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THEORY OF OSTWALD RIPENING IN A TWO-COMPONENT  
SYSTEM - CENTER DIRECTOR'S DISCRETIONARY FUND  
FINAL REPORT

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TABLE OF CONTENTS

	Page
I. INTRODUCTION .....	1
1.1 Physical Picture of Ostwald Ripening .....	1
1.2 Solubility and the Gibbs-Kelvin Equation .....	2
1.3 Continuity Equation .....	5
1.4 Conservation of Mass .....	6
1.5 Grain Size Growth Velocity .....	7
1.5.1 Two Diffusion Theorems .....	9
1.5.2 The Interdiffusion Coefficient .....	11
1.5.3 Rate Coefficient and the Effect of Advection .....	11
1.5.4 Diffusion-Controlled Growth Velocity .....	15
II. EFFECT OF INTER-GRAIN COMPETITION ON THE GRAIN RADIUS GROWTH VELOCITY .....	17
2.1 Macroscopic Equation of Motion and Its Solution .....	17
2.2 Microscopic Equation of Motion and Its Solution .....	21
2.3 Rate Coefficient and Diffusion-Controlled Growth Velocity ...	33
2.3.1 Computation of $\langle\langle \hat{T}_i(\mathbf{k}) \rangle\rangle$ and $K_T(1)$ .....	34
2.3.2 Computation of $\langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \rangle\rangle$ and $K_T(2)$ .....	35
2.3.3 Computation of $\langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) \rangle\rangle$ . $K_T(3)$ , and Higher Order Terms. Use of Diagrams .....	37
2.3.4 Summing Ring Diagrams .....	44
III. DETERMINATION OF THE GRAIN-SIZE DISTRIBUTION FUNCTION AND RELATED PARAMETERS .....	52
3.1 Summary of Governing Equations .....	52
3.2 Introduction of Dimensionless Variables .....	53
3.3 Similarity Transformation .....	56
3.4 Critical Radius and Supersaturation .....	61
3.5 Integration of Eq. (3.3.25) to Obtain $F_0(Z)$ .....	64
3.6 Evaluation of $C'_0$ , $\rho_0$ , and $a_0$ for $\epsilon=0$ .....	68
3.6.1 Evaluation of $C'_0$ .....	68
3.6.2 Evaluation of $\rho_0$ .....	69
3.6.3 Evaluation of $a_0$ .....	70

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TABLE OF CONTENTS (CONCLUDED)

	Page
3.7 Evaluation of $C_0$ , $\rho_0$ , and $a_0$ for $\epsilon \neq 0$ .....	71
3.8 Summary and Discussion .....	73
3.8.1 Results in Terms of Laboratory Parameters .....	73
3.8.2 Application to the System Succinonitrile/Water .....	79
REFERENCES .....	85
APPENDICES	
A. THE DELTA FUNCTION AND ITS PROPERTIES .....	87
B. FICK'S FIRST AND SECOND LAWS WITH DELTA FUNCTION SINKS .....	91
C. THE GREEN'S FUNCTION METHOD .....	95
C.1 General Principles .....	95
C.2 Green's Problem .....	95
C.3 Green's Theorem .....	98
D. FOURIER TRANSFORMS .....	101
D.1 General Principles .....	101
D.2 Fourier Integral Representation of the Delta Function ..	102
D.3 Convolution Theorem of the Fourier Transform .....	103
D.4 Fourier Transform of $\nabla^2 C(\mathbf{r})$ .....	104
D.5 Fourier Transform of $G(\mathbf{r}) = -(4\pi D\mathbf{r})^{-1}$ .....	106
E. SPECIFICATION OF EXPONENTS .....	109
E.1 Proof of $y_1 = x$ .....	109
E.2 Proof of $x = 1/3$ .....	111
F. EXPANSION OF $1/w(z)$ IN PARTIAL FRACTIONS .....	113

LIST OF ILLUSTRATIONS

Figure	Title	Page
1.1	Geometry for Calculating the Diffusion Into a Spherical Grain of Radius, $R$ .....	12
2.1	Coordinates Locating the Centers of Two Grains of Radii $R_1$ and $R_2$ , Respectively .....	22
2.2a	Diagram Representing the Left-Hand Side of Eq. (2.3.18) .....	41
2.2b	Diagram Representing the Left-Hand Side of Eq. (2.3.24) .....	42
2.2c	Ring Diagram for Three Grains .....	42
2.2d	Ring Diagram for Four Grains .....	45
2.2e	Multiply Connected Ring Diagram for Four Grains .....	46
2.3	Diagrammatic Representation of the Sum on the Right-Hand Side of Eq. (2.3.32) .....	46
3.1	Grain Size Distribution Normalization Constant, $\rho_0$ [Eq. (3.3.10)], Supersaturation Constant, $\sigma_1$ [Eq. (3.7.3)], and Mean Radius Constant, $a_0$ [Eq. (3.7.8)], Shown as Functions of the Equilibrium Volume Fraction Occupied by Grains, $\phi_\infty$ [Eq. (3.2.4)] .....	75
3.2	Grain Size Distribution Function, $F_0(Z)$ .....	76
3.3	Maximum Grain Size Constant, $Z_0$ [Eq. (3.7.2)], as a Function of Volume Fraction Occupied by Grains, $\phi_\infty$ [Eq. (3.2.4)] .....	78
3.4	Phase Diagram for the System Succinonitrile/Water .....	80
A.1	Sequence of Functions Representing the Dirac Delta Function in the Limit $n \rightarrow \infty$ .....	88
B.1	(a) Negative Concentration Gradient Showing Direction of Molecular Flux; (b) Positive Concentration Gradient Showing Direction of Molecular Flux .....	91
B.2	Geometry for Derivation of Fick's Second Law .....	92
C.1	Geometry of Origins $O$ and $O'$ .....	96
D.1	Geometry for Computing the Integral in Eq. (D.29) .....	107

LIST OF TABLES

Table	Title	Page
3.1	Thermophysical Data for the System $C_4H_4N_2/H_2O$ at $25\pm 1$ °C .....	80
3.2	Calculated Results for the System $C_4H_4N_2/H_2O$ at $25\pm 1$ °C and $\mu_\infty = 0.1$ .....	83

## TECHNICAL MEMORANDUM

### THEORY OF OSTWALD RIPENING IN A TWO-COMPONENT SYSTEM - CENTER DIRECTOR'S DISCRETIONARY FUND FINAL REPORT

#### I. INTRODUCTION

##### 1.1 Physical Picture of Ostwald Ripening

Imagine a solution containing two chemical components. The solution is supersaturated with solute, and nuclei of a second phase have already started to grow. The supersaturated solution shall be called the parent phase, and the nuclei shall be termed the second phase. The nuclei shall be assumed large enough to have well-defined surfaces so that macroscopic theories such as thermodynamics can be applied. Such nuclei shall be called grains. Of interest is the grain size distribution function and its development over time. The grain size distribution evolves so as to reduce the surface area of contact between the two phases, which also serves to reduce the interfacial free energy. The dynamics of this process is termed Ostwald ripening [1]. Here, it shall be assumed that the transfer of material between the two phases is governed by Fick's laws of diffusion. The two phases may be any pairing of solid, liquid, or gas, except both cannot be gases, since gases are miscible in all proportions.

During Ostwald ripening, the solute supersaturation in the parent phase diminishes with time tending asymptotically to zero. At any given time, the value of the supersaturation determines a critical grain size. Grains larger than this tend to grow, while grains smaller tend to dissolve. The parent phase is the medium through which the grains communicate by way of mass transfer. Associated with each grain are local concentration gradients of solute and solvent. For example, a grain which is growing by concentrating solute and rejecting solvent has about it a positive solute gradient and a negative solvent gradient.

It is a main objective of this report to treat quantitatively the situation where diffusion of both solvent and solute occur in the parent phase. Associated with these diffusion fluxes are bulk transfers of material termed advectations. These shall be treated by referring the diffusion to a coordinate frame in the parent phase which moves with respect to the laboratory [2]. Our result will permit the extension of the current theory of Ostwald ripening [3-5] to the case where both chemical components occur in both phases. Phase separating systems possessing a miscibility gap are an important example.

As the total volume occupied by the grains increases, the grains come closer together, and the associated concentration gradients begin to overlap. Overlapping concentration gradients mean interacting local rates of growth and dissolution. The rate of growth of an individual grain is no longer the same as it would be if it were in isolation; instead, many-body effects come into play.

It is a second main objective of this report to incorporate these many-body effects into the theory of Ostwald ripening. The work of Marqusee and Ross [6] will be followed to accomplish this. An extended, pedagogical development of their original ideas shall be given.

Our program consists essentially of four tasks:

(1) Derive the Gibbs-Kelvin equation relating the solubility of a grain to its size (see Section 1.2).

(2) Taking into account growth and dissolution, develop a continuity equation for the time evolution of the grain size distribution function (see Section 1.3).

(3) At any given time the total masses of solute and solvent are divided between the parent phase and the second phase. This division must satisfy a conservation equation, derived in Section 1.4.

(4) In the continuity equation, there occurs a function depending upon the grain size and the time, which specifies the rate of growth of an individual grain. This growth velocity function, which is derived in Section 1.5, depends on a carefully defined diffusion coefficient. All of Chapter II is occupied with the problem of generalizing this function to take into account the effect of overlapping concentration gradients. This technically involved subject will be treated within the framework of the classical many-body theory of statistical mechanics.

In summary, Chapters I and II are devoted to the program above. The work of combining the results of this program into a single differential equation is presented in Sections 3.1-3.4 of Chapter III. In Section 3.5, that equation is integrated, and the functional form of the grain size distribution function is found. Parameters associated with that distribution are determined as a function of the volume fraction of the system in Sections 3.6-3.7. In Section 3.8, results are presented graphically and by equations in a form ready for comparison with experiment. The system succinonitrile/water is analyzed as an example. At the end of the report are five appendices explaining the mathematical techniques used in Chapters I-III and deriving certain technical details associated with the solution of the continuity equation for the grain size distribution function.

## 1.2 Solubility and the Gibbs-Kelvin Equation

A molecule in the interior of a precipitate grain is bound by forces which are characteristic of the bulk precipitate phase. A molecule in the surface of the grain, however, has some of its atomic bonding contacts satisfied by molecules in the parent phase which are adjacent to it. These contacts provide less stabilizing (negative) energy for the surface molecule than the contacts it would enjoy if it were in the bulk of the grain. Hence, in an algebraic sense the chemical potential of a molecule in the interior of the grain is less than a molecule in the surface.

Suppose now that the parent phase is an ideal solution composed of components A and B with concentrations (molecules/cm<sup>3</sup>)  $C_A$  and  $C_B$ , respectively. The corresponding chemical potentials are  $\mu_A$  and  $\mu_B$ , respectively, which are given by

$$\mu_A = \mu_A^{\circ} + kT \ln C_A \quad (1.2.1)$$

$$\mu_B = \mu_B^{\circ} + kT \ln C_B \quad (1.2.2)$$

where  $\mu_A^{\circ}$  and  $\mu_B^{\circ}$  are the chemical potentials defined in the standard states  $C_A = 1$  and  $C_B = 1$ . Here  $k$  is Boltzmann's constant and  $T$  is the absolute temperature.

Consider a grain which is part of the second phase that has precipitated from the parent phase. Let there be  $n'_A$  and  $n'_B$  molecules of A and B in this grain and let its surface area be  $S'$  and its volume be  $V'$ . The composition of the second phase is, of course, different than that of the parent phase. The chemical potentials of A and B molecules in the bulk of the grain are  $\mu'_A$  and  $\mu'_B$ , respectively. The grain forms a surface with the parent phase with surface energy given by  $\gamma$ . The Gibbs free energy of component A in the grain is

$$G'_A = n'_A \mu'_A + \gamma S' \quad (1.2.3)$$

and of component B

$$G'_B = n'_B \mu'_B + \gamma S' \quad (1.2.4)$$

To obtain chemical potentials for the grain as a whole, we must differentiate Eqs. (1.2.3) and (1.2.4) with respect to  $n'_A$  and  $n'_B$ , respectively. In so doing, we should hold in mind that  $S'$  depends upon the number of molecules,  $n'_A$  and  $n'_B$ , in the grain. In other words, the larger the grain, the larger its surface area. The chemical potential of A' in the grain is



$$\mu_A' = \frac{\partial G_A'}{\partial n_A'} = \mu_A'^o + \gamma \frac{dS'}{dV'} \cdot \frac{\partial V'}{\partial n_A'} \quad (1.2.5)$$

where to compute  $\partial S' / \partial n_A'$  we have used the chain rule with  $V'$  as the intermediate variable.

The derivative  $dS'/dV'$  depends on the geometric shape of the grain. At this point we specialize our analysis to spheres for which  $S' = 4\pi R^2$  and  $V' = (4\pi/3)R^3$  where  $R$  is the radius. The derivative is

$$\frac{dS'}{dV'} = \frac{8\pi R dR}{4\pi R^2 dR} = \frac{2}{R} \quad (1.2.6)$$

The partial molecular volume of component A in the grain is

$$\bar{V}_A' = \frac{\partial V'}{\partial n_A'} \quad (1.2.7)$$

Substituting Eqs. (1.2.6) and (1.2.7) into Eq. (1.2.5), we obtain

$$\mu_A' = \mu_A'^o + \frac{2\gamma \bar{V}_A'}{R} \quad (1.2.8)$$

At equilibrium  $\mu_A' = \mu_A^o$ . This determines the dependence on  $C_A$  on  $R$ . Equating Eqs. (1.2.1) and (1.2.8), we obtain

$$kT \ln C_A(R) = -(\mu_A^o - \mu_A'^o) + \frac{2\gamma \bar{V}_A'}{R} \quad (1.2.9)$$

In the limit  $R \rightarrow \infty$ ,  $C_A(R) \rightarrow C_A(\infty)$ , and according to Eq. (1.2.9)

$$kT \ln C_A(\infty) = -(\mu_A^o - \mu_A'^o) \quad (1.2.10)$$

Equation (1.2.10) gives the solubility,  $C_A(\infty)$ , of a flat surface (infinite radius of curvature) and is the usual equilibrium expression for the concen-

tration of a component distributed between two phases. We substitute Eq. (1.2.10) into Eq. (1.2.9) to obtain

$$C_A(R) = C_A(\infty) \exp(2\bar{V}_A'/kTR) . \quad (1.2.11)$$

Equation (1.2.11) is called the Gibbs-Kelvin equation and shows how the equilibrium solubility of a component outside a curved surface depends upon radius.

Starting from Eqs. (1.2.2) and (1.2.4), we may derive by analogy

$$C_B(R) = C_B(\infty) \exp(2\bar{V}_B'/kTR) . \quad (1.2.12)$$

### 1.3 Continuity Equation

Consider a system at time  $t$  consisting of a large number of grains. Let  $n(R,t)dR$  be the number of grains per unit volume with radii lying between  $R$  and  $R + dR$ . As the grains grow in size, their number must decrease because the total mass in the system must be conserved. Suppose that the time rate of change of the radius of any grain is known and is expressed by the equation

$$\frac{dR(t)}{dt} = V(R(t),t) \quad (1.3.1)$$

where the function  $V(R(t),t)$  contains all of the information specifying the growth dynamics. Suppose further that at a fixed time  $t$ , we are able to determine the grain densities  $n(R(t),t)$  and  $n(R(t) + dR,t)$  at radii  $R(t)$  and  $R(t) + dR$ , respectively. The flux of grains leaving  $R(t)$  is  $n(R(t),t)V(R(t),t)$  while the flux leaving  $R(t) + dR$  is  $n(R(t) + dR,t)V(R(t) + dR,t)$ . The net rate of buildup of grains between  $R(t)$  and  $R(t) + dR$  is  $(\partial n(R(t),t)/\partial t)dR$ . To conserve numbers, we must have

$$\begin{aligned} \frac{\partial n(R(t),t)}{\partial t} dR &= n(R(t),t)V(R(t),t) \\ &- n(R(t) + dR,t)V(R(t) + dR,t) . \end{aligned} \quad (1.3.2)$$

We expand the last term on the right-hand side of Eq. (1.3.2) in a Taylor's series about  $R(t)$ ,

$$n(R(t) + dR, t)V(R(t) + dR, t) - n(R(t), t)V(R(t), t) + \frac{\partial(n(R(t), t)V(R(t), t))}{\partial R} dR = 0 \quad (1.3.3)$$

Substitution of Eq. (1.3.3) into Eq. (1.3.2) and cancellation of  $dR$  yields

$$\frac{\partial n(R(t), t)}{\partial t} + \frac{\partial(n(R(t), t)V(R(t), t))}{\partial R} = 0 \quad (1.3.4)$$

Equation (1.3.4) is called the continuity equation for the grain size density  $n(R(t), t)$ .

A model for the "velocity,"  $V(R(t), t)$ , will be developed in Section 1.5.

#### 1.4 Conservation of Mass

At any time  $t$ , the total mass of any component (say A) is fixed in the system. In the bulk of the parent phase, the concentration of A (molecules/cm<sup>3</sup>) is  $C_A(t)$ . At  $t = 0$ , it was  $C_A(0)$ . Let us say that at  $t = 0$ , the parent phase is supersaturated in A so that  $C_A(0) > C_A(t)$ . Because of conservation of mass, the difference  $C_A(0) - C_A(t)$  is the amount of A deposited in grains at time  $t$ . The volume of a grain of radius  $R$  is  $(4\pi/3)R^3$  while the number of grains per unit volume with this radius is  $n(R, t)dR$ . The average molecular volume in a grain is  $\bar{V}' = X_A' \bar{V}_A' + X_B' \bar{V}_B'$ , where  $X_A'$  and  $X_B'$  are mole fractions describing the composition of a grain. The total number of molecules in grains of size  $R$  is  $(4\pi/3\bar{V}') R^3 n(R, t)dR$ . Of these,  $X_A'$  are molecules of A. Conservation of the total number of molecules of A dictates

$$C_A(0) = C_A(t) + \left(\frac{4\pi}{3\bar{V}'}\right) X_A' \int_0^{\infty} dR R^3 n(R, t) \quad (1.4.1)$$

where the integral on the right-hand side of Eq. (1.4.1) expresses the number of molecules of A in grains of all sizes.

Since  $C_A(0) > C_A(t)$ , the parent phase is rejecting A while the second phase is concentrating it. The reverse must be true for component B. Hence  $C_B(0) < C_B(t)$ , and

$$C_B(t) = C_B(0) + \left(\frac{4\pi}{3V}\right) X_B' \int_0^\infty dR R^3 n(R,t) \quad (1.4.2)$$

expresses the conservation of B.

### 1.5 Grain Size Growth Velocity

In the previous section, we noted that growing grains of the second phase were concentrating A while rejecting B. Hence, in the vicinity of a growing grain, there is a net flux of A toward the grain and a net flux of B away from it. Should the grain be dissolving, the situation is just reversed. In either case, at every point in the parent phase, it is possible to specify local velocities,  $\mathbf{v}_A$  and  $\mathbf{v}_B$ . These velocities are defined in the sense of hydrodynamics and express the transport of A and B, respectively, with respect to the laboratory. We may also define a volume averaged velocity,  $\mathbf{v}^\ddagger$ , given by [2]

$$\mathbf{v}^\ddagger = C_A \bar{V}_A \mathbf{v}_A + C_B \bar{V}_B \mathbf{v}_B \quad (1.5.1)$$

Let  $n_A$  be the number of molecules of A in the parent phase and let  $V_t$  be the total volume of the system. If  $\bar{V}_A$  is the volume occupied by an A molecule in the parent phase, then  $n_A \bar{V}_A$  is the total volume of A whereas  $n_A \bar{V}_A / V_t = C_A \bar{V}_A$  is the volume fraction occupied by A molecules. Likewise  $C_B \bar{V}_B$  is the volume fraction occupied by B molecules. Hence  $\mathbf{v}^\ddagger$  is a linear combination of velocities  $\mathbf{v}_A$  and  $\mathbf{v}_B$  weighted by respective volume fractions. We may also interpret  $\mathbf{v}^\ddagger$  by writing on the basis of the discussion above,

$$V_t \mathbf{v}^\ddagger = (n_A \bar{V}_A) \mathbf{v}_A + (n_B \bar{V}_B) \mathbf{v}_B \quad (1.5.2)$$

If in Eq. (1.5.2), the product  $n_A \bar{V}_A$  were replaced by  $m_A$ , the mass of A, and  $n_B \bar{V}_B$  replaced by  $m_B$ , the mass of B, whereas  $V_t$  were replaced by the total mass,  $m_t = m_A + m_B$ , we would readily recognize  $\mathbf{v}^\ddagger$  as the velocity of the center of mass. As written, however, it is clear that  $\mathbf{v}^\ddagger$  in Eq. (1.5.2) is the velocity of the "center of volume."

Physically, one may indeed see that there must be a velocity associated with the center of volume. Suppose  $\bar{V}_A < \bar{V}_B$  and consider a growing grain which is concentrating A and rejecting B. A molecules are rushing in toward the

grain while B molecules are leaving. Since larger molecules (B) are being replaced by smaller molecules (A), the center of volume is shifting; hence,  $\mathbf{v}^\ddagger \neq 0$ .

It is now useful to define molecular fluxes  $\mathbf{N}_A$  and  $\mathbf{N}_B$  by [2]

$$\mathbf{N}_A = C_A \mathbf{v}_A \quad (1.5.3)$$

$$\mathbf{N}_B = C_B \mathbf{v}_B \quad (1.5.4)$$

After adding and subtracting  $C_A \mathbf{v}^\ddagger$  and  $C_B \mathbf{v}^\ddagger$  from Eqs. (1.5.3) and (1.5.4), respectively, one obtains

$$\mathbf{N}_A = C_A \mathbf{v}^\ddagger + C_A (\mathbf{v}_A - \mathbf{v}^\ddagger) \quad (1.5.5)$$

$$\mathbf{N}_B = C_B \mathbf{v}^\ddagger + C_B (\mathbf{v}_B - \mathbf{v}^\ddagger) \quad (1.5.6)$$

By diffusion, we mean motion with respect to some center within the parent phase. We choose this reference point to be the center of volume. The terms in parentheses on the right-hand sides of Eqs. (1.5.5) and (1.5.6) are the diffusive velocities of A and B, respectively. We write the corresponding diffusive fluxes

$$C_A (\mathbf{v}_A - \mathbf{v}^\ddagger) = -D_A^\ddagger \nabla C_A \quad (1.5.7)$$

$$C_B (\mathbf{v}_B - \mathbf{v}^\ddagger) = -D_B^\ddagger \nabla C_B \quad (1.5.8)$$

Substituting Eqs. (1.5.7) and (1.5.8) into Eqs. (1.5.5) and (1.5.6) gives

$$\mathbf{N}_A = C_A \mathbf{v}^\ddagger - D_A^\ddagger \nabla C_A \quad (1.5.9)$$

$$\mathbf{N}_B = C_B \mathbf{v}^\ddagger - D_B^\ddagger \nabla C_B \quad (1.5.10)$$

The first terms on the right-hand sides of Eqs. (1.5.9) and (1.5.10) give the amount of material transported with respect to laboratory due to the motion of the center of volume. This transport is called "advection." The second terms on the right-hand sides give the material transported by diffusive motion

measured with respect to the center of volume, where  $D_A^\ddagger$  and  $D_B^\ddagger$  are the respective diffusion coefficients referred to that center.

In the remainder of this section, we have two goals. The first is to prove that referred to the center of volume, A and B have the same diffusion coefficient, namely  $D_A^\ddagger = D_B^\ddagger \equiv D$ , where D is termed the "interdiffusion coefficient." The second is to calculate the rate of diffusion into a growing grain, given boundary conditions specifying the concentrations on the surface of the grain and in the bulk of the parent phase. To reach these two goals, we must first demonstrate some theorems associated with diffusion in this frame of reference [2].

### 1.5.1 Two Diffusion Theorems

**Theorem 1:**  $C_A \bar{V}V_A + C_B \bar{V}V_B = 0$

**Proof:** Because the total volume of the parent phase  $V_t = V_t(n_A, n_B)$  is a homogeneous function of first degree, we have by Euler's theorem of thermodynamics

$$V_t = \bar{V}_A n_A + \bar{V}_B n_B \quad . \quad (T.1.1)$$

The function  $V_t(n_A, n_B)$  is also a state function (exact differential), so we have

$$\begin{aligned} dV_t &= \left(\frac{\partial V}{\partial n_A}\right) dn_A + \left(\frac{\partial V}{\partial n_B}\right) dn_B \\ &= \bar{V}_A dn_A + \bar{V}_B dn_B \quad . \end{aligned} \quad (T.1.2)$$

Now form the total differential of Eq. (T.1.1). We find

$$dV_t = \bar{V}_A dn_A + \bar{V}_B dn_B + n_A d\bar{V}_A + n_B d\bar{V}_B \quad . \quad (T.1.3)$$

Because of Eq. (T.1.2), we conclude from Eq. (T.1.3) that

$$n_A d\bar{V}_A + n_B d\bar{V}_B = 0 \quad . \quad (T.1.4)$$

Since the gradient operator involves just linear combinations of derivatives, we may write on the basis of Eq. (T.1.4)

$$n_A \bar{V}_A + n_B \bar{V}_B = 0 . \quad (\text{T.1.5})$$

We divide both sides of Eq. (T.1.5) by  $V_t$  and use  $C_A = n_A/V_t$  and  $C_B = n_B/V_t$  to obtain

$$C_A \bar{V}_A + C_B \bar{V}_B = 0 . \quad \text{Q.E.D. (T.1.6)}$$

**Theorem 2:**  $\bar{V}_A D_A^\ddagger VC_A + \bar{V}_B D_B^\ddagger VC_B = 0$

**Proof:** Multiply Eq. (1.5.7) by  $\bar{V}_A$  and Eq. (1.5.8) by  $\bar{V}_B$  and add the results

$$\begin{aligned} -\bar{V}_A D_A^\ddagger VC_A - \bar{V}_B D_B^\ddagger VC_B &= \bar{V}_A C_A (\mathbf{v}_A - \mathbf{v}^\ddagger) + \bar{V}_B C_B (\mathbf{v}_B - \mathbf{v}^\ddagger) \\ &= (C_A \bar{V}_A \mathbf{v}_A + C_B \bar{V}_B \mathbf{v}_B) - (\bar{V}_A C_A + \bar{V}_B C_B) \mathbf{v}^\ddagger . \end{aligned} \quad (\text{T.2.1})$$

The first term in parentheses in the second line of Eq. (T.2.1) is by Eq. (1.5.1) just  $\mathbf{v}^\ddagger$ . The second term is

$$\bar{V}_A C_A + \bar{V}_B C_B = (\bar{V}_A n_A + \bar{V}_B n_B) / V_t = 1 \quad (\text{T.2.2})$$

because

$$V_t = \bar{V}_A n_A + \bar{V}_B n_B . \quad (\text{T.2.3})$$

Using these results, we find for Eq. (T.2.1)

$$\bar{V}_A D_A^\ddagger VC_A + \bar{V}_B D_B^\ddagger VC_B = -\mathbf{v}^\ddagger + \mathbf{v}^\ddagger = 0 \quad \text{Q.E.D. (T.2.4)}$$

### 1.5.2 The Interdiffusion Coefficient

To show that only one diffusion coefficient is required to describe interdiffusion, we begin by forming the gradient of both sides of Eq. (T.2.2)

$$\begin{aligned} \nabla 1 = 0 &= \nabla(\bar{V}_A C_A + \bar{V}_B C_B) \\ &= C_A \nabla \bar{V}_A + C_B \nabla \bar{V}_B + \bar{V}_A \nabla C_A + \bar{V}_B \nabla C_B \\ &= \bar{V}_A \nabla C_A + \bar{V}_B \nabla C_B \end{aligned} \quad (1.5.11)$$

where we used the results of Theorem 1.

Now solve Eq. (1.5.11) for  $\bar{V}_B \nabla C_B$  and substitute the result into Eq. (T.2.4). One finds

$$0 = (D_A^\ddagger - D_B^\ddagger) \bar{V}_A \nabla C_A \quad (1.5.12)$$

Equation (1.5.12) can be true in general only if

$$D_A^\ddagger = D_B^\ddagger \equiv D \quad (1.5.13)$$

where we refer to the common value as the interdiffusion coefficient and denote it by  $D$ .

### 1.5.3 Rate Coefficient and the Effect of Advection

Consider a system of spherical polar coordinates and a grain of radius  $R$  with its center located at the origin. The geometry is illustrated in Figure 1.1. The fluxes of  $A$  and  $B$  molecules in the vicinity of this grain are given by Eqs. (1.5.9) and (1.5.10). Expressed in spherical polar coordinates, the first of these is

$$N_A = C_A v_A^\ddagger - D \frac{\partial C_A}{\partial r} \quad (1.5.14)$$



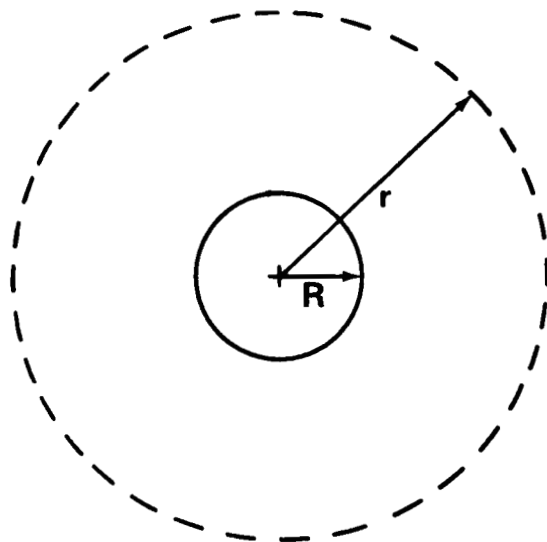


Figure 1.1. Geometry for calculating the diffusion into a spherical grain of radius,  $R$ .

In writing Eq. (1.5.14), we have made note of the fact that Figure 1.1 is spherically symmetric and that  $\mathbf{v}^\ddagger$  has only one component,  $v^\ddagger$ , which is in the radial direction. The term,  $C_A v^\ddagger$ , represents radial advection while the term,  $-D\partial C_A/\partial r$ , expresses radial diffusion. Transport in the two angular directions is prohibited by the symmetry. We also have used the results of Section 1.5.2 and set  $D_A^\ddagger = D$ .

We shall assume that the grain of radius  $R$  is isolated from all other grains and that there are no sinks nor sources for molecules anywhere except on its surface. Thus, molecules which cross the surface at  $R$  must also cross the surface of the larger sphere of radius  $r$  (broken circle in Figure 1.1). The total number of molecules of  $A$  crossing the sphere of radius  $r$  is  $I_A$  and is given by

$$I_A = 4\pi r^2 N_A = 4\pi r^2 C_A v^\ddagger - 4\pi r^2 D \frac{\partial C_A}{\partial r} \quad (1.5.15)$$

Because of mass conservation,  $I_A$  is a constant independent of  $r$ . Now in Eq. (1.5.15) replace  $v^\ddagger$  by its definition given by Eq. (1.5.1). The result is

$$\begin{aligned}
I_A &= (4\pi r^2 (C_{A A} v_A) \bar{V}_A + 4\pi r^2 (C_{B B} v_B) \bar{V}_B) C_A - 4\pi r^2 D \frac{\partial C_A}{\partial r} \\
&= (I_A \bar{V}_A + I_B \bar{V}_B) C_A - 4\pi r^2 D \frac{\partial C_A}{\partial r}
\end{aligned} \tag{1.5.16}$$

where we have used Eqs. (1.5.3), (1.5.4), and (1.5.15). We have noted that

$$I_B = 4\pi r^2 N_B \quad . \tag{1.5.17}$$

Our argument that  $I_A$  is constant also applies to  $I_B$ . This permits us to define a constant rate of flow of volume,  $u$ , by

$$u = I_A \bar{V}_A + I_B \bar{V}_B \quad . \tag{1.5.18}$$

Using Eq. (1.5.18), we may cast Eq. (1.5.16) in the form of an ordinary differential equation of first order to be satisfied by  $C_A$ , namely,

$$\frac{\partial C_A}{\partial r} - \left( \frac{u}{4\pi D r^2} \right) C_A = - \frac{I_A}{4\pi D r^2} \quad . \tag{1.5.19}$$

The general solution to Eq. (1.5.19) is

$$C_A(r) = (I_A/u) + W \exp(-u/4\pi D r) \tag{1.5.20}$$

where  $W$  is a constant of integration.

By a diffusion-controlled precipitation, we mean one where the material just outside a grain is always in equilibrium with the material inside. The equilibrium concentration of A just outside the grain is given by Eq. (1.2.11). Hence, replacing  $C_A(r)$  on the left-hand side of Eq. (1.5.20) by  $C_A(R)$  and setting  $r = R$  on the right-hand side, we find

$$W = \exp(u/4\pi D R) [C_A(R) - (I_A/u)] \quad . \tag{1.5.21}$$

Replacing  $W$  in Eq. (1.5.20) by Eq. (1.5.21), we obtain

$$C_A(r) = \frac{I_A}{u} + (C_A(R) - \frac{I_A}{u}) \exp\left[\frac{u}{4\pi D R} \left(1 - \frac{R}{r}\right)\right] \quad . \tag{1.5.22}$$

Infinitely far from the grain, the concentration of A is undisturbed by the formation of the grain and has the value,  $C_A^{\text{bulk}}$ . Letting  $r \rightarrow \infty$  on the right-hand side of Eq. (1.5.22) and replacing  $C_A(r)$  by  $C_A^{\text{bulk}}$  on the left, we obtain an equation for  $I_A$

$$I_A = u [C_A(R) - C_A^{\text{bulk}}] [\exp(u/4\pi DR) - 1]^{-1} \quad (1.5.23)$$

Define the dimensionless parameter,  $b$ , by

$$b = u/4\pi DR \quad (1.5.24)$$

then Eq. (1.5.23) may be written

$$I_A = 4\pi DR [C_A(R) - C_A^{\text{bulk}}] b [e^b - 1]^{-1} \quad (1.5.25)$$

Since  $b$  depends on  $R$ , Eq. (1.5.25) is a rather complicated function of  $R$  to use in further analyses. We note, however, that near the end of the precipitation (a circumstance which shall be of interest to us), the net rate of growth given by  $u$  diminishes to the point where  $u/4\pi DR \ll 1$ . Letting  $e^b \approx 1 + b$  in Eq. (1.5.25), we find in this limit

$$I_A = 4\pi DR [C_A(R) - C_A^{\text{bulk}}] \quad (1.5.26)$$

Since  $D$  has the units of  $\text{cm}^2 \text{sec}^{-1}$  and  $R$  the units of  $\text{cm}$ , the product,  $4\pi DR$ , has units associated with a bimolecular rate constant, namely,  $\text{cm}^3 \text{sec}^{-1}$ . The two species reacting are A and the grains. The rate constant being a function of  $R$ , we write it as  $K(R)$ , where

$$K(R) = 4\pi DR \quad (1.5.27)$$

An expression for the transport of B, which is the analog of Eq. (1.5.26), can be obtained simply by replacing the subscripts A everywhere in that equation by B. Note also that when  $C_A(R) < C_A^{\text{bulk}}$  in Eq. (1.5.26), transport of A is in the negative  $r$  direction toward the grain. When  $C_A(R) > C_A^{\text{bulk}}$ , it is in the positive  $r$  direction away from the grain.

Because we have made the approximation  $b \ll 1$ , Eq. (1.5.27) has the same form as is found in the absence of advection [7]. The consideration of advection, nevertheless, has forced us to pay careful attention to the definition of the diffusion coefficients of species A and B. We have found that only one diffusion coefficient enters the theory and that it is the one governing interdiffusion. In the case that the parent phase is a liquid, D and its concentration dependence may be measured directly using the diaphragm cell technique [8,9].

#### 1.5.4 Diffusion-Controlled Growth Velocity

The rate of decrease of volume in the parent phase is  $I_A \bar{V}_A + I_B \bar{V}_B$  or  $u$  as defined by Eq. (1.5.18). The rate of increase of volume of the second phase grain is  $I_A \bar{V}'_A + I_B \bar{V}'_B$ . If  $\bar{V}'_A \neq \bar{V}_A$  and  $\bar{V}'_B \neq \bar{V}_B$  then as the precipitation proceeds there is a net change in the overall volume of the system. This introduces a new mechanism for growth in addition to diffusion and advection. Consider a second phase grain which is expanding faster than the parent phase is contracting, i.e.  $(I_A \bar{V}'_A + I_B \bar{V}'_B) > (I_A \bar{V}_A + I_B \bar{V}_B)$ . In this circumstance, the surface of the grain engulfs molecules of the parent phase as it advances [10]. This, however, is not a very important effect and shall be ignored in the remainder of this report.

We have been assuming that the second phase grain maintains its equilibrium composition during growth. The total rate of arrival of molecules to the grain is  $I_A + I_B$ ; hence, for the grain to have its equilibrium composition, the molecular rates,  $I_A$  and  $I_B$ , must satisfy the equations,

$$X'_A = \frac{I_A}{I_A + I_B} \quad (1.5.28)$$

$$X'_B = \frac{I_B}{I_A + I_B} \quad (1.5.29)$$

The volume of the second phase grain is  $(4\pi/3)R^3$ , and the rate of growth of this volume is

$$\frac{d}{dt} \left( \frac{4\pi}{3} R^3 \right) = -(I_A \bar{V}'_A + I_B \bar{V}'_B) \quad (1.5.30)$$

If we multiply and divide the right-hand side of Eq. (1.5.30) through by  $I_A + I_B$  and use Eqs. (1.5.28) and (1.5.29), we obtain

$$\frac{d}{dt} \left( \frac{4\pi}{3} R^3 \right) = -(I_A + I_B) (X'_A \bar{V}'_A + X'_B \bar{V}'_B) \quad (1.5.31)$$

Using Eq. (1.5.28) again, we may eliminate  $I_B$  from the right-hand side of Eq. (1.5.31) and obtain

$$\frac{d}{dt} \left( \frac{4\pi}{3} R^3 \right) = -I_A \cdot \frac{(X'_A \bar{V}'_A + X'_B \bar{V}'_B)}{X'_A} \quad (1.5.32)$$

Finally, we compute the indicated differentiation on the left-hand side of Eq. (1.5.32) and replace  $I_A$  on the right-hand side by Eq. (1.5.26), and obtain

$$\frac{dR}{dt} = \frac{(X'_A \bar{V}'_A + X'_B \bar{V}'_B)}{X'_A} \cdot \frac{D}{R} \cdot (C_A^{\text{bulk}} - C_A(R)) \quad (1.5.33)$$

Introducing the average molecular volume,  $\bar{V}'$ ,

$$\bar{V}' = X'_A \bar{V}'_A + X'_B \bar{V}'_B \quad (1.5.34)$$

Eq. (1.5.33) becomes

$$\frac{dR}{dt} = \frac{\bar{V}' D}{X'_A R} \cdot (C_A^{\text{bulk}} - C_A(R)) \equiv V(R,t) \quad (1.5.35)$$

Equation (1.5.35) is the grain size growth velocity,  $V(R,t)$ , first postulated in Eq. (1.3.1). The next chapter will be devoted to generalizing Eq. (1.5.35) to take into account competitive effects due to neighboring grains.

## II. EFFECT OF INTER-GRAIN COMPETITION ON THE GRAIN RADIUS GROWTH VELOCITY

### 2.1 Macroscopic Equation of Motion and Its Solution

We wish to calculate the rate of disappearance of solute molecules diffusing freely amongst some randomly placed spherical precipitate grains. The grains are stationary, and they and the diffusing molecules are immersed in a continuous medium in which the molecules have diffusion coefficient,  $D$ . Suppressing the subscripts, A and B, introduced in Chapter I, we let  $C(\mathbf{r}, t)$  be the concentration of diffusing molecules at the position,  $\mathbf{r}$ , and time,  $t$ . At the surface of a precipitate grain of radius  $R$ , the solute concentration is determined by the Gibbs-Kelvin equation, which takes the form,

$$C(R) = C(\infty) \exp(2\gamma\bar{V}'/kTR) \quad . \quad (2.1.1)$$

Whether a particular grain is absorbing solute (growing) or emitting solute (dissolving) depends upon the difference  $(C(\mathbf{r}, t) - C(R))$ . If positive, the grain is growing; if negative, it is dissolving. The specific rate of growth (dissolution) is  $K(R)$ , so that the rate is  $K(R)(C(\mathbf{r}, t) - C(R))$ . Let  $P(R)dR$  be the probability that a grain has a radius between  $R$  and  $R + dR$ . For the medium as a whole the rate of change of solute molecules due to the action of the grains is  $\int_0^{\infty} dR P(R) K(R) (C(\mathbf{r}, t) - C(R))$ .

Using this integral to take into account the loss of material by incorporation into grains, Fick's second law for  $C(\mathbf{r}, t)$  is

$$\frac{\partial C(\mathbf{r}, t)}{\partial t} - D\nabla^2 C(\mathbf{r}, t) = \phi(\mathbf{r}) - \int_0^{\infty} dR P(R) K(R) (C(\mathbf{r}, t) - C(R)) \quad (2.1.2)$$

where the function  $\phi(\mathbf{r})$  has been introduced to represent any continuously distributed sources of solute molecules. From a mathematical point of view, the presence of  $\phi(\mathbf{r})$  permits Eq. (2.1.2) to be treated by Green's function techniques. The relevant parts of this and other techniques of mathematical physics have been developed in Appendices A through D for those readers who may not be familiar with them. It is recommended that those appendices be studied now before going further.

The physical meaning of  $\phi(\mathbf{r})$  depends upon the situation, but one might think of  $\phi(\mathbf{r})$  as being equal to the quantum yield times the rate of absorbance of light producing some photochemical product, which is subsequently precipitating. Our results will be wholly independent of the form of  $\phi(\mathbf{r})$ , however.

In the steady state  $\partial C(\mathbf{r},t)/\partial t = 0$  and Eq. (2.1.2) becomes

$$-D\nabla^2 C(\mathbf{r}) = \phi(\mathbf{r}) - \int_0^\infty dR P(R) K(R) (C(\mathbf{r}) - C(R)) . \quad (2.1.3)$$

We may Fourier transform both sides of Eq. (2.1.3) using Eq. (D.26) of Appendix D to compute the transform of  $\nabla^2 C(\mathbf{r})$  and Eq. (D.10) with  $\mathbf{k}' = 0$  to compute the transform of  $\int_0^\infty dR P(R) C(R)$  which is independent of  $\mathbf{r}$ . The result is

$$k^2 \hat{D} \hat{C}(\mathbf{k}) = \hat{\phi}(\mathbf{k}) - \int_0^\infty dR P(R) K(R) (\hat{C}(\mathbf{k}) - (2\pi)^3 C(R) \delta(\mathbf{k})) . \quad (2.1.4)$$

Define

$$K_T = \int_0^\infty dR P(R) K(R) \quad (2.1.5)$$

and write Eq. (2.1.4) in the form

$$(k^2 D + K_T) \hat{C}(\mathbf{k}) = \hat{\phi}(\mathbf{k}) + \int_0^\infty dR P(R) K(R) C(R) (2\pi)^3 \delta(\mathbf{k}) \quad (2.1.6)$$

where  $\delta(\mathbf{k})$  is the Dirac delta function discussed in Appendices A and D. According to Appendix C and Eq. (D.35) of Appendix D, the Fourier transform of the Green's function  $G(\mathbf{r})$  for the operator,  $D\nabla^2$ , is

$$\hat{G}(\mathbf{k}) = -1/k^2 D . \quad (2.1.7)$$

Equation (2.1.7) permits Eq. (2.1.6) to be written

$$-\hat{C}(\mathbf{k}) = (1 - \hat{G}(\mathbf{k}) K_T)^{-1} [\hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) + \hat{G}(\mathbf{k})$$

$$\int_0^{\infty} dRP(R)K(R)C(R)(2\pi)^3\delta(\mathbf{k})] . \quad (2.1.8)$$

We next expand the factor  $(1 - \hat{G}(\mathbf{k})K_T)^{-1}$  in a geometric series

$$\frac{1}{1 - \hat{G}(\mathbf{k})K_T} = 1 + \hat{G}(\mathbf{k})K_T + (\hat{G}(\mathbf{k})K_T)^2 + (\hat{G}(\mathbf{k})K_T)^3 + \dots \quad (2.1.9)$$

and substitute into Eq. (2.1.8) to obtain

$$\begin{aligned} -\hat{C}(\mathbf{k}) = & [1 + (\hat{G}(\mathbf{k})K_T) + (\hat{G}(\mathbf{k})K_T)^2 + (\hat{G}(\mathbf{k})K_T)^3 + \dots] \\ & [\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) + \hat{G}(\mathbf{k}) \int_0^{\infty} dRP(R)K(R)C(R)(2\pi)^3\delta(\mathbf{k})] . \end{aligned} \quad (2.1.10)$$

We multiply out the brackets in Eq. (2.1.10) collecting together like powers of  $K_T$  and  $K(R)$ , since being proportional to the rate of precipitation, they are of the same order of magnitude. The result is

$$\begin{aligned} -\hat{C}(\mathbf{k}) = & \hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) + [\hat{G}(\mathbf{k})K_T\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) + \hat{G}(\mathbf{k}) \int_0^{\infty} dRP(R)K(R)C(R)(2\pi)^3\delta(\mathbf{k})] \\ & + [\hat{G}(\mathbf{k})K_T\hat{G}(\mathbf{k})K_T\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) + \hat{G}(\mathbf{k})K_T\hat{G}(\mathbf{k}) \int_0^{\infty} dRP(R)K(R)C(R)(2\pi)^3\delta(\mathbf{k})] \\ & + [\hat{G}(\mathbf{k})K_T\hat{G}(\mathbf{k})K_T\hat{G}(\mathbf{k})K_T\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) + \hat{G}(\mathbf{k})K_T\hat{G}(\mathbf{k})K_T\hat{G}(\mathbf{k}) \\ & \int_0^{\infty} dRP(R)K(R)C(R)(2\pi)^3\delta(\mathbf{k})] + \dots \end{aligned} \quad (2.1.11)$$

We next expand  $K(R)$  in a series analagous to a cluster expansion in the theory of the equation of state of real gases [11],

$$K(R) = \sum_{d=1}^N K(d|R) , \quad (2.1.12)$$

where  $N$  is the number of grains. The term,  $K(d|R)$ , represents the contribution to  $K(R)$  of an ensemble of grains, "d" in number, all competing for a diffusing solute molecule. Likewise,  $K_T$  which is the average of Eq. (2.1.12)



over the distribution of grain sizes may be developed in a cluster expansion, as

$$K_T = \sum_{d=1}^N K_T(d) \quad (2.1.13)$$

where

$$K_T(d) = \int_0^{\infty} dR P(R) K(d|R) . \quad (2.1.14)$$

We put Eqs. (2.1.12) and (2.1.13) into Eq. (2.1.11). For simplicity of notation, we suppress everywhere the dependence upon the Fourier transform variable,  $\mathbf{k}$ , and write

$$\begin{aligned} -\hat{C} = & \hat{G}_\phi + [\hat{G}(K_T(1) + K_T(2) + K_T(3) + \dots) \hat{G}_\phi + \hat{G} \\ & \int_0^{\infty} dR P(R) (K(1|R) + K(2|R) + K(3|R) + \dots) C(R) (2\pi)^3 \delta] \\ & + [\hat{G}(K_T(1) + K_T(2) + K_T(3) + \dots) \hat{G}(K_T(1) + K_T(2) + K_T(3) + \dots) \\ & \hat{G}_\phi + \hat{G}(K_T(1) + K_T(2) + K_T(3) + \dots) \hat{G} \\ & \int_0^{\infty} dR P(R) (K(1|R) + K(2|R) + K(3|R) + \dots) C(R) (2\pi)^3 \delta] \quad (2.1.15) \\ & + [\hat{G}(K_T(1) + K_T(2) + K_T(3) + \dots) \hat{G}(K_T(1) + K_T(2) + K_T(3) + \dots) \\ & \hat{G}(K_T(1) + K_T(2) + K_T(3) + \dots) \hat{G}_\phi \\ & + \hat{G}(K_T(1) + K_T(2) + K_T(3) + \dots) \hat{G}(K_T(1) + K_T(2) + K_T(3) + \dots) \\ & \hat{G} \int_0^{\infty} dR P(R) (K(1|R) + K(2|R) + K(3|R) + \dots) C(R) (2\pi)^3 \delta] . \end{aligned}$$

On the right-hand side of Eq. (2.1.15), terms of the same order need to be collected together. Note, for example, that  $K_T(2)$  and  $(K_T(1))^2$  are of the same (second) order, while  $(K_T(1))^3$ ,  $K_T(1)K_T(2)$ , and  $K_T(3)$  are of the same (third) order. The result is

$$\begin{aligned}
-\hat{C}(\mathbf{k}) &= \hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) + [\hat{G}(\mathbf{k})K_T(1)\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k})] + [\hat{G}(\mathbf{k})K_T(2)\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k})] \\
&\quad + \hat{G}(\mathbf{k})K_T(1)\hat{G}(\mathbf{k})K_T(1)\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) \\
&+ [\hat{G}(\mathbf{k})K_T(3)\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) + \hat{G}(\mathbf{k})K_T(1)\hat{G}(\mathbf{k})K_T(2)\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k})] \\
&+ \hat{G}(\mathbf{k})K_T(2)\hat{G}(\mathbf{k})K_T(1)\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) + \hat{G}(\mathbf{k})K_T(1)\hat{G}(\mathbf{k})K_T(1)\hat{G}(\mathbf{k})K_T(1)\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) \\
&+ \dots \tag{2.1.16} \\
&+ [\hat{G}(\mathbf{k}) \int_0^\infty dR P(R)K(3|R)C(R)(2\pi)^3 \delta(\mathbf{k}) + \hat{G}(\mathbf{k}) \int_0^\infty dR' P(R')K(1|R')\hat{G}(\mathbf{k}) \int_0^\infty \\
&\quad dR P(R)K(2|R)C(R)(2\pi)^3 \delta(\mathbf{k}) \\
&+ \hat{G}(\mathbf{k}) \int_0^\infty dR' P(R')K(2|R')\hat{G}(\mathbf{k}) \int_0^\infty dR P(R)K(1|R)C(R)(2\pi)^3 \delta(\mathbf{k}) \\
&+ \hat{G}(\mathbf{k}) \int_0^\infty dR'' P(R'')K(1|R'')\hat{G}(\mathbf{k}) \int_0^\infty dR' P(R')K(1|R')\hat{G}(\mathbf{k}) \int_0^\infty \\
&\quad dR P(R)K(1|R)C(R)(2\pi)^3 \delta(\mathbf{k})] \\
&+ \dots
\end{aligned}$$

This completes the analysis based upon a macroscopic point of view. In the next section (Section 2.2), we reanalyze this problem, working on the assumption that the locations of all the grains are known. Subsequently, in Section 2.3, we shall average the result from Section 2.2 over a distribution of grain sizes and locations (configurations) to obtain an equation for comparison with Eq. (2.1.16). This comparison will be carried out in Section 2.3 and will result in a revision of the formula,  $K(R) = 4\pi DR$ , to take into account the effect of grain density on the diffusion process.

## 2.2 Microscopic Equation of Motion and Its Solution

In this section, we seek to represent on a microscopic scale the diffusion of molecules among the grains. We specifically consider a continuous parent phase in which some grains of second phase are imbedded. The grains are

$N$  in number and have centers located by the set of coordinates  $\{\mathbf{r}_i\} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ . Let  $c(\mathbf{r}; \{\mathbf{r}_i\})$  be the concentration of molecules diffusing among the particular configuration,  $\{\mathbf{r}_i\}$ , of the grains. The equation of motion for  $c(\mathbf{r}; \{\mathbf{r}_i\})$  is Fick's second law, which in steady state takes the form

$$D\nabla^2 c(\mathbf{r}) = -\phi(\mathbf{r}) - \sum_{i=1}^N q_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (2.2.1)$$

where we have intentionally suppressed in  $c(\mathbf{r})$  the dependence upon  $\{\mathbf{r}_i\}$ . The  $i$ -th grain is located at  $\mathbf{r}_i$ , has radius  $R_i$ , and "strength"  $q_i$ , which expresses its ability to absorb or emit molecules. The spatial location of this strength is given by  $\delta(\mathbf{r} - \mathbf{r}_i)$ . Inasmuch as  $\delta(\mathbf{r} - \mathbf{r}_i)$  represents the location of a point particle, it is in seeming contradiction with our assignment of a radius,  $R_i$ , to the grain. This concept will be dealt with carefully when we determine the values of the  $\{q_i\}$ . For illustration, the geometry of just two grains is shown in Figure 2.1. More on the Dirac delta function can be found in Appendix A, whereas Fick's laws of diffusion are discussed in Appendix B.

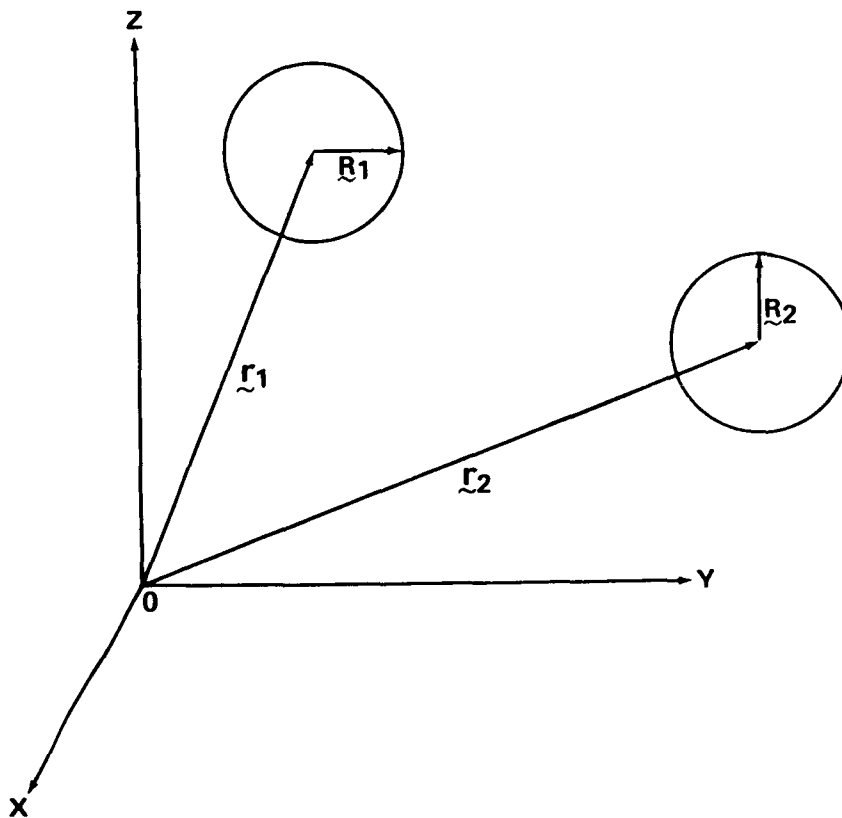


Figure 2.1. Coordinates locating the centers of two grains of radii  $R_1$  and  $R_2$ , respectively.

Each of the  $N$  grains is assumed to be in chemical equilibrium with the parent phase just outside its boundary. Hence, the concentration just outside each grain is specified by the Gibbs-Kelvin equation. Every point on the surface of a grain, in fact, must satisfy the Gibbs-Kelvin equation, so we have

$$c(\mathbf{r}_i + \mathbf{R}_i; \{\mathbf{r}_i\}) = C(R_i) = C(\infty) \exp(2\gamma\bar{V}/kTR_i), \quad i = 1, 2, \dots, M \quad (2.2.2)$$

where  $R_i = |\mathbf{R}_i|$ . If the grains are sufficiently dilute, then  $R_i = |\mathbf{R}_i| \ll |\mathbf{r}_i|$ , and we may to sufficient accuracy replace Eq. (2.2.2) by

$$c(\mathbf{r}_i; \{\mathbf{r}_i\}) = C(R_i) = C(\infty) \exp(2\gamma\bar{V}/kTR_i), \quad i = 1, 2, \dots, M \quad (2.2.3)$$

Eqs. (2.2.3) may be used to determine the  $\{q_i\}$  as follows.

As shown in Appendix C, the Green's function for the operator  $D\nabla^2$  is given by

$$G(\mathbf{r}|\mathbf{r}') = - \frac{1}{4\pi D|\mathbf{r} - \mathbf{r}'|} \quad (2.2.4)$$

which satisfies the boundary conditions

$$\lim_{r \rightarrow \infty} G(\mathbf{r}|\mathbf{r}') = \lim_{r \rightarrow \infty} \nabla G(\mathbf{r}|\mathbf{r}') = 0 \quad (2.2.5)$$

Hence, according to Appendix C, we may apply Green's theorem in the form

$$c(\mathbf{r}) = \int d^3\mathbf{r}' G(\mathbf{r}|\mathbf{r}') f(\mathbf{r}') \quad (2.2.6)$$

If on the right-hand side of Eq. (2.2.1) we replace  $i$  by  $j$  and make the identification

$$f(\mathbf{r}) = - \phi(\mathbf{r}) - \sum_{j=1}^N q_j \delta(\mathbf{r} - \mathbf{r}_j) \quad (2.2.7)$$

then we may solve Eq. (2.2.1) for  $c(\mathbf{r})$  in the form

$$\begin{aligned} -c(\mathbf{r}) &= \int d^3\mathbf{r}' G(\mathbf{r}|\mathbf{r}') [\phi(\mathbf{r}') + \sum_{j=1}^N q_j \delta(\mathbf{r}' - \mathbf{r}_j)] \\ &= \int d^3\mathbf{r}' G(\mathbf{r}|\mathbf{r}') \phi(\mathbf{r}') + \sum_{j=1}^N q_j G(\mathbf{r}|\mathbf{r}_j) \end{aligned} \quad (2.2.8)$$

where we have used Eq. (A.9) of Appendix A to evaluate the integral involving the delta function.

We next use Eq. (2.2.8) to evaluate  $c(\mathbf{r})$  on the boundary of the  $i$ -th grain. We note that this value,  $C(R_i)$  is established by Eq. (2.2.3). We find

$$-C(R_i) = \int d^3\mathbf{r}' G(\mathbf{r}_i|\mathbf{r}') \phi(\mathbf{r}') + q_i G(R_i) + \sum_{\substack{j=1 \\ \neq i}}^N q_j G(\mathbf{r}_i - \mathbf{r}_j). \quad (2.2.9)$$

To obtain Eq. (2.2.9) from Eq. (2.2.8), care has been exercised in evaluating  $G(\mathbf{r}|\mathbf{r}_j)$  on the surface of each sphere. The cases  $i=j$  and  $i \neq j$  must be distinguished. To evaluate  $G(\mathbf{r}|\mathbf{r}_j)$  on the surface of the  $i$ -th sphere where  $i=j$ , we have set  $\mathbf{r} = \mathbf{r}_i + \mathbf{R}_i$ , and written

$$G(\mathbf{r}_i + \mathbf{R}_i|\mathbf{r}_i) = - \frac{1}{4\pi D |\mathbf{r}_i + \mathbf{R}_i - \mathbf{r}_i|} = - \frac{1}{4\pi D |\mathbf{R}_i|} = - \frac{1}{4\pi D R_i} = G(R_i). \quad (2.2.10)$$

This accounts for the term  $q_i G(R_i)$  on the right-hand side of Eq. (2.2.9). To obtain  $G(\mathbf{r}|\mathbf{r}_j)$  on the surface of the  $i$ -th sphere ( $i \neq j$ ), we have set  $\mathbf{r} = \mathbf{r}_i + \mathbf{R}_i$ , and written

$$G(\mathbf{r}_i + \mathbf{R}_i|\mathbf{r}_j) = - \frac{1}{4\pi D |\mathbf{r}_i + \mathbf{R}_i - \mathbf{r}_j|} \approx - \frac{1}{4\pi D |\mathbf{r}_i - \mathbf{r}_j|} = G(\mathbf{r}_i - \mathbf{r}_j) \quad (2.2.11)$$

Eq. (2.2.11) follows because the dilute nature of the sinks which implies  $|\mathbf{R}_i| \ll |\mathbf{r}_i - \mathbf{r}_j|$  and  $|\mathbf{r}_i + \mathbf{R}_i - \mathbf{r}_j| \approx |\mathbf{r}_i - \mathbf{r}_j|$ . Eq. (2.2.11) accounts for all the terms within the sum on the right-hand side of Eq. (2.2.9).

By virtue of Appendix D and the fact that  $G(\mathbf{r}_i | \mathbf{r}') = -(4\pi D)^{-1} |\mathbf{r}_i - \mathbf{r}'|^{-1} = G(\mathbf{r} - \mathbf{r}')$ , we may recognize the integral term on the right-hand side of Eq. (2.2.9) as a convolution and write

$$G^* \phi(\mathbf{r}) = \int d^3 r' G(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') . \quad (2.2.12)$$

Substituting Eqs. (2.2.10) and (2.2.12), we solve Eq. (2.2.9) for  $q_i$ , as

$$q_i = 4\pi D R_i [G^* \phi(\mathbf{r}_i) + \sum_{\substack{j=1 \\ \neq i}}^N G(r_{ij}) q_j + C(R_i)] \quad (2.2.13)$$

where we write  $G(\mathbf{r}_i - \mathbf{r}_j) = G(r_{ij}) = -(4\pi D r_{ij})^{-1}$  with  $r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$ .

As it stands, Eq. (2.2.13) does not determine  $q_i$  because the equation depends for its evaluation upon a knowledge of the  $\{q_j\}$ ,  $j \neq i$ . By the method of successive approximations, however, we may use Eq. (2.2.13) to develop Eq. (2.2.8) in a power series. To do this, we replace  $j$  by  $i$  in Eq. (2.2.8) and write

$$-c(\mathbf{r}) = G^* \phi(\mathbf{r}) + \sum_{i=1}^N q_i G(\mathbf{r} | \mathbf{r}_i) . \quad (2.2.14)$$

Now substitute Eq. (2.2.13) into the right-hand side of Eq. (2.2.14). The result is

$$\begin{aligned} -c(\mathbf{r}) = G^* \phi(\mathbf{r}) + \sum_{i=1}^N G(\mathbf{r} - \mathbf{r}_i) 4\pi D R_i [G^* \phi(\mathbf{r}_i) + \\ \sum_{\substack{j=1 \\ \neq i}}^N G(r_{ij}) q_j + C(R_i)] . \end{aligned} \quad (2.2.15)$$

We expand Eq. (2.2.15) further. In Eq. (2.2.13), replace  $i$  by  $j$  and  $j$  by  $l$  to obtain

$$q_j = 4\pi DR_j [G^*\phi(\mathbf{r}_j) + \sum_{\substack{\ell=1 \\ \ell \neq j}}^N G(\mathbf{r}_{j\ell})q_\ell + C(R_j)] \quad (2.2.16)$$

Substitute Eq. (2.2.16) for  $q_j$  on the right-hand side of Eq. (2.2.15) to obtain

$$\begin{aligned} -c(\mathbf{r}) = & G^*\phi(\mathbf{r}) + \sum_{i=1}^N G(\mathbf{r} - \mathbf{r}_i)4\pi DR_i [G^*\phi(\mathbf{r}_i) + C(R_i)] \\ & + \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N G(\mathbf{r} - \mathbf{r}_i)4\pi DR_i G(\mathbf{r}_{ij})4\pi DR_j [G^*\phi(\mathbf{r}_j) + C(R_j)] \quad (2.2.17) \end{aligned}$$

$$+ \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \sum_{\substack{\ell=1 \\ \ell \neq j}}^N G(\mathbf{r} - \mathbf{r}_i)4\pi DR_i G(\mathbf{r}_{ij})4\pi DR_j G(\mathbf{r}_{j\ell})4\pi DR_\ell [G^*\phi(\mathbf{r}_\ell) + C(R_\ell)] \quad .$$

In Eq. (2.2.17) in the triple sum on the right, we have replaced  $q_\ell$  by  $4\pi DR_\ell [G^*\phi(\mathbf{r}_\ell) + C(R_\ell)]$  which is the leading term in the next substitution. This "closure" step is a necessary approximation if we are to have an equation for  $c(\mathbf{r})$  which is free of explicit dependence upon any of the  $\{q_i\}$ . Equation (2.2.17) is the result of only two successive approximations; the procedure, however, may be carried out to any higher degree of approximation desired.

It is now worthwhile to examine a product such as  $G(\mathbf{r} - \mathbf{r}_i) 4\pi DR_i G^*\phi(\mathbf{r}_i)$  which appears, for example, as a factor within the single sum in Eq. (2.2.17). If we define the "scattering" operator  $T_i(\mathbf{r}, \mathbf{r}')$  by

$$T_i(\mathbf{r}, \mathbf{r}') = 4\pi DR_i \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_i) \quad (2.2.18)$$

then the desired product can be written

$$\begin{aligned} & G(\mathbf{r} - \mathbf{r}_i)4\pi DR_i G^*\phi(\mathbf{r}_i) \\ & = G(\mathbf{r} - \mathbf{r}_i)4\pi DR_i \int d^3 r' G(\mathbf{r}_i - \mathbf{r}') \phi(\mathbf{r}') \quad (2.2.19) \\ & = \int d^3 r'' G(\mathbf{r} - \mathbf{r}'') \int d^3 r''' 4\pi DR_i \delta(\mathbf{r}''' - \mathbf{r}_i) \delta(\mathbf{r}'' - \mathbf{r}_i) \\ & \int d^3 r' G(\mathbf{r}'' - \mathbf{r}') \phi(\mathbf{r}') = G^* T_i^* G^* \phi(\mathbf{r}) \quad . \end{aligned}$$

Using Eqs. (2.2.18) and (2.2.19), we may write Eq. (2.2.17) in the form

$$\begin{aligned}
 -c(\mathbf{r}) &= G*\phi(\mathbf{r}) + \sum_{i=1}^N G*T_i*[G*\phi(\mathbf{r}) + C(R_i)] \\
 &+ \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N G*T_i * G*T_j * [G*\phi(\mathbf{r}) + C(R_j)] \\
 &+ \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \sum_{\substack{\ell=1 \\ \neq j}}^N G*T_i * G*T_j * G*T_\ell * [G*\phi(\mathbf{r}) + C(R_\ell)] + \dots \quad (2.2.20)
 \end{aligned}$$

The ultimate goal of this section is to obtain a result which can be compared with Eq. (2.1.16) of the previous section. In order to do this, we form the Fourier transform of both sides of Eq. (2.2.20). The transform of  $-c(\mathbf{r})$  is  $\hat{-c}(\mathbf{k})$ , but the transform of the right-hand side must be analyzed with some care. Because of the use of the convolution symbol throughout Eq. (2.2.20), it would seem that the transform of each term within the various sums would simply be the product of the individual transforms. However, Eq. (2.2.18) involves the product of delta functions and is not explicitly a function of  $\mathbf{r} - \mathbf{r}'$ , which was a property exploited in going from Eq. (D.14) to (D.15) of Appendix D. We will see, nevertheless, that Eqs. (D.18) and (D.19) apply if we define carefully the transform of  $T_i(\mathbf{r}, \mathbf{r}')$ . Consider the transform of  $G*T_i * G*\phi(\mathbf{r})$ . Since this is a transform of a convolution, we denote it by

$$\begin{aligned}
 (\text{FTC}) &= \int d^3 r e^{-i\mathbf{k}\cdot\mathbf{r}} G*T_i * G*\phi(\mathbf{r}) \\
 &= \int d^3 r e^{-i\mathbf{k}\cdot\mathbf{r}} \int d^3 r''' G(\mathbf{r}-\mathbf{r}''') \int d^3 r'' T_i(\mathbf{r}''', \mathbf{r}'') \int d^3 r' G(\mathbf{r}''-\mathbf{r}') \phi(\mathbf{r}') \\
 &= \int d^3 r \int d^3 r''' \int d^3 r'' \int d^3 r' e^{-i\mathbf{k}\cdot\mathbf{r}} G(\mathbf{r}-\mathbf{r}''') T_i(\mathbf{r}''', \mathbf{r}'') G(\mathbf{r}''-\mathbf{r}') \phi(\mathbf{r}') . \quad (2.2.21)
 \end{aligned}$$

Replace the variable  $\mathbf{r}$  by  $\xi = \mathbf{r} - \mathbf{r}'''$ , where  $d^3 r = d^3 \xi$ , so that Eq. (2.2.21) reads



$$\begin{aligned}
(\text{FTC}) &= \int d^3\xi e^{-i\mathbf{k}\cdot\xi} G(\xi) \int d^3\mathbf{r}''' \\
&\int d^3\mathbf{r}'' \int d^3\mathbf{r}' e^{-i\mathbf{k}\cdot\mathbf{r}'''} T_i(\mathbf{r}''', \mathbf{r}'') G(\mathbf{r}'' - \mathbf{r}') \phi(\mathbf{r}') .
\end{aligned} \tag{2.2.22}$$

Replace  $\mathbf{r}'''$  by  $\rho = \mathbf{r}''' - \mathbf{r}''$ , where  $d^3\mathbf{r}''' = d^3\rho$ , and for  $T_i(\mathbf{r}''', \mathbf{r}'')$  substitute

$$T_i(\mathbf{r}''', \mathbf{r}'') = 4\pi DR_i \delta(\mathbf{r}''' - \mathbf{r}_i) \delta(\mathbf{r}'' - \mathbf{r}_i) \tag{2.2.23}$$

so that Eq. (2.2.22) reads

$$\begin{aligned}
(\text{FTC}) &= \int d^3\xi e^{-i\mathbf{k}\cdot\xi} G(\xi) 4\pi DR_i \int d^3\mathbf{r}'' e^{-i\mathbf{k}\cdot\mathbf{r}''} \delta(\mathbf{r}'' - \mathbf{r}_i) \int d^3\rho e^{-i\mathbf{k}\cdot\rho} \delta(\rho - (\mathbf{r}_i - \mathbf{r}'')) \\
&\quad \times \int d^3\mathbf{r}' G(\mathbf{r}'' - \mathbf{r}') \phi(\mathbf{r}') \\
&= \int d^3\xi e^{-i\mathbf{k}\cdot\xi} G(\xi) 4\pi DR_i \int d^3\mathbf{r}'' e^{-i\mathbf{k}\cdot\mathbf{r}''} \delta(\mathbf{r}'' - \mathbf{r}_i) e^{-i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}'')} \\
&\quad \times \int d^3\mathbf{r}' G(\mathbf{r}'' - \mathbf{r}') \phi(\mathbf{r}') .
\end{aligned} \tag{2.2.24}$$

In Eq. (2.2.24), we have used the right-hand side of Eq. (D.7) to evaluate the integral over  $d^3\rho$ .

For  $\delta(\mathbf{r}'' - \mathbf{r}_i)$ , it is convenient to use the Fourier representation given by Eq. (D.8) which reads

$$\delta(\mathbf{r}'' - \mathbf{r}_i) = \delta(\mathbf{r}_i - \mathbf{r}'') = (1/2\pi)^3 \int d^3\mathbf{k}' e^{i\mathbf{k}'\cdot(\mathbf{r}_i - \mathbf{r}'')} . \tag{2.2.25}$$

In writing Eq. (2.2.25), we have exploited the fact that the delta function is an even function of its argument [see Eq. (A.14) of Appendix A]. Substituting Eq. (2.2.25) into Eq. (2.2.24) yields

$$\begin{aligned}
(\text{FTC}) &= \int d^3 \xi e^{-i\mathbf{k} \cdot \xi} G(\xi) 4\pi \text{DR}_i \int d^3 \mathbf{r}'' e^{-i\mathbf{k} \cdot \mathbf{r}''} \left(\frac{1}{2\pi}\right)^3 \int d^3 \mathbf{k}' e^{i\mathbf{k}' \cdot (\mathbf{r}_i - \mathbf{r}'')} e^{-i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}'')} \\
&\quad \times \int d^3 \mathbf{r}' G(\mathbf{r}'' - \mathbf{r}') \phi(\mathbf{r}') \\
&= \left[ \int d^3 \xi e^{-i\mathbf{k} \cdot \xi} G(\xi) \right] \left[ 4\pi \text{DR}_i \left(\frac{1}{2\pi}\right)^3 \int d^3 \mathbf{k}' e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}_i} \right] \\
&\quad \times \left[ \int d^3 \mathbf{r}'' e^{-i\mathbf{k}' \cdot \mathbf{r}''} \int d^3 \mathbf{r}' G(\mathbf{r}'' - \mathbf{r}') \phi(\mathbf{r}') \right] \tag{2.2.26}
\end{aligned}$$

$$\begin{aligned}
&= \left[ \int d^3 \xi e^{-i\mathbf{k} \cdot \xi} G(\xi) \right] \left[ 4\pi \text{DR}_i \left(\frac{1}{2\pi}\right)^3 \int d^3 \mathbf{k}' e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}_i} P(\mathbf{k}|\mathbf{k}') \right] \\
&\quad \times \left[ \int d^3 \mathbf{r}'' e^{-i\mathbf{k}' \cdot \mathbf{r}''} \int d^3 \mathbf{r}' G(\mathbf{r}'' - \mathbf{r}') \phi(\mathbf{r}') \right] . \tag{2.2.27}
\end{aligned}$$

Note that within the last bracket on the right-hand side of Eq. (2.2.27), we have replaced  $\mathbf{k}'$  by  $\mathbf{k}$ , and in the next to last bracket introduced the symbol,  $P(\mathbf{k}|\mathbf{k}')$ . The effect of  $P(\mathbf{k}|\mathbf{k}')$  is to change  $\mathbf{k}$  to  $\mathbf{k}'$  in all functions on its right. This permits us to go from Eq. (2.2.26) to (2.2.27) and to identify the last bracket as  $\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k})$  using Eqs. (D.18) and (D.19). We further define

$$\hat{T}_i(\mathbf{k}) = 4\pi \text{DR}_i \left(\frac{1}{2\pi}\right)^3 \int d^3 \mathbf{k}' e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}_i} P(\mathbf{k}|\mathbf{k}') . \tag{2.2.28}$$

With Eq. (2.2.28) and the results of this paragraph, we may write Eq. (2.2.27) in the form

$$(\text{FTC}) = \hat{G}(\mathbf{k})\hat{T}_i(\mathbf{k})\hat{G}(\mathbf{k})\hat{\phi}(\mathbf{k}) . \tag{2.2.29}$$

Note carefully that because of the definition of  $P(\mathbf{k}|\mathbf{k}')$ ,  $\hat{T}_i(\mathbf{k})$  is an operator in  $\mathbf{k}$  space, and it and functions of  $\mathbf{k}$ , such as  $\hat{G}(\mathbf{k})$  and  $\hat{\phi}(\mathbf{k})$ , do not commute.

To complete the calculation of the transform of Eq. (2.2.20), we need also to compute the transform of terms of the type  $G*\hat{T}_i*C(R_i)$ . Let the transform of a term of this type be called FTD. The manipulations for computing FTD are the same as Eqs. (2.2.21)-(2.2.27); namely,

$$\begin{aligned}
(\text{FTD}) &= \left[ \int d^3 \xi e^{-i\mathbf{k} \cdot \xi} G(\xi) \right] \left[ 4\pi \text{DR}_i \left(\frac{1}{2\pi}\right)^3 \int d^3 \mathbf{k}' e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}_i} P(\mathbf{k}|\mathbf{k}') \right] \\
&\quad \times \left[ \int d^3 \mathbf{r}'' e^{-i\mathbf{k} \cdot \mathbf{r}''} C(R_i) \right] . \tag{2.2.30}
\end{aligned}$$

Equations (2.2.27) and (2.2.30) are identical except for the last bracket in Eq. (2.2.30) involving the constant  $C(R_i)$ , which replaces  $G^*\phi(\mathbf{r})$  in Eq. (2.2.27). Since  $C(R_i)$  does not involve  $\mathbf{r}''$ , it may be factored out of the bracket. After factoring, if we then compare the last integral in Eq. (2.2.30) with Eq. (D.10) with  $\mathbf{k}' = 0$ , we have

$$C(R_i) \int d^3 \mathbf{r}'' e^{-i\mathbf{k} \cdot \mathbf{r}''} = C(R_i) (2\pi)^3 \delta(\mathbf{k}) . \quad (2.2.31)$$

Combining Eqs. (2.2.30) and (2.2.31) and using the previous results of this section, we find

$$(\text{FTD}) = \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) C(R_i) (2\pi)^3 \delta(\mathbf{k}) . \quad (2.2.32)$$

Applying Eqs. (2.2.29) and (2.2.32) to Eq. (2.2.20), we get

$$\begin{aligned} -\hat{c}(\mathbf{k}) &= \hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) + \sum_{i=1}^N \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) [\hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) + C(R_i) (2\pi)^3 \delta(\mathbf{k})] \\ &+ \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) [\hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) + C(R_j) (2\pi)^3 \delta(\mathbf{k})] \end{aligned} \quad (2.2.33)$$

$$+ \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \sum_{\substack{\ell=1 \\ j \neq \ell}}^N \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) [\hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) + C(R_\ell) (2\pi)^3 \delta(\mathbf{k})] .$$

Equation (2.2.33) applies to a configuration of grains with specified radii and fixed locations. Ordinarily, there are so many grains that it is impossible to specify either their radii or their locations. Rather, only the probability of a given radius and probability of a given location can be specified. In Section 2.1, we let  $P(R)dR$  be the probability of a grain having a radius lying between  $R$  and  $R + dR$ . If the volume of the system is  $V$ , the probability of finding the center of the  $i$ -th grain within an element of volume is  $d^3 \mathbf{r}_i / V$ . We now specify that the grains are randomly located and exert no long range forces on one another. Furthermore, we shall take their concentration small enough so that the fact that they must not overlap may be ignored. For these reasons, their positions are uncorrelated and the

probability of a given configuration (specified set of values for the  $\{r_i\}$ ) is just the product of individual probabilities, namely,  $\prod_{i=1}^N (d^3 r_i / V)$ . In Eq. (2.2.33),  $\hat{c}(\mathbf{k})$  is an implicit function of the radii  $\{R_i\}$  and the positions  $\{r_i\}$ . After drawing the  $\{R_i\}$  from the distribution  $P(R_i)$ , the configurational average of  $\hat{c}(\mathbf{k})$  should be equal to  $\hat{C}(\mathbf{k})$  in Eq. (2.1.16). We define

$$\langle\langle \hat{c}(\mathbf{k}) \rangle\rangle \equiv \prod_{i=1}^N \int_0^\infty dR_i P(R_i) V^{-N} \prod_{j=1}^N \int d^3 r_j \hat{c}(\mathbf{k}) = \hat{C}(\mathbf{k}) \quad (2.2.34)$$

where  $\langle\langle \hat{c}(\mathbf{k}) \rangle\rangle$  symbolizes the average of  $c(\mathbf{k})$  over both the distribution of grain radii and the distribution of grain configurations.

We form the average of both sides of Eq. (2.2.33), taking note that because of (2.2.28),  $\hat{T}_i(\mathbf{k})$  depends upon both  $R_i$  and  $r_i$ . The result is

$$\begin{aligned} \langle\langle \hat{c}(\mathbf{k}) \rangle\rangle &= \hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) + \sum_{i=1}^N [\hat{G}(\mathbf{k}) \langle\langle \hat{T}_i(\mathbf{k}) \rangle\rangle \hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) \\ &+ \hat{G}(\mathbf{k}) \langle\langle \hat{T}_i(\mathbf{k}) C(R_i) \rangle\rangle (2\pi)^3 \delta(\mathbf{k})] \\ &+ \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N [\hat{G}(\mathbf{k}) \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \rangle\rangle \hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) + \\ &+ \hat{G}(\mathbf{k}) \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) C(R_j) \rangle\rangle (2\pi)^3 \delta(\mathbf{k})] \\ &+ \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \sum_{\substack{\ell=1 \\ \neq j}}^N [\hat{G}(\mathbf{k}) \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) \rangle\rangle \hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) + \\ &+ \hat{G}(\mathbf{k}) \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) C(R_\ell) \rangle\rangle (2\pi)^3 \delta(\mathbf{k}) + \dots] \quad (2.2.35) \end{aligned}$$

Note that  $P(R_\ell)$  is normalized to unity, namely,

$$\int_0^\infty dR_\ell P(R_\ell) = 1, \quad \ell = 1, 2, \dots, N \quad (2.2.36)$$

and also that

$$V^{-1} \int d^3 r_\ell = 1, \quad \ell = 1, 2, \dots, N. \quad (2.2.37)$$

Hence, averages of typical terms shown on the right-hand side of Eq. (2.2.35) follow. For example,

$$\langle\langle \hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) \rangle\rangle = \prod_{i=1}^N \int_0^\infty dR_i P(R_i) V^{-N} \prod_{j=1}^N \int d^3 r_j \hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) = \hat{G}(\mathbf{k}) \hat{\phi}(\mathbf{k}) \quad (2.2.38)$$

because neither  $\hat{G}(\mathbf{k})$  nor  $\hat{\phi}(\mathbf{k})$  depends upon any of the  $\{R_i\}$  or  $\{r_j\}$ . Another typical average is

$$\begin{aligned} \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \rangle\rangle &= \prod_{\ell=1}^N \int_0^\infty dR_\ell P(R_\ell) V^{-N} \prod_{m=1}^N \int d^3 r_m \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \\ &= \int_0^\infty dR_i P(R_i) \int_0^\infty dR_j P(R_j) V^{-2} \int d^3 r_i \int d^3 r_j \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \\ &= \prod_{\substack{\ell=1 \\ \neq i \\ \neq j}}^N \int_0^\infty dR_\ell P(R_\ell) V^{-(N-2)} \prod_{\substack{m=1 \\ \neq i \\ \neq j}}^N \int d^3 r_m \\ &= \int_0^\infty dR_i P(R_i) \int_0^\infty dR_j P(R_j) V^{-2} \int d^3 r_i \int d^3 r_j \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}). \quad (2.2.39) \end{aligned}$$

Note that because of Eqs. (2.2.36) and (2.2.37), the integrals involving neither  $i$  nor  $j$  are unity.

This completes the analysis based upon the microscopic point of view.

### 2.3 Rate Coefficient and Diffusion-Controlled Growth Velocity

By virtue of the connection between  $\langle\langle c(\mathbf{k}) \rangle\rangle$  and  $C(\mathbf{k})$  expressed by Eq. (2.2.34), Eqs. (2.1.16) and (2.2.35) express the same thing. Both Eqs. (2.1.16) and (2.2.35) have been organized so that terms of like order have been grouped together. Now comparing terms of like order between the two equations, we obtain

$$K_T(1) = \sum_{i=1}^N \langle\langle \hat{T}_i(\mathbf{k}) \rangle\rangle \quad (2.3.1)$$

$$K_T(2) + K_T(1)\hat{G}K_T(1) = \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \langle\langle \hat{T}_i(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_j(\mathbf{k}) \rangle\rangle \quad (2.3.2)$$

$$K_T(3) + K_T(1)\hat{G}K_T(2) + \hat{G}K_T(2)\hat{G}K_T(1) + K_T(1)\hat{G}K_T(1) = \quad (2.3.3)$$

$$\sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \sum_{\substack{\ell=1 \\ \neq j}}^N \langle\langle \hat{T}_i(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_j(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_\ell(\mathbf{k}) \rangle\rangle,$$

etc. The terms involving the grain surface concentration yield,

$$\int_0^\infty dR P(R) K(1|R) C(R) = \sum_{i=1}^N \langle\langle \hat{T}_i(\mathbf{k}) C(R_i) \rangle\rangle$$

$$\int_0^\infty dR P(R) K(2|R) C(R) + \int_0^\infty dR' P(R') K(1|R') \hat{G} \int_0^\infty dR P(R) K(1|R) C(R) \quad (2.3.4)$$

$$= \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) C(R_j) \rangle\rangle \quad (2.3.5)$$

$$\int_0^\infty dR P(R) K(3|R) C(R) + \int_0^\infty dR' P(R') K(1|R') \hat{G} \int_0^\infty dR P(R) K(2|R) C(R) \\ + \int_0^\infty dR' P(R') K(2|R') \hat{G} \int_0^\infty dR P(R) K(1|R) C(R) \\ + \int_0^\infty dR'' P(R'') K(1|R'') \hat{G} \int_0^\infty dR' P(R') K(1|R') \hat{G} \int_0^\infty dR P(R) K(1|R) C(R)$$

$$= \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \sum_{\substack{\ell=1 \\ \neq j}}^N \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) C(R_\ell) \rangle\rangle . \quad (2.3.6)$$

Equations (2.3.4)-(2.3.6) contain no information not already contained in Eqs. (2.3.1)-(2.3.3); hence, we shall choose Eqs. (2.3.1)-(2.3.3) for further analysis and proceed to the computation of the averages  $\langle\langle \hat{T}_i \rangle\rangle$ ,  $\langle\langle \hat{T}_i \hat{G} \hat{T}_j \rangle\rangle$  and  $\langle\langle \hat{T}_i \hat{G} \hat{T}_j \hat{G} \hat{T}_\ell \rangle\rangle$ .

### 2.3.1 Computation of $\langle\langle \hat{T}_i(\mathbf{k}) \rangle\rangle$ and $K_T(1)$

According to Eq. (2.2.28) and the definition of an ensemble average expressed by Eq. (2.2.34), the meaning of  $\langle\langle \hat{T}_i(\mathbf{k}) \rangle\rangle$  is

$$\langle\langle \hat{T}_i(\mathbf{k}) \rangle\rangle = \int_0^\infty dR_i P(R_i) 4\pi D R_i V^{-1} \int d^3 r_i \left(\frac{1}{2\pi}\right)^3 \int d^3 k' e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_i} P(\mathbf{k}|\mathbf{k}') . \quad (2.3.7)$$

We interchange the order of integration with respect to  $d^3 r_i$  and  $d^3 k'$  on the right-hand side of Eq. (2.3.7) and use Eq. (D.10) to recognize a delta function. Because there is no function (i.e., only unity) to the right of  $P(\mathbf{k}|\mathbf{k}')$  on which it can act, we may set  $P(\mathbf{k}|\mathbf{k}') = 1$ . We find,

$$\begin{aligned}
\langle\langle \hat{T}_i(\mathbf{k}) \rangle\rangle &= \int_0^\infty dR_i P(R_i) 4\pi DR_i V^{-1} \left(\frac{1}{2\pi}\right)^3 \int d^3 k' \int d^3 r_i e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}_i} \\
&= \int_0^\infty dR_i P(R_i) 4\pi DR_i V^{-1} \left(\frac{1}{2\pi}\right)^3 \int d^3 k' (2\pi)^3 \delta(\mathbf{k}'-\mathbf{k}) \\
&= 4\pi DV^{-1} \int_0^\infty dR_i P(R_i) R_i \\
&= 4\pi DV^{-1} \langle R \rangle
\end{aligned} \tag{2.3.8}$$

where we have used Eq. (A.9) with  $\mathbf{r} = \mathbf{k}'$ ,  $\mathbf{r}' = \mathbf{k}$ , and  $f(\mathbf{r}) = 1$ , and where by  $\langle R \rangle$ , we mean

$$\langle R \rangle = \int_0^\infty dR_i P(R_i) R_i \quad . \tag{2.3.9}$$

According to Eqs. (2.3.1) and (2.3.8)

$$K_T(1) = \sum_{i=1}^N \langle\langle \hat{T}_i(\mathbf{k}) \rangle\rangle = \sum_{i=1}^N 4\pi DV^{-1} \langle R \rangle = 4\pi D \langle R \rangle (N/V) \tag{2.3.10}$$

because there are  $N$  terms in Eq. (2.3.10), each equal to  $4\pi D \langle R \rangle V^{-1}$ . Hence,

$$K_T(1) = 4\pi D \rho \langle R \rangle \tag{2.3.11}$$

where

$$\rho = N/V \tag{2.3.12}$$

is the number density of grains.

### 2.3.2 Computation of $\langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \rangle\rangle$ and $K_T(2)$

According to Eqs. (2.2.28) and (2.2.39)

$$\begin{aligned}
&\langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \rangle\rangle \\
&= \int_0^\infty dR_i P(R_i) \int_0^\infty dR_j P(R_j) V^{-1} \int d^3 r_i 4\pi DR_i \left(\frac{1}{2\pi}\right)^3 \int
\end{aligned}$$



$$\begin{aligned}
& d^3 k' e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}_i} P(\mathbf{k}|\mathbf{k}') \hat{G}(\mathbf{k}) \\
& \times V^{-1} \int d^3 r_j 4\pi D R_j \left(\frac{1}{2\pi}\right)^3 \int d^3 k'' e^{i(\mathbf{k}'' - \mathbf{k}) \cdot \mathbf{r}_j} P(\mathbf{k}|\mathbf{k}'') \quad (2.3.13) \\
& = \int_0^\infty dR_i P(R_i) \int_0^\infty dR_j P(R_j) V^{-2} (4\pi D R_i) (4\pi D R_j) \\
& \quad \times \int d^3 k' \hat{G}(\mathbf{k}) \left(\frac{1}{2\pi}\right)^3 \int d^3 r_i e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}_i} \\
& \quad \times \int d^3 k'' \left(\frac{1}{2\pi}\right)^3 \int d^3 r_j e^{i(\mathbf{k}'' - \mathbf{k}') \cdot \mathbf{r}_j}
\end{aligned}$$

where we have used the definition of  $P(\mathbf{k}''|\mathbf{k}')$  to exchange  $\mathbf{k}$  for  $\mathbf{k}'$  in  $\hat{G}(\mathbf{k})$  and in  $e^{i(\mathbf{k}'' - \mathbf{k}') \cdot \mathbf{r}_j}$ .

We have also interchanged the order of integration with respect to  $d^3 r_i$  and  $d^3 k'$  and with respect to  $d^3 r_j$  and  $d^3 k''$ . In Eq. (2.3.13), the integral over  $d^3 r_i$  is equal to  $(2\pi)^3 \delta(\mathbf{k}' - \mathbf{k})$  while the integral over  $d^3 r_j$  is equal to  $(2\pi)^3 \delta(\mathbf{k}'' - \mathbf{k}')$ . After these identifications, we note that  $\int d^3 k' \hat{G}(\mathbf{k}') \delta(\mathbf{k}' - \mathbf{k}) = \hat{G}(\mathbf{k})$  by Eq. (D.12) and  $\int d^3 k'' \delta(\mathbf{k}'' - \mathbf{k}') = 1$  by Eq. (D.11). Equation (2.3.13) becomes

$$\begin{aligned}
\langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \rangle\rangle &= V^{-2} (4\pi D) \int_0^\infty dR_i P(R_i) R_i (4\pi D) \int_0^\infty dR_j P(R_j) R_j \hat{G}(\mathbf{k}) \\
&= V^{-2} (4\pi D \langle R \rangle) (4\pi D \langle R \rangle) \hat{G}(\mathbf{k}) \quad . \quad (2.3.14)
\end{aligned}$$

We observe that on the right-hand side of Eq. (2.3.2) there is a double sum, the inner sum having one less term ( $j \neq i$ ) than the outer. The outer sum (over  $i$ ) has  $N$  terms ( $i = 1, \dots, N$ ) while the inner sum (over  $j$ ) has  $(N-1)$  terms ( $j = 1, \dots, i-1, i+1, \dots, N$ ). Hence, the double sum has  $N(N-1)$  terms. Because  $\hat{G}(\mathbf{k})$  on the right-hand side of Eq. (2.3.14) depends upon neither  $i$  nor  $j$ , each of these terms is identical, and Eq. (2.3.2) becomes

$$\begin{aligned} K_T(2) + K_T(1)\hat{G}(\mathbf{k})K_T(1) &= \left(\frac{N}{V}\right)\left(\frac{N-1}{V}\right)(4\pi D\langle R \rangle)^2 \hat{G}(\mathbf{k}) \\ &= (4\pi D\rho\langle R \rangle)^2 \hat{G}(\mathbf{k}) \end{aligned} \quad (2.3.15)$$

To get Eq. (2.3.15), we have taken the "thermodynamic limit," wherein  $N \rightarrow \infty$ ,  $V \rightarrow \infty$  while the ratio,  $\rho = N/V$ , is held constant. When we substitute Eq. (2.3.11) into the left-hand side of Eq. (2.3.15), we find

$$K_T(2) = 0. \quad (2.3.16)$$

### 2.3.3 Computation of $\langle\langle \hat{T}_i(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_j(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_\ell(\mathbf{k}) \rangle\rangle$ , $K_T(3)$ , and Higher Order Terms. Use of Diagrams

In computing  $\langle\langle \hat{T}_i(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_j(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_\ell(\mathbf{k}) \rangle\rangle$ , we need to distinguish two cases.

Case I:  $i \neq \ell$

In this case, we have

$$\begin{aligned} &\langle\langle \hat{T}_i(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_j(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_\ell(\mathbf{k}) \rangle\rangle \\ &= \int_0^\infty dR_1 P(R_1) \int_0^\infty dR_j P(R_j) \int_0^\infty dR_\ell P(R_\ell) V^{-1} \int d^3 r_1 4\pi DR_1 \left(\frac{1}{2\pi}\right)^3 \int \\ &\quad d^3 k' e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}_1} P(\mathbf{k}|\mathbf{k}') \hat{G}(\mathbf{k}) \\ &\quad \times V^{-1} \int d^3 r_j 4\pi DR_j \left(\frac{1}{2\pi}\right)^3 \int d^3 k'' e^{i(\mathbf{k}''-\mathbf{k})\cdot\mathbf{r}_j} P(\mathbf{k}|\mathbf{k}'') \hat{G}(\mathbf{k}) \\ &\quad \times V^{-1} \int d^3 r_\ell 4\pi DR_\ell \left(\frac{1}{2\pi}\right)^3 \int d^3 k''' e^{i(\mathbf{k}'''-\mathbf{k})\cdot\mathbf{r}_\ell} P(\mathbf{k}|\mathbf{k}''') \end{aligned} \quad (2.3.17)$$

To simplify Eq. (2.3.17), we make repeated use of the techniques employed to go from Eq. (2.3.13) to Eq. (2.3.15). The result is

$$\langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) \rangle\rangle = v^{-3} (4\pi D \langle R \rangle)^3 (\hat{G}(\mathbf{k}))^2. \quad (2.3.18)$$

Case II:  $i=\ell$

Evaluation of the triple sum on the right-hand side of Eq. (2.3.3) requires  $j \neq i$  and  $\ell \neq j$ . Not ruled out, however, by these restrictions is the possibility,  $\ell=i$ . We now treat this case. Because  $\ell=i$ , we must return to Eq. (2.2.39) to reexamine the averaging process. On the basis of Eq. (2.2.38), an average over three  $\{\hat{T}_j(\mathbf{k})\}$  operators is

$$\begin{aligned} \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \rangle\rangle &= \prod_{\ell=1}^N \int_0^\infty dR_\ell P(R_\ell) v^{-N} \prod_{m=1}^N \int \\ & d^3 r_m \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \\ &= \int_0^\infty dR_1 P(R_1) \int_0^\infty dR'_1 P(R'_1) \int_0^\infty dR_j P(R_j) v^{-2} \int d^3 r_1 \int d^3 r_j \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \prod_{\substack{\ell=1 \\ \neq i \\ \neq j}}^N \int_0^\infty \\ & dR_\ell P(R_\ell) \prod_{\substack{m=1 \\ \neq i \\ \neq j}}^N \int d^3 r_m \\ &= \int_0^\infty dR_1 P(R_1) \int_0^\infty dR'_1 P(R'_1) \int_0^\infty dR_j P(R_j) v^{-2} \int d^3 r_1 \int \\ & d^3 r_j \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \end{aligned} \quad (2.3.19)$$

where we used Eqs. (2.2.36) and (2.2.37) to evaluate integrals not involving  $i$  and  $j$ . Substituting Eq. (2.2.28) into Eq. (2.3.19) we obtain

$$\begin{aligned}
& \langle \langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \rangle \rangle \\
&= \int_0^\infty dR_i P(R_i) \int_0^\infty dR'_i P(R'_i) \int_0^\infty dR_j P(R_j) V^{-1} \int d^3 r_i 4\pi DR_i \left(\frac{1}{2\pi}\right)^3 \int \\
&\quad d^3 k' e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}_i} P(\mathbf{k}|\mathbf{k}') \hat{G}(\mathbf{k}) \\
&\quad \times V^{-1} \int d^3 r_j 4\pi DR_j \left(\frac{1}{2\pi}\right)^3 \int d^3 k'' e^{i(\mathbf{k}''-\mathbf{k})\cdot\mathbf{r}_j} P(\mathbf{k}|\mathbf{k}'') \hat{G}(\mathbf{k}) \\
&\quad \times 4\pi DR'_i \left(\frac{1}{2\pi}\right)^3 \int d^3 k''' e^{i(\mathbf{k}'''-\mathbf{k})\cdot\mathbf{r}_i} P(\mathbf{k}|\mathbf{k}''') . \tag{2.3.20}
\end{aligned}$$

In Eq. (2.3.20), we gather together the integrals over  $dR_i$ ,  $dR'_i$ ,  $dR_j$ , compute them, and obtain the result  $(4\pi D \langle R \rangle)^3$ . Operating on unity,  $P(\mathbf{k}|\mathbf{k}''')$  has no effect. The remaining interchange operators must be carefully computed, however. We write the relevant factors from Eq. (2.3.20),

$$\begin{aligned}
& P(\mathbf{k}|\mathbf{k}') \hat{G}(\mathbf{k}) e^{i(\mathbf{k}''-\mathbf{k})\cdot\mathbf{r}_j} P(\mathbf{k}|\mathbf{k}'') \hat{G}(\mathbf{k}) e^{i(\mathbf{k}'''-\mathbf{k})\cdot\mathbf{r}_i} P(\mathbf{k}|\mathbf{k}''') \\
&= P(\mathbf{k}|\mathbf{k}') \hat{G}(\mathbf{k}) e^{i(\mathbf{k}''-\mathbf{k})\cdot\mathbf{r}_j} \hat{G}(\mathbf{k}'') e^{i(\mathbf{k}'''-\mathbf{k}'')\cdot\mathbf{r}_i} \\
&= \hat{G}(\mathbf{k}') e^{i(\mathbf{k}''-\mathbf{k}')\cdot\mathbf{r}_j} \hat{G}(\mathbf{k}'') e^{i(\mathbf{k}'''-\mathbf{k}'')\cdot\mathbf{r}_i} . \tag{2.3.21}
\end{aligned}$$

Taking note of Eq. (2.3.21) and the other results of this paragraph, we write Eq. (2.3.20) in the form

$$\begin{aligned}
& \langle \langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \rangle \rangle \\
&= (4\pi D) \int_0^\infty dR_i P(R_i) R_i (4\pi D) \int_0^\infty dR'_i P(R'_i) R'_i (4\pi D) \int_0^\infty dR_j P(R_j) R_j V^{-2} \left(\frac{1}{2\pi}\right)^3 \int \\
&\quad d^3 k' \hat{G}(\mathbf{k}') \left(\frac{1}{2\pi}\right)^3 \int d^3 k'' \hat{G}(\mathbf{k}'') \left(\frac{1}{2\pi}\right)^3 \int d^3 k''' \\
&\quad \times \left[ \int d^3 r_i e^{-i\mathbf{r}_i \cdot (\mathbf{k} - \mathbf{k}' + \mathbf{k}'' - \mathbf{k}''')} \right] \left[ \int d^3 r_j e^{-i\mathbf{r}_j \cdot (\mathbf{k}' - \mathbf{k}'')} \right]. \quad (2.3.22)
\end{aligned}$$

In Eq. (2.3.22), the first integral in brackets is equal to  $(2\pi)^3 \delta(\mathbf{k} - \mathbf{k}' + \mathbf{k}'' - \mathbf{k}''')$  =  $(2\pi)^3 \delta(\mathbf{k}''' - \mathbf{k}' + \mathbf{k}'' - \mathbf{k})$  =  $(2\pi)^3 \delta(\mathbf{k}''' - (\mathbf{k}' - \mathbf{k}'' + \mathbf{k}))$  because the delta function is even. The second integral in brackets is  $(2\pi)^3 \delta(\mathbf{k}' - \mathbf{k}'')$ . Putting these results in Eq. (2.3.22), we obtain

$$\begin{aligned}
& \langle \langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \rangle \rangle \\
&= (4\pi D \langle R \rangle)^3 V^{-2} \left(\frac{1}{2\pi}\right)^3 \int d^3 k' \hat{G}(\mathbf{k}') \\
&\quad \times \int d^3 k'' \delta(\mathbf{k}'' - \mathbf{k}') \hat{G}(\mathbf{k}'') \int d^3 k''' \delta(\mathbf{k}''' - (\mathbf{k}' - \mathbf{k}'' + \mathbf{k})) \\
&= (4\pi D \langle R \rangle)^3 V^{-2} \left(\frac{1}{2\pi}\right)^3 \int d^3 k' (\hat{G}(\mathbf{k}'))^2. \quad (2.3.23)
\end{aligned}$$

In obtaining the last line of Eq. (2.3.23), we have noted that the integral over  $d^3 k'''$  is unity due to Eq. (D.11) while the integral over  $d^3 k''$  is  $\hat{G}(\mathbf{k}')$  because of Eq. (D.12). To complete the evaluation of Eq. (2.3.23), we need to compute the remaining integral over  $d^3 k'$ . We may replace  $\hat{G}(\mathbf{k}')$  by  $(-1/D(k')^2)$  using Eq. (D.35). Although written  $\hat{G}(\mathbf{k}')$ , this function in fact depends only upon the length of the vector,  $k'$  [see Eq. (D.35)], and not its direction. Hence, it is worthwhile to compute the integral over  $d^3 k'$  using polar coordinates  $(k', \theta_{k'}, \phi_{k'})$  as follows

$$\begin{aligned}
& \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \rangle\rangle \\
&= (4\pi D \langle R \rangle)^3 V^{-2} \left(\frac{1}{2\pi}\right)^3 \int_0^\infty dk' (k')^2 (-1/D(k')^2)^2 \int_0^{2\pi} d\phi_{k'} \int_0^\pi d\theta_{k'} \sin\theta_{k'} \\
&= (4\pi D \langle R \rangle)^3 V^{-2} \cdot \frac{(4\pi)}{(2\pi)^3 D^2} \cdot \int_0^\infty dk' (k')^{-2} = \infty . \tag{2.3.24}
\end{aligned}$$

The integral on the third line of Eq. (2.3.24) is elementary, and also infinite! We deal with this difficulty below.

The left-hand sides of Eqs. (2.3.18) and (2.3.24) may be represented in terms of diagrams. Since  $\hat{G}(\mathbf{k})$  is the Fourier transform of the Green's function for free diffusion (which occurs between the grains), we represent a factor of  $\hat{G}(\mathbf{k})$  by a line containing an arrowhead. On the other hand,  $\hat{T}_i(\mathbf{k})$  is the Fourier transform of the operator describing interaction of a solute molecule with a precipitate grain of radius  $R_i$ . We represent a factor of  $\hat{T}_i(\mathbf{k})$  as a circle. Hence, the left-hand side of Eq. (2.3.18) may be represented as shown in Figure 2.2a

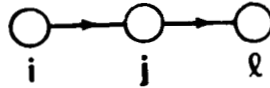


Figure 2.2a. Diagram representing the left-hand side of Eq. (2.3.18).

This may be interpreted as interaction at grain "i," followed by free diffusion, followed by interaction at grain "j," followed by free diffusion, followed by interaction at grain "l." The left-hand side of Eq. (2.3.24) can be represented as shown in Figure 2.2b,

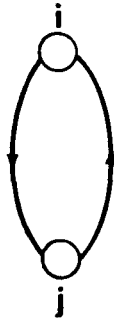


Figure 2.2b. Diagram representing the left-hand side of Eq. (2.3.24).

This may be interpreted as interaction at grain "i," followed by free diffusion, followed by interaction at grain "j," followed by free diffusion back to "i", followed by interaction at "i." For three grains, this diagram in Figure 2.2b is generalized as in Figure 2.2c,

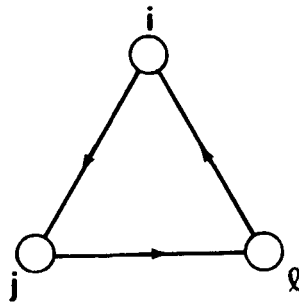


Figure 2.2c. Ring diagram for three grains.

Closed diagrams of the sort represented by Figures 2.2b and 2.2c are called "ring diagrams." Hence, the terms in the triple sum on the right-hand side of Eq. (2.3.3) are of two types: those represented by open diagrams, such as Figure 2.2a, and those represented by ring diagrams, such as Figure 2.2b.

Separating the two types of terms, the triple sum may be written

$$\begin{aligned}
& \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \sum_{\substack{\ell=1 \\ \neq j}}^N \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) \rangle\rangle \\
&= \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i \\ \neq j}}^N \sum_{\ell=1}^N \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) \rangle\rangle \\
&+ \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \rangle\rangle . \tag{2.3.25}
\end{aligned}$$

Making a count of terms of the type represented by Figure 2.2a, we note that there are  $N$  integral values that can be taken on by  $i$ , but once it is fixed, only  $(N-1)$  values can be assigned to  $j$ , and once  $j$  is fixed, only  $(N-2)$  can be assigned to  $\ell$ . Hence there are  $N(N-1)(N-2)$  terms in the triple sum of this type. Counting terms of the second type,  $i$  may be fixed in any of  $N$  ways, which leaves  $(N-1)$  ways of fixing  $j$ . Hence, there are  $N(N-1)$  terms of this type in the triple sum.

Because of Eq. (2.3.18), each term in the triple sum on the right-hand side of Eq. (2.3.25) is identical to every other term in that sum. Likewise, because of Eq. (2.3.24), each term in the double sum on the right-hand side of Eq. (2.3.25) is identical to every other term and is also infinite. Hence, using Eq. (2.3.18), Eq. (2.3.25) may be rewritten

$$\begin{aligned}
& \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \sum_{\substack{\ell=1 \\ \neq i \\ \neq j}}^N \langle\langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) \rangle\rangle \\
&= \left(\frac{N}{V}\right) \left(\frac{N-1}{V}\right) \left(\frac{N-2}{V}\right) (4\pi D \langle R \rangle)^3 (\hat{G}(\mathbf{k}))^2 + \\
&N(N-1) \langle\langle \hat{T}_1(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_2(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_1(\mathbf{k}) \rangle\rangle
\end{aligned}$$



$$= \rho^3 (4\pi D \langle R \rangle)^3 (\hat{G}(\mathbf{k}))^2 + N(N-1) \langle \hat{T}_1(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_2(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_1(\mathbf{k}) \rangle \quad (2.3.26)$$

where in the final step, we have taken the thermodynamic limit. In the second term on the right in each line of Eq. (2.3.26), we have replaced  $\hat{T}_i(\mathbf{k})$  by  $\hat{T}_1(\mathbf{k})$  and  $\hat{T}_j(\mathbf{k})$  by  $\hat{T}_2(\mathbf{k})$ , because Eq. (2.3.24) is independent of  $i$  and  $j$ ; hence, we may choose any convenient values for  $i$  and  $j$  so long as they are different.

We now substitute Eq. (2.3.26) into Eq. (2.3.3) and use Eqs. (2.3.11), and (2.3.16) to simplify the results. We obtain

$$\begin{aligned} K_T(3) + 4\pi D \rho \langle R \rangle \hat{G}(\mathbf{k}) 4\pi D \rho \langle R \rangle \hat{G}(\mathbf{k}) 4\pi D \rho \langle R \rangle \\ = \rho^3 (4\pi D \langle R \rangle)^3 (\hat{G}(\mathbf{k}))^2 + N(N-1) \langle \hat{T}_1(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_2(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_1(\mathbf{k}) \rangle . \end{aligned} \quad (2.3.27)$$

Because the terms involving  $\langle R \rangle$  on either side of Eq. (2.3.27) cancel, we have

$$K_T(3) = N(N-1) \langle \hat{T}_1(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_2(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_1(\mathbf{k}) \rangle \quad (2.3.28)$$

which shows that  $K_T(3)$  is determined solely by the infinite terms in the triple sum.

#### 2.3.4 Summing Ring Diagrams

So far, our analysis has carried us only up to the partial rate coefficient  $K_T(3)$ . If we were to push on to find  $K_T(4)$ , we could do so in complete analogy with the above. We would find

$$K_T(4) = \sum_{i=1}^N \sum_{\substack{j=1 \\ \neq i}}^N \sum_{\substack{\ell=1 \\ \neq j}}^N \langle \hat{T}_i(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_j(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_\ell(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_i(\mathbf{k}) \rangle . \quad (2.3.29)$$

The right-hand side of Eq. (2.3.29) is a sum over ring diagrams involving three grains. The diagrams are of the type shown in Figure 2.2c. When the ring sum in Eq. (2.3.29) is reduced as in the steps leading from Eq. (2.3.25) to Eq. (2.3.28), we find

$$K_T(4) = N(N-1)(N-2) \langle\langle \hat{T}_1(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_2(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_3(\mathbf{k}) \hat{G}(\mathbf{k}) \hat{T}_1(\mathbf{k}) \rangle\rangle . \quad (2.3.30)$$

Now read Eq. (2.3.30) from right to left. Refer respectively to Eqs. (2.2.28) and (2.3.21) for the definition of  $\hat{T}_1(\mathbf{k})$  and for an example of the effect of the operator  $P(\mathbf{k}|\mathbf{k}')$ . In reading Eq. (2.3.30) from right to left, the first  $\hat{T}_1(\mathbf{k})$  operates on unity to its right, which has no effect. Hence, this operator is just a function of  $\mathbf{k}$  in no wise different than  $\hat{G}(\mathbf{k})$ . The next operator encountered in this direction is  $\hat{T}_3(\mathbf{k})$  which replaces  $\mathbf{k}$  by  $\mathbf{k}'$  in the product,  $\hat{G}(\mathbf{k}) \hat{T}_1(\mathbf{k})$  on its right. Once this is accomplished, the product  $\hat{G}(\mathbf{k}) \hat{T}_1(\mathbf{k})$  is no longer a function of  $\mathbf{k}$  although  $\hat{T}_3(\mathbf{k})$  is. The next operator encountered is  $\hat{T}_2(\mathbf{k})$ , which changes  $\mathbf{k}$  to  $\mathbf{k}''$  in the product  $\hat{G}(\mathbf{k}) \hat{T}_3(\mathbf{k})$  to its right. However,  $\mathbf{k}'$  and  $\mathbf{k}''$  are independent variables of integration and may be interchanged (i.e., whichever is immaterial). This means that the order in which the factors of  $\hat{T}_2(\mathbf{k}) \hat{G}(\mathbf{k})$  and  $\hat{T}_3(\mathbf{k}) \hat{G}(\mathbf{k})$  occur in Eq. (2.3.30) is unimportant, and we may group them in arbitrary fashion. Moreover, the integrals implied by the terms  $\hat{T}_2(\mathbf{k}) \hat{G}(\mathbf{k})$  and  $\hat{T}_3(\mathbf{k}) \hat{G}(\mathbf{k})$  are the same so we may write

$$K_T(4) = N(N-1)(N-2) \langle\langle \hat{T}_1(\mathbf{k}) \hat{G}(\mathbf{k}) (\hat{T}_2(\mathbf{k}) \hat{G}(\mathbf{k}))^2 \hat{T}_1(\mathbf{k}) \rangle\rangle . \quad (2.3.31)$$

The right-hand side of Eq. (2.3.31) is infinite just as was found in Eq. (2.3.24).

If we were to generalize Eq. (2.3.29) still further to compute  $K_5(T)$ , we would confront rings of the type shown in Figure 2.2d

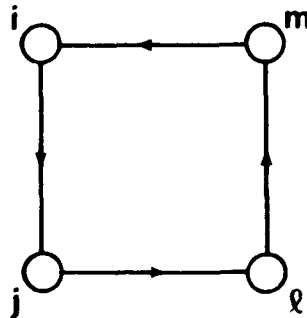


Figure 2.2d. Ring diagram for four grains.

and also multiply connected rings of the type shown in Figure 2.2e.

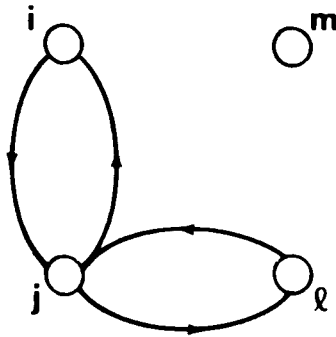


Figure 2.2e. Multiply connected ring diagram for four grains.

The diagrams in Figure 2.2e are less singular than those shown in Figure 2.2d and will be ignored in our subsequent analysis.

Hence, our final result is a sum of terms of the general type displayed in Eqs. (2.3.11), (2.3.28), and (2.3.31). That is

$$K_T = K_T(1) + K_T(3) + K_T(4) + \dots \quad (2.3.32)$$

where  $K_T(2)$  is missing because of Eq. (2.3.16). The sum on the right-hand side of Eq. (2.3.32) is diagrammed in Figure 2.3.

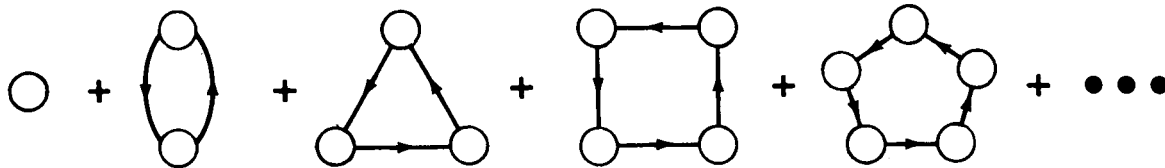


Figure 2.3. Diagrammatic representation of the sum on the right-hand side of Eq. (2.3.32).

If we add and subtract the quantity  $N\langle\langle\hat{T}_1(\mathbf{k})\rangle\rangle\hat{G}(\mathbf{k})\rangle$  to the right-hand side of Eq. (2.3.32) and use Eqs. (2.3.10), (2.3.28) and (2.3.30), we obtain

$$K_T = N\langle\langle\hat{T}_1(\mathbf{k})\rangle\rangle + N\langle\langle\hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_1(\mathbf{k})\rangle\rangle - N\langle\langle\hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_1(\mathbf{k})\rangle\rangle \quad (2.3.33)$$

$$+ N(N-1)\langle\langle\hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k})(\hat{T}_2(\mathbf{k})\hat{G}(\mathbf{k}))\hat{T}_1(\mathbf{k})\rangle\rangle$$

$$+ N(N-1)(N-2)\langle\langle\hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k})(\hat{T}_2(\mathbf{k})\hat{G}(\mathbf{k}))^2\hat{T}_1(\mathbf{k})\rangle\rangle$$

+ ...

By Eq. (2.1.5), we imply that  $K(R)$  is the effective rate coefficient for a single grain, the configurations and radii of all other grains taking on average values. We may obtain a formula for  $K(R)$  at  $R = R_1$  simply by failing to take the average over  $P(R_1)dR_1$  implied by the brackets in Eq. (2.3.33). Also factoring out the common factor  $N$  and grouping other terms, we may write Eq. (2.3.33) in the form

$$K(R_1) = \left(\frac{N}{V}\right) \int d^3 r_1 \left\{ \hat{T}_1(\mathbf{k}) + \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k}) \left[ 1 + (N-1) \langle\langle\hat{T}_2(\mathbf{k})\hat{G}(\mathbf{k})\rangle\rangle \right] \right. \\ \left. + (N-1)(N-2) \langle\langle\hat{T}_2(\mathbf{k})\hat{G}(\mathbf{k})\rangle\rangle^2 + \dots \right\} \hat{T}_1(\mathbf{k}) - \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_1(\mathbf{k}) \}. \quad (2.3.34)$$

Referring to Eqs. (2.3.7) and (2.3.8),  $\langle\langle\hat{T}_2(\mathbf{k})\hat{G}(\mathbf{k})\rangle\rangle$  may be computed as follows:

$$\langle\langle\hat{T}_2(\mathbf{k})\hat{G}(\mathbf{k})\rangle\rangle = \\ \int_0^\infty dR_2 P(R_2) 4\pi DR_2 V^{-1} \left(\frac{1}{2\pi}\right)^3 \int d^3 k' \int d^3 r_2 e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}_2} P(\mathbf{k}|\mathbf{k}') \hat{G}(\mathbf{k}) \\ = \int_0^\infty dR_2 P(R_2) 4\pi DR_2 V^{-1} \left(\frac{1}{2\pi}\right)^3 \int d^3 k' (2\pi)^3 \delta(\mathbf{k}'-\mathbf{k}) \hat{G}(\mathbf{k}') \\ = 4\pi DV^{-1} \langle R \rangle \hat{G}(\mathbf{k}) \}. \quad (2.3.35)$$

where in going from the first to the second lines, we have as usual interchanged the order of integration with respect to  $d^3 k'$  and  $d^3 r_2$  and recognized a delta function. Substitution of Eq. (2.3.35) into Eq. (2.3.34) yields

$$K(R_1) = \left(\frac{N}{V}\right) \int d^3 r_1 \left\{ \hat{T}_1(\mathbf{k}) + \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k}) \left[ 1 + \left(\frac{N-1}{V}\right) (4\pi D \langle R \rangle \hat{G}(\mathbf{k})) \right] \right\}$$

$$\begin{aligned}
& + \left(\frac{N-1}{V}\right)\left(\frac{N-2}{V}\right)(4\pi D\langle R\rangle\hat{G}(\mathbf{k}))^2 + \dots] \hat{T}_1(\mathbf{k}) - \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_1(\mathbf{k}) \} \\
& = \rho \int d^3 r_1 \{ \hat{T}_1(\mathbf{k}) + \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k}) [1 + \rho(4\pi D\langle R\rangle\hat{G}(\mathbf{k})) + \rho^2(4\pi D\langle R\rangle\hat{G}(\mathbf{k}))^2 \\
& \quad + \dots] \hat{T}_1(\mathbf{k}) - \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_1(\mathbf{k}) \} \tag{2.3.36}
\end{aligned}$$

where in the last line we have taken the thermodynamic limit.

In Eq. (2.3.36), the series within the square bracket is a geometric series in the variable,  $4\pi D\rho\langle R\rangle$ , and sums to  $(1 - (4\pi D\rho\langle R\rangle))^{-1}$ . We substitute this result into Eq. (2.3.36) and simplify.

$$\begin{aligned}
K(R_1) &= \rho \int d^3 r_1 \{ \hat{T}_1(\mathbf{k}) + \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k}) [1 - 4\pi D\rho\langle R\rangle\hat{G}(\mathbf{k})]^{-1} \hat{T}_1(\mathbf{k}) - \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k})\hat{T}_1(\mathbf{k}) \} \\
&= \rho \int d^3 r_1 \{ \hat{T}_1(\mathbf{k}) + \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k}) \left[ \frac{1}{1 - 4\pi D\rho\langle R\rangle\hat{G}(\mathbf{k})} - 1 \right] \hat{T}_1(\mathbf{k}) \} \\
&= \rho \int d^3 r_1 \{ \hat{T}_1(\mathbf{k}) + \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k}) \left[ \frac{4\pi D\rho\langle R\rangle\hat{G}(\mathbf{k})}{1 - 4\pi D\rho\langle R\rangle\hat{G}(\mathbf{k})} \right] \hat{T}_1(\mathbf{k}) \} \\
&= \rho \int d^3 r_1 \hat{T}_1(\mathbf{k}) + \rho \int d^3 r_1 \hat{T}_1(\mathbf{k})\hat{G}(\mathbf{k}) \left[ \frac{4\pi D\rho\langle R\rangle\hat{G}(\mathbf{k})}{1 - 4\pi D\rho\langle R\rangle\hat{G}(\mathbf{k})} \right] \hat{T}_1(\mathbf{k}) . \tag{2.3.37}
\end{aligned}$$

The first integral on the right-hand side of the last line in Eq. (2.3.37) is the same as Eq. (2.3.8) except for a factor of  $V^{-1}$  and an average over  $R_1$ . Removing  $V^{-1} \int_0^\infty dR_1 P(R_1)$  from Eq. (2.3.8),  $i = 1$ , and calling the resulting integral  $I_1$ , we have

$$I_1 = \int d^3 r_1 \hat{T}_1(\mathbf{k}) = 4\pi D R_1 . \tag{2.3.38}$$

In the second integral on the right-hand side of Eq. (2.3.37), we replace  $\hat{G}(\mathbf{k})$  within the bracket by Eq. (D.35), replace  $\hat{T}_1(\mathbf{k})$  by its definition in terms of Eq. (2.2.28) and simplify. In evaluating the effect of the  $P(\mathbf{k}|\mathbf{k}')$  operators, we rely upon Eq. (2.3.21). Calling the integral  $I_2$ , we find

$$\begin{aligned}
I_2 &= \int d^3 r_1 \hat{T}_1(\mathbf{k}) \hat{G}(\mathbf{k}) \left[ \frac{4\pi D\rho \langle R \rangle \hat{G}(\mathbf{k})}{1 - 4\pi D\rho \langle R \rangle \hat{G}(\mathbf{k})} \right] \hat{T}_1(\mathbf{k}) \\
&= \int d^3 r_1 (4\pi DR_1) \left(\frac{1}{2\pi}\right)^3 \int d^3 k' e^{i(\mathbf{k}'-\mathbf{k}) \cdot \mathbf{r}_1} P(\mathbf{k}|\mathbf{k}') \hat{G}(\mathbf{k}) \left[ \frac{4\pi D\rho \langle R \rangle (-1/k^2 D)}{1 - 4\pi D\rho \langle R \rangle (-1/k^2 D)} \right] \\
&\quad \times (4\pi DR_1) \left(\frac{1}{2\pi}\right)^3 \int d^3 k'' e^{i(\mathbf{k}''-\mathbf{k}) \cdot \mathbf{r}_1} P(\mathbf{k}|\mathbf{k}'') \\
&= \left(\frac{1}{2\pi}\right)^3 \int d^3 k' \hat{G}(\mathbf{k}') \cdot \frac{(4\pi DR_1)^2 (-4\pi\rho \langle R \rangle)}{(k')^2 + 4\pi\rho \langle R \rangle} \cdot \left(\frac{1}{2\pi}\right)^3 \int d^3 k'' \int d^3 r_1 e^{i(\mathbf{k}''-\mathbf{k}) \cdot \mathbf{r}_1} \\
&= \left(\frac{1}{2\pi}\right)^3 \int d^3 k' \hat{G}(\mathbf{k}') \cdot \frac{(4\pi DR_1)^2 (-4\pi\rho \langle R \rangle)}{(k')^2 + 4\pi\rho \langle R \rangle} \cdot \left(\frac{1}{2\pi}\right)^3 \int d^3 k'' (2\pi)^3 \delta(\mathbf{k}''-\mathbf{k}) \\
&= \left(\frac{1}{2\pi}\right)^3 \int d^3 k' \hat{G}(\mathbf{k}') \cdot \frac{(4\pi DR_1)^2 (-4\pi\rho \langle R \rangle)}{(k')^2 + 4\pi\rho \langle R \rangle} \cdot \quad (2.3.39)
\end{aligned}$$

According to Eq. (D.35)  $\hat{G}(\mathbf{k}')$  depends only upon the length of  $\mathbf{k}'$ ; hence, the integral in Eq. (2.3.39) is spherically symmetrical, and it is especially worthwhile to perform the integration in spherical polar coordinates. We find

$$I_2 = \left(\frac{1}{2\pi}\right)^3 \int_0^\infty dk' (k')^2 \left(\frac{-1}{D(k')^2}\right) \cdot \frac{(4\pi DR_1)^2 (-4\pi\rho \langle R \rangle)}{(k')^2 + 4\pi\rho \langle R \rangle} \cdot$$

$$\int_0^{2\pi} d\phi_{k'} \int_0^{\pi} d\theta_{k'} \sin\theta_{k'}$$

$$= \frac{(4\pi DR_1)^2 (4\pi\rho\langle R \rangle)}{(2\pi)^3 D} \cdot (4\pi) \cdot \int_0^{\infty} \frac{dk'}{(k')^2 + 4\pi\rho\langle R \rangle} \quad (2.3.40)$$

The integral over  $k'$  on the last line of Eq. (2.3.40) can be found in tables and is equal to  $(\pi/2)(4\pi\rho\langle R \rangle)^{-1/2}$ . Hence Eq. (2.3.40) becomes

$$I_2 = \frac{(4\pi DR_1)^2 (4\pi\rho\langle R \rangle) (4\pi)}{(2\pi)^3 D} \cdot \frac{(\pi/2)}{(4\pi\rho\langle R \rangle)^{1/2}}$$

$$= (4\pi DR_1) R_1 (4\pi\rho\langle R \rangle)^{1/2} \quad (2.3.41)$$

Finally, we substitute our evaluations of  $I_1$  and  $I_2$  [Eqs. (2.3.38) and (2.3.41)] into Eq. (2.3.37) to obtain our final result for  $K(R_1)$ , which is

$$K(R_1) = 4\pi DR_1 [1 + R_1 (4\pi\rho\langle R \rangle)^{1/2}] \quad (2.3.42)$$

In the limit of an infinitely dilute system of sinks ( $\rho \rightarrow 0$ ), we have according to Eq. (2.3.42)

$$\lim_{\rho \rightarrow 0} K(R_1) = 4\pi DR_1 \quad (2.3.43)$$

which is identical to Eq. (1.5.27). On the basis of the arguments and results of this section, we have demonstrated that for a slightly concentrated system of sinks that corrections to the infinitely dilute limit rate constant,

$4\pi DR_1$ , depend upon  $\rho^{1/2}$

We now return to Eqs. (1.5.26) and (1.5.35), replacing in the former the factor  $4\pi DR$  by Eq. (2.3.42). The resulting equation is

$$V(R, C_A^{\text{bulk}}) = \frac{dR}{dt} = \frac{\bar{V}'D}{X_A'R} [1 + R(4\pi\rho\langle R \rangle)^{1/2}] [C_A^{\text{bulk}} - C_A(R)] \quad (2.3.44)$$

which gives the rate of growth of the grain radius taking into account the proximity effects associated with neighboring grains.

If the bulk concentration is changing with time, i.e.,  $C_A^{\text{bulk}} = C_A(t)$ , Eq. (2.3.44) may be rewritten

$$V(R, t) = \frac{\bar{V}'D}{X_A'R} [1 + R(4\pi\rho\langle R \rangle)^{1/2}] [C_A(t) - C_A(R)] . \quad (2.3.45)$$

During a precipitation,  $R = R(t)$  will be an implicit function of  $t$ . Eq. (2.3.45) shows that  $V(R, t) = V(R(t), t)$  depends implicitly on  $t$  through  $R(t)$  and explicitly on  $t$  through  $C_A(t)$ .



III. DETERMINATION OF THE GRAIN-SIZE DISTRIBUTION FUNCTION  
AND RELATED PARAMETERS

3.1 Summary of Governing Equations

In Section 1.2, we found that the local solubility in the parent phase of a component A just outside a grain of radius R was given by

$$C_A(R) = C_A(\infty) \exp(2\gamma\bar{V}'_A/kTR) \quad (3.1.1)$$

The grain size distribution function,  $n(R(t), t)$ , was introduced in Section 1.3 and was found to satisfy the continuity equation

$$\frac{\partial n(R(t), t)}{\partial t} + \frac{\partial (n(R(t), t)V(R(t), t))}{\partial R} = 0 \quad (3.1.2)$$

In Section 1.4, the equation,

$$C_A(0) = C_A(t) + \left(\frac{4\pi}{3\bar{V}'_A}\right) X'_A \int_0^\infty dRR^3 n(R, t) \quad (3.1.3)$$

was derived expressing the conservation of component A in the case where the grains were concentrating A while the parent phase was rejecting it. Finally, at the end of Chapter II, we found that the grain radius growth velocity was given by (see Eq. (2.3.45))

$$V(R(t), C_A(t)) = \frac{\bar{V}'_D}{X'_A R} [1 + R(4\pi\rho\langle R \rangle)^{1/2}] [C_A(t) - C_A(R)] \quad (3.1.4)$$

where  $\rho$  is the number density of grains at time  $t$ .

The object of the remainder of this Chapter is to solve Eq. (3.1.2) for  $n(R(t), t)$  subject to the constraint provided by the mass conservation principle expressed by Eq. (3.1.3). To start the process of solution, Eq. (3.1.1) will be used to evaluate  $C_A(R)$  in Eq. (3.1.4) and the resulting formula will be substituted for  $V(R(t), t)$  in Eq. (3.1.2).

### 3.2 Introduction of Dimensionless Variables

Since the parent phase is rejecting the substance A, the concentration  $C_A(t)$  is a monotonically decreasing function of time. When  $t \rightarrow \infty$ , the precipitation is complete, and the parent phase has reached the saturation concentration  $C_A(\infty)$ . Prior to that,  $C_A(t) > C_A(\infty)$ , which permits us to define a dimensionless supersaturation,  $\sigma(t)$ , by

$$\sigma(t) = \frac{C_A(t) - C_A(\infty)}{C_A(\infty)} . \quad (3.2.1)$$

By the time,  $t \rightarrow \infty$ , at least one grain has achieved macroscopic dimensions; mathematically expressed, this means  $R \rightarrow \infty$ . The equilibrium solubility of a macroscopic grain is  $C_A(\infty)$  given by Eq. (3.1.1), which must be identical to the long time limit of  $C_A(t)$ . Hence,

$$\lim_{t \rightarrow \infty} C_A(t) = \lim_{R \rightarrow \infty} C_A(R) = C_A(\infty) . \quad (3.2.2)$$

We conclude that symbols  $C_A(\infty)$  in Eqs. (3.1.1) and (3.2.1) are identical.

The number of grains per unit volume of the system with radii between  $R$  and  $R + dR$  is  $n(R,t)dR$ . Hence, at any time the grain number density is

$$\rho(t) = \int_0^{\infty} dR n(R,t) . \quad (3.2.3)$$

The volume of a grain of radius  $R$  is  $\frac{4\pi}{3}R^3$ . Hence, the fraction of the total volume occupied by grains is  $\int_0^{\infty} dR \frac{4\pi}{3}R^3 n(R,t)$ . As  $t \rightarrow \infty$ , we may define a limiting volume fraction  $\phi_{\infty}$  by

$$\phi_{\infty} = \frac{4\pi}{3} \int_0^{\infty} dR R^3 n(R,\infty) = (C_A(0) - C_A(\infty)) (\bar{V}'/X'_A) \quad (3.2.4)$$

where to obtain the far right-hand side of Eq. (3.2.4), we have used the limit

of Eq. (3.1.3) as  $t \rightarrow \infty$ .

We now define a dimensionless length,  $a$ , by

$$a = R/\alpha \quad (3.2.5)$$

where

$$\alpha = 2\gamma\bar{V}'_A/kT \quad (3.2.6)$$

and a dimensionless time,  $\tau$ , by

$$\tau = tD(\bar{V}'_A/X'_A)C_A(\infty)/\alpha^2 \quad (3.2.7)$$

We convert from  $n(R,t)$  to a dimensionless distribution,  $F(a,\tau)$ , by writing

$$n(R,t) = \left(\frac{\phi_\infty}{4\pi\alpha/3}\right) F(a,\tau) \frac{da}{dR} \quad (3.2.8)$$

Substituting Eqs. (3.2.1), (3.2.4), and (3.2.7) into Eq. (3.1.3) gives

$$\sigma(\tau) = \sigma(0) \left[1 - \int_0^\infty da F(a,\tau) a^3\right] \quad (3.2.9)$$

where

$$\sigma(0) = \frac{C_A(0) - C_A(\infty)}{C_A(\infty)} \quad (3.2.10)$$

Turning to Eq. (3.2.3), we substitute Eq. (3.2.8) and obtain

$$\rho(t) = \left(\frac{\phi_\infty}{4\pi\alpha/3}\right) \tilde{\rho}(\tau) \quad (3.2.11)$$

where

$$\tilde{\rho}(\tau) = \int_0^{\infty} da F(a, \tau) . \quad (3.2.12)$$

It is helpful also to define

$$\langle a \rangle = \frac{\int_0^{\infty} da F(a, \tau) a}{\int_0^{\infty} da F(a, \tau)} . \quad (3.2.13)$$

Next in Eq. (3.1.1), note that  $2\gamma\bar{V}'_A/kTR$  is much less than unity for most substances at room temperature in the form of precipitate grains exceeding a few hundred Angstroms in radius. Hence, we may expand the exponential in Eq. (3.1.1) and write more simply

$$C_A(R) = C_A(\infty) (1 + \alpha/R) . \quad (3.2.14)$$

Substitute Eq. (3.2.14) into (3.1.4) to obtain

$$V(R, t) = \frac{\bar{V}'_D}{X'_A R} [1 + R(4\pi\rho\langle R \rangle)^{1/2}] [(C_A(t) - C_A(\infty)) - \alpha C_A(\infty)/R] . \quad (3.2.15)$$

Next use  $\langle R \rangle = \alpha \langle a \rangle$ , replace  $\rho$  by Eq. (3.2.11), and replace  $C_A(t) - C_A(\infty)$  by Eq. (3.2.1). With these substitutions, Eq. (3.2.15) becomes

$$V(a, \tau) = \frac{\bar{V}'_D C_A(\infty)}{X'_A \alpha a} [\sigma(\tau) - (1/a)] [1 + a(3\phi_{\infty} \tilde{\rho}\langle a \rangle)^{1/2}] . \quad (3.2.16)$$

Next substitute  $dR = \alpha da$ ,  $dt = X'_A \alpha^2 d\tau / D\bar{V}'_A C_A(\infty)$ , Eq. (3.2.8) and Eq. (3.2.16) into Eq. (3.1.2). The result is

$$\frac{\partial F(a, \tau)}{\partial t} + \frac{\partial}{\partial a} \left\{ F(a, \tau) \left( \frac{1}{a} \right) \left[ \sigma(\tau) - \left( \frac{1}{a} \right) \right] \left[ 1 + a(3\phi_{\infty} \tilde{\rho}\langle a \rangle)^{1/2} \right] \right\} = 0 \quad (3.2.17)$$

which may also be written

$$\frac{\partial F(a, \tau)}{\partial \tau} + \frac{\partial [F(a, \tau)W(a, \tau)]}{\partial a} = 0 \quad (3.2.18)$$

where  $W(a, \tau)$  is a dimensionless velocity defined by

$$W(a, \tau) = \left(\frac{1}{a}\right) \left[\sigma(\tau) - \left(\frac{1}{a}\right)\right] \left[1 + a(3\phi_{\infty} \tilde{\rho} \langle a \rangle)^{1/2}\right]. \quad (3.2.19)$$

Summarizing the accomplishments of this section, we may state that we have combined Eqs. (3.1.1) and (3.1.4) and substituted the result into Eq. (3.1.2) which has been expressed in dimensionless variables to obtain Eq. (3.2.17). We have also written Eq. (3.1.3) in dimensionless variables to obtain Eq. (3.2.9). The four equations (Eq. (3.1.1)-(3.1.4)) have been condensed to two equations (Eq. (3.2.9) and (3.2.17)). We must now solve Eq. (3.2.17) for  $F(a, \tau)$  subject to the side condition expressed by Eq. (3.2.9).

### 3.3 Similarity Transformation

Eq. (3.2.18) is a rather complicated first order partial differential equation, whose exact solution does not seem to be known. Hence, we propose to separate variables and search for a series solution of the form good for large  $\tau$ ,

$$F(a, \tau) = \tau^{-y} [F_0(Z) + \tau^{-y_1} F_1(Z) + \dots], \quad (3.3.1)$$

where  $y_1 > y > 0$ . The variable  $Z$  is defined by the similarity transformation

$$a(\tau) = Z(\tau)\tau^x \quad (3.3.2)$$

where  $x$  is some power. If for large  $\tau$ , where Eq. (3.3.1) is meant to apply, we suppose that  $a$  is growing as a power of  $\tau$ , say  $a \sim \tau^x$ , then  $Z$  can depend only weakly upon  $\tau$ . In this sense, it may be said to be the proper or canonical length for the problem.

Substitute Eq. (3.3.1) and (3.3.2) into Eq. (3.2.9). Noting that  $da = \tau^x dz$ . The result is

$$\sigma(\tau) = \sigma(0) \left[ 1 - \tau^{4x-y} \left( \int_0^\infty dz z^3 F_0(z) + \tau^{-y_1} \int_0^\infty dz z^3 F_1(z) + \dots \right) \right]. \quad (3.3.3)$$

For large  $\tau$ ,  $\sigma(\tau) \sim 0$ . Since  $\tau^{-y_1}$  does to zero as  $\tau \rightarrow \infty$ , Eq. (3.3.3) can be satisfied for large  $\tau$  only if

$$y = 4x \quad (3.3.4)$$

and

$$\int_0^\infty dz z^3 F_0(z) = 1. \quad (3.3.5)$$

Equation (3.3.5) is required in order to cancel the leading term of unity within the brackets in Eq. (3.3.3). Using Eqs. (3.3.4) and Eq. (3.3.5), Eq. (3.3.3) may be written to lowest order as

$$\sigma(\tau) \approx \sigma_1 \tau^{-y_1} \quad (3.3.6)$$

where

$$\sigma_1 = -\sigma(0) \int_0^\infty dz z^3 F_1(z). \quad (3.3.7)$$

Keeping only the leading term in Eq. (3.3.1) and using Eq. (3.3.4), we obtain

$$F(a, \tau) \approx \tau^{-4x} F_0(z). \quad (3.3.8)$$

Substitute Eq. (3.3.8) into Eq. (3.2.12). The result is

$$\tilde{\rho}(t) \approx \rho_0 \tau^{-3x} \quad (3.3.9)$$

where

$$\rho_0 = \int_0^{\infty} dz F_0(z) \quad (3.3.10)$$

Likewise substitute Eq. (3.3.8) into Eq. (3.2.13) to obtain

$$\langle a \rangle \approx a_0 \tau^x \quad (3.3.11)$$

where

$$a_0 = \frac{\int_0^{\infty} dz z F_0(z)}{\int_0^{\infty} dz F_0(z)} \quad (3.3.12)$$

We next introduce the canonical length into Eq. (3.2.18). In computing the relevant derivatives, however, it is important to note that  $Z$  is an implicit function of  $\tau$ . Using Eq. (3.3.2), we compute

$$\begin{aligned} \frac{\partial F(a, \tau)}{\partial \tau} &= \frac{\partial}{\partial \tau} (\tau^{-4x} F_0(z)) \\ &= -4x \tau^{-(4x+1)} F_0(z) + \tau^{-4x} \frac{\partial F_0(z)}{\partial z} \frac{\partial z}{\partial \tau} \end{aligned} \quad (3.3.13)$$

According to Eq. (3.3.2)

$$\frac{\partial z}{\partial \tau} = \frac{\partial}{\partial \tau} (\tau^{-x} a) = -x \tau^{-(x+1)} a = -x \tau^{-1} x \quad (3.3.14)$$

so that Eq. (3.3.13) becomes

$$\frac{\partial F(a, \tau)}{\partial \tau} = -4x \tau^{-(4x+1)} F_0(z) - xz \tau^{-(4x+1)} \frac{\partial F_0(z)}{\partial z} \quad (3.3.15)$$

The next derivative to compute is

$$\frac{\partial [F(a, \tau)W(a, \tau)]}{\partial a} = \frac{\partial [F(Z, \tau)W(Z, \tau)]}{\partial Z} \frac{\partial Z}{\partial a} = \tau^{-4x} \frac{\partial [F_o(Z)W(Z, \tau)]}{\partial Z} \frac{\partial Z}{\partial a} . \quad (3.3.16)$$

According to Eq. (3.3.2),

$$\frac{\partial Z}{\partial a} = \tau^{-x} \quad (3.3.17)$$

so that Eq. (3.3.16) becomes

$$\frac{\partial [F(a, \tau)W(a, \tau)]}{\partial a} = \tau^{-5x} \frac{\partial [F_o(Z)W(Z, \tau)]}{\partial Z} . \quad (3.3.18)$$

Substituting Eqs. (3.3.15) and (3.3.18) into Eq. (3.2.18), we obtain

$$-\tau^{-(4x+1)} \left[ 4x F_o(Z) + xZ \frac{\partial F_o(Z)}{\partial Z} \right] = \tau^{-5x} \frac{\partial [F_o(Z)W(Z, \tau)]}{\partial Z} \quad (3.3.19)$$

which suffices to transform Eq. (3.2.18) to canonical variables.

The explicit form of the velocity which appears in Eq. (3.3.19) may be obtained by substituting Eqs. (3.3.2), (3.3.9), and (3.3.11) into Eq. (3.2.19). The result is

$$W(Z, \tau) = (Z\tau)^{-1} [\sigma(\tau) - (1/Z\tau)] [1 + (3\phi_\infty \rho_o a_o)^{1/2} Z] . \quad (3.3.20)$$

If we set

$$\epsilon = (3\phi_\infty \rho_o a_o)^{1/2} \quad (3.3.21)$$

Eq. (3.3.20) may be written simply

$$W(Z, \tau) = (1/Z\tau^x) [\sigma(\tau) - (1/Z\tau^x)] [1 + \epsilon Z] . \quad (3.3.22)$$



The asymptotic form of  $\sigma(\tau)$  is given by Eq. (3.3.6). In Appendix E, we showed that  $y_1 = x$  [see Eq. (E.1.16)]. Combining these results and substituting into Eq. (3.3.22), we obtain

$$W(Z, \tau) \approx \tau^{-2x} (1/Z) [\sigma_1 - (1/Z)] [1 + \epsilon Z] . \quad (3.3.23)$$

Next, we substitute Eq. (3.3.23) into the right-hand side of Eq. (3.3.19). The factor  $\tau^{-2x}$  which leads Eq. (3.3.23) is combined with the factor of  $\tau^{-5x}$  on the right-hand side of Eq. (3.3.19) to produce  $\tau^{-7x}$ . Because of Eq. (E.2.2.), which specifies  $x = 1/3$ , the factor of  $\tau^{-(4x+1)}$  on the left-hand side of Eq. (3.3.19) cancels the factor of  $\tau^{-5x}$  on the right. The end result of these cancellations is shown in Eq. (3.3.24).

$$-4x F_0(Z) - xZ \frac{dF_0(Z)}{dZ} + \frac{d}{dZ} [F_0(Z) Z^{-1} (\sigma_1 - (1/Z)) (1 + \epsilon Z)] = 0 . \quad (3.3.24)$$

Equation (3.3.24) may be cast in a more compact form by adding  $-xZF_0(Z)$  to the terms within the brackets and subtracting  $-(d/dZ)(xZF_0(Z))$  from the terms outside. The result is

$$-F_0(Z) + \frac{d}{dZ} [w(Z) F_0(Z)] = 0 \quad (3.3.25)$$

where we may identify a new dimensionless velocity by

$$w(Z) = \left(\frac{1}{3x}\right) \left[\left(\frac{1}{Z}\right) \left(\sigma_1 - \frac{1}{Z}\right) (1 + \epsilon Z) - \frac{Z}{3}\right] . \quad (3.3.26)$$

We now summarize the progress to this point. In Section 3.2, we were left with Eq. (3.2.18) to be solved for  $F(a, \tau)$  subject to the condition on  $\sigma(\tau)$  expressed by Eq. (3.2.9). By expanding the grain size distribution function as in Eq. (3.3.1) and introducing the variable change specified by Eq. (3.3.2), we have converted Eq. (3.2.9) into Eq. (3.3.6) with  $\sigma_1$  defined by Eq. (3.3.7). The variable change specified by Eq. (3.3.2) plus the simple

asymptotic forms given by Eqs. (3.3.6), (3.3.8), (3.3.9), and (3.3.11) have served to convert the partial differential equation, Eq. (3.2.18), to the ordinary differential equation, Eq. (3.3.25), with  $w(Z)$  defined by Eq. (3.3.26). The constraint expressed by Eq. (3.2.9) has been completely incorporated into Eq. (3.3.26) and no further reference to it is needed to obtain the general solution of Eq. (3.3.25) for  $F_0(Z)$ .

In the process of changing variables from  $a(\tau)$  to  $z(\tau)$ , we have converted Eq. (3.2.12) to the form of Eqs. (3.3.9) and (3.3.10) and converted Eq. (3.2.13) to the form of Eqs. (3.3.11) and (3.3.12). Once we have solved Eq. (3.3.25) for  $F_0(Z)$ , we will use Eq. (3.3.10) to compute the normalization factor for  $F_0(Z)$  and use Eq. (3.3.12) to compute the mean radius. The technique used to solve Eq. (3.3.25) is motivated by some physical arguments which we explore in the next section.

#### 3.4 Critical Radius and Supersaturation

As was explained in Section 1.1, in a distribution of grain sizes maturing through Ostwald ripening, there exists a critical radius specified by the value of the supersaturation. Grains smaller than this critical radius will dissolve while larger grains will grow. As the precipitation evolves, however, the supersaturation diminishes and the critical radius increases. In the case of a grain whose initial radius exceeds the critical radius, there ensues a race between it and the critical size. Even though such a grain is initially growing, it is possible for the critical radius to grow faster and at some time to catch up. When this happens, a grain of this size stops growing, turns around and begins dissolving. In fact, when  $\tau \rightarrow \infty$ , all grains except the largest have disappeared. The sole remaining grain has absorbed all of the available solute and is in stable equilibrium at the saturation concentration.

For large yet finite times ( $\tau \lesssim \infty$ ) there is an asymptotic distribution of grain sizes given by the function  $F_0(Z)$ . Within this distribution, a grain which is neither growing nor dissolving has attained the critical radius. Because it is in equilibrium with the instantaneous supersaturation, its growth velocity, as defined in canonical variables by Eq. (3.3.26) must be zero. The canonical critical radius  $Z_0$  thus satisfies

$$w(Z_0) = 0. \tag{3.4.1}$$

Combining Eqs. (3.3.26) and (E.2.2) and substituting the result into Eq. (3.4.1), we obtain

$$(1/Z_0)(\sigma_1 - (1/Z_0))(1 + \epsilon Z_0) - (1/3) Z_0 = 0 . \quad (3.4.2)$$

Equation (3.4.2) may be rearranged to read

$$\sigma_1 = \frac{Z_0^2}{3(1+\epsilon Z_0)} + \frac{1}{Z_0} \quad (3.4.3)$$

so as to serve as an expression for  $\sigma_1$ .

Now consider a grain with radius,  $Z > Z_0$ . This grain cannot grow forever or else the principal of mass conservation expressed by Eq. (3.3.5) would be violated, and no asymptotic steady state could exist. Hence, asymptotically no velocity larger than the critical velocity,  $w(Z_0) = 0$ , can exist. Therefore  $w(Z)$  must have a maximum at  $Z_0$ . The condition specifying this is

$$\frac{dw(Z)}{dZ} = 0 \text{ at } Z = Z_0 . \quad (3.4.4)$$

Using Eq. (E.2.2) and substituting Eq. (3.3.26) into Eq. (3.4.4), we obtain

$$\left[ -\frac{\sigma_1}{Z_0} + \frac{2}{Z_0^2} \right] (1 + \epsilon Z_0) + \left( \frac{\epsilon}{Z_0} \right) \left[ \sigma_1 - \frac{1}{Z_0} \right] - \frac{1}{3} = 0 . \quad (3.4.5)$$

Equation (3.4.5) may be solved so as to provide another expression for  $\sigma_1$  in terms of  $Z_0$ , namely,

$$\sigma_1 = \frac{2}{Z_0} - \frac{Z_0^2}{3} + \epsilon . \quad (3.4.6)$$

Eliminating  $\sigma_1$  between Eqs. (3.4.3) and (3.4.6) yields a polynomial equation for  $Z_0$ ,

$$\epsilon Z_0^4 + 2Z_0^3 - 3\epsilon^2 Z_0^2 - 6\epsilon Z_0 - 3 = 0 . \quad (3.4.7)$$

For  $\epsilon = 0$ , Eq. (3.4.7) becomes a simple cubic equation, the physically significant root of which is

$$Z_0 = (3/2)^{1/3} . \quad (3.4.8)$$

Equation (3.4.8) serves as a zeroth order estimate of the root of the quartic which is Eq. (3.4.7). Isolating the term in  $Z_0^3$  on the left-hand side, Eq. (3.4.7) may be rewritten

$$Z_0 = \left(\frac{3}{2}\right)^{1/3} \left[ 1 + \left(2Z_0 - \frac{Z_0^4}{3}\right) \epsilon + Z_0^2 \epsilon^2 \right]^{1/3} . \quad (3.4.9)$$

Now substituting Eq. (3.4.8) for  $Z_0$  on the right-hand side of Eq. (3.4.9), one obtains

$$Z_0 \approx \left(\frac{3}{2}\right)^{1/3} \left[ 1 + \left(\frac{3}{2}\right)^{4/3} \epsilon + \left(\frac{3}{2}\right)^{2/3} \epsilon^2 \right]^{1/3} . \quad (3.4.10)$$

Expanding the right-hand side of Eq. (3.4.10) in a binomial series, including terms through order  $\epsilon$ , yields

$$Z_0 \approx \left(\frac{3}{2}\right)^{1/3} \left[ 1 + \left(\frac{1}{2}\right) \left(\frac{3}{2}\right)^{1/3} \epsilon \right] . \quad (3.4.11)$$

Replacing  $\epsilon$  by Eq. (3.3.21), Eq. (3.4.11) becomes

$$Z_0 \approx \left(\frac{3}{2}\right)^{1/3} \left[ 1 + \frac{1}{2} \left(\frac{3}{2}\right)^{1/3} (3\phi_\infty \rho_0 a_0)^{1/2} \right] . \quad (3.4.12)$$

To calculate  $\sigma_1$ , substitute Eq. (3.4.11) for  $Z_0$  in Eq. (3.4.6). The result is

$$\sigma_1 = 2\left(\frac{2}{3}\right)^{1/3} \left[1 - \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)^{1/3} \varepsilon\right]^{-1} - \left(\frac{1}{3}\right)\left(\frac{3}{2}\right)^{2/3} \left[1 + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)^{1/3} \varepsilon\right]^2 + \varepsilon. \quad (3.4.13)$$

The quantities within brackets are next expanded in binomial series up to order  $\varepsilon$ . When coefficients of like terms are collected, one obtains

$$\sigma_1 \approx \left(\frac{9}{4}\right)^{1/3} \left[1 - \left(\frac{1}{2}\right)\left(\frac{4}{9}\right)^{1/3} \varepsilon\right]. \quad (3.4.14)$$

Replacement of  $\varepsilon$  by Eq. (3.3.21) gives finally

$$\sigma_1 \approx \left(\frac{9}{4}\right)^{1/3} \left[1 - \left(\frac{1}{2}\right)\left(\frac{4}{9}\right)^{1/3} (3\phi_\infty \rho_0 a_0)^{1/2}\right]. \quad (3.4.15)$$

### 3.5 Integration of Eq. (3.3.25) to obtain $F_0(Z)$

In Eq. (3.3.25) the indicated differentiation of the quantity within the brackets may be carried out and the result divided through by  $w(Z)F_0(Z)$ . One thus obtains

$$\frac{1}{F_0(Z)} \frac{dF_0(Z)}{dZ} = -\frac{1}{w(Z)} \frac{dw(Z)}{dZ} + \frac{1}{w(Z)}. \quad (3.5.1)$$

Integration of Eq. (3.5.1) yields

$$F_0(Z) = \frac{C_0}{w(Z)} \cdot \exp \left[ \int \frac{dZ}{w(Z)} \right] \quad (3.5.2)$$

where  $C_0$  is a constant of integration.

To compute the integral indicated in Eq. (3.5.2), we begin by combining Eqs. (3.3.26) and (E.2.2) to obtain

$$w(z) = \left(\frac{1}{z}\right) \left[\sigma_1 - \left(\frac{1}{z}\right)\right] (1 + \epsilon z) - \frac{z}{3}. \quad (3.5.3)$$

For  $\sigma_1$ , on the right-hand side of Eq. (3.5.3), substitute Eq. (3.4.6). The result is

$$w(z) = \left(\frac{1}{z}\right) \left[\frac{z_0^2}{z} - \frac{z_0^2}{3} + \epsilon - \frac{1}{z}\right] (1 + \epsilon z) - \frac{z}{3}. \quad (3.5.4)$$

Multiply the right-hand side of Eq. (3.5.4) by  $(-3z_0 z^2)/(-3z_0 z^2)$  to obtain

$$w(z) = \left(\frac{-1}{3z_0 z^2}\right) \{z[(z_0^3 - 6) + 3(z_0/z) - 3z_0 \epsilon][1 + \epsilon z] + z_0 z^3\}. \quad (3.5.5)$$

If on the right-hand side of Eq. (3.5.5) terms of order  $\epsilon$  and higher are dropped, the result is

$$w(z) \approx \left(\frac{-1}{3z_0 z^2}\right) [z_0 z^3 + (z_0^3 - 6) + 3z_0]. \quad (3.5.6)$$

If terms of order  $\epsilon$  and higher are ignored in Eq. (3.4.10), Eq. (3.4.8) applies. Since according to Eq. (3.4.8)  $3 - 2z_0^3 = 0$ , we may add  $(3 - 2z_0^3)z^2$  to the quantity within the bracket in Eq. (3.5.6) to obtain

$$w(z) \approx \left(\frac{-1}{3z_0 z^2}\right) [z_0 z^3 + (3 - 2z_0^3) z^2 + (z_0^3 - 6) z + 3z_0]. \quad (3.5.7)$$

The quantity within the bracket in Eq. (3.5.7) factors so that

$$w(Z) \approx -(1/3Z^2) (Z - z_0)^2 (Z + 3/z_0^2) . \quad (3.5.8)$$

Evaluation of Eq. (3.5.2) calls for  $1/w(Z)$ . Also involved is an integral of this quantity. To compute the integral, we expand  $1/w(Z)$  in partial fractions and arrive at

$$\frac{1}{w(Z)} = -\frac{3z_0^4}{(z_0^3+3)} \cdot \frac{1}{(Z-z_0)^2} - \frac{3z_0^3(z_0^3+6)}{(z_0^3+3)^2} \cdot \frac{1}{(Z-z_0)} - \frac{27}{(z_0^3+3)^2} \cdot \frac{1}{(Z+3/z_0^2)} . \quad (3.5.9)$$

The details associated with the derivation of Eq. (3.5.9) may be found in Appendix F.

After substitution of Eq. (3.5.9) into the integral on the right-hand side of Eq. (3.5.2) and integrating, one obtains

$$\int \frac{dZ}{w(Z)} = -\frac{3z_0^4}{(z_0^3+3)} \cdot \frac{1}{(z_0-z)} - \frac{3z_0^3(z_0^3+6)}{(z_0^3+3)^2} \ln(z_0-z) - \frac{27}{(z_0^3+3)^2} \ln(Z+3/z_0^2) . \quad (3.5.10)$$

In Eq. (3.5.10), we have used the following:

$$\int dZ (Z - z_0)^{-2} = (z_0 - Z)^{-1} \quad (3.5.11)$$

$$\int dZ (Z - z_0)^{-1} = \ln(z_0 - Z) \quad (3.5.12)$$

$$\int dZ (Z + 3/z_0^2)^{-1} = \ln(Z + 3/z_0^2) . \quad (3.5.13)$$

Finally, we substitute Eqs. (3.5.9) and (3.5.10) into Eq. (3.5.2) to obtain

$$F_0(Z) = \frac{c_0 z^2}{(z_0-z)^\alpha (Z+3/z_0^2)^\beta} \cdot \exp(-\delta/(z_0-z)) \quad (3.5.14)$$

where  $\alpha$ ,  $\beta$ , and  $\delta$  are defined by

$$\alpha = \frac{3Z_o^3 Z_o^3 + 6}{(Z_o^3 + 3)^2} + 2 \quad (3.5.15)$$

$$\beta = \frac{27}{(Z_o^3 + 3)^2} + 1 \quad (3.5.16)$$

$$\delta = \frac{3Z_o^4}{(Z_o^3 + 3)} \quad (3.5.17)$$

For later comparison, it is useful to have Eqs. (3.5.15)-(3.5.17) in the limit  $\epsilon \rightarrow 0$  (infinitely dilute system of grains). In this limit,  $Z_o$  is given by Eq. (3.4.8) and according to Eqs. (3.5.15)-(3.5.17),

$$\alpha = \frac{11}{3} \quad (3.5.18)$$

$$\beta = \frac{7}{3} \quad (3.5.19)$$

$$\delta = \left(\frac{3}{2}\right)^{1/3} \quad (3.5.20)$$

Using Eq. (3.5.14),

$$\lim_{\epsilon \rightarrow 0} F_o(Z) = \frac{C_o' Z^2}{[(3/2)^{1/3} - Z]^{11/3} [Z + 2(3/2)^{1/3}]^{7/3}} \cdot \exp\left(-\frac{(3/2)^{1/3}}{[(3/2)^{1/3} - Z]}\right) \quad (3.5.21)$$

where  $C_o'$  is the  $\epsilon = 0$  limit of  $C_o$ .

One should note that  $Z = Z_o$  in Eq. (3.5.14) and  $Z = (3/2)^{1/3}$  in Eq. (3.5.21) cannot be exceeded by  $Z$ , otherwise  $F_o(Z)$  would take on complex values which are unphysical. Hence  $Z = Z_o$  serves as a cut-off in the former while  $Z$



$= (3/2)^{1/3}$  is a cut-off for the latter. For values of  $Z$  larger than these cut-off points, the respective distributions are zero.

### 3.6 Evaluation of $C'_0$ , $\rho_0$ , and $a_0$ for $\epsilon = 0$

#### 3.6.1 Evaluation of $C'_0$

Equation (3.3.5) may be used to determine  $C'_0$ . We note, however, that because of the cut-off at  $Z = Z'_0 = (3/2)^{1/3}$ , integration beyond this point is unnecessary and Eq. (3.3.5) can be rewritten

$$1 = \int_0^{Z'_0} dZ Z^3 F_0(Z) . \quad (3.6.1)$$

If we substitute Eq. (3.5.21) into Eq. (3.6.1) and let  $Z = (2/3)^{2/3} x^{1/3}$ , Eq. (3.6.1) becomes

$$\frac{1}{C'_0} = \frac{1}{3} \int_0^{27/8} dx \frac{x}{((3/2)-x^{1/3})(3+x^{1/3})^{7/3}} \cdot \exp\left(-\frac{1}{1-(2/3)x^{1/3}}\right) . \quad (3.6.2)$$

The integral on the right-hand side of Eq. (3.6.2) has been evaluated numerically by Lifshitz and Slyozov [3] and found to have the value 0.0488. Equation (3.6.2) implies

$$C'_0 = 3/(0.0488) . \quad (3.6.3)$$

Equation (3.5.21) may be transformed to another form by multiplying the right-hand side by  $e$  and dividing  $C'_0$  by  $e$ . Eq. (3.6.3) becomes

$$C'_0 / e = \frac{3}{(0.0488)e} = 22.6 \quad (3.6.4)$$

and Eq. (3.5.21) becomes

$$F_0(z) = \frac{22.6 z^2}{[(3/2)^{1/3} - z]^{11/3} [z + 2(3/2)^{1/3}]^{7/3}} \cdot \exp\left(-\frac{z}{[(3/2)^{1/3} - z]}\right). \quad (3.6.5)$$

### 3.6.2 Evaluation of $\rho_0$

The quantity  $\rho_0$  can be computed using Eq. (3.3.10). Taking into account the cut-off at  $z = z'_0 = (3/2)^{1/3}$  Eq. (3.3.10) becomes

$$\rho_0 = \int_0^{z'_0} dz F_0(z). \quad (3.6.6)$$

Replacing  $(3/2)^{1/3}$  in Eq. (3.5.21) by the symbol,  $z'_0$ , and substituting the result into Eq. (3.6.6), one obtains

$$\rho_0 = \int_0^{z'_0} dz \frac{c'_0 z^2}{(z'_0 - z)^{11/3} (z + 2z'_0)^{7/3}} \cdot \exp\left[-\frac{z}{(z'_0 - z)}\right]. \quad (3.6.7)$$

Now in Eq. (3.6.7), we express binomial terms involving fractional exponents as exponential functions of logarithms. Last, we multiply and divide the integrand by  $(-3)$ . The result is

$$\begin{aligned} \rho_0 &= -\frac{c'_0}{3} \int_0^{z'_0} dz \frac{(-3z^2)}{(z'_0 - z)^2 (z + 2z'_0)} \exp\left[-\left(\frac{z}{z'_0 - z}\right) - \left(\frac{5}{3}\right)\ln(z'_0 - z) - \left(\frac{4}{3}\right)\ln(z + 2z'_0)\right] \\ &= -\frac{c'_0}{3} \int_0^{z'_0} dz \frac{d}{dz} \left\{ \exp\left[-\left(\frac{z}{z'_0 - z}\right) - \left(\frac{5}{3}\right)\ln(z'_0 - z) - \left(\frac{4}{3}\right)\ln(z + 2z'_0)\right] \right\} \\ &= -\frac{c'_0}{3} \left\{ \exp\left[-\left(\frac{z}{z'_0 - z}\right) - \left(\frac{5}{3}\right)\ln(z'_0 - z) - \left(\frac{4}{3}\right)\ln(z + 2z'_0)\right] \right\}_0^{z'_0} \end{aligned}$$

$$= \frac{(C'_0/e)}{9(2)^{1/3}}$$

$$\rho_0 = 1.994 \tag{3.6.8}$$

where in the last line, we have used Eq. (3.6.4).

### 3.6.3 Evaluation of $a_0$

The quantity,  $a_0$ , can be evaluated directly in terms of its definition expressed by Eq. (3.3.12) or indirectly by exploiting the results of Section E.1 of Appendix E. We choose the latter procedure because it is simpler.

On the basis of Eq. (E.1.14), we have letting  $\tau \rightarrow \infty$ ,

$$\lim_{\tau \rightarrow \infty} \int_0^{\infty} dz z^2 F_0(z) \bar{V}(z) \sim \lim_{\tau \rightarrow \infty} \tau^{-y_1} = 0 \tag{3.6.9}$$

since  $y_1 = x = 1/3$ . Into the left-hand side of Eq. (3.6.9), substitute Eq. (E.1.15) to obtain

$$\int_0^{\infty} dz (\sigma_1 z - 1 + \epsilon \sigma_1 z^2 - \epsilon z) F_0(z) = 0 . \tag{3.6.10}$$

Since by definition, the average of  $z^k$  is

$$\langle z^k \rangle \sim \int_0^{\infty} dz z^k F_0(z) , \tag{3.6.11}$$

Eq. (3.6.10) becomes

$$\sigma_1 \langle Z \rangle - 1 + \epsilon \sigma_1 \langle Z^2 \rangle - \epsilon \langle Z \rangle = 0 . \quad (3.6.12)$$

Because of Eq. (3.3.12),  $\langle Z \rangle = a_0$ . Hence when  $\epsilon = 0$ , Eq. (3.6.12) gives

$$a_0 = 1/\sigma_1 = (4/9)^{1/3} \quad (3.6.13)$$

where we have used Eq. (3.4.14) with  $\epsilon = 0$ .

### 3.7 Evaluation of $C_0$ , $\rho_0$ , and $a_0$ for $\epsilon \neq 0$

When  $\epsilon \neq 0$ ,  $C_0$  must be evaluated by numerical iteration. The independent variable is  $\phi_\infty$ , which is the volume fraction under consideration. One then estimates  $\rho_0$  and  $a_0$  by choosing the  $\phi_\infty = 0$  values given by Eqs. (3.6.8) and (3.6.13), respectively. Having specified  $\phi_\infty$ ,  $\rho_0$ , and  $a_0$ , Eq. (3.4.12) gives  $Z_0$ , which in turn determines  $\alpha$ ,  $\beta$ ,  $\delta$  by virtue of Eqs. (3.5.15)-(3.5.17). At this point  $C_0$  can be determined from Eq. (3.3.5). This completes the first iteration.

With  $\phi_\infty$  fixed as before, the second iteration is begun by using the function  $F_0(Z)$  obtained from the first iteration and computing  $\rho_0$  and  $a_0$  using Eqs. (3.3.10) and (3.3.12). Next,  $Z_0$  is recomputed using Eq. (3.4.12). With  $Z_0$  specified,  $C_0$  is determined as before, which completes the second iteration.

The procedure described above converges nicely after a few iterations. Part of the results obtained may also be expressed analytically. Let  $\rho_0$  and  $a_0$  be given by the zero volume fraction results, Eqs. (3.6.8) and (3.6.13). Substituting these into Eq. (3.3.21) gives

$$\epsilon = 2.134(\phi_\infty)^{1/2} . \quad (3.7.1)$$

When Eq. (3.7.1) is substituted into Eq. (3.4.11), we obtain

$$z_0 \approx (3/2)^{1/3} [1 + 1.222(\phi_\infty)^{1/2}] . \quad (3.7.2)$$

Likewise, substitution of Eq. (3.7.1) into Eq. (3.4.14) gives

$$\sigma_1 \approx (9/4)^{1/3} [1 - 0.815(\phi_\infty)^{1/2}] . \quad (3.7.3)$$

To obtain  $a_0$ , we turn to Eq. (3.6.12). We define  $a_2$  by

$$a_2 \equiv \langle z^2 \rangle = \frac{\int_0^\infty dz z^2 F_0(z)}{\int_0^\infty dz F_0(z)} = 0.609 . \quad (3.7.4)$$

The value, 0.609, on the right-hand side of Eq. (3.7.4) was found by replacing the integral in the denominator by Eq. (3.6.8) and computing the integral in the numerator numerically using Eq. (3.6.5). With  $a_2$  thus found, Eq. (3.6.12) may be rewritten

$$a_0 = \frac{1 - \epsilon \sigma_1 a_2}{\sigma_1 - \epsilon} . \quad (3.7.5)$$

Into the right-hand side of Eq. (3.7.5), we substitute Eq. (3.4.14). Up to terms of order  $\epsilon$ , the result may be written

$$a_0 \approx \frac{1 - a_2 (3/2)^{2/3} \epsilon}{(3/2)^{2/3} - (3/2) \epsilon} . \quad (3.7.6)$$

Expanding the denominator of Eq. (3.7.6) in a binomial series and collecting terms up to order  $\epsilon$  gives

$$a_o = \left(\frac{4}{9}\right)^{1/3} \left[1 + \left(\frac{3}{2(3/2)^{2/3}} - a_2(3/2)^{2/3}\right) \epsilon\right]. \quad (3.7.7)$$

We now substitute Eqs. (3.7.1) and (3.7.4) into Eq. (3.7.7). The result is

$$a_o = \left(\frac{4}{9}\right)^{1/3} \left[1 + 0.739 (\phi_\infty)^{1/2}\right]. \quad (3.7.8)$$

This completes the determination of the relevant parameters in the case  $\epsilon \neq 0$ .

### 3.8 Summary and Discussion

#### 3.8.1 Results in Terms of Laboratory Parameters

The use of dimensionless variables for mathematical analysis has led us to a number of important results. In this section, we summarize a set of parameters (mostly dimensional) which are appropriate for expressing these results in a form convenient for laboratory use.

The mean molecular volume in the A-rich phase (the phase consisting of grains which are concentrating A) is

$$\bar{V}' = \frac{X'_A(MW)_A + X'_B(MW)_B}{\rho' N_o} \quad (3.8.1)$$

where  $(MW)_A$  and  $(MW)_B$  are the molecular weights of A and B, respectively, and  $X'_A$  and  $X'_B$  are the mole fractions of these components in the phase. The mass density of the phase is  $\rho'$ , while  $N_o$  is Avagadro's number. The volume occupied by a molecule of A in this phase is

$$\bar{V}'_A = X'_A \bar{V}' . \quad (3.8.2)$$

Using Eq. (3.8.2), we may calculate the natural length scale

$$\alpha = 2\gamma \bar{V}'_A / kT \quad (3.8.3)$$

which was introduced in Eq. (3.2.6);  $\alpha$  is the radius beyond which the curvature of a grain no longer greatly enhances its solubility.

The equilibrium concentration (molecular number density) of A in the B-rich phase (the continuous phase which is rejecting A) is

$$C_A(\infty) = \frac{X_A \rho N_O}{X_A (MW)_A + X_B (MW)_B} \quad (3.8.4)$$

where  $\rho$  is the density of the phase and  $X_A$  and  $X_B$  are the respective mole fractions.

With the quantities defined so far, we may also introduce a natural time scale,

$$\theta = \frac{\alpha^2 X_A'}{\bar{D} \bar{V}' C_A(\infty)} \quad (3.8.5)$$

Having the units of seconds,  $\theta$  is proportional to the time,  $\alpha^2/D$ , required by a molecule to diffuse a distance,  $\alpha$ .

By combining Eqs. (3.2.4) and (3.2.10), we obtain an expression for the initial supersaturation,  $\sigma(0)$ , in terms of the volume fraction,  $\phi_\infty$ , occupied by the A-rich phase at equilibrium,

$$\sigma(0) = \frac{X_A' \phi_\infty}{C_A(\infty) \bar{V}'} \quad (3.8.6)$$

According to Eqs. (3.2.7), (3.3.6), (3.8.5), and (E.2.2), the supersaturation decays with time as

$$\sigma(t) = \sigma_1 (\theta/t)^{1/3} \quad (3.8.7)$$

where  $\sigma_1$  may be determined from the graph in Figure 3.1 or calculated from Eq. (3.7.3).

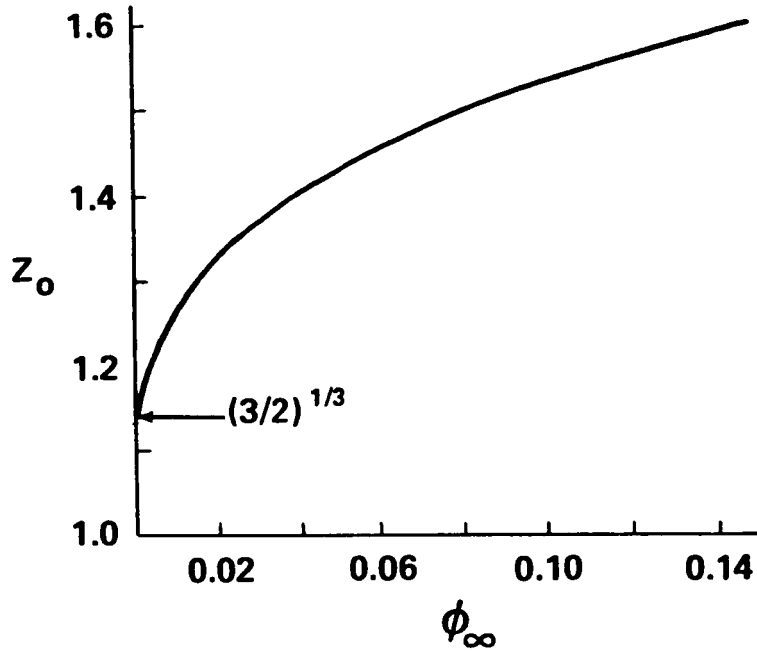


Figure 3.1. Grain size distribution normalization constant,  $\rho_0$  [Eq. (3.3.10)], supersaturation constant,  $\sigma_1$  [Eq. (3.7.3)], and mean radius constant,  $a_0$  [Eq. (3.7.8)], shown as functions of the equilibrium volume fraction occupied by grains,  $\phi_\infty$  [Eq. (3.2.4)].

According to Eqs. (3.2.4), (3.2.7), (3.2.10), (3.2.11), (3.3.9), and (E.2.2), the total number of grains of the A-rich phase per unit volume decreases with time according to

$$\rho(t) = \frac{3\rho_0\sigma(0)}{4\pi\alpha D} \cdot \frac{1}{t} \quad (3.8.8)$$

where  $\rho_0$  may be determined from Figure 3.1.

As we know, within the population,  $\rho(t)$ , there is a distribution of grain sizes. This distribution,  $n(R,t)$ , depends upon both radius and time. Combining Eqs. (3.2.4), (3.2.5), (3.2.8), (3.2.10), (3.3.8), and (E.2.2), we may write

$$n(R,t) = \frac{\sigma(0)}{(D\theta/\alpha)^2} \cdot \frac{F_0(Z)}{(4\pi\alpha^3/3)} \cdot \left(\frac{\theta}{t}\right)^{1/3} \quad (3.8.9)$$



where  $F_0(Z)$  is given by Eq. (3.5.14) and  $Z$  is defined by Eqs. (3.2.5) and (3.3.2), namely,

$$Z = (R/\alpha)(\theta/t)^{1/3} . \quad (3.8.10)$$

The function  $F_0(Z)$  is shown in graphical form in Figure 3.2. Note that with increasing volume fraction,  $\phi_\infty$ ,  $F_0(Z)$  decreases in height and broadens. The broadening is caused because competition increases the rates of both growth and dissolution of grains [see Eq. (2.3.45)]. This means that the large grains grow even faster, shifting both the mean and maximum radii to larger values. With broadening, however, the height must decrease because  $F_0(Z)$  is normalized according to Eq. (3.3.5). Associated with the distribution are a number of radii, which we discuss below:

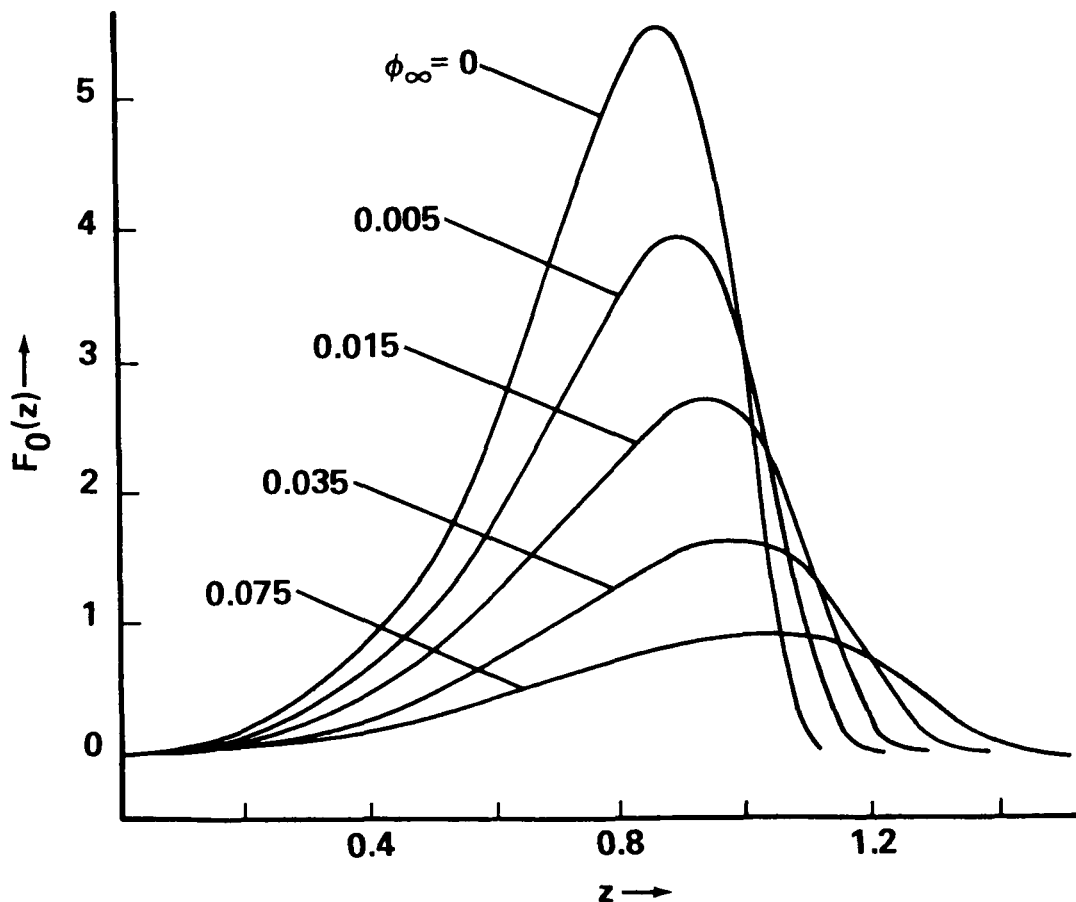


Figure 3.2. Grain size distribution function,  $F_0(Z)$ .

There is no sharp minimum radius in the distribution. To represent an effective minimum radius, however, we arbitrarily select from Figure 3.2,  $Z = 0.2$ , the point where  $F_0(Z)$  diminishes to a few percent of its maximum value. Setting  $Z = 0.2$  in Eq. (3.8.10), we obtain

$$R_{\min} = 0.2 \alpha (t/\theta)^{1/3} . \quad (3.8.11)$$

Inspection of Eq. (3.2.15) reveals that there is a critical value of the radius, call it  $R_{\text{crit}}$ , at which  $V(R,t) = 0$ . Using Eq. (3.2.1), this radius may be written

$$R_{\text{crit}} = \alpha/\sigma(t) . \quad (3.8.12)$$

The value of  $R_{\text{crit}}$  follows the inverse of the supersaturation. Grains whose radii at time  $t$  are greater than  $R_{\text{crit}}$  are growing while grains whose radii are smaller than  $R_{\text{crit}}$  are dissolving.

The mean radius in the distribution is found by combining Eqs. (3.2.5), (3.2.7), (E.2.2), (3.3.11), and (3.8.5). The result is

$$\langle R \rangle = a_0 \alpha (t/\theta)^{1/3} . \quad (3.8.13)$$

The value of  $a_0$  depends upon the volume fraction and may be read from Figure 3.1 or calculated from Eq. (3.7.8). Comparison of Eqs. (3.7.3) and (3.7.8) for  $\phi_\infty = 0$ , shows that  $a_0(\phi_\infty = 0) = 1/\sigma_1(\phi_\infty = 0) = (4/9)^{1/3}$ . Hence, because of Eqs. (3.8.7), (3.8.12), and (3.8.13), we find that  $\langle R \rangle = R_{\text{crit}}$  when  $\phi_\infty = 0$ . For  $\phi_\infty > 0$ , however, Eqs. (3.7.3) and (3.7.8) indicate that  $R_{\text{crit}} > \langle R \rangle$ .

The maximum radius in  $F_0(Z)$  is  $Z = Z_0$  [see Eq. (3.5.14) and the discussion following Eq. (3.5.21)]. Setting  $Z = Z_0$  in Eq. (3.8.10), we obtain

$$R_{\max} = Z_0 \alpha (t/\theta)^{1/3} \quad (3.8.14)$$

where  $Z_0$  may be read from Figure 3.3 or calculated using Eq. (3.7.2). In general  $R_{\min} < \langle R \rangle < R_{\text{crit}} < R_{\max}$ .

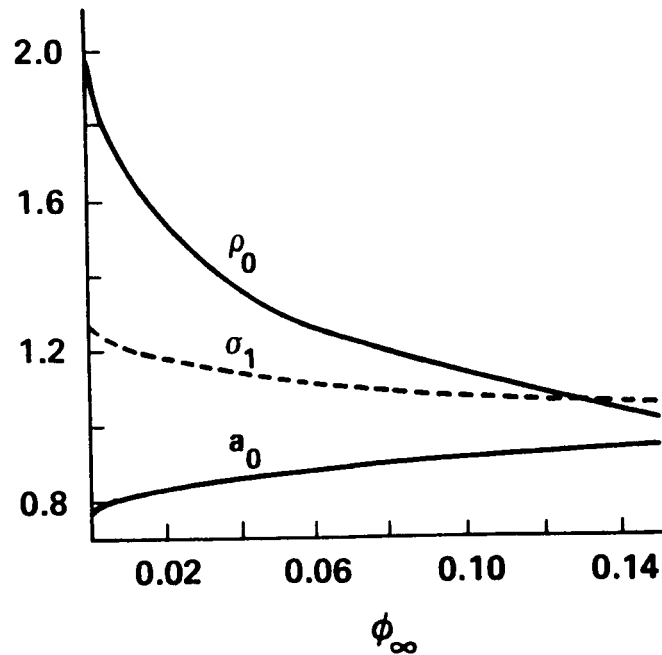


Figure 3.3. Maximum grain size constant,  $Z_0$  [Eq. (3.7.2)], as a function of volume fraction occupied by grains,  $\phi_\infty$  [Eq. (3.2.4)].

Finally, it is worth noting that all quantities which depend upon volume fraction (e.g.,  $\rho(t)$ ,  $\sigma(t)$ ,  $R_{crit}$ ,  $\langle R \rangle$ ,  $R_{max}$ , and  $F_0(Z)$ ) do so as a function of  $(\phi_\infty)^{1/2}$  (see Chapter II above). This has its origin in the growth velocity expressed by Eq. (2.3.45), which encompasses the competition effect. The square root dependence is in contrast with  $(\phi_\infty)^{1/3}$  which might be expected if the competition effect depended upon the mean separation between the grains, which is proportional to the cube root of the volume. In the treatment supplied above, we have assumed that the surface of each grain is in equilibrium with its local environment and that its growth is diffusion-controlled. If, however, the relaxation of the grain radius to accommodate changes in its local environment is not instantaneous, then the growth of the grain is not diffusion-controlled. The volume-fraction effects predicted above diminish as the degree of diffusion-control decreases, becoming zero in the limit that diffusion is infinitely fast. In this limit, the mean radius increases as  $t^{1/2}$ , the number of grains per unit volume decreases as  $t^{2/3}$ , and the grain size distribution function  $F_0(Z)$  is substantially broadened [5].

### 3.8.2 Application to the System Succinonitrile/Water

The growth of grains described above involves an evaporation-condensation mechanism with molecular transport between grains by diffusion. In almost all systems, the continuous phase and the granular phase have different densities, however. This means that the evaporation-condensation mechanism (Ostwald ripening) may be obscured by the gravitational convection and collisional coagulation of the growing grains. Experimentation in the acceleration-free environment of an Earth orbiting laboratory removes the effect of gravitational convection and permits the free observation of the Ostwald ripening of the precipitate grains.

Phase equilibrium in the two component system, succinonitrile ( $\text{NCCH}_2\text{CH}_2\text{CN}$ ) and water is summarized in the phase diagram shown in Figure 3.4. The diagram is marked by a monotectic point (two liquids and solid  $\text{C}_4\text{H}_4\text{N}_2$ ) in equilibrium, which is characteristic of many two-component metal alloys. The system succinonitrile/water has some distinct advantages for studying the process of Ostwald ripening. These are: (1) The system is transparent to visible light at all compositions and temperatures, so that the growth of second phase droplets can be observed photographically. (2) The consolute and monotectic points occur near room temperature, so that little heat is required to keep the system in a liquid state; in space flight where electric power is at a premium, this is an important advantage. (3) The thermophysical properties of the system are rather well studied. (4) Near 41 °C, the droplet and continuous phases have the same density, so that at this temperature the Ostwald ripening process can be observed even in Earth's gravity.

In Table 3.1, we have summarized the thermophysical properties of the succinonitrile/water system at  $25 \pm 1$  °C. The primed symbols refer to the succinonitrile rich phase (droplets). The coefficient for interdiffusion on the water-rich side of the phase diagram (continuous phase) is  $D$ . The interfacial tension is  $\gamma$ . The subscript A refers to succinonitrile while the subscript B refers to water.

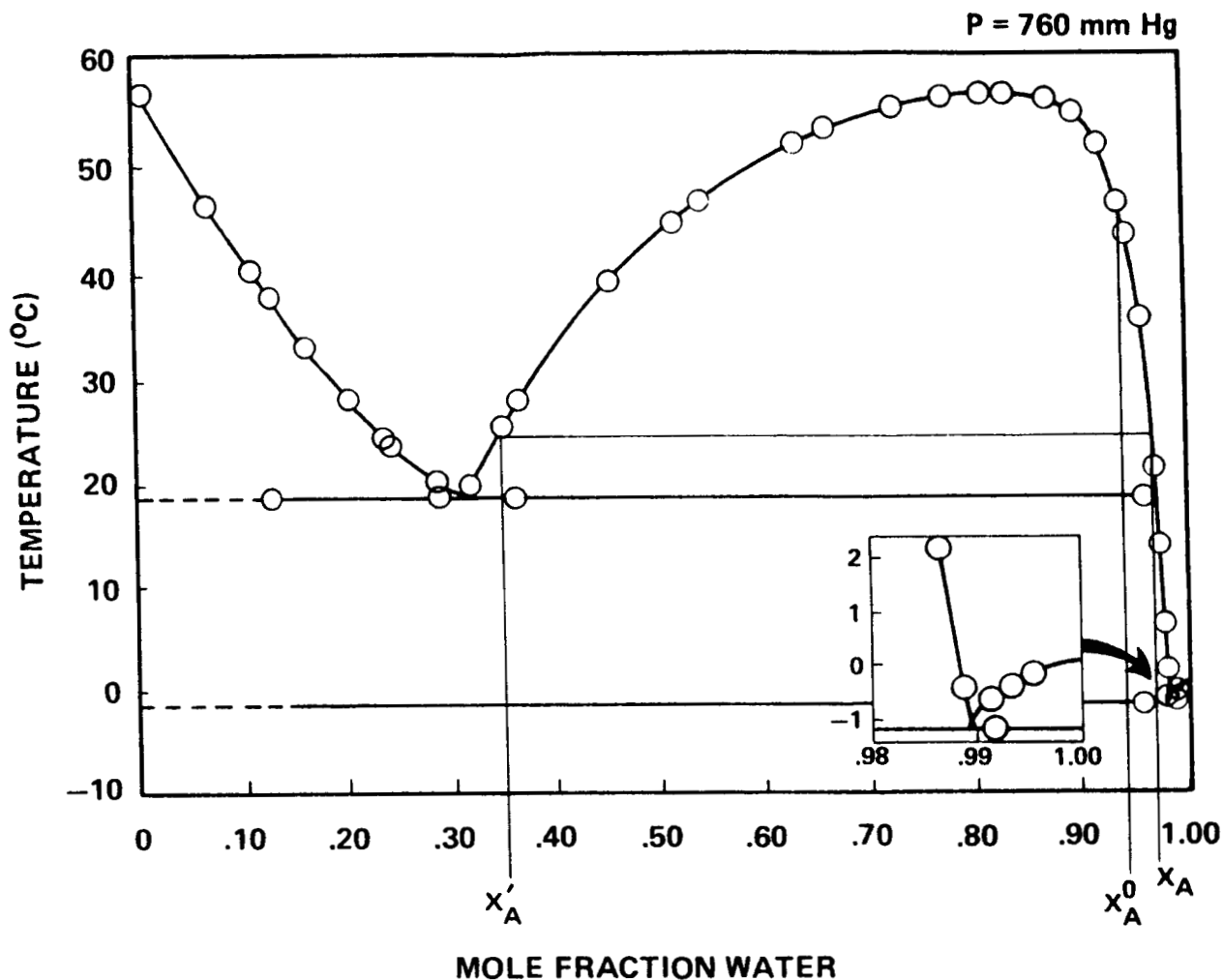


Figure 3.4. Phase diagram for the system succinonitrile/water.

TABLE 3.1 THERMOPHYSICAL DATA FOR THE SYSTEM  $C_4H_4N_2/H_2O$  AT  $25 \pm 1$  °C

A =  $C_4H_4N_2$ , B =  $H_2O$ . Primes on symbols refer to the succinonitrile-rich phase.

Succinonitrile Rich Phase

$$x'_A = 0.646$$

$$x'_B = 0.354$$

$$\rho' = 1.0121 \text{ gm/cm}^3$$

Water Rich Phase

$$x_A = 0.032$$

$$x_B = 0.968$$

$$\rho = 1.0052 \text{ gm/cm}^3$$

Other data:  $\gamma = 2.484 \text{ erg/cm}^2$ ;  $D = 1.27 \times 10^{-5} \text{ cm}^2/\text{sec}$   $(MW)_A = 80 \text{ gm/mole}$ ;  $(MW)_B = 18 \text{ gm/mole}$ .

If the continuous phase is to be water-rich, the initial composition of the system must lie to the right in the phase diagram. By the lever rule, the initial mole fraction of A,  $X_A^O$ , is related to the equilibrium values,  $X_A$  and  $X_A'$ , by

$$\frac{n}{n'} = \frac{X_A' - X_A^O}{X_A^O - X_A} \quad (3.8.15)$$

where  $n'$  and  $n$  are the number of moles of A-rich and B-rich phases, respectively, in the equilibrium mixture. The volumes occupied by the two phases at equilibrium are, respectively,

$$V' = n' \bar{V}' \quad (3.8.16)$$

and

$$V = n \bar{V} \quad (3.8.17)$$

where

$$\bar{V}' = (X_A' (MW)_A + X_B' (MW)_B) / \rho' N_O \quad (3.8.18)$$

and

$$\bar{V} = (X_A (MW)_A + X_B (MW)_B) / \rho N_O \quad (3.8.19)$$

are the respective average molecular volumes in the two phases. the fraction of the total volume occupied by the A-rich phase at equilibrium is

$$\phi_\infty = \frac{V'}{V' + V} = \frac{1}{1 + (V/V')} \quad (3.8.20)$$

where by Eqs. (3.8.16) through (3.8.19),

$$\frac{V}{V'} = \frac{\rho'}{\rho} \cdot \frac{X_A(\text{MW})_A + X_B(\text{MW})_B}{X'_A(\text{MW})_A + X'_B(\text{MW})_B} \cdot \frac{X'_A - X_A^O}{X_A^O - X_A} \quad (3.8.21)$$

The thermophysical data in Table 3.1 are for equilibrium at 25±1 °C. We specify the desired equilibrium volume fraction of the A-rich phase to be  $\phi_\infty = 0.1$ , since this is one of the larger values considered in Figures 3.1-3.2 and can be expected to demonstrate the competition effect. Combining the data in Table 3.1 with  $\phi_\infty = 0.1$  according to Eqs. (3.8.20) and (3.8.21), we find that the system should be prepared initially so that its composition is  $X_A^O = 0.055$ , that is it should be 5.5 mole percent  $C_4H_4N_2$  and 94.5 mole percent water. This and other results are summarized in Table 3.2.

From Eqs. (3.8.1), (3.8.4), and (3.8.6) we find that the initial supersaturation,  $\sigma(0)$ , is 0.70. This means that the initial succinonitrile concentration in the continuous phase is 70% greater than it will be when equilibrium is achieved. This immediately determines the initial critical radius for growth or dissolution through Eq. (3.8.12) with  $t$  set equal to zero. We find  $R_{\text{crit}}(0) = 1.64 \times 10^{-4} \mu\text{m}$  or 1.64 Å.

The other quantities in Table 3.2 cannot be calculated at  $t = 0$ , because the formulae, Eqs. (3.8.7), (3.8.8), (3.8.9), (3.8.11), (3.8.13), and (3.8.14), are all asymptotic and accurate only when  $t \gg \theta$ . We have chosen to evaluate these formulae at a time where the mean radius in the distribution achieves 1  $\mu\text{m}$ , which is a size convenient for holographic photography. This occurs at  $t = 89$  sec, which may be seen from Table 3.2 vastly to exceed  $\theta = 30.4$  ps. At this time, the minimum radius in the distribution is 0.21  $\mu\text{m}$ , while the maximum radius is 1.7  $\mu\text{m}$ . The critical radius, 1.1  $\mu\text{m}$ , slightly exceeds the mean radius. Having been initially 70%, the supersaturation is just  $6.8 \times 10^{-3}\%$ . There are  $2.2 \times 10^{10}$  droplets of the  $C_4H_4N_2$ -rich phase per  $\text{cm}^3$ .

TABLE 3.2 CALCULATED RESULTS FOR THE SYSTEM  $C_4H_4N_2/H_2O$  AT  $25 \pm 1$  °C  
AND  $\mu_\infty = 0.1$

The results in the table are based on the following quantities; the equation or figure used to specify each quantity is shown in parentheses next to the numerical value:  $\bar{V}' = 9.52 \times 10^{-23}$  cm<sup>3</sup>/molecule [Eq. (3.8.1)].  $\bar{V}'_A = 6.15 \times 10^{-23}$  cm<sup>3</sup>/molecule [Eq. (3.8.2)].  $C_A(\infty) = 9.66 \times 10^{20}$  molecules/cm<sup>3</sup> [Eq. (3.8.4)].  $\alpha = 7.43 \times 10^{-9}$  cm [Eq. (3.3.3)].  $\theta = 3.04 \times 10^{-11}$  sec [Eq. (3.8.5)].  $\rho_0 = 1.1$  (Figure 3.1).  $\sigma_1 = 0.97$  (Figure 3.1).  $a_0 = 0.94$  (Figure 3.1).  $Z_0 = 1.6$  (Figure 3.3).  $X_A^0 = 0.055$ .

t(sec)	$\rho$ (cm <sup>-3</sup> )	$\sigma$	$R_{min}$ (μm)	$R_{crit}$ (μm)	$\langle R \rangle$ (μm)	$R_{max}$ (μm)
0	---	$7.0 \times 10^{-1}$	---	$1.1 \times 10^{-4}$	---	---
89	$2.2 \times 10^{10}$	$6.8 \times 10^{-5}$	0.21	1.1	1.0	1.7
$3.45 \times 10^5$	$5.6 \times 10^6$	$4.3 \times 10^{-6}$	3.3	17	16	27

After 4 days (345,600 sec), which might be the length of an experiment carried into orbit by the space shuttle, the mean radius has increased to 16 μm. The minimum radius is 3.3 μm, while the maximum radius is 27 μm. The remaining supersaturation is just  $4.3 \times 10^{-6} = 4.3 \times 10^{-4}\%$ , which is extremely close to equilibrium. The number of droplets has decreased to  $5.6 \times 10^6$  per cm<sup>3</sup>.

Because the characteristic length,  $\alpha = 7.43 \times 10^{-9}$  cm, is quite small, the approximation,  $R > \alpha$ , invoked to obtain Eq. (3.2.14) is established early in this system. In fact, because the interfacial energy,  $\gamma = 2.484$  erg/cm<sup>2</sup>, is small, the approximation becomes good when the droplet has just barely achieved molecular size. It is doubtful that interfacial energy even can be defined at this small size, although this in no way diminishes the power of the approximation.

Likewise, because  $\alpha$  is so small, the characteristic time scale,  $\theta = 30.4$  ps, is very short. For times of the order of 1 ps or less, molecular motion as represented by a diffusion coefficient cannot be defined. Hence, in the system succinonitrile/water, the condition,  $t \gg \theta$ , required for the validity of the asymptotic formulae, is established rapidly. This means that the theory should be applicable as soon as the initial nucleation phase is complete and the surface between the droplet and



the continuous phase is sufficiently established for an interfacial energy to be defined.

It is useful to compare the phase separation of metallic alloys with the system succinonitrile/water. For liquid alloys, the interfacial energy is about a factor of 10 higher, which increases  $\alpha$  by a factor of 10, assuming room temperature. On the other hand, according to Eq. (3.8.5),  $\theta$  increases by a factor of 100. Nevertheless, because of Eq. (3.8.13), droplets of 1  $\mu\text{m}$  size can be expected to be observed after 8.9 sec at room temperature, which is a factor of 10 sooner. On the other hand, in solid non-equilibrium metal alloys, the diffusion coefficient should be about  $10^{-11}$   $\text{cm}^2/\text{sec}$ , implying that  $\theta$  increases by about a factor of  $10^{13}$  over succinonitrile/water. The time to form grains of 1  $\mu\text{m}$  extends to  $8.9 \times 10^{10}$  sec, implying that these non-equilibrium alloys are metastable over times substantially exceeding their expected useful lifetimes.

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APPENDIX A - THE DELTA FUNCTION AND ITS PROPERTIES

To  
 PAUL DIRAC  
 who saw that it must be true,

LAURENT SCHWARTZ  
 who proved it,

and

GEORGE TEMPLE  
 who showed how simple it could be made

The above is from the dedication to the book by M J. Lighthill, Fourier Analysis and Generalized Functions, Cambridge University Press, 1964.

The Dirac delta function has many applications in applied mathematics, not the least of which is its use as a representation of a point source with the partial differential equations of mathematical physics.

The delta function can be represented as a limit of a sequence of functions. Consider, the sequence, defined by (other sequences are also possible),

$$\delta_n(x) = \frac{n}{\pi^{1/2}} \exp(-n^2 x^2), \quad n = 1, 2, \dots \quad (\text{A.1})$$

The delta function is the limit

$$\delta(x) = \lim_{n \rightarrow \infty} \delta_n(x) = \lim_{n \rightarrow \infty} \frac{n}{\pi^{1/2}} \exp(-n^2 x^2) \quad (\text{A.2})$$

In Figure A.1, we show how  $\delta_n(x)$  looks for increasing values of  $n$ . Each  $\delta_n(x)$  gets taller and narrower as  $n$  becomes larger. In the limit  $n \rightarrow \infty$ ,  $\delta_n(x)$  gets infinitely tall and narrow (a point source), and is called the Dirac delta function,  $\delta(x)$ .

Although  $\delta(x)$  is highly singular, it has many uses when it appears within integrals. For example

$$\begin{aligned} \int_{-\infty}^{+\infty} dx \delta(x) &= \int_{-\infty}^{+\infty} dx \lim_{n \rightarrow \infty} \delta_n(x) \\ &= \lim_{n \rightarrow \infty} \frac{n}{\pi^{1/2}} \int_{-\infty}^{+\infty} dx e^{-n^2 x^2} = 1. \end{aligned} \quad (\text{A.3})$$

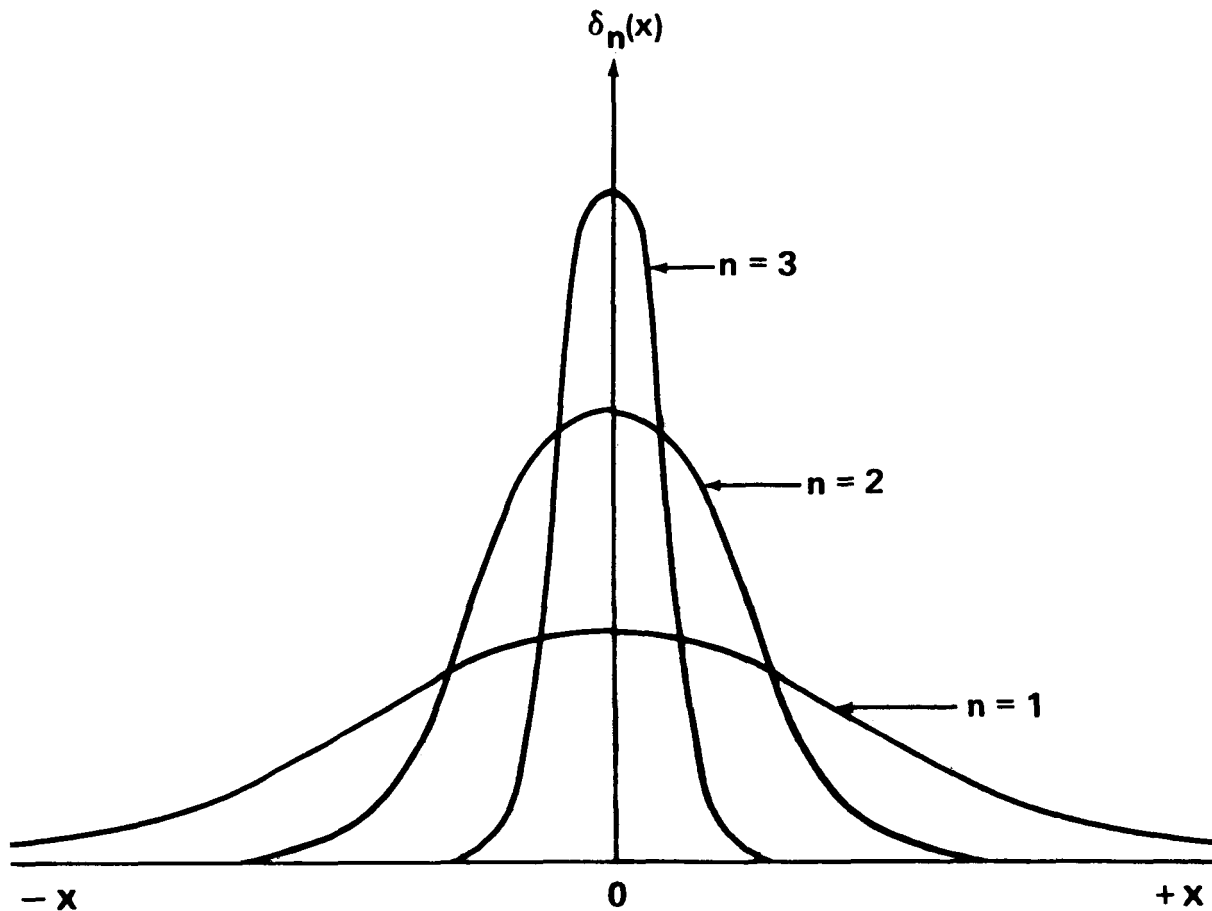


Figure A.1. Sequence of functions representing the Dirac delta function in the limit  $n \rightarrow \infty$ .

Summarizing, this important property is

$$\int_{-\infty}^{+\infty} dx \delta(x) = 1. \quad (\text{A.4})$$

Let  $f(x)$  be an integrable function of  $x$ . Another important property is

$$\int_{-\infty}^{+\infty} dx f(x) \delta(x - x') = f(x'). \quad (\text{A.5})$$

We demonstrate this using Eq. (A.1)

$$\delta(x - x') = \lim_{n \rightarrow \infty} \frac{n}{\pi} \exp[-n^2(x - x')^2]. \quad (\text{A.6})$$

To be specific, let  $f(x) = e^x$ , then

$$\begin{aligned} \int_{-\infty}^{+\infty} dx e^x \delta(x - x') &= \lim_{n \rightarrow \infty} \frac{n}{\pi} \int_{-\infty}^{+\infty} dx e^x e^{-n^2(x - x')^2} \\ &= \lim_{n \rightarrow \infty} \frac{n}{\pi} e^{-n^2 x'^2} \int_{-\infty}^{+\infty} dx e^{-n^2 x^2 + (2n^2 x' + 1)x} \\ &= \lim_{n \rightarrow \infty} \frac{n}{\pi} e^{-n^2 x'^2} \cdot e^{n^2 \left(\frac{2n^2 x' + 1}{2n^2}\right)^2} \int_{-\infty}^{+\infty} dx e^{-n^2 \left[x - \frac{1}{2} \frac{(2n^2 x' + 1)}{n^2}\right]^2} \\ &= \lim_{n \rightarrow \infty} \frac{n}{\pi} e^{-n^2 x'^2} \cdot e^{n^2 \left(\frac{2n^2 x' + 1}{2n^2}\right)^2} \frac{\pi}{n} \\ &= e^{x'} \lim_{n \rightarrow \infty} e^{(1/4n^2)} = e^{x'} \cdot e^0 = e^{x'}. \end{aligned} \quad (\text{A.7})$$

We have shown explicitly that

$$\int_{-\infty}^{+\infty} dx e^x \delta(x - x') = e^{x'}.$$

The delta function can be generalized to three dimensions. In rectangular coordinates,  $\delta(\mathbf{r} - \mathbf{r}')$  means

$$\delta(\mathbf{r} - \mathbf{r}') = \delta(x - x')\delta(y - y')\delta(z - z'). \quad (\text{A.8})$$

The integral property expressed by Eq. (A.5) can be generalized to

$$f(\mathbf{r}') = \int d^3r f(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \quad (\text{A.9})$$

where the symbols in Eq. (A.9) have the meanings:

$$f(\mathbf{r}) \equiv f(x, y, z) \quad (\text{A.10})$$

$$d^3 r \equiv dx dy dz. \quad (\text{A.11})$$

The integral sign in Eq. (A.9) represents a triple integral, namely

$$\int d^3 r \equiv \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz. \quad (\text{A.12})$$

Combining Eqs. (A.8)-(A.12), we can show how the right-hand side of Eq. (A.9) is computed.

$$\begin{aligned} \int d^3 r f(\mathbf{r}) \delta(\mathbf{r}' - \mathbf{r}) &= \int_{-\infty}^{+\infty} dx \delta(x - x') \int_{-\infty}^{+\infty} dy \delta(y - y') \int_{-\infty}^{+\infty} dz \delta(z - z') f(x, y, z) \\ &= \int_{-\infty}^{+\infty} dx \delta(x - x') \int_{-\infty}^{+\infty} dy \delta(y - y') f(x, y, z') \\ &= \int_{-\infty}^{+\infty} dx \delta(x - x') f(x, y', z') = f(x', y', z') \end{aligned} \quad (\text{A.13})$$

where we have used Eq. (A.5) on each coordinate separately.

Finally, it is worth noting that by virtue of Eqs. (A.2) and (A.8), the delta function is an even function of its argument, namely

$$\delta(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r}' - \mathbf{r}). \quad (\text{A.14})$$

APPENDIX B - FICK'S FIRST AND SECOND LAWS WITH DELTA FUNCTION SINKS

Fick's first law of diffusion is

$$J(x) = -D \frac{dC(x)}{dx}$$

where  $C(x)$  is the concentration [say molecules/cm<sup>2</sup>] of the diffusing species and  $J(x)$  [molecules/cm<sup>2</sup> sec] is the flux of that species measured across a plane whose normal points in the +x-direction.

Fick's first law makes physical sense. Consider the concentration profiles shown in Figure B.1.

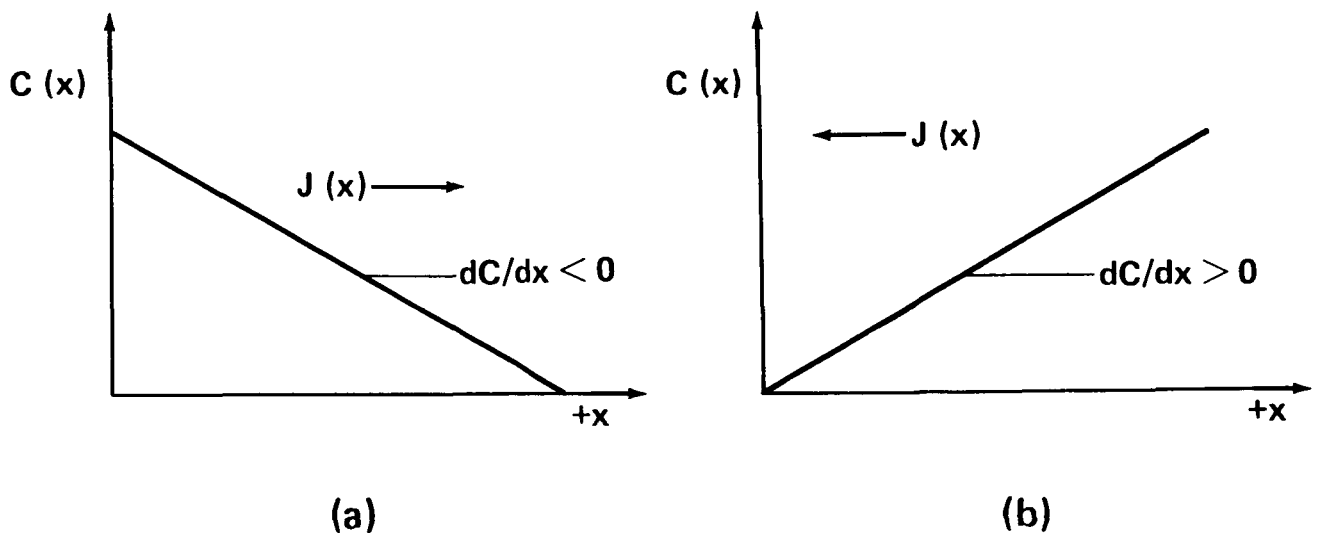


Figure B.1. (a) Negative concentration gradient showing direction of molecular flux; (b) Positive concentration gradient showing direction of molecular flux.

In both cases,  $J(x)$  points in a direction so that particle motion serves to smooth out the concentration gradient.

Generalized to three dimensions, Fick's first law reads

$$J(\mathbf{r}) = -D\nabla C(\mathbf{r}) \tag{B.1}$$

where  $\mathbf{r} = (x,y,z)$  is the position coordinate locating a point in space where the concentration is  $C(\mathbf{r})$ .

Now, return to one dimension and consider the flux  $J(x)$  crossing a plane at  $x$  and another flux  $J(x + dx)$  crossing a plane a distance  $dx$  away at  $x + dx$ . This is depicted in Figure B.2.

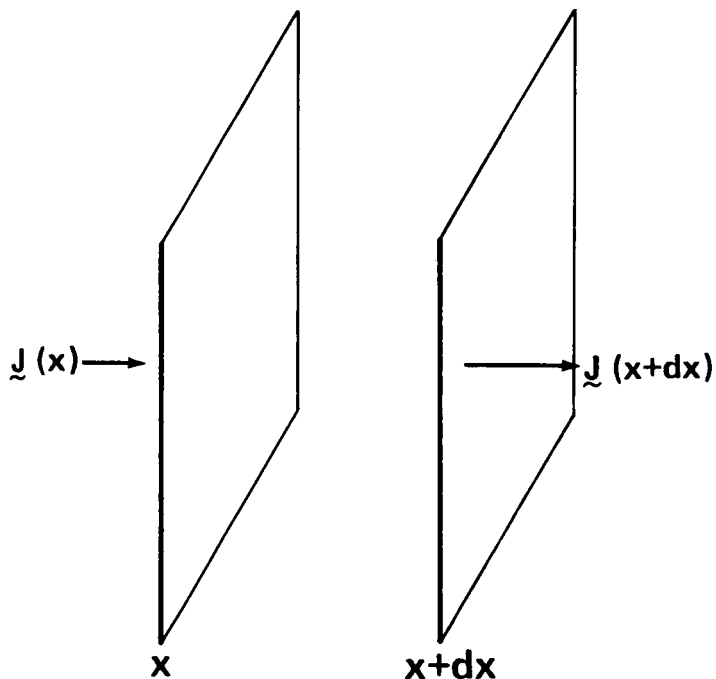


Figure B.2. Geometry for derivation of Fick's second law.

Inside the volume enclosed by the two planes, we allow material to be generated by some sources (e.g., chemical reactions). For mathematical convenience, we may separate these into two types: (1) Continuous sources are defined everywhere and are represented by continuous functions,  $\phi(x)$ . The units of  $\phi(x)$  are, for example, molecules/cm<sup>3</sup> sec. (2) Point sources are represented by delta functions as  $q\delta(x - x')$  where  $q$  is a constant (strength of the source) and  $x'$  lies between  $x$  and  $x + dx$ . If the units of  $x$  are cm, then the units of  $\delta(x - x')$  must be cm<sup>-1</sup> so that the integral

$$\int_{-\infty}^{+\infty} dx \delta(x - x') = 1$$

is dimensionless. This implies that  $q$  has the units molecules/cm<sup>2</sup> sec; hence,  $q\delta(x - x')$  has the units molecules/cm<sup>3</sup> sec.



The distinction between a source and a sink is a matter of sign. Everywhere  $\phi(x) < 0$ , it describes a sink. Likewise, if  $q < 0$ ,  $q\delta(x - x')$  is a point sink.

The buildup (depletion) of material between  $x$  and  $x + dx$  can be described in terms of the fluxes and the sources and sinks. Let the planes at  $x$  and  $x + dx$  have the common cross section,  $A$ . The volume of material between the planes is  $Adx$ , whereas the amount of material is  $C(x)Adx$ . If we allow all functions to depend also upon the time  $t$ , then the net rate of buildup of material within this volume is  $(\partial C(x, t)/\partial t)Adx$  and

$$\frac{\partial C(x, t)}{\partial t} Adx = J(x, t)A - J(x + dx, t)A + \phi(x)Adx + q\delta(x - x')Adx \quad (B.2)$$

where we have allowed for the presence of both continuous and point sources. We expand  $J(x + dx, t)$  in a Taylor series about  $x$ , as

$$J(x + dx, t) = J(x, t) + \frac{\partial J(x, t)}{\partial x} dx \quad (B.3)$$

keeping only terms up to the first order in  $dx$ . We now substitute Eq. (B.3) into Eq. (B.2) to obtain

$$\begin{aligned} \frac{\partial C(x, t)}{\partial t} Adx &= J(x, t)Adx - J(x, t)Adx - \frac{\partial J(x, t)}{\partial x} Adx \\ &+ \phi(x)Adx + q\delta(x - x')Adx \quad . \end{aligned} \quad (B.4)$$

After cancellation of terms of opposite sign, common factors, and algebraic rearrangement

$$\frac{\partial C(x, t)}{\partial t} + \frac{\partial J(x, t)}{\partial x} = \phi(x) + q\delta(x - x') \quad (B.5)$$

Eq. (B.5) can be generalized to three dimensions:

$$\frac{\partial C(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{J}(\mathbf{r}, t) = \phi(\mathbf{r}) + q\delta(\mathbf{r} - \mathbf{r}') \quad (\text{B.6})$$

where we have used the definition of  $\delta(\mathbf{r} - \mathbf{r}')$  given by Eq. (A.8). We substitute Eq. (B.2) and obtain

$$\frac{\partial C(\mathbf{r}, t)}{\partial t} - D\nabla^2 C(\mathbf{r}, t) = \phi(\mathbf{r}) + q\delta(\mathbf{r} - \mathbf{r}') \quad (\text{B.7})$$

which expresses Fick's second law.

In the steady state, the concentration field,  $C(\mathbf{r}, t)$  is no longer a function of time and  $\partial C/\partial t = 0$ , so that Eq. (B.7) becomes

$$D\nabla^2 C(\mathbf{r}) = -\phi(\mathbf{r}) - q\delta(\mathbf{r} - \mathbf{r}') . \quad (\text{B.8})$$

## APPENDIX C - THE GREEN'S FUNCTION METHOD

### C.1 General Principles

The Green's function method is a technique for integrating inhomogeneous partial differential equations. Essentially, it is a generalization of the method of variation of parameters used to solve inhomogeneous ordinary differential equations.

In steady state diffusion, we are faced with the solution of a partial differential equation of the form

$$D\nabla^2 C(\mathbf{r}) = f(\mathbf{r}) \quad (\text{C.1})$$

where  $f(\mathbf{r})$  is a source term which, by virtue of its presence, makes Eq. (C.1) inhomogeneous. There must also be some conditions specifying the value of  $C(\mathbf{r})$  on the boundaries.

### C.2 Green's Problem

In order to solve Eq. (C.1) by the Green's function method, we suppose that we may solve exactly the equation

$$D\nabla^2 G(\mathbf{r}|\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (\text{C.2})$$

where  $G(\mathbf{r}|\mathbf{r}')$  is called the Green's function, whose values we are free to choose on the boundaries. Because of the singular properties of the delta function, Eq. (C.2) is homogeneous everywhere except at the point  $\mathbf{r} = \mathbf{r}'$ . Eq. (C.2) is known as Green's problem.

We proceed to solve Eq. (C.2) for  $G(\mathbf{r}|\mathbf{r}')$ . To accomplish this, we make use of the divergence theorem, which states

$$\int d^3r \nabla \cdot \mathbf{F}(\mathbf{r}) = \int d\mathbf{S} \cdot \mathbf{F}(\mathbf{r}) \quad (\text{C.3})$$

where  $\mathbf{F}(\mathbf{r})$  is a vector-valued function of the position  $\mathbf{r}$  and where in rectangular coordinates,  $\mathbf{r} = (x, y, z)$ . The triple integral covers the entire volume enclosed by the boundary  $S$ .

Consider the vectors,  $\mathbf{r}$  and  $\mathbf{r}'$ , as shown in Figure C.1.

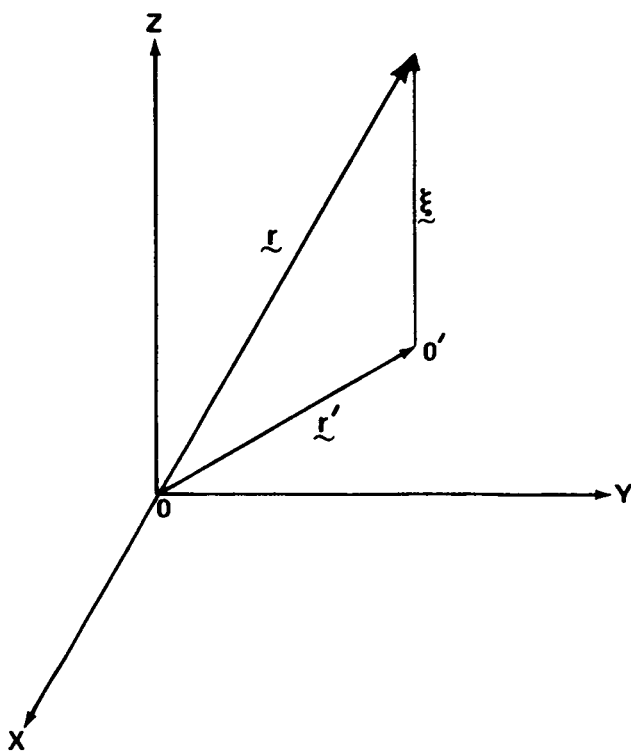


Figure C.1. Geometry of origins  $O$  and  $O'$ .

We define the vector  $\xi$  by

$$\xi = \mathbf{r} - \mathbf{r}' = (x - x', y - y', z - z') \quad (\text{C.4})$$

With  $\mathbf{r}'$  fixed and the origin at  $O'$ ,  $\nabla_{\mathbf{r}}$ , the divergence with respect to  $\mathbf{r}$ , is identical to  $\nabla_{\xi}$ , the divergence with respect to  $\xi$ . This is because

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial (x - x')} \quad (\text{C.5})$$

etc. With the variable change specified by Eq. (C.4), Eq. (C.2) becomes

$$\text{div}_{\xi}^2 G(\xi|\mathbf{r}') = \delta(\xi). \quad (\text{C.6})$$

Note that

$$\nabla_{\xi}^2 G(\xi|\mathbf{r}') = \nabla_{\xi} \cdot (\nabla_{\xi} G(\xi|\mathbf{r}')). \quad (\text{C.7})$$

Integrate Eq. (C.6) over all space starting from the origin at  $O'$ .

$$\begin{aligned} \int d^3\xi \delta(\xi) &= 1 = \int d^3\xi D \nabla_{\xi} \cdot (\nabla_{\xi} G(\xi|\mathbf{r}')) \\ &= D \int dS_{\xi} \cdot \nabla_{\xi} G(\xi|\mathbf{r}') \end{aligned} \quad (\text{C.8})$$

where we have used Eq. (C.3) with  $\mathbf{F}(\mathbf{r}) = \nabla_{\xi} G(\xi|\mathbf{r}')$ . We let our volume of interest be a sphere centered on  $O'$ . The radius of this sphere is  $\xi = |\xi|$  which has surface area  $4\pi\xi^2$ . The normal to the surface of this sphere points in the  $\xi$ -direction. We intend for  $\delta(\xi)$ , to represent a point source (isotropic) centered on  $O'$ ; hence,  $G(\xi|\mathbf{r}')$  must also be isotropic (i.e., depending only upon  $\xi = |\xi|$  and independent of angles). The surface integral in Eq. (C.8) is then equal to

$$D \int dS_{\xi} \cdot \nabla_{\xi} G(\xi|\mathbf{r}') = 4\pi\xi^2 D \frac{\partial G(\xi|\mathbf{r}')}{\partial \xi} \quad (\text{C.9})$$

where  $\partial G/\partial \xi$  is the gradient of  $G$  in the  $\xi$ -direction (the radial direction for spherical polar coordinates centered on  $O'$ ). Putting Eq. (C.9) into Eq. (C.8), we obtain

$$\frac{\partial G(\xi|\mathbf{r}')}{\partial \xi} = \frac{1}{4\pi D \xi^2} \quad (\text{C.10})$$

Eq. (C.10) can be integrated to read

$$G(\xi|\mathbf{r}') = -\frac{1}{4\pi D \xi} + C \quad (\text{C.11})$$

where  $C$  is a constant. We take as boundary condition,  $G(\infty|\mathbf{r}') = 0$ , from which we conclude

$$G(\mathbf{r}|\mathbf{r}') = -\frac{1}{4\pi D |\mathbf{r} - \mathbf{r}'|} \quad (\text{C.12})$$

where we have used Eq. (C.4) and  $\xi = |\xi| = |\mathbf{r} - \mathbf{r}'|$ . The gradient of  $G(\mathbf{r}|\mathbf{r}')$  is

$$\begin{aligned} \nabla G(\mathbf{r}|\mathbf{r}') &= -\frac{1}{4\pi D} \left[ \hat{\mathbf{i}} \frac{\partial}{\partial x} + \hat{\mathbf{j}} \frac{\partial}{\partial y} + \hat{\mathbf{k}} \frac{\partial}{\partial z} \right] \frac{1}{\left( (x-x')^2 + (y-y')^2 + (z-z')^2 \right)^{1/2}} \\ &= \frac{1}{4\pi D} \left[ \frac{(x-x') \hat{\mathbf{i}} + (y-y') \hat{\mathbf{j}} + (z-z') \hat{\mathbf{k}}}{\left( (x-x')^2 + (y-y')^2 + (z-z')^2 \right)^{3/2}} \right] \end{aligned} \quad (\text{C.13})$$

which, in the limit that  $x, y, z$  all go to infinity, is zero. Hence, the Green's function expressed by Eq. (C.12) satisfies the boundary conditions

$$\lim_{r \rightarrow \infty} G(\mathbf{r}|\mathbf{r}') = \lim_{r \rightarrow \infty} \nabla G(\mathbf{r}|\mathbf{r}') = 0. \quad (\text{C.14})$$

Note further that because of the absolute value sign in Eq. (C.12),  $G(\mathbf{r}|\mathbf{r}')$  is symmetric upon interchange of  $\mathbf{r}$  and  $\mathbf{r}'$ , namely

$$G(\mathbf{r}|\mathbf{r}') = G(\mathbf{r}'|\mathbf{r}). \quad (\text{C.15})$$

This is called the reciprocity relation for the Green's function and is due to the fact that the operator  $\nabla^2$  is self-adjoint.

### C.3 Green's Theorem

We propose to solve Eq. (C.1) by expressing  $C(\mathbf{r})$  in terms of some integrals involving  $G(\mathbf{r}|\mathbf{r}')$ ,  $f(\mathbf{r})$ , and the values of  $C(\mathbf{r})$  specified on the boundaries (boundary conditions). To begin, we reexpress Eqs. (C.1) and (C.2) as partial differential equations in terms of the variable,  $\mathbf{r}'$ ,

$$D\nabla'^2 C(\mathbf{r}') = f(\mathbf{r}') \quad (\text{C.16})$$

$$D\nabla'^2 G(\mathbf{r}'|\mathbf{r}) = \delta(\mathbf{r}' - \mathbf{r}) \quad (\text{C.17})$$

where  $\nabla'^2$  is the Laplacian operating on the variable  $\mathbf{r}'$ . Now multiply Eq. (C.16) through by  $G(\mathbf{r}'|\mathbf{r})$  and Eq. (C.17) through by  $C(\mathbf{r}')$  and subtract. The result is

$$G(\mathbf{r}'|\mathbf{r}) D\nabla'^2 C(\mathbf{r}') - C(\mathbf{r}') D\nabla'^2 G(\mathbf{r}'|\mathbf{r}) = G(\mathbf{r}'|\mathbf{r}) f(\mathbf{r}') - C(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}). \quad (\text{C.18})$$

The left-hand side of Eq. (C.18) may be simplified by using the vector identity

$$\nabla' \cdot (A \nabla' B) = \nabla' A \cdot \nabla' B + A \nabla'^2 B \quad (\text{C.19})$$

where  $A(\mathbf{r}')$  and  $B(\mathbf{r}')$  are functions of  $\mathbf{r}'$ . Eq. (C.19) can be rearranged to read

$$A \nabla'^2 B = -\nabla' A \cdot \nabla' B + \nabla' \cdot (A \nabla' B) . \quad (\text{C.20})$$

Using Eq. (C.20) with  $A \equiv G$  and  $B \equiv C$ , the first term on the right-hand side of Eq. (C.18) may be written

$$G(\mathbf{r}' | \mathbf{r}) \nabla'^2 C(\mathbf{r}') = \nabla' \cdot (G(\mathbf{r}' | \mathbf{r}) \nabla' C(\mathbf{r}')) - \nabla' G(\mathbf{r}' | \mathbf{r}) \cdot \nabla' C(\mathbf{r}') \quad (\text{C.21})$$

and using Eq. (C.20) with  $A \equiv C$  and  $B \equiv G$ , the second term on the left-hand side may be written

$$C(\mathbf{r}') \nabla'^2 G(\mathbf{r}' | \mathbf{r}) = \nabla' \cdot (C(\mathbf{r}') \nabla' G(\mathbf{r}' | \mathbf{r})) - \nabla' C(\mathbf{r}') \cdot \nabla' G(\mathbf{r}' | \mathbf{r}) . \quad (\text{C.22})$$

Substituting Eqs. (C.21) and (C.22) into Eq. (C.18), we obtain

$$\nabla' \cdot [G(\mathbf{r}' | \mathbf{r}) \nabla' C(\mathbf{r}') - C(\mathbf{r}') \nabla' G(\mathbf{r}' | \mathbf{r})] = G(\mathbf{r}' | \mathbf{r}) f(\mathbf{r}') - C(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}) . \quad (\text{C.23})$$

We next integrate both sides of Eq. (C.23) over the volume of all space, i.e.,  $\int d^3 r'$ , and apply the divergence theorem to the left-hand side. The result is

$$\begin{aligned} D \int dS' \cdot [G(\mathbf{r}' | \mathbf{r}) \nabla' C(\mathbf{r}') - C(\mathbf{r}') \nabla' G(\mathbf{r}' | \mathbf{r})] \\ = \int d^3 r' G(\mathbf{r}' | \mathbf{r}) f(\mathbf{r}') - \int d^3 r' C(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}) . \end{aligned} \quad (\text{C.24})$$

On the basis of Eq. (A.9), the second term on the right-hand side of Eq. (C.8) (note that the roles of  $\mathbf{r}$  and  $\mathbf{r}'$  have been interchanged) is just equal to  $C(\mathbf{r})$ . Hence, Eq. (C.24) may be rewritten

$$C(\mathbf{r}) = D \int d\mathbf{S}' \cdot [C(\mathbf{r}')\mathbf{V}'G(\mathbf{r}'|\mathbf{r}) - G(\mathbf{r}'|\mathbf{r})\mathbf{V}'C(\mathbf{r}')] + \int d^3\mathbf{r}'G(\mathbf{r}'|\mathbf{r})f(\mathbf{r}'). \quad (\text{C.25})$$

If we let the surface,  $S'$ , recede infinitely far away, i.e.,  $\mathbf{r}' \rightarrow \infty$ , we may employ Eq. (C.14) to evaluate the surface integral in Eq. (C.25). We conclude that so computed this integral is zero. Hence, we obtain finally from Eq. (C.25) the result

$$C(\mathbf{r}) = \int d^3\mathbf{r}'G(\mathbf{r}|\mathbf{r}')f(\mathbf{r}') \quad (\text{C.26})$$

where we have used the reciprocity of  $G(\mathbf{r}|\mathbf{r}')$  expressed by Eq. (C.15). Provided that the integral on the right-hand side of Eq. (C.26) may be computed, this serves to solve Eq. (C.1).



APPENDIX D - FOURIER TRANSFORMS

D.1 General Principles

Let  $\phi(x)$  be a function of the variable  $x$  where  $-\infty < x < +\infty$ . The Fourier transform,  $\hat{\phi}(k)$  of  $\phi(x)$  is

$$\hat{\phi}(k) = \int_{-\infty}^{+\infty} dx d^{-ikx} \phi(x) \quad (D.1)$$

where  $k$  is the transform variable and  $i = (-1)^{1/2}$ . Starting with Eq. (D.1), Fourier showed that  $\hat{\phi}(k)$  and  $\phi(x)$  are also related by

$$\phi(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dk e^{ikx} \hat{\phi}(k) . \quad (D.2)$$

Equation (D.1) may be generalized to three dimensions. Consider

$$\hat{\phi}(k_1, k_2, k_3) = \int_{-\infty}^{+\infty} dx e^{-ik_1x} \int_{-\infty}^{+\infty} dy e^{-ik_2y} \int_{-\infty}^{+\infty} dz e^{-ik_3z} \phi(x,y,z) \quad (D.3)$$

or

$$\hat{\phi}(\mathbf{k}) = \int d^3r d^{-i\mathbf{k}\cdot\mathbf{r}} \phi(\mathbf{r}) \quad (D.4)$$

where the triplet  $(k_1, k_2, k_3)$  is treated as a vector,  $\mathbf{k} = (k_1, k_2, k_3)$  and  $\mathbf{r} = (x, y, z)$ . Equation (D.2) generalized to three dimensions becomes

$$\phi(x,y,z) = \left(\frac{1}{2\pi}\right) \int_{-\infty}^{+\infty} dk_1 e^{ik_1x} \left(\frac{1}{2\pi}\right) \int_{-\infty}^{+\infty} dk_2 e^{ik_2y} \left(\frac{1}{2\pi}\right) \int_{-\infty}^{+\infty} dk_3 e^{ik_3z} \hat{\phi}(\mathbf{k}) \quad (D.5)$$

or

$$\phi(\mathbf{r}) = \left(\frac{1}{2\pi}\right)^3 \int d^3k e^{i\mathbf{k}\cdot\mathbf{r}} \hat{\phi}(\mathbf{k}). \quad (\text{D.6})$$

## D.2 Fourier Integral Representation of the Delta Function

In Eq. (D.4), let  $\phi(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')$ , then

$$\hat{\phi}(\mathbf{k}) = \int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') = e^{-i\mathbf{k}\cdot\mathbf{r}'}. \quad (\text{D.7})$$

We substitute Eq. (D.7) into Eq. (D.6) to obtain

$$\delta(\mathbf{r} - \mathbf{r}') = \left(\frac{1}{2\pi}\right)^3 \int d^3k e^{-i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}')}. \quad (\text{D.8})$$

Equation (D.8) is the very valuable Fourier integral representation of the delta function. It is much more useful than the representation expressed by Eq. (A.2).

An integral representation of the delta function in  $\mathbf{k}$ -space, namely  $\delta(\mathbf{k} - \mathbf{k}')$ , is obtained if in Eq. (D.6) we let  $\hat{\phi}(\mathbf{k}) = \delta(\mathbf{k} - \mathbf{k}')$ . We find

$$\phi(\mathbf{r}) = \left(\frac{1}{2\pi}\right)^3 \int d^3k e^{i\mathbf{k}\cdot\mathbf{r}} \delta(\mathbf{k} - \mathbf{k}') = \left(\frac{1}{2\pi}\right)^3 e^{i\mathbf{k}'\cdot\mathbf{r}}. \quad (\text{D.9})$$

Now substitute Eq. (D.9) into Eq. (D.4)

$$\delta(\mathbf{k} - \mathbf{k}') = \left(\frac{1}{2\pi}\right)^3 \int d^3r e^{-i(\mathbf{k} - \mathbf{k}')\cdot\mathbf{r}}. \quad (\text{D.10})$$

Equation (D.10) is an integral representation of  $\delta(\mathbf{k} - \mathbf{k}')$ .

The delta function in Fourier integral space has properties analogous to those it exhibits in real space, namely

$$\int d^3k' \delta(\mathbf{k}' - \mathbf{k}) = 1 \quad (\text{D.11})$$

$$\int d^3k' \delta(\mathbf{k}' - \mathbf{k}) f(\mathbf{k}') = f(\mathbf{k}). \quad (\text{D.12})$$

### D.3 Convolution Theorem of the Fourier Transform

The function  $f(\mathbf{x})$  is said to be the convolution of the functions  $g(\mathbf{x})$  and  $h(\mathbf{x})$  if

$$f(\mathbf{x}) = \int_{-\infty}^{+\infty} d\mathbf{x}' g(\mathbf{x} - \mathbf{x}') h(\mathbf{x}') \equiv g^*h(\mathbf{x}) \quad (\text{D.13})$$

where  $g^*h(\mathbf{x})$  is the short hand notation for the convolution of  $g(\mathbf{x})$  and  $h(\mathbf{x})$  and is defined by the integral to the left.

The Fourier transform of  $f(\mathbf{x})$  is

$$\hat{f}(\mathbf{k}) = \int_{-\infty}^{+\infty} d\mathbf{x} e^{-i\mathbf{k}\mathbf{x}} \int_{-\infty}^{+\infty} d\mathbf{x}' g(\mathbf{x} - \mathbf{x}') h(\mathbf{x}'). \quad (\text{D.14})$$

In the integrand, let  $\xi = \mathbf{x} - \mathbf{x}'$ ,  $d\xi = d\mathbf{x}$ , so that

$$\begin{aligned} \hat{f}(\mathbf{k}) &= \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} d\mathbf{x}' e^{-i\mathbf{k}(\xi + \mathbf{x}')} g(\xi) h(\mathbf{x}') \\ &= \int_{-\infty}^{+\infty} d\xi e^{-i\mathbf{k}\xi} g(\xi) \int_{-\infty}^{+\infty} d\mathbf{x}' e^{-i\mathbf{k}\mathbf{x}'} h(\mathbf{x}') \\ \hat{f}(\mathbf{k}) &= \hat{g}(\mathbf{k}) \hat{h}(\mathbf{k}) \end{aligned} \quad (\text{D.15})$$

where we have used

$$\hat{g}(\mathbf{k}) = \int_{-\infty}^{+\infty} d\xi e^{-i\mathbf{k}\xi} g(\xi) \quad (\text{D.16})$$

$$\hat{h}(\mathbf{k}) = \int_{-\infty}^{+\infty} dx' e^{-ikx'} h(x'). \quad (\text{D.17})$$

The above results may be generalized to three dimensions, namely

$$f(\mathbf{r}) = \int d^3r' g(\mathbf{r} - \mathbf{r}')h(\mathbf{r}') = g*h(\mathbf{r}) \quad (\text{D.18})$$

and

$$\hat{f}(\mathbf{k}) = \hat{g}(\mathbf{k}) \hat{h}(\mathbf{k}) \quad (\text{D.19})$$

where the transforms are defined in the sense of Eq. (D.4). We conclude that the transform of a convolution is equal to the product of the individual transforms.

#### D.4 Fourier Transform of $\nabla^2 C(\mathbf{r})$

Let  $C(\mathbf{r})$  be a scalar-valued function of the coordinates  $\mathbf{r} = (x, y, z)$ . The Laplacian of  $C(\mathbf{r})$  expressed in Cartesian coordinates is

$$\nabla^2 C(\mathbf{r}) = \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}. \quad (\text{D.20})$$

For simplicity, we compute explicitly only the transform of  $\partial^2 C / \partial x^2$ . We integrate by parts.

$$\begin{aligned} \int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{\partial^2 C}{\partial x^2} &= \int_{-\infty}^{+\infty} dx e^{-ik_1 x} \int_{-\infty}^{+\infty} dy e^{-ik_2 y} \int_{-\infty}^{+\infty} dz e^{-ik_3 z} \frac{\partial^2 C}{\partial x^2} \\ &= \int_{-\infty}^{+\infty} dy e^{-ik_2 y} \int_{-\infty}^{+\infty} dz e^{-ik_3 z} \int_{-\infty}^{+\infty} dx e^{-ik_1 x} \frac{\partial^2 C}{\partial x^2} \end{aligned} \quad (\text{D.21})$$

$$\begin{aligned}
&= \int_{-\infty}^{+\infty} dy e^{-ik_2 y} \int_{-\infty}^{+\infty} dz e^{-ik_3 z} \left\{ \left[ e^{-ik_1 x} \frac{\partial C}{\partial x} \right]_{-\infty}^{+\infty} + ik_1 \left[ e^{-ik_1 x} C \right]_{-\infty}^{+\infty} \right. \\
&\quad \left. - k_1^2 \int_{-\infty}^{+\infty} dx e^{-ik_1 x} C \right\}.
\end{aligned}$$

The boundary conditions are often

$$\lim_{x \rightarrow \pm\infty} C(x, y, z) = \lim_{x \rightarrow \pm\infty} \frac{\partial C(x, y, z)}{\partial x} = 0 \quad (\text{D.22})$$

in which case Eq. (D.21) simplifies to

$$\int d^3 r e^{-i\mathbf{k} \cdot \mathbf{r}} \frac{\partial^2 C}{\partial x^2} = -k_1^2 \int_{-\infty}^{+\infty} dx e^{-ik_1 x} \int_{-\infty}^{+\infty} dy e^{-ik_2 y} \int_{-\infty}^{+\infty} dz e^{-ik_3 z} C(x, y, z) \quad (\text{D.23})$$

or

$$\int d^3 r e^{-i\mathbf{k} \cdot \mathbf{r}} \frac{\partial^2 C}{\partial x^2} = -k_1^2 \hat{C}(\mathbf{k}) \quad (\text{D.24})$$

where

$$\hat{C}(\mathbf{k}) = \int d^3 r e^{-i\mathbf{k} \cdot \mathbf{r}} C(\mathbf{r}). \quad (\text{D.25})$$

Generalizing to three dimensions, the transform of Eq. (D.20) is

$$\int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla^2 C(\mathbf{r}) = -k^2 \hat{C}(\mathbf{k}) \quad (\text{D.26})$$

where

$$k^2 = k_1^2 + k_2^2 + k_3^2 = |\mathbf{k}|^2 . \quad (\text{D.27})$$

#### D.5 Fourier Transform of $G(\mathbf{r}) = -(4\pi D r)^{-1}$

In Appendix C.2, we showed that the solution to Green's problem for the steady state diffusion operator was given by Eq. (C.12). If in Eq. (C.12)  $\mathbf{r}' = 0$ , we obtain

$$G(\mathbf{r}) = -\frac{1}{4\pi D r} . \quad (\text{D.28})$$

It is useful to have the Fourier transform of Eq. (D.28). To compute this, we substitute Eq. (D.28) into Eq. (D.4). The result is

$$\hat{G}(\mathbf{k}) = -(1/4\pi D) \int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} (1/r) . \quad (\text{D.29})$$

We evaluate the integral using spherical polar coordinates. Let  $\mathbf{k}$  and the polar axis ( $z$ -axis) point in the same direction (see Figure D.1). We obtain for the inner product,  $\mathbf{k}\cdot\mathbf{r}$ ,

$$\mathbf{k}\cdot\mathbf{r} = kr \cos\theta, \quad (\text{D.30})$$

and for the volume element

$$d^3r = dr r^2 d\theta \sin\theta d\phi . \quad (\text{D.31})$$

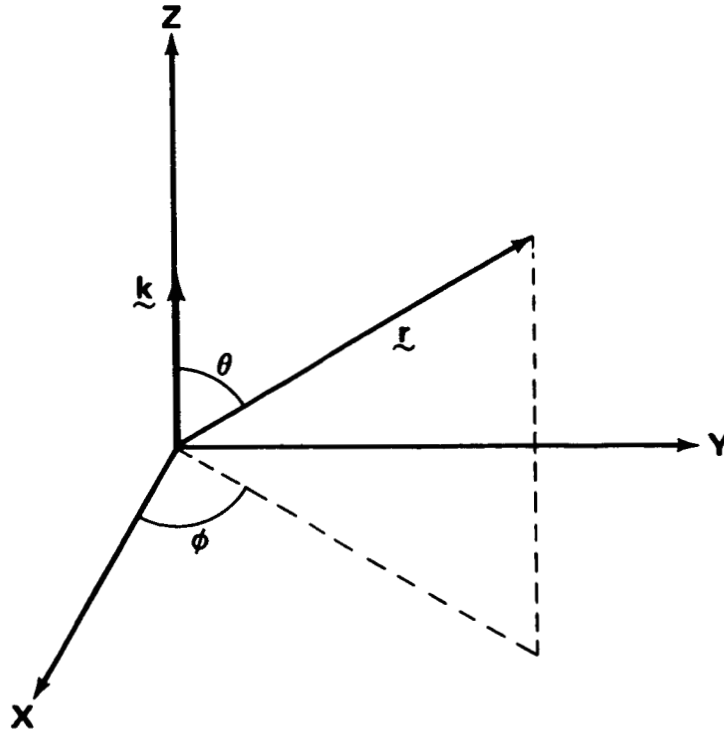


Figure D.1. Geometry for computing the integral in Eq. (D.29).

Transformed to spherical polar coordinates, Eq. (D.29) becomes

$$\hat{G}(k) = -(1/4\pi D) \int_0^{\infty} dr r^2 (1/r) \int_0^{\pi} d\theta \sin\theta e^{-ikr \cos\theta} \int_0^{2\pi} d\phi . \quad (D.32)$$

If we let  $x = \cos\theta$ , and  $dx = -\sin\theta d\theta$

$$\begin{aligned} \hat{G}(k) &= -(1/4\pi D) \int_0^{\infty} dr r^2 (1/r) \int_{-1}^{+1} dx e^{-ikrx} \int_0^{2\pi} d\phi \\ &= -(1/4\pi D) \int_0^{\infty} dr r^2 (1/r) (2/kr) (\sin kr) (2\pi) \\ &= -(1/kD) \int_0^{\infty} dr \sin kr . \end{aligned} \quad (D.33)$$

The remaining integral in Eq. (D.33) may be evaluated by writing  $\sin kr$  in terms of exponentials and inserting an integrating factor as

$$\begin{aligned}
 \int_0^{\infty} dr \sin kr &= \int_0^{\infty} dr \left( \frac{e^{ikr} - e^{-ikr}}{2i} \right) \\
 &= \left( \frac{1}{2i} \right) \left\{ \lim_{\epsilon \rightarrow 0} \int_0^{\infty} dr e^{ikr - \epsilon r} - \lim_{\epsilon \rightarrow 0} \int_0^{\infty} dr e^{-ikr - \epsilon r} \right\} \\
 &= \left( \frac{1}{2i} \right) \left\{ \lim_{\epsilon \rightarrow 0} \left[ \frac{e^{ikr - \epsilon r}}{ikr - \epsilon} \right]_0^{\infty} - \lim_{\epsilon \rightarrow 0} \left[ \frac{e^{-ikr - \epsilon r}}{-(ikr + \epsilon)} \right]_0^{\infty} \right\} \\
 &= \left( \frac{1}{2i} \right) \left\{ \lim_{\epsilon \rightarrow 0} \left[ \frac{-1}{ikr - \epsilon} \right] - \lim_{\epsilon \rightarrow 0} \left[ \frac{1}{ikr + \epsilon} \right] \right\} = 1/k . \tag{D.34}
 \end{aligned}$$

We substitute Eq. (D.34) into Eq. (D.33) and obtain our desired result

$$\hat{G}(k) = - 1/k^2 D . \tag{D.35}$$



APPENDIX E - SPECIFICATION OF EXPONENTS

E.1 Proof of  $y_1 = x$

We first consider the limit of  $W(Z, \tau)$  for large  $\tau$ . To do this, we substitute Eq. (3.3.6) into Eq. (3.3.22) and write

$$W(Z, \tau) = \tau^{-x} (1/Z) [\sigma_1 \tau^{-y_1} - \tau^{-x} (1/Z)] [1 + \epsilon Z] . \quad (E.1.1)$$

The functional form of  $W(Z, \tau)$  for large  $\tau$  depends upon the magnitude of  $y_1$  as compared to  $x$ . Letting  $\tau \rightarrow \infty$  in Eq. (E.1.1), we find the results

$$W(Z, \tau) \approx \begin{cases} -(1/Z)^2 (1+\epsilon Z) \tau^{-2x} & \text{if } y_1 > x \\ (1/Z) (\sigma_1 - (1/Z)) (1+\epsilon Z) \tau^{-2x} & \text{if } y_1 = x \\ (1/Z) \sigma_1 \tau^{-(x+y_1)} & \text{if } y_1 < x \end{cases} . \quad (E.1.2)$$

Equation (E.1.2) in turn may be written as a single equation

$$W(Z, \tau) \approx \tau^{-\eta} \bar{V}(Z) \quad (E.1.3)$$

where both  $\eta$  and  $\bar{V}(Z)$  depend upon the relative magnitudes of  $y_1$  and  $x$ .

Substitute Eq. (E.1.3) into Eq. (3.3.19) and obtain

$$-\tau^{-4(x+1)} \left[ F_0(Z) + xZ \frac{\partial F_0(Z)}{\partial Z} \right] = \tau^{-(5x+\eta)} \frac{\partial [F_0(Z) \bar{V}(Z)]}{\partial Z} . \quad (E.1.4)$$

Equating exponents of  $\tau$  in Eq. (E.1.4), we find

$$\eta = 1 - x . \quad (E.1.5)$$

We next consider the time derivative of the supersaturation  $\sigma(\tau)$  given by Eq. (3.2.9), which we reproduce below

$$\sigma(\tau) = \sigma(0) \left[ 1 - \int_0^{\infty} da F(a, \tau) a^3 \right] . \quad (\text{E.1.6})$$

The derivative of Eq. (E.1.6) with respect to  $\tau$  is

$$\frac{\partial \sigma(\tau)}{\partial \tau} = - \sigma(0) \int_0^{\infty} da \frac{\partial F(a, \tau)}{\partial \tau} a^3 . \quad (\text{E.1.7})$$

We may write Eq. (3.2.18) as

$$\frac{\partial F(a, \tau)}{\partial \tau} = - \frac{\partial [F(a, \tau) W(a, \tau)]}{\partial a} \quad (\text{E.1.8})$$

and substitute into Eq. (E.1.7) to obtain

$$\frac{\partial \sigma(\tau)}{\partial \tau} = \sigma(0) \int_0^{\infty} da a^3 \frac{\partial [F(a, \tau) W(a, \tau)]}{\partial a} . \quad (\text{E.1.9})$$

Using  $F(\infty, \tau) = 0$ , Eq. (E.1.9) may be integrated by parts. The result is

$$\frac{\partial \sigma(\tau)}{\partial \tau} = -3\sigma(0) \int_0^{\infty} da a^2 F(a, \tau) W(a, \tau) . \quad (\text{E.1.10})$$

Using Eq. (3.3.2) to convert Eq. (E.1.10) to an integral over the canonical length  $Z$ , we obtain

$$\frac{\partial \sigma(\tau)}{\partial \tau} = -3\sigma(0) \tau^{3x} \int_0^{\infty} dZ Z^2 F(Z, \tau) W(Z, \tau) . \quad (\text{E.1.11})$$

In the limit  $\tau \rightarrow \infty$ , we may replace  $W(Z, \tau)$  by Eq. (E.1.3) and  $F(Z, \tau)$  by Eq. (3.3.8). In this limit Eq. (E.1.11) becomes

$$\frac{\partial \sigma(\tau)}{\partial \tau} = -3\sigma(0) \tau^{-(x+\eta)} \int_0^{\infty} dz z^2 F_0(z) \bar{V}(z) . \quad (\text{E.1.12})$$

On the other hand, differentiating Eq. (3.3.6), we obtain

$$\frac{\partial \sigma(\tau)}{\partial \tau} = -y_1 \sigma_1 \tau^{-(y_1+1)} \quad (\text{E.1.13})$$

and substituting Eq. (E.1.13) in the left-hand side of Eq. (E.1.12) while using Eq. (E.1.5), we have

$$3\sigma(0) \int_0^{\infty} dz z^2 F_0(z) \bar{V}(z) = y_1 \sigma_1 \tau^{-y_1} . \quad (\text{E.1.14})$$

Since  $y_1 > 0$ ,  $\tau^{-y_1} \rightarrow 0$  as  $\tau \rightarrow \infty$ . The left-hand side of Eq. (E.1.14), however, is independent of  $\tau$ . If the left-hand side is to be zero, the integrand must have compensating positive and negative portions. In as much as  $F_0(z)$  is a distribution function of grain sizes, it is positive definite, which implies that  $\bar{V}(z)$  must possess both positive and negative swings. Referring to Eq. (E.1.2), we find that this is true only for

$$\bar{V}(z) = (1/z)(\sigma_1 - (1/z))(1 + \epsilon z) \quad (\text{E.1.15})$$

which implies

$$y_1 = x . \quad (\text{E.1.16})$$

## E.2 Proof of $x = 1/3$

Since  $y_1 = x$ , we find by comparing Eqs. (E.1.2), (E.1.3), and (E.1.16) that

$$\eta = 2x . \tag{E.2.1}$$

Substituting Eq. (E.2.1) into Eq. (E.1.5), we conclude

$$x = 1/3 . \tag{E.2.2}$$

APPENDIX F - EXPANSION OF  $1/w(z)$  IN PARTIAL FRACTIONS

Rewriting Eq. (3.5.8), we may use partial fractions,

$$-\frac{1}{3w(z)} = \frac{z^2}{(z-z_0)^2(z+3/z_0^2)} = \frac{A_1}{(z-z_0)^2} + \frac{A_2}{(z-z_0)} + \frac{B_1}{(z+3/z_0^2)}. \quad (F.1)$$

The coefficients  $A_1$ ,  $A_2$ , and  $B_1$  are obtained by evaluating

$$A_1 = \left[ \frac{(z-z_0)^2 z^2}{(z-z_0)^2 (z+3/z_0^2)} \right]_{z=z_0} = \frac{z_0^4}{(z_0^3+3)} \quad (F.2)$$

$$A_2 = \frac{d}{dz} \left[ \frac{(z-z_0)^2 z^2}{(z-z_0)^2 (z+3/z_0^2)} \right]_{z=z_0} = \frac{z_0^3(z_0^3+6)}{(z_0^3+3)^2} \quad (F.3)$$

$$B_1 = \left[ \frac{(z+3/z_0^2) z^2}{(z-z_0)^2 (z+3/z_0^2)} \right]_{z=-3/z_0^2} = \frac{9}{(z_0^3+2)^2}, \quad (F.4)$$

respectively. Substitution of Eqs. (F.2)-(F.4) yields

$$\frac{1}{w(z)} = -\frac{3z_0^4}{(z_0^3+3)} \cdot \frac{1}{(z-z_0)^2} - \frac{3z_0^3(z_0^3+6)}{(z_0^3+3)^2} \cdot \frac{1}{(z-z_0)} - \frac{27}{(z_0^3+3)^2} \cdot \frac{1}{(z+3/z_0^2)}. \quad (F.5)$$

APPROVAL

THEORY OF OSTWALD RIPENING IN A TWO-COMPONENT SYSTEM -  
CENTER DIRECTOR'S DISCRETIONARY FUND FINAL REPORT

By James K. Baird, Li Kao Lee, Donald O. Frazier, and Robert J. Naumann

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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16. Abstract  When a two-component system is cooled below the minimum temperature for its stability, it separates into two or more immiscible phases. The initial nucleation produces grains (if solid) or droplets (if liquid) of one of the phases dispersed in the other. The dynamics by which these nuclei proceed toward equilibrium is called Ostwald ripening. We shall assume that the nuclei are spheres, thereby treating the case of droplets rigorously and the case of grains approximately.  The dynamics of growth of the droplets depends upon the following factors: (1) The solubility of the droplet depends upon its radius and the interfacial energy between it and the surrounding (continuous) phase. The equation governing this phenomenon is associated with the names of Gibbs and Kelvin, and we derive it for the case of two components. There is a critical radius determined by the supersaturation in the continuous phase. Droplets with radii smaller than critical dissolve, while droplets with radii larger grow. (2) The droplets concentrate one component and reject the other. The rate at which this occurs is assumed to be determined by the interdiffusion of the two components in the continuous phase. Associated with this diffusion is advection, which is accounted for in our theory to lowest order in the center of volume velocity of the two components. Moreover, when the droplets occupy a finite fraction of the total volume of the system, there occur effects of inter-droplet competition on the concentration field in the continuous phase. This increases the overall rate of growth of the droplet phase. Using diagrammatic techniques and rigorous statistical mechanics, we show that this effect depends upon the square root of the volume fraction associated with the grains, and that it accelerates both the rate of growth and the rate of dissolution of droplets. (3) The Ostwald ripening is constrained by conservation of mass; e.g., the amount of material in the droplet phase plus the remaining supersaturation in the continuous phase must equal the supersaturation available at the start. (4) There is a distribution of droplet sizes associated with a mean droplet radius, which grows continuously with time. This distribution function satisfies a continuity equation, which we solve asymptotically by a similarity transformation method.  The final results of our theoretical analysis consist of the following quantities determined as functions of time: (1) the supersaturation remaining in the continuous phase, (2) the total number of droplets in the continuous phase, (3) the distribution of droplet sizes, (4) the critical droplet radius, (5) the mean droplet radius, and (6) the maximum droplet radius. Each of these is also determined as a function of the volume fraction occupied by the droplets. We apply these results to the system, succinonitrile/water, which separates into two immiscible liquid phases below its consolute temperature at 58 °C. This system is particularly attractive because it is transparent to visible light, so the rate of formation of the droplet phase can be followed photographically. In general, the droplet phase has a different density than the continuous phase. Separation of the two by sedimentation competes with the process of Ostwald ripening. In the acceleration-free environment of an Earth orbiting laboratory, the Ostwald ripening in the system succinonitrile/water should be observable without interference by sedimentation or any other effects associated with gravitation. We provide a complete set of specifications for the design of such an experiment.			
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