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|---|---|
| Title | Modern Theory of Polymer Solutions |
| Author(s) | Yamakawa, Hiromi |
| Citation | Electronic Edition. Harper & Row, 1971, 434p. |
| Issue Date | 1971 |
| URL | http://hdl.handle.net/2433/50527 |
| Right | Copyright © 1971 by Hiromi Yamakawa |
| Type | Book |
| Textversion | publisher |

Kyoto University

Hiromi Yamakawa

# Modern Theory of Polymer Solutions

Harper's Chemistry Series
Under the Editorship of Stuart Alan Rice

# Modern Theory of Polymer Solutions

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Electronic Edition

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# Preface to the Electronic Edition

It has been just thirty years since this volume, *Modern Theory of Polymer Solutions*, was published by Harper & Row, Publishers. It is now out of print but is still in some demand. Furthermore, it is also an introduction to the author's new book, *Helical Wormlike Chains in Polymer Solutions*, published by Springer-Verlag in 1997, although some parts of it are now too old and classical and have only the significance of historical survey. Under these circumstances, the author approved of the preparation of this electronic edition without revision at the Laboratory of Polymer Molecular Science, Department of Polymer Chemistry, Kyoto University. On that occasion, however, he attempted his efforts to correct errors as much as possible. Finally, it is a pleasure to thank Prof. T. Yoshizaki, Mrs. E. Hayashi, and his other collaborators for preparing this electronic edition.

Hiromi Yamakawa

*Kyoto*
*July 2001*

Modern Theory of Polymer Solutions

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For information address Harper & Row, Publishers, Inc., 49 East 33rd Street, New York, N. Y. 10016.

Standard Book Number: 06-047309-6

Library of Congress Catalog Card Number: 71-141173

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# Foreword

*One of the rewards of academic life is the opportunity to meet and work with talented individuals from all over the world. In 1961 Hiromi Yamakawa came to the University of Chicago to work in my laboratory. We had a fruitful collaboration and I learned much from him. I have followed his subsequent work with interest; there are, for me, few pleasures that can compare with the witnessing of the intellectual evolution and continuing contributions of former colleagues.*

*It is in this spirit that I welcome the writing of this book by Professor Hiromi Yamakawa. He has made many contributions to the theory of polymer solutions, and writes from the balanced point of view of research worker and teacher. I believe this book complements those dealing with polymer solutions already published. No other text available so consistently includes the effect of excluded volume on the properties of dilute polymer solutions, and no other so fully develops the distribution function theory approach. For these reasons I recommend the text to research workers and students. Although the presentation is concise, and continuous effort is required to extract all the information implicit in the theory, the reward for such concentration is large.*

**Stuart A. Rice**

# Preface

It is well known that statistical mechanics provides a tool for the description of the relationship between the macroscopic behavior of substances and their atomic and/or molecular properties. Clearly, the same principles apply to polymer science as to the study of small molecules. However, polymeric systems are too complicated to treat rigorously on the basis of molecular mechanics, because polymer molecules have an exceedingly great number of internal degrees of freedom, and thereby also very complicated intramolecular and intermolecular interactions. Thus, it is only for dilute solutions that a molecular theory of polymers can be developed in the spirit of, for instance, the equilibrium and nonequilibrium statistical mechanical theory of simple fluids. In fact, the physical processes which occur in dilute polymer solutions can be described in terms of only a few parameters using the random-flight model. The major purpose of this book is to give a systematic description of the advances made during the past two decades in the distribution-function theory of random-flight models for dilute polymer solutions; this is indicated directly by the title of the book.

The modern theory of polymer solutions has depended on the advances made since the 1940s in the statistical mechanical theory of systems of simple molecules. The random-flight model, which was first investigated by Lord Rayleigh, can now be treated very conveniently by the methods of Markoff and of Wang and Uhlenbeck. Specifically, the latter method has facilitated several advances in the theory of the excluded-volume effect. Except in an ideal state, now called the theta state, all equilibrium and nonequilibrium properties of dilute polymer solutions are influenced by the excluded-volume effect. A large part of this book is concerned with the excluded-volume effect.

The most elementary treatment of the interactions between chain units which leads to the excluded-volume effect is an application of the statistical mechanics of many-particle systems, e.g., the cluster theory of Mayer and McMillan and also the equilibrium theory of liquids. The nonequilibrium properties of the solution are treated by an application of the theory of Brownian motion, or in other words, on the basis of generalized diffusion equations of the Fokker–Planck type. The modern theory of polymer solutions may be classified from the point of view of methodology into these two main subdivisions. Another classification of the several problems is given in Chapter I. We shall consistently emphasize the dependence of dilute-solution properties on polymer molecular weight, as this is an important experimental observable.

The writing of this book was suggested by Professor S. A. Rice in 1961 when the author visited the Institute for the Study of Metals, now the James Franck Institute, of the University of Chicago. Drafts of the first few chapters were written during 1961—1963, but the final draft was not completed then. As in other active fields of science, a large body of new results has accumulated so rapidly that the original design of the book had to be modified. It now seems appropriate to provide a coherent and comprehensive description of the theory of polymer solutions. This does not mean that the theory has been completely established. Rather the author hopes that the appearance of this book at this time will stimulate new developments in the theory of polymer solutions.

This book is not for the beginner, but rather for graduate students and research workers. Much of the research presented has been developed by specialists, and probably has not been read in original form by many research workers and nonspecialists. Thus, the book is intended, on the one hand, to provide an understanding of the modern theory of polymer solutions for these nonspecialists and, on the other hand, to facilitate the research work of specialists in the field and also of physicists and chemists who wish to enter the field. The derivations of most mathematical equations are given in sufficient detail to elucidate the basic physical ideas and the theoretical methods. Although as many references as possible are cited, accidental omissions will occur and are the author's responsibility.

The text is written in the technical terms used in polymer science and statistical mechanics, with only a few exceptions. For instance, the term "configuration" is used instead of the term "conformation," widely employed by polymer chemists at the present time. We choose this notation because this book does not deal with stereochemistry, and the term "configuration integral" or "configurational partition function" is ordinarily used in the statistical mechanics of many-particle systems.

There remains now only the pleasant task of thanking all those who have rendered assistance to the author. The author is indebted to Professor S. A. Rice for his suggestion of this project, constant interest and encouragement for many years, and critical reading of the manuscript with corrections of the English in it. Thanks are also tendered to Professor W. H. Stockmayer for his reading of the manuscript and his lecture at Kyoto University in 1966, which influenced Chapter VI; and to Professor B. H. Zimm for his valuable criticisms of Chapter I and II.

It is a great pleasure to thank Professor Emeritus I. Sakurada for his guidance in polymer chemistry and his general interest and encouragement for many years. The author has carried out much of the research reported with Professor M. Kurata, and benefited from numerous discussions with him. His constant interest and encouragement over the years must also be acknowledged. Professor H. Fujita provided valuable criticisms of the manuscript and ideas in Chapter VII, for which the author wishes to thank him. Needless to say, the writing of this book was made possible by the many papers published in many scientific journals. The author is grateful to these journals and the authors concerned.

Finally, it is a pleasure to acknowledge the assistance of Dr. G. Tanaka who read the manuscript and prepared the figures and the indices, and of Miss S. Sugiura who prepared the typescript and the indices.

Hiromi Yamakawa

# Modern Theory
of Polymer Solutions

# Chapter One

# Introduction

## 1. Survey of the Field

At the very outset of the study of the properties of polymer solutions, in the 1920s, pioneering studies of solution viscosities were carried out by Staudinger. It was his intent to provide evidence supporting the hypothesis that polymers are composed of simple low-molecular-weight compounds connected linearly by covalent bonds. Indeed, the principal objective of early investigations of polymer solutions was to establish methods of molecular weight determination or molecular characterization, and theories of dilute polymer solutions which were developed subsequently are related to this problem in many cases. Emphasis is focused on solution properties because polymer molecules cannot exist in a gaseous state and the characterization of a single polymer molecule is therefore possible only in solutions so dilute that the polymer molecules are well separated from one another.

The first theoretical investigations of the properties of polymers occurred in the 1930s. The foremost of these advances is a statistical treatment of the configurational description of a polymer chain developed independently by Kuhn and by Guth and Mark. These investigators arrived at the significant conclusion that the mean-square end-to-end distance of the chain is proportional to the number of elements constituting it. This deduction provides the foundation for the presently accepted random-flight model in the theory of dilute polymer solutions. Further application of statistical mechanics to the study of the properties of polymer solutions was delayed until the early 1940s. The new developments evolved in two directions. First, there were a number of direct applications of the theory of random-flight statistics to dilute solution properties. The notable results are represented by the theory of light scattering (Debye and Zimm), the theory of intrinsic viscosities (Debye, Kirkwood, and others), and the theory of virial coefficients (Zimm) based on the first general molecular theory of solutions presented by McMillan and Mayer in 1945. The other direction is represented by the lattice theory of polymer solutions, which was developed first by Flory and independently by Huggins in 1942 in order to explain the very large deviations from ideality exhibited by polymer solutions. The Flory–Huggins theory became a standard starting point in the statistical thermodynamics of concentrated polymer solutions. In 1949 and 1950, Flory introduced two new important concepts, now called the excluded-volume effect and the theta state or theta point. Both effects arise from the fact that two elements, possibly remote from each other in sequence along the chain, interact with each other. For example, two elements cannot occupy the same point in space at the same time, thereby generating an excluded volume. The theta state is defined as a sort of ideal state, in the sense that in that state the volume effect apparently vanishes and the chain behaves like an ideal random-flight chain. Thus, by the early 1950s, there had been established the basic physical description of the polymer solution along with the first step in the development of a theory of dilute polymer solutions. The advances made during the last two decades have delineated the relationship between the theory of polymer solutions and other branches of the molecular sciences.

Now, the molecular weight of a given polymeric compound may vary almost continuously from small to very large values, whereas a given low-molecular-weight compound possesses a definite molecular weight characteristic of that compound. In general, the properties of dilute polymer solutions, or more generally polymeric systems, are dependent on their molecular weight. This is an important aspect characteristic of polymeric systems, which is never observed in systems consisting of low-molecular-weight compounds. Thus the molecular weight is an important variable which may in fact be regarded as continuous. This is the reason why a single polymer molecule may be considered a system of the statistical-mechanical ensemble; it is the most fundamental system in the development of the theory. It should be noted that in the theory of dilute polymer solutions the solvent is usually treated as a continuous medium, and not on the molecular level. The principal tool is, of course, classical equilibrium statistical mechanics; nonequilibrium statistical mechanics has not yet been applied to the study of the frictional properties of dilute polymer solutions.

The main part of the theory of polymer solutions consists of a group of theories, now called the two-parameter theory. Within the framework of the two-parameter theory, the properties of dilute polymer solutions, such as average molecular dimensions, second virial coefficients, and intrinsic viscosities, may be expressed in terms of two basic parameters; one is the mean-square end-to-end distance $\langle R^2 \rangle_0$ of a chain in the theta state, and the other is the excluded-volume parameter, which is usually designated by $z$. The parameter $z$ is proportional to the effective excluded volume for a pair of chain elements at infinite dilution and also to the square root of the number of elements in the chain. The excluded volume, and hence the parameter $z$, vanish at the theta point. This is, indeed, the definition of the theta point or theta state. The central problem in the theory is to derive interrelations between the dilute-solution properties and the parameters $\langle R^2 \rangle_0$ and/or $z$, in particular for linear flexible chains. Thus this group of problems is ultimately concerned with the exploration of the dependence of dilute-solution properties on molecular weight.

There is another important group of problems. In these attention is focused primarily on relationships between the chain structure and the dilute-solution properties, especially the average molecular dimensions in the theta state. The chain structure is considered on the atomic level or on the subchain level. The description of the conformational statistics of polymer chains belongs to the first case, in which the local chemical structure of a chain is considered in detail; that is, restrictions on the angles between successive bonds in the chain and steric hindrances to internal rotation about the bonds are explicitly taken into account in a calculation of the quantity $\langle R^2 \rangle_0$ itself. Intramolecular interferences of this sort are of short-range nature, while the excluded-volume effect is of long-range nature. In fact, there have been a number of significant advances in the theory of conformational statistics as well as in the two-parameter theory. For the second case, in which the chain structure on the subchain level is considered, attention is focused on the differences between the dilute-solution properties of linear flexible chains and chains of other types, such as branched and ring polymers and stiff chains.

In the first group of problems, many-body problems are often encountered, and also the self-consistency of theories is an important factor to be discussed. Thus, these have the nature of purely physical problems. On the other hand, the second group of problems is of importance for molecular characterization. It should be noted that both groups of problems have been studied in order to emphasize their interrelations.

## 2. Scope and Introductory Remarks

Many of the chapters of this book will be devoted to the description of the two-parameter theory for linear flexible chain polymers. The reason for this is that the two-parameter theory for linear flexible chains is good enough to provide an understanding of the basic physical processes in dilute polymer solutions and of the theoretical procedures. Studies of the properties of branched and ring polymers and stiff chains will be found in the sections of chapters entitled Remarks or Remarks and Topics. The analysis of the effects of short-range interferences in a chain will be omitted, although not completely, since it must be discussed in the study of conformational statistics. Thus, the basic molecular model used in this book is the random-flight model or its modifications.

Chapter II presents in detail the mathematical foundation of the statistics of ideal random-flight chains, and is also an introduction to the later chapters. In Chapter III there is a detailed description of the theory of the excluded-volume effect, including both the perturbation theory and the other approximate treatments. The present status of the theory is, of course, discussed in detail. No complete solution has as yet been obtained, because the problem is similar to the many-body problem in the theory of simple liquids. Chapter III is, indeed, the core of this book. Chapter IV deals with the theory of virial coefficients on the basis of the McMillan–Mayer general theory of solutions. In particular, the theory of the second virial coefficient is described in detail. Chapter V covers the ordinary theory of light scattering (involving the fluctuation theory), the distribution function theory, and some other topics. Chapter VI deals with the theory of transport properties, such as intrinsic viscosities and friction coefficients. Although the dynamical properties are also discussed, the theory of viscosities is worked out mainly for the case of steady shear rate. The theory of viscosity is very difficult, and no available representation of the viscosity seems to be satisfactory. In Chapter VII, a comparison of the two-parameter theory with experiment is made. In doing this, a fundamental difficulty arises from the fact that the parameter $z$ is not directly observable. This problem is discussed in detail.

The reader who wishes to learn some of the elementary concepts of polymer chemistry, conformational statistics, or the fundamentals of statistical mechanics is referred to some of the books listed below.

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# Chapter Two

# Statistics of Ideal Polymer Chains: Random-Flight Problems

## 3. Introduction

The theory of dilute polymer solutions begins with a formulation of the distribution for a single linear flexible polymer chain in an infinite solvent medium. This simplified system may be realized at infinite dilution where all intermolecular interactions between solute polymers may be neglected. Now, there exist many degrees of internal-rotational freedom about the single bonds in the chain in addition to the irregular translational and rotational motions of the entire molecule due to thermal Brownian motion. As a consequence of this and the great number of elements constituting the chain, an almost limitless number of chain configurations may be realized by the polymer molecule. The instantaneous configuration of the entire chain can be specified by all internal and external coordinates of the molecule. The Cartesian coordinates of the centers of elements in the chain may be chosen as such coordinates. We denote the coordinates of element $j$ by $\mathbf{R}_j$, assuming that the chain is composed of $n+1$ elements joined successively and the elements are numbered 0, 1, 2, …, $n$ from one end to the other. In this book, a portion of the chain belonging to the representative point $\mathbf{R}_j$ will be often referred to as the *segment* instead of the element. In the case of a polymethylene chain, for example, $\mathbf{R}_j$ represents the coordinates of the $j$th carbon atom and the methylene group is considered a segment.[*]

It is evident that the statistical properties of an isolated chain are independent of its external coordinates. Accordingly, suppose that seg-

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[*] In later chapters, by the term "segment" we do not necessarily mean that only one carbon atom is contained in a segment of the backbone chain.

ment 0 is fixed at the origin of the Cartesian coordinate system, as depicted in Fig. II. 1. The configurational partition function $Z$ for the system under consideration may then be written in the form,

$$Z = \int \exp\left[-\frac{U(\{\mathbf{R}_n\})}{kT}\right] d\{\mathbf{R}_n\}\,, \tag{3.1}$$

where $\{\mathbf{R}_n\}$ is a shorthand notation for a set of coordinates $\mathbf{R}_1$, $\mathbf{R}_2$, ..., $\mathbf{R}_n$, and $U$ is the potential energy of the system and may be expressed as

$$U(\{\mathbf{R}_n\}) = \sum_{j=1}^{n} u_j(\mathbf{R}_{j-1}, \mathbf{R}_j) + W(\{\mathbf{R}_n\})\,. \tag{3.2}$$

The potential $u_j$ takes account formally of the fact that the $j-1$th and $j$th segments (or carbon atoms) are connected through a valence bond, and therefore the potential $W$ includes interactions of all other types such as bond angle restrictions and steric hindrances to internal rotation, and also long-range interferences between segments. In Eq. (3.1), it should be understood that integration over coordinates of the solvent molecules has already been performed, and therefore that $W$ plays the role of the potential of mean force. The instantaneous distribution $P(\{\mathbf{R}_n\})$ for the entire chain is given by

$$P(\{\mathbf{R}_n\}) = Z^{-1} \exp\left[-\frac{U(\{\mathbf{R}_n\})}{kT}\right]\,. \tag{3.3}$$

It is often convenient to use, instead of the set of $\mathbf{R}_j$, coordinates $\mathbf{r}_j$ called the *bond vector* and defined by

$$\mathbf{r}_j = \mathbf{R}_j - \mathbf{R}_{j-1}\,. \tag{3.4}$$

Further, we define a distribution function $\tau_j(\mathbf{r}_j)$ by

$$\tau_j(\mathbf{r}_j) = \exp\left[-\frac{u_j(\mathbf{r}_j)}{kT}\right] \tag{3.5}$$

with $u_j(\mathbf{r}_j) = u_j(\mathbf{R}_{j-1}, \mathbf{R}_j)$. The zero of the potential $u_j$ is chosen in such a way that $\tau_j$ is normalized to unity:

$$\int \tau_j(\mathbf{r}_j) d\mathbf{r}_j = 1\,. \tag{3.6}$$

The function $\tau_j$ is referred to as the *bond probability* since $\tau_j d\mathbf{r}_j$ represents the probability that the (vector) length of the $j$th bond lies between $\mathbf{r}_j$ and $\mathbf{r}_j + d\mathbf{r}_j$. Note that by definition $u_j$ and hence $\tau_j$ are spherically symmetric, i.e., functions of $r_j = |\mathbf{r}_j|$ only. Equation (3.1) may then be rewritten in the form,

$$Z = \int \left[\prod_{j=1}^{n} \tau_j(\mathbf{r}_j)\right] \exp\left(-\frac{W}{kT}\right) d\{\mathbf{r}_n\}\,. \tag{3.7}$$

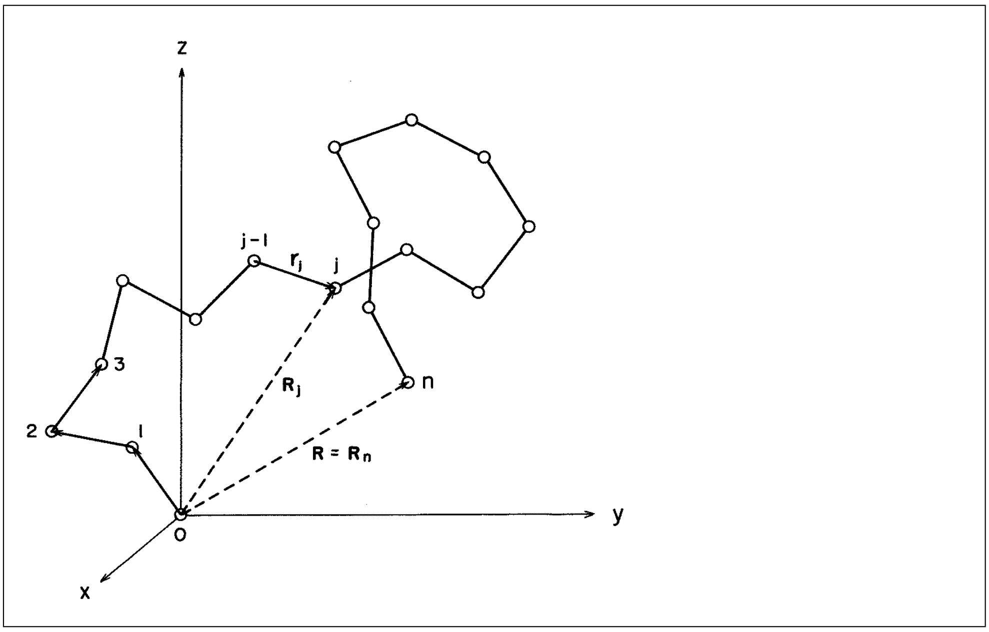

**Fig. II.1.** Configurations of a polymer chain with the 0th segment fixed at the origin of a coordinate system.

The distribution function $P(\mathbf{R})$ of the end-to-end distance $\mathbf{R}$ ($\equiv \mathbf{R}_n$) can be obtained by integrating $P(\{\mathbf{R}_n\})$ over $\{\mathbf{r}_n\}$ under the restriction,

$$\sum_{j=1}^{n} \mathbf{r}_j = \mathbf{R} . \tag{3.8}$$

That is,

$$P(\mathbf{R}) = Z^{-1} \int \left[ \prod_{j=1}^{n} \tau_j(\mathbf{r}_j) \right] \exp\left( -\frac{W}{kT} \right) \frac{d\{\mathbf{r}_n\}}{d\mathbf{R}} , \tag{3.9}$$

which is normalized as

$$\int P(\mathbf{R}) d\mathbf{R} = 1 . \tag{3.10}$$

In this chapter, we shall deal with the ideal case in which $W = 0$. With this assumption, Eq. (3.9) becomes

$$P(\mathbf{R}) = \int \left[ \prod_{j=1}^{n} \tau_j(\mathbf{r}_j) \right] \frac{d\{\mathbf{r}_n\}}{d\mathbf{R}} \tag{3.11}$$

with $Z = 1$. Thus the problem of evaluating $P(\mathbf{R})$ of Eq. (3.11) is equivalent to that of random flights or the Brownian motion of a free particle, which may be stated as follows: "A particle undergoes a sequence of displacements $\mathbf{r}_1,\ \mathbf{r}_2,\ \ldots,\ \mathbf{r}_n$, the magnitude and direction of each displacement being independent of all the preceding ones. The probability that the displacement $\mathbf{r}_j$ lies between $\mathbf{r}_j$ and $\mathbf{r}_j + d\mathbf{r}_j$ is governed by a distribution function $\tau_j(\mathbf{r}_j)$ assigned a priori. We ask: What is the probability $P(\mathbf{R})d\mathbf{R}$ that after $n$ displacements the position $\mathbf{R}(= \mathbf{r}_1 + \mathbf{r}_2 + \cdots + \mathbf{r}_n)$ of the particle lies between $\mathbf{R}$ and $\mathbf{R} + d\mathbf{R}$." For this reason, a chain whose distribution can be determined in terms of only $\tau_j$'s is called a *random-flight chain.* The statistical properties of random-flight chains may be completely analyzed by the use of the Markoff method (Section 4) and the Wang–Uhlenbeck method (Section 6).

## 4. The Markoff Method for the General Problem of Random Flights

Historically the problem of random flights was formulated first by Pearson[1] in terms of the wanderings of a drunkard, and the solution in three dimensions was obtained for small and very large values of $n$, the number of steps, by Rayleigh.[2] In its most general form the problem was formulated by Markoff[3] and subsequently by Chandrasekhar.[4] In this section, we consider a slight generalization of the problem presented in the last section and the method for obtaining its general solution, which can readily be applied to other problems besides that of finding $P(\mathbf{R})$ in later sections. However, this formulation is less general than that of Chandrasekhar.

Consider $n$, three-dimensional vectors,

$$\boldsymbol{\phi}_j = (\phi_{jx}, \phi_{jy}, \phi_{jz}) \qquad (j = 1,\ \ldots,\ n)\,, \tag{4.1}$$

where the components are assumed functions of three coordinates in a Cartesian coordinate system:

$$\phi_{js} = \phi_{js}(x_j, y_j, z_j) \qquad (s = x,\ y,\ z)\,. \tag{4.2}$$

Further, the probability that the $x_j$, $y_j$, $z_j$ occur in the range,

$$x_j \sim x_j + dx_j;\ \ y_j \sim y_j + dy_j;\ \ z_j \sim z_j + dz_j\,,$$

is assumed to be given a priori by

$$\tau_j(x_j, y_j, z_j)dx_j dy_j dz_j \equiv \tau_j(\mathbf{r}_j)d\mathbf{r}_j\,, \tag{4.3}$$

$\tau_j$ satisfying the normalization condition of (3.6). That is, $\tau_j$ is independent of all the preceding vectors $\mathbf{r}_k$ with $k < j$, and the process under consideration is just a simple Markoff process. Now the problem is to find the distribution function $P(\boldsymbol{\Phi})$ of the resultant $\boldsymbol{\Phi}$ of $n$ original vectors,

$$\boldsymbol{\Phi} = \sum_{j=1}^{n} \boldsymbol{\phi}_j\,, \tag{4.4}$$

that is, the probability $P(\mathbf{\Phi})d\mathbf{\Phi}$ that $\mathbf{\Phi}$ lies between $\mathbf{\Phi}$ and $\mathbf{\Phi} + d\mathbf{\Phi}$. Obviously the probability that $\boldsymbol{\phi}_j$ lies between $\boldsymbol{\phi}_j$ and $\boldsymbol{\phi}_j + d\boldsymbol{\phi}_j$ is equal to the probability that $\mathbf{r}_j$ lies between $\mathbf{r}_j$ and $\mathbf{r}_j + d\mathbf{r}_j$. In our notation, $P(\mathbf{\Phi})$ may therefore be written as

$$P(\mathbf{\Phi}) = \int \left[\prod_{j=1}^{n} \tau_j(\mathbf{r}_j)\right] \frac{d\{\mathbf{r}_n\}}{d\mathbf{\Phi}}\,, \tag{4.5}$$

where $d\{\mathbf{r}_n\} = d\mathbf{r}_1 \ldots d\mathbf{r}_n$, and the integration goes over all magnitudes and directions of all $\mathbf{r}_j$ at constant $\mathbf{\Phi}$ with the condition of (4.4).

The restriction on the integration of (4.5) can be removed by introducing Dirichlet's cutoff integral or a Fourier representation of a three-dimensional Dirac delta function as follows,

$$P(\mathbf{\Phi}) = \int \delta(\mathbf{r}) \left[\prod_{j=1}^{n} \tau_j(\mathbf{r}_j) d\mathbf{r}_j\right]\,, \tag{4.6}$$

where

$$\mathbf{r} = \mathbf{\Phi} - \sum_{j=1}^{n} \boldsymbol{\phi}_j\,, \tag{4.7}$$

$$\delta(\mathbf{r}) = (2\pi)^{-3} \int \exp(-i\mathbf{r}\cdot\boldsymbol{\rho}) d\boldsymbol{\rho}\,. \tag{4.8}$$

Equation (4.6) with (4.7) and (4.8) can be rewritten in the form,

$$P(\mathbf{\Phi}) = (2\pi)^{-3} \int K(\boldsymbol{\rho}) \exp(-i\mathbf{\Phi}\cdot\boldsymbol{\rho}) d\boldsymbol{\rho} \tag{4.9}$$

with

$$K(\boldsymbol{\rho}) = \prod_{j=1}^{n} \int \tau_j(\mathbf{r}_j) \exp(i\boldsymbol{\rho}\cdot\boldsymbol{\phi}_j) d\mathbf{r}_j\,. \tag{4.10}$$

From Eq. (4.9) and the Fourier inversion formula, $K(\boldsymbol{\rho})$ is seen to be the three-dimensional Fourier transform of the distribution function $P(\mathbf{\Phi})$:

$$K(\boldsymbol{\rho}) = \int P(\mathbf{\Phi}) \exp(i\boldsymbol{\rho}\cdot\mathbf{\Phi}) d\mathbf{\Phi}\,. \tag{4.11}$$

Thus, the advantage of the method introduced is that $P(\mathbf{\Phi})$ can be obtained by an inverse transformation of $K(\boldsymbol{\rho})$ which can be evaluated from Eq. (4.10) without any restriction on the range of integration. In general, the Fourier transform, $K$, of a distribution function is called the *characteristic function* of that distribution function.

We now examine the properties of the characteristic function. Expanding the exponential in Eq. (4.11), we have

$$K(\boldsymbol{\rho}) = \sum_{k=0}^{\infty} \frac{1}{k!} \int (i\boldsymbol{\rho}\cdot\mathbf{\Phi})^k P(\mathbf{\Phi}) d\mathbf{\Phi}\,. \tag{4.12}$$

If $\Phi_\rho$ is the component of $\boldsymbol{\Phi}$ in the direction of $\boldsymbol{\rho}$, Eq. (4.12) becomes

$$K(\boldsymbol{\rho}) = \sum_{k=0}^{\infty} \frac{1}{k!} \langle {\Phi_\rho}^k \rangle (i\rho)^k \tag{4.13}$$

with

$$\langle {\Phi_\rho}^k \rangle = \int {\Phi_\rho}^k P(\boldsymbol{\Phi}) d\boldsymbol{\Phi} \,. \tag{4.14}$$

In particular, if $P(\boldsymbol{\Phi})$ is spherically symmetric, the integral of (4.14) can be evaluated by using polar coordinates with the $z$ axis in the direction of $\boldsymbol{\rho}$ as follows,

$$\begin{aligned} \langle {\Phi_\rho}^k \rangle &= \frac{1}{k+1} \langle \Phi^k \rangle \qquad && \text{for } k = 2p \,, \\ &= 0 && \text{for } k = 2p+1 \,, \end{aligned} \tag{4.15}$$

where

$$\begin{aligned} \langle \Phi^{2p} \rangle &= \int \Phi^{2p} P(\boldsymbol{\Phi}) d\boldsymbol{\Phi} \\ &= \int_0^\infty \Phi^{2p} P(\boldsymbol{\Phi}) 4\pi \Phi^2 d\Phi \,. \end{aligned} \tag{4.16}$$

Equation (4.13) may then be rewritten in the form,

$$K(\boldsymbol{\rho}) = \sum_{p=0}^{\infty} \frac{(-1)^p}{(2p+1)!} \langle \Phi^{2p} \rangle \rho^{2p} \,. \tag{4.17}$$

Thus the expansion coefficients of the characteristic function yield the moments, $\langle \Phi^{2p} \rangle$, of the distribution function (assuming spherical symmetry). In turn, when all the moments are given the distribution function can be determined completely.

## 5. Distribution of the End-to-End Distance and Related Quantities

It is evident that when we put $\boldsymbol{\Phi} = \mathbf{R}$ and $\boldsymbol{\phi}_j = \mathbf{r}_j$ Eqs. (4.9) and (4.10) become the basic equations from which the distribution function of the end-to-end distance of a polymer chain can be evaluated. For simplicity, we consider a polymer chain, an example of which is a vinyl polymer, whose bond probabilities $\tau_j(\mathbf{r}_j)$ are identical for all $j$, and omit the subscript $j$.* The basic equations may then be written in the forms,

$$P(\mathbf{R}) = (2\pi)^{-3} \int K(\boldsymbol{\rho}) \exp(-i\mathbf{R} \cdot \boldsymbol{\rho}) d\boldsymbol{\rho} \,, \tag{5.1}$$

$$K(\boldsymbol{\rho}) = \left[ \int \tau(\mathbf{r}) \exp(i\boldsymbol{\rho} \cdot \mathbf{r}) d\mathbf{r} \right]^n \,. \tag{5.2}$$

To carry out the calculation the form of $\tau$ must be specified.

*Most of the problems in this book will be discussed on the basis of this model.

## 5a. Exact Expression for the Bond Probability

We may assume that each bond has a constant length $a$, neglecting the deviation of the length of a valence bond from its mean value $a$ due to atomic vibrations in the spine of the chain. The constancy of bond length may be taken into account by expressing the bond probability in terms of a delta function;

$$\tau(\mathbf{r}) = \frac{1}{4\pi a^2}\delta\bigl(|\mathbf{r}| - a\bigr)\,. \tag{5.3}$$

By using polar coordinates with the $z$ axis in the direction of $\boldsymbol{\rho}$, the integral in Eq. (5.2) can then be easily evaluated to give

$$K(\boldsymbol{\rho}) = \left[\frac{\sin(a\rho)}{a\rho}\right]^n\,. \tag{5.4}$$

Substitution of Eq. (5.4) into Eq. (5.1) leads to

$$P(\mathbf{R}) = \frac{1}{2\pi^2 R}\int_0^\infty \rho\sin(R\rho)\left[\frac{\sin(a\rho)}{a\rho}\right]^n d\rho\,, \tag{5.5}$$

where use has been made again of polar coordinates. Note that $P(\mathbf{R})$ is spherically symmetric. In general, if the bond probability is spherically symmetric, so are both the characteristic and distribution functions, provided $\boldsymbol{\phi}_j$ and $\mathbf{r}_j$ are in the same direction for all $j$.

We first evaluate the moments $\langle R^{2p}\rangle$ of the distribution of (5.5) from Eq. (5.4) by the method of cumulants. The logarithm of the characteristic function of (4.13) may be expanded in the form,[5, 6]

$$\begin{aligned}\ln K(\boldsymbol{\rho}) &= \ln\left[\sum_{k=0}^{\infty}\frac{\mu_k}{k!}(i\rho)^k\right]\\ &= \sum_{k=1}^{\infty}\frac{\kappa_k}{k!}(i\rho)^k\end{aligned} \tag{5.6}$$

with $\mu_k \equiv \langle {R_\rho}^k\rangle$ the $k$th moment.* The coefficient $\kappa_k$ is called the $k$th *cumulant* (semiinvariant). The $k$th cumulant can be explicitly represented in terms of only the moments $\mu_j$ with $j \leq k$, and vice versa. Without proof, we use the result,[7]

$$\mu_k = k!\sum_{\mathbf{m}}\prod_{j=1}^{k}\frac{1}{m_j!}\left(\frac{\kappa_j}{j!}\right)^{m_j}\,, \tag{5.7}$$

where $\sum_{\mathbf{m}}$ means the summation over all sets of $m_1, m_2, \ldots$ compatible with

$$\sum_{j=1}^{k} j m_j = k\,.$$

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*Sometimes the *moment generating function* $M(\boldsymbol{\rho}) \equiv K(\boldsymbol{\rho}/i)$, the Laplace transform of the distribution function, is used instead of the characteristic function.

Now the logarithm of Eq. (5.4) can be expanded as

$$\ln K(\boldsymbol{\rho}) = -n \sum_{l=1}^{\infty} \frac{B_l (2a)^{2l}}{(2l)!2l} \rho^{2l} \tag{5.8}$$

with $B_l$ the Bernoulli numbers ($B_l = 1/6$, $B_2 = 1/30$, ...). A comparison of Eq. (5.8) with (5.6) leads to

$$\begin{aligned} \kappa_k &= (-1)^{l-1}(2l)^{-1} B_l n (2a)^{2l} \quad && \text{for } k = 2l\,, \\ &= 0 && \text{for } k = 2l+1\,. \end{aligned} \tag{5.9}$$

Substituting Eq. (5.9) into Eq. (5.7) and recalling that $\langle R^{2p} \rangle = (2p+1)\mu_{2p}$, we obtain

$$\langle R^{2p} \rangle = (-1)^p (2p+1)! \sum_{\mathbf{m}} \prod_{l=1}^{p} \frac{1}{m_l!} \left[ -\frac{B_l n (2a)^{2l}}{(2l)!2l} \right]^{m_l} \tag{5.10}$$

with

$$\sum_{l=1}^{p} l m_l = p\,.$$

In particular, when $p = 1$, Eq. (5.10) yields the mean-square end-to-end distance $\langle R^2 \rangle$ or root-mean-square end-to-end distance $\langle R^2 \rangle^{1/2}$ as a measure of the average size of the random-flightchain,

$$\langle R^2 \rangle = n a^2\,, \tag{5.11}$$

or

$$\langle R^2 \rangle^{1/2} = n^{1/2} a\,. \tag{5.12}$$

It is important to observe that the mean-square end-to-end distance is proportional to the number of bonds or segments in the chain. This characteristic will be referred to as the *Markoff nature* of a chain.

We now proceed to evaluate the integral in Eq. (5.5). This will be done for three cases of interest.

### 5a(i). Exact Solution

The exact solution was obtained by Treloar,[8] by Wang and Guth,[9] by Nagai,[10] and by Hsiung et al.,[11] the mathematical techniques being different from one another. The evaluation is made conveniently using the theory of functions.

Equation (5.5) may be rewritten in the form,

$$P(\mathbf{R}) = -\frac{i}{4\pi^2 a^2 R} \int_{-\infty}^{+\infty} \xi \exp\left(\frac{iR\xi}{a}\right) \cdot \left(\frac{\sin \xi}{\xi}\right)^n d\xi \tag{5.13}$$

with

$$\xi = a\rho\,. \tag{5.14}$$

Using the development,

$$\sin^n \xi = \frac{1}{(2i)^n} \sum_{p=0}^{n} (-1)^p \binom{n}{p} \exp(in\xi - 2ip\xi)\,, \tag{5.15}$$

Eq. (5.13) may be further rewritten in the form,

$$P(\mathbf{R}) = -\frac{1}{2^{n+2} i^{n-1} \pi^2 a^2 R} \sum_{p=0}^{n} (-1)^p \binom{n}{p} \int_{-\infty}^{+\infty} \frac{e^{i(n-2p+R/a)\xi}}{\xi^{n-1}} d\xi\,. \tag{5.16}$$

We now consider the integral,

$$I = \oint \frac{e^{ib\xi}}{(\xi + i\varepsilon)^{n-1}} d\xi \tag{5.17}$$

with $\varepsilon > 0$. When $b > 0$, the contour of integration consists of a large half circle of radius $r$ in the upper complex plane and the real axis between $-r$ and $r$; when $b \leq 0$, a large half circle of radius $r$ in the lower complex plane and the real axis between $-r$ and $r$. When $b > 0$, application of Cauchy's integral formula leads to

$$\int_{-\infty}^{+\infty} \frac{e^{ib\xi}}{\xi^{n-1}} d\xi = \lim_{\substack{r\to\infty \\ \varepsilon\to 0}} I = 0 \qquad (b > 0)\,. \tag{5.18}$$

On the other hand, when $b \leq 0$, application of Goursat's theorem leads to

$$\begin{aligned} \int_{-\infty}^{+\infty} \frac{e^{ib\xi}}{\xi^{n-1}} d\xi &= -\lim_{\substack{r\to\infty \\ \varepsilon\to 0}} I \\ &= -\lim_{\varepsilon\to 0} \frac{2\pi i}{(n-2)!} \left[ \frac{d^{n-2}}{d\xi^{n-2}} e^{ib\xi} \right]_{\xi = -i\varepsilon} \\ &= -\frac{2\pi i^{n-1}}{(n-2)!} b^{n-2} \qquad (b \leq 0)\,. \end{aligned} \tag{5.19}$$

Substituting Eqs. (5.18) and (5.19) with $b = n - 2p + R/a$ into Eq. (5.16) and putting $n - p = k$, we obtain the result,

$$P(\mathbf{R}) = \frac{1}{2^{n+1}(n-2)!\pi a^2 R} \sum_{k=0}^{k \leq (n-R/a)/2} (-1)^k \binom{n}{k} \left( n - 2k - \frac{R}{a} \right)^{n-2}\,. \tag{5.20}$$

Although Wang and Guth[9] have also used the theory of functions to arrive at Eq. (5.20), their procedure is incorrect.

The series displayed in Eq. (5.20) contains, as special cases, the expressions derived by Rayleigh[2] and Chandrasekhar[4] for the first few values of $n$. Since this series is not useful for practical computations in our problems (with $n$ large), we introduce some approximations to obtain a closed expression.

### 5a(ii). Case for $n \gg 1$

The asymptotic solution for large $n$ can be obtained by the method of steepest descents[9] (see Appendix II A). Equation (5.13) may be rewritten in the form,

$$P(\mathbf{R}) = \frac{1}{4i\pi^2 a^2 R} \int_{-\infty}^{+\infty} \xi \exp\big[n f(\xi)\big] d\xi \,, \tag{5.21}$$

where

$$f(\xi) = i\left(\frac{R}{na}\right)\xi + \ln\left(\frac{\sin\xi}{\xi}\right) . \tag{5.22}$$

The integrand of Eq. (5.21) is analytic in the entire finite complex plane. The saddle point, given by the condition

$$f'(\xi) = 0 \,, \tag{5.23}$$

can be shown to be the point $\xi_0 = iy_0$ on the positive imaginary axis with

$$\coth\ y_0 - \frac{1}{y_0} = \mathcal{L}(y_0) = \frac{R}{na} \,, \tag{5.24}$$

where $\mathcal{L}$ is the Langevin function. Further, in the vicinity of the saddle point, $f(\xi)$ may be expanded as

$$f(\xi) = f(\xi_0) + \tfrac{1}{2} f''(\xi_0)(\xi - \xi_0)^2 + \cdots \tag{5.25}$$

with

$$f''(\xi_0) = \operatorname{cosech}^2 y_0 - \frac{1}{y_0^{\,2}} < 0 \,, \tag{5.26}$$

and the contour of integration should therefore be the line through $\xi_0$ and parallel to the real axis. Thus Eq. (5.21) can be approximated by

$$\begin{aligned} P(\mathbf{R}) &= \frac{\exp\big[n f(iy_0)\big]}{4i\pi^2 a^2 R} \int_{-\infty}^{+\infty} (x + iy_0) \exp\big[\tfrac{1}{2} n f''(iy_0) x^2\big] dx \\ &= \left(\frac{y_0}{4\pi^2 a^2 R}\right)\left[-\frac{2\pi}{n f''(iy_0)}\right]^{1/2} \exp\big[n f(iy_0)\big] . \end{aligned} \tag{5.27}$$

That is,

$$P(\mathbf{R}) = \frac{\big[\mathcal{L}^{-1}(t)\big]^2}{(2\pi n a^2)^{3/2} t \big\{1 - \big[\mathcal{L}^{-1}(t) \operatorname{cosech}\ \mathcal{L}^{-1}(t)\big]^2\big\}^{1/2}} \times \left\{\frac{\sinh \mathcal{L}^{-1}(t)}{\mathcal{L}^{-1}(t) \exp\big[t\mathcal{L}^{-1}(t)\big]}\right\}^n \tag{5.28}$$

with

$$t \equiv \frac{R}{na} \,,$$

where $\mathcal{L}^{-1}$ is the inverse Langevin function.

It should be noted that Eq. (5.28) is valid over the whole range of $R$, $0 \leq R \leq na$ (full extension). The problem was also solved by Kuhn and Grün[12] and by James and Guth[13] in a different manner. Their procedure is based on the fact that the problem is essentially equivalent to that of finding the polarization of a gas due to the orientation of permanent magnetic or electric dipoles in an external field of sufficient strength to produce effects approaching complete orientation.

Now, expanding Eq. (5.28) for $R/na \ll 1$ and renormalizing it, we obtain

$$P(\mathbf{R}) = C\left(\frac{3}{2\pi na^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2na^2}\right)\left(1 + \frac{3R^2}{2n^2a^2} - \frac{9R^4}{20n^3a^4} + \cdots\right), \tag{5.29}$$

where $C$ is the normalizing constant. This expansion is equivalent to that obtained by Kuhn and Grün and by James and Guth. We note that originally Eqs. (5.20), (5.28), and (5.29) were derived with the aim of explaining the behavior of polymeric network systems (rubber elasticity) at high extensions.[14]

### 5a(iii). Case for $n \gg 1$ and $R/na \ll 1$

Equation (5.29) is, of course, valid for this case. However, the same result can be obtained in a simpler manner, which we first describe. Equation (5.8) may be rewritten in the form,

$$\begin{aligned} K(\boldsymbol{\rho}) &= \exp\left(-\tfrac{1}{6}na^2\rho^2\right)\exp\left[-n\sum_{l=2}^{\infty}\frac{B_l(2a)^{2l}}{(2l)!2l}\rho^{2l}\right] \\ &= \exp\left(-\tfrac{1}{6}na^2\rho^2\right)\cdot\left[1 - \frac{1}{180}n(a\rho)^4 + \cdots\right]. \end{aligned} \tag{5.30}$$

Integration after substitution of Eqs. (5.4) and (5.30) into Eq. (5.5) leads to

$$\begin{aligned} P(\mathbf{R}) = \left(\frac{3}{2\pi na^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2na^2}\right)\Bigg[1 - \frac{3}{20n}\left(5 - \frac{10R^2}{na^2} + \frac{3R^4}{n^2a^4}\right) \\ + O(n^{-2})\Bigg]. \end{aligned} \tag{5.31}$$

This equation satisfies the normalization condition of (3.10), and Eq. (5.29) becomes identical with Eq. (5.31) when the normalizing constant $C$ is determined.

Evidently the expansion of (5.31) is valid under the present conditions, and asymptotically approaches

$$P(\mathbf{R}) = \left(\frac{3}{2\pi na^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2na^2}\right). \tag{5.32}$$

This Gaussian asymptotic solution is originally due to Rayleigh.[2] Now we consider the moments of (5.10) in the limit of $n \to \infty$. Recalling that the term with the highest power of $n$ in the sum in Eq. (5.10) corresponds to the set, $m_1 = p$, $m_2 = \cdots = m_p = 0$, we retain only this term (for $n \to \infty$) to obtain

$$\langle R^{2p} \rangle = \frac{(2p+1)!}{6^p p!}(na^2)^p \,. \tag{5.33}$$

Substitution of Eq. (5.33) into Eq. (4.17) with $\Phi = R$ leads to

$$K(\boldsymbol{\rho}) = \exp(-\tfrac{1}{6} na^2 \rho^2) \,. \tag{5.34}$$

The inverse Fourier transform of Eq. (5.34) just gives Eq. (5.32). These results state the *central limit theorem* for the random-flight chain. Thus Eqs. (5.33) and (5.34) yield the moments and the characteristic function of the Gaussian distribution. Note that in the particular case of $p = 1$, Eq. (5.33) reduces exactly to Eq. (5.11). When we approximate the distribution function $P(\mathbf{R})$ for the random-flight chain by Eq. (5.32), it is sometimes called the *Gaussian chain*.

## 5b. Approximate Expression for the Bond Probability

Let us approximate the bond probability $\tau$ by a Gaussian function such that it gives the correct mean-square length $a^2$ of the bond; that is,

$$\tau(\mathbf{r}) = \left( \frac{3}{2\pi a^2} \right)^{3/2} \exp\left( -\frac{3r^2}{2a^2} \right) \,. \tag{5.35}$$

Then the Fourier transform of this function is $\exp(-a^2\rho^2/6)$ and the characteristic function becomes equal to Eq. (5.34). Accordingly the distribution function of the end-to-end distance becomes the Gaussian function, Eq. (5.32). This implies that in the statistics of the Gaussian chain the exact bond probability may be replaced by the Gaussian bond probability. In fact, most of the problems in this book will be treated on the basis of the Gaussian chain model with the use of Eq. (5.35). Thus it is worthwhile to describe here further details pertinent to the Gaussian chain.

Using Eq. (5.11), Eq. (5.32) may also be written in the form,

$$P(\mathbf{R}) = \left( \frac{3}{2\pi \langle R^2 \rangle} \right)^{3/2} \exp\left( -\frac{3R^2}{2\langle R^2 \rangle} \right) \,. \tag{5.36}$$

For illustrative purposes, the functions $P(\mathbf{R})$ and $4\pi R^2 P(\mathbf{R})$ (the probability density that $R$ lies between $R$ and $R + dR$ irrespective of the direction of $\mathbf{R}$) for a Gaussian chain with $\langle R^2 \rangle^{1/2} = 300$ (Å) are plotted against $R$ in Fig. II.2. The maximum of $4\pi R^2 P(\mathbf{R})$ occurs at

$$R^* = \left(\tfrac{2}{3}\right)^{1/2} \langle R^2 \rangle^{1/2} \,, \tag{5.37}$$

which represents the most probable value of $R$ and is somewhat smaller than the root-mean-square end-to-end distance.

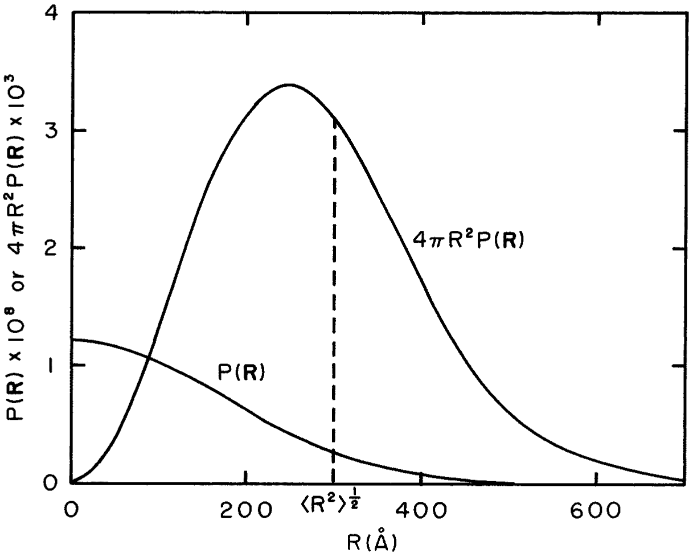

**Fig. II.2.** Gaussian distribution functions of the end-to-end vector **R** and the end-to-end distance *R* of a polymer chain with the root-mean-square end-to-end distance of 300 Å.

In Fig. II.3 a comparison is made of the Gaussian distribution function $4\pi R^2 P(\mathbf{R})$ (broken curve) and the corresponding exact distribution function from Eq. (5.20) (full curve) for $a = 1$ and $n = 10$. It is seen that even for $n = 10$ the asymptotic Gaussian distribution gives surprising accuracy over the whole range. It must however be recognized that the Gaussian distribution has finite, although small, values even for $R > na$, where the exact value is zero; Eq. (5.32) or (5.36) becomes invalid at values of $R$ approaching full extension of the chain.

In general, a linear chain may be considered to be composed of subchains joined successively at their ends. It is then evident that these subchains are mutually independent for the random-flight chain. Thus the distribution function $P(\mathbf{R}_{ij})$ of the distance $\mathbf{R}_{ij}$ between segments $i$ and $j$ $(j > i)$ in the Gaussian chain can readily be written as

$$P(\mathbf{R}_{ij}) = \left(\frac{3}{2\pi\langle R_{ij}^2\rangle}\right)^{3/2} \exp\left(-\frac{3R_{ij}^2}{2\langle R_{ij}^2\rangle}\right) \tag{5.38}$$

with

$$\langle R_{ij}^2\rangle = (j-i)a^2\,, \tag{5.39}$$

where segment $i$, instead of 0, may be supposed to be fixed at the origin.

From the previous discussion, it seems quite adequate to approximate the random-flight chain, which is a basic model for polymer

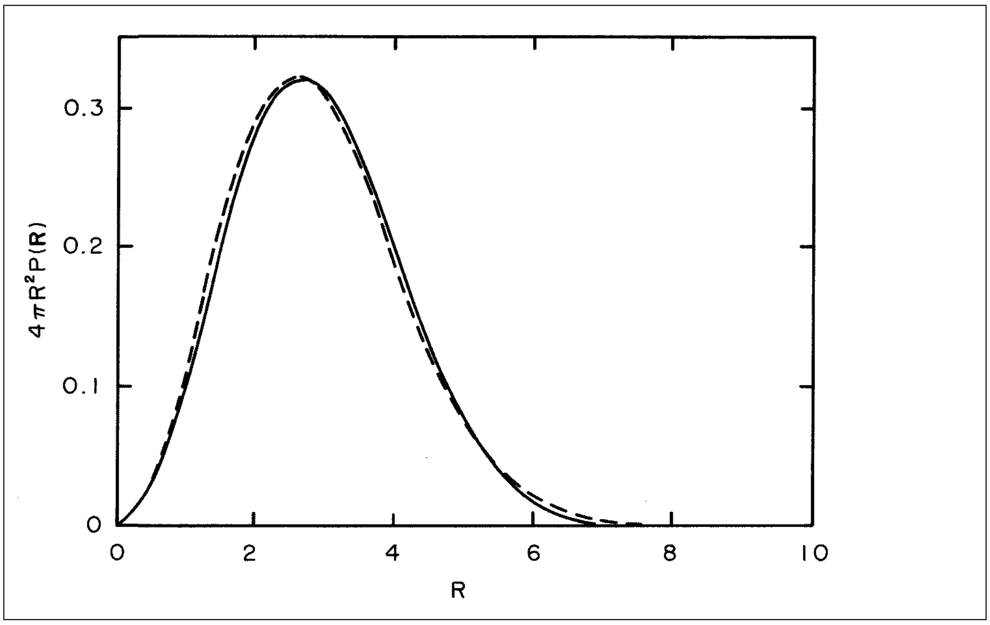

**Fig. II.3.** Comparison of the distribution functions of the end-to-end distances of an exact random-flight chain and of a Gaussian chain, each with $a = 1$ Å and $n = 10$. Full curve: exact random-flight chain. Broken curve: Gaussian chain.

chains, by the Gaussian chain in the theoretical treatment of the properties of dilute polymer solutions. The reasons for this may be summarized as follows: (1) the deviation of the Gaussian distribution from the exact one is small over the range ordinarily of interest, (2) the Gaussian distribution gives the exact value for the mean-square end-to-end distance (the deviation at high extensions has no influence on average chain dimensions), and (3) various calculations can be greatly simplified by the use of the Gaussian distribution, in particular, the Gaussian bond probability.

## 6. The Wang-Uhlenbeck Method for Multivariate Gaussian Distributions

This method is an extension of Markoff's method in the particular case for which the distribution function $\tau_j(\mathbf{r}_j)$ is given by the Gaussian function,

$$\tau_j(\mathbf{r}_j) = \left(\frac{3}{2\pi a_j^2}\right)^{3/2} \exp\left(-\frac{3r_j^2}{2a_j^2}\right), \tag{6.1}$$

where all $a_j$ are assumed not to be equal, for convenience. Let us consider $ns$, three-dimensional vectors $\boldsymbol{\phi}_{kj}$ defined by

$$\boldsymbol{\phi}_{kj} = \psi_{kj}\mathbf{r}_j \qquad \begin{pmatrix} j = 1,\ 2,\ \ldots,\ n \\ k = 1,\ 2,\ \ldots,\ s;\ s \leq n \end{pmatrix}, \tag{6.2}$$

where the $\psi_{kj}$ are constants, and the components of each of these vectors are just functions of $x_j$, $y_j$, and $z_j$ as before. The problem is to find the multivariate distribution function $P(\{\boldsymbol{\Phi}_s\}) = P(\boldsymbol{\Phi}_1, \ldots, \boldsymbol{\Phi}_s)$ or the simultaneous probability density of $s$ resultant vectors,

$$\boldsymbol{\Phi}_k = \sum_{j=1}^{n} \boldsymbol{\phi}_{kj} = \sum_{j=1}^{n} \psi_{kj}\mathbf{r}_j \qquad (k = 1,\ 2,\ \ldots,\ s), \tag{6.3}$$

each being a linear combination of $n$ vectors $\mathbf{r}_j$. The problem in the case of a one-dimensional $r_j$ was formulated first by Wang and Uhlenbeck,[15] and the extension to the three-dimensional case was made by Fixman.[16] Before solving this problem, we note that $P(\{\boldsymbol{\Phi}_s\})$ is normalized as

$$\int P(\{\boldsymbol{\Phi}_s\})d\{\boldsymbol{\Phi}_s\} = 1, \tag{6.4}$$

and that the distribution function $P(\{\boldsymbol{\Phi}_r\})$ of a subset $\{\boldsymbol{\Phi}_r\}$ of the set $\{\boldsymbol{\Phi}_s\}$ is given by

$$P(\{\boldsymbol{\Phi}_r\}) = \int P(\{\boldsymbol{\Phi}_s\})\frac{d\{\boldsymbol{\Phi}_s\}}{d\{\boldsymbol{\Phi}_r\}}, \tag{6.5}$$

Now we many write $P(\{\boldsymbol{\Phi}_s\})$ in the form,

$$P(\{\boldsymbol{\Phi}_s\}) = \int \left[\prod_{j=1}^{n} \tau_j(\mathbf{r}_j)\right] \frac{d\{\mathbf{r}_n\}}{d\{\boldsymbol{\Phi}_s\}}, \tag{6.6}$$

which, by the use of Eq. (6.1) and $s$, three-dimensional Dirac delta functions, reduces to

$$\begin{aligned} P(\{\boldsymbol{\Phi}_s\}) = (2\pi)^{-3s} \int \prod_{j=1}^{n} &\left(\frac{3}{2\pi a_j{}^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{r}_j{}^2}{2a_j{}^2}\right) d\mathbf{r}_j \\ &\times \prod_{k=1}^{s} \exp\left[i\boldsymbol{\rho}_k \cdot \left(\sum_{j=1}^{n} \psi_{kj}\mathbf{r}_j - \boldsymbol{\Phi}_k\right)\right] d\boldsymbol{\rho}_k . \end{aligned} \tag{6.7}$$

That is,

$$P(\{\boldsymbol{\Phi}_s\}) = (2\pi)^{-3s} \int K(\{\boldsymbol{\rho}_s\}) \exp\left(-i\sum_{k=1}^{s} \boldsymbol{\rho}_k \cdot \boldsymbol{\Phi}_k\right) d\{\boldsymbol{\rho}_s\} \tag{6.8}$$

with

$$K(\{\boldsymbol{\rho}_s\}) = \prod_{j=1}^{n} \left(\frac{3}{2\pi a_j{}^2}\right)^{3/2} \int \exp\left(-\frac{3\mathbf{r}_j{}^2}{2a_j{}^2} + i\sum_{k=1}^{s} \psi_{kj}\boldsymbol{\rho}_k \cdot \mathbf{r}_j\right) d\mathbf{r}_j . \tag{6.9}$$

In this case, the characteristic function $K\big(\{\boldsymbol{\rho}_s\}\big)$ is the $3s$-dimensional Fourier transform of the distribution function $P\big(\{\boldsymbol{\Phi}_s\}\big)$;

$$K\big(\{\boldsymbol{\rho}_s\}\big) = \int P\big(\{\boldsymbol{\Phi}_s\}\big) \exp\left(i\sum_{k=1}^{s} \boldsymbol{\rho}_k \cdot \boldsymbol{\Phi}_k\right) d\{\boldsymbol{\Phi}_s\}\,. \tag{6.10}$$

The integral in Eq. (6.9) can be easily evaluated to give

$$K\big(\{\boldsymbol{\rho}_s\}\big) = \exp\left[-\tfrac{1}{6}\langle a^2\rangle \sum_{k=1}^{s}\sum_{l=1}^{s} C_{kl}\boldsymbol{\rho}_k \cdot \boldsymbol{\rho}_l\right], \tag{6.11}$$

where

$$C_{kl} = \sum_{j=1}^{n} \psi_{kj}\psi_{lj}\frac{{a_j}^2}{\langle a^2\rangle}\,, \tag{6.12}$$

$$\langle a^2\rangle = \frac{1}{n}\sum_{j=1}^{n} {a_j}^2\,. \tag{6.13}$$

Substitution of Eq. (6.11) into Eq. (6.8) leads to

$$\begin{aligned} P\big(\{\boldsymbol{\Phi}_s\}\big) = (2\pi)^{-3s} \int \exp\biggl[-\frac{1}{6}\langle a^2\rangle \sum_{k=1}^{s}\sum_{l=1}^{s} C_{kl}\boldsymbol{\rho}_k \cdot \boldsymbol{\rho}_l \\ -i\sum_{k=1}^{s} \boldsymbol{\rho}_k \cdot \boldsymbol{\Phi}_k\biggr] d\{\boldsymbol{\rho}_s\}\,. \end{aligned} \tag{6.14}$$

After an orthogonal transformation of the coordinates the integral in Eq. (6.14) can readily be evaluated, and we obtain the final result (see Appendix II B),

$$\begin{aligned} P\big(\{\boldsymbol{\Phi}_s\}\big) = \left(\frac{3}{2\pi\langle a^2\rangle}\right)^{3s/2} |\mathbf{C}|^{-3/2} \\ \times \exp\biggl[-\left(\frac{3}{2\langle a^2\rangle|\mathbf{C}|}\right)\sum_{k=1}^{s}\sum_{l=1}^{s} C^{kl}\boldsymbol{\Phi}_k \cdot \boldsymbol{\Phi}_l\biggr], \end{aligned} \tag{6.15}$$

where $C^{kl}$ is the cofactor of the element $C_{kl}$ of the $s \times s$ symmetric matrix $\mathbf{C}$, and $|\mathbf{C}|$ is the determinant of $\mathbf{C}$. That is, $P\big(\{\boldsymbol{\Phi}_s\}\big)$ is a multivariate Gaussian distribution.

In the particular case of $s = 1$ and $a_j = a$ for all $j$, Eq. (6.15) reduces to

$$P(\boldsymbol{\Phi}) = \left(\frac{3}{2\pi C a^2}\right)^{3/2} \exp\left(-\frac{3\Phi^2}{2Ca^2}\right) \tag{6.16}$$

with

$$\boldsymbol{\Phi} = \sum_{j=1}^{n} \psi_j \mathbf{r}_j\,, \tag{6.17}$$

$$C = \sum_{j=1}^{n} {\psi_j}^2 \,. \tag{6.18}$$

This result can also be obtained by direct application of Markoff's method. Further, if $\psi_j = 1$ for all $j$, then $C = n$ and Eq. (6.16) reduces to Eq. (5.32).

It will be seen that Eq. (6.15) is of considerable value in developing the theories of the excluded-volume effect (Chapter III) and of the second virial coefficient (Chapter IV), based on the cluster-expansion method.

## 7. Distribution of a Segment About the Center of Mass and Related Quantities

We now proceed to examine the distribution of segments about the center of mass of a polymer chain. The results of this study provide another important measure of the average molecular dimensions, directly related to the properties of dilute solutions. Evaluation of distribution functions will be carried out on the assumption of the Gaussian bond probability of Eq. (5.35). Needless to say, in the present case, the molecular center of mass, instead of segment 0, may be considered to be fixed at the origin.

### 7a. Distribution of a Segment About the Center of Mass

We first consider the distribution function $P_j(\mathbf{S}_j)$ of the distance $\mathbf{S}_j$ from the center of mass to segment $j$. Obviously there is a relation between $\mathbf{S}_j$ and the bond vectors $\mathbf{r}_k$,

$$\begin{aligned} \mathbf{S}_j - \mathbf{S}_i &= \sum_{k=i+1}^{j} \mathbf{r}_k \qquad \text{for } j > i \,, \\ &= -\sum_{k=j+1}^{i} \mathbf{r}_k \quad \text{for } j < i \,. \end{aligned} \tag{7.1}$$

If all the segments have the same mass, by the definition of the center of mass the sum of all the $\mathbf{S}_j$ must be zero,

$$\sum_{i=0}^{n} \mathbf{S}_i = 0 \,. \tag{7.2}$$

By summation of both sides of Eq. (7.1) over $i$, we obtain

$$\mathbf{S}_j = \sum_{i=1}^{n} \psi_{ji} \mathbf{r}_i \tag{7.3}$$

with

$$\psi_{ji} = H(j-i) + \frac{i}{n+1} - 1 \tag{7.4}$$

where $H(x)$ is a unit step function defined as

$$\begin{aligned} H(x) &= 1 \qquad && \text{for } x \geq 0\,, \\ &= 0 && \text{for } x < 0\,. \end{aligned} \tag{7.5}$$

The use of Eq. (6.16) with $\mathbf{\Phi} = \mathbf{S}_j$ and $\psi_j = \psi_{ji}$ leads to

$$P_j(\mathbf{S}_j) = \left(\frac{3}{2\pi\langle {S_j}^2\rangle}\right)^{3/2} \exp\left(-\frac{3{S_j}^2}{2\langle {S_j}^2\rangle}\right) \tag{7.6}$$

with

$$\langle {S_j}^2\rangle = a^2 \sum_{i=1}^{n} {\psi_{ji}}^2\,. \tag{7.7}$$

Since $n$ is large, the summation may be replaced by integration,* and $\langle {S_j}^2\rangle$ can then be evaluated to be

$$\langle {S_j}^2\rangle = \tfrac{1}{3}na^2\left[1 - \frac{3j(n-j)}{n^2}\right]\,. \tag{7.8}$$

Equation (7.6) with (7.8) is the formula obtained by Isihara[17] and by Debye and Bueche.[18] It is seen from Eq. (7.8) that $\langle {S_j}^2\rangle$ takes the maximum value $\frac{1}{3}na^2$ at $j = 0$ or $n$, and the minimum value $\frac{1}{12}na^2$ at $j = \frac{1}{2}n$. In other words, the end segments are located, on the average, at the positions most remote from the center of mass, while the middle segment is nearest to the center of mass.

The function $P_j(\mathbf{S}_j)$ has the meaning of a *specific* distribution function, since $P_j(\mathbf{S}_j)d\mathbf{S}_j$ is the probability of finding a particular segment (the $j$th segment) in the volume element $d\mathbf{S}_j$ at the distance $\mathbf{S}_j$ from the center of mass. On the other hand, a *generic* distribution function $\rho(\mathbf{s})$ is defined as

$$\rho(\mathbf{s}) = \sum_{j=0}^{n} P_j(\mathbf{s}) \tag{7.9}$$

with the normalization condition,

$$\int \rho(\mathbf{s})d\mathbf{s} = n\,. \tag{7.10}$$

That is, $\rho(\mathbf{s})d\mathbf{s}$ is the probability of finding any one of $n$ segments in the volume element $d\mathbf{s}$ at the distance $\mathbf{s}$ from the center of mass; in other words, $\rho(\mathbf{s})$ is the average segment density at $\mathbf{s}$. This function is referred to as the *segment-density distribution function.* It is sometimes convenient to use the distribution function $P(\mathbf{s})$ defined by

$$P(\mathbf{s}) = n^{-1}\rho(\mathbf{s})\,, \tag{7.11}$$

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*The summations of a function of the indices $i$, $j$, ... will be replaced by integrations throughout the remainder of this book except where specified otherwise. In addition, small numbers occurring in such a function will be suppressed compared to $n$.

so that $P(\mathbf{s})$ satisfies the ordinary normalization condition, as defined by Eq. (3.10).

Now $P(\mathbf{s})$ may be written in the form,

$$P(\mathbf{s}) = \frac{1}{n} \sum_j \left( \frac{3}{2\pi \langle S_j{}^2 \rangle} \right)^{3/2} \exp\left( -\frac{3s^2}{2\langle S_j{}^2 \rangle} \right) . \tag{7.12}$$

Using Eq. (5.33), the moments of $P(\mathbf{s})$ can readily be expressed as

$$\langle s^{2p} \rangle = \frac{(2p+1)!}{6^p p! n} \sum_j \langle S_j{}^2 \rangle^p . \tag{7.13}$$

Substituting Eq. (7.8) into Eq. (7.13) and carrying out the summation (integration), we have

$$\langle s^{2p} \rangle = \frac{(2p+1)!}{2^p \cdot 6^{2p} \cdot p!} \left[ \sum_{l=0}^{p} \binom{p}{l} \frac{3^l}{2l+1} \right] (na^2)^p . \tag{7.14}$$

The first three moments are

$$\begin{aligned} \langle s^2 \rangle &= \tfrac{1}{6} na^2 = \tfrac{1}{6} \langle R^2 \rangle , \\ \langle s^4 \rangle &= \frac{1}{18} (na^2)^2 = \frac{1}{30} \langle R^4 \rangle , \\ \langle s^6 \rangle &= \frac{29}{972} (na^2)^3 = \frac{29}{3780} \langle R^6 \rangle . \end{aligned} \tag{7.15}$$

The form of the distribution function $P(\mathbf{s})$ will be considered in Section 8a.

## 7b. Radius of Gyration

We define the *radius of gyration* $S$ of a polymer chain by the equation,*

$$S^2 = \frac{1}{n} \sum_j S_j{}^2 . \tag{7.16}$$

From Eq. (7.13), the mean-square radius of gyration can then be easily obtained as[19]

$$\langle S^2 \rangle = \tfrac{1}{6} \langle R^2 \rangle = \langle s^2 \rangle . \tag{7.17}$$

This is an important relationship between the mean-square radius of gyration and the mean-square end-to-end distance, indicating their interchangeability. However, it is the former that has a direct relation to the solution properties, as will be seen in later chapters. It must be noted that the distribution function, $P(S)$, of the radius of gyration is

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*The term radius of gyration is used in physics with a different meaning, namely, the mean of the square of the radius of a body about an *axis* (not a center). However, to avoid confusion, in this book we shall often use this incorrect nomenclature which is widely used in the extant literatures. Note that $S$ is a scalar.

essentially different from the distribution function $4\pi s^2 P(\mathbf{s})$ of $s$; the form of $P(S)$ will be discussed in Section 8b. For convenience, $s$ will be called the *quasi-radius of gyration*.

Now we derive two other useful formulas for the radius of gyration. From Eqs. (7.7) and (7.16), we have

$$\langle S^2 \rangle = \frac{a^2}{n} \sum_i \sum_j \psi_{ji}^{\ 2} \,. \tag{7.18}$$

On performing the summation only over $j$ after substitution of Eq. (7.4), Eq. (7.18) becomes

$$\langle S^2 \rangle = \frac{a^2}{n^2} \sum_i i(n-i) \,. \tag{7.19}$$

This is the formula derived by Kramers.[20] The meaning of this formula is the following: divide the chain at segment $i$ into two parts, and $\langle S^2 \rangle$ can then be evaluated by summing up the product of the numbers of segments contained in the two parts over all possible divisions. Of course, summation over $i$ in Eq. (7.19) recovers Eq. (7.17).

By definition, there holds the relation,

$$\sum_i \sum_j \mathbf{S}_i \cdot \mathbf{S}_j = 0 \,. \tag{7.20}$$

On the other hand, from the rule of cosines,

$$\mathbf{S}_i \cdot \mathbf{S}_j = \tfrac{1}{2}({S_i}^2 + {S_j}^2 - R_{ij}^{\ 2}) \,,$$

we have

$$\begin{aligned} \sum_i \sum_j \mathbf{S}_i \cdot \mathbf{S}_j &= \frac{n}{2} \sum_i {S_i}^2 + \frac{n}{2} \sum_j {S_j}^2 - \frac{1}{2} \sum_i \sum_j R_{ij}^{\ 2} \\ &= n^2 S^2 - \frac{1}{2} \sum_i \sum_j R_{ij}^{\ 2} \,. \end{aligned} \tag{7.21}$$

From Eqs. (7.20) and (7.21), we obtain

$$S^2 = \frac{1}{2n^2} \sum_i \sum_j R_{ij}^{\ 2} = \frac{1}{n^2} \sum_{i<j}\sum R_{ij}^{\ 2} \,. \tag{7.22}$$

This is the formula derived by Zimm and Stockmayer.[21] On performing the summations after substitution of Eq. (5.39), Eq. (7.22) reduces to Eq. (7.17).

It must be noted that both Eqs. (7.19) and (7.22) hold for branched chains as well as linear chains when the segments are numbered in a proper order (Section 9a). Further, application of Eq. (7.19) is confined to polymer chains which obey random-flight statistics, whereas there is no restriction in the application of Eq. (7.22).

## 7c. Radii of Gyration with **R** Fixed

By the definition of a conditional probability, the distribution function $P_j(\mathbf{S}_j|\mathbf{R})$ of $\mathbf{S}_j$ with the end-to-end vector $\mathbf{R}$ fixed is given by

$$P_j(\mathbf{S}_j|\mathbf{R}) = \frac{P_j(\mathbf{S}_j, \mathbf{R})}{P(\mathbf{R})} \tag{7.23}$$

with the normalization condition,

$$\int P_j(\mathbf{S}_j|\mathbf{R}) d\mathbf{S}_j = 1 \,. \tag{7.24}$$

The bivariate distribution function $P_j(\mathbf{S}_j, \mathbf{R})$ may be evaluated by means of the Wang–Uhlenbeck theorem (Section 6). After a simple algebraic calculation with the use of Eqs. (3.8) and (7.3) with (7.4), we can readily obtain, from Eqs. (6.15) and (7.23),

$$P_j(\mathbf{S}_j|\mathbf{R}) = \left[\frac{3}{2\pi(na^2/12)}\right]^{3/2} \exp\left[-\frac{3L^2}{2(na^2/12)}\right] \tag{7.25}$$

with

$$\mathbf{L} = \mathbf{S}_j + \frac{1}{2n}(n-2j)\mathbf{R} \,, \tag{7.26}$$

where we have used Eq. (5.32).

Now suppose a Cartesian coordinate system $(\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z)$ to be fixed in space, $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ being the unit vectors in the directions of the $x$, $y$, $z$ axes, respectively. Then the mean-square component $\langle(\mathbf{S}_j \cdot \mathbf{e}_x)^2\rangle_{\mathbf{R}}$ of $\mathbf{S}_j$ in the direction of the $x$ axis with $\mathbf{R}$ fixed can be evaluated, from Eq. (7.25) with (7.26), as

$$\begin{aligned} \left\langle(\mathbf{S}_j \cdot \mathbf{e}_x)^2\right\rangle_{\mathbf{R}} &= \int (\mathbf{S}_j \cdot \mathbf{e}_x)^2 P_j(\mathbf{S}_j|\mathbf{R}) d\mathbf{S}_j \\ &= \int \left[(\mathbf{L}\cdot\mathbf{e}_x)^2 + \frac{1}{4n^2}(n-2j)^2(\mathbf{R}\cdot\mathbf{e}_x)^2\right] P_j(\mathbf{S}_j|\mathbf{R}) d\mathbf{L} \\ &= \frac{1}{36}na^2 + \frac{1}{4n^2}(n-2j)^2(\mathbf{R}\cdot\mathbf{e}_x)^2 \,. \end{aligned} \tag{7.27}$$

Defining the mean-square radius of gyration $\langle {S_x}^2\rangle_{\mathbf{R}}$ in the direction of the $x$ axis with $\mathbf{R}$ fixed by the equation,

$$\langle {S_x}^2\rangle_{\mathbf{R}} = \frac{1}{n}\sum_j \left\langle(\mathbf{S}_j \cdot \mathbf{e}_x)^2\right\rangle_{\mathbf{R}} \,, \tag{7.28}$$

We obtain, from Eqs. (7.27) and (7.28),

$$\langle {S_x}^2\rangle_{\mathbf{R}} = \frac{1}{36}na^2\left[1 + \frac{3(\mathbf{R}\cdot\mathbf{e}_x)^2}{na^2}\right] \,. \tag{7.29}$$

Since similar results apply to the $y$ and $z$ components, respectively, we have for the mean-square radius of gyration $\langle S^2\rangle_{\mathbf{R}}$ with $\mathbf{R}$ fixed

$$\begin{aligned}\langle S^2\rangle_{\mathbf{R}} &= \langle {S_x}^2\rangle_{\mathbf{R}} + \langle {S_y}^2\rangle_{\mathbf{R}} + \langle {S_z}^2\rangle_{\mathbf{R}} \\ &= \frac{1}{12}na^2\left(1+\frac{R^2}{na^2}\right) , \end{aligned} \tag{7.30}$$

which reduces to Eq. (7.17), averaged over all values of $\mathbf{R}$. Equations (7.29) and (7.30) are the formulas derived by Hermans and Overbeek[22] using a different method.

In particular, if the $x$ axis is chosen in the direction of $\mathbf{R}$, the three components of $\langle S^2\rangle_{\mathbf{R}}$ become

$$\begin{aligned}\langle {S_x}^2\rangle_{\mathbf{R}} &= \frac{1}{36}na^2\left(1+\frac{3R^2}{na^2}\right) , \\ \langle {S_y}^2\rangle_{\mathbf{R}} &= \langle {S_z}^2\rangle_{\mathbf{R}} = \frac{1}{36}na^2 \end{aligned} \tag{7.31}$$

with $\mathbf{R} = R\mathbf{e}_x$. Thus, when the end segments are fixed, the distribution of segments about the center of mass is no longer spherically symmetric, but may be regarded as approximately ellipsoidal, the major axis of this ellipsoid being in the direction of the end-to-end vector. In this connection, Eq. (7.25) is also to be compared with Eq. (7.6) or (7.12). At full extension of the chain ($R = na$), the component of $\langle S^2\rangle_{\mathbf{R}}$ in the direction of $\mathbf{R}$ takes the value $(na)^2/12$, which is the exact value for $\langle S^2\rangle = \langle {S_x}^2\rangle_{\mathbf{R}}$ of the rod of length $na$. The components perpendicular to $\mathbf{R}$ are predicted to be independent of $R$, whereas the exact values are zero for the rod. Clearly this discrepancy is due to the use of a Gaussian bond probability.

## 8. Distribution of the Radius of Gyration

In this section, we shall discuss the forms of the distribution functions $P(\mathbf{s})$ and $P(S)$. In anticipation of the results, however, we note that closed expressions for neither $P(\mathbf{s})$ nor $P(S)$ can be derived, which are valid over the whole range, even for the Gaussian chain.

### 8a. Distribution of the Quasi-radius of Gyration

The original discussion of the form of the distribution function $P(\mathbf{s})$ of the quasi-radius of gyration $\mathbf{s}$ is due to Debye and Bueche.[18] Replacing the summation by integration in Eq. (7.12), we obtain for $P(\mathbf{s})$ the series forms,

$$\begin{aligned}P(\mathbf{s}) = 2^{1/2}&\left(\frac{3}{2\pi\langle s^2\rangle}\right)^{3/2}\exp\left(-\frac{3t}{4}\right) \\ &\times\left[1-\frac{1}{1\cdot 3}\left(\frac{9t}{2}\right)+\frac{1}{1\cdot 3\cdot 5}\left(\frac{9t}{2}\right)^2-\cdots\right] \quad \text{for small } t\,, \end{aligned} \tag{8.1}$$

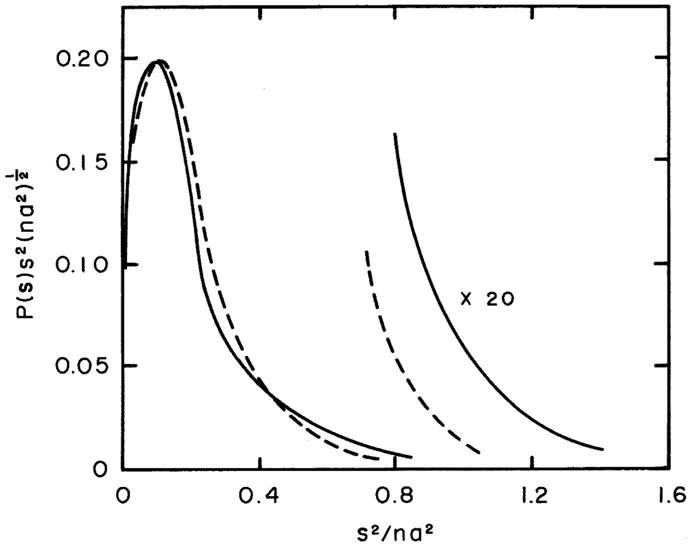

**Fig. II.4.** Comparison of the exact distribution and the approximate Gaussian distribution of the quasi-radius of gyration of a polymer chain. Full curve: exact. Broken curve: approximate.

$$P(\mathbf{s}) = 2^{1/2}\left(\frac{3}{2\pi\langle s^2\rangle}\right)^{3/2}\exp\left(-\frac{3t}{4}\right)\left(\frac{2}{9t}\right)$$
$$\times\left[1+\left(\frac{2}{9t}\right)+1\cdot 3\left(\frac{2}{9t}\right)^2+1\cdot 3\cdot 5\left(\frac{2}{9t}\right)^3+\cdots\right] \quad \text{for large } t\,, \tag{8.2}$$

where

$$t \equiv \frac{s^2}{\langle s^2\rangle} = \frac{6s^2}{na^2}\,. \tag{8.3}$$

The integration has also been carried out graphically, and the result is displayed by the full curve in Fig. II.4. For comparison, the Gaussian distribution of **s**,

$$\left(\frac{3}{2\pi\langle s^2\rangle}\right)^{3/2}\exp\left(-\frac{3\mathbf{s}^2}{2\langle s^2\rangle}\right), \tag{8.4}$$

the second moment of which coincides with that of $P(\mathbf{s})$, is also plotted in the figure.

As seen from Eqs. (8.1) and (8.2) and Fig. II.4, the distribution of the quasi-radius of gyration is not strictly Gaussian in the same approximation which is employed in obtaining the Gaussian distribution of the end-to-end distance and of the distance from the center of mass to a particular segment. However, the agreement between the *exact* distribution and the *approximate* Gaussian distribution is fairly satisfactory except at large values of $s$. Thus the Gaussian approximation for $P(\mathbf{s})$ will still be useful insofar as the dilute-solution properties are described in a crude approximation.

## 8b. Distribution of the Radius of Gyration

The distribution function $P(S)$ of the radius of gyration was first investigated by Fixman[23] and by Forsman and Hughes.[24] For convenience, we describe the procedure of Fixman. However, it should be anticipated that Fixman's calculation involves some error, and the complete numerical results have recently been obtained by Koyama,[25] by Hoffman and Forsman,[26] and by Fujita and Norisuye.[27] The conditional segment-density distribution function with $S$ fixed will also be discussed in Appendix II C. In this section, it is therefore convenient to begin with a formulation of the bivariate distribution function $P_j(\mathbf{S}_j, S^2)$ rather than the desired function $P(S)$. The distribution function $P(S^2)$ of $S^2$ can be obtained from

$$P(S^2) = \int P_j(\mathbf{S}_j, S^2) d\mathbf{S}_j \,. \tag{8.5}$$

Evidently the probability $P(S)dS$ that $S$ lies between $S$ and $S + dS$ is equal to $P(S^2)dS^2$, and we therefore have the relation,

$$P(S) = 2SP(S^2) \,. \tag{8.6}$$

Now, $\mathbf{S}_j$ is given by the linear combination (7.3) of $n$ bond vectors $\mathbf{r}_j$, while from Eqs. (7.3), (7.4), and (7.16) $S^2$ is given by the quadratic form,

$$S^2 = \sum_{k=1}^{n} \sum_{l=1}^{n} g_{kl} \mathbf{r}_k \cdot \mathbf{r}_l \tag{8.7}$$

with

$$\begin{aligned} g_{kl} &= \frac{1}{n} \sum_{j} \psi_{jk} \psi_{jl} = g_{lk} \\ &= n^{-2} \big\{ n \big[ kh(l-k) + lh(k-l) \big] - kl \big\} \,, \end{aligned} \tag{8.8}$$

where $h(x)$ is a unit step function defined as

$$\begin{aligned} h(x) &= 1 \qquad && \text{for } x > 0 \,, \\ &= \tfrac{1}{2} && \text{for } x = 0 \,, \\ &= 0 && \text{for } x < 0 \,. \end{aligned} \tag{8.9}$$

The distribution function $P_j(\mathbf{S}_j, S^2)$ may be written in the form,

$$P_j(\mathbf{S}_j, S^2) = \int \left[ \prod_{j=1}^{n} \tau(\mathbf{r}_j) \right] \frac{d\{\mathbf{r}_n\}}{d\mathbf{S}_j dS^2} \,, \tag{8.10}$$

where we assume the Gaussian bond probability. The range of $S^2$ is taken as $-\infty < S^2 < +\infty$ in the absence of an explicit demonstration that Eq. (8.10) yields the inevitable result, $P_j(\mathbf{S}_j, S^2) \equiv 0$ for $S^2 < 0$. By a slight modification of the Wang–Uhlenbeck method, the integral of (8.10) can be treated easily.

Introducing Fourier representations of the one-and three-dimensional Dirac delta functions and using Eqs. (7.3) and (8.7), we may rewrite Eq. (8.10) in the form,

$$P_j(\mathbf{S}_j, S^2) = (2\pi)^{-4} \int K_j(\boldsymbol{\sigma}, \rho) \exp(-i\rho S^2 - i\boldsymbol{\sigma} \cdot \mathbf{S}_j) d\boldsymbol{\sigma}\, d\rho \tag{8.11}$$

with

$$K_j(\boldsymbol{\sigma}, \rho) = \left(\frac{3}{2\pi a^2}\right)^{3n/2} \int \exp\left[-\frac{3}{2a^2} \sum_k {r_k}^2 \right.$$
$$\left. + i\rho \sum_k \sum_l g_{kl} \mathbf{r}_k \cdot \mathbf{r}_l + i \sum_k \psi_{jk} \boldsymbol{\sigma} \cdot \mathbf{r}_k \right] d\{\mathbf{r}_n\} \,. \tag{8.12}$$

A resolution of the $\mathbf{r}_k$ and $\boldsymbol{\sigma}$ into $x$, $y$, and $z$ components simplifies the evaluation of the integral in Eq. (8.12). That is,

$$K_j(\boldsymbol{\sigma}, \rho) = \left(\frac{3}{2\pi a^2}\right)^{3n/2} \prod_{x,y,z} \Gamma_j(\sigma_x, \rho) \tag{8.13}$$

with

$$\Gamma_j(\sigma_x, \rho) = \int \exp\left[-\sum_k \sum_l A_{kl} x_k x_l + i\sigma_x \sum_k \psi_{jk} x_k\right] dx_1 \cdots dx_n \,, \tag{8.14}$$

$$A_{kl} = \left(\frac{3}{2a^2}\right) \delta_{kl} - i\rho g_{kl} \,, \tag{8.15}$$

where $\delta_{kl}$ is the Kronecker delta. The integral of (8.14) is of a form similar to that of Eq. (6.14), and therefore it can be easily evaluated by an orthogonal transformation of the coordinates (Appendix II B). If $\lambda_k$ are the eigenvalues of the matrix $\mathbf{A}$ with elements $A_{kl}$ and $\boldsymbol{\psi}_j$ is the column vector of the $\psi_{jk}$ with transpose ${\boldsymbol{\psi}_j}^T = (\psi_{j1} \cdots \psi_{jn})$, an orthogonal transformation $\mathbf{Q}$ which diagonalizes $\mathbf{A}$ gives

$$\Gamma_j(\sigma_x, \rho) = \prod_{k=1}^{n} \int_{-\infty}^{+\infty} \exp\left[-\lambda_k {\xi_k}^2 + i\sigma_x ({\boldsymbol{\psi}_j}^T \mathbf{Q})_k \xi_k\right] d\xi_k \,. \tag{8.16}$$

As shown below, the real parts of the $\lambda_k$ are all positive, and hence the integral in Eq. (8.16) is convergent. Thus we find

$$\Gamma_j(\sigma_x, \rho) = \pi^{n/2} \left(\prod_{k=1}^{n} {\lambda_k}^{-1/2}\right) \exp\left[-\frac{{\sigma_x}^2}{4} \sum_k {\lambda_k}^{-1} ({\boldsymbol{\psi}_j}^T \mathbf{Q})_k^2\right] . \tag{8.17}$$

From Eqs. (8.13) and (8.17), the characteristic function $K_j(\boldsymbol{\sigma}, \rho)$ is obtained as

$$K_j(\boldsymbol{\sigma}, \rho) = K(\rho) \exp(-W_j \sigma^2) \tag{8.18}$$

with

$$K(\rho) = K_j(0, \rho) = \left(\frac{3}{2a^2}\right)^{3n/2} \prod_{k=1}^{n} \lambda_k{}^{-3/2}\,, \tag{8.19}$$

$$\begin{aligned} W_j &= \frac{1}{4} \sum_{k=1}^{n} \lambda_k{}^{-1} (\boldsymbol{\psi}_j{}^T \mathbf{Q})_k{}^2 \\ &= \frac{1}{4} \sum_k \lambda_k{}^{-1} \left( \sum_l \psi_{jl} Q_{lk} \right)^2 , \end{aligned} \tag{8.20}$$

where the $Q_{kl}$ are the normalized components of $\mathbf{Q}$. On substitution of Eq. (8.18) into Eq. (8.11) and integration over $\boldsymbol{\sigma}$, we have

$$P_j(\mathbf{S}_j, S^2) = (16\pi^{5/2})^{-1} \int K(\rho) W_j^{-3/2} \exp\left( -i\rho S^2 - \frac{S_j{}^2}{4W_j} \right) d\rho\,, \tag{8.21}$$

and integration over $\mathbf{S}_j$ gives

$$P(S^2) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} K(\rho) \exp(-iS^2\rho) d\rho\,. \tag{8.22}$$

Note that $K(\rho)$ given by Eq. (8.19) is the characteristic function of $P(S^2)$.

We now determine the eigenvalues of $\mathbf{A}$ and the normalized components of $\mathbf{Q}$. If $\mathbf{x}$ is an eigenvector of $\mathbf{A}$, we have

$$\mathbf{A}\mathbf{x} - \lambda \mathbf{x} = 0\,, \tag{8.23}$$

or

$$\sum_{j=1}^{n} A_{ij} x_j = \lambda x_i\,, \tag{8.24}$$

from which there must result $n$ different $\lambda$'s, $\lambda_k$, and $n$ different $x_i$'s, $x_i{}^{(k)}$. The orthogonal matrix $\mathbf{Q}$ may be composed of column vectors $x_i{}^{(k)}$, which form a complete and orthogonal set for functions determined at $n$ points, and

$$\sum_k x_i{}^{(k)} x_j{}^{(k)} = \sum_k x_k{}^{(i)} x_k{}^{(j)} = \delta_{ij}\,. \tag{8.25}$$

Now it proves convenient to convert Eq. (8.24) to an integral equation. This treatment of $i$ and $j$ as continuous variables naturally gives an infinite set of eigenvalues and eigenfunctions from which the proper set may easily be extracted. With $x_i = x(z)$, $A_{ij} = A(z, y)$, and so on, where $z = i/n$ and $y = j/n$, Eqs. (8.8), (8.15), and (8.24) give

$$-\tfrac{3}{2} X^2 \left[ \int_0^z y x(y) dy + z \int_z^1 x(y) dy - z \int_0^1 y x(y) dy \right] = (a^2\lambda - \tfrac{3}{2}) x(z) \tag{8.26}$$

with

$$X^2 \equiv \tfrac{2}{3} i\rho n a^2 \,. \tag{8.27}$$

Equation (8.26) can be solved by two successive differentiations with respect to $z$;

$$-\tfrac{3}{2}X^2 \left[ \int_z^1 x(y)dy - \int_0^1 yx(y)dy \right] = (a^2\lambda - \tfrac{3}{2})x'(z) \,, \tag{8.28}$$

$$\tfrac{3}{2}X^2 x(z) = (a^2\lambda - \tfrac{3}{2})x''(z) \,. \tag{8.29}$$

Equation (8.29) has the solution,

$$x(z) = K_1 \exp\big[zX(\tfrac{2}{3}a^2\lambda - 1)^{-1/2}\big] + K_2 \exp\big[-zX(\tfrac{2}{3}a^2\lambda - 1)^{-1/2}\big] \,. \tag{8.30}$$

Substitution of Eq. (8.30) into Eqs. (8.26) and (8.28) gives

$$x(1) = x(0) = 0 \,. \tag{8.31}$$

The condition $x(0) = 0$ is satisfied by the choice $K_2 = -K_1$, and there results

$$x(z) = K \sin\big[izX(\tfrac{2}{3}a^2\lambda - 1)^{-1/2}\big] \,. \tag{8.32}$$

The condition $x(1) = 0$ then establishes the eigenvalues from the relation,

$$iX(\tfrac{2}{3}a^2\lambda - 1)^{-1/2} = k\pi \qquad (k = \pm 1,\ \pm 2,\ \ldots) \,, \tag{8.33}$$

that is

$$\lambda_k = \frac{3}{2a^2}\left(1 - \frac{X^2}{k^2\pi^2}\right) \,. \tag{8.34}$$

On transformation back from the continuous space of the eigenvectors $x(z)$ to the discrete space of $x_i$, it is evident that the values $k > n$ in Eq. (8.33) are redundant for the expansion of functions on $n$ points. Accordingly the original $n \times n$ matrix $\mathbf{A}$ has eigenvalues given by Eq. (8.34) with $k = 1, \ldots, n$. From Eqs. (8.32) and (8.34), we find for the eigenvectors

$$x_j^{(k)} = K \sin\left(\frac{\pi jk}{n}\right) \,, \tag{8.35}$$

which are just the components $Q_{jk}$ of the matrix $\mathbf{Q}$. The constant $K$ can be determined from Eq. (8.25) as

$$1 = \sum_{j=1}^{n} K^2 \sin^2\left(\frac{\pi jk}{n}\right) = \tfrac{1}{2}nK^2 \,, \tag{8.36}$$

that is,

$$K = \left(\frac{2}{n}\right)^{1/2} \,. \tag{8.37}$$

The normalized components of $\mathbf{Q}$ are therefore given by

$$Q_{jk} = \left(\frac{2}{n}\right)^{1/2} \sin\left(\frac{\pi jk}{n}\right) \,. \tag{8.38}$$

From Eqs. (8.19) and (8.34), we can now obtain for the characteristic function $K(\rho)$

$$K(\rho) = \prod_{k=1}^{n} \left(1 - \frac{X^2}{k^2\pi^2}\right)^{-3/2} . \tag{8.39}$$

It can be shown that the product in Eq. (8.39) may be extended to $k = \infty$ without introduction of any significant error if $n \gg 1$. Then Eq. (8.39) becomes

$$K(\rho) = \left(\frac{\sin X}{X}\right)^{-3/2} . \tag{8.40}$$

Before proceeding to evaluate the distribution function $P(S^2)$, we compute its moments. The logarithm of Eq. (8.40) can be expanded as

$$\ln K(\rho) = \sum_{j=1}^{\infty} \frac{2^{3j-2} B_j}{3^{j-1}(2j)!j} (na^2)^j (i\rho)^j , \tag{8.41}$$

where $B_j$ are the Bernoulli numbers ($B_1 = 1/6$, $B_2 = 1/30$, $\cdots$) as before. We therefore have for the cumulants $\kappa_j$

$$\kappa_j = \frac{2^{3j-2}(j-1)!B_j}{3^{j-1}(2j)!} (na^2)^j . \tag{8.42}$$

Substituting Eq. (8.42) into Eq. (5.7), we obtain for the moments $\mu_k = \langle S^{2k} \rangle$ of $P(S^2)$

$$\langle S^{2k} \rangle = k!(na^2)^k \sum_{\mathbf{m}} \frac{2^{3k-2m}}{3^{k-m}} \prod_{j=1}^{k} \frac{1}{m_j!} \left[\frac{B_j}{j(2j)!}\right]^{m_j} \tag{8.43}$$

with $\sum_j m_j = m$ and $\sum_j jm_j = k$. The first three moments are

$$\begin{aligned} \langle S^2 \rangle &= \tfrac{1}{6} na^2 , \\ \langle S^4 \rangle &= \frac{19}{540}(na^2)^2 = \frac{19}{15} \langle S^2 \rangle^2 , \\ \langle S^6 \rangle &= \frac{631}{68040}(na^2)^3 = \frac{631}{315} \langle S^2 \rangle^3 . \end{aligned} \tag{8.44}$$

It is important to observe that the second moments of the distributions of the radius of gyration and of the quasi-radius of gyration are identical, while the fourth and higher moments are different from each other.

We now turn to the evaluation of $P(S^2)$. Substitution of Eq. (8.40) into Eq. (8.22) leads to

$$P(S^2) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left(\frac{\sin X}{X}\right)^{-3/2} \exp(-\tfrac{1}{4}tX^2) d\rho , \tag{8.45}$$

where

$$t = \frac{S^2}{\langle S^2 \rangle} = \frac{6S^2}{na^2}\,. \tag{8.46}$$

Fujita and Norisuye[27] transformed the integral of (8.45) to a contour integral on the $X$ complex plane, and evaluated it exactly, although only in a series form. The derivation is so lengthy that we do not reproduce it here. If $P(S^2)$ is transformed back to $P(S)$, the result is

$$\begin{aligned} P(S) &= \frac{1}{2^{1/2}\pi \langle S^2 \rangle^{1/2} t^3} \sum_{k=0}^{\infty} \frac{(2k+1)!}{(2^k k!)^2} (4k+3)^{7/2} \exp(-t_k) \\ &\quad \times \left[ \left(1 - \frac{5}{8t_k}\right) K_{1/4}(t_k) + \left(1 - \frac{3}{8t_k}\right) K_{3/4}(t_k) \right] , \end{aligned} \tag{8.47}$$

where $K_s$ are the modified Bessel functions of the second kind and $t_k$ is defined by

$$t_k = \frac{(4k+3)^2}{8t}\,. \tag{8.48}$$

If we use the asymptotic expansions of $K_{1/4}$ and $K_{3/4}$, we have an expansion of $P(S)$ valid for small $t$,

$$\begin{aligned} P(S) &= 18 \left( \frac{6}{\pi \langle S^2 \rangle} \right)^{1/2} t^{-5/2} \exp\left( -\frac{9}{4t} \right) \\ &\quad \times \left( 1 - \frac{19}{36} t + \frac{105}{1296} t^2 - \cdots \right) \qquad \text{(for small } t\text{)}\,. \end{aligned} \tag{8.49}$$

The leading term of this expansion agrees with the result derived by Fixman[23] from Eq. (8.45) by the method of steepest descents.

On the other hand, it is impossible to derive an asymptotic form of $P(S)$ valid for large $t$ from Eq. (8.47). Thus, Fujita and Norisuye turned back to Eq. (8.45) and reevaluated the integral by the choice of a proper contour. The result is

$$\begin{aligned} P(S) &= \frac{2^{1/2}\pi^{5/2}}{\langle S^2 \rangle^{1/2}} t \exp\left( -\frac{\pi^2 t}{4} \right) \\ &\quad \times \left[ 1 + \frac{9}{4\pi^2} \left( \frac{1}{t} \right) + \frac{8\pi^2 + 15}{32\pi^4} \left( \frac{1}{t} \right)^2 + \cdots \right] \qquad \text{(for large } t\text{)}\,. \end{aligned} \tag{8.50}$$

The leading term of this expansion agrees with Forsman's result[24] derived by a different method, but does not agree with Fixman's result,[23]

$$P(S) = \frac{\pi^{5/2} e^{3/2}}{3 \langle S^2 \rangle^{1/2}} t \exp\left( -\frac{\pi^2 t}{4} \right) \qquad \text{(Fixman)}\,, \tag{8.51}$$

which has been derived by the method of steepest descents. However, the difference between the two results is rather small, since $2^{1/2} = 1.414$ and $e^{3/2}/3 = 1.494$. The error in Fixman's calculation arises from the

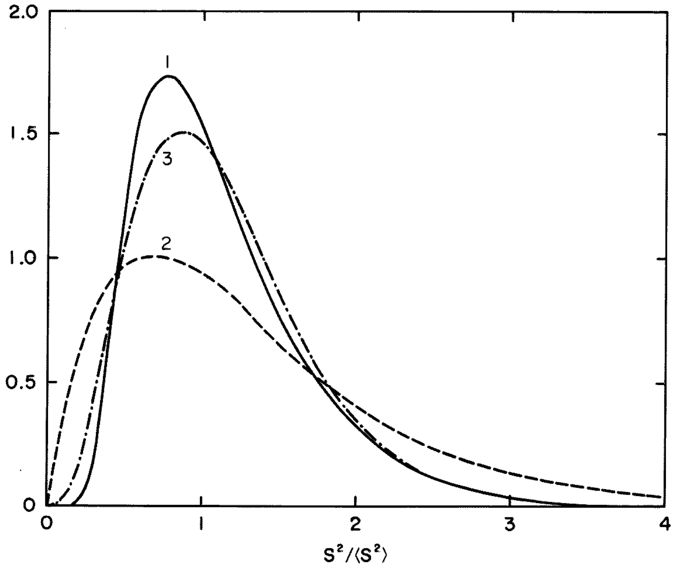

**Fig. II.5.** Comparison of the exact and approximate distributions of the radius of gyration of a polymer chain. Curve 1: exact. Curve 2: the Gaussian distribution. Curve 3: the Flory–Fisk function.

fact that the condition under which the method of steepest descents can be applied is not satisfied at the point he specified as the saddle point for $t \gg 1$. Note that $P(S)$ becomes a Gaussian function at large $S$, although the numerical coefficients are different from those of the usual Gaussian distribution function.

The values of $\langle S^2\rangle^{1/2}P(S)$ as a function of $t$ calculated from Eq. (8.47) are in excellent agreement with those calculated by Koyama[25] from Eq. (8.45) by the use of a computer, and are shown in curve 1 in Fig. II.5. For comparison, the Gaussian distribution of $S$ is shown in curve 2. It is seen that the exact distribution of $S$ converges extremely rapidly to zero at small $S$, and goes more rapidly to zero at large $S$ than does the Gaussian distribution, the former being sharper than the latter. Flory and Fisk[28] assumed as the closed form for $P(S)$

$$P(S) = \text{const. } \langle S^2\rangle^{-1/2} t^m \exp\left[-(m+\tfrac{1}{2})t\right] . \tag{8.52}$$

The value 3 was assigned to $m$, since this choice reproduces fairly well the exact moments of (8.44). Then the numerical constant in Eq. (8.52) is found to be $(343/15)(14/\pi)^{1/2}$. The normalized Flory–Fisk function is shown in curve 3 in Fig. II.5. This function is seen to represent fairly well the salient behavior of the exact distribution of $S$. Further discussion of $P(S)$ will be given in Chapter III.

## 9. Remarks

In this chapter, so far, we have described the mathematical details of the statistics of linear random-flight chains. Although the linear random-flight chain is the basic model in the theory of dilute polymer solutions, it is unrealistic and incomplete from the point of view of the structural restrictions or the conformational statistics of polymer chains. Thus, in this section, we shall describe the statistical properties of those chains which are not placed in a category termed the linear random-flight chain; that is, chains with short-range interferences, branches, or high stiffness.

### 9a. Short-Range Interferences and Unperturbed Molecular Dimensions

In order to make a random-flight chain model more realistic, account should be taken of the fact that the valence angle between successive bonds in the chain is actually a fixed quantity and the angle of rotation about each bond is not uniformly distributed owing to steric hindrances caused by interactions between atomic groups attached to the spine of the chain. In the case of vinyl polymers, for instance, the direction of a given C—C bond, for example, the $j$th bond, is most strongly affected by the direction of its predecessor, the $(j-1)$th bond, due to bond angle restrictions, and is also influenced to some extent by the directions of other neighbors, the $(j-2)$, …, $(j-s)$th bond, due to hindered rotations. It is clear that one bond has no appreciable influence upon the rotation of another bond when they are far apart, and therefore the value of $s$ is relatively small. This is the reason why such interactions between bonds are referred to as the *short-range interference*. In the study of this effect, it would be necessary to take into account a part of the potential $W$ in Eq. (3.2). Then the probability $\tau_j$ of each step depends on the past $s$ steps, and therefore the present problem corresponds to that of random flights with correlations of order $s$, namely the $s$-fold Markoff process. However, it is very difficult to derive generally the distribution function $P(\mathbf{R})$ of the end-to-end distance of the chain with short-range interferences. For convenience, we first evaluate the mean-square end-to-end distance.

### 9a(i). Freely Rotating Chains

Squaring both sides of Eq. (3.8), we have the general expression for the mean-square end-to-end distance of a linear polymer chain,

$$\langle R^2 \rangle = \sum_{i=1}^{n} \langle {\mathbf{r}_i}^2 \rangle + 2 \sum_{1 \le i < j \le n}\sum \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle \,. \tag{9.1}$$

For the random-flight chain without correlations between any two bonds, we have $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = 0$ for $i \neq j$ and $\langle {\mathbf{r}_i}^2 \rangle = a^2$ for all $i$. Thus we can

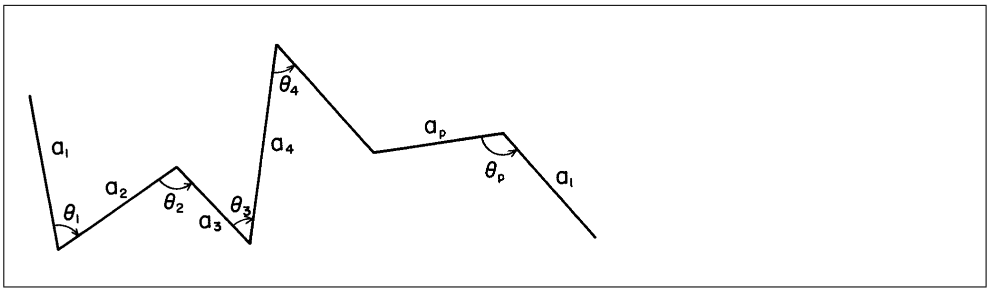

**Fig. II.6.** Schematic representation of a repeating unit of a freely rotating chain.

recover Eq. (5.11). In this subsection, we consider a chain in which the bond angles are restricted but rotations about single bonds are unrestricted. Such a chain is called the *freely rotating chain.*

For convenience, suppose a chain composed of $n/p$ repeating units, each consisting of $p$ bonds of lengths $a_1, \ldots, a_p$ joined successively with angles $\theta_1, \ldots, \theta_p$, where the free rotation about every bond is permitted (see Fig. II.6). Then it is evident that the first sum in Eq. (9.1) is given by

$$\sum_i \langle \mathbf{r}_i{}^2 \rangle = \frac{n}{p} \sum_{i=1}^{p} a_i{}^2 \,. \tag{9.2}$$

By rearrangement of terms with account of the repeating nature, the second sum in Eq. (9.1) may be rewritten as

$$\sum_{i<j}\sum \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \sum_{i=1}^{p} \sum_{\substack{j=1 \\ i<kp+j}}^{p} \sum_{k=0}^{n/p-1} \left( \frac{n}{p} - k \right) \langle \mathbf{r}_i \cdot \mathbf{r}_{kp+j} \rangle \,. \tag{9.3}$$

The averages of scalar products $\mathbf{r}_i \cdot \mathbf{r}_j$ can be easily found. For example, we have $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle = a_1 a_2 \gamma_1$ and $\langle \mathbf{r}_1 \cdot \mathbf{r}_{kp+1} \rangle = a_1{}^2 (\gamma_1 \cdots \gamma_p)^k$ $(k \neq 0)$, where $\gamma_i$ is defined as

$$\gamma_i \equiv -\cos\theta_i \,. \tag{9.4}$$

Then by further rearrangement of terms, Eq. (9.3) may be reduced to a sum of geometrical series. Thus we find

$$\begin{aligned} \langle R^2 \rangle = {} & \frac{n}{p} \sum_{i=1}^{p} a_i{}^2 + \frac{2n}{p(1 - \prod_{i=1}^{p} \gamma_i)} \\ & \times \sum_{i=1}^{p} \left[ a_i{}^2 \prod_{i=1}^{p} \gamma_i + a_i \sum_{j=1}^{i-1} \frac{a_j \prod_{i=1}^{p} \gamma_i}{\prod_{k=j}^{i-1} \gamma_k} + a_i \sum_{j=i+1}^{p} a_j \prod_{k=i}^{j-1} \gamma_k \right] + C \end{aligned} \tag{9.5}$$

with

**TABLE II.1.** PARAMETERS IN EQ. (9.5) FOR VARIOUS TYPES OF POLYMERS

| TYPE[a] | $p$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $\gamma_4$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | $a$ | — | — | — | $\gamma$ | — | — | — |
| 2 | 2 | $a$ | $a$ | — | — | $\gamma_1$ | $\gamma_2$ | — | — |
| 3 | 2 | $a$ | $b$ | — | — | $\gamma_1$ | $\gamma_2$ | — | — |
| 4 | 3 | $a$ | $a$ | $b$ | — | $\gamma_1$ | $\gamma_2$ | $\gamma_2$ | — |
| 5 | 4 | $a$ | $a$ | $b$ | $b$ | $\gamma_1$ | $\gamma_2$ | $\gamma_1$ | $\gamma_2$ |

[a] Type 1: vinyl polymer. Type 2: polyoxymethylene and polydimethylsiloxane. Type 3: *cis*-1, 4'-polysaccharide (amylose) and *cis*-polypeptide. Type 4: *cis*-polybutadiene. Type 5: polycarbonate.

$$C = -\frac{2(\prod_{i=1}^{p}\gamma_i)\left[1-(\prod_{i=1}^{p}\gamma_i)^{n/p}\right]}{(1-\prod_{i=1}^{p}\gamma_i)^2} \times \sum_{i=1}^{p}\left[{a_i}^2 + a_i\sum_{j=1}^{i-1}\frac{a_j}{\prod_{k=j}^{i-1}\gamma_k} + a_i\sum_{j=i+1}^{p}a_j\prod_{k=i}^{j-1}\gamma_k\right]. \tag{9.6}$$

When $n$ is large, the term $C$ becomes independent of $n$ since $|\gamma_i| < 1$, and it may therefore be suppressed in Eq. (9.5); thus $\langle R^2\rangle$ becomes proportional to $n$.

From Eq. (9.5), we can readily obtain expressions for $\langle R^2\rangle$ of various types of freely rotating chains. Some of polymers whose backbones contain structural features such as double bonds or rings can also be reduced to the above model, namely a linear sequence of freely rotating "bonds."For instance, vinyl polymer chains may be represented by the following choice of the parameters: $p = 1$, $a_1 = a$, and $\theta_1 = \theta$. For this case, we have

$$\langle R^2\rangle = na^2\left[\frac{1-\cos\theta}{1+\cos\theta} + \frac{2\cos\theta}{n}\,\frac{1-(-\cos\theta)^n}{(1+\cos\theta)^2}\right], \tag{9.7}$$

which, for large $n$, becomes

$$\langle R^2\rangle = na^2\frac{1-\cos\theta}{1+\cos\theta}\,. \tag{9.8}$$

Equations (9.7) and (9.8) are the formulas derived by Eyring,[29] Wall,[30] and Benoit.[31] In Table II.1 are summarized the parameter assignments for various types of polymers; Type 1: vinyl polymers; Type 2: polyoxymethylene and polydimethylsiloxane[32]; Type 3: *cis*-1,4′-polysaccharide (amylose)[31, 33] and *cis*-polypeptide[34]; Type 4: *cis*-polybutadiene[30, 31, 33]; Type 5: polycarbonate. We note that the expression used by Schulz and Horbach[35] for polycarbonates is incorrect.

There are other types of polymers whose backbone structures cannot be reduced to the above model. However, a similar principle can be applied after use of a maneuver. In fact, calculations have already been made for *trans*-1,4′-polysaccharide (cellulose and pectic acid),[31, 33, 34] *trans*-polybutadiene,[30, 31, 33] and *trans*-polypeptide.[34] In any case, the mean-square end-to-end distance of a freely rotating chain can be easily evaluated when the geometrical structure of the backbone of the chain is given.

## 9a(ii). Chains with Hindered Internal Rotations

For simplicity, we consider vinyl polymers with $a_i = a$ and $\theta_i = \theta$ for all $i$. It is convenient to choose rotation angles $\varphi_1, \varphi_2, \ldots, \varphi_n = \{\varphi_n\}$ as the internal coordinates, assuming $a$ and $\theta$ to be fixed quantities. The configurational partition function of (3.1) may then be rewritten in the form,

$$Z = \int \exp\left[-\frac{U\bigl(\{\varphi_n\}\bigr)}{kT}\right] d\{\varphi_n\}\,, \tag{9.9}$$

where $U$ is the energy of internal rotation (strictly the potential of mean force). The problem is to express the scalar product $\mathbf{r}_i \cdot \mathbf{r}_j$ in Eq. (9.1) in terms of $\{\varphi_n\}$, and then to evaluate its average. This can be done by applying a method, originally suggested by Eyring.[29, 30]

Let us choose a set of Cartesian coordinate systems as follows: the positive direction of the $x_j$ axis of the $j$th coordinate system coincides with the vector $\mathbf{r}_j$, the positive direction of the $y_j$ axis makes an acute angle with the vector $\mathbf{r}_{j-1}$ in the plane containing the two vectors $\mathbf{r}_{j-1}$ and $\mathbf{r}_j$, and the $z_j$ axis constitutes a right-handed rectangular coordinate system with the $x_j$ and $y_j$ axes. The angle between the two planes containing $\mathbf{r}_{j-2}$ and $\mathbf{r}_{j-1}$, and $\mathbf{r}_{j-1}$ and $\mathbf{r}_j$, respectively, defines the rotation angle $\varphi_j$ about the $(j-1)$th bond, which is zero when $\mathbf{r}_{j-2}$ and $\mathbf{r}_j$ are situated in the *trans* position with respect to each other and takes a positive value when $\mathbf{r}_j$ lies in the positive range of $z_{j-1}$ in the $(j-1)$th coordinate system (see Fig. II.7). Then the $j$th coordinate system is transformed into the $(j-1)$th one by the orthogonal matrix,

$$\mathbf{A}_j = \begin{pmatrix} -\cos\theta & \sin\theta & 0 \\ \sin\theta\cos\varphi_j & \cos\theta\cos\varphi_j & \sin\varphi_j \\ \sin\theta\sin\varphi_j & \cos\theta\sin\varphi_j & -\cos\varphi_j \end{pmatrix}. \tag{9.10}$$

The vector $\mathbf{r}_j$ which in its own coordinate system was given by $\mathbf{r}_j = (a\ 0\ 0) \equiv \mathbf{a}$ (column vector) is expressed in the $(j-1)$th system by $\mathbf{A}_j\mathbf{a}$. By repeating this procedure, $\mathbf{r}_j$ can be expressed in the $i$th coordinate system. Thus the average of the scalar product $\mathbf{r}_i \cdot \mathbf{r}_j$ may be written as

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \mathbf{a}^T \left\langle \prod_{k=i+1}^{j} \mathbf{A}_k \right\rangle \mathbf{a}\,, \tag{9.11}$$

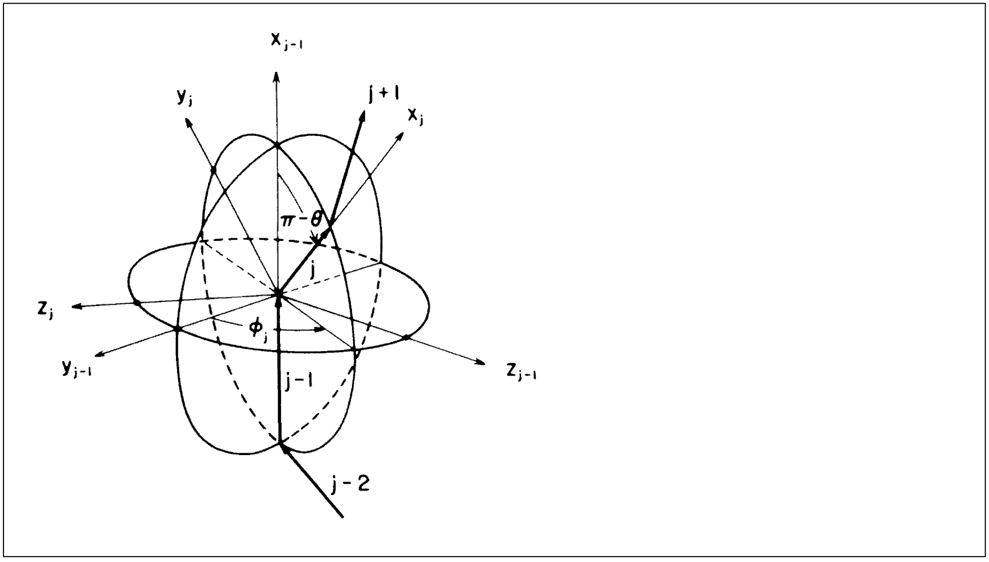

**Fig. II.7.** Transformation of a coordinate system associated with the *j*th bond into a coordinate system associated with the (*j*—1)th bond.

where the superscript $T$ indicates the transpose. The average on the right-hand side is given by

$$\left\langle \prod_{k=i+1}^{j} \mathbf{A}_k \right\rangle = Z^{-1} \int \left( \prod_{k=i+1}^{j} \mathbf{A}_k \right) \exp\left(-\frac{U}{kT}\right) d\{\varphi_n\} . \tag{9.12}$$

The energy $U$ may be decomposed as

$$U\big(\{\varphi_n\}\big) = \sum_{i=1}^{n} u_{1i}(\varphi_i) + \sum_{i=1}^{n} u_{2i}(\varphi_i, \varphi_{i+1}) + \cdots . \tag{9.13}$$

According to the assumed form of $U$, the theories may be classified into three types;

1. independent rotation:

$$U = \sum_{i=1}^{n} u_{1i}(\varphi_i) . \tag{9.14}$$

2. pairwise independent rotation:

$$U = \sum_{i=1}^{n} u_{1i}(\varphi_i) + \sum_{k=1}^{n/2} u_{2,2k}(\varphi_{2k-1}, \varphi_{2k}) . \tag{9.15}$$

3. interdependent rotation:

$$U = \sum_{i=1}^{n} u_{1i}(\varphi_i) + \sum_{i=1}^{n} u_{2i}(\varphi_i, \varphi_{i+1}) . \tag{9.16}$$

It is evident that the third type is most realistic and important since it takes into account completely both first and second neighbor interactions. In the discussion that follows, we assume $u_{1i} = u_1$ and $u_{2i} = u_2$ for all $i$.

We first consider the case of independent rotation. By assumption, Eq. (9.12) becomes

$$\left\langle \prod_{k=i+1}^{j} \mathbf{A}_k \right\rangle = \prod_k \langle \mathbf{A}_k \rangle \equiv \mathbf{A}^{j-i} \,, \tag{9.17}$$

where $\mathbf{A}$ is the transformation matrix of (9.10) with $\eta_1 = \langle \cos\varphi \rangle$ and $\eta_2 = \langle \sin\varphi \rangle$ in place of $\cos\varphi_j$ and $\sin\varphi_j$, respectively, where

$$\langle \cos\varphi \rangle = \frac{\int_{-\pi}^{\pi} \cos\varphi e^{-u_1/kT} d\varphi}{\int_{-\pi}^{\pi} e^{-u_1/kT} d\varphi} \,. \tag{9.18}$$

The matrix $\mathbf{A}$ can be transformed into a diagonal matrix $\boldsymbol{\lambda}$ by a similarity transformation with an appropriate matrix $\mathbf{Q}$,

$$\mathbf{Q}^{-1}\mathbf{A}\mathbf{Q} = \boldsymbol{\lambda} \tag{9.19}$$

the diagonal elements $\lambda_i$ of $\boldsymbol{\lambda}$ (eigenvalues of $\mathbf{A}$) being the roots of the characteristic equation of $\mathbf{A}$,

$$|\lambda\mathbf{E} - \mathbf{A}| = \lambda^3 - c_1\lambda^2 + c_2\lambda - c_3 = 0 \tag{9.20}$$

with $\mathbf{E}$ the unit matrix. From Eqs. (9.1), (9.11), (9.17), and (9.19), we then have

$$\langle R^2 \rangle = na^2 + n\mathbf{a}^T\mathbf{Q}\Lambda\mathbf{Q}^{-1}\mathbf{a} \,, \tag{9.21}$$

where $\Lambda$ is the diagonal matrix given by

$$\Lambda = \frac{2}{n} \sum\sum_{1 \le i < j \le n} \boldsymbol{\lambda}^{j-i} \,. \tag{9.22}$$

Since all of the eigenvalues $\lambda_i$ are smaller than unity, the diagonal elements of $\Lambda$ become $2\lambda_i/(1-\lambda_i)$ for large $n$, and $\Lambda$ may be expressed as

$$\Lambda = K\big[\boldsymbol{\lambda} + c_3\boldsymbol{\lambda}^{-1} + (c_3 - c_2)\mathbf{E}\big] \tag{9.23}$$

with

$$K = 2/(1 - c_1 + c_2 - c_3) \,,$$

where we have used the relations between the roots and coefficients of the cubic equation of (9.20). Equation (9.21) then becomes

$$\langle R^2 \rangle = na^2 + nK\mathbf{a}^T\big[\mathbf{A} + c_3\mathbf{A}^{-1} + (c_3 - c_2)\mathbf{E}\big]\mathbf{a} \,. \tag{9.24}$$

Thus after simple algebraic calculations, we obtain the result,$^{36-39}$

$$\langle R^2 \rangle = na^2 \frac{1 - \cos\theta}{1 + \cos\theta} \, \frac{(1+\eta_1)^2 + {\eta_2}^2}{1 - {\eta_1}^2 - {\eta_2}^2} \,. \tag{9.25}$$

If the potential $u_1(\varphi)$ is an even function of $\varphi$, $\eta_2$ vanishes and Eq. (9.25) reduces to[40−43]

$$\langle R^2 \rangle = na^2 \frac{1-\cos\theta}{1+\cos\theta}\,\frac{1+\eta_1}{1-\eta_1}\,. \tag{9.26}$$

This is a well-known classical formula.

The case of pairwise independent rotation can in principle be treated by the same procedure as above, and we do not reproduce the mathematical details. It is to be noted that calculations belonging to this category have been made by many workers.[38, 39, 44−46]

We now consider the case of interdependent rotation. For this case, it is convenient to introduce the assumption of discrete rotational energy levels or the so-called *rotational-isomeric approximation.* In this approximation, the rotation angle $\varphi_i$ is considered to take only a finite set of fixed values ${\varphi_i}^{(k)}$ ($k = 1, 2, \ldots, s$) corresponding to the minima of the potential. In the following discussion we consider only three available states, $T$ (*trans*, $\varphi = 0°$), $G$ (*gauche*, $\varphi = 120°$), and $G'$ (another *gauche*, $\varphi = -120°$), which are indicated by $k = 1, 2, 3$, respectively. The partition function of (9.9) may then be rewritten in the form,

$$Z = \sum_{\{\varphi_n\}} \prod_{i=1}^{n} p(\varphi_i, \varphi_{i+1}) \tag{9.27}$$

with

$$p(\varphi_i, \varphi_{i+1}) = \exp\left\{-\frac{u_1(\varphi_i) + u_2(\varphi_i, \varphi_{i+1})}{kT}\right\}, \tag{9.28}$$

where we assume $\varphi_{n+1} = \varphi_1$. The sum in Eq. (9.27) extends over all possible values of $\varphi_1, \ldots, \varphi_n$. Thus the problem becomes equivalent to that of a one-dimensional cooperative system, the Ising model.[47] Let us introduce the $3 \times 3$ matrix $\mathbf{p}$ whose elements are

$$p_{kl} = p({\varphi_i}^{(k)}, \varphi_{i+1}^{(l)})\,, \tag{9.29}$$

$p_{kl}$ being independent of $i$. Then $\mathbf{p}$ can be transformed into a diagonal matrix $\mathbf{Q}^{-1}\mathbf{p}\mathbf{Q} = \Lambda(\lambda_i)$ by a similarity transformation, where $\lambda_i$ are the eigenvalues of $\mathbf{p}$, and Eq. (9.27) reduces to

$$\begin{aligned} Z &= \text{trace } \mathbf{p}^n = \sum_{i=1}^{3} {\lambda_i}^n \\ &= \lambda^n \qquad\qquad (\text{for large } n)\,, \end{aligned} \tag{9.30}$$

where $\lambda$ is the largest eigenvalue (assuming its nondegeneracy). Similarly the average of product of functions $f_i(\varphi_i)$ may be expressed as

$$\begin{aligned} \left\langle \prod_{k=i+1}^{j} f_k(\varphi_k) \right\rangle &= Z^{-1} \sum_{\{\varphi_n\}} \left[\prod_{k=i+1}^{j} f_k(\varphi_k)\right] \left[\prod_{i=1}^{n} p(\varphi_i, \varphi_{i+1})\right] \\ &= Z^{-1} \text{trace } \mathbf{f}_{i+1} \left[\prod_{k=i+2}^{j} (\mathbf{p}\mathbf{f}_k)\right] \mathbf{p}^{n-(j-i-1)} \end{aligned}$$

$$= \mathbf{y}\mathbf{f}_{i+1} \left[ \prod_{k=i+2}^{j} (\lambda^{-1}\mathbf{p}\mathbf{f}_k) \right] \mathbf{x} \quad (\text{for large } n)\,, \tag{9.31}$$

where $\mathbf{f}_i$ is the diagonal matrix with diagonal elements $f_i(\varphi^{(k)})$ ($k =$ 1, 2, 3), and $\mathbf{x}$ and $\mathbf{y}$ are the normalized right-hand and left-hand eigenvectors associated with $\lambda$, respectively; i.e.,

$$\mathbf{p}\mathbf{x} = \lambda\mathbf{x}\,, \qquad \mathbf{y}\mathbf{p} = \lambda\mathbf{y}\,, \qquad \mathbf{y}\mathbf{x} = 1\,. \tag{9.32}$$

Recalling that the element $A_{rs}$ of the product of the transformation matrices $\mathbf{A}_k$ is a sum of terms of the form $f_{i+1} \cdots f_j$, we can readily obtain, from Eq. (9.31),

$$\langle A_{rs} \rangle = \mathbf{y} \sum_t \cdots \sum_v \mathbf{a}_{rt}(\lambda^{-1}\mathbf{p}\mathbf{a}_{tu}) \cdots (\lambda^{-1}\mathbf{p}\mathbf{a}_{vs})\mathbf{x}\,, \tag{9.33}$$

where $\mathbf{a}_{ij}$ is the diagonal matrix with diagonal elements $a_{ij}(\varphi^{(k)})$ ($k =$ 1, 2, 3) with $a_{ij}(\varphi)$ the elements of the transformation matrix. In matrix notation, Eq. (9.33) may be written as

$$\left\langle \prod_{k=i+1}^{j} \mathbf{A}_k \right\rangle = \mathbf{Y}\mathbf{T}\mathbf{S}^{j-i-1}\mathbf{X} \tag{9.34}$$

with

$$\mathbf{S} = \lambda^{-1}\mathbf{P}\mathbf{T}\,, \tag{9.35}$$

where $\mathbf{T}$ is the matrix with "elements" $\mathbf{a}_{ij}$, and $\mathbf{P}$, $\mathbf{X}$, and $\mathbf{Y}$ are the direct products,

$$\mathbf{P} = \mathbf{p} \times \mathbf{E}_3\,, \quad \mathbf{X} = \mathbf{x} \times \mathbf{E}_3\,, \quad \mathbf{Y} = \mathbf{y} \times \mathbf{E}_3 \tag{9.36}$$

with $\mathbf{E}_s$ the $s \times s$ unit matrix. From Eqs. (9.1), (9.11), and (9.34), we obtain

$$\langle R^2 \rangle = na^2 \left[ 1 + 2\mathbf{e}^{\mathbf{T}}\mathbf{Y}\mathbf{T}(\mathbf{E}_9 - \mathbf{S})^{-1}\mathbf{X}\mathbf{e} \right] \tag{9.37}$$

with $\mathbf{e} = (1\ 0\ 0)$ the unit bond vector. This is the equation derived independently by Lifson[48] and by Nagai.[49] Equivalent expressions have also been derived by Birshtein et al.[50] and by Hoeve.[51]

We have described the method of evaluating the mean-square end-to-end distance of a chain with hindered internal rotations for the simplest types of molecules. For other types of molecules, suitable forms of the potentials $u_{1i}$, $u_{2i}$, and so on in Eq. (9.13) must be chosen in order to reflect the structure of the backbone and side groups or the stereochemical structures of a given polymer chain. However, the evaluation becomes very complicated, and numerical results cannot be obtained without a computer calculation in most cases. In addition, there is some ambiguity in the assignment of values to the energy parameters introduced. The main reason for this is that, strictly, the energy of internal rotation is the potential of mean force. For this reason we give only a brief description of the numerical results obtained from Eq. (9.37) for polyethylene, which has the same backbone as do vinyl polymer chains, and the result is quite significant. Now let us choose the potential $u_1(\varphi^{(1)})$ in the *trans* state as the zero of energy, and assume the following statistical weights for the conformations indicated: $1(T)$, $\omega_1(G, G')$, $1(TT, TG, TG', GT, G'T, GG, G'G')$, and $\omega_2(GG', G'G)$. Then the matrix $\mathbf{p}$ of (9.29) becomes

$$\mathbf{p} = \begin{pmatrix} 1 & 1 & 1 \\ \omega_1 & \omega_1 & \omega_1\omega_2 \\ \omega_1 & \omega_1\omega_2 & \omega_1 \end{pmatrix} . \tag{9.38}$$

Note that $\omega_1 = \exp(-\Delta {u_1}^{(2)}/kT)$ with $\Delta {u_1}^{(2)}$ the difference between energies in the *gauche* and *trans* states. The weight $\omega_2$ may be regarded as very small because of the so-called *pentane effect*[43, 52]; the first and fifth carbon atoms of $n$-pentane come within the range of repulsion for the $GG'$ or $G'G$ conformation. Nagai[53] has obtained the value 8.0 for $\langle R^2 \rangle / na^2$ of polyethylene (at 140°C), assuming $\omega_2 = 0$ and adopting the value 800 cal/mole for $\Delta {u_1}^{(2)}$ estimated by Pitzer[52] from heat capacity data on gaseous $n$-butane. We note that in this case $\langle R^2 \rangle$ decreases with increasing temperature since the transition $T \rightarrow G$ is caused by an increase in temperature. Hoeve[54] has also obtained the value 6.75 for the corresponding ratio (at 160°C), assigning somewhat different values to $\Delta {u_1}^{(2)}$ and $\omega_2$. On the other hand, the corresponding value of $\langle R^2 \rangle / na^2$ estimated by Nagai[53] from Eq. (9.26) for the independent-rotation model is 4.4, which is much smaller than the above value for the interdependent-rotation model. This difference is, of course, due to the exclusion of the $GG'$ and $G'G$ conformations in the latter.

In sum, the mean-square end-to-end distance of a polymer chain with short-range interferences may be expressed in the form,

$$\langle R^2 \rangle = \langle R^2 \rangle_f \sigma^2 \, , \tag{9.39}$$

where $\langle R^2 \rangle_f$ is the mean-square end-to-end distance of the chain in the freely rotating state, and $\sigma$ represents the effect of steric hindrances to internal rotations. For the case of vinyl polymers with a tetrahedral bond angle ($\cos\theta = -1/3$), we have $\langle R^2 \rangle_f = 2na^2$ from Eq. (9.8). For polyethylene, we therefore have $\sigma = 1.8 \sim 2.0$, assuming Nagai and Hoeve's values for $\langle R^2 \rangle / na^2$. The parameter $\sigma$ is referred to as the *conformation factor.* It is important to note that the factor $\sigma$ depends generally on temperature and sometimes also on the solvent, whereas $\langle R^2 \rangle_f$ is a geometrical quantity independent of thermodynamic variables. For high-molecular-weight polymers of ordinary interest, $\langle R^2 \rangle_f$ is proportional to $n$ but $\sigma$ is independent of $n$, and therefore the Markoff nature of the chain is still preserved. The chain with only short-range interferences is called the *ideal chain* or *unperturbed chain*, and its molecular dimension ($\langle R^2 \rangle$ or $\langle S^2 \rangle$) is called the *unperturbed dimension.* By the term "unperturbed," we mean that the chain is not perturbed by long-range interferences, namely the excluded-volume effect. We note that the unperturbed chain does not necessarily possess the Markoff nature; it breaks down for short chains or stiff chains. The Markoff nature of the unperturbed chain is rather the definition of *flexible* chains. In other words, the unperturbed state of a flexible polymer chain is characterized by the Markoff nature.

### 9a(iii). Distribution of the End-to-End Distance

We now consider the distribution function $P(\mathbf{R})$ for a chain with short-range interferences. Needless to say, it is impossible to derive an expression for $P(\mathbf{R})$ which is valid for all values of $n$ and $R$, and our attention is directed to only the form of $P(\mathbf{R})$ for large $n$. We have already shown that $\langle R^2 \rangle$ is proportional to $n$ for large $n$, and that the sequence of bonds forms a Markoff process. From these facts, it may be expected that $P(\mathbf{R})$ is Gaussian for large $n$.

We first consider the freely rotating chain with identical bond lengths and bond angles.[55] Recalling that $P(\mathbf{R})$ is spherically symmetric and $\mathbf{R}$ is the resultant of the $\mathbf{r}_i$'s, we have, from Eq. (4.12), for the characteristic function

$$K(\boldsymbol{\rho}) = \sum_{p=0}^{\infty} \frac{(-1)^p}{(2p)!} \sum_{i=1}^{n} \sum_{j=1}^{n} \cdots \sum_{s=1}^{n} \sum_{t=1}^{n} I_{ij\cdots st} \tag{9.40}$$

with

$$I_{ij\cdots st} = \big\langle (\boldsymbol{\rho} \cdot \mathbf{r}_i)(\boldsymbol{\rho} \cdot \mathbf{r}_j) \cdots (\boldsymbol{\rho} \cdot \mathbf{r}_t) \big\rangle \,, \tag{9.41}$$

where the number of the indices $i$, $j$, $\ldots$, $t$ is $2p$. When $p = 1$, $I_{ij}$ can readily be obtained by means of the projection method used in Section 9a(i); if $\psi$ is the angle between $\boldsymbol{\rho}$ and $\mathbf{r}_i$, we have (for $i \leq j$)

$$I_{ij} = \rho^2 a^2 (-\cos\theta)^{j-i} \langle \cos^2 \psi \rangle = \tfrac{1}{3} \rho^2 a^2 (-\cos\theta)^{j-i} \,. \tag{9.42}$$

Obviously we have $I_{ij\cdots t} = I_{ij} I_{kl} \cdots I_{st}$ for $i < j < k < \cdots < s < t$ provided the difference between the nearest members of two adjacent pairs of indices is not too small. The sum over indices may then be written as

$$\frac{1}{(2p)!} \sum_i \sum_j \cdots \sum_s \sum_t I_{ij\cdots st} = \sum_{i \leq j < \cdots < s \leq t}{}' \!\!\sum{}' \cdots \sum{}' \, I_{ij} \cdots I_{st} \,, \tag{9.43}$$

where the prime indicates that for $i = j$, $I_{ij}$ is to be replaced by $I_{ij}/2$. On the other hand, we have

$$\begin{aligned} \left( \frac{1}{2} \sum_i \sum_j I_{ij} \right)^p &= \sum_{i \leq j}{}' \!\!\sum{}' \cdots \sum_{s \leq t}{}' \!\!\sum{}' \, I_{ij} \cdots I_{st} \\ &= p! \sum_{i \leq j < \cdots < s \leq t}{}' \!\!\sum{}' \cdots \sum{}' \, I_{ij} \cdots I_{st} \,, \end{aligned} \tag{9.44}$$

where in obtaining the second line we have retained only terms without overlap of pairs of indices, since the contribution of overlapping terms is very small compared to that of nonoverlapping terms because of $|\cos\theta| < 1$. From Eqs. (9.40), (9.43), and (9.44), we have

$$\begin{aligned} K(\boldsymbol{\rho}) &= \exp\left(-\frac{1}{2}\sum_i\sum_j I_{ij}\right) \\ &= \exp\left(-\frac{\rho^2}{6}na^2\frac{1-\cos\theta}{1+\cos\theta}\right) \qquad \text{(for large } n\text{)}\,. \end{aligned} \tag{9.45}$$

This is the characteristic function of a Gaussian distribution whose second moment is given by Eq. (9.8). Thus $P(\mathbf{R})$ is Gaussian for large $n$.

Next we consider a general case. The necessary and sufficient condition under which the chain has the Markoff nature is that the sum $n^{-1}\sum\sum_{i<j}\langle\mathbf{r}_i\cdot\mathbf{r}_j\rangle$ is convergent. When the chain is flexible, the correlation between the $i$th and $j$th bonds must therefore vanish for some value of $j-i$ negligibly small compared to $n$. Suppose that $i$ and $n-j$ are of order $n$, and that $j-i$ is of order unity but is so large that the correlation between $\mathbf{r}_i$ and $\mathbf{r}_j$ may be neglected. Then we have $n-j \simeq n-i$ for very large $n$, and the distribution function may be written in the form,

$$P^{(n)}(\mathbf{R}) = \int P^{(i)}(\mathbf{R}_i)P^{(n-i)}(\mathbf{R}-\mathbf{R}_i)d\mathbf{R}_i\,, \tag{9.46}$$

where $P^{(n)}$ is the distribution of the end-to-end distance of the chain of $n$ bonds. Using Eq. (9.46) and the partition function for the chain subject to an external force, Nagai[56] has shown that $P(\mathbf{R})$ becomes Gaussian. However, the introduction of the external field is unnecessary, and the central limit theorem under consideration is a straightforward consequence of Eq. (9.46), as shown below. The integral of (9.46) is of a convolution type, and there is the relation for the characteristic function,

$$K^{(n)}(\boldsymbol{\rho}) = K^{(i)}(\boldsymbol{\rho})K^{(n-i)}(\boldsymbol{\rho})\,. \tag{9.47}$$

Then the $2l$th cumulant $\kappa_{2l}$, as a function of $n$, satisfies the equation,

$$\kappa_{2l}(n) = \kappa_{2l}(i) + \kappa_{2l}(n-i)\,. \tag{9.48}$$

The solution of this equation is

$$\kappa_{2l} = c_l n\,, \tag{9.49}$$

where $c_l$ is a constant independent of $n$. From Eq. (5.7), the moment $\langle R^{2p}\rangle$ is given by

$$\langle R^{2p}\rangle = (2p+1)!\sum_{\mathbf{m}}\prod_{l=1}^{p}\frac{1}{m_l!}\left[\frac{\kappa_{2l}}{(2l)!}\right]^{m_l} \tag{9.50}$$

with $\sum_l lm_l = p$. Retaining only the term with the highest power of $n$ as in Section 5a(iii), we obtain (for large $n$)

$$\langle R^{2p} \rangle = \frac{(2p+1)!}{p!} \left( \frac{\kappa_2}{2} \right)^p . \tag{9.51}$$

Noting that $\langle R^2 \rangle = 3\kappa_2$, we have

$$\langle R^{2p} \rangle = \frac{(2p+1)!}{6^p p!} \langle R^2 \rangle^p . \tag{9.52}$$

These are the moments of the Gaussian distribution; thus $P(\mathbf{R})$ is Gaussian for large $n$.

Thus, we introduce the postulate that the distribution of the unperturbed flexible polymer chain is Gaussian. This postulate alone is insufficient to enable the development of the theory of dilute polymer solutions; it is necessary to introduce a more restrictive postulate, the concept of an *equivalent chain.*[57] In this approximation, the unperturbed polymer chain is replaced by a random-flight chain which is composed of $N$ bonds of length $A$ and has a mean-square end-to-end distance equal to that of the unperturbed chain under consideration; that is,

$$\langle R^2 \rangle = NA^2 . \tag{9.53}$$

Now the question that arises is: What is the number $N$? It may be determined from Eq. (9.53) with the additional condition that both the chains have the same end-to-end distance $R_m$ at full extension,

$$R_m = NA ; \tag{9.54}$$

that is,

$$N = \frac{{R_m}^2}{\langle R^2 \rangle} , \qquad A = \frac{\langle R^2 \rangle}{R_m} . \tag{9.55}$$

The bond length $A$ given by Eq. (9.55) is called the *Kuhn statistical segment length.* In the case of vinyl polymers, for example, we have

$$\langle R^2 \rangle = na^2 \frac{1-\cos\theta}{1+\cos\theta} \sigma^2 , \quad R_m = na \sin\left( \frac{\theta}{2} \right) , \tag{9.56}$$

$$N = \frac{n}{2\sigma^2}(1+\cos\theta) , \quad A = 2a \frac{\sin(\theta/2)}{1+\cos\theta} \sigma^2 . \tag{9.57}$$

As will be shown in later chapters, however, the parameters $N$ and $A$ never appear separately in the theory of dilute solutions as far as the flexible chain is concerned, and the individual values of $N$ and $A$ have no great significance. It may therefore be supposed that $N$ is, to some extent, arbitrary, and then $A$ does not necessarily have to be the Kuhn statistical length. In the remainder of this book, we shall use the symbols $n$ and $a$ in place of $N$ and $A$, respectively, unless specified otherwise. Thus we rewrite Eq. (9.53) as

$$\langle R^2 \rangle = na^2 . \tag{9.58}$$

This redefined length $a$ is referred to as the *unperturbed effective bond length.* It may then be understood that the statistical properties of the random-flight chain described in the preceding sections apply to the unperturbed flexible chain with short-range interferences, considering $a$ to have the new meaning.

## 9b. Branched and Ring Polymers

Some natural or synthetic polymer molecules contain branches or rings. For such structures, it is convenient to use the mean-square radius of gyration as a measure of the average size of the molecule rather than the mean-square end-to-end distance, because the multiplicity or absence of the ends leads to an ambiguity of the definition of the latter. Evaluation is carried out for unperturbed chains obeying random-flight statistics. It may then be easily shown that the Zimm–Stockmayer relation (7.22) can be applied to both branched and ring polymers, whereas the Kramers relation (7.19) can be applied only to molecules containing no rings.

### 9b(i). Branched Polymers

We first consider a branched molecule containing no loops, as illustrated in Fig. II.8, and define a factor $g$ as the ratio of the mean-square radius of the branched molecule to that of a linear chain possessing the same number $n$ of segments; that is,

$$\langle S^2\rangle_b = g\langle S^2\rangle_l = \tfrac{1}{6}na^2g\,, \tag{9.59}$$

where the subscripts $b$ and $l$ indicate branched and linear chains, respectively, and $a$ is the unperturbed effective bond length. As seen from Fig. II.8, some segments are attached to three or more branches. Such segments will be called *branch units*, and are indicated by small circles in the figure. The number of segments attached to a branch unit will be called the *functionality* of the branch unit. A portion of the molecule between two adjacent branch units or between adjacent end and branch units will be called the *subchain.* Thus the functionality of a branch unit is equal to the number of subchains which grow from it. The molecule is assumed to have $m$ branch units and $p$ subchains. If $n_\lambda$ is the number of segments in the $\lambda$th subchain, we must have

$$n = \sum_{\lambda=1}^{p} n_\lambda\,. \tag{9.60}$$

From Eq. (7.22), $\langle S^2\rangle_b$ may be written in the form,

$$\langle S^2\rangle_b = \frac{1}{n^2}\sum_{(i_\lambda,j_\mu)}\langle {R_{i_\lambda j_\mu}}^2\rangle\,, \tag{9.61}$$

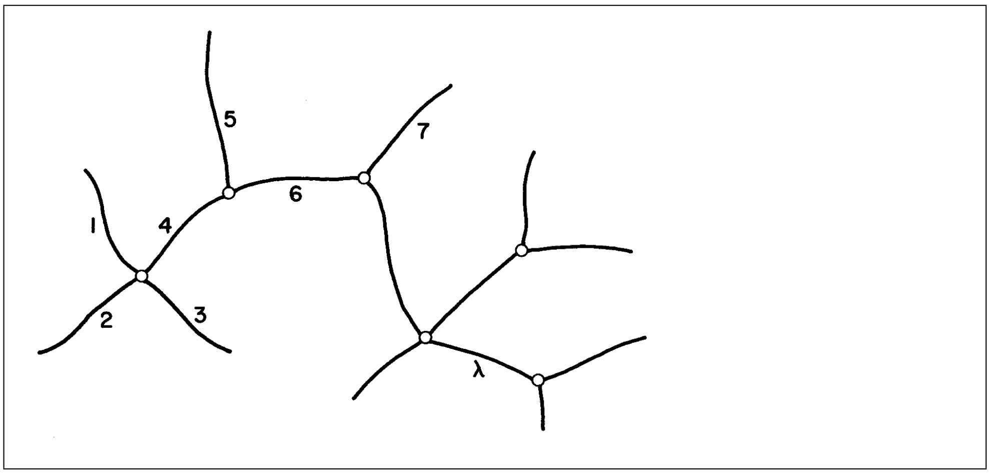

**Fig. II.8.** Schematic representation of a branched polymer molecule containing no ring. The small circles indicate the branch units.

where $R_{i_\lambda j_\mu}$ is the distance between the $i$th segment in the $\lambda$th subchain and the $j$th segment in the $\mu$th subchain, and the summation is carried out over all $i_\lambda$, $j_\mu$ pairs.

Since by assumption the molecule contains no rings, there exists only one way to reach one segment from another along subchains. In addition, each subchain obeys the random-flight statistics. We therefore have

$$\begin{aligned} \langle {R_{i_\lambda j_\mu}}^2 \rangle &= |j_\lambda - i_\lambda| a^2 && \text{for } \lambda = \mu \\ &= (n_{\lambda\mu} + i_\lambda + j_\mu) a^2 && \text{for } \lambda \neq \mu \,, \end{aligned} \tag{9.62}$$

where $n_{\lambda\mu}$ is the number of segments in one or more subchains lying between the $\lambda$th and $\mu$th subchains. In Fig. II.8, for example, $n_{27} = n_4 + n_6$ and $n_{13} = 0$. The segments of the $\lambda$th and $\mu$th subchains are numbered so that $(n_{\lambda\mu} + i_\lambda + j_\mu)$ just gives the number of segments existing on the way from segment $i_\lambda$ to segment $j_\mu$, and therefore the order of the segment numbers in the $\lambda$th subchain may be inverted for a $\lambda$, $\mu$ pair. The sum in Eq. (9.61) can easily be evaluated, and we obtain for the factor $g$

$$g = \frac{1}{n^3} \left[ \sum_{\lambda=1}^{p} (3n{n_\lambda}^2 - 2{n_\lambda}^3) + 6 \sum_{(\lambda,\mu)} n_\lambda n_{\lambda\mu} n_\mu \right] , \tag{9.63}$$

where $\sum_{(\lambda,\mu)}$ means the sum over $\lambda$, $\mu$ pairs. This is the general formula derived by Kataoka.[58, 59] Special cases derived by Zimm and Stockmayer [Eqs. (15a), (18), and (19) of Ref. 21] can readily be obtained from Eq. (9.63). In particular, for star molecules of one branch unit of

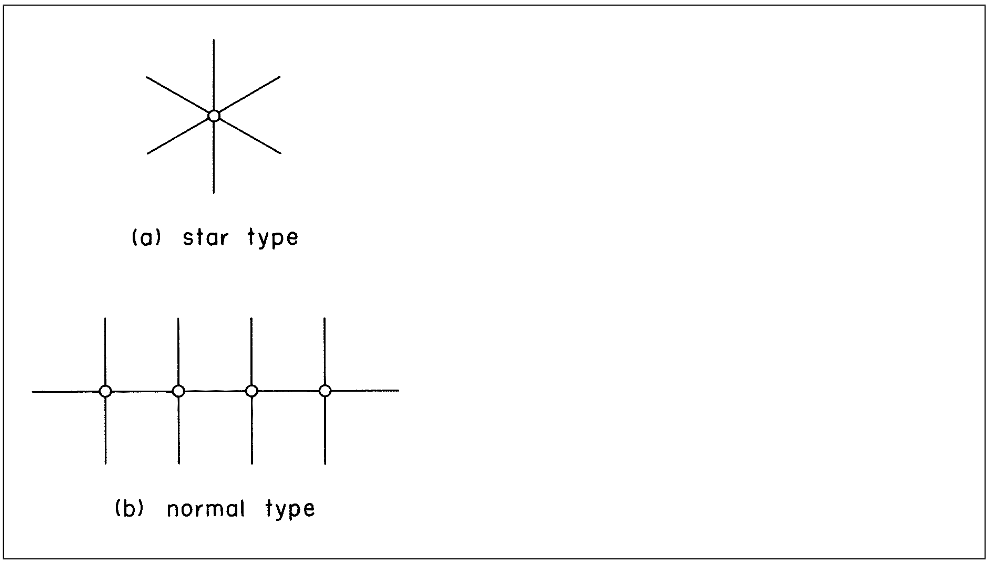

**Fig. II.9.** Two types of branched molecules. (a) Star type with $f = 6$. (b) Normal type with $f = 4$.

functionality $f$ [see Fig. II.9(a)], Eq. (9.63) becomes

$$g = \frac{1}{n^3} \sum_{\lambda=1}^{f} (3nn_\lambda{}^2 - 2n_\lambda{}^3) . \tag{9.64}$$

This result has also been derived by Orofino[60] from the Kramers equation.

Equation (9.63) is valid for a branched molecule having a given type of branching. However, even if the molecular weight or $n$ is uniform, any real polymeric material will have distributions of subchain lengths, of the number of branch units per molecule, of branch units in the molecule, and so on. In what follows, we assume that $n$ and $m$ are fixed, and that all branch units have the same functionality $f$, for simplicity. We then have the relation,

$$p = (f - 1)m + 1 . \tag{9.65}$$

As for the distributions of subchain lengths ($n_\lambda$), we consider two types, for the sake of comparison; one is the *uniform* distribution[61] and the other is the *random* distribution.[21]

The uniform distribution is defined by $n_\lambda = n/p$ for all $\lambda$. If $\nu_{\lambda\mu}$ is the number of subchains between the $\lambda$th and $\mu$th subchains (for example, $\nu_{27} = 2$ in Fig. II.8), we then have $n_{\lambda\mu} = \nu_{\lambda\mu} n/p$, and Eq. (9.63) becomes

$$g_u = \frac{3p - 2}{p^2} + \frac{6}{p^3} \sum_{(\lambda,\mu)} \nu_{\lambda\mu} , \tag{9.66}$$

where the subscript $u$ indicates the uniform distribution.

The random distribution is defined as follows: the number of segments in each subchain varies with an equal probability of occurrence of a set of $n_1$, $n_2$, …, $n_p$ values. Then a quantity $X\bigl(\{n_p\}\bigr)$ as a function of a set of $p$ numbers, $n_1$, $n_2$, …, $n_p$, may be replaced by its average $\langle X \rangle$ given by[21, 59]

$$\langle X \rangle = \frac{\displaystyle\int_0^n dn_{p-1} \int_0^{n-n_{p-1}} dn_{p-2} \cdots \int_0^{n-\sum_{\lambda=2}^{p-1} n_\lambda} X(\{n_p\}) dn_1}{\displaystyle\int_0^n dn_{p-1} \int_0^{n-n_{p-1}} dn_{p-2} \cdots \int_0^{n-\sum_{\lambda=2}^{p-1} n_\lambda} dn_1} . \tag{9.67}$$

As seen from Eq. (9.63), the quantity $X$ to be averaged generally has the form, $n_\lambda{}^x n_\mu{}^y n_\nu{}^z$, and the integrations in Eq. (9.67) can be easily performed. Thus we have

$$g_r = \frac{6}{p(p+1)(p+2)} (p^2 + \sum_{(\lambda,\mu)} \nu_{\lambda\mu}) , \tag{9.68}$$

where the subscript $r$ indicates the random distribution.

We now consider three types of branching for each distribution: *star* type, *normal* (*comb*) type, and *random* type. The normal type of branched molecule contains a linear sequence of $m$ branch units (each of functionality $f$), as illustrated in Fig. II.9(b). The random type contains a random mixture of structural isomers (with $n$ and $m$ fixed and with branch units of the same functionality $f$).

For the star type ($m = 1$, $\nu_{\lambda\mu} = 0$), we readily have, from Eqs. (9.66) and (9.68),

$$g_u(\text{star}) = \frac{3f-2}{f^2} , \tag{9.69}$$

$$g_r(\text{star}) = \frac{6f}{(f+1)(f+2)} . \tag{9.70}$$

In the normal type, there are $(f-2)$ side chains attached to every branch unit; a pair of two branch units separated by $\nu$ subchains forms $(f-1)^2$ pairs of subchains separated by $\nu$ subchains. Further, there are $(m-\nu)$ different pairs of branch units separated by $\nu$ subchains. We therefore have

$$\sum_{(\lambda,\mu)} \nu_{\lambda\mu} = \sum_{\nu=1}^{m-1} (f-1)^2 (m-\nu)\nu = \tfrac{1}{6}(f-1)^2 m(m^2-1) . \tag{9.71}$$

Substitution of Eq. (9.71) into Eqs. (9.66) and (9.68) leads to

$$g_u(\text{normal}) = \frac{3p-2}{p^2} + \frac{1}{p^3}(f-1)^2 m(m^2-1) , \tag{9.72}$$

$$g_r(\text{normal}) = \frac{6}{p(p+1)(p+2)} \bigl[p^2 + \tfrac{1}{6}(f-1)^2 m(m^2-1)\bigr] . \tag{9.73}$$

**TABLE II.2.** NUMERICAL VALUES OF THE FACTOR $g$

| | | RANDOM | | NORMAL | |
|---|---|---|---|---|---|
| $f$ | $m$ | $g_r$ | $g_u$ | $g_r$ | $g_u$ |
| 3 | 1 | 0.900 | 0.778 | — | — |
| | 2 | 0.829 | 0.712 | — | — |
| | 3 | 0.774 | 0.668 | — | — |
| | 4 | 0.730 | 0.633 | 0.733 | 0.638 |
| | 5 | 0.694 | 0.605 | 0.703 | 0.617 |
| | 10 | 0.573 | 0.510 | 0.622 | 0.566 |
| | 15 | 0.505 | 0.454 | 0.587 | 0.546 |
| | 20 | 0.454 | 0.414 | 0.567 | 0.535 |
| | 25 | 0.418 | 0.384 | 0.555 | 0.529 |
| 4 | 1 | 0.800 | 0.625 | — | — |
| | 2 | 0.691 | 0.545 | — | — |
| | 3 | 0.618 | 0.496 | — | — |
| | 4 | 0.566 | 0.460 | 0.569 | 0.465 |
| | 5 | 0.525 | 0.432 | 0.534 | 0.443 |
| | 10 | 0.406 | 0.347 | 0.448 | 0.394 |
| | 15 | 0.344 | 0.301 | 0.414 | 0.375 |
| | 20 | 0.305 | 0.270 | 0.395 | 0.365 |
| | 25 | 0.277 | 0.248 | 0.384 | 0.359 |

Equations (9.72) and (9.73) are the results derived by Kurata and Fukatsu.[61]

For the random type, the sum $\sum \nu_{\lambda\mu}$ must be replaced by its average over all possible structural isomers. This has been done by Kurata and Fukatsu[61] by means of generating functions, but the details are omitted here. The results are

$$g_u(\text{random}) = \frac{3p-2}{p^2} + \frac{6}{p^3} h(f,m)\,, \tag{9.74}$$

$$g_r(\text{random}) = \frac{6}{p(p+1)(p+2)} \left[p^2 + h(f,m)\right], \tag{9.75}$$

where

$$\begin{aligned} h(f,m) = \tfrac{1}{2}(f-1)^2 m(m-1) \sum_{\nu=1}^{m-1} \frac{(fm-m-\nu)!(m-2)!}{(fm-m)!(m-\nu-1)!} \\ \times (f-1)^{\nu-1}(f\nu - 2\nu + f)\nu\,. \end{aligned} \tag{9.76}$$

We note that Zimm and Stockmayer[21] have obtained an alternative but equivalent expression for $g_r$ (random) from the Kramers equation.

In table II.2 are given some numerical values of $g$ calculated by Kurata and Fukatsu. In all cases, $g$ is seen to be smaller than unity.

For given values of $f$ and $m$, it is observed that $g(\text{star}) < g\ (\text{random}) < g(\text{normal})$ for both uniform and random distributions, and that $g_u < g_r$ for each type of branching.

The effect of the heterogeneity in $n$ has been studied by Zimm and Stockmayer[21] and by Orofino,[62] but we do not reproduce it here.

## 9b(ii). Ring Polymers

For simplicity, we consider a single-ring molecule. It may be formed by joining the ends of a linear chain of $n$ segments. The distribution function $P_r(\mathbf{R}_{ij})$ of the distance between segments $i$ and $j$ of the ring molecule may then be expressed in terms of the bivariate distribution $P(\mathbf{R}_{ij}, \mathbf{R})$ for the linear chain as follows,

$$P_r(\mathbf{R}_{ij}) = P(\mathbf{R}_{ij}|\mathbf{R})_{\mathbf{R}=0} \equiv P(\mathbf{R}_{ij}|0)\,, \tag{9.77}$$

where

$$P(\mathbf{R}_{ij}|\mathbf{R}) = P(\mathbf{R}_{ij}, \mathbf{R})/P(\mathbf{R})\,. \tag{9.78}$$

Thus $P_r(\mathbf{R}_{ij})$ can be evaluated by the use of the Wang–Uhlenbeck theorem, and the result is

$$P_r(\mathbf{R}_{ij}) = \left(\frac{3}{2\pi\mu a^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}_{ij}^2}{2\mu a^2}\right) \tag{9.79}$$

with

$$\mu = (j-i)\left(1 - \frac{j-i}{n}\right)\,. \tag{9.80}$$

We therefore have

$$\langle R_{ij}^2 \rangle_r = \mu a^2\,, \tag{9.81}$$

and from Eqs. (7.22) and (9.81)

$$\langle S^2 \rangle_r = \tfrac{1}{12} n a^2\,, \tag{9.82}$$

or

$$\langle S^2 \rangle_r = \tfrac{1}{2} \langle S^2 \rangle_l\,. \tag{9.83}$$

Equation (9.82) or (9.83) is the result obtained by Kramers[20] and by Zimm and Stockmayer[21]; it implies that the mean-square radius of a single-ring molecule is just one half of that of a linear chain having the same number of segments.

In general, the mean-square radii of multiple-ring molecules can also be evaluated by the use of the Wang–Uhlenbeck theorem.

## 9c. Wormlike Chain Model for Stiff Chains

In Section 9a, we have seen that, even for the case of vinyl polymers, unperturbed chains do not have the Markoff nature (the proportionality of $\langle R^2 \rangle$ to $n$) when they are short. This arises from the fact that the correlation between the two end bonds does not vanish for short chains, and the chains may be regarded as stiff or semiflexible. Typical examples placed in this category are short chains of cellulose derivatives, polypeptides in the helical state, and DNA (deoxyribonucleic acids). A useful molecular model of a stiff chain is the one called the *wormlike chain*, the concept of which was first introduced by Kratky and Porod[63] in interpreting small angle x-ray scattering measurements of polymer solutions. In this section, we give a brief description of the statistical treatment of the wormlike chain.

## 9c(i). The Concept and the Moments

We first consider a model chain composed of $n$ bonds of length $a$ joined linearly with bond angle $\theta$, where the free rotation about bonds is permitted and $\theta$ dose not necessarily stand for the true valence angle. The mean-square end-to-end distance of this chain is given by Eq. (9.7). Suppose now that the first bond $\mathbf{r}_1$ is placed in the direction of the $z$ axis. Then the average of the $z$ component of the end-to-end vector $\mathbf{R}$ is given by $\langle \mathbf{R} \cdot \mathbf{e}_z \rangle = a^{-1} \sum_i \langle \mathbf{r}_1 \cdot \mathbf{r}_i \rangle$. The projection method yields $\langle \mathbf{r}_1 \cdot \mathbf{r}_i \rangle = a^2(-\cos\theta)^{i-1}$ as before, and we have

$$\langle \mathbf{R} \cdot \mathbf{e}_z \rangle = a \frac{1 - (-\cos\theta)^n}{1 + \cos\theta}\,, \tag{9.84}$$

and for large $n$

$$\lim_{n\to\infty} \langle \mathbf{R} \cdot \mathbf{e}_z \rangle = \frac{a}{1+\cos\theta} \equiv \frac{1}{2\lambda}\,, \tag{9.85}$$

assuming that $|\cos\theta| < 1$. The length $(2\lambda)^{-1}$ is referred to as the *persistence length.* The situation is similar to that encountered in the kinetic theory of gases, in which some component of the velocity of a particle *persists* after collisions.

The wormlike chain is defined as a limiting continuous chain formed from the above discrete chain by letting $a \to 0$ and $\theta \to \pi$ under the restriction that $a/(1+\cos\theta) = (2\lambda)^{-1}$ and $na \equiv L$ remain constant.[63, 64] For the wormlike chain, we therefore have, from Eqs. (9.84) and (9.7),

$$\langle \mathbf{R} \cdot \mathbf{e}_z \rangle = \frac{1}{2\lambda}(1 - e^{-2\lambda L})\,, \tag{9.86}$$

$$\langle R^2 \rangle = \frac{L}{\lambda} - \frac{1}{2\lambda^2}(1 - e^{-2\lambda L})\,. \tag{9.87}$$

Similarly, by evaluating $\langle R^4 \rangle$ of the discrete chain, for the limiting case we obtain[65, 66]

$$\langle R^4 \rangle = \frac{5L^2}{3\lambda^2} - \frac{26L}{9\lambda^3} - \frac{1}{54\lambda^4}(1 - e^{-6\lambda L}) + \frac{2}{\lambda^4}(1 - e^{-2\lambda L}) - \frac{L}{\lambda^3}e^{-2\lambda L}\,. \tag{9.88}$$

Equations (9.87) and (9.88) have also been derived by Hermans and Ullman[67] and by Saito et al.[68] by different methods.

The random-flight chain and rod may be considered the extremes, $\lambda L \gg 1$ and $\lambda L \ll 1$, of the wormlike chain, respectively. In fact, we have, from Eqs. (9.87) and (9.88),

$$\left.\begin{aligned} \lim_{\lambda L\to\infty} \langle R^2\rangle &= \frac{L}{\lambda}\,, \\ \lim_{\lambda L\to\infty} \langle R^4\rangle &= \frac{5}{3}\left(\frac{L}{\lambda}\right)^2, \end{aligned}\right\} \quad \text{(for random flights)} \tag{9.89}$$

$$\left.\begin{aligned} \lim_{\lambda L\to 0} \langle R^2\rangle &= L^2\,, \\ \lim_{\lambda L\to 0} \langle R^4\rangle &= L^4\,. \end{aligned}\right\} \quad \text{(for rods)} \tag{9.90}$$

The quantity $L$ is the contour length of the chain and is equal to $R_m$ of Eq. (9.54), the end-to-end distance at full extension. Thus, for the random-flight chain, we have $A = \langle R^2\rangle/L = \lambda^{-1}$; that is, the Kuhn statistical segment length is just twice the persistence length. The parameter $\lambda$ is a measure of chain stiffness or flexibility; the stiffer the chain, the smaller the parameter $\lambda$.

## 9c(ii). Treatments as a Space Curve

The wormlike chain may be regarded as a differentiable space curve, and from this point of view the statistical theory of a stiff chain has recently been developed.[68, 69] For convenience, we describe it following the procedure of Saito et al.[68]

Let $\mathbf{r}(s)$ be the radius vector of an arbitrary point of the space curve as a function of the contour distance $s$ from one end to that point. Then the unit vector $\mathbf{u}(s)$ tangential to the curve at the point $s$ is given by

$$\mathbf{u} = \frac{\partial \mathbf{r}}{\partial s} \tag{9.91}$$

with

$$\mathbf{u}^2 = \left(\frac{\partial \mathbf{r}}{\partial s}\right)^2 = 1\,. \tag{9.92}$$

The derivative $\partial\mathbf{u}/\partial s$ is the curvature vector, its magnitude being equal to the inverse of the radius of curvature. The energy of a bending rod (per unit length) is equal to $\frac{1}{2}\varepsilon(\text{radius of curvature})^{-2}$, where $\varepsilon$ is a bending force constant.[70] Thus the potential energy of the chain of contour length $s$ is given by

$$U = \tfrac{1}{2}\varepsilon \int_0^s \left(\frac{\partial \mathbf{u}}{\partial s}\right)^2 ds\,. \tag{9.93}$$

The configurational partition function $Z(\mathbf{u}, s)$ with the unit tangent vector $\mathbf{u}(s)$ (at the end $s$) fixed may be written in the form,

$$Z(\mathbf{u}, s) = \int \exp\left[-\frac{\varepsilon}{2kT}\int_0^s \left(\frac{\partial \mathbf{u}}{\partial s}\right)^2 ds\right] d\{\mathbf{r}\}\,, \tag{9.94}$$

where the integration over $\{\mathbf{r}\}$ is carried out over all possible configurations of the chain with $\mathbf{u}(s)$ fixed, and may be considered a kind of path integral.

Now, Eq. (9.94) is of the same form as the integral representation of the wave function $\psi(\mathbf{r}, t)$ for a free particle,[71] the correspondence between the parameters in the two expressions being $\varepsilon/2kT \leftrightarrow \pi m/ih$. The wave function for a free particle satisfies the Schrödinger equation,

$$\frac{\partial\psi}{\partial t} = \frac{ih}{4\pi m}{\nabla_{\mathbf{r}}}^2\psi\,. \tag{9.95}$$

Thus we can readily write down the differential equation satisfied by $Z$ as follows,

$$\frac{\partial Z}{\partial s} = \lambda{\nabla_{\mathbf{u}}}^2 Z \tag{9.96}$$

with

$$\lambda = \frac{kT}{2\varepsilon}\,. \tag{9.97}$$

In polar coordinates, the general solution of Eq. (9.96) under the restriction of (9.92) may be expanded in terms of spherical harmonics,

$$Z(\theta, \varphi, s) = \frac{1}{4\pi}\sum_{n,m}(2n+1)e^{-n(n+1)(s-s')\lambda}({A_{nm}}^e {Y_{nm}}^e + {A_{nm}}^0 {Y_{nm}}^0)\,, \tag{9.98}$$

where ${Y_{nm}}^e$ and ${Y_{nm}}^0$ are the even and odd spherical harmonics,

$${Y_{nm}}^e = \cos(m\varphi){P_n}^m(\cos\theta)\,, \quad {Y_{nm}}^0 = \sin(m\varphi){P_n}^m(\cos\theta) \tag{9.99}$$

with ${P_n}^m(\cos\theta)$ the associated Legendre function, and the coefficients $A_{nm}(= {A_{nm}}^e$ or ${A_{nm}}^0$, as $Y_{nm} = {Y_{nm}}^e$ or ${Y_{nm}}^0)$ are given by

$$A_{nm} = e_m\frac{(n-m)!}{(n+m)!}\int_0^\pi\int_0^{2\pi} Z(\theta', \varphi', s')Y_{nm}(\theta', \varphi')\sin\theta' d\theta' d\varphi' \tag{9.100}$$

with $e_0 = 1$ and $e_m = 2$ for $m = 1, 2, \ldots$ Equation (9.98) may be rewritten as

$$Z(\theta, \varphi, s) = \int_0^\pi\int_0^{2\pi} Z(\theta', \varphi', s')G(\theta, \varphi, s|\theta', \varphi', s')\sin\theta' d\theta' d\varphi'\,, \tag{9.101}$$

where $G$ is the Green's function[72] of the differential equation of (9.96) and is given by

$$G(\theta, \varphi, s|\theta', \varphi', s') = \frac{1}{4\pi}\sum_{n=0}^{\infty}(2n+1)e^{-n(n+1)\lambda|s-s'|}\sum_{m=0}^{n} e_m \\ \times\frac{(n-m)!}{(n+m)!}{P_n}^m(\cos\theta){P_n}^m(\cos\theta')\cos\big[m(\varphi-\varphi')\big]\,. \tag{9.102}$$

Note that for the present case $G$ has the meaning of a conditional probability. In particular, we have

$$G(\theta, \varphi, s|0, 0, s') = \frac{1}{4\pi} \sum_n (2n+1) e^{-n(n+1)\lambda|s-s'|} P_n(\cos\theta) P_n(1) \tag{9.103}$$

with $P_n$ the ordinary Legendre polynomials.

The mean-square end-to-end distance of a discrete chain may be expressed as $\langle R^2 \rangle = \sum_i \sum_j \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle$. For the continuous chain of contour length $L$, this may be converted to

$$\langle R^2 \rangle = \int_0^L \int_0^L \big\langle \mathbf{u}(s_1) \cdot \mathbf{u}(s_2) \big\rangle ds_1 ds_2 \,. \tag{9.104}$$

The integrand can be evaluated, by the use of Eq. (9.103), as

$$\begin{aligned} \big\langle \mathbf{u}(s_1) \cdot \mathbf{u}(s_2) \big\rangle &= \int_0^\pi \int_0^{2\pi} \cos\theta G(\theta, \varphi, s_2|0, 0, s_1) \sin\theta d\theta d\varphi \\ &= e^{-2\lambda|s_2 - s_1|} \,. \end{aligned} \tag{9.105}$$

Substitution of Eq. (9.105) into Eq. (9.104) leads to Eq. (9.87). Similarly, $\langle R^4 \rangle$ may be written as

$$\langle R^4 \rangle = \int_0^L \cdots \int_0^L \Big\langle \big[\mathbf{u}(s_1) \cdot \mathbf{u}(s_2)\big] \big[\mathbf{u}(s_3) \cdot \mathbf{u}(s_4)\big] \Big\rangle ds_1 \cdots ds_4 \,. \tag{9.106}$$

After a rather lengthy calculation with the use of Eq. (9.102), we recover Eq. (9.88). Thus the parameter $\lambda$ defined by Eq. (9.97) is identical with that introduced in Eq. (9.85).

The mean-square radius of gyration may be calculated from the equivalent of Eq. (7.22),

$$\langle S^2 \rangle = \frac{1}{L^2} \int_0^L (L - l) \langle {R_l}^2 \rangle dl \,, \tag{9.107}$$

where $\langle {R_l}^2 \rangle$ is the mean-square end-to-end distance of the chain of contour length $l$ and is given by Eq. (9.87) with $L = l$. The result is

$$\langle S^2 \rangle = \frac{L}{6\lambda} - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^3 L} - \frac{1}{8\lambda^4 L^2} (1 - e^{-2\lambda L}) \,. \tag{9.108}$$

In the two limiting cases, we have

$$\lim_{\lambda L \to \infty} \langle S^2 \rangle = \frac{L}{6\lambda} \qquad \text{(for random flights)} \,, \tag{9.109}$$

$$\lim_{\lambda L \to 0} \langle S^2 \rangle = \frac{L^2}{12} \qquad \text{(for rods)} \,. \tag{9.110}$$

### 9c(iii). Distribution of the End-to-End Distance

Our attention is directed to the distribution function $P(\mathbf{R}, \mathbf{u}_0)$ for the continuous chain with the unit tangent vector $\mathbf{u}_0$ at one end fixed. Daniels[73] has treated the problem as a Markoff process, and derived a differential equation for $P$ from a Markoff integral equation.* A similar approach has been made by Hermans and Ullman.[67] However, the details are omitted here. The result can be obtained only in a series form; in polar coordinates, it reads[73]

$$\begin{aligned} P(\mathbf{R}, \mathbf{u}_0)d\mathbf{R} = {} & (3\lambda/2\pi L)^{3/2} \exp(-3\lambda R^2/2L) \\ & \times \big[(1 - 5/8\lambda L + 2R^2/L^2 - 33\lambda R^4/40L^3) + (3R/2L \\ & - 25R/16\lambda L^2 + 153R^3/40L^3 - 99\lambda R^5/80L^4)P_1(\cos\theta) \\ & + (R^2/2L^2)P_2(\cos\theta) + \cdots\big] R^2 \sin\theta \, dR \, d\theta \, d\varphi \qquad (9.111) \end{aligned}$$

with $\mathbf{u}_0$ in the direction of the polar axis. Integrating over $\theta$ and $\varphi$, we have

$$\begin{aligned} P(R, \mathbf{u}_0)dR = {} & (3\lambda/2\pi L)^{3/2} \exp(-3\lambda R^2/2L) \\ & \times (1 - 5/8\lambda L + 2R^2/L^2 - 33\lambda R^4/40L^3 + \cdots) 4\pi R^2 dR \,. \qquad (9.112) \end{aligned}$$

From Eqs. (9.111) and (9.112), we obtain for the moments of the Daniels distribution

$$\left. \begin{aligned} \langle \mathbf{R} \cdot \mathbf{e}_z \rangle &= \frac{1}{2\lambda} \,, \\ \langle R^2 \rangle &= \frac{L}{\lambda} - \frac{1}{2\lambda^2} \,, \\ \langle R^4 \rangle &= \frac{5L^2}{3\lambda^2} - \frac{26L}{9\lambda^3} \,. \end{aligned} \right\} \quad \text{(Daniels)} \qquad (9.113)$$

These are to be compared with the exact values given by Eqs. (9.86) to (9.88). Thus the Daniels distribution is seen to be a good approximation to the actual distribution for large $\lambda L$; it includes a first-order correction to the Gaussian distribution due to chain stiffness.

## Appendix II A. Method of Steepest Descents

We consider the problem of finding the asymptotic form of a contour integral,

$$J(z) = \int_\Gamma g(\xi) \exp\big[z f(\xi)\big] d\xi \,, \qquad \text{(II A.1)}$$

as $|z| \to \infty$, where $z$ and $\xi$ are complex variables, $g(\xi)$ and $f(\xi)$ are analytic functions of $\xi$, and the contour $\Gamma$ is such that the integrand becomes zero at the ends $A$ and $B$ of the contour. This can be done by a procedure known as the method of steepest descents or the saddle point method.[74] In the following, we give only a short sketch of the method which will be sufficient for practical use.

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*This approach to the chain statistics will be described in Chapter III.

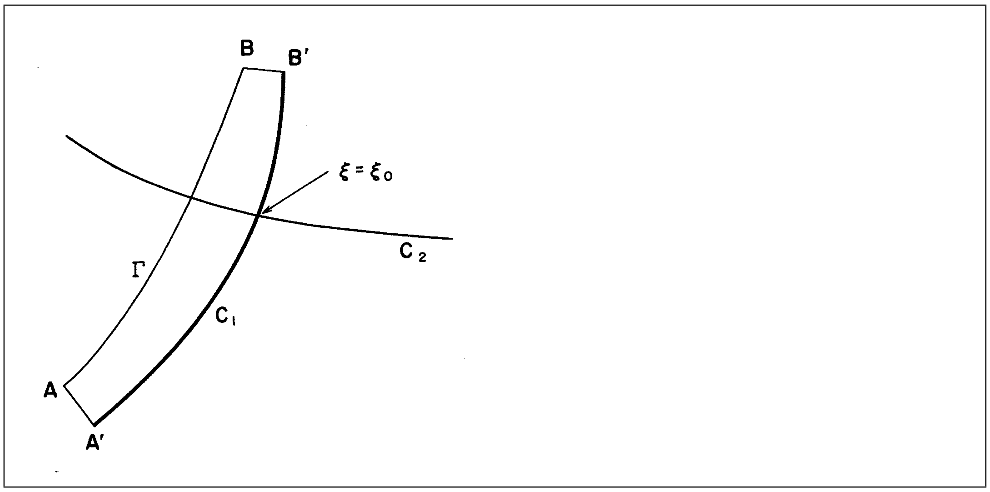

**Fig. II.10.** Two paths $C_1$ and $C_2$ passing through the saddle point. Path $C_1$ is the distorted contour, while $\Gamma$ is the original contour.

Let us examine the behavior of the real part $|z|u(\xi)$ of $zf(\xi) = |z|u(\xi) + i|z|v(\xi)$ near the point $\xi = \xi_0$ determined by

$$f'(\xi_0) = 0\,. \tag{II A.2}$$

It is convenient to plot the surface, $|z|u(\xi)$ =vertical coordinate perpendicular to the $x$, $y$ complex plane ($\xi = x + iy$); at every point $\xi$ in the $x$, $y$ plane the surface is at a height above the horizontal given by $|z|u(\xi)$ at that point. Now, according to the theory of functions, the real part of an analytic function of a complex variable (and also the imaginary part and the absolute value) can have neither a maximum nor a minimum. The above surface can therefore be neither a mountain top nor a valley in the neighborhood of $\xi_0$, though it must be flat there because of Eq. (II A.2). Thus the point $\xi_0$ must be a minimax (or a saddle point). Two curves $C_1$ and $C_2$ passing through $\xi_0$ can be drawn on the surface so as to satisfy the following condition: the point $\xi_0$ is the sharpest maximum for curve $C_1$ running from one valley to another and is the sharpest minimum for curve $C_2$ running from one mountain top to another, while the imaginary part $|z|v(\xi)$ is kept constant along paths $C_1$ and $C_2$ (projections of $C_1$ and $C_2$ on the $x$, $y$ plane). Along path $C_1$ the integrand of Eq. (II A.1) approaches its end-point value of zero at $A'$ or $B'$ as $|z|u(\xi)$ descends towards the valley on either side of the saddle point. Path $C_1$ may then be chosen as a new distorted contour in place of $\Gamma$, assuming that the integrand is zero along paths $AA'$ and $BB'$ (see Fig. II.10). Thus Eq. (II A.1) may be rewritten as

$$J(z) = \exp\big[i|z|v(\xi)\big] \int_{C_1} g(\xi) \exp\big[|z|u(\xi)\big] d\xi\,. \tag{II A.3}$$

The dominant contribution to this integral comes from the neighborhood of the saddle point. This becomes increasingly true as $|z| \to \infty$, since the maximum of $|z|u(\xi)$ along $C_1$ becomes sharper and the descent to the end-point value more rapid.

To illustrate the above statement more clearly, let us find the first term in the asymptotic expansion of $J(z)$. In the neighborhood of $\xi_0$, $zf(\xi)$ may be expanded as

$$\begin{aligned} zf(\xi) &= zf(\xi_0) + \tfrac{1}{2}zf''(\xi_0)(\xi-\xi_0)^2 + \cdots \\ &= zf(\xi_0) + \tfrac{1}{2}|zf''(\xi_0)|r^2 e^{i(2\theta+\alpha)} + \cdots\,, \end{aligned} \tag{II A.4}$$

where $r$ is the absolute value of $(\xi - \xi_0)$, and $\theta$ and $\alpha$ are the arguments of $(\xi - \xi_0)$ and $zf''(\xi_0)$, respectively. The real part of $zf(\xi)$ is

$$|z|u(\xi) = |z|u(\xi_0) + \tfrac{1}{2}|zf''(\xi_0)|r^2\cos(2\theta+\alpha) + \cdots\,, \tag{II A.5}$$

Thus the steepest-descent direction $C_1$ at $\xi_0$ is such that $\cos(2\theta+\alpha) = -1$, and therefore such that $zf''(\xi_0)(\xi-\xi_0)^2$ is real and negative. Along path $C_2$ perpendicular to $C_1$ at the point $\xi_0$, it is the sharpest minimum. Along paths $C_1$ and $C_2$, we have

$$|z|v(\xi) = |z|v(\xi_0) + \cdots\,, \tag{II A.6}$$

which is independent of $\xi$. Thus the integral $J(z)$ may be approximated by

$$J(z) = \exp\big[zf(\xi_0)\big]\int_{C_1} g(\xi)\exp\big[\tfrac{1}{2}zf''(\xi_0)(\xi-\xi_0)^2\big]d\xi\,. \tag{II A.7}$$

For instance, suppose that $g(\xi) \equiv 1$, and that $zf''(\xi_0)$ is real and negative. Then the contour should pass through $\xi_0$ parallel to the real axis. Upon putting $\xi = x + iy_0$ and $\xi_0 = x_0 + iy_0$, Eq. (II A.7) becomes an integral with respect to $x$ covering the range from $-\infty$ to $+\infty$. The direction of integration over $x$ is determined by the original contour. If it is assumed that the direction of integration along the contour is such that the integration over $x$ is from $-\infty$ to $+\infty$, $J(z)$ can be evaluated as

$$\begin{aligned} J(z) &= \exp\big[zf(\xi_0)\big]\int_{-\infty}^{+\infty}\exp\big[-\tfrac{1}{2}|zf''(\xi_0)|(x-x_0)^2\big]dx \\ &= \big[2\pi/|zf''(\xi_0)|\big]^{1/2}\exp\big[zf(\xi_0)\big]\,. \end{aligned} \tag{II A.8}$$

## Appendix II B. Orthogonal Transformations

For the evaluation of the integral of Eq. (6.14), it is convenient to resolve $\boldsymbol{\rho}_j$ into $x$, $y$, and $z$ components, giving

$$P\big(\{\boldsymbol{\Phi}_s\}\big) = P_x\big(\{\Phi_{sx}\}\big)P_y\big(\{\Phi_{sy}\}\big)P_z\big(\{\Phi_{sz}\}\big)\,, \tag{II B.1}$$

where

$$P_x\bigl(\{\Phi_{sx}\}\bigr) = (2\pi)^{-s} \int \exp\biggl[-\frac{\langle a^2\rangle}{6}\sum_k\sum_l C_{kl}\rho_{kx}\rho_{lx} - i\sum_k \rho_{kx}\Phi_{kx}\biggr] d\{\rho_{sx}\}\,, \tag{II B.2}$$

and so on. In the material that follows the subscript $x$ will be omitted for simplicity.

As is well known, a vector may be represented as a matrix consisting of one single row or one single column, and is called a row vector or a column vector, as the case may be. Now suppose $\boldsymbol{\rho}$ and $\boldsymbol{\Phi}$ to be column vectors,

$$\boldsymbol{\rho} = \begin{pmatrix} \rho_1 \\ \vdots \\ \rho_s \end{pmatrix}, \qquad \boldsymbol{\Phi} = \begin{pmatrix} \Phi_1 \\ \vdots \\ \Phi_s \end{pmatrix}, \tag{II B.3}$$

so that the transposes $\boldsymbol{\rho}^T$ and $\boldsymbol{\Phi}^T$ of $\boldsymbol{\rho}$ and $\boldsymbol{\Phi}$ are the row vectors,

$$\boldsymbol{\rho}^T = (\rho_1 \cdots \rho_s)\,, \quad \boldsymbol{\Phi}^T = (\Phi_1 \cdots \Phi_s)\,. \tag{II B.4}$$

In matrix notation, Eq. (II B.2) may then be rewritten as

$$P_x\bigl(\{\boldsymbol{\Phi}_s\}\bigr) = (2\pi)^{-s} \int \exp\left[-\frac{\langle a^2\rangle}{6}\boldsymbol{\rho}^T\mathbf{C}\boldsymbol{\rho} - i\boldsymbol{\Phi}^T\boldsymbol{\rho}\right] d\boldsymbol{\rho} \tag{II B.5}$$

with

$$\boldsymbol{\rho}^T\mathbf{C}\boldsymbol{\rho} = \sum_k\sum_l C_{kl}\rho_k\rho_l\,, \tag{II B.6}$$

$$\boldsymbol{\Phi}^T\boldsymbol{\rho} = \sum_k \Phi_k\rho_k\,, \tag{II B.7}$$

where $\mathbf{C}$ is the $s \times s$ symmetric matrix with elements $C_{kl}$ and the quadratic form of (II B.6) is assumed positive definite.

The matrix $\mathbf{C}$ can be transformed into a diagonal matrix $\boldsymbol{\Lambda}$ with an appropriate orthogonal matrix $\mathbf{Q}(\mathbf{Q}^{-1} = \mathbf{Q}^T)$,

$$\mathbf{Q}^{-1}\mathbf{C}\mathbf{Q} = \boldsymbol{\Lambda}\,, \tag{II B.8}$$

and at the same time $\boldsymbol{\rho}$ and $\boldsymbol{\Phi}$ are transformed into $\boldsymbol{\xi}$ and $\boldsymbol{\Psi}$, respectively,

$$\boldsymbol{\rho} = \mathbf{Q}\boldsymbol{\xi}\,, \tag{II B.9}$$

$$\boldsymbol{\Phi} = \mathbf{Q}\boldsymbol{\Psi}\,. \tag{II B.10}$$

Then, in the new coordinate system $\boldsymbol{\xi}$, the quantities $\boldsymbol{\rho}^T\mathbf{C}\boldsymbol{\rho}$ and $\boldsymbol{\Phi}^T\boldsymbol{\rho}$ may be expressed as

$$\boldsymbol{\rho}^T\mathbf{C}\boldsymbol{\rho} = (\mathbf{Q}\boldsymbol{\xi})^T\mathbf{C}\boldsymbol{\rho} = \boldsymbol{\xi}^T\mathbf{Q}^T\mathbf{C}\mathbf{Q}\boldsymbol{\xi} = \boldsymbol{\xi}^T\boldsymbol{\Lambda}\boldsymbol{\xi} = \sum_j \lambda_j{\xi_j}^2\,, \tag{II B.11}$$

$$\mathbf{\Phi}^T \boldsymbol{\rho} = \mathbf{\Phi}^T \mathbf{Q}\boldsymbol{\xi} = (\mathbf{Q}^{-1}\mathbf{\Phi})^T \boldsymbol{\xi} = \mathbf{\Psi}^T \boldsymbol{\xi} = \sum_j \Psi_j \xi_j \,, \tag{II B.12}$$

where the $\lambda_j$'s are the diagonal elements of $\mathbf{\Lambda}$. Further, the Jacobian of the transformation is

$$\left| \frac{\partial \boldsymbol{\rho}}{\partial \boldsymbol{\xi}} \right| = \text{absolute value of } |\mathbf{Q}| = 1 \tag{II B.13}$$

with $|\mathbf{Q}|$ the determinant of $\mathbf{Q}$. Accordingly Eq. (II B.5) becomes

$$\begin{aligned} P_x\big(\{\Phi_s\}\big) &= (2\pi)^{-s} \int \exp\left[ -\frac{\langle a^2 \rangle}{6} \boldsymbol{\xi}^T \mathbf{\Lambda} \boldsymbol{\xi} - i \mathbf{\Psi}^T \boldsymbol{\xi} \right] d\boldsymbol{\xi} \\ &= (2\pi)^{-s} \prod_{j=1}^{s} \int_{-\infty}^{+\infty} \exp\left[ -\frac{\langle a^2 \rangle}{6} \lambda_j {\xi_j}^2 - i \Psi_j \xi_j \right] d\xi_j \,. \end{aligned} \tag{II B.14}$$

Since by assumption $\boldsymbol{\rho}^T \mathbf{C} \boldsymbol{\rho}$ is positive definite, all the eigenvalues $\lambda_j$ are positive, and thus it can be easily found that

$$P_x\big(\{\Phi_s\}\big) = \left( \frac{3}{2\pi \langle a^2 \rangle} \right)^{s/2} \left( \prod_{j=1}^{s} {\lambda_j}^{-1/2} \right) \exp\left( -\frac{3}{2\langle a^2 \rangle} \sum_{j=1}^{s} \frac{{\Psi_j}^2}{\lambda_j} \right) . \tag{II B.15}$$

Now we recall that

$$\prod_j \lambda_j = |\mathbf{\Lambda}| = |\mathbf{C}| \,, \tag{II B.16}$$

$$\begin{aligned} \sum_j \frac{{\Psi_j}^2}{\lambda_j} &= \mathbf{\Psi}^T \mathbf{\Lambda}^{-1} \mathbf{\Psi} = \mathbf{\Phi}^T \mathbf{Q} \mathbf{\Lambda}^{-1} \mathbf{Q}^{-1} \mathbf{\Phi} \\ &= \mathbf{\Phi}^T \mathbf{C}^{-1} \mathbf{\Phi} = \sum_k \sum_l \frac{C^{kl}}{|\mathbf{C}|} \Phi_k \Phi_l \,, \end{aligned} \tag{II B.17}$$

where $C^{kl}$ is the cofactor of the element $C_{kl}$ of $\mathbf{C}$. Equation (II B.15) may then be rewritten as

$$P_x\big(\{\Phi_s\}\big) = \left( \frac{3}{2\pi \langle a^2 \rangle} \right)^{s/2} |\mathbf{C}|^{-1/2} \exp\left( -\frac{3}{2\langle a^2 \rangle |\mathbf{C}|} \sum_k \sum_l C^{kl} \Phi_k \Phi_l \right) . \tag{II B.18}$$

Substitution of Eq. (II B.18) and similar equations for the $y$ and $z$ components into Eq. (II B.1) leads to

$$\begin{aligned} P\big(\{\mathbf{\Phi}_s\}\big) &= \left( \frac{3}{2\pi \langle a^2 \rangle} \right)^{3s/2} |\mathbf{C}|^{-3/2} \\ &\quad \times \exp\left[ -\frac{3}{2\langle a^2 \rangle |\mathbf{C}|} \sum_k \sum_l C^{kl} (\Phi_{kx}\Phi_{lx} + \Phi_{ky}\Phi_{ly} + \Phi_{kz}\Phi_{lz}) \right] . \end{aligned} \tag{II B.19}$$

This is equivalent to Eq. (6.15).

## Appendix II C. Distribution of the Quasi-radius of Gyration with S Fixed

In this appendix, we evaluate, from Eq. (8.21), the conditional probability density $P(\mathbf{s}|S)$ of the quasi-radius of gyration $\mathbf{s}$ with the radius of gyration $S$ fixed. A very interesting conclusion will be drawn concerning the segment density. The evaluation is due to Fixman.[75]

We begin by describing some basic equations. As in the case of $P(\mathbf{s})$, $P(\mathbf{s}|S)$ is given by the sum of the bivariate distribution functions $P_j(\mathbf{s}, S^2)$ of Eq. (8.21) with $\mathbf{S}_j = \mathbf{s}$,

$$\begin{aligned} P(\mathbf{s}|S) &= \left[nP(S^2)\right]^{-1}\sum_j P_j(\mathbf{s}, S^2) = \left[nP(S)\right]^{-1}\sum_j P_j(\mathbf{s}, S) \\ &= \frac{1}{n}\sum_j P_j(\mathbf{s}|S)\,, \end{aligned} \tag{II C.1}$$

and also is related to the segment-density distribution function $\rho(\mathbf{s}|S)$ with $S$ fixed by the equation,

$$P(\mathbf{s}|S) = \frac{1}{n}\rho(\mathbf{s}|S)\,. \tag{II C.2}$$

The function $P(\mathbf{s}|S)$ averaged over all values of $S$ gives the distribution function $P(\mathbf{s})$ of the quasi-radius of gyration, and the second moments of $P(\mathbf{s})$ and $P(S)$ are identical as mentioned earlier; that is,

$$P(\mathbf{s}) = \int P(\mathbf{s}|S)P(S)dS\,, \tag{II C.3}$$

$$\begin{aligned} \langle S^2\rangle &= \int S^2P(S)dS = \int s^2P(\mathbf{s})d\mathbf{s} \\ &= \int s^2P(\mathbf{s}|S)P(S)d\mathbf{s}\; dS\,. \end{aligned} \tag{II C.4}$$

Further, it must be true that

$$S^2 = \int s^2P(\mathbf{s}|S)d\mathbf{s}\,. \tag{II C.5}$$

This equality follows from the fact that the square of the radius of gyration in any instantaneous configuration is

$$\frac{1}{n}\sum_j {S_j}^2 = \frac{1}{n}\int s^2\sum_j \delta(\mathbf{s}-\mathbf{S}_j)d\mathbf{s}\,,$$

where $\sum\delta(\mathbf{s}-\mathbf{S}_j)$ is the segment density in the given configuration. Equation (II C.5) results from a conditional average over all configurations, the condition being that $S^2 = n^{-1}\sum {S_j}^2$. Equations (II C.4) and (II C.5) are general relations between $S$ and $P(\mathbf{s}|S)$.

Now we evaluate the quantity $W_j$ of (8.20), which appears in $P_j(\mathbf{S}_j, S^2)$ of (8.21). Substitution of Eqs. (7.4) and (8.38) and conversion of the sum to an integral leads to

$$\sum_{l=1}^{n} \psi_{jl} Q_{lk} = -(2n)^{1/2}(\pi k)^{-1} \cos(\pi jk/n)\,. \tag{II C.6}$$

Substituting Eqs. (8.34) and (II C.6) into Eq. (8.20), we can obtain (for $n \gg 1$)

$$W_j = (na^2/12X^2)\big\{2-(X/\sin X)\big[\cos X+\cos(X-2jX/n)\big]\big\}\,. \tag{II C.7}$$

The problem is to evaluate the integral in Eq. (8.21) with Eq. (II C.7).

No closed expression for $P(S)$ valid for all $S$ has been obtained, and therefore it will not be surprising that the integration in Eq. (8.21) also proves refractory. Thus we shall confine ourselves to the solution for large $S$. Even for this situation, however, a steepest-descent calculation of the integral is so complicated that it is easier to compute the moments of $P_j(\mathbf{S}_j, S^2)$, and from these to infer the distribution. The moments $\langle {S_j}^{2p}\rangle_S$ of $P_j(\mathbf{S}_j|S)$ are given by

$$\begin{aligned}\langle {S_j}^{2p}\rangle_S &= \int {S_j}^{2p} P_j(\mathbf{S}_j|S)d\mathbf{S}_j \\ &= \big[P(S^2)\big]^{-1}\int {S_j}^{2p} P_j(\mathbf{S}_j, S^2)d\mathbf{S}_j\,. \end{aligned} \tag{II C.8}$$

Substitution of Eq. (8.21) into Eq. (II C.8) and integration over $\mathbf{S}_j$ gives

$$\begin{aligned}P(S^2)\langle {S_j}^{2p}\rangle_S = {}& (2\pi)^{-1}2^n\big[1\cdot 3\cdots(2p+1)\big] \\ & \times \int_{-\infty}^{+\infty} K(\rho){W_j}^p \exp(-i\rho S^2)d\rho\,. \end{aligned} \tag{II C.9}$$

It should be noted that a summation of Eq. (II C.9) over all $j$, for $p = 1$, must lead to

$$\sum_j \langle {S_j}^2\rangle_S = nS^2\,, \tag{II C.10}$$

which can easily be verified from Eqs. (II C.1) and (II C.5).

The integral in Eq. (II C.9) was evaluated by Fixman for large $S$ by the method of steepest descents. The result is

$$\begin{aligned}P(S^2)\langle {S_j}^{2p}\rangle_S = {}& 2^{-1/2}3^{3/2}\pi^{5/2}(na^2)^{-3/2}S^{2p+1}(p+\tfrac{3}{2})^{-(p+1)} \\ & \times \big[1\cdot 3\cdots(2p+1)\big]\cos^{2p}(\pi j/n)\exp\big[(p+\tfrac{3}{2})-(3\pi^2S^2/2na^2)\big]\,. \end{aligned} \tag{II C.11}$$

It must however be pointed out that Eq. (II C.11) is not the correct asymptotic form for large $n$ and $S$, but is slightly erroneous. When $p = 0$, Eq. (II C.11) reduces to the Fixman equation (8.51) for $P(S)$, which is also slightly erroneous as already discussed. From Eqs. (II C.11) and (8.51) we obtain for $\langle {S_j}^{2p}\rangle_S$ at large $S$

$$\langle {S_j}^{2p}\rangle_S = {\alpha_j}^p \beta_p \tag{II C.12}$$

with

$$\alpha_j = 2S^2\cos^2(\pi j/n)\,, \tag{II C.13}$$

$$\beta_p = 3e^p\big[1\cdot 3\cdots(2p+1)\big](2p+3)^{-(p+1)}\,. \tag{II C.14}$$

If Stirling's approximation is applied to the product $\big[1\cdot 3\cdots(2p+1)\big]$, Eq. (II C.14) becomes

$$\beta_p = 0.9467\big\{1+\big[12(p+\tfrac{3}{2})\big]^{-1}+\cdots\big\}\,. \tag{II C.15}$$

The first two terms in this series suffice to give $\beta_p$ with an error less than 0.001 for $p=0$, and smaller error for larger $p$. From Eq. (II C.12) with (II C.13) and (II C.15), we have

$$\sum_j \langle {S_j}^2\rangle_S = 0.98nS^2\,. \tag{II C.16}$$

The coefficient should, of course, equal unity according to Eq. (II C.10), and we can only presume that this small error is connected with the inadequate treatment of the steepest-descent calculation stated above.

Equation (II C.15) shows that no moment would be computed with an error greater than 5% if $\beta_p$ were put equal to unity for all $p$. (Indeed, the coefficient in Eq. (II C.16) would become unity.) Because of the small error consequent on this approximation and the enormous simplification, we therefore take

$$\langle {S_j}^{2p}\rangle_S = {\alpha_j}^p\,. \tag{II C.17}$$

It is rather obvious from Eq. (II C.17) that the probability density has now been approximated by a delta function. To develop this conclusion formally let ${S_j}^2 = x_j$,

$$\langle {S_j}^{2p}\rangle_S = \int {x_j}^p P_j(x_j|S)dx_j\,. \tag{II C.18}$$

$P_j(x|S)$ is related to its characteristic function $\phi_j(\rho)$ by

$$P_j(x|S) = \frac{1}{2\pi}\int \phi_j(\rho)\exp(-i\rho x)d\rho\,, \tag{II C.19}$$

and according to Eq. (4.13) $\phi_j(\rho)$ is related to the moments of $P_j(x|S)$ by

$$\phi_j(\rho) = \sum_{p=0}^{\infty}\frac{1}{p!}\langle {x_j}^p\rangle_S (i\rho)^p = \exp(i\rho\alpha_j)\,, \tag{II C.20}$$

where the last equality has been obtained by substitution of Eq. (II C.17). Substitution of Eq. (II C.20) into Eq. (II C.19) leads to a Fourier representation of the one-dimensional delta function; that is,

$$P_j(x_j|S) = \delta(x_j - \alpha_j)\,. \tag{II C.21}$$

The result can be rewritten in terms of $P_j(\mathbf{S}_j|S)$ as

$$\begin{aligned} P_j({S_j}^2|S)d{S_j}^2 &= P_j(\mathbf{S}_j|S)4\pi {S_j}^2 dS_j\,,\\ P_j(\mathbf{S}_j|S) &= \frac{1}{2\pi S_j}\delta({S_j}^2 - \alpha_j)\,. \end{aligned} \tag{II C.22}$$

Now conversion of the sum in Eq. (II C.1) to an integral gives

$$\begin{aligned} P(\mathbf{s}|S) &= \frac{1}{n}\int_0^n P_j(\mathbf{s}|S)dj\\ &= \frac{1}{2\pi ns}\int_0^n \delta(s^2 - \alpha_j)dj\\ &= \frac{1}{\pi ns}\int_0^{2S^2} \delta(s^2 - \alpha_j)\left|\frac{\partial\alpha_j}{\partial j}\right|^{-1} d\alpha_j\,. \end{aligned} \tag{II C.23}$$

From Eq. (II C.13), $|\partial\alpha_j/\partial j|$ is obtained as

$$\left|\frac{\partial\alpha_j}{\partial j}\right| = (2\pi/n){\alpha_j}^{1/2}(2S^2 - \alpha_j)^{1/2}\,. \tag{II C.24}$$

We therefore have

$$P(\mathbf{s}|S) = H(2S^2 - s^2)/2\pi^2 s^2(2S^2 - s^2)^{1/2}\,, \tag{II C.25}$$

where $H$ is the unit step function defined by Eq. (7.5). It may easily be seen that Eq. (II C.25) satisfies Eq. (II C.5), and the step function $H(2S^2 - s^2)$ makes the segment density zero for $s > \sqrt{2}S$.

Equation (II C.25) has several interesting features. There is a sharp boundary to the molecule, and the segment density has a maximum on that boundary. However, there is also a nonnegligible distribution of segments in the interior of the molecule, the segment density being minimized at $s = (4/3)^{1/2}S$. Far in the interior of the molecule the segment density varies as $(s^2 S)^{-1}$. In summary, the qualitative effect of the constraint on $S$ is a shift of segments from the interior of the segment cloud to its boundary, the effect being so large that the cloud acquires a minimum density on an interior shell.

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# Chapter Three

# Statistics of Real Polymer Chains: Excluded-Volume Effect

## 10. Introduction

In the statistics of unperturbed chains we have described so far, account has been taken only of short-range interferences between segments separated by a relatively small number of bonds [through the first few terms in the expansion of the internal-rotational potential of (9.13)]. However, two or more segments remote from one another along the chain cannot occupy the same volume element at the same time because of their finite volumes; in other words, repulsive forces will act between these segments when close to one another. In addition, this repulsive force will, to some extent, be altered by the existence of solvent molecules. That is, there exist general van der Waals interactions among these segments. Intramolecular interactions of this sort are usually referred to as the *excluded-volume effect* in a polymer chain. This effect may be represented by higher-order terms in the expansion of (9.13), and therefore is of long-range nature. Thus it is also often called the long-range (intramolecular) interference effect. The description in this chapter is mostly concerned with the excluded volume of a linear flexible chain.

The basic molecular model we adopt for the present problem is the random-flight (Gaussian) chain of $(n + 1)$ identical segments with the effective bond length $a$, as discussed in Section 9a(iii). The reasons for this simplification are the following: (1) the distribution function is very complicated even for the unperturbed chain with only short-range interferences, and (2) there is no fundamental way in which the total intramolecular potential of (9.13) may be split into the potentials corresponding to short-range and long-range interferences. With this assumption, the configurational partition function for the system may be given formally by Eq. (3.7),

$$Z = \int \left[ \prod_{j=1}^{n} \tau(\mathbf{r}_j) \right] \exp \left[ -\frac{W\big(\{\mathbf{R}_n\}\big)}{kT} \right] d\{\mathbf{r}_n\} \,. \tag{10.1}$$

However, $\tau$ and $W$ are to be redefined as follows: $\tau$ is the (effective) bond probability given by Eq. (5.3) or (5.35) with $a$ being the effective bond length, and $W$ represents only the potential of mean force due to long-range interferences, so that the effect of short-range interferences is absorbed into the parameter $a$.

Now it is evident that the real chain with excluded volume will tend to be more extended, especially in a *good* solvent, than is expected from the statistics of unperturbed chains. Thus it is adequate to express the mean-square end-to-end distance $\langle R^2 \rangle$ and mean-square radius of gyration $\langle S^2 \rangle$ of the real chain in the forms,

$$\langle R^2 \rangle = \langle R^2 \rangle_0 \alpha_R{}^2 \,, \tag{10.2}$$

$$\langle S^2 \rangle = \langle S^2 \rangle_0 \alpha_S{}^2 \,, \tag{10.3}$$

where the subscript 0 refers to the unperturbed chain.* In particular, the unperturbed dimensions of the linear flexible chain may be written as

$$\langle R^2 \rangle_0 = na^2 \,, \tag{10.4}$$

$$\langle S^2 \rangle_0 = \tfrac{1}{6} na^2 \,, \tag{10.5}$$

as discussed in Section 9a(iii). The parameter $\alpha_R$ or $\alpha_S$ is referred to as the (*linear*) *expansion factor* of the polymer chain. It measures the extent to which a linear molecular dimension is perturbed by the excluded-volume effect and thereby differs from a linear unperturbed dimension. When the potential $W$ in Eq. (10.1) vanishes, the chain must become the unperturbed chain with $\alpha_R = \alpha_S = 1$.

For the treatment of the partition function of (10.1), it is necessary to make the superposition approximation[1, 2] in the potential of mean force $W$,

$$W\big(\{\mathbf{R}_n\}\big) = \sum_{0 \leq i < j \leq n} w(\mathbf{R}_{ij}) \,, \tag{10.6}$$

where $w(\mathbf{R}_{ij})$ is the pair potential of mean force between the $i$th and $j$th segments as a function of separation $\mathbf{R}_{ij}$. Further, it is assumed that the pair potential $w$ is short-ranged. Then the problem becomes very similar to that in the theory of simple fluids[1, 2]; it is the many-body problem. In fact, there are two approaches to the theory of the expansion factor. The first approach, which corresponds to the theory of imperfect gases, is valid for small excluded volume, and the expansion factor is expressed in a series form. The second approach focuses

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*Throughout the remainder of this book, the subscript 0 will be used to indicate the unperturbed state unless specified otherwise.

on deriving a theory valid at large excluded volume, and therefore corresponds to the theory of liquids at high densities. Naturally, the latter encounters many mathematical difficulties inherent in the many-body problem, and an exact solution for the case of large excluded volume has not yet been obtained. However, both the approaches lead to the conclusion that the expansion factor depends on the number of segments in the chain, and therefore the chain with excluded volume is of the non-Markoff nature. These developments, based on Eq. (10.1), will be described in Sections 13 to 16.

Our procedure is as follows: we first describe the theory of Flory,[3, 4] who was among the first to demonstrate the non-Markoff nature of the excluded-volume effect. Then we give a brief description of various attempts made by many workers following Flory, whose studies preceded the establishment of the dependence of $\alpha$ on $n$.

## 11. The Flory Theory

In the model used by Flory, the polymer molecule is regarded as a continuous cloud of segments distributed about the molecular center of mass in accordance with a Gaussian function. Irrespective of the form of the segment distribution, such a model is referred to as the *smoothed-density model.* For this model, the expansion factors $\alpha_R$ and $\alpha_S$ cannot be distinguished from each other, and we represent them both by $\alpha$. In Flory's treatment the equilibrium value of $\alpha$ is calculated from the balance between the osmotic force which tends to swell the molecule in solution and the elastic force arising from the resulting molecular expansion to a less probable configuration. For the sake of comparison with our later developments, however, we adopt an alternative method somewhat different from that used by Flory, but physically equivalent to that of Flory.

The distribution function $P(S)$ of the radius of gyration may be obtained by integrating the instantaneous distribution, the integrand of Eq. (10.1) divided by $Z$, over $\{\mathbf{r}_n\}$ under the restriction that $S$ has a specified value, as in Eq. (3.9) for $P(\mathbf{R})$. The result may be written formally in the form,

$$P(S) = Z^{-1} P_0(S) \exp\left[-\frac{V(S)}{kT}\right] \tag{11.1}$$

with

$$Z = \int P_0(S) \exp\left[-\frac{V(S)}{kT}\right] dS\,, \tag{11.2}$$

where $V(S)$ is the intramolecular potential of mean force with $S$ fixed, and $Z^{-1}$ has the meaning of a normalizing constant. Equation (11.1) is rather a defining equation for $V(S)$. The complete form of the unperturbed distribution $P_0(S)$ is very complicated, as seen in Section 8b.

For convenience, it is therefore assumed to be a Gaussian function,

$$P_0(S) = \left(\frac{3}{2\pi\langle S^2\rangle_0}\right)^{3/2} \exp\left(-\frac{3S^2}{2\langle S^2\rangle_0}\right) \cdot 4\pi S^2 \,. \tag{11.3}$$

Now the problem is to evaluate $V(S)$. When the zero of energy is chosen appropriately, the potential of mean force $V(S)$ will be a Helmholtz free energy of mixing segments (of one polymer molecule) and solvent molecules for a specified value of $S$ with the polymer molecular center of mass fixed in space. Let $\varphi(\mathbf{s}|S)$ be the volume fraction of polymer segments at the distance $\mathbf{s}$ from the molecular center of mass with $S$ fixed. Then the local free energy $\varepsilon_{\mathbf{s}}$ of mixing per unit volume at the point $\mathbf{s}$ is a function of $\varphi$,

$$\varepsilon_{\mathbf{s}} = \varepsilon\big[\varphi(\mathbf{s}|S)\big] \,, \tag{11.4}$$

and $V(S)$ is given by[5, 6]

$$V(S) = \int \varepsilon_{\mathbf{s}} d\mathbf{s} \,. \tag{11.5}$$

Since the average segment density within a single polymer molecule is very low, we may expand $\varepsilon_{\mathbf{s}}$ in a Taylor series around $\varphi = 0$,

$$\varepsilon_{\mathbf{s}} = \varepsilon(0) + \varepsilon^{(1)}(0)\varphi + \tfrac{1}{2}\varepsilon^{(2)}(0)\varphi^2 + \cdots \tag{11.6}$$

with

$$\varepsilon^{(k)}(\varphi) = \frac{d^k\varepsilon(\varphi)}{d\varphi^k} \,, \tag{11.7}$$

and neglect cubic and higher-order terms. The first term of Eq. (11.6) gives a constant term in $V(S)$. Now $\varphi$ may be expressed in terms of the segment-density distribution function $\rho(\mathbf{s}|S)$ with $S$ fixed,

$$\varphi(\mathbf{s}|S) = V_s \rho(\mathbf{s}|S) \tag{11.8}$$

with $V_s$ the volume of the polymer segment. Since the integral of $\rho$ over $\mathbf{s}$ is equal to $n$, the second term of Eq. (11.6) also gives a constant term in $V(S)$. These constant terms have no contribution to the distribution $P(S)$. We therefore have for $V(S)$ (with omission of constant terms)

$$V(S) = \tfrac{1}{2}\varepsilon^{(2)}(0){V_s}^2 \int \big[\rho(\mathbf{s}|S)\big]^2 d\mathbf{s} \,. \tag{11.9}$$

The complete form of $\rho(\mathbf{s}|S)$ is unknown, as discussed in Appendix II C, and we therefore approximate it by a Gaussian function. Equations (II C.2) and (II C.5) require the relation,

$$S^2 = n^{-1} \int s^2 \rho(\mathbf{s}|S) d\mathbf{s} \,. \tag{11.10}$$

The Gaussian function satisfying this necessary condition is

$$\rho(\mathbf{s}|S) = n\left(\frac{3}{2\pi S^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{s}^2}{2S^2}\right) \,. \tag{11.11}$$

Substitution of Eq. (11.11) into Eq. (11.9) leads to

$$V(S) = (3^{3/2}/16\pi^{3/2})n^2 {V_s}^2 \varepsilon^{(2)}(0) S^{-3} \,. \tag{11.12}$$

Now we adopt the Flory–Huggins equation$^{7-9}$ for the free energy of mixing polymer and solvent. Then $\varepsilon$ may be written in the form,

$$\varepsilon(\varphi) = {V_0}^{-1} kT \bigl[(1-\varphi)\ln(1-\varphi) + \chi\varphi(1-\varphi)\bigr] \,, \tag{11.13}$$

where $V_0$ is the molecular volume of the solvent and $\chi$ is the thermodynamic interaction parameter for a given polymer-solvent pair. In Eq. (11.13), the term involving $\ln\varphi$ has been dropped because of the assumed fixed position of the polymer molecular center of mass.[8] From Eqs. (11.7) and (11.13), we obtain

$$\begin{aligned} \varepsilon^{(2)}(0) &= 2{V_0}^{-1} kT \bigl(\tfrac{1}{2} - \chi\bigr) \\ &= 2{V_0}^{-1} kT \psi (1 - \Theta/T) \,, \end{aligned} \tag{11.14}$$

where $\psi$ is the entropy parameter, and $\Theta$ is the parameter called the *theta temperature*; both were introduced by Flory.[8] Recalling that $nV_s = M\bar{v}/N_{\mathrm{A}}$ with $N_{\mathrm{A}}$ the Avogadro number, $M$ the polymer molecular weight, and $\bar{v}$ the polymer partial specific volume, we may then rewrite Eq. (11.12) in the form,

$$V(S)/kT = 2C_M \psi (1 - \Theta/T) M^{1/2} x^{-3} \tag{11.15}$$

with

$$C_M = (27/2^{5/2}\pi^{3/2})(\bar{v}^2/{N_{\mathrm{A}}}^2 V_0)\bigl(\langle R^2\rangle_0/M\bigr)^{-3/2} \,, \tag{11.16}$$

$$x = S/{\langle S^2\rangle_0}^{1/2} \,. \tag{11.17}$$

The mean-square radius $\langle S^2\rangle$ or the squared expansion factor $\alpha^2$ may be calculated from Eq. (4.16) with (11.1) to (11.3); that is,

$$\begin{aligned} \langle S^2\rangle/\langle S^2\rangle_0 &= \alpha^2 \\ &= \frac{\int_0^\infty x^4 \exp\bigl[-3x^2/2 - V(x)/kT\bigr]dx}{\int_0^\infty x^2 \exp\bigl[-3x^2/2 - V(x)/kT\bigr]dx} \,, \end{aligned} \tag{11.18}$$

where $x$ is defined by Eq. (11.17). The ratio of the two integrals in Eq. (11.18) may be evaluated approximately following the procedure of Hermans and Overbeek[10]; the approximate value of $\alpha$ is equal to the value of $x$ at which the function $x^3 \exp\bigl[-3x^2/2 - V(x)/kT\bigr]$ is a maximum. In other words, if $V(x) > 0$, $x^3 \exp[\quad]$ may be regarded as a delta function $\delta(x-\alpha)$, which satisfies Eq. (11.18).[11] This maximizing condition is

$$\frac{\partial}{\partial\alpha}\left[\ln\alpha^3 - \tfrac{3}{2}\alpha^2 - \frac{V(\alpha)}{kT}\right] = 0 \,, \tag{11.19}$$

which is equivalent to the equilibrium condition of Flory for the balance between the osmotic and elastic forces. Substitution of Eq. (11.15) into Eq. (11.19) leads to

$$\alpha^5 - \alpha^3 = 2C_M \psi (1 - \Theta/T) M^{1/2} . \tag{11.20}$$

This is the well-known Flory equation for the expansion factor.

A number of significant conclusions may be drawn from Eq. (11.20). First, the quantity $(\alpha^5 - \alpha^3)$ is seen to be proportional to the square root of the polymer molecular weight $M$ except at $T = \Theta$, since the constants $C_M$, $\psi$, and $\Theta$ are independent of $M$ for high-molecular-weight polymers of ordinary interest.[8] Therefore it follows that $\alpha$ increases slowly with molecular weight (assuming that $\psi(1 - \Theta/T) > 0$) and without limit even when the molecular weight becomes very large. Since $\alpha^5$ is proportional to $M^{1/2}$ as $M$ approaches infinity, the dependence of the mean-square end-to-end distance on the molecular weight may be expressed, from Eq. (10.2), as

$$\langle R^2 \rangle \propto M^\delta \propto n^\delta , \qquad 1 \leq \delta \leq 1.2 . \tag{11.21}$$

Thus $\langle R^2 \rangle$ is no longer proportional to the number of the segments in the chain, and the real chain with excluded volume is of the non-Markoff nature. This is the most important conclusion of the Flory theory.

Secondly, $\alpha$ depends on the factor $\psi(1 - \Theta/T)$. This factor represents the solvent power of the "goodness" of the solvent; the larger this factor, the better the solvent. Therefore, the better the solvent, the greater the value of $\alpha$ for a given molecular weight. The parameter $\psi$ is ordinarily positive, and a system having $\Theta$ above or below room temperatures is called a *poor-solvent* or *good-solvent system* empirically, as the case may be. Thus $\alpha$ may be expected to increase as the temperature is increased in a poor solvent. Furthermore, $\alpha$ is greater or smaller than unity, as the temperature is above or below $\Theta$.

The important point is that at the theta temperature $\alpha$ must equal unity irrespective of $M$; that is, at $T = \Theta$ the molecular dimension is unperturbed by long-range interferences, and the chain behaves just like an unperturbed chain. From a physical point of view, the theta point arises because of the apparent cancellation at this temperature of the effect of volume exclusion of the segments, which tends to enlarge the molecule, and the effect of van der Waals attractions between segments, which contracts the molecule. As will be seen in Chapter IV, the second virial coefficient of polymer solutions vanishes at the theta temperature. Thus it corresponds to the Boyle point of an imperfect gas. The theta temperature may often be experimentally realized by suitable choice of a single (or mixed) solvent near room temperatures. Such poor solvents are called *theta solvents* for a given polymer. A number of theta-solvent systems have been studied.

Our final discussion is concerned with the parameter $C_M$ defined by Eq. (11.16). It involves the unperturbed dimension $\langle R^2 \rangle_0$, which depends on the temperature through the effective bond length $a$ as mentioned in Section 9a. In most cases, however, $C_M$ is less dependent on the temperature than the factor $\psi(1-\Theta/T)$; the temperature dependence of $\alpha$ will then be governed by the factors discussed above. On the other hand, $C_M$ is inversely proportional to the molecular volume, $V_0$, of the solvent, and therefore if $\chi = 0$, $\alpha$ may be expected to decrease with increasing $V_0$. Consider now a polymer molecule dispersed in a "solvent" consisting of other polymers of the same kind. Necessarily $\chi$ will then be zero, and $V_0$ is very large. Thus $\alpha$ will be very nearly unity. This suggests that $\alpha$ will decrease with increasing concentration of the polymer. A quantitative treatment of the dependence of $\alpha$ on concentration will be made in Chapter V.

In conclusion, it must be pointed out that in 1948 Hermans and Overbeek[10] evaluated the expansion factor of a polyelectrolyte chain with electrostatic interactions and showed its dependence on $n$. Strictly speaking, therefore, they were the first to demonstrate the excluded-volume effect in a wide sense. Nevertheless, the noteworthy contribution of Flory consists in his emphasis of the significance of this effect and his establishment of the concept of the theta state.

## 12. The Direction of Developments Following the Flory Theory

In its original form the Flory theory cannot be considered a theory developed logically from the formalism of statistical mechanics. If the chain with excluded volume truly has a non-Markoff nature, as concluded by Flory, the non-Markoff nature will have a large influence on the properties of dilute polymer solutions, especially on the molecular weight dependences. Because the excluded-volume problem itself is of great interest both physically and mathematically, following the publication of the Flory theory, a number of different attacks on the problem were made. Among these, there were several whose conclusions disagreed with those of Flory. Indeed, it was not until the mid-1950s that Flory's concepts gained wide acceptance. It seems worthwhile to make a survey of these early investigations, since these will help us to understand the salient aspects of the excluded-volume effect, and also our later developments. The published work may be classified into three groups: ideal-chain type, production-chain type, and real-chain type.[12, 13] There are discussed in order.

### 12a. Ideal-Chain Type

The work of Hermans[14] and Grimley[15] belongs to this group; the conclusion is that the excluded-volume effect is negligible, so that the mean-square end-to-end distance retains exactly the form it would have if long-range interferences were absent.

We have already pointed out the equivalence of an ideal random-flight chain to a simple Markoff chain, and it is known that the Gaussian distribution of its end-to-end distance can be obtained as the solution of a Markoff integral equation or a diffusion equation with an appropriate boundary condition. Hermans[14] approached the problem from this standpoint. Suppose now that the 0th segment of a chain of $n$ bonds is fixed at the origin of a coordinate system, and the position of the $j$th segment is $\mathbf{R}_j$, as before (see Fig. III.1). Then, by definition, the bivariate distribution, or the joint probability, $P(\mathbf{R}_j, \mathbf{R}_{j+1})$ is given by the product of the singlet distribution $P(\mathbf{R}_j)$ and the conditional probability $\psi(\mathbf{R}_{j+1}|\mathbf{R}_j)$,

$$P(\mathbf{R}_j, \mathbf{R}_{j+1}) = P(\mathbf{R}_j)\psi(\mathbf{R}_{j+1}|\mathbf{R}_j) \tag{12.1}$$

irrespective of the existence of long-range interferences, $P$ and $\psi$ being normalized as

$$\int P(\mathbf{R}_j)d\mathbf{R}_j = 1\,, \tag{12.2}$$

$$\int \psi(\mathbf{R}_{j+1}|\mathbf{R}_j)d\mathbf{R}_{j+1} = 1\,. \tag{12.3}$$

Integration of Eq. (12.1) over $\mathbf{R}_j$ gives

$$P(\mathbf{R}_{j+1}) = \int P(\mathbf{R}_j)\psi(\mathbf{R}_{j+1}|\mathbf{R}_j)d\mathbf{R}_j\,. \tag{12.4}$$

If we use the symbols $(\mathbf{R}, j+1)$ and $(\mathbf{R}-\mathbf{r}, j)$ in place of $\mathbf{R}_{j+1}$ and $\mathbf{R}_j$, respectively, Eq. (12.4) may be rewritten in the form,

$$P(\mathbf{R}, j+1) = \int P(\mathbf{R}-\mathbf{r}, j)\psi(\mathbf{R}-\mathbf{r}, j; \mathbf{r})d\mathbf{r} \tag{12.5}$$

with

$$\int \psi(\mathbf{R}, j; \mathbf{r})d\mathbf{r} = 1\,. \tag{12.6}$$

Equation (12.5) is a *Markoff integral equation*, sometimes referred to as the *Chapman–Kolmogoroff equation*,[16] $\psi$ being the *transition probability* for $\mathbf{R}-\mathbf{r} \rightarrow \mathbf{R}$. In the present case, $\psi\, d\mathbf{r}$ is the conditional probability that when the $j$th segment is at $(\mathbf{R}-\mathbf{r})$ the $(j+1)$th bond vector lies between $\mathbf{r}$ and $\mathbf{r}+d\mathbf{r}$. The integral equation of (12.5) can be transformed into a differential equation for the distribution function, called the *Fokker–Planck equation* (see Appendix III A). If the form of $\psi$ is assumed, the solution for $P(\mathbf{R}, j)$ can in principle be obtained.

Hermans assumed for the form of the transition probability (for $\mathbf{R} \rightarrow \mathbf{R}+\mathbf{r}$)

$$\psi(\mathbf{R}, j; \mathbf{r}) = C(\mathbf{R})\tau(\mathbf{r})\left[1 - \beta_0\rho(\mathbf{R}+\mathbf{r}|\mathbf{R})\right], \tag{12.7}$$

where $C(\mathbf{R})$ is the normalizing function dependent on $\mathbf{R}$, $\tau(\mathbf{r})$ is the bond probability, $\beta_0$ is the volume excluded to one segment by the presence of another, and $\rho(\mathbf{R}+\mathbf{r}|\mathbf{R})$ is the average segment density

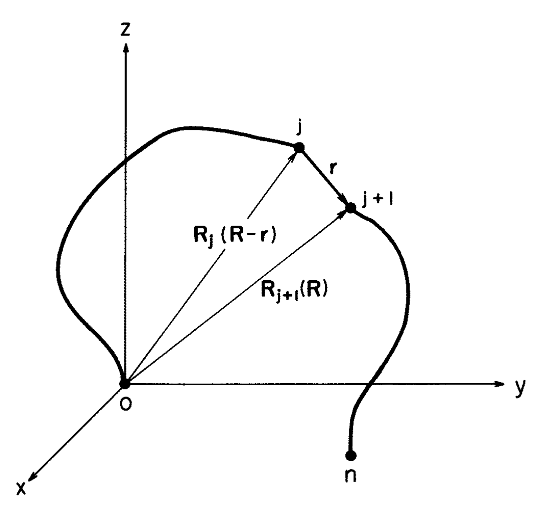

**Fig. III.1.** Schematic representation of the coordinates of segments appearing in the Markoff integral equation for the distribution function.

at $(\mathbf{R}+\mathbf{r})$ when the $j$th segment is at $\mathbf{R}$. The physical meaning of Eq. (12.7) is obvious: $\beta_0\rho$ is the fraction of the total volume excluded to the $(j+1)$th segment at $(\mathbf{R}+\mathbf{r})$ by the presence of others, and therefore the factor $(1-\beta_0\rho)$ represents the volume fraction available for occupancy by the $(j+1)$th segment in the volume element $d\mathbf{r}$ at $(\mathbf{R}+\mathbf{r})$. Evidently $\rho(\mathbf{R}+\mathbf{r}|\mathbf{R})$ is given by the sum over the conditional probability density $P_k(\mathbf{R}+\mathbf{r}|\mathbf{R})$ that the $k$th segment is in $d\mathbf{r}$ at $(\mathbf{R}+\mathbf{r})$ when the $j$th segment is at $\mathbf{R}$; that is,

$$\rho(\mathbf{R}+\mathbf{r}|\mathbf{R}) = \sum_{k=1}^{n} P_k(\mathbf{R}+\mathbf{r}|\mathbf{R})\,. \tag{12.8}$$

Hermans approximated $P_k(\mathbf{R}+\mathbf{r}|\mathbf{R}) \equiv P_k(\mathbf{R}_k|\mathbf{R}_j)$ by $P_k(\mathbf{R}_k)$ without $\mathbf{R}_j$ fixed, and used the unperturbed distribution function for $P_k(\mathbf{R}_k)$. His final result is

$$\langle R^2\rangle = na^2\left[1+0.78(\beta_0/a^3n^{1/2})\right]. \tag{12.9}$$

Thus $\langle R^2\rangle$ becomes equal to $na^2$ as $n$ is increased. The average segment density at $(\mathbf{R}+\mathbf{r})$ will be much higher when the $j$th segment is at $\mathbf{R}$ than when it is free. Apart from the expression for $\psi$, therefore, Hermans' approximation to $P_k$ underestimates the excluded-volume effect and is invalid.

Next we discuss the treatment of Grimley.[15] His starting point is Eq. (10.1) with (10.6). Now the product of $\tau$ in the integrand of Eq. (10.1) is just the instantaneous distribution $P_0(\{\mathbf{R}_n\})$ for the unperturbed chain. Grimley approximated $P_0(\{\mathbf{R}_n\})$ by the product of independent distributions,

$$P_0\bigl(\{\mathbf{R}_n\}\bigr) = \prod_{j=1}^{n} P_{0j}(\mathbf{R}_j)\,. \tag{12.10}$$

Integration of $P\bigl(\{\mathbf{R}_n\}\bigr)$ over $\{\mathbf{R}_{n-1}\}$ leads then to

$$P(\mathbf{R}) = CP_0(\mathbf{R})\bigl[1 - \beta_0\rho_0(\mathbf{R})\bigr]\,, \tag{12.11}$$

where $C$ is the normalizing constant, and $\rho_0(\mathbf{R})$ is the average segment density at $\mathbf{R}(\equiv \mathbf{R}_n)$ in the unperturbed state. From Eq. (12.11), we can obtain

$$\langle R^2\rangle = na^2\bigl[1 + 0.143(\beta_0/a^3n^{1/2})\bigr]\,. \tag{12.12}$$

Thus the conclusion of Grimley is the same as that of Hermans. The approximation of (12.10) is incorrect, because all intramolecular interactions cannot be taken into account in this approximation but only interactions of the $n$th segment with the others contribute to the excluded-volume effect.

## 12b. Production-Chain Type

The conclusion is that the effect increases $\langle R^2\rangle$ but does not alter the Markoff nature of the chain; that is, it behaves just like the short-range effect. The theories of Hermans, Klamkin, and Ullman,[17] Debye and Rubin,[18] and Montroll[19] are placed in this category.

Hermans et al.[17] again started at Eq. (12.5) with (12.7) but used the correct expression for the conditional segment density $\rho(\mathbf{R}+\mathbf{r}|\mathbf{R})$, though it was evaluated in the unperturbed state. Their result is

$$\langle R^2\rangle = na^2\bigl[1 + 1.72(\beta_0/a^3)\bigr]\,. \tag{12.13}$$

Thus the Markoff nature of the chain is preserved, although $\langle R^2\rangle$ becomes greater than the unperturbed value $na^2$. We must note that the segments $k > j+1$ make no contribution to the final result. Indeed, Debye and Rubin[18] used Eq. (12.8) from the outset without $P_k$ for $k > j+1$ and naturally arrived at the same conclusion as Hermans et al.[17] In these treatments, the entire chain may be considered to be "produced" by adding bonds one by one, the direction of each step depending only on the past steps. If the problem is formulated by Eq. (12.5), $\psi(\mathbf{R}, j; \mathbf{r})$ should represent the transition probability for $\mathbf{R} \to \mathbf{R}+\mathbf{r}$ when all intramolecular long-range interactions are taken into account. Each step or $\psi$ must therefore be affected by all the steps in the past and future, and also by correlations between them. Thus the real chain must be different in nature from the simple Markoff chain.

On the other hand, Montroll[19] treated the effect in a two-dimensional square lattice chain, applying the theory of Markoff processes. For a completely random-flight chain, excluding only first-order overlaps which occur between bonds four removed from each other, his result is similar to that of Hermans et al.[17] This is to be expected, since the effect is regarded as of short-range nature. Frisch, Collins, and Friedman[20] also attempted a similar approach, using the two-dimensional square lattice, the hexagonal lattice, and the diamond lattice, but did not come to any conclusion about $\langle R^2 \rangle$.

## 12c. Real-Chain Type

The conclusion is that the effect causes $\langle R^2 \rangle$ to become asymptotically proportional to a power of $n$ higher than the first, or at least $\langle R^2 \rangle / n$ does not approach a finite limit as $n$ increases without limit. This point of view, the non-Markoff nature of the real chain, is in agreement with the conclusion of Flory and is widely accepted at the present time.

Many papers in this group have been published since 1951 (after the Flory theory). All of them start with the partition function of (10.1), using the superposition approximation of (10.6) to the potential of mean force but discarding the factorization approximation of (12.10) to the unperturbed instantaneous distribution. Necessarily this leads to the correct result. The foremost of these theories is the development of the partition function by Teramoto,[12, 21] based on the cluster expansion method of Ursell and Mayer in the theory of imperfect gases.[22] Subsequent developments in this direction were made by many workers.[23–26] The most general formulation, made by Fixman[26] in 1955, and subsequent advances will be described in detail in Section 14. Another direction of study is the derivation of the Markoff integral equation for the distribution function, or the equivalent diffusion equation, from the partition function. Contrary to the work of Herman et al.[17] and others,[18] however, no assumption is made about the form of the transition probability $\psi$; there results a physically plausible form for $\psi$ as a straightforward consequence of the partition function. Such investigations were made by Grimley[27] and by Zimm, Stockmayer, and Fixman,[13] and will be described in Section 13. Saito[28] also treated the problem in a similar manner, deriving an integrodifferential equation for the distribution function by means of the coupling parameter method.[1, 29] All these early investigations of the real-chain type lead to a theory, now called the *first-order perturbation theory*. It must be pointed out that although the theory of James[30] also gives the correct result, his treatment is somewhat different from those cited above. Regarding the problem as equivalent to a diffusion problem, he still started at the Markoff integral equation but assumed for the transition probability

$$\psi(\mathbf{R}, j; \mathbf{r}) = \tau(\mathbf{r}) \left[ 1 - \beta_0 \rho(\mathbf{R} + \mathbf{r} | \mathbf{R}) \right] . \tag{12.14}$$

The existence of the segments $k > j + 1$ was not considered from the outset because of the formulation as a diffusion process. The essential difference between the theories of Hermans et al.[17] and James[30] consists in the normalization condition; that is, in the latter neither $\psi(\mathbf{R},\ j;\ \mathbf{r})$ nor $P(\mathbf{R},\ j)$ is subject to any normalization condition. After normalization, however, his distribution function becomes exactly

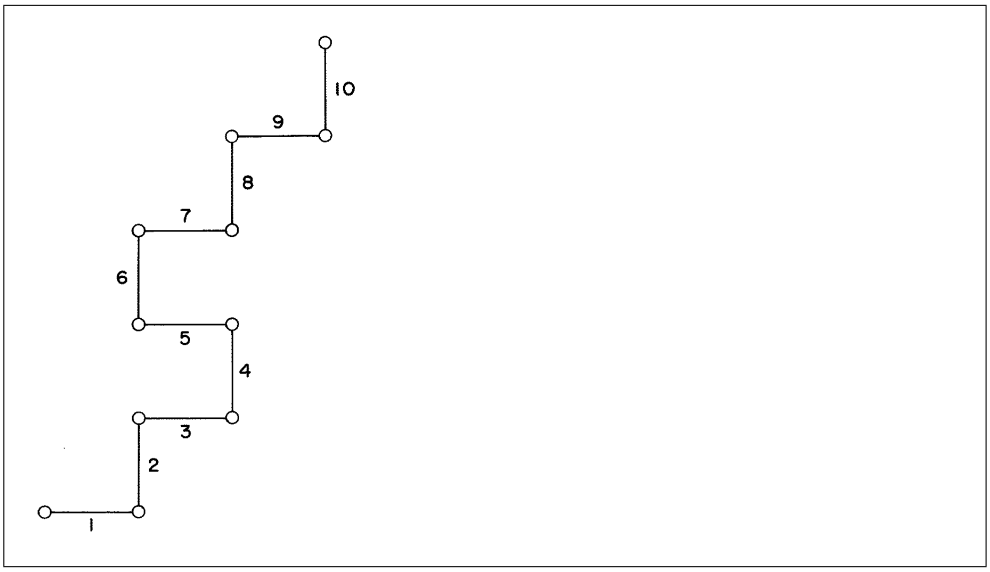

**Fig. III.2.** A two-dimensional square lattice chain of ten bonds and with bond angle 90°.

the same as that of Grimley[27] and Zimm et al.[13] in the first-order perturbation approximation. A statistical-mechanical justification of the formulation of James will be given in Section 16.

Finally, from a different point of view, we now discuss the differences between the theories classed under the ideal, production, and real chains.[12, 31] Let us consider the two-dimensional square lattice chain with bond angle 90°, and suppose this chain to be constructed by attaching one bond after another consecutively just as in the diffusion of a free particle. A configuration of such a chain of ten bonds is shown in Fig. III.2. If this configuration is one of the configurations of the *ideal* chain in which overlaps of bonds are allowed, the probability of its occurrence is $(1/4)\cdot(1/2)^9 = 1/2048$, since each bond can be placed in two ways (on the right or left side of a foregoing one) except the first bond which has four possible directions. The total number of possible configurations is of course 2048 in this case. If we take the configuration in Fig. III.2 as one of the configurations of the *production* chain, its probability is $(1/4)\cdot(1/2)^4\cdot 1\cdot(1/2)\cdot 1\cdot(1/2)^2 = 1/512$, since the first step goes to the right with probability one-fourth, the next step goes upwards with probability one-half, after three steps with the same probability the sixth step goes certainly upwards with probability unity, and so on. Thus, all possible configurations do not occur with the same probability, and the probability of placing each bond is normalized in such a way that overlaps of bonds occur with probability zero. For instance, the sixth step goes upwards with probability unity and downwards with probability zero $(1+0=1)$. Therefore this corresponds to the normalized transition probability of Hermans et al.[17] On the other hand, a complete enumeration shows that if the overlaps between bonds are completely excluded, only 440 configurations are allowable. For the real chain, therefore, the probability of the configuration in Fig. III.2 is 1/440, since all possible configurations must be a priori equally probable. In this case, each configuration has the same relative probability $1/2048 = (1/4) \cdot (1/2)^9$, and the probability of placing each bond is not always normalized. For instance, the sixth step goes upwards with probability one-half and downwards with probability zero. Therefore this corresponds to the unnormalized transition probability of James.[30] If the overlap between bonds is regarded as the arrival at a barrier of a diffusing particle, the problem of the production chain is equivalent to that of a random walk with *reflecting barriers*, while the problem of the real chain is equivalent to that of a random walk with *absorbing barriers.* Note that a diffusing particle reflects with probability unity at a reflecting barrier, while it cannot suffer further displacements after arrival at an absorbing barrier and the sequence of the random walk terminates there.[32]

## 13. Perturbation Theory (A): Distribution Function Method

The primary purpose of this section is to derive an exact expression for the transition probability $\psi$ and a differential equation for the distribution function from the partition function of (10.1). This has been done by several authors, as mentioned in the previous section. For convenience, we describe it following the procedure of Zimm, Stockmayer, and Fixman,[13] which will be very helpful in understanding the difference between the real polymer chain and a simple Markoff chain. We shall also discuss the approximations used here and common to all other theories of dilute solutions of flexible chain polymers. Although the original theory of Zimm et al. was worked out on the distribution $P(\mathbf{R}_{ij})$ of the distance between the $i$th and $j$th segments, we consider simply the distribution $P(\mathbf{R})$, since the former can be treated more conveniently by the cluster expansion method.

We begin by discussing the superposition approximation of (10.6). In general, the pairwise decomposability of the potential energy is moderately accurate, whereas the potential of mean force is exactly expressed as a sum of terms of all kinds of component potentials, $w^{(2)}$ for two molecules, $w^{(3)}$ for three molecules, and so on[33]; the approximation of (10.6) neglecting higher component potentials is inexact. A justification of the superposition approximation is difficult, although its adequacy has been proved for the dense hard sphere fluid. In the present problem, however, the superposition approximation may be expected to cause little error for the final result, because the average segment density within a polymer molecule is very low and three or more nonbonded segments will not be simultaneously close to one another [the component potential $w^{(\nu)}$ approaches zero if one of the molecules (segments) of the subset of $\nu$ molecules is distant from all the other molecules of the subset].

The second approximation to be used is concerned with the form of the pair potential $w(\mathbf{R}_{ij})$ in Eq. (10.6). The potential $w$, although formally taking the place of a potential energy for solute-solute interactions, depends intimately on solvent-solute and solvent-solvent interactions as well. In addition, $w$ is a complicated function of separation even in the simplest systems. More explicitly, $w$ is related to the pair correlation function $g(\mathbf{R}_{ij})$ for solute molecules (segments) at infinite dilution by the equation,

$$g(\mathbf{R}_{ij}) = \exp\left[-\frac{w(\mathbf{R}_{ij})}{kT}\right] , \tag{13.1}$$

where the zero of $w$ is chosen so that $g \to 1$ as $\mathbf{R}_{ij} \to \infty$. For a fluid mixture of monatomic isotopes, for example, $g$ is exactly the radial distribution function for any pair of molecules in the fluid, and would oscillate at short range, as would $w$, even if the molecules were hard spheres without attraction.[1, 2] It is therefore physically of no great significance to speculate about the detailed behavior of polymer solutions by using special simple forms for $w$, e.g., a Lennard–Jones 6–12 potential; almost any function can be used with impunity, provided its short-range nature is preserved.[34, 35] Thus we simply put

$$\chi_{ij} \equiv g(\mathbf{R}_{ij}) - 1 = -\beta\delta(\mathbf{R}_{ij}) \tag{13.2}$$

with

$$\beta = \int \big[1 - g(\mathbf{R}_{ij})\big] d\mathbf{R}_{ij} \, , \tag{13.3}$$

where $\delta$ is a three-dimensional Dirac delta function. The parameter $\beta$ is called the *binary cluster integral* for a pair of segments (strictly the cluster integral is the negative of $\beta$); it represents the effective volume excluded to one segment by the presence of another.[*] We note that any function $w$ with a repulsive core at small separation and attraction for some range of separation will give positive $\beta$ at high temperature, negative $\beta$ at low temperature, and vanishing $\beta$ at an intermediate Boyle temperature, namely the theta temperature. Generally, $\beta$ will have large positive values in good-solvent systems where preferential attractions occur between the polymer segment and solvent molecule, and small positive, zero, or negative values in poor-solvent systems. The approximations of (10.6) and (13.2) are fundamental and common to all the theories of dilute polymer solutions.

Now we proceed to consider the present problem. From Eq. (10.1), the instantaneous distribution $P\big(\{\mathbf{R}_n\}\big)$ for the entire chain may be

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[*] For a very dilute gas of hard spheres, $\beta$ is equal to $8V_0$ with $V_0$ the molecular volume. For a fluid mixture of monatomic isotopes, $\beta$ is approximately equal to $V_0$ at high densities where the compressibility of the fluid may be neglected.

written as

$$P\big(\{\mathbf{R}_n\}\big) = Z^{-1}\left[\prod_{i=1}^{n}\tau(\mathbf{r}_i)\right]\exp\left(-\frac{W}{kT}\right), \tag{13.4}$$

where the 0th segment is fixed at the origin of a coordinate system, as before (see Fig. III.1). With the use of Eqs. (10.6), (13.1), and (13.2), Eq. (13.4) may be rewritten in the form,

$$P\big(\{\mathbf{R}_n\}\big) = Z^{-1}\left[\prod_{i=1}^{n}\tau(\mathbf{r}_i)\right]\left[\prod_{0\le k<l\le n}(1+\chi_{kl})\right]. \tag{13.5}$$

From Eq. (13.5), $P\big(\{\mathbf{R}_n\}\big)$ is seen to reduce to the unperturbed distribution at the theta temperature at which $\beta$ and $\chi_{ij}$ vanish. Now we designate the partition function and instantaneous distribution for the chain of $j$ bonds (with the first segment fixed) by $Z_j$ and $P^{(j)}\big(\{\mathbf{R}_j\}\big)$, respectively, $P^{(j)}$ being written as

$$P^{(j)}\big(\{\mathbf{R}_j\}\big) = {Z_j}^{-1}\left[\prod_{i=1}^{j}\tau(\mathbf{r}_i)\right]\left[\prod_{0\le k<l\le j}(1+\chi_{kl})\right]. \tag{13.6}$$

If $t = n-(j+1)$ and $\{\mathbf{R}_t\} = (\mathbf{R}_{j+2},\ \ldots,\ \mathbf{R}_n)$, the instantaneous distribution for the chain of $t$ bonds is

$$P^{(t)}\big(\{\mathbf{R}_t\}\big) = {Z_t}^{-1}\left[\prod_{i=j+2}^{n}\tau(\mathbf{r}_i)\right]\left[\prod_{j+1\le k<l\le n}(1+\chi_{kl})\right]. \tag{13.7}$$

Further, we define a function $H_{jt}$ by

$$1 + H_{jt} = \prod_{\substack{0\le k\le j\\ j+1\le l\le n}}(1+\chi_{kl}). \tag{13.8}$$

Then the distribution of (13.5) may be factored as

$$P\big(\{\mathbf{R}_n\}\big) = Z^{-1}Z_jZ_t\tau(\mathbf{r}_{j+1})P^{(j)}\big(\{\mathbf{R}_j\}\big)P^{(t)}\big(\{\mathbf{R}_t\}\big)(1+H_{jt}). \tag{13.9}$$

This factorization is the basis for several useful results, and provides a means of relating the intramolecular long-range effects on the $(j+1)$th bond in the chain of $n$ bonds to the interactions between the two parts of the chain on either side of the specified bond.

Integrating $P\big(\{\mathbf{R}_n\}\big)$ over $\{\mathbf{R}_n\}$ under the restriction that $\mathbf{R}_j$ and $\mathbf{R}_{j+1}$ are fixed, we obtain the joint probability,

$$P(\mathbf{R}_j, \mathbf{R}_{j+1}) = Z^{-1}Z_jZ_t\tau(\mathbf{r}_{j+1})\int P^{(j)}P^{(t)}(1+H_{jt})\frac{d\{\mathbf{R}_n\}}{d\mathbf{R}_j d\mathbf{R}_{j+1}}, \tag{13.10}$$

where for brevity the explicit coordinates of $P^{(j)}$ and $P^{(t)}$ have been suppressed. Dividing both sides by the singlet distribution $P(\mathbf{R}_j)$,

$$P(\mathbf{R}_j) = \int P(\mathbf{R}_j, \mathbf{R}_{j+1}) d\mathbf{R}_{j+1}\,, \tag{13.11}$$

we have for the transition probability

$$\psi(\mathbf{R}_{j+1}|\mathbf{R}_j) = \gamma(\mathbf{R}_j)\tau(\mathbf{r}_{j+1}) \int P^{(j)} P^{(t)} (1 + H_{jt}) \frac{d\{\mathbf{R}_n\}}{d\mathbf{R}_j d\mathbf{R}_{j+1}}\,, \tag{13.12}$$

where $\gamma(\mathbf{R}_j) = Z^{-1} Z_j Z_t / P(\mathbf{R}_j)$ is a normalizing function to be determined from Eq. (12.3). It will be convenient to express $\psi$ in another form. The integral in Eq. (13.12) is the sum of two parts, the first of which is easily split into a product of two independent factors,

$$\begin{aligned} &\int P^{(j)} P^{(t)} \frac{d\{\mathbf{R}_n\}}{d\mathbf{R}_j d\mathbf{R}_{j+1}} \\ &\quad = \left[\int P^{(j)} \frac{d\{\mathbf{R}_j\}}{d\mathbf{R}_j}\right] \cdot \left[\int P^{(t)} d\{\mathbf{R}_t\}\right] = P^{(j)}(\mathbf{R}_j) \cdot 1\,, \end{aligned} \tag{13.13}$$

where $P^{(j)}(\mathbf{R}_j)$ is just the distribution function of the end-to-end distance of the chain of $j$ bonds. The second term cannot be simply reduced, and is of special interest; we denote it by $J(\mathbf{R}_j, \mathbf{R}_{j+1})$,

$$J(\mathbf{R}_j, \mathbf{R}_{j+1}) = \int P^{(j)} P^{(t)} H_{jt} \frac{d\{\mathbf{R}_n\}}{d\mathbf{R}_j d\mathbf{R}_{j+1}}\,. \tag{13.14}$$

With these relations, Eq. (13.12) may be rewritten in the form,

$$\psi(\mathbf{R}_{j+1}|\mathbf{R}_j) = C(\mathbf{R}_j)\tau(\mathbf{r}_{j+1}) \left[1 + \frac{J(\mathbf{R}_j, \mathbf{R}_{j+1})}{P^{(j)}(\mathbf{R}_j)}\right]\,, \tag{13.15}$$

where $C(\mathbf{R}_j) = \gamma(\mathbf{R}_j) P^{(j)}(\mathbf{R}_j)$ is a new normalizing function.

From Eq. (13.8), the function $H_{jt}$ is seen to involve interaction terms $\chi_{kl}$ between all the segments in the first part of the chain [i.e., the first $(j + 1)$ segments] and all of those in the other part. This effect reflects on the transition probability through the function $J$. In other words, the transition probability $\psi$ for $j \to j + 1$ is affected not only by the existence of the segments $k \leq j$ but also by the segments $l > j + 1$. The real chain must therefore be distinguished from a simple Markoff chain, for which $\psi$ is governed only by the $j$th segment. On the other hand, in the transition probability of Hermans et al.[17] and Debye and Rubin,[18] only the interaction of the $(j + 1)$th segment with the others is considered. It is evident that such special assumptions about $\psi$ cannot lead to a correct conclusion concerning the excluded-volume effect, since Eq. (13.15) is a straightforward consequence of the partition function.

Now the problem is to derive a differential equation for $P(\mathbf{R}_j)$. This can usually be done from the Markoff integral equation of (12.4) or (12.5). However, it is more convenient to go back to the joint probability of (13.10). Integrating it over $\mathbf{R}_{j+1}$ or $\mathbf{R}_j$, we have the singlet distributions,

$$P(\mathbf{R}_j) = Q\left[P^{(j)}(\mathbf{R}_j) + \int \tau(\mathbf{r}_{j+1}) J(\mathbf{R}_j, \mathbf{R}_{j+1}) d\mathbf{R}_{j+1}\right], \tag{13.16}$$

$$P(\mathbf{R}_{j+1}) = Q \int \tau(\mathbf{r}_{j+1}) \big[P^{(j)}(\mathbf{R}_j) + J(\mathbf{R}_j, \mathbf{R}_{j+1})\big] d\mathbf{R}_j\,, \tag{13.17}$$

where we have used Eqs. (13.13) and (13.14), and $Q = Z^{-1} Z_j Z_t$ is a normalizing constant and is given by

$$Q^{-1} = 1 + \int \tau(\mathbf{r}_{j+1}) J(\mathbf{R}_j, \mathbf{R}_{j+1}) d\mathbf{R}_j d\mathbf{R}_{j+1}\,. \tag{13.18}$$

In the alternative notation, as in Eq. (12.5), Eqs. (13.16) to (13.18) may be rewritten as

$$P(\mathbf{R}, j) = Q\left[P^{(j)}(\mathbf{R}, j) + \int \tau(\mathbf{r}) J(\mathbf{R}, \mathbf{R}+\mathbf{r}) d\mathbf{r}\right], \tag{13.19}$$

$$P(\mathbf{R}, j+1) = Q \int \tau(\mathbf{r}) \big[P^{(j)}(\mathbf{R}-\mathbf{r}, j) + J(\mathbf{R}-\mathbf{r}, \mathbf{R})\big] d\mathbf{r}\,, \tag{13.20}$$

$$Q^{-1} = 1 + \int \tau(\mathbf{r}) J(\mathbf{R}, \mathbf{R}+\mathbf{r}) d\mathbf{R}\; d\mathbf{r}\,. \tag{13.21}$$

Expanding $P^{(j)}(\mathbf{R}-\mathbf{r}, j)$ around $\mathbf{R}$, and $J(\mathbf{R}, \mathbf{R}+\mathbf{r})$ and $J(\mathbf{R}-\mathbf{r}, \mathbf{R})$ around $(\mathbf{R}, \mathbf{R})$, we obtain (see Appendix III A)

$$P(\mathbf{R}, j+1) - P(\mathbf{R}, j) = \tfrac{1}{6} a^2 Q \big[\nabla_j{}^2 P^{(j)} + (\nabla_j{}^2 J - \nabla_{j+1}{}^2 J)_{\mathbf{R},\mathbf{R}} + \cdots\big]\,, \tag{13.22}$$

where we have used the normalization condition on $\tau$ and the fact that the second moment of $\tau$ is $a^2$, and terms of order $a^3$ and higher have been dropped. The symbols $\nabla_j{}^2$ and $\nabla_{j+1}{}^2$ denote Laplacian operators with respect to the coordinates of the $j$th and $(j+1)$th segments, respectively, and the subscript $(\mathbf{R}, \mathbf{R})$ means that the value of the function so designated is to be taken when the coordinates of both these segments are at $\mathbf{R}$. Similarly we have

$$Q^{-1} = 1 + \int J(\mathbf{R}, \mathbf{R}) d\mathbf{R} + \cdots\,. \tag{13.23}$$

The right-hand side of Eq. (13.22) may be equated to $\partial P(\mathbf{R}, j)/\partial j$, and we therefore have for the desired differential equation

$$\frac{6}{a^2}\frac{\partial P}{\partial j} = Q\big[\nabla_j{}^2 P^{(j)} + (\nabla_j{}^2 J - \nabla_{j+1}{}^2 J)_{\mathbf{R},\mathbf{R}}\big]\,. \tag{13.24}$$

We do not deal further with the distribution function itself, but turn our attention now to the mean-square distance $\langle R_j{}^2\rangle$. Multiply both sides of Eq. (13.24) by $R^2 d\mathbf{R}$ and integrate. Noting that by Green's theorem

$$\int ({\nabla_j}^2 P^{(j)}) R^2 d\mathbf{R} = 6\,, \tag{13.25}$$

we then obtain

$$\frac{1}{a^2}\frac{d\langle {R_j}^2\rangle}{dj} = \frac{1 + \frac{1}{6}\int ({\nabla_j}^2 J - \nabla_{j+1}^2 J)_{\mathbf{R},\mathbf{R}} R^2 d\mathbf{R}}{1 + \int J(\mathbf{R},\mathbf{R}) d\mathbf{R}}\,. \tag{13.26}$$

As seen from Eq. (13.8), the function $H_{jt}$ is given by the sum of products of the $\chi$ functions. We now approximate $H_{jt}$ by terms involving only one of the $\chi$ functions; that is,

$$H_{jt} = \sum_{0\le k\le j}\ \sum_{j+1\le l\le n} \chi_{kl}\,. \tag{13.27}$$

Such an approximation is called the *single-contact approximation.* In this approximation, only those configurations are considered in which a single pair of segments is interacting (i.e., only one of the $\chi$ functions differs appreciably from zero). Higher-order approximations for multiple contacts will be introduced in the next section. In the single-contact approximation, we may further approximate the functions $P^{(j)}$ and $P^{(t)}$ by their unperturbed values ${P_0}^{(j)}$ and ${P_0}^{(t)}$, respectively. From Eq. (13.14), we then have

$$J(\mathbf{R}_j, \mathbf{R}_{j+1}) = \sum_k \sum_l \int \chi_{kl} {P_0}^{(j)}(\mathbf{R}_k, \mathbf{R}_j) \times {P_0}^{(l-j-1)}(\mathbf{R}_l - \mathbf{R}_{j+1}) d\mathbf{R}_k\; d\mathbf{R}_l\,. \tag{13.28}$$

Substitution of Eq. (13.2) for $\chi_{kl}$ and integration over $\mathbf{R}_l$ leads to a contact of the $k$th and $l$th segments because of the delta function,

$$J(\mathbf{R}_j, \mathbf{R}_{j+1}) = -\beta \sum_k \sum_l \int {P_0}^{(j)}(\mathbf{R}_k, \mathbf{R}_j) \times {P_0}^{(l-j-1)}(\mathbf{R}_k - \mathbf{R}_{j+1}) d\mathbf{R}_k\,. \tag{13.29}$$

The unperturbed bivariate distribution ${P_0}^{(j)}(\mathbf{R}_k, \mathbf{R}_j)$ may be factored as

$${P_0}^{(j)}(\mathbf{R}_k, \mathbf{R}_j) = {P_0}^{(k)}(\mathbf{R}_k) {P_0}^{(j-k)}(\mathbf{R}_j - \mathbf{R}_k)\,. \tag{13.30}$$

Then, if we use Gaussian functions for all the $P_0$'s, the integral in Eq. (13.29) may be evaluated in a straightforward manner, and the result can be used in Eq. (13.26).

We omit further details. The derivative of $\langle {R_j}^2\rangle$ becomes

$$\frac{1}{a^2}\frac{d\langle {R_j}^2\rangle}{dj} = 1 + \tfrac{8}{3} z\big[2y^{1/2} + (1-y)^{1/2} - 1 - y\big] + \cdots\,, \tag{13.31}$$

where

$$\begin{aligned} y &= \frac{j}{n}\,, \\ z &= \left(\frac{3}{2\pi a^2}\right)^{3/2} \beta n^{1/2} \\ &= \left(\frac{3}{2\pi \langle R^2\rangle_0}\right)^{3/2} \beta n^2\,. \end{aligned} \tag{13.32}$$

Integration now yields $\langle R_n{}^2\rangle \equiv \langle R^2\rangle$,

$$\frac{\langle R^2\rangle}{na^2} = \alpha_R{}^2 = 1 + \tfrac{4}{3}z + \cdots\,. \tag{13.33}$$

This is the first-order perturbation theory of the mean-square end-to-end distance, and has been derived by many authors as cited in Section 12c. From Eqs. (13.32) and (13.33), the expansion factor is seen to increase with $n$ (assuming that $\beta > 0$). Thus the present theory gives support to the conclusion of Flory. A further discussion of the perturbation theory of $\alpha$ is deferred to the next section.

## 14. Perturbation Theory (B): Cluster Expansion Method

As mentioned in Section 12c, the approach to the problem analogous to the Ursell–Mayer theory of imperfect gases was attempted first by Teramoto,[12, 21] and subsequently pursued by many investigators. Various statistical properties can be calculated more easily than in the previous section, although the results are obtained in series forms. The formulation presented here is due to Fixman.[26]

It is convenient to formulate, instead of $P(\mathbf{R})$, the distribution function $P(\mathbf{R}_{ij})$ of the distance $\mathbf{R}_{ij}$ between the $i$th and $j$th segments ($j > i$). Suppose the $i$th segment to be fixed at the origin of a coordinate system. Then the partition function is still given by Eq. (10.1), and $P(\mathbf{R}_{ij})$ may be written in the form,

$$P(\mathbf{R}_{ij}) = Z^{-1} \int \left[\prod_{j=1}^{n} \tau(\mathbf{r}_j)\right] \exp\left(-\frac{W}{kT}\right) \frac{d\{\mathbf{r}_n\}}{d\mathbf{R}_{ij}}\,. \tag{14.1}$$

The exponential in the integrand may be expanded in terms of the $\chi$ functions as follows,

$$\begin{aligned} \exp(-W/kT) &= \prod_{k<l} (1 + \chi_{kl}) \\ &= 1 + \sum_{k<l} \chi_{kl} + \sum_{\substack{k<l \\ k<p}} \sum_{p<q} \chi_{kl}\chi_{pq} + \cdots \\ &\quad + \sum_{k<l} \sum_{p<q} \cdots \sum_{\substack{u<v \\ k<p<\cdots<u}} \chi_{kl}\chi_{pq}\cdots\chi_{uv} + \cdots\,. \end{aligned} \tag{14.2}$$

We now introduce the unperturbed multivariate distribution function $P_0(\mathbf{R}_{ij}, \mathbf{R}_{kl}, \ldots, \mathbf{R}_{uv})$ of vectors $\mathbf{R}_{ij}$, $\mathbf{R}_{kl}$, …, $\mathbf{R}_{uv}$,

$$P_0(\mathbf{R}_{ij}, \mathbf{R}_{kl}, \ldots, \mathbf{R}_{uv}) = \int \left[\prod_{j=1}^{n} \tau(\mathbf{r}_j)\right] \frac{d\{\mathbf{r}_n\}}{d\mathbf{R}_{ij} d\mathbf{R}_{kl} \cdots d\mathbf{R}_{uv}} \,. \tag{14.3}$$

With the use of Eqs. (14.2) and (14.3), $P(\mathbf{R}_{ij})$ of (14.1) may then be expanded as

$$\begin{aligned} P(\mathbf{R}_{ij}) = Z^{-1} \Big[ & P_0(\mathbf{R}_{ij}) + \sum \int \chi_{kl} P_0(\mathbf{R}_{ij}, \mathbf{R}_{kl}) d\mathbf{R}_{kl} \\ & + \sum \sum \int \chi_{kl} \chi_{pq} P_0(\mathbf{R}_{ij}, \mathbf{R}_{kl}, \mathbf{R}_{pq}) d\mathbf{R}_{kl} d\mathbf{R}_{pq} + \cdots \Big] \,. \end{aligned} \tag{14.4}$$

Recalling that

$$P_0(\mathbf{R}_{kl}, \ldots, \mathbf{R}_{uv}) = \int P_0(\mathbf{R}_{ij}, \mathbf{R}_{kl}, \ldots, \mathbf{R}_{uv}) d\mathbf{R}_{ij} \,, \tag{14.5}$$

we integrate both sides of Eq. (14.4) over $\mathbf{R}_{ij}$ to obtain

$$\begin{aligned} Z = 1 & + \sum \int \chi_{kl} P_0(\mathbf{R}_{kl}) d\mathbf{R}_{kl} \\ & + \sum \sum \int \chi_{kl} \chi_{pq} P_0(\mathbf{R}_{kl}, \mathbf{R}_{pq}) d\mathbf{R}_{kl} \; d\mathbf{R}_{pq} + \cdots \,. \end{aligned} \tag{14.6}$$

Substitution of Eq. (13.2) into Eqs. (14.4) and (14.6) and integration leads to

$$\begin{aligned} P(\mathbf{R}_{ij}) = Z^{-1} \big[ & P_0(\mathbf{R}_{ij}) - \beta \sum P_0(\mathbf{R}_{ij}, 0_{kl}) \\ & + \beta^2 \sum \sum P_0(\mathbf{R}_{ij}, 0_{kl}, 0_{pq}) + \cdots \big] \end{aligned} \tag{14.7}$$

with

$$Z = 1 - \beta \sum P_0(0_{kl}) + \beta^2 \sum \sum P_0(0_{kl}, 0_{pq}) + \cdots \,, \tag{14.8}$$

where $0_{kl}$, $0_{pq}$, … mean that $\mathbf{R}_{kl} = 0$, $\mathbf{R}_{pq} = 0$, …. Now $Z$ certainly lies between zero and unity if $\beta > 0$. We may therefore expand the denominator of the right-hand side of Eq. (14.7) with (14.8) in a geometric series and collect powers of $\beta$; that is,

$$\begin{aligned} P(\mathbf{R}_{ij}) = P_0(\mathbf{R}_{ij}) & + \beta \sum_{k<l} Q_0(\mathbf{R}_{ij}, 0_{kl}) - \beta^2 \sum_{\substack{k<l \\ k<p}} \sum_{p<q} Q_0(\mathbf{R}_{ij}, 0_{kl}, 0_{pq}) \\ & + \beta^3 \sum_{\substack{k<l \\ k<p<s}} \sum_{p<q} \sum_{s<t} Q_0(\mathbf{R}_{ij}, 0_{kl}, 0_{pq}, 0_{st}) - \cdots \,, \end{aligned} \tag{14.9}$$

where

$$Q_0(\mathbf{R}_{ij}, 0_{kl}) = P_0(\mathbf{R}_{ij}) P_0(0_{kl}) - P_0(\mathbf{R}_{ij}, 0_{kl}) \,, \tag{14.10}$$

$$\begin{aligned} Q_0(\mathbf{R}_{ij}, 0_{kl}, 0_{pq}) = {} & P_0(\mathbf{R}_{ij})P_0(0_{kl}, 0_{pq}) - P_0(\mathbf{R}_{ij}, 0_{kl}, 0_{pq}) \\ & + P_0(\mathbf{R}_{ij}, 0_{kl})P_0(0_{pq}) + P_0(\mathbf{R}_{ij}, 0_{pq})P_0(0_{kl}) \\ & - 2P_0(\mathbf{R}_{ij})P_0(0_{kl})P_0(0_{pq}) \,, \end{aligned} \tag{14.11}$$

$$\begin{aligned} Q_0(\mathbf{R}_{ij}, 0_{kl}, 0_{pq}, 0_{st}) = {} & P_0(\mathbf{R}_{ij})P_0(0_{kl}, 0_{pq}, 0_{st}) - P_0(\mathbf{R}_{ij}, 0_{kl}, 0_{pq}, 0_{st}) \\ & + P_0(\mathbf{R}_{ij}, 0_{pq}, 0_{st})P_0(0_{kl}) + P_0(\mathbf{R}_{ij}, 0_{kl}) \\ & \times P_0(0_{pq}, 0_{st}) - 2P_0(\mathbf{R}_{ij})P_0(0_{kl})P_0(0_{pq}, 0_{st}) \\ & + P_0(\mathbf{R}_{ij}, 0_{kl}, 0_{st})P_0(0_{pq}) + P_0(\mathbf{R}_{ij}, 0_{pq}) \\ & \times P_0(0_{kl}, 0_{st}) - 2P_0(\mathbf{R}_{ij})P_0(0_{pq})P_0(0_{kl}, 0_{st}) \\ & + P_0(\mathbf{R}_{ij}, 0_{kl}, 0_{pq})P_0(0_{st}) + P_0(\mathbf{R}_{ij}, 0_{st}) \\ & \times P_0(0_{kl}, 0_{pq}) - 2P_0(\mathbf{R}_{ij})P_0(0_{st})P_0(0_{kl}, 0_{pq}) \\ & - 2P_0(\mathbf{R}_{ij}, 0_{kl})P_0(0_{pq})P_0(0_{st}) \\ & - 2P_0(\mathbf{R}_{ij}, 0_{pq})P_0(0_{kl})P_0(0_{st}) \\ & - 2P_0(\mathbf{R}_{ij}, 0_{st})P_0(0_{kl})P_0(0_{pq}) \\ & + 6P_0(\mathbf{R}_{ij})P_0(0_{kl})P_0(0_{pq})P_0(0_{st}) \,. \end{aligned} \tag{14.12}$$

As seen from Eq. (14.3), if we use the Gaussian function of (5.35) for the bond probability, all the $P_0$'s can be easily evaluated by the Wang–Uhlenbeck theorem (Section 6). Some of these, which are frequently used, are given in Appendix III B. Thus each term in $Q_0$ becomes a Gaussian function.

We do not again deal further with the distribution function itself, but proceed to the evaluation of its moments. For example, the mean-square end-to-end distance can be obtained by multiplying Eq. (14.9) with $i = 0$ and $j = n$ by $R^2 d\mathbf{R}$ and integrating. All the results may be expressed as power series in $\beta$, as seen from Eq. (14.9). The linear term, the square term, and so on are called the *single-contact term*,the *double-contact term*, and so on, respectively. The theory obtained by retaining terms only up to the $k$th power of $\beta$ is referred to as the k*th-order perturbation theory.*

We first evaluate the mean-square end-to-end distance. The final result may be expressed as a power series in the parameter $z$ defined by Eq. (13.32),

$$\langle R^2 \rangle / \langle R^2 \rangle_0 = \alpha_R^{\,2} = 1 + C_1 z - C_2 z^2 + C_3 z^3 - \cdots \,. \tag{14.13}$$

Let us now consider the symmetric matrix $\mathbf{C}$ appearing in Eq. (6.15) for the distribution function $P_0(\mathbf{\Phi}_1, \mathbf{\Phi}_2, \ldots)$ with $\mathbf{\Phi}_1 = \mathbf{R}$, $\mathbf{\Phi}_2 = \mathbf{R}_{kl}$, $\mathbf{\Phi}_3 = \mathbf{R}_{pq}$, $\mathbf{\Phi}_4 = \mathbf{R}_{st}$, $\ldots$. From Eqs. (6.3) and (6.12), it is seen that for the present case the diagonal element $C_{jj}$ is equal to the number of bonds contained in the part of the chain between the two ends of the vector $\mathbf{\Phi}_j$, while the off-diagonal element $C_{ij}$ is equal to the number of

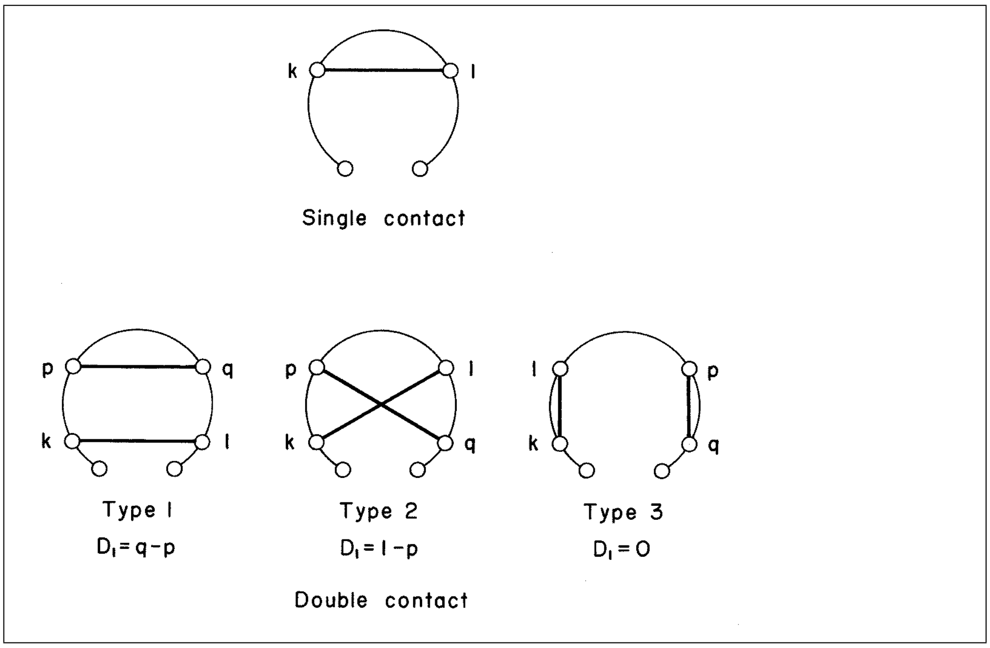

**Fig. III.3.** Representative cluster diagrams for the single- and double-contact terms of the mean-square end-to-end distance.

bonds contained commonly in the two parts of the chain between the ends of $\mathbf{\Phi}_i$ and between the ends of $\mathbf{\Phi}_j$. Thus we have

$$\mathbf{C} = \begin{pmatrix} n & l-k & q-p & t-s & \cdots \\ l-k & l-k & D_1 & D_2 & \cdots \\ q-p & D_1 & q-p & D_3 & \cdots \\ t-s & D_2 & D_3 & t-s & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} . \tag{14.14}$$

The coefficients in Eq. (14.13) can be expressed in terms of the matrix elements of (14.14),

$$C_1 = n^{-3/2} \sum_{k<l} (l-k)^{-1/2} , \tag{14.15}$$

$$C_2 = n^{-2} \sum_{\substack{k<l \\ k<p}} \sum_{p<q} \left\{ \frac{(l-k)(q-p)\left[2D_1 - (l-k) - (q-p)\right]}{\left[(l-k)(q-p) - {D_1}^2\right]^{5/2}} \right.$$

$$\left. + (l-k)^{-1/2}(q-p)^{-3/2} + (l-k)^{-3/2}(q-p)^{-1/2} \right\} , \tag{14.16}$$

$$C_3 = n^{-5/2} \sum_{\substack{k<l \\ k<p<s}} \sum_{p<q} \sum_{s<t} f(k, \ldots, t, D_1, D_2, D_3) , \tag{14.17}$$

**TABLE III.1.** THE MATRIX ELEMENTS $D_1$, $D_2$, and $D_3$ FOR THE CLUSTER TYPES IN THE TRIPLE-CONTACT TERM OF $\langle R^2 \rangle$ FOR WHICH THE SUMMATION IS REQUIRED

| $D_1 = q - p$ | | | | $D_1 = l - p$ | | | |
|---|---|---|---|---|---|---|---|
| TYPE | $\sigma$ | $D_2$ | $D_3$ | TYPE | $\sigma$ | $D_2$ | $D_3$ |
| 1 | 1 | $t - s$ | $t - s$ | 5 | 1 | $t - s$ | $t - s$ |
| 2 | 1 | $t - s$ | 0 | 6 | 1 | 0 | $q - s$ |
| 3 | 1 | $t - s$ | $q - s$ | 7 | 2 | $l - s$ | $t - s$ |
| 4 | 2 | $l - s$ | 0 | 8 | 1 | $l - s$ | $q - s$ |

where the explicit expression for $f$ has been omitted because of its length. The elements $D_1$, $D_2$, and so on can be determined by a cluster-diagram analysis. In Fig. III.3 are depicted representative cluster diagrams for all possible contact types in the single- and double-contact terms. There is only one type of contact in the single-contact term, and three types in the double-contact term. For the latter, we have

$$\begin{aligned} D_1 &= q - p && \text{for type } 1\,, \\ &= l - p && \text{for type } 2\,, \\ &= 0 && \text{for type } 3\,. \end{aligned} \tag{14.18}$$

When $D_1 = 0$, the quantity in curly brackets of Eq. (14.16) is identically equal to zero; terms of type 3 do not contribute to $C_2$, and only two types require the multiple summations in Eq. (14.16). In general, a diagram, in which the chain can be divided into at least two subchains statistically independent of each other, does not contribute to the final result. In the triple-contact term, there are, in all, 15 possible types of contacts. Of these, five types make no contribution, for which $f$ is identically equal to zero. In addition, there is mirror image symmetry between two other types of contacts; two types related by mirror image symmetry lead to the same numerical contribution once the summation has been carried out. There are two symmetric pairs of types among the remaining ten types in $C_3$. Thus the number of types of contacts that require the multiple summations in Eq. (14.17) is reduced to eight. In Table III.1 are given the elements $D_1$, $D_2$, and $D_3$ for these eight types of contacts together with a symmetry factor $\sigma(= 1$ or $2)$ to be applied to each type.

The sums in Eqs. (14.15) to (14.17) may now be converted to integrals for $n^{1/2} \gg 1$. The integrals for $C_1$ and $C_2$ can be evaluated analytically. The integrals for types 1 to 5 in $C_3$ can also be evaluated analytically, but the remaining require numerical integration. The results are

$$\begin{aligned} C_1 &= \tfrac{4}{3} = 1.333\,, \\ C_2 &= \frac{16}{3} - \frac{28}{27}\pi = 2.075\,, \\ C_3 &= \frac{64}{3} - \left(\frac{73679}{8100} - \frac{13202}{2025}\ln 2 + \frac{1616}{405}\ln\frac{3}{2}\right)\pi + \frac{512}{45} I_A \\ &= 6.459\,, \end{aligned} \tag{14.19}$$

where

$$I_A = \int_0^{\pi/2} \frac{\theta^2}{1 + 3\sin^2\theta}\, d\theta = 0.40325\,.$$

The integral $I_A$ was evaluated numerically. The first coefficient $C_1$ is in agreement with that in Eq. (13.33), and $C_2$ and $C_3$ are due to Fixman[26] and Yamakawa and Tanaka.[36] It is of interest to note that, using a numerical extrapolation method, Subirana et al.[37] found $C_2 = 2.05$ and $C_3 = 6.3 \pm 0.2$, which are very close to the exact values of (14.19). The evaluation of higher coefficients requires the use of digital computers.

Next we evaluate the mean-square radius of gyration in the double-contact approximation. For this purpose, we can use Eq. (7.22) or

$$\langle S^2 \rangle = n^{-2} \sum_{i<j} \langle {R_{ij}}^2 \rangle\,, \tag{14.20}$$

where $\langle {R_{ij}}^2 \rangle$ can be obtained from Eq. (14.9). We may write the result as

$$\langle S^2 \rangle / \langle S^2 \rangle_0 = \alpha_S^{\,2} = 1 + {C_1}' z - {C_2}' z^2 + \cdots\,. \tag{14.21}$$

The matrix $\mathbf{C}'$ associated with the distribution function $P_0(\mathbf{R}_{ij}, \mathbf{R}_{kl}, \mathbf{R}_{pq}, \ldots)$ is

$$\mathbf{C}' = \begin{pmatrix} j - i & {D_1}' & {D_2}' & \cdots \\ {D_1}' & l - k & {D_3}' & \cdots \\ {D_2}' & {D_3}' & q - p & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{14.22}$$

The coefficients in Eq. (14.21) may then be written as

$${C_1}' = 6n^{-7/2} \sum_{i<j} \sum_{k<l} ({D_1}')^2 (l-k)^{-5/2}\,, \tag{14.23}$$

$$\begin{aligned} {C_2}' = 6n^{-4} \sum_{i<j} \sum_{\substack{k<l \\ k<p}} \sum_{p<q} \Big\{ & \big[(q-p)({D_1}')^2 + (l-k)({D_2}')^2 \\ & - 2{D_1}'{D_2}'{D_3}'\big] \big[(l-k)(q-p) - ({D_3}')^2\big]^{-5/2} \\ & - ({D_1}')^2 (l-k)^{-5/2} (q-p)^{-3/2} - ({D_2}')^2 (l-k)^{-3/2} (q-p)^{-5/2} \Big\}\,. \end{aligned} \tag{14.24}$$

We omit further details, and merely note that there are three types of clusters in ${C_1}'$ and 16 types in ${C_2}'$ that require the multiple summations. The sums may be converted to integrals; they can be evaluated analytically. The results are

$$\begin{aligned} {C_1}' &= \frac{134}{105} = 1.276, \\ {C_2}' &= \frac{536}{105} - \frac{1247}{1296}\pi = 2.082\,. \end{aligned} \tag{14.25}$$

The first coefficient was obtained by Zimm, Stockmayer, and Fixman,[13, 26] and the second coefficient, by Yamakawa, Aoki, and Tanaka.[38] The evaluation of ${C_3}'$ and higher coefficients cannot be carried through without numerical calculation.

Other statistical averages can also be evaluated easily in the single-contact approximation. For example, we can calculate $\langle {R_{ij}}^{2p} \rangle$. In particular, we obtain for $\langle R^{2p} \rangle$ and $\langle {R_{ij}}^2 \rangle$

$$\langle R^{2p} \rangle = \langle R^{2p} \rangle_0 (1 + K^{(p)} z - \cdots) \tag{14.26}$$

with

$$K^{(p)} = \sum_{m=1}^{p} \frac{(-1)^{m+1}}{m^2 - \frac{1}{4}} \binom{p}{m} = 2\left[ \frac{\pi^{1/2}(p+1)!}{\Gamma(p+\frac{3}{2})} - 2 \right], \tag{14.27}$$

$$\langle {R_{ij}}^2 \rangle = \langle {R_{ij}}^2 \rangle_0 (1 + K_{ij} z - \cdots) \tag{14.28}$$

with

$$\begin{aligned} K_{ij} = \tfrac{4}{3}\big\{ &\tfrac{8}{3}(y-x)^{1/2} - 4(1-x)^{1/2} - 4y^{1/2} + (y-x) \\ &- \tfrac{8}{3}(y-x)^{-1}\big[(1-y)^{3/2} - (1-x)^{3/2} - y^{3/2} + x^{3/2}\big]\big\}\,, \\ &x = i/n\,, \qquad y = j/n\,. \end{aligned} \tag{14.29}$$

Substituting Eqs. (14.21) and (14.28) into the relation,

$$\langle {S_j}^2 \rangle = n^{-1} \left( \sum_{i=0}^{j-1} \langle {R_{ij}}^2 \rangle + \sum_{i=j+1}^{n} \langle {R_{ji}}^2 \rangle \right) - \langle S^2 \rangle\,, \tag{14.30}$$

we obtain

$$\langle {S_j}^2 \rangle = \langle {S_j}^2 \rangle_0 (1 + K_j z - \cdots) \tag{14.31}$$

with

$$\begin{aligned} K_j = (1 - 3y + 3y^2)^{-1} \bigg\{ &\frac{121}{21} - \frac{32}{3}\big[y^{3/2} + (1-y)^{3/2}\big] \\ &+ \frac{24}{5}\big[y^{5/2} + (1-y)^{5/2}\big] + \tfrac{4}{3}\big[y^3 + (1-y)^3\big] \bigg\}\,. \end{aligned} \tag{14.32}$$

The results given by Eqs. (14.26) to (14.32) are due to Yamakawa and Kurata.[39, 40]

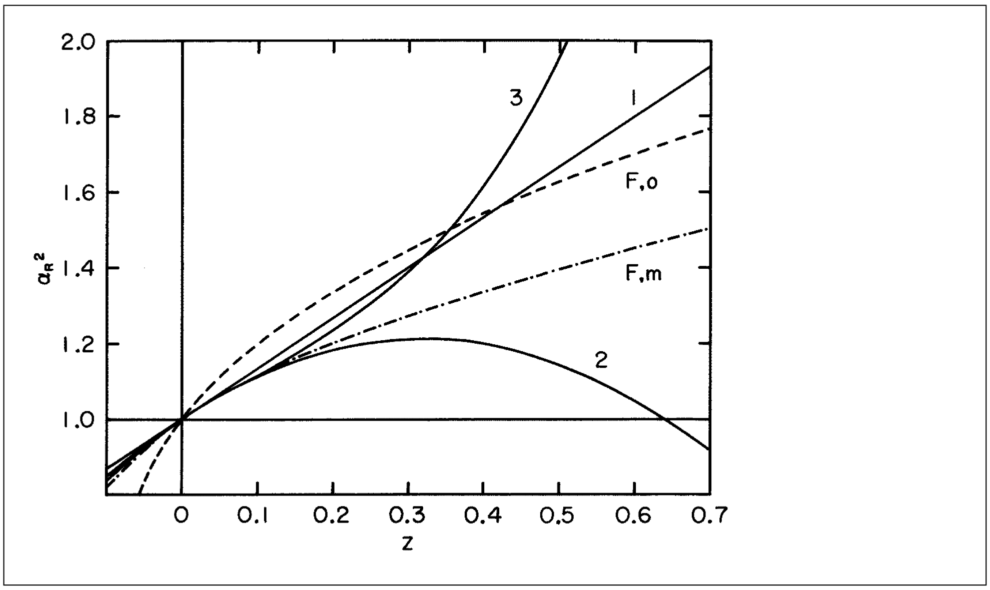

**Fig. III.4.** Theoretical values of $\alpha_R^2$ at small $z$. Curves 1 to 3: the first-,second-, and third-order perturbation theories, respectively. Curve F,o: the original Flory theory, Eq. (14.39). Curve F,m: the modified Flory theory, Eq. (14.40).

As seen from the analysis described so far, the average molecular dimensions may be expressed in terms of three parameters: the number $n$ of segments in the chain, the effective bond length $a$, and the binary cluster integral $\beta$ for a pair of segments, provided that the superposition approximation and the assumption of the short-range nature of the pair potential are valid and $n$ is large. However, it is important to observe that these three parameters never appear separately but only in two combinations $na^2$ and $n^2\beta$. For this reason, a theory of the type described is referred to as the *two-parameter theory* of polymer solutions. The quantity $na^2$ is nothing but the unperturbed mean-square end-to-end distance of the linear chain, while the quantity $n^2\beta$ is just twice the total excluded volume between segments. Thus these two quantities represent short-range and long-range interferences in the chain, respectively.

The most significant results obtained in this section are the perturbation theoretic predictions of the expansion factors,

$$\alpha_R^2 = 1 + 1.333z - 2.075z^2 + 6.459z^3 - \cdots , \qquad (14.33)$$

$$\alpha_S^2 = 1 + 1.276z - 2.082z^2 + \cdots . \qquad (14.34)$$

These equations represent the exact and standard theory of the excluded-volume effect within the framework of the two-parameter theory, although the series are very slowly convergent and therefore their validity is confined to the range of small $z$, i.e., the very vicinity of the theta temperature. The expansion coefficients in Eq. (14.33) or (14.34) may be used as a criterion for excellence of an approximate theory at least over the range of relatively small $z$. In order to illustrate the slow convergence of the series, in Fig. III.4 are shown the values of $\alpha_R^2$ predicted by the first-, second-, and third-order perturbation theories by curves 1, 2, and 3, respectively. The second- and third-order perturbation theories are seen to predict almost the same values of $\alpha_R$ for $|z| < 0.15$, but depart markedly from each other beyond this region. These perturbation theories are believed to predict the correct trend of the increase in $\alpha_R$ over the range of $z < 0.15$. Also, it is important to note that for small $z$ both the second- and third-order perturbation theories predict values of $\alpha_R$ smaller (not greater) than those predicted by the first-order perturbation theory.

From the first-order perturbation theory, we can deduce some interesting aspects of the excluded-volume effect.[39, 40] First, consider a Gaussian distribution function of the end-to-end distance, whose second moment is given by the exact first-order perturbation theory. Its $2p$th moments, which we designate by $\langle R^{2p}\rangle^*$, can then be obtained as

$$\langle R^{2p}\rangle^* = \langle R^{2p}\rangle_0(1 + \tfrac{4}{3}pz - \cdots)\,. \tag{14.35}$$

By a comparison of this and Eq. (14.26) with (14.27), we immediately find that $\langle R^{2p}\rangle^*$ are always larger than the corresponding exact values for positive small $z$ and $p \geq 2$. Secondly, the ratio of $\langle R^2\rangle$ to $\langle S^2\rangle$ may be expressed as

$$\frac{\langle R^2\rangle}{\langle S^2\rangle} = 6\left(1 + \frac{2}{35}z - \cdots\right)\,. \tag{14.36}$$

In other words, the ratio is larger than the value 6 for the random-flight chain for positive $z$, and tends to increase with increasing $z$. Thirdly, from Eq. (14.31) with (14.32), we have

$$\begin{aligned}\langle {S_j}^2\rangle &= \tfrac{1}{3}na^2(1 + 1.23z - \cdots) \qquad \text{for } j = 0, n\,,\\ &= \frac{1}{12}na^2(1 + 1.00z - \cdots) \quad \text{for } j = \tfrac{1}{2}n\,.\end{aligned} \tag{14.37}$$

Equations (14.37) indicate that the excluded-volume effect has a larger influence on the segments near the ends of the chain than on the intermediate segments; the expansion of the polymer molecule does not occur *uniformly*, but is greater in the outer shells than in the interior of the molecule. All these aspects of the effect may be represented in terms of the *non-Gaussian nature* of the real polymer chain.

Finally, we discuss briefly the Flory theory from the point of view of the two-parameter theory. As will be shown in Chapter IV, a correspondence exists between Flory's notation and ours,[35, 41]

$$\begin{aligned}z &= (4/3^{3/2})C_M\psi(1 - \Theta/T)M^{1/2}\,,\\ \beta &= 2{V_0}^{-1}{V_s}^2\psi(1 - \Theta/T)\,.\end{aligned} \tag{14.38}$$

In our notation the Flory equation (11.20) may be rewritten as

$$\alpha^5 - \alpha^3 = 2.60z\,. \qquad (\mathrm{F, o}) \tag{14.39}$$

At small $z$, Eq. (14.39) may be expanded as $\alpha^2 = 1 + 2.60z - \cdots$; the coefficient $2.60(= 3^{3/2}/2)$ is about two times greater than the exact value of (14.19) or (14.25). Thus Stockmayer[35, 41] recommended an adjustment of the coefficient on the right-hand side of Eq. (14.39) so that it gives the exact first-order perturbation theory;

$$\alpha_R^5 - \alpha_R^3 = \tfrac{4}{3}z\,, \qquad (\mathrm{F,m}) \tag{14.40}$$

$$\alpha_S^5 - \alpha_S^3 = \frac{134}{105}z\,. \qquad (\mathrm{F,m}) \tag{14.41}$$

Equation (14.39) is referred to as the *original* Flory equation (F,o), and Eqs. (14.40) and (14.41), as the *modified* Flory equations (F,m). In Fig. III.4 are also plotted the values of $\alpha_R^2$ predicted by the original and modified Flory equations. The modified Flory theory prediction is seen to lie between the second- and third-order perturbation theory predictions for positive $z$, and seems rather better than the original Flory theory. However, Eq. (14.40) or (14.41) is semiempirical in nature, and the adequacy of these equations at large $z$ must be examined by further investigations.

## 15. Approximate Closed Expressions

As described in the preceding sections, the expansion factor is a function only of the excluded-volume parameter $z$ within the framework of the two-parameter theory. Although the perturbation theory is exact, its validity is confined to a very small range near $z = 0$. We now wish to derive an equation which can describe correctly the behavior of the expansion factor over a wide range of $z$. There is, of course, no promise that we can obtain an exact solution of the problem, since it is a many-body problem. Since the mid-1950s, the general excluded-volume problem has been approached from two starting points. One begins with the potential of mean force with the end-to-end distance or the radius of gyration fixed, and the other is a derivation of a differential equation for the expansion factor. Although all the theories predict that $\alpha$ increases with $z$ without limit, in conformity with the Flory theory, there are appreciable differences among the values of $\alpha$ predicted by them, depending primarily on the method used to decouple the many-body problem. In particular, although all expressions for $\alpha$ have the asymptotic form,

$$\lim_{z\to\infty} \alpha^{\nu} = \text{const. } z\,, \tag{15.1}$$

where $\nu$ is a constant independent of $z$, several values between one and five for $\nu$ have been predicted. In the present and next sections, we give a detailed discussion of the present status of the problem.

## 15a. Approximate Expressions Derived from the Potential of Mean Force with $R$ or $S$ Fixed

In Section 11, we assumed a form for the potential $V(S)$ in Eq. (11.1) without proof. We begin by deriving a formal but exact expression for the potential $V(R)$ or $V(S)$. The distribution function $P(\mathbf{R})$ of the end-to-end distance may be written in the form,

$$P(\mathbf{R}) = Z^{-1} \int P_0\bigl(\{\mathbf{R}_n\}\bigr) \exp\left(-\frac{W}{kT}\right) \frac{d\{\mathbf{r}_n\}}{d\mathbf{R}} \tag{15.2}$$

with

$$Z = \int P_0\bigl(\{\mathbf{R}_n\}\bigr) \exp\left(-\frac{W}{kT}\right) d\{\mathbf{r}_n\}\,, \tag{15.3}$$

$$\exp\left(-\frac{W}{kT}\right) = \prod_{i<j} (1 - \beta\delta_{ij})\,, \tag{15.4}$$

where $\delta_{ij}$ is shorthand for $\delta(\mathbf{R}_{ij})$ and $P_0\bigl(\{\mathbf{R}_n\}\bigr)$ represents the product of the bond probabilities, namely the unperturbed instantaneous distribution. Now, differentiation of $ZP(\mathbf{R})$ with respect to $\beta$ leads to

$$\frac{\partial ZP(\mathbf{R})}{\partial\beta} = -\sum_{i<j} \int \delta_{ij} P_0\bigl(\{\mathbf{R}_n\}\bigr) \exp\left(-\frac{W}{kT}\right) \frac{d\{\mathbf{r}_n\}}{d\mathbf{R}}\,. \tag{15.5}$$

Dividing both sides of Eq. (15.5) by $Z$, we obtain

$$\begin{aligned} Z^{-1}\frac{\partial ZP(\mathbf{R})}{\partial\beta} &= -\sum_{i<j} \int \delta_{ij} P\bigl(\{\mathbf{R}_n\}\bigr) \frac{d\{\mathbf{r}_n\}}{d\mathbf{R}} \\ &= -\sum_{i<j} \int \delta_{ij} P(\mathbf{R}, \mathbf{R}_{ij}) d\mathbf{R}_{ij}\,. \end{aligned} \tag{15.6}$$

Dividing both sides of Eq. (15.6) by $P(\mathbf{R})$, we have

$$\begin{aligned} \frac{\partial \ln ZP(\mathbf{R})}{\partial\beta} &= -\sum_{i<j} \int \delta_{ij} P(\mathbf{R}_{ij}|\mathbf{R}) d\mathbf{R}_{ij} \\ &= -\sum_{i<j} P(0_{ij}|\mathbf{R})\,. \end{aligned} \tag{15.7}$$

Integration of Eq. (15.7) over $\beta$ from 0 to $\beta$ leads to

$$P(\mathbf{R}) = Z^{-1} P_0(\mathbf{R}) \exp\left[-\frac{V(\mathbf{R})}{kT}\right]\,, \tag{15.8}$$

where

$$Z = \int P_0(\mathbf{R}) \exp\left[-\frac{V(\mathbf{R})}{kT}\right] d\mathbf{R}\,, \tag{15.9}$$

$$\frac{V(\mathbf{R})}{kT} = \sum_{i<j} \int_0^\beta P(0_{ij}|\mathbf{R}) d\beta\,. \tag{15.10}$$

The conditional probability density $P(0_{ij}|\mathbf{R})$ in Eq. (15.10) is to be evaluated in the (intermediate) perturbed state. Equation (15.10) is due to Fujita et al.[42]

Similarly, we can obtain for the distribution function $P(S)$ of the radius of gyration

$$P(S) = Z^{-1} P_0(S) \exp\left[-\frac{V(S)}{kT}\right] \tag{15.11}$$

with

$$Z = \int P_0(S) \exp\left[-\frac{V(S)}{kT}\right] dS\,, \tag{15.12}$$

$$\frac{V(S)}{kT} = \sum_{i<j} \int_0^\beta P(0_{ij}|S) d\beta\,. \tag{15.13}$$

We note that the approximation of Eq. (15.4) by[26]

$$\frac{W}{kT} = \beta \sum_{i<j} \delta_{ij} \tag{15.14}$$

in Eq. (15.2) and the corresponding expression for $P(S)$ give the same results as Eqs. (15.10) and (15.13), respectively. This means that the effect of interactions between two particular segments on statistical averages is negligibly small provided $n$ is large. With Eq. (15.14), the differentiation with respect to $\beta$ can be conveniently performed. Equations (15.10) and (15.13) are formally exact within the framework of the two-parameter theory.

Now we may use the Gaussian function for $P_0(\mathbf{R})$. Adopting the Hermans–Overbeek procedure, used in Section 11, the expansion factor $\alpha_R$ may then be equated to the value of $x = R/\langle R^2\rangle_0^{1/2}$ satisfying the equation,

$$x - \frac{1}{x} = -\frac{1}{3kT}\frac{\partial V(\mathbf{R})}{\partial x}\,. \tag{15.15}$$

However, the exact expression for $P_0(S)$, as given by Eq. (8.47), is too complicated to derive a closed expression for $\alpha_S$. In the first approximation, we therefore use the Gaussian function for $P_0(S)$ as in Section 11, and then $\alpha_S$ can be determined from Eq. (15.15) with $x = S/\langle S^2\rangle_0^{1/2}$ and $V(S)$ in place of $V(\mathbf{R})$.

Thus the problem comes down to an evaluation of the conditional probability density $P(0_{ij}|\mathbf{R})$ or $P(0_{ij}|S)$ in Eq. (15.10) or (15.13). Dependent on the approximation made in $P(0_{ij}|\mathbf{R})$ or $P(0_{ij}|S)$, the published work may be classified into three groups.

### 15a(i). Theories with $P(0_{ij}|\mathbf{R})$ in the Unperturbed State

We approximate $P(0_{ij}|\mathbf{R})$ by its value at $\beta = 0$ corresponding to the lower limit of integration in Eq. (15.10). We then have

$$\frac{V(\mathbf{R})}{kT} = \beta \sum_{i<j} P_0(0_{ij}|\mathbf{R}) \,. \tag{15.16}$$

For the random-flight model, $P_0(0_{ij}|\mathbf{R})$ can be evaluated straightforwardly, and we have

$$\frac{V(\mathbf{R})}{kT} = zn \sum_{i<j} (j-i)^{-3/2}(n-j+i)^{-3/2} \exp\left[-\frac{3(j-i)R^2}{2n(n-j+i)a^2}\right] . \tag{15.17}$$

Replacing the summation by integration, we obtain (with omission of a constant term)

$$V(\mathbf{R})/3kT = -(2\pi/3)^{1/2} zx \tag{15.18}$$

for $a \ll R \ll na$. From Eqs. (15.15) and (15.18), we have the result, $\alpha_R^2 - 1 = (2\pi/3)^{1/2}\alpha_R z$. Now the Hermans–Overbeek procedure correctly defines the asymptotic solution for large $z$. We replace the coefficient $(2\pi/3)^{1/2} = 1.446$ by 4/3 over the range of ordinary interest, since the difference between the two coefficients is small and at small $z$ the latter gives the exact first-order perturbation theory. Thus we rewrite the result as

$$\alpha_R^2 - 1 = \tfrac{4}{3}\alpha_R z \,. \qquad \text{(BJ)} \tag{15.19}$$

This equation is due to Bueche[25] and to James.[30] The BJ equation predicts that at large $z$, $\alpha_R$ is proportional to $z$, i.e., $\nu = 1$ in Eq. (15.1). Such an equation for $\alpha$ is referred to as an equation of the *first-power type*; it predicts that the root-mean-square end-to-end distance is proportional to $n$ at large $z$ so that the chain behaves like a rod molecule. This seems an implausible result.

Next we consider the smoothed-density model. It is convenient to rewrite $P_0(0_{ij}|\mathbf{R})$ as

$$P_0(0_{ij}|\mathbf{R}) = \int \delta(\mathbf{S}_j - \mathbf{S}_i) P_0(\mathbf{S}_i, \mathbf{S}_j|\mathbf{R}) d\mathbf{S}_i \, d\mathbf{S}_j \,, \tag{15.20}$$

where $\mathbf{S}_i$ is the distance of the $i$th segment from the molecular center of mass, as before. We now introduce the factorization approximation,

$$P_0(\mathbf{S}_i, \mathbf{S}_j|\mathbf{R}) = P_{0i}(\mathbf{S}_i|\mathbf{R}) P_{0j}(\mathbf{S}_j|\mathbf{R}) \tag{15.21}$$

with $P_{0i}(\mathbf{S}_i|\mathbf{R})$ the unperturbed distribution of $\mathbf{S}_i$ with $\mathbf{R}$ fixed. Substitution of Eq. (15.21) into Eq. (15.20) leads to

$$P_0(0_{ij}|\mathbf{R}) = \int P_{0i}(\mathbf{s}|\mathbf{R}) P_{0j}(\mathbf{s}|\mathbf{R}) d\mathbf{s} \,. \tag{15.22}$$

Recalling that the (unperturbed) conditional segment-density distribution $\rho_0(\mathbf{s}|\mathbf{R})$ is given by

$$\rho_0(\mathbf{s}|\mathbf{R}) = \sum_j P_{0j}(\mathbf{s}|\mathbf{R})\,, \tag{15.23}$$

we have, from Eqs. (15.16), (15.22), and (15.23),

$$V(\mathbf{R})/kT = \tfrac{1}{2}\beta \int \left[\rho_0(\mathbf{s}|\mathbf{R})\right]^2 d\mathbf{s}\,. \tag{15.24}$$

Similarly, we can obtain

$$V(S)/kT = \tfrac{1}{2}\beta \int \left[\rho_0(\mathbf{s}|S)\right]^2 d\mathbf{s}\,. \tag{15.25}$$

Substitution of Eq. (11.11) into Eq. (15.25) leads to

$$V(S)/kT = (3^{3/2}/2)zx^{-3}\,. \qquad (\mathrm{F,o}) \tag{15.26}$$

If we use Eq. (15.26) and the Gaussian function for $P_0(S)$, we find the original Flory equation. As pointed out by Fixman,[26] however, to derive the equations of the Flory type, it suffices merely to assume that the spatial distribution of segments about the center of mass is spherically symmetric; $\rho_0(\mathbf{s}|S)$ is a function only of $n$, $s$, and $S$. Thus $\rho_0(\mathbf{s}|S)$ must be of the form,

$$\rho_0(\mathbf{s}|S) = nS^{-3}f(s/S)\,, \tag{15.27}$$

where $f$ is some unknown function of $s/S$. We then have

$$\begin{aligned} V(S)/kT &= \tfrac{1}{2}\beta n^2 S^{-3} \int_0^\infty \left[f(s/S)\right]^2 4\pi (s/S)^2 d(s/S) \\ &= Czx^{-3}\,. \end{aligned} \tag{15.28}$$

Use of Eq. (15.28) and the Gaussian function for $P_0(S)$ leads to

$$\alpha_S^5 - \alpha_S^3 = Cz\,. \tag{15.29}$$

If the coefficient $C$ is adjusted to give the exact first-order perturbation theory, Eq. (15.29) becomes the modified Flory equation of (14.41) for $\alpha_S$. If we assume that $\rho_0(\mathbf{s}|\mathbf{R})$ is also spherically symmetric, by the same argument as above we can find the modified Flory equation of (14.40) for $\alpha_R$. All the equations of the Flory type predict that $\nu = 5$ in Eq. (15.1); they are of the *fifth-power type.*

Flory and Fisk[43] introduced a device to improve the theory by using the Flory–Fisk function given by Eq. (8.52) with $m = 3$ for $P_0(S)$ instead of the Gaussian function. Equation (15.28) was still adopted for $V(S)$, adjusting the coefficient $C$ to force agreement with the exact first-order perturbation theory. Carrying out the integration over $S$

numerically (without use of the Hermans–Overbeek procedure), they obtained the result,

$$\alpha_S^5 - \alpha_S^3 = 0.648z\left[1 + 0.969(1 + 10z/\alpha_S^3)^{-2/3}\right]. \qquad \text{(FF)} \qquad (15.30)$$

The FF equation predicts that at large $z$, $\alpha_S^5 = 0.648z$; it is of the fifth-power type, but the constant 0.648 in this asymptotic form is about one-half of the corresponding constant in the F,m equation. We note that the boson representation approach of Fixman and Stidham [44, 45] also predicts similar dependences of $\alpha_R$ and $\alpha_S$ on $z$; the numerical results will be shown at the end of this section, though the derivation is too complicated to reproduce herein [see Section 35a(iii)].

Fujita and Norisuye[46] improved the FF theory by using their exact expression for $P_0(S)$ given by Eq. (8.47) and still adopting Eq. (15.28) for $V(S)$. The coefficient $C$ may be again adjusted to force agreement with the exact first-order perturbation theory. This can be done conveniently following the procedure of Fixman.[47] If the general expression for $\langle S^2\rangle$, analogous to Eq. (11.18), is expanded in powers of $Cz$, the coefficients of these powers are various combinations of $\langle S^{-2p}\rangle_0$. These moments can be calculated if $P_0(S)$ or $P_0(S^2)$ is expressed as Eq. (8.45) and the integration over $S$ is carried out first. The result is*

$$\alpha_S^2 = 1 + 0.4649(Cz) - 0.2458(Cz)^2 + \cdots . \qquad (15.31)$$

If the coefficient of $z$ is equated to 134/105, $C$ is found to be 2.745. Note that this $C$ value yields the value $-1.852$ for the coefficient of $z^2$ in Eq. (15.31), which is in good agreement with the exact value. The Fujita–Norisuye theory is also of the fifth-power type and gives, of course, only numerical results. As will be shown later, it predicts values of $\alpha_S$ somewhat greater than those predicted by the FF theory.

The following question now arises: is $\rho_0(\mathbf{s}|\mathbf{R})$ spherically symmetric? Obviously, it is not, since it is the sum over $P_{0j}(\mathbf{s}|\mathbf{R})$ given by Eq. (7.25) with (7.26). Although its evaluation is straightforward,Kurata, Stockmayer, and Roig[48] simply adopted an ellipsoid model such that the distribution of segments is uniform within an ellipsoid having its principal axes proportional to the root-mean-square radii of the chain with $\mathbf{R}$ fixed. From Eqs. (7.31), the volume $V_R$ of this ellipsoid is given by

$$\begin{aligned} V_R &= \text{const.}\left(\langle {S_x}^2\rangle_{\mathbf{R}}\langle {S_y}^2\rangle_{\mathbf{R}}\langle {S_z}^2\rangle_{\mathbf{R}}\right)^{1/2} \\ &= \text{const.}\langle R^2\rangle_0 R\left(1 + \langle R^2\rangle_0/3R^2\right)^{1/2}. \end{aligned} \qquad (15.32)$$

we then have

$$\begin{aligned} \rho_0(\mathbf{s}|\mathbf{R}) &= n/V_R \qquad \text{within the ellipsoid}, \\ &= 0 \qquad \text{outside the ellipsoid}, \end{aligned} \qquad (15.33)$$

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*Fixman's original result is erroneous and corrected in the paper of Fujita and Norisuye.[46]

and therefore obtain, from Eqs. (15.24) and (15.33),

$$\begin{aligned} V(\mathbf{R})/kT &= \beta n^2/2V_R \\ &= 3Cz(x^2 + \tfrac{1}{3})^{-1/2} . \end{aligned} \tag{15.34}$$

From Eqs. (15.15) and (15.34), we find

$$\alpha_R^{\,3} - \alpha_R = 2.053z \left(1 + \frac{1}{3\alpha_R^{\,2}}\right)^{-3/2} , \qquad \text{(KSR)} \tag{15.35}$$

where the choice of $C = (4/3)^{5/2} = 2.053$ has been taken to give the exact first-order perturbation theory. The KSR equation is seen to be of the *third-power type*. This arises from the fact that the KSR potential falls off as $R^{-1}$ instead of $R^{-3}$ as in the potential of the Flory type.

Koyama[49] assumed $\rho_0(\mathbf{s}|S)$ to be an ellipsoidal distribution, and arrived at an equation for $\alpha_S$ of the third-power type with the use of Eq. (8.52). As mentioned already, however, Eq. (8.52) is not necessarily correct. In addition, there is no reason why $\rho_0(\mathbf{s}|S)$ should not be spherically symmetric for the smoothed-density model; the ellipsoidal distribution is inconsistent with the factorization approximation to $P_0(\mathbf{S}_i, \mathbf{S}_j|S)$ as in Eq. (15.21). Thus the significance of this improvement seems obscure.

### 15a(ii). Theories with $P(0_{ij}|\mathbf{R})$ in the Fully Perturbed State

We approximate $P(0_{ij}|\mathbf{R})$ by its value at $\beta = \beta$ corresponding to the upper limit of integration in Eq. (15.10). We then have

$$\frac{V(\mathbf{R})}{kT} = \beta \sum_{i<j} P(0_{ij}|\mathbf{R}) , \tag{15.36}$$

where $P(0_{ij}|\mathbf{R})$ is to be evaluated in the fully perturbed state. This case was studied by Fujita.[42] For simplicity, we approximate $P(0_{ij}|\mathbf{R})$ in Eq. (15.36) by $P_0(0_{ij}|\mathbf{R})$ with $a\alpha_R$ in place of $a$. Such an approximation is referred to as the *uniform-expansion approximation.*

For the random-flight model, we have

$$V(\mathbf{R})/3kT = -(2\pi/3)^{1/2} zx\alpha_R^{\,-4} . \tag{15.37}$$

This equation can readily be obtained from Eq. (15.18) by replacing $z$ and $x$ by $z/\alpha_R^3$ and $x/\alpha_R$, respectively. If the coefficient $(2\pi/3)^{1/2}$ is again replaced by 4/3, we find the F,m equation,

$$\alpha_R^{\,5} - \alpha_R^{\,3} = \tfrac{4}{3} z .$$

Next we consider the smoothed-density model. In the case of the spherically symmetric distribution of segments, Eq. (15.28) remains unchanged, and we therefore recover the F,m equation. In the case of the ellipsoidal distribution of segments, Eq. (15.34) must be replaced by

$$\frac{V(\mathbf{R})}{3kT} = Cz\left(x^2 + \frac{\alpha_R^2}{3}\right)^{-1/2} \alpha_R^{-2}\,. \tag{15.38}$$

This potential also leads to the F,m equation.

The result is quite interesting; irrespective of the form of $P(0_{ij}|\mathbf{R})$, the present case leads exactly to the F,m equation of the fifth-power type. From the analysis described so far, we may expect that the BJ and F,m equations give the upper and lower bounds of $\alpha_R$ at a given $z$, respectively.

### 15a(iii). Theories with $P(0_{ij}|\mathbf{R})$ in the Intermediate Perturbed State

We still introduce the uniform-expansion approximation, but use, instead of $\alpha_R(z)$, a scale factor $\alpha_R(z')$ with $z'$ the excluded-volume parameter in the intermediate perturbed state ($0 \leq z' \leq z$). The potential can then be obtained, according to Eq. (15.10) or (15.13), by replacing $\alpha_R$ by $\alpha_R(z')$ in the potential used in Section 15a(ii) and integrating $z^{-1}V$ so obtained over $z'$ from 0 to $z$.

For the random-flight model, the equation determining $\alpha_R$ becomes

$$\alpha_R - \frac{1}{\alpha_R} = (2\pi/3)^{1/2} \int_0^z \frac{dz'}{\alpha_R^4(z')} \tag{15.39}$$

with $\alpha_R \equiv \alpha_R(z)$. Differentiation of both sides with respect to $z$ leads to

$$(2\pi/3)^{1/2} \frac{dz}{d\alpha_R} = \alpha_R^4 + \alpha_R^2\,. \tag{15.40}$$

Integration gives

$$\tfrac{1}{5}(\alpha_R^5 - 1) + \tfrac{1}{3}(\alpha_R^3 - 1) = \tfrac{4}{3}z\,, \qquad \text{(K)} \tag{15.41}$$

where the coefficient $(2\pi/3)^{1/2}$ has been replaced by 4/3 again. Equation (15.41) is due to Kurata.[50] The K equation predicts that at large $z$, $\alpha_R^5 = 6.67z$; it is of the fifth-power type. A similar calculation was also carried out by Alexandrowicz.[51]

In the case of the spherically symmetric distribution of segments, the result is the same as in Section 15a(ii), i.e., the F,m equation. In other words, the potential which is proportional to $R^{-3}$ or $S^{-3}$ leads to the F,m equation irrespective of the presence of a scale factor in the fully or intermediately perturbed state. In the case of the ellipsoidal distribution of segments, with the modification of Eq. (15.38) we have for the equation determining $\alpha_R = \alpha_R(z)$.

$$1 - \frac{1}{\alpha_R^2} = C \int_0^z \frac{dz'}{\alpha_R^2(z')\big[\alpha_R^2 + \frac{1}{3}\alpha_R^2(z')\big]^{3/2}}\,. \tag{15.42}$$

If we put $\alpha_R(z) = y$, $\alpha_R(z') = t$, and $dz/dy = \phi(y)$, Eq. (15.42) may be rewritten as

$$y^3 - y = C \int_1^y t^{-2} \left(1 + \frac{t^2}{3y^2}\right)^{-3/2} \phi(t)dt\,. \tag{15.43}$$

This is a linear integral equation of the Volterra type for $\phi$. Over the range of integration, Fujita, Okita, and Norisuye[42] represented the kernel to a very good approximation by the quadratic form, $0.9990 - 0.4771(t/y)^2 + 0.1304(t/y)^4$. Then Eq. (15.43) can be solved analytically, and the final result is

$$\begin{aligned}&\alpha_R^{\,5} - 0.4931\alpha_R^{\,3} - 0.2499\alpha_R^{\,-1.332} \sin(1.073 \ln \alpha_R)\\ &\quad - 0.5069\alpha_R^{\,-1.332} \cos(1.073 \ln \alpha_R) = 2.630z\,, \qquad \text{(FON)}\end{aligned} \tag{15.44}$$

where the coefficient $C$ has been put equal to 2.053, as before. The FON equation predicts that at large $z$, $\alpha_R^{\,5} = 2.63z$; it is also of the fifth-power type.

Finally, we describe briefly two other theories, which were not developed on the basis of Eq. (15.10), but may be considered to belong to the present category. Bueche[25] assumed for the potential

$$\frac{V(\mathbf{R})}{kT} = \beta \sum_{i<j} P^*(0_{ij}, i, n-j|\mathbf{R})\,, \tag{15.45}$$

where $P^*(0_{ij}, i, n-j|\mathbf{R})$ has the same meaning as $P_0(0_{ij}|\mathbf{R})$ except that the two parts of the chain between the 0th and $i$th segments and between the $j$th and $n$th segments are in the fully perturbed state. The justification of this approximation given by Bueche is the following: the main contribution to the potential comes from $P(0_{ij}|\mathbf{R})$ with small $(j-i)$, and then the middle part of the chain (between $i$ and $j$) may be regarded as an unperturbed chain. With $P^*$ evaluated for the random-flight model with a scale factor, we obtain

$$\alpha_R^{\,4} - \alpha_R^{\,2} = \frac{48}{69} z \left(1 + \frac{2}{3\alpha_R^{\,2}} + \frac{1}{4\alpha_R^{\,4}}\right). \qquad \text{(B)} \tag{15.46}$$

The B equation is of the fourth-power type. On the other hand, Alexandrowicz[52] derived the approximate expression for the potential,

$$\frac{V(\mathbf{R})}{kT} = \beta \sum_{i<j} P^*(0_{ij}, n-i|\mathbf{R})\,. \tag{15.47}$$

For this $P^*$, the part of the chain between the $i$th and $n$th segments is in the fully perturbed state. For the random-flight model, the final result was obtained numerically, though the asymptotic solution could be obtained analytically. It predicts that $\nu = 4.24$ in Eq. (15.1).

## 15b. The Differential-Equation Approach

This approach was attempted first by Fixman,[26, 47] and further developments were made by Ptitsyn[53] and by Yamakawa and Tanaka.[36]

## 15b(i). The Fixman Theory

Differentiation of Eq. (15.2) with (15.3) and (15.4) with respect to $\beta$ leads to

$$\frac{\partial P(\mathbf{R})}{\partial \beta} = \sum_{i<j} \big[P(\mathbf{R})P(0_{ij}) - P(\mathbf{R}, 0_{ij})\big] . \tag{15.48}$$

Multiplying both sides by $R^2 d\mathbf{R}$ and integrating, we have

$$\frac{\partial \langle R^2 \rangle}{\partial \beta} = \sum_{i<j} \int R^2 \big[P(\mathbf{R})P(0_{ij}) - P(\mathbf{R}, 0_{ij})\big] d\mathbf{R} . \tag{15.49}$$

This equation is formally exact. We now introduce the uniform-expansion approximation; that is, we approximate the $P$ by the $P_0$ with $a\alpha$ in place of $a$, where we suppress temporarily the subscript $R$ on $\alpha$. Recalling that the quantity in square brackets in Eq. (15.49) is equal to $Q_0(\mathbf{R}, 0_{ij})$ of (14.10) with the scale factor, we readily obtain

$$\frac{\partial \langle R^2 \rangle}{\partial \beta} = C_1 (3/2\pi a^2)^{3/2} n^{1/2} (na^2) \alpha^{-1} , \tag{15.50}$$

or

$$\frac{d\alpha^2}{dz} = \frac{C_1}{\alpha} , \tag{15.51}$$

where $C_1$ is given by Eq. (14.19). Integration of Eq. (15.51) leads to

$$\alpha^3 = 1 + \tfrac{3}{2} C_1 z . \tag{15.52}$$

The differential equation (15.51) may be considered to hold for both $\alpha_R$ and $\alpha_S$ if the first coefficients in the perturbation theories are used for $C_1$. Thus we have

$$\alpha_R{}^3 = 1 + 2z , \qquad (\mathrm{F}_1) \tag{15.53}$$

$$\alpha_S{}^3 = 1 + 1.914z . \qquad (\mathrm{F}_1) \tag{15.54}$$

The $\mathrm{F}_1$ equations are of the third-power type; the subscript 1 is used to distinguish the present theory from Fixman's second theory ($\mathrm{F}_2$) using the boson representation.

## 15b(ii). The Ptitsyn Theory

Equation (15.52) may be improved if we take into account the fact that the scale factor $\alpha$ entering into the right-hand side of Eq. (15.49) through the replacement of $a$ by $a\alpha$ in fact is not equal to $\langle R^2 \rangle^{1/2} / \langle R^2 \rangle_0^{1/2}$ because of the non-Gaussian nature of the chain. Designating this scale factor by $\alpha^*$, we have, instead of Eq. (15.51),

$$\frac{d\alpha^2}{dz} = \frac{C_1}{\alpha^*} . \tag{15.55}$$

From the perturbation theory, $(\alpha^*)^2$ may be expanded as

$$(\alpha^*)^2 = 1 + (4C_2/C_1)z - \cdots\,. \tag{15.56}$$

We therefore have

$$\left[\frac{d(\alpha^*)^2}{dz}\right]_{z=0} = \frac{4C_2}{C_1}\,. \tag{15.57}$$

We now assume that $\alpha^*$ satisfies a differential equation of the same form as Eq. (15.51); that is,

$$\frac{d(\alpha^*)^2}{dz} = \frac{4C_2}{C_1\alpha^*}\,, \tag{15.58}$$

where we have used Eq. (15.57). The solution of Eq. (15.58) is

$$(\alpha^*)^3 = 1 + (6C_2/C_1)z\,. \tag{15.59}$$

Substitution of Eq. (15.59) into Eq. (15.55) and integration leads to

$$\alpha^2 = \frac{{C_1}^2}{4C_2}\left[\frac{4C_2}{{C_1}^2} - 1 + \left(1 + \frac{6C_2}{C_1}z\right)^{2/3}\right]. \tag{15.60}$$

Using the exact values for $C_1$ and $C_2$ of (14.19) and (14.25), as before, we obtain the results,

$$4.67\alpha_R^2 = 3.67 + (1 + 9.34z)^{2/3}\,, \qquad \text{(P)} \tag{15.61}$$

$$5.12\alpha_S^2 = 4.12 + (1 + 9.79z)^{2/3}\,. \qquad \text{(P)} \tag{15.62}$$

Although the P equation is still of the third-power type, it predicts that at large $z$, $\alpha_R^3 = 0.93z$, while the $\mathrm{F}_1$ equation predicts that at large $z$, $\alpha_R^3 = 2z$. There is a similar relation between the $\mathrm{F}_1$ and P equations for $\alpha_S$.

## 15b(iii). The Yamakawa–Tanaka Theory

As we have seen in the preceding sections, the Fixman theory deals with a differential equation of the first order for $\alpha$ including the first expansion coefficient $C_1$, while the Ptitsyn theory deals with a differential equation of the second order including the coefficients $C_1$ and $C_2$. This suggests a derivation of differential equations of higher orders. Necessarily, the derived equations form a hierarchy, and the present idea consists in obtaining an approximate solution for $\alpha$ by truncating the hierarchy at some step including at least the first three expansion coefficients.

Now we differentiate further Eq. (15.49) with respect to $\beta$ to obtain

$$\frac{\partial^2\langle R^2\rangle}{\partial\beta^2} = \sum_{i<j}\int R^2\left[\frac{\partial P(\mathbf{R})}{\partial\beta}P(0_{ij}) + P(\mathbf{R})\frac{\partial P(0_{ij})}{\partial\beta} - \frac{\partial P(\mathbf{R},0_{ij})}{\partial\beta}\right]d\mathbf{R}\,. \tag{15.63}$$

Differentiating the formal expressions for $P(\mathbf{R}_{ij})$ and $P(\mathbf{R}, \mathbf{R}_{ij})$ with respect to $\beta$, we can obtain the equations, similar to Eq. (15.48),

$$\frac{\partial P(0_{ij})}{\partial \beta} = \sum_{k<l} \big[ P(0_{ij}) P(0_{kl}) - P(0_{ij}, 0_{kl}) \big] \,, \tag{15.64}$$

$$\frac{\partial P(\mathbf{R}, 0_{ij})}{\partial \beta} = \sum_{k<l} \big[ P(\mathbf{R}, 0_{ij}) P(0_{kl}) - P(\mathbf{R}, 0_{ij}, 0_{kl}) \big] \,. \tag{15.65}$$

Substitution of Eqs. (15.48),(15.64), and (15.65) into Eq. (15.63) leads to

$$\frac{\partial^2 \langle R^2 \rangle}{\partial \beta^2} = - \sum_{i<j} \sum_{k<l} \int R^2 Q(\mathbf{R}, 0_{ij}, 0_{kl}) d\mathbf{R} \,, \tag{15.66}$$

where $Q(\mathbf{R}, 0_{ij}, 0_{kl})$ is given by $Q_0(\mathbf{R}, 0_{ij}, 0_{kl})$ of (14.11) evaluated in the perturbed state. Similarly, we can obtain for the third derivative

$$\frac{\partial^3 \langle R^2 \rangle}{\partial \beta^3} = \sum_{i<j} \sum_{k<l} \sum_{s<t} \int R^2 Q(\mathbf{R}, 0_{ij}, 0_{kl}, 0_{st}) d\mathbf{R} \,. \tag{15.67}$$

Equations (15.49), (15.66), (15.67), and so on may then be rewritten as

$$\begin{aligned}
\frac{\partial \alpha^2}{\partial \beta} &= \alpha^2 \sum_{i<j} \left[ P(0_{ij}) - \langle R^2 \rangle^{-1} \int R^2 P(\mathbf{R}, 0_{ij}) d\mathbf{R} \right] \,, \\
\frac{\partial^2 \alpha^2}{\partial \beta^2} &= -\alpha^2 \sum_{i<j} \sum_{k<l} \Bigg\{ P(0_{ij}, 0_{kl}) - 2P(0_{ij}) P(0_{kl}) - \langle R^2 \rangle^{-1} \int R^2 \\
&\qquad \times \big[ P(\mathbf{R}, 0_{ij}, 0_{kl}) - P(\mathbf{R}, 0_{ij}) P(0_{kl}) - P(\mathbf{R}, 0_{kl}) P(0_{ij}) \big] d\mathbf{R} \Bigg\} \,, \\
\frac{\partial^k \alpha^2}{\partial \beta^k} &= (-1)^{k+1} \alpha^2 \sum_{i<j} \cdots \sum_{s<t} \big[ P(0_{ij}, \ldots, 0_{st}) + \cdots \big] \,.
\end{aligned} \tag{15.68}$$

Recalling that removal of the lower restrictions on the summations in the $\beta^k$ term of Eq. (14.9) introduces the factor $k!$, we obtain, from Eqs. (14.9) (with $\mathbf{R}_{ij} = \mathbf{R}$) and (15.68),

$$\left[ \frac{\partial^k \alpha^2}{\partial z^k} \right]_{z=0} = (-1)^{k+1} k! C_k \,, \tag{15.69}$$

where $C_k$ is the coefficient of $z^k$ in the expansion of $\alpha^2$, $\alpha^2 = \sum (-1)^{k+1} C_k z^k$.

If the sum in Eq. (15.68) is evaluated in the unperturbed state, followed by the replacement of $a$ by $a\bar{\alpha}_k$, we have

$$\frac{d^k \alpha^2}{dz^k} = (-1)^{k+1} k! C_k \frac{\alpha^2}{\bar{\alpha}_k^{3k}} \qquad (k = 1, 2, \ldots) \,. \tag{15.70}$$

Equations (15.70) may be considered to be defining equations for the new scale factors $\bar{\alpha}_k$. Equation (15.70) can be obtained more conveniently following Fixman's dimensional argument in deriving Eq.

(15.51).[47] The derivative $\partial^k \langle R^2 \rangle / \partial \beta^k$ has the dimension of (length)$^2$/(length)$^{3k}$, and must therefore be proportional to $(a\alpha)^2/(a\bar{\alpha}_k)^{3k}$ if the scale factors to be introduced in the denominator and numerator are distinguished from each other. On the other hand, $\partial^k \langle R^2 \rangle / \partial \beta^k$ is proportional to $a^2 \partial^k \alpha^2 / \partial \beta^k$, and $n$ must enter in such a way as to make $\alpha$ and $\bar{\alpha}_k$ functions of $z$. We then have $d^k \alpha^2 / dz^k \propto \alpha^2 / \bar{\alpha}_k{}^{3k}$, the proportionality constant being determined from Eq. (15.69). We now define new scale factors $\alpha_k$ by

$$\bar{\alpha}_k = \left( \prod_{i=1}^{k} \alpha_i \right)^{1/k} \tag{15.71}$$

(with $\bar{\alpha}_1 = \alpha_1$), and eliminate $\alpha^2$ from Eqs. (15.70) with (15.71) to obtain

$$\frac{d\alpha_k{}^3}{dz} = \frac{(k+1)C_{k+1}}{C_k} \frac{\alpha_k{}^3}{\alpha_{k+1}{}^3} - \frac{kC_k}{C_{k-1}} \quad (k = 1, 2, \ldots) \tag{15.72}$$

with $C_0 \equiv -1$. Equation (15.72) may be considered to form a hierarchy of differential equations for $\alpha_k$; the solution for $\alpha_1$ requires the solution for $\alpha_2$, the solution for $\alpha_2$ requires the solution for $\alpha_3$, and so on. If the hierarchy is truncated by some approximation, we can find an approximate solution for $\alpha_1$ and then obtain $\alpha_2$ from the $k = 1$ equation of (15.70),

$$\frac{d\alpha^2}{dz} = C_1 \frac{\alpha^2}{\alpha_1{}^3} \, . \tag{15.73}$$

We note that the Fixman and Ptitsyn equations can be obtained from the different hierarchy of differential equations,

$$\frac{d^k \alpha^2}{dz^k} = (-1)^{k+1} k! C_k \frac{1}{(\alpha_k{}^*)^{3k-2}} \, , \tag{15.74}$$

by truncating it with $\alpha = \alpha_1{}^*$ and $\alpha_1{}^* = \alpha_2{}^*$, respectively. However, when it is truncated with $\alpha_2{}^* = \alpha_3{}^*$ and the exact values for $C_1$ to $C_3$ are used, there is no physically reasonable solution for $\alpha$ in the sense that $\alpha$ must be a monotonically increasing function of $z$.

Before proceeding to solve Eq. (15.72), we examine the behavior of $\alpha_k$. First, $\alpha_k$ must be unity at $z = 0$, and at small $z$, $\alpha_k{}^3$ may be expanded, from Eq. (15.72), as follows,

$$\alpha_k{}^3 = 1 + \left[ \frac{(k+1)C_{k+1}}{C_k} - \frac{kC_k}{C_{k-1}} \right] z - \cdots \, . \tag{15.75}$$

Inserting the values of (14.19) for $C_1$ to $C_3$, we have

$$\begin{aligned} \alpha_1{}^3 &= 1 + 4.45z - \cdots \, , \\ \alpha_2{}^3 &= 1 + 6.23z - \cdots \, . \end{aligned} \tag{15.76}$$

Since the corresponding expansion for the original $\alpha (= \alpha_R)$ is $\alpha^3 = 1 + 2z - \cdots$, there must exist the inequalities, $\alpha < \alpha_1 < \alpha_2$, provided $z$

is positive and small. Next, in order to examine the behavior of $\alpha_k$ at very large $z$, we assume the asymptotic forms $\alpha^{\nu} = \gamma z$ and ${\alpha_k}^{\nu_k} = \gamma_k z$. Substitution of these relations into Eqs. (15.72) and (15.73) leads to

$$\nu = \frac{2{\gamma_1}^{3/\nu_1}}{C_1} z^{3/\nu_1 - 1} \,, \tag{15.77}$$

$$\frac{3{\gamma_k}^{3/\nu_k}}{\nu_k} z^{3/\nu_k - 1} = \frac{(k+1)C_{k+1}}{C_k} \frac{{\gamma_k}^{3/\nu_k}}{{\gamma_{k+1}}^{3/\nu_{k+1}}} z^{3(1/\nu_k - 1/\nu_{k+1})} - \frac{kC_k}{C_{k-1}} \,. \tag{15.78}$$

Since Eq. (15.77) must hold for all large values of $z$, there must exist the relations,

$$\nu = \frac{2\gamma_1}{C_1} \,, \qquad \nu_1 = 3 \,. \tag{15.79}$$

By the same argument, substitution of $\nu_1 = 3$ into the $k = 1$ equation of (15.78) leads to $\nu_2 = 3$, substitution of $\nu_2 = 3$ into the $k = 2$ equation to $\nu_3 = 3$, and so on; and we therefore have $\nu_k = 3$ for all $k$; that is,

$$\lim_{z \to \infty} {\alpha_k}^3 = \gamma_k z \qquad (\text{for all } k) \,. \tag{15.80}$$

In other words, the equations for $\alpha_k$ must be of the third-power type. Equation (15.78) may then be reduced to

$$\frac{(k+1)C_{k+1}}{C_k \gamma_{k+1}} - \frac{kC_k}{C_{k-1}\gamma_k} = 1 \,. \tag{15.81}$$

This is a difference equation for $\gamma_k$, and the solution must be of the form,

$$\gamma_k = \frac{kC_k}{(k - 1 - \sigma)C_{k-1}} \,, \tag{15.82}$$

where $\sigma$ is an unknown positive constant independent of $k$. From the equation for $\gamma_1$ and the first of Eqs. (15.79), we have

$$\nu = \frac{2}{\sigma} \,. \tag{15.83}$$

Now, it seems reasonable to assume that $3 \leq \nu \leq 5$, considering the predictions of the various approximate theories already described. Then, from Eqs. (15.82) and (15.83) and the values of (14.19) for $C_1$ to $C_3$, we have $\gamma_1 = 2$, $\gamma_2 = 9.34$, and $\gamma_3 = 7.00$ if $\nu = 3$, and $\gamma_1 = 3.33$, $\gamma_2 = 5.19$, and $\gamma_3 = 5.84$ if $\nu = 5$. From these values and the analysis above, we expect that $\alpha < \alpha_1 < \alpha_2$ at an arbitrary positive value of $z$. However, the values of $\gamma_1$ to $\gamma_3$ suggest that $\alpha_k$ levels off at large $k$. This conclusion is reached as follows: qualitatively, $\alpha_k$ will be related to the expansion factor associated with the conditional probability that when there are $(k-1)$ intramolecular contacts between segments, an additional contact occurs; and the expansion factor will increase with increasing number of contacts because the average segment density is increased, but the rate of increase in $\alpha_k$ with $k$ will decrease because

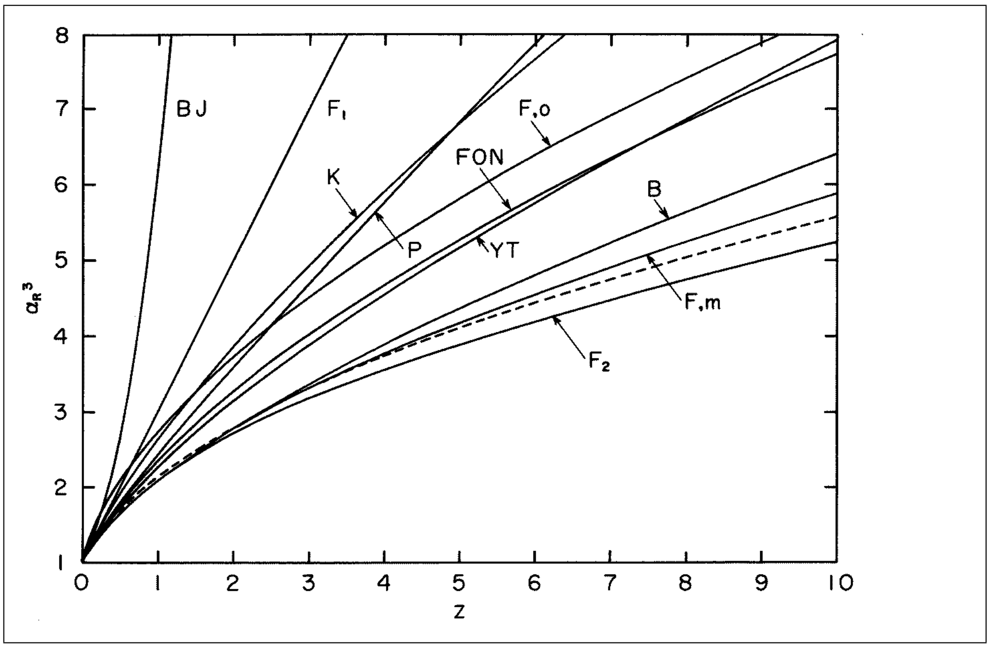

**Fig. III.5.** Theoretical values of $\alpha_R^3$ calculated from various approximate theories. Curve BJ: the Bueche–James theory, Eq. (15.19). Curve $F_1$: the Fixman theory, Eq. (15.53). Curve P: the Ptitsyn theory, Eq. (15.61). Curve K: the Kurata theory, Eq. (15.41). Curve F,o: the original Flory theory, Eq. (14.39). Curve FON: the Fujita–Okita–Norisuye theory, Eq. (15.44). Curve YT: the Yamakawa–Tanaka theory, Eq. (15.94). Curve B: the Bueche theory, Eq. (15.46). Curve F,m: the modified Flory theory, Eq. (14.40). Curve $F_2$: the boson representation theory of Fixman. Broken curve: Eq. (15.96).

the increase in the number of contacts tends to suppress the expansions of subchains between contact segments, which become short with increasing number of contacts. Thus we impose the following condition on $\alpha_k$,

$$\alpha_k = \alpha_{k+1} \qquad \text{(at large } k\text{)}\,. \tag{15.84}$$

We now solve Eq. (15.72) under the conditions of (15.80) and (15.84). Equation (15.84) requires that $\alpha_k$ be the same for all values of $k$ greater than some boundary value. We first determine that value of $k$. Putting ${\alpha_k}^3 = x_k$ and $kC_k/C_{k-1} = a_k$, we have, from Eq. (15.72) with (15.84),

$$\frac{dx_k}{dz} = a_{k+1} - a_k \equiv K_k \tag{15.85}$$

for some large value of $k$. It is evident that $a_1 = -C_1 < 0$, $a_k > 0$ (for $k \geq 2$), and $K_k > 0$ (for $k \geq 1$). Integration of Eq. (15.85) leads to

$$x_k = 1 + K_k z\,. \tag{15.86}$$

**TABLE III.2.** THE COEFFICIENTS $C_1$ TO $C_3$ IN THE EXPANSION OF $\alpha_R^2$ FROM VARIOUS APPROXIMATE THEORIES

| | $C_1$ | $C_2$ | $C_3$ |
|---|---|---|---|
| Exact | 1.33 | 2.08 | 6.46 |
| BJ | 1.33 | −0.89 | 0.30 |
| $F_1$ | 1.33 | 0.44 | 0.40 |
| K | 1.33 | 0.89 | 1.09 |
| P | 1.33 | 2.08 | 8.61 |
| FON | 1.33 | 1.50 | 2.96 |
| YT | 1.33 | 2.08 | 6.46 |
| B | 1.33 | 2.86 | 11.70 |
| F,m | 1.33 | 2.67 | 9.78 |
| Eq. (15.96) | 1.33 | 2.08 | 5.24 |

Substitution of Eq. (15.86) into Eq. (15.72) leads to

$$(1+K_k z)\frac{dx_{k-1}}{dz} - a_k x_{k-1} = -a_{k-1}(1+K_k z)\,. \tag{15.87}$$

This is an Euler differential equation. If $K_k \neq a_k$, the solution for $x_{k-1}$ which satisfies the condition of (15.80) is obtained as

$$x_{k-1} = \left(1+\frac{a_{k-1}}{K_k - a_k}\right)(1+K_k z)^{a_k/K_k} - \frac{a_{k-1}}{K_k - a_k}(1+K_k z)\,. \tag{15.88}$$

In Eq. (15.88) $K_k$ must be smaller than $a_k$ because if $K_k > a_k$, $x_{k-1}$ becomes $-\infty$ as $z$ is increased to $\infty$. The condition of (15.80) then requires that the first term on the right-hand side of Eq. (15.88) be identically equal to zero so that there must hold the relation, $a_k - a_{k-1} = K_k$, i.e., $K_{k-1} = K_k$. We therefore have $x_{k-1} = 1 + K_{k-1}z$ with $K_{k-1} = K_k$. Thus, repeating the above procedure, we arrive at

$$x_k = 1 + Kz \qquad (\text{for } k \geq 2) \tag{15.89}$$

with

$$K = K_2 = a_3 - a_2\,. \tag{15.90}$$

After substitution of Eq. (15.89) for $x_2$ in the $k = 1$ equation of (15.72), integration leads to

$$\alpha_1{}^3 = (1-A)(1+Kz)^{1-\mu} + A(1+Kz) \tag{15.91}$$

with

$$A = \frac{C_1}{K - a_2}\,, \quad \mu = \frac{K - a_2}{K}\,. \tag{15.92}$$

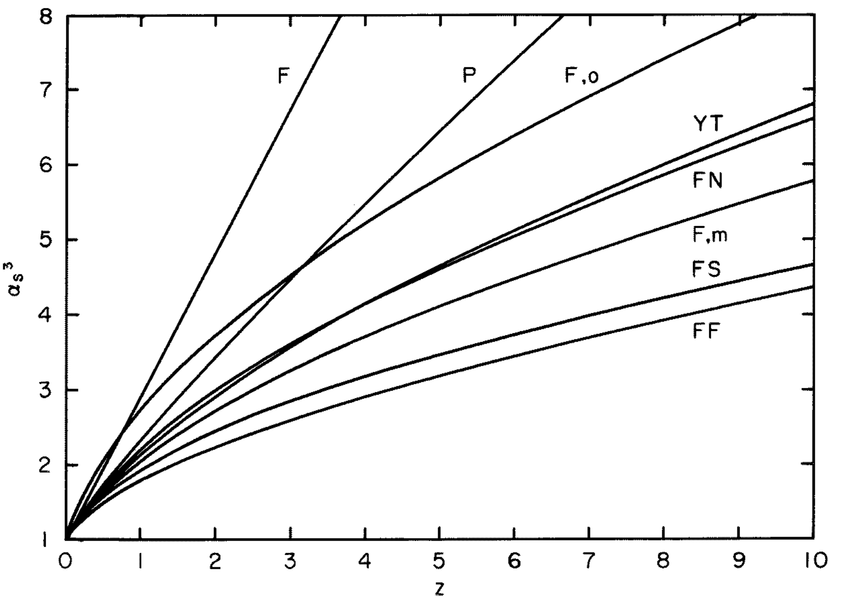

**Fig. III.6.** Theoretical values of $\alpha_S^3$ calculated from various approximate theories. Curve F: the Fixman theory, Eq. (15.54). Curve P: the Ptitsyn theory, Eq. (15.62). Curve F,o: the original Flory theory, Eq. (14.39). Curve YT: the Yamakawa–Tanaka theory, Eq. (15.95). Curve FN: the Fujita–Norisuye theory. Curve F,m: the modified Flory theory, Eq. (14.41). Curve FS: the boson representation theory of Fixman and Stidham. Curve FF: the Flory–Fisk theory, Eq. (15.30).

Substituting Eq. (15.91) for $\alpha_1{}^3$ in Eq. (15.73) and integrating, we obtain

$$\alpha^2 = 1 - A + A(1 + Kz)^{\mu} . \tag{15.93}$$

This solution gives the sequence $\alpha < \alpha_1 < \alpha_2 = \alpha_3 = \cdots$. If we use the values of (14.19) for $C_1$ to $C_3$, the equation for $\alpha_R$ is obtained from Eq. (15.93). From Eqs. (14.19) and (14.25), the coefficient $C_2{}'$ in the expansion of $\alpha_S^2$ is seen to be very close to $C_2$ for $\alpha_R^2$, and we therefore assume that $C_3{}'$ is nearly equal to $C_3$. With these $C_1{}'$ to $C_3{}'$ instead of $C_1$ to $C_3$ ($C_3{}' = C_3$), the equation for $\alpha_S$ is also obtained from Eq. (15.93). The results are

$$\alpha_R^2 = 0.572 + 0.428(1 + 6.23z)^{1/2} , \quad \text{(YT)} \tag{15.94}$$

$$\alpha_S^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} . \quad \text{(YT)} \tag{15.95}$$

If our hierarchy is truncated with $\alpha = \alpha_1$, the Fixman equation is obtained, while if it is truncated with $\alpha_1 = \alpha_2$, there is obtained for $\alpha_R$

$$\alpha_R^{6.67} = 1 + 4.45z \qquad (\text{for } \alpha_1 = \alpha_2) . \tag{15.96}$$

We note that the Fixman equation can also be obtained from Eq. (15.93) with $C_1 = C_1$, $C_2 = {C_1}^2/4$, and $C_3 = {C_1}^3/6$, and the Ptitsyn equation from Eq. (15.93) with $C_1 = C_1$, $C_2 = C_2$, and $C_3 = 8{C_2}^2/3C_1$.

Finally, we compare numerical results obtained from the various approximate theories. In Fig. III.5 are plotted the values of $\alpha_R^{\ 3}$ predicted by the BJ theory, Eq. (15.19), the $\mathrm{F}_1$ theory, Eq. (15.53), the P theory, Eq. (15.61), the K theory, Eq. (15.41), the FON theory, Eq. (15.44), the YT theory, Eq. (15.94), the B theory, Eq. (15.46), and the F,m theory, Eq. (14.40); the broken curve represents the values from Eq. (15.96). At small $z$, all these theories give at least the exact first-order perturbation theory. In the figure are also shown the values predicted by the F,o theory, Eq. (14.39), and the boson representation theory of Fixman ($\mathrm{F}_2$); the $\mathrm{F}_2$ theory gives only numerical results (see Chapter VI). The values predicted by the KSR theory, Eq. (15.35), and by the Alexandrowicz theory[52] are close to those predicted by the $\mathrm{F}_1$ theory over the range of $\alpha_R^{\ 3}$ displayed in the figure. In Table III.2 are given the values for the first three coefficients in the expansion of $\alpha_R^{\ 2}$ from various approximate theories. The values of $C_2$ and $C_3$ from the BJ, $\mathrm{F}_1$, and K theories are seen to be too small compared with the exact values. It is of interest to observe that the values of $C_3$ from the P theory and Eq. (15.96) bracket the exact value, their values of $C_1$ and $C_2$ being exact. In addition, the values of $\alpha_R^{\ 3}$ predicted by the B, F,m, and $\mathrm{F}_2$ theories and Eq. (15.96) are very close to one another over the range of $\alpha_R^{\ 3}$ of ordinary interest, as seen from Fig. III.5. We may therefore expect that at small $z$ the P theory gives the upper bound of $\alpha_R$, and Eq. (15.96) and the B,F,m, and $\mathrm{F}_2$ theories give the lower bound.

In Fig. III.6 are plotted the values of $\alpha_S^{\ 3}$ predicted by the F,o theory, Eq. (14.39), the F,m theory, Eq. (14.41), the F theory, Eq. (15.54), the P theory, Eq. (15.62), the FF theory, Eq. (15.30), and the YT theory, Eq. (15.95). In the figure are also shown the values predicted by the boson representation theory of Fixman and Stidham (FS) and the Fujita–Norisuye theory (FN), both giving only numerical results. It is seen that the values of $\alpha_S^{\ 3}$ predicted by the FN theory are very close to those predicted by the YT theory. It must now be recalled that an approximate expression for $P_0(S)$ is used in the FF theory, whereas the exact expression for $P_0(S)$ is used in the FN theory. Thus the FF theory and also the FS theory seem to underestimate $\alpha_S$. Curves F,o, F,m, F, P, and YT correspond to the curves indicated by the same symbols in Fig. III.5, respectively.

## 16. Asymptotic Solution at Large z

In most of the approximate theories described in Section 15a, adjustable constants were chosen to force agreement with the exact first-order perturbation theory, and in the differential-equation approach, the theory was still developed on the basis of the first few expansion coefficients. It is therefore not possible to deduce the asymptotic behavior of $\alpha$ at extremely large $z$ from these approximate closed expressions. To proceed further, we must resort to a different approach. The result will serve to select several good approximate expressions for $\alpha$ from those derived in the previous section.

We first describe the self-consistent-field approach to the solution for $\alpha_R$. The following formulation of the self-consistent potential is due to Reiss.[54] Suppose the 0th segment to be fixed at the origin of a coordinate system, as before. Then the instantaneous distribution for the chain is given by Eq. (13.4); that is,

$$P\bigl(\{\mathbf{R}_n\}\bigr) = Z^{-1} P_0\bigl(\{\mathbf{R}_n\}\bigr) \exp\left(-\frac{W}{kT}\right) , \tag{16.1}$$

where $W$ is given by the sum of all pair potentials between segments, as in Eq. (10.6). We now wish to express $P$ in order to decouple the many-body problem;

$$P\bigl(\{\mathbf{R}_n\}\bigr) = Z^{-1} P_0\bigl(\{\mathbf{R}_n\}\bigr) \prod_{j=1}^{n} \exp\left[-\frac{\phi_j(\mathbf{R}_j)}{kT}\right] \tag{16.2}$$

with

$$Z = \int P_0\bigl(\{\mathbf{R}_n\}\bigr) \left\{\prod_{j=1}^{n} \exp\left[-\frac{\phi_j(\mathbf{R}_j)}{kT}\right]\right\} d\{\mathbf{R}_n\} . \tag{16.3}$$

The form of $P$ given by Eq. (16.2) will prove to be especially convenient in deriving an integral equation or a diffusion equation for the distribution function. In Eq. (16.2), the part of the distribution dealing with long-range interactions is approximated by a product of single-segment distributions. The process is quite analogous to the Hartree–Fock self-consistent-field method of determining wave functions in many-particle quantum-mechanical systems. Our problem is to determine the form of the function $\phi_j$, which is a self-consistent field, as will be seen later. This can be achieved by applying the variation principle. In the present case, the variation principle consists of finding an extremal of configurational free energy rather than of the energy as in quantum mechanics.

For the classical case of canonical ensemble under consideration, the configurational Helmholtz free energy $A$ of the system may be written in the form,

$$A = \int U P \, d\{\mathbf{R}_n\} + kT \int P \ln P \, d\{\mathbf{R}_n\} , \tag{16.4}$$

where $U$ is the *exact* configurational energy, while $P$ is constrained to be given by Eq. (16.2) with (16.3), differing from Eq. (16.1). The potential $U$ is composed of two parts, as in Eq. (3.2): one is the formal potential $U_0$ representing the connection of segments, and the other is $W$. These may be written as

$$U_0 = -kT \ln P_0\bigl(\{\mathbf{R}_n\}\bigr) , \tag{16.5}$$

$$W = \frac{1}{2} \sum_{i} \sum_{\substack{j \\ i \neq j}} w_{ij} \tag{16.6}$$

with $w_{ij} \equiv w(\mathbf{R}_{ij})$ the pair potential between the $i$th and $j$th segments. Equation (16.4) may then be reduced to

$$A = \frac{1}{2} \sum_{i \neq j} \sum \int w_{ij} P \, d\{\mathbf{R}_n\} - \sum_{j} \int \phi_j P \, d\{\mathbf{R}_n\} - kT \ln Z \int P \, d\{\mathbf{R}_n\} \, . \tag{16.7}$$

Regarding $A$ as a functional of $\phi_j$, we may determine $\phi_j$ from the extremalization condition that the variation $\delta A$ due to variations $\delta \phi_l$ is zero at the extremal point, $\delta \phi_l$ being taken subject to the normalization condition of $P$; that is,

$$\delta A = 0 \tag{16.8}$$

subject to the constraint,

$$\int P \, d\{\mathbf{R}_n\} = 1 \, . \tag{16.9}$$

After tedious algebraic calculations, we obtain, from Eqs. (16.7) to (16.9),

$$kT \delta A = \sum_{l} \int \delta \phi_l F_l \, d\mathbf{R}_l = 0 \, , \tag{16.10}$$

where

$$\begin{aligned} F_l = & \left[ \phi_l P(\mathbf{R}_l) - \sum_{j \neq l} \int w_{lj} P(\mathbf{R}_l, \mathbf{R}_j) d\mathbf{R}_j \right] \\ & - P(\mathbf{R}_l) \int \left[ \phi_l P(\mathbf{R}_l) - \sum_{j \neq l} \int w_{lj} P(\mathbf{R}_l, \mathbf{R}_j) d\mathbf{R}_j \right] d\mathbf{R}_l \\ & + \sum_{i \neq l} \int \Bigg\{ \phi_i \left[ P(\mathbf{R}_i, \mathbf{R}_l) - P(\mathbf{R}_i) P(\mathbf{R}_l) \right] \\ & - \frac{1}{2} \sum_{\substack{j \neq i \\ \neq l}} \int w_{ij} \left[ P(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_l) - P(\mathbf{R}_i, \mathbf{R}_j) P(\mathbf{R}_l) \right] d\mathbf{R}_j \Bigg\} d\mathbf{R}_i \, . \end{aligned} \tag{16.11}$$

Equation (16.10) must now hold for arbitrary variations $\delta \phi_l$, and therefore $F_l$ must be identically equal to zero. At this stage, we introduce the approximations $P(\mathbf{R}_i, \mathbf{R}_l) = P(\mathbf{R}_i) P(\mathbf{R}_l)$ and $P(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_l) = P(\mathbf{R}_i, \mathbf{R}_j) P(\mathbf{R}_l)$, but do not factor $P(\mathbf{R}_i, \mathbf{R}_j)$ appearing in the products $w_{ij} P(\mathbf{R}_i, \mathbf{R}_j)$, the latter having significant influence on the averaging of $w_{ij}$. Then the third term in $F_l$ vanishes, and the first and second terms vanish if we set

$$\phi_l P(\mathbf{R}_l) - \sum_{j \neq l} \int w_{lj} P(\mathbf{R}_l, \mathbf{R}_j) d\mathbf{R}_j = 0 \, ,$$

or

$$\phi_j(\mathbf{R}_j) = \sum_{\substack{i=1 \\ \neq j}}^{n} \int w(\mathbf{R}_{ij}) P(\mathbf{R}_{ij}|\mathbf{R}_j) d\mathbf{R}_i \,. \tag{16.12}$$

This is the desired approximate solution for $\phi_j$. The function $\phi_j$ is seen to be given by a sum of the physically exact pair potentials over all pairs of segments including the $j$th, averaged over the desired distribution, and therefore it represents a self-consistent potential. We note that Edwards[55] also introduced a self-consistent field. As pointed out by Reiss,[54] however, Edwards' field is equivalent to assuming $P(\mathbf{R}_{ij}|\mathbf{R}_j) = P(\mathbf{R}_i)$ in Eq. (16.12). Further, we note that although Reiss' equation [Eq. (25) of Ref.54] determining $\phi_j$ is incorrect, its incorrect solution led accidentally to Eq. (16.12). Therefore, any attempt[56] to obtain a complete solution of Reiss' equation is meaningless.

Our problem is now to derive an integral equation for the distribution function, and to solve it after transformation into a differential equation. This was done by Reiss,[54] but his integral equation is incorrect, since an important factor was dropped. Further developments are due to Yamakawa.[57] Expressing $P_0\big(\{\mathbf{R}_n\}\big)$ by the product of the bond probabilities, as before, we define functions $\hat{P}(\mathbf{R}_j)$ and $G(\mathbf{R}_{j+1})$ by

$$\hat{P}(\mathbf{R}_j) = \int \prod_{i=1}^{j} \big\{\tau(\mathbf{r}_i)\exp(-\phi_i/kT)d\mathbf{r}_i\big\}/d\mathbf{R}_j \,, \tag{16.13}$$

$$G(\mathbf{R}_{j+1}) = \int \prod_{i=j+2}^{n} \big\{\tau(\mathbf{r}_i)\exp(-\phi_i/kT)d\mathbf{r}_i\big\}/d\mathbf{R}_{j+1} \,. \tag{16.14}$$

With these relations, the joint probability $P(\mathbf{R}_j, \mathbf{R}_{j+1})$ may be expressed, from Eq. (16.2), as

$$P(\mathbf{R}_j, \mathbf{R}_{j+1}) = Z^{-1}\hat{P}(\mathbf{R}_j)G(\mathbf{R}_{j+1})\tau(\mathbf{r}_{j+1})\exp\left(-\frac{\phi_{j+1}}{kT}\right) . \tag{16.15}$$

We then have the Markoff integral equation of (12.4), where the transition probability $\psi$ is given by

$$\psi(\mathbf{R}_{j+1}|\mathbf{R}_j) = C(\mathbf{R}_j)\tau(\mathbf{r}_{j+1})G(\mathbf{R}_{j+1})\exp\left(-\frac{\phi_{j+1}}{kT}\right) , \tag{16.16}$$

with $C$ the normalizing function to be determined from Eq. (12.3). We note that Reiss omitted the factor $G$ in Eq. (16.16), and that if the exponential in Eq. (16.16) is linearized the integral equation of (12.4) without $G$ in $\psi$ is equivalent to that of Hermans, Klamkin, and Ullman which does not lead to the excluded-volume effect (see Section 12b). The transition probability given by Eq. (16.16) resembles that of Zimm, Stockmayer, and Fixman, Eq. (13.15), which involves the effects of the segments $k > j+1$ as well as the segments $k \leq j$. In Eq. (16.16), there are two kinds of effects of segments beyond the $(j+1)$th. One is the direct effect arising from interactions between the $(j+1)$th segment and some segment further down the chain, as summarized in Eq. (16.12). The other is an effect which is transmitted along the backbone of the chain. Such an effect ultimately appears through the influence of the $(j+1)$th segment on the $j$th, and this effect is represented by the factor $G$. However, an evaluation of $G$ is as formidable as a direct evaluation of the distribution function $P(\mathbf{R})$ of the end-to-end distance from Eq. (16.2). It is more convenient to work with an integral equation for the function $\hat{P}$ defined in Eq. (16.13). Evidently, when $j = n$, normalization of $\hat{P}(\mathbf{R}_j)$ yields $P(\mathbf{R})$. Indeed, the advantage of the self-consistent-field approach consists in deriving an integral equation for $\hat{P}$ amenable to mathematical treatment.

Now we can readily have, from the defining equation for $\hat{P}(\mathbf{R}_{j+1})$,

$$\hat{P}(\mathbf{R}_{j+1}) = \int \hat{P}(\mathbf{R}_j)\tau(\mathbf{r}_{j+1}) \exp\left[-\frac{\phi_{j+1}(\mathbf{R}_{j+1})}{kT}\right] d\mathbf{R}_j \,, \tag{16.17}$$

or in the alternative notation,

$$\hat{P}(\mathbf{R}, j+1) = \int \hat{P}(\mathbf{R}-\mathbf{r}, j)\hat{\psi}(\mathbf{R}-\mathbf{r}, j; \mathbf{r})d\mathbf{r} \tag{16.18}$$

with

$$\hat{\psi}(\mathbf{R}-\mathbf{r}, j; \mathbf{r}) = \tau(\mathbf{r}) \exp\left[-\frac{\phi(\mathbf{R}, j+1)}{kT}\right] . \tag{16.19}$$

This new transition probability is subject to no normalization condition, and is equivalent to that of James, Eq. (12.14), if the exponential in Eq. (16.19) is linearized. Equation (16.18) can be easily transformed into a differential equation. Recalling that the second moment of $\tau$ is $a^2$, and expanding $\hat{P}(\mathbf{R}-\mathbf{r}, j)$ around $\mathbf{R}$ with neglect of terms of order $a^3$ and higher, we obtain

$$\frac{\partial \hat{P}(\mathbf{R}, j)}{\partial j} - \frac{a^2}{6}\nabla^2 \hat{P}(\mathbf{R}, j) = \Lambda(\mathbf{R}, j)\hat{P}(\mathbf{R}, j) \,, \tag{16.20}$$

where

$$\Lambda(\mathbf{R}, j) = \exp\left[-\frac{\phi(\mathbf{R}, j)}{kT}\right] - 1 \,. \tag{16.21}$$

In Eq. (16.20), we have also neglected terms of order $j^{-2}\hat{P}$ and $\Lambda j^{-1}\hat{P}$, which are small compared to $j^{-1}\hat{P}$ for $j \gg 1$.

In order to complete the differential equation of (16.20), we evaluate the self-consistent potential. As in Eq. (15.14), we express the pair potential as

$$w(\mathbf{R}_{ij}) = kT\beta\delta(\mathbf{R}_{ij}) \,. \tag{16.22}$$

Substitution of Eq. (16.22) into Eq. (16.12) leads to

$$\frac{\phi(\mathbf{R}, j)}{kT} = \beta \sum_i P(0_{ij}|\mathbf{R}) \,. \tag{16.23}$$

As seen from the derivation of Eq. (16.12), $P(0_{ij}|\mathbf{R})$ should be evaluated in the perturbed state. Thus we make the uniform-expansion approximation in $P(0_{ij}|\mathbf{R})$; that is, we replace it by $P_0(0_{ij}|\mathbf{R})$ with $a\alpha$ in place of $a$, where $\alpha$ is the expansion factor for the end-to-end distance of the entire chain of $n$ bonds (not of $j$ bonds) with temporary omission of the subscript $R$ on $\alpha$. Under the condition that

$$a\alpha \ll R \ll ja\alpha\,, \tag{16.24}$$

for the random-flight model $\phi$ may then be evaluated to be (with omission of a constant term)

$$\frac{\phi(\mathbf{R},j)}{kT} = (2\pi/3)^{1/2}\xi\left(\frac{a}{\alpha^2 R} - \frac{3R}{ja\alpha^4}\right) \tag{16.25}$$

with

$$\xi = z/n^{1/2}\,. \tag{16.26}$$

From Eq. (16.25), $\phi$ is seen to be very small compared to $kT$ under the condition of (16.24). The exponential in $\Lambda$ may therefore be linearized. Substitution of Eq. (16.21) with (16.25) into Eq. (16.20) then leads to

$$\frac{\partial \hat{P}}{\partial j} - \frac{1}{6}\nabla^2\hat{P} = -(2\pi/3)^{1/2}\xi\left(\frac{1}{\alpha^2 y} - \frac{3y}{j\alpha^4}\right)\hat{P}\,, \tag{16.27}$$

where we have introduced the dimensionless variable $y = R/a$. We note that if $\alpha$ is set equal to unity, Eq. (16.27) is equivalent to the differential equation of James, and it has a simple analytic solution.

We now proceed to solve Eq. (16.27). As is well known, when $z = \xi = 0$ the solution of Eq. (16.27) satisfying the boundary condition, $\hat{P}(\mathbf{R},0) = \delta(\mathbf{R})$, is $\hat{P}(\mathbf{R},j) = P_0(\mathbf{R},j)$, the Gaussian distribution (see Appendix III A). Unless $\xi = 0$, it is difficult to find an analytic solution of Eq. (16.27) which is valid over the unlimited ranges of the variables. Thus, following the procedure of Reiss, we consider an associated differential equation which becomes identical with the given equation under appropriate conditions. In the present case, such an equation is

$$\frac{\partial \hat{P}}{\partial j} - \frac{1}{6}\nabla^2\hat{P} = (\Lambda_1 + \Lambda_2)\hat{P} \tag{16.28}$$

with

$$\Lambda_1 = -(2\pi/3)^{1/2}\xi\left[\frac{1}{\alpha^2 y}\left(1 + \frac{1}{\alpha^2}\right) - \frac{3y}{j\alpha^4} + \frac{j}{3\alpha^2 y^3}\right], \tag{16.29}$$

$$\Lambda_2 = -(4\pi/3)\xi^2\left[1 + \frac{j\alpha^2}{3y^2}\ln\left(\frac{y}{j^{1/2}\alpha}\right)\right]\left(\frac{j}{\alpha^6 y^2}\right)\ln\left(\frac{y}{j^{1/2}\alpha}\right). \tag{16.30}$$

The exact solution of Eq. (16.28) satisfying the same boundary condition as above is

$$\begin{aligned}\hat{P}(\mathbf{R},j) &= P_0(\mathbf{R},j)\exp(\pi\xi^2 j/\alpha^8)\\ &\quad\times\exp\left(-(2\pi/3)^{1/2}\xi\left\{\frac{2j}{\alpha^2 y}\left[1 + \ln\left(\frac{y}{j^{1/2}\alpha}\right)\right] - \frac{3y}{\alpha^4}\right\}\right).\end{aligned} \tag{16.31}$$

Let us now demonstrate that Eq. (16.28) reduces to Eq. (16.27) under appropriate conditions. Suppose that

$$j = O(n) \quad \text{and} \quad n \to \infty \,. \tag{16.32}$$

We then have $y = O(n^{1/2}\alpha)$ over the important range of $y$. Therefore, the first and second terms of $\Lambda_1$ are of order $\xi/n^{1/2}\alpha^3$, whereas the last term is of order $\xi/n^{1/2}\alpha^5$; the last term is negligibly small compared to the first two, provided $\alpha$ becomes indefinitely large as $n$ is increased. Thus $\Lambda_1$ may be expected to tend to

$$\Lambda_1 \to -(2\pi/3)^{1/2}\xi\left(\frac{1}{\alpha^2 y} - \frac{3y}{j\alpha^4}\right) = O(\xi/n^{1/2}\alpha^3)\,. \tag{16.33}$$

On the other hand, the quantity in square brackets of Eq. (16.30) is of order unity, and we therefore have

$$\Lambda_2 = O\big[(\xi^2/\alpha^8)\ln(y/j^{1/2}\alpha)\big]\,. \tag{16.34}$$

We now assume that $\alpha^\nu = \text{const}.n^{1/2}$, or $\alpha^2 = \text{const}.n^\varepsilon$ for extremely large $n$. Equations (16.33) and (16.34) may then be rewritten as $\Lambda_1 = O(\xi/n^{(1+3\varepsilon)/2})$ and $\Lambda_2 = O\big[(\xi^2/n^{4\varepsilon})\ln(y/j^{1/2}\alpha)\big]$, respectively. If $\varepsilon > 0.2$, or $\nu < 5$, we have $4\varepsilon > (1+3\varepsilon)/2$, and therefore $\Lambda_2$ is negligibly small compared to $\Lambda_1$, since $\xi$ is at most of order unity and the logarithm in Eq. (16.34) is also of order unity. If $\varepsilon = 0.2$, or $\nu = 5$, $\Lambda_2$ is still negligibly small compared to $\Lambda_1$ as long as $y$ is very close to $j^{1/2}\alpha$. Thus, when the conditions, $\nu \le 5$ and $y \approx j^{1/2}\alpha$, together with (16.32) are fulfilled, $(\Lambda_1 + \Lambda_2)$ becomes equal to $\Lambda_1$ given by Eq. (16.33), and Eq. (16.28) reduces to Eq. (16.27). In other words, the $\hat{P}$ given by Eq. (16.31) is the solution of Eq. (16.27) under these conditions.

Putting $j = n$ in Eq. (16.31) and normalizing it, we obtain the distribution function of the end-to-end distance $\mathbf{R}$ of the chain of $n$ bonds, which may be written as Eq. (15.8) with the potential

$$\frac{V(\mathbf{R})}{kT} = (2\pi/3)^{1/2} z\left\{\frac{2}{\alpha_R^2 x}\left[1 + \ln\left(\frac{x}{\alpha_R}\right)\right] - \frac{3x}{\alpha_R^4}\right\}, \tag{16.35}$$

where $x = R/\langle R^2\rangle_0^{1/2}$, as before. Equation (16.35) is valid only when $R \approx \langle R^2\rangle^{1/2}$, $\nu \le 5$, and $z \to \infty$. The asymptotic solution for $\langle R^2\rangle$ can be obtained exactly by means of the Hermans–Overbeek procedure or from the value of $R$ corresponding to the peak of the distribution. Therefore, the restriction, $R \approx \langle R^2\rangle^{1/2}$, does not affect the final result; the localized solution of (16.35) suffices for the present purpose. Thus, we find, from Eqs. (15.8) and (16.35),

$$\lim_{z\to\infty} \alpha_R^5 = (2\pi/3)^{1/2} z = 1.45z\,. \tag{16.36}$$

This is the self-consistent asymptotic solution for $\alpha_R$ in the present treatment, since the solution is $\nu = 5$ on the assumption that $\nu \le 5$.

Equation (16.36) predicts values of $\alpha_R$ (at large $z$) slightly larger than those predicted by the corresponding F,m equation, $\alpha_R^5 = 1.33z$. The result suggests that $P(0_{ij}|\mathbf{R})$ in Eq. (15.10) may be evaluated in the fully perturbed state in a first approximation, since the potential of (15.37) gives the same result as Eq. (16.36).

Whether the probability density appearing in the potential is evaluated in the fully perturbed state or in the intermediate perturbed state, it is evident that the uniform-expansion approximation made in it is responsible for an equation of the fifth-power type for $\alpha_R$. This can be seen more explicitly as follows. Assume that the potential $V$ is proportional to $R^{-\mu}$, or more generally that $V$ is a linear combination of such terms. From a dimensional consideration, $V$ may then be written in the form

$$V(\mathbf{R})/kT = z \sum_i c_i \left(\langle R^2 \rangle_0{}^{1/2}/R\right)^{\mu_i} \alpha_R{}^{\mu_i - 3} , \tag{16.37}$$

where $c_i$ are numerical constants and we have introduced the uniform-expansion approximation (the replacement of $a$ by $a\alpha_R$). From Eqs. (15.8) and (16.37), we obtain

$$\lim_{z \to \infty} \alpha_R^5 = \frac{1}{3} \sum_i c_i \mu_i z \, . \tag{16.38}$$

However, the uniform-expansion approximation of this kind is difficult to justify from a theoretical point of view.

Several authors[58, 59] have recently attempted to apply the technique used in the theory of simple liquids, i.e., the Born–Green–Yvon–Kirkwood method or the Percus–Yevick method of deriving an integral equation for the pair correlation function. However, these approaches will need further investigations, and we do not reproduce them here.

Next we discuss briefly the asymptotic behavior of $\alpha_S$. For this case, the important range of $S$ is $S \approx \langle S^2 \rangle_0{}^{1/2} \alpha_S$ or $S \gg \langle S^2 \rangle_0{}^{1/2}$. We should therefore use Eq. (8.50) for $P_0(S)$, or its leading term,

$$P_0(S) = \text{const.}\ S^2 \exp\left(-\frac{\pi^2 S^2}{4\langle S^2 \rangle_0}\right) . \tag{16.39}$$

Then the asymptotic value of $\alpha_S$ is exactly given by the value of $x = S/\langle S^2 \rangle_0{}^{1/2}$ satisfying the equation,

$$x = -\frac{2}{\pi^2 kT} \frac{\partial V(S)}{\partial x} \, . \tag{16.40}$$

If we use the Fujita–Norisuye–Fixman potential given by Eq. (15.28) with $C = 2.745$, we have, from Eq. (16.40),

$$\lim_{z \to \infty} \alpha_S^5 = 1.67z \, . \tag{16.41}$$

If we use the original Flory potential given by Eq. (15.26), we have the numerical coefficient 1.58 instead of 1.67 in Eq. (16.41).[60] These equations predict values of $\alpha_S$ (at large $z$) somewhat larger than those predicted by the corresponding F,m equation, $\alpha_S^5 = 1.276z$, but definitely smaller than those by the corresponding F,o equation, $\alpha_S^5 = 2.60z$.

From the previous analysis, it follows that the asymptotic form of the fifth-power type, $\alpha^5 = \gamma z$, as suggested first by Flory, may be accepted, and that the value of $\gamma$ will be nearly equal to or slightly above the F,m value (1.333 for $\alpha_R$ and 1.276 for $\alpha_S$). From this conclusion and the statement at the end of Section 15b, we may deduce that the F,m, B, $F_2$, FON, or YT equation for $\alpha_R$ and the F,m or YT equation for $\alpha_S$ will provide a fairly satisfactory description of the behavior of the expansion factors over the range of $z$ experimentally accessible (see Figs. III.5 and III.6).

## 17. Remarks

### 17a. Branched and Ring Polymers

We describe only the first-order perturbation theory. The mean-square radii may be evaluated conveniently by the cluster expansion method with the use of the Zimm–Stockmayer relation of (7.22), as in the case of a linear chain. The evaluation is tedious but straightforward, and we omit the mathematical details.

For branched molecules, we may write

$$\langle S^2 \rangle_b = \tfrac{1}{6} n a^2 g (1 + Kz - \cdots) \,. \tag{17.1}$$

For convenience, we consider only two types of structures: one is a uniform star molecule of functionality $f$, and the other is a uniform normal (comb) molecule of $m$ branch units of functionality 3. For this star molecule, the factor $g$ is given by Eq. (9.69) and the coefficient $K$ was evaluated by Kron and Ptitsyn[61] and by Berry and Orofino[62] as follows,

$$\begin{aligned} K_u(\mathrm{star}) = \frac{3}{f^{1/2}(3f-2)} \bigg[ & \frac{67 \cdot 2^{7/2}}{315}(f-1) - \frac{134}{315}(f-2) \\ & + \frac{4}{45}(101 \cdot 2^{1/2} - 138)(f-1)(f-2) \bigg] \,. \end{aligned} \tag{17.2}$$

In Table III.3 are given the values of $K$ calculated from Eq. (17.2) for various values of $f$. The coefficient $K$ is seen to increase with $f$ from the value 1.276 for the linear chain. We note that for a cruciform molecule (with $f = 4$) Fixman[26] obtained the value 1.12 for $K$, using the equation[63]

$$\langle S^2 \rangle_b = n^{-1} f \sum_{k=1}^{n/f} \langle L_k{}^2 \rangle - \langle Z^2 \rangle \,, \tag{17.3}$$

**TABLE III.3.** VALUES OF $K$ FOR UNIFORM STAR MOLECULES OF FUNCTIONALITY $f$[62]

| $f$ | $K$ |
|---|---|
| 1 | 1.276 |
| 2 | 1.276 |
| 3 | 1.298 |
| 4 | 1.342 |
| 5 | 1.394 |
| 6 | 1.449 |
| 8 | 1.559 |
| 12 | 1.770 |
| $\infty$ | $0.430f^{1/2}$ |

where $L_k$ is the distance between the branch unit and the $k$th segment of a particular branch, and $Z$ is the distance from the branch unit to the center of mass. Equation (17.3) is, of course, valid for a uniform star molecule even with excluded volume, and there is some error in his evaluation; Eq. (17.3) also gives the correct result of (17.2).[64] For the uniform normal molecule mentioned above, the factor $g$ is given by Eq. (9.72) with $f = 3$ and $p = 2m + 1$, and numerical values of $K$ obtained by Berry and Orofino[62] are given in Table III.4. The coefficient $K$ is seen to increase with increasing number of branch units. The results given in Tables III.3 and III.4 are easy to understand: the chance of segment contacts is increased as the degree of branching is increased, because the unperturbed dimension decreases with increasing branching; and the greater the chance of segment contacts, the larger the expansion of the molecule.

For a single-ring molecule, Casassa[65] obtained the result,

$$\langle S^2 \rangle_r = \frac{1}{12} n a^2 \left( 1 + \frac{\pi}{2} z - \cdots \right) , \tag{17.4}$$

where the unperturbed dimension has already been obtained in Section 9b(ii). The coefficient of $z$ is larger than the value 1.276 for the linear chain. Thus the decrease in the molecular dimension due to branching or formation of a ring is compensated in part by the excluded-volume effect.

## 17b. Numerical Calculations on Lattice Chains

In parallel with various theoretical attempts to solve the excluded-volume problem in a linear polymer chain, there have been made a number of numerical computations for nonintersecting random walks on various lattices. These investigations may be classified into two

**TABLE III.4.** VALUES OF $K$ FOR UNIFORM NORMAL (COMB) MOLECULES OF $m$ BRANCH UNITS OF FUNCTIONALITY 3[62]

| $m$ | $K$ |
|---|---|
| 2 | 1.386 |
| 3 | 1.455 |
| 4 | 1.522 |
| 5 | 1.587 |
| 10 | 1.849 |
| 15 | 2.032 |
| 20 | 2.167 |
| 25 | 2.271 |

groups: one is the exact enumeration method, and the other is the statistical or Monte Carlo method. Both approaches lead to the conclusion that the dependence of $\langle R^2 \rangle$ on $n$ may be expressed as

$$\langle R^2 \rangle \propto n^{\delta}\,, \tag{17.5}$$

and most attention is focused on the value of $\delta$. A brief summary of the results follows.

### 17b(i). Exact Enumeration Method

If $C_n$ is the number of all possible nonintersecting random walks of $n$ steps on a lattice and $f_n(\mathbf{R})\Delta\mathbf{R}$ is the number of those walks whose end points lie between $\mathbf{R}$ and $\mathbf{R}+\Delta\mathbf{R}$ from the origin, we have

$$P(\mathbf{R})\Delta\mathbf{R} = {C_n}^{-1} f_n(\mathbf{R})\Delta\mathbf{R}\,, \tag{17.6}$$

$$\langle R^2 \rangle = {C_n}^{-1} \sum_{\mathbf{R}} R^2 f_n(\mathbf{R})\Delta\mathbf{R}\,, \tag{17.7}$$

because all possible configurations are a priori equally probable. The present method consists in carrying out a direct and exact enumeration of $C_n$ and $f_n(\mathbf{R})$ for short chains.

Teramoto et al.,[12, 31] who were among the first to attempt this approach, investigated the statistical properties of the two-dimensional square lattice chain with bond angle 90° (right-left two choice), two-dimensional square lattice chain with bond angles 90° and 180° (three choice), and three-dimensional simple cubic lattice chain with bond angle 90° (four choice). In every case of nonintersecting walks, it was observed that $\langle R^2 \rangle / n$ tends to increase and diverge as $n$ is increased. In addition, it was found that $\langle R^2 \rangle / \langle S^2 \rangle = 7.41$ for the two-choice, two-dimensional, square lattice chain of 17 bonds, which is greater than the value 6 for the random-flight chain. It is pertinent to note that the first-order perturbation theories of $\langle R^2 \rangle$ and $\langle S^2 \rangle$ for a two-dimensional chain read[66] (see Appendix III C)

$$\langle R^2 \rangle = na^2(1 + \tfrac{1}{2}z^* - \cdots) , \tag{17.8}$$

$$\langle S^2 \rangle = \tfrac{1}{6}na^2 \left(1 + \frac{11}{24}z^* - \cdots \right) , \tag{17.9}$$

where

$$z^* = (1/\pi a^2)\beta^* n \tag{17.10}$$

with $\beta^*$ the two-dimensional binary cluster integral for a pair of segments. From these equations, we may expect that $\langle R^2 \rangle$ of $\langle S^2 \rangle$ for the two-dimensional chain has a greater dependence on $n$ than for the corresponding three-dimensional chain, and that $\langle R^2 \rangle / \langle S^2 \rangle$ is greater than 6 also for the two-dimensional chain (assuming $z^* > 0$).

Fisher et al.[67, 68] made an attempt to determine the value of $\delta$ in Eq. (17.5) for $n \to \infty$ from a knowledge of short chains by suitable extrapolation, applying a "chain counting theorem" of Domb.[69, 70] This theorem enables one to calculate $C_n$ recursively in terms of the number of certain closed configurations of $n$ bonds, which is much less than $C_n$ and can be enumerated with less labor. With values of $\langle R^2 \rangle = \langle {R_n}^2 \rangle$ thus evaluated, they found that the sequence of points in a plot of the ratio $A_n = \langle {R_{n+1}}^2 \rangle / \langle {R_n}^2 \rangle$ against $1/n$ approach a straight line of slope $\delta$ which extrapolates to $A_\infty = 1$. From this linearity, it was proved that Eq. (17.5) holds for $n \to \infty$. A sequence of estimates for the index $\delta$ may then be calculated from $\delta_n = n(A_n - 1)$. The sequence 1 of points in Fig. III.7 represents the values of $\delta_n$ for the completely random, two-dimensional, square lattice chain; the slope is zero and the limit is $\delta_n = \delta = 1$ as expected. The sequence 2 corresponds to a similar chain but with only immediate reversals forbidden (three-choice, two-dimensional, square lattice chain subject to no volume exclusions). These points lie on a slightly irregular sloping curve which, however, clearly extrapolates to $\delta_\infty = 1$. The results for the three-choice, two-dimensional, square lattice chain subject to volume exclusions yield the sequence 3. The points exhibit the characteristic odd-even oscillation about a straight line. The amplitude of oscillations can be markedly reduced by forming the means $\frac{1}{2}(\delta_n + \delta_{n+1})$, which lie very close to a straight line of small slope and quite well defined intercept (sequence 4). The estimate thus obtained is $\delta = 1.47 \pm 0.02$.[68] Similar treatments for the five-choice, three-dimensional, simple cubic lattice chain lead to the estimate, $\delta = 1.21 \pm 0.02$.[68] Subsequently, Domb[71] obtained extensive data for longer lattice chains, and concluded that $\delta = 1.50$ for all two-dimensional nonintersecting chains and $\delta = 1.20$ for all three-dimensional non-intersecting chains. This indicates the adequacy of the asymptotic form of $\alpha_R$ of the fifth-power type for a polymer chain.

Next we discuss briefly the shape of the distribution of $R$. The function $2\pi RP(\mathbf{R})$ obtained by Teramoto et al.[31] for the two-choice, two-dimensional, square lattice chain of $n = 17$ and unit bond length is shown by the histogram in Fig. III.8. For comparison, in the figure are

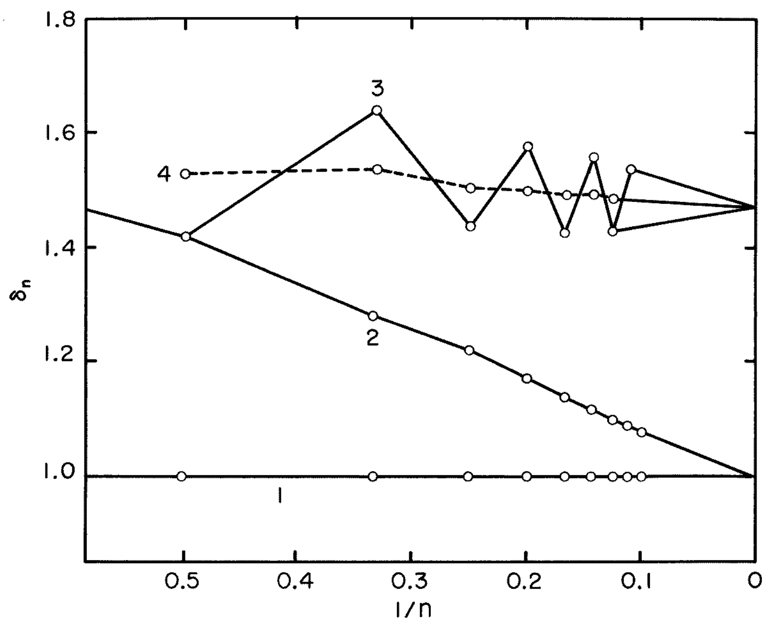

**Fig. III.7.** Successive estimates of $\delta$ for two-dimensional square lattice chains.[68] 1: completely random-flight chains. 2: chains only with immediate reversals forbidden. 3: three-choice, nonintersecting chains. 4: sequence of the means $\frac{1}{2}(\delta_n + \delta_{n+1})$ for case 3.

also shown the Gaussian distributions with the ideal value 17 of $\langle R^2 \rangle_0$ and with the same value 48.8 of $\langle R^2 \rangle$ as the histogram by the broken and full curves, respectively. From the figure, it is seen that the Gaussian distribution decreases gradually beyond the most probable value of $R$, while the distribution of $R$ for the real (lattice) chain subject to volume exclusions falls off to zero suddenly. Domb et al.[72] also arrived at the conclusion that in the limiting case the distribution of $R$ is a skew Gaussian function.

## 17b(ii). Monte Carlo Method

This method consists of generating nonintersecting random walks for various lattice systems on an electronic computer and accumulating statistical data describing the average behavior of the chain. Contrary to the exact enumeration, the Monte Carlo method is thus restricted in accuracy by statistical fluctuations, but long walks ($n = 50$ to 2000) can be sampled. This approach has been developed by many investigators, but especially by Wall and his co-workers.

Early investigations of Wall et al.[73, 74] were confined to relatively short chains of up to 50 to 100 bonds, and led to the estimates, $\delta = 1.45$

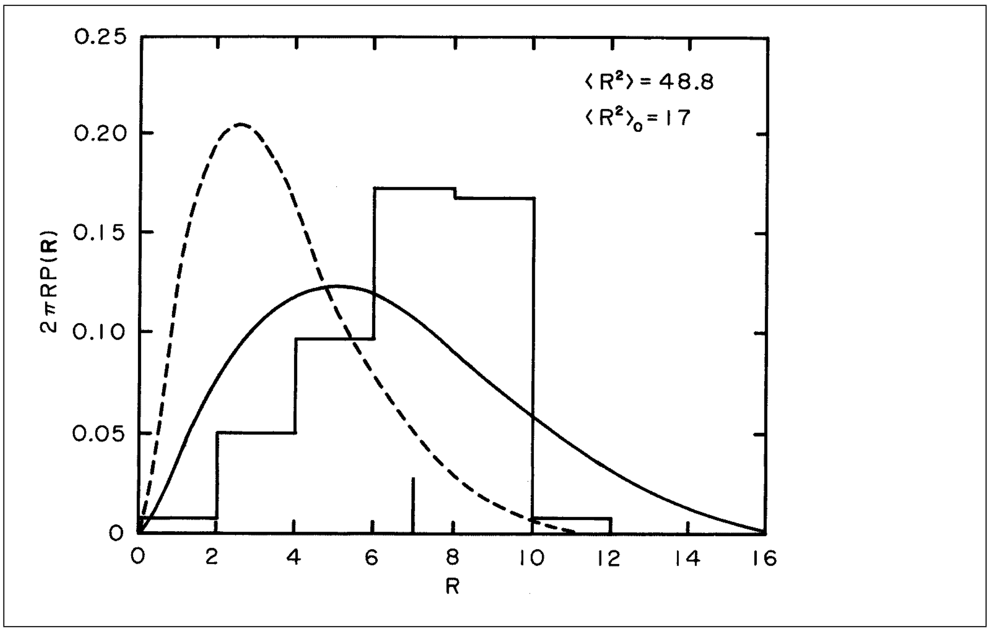

**Fig. III.8.** The distribution functions of $R$ of the two-choice, two-dimensional, square lattice chain of 17 bonds with unit bond length. Histogram: exact enumeration.[31] Broken curve: unperturbed Gaussian function. Full curve: Gaussian function with the same value of $\langle R^2 \rangle$ as the histogram. The vertical line segment indicates $\langle R^2 \rangle^{1/2}$.

for two-dimensional chains and $\delta = 1.22$ for three-dimensional chains. Rosenbluth and Rosenbluth[75] also obtained the same results. Subsequently, however, much longer walks were generated by Wall and Erpenbeck[76] and by Suzuki[77] on the three-dimensional tetrahedral lattice, and by Kron and Ptitsyn[78] on the five-choice, three-dimensional, simple cubic lattice. The results are given in Tables III.5 and III.6, where the bond length is taken as unity. These data lead to the estimate, $\delta = 1.19$, very close to the value 1.20 from the exact enumeration. In addition, the ratio $\langle R^2 \rangle / \langle S^2 \rangle$ is observed to be almost independent of $n$; its average values are 6.4 and 6.3 for the tetrahedral and simple cubic lattices, respectively.

We now consider the problem of estimating $\alpha$ and $z$ for lattice chains and compare the results with the analytical theory. For this purpose, it is necessary and sufficient to determine the values of $\langle R^2 \rangle_0$ (or $\langle S^2 \rangle_0 = \langle R^2 \rangle_0 / 6$) and $\beta$ for a given lattice system. The reverse step in nonintersecting random walks is usually considered to be a short-range effect, which is absorbed into the unperturbed dimension.[35, 66] For $(z_c - 1)$-choice walks on a lattice of coordination number $z_c$, we

**TABLE III.5.** MEAN-SQUARE END-TO-END DISTANCES AND RADII OF THREE-DIMENSIONAL TETRAHEDRAL LATTICE CHAINS WITH UNIT BOND LENGTH

| | WALL–ERPENBECK[76] | | SUZUKI[77] |
|---|---|---|---|
| $n$ | $\langle R^2\rangle$ | $\langle S^2\rangle$ | $\langle S^2\rangle$ |
| 16 | — | — | 5.56 |
| 32 | — | — | 12.78 |
| 40 | 108 | 17.0 | — |
| 64 | — | — | 29.31 |
| 80 | 243 | 38.3 | — |
| 120 | 431 | 67.0 | — |
| 128 | — | — | 67.37 |
| 160 | 568 | 89.3 | — |
| 200 | 726 | 115.0 | — |
| 240 | 880 | 141.7 | — |
| 256 | — | — | 153.4 |
| 280 | 1075 | 168.7 | — |
| 320 | 1255 | 196.3 | — |
| 360 | 1456 | 225.0 | — |
| 400 | 1648 | 256.3 | — |
| 440 | 1885 | 293.0 | — |
| 480 | 2056 | 324.3 | — |
| 512 | — | — | 350.3 |
| 520 | 2259 | 354.3 | — |
| 560 | 2501 | 389.7 | — |
| 600 | 2708 | 425.0 | — |
| 1024 | — | — | 787.0 |
| 2048 | — | — | 1740 |

then have (except for short chains)

$$\langle R^2\rangle_0 = nl^2 \frac{1+(z_c-1)^{-1}}{1-(z_c-1)^{-1}} \tag{17.11}$$

with $l$ the bond length. For example, we have $\langle R^2\rangle_0 = 2nl^2$ for the three-dimensional tetrahedral lattice, and $\langle R^2\rangle_0 = \frac{2}{3}nl^2$ for the five-choice, three-dimensional, simple cubic lattice. For the estimation of the binary cluster integral $\beta$, it is adequate to use the Ornstein–Zernike equation relating the pair correlation function $g(\mathbf{R}_1, \mathbf{R}_2)$ to the isothermal compressibility $\kappa$ for a one-component system of monatomic molecules[2, 35]; that is,

$$\frac{1}{\rho V}\int \rho^{(1)}(\mathbf{R}_1)\rho^{(1)}(\mathbf{R}_2)\big[g(\mathbf{R}_1,\mathbf{R}_2)-1\big]d\mathbf{R}_1 d\mathbf{R}_2 = \rho\kappa kT - 1 \tag{17.12}$$

**TABLE III.6.** MEAN-SQUARE END-TO-END DISTANCES AND RADII OF FIVE-CHOICE, THREE-DIMENSIONAL, SIMPLE CUBIC LATTICE CHAINS WITH UNIT BOND LENGTH.[78]

| $n$ | $\langle R^2 \rangle$ | $\langle S^2 \rangle$ |
|---|---|---|
| 47 | 107.6 | — |
| 197 | 591.8 | 93.2 |
| 407 | 1408 | 223 |
| 617 | 2293 | 366 |
| 1007 | 4088 | 653 |
| 1517 | 6720 | 1071 |
| 1997 | 9314 | 1474 |

with $\rho = N/V$, the number density of the component, and $\rho^{(1)}$ the singlet generic molecular distribution function. (For the complete definition of $\rho^{(n)}$, we refer the reader ahead to Section 19.) For fluids, we have $\rho^{(1)} = \rho$, and the compressibility term $\rho\kappa kT$ may be neglected compared to unity below the normal boiling point. From Eqs. (13.3) and (17.12), we then find $\beta = \rho^{-1}$; that is, $\beta$ is equal to the molecular volume. For perfect lattice systems, $\rho^{(1)}$ may be expressed as a sum of delta functions,

$$\rho^{(1)}(\mathbf{R}_1) = \sum_i \delta(\mathbf{R}_1 - \mathbf{l}_i) \tag{17.13}$$

with $\mathbf{l}_i$ the coordinates of the $i$th lattice point. Substitution of Eq. (17.13) into Eq. (17.12) leads to (with $\kappa = 0$)

$$\int \rho^{(1)}(\mathbf{R}_1)\big[g(\mathbf{R}_1, \mathbf{l}_i) - 1\big] d\mathbf{R}_1 = -1\,. \tag{17.14}$$

This equation is an obvious consequence of the fact that $g$ is unity when $\mathbf{R}_1$ and $\mathbf{R}_2$ are at two different lattice points, and zero when both molecules are at the same lattice point. We then have the equivalent of Eq. (13.3),

$$\beta = \rho^{-1} \int \rho^{(1)}(\mathbf{R}_1)\big[1 - g(\mathbf{R}_1, \mathbf{l}_i)\big] d\mathbf{R}_1 = \rho^{-1}\,. \tag{17.15}$$

Thus $\beta$ is equal to the volume per lattice point. For example, we have $\beta = 1.53 l^3$ for the tetrahedral lattice, and $\beta = l^3$ for the simple cubic lattice.

Having determined the values of $\langle R^2 \rangle_0$ and $\beta$, we evaluate $\alpha_S{}^2 = 6\langle S^2 \rangle / \langle R^2 \rangle_0$ and $z = (3/2\pi \langle R^2 \rangle_0)^{3/2} \beta n^2$ (with $l = 1$), as functions of $n$, with the values given in Tables III.5 and III.6. In Fig. III.9 are shown the values of $\alpha_S{}^3$ as a function of $z$ so obtained by the open circles, triangles (tetrahedral lattice), and squares (simple cubic lattice). For

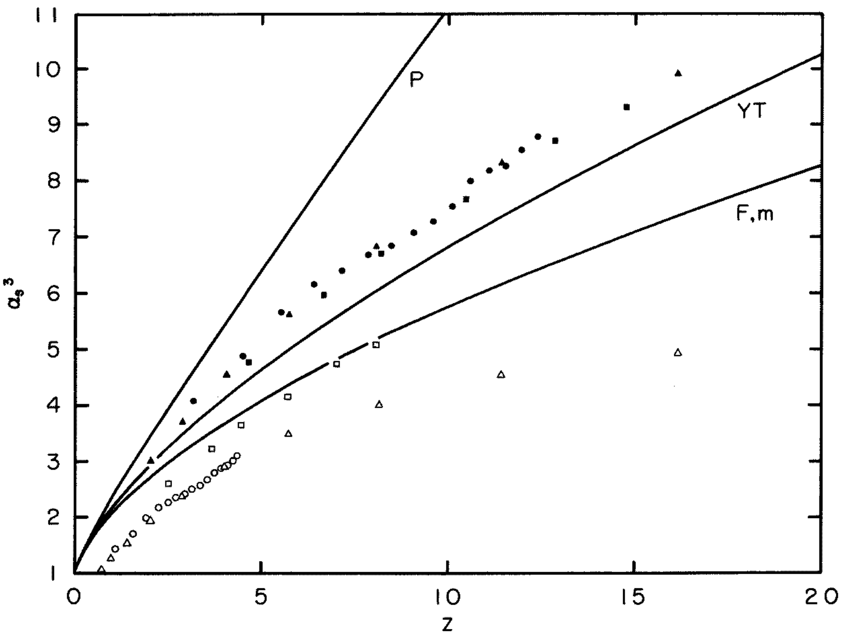

**Fig. III.9.** Values of $\alpha_S^3$ calculated from Monte Carlo data. The open circles, triangles, and squares were obtained assuming Eq. (17.11), while the filled circles, triangles, and squares were obtained assuming $\langle R^2\rangle_0 = nl^2$. Circles and triangles: tetrahedral lattice.[76, 77] Squares: simple cubic lattice.[78] Curve P: the Ptitsyn theory, Eq. (15.62). Curve YT: the Yamakawa–Tanaka theory, Eq. (15.95). Curve F,m: the modified Flory theory, Eq. (14.41).

comparison, the values calculated from the F,m equation (14.41), the P equation (15.62), and the YT equation (15.95) are also plotted in the figure. The points for the tetrahedral and simple cubic lattices are seen to form two different curves; the result is inconsistent with the requirement of the two-parameter theory that $\alpha$ be a universal function of $z$. This is probably due to the fact that the bond probability is spherically symmetric in the two-parameter theory for a polymer chain,whereas this is not the case for the lattice chains with $\langle R^2\rangle_0$ given by Eq. (17.11). If we regard the overlap between bonds due to the reverse step as the excluded-volume effect, and take $\langle R^2\rangle_0 = nl^2$, we obtain the filled points in Fig. III.9. These points seem to form a single-composite curve, which is close to the YT curve. However, there arises the question of whether these data may be used to test an approximate analytical theory of $\alpha$ regarding its dependence of $z$, since there is still a gap between the discrete lattice chain and the model used in the theory for a polymer chain. At present, there is no definite answer to this question.

Finally, we note that numerical studies have been made also of the effects of solvent[79−83] and of branching,[84] but we shall not reproduce the results here.

## 17c. General Comments

In this chapter we have described various attempts made so far to solve the excluded-volume problem, and may now definitely accept the conclusion that $\alpha$ increases and diverges as $n$ or $z$ is increased. However, there has been controversy on the question of whether the behavior of $\alpha$ obeys an equation of the fifth-power type or of the third-power type. On the one hand, the modified Flory equation, proposed at the early stage of improvements of the Flory theory, has been frequently used for the treatment of experimental data, although not accepted by Flory for a long time. In 1960, on the other hand, Kurata et al. derived the KSR equation of the third-power type, numerically equivalent to the $\mathrm{F}_1$ equation, and rejected both the original and modified Flory equations of the fifth-power type. Their grounds for the superiority of the equation of the third-power type were the following: (1) the available Monte Carlo data of Wall and Erpenbeck (the open circles in Fig. III.9) indicated a linear relationship between $\alpha^3$ and $n^{1/2}$, and (2) there existed a similar relationship between the intrinsic viscosity and the molecular weight, namely the Stockmayer–Fixman–Kurata plot.[66, 85] However, the recent Monte Carlo data for much longer chains show that $\alpha^3$ is not linear in $z$ (see Fig. III.9). Also from the theoretical point of view, an equation of the fifth-power type is more plausible than that of the third-power type, as discussed in Sections 15 and 16. The SFK plot of the intrinsic viscosity will be discussed in Chapter VII.

We must now refer to a comparison of theory with experiment. There is a fundamental difficulty in testing a theory of $\alpha$ regarding its dependence on $z$. Light scattering measurements can afford *experimental* values of $\alpha_S$, whereas the binary cluster integral $\beta$ and, hence, the parameter $z$ are not directly observable quantities. Thus some additional information is necessary. For example, we must know the two-parameter theory value of the second virial coefficient, which will be developed in the next chapter. Emphasis must then be focused on the self-consistency of the intramolecular and intermolecular theories of interaction. However, a complete comparison of theory with experiment cannot be completed even in conjunction with the theory of the second virial coefficient. Deferring this problem to Chapter VII, we here discuss treatments of experimental data which are based on the Flory expression for $\beta$ or $z$, Eq. (14.38). If Eq. (14.38) were assumed, the value of $\psi$ could be determined from the temperature dependence of the second virial coefficient near the theta temperature, and therefore values of $z$ could be determined at various temperatures and molecular weights. However, such an analysis is inadequate, since Flory's expression for $\beta$ corresponds to the Bragg–Williams approximation in the theory of mixtures and is not always accurate over a wide range of temperature. In this book, we therefore adopt $\beta$ as a basic *parame-*

*ter* representing interactions between segments and do not attempt to calculate $\beta$.

## Appendix III A. The Distribution Function, Markoff Process, and Diffusion Equation

We give here a brief description of the Markoff process which suffices for an application to polymer-chain statistics. For the details, the reader is referred to Refs. 32, 86, and 87. As an example, consider the Brownian motion of a free particle. If $\mathbf{u}(t)$ is the displacement or velocity of the particle, it forms a random process defined as follows: the variable $\mathbf{u}$ does not depend in a completely definite way on the independent variable $t$ (time), and the process is completely described only by the probabilities $P_n(\mathbf{u}_1, t_1; \mathbf{u}_2, t_2; \ldots; \mathbf{u}_n, t_n)d\mathbf{u}_1 d\mathbf{u}_2 \ldots d\mathbf{u}_n$ ($n = 1, 2, \ldots$) of finding $\mathbf{u}$ in the range $(\mathbf{u}_1, \mathbf{u}_1 + d\mathbf{u}_1)$ at time $t_1$, in the range $(\mathbf{u}_2, \mathbf{u}_2 + d\mathbf{u}_2)$ at time $t_2$, …, and in the range $(\mathbf{u}_n, \mathbf{u}_n + d\mathbf{u}_n)$ at time $t_n$. In our example, all the information about the process is contained in $P_2$. Such a process is called a (simple) Markoff process. If $\psi_1(\mathbf{u}_2, t_2|\mathbf{u}_1, t_1)d\mathbf{u}_2$ is the conditional probability that $\mathbf{u}$ lies in the range $(\mathbf{u}_2, \mathbf{u}_2 + d\mathbf{u}_2)$ at $t_2$, given that $\mathbf{u}$ has the value $\mathbf{u}_1$ at $t_1$, we have

$$P_2(\mathbf{u}_1, t_1; \mathbf{u}_2, t_2) = P_1(\mathbf{u}_1, t_1)\psi_1(\mathbf{u}_2, t_2|\mathbf{u}_1, t_1)\,. \qquad \text{(III A.1)}$$

Evidently we have also

$$\int \psi_1(\mathbf{u}_2, t_2|\mathbf{u}_1, t_1)d\mathbf{u}_2 = 1\,, \qquad \text{(III A.2)}$$

$$P_1(\mathbf{u}_2, t_2) = \int P_1(\mathbf{u}_1, t_1)\psi_1(\mathbf{u}_2, t_2|\mathbf{u}_1, t_1)d\mathbf{u}_1\,. \qquad \text{(III A.3)}$$

This is the Markoff integral equation with the transition probability $\psi_1$. A Markoff process can now be defined alternatively by stating that for such a process the transition probability of finding $\mathbf{u}$ in the range $(\mathbf{u}_n, \mathbf{u}_n + d\mathbf{u}_n)$ at $t_n$ depends on $(\mathbf{u}_n, t_n)$ and only on the value of $\mathbf{u}$ at the previous time $t_{n-1}$.

If the changes in the variable are frequent and small, as in the present case, there exists an interval $\Delta t$ of time which is long compared to intervals during which the changes in the variable occur but short compared to intervals during which the distribution function changes by appreciable amounts. Then a differential equation for the distribution function $P_1$ can be derived. If we take the interval $\Delta t$ equal to $(t_2 - t_1)$, and set $\mathbf{u}_1 = \mathbf{u} - \mathbf{r}$ and $\mathbf{u}_2 = \mathbf{u}$, Eq. (III A.3) may be rewritten in the form,

$$P(\mathbf{u}, t + \Delta t) = \int P(\mathbf{u} - \mathbf{r}, t)\psi(\mathbf{u} - \mathbf{r}, t; \mathbf{r})\,d\mathbf{r} \qquad \text{(III A.4)}$$

with

$$\int \psi(\mathbf{u}, t; \mathbf{r})\,d\mathbf{r} = 1\,, \qquad \text{(III A.5)}$$

where the subscripts 1 on $P$ and $\psi$ have been omitted, and $\psi(\mathbf{u}, t; \mathbf{r})$ is the transition probability that $\mathbf{u}$ suffers the increment $\mathbf{r}$ in the interval $\Delta t$.

Under the conditions stated above, we may expand $P(\mathbf{u}, t + \Delta t)$, $P(\mathbf{u} - \mathbf{r}, t)$, and $\psi(\mathbf{u} - \mathbf{r}, t; \mathbf{r})$ in Taylor series as follows,

$$\begin{aligned} &P(\mathbf{u}, t + \Delta t) = P(\mathbf{u}, t) + \frac{\partial P}{\partial t} \Delta t + \cdots\,, \\ &P(\mathbf{u} - \mathbf{r}, t) = P(\mathbf{u}, t) - \mathbf{r} \cdot \nabla P + \tfrac{1}{2} \mathbf{rr} : \nabla\nabla P - \cdots\,, \\ &\psi(\mathbf{u} - \mathbf{r}, t; \mathbf{r}) = \psi(\mathbf{u}, t; \mathbf{r}) - \mathbf{r} \cdot \nabla \psi + \tfrac{1}{2} \mathbf{rr} : \nabla\nabla \psi - \cdots\,, \end{aligned} \tag{III A.6}$$

where $\nabla$ is the differential operator with respect to $\mathbf{u}$. We now define the average of any function $\varphi(\mathbf{r})$ of $\mathbf{r}$ by

$$\langle \varphi(\mathbf{r}) \rangle = \int \varphi(\mathbf{r}) \psi(\mathbf{u}, t; \mathbf{r})\, d\mathbf{r}\,. \tag{III A.7}$$

For the Brownian motion under consideration, this average depends generally on $\mathbf{u}$, but does not depend on $t$. With Eqs. (III A.6) and (III A.7), Eq. (III A.4) may be rewritten as (with omission of higher-order terms)

$$\frac{\partial P}{\partial t} \Delta t = -\nabla \cdot \big( \langle \mathbf{r} \rangle P \big) + \tfrac{1}{2} \nabla\nabla : \big( \langle \mathbf{rr} \rangle P \big)\,. \tag{III A.8}$$

This is the Fokker–Planck equation in the position or velocity space. We note that the moments $\langle \mathbf{r} \rangle$ and $\langle \mathbf{rr} \rangle$ are proportional to $\Delta t$ or vanish.

We now consider the problem of ideal random-flight chains, which is obviously equivalent to that of the Brownian motion of a free particle. We may regard $P(\mathbf{u}, t)$ as the distribution function of the end-to-end distance $\mathbf{u}$ of the chain of $t$ bonds. For large $t$, it may be considered a continuous variable, and we may simply take $\Delta t = 1$. Then $\psi(\mathbf{u}, t; \mathbf{r})$ becomes equal to the bond probability $\tau(\mathbf{r})$. Since $\tau(\mathbf{r})$ is spherically symmetric, we have

$$\begin{aligned} &\langle \mathbf{r} \rangle = 0\,, \\ &\langle \mathbf{rr} \rangle = \tfrac{1}{3} \langle r^2 \rangle \mathbf{I} = \frac{a^2}{3} \mathbf{I} \end{aligned} \tag{III A.9}$$

with $\mathbf{I}$ the unit tensor. Substitution of these relations into Eq. (III A.8) leads to

$$\frac{\partial P}{\partial t} = \frac{a^2}{6} \nabla^2 P\,, \tag{III A.10}$$

which is the diffusion equation with diffusion coefficient $a^2/6$. It is well known that the solution of Eq. (III A.10) with the boundary condition, $P(\mathbf{u}, 0) = \delta(\mathbf{u})$, proper to the present problem, is the Gaussian function,[88]

$$P(\mathbf{u}, t) = (3/2\pi t a^2)^{3/2} \exp(-3u^2/2ta^2)\,. \tag{III A.11}$$

This is in agreement with the result obtained in Chapter II.

## Appendix III B. The Probability Densities for Segment Contacts

We give some of the unperturbed probability densities for segment contacts, which can readily be obtained by the use of the Wang–Uhlenbeck theorem.

$$\begin{aligned} P_0(\mathbf{R}, 0_{ij}) &= (3/2\pi a^2)^3 (j-i)^{-3/2} (n-j+i)^{-3/2} \\ &\quad \times \exp\left[-3R^2/2(n-j+i)a^2\right] , \qquad \text{(III B.1)} \\ P_0(0_{ij}) &= (3/2\pi a^2)^{3/2} (j-i)^{-3/2} , \qquad \text{(III B.2)} \\ P_0(\mathbf{R}, 0_{ij}, 0_{kl}) &= (3/2\pi a^2)^{9/2} \left[(j-i)(l-k) - L^2\right]^{-3/2} \mu^{-3/2} \\ &\quad \times \exp(-3R^2/2\mu a^2) , \qquad \text{(III B.3)} \\ P_0(0_{ij}, 0_{kl}) &= (3/2\pi a^2)^3 \left[(j-i)(l-k) - L^2\right]^{-3/2} \qquad \text{(III B.4)} \end{aligned}$$

with

$$\begin{aligned} L &= l - k && \text{for } i < k < l < j , \\ &= j - k && \text{for } i < k < j < l , \\ &= 0 && \text{for } i < j < k < l , \end{aligned}$$

$$\mu = n + \frac{(j-i)(l-k)\left[2L - (j-i) - (l-k)\right]}{(j-i)(l-k) - L^2} .$$

## Appendix III C. Perturbation Theory for a Two-Dimensional Chain

For brevity, we describe only a first-order perturbation theory of the mean-square end-to-end distance. In the two-dimensional case, the unperturbed distribution $P_0(\mathbf{R})$ and the Gaussian bond probability $\tau(\mathbf{r})$ are given by

$$P_0(\mathbf{R}) = (1/\pi\langle R^2\rangle_0) \exp(-R^2/\langle R^2\rangle_0) , \qquad \text{(III C.1)}$$

$$\tau(\mathbf{r}) = (1/\pi a^2) \exp(-r^2/a^2) . \qquad \text{(III C.2)}$$

Of course, the relations, $\langle R^2\rangle_0 = na^2$ and $\langle S^2\rangle_0 = \frac{1}{6}na^2$, hold for both two- and three-dimensional chains. The Wang-Uhlenbeck theorem (with $a_j = a$) must now be replaced by

$$P\big(\{\mathbf{\Phi}_s\}\big) = (1/\pi a^2)^s |\mathbf{C}|^{-1} \exp\left[-(1/a^2|\mathbf{C}|) \sum_{k=1}^{s} \sum_{l=1}^{s} C^{kl} \mathbf{\Phi}_k \cdot \mathbf{\Phi}_l\right] . \qquad \text{(III C.3)}$$

As in Eq. (14.9), $P(\mathbf{R})$ may be expanded as

$$P(\mathbf{R}) = P_0(\mathbf{R}) + \beta^* \sum_{i<j} \left[P_0(\mathbf{R}) P_0(0_{ij}) - P_0(\mathbf{R}, 0_{ij})\right] - \cdots , \qquad \text{(III C.4)}$$

where $\beta^*$ is the two-dimensional binary cluster integral, and is defined by

$$\beta^* = \int_0^\infty \left[1 - \exp(-w_{ij}/kT)\right] 2\pi R_{ij}\, dR_{ij} \tag{III C.5}$$

with $w_{ij}$ the pair potential between segments. The probability densities $P_0(\mathbf{R}, 0_{ij})$ and $P_0(0_{ij})$ in Eq. (III C.4) can easily be evaluated from Eq. (III C.3), and we obtain

$$\begin{aligned}\langle R^2 \rangle &= \int_0^\infty R^2 P(\mathbf{R}) 2\pi R\, dR \\ &= na^2(1 + \tfrac{1}{2}z^* - \cdots)\end{aligned} \tag{III C.6}$$

with

$$z^* = (1/\pi a^2)\beta^* n\,. \tag{III C.7}$$

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# Chapter Four
# Thermodynamic Properties of Dilute Solutions

## 18. Introduction

Having developed a detailed analysis of the statistical properties of a single polymer chain in dilute solution in the two chapters preceding, we now turn to the study of the thermodynamic behavior of polymer solutions. Intermolecular (solute-solute) interactions, which have not been considered so far, as well as solvent-solute and solvent-solvent interactions, play an important role in the present problem. An extremely unsymmetrical nature with respect to the sizes of the components is the primary characteristic of polymer solutions. This leads to large intermolecular interactions which are unusual in solutions of simple molecules. Thus, polymer solutions exhibit very large deviations from ideality, as defined by Raoult's and van't Hoff's laws. However, at infinite dilution; where the intermolecular interactions may be neglected, the ideal solution properties must be approached as an asymptotic limit even in polymer solutions.

As is well known, the thermodynamic properties of a solution are uniquely determined once the chemical potential of the solvent, $\mu_0$, in the solution is known as a function of temperature and solute concentration. $\mu_0$ is related to the Gibbs free energy, $G$ , of the solution, the activity $a_o$ of the solvent in the solution, and the osmotic pressure $\pi$ by the equations,

$$\mu_0 = \left(\frac{\partial G}{\partial N_0}\right)_{T,P,N_1} , \quad {\mu_0}^0 = \left(\frac{\partial G^0}{\partial N_0}\right)_{T,P,N_1} , \tag{18.1}$$

$$\Delta\mu_0 \equiv \mu_0 - {\mu_0}^0 = kT \ \ln \ a_0 = -{V_0}^0\pi \, , \tag{18.2}$$

where the superscript 0 refers to the pure solvent state, ${V_0}^0$ is the molecular volume of the solvent,and $N_0$ and $N_1$ are the numbers of the solvent and solute molecules in the solution, respectively, assuming a binary solution. Thus our problem is to derive theoretical expressions for $G$ or $\pi$ with the tools of statistical mechanics, assuming appropriate models for the polymer solutions.

There are two lines of approach to the problem : one uses a discrete model and the other a continuum model. The first model leads to a lattice theory, and was the basis of the statistical thermodynamics of polymer solutions in the 1940s. It is still useful to interpret the behavior of the solvent activity over the whole concentration range. The second model leads to the distribution function theory, in which the osmotic pressure may be expressed in terms of the molecular distribution functions, and therefore is in the spirit of the preceding chapters. Treatments of polymer solutions along this line are based on either the general solution theory of McMillan and Mayer[1] or the pair correlation function approach in the theory of simple liquids.[2, 3] The McMillan–Mayer theory is particularly convenient for the study of dilute solutions, while it is in practice not possible to actually carry out calculations for the case of concentrated solutions where the latter approach becomes more useful. It should be noted that Kirkwood and Buff[4] have developed an alternative general solution theory which is necessarily equivalent to the McMillan–Mayer theory since both are formally exact. The McMillan–Mayer approach is more useful than the Kirkwood–Buff approach if the osmotic pressure is to be calculated.

Now, the McMillan–Mayer theory verifies that there exists a formal analogy between the osmotic pressure and gas pressure ; corresponding to the *virial expansion* for the gas pressure, the osmotic pressure $\pi$ may be expanded in powers of the solute concentration $c$ (in grams per unit volume) as follows,

$$\pi = RT\left(\frac{1}{M}c + A_2c^2 + A_3c^3 + \cdots\right), \tag{18.3}$$

where $R$ is the gas constant and $M$ is the molecular weight of the solute. The coefficients $A_j$ are called the j*th virial coefficients*, and can be written in terms of the molecular distribution functions. From Eq. (18.3), van't Hoff's law is seen to hold asymptotically at infinite dilution, and even to be valid under certain conditions over a finite range of concentration when the second virial coefficient and also higher virial coefficients vanish.

A large part of the present chapter will be devoted to a calculation of the second virial coefficient for linear flexible chains. This then completes the two-parameter theory for the equilibrium properties of dilute polymer solutions in conjunction with the theory of excluded-volume effects described in the preceding chapter. Some discussion of the third virial coefficient and the effects of molecular weight heterogeneity and branching will also be given in the later sections of this chapter. It will be convenient to give first a relatively brief description of the McMillan–Mayer theory in a form convenient for use in our applications.

## 19. The McMillan–Mayer General Theory of Solutions

The McMillan–Mayer theory[1, 2] is an extension of the Ursell–Mayer theory of imperfect gases to multicomponent systems. It is developed conveniently from the grand canonical ensemble, which ensemble is very useful in the statistical-mechanical theory of multicomponent systems. The system to be considered is of volume $V$, in a large heat bath at temperature $T$, and is open with respect to the molecules in the system. That is, both heat (energy) and matter (molecules) can be transported across the walls of the system so that the energy and the numbers $N_1$, $N_2$, …, $N_r$ of molecules of the $r$ species present, 1, 2, …, $r$, may fluctuate about their mean values. The independent thermodynamic variables are then $V, T$ and the chemical potentials $\mu_1$, $\mu_2$, …, $\mu_r$. The grand partition function $\Xi(\boldsymbol{\mu}, V, T)$ is related to the thermodynamic function $pV$ for the variables $\boldsymbol{\mu}$, $V$ and $T$ by the equation,

$$\Xi(\boldsymbol{\mu}, V, T) = e^{pV/kT}\,, \tag{19.1}$$

where $\boldsymbol{\mu}$ denotes a set of chemical potentials, $\boldsymbol{\mu} = \mu_1,\ \mu_2,\ \ldots,\ \mu_r$, and $p$ is the pressure of the system. The idea of McMillan and Mayer consists in expressing the pressure and the distribution functions at any chemical potential set $\boldsymbol{\mu}$ (or activity set) in terms of those at any other chemical potential set $\boldsymbol{\mu}^*$, and then deriving an expression for the gas pressure or the osmotic pressure by a suitable choice of the reference state indicated by $\boldsymbol{\mu}^*$.

Before proceeding to develop the theory, it is appropriate to describe the McMillan–Mayer symbolism which makes the resulting equations appear relatively simple. The symbol $(i_s) = q_{1i_s}, q_{2i_s}, \ldots, q_{f_s i_s}$ denotes all the coordinates (internal and external) of the $i$th molecule of species $s$ in the Cartesian space of the atoms composing the molecules, where $f_s$ is the number of (classical) translational and rotational (internal and external) degrees of freedom of an $s$ molecule. Note that for the classical case in which we are interested, the internal-vibrational degree of freedom and the electronic contributions may be neglected. The position and configuration of the molecule are determined completely by the $f_s$ coordinates, $q_{1i_s}, \ldots, q_{f_s i_s}$. The coordinates of $N_s$ molecules of species $s$ are represented by $\{N_s\} = (1_s), (2_s), \ldots, (i_s), \ldots, (N_s)$. In general, any boldface symbol indicates a set of numbers or variables, one for each species. Thus, as in the definition of $\boldsymbol{\mu}$, the boldface $\mathbf{N}$ is used to indicate a set of numbers of molecules : $\mathbf{N} = N_1$, $N_2$, …, $N_s$, …, $N_r$, the number of molecules under consideration being $N = \sum_{s=1}^{r} N_s$. The coordinates of all the molecules of such a set $\mathbf{N}$ are represented by $\{\mathbf{N}\} = \{N_1\}, \{N_2\}, \ldots, \{N_r\}$. The differential volume elements are similarly defined by $d(i_s) = dq_{1i_s} dq_{2i_s} \cdots dq_{f_s i_s}$, $d\{N_s\} = d(1_s)d(2_s) \cdots d(N_s)$, and $d\{\mathbf{N}\} = d\{N_1\}d\{N_2\} \cdots d\{N_r\}$.

We now begin by considering a closed system containing a set of molecules $\mathbf{N}$. The partition function $Q_{\mathbf{N}}(\mathbf{N}, V, T)$ (canonical ensemble) may be written as

$$Q_{\mathbf{N}} = \frac{Z_{\mathbf{N}}}{\prod_s (N_s! {\Lambda_s}^{3N_s})} \tag{19.2}$$

with

$$Z_{\mathbf{N}} = \int \exp\left(-\frac{U_{\mathbf{N}}}{kT}\right) d\{\mathbf{N}\}\,, \tag{19.3}$$

where $Z_{\mathbf{N}}$ is the configurational partition function and $U_{\mathbf{N}} \equiv U_{\mathbf{N}}(\{\mathbf{N}\})$ is the potential energy of the system. The constants $\Lambda_s$ (thermal de Broglie wavelengths) result from integration of $\exp(-H_{\mathbf{N}}/kT)$ over the momenta, where $H_{\mathbf{N}}$ is the Hamiltonian. For example, in the simple case of a classical monatomic fluid mixture, $\Lambda_s = h/(2\pi m_s kT)^{1/2}$ where $h$ is Planck's constant and $m_s$ is the mass of species $s$. The zero of potential energy for intermolecular interactions is chosen at infinite separation of all molecules, while the zero for intramolecular interactions is chosen in such a way that $Z_{\mathbf{N}} = \Pi_s V^{N_s}$ for a perfect-gas mixture. Let $\mathbf{n}$ be a particular subset of molecules. The (specific) probability density of finding the set $\mathbf{n}$ in the volume element $d\{\mathbf{n}\}$ at $\{\mathbf{n}\}$ irrespective of the coordinates of the remaining molecules $(\mathbf{N} - \mathbf{n})$ is

$$P_{\mathbf{N}}^{(\mathbf{n})}(\{\mathbf{n}\}) = Z_{\mathbf{N}}^{-1} \int \exp\left[-\frac{U_{\mathbf{N}}(\{\mathbf{N}\})}{kT}\right] d\{\mathbf{N} - \mathbf{n}\} \tag{19.4}$$

with

$$\int P_{\mathbf{N}}^{(\mathbf{n})}(\{\mathbf{n}\})\, d\{\mathbf{n}\} = 1\,. \tag{19.5}$$

If $\rho_{\mathbf{N}}^{(\mathbf{n})}(\{\mathbf{n}\})$ is the (generic) probability density of finding any $n_1$ molecules of species 1 (out of $N_1$), ..., any $n_r$ molecules of species $r$ (out of $N_r$) in $d\{\mathbf{n}\}$ at $\{\mathbf{n}\}$, we have

$$\rho_{\mathbf{N}}^{(\mathbf{n})}(\{\mathbf{n}\}) = \left[\prod_s \frac{N_s!}{(N_s - n_s)!}\right] P_{\mathbf{N}}^{(\mathbf{n})}(\{\mathbf{n}\}) \tag{19.6}$$

with

$$\int \rho_{\mathbf{N}}^{(\mathbf{n})}(\{\mathbf{n}\})\, d\{\mathbf{n}\} = \prod_s \frac{N_s!}{(N_s - n_s)!}\,. \tag{19.7}$$

Next, in an open system, the grand partition function is

$$\begin{aligned} \boldsymbol{\Xi} = e^{pV/kT} &= \sum_{\mathbf{N} \geq \mathbf{0}} e^{\mathbf{N}\cdot\boldsymbol{\mu}/kT} Q_{\mathbf{N}} \\ &= \sum_{\mathbf{N} \geq 0} \left(\prod_s \frac{{z_s}^{N_s}}{N_s\,!}\right) Z_{\mathbf{N}} \end{aligned} \tag{19.8}$$

with

$$z_s \equiv \frac{e^{\mu_s/kT}}{{\Lambda_s}^3}\,, \tag{19.9}$$

where we have used Eq. (19.2) and the summation runs over all sets of numbers $\mathbf{N}$,i.e., $0 \leq N_s \leq \infty$ for all $s$. The quantity $z_s$ defined by Eq. (19.9) is called the *fugacity* (activity) of species $s$. The probability $P_{\mathbf{N}}$ of the open system containing exactly the numbers $\mathbf{N}$ of molecules is given by

$$P_{\mathbf{N}} = \Xi^{-1}\left(\prod_s \frac{{Z_s}^{N_s}}{N_s\,!}\right) Z_{\mathbf{N}}\,. \tag{19.10}$$

Therefore,the generic probability density, in an open system, of finding any $n_1$ molecules of species 1,etc., in $d\{\mathbf{n}\}$ at $\{\mathbf{n}\}$ is

$$\rho^{(\mathbf{n})}(\{\mathbf{n}\}) = \sum_{\mathbf{N}\geq\mathbf{n}} P_{\mathbf{N}}{\rho_{\mathbf{N}}}^{(\mathbf{n})}(\{\mathbf{n}\}) \tag{19.11}$$

with

$$\int \rho^{(\mathbf{n})}(\{\mathbf{n}\})\;d\{\mathbf{n}\} = \sum_{\mathbf{N}\geq\mathbf{n}} P_{\mathbf{N}}\left[\prod_s \frac{N_s!}{(N_s-n_s)!}\right] = \left\langle \prod_s \frac{N_s!}{(N_s-n_s)!}\right\rangle\,. \tag{19.12}$$

In particular,if $\mathbf{n}$ is a single molecule of species $s$, Eq. (19.12) reduces to

$$\int \rho^{(1)}(i_s)\;d(i_s) = \langle N_s\rangle\,. \tag{19.13}$$

Further, $\rho^{(1)}$ depends on the internal coordinates $(i_s)_{\text{int}}$ but not on the external coordinates $(i_s)_{\text{ext}}$, and we therefore have

$$\int \rho^{(1)}(i_s)\;d(i_s)_{\text{int}} = \langle N_s\rangle/V = \rho_s \tag{19.14}$$

with $\rho_s$ the number density of species $s$. On putting $\mathbf{m} = \mathbf{N} - \mathbf{n}$, Eqs. (19.4), (19.6), and (19.10), when substituted in Eq. (19.11), lead to

$$\frac{\Xi(\mathbf{z}, V, T)}{\prod_s {z_s}^{n_s}}\rho^{(\mathbf{n})}(\{\mathbf{n}\}, \mathbf{z}, T) = \sum_{\mathbf{m}\geq\mathbf{0}}\left(\prod_s \frac{{z_s}^{m_s}}{m_s!}\right)\int \exp\left(-\frac{U_{\mathbf{m}+\mathbf{n}}}{kT}\right) d\{\mathbf{m}\}\,, \tag{19.15}$$

where we have indicated explicitly that $\rho^{(\mathbf{n})}$ is also a function of $T$ and the fugacity set $\mathbf{z} = z_1, \ldots, z_r$ with the independent variables changed from $\boldsymbol{\mu}$ to $\mathbf{z}$. Note that in a macroscopic system ($V \to \infty$), $\rho^{(\mathbf{n})}$ is independent of $V$.

In the limit of $\mathbf{z} = \mathbf{0}$ (perfect gas), Eq. (19.8) becomes

$$pV/kT = \ln \Xi = V\sum_s z_s + \cdots\,. \tag{19.16}$$

From the general relation for an open system,

$$\langle N_s \rangle = z_s \left( \frac{\partial \ln \Xi}{\partial z_s} \right)_{V,T,z_{\alpha \neq s}} , \tag{19.17}$$

we then find that $\langle N_s \rangle = V z_s$, or $\rho_s = z_s$ in a perfect gas. That is, $z_s$ is normalized so that $z_s \to \rho_s$ as $\mathbf{z}$ (and $\boldsymbol{\rho}$ )$\to \mathbf{0}$. In the limit of $\mathbf{z} = \mathbf{0}$, Eq. (19.15) reduces to

$$\rho^{(\mathbf{n})}(\{\mathbf{n}\}, \mathbf{0}, T) = \left( \prod_s {\rho_s}^{n_s} \right) \exp \left[ -\frac{U_{\mathbf{n}}(\{\mathbf{n}\})}{kT} \right] . \tag{19.18}$$

We now define the distribution function $F_{\mathbf{n}}(\{\mathbf{n}\})$ by

$$F_n(\{\mathbf{n}\}) = \frac{\rho^{(\mathbf{n})}(\{\mathbf{n}\})}{\prod\limits_s {\rho_s}^{n_s}} . \tag{19.19}$$

For the case of a monatomic fluid, this function is identical with the correlation function $g^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n)$. Because of the definition of $\rho^{(\mathbf{n})}$, when all the molecules of the set $\mathbf{n}$ are widely separated,

$$\rho^{(\mathbf{n})}(\{\mathbf{n}\}) \to \prod_s \rho^{(1)}(1_s) \rho^{(1)}(2_s) \cdots \rho^{(1)}(n_s) ,$$

and therefore from Eq. (19.14) we have

$$\int F_{\mathbf{n}}(\{\mathbf{n}\}) d\{\mathbf{n}\}_{\text{int}} \to 1 . \tag{19.20}$$

Thus, in a macroscopic system ($V \to \infty$), $F_{\mathbf{n}}$ is normalized as

$$V^{-n} \int F_{\mathbf{n}}(\{\mathbf{n}\}) d\{\mathbf{n}\} = 1 . \tag{19.21}$$

This normalization property of $F_{\mathbf{n}}$ is very useful. It is to be noted that $F_{\mathbf{n}}$ is also a function of $\mathbf{z}$ and $T$. In what follows, the equations are written in terms of $F_{\mathbf{n}}$ instead of $\rho^{(\mathbf{n})}$. Before discussing further developments, it is pertinent to consider the physical meaning of $F_{\mathbf{n}}$ from a different point of view.

Let us define a quantity $W_{\mathbf{n}}$ by the equation,

$$\exp \left[ -\frac{W_{\mathbf{n}}(\{\mathbf{n}\}, \mathbf{z}, T)}{kT} \right] = F_{\mathbf{n}}(\{\mathbf{n}\}, \mathbf{z}, T) . \tag{19.22}$$

When there are $\mathbf{N}$ molecules in the system in the configuration $\{\mathbf{N}\}$, including the set $\mathbf{n}$ in the configuration $\{\mathbf{n}\}$, the component $f_{q_{\mathbf{n}}}$ of force along an arbitrary coordinate $q_{\mathbf{n}}$ associated with one of the molecules of the set $\mathbf{n}$, owing to intra-and intermolecular interactions, is given by

$$f_{q_{\mathbf{n}}} = -\frac{\partial U_{\mathbf{N}}}{\partial q_{\mathbf{n}}} . \tag{19.23}$$

Now if we keep the set of molecules $\mathbf{n}$ fixed in the configuration $\{\mathbf{n}\}$, but average this force over all configurations of the remaining $(\mathbf{N}-\mathbf{n})$ molecules, we obtain

$$\langle f_{q_\mathbf{n}}\rangle_\mathbf{N}^{(\mathbf{n})} = \frac{\int(-\partial U_\mathbf{N}/\partial q_\mathbf{n})\exp(-U_\mathbf{N}/kT)d\{\mathbf{N}-\mathbf{n}\}}{\int\exp(-U_\mathbf{N}/kT)d\{\mathbf{N}-\mathbf{n}\}}\,, \tag{19.24}$$

and therefore from Eqs. (19.4),(19.6) ,and(19.24)

$$\langle f_{q_\mathbf{n}}\rangle_\mathbf{N}^{(\mathbf{n})} = kT\frac{\partial}{\partial q_\mathbf{n}}\ln\rho_\mathbf{N}^{(\mathbf{n})}\,. \tag{19.25}$$

The probability density that the system contains $\mathbf{N}$ molecules and a set of molecules $\mathbf{n}$ is found in $d\{\mathbf{n}\}$ at $\{\mathbf{n}\}$ is $P_\mathbf{N}\rho_\mathbf{N}^{(\mathbf{n})}$ , and $\langle f_{\mathbf{q_n}}\rangle_\mathbf{N}^{(\mathbf{n})}$ is the average component of force along $q_\mathbf{n}$ under these conditions. Therefore, the further average over all values of $\mathbf{N}$ for the open system is

$$\langle f_{q_\mathbf{n}}\rangle^{(\mathbf{n})} = \frac{\sum_{\mathbf{N}\geq\mathbf{n}}P_\mathbf{N}\rho_\mathbf{N}^{(\mathbf{n})}\langle f_{q_\mathbf{n}}\rangle_\mathbf{N}^{(\mathbf{n})}}{\sum_{\mathbf{N}\geq\mathbf{n}}P_\mathbf{N}\rho_\mathbf{N}^{(\mathbf{n})}}\,. \tag{19.26}$$

On the other hand, from Eqs. (19.11), (19.19), and (19.22) we have

$$\exp\left(-\frac{W_\mathbf{n}}{kT}\right) = \frac{\sum_{\mathbf{N}\geq\mathbf{n}}P_\mathbf{N}\rho_\mathbf{N}^{(\mathbf{n})}}{\prod_s{\rho_s}^{n_s}}\,. \tag{19.27}$$

Differentiating both sides of Eq. (19.27) with respect to $q_\mathbf{n}$ and comparing the resulting equation with Eq. (19.26) with substitution of Eq. (19.25), we find

$$\langle f_{q_\mathbf{n}}\rangle^{(\mathbf{n})} = -\frac{\partial W_\mathbf{n}}{\partial q_\mathbf{n}}\,. \tag{19.28}$$

Thus $W_\mathbf{n}$ (and also $W_\mathbf{n}$+const.) is the *potential of mean force.* A particular case of $W_\mathbf{n}$ has already been introduced in the preceding chapters. In the limit of $\mathbf{z}$ (or $\boldsymbol{\rho}$) $= \mathbf{0}$, $W_\mathbf{n}$ becomes $U_\mathbf{n}$, as seen from Eqs. (19.18), (19.19), and (19.22). As already mentioned in Section 13, the potential energy $U_\mathbf{n}$ may be expressed as a sum of component potential energies $u_{ij}$ arising from the interaction between pairs of molecules only, but the potential of mean force $W_\mathbf{n}$ must be expressed as a sum of terms of all kinds of component potentials $w_{\boldsymbol{\nu}}$. That is, if we denote a subset of the set of coordinates $\{\mathbf{n}\}$ of $\mathbf{n}$ molecules by the symbol $\{\boldsymbol{\nu}\}_\mathbf{n}$, we may write

$$W_\mathbf{n} = \sum_{\boldsymbol{\nu}_\mathbf{n}} w_{\boldsymbol{\nu}}\,, \tag{19.29}$$

where the sum is taken over all possible subsets, and the terms $w_{\boldsymbol{\nu}}$ for $\nu > 2$ may be regarded as corrections for the deviation of $W_\mathbf{n}$ from a sum of pair terms only.

We return now to the grand partition function. Denote either side of Eq. (19.15) by $f(\mathbf{z})$. The right-hand side of Eq. (19.15) may be considered to be the expansion of $f(\mathbf{z})$ around $\mathbf{z} = \mathbf{0}$, the expansion coefficients being integrals of the distribution functions $F_{\mathbf{n}+\mathbf{m}}(\{\mathbf{n}+\mathbf{m}\}, \mathbf{0}, T)$. Using Taylor's theorem,

$$f(\mathbf{z}) = \sum_{\mathbf{l}\geq\mathbf{0}} \left[\prod_s \frac{(z_s - {z_s}^*)^{l_s}}{l_s!}\right] \left[\frac{\partial^{l_1+\cdots+l_r} f(\mathbf{z})}{\partial {z_1}^{l_1}\cdots\partial {z_r}^{l_r}}\right]_{\mathbf{z}=\mathbf{z}^*} \tag{19.30}$$

is the expansion of $f(\mathbf{z})$ around $\mathbf{z} = \mathbf{z}^*$, where $\mathbf{z}^*$ is some particular fugacity set. On putting $\mathbf{m} = \mathbf{l} + \mathbf{q}$, differentiation of the right-hand side of Eq. (19.15) for $f(\mathbf{z})$ gives

$$\frac{\partial^{l_1+\cdots+l_r} f(\mathbf{z})}{\partial {z_1}^{l_1}\cdots\partial {z_r}^{l_r}} = \sum_{\mathbf{q}\geq\mathbf{0}} \left(\prod_s \frac{{z_s}^{q_s}}{q_s!}\right) \int \exp\left(-\frac{U_{\mathbf{n}+\mathbf{l}+\mathbf{q}}}{kT}\right) d\{\mathbf{l}+\mathbf{q}\}\,. \tag{19.31}$$

Next, in Eq. (19.15), we replace $\mathbf{n}$ by $(\mathbf{n} + \mathbf{l})$ and $\mathbf{m}$ by $\mathbf{q}$, and integrate both sides of the equation over $\{\mathbf{l}\}$. Comparing the result with Eq. (19.31), we find

$$\frac{\partial^{l_1+\cdots+l_r} f(\mathbf{z})}{\partial {z_1}^{l_1}\cdots\partial {z_r}^{l_r}} = \frac{\Xi(\mathbf{z})}{\prod_s {z_s}^{n_s+l_s}} \int \rho^{(\mathbf{n}+\mathbf{l})}(\{\mathbf{n}+\mathbf{l}\}, \mathbf{z})d\{\mathbf{l}\}\,. \tag{19.32}$$

Substituting Eq. (19.32) into Eq. (19.30), we have the desired result (writing $\mathbf{m}$ instead of $\mathbf{l}$)

$$\begin{aligned}\frac{\Xi(\mathbf{z})}{\prod_s {\gamma_s}^{n_s}} F_{\mathbf{n}}(\{\mathbf{n}\}, \mathbf{z}) = \Xi(\mathbf{z}^*) \sum_{\mathbf{m}\geq\mathbf{0}} &\left[\prod_s \frac{(z_s - {z_s}^*)^{m_s}}{m_s!({\gamma_s}^*)^{n_s+m_s}}\right] \\ &\times \int F_{\mathbf{n}+\mathbf{m}}(\{\mathbf{n}+\mathbf{m}\}, \mathbf{z}^*)d\{\mathbf{m}\}\,,\end{aligned} \tag{19.33}$$

where we have used Eq. (19.19), and $\gamma_s$ is an activity coefficient defined by $\gamma_s = z_s/\rho_s$ with $\gamma_s \equiv \gamma_s(\mathbf{z})$ and $\rho_s \equiv \rho_s(\mathbf{z})$, so that ${\gamma_s}^* = {z_s}^*/{\rho_s}^*$. Equation (19.33) is a generalized form of the grand partition function for a multicomponent system. It enables us to calculate the pressure $p(\mathbf{z})$, the activity coefficients $\gamma_s(\mathbf{z})$, and the distribution functions $F_{\mathbf{n}}(\{\mathbf{n}\}, \mathbf{z})$, at any fugacity set $\mathbf{z}$ in terms of the pressure $p(\mathbf{z}^*)$, the activity coefficients $\gamma_s(\mathbf{z}^*)$, and the distribution functions $F_{\mathbf{n}}(\{\mathbf{n}\}, \mathbf{z}^*)$, at any other fugacity set $\mathbf{z}^*$. In particular, if $\mathbf{n} = \mathbf{0}$ in Eq. (19.33), since by definition $\rho^{(\mathbf{0})} = F_{\mathbf{0}} = 1$, we obtain for the difference between pressures at different fugacities (writing $\mathbf{M}$ instead of $\mathbf{m}$)

$$\begin{aligned}\frac{\Xi(\mathbf{z})}{\Xi(\mathbf{z}^*)} &= \exp\left\{\frac{[p(\mathbf{z}) - p(\mathbf{z}^*)]V}{kT}\right\} \\ &= \sum_{\mathbf{M}\geq\mathbf{0}} \left[\prod_s \frac{1}{M_s!}\left(\frac{z_s - {z_s}^*}{{\gamma_s}^*}\right)^{\mathbf{M}_s}\right] \int F_{\mathbf{M}}(\{\mathbf{M}\}, \mathbf{z}^*)d\{\mathbf{M}\}\,.\end{aligned} \tag{19.34}$$

We now proceed to deduce the *cluster expansion* for the pressure. We denote, as before, a subset of coordinates of $\mathbf{m}$ particular molecules of the set $\mathbf{M}$ by the symbol $\{\mathbf{m}\}_{\mathbf{M}}$, and a complete set of $k$ unconnected subsets $\{\mathbf{m}_i\}_{\mathbf{M}}$ $(1 \le i \le k)$ of the set $\mathbf{M}$ by the symbol $\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}$ with $\sum_{i=1}^{k} \mathbf{m}_i = \mathbf{M}$. By unconnected subsets we mean that no molecule occurs in more than one subset, but every molecule of the set $\mathbf{M}$ occurs in one of the $k$ subsets. Further, it must be noted that two subsets of identical size are different if they do not contain the same particular molecules. We then define $g$ functions implicitly by

$$F_{\mathbf{M}}(\{\mathbf{M}\}, \mathbf{z}) = \sum_{\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}} \prod_{i=1}^{k} g_{\mathbf{m}}(\{\mathbf{m}_i\}_{\mathbf{M}}, \mathbf{z}) \,, \tag{19.35}$$

where the sum is taken over all possible sets of unconnected subsets. For example, if molecules of the set $\mathbf{M}$ are of the same species and $M = 1$, 2, or 3, we have

$$\begin{aligned} F_1(1) &= g_1(1) \,, \\ F_2(1,2) &= g_2(1,2) + g_1(1)g_1(2) \,, \\ F_3(1,2,3) &= g_3(1,2,3) + g_2(2,3)g_1(1) + g_2(1,3)g_1(2) \,, \\ &\quad + g_2(1,2)g_1(3) + g_1(1)g_1(2)g_1(3) \,, \end{aligned} \tag{19.36}$$

where we have used the symbol (1,2,..., $n$) to represent explicitly the set of coordinates $\{n\}$ of $n$ molecules of the same species. The functions $g_{\mathbf{m}}(\{\mathbf{m}\}, \mathbf{z})$ are so defined that they approach zero if the values of the coordinates $\{\mathbf{m}\}$ are such that there exist two subsets $\{\boldsymbol{\mu}\}$ and $\{\boldsymbol{\nu}\}$ $(\boldsymbol{\mu} + \boldsymbol{\nu} = \mathbf{m})$ with all distances large between any molecule of $\{\boldsymbol{\mu}\}$ and any molecule of $\{\boldsymbol{\nu}\}$. For example, $g_2(1,2) = F_2(1,2) - F_1(1)F_1(2) \to 0$, as the distance $R_{12}$ between molecules 1 and 2 $\to \infty$, since by definition $F_2(1,2) \to F_1(1)F_1(2)$ [and $W_2(1,2) \to W_1(1) + W_1(2)$ ], as $R_{12} \to \infty$; $g_2(1,2)$ represents the amount by which $F_2(1,2)$ deviates from the simple product $F_1(1)F_1(2)$. We further define *cluster integrals* $b_{\mathbf{m}}(\mathbf{z})$ by

$$V\left(\prod_s m_s!\right) b_{\mathbf{m}}(\mathbf{z}) = \int g_{\mathbf{m}}(\{\mathbf{m}\}_{\mathbf{M}}, \mathbf{z}) d\{\mathbf{m}\}_{\mathbf{M}} \,. \tag{19.37}$$

It must be noted that the integrals of (19.37) depend only on the numerical value of $\mathbf{m} = m_1, \ldots, m_r$, and not on which of the $M_s$ molecules constitute the $m_s$, and that in a macroscopic system, $b_{\mathbf{m}}(\mathbf{z})$ is independent of $V$ if the interaction forces drop to zero sufficiently rapidly with increasing separation. A subdivision of the set $\mathbf{M}$ into $\mu_{\mathbf{m}}$ subsets of size $\mathbf{m}$ may be obtained in $\prod_s M_s! / \prod_{\mathbf{m}} (\prod_s m_s!)^{\mu_{\mathbf{m}}} \mu_{\mathbf{m}}!$ different ways, all of which appear in the sum of (19.35). Integration over $\{\mathbf{M}\}$ thus gives

$$\int F_{\mathbf{M}}(\{\mathbf{M}\}, \mathbf{z}) d\{\mathbf{M}\} = \left(\prod_s M_s!\right) \sum_{\mu_{\mathbf{m}}} \prod_{\mathbf{m}} [V b_{\mathbf{m}}(\mathbf{z})]^{\mu_{\mathbf{m}}} / \mu_{\mathbf{m}}! \,, \tag{19.38}$$

where the sum over $\mu_{\mathbf{m}}$ is subject to the restriction $\sum_{\mathbf{m}} \mathbf{m} \mu_{\mathbf{m}} = \mathbf{M}$, i.e., $\sum_{\mathbf{m}} m_s \mu_{\mathbf{m}} = M_s$ for all $s$. Substitution of Eq. (19.38) into Eq. (19.34) leads to

$$\exp\left\{\frac{\{[p(\mathbf{z})-p(\mathbf{z}^*)]V}{kT}\right\} = \sum_{\mu_{\mathbf{m}}}\prod_{\mathbf{m}}\frac{1}{\mu_{\mathbf{m}}!}\left[Vb_{\mathbf{m}}(\mathbf{z}^*)\prod_s\left(\frac{z_s-{z_s}^*}{{\gamma_s}^*}\right)^{m_s}\right]^{\mu_{\mathbf{m}}}$$
$$= \exp\sum_{\mathbf{m}\geq\mathbf{0}}\left[Vb_{\mathbf{m}}(\mathbf{z}^*)\prod_s\left(\frac{z_s-{z_s}^*}{{\gamma_s}^*}\right)^{m_s}\right], \tag{19.39}$$

where the summation over $\mathbf{M}$ removes the restriction on the $\mu_{\mathbf{m}}$, and the sum of the first line is just the expansion of the exponential of the second line. We therefore have

$$p(\mathbf{z})-p(\mathbf{z}^*) = kT\sum_{\mathbf{m}\geq\mathbf{0}} b_{\mathbf{m}}(\mathbf{z}^*)\prod_s\left(\frac{z_s-{z_s}^*}{{\gamma_s}^*}\right)^{m_s}, \tag{19.40}$$

where $b_{\mathbf{0}} = 0$, and $b_{\mathbf{m}} = 1$ for the subscript set $m_s = \delta_{rs}$. Equation (19.40) is the cluster expansion for the pressure. We note that the integrals of $F_{\mathbf{M}}$ relate to the integrals of $g_{\mathbf{m}}$ according to the relationship between the moments and cumulants. Since from Eq. (19.17) we have the relation, $(\partial p/\partial z_s)_{T,z_{\alpha\neq s}} = kT\rho_s/z_s$, differentiation of Eq. (19.40) leads to a similar expansion for the density,

$$\rho_s(\mathbf{z}) = \left(\frac{z_s}{z_s-{z_s}^*}\right)\sum_{\mathbf{m}\geq\mathbf{0}} m_s b_{\mathbf{m}}(\mathbf{z}^*)\prod_r\left(\frac{z_r-{z_r}^*}{{\gamma_r}^*}\right)^{m_r}. \tag{19.41}$$

Equations (19.40) and (19.41) lead to the virial expansion for the gas pressure or the osmotic pressure;the pressure may be expanded in powers of the densities instead of the fugacity differences by inverting the series of (19.41). Although we have a general method for doing this, the procedure followed is to evaluate explicitly the first few coefficients in the virial expansions.

Gas Pressure. As an illustration, we consider a one-component gas, and drop the subscript $s$. Set $z^* = 0$, in which case $\gamma^* = 1$ and $p(z^*) = 0$, and then Eqs. (19.40) and (19.41) become

$$p(z) = kT\sum_{m\geq 1} b_m^0 z^m, \tag{19.42}$$

$$\rho(z) = \sum_{m\geq 1} m b_m^0 z^m, \tag{19.43}$$

where $b_m^0 = b_m(0)$; that is, the cluster integrals are to be evaluated at zero fugacity or density. The coefficients $a_2$, $a_3$, … in the inverted series, $z = \rho + a_2\rho^2 + a_3\rho^3 + \cdots$, are found by substituting this series into Eq.(19.43) for $z$. Having found the coefficients, the inverted series is then introduced in Eq. (19.42), and we obtain the virial expansion for the gas pressure,

$$\begin{aligned} p &= kT(\rho - \tfrac{1}{2}{\beta_1}^0\rho^2 - \tfrac{2}{3}{\beta_2}^0\rho^3 - \cdots) \\ &= kT(\rho + {B_2}^0\rho^2 + {B_3}^0\rho^3 + \cdots)\,, \end{aligned} \tag{19.44}$$

where

$${B_n}^0 = -\frac{n-1}{n}{\beta_{n-1}}^0\,, \tag{19.45}$$

$$\begin{aligned} {\beta_1}^0 &= 2{b_2}^0\,, \\ {\beta_2}^0 &= 3{b_3}^0 - 6({b_2}^0)^2\,. \end{aligned} \tag{19.46}$$

The quantity $\beta_n$ is called the n*th irreducible cluster integral.*

Osmotic Pressure. We consider a solution composed of a solvent, species 0, and solutes, species 1, 2, ..., $\sigma$, ..., $\tau$, ..., $r$. Suppose we have a membrane permeable to solvent species 0 but not to solute species 1, ..., $r$. Let the state $\mathbf{z}^*$ in Eqs. (19.40) and (19.41) refer to pure solvent on one side of the membrane (which therefore contains species 0 only). Let the value of $z_0$ be denoted by ${z_0}^*$, while each $z_\sigma = \rho_\sigma = 0$. We summarize this by $\mathbf{z}^* = {z_0}^*,\ \mathbf{0}_\sigma$. Let the state $\mathbf{z}$ in Eqs. (19.40) and (19.41) refer to a solution on the other side of the membrane which contains species 0, 1, ..., $r$ and which is in equilibrium, with respect to solvent species 0, with the pure solvent. We represent this by $\mathbf{z} = {z_0}^*$, $\mathbf{z}_\sigma$, since at equilibrium $z_0$ must have the same value, ${z_0}^*$, on the solvent and solution sides of the membrane. Under these conditions (osmotic conditions) the pressure difference across the membrane $[p(\mathbf{z}) - p(\mathbf{z}^*)]$ is, by definition, just the osmotic pressure $\pi$. With this particular choice of $\mathbf{z}$ and $\mathbf{z}^*$ in Eqs. (19.40) and (19.41), the only terms in the sums that contribute to $\pi$ and $\rho_\sigma$ are those for which $\mathbf{m}$ represents a set of solute molecules only, that is, $\mathbf{m} = m_1, \ldots, m_r$. Thus we have

$$\pi = kT \sum_{\mathbf{m}\geq\mathbf{0}} b_{\mathbf{m}}^0 \prod_{\sigma=1}^{r} {\alpha_\sigma}^{m_\sigma}\,, \tag{19.47}$$

$$\rho_\sigma = \sum_{\mathbf{m}\geq\mathbf{0}} m_\sigma b_{\mathbf{m}}^0 \prod_{\tau=1}^{r} {\alpha_\tau}^{m_\tau}\,, \tag{19.48}$$

where $\alpha_\sigma = (z_\sigma - {z_\sigma}^*)/{\gamma_\sigma}^* = z_\sigma/{\gamma_\sigma}^0$ with ${\gamma_\sigma}^0(\equiv {\gamma_\sigma}^*)$ the activity coefficient of solute species $\sigma$ in the pure solvent with fugacity set ${z_0}^*$, $\mathbf{0}_\sigma$, that is, in a solution which is *infinitely dilute* with respect to all solute species but not with respect to solvent species. Similarly, $b_{\mathbf{m}}^0$ is the cluster integral for a set of solute molecules $\mathbf{m}$ in a solution which is infinitely dilute with respect to solute molecules, that is, for a set of solute molecules in a pure solvent. Thus Eqs. (19.42), (19.43), (19.47), and (19.48) show that the gas pressure as a function of the densities of all the species present, and the osmotic pressure as a function of the densities of the solutes present may be expressed formally in the same form;

the only difference is that the cluster integrals are evaluated in different states. Since $z_\sigma = \gamma_\sigma \rho_\sigma$, the quantity $\alpha_\sigma$ in Eqs. (19.47) and (19.48) may be written as $(\gamma_\sigma/{\gamma_\sigma}^0)\rho_\sigma$. Thus $\gamma_\sigma/{\gamma_\sigma}^0$ is a number-concentration activity coefficient and $\alpha_\sigma$ is a number-concentration activity such that, as the solution becomes dilute with respect to all solutes, $\gamma_\sigma/{\gamma_\sigma}^0 \to 1$ and $\alpha_\sigma \to \rho_\sigma$.

The first few terms in Eqs. (19.47) and (19.48) may be written explicitly in the form,

$$\pi = kT\left(\sum_\sigma \alpha_\sigma - \sum_\sigma \sum_\tau B_{2,\sigma\tau}^{\,0} \alpha_\sigma \alpha_\tau - \cdots\right), \tag{19.49}$$

$$\rho_\sigma = \alpha_\sigma - 2\sum_\tau B_{2,\sigma\tau}^{\,0} \alpha_\sigma \alpha_\tau - \cdots \tag{19.50}$$

with

$$B_{2,\sigma\tau}^0 = -\tfrac{1}{2}(1+\delta_{\sigma\tau}) b_{2,\sigma\tau}^0 \,, \tag{19.51}$$

where $b_{2,\sigma\tau}^{\,0}$ is the cluster integral for the set of a single molecule of solute species $\sigma$ and a single molecule of solute species $\tau$, and is to be evaluated at zero solute concentration. By inversion of the series of (19.50), we obtain

$$\pi = kT\left(\sum_\sigma \rho_\sigma + \sum_\sigma \sum_\tau B_{2,\sigma\tau}^{\,0} \rho_\sigma \rho_\tau + \cdots\right), \tag{19.52}$$

Finally, in the case of a single solute species in a solvent, from the discussion above and Eq. (19.44) the osmotic pressure may be written as

$$\pi = kT(\rho + {B_2}^0\rho^2 + {B_3}^0\rho^3 + \cdots)\,, \tag{19.53}$$

where $\rho$ is the density of the solute and the coefficients ${B_2}^0$, ${B_3}^0$, ... are given formally by Eqs. (19.45) and (19.46). Thus, by use of the relation $\rho = N_A c/M$ with $N_A$ the Avogadro number, $c$ the solute concentration (g/cc), and $M$ the solute molecular weight, from Eqs. (19.36), (19.37), (19.45), (19.46), and (19.53) we obtain the final results,

$$\pi = RT\left(\frac{1}{M}c + A_2c^2 + A_3c^3 + \cdots\right), \tag{19.54}$$

where

$$A_2 = -\frac{N_A}{2VM^2}\int g_2(1,2)d\{2\}\,, \tag{19.55}$$

$$A_3 = -\frac{{N_A}^2}{3VM^3}\int g_3(1,2,3)d\{3\} + 4{A_2}^2M\,, \tag{19.56}$$

$$g_2(1,2) = F_2(1,2) - F_1(1)F_1(2)\,, \tag{19.57}$$

$$\begin{aligned} g_3(1,2,3) = F_3(1,2,3) &- F_2(2,3)F_1(1) - F_2(1,3)F_1(2) \\ &- F_2(1,2)F_1(3) + 2F_1(1)F_1(2)F_1(3)\,. \end{aligned} \tag{19.58}$$

Here, the distribution functions $F_1$, $F_2$, and $F_3$ for the solute molecules are to be evaluated at zero concentration. In practice, calculations of the virial coefficients begin with assumed forms for the potentials of mean force guessed to be suitable to a given system.

## 20. The Second Virial Coefficient (A): Random-Flight Chains

The first application of the McMillan–Mayer theory to solutions of flexible chain polymers was made by Zimm.[5] The calculations led to a dependence on the polymer molecular weight of the second virial coefficient in contradiction with the early lattice theories. About the same time, a molecular weight dependence was suggested independently by Flory,[6] who used the uniform-density sphere model of a polymer molecule. Subsequently, using a Gaussian chain model, Flory and Krigbaum[7] developed an approximate theory which shows explicitly that the second virial coefficient is a decreasing function of the polymer molecular weight. This prediction is qualitatively in accord with experimental results but underestimates the molecular weight dependence of the second virial coefficient. As a result of this discrepancy, a number of attacks on the problem have been made since the mid-1950s. In this section and the succeeding sections we shall give a detailed description of these investigations. However, it must be pointed out that there is a difficulty in the theory which is similar to that encountered in the excluded-volume problem, namely the many-body problem. For mathematical convenience, the present section is confined to the use of the random-flight model for a monodisperse system of linear chains. The effect of the intramolecular excluded volume on the second virial coefficient will be treated in the next section. Further, a treatment of solutions of rigid macromolecules is given in Appendix IV A to provide an elementary description of the physical meaning of the second virial coefficient.

### 20a. Perturbation Theory

It will be desirable to describe first the exact form of perturbation theory which can be developed by the cluster expansion method, as used in the perturbation theory of the excluded-volume effect. In the present problem, the expansion is made with respect to intermolecular clusters formed among segments of two polymer chains at infinite dilution. The formulation presented here is due to Zimm[5] and Albrecht.[8]

The second virial coefficient $A_2$ may be expressed, from Eqs. (19.22), (19.55), and (19.57), as

$$A_2 = -\frac{N_A}{2VM^2}\int [F_2(1,2) - F_1(1)F_1(2)]d(1,2) \tag{20.1}$$

with

$$F_2(1,2) = \exp\left[-\frac{W_2(1,2)}{kT}\right],$$
$$F_1(1) = \exp\left[-\frac{W_1(1)}{kT}\right]. \tag{20.2}$$

From Eq. (19.29), the potential $W_2(1,2)$ of mean force on two polymer molecules 1 and 2 at infinite dilution is given by a sum of the self-potentials $W_1(1)$ and $W_1(2)$ of the two molecules and the intermolecular potential $W_{12}(1,2)$, where $W_1 = w_1$ and $W_{12} \equiv w_2$. The potential $W_{12}$ may be assumed to be a sum of the pair potentials of mean force between the segments $w(\mathbf{R}_{i_1i_2})$, where $\mathbf{R}_{i_1i_2}$ is the distance between the $i_1$th segment of molecule 1 and the $i_2$th segment of molecule 2. That is,

$$W_2(1,2) = W_1(1) + W_1(2) + W_{12}(1,2) \tag{20.3}$$

with

$$W_{12}(1,2) = \sum_{i_1=0}^{n}\sum_{i_2=0}^{n} w(\mathbf{R}_{i_1i_2}). \tag{20.4}$$

The distribution function $F_2(1,2)$ for the two molecules may then be written as

$$F_2(1,2) = F_1(1)F_1(2)\exp\left[-\sum_{i_1,i_2}\frac{w(\mathbf{R}_{i_1i_2})}{kT}\right]. \tag{20.5}$$

Substitution of Eq. (20.5) into Eq. (20.1) leads to

$$A_2 = -\frac{N_A}{2VM^2}\int F_1(1)F_1(2)\left[\prod_{i_1,i_2}(1+\chi_{i_1i_2}) - 1\right]d(1,2), \tag{20.6}$$

where $\chi_{i_1i_2}$ is a short-range function as defined by Eqs. (13.1) and (13.2). Necessarily the potentials of mean force between the segments of the same molecule and between the segments of the two different molecules must be of the same form. Thus $\chi_{i_1i_2}$ may be expressed in terms of the same binary cluster integral $\beta$ as for intramolecular interactions; that is,

$$\chi_{i_1i_2} = -\beta\,\delta(\mathbf{R}_{i_1i_2}). \tag{20.7}$$

The distribution function $F_1(1)$ for a single molecule depends only on the internal coordinates and is just identical with the instantaneous distribution $P(\{\mathbf{r}_n\})$ for the entire chain introduced in the preceding chapter,

$$F_1(1) = Z^{-1}\left[\prod_{i_1=1}^{n}\tau(\mathbf{r}_{i_1})\right]\exp\left(-\frac{W}{kT}\right), \tag{20.8}$$

where $Z$ is the configurational partition function for the chain with the external coordinates fixed and $W$ is given by Eq. (10.6). Clearly, Eq. (20.8) satisfies the normalization condition of (19.21), since the integral of $F_1(1)$ over the internal coordinates $\{\mathbf{r}_n\}$ is just unity. Equations (20.2) and (20.8) give

$$W_1(1) = U_0(1) + W(1) + kT \ln Z\,, \tag{20.9}$$

where $U_0$ is the formal potential associated with $\tau(\mathbf{r})$ and is given by Eq. (16.5). Thus $W_1$ is equivalent to the potential $U$ of (3.2) except for a constant term. In this section we consider the case $W(1) = W(2) = 0$, the random-flight chain without intramolecular excluded volumes. Equation (20.8) then reduces to

$$F_1{}^0(1) = \prod_{i_1=1}^{n} \tau(\mathbf{r}_{i_1})\,. \tag{20.10}$$

We now expand the integrand in Eq. (20.6) as follows,

$$\begin{aligned} A_2 = &-\frac{N_A}{2VM^2} \int F_1{}^0(1) F_1{}^0(2) \\ &\times \left( \sum_{i_1,i_2} \chi_{i_1 i_2} + \sum_{i_1,i_2} \sum_{j_1,j_2} \chi_{i_1 i_2} \chi_{j_1 j_2} + \cdots \right) d(1,2)\,, \end{aligned} \tag{20.11}$$

where there exist restrictions on the summations, which will be indicated later using cluster diagrams. For convenience, each term of this expansion is referred to as *Term* and the individual terms arising from the multiple summations are referred to simply as terms, without capitalizing or italicizing. Thus, altogether there are $(n+1)^2$ *Terms*, the $\sigma$th *Term* ($\sigma$-ple contact term) having $\binom{(n+1)^2}{\sigma} \simeq \binom{n^2}{\sigma}$ terms when the multiple summation is expanded. A given term of the $\sigma$th *Term* in the integral in Eq. (20.11) may be written as

$$\begin{aligned} J^{(\sigma)} &= \int F_1{}^0(1) F_1{}^0(2) \prod_{\sigma \text{ pairs}} \chi_{i_1 i_2} d(1,2) \\ &= (-1)^\sigma \beta^\sigma \int F_1{}^0(1) F_1{}^0(2) \prod_{\sigma \text{ pairs}} \delta(\mathbf{R}_{i_1 i_2}) d(1,2)\,, \end{aligned} \tag{20.12}$$

where we have used Eq. (20.7). First, integration is performed over coordinates specifying the relative positions of segments $i_1$ and $i_2$. These segments are arbitrarily chosen to take part in the first of $\sigma$ intermolecular contacts. This integration yields a new distribution function which we write as $F_1{}^0(1*2)$ to symbolize the fact that the presence of $\delta(\mathbf{R}_{i_1 i_2})$ in the integrand has brought molecules 1 and 2 into contact forming a single star molecule of functionality 4 whose configuration is symbolized by $(1*2)$. Then integration is performed over the external coordinates of the star molecule. Since $F_1{}^0(1*2)$ is independent of the external coordinates, this integration gives $VF_1{}^0(1*2)$ which we write as $VF_1{}^0(1*2)_{\text{int}}$ to indicate explicitly that the integration over the external coordinates has been carried out. The unperturbed distribution function ${F_1}^0(1*2)_{\rm int}$ is given by

$$ {F_1}^0(1*2)_{\rm int}\, d(1*2)_{\rm int} = \prod_{i_1=1}^{n} \prod_{i_2=1}^{n} \tau(\mathbf{r}_{i_1})\tau(\mathbf{r}_{i_2}) d\mathbf{r}_{i_1} d\mathbf{r}_{i_2} \bigg|_{\mathbf{R}_{i_1 i_2}=0} \tag{20.13} $$

with

$$ \int {F_1}^0(1*2)_{\rm int}\, d(1*2)_{\rm int} = 1\,. $$

Thus Eq, (20.12) becomes

$$ J^{(\sigma)} = (-1)^\sigma \beta^\sigma V \int {F_1}^0(1*2)_{\rm int} \prod_{(\sigma-1)\ \rm pairs} \delta(\mathbf{R}_{j_1 j_2})\, d(1*2)_{\rm int}\,. \tag{20.14} $$

We now introduce the distribution function $P_0(\mathbf{R}_{j_1 j_2}, \mathbf{R}_{k_1 k_2}, \ldots, \mathbf{R}_{t_1 t_2})_{i_1 i_2}$ of $(\sigma-1)$ vectors, $\mathbf{R}_{j_1 j_2}$, $\mathbf{R}_{k_1 k_2}$, ..., $\mathbf{R}_{t_1 t_2}$, for the unperturbed star molecule,

$$ \begin{aligned} & P_0(\mathbf{R}_{j_1 j_2}, \mathbf{R}_{k_1 k_2}, \ldots, \mathbf{R}_{t_1 t_2})_{i_1 i_2} \\ & \quad = \int {F_1}^0(1*2)_{\rm int}\, d(1*2)_{\rm int} / d\mathbf{R}_{j_1 j_2}\, d\mathbf{R}_{k_1 k_2} \ldots d\mathbf{R}_{t_1 t_2}\,, \end{aligned} \tag{20.15} $$

where the subscript $i_1 i_2$ indicates that segments $i_1$ and $i_2$ are in contact. Equation (20.14) then becomes

$$ \begin{aligned} J^{(\sigma)} &= (-1)^\sigma \beta^\sigma V \int P_0(\mathbf{R}_{j_1 j_2}, \ldots, \mathbf{R}_{t_1 t_2})_{i_1 i_2} \\ & \quad \times \prod_{(\sigma-1)\ \rm pairs} \delta(\mathbf{R}_{j_1 j_2}) d\mathbf{R}_{j_1 j_2} \cdots d\mathbf{R}_{t_1 t_2} \\ &= (-1)^\sigma \beta^\sigma V P_0(0_{j_1 j_2}, \ldots, 0_{t_1 t_2})_{i_1 i_2} \end{aligned} \tag{20.16} $$

with $J^{(1)} = -\beta V$. The quantity $P_0(0_{j_1 j_2}, \ldots, 0_{t_1 t_2})_{i_1 i_2}$ represents a conditional probability density that, given an initial contact between segments $i_1$ and $i_2$, there are $(\sigma-1)$ additional specified contacts between segments $j_1$ and $j_2$, ..., and $t_1$ and $t_2$. From Eqs. (20.11) and (20.16), we obtain

$$ \begin{aligned} A_2 = \frac{N_A n^2 \beta}{2M^2} \bigg[ & 1 - \beta n^{-2} \sum_{i_1, i_2} \sum_{j_1, j_2} P_0(0_{j_1 j_2})_{i_1 i_2} \\ & + \beta^2 n^{-2} \sum_{i_1, i_2} \sum_{j_1, j_2} \sum_{k_1, k_2} P_0(0_{j_1 j_2}, 0_{k_1 k_2})_{i_1 i_2} - \cdots \bigg]\,. \end{aligned} \tag{20.17} $$

Since each of the $(\sigma-1)$ victors, $\mathbf{R}_{j_1 j_2}, \ldots, \mathbf{R}_{t_1 t_2}$, is given by a linear combination of the $2n$ bond vectors, $\mathbf{r}_{1_1}$, ..., $\mathbf{r}_{n_1}$, $\mathbf{r}_{1_2}$, ..., $\mathbf{r}_{n_2}$, by the use of the Wang–Uhlenbeck theorem (Section 6), we find

$$ P_0(0_{j_1 j_2}, \ldots, 0_{t_1 t_2})_{i_1 i_2} = (3/2\pi a^2)^{3s/2} {C_s}^{-3/2}\,, \tag{20.18} $$

where $s = \sigma - 1$, $a$ is the effective bond length, and $C_s$ is the determinant of the $s \times s$ symmetric matrix with elements $C_{kl}$ formally defined by

Eqs. (6.3) and (6.12). Thus, in terms of the parameter $z$ defined by Eq. (13.32), $A_2$ may be written in the form,

$$A_2 = (N_A n^2 \beta / 2M^2) h_0(z) \tag{20.19}$$

with

$$h_0(z) = 1 - z n^{-5/2} \sum_{i_1, i_2, j_1, j_2} {C_1}^{-3/2} + z^2 n^{-3} \sum_{i_1, i_2, j_1, j_2, k_1, k_2} {C_2}^{-3/2} - \cdots \,, \tag{20.20}$$

where the subscript 0 on $h$ indicates that there are no intramolecular interactions. The problem now reduces to an evaluation of the determinants followed by the multiple summations.

Let us consider the general properties of $C_s$. This is the determinant belonging to the $(s+1)$th *Term*, for which molecules 1 and 2 may be considered in simultaneous contact at $(s+1)$ points. Choosing one point of contact as a reference point, it is possible to associate with each of the $s$ additional contacts a loop containing parts of both molecules. The loop to be associated with the $k$th additional contact, for example, begins at the reference point, includes a part of molecule 1 up to the point of the $k$th additional contact, and closes by including the part of molecule 2 which leads back to the reference contact. The diagonal element $C_{kk}$ represents the number of segments contained in the loop just described. The $s$ loops so defined obviously contain certain segments in common. The number of segments contained commonly by loops $k$ and $l$ is represented by the off-diagonal element $C_{kl}$ $(= C_{lk})$.

Now the detailed conditions on the multiple summations in Eq. (20.20) indicate that while the order of contact segments on molecule 1 is preserved $(i_1 \leq j_1 \leq k_1 \leq \cdots \leq t_1)$ the contact segments of molecule 2 $(i_2, j_2, \ldots, t_2)$ are allowed to vary independently. This gives rise to a set of types of multiple contacts, each type corresponding to one of the $\sigma!$ (for $\sigma$ contacts) possible orderings of the contact segments of molecule 2. This division into types is necessary, since in general the $C_s$, determined as just described, are not the same for all types. The discussion of the various types of contacts is greatly aided by the use of cluster diagram technique as in Section 14. In Fig. IV.1 are depicted the two (2!) possible types which can appear in the double-contact term and the six (3!) types which appear in the triple-contact term. As seen from the figure, in general, to generate all possible types of $\sigma$ contacts, for example, we need only write all permutations of the index set $i_2$, $j_2$, …, $t_2$ for the $\sigma$ segments of molecule 2 and interpret each permutation in the diagrammatic sense.

Consider now diagrams $C_{1-1}$ $(i_1 \leq j_1, i_2 \leq j_2)$, $C_{2-1}$ $(i_1 \leq j_1 \leq k_1, i_2 \leq j_2 \leq k_2)$, and $C_{2-3}$ $(i_1 \leq j_1 \leq k_1, j_2 \leq i_2 \leq k_2)$ of Fig. IV.1. If we denote the number of segments separating the contact segments of molecule 1 and of molecule 2 by $x_i$ and $y_i$, respectively, as shown in the figure, following the procedure outlined above we obtain for the corresponding determinants

$$C_{1-1} = x_1 + y_1 \,,$$

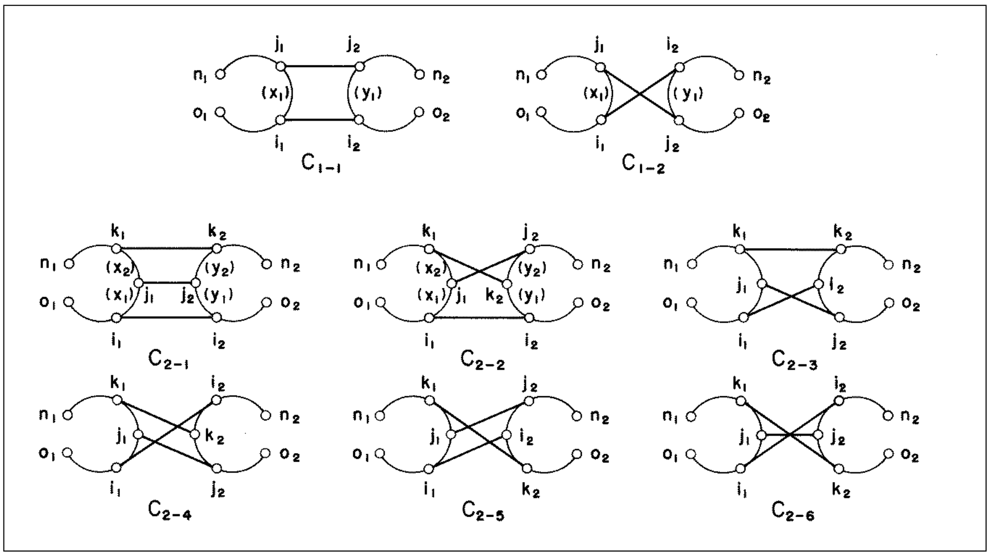

**Fig. IV.1.** Cluster diagrams for the double and triple intermolecular contact terms. The heavy lines connect the contact segments.

$$C_{2-1} = \begin{vmatrix} x_1 + y_1 & x_1 + y_1 \\ x_1 + y_1 & x_1 + x_2 + y_1 + y_2 \end{vmatrix},$$

$$C_{2-3} = \begin{vmatrix} x_1 + y_1 & y_1 \\ y_1 & x_2 + y_1 + y_2 \end{vmatrix}, \tag{20.21}$$

where we have chosen $(i_1 i_2)$ and $(j_1 j_2)$ as the reference contacts in $C_{2-1}$ and $C_{2-3}$, respectively. Upon simple transformation, from $C_{2-1}$ there is obtained a diagonal determinant with diagonal elements $(x_1 + y_1)$ and $(x_2 + y_2)$. The formal definition of $C_s$ is, as expected, not unique, since determinants are invariant to a variety of transformations. In fact, every equivalent representation of $C_s$ corresponds to a particular manner in which $s$ loops are chosen. This suggests that an alternative method of defining loops be adopted in order to lead directly to a simplified form for $C_s$. If the $s$ loops are chosen in a manner such that there is a minimum number of loops which overlap (contain common segments), the desired simplification of $C_s$ is obtained.

This method of choosing loops leads directly to two classes of contact types: Class I, containing those types for which $C_s$ is diagonal (e.g., $C_{2-1}$); and Class II, containing all those types (the remainder) for which $C_s$ cannot be diagonalized (e.g., $C_{2-3}$). It can be shown that there are only two types which belong to Class I for a given *Term*. These are the types whose representative permutation is either the perfectly ordered set $i_2$, $j_2$, $k_2$, ..., $t_2$ or the reverse perfectly ordered set $t_2$, ..., $k_2$, $j_2$, $i_2$. The remaining types ($\sigma! - 2$ for the $\sigma$th *Term*) belong to Class II. The Class I representatives in Fig. IV.1 are diagrams $C_{1-1}$ and $C_{1-2}$ for $\sigma = 2$ and diagrams $C_{2-1}$ and $C_{2-6}$ for $\sigma = 3$.

There are two kinds of symmetry which appear among the types.

The first symmetry is a property common to both classes; the second belongs only to Class II. The first is a symmetry which causes two different types to yield two $C_s$ differing only in that in one the $y_i$ are labeled in just the reverse manner; these lead to equivalent contributions once the sum has been carried out. This corresponds to the two permutations $i_2$, $j_2$, …, $t_2$ and $t_2$, …, $j_2$, $i_2$ for Class I, and similarly (for Class II) to all other pairs of representative permutations achieved by analogous transpositions on the ordered and reverse ordered sets. Thus, each of the following pairs of diagrams in Fig IV.1 has equivalent contributions:$C_{1-1}$, $C_{1-2}$; $C_{2-1}$, $C_{2-6}$; $C_{2-3}$, $C_{2-5}$; and $C_{2-2}$, $C_{2-4}$. The second symmetry can be seen as follows. Consider a plane normal to and bisecting the two are lines (polymer chains) of a given diagram. It can make no physical difference whether the overlap occurs on one side or at its mirror image through this plane. Types so related must lead to the same contribution. In Fig. IV.1, therefore, the contribution of type $C_{2-2}$ is equal to that of $C_{2-3}$ and the contribution of type $C_{2-4}$ is equal to that of $C_{2-5}$. The number of unique $C_s$ that require evaluation in the sense of performing the multiple summation is not $\sigma!$ but $(\sigma! + 2)/4$, the symmetry factors being appropriately applied to give the correct final answer.

We now turn to the evaluation of the function $h_0(z)$ through the third *Term.* According to the discussion above, we have the two Class I types for the double-contact term, and the two Class I types and the four Class II types for the triple-contact term. The required sums in Eq.(20.20) may be written as

$$\sum {C_1}^{-3/2} = 2 \sum_{i_1 \leq j_1} \sum_{i_2 \leq j_2} {C_{1-1}}^{-3/2} ,$$

$$\sum {C_2}^{-3/2} = 2 \sum_{i_1 \leq j_1 \leq k_1} \sum_{i_2 \leq j_2 \leq k_2} {C_{2-1}}^{-3/2} + 4 \sum_{i_1 \leq j_1 \leq k_1} \sum_{j_2 \leq i_2 \leq k_2} {C_{2-3}}^{-3/2} , \tag{20.22}$$

where $C_{1-1}$, $C_{2-1}$, and $C_{2-3}$ are given by Eqs. (20.21). The sums may be converted to integrals in the usual fashion. The integrals for types $C_{1-1}$ and $C_{2-1}$ can be evaluated analytically, while the integral for type $C_{2-3}$ requires a numerical integration. Thus the final result is

$$h_0(z) = 1 - 2.865z + 9.202z^2 - \cdots . \tag{20.23}$$

Equation (20.19) with (20.23) represents the second-order perturbation theory of the second virial coefficient for the random-flight chain. The double-contact term was obtained by Zimm[5] (where the symmetry factor of 2 was erroneously omitted) and Fixman[9]; the triple-contact term is due to Albrecht,[8] and Tagami and Casassa,[10] Albrecht's original value being 9.726 instead of 9.202.

In general, it is possible to evaluate the contribution $2T_\sigma(-z)^{\sigma-1}$ of the Class I types to the $\sigma$th *Term.* The associated determinant ${C_s}^I$

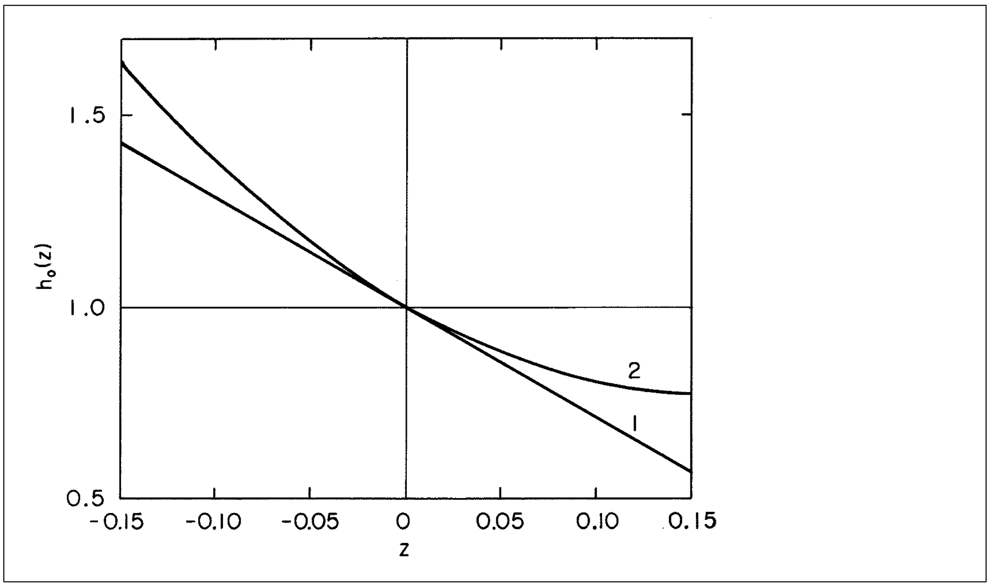

**Fig. IV.2.** Theoretical values of $h_0(z)$ at small $z$. Line 1: the first-order perturbation theory. Curve 2: the second-order perturbation theory.

being diagonal, reads simply

$$C_s{}^I = \prod_{i=1}^{\sigma-1}(x_i + y_i)\,. \tag{20.24}$$

If reduced variables $x_i{}' = x_i/n$ and $y_i{}' = y_i/n$ are introduced together with $X' = \sum x_i{}'$ and $Y' = \sum y_i{}'$ and the primes are immediately suppressed, $T_\sigma$ is found to be

$$\begin{aligned} T_\sigma = & \int\limits_{\substack{0\le\sum x_i = X \le 1\\ 0\le\sum y_i = Y\le 1}} \cdots \int (1-X)(1-Y)\prod_{i=1}^{\sigma-1}[(x_i+y_i)^{-3/2}dx_i dy_i]dXdY \\ = & \frac{2^{\sigma+2}\pi^{(\sigma-2)/2}}{(\sigma+1)(\sigma+3)\Gamma(\sigma/2)}[(\sigma^2+3)I_{\sigma-1} - (\sigma-1)2^{-(\sigma-1)/2}] \end{aligned} \tag{20.25}$$

with

$$I_{\sigma-1} = \int_0^{\pi/4} \sin^{\sigma-1}\theta\, d\theta \simeq 2^{-\sigma(\sigma+1)/2(\sigma+2)}/\sigma\,. \tag{20.26}$$

The integrals for types $C_{1-1}$ and $C_{2-1}$ are particular cases of the integral of (20.25). However, it appears extremely difficult to evaluate exactly all the contributions of Class II, although it can be shown that type for type the contribution of Class II must be smaller than that of Class I.

From the above analysis, $h_0$ is seen to be a function of the parameter $z$ only. Thus Eq. (20.19) with (20.23) represents a two-parameter theory of the second virial coefficient; $A_2$ may be expressed in terms of only the two parameters $na^2$ and $n^2\beta$ as in the theory of excluded-volume effects. Equations (20.19) and (20.23) predict that $A_2 = 0$ and $h_0(z) = 1$ at the theta temperature at which $\beta$ and $z$ vanish. Further, $A_2$ is seen to depend on the polymer molecular weight $M$ through the function $h_0(z)(z \propto M^{1/2})$, since the quantity $N_A n^2 \beta / 2M^2$ is independent of $M$. In Fig. IV.2 are shown the values of $h_0(z)$ predicted by the first-and second-order perturbation theories. The series of (20.23) is very slowly convergent, and is valid only for $|z| < 0.15$, near the theta temperature.

## 20b. Approximate Closed Expressions

Corresponding to the theory of the excluded-volume effect, we now wish to derive an equation which can describe the behavior of the function $h_0(z)$ over a wide range of $z$. It may be easily recognized that the present problem is very similar to the excluded-volume problem in nature. Indeed, various attempts have been made to solve the $A_2$ problem in parallel with the excluded-volume problem, although some of these lead only to numerical results. All these theories, although differing in the functional form of $h_0(z)$, predict that $h_0(z)$ is a decreasing function of $z$. It will be convenient to classify these investigation into three groups.

### 20b(i). The Smoothed-Density Model

The theories developed by Flory and Krigbaum,[6, 7] by Grimley,[11] and by Isihara and Koyama[12] may be discussed together, in a category termed the smoothed-density theory. We begin by deriving an approximate general expression for $A_2$, written in terms of the average segment density around the molecular center of mass, from which there result these theories by assuming appropriate forms for the density function.

Denoting the distance between the center of mass and the $i_1$th segment of molecule 1 by $\mathbf{S}_{i_1}$, we introduce the distribution function $P_0(\mathbf{S}_{i_1}, \mathbf{S}_{j_1}, \ldots, \mathbf{S}_{t_1})$ of $\sigma$ vectors, $\mathbf{S}_{i_1}$, …, $\mathbf{S}_{t_1}$, for the unperturbed chain [and also $P_0(\mathbf{S}_{i_2}, \ldots, \mathbf{S}_{t_2})$],

$$P_0(\mathbf{S}_{i_1}, \mathbf{S}_{j_1}, \ldots, \mathbf{S}_{t_1}) = \int {F_1}^0(1) d(1)_{\text{int}} / d\mathbf{S}_{i_1}, d\mathbf{S}_{j_1} \cdots d\mathbf{S}_{t_1} \,. \quad (20.27)$$

If $\mathbf{S}_{12}$ is the distance between the centers of mass of molecules 1 and 2, Eq. (20.12) may be rewritten, by the use of Eq. (20.27), as

$$\begin{aligned} J^{(\sigma)} &= (-1)^\sigma \beta^\sigma V \int {F_1}^0(1) {F_1}^0(2) \prod_{\sigma \text{ pairs}} \delta(\mathbf{R}_{i_1 i_2}) d(1)_{\text{int}} d(2)_{\text{int}} d\mathbf{S}_{12} \\ &= (-1)^\sigma \beta^\sigma V \int P_0(\mathbf{S}_{i_1}, \ldots, \mathbf{S}_{t_1}) P_0(\mathbf{S}_{i_1} - \mathbf{S}_{12}, \ldots, \mathbf{S}_{t_1} - \mathbf{S}_{12}) \end{aligned}$$

$$\times d\mathbf{S}_{i_1} \cdots d\mathbf{S}_{t_1} d\mathbf{S}_{12}\,, \tag{20.28}$$

where we have used the relation, $\mathbf{S}_{12} = \mathbf{S}_{i_1} - \mathbf{S}_{i_2} + \mathbf{R}_{i_1 i_2}$. We now introduce the factorization approximation,

$$P_0(\mathbf{S}_{i_1}, \ldots, \mathbf{S}_{t_1}) = P_{0i_1}(\mathbf{S}_{i_1}) \cdots P_{0t_1}(\mathbf{S}_{t_1})\,, \tag{20.29}$$

and a similar approximation for molecule 2, where $P_{0i_1}(\mathbf{S}_{i_1}) \equiv P_0(\mathbf{S}_{i_1})$. With these approximation, we then obtain, from Eqs. (20.11) and (20.28)

$$\begin{aligned} A_2 = \frac{N_A}{2M^2} \int \Bigg[ & \beta \sum_{i_1, i_2} \int P_{0i_1}(\mathbf{S}_{i_1}) P_{0i_2}(\mathbf{S}_{i_1} - \mathbf{S}_{12}) d\mathbf{S}_{i_1} \\ & -\beta^2 \sum_{i_1, i_2} \sum_{j_1, j_2} \int P_{0i_1}(\mathbf{S}_{i_1}) P_{0i_2}(\mathbf{S}_{i_1} - \mathbf{S}_{12}) d\mathbf{S}_{i_1} \\ & \times \int P_{0j_1}(\mathbf{S}_{j_1}) P_{0j_2}(\mathbf{S}_{j_1} - \mathbf{S}_{12}) d\mathbf{S}_{j_1} + \cdots \Bigg] d\mathbf{S}_{12}\,. \end{aligned} \tag{20.30}$$

As mentioned already, the number of terms of the $\sigma$th *Term* is $\binom{(n+1)^2}{\sigma}$, which may be approximated by $n^{2\sigma}/\sigma!$ provided that $n$ is large. In other words, the restrictions on the summations in Eq. (20.30) may be removed by introducing a factor $1/\sigma!$ in the $\sigma$th *Term*. Then the series in the integrand of the integral over $\mathbf{S}_{12}$ can be summed to yield an exponential form, and we obtain

$$A_2 = \frac{N_A}{2M^2} \int \left\{ 1 - \exp\left[ -\frac{V_{12}(\mathbf{S}_{12})}{kT} \right] \right\} d\mathbf{S}_{12} \tag{20.31}$$

with

$$\frac{V_{12}(\mathbf{S}_{12})}{kT} = \beta \sum_{i_1=0}^{n} \sum_{i_2=0}^{n} \int P_{0i_1}(\mathbf{s}) P_{0i_2}(\mathbf{s} - \mathbf{S}_{12}) d\mathbf{s}\,, \tag{20.32}$$

where we have used $\mathbf{s}$ in place of $\mathbf{S}_{i_1}$. Since $P_{0i_1}(\mathbf{s})$ is the distribution function of the distance of the $i_1$th segment from the center of mass of molecule 1, Eq. (20.32) may be rewritten, by the used of Eq. (7.9), as

$$\frac{V_{12}(\mathbf{S}_{12})}{kT} = \beta \int \rho_{01}(\mathbf{s}) \rho_{02}(\mathbf{s} - \mathbf{S}_{12}) d\mathbf{s}\,, \tag{20.33}$$

where $\rho_{0i}(\mathbf{s})$ represents the average segment density at distance $\mathbf{s}$ from the center of mass of isolated unperturbed chain $i$. $V_{12}$ may be considered to be the average intermolecular potential as a function of separation, corresponding to the average intramolecular potential $V(S)$ of (15.25). The integral in Eq. (20.31) may be regarded as the effective volume excluded to one *molecule* by the presence of another, the intermolecular excluded volume [compare with Eq. (13.3) for $\beta$]. We note that Eq. (20.33) can also be derived by a procedure similar to that used in Section 11.[7],[13] We first consider the uniform-density sphere model of Flory.[6] In this case, $\rho_0(\mathbf{s})$ (with omission of the subscript 1 or 2) is obviously given by

$$\begin{aligned} \rho_0(\mathbf{s}) &= n/(\tfrac{4}{3}\pi\bar{S}^3) && \text{for } 0 \leq s \leq \bar{S} \\ &= 0 && \text{for } s > \bar{S}\,, \end{aligned} \tag{20.34}$$

where $\bar{S}$ is the radius of the sphere. We therefore have, from Eqs. (20.33) and (20.34),

$$V_{12}(\mathbf{S}_{12})/kT = \beta(n/\tfrac{4}{3}\pi\bar{S}^3)^2\mathcal{V}(S_{12})\,, \tag{20.35}$$

where $\mathcal{V}(S_{12})$ is the volume common to two spheres of radius $\bar{S}$ with a distance $S_{12}$ between the centers, and is given by

$$\mathcal{V}(S_{12}) = \tfrac{2}{3}\pi\bar{S}^3\left(1-\frac{S_{12}}{2\bar{S}}\right)^2\left(2+\frac{S_{12}}{2\bar{S}}\right) \qquad (0 \leq S_{12} \leq 2\bar{S})\,. \tag{20.36}$$

On putting $t = S_{12}/2\bar{S}$ and $\bar{S} \propto n^{1/2}a$ (for a random-flight chain), we obtain, from Eqs. (20.31), (20.35), and (20.36), for the function $h_0(z)$

$$h_0(z) = (12/Kz)\int_0^1 \{1-\exp[-Kz(1-t)^2(2+t)]\}t^2dt, \qquad \text{(F)} \tag{20.37}$$

where $K$ is a constant. This integral must be evaluated numerically, and the result will be discussed later.

Secondly, we approximate $\rho_0(\mathbf{s})$ by the Gaussian function of (8.4). Performing the integration over $\mathbf{s}$ in Eq.(20.33), we find

$$\frac{V_{12}(\mathbf{S}_{12})}{kT} = n^2\beta\left(\frac{3}{4\pi\langle S^2\rangle_0}\right)^{3/2}\exp\left(-\frac{3S_{12}^2}{4\langle S^2\rangle_0}\right) \tag{20.38}$$

with $\langle S^2\rangle_0$ the unperturbed mean-square radius of gyration. This potential is usually called the Flory–Krigbaum potential. Substituting Eq.(20.38) into Eq.(20.31) and putting $t^2 = 9S_{12}^2/2na^2$, we obtain

$$\begin{aligned} h_0(z) &= (4/\pi^{1/2})(3^{3/2}z)^{-1}\int_0^\infty \{1-\exp[-(3^{3/2}z)\exp(-t^2)]\}t^2dt \\ &= \sum_{k=1}^{\infty}\frac{(-3^{3/2}z)^{k-1}}{k!k^{3/2}}. \qquad \text{(FKG)} \end{aligned} \tag{20.39}$$

This is the result derived first by Flory and Krigbaum,[7] and subsequently by Grimley.[11] In order to obtain numerical results, the integral in Eq. (20.39) must be evaluated numerically.

Finally, we insert the expression (7.6) for $P_{0i_1}$ and $P_{0i_2}$ in Eq. (20.32) without using the Gaussian approximation to $\rho_0(\mathbf{s})$. We then find

$$\begin{aligned} \frac{V_{12}(\mathbf{S}_{12})}{kT} = \beta\sum_{i_1,i_2}&\left[\frac{3}{2\pi(\langle S_{i_1}{}^2\rangle_0+\langle S_{i_2}{}^2\rangle_0)}\right]^{3/2} \\ &\times\exp\left[-\frac{3S_{12}^2}{2(\langle S_{i_1}{}^2\rangle_0+\langle S_{i_2}{}^2\rangle_0)}\right], \end{aligned} \tag{20.40}$$

where $\langle {S_i}^2 \rangle_0$ is the unperturbed mean-square distance from the center of mass to the $i$th segment and is given by Eq. (7.8). Substitution of Eq. (20.40) into Eq. (20.31) leads to the Isihara–Koyama equation,[12]

$$h_0(z) = (4/\pi^{1/2})(3^{3/2}z)^{-1} \int_0^\infty \{1 - \exp[-(3^{3/2}z)f(t)]\} t^2 dt \qquad \text{(IK)} \tag{20.41}$$

with

$$f(t) = (4/3)^{3/2} \int_0^1 \int_0^1 (x^2 + y^2 + \tfrac{2}{3})^{-3/2} \exp[-4t^2/3(x^2 + y^2 + \tfrac{2}{3})] dx dy \,, \tag{20.42}$$

where $x = 2(i_1/n) - 1$ and $y = 2(i_2/n) - 1$, and the sums have been converted to integrals. The numerical results obtained by Isihara and Koyama show that the IK function is very close to the FKG function despite the improvement of the distribution function for a segment about the molecular center of mass. This is to be expected, since as discussed in Section 8a, the agreement between the exact distribution $\rho_0(\mathbf{s})$ and the approximate Gaussian distribution of (8.4) is fairly satisfactory.

By a semiempirical procedure, Orofino and Flory[14] found that the FKG function may be approximated by the close form,

$$h_0(z) = \frac{1}{2.30z} \ln(1 + 2.30z) \,. \qquad \text{(FKO , o)} \tag{20.43}$$

This is referred to as the original Flory–Krigbaum–Orofino function. The FKO,o function is in agreement with the FKG function with an accuracy of a few percents over the range of $z$ of interest. In analogy with a maneuver used in Chapter III, however, Stockmayer[15] recommended that the numerical constant 2.30 in Eq. (20.43) be changed to 5.73 to yield the exact first-order perturbation theory;that is,

$$h_0(z) = \frac{1}{5.73z} \ln(1 + 5.73z) \,. \qquad \text{(FKO , m)} \tag{20.44}$$

This function is referred to as the modified Flory–Krigbaum–Orofino function. By a similar argument, the value of the constant $K$ in Eq. (20.37) can be found to be 8.85 when forced to fit the exact first-order perturbation theory. The F function for the uniform-density sphere model so determined has a little smaller value than the FKO,m function at a given positive value of $z$. A comparison of the values of $h_0(z)$ from various approximate theories will be deferred to the end of this section.

Our final problem is to show the correspondence between our notation and Flory's notation. The parameter $X$ used by Flory and Krigbaum is equal to $4C_M \psi(1 - \Theta/T)M^{1/2}/\alpha^3 \equiv X'/\alpha^3$, and for the random-flight chain model $X'$ must be equated $3^{3/2}z$ appearing in Eq. (20.39); that is

$$z = (4/3^{3/2})C_M \psi(1 - \Theta/T)M^{1/2} \,. \tag{20.45}$$

Further, the single-contact term $N_A n^2 \beta / 2M^2$ in Eq. (20.19) must be equated to the corresponding term, $(\bar{v}^2/N_A V_0)\psi(1-\Theta/T)$, of Flory and Krigbaum, where $\bar{v}$ is the partial specific volume of the polymer and $V_0$ is the molecular volume of the solvent. Recalling that $nV_s = M\bar{v}/N_A$ with $V_s$ the volume of the segment, we therefore have

$$\beta = 2{V_0}^{-1}{V_s}^2\psi(1-\Theta/T)\,. \tag{20.46}$$

Equations (20.45) and (20.46) have already been used in Section 14 without proof.

## 20b(ii). The Factored Random-Flight Model

This model is similar to the smoothed-density model, but the segment distribution function is factored in a different manner. The Fixman–Casassa–Markovitz theory[9, 16, 17]belongs to this class.

We introduce the following factorization approximation to the conditional probability density for segment contacts, $P_0(0_{j_1j_2},\ 0_{k_1k_2},\ \ldots,\ 0_{t_1t_2})_{i_1i_2}$, appearing in Eq. (20.16)

$$P_0(0_{j_1j_2},\ldots,0_{t_1t_2})_{i_1i_2} = P_0(0_{j_1j_2})_{i_1i_2}\cdots P_0(0_{t_1t_2})_{i_1i_2}\,. \tag{20.47}$$

This approximation is equivalent to introducing the alternative factorization approximation,

$$P_0(\mathbf{R}_{i_1j_1},\mathbf{R}_{i_1k_1},\ldots,\mathbf{R}_{i_1t_1}) = P_0(\mathbf{R}_{i_1j_1})P_0(\mathbf{R}_{i_1k_1})\cdots P_0(\mathbf{R}_{i_1t_1})\,, \tag{20.48}$$

and also a similar approximation for molecule 2. Substitution of Eq. (20.16) with (20.47) into Eq. (20.11) leads to

$$\begin{aligned} n^2h_0(z) = {} & \sum_{i_1,i_2} 1 - \beta \sum_{i_1,i_2}\sum_{j_1,j_2} P_0(0_{j_1j_2})_{i_1i_2} \\ & +\beta^2 \sum_{i_1,i_2}\sum_{j_1,j_2}\sum_{k_1,k_2} P_0(0_{j_1j_2})_{i_1i_2}P_0(0_{k_1k_2})_{i_1i_2} - \cdots\,. \end{aligned} \tag{20.49}$$

We now remove, as before, the restrictions on the summations by introducing a factor $1/\sigma!$ in the $\sigma$th *Term.* Equation (20.49) then becomes

$$h_0(z) = n^{-2}\sum_{i_1=0}^{n}\sum_{i_2=0}^{n}\sum_{\sigma=0}^{\infty}\frac{1}{(\sigma+1)!}\left[-\beta\sum_{j_1=0}^{n}\sum_{j_2=0}^{n}P_0(0_{j_1j_2})_{i_1i_2}\right]^{\sigma}\,, \tag{20.50}$$

where $P_0(0_{j_1j_2})_{i_1i_2}$ is given by Eq. (20.18) with $C_1 = |j_1-i_1|+|j_2-i_2|$. Recalling that the series in $\beta$ of Eq. (20.50) may be summed in exponential form, and replacing the summations over the indices by integrations, we obtain

$$h_0(z) = \int_0^1\int_0^1 \frac{1-\exp[-4zw(x,y)]}{4zw(x,y)}dxdy \tag{20.51}$$

with

$$\begin{aligned} w(x,y) &= 2x^{1/2} + 2y^{1/2} + 2(1-x)^{1/2} + 2(1-y)^{1/2} \\ &\quad - (x+y)^{1/2} - (1-x+y)^{1/2} - (1+x-y)^{1/2} - (2-x-y)^{1/2}\,, \end{aligned} \tag{20.52}$$

$$x = i_1/n, \qquad y = i_2/n\,.$$

The surface representing $w(x,y)$ over the range of integration ($0 \le x \le 1$, $0 \le y \le 1$) is quite flat, falling away rapidly only near the edges. Therefore, a reasonable approximation can be obtained by replacing the actual surface with a rectangular box of height $w_0$ and enclosing the same volume.[17] In other words, $w(x,y)$ may be replaced by $w_0$ given by

$$w_0 = \int_0^1 \int_0^1 w(x,y)dx\,dy = \frac{16}{15}(7 - 4 \cdot 2^{1/2}) = 1.4327\,. \tag{20.53}$$

This replacement is equivalent to approximating $P_0(0_{j_1j_2})_{i_1i_2}$ by its value averaged over $i_1$, $i_2$ pairs,[9]

$$P_0(0_{j_1j_2})_{i_1i_2} \simeq n^{-2} \sum_{i_1=0}^{n} \sum_{i_2=0}^{n} P_0(0_{j_1j_2})_{i_1i_2}\,. \tag{20.54}$$

Thus we have

$$h_0(z) = \frac{1 - \exp(-5.73z)}{5.73z}\,. \qquad \text{(FCM)} \tag{20.55}$$

By numerical calculation Casassa Markovitz[17] showed that the deviation of the FCM function from $h_0(z)$ given by Eq. (20.51) with (20.52) never exceeds 1.8%. To minimize the error over the important range, they proposed that the value 5.73 in Eq. (20.55) be changed to 5.68. However, we retain the value 5.73, since Eq.(20.55) yields the exact first-order perturbation theory result for $h_0(z)$.

The essential difference between the smoothed-density theory and the present theory consists in the manner of factoring the segment distribution function. That is, the molecular center of mass is chosen as the reference point for factorization in the former, whereas an arbitrary initial contact point is taken in the latter. The former approximation causes an appreciable error in taking into account the connective nature of the polymer chain (the error appears first in the double-contact term as evidenced by the failure to give the correct linear term). Further, we note that the FCM factorization approximation is the same as the Grimley approximation of (12.10). It must be recalled that this approximation failed in the description of the intramolecular excluded-volume effect.

## 20b(iii). The Differential-Equation Approach

This approach is similar to the differential-equation approach to the excluded-volume problem described in Section 15b. Kurata et al.[18] developed a theory corresponding to the $F_1$ theory of $\alpha$ described in Section 15b(i). Subsequently Yamakawa[19] generalized the procedure; it is consistent with the hierarchy approach in the theory of $\alpha$ described in Section 15b(iii).

By analogy with Eq. (15.14), the intermolecular potential may be expressed as

$$\frac{W_{12}(1,2)}{kT} = \beta \sum_{i_1=0}^{n} \sum_{i_2=0}^{n} \delta_{i_1 i_2} \,, \tag{20.56}$$

where $\delta_{i_1 i_2}$ is a shorthand notation for $\delta(\mathbf{R}_{i_1 i_2})$. For the random-flight chain model, Eq. (20.1) then becomes

$$A_2 = -\frac{N_A}{2VM^2} \int {F_1}^0(1){F_1}^0(2) \left[ \exp\left( -\beta \sum_{i_1, i_2} \delta_{i_1 i_2} \right) - 1 \right] d(1,2) \,. \tag{20.57}$$

Differentiation of Eq. (20.57) with respect to $\beta$ leads to

$$\frac{\partial A_2}{\partial \beta} = \frac{N_A n^2}{2M^2} \psi \,, \tag{20.58}$$

where

$$\psi = n^{-2} \sum_{i_1=0}^{n} \sum_{i_2=0}^{n} \psi_{i_1 i_2} \,, \tag{20.59}$$

$$\begin{aligned} \psi_{i_1 i_2} &= V^{-1} \int \delta_{i_1 i_2} {F_1}^0(1){F_1}^0(2) \exp\left( -\frac{W_{12}}{kT} \right) d(1,2) \\ &= \int {F_1}^0(1*2)_{\mathrm{int}} \exp\left( -\frac{W_{12}}{kT} \right) d(1*2)_{\mathrm{int}} \,. \end{aligned} \tag{20.60}$$

The second line of Eqs. (20.60) has been obtained from the first line by the same procedure as used in going from Eq. (20.12) to Eq. (20.14), and ${F_1}^0(1*2)_{\mathrm{int}}$ is, as before, the unperturbed distribution function which describes the internal configuration of a star molecule of functionality 4 (joined at $i_1$ and $i_2$). On the other hand, differentiation of Eq. (20.19) with respect to $\beta$ leads to

$$\frac{\partial A_2}{\partial \beta} = \left( \frac{\partial A_2}{\partial z} \right)_n \frac{\partial z}{\partial \beta} = \frac{N_A n^2}{2M^2} \frac{\partial}{\partial z} [z h_0(z)] \,. \tag{20.61}$$

Comparing Eq. (20.61) with Eq. (20.58), we have

$$\psi = \frac{\partial}{\partial z} [z h_0(z)] \,. \tag{20.62}$$

Thus our problem is to derive a differential equation for $\psi$.

Now, successive differentiation of Eq. (20.60) leads to

$$\frac{\partial\psi_{i_1i_2}}{\partial\beta} = -\sum_{j_1,j_2}\int \delta_{j_1j_2}{F_1}^0(1*2)_{\text{int}}\exp\biggl(-\frac{W_{12}}{kT}\biggr)d(1*2)_{\text{int}}\,,$$
$$\frac{\partial^2\psi_{i_1i_2}}{\partial\beta^2} = \sum_{j_1,j_2}\sum_{k_1,k_2}\int \delta_{j_1j_2}\delta_{k_1k_2}{F_1}^0(1*2)_{\text{int}}\exp\biggl(-\frac{W_{12}}{kT}\biggr)d(1*2)_{\text{int}}\,,$$
$$\frac{\partial^k\psi_{i_1i_2}}{\partial\beta^k} = (-1)^k\sum_{j_1,j_2}\cdots\int\biggl(\prod_{k\ \text{pairs}}\delta_{j_1j_2}\biggr){F_1}^0(1*2)_{\text{int}}\exp\biggl(-\frac{W_{12}}{kT}\biggr)$$
$$\times d(1*2)_{\text{int}}\,. \quad (20.63)$$

Let us introduce the perturbed distribution function,

$$F_1{}'(1*2)_{\text{int}} = {\psi_{i_1i_2}}^{-1}{F_1}^0(1*2)_{\text{int}}\exp\biggl(-\frac{W_{12}}{kT}\biggr) \quad (20.64)$$

with

$$\int F_1{}'(1*2)_{\text{int}}d(1*2)_{\text{int}} = 1\,.$$

The prime on $F_1$ indicates that interactions exist only between two parent chains 1 and 2. Note that the quantity ${\psi_{i_1i_2}}^{-1}$ plays the role of a normalizing constant. Given the distribution function $F_1{}'(1*2)_{\text{int}}$, the distribution function $P'(\mathbf{R}_{j_1j_2},\ldots,\mathbf{R}_{t_1t_2})_{i_1i_2}$ of $k(=\sigma-1)$ vectors $\mathbf{R}_{j_1j_2}$, …, $\mathbf{R}_{t_1t_2}$ for this star molecule may be defined as in Eq. (20.15).From Eqs. (20.59), (20.63), and (20.64), we then obtain

$$\frac{\partial^k\psi}{\partial\beta^k} = (-1)^k n^{-2}\sum_{i_1,i_2}\sum_{j_1,j_2}\cdots\sum_{t_1,t_2}\psi_{i_1i_2}P'(0_{j_1j_2},\ldots,0_{t_1t_2})_{i_1i_2}\,. \quad (20.65)$$

This equation is formally exact. It is easy to see that at $\beta = 0$ the right-hand side of Eq. (20.65) becomes equal to the coefficient of $\beta^k$ in the series in square brackets of Eq.(20.17) if the restrictions, $i_1 \leq j_1 \leq \cdots \leq t_1$, on the summations are introduced. We therefore have

$$\left[\frac{\partial^k\psi}{\partial z^k}\right]_{z=0} = (-1)^k(k+1)!C_k\,, \quad (20.66)$$

where $C_k$ are the coefficients in the expansion,

$$h_0(z) = 1 - C_1z + C_2z^2 - \cdots + (-1)^kC_kz^k + \cdots\,, \quad (20.67)$$

$C_1$ and $C_2$ being 2.865 and 9.202, respectively (not to be confused with the determinants $C_s$).

We now approximate $P'$ in Eq. (20.65) by its value averaged over $i_1$, $i_2$ pairs, as in Eq.(20.54); that is,

$$P'(0_{j_1j_2},\ldots,0_{t_1t_2})_{i_1i_2} \simeq n^{-2}\sum_{i_1,i_2}P'(0_{j_1j_2},\ldots,0_{t_1t_2})_{i_1i_2}\,, \quad (20.68)$$

which gives

$$\frac{\partial^k \psi}{\partial \beta^k} = (-1)^k \psi n^{-2} \sum_{i_1,i_2} \cdots \sum_{t_1,t_2} P'(0_{j_1j_2}, \ldots, 0_{t_1t_2})_{i_1i_2} \,. \tag{20.69}$$

We evaluate the sum in Eq. (20.69) in the unperturbed state, followed by the replacement of $a$ by $a\bar{\alpha}_k$; and we obtain

$$\frac{d^k \psi}{dz^k} = (-1)^k (k+1)! C_k \frac{\psi}{{\bar{\alpha}_k}^{3k}} \qquad (k = 1, 2, \ldots) \,. \tag{20.70}$$

This is to be compared with Eq. (15.70), $\psi$ corresponding to $\alpha^2$. Equation (20.70) may be considered rather defining equations for the scale factors $\bar{\alpha}_k$. Defining new factors $\alpha_k$ by

$$\bar{\alpha}_k = \left( \prod_{i=1}^{k} \alpha_i \right)^{1/k} \tag{20.71}$$

(with $\bar{\alpha}_1 = \alpha_1$) as before, we eliminate $\psi$ from Eqs. (20.70) with (20.71) to obtain

$$\frac{d{\alpha_k}^3}{dz} = \frac{(k+2)C_{k+1}}{C_k} \frac{{\alpha_k}^3}{{\alpha_{k+1}}^3} - \frac{(k+1)C_k}{C_{k-1}} \qquad (k = 1, 2, \ldots) \,. \tag{20.72}$$

with $C_0 \equiv 1$. Equations (20.72) form a hierarchy of differential equations for ${\alpha_k}^3$ which can be truncated to obtain the solution for ${\alpha_1}^3$. The solution for $\psi$ can then be obtained from the $k = 1$ equation of (20.70),

$$\frac{d\psi}{dz} = -2C_1 \frac{\psi}{{\alpha_1}^3} \,, \tag{20.73}$$

and from Eq. (20.62), the function $h_0(z)$ can be found by integration of $\psi$.

Before proceeding to further developments using the hierarchy, we describe briefly the procedure of Kurata et al.[18] The scale factor $\alpha_1$ may be considered to be the expansion factor of the star molecule (joined at $i_1$ and $i_2$) with partial intramolecular interactions between parent chains 1 and 2, averaged over $i_1$, $i_2$ pairs. Thus we may evaluate it approximately from

$$na^2{\alpha_1}^2 = n^{-2} \sum_{i_1,i_2} \langle {R_1}^2 \rangle_{i_1i_2} \,, \tag{20.74}$$

where $R_1$ is the end-to-end distance of parent chain 1. Note that the average of $\langle {R_2}^2 \rangle_{i_1i_2}$ for parent chain 2 also gives the same $\alpha_1$. As in Eq. (15.49), differentiation of the general expression for $\langle {R_1}^2 \rangle_{i_1i_2}$ with respect to $\beta$ leads to

$$\frac{\partial \langle {R_1}^2 \rangle_{i_1i_2}}{\partial \beta} = \sum_{j_1,j_2} \int {R_1}^2 [P'(\mathbf{R}_1)_{i_1i_2} P'(0_{j_1j_2})_{i_1i_2} - P'(\mathbf{R}_1, 0_{j_1j_2})_{i_1i_2}] d\mathbf{R}_1 \,. \tag{20.75}$$

In a first approximation, we replace the $P'$ by the $P_0$ with $a\alpha_1$ in place of $a$. Equation (20.75) then reduces to a differential equation for $\alpha_1$ of the Fixman type, and we have the solution,

$$\alpha_1{}^3 = 1 + 0.683z\,. \tag{20.76}$$

Since $\psi(0) = h_0(0) = 1$, from Eqs. (20.62), (20.73), and (20.76) we find

$$h_0(z) = \frac{1-(1+0.683z)^{-7.39}}{5.047z}\,. \qquad \text{(K)} \tag{20.77}$$

We now turn to the hierarchy approach. In order to examine the behavior of $\alpha_k$, we assume the forms $\psi = \gamma z^{-\nu}$ and $\alpha_k{}^{\nu_k} = \gamma_k z$ at large $z$. In particular, if we consider only the contribution $2T_\sigma$ of the Class I type clusters to the $\sigma$th *Term*, which is given by Eq. (20.25), it can be shown that $\nu = 2$.[8] By the same argument as in Section 15b(iii), substitution of these asymptotic forms into Eqs. (20.72) and (20.73) leads to

$$\lim_{z\to\infty} \alpha_k{}^3 = \gamma_k z\,. \tag{20.78}$$

We impose the following condition on $\alpha_k$ as before,

$$\alpha_k = \alpha_{k+1} \qquad (\text{for large } k)\,. \tag{20.79}$$

It is then straightforward to find approximate solutions for $\alpha_k$, since the differential equations of (20.72) and the conditions of (20.78) and (20.79) are formally the same as those in the YT theory of $\alpha$. By the same argument as before, we therefore arrive at

$$\alpha_k{}^3 = 1 + Kz \qquad (\text{for } k \geq 1) \tag{20.80}$$

with

$$K = \frac{3C_2}{C_1} - 2C_1\,. \tag{20.81}$$

Thus our approximate theory yields the sequence $\alpha_1 = \alpha_2 = \alpha_3 = \cdots$. It is important to recall that in the theory of $\alpha$ the corresponding factors $\alpha_k$ become equal for $k \geq 2$. This difference arises from the fact that $C_0$ is positive in the present case, whereas $C_0$ is negative in the case of the theory of the expansion factor $\alpha$. From Eqs. (20.62), (20.73), and (20.80) we find

$$h_0(z) = \frac{1-(1+Kz)^{-(2C_1-K)/K}}{(2C_1-K)z}\,. \tag{20.82}$$

If we use the exact values for the coefficients $C_1$ and $C_2$, we have

$$h_0(z) = \frac{1-(1+3.903z)^{-0.4683}}{1.828z}\,. \qquad \text{(KY)} \tag{20.83}$$

Naturally Eq. (20.83) yields the exact second-order perturbation theory.

All the approximate expressions for $h_0(z)$ described so far can be reproduced from Eq. (20.82). Suppose $K$ in Eq. (20.82) is taken to be

**TABLE IV.1.** THE COEFFICIENTS $C_1$ AND $C_2$ IN THE EXPANSION OF $h_0(z)$ FROM VARIOUS APPROXIMATE THEORIES

| | $C_1$ | $C_2$ |
|---|---|---|
| Exact | 2.865 | 9.202 |
| FKG | 0.918 | 0.867 |
| IK | 1.043 | 1.135 |
| FKO,o | 1.151 | 1.767 |
| FKO,m | 2.865 | 10.944 |
| KY | 2.865 | 9.202 |
| S | 2.865 | 8.208 |
| K | 2.865 | 6.124 |
| FCM | 2.865 | 5.472 |

an arbitrary constant ranging from 0 to $2C_1$, where $C_1$ is kept equal to 2.865. Then if $K = 0$, Eq. (20.82)reduces to the FCM function of (20.55), in which all $\alpha_k$ are identically equal to unity. If $K = 0.683$, Eq. (20.82) reduces to the K function of (20.77). If $K = C_1$, Eq. (20.82) becomes

$$h_0(z) = \frac{1}{1 + 2.865z}\,. \qquad \text{(S)} \qquad (20.84)$$

This is a semi-empirical equation proposed by Stockmayer.[15] Further, Eq. (20.82) can be shown to reduce to the FKO,m function of (20.44) in the limit for $K = 2C_1$. In Table IV.1 are given the values for the first two coefficients in the expansion of $h_0(z)$ from various approximate theories. The second coefficient is seen to vary from 5.472 (the FCM value) to 10.944(the FKO,m value) as $K$ in Eq.(20.82) is increased from 0 to 5.73, $C_1$ being kept equal to 2.865.

We now compare the numerical results obtained from various approximate theories. In Fig. IV.3 are plotted the values of $h_0(z)$ predicted by the FKO,o theory, Eq. (20.43), the FKO,m theory, Eq. (20.44), The KY theory, Eq. (20.83), the S theory, Eq. (20.84), the K theory, Eq. (20.77), and the FCM theory, Eq. (20.55). The values predicted by the FKG theory, Eq. (20.39),and the IK theory, Eq. (20.41), are very close to those predicted by the FKO,o theory. All the functions $h_0(z)$ but the FKO,o (and also FKG and IK) function have the correct initial slope, and there is seen to be a correlation between the value of $K$ in Eq. (20.82) and the rate of decrease of $h_0(z)$. The FKO,o function decreases with increasing $z$ less rapidly than the others. It is because of this behavior that a number of attempts have been made to improve the theory.

Finally, we give a brief discussion of the asymptotic behavior of $h_0(z)$ for large $z$.Albrecht[8] showed that $h_0(z)$ is asymptotically proportional to $z^{-1}$ for large $z$, considering only the contribution $2T_\sigma$

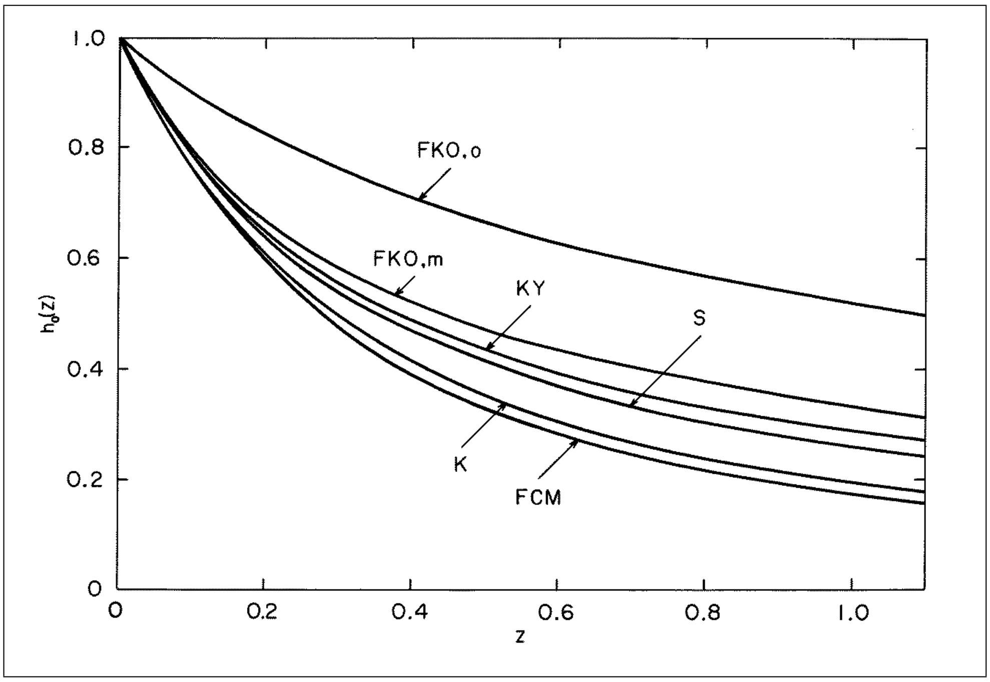

**Fig. IV.3.** Theoretical values of $h_0(z)$ calculated from various approximate theories. Curve FKO,o: the original Flory–Krigbaum–Orofino theory, Eq. (20.43). Curve FKO,m: the modified Flory–Krigbaum–Orofino theory, Eq. (20.44). Curve KY: the Kurata–Yamakawa theory, Eq. (20.83). Curve S: the Stockmayer equation, Eq. (20.84). Curve K: the Kurata theory, Eq. (20.77). Curve FCM: the Fixman–Casassa–Markovitz theory, Eq. (20.55).

of the Class I type clusters to the $\sigma$th *Term*. It can now be shown that both the FKG and IK functions have the asymptotic form, const. $z^{-1}(\ln z)^{3/2}$, while the FKO,o or FKO,m function has the form, $z^{-1}\ln z$. For extremely large $z$, these functions vary as $z^{-1}$. Further, it is easy to see that variation of $h_0(z)$ with $z^{-1}$ at large $z$ is also given by Flory's uniform-density sphere model and by Eq. (20.82) including the KY, S, K, and FCM functions. Thus all the theories of $A_2$ described above predict that

$$\lim_{z\to\infty} h_0(z) = \text{const.} z^{-1} \,. \tag{20.85}$$

## 21. The Second Virial Coefficient (B): Real Polymer Chains with Intramolecular Interactions

Since the effect of intramolecular interactions has been neglected throughout the preceding treatment of the second virial coefficient, the theory thus far presented is not self-consistent at nonzero values of the parameter $z$. Our problem in the present section is to investigate this effect and complete the theory of $A_2$ for linear flexible chains. We shall first describe the perturbation theory and then approximate treatments. Finally, a general analysis of the behavior of $A_2$ will be given.

## 21a. Perturbation Theory

We consider the effect of intramolecular interactions only through the single-contact term in the one-body molecular distribution function $F_1(1)$ or $F_1(2)$. The cluster analysis for this case was first presented by Yamakawa and Kurata.[20] We expand the double product in the integrand of Eq. (20.6) and split the integral into two parts,

$$A_2 = -\frac{N_A}{2VM^2}\Bigg[\int F_1(1)F_1(2)\sum_{i_1,i_2}\chi_{i_1i_2}d(1,2)$$
$$+\int F_1(1)F_1(2)\Bigg(\sum_{i_1,i_2}\sum_{j_1,j_2}\chi_{i_1i_2}\chi_{j_1j_2}+\sum_{i_1,i_2}\sum_{j_1,j_2}\sum_{k_1,k_2}\chi_{i_1i_2}\chi_{j_1j_2}\chi_{k_1k_2}$$
$$+\cdots\Bigg)d(1,2)\Bigg]\,. \tag{21.1}$$

Since the distribution functions $F_1(1)$ and $F_1(2)$ depend only on the internal coordinates, the first integral is easily seen to yield the value, $-Vn^2\beta$. We now use Eq. (20.8) instead of Eq. (20.10) for the $F_1(1)$ appearing in the second integral. Recalling that the Boltzmann factor in Eq. (20.8) is identical with that in Eq.(14.1), $F_1(1)$ may be expanded as

$$F_1(1) = Z^{-1}{F_1}^0(1)\Bigg(1+\sum_{s_1<t_1}\chi_{s_1t_1}+\cdots\Bigg) \tag{21.2}$$

with

$$Z = 1-\beta\sum_{s_1<t_1}P_0(0_{s_1t_1})+\cdots\,. \tag{21.3}$$

A similar expansion is possible for $F_1(2)$. Equation (21.1) may therefore be rewritten as

$$A_2 = -\frac{N_A}{2VM^2}\Bigg[-Vn^2\beta+Z^{-2}\int {F_1}^0(1){F_1}^0(2)\big(\textstyle\sum\sum\chi_{i_1i_2}\chi_{j_1j_2}$$
$$+\textstyle\sum\sum\sum\chi_{i_1i_2}\chi_{j_1j_2}\chi_{s_1t_1}+\sum\sum\sum\chi_{i_1i_2}\chi_{j_1j_2}\chi_{s_2t_2}+\cdots\big)d(1,2)\Bigg]\,, \tag{21.4}$$

where the second and third *Terms* of the integrand are new triple-contact terms which correspond to single intramolecular and double intermolecular contacts in coexistence. The integrations in Eq. (21.4) can be performed using the same procedure as that of Section 20a; the result may be expressed in terms of the probability densities for

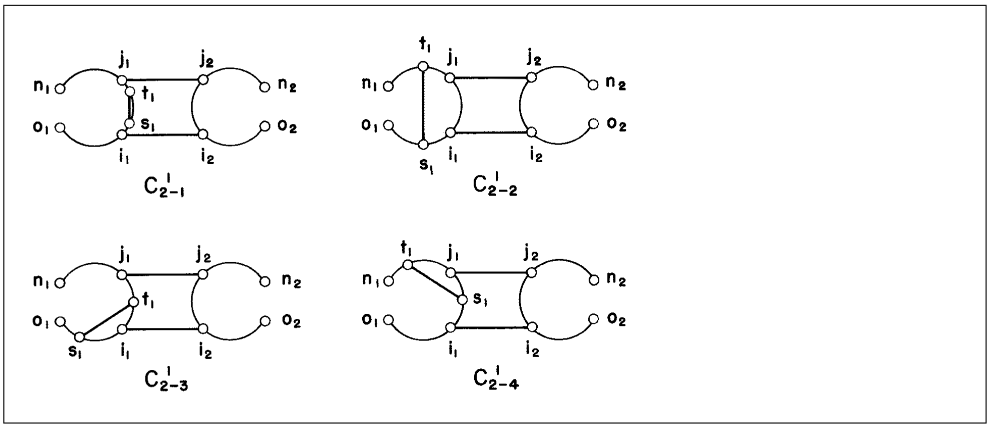

**Fig. IV.4.** Cluster diagrams for the double intermolecular contact term with a single intramolecular contact.

segment contacts. Expanding $Z^{-2}$ in a geometric series and collecting powers of $\beta$, we obtain

$$A_2 = (N_A n^2 \beta / 2M^2) h(z) \tag{21.5}$$

with

$$\begin{aligned} h(z) = h_0(z) + 2\beta n^{-2} \textstyle\sum\sum\sum \big[\, & P_0(0_{j_1 j_2}, 0_{s_1 t_1})_{i_1 i_2} \\ & - P_0(0_{j_1 j_2})_{i_1 i_2} P_0(0_{s_1 t_1}) \,\big] + \cdots , \end{aligned} \tag{21.6}$$

where $h_0(z)$ is given by Eq. (20.23). The symmetry factor of 2 in Eq. (21.6) arises from the fact that the two new triple-contact terms of Eq. (21.4) lead to equivalent contributions, since it can make no difference whether the single intramolecular contact exists in chain 1 or 2. From Eqs. (21.5) and (21.6), intramolecular interactions are seen to have no influence on the single- and double-contact terms of $A_2$ but do alter the higher-order terms. Equation (21.6) can readily be rewritten as

$$h(z) = 1 - 2.865z + (9.202 + D)z^2 - \cdots \tag{21.7}$$

with

$$D = 2n^{-3} \sum [({C_2}^1)^{-3/2} - C_1^{-3/2} (C^1)^{-3/2}] \,, \tag{21.8}$$

where ${C_2}^1$, $C_1$, and $C^1$ are the determinants associated with the probability densities $P_0(0_{j_1 j_2}, 0_{s_1 t_1})_{i_1 i_2}$, $P_0(0_{j_1 j_2})_{i_1 i_2}$, and $P_0(0_{s_1 t_1})$ in Eq. (21.6), respectively, and the sum is taken over the indices.

We now make a cluster analysis. Twelve possible types of triple contacts can appear in ${C_2}^1$. However there is inherent symmetry which causes two different types to yield two ${C_2}^1$ differing only in that in one the indices $i_2$ and $j_2$ are labeled in just the reverse manner; these lead to equivalent contributions. This symmetry occurs also in $C_1$ and is just the first kind of symmetry discussed in Section 20a. Thus we need only consider the six types with $i_1 \leq j_1$ and $i_2 \leq j_2$, applying the symmetry factor of two to each of them. Among these six types, two types (with $s_1 < t_1 < i_1$ and $j_1 < s_1 < t_1$) make no contribution, since for these types ${C_2}^1 = C_1C^1$. In Fig. IV.4 there are depicted the remaining four types which contribute to $D$. Now types ${C_{2-3}}^1$ and ${C_{2-4}}^1$ are easily seen to lead to equivalent contributions once the sum has been evaluated. Thus the types that require evaluation are ${C_{2-1}}^1$, ${C_{2-2}}^1$, and ${C_{2-3}}^1$, the symmetry factors to be applied being 4, 4, and 8, respectively [with inclusion of the factor of 2 in Eq. (21.8)]. The sums may be converted to integrals. Denoting the integrals corresponding to the above three types by $D_1$, $D_2$, and $D_3$, respectively, we have $D = 4D_1 + 4D_2 + 8D_3$. The integrals $D_1$ and $D_2$ can be evaluated analytically, but $D_3$ requires a numerical integration. The result is[10, 18]

$$D = 5.076\,. \tag{21.9}$$

We note that $D_1$ was first erroneously evaluated by Yamakawa and Kurata,[20] and then Kurata et al.[18] corrected it and evaluated $D_2$ and $D_3$ with the result $D = 5.097$, and finally Tagami and Casassa[10] reevaluated $D_3$ and arrived at Eq. (21.9).

Substitution of Eq. (21.9) into Eq.(21.7) leads to

$$h(z) = 1 - 2.865z + 14.278z^2 - \cdots\,. \tag{21.10}$$

Equation (21.5) with (21.10) represents the second-order perturbation theory of the second virial coefficient for real polymer chains with intramolecular interactions. Equation (21.10) is to be compared with Eq. (20.23) for the function $h_0(z)$.

## 21b. Approximate Treatments

We must now derive an approximate closed expression for the function $h(z)$ which can be applied also when $z$ is large. Equations (20.11) and (21.1) suggest that in the uniform-expansion approximation the distribution function $F_1(i)$ may be replaced by ${F_1}^0(i)$ with an effective bond length $a\alpha^*$ in place of $a$, where $a^*$ is the expansion factor of one polymer molecule in contact with another. We then obtain

$$h(z) = h_0(\bar{z}) \tag{21.11}$$

with

$$\bar{z} = z/(\alpha^*)^3\,. \tag{21.12}$$

This implies that $h(z)$ may be approximated by the function $h_0$ with the argument $\bar{z}$ in place of $z$. In other words, an approximate theory of $A_2$ is given by Eq. (21.5) with (21.11) if any of the approximate closed expressions for $h_0$ as described in Section 20b is adopted in conjunction with an expression for $\alpha^*$. Thus the problem is to find a closed expression for $\alpha^*$.

The first-order perturbation theory of $\alpha^*$ can readily be derived. Let us expand $(\alpha^*)^2$ in powers of $z$,

$$(\alpha^*)^2 = 1 + Az - \cdots \,. \tag{21.13}$$

By assumption, $h(z)$ may be expanded in the form,

$$h(z) = 1 - 2.865(z/\alpha^{*3}) + 9.202(z/\alpha^{*3})^2 - \cdots \,. \tag{21.14}$$

Substituting Eq. (21.13) into Eq. (21.14) and setting the coefficient of $z^2$ equal to that in Eq.(21.10), we find

$$A = 1.181 \,. \tag{21.15}$$

This value is a little smaller than the value of 1.276 for the corresponding coefficient in the expansion of ${\alpha_s}^2$ for an isolated molecule. The reason for the differences is easy to understand:the expansion of one molecule is suppressed by intermolecular interactions with another. However, this difference is of rather minor importance; and for practical purpose, we may assume that $\alpha^* = \alpha_S$, as was done by Flory and Krigbaum.[7] Thus we redefine the parameter $\bar{z}$ by

$$\bar{z} = z/{\alpha_S}^3 \,. \tag{21.16}$$

Casassa[21] and Ptitsyn and Eizner[22] obtained the values 1.858 and 2.93 for the coefficient $A$, respectively, using different assumptions, and adopted an equation for $\alpha^*$ of Flory type, $(\alpha^*)^5 - (\alpha^*)^3 = Az$. However, their values for $A$ have no great significance, since the exact value is now available.

We now proceed to a general analysis of the behavior of the second virial coefficient. If Eq (21.16) is combined with any of the equations for $\alpha_s$ with the exponent $\nu$ in Eq. (15.1) greater than three, the parameter $\bar{z}$ is seen to increase with $z$. Therefore, $h(z)$ is still a decreasing function of $z$, and $A_2$ decreases with increasing molecular weight. Also, the previous conclusion that $A_2 = 0$ at $T = \Theta$ or at $\beta = z = 0$ remains unaltered. Thus, we use the vanishing of $A_2$ to define the theta temperature. Equation (21.5) with (21.11) and (21.16) may now be rewritten as

$$A_2 = 4\pi^{3/2} N_A \frac{\langle S^2 \rangle^{3/2}}{M^2} \Psi \tag{21.17}$$

with

$$\Psi = \bar{z} h_0(\bar{z}) \,. \tag{21.18}$$

The values of $\Psi$ from various approximate theories of $h_0$ are plotted against $\bar{z}$ in Fig. IV.5. It is seen that $\Psi$ is an increasing function of $\bar{z}$, and hence of $z$. In addition, the mean-square radius $\langle S^2 \rangle$ is an increasing function of $\beta$. Thus $A_2$ increases with $\beta$; the greater the solvent power, the larger the second virial coefficient. From Eq. (20.85), $\Psi$ is predicted to approach a constant as $\bar{z}$ tends to infinity. Then $A_2$ becomes proportional to $\langle S^2 \rangle^{3/2}/M^2$ in the limit of $z = \infty$. This form

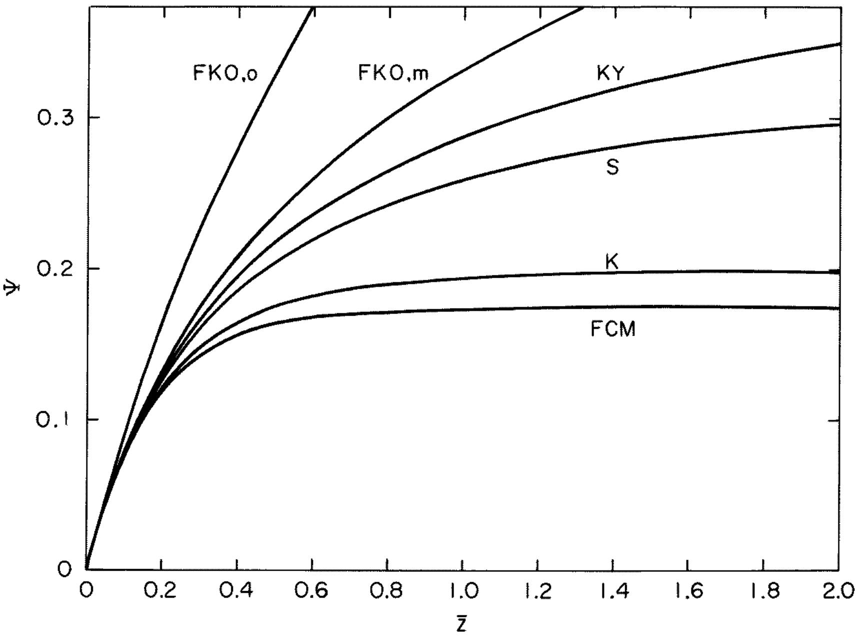

**Fig. IV.5.** Theoretical values of $\Psi$ as a function of $\bar{z}$ from various approximate theories. The curves correspond to those in Fig.IV.3.

of $A_2$ is equivalent to that for rigid sphere molecules with a diameter proportional to $\langle S^2 \rangle^{1/2}$ (see Appendix IV A). Therefore polymer chains in very good solvents may be regarded as thermodynamically noninterpenetrating spheres. On the other hand, polymer molecules are completely interpenetrable at the theta temperature, at which $\Psi$ vanishes. Thus the function $\Psi$ represents the degree of interpenetration of polymer molecules in dilute solution.

We now ask the following question: which expression for $\alpha_S$ is to be combined with a given expression for $h_0$ in order to complete the form of $\Psi$ as a function of $z$. Necessarily this must be done from the point of view of maintaining the self-consistency of the intramolecular and intermolecular theories. First, there is no reason why the FKO,o equation for $h_0$ should not be combined with the F,o equation for $\alpha_S$, since both are based on the smoothed Gaussian density model. Similarly, the FKO,m equation for $h_0$ should be combined with the F,m equation for $\alpha_S$. Further, the KY equation for $h_0$ may be combined with the YT equation for $\alpha_S$, since both were derived by the hierarchy approach. However, there is no explicit justification of any other combination. The above three combinations will be tested by comparison with experiment in Chapter VII.

## 22. The Third Virial Coefficient

The first investigation of the third virial coefficient, $A_3$, for flexible chain polymers is again Zimm's formulation,[5] developed on the basis of the McMillan–Mayer theory. To avoid complications, Flory and Krigbaum[7] simply assumed that $A_3$ has the same relation to $A_2$ as in the case of rigid sphere molecules; that is (see Appendix IV B),

$$A_3/{A_2}^2M = \tfrac{5}{8}\,. \tag{22.1}$$

Subsequently, smoothed-density theories of $A_3$ were developed by Stockmayer and Casassa[23] and by Koyama,[24] and an approximate closed expression for $A_3$ was derived by Yamakawa.[25] Investigations of the third virial coefficient are very few in number compared to the numerous theories of the second virial coefficient. Nevertheless some knowledge of $A_3$ is required for the accurate evaluation of $M$ and $A_2$ by extrapolation of experimental data to infinite dilution, especially in the case of high-molecular-weight polymers in good solvents.

### 22a. Perturbation Theory

The perturbation theory of $A_3$ was formulated first by Zimm[5] and subsequently developed by Stockmayer[15] and Yamakawa.[25] Our starting point is Eq. (19.56) with (19.58). Integrations must then be performed over the distribution function $F_3$(1,2,3) related to the potential $W_3$(1,2,3) as well as over $F_2$ related to $W_2$. Although $W_2$(1,2) is given exactly by Eq. (20.3), it is necessary to make the superposition approximation in $W_3$(1,2,3). In this approximation, the component potential $w_3$ is neglected in Eq. (19.29) with $n = 3$ and $W_3$ may be expressed as a sum of self and pair potentials only; that is,

$$\begin{aligned} W_3(1,2,3) = {} & W_1(1) + W_1(2) + W_1(3) \\ & + W_{12}(1,2) + W_{23}(2,3) + W_{13}(1,3)\,. \end{aligned} \tag{22.2}$$

In terms of the distribution functions, the superposition approximation reads, from Eqs. (19.22), (20.3), and (22.2),

$$F_3(1,2,3) = \frac{F_2(1,2)F_2(2,3)F_2(1,3)}{F_1(1)F_1(2)F_1(3)}\,. \tag{22.3}$$

From Eqs. (19.57), (19.58), and (22.3), the function $g_3$(1,2,3) may then be reduced to

$$\begin{aligned} g_3(1,2,3) = {} & \frac{g_2(1,2)g_2(2,3)g_2(1,3)}{F_1(1)F_1(2)F_1(3)} + \frac{g_2(1,2)g_2(1,3)}{F_1(1)} \\ & + \frac{g_2(2,3)g_2(1,2)}{F_1(2)} + \frac{g_2(1,3)g_2(2,3)}{F_1(3)}\,. \end{aligned} \tag{22.4}$$

The last three terms on the right-hand side of Eq. (22.4) lead to equivalent contributions to $A_3$ after integration over (1,2,3). From Eqs. (19.56) and (22.4), we therefore have

$$\begin{aligned} A_3 = & -\frac{N_A^2}{3VM^3}\int \frac{g_2(1,2)g_2(2,3)g_2(1,3)}{F_1(1)F_1(2)F_1(3)}d(1,2,3) \\ & -\frac{N_A^2}{VM^3}\int \frac{g_2(1,2)g_2(1,3)}{F_1(1)}d(1,2,3) + 4{A_2}^2M\,. \end{aligned} \tag{22.5}$$

Zimm[5] and Stockmayer and Casassa[23] used Eq. (22.5) with omission of the last two terms. These two terms, in fact, cancel each other for rigid sphere molecules and also for smoothed-density models, but this is not necessarily the case for random-flight chain models.[25]

To proceed further, we assume the random-flight chain to be expanded uniformly by the factor $\alpha_S$, as in Section 21b. The distribution function $F_1(i)$ then reduces to ${F_1}^0(i)$ of (20.10) with $a\alpha_S$ in place of $a$. This approximation is used throughout Section 22. Now Eq. (20.4) and similar equations are used for the pair potentials $W_{ij}$, and the $\chi$ functions, as given by Eq. (20.7), are introduced. The ternary cluster integral $\beta_2$ as well as the binary cluster integral $\beta$ will then occur in $A_3$[5, 15, 26] where $\beta_2$ may be defined by

$$\beta_2 = -\int' \chi_{i_1i_2}\chi_{i_2i_3}\chi_{i_1i_3}d\mathbf{R}_{i_1i_2}d\mathbf{R}_{i_2i_3}d\mathbf{R}_{i_1i_3}\,. \tag{22.6}$$

The prime indicates that the integration is carried out under the condition, $\mathbf{R}_{i_1i_2}+\mathbf{R}_{i_2i_3}+\mathbf{R}_{i_3i_1}=0$. Now, experimentally, $A_3$ is nearly equal to zero at the theta temperature at which $A_2$ and $\beta$ vanish.[27, 28] Furthermore, possibilities for ternary clustering will be much smaller than those for binary clustering, provided $n$ is very large. Thus we here neglect $\beta_2$. Introduction of this approximation leads to a two-parameter theory of $A_3$.

The perturbation theory can now be formulated without difficulty. Expanding Eq. (22.5) and integrating, we may write $A_3$ in the form,

$$\begin{aligned} A_3 = & ({N_A}^2n^4\beta^2/3M^3)\{\bar{z}n^{-9/2}\textstyle\sum D_1^{-3/2} \\ & -3\bar{z}^2n^{-5}[\textstyle\sum {D_2}^{-3/2}+\sum {K_2}^{-3/2}-(\sum {C_1}^{-3/2})^2]+\cdots\}\,, \end{aligned} \tag{22.7}$$

where $\bar{z}$ is given by Eq. (21.16). The summations in Eq. (22.7) are performed with respect to the indices $k_1$, $k_2$, $i_2$, $i_3$, and so on. $D_1$, $D_2$, …, $D_s$, … are the determinants arising from the conditional probability densities $P_0(0_{i_2i_3},\ldots)_{j_1j_3,k_1k_2}$, that, when two initial contacts between segments $j_1$ and $j_3$, and $k_1$ and $k_2$ exist, there also exist $s$ additional specified contacts between segments $i_2$ and $i_3$, …, and so on, where at least one of the $s$ additional contacts must exist between segments of molecules 2 and 3. Similarly, the determinant $K_2$ arises from $P_0(0_{l_1l_2},0_{m_1m_3})_{j_1j_3,k_1k_2}$, and $C_1$ from Eq. (20.18). It must be noted that the terms involving $D_1$, $D_2$, …, in Eq. (22.7) result from the leading term on the right-hand side of Eq. (22.5), and the terms involving $K_2$ and $C_1$ from the second and last terms of Eq. (22.5), respectively.

Thus an approximation to $A_3$ by the leading term of Eq. (22.5) is seen to yield the correct term linear in $\bar{z}$, but not the correct higher-order terms.

We evaluate only the first term in the expansion of (22.7), the evaluation of the second term being too laborious to present. Replacing the summations by integrations, we find

$$A_3 = (N_A{}^2 n^4 \beta^2 / 3M^3)(\lambda_1 \bar{z} - \cdots) \tag{22.8}$$

with

$$\lambda_1 = 8 \int_0^1 \int_0^1 \int_0^1 \int_0^X \int_0^Y \int_0^Z (x+y+z)^{-3/2} dX\,dY\,dZ\,dx\,dy\,dz = 1.664\,. \tag{22.9}$$

Equation (22.8) with (22.9) represents the first-order perturbation theory of $A_3$ developed by Stockmayer[15] (where a symmetry factor of 4 was erroneously introduced) and by Yamakawa.[25]

## 22b. Approximate Closed Expressions

For convenience, we first describe a smoothed-density theory following Stockmayer and Casassa.[23] This theory may be considered to be an extension of the $A_2$ theory of Flory and Krigbaum. For the Gaussian smoothed-density model, $A_3$ may be approximated by the leading term on the right-hand side of Eq. (22.5), which becomes equivalent to the expression for $A_3$ for rigid sphere molecules,

$$A_3 = -\frac{N_A{}^2}{3M^3} \int' f_{12} f_{23} f_{13} d\mathbf{S}_{12} d\mathbf{S}_{23} d\mathbf{S}_{13} \tag{22.10}$$

with

$$f_{ij} = \exp(-V_{ij}/kT) - 1\,, \tag{22.11}$$

where $\mathbf{S}_{ij}$ is the distance between the centers of molecules $i$ and $j$, and $V_{ij}$ is the Flory–Krigbaum potential,

$$V_{ij}/kT = 3^{3/2} \bar{z} \exp(-3S_{ij}{}^2 / 4\langle S^2 \rangle) \tag{22.12}$$

[compare with Eq. (20.38)]. Equation (22.12) leads to Eq. (21.17) for $A_2$ with $h_0(\bar{z})$ given by Eq. (20.39) with $\bar{z}$ in place of $z$. Since $A_3$ is not easily obtained from Eqs. (22.10) to (22.12), we consider another expression for $V_{ij}$ or $f_{ij}$,

$$f_{ij} = -A \;\exp(-B^2 S_{ij}{}^2)\,, \tag{22.13}$$

where the parameters $A$ and $B$ will be determined later. Equations (22.13) gives the second and third virial coefficients,

$$A_2 = \pi^{3/2} N_A A / 2M^2 B^3\,, \tag{22.14}$$

$$A_3 = \pi^3 N_A{}^2 A^3 / 3^{5/2} M^3 B^6\,. \tag{22.15}$$

From these equations, we have

$$A_3/A_2{}^2M = 0.257A\,. \tag{22.16}$$

Now we determine the parameters $A$ and $B$. On assuming that the Flory–Krigbaum potential is valid, the requirement that the second virial coefficients of (21.17) and (22.14) be the same gives one condition,

$$B^3\Psi = A/8\langle S^2\rangle^{3/2}\,. \tag{22.17}$$

However, another condition is still required to fix $A$ and $B$ uniquely. Probably the most trustworthy second condition is obtained in the following manner. Let us define a function $\varphi(S_{ij})$ by

$$S_{ij}f_{ij} = -(2\langle S^2\rangle^{1/2}/3^{1/2})\varphi(S_{ij})\,. \tag{22.18}$$

The alternative expressions for $\varphi$ given by Eqs. (22.12) and (22.13) are then

$$\varphi_1(t) = t\{1 - \exp[-3^{3/2}\bar{z}\exp(-t^2)]\}\,, \tag{22.19}$$

$$\varphi_2(t) = At\ \exp[-(A/3^{3/2}\Psi)^{2/3}t^2]\,, \tag{22.20}$$

respectively, where we have put $t^2 = 3S_{ij}{}^2/4\langle S^2\rangle$, and applied the condition of (22.17) in writing $\varphi_2$. Plots of $\varphi_1(t)$ and $\varphi_2(t)$ against $t$ are then compared and that value of $A$ is chosen which causes the two curves to coincide as nearly as possible. Thus we can find the values of $A$, and therefore of $A_3/A_2{}^2M$ from Eq. (22.16), as functions of $\bar{z}$. The results are shown by the points in Fig. IV.6, where the horizontal line segment indicates the asymptotic value (rigid sphere value) for large $\bar{z}$. The present theory predicts that $A_3/A_2{}^2M$ becomes zero at $z = 0$, and increases monotonically with increasing $\bar{z}$ or $z$.

Next we describe briefly the differential-equation approach of Yamakawa,[25] which is in the spirit of Section 20b(iii). For our present purposes, it is better to use different coupling parameters for the potentials $W_{23}$, $W_{13}$, and $W_{12}$, and differentiate $A_3$ with respect to the coupling parameters. The procedure is similar to the coupling-parameter method in the theory of liquids.[2, 3] Thus, we write the above potentials in the form,

$$\frac{W_{23}(2,3;\xi_1)}{kT} = \xi_1\beta\sum_{i_2,i_3}\delta_{i_2i_3}\,, \tag{22.21}$$

and similar equations for $W_{13}(1,3;\xi_2)$ and $W_{12}(1,2;\xi_3)$. Each of the $\xi_i$'s ranges from zero to unity. The real system has $\xi_1 = \xi_2 = \xi_3 = 1$. The third virial coefficient $A_3(\boldsymbol{\xi})$ as a function of $\boldsymbol{\xi} = (\xi_1,\xi_2,\xi_3)$ consists of three parts,

$$A_3(\boldsymbol{\xi}) = A_3{}^{(1)}(\boldsymbol{\xi}) + A_3{}^{(2)}(\boldsymbol{\xi}) + A_3{}^{(3)}(\boldsymbol{\xi})\,, \tag{22.22}$$

where $A_3{}^{(1)}$, $A_3{}^{(2)}$, and $A_3{}^{(3)}$ correspond to the first, second, and last terms on the right-hand side of Eq. (22.5), respectively. Now successive differentiations of $A_3(\boldsymbol{\xi})$ with respect to $\xi_1$, $\xi_2$, and $\xi_3$, lead to

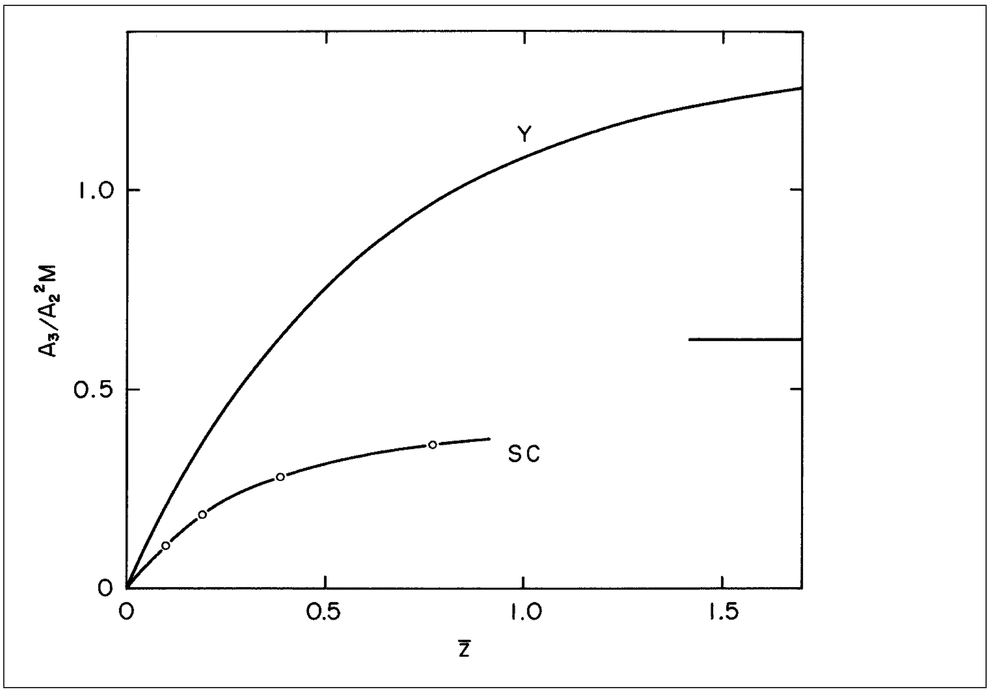

**Fig. IV.6.** Theoretical values of $A_3/A_2^{\,2}M$ as a function of $\bar{z}$. Curve SC: the Stockmayer–Casassa theory. Curve Y: the Yamakawa theory, Eq. (22.32). The horizontal line segment indicates the rigid sphere value of 5/8.

$$\frac{\partial^3 A_3}{\partial\xi_1\,\partial\xi_2\,\partial\xi_3} = \frac{\partial^3 A_3^{\,(1)}}{\partial\xi_1\,\partial\xi_2\,\partial\xi_3} = -\frac{N_A^{\,2}n^4\beta^2}{3M^3}H\,, \tag{22.23}$$

where

$$H = \frac{1}{3}\sum_{i=1}^{3}\frac{\partial I_i}{\partial\xi_i}\,, \tag{22.24}$$

$$\frac{\partial I_1}{\partial\xi_1} = -\beta n^{-4}I_1\sum_{i_2,i_3}\sum_{j_1,j_3}\sum_{k_1,k_2}P'(0_{i_2i_3})_{j_1j_3,k_1k_2}\,, \tag{22.25}$$

and similar equations for $I_2$ and $I_3$. In obtaining Eq. (22.25), we have used an approximation analogous to Eq. (20.54). The prime on $P$ indicates, as before, that there are interactions only among three parent chains. For simplicity, we now introduce the Fixman–Casassa–Markovitz approximation, in which the scale factor $\alpha_1$ appearing in $P'$ is set equal to unity. Equation (22.25) then reduces to

$$\frac{\partial \ln I_1}{\partial\xi_1} = -\lambda_1\bar{z}\,, \tag{22.26}$$

where $\lambda_1$ is given by Eq. (22.9). In the same approximation, it can easily be verified that

$$A_3^{\,(2)} + A_3^{\,(3)} = 0\,, \tag{22.27}$$

$$I_1(0,\xi_2,\xi_3) = \psi(\xi_2)\psi(\xi_3) = \exp[-2C_1\bar{z}(\xi_2+\xi_3)]\,, \tag{22.28}$$

where $\psi$ is the same function as that appearing in Eq. (20.58), and $C_1 = 2.865$.

Now integration of Eq. (22.26) leads to

$$\begin{aligned} I_1 &= I_1(0,\xi_2,\xi_3)\exp(-\lambda_1\bar{z}\xi_1) \\ &= \exp[-\lambda_1\bar{z}\xi_1 - 2C_1\bar{z}(\xi_2+\xi_3)]\,, \end{aligned} \tag{22.29}$$

where we have used Eq. (22.28). Solutions for $I_2$ and $I_3$ can easily be written down by exchanging $\xi_1$ and $\xi_2$, and $\xi_1$ and $\xi_3$, respectively, in Eq. (22.29). From these equations and Eqs. (22.23) and (22.24), we obtain the desired solution with $\boldsymbol{\xi} = \mathbf{1}$,

$$A_3 = ({N_A}^2 n^4\beta^2/3M^3)[1-\exp(-\lambda_1\bar{z})][1-\exp(-2C_1\bar{z})]^2/(2C_1\bar{z})^2\,. \tag{22.30}$$

At small $\bar{z}$, Eq. (22.30) may be expanded in the form,

$$A_3 = ({N_A}^2 n^4\beta^2/3M^3)(1.664\bar{z} - 10.920\bar{z}^2 + \cdots)\,. \tag{22.31}$$

Thus Eq. (22.30) is seen to yield the exact first-order perturbation theory result, as expected. Necessarily Eq. (22.30) should be combined with the FCM theory of $A_2$, and we therefore have

$$A_3/{A_2}^2M = \tfrac{4}{3}[1-\exp(-\lambda_1\bar{z})]\,. \tag{22.32}$$

The present theory predicts that $A_3/{A_2}^2M$ is zero at the theta temperature, and has the asymptotic value 1.333, which is greater than the hard sphere value. We note that Koyama[24] obtained the corresponding value of 0.704 for the Gaussian smoothed-density model of IK. The values of $A_3/{A_2}^2M$ from Eq. (22.32) are shown by curve Y in Fig. IV.6. In any case, it may be concluded that for flexible chains $A_3/{A_2}^2M$ is an increasing function of $z$. A comparison of theory and experiment based on osmotic pressure data will be considered in Chapter VII.

## 23. Remarks

### 23a. Heterogeneous Polymers

The osmotic pressure of a solution of heterogeneous polymers may easily be formulated through the second term of the virial expansion. The solute is considered to be a mixture of chain polymers differing only in molecular weight. If $N_i$ is the number of polymer species $i$ of molecular weight $M_i$ in the solution, the number density $\rho_i$ and concentration $c_i$(g/cc) of species $i$ and the whole concentration $c$ are given by

$$\begin{aligned} \rho_i &= N_A c_i/M_i\,, \\ c_i &= M_i N_i/N_A V\,, \\ c &= \sum_i c_i\,. \end{aligned} \tag{23.1}$$

For this case, the osmotic pressure $\pi$ may be written, from Eq. (19.52), as

$$\pi = RT\left(\frac{1}{\langle M\rangle_n}c + A_2c^2 + \cdots\right), \tag{23.2}$$

where

$$\langle M\rangle_n = \sum_i M_iN_i \Big/ \sum_i N_i\,, \tag{23.3}$$

$$A_2 = \sum_i\sum_j N_A {B_2}^0{}_{,ij}N_iN_j \bigg/ \left(\sum_i M_iN_i\right)^2. \tag{23.4}$$

The quantity $\langle M\rangle_n$ is referred to as the *number-average molecular weight* of the polymer.

We now introduce the weight fraction $w_i$ of polymer species $i$ defined by

$$w_i = M_iN_i \Big/ \sum_i M_iN_i\,. \tag{23.5}$$

The alternative expressions for $\langle M\rangle_n$ and $A_2$ are[5, 7, 29]

$$\langle M\rangle_n = 1\Big/\sum_i (w_i/M_i)\,, \tag{23.6}$$

$$A_2 = \sum_i\sum_j A_{ij}w_iw_j \tag{23.7}$$

with

$$A_{ij} = -\frac{N_A}{2VM_iM_j}\int g_2(i,j)d(i,j)\,, \tag{23.8}$$

where we have used Eqs. (19.37) and (19.51) in writing $A_2$. The discrete function $w_i$ is often replaced by a continuous function $w(M)$, which represents the molecular-weight distribution of the whole polymer such that $w(M)dM$ is the weight fraction of polymer of molecular weight between $M$ and $M + dM$. Equations (23.6) and (23.7) may then be rewritten as

$$\langle M\rangle_n = 1\bigg/\int_0^\infty M^{-1}w(M)\,dM\,, \tag{23.9}$$

$$A_2 = \int_0^\infty\int_0^\infty A_{ij}w(M_i)w(M_j)dM_idM_j\,. \tag{23.10}$$

In the particular case of homogeneous polymers, $w$ is represented by a delta function, $w(M_i) = \delta(M_i - M)$, and Eq. (23.10) reduces to Eq. (19.55). The problem is to evaluate $A_2$ from Eq. (23.10) assuming an appropriate form for the distribution $w$. This problem is deferred to the next chapter, where another average of $A_{ij}$ will be defined in formulating the intensity of light scattering from a multicomponent system, and the two kinds of second virial coefficients will be compared with each other.

**TABLE IV.2.** VALUES OF $C$ FOR UNIFORM STAR MOLECULES OF FUNCTIONALITY $f$[30]

| $f$ | $C$ |
|---|---|
| 1 | 2.865 |
| 2 | 2.865 |
| 3 | 3.279 |
| 4 | 3.873 |
| 5 | 4.586 |
| 6 | 5.390 |
| 8 | 7.219 |
| 12 | 11.585 |
| $\infty$ | $0.2201f^{3/2}$ |

## 23b. Branched and Ring Polymers

We consider the effects of branching and ring formation on the second virial coefficient for the same types of molecules as those discussed in Section 17a. We first describe the first-order perturbation theory. Evidently the differences in molecular structure do not alter the single-contact term for given values of $n$ and $\beta$. We may therefore write

$$A_2 = (N_A n^2 \beta / 2M^2)(1 - Cz + \cdots)\,. \tag{23.11}$$

The evaluation of the coefficient $C$ involves no fundamental difficulty, and the details are omitted. For a uniform star molecule of functionality $f$, $C$ is given by[30]

$$\begin{aligned} C_u(\text{star}) = \frac{32}{15f^{1/2}}[&7 - 4\cdot 2^{1/2} + (f-1)(17\cdot 2^{1/2} - 9\cdot 3^{1/2} - 8) \\ &+ (f-1)^2(9\cdot 3^{1/2} - 6\cdot 2^{1/2} - 7)]\,. \end{aligned} \tag{23.12}$$

In Table IV.2 are given the values of $C$ calculated from Eq. (23.12) for various values of $f$. The coefficient $C$ increases with $f$ from the value 2.865 for the linear chain. For a uniform normal (comb) molecule of $m$ branch units of functionality 3, the coefficient $C$ cannot be expressed in simple analytic form; the numerical results obtained by Casassa[31] are given in Table IV.3. The coefficient $C$ is seen to increase with increasing number of branch units. More general types of comb molecules have also been investigated,[31, 32] but we do not reproduce the resultant expressions here. For a single-ring molecule, Casassa[33] obtained the result,

$$C(\text{ring}) = 4.457\,, \tag{23.13}$$

which is also greater than the value for the linear chain.

We now examine the effects at large $z$, using a semiempirical procedure. Let $A_{2,l}$, $A_{2,b}$, and $A_{2,r}$, be the second virial coefficients for

**TABLE IV.3.** VALUES OF $C$ FOR UNIFORM NORMAL (COMB) MOLECULES OF $m$ BRANCH UNITS OF FUNCTIONALITY 3[31]

| $m$ | $C$ |
|---|---|
| 2 | 3.536 |
| 3 | 3.753 |
| 4 | 3.939 |
| 5 | 4.100 |
| 10 | 4.672 |
| 20 | 5.293 |

linear, branched, and ring molecules, respectively. For given values of $n$ and $\beta$, we then have

$$A_{2,b}/A_{2,l} = [h_0(\bar{z})]_b/[h_0(\bar{z})]_l \,, \tag{23.14}$$

and a similar equation for $A_{2,r}/A_{2,l}$ where $\bar{z} = z/\alpha_S{}^3$, as before. For convenience, we assume the FKO,m equation for $h_0$ and the F,m equation for $\alpha_S$;

$$h_0(\bar{z}) = \frac{1}{2C\bar{z}} \ln(1 + 2C\bar{z}) \,, \tag{23.15}$$

$$\alpha_S{}^5 - \alpha_S{}^3 = Kz \,. \tag{23.16}$$

In Fig. IV.7 are plotted the values of $A_{2,b}/A_{2,l}$ and $A_{2,r}/A_{2,l}$ as functions of $z$ calculated from Eqs. (23.14) to (23.16) using the values of $K$ and $C$ given in Tables III.3, III.4, IV.2 and IV.3, and in Eqs. (17.4) and (23.13). The second virial coefficient (for $z > 0$) is seen to be diminished by branching or ring formation, the effects being exaggerated for high-molecular-weight polymers in good solvents.

## 23c. General Comments

In the preceding and present chapters, we have discussed in detail the most important equilibrium properties of dilute polymer solutions, namely the expansion factor and the second virial coefficient. All the theories of these properties described so far are within the framework of the two-parameter theory, and emphasis has been focused on the dependences of the properties on the excluded-volume parameter $z$. Quantitatively these theories predict different dependences on $z$, but the two-parameter theory may be considered to provide a correct description of the qualitative aspects of the solution properties insofar as it is concerned with very dilute solutions of the flexible-chain polymers of high molecular weights of ordinary interest.

The two-parameter theory will break down for stiff chains, and also for concentrated solutions. Some effects of chain stiffness on the

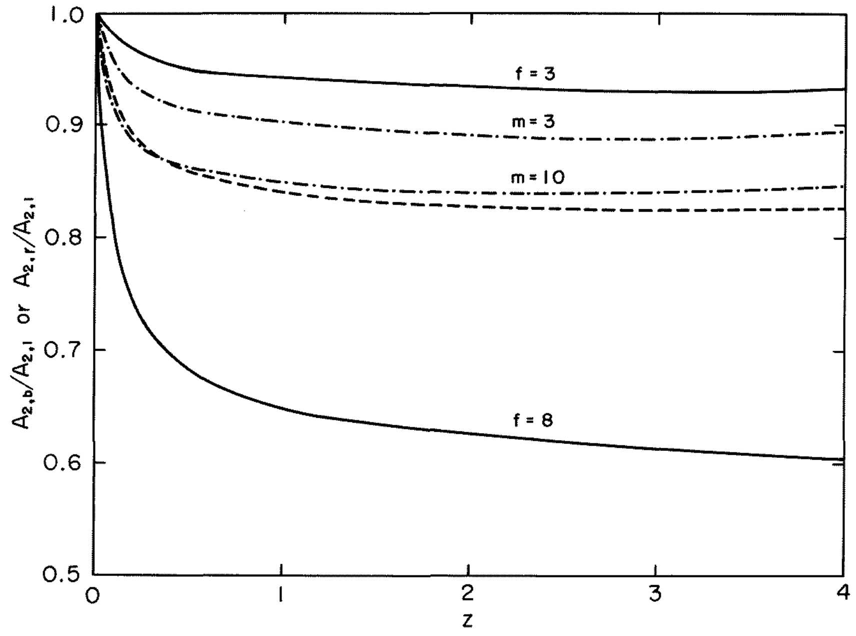

**Fig. IV.7.** Ratios of the second virial coefficients for branched and ring polymers to those for linear chains. Full curves: uniform star molecules of functionality *f*. Chain curves: uniform normal (comb) molecules of *m* branch units of functionality 3. Broken curve : ring polymer.

expansion factor and the second virial coefficient were discussed by Yamakawa.[34] However, no available theory of $\alpha$ and $A_2$ has as yet been derived for wormlike chains. Thus our further comments are limited to the thermodynamics of concentrated solutions. The McMillan–Mayer theory ceases to be convenient when the fourth and higher virial coefficients are important. One of the possible approaches is to use the pair correlation function familiar from the theory of simple fluids. If the potential of mean force for solute molecules is pairwise decomposable (superposition approximation), for the smoothed-density model the osmotic pressure $\pi$ may be expressed in the closed form,[2, 3]

$$\pi = \rho kT - \frac{\rho^2}{6} \int S_{12} V_{12}{}'(S_{12}) g(S_{12}) d\mathbf{S}_{12} \,, \tag{23.17}$$

where $V_{12}{}' = \partial V_{12}/\partial S_{12}$, and $\mathbf{S}_{12}$ is the distance between the centers of two molecules, as before. The pair correlation function $g$ and the intermolecular potential $V_{12}$ in Eq. (23.17) are dependent on concentration. Fixman[35, 36] adopted the Flory–Krigbaum potential and used an approximate solution of the Born–Green–Yvon–Kirkwood equation for $g$. A similar approach was also attempted by Yamakawa[37] for random flight chains. These theories are still within the framework of the two-parameter theory, and are valid for solutions up to a polymer volume fraction of about 0.1, at which concentration a particular polymer molecule begins to overlap considerably the domain occupied by other molecules. At higher concentrations, the ternary and higher-order cluster integrals for segments become important, and the Flory–Huggins entropy plays an important role. Thus, Fixman[13] attempted to derive a theory which reduces to the two-parameter theory at low concentrations and to the Flory–Huggins theory at high concentrations, expanding the local free energy of mixing in a Taylor series around the bulk volume fraction, instead of around zero concentration as in Eq. (11.6). However, no numerical results were obtained.

As is well known, a lattice theory is the alternative convenient approach to the problem of the thermodynamics of concentrated solutions. Extensive investigations based on this model were made in the 1940s, and are well reviewed in the books by Flory[38], Muenster,[39] and Tompa.[40] Subsequent investigations are very few in number.[*] We merely note here that Kurata[41, 42] developed a lattice theory which can account for the decrease of $A_2$ with increasing $M$; early theories failed in predicting the molecular weight dependence of $A_2$. Some other topics in this field, although not very recent, are the lattice theory of solutions of stiff chains developed by Flory,[43] and the simple model of solutions of polar polymers introduced by Yamakawa et al.[44]

## Appendix IV A. The Second Virial Coefficient for Rigid Macromolecules

There are several features which arise in applying the McMillan–Mayer theory to solutions of rigid macromolecules. First, since the solute molecules are so large that the solvent may be considered a continuous medium, the effect of averaging the intermolecular force with respect to all coordinates of the solvent molecules disappears. Thus the superposition approximation becomes asymptotically exact;the pair potential of mean force on solute molecules is not essentially different from the potential energy of interaction between molecules of a gas except that the force constants in a solution are to be modified by taking account of the presence of the solvent molecules. Secondly, for most nonelectrolyte solutions, the range of the intermolecular forces is negligibly small compared to the dimensions of the solute molecules, and thus only the (repulsive) core part of the intermolecular potential need be considered. Thirdly, the solute molecule has no internal-rotational freedom, and the integrals over the molecular distribution functions can be evaluated exactly in many cases.

In the present problem, the second virial coefficient may be written,

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[*] Many papers on the cell-theory approach have recently been published, especially by Flory and his co-workers, but we omit the literatures.

from Eq. (19.55), as

$$A_2 = -(N_A C^2/2VM^2) \int f_{12} d(1)' d(2)' \qquad \text{(IV A.1)}$$

with

$$f_{12} = \exp(-V_{12}/kT) - 1\,, \qquad \text{(IV A.2)}$$

$$F_1(1) = F_1(2) = C\,, \qquad \text{(IV A.3)}$$

where $(1)'$ and $(2)'$ represent all translational and external-rotational coordinates of solute molecules 1 and 2, respectively, $V_{12}$ is the intermolecular potential depending on the relative positions and orientations of the two molecules and hence on the molecular size and shape, and $C$ is a constant independent of the molecular coordinates and determined from the normalization condition of (19.21).

We first consider rigid sphere molecules of radius $\bar{S}$. If $S_{12}$ is the distance between the centers of spheres 1 and 2, $V_{12}$ may be expressed as

$$\begin{aligned} V_{12} &= +\infty \qquad \text{for } 0 \leq S_{12} \leq 2\bar{S} \\ &= 0 \qquad \text{for } S_{12} > 2\bar{S}\,. \end{aligned} \qquad \text{(IV A.4)}$$

From Eqs. (IV A.1) and (IV A.4), we readily obtain (with $C = 1$)

$$\begin{aligned} A_2 &= (N_A/2M^2) \int_0^{2\bar{S}} (1 - e^{-V_{12}/kT}) 4\pi {S_{12}}^2 dS_{12} \\ &= 16\pi N_A \bar{S}^3/3M^2\,, \end{aligned} \qquad \text{(IV A.5)}$$

which are to be compared with Eqs. (20.31) and (21.17), respectively. If $v_m$ is the volume of the solute molecule, Eq. (IV A.5) may be rewritten as

$$A_2 = 4N_A v_m/M^2\,. \qquad \text{(IV A.6)}$$

Since the volume of a spherical molecule is proportional to the molecular weight $M$, the second virial coefficient for rigid sphere molecules is inversely proportional to $M$.

We next consider rigid rod molecules of diameter $d$ and length $l$, with $l$ much greater than $d$. To describe the position and direction of rod 1, we use three Cartesian coordinates $x_1$, $y_1$, and $z_1$ of one end of the rod, and two polar angles $\theta_1$ and $\varphi_1$. As in the case of spheres, the potential $V_{12}$ becomes infinite in the region in which overlapping of the two molecules occurs, and vanishes elsewhere. Thus, only those configurations are considered in which the two rods overlap, as depicted in Fig. IV.8. Then, to specify the direction of the axis of rod 2, we use two polar angles $\theta_2$ and $\varphi_2$ as shown in the figure, assuming $l \gg d$. At constant $\theta_2$ and $\varphi_2$, these configurations will occur when the center of rod 2 lies within the parallelepiped of volume $2dl^2 \sin\theta_2$ as shown in

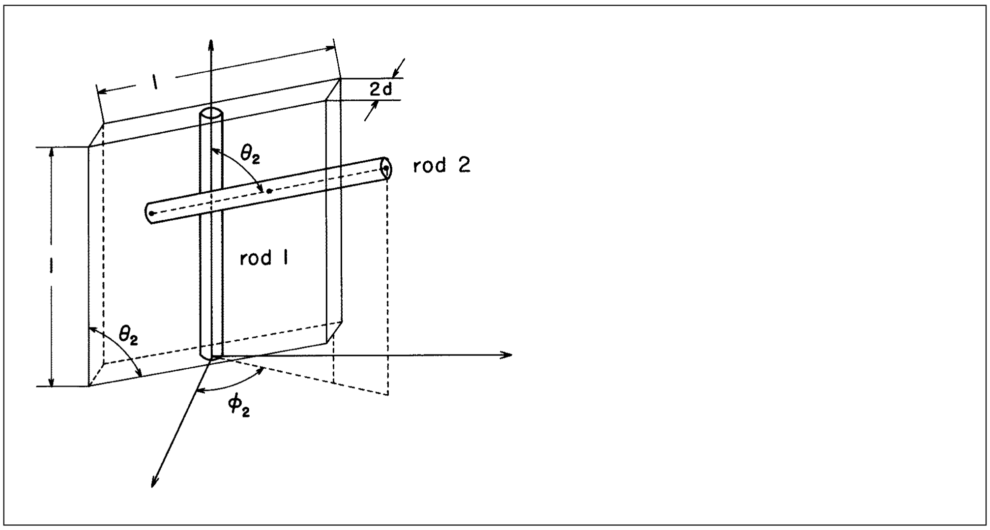

**Fig. IV.8.** Overlapping of two rods of diameter *d* and length *l*, with *l* much greater than *d*.

the figure. From Eqs. (IV A.1) and (19.21), we therefore have

$$\begin{aligned} A_2 = (N_A/2M^2)C^2 &\int_0^{\pi} \int_0^{2\pi} \sin\,\theta_1\,d\theta_1\,d\varphi_1 \\ \times &\int_0^{\pi} \int_0^{2\pi} (2dl^2 \sin\,\theta_2) \sin\,\theta_2\,d\theta_2\,d\varphi_2\,. \\ C &\int_0^{\pi} \int_0^{2\pi} \sin\,\theta_1\,d\theta_1\,d\varphi_1 = 1\,, \end{aligned}$$

where integration over $x_1$, $y_1$, and $z_1$ has been carried out to yield $V$. Thus we obtain[5]

$$A_2 = \pi N_A d l^2 / 4M^2\,. \tag{IV A.7}$$

Since $l$ is proportional to $M$ at constant $d$, the second virial coefficient for rigid rod molecules is independent of the molecular weight. We note that the single-contact term of $A_2$ for flexible chains is independent of chain configurations, and is equivalent to the second virial coefficient for rigid rod molecules.

Finally, we consider briefly arbitrary rigid ovaloid molecules. According to Isihara,[45, 46] the second virial coefficient for rigid nonspherical molecules may be written in the general form,

$$A_2 = (4N_A v_m/M^2)f\,, \tag{IV A.8}$$

where $f$ is a factor (always greater than unity) which represents deviation from the rigid sphere behavior and depends only on the molecular shape. When $f = 1$, Eq. (IV A.8) reduces to Eq. (IV A.6). Isihara has shown how to evaluate the factor $f$ for any rigid ovaloid molecule by the use of group theory and differential geometry; it has been calculated for a number of such molecules.[47, 48] Without reproducing the details, we describe the results of interest to us. For example, for ellipsoids of revolution $f$ is given by

$$f = \tfrac{1}{4} + \tfrac{3}{16}[1 + (1-\varepsilon^2)^{-1/2}(\sin^{-1}\varepsilon)/\varepsilon]\{1 + [(1-\varepsilon^2)/2\varepsilon] \times \ln[(1+\varepsilon)/(1-\varepsilon)]\}\,, \qquad \text{(IV A.9)}$$

where $\varepsilon$ is the eccentricity defined by $\varepsilon^2 = (l^2 - d^2)/l^2$, $l$ and $d$ being the major and minor axes of the generating ellipse, respectively. At small $\varepsilon$, Eq. (IV A.9) may be expanded as

$$f = 1 + \frac{1}{15}\varepsilon^4 + \frac{1}{15}\varepsilon^6 + \cdots\,. \qquad \text{(IV A.10)}$$

Another example is a rod molecule, for which $f$ is given by

$$f = \tfrac{1}{4}[1 + (l/d)(1 + d/2l)(1 + \pi d/2l)]\,. \qquad \text{(IV A.11)}$$

In the case $l \gg d$, Eq. (IV A.8) with (IV A.11) reduces to Eq. (IV A.7), since $v_m = \pi d^2 l/4$.

## Appendix IV B. The Third Virial Coefficient for Rigid Sphere Molecules

The third virial coefficient for rigid sphere molecules may be written, from Eq. (19.56), as

$$A_3 = -(N_A{}^2/3M^3)\int' f_{12}f_{23}f_{13}d\mathbf{S}_{12}d\mathbf{S}_{23}d\mathbf{S}_{13}\,, \qquad \text{(IV B.1)}$$

where the functions $f_{ij}$ are given by Eq. (IV A.2) and similar equations, and the $\mathbf{S}_{ij}$ are the distances between the centers of spheres $i$ and $j$. The prime indicates that integration is carried out under the condition, $\mathbf{S}_{12} + \mathbf{S}_{23} + \mathbf{S}_{31} = 0$. Equation (IV B.1) is equivalent to Eq. (22.10).

Now the integral in Eq. (IV B.1) is nonzero only for $0 \le S_{12} \le 2\bar{S}$, $0 \le S_{23} \le 2\bar{S}$, and $0 \le S_{13} \le 2\bar{S}$, where $\bar{S}$ is the radius of the sphere. Therefore, if $\mathbf{S}_{12}$ is fixed, the integral is nonzero when the center of sphere 3 lies in the region overlapped by two spheres of radius $2\bar{S}$ and concentric with spheres 1 and 2, respectively. The volume $\mathcal{V}'$ of this region is given, from Eq. (20.36), by

$$\mathcal{V}' = \tfrac{2}{3}\pi(2\bar{S})^3\left(1 - \frac{S_{12}}{4\bar{S}}\right)^2\left(2 + \frac{S_{12}}{4\bar{S}}\right). \qquad \text{(IV B.2)}$$

Thus, we obtain

$$\begin{aligned} A_3 &= (N_A{}^2/3M^3)\int_0^{2\bar{S}} \mathcal{V}' 4\pi S_{12}^{\,2} dS_{12} \\ &= 160\pi^2 N_A{}^2\bar{S}^6/9M^3\,. \end{aligned} \qquad \text{(IV B.3)}$$

From Eqs. (IV A.5) and (IV B.3), we have

$$A_3/A_2{}^2M = \tfrac{5}{8}\,. \qquad \text{(IV B.4)}$$

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# Chapter Five
# Light Scattering from Dilute Solutions

## 24. Introduction

The scattering of light by the molecules of a gas or by colloidal particles suspended in a liquid medium has been known for many years under the name Rayleigh scattering.[1] The first application of Rayleigh scattering to the study of polymer solutions was made by Debye and his co-workers[2−4] in the 1940s. Further progress was made principally by Zimm and co-workers,[5−8] and the theoretical and experimental foundations were essentially complete by 1950. Measurements of light scattering from dilute polymer solutions are the principal method in use at the present time for the determination of molecular weights, second virial coefficients, and average molecular dimensions. The object of this chapter is to derive equations for the intensity of scattered light, and also to describe various aspects of the utility of light-scattering measurements in polymer solutions.

When a light beam falls upon matter, the electric field associated with the incident light induces oscillating electric dipoles on the particles (molecules) constituting the matter. The induced oscillating dipoles then become secondary sources of light and give rise to electromagnetic radiation, Rayleigh scattering. For the case of an ideal gas, in which the molecules are randomly distributed, there are no particular phase relationships between the scattered waves, and the total intensity of scattered light is simply the sum of the contributions from the individual molecules in the system. On the other hand, for the case of a perfect crystal, in which the particles are fixed at the points of a perfect lattice, there occurs destructive interference between the scattered waves because of the particular phase relationships, and no light is scattered, i.e., a perfect crystal is transparent. This is true provided the wavelength of light is much greater than the distance between the particles. However, this is not so for a perfect crystal when the wavelength is of the same order of magnitude as the distance between the particles; that is, in the scattering of x-rays there occurs constructive interference according to Bragg's law. A pure liquid is intermediate between an ideal gas and a perfect crystal in that the molecular distribution has some short-range order but no long-range order. Therefore, a pure liquid is not perfectly transparent, but the intensity of scattered light is much less than that for a gas of the same density. For the case of a solution, there is an excess scattering from the solute particles over that of the solvent alone. When considering the excess intensity of scattered light, we note that at infinite dilution the situation is similar to that of an ideal gas. If the concentration is increased, there occurs destructive interference between the waves scattered from the different solute particles. When the solute molecules are large, as in polymer solutions, there is intramolecular destructive interference even at infinite dilution.

As seen from the above arguments, the problem of evaluating the intensities of light scattered from liquids or solutions may be approached conveniently from two standpoints. One is the fluctuation theory approach suggested originally by Smoluchowski[9] and by Einstein.[10] The fact that a perfect crystal is transparent means that no scattered light is observed when there is no optical inhomogeneity in the region of volume of the order of magnitude of (wavelength)$^3$. If optical inhomogeneities exist in such a region, light is scattered. For the case of a liquid or solution, the optical inhomogeneities arise from the fluctuations in local density or concentration because of the thermal Brownian motions of the molecules. Thus, the problem is reduced to that of evaluating the density or composition fluctuations in the fluid. This approach will be described in Section 26. The other is the distribution function approach, which will be described in Section 27. This approach is easy to understand : the intensity of scattered light is strongly affected by the distribution of the scattering particles in the system, as mentioned above, and therefore the intensity may be expressed in terms of the molecular distribution functions.

However, both the approaches begin with an equation for the intensity of light scattered by a single-small particle. In the next section, we therefore describe some of the fundamental physics of this simplest system and also describe the properties of a system of independent small particles. Most of the calculations are carried out using the assumption that the scattering particles are optically isotropic. The effects of the optical anisotropies will be discussed in Section 28. In that section, some other topics will also be described.

## 25. Scattering by Independent Small Isotropic Particles

We begin by discussing the radiation field around a single small isotropic particle in a homogeneous medium of optical refractive index $\tilde{n}$. Suppose that the incident light is plane-polarized, and that the electric field $\mathbf{E}^0$ associated with the incident light at the point of location of the particle oscillates according to the equation,

$$\mathbf{E}^0 = {\mathbf{E}_0}^0 \exp(i\omega t) \tag{25.1}$$

with ${\mathbf{E}_0}^0$ the amplitude, $\omega$ the angular frequency, and $t$ the time. The field $\mathbf{E}^0$ then induces an oscillating electric dipole $\mathbf{p}$ on the particle,

$$\begin{aligned} \mathbf{p} &= \alpha \mathbf{E}^0 \\ &= \mathbf{p}_0 \exp(i\omega t) \end{aligned} \tag{25.2}$$

with

$$\mathbf{p}_0 = \alpha {\mathbf{E}_0}^0 , \tag{25.3}$$

where $\alpha$ is the polarizability of the particle, and is, by assumption, a scalar quantity. This oscillating dipole radiates electromagnetic waves, and the radiation electric field $\mathbf{E}$ and magnetic field $\mathbf{H}$ at the distance $\mathbf{r}$ from the particle can be calculated by a simple application of electromagnetic theory. The results are (see Appendix V A)

$$\mathbf{E} = -\left(\frac{\omega}{\tilde{c}}\right)^2 \frac{\mathbf{r} \times (\mathbf{r} \times \{\mathbf{p}\})}{r^3} , \tag{25.4}$$

$$\mathbf{H} = \tilde{n}\left(\frac{\omega}{\tilde{c}}\right)^2 \frac{\mathbf{r} \times \{\mathbf{p}\}}{r^2} , \tag{25.5}$$

where $\tilde{c}$ is the velocity of light in a vacuum, and the curly brackets indicate that $\mathbf{p}$ is to be evaluated at the retarded time $(t - r/\tilde{c'})$ with $\tilde{c'} = \tilde{c}/\tilde{n}$ the velocity of light in the medium. Equations (25.4) and (25.5) give the field associated with the scattered light.

Suppose, now, that the particle lies at the origin of a coordinate system, the incident light travels along the $z$ axis, and $\mathbf{E}^0$ is parallel to the $x$ axis (see Fig. V.1). Then $\mathbf{E}$ lies in the plane containing the vector $\mathbf{r}$ and the $x$ axis and is perpendicular to $\mathbf{r}$, while $\mathbf{H}$ is perpendicular to $\mathbf{E}$ and $\mathbf{r}$. If $\theta_x$ is the angle between the vector $\mathbf{r}$ and $x$ axis, the magnitudes (real parts) of $\mathbf{E}$ and $\mathbf{H}$ are given by

$$E = p_0 \left(\frac{\omega}{\tilde{c}}\right)^2 \frac{\sin\theta_x}{r} \cos\left[\omega\left(t - \frac{r}{\tilde{c}'}\right)\right] , \tag{25.6}$$

$$H = \tilde{n} E . \tag{25.7}$$

Next we consider the case for which the incident light is unpolarized (natural light). It is then convenient to decompose $\mathbf{E}^0$ into the $x$ and $y$ components,

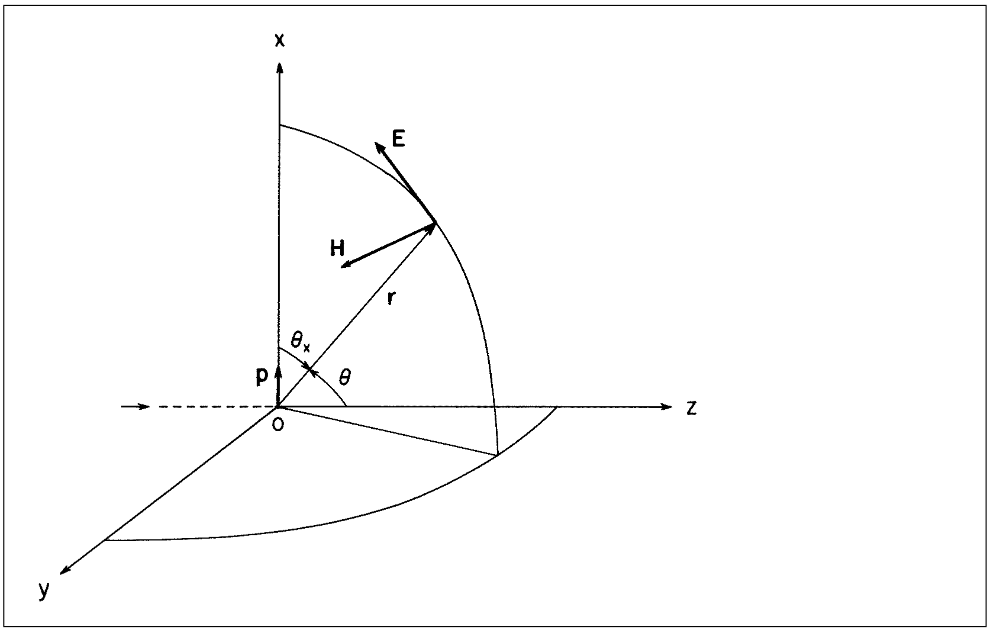

**Fig. V.1.** Electromagnetic field due to an oscillating electric dipole.

$$\begin{aligned} {E_x}^0 &= {E_{0x}}^0 \exp[i(\omega t + \delta_x)] \,, \\ {E_y}^0 &= {E_{0y}}^0 \exp[i(\omega t + \delta_y)] \,. \end{aligned} \tag{25.8}$$

In the present case (unpolarized light) the amplitudes and also the difference between the phases $\delta_x$ and $\delta_y$ vary with time irregularly, but on the average ${E_{0x}}^0 = {E_{0y}}^0 \equiv {E_0}^0$. The induced moments $\mathbf{p}_x$ and $\mathbf{p}_y$ in the directions of the $x$ and $y$ axes are

$$\begin{aligned} \mathbf{p}_x &= \mathbf{e}_x p_0 \exp[i(\omega t + \delta_x)] \,, \\ \mathbf{p}_y &= \mathbf{e}_y p_0 \exp[i(\omega t + \delta_y)] \,, \end{aligned} \tag{25.9}$$

where $\mathbf{e}_x$ and $\mathbf{e}_y$ are the unit vectors, and $p_0 = \alpha {E_0}^0$. If $\mathbf{E}_1$ and $\mathbf{H}_1$ are the contributions of $\mathbf{p}_x$ to the electric and magnetic radiation fields at $\mathbf{r}$, respectively, and $\mathbf{E}_2$ and $\mathbf{H}_2$ are those of $\mathbf{p}_y$, the total radiation fields at $\mathbf{r}$ are

$$\begin{aligned} \mathbf{E} &= \mathbf{E}_1 + \mathbf{E}_2 \,, \\ \mathbf{H} &= \mathbf{H}_1 + \mathbf{H}_2 \,, \end{aligned} \tag{25.10}$$

where $\mathbf{E}_1$ and $\mathbf{H}_1$ are given by Eqs. (25.4) and (25.5) with $\{\mathbf{p}_x\}$ in place of $\{\mathbf{p}\}$, respectively, and $\mathbf{E}_2$ and $\mathbf{H}_2$ are also given by the same equations with $\{\mathbf{p}_y\}$ in place of $\{\mathbf{p}\}$. The equations for $E_1$ and $H_1$ are the same as Eqs. (25.6) and (25.7), respectively, except that the cosine factor involves the phase $\delta_x$, and $E_2$ and $H_2$ are obtained from $E_1$ and $H_1$ by replacing $\delta_x$ and $\theta_x$ by $\delta_y$ and $\theta_y$, respectively, where $\theta_y$ is the angle between $\mathbf{r}$ and the $y$ axis. We note that $\mathbf{E}_i$ and $\mathbf{H}_i$, and also $\mathbf{E}$

and **H**, are perpendicular to each other, but this is not always the case for $\mathbf{E}_1$ and $\mathbf{E}_2$, and for $\mathbf{H}_1$ and $\mathbf{H}_2$.

We now derive equations for the intensity of the scattered light. The intensity of an electromagnetic wave is defined as the time average of the energy per unit time which crosses a unit area perpendicular to the direction of the propagation of the electromagnetic wave. The energy flow across an infinitesimal area $d\mathbf{A}$ per unit time is equal to $\mathbf{S} \cdot d\mathbf{A}$ with **S** the Poynting vector defined by

$$\mathbf{S} = \frac{\tilde{c}}{4\pi}(\mathbf{E} \times \mathbf{H})\,. \tag{25.11}$$

The intensity is therefore equal to $\bar{S}$;

$$\bar{S} = \frac{\tilde{n}\tilde{c}}{4\pi}\overline{E^2} \equiv \frac{\tilde{n}\tilde{c}}{8\pi}I\,, \tag{25.12}$$

where we have used Eq. (25.7), and the bar indicates the time average. Thus, we may define the intensity by the quantity $I$ in Eq. (25.12) instead of $\bar{S}$; that is,

$$I = 2\overline{E^2} = 2(\overline{E_x^{\,2}} + \overline{E_y^{\,2}})\,, \tag{25.13}$$

where $E_x$ and $E_y$ are the $x$ and $y$ components of **E**, and are to be written in the cosine representation. Recalling that $\overline{\cos^2(\omega t + \delta)} = \frac{1}{2}$, we have

$$\begin{aligned} I &= {E_{0x}}^2 + {E_{0y}}^2 \\ &= |E_x|^2 + |E_y|^2\,, \end{aligned} \tag{25.14}$$

where $E_{0x} = |E_x|$ and $E_{0y} = |E_y|$ are the amplitudes of $E_x$ and $E_y$, respectively, and the second line of Eqs. (25.14) is useful when **E** is written in the complex representation. We note that $I_x = {E_{0x}}^2$ and $I_y = {E_{0y}}^2$ are the intensities in the directions of the $x$ and $y$ axes, respectively.

For the case of plane-polarized incident light, from Eqs. (25.6) and (25.14) we obtain for the intensity of scattered light.

$$I = {p_0}^2\left(\frac{\omega}{\tilde{c}}\right)^4\frac{\sin^2\theta_x}{r^2}\,. \tag{25.15}$$

Since the intensity $I^0$ of the incident light is $I^0 = ({E_0}^0)^2 = {p_0}^2/\alpha^2$, we find

$$\frac{I}{I^0} = \frac{16\pi^4\alpha^2}{\lambda^4 r^2}\sin^2\theta_x\,, \tag{25.16}$$

where we have used the relation $\omega/\tilde{c} = 2\pi/\lambda$ with $\lambda$ the wavelength of the incident light (and also of the scattered light) in vacuum. In this case, the scattered light is also plane-polarized. When **r** lies in the $yz$ plane, Eq. (25.15) with $\sin\theta_x = 1$ gives the intensity of scattered light in the direction of the $x$ axis, and the intensity in the direction perpendicular to this is zero.

For the case of unpolarized incident light, the intensity of scattered light may be written, from Eqs. (25.10) and (25.13), as

$$\begin{aligned} I &= 2\overline{(\mathbf{E}_1 + \mathbf{E}_2)^2} \\ &= 2(\overline{E_1}^2 + \overline{E_2}^2 + 2\overline{\mathbf{E}_1 \cdot \mathbf{E}_2})\,. \end{aligned} \tag{25.17}$$

Since there is no correlation between $\mathbf{E}_1$ and $\mathbf{E}_2$, the average of $\mathbf{E}_1 \cdot \mathbf{E}_2$, vanishes, and we obtain

$$\begin{aligned} I &= {E_{01}}^2 + {E_{02}}^2 \\ &= {p_0}^2 \left(\frac{\omega}{\tilde{c}}\right)^4 \frac{\sin^2\theta_x + \sin^2\theta_y}{r^2} \\ &= {p_0}^2 \left(\frac{\omega}{\tilde{c}}\right)^4 \frac{1 + \cos^2\theta}{r^2}\,, \end{aligned} \tag{25.18}$$

where $\theta$ is the angle between $\mathbf{r}$ and the $z$ axis, i.e., the angle between the incident and scattered rays. The intensity of the incident light is $I^0 = ({E_{0x}}^0)^2 + ({E_{0y}}^0)^2 = 2({E_0}^0)^2 = 2{p_0}^2/\alpha^2$, and we therefore have

$$\frac{I}{I^0} = \frac{8\pi^4\alpha^2}{\lambda^4 r^2}(1 + \cos^2\theta)\,. \tag{25.19}$$

In particular, when $\mathbf{r}$ lies in the $yz$ plane, $\mathbf{E}_1$ and $\mathbf{E}_2$ are perpendicular to each other, $\mathbf{E}_1$ being parallel to the $x$ axis. The term unity of the factor $(1 + \cos^2\theta)$ corresponds to the intensity of $\mathbf{E}_1$, while the term $\cos^2\theta$ corresponds to the intensity of $\mathbf{E}_2$.

We now proceed to discuss a system of volume $V$ containing $N$ independent identical scattering particles. Since Eq. (25.16) for the case of polarized incident light is obtained from Eq. (25.19) for the case of unpolarized incident light by replacing the factor $(1+\cos^2\theta)$ by $2\sin^2\theta_x$, the following discussion is confined to the latter case. Then the total intensity $I$ of light scattering from the system is

$$\frac{I}{I^0} = \frac{8\pi^4\alpha^2 N}{\lambda^4 r^2}(1 + \cos^2\theta)\,. \tag{25.20}$$

Defining the *Rayleigh ratio* $R_\theta$ (experimentally determinable) by

$$R_\theta = \frac{r^2 I}{V I^0 (1 + \cos^2\theta)}\,, \tag{25.21}$$

we have

$$R_\theta = \frac{8\pi^4\alpha^2}{\lambda^4}\rho \tag{25.22}$$

with $\rho = N/V$. Thus the problem remaining is to express $\alpha$ in terms of a measurable quantity. For the case of solution, the $R_\theta$ given by Eq. (25.22) is the excess intensity over that of the solvent alone, with $\rho$

the number density of the solute, and $\alpha$ the *excess* polarizability. Then, $\alpha$ may be related to the dielectric constants $\varepsilon$ and $\varepsilon_0$ of the solution and solvent by the equation,

$$\varepsilon - \varepsilon_0 = 4\pi\rho\alpha \,. \tag{25.23}$$

For a dilute solution, Eq. (25.23) may be rewritten as

$$\alpha = \frac{1}{4\pi}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_0 = \frac{M}{2\pi N_A}\tilde{n}_0\left(\frac{\partial\tilde{n}}{\partial c}\right)_0 , \tag{25.24}$$

where we have used the relations $\varepsilon = \tilde{n}^2$ and $\rho = N_A c/M$ with $N_A$ the Avogadro number, $M$ the molecular weight of the solute, and $c$ the concentration in grams per unit volume. Note that for the case of a gas $\varepsilon_0 = \tilde{n}_0 = 1$. Substitution of Eq. (25.24) into Eq. (25.22) leads to

$$R_\theta = KMc \tag{25.25}$$

with

$$K = \frac{2\pi^2\tilde{n}_0^{\,2}}{N_A\lambda^4}\left(\frac{\partial\tilde{n}}{\partial c}\right)_0^2 . \tag{25.26}$$

The constant $K$ is determinable experimentally.

In light-scattering experiments, the *turbidity* $\tau$ is sometimes measured instead of $R_\theta$. Suppose that the intensity $I^0$ of light decreases, as a result of scattering, by the amount $-\Delta I$, in traveling the distance $\Delta l$ through a medium containing scattering particles. Then the turbidity $\tau$ of the system is defined by

$$\Delta I = -\tau I^0 \Delta l \,. \tag{25.27}$$

Consider now an area $\Delta A$ perpendicular to the direction of propagation of the light in the medium. The principle of conservation of energy requires that the average energy (per unit time) flowing into a domain of volume $V = \Delta A \Delta l$ across $\Delta A$ be equal to the average energy flowing out of the domain; that is,

$$I^0\Delta A = (I^0 + \Delta I)\Delta A + 2\pi\int_0^\pi I r^2 \sin\theta d\theta \,, \tag{25.28}$$

where the second term on the right-hand side represents the average energy of radiation in all directions, and $I$ in the integrand is the intensity of scattered light. From Eqs. (25.20), (25.27), and (25.28), we obtain for the turbidity

$$\tau = \frac{128\pi^5\alpha^2}{3\lambda^4}\rho \,, \tag{25.29}$$

or

$$\tau = HMc \tag{25.30}$$

with

$$H = \frac{32\pi^3\tilde{n}_0^{\,2}}{3N_A\lambda^4}\left(\frac{\partial\tilde{n}}{\partial c}\right)_0^2 . \tag{25.31}$$

Note that the constant $H$ is also determinable experimentally, and that for a solution the $\tau$ given by Eq. (25.29) or (25.30) is the excess turbidity.

## 26. Fluctuation Theory

Consider a region (element) of volume $V$ of a liquid of solution which is small compared to the wavelength of the incident light, but which is large enough to contain many molecules. ($V$ is not to be confused with the volume of the whole scattering system.) The fluctuation in the number of molecules in the subvolume just defined will cause the dielectric constant $\varepsilon$ therein to fluctuate about its mean value $\langle\varepsilon\rangle$. At any instant, any particular region may be considered to be a small particle with (excess) dielectric constant $\Delta\varepsilon = \varepsilon - \langle\varepsilon\rangle$ which is immersed in the surrounding homogeneous medium of dielectric constant $\langle\varepsilon\rangle$. The instantaneous excess polarizability, $\Delta\alpha = \alpha - \langle\alpha\rangle$, of the region is given by

$$\Delta\alpha = \frac{V}{4\pi}\Delta\varepsilon = \frac{V}{2\pi}\tilde{n}\Delta\tilde{n}\,. \tag{26.1}$$

Since the inhomogeneities are randomly distributed throughout the whole system, the total intensity of scattered light is the sum of the contributions from each of the regions. The Rayleigh ratio is then obtained from Eq. (25.22) by replacing $\alpha^2$ and $\rho$ by $\overline{(\Delta\alpha)^2}$ and $V^{-1}$, respectively. The time average may be replaced by the ensemble average, and we therefore obtain in the basic equation for the Rayleigh ratio,

$$R_\theta{}^* = \frac{2\pi^2\tilde{n}^2V}{\lambda^4}\langle(\Delta\tilde{n})^2\rangle\,, \tag{26.2}$$

where the asterisk indicates that $R_\theta{}^*$ includes the scattering from the pure solvent. Similarly, the turbidity may be expressed, from Eq. (25.29), in the form,

$$\tau^{\,*} = \frac{32\pi^3\tilde{n}^2V}{3\lambda^4}\langle(\Delta\tilde{n})^2\rangle\,. \tag{26.3}$$

To use Eq. (26.2) or (26.3) we must evaluate $\langle(\Delta\tilde{n})^2\rangle$. In the next subsection, we discuss the fluctuation in $\tilde{n}$ arising from the density and composition fluctuations in a multicomponent system. The general theory is then applied to special cases of interest, such as a two-component system, heterogeneous polymers in a single solvent, and a single polymer in a mixed solvent. We note that Eqs. (26.2) and (26.3) cannot account for intramolecular destructive interferences and,strictly, Eq. (26.2) is valid only at $\theta = 0$. However, effects of thermodynamic interactions between molecules can be taken into account.

### 26a. General Theory

The theory of light scattering arising from density and composition fluctuations in multicomponent systems was developed by Brinkman and Hermans,[11] by Kirkwood and Goldberg,[12] and by Stockmayer.[13] Kirkwood and Goldberg, and also Brinkman and Hermans, used the grand canonical ensemble to evaluate these fluctuations. Alternatively, we may use a "hybrid" ensemble, as shown by Stockmayer. Since the grand canonical ensemble approach is discussed in detail in the book by Hill,[14] the hybrid ensemble approach is described here.

The system to be considered is of volume $V$ at constant temperature $T$ and pressure $p$ containing a constant number $N_0$ of molecules of species 0. The energy, the volume, and the numbers $N_1$, $N_2$, …, $N_r$ of molecules of the other $r$ species present, 1, 2, …, $r$ may fluctuate about their mean values $\langle E\rangle$, $\langle V\rangle$, $\langle N_1\rangle$, …, $\langle N_r\rangle$. The independent thermodynamic variables are then $T$, $p$, $N_0$, and the chemical potentials $\mu_1$, $\mu_2$, …, $\mu_r$. If we use the symbols $\mathbf{N} = N_0$, $N_1$, …, $N_r$, $\mathbf{N}' = N_1$, …, $N_r$, and $\boldsymbol{\mu}' = \mu_1$, …, $\mu_r$, the partition function $\Gamma(T, p, N_0, \boldsymbol{\mu}')$ for the hybrid ensemble, a collection of the systems just described, is given by

$$\Gamma(T, p, N_0, \boldsymbol{\mu}') = \sum_{V} \sum_{\mathbf{N}' \geq \mathbf{0}} e^{-pV/kT} e^{\mathbf{N}' \cdot \boldsymbol{\mu}'/kT} Q(T, V, \mathbf{N}) , \tag{26.4}$$

where $Q$ is the canonical ensemble partition function. $\Gamma$ is also related to the thermodynamic function $N_0\mu_0$ for the variables $T, p, N_0$ and $\boldsymbol{\mu}'$ by the equation,

$$\Gamma(T, p, N_0, \boldsymbol{\mu}') = e^{-N_0\mu_0/kT} . \tag{26.5}$$

The probability $P(V, \mathbf{N}'; T, p, N_0, \boldsymbol{\mu}')$ that the system has exactly the volume $V$ and contains exactly the number of molecules $\mathbf{N}'$ for given $T$, $p$, $N_0$, and $\boldsymbol{\mu}'$ is

$$P(V, \mathbf{N}') = \Gamma^{-1} \exp\left[\left(-pV + \sum_{i=1}^{r} N_i\mu_i - A\right)\Big/ kT\right] , \tag{26.6}$$

where $A = -kT \ln Q$ is the Helmholtz free energy in the canonical ensemble for $T$, $V$, and $\mathbf{N}$.

We now derive the fluctuation distribution function. We recall that except for critical phases, fluctuations are so small that the mean values are also the most probable values and a Gaussian distribution about the most probable values may be used. We therefore expand $\ln P(V, \mathbf{N}')$ about $\langle V\rangle$, $\langle N_1\rangle$, …, $\langle N_r\rangle$, and obtain (with neglect of terms higher than quadratic)

$$P(V, \mathbf{N}') = C \exp(-\varphi/kT) \tag{26.7}$$

with

$$\begin{aligned}\varphi = \frac{1}{2}\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,\mathbf{N}} (\Delta V)^2 + \sum_{i=1}^{r}\left(\frac{\partial^2 A}{\partial V \partial N_i}\right)_{T,V,N_k} \Delta V \Delta N_i \\ + \frac{1}{2}\sum_{i=1}^{r}\sum_{j=1}^{r}\left(\frac{\partial^2 A}{\partial N_i \partial N_j}\right)_{T,V,N_k} \Delta N_i \Delta N_j ,\end{aligned} \tag{26.8}$$

where $C$ is the normalizing constant, $\Delta V = V - \langle V\rangle$, and $\Delta N_i = N_i - \langle N_i\rangle$. Note that linear terms drop out since $\ln P$ has a maximum at $\langle V\rangle$, $\langle N_1\rangle$, …, $\langle N_r\rangle$, and that the derivatives are to be evaluated at $\langle V\rangle$, $\langle N_1\rangle$, …, $\langle N_r\rangle$.

From thermodynamics, we have

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,\mathbf{N}} = -\left(\frac{\partial p}{\partial V}\right)_{T,\mathbf{N}} = \frac{1}{\kappa\langle V\rangle}\,, \tag{26.9}$$

$$\left(\frac{\partial^2 A}{\partial V \partial N_i}\right)_{T,V,N_k} = -\left(\frac{\partial p}{\partial N_i}\right)_{T,V,N_k} = \frac{(\partial V/\partial N_i)_{T,p,N_k}}{(\partial V/\partial p)_{T,\mathbf{N}}} = -\frac{V_i}{\kappa\langle V\rangle}\,, \tag{26.10}$$

where $V_i$ is the partial molecular volume of species $i$, and $\kappa$ is the isothermal compressibility defined by

$$\kappa = -\frac{1}{\langle V\rangle}\left(\frac{\partial V}{\partial p}\right)_{T,\mathbf{N}}\,. \tag{26.11}$$

Further, we may use the relations

$$\begin{aligned}\left(\frac{\partial^2 A}{\partial N_i \partial N_j}\right)_{T,V,N_k} &= \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,V,N_k} = \left(\frac{\partial \mu_j}{\partial N_i}\right)_{T,V,N_k} \\ &= \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\mathbf{N}}\left(\frac{\partial p}{\partial N_j}\right)_{T,V,N_k} + \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,p,N_k}\,.\end{aligned} \tag{26.12}$$

Using Eq. (26.10) for $(\partial p/\partial N_j)_{T,V,N_k}$ and

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\mathbf{N}} = V_i\,, \tag{26.13}$$

Eq. (26.12) may be rewritten as

$$\left(\frac{\partial^2 A}{\partial N_i \partial N_j}\right)_{T,V,N_k} = \frac{V_i V_j}{\kappa\langle V\rangle} + \frac{M_j}{M_0 N_0}\left(\frac{\partial \mu_i}{\partial m_j}\right)_{T,p,m_k}\,, \tag{26.14}$$

where we have introduced concentrations of species $i$,

$$m_i = M_i N_i / M_0 N_0 \tag{26.15}$$

with $M_i$ the molecular weight of species $i$, as was done by Kirkwood and Goldberg and by Stockmayer. We note that the composition fluctuation cannot be simply treated with concentrations in conventional units (g/cc). Let us introduce the reduced variables,

$$\xi = -\frac{\Delta V}{\langle V\rangle} + \sum_{i=1}^{r} \frac{V_i \Delta N_i}{\langle V\rangle}\,, \tag{26.16}$$

$$x_i = \frac{\Delta N_i}{\langle N_i\rangle} = \frac{\Delta m_i}{\langle m_i\rangle} \quad (i = 1, \ldots, r)\,. \tag{26.17}$$

Substitution of Eqs. (26.9), (26.10), and (26.14) into Eq. (26.8) then leads to

$$\varphi = \frac{V}{2\kappa}\xi^2 + \frac{M_0 N_0}{2}\sum_{i=1}^{r}\sum_{j=1}^{r}\frac{m_i m_j}{M_i}\left(\frac{\partial \mu_i}{\partial m_j}\right)_{T,p,m_k} x_i x_j\,, \tag{26.18}$$

where we have replaced $\langle V\rangle$ and $\langle m_j\rangle$ by $V$ and $m_j$, respectively, and it is to be understood that $V$ and $m_i$ in Eq. (26.18) are thermodynamic quantities. The physical meaning of the variable $\xi$ is easily seen as follows. From thermodynamics, we have

$$\kappa V\Delta p = -\Delta V + \sum_{i=1}^{r} V_i \Delta N_i \tag{26.19}$$

as constant $T$ and $N_0$. From Eqs. (26.16) and (26.19), we find $\xi = \kappa\Delta p$, where $\Delta p$ is the change in pressure of the system at constant $T$ and $N_0$ which would accompany the variations $\Delta V$, $\Delta N_1$, …, $\Delta N_r$, if the pressure were *not* held fixed.

Having changed independent variables from $V$, $N_1$, …, $N_r$, or $\Delta V$, $\Delta N_1$, …, $\Delta N_r$, to $\xi$, $x_1$, …, $x_r$, the fluctuation distribution function now becomes

$$P(\xi, x_1, \ldots, x_r) = C\exp\left(-\frac{V}{2\kappa kT}\xi^2 - \frac{M_0N_0}{2}\sum_{i=1}^{r}\sum_{j=1}^{r}\psi_{ij}x_ix_j\right), \tag{26.20}$$

where

$$\psi_{ij} = \frac{m_im_j}{M_ikT}\left(\frac{\partial\mu_i}{\partial m_j}\right)_{T,p,m_k} = \psi_{ji}\,. \tag{26.21}$$

From Eq. (26.20), we can readily deduce that

$$\langle\xi x_i\rangle = 0\,. \tag{26.22}$$

In order to evaluate the averages $\langle\xi^2\rangle$ and $\langle x_ix_j\rangle$, we must first determine the normalizing constant $C$. To do this, we transform the coordinates $x_1$, …, $x_r$ into $\xi_1$, …, $\xi_r$ with an orthogonal matrix $\mathbf{Q}$; that is, $\mathbf{x} = \mathbf{Q}\boldsymbol{\xi}$ and $\mathbf{Q}^{-1}\boldsymbol{\psi}\mathbf{Q} = \boldsymbol{\Lambda}$, where $\boldsymbol{\psi}$ is the $r \times r$ symmetric matrix with elements $\psi_{ij}$, and $\boldsymbol{\Lambda}$ is a diagonal matrix (see Appendix II B). Equation (26.20) then becomes

$$P = C\exp\left(-\frac{V}{2\kappa kT}\xi^2 - \frac{M_0N_0}{2}\sum_{i=1}^{r}\lambda_i{\xi_i}^2\right), \tag{26.23}$$

where the $\lambda_i$'s are the diagonal elements of $\boldsymbol{\Lambda}$. Integration of $P$ over $\xi$, $\xi_1$, …, $\xi_r$ from $-\infty$ to $+\infty$ must give unity, and we therefore find

$$C = \left[\frac{V(M_0N_0/2)^r|\psi|}{2\pi^{r+1}\kappa kT}\right]^{1/2}, \tag{26.24}$$

where $|\psi|$ is the determinant of $\boldsymbol{\psi}$. From Eq. (26.23) with (26.24), we readily obtain

$$\langle\xi^2\rangle = \frac{\kappa kT}{V}\,. \tag{26.25}$$

Further, recalling that

$$x_ix_j = \sum_k\sum_l Q_{ik}Q_{jl}\xi_k\xi_l$$

with $\mathcal{Q}_{ij}$ the elements of $\mathbf{Q}$, we obtain

$$\langle x_i x_j \rangle = \sum_k \mathcal{Q}_{ik} \mathcal{Q}_{jk} \langle {\xi_k}^2 \rangle = \frac{1}{M_0 N_0} \sum_k \frac{\mathcal{Q}_{ik} \mathcal{Q}_{jk}}{\lambda_k} \,. \tag{26.26}$$

The sum in Eq. (26.26) may be rewritten as

$$\begin{aligned} \sum_k \frac{\mathcal{Q}_{ik} \mathcal{Q}_{jk}}{\lambda_k} &= (\mathbf{Q} \boldsymbol{\Lambda}^{-1} \mathbf{Q}^T)_{ij} \\ &= (\boldsymbol{\psi}^{-1})_{ij} = \psi^{ij} |\psi|^{-1} \end{aligned} \tag{26.27}$$

with $\psi^{ij}$ the cofactor of the element $\psi_{ij}$ of $\boldsymbol{\psi}$. We therefore have

$$\langle x_i x_j \rangle = \frac{\psi^{ij}}{M_0 N_0 |\psi|} \,. \tag{26.28}$$

We now consider the meaning of $\langle \xi^2 \rangle$. In particular, at constant composition, we have $\Delta N_i = 0$ for $i = 1, \ldots, r$ since $N_0$ is fixed in the hybrid ensemble. Equation (26.16) then reduces to

$$\xi = -\frac{\Delta V}{\langle V \rangle} \,. \tag{26.29}$$

Recalling that $-\Delta V / \langle V \rangle = \Delta \rho / \langle \rho \rangle$ with $\rho = \langle N \rangle / V$ and $N = \sum_{i=0}^r N_i$, we obtain from Eq. (26.29)

$$\langle \xi^2 \rangle = \langle (\Delta \rho)^2 \rangle / \langle \rho \rangle^2 \,. \tag{26.30}$$

Thus $\langle \xi^2 \rangle$ represents the density fluctuation at constant composition. Note that the quantity $\kappa k T / V$ of (26.25) is just the density fluctuation in a one-component system. From Eq. (26.17), it is easily seen that $\langle x_i x_j \rangle$ represents the composition or concentration fluctuation.

The fluctuation in optical refractive index $\tilde{n}$ may be expressed in terms of $\langle \xi^2 \rangle$ and $\langle x_i x_j \rangle$. In the hybrid ensemble, the variation in $\tilde{n}$ is

$$\Delta \tilde{n} = \left( \frac{\partial \tilde{n}}{\partial V} \right)_{T, \mathbf{N}} \Delta V + \sum_{i=1}^r \left( \frac{\partial \tilde{n}}{\partial N_i} \right)_{T, V, N_k} \Delta N_i \,. \tag{26.31}$$

From thermodynamics, we have

$$\left( \frac{\partial \tilde{n}}{\partial V} \right)_{T, \mathbf{N}} = \left( \frac{\partial \tilde{n}}{\partial p} \right)_{T, \mathbf{m}} \left( \frac{\partial p}{\partial V} \right)_{T, \mathbf{N}} = -\frac{1}{\kappa V} \left( \frac{\partial \tilde{n}}{\partial p} \right)_{T, \mathbf{m}} , \tag{26.32}$$

$$\begin{aligned} \left( \frac{\partial \tilde{n}}{\partial N_i} \right)_{T, V, N_k} &= \left( \frac{\partial \tilde{n}}{\partial p} \right)_{T, \mathbf{m}} \left( \frac{\partial p}{\partial N_i} \right)_{T, V, N_k} + \left( \frac{\partial \tilde{n}}{\partial N_i} \right)_{T, p, N_k} \\ &= \frac{V_i}{\kappa V} \left( \frac{\partial \tilde{n}}{\partial p} \right)_{T, \mathbf{m}} + \frac{M_i}{M_0 N_0} \left( \frac{\partial \tilde{n}}{\partial m_i} \right)_{T, p, m_k} , \end{aligned} \tag{26.33}$$

where we have replaced $\langle V \rangle$ by $V$ as before. Introducing the reduced variables $\xi$ and $x_i$, we obtain, from Eqs. (26.31) to (26.33),

$$\begin{aligned}\langle(\Delta\tilde{n})^2\rangle = {} & \frac{\langle\xi^2\rangle}{\kappa^2}\left(\frac{\partial\tilde{n}}{\partial p}\right)_{T,\mathbf{m}}^2 \\ & + \sum_i\sum_j m_i m_j \langle x_i x_j\rangle \left(\frac{\partial\tilde{n}}{\partial m_i}\right)_{T,p,m_k}\left(\frac{\partial\tilde{n}}{\partial m_j}\right)_{T,p,m_k}, \end{aligned} \tag{26.34}$$

where we have used Eq. (26.22).

Thus, substituting Eq. (26.34) with (26.25) and (26.28) into Eq. (26.2), we obtain for the Rayleigh ratio

$$R_\theta{}^* = R_{\theta,0} + R_\theta \tag{26.35}$$

with

$$R_{\theta,0} = \frac{2\pi^2\tilde{n}^2 kT}{\lambda^4\kappa}\left(\frac{\partial\tilde{n}}{\partial p}\right)_{T,\mathbf{m}}^2, \tag{26.36}$$

$$R_\theta = \frac{2\pi^2\tilde{n}^2}{N_A\lambda^4 c_0}\sum_{i=1}^{r}\sum_{j=1}^{r} m_i m_j \frac{\psi^{ij}}{|\psi|}\left(\frac{\partial\tilde{n}}{\partial m_i}\right)_{T,p,m_k}\left(\frac{\partial\tilde{n}}{\partial m_j}\right)_{T,p,m_k}, \tag{26.37}$$

where $c_0$ is the concentration of species 0 in g/cc, $c_0 = M_0 N_0/N_A V$. $R_{\theta,0}$ is the scattering arising from the density fluctuation, while $R_\theta$ is the (excess) scattering arising from the concentration fluctuation. The corresponding turbidities $\tau_0$ and $\tau$ can be written down by replacing the factor $2\pi^2$ in $R_{\theta,0}$ and $R_\theta$ by $32\pi^3/3$. Necessarily the results are exactly the same as those obtained by Kirkwood and Goldberg using the grand canonical ensemble.

In the study of light scattering from polymer solutions, our attention is directed to only the excess scattering $R_\theta$. It is then convenient to expand the excess chemical potentials in a power series in the concentrations $m_i$; that is,

$$\mu_i = \mu_i{}^0(T, p) + kT\ln\gamma_i\ m_i \qquad (i = 1, \ldots, r) \tag{26.38}$$

with

$$\ln\gamma_i = M_i\left(\sum_{j=1}^{r} B_{2,ij}m_j + \sum_{j=1}^{r}\sum_{k=1}^{r} B_{3,ijk}m_j m_k + \cdots\right), \tag{26.39}$$

so that $\gamma_i$ is an activity coefficient such that $\gamma_i \to 1$ as $m_1, \ldots, m_r \to 0$.

For a two-component system, a useful result can readily be derived from Eq. (26.37). Let species 0 and 1 be a solvent and a solute, respectively. For this case, $\psi^{11}|\psi|^{-1}$ is equal to $\psi_{11}{}^{-1}$, and Eq. (26.37) reduces to

$$R_\theta = \frac{2\pi^2\tilde{n}^2 M_1 kT}{N_A\lambda^4 c_0}\left(\frac{\partial\tilde{n}}{\partial m_1}\right)_{T,p}^2\Big/\left(\frac{\partial\mu_1}{\partial m_1}\right)_{T,p}. \tag{26.40}$$

From the Gibbs–Duhem equation, we have

$$\left(\frac{\partial\mu_1}{\partial m_1}\right)_{T,p} = -\frac{N_0}{N_1}\left(\frac{\partial\mu_0}{\partial m_1}\right)_{T,p}. \tag{26.41}$$

Furthermore, if we denote the solute concentration in g/cc by $c = M_1N_1/N_AV$, the differential operator is transformed by

$$\left(\frac{\partial}{\partial m_1}\right)_{T,p} = \frac{c_0V_0N_0}{V}\left(\frac{\partial}{\partial c}\right)_{T,p}. \tag{26.42}$$

Now using Eq. (18.2)

$$\mu_0 - {\mu_0}^0 = -{V_0}^0\pi\,, \tag{26.43}$$

we have

$$\begin{aligned}\left(\frac{\partial\mu_0}{\partial c}\right)_{T,p} &= -{V_0}^0\frac{\partial\pi}{\partial c}\\ &= -{V_0}^0RT\left(\frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots\right), \end{aligned}\tag{26.44}$$

where we have used Eq. (18.3), and $M$ is the molecular weight of the solute(with omission of the subscript 1). For dilute solutions, $V_0 \simeq {V_0}^0$ and $\tilde{n} \simeq \tilde{n}_0$, and Eq. (26.40) therefore becomes

$$\frac{Kc}{R_\theta} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots\,, \tag{26.45}$$

where $K$ is given by Eq. (25.26). At infinite dilution, Eq. (26.45) reduces to Eq. (26.25). Equation (26.45) is strictly valid at $\theta = 0$, as mentioned already, and it is seen that the solute molecular weight $M$ and the second virial coefficient $A_2$ may be determined from the observed values of $Kc/R_\theta$ plotted against $c$.

## 26b. Heterogeneous Polymers

We consider a solution containing a single solvent (species 0) and polymer species $i$ ($\geq 1$) differing only in molecular weight. From Eqs. (26.21) and (26.38) with (26.39), $\psi_{ij}$ may be expanded as

$$\psi_{ij} = \frac{m_j}{M_i}(\delta_{ij} + M_iB_{2,ij}m_i + \cdots) \tag{26.46}$$

with $\delta_{ij}$ the Kronecker delta. In order to expand the quantity $\psi^{ij}|\psi|^{-1}$ in Eq. (26.37) in powers of $m_1$, $m_2$, …, we expand the determinant $|\psi|$ in the form,

$$|\psi| = \left(\prod_i \psi_{ij}\right)\left(1 - \sum_{i<j}\frac{\psi_{ij}\psi_{ji}}{\psi_{ii}\psi_{jj}} + \cdots\right). \tag{26.47}$$

Recalling that the cofactor of $\psi_{ij}$ is equal to $\psi^{ij} = \partial|\psi|/\partial\psi_{ij}$, we obtain, from Eqs. (26.46) and (26.47),

$$\frac{\psi^{ij}}{|\psi|} = \frac{M_i}{m_i}\delta_{ij} - M_iM_jB_{2,ij} + \cdots\,, \tag{26.48}$$

where $B_{2,ij} = B_{2,ji}$, since $\psi_{ij} = \psi_{ji}$ and $\psi^{ij} = \psi^{ji}$. Now, the refractive increment is independent of the polymer molecular weight, and we therefore assume that

$$\left(\frac{\partial \tilde{n}}{\partial m_i}\right)_{T,p,m_k} = \left(\frac{\partial \tilde{n}}{\partial m}\right)_{T,p} \quad \text{for all } i \tag{26.49}$$

with

$$m = \sum_i m_i \,. \tag{26.50}$$

Substitution of Eqs. (26.48) and (26.49) into Eq. (26.37) leads to

$$\begin{aligned} R_\theta &= \frac{2\pi^2\tilde{n}^2}{N_A\lambda^4 c_0}\left(\frac{\partial \tilde{n}}{\partial m}\right)^2 \left(\sum_i M_i m_i - \sum_i\sum_j M_i M_j B_{2,ij} m_i m_j + \cdots\right) \\ &= \frac{2\pi^2\tilde{n}^2}{N_A\lambda^4 c_0}\left(\frac{\partial \tilde{n}}{\partial m}\right)^2 \left(\langle M\rangle_w m - \sum_i\sum_j M_i M_j B_{2,ij} w_i w_j m^2 + \cdots\right), \end{aligned} \tag{26.51}$$

where $\langle M\rangle_w$ is the *weight-average molecular weight* of the polymer defined by

$$\langle M\rangle_w = \sum_i {M_i}^2 N_i / \sum_i M_i N_i \,, \tag{26.52}$$

and $w_i (= m_i/m)$ is the weight fraction of polymer species $i$ (in the whole polymer) and is also given by Eq. (23.5).

Let us now convert the concentration $m$ to the concentration $c$ in conventional units, $c$ being given by Eqs. (23.1). If the partial specific volume $\bar{v}$ of the polymer is assumed to be independent of $M_i$, the relations

$$m = \frac{c}{c_0} = \frac{N_A V_0}{M_0}\frac{c}{1-\bar{v}c}\,, \tag{26.53}$$

$$\frac{\partial}{\partial m} = \frac{c_0 N_0 V_0}{V}\frac{\partial}{\partial c} \tag{26.54}$$

are valid. Equation (26.51) may then be rewritten as

$$\frac{R_\theta}{K} = \langle M\rangle_w c - 2\sum_i\sum_j M_i M_j \left[\frac{\bar{v}_0}{2}B_{2,ij} + \frac{\bar{v}}{2}\left(\frac{1}{M_i}+\frac{1}{M_j}\right)\right] w_i w_j c^2 + \cdots\,, \tag{26.55}$$

where $\bar{v}_0 (= N_A V_0/M_0)$ is the partial specific volume of the solvent. In order to compare Eq. (26.55) with the virial expansion for the osmotic pressure $\pi$, we must expand $\pi$ in terms of $B_{2,ij}$. From the Gibbs–Duhem equation with Eqs. (26.38) and (26.39), we have

$$-N_0 d\mu_0 = kT\sum_i N_i d\ln \gamma_i m_i \,, \tag{26.56}$$

or

$$-d\mu_0 = kTM_0\left(\sum_i \frac{1}{M_i}dm_i + \sum_i\sum_j B_{2,ij} m_i dm_j + \cdots\right). \tag{26.57}$$

Integration over $m_1$, $m_2$, … gives

$$\begin{aligned}\pi = -\frac{\mu_0 - {\mu_0}^0}{{V_0}^0} &= \frac{RTM_0}{N_A {V_0}^0}\left(\sum_i \frac{1}{M_i} m_i + \frac{1}{2}\sum_i \sum_j B_{2,ij} m_i m_j + \cdots\right) \\ &= \frac{RTM_0}{N_A V_0}\left(\frac{1}{\langle M\rangle_n} m + \frac{1}{2}\sum_i \sum_j B_{2,ij} w_i w_j m^2 + \cdots\right), \end{aligned} \tag{26.58}$$

where we have replaced ${V_0}^0$ by $V_0$. Equation (26.58) may be rewritten as

$$\frac{\pi}{RT} = \frac{1}{\langle M\rangle_n} c + \sum_i \sum_j \left[\frac{\bar{v}_0}{2} B_{2,ij} + \frac{\bar{v}}{2}\left(\frac{1}{M_i} + \frac{1}{M_j}\right)\right] w_i w_j c^2 + \cdots . \tag{26.59}$$

On the other hand, we have, from Eqs. (23.2) and (23.7),

$$\frac{\pi}{RT} = \frac{1}{\langle M\rangle_n} c + \sum_i \sum_j A_{ij} w_i w_j c^2 + \cdots . \tag{26.60}$$

Comparing Eq. (26.59) with Eq. (26.60), we obtain the relation between $A_{ij}$ and $B_{2,ij}$,

$$A_{ij} = \frac{\bar{v}_0}{2} B_{2,ij} + \frac{\bar{v}}{2}\left(\frac{1}{M_i} + \frac{1}{M_j}\right). \tag{26.61}$$

Thus, substitution of Eq. (26.61) into Eq. (26.55) leads to

$$\frac{Kc}{R_\theta} = \frac{1}{\langle M\rangle_w} + 2A_2 c + \cdots , \tag{26.62}$$

where

$$A_2 = \frac{1}{\langle M\rangle_w^2} \sum_i \sum_j M_i M_j A_{ij} w_i w_j . \tag{26.63}$$

Equation (26.63) is to compared with Eq. (23.7). For heterogeneous polymers, the osmotic and light-scattering second virial coefficients, $A_2$, are seen to differ from each other. For a monodisperse system, both are, of course, the same, and Eq. (26.62) reduces to Eq. (26.45). Further analysis of the second virial coefficients of heterogeneous polymers will be deferred to Section 27d.

## 26c. Mixed-Solvent Systems

We consider a solution containing two solvents (species 0 and 1) and a single polymer (species 2). In this case, $R_\theta$ may be written in the form,

$$\begin{aligned} R_\theta = \frac{2\pi^2 \tilde{n}^2}{N_A \lambda^4 c_0 |\psi|} \Bigg[ &\left(\frac{\partial \tilde{n}}{\partial m_1}\right)^2 {m_1}^2 \psi_{22} - 2\left(\frac{\partial \tilde{n}}{\partial m_1}\right)\left(\frac{\partial \tilde{n}}{\partial m_2}\right) m_1 m_2 \psi_{12} \\ &+ \left(\frac{\partial \tilde{n}}{\partial m_2}\right)^2 {m_2}^2 \psi_{11} \Bigg] , \end{aligned} \tag{26.64}$$

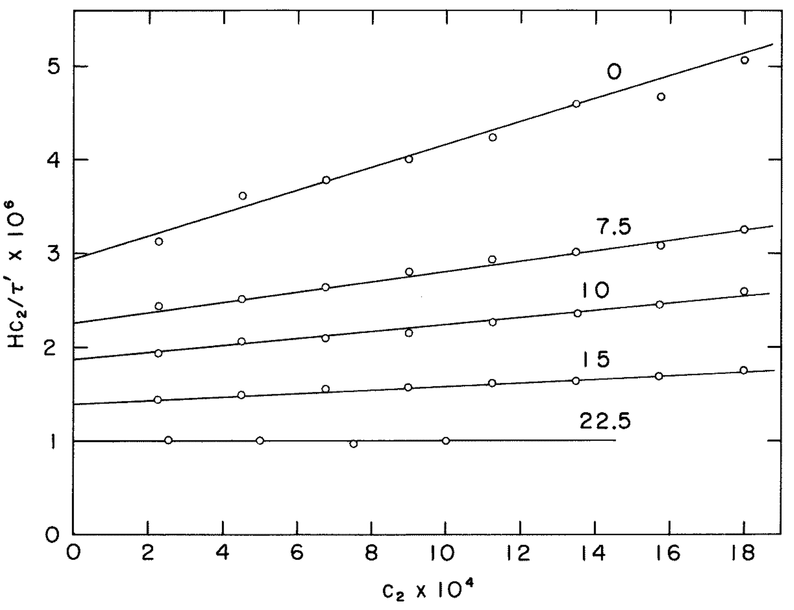

**Fig. V.2.** $Hc_2/\tau'$ as a function of concentration $c_2$ of polystyrene in benzene–methanol mixtures.[3] The number attached to each curve indicates the concentration (%) of methanol in the mixed solvent.

where we have abbreviated $(\partial\tilde{n}/\partial m_i)_{T,p,m_j}$ to $\partial\tilde{n}/\partial m_i$. From Eqs. (26.21) and (26.38) with (26.39), $\psi_{ij}$ may be expanded in the form

$$\psi_{ij} = \frac{m_j}{M_i}\left(\delta_{ij} + M_i B_{2,ij} m_i + 2M_i \sum_{k=1}^{2} B_{3,ijk} m_i m_k + \cdots\right), \tag{26.65}$$

where we have used the symmetry property that permutation of the indices $i$, $j$, $k$, does not alter the value of $B_{3,ijk}$. Suppose now that $R_\theta$ becomes $R_\theta{}^0$ as $m_2$ goes to zero at constant $m_1$. Then the quantity $R_\theta{}' \equiv R_\theta - R_\theta{}^0$ represents the excess scattering over that of the mixed solvent of composition $m_1$. After a tedious calculation, we obtain for $R_\theta{}'$

$$\frac{K_m m_2}{R_\theta{}'} = \frac{1}{M_{2,\mathrm{ap}}} + 2B_{2,\mathrm{ap}} m_2 + \cdots, \tag{26.66}$$

where

$$K_m = \frac{2\pi^2\tilde{n}^2}{N_A \lambda^4 c_0}\left(\frac{\partial\tilde{n}}{\partial m_2}\right)^2, \tag{26.67}$$

$$M_{2,\mathrm{ap}} = M_2(1 - 2\gamma_m M_1 B_{2,12} m_1 + \cdots), \tag{26.68}$$

$$\begin{aligned} B_{2,\mathrm{ap}} = {} & \tfrac{1}{2}B_{2,22} + [(1 + 2\gamma_m M_1 M_2{}^{-1})B_{3,122} \\ & - \tfrac{1}{2}M_1 B_{2,12}^2 + \gamma_m M_1 B_{2,12} B_{2,22}] m_1 + \cdots, \end{aligned} \tag{26.69}$$

$$\gamma_m = \left(\frac{\partial \tilde{n}}{\partial m_1}\right) \bigg/ \left(\frac{\partial \tilde{n}}{\partial m_2}\right) . \tag{26.70}$$

We do not here convert $m_i$ to $c_i$, since the distribution function theory (Section 27e) gives the equivalent of Eq. (26.66) written in terms of the $c$-concentration units.

From Eqs. (26.66) and (26.68), the intercept ${M_{2,\mathrm{ap}}}^{-1}$ of a plot of $K_m m_2/R_\theta{}'$ against $m_2$ is seen to depend on the composition of the mixed solvent unless $\gamma_m = 0$, and not to give the true molecular weight $M_2$ of the polymer. Thus the quantity $M_{2,\mathrm{ap}}$ is called the *apparent* molecular weight. In addition, one-half of the slope of the same plot, $B_{2,\mathrm{ap}}$, is not the true second virial coefficient (in the $m$-concentration units) for polymer molecules in the mixed solvent, and is called the *apparent* second virial coefficient. For illustrative purposes, in Fig V.2 are shown the turbidity data of Ewart et al.[3] on solutions of polystyrene in benzene-methanol mixtures, where the $c$-concentration scale is used, and methanol is assumed to be species 1. An analysis of the data by means of Eqs. (26.68) to (26.70) yields some information concerning thermodynamic interactions. For example, the values of $B_{2,12}$ and $B_{2,22}$ estimated by Kirkwood and Goldberg[12] for this system are the following: $B_{2,12} = 3.3 \times 10^{-2}$ and $B_{2,22} = 9.9 \times 10^{-4}$. The positive value of the coefficient $B_{2,12}$ for polystyrene and methanol means that a polystyrene molecule exhibits a preference for benzene molecules in its statistical environment. This is consistent with the fact that benzene is a good solvent for polystyrene, but methanol is a nonsolvent.

We now consider the problem of determining the true molecular weight of the polymer and the second virial coefficient from light-scattering measurements in mixed-solvent systems. Suppose that there is a membrane permeable to species 0 and 1 but not to species 2, and two solutions of concentrations $(c_1, c_2)$ and $(c_1', 0)$, or $(m_1, m_2)$ and $(m_1', 0)$, are in equilibrium with each other separated by the membrane. The concentration of species 1 on one side is different from that on the other, but the chemical potentials $\mu_0$ and $\mu_1$ of species 0 and 1 have the same values in the two solutions, respectively. From the McMillan–Mayer theory (Section 19), the pressure difference $p(c_1, c_2) - p(c_1', 0)$, i.e., the osmotic pressure $\pi(c_1, c_2|c_1', 0)$, may then be expanded in the form

$$\pi(c_1, c_2|c_1{}', 0) = RT\left[\frac{1}{M_2}c_2 + A_{2,22}(c_1{}')c_2{}^2 + \cdots\right] , \tag{26.71}$$

where $A_{2,22}(c_1{}')$ is the second virial coefficient for polymer molecules in the mixed solvent, and may also be defined in terms of the distribution functions for polymer molecules at concentrations $(c_1{}', 0)$. We anticipate that the quantities $M_2$ and $A_{2,22}(c_1{}')$ may be determined from light-scattering measurements if we study solutions of concentrations $(c_1, c_2)$ at constant chemical potential $\mu_1$. This method was suggested by Casassa and Eisenberg,[15–17] and is called the "dialysis" technique.

In order to demonstrate the above statement, we rewrite Eq. (26.64) as

$$\frac{R_\theta}{K'} = \frac{1}{c_0({\psi_{22}} - {\psi_{12}}^2/\psi_{11})}\left[m_2\left(\frac{\partial\tilde{n}}{\partial m_2}\right) - m_1\left(\frac{\partial\tilde{n}}{\partial m_1}\right)\frac{\psi_{12}}{\psi_{11}}\right]^2 + \left(\frac{\partial\tilde{n}}{\partial m_1}\right)^2\frac{{m_1}^2}{c_0\psi_{11}} \tag{26.72}$$

with

$$K' = \frac{2\pi^2\tilde{n}^2}{N_A\lambda^4}\,. \tag{26.73}$$

Let us now examine the thermodynamic properties of the solution with concentration $(m_1, m_2)$. Since $Vd\pi = Vdp = N_2 d\mu_2$ at constant $T$, $\mu_0$, and $\mu_1$, we have

$$\frac{V}{N_2}\left(\frac{\partial\pi}{\partial m_2}\right)_{T,\mu_1} = \left(\frac{\partial\mu_2}{\partial m_2}\right)_{T,\mu_0,\mu_1}. \tag{26.74}$$

We write the chemical potentials $\mu_i (i = 1, 2)$ as functions of $m_1$, $m_2$, and $p$; that is

$$d\mu_i = \left(\frac{\partial\mu_i}{\partial m_1}\right)_{T,p,m_2} dm_1 + \left(\frac{\partial\mu_i}{\partial m_2}\right)_{T,p,m_1} dm_2 + V_i dp\,. \tag{26.75}$$

We obtain, from Eq. (26.75) with $i = 2$,

$$\left(\frac{\partial\mu_2}{\partial m_2}\right)_{T,\mu_0,\mu_1} = \left(\frac{\partial\mu_2}{\partial m_1}\right)_{T,p,m_2}\left(\frac{\partial m_1}{\partial m_2}\right)_{T,\mu_0,\mu_1} + \left(\frac{\partial\mu_2}{\partial m_2}\right)_{T,p,m_1} + V_2\left(\frac{\partial\pi}{\partial m_2}\right)_{T,\mu_1}, \tag{26.76}$$

and from Eq. (26.75) with $i = 1$,

$$\left(\frac{\partial\mu_1}{\partial m_1}\right)_{T,p,m_2}\left(\frac{\partial m_1}{\partial m_2}\right)_{T,\mu_0,\mu_1} = -\left(\frac{\partial\mu_1}{\partial m_2}\right)_{T,p,m_1} - V_1\left(\frac{\partial\pi}{\partial m_2}\right)_{T,\mu_1}, \tag{26.77}$$

$$\left(\frac{\partial m_1}{\partial m_2}\right)_{T,p,\mu_1} = -\left(\frac{\partial\mu_1}{\partial m_2}\right)_{T,p,m_1}\Bigg/\left(\frac{\partial\mu_1}{\partial m_1}\right)_{T,p,m_2}. \tag{26.78}$$

Since $dV = V_1 dN_1 + V_2 dN_2$ at constant $T$ and $p$ ($N_0$ is fixed as before), we have

$$\begin{aligned} {V_2}^* \equiv \left(\frac{\partial V}{\partial N_2}\right)_{T,p,\mu_1} &= V_2 + \frac{V_1 M_2}{M_1}\left(\frac{\partial m_1}{\partial m_2}\right)_{T,p,\mu_1} \\ &= V_2 - \frac{V_1 M_2}{M_1}\left(\frac{\partial\mu_1}{\partial m_2}\right)_{T,p,m_1}\Bigg/\left(\frac{\partial\mu_1}{\partial m_1}\right)_{T,p,m_2}, \end{aligned} \tag{26.79}$$

where we have used Eq. (26.78) in obtaining the second line. Substituting Eqs. (26.76), (26.77), and (26.79) with (26.21) into Eq. (26.74), we obtain

$$c_0\left(\psi_{22} - \frac{{\psi_{12}}^2}{\psi_{11}}\right) = \frac{m_2(1 - {V_2}^*\rho_2)}{RT}\left(\frac{\partial\pi}{\partial m_2}\right)_{T,\mu_1} \tag{26.80}$$

with $\rho_2 = N_2/V$. Further, we write the refractive index $\tilde{n}$ as a function of $m_1$ and $m_2$,

$$d\tilde{n} = \left(\frac{\partial\tilde{n}}{\partial m_1}\right)_{T,p,m_2} dm_1 + \left(\frac{\partial\tilde{n}}{\partial m_2}\right)_{T,p,m_1} dm_2\,, \tag{26.81}$$

and obtain

$$m_2\left(\frac{\partial\tilde{n}}{\partial m_2}\right)_{T,p,\mu_1} = m_2\left(\frac{\partial\tilde{n}}{\partial m_2}\right)_{T,p,m_1} - m_1\left(\frac{\partial\tilde{n}}{\partial m_1}\right)_{T,p,m_2}\frac{\psi_{12}}{\psi_{11}}\,, \tag{26.82}$$

where we have used Eqs. (26.21) and (26.78).

Now, if $R_\theta$ approaches ${R_\theta}^0$ as $m_2$ becomes zero at constant $T$, $p$, and $\mu_1$, the quantity $R_\theta - {R_\theta}^0 \equiv {R_\theta}^*$ represents the excess scattering over that of the mixed solvent of composition ${m_1}'$. For solutions dilute with respect to the polymer the refractive index and the last term on the right-hand side of Eq. (26.72) may be assumed to be independent of $m_2$. Substitution of Eqs. (26.80) and (26.82) into Eq. (26.72) then leads to

$$\frac{{R_\theta}^*}{K'} = \left(\frac{\partial\tilde{n}}{\partial m_2}\right)^2_{T,p,\mu_1}\left(\frac{\partial\pi}{\partial m_2}\right)^{-1}_{T,\mu_1}\frac{RTm_2}{1 - {V_2}^*\rho_2}\,. \tag{26.83}$$

We now convert $m_2$ to $c_2$ by the use of the relation, $m_2 = c_2/c_0 = N_A V c_2/M_0 N_0$ and

$$\left(\frac{\partial}{\partial m_2}\right)_{T,p,\mu_1} = c_0(1 - {V_2}^*\rho_2)\left(\frac{\partial}{\partial c_2}\right)_{T,p,\mu_1}\,. \tag{26.84}$$

The result is

$$\frac{K^* c_2}{{R_\theta}^*} = \frac{1}{M_2} + 2A_{2,22}(c_1^{'})c_2 + \cdots\,, \tag{26.85}$$

where we have used Eq. (26.71), and $K^*$ is defined by

$$K^* = \frac{2\pi^2\tilde{n}^2}{N_A\lambda^4}\left(\frac{\partial\tilde{n}}{\partial c_2}\right)^2_{T,p,\mu_1}\,. \tag{26.86}$$

Equation (26.85) with (26.86) implies that the equation for a three-component system is formally identical with that for a two-component system when the chemical potential of species 1 is kept constant; it enables us to determine $M_2$ and $A_{2,22}({c_1}')$. The theory may easily be extended to a multicomponent system containing two or more "diffusible "species. In particular, the dialysis technique is useful in light-scattering studies of polyelectrolyte solutions.[16, 18]

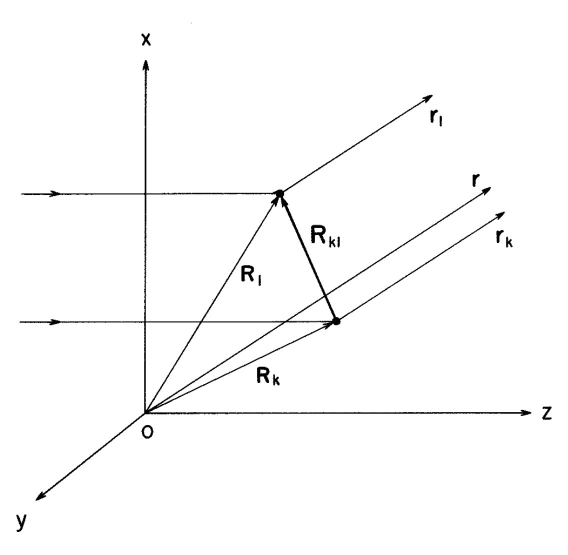

**Fig. V.3.** Paths of light scattered from two different scattering units.

## 27. Distribution Function Theory

The fluctuation theory of light scattering is valid only at zero scattering angle or, strictly, for a system of small scattering particles. In order to discuss the effect of intramolecular destructive interference in a system of large molecules, we must return to the distribution function approach.

Consider first a localized system of volume $V$ containing $N$ scattering units, not all identical. Let the $k$th unit be at the distance $\mathbf{R}_k$ from the origin of a coordinate system, and the incident light be plane-polarized, its electric field and the direction of propagation being parallel to the $x$ and $z$ axes, respectively. The moment $\mathbf{p}_k$ induced on the $k$th unit may then be written as (see Fig. V.3)

$$\mathbf{p}_k = \mathbf{e}_x p_{0k} \exp\left[i\omega\left(t - \frac{\mathbf{R}_k \cdot \mathbf{e}_z}{\tilde{c}'}\right)\right] . \tag{27.1}$$

From Eq. (25.4), the magnitude of the radiation electric field $\mathbf{E}_k$ due to $\mathbf{p}_k$ is given by

$$E_k = p_{0k}\left(\frac{\omega}{\tilde{c}}\right)^2 \frac{\sin\theta_x}{r_k} \exp\left[i\omega\left(t - \frac{r_k + \mathbf{R}_k \cdot \mathbf{e}_z}{\tilde{c}'}\right)\right] , \tag{27.2}$$

where $r_k$ is the distance between the $k$th unit and the observer. If $r$ is the distance between the origin and the observer, $r_k = r - \mathbf{R}_k \cdot \mathbf{e}_r$ with $\mathbf{e}_r$ the unit vector in the direction of $\mathbf{r}$, and $r_k^{-1} \simeq r^{-1}$ since $r \gg V^{1/3}$. Further, $\mathbf{E}_k$ is parallel to $\mathbf{E}_l$ for all $k$, $l$, pairs. We therefore obtain for the total radiation field $E$

$$E = \sum_{k=1}^{N} E_k = \left(\frac{\omega}{\tilde{c}}\right)^2 \frac{\sin\theta_x}{r} \exp\left[i\omega\left(t - \frac{r}{\tilde{c}'}\right)\right] \sum_k p_{0k} \exp(\mathbf{s}' \cdot \mathbf{R}_k)\,, \tag{27.3}$$

where

$$\begin{aligned} \mathbf{s}' &= 2\pi i \mathbf{s}/\lambda'\,, \\ \mathbf{s} &= \mathbf{e}_r - \mathbf{e}_z\,, \\ s &= 2\sin(\theta/2) \end{aligned} \tag{27.4}$$

with $\lambda'$ the wavelength of light in the medium. Recalling that $I = |E|^2 = EE^*$ with $E^*$ the complex conjugate of $E$, $I^0 = ({E_0}^0)^2$, and $p_{0k} = \alpha_k {E_0}^0$ with $\alpha_k$ the polarizability of the $k$th unit, we obtain

$$\frac{I}{I^0} = \frac{16\pi^4 \sin^2\theta_x}{\lambda^4 r^2} G\,, \tag{27.5}$$

where

$$G = \sum_{k=1}^{N}\sum_{l=1}^{N} \alpha_k \alpha_l \exp(\mathbf{s}' \cdot \mathbf{R}_{kl}) \tag{27.6}$$

with $\mathbf{R}_{kl}$ the distance between the $k$th and $l$th units. When the incident light is unpolarized, it is easy to see that we have, instead of Eq. (27.5),

$$\frac{I}{I^0} = \frac{8\pi^4(1+\cos^2\theta)}{\lambda^4 r^2} G\,. \tag{27.7}$$

For a nonlocalized system, $G$ must be replaced by the ensemble average,

$$\langle G \rangle = \sum_k \sum_l \alpha_k \alpha_l \int P(\mathbf{R}_{kl}) \exp(\mathbf{s}' \cdot \mathbf{R}_{kl}) d\mathbf{R}_{kl}\,, \tag{27.8}$$

where $P(\mathbf{R}_{kl})$ is the distribution function of $\mathbf{R}_{kl}$. Then the Rayleigh ratio is given by

$$R_\theta = \frac{8\pi^4}{\lambda^4} \frac{\langle G \rangle}{V}\,. \tag{27.9}$$

It is to be understood that the $R_\theta$ given by Eq. (27.9) is the excess scattering over that of species 0 alone, and we do not discuss the scattering of a pure liquid. We note that Fixman[19] has developed the molecular theory of light scattering for a one-component system, results of which are in agreement with the fluctuation theory. Thus, our problem is to evaluate the integral in $\langle G \rangle$ with the distribution functions for "solute" molecules.

## 27a. General Theory

The distribution function theory for a two-component system was developed by Zimm[6] and Albrecht,[20] and subsequently the theory was extended to a multicomponent system by Yamakawa.[21] Consider a solution of volume $V$ containing molecules of species 0, 1, 2, ..., $r$, and let $N_\sigma$ be the number of molecules of species $\sigma$ in $V$. Suppose that a molecule of species $\sigma$ is composed of $n_\sigma$ identical scattering units. Then the total number of scattering units entering into Eq. (27.8) is

$$N = \sum_{\sigma=1}^{r} N_\sigma n_\sigma \, . \tag{27.10}$$

The $\alpha_k$'s in Eq. (27.8) are the same for $N_\sigma n_\sigma$ units, and we put $\alpha_k = \alpha_\sigma$ if the $k$th unit belongs to a molecule of species $\sigma$.

Now, the integral in Eq. (27.8) depends upon which species the $k$th and $l$th units belong to, and also upon which units of molecules of those species they are, but not upon which molecules of those species they belong to. We therefore separate the $N^2$ terms of the double summation into intramolecular and intermolecular terms, and it is sufficient to consider the distribution function $P(\mathbf{R}_{i_1 j_1})$ of the distance $\mathbf{R}_{i_1 j_1}$ between the $i_1$th and $j_1$th units of molecule 1 of species $\sigma$ and the distribution function $P(\mathbf{R}_{i_1 i_2})$ of the distance $\mathbf{R}_{i_1 i_2}$ between the $i_1$th unit of molecule 1 and the $i_2$th unit of molecule 2, where molecules 1 and 2 are assumed to be those of species $\sigma$ and $\tau$, respectively. Clearly, these functions may be expressed in terms of the McMillan–Mayer distribution functions defined by Eq. (19.19) with (19.21); that is,

$$P(\mathbf{R}_{i_1 j_1}) = V^{-1} \int F_1(1_\sigma) d(1_\sigma)/d\mathbf{R}_{i_1 j_1} \, , \tag{27.11}$$

$$P(\mathbf{R}_{i_1 i_2}) = V^{-2} \int F_2(1_\sigma, 2_\tau) d(1_\sigma, 2_\tau)/d\mathbf{R}_{i_1 i_2} \, . \tag{27.12}$$

Equation (27.8) may then be rewritten as

$$\begin{aligned}
\langle G \rangle &= \sum_{\sigma=1}^{r} N_\sigma {\alpha_\sigma}^2 \sum_{i_1=1}^{n_\sigma} \sum_{j_1=1}^{n_\sigma} V^{-1} \int F_1(1_\sigma) \exp(\mathbf{s}' \cdot \mathbf{R}_{i_1 j_1}) d(1_\sigma) \\
&+ \sum_{\sigma=1}^{r} N_\sigma (N_\sigma - 1) {\alpha_\sigma}^2 \sum_{i_1=1}^{n_\sigma} \sum_{i_2=1}^{n_\sigma} V^{-2} \\
&\times \int F_2(1_\sigma, 2_\sigma) \exp(\mathbf{s}' \cdot \mathbf{R}_{i_1 i_2}) d(1_\sigma, 2_\sigma) \\
&+ \sum_{\substack{\sigma=1 \\ \sigma \neq \tau}}^{r} \sum_{\tau=1}^{r} N_\sigma N_\tau \alpha_\sigma \alpha_\tau \sum_{i_1=1}^{n_\sigma} \sum_{i_2=1}^{n_\tau} V^{-2} \\
&\times \int F_2(1_\sigma, 2_\tau) \exp(\mathbf{s}', \mathbf{R}_{i_1 i_2}) d(1_\sigma, 2_\tau) \, .
\end{aligned} \tag{27.13}$$

We note that $F_1$ and $F_2$ in Eqs. (27.11) to (27.13) are also functions of a set of concentrations $\mathbf{c} = c_1, c_2, \ldots, c_r$, with $c_\sigma = M_\sigma N_\sigma / N_\mathrm{A} V$ the concentration (g/cc) of species $\sigma$.

When the distribution of the molecules is random, as it will be if there are no intermolecular interactions, the second and last terms on the right-hand side of Eq. (27.13) make no contribution to the scattering. In fact, this conclusion can be verified as follows. For the random distribution we have $F_2(1_\sigma, 2_\tau) = F_1(1_\sigma)F_1(2_\tau)$, and the integral in the second or last term becomes

$$\int F_1(1_\sigma)F_1(2_\tau)\exp(\mathbf{s}' \cdot \mathbf{R}_{i_1 i_2})d(1_\sigma, 2_\tau) = V \int \exp(\mathbf{s}' \cdot \mathbf{R}_{i_1 i_2})d\mathbf{R}_{i_1 i_2}\,, \tag{27.14}$$

where the normalization condition on $F_1$ has been used. The right-hand side is just a Fourier representation of the three-dimensional delta function, i.e., $(\lambda')^3\delta(\mathbf{s})$, and is therefore zero except at $\theta = 0$. Thus we may replace $F_2(1_\sigma, 2_\sigma)$ and $F_2(1_\sigma, 2_\tau)$ by the $g$ functions $g_2(1_\sigma, 2_\sigma)$ and $g_2(1_\sigma, 2_\tau)$, respectively, in Eq. (27.13);

$$g_2(1_\sigma, 2_\tau, \mathbf{c}) = F_2(1_\sigma, 2_\tau, \mathbf{c}) - F_1(1_\sigma, \mathbf{c})F_1(2_\tau, \mathbf{c})\,, \tag{27.15}$$

where we have indicated explicitly that $F_1$, $F_2$, and $g_2$, are functions of $\mathbf{c}$.

We now introduce an *intramolecular interference factor* $P_{1,\sigma}(\theta, \mathbf{c})$ and *intermolecular interference factor* $P_{2,\sigma\tau}(\theta, \mathbf{c})$ defined by

$$P_{1,\sigma}(\theta, \mathbf{c}) = n_\sigma{}^{-2} \sum_{i_1=1}^{n_\sigma} \sum_{j_1=1}^{n_\sigma} V^{-1} \int F_1(1_\sigma, \mathbf{c}) \exp(\mathbf{s}' \cdot \mathbf{R}_{i_1 j_1}) d(1_\sigma)\,, \tag{27.16}$$

$$P_{2,\sigma\tau}(\theta, \mathbf{c}) = (n_\sigma n_\tau)^{-1} \sum_{i_1=1}^{n_\sigma} \sum_{i_2=1}^{n_\tau} \frac{\int g_2(1_\sigma, 2_\tau, \mathbf{c}) \exp(\mathbf{s}' \cdot \mathbf{R}_{i_1 i_2}) d(1_\sigma, 2_\tau)}{\int g_2(1_\sigma, 2_\tau, \mathbf{c}) d(1_\sigma, 2_\tau)}\,. \tag{27.17}$$

In the limit of $\mathbf{s}' = 0$ (or $\theta = 0$), we have

$$\begin{aligned} \lim_{\theta \to 0} P_{1,\sigma}(\theta, \mathbf{c}) &= 1\,, \\ \lim_{\theta \to 0} P_{2,\sigma\tau}(\theta, \mathbf{c}) &= 1\,, \end{aligned} \tag{27.18}$$

irrespective of the values of $\mathbf{c}$. Further, we define a coefficient $A_{2,\sigma\tau}(\mathbf{c})$ by

$$A_{2,\sigma\tau}(\mathbf{c}) = -\frac{N_\mathrm{A}}{2VM_\sigma M_\tau} \int g_2(1_\sigma, 2_\tau, \mathbf{c}) d(1_\sigma, 2_\tau)\,, \tag{27.19}$$

which represents interactions between a molecule of species $\sigma$ and a molecule of species $\tau$ at concentrations $\mathbf{c}$, and is equal to the ordinary second virial coefficient at $\mathbf{c} = 0$. By the use of Eqs. (27.16), (27.17), and (27.19), Eq. (27.13) may then be simplified (for $N_\sigma \gg 1$) to

$$\begin{aligned} \frac{\langle G \rangle}{N_\mathrm{A} V} &= \sum_{\sigma=1}^{r} (n_\sigma \alpha_\sigma)^2 M_\sigma{}^{-1} P_{1,\sigma}(\theta, \mathbf{c}) c_\sigma \\ &\quad -2 \sum_{\sigma=1}^{r} \sum_{\tau=1}^{r} (n_\sigma \alpha_\sigma)(n_\tau \alpha_\tau) A_{2,\sigma\tau}(\mathbf{c}) P_{2,\sigma\tau}(\theta, \mathbf{c}) c_\sigma c_\tau\,, \end{aligned} \tag{27.20}$$

where the second and third terms on the right-hand side of Eq. (27.13) have been combined to yield the last term of Eq. (27.20).

Let us now express the excess polarizability $\alpha_\sigma$ in terms of the refractive index increment. Assuming that the dielectric increment is independent of $M_\sigma$, we have

$$\tilde{n}^2 - \tilde{n}_0{}^2 = 4\pi N_{\mathrm{A}} \sum_{\sigma=1}^{r} \frac{n_\sigma}{M_\sigma} \alpha_\sigma c_\sigma \tag{27.21}$$

with $\tilde{n}_0$ the refractive index of species 0. To solve Eq. (27.21), we further assume that $\alpha_\sigma$ is independent of $\mathbf{c}$ in a first approximation. Then differentiation of Eq. (27.21) with respect to $c_\sigma$ leads to

$$n_\sigma \alpha_\sigma = \frac{M_\sigma \tilde{n}_0}{2\pi N_{\mathrm{A}}} \left( \frac{\partial \tilde{n}}{\partial c_\sigma} \right)_0 , \tag{27.22}$$

where the derivative is to be evaluated at infinite dilution with respect to all "solute"species $\sigma(\geq 1)$.

Substituting Eq. (27.20) with (27.22) into Eq. (27.9), we obtain for the Rayleigh ratio

$$\begin{aligned} \frac{R_\theta}{K'} = & \sum_{\sigma=1}^{r} \left( \frac{\partial \tilde{n}}{\partial c_\sigma} \right)_0^2 M_\sigma P_{1,\sigma}(\theta, \mathbf{c}) c_\sigma \\ & -2 \sum_{\sigma=1}^{r} \sum_{\tau=1}^{r} \left( \frac{\partial \tilde{n}}{\partial c_\sigma} \right)_0 \left( \frac{\partial \tilde{n}}{\partial c_\tau} \right)_0 M_\sigma M_\tau A_{2,\sigma\tau}(\mathbf{c}) P_{2,\sigma\tau}(\theta, \mathbf{c}) c_\sigma c_\tau , \end{aligned} \tag{27.23}$$

where $K'$ is given by Eq. (26.73) with $\tilde{n} = \tilde{n}_0$. Equation (27.23) is the basic equation in the distribution function theory of light scattering for a multicomponent system, from which various cases of interest can be derived.

In particular, for a two-component system, Eq. (27.23) becomes

$$\frac{R_\theta}{K} = M P_1(\theta, c) c - 2M^2 A_2(c) P_2(\theta, c) c^2 , \tag{27.24}$$

where the subscript $\sigma(=1)$ has been omitted, and $K$ is given by Eq. (25.26). We expand $P_1(\theta, c)$ in powers of $c$,

$$P_1(\theta, c) = P_1(\theta) + P_1{}^{(1)}(\theta) c + \cdots \tag{27.25}$$

with $P_1(\theta) \equiv P_1(\theta, 0)$. With the shorthand notation, $A_2(0) \equiv A_2$ and $P_2(\theta, 0) \equiv P_2(\theta)$, Eq. (27.24) may then be rewritten as

$$\frac{Kc}{R_\theta} = \frac{1}{M P_1(\theta)} + 2A_2 Q(\theta) c + \cdots , \tag{27.26}$$

where

$$Q(\theta) = Q_2(\theta) - Q_1(\theta) , \tag{27.27}$$

$$Q_1(\theta) = \frac{{P_1}^{(1)}(\theta)}{2MA_2{P_1}^2(\theta)}\,, \tag{27.28}$$

$$Q_2(\theta) = \frac{P_2(\theta)}{{P_1}^2(\theta)}\,. \tag{27.29}$$

In the limit of $\theta = 0$, Eq. (27.26) becomes identical with Eq. (26.45).

## 27b. Intramolecular Interferences and Angular Dissymmetries

In this section, we examine the behavior of the intramolecular interference factor $P_1(\theta, c)$ as a function of $\theta$ and $c$ for a two-component system. For a system of small scattering particles $P_1(\theta)$ is identically equal to unity, and the intensity $I$ of scattered light depends on the angle only through the factor $(1 + \cos^2\theta)$ (for unpolarized incident light). In this case $I$ is symmetric about $\theta = 90°$. For large molecules, $P_1(\theta)$ depends on the size and shape of the molecule as well as on the angle, and the angular symmetry of $I$ is lost. This enables us to determine the molecular dimensions from light-scattering measurements. For flexible chain polymers, $P_1$ depends also on the concentration $c$ through the distribution function $F_1(1, c)$, whereas for rigid molecules $P_1$ is independent of $c$.

### 27b(i). The Intramolecular Interference Factor at Infinite Dilution

We consider a flexible chain polymer composed of $n$ segments. There arises some ambiguity in defining the scattering unit of molecule. However, since the number of effective segments in the chain is, to some extent, arbitrary, as discussed already, we regard the segment as the scattering unit. At infinite dilution, the intramolecular interference factor may then be written in the form,

$$P_1(\theta) = n^{-2}\sum_i\sum_j\int P(\mathbf{R}_{ij})\exp(\mathbf{s}'\cdot\mathbf{R}_{ij})d\mathbf{R}_{ij}\,, \tag{27.30}$$

where $P(\mathbf{R}_{ij})$ is the distribution of the distance $\mathbf{R}_{ij}$ between the $i$th and $j$th segments of the chain. Since the integral in Eq. (27.30) is of the same form as that of (4.11), and $P(\mathbf{R}_{ij})$ is spherically symmetric, $P_1(\theta)$ may be expanded in terms of the moments $\langle {R_{ij}}^{2p}\rangle$ as

$$P_1(\theta) = 2\sum_{p=0}^{\infty}\frac{(-1)^p}{(2p+1)!}\left(\frac{4\pi}{\lambda'}\right)^{2p} n^{-2}\sum_{i<j}\langle {R_{ij}}^{2p}\rangle \sin^{2p}(\theta/2)\,, \tag{27.31}$$

and at small $\theta$,

$$P_1(\theta) = 1 - \frac{16\pi^2}{3(\lambda')^2}\langle S^2\rangle \sin^2(\theta/2) + \cdots\,, \tag{27.32}$$

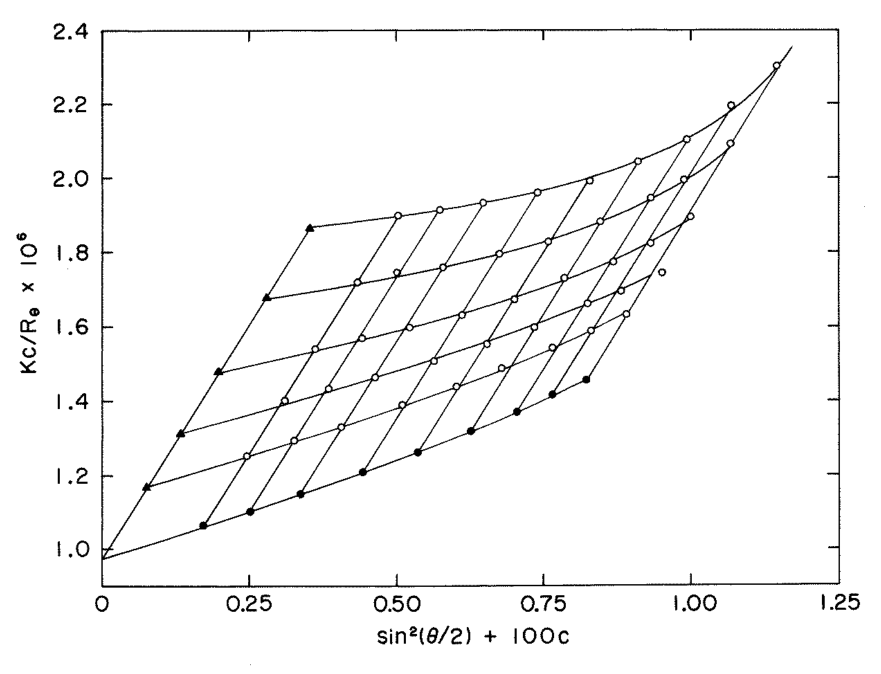

**Fig. V.4.** Zimm plot for the light-scattering data on solutions of polystyrene in methyl ethyl ketone.[25] Filled circles: extrapolation to $c = 0$. Filled triangles: extrapolation to $\theta = 0$.

where we have used Eq. (7.22) for the mean-square radius of gyration $\langle S^2 \rangle$.

In particular, for an unperturbed linear chain, we have, by the use of Eq. (5.33),

$$n^{-2} \sum_{i<j} \langle R_{ij}{}^{2p} \rangle_0 = \frac{(2p+1)!}{6^p (p+2)!} \langle R^2 \rangle_0{}^p \,. \tag{27.33}$$

On substituting Eq. (27.33) into Eq. (27.31), the series in $\sin^2(\theta/2)$ may be summed in exponential form to yield[4, 6, 22]

$$P_1{}^0(\theta) = \frac{2}{u^2}(e^{-u} - 1 + u) \tag{27.34}$$

with

$$u = \frac{8\pi^2}{3(\lambda')^2} \langle R^2 \rangle_0 \sin^2(\theta/2) \,. \tag{27.35}$$

The superscript 0 on $P_1$ refers to the unperturbed state. Although similar calculations have been carried out for unperturbed branched and ring molecules,[23, 24] we do not reproduce them here. The evaluation of $P_1(\theta)$ for rigid sphere and rod molecules is given in Appendix V B.

From Eqs.(27.26) and (27.32), we have

$$\lim_{c\to 0}\frac{Kc}{R_\theta}=\frac{1}{M}+\frac{16\pi^2}{3(\lambda')^2M}\langle S^2\rangle\sin^2(\theta/2)+\cdots\,, \tag{27.36}$$

This implies that $\langle S^2\rangle$ can be determined from the initial slope of a plot of $(Kc/R_\theta)_{c=0}$ against $\sin^2(\theta/2)$. It is important to note that Eq. (27.36), and hence this procedure of determining $\langle S^2\rangle$, are independent of the molecular model (or of whether the chain is linear, branched, or stiff). In practice, the data are often treated by a procedure known as making a *Zimm plot*.[6] This procedure consists of plotting $Kc/R_\theta$ against $\sin^2(\theta/2)+k'c$, where $k'$ is an arbitrary constant chosen for convenience. An example of a Zimm plot is shown in Fig. V.4, using the data of Doty and Steiner[25] on solutions of polystyrene in methyl ethyl ketone. Extrapolating to $c=0$ and $\theta=0$, we obtain the two limiting curves drawn through the filled circles and triangles, respectively. We can then determine $M$, $\langle S^2\rangle$, and $A_2$ from the intercept of these two curves at $c=\theta=0$, and their initial slopes, respectively.

## 27b(ii). Molecular Dimensions at Finite Concentrations

Evidently, $P_1(\theta,c)$ is given by Eq. (27.30) with $P(\mathbf{R}_{ij},c)$ in place of $P(\mathbf{R}_{ij})$, or by Eq. (27.31) with $\langle {R_{ij}}^{2p}(c)\rangle$ in place of $\langle {R_{ij}}^{2p}\rangle$, where $\langle {R_{ij}}^{2p}(c)\rangle$ are the moments at concentration $c$. At small $\theta$, we therefore have

$$P_1(\theta,c)=1-\frac{16\pi^2}{3(\lambda')^2}\langle S^2(c)\rangle\sin^2(\theta/2)+\cdots\,. \tag{27.37}$$

Thus our problem is to evaluate $\langle S^2(c)\rangle$, or the expansion factors $\alpha_S(c)=\langle S^2(c)\rangle^{1/2}/{\langle S^2\rangle_0}^{1/2}$ and $\alpha_R(c)=\langle R^2(c)\rangle^{1/2}/{\langle R^2\rangle_0}^{1/2}$ at finite concentrations.

First, we express the expansion factor as a power series in $c$, and evaluate the term linear in $c$. For this purpose, we expand $F_1(1,c)$ in powers of $c$. In general, the expansion of the component potential $w_\nu$ in Eq. (19.29) can be obtained from Eq. (19.33) by a procedure similar to that used in deriving the virial expansion for the osmotic pressure from Eq. (19.33). Recalling that $F_1(1,c)=\exp[-W_1(1,c)/kT]$ with $W_1=w_1$, we obtain the expansion,[26]

$$F_1(1,c)=F_1(1)+\left[\frac{N_\mathrm{A}}{M}\int g_2(1,2)d(2)+2MA_2F_1(1)\right]c+\cdots\,. \tag{27.38}$$

The detailed steps by which Eq. (27.38) is obtained are omitted here. The expansion coefficients in Eq. (27.38) are to be evaluated at $c=0$. We note that the $F_1(1,c)$ given by Eq. (27.38) is the distribution function at the standard atmospheric pressure plus the osmotic pressure. Under ordinary conditions, however, the molecular distribution functions may be assumed to be independent of pressure, and the effect of the pressure difference may be neglected. If $R_{ij}$ is the distance between segments of molecule 1, we obtain, by the use of Eq. (27.38),

$$\langle {R_{ij}}^2(c)\rangle = \langle {R_{ij}}^2\rangle + \left[\frac{N_{\text{A}}}{VM}\int {R_{ij}}^2 g_2(1,2)d(1,2) + 2MA_2\langle {R_{ij}}^2\rangle\right] c + \cdots . \tag{27.39}$$

As in Eq. (20.17), the coefficient of $c$ in Eq. (27.39) may be expanded in terms of the binary cluster integral $\beta$ for a pair of segments;

$$\begin{aligned}[\quad] = (N_{\text{A}}n^2\beta/M)\Bigg\{\beta n^{-2}\sum_{k_1,k_2}\sum_{l_1,l_2}\int R_{ij}^2 \\ \times[P(\mathbf{R}_{ij},0_{l_1l_2})_{k_1k_2} - P(\mathbf{R}_{ij})P(0_{l_1l_2})_{k_1k_2}]d\mathbf{R}_{ij} + O(\beta^2)\Bigg\} .\end{aligned} \tag{27.40}$$

If the uniform-expansion approximation is made in the probability densities for segment contacts, the leading term of Eq. (27.40) may be evaluated straightforwardly. Thus, for a linear chain, we obtain

$$\alpha_S(c) = \alpha_S[1 - (N_{\text{A}}n^2\beta/M)(0.1025\bar{z} + \cdots)c + \cdots] , \tag{27.41}$$

$$\alpha_R(c) = \alpha_R[1 - (N_{\text{A}}n^2\beta/M)(0.1138\bar{z} + \cdots)c + \cdots] , \tag{27.42}$$

where $\alpha_S = \alpha_S(0)$, $\alpha_R = \alpha_R(0)$, and $\bar{z}$ is given by Eq. (21.16). Equations (27.41) and (27.42) are the results obtained by Yamakawa,[26] Eizner,[27] and Kotin.[28] A similar expansion has also been obtained by Grimley.[29] Equations (27.41) and (27.42), although valid only at small $z$ and $c$, predict that the expansion factors of the polymer chain decrease with increasing concentration except at the theta temperature. This may be considered to arise from the fact that intramolecular interactions are compensated by intermolecular interactions.

Closed expressions for $\alpha(c)$ have been derived by several workers.[30−33] For example, by the differential-equation approach as in the theories of $A_2$ and $A_3$, Yamakawa[31] derived the equation,

$$\alpha_R(c) = \alpha_R \exp\{-0.0397(N_{\text{A}}n^2\beta/M)[1 - h_0(\bar{z})]c\} , \tag{27.43}$$

where $h_0(\bar{z})$ is the FCM function given by Eq. (20.55) with $\bar{z}$ in place of $z$. Equation (27.43) is valid over the range of relatively small $c$ in which extensive overlapping of polymer domains does no occur, because it was derived within the framework of the two-parameter theory. On the other hand, Fixman and Peterson[33] adopted the Born–Green–Yvon–Kirkwood approach in the theory of liquids to evaluate the potential $V(S)$ of (11.9) at concentration $c$. Their theory predicts that $\alpha(c)$ decreases first rapidly and then gradually from $\alpha(0)$ as $c$ increases, the dominant behavior being that $\alpha^2(c) - 1$ is proportional to $c^{-1}$. This behavior continues until the solvent volume fraction drops below about $10^{-1}$ to $10^{-3}$, depending on the polymer molecular weight. At present, however, we cannot answer the question of whether $\alpha$ is or is not equal to unity in the pure melt or bulk state.

As easily seen from Eq. (27.24), $\langle S^2(c)\rangle$ cannot be determined from light-scattering measurements, since the slope of a plot of $Kc/R_\theta$ against $\sin^2(\theta/2)$ at concentration $c$ involves the contribution from $P_2(\theta, c)$. However, for a particular system containing one solvent and two polymers (1 and 2) with the refractive index of polymer 2 equal to that of the solvent, we have $(\partial\tilde{n}/\partial c_2)_0 = 0$, and therefore from Eq. (27.23),

$$\lim_{c_1\to 0} \frac{Kc_1}{R_\theta} = \frac{1}{M_1 P_{1,1}(\theta, c_2)} \tag{27.44}$$

with $K = 2\pi^2 {\tilde{n}_0}^2 (\partial\tilde{n}/\partial c_1)_0{}^2/N_\mathrm{A}\lambda^4$. Thus we can determine the mean-square radius of a chain of polymer 1 at zero concentration of polymer 1 but a finite concentration of polymer 2.

## 27c. Intermolecular Interferences

We evaluate the function $Q_2(\theta)$ defined by Eq. (27.29) for linear chains at infinite dilution. For this case, the intermolecular interference factor may be written in the form,

$$P_2(\theta) = n^{-2} \sum_{i_1,i_2} \frac{\int g_2(1,2)\exp(\mathbf{s}'\cdot\mathbf{R}_{i_1i_2})d(1,2)}{\int g_2(1,2)d(1,2)}\,. \tag{27.45}$$

As in Eq. (27.31), $P_2(\theta)$ may be expanded in the form,

$$P_2(\theta) = \sum_{p=0}^{\infty} \frac{(-1)^p}{(2p+1)!}\left(\frac{4\pi}{\lambda'}\right)^{2p} n^{-2}\sum_{i_1,i_2}\langle {R_{i_1i_2}}^{2p}\rangle \sin^{2p}(\theta/2) \tag{27.46}$$

with

$$\langle {R_{i_1i_2}}^{2p}\rangle = \frac{\int {R_{i_1i_2}}^{2p} g_2(1,2)d(1,2)}{\int g_2(1,2)d(1,2)}\,. \tag{27.47}$$

If we confine ourselves to the range of small $\theta$, we have, from Eqs. (27.29), (27.32), and (27.46),

$$Q_2(\theta) = 1 - \frac{8\pi^2}{3(\lambda')^2}\left[n^{-2}\sum_{i_1,i_2}\langle {R_{i_1i_2}}^2\rangle - 4\langle S^2\rangle\right]\sin^2(\theta/2) + \cdots\,. \tag{27.48}$$

Let us evaluate the first term in the square brackets of Eq. (27.48) for the random-flight model with the uniform-expansion approximation. Recalling that the denominator of Eq. (27.47) is equal to $-Vn^2\beta h_0(\bar{z})$ with $h_0(\bar{z})$ the function appearing in $A_2$, we expand the numerator in terms of $\beta$ (as in the perturbation theory of $A_2$) to obtain

$$\begin{aligned} n^{-2}\sum_{i_1,i_2}\langle {R_{i_1i_2}}^2\rangle = [h_0(\bar{z})]^{-1} n^{-4} \sum_{i_1,i_2} \int {R_{i_1i_2}}^2 \Bigg[ & \sum_{j_1,j_2} P(\mathbf{R}_{i_1i_2})_{j_1j_2} \\ & -\beta \sum_{j_1,j_2}\sum_{k_1,k_2} P(\mathbf{R}_{i_1i_2}, 0_{k_1k_2})_{j_1j_2} + \cdots \Bigg] d\mathbf{R}_{i_1i_2}\,, \end{aligned} \tag{27.49}$$

where restrictions exist on the summations over $j_1$, $j_2$, $k_1$, $k_2$, $\ldots$ as in Eq. (20.11) or (20.17). We now define a moment $\langle {R_{12}}^2\rangle_\sigma$ by

$$\langle {R_{12}}^2\rangle_\sigma = \frac{\displaystyle\sum_{i_1,i_2}\sum_{j_1,j_2}\cdots\int {R_{i_1i_2}}^2 P(\mathbf{R}_{i_1i_2}, 0_{k_1k_2},\ldots)_{j_1j_2}d\mathbf{R}_{i_1i_2}}{\displaystyle\sum_{i_1,i_2}\sum_{j_1,j_2}\cdots\int P(\mathbf{R}_{i_1i_2}, 0_{k_1k_2},\ldots)_{j_1j_2}d\mathbf{R}_{i_1i_2}}\,. \quad (27.50)$$

The moment $\langle {R_{12}}^2\rangle_\sigma$ represents the mean-square distance $\langle {R_{i_1i_2}}^2\rangle$ between segments $i_1$ and $i_2$ when $\sigma$ contacts exist between segments $j_1$ and $j_2$, $k_1$ and $k_2$, $\ldots$, averaged over $i_1$, $i_2-$, $j_1$, $j_2-$, $\ldots$ pairs. Recalling that integration of $P(\mathbf{R}_{i_1i_2}, 0_{k_1k_2},\ldots)_{j_1j_2}$ over $\mathbf{R}_{i_1i_2}$ gives $P(0_{k_1k_2},\ldots)_{j_1j_2}$, Eq. (27.49) may be rewritten as

$$n^{-2}\sum_{i_1,i_2}\langle {R_{i_1i_2}}^2\rangle = [h_0(\bar{z})]^{-1}\Bigg[\langle {R_{12}}^2\rangle_1 \\ -\beta n^{-2}\sum_{j_1,j_2}\sum_{k_1,k_2}P(0_{k_1k_2})_{j_1j_2}\langle {R_{12}}^2\rangle_2 + \cdots\Bigg]\,, \quad (27.51)$$

From Eq. (20.17), the coefficient of $\langle {R_{12}}^2\rangle_2$ in Eq. (27.51) is seen to equal $C_1\bar{z}$ with $C_1(= 2.865)$ the coefficient of $\bar{z}$ in the expansion $h_0(\bar{z}) = 1 - C_1\bar{z} + \cdots$, We therefore have

$$n^{-2}\sum_{i_1,i_2}\langle {R_{i_1i_2}}^2\rangle = \langle {R_{12}}^2\rangle_1 + C_1\bar{z}[\langle {R_{12}}^2\rangle_1 - \langle {R_{12}}^2\rangle_2] + O(\bar{z}^2)\,. \quad (27.52)$$

Now the moment $\langle {R_{12}}^2\rangle_1$ is given by

$$\langle {R_{12}}^2\rangle_1 = n^{-4}\sum_{i_1,i_2}\sum_{j_1,j_2}\int {R_{i_1i_2}}^2 P(\mathbf{R}_{i_1i_2})_{j_1j_2}d\mathbf{R}_{i_1i_2}\,. \quad (27.53)$$

Writing $\mathbf{R}_{i_1i_2} = \mathbf{R}_{i_1j_1} + \mathbf{R}_{j_2i_2}(\mathbf{R}_{j_1j_2} = 0)$ in Eq. (27.53), and recalling that $\langle \mathbf{R}_{i_1j_1}\cdot\mathbf{R}_{j_2i_2}\rangle_{j_1j_2} = 0$, we have

$$\begin{aligned}\langle {R_{12}}^2\rangle_1 &= n^{-4}\sum_{i_1,i_2}\sum_{j_1,j_2}(\langle {R_{i_1j_1}}^2\rangle + \langle {R_{j_2i_2}}^2\rangle) \\ &= 4\langle S^2\rangle\,. \end{aligned} \quad (27.54)$$

The evaluation of $\langle {R_{12}}^2\rangle_2$ is less simple, but may be carried out straightforwardly using a cluster diagram technique. The result is (with omission of the details)

$$\langle {R_{12}}^2\rangle_2 = 0.563na^2{\alpha_s}^2\,. \quad (27.55)$$

Substitution of Eqs. (27.52), (27.54), and (27.55) into Eq. (27.48) leads to

$$Q_2(\theta) = 1 - 0.296\bar{z}\bar{u} + \cdots \quad (27.56)$$

with

$$\bar{u} = \frac{8\pi^2}{3(\lambda')^2}na^2\alpha_s^2\sin^2(\theta/2)\,. \quad (27.57)$$

This is the result derived by Albrecht.[20] Note that Eq. (27.56) is valid only at small $z$ and $\theta$. Similar calculations for the smoothed-density models have been made by Albrecht[20] and by Flory and Bueche.[34] However, we do not reproduce them here.

On the other hand, from Eqs. (27.25), (27.37), and (27.41), we have for the function $Q_1(\theta)$ defined by Eq. (27.28)

$$Q_1(\theta) = 0.068\bar{z}\bar{u} + \cdots \tag{27.58}$$

in the same approximation as that used in deriving Eq. (27.56). From Eqs. (27.27),(27.56), and (27.58), we obtain for the factor $Q(\theta)$ in Eq. (27.26)

$$Q(\theta) = 1 - 0.364\bar{z}\bar{u} + \cdots \,. \tag{27.59}$$

Thus the theory predicts that the slope of a plot of $Kc/R_\theta$ against $c$ decreases with increasing $\theta$ for positive $z$. This is in agreement with experiment.

## 27d. Heterogeneous Polymers

In Section 26b, we derived the equation for $R_\theta$ which is valid at $\theta = 0$ for heterogeneous polymers. The same result can readily be obtained from the distribution function theory. If we assume that $(\partial\tilde{n}/\partial c_i)_0 = (\partial\tilde{n}/\partial c)_0$ for all polymers of molecular weights $M_i$ with $c = \sum_i c_i$, as before, we have, from Eq. (27.23),

$$\frac{Kc}{R_\theta} = \frac{1}{\langle M\rangle_w \langle P_1(\theta)\rangle} + 2A_2c + \cdots \,, \tag{27.60}$$

where the factor $Q(\theta)$ has been omitted, $A_2$ is given by Eq. (26.63), and $\langle P_1(\theta)\rangle$ is defined by

$$\langle P_1(\theta)\rangle = \langle M\rangle_w^{-1} \sum_i M_i P_{1,i}(\theta) w_i \,. \tag{27.61}$$

At $\theta = 0$, Eq. (27.60) reduces to Eq. (26.62). In this section, we evaluate the average $\langle P_1(\theta)\rangle$ of the intramolecular interference factor, and also the light-scattering and osmotic second virial coefficients, assuming a particular form for the molecular weight distribution.

### 27d(i). The Intramolecular Interference Factor

The average $\langle P_1(\theta)\rangle$ for small $\theta$ may be expressed, from Eqs. (27.32) and (27.61), as

$$\langle P_1(\theta)\rangle = 1 - \frac{16\pi^2}{3(\lambda')^2}\langle S^2\rangle_z \sin^2(\theta/2) + \cdots \,, \tag{27.62}$$

where

$$\langle S^2\rangle_z = \langle M\rangle_w^{-1} \sum_i M_i \langle S^2\rangle_i w_i \tag{27.63}$$

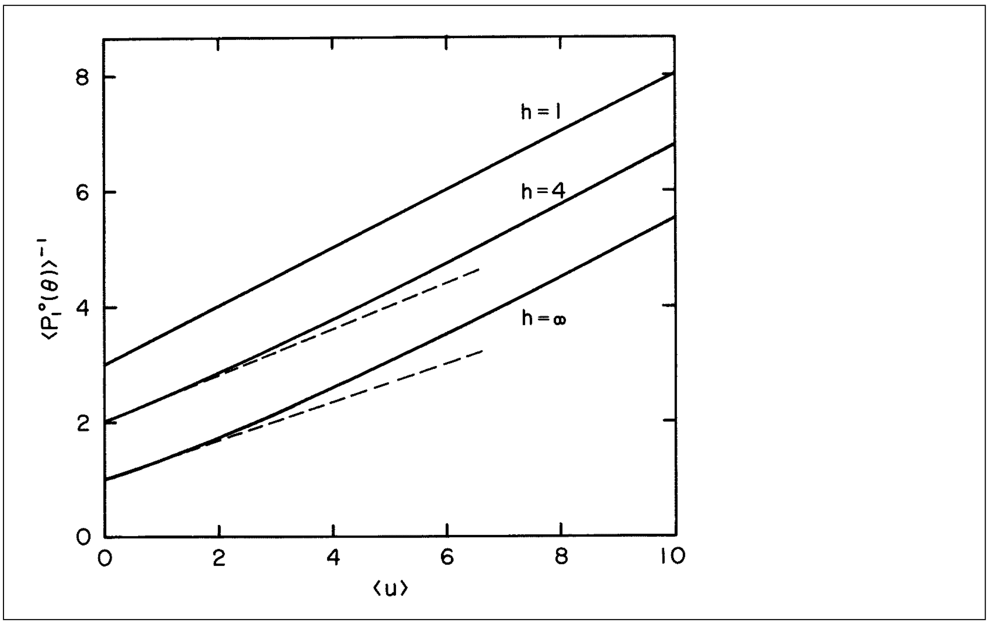

**Fig. V.5.** $\langle P_1{}^0(\theta)\rangle^{-1}$ plotted against $\langle u\rangle$ for three values of $h$. The curve for $h = 4$ is displaced upward one unit and that for $h = 1$ two units.[6] The broken lines indicate the initial slopes.

with $\langle S^2\rangle_i$ the mean-square radius for the homogeneous polymer of molecular weight $M_i$. The quantity $\langle S^2\rangle_z$ is called the z-*average* of the mean-square radius, corresponding to the z-*average molecular weight* defined by

$$\begin{aligned}\langle M\rangle_z &= \langle M\rangle_w{}^{-1}\sum_i M_i{}^2 w_i \\ &= \sum_i M_i{}^3 N_i \Big/ \sum_i M_i{}^2 N_i\,. \end{aligned} \tag{27.64}$$

We now examine the behavior of $\langle P_1(\theta)\rangle$ over a wide range of $\theta$ for the unperturbed chain, the perturbed chain being too difficult to treat. If we use the continuous molecular weight distribution $w(M)$ introduced in Section 23a, Eq. (27.61) may be rewritten in the form,

$$\langle P_1(\theta)\rangle = \langle M\rangle_w{}^{-1}\int_0^\infty MP_1(\theta)w(M)dM\,. \tag{27.65}$$

In order to evaluate the integral, we must assume a suitable form for $w(M)$. One of the forms frequently used is the Schulz distribution,[6, 35]

$$w(M) = \frac{y^{h+1}}{\Gamma(h+1)}M^h e^{-yM}\,, \tag{27.66}$$

where $\Gamma$ is the gamma function, and the parameter $y$ is related to the various average molecular weights by

$$y = \frac{h}{\langle M\rangle_n} = \frac{h+1}{\langle M\rangle_w} = \frac{h+2}{\langle M\rangle_z}\,. \tag{27.67}$$

The $w(M)$ given by Eq. (27.66) is a function with a single peak whose width is determined by the parameter $h$; for the homogeneous system $h = \infty$ (at which $w(M)$ is a delta function), and the smaller the parameter $h$, the broader the distribution. Since the variable $u$ defined by Eq. (27.35) is proportional to $M$, i.e., $CM$, we define an average $\langle u\rangle$ by $\langle u\rangle = C\langle M\rangle_w$, and obtain, by the use of Eqs. (27.34) and (27.66),[6]

$$\langle {P_1}^0(\theta)\rangle = \frac{2}{h\langle u\rangle^2}\left[\frac{(h+1)^{h+1}}{(\langle u\rangle + h + 1)^h} + h\langle u\rangle - (h+1)\right]. \tag{27.68}$$

The inverse of $\langle {P_1}^0(\theta)\rangle$ is plotted in Fig. V.5 against $\langle u\rangle$ for $h = 1$, 4, and $\infty$. From the figure, it is seen that the curve is concave upward for the homogeneous system, and the curvature becomes small as the system becomes heterogeneous.

In the particular case $h = 1$, we have

$$\langle {P_1}^0(\theta)\rangle^{-1} = 1 + \tfrac{1}{2}\langle u\rangle\,. \tag{27.69}$$

That is, $\langle {P_1}^0(\theta)\rangle^{-1}$ is linear in $\langle u\rangle$. In general, $\langle {P_1}^0(\theta)\rangle$ approaches unity as $\langle u\rangle$ becomes zero, while the curve of $\langle {P_1}^0(\theta)\rangle^{-1}$ approaches an asymptotic straight line as $\langle u\rangle$ becomes infinite; that is,

$$\begin{aligned}\lim_{\langle u\rangle\to\infty} = \frac{1}{\langle M\rangle_w\langle {P_1}^0(\theta)\rangle} &= \frac{h+1}{2\langle M\rangle_w h} + \frac{1}{2}\langle u\rangle \\ &= \frac{1}{2\langle M\rangle_n} + \frac{1}{2}\langle u\rangle\,. \end{aligned}\tag{27.70}$$

This suggests that $\langle M\rangle_n$ may be determined from the intercept of the asymptote of (27.70) at $\theta = 0$. In practice, however, this procedure does not lead to an accurate determination of $\langle M\rangle_n$.

## 27d(ii). The Second Virial Coefficients

Let $A_2^{(\pi)}$ and $A_2^{(R)}$ be the osmotic and light-scattering second virial coefficients, respectively. As shown already, with the use of the continuous molecular weight distribution, $A_2^{(\pi)}$ and $A_2^{(R)}$ may be written as

$$A_2^{(\pi)} = \int_0^\infty\int_0^\infty A_{ij}w(M_i)w(M_j)dM_i dM_j\,, \tag{27.71}$$

$$A_2^{(R)} = {\langle M\rangle_w}^{-2}\int_0^\infty\int_0^\infty M_iM_jA_{ij}w(M_i)w(M_j)dM_i dM_j\,, \tag{27.72}$$

where

$$A_{ij} = -\frac{N_{\mathrm{A}}}{2VM_iM_j}\int g_2(i,j)d(i,j)\,. \tag{27.73}$$

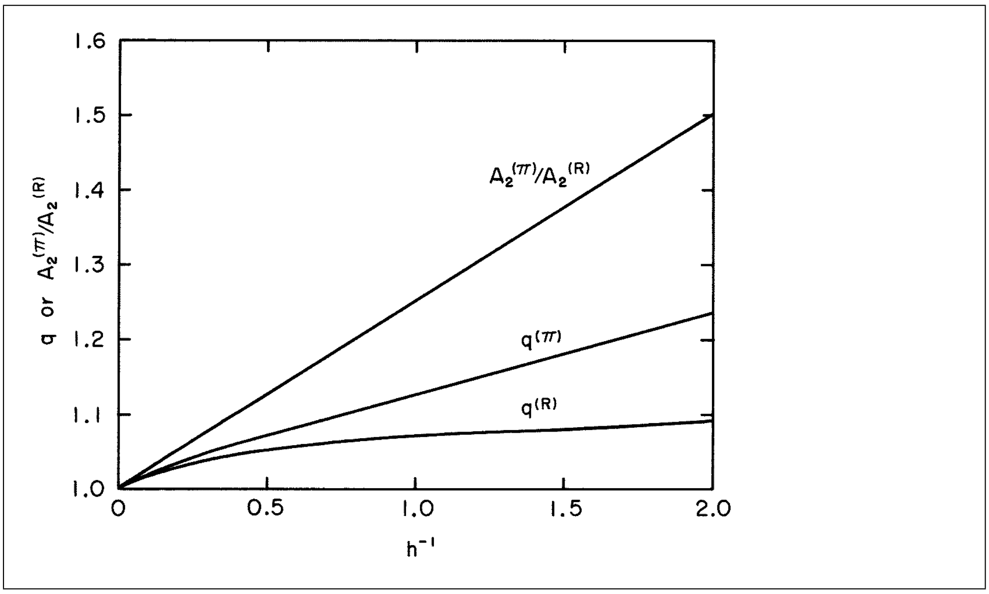

**Fig. V.6.** $q^{(\pi)}$, $q^{(R)}$, and $A_2^{(\pi)}/A_2^{(R)}$ plotted against $h^{-1}$ for $\nu = \frac{1}{4}$.[37]

For small $z$, it is easy to calculate $A_{ij}$, and therefore $A_2^{(\pi)}$ and $A_2^{(R)}$ using the Schulz distribution. The first-order perturbation theory result shows that $A_2^{(\pi)}$ is slightly greater than $A_2^{(R)}$ at small $z$.[36] For large $z$, an exact evaluation of $A_{ij}$ is, of course, hopelessly difficult, and we describe the approximate treatment of Casassa.[37] We assume that the second virial coefficient for homogeneous polymers is of the form,

$$A_2 = A_0 M^{-\nu}\,, \tag{27.74}$$

where $A_0$ and $\nu$ are constants independent of $M$. Further, $A_{ij}$ is assumed to equal the second virial coefficient for hard spheres of radii $\bar{S}_i$ and $\bar{S}_j$; that is (see Appendix IV A)

$$A_{ij} = 2\pi N_{\rm A}(\bar{S}_i + \bar{S}_j)^3/3M_iM_j\,. \tag{27.75}$$

$A_{ii}$ is the second virial coefficient for homogeneous spheres of radius $\bar{S}_i$,

$$A_{ii} = 16\pi N_{\rm A}\bar{S}_i{}^3/3M_i{}^2 = A_0 M_i{}^{-\nu}\,. \tag{27.76}$$

From Eqs. (27.75) and (27.76), we then have

$$A_{ij} = \frac{A_0}{8M_iM_j}(M_i{}^{(2-\nu)/3} + M_j{}^{(2-\nu)/3})^3\,. \tag{27.77}$$

Using the Schulz distribution, $A_2^{(\pi)}$ and $A_2^{(R)}$ may now be calculated straightforwardly. If $A_{2,n}$ and $A_{2,w}$ are the second virial coefficients for homogeneous polymers with $M = \langle M\rangle_n$ and $\langle M\rangle_w$, respectively, the results are

$$\begin{aligned} A_2^{(\pi)} &= q^{(\pi)} A_{2,n} \,, \\ A_2^{(R)} &= q^{(R)} A_{2,w} \,, \end{aligned} \tag{27.78}$$

where

$$\begin{aligned} q^{(\pi)}(h,\nu) = \frac{h^\nu}{4[\Gamma(h+1)]^2} & [\Gamma(h-\nu+2)\Gamma(h) \\ & +3\Gamma(h-\tfrac{2}{3}\nu+\tfrac{4}{3})\Gamma(h-\tfrac{1}{3}\nu+\tfrac{2}{3})] \,, \\ q^{(R)}(h,\nu) &= q^{(\pi)}(h+1,\nu) \,. \end{aligned} \tag{27.79}$$

The coefficients $q^{(\pi)}$ and $q^{(R)}$ and ratio $A_2^{(\pi)}/A_2^{(R)}$ are plotted in Fig. V.6 against $h^{-1}$ for $\nu = \frac{1}{4}$. $A_2^{(\pi)}$ is seen to be still greater than $A_2^{(R)}$. However, it is important to observe that for $h > 5$ or $\langle M \rangle_w / \langle M \rangle_n < 1.2$, the coefficients $q^{(\pi)}$ and $q^{(R)}$ do not differ appreciably from unity. This suggests that values of $A_2^{(\pi)}$ or $A_2^{(R)}$ observed for well-fractionated samples may be analyzed by means of the theory for homogeneous polymers, considering an experimental error in determination of $A_2^{(\pi)}$ or $A_2^{(R)}$.

Similar calculations for a mixture of two homogeneous polymers differing in molecular weight have also been carried out by Flory and Krigbaum[38] and by Casassa.[37] The theory predicts that under certain conditions both $A_2^{(\pi)}$ and $A_2^{(R)}$ exhibit a maximum as functions of the relative compositions of the two polymers. Experimental examples are provided by the work of Krigbaum and Flory[39] on solutions of polystyrene in toluene, and of polyisobutylene in cyclohexane, and that of Kato, Miyaso, and Nagasawa[40] on solutions of poly-$\alpha$-methylstyrene in cyclohexane.

## 27e. Mixed-Solvent Systems

The distribution function theory of light scattering for mixed-solvent systems was developed by Yamakawa.[21] Let species 0, 1, and 2 be a first solvent (good solvent), a second solvent (poor solvent), and a polymer, respectively. We consider the excess scattering $R_\theta{}' = R_\theta - R_\theta{}^0$ over that of the mixed solvent, $R_\theta$ approaching $R_\theta{}^0$ as $c_2$ becomes zero at constant $c_1$. For practical purposes, $R_\theta$ may be considered to approach the same limiting value $R_\theta{}^0$ as $c_2$ becomes zero at constant $m_1$ $(= M_1 N_1 / M_0 N_0)$, since $c_2$ is usually very small. Now, since the second solvent is a low-molecular-weight species, $P_{1,1}(\theta, \mathbf{c})$ is identically equal to unity. In addition, there are the symmetric relations, $A_{2,12}(\mathbf{c}) = A_{2,21}(\mathbf{c})$ and $P_{2,12}(\theta, \mathbf{c}) = P_{2,21}(\theta, \mathbf{c})$. Further, we use the shorthand notation, $A(c_1, 0) = A(c_1)$, $A(0, c_2) = A(c_2)$, and $A(0,0) = A$ for any function $A(c_1, c_2)$ of $c_1$ and $c_2$. We then have, from Eq. (27.23),

$$\begin{aligned} \frac{R_\theta{}'}{KM_2 c_2} &= P_{1,2}(\theta, c_1, c_2) - 2M_2 A_{2,22}(c_1, c_2) P_{2,22}(\theta, c_1, c_2) c_2 \\ & \quad -4\gamma M_1 A_{2,12}(c_1, c_2) P_{2,12}(\theta, c_1, c_2) c_1 + f(\theta, c_1, c_2) \,, \end{aligned} \tag{27.80}$$

where $K$ is given by Eq. (25.26) with $c = c_2$, and $\gamma$ and $f$ are defined by

$$\gamma = \left(\frac{\partial \tilde{n}}{\partial c_1}\right)_0 \Bigg/ \left(\frac{\partial \tilde{n}}{\partial c_2}\right)_0 , \tag{27.81}$$

$$\begin{aligned} f(\theta, c_1, c_2) = -2\gamma^2 {M_1}^2 {M_2}^{-1} [&A_{2,11}(c_1, c_2) P_{2,11}(\theta, c_1, c_2) \\ &- A_{2,11}(c_1) P_{2,11}(\theta, c_1)] {c_1}^2 {c_2}^{-1} . \end{aligned} \tag{27.82}$$

In the following subsections, we consider three cases of interest:(1) the case for $\gamma = 0$, (2) the case for $\gamma \neq 0$ and $\theta = 0$, and (3) the case for $\gamma \neq 0$ and $c_2 = 0$.

## 27e(i). Case for $\gamma = 0$

In this case, for which the refractive index of the second solvent is equal to that of the first solvent, Eq. (27.80) reduces to [with omission of the factor $Q(\theta)$]

$$\frac{Kc_2}{R_\theta{}'} = \frac{1}{M_2 P_{1,2}(\theta, c_1)} + 2A_{2,22}(c_1) c_2 + \cdots . \tag{27.83}$$

Thus, the polymer molecular weight $M_2$ and the mean-square radius $\langle S^2(c_1)\rangle$ and second virial coefficient $A_{2,22}(c_1)$ for the polymer in the mixed solvent of concentration $c_1$, can be determined from the usual light-scattering measurements, $A_{2,22}(c_1)$ being identical with the second coefficient in Eq. (26.71). In particular, the temperature at which $A_{2,22}(c_1)$ becomes zero corresponds to the theta point in the binary system, and under this condition unperturbed dimensions $\langle S^2(c_1)\rangle_0$ in mixed solvents can be determined.

## 27e(ii). Limit of $\theta = 0$

Recalling that $P_1(\theta, \mathbf{c})$ and $P_2(\theta, \mathbf{c})$ approach unity as $\theta$ becomes zero, we obtain from Eq. (27.80)

$$\begin{aligned} \lim_{\theta \to 0} \frac{R_\theta{}'}{KM_2 c_2} = 1 &- 2M_2 A_{2,22}(c_1, c_2) c_2 - 4\gamma M_1 A_{2,12}(c_1, c_2) c_1 \\ &+ f(0, c_1, c_2) \end{aligned} \tag{27.84}$$

with

$$f(0, c_1, c_2) = -2\gamma^2 {M_1}^2 {M_2}^{-1} [A_{2,11}(c_1, c_2) - A_{2,11}(c_1)] {c_1}^2 {c_2}^{-1} . \tag{27.85}$$

We now wish to expand $A_{2,22}(c_1, c_2)$ and $A_{2,12}(c_1, c_2)$ in powers of $c_1$ and $c_2$. This can be done by expanding the distribution functions $F_1$ and $F_2$ as in Eq. (27.38) and substituting the results into Eq. (27.19). If we make superposition approximation in the three-body distribution function $F_3$, we find

$$\begin{aligned} A_{2,22}(c_1, c_2) = A_{2,22} &+ [\tfrac{3}{2} A_{3,122} - 2M_1 (A_{2,12})^2] c_1 \\ &+ [\tfrac{3}{2} A_{3,222} - 2M_2 (A_{2,22})^2] c_2 + \cdots , \end{aligned} \tag{27.86}$$

$$A_{2,12}(c_1, c_2) = A_{2,12} + (\tfrac{3}{2}A_{3,122} - 2M_2 A_{2,12} A_{2,22})c_2 + \cdots \,. \tag{27.87}$$

The $c_1$ term has been omitted in Eq. (27.87), because we neglect the ${c_1}^2$ term in the final result. The coefficients $A_{2,22}$ and $A_{3,222}$ are just the second and third virial coefficients ($A_2$ and $A_3$) for the two-component system containing species 0 and 2, respectively, $A_{3,222}$ being given by Eq. (19.56). The coefficient $A_{3,122}$ may be written as

$$\begin{aligned} A_{3,122} = &-\frac{{N_{\mathrm{A}}}^2}{3VM_1{M_2}^2}\int g_3(1_1, 2_2, 3_2)d(1_1, 2_2, 3_2) + \tfrac{4}{3}M_1(A_{2,12})^2 \\ &+ \tfrac{8}{3}M_2 A_{2,12} A_{2,22} \,. \end{aligned} \tag{27.88}$$

When species 1 and 2 are identical, Eq. (27.88) reduces to Eq. (19.56). We note that the coefficients in Eqs. (27.86) and (27.87) appear in the virial expansion for the three-component system. Suppose that two solutions of concentrations $(c_1, c_2)$ and (0,0) are in equilibrium with each other separated by membrane permeable only to species 0. From the McMillan–Mayer theory, the pressure difference $p(c_1, c_2) - p(0, 0)$, i.e., the osmotic pressure $\pi(c_1, c_2|0, 0)$ may then be expanded in the form,

$$\begin{aligned} \frac{\pi(c_1, c_2|0, 0)}{RT} = &\frac{1}{M_1}c_1 + \frac{1}{M_2}c_2 + A_{2,11}{c_1}^2 + A_{2,22}{c_2}^2 + 2A_{2,12}c_1c_2 \\ &+ A_{3,111}{c_1}^3 + A_{3,222}{c_2}^3 + 3A_{3,112}{c_1}^2c_2 + 3A_{3,122}c_1{c_2}^2 + \cdots \,, \end{aligned} \tag{27.89}$$

where all coefficients may be expressed in terms of the molecular distribution functions at concentration (0,0).

Next, we expand the coefficient $A_{2,11}(c_1, c_2)$ in the form,

$$A_{2,11}(c_1, c_2) = A_{2,11}(c_1) + {A_{2,11}}^{(1)}(c_1)c_2 + \cdots \,. \tag{27.90}$$

Equation (27.85) then reduces to

$$f(0, c_1, c_2) = -2\gamma^2{M_1}^2{M_2}^{-1}[{A_{2,11}}^{(1)}(c_1) + O(c_2)]{c_1}^2 \,. \tag{27.91}$$

The coefficient ${A_{2,11}}^{(1)}(c_1)$ can be evaluated by the same procedure as used above when we choose the solution of concentration $(c_1, 0)$ instead of (0,0) as the reference states. The result is

$${A_{2,11}}^{(1)}(c_1) = \tfrac{3}{2}A_{3,112}(c_1) - 2M_2[A_{2,12}(c_1)]^2 \,. \tag{27.92}$$

The quantity $A_{3,112}(c_1)$ is comparable in magnitude with $M_2[A_{2,12}(c_1)]^2$ and $M_1A_{2,11}(c_1)A_{2,12}(c_1)$. Since $M_1 < M_2$ and $0 < A_{2,11} < A_{2,12}$ in the system under consideration for which species 1 is a poor solvent for the polymer, the inequalities, $0 < M_1A_{2,11}(c_1)A_{2,12}(c_1) < M_2[A_{2,12}(c_1)]^2$ must be valid. Therefore, $A_{3,112}(c_1)$ must be at most of the same order of magnitude as $M_2[A_{2,12}(c_1)]^2$. Thus, $|{A_{2,11}}^{(1)}(c_1)|$ will not exceed $2M_2[A_{2,12}(c_1)]^2$, and at small $c_2$

$$|f(0, c_1, c_2)| < 4[\gamma M_1 A_{2,12}(c_1)c_1]^2 \,. \tag{27.93}$$

Now, $|\gamma|$ is at most of order unity, and $A_{2,12}$ must be of order $10^{-3} \sim 10^{-2}$ in the present system. (Note that $A_{2,22}$ is of order $10^{-4}$ since species 0 is assumed to be a good solvent for the polymer.) Under these conditions, the quantity $\gamma M_1 A_{2,12}(c_1)c_1$ is at most of order $10^{-2}$, and therefore the term $f$ is definitely negligible compared to unity in Eq. (27.84).

Thus, by the use of Eqs. (27.86) and (27.87), we obtain from Eq. (27.84)

$$\lim_{\theta \to 0} \frac{Kc_2}{R_\theta{}'} = \frac{1}{M_{2,\mathrm{ap}}} + 2A_{2,\mathrm{ap}}c_2 + 3A_{3,\mathrm{ap}}{c_2}^2 + \cdots \tag{27.94}$$

with

$$\begin{aligned} M_{2,\mathrm{ap}} &= M_2[1 - 4\gamma M_1 A_{2,12}(c_1)c_1] \\ &= M_2[1 - 4\gamma M_1 A_{2,12}c_1 + O({c_1}^2)] \,, \end{aligned} \tag{27.95}$$

$$\begin{aligned} A_{2,\mathrm{ap}} = A_{2,22} + [\tfrac{3}{2}(1 + 2\gamma M_1 {M_2}^{-1})A_{3,122} - 2M_1(A_{2,12})^2 \\ +4\gamma M_1 A_{2,12}A_{2,22}]c_1 + O({c_1}^2) \,, \end{aligned} \tag{27.96}$$

$$A_{3,\mathrm{ap}} = A_{3,222} + O(c_1) \,. \tag{27.97}$$

Equations (27.95) and (27.96) are to be compared with Eqs. (26.68) and (26.69), respectively. The term $2\gamma M_1 {M_2}^{-1}$ in Eq. (27.96) may be suppressed compared to unity, and we therefore obtain, from Eqs. (27.86) and (27.96),

$$A_{2,\mathrm{ap}} = A_{2,22}(c_1)(1 + 4\gamma M_1 A_{2,12}c_1 + \cdots) \,, \tag{27.98}$$

or, combining this with Eq. (27.95), at small $c_1$

$$A_{2,22}(c_1) = (M_{2,\mathrm{ap}}/M_2)A_{2,\mathrm{ap}} \,. \tag{27.99}$$

This suggests that $A_{2,22}(c_1)$ can be determined from observed values of $M_2$, $M_{2,\mathrm{ap}}$, and $A_{2,\mathrm{ap}}$ provided the concentration of the second solvent is low.

The conditions under which the term $f$ can be suppressed may now be stated in a more convenient form. If $M_{2,\mathrm{ap}} = 1.3M_2$, or $\gamma M_1 A_{2,12}(c_1)c_1 \simeq -0.075$, $f$ is smaller than 0.023 and may be neglected. Thus we have the condition, $0.7 < M_{2,\mathrm{ap}}/M_2 < 1.3$, or more strictly,

$$0.8 < M_{2,\mathrm{ap}}/M_2 < 1.2 \,. \tag{27.100}$$

This is, of course, a sufficient condition, and not a necessary condition. For practical purposes, it is desirable to find experimentally a condition under which values of $A_{2,22}(c_1)$ determined from Eq. (27.99) are in agreement with those determined using the dialysis technique described in Section 26c.

### 27e(iii). Limit of $c_2 = 0$

In this limit, Eq. (27.80) reduces to

$$\lim_{c_2 \to 0} \frac{R_\theta{}'}{KM_2 c_2} = P_{1,2}(\theta, c_1) - 4\gamma M_1 A_{2,12}(c_1) P_{2.12}(\theta, c_1) c_1 + f(\theta, c_1)\,. \tag{27.101}$$

The function $P_{2,11}(\theta, c_1, c_2)$ appearing in $f(\theta, c_1, c_2)$ may be written, from Eq. (27.17) (with $n_1 = 1$), in the form,

$$P_{2,11}(\theta, \mathbf{c}) = \frac{\int [g(\mathbf{R}_{12}, \mathbf{c}) - 1] \exp(\mathbf{s}' \cdot \mathbf{R}_{12}) d\mathbf{R}_{12}}{\int [g(\mathbf{R}_{12}, \mathbf{c}) - 1] d\mathbf{R}_{12}}\,, \tag{27.102}$$

where $\mathbf{R}_{12}$ is the distance between molecules 1 and 2 of species 1, and $g$ is the pair correlation function for these molecules. Evidently, $g - 1$ differs appreciably from zero only for $\mathbf{R}_{12} \ll \lambda'$. Since the exponential in Eq. (27.102) is effectively unity when $\mathbf{R}_{12} \ll \lambda'$, we have

$$P_{2,11}(\theta, c_1, c_2) = 1\,, \tag{27.103}$$

and therefore $f(\theta, c_1)$ becomes equal to $f(0, c_1)$, which is given by Eq. (27.91) with $c_2 = 0$. Thus, the term $f$ may be neglected in Eq. (27.101), because $P_{1,2}(\theta, c_1)$ must be ordinarily of order $10^{-1} \sim 1$.

Next we evaluate the function $P_{2,12}(\theta, c_1)$. It may be written as

$$P_{2,12}(\theta, c_1) = {n_2}^{-1} \sum_{i_2=1}^{n_2} \frac{\int g_2(1_1, 2_2, c_1) \exp(\mathbf{s}' \cdot \mathbf{R}_{1i_2}) d(1_1, 2_2)}{\int g_2(1_1, 2_2, c_1) d(1_1, 2_2)}\,, \tag{27.104}$$

where $\mathbf{R}_{1i_2} = \mathbf{R}_{i_1 i_2}$ with $i_1 \equiv 1$. The potential of mean force between a molecule of species 1 and a polymer segment (at concentration $c_1$) must also differ appreciably from zero when $R_{1i_2} \ll \lambda'$. As in the perturbation theory of $A_2$, the function $g_2$ in Eq. (27.104) may therefore be expanded in terms of short-range functions $\chi_{1i_2}$ [with $F_1(1_1, c_1) = 1$],

$$g_2(1_1, 2_2, c_1) = F_1(2_2, c_1) \Bigl( \sum_{j_2} \chi_{1j_2} + \sum_{j_2 < k_2}\sum \chi_{1j_2} \chi_{1k_2} + \cdots \Bigr) \tag{27.105}$$

with

$$\chi_{1j_2} = -\beta_{12} \delta(\mathbf{R}_{1j_2})\,, \tag{27.106}$$

where $\beta_{12}$ is the binary cluster integral representing interactions between a molecule of species 1 and a polymer segment at concentration $c_1$. The second term on the right-hand side of Eq. (27.105) is not a pure double-contact term, but rather corresponds to a ternary clustering. It is then expected that this and higher terms may be neglected provided $n_2$ is very large, and therefore that $P_{2,12}(\theta, c_1)$ may be evaluated in the single-contact approximation. This can be explicitly demonstrated,[21] but we do not reproduce the analysis here. Thus, we obtain, from

Eqs. (27.104) to (27.106),

$$\begin{aligned} P_{2,12}(\theta, c_1) &= -{\beta_{12}}^{-1}{n_2}^{-2}\sum_{i_2,j_2} V^{-1} \\ &\qquad \times \int F_1(2_2, c_1)\chi_{1j_2}\exp(\mathbf{s}'\cdot\mathbf{R}_{1i_2})d(1_1, 2_2) \\ &= {n_2}^{-2}\sum_{i_2,j_2} V^{-1}\int F_1(2_2, c_1)\exp(\mathbf{s}'\cdot\mathbf{R}_{i_2j_2})d(2_2)\,. \end{aligned} \tag{27.107}$$

Comparing Eq. (27.16) with Eq. (27.107), we find

$$P_{2,12}(\theta, c_1) = P_{1,2}(\theta, c_1)\,. \tag{27.108}$$

Now substitution of Eq. (27.108) into Eq. (27.101) leads to (with omission of $f$)

$$\lim_{c_2\to 0}\frac{Kc_2}{{R_\theta}'} = \frac{1}{M_{2,\mathrm{ap}}P_{1,2}(\theta, c_1)}\,, \tag{27.109}$$

where we have used Eq. (27.95). This implies that the molecular dimensions $\langle S^2(c_1)\rangle$ in mixed solvents can be determined from the usual light-scattering measurements even if the refractive index increment with respect to the second solvent does not vanish completely. In particular, this procedure should be useful in the determination of unperturbed dimensions when the theta points cannot be realized without the use of mixed solvents.

## 28. Remarks and Topics

### 28a. Effects of the Optical Anisotropies

In the previous sections, we have assumed that the scattering particles are optically isotropic. In this section, we study the effects of the optical anisotropy on the intensity of scattered light. For this case, Eq. (25.3) for the amplitude of the induced moment must be replaced by

$$\mathbf{p}_0 = \boldsymbol{\alpha}{\mathbf{E}_0}^0\,, \tag{28.1}$$

where the polarizability $\boldsymbol{\alpha}$ is a (symmetric) tensor, instead of a scalar. For convenience, we first consider a system of independent small particles, and then a solution of polymers composed of anisotropic segments.

### 28a(i). Systems of Independent Small Particles

Suppose that the incident light is plane-polarized, and the scattered light is observed with an analyzer, its transmission axis being in the direction $\boldsymbol{\xi}$ perpendicular to $\mathbf{r}$. From Eq. (25.4), the component of the total radiation field $\mathbf{E}$ in the direction of $\boldsymbol{\xi}$ is then given by

$$\mathbf{E}\cdot\mathbf{e}_\xi = \left(\frac{\omega}{\tilde{c}}\right)^2\frac{N}{r^3}[r^2\{\mathbf{p}\} - (\mathbf{r}\cdot\{\mathbf{p}\})\mathbf{r}]\cdot\mathbf{e}_\xi$$

$$= \left(\frac{\omega}{\tilde{c}}\right)^2 \frac{N}{r} \{\mathbf{p}\} \cdot \mathbf{e}_\xi \tag{28.2}$$

with $N$ the number of scattering particles in the system. The total intensity $I_\xi$ of scattered light in the direction of $\boldsymbol{\xi}$ may therefore be written in the form,

$$I_\xi = A\langle(\boldsymbol{\alpha}\mathbf{e}_0 \cdot \mathbf{e}_\xi)^2\rangle I^0 \tag{28.3}$$

with

$$A = 16\pi^4 N/\lambda^4 r^2 \,, \tag{28.4}$$

where $\mathbf{e}_0$ is the unit vector in the direction of ${E_0}^0$, and the average in Eq. (28.3) is taken over all orientations of the particle.

If a coordinate system $(X, Y, Z)$ fixed in the particle is properly chosen, the polarizability tensor $\boldsymbol{\alpha}$ may be expressed as a diagonal tensor in that molecular coordinate system, whose diagonal elements $(\alpha_1,\alpha_2,\alpha_3)$ are the principal values of $\boldsymbol{\alpha}$. After an orthogonal transformation of the coordinate system $(x, y, z)$ fixed in space into $(X, Y, Z)$, the average in Eq. (28.3) can readily be evaluated by the use of the averages of products of the direction cosines of the coordinate axes, assuming that the orientation of the particle is uniform in all directions. The result is

$$\langle(\boldsymbol{\alpha}\mathbf{e}_0 \cdot \mathbf{e}_\xi)^2\rangle = \alpha^2 \cos^2\varphi + \frac{B^2}{2}(1 + \tfrac{1}{3}\cos^2\varphi)\,, \tag{28.5}$$

where $\varphi$ is the angle between $\mathbf{e}_0$ and $\mathbf{e}_\xi$, and $\alpha$ and $B$ are defined by

$$\alpha = \tfrac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3)\,, \tag{28.6}$$

$$B^2 = \tfrac{1}{15}[(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2]\,. \tag{28.7}$$

The $\alpha$ defined by Eq. (28.6) is equal to one-third of the trace of $\boldsymbol{\alpha}$, and is the average polarizability related to the optical refractive index by Eq. (25.24). Note that for isotropic particles $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$ and $B = 0$.

In particular, we use the subscript $v$ or $h$ as $\mathbf{e}_0$ is parallel to the $x$ axis (vertical) or to the $y$ axis (horizontal), and the subscript $V$ or $H$ as $\mathbf{e}_\xi$ is vertical or horizontal (see Fig. V.7). For example, $I_{V_h}$ represents the vertical component of the scattered intensity when the incident light is horizontally polarized. From Eqs. (28.3) and (28.5), we then have

$$\begin{aligned}
\frac{I_{V_v}}{{I_v}^0} &= A(\alpha^2 + \tfrac{2}{3}B^2)\,,\\
\frac{I_{H_v}}{{I_v}^0} &= \frac{I_{V_h}}{{I_h}^0} = A(\tfrac{1}{2}B^2)\,,\\
\frac{I_{H_h}}{{I_h}^0} &= A\left[\alpha^2\cos^2\theta + \frac{B^2}{2}(1 + \tfrac{1}{3}\cos^2\theta)\right].
\end{aligned} \tag{28.8}$$

Next we consider the case for which the incident light is unpolarized. In this case, the intensity of the incident light is formally given by

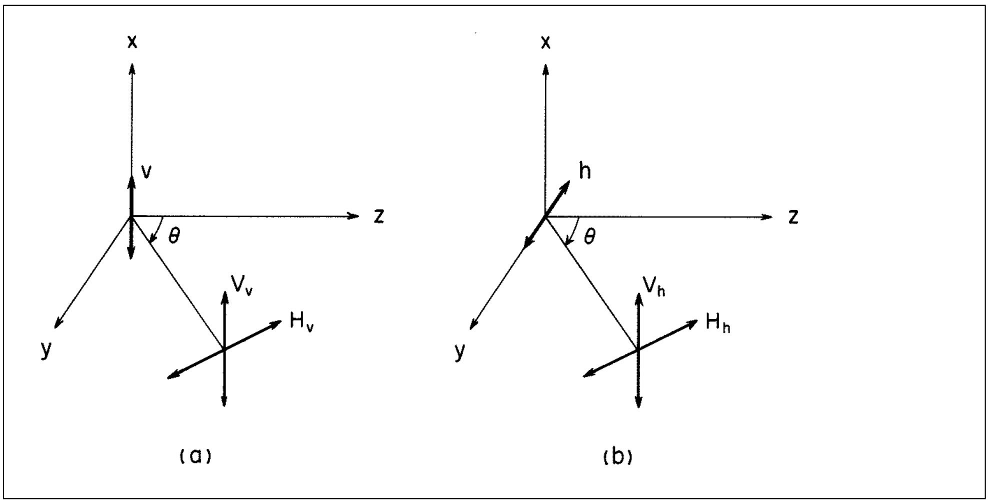

**Fig. V.7.** Vertical and horizontal components of the scattered intensity. (a) The incident light is vertically polarized. (b) The incident light is horizontally polarized.

$I_0 = {I_v}^0 + {I_h}^0 = 2{I_v}^0 = 2{I_h}^0$, and the two components of the scattered intensity by $I_V = I_{V_v} + I_{V_h}$ and $I_H = I_{H_v} + I_{H_h}$. We therefore obtain, from Eqs. (28.8),

$$\begin{aligned} \frac{I_V}{I^0} &= \frac{A}{2}(\alpha^2 + \tfrac{7}{6}B^2)\,, \\ \frac{I_H}{I^0} &= \frac{A}{2}[\alpha^2 \cos^2\theta + B^2(1 + \tfrac{1}{6}\cos^2\theta)]\,. \end{aligned} \tag{28.9}$$

Without the analyzer, the total scattered intensity is given by $I = I_V + I_H$, and we obtain for the Rayleigh ratio

$$R_\theta = \frac{8\pi^4\alpha^2\rho}{\lambda^4}\frac{6}{6-7\Delta}\left(1 + \Delta\frac{1-\cos^2\theta}{1+\cos^2\theta}\right), \tag{28.10}$$

where

$$\Delta = \frac{B^2}{\alpha^2 + \frac{7}{6}B^2}\,. \tag{28.11}$$

Equation (28.10) is to be compared with Eq. (25.22). From Eqs. (28.9) and (28.11), it is seen that[41]

$$\Delta = \left(\frac{I_H}{I_V}\right)_{\theta=90^\circ}. \tag{28.12}$$

This implies that the quantity $\Delta$ can be determined experimentally, and thus the anisotropy correction to $R_\theta$ can be made according to Eq. (28.10) to determine the correct molecular weight. For isotropic particles, $I_H = 0$ at $\theta = 90°$; that is, the scattered light is completely vertically polarized at $\theta = 90°$ Thus $\Delta$ is called the *degree of depolarization.* The turbidity $\tau$ is readily obtained, from Eq. (28.10), as

$$\tau = \frac{128\pi^5\alpha^2}{3\lambda^4}\rho f \tag{28.13}$$

with

$$f = \frac{6+3\Delta}{6-7\Delta}\,. \tag{28.14}$$

The correction factor $f$ is called the *Cabannes factor*.

## 28a(ii). Polymer Composed of Anisotropic Segments

The usual light-scattering measurements give apparently negative values of $\langle S^2\rangle$ for certain polymers, and it was pointed out first by Nakagaki[42] that this anomaly arises from the optical anisotropy of polymer segments. Subsequently, Utiyama[43, 44] derived an equation for $R_\theta$ with anisotropy corrections, and showed how to determine correctly molecular weights, molecular dimensions, and second virial coefficients.

We consider a binary solution containing $N$ polymer molecules, each composed of $n$ identical anisotropic segments. When the incident light is plane-polarized, the component of the total radiation field is given by

$$\begin{aligned}\mathbf{E}\cdot\mathbf{e}_\xi &= \sum_{k=1}^{Nn}\mathbf{E}_k\cdot\mathbf{e}_\xi\\ &= \left(\frac{\omega}{\tilde{c}}\right)^2\frac{E_0{}^0}{r}\exp\left[i\omega\left(t-\frac{r}{\tilde{c}'}\right)\right]\sum_k(\boldsymbol{\alpha}_k\mathbf{e}_0\cdot\mathbf{e}_\xi)\exp(\mathbf{s}'\cdot\mathbf{R}_k)\end{aligned} \tag{28.15}$$

instead of Eq. (27.3). The component $I_\xi$ of the scattered intensity may therefore be written in the form,

$$\frac{I_\xi}{I^0} = \frac{16\pi^4}{\lambda^4 r^2}\langle G'\rangle \tag{28.16}$$

with

$$\langle G'\rangle = \sum_k\sum_l\langle(\boldsymbol{\alpha}_k\mathbf{e}_0\cdot\mathbf{e}_\xi)(\boldsymbol{\alpha}_l\mathbf{e}_0\cdot\mathbf{e}_\xi)\rangle\int P(\mathbf{R}_{kl})\exp(\mathbf{s}'\cdot\mathbf{R}_{kl})d\mathbf{R}_{kl}\,. \tag{28.17}$$

The symbol $\langle\quad\rangle$ on the right-hand side of Eq. (28.17) indicates the average over all orientations of the two segments $k$ and $l$. If we assume that there is no correlation between orientations of segments $k$ and $l$, we have

$$\begin{aligned}\langle(\boldsymbol{\alpha}_k\mathbf{e}_0\cdot\mathbf{e}_\xi)(\boldsymbol{\alpha}_l\mathbf{e}_0\cdot\mathbf{e}_\xi)\rangle &= \langle(\boldsymbol{\alpha}\mathbf{e}_0\cdot\mathbf{e}_\xi)^2\rangle \qquad \text{for } k=l\\ &= \langle\boldsymbol{\alpha}\mathbf{e}_0\cdot\mathbf{e}_\xi\rangle^2 \qquad \text{for } k\neq l\,,\end{aligned} \tag{28.18}$$

where we have omitted the subscripts $k$ and $l$ on the right-hand side since all the segments are identical. Substitution of Eq. (28.18) into Eq. (28.17) leads to

$$\langle G' \rangle = Nn[\langle (\boldsymbol{\alpha}\mathbf{e}_0 \cdot \mathbf{e}_\xi)^2 \rangle - \langle \boldsymbol{\alpha}\mathbf{e}_0 \cdot \mathbf{e}_\xi \rangle^2] + \alpha^{-2} \langle \boldsymbol{\alpha}\mathbf{e}_0 \cdot \mathbf{e}_\xi \rangle^2 \langle G \rangle \,, \tag{28.19}$$

where $\langle G \rangle$ is given by Eq. (27.20) with $r = 1$, and $\langle (\boldsymbol{\alpha}\mathbf{e}_0 \cdot \mathbf{e}_\xi)^2 \rangle$ is given by Eq. (28.5). $\langle \boldsymbol{\alpha}\mathbf{e}_0 \cdot \mathbf{e}_\xi \rangle^2$ may also be simply evaluated to be

$$\langle \boldsymbol{\alpha}\mathbf{e}_0 \cdot \mathbf{e}_\xi \rangle^2 = \alpha^2 \cos^2 \varphi \,. \tag{28.20}$$

Thus Eq. (28.16) becomes

$$\frac{r^2 I_\xi}{2VI^0KMc} = \frac{B^2}{2\alpha^2 n}(1 + \tfrac{1}{3}\cos^2\varphi) + \cos^2\varphi[P_1(\theta) - 2MA_2P_2(\theta)c + \cdots] \,, \tag{28.21}$$

where $K$ is given by Eq. (25.26).

From Eq. (28.21), the vertical and horizontal components of the scattered intensity are obtained as

$$\begin{aligned}
\frac{r^2 I_{V_v}}{2V{I_v}^0KMc} &= 4\delta + P_1(\theta) - 2MA_2P_2(\theta)c + \cdots \,, \\
\frac{r^2 I_{H_v}}{2V{I_v}^0KMc} &= \frac{r^2 I_{V_h}}{2V{I_h}^0KMc} = 3\delta \,, \\
\frac{r^2 I_{H_h}}{2V{I_h}^0KMc} &= 3\delta(1 + \tfrac{1}{3}\cos^2\theta) + \cos^2\theta[P_1(\theta) - 2MA_2P_2(\theta)c + \cdots]
\end{aligned} \tag{28.22}$$

with

$$\delta = \frac{B^2}{6\alpha^2 n} \,. \tag{28.23}$$

For the case when unpolarized incident light is used, without the analyzer, we obtain for the Rayleigh ratio from Eqs. (28.22)

$$R_\theta/KMc = \delta + 12\delta(1+\cos^2\theta)^{-1} + P_1(\theta) - 2MA_2P_2(\theta)c + \cdots \,. \tag{28.24}$$

In particular, in the limit $\theta = 0$ or $c = 0$, we have

$$\lim_{\theta\to 0} \frac{Kc}{R_\theta} = \frac{1}{M_{\mathrm{ap}}} + 2A_{2,\mathrm{ap}}c + \cdots \,, \tag{28.25}$$

$$\lim_{c\to 0} \frac{Kc}{R_\theta} = \frac{1}{M_{\mathrm{ap}}} \left[ 1 + \frac{16\pi^2}{3(\lambda')^2} \langle S^2 \rangle_{\mathrm{ap}} \sin^2(\theta/2) + \cdots \right] \,, \tag{28.26}$$

where

$$M_{\mathrm{ap}} = M(1 + 7\delta) \,, \tag{28.27}$$

$$A_{2,\mathrm{ap}} = A_2(1 + 7\delta)^{-2} \,, \tag{28.28}$$

$$\langle S^2 \rangle_{\mathrm{ap}} = \frac{\langle S^2 \rangle}{1 + 7\delta} - \frac{9(\lambda')^2\delta}{4\pi^2(1 + 7\delta)} \,. \tag{28.29}$$

Thus, apparent molecular weights, virial coefficients, and molecular dimensions determined from the usual light-scattering measurements must be corrected by means of Eqs. (28.27) to (28.29).

Now, it is seen from Eqs. (28.22) that $I_{H_v}/c$ and $I_{V_h}/c$ are independent of $c$ and $\theta$, and $I_{H_h}(\theta = 90°)/c$ is independent of $c$; and from observed values of these quantities (or any one of them), we can determine values of $M\delta$. From observed values of $M\delta$ and $M_{\text{ap}} = M(1+7\delta)$, we can therefore estimate the parameter $\delta$. The parameter $\delta$ is, by definition, inversely proportional to $n$, and therefore the effect of anisotropy is negligibly small for ordinary polymers of high molecular weight. (Note that the correction factor for the molecular weight is different from that for the case of small molecules.) For example, Utiyama[43] found $\delta = 0.86 \times 10^{-3}$ for atactic polystyrene of $M = 5.1 \times 10^5$ in monochlorobenzene. On the other hand, for isotactic polystyrene of $M = 3.41 \times 10^5$, $\delta$ was estimated to be $53.3 \times 10^{-3}$, and the effect of anisotropy is so large that $\langle S^2 \rangle_{\text{ap}}$ is negative.[43]

We note that the effect of anisotropy may be eliminated by using the observed values of the quantity $(I_{V_v} - \frac{4}{3} I_{H_v})$, which does not involve $\delta$. Further, Utiyama[44] also proposed a procedure to estimate $\delta$ even when measurements are carried out with unpolarized light, but we do not reproduce it here.

## 28b. Copolymers

It was found first by Tremblay et al.[45] that the apparent molecular weight determined from the usual light-scattering measurements on solutions of butadiene-styrene copolymer varied with the refractive index of the solvent, and it was suggested that this anomaly arises from heterogeneities in the composition of the copolymer. Further investigations on this problem were made by Stockmayer et al.[46] and by Bushuk and Benoit.[47]

In this section, we consider effects of the heterogeneity in composition as well as in molecular weight on the apparent molecular weight of binary copolymers composed of monomeric units $A$ and $B$, following the procedure of Bushuk and Benoit. The equations derived are general, and are applicable to random, block, or graft copolymers. Suppose now that copolymer species $i$ is characterized by the molecular weight $M_i$ and the composition $w_{Ai}$ that is the weight fraction of $A$ in a molecule of that species. The total concentration of the copolymer is given by $c = \sum_i c_i$, and from Eq. (27.23) we obtain

$$\lim_{\substack{\theta \to 0 \\ c \to 0}} \frac{Kc}{R_\theta} = \frac{1}{M_{\text{ap}}}\,, \tag{28.30}$$

where

$$M_{\text{ap}} = \left(\frac{\partial \tilde{n}}{\partial c}\right)_0^{-2} \sum_i \left(\frac{\partial \tilde{n}}{\partial c_i}\right)_0^2 M_i w_i \tag{28.31}$$

with $w_i = c_i/c$. If $c_A$ and $c_B$ are the concentrations of $A$ and $B$, respectively, we have $c = c_A + c_B$, and

$$\begin{aligned} c_A &= \sum_i w_{Ai} c_i \,, \\ c_B &= \sum_i w_{Bi} c_i \,. \end{aligned} \tag{28.32}$$

Since the over-all weight fractions of $A$ and $B$ in the whole copolymer are given by $c_A/c = w_A$ and $c_B/c = w_B$, respectively, Eqs.(28.32) may be rewritten as

$$\begin{aligned} w_A &= \sum_i w_{Ai} w_i \,, \\ w_B &= \sum_i w_{Bi} w_i \,. \end{aligned} \tag{28.33}$$

The refractive index increments may then be written in the forms,

$$\nu_i \equiv \left(\frac{\partial \tilde{n}}{\partial c_i}\right)_0 = \left(\frac{\partial \tilde{n}}{\partial c_A}\right)_0 \frac{\partial c_A}{\partial c_i} + \left(\frac{\partial \tilde{n}}{\partial c_B}\right)_0 \frac{\partial c_B}{\partial c_i} = w_{Ai}\nu_A + w_{Bi}\nu_B \,, \tag{28.34}$$

$$\nu \equiv \left(\frac{\partial \tilde{n}}{\partial c}\right)_0 = w_A\nu_A + w_B\nu_B \,, \tag{28.35}$$

where

$$\nu_A \equiv \left(\frac{\partial \tilde{n}}{\partial c_A}\right)_0 , \qquad \nu_B \equiv \left(\frac{\partial \tilde{n}}{\partial c_B}\right)_0 . \tag{28.36}$$

Substituting Eq. (28.34) into Eq. (28.31), we obtain for the apparent molecular weight

$$M_{\text{ap}} = \nu^{-2}[\nu_A\nu_B\langle M\rangle_w + \nu_A(\nu_A - \nu_B)\langle M\rangle_A w_A + \nu_B(\nu_B + \nu_A)\langle M\rangle_B w_B] \,, \tag{28.37}$$

where $\langle M\rangle_w$ is the weight-average molecular weight of the copolymer, and $\langle M\rangle_A$ and $\langle M\rangle_B$ are defined by

$$\begin{aligned} \langle M\rangle_A &= \sum_i M_i w_i w_{Ai}^2 / w_A \\ &= \sum_i (M_i w_{Ai})(w_{Ai} w_i) \Big/ \sum_i w_{Ai} w_i \,, \\ \langle M\rangle_B &= \sum_i M_i w_i w_{Bi}^2 / w_B \\ &= \sum_i (M_i w_{Bi})(w_{Bi} w_i) \Big/ \sum_i w_{Bi} w_i \,. \end{aligned} \tag{28.38}$$

From Eqs. (28.38), $\langle M\rangle_A$ and $\langle M\rangle_B$ are seen to be the weight-average molecular weights of the parts of the copolymer formed of monomeric units $A$ and $B$, respectively. Equation (28.37) shows that from measurements in three solvents it is possible, in principle, to solve for the three quantities $\langle M\rangle_w$, $\langle M\rangle_A$ and $\langle M\rangle_B$.

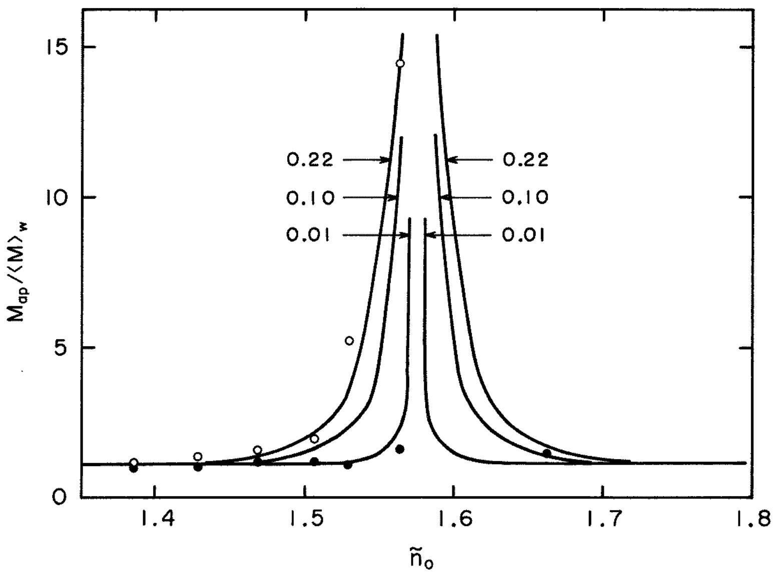

**Fig. V.8.** $M_{\text{ap}}/\langle M\rangle_w$ plotted against $n_0$ for copolymers of styrene and methylmethacrylate.[47] The points indicate the experimental data. Open circles: random copolymer. Filled circles: block copolymer. The curves represent the values calculated from Eq. (28.41) with $P = 0$ and $Q/\langle M\rangle_w$ as indicated.

However, apparent molecular weight may be expressed in a more convenient form if we introduce the deviation, $\delta w_i$, in composition of molecules of species $i$ from the average value. This deviation is defined by

$$\delta w_i = w_{Ai} - w_A = w_B - w_{Bi}\,. \tag{28.39}$$

From Eqs. (28.34), (28.35), and (28.39), we have

$$\nu_i = \nu + (\nu_A - \nu_B)\delta w_i\,. \tag{28.40}$$

Substitution of Eq. (28.40) into Eq. (28.31) leads to

$$M_{\text{ap}} = \langle M\rangle_w + 2P\left(\frac{\nu_A - \nu_B}{\nu}\right) + Q\left(\frac{\nu_A - \nu_B}{\nu}\right)^2 \tag{28.41}$$

with

$$P = \sum_i M_i w_i \delta w_i\,, \tag{28.42}$$

$$Q = \sum_i M_i w_i (\delta w_i)^2\,. \tag{28.43}$$

By the use of Eqs. (28.38), Eqs. (28.42) and (28.43) may be rewritten as

$$2P = (\langle M\rangle_A - \langle M\rangle_w)w_A + (\langle M\rangle_w - \langle M\rangle_B)w_B\,, \tag{28.44}$$

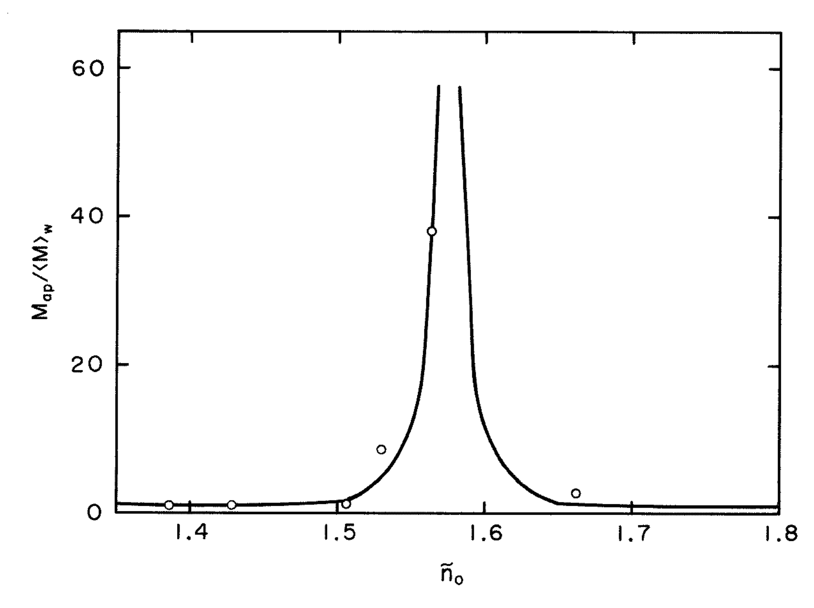

**Fig. V.9.** $M_{\rm ap}/\langle M\rangle_w$ plotted against $\tilde{n}_0$ for a mixture of 65% polystyrene and 35% polymethylmethacrylate.[47] Open circles: experimental data. The curves represent the values calculated from Eq. (28.48)

$$Q = (\langle M\rangle_A + \langle M\rangle_B - \langle M\rangle_w)w_A w_B\,. \tag{28.45}$$

It can easily be shown that Eq. (28.41) is equivalent to Eq. (28.37). According to Eq. (28.41), if $M_{\rm ap}$ is plotted against $(\nu_A - \nu_B)/\nu$, which varies with the refractive index of the solvent, the points must describe a parabola from which the values of $\langle M\rangle_w$, $P$, and $Q$ can be estimated. The value of $\langle M\rangle_w$ must agree with that determined from Eq. (28.37). The parameters $P$ and $Q$ are related to the heterogeneity in composition of the sample, and must be constant for a given copolymer. In general, $P$ and $Q$ will vary between the following limits:

$$\begin{aligned} -\langle M\rangle_w w_A \le P \le \langle M\rangle_w w_B\,, \\ 0 \le Q \le \langle M\rangle_w(1 - w_A w_B)\,. \end{aligned} \tag{28.46}$$

If the copolymer is homogeneous in molecular weight or if the composition is independent of molecular weight, $P$ is identically equal to zero and the range of $Q$ becomes

$$0 \le Q \le \langle M\rangle_w w_A w_B\,. \tag{28.47}$$

We note that the maximum value of $Q$ may be realized only with a mixture of two homopolymers $A$ and $B$. As seen from the definition, the parameter $Q/\langle M\rangle_w$ for a particular copolymer may be defined as a measure of the heterogeneity in composition. If the composition is homogeneous, we have, of course, $\delta w_i = 0$ and $M_{\rm ap} = \langle M\rangle_w$.

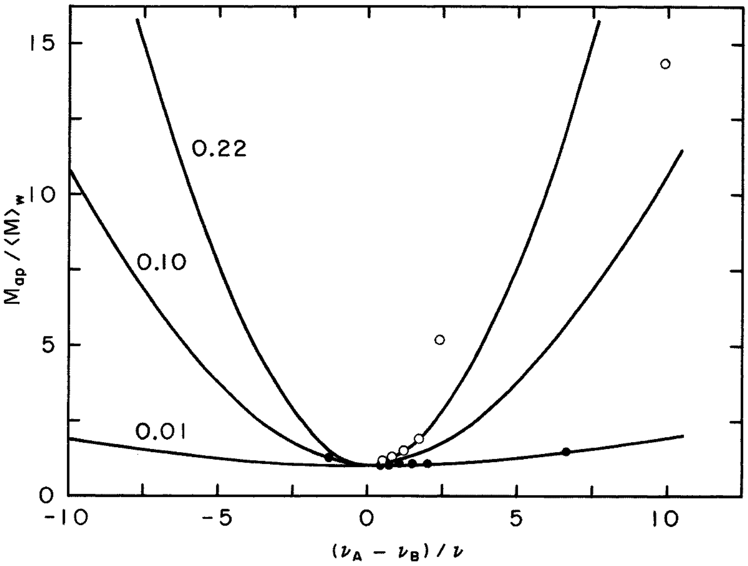

**Fig. V.10.** $M_{\mathrm{ap}}/\langle M\rangle_w$ plotted against $(\nu_A - \nu_B)/\nu$.[47] The points and curves correspond to those shown in Fig.V.8, respectively.

The values of $M_{\mathrm{ap}}/\langle M\rangle_w$ of copolymers of styrene and methylmethacrylate obtained by Bushuk and Benoit are plotted in Fig. V.8 against the refractive index of solvent. The open and filled circles represent the experimental data for the random and block copolymers, respectively, and the curves represent the theoretical values calculated from Eq. (28.41) with $P = 0$ and $Q/\langle M\rangle_w$ as indicated. $M_{\mathrm{ap}}$ becomes infinite at the value of $\tilde{n}_0$ which corresponds to $\nu = 0$. A mixture of two homopolymers $A$ and $B$ may be considered to be an extreme case of a copolymer. For the sake of comparison, in Fig. V.9 are also plotted the values of $M_{\mathrm{ap}}/\langle M\rangle_w$ of a mixture of 65% polystyrene and 35% polymethylmethacrylate against the refractive index of solvent.[46] The curves represent the values of $M_{\mathrm{ap}}/\langle M\rangle_w$ calculated from the equation,

$$M_{\mathrm{ap}} = \nu^{-2}(\nu_A^2\langle M\rangle_A w_A + \nu_B^2\langle M\rangle_B w_B)\,. \tag{28.48}$$

In Fig. V.10 are plotted the data of Fig. V.8 against $(\nu_A - \nu_B)/\nu$. From this figure, it is possible to estimate the value of $Q/\langle M\rangle_w$ that will best fit the experimental data. The values of $Q/\langle M\rangle_w$ thus obtained for the random and block copolymers are 0.16 and 0.01, respectively. For both copolymers, the maximum value of $Q/\langle M\rangle_w$ calculated from Eq. (28.47) is about 0.22. Thus, this random copolymer is seen to be highly heterogeneous in composition.

Finally, we note that mean-square radii of gyration and second virial coefficients for copolymers, although well-defined physical quantities, cannot be determined from light-scattering measurements. Although the intramolecular interference factor $P_1(\theta)$ for a copolymer has been evaluated by Benoit and Wippler,[48] the derived equation for $P_1(\theta)$ involves $\nu_A$ and $\nu_B$, and is not of a form accessible to determination of $\langle S^2 \rangle$.

## 28c. Critical Opalescence

In the fluctuation theory described in Section 26a, we have confined ourselves to "normal " fluctuations, excluding critical and two-phase regions. The normal density fluctuation, $\langle (\Delta\rho)^2 \rangle / \rho^2$, is of order $N^{-1}$. However, at a critical point or in a two-phase system, $\langle (\Delta\rho)^2 \rangle / \rho^2$, is of order unity.[49] That is, at a critical point, the density or concentration fluctuation is so large that the scattered intensity becomes extremely high. This phenomenon is well known as the *critical opalescence.*

According to the fluctuation theory,the Rayleigh ratio $R_{\theta,0}$ for a one-component system may be written, from Eq. (26.36), in the form,

$$R_{\theta,0} = \frac{2\pi^2 \tilde{n}}{\lambda^4} \left( \frac{\partial \tilde{n}}{\partial \rho} \right)_T^2 kT\rho \bigg/ \left( \frac{\partial p}{\partial \rho} \right)_T , \tag{28.49}$$

where we have used the relation $(\partial p / \partial \rho)_T = (\rho\kappa)^{-1}$ with $\kappa$ the isothermal compressibility. Equation (26.40) for the (excess) Rayleigh ratio for a two-component system may be rewritten in a similar form;

$$R_\theta = \frac{2\pi^2 \tilde{n}^2}{\lambda^4} \left( \frac{\partial \tilde{n}}{\partial c} \right)_{T,p}^2 kTc \bigg/ \left( \frac{\partial \pi}{\partial c} \right)_T . \tag{28.50}$$

At a critical point for a pure liquid, $(\partial p / \partial \rho)_T = 0$ or $\kappa = \infty$, and $R_{\theta,0}$ becomes infinite. Similarly, at a critical point (critical solution temperature) for a solution, $(\partial \pi / \partial c)_T = -{V_0}^{-1} (\partial \mu_0 / \partial c)_{T,p} = 0$, and $R_\theta$ becomes infinite. In fact, however, at the critical point the scattered intensity is very large, but finite. The inadequacy of Eq. (28.49) or (28.50) near the critical point is due to the fact that in deriving them there have been neglected correlations between density or concentration fluctuations in two volume elements. This problem was solved first by Ornstein and Zernike,[50] using a pair correlation function approach. Subsequently several authors[51−54] attempted different approaches, and Fixman[54] showed the equivalence of these approaches to that of Ornstein and Zernike. In this section, we first describe the pair correlation function approach for one-component simple fluids, and then apply the result to a binary solution.

We begin by deriving a basic equation for $R_{\theta,0}$. Let $\alpha_i$ be the instantaneous polarizability in the volume element $d\mathbf{R}_i$ at $\mathbf{R}_i$, and $\alpha$ its mean value. The instantaneous change $\Delta\alpha_i (= \alpha_i - \alpha)$ in $\alpha_i$ may then be written, from Eq. (26.1), in the form,

$$\begin{aligned} \Delta\alpha_i &= \frac{\tilde{n}}{2\pi} \Delta\tilde{n}_i d\mathbf{R}_i \\ &= \frac{\tilde{n}}{2\pi} \left( \frac{\partial \tilde{n}}{\partial \rho} \right)_T \Delta\rho_i d\mathbf{R}_i \, , \end{aligned} \tag{28.51}$$

where $\Delta\tilde{n}_i$ and $\Delta\rho_i$ are the instantaneous changes in refractive index and (number) density at $\mathbf{R}_i$. Replacing $\alpha_i$ in Eq. (27.6) by $\Delta\alpha_i$, we obtain for the scattered intensity $I$

$$\frac{I}{I^0} = \frac{8\pi^4(1+\cos^2\theta)}{\lambda^4 r^2}\langle G\rangle \tag{28.52}$$

with

$$\langle G\rangle = \frac{\tilde{n}}{4\pi^2}\left(\frac{\partial\tilde{n}}{\partial\rho}\right)_T^2 \sum_i\sum_j \langle\Delta\rho_i\Delta\rho_j\rangle \exp(\mathbf{s}'\cdot\mathbf{R}_{ij})d\mathbf{R}_i d\mathbf{R}_j\,, \tag{28.53}$$

where the average of $G$ is assumed to be the grand canonical ensemble average. Converting the sums to integrals in Eq. (28.53), we obtain for the Rayleigh ratio $R_{\theta,0}$

$$R_{\theta,0} = \frac{2\pi^2\tilde{n}^2}{\lambda^4}\left(\frac{\partial\tilde{n}}{\partial\rho}\right)_T^2 \int\langle\Delta\rho_1\Delta\rho_2\rangle\exp(\mathbf{s}'\cdot\mathbf{R})d\mathbf{R} \tag{28.54}$$

with $\mathbf{R}\equiv\mathbf{R}_{12}(=\mathbf{R}_2-\mathbf{R}_1)$.

Let us now express the correlation of density fluctuations in terms of the pair correlation function $g(\mathbf{R})$. For specified configurations, $\{R_N{}'\}$, of all of the molecules, the singlet density $\nu^{(1)}(\mathbf{R}_1)$ of molecules at $\mathbf{R}_1$ and the pair density $\nu^{(2)}(\mathbf{R}_1,\mathbf{R}_2)$ of molecules at $\mathbf{R}_1$ and $\mathbf{R}_2$ are given by[55]

$$\begin{aligned}\nu^{(1)}(\mathbf{R}_1) &= \sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{R}_i{}')\,,\\ \nu^{(2)}(\mathbf{R}_1,\mathbf{R}_2) &= \sum_{\substack{i=1\\ i\neq j}}^{N}\sum_{j=1}^{N}\delta(\mathbf{R}_1-\mathbf{R}_i{}')\delta(\mathbf{R}_2-\mathbf{R}_j{}')\,.\end{aligned} \tag{28.55}$$

The averages of $\nu^{(1)}$ and $\nu^{(2)}$ are equal to the singlet and pair distribution functions $\rho^{(1)}$ and $\rho^{(2)}$ given by Eq. (19.11), respectively;

$$\begin{aligned}\langle\nu^{(1)}(\mathbf{R}_1)\rangle &= \rho^{(1)}(\mathbf{R}_1) = \rho\,,\\ \langle\nu^{(2)}(\mathbf{R}_1,\mathbf{R}_2)\rangle &= \rho^{(2)}(\mathbf{R}_1,\mathbf{R}_2)\equiv\rho^2 g(\mathbf{R}_{12})\,.\end{aligned} \tag{28.56}$$

Since $\Delta\rho_1$ and $\Delta\rho_2$ are given by

$$\Delta\rho_1 = \nu^{(1)}(\mathbf{R}_1)-\rho\,,\qquad \Delta\rho_2 = \nu^{(1)}(\mathbf{R}_2)-\rho\,, \tag{28.57}$$

we have

$$\begin{aligned}\Delta\rho_1\Delta\rho_2 = &\sum_i\delta(\mathbf{R}_1-\mathbf{R}_i{}')\delta(\mathbf{R}_2-\mathbf{R}_i{}')+\nu^{(2)}(\mathbf{R}_1,\mathbf{R}_2)\\ &-\rho[\nu^{(1)}(\mathbf{R}_1)+\nu^{(1)}(\mathbf{R}_2)]+\rho^2\,.\end{aligned} \tag{28.58}$$

It is evident that the first term on the right-hand side of Eq. (28.58) is equal to $\delta(\mathbf{R}_{12})\nu^{(1)}(\mathbf{R}_1)$, and we therefore obtain, from Eqs. (28.56) and (28.58),[56]

$$\langle \Delta\rho_1 \Delta\rho_2 \rangle = \rho\{\delta(\mathbf{R}) + \rho[g(\mathbf{R}) - 1]\}\,. \tag{28.59}$$

The great increase in the intensity of scattered light at the critical point may be ascribed to the great extension of the range of $R$ in which $[g(R) - 1]$ is sensibly nonvanishing; and the contribution of $g(R)$ for small $R$ to the integral of (28.54) is of minor importance. We may therefore use the asymptotic form of $g(R)$ in Eq. (28.54) with (28.59). Now, the pair correlation function or the function $G(\mathbf{R}) \equiv g(\mathbf{R}) - 1$ is related to the *direct* correlation function $X(\mathbf{R})$ by the Ornstein–Zernike equation,[57]

$$G(\mathbf{R}_{12}) = X(\mathbf{R}_{12}) + \rho \int X(\mathbf{R}_{13}) G(\mathbf{R}_{32}) d\mathbf{R}_3\,. \tag{28.60}$$

When $X$ is explicitly given, Eq. (28.60) is an integral equation for $g$. For example, in the Percus–Yevick equation, $X$ is simply given by $X = g(1 - e^{u/kT})$,[58, 59] where $u$ is the intermolecular potential energy. In general, $X$ is a short-range function ($X \to 0$ and $g \to 1$, as $R \to \infty$). Therefore, we expand the function $G(\mathbf{R}_{32})$ around $\mathbf{R}_{13} = 0$ in the integrand of Eq. (28.60);

$$\begin{aligned} G(\mathbf{R}_{32}) &= G(\mathbf{R}_{12} - \mathbf{R}_{13}) \\ &= G(\mathbf{R}_{12}) + \mathbf{R}_{13} \cdot \nabla_1 G(\mathbf{R}_{12}) + \tfrac{1}{2} \mathbf{R}_{13}\mathbf{R}_{13} : \nabla_1 \nabla_1 G(\mathbf{R}_{12}) + \cdots\,, \end{aligned} \tag{28.61}$$

where we neglect terms higher than $\mathbf{R}_{13}\mathbf{R}_{13}$. Recalling that $X$ is spherically symmetric, substitution of Eq. (28.61) into Eq. (28.60) leads to

$$\begin{aligned} G(\mathbf{R}_{12}) = X(\mathbf{R}_{12}) &+ \rho \int X(\mathbf{R}_{13}) d\mathbf{R}_{13} G(\mathbf{R}_{12}) \\ &+ \frac{\rho}{6} \int {R_{13}}^2 X(\mathbf{R}_{13}) d\mathbf{R}_{13} {\nabla_1}^2 G(\mathbf{R}_{12})\,. \end{aligned} \tag{28.62}$$

At large $R_{12}$, the leading term on the right-hand side of Eq. (28.62) may be put equal to zero. Then Eq. (28.62) reduces to the differential equation,

$$\nabla^2 G - \sigma^2 G = 0\,, \tag{28.63}$$

where

$$\sigma^2 = \frac{6}{l^2}\left[\frac{1}{\rho \int X(\mathbf{R}) d\mathbf{R}} - 1\right] \tag{28.64}$$

with

$$l^2 \equiv \frac{\int R^2 X(\mathbf{R}) d\mathbf{R}}{\int X(\mathbf{R}) d\mathbf{R}}\,. \tag{28.65}$$

Clearly, the parameter $l$ is a measure of the range of intermolecular forces. The spherically symmetric solution of Eq. (28.63) gives the desired asymptotic form of $G$, that is,[50, 52, 60]

$$G(\mathbf{R}) = \frac{A}{R} e^{-\sigma R} . \tag{28.66}$$

The constants $\sigma$ and $A$ may be determined from the compressibility equation of (17.12), that is,

$$\rho \int G(\mathbf{R}) d\mathbf{R} = \rho \kappa k T - 1 . \tag{28.67}$$

Integrating both sides of Eq. (28.60) over $\mathbf{R}_{12}$ and combining the result with Eq. (28.67), we obtain

$$\rho \int X(\mathbf{R}) d\mathbf{R} = 1 - \frac{1}{\rho \kappa k T} . \tag{28.68}$$

Substitution of Eq. (28.68) into Eq. (28.64) leads to

$$\sigma^2 = \frac{6}{l^2(\rho \kappa k T - 1)} . \tag{28.69}$$

Substitution of Eq. (28.66) into Eq. (28.67) with the use of Eq. (28.69) leads to

$$A = \frac{3}{2\pi \rho l^2} . \tag{28.70}$$

By the use of Eq. (28.59) with (28.66), the integral in Eq. (28.54) may now be evaluated to be

$$\int \langle \Delta\rho_1 \Delta\rho_2 \rangle \exp(\mathbf{s}' \cdot \mathbf{R}) d\mathbf{R} = \rho \left[ 1 + \frac{6}{l^2(\sigma^2 + v^2)} \right] \tag{28.71}$$

with

$$v = \frac{4\pi}{\lambda'} \sin(\theta/2) . \tag{28.72}$$

Since $l/\lambda' \ll 1$, and near the critical point $l\sigma \ll 1 (\kappa \approx \infty)$, the first term on the right-hand side of Eq. (28.71) is negligible compared to the second term. From Eqs. (28.54) and (28.71), we then have

$$R_{\theta,0} = \frac{2\pi^2 \tilde{n}^2}{\lambda^4} \left( \frac{\partial \tilde{n}}{\partial \rho} \right)_T^2 kT\rho \Big/ \left[ \left( \frac{\partial p}{\partial \rho} \right)_T + \frac{1}{6} kTl^2 v^2 \right] . \tag{28.73}$$

This result is equivalent to those obtained by Ornstein and Zernike[50] and by Fixman.[54] When the $v^2$ term is negligible compared to $(\partial p/\partial \rho)_T$, Eq. (28.73) reduces to Eq. (28.49). We note that at the critical point $[(\partial p/\partial \rho)_T = 0]$ the $R_{\theta,0}$ given by Eq. (28.73) is finite except at $\theta = 0$ and is proportional to $\lambda^{-2}$ instead of $\lambda^{-4}$.

Next we discuss the critical opalescence of a binary solution. Debye[53] solved this problem, based on the contribution of the square of the concentration gradient to the local free energy. However, the excess Rayleigh ratio may be obtained indirectly from Eq. (28.73) by replacing the pressure $p$ by the osmotic pressure $\pi$ and regarding $\rho$ as the number of solute molecules per unit volume of solution. That is,

$$\frac{N_{\mathrm{A}} K c^2}{R_\theta} = \frac{\phi}{kT}\left(\frac{\partial \pi}{\partial \phi}\right)_T + \frac{\phi l^2 v^2}{6 V_0 x}\,, \tag{28.74}$$

where $K$ is given by Eq. (25.26), $\phi$ is the volume fraction of the solute, $V_0$ is the molecular volume of the solvent, and $x$ is the ratio of the molecular volumes of the solute and solvent (note that $\rho = \phi / V_0 x \propto c$). We adopt the Flory–Huggins expression for the chemical potential $\mu_0$ of the solvent,[61]

$$\mu_0 / kT = \ln(1-\phi) + (1 - x^{-1})\phi + \chi \phi^2\,, \tag{28.75}$$

where the parameter $\chi$ is the same as that appearing in Eq. (11.13). From Eqs. (26.43) and (28.75), we then have

$$\frac{\phi}{kT}\left(\frac{\partial \pi}{\partial \phi}\right)_T = \phi^2 \left[\frac{1}{V_0(1-\phi)} + \frac{1}{V_0 x \phi} - \frac{2\chi}{V_0}\right]. \tag{28.76}$$

Since at the critical point $(\partial \mu_0 / \partial \phi)_{T,p} = 0$, and $(\partial^2 \mu_0 / \partial \phi^2)_{T,p} = 0$, we obtain[62]

$$\phi_c = \frac{1}{1 + x^{1/2}}\,, \tag{28.77}$$

$$\chi_c = \frac{(1 + x^{1/2})^2}{2x}\,, \tag{28.78}$$

where the subscript $c$ refers to the critical point. Let us now assume that an experiment is carried out with a homogeneous solution above the critical temperature $T_c$ at the critical concentration $\phi_c$, and that the temperature is gradually lowered until $T$ reaches $T_c$. Further we assume that near the critical point $\chi$ is given by

$$\chi = \frac{1}{2} + \frac{1}{2x^{1/2}} + \frac{B V_0}{2kT}\,. \tag{28.79}$$

From Eqs. (28.76) to (28.79), we then obtain

$$\frac{\phi_c}{kT}\left(\frac{\partial \pi}{\partial \phi}\right)_{T,\phi_c} = \frac{2{\phi_c}^2}{V_0}(\chi_c - \chi) = \frac{B {\phi_c}^2}{kT}\left(\frac{T}{T_c} - 1\right), \tag{28.80}$$

$$x V_0 B \phi_c = k T_c\,. \tag{28.81}$$

With these relations, Eq. (28.74) may be rewritten in the form,

$$\frac{C}{R_\theta} = \frac{T_c}{T}\left[\left(\frac{T_c}{T} - 1\right) + \frac{8\pi^2 l^2}{3(\lambda')^2}\sin^2(\theta/2)\right], \tag{28.82}$$

where we have assumed $T \approx T_c$ in the second term in the square brackets, and $C$ is a constant characteristic of the system at the critical point. Equation (28.82) is equivalent to the result derived by Debye.

**TABLE V.1.** OBSERVED VALUES OF THE PARAMETER $l$ FOR POLYSTYRENE IN CYCLOHEXANE[63, 64]

| $\langle M\rangle_w \times 10^{-4}$ | $T_c$ (°C) | $\phi_c$ (%) | $l$ (Å) | $\langle S^2\rangle^{1/2}$ (Å) |
|---|---|---|---|---|
| 8.0 | 19.24 | 6.8 | 23.8 | — |
| 12.3 | 21.82 | 5.6 | 26.6 | — |
| 15.3 | 23.19 | 5.0 | 28.4 | — |
| 23.9 | 24.95 | 4.6 | 30.0 | — |
| 25.3 | 25.09 | 4.3 | 33.3 | — |
| 56.9 | 27.79 | 2.8 | 42.1 | — |
| 119 | 29.00 | 2.0 | 50.1 | 143 (30°C) |
| 350 | 29.18 | 1.25 | 66.1 | 186 (45°C) |

From Eq. (28.82), the intensity of light scattered from a solution near the critical point is seen to exhibit very large angular dissymmetry. Thus, for the case of solutions of polymers of relatively low molecular weights, Debye attempted to determine the parameter $l$ by means of Eq. (28.82), regarding $l^2$ as equal to the mean-square radius $\langle S^2\rangle$ of the polymer. In this connection, we note that for polymers of low molecular weight such that $\langle S^2\rangle^{1/2} < \lambda/20$, the angular dissymmetry of scattered light is so small that the usual method based on Eq. (27.36) fails in the accurate determination of $\langle S^2\rangle$. In practice, the usual method is confined to the case for which $\langle S^2\rangle^{1/2} > 200$ Å. On the contrary, Eq. (28.82) may be used to determine much smaller $l$ when $T$ approaches $T_c$. In Table V.1 are given the data obtained by Debye et al.[63, 64] for polystyrene in cyclohexane. It is seen that $l$ is unexpectedly much smaller than $\langle S^2\rangle^{1/2}$. There is, of course, no explicit relation between the defining equations for $l^2$ and $\langle S^2\rangle$, and we do not further discuss the differences between their observed values.

## 28d. Some Other Topics

In this chapter, so far, we have not considered the difference between the frequencies of the incident and scattered light. However, there will be a frequency distribution of the scattered light about the Rayleigh line (of the same frequency as that of the incident light), which arises from the thermal Brownian motion of scattering particles. Such *Doppler shifts* are, of course, small; their region is much closer to the Rayleigh line than the Raman region. However, the recent development of the optical maser offers hope for future high precision experimental work in this field, which will yield valuable information concerning thermal motions in pure liquids and in polymer solutions. Thus, we give a brief description of the theory of Pecora,[65] which will be useful for the analysis of such experiments. Now, the quantity that we need in this case is not the total scattered intensity, but the intensity, $I(\omega)d\omega$, of the scattered light whose angular frequency is between $\omega$ and $\omega + d\omega$. The quantity $I(\omega)$, called the *spectral density*, may be defined by[56, 66]

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle \mathbf{E}(0) \cdot \mathbf{E}^*(t) \rangle \exp(i\omega t) dt \,, \tag{28.83}$$

where $\mathbf{E}(t)$ is the radiation field at time $t$, and asterisk indicates the complex conjugate. Starting with Eq. (27.3), we obtain for the Rayleigh ratio $R_{\theta,0}(\omega)$ associated with $I(\omega)$ for pure liquids

$$R_{\theta,0}(\omega) = \frac{\pi \tilde{n}^2}{\lambda^4} \left( \frac{\partial \tilde{n}}{\partial \rho} \right)_T^2 \int \langle \Delta\rho_1(0) \Delta\rho_2(t) \rangle \exp(\mathbf{s}' \cdot \mathbf{R} - it\Delta\omega) d\mathbf{R}\, dt \,, \tag{28.84}$$

where $\Delta\omega$ is the difference between the angular frequencies of the incident and scattered waves. Integration of $R_{\theta,0}(\omega)$ over $\omega$ from $-\infty$ to $+\infty$ gives the $R_{\theta,0}$ given by Eq. (28.54), because the integral of $\exp(-it\Delta\omega)$ is $2\pi\delta(t)$. It is convenient to introduce a *space-time correlation function* $C(\mathbf{R}, t)$ defined by

$$\langle \Delta\rho_1(0) \Delta\rho_2(t) \rangle = \rho[C(\mathbf{R}, t) - \rho] \,. \tag{28.85}$$

For a more explicit definition of $C(\mathbf{R}, t)$, see Appendix V C. The function $C(\mathbf{R}, t)$ is the probability density that if there was a molecule at the origin at time zero, then there will be one at $\mathbf{R}$ at time $t$. For the case of polymer solutions, $R_\theta(\omega)$ may easily be obtained, from Eq. (28.84), as

$$R_\theta(\omega) = \frac{KMc}{2\pi n} \int C_0(\mathbf{R}, t) C_I(\mathbf{R}', t) \exp[\mathbf{s}' \cdot (\mathbf{R} + \mathbf{R}') - it\Delta\omega] d\mathbf{R} d\mathbf{R}' dt \,, \tag{28.86}$$

where $C_0(\mathbf{R}, t)$ is the space-time correlation function for the center of mass of the same molecule, and $C_I(\mathbf{R}', t)$ is that for two segments of the same molecule. Evaluation of $C_0$ and $C_I$ requires a knowledge of polymer dynamics (Chapter VI). Thus we describe only the final results. For flexible-chain polymers, the spectrum associated with the center of mass is approximately Lorentzian with a half-width of order $10\ \text{sec}^{-1}$; and the spectrum associated with segmental motions is a sum of Lorentzians centered about the incident frequency each with a half-width inversely proportional to the relaxation time of a given normal mode. The longest mode contributes most to the line intensity, and the half-width due to it is of order $10^4\ \text{sec}^{-1}$. The spectrum associated with the rotation of a rod molecule about its center of mass is also Lorentzian with a half-width of order $10^2 - 10^6\ \text{sec}^{-1}$.

Our final remarks are concerned with the effects of short-range interferences in a polymer chain on the scattered intensity. As mentioned in Section 9a, even for unperturbed chains, the Markoff nature dose not hold for short chains, and $\langle {R_{ij}}^2 \rangle_0$ is not proportional to $|j - i|$ when $|j - i|$ is small. Strictly, therefore, Eqs. (27.33) and (27.34) are not exact. Recently Flory and Jernigan[67] investigated this problem on the basis of the rotational isomeric state model, and concluded that Eq. (27.34) is remarkably accurate even for short chains in the case of polymethylene. In a similar sense, the second line of Eq. (28.18) is not exact, since it has been derived on the assumption that there is no correlation between bonds in a polymer chain. Without this assumption, it is, of course, quite difficult to develop a theory of light scattering from polymers composed of optically anisotropic segments. However, we note that Jernigan and Flory[68] have estimated the degree of depolarization for $n$-alkanes, still using the rotational isomeric approximation.

## Appendix V A. The Electromagnetic Field Due to an Oscillating Electric Dipole

We show a calculation of the radiation field due to an oscillating electric dipole in a homogeneous dielectric medium of dielectric constant $\varepsilon = \tilde{n}^2$ with $\tilde{n}$ its optical refractive index. This is an elementary application of electromagnetic theory (Maxwell's equations).[69] For simplicity, suppose that the oscillating dipole is induced along a wire of length $L$ which is placed on the $x$ axis with its center at the origin, as depicted in Fig. V.II.[70] The oscillating dipole moment $\mathbf{p}$ may then be written in the form,

$$\begin{aligned}\mathbf{p} &= \mathbf{p}_0 \exp(i\omega t) \\ &= q\mathbf{L} = qL\mathbf{e}_x\,, \end{aligned} \tag{V A.1}$$

where $\omega$ is the angular frequency, and $q$ is the electric charge on the upper end of the wire, the charge on the lower end being $-q$. Therefore, $q$ is given by

$$q = q_0 \exp(i\omega t) \tag{V A.2}$$

with $p_0 = q_0 L$. Thus, an electric current flows in the wire, and its magnitude $J$ is given by

$$J = \frac{dq}{dt} = i\omega q_0 \exp(i\omega t)\,, \tag{V A.3}$$

the positive direction of $J$ being that of $\mathbf{e}_x$.

Now, the retarded magnetic vector potential $\mathbf{A}(\mathbf{r}, t)$ at the point $P(\mathbf{r})$ of observation, which is produced by the time-varying current $J$, may be expressed in the form,

$$\mathbf{A}(\mathbf{r}, t) = \frac{\mathbf{e}_x}{\tilde{c}} \int_{-L/2}^{L/2} \frac{1}{R} J(x', y', z', t - R/\tilde{c}')dx'\,, \tag{V A.4}$$

where $\tilde{c}$ and $\tilde{c}'$ are the velocities of light in a vacuum and the medium, respectively, and $R$ is the distance between the point $P'(x', y', z')$ (with $y' = z' = 0$) on the wire and the point $P$. We now assume that $L \ll r$ and that $L \ll \lambda'$ with $\lambda'$ the wavelength of light in the medium. From the first assumption, we may have $R^{-1} \approx r^{-1}$ in the integrand of Eq.

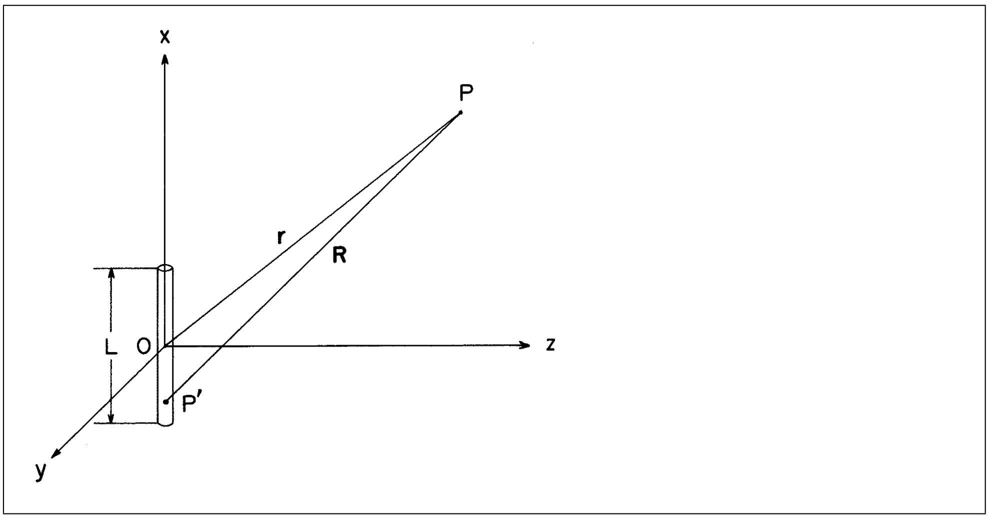

**Fig. V.11.** Model of an oscillating electric dipole.

(V A.4). From the second assumption, the quantity $\omega(t-R/\tilde{c}')$ may be replaced by $\omega(t-r/\tilde{c}')$, because the error is at most $\omega L/\tilde{c}' = 2\pi L/\lambda'$. Then, the integrand of Eq. (V A.4) becomes independent of $x'$, and we therefore have

$$\begin{aligned}\mathbf{A}(\mathbf{r},t) &= \mathbf{e}_x\frac{i\omega q_0 L}{\tilde{c}r}\exp[i\omega(t-r/\tilde{c}')] \\ &= \{\dot{\mathbf{p}}\}/\tilde{c}r\,, \end{aligned} \tag{V A.5}$$

where the curly brackets indicate that $t$ is to be replaced by the retarded time $(t-r/\tilde{c}')$, and $\{\dot{\mathbf{p}}\} = d\{\mathbf{p}\}/dt$. The magnetic field $\mathbf{H}$ due to the current $J$ is

$$\mathbf{H} = \nabla\times\mathbf{A}\,. \tag{V A.6}$$

Using the Maxwell equation for a nonconducting dielectric medium,

$$\nabla\times\mathbf{H} = \frac{\varepsilon}{\tilde{c}}\frac{\partial\mathbf{E}}{\partial t}\,, \tag{V A.7}$$

We obtain for the electric field $\mathbf{E}$ at $\mathbf{r}$

$$\mathbf{E} = \frac{\tilde{c}}{\varepsilon}\int(\nabla\times\mathbf{H})dt = \frac{\tilde{c}}{\varepsilon}\nabla\times\nabla\times\int\mathbf{A}\,dt\,. \tag{V A.8}$$

Substitution of Eq. (V A.5) into Eqs. (V A.8) and (V A.6) leads to

$$\mathbf{E} = \frac{1}{\varepsilon}\nabla\times\nabla\times\frac{\{\mathbf{p}\}}{r}\,, \tag{V A.9}$$

$$\mathbf{H} = \frac{1}{\tilde{c}}\nabla\times\frac{\{\dot{\mathbf{p}}\}}{r}\,. \tag{V A.10}$$

Equations (V A.9) and (V A.10) may be rewritten as

$$\mathbf{E} = \frac{\mathbf{r} \times (\mathbf{r} \times \{\ddot{\mathbf{p}}\})}{\varepsilon(\tilde{c}')^2 r^3} + \frac{\mathbf{r} \times (\mathbf{r} \times \{\dot{\mathbf{p}}\}) + 2\mathbf{r}(\mathbf{r} \cdot \{\dot{\mathbf{p}}\})}{\varepsilon \tilde{c}' r^4} + \frac{3\mathbf{r}(\mathbf{r} \cdot \{\mathbf{p}\}) - r^2\{\mathbf{p}\}}{\varepsilon r^5}\,, \tag{V A.11}$$

$$\mathbf{H} = -\frac{\mathbf{r} \times \{\ddot{\mathbf{p}}\}}{\tilde{c}\tilde{c}' r^2} - \frac{\mathbf{r} \times \{\dot{\mathbf{p}}\}}{\tilde{c} r^3}\,. \tag{V A.12}$$

If $r \gg \lambda'$, $\mathbf{E}$ and $\mathbf{H}$ may be approximated by the leading terms in Eqs (V A.11) and (V A.12), respectively;

$$\mathbf{E} = -\left(\frac{\omega}{\tilde{c}}\right)^2 \frac{\mathbf{r} \times (\mathbf{r} \times \{\mathbf{p}\})}{r^3}\,, \tag{V A.13}$$

$$\mathbf{H} = \tilde{n}\left(\frac{\omega}{\tilde{c}}\right)^2 \frac{\mathbf{r} \times \{\mathbf{p}\}}{r^2}\,, \tag{V A.14}$$

where we have used the relations, $\{\dot{\mathbf{p}}\} = i\omega\{\mathbf{p}\}$, $\{\ddot{\mathbf{p}}\} = -\omega^2\{\mathbf{p}\}$, $\tilde{c}' = \tilde{c}/\tilde{n}$, and $\varepsilon = \tilde{n}^2$. Equations (V A.13) and (V A.14) give the desired radiation field.

## Appendix V B. Angular Distributions for Rigid Sphere and Rod Molecules

In this appendix, we discuss the intramolecular interference factor $P_1(\theta)$ for rigid macromolecules. A rigid macromolecule may be treated as a continuum of scattering units, and $P_1(\theta)$ may be evaluated from Eq. (27.30). Then, the Rayleigh ratio is given by $R_\theta = KMcP_1(\theta)$ at infinite dilution. However, we note that this is true when the difference between the refractive indices of the particle and medium is small as in the case of polymer solutions; otherwise, a very complicated scattering pattern is observed, arising from the Mie effect,[22, 71] i.e., interactions of the field and the scattering units.

We first consider a rigid sphere molecule of radius $\bar{S}$. In this case, the scattering units of the sphere may be regarded as localized, and it is unnecessary to take the configurational average in Eq. (27.30). $P_1(\theta)$ may then be calculated from

$$P_1(\theta) = \left| n^{-1} \sum_i \exp(\mathbf{s}' \cdot \mathbf{S}_i) \right|^2, \tag{V B.1}$$

where $\mathbf{S}_i$ is the distance between the $i$th unit (volume element) and the center of the sphere. The sum in Eq. (V B.1) may be converted to an integral. Using polar coordinates with the $z$ axis in the direction of $\mathbf{s}'$, Eq. (V B.1) may be rewritten in the form,

$$P_1(\theta) = \left[ \frac{2\pi}{v_m} \int_0^S \int_0^\pi \exp(\mathbf{s}' \cdot \mathbf{r}) r^2 \sin\theta' \; dr \; d\theta' \right]^2, \tag{V B.2}$$

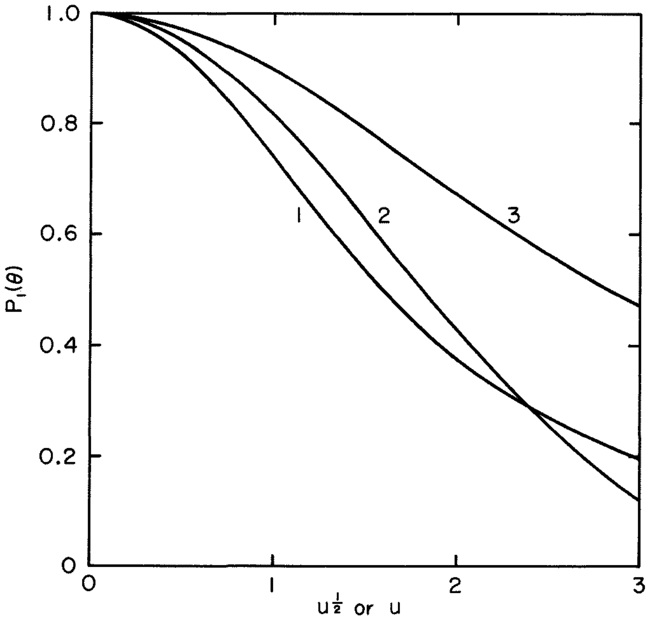

**Fig. V.12.** $P_1(\theta)$ plotted against $u^{1/2}$ (for unperturbed flexible chains) or $u$ (for spheres and rods).[25] Curve 1: unperturbed flexible chains. Curve 2: spheres Curve 3: rods.

with $v_m$ the volume of the sphere. The result is[4, 72]

$$P_1(\theta) = [3u^{-3}(\sin u - u\cos u)]^2 \qquad \text{(for spheres)} \qquad \text{(V B.3)}$$

with

$$u = (4\pi\bar{S}/\lambda')\sin(\theta/2)\,. \qquad \text{(V B.4)}$$

In general, for rigid molecules other than spheres, the configurational average is concerned with the orientation of the molecule. This orientation may be assumed to be uniform in all directions, and Eq. (27.30) may be rewritten in the form,

$$\begin{aligned} P_1(\theta) &= n^{-2}\sum_i\sum_j \frac{1}{2}\int_0^\pi \exp(\mathbf{s}'\cdot\mathbf{R}_{ij})\sin\theta'\,d\theta' \\ &= n^{-2}\sum_i\sum_j \frac{\sin(2\pi sR_{ij}/\lambda')}{(2\pi sR_{ij}/\lambda')}\,. \qquad \text{(V B.5)} \end{aligned}$$

For example, $P_1(\theta)$ for a rod molecule of length $l$ may be conveniently calculated from Eq. (V B.5). Replacing the summations by integrations, we obtain

$$P_1(\theta) = \frac{2}{l^2}\int_0^l (l-r)\frac{\sin(2\pi sr/\lambda')}{(2\pi sr/\lambda')}dr\,,$$

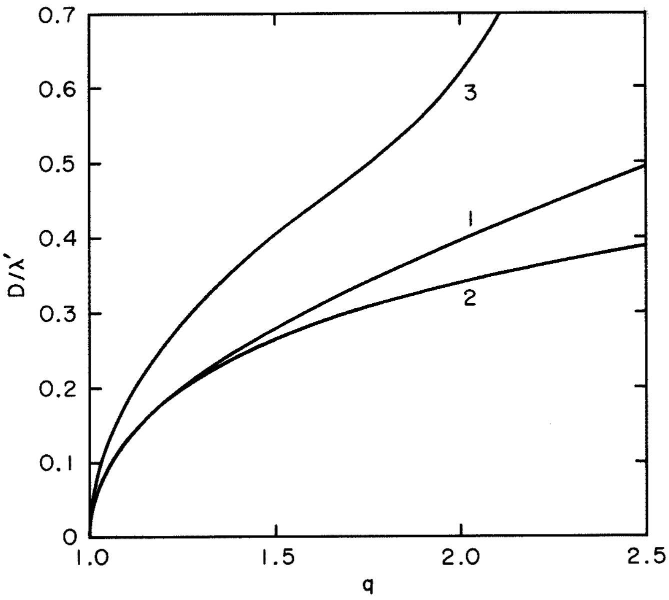

**Fig. V.13.** $D/\lambda'$ as a function of the dissymmetry ratio $q$.[25] Curve 1: unperturbed flexible chains. Curve 2: spheres. Curve 3: rods.

that is,[4, 73, 74]

$$P_1(\theta) = \frac{1}{u}\int_0^{2u} \frac{\sin x}{x} dx - \left(\frac{\sin u}{u}\right)^2 \qquad \text{(for rods)} \tag{V B.6}$$

with

$$u = (2\pi l/\lambda')\sin(\theta/2)\,. \tag{V B.7}$$

Although similar calculations for rigid macromolecules of other shapes have also been made,[75, 76] the results can be expressed only in series forms, and we do not reproduce them here.

For illustrative purposes, in Fig. V.12 are plotted the values of $P_1(\theta)$ calculated from Eq. (27.34) for unperturbed flexible chains, Eq. (V B.3) for spheres, and Eq. (V B.6) for rods against $u^{1/2}$ (for chains) or $u$ (for spheres and rods). Let us now define a *dissymmetry ratio* $q$ by $q = P_1(45°)/P_1(135°)$. The ratio $D/\lambda'$ with $D = 2\bar{S}$, $l$, or $\langle R^2\rangle_0{}^{1/2}$ is plotted in Fig. V.13 against $q$. This indicates that measurements of $q$ enable us to determine molecular dimensions when the molecular shape is known.

Finally, we note that Jennings and Jerrard[77] have recently reported light-scattering studies on solutions of polar or electrically anisotropic rod molecules (tobacco mosaic virus) in the presence of an applied electric field, which results in changes of the angular distribution of the scattered intensity, and leads to a determination of the permanent dipole moment of the molecule.

## Appendix V C. The Space-Time Correlation Function

For specified configurations, $\{\mathbf{R}_N{}'(t)\}$, of all of the molecules at time $t$, the density fluctuation $\Delta\rho_j(t)$ at $\mathbf{R}_j$ is given by

$$\Delta\rho_j(t) = \sum_{i=1}^{N} \delta[\mathbf{R}_j - \mathbf{R}_i{}'(t)] - \rho\,. \tag{V C.1}$$

We therefore have

$$\langle \Delta\rho_1(0)\Delta\rho_2(t)\rangle = \left\langle \sum_i \sum_j \delta[\mathbf{R}_1 - \mathbf{R}_i{}'(0)]\delta[\mathbf{R}_2 - \mathbf{R}_j{}'(t)]\right\rangle - \rho^2\,. \tag{V C.2}$$

Comparing Eq. (28.85) with Eq. (V C.2), we find an alternative explicit expression for the space-time correlation function $C(\mathbf{R}, t)$ with $\mathbf{R} \equiv \mathbf{R}_{12}$,

$$C(\mathbf{R}, t) = \frac{1}{\rho}\left\langle \sum_i \sum_j \delta[\mathbf{R}_1 - \mathbf{R}_i{}'(0)]\delta[\mathbf{R}_2 - \mathbf{R}_j{}'(t)]\right\rangle. \tag{V C.3}$$

Now, taking the Fourier transform of both sides of Eq. (V C.3), we obtain

$$\begin{aligned}\int C(\mathbf{R}, t)\exp(\mathbf{s}'\cdot\mathbf{R})d\mathbf{R} &= \frac{1}{V}\int C(\mathbf{R}, t)\exp[-\mathbf{s}'\cdot(\mathbf{R}_1 - \mathbf{R}_2)]d\mathbf{R}_1\, d\mathbf{R}_2\\ &= \frac{1}{N}\left\langle \sum_i \sum_j \exp\{-\mathbf{s}'\cdot[\mathbf{R}_i{}'(0) - \mathbf{R}_j{}'(t)]\}\right\rangle.\end{aligned} \tag{V C.4}$$

Then inverse Fourier transformation leads to

$$\begin{aligned}C(\mathbf{R}, t) = \frac{1}{8\pi^3 N}\int &\left\langle \sum_i \sum_j \exp\{-\mathbf{s}'\cdot[\mathbf{R}_i{}'(0) - \mathbf{R}_j{}'(t)]\}\right\rangle\\ &\times \exp\{-\mathbf{s}'\cdot\mathbf{R})d(\mathbf{s}'/i)\,.\end{aligned} \tag{V C.5}$$

This is the original definition of $C(\mathbf{R}, t)$ by Van Hove.$^{78}$

When $t = 0$, Eq. (V C.4) reduces to

$$\left\langle \sum_i \sum_j \exp(\mathbf{s}'\cdot\mathbf{R}_{ij})\right\rangle = N\int C(\mathbf{R}, 0)\exp(\mathbf{s}'\cdot\mathbf{R})d\mathbf{R} \tag{V C.6}$$

with $\mathbf{R}_{ij} = \mathbf{R}_j{}'(0) - \mathbf{R}_i{}'(0)$. The ensemble average on the left-hand side of Eq. (V C.6) may easily be written as

$$\left\langle \sum_i \sum_j \exp(\mathbf{s}'\cdot\mathbf{R}_{ij})\right\rangle = N\int [\delta(\mathbf{R}) + \rho g(\mathbf{R})]\exp(\mathbf{s}'\cdot\mathbf{R})d\mathbf{R}\,. \tag{V C.7}$$

From Eqs. (V C.6) and (V C.7), we have

$$C(\mathbf{R}, 0) = \delta(\mathbf{R}) + \rho g(\mathbf{R})\,. \tag{V C.8}$$

This is consistent with the result obtained from Eqs. (28.59) and (28.85).

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# Chapter Six

# Frictional and Dynamical Properties of Dilute Solutions

## 29. Introduction

In this chapter we turn to the study of the nonequilibrium properties of dilute polymer solutions, for example, the viscosity, the sedimentation coefficient, and the diffusion coefficient. When the solution is infinitely dilute, all these properties are intimately related to the molecular dimensions discussed in Chapters II and III, and their measurement provides a useful method of molecular characterization. Theoretical investigation of the solution viscosities of flexible-chain polymers was pioneered by a number of workers[1–5] in the late 1930s through the mid-1940s. Most of the investigations were intended to deduce the so-called Staudinger rule which states that the quantity $[\eta]$, now called the *intrinsic viscosity*, is proportional to the polymer molecular weight. However, it was the Kirkwood–Riseman theory,[6] published in 1948, which provided the foundation for later significant advances in this field. Besides the frictional properties such as the viscosity in steady flow, the sedimentation velocity, and the diffusion coefficient, the nonequilibrium properties of polymer solutions include those dynamical phenomena which involve fluid flow and mechanical and electrical responses to an external applied force, mechanical or electrical, varying with time. Some of these problems are also discussed in this chapter.

There are three basic ideas in the development of the theory of the frictional properties of polymer solutions. First, the solvent is regarded as a continuous viscous fluid. For rigid solute molecules, hydrodynamics may then be used to calculate the viscosity and friction coefficients. Typical examples are provided by Stokes' law and Einstein's calculation[7] of the intrinsic viscosity of rigid sphere molecules. The second point is concerned with chain polymers. For these molecules, the elements or segments constituting the polymer chain may be considered to be the centers of resistance to the flow. Then the fluid velocity at the point of location of each segment will be perturbed by the presence of the other segments. The effects of these perturbations are cooperative and lead to specific hydrodynamic interactions. When the solution is not dilute, there exist not only intramolecular but also intermolecular hydrodynamic interactions. A discussion of hydrodynamic interactions was given first by Burgers,[8] and subsequently by Hermans,[3] Peterlin,[9] and Kirkwood and Riseman,[6] using the Oseen formula[10] which arises as a solution of the Navier–Stokes equation of hydrodynamics. In all the later developments, the formulation of the hydrodynamic interaction is based on the Kirkwood–Riseman method. The third basic point is that it is necessary to take into account the Brownian motion of the solute molecule. A nonspherical molecule under the influence of an external force field, or fluid flow, will undergo irregular motion such as is characteristic of Brownian motion, in addition to a regular motion determined by the force field. For example, the disorienting effect of Brownian motion on a rod molecule in shear flow is well known. Of course, this particular effect disappears for rigid sphere molecules. In the case of flexible-chain polymers, the influence of internal (segmental) Brownian motion becomes important. In general, the analysis of the motion of the molecule under these circumstances may be conveniently carried through using the generalized diffusion equation which is satisfied by the molecular distribution function.

One of the important objectives of this chapter is to study the effects of the excluded volume on the frictional properties in order to complete the two-parameter theory of the equilibrium and nonequilibrium properties of dilute polymer solutions. However, very few such investigations have been published, and many of the sections of this chapter are necessarily restricted to the study of unperturbed chains. Indeed, there have been a number of significant advances in the theory of the frictional properties of unperturbed chains, especially in relation to the problems of the chain structure. This newly developing field is reviewed in Section 36.

## 30. Some Fundamentals

This section presents the fundamental physical analysis of the frictional properties of polymer solutions. We give a brief description of the phenomenological theory of viscosity, sedimentation, and diffusion along with the terminology and the definitions of the physical quantities to be evaluated in this chapter. Basic expressions for some of these quantities are derived. We also describe briefly the theory of Brownian motion in order to make clear the relationship between the friction and diffusion coefficients, and to underpin our discussion of the generalized diffusion problem.

## 30a. The Viscosity Coefficient

### 30a(i). Stress and Strain Tensors

Consider three planes passing through a point in a continuous viscous fluid, and perpendicular to the $x$, $y$, and $z$ axes of a Cartesian coordinate system. The force, per unit area, exerted across the first plane by the fluid on the positive side of that plane on the fluid on the negative side of that plane may be decomposed into $x$, $y$, and $z$ components, which we denote by $\sigma_{xx}$, $\sigma_{xy}$, $\sigma_{xz}$, respectively. Similarly, the force across the second plane may be decomposed into $\sigma_{yx}$, $\sigma_{yy}$, $\sigma_{yz}$, and the force across the third plane into $\sigma_{zx}$, $\sigma_{zy}$, $\sigma_{zz}$. The force $\boldsymbol{\sigma}_\nu$ per unit area, i.e., the stress, exerted across any surface with unit normal vector $\mathbf{e}_\nu$ by the fluid on the positive side[*] on the fluid on the negative side may be expressed in terms of these nine components of the force; that is,

$$\boldsymbol{\sigma}_\nu = \boldsymbol{\sigma}\mathbf{e}_\nu \,, \tag{30.1}$$

where $\boldsymbol{\sigma}$ is the *stress tensor* (whose components are $\sigma_{xx}$, $\sigma_{xy}$, and so on). When the fluid on one side of the surface moves with respect to the other, the tangential component of $\boldsymbol{\sigma}_\nu$ does not vanish. This is the fundamental characteristic of a viscous fluid. It can be shown that the stress tensor is symmetric. It is sometimes convenient to use the subscript $i$, $j$, …, instead of $x$, $y$, and $z$; $i$, $j$, …, take the values 1, 2, and 3, corresponding to the components of vectors and tensors along the $x$, $y$, and $z$ axes, respectively. We may then write

$$\sigma_{ij} = \sigma_{ji} \,. \tag{30.2}$$

Let $\mathbf{v}$ be the velocity of the fluid at the point $\mathbf{r} = (x, y, z) = (x_1, x_2, x_3)$. We then have

$$d\mathbf{v} = \mathbf{g} d\mathbf{r} \,, \tag{30.3}$$

where $\mathbf{g}$ is a tensor whose components are given by

$$g_{ij} = \frac{\partial v_i}{\partial x_j} \,. \tag{30.4}$$

Now $\mathbf{g}$ may be split into symmetric and antisymmetric parts:

$$\mathbf{g} = \mathbf{f} + \boldsymbol{\Omega} \,, \tag{30.5}$$

the components of $\mathbf{f}$ and $\boldsymbol{\Omega}$ being

$$f_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) = f_{ji} \,, \tag{30.6}$$

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[*] The positive side of a surface is taken as the side on which the unit normal vector of the surface is positive.

$$\Omega_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i}\right) = -\Omega_{ji}\,. \tag{30.7}$$

The contribution of $\boldsymbol{\Omega}$ to $d\mathbf{v}$ may be written as

$$\boldsymbol{\Omega} d\mathbf{r} = \boldsymbol{\omega} \times d\mathbf{r}\,, \tag{30.8}$$

where $\boldsymbol{\omega}$ is a vector whose components are $\Omega_{32}$, $\Omega_{13}$, and $\Omega_{21}$. In other words, the antisymmetric tensor $\boldsymbol{\Omega}$ is associated with the rotation of the fluid about the point $\mathbf{r}$, the angular velocity being $\boldsymbol{\omega}$. Thus, the symmetric tensor $\mathbf{f}$ represents the deformation of the fluid, and is called the *strain tensor.* For an incompressible fluid, the volume is constant, and we therefore have

$$\nabla \cdot \mathbf{v} = \text{trace}\ \mathbf{f} = 0\,. \tag{30.9}$$

In the classical hydrodynamics of viscous incompressible fluids, the relationship between the stress and strain is given by[11]

$$\sigma_{ij} = -p\delta_{ij} + 2\eta f_{ij}\,, \tag{30.10}$$

where $p$ is the pressure, and the quantity $\eta$ is called the *shear viscosity coefficient.* That is,

$$\begin{aligned} \sigma_{ij} &= \eta\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) \qquad \text{for } i \neq j \\ &= -p + 2\eta\frac{\partial v_i}{\partial x_i} \qquad\quad \text{for } i = j\,. \end{aligned} \tag{30.11}$$

The off-diagonal components $\sigma_{ij}$ are called the shear stresses, while the diagonal components $\sigma_{ii}$ represent the normal stresses.

We now consider the simple case for which the velocity field of the fluid is given by

$$v_x = gy\,, \qquad v_y = 0\,, \qquad v_z = 0\,. \tag{30.12}$$

This two-dimensional flow can be generated by the motion of one of two parallel plates. If the plates are both perpendicular to the $y$ axis, and one is moved with a constant velocity in the direction of the $x$ axis, as depicted in Fig. VI.1, then Eq. (30.12) describes the flow field. The *rate of shear* or *velocity gradient* is $g$. In this case, the shear stress $\sigma_{xy}$ becomes

$$\sigma_{xy} = \eta\frac{\partial v_x}{\partial y} = \eta g\,. \tag{30.13}$$

Further, we may write $\mathbf{v} = \mathbf{g}\mathbf{r}$, and the symmetric and antisymmetric parts of $\mathbf{g}$ are then given by

$$\mathbf{f} = \begin{pmatrix} 0 & \frac{1}{2}g & 0 \\ \frac{1}{2}g & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\,, \tag{30.14}$$

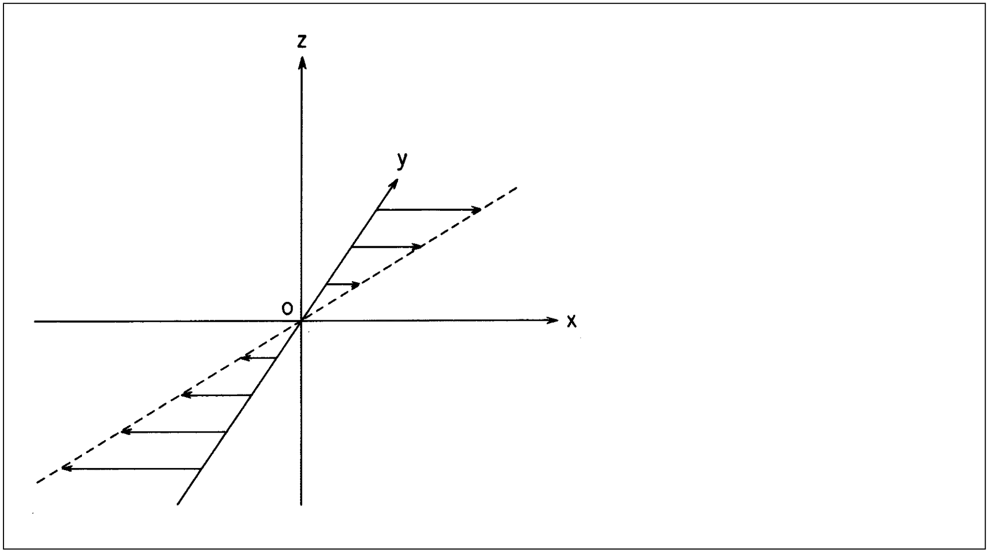

**Fig. VI.1.** The velocity field given by Eq. (30.12).

$$\mathbf{\Omega} = \begin{pmatrix} 0 & \frac{1}{2}g & 0 \\ -\frac{1}{2}g & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} . \tag{30.15}$$

The angular velocity associated with the $\mathbf{\Omega}$ given by Eq. (30.15) is $\boldsymbol{\omega} = (0, 0, -\frac{1}{2}g)$, corresponding to rotation of the fluid about the $z$ axis. On the other hand, the velocity associated with the deformation is $\mathbf{fr} = (\frac{1}{2}gy, \frac{1}{2}gx, 0)$. The stram lines for this part of the flow can be determined from the differential equation, $dx/(\mathbf{fr})_x = dy/(\mathbf{fr})_y$; that is, they are hyperbolas with the equation, $x^2 - y^2 =$const. The deformation and rotation components of the flow (30.12) are shown in Fig. VI.2.

A fluid whose shear viscosity is independent of $g$ is called a *Newtonian* fluid, while a fluid whose shear viscosity depends on $g$ is called a *non-Newtonian* fluid. In general, polymer solutions exhibit non-Newtonian viscosities at large $g$. In this book, however, most of the calculations are limited to consideration of the zero-shear viscosity.

### 30a(ii). Intrinsic Viscosity

Let $\eta$ and $\eta_0$ be the viscosity coefficients of the solution and solvent, respectively. For dilute solutions $\eta$ may be expanded in powers of the solute concentration $c(g/cc)$;

$$\eta = \eta_0(1 + a_1 c + a_2 c^2 + \cdots) . \tag{30.16}$$

Clearly, the coefficient $a_1$ represents the relative increase in viscosity per solute molecule, and is a quantity concerned with a single solute molecule. This coefficient is called the *intrinsic viscosity* and denoted

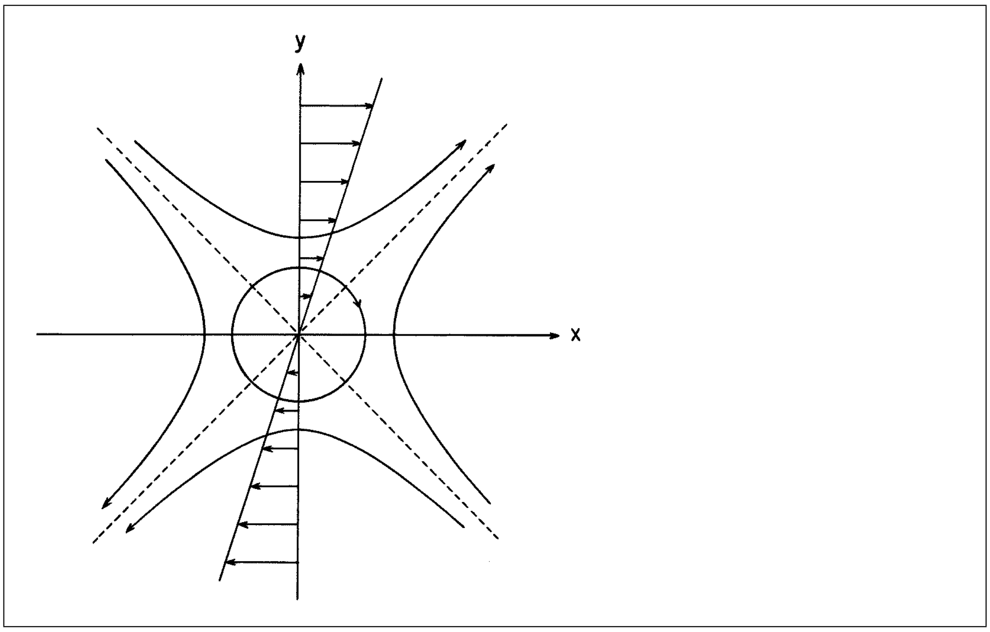

**Fig. VI.2.** Stream lines for the deformation and rotation components of the flow given by Eq. (30.12).

by $[\eta]$. We then have

$$a_1 \equiv [\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c} . \tag{30.17}$$

We now derive a basic expression for the intrinsic viscosity of flexible-chain polymers. Suppose that before and after the introduction of the solute molecules, the fluids (solvent and solution) have the same velocity field given by Eq. (30.12), i.e., $\mathbf{v} = (gy, 0, 0)$. Let $\boldsymbol{\sigma}_\nu$ and ${\boldsymbol{\sigma}_\nu}^0$ be the stresses exerted across a unit area $S$ with unit normal vector $\mathbf{e}_\nu$ in the solution and solvent, respectively. We evaluate the increase $(\boldsymbol{\sigma}_\nu - {\boldsymbol{\sigma}_\nu}^0)$ in stress (at constant rate of shear) due to the introduction of the polymer molecules, following the procedure of Kramers.[4] The stress will be increased only when the bonds of the polymer chains intersect the plane $S$, and the tensions in the bonds are transformed into the stress. That is, the tension $\mathbf{T}_j$ in the $j$th (effective) bond of a chain is just its contribution to $(\boldsymbol{\sigma}_\nu - {\boldsymbol{\sigma}_\nu}^0)$ if the sign of $\mathbf{T}_j$ is chosen as shown in Fig. VI.3. If $\mathbf{r}_j$ is the $j$th bond vector and $\rho$ is the number of polymer molecules in a unit volume, the number of the $j$th bonds which intersect the plane $S$ is $\rho(\mathbf{r}_j \cdot \mathbf{e}_\nu)P(\{\mathbf{r}_n\})d\{\mathbf{r}_n\}$ for a given configuration $\{\mathbf{r}_n\}$. Since all bonds of a chain (of $n$ bonds) and all configurations contribute to the excess stress, we obtain

$$\boldsymbol{\sigma}_\nu = {\boldsymbol{\sigma}_\nu}^0 + \rho \sum_{j=1}^{n} \int \mathbf{T}_j (\mathbf{r}_j \cdot \mathbf{e}_\nu) P(\{\mathbf{r}_n\}) d\{\mathbf{r}_n\}$$

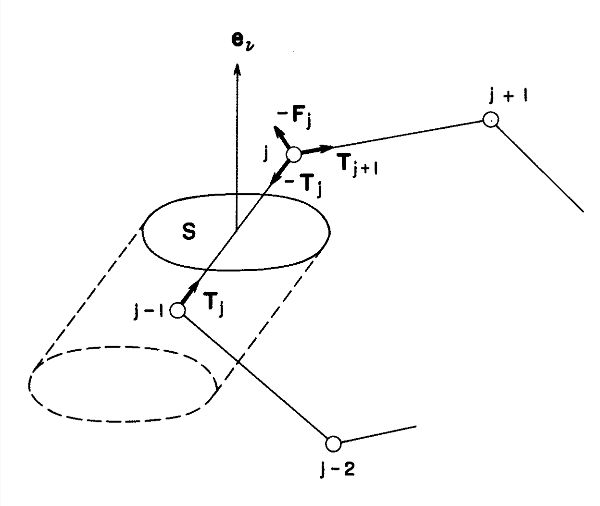

**Fig. VI.3.** Contribution of the tension in the *j*th bond of a chain to the excess stress across a plane *S*.

$$= \boldsymbol{\sigma}_\nu{}^0 + \rho \sum_j \langle \mathbf{T}_j (\mathbf{r}_j \cdot \mathbf{e}_\nu) \rangle \,. \tag{30.18}$$

Now, the equation of motion for the $j$th segment, or "bead,"of mass $m$ is

$$m\ddot{\mathbf{R}}_j = \mathbf{T}_{j+1} - \mathbf{T}_j - \mathbf{F}_j \tag{30.19}$$

where $\mathbf{R}_j$ is the position vector of the $j$th segment, and $-\mathbf{F}_j$ is the frictional force exerted by the fluid on the $j$th segment.* Since the inertia term may be neglected, Eq. (30.19) reduces to

$$\mathbf{F}_j = \mathbf{T}_{j+1} - \mathbf{T}_j \quad (j = 0, 1, 2, \ldots, n) \tag{30.20}$$

with $\mathbf{T}_0 = \mathbf{T}_{n+1} = 0$. Substitution of Eq. (30.20) into Eq. (30.18) leads to

$$\boldsymbol{\sigma}_\nu = \boldsymbol{\sigma}_\nu{}^0 - \rho \sum_j \langle \mathbf{F}_j (\mathbf{R}_j \cdot \mathbf{e}_\nu) \rangle \,, \tag{30.21}$$

where we have used the relation, $\mathbf{r}_j = \mathbf{R}_j - \mathbf{R}_{j-1}$ In particular, if we take $\mathbf{e}_\nu = \mathbf{e}_y$, the $x$ component of $\boldsymbol{\sigma}_\nu$ becomes

$$\sigma_{xy} = \sigma_{xy}{}^0 - \rho \sum_j \langle (\mathbf{F}_j \cdot \mathbf{e}_x)(\mathbf{R}_j \cdot \mathbf{e}_y) \rangle \,. \tag{30.22}$$

Recalling that $\sigma_{xy} = \eta g$ for the flow under consideration, we obtain

$$\eta = \eta_0 - \frac{\rho}{g} \sum_j \langle (\mathbf{F}_j \cdot \mathbf{e}_x)(\mathbf{R}_j \cdot \mathbf{e}_y) \rangle \,. \tag{30.23}$$

*The $j$th segment exerts the force $\mathbf{F}_j$ on the fluid. In Eq. (30.19), we have omitted a fluctuating force, which makes no contribution to the final result. For a discussion of the role of the fluctuating force, see the next section.

From Eqs. (30.17) and (30.23), we find

$$\begin{aligned}[\eta] &= -\frac{N_\mathrm{A}}{M\eta_0 g}\sum_j \langle (\mathbf{F}_j\cdot\mathbf{e}_x)(\mathbf{R}_j\cdot\mathbf{e}_y)\rangle \\ &= -\frac{N_\mathrm{A}}{M\eta_0 g}\sum_j \langle F_{jx}y_j\rangle\,, \end{aligned} \tag{30.24}$$

where $N_\mathrm{A}$ is the Avogadro number, $M$ is the molecular weight of the polymer, and in the second line we have put $\mathbf{F}_j\cdot\mathbf{e}_x = F_{jx}$ and $\mathbf{R}_j\cdot\mathbf{e}_y = y_j$, for simplicity. The configurational average in Eq. (30.24) is to be evaluated at infinite dilution.

Alternatively the basic equation (30.24) for the intrinsic viscosity may be obtained from a consideration of energy dissipation. If ${\mathbf{v}_j}^0$ is the original velocity of the solvent fluid at the point of location of the $j$th segment, the work done in unit time by the fluid for the $j$th segment is $-\mathbf{F}_j\cdot{\mathbf{v}_j}^0$, which is equal to $-gF_{jx}y_j$ since ${\mathbf{v}_j}^0 = (gy_j, 0, 0)$. The increase in energy loss in unit time and in unit volume due to the presence of polymer molecules is therefore, on the average, equal to

$$w = -\rho g \sum_j \langle F_{jx}y_j\rangle\,. \tag{30.25}$$

Suppose now that one of the two parallel plates of area $A$ at a distance $h$ is moving with the velocity $v = gh$ with respect to the other (which is at rest). Then the frictional force on the moving plate of $F = \eta g A$, and the displacement of this plate per unit time is $v = gh$. Furthermore, the total amount of work dissipated in the volume $Ah$ per unit time is $Fv = \eta g^2 Ah$, and we have

$$w = (\eta - \eta_0)g^2\,. \tag{30.26}$$

From Eqs. (30.25) and (30.26), we recover Eq. (30.23), and therefore Eq. (30.24).

Finally, we consider the case for which the rate of shear is harmonic function of time,

$$g = g_0 \exp(i\omega t)\,. \tag{30.27}$$

Then, the viscosity coefficient of a polymer solution is complex, and we denote it by $\bar\eta = \eta' - i\eta''$. The complex viscosity coefficient $\bar\eta$ is phenomenologically related to the complex rigidity modulus $\bar G = G' + iG''$ by the equation,

$$\bar G = i\omega\bar\eta\,. \tag{30.28}$$

The *complex intrinsic viscosity* $[\bar\eta]$ and *complex intrinsic rigidity* $[\bar G]$ are defined by

$$[\bar\eta] \equiv \lim_{c\to 0}\frac{\bar\eta - \eta_0}{\eta_0 c} = [\eta'] - i[\eta'']\,, \tag{30.29}$$

$$[\bar G] \equiv \lim_{c\to 0}\frac{\bar G - i\omega\eta_0}{c} = [G'] + i[G'']\,. \tag{30.30}$$

From Eqs. (30.28) to (30.30), we obtain

$$\begin{aligned} [\bar{G}] &= i\omega\eta_0[\bar{\eta}]\,, \\ [G'] &= \omega\eta_0[\eta'']\,, \\ [G''] &= \omega\eta_0[\eta']\,. \end{aligned} \tag{30.31}$$

Clearly $[\bar{\eta}]$ is given by Eq. (30.24) with Eq. (30.27). At high frequency, the imaginary part of $[\bar{\eta}]$ does not vanish as seen in later sections, and the polymer solution exhibits rigidity. Sometimes $[\eta']$ is called the *intrinsic dynamic viscosity*, and $[G']$ and $[G'']$ are called the *intrinsic storage modulus* and the *intrinsic loss modulus*, respectively.

## 30b. The Friction Coefficient

If $\mathbf{F}$ is the force applied in the center of mass of a molecule immersed in a solvent to produce its velocity $\mathbf{u}$, the (translational) *friction coefficient* $f$ of the molecule is defined by

$$\mathbf{F} = f\mathbf{u}\,. \tag{30.32}$$

For flexible-chain polymers, $\mathbf{F}$ is equal to the sum of the average forces exerted on the fluid by the individual segments of the molecule,

$$\mathbf{F} = \sum_{j=0}^{n} \langle \mathbf{F}_j \rangle\,. \tag{30.33}$$

The friction coefficient is one of the important quantities to be evaluated in this chapter, and is related to the sedimentation and diffusion coefficients which can be determined experimentally.

### 30b(i). Sedimentation Coefficient

A force field as great as several hundred thousand times the acceleration of gravity can be obtained by the use of an ultracentrifuge. In such a field there results a flow of polymer, recognizable as a velocity $u$ of the polymer molecule in solution. The centrifugal force acting on the molecule located at a distance $r$ from the axis of rotation is $F = (M/N_\mathrm{A}) \times (1 - \bar{v}\bar{\rho})\omega^2 r$, with $\omega$ the angular velocity, $\bar{v}$ the partial specific volume of the polymer, and $\bar{\rho}$ the density of the solution, $(1 - \bar{v}\bar{\rho})$ being the correction factor for buoyancy. This force is equal to the frictional force $fu$. The *sedimentation coefficient* $s$ is then defined by

$$s \equiv \frac{u}{\omega^2 r} = \frac{M(1 - \bar{v}\bar{\rho})}{N_\mathrm{A} f}\,. \tag{30.34}$$

In general, $f$ and $s$ depend on concentration, and may be expanded as follows,

$$f = f_0(1 + k_s c + \cdots)\,, \tag{30.35}$$

$$\frac{1}{s} = \frac{1}{s_0}(1 + k_s c + \cdots) \tag{30.36}$$

with $f_0$ and $s_0$ the friction and sedimentation coefficients at infinite dilution, respectively.

We note that Eq. (30.34) for the sedimentation velocity is valid only when the ultracentrifuge is operated with high speed. In the case of low-speed operation, the effect of diffusion, of Brownian motion, must be taken into account. The concentration as a function of the position and time is then given by a solution of a partial differential equation for the diffusion process under the influence of an external force [see Section 30c], namely the Lamm equation.[12] The approach to sedimentation equilibrium will not be discussed here.

### 30b(ii). Diffusion Coefficient

When there is a concentration gradient in solution, it gives rise to a flow of matter which tends to make the concentration uniform throughout the solution. This is the diffusion process. Suppose that a concentration gradient exists in the direction of the $x$ axis. The current density $J$ (i.e., the flow of solute molecules per unit time across a unit area perpendicular to the $x$ axis) is given by Fick's equation,

$$J = -D\frac{\partial c}{\partial x}\,. \tag{30.37}$$

The coefficient $D$ is known as the (translational) *diffusion coefficient.* Combining Eq. (30.37) with the equation of continuity.

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}\,, \tag{30.38}$$

we obtain the (one-dimensional) diffusion equation,

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}\,. \tag{30.39}$$

In general, $D$ is also dependent on concentration, and we may expand it in the form,

$$D = D_0(1 + k_D c + \cdots) \tag{30.40}$$

with $D_0$ the diffusion coefficient at infinite dilution.

Now, according to thermodynamics of irreversible processes,[13] the flux $J$ is proportional to the force $X$ (per molecule) which causes the flow. In the present case, $X$ is equal to the negative gradient of the solute chemical potential $\mu_1$ (per molecule); that is,

$$J = LX = -L\frac{\partial \mu_1}{\partial x}\,. \tag{30.41}$$

Since the velocity of the flow is $J/c = X/f$, we find $L = c/f$. Further, we have

$$\frac{\partial \mu_1}{\partial x} = \frac{\partial \mu_1}{\partial c}\frac{\partial c}{\partial x} = \frac{M}{N_A c}(1 - \bar{v}c)\frac{\partial \pi}{\partial c}\frac{\partial c}{\partial x}\,, \tag{30.42}$$

where $\pi$ is the osmotic pressure, and we have used the Gibbs–Duhem equation in obtaining the second equality. From Eqs. (30.37), (30.41), and (30.42), we then obtain

$$\begin{aligned} D &= \frac{M}{N_\mathrm{A} f}(1 - \bar{v}c)\frac{\partial \pi}{\partial c} \\ &= \frac{kT}{f}(1 - \bar{v}c)(1 + 2A_2 Mc + \cdots)\,, \end{aligned} \tag{30.43}$$

and therefore

$$D_0 = \frac{kT}{f_0}\,, \tag{30.44}$$

$$k_s + k_D = 2A_2 M - \bar{v}\,. \tag{30.45}$$

Equation (30.44), is Einstein's relation between the diffusion and friction coefficients.

## 30c. Brownian Motion

The dynamical behavior of a Brownian particle may be described by the Langevin equation,[14, 15]

$$m\frac{d\mathbf{u}}{dt} = -\zeta\mathbf{u} + \mathbf{F} + \mathbf{A}(t)\,, \tag{30.46}$$

where $\mathbf{u}$ is the velocity of the particle with mass $m$ and friction coefficient $\zeta$, and the right-hand side of the equation represents the forces acting on the particle. These consist of an external force field $\mathbf{F}$ and forces exerted by the surrounding medium. The influence of the surrounding medium on the motion of the particle can be split into two parts; one is a systematic part $-\zeta\mathbf{u}$ representing a frictional force exerted on the particle, and the other is a fluctuating part $\mathbf{A}(t)$ which is characteristic of the Brownian motion. Equation (30.46) is not an ordinary differential equation in that $\mathbf{u}$ is not determinable as a function of the quantities on the right-hand side of the equation. Rather, since the right-hand side contains a fluctuating term, $\mathbf{u}$ is to be regarded as a stochastic variable characterized by a distribution function. Thus, to solve the stochastic differential equation (30.46) is to find the distribution function describing the Brownian motion of the particle, i.e., the probability that the particle at a particular time will be located at some specified position with a specified velocity. In our problems, the velocity distribution is not of interest, and we need only consider the configurational distribution function.

As already described in Appendix III A, when the changes in the variable are frequent and small, the distribution function can also be obtained from the Fokker–Planck equation. For a free Brownian particle, the configurational distribution function $P(\mathbf{R}, t)$ satisfies Eq. (III A.8), and the transition probability that $\mathbf{R}$ suffers an increment $\mathbf{r}$ in time $\Delta t$ is given by

$$\psi(\mathbf{R}, t; \mathbf{r}) = (4\pi D\Delta t)^{-3/2} \exp(-r^2/4D\Delta t) \tag{30.47}$$

with

$$D = kT/\zeta\,. \tag{30.48}$$

We then have $\langle \mathbf{r} \rangle = 0$ and $\langle \mathbf{rr} \rangle = 2D\Delta t\mathbf{I}$ in Eq. (III A.8), from which we obtain

$$\frac{\partial P}{\partial t} = D\nabla^2 P\,. \tag{30.49}$$

This is the diffusion equation. Since the solute concentration $c$ is proportional to $P$, for the one-dimensional diffusion Eq. (30.49) reduces to Eq. (30.39). When there exists an external force field $\mathbf{F}$, by a generalization of the Fokker–Planck equation we can obtain the differential equation[14, 16]

$$\frac{\partial P}{\partial t} = \nabla \cdot \left( D\nabla P - \frac{\mathbf{F}}{\zeta} P \right), \tag{30.50}$$

which is often referred to as *Smoluchowski's equation.* Equation (30.50) from which the configurational distribution function can be obtained may be written in the form of the continuity equation,

$$\frac{\partial P}{\partial t} = -\nabla \cdot \mathbf{J} \tag{30.51}$$

with

$$\mathbf{J} = P\mathbf{F}/\zeta - D\nabla P\,. \tag{30.52}$$

The current density $\mathbf{J}$ is made up of a convective part and a diffusive part. If the solvent in which the particle is immersed has a velocity field $\mathbf{v}$, this contribution to the convective part must be added; that is,

$$\mathbf{J} = P\mathbf{v} + P\mathbf{F}/\zeta - D\nabla P\,. \tag{30.53}$$

If $\mathbf{F}$ can be derived from a potential $U$ so that $\mathbf{F} = -\nabla U$, then at equilibrium we have $P = \text{const. } \exp(-U/kT)$ with $\mathbf{J} = \mathbf{v} = 0$ and we recover Eq. (30.48).

The above discussion has been concerned with a simple particle with scalar translational friction and diffusion coefficients. It is well known, however, that a rigid molecule such as an ellipsoid shows a resistance to motion through a fluid which varies with the orientation of the molecule to the flow. For this case three different friction coefficients corresponding to translations parallel to the symmetry axes are needed. Correspondingly, we have three diffusion coefficients. The friction coefficient, and also the diffusion coefficient, then become tensors and will normally consist of nine components, which reduce to three when the principal axes are used as the reference system. Similar considerations apply to rotatory motions and correspondingly to *rotatory friction* and *diffusion coefficients.* A flexible polymer chain will add new degrees of freedom corresponding to bonds which can also undergo Brownian motion. That is, segments of the chain can move subject to the constraints that characterize the molecule. This type of Brownian motion is referred to as the *internal* or *micro-Brownian motion.* There will again be not one but a multitude of diffusion coefficients describing the motions of different sections of the chain, and these will constitute the components of the *internal* or *microdiffusion tensor*. The number of such components depend on the number of degrees of internal freedom. The generalized diffusion equation and the diffusion tensor for a flexible chain will be given in Section 32.

## 31. The Hydrodynamic Interaction: The Kirkwood–Riseman Theory

When a polymer chain is placed in a fluid in which there is a velocity field, the flow is perturbed by the resistance offered by each polymer segment. The change in flow at any point in the fluid is therefore the sum of the perturbations to the fluid flow of each of the segments. In addition, the general effects of the perturbations are cooperative in that effects at one segment are felt at another. In general, when there are two or more centers of resistance to a flow of fluid, there always occurs *hydrodynamic interaction* between the resistance centers. The flow perturbations and the hydrodynamic interaction between segments may be obtained by the use of the method of Oseen.[8, 10] This method is based on a solution of the Navier–Stokes equation of hydrodynamics (Appendix VI A) possessing a singularity arising from the point force exerted on the fluid. It describes the velocity perturbation $\mathbf{v}'$ in the fluid at a distance $\mathbf{r}$ from a point at which a force $\mathbf{F}$ is exerted on the fluid;

$$\mathbf{v}' = \mathbf{T}\mathbf{F} \tag{31.1}$$

with

$$\mathbf{T} = \frac{1}{8\pi\eta_0 r}\left(\mathbf{I} + \frac{\mathbf{r}\mathbf{r}}{r^2}\right), \tag{31.2}$$

where $\mathbf{I}$ is the unit tensor. The tensor $\mathbf{T}$ is referred to as the *Oseen tensor*, and the derivation is given in Appendix VI B. We note that the velocity perturbation given by the Oseen formula is independent of the original flow because of the Stokes approximation employed in deriving it.

If $\mathbf{u}_i$ is the velocity of the $i$th segment of a polymer chain and $\mathbf{v}_i$ is the velocity the fluid would possess at the point of location of the $i$th segment if that segment were absent, the force $\mathbf{F}_i$ exerted on the fluid by the $i$th segment is given by

$$\mathbf{F}_i = \zeta(\mathbf{u}_i - \mathbf{v}_i) \tag{31.3}$$

with $\zeta$ the (translational) friction coefficient of the segment. $\zeta$ depends both on the fluid and the structure of segment. The fluid velocity $\mathbf{v}_i$ is the sum of the original velocity ${\mathbf{v}_i}^0$ existing in the fluid in the absence of the polymer molecule and the summed Oseen perturbations from all other segments of the same molecule (at infinite dilution); that is,

$$\mathbf{v}_i = {\mathbf{v}_i}^0 + {\mathbf{v}_i}' \tag{31.4}$$

with

$$\mathbf{v}_i{}' = \sum_{\substack{j=0 \\ \neq i}}^{n} \mathbf{T}_{ij}\mathbf{F}_j \,, \tag{31.5}$$

$$\mathbf{T}_{ij} = \frac{1}{8\pi\eta_0 R_{ij}}\left(\mathbf{I} + \frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{{R_{ij}}^2}\right), \tag{31.6}$$

where $\mathbf{R}_{ij}$ is the distance between the $i$th and $j$th segments. Substitution of Eqs. (31.4) and (31.5) into Eq. (31.3) leads to a set of linear equations for $\mathbf{F}_i$,

$$\mathbf{F}_i = \zeta(\mathbf{u}_i - {\mathbf{v}_i}^0) - \zeta \sum_{\substack{j=0 \\ \neq i}}^{n} \mathbf{T}_{ij}\mathbf{F}_j \,. \tag{31.7}$$

Equation (31.7) is the basis of the Kirkwood–Riseman theory[6] of the intrinsic viscosity and the friction coefficient of polymer molecules. Their evaluation of (31.7) is carried out for the unperturbed linear flexible chain without explicit consideration of micro-Brownian motion.

## 31a. Intrinsic Viscosities

Suppose that the solvent has the unperturbed velocity field given by Eq. (30.12) in the absence of the polymer molecule. When a polymer molecule is introduced into the system, the molecular center of mass acquires a mean velocity equal to the local velocity of the solvent. Therefore, the molecular center of mass may be considered to be fixed at the origin of the coordinate system, and we have

$${\mathbf{v}_i}^0 = g(\mathbf{S}_i \cdot \mathbf{e}_y)\mathbf{e}_x \,, \tag{31.8}$$

where $\mathbf{S}_i$ is the distance between the $i$th segment and the center of mass. The molecule will then rotate as a whole around the $z$ axis with the rotational part of the solvent flow, the angular velocity of rotation being $\boldsymbol{\omega} = -\frac{1}{2}g\mathbf{e}_z$, provided that the velocity gradient is constant and small. This conclusion can also be obtained from the condition that the average torque (moment of the frictional force) around the center of mass is zero in steady flow. Thus we have

$$\mathbf{u}_i = \tfrac{1}{2}g(\mathbf{S}_i \times \mathbf{e}_z) \,, \tag{31.9}$$

and Eq. (31.7) becomes

$$\mathbf{F}_i = -\tfrac{1}{2}\zeta g(y_i\mathbf{e}_x + x_i\mathbf{e}_y) - \zeta \sum_{\substack{j=0 \\ \neq i}}^{n} \mathbf{T}_{ij}\mathbf{F}_j \,, \tag{31.10}$$

where we have put $\mathbf{S}_i \cdot \mathbf{e}_x = x_i$ and $\mathbf{S}_i \cdot \mathbf{e}_y = y_i$ since $\mathbf{R}_i = \mathbf{S}_i$. Multiplying the $x$ components of both sides of Eq. (31.10) by $y_k$ and taking the configurational average, we obtain

$$\langle F_{ix} y_k \rangle = -\tfrac{1}{2}\zeta g \langle y_i y_k \rangle - \zeta \sum_j \langle (\mathbf{T}_{ij}\mathbf{F}_j) \cdot \mathbf{e}_x y_k \rangle \,. \tag{31.11}$$

We now approximate $\mathbf{T}_{ij}$ by its average $\langle \mathbf{T}_{ij} \rangle$; that is, we set

$$\langle (\mathbf{T}_{ij}\mathbf{F}_j) \cdot \mathbf{e}_x y_k \rangle = \langle (\langle \mathbf{T}_{ij} \rangle \mathbf{F}_j) \cdot \mathbf{e}_x y_k \rangle \,, \tag{31.12}$$

where

$$\langle \mathbf{T}_{ij} \rangle = \frac{1}{6\pi\eta_0} \left\langle \frac{1}{R_{ij}} \right\rangle \mathbf{I} \,, \tag{31.13}$$

because the distribution of $\mathbf{R}_{ij}$ is spherically symmetric. Equation (31.11) then reduces to

$$\langle F_{ix} y_k \rangle = -\tfrac{1}{2}\zeta g \langle y_i y_k \rangle - \frac{\zeta}{6\pi\eta_0} \sum_j \left\langle \frac{1}{R_{ij}} \right\rangle \langle F_{jx} y_k \rangle \,. \tag{31.14}$$

If we define the quantity $\varphi_{ik}$ by the equation,

$$\varphi_{ik} = -\frac{18}{na^2 \zeta g} \langle F_{ix} y_k \rangle \tag{31.15}$$

with $a$ the effective bond length of the chain, the intrinsic viscosity may then be written, from Eqs. (30.24) and (31.15), in the form,

$$[\eta] = \frac{N_{\mathrm{A}} \zeta n^2 a^2}{36 \eta_0 M} F \tag{31.16}$$

with

$$F = \frac{2}{n} \sum_{i=0}^{n} \varphi_{ii} \,, \tag{31.17}$$

and Eq. (31.14) becomes

$$\varphi_{ik} = \frac{9}{na^2} \langle y_i y_k \rangle - \frac{\zeta}{6\pi\eta_0} \sum_j \left\langle \frac{1}{R_{ij}} \right\rangle \varphi_{jk} \,. \tag{31.18}$$

Since at small $g$ (strictly $g \rightarrow 0$) the equilibrium distribution function subject to no applied field may be used, for the unperturbed linear chain we obtain, from Eqs. (5.39) and (7.8),

$$\begin{aligned} \langle y_i y_j \rangle_0 &= \tfrac{1}{3} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_0 = \tfrac{1}{6} (\langle {S_i}^2 \rangle_0 + \langle {S_j}^2 \rangle_0 - \langle {R_{ij}}^2 \rangle_0) \\ &= \tfrac{1}{9} na^2 \left[ 1 - \frac{3}{2n} (i + j + |i - j|) + \frac{3}{2n^2} (i^2 + j^2) \right] . \end{aligned} \tag{31.19}$$

Further, we find by the use of the Gaussian distribution

$$\left\langle \frac{1}{R_{ij}} \right\rangle_0 = \frac{6^{1/2}}{\pi^{1/2} |i - j|^{1/2} a} \,. \tag{31.20}$$

Substitution of Eqs. (31.19) and (31.20) into Eq. (31.18) and conversion of the sum to an integral leads to an integral equation for the function $\varphi(x, y) \equiv \varphi_{ik}$ with $x = 2i/n - 1$ and $y = 2k/n - 1$,

$$\varphi(x, y) = f(x, y) - h \int_{-1}^{1} \frac{\varphi(t, y)}{|x - t|^{1/2}} dt \,, \tag{31.21}$$

where

$$f(x,y) = \tfrac{1}{8}[3(x^2+y^2) - 6|x-y| + 2]\,, \tag{31.22}$$

$$h = \zeta n^{1/2}/(12\pi^3)^{1/2}\eta_0 a\,. \tag{31.23}$$

The quantity $F$ defined by Eq. (31.17) may then be calculated from

$$F = \int_{-1}^{1} \varphi(x,x)dx\,. \tag{31.24}$$

The problem is now to solve the integral equation (31.21). It is, however, to be anticipated that we cannot obtain an analytical solution for $\varphi$ which is valid for any positive value of $h$. We first find the approximate analytical solution of Kirkwood and Riseman. Let us expand $\varphi(x,y)$ and $f(x,y)$ in Fourier series of the form,

$$\begin{aligned} \varphi(x,y) &= \sum_{k=-\infty}^{+\infty} \varphi_k(y)e^{i\pi kx}\,, \\ f(x,y) &= \sum_{k=-\infty}^{+\infty} f_k(y)e^{i\pi kx}\,. \end{aligned} \tag{31.25}$$

The integral equation of (31.21) then leads to the set of linear equations for the Fourier coefficients $\varphi_k(y)$,

$$\varphi_k(y) + h\sum_{l=-\infty}^{+\infty} a_{kl}\varphi_l(y) = f_k(y) \qquad (k = 0, \pm 1, \pm 2, \ldots)\,, \tag{31.26}$$

where the coefficients $f_k(y)$ and the matrix elements $a_{kl}$ can easily be determined. The Kirkwood–Riseman approximation consists in replacing $a_{kl}$ by the values asymptotically valid for large $|k|$ and $|l|$; that is,

$$\begin{aligned} a_{kl} &= 8\sqrt{2}/3 && \text{for } k = l = 0 \\ &= (2/|k|)^{1/2}\delta_{kl} && \text{for } k \neq 0\,. \end{aligned} \tag{31.27}$$

With this approximation we can readily solve Eqs. (31.26) and obtain

$$\varphi(x,y) = \sum_{\substack{k=-\infty \\ \neq 0}}^{+\infty} \frac{f_k(y)e^{i\pi kx}}{1 + h(2/|k|)^{1/2}} \tag{31.28}$$

with

$$f_k(y) = (3/4\pi^2k^2)e^{-i\pi ky} + (-1)^k(3iy/4\pi k)\,. \tag{31.29}$$

From Eqs. (31.24), (31.28), and (31.29), we find the Kirkwood–Riseman function,

$$F(X) = \frac{6}{\pi^2}\sum_{k=1}^{\infty} \frac{1}{k^2(1 + X/k^{1/2})}\,, \tag{31.30}$$

**TABLE VI.1.** NUMERICAL VALUES OF $XF(X)$ AS A FUNCTION OF $X$[6, 17]

| $X$ | KR | KZP | REVISED |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0.1 | 0.092 | 0.09 | 0.073 |
| 0.2 | 0.172 | 0.17 | 0.136 |
| 0.3 | 0.242 | 0.24 | 0.192 |
| 0.4 | 0.304 | 0.30 | 0.241 |
| 0.5 | 0.358 | 0.35 | 0.284 |
| 1.0 | 0.564 | 0.54 | 0.447 |
| 2.0 | 0.800 | 0.75 | 0.634 |
| 3.0 | 0.936 | 0.88 | 0.742 |
| 4.0 | 1.024 | 0.96 | 0.812 |
| 5.0 | 1.090 | 1.02 | 0.864 |
| 10.0 | 1.260 | 1.17 | 0.999 |
| 20.0 | 1.400 | 1.31 | 1.110 |
| 50.0 | 1.486 | — | 1.178 |
| 100.0 | 1.528 | — | 1.212 |
| $\infty$ | 1.588 | 1.48 | 1.259[a] |

[a] This value is due to Auer and Gardner.[18]

where

$$X = 2^{1/2}h\,. \tag{31.31}$$

The values of $XF(X)$ as a function of $X$ calculated from Eq. (31.30) are given in the second column of Table VI.1. Kirkwood, Zwanzig, and Plock[17] improved the solution by solving Eqs. (31.26) numerically by inversion of the matrix $\delta_{kl} + ha_{kl}$ by a method of successive approximation which involves the neglect of all off-diagonal elements for which $|k|$ and $|l|$ are greater than an assigned integer $m$. Their values are given in the third column of same table.

In the two limiting cases $X = 0$ and $X = \infty$, we can find the exact solutions of the integral equation of (31.21). In the case $X = 0$, we readily obtain $\varphi(x, y) = f(x, y)$ and $F(X) = 1$, and therefore

$$[\eta] = \frac{N_{\mathrm{A}}\zeta n^2 a^2}{36\eta_0 M} = \frac{N_{\mathrm{A}}\zeta n}{6\eta_0 M}\langle S^2\rangle_0 \qquad (\text{for } X = 0)\,. \tag{31.32}$$

In the case $X = \infty$, Eq. (31.21) reduces to the integral equation of the first kind,

$$f(x, y) = \int_{-1}^{1} \frac{\bar{\varphi}(t, y)}{|x - t|^{1/2}}dt \tag{31.33}$$

with $\bar{\varphi} \equiv h\varphi$. Auer and Gardner[18] solved this integral equation using a Gegenbauer polynomial expansion, and obtained the result $XF(X) = 1.259$ for $X = \infty$. It is now observed that the ratio of the KR function to the KZP function is approximately independent of $X$. For practical purposes, we may therefore use the revised values of $XF(X)$ given in the fourth column of Table VI.1, which values were obtained by multiplying the KR values by the factor 0.793 (= 1.259/1.588).

In the case $X = 0$, there are no Oseen perturbations. In other words, there is no hydrodynamic interaction between segments, and the velocity field is given by Eq. (31.8) even in the presence of the polymer segments. Thus this limiting case is referred to as *free-draining* case. From Eq. (31.32), the intrinsic viscosity is seen to be directly proportional to the molecular weight for the (unperturbed) free-draining molecule. This conclusion has been obtained independently by several authors[1,3–5] all of whom neglected the hydrodynamic interaction from the outset. Equation (31.32) is a theoretical interpretation of Staudinger's rule. In order to discuss the other limiting case, it is convenient to rewrite Eq. (31.16) in the form

$$\begin{aligned}[\eta] &= \Phi_0 \frac{{\langle R^2 \rangle_0}^{3/2}}{M} \\ &= 6^{3/2} \Phi_0 \frac{{\langle S^2 \rangle_0}^{3/2}}{M} \,, \end{aligned} \tag{31.34}$$

where

$$\Phi_0 = (\pi/6)^{3/2} N_{\mathrm{A}} [XF(X)] \,. \tag{31.35}$$

If $X$ becomes infinite, $\Phi_0$ approaches the constant $2.87 \times 10^{23}$ corresponding to the value 1.259 for $XF(X)$, and $[\eta]$ becomes proportional to ${\langle S^2 \rangle_0}^{3/2}/M$. This form of $[\eta]$ is equivalent to that for rigid sphere molecules with a radius proportional to ${\langle S^2 \rangle_0}^{1/2}$ (see Appendix VI.C). Therefore , flexible polymer chains in this limit behave hydrodynamically as rigid sphere molecules. This limit corresponds, of course, to very large hydrodynamic interaction between segments, and is referred to as the *non-free-draining case.* The present theory predicts that $[\eta]$ is proportional to $M^{1/2}$ for the (unperturbed) non-free-draining chain. This result was also derived by Kuhn and Kuhn[2] and Peterlin.[9] In general, $\Phi_0$ increases from zero to its asymptotic value as $X$ is increased from zero to infinity. Therefore, the variable $X$ or $h$ represents the degree of drainage of the solvent through the polymer molecular domain, and is called the *draining parameter.* The ratio $\Phi_0(X)/\Phi_0(\infty)$ may be regarded as the correction factor by which the hydrodynamically effective volume of the molecule is decreased by the draining effect. A theory physically equivalent to the KR theory was developed independently by Debye and Bueche,[19] who solved the Navier–Stokes equation with appropriate boundary conditions for the uniform-density sphere model.

It is important to note that Staudinger's formula is not always valid. The presently accepted empirical relationship between $[\eta]$ and $M$ (which is valid over a given range of $M$) is of the form,[20–22]

$$[\eta] \propto M^{\nu} \,, \tag{31.36}$$

where $\nu$ is a constant independent of $M$ and ordinarily lies between 0.5 and 1.0 for flexible-chain polymers. It was the intent of Kirkwood and Riseman, and also of Debye and Bueche, to interpret the intermediate values of $\nu$ (between 0.5 and 1.0) as arising from the draining effect. At the present time, however, this interpretation is not always accepted. We discuss this matter further in later sections. It is also important to examine the relationship between the friction coefficient $\zeta$ of the segment and the molecular model discussed above. According to the present theory, for random-flight chains, the intrinsic viscosity may be expressed in terms of three parameters: $n$, $a$, and $\zeta$. However, these parameters never appear separately but only in two combinations $na^2$ and $n\zeta$, since $h$ or $X$ is proportional to $(n\zeta)/\eta_0(na^2)^{1/2}$. Therefore the value to be assigned to $\zeta$ is arbitrary to the extent that a division of the chain into $n$ effective bonds is arbitrary. The same argument applies to the friction coefficient of the entire molecule.

## 31b. Translational and Rotatory Friction Coefficients

The translational friction coefficient $f_0$ of the entire molecule at infinite dilution may be evaluated from Eqs. (30.32) and (30.33) with (31.7). We suppose that there is no original velocity field, and that the average velocities of the segments may be equated to the drift velocity; that is, $\mathbf{v}_i{}^0 = 0$ and $\langle \mathbf{u}_i \rangle = \mathbf{u}$ for all $i$. From Eq. (31.7), we then have

$$\langle \mathbf{F}_i \rangle = \zeta \mathbf{u} - \zeta \sum_j \langle \mathbf{T}_{ij} \mathbf{F}_j \rangle \,. \tag{31.37}$$

If we replace $\mathbf{T}_{ij}$ by $\langle \mathbf{T}_{ij} \rangle$ as before, that is, set

$$\langle \mathbf{T}_{ij} \mathbf{F}_j \rangle = \langle \mathbf{T}_{ij} \rangle \langle \mathbf{F}_j \rangle \,, \tag{31.38}$$

Eq. (31.37) becomes

$$\langle \mathbf{F}_i \rangle = \zeta \mathbf{u} - \frac{\zeta}{6\pi\eta_0} \sum_j \left\langle \frac{1}{R_{ij}} \right\rangle \langle \mathbf{F}_j \rangle \,. \tag{31.39}$$

We now define the quantity $\psi_i$ by the equation,

$$\langle \mathbf{F}_i \rangle = \zeta \psi_i \mathbf{u} \,, \tag{31.40}$$

and convert the sums to integrals. Then, Eq. (31.39) becomes an integral equation for the function $\psi(x) \equiv \psi_i$ with $x = 2i/n - 1$,

$$\psi(x) = 1 - h \int_{-1}^{1} \frac{\psi(t)}{|x-t|^{1/2}} dt \,, \tag{31.41}$$

and the friction coefficient may be expressed, from Eqs. (30.32) and (30.33), in the form

$$f = \tfrac{1}{2} n\zeta \int_{-1}^{1} \psi(x) dx \,, \tag{31.42}$$

where we have suppressed the subscript 0 on $f$ for simplicity.

If we expand the function $\psi(x)$ in a Fourier series of the form,

$$\psi(x) = \sum_{k=-\infty}^{+\infty} \psi_k e^{i\pi kx} \,, \tag{31.43}$$

$f$ may be simply expressed as

$$f = n\zeta\psi_0 \,. \tag{31.44}$$

The coefficients $\psi_k$ satisfy a set of linear equations analogous to Eqs. (31.26). Therefore, if we use the approximation of (31.27), we can easily find the solution for $\psi_0$ and obtain for the translational friction coefficient

$$f = \frac{n\zeta}{1 + \frac{8}{3}X} \,. \tag{31.45}$$

The sedimentation coefficient and translational diffusion coefficient (at infinite dilution) can now be readily written down. For example, the latter reads

$$D = \frac{kT}{n\zeta}(1 + \tfrac{8}{3}X) \,. \tag{31.46}$$

Equations (31.45) and (31.46) are equivalent to the results derived by Hermans[3] and by Debye and Bueche.[19]

In the two limiting cases already cited we have from Eqs. (31.45) and (31.46)

$$\left.\begin{aligned} f &= n\zeta \\ D &= kT/n\zeta \end{aligned}\right\} \quad (\text{for } X = 0) \,, \tag{31.47}$$

$$\left.\begin{aligned} f &= (9\pi^{3/2}/4)\eta_0\langle S^2\rangle_0^{\,1/2} \\ D &= 0.196kT/\eta_0\langle R^2\rangle_0^{\,1/2} \end{aligned}\right\} \quad (\text{for } X = \infty) \,. \tag{31.48}$$

In the free-draining case, the translational friction coefficient of the entire molecule is simply the sum of the friction coefficient of the individual segments, as expected. In the non-free-draining case, Stokes' law is seen to be apparently satisfied, indicating that the molecule behaves as a hard sphere. We note that Eqs. (31.47) are exact, but the numerical constants in Eqs. (31.48) are incorrect, since the $f$ given by Eq. (31.45) is an approximate solution. The exact asymptotic solution of the integral equation of (31.41) was obtained by Kurata and Yamakawa,[23] and it gives the numerical factor 0.192 instead of 0.196 in $D$ of Eqs. (31.48). The difference between the two values is rather small, and therefore Eqs. (31.45) and (31.46) are fairly satisfactory.

Next, we evaluate the rotatory friction coefficient of the molecule as a whole. This can easily be done[24] when the equations derived in the previous section are used. If $\mathbf{T}$ is the torque required to produce the angular velocity $\boldsymbol{\omega}$ of the molecule around the center of mass, the rotatory friction coefficient $f_r$ is defined by

$$\mathbf{T} = f_r\boldsymbol{\omega} \,. \tag{31.49}$$

In the present case, $\mathbf{T}$ is the sum of the average torques of the individual segments of the molecule,

$$\mathbf{T} = \sum_i \langle \mathbf{S}_i \times \mathbf{F}_i \rangle \,. \tag{31.50}$$

Recalling that ${\mathbf{v}_i}^0 = 0$ and $\mathbf{u}_i = \boldsymbol{\omega} \times \mathbf{S}_i$, we obtain from Eq. (31.7)

$$\begin{aligned} \langle \mathbf{S}_k \times \mathbf{F}_i \rangle &= \zeta \langle \mathbf{S}_k \times (\boldsymbol{\omega} \times \mathbf{S}_i) \rangle - \zeta \sum_j \langle \mathbf{S}_k \times \mathbf{T}_{ij} \mathbf{F}_j \rangle \\ &= \tfrac{2}{3} \zeta \langle \mathbf{S}_i \cdot \mathbf{S}_k \rangle \boldsymbol{\omega} - \frac{\zeta}{6\pi\eta_0} \sum_j \left\langle \frac{1}{R_{ij}} \right\rangle \langle \mathbf{S}_k \times \mathbf{F}_j \rangle \,, \end{aligned} \tag{31.51}$$

where in the second line we have replaced $\mathbf{T}_{ij}$ by $\langle \mathbf{T}_{ij} \rangle$, as before. If we define the quantity $\varphi_{ik}$ by

$$\frac{9}{2na^2\zeta} \langle \mathbf{S}_k \times \mathbf{F}_i \rangle = \varphi_{ik} \boldsymbol{\omega} \,, \tag{31.52}$$

Eq. (31.51) becomes a set of linear equations for $\varphi_{ik}$ which is identical to Eq. (31.18). Therefore, we readily find from Eqs. (31.49), (31.50), and (31.52)

$$f_r = \tfrac{1}{9} \zeta n^2 a^2 F(X) \,, \tag{31.53}$$

where $F(X)$ is the same function as that appearing in the intrinsic viscosity. Since the Einstein relation holds also in the present case, we have for the rotatory diffusion coefficient $D_r (= kT/f_r)$

$$D_r = 9kT/\zeta n^2 a^2 F(X) \,. \tag{31.54}$$

In particular, for the non-free-draining molecule, we have $f_r =$ const. $\times \eta_0 {\langle S^2 \rangle_0}^{3/2}$. This is to be compared with the Stokes formula, $f_r = 8\pi\eta_0 \bar{S}^3$, for a hard sphere of radius $\bar{S}$.

Combining Eq. (31.16) with Eqs. (31.53) and (31.54), we obtain a simple relationship between the intrinsic viscosity and the rotatory friction or diffusion coefficient,

$$f_r = 4{N_{\mathrm{A}}}^{-1} \eta_0 M[\eta] \,, \tag{31.55}$$

$$D_r = N_{\mathrm{A}} kT / 4\eta_0 M[\eta] \,. \tag{31.56}$$

It is important to note that Eqs. (31.55) and (31.56) hold irrespective of the presence of the draining effect and of the excluded-volume effect, as seen from the derivation. The rotatory diffusion coefficient may be determined from *flow birefringence* experiments, and Eq. (31.56) has been confirmed by extensive data.[25] Although a similar calculation of the internal rotatory diffusion tensor has also been carried out,[24] we do not reproduce it here.

## 32. The Diffusion-Equation Approach (A): The Kirkwood General Theory

In the viscosity theory described in the previous section, the equilibrium molecular distribution function could be employed to take the configurational averages on the assumption that the rate of shear was very small. However, when the applied forces are not small or vary with time, the distribution function deviates from its equilibrium form. As already mentioned, the nonequilibrium distribution function may be conveniently obtained from a diffusion equation which describes the Brownian motion of the molecule under the influence of an external force field. In this section, we formulate in its most general form, a theory of irreversible processes in dilute polymer solutions, following Kirkwood.[26, 27]

Consider a single polymer molecule composed of $(n+1)$ segments, and let $P(\{\mathbf{R}_{n+1}\}, t)$ be the instantaneous distribution for the entire molecule at time $t$, $\mathbf{R}_j$ being the coordinates of the $j$th segment in a Cartesian coordinate system. Equation (30.51) with (30.53) may then be easily generalized to the diffusion equation for $P(\{\mathbf{R}_{n+1}\}, t)$,

$$\frac{\partial P}{\partial t} = -\sum_{i=0}^{n} \nabla_i \cdot \mathbf{J}_i \,, \tag{32.1}$$

where

$$\mathbf{J}_i = P\mathbf{v}_i + \frac{P}{\zeta}(-\nabla_i U + \mathbf{X}_i) - \frac{kT}{\zeta}\nabla_i P \tag{32.2}$$

with $\mathbf{v}_i$ the velocity of the solvent at $\mathbf{R}_i$ and $\zeta$ the friction coefficient of the segment, as before. The external force acting on the $i$th segment has been split into two parts; one arises from the intramolecular potential of mean force $U$ given by Eq. (3.2), and the other is the pure external force $\mathbf{X}_i$, centrifugal, electric, or magnetic. Since the current density $\mathbf{J}_i$ is equal to $P\mathbf{u}_i$ with $\mathbf{u}_i$ the velocity of the $i$th segment, Eq. (32.2) may be rewritten as

$$-\mathbf{F}_i - \nabla_i U + \mathbf{X}_i - kT\nabla_i \ln P = 0 \,. \tag{32.3}$$

Equation (32.3) may be obtained *formally* from the Langevin equation for the $i$th segment if the inertia term is neglected and the fluctuating force is replaced by the diffusion force $-kT\nabla_i \ln P$, a sort of statistical average value. Thus, under these circumstances, the sum of the forces acting on each segment is equal to zero. Equations (32.2) or (32.3) serve to determine the velocity of the segment under the influence of Brownian motion. In the Kirkwood–Riseman theory of viscosity, $\mathbf{u}_i$ was determined from the condition that the average external frictional torque on the molecule is equal to zero in steady shear flow.

Kirkwood's approach[26, 27] consists of writing the diffusion equation in terms of generalized curvilinear coordinates in Riemann space to obtain useful results. We note that the original theory of Kirkwood was not completely correct; it has been corrected by Ikeda[28] and subsequently by Erpenbeck and Kirkwood.[29] The general theory is developed so as to be applicable to any type of molecule, flexible or stiff, and linear, branched, or ring shaped. That is, we do not use the random-flight model, but impose structural constraints, constant bond length, bond angle, and so on, upon the model molecule composed of $(n+1)$ identical segments. Because of these constraints, the molecule will then possess a number of degrees of freedom, $m$, which is less than $3(n+1)$. The $m$-dimensional molecular configuration space is referred to as the $m$-space, and the complete $3(n+1)$-dimensional configuration space of the $(n+1)$ segments as the $e$-space; $m$-space is a subspace of the $e$-space subject to the structural constraints characteristic of the molecule. The coordinates associated with the $m$-space are denoted by $q^1$, $q^2$, …, $q^m$. In the case of a linear flexible chain, for instance, these include the $(n-1)$ angles of internal rotation, the three coordinates of the center of mass relative to an external coordinate system, and the two orientation angles of the molecule in the external system; that is, $m = n+4$. We denote the $(3n+3-m)$ coordinates of $e$-space complementary to those of the $m$-space by $q^{m+1}$, $q^{m+2}$, …, $q^{3n+3}$. These could be chosen in a large number of ways. The coordinates $q^1$, …, $q^{3n+3}$ may be regarded as generalized curvilinear coordinates.

If $\mathbf{R}$ is the $3(n+1)$-dimensional vector specifying the position of the $(n+1)$ segments in the $e$-space, we may span the $e$-space by the covariant basis vectors,

$$\mathbf{a}_\alpha = \frac{\partial \mathbf{R}}{\partial q^\alpha} = \sum_{i=0}^{n} \frac{\partial \mathbf{R}^i}{\partial q^\alpha} \qquad (\alpha = 1, \ldots, 3n+3) \tag{32.4}$$

with

$$\mathbf{R} = \sum_{i=0}^{n} \mathbf{R}^i \,, \tag{32.5}$$

where $\mathbf{R}^i$ is the position vector of the $i$th segment in the three-dimensional space of the segment. A set of basis vectors, $\mathbf{a}_1$, $\mathbf{a}_2$, …, $\mathbf{a}_{3n+3}$ defines a localized coordinate system in the $e$-space. The metric tensor of the $e$-space is given by

$$g_{\alpha\beta} = \mathbf{a}_\alpha \cdot \mathbf{a}_\beta = \sum_{i=0}^{n} \frac{\partial \mathbf{R}^i}{\partial q^\alpha} \cdot \frac{\partial \mathbf{R}^i}{\partial q^\beta} \,. \tag{32.6}$$

The contravariant basis vectors $\mathbf{a}^\alpha$ are given by

$$\mathbf{a}^\alpha = \sum_\beta g^{\alpha\beta} \mathbf{a}_\beta \,, \tag{32.7}$$

where $g^{\alpha\beta}$ are the elements of the reciprocal of the matrix $g_{\alpha\beta}$, i.e., $g^{\alpha\beta} = |g|_{\alpha\beta}/g$ with $|g|_{\alpha\beta}$ the cofactor of $g_{\alpha\beta}$ in the determinant $g = |g_{\alpha\beta}|$. The components of $g_{\alpha\beta}$ involving the complementary space depend on the choice of $q^{m+1}$, $q^{m+2}$, …, $q^{3n+3}$. We assume that these have been chosen orthogonal to $m$-space coordinates, so that the components of the metric tensor are zero between the $m$-space and its complementary space, i.e., $g_{\alpha\beta} = 0$ for $1 \leq \alpha \leq m$ and $m+1 \leq \beta \leq 3n+3$. Then, the $g^{\alpha\beta}$ also disappear between the $m$-space and its complementary space. Further, note that $g$ is equal to the product of two determinants, one for the $m$-space and one for the orthogonal complementary space.

The covariant components of any $3(n+1)$-dimensional vector or tensor are given by

$$\begin{aligned} F_\alpha &= \mathbf{F} \cdot \mathbf{a}_\alpha \,, \\ T_{\alpha\beta} &= \mathbf{a}_\alpha \mathbf{T} \mathbf{a}_\beta \,. \end{aligned} \tag{32.8}$$

The contravariant components are obtained as

$$\begin{aligned} F^\alpha &= \mathbf{F} \cdot \mathbf{a}^\alpha = \sum_\beta g^{\alpha\beta} F_\beta \,, \\ T^{\alpha\beta} &= \mathbf{a}^\alpha \mathbf{T} \mathbf{a}^\beta = \sum_\mu \sum_\nu g^{\alpha\mu} g^{\beta\nu} T_{\mu\nu} \,. \end{aligned} \tag{32.9}$$

We can obtain the mixed components $T_\alpha{}^\beta$ in a similar fashion.

We now introduce the following conventions in the notation. Greek subscripts and superscripts are used for components along the basis vectors $\mathbf{a}_\alpha$ and $\mathbf{a}^\alpha$, respectively. Latin superscripts are used for the projections of $3(n+1)$-dimensional vectors and tensors onto the three-dimensional Cartesian coordinate system of the indicated segment. Latin subscripts are used for these same projections when referred to the Cartesian system common to all segments. The previous meanings of $\mathbf{F}_i$, $\mathbf{v}_i{}^0$, $\mathbf{v}_i$, $\mathbf{u}_i$, $\mathbf{J}_i$, etc. are retained. These three-dimensional vectors may be generalized to the $3(n+1)$-dimensional $e$-space vectors $\mathbf{F}$, $\mathbf{v}^0$, $\mathbf{v}$, $\mathbf{u}$, $\mathbf{J}$, etc. as in the case of $\mathbf{R}$. In general, these generalized vectors have components in $m$-space and complementary space. However, $\mathbf{u}$ and $\mathbf{J}$ have only $m$-space components because of the structural constraints. We then have for the generalized frictional force

$$\mathbf{F} = \sum_{i=0}^{n} \mathbf{F}^i = \zeta(\mathbf{u} - \mathbf{v}) \,. \tag{32.10}$$

The generalized velocity of the solvent may be written , from Eqs. (31.4) and (31.5), in the form,

$$\mathbf{v} = \mathbf{v}^0 + \mathbf{T}\mathbf{F} \tag{32.11}$$

with

$$\mathbf{T} = \sum_{\substack{i,j \\ i \neq j}} \mathbf{T}^{ij} = \sum_{\substack{i,j \\ i \neq j}} \frac{1}{8\pi\eta_0 R_{ij}} \left( \mathbf{I}^{ij} + \frac{\mathbf{R}_{ij}{}^i \mathbf{R}_{ij}{}^j}{R_{ij}{}^2} \right) , \tag{32.12}$$

where $\mathbf{T}$ may be considered to be the $(n+1) \times (n+1)$ matrix whose elements are $\mathbf{T}^{ij}$ with $\mathbf{T}^{ij} = 0$. If we define a friction tensor $\boldsymbol{\zeta}$ in the

$e$-space by the equation,

$$\mathbf{F} = \boldsymbol{\zeta}(\mathbf{u} - \mathbf{v}^0)\,, \tag{32.13}$$

we obtain, from Eqs. (32.10) and (32.11), the relation $(\mathbf{I} + \zeta\mathbf{T})\mathbf{F} = \zeta(\mathbf{u} - \mathbf{v}^0)$. From this equation and Eq. (32.13), we find

$$\begin{aligned} \boldsymbol{\zeta} &= \zeta(\mathbf{I} + \zeta\mathbf{T})^{-1} \\ &= \zeta(\mathbf{I} - \zeta\mathbf{T} + \zeta^2\mathbf{T}^2 - \cdots)\,. \end{aligned} \tag{32.14}$$

Now let $P(\{q^m\}, t)$ be the distribution function for the molecule in $m$-space where $\{q^m\}$ denotes the $m$-space coordinates $q^1$, $q^2$, $\ldots$, $q^m$. By the use of the divergence operator in Riemann space, the continuity equation of (32.1) may then be generalized to

$$\frac{\partial P}{\partial t} = -\frac{1}{g^{1/2}} \sum_{\alpha=1}^{m} \frac{\partial(g^{1/2} J^\alpha)}{\partial q^\alpha}\,. \tag{32.15}$$

Equation (32.3) may also be generalized to the equation for the current density $\mathbf{J}$

$$\boldsymbol{\zeta}\mathbf{J} = \boldsymbol{\zeta}\mathbf{v}^0 P + (-\nabla V + \mathbf{X} + \mathbf{X}')P - kT\nabla P\,, \tag{32.16}$$

where we have used Eq. (32.13) and the relation $\mathbf{J} = \mathbf{u}P$. The force $-\nabla U$ has been split into two parts; one is the force $\mathbf{X}'$ associated with the structural constraints, and the other is the remaining part, $-\nabla V$, which arises from the potential of mean force, $V$, associated with the internal rotation and the excluded-volume effect. $\mathbf{v}^0$ and $\mathbf{X}$ have both $m$-space and complementary space components, while $\mathbf{J}$, $\nabla V$, and $\nabla P$ have only $m$-space components, and $\mathbf{X}'$ has only complementary space components. Therefore, taking covariant components of both sides of Eq. (32.16), we obtain

$$\sum_{\beta=1}^{m} \zeta_{\alpha\beta} J^\beta = (\boldsymbol{\zeta}\mathbf{v}^0)_\alpha P + \left(-\frac{\partial V}{\partial q^\alpha} + X_\alpha\right)P - kT\frac{\partial P}{\partial q^\alpha} \qquad (\alpha = 1, \ldots, m)\,. \tag{32.17}$$

Solving Eqs. (32.17) for $J^\alpha (\alpha = 1, \ldots, m)$, we find

$$J^\alpha = \sum_{\beta=1}^{m} \frac{D^{\alpha\beta}}{kT} \left[(\boldsymbol{\zeta}\mathbf{v}^0)_\beta P + \left(-\frac{\partial V}{\partial q^\beta} + X_\beta\right)P - kT\frac{\partial P}{\partial q^\beta}\right], \tag{32.18}$$

where $D^{\alpha\beta}/kT$ are the elements of the reciprocal of the $m \times m$ matrix $\zeta_{\alpha\beta}$; that is,

$$\sum_{\beta=1}^{m} (D^{\alpha\beta}/kT)\zeta_{\beta\gamma} = \delta_\gamma{}^\alpha \tag{32.19}$$

with $\delta_\alpha{}^\alpha = 1$ and $\delta_\gamma{}^\alpha = 0$ for $\alpha \neq \gamma$. $D^{\alpha\beta}$ are the components of the diffusion tensor. Recalling that

$$\begin{aligned}\sum_{\beta=1}^{m} \frac{D^{\alpha\beta}}{kT} (\boldsymbol{\zeta}\mathbf{v}^0)_\beta &= \sum_{\beta=1}^{m} \frac{D^{\alpha\beta}}{kT} \sum_{\gamma=1}^{3n+3} \zeta_{\beta\gamma} v^{0\gamma} \\ &= \sum_{\beta=1}^{m} g^{\alpha\beta} {v_\beta}^0 + \sum_{\beta=1}^{m} \frac{D^{\alpha\beta}}{kT} \sum_{\gamma=m+1}^{3n+3} \zeta_{\beta\gamma} v^{0\gamma} \,, \quad (32.20)\end{aligned}$$

Eq. (32.18) may be rewritten as

$$\begin{aligned}J^\alpha = \sum_{\beta=1}^{m} \Bigg[ & g^{\alpha\beta} {v_\beta}^0 P + \frac{D^{\alpha\beta}}{kT} \left( -\frac{\partial V}{\partial q^\beta} + X_\beta \right) P \\ & - D^{\alpha\beta} \frac{\partial P}{\partial q^\beta} + \frac{D^{\alpha\beta}}{kT} \sum_{\gamma=m+1}^{3n+3} \zeta_{\beta\gamma} v^{0\gamma} P \Bigg] \,. \quad (32.21)\end{aligned}$$

The terms involving $\zeta_{\beta\gamma}$ with $\gamma \geq m+1$ were omitted in the original theory of Kirkwood. Equation (32.15) with (32.21) gives the generalized diffusion equation. The average value of a function $\varphi(\{q^m\})$ of the coordinates $\{q^m\}$ is given by

$$\langle \varphi(t) \rangle = \int g^{1/2} \varphi(\{q^m\}) P(\{q^m\}, t) d\{q^m\} \,. \qquad (32.22)$$

The problem we face is to solve the diffusion equation for $P(\{q^m\}, t)$. This can be formally done by the use of perturbation theory. We define the function $\rho(\{q^m\}, t)$ by

$$P(\{q^m\}, t) = {P_0}^{1/2}(\{q^m\}) \rho(\{q^m\}, t) \,, \qquad (32.23)$$

where $P_0(\{q^m\})$ is the equilibrium distribution function,

$$P_0(\{q^m\}) = \exp(-V/kT) \,. \qquad (32.24)$$

Then Eq. (32.15) with (32.21) becomes

$$L\rho - \frac{\partial \rho}{\partial t} = -Q\rho \qquad (32.25)$$

with

$$L = \sum_{\alpha,\beta=1}^{m} \frac{1}{g^{1/2}} \frac{\partial}{\partial q^\alpha} g^{1/2} D^{\alpha\beta} \frac{\partial}{\partial q^\beta} + W \,, \qquad (32.26)$$

$$W = \frac{1}{2kT} \sum_{\alpha,\beta=1}^{m} \frac{1}{g^{1/2}} \frac{\partial}{\partial q^\alpha} g^{1/2} D^{\alpha\beta} \frac{\partial V}{\partial q^\beta} - \frac{1}{(2kT)^2} \sum_{\alpha,\beta=1}^{m} D^{\alpha\beta} \frac{\partial V}{\partial q^\alpha} \frac{\partial V}{\partial q^\beta} \,, \qquad (32.27)$$

$$Q = -{P_0}^{-1/2} \sum_{\alpha,\beta=1}^{m} \frac{1}{g^{1/2}} \frac{\partial}{\partial q^\alpha} g^{1/2} \frac{D^{\alpha\beta}}{kT} \left( X_\beta + \sum_{\gamma=1}^{3n+3} \zeta_{\beta\gamma} v^{0\gamma} \right) {P_0}^{1/2} \,. \qquad (32.28)$$

The differential operator $L$ is self-adjoint, and therefore possesses a complete orthonormal set of eigenfunctions $\psi_j$:

$$L\psi_j + \lambda_j \psi_j = 0 \tag{32.29}$$

with negative eigenvalues $-\lambda_j$. Suppose now that the operator $Q$ and the function $\rho$ may be expanded in powers of a perturbation parameter $\gamma$ (e.g., the magnitude of the rate of shear),

$$\begin{aligned} Q &= \sum_{s=1}^{\infty} \gamma^s Q^{(s)} \,, \\ \rho &= {P_0}^{1/2} + \sum_{s=1}^{\infty} \rho^{(s)} \gamma^s \,. \end{aligned} \tag{32.30}$$

Equations. (32.25) and (32.30) then give a system of inhomogeneous differential equations for $\rho^{(s)}(\{q^m\}, t)$. The first-order perturbation calculation leads to

$$\rho^{(1)} = \int_{-\infty}^{+\infty} G^{(1)}(\{q^m\}, \omega) e^{i\omega t} d\omega \,, \tag{32.31}$$

where

$$\begin{aligned} G^{(1)}(\{q^m\}, \omega) &= \sum_j \frac{{B_j}^{(1)}(\omega)}{\lambda_j + i\omega} \psi_j(\{q^m\}) \,, \\ {B_j}^{(1)}(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} (Q^{(1)} {P_0}^{1/2})_j e^{-i\omega t} dt \,, \\ (Q^{(1)} {P_0}^{1/2})_j &= \int g^{1/2} {\psi_j}^* Q^{(1)} {P_0}^{1/2} d\{q^m\} \,. \end{aligned} \tag{32.32}$$

The average $\langle \varphi(t) \rangle$ may be expanded in the form,

$$\langle \varphi(t) \rangle = \sum_{s=0}^{\infty} \langle \varphi^{(s)}(t) \rangle \gamma^s \tag{32.33}$$

with

$$\langle \varphi^{(s)}(t) \rangle = \int g^{1/2} \varphi {P_0}^{1/2} \rho^{(s)} d\{q^m\} \,. \tag{32.34}$$

The techniques useful in determining the eigenfunctions and eigenvalues of the operator $L$ are identical with those employed in the solution of the Schrödinger equation in quantum mechanics.

We now consider the diffusion tensor. From Eqs. (32.14) and (32.19), $D^{\alpha\beta}$ may be expanded in the form,[28]

$$\frac{D^{\alpha\beta}}{kT} = \frac{1}{\zeta} \left[ g^{\alpha\beta} + \zeta T^{\alpha\beta} + \zeta^2 \left( \sum_{\mu,\nu} g_{\mu\nu} T^{\alpha\mu} T^{\nu\beta} - \mathbf{a}^\alpha \mathbf{T}^2 \mathbf{a}^\beta \right) + \cdots \right] . \tag{32.35}$$

In the original theory of Kirkwood, the third and higher terms on the right-hand side of Eq. (32.35) were dropped. In other words, Kirkwood obtained the diffusion tensor from the incorrect equation $D^{\alpha\beta}/kT = \mathbf{a}^{\alpha}\boldsymbol{\zeta}^{-1}\mathbf{a}^{\beta}$;

$$\frac{D^{\alpha\beta}}{kT} = \frac{g^{\alpha\beta}}{\zeta} + T^{\alpha\beta} . \qquad \text{(Kirkwood)} \tag{32.36}$$

The neglected terms vanish when the components of the generalized Oseen tensor $\mathbf{T}$ disappear between the $m$-space and its complementary space, but this is not generally the case. The contravariant components of $\mathbf{T}$ may be obtained, from Eqs. (32.9) and (32.12), as

$$T^{\alpha\beta} = \sum_{\substack{i,j \\ i\neq j}} T_{ij}{}^{\alpha\beta} \tag{32.37}$$

with

$$T_{ij}{}^{\alpha\beta} = \frac{1}{8\pi\eta_0 R_{ij}} \sum_{\mu,\nu=1}^{m} g^{\alpha\mu} g^{\beta\nu} \left[ \frac{\partial \mathbf{R}_i}{\partial q^{\mu}} \cdot \frac{\partial \mathbf{R}_j}{\partial q^{\nu}} + \frac{1}{R_{ij}{}^2} \left( \mathbf{R}_{ij} \cdot \frac{\partial \mathbf{R}_i}{\partial q^{\mu}} \right) \left( \mathbf{R}_{ij} \cdot \frac{\partial \mathbf{R}_j}{\partial q^{\nu}} \right) \right] . \tag{32.38}$$

If the Kirkwood approximation of (32.36) is adopted, we can derive a simple expression for the translational diffusion coefficient. Let $q^1$, $q^2$, and $q^3$ be the coordinates specifying the position of the center of mass in an external Cartesian coordinate system. Then, $\partial \mathbf{R}^i/\partial q^{\alpha} (\alpha = 1, 2, 3)$ are the unit vectors $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$, and the coordinates $q^1$, $q^2$, and $q^3$ are separable from, or orthogonal to, the remaining $(m - 3)$ coordinates. We therefore have (for $n \gg 1$)

$$g_{\alpha\beta} = n\delta_{\alpha\beta} ,$$

$$g^{\alpha\beta} = n^{-1}\delta^{\alpha\beta} \qquad (\alpha = 1, 2, 3;\ \beta = 1, 2 \ldots, m) . \tag{32.39}$$

From Eqs. (32.36) to (32.39), we obtain for the translational components of the diffusion tensor

$$\frac{D^{\alpha\beta}}{kT} = \frac{\delta_{\alpha\beta}}{n\zeta} + \frac{1}{8\pi\eta_0 n^2} \sum_{\substack{i=0 \\ i\neq j}}^{n} \sum_{j=0}^{n} \left[ \frac{\delta_{\alpha\beta}}{R_{ij}} + \frac{(\mathbf{R}_{ij}\cdot\mathbf{e}_{\alpha})(\mathbf{R}_{ij}\cdot\mathbf{e}_{\beta})}{R_{ij}{}^3} \right] \qquad (\alpha,\ \beta = 1, 2, 3) . \tag{32.40}$$

The (mean) translational diffusion coefficient $D$ is equal to one-third of the trace of $D^{\alpha\beta}$, averaged over the internal coordinates;

$$D = \frac{kT}{n\zeta} \left( 1 + \frac{\zeta}{6\pi\eta_0 n} \sum_{\substack{i \\ i\neq j}} \sum_{j} \left\langle \frac{1}{R_{ij}} \right\rangle \right) . \tag{32.41}$$

The sedimentation coefficient is then given by

$$s = \frac{M(1-\bar{v}\bar{\rho})}{N_{\mathrm{A}} n\zeta}\left(1 + \frac{\zeta}{6\pi\eta_0 n}\sum_{i}\sum_{\substack{j \\ i\neq j}}\left\langle\frac{1}{R_{ij}}\right\rangle\right). \tag{32.42}$$

These are the famous equations of Kirkwood; they are not exact, but rather involve the approximations cited.

For an unperturbed linear flexible chain it is interesting to note that Eq. (32.41) yields the same result as that obtained previously in an approximate manner, Eq. (31.46). For a rigid rod, recalling that $\langle {R_{ij}}^{-1}\rangle = 1/|i-j|a$, we obtain from Eq. (32.41)

$$\begin{aligned} D(\text{rod}) &= \frac{kT}{n\zeta}\left[1 + \frac{\zeta}{3\pi\eta_0 a}(\ln n - 1 + \gamma)\right] \\ &= \frac{kT\ln(L/a)}{3\pi\eta_0 L} \qquad (\text{for large } n)\,, \end{aligned} \tag{32.43}$$

where $L$ is the length of the rod and $\gamma$ is the Euler constant (0.5772). (If the summations in Eq. (32.41) are replaced by integrations, $\gamma$ does not appear.) Equations. (32.43) without $\gamma$ can also be obtained by the method of Kirkwood and Riseman described in the previous section.[30] The translational diffusion coefficient of a rigid ring, when calculated from Eq. (32.41), is also given by Eq. (32.43) in the limit of large $L$, if $L$ is the contour length of the ring and $a$ is the arc length of a bond. On the other hand, the correct diffusion coefficient of a rigid ring calculated by Zwanzig[31] by a different method is

$$D(\text{rigid ring}) = \frac{11kT\ln(L/a)}{36\pi\eta_0 L}\,. \quad (\text{correct}) \tag{32.44}$$

Thus, the correct result is smaller than the incorrect one by a factor 11/12. Examination of the results for linear flexible chains and rigid rods suggests that Kirkwood's formula for $D$ has some practical value, even if it is not generally correct.

## 33. The Diffusion-Equation Approach (B): The Spring and Bead Model

Solutions of the Kirkwood diffusion equation, as shown in the previous section, are not in general derived without the use of mathematical approximations. For flexible chains it is convenient to use the random-flight model with the Gaussian bond probability to obtain numerical results. This model is dynamically equivalent to a chain composed of $(n+1)$ segments, or beads, with friction coefficient $\zeta$, joined together with a Hooke's law spring, and is referred to as the *spring and bead model.* The development of the dynamical theory based on this model was initiated by Rouse,[32] Bueche,[33] Zimm,[34] and others.[35, 36] The general mathematical problem is similar to that in the Debye theory of lattice vibrations, or in the theory of Brownian motion of a system of coupled harmonic oscillators. The model will, therefore, be a valid description of low-frequency dynamical processes. As hinted the present theory may be developed conveniently by the use of a transformation into normal coordinates, but use of this model limits the range of application. In this section we adopt the procedure of Zimm, and evaluate the intrinsic viscosity and the translational diffusion coefficient for unperturbed linear chains.

We begin by deriving the diffusion equation for the spring and bead model. If the fluid velocity $\mathbf{v}_i$ is split into the unperturbed velocity ${\mathbf{v}_i}^0$ and the Oseen perturbations according to Eq. (31.4) with (31.5), Eq. (32.2) for the current density may be rewritten as

$$\mathbf{J}_i = P{\mathbf{v}_i}^0 + \sum_{j=0}^{n} \mathbf{D}_{ij}[P(-\nabla_j U + \mathbf{X}_j) - kT\nabla_j P] \,, \tag{33.1}$$

where we have used Eq. (32.3) for the frictional force, and the tensor $\mathbf{D}_{ij}$ is given by

$$\mathbf{D}_{ij} = \zeta^{-1}\delta_{ij}\mathbf{I} + \mathbf{T}_{ij} \tag{33.2}$$

with

$$\mathbf{T}_{ii} = 0 \,.$$

For present purposes, it is convenient to write

$$\begin{aligned} U &= U_0 + W \,, \\ \mathbf{X}_i &= -\nabla_i U_e \,, \end{aligned} \tag{33.3}$$

where $U_0$ is the potential representing the connection of segments, $W$ is the intramolecular excluded-volume potential, and $U_e$ is the external potential. If $\tau(\mathbf{r}_i)$ is the bond probability given by Eq. (5.35), the elastic force exerted on the $i$th segment by the $i$th bond (spring) is

$$kT\frac{\mathbf{r}_i}{r_i}\frac{\partial \ln \tau(\mathbf{r}_i)}{\partial r_i} = -\kappa\mathbf{r}_i = -\kappa(\mathbf{R}_i - \mathbf{R}_{i-1}) \,, \tag{33.4}$$

where $\kappa$ is the force constant of the spring and is given by $\kappa = 3kT/a^2$. The elastic force exerted on the $i$th segment by the $(i+1)$th bond is equal to $\kappa(\mathbf{R}_{i+1} - \mathbf{R}_i)$. For a linear chain we therefore have

$$\begin{aligned} \nabla_i U_0 &= \kappa(\mathbf{R}_0 - \mathbf{R}_1) && \text{for } i = 0 \\ &= \kappa(-\mathbf{R}_{i-1} + 2\mathbf{R}_i - \mathbf{R}_{i+1}) && \text{for } 1 \le i \le n-1 \\ &= \kappa(-\mathbf{R}_{n-1} + \mathbf{R}_n) && \text{for } i = n \,. \end{aligned} \tag{33.5}$$

We approximate the Oseen tensor $\mathbf{T}_{ij}$ by its average value [$\langle \mathbf{T}_{ij} \rangle$ of (31.13)] in Eq. (33.2), and define the $(n+1) \times (n+1)$ matrix $\mathbf{H}$ whose elements are

$$\begin{aligned} H_{ij} &= 1 && \text{for } i = j \\ &= \frac{\zeta}{6\pi\eta_0}\left\langle \frac{1}{R_{ij}} \right\rangle && \text{for } i \ne j \,. \end{aligned} \tag{33.6}$$

It is then convenient to write the diffusion equation (32.1) with (33.1) in matrix notation. Let $\mathbf{F}$ be any column vector whose components are three-dimensional vector $\mathbf{F}_i (0 \leq i \leq n)$. The row vector $\mathbf{F}^T$ is

$$\mathbf{F}^T = (\mathbf{F}_0 \, \mathbf{F}_1 \cdots \mathbf{F}_n) \, , \tag{33.7}$$

where the superscript $T$ indicates the transpose. The differential operator with respect to $\mathbf{R}$ may therefore be written as

$$\nabla^T = (\nabla_0 \, \nabla_1 \cdots \nabla_n) \, . \tag{33.8}$$

We now introduce the $(n+1) \times (n+1)$ matrix $\mathbf{A} = \mathbf{a}^T \mathbf{a}$ with $a_{ij} = \delta_{ij} - \delta_{i,j-1}$; that is,

$$\mathbf{A} = \begin{pmatrix} 1 & -1 & 0 & 0 & \cdots & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & \cdots & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & \cdots & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & \cdots & 0 & -1 & 1 \end{pmatrix} . \tag{33.9}$$

The operator $\kappa \mathbf{A}$ transforms a position vector into a force vector, while $\zeta^{-1}\mathbf{H}$ is the hydrodynamic mobility operator which transforms a force vector into a velocity vector. The diffusion equation and the frictional force may then be written as

$$\frac{\partial P}{\partial t} = -\nabla^T P \mathbf{v}^0 + \zeta^{-1} \nabla^T \mathbf{H} [\kappa P \mathbf{A} \mathbf{R} + P \nabla (W + U_e) + kT \nabla P] \, , \tag{33.10}$$

$$\mathbf{F} = -\kappa \mathbf{A} \mathbf{R} - \nabla (W + U_e) - kT \nabla \ln P \, . \tag{33.11}$$

Further developments are facilitated by a coordinate transformation into normal coordinates. The matrix $\mathbf{HA}$ can be transformed into a diagonal matrix $\boldsymbol{\Lambda}$ with elements $\lambda_j$ by a similarity transformation with an appropriate matrix $\mathbf{Q}$,

$$\mathbf{Q}^{-1} \mathbf{H} \mathbf{A} \mathbf{Q} = \boldsymbol{\Lambda} \, . \tag{33.12}$$

If $\boldsymbol{\alpha}_j$ is the eigenvector of $\mathbf{HA}$ corresponding to the eigenvalue $\lambda_j$, we have the eigenvalue equation,

$$\mathbf{H} \mathbf{A} \boldsymbol{\alpha}_j = \lambda_j \boldsymbol{\alpha}_j \qquad (0 \leq j \leq n) \, , \tag{33.13}$$

and $\mathbf{Q}$ is composed of $(n+1)$ column vectors $\boldsymbol{\alpha}_j$. Note that $\mathbf{HA}$ is not in general symmetric and $\mathbf{Q}$ is not orthogonal. The same matrix $\mathbf{Q}$ can also be used to diagonalize the matrices $\mathbf{H}$ and $\mathbf{A}$ separately, although not by similarity transformations. We first establish that

$$\boldsymbol{\alpha}_j{}^T \mathbf{A} \mathbf{H} = (\mathbf{H}^T \mathbf{A}^T \boldsymbol{\alpha}_j)^T = (\mathbf{H} \mathbf{A} \boldsymbol{\alpha}_j)^T = \lambda_j \boldsymbol{\alpha}_j{}^T \, , \tag{33.14}$$

since **H** and **A** are symmetric. We therefore have

$$\boldsymbol{\alpha}_j{}^T\mathbf{AHA}\boldsymbol{\alpha}_k = (\boldsymbol{\alpha}_j{}^T\mathbf{AH})\mathbf{A}\boldsymbol{\alpha}_k = \lambda_j\boldsymbol{\alpha}_j{}^T\mathbf{A}\boldsymbol{\alpha}_k\,, \tag{33.15}$$

and also

$$\boldsymbol{\alpha}_j{}^T\mathbf{AHA}\boldsymbol{\alpha}_k = \boldsymbol{\alpha}_j{}^T\mathbf{A}(\mathbf{HA}\boldsymbol{\alpha}_k) = \lambda_k\boldsymbol{\alpha}_j{}^T\mathbf{A}\boldsymbol{\alpha}_k\,. \tag{33.16}$$

Equations (33.15) and (33.16) can both be true only if

$$\boldsymbol{\alpha}_j{}^T\mathbf{A}\boldsymbol{\alpha}_k = 0 \qquad \text{for } j \neq k\,, \tag{33.17}$$

unless $\lambda_j = \lambda_k$. Therefore, if all the eigenvalues are distinct (as turns out to be the case), **A** is diagonalized by the congruent transformation,

$$\mathbf{Q}^T\mathbf{AQ} = \mathbf{M}\,, \tag{33.18}$$

where **M** is the diagonal matrix with elements $\mu_j$. Next, define a set of $(n+1)$ vectors $\boldsymbol{\beta}_j$ as the column vectors of $\mathbf{Q}^{-1T}$. Since we find $\mathbf{Q}^T\mathbf{AHQ}^{-1T} = \boldsymbol{\Lambda}$ from Eq. (33.12), the $\boldsymbol{\beta}_j$ are the eigenvectors of **AH** with eigenvalues $\lambda_j$. With these we can also diagonalize **H** by a congruent transformation. If we obtain **AQ** from Eq. (33.18) and substitute it into Eq. (33.12), we find

$$\mathbf{Q}^{-1}\mathbf{HQ}^{-1T} = \boldsymbol{\Lambda}\mathbf{M}^{-1} = \mathbf{N}\,, \tag{33.19}$$

where **N** is diagonal with elements $\nu_j$.

$$\begin{aligned}\nu_j &= \boldsymbol{\beta}_j{}^T\mathbf{H}\boldsymbol{\beta}_j \\ &= \lambda_j/\mu_j\,.\end{aligned} \tag{33.20}$$

The element $\nu_0$ is indeterminate in the second line of Eqs. (33.20), since both $\lambda_0$ and $\mu_0$ turn out to be zero. On the other hand, while the first line of Eqs. (33.20) is valid by definition for all $j$, it requires the inversion of **Q** to determine the $\boldsymbol{\beta}_j$. Multiplying Eq. (33.19) from the left with $\mathbf{N}^{-1}$, we can show that

$$\boldsymbol{\alpha}_j = \frac{1}{\nu_j}\mathbf{H}\boldsymbol{\beta}_j\,, \tag{33.21}$$

from which we obtain, by the use of the relation $\boldsymbol{\alpha}_i{}^T\boldsymbol{\beta}_j = \delta_{ij}$,

$$\nu_j{}^{-1} = \boldsymbol{\alpha}_j{}^T\mathbf{H}^{\,-1}\boldsymbol{\alpha}_j\,. \tag{33.22}$$

This relation is valid for all $j$ including zero, but requires the inversion of **H**.

An important property of **A** is its possession of a zero eigenvalue, since the determinant of **A** vanishes. This may be demonstrated by adding all the rows of the determinant, except the first, to the first row, whereupon the first row is reduced to zero. As a consequence **HA** also has a zero eigenvalue. The eigenvector in each case can be shown to be a constant vector. This corresponds to a simple translation of the molecule in space, as will be discussed later. We designate $\lambda_0$ as the vanishing eigenvalue of **HA**.

The matrix **Q** is used to transform the coordinates **R** into *normal coordinates* $\boldsymbol{\xi}$;

$$\begin{aligned}\mathbf{R} &= \mathbf{Q}\boldsymbol{\xi}\,,\\ \boldsymbol{\xi} &= \mathbf{Q}^{-1}\mathbf{R}\end{aligned}\tag{33.23}$$

with $\boldsymbol{\xi}^T = (\boldsymbol{\xi}_0\,\boldsymbol{\xi}_1\,\cdots\,\boldsymbol{\xi}_n)$. By the usual rules for transforming partial derivatives, we also find

$$\begin{aligned}\nabla &= \mathbf{Q}^{-1T}\nabla_{\boldsymbol{\xi}}\,,\\ \nabla^T &= \nabla_{\boldsymbol{\xi}}{}^T\mathbf{Q}^{-1}\,,\end{aligned}\tag{33.24}$$

where $\nabla_{\boldsymbol{\xi}}$ is the differential operator with respect to $\boldsymbol{\xi}$. In the new coordinates the diffusion equation (33.10) becomes

$$\frac{\partial P}{\partial t} = -\nabla_{\boldsymbol{\xi}}{}^T\mathbf{v}_{\boldsymbol{\xi}}{}^0P + \zeta^{-1}\nabla_{\boldsymbol{\xi}}{}^T[\kappa\boldsymbol{\Lambda}\boldsymbol{\xi}P + \mathbf{N}P\nabla_{\boldsymbol{\xi}}(W+U_e) + kT\mathbf{N}\nabla_{\boldsymbol{\xi}}P]\tag{33.25}$$

with $\mathbf{v}_{\boldsymbol{\xi}}{}^0 = \mathbf{Q}^{-1}\mathbf{v}^0$.

In what follows we consider the unperturbed linear chain subject to no external field; that is, $W + U_e = \text{const}$. In order to reduce the unperturbed velocity term in the diffusion equation, it is convenient to use the explicit Cartesian components $x_i$, $y_i$, and $z_i$ of the vector $\mathbf{R}_i$ and $X_i$, $Y_i$, and $Z_i$ of the normal coordinate vector $\boldsymbol{\xi}_i$. Suppose that the unperturbed velocity field is given by Eq. (30.12), i.e., $\mathbf{v}_i{}^0 = (gy_i, 0, 0)$, and the rate of shear $g$ is given by the harmonic function of time, Eq. (30.27). Then Eq. (33.25) reduces to

$$\frac{\partial P}{\partial t} = \sum_{j=0}^{n}\left[-gY_j\frac{\partial P}{\partial X_j} + \frac{\kappa\lambda_j}{\zeta}\nabla_j\cdot(\boldsymbol{\xi}_jP) + \frac{kT\nu_j}{\zeta}\nabla_j{}^2P\right],\tag{33.26}$$

where $\nabla_j$ is the differential operator with respect to $\boldsymbol{\xi}_j$ (not to $\mathbf{R}_j$). Both closed-form and perturbation solutions of Eq. (33.26) can be found. For many purposes, however, this is not necessary, since the average values of certain functions of the coordinates can be obtained exactly without finding the distribution function $P$ itself.

We now evaluate the complex intrinsic viscosity $[\bar{\eta}]$. If we introduce the vectors $\mathbf{x}^T = (x_0x_1\cdots x_n)$ and $\mathbf{F}_x{}^T = (F_{0x}F_{1x}\cdots F_{nx})$ and the operator $\nabla_x{}^T = (\partial/\partial x_0\;\partial/\partial x_1\;\cdots\;\partial/\partial x_n)$, we have from Eq. (33.11)

$$\mathbf{F}_x = -\kappa\mathbf{A}\mathbf{x} - kT\nabla_x\ln P\,.\tag{33.27}$$

The sum of the average values $\langle F_{jx}y_j\rangle$ appearing in $[\bar{\eta}]$ then becomes

$$\begin{aligned} -\sum_{j=0}^{n} \langle F_{jx} y_i \rangle &= -\langle \mathbf{y}^T \mathbf{F}_x \rangle \\ &= \int (\kappa \mathbf{y}^T \mathbf{A} \mathbf{x} + kT \mathbf{y}^T \nabla_x \ln P) P \, d\mathbf{R} \\ &= \kappa \langle \mathbf{y}^T \mathbf{A} \mathbf{x} \rangle = \kappa \langle \mathbf{Y}^T \mathbf{M} \mathbf{X} \rangle = \sum_{j=1}^{n} \kappa \mu_j \langle X_j Y_j \rangle \,, \end{aligned} \tag{33.28}$$

where the second term in the second line drops out on integration since $P$ vanishes at infinity, and in the third line we have excluded the term with $j = 0$ since $\mu_0 = 0$. Now, again making use of the fact that $P$ vanishes at infinity, we multiply Eq. (33.26) by $X_j Y_j$ or ${Y_j}^2$ and integrate over the space coordinates. After an integration by parts we obtain the differential equations,

$$\frac{\partial \langle X_j Y_j \rangle}{\partial t} = -\frac{2\kappa\lambda_j}{\zeta} \langle X_j Y_j \rangle + g \langle {Y_j}^2 \rangle \,, \tag{33.29}$$

$$\frac{\partial \langle {Y_j}^2 \rangle}{\partial t} = -\frac{2\kappa\lambda_j}{\zeta} \langle {Y_j}^2 \rangle + \frac{2kT\nu_j}{\zeta} \,. \tag{33.30}$$

The solution of Eq. (33.30) is

$$\langle {Y_j}^2 \rangle = kT/\kappa\mu_j + C \exp(-2\kappa\lambda_j t/\zeta) \,, \tag{33.31}$$

where $C$ is the constant of integration, and in the stationary state we may suppress the second term on the right-hand side (the transient term). Then substitution of Eq. (33.31) into Eq. (33.29) and solution (with omission of the transient term) leads to

$$\langle X_j Y_j \rangle = \frac{kTg}{\kappa\mu_j (2\kappa\lambda_j/\zeta + i\omega)} \,. \tag{33.32}$$

Thus we obtain from Eqs. (30.24), (33.28), and (33.32)

$$[\bar{\eta}] = \frac{RT}{M\eta_0} \sum_{j=1}^{n} \frac{\tau_j}{1 + i\omega\tau_j} \,, \tag{33.33}$$

where $R$ is the gas constant, and $\tau_j$ are the *relaxation times* given by

$$\tau_j = \frac{\zeta}{2\kappa\lambda_j} = \frac{M\eta_0[\eta]}{RT\lambda_j \left( \displaystyle\sum_{j=1}^{n} {\lambda_j}^{-1} \right)} \tag{33.34}$$

with $[\eta]$ the zero-frequency intrinsic viscosity. The qualitative aspects of the present theory are as follows: the resultant of all the motions of the segments of the chain can be decomposed into a series of independent normal modes of motion, with each mode represented by a normal coordinate and having a relaxation time during which the transition to the equilibrium distribution occurs. Further, we note that the intrinsic viscosity is independent of the rate of shear. This result is not in agreement with experiment. A discussion of the non-Newtonian viscosity is deferred to Section 36b.

We can readily obtain the real and imaginary parts of the complex intrinsic viscosity, or the complex intrinsic rigidity $[\bar{G}]$. According to Eqs. (30.29) and (30.31),

$$\begin{aligned} [G'] &= \frac{RT}{M} \sum_{j=1}^{n} \frac{\omega^2 {\tau_j}^2}{1 + \omega^2 {\tau_j}^2} \,, \\ [G''] &= \frac{RT}{M} \sum_{j=1}^{n} \frac{\omega \tau_j}{1 + \omega^2 {\tau_j}^2} \,. \end{aligned} \tag{33.35}$$

The nonvanishing of $[\eta''] = [G']/\omega\eta_0$ except at $\omega = 0$ indicates that for an alternating shear strain, the distribution function and also the shear stress exhibit a lag in phase relative to the rate of shear, and the solution possesses rigidity. The rigidity of polymer solutions was first observed experimentally by Mason, Baker, and their co-workers.[37]

The problem is now to solve the eigenvalue equation,

$$\mathbf{HA}\boldsymbol{\alpha} = \lambda \boldsymbol{\alpha} \,. \tag{33.36}$$

When $n$ is large the components $\alpha_i$ of $\boldsymbol{\alpha}$ vary slowly with the index $i$ so that they may be represented by a continuous function $\alpha(r)$ with the relations between indices $i$ and $j$ and the variables $r$ and $s$ given by $r = 2i/n - 1$ and $s = 2j/n - 1$. For the unperturbed linear chain Eq. (33.36) then becomes the integrodifferential equation,

$$\alpha''(r) + h \int_{-1}^{1} \frac{\alpha''(s)}{|r - s|^{1/2}} ds = -\frac{n^2 \lambda}{4} \alpha(r) \tag{33.37}$$

with the free-end boundary conditions,

$$\alpha'(\pm 1) = 0 \,, \tag{33.38}$$

where we have used Eq. (33.6) with (31.20) for the elements $H_{ij}$, the primes indicate differentiation, and $h$ is the draining parameter defined by Eq. (31.23). If we use the variables $x = i/n$ and $y = j/n$ instead of $r$ and $s$, Eq. (33.37) with (33.38) must be replaced by

$$\alpha''(x) + 2^{1/2} h \int_{0}^{1} \frac{\alpha''(y)}{|x - y|^{1/2}} dy = -n^2 \lambda \alpha(x) \tag{33.39}$$

with

$$\alpha'(0) = \alpha'(1) = 0 \,. \tag{33.40}$$

Necessarily Eqs. (33.37) and (33.39) yield the same eigenvalues but different forms of eigenfunctions. Also, the eigenvalues depend on the parameter $h$.

In the free-draining case ($h = 0$), the eigenvalues are obtained as

$$\lambda_j = \pi^2 j^2/n^2 \qquad (j = 0, 1, \ldots, n)\,. \tag{33.41}$$

These are called the Rouse eigenvalues. We obtain for the corresponding normalized Rouse eigenfunctions from Eq. (33.37)

$$\begin{aligned} \alpha_j(r) &= (2/n)^{1/2}\cos(\pi jr/2) \qquad \text{for even } j \\ &= (2/n)^{1/2}\sin(\pi jr/2) \qquad \text{for odd } j\,, \end{aligned} \tag{33.42}$$

and from Eq. (33.39)

$$\alpha_j(x) = (2/n)^{1/2}\cos(\pi jx)\,. \tag{33.43}$$

The Rouse eigenfunctions are quite good approximations to the exact solutions of Eq. (33.37) or (33.39) for any value of $h$, since the integral in each equation is well approximated by $\alpha(r)$ of $\alpha(x)$ multiplied by a slowly varying function of $r$ or $x$. Calculations with the Rouse eigenfunctions are especially easy, because then the matrix $\mathbf{Q}$ is symmetric, i.e., $\mathbf{Q}^T = \mathbf{Q}$, and moreover $\mathbf{Q}^T = \mathbf{Q}^{-1}$, and hence $\boldsymbol{\alpha}_j = \boldsymbol{\beta}_j$. From Eqs. (33.33) and (33.41) with the value of the Riemann zeta function, we find the previously derived result, Eq. (31.32), for the zero-frequency intrinsic viscosity. Further, we obtain for the relaxation times

$$\tau_j = \frac{6M\eta_0[\eta]}{\pi^2 RTj^2} \qquad (\text{for } h = 0)\,. \tag{33.44}$$

In the non-free-draining case ($h = \infty$), the integral equation [without $\alpha''(r)$] that results from Eq. (33.37) has been solved numerically by Zimm, Roe, and Epstein[38] by transforming it into a set of homogeneous linear equations for the coefficients ${}^j\alpha_k$ in the Fourier series expansion of $\alpha_j(r)$,

$$\mathbf{G}\,{}^j\mathbf{a} = \lambda_j{}'\,{}^j\mathbf{a} \tag{33.45}$$

with

$$\lambda_j = (4h/n^2)\lambda_j{}'\,. \tag{33.46}$$

The matrix $\mathbf{G}$ is almost diagonal, so that the off-diagonal elements may be treated by a perturbation method to find

$$\lambda_j{}' = G_{jj} - \sum_{\substack{k=0\\ \neq j}}^{\infty} \frac{G_{jk}G_{kj}}{G_{kk} - G_{jj}}\,. \tag{33.47}$$

In particular, the diagonal elements are given by

$$G_{jj} = \pi j^{1/2}[\pi jC(\pi j) - \tfrac{1}{2}S(\pi j)]\,, \tag{33.48}$$

where $C(x)$ and $S(x)$ are the Fresnel integrals defined by

$$\begin{aligned} C(x) &= (2\pi)^{-1/2}\int_0^x t^{-1/2}\cos t\,dt\,, \\ S(x) &= (2\pi)^{-1/2}\int_0^x t^{-1/2}\sin t\,dt\,. \end{aligned} \tag{33.49}$$

**TABLE VI.2.** THE REDUCED EIGENVALUES $\lambda_j{}'$ IN THE NON-FREE-DRAINING LIMIT[34]

|  | $\lambda_j{}'$ |  |
|---|---|---|
| $j$ | ZIMM | HEARST |
| 0 | 0 | 0 |
| 1 | 4.04 | 4.10 |
| 2 | 12.79 | 12.87 |
| 3 | 24.2 | 24.3 |
| 4 | 37.9 | 37.9 |
| 5 | 53.5 | 53.4 |
| 6 | 70.7 | 70.6 |
| 7 | 89.4 | 89.3 |

The $\lambda_j{}'$ for $j = 0$ to 7 are tabulated in the second column of Table VI.2. For large $j$ they are well approximated by $\lambda_j{}' = \frac{1}{2}\pi^2 j^{3/2}(1 - 1/2\pi j)$. With these eigenvalues we obtain Eq. (31.34) for the zero-frequency intrinsic viscosity with $\Phi_0 = 2.84 \times 10^{23}$. This value of $\Phi_0$ is to be compared with the value $2.87 \times 10^{23}$ obtained in Section 31a. The relaxation times are given by

$$\tau_j = \frac{M\eta_0[\eta]}{0.586RT\lambda_j{}'} \qquad (\text{for } h = \infty)\,. \tag{33.50}$$

The eigenvalues for intermediate values of $h$ were calculated by Hearst[39] and by Tschoegl.[40] Hearst's calculations are particularly simple, because the Rouse eigenfunctions were used. The use of the Rouse eigenfunctions in the non-free-draining limit is equivalent to neglecting the off-diagonal elements in Eq. (33.47), i.e., $\lambda_j{}' = G_{jj}$. These $\lambda_j{}'$ are tabulated in the third column of Table VI.2. The eigenvalues $\lambda_j$ (for any value of $h$) within this approximation are the sum of the free-draining and non-free-draining contributions,

$$\lambda_j = \frac{\pi^2}{n^2}\left(j^2 + \frac{4h\lambda_j{}'}{\pi^2}\right). \tag{33.51}$$

Hearst's calculations give $\Phi_0(\infty) = 2.82 \times 10^{23}$, which is very close to Zimm's value. The values of the ratio $\Phi_0(h)/\Phi_0(\infty)$ as a function of log $h$ calculated with the use of Hearst's eigenvalues are shown by curve H in Fig. VI.4. For comparison, the corresponding values from the Kirkwood-Riseman theory are shown by curve KR. Note the good agreement between the calculations. Thus, for the zero-frequency intrinsic viscosity of flexible chains, almost the same predictions are obtained whether Brownian motion is explicitly considered or not.

We now turn to the study of the translational diffusion coefficient $D$. The elements of the vector $\boldsymbol{\alpha}_0$ are all the same constant, whose value

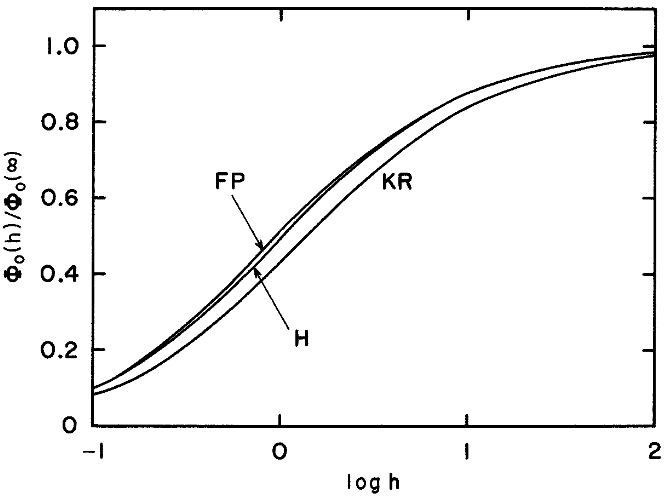

**Fig. VI.4.** The ratio $\Phi_0(h)/\Phi_0(\infty)$ plotted against log $h$. Curve KR: the Kirkwood–Riseman theory. Curve H: Hearst's version of the Zimm theory. Curve FP: the Fixman–Pyun theory.

may be chosen to be $n^{-1/2}$ to normalize $\boldsymbol{\alpha}_0$ ; that is, $\boldsymbol{\alpha}_0 = n^{-1/2}\mathbf{I}$ with $\mathbf{I}$ the unit vector. Then, from Eqs. (33.23), the normal coordinate $X_0$ is seen to represent a translation of the whole molecule by the amount $X_0/n^{1/2}$ in the direction of the $x$ axis. The meaning of $\boldsymbol{\beta}_0$ is exposed by Eq. (33.21) and the physical interpretation of $\zeta^{-1}\mathbf{H}$ as the operator that converts force into velocity; $\boldsymbol{\beta}_0$ is the force vector which is produced by a uniform translational velocity of the molecule relative to the fluid with a magnitude $\nu_0/n^{1/2}\zeta$. We can then define a *center of resistance*, whose $x$-coordinate is $x_r$, as that point about which the net torque vanishes when the force vector $\boldsymbol{\beta}_0$ arising from uniform translation is applied to the molecule and equivalent total force is applied to the point. In symbols,

$$\boldsymbol{\beta}_0{}^T(\mathbf{x} - x_r\mathbf{I}) = 0\,, \tag{33.52}$$

where $\mathbf{x}$ is an arbitrary vector, and the left-hand side is the net torque. The solution of Eq. (33.52) is

$$X_0 = n^{1/2}x_r\,. \tag{33.53}$$

Therefore, the zeroth normal coordinates $\boldsymbol{\xi}_0$ measure the position of the center of resistance. For the case of steady flow, it can be shown that the molecule rotates with the angular velocity $\frac{1}{2}g$ around its center of resistance instead of around its center of mass as in the Kirkwood-Riseman theory. The translational diffusion coefficient is related to the number $\nu_0$. In Eq. (33.26) the diffusion coefficient associated with $\partial^2 P/\partial {X_0}^2$ is $kT\nu_0/\zeta$, but $X_0$ is $n^{1/2}$ times the magnitude of a translation of the

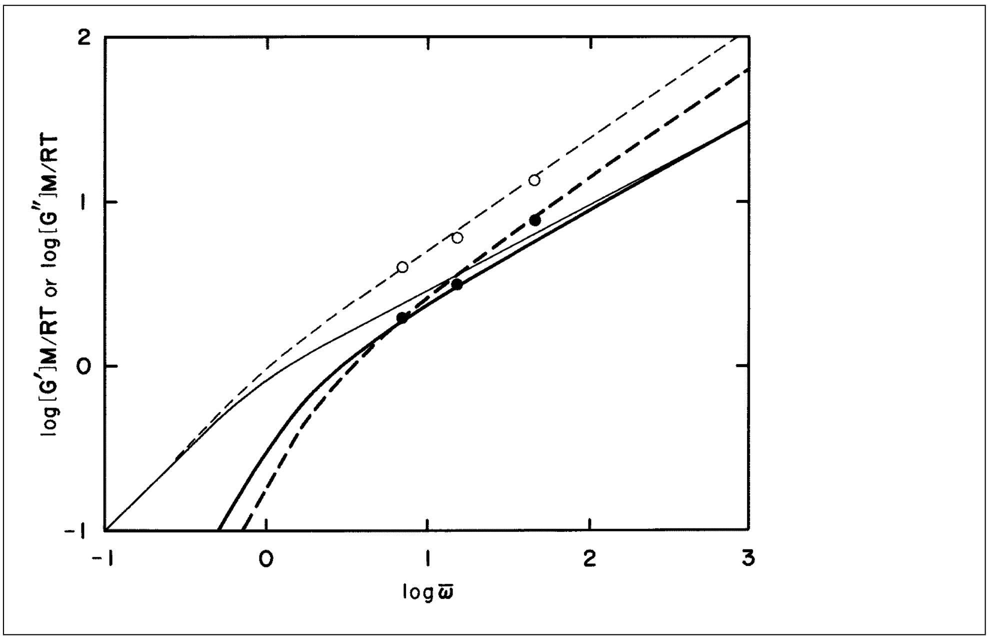

**Fig. VI.5.** The dimensionless intrinsic storage and loss moduli as functions of the reduced angular frequency. Full curves: the Rouse theory (the free-draining case). Broken curves: the Zimm theory (the non-free-draining case). Heavy curves: $[G']$. Light curves: $[G'']$. Filled circles ($[G']$) and open circles ($[G'']$): data on a polyisobutylene fraction (with $M = 1.76 \times 10^6$) in benzene at the $\Theta$ temperature (24.0 °C).[41]

center of resistance, so that

$$D = kT\nu_0/n\zeta\,. \tag{33.54}$$

In the free-draining case, we find $\nu_0 = 1$ from Eq. (33.22) and recover Eq. (31.47). For the non-free-draining case, Zimm gave the numerical constant 0.192 instead of 0.196 in $D$ of Eq. (31.48). This result is the same as that obtained from the exact asymptotic solution of the Kirkwood–Riseman integral equation of (31.41). It is interesting to note that if we use the Rouse eigenfunctions, we have $\boldsymbol{\beta}_0 = n^{-1/2}\mathbf{I}$, and from this and Eqs. (33.20) and (33.54) obtain the Kirkwood expression for $D$, Eq. (32.41).

Finally, we make a comparison of theory with experiment with respect to the frequency dependence of the complex intrinsic rigidity or viscosity, since this can be done without fundamental difficulty. The dimensionless quantity $\omega\tau_j$ in Eqs. (33.35) may be written in the form,

$$\omega\tau_j = \frac{\bar{\omega}}{\lambda_j\left(\sum_j \lambda_j^{-1}\right)}\,, \tag{33.55}$$

where $\bar{\omega}$ is the reduced angular frequency defined by

$$\bar{\omega} = \omega M \eta_0 [\eta]/RT \,. \tag{33.56}$$

Then the quantities $[G']M/RT$ and $[G'']M/RT$ are dimensionless functions only of $\bar{\omega}$ and $h$ for unperturbed flexible chains. This is also the case for the dimensionless functions $[\eta']/[\eta]$ and $[\eta'']/[\eta]$. Experimental data satisfying the conditions (of infinite dilution and theta state) required by the present theory are the ones obtained by Sakanishi[41] for a polyisobutylene fraction (of $M = 1.76 \times 10^6$) in benzene at the theta temperature (24.0°C) by the torsional crystal method. In Fig. VI.5 are shown plots of log $[G']M/RT$ or log $[G'']M/RT$ against log $\bar{\omega}$. The filled and open circles represent the data for $[G']$ and $[G'']$, respectively. The full and broken curves represent the theoretical values for the free-draining case (Rouse theory) and the non-free-draining case (Zimm theory), respectively, $[G']$ and $[G'']$ being indicated by the heavy and light curves. Clearly, this polymer system is well described by the Zimm theory, indicating that there is no draining effect.

## 34. The Nonaveraged Oseen Tensor and the Viscosity Constant $\Phi_0$

Apart from the model adopted the only mathematical approximation made in the Zimm theory is the use of the preaveraged Oseen tensor. In this section we avoid preaveraging the Oseen tensor in order to further investigate the behavior of the viscosity function $\Phi_0(h)$ for unperturbed linear chains in steady flow. We again use the spring and bead model, employing a procedure due to Fixman and Pyun.[42, 43] Their idea consists of using, in zeroth approximation, only the diagonal part of the time evolution operator of the distribution function in the free-draining basis representation, and treating the off-diagonal part by perturbation theory. The (zeroth-order) diagonal approximation corresponds to the adoption of the Rouse free-draining normal modes, which we have noted are good approximations to the exact modes.

We start from the diffusion equation (32.1) with (33.1), where for the present case $W$ and $U_e$ are constant. In the matrix notation introduced in the previous section, it may be written in the form

$$\frac{\partial P}{\partial t} = -\nabla^T \mathbf{v}^0 P + \nabla^T \mathbf{D}(P \nabla U_0 + kT \nabla P) \tag{34.1}$$

with

$$\mathbf{D} = \zeta^{-1}\mathbf{I} + \mathbf{T} \,, \tag{34.2}$$

the elements of $\mathbf{D}$ being the $\mathbf{D}_{ij}$ given Eq. (33.2). In order to obtain a perturbation solution of the diffusion equation in the Kirkwood general theory, the function ${PP_0}^{-1/2}$ was introduced to make the operator on it self-adjoint. Here $P_0$ is the equilibrium distribution function,

$$P_0 = C_0 \exp(-U_0/kT) \tag{34.3}$$

with

$$C_0{}^{-1} = \int \exp(-U_0/kT) d\{\mathbf{R}_{n+1}\} . \tag{34.4}$$

However, there are many disadvantages in such a procedure if we wish actually to carry through calculations. In the present theory we put

$$P = P_0 \rho . \tag{34.5}$$

Then Eq. (34.1) becomes

$$\frac{\partial \rho}{\partial t} + \mathcal{L}\rho = 0 , \tag{34.6}$$

where

$$\mathcal{L} = \mathcal{A} + \mathcal{B} , \tag{34.7}$$

$$\mathcal{A} = -kT\nabla^T \mathbf{D}\nabla + (\nabla^T U_0)\mathbf{D}\nabla , \tag{34.8}$$

$$\mathcal{B} = \nabla^T \mathbf{v}^0 - (1/kT)(\nabla^T U_0)\mathbf{v}^0 . \tag{34.9}$$

The operator $\mathcal{A}$ is not self-adjoint in itself, but becomes self-adjoint, i.e., $\langle g, \mathcal{A}f\rangle = \langle \mathcal{A}g, f\rangle$, if the scalar product $\langle g, h\rangle$ of any two functions $g$ and $h$ is defined with weighting function $P_0$,

$$\langle g, h\rangle = \int P_0 gh \, d\{\mathbf{R}_{n+1}\} = \langle gh\rangle_0 . \tag{34.10}$$

Then the operator $\mathcal{A}$ possesses a complete orthonormal set of eigenfunctions. It is particularly convenient to choose as our basis set the free-draining eigenfunctions $\psi_k$ which are determined by

$$\mathcal{A}^0 \psi_k = \bar{\lambda}_k{}^0 \psi_k \tag{34.11}$$

with

$$\mathcal{A}^0 = -(kT/\zeta)\nabla^T\nabla + \zeta^{-1}(\nabla^T U_0)\nabla . \tag{34.12}$$

The free-draining operator $\mathcal{A}^0$ is obtained from $\mathcal{A}$ of (34.8), with the elements of $\mathbf{D}$ given by only the first term of Eq. (34.2) thereby completely neglecting the hydrodynamic interaction between segments ($\mathbf{T}_{ij} = 0$ for all $i$ and $j$).

We now expand the function $\rho$ in terms of $\psi_k$,

$$\rho = \sum_k f_k \psi_k , \tag{34.13}$$

where $f_k$ are the components of $\rho$ in the basis $\{\psi_k\}$, and are given by

$$f_k = \langle \psi_k, \rho\rangle = \int P\psi_k d\{\mathbf{R}_{n+1}\} . \tag{34.14}$$

Then Eq. (34.6) has the matrix representation,

$$\frac{\partial f}{\partial t} + Lf = 0 , \tag{34.15}$$

where $f$ is the column vector whose components are $f_k$, and $L$ is the matrix with elements $L_{kl} = \langle \psi_k, \mathcal{L}\psi_l \rangle = \langle \psi_k \mathcal{L} \psi_l \rangle_0$, namely the matrix representation of $\mathcal{L}$. Put

$$f = f^0 + f' \,, \tag{34.16}$$

$$\rho = \rho^0 + \rho' \,, \tag{34.17}$$

where $f^0$ and $\rho^0$ are the equilibrium (or ground) states of $f$ and $\rho$, respectively. Clearly we have $\rho^0 = 1$ from Eq. (34.5). Furthermore, since $\psi_0 = 1$, as seen later, from Eq. (34.14) we have $f_0 = 1$, and hence ${f_k}^0 = \delta_{k0}$. Therefore, Eq. (34.13) becomes

$$\rho = 1 + \sum_{k \neq 0} {f_k}' \psi_k \,. \tag{34.18}$$

The matrix $L$ may be separated into

$$L = L^a + L^b \,, \tag{34.19}$$

where $L^a$ and $L^b$ are the matrix representations of the operators $\mathcal{A}$ and $\mathcal{B}$, respectively. Obviously we have

$$L^a f^0 = 0 \,, \tag{34.20}$$

and for steady flow Eq. (34.15) becomes

$$(L^a + L^b) f' = -L^b f^0 \,. \tag{34.21}$$

By inversion of Eq. (34.21), we find

$$\begin{aligned} {f_k}' = &-\frac{{L_{k0}}^b}{\bar{\lambda}_k} + \frac{1}{\bar{\lambda}_k} \sum_{\substack{l \\ \neq k}} \left( \frac{{L_{kl}}^a {L_{l0}}^b}{\bar{\lambda}_l} + \frac{{L_{kl}}^b {L_{l0}}^b}{\bar{\lambda}_l} \right) \\ &-\frac{1}{\bar{\lambda}_k} \sum_{\substack{l \\ l \neq k,m}} \sum_{m} \left( \frac{{L_{kl}}^a {L_{lm}}^a {L_{m0}}^b}{\bar{\lambda}_l \bar{\lambda}_m} + \frac{{L_{kl}}^a {L_{lm}}^b {L_{m0}}^b}{\bar{\lambda}_l \bar{\lambda}_m} \right. \\ &\left. + \frac{{L_{kl}}^b {L_{lm}}^a {L_{m0}}^b}{\bar{\lambda}_l \bar{\lambda}_m} + \frac{{L_{kl}}^b {L_{lm}}^b {L_{m0}}^b}{\bar{\lambda}_l \bar{\lambda}_m} \right) + \cdots \end{aligned} \tag{34.22}$$

with $\bar{\lambda}_k = {L_{kk}}^a$. We separate $L^a$ into

$$L^a = A^0 + A' \,, \tag{34.23}$$

where $A^0$ is the matrix representation of $\mathcal{A}^0$, and $A'$ is the representation of $\mathcal{A}' = \mathcal{A} - \mathcal{A}^0$,

$$\mathcal{A}' = -kT \nabla^T \mathbf{T} \nabla + (\nabla^T U_0) \mathbf{T} \nabla \,. \tag{34.24}$$

$A^0$ is diagonal with elements ${A_{kk}}^0 = {\bar{\lambda}_k}^0$, since $\langle \psi_k, \psi_l \rangle = \delta_{kl}$. We therefore have

$$\begin{aligned} {L_{kl}}^a &= \bar{\lambda}_k = {\bar{\lambda}_k}^0 + {A_{kk}}' \qquad && \text{for } k = l \\ &= {A_{kl}}' && \text{for } k \neq l \,. \end{aligned} \tag{34.25}$$

Equation (34.18) with (34.22) establishes a perturbation solution for $\rho$.

In order to proceed further, we must solve the eigenvalue equation (34.11). The spring potential $U_0$ may be written as

$$U_0 = \tfrac{1}{2}\kappa \mathbf{R}^T \mathbf{A}\mathbf{R}\,, \tag{34.26}$$

where $\kappa$ is the force constant and $A$ is the matrix given by Eq. (33.9). The matrix $\mathbf{A}$ can be transformed into a diagonal matrix $\Lambda$ with a matrix $\mathbf{Q}$; that is, $\mathbf{Q}^{-1}\mathbf{A}\mathbf{Q} = \Lambda$. This is a special case of the transformation of (33.12), i.e., the free-draining case with $\mathbf{H}$ the unit matrix. Therefore, the diagonal elements $\lambda_j$ of $\Lambda$ are given by Eq. (33.41),

$$\lambda_j = \pi^2 j^2/n^2\,, \tag{34.27}$$

and $\mathbf{Q}$ is orthogonal and symmetric, $\mathbf{Q}^{-1} = \mathbf{Q}^T = \mathbf{Q}$, its elements being, from Eq. (33.43),

$$Q_{ij} = (2/n)^{1/2}\cos(\pi i j/n)\,. \tag{34.28}$$

Then, the coordinates $\boldsymbol{\xi}$ given by Eq. (33.23) are the Rouse free-draining normal coordinates, and the operator $\mathcal{A}^0$ is transformed into

$$\begin{aligned}\mathcal{A}^0 &= -(kT/\zeta)\nabla_{\boldsymbol{\xi}}{}^T\nabla_{\boldsymbol{\xi}} + (\kappa/2\zeta)\nabla_{\boldsymbol{\xi}}{}^T(\boldsymbol{\xi}^T\Lambda\boldsymbol{\xi})\nabla_{\boldsymbol{\xi}} \\ &= -(kT/\zeta)\sum_{j=0}^{n}\nabla_{\boldsymbol{\xi}_j}{}^2 + (\kappa/\zeta)\sum_{j=0}^{n}\lambda_j\boldsymbol{\xi}_j\cdot\nabla_{\boldsymbol{\xi}_j}\,.\end{aligned} \tag{34.29}$$

The separation of variables in Eq. (34.29) allows the eigenfunctions $\psi_k$ to be written as

$$\psi_k = \prod_{j=1}^{n}\phi_{k(j)}(\boldsymbol{\xi}_j) \tag{34.30}$$

with

$$\phi_{k(j)}(\boldsymbol{\xi}_j) = \phi_{k(jX)}(X_j)\phi_{k(jY)}(Y_j)\phi_{k(jZ)}(Z_j)\,, \tag{34.31}$$

where we have omitted the contribution of a simple translation of the molecule. From Eq. (34.11), the equations for $\phi_{k(j)}$ are

$$-(kT/\zeta)\nabla_{\boldsymbol{\xi}_j}{}^2\phi_{k(j)} + (\kappa/\zeta)\lambda_j\boldsymbol{\xi}_j\cdot\nabla_{\boldsymbol{\xi}_j}\phi_{k(j)} = \bar{\lambda}_{k(j)}{}^0\phi_{k(j)} \quad (j = 1,\ldots,n) \tag{34.32}$$

with

$$\begin{aligned}\bar{\lambda}_k{}^0 &= \sum_j \bar{\lambda}_{k(j)}{}^0\,, \\ \bar{\lambda}_{k(j)}{}^0 &= \bar{\lambda}_{k(jX)}{}^0 + \bar{\lambda}_{k(jY)}{}^0 + \bar{\lambda}_{k(jZ)}{}^0\,.\end{aligned} \tag{34.33}$$

The single subscript $k$ denotes a set of $n$ $k(j)'$s, and each $k(j)$ denotes the set $k(jX)$, $k(jY)$, $k(jZ)$. Equation (34.32) may be reduced to the standard Hermite differential equation, and then solved to give

$$\phi_{k(jX)}(X_j) = A_{k(jX)}H_{k(jX)}(\sigma_j X_j)\,, \tag{34.34}$$

and similar equations for the $Y$ and $Z$ components. Here $\sigma_j$ and $\bar{\lambda}_{k(jX)}{}^0$ are defined by

$$\sigma_j{}^2 = 3\lambda_j/2a^2\,, \tag{34.35}$$

$$\bar{\lambda}_{k(jX)}{}^0 = \pi^2(\kappa/\zeta)j^2k(jX)/n^2\,. \tag{34.36}$$

$H_{k(jX)}$ is the Hermite polynomial degree $k(jX)$ which is an integer. $A_{k(jX)}$, etc., given by $A_{k(j)} = A_{k(jX)}A_{k(jY)}A_{k(jZ)}$, are the normalizing constants to be determined by $\langle \psi_k, \psi_l \rangle = \delta_{kl}$ and

$$\psi_k = A_k H_k(\{\boldsymbol{\xi}_n\}) = \prod_j A_{k(j)}H_{k(j)}(\sigma_j \boldsymbol{\xi}_j)\,, \tag{34.37}$$

where $H_{k(j)}(\sigma_j\boldsymbol{\xi}_j)$ again denotes $H_{k(jX)}(\sigma_jX_j)H_{k(jY)}(\sigma_jY_j)$ $\times H_{k(jZ)}(\sigma_jZ_j)$.

In the normal coordinates, the potential $U_0$ becomes

$$U_0 = kT\sum_j \sigma_j{}^2\xi_j{}^2\,, \tag{34.38}$$

and the normalizing constant $C_0$ in Eq. (34.3) is found to be

$$C_0 = \pi^{-3n/2}\prod_{j=1}^{n}\sigma_j{}^3\,. \tag{34.39}$$

We then obtain

$$A_k = \prod_{j=1}^{n}[2^{k(jX)+k(jY)+k(jZ)}k(jX)!k(jY)!k(jZ)!]^{-1/2}\,. \tag{34.40}$$

Clearly we have

$$\begin{aligned} \psi_0 &= A_0H_0 = 1\,, \\ \bar{\lambda}_0{}^0 &= 0\,. \end{aligned} \tag{34.41}$$

Now, by the use of Eq. (33.28) with $\mu_j = \lambda_j$, the intrinsic viscosity may be written as

$$[\eta] = \frac{N_{\mathrm{A}}\kappa}{M\eta_0 g}\sum_{j=1}^{n}\lambda_j\langle X_jY_j\rangle\,, \tag{34.42}$$

where $g$ is independent of time. $\langle X_jY_j\rangle$ may be evaluated as follows,

$$\begin{aligned} \langle X_jY_j\rangle &= \int X_jY_jP\; d\{\boldsymbol{\xi}_n\} \\ &= \sum_{k\neq 0} f_k{}'\int X_jY_jP_0\psi_k\; d\{\boldsymbol{\xi}_n\} \\ &= f_{(j)}{}'\int X_jY_jP_0\psi_{(j)}d\{\boldsymbol{\xi}_n\} = f_{(j)}{}'(2\sigma_j{}^2)^{-1}\,, \end{aligned} \tag{34.43}$$

where we have used Eq. (34.5) with (34.18) in the second line, and the properties of the Hermite polynomials in the third line. The states indicated by the subscript $(j)$ ($j = 1, \ldots, n$) are those in which $X$ and $Y$ components of one normal mode are excited from the zeroth order to the first-order Hermite polynomial, the other component and all other modes being in their ground states; that is,

$$\psi_{(j)} = A_{(j)} H_{(j)} = \tfrac{1}{2} H_1(\sigma_j X_j) H_1(\sigma_j Y_j)\,, \tag{34.44}$$

$$\bar{\lambda}_{(j)}{}^0 = 2\pi^2 (\kappa/\zeta) j^2/n^2\,. \tag{34.45}$$

Substitution of Eq. (34.43) with (34.35) into Eq. (34.42) leads to

$$[\eta] = \frac{N_{\mathrm{A}} kT}{M\eta_0 g} \sum_{j=1}^{n} f_{(j)}{}'\,. \tag{34.46}$$

Thus the only $\psi_k$ which can contribute to the intrinsic viscosity are of the type $\psi_{(j)}$.

For the flow under consideration the operator $\mathcal{B}$ is transformed into

$$\mathcal{B} = g \sum_j Y_j \frac{\partial}{\partial X_j} - \frac{3g}{a^2} \sum_j \lambda_j X_j Y_j\,. \tag{34.47}$$

The matrix representation of $\mathcal{B}$ is found to be

$$\begin{aligned} L_{kl}{}^b = & -g \sum_{j=1}^{n} \Bigg( \prod_{\substack{i=1 \\ \neq j}}^{n} \delta_{k(i),l(i)} \Bigg) \delta_{k(jZ),l(jZ)} [k(jX)]^{1/2} \delta_{k(jX)-1,l(jX)} \\ & \times \left\{ [k(jY)]^{1/2} \delta_{k(jY)-1,l(jY)} + [k(jY)+1]^{1/2} \delta_{k(jY)+1,l(jY)} \right\}, \end{aligned} \tag{34.48}$$

where $\delta_{k(i),l(i)}$ is the abbreviation for the product $\delta_{k(iX),l(iX)} \delta_{k(iY),l(iY)} \times \delta_{k(iZ),l(iZ)}$. It is evident that

$$L_{kk}{}^b = 0\,, \tag{34.49}$$

and that the only $\psi_k$ which give nonvanishing $L_{k0}{}^b$ are of the type $\psi_{(j)}$ and then

$$L_{(j)0}{}^b = -g\,. \tag{34.50}$$

It is now seen that any term in $f_k{}'$ of (34.22) which contains only products of elements from $L^b$, and no elements from $L^a$, makes no contribution to $[\eta]$. For, each $L_{kl}{}^b$ raises by one the excitation level of the $X$ component of a normal mode according to Eq. (34.48), and only $f_{(j)}{}'$ contribute to $[\eta]$.

If we consider the limiting case $g \to 0$, Eq. (34.22) with $k = (j)$ becomes

$$\frac{f_{(j)}{}'}{g} = \frac{1}{\bar{\lambda}_{(j)}} \left[ 1 - \sum_{\substack{l \\ \neq j}} \frac{A_{(j)(l)}{}'}{\bar{\lambda}_{(l)}} + \sum_{\substack{l \\ l \neq (j),(m)}} \sum_{m} \frac{A_{(j)l}{}' A_{l(m)}{}'}{\bar{\lambda}_l \bar{\lambda}_{(m)}} + \cdots \right] \tag{34.51}$$

with

$$\bar{\lambda}_{(j)} = \bar{\lambda}_{(j)}^{\,0} + A_{(j)(j)}{}'\,. \tag{34.52}$$

Equation (34.46) with (34.51) gives the desired perturbation theory of the intrinsic viscosity. The zeroth-order theory includes only the first term on the right-hand side of Eq. (34.51). This is equivalent to neglecting the off-diagonal elements of $L^a$, and is called the diagonal $L^a$ approximation. In order to obtain numerical results we must evaluate $A_{kl}{}'$. It is given by

$$\begin{aligned} A_{kl}{}' &= \int P_0 \psi_k \mathcal{A}' \psi_l d\{\mathbf{R}_n\} \\ &= kT \int P_0 (\nabla^T \psi_k) \mathbf{T} (\nabla \psi_l) d\{\mathbf{R}_n\} . \end{aligned} \tag{34.53}$$

In particular, we have from Eq. (34.44).

$$A_{(i)(j)}{}' = \tfrac{1}{4} kT \sum_{\substack{l \\ l \neq m}} \sum_{m} \langle (\nabla_l H_{(i)}) \mathbf{T}_{lm} (\nabla_m H_{(j)}) \rangle_0 , \tag{34.54}$$

where

$$H_{(j)} = 4{\sigma_j}^2 \left( \sum_k \mathcal{Q}_{jk} x_k \right) \left( \sum_k \mathcal{Q}_{jk} y_k \right) . \tag{34.55}$$

The equilibrium average in Eq. (34.54) may be evaluated straightforwardly by means of the Wang-Uhlenbeck theorem, and the sums may be converted to integrals. For example, $A_{(j)(j)}{}'$ is found to be

$$A_{(j)(j)}{}' = \frac{8\kappa h}{n^2 \zeta} [I_1(j) + I_2(j)] , \tag{34.56}$$

where $h$ is the draining parameter defined by Eq. (31.23), $I_1(j)$ is equal to Hearst's $\lambda_j'$, i.e., $G_{jj}$ given by Eq. (33.48), and $I_2(j)$ is given by

$$\begin{aligned} I_2(j) = \frac{3\sqrt{2}}{40} \bigg[ &-20 + (-1)^j 12 + 12\pi (2j)^{1/2} S(\pi j) - 8\pi j^{1/2} S(2\pi j) \\ &+ 17 \left( \frac{2}{j} \right)^{1/2} C(\pi j) - \frac{22}{j^{1/2}} C(2\pi j) + 3 \left( \frac{6}{j} \right)^{1/2} C(3\pi j) \bigg] \end{aligned} \tag{34.57}$$

with $C$ and $S$ Fresnel integrals defined by Eqs. (33.49).

Now, in the diagonal $L^a$ approximation, the intrinsic viscosity or the viscosity function $\Phi_0(h)$ can readily be written down,

$$\Phi_0(h) = \frac{2N_{\mathrm{A}} h}{(12\pi)^{1/2}} \sum_{j=1}^{n} \frac{1}{j^2 + (4h/\pi^2)[I_1(j) + I_2(j)]} . \tag{34.58}$$

Equation (34.58) gives $\Phi_0(\infty) = 2.68 \times 10^{23}$, and the values of $\Phi_0(h)/\Phi_0(\infty)$ are shown by curve FP in Fig. VI.4. If $\mathbf{T}_{lm}$ is replaced by its average value in Eq. (34.54), the $\Phi_0(h)$ given by Eq. (34.58) includes no contribution from $I_2(j)$, and becomes identical with Hearst's $\Phi_0(h)$

**TABLE VI.3.** THE VISCOSITY CONSTANT $\Phi_0$ FROM VARIOUS THEORIES FOR LINEAR FLEXIBLE CHAINS

| | $\Phi_0 \times 10^{-23}$ |
|---|---|
| KRAG | 2.87 |
| Z | 2.84 |
| H | 2.82 |
| FP (0th order) | 2.68 |
| (1st order) | 1.81 |
| (2nd order) | 2.66 |
| HT[a] | 2.19 |

[a] See Section 36d(ii).

with $\Phi_0(\infty) = 2.82 \times 10^{23}$ as obtained in the previous section. The difference between these two values of $\Phi_0(\infty)$ is obviously due to the present avoidance of preaveraging the Oseen tensor. Consider now the non-free-draining limit. As seen from Eq. (34.51), the first-order perturbation theory result is obtained when the off-diagonal elements $A_{(i)(j)}{}'$ are evaluated from Eq. (34.54); one finds $\Phi_0(\infty) = 1.81 \times 10^{23}$. In the second-order perturbation theory we need evaluate not only the terms $A_{(j)(l)}{}'A_{(l)(m)}{}'$ but also $A_{(j)l}{}'A_{l(m)}{}'$ with $l \neq (l)$. The contribution of the terms of the former type to $\Phi_0(\infty)$ is $2.19 \times 10^{23}$, while the contribution of the latter is found to be $0.47 \times 10^{23}$. Thus the second-order perturbation theory result is $\Phi_0(\infty) = 2.66 \times 10^{23}$. The convergence of the perturbation series is clearly not as good as could be hoped for. The values of $\Phi_0(\infty)$ obtained from the various theories are summarized in Table VI.3. For convenience, $\Phi_0(\infty)$ will be referred to as the *viscosity constant.*

All the theories of the intrinsic viscosity described so far predict that the viscosity function $\Phi_0(h)$ for flexible chains increases with increasing $h$, and hence with molecular weight $M$, since $h$ is proportional to $M^{1/2}$. Then it follows from Eq. (31.34) that $[\eta]/M^{1/2}$ must be an increasing function of $M$ at the theta temperature. However, experimental data are not in agreement with this conclusion, indicating rather that $[\eta]/M^{1/2}$ is independent of $M$ at the theta temperature for molecular weights of ordinary interest, and therefore that there is no draining effect. As an illustration, in Fig. VI.6 are shown plots of $[\eta]/M^{1/2}$ against $M^{1/2}$ using the data obtained by Krigbaum and Flory[44] for polystyrene in cyclohexane at the theta temperature, 34°C (open circles) and polyisobutylene in benzene at the theta temperature, 24°C (filled circles). It is seen that $[\eta]/M^{1/2}$ remains constant until the molecular weight goes down to about ten thousand. If we assume Stokes' law to determine the friction coefficient of the segment, $\zeta = 3\pi\eta_0 b$ with $b$ the diameter of the segment, and further assume that $n = M/52$, $a = 5$ Å,

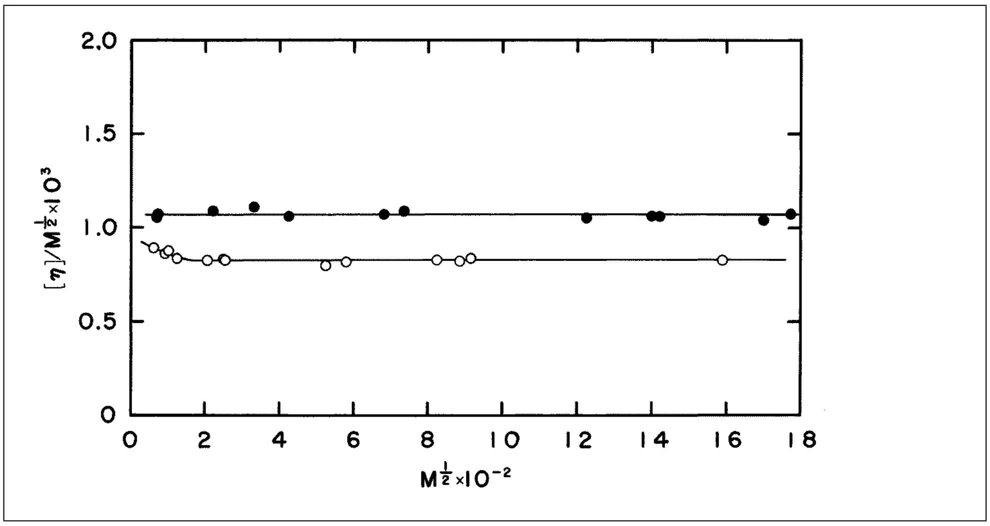

**Fig. VI.6.** $[\eta]/M^{1/2}$ plotted against $M^{1/2}$ ($[\eta]$ in dl/g). Open circles: polystyrene in cyclohexane at $\Theta = 34.0$ °C.[44] Filled circles: polyisobutylene in benzene at $\Theta = 24$ °C.[44]

and $b = 5$ Å for polystyrene, we obtain $h \simeq 6 \times 10^{-2} M^{1/2}$. When $M = 10^4$, we have $h = 6$, and $\Phi_0(h)/\Phi_0(\infty) \simeq 0.8$ from Fig. VI.4. In order words, the theory predicts a 20% decrease in $[\eta]/M^{1/2}$ when the molecular weight is decreased from very large values to about ten thousand. There are at least two reasons for this disagreement between theory and experiment. One source of discrepancy arises from the use of the random-flight model, and the other from the inadequacy of the Oseen tensor as a description of the hydrodynamic interaction. A complete theory of the viscosity has not yet been given, and further investigations are needed.

Thus, at least for flexible-chain polymers, the theory may be considered to have a significance only in the non-free-draining limit, and we may assume that the viscosity function is constant and equal to $\Phi_0(\infty)$ over a wide range of molecular weight. The viscosity constant $\Phi_0$ has practical importance, because exploitation of the relationship between intrinsic viscosity and molecular weight enables us to determine the unperturbed molecular dimensions from Eq. (31.34) when $\Phi_0$ is given. As seen from Table VI.3, however, the theoretical values of $\Phi_0$ scatter, although not appreciably. Further discussion of this subject will be found in the next chapter.

## 35. Excluded-Volume Effects

In this section we study the effects of excluded volume on the zero-frequency intrinsic viscosity and the translational friction coefficient of linear flexible chains. In particular, the intrinsic viscosity of perturbed chains is the more important property, since it is very often used, along with the molecular dimensions and the second virial coefficient, to characterize the polymer. The theory is developed on the basis of the previous theory of intrinsic viscosities or friction coefficients of unperturbed chains.

## 35a. Intrinsic Viscosities

If the draining effect is assumed to be negligibly small for ordinary flexible chains, as discussed in the last section, then the theory thus far developed predicts that the intrinsic viscosity is proportional to the square root of the molecular weight, and that a value of $\nu$ greater than 0.5 in the $[\eta] - M$ relationship of (31.36) must be interpreted as arising from the excluded-volume effect. Indeed it was from this point of view that Flory[45, 46] introduced the discussion of the excluded-volume effect in a polymer chain. Replacing $\langle S^2 \rangle_0$ by $\langle S^2 \rangle$ in Eq. (31.34), Flory and Fox[46, 47] proposed the empirical equation,

$$[\eta] = 6^{3/2} \Phi \frac{\langle S^2 \rangle^{3/2}}{M} , \tag{35.1}$$

where they originally regarded $\Phi$ as equal to the (universal) viscosity constant $\Phi_0$. In general, however, $\Phi$ depends on the excluded volume, although not on the draining parameter. Let $[\eta]_\theta$ be the intrinsic viscosity of unperturbed chains. The radius expansion factor $\alpha_\eta$ for the viscosity is then defined by

$$\begin{aligned} [\eta] &= [\eta]_\theta {\alpha_\eta}^3 \\ &= 6^{3/2} \Phi_0 \frac{{\langle S^2 \rangle_0}^{3/2}}{M} {\alpha_\eta}^3 . \end{aligned} \tag{35.2}$$

From Eqs. (35.1) and (35.2), $\Phi$ may be expressed as

$$\Phi = \Phi_0 \left( \frac{\alpha_\eta}{\alpha_S} \right)^3 . \tag{35.3}$$

In the original theory of Flory there is no distinction made between the various possible expansion factors. Our problem is to evaluate $\alpha_\eta$ or $\Phi$.

## 35a(i). The Kirkwood–Riseman Scheme

Kurata and Yamakawa[23, 48] developed an approximate first-order perturbation theory of the intrinsic viscosity on the basis of the Kirkwood–Riseman theory, and were the first to emphasize the difference between $\alpha_\eta$ and $\alpha_S$. In Eq. (31.18) we use the perturbed statistical averages evaluated in the single-contact approximation. From Eqs. (14.28) and (14.31) the exact first-order perturbation theory value of $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ is obtained as

$$\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_0 + \tfrac{1}{3} n a^2 I_{ij} z - \cdots , \tag{35.4}$$

where $z$ is the excluded-volume parameter defined by Eq. (13.32), and the coefficient $I_{ij}$ (for $j > i$) is given by

$$\begin{aligned} I_{ij} = {} & \frac{121}{21} - \frac{32}{3n^{3/2}} \\ & \times \{ j^{3/2} + (n-i)^{3/2} + \tfrac{1}{2}(j-i)^{3/2} - \tfrac{3}{4}(j-i)[j^{1/2} + (n-i)^{1/2}] \} \\ & - \frac{2}{n^2}(j-i)^2 + \frac{12}{5n^{5/2}}[j^{5/2} + i^{5/2} + (n-j)^{5/2} + (n-i)^{5/2}] \\ & + \frac{2}{3n^3}[j^3 + i^3 + (n-j)^3 + (n-i)^3] \, . \end{aligned} \tag{35.5}$$

We can also derive the exact first-order perturbation theory value of $\langle {R_{ij}}^{-1} \rangle$, but it is so complicated that further developments become intractable. Therefore, we introduce the approximation,

$$\langle {R_{ij}}^{-1} \rangle = \tilde{\alpha}^{\,-1} \langle {R_{ij}}^{-1} \rangle_0 \tag{35.6}$$

with

$$\tilde{\alpha}^{\,-1} = \frac{\displaystyle\sum_{i<j} {\alpha_{ij}}^{-1} \langle {R_{ij}}^{-1} \rangle_0}{\displaystyle\sum_{i<j} \langle {R_{ij}}^{-1} \rangle_0} \, , \tag{35.7}$$

$${\alpha_{ij}}^2 = \langle {R_{ij}}^2 \rangle / \langle {R_{ij}}^2 \rangle_0 \, . \tag{35.8}$$

The expansion factor $\tilde{\alpha}$ is then evaluated to be

$$\tilde{\alpha}^{-1} = 1 - 0.416z + \cdots \, . \tag{35.9}$$

The approximation of (35.6) with (35.9) seems more plausible than does the uniform-expansion approximation $\langle {R_{ij}}^{-1} \rangle = {\alpha_S}^{-1} \langle {R_{ij}}^{-1} \rangle_0$ with ${\alpha_S}^{-1} = 1 - 0.638z + \cdots$.

Now, substitution of Eqs. (35.4) and (35.6) into Eq. (31.18) leads to an integral equation of the same type as the Kirkwood–Riseman equation (31.21). Therefore, if we use the Kirkwood–Riseman approximation of (31.27) as before, we obtain for the function $F(X)$ appearing in Eq. (31.16) for $[\eta]$

$$\frac{F(X)}{F_0(X)} = 1 + \left[ \frac{{F_1}^{(1)}(X) + {F_1}^{(2)}(X)}{F_0(X)} \right] z + \cdots \, , \tag{35.10}$$

where $F_0(X)$ is identical with the $F(X)$ (at $z = 0$) given by Eq. (31.30), and ${F_1}^{(1)}(X)$ and ${F_1}^{(2)}(X)$ are given by

$$\begin{aligned} {F_1}^{(1)}(X) = {} & \frac{4}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2(1 + X/k^{1/2})} \\ & \times \left[ 1 + 2\pi^{1/2} \frac{C(2\pi k)}{(\pi k)^{1/2}} + \tfrac{3}{2}\pi^{1/2} \frac{S(2\pi k)}{(\pi k)^{3/2}} \right] , \end{aligned} \tag{35.11}$$

$$F_1{}^{(2)}(X) = 0.416 \times \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{X}{k^{5/2}(1 + X/k^{1/2})^2} \tag{35.12}$$

with $C$ and $S$ the Fresnel integrals. Ullman[49] has solved our integral equation for several values of $X$ and $z$ using a computer, but we do not reproduce the results here.

Since ${\alpha_\eta}^3 = F(\infty)/F_0(\infty)$, we find (in the non-free-draining limit)

$${\alpha_\eta}^3 = 1 + 1.55z - \cdots\,, \tag{35.13}$$

$$\Phi/\Phi_0 = 1 - 0.36z + \cdots\,. \tag{35.14}$$

We note that the contributions of $F_1{}^{(1)}$ and $F_1{}^{(2)}$ to the coefficient 1.55 of $z$ in ${\alpha_\eta}^3$ are 1.135 and 0.416, respectively. If we use the uniform-expansion approximations $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_0 \alpha_S^2$ and $\langle {R_{ij}}^{-1} \rangle = \langle {R_{ij}}^{-1} \rangle_0 {\alpha_S}^{-1}$ in Eq. (31.18), the corresponding contributions become 1.276 and 0.638, respectively, and necessarily we have ${\alpha_\eta}^3 = \alpha_S^3 = 1 + 1.914z - \cdots$. Subsequently, however, Ptitsyn and Eizner[50] solved, with the use of the Gegenbauer polynomial expansion, the integral equation that results from the assumptions of (35.4) and $\langle {R_{ij}}^{-1} \rangle = \langle {R_{ij}}^{-1} \rangle_0$, and showed that the uniform-expansion approximation to $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ is very good.

Equation (35.1) with (35.14) gives the two-parameter theory of the intrinsic viscosity; this theory is similar to the theory of the excluded-volume effect described in Chapter III. The present analysis predicts that ${\alpha_\eta}^3$ is smaller than $\alpha_S^3$ for positive $z$, and that $\Phi$ is a decreasing function of $z$. Kurata and Yamakawa have proposed a semiempirical closed expression for ${\alpha_\eta}^3$,

$${\alpha_\eta}^3 = \alpha_S^{2.43} \tag{35.15}$$

to give Eq. (35.13) at small $z$.

## 35a(ii). The Zimm-Peterlin Scheme

The intrinsic viscosity for large excluded volume has been investigated by Ptitsyn and Eizner,[51] Tschoegl,[52] and Bloomfield and Zimm,[53] using the Zimm theory of the spring and bead model and the Peterlin method[54] of treating the excluded-volume effect. We first describe briefly the procedure proposed by Peterlin. In order to take into account the non-Markoff nature of the polymer chain we assume the form of $\langle {R_{ij}}^2 \rangle$ to be

$$\langle {R_{ij}}^2 \rangle = a^2 |j - i|^{1+\varepsilon}\,, \tag{35.16}$$

so that $\langle R^2 \rangle = a^2 n^{1+\varepsilon}$. We note that $\varepsilon$ is a monotonically increasing function of $z$ since it is determined from $\varepsilon = \frac{1}{2} \partial \ln \alpha_R^2 / \partial \ln\ z$. Further, the distribution of $R_{ij}$ is assumed to be Gaussian with second moment just equal to that given by Eq. (35.16). We then have

$$\begin{aligned}\langle {R_{ij}}^{-1}\rangle &= (6/\pi)^{1/2}\langle {R_{ij}}^{2}\rangle^{-1/2}\\ &= (6/\pi)^{1/2}/|j-i|^{(1+\varepsilon)/2}a\,,\end{aligned} \tag{35.17}$$

and from Eqs. (7.22) and (35.16)

$$\langle S^2\rangle = a^2 n^{1+\varepsilon}(6+5\varepsilon+\varepsilon^2)^{-1}\,. \tag{35.18}$$

Thus, the ratio $\langle R^2\rangle/\langle S^2\rangle$ becomes dependent on the parameter $\varepsilon$, thereby displaying the non-Gaussian nature of the perturbed chain.

We must now solve the diffusion equation (33.10) with a nonvanishing excluded-volume force term $\nabla W$. However, this equation is so complicated that we use the spring potential $U_0$ with $a\alpha_S$ in place of $a$ to suppress the term $\nabla W$ in Eq. (33.10). In this approximation the spring force constant $\kappa$ may simply be replaced by $\kappa/\alpha_S^{\,2}$, and Eq. (33.33) with (33.34) becomes

$$[\eta] = \frac{N_{\mathrm{A}}\langle S^2\rangle\zeta}{nM\eta_0}\sum_j {\lambda_j}^{-1}\,. \tag{35.19}$$

This approximation is equivalent to making the uniform-expansion approximation in $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$ but not in $\langle {R_{ij}}^{-1}\rangle$ in the Kirkwood-Riseman scheme, which is very good, as mentioned in the last subsection.

The eigenvalues $\lambda_j$ are determined by

$$\alpha''(r) + h(\varepsilon)\int_{-1}^{1}\frac{\alpha''(s)}{|r-s|^{(1+\varepsilon)/2}}ds = -\frac{n^2\lambda}{4}\alpha(r) \tag{35.20}$$

with the boundary conditions of (33.38). In Eq. (35.20) we have used Eq. (35.17), and $h(\varepsilon)$ is defined by

$$h(\varepsilon) = 2^{\varepsilon/2}\zeta n^{(1-\varepsilon)/2}/(12\pi^3)^{1/2}\eta_0 a\,, \tag{35.21}$$

which reduces to Eq. (31.23) when $\varepsilon=0$. We then have for the function $\Phi$ in Eq. (35.1) (in the non-free-draining limit)

$$\Phi = \frac{(2\pi^3)^{1/2}N_{\mathrm{A}}}{24}2^{-\varepsilon/2}(6+5\varepsilon+\varepsilon^2)^{1/2}\sum_j {\lambda_j}'^{-1}\,, \tag{35.22}$$

where ${\lambda_j}'$ is defined by Eq. (33.46) with $h(\varepsilon)$ in place of $h$. In the Hearst diagonal approximation, we obtain from Eq. (35.20)

$${\lambda_j}' = (2\pi)^{1/2}2^{-\delta}(\pi j)^{\delta}[\pi j C_\delta(\pi j) - \delta S_\delta(\pi j)] \tag{35.23}$$

with

$$\delta = \tfrac{1}{2}(1+\varepsilon)\,,$$

where $C_\delta$ and $S_\delta$ are the modified Fresnel integrals which are obtained by replacing $t^{-1/2}$ by $t^{-\delta}$ in Eqs. (33.49).

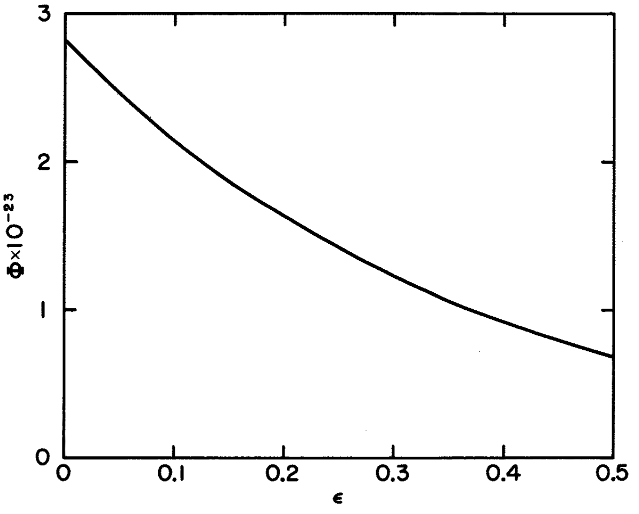

**Fig. VI.7.** The viscosity function $\Phi$ plotted against Peterlin's excluded-volume parameter $\varepsilon$.

The values of $\Phi$ calculated from Eq. (35.22) are plotted against $\varepsilon$ in Fig. VI.7. Ptitsyn and Eizner[51] carried out the calculation with $\varepsilon = 0$ to 0.2; the case $\varepsilon = 0.2$ corresponds to an expansion of the fifth-power type. The case $\varepsilon = \frac{1}{3}$ corresponding to third-power type expansion was considered by Tschoegl,[52] and the case $\varepsilon = 0.5$ was given by Bloomfield and Zimm[53] to apply to stiff chains. $\Phi$ is seen to decrease with increasing $\varepsilon$, and hence $z$.

## 35a(iii). The Boson Representation

In this subsection we describe a method of operator representation satisfying boson commutation rules which was introduced by Fixman.[55, 56] The introduction of this technique makes not only an explicit consideration of the excluded-volume potential possible, but also renders the matrix formalism introduced in Section 34 more tractable.

We first put $P = P^{\alpha}\rho$, where $P^{\alpha}$ is equal to the $P_0$ given by Eq. (34.3) with $\bar{a} = a\alpha$ in place of $a$, i.e., the scaled Gaussian distribution,

$$P^{\alpha} = C^{\alpha}\exp(-U^{\alpha}/kT) \tag{35.24}$$

with

$$U^{\alpha} = U_0/\alpha^2\,, \tag{35.25}$$

where $C^{\alpha}$ is the normalizing constant and $U_0$ is the spring potential given by Eq. (34.26). The parameter $\alpha$ cannot be equal to the expansion factor of any particular measure of molecular dimensions ($\alpha_R$ or $\alpha_S$), but is chosen to make the new $\rho$ defined above come as close as possible to the basis set unity, which forms the zeroth approximation to the equilibrium $\rho$. The new $\rho$ satisfies Eq. (34.6) if $\mathcal{L}$ is defined by

$$\mathcal{L} = \mathcal{L}^a + \mathcal{L}^b \tag{35.26}$$

with

$$\mathcal{L}^a = -kT[\nabla^T - (\nabla^T U^\alpha/kT)]\mathbf{D}(\nabla + \nabla V)\,, \tag{35.27}$$

$$\mathcal{L}^b = [\nabla^T - (\nabla^T U^\alpha/kT)]\mathbf{v}^0\,, \tag{35.28}$$

$$V = (U - U^\alpha)/kT = (U_0 - U^\alpha + W)/kT\,. \tag{35.29}$$

When $\alpha = 1$ and $W = 0$, $V$ vanishes, and $\mathcal{L}^a$ and $\mathcal{L}^b$ become $\mathcal{A}$ and $\mathcal{B}$ given by Eqs. (34.8) and (34.9), respectively. If we use the Rouse free-draining normal coordinates as before, $U^\alpha$ may be written as

$$U^\alpha = kT\sum_{l=1}^{n} \bar{\sigma}_l{}^2 \xi_l{}^2\,, \tag{35.30}$$

where $\bar{\sigma}_l = \sigma_l/\alpha$ with $\sigma_l$ given by Eq. (34.35). We can also write down $\mathcal{L}^a$ and $\mathcal{L}^b$ in the normal coordinates. The scalar product is defined with weight function $P^\alpha$ instead of $P_0$, and a matrix representation of $\mathcal{L}^a$, $\mathcal{L}^b$, and $\rho$ is formed from the same Hermite polynomial basis set as before except that $\sigma_l$ is replaced by $\bar{\sigma}_l$.

The operators $\mathcal{L}^a$ and $\mathcal{L}^b$ are composed of differential operators and functions of the normal coordinates. The latter must be treated as operators since they do not commute with the differential operators. Consider therefore the matrix representation of $\partial/\partial\xi_{ls}$ and $\xi_{ls}$, where $\xi_{ls}$ with $s = 1$, 2, and 3 represent $X_l$, $Y_l$, and $Z_l$, respectively. The operator $\partial/\partial\xi_{ls}$ or $\xi_{ls}$ can connect only different excitations of $\phi_{p(ls)}(\xi_{ls})$, other components of the basis function $\psi_p$ being unchanged. The matrix elements between different excitations $p$ and $q$ the $s$th component of the $l$th mode are obtained as

$$(\partial/\partial\xi_{ls})_{pq} = (2q)^{1/2}\bar{\sigma}_l\delta_{p,q-1}\,, \tag{35.31}$$

$$(\xi_{ls})_{pq} = (1/2^{1/2}\bar{\sigma}_l)[q^{1/2}\delta_{p,q-1} + (q+1)^{1/2}\delta_{p,q+1}]\,. \tag{35.32}$$

These elements can be expressed as the matrix elements of creation and annihilation operators as follows. We denote the occupation number representation of $\psi_q$ by

$$|q\rangle = |q(1X)q(1Y)q(1Z)\cdots q(nX)q(nY)q(nZ)\rangle\,, \tag{35.33}$$

$$\langle\psi_p, \psi_q\rangle = \langle p|q\rangle = \delta_{pq}\,. \tag{35.34}$$

That is, $|q\rangle$ is the matrix representative of the function $\psi_q$ formed on the basis set $\psi_p$. Let $b_{ls}^\dagger$ be an operator acting on a basis vector $|q\rangle$ which raises $q(ls)$ to $q + 1(ls)$, and leaves other occupation numbers unchanged. With the normal mode to which $q$ refers left implicit, the defining equation is

$$b_{ls}^\dagger|q\rangle = (q+1)^{1/2}|q+1\rangle\,. \tag{35.35}$$

We therefore have

$$\langle p|b_{ls}^{\dagger}|q\rangle = (q+1)^{1/2}\delta_{p,q+1}\,. \tag{35.36}$$

Similarly, the annihilation operator is defined to have the property,

$$b_{ls}|q\rangle = q^{1/2}|q-1\rangle\,. \tag{35.37}$$

$$\langle p|\,b_{ls}\,|q\rangle = q^{1/2}\delta_{p,q-1}\,. \tag{35.38}$$

Comparison of Eqs. (35.36) and (35.38) with Eqs. (35.31) and (35.32) gives

$$\nabla_{\boldsymbol{\xi}_l} = 2^{1/2}\bar{\sigma}_l\mathbf{b}_l\,, \tag{35.39}$$

$$\boldsymbol{\xi}_l = (1/2^{1/2}\bar{\sigma}_l)(\mathbf{b}_l + \mathbf{b}_l{}^{\dagger})\,, \tag{35.40}$$

where

$$\mathbf{b}_l = \sum_{s=1}^{3} b_{ls}\mathbf{e}_s\,, \qquad \mathbf{b}_l{}^{\dagger} = \sum_{s=1}^{3} b_{ls}{}^{\dagger}\mathbf{e}_s\,. \tag{35.41}$$

If the commutator is defined by $(a,b) = ab - ba$, from Eqs. (35.35) and (35.37) there result the usual commutation properties of boson operator,

$$(b_{ks}, b_{lt}) = 0\,, \qquad (b_{ks}^{\dagger}, b_{lt}^{\dagger}) = 0\,, \qquad (b_{ks}, b_{lt}^{\dagger}) = \delta_{kl}\delta_{st}\,. \tag{35.42}$$

With the understanding that all functions of coordinates are given a boson representation through Eqs. (35.39) and (35.40), $\mathcal{L}^a$ and $\mathcal{L}^b$ may be brought into boson form. It is necessary first to put

$$\nabla_{\boldsymbol{\xi}_l} V = (\nabla_{\boldsymbol{\xi}_l}, V)\,, \tag{35.43}$$

where the derivative in the commutator acts on any function to its right. We then have

$$\mathcal{L}^a = \sum_{k=1}^{n}\sum_{l=1}^{n} \mathbf{b}_k{}^{\dagger}\cdot\boldsymbol{\Lambda}_{kl}[\mathbf{b}_l + (\mathbf{b}_l, V)]\,, \tag{35.44}$$

$$\mathcal{L}^b = -g\sum_{l=1}^{n} \mathbf{b}_l{}^{\dagger}\cdot(\mathbf{e}_x\mathbf{e}_y)(\mathbf{b}_l + \mathbf{b}_l{}^{\dagger}) \tag{35.45}$$

with

$$\boldsymbol{\Lambda}_{kl} = 2kT\bar{\sigma}_k\bar{\sigma}_l\sum_i\sum_j Q_{ki}Q_{lj}[\zeta^{-1}\delta_{ij}\mathbf{I} + \mathbf{T}(\mathbf{R}_{ij})]\,, \tag{35.46}$$

where $g$ is the time-independent velocity gradient, $Q_{ij}$ is given by Eq. (34.28), and $\mathbf{T}(\mathbf{R}_{ij}) = \mathbf{T}_{ij}$ is the Oseen tensor in the boson representation. The boson representation of functions of $\mathbf{R}_{ij}$ may be obtained through the equation,

$$f(\mathbf{R}_{ij}) = \int f(\mathbf{R})\delta(\mathbf{R} - \mathbf{R}_{ij})d\mathbf{R} \tag{35.47}$$

with the use of the boson representation of the delta function. Although we omit the derivation of the representation of the delta function, we note that

$$\mathbf{R}_i = \sum_{l=1}^{n} (Q_{il}/2^{1/2}\bar{\sigma}_l)(\mathbf{b}_l + \mathbf{b}_l{}^{\dagger})\,, \tag{35.48}$$

$$\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i = \sum_{l=1}^{n} f_l(\mathbf{b}_l + \mathbf{b}_l{}^{\dagger}) \tag{35.49}$$

with

$$f_l = (Q_{lj} - Q_{li})/2^{1/2}\bar{\sigma}_l\,. \tag{35.50}$$

We now derive the representation of $V$ in Eq. (35.44). We first obtain from Eqs. (35.30) and (35.40)

$$U^{\alpha} = \tfrac{1}{2}kT \sum_{l} (\mathbf{b}_l + \mathbf{b}_l{}^{\dagger}) \cdot (\mathbf{b}_l + \mathbf{b}_l{}^{\dagger})\,, \tag{35.51}$$

and $U_0 = \alpha^2 U^{\alpha}$. The excluded-volume potential $W$ may be given by Eq. (15.14),

$$W = kT\beta \sum_{i<j} \delta(\mathbf{R}_{ij})\,, \tag{35.52}$$

and its representation is obtained by the use of the representation of the delta function. However, we neglect terms higher than quadratic in the boson operators. Then, substitution of the result with Eq. (35.51) into Eq. (35.29) leads to

$$V = \frac{1}{2} \sum_{l} G_l(\mathbf{b}_l + \mathbf{b}_l{}^{\dagger}) \cdot (\mathbf{b}_l + \mathbf{b}_l{}^{\dagger})\,, \tag{35.53}$$

where

$$G_l = (\alpha^2 - 1) - (z/\alpha^3)g_l\,, \tag{35.54}$$

$$\begin{aligned} g_l = \tfrac{1}{2}l^{-3/2}(8\sqrt{2}/3\pi)\{&[4/\pi(2l)^{1/2}][1 - (-1)^l] \\ &+ (4/\sqrt{2})S(2\pi l) - 5S(\pi l) + 2\pi l C(\pi l)\} \end{aligned} \tag{35.55}$$

with $C$ and $S$ the Fresnel integrals. From Eqs. (35.42) and (35.53) we fine for the commutator in Eq. (35.44)

$$(\mathbf{b}_l, V) = G_l(\mathbf{b}_l + \mathbf{b}_l{}^{\dagger})\,. \tag{35.56}$$

The average of any function $\varphi$ of coordinates is given by

$$\langle \varphi \rangle = \int P^{\alpha}\rho\varphi \, d\{\boldsymbol{\xi}_n\} = \langle 0|\, \varphi \,|\rho\rangle\,, \tag{35.57}$$

where $\varphi$ and $\rho$ are expressed in the boson representation, and $\langle 0|$ or $|0\rangle$ denotes the ground states of the basis set. The equation applies to both equilibrium and nonequilibrium $\rho$. For steady flow $\rho$ satisfies

$$\mathcal{L}\rho = 0\,. \tag{35.58}$$

In order to solve Eq. (35.58) we introduce the approximation

$$\mathbf{\Lambda}_{kl} = \mathbf{\Lambda}_l \delta_{kl}\,, \tag{35.59}$$

with $\mathbf{\Lambda}_l = \mathbf{\Lambda}_{ll}$. Further, we replace $\mathbf{\Lambda}_l$ by its steady-state average. It may then be written in the form,

$$\mathbf{\Lambda}_l = {\Lambda_l}^0(\mathbf{I} + \mathbf{\Lambda}_l{}')\,, \tag{35.60}$$

where ${\Lambda_l}^0\mathbf{I}$ is the ground-state average, $\langle 0|\mathbf{\Lambda}_{ll}|0\rangle$, of $\mathbf{\Lambda}_{ll}$, and $\mathbf{\Lambda}_l{}'$ is the remainder. In the non-free-draining limit ${\Lambda_l}^0$ is evaluated to be

$${\Lambda_l}^0 = \alpha^{-3}[12kT/(12\pi^3)^{1/2}\eta_0 {\langle R^2\rangle_0}^{3/2}]\lambda_l{}' \tag{35.61}$$

with $\lambda_l{}'$ the Hearst eigenvalues given by Eq. (33.48). Now the solution for $\rho$ can be found to be

$$|\rho\rangle = \exp\left(\sum_l {\mathbf{b}_l}^\dagger \cdot \mathbf{M}_l {\mathbf{b}_l}^\dagger\right)|0\rangle \tag{35.62}$$

with

$$\mathbf{M}_l = -\tfrac{1}{2}G_l(1+G_l)^{-1}\mathbf{I} + \mathbf{N}_l + \mathbf{N}_l{}'\,, \tag{35.63}$$

where the $\mathbf{N}_l$ and $\mathbf{N}_l{}'$ are symmetric dyadics and are related to ${\Lambda_l}^0$ and $\Lambda_l{}'$, respectively. For example, the $xy$ component of $\mathbf{N}_l$, which we need, is given by

$$(\mathbf{N}_l)_{xy} = (\mathbf{N}_l)_{yx} = \tfrac{1}{4}g[{\Lambda_l}^0(1+G_l)^2]^{-1}\,. \tag{35.64}$$

We note that in equilibrium $\mathbf{N}_l = \mathbf{N}_l{}' = 0$, and that at small $g$, $\mathbf{N}_l{}'$ may be neglected compared to $\mathbf{N}_l$.

For the present purpose it is convenient to write the intrinsic viscosity, from Eqs. (30.24) and (33.11), as

$$[\eta] = \frac{N_{\mathrm{A}}}{M\eta_0 g}\sum_j \left\langle y_j \frac{\partial U}{\partial x_j}\right\rangle \tag{35.65}$$

with $U = kTV + U^\alpha$. After transformation into the normal coordinates we can obtain the boson representation of $y_j\partial U/\partial x_j$, and by the use of Eqs. (35.57) and (35.62) write

$$[\eta] = \frac{2N_{\mathrm{A}}kT}{M\eta_0 g}\sum_l (1+G_l)(\mathbf{N}_l + \mathbf{N}_l{}')_{xy}\,. \tag{35.66}$$

In the limit $g \rightarrow 0$ (with omission of $\mathbf{N}_l{}'$), substitution of Eqs. (35.61) and (35.64) into Eq. (35.66) leads to

$$\Phi = 4.84 \times 10^{23}\left(\frac{\alpha}{\alpha_S}\right)^3 \sum_l \frac{1}{\lambda_l{}'(1+G_l)}\,. \tag{35.67}$$

The problems remaining are to determine $\alpha$ and $G_l$, and to evaluate $\alpha_R$, $\alpha_S$, and $\Phi$ as functions of $z$.

From Eqs. (35.62) and (35.63) the equilibrium $\rho$ is given by

$$|\rho\rangle = \exp\left[-\frac{1}{2}\sum_l G_l(1+G_l)^{-1}\mathbf{b}_l{}^\dagger \cdot \mathbf{b}_l{}^\dagger\right] |0\rangle \,. \tag{35.68}$$

As mentioned already, $\alpha$ is chosen to make this $\rho$ as close to unity as possible. In other words, the $G_l$ should be made as small as possible by the choice of $\alpha$. It is obvious that all $G_l$ cannot be made to vanish by the same value of $\alpha$. The best choice of $\alpha$ is obtained by making $G_1$ vanish. We then have

$$\alpha^5 - \alpha^3 = g_1 z = 1.516z\,, \tag{35.69}$$

$$G_l = (z/\alpha^3)(g_1 - g_l)\,. \tag{35.70}$$

By the use of Eq. (35.49), the squared end-to-end distance may be expressed in the form

$$R^2 = R_{0n}{}^2 = \sum_k\sum_l f_k f_l(\mathbf{b}_k + \mathbf{b}_k{}^\dagger)\cdot(\mathbf{b}_l + \mathbf{b}_l{}^\dagger)\,. \tag{35.71}$$

$\langle R^2\rangle$ may be evaluated from Eq. (35.57) with (35.68) and (35.71). Using Eqs. (35.34) to (35.38) and the commutation rules after expansion of the exponential in Eq. (35.68), we find

$$\langle R^2\rangle = 3\sum_l f_l{}^2(1+G_l)^{-1}\,, \tag{35.72}$$

and therefore

$$\alpha_R{}^2 = 2\pi^{-2}\alpha^2\sum_{l=1}^{\infty} l^{-2}[(-1)^l - 1]^2(1+G_l)^{-1}\,. \tag{35.73}$$

Similarly, we can obtain $\langle S^2\rangle$ by the use of Eqs. (7.22) and (35.49).[57] The result is

$$\alpha_S{}^2 = 6\pi^{-2}\alpha^2\sum_{l=1}^{\infty} l^{-2}(1+G_l)^{-1}\,. \tag{35.74}$$

At small $z$ Eqs. (35.73) and (35.74) give

$$\alpha_R{}^2 = 1 + 1.377z - 3.229z^2 + \cdots\,, \tag{35.75}$$

$$\alpha_S{}^2 = 1 + 1.276z - 3.089z^2 + \cdots\,, \tag{35.76}$$

where we have used Eqs. (35.69) and (35.70). The coefficient of $z$ in $\alpha_R{}^2$ is in fairly good agreement with the exact value 1.333, while the corresponding coefficient in $\alpha_S{}^2$ is exact, both the coefficients of $z^2$ being too large [see Eqs. (14.33) and (14.34)]. The values of $\alpha_R{}^3$ and $\alpha_S{}^3$ calculated from Eqs. (35.73) and (35.74) were already shown in curves $F_2$ and FS in Figs. III.5 and III.6, respectively, and values of

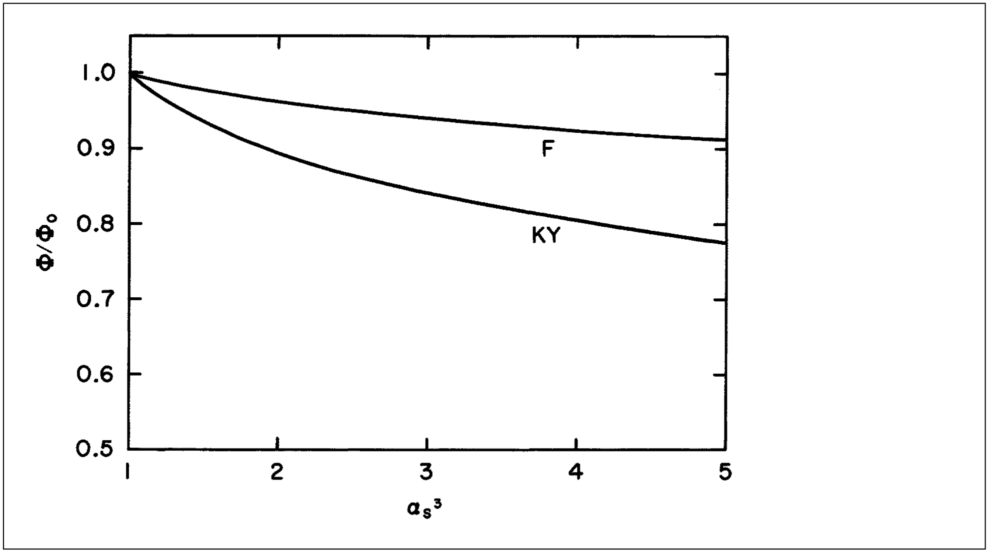

**Fig. VI.8.** Theoretical values of the ratio $\Phi/\Phi_0$ plotted against $\alpha_S{}^3$. Curve KY: the Kurata–Yamakawa theory, Eq (35.3) with (35.15). Curve F: the Fixman theory, Eq (35.67) with (35.74).

$\alpha_S$ predicted by Eq. (35.74) are smaller than those predicted by the modified Flory equation (14.41).

Now the values of $\Phi$ as a function of $z$ or $\alpha_S$ can be calculated from Eq. (35.67). The results are shown in curve F in Fig. VI.8. $\Phi$ is again seen to decrease with increasing $z$ or $\alpha_S$. For comparison, the corresponding values predicted by Eqs. (35.3) and (35.15) are shown in curve KY in the same figure. Finally, we note that similar results to those described have been derived by Chikahisa[58] and Koyama[59] using an ellipsoid model. For example, Koyama finds $\alpha_\eta{}^3 = \alpha_S{}^{2.45}$.

## 35b. Friction Coefficients

By analogy with the empirical equation for the intrinsic viscosity with neglect of the draining effect, Mandelkern and Flory[60] deduced, from Eq. (31.48), an empirical equation for the translational friction coefficient,

$$\frac{f}{\eta_0} = 6^{1/2} P \langle S^2 \rangle^{1/2} , \tag{35.77}$$

where they considered $P$ to be a universal constant. We now introduce the expansion factor $\alpha_f$, corresponding to $\alpha_\eta$, by the equation

$$\frac{f}{\eta_0} = \frac{f_\Theta}{\eta_0} \alpha_f = 6^{1/2} P_0 \langle S^2 \rangle_0{}^{1/2} \alpha_f \tag{35.78}$$

with $f_\Theta$ the friction coefficient of unperturbed chains. Then $P$ may be written as

$$P = P_0\left(\frac{\alpha_f}{\alpha_S}\right). \tag{35.79}$$

The original Kirkwood–Riseman theory, Eq. (31.48), gives $P_0 = 5.11$.

Now, $\alpha_f$ or $P$ may be evaluated from the Kirkwood equation (32.41) for the diffusion coefficient (neglecting the small error inherent in it). Then we need merely evaluate the double sum of the equilibrium statistical average $\langle {R_{ij}}^{-1}\rangle$ over $i$ and $j$. The Kurata–Yamakawa approximation of (35.6) with (35.9) gives

$$\alpha_f = \tilde{a} = 1 + 0.416z - \cdots\,, \qquad \text{(KY)} \tag{35.80}$$

$$P = P_0(1 - 0.222z + \cdots)\,. \qquad \text{(KY)} \tag{35.81}$$

By the use of the boson operator technique, Horta and Fixman[61] have obtained the value 0.415 for the coefficient of $z$ in $\alpha_f$, which is very close to the KY value. However, Stockmayer and Albrecht[62] have derived the exact first-order perturbation theory value

$$\alpha_f = 1 + 0.609z - \cdots\,, \tag{35.82}$$

$$P = P_0(1 - 0.029z + \cdots)\,. \qquad \text{(SA ; exact)} \tag{35.83}$$

Both the exact and approximate theories predict that $\alpha_f$ is smaller than $\alpha_S$ for positive $z$, and that $P$ decreases with increasing $z$, although the decrease in $P$ predicted by the approximate theories seems too large. If we use Eq. (35.17), we obtain[53]

$$P = (\pi^{3/2}/8)(1-\varepsilon)(3-\varepsilon)(6+5\varepsilon+\varepsilon^2)^{1/2}\,. \tag{35.84}$$

This $P$ also decreases from 5.11 as $\varepsilon$ is increased from zero.

## 36. Remarks and Some Other Topics

### 36a. Concentration Dependence

In order to study the behavior of the viscosity coefficient $\eta$ and the friction coefficient $f$ up to moderate concentrations, we must evaluate the coefficient $a_2$ of $c^2$ in Eq. (30.16) for $\eta$ and the coefficient $k_s$ of $c$ in Eq. (30.35) for $f$, considering a system of many solute particles instead of a single particle. We first consider the viscosity. It is convenient to rewrite Eq. (30.16) in the form,

$$\eta = \eta_0(1 + [\eta]c + k'[\eta]^2c^2 + \cdots)\,, \tag{36.1}$$

where the $k'$ is called the Huggins coefficient,[63] and is to be studied here. Unfortunately, many different numerical estimates of $k'$ have been published even for rigid sphere molecules.[64] One of the reasons for this is that the hydrodynamic problem we face involves a fundamental difficulty. We manifest the problem following the procedure of Burgers[8] and Saito.[65] Suppose that the velocity field given by Eq. (30.12) is produced by the motion of one of two parallel plates perpendicular to the $y$ axis,moving in the direction of the $x$ axis. At constant shear stress,

$$\eta g = \eta_0 g_0 \,, \tag{36.2}$$

where $g$ and $g_0$ are the velocity gradients of the solution and solvent, respectively. That is, the velocity gradient is decreased from $g_0$ to $g$ by the introduction of the solute molecules. In the case of a solution of hard spheres of radius $\bar{S}$, whose number density is $\rho$, $g$ is given by

$$g = g_0 - \frac{20\pi}{3}\langle f_{12}\rangle \rho \bar{S}^3 \,, \tag{36.3}$$

where $f_{12}$ is defined by Eq. (30.6). The average of $\langle f_{12}\rangle$ is defined by[11]

$$\langle f_{12}\rangle = V^{-1}\left\langle \int f_{12} d\mathbf{r} \right\rangle , \tag{36.4}$$

where $V$ is the volume of the system, and the average $\langle \quad \rangle$ on the right-hand side is taken over all configurations. If $\mathbf{v}'$ is the velocity perturbation at $\mathbf{r}$ due to a sphere present at the origin, $\langle f_{12}\rangle$ is obtained to the first order in $\rho$ as[66]

$$\langle f_{12}\rangle = \tfrac{1}{2}(1-\varphi)g_0 + \frac{\rho}{2}\int_{r>2S}\left(\frac{\partial {v_1}'}{\partial x_2} + \frac{\partial {v_2}'}{\partial x_1}\right) d\mathbf{r} \,, \tag{36.5}$$

where $\varphi$ is the volume fraction of the spheres, and we have used the fact that the symmetric velocity gradient vanishes inside the spheres. At infinite dilution $\langle f_{12}\rangle = \frac{1}{2}g_0$, and Eq. (36.2) with (36.3) gives the Einstein equation for the intrinsic viscosity. As shown in Appendix VI C, $v'$ is asymptotically proportional to $r^{-2}$ in the Stokes approximation. Then the integrand in Eq. (36.5) is asymptotically proportional to $r^{-3}$, and the integral, which is related to the Huggins coefficient, becomes indeterminate, depending on the size and shape of the system. In the calculation of $k'$ for linear flexible chains, Riseman and Ullman[67] also encountered an integral similar to that in Eq. (36.5), and their value 0.6 for $k'$ is inconclusive.

As an alternative intended to resolve this unpleasant situation Saito[65] has proposed a nonlinear theory of $k'$ which utilizes Oseen rather than Stokes perturbation theory, but a numerical result for $k'$ has not yet been obtained. On the other hand, Brinkman[68] has derived a difference equation for $\eta$, considering the increase in $\eta$ as a result of adding one more solute molecule to the solution. The solution of the difference equation gives the value 0.7 for $k'$. Experiments show that $k'$ lies between 0.5 and 0.7 at the theta temperature, and decreases monotonically to about 0.3 as $z$ is increased.[69] Yamakawa[70] has attempted to derive the decrease in $k'$ with $z$ from the Brinkman equation by taking into account only the effect of the concentration dependence of the molecular dimensions.

The hydrodynamic problem described has been recently reconsidered by Peterson and Fixman.[66] They have pointed out that the physical and mathematical problems connected with $k'$ are quite like those connected with the theory of light scattering for a simple liquid, which were already discussed by Fixman.[71] In the light scattering theory the problem is that the electric field of a dipole vanishes as $r^{-3}$, and it is not immediately clear that the dielectric properties of one part of an inhomogeneous medium are independent of the surface polarization. In the light scattering problem Fixman used the following considerations:(1) the constitutive coefficients of macroscopic electrodynamics ought to permit a local definition in inhomogeneous media, (2) local electric fields and polarizations are well known to depend on sample size and shape, and (3) therefore a calculation of a constitutive coefficient ought to be based on a calculation of both the field and the polarization, so that the ratio, which is the desired coefficient, can be shown independent of surface effects. Peterson and Fixman have carried out a hydrodynamic calculation from the same point of view, i.e., carried out a calculation of both the average stress and the average velocity gradient. Their starting equation is

$$\langle \sigma_{ij} \rangle = 2\eta_0 \langle f_{ij} \rangle - \langle p \rangle \delta_{ij} + V^{-1} \left\langle \int (\sigma_{ij} - 2\eta_0 f_{ij} + p\delta_{ij}) d\mathbf{r} \right\rangle , \quad (36.6)$$

which is obtained from Eq. (30.10). We note that since Eq. (30.10) holds in the solvent, the integrand in Eq. (36.6) is nonvanishing only inside the spheres, and that the pressure terms may be suppressed, since the average of $p$ either inside or outside the spheres must vanish. The average $\langle f_{ij} \rangle$ may be expressed as Eq. (36.5). Then, the viscosity coefficient is given by the ratio $\langle \sigma_{ij} \rangle / 2\langle f_{ij} \rangle$, and has been shown independent of surface effects in the Stokes approximation. In this way the value 0.691 has been obtained for the Huggins coefficient $k_{\varphi}{}'$ for hard spheres, in volume-fraction concentration units. To obtain $k'$ for flexible chains Peterson and Fixman used the uniform-density sphere model, and also used the intermolecular potential appearing in Eq. (20.37). The calculation involves several approximations. The parameter $A$ introduced by them may be set equal to $8.85\bar{z}$ with $\bar{z} = z/\alpha_S^3$. Then $k'$ becomes a function of $\bar{z}$, and is plotted in Fig. VI.9, $k'$ being equal to 0.883 at the theta temperature. Unfortunately, the theory never agrees with the experimental results mentioned above. Although Sakai[72] has attempted to make some improvements on the approximations of Peterson and Fixman, a satisfactory theory of $k'$ has not yet been published.

Next we consider the friction coefficient. The basic problem in the theory of $k_s$ is similar to that of the Huggins coefficient. The velocity perturbation around a sphere moving in a fluid is asymptotically proportional to $r^{-1}$ in the Stokes approximation. Thus a direct summation of this long-ranged perturbation for a finite system results in a coefficient $k_s$ which depends on the size and shape of the system. However, the friction coefficient ought to be independent of surface effects. The difficulty is removed by the use of the drift velocity $\mathbf{u}'$ in

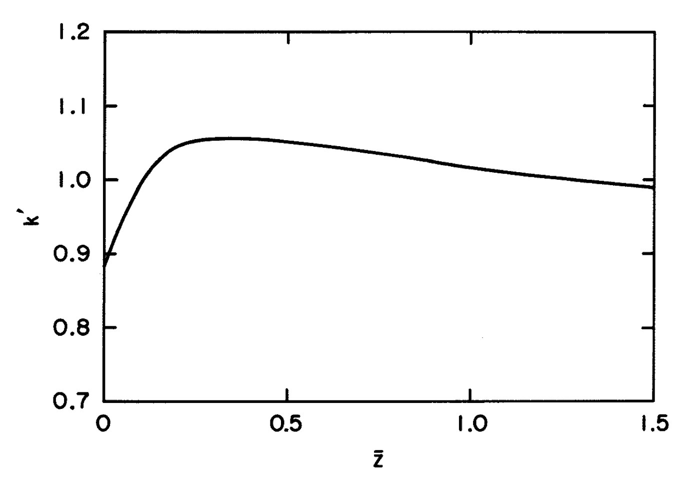

**Fig. VI.9.** Values of the Huggins coefficient $k'$ predicted by the Peterson–Fixman theory as a function of $\bar{z} = z/\alpha_S^3$.

place of the simple average velocity **u** of polymer molecules, as shown by Yamakawa[73] and by Pyun and Fixman.[74] That is, the friction coefficient $\xi$ defined as the ratio of the external force on a polymer molecule to the average translational velocity **u**' of the polymer molecule relative to the solvent is a property independent of the surface effect. Switching from this frame of reference to that of the experimental observation may be achieved by considering the conservation of the solution volume in any volume element in the system. Thus we obtain

$$f = \xi(1+\varphi)\,, \tag{36.7}$$

which is correct to the first order in $\varphi$. $\xi$ may be expanded as

$$\xi = \xi_0(1 + k_s{}'c + \cdots)\,, \tag{36.8}$$

and we therefore have

$$k_s = k_s{}' + N_{\mathrm{A}}v_m/M\,, \tag{36.9}$$

where $v_m$ is the hydrodynamic volume of the solute molecule. Note that at infinite dilution $\mathbf{u}' = \mathbf{u}$ and $f_0 = \xi_0$.

For the random-flight model Yamakawa[73] has derived the expression $k_s{}' = 1.2A_2M$ by an extension of the Kirkwood–Riseman theory of $f_0$. This $k_s{}'$ vanishes at the theta temperature. For hard spheres, Pyun and Fixman[74] have obtained $k_{s,\varphi}{}' = 6.16$, and hence $k_{s,\varphi} = 7.16$ (in volume-fraction concentration units) by a calculation similar to that of $k'$ by Peterson and Fixman. This value of $k_{s,\varphi}$ is close to the earlier Burgers value 55/8=6.88.[75] For the uniform-density sphere model Pyun and Fixman have shown that $k_{s,\varphi}{}' = 1.23$ and $k_{s,\varphi} = 2.23$ at the theta temperature, and that $k_{s,\varphi}$ increases monotonically to the hard sphere value 7.16 as $\bar{z}$ is increased. Note that $k_{s,\varphi}$ is related to $k_s$ by the relation $k_s = k_{s,\varphi}(N_{\mathrm{A}}v_m/M)$. Now, if we assume $f_0 = 6\pi\eta_0\bar{S}$ with $v_m = \frac{4}{3}\pi\bar{S}^3$, we have from Eqs. (35.1) and (35.77)[76]

$$\frac{N_{\mathrm{A}}v_m}{M} = \frac{N_{\mathrm{A}}(P^3/\Phi)[\eta]}{162\pi^2}\,. \tag{36.10}$$

Further, we assume $P = 5.1$ and $\Phi = 2.5 \times 10^{23}$, neglecting the dependences of $P$ and $\Phi$ on $z$. Then we find $N_{\mathrm{A}}v_m/M = 0.2[\eta]$, and the results obtained by Yamakawa and by Pyun and Fixman may be written as

$$k_s/[\eta] = 1.2A_2M/[\eta] + 0.2\,, \qquad \text{(Y)} \tag{36.11}$$

$$k_s/[\eta] = 0.2k_{s,\varphi}\,. \qquad \text{(PF)} \tag{36.12}$$

An experimental value for $k_s/[\eta]$ in good solvents is about 1.6 for flexible chains.[76] Equation (36.11) and (35.12) are in fairly good agreement with experiment. Note that $A_2M/[\eta] = 1.0 - 1.2$ for flexible chains in good solvents.

## 36b. Non-Newtonian Viscosities

Rigid nonspherical particles in solution will tend to be oriented at high rates of shear, so that the energy dissipation is diminished below that at zero rate of shear. As a result, the intrinsic viscosity is decreased as the rate of shear $g$ is increased. Such behavior, called non-Newtonian viscosity, is observed also in solutions of flexible-chain polymers. The effect is nonvanishing even at the theta temperature, and is exaggerated for high-molecular-weight polymers in good solvents. As pointed out in Section 33, however, the Rouse-Zimm theory for the spring and bead model fails in interpreting the non-Newtonian viscosity. Theoretical attempts made so far to predict the shear dependence of $[\eta]$ for flexible chains may be classified into three groups: (1) improvement of the model, (2) refinement of the calculation of hydrodynamic interaction, and (3) explicit consideration of the excluded-volume effect. We summarize these investigations in the following discussion.

The model has been improved so as to take into account the fact that the real chain possesses some rigidity because of restrictions on the bond angles and steric hindrances to internal rotation. As early as 1945, Kuhn and Kuhn[77] approximated this effect by the introduction of the concept of the *internal viscosity.* They simply replaced the random-flight chain by an elastic dumbbell, and defined the internal viscosity coefficient as the ratio of the force required to separate the chain ends to the velocity of separation. Subsequently, Cerf[78] redefined the internal viscosity coefficient $\eta_{\mathrm{in}}$ associated with a bond of the chain in terms of the force $\mathbf{F}_{\mathrm{in}}$ required to produce a difference in the radial components of the velocities of two adjacent segments;

$$\mathbf{F}_{\mathrm{in}} = \eta_{\mathrm{in}}(\mathbf{u}_{j+1}{}^{r} - \mathbf{u}_{j}{}^{r}) \tag{36.13}$$

with

$$\mathbf{u}_j{}^r = \mathbf{u}_j - \boldsymbol{\omega} \times \mathbf{S}_j \,, \tag{36.14}$$

where $\mathbf{u}_j$ is the velocity of the $j$th segment and $\boldsymbol{\omega}$ is the angular velocity of the molecule around the center of mass. From a different point of view Reinhold and Peterlin[79] have taken into account the finite deformability of the chain because of the constancy of the bond length. Chain rigidity of this sort seems to be of minor importance in steady shear flow.

Peterlin and Čopič[80] and Ikeda[81] have considered the possible effects of the anisotropy of the effective friction coefficient of a segment (or the difference between the radial and transverse components of the effective diffusion tensor of a segment) which arises from the nonspherical distribution of segments around the specified segment when there exists hydrodynamic interaction. However, we must always remember that the more serious approximation than neglect of anisotropy has been made in the hydrodynamic interaction in the Zimm theory; that is, the Oseen tensor has been replaced by its equilibrium average. It would be more consistent, in the present case, to use the steady-state average.[56, 82, 83] Peterlin[82] has evaluated $\langle R_{ij}{}^{-1} \rangle$ by the use of the steady-state distribution function, and in the boson formulation of Fixman described in Section 35a(iii) the appropriate steady state is used. It is found that the shear dependence of $[\eta]$ may be derived from Eq. (35.66) by evaluating $G_l$, and hence $\mathbf{N}_l$ and $\mathbf{N}_l{}'$, in the steady state.

Clearly, the Fixman theory includes the excluded-volume effect. The influence of excluded volume has also been considered by Chikahisa,[84] using the smoothed-density ellipsoid model. Both theories predict there to be shear dependence of $[\eta]$ even at the theta temperature. Although Subirana[85] and Okano et al.[86] have investigated the excluded-volume effect, their treatments are inadequate, since the shear dependence is attributed to this effect alone and is not predicted to remain finite at the theta temperature. Further, we note that several incorrect attempts[87, 88] have been made to predict the shear dependence for the spring and bead model only by reconsideration of the molecular motion.

The theories cited above predict that the ratio of the intrinsic viscosity $[\eta]$ at finite rate of shear to its value $[\eta]_0$ at zero shear is a function of only the excluded-volume parameter $z$ and the reduced rate of shear $\beta_0$ defined by

$$\beta_0 = (M\eta_0[\eta]_0/RT)g \,. \tag{36.15}$$

Since the shear dependence does not change when the sign of $g$ is reversed, at small $\beta_0$ the ratio $[\eta]/[\eta]_0$ may be expanded in even powers of $\beta_0$,

$$[\eta]/[\eta]_0 = 1 - A\beta_0{}^2 + \cdots \,, \tag{36.16}$$

where $A$ is positive. The expansion coefficients depend on the excluded-volume parameter $z$, but do not vanish at the theta temperature.

In Fig. VI.10 is shown a comparison of theory with experiment, using the data obtained by Kotaka et al.[89] on polystyrene with $M =$

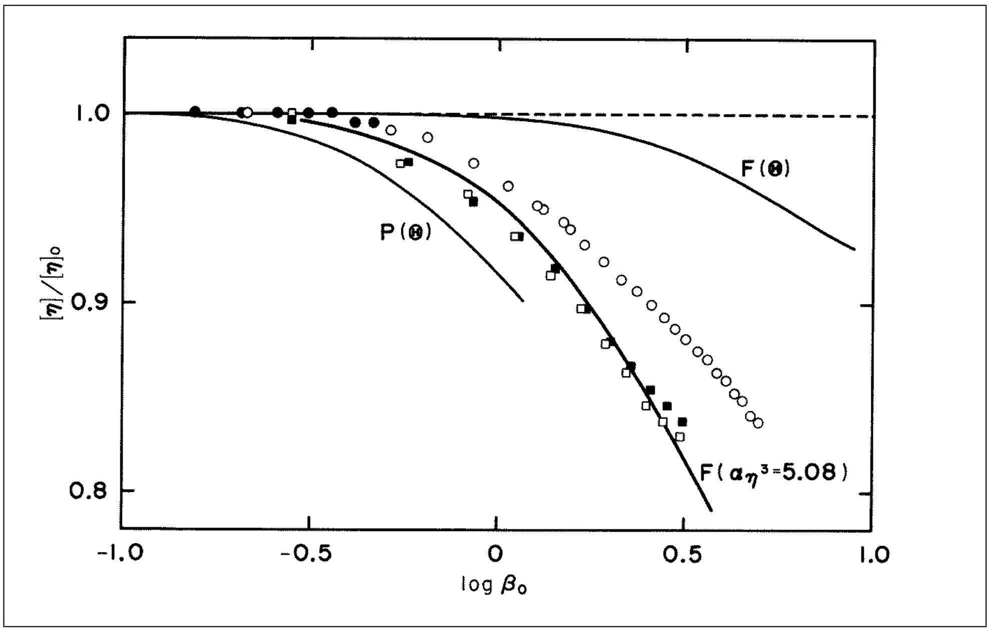

**Fig. VI.10.** Dependence of the reduced intrinsic viscosity $[\eta]/[\eta]_0$ on the reduced rate of shear $\beta_0$. Points: data on a polystyrene fraction (with $M = 6.2\times10^6$) in various solvents.[89] Filled circles: cyclohexane (34.8 °C). Open circles: Aroclor (40 °C). Filled squares: benzene (30 °C). Open squares: benzene (40 °C). Curve P: the Peterlin theory. Curves F: the Fixman theory.

$6.2 \times 10^6$. The circles represent the data at and near the theta temperature, and the squares the data in benzene (good solvent). The curves represent the values predicted by the theories of Peterlin[82] and Fixman.[56] At the theta temperature the Peterlin theory overestimates the shear dependence, while the Fixman theory underestimates it. Further, the latter overestimates the effect of excluded volume on the shear dependence. Thus there seems to be no satisfactory theory of the non-Newtonian intrinsic viscosity now available.

## 36c. Branched and Ring Polymers

The unperturbed and perturbed dimensions and the second virial coefficients of branched and flexible-ring molecules have already been studied in the preceding chapters. In this section we evaluate the zero-frequency intrinsic viscosity and the translational friction coefficient of these non-linear molecules. Indeed, measurements of the frictional properties are the most useful method of distinguishing between non-linear and linear molecules. Natural or synthetic branched polymers have been known for some time, and certain types of branching have recently been regulated by anionic polymerization. Recent growth in interest in the properties of ring molecules dates from 1962 when Fiers and Sinsheimer[90] suggested that single-stranded DNA from bacteriophage may exist in the native form as a ring-shaped molecule.

## 36c(i). Branched Polymers

We first study the intrinsic viscosity of unperturbed branched chains, using the spring and bead model. The free-draining case was treated by Ham,[91] and the non-free-draining case by Zimm and Kilb[92] by an extension of the Zimm theory described in Section 33. For simplicity, we consider uniform star molecules of functionality $f$. Then the mean reciprocal distance between the $i$th segment of the $\lambda$th subchain and the $j$th segment of the $\mu$th subchain is given by

$$\begin{aligned}\langle R_{i_\lambda j_\mu}{}^{-1}\rangle_0 &= (6/\pi)^{1/2}/a|i_\lambda - j_\mu|^{1/2} \qquad \text{for } \lambda = \mu \\ &= (6/\pi)^{1/2}/a|i_\lambda + j_\mu|^{1/2} \qquad \text{for } \lambda \neq \mu\,, \qquad (36.17)\end{aligned}$$

and the matrix $\mathbf{H}$ in the Zimm formulation has a form different from that for a linear chain. The matrix $\mathbf{A}$ must also be modified. In this case, the matrix $\mathbf{HA}$ has degenerate eigenvalues. However, it can be demonstrated that Eq. (33.18) still holds. If $\alpha_\mu(r)$ is the eigenfunction associated with the $\mu$th subchain, where $r = fi/n (0 \leq r \leq 1)$ and $r = 0$ at the branch unit, the eigenvalue equation becomes

$$\begin{aligned}\alpha_\mu{}''(r) + h\left(\frac{2}{f}\right)^{1/2} \int_0^1 \frac{\alpha_\mu{}''(s)}{|r-s|^{1/2}} ds + h\left(\frac{2}{f}\right)^{1/2} \\ \times \sum_{\substack{\mu'=1 \\ \neq \mu}}^{f} \int_0^1 \frac{\alpha_{\mu'}{}''(s)}{|r+s|^{1/2}} ds = -\frac{n^2\lambda}{f^2}\alpha_\mu(r) \qquad (36.18)\end{aligned}$$

with the boundary conditions,

$$\begin{aligned}\alpha_\mu{}'(1) &= 0\,, \\ \sum_{\mu=1}^{f} \alpha_\mu{}'(0) &= 0\,. \qquad (36.19)\end{aligned}$$

For the non-free-draining case, we define the reduced eigenvalues $\lambda_j{}'$ by

$$\lambda_j{}' = \frac{n^2}{4h}\left(\frac{2}{f}\right)^{3/2} \lambda_j\,, \qquad (36.20)$$

which reduces to Eq. (33.46) for a linear chain when $f = 2$. We then find

$$\begin{aligned}\sum_j \frac{1}{\lambda_j} &\simeq \frac{n^2}{4h}\left(\frac{2}{f}\right)^{3/2} \left[(f-1)\sum_{\text{odd } j} \frac{1}{\lambda_{j,l}{}'} + \sum_{\text{even } j} \frac{1}{\lambda_{j,l}{}'}\right] \\ &= \frac{n^2}{4h}\left(\frac{2}{f}\right)^{3/2} [0.390(f-1) + 0.196]\,, \qquad (36.21)\end{aligned}$$

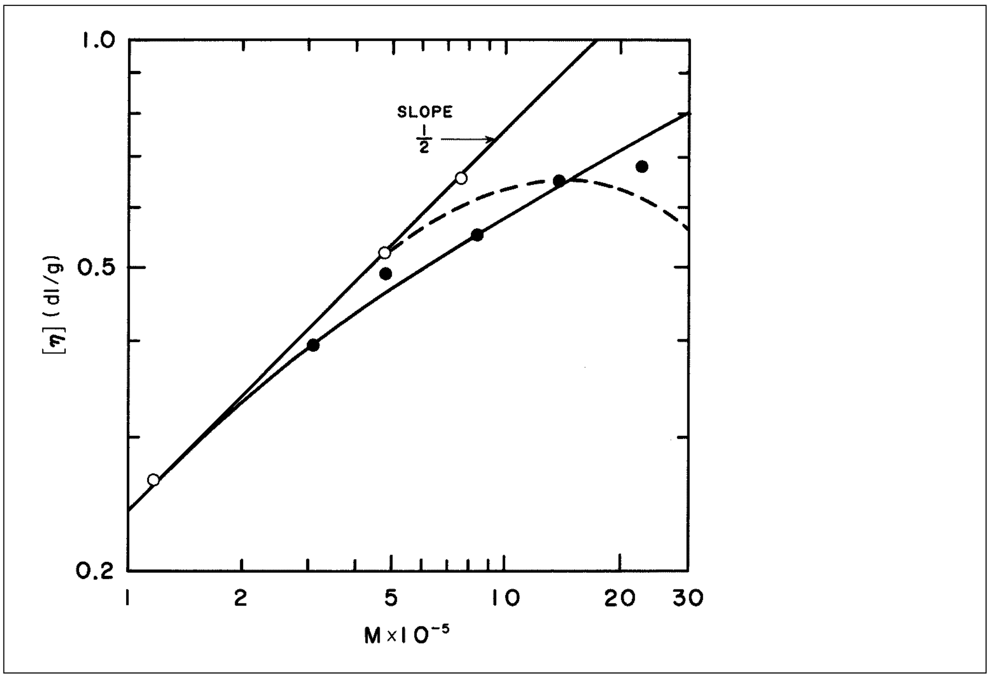

**Fig. VI.11.** Effect of branching on the intrinsic viscosity. Open and filled circles: data on linear and branched polystyrene fractions in methyl ethyl ketone-16.5% propanol mixtures.[94] Full curve: theoretical values calculated from Eq. (36.23). Broken curve: theoretical values calculated from Eq. (36.24).

where the subscript $l$ refers to a linear chain, and the $\lambda_j$ are $(f-1)$-fold degenerate when $j$ is odd. We therefore obtain for the ratio of the intrinsic viscosities of branched (uniform star) and linear chains of the same number of segments

$$[\eta]_b/[\eta]_l = (2/f)^{3/2}[0.390(f-1)+0.196]/0.586\,. \tag{36.22}$$

Comparing numerical values of this ratio and the factor $g = \langle S^2\rangle_b/\langle S^2\rangle_l$ of (9.69), we find

$$[\eta]_b/[\eta]_l \simeq g^{1/2}\,. \tag{36.23}$$

Note that $[\eta]_b/[\eta]_l = 1.88f^{-1/2}$ and $g^{1/2} = 1.73f^{-1/2}$ for large $f$. Zimm and Kilb assumed that Eq. (36.23) is valid for all kinds of branched molecules. However, if $[\eta]$ is assumed to be proportional to $\langle S^2\rangle^{3/2}/M$ as in the Flory–Fox theory, we readily find, instead of Eq. (36.23)

$$[\eta]_b/[\eta]_l = g^{3/2}\,. \tag{36.24}$$

There are several experimental results supporting Eq. (36.23) rather than Eq. (36.24). The first example comes from the work of Schaefgen and Flory[93] on the intrinsic viscosity-molecular weight relationships for polyamide star molecules of $f = 4$ or 8 with a random distribution of subchain lengths. As a second example, we take the intrinsic viscosity data of Thurmond and Zimm[94] on a series of fractions of branched polystyrene in methyl ethyl ketone-16.5% propanol mixtures. In this series the number of branch units per molecule varies with the molecular weight. The results are shown in Fig. VI.11. The open and filled circles represent the data on linear and branched chains, respectively. The full curve represents the theoretical values calculated from Eq. (36.23) taking account of the variation of the number of branch units, while the broken curve represents Eq. (36.24). Now, for good-solvent systems, Eq. (36.23) must be replaced by

$$[\eta]_b/[\eta]_l = g^{1/2}(\alpha_{\eta,b}/\alpha_{\eta,l})^3\,, \tag{36.25}$$

where $\alpha_\eta$ denotes the expansion factor of the viscosity radius. According to the work of Orofino and Wenger[95] on polystyrene star molecules, the factor $(\alpha_{\eta,b}/\alpha_{\eta,l})^3$ is slightly greater than unity.

Next we consider the friction coefficient $f_b$ of branched molecules. $f_b$ may be evaluated from the Kirkwood equation (32.41), and for the non-free-draining case,

$$f_b{}^{-1} = \frac{1}{3\pi\eta_0 n^2} \sum_{(i_\lambda, j_\mu)} \langle R_{i_\lambda j_\mu}{}^{-1} \rangle\,, \tag{36.26}$$

where the sum is taken over all $i_\lambda$, $j_\mu$ pairs. We define a factor $h$ as the ratio of the friction coefficients of branched and linear chains of the same number of segments,

$$h = f_b/f_l = \bar{S}_b/\bar{S}_l \tag{36.27}$$

with $\bar{S}$ the Stokes radius of the molecule. The problem is to evaluate the statistical average and the sum in Eq. (36.26).

For star molecules with a uniform or random distribution of subchain lengths, we easily obtain for the factor $h$

$$h_u{}^{-1}(\mathrm{star}) = (\sqrt{2}-1)f^{1/2} + (2-\sqrt{2})f^{-1/2}\,, \tag{36.28}$$

$$h_r{}^{-1}(\mathrm{star}) = \frac{3\pi^{1/2}(f+3)\Gamma(f+1)}{16\Gamma(f+\frac{3}{2})}\,. \tag{36.29}$$

Equations (36.28) and (36.29) were first derived by Stockmayer and Fixman[96] and by Ptitsyn,[97]respectively. For the normal or random type of branching, the method of Kurata and Fukatsu described in Section 9b(i) is again useful. The results are[98]

$$\begin{aligned} h_u{}^{-1}(\mathrm{normal}) = p^{-3/2}\Bigg\{ & p + (\sqrt{2}-1)f(f-1)m + (f-1)^2 \\ & \times \sum_{\nu=1}^{m-1} [(\nu+2)^{3/2} - 2(\nu+1)^{3/2} + \nu^{3/2}](m-\nu) \Bigg\}\,, \end{aligned} \tag{36.30}$$

$$h_r{}^{-1}(\text{normal}) = \frac{3\pi^{1/2}\Gamma(p)}{4\Gamma(p+\frac{3}{2})}\Bigg\{p + \tfrac{1}{4}f(f-1)m + (f-1)^2 \times \sum_{\nu=1}^{m-1} \frac{(2\nu+2)!(m-\nu)}{[(\nu+1)!2^{\nu+1}]^2}\Bigg\} \tag{36.31}$$

$$h_u{}^{-1}(\text{random}) = p^{-3/2}\Bigg\{p + (\sqrt{2}-1)f(f-1)m + \tfrac{1}{2}(f-1)^2 m(m-1) \times \sum_{\nu=1}^{m-1}[(\nu+2)^{3/2} - 2(\nu+1)^{3/2} + \nu^{3/2}]K_\nu(f,m)\Bigg\}, \tag{36.32}$$

$$h_r{}^{-1}(\text{random}) = \frac{3\pi^{1/2}\Gamma(p)}{4\Gamma(p+\frac{3}{2})}\Bigg\{p + \tfrac{1}{4}f(f-1)m + \tfrac{1}{2}(f-1)^2 m(m-1) \times \sum_{\nu=1}^{m-1} \frac{(2\nu+2)!}{[(\nu+1)!2^{\nu+1}]^2}K_\nu(f,m)\Bigg\} \tag{36.33}$$

with

$$K_\nu(f,m) = \frac{(fm-m-\nu)!(m-2)!}{(fm-m)!(m-\nu-1)!}(f-1)^{\nu-1}(f\nu - 2\nu + f), \tag{36.34}$$

where we have used the same notation as that in Section 9b(i). Equations (36.30) and (36.31) include the special cases derived by Ptitsyn.[97]

In Table VI.4 are given some numerical values of $h$ calculated from Eqs. (36.30) and (36.33) by Kurata and Fukatsu. In all cases $h$ is seen to be smaller than unity. Further, comparing these values with the corresponding values of the factor $g$ given in Table II.2, we find that

$$1 \leq h/g^{1/2} \leq 1.39\,. \tag{36.35}$$

This implies that the effect of branching is greater in the intrinsic viscosity than in the friction coefficient. Although both properties may be, of course, effectively used to distinguish between branched and linear chains, we must assume we know the type of branching in order to determine the number of subchains and/or the number of branch units per molecule.

## 36c(ii). Ring Polymers

The intrinsic viscosity of single-ring molecules was first evaluated by Bloomfield and Zimm[53] and Fukatsu and Kurata.[99] Both theories give the same result for the unperturbed ring, but are in conflict with each other regarding the prediction of the effect of excluded volume, which was treated by the Peterlin method as in Section 35a(ii) in the former

**TABLE VI.4.** NUMERICAL VALUES OF THE FACTOR $h^{98}$

| | | RANDOM | | NORMAL | |
|---|---|---|---|---|---|
| $f$ | $m$ | $h_u$ | $h_r$ | $h_u$ | $h_r$ |
| 3 | 1 | 0.947 | 0.972 | — | — |
| | 2 | 0.992 | 0.950 | — | — |
| | 3 | 0.903 | 0.931 | — | — |
| | 4 | 0.887 | 0.915 | 0.888 | 0.916 |
| | 5 | 0.873 | 0.901 | 0.876 | 0.903 |
| | 10 | 0.823 | 0.846 | 0.840 | 0.862 |
| | 15 | 0.788 | 0.808 | 0.820 | 0.839 |
| | 20 | 0.760 | 0.779 | 0.807 | 0.825 |
| | 25 | 0.739 | 0.756 | 0.798 | 0.814 |
| 4 | 1 | 0.892 | 0.938 | — | — |
| | 2 | 0.850 | 0.891 | — | — |
| | 3 | 0.820 | 0.864 | — | — |
| | 4 | 0.797 | 0.838 | 0.799 | 0.840 |
| | 5 | 0.778 | 0.817 | 0.782 | 0.820 |
| | 10 | 0.713 | 0.743 | 0.733 | 0.763 |
| | 15 | 0.672 | 0.697 | 0.708 | 0.733 |
| | 20 | 0.642 | 0.664 | 0.692 | 0.714 |
| | 25 | 0.619 | 0.638 | 0.681 | 0.701 |

and by an approximate perturbation theory in the latter. Moreover, the Bloomfield–Zimm theory predicts that $\langle S^2\rangle_r/\langle S^2\rangle_l$ decreases with increasing excluded volume; this is not in agreement with the perturbation theory given in Section 17. For this reason the problem was later reexamined by Yu and Fujita.[100]

If we take into account the excluded-volume effect by the Peterlin method, it is found that

$$\langle {R_{ij}}^{-1}\rangle = (6/\pi)^{1/2}\langle {R_{ij}}^2\rangle^{-1/2}\,. \tag{36.36}$$

For the unperturbed ring, $\langle {R_{ij}}^2\rangle_{0,r}$ is given by Eq. (9.81) with (9.80). For the perturbed ring, Bloomfield and Zimm assumed

$$\langle {R_{ij}}^2\rangle_r = a^2\frac{|j-i|^{1+\varepsilon}(n-|j-i|)^{1+\varepsilon}}{|j-i|^{1+\varepsilon}+(n-|j-i|)^{1+\varepsilon}}\,, \qquad \text{(BZ)} \tag{36.37}$$

while Yu and Fujita assumed

$$\langle {R_{ij}}^2\rangle_r = a^2|j-i|^{1+\varepsilon}(n^{1+\varepsilon}-|j-i|^{1+\varepsilon})/n^{1+\varepsilon}\,. \qquad \text{(YF)} \tag{36.38}$$

Of course, both Eqs. (36.37) and (36.38) satisfy the circularity condition that the sum of the two factors in the numerator is equal to the denominator. From Eq. (36.38) we obtain

$$\langle S^2\rangle_r = \frac{a^2 n^{1+\varepsilon}}{2(6+5\varepsilon+\varepsilon^2)}\left(1+\frac{\varepsilon}{3+2\varepsilon}\right), \tag{36.39}$$

$$\langle S^2\rangle_r/\langle S^2\rangle_l = \frac{1}{2}\left(1+\frac{\varepsilon}{3+2\varepsilon}\right). \tag{36.40}$$

That is , $\langle S^2\rangle_r/\langle S^2\rangle_l$ increases with increasing $\varepsilon$; this is consistent with the exact perturbation theory. Equation (36.37) leads to the opposite conclusion. We therefore adopt Eq. (36.38).

Now, the intrinsic viscosity of ring molecules may be expressed in the form,

$$[\eta]_r = \frac{2N_{\mathrm{A}}\langle S^2\rangle_r \zeta}{nM\eta_0}\sum_j g_j {\lambda_j}^{-1}, \tag{36.41}$$

corresponding to Eq. (35.19) for linear chain, where $g_j$ is the degeneracy of the $j$th eigenvalue and is shown to equal 2 for all $j$. We define the function $\Phi_r$ by

$$[\eta]_r = 12^{3/2}\Phi_r \frac{{\langle S^2\rangle_r}^{3/2}}{M}. \tag{36.42}$$

From Eqs. (36.39), (36.41), and (36.42), we then have

$$\Phi_r = \frac{(2\pi^3)^{1/2}N_{\mathrm{A}}}{12}2^{-\varepsilon/2}(6+5\varepsilon+\varepsilon^2)^{1/2}\left(1+\frac{\varepsilon}{3+2\varepsilon}\right)^{-1/2}\sum_j {\lambda_j}'^{-1}, \tag{36.43}$$

where the definition of ${\lambda_j}'$ is the same as that in Eq. (35.22), and we have put $g_j = 2$.

The eigenvalue equation becomes

$$\alpha''(r) + h(\varepsilon)\int_{-1}^{1}\frac{\alpha''(s)}{|r-s|^{(1+\varepsilon)/2}[1-(\frac{1}{2}|r-s|)^{1+\varepsilon}]^{1/2}}ds = -\frac{n^2\lambda}{4}\alpha(r) \tag{36.44}$$

with the circularity boundary conditions,

$$\alpha(1) = \alpha(-1), \quad \alpha'(1) = \alpha'(-1). \tag{36.45}$$

The eigenfunctions turn out to be doubly degenerate simple cosine or sine functions. If we adopt the cosine functions, for the non-free-draining case we find (for $j = 1, 2, \ldots, \frac{1}{2}n$)

$${\lambda_j}' = 2^{1-\delta}\pi^2 j^2\int_0^1 (x/2)^{-\delta}[1-(x/2)^{2\delta}]^{-1/2}\cos(\pi jx)dx \tag{36.46}$$

with $\delta = \frac{1}{2}(1+\varepsilon)$. When $\varepsilon = 0$, Eq. (36.46) may be rewritten in terms of the Bessel function of the zeroth order, and becomes identical with the equations obtained by Bloomfield and Zimm and by Fukatsu and Kurata.

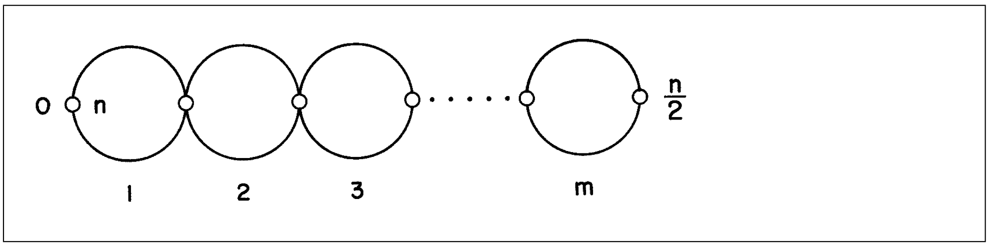

**Fig. VI.12.** A multiple-ring molecule composed of $m$ rings of equal size.

All these theories predict that $[\eta]_r/[\eta]_l = 0.662$ at the theta temperature, where $[\eta]_l$ is the intrinsic viscosity of linear chains of the same number of segments. For $\varepsilon \neq 0$, Yu and Fujita evaluated numerically the integral in Eq. (36.46), and showed that $[\eta]_r/[\eta]_l$ decreases from 0.662 to 0.633 as $\varepsilon$ is increased from 0 to 0.5. That is, $[\eta]_r/[\eta]_l$ is almost independent of the excluded-volume effect. The theory of Bloomfield and Zimm predicts that $[\eta]_r/[\eta]_l$ is a more rapidly decreasing function of $\varepsilon$. On the other hand, Fukatsu and Kurata arrived at the opposite conclusion by using the exact first-order perturbation theory result for $\langle S^2\rangle_r/\langle S^2\rangle_l$ appearing in the ratio $[\eta]_r/[\eta]_l$, but considering only approximately the effect of excluded volume on the ratio $\sum_j \lambda_{j,r}{}^{-1}/\sum_j \lambda_{j,l}{}^{-1}$.

The friction coefficient of single-ring molecules may be evaluated straightforwardly by the use of the Kirkwood equation. We consider only the non-free-draining case. First, the exact first-order perturbation theory of the ratio $f_l/f_r$ of the friction coefficients is given by

$$f_l/f_r = s_r/s_l = \tfrac{3}{8}\pi(1 - 0.021z + \cdots) \tag{36.47}$$

with $s$ the sedimentation coefficient. Equation (36.47) is due to Fukatsu and Kurata.[99] At $z = 0$, we have $s_r/s_l = \frac{3}{8}\pi = 1.178$, the result obtained also by Ptitsyn[97] and Bloomfield and Zimm.[53] In the Peterlin scheme, Yu and Fujita[100] obtained by the use of Eqs. (36.36) and (36.38)

$$\begin{aligned} s_r/s_l = {} & (\pi^{1/2}/2)\delta^{-1}(1-\delta)(2-\delta) \\ & \times \left[\Gamma\left(\frac{1}{2\delta} - \frac{1}{2}\right)\Big/\Gamma\left(\frac{1}{2\delta}\right) - \Gamma\left(\frac{1}{\delta} - \frac{1}{2}\right)\Big/\Gamma\left(\frac{1}{\delta}\right)\right]. \end{aligned} \tag{36.48}$$

This equation predicts that $s_r/s_l$ decreases from 1.178 to 1.055 as $\varepsilon$ is increased from 0 to 0.5; $s_r/s_l$ is also almost independent of the excluded-volume effect. We note that the friction or sedimentation coefficient is less sensitive to the ring formation than is the intrinsic viscosity.

Finally, we consider a multiple-ring molecule composed of $m$ rings of equal size linearly connected, as depicted schematically in Fig. VI.12. This molecule can be formed from a linear chain of $n + 1$ segments

**TABLE VI.5.** EFFECT OF RING FORMATION ON THE SEDIMENTATION COEFFICIENT[99]

| NUMBER OF RINGS | $s_r/s_l$ |
|---|---|
| 1 | 1.178 |
| 2 | 1.321 |
| 3 | 1.400 |
| 4 | 1.458 |
| 5 | 1.500 |
| 10 | 1.617 |
| $\infty$ | 2.000 |

by joining the $(ni/2m)$th and $(n - ni/2m)$th segments with $i = 0, 1, \ldots, m - 1$. For the unperturbed molecules, $s_r/s_l$ was evaluated as a function of $m$ by Fukatsu and Kurata.[99] The results are summarized in Table VI.5. In this connection it is pertinent to refer to the work of Weil and Vinograd,[101] who showed by means of the band-centrifugation technique that polyoma viral DNA consists of three components I, II, and III, and assigned these components to the twisted (multiple) ring, untwisted (single) ring, and linear forms of DNA, respectively. The ratios of the sedimentation coefficients of I and III and of II and III were 1.44 and 1.14, respectively.

## 36d. Rigid Rods and Stiff Chains

Some of the equilibrium properties of rod and stiff-chain molecules, such as tobacco mosaic virus, helical polypeptides, and DNA, have already been discussed in the preceding chapters. Measurements of the frictional properties are, of course, useful in obtaining conformational information about such molecules. Stiff chains may be well represented by the wormlike chain model, as described in Section 9c, and for this model we now evaluate the intrinsic viscosity and the diffusion or sedimentation coefficient. Although rod molecules may be regarded as a limiting case of the wormlike chain, we begin by discussing the dynamical properties of rod molecules since these have been thoroughly investigated. In this section the evaluation is carried out taking into account the draining effect, which has often been neglected for flexible chains.

### 36d(i). Straight and Once-Broken Rods

Many years ago Simha[102] extended the Einstein theory of the intrinsic viscosity of spherical particles to ellipsoidal particles, which may be regarded as rod molecules when the axial ratio is very large. On the other hand, Huggins,[1] Kuhn,[77] and succeeding investigators[30, 103] used the fully-extended random-flight model to represent a rod molecule, as described in our study of the Kirkwood equation for the diffusion coefficient (Section 32). Riseman and Kirkwood[30] also developed a theory for the fully-extended chain model; this theory is analogous to their theory of flexible chains as described in Section 31. Subsequently, Kirkwood and Auer[103] applied the general theory of Kirkwood to the same model, and first accounted for the rigidity of polymer solutions. We describe here the approach of Kirkwood and Auer.

Suppose that the middle ($\frac{1}{2}n$th) segment of the rod is fixed at the origin of a polar coordinate system ($r$, $\theta$, $\varphi$). The two angles $\theta$ and $\varphi$ suffice to specify the orientation of the rod, and may be chosen as generalized coordinates. If $\mathbf{e}_\theta$ and $\mathbf{e}_\varphi$ are unit vectors in the directions of $\theta$ and $\varphi$, respectively, we readily have in the same notation as in Section 32

$$\frac{\partial \mathbf{R}^i}{\partial q^1} = al\mathbf{e}_\theta \, , \qquad \frac{\partial \mathbf{R}^i}{\partial q^2} = al \, \sin\theta \, \mathbf{e}_\varphi \tag{36.49}$$

with $a$ the spacing between segments and $l = i - \frac{1}{2}n$. The components of the metric tensor in this space are

$$g_{\theta\theta} = a^2\nu \, , \qquad g_{\varphi\varphi} = a^2\nu \, \sin^2\theta \tag{36.50}$$

with

$$\nu = \sum_{l=-n/2}^{n/2} l^2 = \frac{1}{12}n^3 \, . \tag{36.51}$$

We then have $g^{\theta\theta} = {g_{\theta\theta}}^{-1}$ and $g^{\varphi\varphi} = {g_{\varphi\varphi}}^{-1}$ since $g_{\theta\varphi} = 0$ and the $q^1$ and $q^2$ are separable from the remaining $3n + 3 - 2$ coordinates. In this case the approximate general theory of Kirkwood gives the correct result for very large $n$, as will be seen later. We may therefore use Eqs. (32.36) to (32.38) to find for the rotatory diffusion coefficients

$$D^{\theta\theta} = D^{\varphi\varphi} \sin^2\theta = kT(1+\mu)/\zeta a^2\nu \, , \tag{36.52}$$

where

$$\mu = \frac{2\lambda_0}{\nu} \sum\sum_{-n/2 \le s < l \le n/2} \frac{ls}{l-s} \, , \tag{36.53}$$

$$\lambda_0 = \zeta / 8\pi\eta_0 a \, . \tag{36.54}$$

The diffusion equation for the distribution function $P(\theta, \varphi, t)$ may be written in the form,

$$\frac{\partial P}{\partial t} = \frac{1}{g'^{1/2}} \sum_{\alpha=1}^{2} \frac{\partial}{\partial q^\alpha} g'^{1/2} \left( D^{\alpha\alpha} \frac{\partial P}{\partial q^\alpha} - g^{\alpha\alpha} \sum_i {\mathbf{v}_i}^0 \cdot \frac{\partial \mathbf{R}^i}{\partial q^\alpha} P \right) , \tag{36.55}$$

where $g' = g_{\theta\theta} g_{\varphi\varphi}$, and we have suppressed the $\zeta_{\beta\gamma}$ terms in Eq. (32.21) for the same reason as above. After expressing ${\mathbf{v}_i}^0$ in polar coordinates, Eq. (36.55) may be explicitly rewritten as

$$\begin{aligned} 6\tau \frac{\partial P}{\partial t} - \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial P}{\partial \theta} \right) - \frac{1}{\sin^2\theta} \frac{\partial^2 P}{\partial \varphi^2} \\ = 9\tau g P \sin^2\theta \, \sin 2\varphi + O(g^2) \, , \end{aligned} \tag{36.56}$$

where $g$ is assumed to be the time-dependent rate of shear, and $\tau$ is the relaxation time defined by

$$\tau = 1/6D^{\theta\theta}\,. \tag{36.57}$$

Note that this $\tau$ corresponds to Zimm's $\tau_1$. At small $g$ the solution of Eq. (36.56) is

$$4\pi P = 1 + \tfrac{3}{2}g\left(\frac{\tau}{1+i\omega\tau}\right)\sin^2\theta\sin 2\varphi + O(g^2)\,. \tag{36.58}$$

Now we derive a set of equations determining the frictional forces $\mathbf{F}_i$. Since the generalized velocity of the segment is given by

$$\mathbf{u} = \sum_i \mathbf{u}^i = \sum_i\sum_\alpha u^\alpha \frac{\partial \mathbf{R}^i}{\partial q^\alpha}\,, \tag{36.59}$$

we have for the velocity of the $i$th segment

$$\mathbf{u}_i = \sum_\alpha u^\alpha \frac{\partial \mathbf{R}^i}{\partial q^\alpha} = \sum_\alpha \frac{J^\alpha}{P}\frac{\partial \mathbf{R}^i}{\partial q^\alpha}\,. \tag{36.60}$$

Substitution of Eq. (32.21) into Eq. (36.60) leads to

$$\mathbf{u}_i = -\sum_\alpha\sum_\beta \frac{\partial \mathbf{R}^i}{\partial q^\alpha}\left(D^{\alpha\beta}\frac{\partial \ln P}{\partial q^\beta} - g^{\alpha\beta}\sum_i {\mathbf{v}_i}^0\cdot\frac{\partial \mathbf{R}^i}{\partial q^\beta}\right). \tag{36.61}$$

Substitution of Eq. (36.61) into Eq. (31.7) gives a general equation determining the frictional forces (in the Kirkwood approximation). For the present case it may be written as

$$\begin{aligned}\mathbf{F}_l &+ \lambda_0 \sum_{\substack{s=-n/2\\ \neq l}}^{n/2} \frac{\mathbf{I}+\mathbf{e}_r\mathbf{e}_r}{|l-s|}\mathbf{F}_s \\ &= -\zeta l a\left(\tfrac{1}{2}g\,\sin^2\theta\sin\,2\varphi\,\mathbf{e}_r + D^{\theta\theta}\frac{\partial \ln P}{\partial\theta}\mathbf{e}_\theta + D^{\varphi\varphi}\sin\,\theta\frac{\partial \ln P}{\partial\varphi}\mathbf{e}_\varphi\right).\end{aligned} \tag{36.62}$$

Substitution of Eq. (36.58) into Eq. (36.62) leads to the equations for $\mathbf{F}_l$ up to terms linear in $g$,

$$\begin{aligned}\mathbf{F}_l\cdot\mathbf{e}_r &= -\tfrac{1}{2}g\zeta a\psi_l(2\lambda_0)\sin^2\theta\,\sin\,2\varphi\,,\\ \mathbf{F}_l\cdot\mathbf{e}_\theta &= -\tfrac{1}{4}g\zeta a\psi_l(\lambda_0)\frac{\sin\,2\theta\,\sin\,2\varphi}{1+i\omega\tau}\,,\\ \mathbf{F}_l\cdot\mathbf{e}_\varphi &= -\tfrac{1}{2}g\zeta a\psi_l(\lambda_0)\frac{\sin\,\theta\,\cos\,2\varphi}{1+i\omega\tau}\,,\end{aligned} \tag{36.63}$$

where the functions $\psi_l(\lambda)$ satisfy the set of equations,

$$\psi_l + \lambda \sum_{\substack{s=-n/2\\ \neq l}}^{n/2} \frac{\psi_s}{|l-s|} = l \qquad \left(-\frac{n}{2} \le l \le \frac{n}{2}\right). \tag{36.64}$$

Equations (36.64) may be transformed into an integral equation. Riseman and Kirkwood solved this integral equation by the Fourier series expansion method, as in the case of the Kirkwood–Riseman theory for flexible chains. As in that case, the solution is only approximate. However, Ullman[104] has shown that the Riseman–Kirkwood solution for $\psi_l$ is asymptotically correct for large $n$.

If the results for $\mathbf{F}_l$ are substituted in Eq. (30.24) rewritten in polar coordinates, we find the Newtonian complex intrinsic viscosity $[\bar{\eta}]$. As is easily seen from the derivation, the result so obtained is free of possible error arising from the preaveraging of the Oseen tensor. For large $n$ we obtain for the intrinsic dynamic viscosity, intrinsic storage modulus, and rotatory diffusion coefficient

$$[\eta'] = \frac{\pi N_\mathrm{A} L^3}{90 M \ln(L/a)} \left( 1 + \frac{3}{1 + \omega^2 \tau^2} \right), \tag{36.65}$$

$$[G'] = \frac{3RT}{5M} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}, \tag{36.66}$$

$$\frac{\eta_0 D^{\theta\theta}}{kT} = \frac{3 \ln(L/a)}{\pi L^3} \tag{36.67}$$

with $L$ $(= na)$ the length of the rod. The intrinsic dynamic viscosity is seen to have a finite value even in the limit $\omega = \infty$, while the Rouse–Zimm theory for flexible chains predicts vanishing of $[\eta']$ at $\omega = \infty$. At $\omega = 0$ Eq. (36.65) reduces to

$$[\eta] = \frac{2\pi N_\mathrm{A} L^3}{45 M \ \ln(L/a)}. \tag{36.68}$$

Simha's equation for the intrinsic viscosity of prolate ellipsoids is

$$[\eta] = \frac{N_\mathrm{A} v_m}{M} \left[ \frac{14}{15} + \frac{p^2}{15(\ln 2p - \frac{3}{2})} + \frac{p^2}{5(\ln 2p - \frac{1}{2})} \right] \tag{36.69}$$

with $v_m$ the volume of the ellipsoid and $p$ the axial ratio. Since $p^2 v_m$ may be set equal to $\pi L^3/6$, Eq. (36.68) is in agreement with Eq. (36.69) for very large $p$. Since $L$ is proportional to the molecular weight $M$, the dependence of $[\eta]$ on $M$ for long rods may be expressed in the form,

$$[\eta] = CM^2 / \ln M \,, \tag{36.70}$$

where $C$ is a constant independent of $M$.

Yu and Stockmayer[105] extended the above theory to a once-broken rod, i.e., two rods of equal length $(L/2)$ connected by a flexible joint. The result for the zero-frequency intrinsic viscosity is (for large $n$)

$$[\eta]_b = \frac{73\pi N_\mathrm{A} L^3}{1920 M \ \ln(L/a)}. \tag{36.71}$$

From Eqs. (36.68) and (36.71), we obtain $[\eta]_b/[\eta]_s = 0.85$, where $[\eta]_s$ is the intrinsic viscosity of straight rods of the same molecular weight.

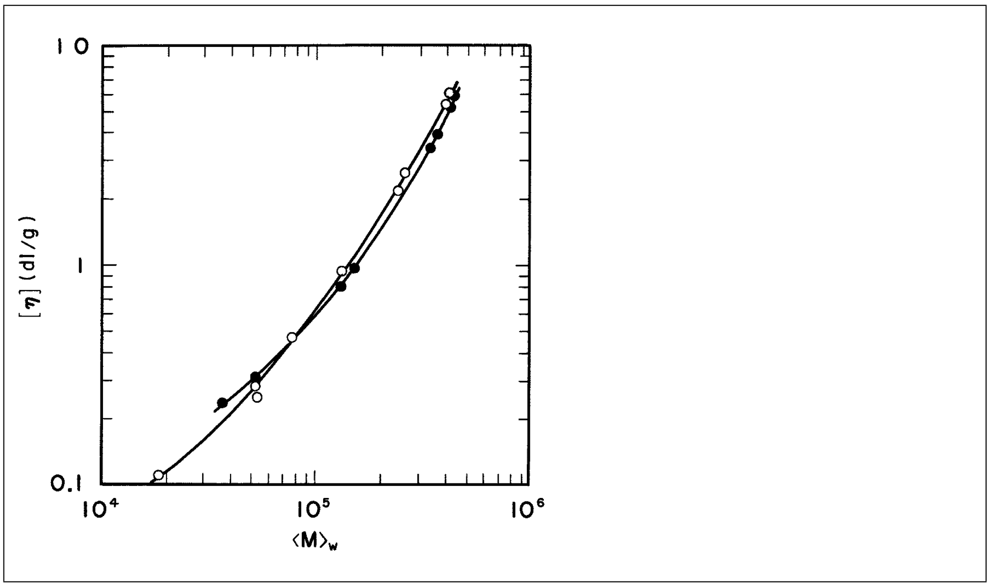

**Fig. VI.13.** Intrinsic viscosities of poly-$\gamma$-benzyl-L-glutamates (PBLG) in dimethylformamide at 25 °C.[106, 107] Open circles: PBLG-A (straight rods). Filled circles: PBLG-B (once-broken rods).

Next we evaluate the translational diffusion or sedimentation coefficient using the Kirkwood equation (32.41). The diffusion coefficient of straight rods has already been evaluated and is given by Eq. (32.43). The evaluation can easily be extended to broken rods composed of two subsections of lengths $L\sigma$ and $L(1-\sigma)(\frac{1}{2} \leq \sigma \leq 1)$. The result is

$$D_b = \frac{kT}{n\zeta}\left\{1 + \frac{\zeta}{3\pi\eta_0 a}[\ln n - 1 + \gamma + g(\sigma)]\right\}, \tag{36.72}$$

where $\gamma$ is the Euler constant, and $g(\sigma)$ is given by

$$g(\sigma) = \ln \sigma + 2(1-\sigma). \tag{36.73}$$

When $\sigma = 1$, $g(\sigma)$ vanishes, and Eq. (36.72) reduces to Eq. (32.43). Equation (36.72) is due to Teramoto, Yamashita, and Fujita.[106] The molecular weight dependence of the sedimentation coefficient of once-broken rods may be expressed in the form,

$$s_b = C \ln M + C' + Cg(\sigma), \tag{36.74}$$

where $C$ and $C'$ are constants independent of $M$ and $\sigma$.

Finally, we give a brief description of experimental results obtained by Fujita et al.[106, 107] for poly-$\gamma$-benzyl-L-glutamates (PBLG) in dimethylformamide (helicogenic solvent). In Fig. VI.13 are shown the double logarithmic plots of $[\eta]$ (dl/g) against the weight-average molecular weight $\langle M \rangle_w$. The open circles represent the data for triethylamine

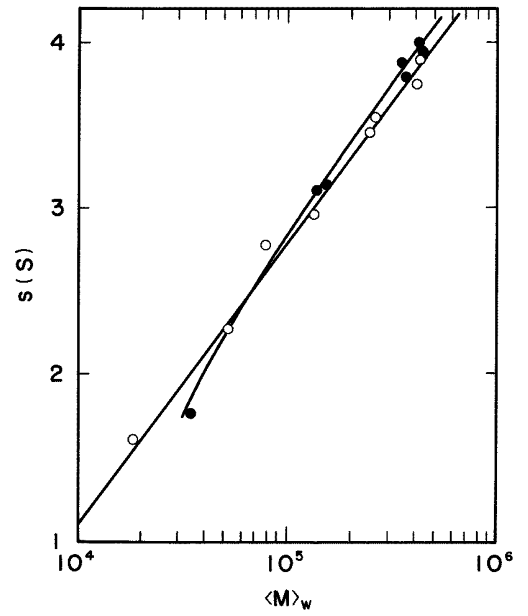

**Fig. VI.14.** Sedimentation coefficients (in svedbergs) of poly-$\gamma$-benzyl-L-glutamates (PBLG) in dimethylformamide at 25 °C.[106, 107] Open circles: PBLG-A. Filled circles: PBLG-B.

or sodium methoxide-initiated samples (PBLG-A), and the filled circles for trimethylenediamine-initiated samples (PBLG-B). The PBLG-A molecules in dimethylformamide may be regarded as straight rods. This was first demonstrated by Doty et al.[108] On the other hand, the PBLG-B molecules in the same solvent may be represented by the once-broken rod model. The data show that for $\langle M\rangle_w$ above $10^5$ the introduction of one flexible joint into a straight rod lowers $[\eta]$ by a factor of about 14%, almost independent of $\langle M\rangle_w$. This compares well with the theory of Yu and Stockmayer. Figure VI.14 shows plots of the sedimentation coefficient $s$ (in svedbergs, 1 S $= 10^{-13}$ sec) against log $\langle M\rangle_w$ for the same systems as above. Again for $\langle M\rangle_w > 10^5$, the relationship (36.74) is seen to be fulfilled.

## 36d(ii). Wormlike Chains without Excluded Volume

In the early 1950s the effects of chain stiffness on the frictional properties of polymers were investigated by Kuhn, Kuhn, and Silberberg,[109, 110] and by Peterlin[111] using rather simple models, and since the 1960s, extensive investigations of the frictional properties of wormlike chains have been published. These studies were often undertaken so as to obtain conformational information about DNA. Now, the evaluation of $[\eta]$ and $s$ requires the average $\langle {R_{ij}}^{-1}\rangle$ and its sum over $i$ and $j$. For convenience let $R_t$ be the distance between two points in the wormlike chain separated by a contour length $t = |j - i|a$. As shown in Section 9c, the averages of the positive powers of any displacement length or its components can be exactly calculated for wormlike chains, while this is not the case for the mean reciprocal distance $\langle {R_t}^{-1} \rangle$. Thus we must introduce some approximations.

Recalling that the distribution of $R_t$ may be well approximated by the Daniels distribution for large $\lambda t$ with $\lambda^{-1}$ the Kuhn statistical length, we write

$$\begin{aligned}\langle {R_t}^{-1} \rangle &= \int_0^\infty {R_t}^{-1} P_D(R_t) dR_t \quad \text{for } \lambda t > \sigma \\ &= \int_0^\infty {R_t}^{-1} P(R_t) dR_t \quad \text{for } 0 \le \lambda t \le \sigma \,, \end{aligned} \tag{36.75}$$

where $\sigma$ is some positive constant, $P_D$ is Daniels distribution given by Eq. (9.112), and $P$ is the exact distribution for the wormlike chain. Hearst and Stockmayer[112] have approximated $t\langle {R_t}^{-1} \rangle$ by a cubic equation for $0 \le \lambda t \le \sigma$, i.e., the set

$$\begin{aligned}t\langle {R_t}^{-1} \rangle &= (6/\pi)^{1/2} (\lambda t)^{1/2} [1 - \tfrac{1}{40} (\lambda t)^{-1}] \quad \text{for } \lambda t > \sigma \\ &= 1 + \tfrac{1}{3} \lambda t + c_1 (\lambda t)^2 + c_2 (\lambda t)^3 \quad \text{for } 0 \le \lambda t \le \sigma \,, \end{aligned} \tag{36.76}$$

where the first line is obtained by the use of Eq. (9.112). Clearly, $t\langle {R_t}^{-1} \rangle$ is equal to unity for a rod ($\lambda t = 0$), and it can easily be shown that the initial slope of $t\langle {R_t}^{-1} \rangle$ at $\lambda t = 0$ is $\frac{1}{3}$. The constants $\sigma$, $c_1$, and $c_2$ have been determined in such a way that at $\lambda t = \sigma$ the two curves of $t\langle {R_t}^{-1} \rangle$ given by the first and second lines of Eqs. (36.76) intersect each other and have the same first and second derivatives. The results are

$$\sigma = 2.20, \quad c_1 = 0.118, \quad c_2 = -0.026 \,. \tag{36.77}$$

The values of $t\langle {R_t}^{-1} \rangle$ calculated from Eqs. (36.76) with (36.77) are plotted against $\lambda t$ in Fig. VI.15.

An alternative approximation has been introduced by Ptitsyn and Eizner.[113] They have approximated the distribution function $P(R_t)$ by a linear combination of a Gaussian distribution for the random-flight chain and a delta function for the rod so as to be able to interpolate to intermediate values of $\lambda t$;

$$P(R_t) = \frac{3}{2} \left( \frac{\langle {R_t}^4 \rangle}{\langle {R_t}^2 \rangle^2} - 1 \right) P_G(R_t) + \left( \frac{5}{2} - \frac{3}{2} \frac{\langle {R_t}^4 \rangle}{\langle {R_t}^2 \rangle^2} \right) \delta(R_t - \langle {R_t}^2 \rangle^{1/2}) \,, \tag{36.78}$$

where $P_G(R_t)$ is the Gaussian distribution whose second moment is $\langle {R_t}^2 \rangle$, and $\langle {R_t}^2 \rangle$ and $\langle {R_t}^4 \rangle$ are given by Eqs. (9.87) and (9.88) with $L = t$, respectively. Equation (36.78) gives

$$\langle {R_t}^{-1} \rangle = \psi(\lambda t) \langle {R_t}^2 \rangle^{-1/2} \tag{36.79}$$

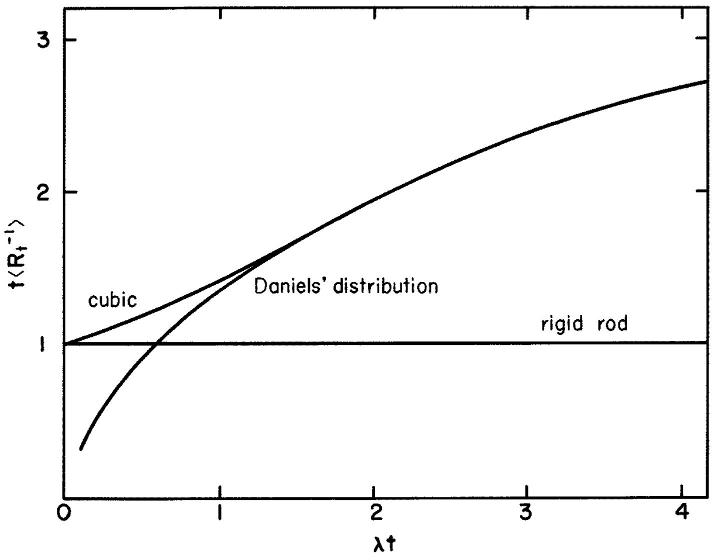

**Fig. VI.15.** The values of the contour length times the mean reciprocal end-to-end distance for a rigid rod, a Daniels wormlike chain, and a Daniels wormlike chain with the cubic correction for small $\lambda t$.[112]

with

$$\begin{aligned}\psi(\lambda t) = 0.427 + 0.573[180(\lambda t)^2 - 312\lambda t + 214 \\ -108(2+\lambda t)e^{-2\lambda t} + 2e^{-6\lambda t}]/27(2\lambda t - 1 + e^{-2\lambda t})^2\,. \quad (36.80)\end{aligned}$$

First we apply the general theory of Kirkwood to wormlike chains, following Hearst.[114, 115] If the direction of the tangent to the chain at the midpoint of its contour is fixed, the segment distribution may be considered to be cylindrically symmetric about that tangent (the cylindrical axis). We choose the midpoint of the contour as the origin of a coordinate system, and denote the internal (Cartesian) coordinates of the $i$th segment by $l_{1i}$, $l_{2i}$, and $l_{3i}$, the last of these being measured along the cylindrical axis. The Euler angles $\theta$, $\varphi$, and $\psi$ are introduced to specify this coordinate system relative to a fixed laboratory coordinate system $(x, y, z)$ with the same origin. The external rotation of the cylindrical distribution of segments may be specified by the angles $\theta$, $\varphi$, $\psi$. The components of the metric tensor associated with these coordinates are

$$\begin{aligned} g_{\theta\theta} &= A + B\,, & g_{\theta\varphi} &= 0\,, \\ g_{\varphi\varphi} &= A(1+\cos^2\theta) + B\sin^2\theta\,, & g_{\theta\psi} &= 0\,, \\ g_{\psi\psi} &= 2A\,, & g_{\varphi\psi} &= 2A\cos\theta\,, \quad (36.81) \end{aligned}$$

where

$$A = \sum_i \langle {l_{1i}}^2 \rangle = \sum_i \langle {l_{2i}}^2 \rangle \,, \qquad B = \sum_i \langle {l_{3i}}^2 \rangle \,, \tag{36.82}$$

and terms of type $l_{1i}l_{3i}$ have been dropped because of the averaging over internal coordinates subject to the cylindrical distribution. The quantities $A$ and $B$ can easily be evaluated for wormlike chains. We evaluate the rotatory diffusion coefficient $D^{\theta\theta}$ from Eqs. (32.36) to (32.38), $D^{\varphi\varphi}$ being given by $D^{\varphi\varphi} = D^{\theta\theta}/\sin^2\theta$. In doing this, we use Eqs. (36.76) for $\langle {R_t}^{-1} \rangle$, and replace the sums over $i$ and $j$ by integrals, taking the lower limit of $t$ as $a$, corresponding to $|j - i| = 1$. The choice of the lower limit of integration is, to some extent, arbitrary, and has influence upon the final results. The results thus obtained are

$$\eta_0 D^{\theta\theta}/kT = (\lambda/L^2)[0.716(\lambda L)^{1/2} - 0.636\ln(\lambda a) - 1.548 + 0.640(a/b)] \qquad \text{for } \lambda L \gg 1 \,, \tag{36.83}$$

$$\begin{aligned} \eta_0 D^{\theta\theta}/kT = (1/\pi L^3)\{&3\ \ln(L/a) - 7.00 + 4(a/b) \\ &+\lambda L[2.25\ \ln(L/a) - 6.66 + 2(a/b)]\} \end{aligned} \qquad \text{for } \lambda L \ll 1,\ L/a \gg 1 \,, \tag{36.84}$$

where $L$ is the contour length of the chain and $b = \zeta/3\pi\eta_0$ is Stokes diameter of the segment. Equations (36.83) and (36.84) describe deviations from the random-flight chain rod, respectively. Equation (36.84) becomes Eq. (36.67) in the asymptotic limit $\lambda L = 0$.

The diffusion equation for the distribution function $P(\theta, \varphi, t)$ describing the orientation of the cylindrical distribution of segments is readily obtained as

$$\begin{aligned} 6\tau\frac{\partial P}{\partial t} - \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial t}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2 P}{\partial\varphi^2} \\ = 9\tau g\left(\frac{B-A}{B+A}\right)P\sin^2\theta\sin 2\varphi + O(g^2) \,, \end{aligned} \tag{36.85}$$

where $\tau$ is given by Eq. (36.57) with (36.83) or (36.84). The solution of Eq. (36.85) is

$$4\pi P = 1 + \tfrac{3}{2}g\left(\frac{B-A}{B+A}\right)\left(\frac{\tau}{1+i\omega\tau}\right)\sin^2\theta\sin 2\varphi + O(g^2) \,. \tag{36.86}$$

When $A = 0$, Eqs. (36.85) and (36.86) reduce to Eqs. (36.56) and (36.58) for rods, respectively.

Now we proceed to evaluate the intrinsic viscosity. For the present model, $[\eta]$ may be obtained more conveniently by evaluating $\sum_i \langle \mathbf{F}_i \cdot {\mathbf{v}_i}^0 \rangle$ rather than $\sum_i \langle F_{ix} y_i \rangle$ in Eq. (30.24). Recalling that

$$\mathbf{F}_i = \sum_\alpha [\zeta(\mathbf{u} - \mathbf{v}^0)]^\alpha \frac{\partial \mathbf{R}^i}{\partial q^\alpha} \,, \tag{36.87}$$

$${\mathbf{v}_i}^0 = \sum_\alpha v^{0\alpha}\frac{\partial \mathbf{R}^i}{\partial q^\alpha} \,, \tag{36.88}$$

**TABLE VI.6.** GENERALIZED COORDINATES FOR THE CYLINDRICAL DISTRIBUTION OF SEGMENTS[116]

| COORDINATE NUMBER | COORDINATE | METRIC TENSOR |
|---|---|---|
| 1 | $dl_1/l_1$ | $g_{11} = A$ |
| 2 | $dl_2/l_2$ | $g_{22} = A$ |
| 3 | $dl_3/l_3$ | $g_{33} = B$ |
| 4 | $\frac{1}{2}(dl_2/l_3 + dl_3/l_2)$ | $g_{44} = \frac{1}{2}(A + B)$ |
| 5 | $\frac{1}{2}(dl_3/l_1 + dl_1/l_3)$ | $g_{55} = \frac{1}{2}(A + B)$ |
| 6 | $\frac{1}{2}(dl_1/l_2 + dl_2/l_1)$ | $g_{66} = A$ |

we find through straightforward tensor algebra

$$\sum_i \mathbf{F}_i \cdot \mathbf{v}_i{}^0 = \sum_{\alpha,\beta,\mu,\nu} g^{\alpha\mu} g^{\beta\nu} \zeta_{\alpha\beta} \sum_i \sum_j \left( \mathbf{v}_i{}^0 \cdot \frac{\partial \mathbf{R}^i}{\partial q^\mu} \right) \left[ (\mathbf{u}_j - \mathbf{v}_j{}^0) \cdot \frac{\partial \mathbf{R}^j}{\partial q^\nu} \right] . \tag{36.89}$$

The velocity of the $j$th segment $\mathbf{u}_j$ may be calculated from Eq. (36.61) by substitution of Eq. (36.86) for $P$, in which $\alpha$ and $\beta$ are summed over $\theta$, $\varphi$, and $\psi$. The evaluation of the sum of (36.89) requires a set of generalized coordinates with which all forces on the distribution of segments may be expressed. There are three stretching coordinates referring to stretches in the $l_1$, $l_2$, and $l_3$ directions. Three mutually perpendicular shear planes pass through the origin. For each such plane, there are two orthogonal directions of shear, introducing six shearing coordinates. Thus Hearst and Tagami[116] have introduced the set of coordinates listed in Table VI.6 in the form of differential displacements together with a number which identifies them and the component of the metric tensor. This set has been chosen so as to make the metric and friction tensors diagonal. Then we readily find the contravariant components $g^{\alpha\alpha}$ and the reciprocal friction tensor, and obtain $\zeta_{\alpha\alpha}$ by inversion. Averaging the sum of (36.89) thus obtained over all orientations, we find

$$[\eta] = 2.19 \times 10^{23} \frac{(L/\lambda)^{3/2}}{M} \{1 - 0.891[\ln(\lambda a) + 2.431 - a/b](\lambda L)^{-1/2}\}^{-1} \quad \text{for } \lambda L \gg 1 \, , \tag{36.90}$$

$$[\eta] = \frac{\pi N_{\mathrm{A}} L^3}{90M} \left[ \frac{1}{\ln(L/a) - 2.72 + 0.66(a/b)} + \frac{3}{\ln(L/a) - 2.72 + 1.33(a/b)} \right] \quad \text{for } \lambda L \ll 1, \ L/a \gg 1 \, . \tag{36.91}$$

Equation (36.91) becomes Eq. (36.68) for rods in the asymptotic limit.

In the non-free-draining limit, from Eq. (36.90), we have $\Phi_0 = 2.19 \times 10^{23}$ for the viscosity constant. For the sake of comparison this

Hearst–Tagami value of $\Phi_0$ for random-flight chains is also included in Table VI.3. It is seen that for some value of $\lambda$ the second term in the curly brackets in Eq. (36.90) vanishes and $[\eta]$ is therefore proportional to $M^{1/2}$ for any value of $M$. Thus Hearst has attributed proportionality of $[\eta]$ to $M^{1/2}$ observed for flexible chains such as vinyl polymers to their finite stiffness, corresponding to the above value of $\lambda$. However, this interpretation seems artificial. In general, for $\lambda L \gg 1$ the molecular weight dependence of $[\eta]$ may be written in the form,

$$[\eta] = C_\eta M^{1/2} - C_\eta{}' \,, \tag{36.92}$$

where $C_\eta$ and $C_\eta{}'$ are constants independent of $M$.

Eizner and Ptitsyn[117, 118] and Sharp and Bloomfield[119] have evaluated the intrinsic viscosity of wormlike chains by the use of the semiempirical equation of Peterlin,[82, 120]

$$[\eta] = \frac{N_\mathrm{A}\zeta n\langle S^2\rangle}{6\eta_0 M}\left[1 + \frac{4\zeta}{9\pi\eta_0 n^2}\sum_{\substack{i=0 \\ i\neq j}}^{n/2}\sum_{j=0}^{n}(n-2j)\langle R_{ij}{}^{-1}\rangle\right]^{-1} . \tag{36.93}$$

Eizner and Ptitsyn have used Eq. (36.79) with (36.80) for $\langle R_{ij}{}^{-1}\rangle$, while Sharp and Bloomfield Eqs. (36.76) for $\langle R_{ij}{}^{-1}\rangle$. We write the results in the form of Eq. (35.1), where $\langle S^2\rangle$ is given by Eq. (9.108). The values of $\Phi$ are plotted in Fig. VI.16 against $n$ for $\lambda a = 1/20$ and $a = b$, the values from the theory of Hearst and Tagami, Eq. (36.90), being also included. We note that Ullman[121] has also calculated the intrinsic viscosity on the basis of the Kirkwood–Riseman integral equation, but omit the details here.

The diffusion and sedimentation coefficients can be evaluated straightforwardly by the use of the Kirkwood equation. Using Eqs. (36.76) for $\langle R_{ij}{}^{-1}\rangle$, Hearst and Stockmayer[112] have derived

$$s = \frac{M_L(1-\bar{v}\bar{\rho})}{3\pi\eta_0 N_\mathrm{A}}[1.843(\lambda L)^{1/2} - \ln(\lambda a) - 2.431 - a/b] \quad \text{for } \lambda L \gg 1\,, \tag{36.94}$$

$$s = \frac{M_L(1-\bar{v}\bar{\rho})}{3\pi\eta_0 N_\mathrm{A}}[\ln(L/a) + 0.166\lambda L - 1 + a/b] \quad \text{for } \lambda L \ll 1, L/a \gg 1\,, \tag{36.95}$$

where $M_L(= M/L)$ is the molecular weight per unit contour length. For $\lambda L \gg 1$, the molecular weight dependence of a may be written in the form

$$s = C_s M^{1/2} + C_s{}' \,, \tag{36.96}$$

where $C_s$ and $C_s{}'$ are constants independent of $M$. Ptitsyn and Eizner[113, 118] have also carried out similar calculations using Eq. (36.79) with (36.80) for $\langle R_{ij}{}^{-1}\rangle$.

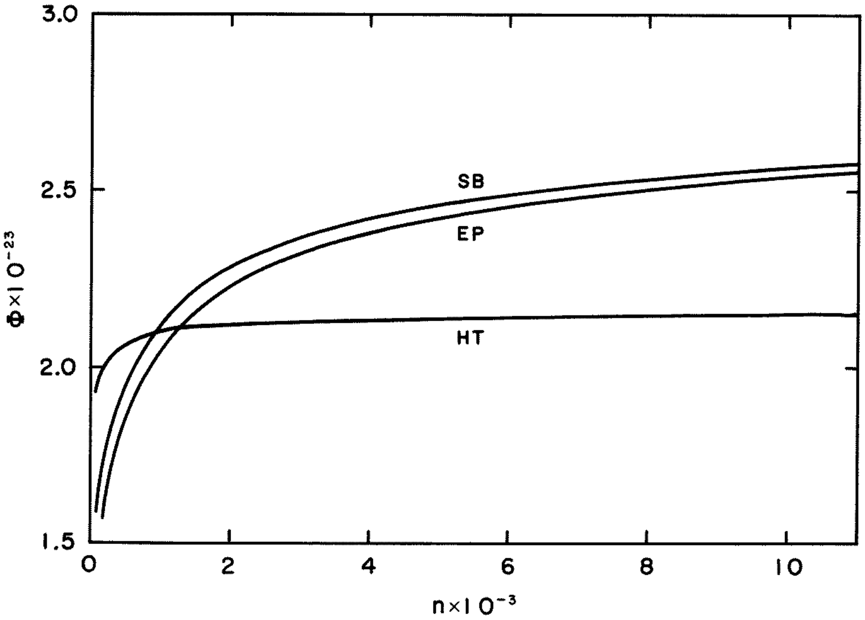

**Fig. VI.16.** Dependence of the viscosity function $\Phi$ on the number of segments, *n*, for wormlike chains with $\lambda a = 1/20$ and $a = b$ and without excluded volume. Curve HT: the Hearst–Tagami theory. Curve EP: the Eizner–Ptitsyn theory. Curve SB: the Sharp–Bloomfield theory.

## 36d(iii). Wormlike Chains with Excluded Volume

Crothers and Zimm[122] have summarized viscosity and sedimentation data[122–125] for DNA in buffers of ionic strength near 0.2 as shown in Fig. VI.17 and obtained empirical relations,

$$[\eta] = 0.001371M^{0.665} - 5\,, \tag{36.97}$$

$$s = 0.01517M^{0.445} + 2.7\,, \tag{36.98}$$

where $[\eta]$ is expressed in deciliters per gram and $s$ in svedbergs. That is, $[\eta]$ and $s$ are not linear in $M^{1/2}$. This suggests that there are excluded-volume effects in the DNA molecule.

The effect of excluded volume on the intrinsic viscosity of wormlike chains has been investigated by Sharp and Bloomfield[119]using Peterlin's equation (36.93) and the $\varepsilon$-method. For random-flight chains the Kuhn statistical segment length $A$ is related to the parameter $\lambda$ by $A = \lambda^{-1}$ and $NA^2 = L/\lambda$, and therefore there is the relation $\lambda L = N$. Thus we may write $\langle R^2 \rangle = A^2 N^{1+\varepsilon} = \langle R^2 \rangle_0 N^{\varepsilon} = \langle R^2 \rangle_0 (\lambda L)^{\varepsilon}$ and $\langle R^{-1} \rangle = \langle R^{-1} \rangle_0 (\lambda L)^{-\varepsilon/2}$ for random-flight chains with excluded volume. Sharp and Bloomfield have assumed equivalent expressions for $\langle {R_t}^{-1} \rangle$ and $\langle {R_t}^2 \rangle$ for wormlike chains together with the cubic approximation of

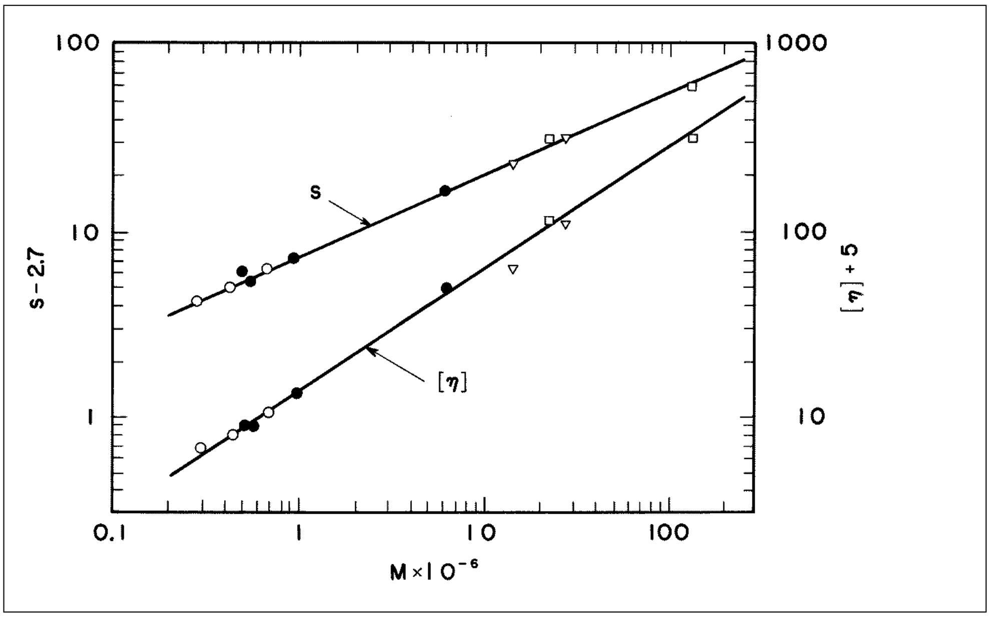

**Fig. VI.17.** Intrinsic viscosities and sedimentation coefficients of DNA in buffers of ionic strength near 0.2 obtained by various investigators.[122–125]

Hearst and Stockmayer;

$$\begin{aligned} t\langle {R_t}^{-1}\rangle &= t\langle {R_t}^{-1}\rangle_0(\lambda t)^{-\varepsilon/2} && \text{for } \lambda t > \sigma \\ &= 1 + \tfrac{1}{3}\lambda t + c_1(\lambda t)^2 + c_2(\lambda t)^3 && \text{for } 0 \le \lambda t \le \sigma\,, \end{aligned} \tag{36.99}$$

$$\begin{aligned} t^{-2}\langle {R_t}^2\rangle &= t^{-2}\langle {R_t}^2\rangle_0(\lambda t)^{\varepsilon} && \text{for } \lambda t > \sigma' \\ &= 1 - \tfrac{2}{3}\lambda t + c_1{}'(\lambda t)^2 + c_2{}'(\lambda t)^3 && \text{for } 0 \le \lambda t \le \sigma'\,, \end{aligned} \tag{36.100}$$

where $\langle {R_t}^{-1}\rangle_0$ and $\langle {R_t}^2\rangle_0$ are given by the first of Eqs. (36.76) and (9.87), respectively. The values of the constants in Eqs. (36.99) and (36.100) can be determined as functions of $\varepsilon$, as before, by matching the values and the first and second derivatives of the two expressions. Equation (36.100) is used to evaluate $\langle S^2\rangle$. Thus Sharp and Bloomfield have shown that $[\eta]$ is linear in $M^{(1+3\varepsilon)/2}$. Similar calculations of the sedimentation coefficient have been carried out by Gray, Bloomfield, and Hearst,[126] leading to the result that $s$ is a linear function of $M^{(1-\varepsilon)/2}$. Comparing these powers of $M$ with those in Eqs. (36.97) and (36.98), we find $\varepsilon = 0.110$ for DNA. Further, we can estimate $\lambda^{-1}$ and $b$ from the numerical constants in Eq. (36.97) or (36.98) using the theoretical expression for $[\eta]$ or $s$, assuming $a = b$. The results are given in Table VI.7, where the estimates from the Hearst–Stockmayer equation (36.94) for $s$ are also included. The SB value of the hydrodynamic diameter $b$ for DNA is too large even if it is assumed to be the

**TABLE VI.7.** ESTIMATES OF $\lambda^{-1}$ AND $b$ FOR DNA

| THEORY | DATA | $\lambda^{-1}$ (Å) | $b$ (Å) |
|---|---|---|---|
| SB[a] | $[\eta]$ | 542 | 79-82 |
| GBH[a] | $s$ | 900 | 26-27 |
| HS[b] | $s$ | 717 | 30-41 |

[a] With the excluded-volume effect.

[b] Without the excluded-volume effect.

hydrated diameter. This is probably due to the use of the approximate Peterlin expression $[\eta]$.

Finally, we must note that the dynamics of the space curve model has been developed by Harris and Hearst,[127-129] but we do not reproduce the results here.

## 36e. Some Other Problems

In this section we discuss some of the other nonequilibrium properties of dilute polymer solutions, e.g., normal stress effects, flow birefringence, and dielectric dispersion. We also add some comments on the Rouse–Zimm theory in relation to these properties.

### 36e(i). Normal Stress Effects

Consider the steady shear flow given by Eq. (30.12). At infinite dilution the Rouse–Zimm theory then gives the shear stress,

$$\sigma_{xy} - \eta_0 g = \frac{RTc}{M} \sum_j \tau_j g \,, \tag{36.101}$$

$$\sigma_{yz} = \sigma_{zx} = 0 \,, \tag{36.102}$$

where Eq. (36.101) has been obtained from Eq. (33.33). Similarly, from Eq. (30.21) we can easily derive for the normal stresses the expressions

$$\sigma_{xx} - \sigma_{yy} = \frac{2RTc}{M} \sum_j {\tau_j}^2 g^2 = \frac{2\gamma Mc}{RT} (\eta_0 [\eta] g)^2 \,, \tag{36.103}$$

$$\sigma_{yy} - \sigma_{zz} = 0 \,, \tag{36.104}$$

where $\gamma$ is defined by

$$\gamma = \sum_j {\lambda_j}^{-2} \bigg/ \left( \sum_j {\lambda_j}^{-1} \right)^2 \tag{36.105}$$

with $\lambda_j$ the eigenvalues of Rouse and Zimm. $\gamma$ is equal to 0.4 and 0.205 in the free-draining and non-free-draining limits, respectively. The nonvanishing of $\sigma_{xx} - \sigma_{yy}$ is called the *normal stress effect* or the

*Weissenberg effect.*[130] The Rouse–Zimm theory predicts that $(\sigma_{xx} - \sigma_{yy})/g^2$ is independent of the rate of shear $g$. Experimentally, however, this quantity decreases with increasing $g$ as does $(\sigma_{xy} - \eta_0 g)/g$ (non-Newtonian viscosity), although there exists a linear relationship between $\sigma_{xx} - \sigma_{yy}$ and $g^2$ for small $g$.[131] Further, for small $g$ the Zimm theory does work well for flexible chains, indicating again absence of the draining effect.

Now, from Eq. (33.35) we obtain for the storage modulus at small $\omega$

$$\lim_{\omega \to 0} \frac{G'}{\omega^2} = \frac{RTc}{M} \sum_j {\tau_j}^2 \,. \tag{36.106}$$

Comparison of Eqs. (36.103) and (36.106) leads to a relationship between the storage modulus and the normal stress,

$$\lim_{\omega \to 0} \frac{G'}{\omega^2} = \frac{\sigma_{xx} - \sigma_{yy}}{2g^2} \,. \tag{36.107}$$

This equation is found to be valid in the region of Newtonian flow.[131]

Thus we have seen that the Zimm theory for non-free-draining flexible molecules works well for most phenomena, but breaks down in interpreting the nonlinear viscoelastic behavior, i.e., the non-Newtonian viscosity and the nonquadratic-dependent normal stress effect. Another defect of this theory is that it predicts the vanishing of the intrinsic dynamic viscosity $[\eta']$ at $\omega = \infty$, whereas experiments show that $[\eta']$ remains finite at $\omega = \infty$.[132, 133] The observed behavior may be deduced from theory by introducing some rigidity or internal viscosity into the spring and bead model, as shown by Peterlin.[134]

## 36e(ii). Flow Birefringence

The orientation of nonspherical particles or deformed flexible chains in a shear flow leads to an optical anisotropy of the solution which may be observed by examining the flow birefringence.[25] The degree of orientation is determined by the balance between the orienting effect arising from shear flow and the disorienting effect arising from rotatory diffusion. Thus, the flow birefringence may be used to determine the rotatory diffusion coefficient, as already mentioned. Using the spring and bead model we now derive theoretical expressions for two important quantities observed in flow birefringence experiments, the *extinction angle* $\chi$ and the magnitude of birefringence $\Delta\tilde{n}$.

Let $\gamma_1$ be the polarizability component along the end-to-end vector $\mathbf{R}$ of the chain of $n$ bonds and $\gamma_2$ be the value of the two equal components normal to $\mathbf{R}$, averaged over all configurations with $\mathbf{R}$ fixed. For the Gaussian chain Kuhn and Grün[135] have derived expressions for $\gamma_1$ and $\gamma_2$:

$$\gamma_1 = \frac{n}{3}(\alpha_1 + 2\alpha_2) + \frac{2(\alpha_1 - \alpha_2)}{5\langle R^2 \rangle_0} R^2 \,,$$

$$\gamma_2 = \frac{n}{3}(\alpha_1 + 2\alpha_2) - \frac{(\alpha_1 - \alpha_2)}{5\langle R^2 \rangle_0} R^2 \,, \tag{36.108}$$

where $\alpha_1$ is the component of polarizability of the bond along its vector, and $\alpha_2$ is the value of the two equal components normal to the bond vector. We may use Eqs. (36.108) for individual Gaussian springs in the spring and bead model, and write their polarizability components in the form

$$\begin{aligned} {\gamma_1}' &= p + 2qr^2 \,, \\ {\gamma_2}' &= p - qr^2 \,, \end{aligned} \tag{36.109}$$

where $p$ and $q$ are constants independent of the length of the spring $r$. The polarizability of the whole molecule is the sum of the polarizabilities of the individual springs, and the average of this is designated by $\mathbf{\Gamma}$. When all the individual polarizability tensors are referred to the $x$, $y$, $z$ coordinate system and added, we find

$$\mathbf{\Gamma} = n(p-q)\mathbf{I} + 3q \begin{pmatrix} \langle \mathbf{x}^T\mathbf{A}\mathbf{x} \rangle & \langle \mathbf{x}^T\mathbf{A}\mathbf{y} \rangle & \langle \mathbf{x}^T\mathbf{A}\mathbf{z} \rangle \\ \langle \mathbf{y}^T\mathbf{A}\mathbf{x} \rangle & \langle \mathbf{y}^T\mathbf{A}\mathbf{y} \rangle & \langle \mathbf{y}^T\mathbf{A}\mathbf{z} \rangle \\ \langle \mathbf{z}^T\mathbf{A}\mathbf{x} \rangle & \langle \mathbf{z}^T\mathbf{A}\mathbf{y} \rangle & \langle \mathbf{z}^T\mathbf{A}\mathbf{z} \rangle \end{pmatrix} \,, \tag{36.110}$$

where we have used the same matrix notation as in Eq. (33.28).

If we consider a shear flow given by Eq. (30.12) and a light beam propagating along the $z$ axis, the electric vectors in the $xy$ plane are the only ones of interest, and we may omit the third row and column of the tensor in Eq. (36.110). The extinction angle is equal to the smaller angle between the principal axes of the tensor $\Gamma$ and the $x$ axis (stream lines). Therefore, diagonalizing this tensor, we find

$$\tan 2\chi = \frac{2\langle \mathbf{x}^T\mathbf{A}\mathbf{y} \rangle}{\langle \mathbf{x}^T\mathbf{A}\mathbf{x} \rangle - \langle \mathbf{y}^T\mathbf{A}\mathbf{y} \rangle} \,. \tag{36.111}$$

The difference of the polarizabilities along the principal axes, $\Delta\Gamma$, is

$$\Delta\Gamma = 3q[(\langle \mathbf{x}^T\mathbf{A}\mathbf{x} \rangle - \langle \mathbf{y}^T\mathbf{A}\mathbf{y} \rangle)^2 + 4\langle \mathbf{x}^T\mathbf{A}\mathbf{y} \rangle^2]^{1/2} \,. \tag{36.112}$$

The magnitude of the refringence of the solution, $\Delta\tilde{n}$, is proportional to this expression multiplied by the number of molecules per unit volume, $cN_\mathrm{A}/M$.

After transformation to normal coordinates we can evaluate the averages in Eqs. (36.111) and (36.112). The results for steady flow are

$$\tan 2\chi = \frac{\sum_j \tau_j}{g \sum_j {\tau_j}^2} \,, \tag{36.113}$$

$$\Delta\tilde{n} = q' \frac{cna^2[\eta]\eta_0 g}{MRT} \mathrm{cosec} 2\chi \,, \tag{36.114}$$

where $q'$ is an optical constant characteristic of the system. Equation (36.113) may be rewritten as

$$\tan 2\chi = \frac{RT}{\gamma g \eta_0 M[\eta]} = \frac{4D_r}{\gamma g} \,, \tag{36.115}$$

where the second equality has been obtained by the use of Eq. (31.56) for the rotatory diffusion coefficient $D_r$, and $\gamma$ is defined by Eq. (36.105). The extinction angle is equal to $\pi/4$ in the limit $g = 0$, and decreases with increasing $g/D_r$.

## 36e(iii). Dielectric Dispersion

Consider the application of the alternating electric field $E = E_0 \exp(i\omega t)$ to a dielectric substance with complex dielectric constant $\bar{\varepsilon} = \varepsilon' - i\varepsilon''$, where $\varepsilon'$ and $\varepsilon''$ are dependent on $\omega$. The frequency dependences of $\varepsilon'$ and $\varepsilon''$ are usually referred to as *dielectric dispersion.* As is well known, dispersion of the Debye type (single relaxation time) is given by

$$\bar{\varepsilon} - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}\,, \tag{36.116}$$

where $\varepsilon_s$ and $\varepsilon_\infty$ are the values of $\varepsilon'$ at $\omega = 0$ and $\infty$, respectively. $\tau$ is the relaxation time during which the transition from one equilibrium orientation of dipoles to another occurs. The imaginary part (dielectric loss) $\varepsilon''$ has a maximum at $\omega = \tau^{-1}$. For both polymeric and nonpolymeric substances deviations from the Debye equation occur frequently. However, we do not discuss this problem here; rather, we study the relationship between the relaxation time and molecular parameters.

The dielectric dispersion of rigid macromolecules (globular proteins) has been investigated by Oncley.[136] He has estimated the dimensions of the particles from the relaxation times, which are associated with their rotational motions and are inversely proportional to the rotatory diffusion coefficients. In the case of rod molecules, for example, the dielectric relaxation time $\tau$ is related to the rotatory diffusion coefficient $D^{\theta\theta}$ by the equation,

$$\tau = 1/2D^{\theta\theta}\,. \tag{36.117}$$

Note that this $\tau$ is different from the viscoelastic relaxation time defined by Eq. (36.57). For very long rods, $D^{\theta\theta}$ is given by Eq. (36.67). Yu et al.[137] have determined the molecular dimensions of helical polyisocyanates by the use of Eq. (36.117).

Now we consider the dielectric dispersion of flexible chain polymers. Our discussion is limited to a chain whose repeating units possess dipoles rigidly attached to the backbone. Then dipoles in the repeating units may be classified geometrically into two types. If the dipoles are along the chain contour, they are referred to as Type A dipoles; on the other hand, the dipoles attached perpendicular to the chain contour are referred to as Type B dipoles. For a sequence of end-to-end Type A dipoles, there must be a complete correlation between the dipole moment $\boldsymbol{\mu}$ of the whole chain and the end-to-end distance; that is $\langle \boldsymbol{\mu} \cdot \mathbf{R} \rangle =$ const. $\langle R^2 \rangle$. For this case, the mean-square dipole moment $\langle \mu^2 \rangle$ has the same excluded-volume effect as $\langle R^2 \rangle$, and the low-frequency relaxation time, associated with a rotation of the whole molecule, depends on the molecular weight. On the other hand, for chains possessing Type B dipoles, there is no correlation between $\boldsymbol{\mu}$ and $\mathbf{R}$, i.e., $\langle \boldsymbol{\mu} \cdot \mathbf{R} \rangle = 0$. For this case, the mean-square dipole moment is subject to no excluded-volume effect, and the relaxation time is independent of the molecular weight, since the dipole relaxation is associated with local segmental motions.

Although it is difficult to develop a dielectric theory for chains possessing Type B dipoles, Type A dipoles can easily be treated using the spring and bead model. We describe this following Stockmayer and Baur.[138] Let $e_i$ be the charge on the $i$th bead, all charges being represented by a column vector $\mathbf{e}$. Without loss of generality, suppose that the field $E$ is along the $x$ axis. Then the external force acting on the $i$th bead is

$$-\nabla_i U_e = e_i E \mathbf{e}_x \,. \tag{36.118}$$

We introduce the vector $\boldsymbol{\varepsilon}$ defined by

$$\boldsymbol{\varepsilon} = \mathbf{Q}^T \mathbf{e} \tag{36.119}$$

with $\mathbf{Q}$ the transformation matrix in Eqs. (33.23). If we ignore the free diffusion in the $y$ and $z$ directions, the diffusion equation (33.25) in normal coordinates becomes

$$\frac{\partial P}{\partial t} = \sum_j \left[ \frac{\kappa \lambda_j}{\zeta} - \frac{\partial (X_j P)}{\partial X_j} - \frac{E \nu_j \varepsilon_j}{\zeta} \frac{\partial P}{\partial X_j} + \frac{k T \nu_j}{\zeta} \frac{\partial^2 P}{\partial {X_j}^2} \right] . \tag{36.120}$$

The average moment of the whole molecule is given by

$$\langle p \rangle = \langle \mathbf{e}^T \mathbf{x} \rangle = \langle \boldsymbol{\varepsilon}^T \mathbf{X} \rangle = \sum_j \varepsilon_j \langle X_j \rangle \,. \tag{36.121}$$

As before, we derive the differential equation for $\langle X_j \rangle$ from Eq. (36.120) to find (for the alternating field)

$$\langle X_j \rangle = \frac{a^2 \varepsilon_j}{3 k T \mu_j} \frac{E}{1 + i \omega {\tau_j}'} \,, \tag{36.122}$$

where ${\tau_j}'$ are the dielectric relaxation times and just twice the viscoelastic relaxation times,

$${\tau_j}' = \frac{\zeta}{\kappa \lambda_j} = 2 \tau_j \,. \tag{36.123}$$

Now, if we consider the local field in the nonpolar solvent with dielectric constant $\varepsilon_0$, the excess dielectric constant over that of the solvent alone is

$$\Delta \bar{\varepsilon} - \Delta \varepsilon_\infty = 4 \pi \rho \left( \frac{\varepsilon_0 + 2}{3} \right)^2 \frac{\langle p \rangle}{E} \tag{36.124}$$

with $\rho$ the number of solute molecules per unit volume. Substitution of Eq. (36.121) with (36.122) into Eq. (36.124) leads to

$$\Delta \bar{\varepsilon} - \Delta \varepsilon_\infty = \frac{4 \pi {N_\mathrm{A}}^2 (\varepsilon_0 + 2)^2 c}{27 R T M} \sum_j \frac{{p_j}^2}{1 + i \omega {\tau_j}'} \,, \tag{36.125}$$

where

$$p_j = a\varepsilon_j/\mu_j^{1/2}\,. \tag{36.126}$$

If we use the Rouse eigenfunctions, we have $\mu_j = \pi^2 j^2/n^2$ and

$$p_j = \frac{na}{\pi j}\sum_i e_i Q_{ij} = \frac{(2na^2)^{1/2}}{\pi j}\int_0^1 e(s)\cos(\pi j s)ds\,, \tag{36.127}$$

where $e(s)$ is an appropriately defined charge density along the chain contour, expressible in terms of the magnitude and disposition of the Type A dipoles. Note that the $\varepsilon_j$ are just the Fourier components of the charge distribution.

We now discuss two particular cases. First, in the case specifically worked out by Zimm,[34] only the two end beads of the chain carry charges; we have $e_0 = -e$, $e_n = +e$, and all other $e_i = 0$, and therefore $\varepsilon_j = e(Q_{nj} - Q_{0j}) = e(8/n)^{1/2}$ for odd $j$ and zero for even $j$. Then the frequency dependent part in Eq. (36.125) becomes $\sum_{\text{odd}} j^{-2}(1 + i\omega\tau_j{}')^{-1}$. Thus, the dielectric spectrum consists of a single peak, not too much broader than a Debye dispersion, with a relaxation time that is essentially equal to the longest relaxation time $\tau_1{}'$ of the molecule, which corresponds in large measure to a molecular rotation, and which can be estimated from viscosity data;

$$\tau_1{}' = 1.21M\eta_0[\eta]/RT \qquad (\text{for } h = 0)\,, \tag{36.128}$$

$$\tau_1{}' = 0.85M\eta_0[\eta]/RT \qquad (\text{for } h = \infty)\,. \tag{36.129}$$

Secondly, let the charges on the beads alternate in sign and be equal in magnitude; $n$ is odd and $e_i = (-1)^i e$. This model was studied by Van Beek and Hermans.[139] In this case there are two dispersion peaks: one near $\tau_1{}'$ and the other near $\tau_n{}'$. The low-frequency relaxation can be reduced to negligible proportions by halving the charges on the two end beads, thus eliminating the elements $\varepsilon_j$ of low $j$ values, which correspond to the slow relaxation processes. As concerns the high-frequency dispersion, it can only be said that the model parameters which enter can be given no molecular significance, since the value of $\tau_n{}'$ depends on the value of $n$, which is number to be chosen arbitrarily.

Finally, we note that the charged spring and bead model may also be used to study relaxation processes in the birefringence produced by an electric field (the Kerr effect) and in light scattering under an electric field (the Benoit–Wippler effect),[140] provided the chains possess Type A dipoles.

### 36e(iv). Some Further Comments on the Spring and Bead Model

We have seen that the Rouse–Zimm theory for the spring and bead model is very successful in providing an understanding of various dynamical properties of flexible-chain polymers in dilute solution, except at high frequencies or when nonlinearity is important. Although we have thus far considered an alternating external field, the theory also works well for transient relaxations provided that the processes correspond to slow relaxations.[138, 141, 142] In general, the number $n$ of segments in the random-flight model is, to some extent, arbitrary. Therefore the Rouse-Zimm theory should be valid for those problems in which the final equations are invariant to the choice of $n$. It turns out that this is true for slow or low-frequency dynamical properties, since then only the combinations $na^2$ and $n\zeta$ appear in the final equations. As already pointed out, a good analog is furnished by the Debye theory of the heat capacity of crystals, which correctly describes the low-frequency vibrations but which is not reliable for the description of the high frequency part of the vibrational spectrum, where greater knowledge of the crystal structure is needed.

Consider again the spring and bead model without hydrodynamic interaction and excluded volume, i.e., the so-called Rouse model. For convenience, let the model have $n$ beads (0, 1, 2, ..., $n-1$). For finite $n$ the eigenvalues of the matrix $\mathbf{A}$ of (33.9) and the elements of the orthogonal transformation matrix $\mathbf{Q}$ are then given exactly by

$$\lambda_j = 4\sin^2(\pi j/2n) \quad (j = 0, 1, \ldots, n-1)\,, \tag{36.130}$$

$$Q_{ij} = (2/n)^{1/2}\cos[\pi(i + \tfrac{1}{2})j/n] \quad (i, j = 0, 1, \ldots, n-1)\,, \tag{36.131}$$

the coordinates being transformed by

$$\mathbf{R}_i = \sum_{j=0}^{n-1} Q_{ij}\boldsymbol{\xi}_j\,. \tag{36.132}$$

For large $n$, Eqs. (36.130) and (36.131) become Eqs. (34.27) and (34.28), respectively. If we put $g = 0$ and $\nu_j = 1$ in Eq. (33.26), the equation for configurational diffusion subject to no external field is

$$\frac{\partial P}{\partial t} = \sum_{j=0}^{n-1}\left[\frac{kT}{\zeta}{\nabla_j}^2 P + \frac{1}{{\tau_j}'}\nabla_j \cdot (\boldsymbol{\xi}_j P)\right] \tag{36.133}$$

with ${\tau_j}'$ the relaxation times defined by Eq. (36.123). Equation (36.133) is just the Fokker–Planck equation for Brownian motion of a system of coupled harmonic oscillators investigated by Wang and Uhlenbeck,[143] and its fundamental solution is now available. However, the average of a scalar function $f(\boldsymbol{\xi}_0, \boldsymbol{\xi}_1, \ldots, \boldsymbol{\xi}_{n-1})$ of normal coordinates may be calculated from

$$\frac{d\langle f\rangle}{dt} = \frac{kT}{\zeta}\sum_{j=0}^{n-1}\langle{\nabla_j}^2 f\rangle - \sum_{j=0}^{n-1}\frac{1}{{\tau_j}'}\langle\boldsymbol{\xi}_j \cdot \nabla_j f\rangle\,, \tag{36.134}$$

which is obtained by multiplying both sides of Eq. (36.133) by $f$ and integrating. For example, if $f = \boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_j$, we obtain

$$\langle\boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_j\rangle_e = 6kT\delta_{ij}/\zeta({\tau_i}'^{-1} + {\tau_j}'^{-1})\,, \tag{36.135}$$

$$\langle\boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_j\rangle = \langle\boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_j\rangle_\mathrm{e} + (\langle\boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_j\rangle_0 - \langle\boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_j\rangle_\mathrm{e})\exp[-t({\tau_i}'^{-1} + {\tau_j}'^{-1})]\,, \tag{36.136}$$

where the subscripts 0 and e refer to the initial and equilibrium states ($t = 0$ and $\infty$), respectively.

In order to study chain relaxation, we consider the correlation function $\rho(f, g, t)$ for two functions $f$ and $g$.[144] In general, correlation functions (or better, time-correlation functions) play the dominant role in the theory of linear irreversible processes, just as partition functions play the dominant role in equilibrium statistical mechanics.[16, 145] $\rho(f, g, t)$ may be defined by

$$\rho(f, g, t) = \frac{\langle f(t_0) g(t_0 + t)\rangle - \langle f\rangle_\mathrm{e}\langle g\rangle_\mathrm{e}}{(\langle f^2\rangle_\mathrm{e} - \langle f\rangle_\mathrm{e}{}^2)^{1/2}(\langle g^2\rangle_\mathrm{e} - \langle g\rangle_\mathrm{e}{}^2)^{1/2}} \,. \tag{36.137}$$

In the particular case for which $f$ and $g$ are of the forms $f = \sum_{i,j} f_{ij}\boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_j$ and $g = \sum_{i,j} g_{ij}\boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_j$, Verdier[144] has obtained an expression for $\rho(f, g, t)$ by the use of Eqs. (36.134) to (36.136). The result is

$$\rho(f, g, t) = \frac{\sum_{i,j} f_{ij}(g_{ij} + g_{ji})\tau_i{}'\tau_j{}' \exp[-t(\tau_i{}'^{-1} + \tau_j{}'^{-1})]}{[\sum_{i,j} f_{ij}(f_{ij} + f_{ji})\tau_i{}'\tau_j{}']^{1/2}[\sum_{i,j} g_{ij}(g_{ij} + g_{ji})\tau_i{}'\tau_j{}']^{1/2}} \,. \tag{36.138}$$

In particular, when $f \equiv g$, Eq. (36.138) leads to and expression for the *autocorrelation function*:

$$\rho(f, f, t) = \frac{\sum_{i,j} f_{ij}(f_{ij} + f_{ji})\tau_i{}'\tau_j{}' \exp[-t(\tau_i{}'^{-1} + \tau_j{}'^{-1})]}{\sum_{i,j} f_{ij}(f_{ij} + f_{ji})\tau_i{}'\tau_j{}'} \,. \tag{36.139}$$

We can find correlation functions for a number of quantities of interest by direct substitution in Eq. (36.138) or (36.139). For the autocorrelation function of the squared end-to end distance $R^2$, we have $f \equiv R^2 = (R_{n-1} - R_0)^2$, and

$$f_{ij} = c_i c_j \tag{36.140}$$

with

$$\begin{aligned} c_i &= (8/n)^{1/2}\cos(\pi i/2n) && \text{for odd } i \\ &= 0 && \text{for even } i \end{aligned} \tag{36.141}$$

Therefore, we obtain

$$\rho(R^2, R^2, t) = \phi^2(t/\tau_1{}') \,, \tag{36.142}$$

where

$$\phi(x) = \frac{2}{n(n-2)} \sum_{\text{odd } j} \cot^2(\pi j/2n) \exp(-x\tau_1{}'/\tau_j{}') \tag{36.143}$$

with $\phi(0) = 1$ and $\phi(\infty) = 0$. For large $n$, Eq. (36.143) becomes

$$\phi(x) = (8/n^2) \sum_{\text{odd } j} j^{-2} \exp(-j^2 x) \,. \tag{36.144}$$

For example, the relaxation of the mean-square end-to-end distance may be expressed in terms of $\rho(R^2, R^2, t)$ as[146]

$$\langle R^2(t) \rangle - \langle R^2 \rangle_{\mathrm{e}} = (na)^2 \rho(R^2, R^2, t) - \langle R^2 \rangle_{\mathrm{e}} \rho^{1/2}(R^2, R^2, t) \,, \quad (36.145)$$

where the initial state corresponds to the full extension of the chain, $\langle R^2 \rangle_0 = (na)^2$.

Verdier and Stockmayer[146, 147] have investigated the relaxation behavior of the end-to-end distance by simulating the motion of lattice-model chains on a high-speed digital computer. For simplicity they have used simple cubic lattice chains together with the following set of rules for moving the chain, in a random way, from one configuration to another. Select a bead at random along the chain. If it is not an end bead, calculate a new position $\mathbf{R}_j{}'$ for it as

$$\mathbf{R}_j{}' = \mathbf{R}_{j-1} + \mathbf{R}_{j+1} - \mathbf{R}_j \,. \quad (36.146)$$

If it is an end bead, pick its new position at random from the four possibilities satisfying

$$(\mathbf{R}'_{\mathrm{end}} - \mathbf{R}_{\mathrm{next}}) \cdot (\mathbf{R}_{\mathrm{end}} - \mathbf{R}_{\mathrm{next}}) = 0 \,. \quad (36.147)$$

These rules may also be stated as follows. If beads $j-1$, $j$, and $j+1$ lie in a straight line, there can be no movement of the $j$th bead. If the beads lie at three corners of a square, the $j$th bead moves across the diagonal of the square to the opposite corner. For the chain without excluded volume, there is the possibility that $(\mathbf{R}_j - \mathbf{R}_{j-1}) + (\mathbf{R}_{j+1} - \mathbf{R}_j) = 0$. Then the $j$th bead moves to the opposite position beyond the point $\mathbf{R}_{j+1}(\mathbf{R}_{j-1})$, so that beads $j$, $j+1(j-1)$, and $j'$ lie in a straight line. An end bead moves across the diagonal of a square in such a way that the bond connecting it with the next-to-end bead moves through a right angle. Lattice chains moving according to these rules correspond to Rouse chains without hydrodynamic interaction. We refer to the process of picking a bead at random and computing and testing a new position for it as a bead cycle whether or not the process results in actually moving the bead. We assume that a bead cycle in the simulation model corresponds to a fixed increment of time in the real world.

The autocorrelation functions $\rho$ of $R^2$ obtained for the lattice chains without excluded volume are plotted in Fig. VI.18 against log $t$. The curves represent the values calculated from Eq. (36.142) with (36.143) for the Rouse model, values of $\tau_1{}'$ at each $n$ having been chosen to force the Rouse-model and the lattice-model correlation functions to agree at $\rho = 0.3$. Similar results are shown in Fig. VI.19 for the lattice chains with excluded volume. From the figure, it is seen that the relaxation behavior of the lattice chains without excluded volume is remarkably similar to that of the Rouse chains even for $n = 8$, the marked departures from the Rouse-model behavior being due to the excluded-volume effect. In this connection, Iwata and Kurata[148] have

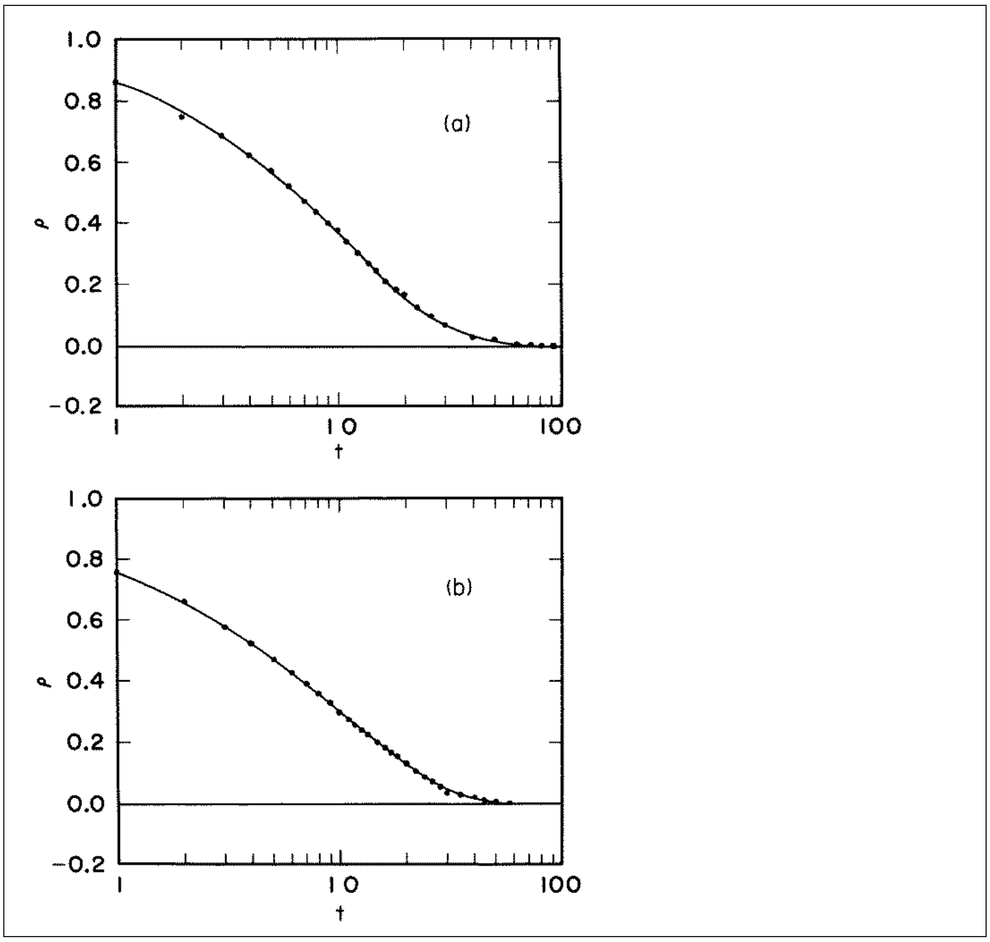

**Fig. VI.18.** Autocorrelation functions of $R^2$ for chains without excluded volume.[147] Points: Monte Carlo data on simple cubic lattice chains. Curves: the Rouse theory. (a) $n = 8$. (b) $n = 64$.

developed an analytical theory for the Brownian motion of a simple cubic lattice chain, and derived a Fokker–Planck equation of the same form as Eq. (36.133). Orwoll and Stockmayer[149] have also developed a similar theory for the exact random-flight model with the bond probability given by Eq. (5.3), and demonstrated that the long relaxation times of the model are identical with those of the Rouse model. These results provide a theoretical interpretation of the lattice chain dynamics data obtained by Verdier.

Further, Orwoll and Stockmayer have investigated a one-dimensional chain with bond correlations. The results show that this model also conforms to a Rouse chain, as far as the slow relaxations are concerned, the ratio $\tau_j{}'/\tau_1{}'$ being equal to $j^{-2}$ for $j \ll n$ as in the Rouse model, but that for higher modes, the ratio $\tau_j{}'/\tau_1{}'$ becomes sensitive to the

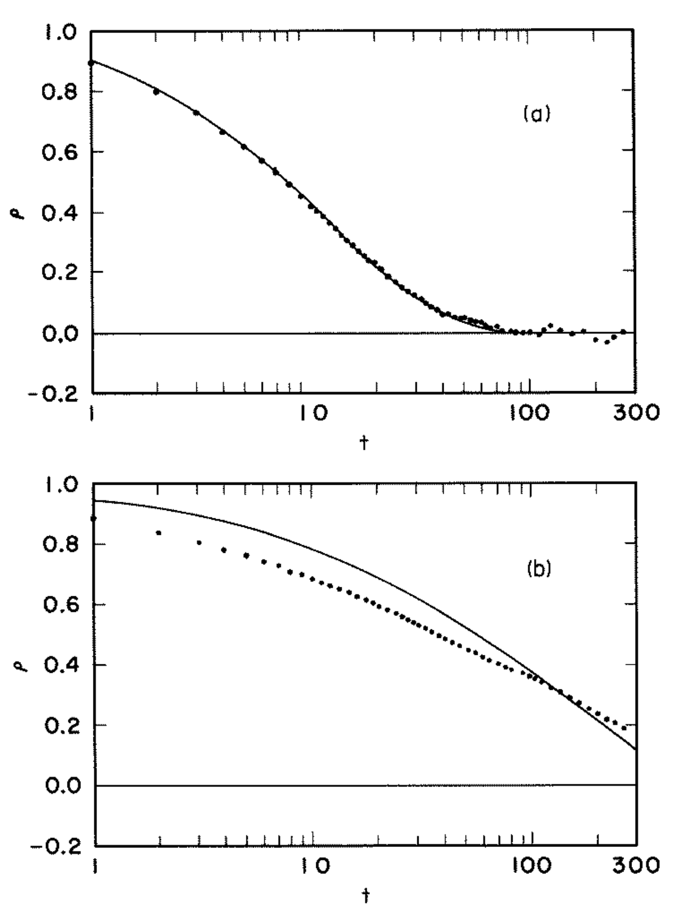

**Fig. VI.19.** Autocorrelation functions of $R^2$ for chains with excluded volume.[147] All symbols have the same significance as those in Fig. VI.18.

bond correlations. The relaxation spectrum is broadened as the energetic preference for extended configurations is increased. Thus, the effect of such bond correlations, or local stiffness, counteracts the effect of hydrodynamic interactions in the spring and bead model.[150] On the contrary, the relaxation spectrum of the one-dimensional chain is narrowed when compact chain configurations are favored. In this connection we note that the introduction of internal viscosity into the spring and bead model produces a narrowing of the spectrum.[151]

## Appendix VI A. The Equation of Motion for Viscous Fluids

Let $\mathbf{v}$ be the velocity of a fluid at the point $(x, y, z)$ or $(x_1, x_2, x_3)$ at time $t$, and $\mathbf{X}$ be the external force exerted on the fluid per unit volume at the same point at the same time. The equation of motion for the fluid may then be written in the form,

$$\bar{\rho}\frac{D\mathbf{v}}{Dt} = \mathbf{X} + \nabla \cdot \boldsymbol{\sigma} \,, \tag{VI A.1}$$

where $\bar{\rho}$ is the mass density of the fluid, $\boldsymbol{\sigma}$ is the stress tensor, and $D/Dt$ denotes a differentiation following the motion of the fluid and is given by

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla) \,. \tag{VI A.2}$$

The stress tensor is given by

$$\begin{aligned} \sigma_{ij} &= \eta \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) && \text{for } i \neq j \\ &= 2\eta \frac{\partial v_i}{\partial x_i} - p - \tfrac{2}{3}\eta \nabla \cdot \mathbf{v} && \text{for } i = j \,, \end{aligned} \tag{VI A.3}$$

and may be simply written in the form,

$$\boldsymbol{\sigma} = 2\eta(\nabla \mathbf{v})^s - (p + \tfrac{2}{3}\eta \nabla \cdot \mathbf{v})\mathbf{I} \,, \tag{VI A.4}$$

where the superscript $s$ indicates the symmetric part of the tensor, $p$ is the pressure, and $\eta$ is the viscosity coefficient of the fluid. Substitution of Eq. (VI A.4) into Eq. (VI A.1) leads to

$$\bar{\rho}\left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v}\right] = \mathbf{X} - \nabla p + \tfrac{1}{3}\eta \nabla(\nabla \cdot \mathbf{v}) + \eta \nabla^2 \mathbf{v} \,. \tag{VI A.5}$$

This is the *Navier-Stokes equation.* For incompressible fluids,

$$\nabla \cdot \mathbf{v} = 0 \,, \tag{VI A.6}$$

and therefore Eq. (IV A.3) or (IV A.4) reduces to Eq. (30.11) and Eq. (IV A.5) becomes

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v} = \frac{1}{\bar{\rho}}\mathbf{X} - \frac{1}{\bar{\rho}}\nabla p + \frac{\eta}{\bar{\rho}}\nabla^2 \mathbf{v} \,. \tag{VI A.7}$$

We note that for steady flow $\partial \mathbf{v}/\partial t = 0$.

Equation (IV A.7) is a nonlinear differential equation, and it is difficult to find its solution. Thus we neglect the inertia term $\bar{\rho}(\mathbf{v} \cdot \nabla)\mathbf{v}$ compared to the viscosity term $\eta \nabla^2 \mathbf{v}$. In general, this approximation, called the *Stokes approximation*, is valid if the Reynolds number is small. Then Eq. (IV A.7) becomes

$$\frac{\partial \mathbf{v}}{\partial t} = \frac{1}{\bar{\rho}}\mathbf{X} - \frac{1}{\bar{\rho}}\nabla p + \frac{\eta}{\bar{\rho}}\nabla^2 \mathbf{v} \,. \tag{VI A.8}$$

This is called the *Stokes equation* for incompressible fluids. A higher approximation was studied by Oseen. He considered the case in which the velocity field is given by $\mathbf{v} = (-v^0 + v_1{}', v_2{}', v_3{}')$, where $v^0$ is a positive constant and $\mathbf{v}'$ is small and vanishes at infinity, and retained the term $-v^0 \partial \mathbf{v}'/\partial x_1$ in $(\mathbf{v} \cdot \nabla)\mathbf{v}$. This is called the *Oseen approximation* for a uniform flow. Most cases, but not all, can be treated in the Stokes approximation.

## Appendix VI B. The Oseen Hydrodynamic Interaction Tensor

We consider the problem of finding the fundamental solution of the Stokes equation for incompressible fluids in steady flow,

$$\eta\nabla^2\mathbf{v} - \nabla p + \mathbf{X} = 0 \tag{VI B.1}$$

with

$$\nabla\cdot\mathbf{v} = 0\,. \tag{VI B.2}$$

We follow the procedure of Oseen.[10]

We assume that in a domain $V$ there exist the solution $(\mathbf{v}, p)$ of Eq. (IV B.1) with (IV B.2) and the solution $(\mathbf{v}', p')$ of Eq. (IV B.1) with (IV B.2) and $\mathbf{X} = 0$, and that in the same domain, $\mathbf{v}$ and $\mathbf{v}'$ are single-valued, continuous, and twice differentiable, and $p$ and $p'$ are single-valued, continuous, and differentiable. We then have

$$\int_V [\mathbf{v}'\cdot(\eta\nabla^2\mathbf{v} - \nabla p + \mathbf{X}) - \mathbf{v}\cdot(\eta\nabla^2\mathbf{v}' - \nabla p')]dV = 0\,. \tag{VI B.3}$$

By the use of Green's formula we transform the volume integral to a surface integral as follows:

$$\sum_{i=1}^{3}\int_S\left[{v_i}'\left(\eta\frac{dv_i}{d\nu} - p\nu_i\right) - v_i\left(\eta\frac{d{v_i}'}{d\nu} - p'\nu_i\right)\right]dS + \int_V \mathbf{v}'\cdot\mathbf{X}dV = 0\,, \tag{VI B.4}$$

where $\mathbf{v}$ is the unit vector normal to the surface $S$, the domain $V$ being taken as the negative side of that surface. In order to express three components of $\mathbf{v}$ on the surface $S$, we need three pairs of solutions $(\mathbf{v}', p')$. These nine components of $\mathbf{v}'$ may be chosen so as to depend only on the distance $r$ between two points $P = (x_1, x_2, x_3)$ and $P^0 = ({x_1}^0, {x_2}^0, {x_3}^0)$ and not to depend on the choice of a coordinate system, and may therefore be considered nine components of a tensor invariant to coordinate transformation.

Thus we introduce a tensor $\mathbf{t}$ defined by

$$\mathbf{t} = \mathbf{I}\nabla^2\Phi(r) - \nabla\nabla\Phi(r) \tag{VI B.5}$$

with

$$r^2 = \sum_{i=1}^{3}(x_i - {x_i}^0)^2\,, \tag{VI B.6}$$

where $\Phi$ is scalar function of $r$ and $\nabla$ is the differential operator with respect to $x_1, x_2$, and $x_3$. If $t_{ij}$ are the components of $\mathbf{t}$, the vectors $\mathbf{t}_j = (t_{1j}, t_{2j}, t_{3j})$ satisfy the equation,

$$\nabla\cdot\mathbf{t}_j = 0\,. \tag{VI B.7}$$

If we assume that

$$\nabla^2(\nabla^2\Phi) = 0\,, \tag{VI B.8}$$

and put

$$-\eta\frac{\partial}{\partial x_j}\nabla^2\Phi = p_j\,, \tag{VI B.9}$$

we then have

$$\eta\nabla^2\mathbf{t}_j - \nabla p_j = 0\,. \tag{VI B.10}$$

Equations (VI B.7) and (VI B.10) imply that the $\mathbf{t}_j$ and $p_j$ $(j = 1, 2, 3)$ determined by Eqs. (VI B.5), (VI B.8), and (VI B.9) are three solutions of the Stokes equation (VI B.1) with $X = 0$. Equation (VI B.8) may be rewritten as $d^4(r\Phi)/dr^4 = 0$, whose general solution is of the form $\Phi = ar^2 + br + c + dr^{-1}$. If we put $\Phi = r$, we have $\nabla^2\Phi = 2/r$ and substitution of these relations into Eqs. (VI B.5) and (VI B.9) leads to

$$t_{ij} = \frac{\delta_{ij}}{r} + \frac{(x_i - x_i{}^0)(x_j - x_j{}^0)}{r^3}\,, \tag{VI B.11}$$

$$p_j = -2\eta\frac{\partial}{\partial x_j}\frac{1}{r} = 2\eta\frac{x_j - x_j{}^0}{r^3}\,. \tag{VI B.12}$$

These $t_{ij}$ and $p_j$ $(j = 1, 2, 3)$ are the three desired solutions for $\mathbf{v}'$ and $p'$, respectively.

Now, suppose that $V$ is the domain between the spherical surface with the center at $P^0$ and radius $\varepsilon$ $(\to 0)$ and a large closed surface $S'$ enclosing the sphere. We then have

$$\lim_{\varepsilon\to 0}\sum_i\int_{r=\varepsilon} t_{ij}\left(\eta\frac{dv_i}{d\nu} - p\nu_i\right)dS = 0\,, \tag{VI B.13}$$

$$\begin{aligned}\lim_{\varepsilon\to 0}&\sum_i\int_{r=\varepsilon} v_i\left(\eta\frac{dt_{ij}}{d\nu} - p_j\nu_i\right)dS\\ &= \lim_{\varepsilon\to 0}\eta\int_{r=\varepsilon}\left[v_j + 3\sum_i v_i\frac{(x_i - x_i{}^0)(x_j - x_j{}^0)}{r^2}\right]\frac{dS}{r^2} = 8\pi\eta v_j(P^0)\,.\end{aligned} \tag{VI B.14}$$

We therefore obtain from Eqs. (VI B.4), (VI B.13), and (VI B.14)

$$\begin{aligned}v_j(P^0) = \frac{1}{8\pi\eta}\int_{S'}\sum_i&\left[t_{ij}\left(\eta\frac{dv_i}{d\nu} - p\nu_i\right) - v_i\left(\eta\frac{dt_{ij}}{d\nu} - p_j\nu_i\right)\right]dS\\ &+\frac{1}{8\pi\eta}\int_V\sum_i t_{ij}X_i dV\,.\end{aligned} \tag{VI B.15}$$

When the surface $S'$ goes to infinity the surface integral must vanish, and Eq. (VI B.15) becomes

$$\mathbf{v}(P^0) = \frac{1}{8\pi\eta}\int\mathbf{tX}dV\,, \tag{VI B.16}$$

where the integration extends over the whole space.

In particular, if the external force is exerted only at the origin, i.e.,

$$\mathbf{X} = \mathbf{F}\delta(\mathbf{R}) \tag{VI B.17}$$

with $d\mathbf{R} = dV$, and if the point $P^0$ is at the distance $\mathbf{r}$ from the origin, we have

$$\mathbf{v}(\mathbf{r}) = \mathbf{T}(\mathbf{r})\mathbf{F} \tag{VI B.18}$$

with

$$\mathbf{T} = \frac{\mathbf{t}}{8\pi\eta} = \frac{1}{8\pi\eta r}\left(\mathbf{I} + \frac{\mathbf{rr}}{r^2}\right). \tag{VI B.19}$$

This is Oseen tensor. Note that it has been derived in the Stokes approximation, and not in the Oseen approximation, and that it does not depend on the original velocity field.

## Appendix VI C. The Intrinsic Viscosity and Friction Coefficient of Rigid Sphere Macromolecules

The Einstein equation for the viscosity of solutions of rigid spheres and the Stokes formula for the friction coefficient of rigid spheres are well known. In this appendix we describe some recently clarified aspects of these theories.

Consider a single sphere of radius $\bar{S}$ located at the origin of a coordinate system. The motion of the surrounding fluid with viscosity coefficient $\eta_0$ may be determined by the Stokes equation, which may be rewritten in the form,

$$\nabla \cdot \boldsymbol{\sigma} = 0 \tag{VI C.1}$$

with

$$\boldsymbol{\sigma} = 2\eta_0\mathbf{f} - p\mathbf{I}\,, \tag{VI C.2}$$

$$\nabla \cdot \mathbf{v} = 0\,, \tag{VI C.3}$$

where we have assumed the incompressibility of the fluid and $\mathbf{f}$ denotes the symmetric part of $\nabla\mathbf{v}$.

First we consider the viscosity. Suppose that the unperturbed velocity $\mathbf{v}^0$ in the absence of the sphere is given by $\mathbf{v}^0 = \mathbf{g}^0\mathbf{r}$, where $\mathbf{g}^0$ is a constant tensor, i.e., $\mathbf{g}^0 = \nabla\mathbf{v}^0$, and let $\mathbf{f}^0$ be the symmetric part of $\mathbf{g}^0$. The rotational velocity of the sphere is $\boldsymbol{\Omega}^0\mathbf{r}$, where $\boldsymbol{\Omega}^0$ is the antisymmetric part of $\mathbf{g}^0$. We denote the solutions of Eqs. (VI C.1) to (VI C.3) in the presence of the sphere by $\mathbf{v} = \mathbf{v}^0 + \mathbf{v}'$ and $p = p^0 + p'$, where $p^0$ is the constant unperturbed pressure. With the boundary conditions that the sphere and fluid velocities match at the surface of the sphere, and that $\mathbf{v}'$ vanishes at infinity, we find for the velocity and pressure perturbations[11]

$$\mathbf{v}' = \nabla \times \nabla \times (\mathbf{f}^0 \cdot \nabla\psi)\,, \tag{VI C.4}$$

$$p' = \eta_0\mathbf{f}^0 : \nabla\nabla(\nabla^2\psi) \tag{VI C.5}$$

with

$$\psi = -\tfrac{1}{6}(5\bar{S}^3 r + \bar{S}^5 r^{-1})\,, \tag{VI C.6}$$

that is,

$$v_i{}' = \frac{5}{2}\left(\frac{\bar{S}^5}{r^4} - \frac{\bar{S}^3}{r^2}\right)\sum_j\sum_k f_{jk}{}^0 \nu_i\nu_j\nu_k - \frac{\bar{S}^5}{r^4}\sum_j f_{ij}{}^0\nu_j\,, \tag{VI C.7}$$

$$p' = -5\eta_0\frac{\bar{S}^3}{r^3}\sum_i\sum_j f_{ij}{}^0\nu_i\nu_j\,, \tag{VI C.8}$$

where $\boldsymbol{\nu}$ is a unit vector in the direction of the radius vector $\mathbf{r}$.

Now we consider a solution of volume $V$ containing $N$ spheres. The average stress tensor is given by Eq. (36.6),

$$\langle\boldsymbol{\sigma}\rangle = 2\eta_0\langle\mathbf{f}\rangle + V^{-1}\left\langle\int(\boldsymbol{\sigma} - 2\eta_0\mathbf{f})dV\right\rangle, \tag{VI C.9}$$

where we have suppressed the pressure terms. The integrand in Eq. (VI C.9) is nonvanishing only inside the spheres. When the solution is very dilute the second term on the right-hand side of Eq. (VI C.9), which we denote by $\boldsymbol{\sigma}'$, may be equated to the integral for a single sphere multiplied by $\rho = N/V$. Further, at a point inside the sphere undergoing rigid rotation, the symmetric gradient of velocity vanishes. We therefore have[66]

$$\boldsymbol{\sigma}' = \rho\int_{v_m}\boldsymbol{\sigma}d\mathbf{r}\,, \tag{VI C.10}$$

where $v_m$ is the volume of the sphere. Equation (VI C.1) leads to the identity,

$$\sigma_{ij} = \sum_k\frac{\partial(\sigma_{ik}x_j)}{\partial x_k}\,, \tag{VI C.11}$$

and the integral in Eq. (VI C.10) is therefore converted to the integral over the surface of the sphere,

$$\sigma_{ij}{}' = \rho\int_{r=\bar{S}}\sum_k\sigma_{ik}\nu_k x_j dS\,. \tag{VI C.12}$$

Substitution of Eq. (VI C.2) with (VI C.7) and (VI C.8) into Eq. (VI C.12) leads to

$$\boldsymbol{\sigma}' = 5\eta_0\varphi\mathbf{f}^0 \tag{VI C.13}$$

with $\varphi = v_m\rho$. Since for the solution $\langle\boldsymbol{\sigma}\rangle = 2\eta\langle\mathbf{f}\rangle$ and $\mathbf{f} \simeq \mathbf{f}^0$ at small $\varphi$, we obtain from Eqs. (VI C.9) and (VI C.13)

$$\eta = \eta_0(1 + \tfrac{5}{2}\varphi)\,, \tag{VI C.14}$$

and therefore

$$[\eta] = \frac{10\pi}{3}N_{\mathrm{A}}\frac{\bar{S}^3}{M}\,. \tag{VI C.15}$$

Next we evaluate the friction constant. We write the velocity field around a single sphere fixed at the origin as $\mathbf{v} = \mathbf{u} + \mathbf{v}'$, where $\mathbf{u}$ is a constant unperturbed velocity. With the boundary conditions that $\mathbf{v} = 0$ at $r = \bar{S}$, and that $\mathbf{v}' = 0$ at infinity, the velocity and pressure perturbations are obtain as[11]

$$\mathbf{v}' = \nabla \times \nabla \times (\psi \mathbf{u}) \,, \tag{VI C.16}$$

$$p' = \eta_0 \mathbf{u} \cdot \nabla(\nabla^2 \psi) \tag{VI C.17}$$

with

$$\psi = \tfrac{1}{4}(3\bar{S}r + \bar{S}^3 r^{-1}) \,. \tag{VI C.18}$$

The stress tensor is obtained from Eq. (VI C.2) with (VI C.16) to (VI C.18). Then the frictional force $\mathbf{F}$ exerted by the sphere on the fluid is obtained by integrating $\boldsymbol{\sigma\nu}$ over the surface of the sphere. The result is

$$\mathbf{F} = -6\pi\eta_0 \bar{S}\mathbf{u} \,, \tag{VI C.19}$$

and therefore the friction coefficient $f$ is

$$f = 6\pi\eta_0 \bar{S} \,. \tag{VI C.20}$$

The Stokes formula may be derived more simply by the use of the Oseen velocity perturbation.[8] We approximate $\mathbf{v}'$ by $\mathbf{TF}$, with $\mathbf{T}$ the Oseen tensor, and make the average fluid velocity, $\langle \mathbf{u} + \mathbf{v}' \rangle = \mathbf{u} + \langle \mathbf{v}' \rangle$, vanish at the surface of the sphere. Since $\langle \mathbf{v}' \rangle = \mathbf{F}/6\pi\eta_0\bar{S}$ at $r = \bar{S}$, we recover Eq. (VI C.19).

Bloomfield et al.[152] have used the Kirkwood equation (32.41) to evaluate the friction coefficient of a shell model, i.e., a large number of small spheres distributed in a spherical shell of radius $\bar{S}$, each obeying Stokes' law. They have shown that in the limit of a continuous surface distribution of small spheres the friction coefficient of the shell is given by Eq. (VI C.20), and that Eq. (VI C.20) still holds quite accurately even when a large fraction (about 60%) of the small spheres are removed. This suggests the inadequacy of free-draining models for certain structures of frictional elements.

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Chapter Seven

# Comparison with Experiment

## 37. Introduction

In the preceding chapters we have seen that a theoretical description of the equilibrium and nonequilibrium properties of dilute solutions of flexible-chain polymers requires (except in the theta state) two basic molecular parameters, the effective bond length $a$ and the binary cluster integral $\beta$ for a pair of segments, and that these parameters suffice as long as we do not inquire into the detailed chemical structure of the polymer and solvent molecules. In particular, the molecular dimensions, second virial coefficients, and intrinsic viscosities of linear flexible chains may be expressed in terms of only these two parameters. The primary purpose of this chapter is to make a comparison of the so-called two-parameter theories of these fundamental properties with experiment, with special attention to their dependence on the excluded-volume parameter $z$. As already discussed, a fundamental difficulty then arises from the fact that the parameter $z$ is not directly observable. It is therefore impossible to make an explicit comparison of theory with experiment in the usual sense, and it is necessary to set forth some criteria for this purpose. For this reason a description of this subject has been deferred to the present chapter.

We begin by making some comments on the experimental determination of molecular weights, second virial coefficients, and molecular dimensions, since observed values of these quantities depend markedly on the method of treating experimental data. We also discuss the method of determining unperturbed molecular dimensions from intrinsic viscosity data. Finally, we give a simple analysis of the two basic molecular parameters estimated for several systems.

## 38. Determination of Molecular Weights, Molecular Dimensions, and Second Virial Coefficients

There are several direct methods of determining molecular weights of polymers. Of those, the light-scattering method is most important, since it yields not only molecular weights but also molecular dimensions and second virial coefficients, i.e., the equilibrium properties for which a comparison of theory with experiment is made in later sections. Molecular weights and second virial coefficients may also be determined from osmotic pressure measurements. In this section, we discuss only these two methods.

The basic equations for osmotic pressure and light-scattering measurements are given by Eqs. (18.3), (26.45), and (27.36);

$$\frac{\pi}{c} = RT\left(\frac{1}{M} + A_2c + A_3c^2 + \cdots\right), \tag{38.1}$$

$$\left(\frac{Kc}{R_\theta}\right)_{\theta=0} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots , \tag{38.2}$$

$$\left(\frac{Kc}{R_\theta}\right)_{c=0} = \frac{1}{M} + \frac{16\pi^2}{3(\lambda')^2M}\langle S^2\rangle \sin^2(\theta/2) + \cdots , \tag{38.3}$$

where the symbols have the same meaning as before. As seen from these equations, the determinations of molecular weights, molecular dimensions, and second virial coefficients require extrapolations to infinite dilution from measurements made at finite but low concentrations.

In the conventional extrapolations, $\pi/c$ and $(Kc/R_\theta)_{\theta=0}$ are plotted against $c$ to determine molecular weights and second virial coefficients. These plots exhibit deviations from linearity over the concentration range in which measurements are made, because of the contributions of the third and higher virial coefficients, especially for high-molecular-weight polymers in good solvents. This leads to some ambiguity in estimates of molecular weights and second virial coefficients. In order to avoid this difficulty, the so-called square-root plots are used; that is, $(\pi/c)^{1/2}$ and $(Kc/R_\theta)_{\theta=0}^{1/2}$ are plotted against $c$.[1, 2] These plots are linear in many cases, and are better than the conventional plots. However, we must examine the limitations of application of the square-root plots. In what follows, the discussion is confined to linear flexible chains.

Assuming that the solution is so dilute that the fourth and higher virial coefficients may be neglected, we rewrite Eqs. (38.1) and (38.2) as

$$M\pi/RTc = 1 + v + gv^2 , \tag{38.4}$$

$$(MKc/R_\theta)_{\theta=0} = 1 + 2v + 3gv^2 , \tag{38.5}$$

**TABLE VII.1.** UPPER LIMITS OF MOLECULAR WEIGHT IN THE SQUARE-ROOT PLOTS OF OSMOTIC PRESSURE AND LIGHT-SCATTERING DATA

| | | OS[a] | | LS[b] | |
|---|---|---|---|---|---|
| $z$ | $g$ | $v_m$ | $M_m \times 10^{-5}$ | $v_m$ | $M_m \times 10^{-5}$ |
| 0.115 | 0.108 | 0.5 | 159 | 0.3 | 57.2 |
| 0.267 | 0.185 | 0.5 | 40.7 | 0.4 | 26.0 |
| 0.701 | 0.280 | 0.5 | 9.67 | 0.6 | 13.9 |
| 2.149 | 0.360 | 0.5 | 1.95 | 1.0 | 7.82 |

[a] Osmotic pressure.
[b] Light scattering.

where

$$v = A_2 M c\,, \tag{38.6}$$

$$g = A_3 / {A_2}^2 M\,. \tag{38.7}$$

For convenience, we adopt the values of $g$ evaluated by Stockmayer and Casassa for the Gaussian smoothed-density model and shown in Fig. IV.6 as a function of $\bar{z} = z/\alpha_S^3$. If we use the modified Flory equation for $\alpha_S$ consistent with this model, we find the corresponding values of $z$. The values of $g$ as a function of $z$ thus obtained are given in Table VII.1. For these values of $g$, $(M\pi/RTc)^{1/2}$ and $(MKc/R_\theta)_{\theta=0}^{1/2}$ are plotted against $v$ in Figs. VII.1 and VII.2, respectively. From Eqs. (38.4) and (38.5), $(M\pi/RTc)^{1/2}$ and $(MKc/R_\theta)_{\theta=0}^{1/2}$ are seen to be linear in $v$ for $g = \frac{1}{4}$ and $\frac{1}{3}$, respectively. These cases are also shown in the figures. The plots deviate from linearity except at small $v$ unless $g$ takes the particular values cited; the plots are approximately linear for values of $v$ smaller than those indicated by $v_m$ in Table VII.1. In the conventional plots, of course, deviations from linearity occur at values of $v$ much smaller than $v_m$. Now, we can estimate the upper limits of molecular weight, $M_m$, such that for $M < M_m$ the square-root plots are linear over a given range of concentration. If it is required that the square-root plots be linear for $c < 0.5 \times 10^{-2}$ $(g/cc)$, the corresponding values of $M_m$ may be calculated from

$$200 v_m = 4\pi^{3/2} N_{\mathrm{A}} \left( \frac{\langle S^2 \rangle_0}{M} \right)^{3/2} {\alpha_S}^3 \Psi {M_m}^{1/2}\,, \tag{38.8}$$

where we have used Eqs. (38.6) and (21.17). In Table VII.1 are given the values of $M_m$ thus obtained as a function of $z$, adopting the modified Flory equation for $\alpha_S$ and the modified Flory–Krigbaum–Orofino equation (20.44) with $\langle S^2 \rangle_0 / M = 7.6 \times 10^{-18}$ (observed value for polystyrene).[2] Now, $M_m$ may be considered to ba a function of the

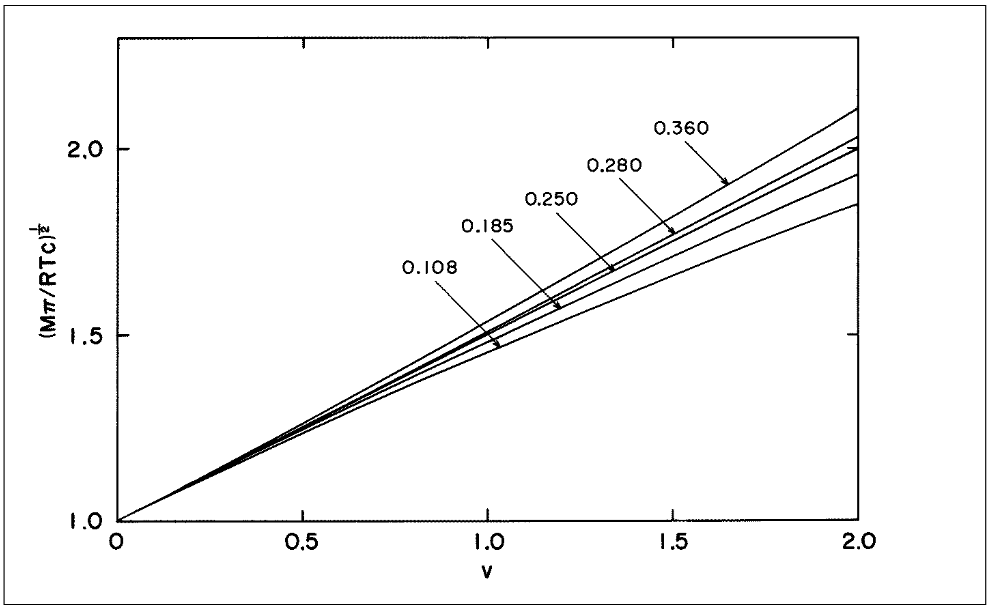

**Fig. VII.1.** $(M\pi/RTc)^{1/2}$ plotted against $v = A_2Mc$ for the indicated values of $g = A_3/A_2^2M$. The plot is linear for $g = 0.250$.

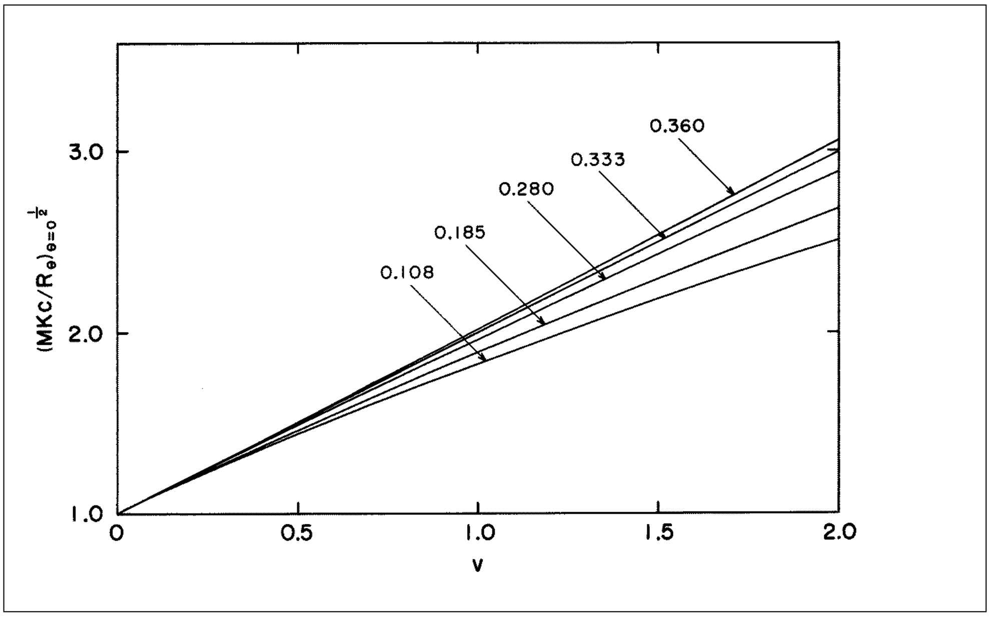

**Fig. VII.2.** $(MKc/R_\theta)_{\theta=0}^{1/2}$ plotted against $v = A_2Mc$ for the indicated values of $g = A_3/A_2^2M$. The plot is linear for $g = 0.333$.

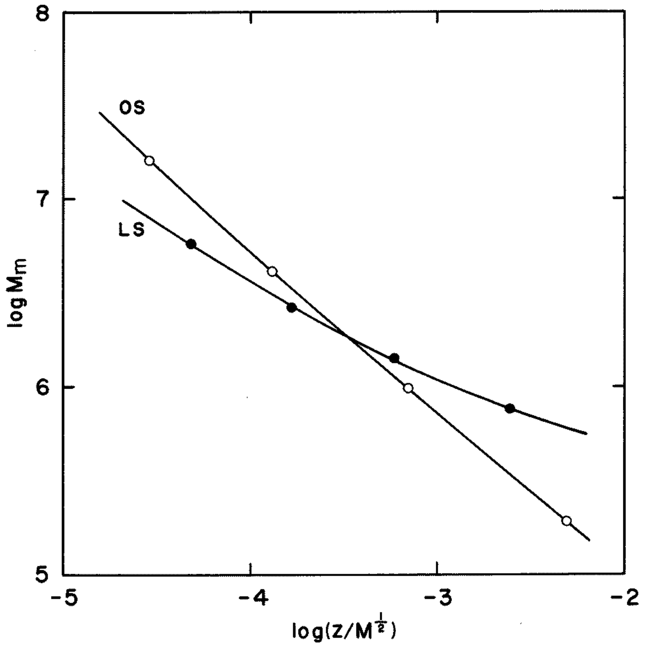

**Fig. VII.3.** Double logarithmic plots of $M_m$ against $z/M^{1/2}$. OS: osmotic pressure. LS: light scattering.

ratio $z/M^{1/2}$, which is independent of molecular weight and proportional to the binary cluster integral, or the solvent power, and which is to be equated to $z/M_m^{1/2}$. That is, $M_m$ represents the upper limit of molecular weight for a given value of solvent power under the condition stated above. Double logarithmic plots of $M_m$ against $z/M^{1/2}$ are shown in Fig. VII.3, using the values given in Table VII.1. It is seen that $M_m$ decreases with increasing solvent power, as expected, and that for poor-solvent systems both osmotic pressure and light-scattering data may be treated using the square-root plots for almost all molecular weights experimentally accessible. However, the square-root plots as well as the conventional plots fail to yield accurate estimates of molecular weights and second virial coefficients. In the case of polystyrene in toluene, for example, $z/M^{1/2}$ is about $2.5 \times 10^{-3}$, as shown later, and the $M_m$ are about $3 \times 10^5$ and $8 \times 10^5$ for osmotic pressure and light scattering, respectively. These values, although depending on theories used for $g$, $\alpha_S$, and $\Psi$, suggest the limitations of application of the square-root plots.

Next we consider the determination of molecular dimensions. The conventional plot of $(Kc/R_\theta)_{c=0}$ against $\sin^2(\theta/2)$ is not linear in most cases. Now, the quantity $(MKc/R_\theta)_{c=0}$ is equal to the inverse of the intramolecular interference factor $P_1(\theta)$. For unperturbed linear chains,

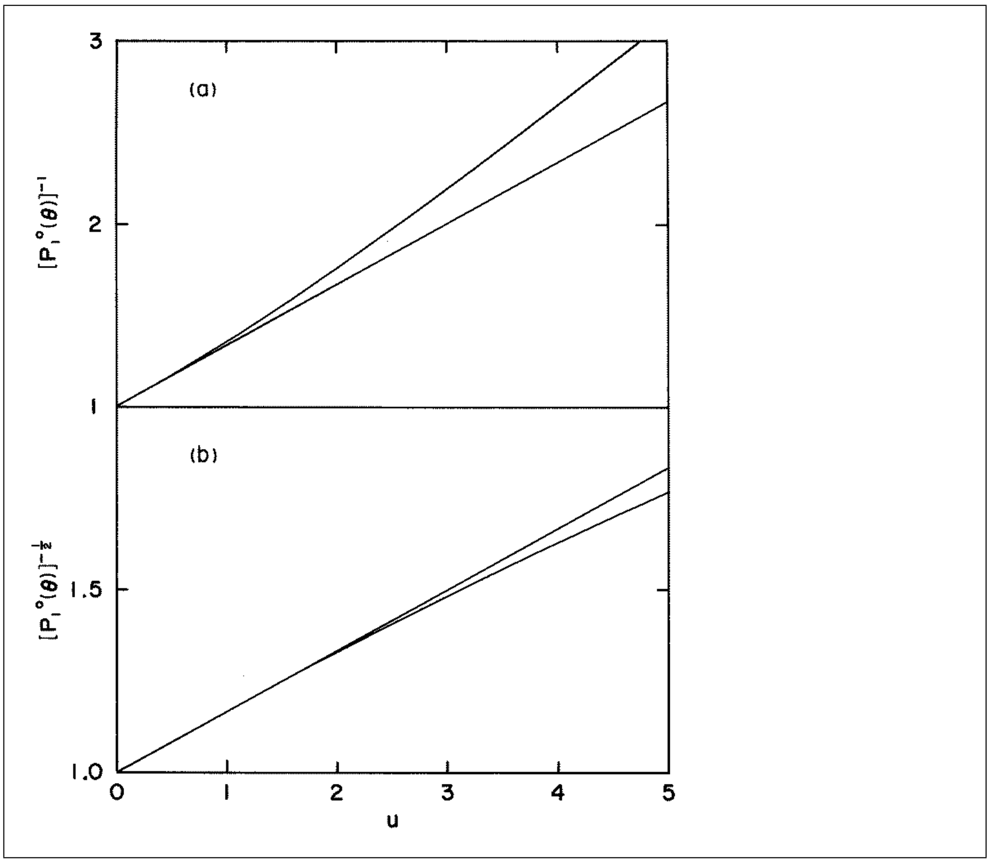

**Fig. VII.4.** The intramolecular (scattering) interference factor $P_1{}^0(\theta)$ as a function of $u$ for linear unperturbed chains. (a) The conventional plot. (b) The square-root plot.

$P_1(\theta)$ is given by Eq. (27.34),

$$P_1{}^0(\theta) = \frac{2}{u^2}(e^{-u} - 1 + u) \tag{38.9}$$

with

$$u = \frac{16\pi^2}{(\lambda')^2}\langle S^2\rangle_0 \sin^2(\theta/2)\,. \tag{38.10}$$

The inverse of the function $P_1{}^0(\theta)$ is plotted against $u$ in Fig. VII.4(a), while Fig. VII.4(b) shows $[P_1{}^0(\theta)]^{-1/2}$ plotted against $u$. Clearly, this indicates that linear extrapolation on the plot of $(Kc/R_\theta)^{1/2}_{c=0}$ against $\sin^2(\theta/2)$ yields a much more reliable estimate of $\langle S^2\rangle_0$ than the conventional plot.[2] Smith and Carpenter[3] have shown experimentally that the function $P_1(\theta)$ given by Eq. (38.9) is approximately valid even for perturbed chains if we redefine $u$ by Eq. (38.10) with $\langle S^2\rangle$ in place of $\langle S^2\rangle_0$. Therefore, the square-root plot for the determination of molecular dimensions may be applied to good-solvent systems. As seen from Fig. VII.4(b), however, this plot also becomes unreliable for high-molecular-weight polymers in good solvents.

In later sections, light-scattering data, which are to be used for a test of the two-parameter theory, will be treated by means of the square-root plot. We must then keep in mind the limitations discussed above.

## 39. Determination of Unperturbed Molecular Dimensions

The unperturbed mean-square radius $\langle S^2 \rangle_0$ is one of the two basic molecular parameters, which represents short-range interferences in the chain, and from which valuable information concerning the chain structure is obtained. In addition, in order to estimate the expansion factor, as defined by the ratio of the mean-square radius to its unperturbed value, we must determine the latter. Thus, it is very often necessary to estimate unperturbed molecular dimensions. This can, of course, be done from light-scattering measurements at theta temperatures. In this section we describe several indirect or extrapolation methods of estimating unperturbed molecular dimensions.

First we discuss the methods using intrinsic viscosity-molecular weight data. The intrinsic viscosity may be expressed in the form,

$$[\eta] = [\eta]_\theta {\alpha_\eta}^3 \,, \tag{39.1}$$

where the intrinsic viscosity $[\eta]_\theta$ at the theta temperature, or in the unperturbed state, is proportional to the square-root of the molecular weight for flexible chains with ordinary molecular weights and without hydrodynamic interactions; that is,

$$[\eta]_\theta = KM^{1/2} \,, \tag{39.2}$$

so that

$${\alpha_\eta}^3 = [\eta]/KM^{1/2} \tag{39.3}$$

with

$$K = \Phi_0 A^3 \,, \tag{39.4}$$

$$A^2 = \langle R^2 \rangle_0 / M \,. \tag{39.5}$$

Equation (39.2) with (39.4) and (39.5) suggests that measurements of intrinsic viscosities at theta temperatures for various molecular weights yield values of $K$ (see Fig. VI.6), from which the parameter $A$ can be estimated when the value of the viscosity constant $\Phi_0$ is given. Various theoretical values of $\Phi_0$ have been obtained, as summarized in Table VI.3. On the other hand, the best experimental value of $\Phi_0$ that was established from viscosity and light-scattering measurements for a number of systems seems to be $2.5 \times 10^{23}$ (cgs). For the present purpose, we adopt this value for $\Phi_0$.

Now, under non-theta conditions, the radius expansion factor $\alpha_\eta$ for the viscosity is an increasing function of the excluded-volume parameter $z$. For convenience, we rewrite this paramere in the form,

$$z = (3/2\pi)^{3/2}(B/A^3)M^{1/2}\,, \tag{39.6}$$

where

$$B = \beta/{M_s}^2 \tag{39.7}$$

with $M_s$ the molecular weight of the segment. The factor $\alpha_\eta$ must become unity as the molecular weight is decreased to zero, since $\alpha_\eta = 1$ at $z = 0$. In other words, the excluded-volume effect is negligibly small for short chains. This fact suggests that values of $[\eta]_\theta$ or $K$ may be obtained by extrapolation to zero molecular weight from intrinsic viscosity data obtained in an ordinary range of molecular weight in good or non-theta solvents. There have been proposed several graphical methods for extrapolation, all based on approximate closed expressions for the expansion factor.

The foremost of these investigations is a viscosity plot attempted by Flory, Fox, and Schaefgen.[4] If we assume that $\alpha_\eta = \alpha_S$, and substitute Eq. (39.3) into the original Flory equation for $\alpha_S$, we obtain

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + 0.858K^{2/3}\Phi_0 BM/[\eta]\,. \quad \text{(FFS)} \tag{39.8}$$

Thus the constant $K$ could be estimated from the ordinate intercept of a plot of $[\eta]^{2/3}/M^{1/3}$ against $M/[\eta]$, the slope giving the parameter $B$. This is the so-called Flory–Fox–Schaefgen plot. Figure VII.5 shows the FFS plots for polystyrene in various solvents, $[\eta]$ being expressed in deciliters per gram. The filled circles represent the data in benzene at 30°C,[5] the squares represent the data in toluene at 25°C,[6] the semifilled circles represent the data in methyl ethyl ketone at 22°C,[7] and the open circles represent the data in cyclohexane at $\Theta = 34.5$°C.[5] The remarkable feature of the FFS plot is that for very good solvent systems linear extrapolation from large values of $M$ yields a negative intercept. This demonstrates the inadequacy of the Flory equation for $\alpha_S$ $(= \alpha_R)$ or of the assumption $\alpha_\eta = \alpha_S$. If we assume that values of $K$ or unperturbed dimensions are insensitive to the nature of the solvent, extrapolations in the region of small $M$ must be made along the broken curves in the figure. Such extrapolations are difficult, and the FFS plot was discarded by Flory himself.

Kurata and Stockmayer[8] attributed the defects of the FFS plot to the inadequacy of the Flory equation which is of the fifth-power type for $\alpha$. They proposed a new viscosity plot based on the Kurata–Stockmayer–Roig equation, which is of the third-power type for $\alpha_R$. Kurata and Stockmayer have assumed that $\alpha_\eta$ has the same functional form as the KSR equation for $\alpha_R$, and readjusted the numerical coefficient involved in it so that at small $z$ the assumed equation for $\alpha_\eta$ agrees with an empirical equation

$${\alpha_\eta}^3 = \alpha_R^{5/2}\,, \tag{39.9}$$

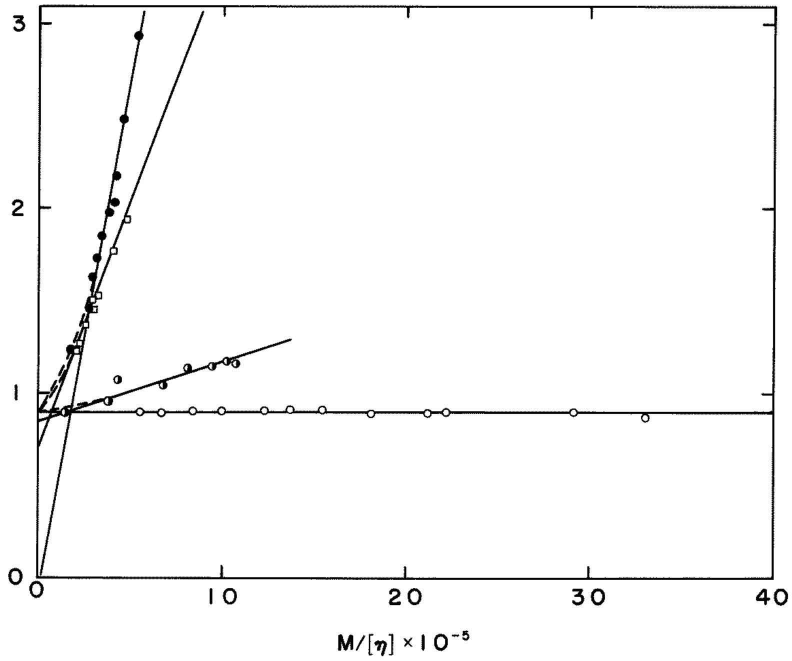

**Fig. VII.5.** The Flory–Fox–Schaefgen plots for polystyrene in benzene at 30 °C (filled circles),[5] toluene at 25 °C (squares),[6] methyl ethyl ketone at 22 °C (semi-filled circles),[7] and cyclohexane at $\Theta = 34.5$ °C (open circles).[5]

which is an analog of Eq. (35.15). Substituting Eq. (39.3), we then find

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + 0.363\Phi_0 B g(\alpha_\eta) M^{2/3}/[\eta]^{1/3} \quad \text{(KS)} \qquad (39.10)$$

with

$$g(\alpha_\eta) = 8{\alpha_\eta}^3/(3{\alpha_\eta}^2 + 1)^{3/2}\,. \qquad (39.11)$$

In the KS plot we first plot $[\eta]^{2/3}/M^{1/3}$ against $M^{2/3}/[\eta]^{1/3}$ to find a first-order approximate value of $K$, and then replot $[\eta]^{2/3}/M^{1/3}$ against $g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}$, where $g(\alpha_\eta)$ is calculated from Eqs. (39.3) and (39.11) with the first-order value of $K$. Examples of this plot are shown in Fig. VII.6, the data being the same as those in Fig. VII.5. It is observed that the KS plot leads to a much more reliable estimate of $K$ than the FFS plot. Kurata and Stockmayer[8] have analyzed a wide variety of polymer–solvent systems using the KS plot, and shown that the plots are always linear at least for vinyl polymers. However, some of the viscosity data accumulated to date deviate from linearity, especially for high molecular weights in good solvents, e.g., for polystyrene in benzene and toluene, as shown in Fig. VII.6.

As already mentioned, the Kurata–Stockmayer–Roig equation is numerically very close to the Fixman equation of the third-power type for

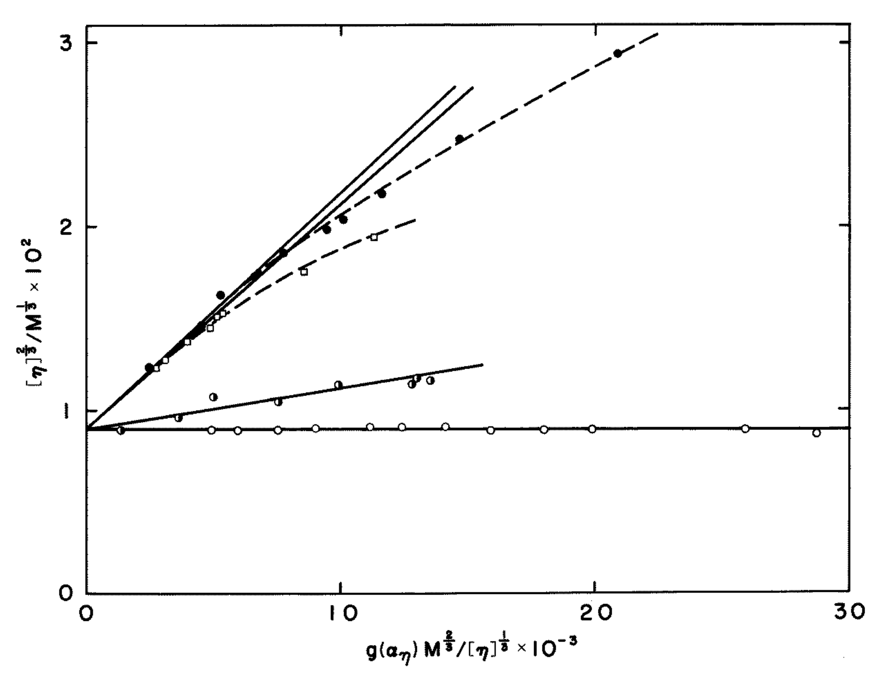

**Fig. VII.6.** The Kurata–Stockmayer plots for polystyrene in various solvents. The symbols have the same significance as those in Fig. VII.5.

$\alpha_R$. Based on the latter, Stockmayer and Fixman[9] have proposed a simpler equation,

$$[\eta]/M^{1/2} = K + 0.51\Phi_0 B M^{1/2}\,. \quad \text{(SF)} \qquad (39.12)$$

Equation (39.12) is obtained by substitution of Eq. (39.3) into Eq. (35.13) with omission of higher terms. According to Eq. (39.12), we may simply plot $[\eta]/M^{1/2}$ against $M^{1/2}$ which is clearly less laborious than making the KS plot. Figure VII.7 shows the SF plots for the same systems as before. The SF plot is also seen to yield accurate estimates of $K$. For good-solvent systems, however, the plots deviate from linearity in the region of large $M$, as in the case of the KS plot.

Thus, both KS and SF plots lead to overestimates of $K$ when for good-solvent systems only high-molecular-weight data are available. In order to avoid the possible errors in extrapolation under these circumstances, various devices have been proposed.[5, 10–14] For example, Inagaki[5] has proposed the equation,

$$[\eta]^{4/5}/M^{2/5} = 0.786K^{4/5} + 0.454K^{2/15}\Phi_0^{\;2/3}B^{2/3}M^{1/3}\,. \quad \text{(IP)} \quad (39.13)$$

This equation is obtained by substitution of Eqs. (39.3) and (39.9) into the asymptote of the Ptitsyn equation for $\alpha_R$. In this case we

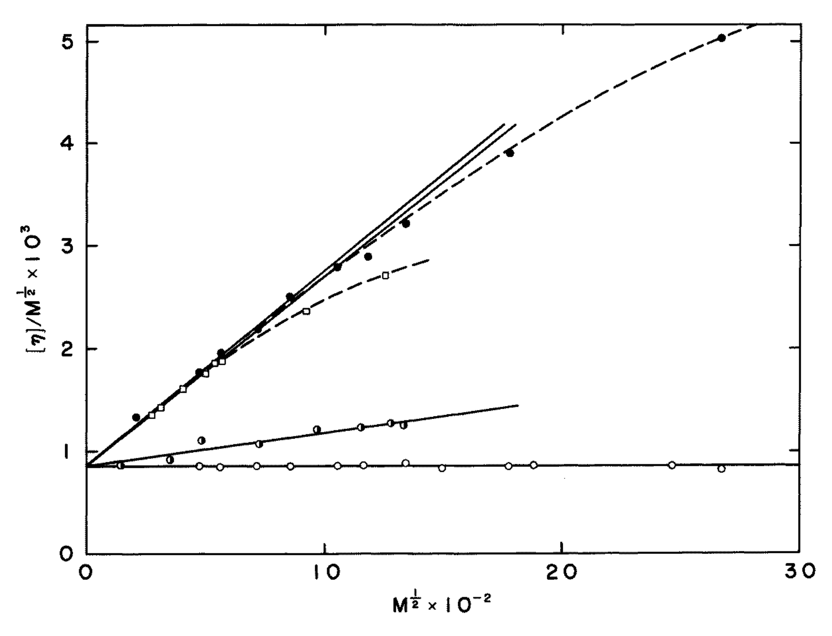

**Fig. VII.7.** The Stockmayer–Fixman plots for polystyrene in various solvents. The symbols have the same significance as those in Fig. VII.5.

plot $[\eta]^{4/5}/M^{2/5}$ against $M^{1/3}$. In Fig. VII.8 are shown the IP plots for the same systems as before. It is important to note that linear extrapolation to zero molecular weight from large values of $M$ gives the intercept $0.786K^{4/5}$, and not $K^{4/5}$, and that the IP plot applies only to high-molecular-weight polymers in good solvents. In Fig. VII.8, the broken curves indicate extrapolations to $[\eta]^{4/5}/M^{2/5} = K^{4/5}$ following actual experimental points in the region of small $M$ if they are available.

In Table VII.2 are summarized the values of the parameters $A$ and $B$ estimated from the straight lines in Figs. VII.6 to VII.8. The KS, SF, and IP plots are seen to give the same values of $A$ but different values of $B$ for a given system. Furthermore, we see that the unperturbed

**TABLE VII.2.** VALUES OF $A$ AND $B$ ESTIMATED FROM VISCOSITY PLOTS FOR POLYSTYRENE

| | | $B \times 10^{27}$ (cm$^3$) | | |
|---|---|---|---|---|
| PLOTS | $A \times 10^8$(cm) | BENZENE (30°C) | TOLUENE(25°C) | METHYL ETHYL KETONE(22°C) |
| KS | 0.698 | 1.41 | 1.35 | 0.248 |
| SF | 0.698 | 1.48 | 1.43 | 0.251 |
| IP | 0.698 | 2.55 | 2.11 | 0.387 |

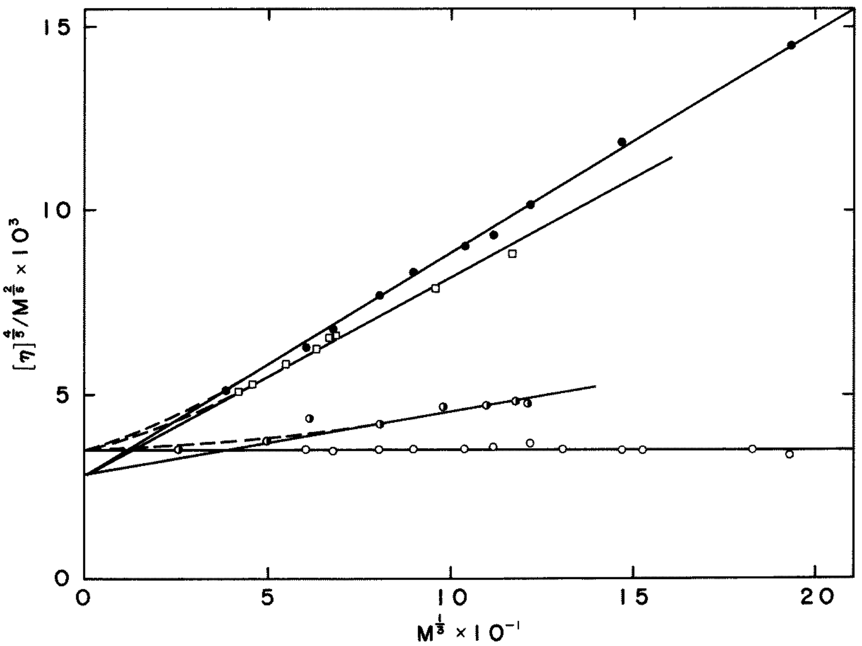

**Fig. VII.8.** The Inagaki–Ptitsyn plots for polystyrene in various solvents. The symbols have the same significance as those in Fig. VII.5.

dimension is, in fact, almost independent of solvent for the systems under consideration. We may therefore use properly any of these viscosity plots to estimate unperturbed dimensions. However, it is not satisfactory to apply these procedures to the estimation of the parameter $B$. Clearly, estimates of $B$ depend appreciably on the functional form of $\alpha$ to be used, and also on the assumed relation between $\alpha_\eta$ and $\alpha$. Therefore, a more rigorous experimental test of the theories of $\alpha_S$ and $\alpha_\eta$ is needed before we can establish a basic equation for viscosity plots to be used for the estimation of $B$.

Next we discuss extrapolation methods using data for second virial coefficients.Krigbaum[15] has proposed a semiempirical equation relating the second virial coefficient to the intrinsic viscosity,

$$[\eta] = [\eta]_\theta + 5.0 \times 10^{-3} A_2 M\,, \tag{39.14}$$

$[\eta]$ being expressed in deciliters per gram. Values of $[\eta]_\theta$ and hence $K$ can be calculated from this equation using experimental values of $M$, $[\eta]$, and $A_2$. If we neglect the dependence of $A_2$ on $M$, Eq. (39.14) is seen to be equivalent to Eq. (39.12) for the SF plot. Kurata et al.[16] have derived an equation for $A_2$-plots from the asymptote of Eq. (21.17) for $A_2$ with K function $h_0(\bar{z})$ given by Eq. (20.77) (with $\bar{z}$ in place of

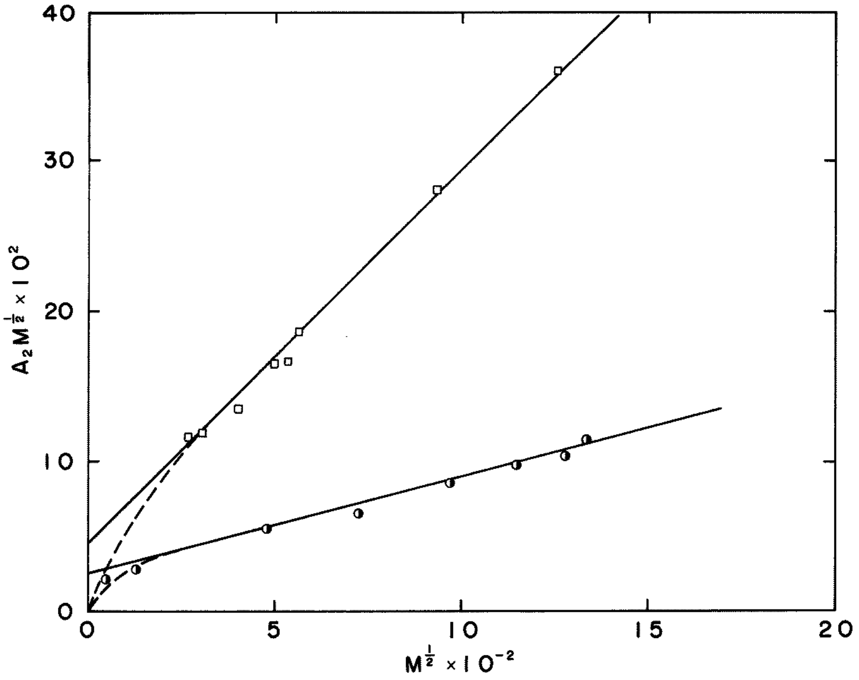

**Fig. VII.9.** The Kurata plots of the second virial coefficient for polystyrene in toluene (squares)[6] and methyl ethyl ketone (semifilled circles).[7]

$z$) and the third-power type equation for $\alpha$; that is,

$$A_2M^{1/2} = 1.65 \times 10^{23}A^3 + 0.968 \times 10^{23}BM^{1/2}\,. \tag{39.15}$$

Thus, this equation corresponds to Eq. (39.12) for the SF plot, which is based on the third-power type equation for $\alpha$. According to Eq. (39.15), values of $A$ and $B$ can be obtained from the intercept and slope of a plot of $A_2M^{1/2}$ against $M^{1/2}$. This is called the Kurata plot of the second virial coefficient. Figure VII.9 shows the K plots for polystyrene in toluene[6] and methyl ethyl ketone.[7] Clearly, $A_2M^{1/2}$ must become zero as $M$ is decreased to zero, and the broken curves in the figure indicate this fact. In Table VII.3 are given the values of $A$ and $B$ estimated from the straight lines in Fig. VII.9. In the case of toluene the value of $A$

**TABLE VII.3.** VALUES OF $A$ AND $B$ ESTIMATED FROM THE KURATA PLOTS OF $A_2$ FOR POLYSTYRENE

| SOLVENT | $A \times 10^8$ (cm) | $B \times 10^{27}$ (cm$^3$) |
|---|---|---|
| Toluene (25°C) | 0.648 | 2.56 |
| Methyl ethyl ketone (22°C) | 0.533 | 0.667 |

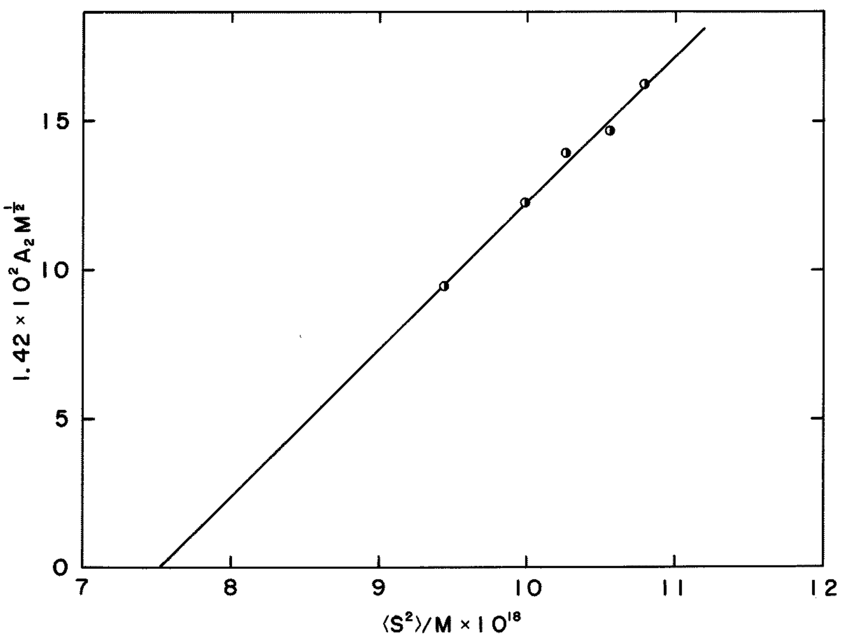

**Fig. VII.10.** The Berry plot of the second virial coefficient for polystyrene in methyl ethyl ketone.[7]

is in fair agreement with those obtained from the viscosity plots, while in the case of methyl ethyl ketone the agreement is not good (compare Tables VII.2 and VII.3). This is not surprising, since Eq. (39.15) is invalid for poor-solvent systems. Furthermore, it is seen that the values of $B$ from the K plots are not in agreement with those from the SF plots. This means that the K theory of the second virial coefficient does not correlate well with the third-power type equation for the expansion factor. This point will be discussed again in the next section. In any case, Eq. (39.15) may not be used to estimate the parameter $B$.

Berry[2] has recently found that $A_2M^{1/2}$ is proportional to $\alpha_S^2 - 1$, where the proportionality constant must be of the form, const.$(\langle S^2\rangle_0/M)^{3/2}$, from dimensional considerations. With the numerical constant determined experimentally, we may write

$$1.42 \times 10^{-24} A_2 M^{1/2} = -A^3 + 6A\langle S^2\rangle/M\,. \qquad (39.16)$$

Thus the Berry plot consists of plotting $A_2M^{1/2}$ against $\langle S^2\rangle/M$. Figure VII.10 shows the B plot for polystyrene in methyl ethyl ketone. The parameter $A$ may be estimated from the abscissa intercept $(= A^2/6)$. The value of $A$ so determined for this system is $0.672 \times 10^{-8}$, which compares well with the value from the viscosity plots given in Table VII.2. The Berry plot seems to yield a more reliable estimate of $A$ than Eq. (39.14) or (39.15).

In the above discussion, we have assumed, from the outset, that the expansion factors and the dimensionless ratio $A_2M^2/\langle S^2\rangle_0{}^{3/2}$ are functions of only the parameter $z$, following the theoretical conclusions reached in Chapters III and IV. However, this is to be examined experimentally.

## 40. Correlations Between the Expansion Factor and the Second Virial Coefficient

As already mentioned in Section 17c, Kurata[8] claimed that an equation of the third-power type for $\alpha_R$ and $\alpha_S$ is superior to that of the fifth-power type on the grounds that the KS or SF plots of intrinsic viscosities gave reliable estimates of unperturbed dimensions, and also that the available Monte Carlo data of Wall and Erpenbeck[17] indicated a linear relationship between $\alpha_R^3$ (or $\alpha_S^3$) and $n^{1/2}$. Further, Kurata[16] developed a theory of the second virial coefficient corresponding to the Fixman-type theory of the expansion factor, as described in Section 20b. This was the basis of Eq. (39.15) for the K plot. As seen in the last section, however, the KS of SF plots are not always linear, and moreover, there is no agreement between values of $B$ estimated from the SF plots of intrinsic viscosities and from the K plots of second virial coefficients. These facts led to the re-reexamination of the theory of the excluded-volume effect. Indeed, most of the work published since the mid-1960s, especially the theories of Flory and Fisk,[18] Reiss,[19] Fujita,[20, 21] Alexandrowicz,[22] and Yamakawa,[23, 24] were intended to answer the question of which of the third-power type and fifth-power type equations is better. These investigations have already been described in Chapter III. Since that time, great efforts have also been made especially by Berry[2, 14] to achieve a direct experimental test of the theory, instead of the indirect test provided by viscosity plots.

Now, the binary cluster integral $\beta$, and hence the parameter $z$, cannot be estimated directly from experiment. However, Berry has attempted to estimate $\beta$, or $B$, assuming the temperature dependence

$$B = B_0(1 - \Theta/T)\,, \tag{40.1}$$

as suggested originally by Flory,[25] where $B_0$ is a constant independent of temperature, and can be determined from the temperature dependence of the second virial coefficient near the theta temperature. Thus Berry has determined values of $z$ for polystyrene in decalin and toluene, and plotted $\alpha_S^2$, and also $\alpha_\eta{}^3$, against $z$. We believe that it is the best way to use, if possible, these plots as a criterion of validity for a theory of the excluded-volume effect. To our knowledge, there has not yet been given a theoretical or experimental justification of the assumption (40.1). Therefore, we wish to examine the agreement between theory and experiment without the use of any *ad hoc* assumption. In this section, our discussion is confined to the equilibrium properties, $\alpha_S$ and $A_2$.

Yamakawa[26] and Fujita[27] have proposed a procedure for examining the agreement between theory and experiment,which is based on the correlation between the expansion factor and the second virial coefficient. What have been adopted as criteria of validity of a theory are the following: (1) consistency in the values of $z$ determined from observed values of $\alpha_S$ and from observed values of the function $\Psi$ defined by

$$\Psi = A_2 M^2 / 4\pi^{3/2} N_{\mathrm{A}} \langle S^2 \rangle^{3/2} \,, \tag{40.2}$$

using the theoretical expressions for $\alpha_S$ and $\Psi$, and (2) linearity between $M^{1/2}$ and $z$ determined from observed values of $\alpha_S$ using its theoretical expression. The first criterion arises from the fact that the binary cluster integral for segments in the same chain must be the same as that for two segments belonging to different chains. Clearly the second criterion is required by the definition of $z$. These two criteria involve no assumptions.

Although various approximate theories of $\alpha_S$ and $\Psi$ have been developed, as seen in Chapters III and IV, there are very few expressions for $\Psi$ which can be chosen for a given theory of $\alpha_S$ if we insist on the self-consistency of intramolecular and intermolecular theories of interaction. Strictly, there are only three such self-consistent combinations: (1) the original Flory–Krigbaum–Orofino theory of $\Psi$ and the original Flory theory of $\alpha_S$, (2) the modified Flory–Krigbaum–Orofino theory of $\Psi$ and the modified Flory theory of $\alpha_S$, and (3) the Kurata–Yamakawa theory of $\Psi$ and the Yamakawa–Tanaka theory of $\alpha_S$. That is,
Combination (1):

$$\Psi = [\ln(1 + 2.30\bar{z})]/2.30 \,, \qquad \text{(FKO,o)} \tag{40.3}$$

$$\alpha_S^{\,5} - \alpha_S^{\,3} = 2.60 z \,, \qquad \text{(F,o)} \tag{40.4}$$

Combination (2):

$$\Psi = [\ln(1 + 5.73\bar{z})]/5.73 \,, \qquad \text{(FKO,m)} \tag{40.5}$$

$$\alpha_S^{\,5} - \alpha_S^{\,3} = 1.276 z \,, \qquad \text{(F,m)} \tag{40.6}$$

Combination (3):

$$\Psi = 0.547[1 - (1 + 3.903\bar{z})^{-0.4683}] \,, \quad \text{(KY)} \tag{40.7}$$

$$\alpha_S^{\,2} = 0.541 + 0.459(1 + 6.04z)^{0.46} \,, \quad \text{(YT)} \tag{40.8}$$

where $\bar{z}$ is defined by Eq. (21.16),

$$\bar{z} = z/\alpha_S^{\,3} \,. \tag{40.9}$$

Now, $\Psi$ may be considered to be a function of $\alpha_S$ when $z$ is eliminated from $\Psi$ and $\alpha_S$. Values of $\Psi$ may be calculated from Eq. (40.2) with values of $\langle M \rangle_w$, $A_2$, and $\langle S^2 \rangle$ obtained from light-scattering measurements, while $\alpha_S$ may be calculated from $\alpha_S^{\,2} = \langle S^2 \rangle / \langle S^2 \rangle_0$ with values of $\langle S^2 \rangle_0$ at the theta temperature; that is, *observed* values of $\Psi$

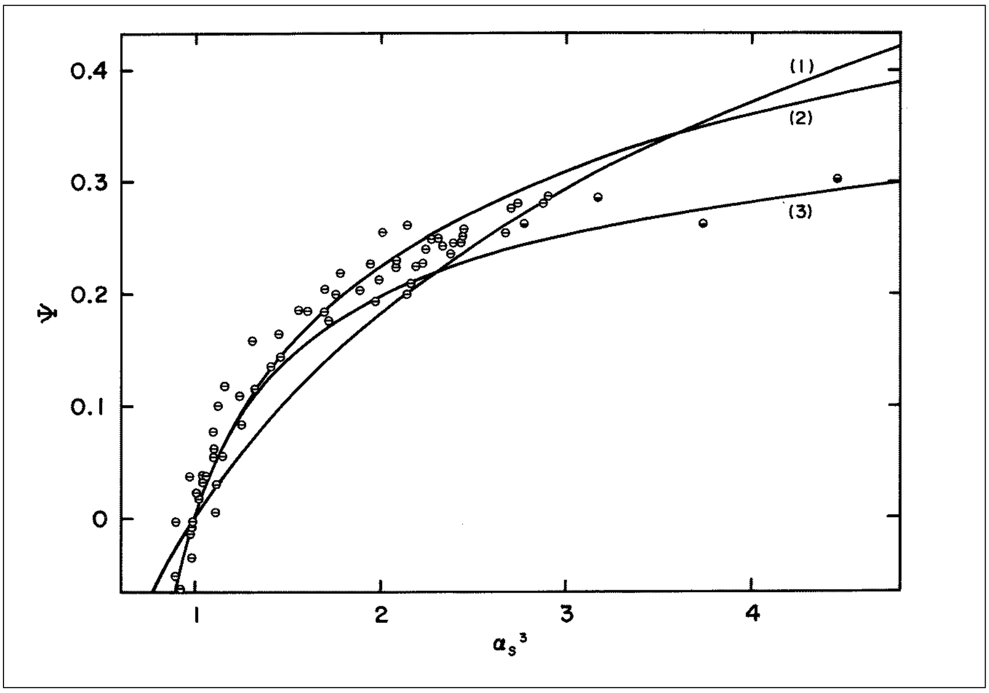

**Fig. VII.11.** Plots of $\Psi$ against $\alpha_S^3$ for fractions of polystyrene;[2] ◒, in toluene at 12 °C; ⊖, in decalin at various temperatures. Curves (1) to (3) represent the theoretical values calculated from combinations (1) to (3) of equations for $\Psi$ and $\alpha_S$, respectively.

and $\alpha_S$ are both available. Therefore, we first test each of the above three combinations with respect to the functional dependence of $\Psi$ on $\alpha_S$, following Fujita.[27] This is equivalent to examining the fulfillment of criterion (1), and can be done without any assumption. Figures VII.11 and VII.12 show plots of $\Psi$ against $\alpha_S^3$ for fractions of polystyrene and polychloroprene in various solvents, respectively, the data being due to Berry[2] (polystyrene) and Norisuye et al.[27] (polychloroprene). In each case, the data points are seen to form a single composite curve. This implies that the two-parameter scheme is good enough to describe the intramolecular and intermolecular interactions. Curves (1) to (3) in the figures represent the values calculated from combinations (1) to (3) of intramolecular and intermolecular theories, respectively. It is seen that curves (2) and (3) fit the data well; combination (3) is particularly satisfactory.

As seen from Fig. IV.5, the Kurata theory and the Fixman–Casassa–Markovitz theory predict that $\Psi$ does not exceed 0.2. This prediction is not in agreement with experiment, as seen from Figs. VII.11 and VII.12. This is one of the reasons why there is no agreement between values of $B$ estimated from the SF plots of intrinsic viscosities and from the K plots of second virial coefficients.

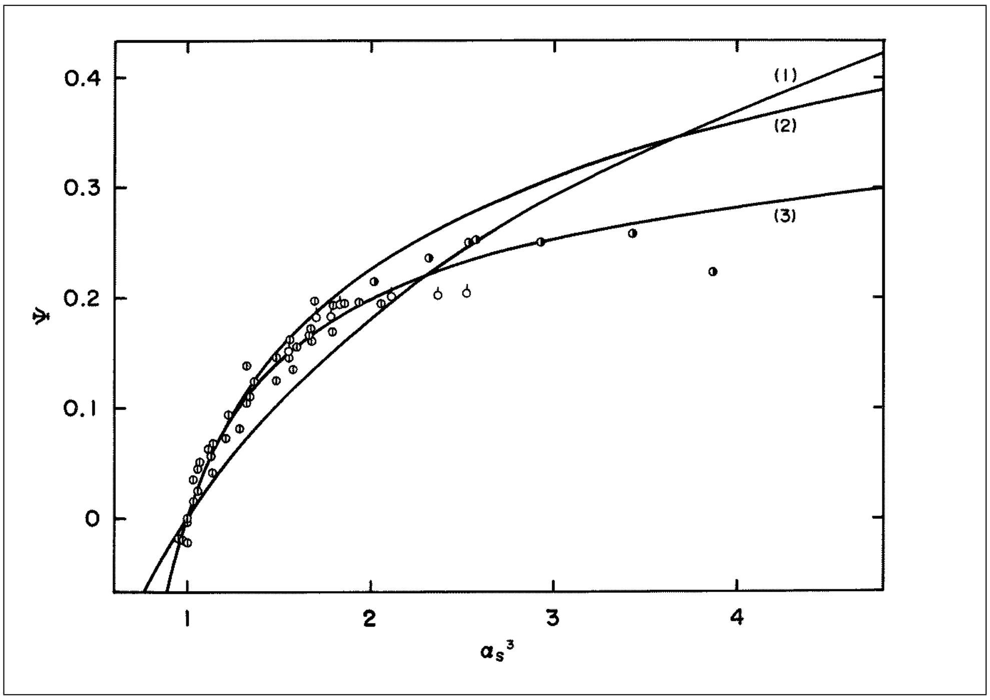

**Fig. VII.12.** Plots of $\Psi$ against $\alpha_S^3$ for fractions of polychloroprene;[27] ◑, in carbon tetrachloride at 25 °C; ȯ, in $n$-butyl acetate at 25 °C; ⦶, in *trans*-decalin at various temperatures. The curves have the same significance as those in Fig. VII.11.

Next we examine the fulfillment of criterion (1) only for combination (3). We first determine values of $\bar{z}$ from observed values of $\Psi$ using Eq. (40.7). From these values of $\bar{z}$ and the corresponding observed values of $\alpha_S$, we can then estimate values of $z$ by the use of Eq. (40.9). Thus we can plot values of $\alpha_S$ (usually $\alpha_S^3$) against the corresponding values of $z$ so determined. Figure VII.13 shows such plots for Berry's polystyrene in decalin and toluene. If combination (3) satisfies criterion (1), curve YT, which represent the theoretical values calculated from Eq. (40.8), must fit the data points. This seems to be true, though the data are scattered. In Fig. VII.13 are also shown the values predicted by other theories: the original Flory theory (F,o), Eq. (40.4), the modified Flory theory (F,m), Eq. (40.6), the Fixman theory (F), the Ptitsyn theory (P), the Flory–Fisk theory (FF), the Fixman–Stidham theory (FS), and the Fujita–Norisuye theory (FN). The F,P, and FF theories read

$$\alpha_S^3 = 1 + 1.914z\,, \qquad \text{(F)} \quad (40.10)$$

$$5.12\alpha_S^2 = 4.12 + (1 + 9.79z)^{2/3}\,, \qquad \text{(P)} \quad (40.11)$$

$$\alpha_S^5 - \alpha_S^3 = 0.648z[1 + 0.969(1 + 10z/\alpha_S^3)^{-2/3}]\,. \qquad \text{(FF)} \quad (40.12)$$

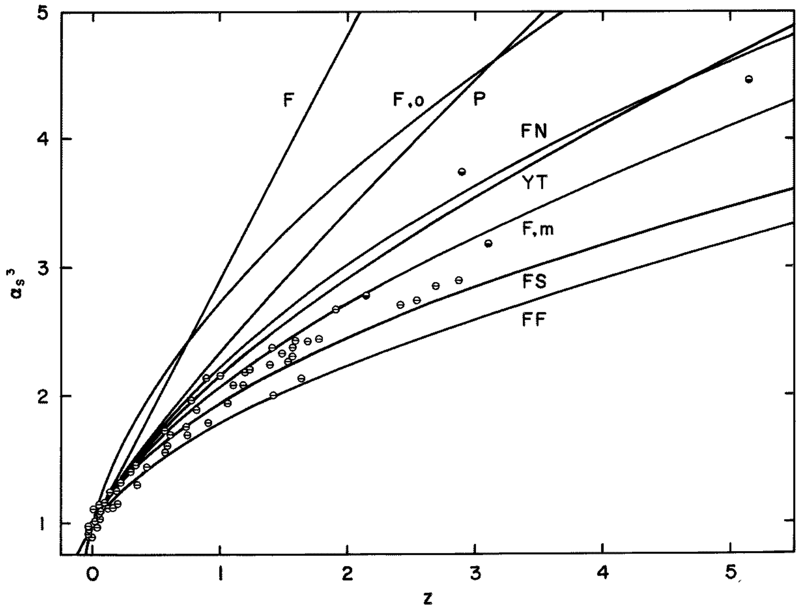

**Fig. VII.13.** Plots of $\alpha_S^3$ against $z$ for fractions of polystyrene in toluene and decalin.[2] The values of $z$ were determined from observed values of $\Psi$ by the use of Eq. (40.7). The curves represent the values predicted by the indicated theories.

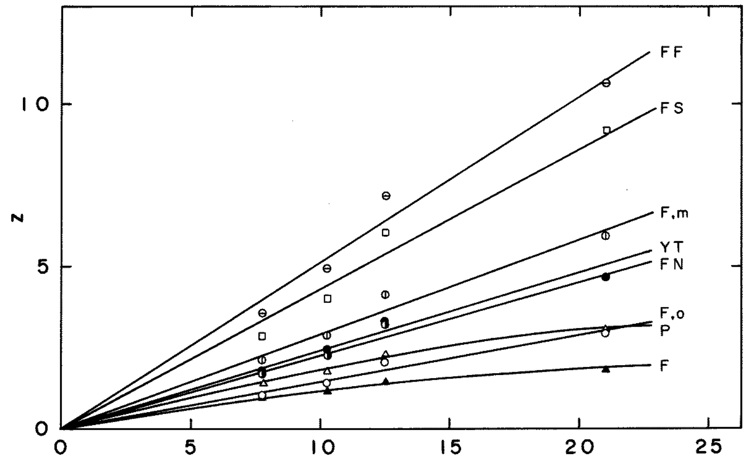

**Fig. VII.14.** Test of the linearity between $z$ and $\langle M\rangle_w^{1/2}$ with data for polystyrene in toluene at 12°C.[2] The values of $z$ were calculated from various theories of $\alpha_S$; ⊖, from the FF theory; □, from the FS theory; ⦶, from the F,m theory; ●, from the YT theory; ◑, from the FN theory; ○, from the F,o theory; △, from the P theory; ▲, from the F theory.

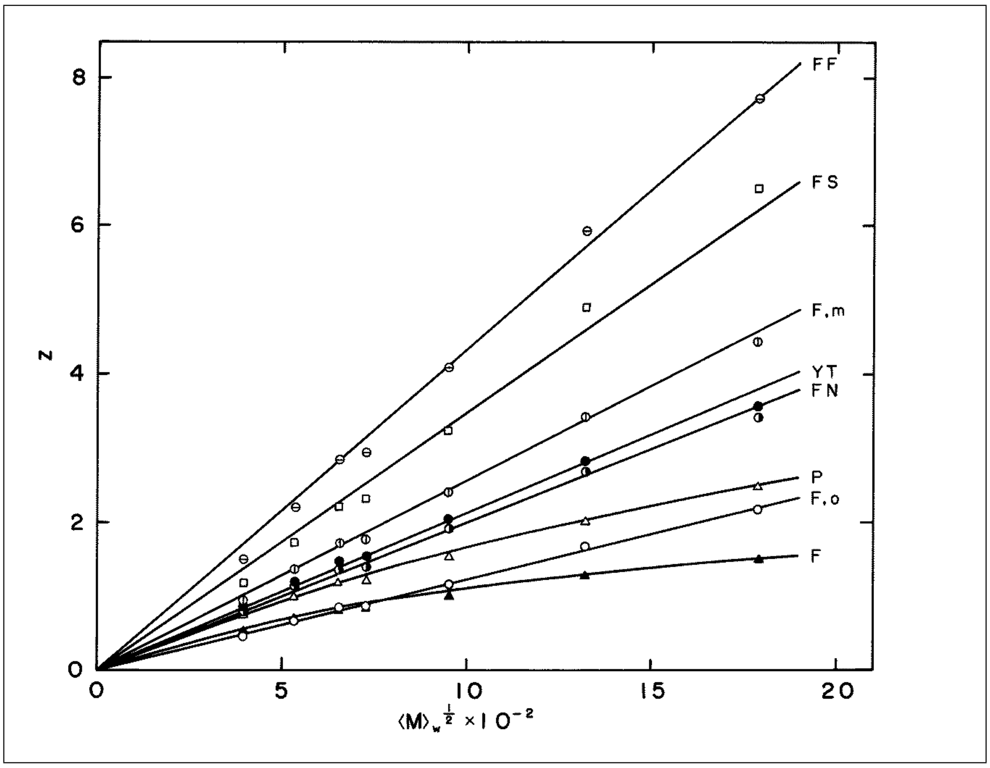

**Fig. VII.15.** Test of the linearity between $z$ and $\langle M\rangle_w^{1/2}$ with data for polychloroprene in carbon tetrachloride at 25 °C.[27] The symbols have the same significance as those in Fig. VII.14.

The FS and FN theory results have been obtained only numerically. We note that Berry's assumption of (40.1) leads to estimates of $z$ greater than ours; he has concluded that the FF theory is in good agreement with experiment.

As already noted in Chapter III, the above theories of $\alpha_S$ other than the F,o theory give the exact first-order perturbation theory at small $z$. Indeed, it is seen that the F,o theory does not predict the correct initial increase in $\alpha_S^3$. The corresponding defect of the FKO,o function $\Psi$ has already been observed in Figs. VII.11 and VII.12. The modified Flory theory was designed to remove this defect, and was the first step to improvements of the theory. We note that this earliest improvement is fairly satisfactory; there have been many subsequent improvements, as seen from Figs. VII.11 and VII.12.

We now turn to the examination of criterion (2). Figures. VII.14 and VII.15 show plots of $z$ against $\langle M\rangle_w^{1/2}$ for polystyrene in toluene[2] and polychloroprene in carbon tetrachloride,[27] respectively, where the values of $z$ have been estimated from observed values of $\alpha_S$ using the theories indicated. The data points obtained from the F,o, F,m, YT,

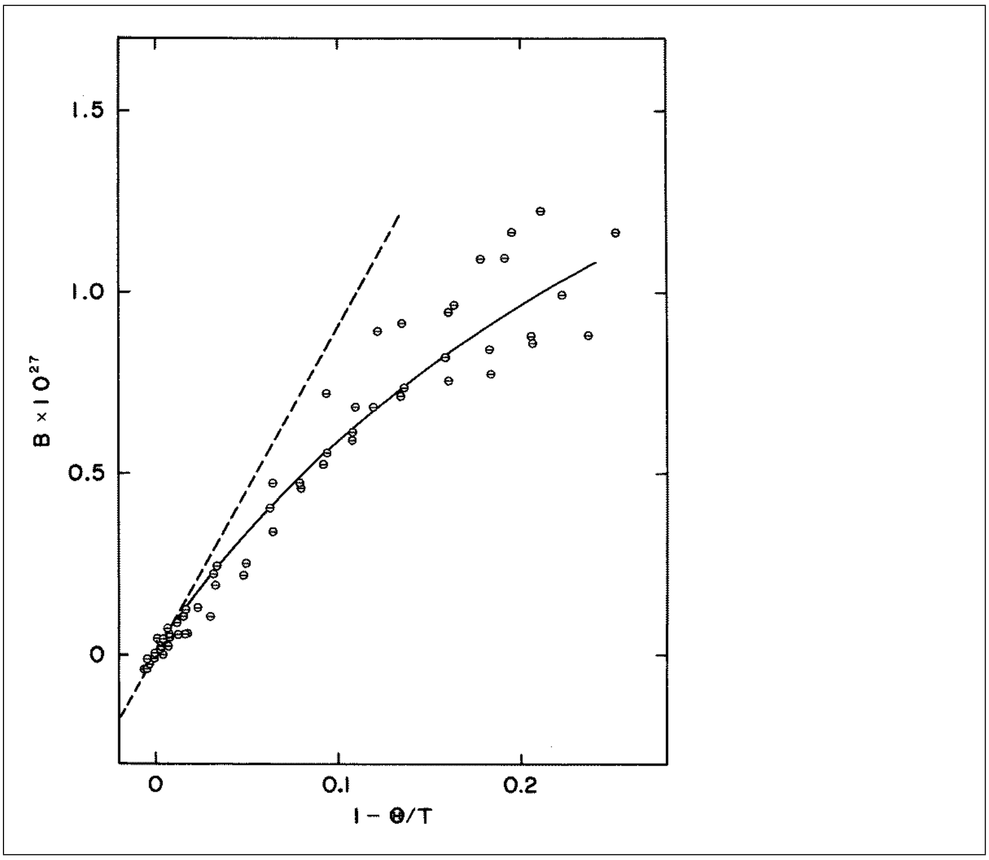

**Fig. VII.16.** Plots of $B$ against $1 - \Theta/T$ for fractions of polystyrene in decalin.[2] The values of $B$ were calculated from values of $\alpha_S$ by the use of Eq. (40.8) with (39.6). The full curve is an empirical fit to the data. The broken line represents the temperature dependence of $B$ determined by Berry from second virial coefficients.

FF, FS, and FN theories are seen to fall close to respective straight lines passing through the origin, indicating that these theories satisfy criterion (2). On the other hand, the F and P equations are seen to lead to nonlinear relations between $z$ and $M^{1/2}$, indicating an inadequacy of equations of the third-power type. However, we note that for intermediate or poor solvent systems all the theories cited above lead to linear relations between $z$ and $M^{1/2}$, and criterion (2) is not sufficiently sensitive to be a test of validity of a theory.

From the above analysis, we may conclude that combinations (2) and (3) satisfy both criteria (1) and (2); in particular, combination (3) is satisfactory even for good solvent systems. Thus, in what follows, we adopt the YT equation (40.8) to determine values of $z$ from observed values of $\alpha_S$.

Finally, we examine the temperature dependence of the parameter

$B$. Figure VII.16 shows plots of $B$ against $1 - \Theta/T$ for polystyrene in decalin,[2] where values of $B$ have been calculated from values of $\alpha_S$ using Eq. (40.8) with (39.6) and $10^{18}\langle S^2\rangle_0/M = 7.6$ (for the homogeneous polymer). The full curve is an empirical fit to the data. The broken straight line is given by

$$B = 9.04 \times 10^{-27}(1 - \Theta/T)\,, \tag{40.13}$$

which has been determined by Berry[2] from the temperature dependence of the second virial coefficient near the theta temperature. This straight line is seen to represent closely the initial tangent to the curve in the figure. This also implies that values of $B$ determined from Eq. (40.8) are consistent with those from second virial coefficients. Further, it is seen that the curve in the figure is concave downward, and therefore that Berry's assumption of (40.1) leads to overestimates of $B$, and hence $z$, except near the theta temperature. The validity of this assumption is confined to a very narrow range near the theta temperature.

## 41. Correlations Between the Expansion Factor and the Intrinsic Viscosity

Berry[14] has found that for polystyrene the viscosity-radius expansion factor $\alpha_\eta$ is not a function of only the parameter $z$, again making use of the values of $z$ determined on the basis of the assumption (40.1). This result has been interpreted in terms of the draining effect. As already mentioned in Section 34, however, this effect has never been observed for flexible chains, at least at theta temperatures. Then, there arises the question of whether the draining effect exists for $z > 0$. We begin by considering this problem.

Figure VII.17 shows plots of $A_2\langle M\rangle_w/[\eta]$ against $\alpha_S{}^2 - 1$ for fractions of polychloroprene[27, 28] and poly-$p$-methylstyrene[29] in various solvents, $[\eta]$ being expressed in deciliters per gram. It is seen that the plots may be well represented by a single-composite curve. This suggests that the two-parameter theory does work well for the intrinsic viscosity as well as the equilibrium properties, and therefore that there is no draining effect irrespective of the value of $z$. We note that the behavior of the above dimensionless ratio as a function of $\alpha_S$ has been frequently examined for various systems, and earlier data have been found to scatter remarkably when plotted against $\alpha_\eta{}^2 - 1$, or $\alpha_S{}^2 - 1$.[8, 30] This is probably due to the inaccuracy of the estimates of the second virial coefficient obtained from the conventional plots; the light-scattering data used in Fig. VII.17 were obtained from the square-root plots, as described in Section 38.

Now, whether the draining effect exists or does not for $z > 0$ may be examined more explicitly as follows. If $\alpha_\eta$ is a function of only $\alpha_S$, then $\alpha_\eta$ must be a function of only $z$ since $\alpha_S$ has been proved to be a function of only $z$. In order to demonstrate this and also make a comparison of theory with experiment, Fujita et al.[28, 31] have proposed to plot

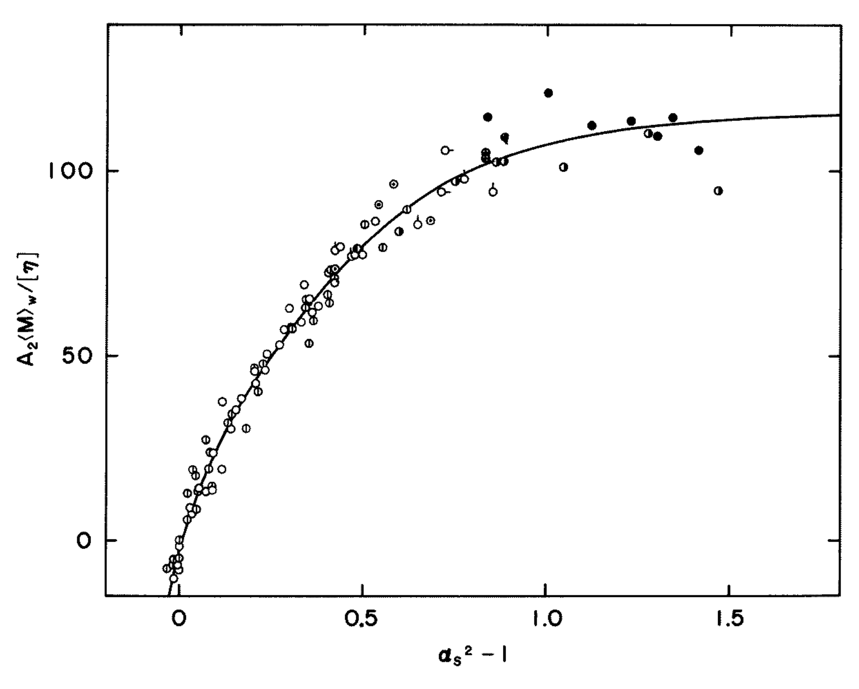

**Fig. VII.17.** Plots of $A_2\langle M\rangle_w/[\eta]$ against $\alpha_S^2 - 1$ for fractions of polychloroprene[27, 28] in carbon tetrachloride at 25 °C (◑), *n*-butyl acetate at 25 °C (o̍), and *trans*-decalin at various temperatures (⦶), and for fractions of poly-*p*-methylstyrene[29] in toluene at 30 °C (●), dichloroethane at 30 °C (⊕), cyclohexane at 30 °C (o-), methyl ethyl ketone at 30 °C (⊙), and diethyl succinate at various temperatures (○). The curve is an empirical fit to the data.

$\log\alpha_\eta^3$ against $\log\alpha_S^3$. Such plots can be made without any assumption, and are shown in Fig. VII.18, where we have used almost all the published data for polystyrene,[14, 32] polymethylmethacrylate,[33] poly-$\alpha$-methylstyrene,[34] polychloroprene,[27, 28] and poly-*p*-methylstyrene[29] in various solvents. It is seen that the plots form a single-composite curve, the full curve being an empirical fit to the data. Thus we have support for the earlier conclusion that there is no draining effect for flexible chains irrespective of the value of $z$, as advocated first by Flory[4] and assumed in Section 35. We believe that Berry's conclusion conflicts with ours because of his incorrect estimates of $z$.

Our next problem is then to test the (two-parameter) theory of the intrinsic viscosity in the non-free-draining limit. In Fig. VII.18 are shown the values calculated from three theories: the Flory–Fox theory (FF), $\alpha_\eta = \alpha_S$, the Kurata–Yamakawa theory (KY), Eq. (35.15),

$$\alpha_\eta^3 = \alpha_S^{2.43}, \tag{41.1}$$

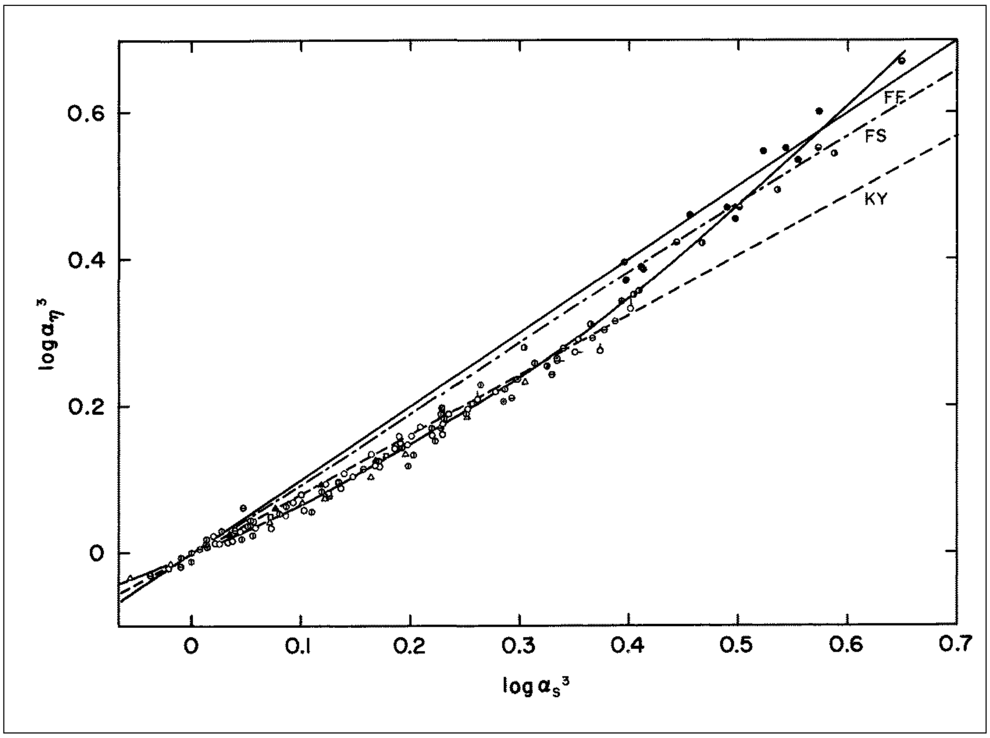

**Fig. VII.18.** Double logarithmic plots of ${\alpha_\eta}^3$ against $\alpha_S^3$ for polystyrene in toluene (◒), decalin (⊖), and cyclohexane(□),[2, 14, 32] polymethylmethacrylate in *n*-butylchloride(△),[33] poly-$\alpha$-methylstyrene in cyclohexane(▲),[34] and polychloroprene[27, 28] and poly-*p*-methylstyrene[29] in various solvents. For the last two polymers, the same symbols as those in Fig. VII.17 are used. The full curve is an empirical fit to the data. Full line FF : the Flory–Fox theory. Broken line KY : the Kurata–Yamakawa theory. Chain curve FS : the Fixman–Stidham theory.

or

$$\log {\alpha_\eta}^3 = 0.81 \log \alpha_S^3 \,, \tag{41.2}$$

and the Fixman–Stidham theory (FS), Eq. (35.67) with (35.74). It is seen that most of the data points lie below the straight line FF. Such behavior of $\alpha_\eta$ was found first by Krigbaum and Carpenter[32] for polystyrene in cyclohexane near the theta temperature. Indeed this observation stimulated further investigations of the intrinsic viscosity following the Flory–Fox theory, as described in Section 35. However, it is important to observe that both of the improved theories of Kurata and Yamakawa, and Fixman and Stidham, still overestimate $\alpha_\eta$ near the theta temperature. In other words, the coefficient $C_1$ in the expansion, ${\alpha_\eta}^3 = 1 + C_1 z + \cdots$, is definitely smaller than 1.55, the value predicted by Kurata and Yamakawa. Further, it is seen that there is not linearity between log ${\alpha_\eta}^3$ and log $\alpha_S^3$, as predicted by Kurata and

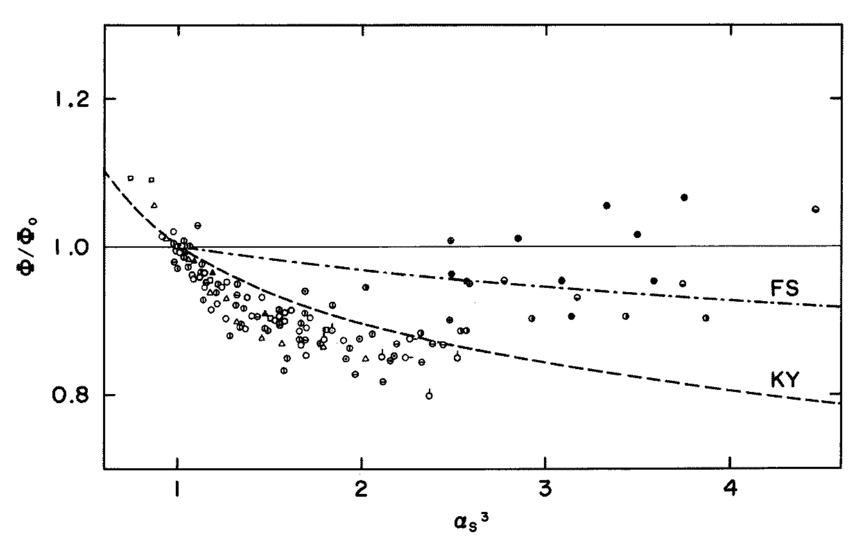

**Fig. VII.19.** Plots of $\Phi/\Phi_0$ against $\alpha_S^3$ for various polymer-solvent systems. The symbols have the same significance as those in Fig. VII.18. Curve KY : the Kurata–Yamakawa theory. Curve FS : the Fixman–Stidham theory.

Yamakawa.

This conclusion can be made clearer if we examine the behavior of the viscosity constant $\Phi$, or the ratio

$$\Phi/\Phi_0 = {\alpha_\eta}^3/\alpha_S^3 \,. \tag{41.3}$$

Figure VII.19 shows plots of $\Phi/\Phi_0$ against $\alpha_S^3$, the data being the same as those in Fig. VII.18. The horizontal line, and curves KY and FS represent the values predicted by the Flory–Fox theory, the Kurata–Yamakawa theory,

$$\Phi/\Phi_0 = {\alpha_S}^{-0.57} \,, \tag{41.4}$$

and the Fixman–Stidham theory, respectively. The observed $\Phi/\Phi_0$ is seen to decrease first more rapidly with increasing $\alpha_S$ than do any of the theoretical values, and then increase gradually. Although the data scatter appreciably for large $\alpha_S$, it is reasonable to consider $\Phi/\Phi_0$ to approach unity asymptotically. Thus there is no satisfactory theory of $\alpha_\eta$ or $\Phi$.

Now we examine the behavior of ${\alpha_\eta}^3$ as a-function of $z$. As suggested in the last section, values of $z$ may be determined from values of $\alpha_S$ using Eq. (40.8). In Fig. VII.20 are plotted values of ${\alpha_\eta}^3$ against the values of $z$ thus determined using the same data as those in Figs. VII.18 and VII.19. The full curve is an empirical fit to the data, which has only slight curvature. As pointed out first by Fujita et al.,[28] this characteristic of the plot accounts for why there is a linearity

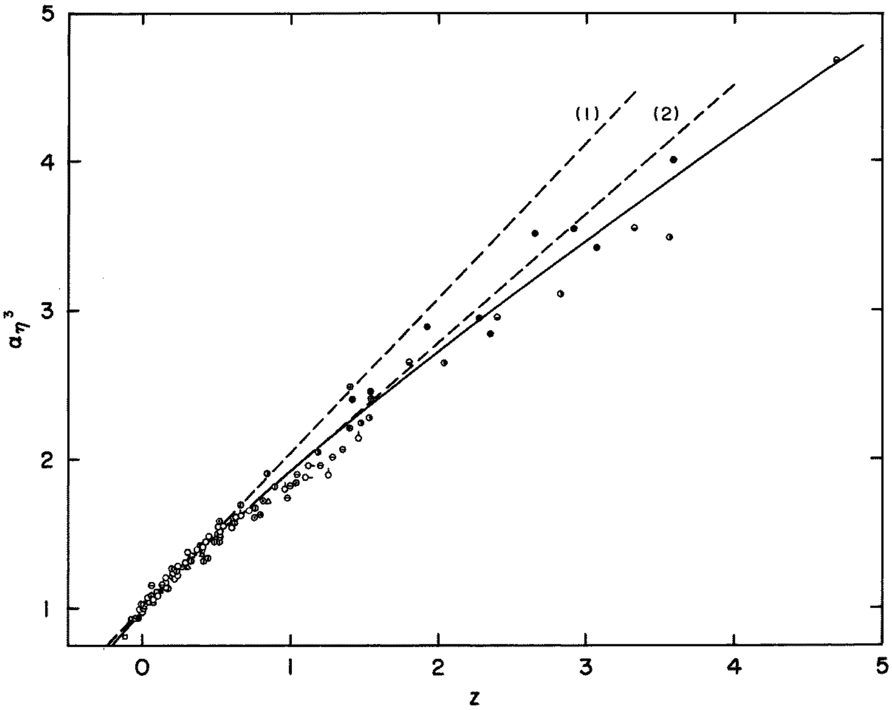

**Fig. VII.20.** Plots of $\alpha_\eta{}^3$ against $z$ for various polymer-solvent systems. The symbols have the same significance as those in Fig. VII.18. The values of $z$ were calculated from values of $\alpha_S$ by the use of Eq. (40.8). The full curve is an empirical fit to the data. Broken line (1) and (2) are the best fits over the ranges $0 < \alpha_\eta{}^3 < 1.6$ and $0 < \alpha_\eta{}^3 < 2.5$, and are given by Eqs. (41.5) and (41.6), respectively.

between $[\eta]/M^{1/2}$ and $M^{1/2}$ over a relatively wide range of $M$ as seen in Fig. VII.7, and thus the Stockmayer-Fixman plot gives a reasonable estimate of $K$ when extrapolated linearly to $M = 0$. Note that the plot of $\alpha_\eta{}^3$ against $z$ is essentially equivalent to the SF plot since $\alpha_\eta{}^3 = [\eta]/KM^{1/2}$ and $z \propto M^{1/2}$. As already mentioned, Kurata and Stockmayer concluded that an equation of the third-power type for $\alpha_S$ is better than an equation of the fifth-power type because of the superiority of the Stockmayer–Fixman or Kurata–Stockmayer plot to the Flory–Fox–Schaefgen plot. However, this conclusion requires modification in the light of the above analysis. It is now clear that the adequacy of the Stockmayer–Fixman equation for $\alpha_\eta$ is not a consequence of the third-power type equation for $\alpha_S$, but arises from the resultant effect of the F,m or YT equation for $\alpha_S$ and the characteristic dependence of $\Phi/\Phi_0$ on $\alpha_S$. The curvature of the plot of $\alpha_S^3$ against $z$ is diminished by the opposite curvature of the curve of $\Phi/\Phi_0$, leading to the weak curvature of $\alpha_\eta{}^3$. Since the F,m equation for $\alpha_S$ has been found to be fairly satisfactory, the defect of the FFS plot must be attributed to the assumption $\alpha_S = \alpha_\eta$. We cannot support Flory's claim[35] that none of the viscosity plots is valid because of the breakdown of the theory of $\alpha_S$ in the range of low molecular weights where short chain effects come out.

Straight lines (1) and (2) in Fig. VII.20, which are represented by

$$\alpha_\eta{}^3 = 1 + 1.05z \qquad \text{for } 0 < \alpha_\eta{}^3 < 1.6\,, \tag{41.5}$$

$$\alpha_\eta{}^3 = 1.05 + 0.87z \qquad \text{for } 0 < \alpha_\eta{}^3 < 2.5\,, \tag{41.6}$$

respectively, are the best fits to the data over the indicated ranges. The coefficient 1.05 in Eq. (41.5) is not necessarily equal to the first coefficient $C_1$ in the exact perturbation series, $\alpha_\eta{}^3 = 1 + C_1 z - \cdots$, since the perturbation theory is valid only for $|z| < 0.15$. Rather $C_1$ may be regarded as greater than 1.05. On the other hand, we have already seen in Fig. VII.18 that $C_1$ is smaller than 1.55. Thus the exact $C_1$, which is unknown theoretically, must be

$$1.05 < C_1 < 1.55\,. \tag{41.7}$$

To derive such a value of $C_1$ is a future theoretical problem.*

The new empirical equation (41.5) and (41.6) for $\alpha_\eta$ lead to

$$[\eta]/M^{1/2} = K + 0.346\Phi_0 B M^{1/2} \qquad \text{for } 0 < \alpha_\eta{}^3 < 1.6\,, \tag{41.8}$$

$$[\eta]/M^{1/2} = 1.05K + 0.287\Phi_0 B M^{1/2} \qquad \text{for } 0 < \alpha_\eta{}^3 < 2.5\,. \tag{41.9}$$

These equations yield estimates of $B$ different from those derived from the Stockmayer–Fixman equation (39.12). Equations (41.8) and (41.9) are called the modified Stockmayer–Fixman equations. For polystyrene in decalin near the theta temperature, Inagaki et al.[36] have obtained the value $6.0 \times 10^{-27}$ for the constant $B_0$ in Eq. (40.1) from intrinsic viscosity data using Eq. (39.12) or the equation, $\alpha_\eta{}^3 = 1 + 1.55z$. This value for $B_0$ is smaller than Berry's value $9.04 \times 10^{-27}$, as given in Eq. (40.13), estimated from second virial coefficients. Clearly this disagreement arises from the inaccuracy of the numerical coefficient in Eq. (39.12). If we use Eq. (41.5) or (41.8) instead of Eq. (39.12), Inagaki's value for $B_0$ is revised to $8.85 \times 10^{-27}$ and the agreement with Berry's value becomes better. Thus the modified SF equations will, in general, lead to more nearly correct estimates of $B$ than does the original SF equation, the latter giving underestimates of $B$.

Finally, we estimate $B$ for several systems from the modified SF equations, and compare the results with those from expansion factors $\alpha_S$. Figure VII.21 shows the SF plots for poly-*p*-methylstyrene in toluene at 30°C (filled circles), methyl ethyl ketone at 30°C (center-filled circles), and diethyl succinate at the theta temperature 16.4°C

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*Recently, H. Yamakawa and G. Tanaka [*J.Chem.Phys.*, to be published] have obtained $C_1 = 1.06$ theoretically, introducing exactly the excluded-volume effect into the Zimm–Hearst theory.

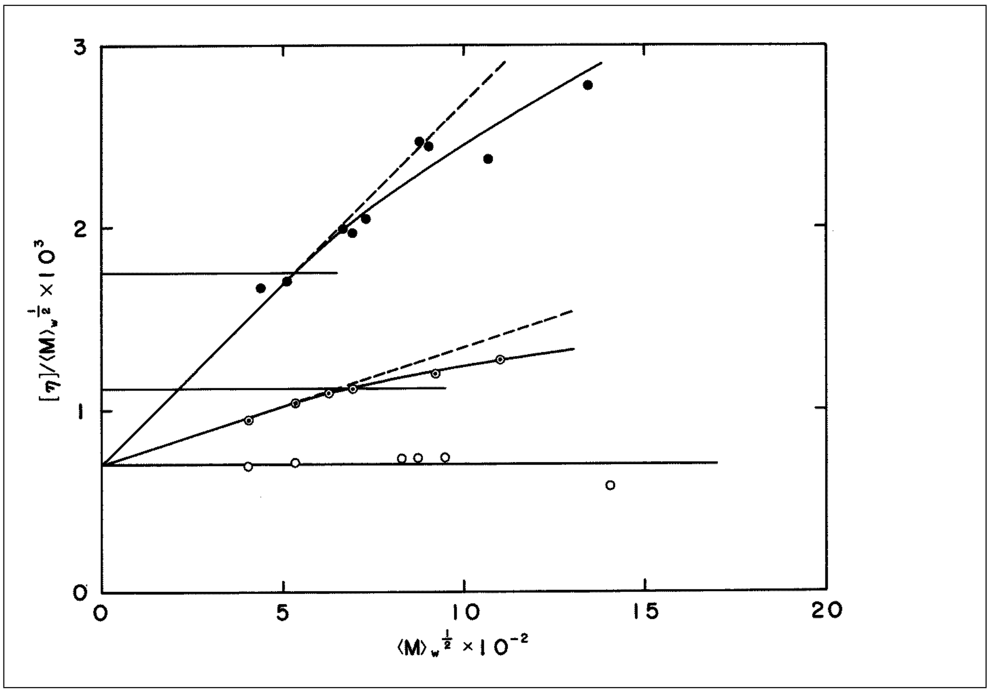

**Fig. VII.21.** The Stockmayer–Fixman plots for poly-*p*-methylstyrene: ●, in toluene at 30 °C; ⊙, in methyl ethyl ketone at 30 °C; ○, in diethyl succinate at 16.4 °C (Θ).[29] The broken lines are the initial tangents. The two thin horizontal lines indicate the upper bounds given in Eqs. (41.5) and (41.6).

(open circles),[29] $[\eta]$ being expressed in deciliters per gram. Extrapolations to $M = 0$ are carried out so as to yield the same ordinate intercept $10^3 K = 0.7$. The two thin horizontal lines in the figure indicate the upper bounds below which Eqs. (41.8) and (41.9) are applicable, corresponding to $[\eta]/KM^{1/2} = 1.6$ and 2.5, respectively. Linear extrapolations may be carried out over these regions for toluene and methyl ethyl ketone solutions, and the tangents to the linear parts are indicated by the broken lines. Values of B may then be determined from the slopes of these broken lines using Eq. (41.8) for methyl ethyl ketone solutions, and Eq. (41.9) for toluene solutions, where we simply replace the coefficient 1.05 in Eq. (41.9) by unity. Similar analyses have been made using the data for polystyrene,[14] poly-*p*-chlorostyrene,[37] poly-*p*-bromostyrene,[37] and polychloroprene.[28] The results are summarized in Table VII.4. In the last column of the table are given the corresponding values of $B$ estimated from the slopes of the plots of $z$ against $\langle M\rangle_w^{1/2}$ with the values of $A$ or $\langle S^2\rangle_0/M$ (for the homogeneous polymers), where values of $z$ have been calculated from values of $\alpha_S$ using Eq. (40.8). It is seen that there is good agreement between the values of $B$ estimated from $[\eta]$ and $\alpha_S$.

As easily recognized from the preceding discussion, one of the im-

**TABLE VII.4.** VALUES OF $B$ ESTIMATED FROM INTRINSIC VISCOSITIES AND STATISTICAL RADIUS EXPANSION FACTORS

| | | $B \times 10^{27}(\mathrm{cm}^3)$ | |
|---|---|---|---|
| POLYMER | SOLVENT | FROM $[\eta]$ | FROM $\alpha_S$ |
| Polystyrene[2, 14] | Toluene (12°C) | 2.11 | 2.19 |
| Poly-*p*-methylstyrene[29] | Toluene (30°C) | 2.73 | 2.90 |
| Poly-*p*-methylstyrene[29] | Methyl ethyl ketone (30°C) | 0.74 | 0.89 |
| Poly-*p*-chlorostyrene[37] | Toluene (30°C) | 0.51 | 0.52 |
| Poly-*p*-bromostyrene[37] | Toluene (30°C) | 0.058 | 0.055 |
| Polychloroprene[27, 28] | Carbon tetrachloride (25°C) | 3.22 | 2.87 |
| Polychloroprene[27, 28] | *n*-Butyl acetate (25°C) | 1.20 | 1.23 |

portant theoretical problems which remains is to derive the relation between ${\alpha_\eta}^3$ and $z$, as displayed in Fig. VII.20. This will complete a consistent system of two-parameter theories along with the theory of the equilibrium properties of dilute polymer solutions.

## 42. The Two Molecular Parameters

In the previous sections, we have seen that the two-parameter scheme is good enough to describe the properties of dilute solutions of long flexible chain polymers, and we established a procedure for estimating the two parameters $A$ and $B$, as defined by

$$na^2 = \langle R^2 \rangle_0 = MA^2 \,, \tag{42.1}$$

$$n^2\beta = M^2 B \,. \tag{42.2}$$

The estimation of $A$ and $B$ is independent of the choice of the number of segments, $n$, in the model chain, and their values can be determined uniquely. The reason is obvious: all the two-parameter theory results may be written in terms of the above two-parameter combinations $na^2$ and $n^2\beta$, and the parameters $n$ and $a$, and also $n$ and $\beta$, never appear separately in the final equations. In other words, the final equations are invariant to the choice of $n$, and the value of $n$ is, to some extent, arbitrary. Further analysis of the parameter $A$, or the ratio $\langle R^2 \rangle_0/M$, thus estimated is free from this arbitrariness, and the conformation factor $\sigma$, as defined by Eq. (9.39), can readily be calculated from

$$\sigma = A/(\langle R^2 \rangle_{0,f}/M)^{1/2} \,, \tag{42.3}$$

where $\langle R^2 \rangle_{0,f}$ is the mean-square end-to-end distance of the chain in the freely rotating state. As described in Section 9a, the theoretical investigation of $\sigma$ has recently progressed at a rapid rate. On the other hand, the molecular parameter related to $B$ is the binary cluster integral $\beta$ for a pair of segments, and its analysis requires a definite choice of $n$, or the assumption of the size of a segment, as seen from Eq. (42.2). Very few investigations of $\beta$ have been published. In this final section we give a brief summary of the investigations of the parameters $\sigma$ and $\beta$.

## 42a. The Conformation Factor

The unperturbed mean-square end-to-end distance is determined by its value in the freely rotating state and the conformation factor. The former is a geometrical quantity and can easily be estimated by the use of appropriate spectroscopic data for bond lengths and bond angles, while the latter is a purely statistical–mechanical quantity and yields useful information about chain conformation. However, it is not always convenient to separate the factor $\sigma$ and discuss it alone; recall the case of stiff chains. In 1963, Kurata and Stockmayer[8] published a tabulation of the values of the conformation factor $\sigma$ for various types of polymers which were obtained from extensive viscosity data by means of the Kurata–Stockmayer plot. A large part of their qualitative interpretation of the results remains correct. Subsequently, theoretical values of $\sigma$ (strictly $\langle R^2\rangle_0$) for various polymers have been published, especially by Flory and collaborators.

In Table VII.5 are given observed values of $\sigma$ for several typical polymers.[2, 29, 32, 38–49] They were obtained from light-scattering or viscosity data at theta temperatures, or from the Stockmayer–Fixman viscosity plots. Viscosity data were analyzed assuming $\Phi_0 = 2.5 \times 10^{23}$ (cgs). The salient features of the results together with some comments on the theoretical values may be summarized as follows.

1. The value 1.83 for $\sigma$ for polyethylene compares well with the theoretical values 1.84 (at 160°C) and 2.00 (at 140°C) obtained by Hoeve[50] and by Nagai,[51] respectively. Recall that the theoretical values have been obtained on the basis of the interdependent-rotation model, taking into account the difference between energies in the *trans* ($T$) and *gauche* ($G$) states and also the pentane effect, i.e., the exclusion of the $GG'$ or $G'G$ conformation [see Section 9a(ii)]. The latter effect is common to most polymers.

2. The value of $\sigma$ for polystyrene is greater than that for polyethylene. For vinyl polymers, in general, $\sigma$ lies between 1.8 and 2.5. The result may be interpreted as arising from the hindrances to internal rotation due to the repulsion between side groups attached to the chain backbone in addition to those as in a polymethylene chain.

3. Values of $\sigma$ for diene polymers are smaller than that for polyethylene, and moreover, values of $\sigma$ for *trans*-polymers are smaller than those for the *cis*-polymers. The reason is that the introduction of double bonds into the backbone is equivalent to lengthening the single bonds, thereby weakening the hindrances to internal rotation, the effect being exaggerated for the *trans*-polymers. Although a theoretical calculation has been carried out for *cis*-polybutadiene, it requires adjustment of parameter values.[52]

**TABLE VII.5.** OBSERVED VALUES OF THE CONFORMATION FACTOR $\sigma$ FOR VARIOUS POLYMERS

| POLYMER | SOLVENT | TEMP. (°C) | $10^{18}\langle R^2\rangle_{0,f}/M$ | $\sigma$ | REF. |
|---|---|---|---|---|---|
| Polyethylene | Diphenyl ether | 161.4(Θ) | 33.5 | 1.83 | 38 |
| Polystyrene | Cyclohexane | 34.8(Θ) | 9.01 | 2.25 | 2, 32 |
| Poly-*p*-methylstyrene | Diethyl succinate | 16.4(Θ) | 7.94 | 2.41 | 29 |
| *cis*-Polybutadiene | Isobutyl acetate | 20.5(Θ) | 30.6 | 1.64 | 39 |
| *trans*-Polybutadiene | Diethyl ketone | 5 (Θ) | 62.2 | 1.15 | 40 |
| *trans*-Polybutadiene | Diethyl ketone | 24 (Θ) | 62.2 | 1.32 | 40 |
| *cis*-Polyisoprene | Methyl *n*-propyl ketone | 14.5(Θ) | 23.5 | 1.61 | 41 |
| *trans*-Polyisoprene | *n*-Propyl acetate | 60 (Θ) | 49.4 | 1.39 | 41 |
| Polydimethylsiloxane | Methyl ethyl ketone | 20 (Θ) | 23.8 | 1.39 | 42 |
| Polydimethylsiloxane | Alkane mixture | 22.5(Θ) | 23.8 | 1.54 | 42 |
| Polyoxymethylene | Phenol | 90 | 27.3 | 1.99 | 43 |
| Polyoxymethylene | Hexafluoroacetone(0.84)–water(0.16) | 25 | 27.3 | 2.29 | 44 |
| Polyoxymethylene | 0.45 $M$ $K_2SO_4$ | 35 (Θ) | 22.0 | 1.65 | 45 |
| Polycarbonate | *n*-Butyl benzyl ether | 170 (Θ) | 46.7 | 1.38 | 46 |
| Polyethylene terephthalate | Phenol(0.50)–tetrachloroethane(0.50) | 25 | 47.1 | 1.30 | 47 |
| Poly-$\gamma$-benzyl-L-glutamate | Dichloroacetic acid | 25 | 12.7 | 1.84 | 48, 49 |

4. Values of $\sigma$ for polymers, such as polydimethylsiloxane and polyethers, whose backbones contain oxygen atoms are smaller than that for polyethylene, an exception being polyoxymethylene. The reduction in $\sigma$ arises from the fact that there are no hydrogen-atom substituents on the backbone oxygen atoms, thereby weakening the pentane effect. Indeed, Flory et al.[53] have carried out a theoretical calculation for polydimethylsiloxane, excluding the $GG'$ conformation completely for the sequence of bonds Si–O–Si–O–Si but partially for the sequence O–Si–O–Si–O. Similarly, for polyoxyethylene, Mark and Flory[54] have excluded the $GG'$ conformation completely for the sequence C–C–O–C–C but partially for the sequence O–C–C–O–C. On the other hand, in order to account for the relatively large values of $\sigma$ for polyoxymethylene, it is necessary to exclude completely the $GG'$conformation.[55] The reason will probably be that the C–O bond is shorter than the C–C bond.

5. Aromatic polyesters, such as polycarbonate and polyethylene terephthalate, have small $\sigma$ values. The situation is similar to that in diene polymers; note that the introduction of the six-membered rings into the backbone reduces the hindrances to internal rotation. For polyethylene terephthalate, Williams and Flory[56] have obtained a the-

oretical value of 1.40 for $\sigma$. This value is in fairly good agreement with the observed one.

Thus the values of $\sigma$ for various types of polymers as cited above may be well understood from the point of view of the chain structure. We note that theoretical calculations have also been carried out for some other polymers, e.g., polyamides[57] and polypeptides,[58] which we have not cited above. Although the method of evaluating $\sigma$ is well established, numerical results involve some ambiguity arising from the assignment of proper values to the energy parameters.

We must now discuss the conformation factors of cellulose, amylose, and their derivatives. Kurata and Stockmayer[8] applied the KS plot to these polymers, assuming that the two-parameter scheme is valid for them, as for flexible polymers, with neglect of the draining effect, and obtained the following conclusions. First, unperturbed dimensions for cellulose derivatives are independent of the solvent, since the KS plot gives the same intercept for the same polymer in different solvents. Second, values of $\sigma$ for cellulose derivatives are not so different from those for vinyl polymers, i.e., about two. This result was interpreted as arising from the existence of the pyranose rings in the backbone. In this sence, cellulose derivatives may be considered rather flexible polymers. Third, the viscosity plots for cellulose derivatives in good solvents lead to very large values of $B$, and therefore large expansion factors. These conclusions are in conflict with earlier conclusions that unperturbed dimensions for cellulose derivatives are dependent on the solvent and temperature, and that they have large average dimensions but small expansion factors.

Naturally Flory[35] has criticized the new version of Kurata and Stockmayer, and supported the earlier conclusions about the chain conformation of cellulose derivatives.Flory's grounds for objection are the following: (1) the KS plot requires extrapolation into the (short-chain) region where breakdown of the theory on which the plot is based is to be expected; thus the result that the KS plot gives the same intercept for the same cellulose derivative in different solvents is accidental, and (2) the KS plot predicts the value of $B$ for hydroxyethyl cellulose in water to be greater than that in cadoxen, while the data for the second virial coefficient leads to the opposite conclusion.[59]

However, Flory has not given an explicit theoretical interpretation of the *apparent* success of the KS plot for cellulose derivatives—the experimental result. Further, we must note that some cellulose derivatives exhibit the draining effect, i.e., the dependence of the viscosity constant $\Phi$ on the molecular weight $M$,[60, 61] and for others $[\eta]_\theta/M^{1/2}$ is independent of $M$ over a wide range of $M$.[62, 63] On the other hand, if the two-parameter scheme is assumed to be valid for cellulose derivatives, the KS or SF plot gives values of $B$ about twice as large as those predicted from values of $A_2M/[\eta]$.[64] Both Flory's and Kurata's versions involve several weak points, as mentioned above, and seem inconclusive. Further theoretical and experimental investigations of cellulose derivatives are needed.

**TABLE VII.6.** WHOLE AND EXCESS BINARY CLUSTER INTEGRALS PER MONOMERIC UNIT FOR POLYSTYRENE AND ITS DERIVATIVES IN TOLUENE AT 30°C

| | | $\beta_e \times 10^{24}(\text{cm}^3)$ | |
|---|---|---|---|
| POLYMER | $\beta \times 10^{24}(\text{cm}^3)$ | OBSERVED | THEORETICAL |
| Polystyrene | 23.7 | — | — |
| Poly-*p*-methylstyrene | 40.4 | — | — |
| Poly-*p*-chlorostyrene | 9.90 | −30.5 | −44.0 |
| Poly-*p*-bromostyrene | 1.84 | −38.6 | −49.3 |

## 42b. The Binary Cluster Integral

In this section our discussion is confined to polystyrene and *p*-substituted polystyrenes. As already noted, an analysis of the binary cluster integral $\beta$ itself requires the assumption of the size of a segment. For homopolymers possessing structurally similar backbones, as in the present case, it is convenient to consider the binary cluster integral per *monomeric unit.* With this assumption, we obtain the values of $\beta$, given in Table VII.6, for polystyrene and its derivatives in toluene at 30°C. (Although the data for polystyrene in toluene were obtained at 12°C, the temperature dependence of $\beta$ for this system is very small.) These values were calculated from the values of $B$ given in the last column of Table VII.4.

Now, $\beta$ is defined by Eq. (13.3),

$$\beta = \int [1 - g(R)] d\mathbf{R} \,, \tag{42.4}$$

where $g(R)$ is the pair correlation function between segments (monomeric units) with $R$ the separation at infinite dilution. As discussed in Section 13, $g(R)$ is a very complicated function of $R$. Thus Yamakawa, Rice, and collaborators[65] have considered only the excess binary cluster integral $\beta_e$ over a reference value $\beta_0$; that is,

$$\beta = \beta_0 + \beta_e \,. \tag{42.5}$$

In the case of polar polymers such as poly-*p*-chlorostyrene and poly-*p*-bromostyrene, $\beta_0$ and $\beta_e$ are the nonpolar and polar contributions, respectively, and $\beta_0$ may be taken as equal to the whole $\beta$ for the structurally similar, nonpolar polymer, poly-*p*-methylstyrene, in the same solvent.

The excess binary cluster integral arising from the long-range dipolar interaction, which falls off as $R^{-6}$, has been evaluated on the basis of the Onsager approximation, involving the use of cavity field and reaction field arguments.[65] The result is

$$\beta_e = -\frac{4\pi^2}{3V_s}\frac{1}{{\varepsilon_0}^2}\left(\frac{3\varepsilon_0}{2\varepsilon_0+1}\right)^4\left(\frac{\mu^{*2}}{3kT}\right)\left(\frac{\mu^{*2}}{3kT}+\alpha^*\right), \tag{42.6}$$

where

$$\mu^* = \frac{(2\varepsilon_0+1)(\tilde{n}^2+2)}{3(2\varepsilon_0+\tilde{n}^2)}\mu\,, \tag{42.7}$$

$$\alpha^* = \frac{(2\varepsilon_0+1)(\tilde{n}^2+2)}{3(2\varepsilon_0+\tilde{n}^2)}\alpha\,, \tag{42.8}$$

$$\alpha = \frac{3V_s}{4\pi}\frac{\tilde{n}^2-1}{\tilde{n}^2+2}\,, \tag{42.9}$$

with $\varepsilon_0$ the dielectric constant of the solvent, and $V_s$, $\mu$, $\alpha$, and $\tilde{n}$ the volume, dipole moment (*in vacuo*), polarizability, and refractive index of a spherical segment (monomeric unit). Values of $\beta_e$ for poly-*p*-chlorostyrene and poly-*p*-bromostyrene in toluene at 30°C calculated from Eqs. (42.6) to (42.9) are given in the last column of Table VII.6, where we have adopted the following values: $\varepsilon_0 = 2.36$, $V_s = 188 \times 10^{-24}$ cm$^3$, $\mu = 1.70 \times 10^{-18}$ esu and $\tilde{n}^2 = 2.31$ for poly-*p*-chlorosyrene, and $\mu = 1.73 \times 10^{-18}$ esu and $\tilde{n}^2 = 2.42$ for poly-*p*-bromostyrene. It is seen that there is fairly good agreement between the observed and theoretical values of $\beta_e$.

The monomeric unit of polystyrene has a dipole moment of about $0.4 \times 10^{-18}$ esu, while poly-*p*-methylstyrene may be regarded as completely nonpolar. In addition, the value of $V_s$ for polystyrene is smaller than that for poly-*p*-methylstyrene. These two effects account semi-quantitatively for the observation that the binary cluster integral for polystyrene is smaller than that for poly-*p*-methylstyrene in the same solvent. In this case, however, Eq. (42.6) cannot be applied, since there is the significant difference in $V_s$ between these polymers.

Now, if the monomeric units were identical with the solvent molecules, $g(R)$ in Eq. (42.4) would become equal to the pair correlation function for the pure solvent, and $\beta$ would be equal to the molecular volume of the solvent (see Section 13). Therefore, if the monomeric unit of polystyrene may be regarded as identical with a toluene molecule, $\beta$ for polystyrene in toluene would be equal to the molecular volume of toluene, $178 \times 10^{-24}$ cm$^3$ (at 30°C). This value is much larger than the observed value, $23.7 \times 10^{-24}$ cm$^3$. This difference cannot be considered to arise from only the difference between the volumes of the monomeric unit and the solvent molecule, and suggests that there is a preferential attraction between the monomeric units of polystyrene in toluene.

In conclusion, a complete theoretical calculation of the whole $\beta$ should be based on Eq. (42.4) with the use of the theory of simple liquids.

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## Chapter Eight

# Concluding Remarks

This book has been devoted to the development of the theory of the equilibrium and nonequilibrium properties of dilute polymer solutions; the main subjects have been the excluded-volume effect and related equilibrium properties, and the transport properties for linear flexible polymer chains. Throughout the book we have emphasized the establishment of the two-parameter theory in a systematic way, the historical significance of the individual theories and their interrelations, and the distinction between the solved and unsolved problems. Now the problematical points which require further investigations are summarized as follows.

1. The two-parameter theory has been developed on the basis of the random-flight model and the use of the approximation that the potentials between segments are short-ranged and pairwise additive. Within this framework, the formulation of the partition function for a single chain is well established. However, its evaluation is a many-body problem and there has not yet been obtained the exact solution of the excluded-volume problem; the problem of short-range interferences in the chain can be reduced to that in linear cooperative systems and is amenable to exact solution. Thus, to find, specifically, the asymptotic solution for the expansion factor remains as a mathematical–physical problem which is of particular interest to theoreticians. On the other hand, we must remember that several approximate theories may account for the experimental data.

2. The theory of the frictional properties has been developed using the Oseen hydrodynamic interaction tensor. This procedure has been common to almost all theories in the field since the Kirkwood–Riseman

theory. For flexible polymers, nevertheless, the draining effect has not been observed which is predicted by a theory of this type. In this connection, we must refer to the recent work of Zwanzig, Kiefer, and Weiss [*Proc. Natl. Acad. Sci. U.S.*, **60**, 381 (1968)]. They have pointed out that the solutions of a set of linear equations of the Kirkwood–Riseman type determining the frictional forces on the segments possess singularities for some values of the draining parameter, and these singularities lead to unphysical behavior of the transport properties, e.g., negative translational diffusion coefficients. The main source of error seems to be the treatment of segments as point sources of friction. Indeed, Rotne and Prager [*J. Chem. Phys.*, **50**, 4831 (1969)] have derived an approximate diffusion tensor which is positive definite for all chain configurations and approaches the Kirkwood–Riseman diffusion tensor at large separations between segments. These analyses suggest that the size of segments must be taken into account more accurately. The problem of the hydrodynamic interaction requires much more investigations. However, we must also remember the apparent success of approximate solutions of the Kirkwood–Riseman equations, especially in the non-free-draining limit

3. There is no satisfactory theory of the viscosity-radius expansion factor. This problem is very difficult to solve, since it involves the problems of the excluded-volume effect and the hydrodynamic interaction which have not been completely solved. Further investigations are needed in order to make the two-parameter theoretical description of the behavior of dilute polymer solutions more complete.

4. DNA molecules have been found to be fairly well represented by wormlike chains, specifically in describing their frictional behavior. Although the wormlike chain model has also been applied to cellulose derivatives by several authors, there have not yet been obtained definite conclusions regarding the chain conformation and dilute solution behavior of cellulose derivatives. In this connection, further research on wormlike chains with excluded volume is needed. This will necessarily lead to a three-parameter theory. It is, of course, questionable whether the dilute solution behavior of cellulose derivatives may or may not be described by a three-parameter theory of this type.

5. In Section 9a(ii) we have defined flexible chains as those which have the Markoff nature in the unperturbed state. It is clear that even such chains have stiffness to some extent; different kinds of chains have different flexibilities. Then what is the quantitative definition of chain flexibility? In many cases we may use the persistence length or the Kuhn statistical segment length for this purpose. In particular, for chains possessing the same type of backbone, we may use the conformation factor which measures the degree of hindrance to internal rotation. However, there will be some cases for which it is not convenient to use the persistence length. In other words, there is no unique quantitative definition of chain flexibility; it depends on the molecular model on the basis of which a theory is developed.

In closing the book, we hope that it will provide a thorough understanding of the theory of dilute polymer solutions and stimulate further research in this field.

# Indexes

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