"Rigorous Statistical Mechanics of Selected Classical Systems at Real or Complex Fugacities".

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by

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ABSTRACT

The rigorous statistical mechanics of various classical systems of particles at real or complex fugacities is studied. Some existing techniques for deriving the equation of state at positive fugacities are surveyed & one of them is partially extended. Several theorems are proved (for systems which are, effectively, one-dimensional) concerning the distribution of limit points of zeros of the grand partition function in the complex fugacity —(z)— plane, as the size of the system becomes infinite. The main new result is a criterion for the unique determination of this distribution from the equation of state. This is important because it allows unambiguous application of the Yang-Lee theorems (1952), which show that a phase transition can occur only if the zero-distribution meets the real positive z-axis. The calculation in Chapter VI & the work of Kac, Uhlenbeck & Hemmer (1963), & Lebowitz & Penrose (1966), show that our criterion fails for certain systems with forces of infinite range; but the most general conditions for this or a modified uniqueness criterion to hold have still to be found.

P R E F A C E

The research in this thesis concerns a single problem:

to determine the thermodynamic pressure at fixed temperature, of a classical system of interacting particles, throughout the complex plane of the fugacity variable, z.

It was shown by Yang and Lee (1952) that the singularities of the complete analytic function, say $\Pi(z)$, obtained by analytic continuation from the equation of state at positive fugacity, coincide with the limit points of zeros of the grand partition function as the size of the system becomes infinite. Chapter I is designed primarily to motivate and explain the theory of phase transitions due to Yang and Lee (1952), in which the above zero-distribution plays a central role. In Chapter II we analyse some rigorous techniques for studying the equation of state of a classical, one-dimensional continuum system. Our original intention was to tackle the main problem with the help of these techniques, but the mathematical obstacles to this procedure have so far proved insurmountable and we have had to develop different methods. It was shown by Kac (1959) how the grand canonical pressure of a one-dimensional system could be determined implicitly if the pair interaction potential was equal to the autocovariance of a stationary, one-dimensional, Gaussian Markov process. We have extended this method in Chapter III to study a system for which the potential is an element of the autocovariance matrix of a two-dimensional Markov process. However, the integral equation we obtain does not

share the symmetry of Kac's equation, so we have only been able to derive formal results.

Chapter IV consists of a paper,

The Yang - Lee Distribution of Zeros for a Classical One-dimensional system, by

O. Penrose & J.S.N. Elvey,

which has been submitted for publication in the Journal of Mathematical Physics.* For this reason the numbering of equations in chapter IV differs from that in the other chapters, but this difference causes no difficulties. In all chapters except Chapter IV each equation has a three-part number; for example (II 6 · 18) means Chapter II, section 6, equation 18. For reference within a chapter the chapter number is omitted. Finally, cross - references to Chapter IV, where the equations are numbered consecutivily from 1 to 74, consist of just two numbers; for instance (IV 31).

Our main result in Chapter IV states that when there is a unique branch of $\Pi(z)$ having largest real part, and this branch is regular, then it is equal to the pressure at fugacity z. The set of values of the fugacity for which no such branch exists is shown to coincide with the set of limit points of zeros of the grand partition function. These results are proved for a classical, one-dimensional continuum system of particles with hard cores and nearest-neighbour interactions.

If lattice gases are considered, however, the principal theorems of Chapter IV may be extended to a class of systems in one, two or three dimensions, provided that the lattices grow only one-

* Written in error; accepted by Proc. Phys. Soc. (London) July, 1968.

dimensionally. These extensions are achieved in Chapter V, where the problem of proving similar generalisations for continuum systems, by making the lattice spacing tend to zero in a suitable way, is also discussed, though no rigorous results are obtained.

All of the theorems proved in Chapters IV and V may be generalized at once to the case where the temperature is fixed but complex. *

The work of Kac, Uhlenbeck and Hemmer (1963) shows that a continuum system of hard rods with exponentially decreasing attractive forces rigorously obeys Van der Waal's equation of state (modified by Maxwell's rule) in the limit that the range of interaction becomes infinite while its strength decreases to zero. This property has been generalized by Lebowitz and Penrose (1966) to a class of three-dimensional systems. Therefore it seems interesting to examine the consequences of assuming our theorems for a Van der Waals gas, and our final Chapter (VI) contains an approximate calculation in which this is done. Our results are found to be consistent with thermodynamics at or below the critical temperature, Tc, but lead to incorrect conclusions above Tc.

References.

Kac (1959), Phys. Fluids 2, 8;

Kac, Uhlenbeck & Hemmer (1963), J. Math. Phys. 4, 216;

Lebowitz & Penrose (1966), J. Math. Phys. 7, 98;

Yang & Lee (1952), Phys. Rev. 87, 404.

* Except for theorem V, which probably holds, though the generalization does not seem trivial.

All of this work, except for the proof of theorem III (P.104), the alternative proof of theorem V (cited but not quoted on P.~~148~~ 143) & the basic scheme for the calculation in chapter VI (all of which are due to Penrose alone) was done in the course of my Ph.D. research under the supervision of Dr. O. Penrose, in the Mathematics Department, Imperial College, London.

All other work quoted or referred to for comparison or review is explicitly acknowledged either in the text or in footnotes.

Full time work on this thesis occupied the period from May 1965 to August 1967.

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C O N T E N T S

		Page
Chapter I	General Considerations.	8
Chapter II	Some Methods for Studying the Equation of State of a One-dimensional System - a Survey.	35
Chapter III	Another Application of the Covariance Method.	63
Chapter IV	The Yang - Lee Distribution of Zeros for a Classical One-dimensional System.	78
Chapter V	The Yang - Lee Distribution of Zeros for a Lattice Gas.	128
Chapter VI	An Approximate Test of Theorem I for a Van der Waals Gas.	158

C H A P T E R 1

General Considerations.

§1 The Basic Aims of Statistical Mechanics and Thermodynamics.

The aim of statistical mechanics is to explain and predict the behaviour of matter in bulk from the dynamical behaviour of its constituent particles. That is, given the Hamiltonian representing a physical object, such as a volume of gas in a container, to determine the observational properties of this object - for instance its specific heat or its entropy.

A procedure whereby this aim can be achieved completely (at least in principle) was introduced by Gibbs (1902) for systems whose constituent particles move according to Newton's Laws of motion. The essential step in extending Gibbs' procedure to systems whose particles obey the laws of quantum mechanics was taken by Dirac (1930).

The basis of Gibbs' method lies in accepting our practical inability to determine the precise dynamical state of a system of particles (that is, the position and momentum of each particle) at a given time, and to use instead a probability distribution over the phase space of the system. The natural form of ~~distribution~~ average, ~~describing~~ over the change of state of the system in time, makes the calculations intractable; but the ergodic theorem (cf. Khinchin, 1949 Ch. 3)* provides sufficient conditions for the time averages of dynamical variables to be replaced by expectation values over an appropriate ensemble consisting of systems identical to the one under consideration.

* See also Farquhar (1964) for a more recent and fuller account.

The introduction of probability from the outset envisages thermodynamic variables as ensemble - averages of dynamical variables: for instance, the temperature corresponds to the mean kinetic energy of the system, and the total internal energy to the mean value of the Hamiltonian. Accordingly, the fundamental problem which Gibbs set himself was to specify suitable probability distributions and to construct from them analogues of thermodynamic quantities. In Sections 2 and 3 of this chapter the essentials of Gibbs' method are outlined.

In classical thermodynamics it is postulated that a complete description of a physical object is provided by a set of independent variables, say R and a function, say Φ_R, of these variables. The set R is called a (thermodynamic) representation, Φ_R being the corresponding (thermodynamic) potential. In general R consists of both intensive and extensive variables, though it is often convenient to consider 'reduced' representations, r, in which all extensive variables in R are replaced by densities (per unit volume). It is assumed that the set of macroscopic quantities constituting a full description of the observational state of the system can be specified; the manifold difficulties inherent in making this specification do not concern us here. In terms of R and Φ_R, the set, $\mathcal{O}$, of variables which determine the observational state, may be expressed as

$$\mathcal{O} = R \cup \frac{\partial}{\partial R}\Phi_R , \qquad (\text{I } 1.1)$$

where the right - hand side of (1·1) denotes the union of the set R and the set $(\partial \Phi_R / \partial \mathcal{R})$ of dependent variables obtained from Φ_R by partial differentiation in the variables of R.

If an equilibrium state of an isolated composite system subject to internal constraints, such as partitions, is specified, in the representation R, then the new equilibrium state eventually attained when a constraint is relaxed, may be determined by solving the variational problem

$$\left.\begin{aligned} d\Phi_R &= 0 \\ d^2\Phi_R &\neq 0 \end{aligned}\right\} \qquad (\text{I } 1\text{-}2)$$

for the variables in R subject to all of the remaining constraints, the sign $(\pm)$ required of $d^2\Phi_R$ depending upon whether Φ_R is to be minimized (like the internal energy, U) or maximized (like the entrophy, S). That is, the linear differential form, $d\Phi_R$, must vanish, while the quadratic differential form, $d^2\Phi_R$, must be (positive or negative) definite. Following Callen (1960 Ch.8), it may be shown that the statements (1·1) and (1·2) imply all of the usual thermodynamic stability conditions.

If $\alpha \in R$ then $\partial \Phi_R / \partial \alpha$ and α are called conjugate variables for R (an example is the pair T, S). A pair of conjugate variables always consists of one extensive variable and one intensive variable (except when one deals with reduced potentials, when both variables are necessarily intensive).

Further, if the representation $\tilde{R}$ is derived from R by replacing α with $\partial \underline{\Phi}_R / \partial \alpha$ then we have

$$\underline{\Phi}_{\tilde{R}} = \underline{\Phi}_R - \alpha \frac{\partial \underline{\Phi}_R}{\partial \alpha} \qquad (\underline{I}\ 1{\cdot}3)$$

Evidently the effect of the Legendre transformation (3) is to make $\partial \underline{\Phi}_R / \partial \alpha$ an independent variable and α a dependent variable. The basic result (1) applied to (3) yields the thermodynamic state in representation $\tilde{R}$.

§2 The Link Between Statistical Mechanics and Thermodynamics.

Gibbs' prescription for constructing analogues of the 'reduced potentials' $\phi_r \equiv \Phi_R/V$ when R includes at least one extensive variable, may be expressed succently in the form

$$V^{-1} \log \Psi_R \sim \phi_r , \qquad (\text{I } 2{\cdot}1)$$

where Ψ_R denotes the normalizing factor (structure function) of the normalized probability distribution, $D_R(\xi)$, for the ensemble representing a system in which the variables of R are fixed, and ξ denotes a point in the phase space of the system. The asymptotic equality indicated in (2·1) holds as the volume, V, becomes infinite. If α is extensive, it may be shown (cf. Sack, 1959) that $\Psi_{\tilde{R}}$ is the Laplace transform of Ψ_R, where $\tilde{R}$ and R are related by (1·3).

The guiding principles for the assignment of phase - space density functions are Lionville's theorem ($D_R(\xi)$ is conserved along a phase - space trajectory), and the requirement that the functions Φ_R should be strictly additive for a composite system comprizing two or more mutually isolated subsystems. Lionville's theorem implies that $D_R(\xi)$ must be a function of constants of the motion of the system. Moreover, the multiplicative law for the joint probability of a pair of independent events implies that

$$D_R(\xi) = D_R(\xi^{\mathrm{I}}) D_R(\xi^{\mathrm{II}}) \qquad (\text{I } 2{\cdot}2)$$

whenever the phase space, Γ, of the whole system may be written as the topological product, $\Gamma^{I} \otimes \Gamma^{II}$, of two subspaces with representative points ξ^{I}, ξ^{II} respectively. Physically, (1·5) means that the system consists of two mutually isolated parts. The expectation value of any classical - dynamical variable, say v, is found by intergrating $v(\xi) D_R(\xi)$ over Γ.

For quantum mechanical systems the uncertainty relations preclude the definition of a phase space. Nevertheless, following Dirac (1930),* one can still introduce a density operator, $\hat{D}_R$, which is simply a weighted sum of projection operators onto all possible linearly independent quantum states, $|c\rangle$, compatible with what is known about the system, each weight being the probability that a particular one of these states is attained. When the system consists of N particles, the domain of $\hat{D}_R$ is a subspace of the Hilbert space of square - integrable functions of N variables. For example, a hard - sphere Bose gas in a container would correspond to a subspace in which the wave - functions were totally symmetric in all N arguments and vanished if two particles overlapped or a particle was outside the container.

The probability of finding a specified quantum state, say $|c\rangle$, is then found to be $\langle c|\hat{D}_R|c\rangle$ (in Dirac's notation), so that the expectation value $\langle \hat{v} \rangle$ of any quantum - dynamical variable, $\hat{v}$, equals $tr(\hat{v}\hat{D}_R)$, where the symbol $tr\hat{A}$ indicates the trace of an operator $\hat{A}$, taken with respect to any complete set of wave funotions of suitable symmetry. It is readily shown that

* See Dirac (1958) Ch. V § 33

$\langle \hat{\mathcal{O}} \rangle$ is independent of the (quantum mechanical) representation with respect to which the trace is taken. The function Ψ_R of equation (1·4) now becomes $tr\ \hat{D}_R$, while equation (2.5) generalizes to the case where the Hilbert space of the system is separable.

The Basic Functions of Statistical Mechanics.

For future reference, we now define the principal functions of classical statistical mechanics; all of them have quantum mechanical analogues but we omit these, since this thesis is concerned only with classical systems.

For a system of N identical particles of mass m, moving in a ν-dimensional container, Ω, of volume V (area A in two dimensions, length L in one dimension), interacting with one another through pair-wise forces only, the Hamiltonian is defined by

$$\mathcal{H}_N(\xi) \equiv U(\underset{\sim}{x})_N + T(\underset{\sim}{p})_N + \gamma_\Omega, \qquad (\text{I } 3{\cdot}1)$$

where

$$U(\underset{\sim}{x})_N \equiv U(\underset{\sim}{x}_1 \cdots \underset{\sim}{x}_N) \equiv \sum_{i=1}^{N-1} \sum_{j=1+i}^{N} u(\underset{\sim}{x}_i - \underset{\sim}{x}_j) \qquad (\text{I } 3{\cdot}2)$$

denotes the total potential energy of the particles,

$$T(\underset{\sim}{p})_N \equiv T(\underset{\sim}{p}_1 \cdots \underset{\sim}{p}_N) \equiv \sum_{i=1}^{N} \frac{|\underset{\sim}{p}_i|^2}{2m} \qquad (\text{I } 3{\cdot}3)$$

is the total kinetic energy and γ_Ω accounts for the interactions of the particles with the walls of the container. As before, ξ denotes a point in the phase space, Γ, of the system.

It may be demonstrated (of Khinchin, 1949, Ch. V, Huang, 1964 Chs. 7 and 8) that the probability density functions,

can be determined from the conditions mentioned in § 2 (see Table 1 for details). The explicit forms of $\underline{\Psi}_R$ in the cases of interest to us are as follows, the representation, R, being specified by the independent variables appearing on the left-hand sides of the defining equations.

First, one finds that

$$W(E,N,V) = \frac{1}{N!} \int_{\Gamma} d\xi \, \Delta[E - \mathcal{H}_N(\xi)] \qquad (\text{I } 3.4)$$

where

$$\Delta(x) \equiv \begin{cases} 1, & |x| \leq \eta \\ 0, & |x| > \eta \end{cases} \qquad (\text{I } 3.5)$$

and the integral of $\Delta(x)$ over all real x is positive. In the present context, η is to be interpreted as the maximal uncertainty in the value of the energy, E ~~; many authors take η to be zero, so that $\Delta(x)$ reduces to a multiple of the Dirac δ-function.~~

The factor $(1/N!)$ is included here and elsewhere to make the entropy, which is found to be proportional to $\log W$, an additive function of each of its arguements.

Next, we have

$$Z(\beta,N,V) = \frac{1}{N!} \int_{\Gamma} d\xi \, \exp\{-\beta \mathcal{H}_N(\xi)\}, \qquad (\text{I } 3.6)$$

where $(k\beta)^{-1}$ is the absolute temperature, k being Boltzmann's Constant. Finally, one obtains for the grand partition function

$$\Xi(\beta,\lambda,V) = 1 + \sum_{N=1}^{\infty} \lambda^N Z(\beta,N,V), \qquad (\text{I } 3.7)$$

where λ, the Activity of the system, is given by

$$\lambda \equiv e^{\beta\mu}, \qquad (\text{I } 3.8)$$

$$\mu \equiv -\beta^{-1} \frac{\partial}{\partial N} \log Z(\beta,N,V). \qquad (\text{I } 3.9)$$

For convenience of presentation, the variable β will be shown explicitly only when its omission would lead to loss of clarity in the arguements.

The function μ, called the chemical potential, measures the 'tendency of the system to exchange particles' with its surroundings; hence μ is meaningful only in ensembles such as the grand canonical or constant pressure ensembles.

In the next section we consider the 'bulk limit', in which (2·1) holds; it will then be possible to obtain the equation of state for each representation R, though we shall not do so in detail.

R	$D_R(\xi)$	$\underline{\Psi}_R$	$\underline{\Phi}_R$	ENSEMBLE
$\{E,N,V\}$	$(N!)^{-1}\Delta(E-\mathcal{H}_N(\xi))$	$W(E,N,V)$	$\log W$	MICROCANONICAL
$\{\beta,N,V\}$	$(N!)^{-1}\exp[-\beta\mathcal{H}_N(\xi)]$	$Z(\beta,N,V)$	$\log Z$	CANONICAL
$\{\beta,\lambda,V\}$	$(N!)^{-1}\lambda^N\exp[-\beta\mathcal{H}_N(\xi)]$	$\Xi(\beta,\lambda,V)$	$\log \Xi$	GRAND CANONICAL

TABLE 1

THE PRINCIPAL ENSEMBLES OF STATISTICAL MECHANICS

§4 The Bulk Limit

It is a basic assumption in equilibrium thermodynamics that the variables constituting an observational state are sharply (cf Callen, 1960, P.267) determined and do not fluctuate about mean values. This condition holds for the statistical expectations, $\langle A \rangle$, of dynamical variables, A, for a system consisting of N particles, only in the limit that N becomes infinite, the standard deviation of A being of order $N^{-\frac{1}{2}}$ (cf. Landau and Liftshitz, 1958).* The variable must be a 'bulk variable' and not a 'sum-variable' such as the kinetic energy.

The bridging operation which must be applied in a rigorous derivation of the laws of thermodynamics from statistical mechanics therefore consists of making the volume of the sample constituting the system tend to infinity at constant particle density. We shall refer to this operation (following Penrose, Statistical Mechanics, to be published by Pergamon Press) as 'taking the bulk limit'. Another reason for taking the bulk limit will be given in §6, where the Yang - Lee theory of condensation is outlined.

The question of the existence and analitical properties of the reduced potentials, ϕ_r, defined in equation (1·4), was first considered by Van Hove (1949), who studied the convergence of the free - energy density in the bulk limit. Subsequently, Yang and Lee treated the same problem for the grand canonical pressure, while Whitten (1954) showed that the conditions assumed by Yang and Lee could be weakened. The problem has been solved generally

* The system is assumed to be in a single phase and to behave classically; see also Farquhar (1964) Ch. 2 (§2·5). It is also supposed that A is not a 'sum-variable', such as the kinetic energy.

only quite recently, in the work of Ruelle (1963), Fisher (1964), Griffiths (1964), Van der Linden (1966) and Van der Linden and Mazur (1967).

This general solution provides an answer to the following questions:-

(1) What are the conditions (a) on the interaction potential, (b) on the shapes assumed by the container as its volume, V, becomes infinite, sufficient for the existence of ϕ_γ ?

(2) Does ϕ_γ depend on the shapes assumed by the container as its volume increases?

(3) If γ_1, γ_2 are distinct reduced representations, do the limit functions $\phi_{\gamma_1}, \phi_{\gamma_2}$ generate the same numerical values when used to calculate the same thermodynamic quantity?

Question (1) is most readily answered in two stages. In the first stage it is assumed that, as V increases, the shape of Ω remains unchanged, so that the functions of the sequence $\{V^{-1}\log \Xi_R\}$ depend only on V ; the existence of ϕ_γ may then be inferred if one can show that this sequence is monotonic and (suitably) bounded. This, in turn may be demonstrated very simply provided that (i) the binding energy per particle is bounded, uniformly over all configurations and all values of N - the total number of particles;

(ii) the mutual potential energy of two groups of particles becomes negative whenever the minimum separation of particles in different groups exceeds a fixed number, say d.

Much work has been done recently to find conditions sufficient for (i), which is known as the stability condition.* It is plausible on physical grounds provided that the particles have hard cores or, at least, that the forces become repulsive at small enough separations; moreover, it has been proved (Dyson and Lenard, 1967) that a system of charged point particles, moving quantum mechanically, is stable in this sense, even when charges of both signs are present.

The requirement (ii), known as 'strong tempering', is also likely to be satisfied in real systems since the intermolecular 'Van der Waals', forces are attractive and of long range. An example of a stable, strongly tempered potential is the Lennard - Jones (6 - 12) potential in three dimensions* Fisher (1964) has shown that the strong tempering condition may be replaced by that of 'weak tempering', in which the interactions may remain repulsive for arbitrarily large separations, but this possibility seems to be of little physical interest. Fisher is also the only author to consider many-body forces though, again, it appears that such forces are not understood well enough to make it clear whether their inclusion affects the convergence of the sequence $\{V^{-1} \log \Xi_R\}$ in realistic cases.

* cf. Ruelle (1963c), Fisher (1964).

In answer to question 1(b), Fisher postulates certain 'regularity' conditions on the domains Ω, which ensure that they are not too violently crennellated and do not grow too anisotropically. It is then shown that Ω can be approximated sufficiently closely by a union of standard (cubical) domains, for which the existence of ϕ_r has already been demonstrated, and this also yields a negative answer to question 2.

Detailed proofs of these properties may be found in the references quoted. However, one can see roughly from (3.4) - (3.9) and Table 1 that the stability condition ((i)) on the interaction potential implies bounds on the function Ψ_R. Further, by considering the form of Ψ_R when Ω is a cube constructed from a union of smaller cubes at mutual separation at least a (so that the forces between particles in different subcubes are attractive) and supposing that no particles move in the 'corridor' between the subcubes, one can also establish the monotonicity of $V^{-1} \log \Psi_R$. Notice that, in the process just indicated, the shape of Ω remains unchanged as V increases, though it has to be proved that the exclusion of the particles from the 'corridor' has no effect on the resulting limit functions, ϕ_r.

§5 Equivalence of Representations:

Equations of state

It is a natural consistency condition on the formalism of thermodynamics that if the same thermodynamical quantity is calculated for an object using two distinct representations, then the numerical results of the two calculations should be the same. The problem of showing that Gibbs' reduced potentials, ϕ_r, satisfy this condition has been posed in §4 as question 3.

To put it another way, does the equation of state in one representation imply those in all other representations? Ruelle (1963a, 1963b) and Fisher (1964) prove the equivalence of the canonical&grand canonical ensembles both for classical and quantum mechanical systems. Their methods, which are essentially the same, cannot be cast in a form suitable for proving the equivalence of all ensembles, but very recently the problem has been solved generally for classical systems by Van der Linden (1966) and Van der Linden and Mazur (1967). The main features of their work are (a) use of the central limit theorem of probability theory in establishing the existence of the reduced potentials (or bulk limit functions) (b) systematic application of a theorem due to Griffiths (1964), giving sufficient conditions for interchanging the operations of differentiation in a thermodynamic variable and taking the bulk limit. It appears that this general method could be extended to quantum mechanical systems.

For our purposes, only the equations of state in the canonical and grand canonical ensembles will be required. Denoting by $f(\beta, v)$, $\pi(\beta, z)$ respectively the reduced potentials (5) for these ensembles, one has, by definition, the relations (see Ruelle 1963) that

$$p(\beta, v) = -\beta^{-1} \frac{\partial}{\partial v} f(\beta, v) \qquad (\text{I } 5.1)$$

where $p(\beta, v)$ denotes the canonical pressure (at infinite volume) and v the specific volume; and that

$$\beta \bar{p}(\beta, z) = \pi(\beta, z) \equiv \lim V^{-1} \log \Xi(\beta, z, V), \qquad (\text{I } 5.2)$$

$$\bar{v}(\beta, z) = z \frac{\partial}{\partial z} \pi(\beta, z), \qquad (\text{I } 5.3)$$

where $\bar{p}(\beta, z)$ stands for the grand canonical pressure at infinite volume and the fugacity variable, z, is related to the activity, λ, by

$$z = \lambda (2\pi m/\beta)^{\frac{\nu}{2}} \qquad (\text{I } 5.4)$$

~~denotes the grand canonical pressure (at infinite volume).~~

The equivalence of the equations (5·2) and 5·3) to 5·1) is reflected in the relation (cf Van der Linden, 1966)

$$\Pi(\beta,z) = \beta\, p[\bar{v}(\beta,z)] \qquad (I\ 5.5)$$

which holds for all values of z such that the system is in a single phase. All of the usual thermodynamic stability conditions, such as the requirement that $\partial p/\partial v$ be non positive, may be established from the convexity properties of the functions $f(\beta,v)$ (convex in β, concave in v) and $\Pi(\beta,z)$ (convex in $\log z$).

§6 The Theory of Yang and Lee.

The grand canonical pressure at finite volume is defined by

$$\bar{P}(\beta, z, V) \equiv (\beta V)^{-1} \log \Xi(\beta, z, V) \quad (\text{I } 6{\cdot}1)$$

where $\Xi(\beta, z, V)$ is the function obtained from (6·1) by substituting for λ from (5·4). Since the factor $(\beta/2\pi m)^{\frac{\nu}{2}}$ is obtained by performing the momentum integration for a single particle in (3·6), it follows that the grand partition function may be written in the alternative form

$$\Xi(\beta, z, V) = 1 + \sum_{N=1}^{\infty} z^N Q(\beta, N, V) \quad (\text{I } 6{\cdot}2)$$

where the configurational integral is defined by

$$Q(\beta, N, V) \equiv \frac{1}{N!} \int_{\{\Omega\}^N} d(\underset{\sim}{x})_N \exp\{-\beta U(\underset{\sim}{x})_N\} \quad (\text{I } 6{\cdot}3)$$

$U(\underset{\sim}{x})_N$ being given by (3·2).

Throughout this thesis we denote by $(\underset{\sim}{x})_N$ any configuration of N particles whose centres occupy the positions $\underset{\sim}{x}_1, \underset{\sim}{x}_2, \ldots\ldots \underset{\sim}{x}_N$ within a ν - dimensional container, Ω, and by $\int d(\underset{\sim}{x})_N$ the symbol specifying integration over $(x)N$. Functions of $\underset{\sim}{x}_1 \ldots\ldots \underset{\sim}{x}_N$ will be written as $F(\underset{\sim}{x}_1 \ldots\ldots \underset{\sim}{x}_N) \equiv F(\underset{\sim}{x})N$. This

notation seems to be due to Ruelle (1963), who used it in his work on the bulk - limit problem. The symbol $\{\Omega\}^N$ for the domain of integration in (6·3) indicates that all of the N particles are free to move throughout the container, Ω .

The existence of the grand canonical pressure at infinite volume has been discussed, *inter alia*, in paragraph 4 ; here, however, a different point of view will be adopted, our interest being in the convergence of the sequence (6·1) when z is complex.

When the pair interaction potential, $u(x)$, has a hard core, say of diameter a, (so that $u(\underset{\sim}{x})$ equals plus infinity whenever $|\underset{\sim}{x}|$ is less than a), the integral (6·3) vanishes if N exceeds $(V/\frac{4}{3}\pi a^3)$, and the right hand side of (6·2) becomes a polynomial in z, whose degree equals the greatest integer less than $(V/\frac{4}{3}\pi a^3)$. Moreover, since Q(N, V) is positive, this polynomial has no positive zeros and hence $\bar{p}(z, V)$ is analytic in the neighbourhood of every positive value of z. This, in turn, implies the analyticity of $\bar{v}(z, V)$, and finally that $p(v, V)$ is analytic for all positive v. The functions $\bar{v}(z, V)$, $p(v, V)$ denote respectively the grand canonical specific volume and the canonical pressure - both at volume V.

Yang and Lee (1952) realized that the only possibility for $p(v) \equiv \lim_{V\to\infty} p(v,V)$ to be non analytic at some positive value, say v_0, of v, occurred when v_0 was given by

$$v_0 = \bar{v}(z_0),$$

where z_0 was a limit point of zeros of $\Xi(z,V)$. Their first theorem, concerned with the existence of $\pi(z)$, is a special case of the 'bulk limit' problem. One form of their Theorem II is as follows:

> If R denotes any bounded, simply connected region containing a segment of the real positive z- axis and free from zeros of $\Xi(z,V)$ for all sufficiently large V, then
>
> (1) $\beta \bar{p}(z,V)$ converges to $\pi(z)$. uniformly for z in R, and hence
>
> (2) $\pi(z)$ is analytic throughout R.

The uniformity of convergence justifies the relation

$$\beta \lim_{V\to\infty} \frac{\partial}{\partial z} \bar{p}(z,V) = \frac{\partial}{\partial z} \pi(z) \qquad (\text{I } 6{\cdot}4)$$

for z in R, so that, since all of the derivatives of an analytic function are themselves analytic, one concludes that $p(v)$ is analytic in the neighbourhood of every positive v.

In order to relate the theorem just stated to the study of phase transitions, we must give a mathematical characterization of these transitions. We shall say that a system undergoes a phase transition when at least one of the thermodynamic variables used to specify it suffers a jump discontinuity. Since we are supposing the bulk limit to have been taken, we shall always deal with reduced representations. (see paragraph 1). This definition of phase transitions, attributed to Ehrenfest, is not comprehensive. For example, it does not include the 'anomalies' associated with order - disorder phenomena, such as the 'infinity' in the specific heat of the two dimensional Ising model in zero magnetic field, as the critical temperature is approached.

But a wide variety of phase transitions <u>are</u> included in the Ehrenfest classification (for instance the vapour - liquid transition first studied by Van der Waals (1873) and Maxwell) and one can see at once that the theorems of Yang and Lee furnish a necessary condition for the occurrence of a transition of Ehrenfest type. For, their theorems provide sufficient conditions for the existence and analyticity of $\mathcal{P}(z)$, the grand canonical pressure at infinite volume, for positive values of z; then the derivatives (of all orders) of $\mathcal{P}(z)$ are also analytic

and hence transitions of Ehrenfest type are precluded. Moreover, If π or one of its derivatives is non-analytic in the neighbourhood of a positive value of z, then a phase transition occurs as z passes through this value along the real positive axis (though this transition is not necessarily of Ehrenfest type).

The Yang - Lee theorems may be stated more simply if we use explicitly the notion of limit points of zeros of Ξ. We define the point z' to be a limit point of zeros of $\Xi(z,V)$ when the following condition is satisfied:

> Given any neighbourhood $\mathcal{N}$ of z' and any positive number K, there exists a z in $\mathcal{N}$ and a $V > K$, such that $\Xi(z,V) = 0$

The two theorems of Yang and Lee may then be combined into a single theorem:

Theorem

Let R denote a bounded, simply connected region in the $z-$ plane containing a segment of the real positive axis. Then a sufficient condition for the existence and analyticity of $\pi(z) \equiv \lim V^{-1} \log \Xi(z,V)$ throughout R is that R is free from limit points of zeros of $\Xi(z,V)$

If we denote by C the set of all limit points of zeros of Ξ and by χ_+ the real positive $z-$ axis, then it follows from the theorem just stated and the definition of phase transitions adopted here, that

'the open segment $R \cap \mathcal{X}_+$ of values of z corresponds to a single phase of the system if and only if $R \cap \mathcal{X}_+$ contains no points of C.'

The major part of the research described in this thesis deals with the problem of specifying C rigorously; this work is explained in Chs IV and V .

An analogue of Yang and Lee's theorems, referring to the uniform convergence of the canonical pressure at complex density, as the volume becomes infinite, has been proved by Lebowitz and Penrose (1966). A second analogue of these theorems (Jones, 1966) deals with the uniform convergence of the grand canonical pressure, regarded as a function of the complex variable β at fixed (possibly complex) z , as V tends to infinity.

REFERENCES

Callen (1960), Thermodynamics (John Wiley & Sons Inc., New York);

Dirac (1958), Quantum Mechanics, Fourth Edition, (Oxford University Press);

Dyson & Lenard (1967), J. Math. Phys. 8, 423;

Farquhar (1964), 'Ergodic Theory in Statistical Mechanics' (Interscience Publishers, Inc.);

Fisher (1964), Arch. Rational Mech. & Anal. 17, 377;

Gibbs (1902), Elementary Principles in Statistical Mechanics (Dover reprint, 1960);

Griffiths (1964), J. Math. Phys. 5, 1215;

Van Hove (1949), Physica 15, 951;

Huang (1964), Statistical Mechanics, John Wiley & Sons Inc., New York;

Jones (1966), J. Math. Phys. 7, 2000;

Khinchin (1949), Mathematical Foundations of Statistical Mechanics, Dover edition, translated by G. Gamow.

Landau & Lifshitz (1958), Statistical Physics, translated by R.E. & R.M. Peierls, Pergammon Press;

Lebowitz & Penrose (1966), J. Math. Phys. 7, 98;

Van der Linden (1966), Physica 32, 642;

Van der Linden & Mazur (1967), Preprint (Leiden).

Ruelle (1963a), Helv. Physica Acta 36, 183;

Ruelle (1963b), Helv. Physica Acta 36, 789;

Yang & Lee (1952), Phys. Rev. 87, 404.

Closely Related References.

Fisher (1964), 'The Nature of Critical Points', Lectures in Theoretical Physics VII C (Boulder, Colorado);

Ruelle (1963c), 'Rigorous Results in Statistical Mechanics', Lectures in Theoretical Physics (VI (Boulder, Colorado).

CHAPTER II

Some Methods for Studying the Equation of State of a One - dimensional System - a Survey.

§ 1 The systems to be considered in this chapter consist of N particles moving continuously on a line of length L. The essential simplification characteristic of one - dimensional continuum systems is that, even when the particles do not have hard cores, a fixed ordering of the particles may be defined and maintained throughout all calculations. This simplification reflects the total symmetry in its arguments of the potential energy function of N identical particles, which implies that the integrand of the configurational integral is invariant under changes in the order of the particles. For continuum systems in two or three dimensions, total ordering is impossible and the methods of this chapter break down.

The term one - dimensional is, however, less definite when applied to lattice gases since such systems, even when they are nominally two - or three - dimensional, may often be considered to consist of particles with internal degrees of freedom, whose possible positions are restricted to the sites of a linear lattice (see Ch. V).

§2 Classification of Methods.

Although the distinctions between various techniques are not always clear-cut, the following classification seems to be justified.

(i) Iterative Methods, in which either N or L is increased in regular steps, whence Q(N,L) may be 'calculated' recursively. (Von Hove, 1950; Kummer, 1962; Baur and Nosanow, 1962).

(ii) Use of external potentials, in which Q(N,L) is shown to satisfy an operator equation with respect to variations in the 'external parameters'. (Baxter, 1964, 1965; cf Leff and Coopersmith, 1967, Coopersmith and Leff, 1967,* for a similar method applied to the study of distribution functions.)

(iii) Use of random processes, in which $\Xi(z)$ may be obtained implicitly with the help of the theory of Gaussian Markov processes (Kac, 1959; Edwards and Lenard, 1962; Kac, Uhlenbeck and Hemmer, 1963; Kac and Helfand, 1963.)

In the following survey this classification helps us to identify the crucial assumptions responsible for the success of a particular technique, though no explicit reference to it will be made. (Some of the methods discussed in this chapter are also considered, briefly, in the book, Mathematical Physics in One Dimension, edited by E. Lieb & D. Mattis (Interscience Publishers Inc., 1966)).

* J. Math. Phys. 8, 306; 8, 434.

§3 Van Hove's Method: Impossibility of phase transitions when the forces are of finite range.

Suppose that the particles have hard cores, that the interactions extend to h^{th} - nearest neighbours and that the potential is bounded below. Starting from a set of $t = h+1$ particles on a line of length L, one can assemble a system of $N = t + mh$ particles by adding, successively, 'strings' of h particles. The hard core condition makes it possible to maintain a definite ordering of the particles throughout this process, so that we have

$$Q(t+mh;L) = \int d(1) \int d(m+1)\, K^{(m)}(1, m+1), \qquad (\text{II } 3\cdot 1)$$

where the symbol $\int d(j)$ denotes integration over all possible configurations of the j th string (compatible with the chosen ordering of the particles). The kernel $K(i,j)$, of which $K^{(m)}$ stands for the m th iterate, is defined by

$$K(i,j) \equiv \exp\{-\beta \Phi_{int}(i,j)\}\exp(-\beta U(j)) \qquad (\text{II } 3\cdot 2)$$

$\Phi_{int}(i,j)$ being the mutual potential energy of the ith and jth strings.* Thus $K(i,j)$ has the constant value 1 for all configurations of the strings i, j unless $|i-j| = 1$

By introducing instead of K(i,j) the kernel

$$\mathcal{K}(i,j;p) \equiv K(i,j)\exp\{-p\lambda_i\} \qquad (\text{II } 3\cdot 3)$$

* $U(j)$ denotes the self-enorgy of the jth string.

where, for each configuration of the ith string, λ_i denotes the distance between its first and last particles, one can express the Laplace transform, $I(N,P)$, of $Q(t+mh)$ in terms of the mth iterate $K^{(m)}(i,j;p)$ of $K(i,j;p)$, though the range of integrations in each of the $2h$ particle co-ordinates is now infinite. By making the change of variable: $p^{-1}\exp(-px) \equiv y$, where x denotes the separation of a pair of particles, Van Hove succeeds in reducing the problem of calculating the Gibbs free energy per particle, $g(p)$, to finding the eigen-value of maximum modulus of a Fredholm integral equation. The modulus of this eigen-value equals the radius of convergence of the resolvent series of the kernel of the equation, and this expansion is used by Van Hove to show that

$$g(p) = (t-1)\,K_{max}(p), \qquad (\text{II } 3.4)$$

where $(t-1)$ is the number of particles in a string, from which the equation of state is

$$\zeta(p) = \frac{\partial}{\partial p} g(p) = (t-1)\frac{\partial}{\partial p} K_{max}(p), \qquad (\text{II } 3.5)$$

corresponding to the constant pressure ensemble (cf. Brown 1958, Sack 1959). Finally, the existence and analyticity of $K_{max}(p)$ are justified for positive p by virtue of a theorem of Jentzsch (1912), whence (3.5) implies that a phase transition (in the sense of Ch. I §6) cannot occur.

Kummer (1962) has generalized Van Hove's method to the case of a 'quasi two - dimensional' system, consisting of 'hard squares' free to move parallel to the sides of a rectangular container, one side of which remains of fixed length while the other may increase without bound. A procedure similar to Van Hove's but also based on the matrix method of Kramers and Wannier (1941) has been used by Baur and Nosanow (1962) in their treatment of lattice gases.

In explicit calculation of the equation of state Van Hove's method is of little use, since the kernel $K(i,j;p)$ and its transform under the change of variable $x \rightarrow y$ are neither symmetric, (except when $p>0$ & $t=2$) nor Hermition when p is complex, so that analytical calculation of $K_{max}(p)$ is, ingeneral, not possible. Moreover, the total number, N, of particles must have the form $N = t + m\,h$, which makes it impossible* to consider the grand partition function. This difficulty may be avoided when dealing with lattice gases, since the grand partition function of a lattice gas equals the 'configurational sum' of a suitably defined spin system (see Ch. V).

* In fact it is possible but not useful to consider the grand partition function.

§4 Another Iterative Method.

A method closely parallel to Van Hove's but avoiding the requirement that N has a special form, (except that N must exceed t), has been suggested by Penrose (unpublished). The conditions on the interaction are the same as Van Hove's. Suppose that $(x)_N$ denotes any configuration of N particles on a line, numbered from 1 to N, increasing with displacement to the right, and that Y denotes a fixed configuration of t particles (of the same species as the moveable particles) constituting a 'wall' to the right of all the particles at x_i, the other end of the container being closed at the origin of displacement coördinates by a perfectly hard particle. That is, the x_i, y_j satisfy

$$0 \leqslant x_1 < x_2 < \cdots < x_N < y_1 < \cdots < y_t \leqslant L \quad . \quad (\text{II } 4{\cdot}1)$$

We define a modified configurational integral, $\psi_L(N;Y)$, by

$$\psi_L(N,Y) \equiv \int d(x)_N \exp\{-\beta U[(x)_N;Y]\} \quad (\text{II } 4{\cdot}2)$$

where $U[(x)_N;Y]$ denotes the total potential energy of the N particles in configuration $(x)_N$ in the presence of the wall Y, and the integration is taken over all such configurations. Since the interaction extends from a given particle to at most (t - 1) particles on its left, it follows from (4.2) that ψ_L satisfies the recurrence relation

$$\psi_L(N+1;Y) = \int_0^{y_1} dy_0 \prod_{k=0}^{t-1} \exp[-\beta u(y_t - y_k)]\, \psi_L(N;y_0,Y), \qquad (\text{II } 4\cdot3)$$

$u(x)$ being the interaction potential.

This may be written in the operational form

$$\psi_L(N+1;Y) = \hat{K}\psi_L(N;Y), \qquad (\text{II } 4\cdot4)$$

which may be regarded as defining the operator $\hat{K}$. Since the effect of applying $\hat{K}$ is to introduce one more particle to the system, we may build a system of N particles from an empty container with the wall Y at one end, by repeated use of $\hat{K}$. Therefore we have

$$\psi_L(N;Y) = \hat{K}^N \psi_L(0;Y), \qquad (\text{II } 4\cdot5)$$

where

$$\psi_L(0;Y) \equiv \exp[-\beta U(Y;L)] \qquad (\text{II } 4\cdot6)$$

and $U(Y;L)$ is the potential energy of the fixed configuration of particles constiuting the wall. The usual configurational integral may now be found from (4.2) and (4.5) to be

$$Q(N,L) = \int dY\, \hat{K}^N \psi_L(0;Y), \qquad (\text{II } 4\cdot7)$$

where the integrations over $y_1 \cdots y_t$ are subject to the condition (4.1) (though the lower limit for y_1 is now 0 because the x - integrations have been done).

One expects that it should be possible to obtain from (4.7) a formal expression for $f(v)$, the canonical free energy per particle, analogous to Van Hove's formula (3.4) and so to reach the same conclusion regarding the impossibility of phase transitions. The rigorous justification of such a procedure would, however, entail a full study of the operator $\hat{K}$.

If we keep the wall fixed, so that the effective length of the container is y_1, and define a modified grand partition function, $\Xi(z; y_1, Y; L)$, by

$$\Xi(z; y_1, Y; L) \equiv 1 + \sum_{N=1}^{\infty} z^N \psi_L(N; Y)$$

$$= 1 + \sum_{N=1}^{\infty} (z\hat{K})^N \psi_L(0; Y), \qquad (\text{II } 4\cdot 8)$$

by (4.5), then for all sufficiently small $|z|$ we obtain

$$\Xi(z; y_1, Y; L) = (1 - z\hat{K})^{-1} \psi_L(0; Y). \qquad (\text{II } 4\cdot 9)$$

The expression (4.9) has a misleading simplicity, it being difficult to introduce a suitable norm for the operator $\hat{K}$ and hence give a precise meaning to the ~~phase~~ phase 'for all sufficiently small $|z|$ ', used above. However, if t = 2 (nearest neighbour forces) one may verify that the method of this section is equivalent to that of Takahasi (1942) and Gürsey (1950), though their methods are preferable in this simple case. Our original intention in deriving (4.9) was to relate $\Pi(z)$ to the eigen-values of an operator, but we have not been able to see a simple way to study the spectrum of $\hat{K}$ and so the method is mainly of formal interest.

§5 Baxter's Method.

This method was designed to show formally how the function $\bar{p}(z)$ can be obtained, for positive z, as the largest real eigen-value of an operator, while the correlation functions may be calculated from a related operator. The argument is formulated for one - dimensional continuum systems and is shown to be valid both for particles with hard cores and for those with bounded interactions.

The basic idea is that the configurational integral, Q (N.L), defined by(I6.3) is differentiable in L, and that the operation $\partial/\partial L$ may be performed before the integration over configurations. In order to make variations in L 'perceptible', an external potential, say g(r), is centred at the moveable end of the container. We define a modified configurational integral by

$$\tilde{Q}(N,L) \equiv \int\cdots\int_{0\le x_1\cdots<x_N\le L} dx_1\cdots dx_N \exp\{-W\}, \qquad (\text{II } 5\cdot1)$$

where

$$W(x_1\cdots x_N; L; g) \equiv \beta\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u(x_i-x_j) + \beta\sum_{l=1}^{N} g(L-x_l). \qquad (\text{II } 5\cdot2)$$

Differentiating (5.1) in L, we obtain

$$\frac{\partial}{\partial L}\tilde{Q}(N,L) = \int\cdots\int_{0\le x_1\cdots<x_{N-1}\le L} dx_1\cdots dx_{N-1}\left[\exp(-W)\right]_{x_N=L}$$

$$+\int\cdots\int_{0\le x_1\cdots<x_N\le L} dx_1\cdots dx_N \frac{\partial}{\partial L}\exp(-W). \qquad (\text{II } 5\cdot3)$$

If the external potential can be made to depend on parameters $v_0 \cdots\cdots v_k$ in such a way that

$$g(L-x; v_0'\cdots\cdots v_k') + u(L-x) = g(L-x; v_0''\cdots\cdots v_k'') \qquad (\text{II } 5\cdot4)$$

$$\frac{\partial}{\partial L} g(L-x; v_0\cdots\cdots v_k) = \hat{J}\, g(L-x; v_0\cdots\cdots v_k) \qquad (\text{II } 5\cdot5)$$

where $\hat{J}$ is an operator acting only on the parameters v_j, then it follows from (5.1) - (5.3) that Q(N,L) satisfies the equation

$$\frac{\partial}{\partial L}\tilde{Q}(N,L) = \int\cdots\int_{0\le x_1\cdots<x_{N-1}\le L} dx_1\cdots dx_{N-1}\left[\exp(-W)\right]_{x_N=L}$$

$$+\hat{J}\,\tilde{Q}(N,L). \qquad (\text{II } 5\cdot6)$$

Notice that if the particles have hard cores, say of diameter a, then the domain of integration in (5.5) becomes $0 \leq x_1 < x_2 \cdots < x_{N-1} \leq L-a$. Moreover, if the pair interaction potential, $u(r)$, satisfies an ordinary differential equation of order k with constant coefficients, the conditions (5.3) and (5.4) can be satisfied by functions g of the form

$$g(r; v_0 \cdots v_k) = \sum_{l=0}^{k} v_l u^{(l)}(r), \quad (\text{II } 5.7)$$

where $u^{(l)}(r)$ means $d^l u(r)/dr^l$, and in this case $\hat{J}$ becomes a differential operator in one or more of the v_j. It may be shown, also, that the first term on the right-hand side of (5.4) has the form $\hat{K}\tilde{Q}(N-1,L)$ [or $\hat{K}\tilde{Q}(N-1,L-a)$ when the particles have hard cores], where $\hat{K}$ is the exponential of a differential operator in one or more of the v_j. More general formal representations may be obtained for $\hat{J}, \hat{K}$ as functional differential operators even when $u(x)$ does not satisfy a differential equation, but these seem to be of little practical use (see Baxter, 1964).

As a simple illustrative example (R.J. Baxter, 1966, private communication) consider a superposition of Kac potentials:

$$u(r) = \sum_{\alpha=1}^{k} c_\alpha \exp(-\gamma_\alpha |r|).$$

According to (5.5) we may write

$$g(r; v \cdots v_k) = \sum_{\alpha=1}^{k^*} v_\alpha \exp(-\lambda_\alpha r) ;$$

(note that the argument, L - x, of g in (5.2) is non negative, so that we may write r instead of $|r|$ when dealing with g). Using these expressions for u(r) and g(r) one can show by manipulating (5.3) that

$$\frac{\partial}{\partial L} \tilde{Q}(N,L) = e^{-\sum_\alpha v_\alpha} \tilde{Q}(N-1, L; v_1 + c_1, v_2 + c_2 \cdots) - \sum_\alpha \lambda_\alpha v_\alpha \frac{\partial}{\partial v_\alpha} \tilde{Q}(N,L; v_1, v_2 \cdots) .$$

By considering the first term on the right-hand side as a multible Taylor series one obtains, formally,

$$\hat{K} = \exp\left[\sum_\alpha \left(-v_\alpha + c_\alpha \frac{\partial}{\partial v_\alpha}\right)\right] ,$$

while comparison with the general equation (5.5) yields

$$\hat{J} = - \sum_\alpha \lambda_\alpha v_\alpha \frac{\partial}{\partial v_\alpha} .$$

On introducing K in (5.5), multiplying by z^N and summing over all positive integers N, one obtains a differential equation for the function

$$f(z,L) \equiv 1 + \sum_{N=1}^{\infty} z^N \tilde{Q}(N,L)$$

(or for both $f(z,L)$ & $f(z,L-a)$ when the particles have hard cores). When g(r) vanishes identically for $r \geq 0$ $f(z,L)$ coincides with $\Xi(z,L)$, the grand partition function. Finally, if one assumes that the differential equation for f has a separable solution of the form

$$f(z,L) = \sum_j h_j(z) \exp(k_j L)$$

then an eigen-value equation (with eigen-values k_j and eigen-functions h_j) is obtained. The desired formula for $\bar{p}(z)$, the pressure, results if there exists a real eigen-value, say Kmax, exceeding the real parts of all other eigen-values. For we have then

$$\bar{p}(z) \equiv \lim_{L\to\infty} (\beta L)^{-1} \log \Xi(z,L) = K_{max}(z). \qquad (\text{II } 5.8)$$

Evidently, Baxter's treatment is rather schematic, but he has considered specific cases. For a system with potential $u(r) = -\alpha\gamma \exp(-\gamma|r|)$, outside

a hard core (to be discussed further in our next section) he has obtained the Van der Waals phase transition (in the limit $\gamma \to 0^+$) which was first derived by Kac, Uhlenbeck and Hemmer (1963(a)). He has also obtained results for a system of charged hard rods; the previous results for charged one - dimensional systems (Lenard 1962, Edwards and Lenard 1962, Prager 1961) depend on the assumption that the particles do not have hard cores. Baxter shows how his method may be used to obtain the distribution functions; essentially, he carries out the same procedure as we have outlined, but starting with the (unnormalized) distribution function,

$$\int \cdots \int_{x_r < x_{r+1} \cdots < x_N \leq L} dx_{r+1} \cdots dx_N \exp(-W)$$

instead of $\tilde{Q}(N, L)$.

This technique, depending on continuous variation of L, has no direct analogue for lattice gases, but the representation of the pressure as the largest eigen value of an operator has been demonstrated by Kramers and Wannier (1941) and Baur and Nosanow (1962).

§6 The Covariance Method.

The technique of this section allows a complete calculation of the Laplace transform of the configurational integral for any system whose pair potential, u(r), may be regarded as the auto - covariance of a Gaussian Markov process. We illustrate the method by giving a fairly detailed derivation of the Kac integral equation (Kac, 1959), which serves, also, as a preparation for our derivation of an analogous integral equation, described in Chapter III of this thesis.

Since the elements of the autocovariance matrix of an l-dimensional Markov process satisfy a linear differential equation of order l (of de Groot and Mazur 1962, Ch. VIII) with constant coefficients, - which is just the condition for Baxter's method to be used effectively - it is possible that the two methods are equivalent, for a class of interaction potentials. However, we have been unable to apply Baxter's method successfully to the system with pair potential $u(r) = -h \cos kr\, e^{-\lambda|r|}$ (see Ch. III), which satisfies a second order differential equation with constant coefficients. In practice, therefore, it appears that Baxter's technique is effective only when the potential is proportional to $|x|$ or to $e^{-\alpha|x|}$.

Kac based his calculation on the identity (cf. Wilks, 1963, Sec. 7.4)

$$e^{-\frac{1}{2}(\xi, C\xi)} = (2\pi)^{-\frac{N}{2}} |C|^{-\frac{1}{2}} \int_{-\infty}^{\infty} d(\eta)_N \cdot e^{-\frac{1}{2}(\eta, C^{-1}\eta) + i(\xi, \eta)} \qquad (\text{II } 6.1)$$

where $\xi \equiv (\xi_1 \cdots \xi_N)$ denotes any vector with N (real or complex) components, C is a real, symmetric, positive-definite matrix and (A,B) means the scalar product of vectors A, B. The integration extends over all real values of the N components $\eta_1 \cdots \eta_N$ of the vector η and $|C|$ denotes the determinant of C. The proof of (6·1) is immediate if one writes

$$T\xi = \mu \quad , \quad T\eta = \nu,$$

where the matrix T has been chosen so that $T'CT$ is a diagonal matrix whose eigen-values are, say, $\lambda_1 \cdots \lambda_N$, T' being the transpose of T. For, (6·1) is then transformed into the identity

$$(2\pi)^{\frac{N}{2}} |C|^{\frac{1}{2}} \equiv \int_{-\infty}^{\infty} d(\nu)_N \prod_{k=1}^{N} e^{-\frac{1}{2}\theta_k^2(\nu_k)}, \qquad (\text{II } 6.2)$$

where

$$\theta_k(\nu_k) \equiv i\mu_k\sqrt{\lambda_k} + \nu_k/\sqrt{\lambda_k}, \qquad (\text{II } 6.3)$$

and the identity (6.2) may be verified at once by integration.

By setting all of the ξ_k equal to 0, one finds (cf Siegert, 1963) that

$$\rho(\eta) \equiv (2\pi)^{-\frac{N}{2}}|C|^{-\frac{1}{2}} e^{-\frac{1}{2}(\eta, C^{-1}\eta)} \qquad (\text{II } 6.4)$$

is the joint probability density for the components of a 'random vector' η. Moreover, we have from (6.1) the relations

$$\lim_{\text{all } \xi_j \to 0} \frac{\partial}{\partial \xi_k} e^{-\frac{1}{2}(\xi, C\xi)} = i\langle \eta_k \rangle = 0, \qquad (\text{II } 6.5)$$

$$\lim_{\text{all } \xi_j \to 0} \frac{\partial^2}{\partial \xi_k \partial \xi_\ell} e^{-\frac{1}{2}(\xi, C\xi)} = -C_{k\ell} = -\langle \eta_k \eta_\ell \rangle, \qquad (\text{II } 6.6)$$

where $\langle\ \rangle$ denotes expectation value subject to the probability density $\rho(\eta)$. Hence the components $\eta_1 \cdots \eta_N$ constitute Gaussian random variables with mean zero and covariance $C_{k\ell}$. An extension of this technique will be discussed in Ch. III.

Kac considered a system of particles moving on a line of length L under pairwise forces with interaction potential, u(r), defined by

$$u(r) \equiv \begin{cases} +\infty, & r < a \\ -\alpha e^{-\gamma r}, & r \geq a \end{cases} . \quad (\text{II } 6.7)$$

The configuration integral for this system is therefore

$$Q(N,L) = \int \cdots \int_{0<x_1<\cdots<x_N<L} dx_1 \cdots dx_N \prod_{j=1}^{N-1} \left[1 - \phi(x_{j+1}-x_j)\right]$$

$$\cdot \exp\left[\frac{1}{2}\alpha\beta \sum_{k=1}^{N}\sum_{l=1}^{N} e^{-\gamma|x_k - x_l|} - \frac{1}{2}N\alpha\beta\right], \quad (\text{II } 6.8)$$

where $\phi(r)$ denotes the step function:

$$\phi(r) = \begin{cases} 1, & |r| < a \\ 0, & |r| > a \end{cases} . \quad (\text{II } 6.9)$$

In order to make use of (6·1) we consider the Gaussion random process, say $\eta(x)$, whose autocovariance is equal to $\exp(-\lambda|x|)$. This process is known to be Markovian, (Ornstein and Uhlenbeck, 1930), which means that the probability density function for a random vector, $(\eta_1 \cdots\cdots \eta_N) \equiv (\eta(x_1) \cdots, \ldots, \eta(x_N))$ has the form

$$\rho(\eta_1 \cdots \eta_N) = W(\eta_1) \prod_{j=1}^{N-1} P(\eta_j | \eta_{j+1}; x_{j+1} - x_j), \qquad (\text{II } 6\cdot 10)$$

where $W(\eta_1)$ is the unconditional probability density of η_1 and $P(\eta_j | \eta_{j+1}; x_{j+1} - x_j)$ denotes the conditional probability that $\eta(x_{j+1}) = \eta_{j+1}$, given that $\eta(x_j) = \eta_j$. , We may now use (6·1), obtaining by comparison with (6·8)

$$Q(N, L) = e^{-\frac{1}{2}N\alpha\beta} \int \cdots \int_{0 < x_1 \cdots < x_N < L} dx_1 \cdots dx_N \prod_{j=1}^{N-1} \left(1 - \phi(x_{j+1} - x_j)\right) \qquad (\text{II } 6\cdot 11)$$
$$\cdot \left\langle \exp\{(a, \eta)\} \right\rangle_{\rho(\eta)},$$

Where $\rho(\eta)$ is given by (6·10), a denotes the N - dimensional vector $((\alpha\beta)^{\frac{1}{2}} \cdots, (\alpha\beta)^{\frac{1}{2}})$ and the average is taken by integrating over each of $\eta_1 \cdots\cdots \eta_N$ from $-\infty$ to $+\infty$ (so that, since $\rho(-\eta) = \rho(+\eta)$, we have $\left\langle \exp\{-(a, \eta)\} \right\rangle_\rho = \left\langle \exp\{(a, \eta)\} \right\rangle_\rho$). Moreover, the function $\rho(\eta)$

is known explicitly in this case (Ornstein and Uhlenbeck, 1930).

On making the transformation

$$\tau_1 = x_1, \quad \tau_j = x_j - x_{j-1} \ (2 \leq j \leq N), \quad \tau_{N+1} = L - x_N, \tag{II 6·12}$$

with unit Jacobian, we obtain for $N \geq 2$, after changing the order of integration and integrating twice by parts,

$$I_N(p) \equiv \int_0^\infty dL\, e^{-pL} Q(N,L) = \frac{e^{-\frac{1}{2}N\alpha\beta}}{p^2} \left\langle \exp\{(a,\eta)\} \right\rangle_{\tilde{\rho}(\eta,p)}, \tag{II 6·13}$$

where $\tilde{\rho}$ is the density function

$$\tilde{\rho}(\eta,p) \equiv W(\eta_1) \prod_{j=1}^{N-1} \int_a^\infty e^{-p r_j} P(\eta_j | \eta_{j+1}; r_j). \tag{II 6·14}$$

The crucial point is that the right hand side of (6·13) may be expressed in the form

$$p^{-2} e^{-\frac{1}{2}N\alpha\beta} \int_{-\infty}^{\infty}\int d\eta_1 d\eta_N \, K_p^{(N-1)}(\eta_1, \eta_N)$$

$$\cdot \left[W(\eta_1) W(\eta_N) \exp\{(\alpha\beta)^{\frac{1}{2}}(\eta_1 + \eta_N)\} \right]^{\frac{1}{2}}, \tag{II 6·15}$$

Where $K_p^{(N-1)}(\eta_1, \eta_N)$ is obtained by iterating the basic kernel

$$K_p^{(1)}(u,v) \equiv \left[\exp\left\{(\alpha\beta)^{\frac{1}{2}}(u+v)\right\} W(u)/W(v)\right]^{\frac{1}{2}} \cdot \int_a^\infty dr\, e^{-pr} P(u|v;r). \quad (\text{II } 6.16)$$

The ultimate success of Kac's calculation depends on the fact (which he proves) that $K_p(u, v)$ is a Hilbert - Schmidt kernel (cf. Courant and Hilbert, 1953, Ch. 2) so that $K_p^{(l)}(u, v)$ may be written as

$$K_p^{(l)}(u,v) = \sum_{j=1}^{\infty} \lambda_j^l(p)\, \psi_j(u,p)\, \psi_j(v,p), \quad (\text{II } 6.17)$$

where the spectrum of K_p is discrete and bounded and all of the eigenvalues, λ_j, are positive. Since the abscissa of convergence of the Laplace transform (cf Widder, 1941, p.37) of $\Xi(z, L)$ equals $\Pi(z)$, as defined by (I5·2), it is then possible to relate $\Pi(z)$ to the largest eigenvalue, say $\lambda_1(p)$, of K. In this way Kac obtains $\Pi(z)$

implicitly through the relation

$$\lambda_1[\Pi(z)] = z^{-1}\exp(\tfrac{1}{2}\alpha\beta), \quad (\text{II } 6{\cdot}18)$$

whence he is able to show that $\Pi(z)$ is analytic for all positive z, thus precluding a phase transition. His result extends those of Van Hove (1950) and Yang and Lee (1952), since the potential (6·7) has infinite range.

More recently, Kac, Uhlenbeck and Hemmer (1963), building on the result (6·18), have shown that if α is replaced by $\alpha_0\gamma$ in (6·7) then, in the limit as $\gamma \to 0^+$, the 'Van der Waals limit', the system exhibits a phase transition described exactly be Van der Waals' equation, modified by Maxwells' 'equal area construction'. The fact that Maxwell's rule is 'built into' the calculation reflects the convexity properties of the bulk limit functions (I §5) which show that Van der Waals 'loops' cannot occur when the isotherms are calculated rigorously; indeed, the interaction potential (6·7) is both stable and strongly tempered - the simplest conditions sufficient for the existence of the functions $p(v)$, $\Pi(z)$ [cf. I §4]. Kac and Helfand (1963) have studied several lattice systems using the technique of this section and

Siegert (1963) has formulated the Ising problem in terms of random variables.

The one - dimensional plasma problem has been treated by Edwards and Lenard (1962) using the method of functional integration, of which the covariance method is a special case (as they explain). Specifically, they show that the G.P.F. for a system of several species of charged particles equals the average of a functional whose argument function describes the position of a Brownian particle (Wiener Process; Wiener (1923)). By using a theorem due to Kac (1951) they prove that this functional is the fundamental solution of a diffusion equation, thus obtaining, like Baxter, an explicit eigenvalue equation whose largest real eigenvalue equals $\Pi(z)$ when z is positive.

The occurrence of phase transitions in the systems considered in this chapter may be characterized very simply. It is found that as z moves along the real positive axis $\Pi(z)$, being the largest real eigenvalue of an eigenvalue equation, is analytic so long as there is only <u>one</u> such eigenvalue. If, on the other hand, two or more eigenvalues become equal and larger than the real parts of all others as z tends to z' then $\Pi(z)$ would be nonanalytic at z', and a phase

transition could occur. This idea is used by Helfand (1964) to study the way in which a phase transition can 'grow' as a result of some limiting operations (for example, the Van der Waals limit).

The basic aim of the research described in Chapters IV and V is to locate the set of points $\{z'\}$ in the complex plane, at which $\pi(z)$ is non analytic(or does not exist). According to the theory of Yang and Lee (1952) the set $\{z'\}$ should coincide with C, the set of all limit points of zeros of $\Xi(z,L)$, and it will be seen that this is so.

REFERENCES

Baxter (1964), Phys. Fluids 7, 38;

Baxter (1965), Phys. Fluids 8, 687;

Baur & Nosonow (1962), J. Chem. Phys. 37, 153;

Brown (1958), Mol. Phys. 1, 68;

Courant & Hilbert (1953), Methods of Mathematical Physics, Volume I (Interscience Publishers Inc.);

Edwards & Lenard (1962), J. Math. Phys. 3, 778;

de Groot & Magur (1962), Nonequilibrium Thermodynamics, (North Holland Publishing Company, Amsterdam.)

Helfand (1964), J. Math. Phys. 5, 127;

Van Hove (1950), Physica 16, 137;

Jentzsch (1912) Journal Fur Math. 141, 235;

Kac (1951), Proc. Second Berkeley Symp. on Prob. & Stat. p.189;

Kac (1959), Phys. Fluids 2, 8;

Kac, Uhlenbeck & Hemmer (1963), J. Math. Phys. 4, 216;

Kramers & Wannier (1941) Phys. Rev. 60, 252;

Kummer (1962), Helv. Physica Acta 35,457;

Ornstein & Uhlenbeck (1930), Phys. Rev. 36, 823;

Prager (1961), Adv. Chem. Phys. Vol. IV, edited by I. Prigogine, (Interscience Publishers Inc., New York);

Sak (1959), Mol. Phys. 2, 8;

Siegert (1963), Brandeis University Summer Institute Lectures in Theoretical Physics (delivered in 1962, published in 196

Widder (1941), The Laplace Transform, (Princeton Mathematical Series, 6);

Wiener (1923), J. Math. & Phys. 2, 131;

Wilks (1963), Mathematical Statistics, (John Wiley & Sons Inc. New York);

Yang & Lee (1952), Phys. Rev. 87, 404.

Closely Related References.

Lenard (1961), J. Math. Phys. 2, 682;

Lenard (1963), J. Math. Phys. 4, 533;
(Both of these papers deal with the one-dimensional Coulomb System).

Newman (1964), J. Math. Phys. 5, 1153;
(Covariance method for a one-dimensional system with weak, long - range repulsive forces).

Zaanen (1953), Linear Analysis (North Holland Publishing Co. Amsterdam);
(A more recent proof of Jentzsch's theorem is given on pp 495-9).

C H A P T E R III

Another Application of the Covariance Method.

§ 1 In this chapter we present a generalization of the relation (II·6·13) giving $\Pi(N, p)$ as a stochastic average. With certain assumptions, which will be stated, it will be shown how the equation of state may be obtained implicitly, in analogy with (II 6·18). These assumptions seem difficult to verify, so the second part of the calculation is hypothetical.

§2 We consider a one - dimensional system of particles interacting through two - body forces; the interaction potential is defined to be

$$u(x) \equiv \begin{cases} +\infty, & x < a \\ -h\cos kx\, e^{-\gamma x}, & x \geqslant a \end{cases} \quad (\text{III } 2\cdot1)$$

where h, k and γ are positive constants. Our original aim in considering this highly unrealistic potential was to see whether some form of fluid - solid phase transition might appear in the limit as $\gamma \to 0^+$, induced by the periodic factor, $\cos kx$.

However, since this calculation was done, it has been pointed out that when $u(x)$ is given by (2·1), the integral of $u(x)$ (over all $x \geqslant a$) tends to 0 with γ, so that it is not clear how the Van der Waals limit ($\gamma \to 0^+$) can be taken in a more useful way. For, the work of Lebowitz and Penrose (1966), in which the long - range forces contribute a term proportional to $\int u(x)\,dx$ to the equation of state, indicates that this integral (or its limit as $\gamma \to 0^+$) should not vanish, if there is to be any hope of finding a phase transition. This difficulty has still to be resolved.

The configurational integral for the potential (2·1) is (cf (II 6·8))

$$Q(N,L) = \int_{0<x_1<\cdots<x_N<L} \cdots \int dx_1 \cdots dx_N \prod_{j=1}^{N-1} \left(1-\phi(x_{j+1}-x_j)\right)$$

$$\cdot \exp\left\{\frac{1}{2} h\beta \sum_{i=1}^{N}\sum_{j=1}^{N} \cos k(x_i-x_j) e^{-\lambda|x_i-x_j|} - \frac{1}{2} Nh\beta\right\}. \qquad (\text{III } 2\cdot2)$$

We aim to show that the Laplace transform of Q(N,L) may be calculated as a stochastic average, analogous to that defined by (II 6·13).

§3 Since the function $\cos kx\, e^{-\gamma x}$ satisfies a second order differential equation in x, we must find a two-dimensional stationary Markov process for which $\cos kx\, e^{-\gamma x}$ is an element of the (2 X 2) auto - covariance matrix. A theorem of Doob (1944) requires that this matrix have the form

$$\begin{matrix} \exp(Ax) & , x > 0 \\ \exp(-A'x) & , x < 0 \end{matrix} \quad , \qquad (\text{III } 3.1)$$

Where A is a constant matrix, A' denotes the transpose of A and it is understood that x is multiplied by the unit matrix of order 2. (cf. Wang and Uhlenbeck, 1945, Appendix, for a direct proof - due to Kac). By using Cauchy's formula, one obtains (cf. Goertzel and Tralli, 1960, Ch. 3)

$$\left[\exp(Ax)\right]_{jl} = \frac{1}{2\pi i} \oint dw \frac{e^{wx}}{(w\mathbb{1} - A)_{jl}} , \qquad (\text{III } 3.2)$$

Where $\mathbb{1}$ stands for the (2 X 2) unit matrix and the contour of integration encloses no eigenvalues of $(w\mathbb{1} - A)$, whence it may be shown that

$$\exp\left[\begin{pmatrix} -\gamma & k \\ -k & -\gamma \end{pmatrix} x\right] = \begin{pmatrix} c & -s \\ s & c \end{pmatrix} . \qquad (\text{III } 3.3)$$

For convenience in the forth coming calculations we have written

$$\left.\begin{aligned} c \equiv c(x) &\equiv \cos kx\, e^{-\gamma x} \\ s \equiv s(x) &\equiv \sin kx\, e^{-\gamma x} \end{aligned}\right\}. \qquad (\text{III } 3\cdot 4)$$

Instead of the vector $\eta \equiv (\eta_1 \cdots \eta_N)$ considered in III§ 6, we now introduce the 'vector' $Y \equiv (\underset{\sim}{y}_1 \cdots \underset{\sim}{y}_N)$, where

$$\underset{\sim}{y}_k \equiv \underset{\sim}{y}(x_k) \equiv \begin{bmatrix} \alpha_1(x_k) \\ \alpha_2(x_k) \end{bmatrix} \qquad (\text{III } 3\cdot 5)$$

and $\underset{\sim}{y}(x)$ is the process whose autocovariance is given by (3·1). Since $\underset{\sim}{y}(x)$ is a Markov process, the density function $p(Y)$, the analogue of $p(\eta)$ in III§ 6, has the form

$$p(Y) = W(\underset{\sim}{y}_1) \prod_{j=1}^{N-1} P(\underset{\sim}{y}_j | \underset{\sim}{y}_{j+1}; x_{j+1} - x_j), \qquad (\text{III } 3\cdot 6)$$

so that our task is reduced to that of calculating the transition probabilities $P(\underset{\sim}{y}_j | \underset{\sim}{y}_{j+1}; x_{j+1} - x_j)$. This, in turn, may be done by use of (II 6·1) successively for $N = 1$ and $N = 2$ (and with η replaced by Y).

For $N = 1$, we obtain at once

$$W(\underset{\sim}{y}_1) = (2\pi)^{-\frac{1}{2}} \exp\{-\tfrac{1}{2}(\alpha_1^2 + \alpha_2^2)\}. \quad (\text{III } 3\cdot 7)$$

In order to determine $W(\underset{\sim}{y}_1, \underset{\sim}{y}_2)$ we must consider the matrix

$$R(x) \equiv \begin{bmatrix} \langle \underset{\sim}{y}_1 \underset{\sim}{y}_1 \rangle & \langle \underset{\sim}{y}_1 \underset{\sim}{y}_2 \rangle \\ \langle \underset{\sim}{y}_2 \underset{\sim}{y}_1 \rangle & \langle \underset{\sim}{y}_2 \underset{\sim}{y}_2 \rangle \end{bmatrix}, \quad (\text{III } 3\cdot 8)$$

which corresponds to the covariance matrix C of Ch. II §6.

The explicit form of R is found from (3.3) to be

$$R = \begin{bmatrix} 1 & 0 & c & -s \\ 0 & 1 & s & c \\ c & s & 1 & 0 \\ -s & c & 0 & 1 \end{bmatrix}. \quad (\text{III } 3\cdot 9)$$

In order to generalize (II 6·1) to the present case we must invert R. After a straight-forward computation we obtain

$$R^{-1} = (1-c^2-s^2)^{-1} \begin{bmatrix} 1 & 0 & -c & s \\ 0 & 1 & -s & -c \\ -c & -s & 1 & 0 \\ s & -c & 0 & 1 \end{bmatrix}. \quad (\text{III } 3\cdot 10)$$

On using (3·7) - (3·10), one finds by analogy with (II 6·7), after some routine algebra, that the transition probabilities are given by

$$P(\alpha_1\alpha_2|\alpha_1'\alpha_2';x) = [2\pi(\theta-1)]^{-1}$$

$$\cdot \exp\left\{-\frac{\theta}{2(\theta-1)}\left[\left(\alpha_1-\frac{c}{\theta}\alpha_1'+\frac{s}{\theta}\alpha_2'\right)^2+\left(\alpha_2-\frac{s}{\theta}\alpha_1'-\frac{c}{\theta}\alpha_2'\right)^2\right.\right.$$

$$\left.\left.+\frac{1}{\theta}\left(1-\frac{c^2}{\theta}-\frac{s^2}{\theta}\right)\left(\alpha_1'^2+\alpha_2'^2\right)\right]\right\},$$

(III 3·11)

Where we have set

$$2-c^2-s^2 \equiv \theta. \qquad \text{(III 3·12)}$$

One may verify, by using the representation

$$\delta(t) = \lim_{n\to\infty}\left(\frac{n}{\pi}\right)^{\frac{1}{2}}\exp[-nt^2]$$

(cf. Lighthill, 1958 p.17 ex. 6), that

$$\lim_{x\to 0+} P(\alpha_1\alpha_2|\alpha_1'\alpha_2';x) = \delta(\alpha_1-\alpha_1')\delta(\alpha_2-\alpha_2'), \qquad \text{(III 3·13)}$$

as we should expect. Moreover, we have also the 'Time - reversal condition'

$$W(\alpha_1\alpha_2)P(\alpha_1\alpha_2|\alpha_1'\alpha_2';x) = W(\alpha_1'\alpha_2')P(\alpha_1'\alpha_2'|\alpha_1\alpha_2;-x), \qquad \text{(III 3·14)}$$

As may be checked directly from (3.5), (3.7) and (3.11).

§4 We may now return to the problem of generalizing (II 6·13). Let us take the vector, ξ, of (II 6·1) to be

$$\xi = \mathfrak{x} \equiv (\hbar\beta/2)^{\frac{1}{2}}(1,0,1,0 \cdots 1,0), \qquad (\text{III } 4\cdot1)$$

where $\mathfrak{x}$ has $2N$ components. Then we obtain from (2·2) and (3·6), by analogy with (II 6·1), (II 6·11),

$$Q(N,L) = e^{-\frac{1}{2}\hbar\beta N} \int\cdots\int_{0<x_1<\cdots<x_N<L} dx_1 \cdots dx_N$$

$$\cdot \left\langle \exp\{(\mathfrak{x},Y)\} \right\rangle_{\rho(Y)} \prod_{j=1}^{N-1} (1-\phi(x_{j+1}-x_j)) \cdot \qquad (\text{III } 4\cdot2)$$

Finally, by carrying out exactly the same procedure as that leading from (II 6·11) to (II 6·13), we reach the result

$$I_N(p) = p^{-2} e^{-\frac{1}{2}\hbar\beta N} \left\langle \exp\{(\mathfrak{x},Y)\} \right\rangle_{\tilde{\rho}(Y,p)}, \qquad (\text{III } 4\cdot3)$$

where

$$\tilde{\rho}(Y,p) \equiv W(\underset{\sim}{y}_1) \prod_{j=1}^{N-1} \int_a^\infty dr_j\, e^{-pr_j} P(\underset{\sim}{y}_j | \underset{\sim}{y}_{j+1}; r_j) \qquad (\text{III } 4\cdot4)$$

and we have set $x_{j+1} - x_j$ equal to r_j. The explicit expression for $\tilde{\rho}(Y)$ may be found by substituting (3.11) into (4·4).

§5 The next step towards determining $\Pi(z)$ should be, following Kac (1959), to express the Laplace transform of $\Xi(z,L)$ as an eigen-function expansion. This step is problematical in the present case because it does not seem possible to introduce a Hilbert - Schmidt kernel into the calculation. The symmetry property

$$W(\eta_1)P(\eta_1|\eta_2;x) = W(\eta_2)P(\eta_2|\eta_1;x),$$

valid for the Ornstein - Uhlenbeck process (used by Kac), is not true of the functions, $W(\underset{\sim}{\eta}_1)P(\underset{\sim}{\eta}_1|\underset{\sim}{\eta}_2;x)$, considered in this chapter; it was precisely this symmentry in η_1, η_2 that allowed the construction of a symmetric kernel.

We may, however, define a <u>positive</u> kernel by

$$K_p(\alpha_1\alpha_2|\alpha_1'\alpha_2') \equiv \int_a^\infty dx\, e^{-px} \cdot P(\alpha_1\alpha_2|\alpha_1'\alpha_2';x)\exp\{q(\alpha_1'+\alpha_1)\}, \qquad (\text{III } 5\cdot1)$$

where

$$q \equiv \left(\tfrac{1}{2}h\beta\right)^{\frac{1}{2}} . \qquad (\text{III } 5\cdot2)$$

When p is positive the kernel (5·1) is also positive and it follows from the theorem of Jentzsch (1912), quoted in II § 3 in connection with Van Hove's work, that K_p possesses a simple eigenvalue which is positive and exceeds the real parts of all other eigenvalues.

In terms of the kernel K_p, we have at once from (4·3) the relation

$$I(N,p) = p^{-2}\exp(-q^2N)\int_0^\infty\int_0^\infty\int_0^\infty\int_0^\infty dr\,ds\,du\,dv$$
$$\cdot W(rs)\,K_p^{(N-1)}(rs|uv)\exp[q(r+u)], \qquad (\text{III } 5\cdot3)$$

where rs, uv, are the components of two column vectors α, defined in (3·5), and q is defined by (5·2).

Since the potential (2·1) is stable (in the sense of I § 4), it follows from (I 6·2) and (I 6·3) that the Laplace transform of $\Xi(z,L)$ exists for all sufficiently large p (depending on z). Moreover, the sequence of partial sums

$$S_m \equiv \sum_{j=1}^{m} e^{-pL} z^j Q(j,L)$$

converges uniformly for all positive L, as may be seen by applying Dini's theorem (cf. Apostol, 1957, p. 425 ex 13.7(a))

to the functions S_m, and hence we have (cf. Titchmarsh, 1939, p 45)

$$\Upsilon(z,p) \equiv \int_0^\infty dL\, e^{-pL}\, \Xi(z,L)$$

$$= p^{-1} + \sum_{N=1}^{\infty} z^N I_N(p), \quad (\text{III } 5\cdot4)$$

for all sufficiently large p, where we have used (5·4) to define $\Upsilon(z,p)$. On substituting for $I_N(p)$ from (5·3), we obtain

$$\Upsilon(z,p) = p^{-1} + p^{-2} z e^{-q^2} \Big\{ 1 + \sum_{N=2}^{\infty} \left(z e^{-q^2}\right)^{N-1} \cdot \int_{-\infty}^{\infty}\int\int\int\int dr\,ds\,du\,dv\, W(rs)\, K_p^{(N-1)}(rs|uv)\, e^{q(r+u)} \Big\}. \quad (\text{III } 5\cdot5)$$

As we mentioned in paragraph 1 of this chapter, the equation of state may be determined implicitly from (5.5) only if an assumption is made about K_p. Despite the asymmetry of K_p, it is possible that it may be expanded in the form

$$K_p(rs|uv) = \sum_{l=1}^{\infty} \lambda_l(p)\, \chi_l^*(rs,p)\, \psi_l(uv,p), \quad (\text{III } 5\cdot6)$$

where the λ_l are eigenvalues, χ_l, ψ_l are respectively the corresponding left and right eigenfunctions and the asterisk denotes complex conjugates. If, in addition, the pairs of functions χ_j, ψ_l were orthonormal, we should obtain from (5·6) and (5·5) the result

$$\Upsilon(z,p) = p^{-1} + p^{-2} z e^{-q^2} \sum_{l=1}^{\infty} \cdot \left\{ \int_{-\infty}^{\infty} dr\, ds\, W(rs)\, e^{qr} \right\}^2 \left\{ 1 - z e^{-q^2} \lambda_l(p) \right\}^{-1} \qquad (\text{III } 5\cdot 7)$$

(cf. Kac, 1959, eq. (6·2), except that Kac omits the term p^{-1} because of his definition of Ξ). By an argument formally identical to that by which we obtained (II 6·18) we now find that the equation of state is given implicitly by the condition

$$\lambda_1 [\pi(z)] = z^{-1} e^{q^2}, \qquad (\text{III } 5\cdot 8)$$

where the positive eigenvalue λ_1 exceeds the real parts of all other eigenvalues of K_p.

Evidently, it is not worth trying to continue the present calculation unless we can establish the validity of (5.6), which we cannot see how to do. This obstacle to further progress suggests that one should start by introducing as the pair potential the autocovariance of an arbitrary ℓ-dimensional Markov process, and then try to choose the parameters (including ℓ) characterizing this process, so that a symmetric kernel was obtained.

REFERENCES

Apostol (1957) Mathematical Analysis, (Addison Wesley Publishing Co. Inc., Reading, Mass.)

Doob (1944) Ann. Am. Stat. 15, 229;

Goertzel & Tralli (1960), Some Mathematical Methods of Physics, (McGraw - Hill Book Co. Inc.);

Jentzsch (1912) Journal for Math. 141, 235;

Kac (1959), Phys. Fluids 2, 8;

Lebowitz & Penrose (1966) J. Math. Phys. 7, 98;

Lighthill (1958), Introduction to Fourier, Analysis & Generalized Functions. (Cambridge University Press).

C H A P T E R IV

The Yang-Lee Distribution of Zeros of a Classical One-dimensional System

(By O.Penrose and J.S.N.Elvey)

ABSTRACT

A classical one-dimensional continuum system of particles with hard cores and nearest-neighbour forces is considered. It is proved that the pressure at constant absolute temperature $(k\beta)^{-1}$ (> 0) and complex fugacity, z, is equal to $\Pi_{max}(\beta, z)$, the branch of largest real part of the complete analytic function, $\Pi(\beta, z)$, with branches $\Pi_e(\beta, z)$, obtained by analytic continuation of the equation of state for positive β, z. It is proved, further, that $\lambda_{max}(z)$ Max_e $[\text{Rl}\, \Pi_e(z)]$ exists and is subharmonic throughout the z-plane, and that the regions where λ_{max} is harmonic become free from zeros of the grand partition function for all sufficiently large values of L, the length of the container. On this basis the set, C, of limit points of zeros of the grand partition function, is shown to consist of arcs and its complement, C', is shown to be simply connected. The arcs C are determined for a system of hard rods. Various generalizations of this work are discussed.

I. Introduction

Yang and Lee have shown[1,2] how the possible occurrence of phase transitions in a classical system of particles can be related to the behaviour of the zeros of the grand partition function Ξ in the complex plane of the fugacity variable z, in the limit where the size of the system becomes infinite. In this paper we shall consider one-dimensional continuum systems only, and we shall denote the grand partition function for such a system at absolute temperature $(k\beta)^{-1}$ and fugacity z on a line of length L by $\Xi(z,L)$ (eqn (5)). Until §XII, we shall treat β as a (possibly complex) constant, and therefore suppress the dependence of Ξ on β. A point z_o in the complex z-plane will be called a limit point of zeros of Ξ when the following condition is satisfied: for every neighbourhood $\mathcal{N}$ of z_o and every number K, there exists a number $L > K$ and a z in $\mathcal{N}$ such that $\Xi(\beta,z,L) = 0$.

Under the assumption that the set C comprising all the limit points of zeros of Ξ is a system of curves in the complex z-plane, the Yang-Lee theory shows[1,2] that phase transitions can occur only at those values of z where C meets the real positive z-axis.

Recently, Hemmer and Hauge have published systems of curves C for some one-dimensional models[3] and for a gas obeying van der Waals' equation of state.[4] From the equation of state one can determine

$$\mathcal{J}(\beta,z) \equiv \lim_{L\to\infty} L^{-1} \log \Xi(z,L) \qquad (1)$$

when z and β are real and positive. Their method consists of continuing $\mathcal{J}(z)$ analytically into the complex z-plane, cut in accordance with the condition that Rl $\mathcal{J}(\beta,z)$ must be continuous for all z, β being fixed and positive. The curves C are identified with these cuts. However, this procedure does not yield a unique set of curves. To show this, let us consider the system of curves C_1 obtained by replacing any arc XY of C by a simple closed curve G, which encloses no part of C except the arc XY, and does not meet the real positive z-axis. Outside G the function corresponding to $\mathcal{J}(\beta,z)$, which we shall denote by $\mathcal{J}_1(z)$, may be found as before by analytic continuation from the real, positive z-axis. Inside G the real part of an analytic function $\mathcal{J}(z)$ may be determined by solving Laplace's equation in two dimensions, subject to the boundary condition that Rl $\mathcal{J}_1(z)$ is continuous across G. The imaginary part of $\mathcal{J}_1(z)$ inside G is then determined (up to a constant) by the Cauchy-Riemann equations. Thus the system C_1 also satisfies Hemmer and Hauge's condition.[5]

A second condition employed by Hauge and Hemmer, based on the total 'measure' of the set of limit points, also fails to distinguish between C and C_1. For, equation (74)

of the present paper shows that, when such a measure can be calculated for any arc, say XY, of C, it depends only on the end points X, Y of this arc.

The purpose of this work is to propose a prescription for determining C uniquely from the equation of state. Our proposed prescription is to construct, by analytic continuation, the complete analytic function, (C.A.F.) $\overline{\Pi}(z)$ that is equal to $\Pi(z)$ for real positive z (& β), and then to take $\Pi(z)$ to be the branch of $\overline{\Pi}(z)$ having largest real part (when this branch is unique and regular). The set C would then comprise all points at which (a) two or more regular branches of $\overline{\Pi}$ have equal real parts, larger than those of all other branches; or (b) the unique branch of largest real part has a branch point; or (c) $\overline{\Pi}(z)$ is not defined at all. In the present paper we shall justify this prescription for the special case of a one-dimensional continuum system with nearest-neighbour interactions by proving the following theorems.

We define[5] $\lambda_{max}(z)$ to be the supremum of the real parts of the branches of $\overline{\Pi}(z)$. We shall show that $\lambda_{max}(z)$ exists for all z. When there is a unique branch of $\overline{\Pi}(z)$, regular near z and having real part $\lambda_{max}(z)$, we denote this branch by $\overline{\Pi}_{max}(z)$.

Theorem I

If $\overline{\Pi}_{max}(\mathcal{Z})$ exists then

(1) $\lim_{L\to\infty} L^{-1} \log \widehat{\Xi}(\mathcal{Z}, L) = \overline{\Pi}_{max}(\mathcal{Z})$

(2) $\mathcal{Z}$ is not a point of C.

Theorem II

The function $\lambda_{max}(\mathcal{Z})$ is subharmonic throughout the $\mathcal{Z}$-plane.

Theorem III

The set of points $\mathcal{Z}$ at which $\lambda_{max}(\mathcal{Z})$ is harmonic is simply connected.

Theorem IV

The set S of points $\mathcal{Z}$ at which $\lambda_{max}(\mathcal{Z})$ is not harmonic consists of arcs and their limit points.

Theorem V

C = S

In section XIV these theorems are used to determine C for a system of hard rods. Finally, in section XV we discuss the possibilities of obtaining various generalizations of Theorems I-V

II. Preliminaries

We consider a classical one-dimensional system of particles free to move on a line of length L. It is assumed that there are two-body forces only, with interaction potential

$$u(r) = \begin{cases} +\infty, & r < a \\ \phi(r), & a \leq r \leq 2a \\ 0, & 2a < r \end{cases} \qquad (2)$$

so that only nearest neighbours can interact. The function $\phi(r)$ is assumed to be bounded, Riemann-integrable and piecewise continuous.

The configurational integral for a classical n-particle system is

$$Q_n(L) \equiv \frac{1}{n!} \int_0^L \cdots \int dx_1 \cdots dx_n \exp\{-\beta U_n(x_1 \cdots x_n)\} \qquad (3)$$

where $U_n(x_1 \ldots x_n)$ means the total potential energy of n particles at $x_1 \ldots x_n$. By virtue of (2) one can simplify (3) by using the total symmetry of $U(x_1 \ldots x_n)$ in $x_1 \ldots x_n$, and specifying once and for all a particular ordering of the particles. One then obtains (for $n \geq 1$)

$$Q_n(L) = \int \cdots \int_{0<x_1<x_2 \cdots < x_n < L} \prod_{t=1}^{n-1} \exp\{-\beta u(x_{t+1} - x_t)\} \qquad (4)$$

The grand partition function is defined for all z as

$$\Xi(z,L) \equiv 1 + \sum_{n=1}^{\infty} z^n Q_n(L) \tag{5}$$

III. The Laplace transform of Ξ

It was shown by Takahasi[6] that the Laplace transform of the configurational integral for the system considered here can be evaluated in a simple way. Here we shall take advantage of the further simplification that can be obtained[7] by using instead the Laplace transform of the grand partition function, which is defined by

$$\Upsilon(z,p) \equiv \int_0^{\infty} dL\, e^{-pL}\, \Xi(z,L) \tag{6}$$

for all values of z and p such that the integral converges. We shall show later (§ VI) how to extend this definition to all values of z and p.

To study the convergence of the integral in (6) we note that (2) and (4) imply

$$Q_n(L) \leq \frac{L^n}{n!} \exp\{(n-1)\beta u_{min}\}, \tag{7}$$

where u_{min} is the greatest lower bound of the function u(r). Hence we have from (5)

$$|\Xi(z,L)| \leq \exp\{|z| L e^{-\beta u_{min}} + \beta u_{min}\}. \tag{8}$$

For all z, therefore, the integral in (6) converges absolutely to an analytic function of p throughout the region of the complex p-place defined by

$$\lambda > |z|\, e^{-\beta u_{min}} \tag{9}$$

where $p \equiv \lambda + i\mu$.

IV. Inversion of the Laplace Transform

The inversion formula for the Laplace transform (6) is[8]

$$\lim_{\Lambda\to\infty} \int_{c-i\Lambda}^{c+i\Lambda} dp\, e^{pL}\, \Upsilon(z,p) = \frac{1}{2}\left[\Xi(z,L+0)+\Xi(z,L-0)\right] \tag{10}$$

where c is any real number exceeding the abscissa of convergence of (6). The condition of validity for this formula, that

$$\int_0^R dL\, |\Xi(z,L)| < \infty$$

for all finite R, is satisfied here because of (8). Since the series (5) terminates because of the hard core condition in (2), and since $Q_n(L)$ is continuous in L by (4) and (2), the function $\Xi(z,L)$ is continuous in L, so that (10) simplifies to

$$\lim_{\Lambda\to\infty} \int_{c-i\Lambda}^{c+i\Lambda} dp\, e^{pL}\, \Upsilon(z,p) = \Xi(z,L) \ . \tag{11}$$

V. Calculation of $\underline{\gamma}(z,p)$

To calculate $\underline{\gamma}(z,p)$ we substitute (5) into (6), obtaining

$$\underline{\gamma}(z,p) = p^{-1} + \int_0^\infty dL\, e^{-pL} \sum_{n=1}^\infty z^n Q_n(L) . \qquad (12)$$

By Dini's theorem[9] applied to the sequence of functions

$$S_N \equiv \sum_{n=1}^{N} z^n e^{-pL} Q_n(L) ,$$

it can be shown that the series $\sum_{n=1}^{\infty} z^n e^{-pL} Q_n(L)$ is uniformly convergent in L for all $L > 0$; consequently,[10] the summation and integration in (12) may be interchanged, giving

$$\underline{\gamma}(z,p) = p^{-1} + \sum_{n=1}^\infty z^n I_n(p) , \qquad (13)$$

where

$$I_n(p) \equiv \int_0^\infty dL\, e^{-pL} Q_n(L) .$$

Using (4), we can calculate $I_n(p)$, obtaining[11]

$$I_n(p) = \int_0^\infty dx_1\, e^{-x_1 p} \int_{x_1}^\infty dx_2\, e^{-(x_2-x_1)p - \beta u(x_2-x_1)}$$

$$\cdots \int_{x_n}^\infty dL\, e^{-(L-x_n)p} = p^{-2} [\psi(p)]^{n-1} \qquad (14)$$

when $n \geq 1$. The function $\psi(p)$ is defined as

$$\psi(p) \equiv \int_0^\infty dr\, e^{-\beta u(r) - pr} . \tag{15}$$

Substituting (14) into (13) we obtain

$$\Gamma(z,p) = p^{-1} + p^{-2} z \left[1 - z\psi(p)\right]^{-1}, \tag{16}$$

for all p satisfying (9).

VI. Analytic Continuation of $\gamma(z,p)$

Without loss of generality we may assume that $\phi(r)$ has only one discontinuity, say at $r = b$, where $a < b < 2a$. Then, by (15) and (2) $\psi(p)$ may be written as

$$\psi(p) = \int_a^b dr\, e^{-\beta\phi(r) - pr} + \int_b^{2a} dr\, e^{-\beta\phi(r) - pr} + \int_{2a}^\infty dr\, e^{-pr} . \tag{17}$$

Now the function $p^{-1}e^{-2ap}$ coincides with $\int_{2a}^\infty dr\, e^{-pr}$ throughout the half-plane Rl $p > 0$ and is analytic for all p. Therefore, $p^{-1}e^{-2ap}$ is the (unique) analytic continuation of $\int_{2a}^\infty dr\, e^{-pr}$ from the region Rl $p > 0$ into the whole p-plane. Further, when p is finite and r is a point of either of the subintervals $a < r < b$, $b < r < 2a$, the function $e^{-\beta\phi(r) - pr}$ is jointly continuous in p and r (since $\phi(r)$ is bounded, Riemann-integrable,

and continuous in both subintervals), and analytic in p. It follows[12] that each of the first two terms on the right-hand side of (17) is analytic in p for all finite p, and finally, that

$$\psi(p) = \int_a^b dr\, e^{-\beta\phi(r)-pr} + \int_b^{2a} dr\, e^{-\beta\phi(r)-pr} + p^{-1}e^{-2ap} \qquad (18)$$

is the analytic continuation of the right-hand member of (17) into the whole p-plane. The analytic continuation of $\underline{\gamma}(z,p)$ into the whole p-plane is therefore obtained by substituting (18) into (16).

VII. The poles of $\underline{\gamma}(z,p)$

In the next section we shall use the method of residues to estimate the integral in (11) for large L and fixed z. We shall find that the behaviour of this integral is dominated by the contribution from the poles of $\underline{\gamma}(z,p)$ which lie farthest to the right in the p-plane. In the present section we shall show that, with the exception of at most two values of z, the function $\underline{\gamma}(z,p)$ has at least one pole in the p-plane and has a finite number of poles $p_1 \ldots p_k$ (where k depends an z) whose real parts are equal and exceed the real parts of all the other poles. We shall call the poles $p_1 \ldots p_k$ the poles of largest real part (L.R.P.), and we denote their common real part by $\lambda_{max}(z)$. When there is a unique branch of Π, regular near z and having real part λ_{max}, we denote this branch by $\Pi_{max}(z)$.

Equation (16) implies[13] that p is a pole of $\underline{\gamma}(z,p)$ if and only if

$$\psi(p) = z^{-1} . \tag{19}$$

Moreover, this pole is simple if and only if

$$\psi'(p) \equiv \frac{d\psi(p)}{dp} \neq 0 . \tag{20}$$

We shall prove[14] that $\psi(p)$ assumes every possible value in the complex plane, so that $\underline{\gamma}(z,p)$ has at least one pole for all values of z and hence $K \geq 1$. For suppose, to the contrary, that $\psi(p)$ does not take some value a; then $p[\psi(p) - a]$ would be, by (18), an entire function of p of order 1 with no zeros, which therefore would have the form $\exp(Ap + B)$, by Hadamard's factorization theorem, and so we should have

$$\psi(p) = a + p^{-1}e^{Ap+B}$$

, where $A \leq 0$.

Since both $\psi(p)$ and $p^{-1}\exp(Ap + B)$ tend to 0 as p tends to $+\infty$, it follows that $a = 0$, which in our case corresponds to $z = \infty$. This completes the proof.

To show that K is finite we show that for any constant λ_o, the number of poles to right of the line $\lambda \equiv \mathrm{Rl}\ p = \lambda_o$ in the p-plane is finite. First, all of these poles must lie to the left of the line $\lambda = z\, e^{-\beta u_{min}}$

since the integral (6) for $\underline{\gamma}(z,p)$ converges whenever (9) is satisfied. Secondly, the Riemann-Lebesgue lemma[15] implies that the right side of (18) tends to O as $\mu \equiv \mathrm{Im}\, p$ tends to $\pm\infty$ at fixed λ and z, and hence (19) cannot be satisfied for arbitrarily large μ (unless z = O, in which case $\underline{\gamma} = 1/p$). Consequently all the poles of $\underline{\gamma}(z,p)$ whose real parts exceed λ_o lie inside a bounded part of the strip

$$\lambda_o \leq \lambda \leq z\, e^{-\beta u_{min}}$$

By (18), $\underline{\gamma}(z,p)$ is meromorphic in p and can therefore have only a finite number of poles in this bounded region, and a fortiori K must be finite.

VIII. Application of the residue theorem

The estimation of $\Xi(z,L)$ is simplest for values of z such that $\underline{\gamma}(z,p)$ has only one pole of L.P.D. in the p-plane and this pole is simple, having affix $p_1(z)$. Let λ' be any non-vanishing constant less than the real part of the affix of the pole of L.R.P.,

$$\lambda' < \lambda_1, \tag{21}$$

but greater than those of all the other poles, and deform the contour of integration in (11) to lie along the line

$$\lambda = \lambda'$$

indented round the pole of L.R.P. (see fig.2).

Applying the residue theorem, we obtain

$$\Xi(z,L) = e^{p_1(z)L}\{A_1(z) + \mathcal{E}(z,L)\}, \qquad (22)$$

where

$$A_1(z) \equiv \operatorname*{Res}_{p=p_1(z)} \Upsilon(z,p) \qquad (23)$$

and

$$\mathcal{E}(z,L) \equiv \frac{e^{[\lambda'-p_1(z)]L}}{2\pi} \int_{-\infty}^{\infty} d\mu\, e^{i\mu L}\, \Upsilon(z,\lambda'+i\mu). \qquad (24)$$

Substituting from (16) into (24) we obtain

$$\mathcal{E}(z,L) = \frac{e^{(\lambda'-p_1)L}}{2\pi}\left\{\int_{-\infty}^{\infty} d\mu \frac{e^{i\mu L}}{\lambda'+i\mu} + \int_{-\infty}^{\infty} \frac{d\mu\, z\, e^{i\mu L}}{(\lambda+i\mu)^2[1-z\psi(\lambda'+i\mu)]}\right\} \qquad (25)$$

The first integral is equal to $2\pi e^{-\lambda' L}$ if $\lambda' > 0$, and to 0 if $\lambda' < 0$. Since Rl $p_1 > \lambda'$ by (21), the contribution of this first integral to $\mathcal{E}(z,L)$ is either $e^{-p_1 L}$ with Rl $p_1 > 0$, or else zero. In either case, this contribution tends to 0 as L tends to ∞. To estimate the second integral we use the Riemann-Lebesgue lemma[15], which when applied to (16) shows

that $\lim_{|\mu| \to \infty} \psi(\lambda' + i\mu) = 0$. It follows that the second integral in (25) converges absolutely and so has an upper bound which is independent of L. Since Rl $p_1 > \lambda'$, the contribution of this second integral to $\mathcal{E}(z,L)$ also tends to O for large L, so that

$$\lim_{L \to \infty} \mathcal{E}(z,L) = 0 . \qquad (26)$$

Since p_1 is a simple pole, $A_1(z)$ cannot vanish, and it follows from (22) that

$$\lim_{L \to \infty} L^{-1} \log \Xi(z,L) = P_1(z) , \qquad (27)$$

for a suitably chosen branch of the multi-valued function log Ξ (z,L). A definite choise of log Ξ is made in § XIII .

It will be seen that in the next section the conditions under which we have proved (27) are precisely those conditions which are assumed in the statement of theorem I. Consequently, we need not consider the existence or properties of the left member of (27) in any other case.

IX. The Connection between $\Pi(z)$ and the poles of $\underline{\gamma}(z,p)$

In order to prove Theorem I from (27) we must relate $p_1(z)$ to the complete analytic function $\Pi(z)$ obtained by analytic continuation from $\pi(z)$, the function giving the thermodynamic pressure for real positive z.

This relationship is described by the following result:

Lemma 1. The branches of the complete analytic function $\overline{\Pi}(z)$ are the values of p at which $\chi(z,p)$, regarded as a function of p, has poles, and these poles are simple except at the branch points of $\overline{\Pi}(z)$.

Proof. When z is small, $\psi(p)$ must be large near a pole of $\chi(z,p)$. Hence, by (18) either p is small or else it has a large negative real part. For small z, the pole of largest real part is therefore near p = 0. Eqn (18) also implies that $1/\psi(p)$ has a simple zero at p = 0 and hence the functional relation $z = 1/\psi(p)$ may be inverted uniquely, so that for small z there is just one simple pole of largest real part, and this pole, $p_1(z)$, is an analytic function of z, vanishing at z = 0. Applying (1) and (26) we see that

$$\pi(z) = p_1(z) \quad \text{for small positive } z, \tag{28}$$

where

$$\psi(p_1(z)) = 1/z \tag{29}$$

and $p_1(z)$ is small.

From (28) it follows by analytic continuation that

$$\overline{\Pi}(z) = P(z) \tag{30}$$

where P(z) is the complete analytic function one of whose elements is $p_1(z)$ when z is small. From (29), it follows that every branch of $\Pi(z)$ satisfies

$$\psi(\Pi(z)) = 1/z \qquad (31)$$

and therefore, by (19), coincides with a pole of $\underline{\gamma}(p,z)$. Moreover, if $\Pi(z)$ does not have a branch point then the derivative $\psi'(\Pi(z))$ does not vanish, and hence by (20) the pole is simple.

Conversely, if z_o is any point in the Z—plane and p_o is any simple pole of $\underline{\gamma}(z_o,p)$, then we may joint the point p_o to the origin by a continuous path in the p-plane, avoiding the isolated points at which either $\psi(p)$ or $d\psi/dp$ vanishes; under the mapping $\psi(p) = 1/z$ this path has a unique continuous image in the z-plane, one end of which is at the origin, and by continuing the function $p_1(z)$ analytically outwards along this image path we obtain a branch of P(z) taking the value p_o when $z = z_o$. This completes the proof of lemma I.

For any $\ell \leq K(Z)$ we may therefore define the branches $\Pi_1(Z) \ldots \Pi_\ell(Z)$ to have L.R.P. when their common real part equals $\lambda_{max}(Z)$, where $K(Z)$ and $\lambda_{max}(Z)$ are defined in §VII.

Using Lemma I, we can prove a second Lemma, which will be used several times in the sequel.

Lemma II

Two branches of $\Pi(z)$ cannot have equal real parts throughout a domain of values of z.

Proof

Suppose, on the contrary, that two branches, Π_1, Π_2 of $\Pi(z)$ satisfy the condition

$$\mathrm{Rl}\ \Pi_1(z) = \mathrm{Rl}\ \Pi_2(z)$$

for all z in a domain $\mathcal{D}$. Then the Cauchy-Riemann conditions imply that the function $\Pi_1 - \Pi_2$ has a constant value, say $i\omega$, for all z in $\mathcal{D}$, where ω is real. Since each of Π_1, Π_2 satisfies (31), we have

$$\psi\{\Pi_1(z)\} = \psi\{\Pi_1(z) - i\omega\}$$

for all z in $\mathcal{D}$ whence, by analytic continuation,

$$\psi(p) = \psi(p - i\omega)$$

for all p. But this cannot happen, for we have shown in §VII that $\psi(p)$ tends to C as $|\mathrm{Im}\ p|$ tends to ∞. This completes the proof of Lemma II.

X. Proof of Theorem I

Theorem I states that if z' is a point such that $\Pi_{Max}(z')$ exists then

(1) $$\lim_{L\to\infty} L^{-1} \log \Xi(z', L) = \Pi_{max}(z')$$

(2) z' is not a point of C.

The proof of (1) follows at once from Lemma I and equation (27). To prove (2) we show that there is a closed disk $\mathcal{D}_\eta(z)$ of radius η, centred at the point $z = z'$ in the $z-$ plane with the properties

(a) $\Xi(z,L)$ is given by (22) throughout $\mathcal{D}$,

(b) $A_1(z)$ is bounded away from zero throughout $\mathcal{D}$,

(c) $\mathcal{E}(z,L)$ tends uniformly to zero throughout $\mathcal{D}$,

so that for all sufficiently large L there con be no zeros of $\Xi(z,L)$ with z in $\mathcal{D}_\eta(z')$.

By the continuity of all branches of $\Pi(z)$, it is possible to find numbers λ', λ'', ond η such that $\lambda' \neq C$ and

$$\mathrm{Rl}\ \Pi_j(z) < \lambda' < \lambda'' < \mathrm{Rl}\ \Pi_{max}(z) \qquad (32)$$

holds throughout $\mathcal{D}_\eta(z)$ for any branch $\Pi_j(z)$ other than $\Pi_{max}(z)$. We sholl show thot $\mathcal{D}_\eta(z)$ has the properties (a), (b) ond (c). It has

the property (a) because throughout $\mathcal{D}_\eta(z')$ there is, by Lemma I, a unique pole of $\underline{\gamma}(Z,p)$ having largest real part. It has the property (b) because $A_1(Z)$ is the residue of $\underline{\gamma}(Z,p)$ at a simple pole, and is therefore analytic and non-vanishing throughout the closed disk $\mathcal{D}_\eta(z')$.

Finally, to establish (c), we note that λ' defined in (32) satisfies the conditions stated in IX, so that we may estimate $\mathcal{E}(Z,L)$ from (25). It has already been shown in §IX that the contribution to $\mathcal{E}(z,L)$ from the first integral in (24) is $e^{-p_1 L}$ if $\lambda' > 0$ and 0 if $\lambda' < 0$; hence, by lemma I and (32), this contribution tends uniformly to zero throughout $\mathcal{D}_\eta(z')$ for either sign of λ'. To estimate the second integral we use the fact that $\underline{\gamma}(Z,p)$ has no poles when Z is in $\mathcal{D}_\eta(z')$, which implies by (19) that $Z^{-1} - \psi(\lambda' + i\mu)$ cannot vanish if μ is real and Z is in $\mathcal{D}_\eta(z')$. Further, by (18) and the Riemann-Lebesgue lemma, $\psi(\lambda' + i\mu)$ tends to 0 for large $|\mu|$, and consequently, since $\mathcal{D}_\eta(z')$ is closed, the quantity $|Z^{-1} - \psi(\lambda'+i\mu)|$ has a positive lower bound, say α, valid for all Z in $\mathcal{D}_\eta(z')$ and all real μ. The absolute value of the contribution of the second integral in (25) to $\mathcal{E}(Z,L)$ is therefore at most

$$\frac{e^{(\lambda'-\lambda_1)L}}{2\pi\alpha}\int_{-\infty}^{\infty}\frac{d\mu}{|\lambda'+i\mu|^2}$$

where $\lambda_1 \equiv \mathrm{Rl}\, p_1$. By Lemma I and (32), this contribution has the upper bound $(2\lambda' a)^{-1} \exp(\lambda' - \lambda'')L$, and therefore tends uniformly to O as $L \longrightarrow \infty$. This completes the proof of (c), and hence of Theorem I.

In the next three sections we shall establish several general properties of the function $\lambda_{max}(\mathcal{Z})$. Although these properties are of interest in themselves, it will be apparent by the time we embark on the proof of theorem V, that they are essential for the unique determination of C.

XI. Subharmonicity of $\lambda_{max}(\mathcal{Z})$

Theorem II

The function $\lambda_{max}(\mathcal{Z})$ is subharmonic throughout the $\mathcal{Z}$ -plane.

Proof

By virtue of the arguments given in §VII, the function $\lambda_{max}(\mathcal{Z})$ exists and is continuous for all $\mathcal{Z}$. Suppose that z' is any value of $\mathcal{Z}$ and denote by $p_1, \ldots, p_k$ the poles of $\underline{\gamma}(z', p)$ having L.R.P., where the integer K depends on z' but is always finite, (see §VII). Let p_k be any one of these poles and m_k (≥ 1) its multiplicity. Then, by (20), the first non-vanishing derivative of $\psi(p)$ at $p = p_k$ is of order m_k, which shows that m_k must be finite, since $\psi(p)$ is nonconstant. Consequently, by Lemma I and a general theorem on the inversion of power

series[17], there are m_k branches of $\overline{\Pi}(Z)$, all of which take the value p_k at z', and the point z' is an algebraic branch point of order $m_k - 1$ for each of these branches.

We shall now use the following result:[18]

If a complete analytic function has an algebraic branch point of order $n - 1$ $(n \geq 2)$ at the point $z' (\neq \infty)$ then each branch having a branch point at z' may be represented in the form $\Phi\{(Z-Z')^{\frac{1}{n}}\}$, where Φ is meromorphic for all Z in an annular neighbourhood of z'.

By applying this result to the complete analytic function $\overline{\Pi}(Z)$ in an annular neighbourhood of z', we deduce that the function $T_k(Z)$, defined to be the sum of all the branches of $\overline{\Pi}$ which take the value p_k when $Z = z'$, is analytic throughout a closed disk with centre z' and radius r_k, depending on z'. For, each of these branches may be expanded as a series of the form $p_k + \sum_{l=1}^{\infty} c_l t_j^l (Z)$, $j = 1,\ldots,n$, where $t_1 \ldots t_n$ denote the n distinct values of $(Z - z')^{\frac{1}{n}}$. Unless l is an integer multiple of n the sum $\sum_{j=1}^{n} t_j^l (Z)$ is zero and hence the Taylor expansion for T_k contains only integral powers of $(Z - z')$. On setting

$$r_{min} \equiv Min\{r_1, r_2, \ldots, r_K\}, \tag{36}$$

$$\overline{T}(Z) \equiv K^{-1} \sum_{k=1}^{K} m_k^{-1} T_k(Z) \tag{37}$$

we obtain a function $T(z)$, which is analytic throughout the closed disk with centre z' and radius r_{min} and satisfies the condition

$$Rl\, T(z) \leq \lambda_{max}(z), \tag{38}$$

with equality, in particular, at z'. Using (38) and applying the mean value theorem for harmonic functions[19] to Rl $T(z)$, we obtain:

$$\lambda_{max}(z') = Rl\, T(z') = \frac{1}{2\pi}\int_0^{2\pi} d\theta\, Rl\{T(z'+re^{i\theta})\}$$

$$\leq \frac{1}{2\pi}\int_0^{2\pi} d\theta\, \lambda_{max}(z'+re^{i\theta}), \tag{39}$$

for all $r \leq r(z)$. Conditions (35) and (39) imply[20] that $\lambda_{max}(z)$ is sub-harmonic throughout the Z -plane.

Corollary

If $\lambda_{max}(Z)$ is harmonic in a neighbourhood $\mathcal{N}$ then $\overline{\Pi}_{max}(Z)$ exists throughout $\mathcal{N}$.

Proof

Suppose that $\mathcal{N}$ is an open disk with centre z'; then there is a closed disk, say D centred at z', throughout which $\lambda_{max}(Z)$ is harmonic. Therefore[21] there exists a branch, say $\overline{\Pi}_1$, of $\overline{\Pi}$, which is regular and has real part $\lambda_{max}(Z)$ for Z in D.

To complete the proof of this corollary we shall show that, within D, $\overline{\Pi}_1(Z)$ is the only branch of $\overline{\Pi}$ having L.R.P. To see this, consider the function $F(Z) \equiv \mathrm{Rl}\ T(Z) - \lambda_{max}(Z)$. Since $T(Z)$ is analytic (as shown in the proof of Theorem II) and $\lambda_{max}(Z)$ is harmonic within D (by the hypothesis of this corollary) the inequality in (39) becomes an equation. Consequently, $F(Z)$ vanishes for all Z on the boundary of D and hence[22] throughout D. Moreover, $\mathrm{Rl}\ T(Z)$, being the arithmetic mean of the real parts of all branches of $\overline{\Pi}$ having L.R.P. at z' is less than $\lambda_{max}(Z)$ unless each of these branches has real part equal to $\lambda_{max}(Z)$. Therefore, the vanishing of $F(Z)$ entails that two or more branches of $\overline{\Pi}(Z)$ have L.R.P. for all Z in D, and this violates Lemma II. Q.E.D.

XII. The Sets $S_0, S_1, S_2, \ldots$.

One of our aims in this paper is to verify rigorously the assumption made by Yang and Lee (which they verified[2] in the case of a classical lattice gas with purely attractive forces), that the limit points of zeros fall on curves in the Z-plane. To this end we define the following disjoint sets $S_1, S_2, \ldots$ of points in the Z-plane.

For $k = 1,2,3,\ldots$

$Z \in S_k$ if and only if $\Pi(Z)$ has exactly $\underline{k}$ branches of L.R.P. at — all regular . (40)

We also define a set S_o:

$Z \in S_o$ if and only if

<u>either</u> $\Pi(Z)$ has no branch of L.R.P.

<u>or</u> = z is a branch point of Π_{max}.

Evidently the sets $S_o, S_1, S_2 \ldots$ partition the whole Z -plane, so that we have at once

$$S_1' = S_o \cup S_2 \cup S_3 \cup \ldots\ldots, \tag{41}$$

where S_1' means the complement of S_1. It follows from the corollary to theorem II that S_1 may also be defined as the set of all points in the Z -plane at which $\lambda_{max}(Z)$ is harmonic.

As a first step towards showing that C consists of arcs we prove the following theorem;

Theorem III

The set S_1 is simply connected.

Proof

We shall show [23] that every simple closed curve contained in S_1 encloses only points of S_1 .

Let Σ denote any simple, closed curve contained in S_1 and let D denote the domain consisting of Σ and all points interior to Σ . Since $\lambda_{max}(Z) \equiv Rl\,\Pi_{max}(Z)$ is subharmonic (Theorem II) we have the inequality [20] (cf. Rado, 1949, §4.31)

$$\oint_{\Sigma} \frac{\partial}{\partial n} \lambda_{max}\, d\Sigma \geqslant 0 , \tag{42}$$

Where the two sides of (42) are equal if and only if $\lambda_{max}(Z)$ is harmonic throughout D.

But $\Pi_{max}(Z)$ exists in a neighbourhood of every point of Σ (by the corollary to theorem II) and hence, by the Cauchy-Riemann conditions,

$$\oint_{\Sigma} \frac{\partial}{\partial n} \lambda_{max}\, d\Sigma = \oint_{\Sigma} \frac{\partial \mu_{max}}{\partial s}\, d\Sigma = 0 \tag{43}$$

where $\mu_{max} \equiv Im\,\Pi_{max}$; for, $\Pi_{max}(Z)$ must be single-valued because of Lemma II. Hence $\lambda_{max}(Z)$ is harmonic for all Z in D and so (by a second application of Lemma II) $\Pi_{max}(Z)$ exists throughout D, showing that $D \subset S_1$. Q.E.D.

* This proof is due to Penrose

** In this notation n stands for the normal to Σ and hence ds coincides with $d\Sigma$.

Theorem IV

The set S of points z at which $\lambda_{max}(z)$ is not harmonic is a closed system of arcs.

Proof

It follows from (41) and the corollary to Theorem II that the sets S, S_1' are identical. Let z' be the affix of any point of S_2 and denote by p_1, p_2 the two simple poles of $\underline{y}(z,p)$ having L.R.P. It follows from Lemma I that $p_1 = \Pi_1(z)$ and $p_2 = \Pi_2(z)$ where Π_1 and Π_2 are branches of $\Pi(z)$. Since all branches of $\Pi(z)$ are continuous there exists a neighbourhood of z', say $\mathcal{N}$, throughout which $\Pi_1(z)$ and $\Pi_2(z)$ are regular and have larger real parts than any other branch of $\Pi(z)$. For all z within $\mathcal{N}$, Taylor's theorem gives

$$\Pi_1(z) - \Pi_2(z) = p_1 - p_2 + \sum r^{\ell} e^{i\ell\theta} R_{\ell} e^{i\Theta_L} \qquad (44)$$

where

$$re^{i\theta} \equiv z - z' \,, \tag{45}$$

$$R_\ell e^{i\Theta_\ell} \equiv \frac{1}{\ell!}\left\{\left(\frac{d}{dz}\right)^\ell \left[\overline{\Pi}_1(z) - \overline{\Pi}_2(z)\right]\right\}_{z=z'} \tag{46}$$

and M is the order of the first nonvanishing derivative of $(\overline{\Pi}_1 - \overline{\Pi}_2)$ at $z = z'$. The value of M must be finite; for otherwise $\overline{\Pi}_1(z) - \overline{\Pi}_2(z)$ would be equal to the imaginary constant $p_1 - p_2$ throughout $\mathcal{N}$, in violation of Lemma II. Taking the real part of (44) and using (45), (35) and Lemma I, we find the condition for a point of $\mathcal{N}$ to belong to S_2 to be

$$0 = (rR)^M \cos(M\theta + \Theta_M) + o(r^M R^M), \tag{47}$$

where $O(r^M R^M)$ denotes a quantity which tends to zero faster than $r^M R^M$ as r tends to zero. Therefore the points of S_2 within $\mathcal{N}$ form a set of M arcs intersecting at z' at angles of π/M, or a single arc if $M = 1$.

If $z \in S_k$, where $k \geq 3$, and $\overline{\Pi}_1, \ldots, \overline{\Pi}_k$ denote the branches of $\overline{\Pi}$ having L.R.P. at z, then each of the functions $\mathrm{RI}\{\overline{\Pi}_i - \overline{\Pi}_j\}$, $1 \leq i < j \leq k$, must vanish at all points of S_k

in a neighbourhood of Z . We conclude, from an argument similar to that used in considering S_2, that for $k \geq 3$ S_k consists at most of arcs and isolated points.

Since ψ (p) is meromorphic and nonconstant, it follows from (20) and Lemma I that the set S_o consists of isolated points. Moreover, since S_1 is simply connected (Theorem III) the complement, S_1', of S_1 cannot contain isolated points. Finally, by the corollary to Theorem II, the limit points of S_k for $k \geq 2$ cannot belong to S_1; for $\lambda_{max}(Z)$ is not harmonic at these points. This completes the proof of Theorem IV. We have also shown that S is a closed set.

XIII. Determination of C

We are now in a position to determine the set C of limit points of zeros of $\underline{\underline{\Xi}}(Z,L)$; this determination is accomplished in the following theorem.

Theorem V

$$C = S.$$

Proof

Define the set S^- to consist of all points Z interior to exactly one arc of S. Suppose that Z_Y is the affix of any point Y of an arc

σ of S^-. Then one can find a closed disk $\mathcal{D}_\delta(Y)$ with centre z_Y and radius δ, containing only points of σ and points of S_1, and split by σ into two disjoint regions, say R_1, R_2. Further, denote by $K_r(Y)$ the circle with centre z_Y and radius r ($< \delta$), and by z_A, z_B the affixes of the distinct points A, B in which K_r cuts σ.

We shall show now that $\overline{\Pi}_{max}(z)$ may be represented in the form

$$\overline{\Pi}_{max}(z) = \begin{cases} \overline{\Pi}_1(z), & \text{if } z \in R_1 \\ \overline{\Pi}_2(z), & \text{if } z \in R_2, \end{cases} \tag{48}$$

where $\overline{\Pi}_1$, $\overline{\Pi}_2$ are distinct branches of $\overline{\Pi}$, regular throughout $\mathcal{D}$ and satisfying the condition

$$\mathrm{Re}\,\overline{\Pi}_1(z) = \mathrm{Re}\,\overline{\Pi}_2(z) = \lambda_{max}(z) \tag{49}$$

when z is on σ.

To see this, suppose that σ is an arc of S_k; then there exists exactly k distinct branches of $\overline{\Pi}$ having real part $\lambda_{max}(z)$ at points of σ, and all regular throughout $\mathcal{D}$. Since R_1, R_2 are subsets of S_1, we may define $\overline{\Pi}_1$ to be the unique branch of $\overline{\Pi}$ having L.R.P. within R_1. If $\overline{\Pi}_1$ had the same property with R_2 and $\overline{\Pi}_2$ were any

other branch of $\overline{\Pi}$ having real part λ_{max} on σ, then the integral mean of the harmonic function $Re(\overline{\Pi}_1 - \overline{\Pi}_2)$ over the boundary of $\mathcal{D}$ would be positive and so different from the value (zero) of $Re(\overline{\Pi}_1 - \overline{\Pi}_2)$ at the centre of $\mathcal{D}$, in violation of the mean value theorem for harmonic functions.[18] Hence $\overline{\Pi}_1$ cannot have L.R.P. within R_2 and we may suppose (after relabelling the branches if necessary) that $\overline{\Pi}_2$ has L.R.P. throughout R_2, thus justifying (51).

Let us choose R_1 to lie to the left and R_2 to the right of σ when σ has the sense of the directed segment AB. We shall prove Theorem V by obtaining bounds on the function $L^{-1}N_r(L)$ for large L, where $N_r(L)$ denotes the number of zeros of $\overline{\Xi}(z,L)$ inside or on K_r. To establish these bounds we shall apply the argument principle, but before this can be done, a definite branch of the multivalued function $\arg \overline{\Xi}(z,L)$ must be chosen. By virtue of (22), which holds at all points of S_1, we may choose the branch

$$Arg\, \overline{\Xi}(z,L) \equiv \mu_{max}(z)L + Arg\, A_{max}(z) + o(1), \quad (50)$$

where $\mu_{max}(z)$ is defined to be the imaginary part of $\overline{\Pi}_{max}(z)$ and, in view of Lemma I, $A_{max}(z)$ equals $A_1(z)$ as defined in (23). The function $Arg\, A_{max}(z)$ is defined so that it varies continuously as z varies on $K_r \cap \sigma'$, σ' being the complement of σ.

Finally, the term O(1) in (50) denotes a quantity which, for each Z, tends to O as L tends to ∞.

We now define a broken contour, Γ, consisting of two segments $P'Q'$, $P''Q''$ of K_r such that:

(i) $P'Q'$, $P''Q''$ are on opposite sides of σ;

(ii) Each of $P'Q'$, $P''Q''$ has the same sense as AB;

(iii) Each of the straight lines $P'P''$, $Q'Q''$ has length $\eta > 0$

(See Figure 3).

It follows from (22) and the fact that, for Z in any close subset of S_1, $\mathcal{E}(Z,L)$ tends uniformly to O as L tends to ∞ (see the proof of Theorem I(2), §X for the reasoning) that the term O(1) in (50) is uniform in Z on Γ. Further, we define a function $\Delta_\Gamma(L;\eta)$ by

$$\Delta_\Gamma(L;\eta) \equiv \left(\operatorname{Arg} \Xi_{P'} - \operatorname{Arg} \Xi_{Q'}\right) + \left(\operatorname{Arg} \Xi_{Q''} - \operatorname{Arg} \Xi_{P''}\right), \quad (51)$$

where (for $X = P', P'', Q', Q''$) $\operatorname{Arg} \Xi_X$ means the numerical value of the right side of (50) at Z_X. To complete the preliminaries to the use of the argument principle, we introduce the circle K_1 with centre Z_Y and radius r_1, where

$$0 < r < r_1 < \delta \quad (52)$$

In order to obtain an upper bound on $\Delta_T(L;\eta)$, we consider separately the contributions from zeros of Ξ (a) inside or on K_1, (b) outside K_1. Denoting by N the total number of zeros of Ξ (as before) and by N_1 the number inside or on K_1. we obtain the bound:

$$\Delta_T(L;\eta) < 2\pi N_1 + (N-N_1)(\theta_P + \theta_Q), \qquad (53)$$

where,
(for X = P or Q),

θ_X means the greatest angle subtended by the chord X'X'' at points outside K_1 (see Figure 3). The simplest way to derive the bound is to consider the contribution of one particular zero, say z', of Ξ, taking the axis from which Arg Ξ is measured to pass through this zero. Since $(z - z')$ is a factor of $\Xi(z,L)$, it follows from (54) that the numbers 2π, $(\phi_Q + \phi_Q)$, constitute upper bounds on the contribution to $\Delta_{T-1}(L;\eta)$ from a zero z' in the regions (a), (b), respectively. By this method, all zeros of Ξ are counted according to their multiplicities. The angles θ_X depend on η ; in particular, we have

$$\lim_{\eta \to 0} \theta_X(\eta) = 0 \qquad (54)$$

On dividing both sides of (53) by L and then letting L tend to ∞, we obtain

$$\lim_{L\to\infty} L^{-1}\Delta_\Gamma(L;\eta) \leqslant \liminf\left[2\pi L^{-1}N_1 + L^{-1}(N-N_1)(\theta_P+\theta_Q)\right]. \tag{55}$$

Let $\lim_{\eta\to 0}$ mean that η tends to O while all of the conditions (i)-(iii) on Γ^{-1} are maintained. Then we obtain from (57) and (58) the inequality

$$\lim_{\eta\to 0}\lim_{L\to\infty} L^{-1}\Delta_\Gamma(L;\eta) \leqslant 2\pi \liminf_{L\to\infty} L^{-1}N_1(L). \tag{56}$$

For all Z in D we define

$$\Delta\Pi_{Max}(Z) \equiv \Pi_1(Z) - \Pi_2(Z) \quad . \tag{57}$$

According to (48), $(\partial/\partial n)$Rl $\Delta\Pi_{max}(Z)$ is nonnegative, where $(\partial/\partial n)$ denotes differentiation along the normal to σ drawn from R_2 into R_1. Taking this normal as the Rl Z —axis of a right-handed pair of axes, we obtain from the Cauchy-Riemann equations

$$\frac{\partial}{\partial s}\,\mathrm{Im}\,\Delta\Pi_{max}(Z) \geqslant 0, \tag{58}$$

where $\partial/\partial s$ denotes differentiation along σ in the direction BA. Since Rl $\Delta\Pi_{max}(Z)$ vanishes along σ, the left side of (58) can

vanish only at isolated points (otherwise $\Delta\Pi_{max}(z) \equiv 0$ in D, in violation of Lemma II). Consequently, the left side of (56), which by (50), (51) and (57) equals $\mathrm{Im}\{\Delta\Pi_{max}(z_A) - \Delta\Pi_{max}(z_B)$, is positive for all positive values of r_1 and hence z_γ is a limit point of zeros of $\Xi(z,L)$.

Moreover, z_γ may be chosen arbitrarily on σ and σ itself denotes any arc of S^-, so we have shown that S^- is a subset of C. Since C is closed it follows that the closure of S^- is also a subset of C. Further, in view of Theorem IV and the definition of S^-, the closure of S^- coincides with S, so that S is a subset of C. We can also show, however, that C is a subset of S; for theorem I(2) implies that C is a subset of S_1', and the result proved immediately after (41) shows that S_1' coincides with S. Since C and S are subsets of each other, it follows that

$$C = S, \tag{59}$$

which is the statement of theorem V.

XIV. The Hard Rod System

In this section the set of arcs C is determined uniquely for a system of hard rods. Here the interaction potential is

$$U(r) = \begin{cases} +\infty, & r < 1 \\ 0, & r \geq 1 \end{cases} \tag{60}$$

For this model we have, from (18),

$$\psi_{h.r}(p) = p^{-1}e^{-p}, \tag{61}$$

so that p is a pole of $\gamma_{h.r.}(Z, p)$ if and only if

$$pe^{p} = Z . \tag{62}$$

The argument given immediately after (20) implies that there is at least one value of p satisfying (62) for each value of Z. The arcs C will be determined by use of Theorems I - V in conjunction with the following properties of $\gamma_{h.r.}$:

(i) If $\gamma_{h.r.}(Z, p)$ has two poles of L.R.P., both simple, then Z is real;

(ii) If $Z > -e^{-1}$ then $\gamma_{h.r.}(Z, p)$ has exactly one pole of L.R.P., and this pole is simple.

(iii) If $Z < -e^{-1}$ then $\gamma_{h.r.}(Z, p)$ has exactly two poles of L.R.P., both simple.

Proof of (i)

Taking the modulus of both sides of (62) we see that

$p \equiv \lambda + i\mu$ is a pole of $\mathcal{P}_{h.r.}(z,p)$ if and only if

$$\mu^2 = |z|^2 e^{-2\lambda} - \lambda^2 \quad . \tag{63}$$

If two distinct simple poles p_1, p_2 have L.F.P. then

$$\left.\begin{aligned} \lambda_1 &= \lambda_2 = \lambda_{max} \\ \mu_1 &\neq \mu_2 \end{aligned}\right\} , \tag{64}$$

$$p_1 e^{p_1} = p_2 e^{p_2} = z \quad . \tag{65}$$

Conditions (63)-(65) imply that

$$\mu_2 = -\mu_1 , \tag{66}$$

whence

$$p_1 = \bar{p}_2 \tag{67}$$

and $$z = p_1 e^{p_1} = \bar{p}_2 e^{\bar{p}_2} = \bar{z} \tag{68}$$

That is, z is real.

The branch points of p(z) may be found, from the condition (dz/dp) = O, applied to the function (74), to be $z_1 = O$, $z_2 = -e^{-1}$, both of which are real.

When $Z = 0$, it follows at once from (5) and (6) that $\underline{\gamma}(Z, p)$ has exactly one pole, at $p = 0$, and that this pole is simple. Consequently we deduce from (20) and (65) that all of the poles of $\underline{\gamma}(Z, p)$ are simple except when $Z = -e^{-1}$. Consequently, when $Z \neq -e^{-1}$ every solution of (74) corresponds to a simple pole $\underline{\gamma}$.

Proof of (ii)

When $Z > 0$ there is always a unique $p > 0$ which satisfies (65), and this is the unique simple pole of L.R.P. since, when $\lambda > 0$, the maximum value of λ for which $(\lambda^2 + \mu^2)^{\frac{1}{2}} e^{\lambda} = Z$ (= const. > 0) occurs when $\mu = 0$. Further, when

$$-e^{-1} < Z \leq 0 \tag{69}$$

there is a unique solution, p, of (62) which is real and > -1, and once again, this value of p corresponds to the unique simple pole of $\underline{\gamma}$ having L.R.P.

To see this, suppose that

$$\left.\begin{aligned} -1 < \lambda \\ \mu \neq 0 \end{aligned}\right\}, \tag{70}$$

and that Z (= $(\lambda + i\mu)\exp\{\lambda + i\mu\}$) is real (so that $\lambda = -\mu \cot \mu$); then we obtain, by substituting into (62)

$$Z = -\mu \operatorname{cosec} \mu \, e^{-\mu \cot \mu} . \qquad (71)$$

To make Z negative, we must take only those values of μ for which $\mu \operatorname{cosec} \mu$ is positive, that is

$$2k\pi < |\mu| < (2k+1)\pi , \qquad (72)$$

$k = 0,1,2,\ldots$. But since $|\mu \operatorname{cosec} \mu|$ is an increasing function of $|\mu|$ and tends to 1 as $|\mu|$ tends to 0, (74) and (75) imply that Z is less than $-e^{-1}$, which is incompatible with our initial assumption (72). Thus statement (ii) is proved.

Proof of (iii)

When $Z < -e^{-1}$, equation (62) has no real roots and it follows from (66) that there are for each λ precisely two roots, which are complex conjugates of each other. Moreover, by (20) these roots correspond to simple poles of $\underline{\gamma}_{h.r.}$; by the argument of §VII, $\underline{\gamma}_{h.r.}(z,p)$ has a finite number of poles of L.R.P. Therefore for all real Z less than $-e^{-1}$, $\underline{\gamma}_{h.r.}$ has exactly two poles of L.R.P., both simple, and they are complex conjugates of one another. From theorems $\underline{I}$ and $\underline{V}$ we now find at once that C is the semi-infinite straight line

$$-\infty < Z \leq -e^{-1} . \qquad (73)$$

This confirms the result obtained by Hauge and Hemmer using a non-rigorous method.

XV. Discussion

The problem of determining the Yang-Lee zero distribution uniquely has been considered by Byckling,[25] whose criteria are less explicit than ours but not in conflict with them.

The fact that $\mathrm{Rl}\ \pi(\beta, z)$ is equal to the abscissa of convergence of the Laplace transform of $\Xi(\beta, z, L)$ when β and z are positive, seems to have been used first by Kac[27] to calculate the equation of state of a system of hard rods with exponentially decreasing attractive forces. This property is also valid[28] for three-dimensional systems when the Laplace transform of $\Xi(\beta, z, V)$ is taken with respect to the volume, V. Our work generalizes this property to some one-dimensional systems at complex fugacities.

Recently it has been shown[29] that, by redefining the configuration space of the system to consist of only those configurations in which no pair of particles overlap, one can prove analogues, referring to the complex β-plane, of the theorems of Yang and Lee.[12] From this it follows that the relation $\psi(\beta, p) = z^{-1}$ which, as we have shown in §IX, is satisfied by the complete analytic function $\Pi(z)$, may equally well be used to generate an analytic function $P(\beta)$, for a fixed value z' of z. It seems likely that all of the theorems we have proved for $\Pi(z)$ can also be established for the C.A.F. obtained by analytic continuation in the

β-plane from $\pi(\beta,z)$. We shall not attempt this task here since no new ideas are involved. The only difficulties in this process requiring further investigation are: (1) to verify that the branch points of $P(\beta)$ form an isolated set and to locate these points in the β-plane, (so that the analogue of Lemma I may be proved); (2) to modify the proof of theorem V to take account of the fact that, even for finite L, $\Xi(\beta,L)$ has in general infinitely many zeros in the β-plane.

The well-known formula[26]

$$g(\tau) = (2\pi i)^{-1} \frac{\partial}{\partial \tau} \Delta \Pi_{max}(Z(\tau)) \qquad (74)$$

for the density of limit points of zeros of Ξ (per unit length of the container of the system) at a point of arc length τ on S^-, can be derived from our analysis if it can be shown that (56) holds with equality, and with lim ln $fL^{-1}N_1$ replaced by lim $L^{-1}N_1$. However, we have been unable to prove that these conditions hold.

Theorem I of this paper may be extended to the case of a classical one-dimensional lattice gas with interaction potential, U(r), defined in (1). The method of proof is unchanged except for the replacement of integrals by sums. However, the lattice gas analogue of $\psi(p)$ has period $2\pi i\delta^{-1}$, δ being the (uniform) lattice spacing, so that the pressure is no longer single-valued and all of the proofs

in the present paper which depend on the aperiodicity of $\psi(p)$ break down for a lattice gas. It appears that Theorems I, II, IV and V may be extended to lattice gases, though parts of the proofs would have to be changed, but that Lemma II, the Corollary to Theorem II and Theorem III cannot be so extended.

The restriction to nearest-neighbour forces in one dimension excludes all cases where a phase transition can occur,[30] such as the model with forces of infinite range studied by Kac, Uhlenbeck and Hemmer.[31] However, it should be emphasized that many of the proofs given in the present paper are sufficiently general to be valid, with only minor modifications, for more general one-dimensional systems, including those with forces of infinite range, and even for some systems in more than one dimension. The most difficult problem, to generalize Theorem I, is currently being considered.

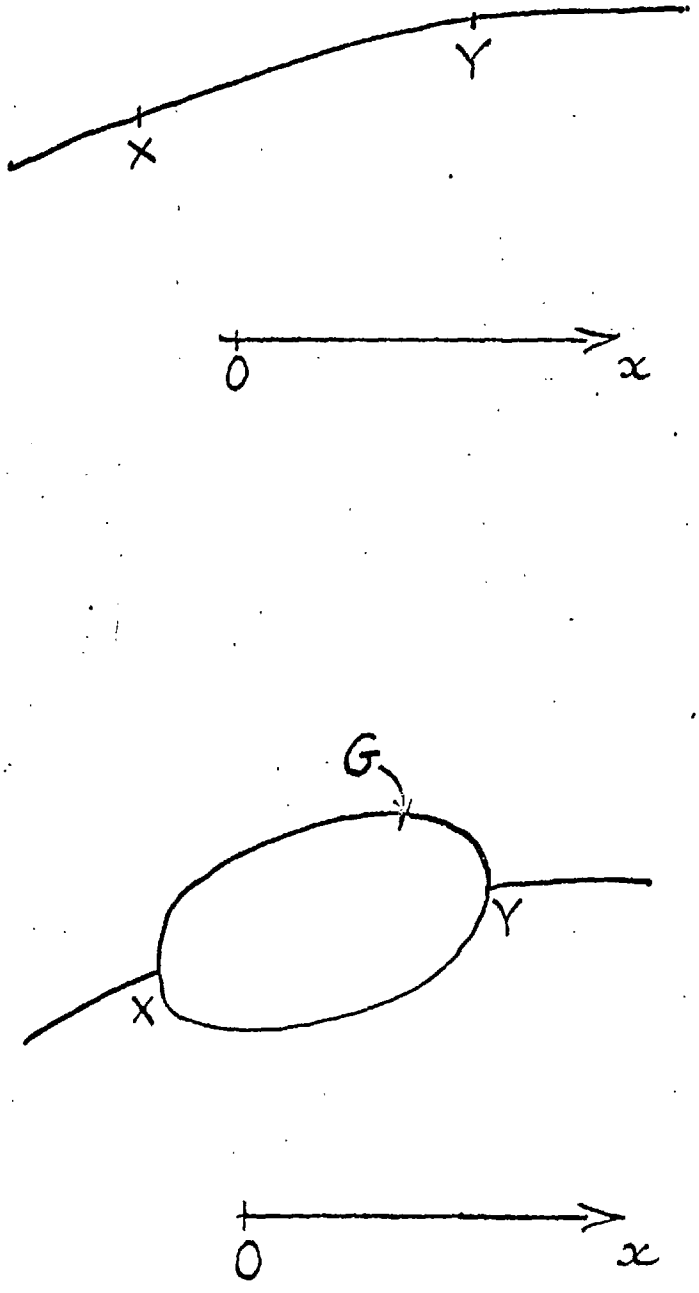

FIGURE 1.

ILLUSTRATING THAT THE ARCS C CANNOT BE DETERMINED UNIQUELY BY REQUIRING ONLY THAT $\overline{\Pi}(z)$ BE CONTINUOUS FOR ALL $z \equiv x+iy$

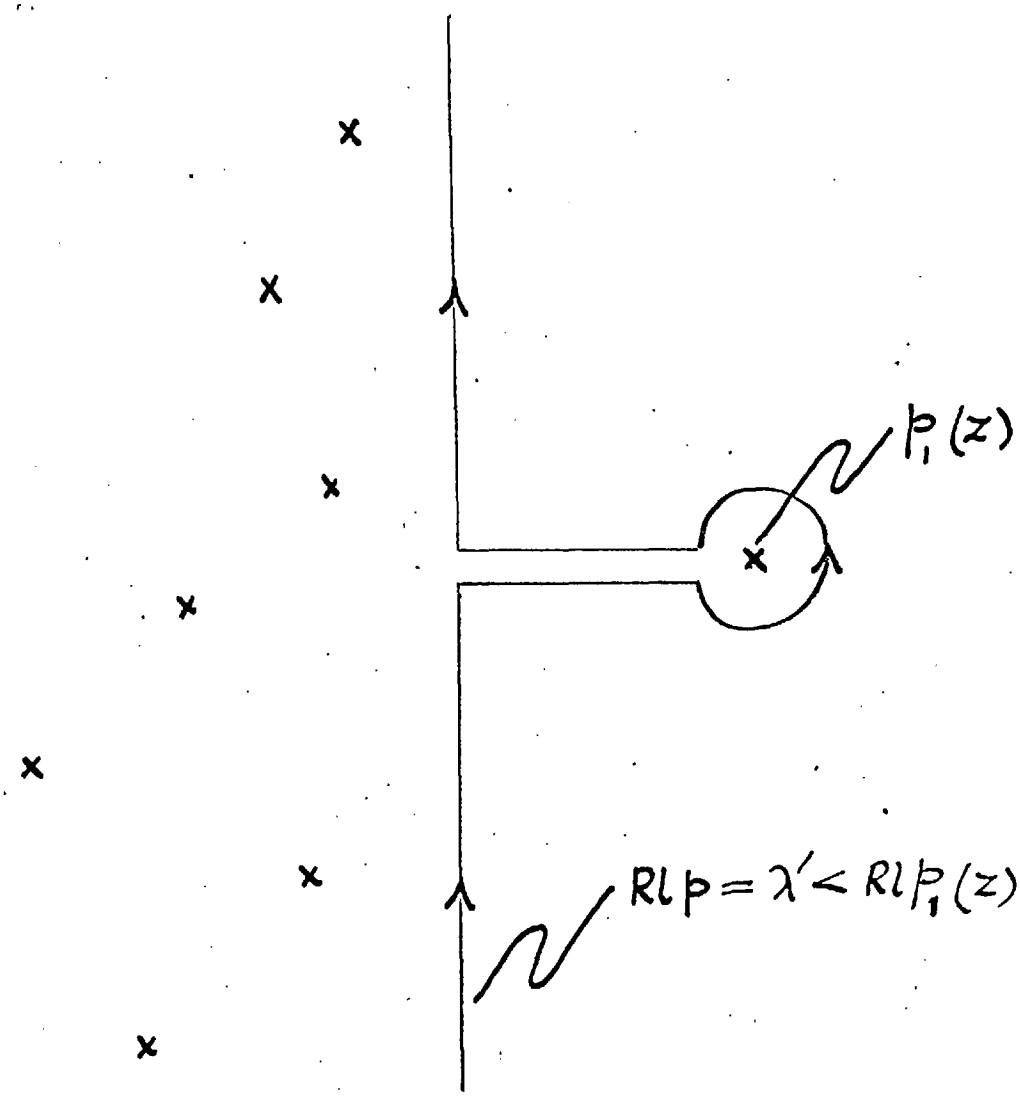

FIGURE 2.

CONTOUR OF INTEGRATION USED TO INVERT THE LAPLACE TRANSFORM OF Ξ

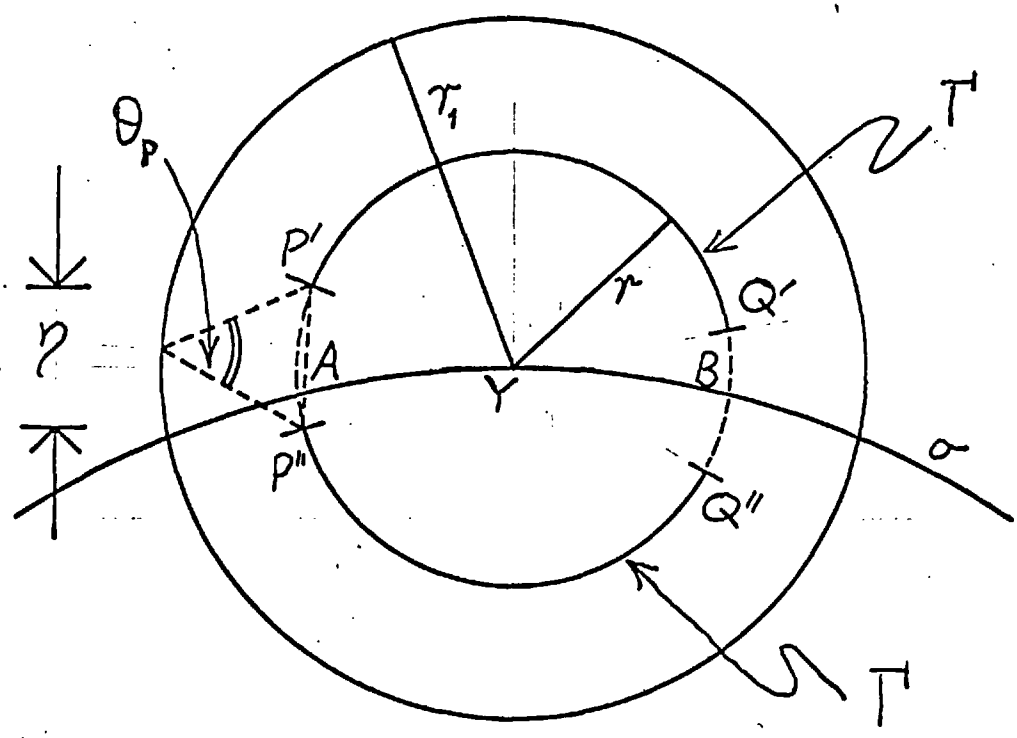

FIGURE 3.

CONTOURS USED TO CONSTRUCT A BOUND ON $\Delta_T(L; D)$.

FOOTNOTES

1. C. N. Yang and T.D. Lee, Phys.Rev. 87, 404 (1952).

2. T. D. Lee and C. N. Yang, Phys.Rev. 87, 410 (1952).

3. E. H. Hauge and P. C. Hemmer, Physica 29, 1338 (1963).

4. P. C. Hemmer and E. H. Hauge, Phys.Rev. 133A, 1010 (1964).

5. For convenience of presentation we anticipate the definitions of $\lambda_{max}(z)$, $\overline{\Pi}_{max}(z)$ which are given, in logical sequence, in § VII.

6. H. Takahasi, Proc.Math.Phys.Soc.Japan, 24, 60 (1942); see also F. Gürsey, Proc.Camb.Phil.Soc. 46, 182 (1950).

7. H. Longuet-Higgins, Mol.Phys. 1, 83 (1958), has used the Laplace transform of the ground partition function in treating one-dimensional mixtures, for real values of β,

8. D. V. Widder, The Laplace Transform (Princeton U.P., 1941) pp.37, 63.

9. T. M. Apostol, Mathematical Analysis (Addison-Wesley Publ.Co.Inc., Reading, Mass., first ed.1957) p.425, Ex.13.7(a).

10. E. C. Titchmarsh, The Theory of Functions (Oxford U.P., 2nd Ed., 1939) p.45. If we were using Lebesgue integrals eq.(15) would be an immediate consequence of the existence of the Laplace transform of $|\Xi(z,L)|$; see Titchmarsh, this reference, p.346.

11. This function has been calculated under different boundary conditions by F. Gürsey, Proc.Camb.Phil.Soc. 46, 182 (1950) and by W. B. Brown, Mol.Phys. 1, 68 (1958); see also H. Takahasi, Proc.Math.Phys.Soc. Japan, 24, 60 (1942).

12. E. T. Copson, An Introduction to the Theory of Functions of a Complex Variable, (Oxford U.P., 1935), p.108.

13. When $Z \neq 0$, one may verify from (16) and (18) that $\chi(Z,p)$ tends to 0 with p, so that $p = 0$ is not a pole.

14. We owe this argument to W. K. Hayman (Oxford Mathematical Monographs, No.), p.

15. M.J. Lighthill, Fourier Analysis and Generalized Functions (Cambridge U.P., 1958) Chapter 4.

16. See § eq.(55).

17. P. Dienes, The Taylor Series (Oxford, Clarendon Press, 1931), p.263.

18. S. Saks and A. Zygmund, Analytic Functions, translated by E.J. Scott (P.W.N. - Polish Scientific Publishers, 2nd Ed., 1965), p267.

19. Reference 18, p.459.

20. Reference 18, p.465, Theorem 8.10, Condition (A); we also use the fact that a function subharmonic in an annular neighbourhood of a point z' and tending to $-\infty$ as Z tends to z' is also subharmonic at z' (since it satisfies the criterion (A) at $Z = z'$).

21. Reference 18, p.447, § 1, Theorem 1.11.

22. Reference 18, p.470, Theorem 5.4

23. This statement includes the possibility that S_1 is the union of two or more sets.

24. T. Rado, Subharmonic Functions (Chelsea Publishing Co. New York 1949).

25. E. Byckling, Phys. Rev. 140 A, 1165 (1965)

26. See Hemmer and Hauge (reference 4) and Byckling (reference **25**). In both cases the following additional assumptions are made in order to derive the formula: (1) C is a system of arcs; (2) a definite branch of arg Ξ can be defined; (3) L^{-1} arg $\Xi(Z,L)$ tends to $\lim_{n\to\infty} \prod(Z)$ as L tends to ∞. Byckling also imposes conditions on $d\prod(Z)/dZ$.

27. M. Kac, Phys.Fluids 2, 8(1959).

28. R.A. Sack, Mol.Phys. 2, 8 (1959).

29. G.L. Jones, J.Math.Phys. 7, 2000 (1966).

30. L. Van Hove, Physica, 16, 137 (1950).

31. M. Kac, G.E. Uhlenbeck and P.C. Hemmer, J.Math.Phys., 4, 216(1963).

C H A P T E R V

The Yang - Lee Distribution of Zeros for a Classical Lattice Gas.

§ 1. In this Chapter it will be shown that the principal results of Chapter IV may be extended to classical lattice gases when the particles have hard cores and an arbitrary but finite range of interaction. Moreover, it will be found that the basic lattice may have any dimensionality, provided that it is simple and grows only one - dimensionally; but the pressure at complex z will, in general, now be multivalued, so that only its real part can be determined uniquely.

The functions occurring in this chapter depend on several variables; for simplicity we show in each section at most those variables directly involved in the reasoning. The full dependence of all functions may be ascertained from their definitions.

The technique used in this chapter is similar to the matrix method of Kramers & Wannier (1941); they considered only nearest - neighbour interactions (two-dimensional Ising model) but allowed the lattice to grow two-dimensionally. It is possible, also, that the results of Baur & Nosanow (1962) on one-dimensional lattice gases, in which the range of interaction may have any finite value and the particles may have any finite number of internal degrees of freedom, could be adapted for use in the present work; however, the treatment given here is simpler and seems more elegant.

§2

Consider a lattice comprising M equally spaced sites on a line. Suppose that the two body interaction potential for the corresponding lattice gas is defined by

$$u(i,j) \quad \begin{cases} +\infty & , \ 0 \leq |i-j| < s \\ \varphi(|i-j|) & , \ s \leq |i-j| \leq t-1 \\ 0 & , \ t \leq |i-j| \leq M-1 \end{cases} , \qquad (\overline{V}\,2\cdot1)$$

Where we take the distance between neighbouring sites as the unit of length, so that s and t are integers, and the function $\varphi(|i-j|)$ is taken to be bounded. Next, consider the model consisting of an array of spins, one per site, denoted by $\sigma_1 \ldots \sigma_M$ and capable of just two orientations, 'up' ($\uparrow$), or 'down' ($\downarrow$). For this model, in the presence of a magnetic field of strength $\mathcal{H}$ (in suitable units), we specify the following interaction:

$$v(i,j) = \begin{cases} u(i,j) & , \text{ if both of } \sigma_i, \sigma_j \text{ are } \uparrow \\ 0 & , \text{ otherwise} \end{cases} \qquad (\overline{V}\,2\cdot2)$$

$$\epsilon_i(\mathcal{H}) = n_i \mathcal{H} \ , \qquad (\overline{V}\,2\cdot3)$$

where

$$n_i \equiv \begin{cases} 1 & , \text{ if } \sigma_i \text{ is } \uparrow \\ 0 & , \text{ if } \sigma_i \text{ is } \downarrow \end{cases} , \qquad (\overline{V}\,2\cdot4)$$

$v(i,j)$ denotes the two-spin potential, $u(i,j)$ is defined by (2·1) and $\epsilon_i(\mathcal{H})$ accounts for the interactions of the separate spins with the external magnetic field. It should be stressed that the somewhat peculiar conditions (2.2), (2.3) have been imposed only as a formal device and are not intended to be physically realistic.

By virtue of (2·2) and (2·3), the configurational sum (canonical partition function) for the spin system may be written as

$$Q_s(M,\mathcal{H}) = \sum_{\{n_i\}} \exp\left[-\beta U_{\mathcal{H}}(n)_M\right], \qquad (\underline{V}\ 2\cdot5)$$

where

$$U_{\mathcal{H}}(n)_M \equiv \sum_{i=1}^{M-1}\sum_{j=i+1}^{M} n_i n_j \mathcal{W}(i,j) + \sum_{l=1}^{M} n_l \mathcal{H} \qquad (\underline{V}\ 2\cdot6)$$

and the summation in (2·5) extends over all of the 2^M possible configurations of the spins $\sigma_1 \cdots \sigma_M$. Following Lee and Yang (1952), we may identify an 'up' spin σ_l in the spin system with a particle on the l^{th} site in the lattice gas, thus obtaining from (2·4) - (2·6) the correspondence

$$Q_s(M,\mathcal{H}) = \underline{\Xi}_l\left(z = e^{-\beta\mathcal{H}}, M\right), \qquad (\underline{V}\ 2\cdot7)$$

$\underline{\Xi}_l$ being the grand partition function of the lattice gas at fugacity $z = \exp(-\beta\mathcal{H})$.

§3 We aim to show that $Q_\Delta(M,\mathcal{H})$ equals the trace of a suitably defined matrix; therefore we adopt cyclic boundary conditions, so that all sites on the lattice are numbered unodulo M. In the limit as M tends to ∞ (the lattice analogue of the bulk limit discussed in I §4) the grand canonical pressure, $\beta^{-1}\Pi(z)$, is not affected by these boundary conditions, provided that the potential is stable, and this is the only case in which we are interested.

The required matrix, say T, may be specified as follows. Denote by $X \equiv (x_1 \cdots\cdots x_{t-1})$, $Y \equiv (y_1 \cdots\cdots y_{t-1})$, any configurations * of $(t-1)$ spins taken in clockwise order round the lattice. Then we may define T by

$$T_{XY}(z;t) \equiv \begin{cases} \mathcal{B}\{y_{t-1}|X;\mathcal{H}\}, & \text{if } y_{\ell-1}=x_\ell,\ 2\le\ell\le t-1 \\ 0, & \text{otherwise} \end{cases} \qquad (\text{V } 3\cdot1)$$

Where $\mathcal{B}\{y_{t-1}|X;\mathcal{H}\}$ denotes the Boltzmann factor of the spin σ in state y_{t-1}, in the presence of the configuration of spins, X, and the magnetic field, $\mathcal{H}$. Thus T is a square matrix of order 2^{t-1}, independent of M.

In terms of the matrix T we have at once from (2·5) - (2·7) the basic result:

$$\Xi_\ell(z=e^{-\beta\mathcal{H}},M) = tr\{T^M\} = \sum_{k=1}^{m} \rho_k^M, \quad (m=2^{t-1})$$

* More precisely, for any $k=0,\cdots M-1$, let X (V 3·2)
Denote any configuration of the spins $\sigma_{k+1}\cdots\sigma_{k+t-1}$
And Y any configuration of $\sigma_{k+2}\cdots\sigma_{k+t}$

Where $\rho_k(z)$ are the eigenvalues of T. It follows from (3·1) that the characteristic equation for the eigenvalues of T has the form

$$\rho^m + \sum_{j=1}^{m} B_j(z)\rho^{m-j} = 0, \quad [m \equiv 2^{t-1}] \qquad (\overline{V}\ 3\cdot3)$$

in which the 'coefficients', $B_j(z)$ are polynomials of degree at most j in z. Consequently, if the left-hand member of (3·3) is identically decomposable into r irreducible polynomial factors of degrees, say, $d_1 \cdots d_r$, then the condition (3·3) determines a set of algebraic functions, $\rho^{(1)}(z), \ldots, \rho^{(r)}(z)$, where $\rho^{(k)}(z)$ has d_k branches and $d_1 + d_2 + \cdots + d_r = m$ (cf. Saks and Zygmund, 1965, pp273-5). When there is a unique eigenvalue of T having largest modulus, and this eigenvalue is simple, we shall denote it by $\rho_{max}(z)$. For a given value of z the sum $(\rho_{max}^{-M} \operatorname{tr} T^M)$ tends to 1 as M tends to ∞. Therefore we may 'define' the argument of $\Xi_\ell(z, M)$ by

$$\arg \Xi_\ell(z, M) \equiv M \arg \rho_{max}(z) + o(1), \qquad (\overline{V}\ 3\cdot4)$$

where $o(1)$ denotes a quantity which tends to 0 as M tends to ∞. Of course this is not yet a proper definition, since arg ρ_{max} is a multi-valued function. There are now two possibilities: (a) One can choose the principal value of the argument of ρ_{max} thus making the argument of Ξ_ℓ single-valued but discontinuous as z varies; or (b) One can define a function, say $\operatorname{Arg} \rho_{max}(z)$, to vary continuously with z

throughout the domain of existence of $\eta_{\max}(z)$, rendering the argument of Ξ_ℓ continuous but multi - valued. We shall denote these values of $\arg \Xi_\ell$ by $\operatorname{Arg} \Xi_\ell$, $\operatorname{Arg} \Xi_\ell$, respectively (cf (IV eq (50)). Thus, when $\eta_{max}(z)$ exists, we obtain from (3.2), by taking logarithms, dividing by M and then letting M tend to ∞, the results

$$\Pi_\ell(z) \equiv \lim_{M\to\infty} M^{-1} \log \Xi_\ell(z,M) = \begin{cases} \log|\eta_{max}| + i \operatorname{Arg} \eta_{max} \\ \log|\eta_{max}| + i \operatorname{Arg} \eta_{max} \end{cases}$$

, depending on our choice of $\arg \Xi_\ell$. (V 3.5)

When z is positive so is $\Xi_\ell(z)$, but in general, the imaginary part of $\log \Xi_\ell$ is quite arbitrary. Thus only the real part of the pressure is uniquely determined by (3 - 5). This arbitrariness in the imaginary part of the pressure also extends to the system studied in Chapter IV, where an apparently stronger result (Th I(1)) was stated.

§4 Equation (3·5) generalizes the relation (eqn. 27) of Chapter IV to the case of a lattice gas consisting of simple particles (that is, particles having no internal degrees of freedom) with an abitrary but finite range of interaction, whose possible positions are limited to the sites of a linear, equally-spaced lattice. Before discussing some consequences of (3·6), we shall show how this, in turn, may be extended to include three-dimensional (or two-dimensional) lattices which grow one-dimensionally.

Consider a simple cubic lattice in the form of a rectangular parallelepiped comprizing $q \times q \times M$ cells. If we retain as the unit of length the separation of a pair of neighbouring sites, we may regard this lattice as consisting of M square sheets of side q, the mutual spacing of neighbouring sheets being unity. We denote the sheets by S_i, and suppose that each sheet can assume $\nu \equiv 2^{q^2}$ distinct internal states, say σ_{ik}, $k = 1, 2, \ldots, \nu$, corresponding to the total number of distinct configurations of the 'compound spin' σ_i formed by placing a simple, 'up - down' spin on each of the q^2 lattice sites of S_i. For the simple spins at positions r_i, r_j, we introduce the two-spin interaction

$$\tilde{v}(i,j) = \begin{cases} \tilde{u}(i,j), & \text{if the spins at } r_i, r_j \text{ are both } \uparrow \\ 0; & \text{otherwise} \end{cases} \qquad (V\ 4\cdot1)$$

where

$$\tilde{u}(i,j) \equiv \begin{cases} +\infty, & r_{ij} < s \\ \varphi(r_{ij}), & s \leqslant r_{ij} \leqslant t-1 \\ 0, & t-1 \leqslant r_{ij} \leqslant b \end{cases}, \qquad (\text{V } 4.2)$$

$r_{ij} \equiv |x_i - x_j|$, $b \equiv (2q^2 + M^2)^{\frac{1}{2}}$ and $\varphi(r_{ij})$ is bounded.

We also introduce the spin - field interaction energy, $\epsilon_{ik} \equiv \epsilon(\delta_{ik})$, defined by

$$\epsilon_{ik} \equiv \mathcal{H}\delta_{ik}, \qquad (\text{V } 4.3)$$

where $\delta_{ik}\,(\geqslant 0)$ denotes the total number of 'up' spins in the k^{th} internal state, σ_{ik}, of σ_i, and $\mathcal{H}$ denotes the field strength of a constant external magnetic field (again, in such units that the sp magnetic moment does not appear explicitly). Finally, for two compound spins, we define the interaction by

$$\tilde{V}_{ik,jl} \equiv \begin{cases} F(\sigma_{ik}, \sigma_{jl}; |i-j|), & \delta_{ik}\delta_{jl} > 0 \\ 0 & \delta_{ik}\delta_{jl} = 0 \end{cases} \qquad (\text{V } 4.4)$$

where $F(\sigma_{ik}, \sigma_{jl}; |i-j|)$ stands for the interaction energy of a pair of compound spins, σ_{ik}, σ_{jl}, the interaction of simple spins being defined by (4.1).

If we adopt cyclic boundary conditions, so that the sheets, Λ_i, are numbered modulo M and, say, in clockwise order, we may generalize the method of section 3 by defining a matrix, $\tilde{\tilde{T}}$, as follows. Denote by $\tilde{X} \equiv (\tilde{x}_1, \ldots\ldots \tilde{x}_{t-1})$, $\tilde{Y} \equiv (\tilde{y}_1, \ldots\ldots \tilde{y}_{t-1})$ any configurations of $(t-1)$ consecutive compound spins, σ_i, in clockwise order.* Define the matrix $\tilde{\tilde{T}}$ by

$$\tilde{\tilde{T}}_{\tilde{X}\tilde{Y}}(z,t) \equiv \begin{cases} \mathcal{B}\{\tilde{y}_{t-1} | \tilde{X}; \mathcal{H}\}, & \text{if } \tilde{y}_{t-1} = \tilde{x}_t, \ 2 \le l \le t-1 \\ 0, & \text{otherwise.} \end{cases} \quad (\text{V } 4\cdot 5)$$

The Boltzmann factor $\mathcal{B}\{\tilde{y}_{t-1} | \tilde{X}; \mathcal{H}\}$ is now supposed to include both the internal energy of the compound spin $\tilde{y}_{t-1}$ and the interaction energy of $\tilde{y}_{t-1}$ with the compound spins $\tilde{X}$ and the magnetic field, $\mathcal{H}$.

Finally, if we identify pairs of simple 'up' spins with pairs of particles interacting via the potential (4·2), it follows from (4·1) – (4·5) that the grand partition function for the lattice gas consisting of these particles is given by

$$\Xi_t(z = e^{-\beta\mathcal{H}}, q^2 M) = tr\{\tilde{\tilde{T}}^M\} = \sum_{k=1}^{mq^2} \tilde{\nu}_k^M \cdot \quad (\text{V } 4\cdot 6)$$

In analogy with (3.3) we now obtain an eigenvalue equation of the form

$$F(\tilde{\nu}, z) \equiv \tilde{\nu}^K + \tilde{B}_1(z)\tilde{\nu}^{K-1} + \cdots + \tilde{B}_K(z) = 0, \quad (K \equiv mq^2) \quad (\text{V } 4\cdot 7)$$

* SEE THE FOOTNOTE ON P. 132.

for the eigenvalues, $\tilde{\eta}_k$, of $\tilde{T}$, the coefficients $\tilde{B}_j$ being polynomials in z, so that (4·7) determines a set of algebraic functions, say $\tilde{\rho}^{(1)}(z), \ldots, \tilde{\rho}^{(h)}(z)$ of degrees $\tilde{d}_1, \ldots, \tilde{d}_h$, where $\tilde{d}_1 + \cdots + \tilde{d}_h = K$. If $\tilde{T}$ has a unique, eigenvalue, say $\tilde{\eta}_{max}(z)$ of largest modulus and this eigenvalue is simple, then we obtain from (4·6) the basic result

$$\pi_l(z) = \begin{cases} \log|\tilde{\eta}_{max}(z)| + i \operatorname{Arg} \tilde{\eta}_{max}(z) \\ \log|\tilde{\eta}_{max}(z)| + i \operatorname{Arg} \tilde{\eta}_{max}(z) \end{cases}, \quad (\overline{V}\,4\cdot8)$$

according to our choice of $\arg \Xi_l$, where the dependence of all functions on q has not been shown explicitly.

The formula (4·8) extends (3.5) to a class of three - dimensional (or two - dimensional) lattice gases. Apart from the fact that the functions $\tilde{\eta}_k(z)$ depend on q, (3.5) and (4·8) are formally identical. Therefore we may omit the tilda in (4·8) and all of the observations made in the rest of this chapter will apply equally to lattice gases in one, two or three dimensions, provided that the lattices grow only one - dimensionally (that is, q is constant).

The analogue of the second part of theorem I is that if T has a unique eigenvalue, $\eta_1(z)$, of largest modulus, and η_1 is simple, then z is not a limit point of zeros of $\Xi_l(z, q^2 M)$. The only change needed in the proof (Ch. IV § X) is that the function $\mathcal{E}(z, L)$ defined by (IV 24) must now be replaced by

$$\mathcal{E}(z,M) \equiv \sum_{k=2}^{mq^2} \left(\eta_k/\eta_{max}\right)^M$$ (where we have numbered the η_k so that $\eta_{max} = \eta_1$), and it must be shown that $\mathcal{E}(z,M)$ tends uniformly to 0 in a neighbourhood of z. To prove this property we use the continuity of all branches of $\eta(z)$. If D denotes any sufficiently small closed disk centred at z, then the number

$$\alpha \equiv \underset{z \in D}{Max} \left\{ \left| \eta_k/\eta_{max} \right| \right\} \quad (2 \leq k \leq mq^2)$$

exists and is less than 1.

Hence we have

$$\left| \mathcal{E}(z,M) \right| \leq \left(mq^2 - 1\right) \alpha^M$$

which tends to 0 uniformly for z in D.

From now on we shall suppose that $F(\eta, z)$ is irreducible to a product of two or more polynomials in η, z. This has the important consequence that the relation $\log \eta_\ell(z) = \log \eta_m(z) + 2\omega$ (ω a real constant) cannot hold over a domain of values of z unless $\omega = 2\pi n$ ($n = 0, \pm 1, \pm 2, \cdots$) and $\log \eta_\ell$, $\log \eta_m$ are two values of the logarithm of the <u>same simple</u> zero of $F(\eta, z)$ (For otherwise F would be reducible). Since the precise form of F is determined by the interaction potential, we may regard the irreducibility of F as a property of the models considered. For such models, two branches of the pressure corresponding to distinct zeros of F cannot differ by an imaginary constant (and so cannot have equal real parts) over a region in the Z-plane; but the multi[illegible]-valuedness of $\log \eta_\ell$ for given η_ℓ still implies that theorem III of Chapter IV is, in general, false for lattice gases.

§ 5 We have seen that the function $\eta(z)$ defined by (4.7) is algebraic, which implies that it has only a finite number of branch points, each of finite order. (cf. Saks and Zygmund, 1965, p.275). Instead of the sets S_k (Ch. IV · § XII) we now introduce sets, J_k, of points in the z-plane, defined by the condition :

for $k = 1, 2, \cdots, K$

$z \in J_k$ if and only if T has exactly k eigenvalues, say $\eta_1, \cdots, \eta_k$, whose common modulus exceeds those of all others, and all of these eigenvalues are simple.

We shall say that the eigenvalues $\eta_1, \cdots, \eta_k$ have largest modulus (LM). We also introduce a set of points, J_0, where $z \in J_0$ if and only if $\eta(z)$ has at least one multiple eigenvalue of LM.

The sets $J_0, J_1, J_2, \cdots$ partition the z-plane.

Finally, we shall write

$$\gamma_{max}(z) \equiv \max_{1 \le j \le K} \{ |\eta_j(z)| \}, \qquad (V\ 5.1)$$

so that $\gamma_{max}(z)$ is defined and continuous for all z, though $\eta_{max}(z)$ exists only when $z \in J_1$, in agreement with the notation used in sections 3 and 4.

According to (4.7), a necessary condition for $\eta(z)$ to have a branch point is that $F(\eta, z)$, regarded as a function

of ρ, has a multiple zero. (cf. Forsyth, 1918, p. 197). Since the definition of J_k for $k \geq 1$ requires that $\rho_1, \ldots, \rho_k$ are simple zeros of $F(\rho, z)$, it follows that each of $\rho_1(z), \ldots, \rho_k(z)$ is regular near a point of J_k. Consequently we may also define J_k by the conditions:

for $k = 1, 2, \ldots, m$, $z \in J_k$ if and only if $\rho(z)$ has exactly k branches of L.M., all regular.

Suppose now that $z \in J_2$; then $\rho_1(z)$, $\rho_2(z)$ have L.M. and are therefore non vanishing throughout a neighbourhood, say N of z. Therefore the function $[\log \rho_1(z) - \log \rho_2(z)]$ is regular within N and so may be expanded in a Taylor series. By repeating the arguments used in proving theorem IV (Ch. IV § XII) with $(\log \rho_1 - \log \rho_2)$ in place of $(\Pi_1 - \Pi_2)$ we conclude that the points of J_2 within N constitute a set of arcs intersecting at z, or possibly a single arc passing through z, so that J_2 as a whole consists of arcs. We also find that the sets $J_3, J_4, \ldots, J_m$ consist of (at most) arcs and isolated points. However, the analyticity of $\log \rho_i(z) - \log \rho_j(z)$, $i \neq j$, $1 \leq i, j \leq k$, in the neighbourhood of a point of J_k shows that $J_k \cup J_2$ contains no isolated points (for, otherwise the harmonic function $Rl\{\log \rho_i - \log \rho_j\}$ would vanish at isolated points - an impossibility). Thus the union, say J, of the sets $J_2, \ldots, J_m$

consists of arcs in the z-plane. We define J to be the set of all points z interior to exactly one arc of J (cf. the definition of S, Ch. IV § XIII).

It remains to consider the set J_0, which contains as a subset all of the branch points of $\eta(z)$. All of the simple terminal points of arcs of J are points of J_0 (and, probably, branch points of $\eta(z)$), since the moduli of two branches of $\eta(z)$ cannot be equal throughout a domain of values of z. For the continuum system of Chapter IV, we showed that S_0 was a subset of S (Ch IV § XII), but this was a consequence of Theorem III, which, as we have mentioned, breaks down for lattice gases. So we cannot exclude the possibility that the union of the sets J, J_0, contains a finite number of isolated points.

We shall indicate now the proof that the function $\log \delta_{max}(z)$ is subharmonic throughout the z-plane; again the reasoning closely parallels that in Chapter IV (§ XI).

Let z' be any point ($\neq \infty$) in the z- plane and $\eta_1, \ldots, \eta_k$ the branches of $\eta(z)$ having L.M. Then $\eta_1(z), \ldots, \eta_k(z)$ are nonvanishing throughout a neighbourhood, say $\mathcal{N}$, of z' and hence the functions $\log \eta_1(z)$ $\log \eta_k(z)$ have branch points only at the branch points of $\eta_1 \ldots \eta_k$. Therefore, within an annular neighbourhood of z', each of the functions $\log \eta_j(z)$ having a (necessarily algebrain) branch point at z', say of order $n_j - 1 (\geq 0)$ may be expressed as a meromorphic function of (a definite branch of) $(z-z')^{\frac{1}{n_j}}$

(cf. Saks and Zygmund, 1965, p.267). (The value $n_j = 1$ is to be taken whenever $\eta_j(z)$ is regular throughout $\mathcal{N}$). We may now apply the arguments used in the proof of theorem II (Ch. IV § XI) to the function

$$T_\ell(z) \equiv K^{-1} \sum_{k=1}^{K} \log \eta_k(z),$$

obtaining, after taking real parts,

$$\log \gamma_{max}(z') \leq \frac{1}{2\pi} \int_0^{2\pi} d\theta \log \gamma_{max}(z' + re^{i\theta}) \qquad (V\ 5\cdot 2)$$

for all sufficiently small values of r, which proves that $\log \gamma_{max}(z)$ is subharmonic throughout the z-plane. (cf. Saks and Zygmund, 1965, p.485).

Lastly, we want to generalize theorem V of Chapter IV and so determine the set, C_ℓ, of limit points of zeros of $\Xi_\ell(z, q^2 M)$.

If we define $\Delta_{\Gamma_\ell'}(M;\rho)$ to be the change in $\operatorname{Arg} \Xi_\ell(z, q^2 M)$ when z describes the broken contour, Γ_ℓ', corresponding to Γ' in figure 3 (but with σ now denoting an arc of J and ρ replacing ρ to avoid ambiguities in the notation) then the proof given in Chapter IV (§ XIII) may be extended to show that J is a subset of C_ℓ. We can show, also, that C_ℓ is a subset of $J \cup J_0$, but this does not permit us to identify J and C_ℓ. Thus our analysis does not preclude the existence of a finite number of isolated limit points of zeros of $\Xi_\ell(z, q^2 M)$,

which is consistent with the fact that the grand partition function for a lattice gas of noninteracting point particles equals $(1+z)^{2M}$, for the lattice considered here, so that $z=-1$ is an isolated limit point of zeros.

An alternative proof of theorem V, for the system considered in Chapter IV or for the lattice gases considered here, is due to Penrose (to be published in the paper by O. Penrose & J.S.N.Elvey, of which Chapter IV of this thesis is a preliminary version). Penrose's proof is based on Jensen's formula (for the number of zeros of an entire function (here $\Xi(z,L)$, or $\Xi_1(z,M)$ for lattice gases) within the circle $|z|=\rho$. As a by-product of this proof, one obtains a formula for the total measure of the set of limit points of zeros on any arc in the $z-$ plane; the formula is equivalent to one used by Hemmer & Hauge (1964).

§6 Unsolved Problems.

The problem of generalizing theorem I (ch. IV § X) to continuum systems with forces of arbitrary but finite range (and ultimately to those where the forces have infinite range) is a formidable one, involving the asymptotic evaluation of $\Xi(z, L)$ for large L. Ostensibly, the techniques of Chapter II yield estimates of $\Xi(z,L)$, either directly, as in Baxter's work, or indirectly, by inverting the Laplace transform of Ξ — an extension of the method employed in Chapter IV. But closer study reveals the difficulty of analysing the spectra of the operators encountered in estimating $\Xi(z,L)$ when z is complex.

As explained in Chapter II (§ 6), Kac (1959) has derived an eigen-function expansion for the Laplace transform of $\Xi(z,L)$, of which our equation (III 5·7) is an extension (subject to our assumption about the kernel). When p is allowed to take complex values, however, as it must when z is complex, Kac's kernel becomes non hermitian and the validity of the expansion is no longer assured.

In view of these difficulties, it seems that the most promising method of attacking the problem consists of studying the limiting form of the pressure of a lattice gas as the lattice spacing tends to zero in a suitable way. We shall refer to this limit operation as 'taking the continuum limit'. It will become

clear that all of the problems encountered in seeking a complete generalization of theorem I reduce to showing that pairs of limit operations commute with oneanother. In this section we reformulate the calculation of section 4 so that the continuum limit can be discussed. The possibility of treating interactions of infinite range is also considered, though it is only for one - dimensional systems that this extension is essential in the study of phase transitions, (see Ch. II § 3).

We suppose that the lattice spacing is

$$\delta_n \equiv n^{-1}, \qquad (\overline{V}\ 6\cdot1)$$

where n is an integer, and that

$$M = M_0 n, \qquad (\overline{V}\ 6\cdot2)$$

$$q = q_0 n, \qquad (\overline{V}\ 6\cdot3)$$

so that the total number of cells of edge δ_n, say N_n, is

$$N_n = n^3 q_0^2 M_0 \qquad (\overline{V}\ 6\cdot4)$$

The basic result (4·5) now becomes

$$\Xi_\ell(z, M_0, q_0, n, t) = \sum_{k=1}^{2^{(t-1)q^2}} \rho_k^{M_0 n}(z, q_0, n, t) \qquad (\overline{V}\ 6\cdot5)$$

all of the arguments of Ξ_ℓ, ρ_k, being shown to make it easier to follow the coming limit operations. In order to suggest one possible way of tackling the limit problems of this section, we replace the variables M_0, q_0, n, t temporarily by $\alpha_1, \alpha_2, \alpha_3, \alpha_4$,

respectively, purely for notational convenience, and define the following operations:

$$\hat{L}_h : \alpha_h \to \infty \text{ at fixed } \alpha_i, \alpha_j, \alpha_k ;$$

$$\hat{L}_{hi} : \alpha_h, \alpha_i \to \infty \text{ at fixed } \alpha_j, \alpha_k ;$$

$$\hat{L}_{hij} : \alpha_h, \alpha_i, \alpha_j \to \infty \text{ at fixed } \alpha_k ;$$

$$\hat{L}_{hijk} : \alpha_h, \alpha_i, \alpha_j, \alpha_k \to \infty .$$

The set $\{h,i,j,k\}$ stands for any permutation of $\{1,2,3,4\}$. Evidently, all of the $\hat{L}$-operators are totally symmetric in their indices.

We now quote two theorems on double sequences, whose generalizations to the case of sequences having more than two indices are immediate.

Theorem 1.

If $\hat{L}_{hi} f_{hi}$ and $\hat{L}_i f_{hi}$ exist,

then so does $\hat{L}_h \hat{L}_i f_{hi}$ and

$$\hat{L}_h \hat{L}_i f_{hi} = \hat{L}_i \hat{L}_h f_{hi} .$$

Theorem 2.

If $\hat{L}_h f_{hi}$ exists uniformly in α_i

then the existence of $\hat{L}_i \hat{L}_h f_{hi}$ implies that of $\hat{L}_{ih} f_{hi}$, and the two limits are equal.

(cf. Apostol, 1957, Section 12-14).

In these theorems, f_{hi} denotes a known function, $f(\alpha_h, \alpha_i)$.

We present now a plausibility argument to show that the problem of extending theorem I may be reduced to proving that the single - index operators, $\hat{L}_h$, intercommute. The idea is that the existence of $\pi(z)$ for a class of three - dimensional continuum systems with forces of infinite range has already been demonstrated for positive z. These results may be extended to some complex values of z by analytic continuation. On the other hand, we shall make it plausible that the iterated limit

$$\hat{L}_t \hat{L}_n \hat{L}_{q_0} \hat{L}_{M_0} \left\{ (M_0 q_0^2)^{-1} \log \Xi_\ell (z, M_0, q_0, n, t) \right\}$$

also exists and would be equal to $\pi(z)$ if the order of the $\hat{L}$- operators could be changed.

We denote by $u_t(r_{ij})$ the interaction potential (4·2) and by $u_\infty(r_{ij})$ the potential, of infinite range, obtained formally from (4·2) by making t infinite. We suppose that $u_\infty(r_{ij})$ is stable (in the sense of Ch. I § 4) and such that the grand canonical pressure exists in the bulk limit for a three -

dimensional continuum system at positive fugacity and with interaction potential $u_\infty(r_{ij})$. The results cited in Chapter I (§ 4) show that this is possible.

The configurational sum for a lattice gas consisting of k particles is defined by

$$Q_\ell(k, M_0, q_0, n, t) \equiv \frac{\delta_n^{\nu k}}{k!} \sum_{x_1, \ldots, x_k} \exp\{-\beta U(\underline{x})_k\}, \qquad (V\ 6\cdot6)$$

where the summation ranges over all possible configurations of particles on a rectangular lattice of N_n sites, N_n being defined by (6·4). In terms of Q_ℓ, we have

$$\Xi_\ell = 1 + \sum_{k=1}^{N_n} z^k Q_\ell(k). \qquad (V\ 6\cdot7)$$

Moreover, the stability of $u_\infty(r_{ij})$ implies that there exists a positive number, say B_∞, such that

$$U_t(\underline{x})_k \geqslant U_\infty(\underline{x})_k \geqslant -kB_\infty \qquad (V\ 6\cdot8)$$

for all values of $k\ (\leqslant N_n)$ and all configurations $(\underline{x})_k$; the subscripts 't', '∞' in (6·8) indicate, respectively, the total potential energy calculated with interaction potential u_t, u_∞.

If $z \in J_1$, so that the matrix, T, defined by (4·5) has a unique eigenvalue of largest modulus, say $p_1(z)$, and p_1 is simple, we obtain from (6·5) – (6·8) the inequalities

$$\exp\{M_0 q_0^2 |z| e^{\beta B_\infty}\} > |\Xi_\ell| \geqslant |p_1|^M \left(1 - \sum_{j=2}^{2^{(t-1)q^2}} |p_j/p_1|^M\right), \qquad (V\ 6\cdot9)$$

On taking logarithms in (6·9), dividing by $M_0 q_0^2$ and making M_0 tend to infinity, we obtain

$$q_0^{-2} n \log |P_1[z, q_0, n, t]| < |z| e^{\beta B_\infty}, \qquad (\overline{V}\ 6\cdot 10)$$

showing the left member of (6·10) to be uniformly bounded in q_0, n, t. From the Boltzano - Weierstrass theorem and (6·10) it now follows that the sequence

$$\{ q_0^{-2} n \log |P_1[z, q_0, n, t]| \}$$

has at least one point of accumulation when q_0, n, t, tend to ∞, successively or together.

We have assumed from the outset that the grand canonical pressure at infinite volume exists for a three - dimensional continuum system with potential $u_\infty(r_{ij})$ That is, we have supposed that

$$\hat{L}_{q_0} \hat{L}_{M_0} \hat{L}_n \hat{L}_t \left\{ (q_0^2 M_0)^{-1} \log \Xi_\ell(z, M_0, q_0, n, t) \right\} = \Pi(z) \qquad (\overline{V}\ 6\cdot 11)$$

for positive values of z. The result (6·11) would also hold, by analytic continuation, within a region of the complex z-plane. However, we must take the limits in a different order, since our calculation rests on the use of the matrix T. Instead of (6·11), we have considered the limit

$$\hat{L}_t \hat{L}_n \hat{L}_{q_0} \hat{L}_{M_0} \left\{ (q_0^2 M_0)^{-1} \log \Xi_\ell(z, M_0, q_0, n, t) \right\} . \qquad (\overline{V}\ 6\cdot 12)$$

The symmetry of the (rectangular) lattice implies that the operations $\hat{L}_{q_1}, \hat{L}_{q_2}, \hat{L}_{q_3}$, intercommute, for a lattice with edges of length q_1, q_2, q_3. It has been shown by Van der Linden and Mazur (1967) that the iterated limit, in which q_1, q_2, q_3 tend successively to ∞, exists and equals the usual bulk limit, for the reduced potentials such as the free energy density or entropy density (see Ch. I § 4). Although they considered continuum systems, it is probable that their method works for lattice gases, thus making it possible (again, by analytic continuation) to extend our theorem I to some complex values of z for genuinely three - dimensional lattice gases with forces of finite range.

The most difficult task seems to be the proof that the operation $\hat{L}_n$ commutes with $\hat{L}_{M_0}$. Preliminary investigation of this problem using a subdivision of the configuration space of the system into 'hypercubical' cells of edge - length equal to the lattice spacing, indicates that when z is positive and $q = 1$, we have

$$\hat{L}_{M_0} \hat{L}_n g_{M_0 n} = \hat{L}_n \hat{L}_{M_0} g_{M_0 n}, \quad (\text{V } 6.13)$$

where

$$g_{M_0 n}(k) \equiv M_0^{-1} \log Q_\ell(k, M_0, n) \quad (\text{V } 6.14)$$

and Q_ℓ is defined by (6.6). The estimates from which (6.13) was derived are too crude to be used for the grand canonical pressure, but more refined estimates can certainly be found. A rigorous proof that the operators $\hat{L}_h$ inter-commute may be envisaged in terms the theorems on double sequences (and their generalizations to multiple sequences). Despite the great difficulties in such a proof, the impossibility of calculating $\pi(z)$ for a three - dimensional continuum system with realistic interactions shows that our method is the only one available at present.

REFERENCES

Baur and Nosanow (1962), J. Chem. Phys. 37, 153;

Forsyth (1918), Theory of Functions, Third Edition (Cambridge);

Kramers & Wannier (1941), Phys. Rev. 60, 252;

Lee and Yang (1952), Phys. Rev. 87, 410;

Saks and Zygmund (1965), Analytic Functions, translated by E.J. Scott, (P.W.N - Polish Scientific Publishers; Warszaw

Closely Related References.

Hemmer, Hauge & Aasen (1966), J. Math. Phys. 7, 35;

Nilsen & Hemmer (1967), J. Chem. Phys. 46, 2640.

CHAPTER VI

THE VANDER WAALS FLUID NEAR THE CRITICAL POINT

The calculations of Kac, Uylenbeck & Hemmer (1963) on a one-dimensional hard-core fluid model with weak, long-range attractive forces, showed that the equation of state for this system is vigorously Van der Waals' equation (plus Maxwell's construction) in the limit that the range of the interaction becomes infinite, while its strength tends to zero. (See Baxter (1965) for another derivation of this result; see also Lebowitz & Penrose (1966) for several generalizations to three-dimensional systems). It is therefore of interest to investigate whether the "LRP" criterion, introduced in Chapter IV, yields results consistent with the known thermodynamic behaviour, for a fluid obeying Van der Waals' equation of state.

The present chapter consists of an approximate calculation of the pressure (as a function of β, z) near the critical point. We shall show that L.R.P. yields physically consistent results at or below the critical temperature, Tc, but that the criterion fails above Tc. Thus the problem of exactly when L.R.P. holds (in general) and if what should replace it when it fails is still very much open. The Van der Waals equation of state is

$$\Pi(\rho,\nu) = \frac{\rho}{1-\rho} - \nu\rho^2 \qquad \text{VI(1)}$$

where $\nu \equiv a/kT$ and a is a positive constant. This form of the equation is obtained when the particles are assumed to be hard spheres of unit diameter interacting through weak, long-range, attractive forces; then (-a) is the integral of the attractive

potential over all possible separations.
By using the relation $\rho = z\partial\pi[\rho(z)]/\partial z$ together with the 'infinite dilution' boundary condition $z \sim \rho$ as $\rho \to 0^+$, one obtains from (1) the relation (cf Hemmer & Hauge(1964))

$$z = \frac{\rho}{1-\rho} \exp\left[\frac{\rho}{1-\rho} - 2\nu\rho\right] \qquad \text{VI(2)}$$

The critical values of ρ, ν are

$$\rho_c = \frac{1}{3}, \quad \nu_c = \frac{27}{8} \qquad \text{VI(3)}$$

On substituting

$$\rho = \frac{1}{3}(1+2\theta)$$
$$\nu = \frac{27}{8}(1+3k^2) \qquad \text{VI(4)}$$

into (1), (2) one obtains the expansions

$$\hat{\pi}(\theta,k) = -9k^2 - 36k^2(\theta+\theta^2) + 12(\theta^3+\theta^4) + O(\theta^4) \qquad \text{VI(5)}$$

$$\sigma(\theta,k) \equiv \frac{2}{27k^3}\left(\hat{z} + \frac{27}{4}k^2\right)$$
$$= \frac{27}{16}k + \frac{1}{3}\left(\frac{\theta}{k}\right)^3 - \frac{\theta}{k} - \frac{1}{6}\frac{\theta^4}{k^3} + o\{|k| + |k||\theta/k|^4\} \qquad \text{VI(6)}$$

Where we have assumed that $k \neq 0$, &

$$\hat{\pi} \equiv \pi_c^{-1}(\pi - \pi_c)$$
$$\hat{z} \equiv z_c^{-1}(z - z_c) \qquad \text{VI(7)}$$

The notation

$$x(t) = o(y(t)) \text{ as } t \to \alpha$$

means that $|x/y| \to 0$ as $t \to \alpha$

We shall also use the notation

$$f(t) = e^{O(1)} \quad \text{as } t \to \alpha$$

to mean that there exist positive numbers b. B, independent of t, where b <B, such that

$$b < |f(t)| < B \quad \text{as } t \to \alpha$$

We shall denote by O(1) any quantity which is bounded; for instance

$$\sigma = O(1)$$

means that a bounded value of σ is considered, the values of θ, k in (6) being assumed compatible with this condition.
Finally, $f(t) = o(1)$ as $t \to \alpha$ means that $f(t) \to 0$ as $t \to \alpha$

Our general plan is now as follows. We want to 'substitute for θ' from (6) into (5);θ is a multi valued function of σ, K, so we shall obtain, in turn, a multi valued function $\hat{\pi}(\hat{\sigma}, K)$. When z & y are both positive, it will always be possible to identify the 'physical branch(es)' of $\hat{\pi}$ (σ, K) by using the continuity and reality of the pressure. It will then be possible to test the L.R.P. criterion.
The form of (6) suggests that we define a function $f(\sigma)$ by

$$\frac{1}{3} f^3(\sigma) - f(\sigma) = \sigma \qquad \text{VI(8)}$$

and then write

$$\theta = K(f(\sigma)+\delta) \qquad \text{VI(9)}$$

Substitution of (9) into (6) and comparison with (8) yields the following equation, in which the 'O' & 'o' symbols refer to the limit process $K \to 0$. (We shall always suppose that $|\delta| <$

the calculation is self-consistent in the sense that the functions δ that we obtain always satisfy this condition.)

$$0 = \frac{27}{16}k + \frac{1}{3}[(f+\delta)^3 - (f+\delta-f) - f^3] - [(f+\delta)-f]$$

$$- \frac{1}{6}k(f+\delta)^4 + o\{|k| + |k|\,|(f+\delta)^4|\},$$

which may be written

$$(1-f^2)\delta - f\delta^2 = \frac{\delta^3}{3} + k\{\frac{27}{16} - \frac{(f+\delta)^4}{6}\}$$

$$+ o\{|k| + |k|\,|(f+\delta)^4|\} \qquad \text{VI(10)}$$

There are several cases to consider.

Case A $\quad 1 - f^2 = e^{O(1)}$, $f = e^{O(1)}$.

(10) gives

$$\delta = \frac{k}{1-f^2}\left(\frac{27}{16} - \frac{f^4}{6}\right) + o(k) \qquad \text{VI(11)}$$

Case B

$1-f^2 = O(1)$; then δ must be determined (to lowest order in k) from the quadratic equation

$$f\delta^2 - (1-f^2)\delta + k\left(\frac{27}{16} - \frac{f^4}{6}\right) = 0,$$

with solution

$$2f\delta = 1-f^2 \pm [(1-f^2)^2 - 4fk\left(\frac{27}{16} - \frac{f^4}{6}\right)]^{\frac{1}{2}} \qquad \text{VI(12)}$$

(i) If $1-f^2 = O(k^{\frac{1}{2}})$, then (12) gives

$$\delta^2 = \frac{-k}{f}\left(\frac{27}{16} - \frac{f^4}{6}\right) + O(k) \qquad \text{VI(13)}$$

while if

(ii) $(1-f^2)^{-1} = o(k^{-\frac{1}{2}})$ we obtain

$$\delta = f^{-1}(1-f^2) + o(1-f^2) \qquad \text{VI(14)}$$

Case C

If $f = o(1)$; then (10) yields

$$\delta = \frac{27}{16}\frac{k}{1-f^2} + o(k) \qquad \text{VI(15)}$$

We define the notation $\sigma \approx 0$ to mean that there is a root of equation (8) satisfying case C.
The essential point of equations (11) - (15) is that, whatever the value of f, δ is small compared with 1 & (except in case C) compared with f.

On subtracting the single-valued function $\sigma - \frac{27}{16}k$ from $\frac{\hat{\pi}+9k^2}{36k^3}$, using (5) & (6), we obtain

$$\frac{\hat{\pi}+9k^2}{36\,k^3} - \sigma + \frac{27}{16}k = \tfrac{1}{2}\frac{\theta^4}{k^3} - \frac{\theta^2}{K} + O\{|k| + |k||\theta/k|^4\} \qquad \text{VI(16)}$$

Let us now suppose that σ is O(1); then, by (8) f is O(1). If we define $h(k,f)$ to be the left member of (16), regarded as a function of k, f, then we find, on using (9) in (16) that

$$h(k,f) = \tfrac{1}{2}k(f^4-2f^2) + o(k) \qquad \text{VI(17)}$$

in Case A or Case B, while, by (15) $h(k,f) = o(k)$ in Case C. VI(18)
It follows from (17) that, in the present approximations, the 'physical value', $f_p(\sigma)$, of $f(\sigma)$ may be found from the condition that $f_p^4 - 2f_p^2$ must be real when the fugacity & temperature variables are positive (except in case C for $T>T_c$, when f_p is identified by continuity from its value in case A or case B).
Using this criterion, we may classify the roots of (8) as follows.

For $T<T_c$ (σ, k real), $f_1(\sigma)$ is continuous for all (real) σ & vanishes at $\sigma = 0$, while $f_2(\sigma)$, $f_p(\sigma)$ are continuous for all nonvanishing real σ & satisfy the conditions

$$\begin{cases} \lim_{\sigma\to 0^+} f_p(\sigma) = -\lim_{\sigma\to 0^+} f_2(\sigma) = +\sqrt{3} \\ \lim_{\sigma\to 0^-} f_p(\sigma) = -\lim_{\sigma\to 0^-} f_2(\sigma) = -\sqrt{3} \end{cases} \qquad \text{VI(19)}$$

For $T>T_c$ (σ, k imaginary) we make the change of variable

$$f = 2 \sin w, \quad w \equiv u + iv \qquad \text{VI(20)}$$

so that (8) gives

$$\sigma = -\frac{2}{3} \sin 3w \qquad \text{VI(21)}$$

Since σ is purely imaginary, we may, without loss of generality, take u equal to 0. Then all of the roots of (8) are continuous, &

$$f_p(\sigma) \equiv f_p(-\tfrac{2}{3} i \operatorname{sh} 3v) = 2 i \operatorname{sh} v \qquad \text{VI(22)}$$

for all real v, while we adopt the convention that

$$\left.\begin{aligned} f_1(\sigma) &\equiv +\sqrt{3} \operatorname{ch} v - i \operatorname{sh} v \\ f_2(\sigma) &\equiv -\sqrt{3} \operatorname{ch} v - i \operatorname{sh} v \end{aligned}\right\} \qquad \text{VI(23)}$$

We define functions $d_r(\sigma)$, for $r = 1$ or 2, by

$$d_r(\sigma) \equiv \frac{2}{k} \mathrm{Rl}\,[h(k, f_p) - h(k, f_r)] \qquad \text{VI(24)}$$

where Rl[X] means the real part of X.

From (19) & the continuity of all roots of (8), as labelled here, for $\sigma \neq 0$ & $T \neq T_c$, it follows that $d_1(\sigma)$, $d_2(\sigma)$ are continuous for all (real or imaginary) bounded values of σ. Moreover we have the criterion that, when σ is given, the LRP rule is valid if & only if both of $d_1(\sigma)$, $d_2(\sigma)$ are positive.

We shall show that when $T<T_c$, both d_1 & d_2 are positive for all bounded (positive) values of $|\sigma|$, while, above T_c, there is a positive number, J, such that both of d_1, d_2 are negative for $0 < |\sigma| < J$, zero for $|\sigma| = J$ & positive for all bounded $|\sigma| > J$. The point $\sigma = 0$ is the "transition point" for temperatures below T_c.

Using (8) in (17) & substituting the result into (24), we obtain:

$$d_r(\sigma) = 3\,\mathrm{Rl}[\sigma f_p - \sigma f_r] + \mathrm{Rl}[f_p^2 - f_r^2] \qquad \text{VI(25)}$$

for all $T \neq T_c$ in cases A & B, while we have in Case C,

$$\left.\begin{aligned} d_1(\sigma) &= 3\,\mathrm{Rl}[\sigma f_p] + \mathrm{Rl}[f_p^2] + o(1) \\ d_2(\sigma) &= 3\,\mathrm{Rl}[\sigma f_p - \sigma f_2] + \mathrm{Rl}[f_p^2 - f_2^2] \end{aligned}\right\} \qquad \text{VI(26)}$$

for $T<T_c$;

$$d_r(\sigma) = o(1) - 3\,\mathrm{Rl}[\sigma f_r] - \mathrm{Rl}\,[f_r^2] \qquad \text{VI(27)}$$

for $T>T_c$.

Since the sum of the roots of (8) is zero, we have

$$f_p + f_1 + f_2 = 0 \qquad \text{VI(28)}$$

Further, by (19), (22) & the continuity of all roots when $\sigma \neq 0$, we find that

$$\sigma f_p(\sigma) > 0 \qquad \text{VI(29)}$$

for all (real or imaginary) bounded σ, ($\neq 0$) so that the identity $\frac{1}{3}\sigma f_p f_1 f_2 = \sigma^2$ (an immediate consequence of (8)) implies that

$$\text{sgn}\,(f_1 f_2) = \text{sgn}\,(\sigma^2) = \text{sgn}\,(T_c - T) \qquad \text{VI(30)}$$

where sgn (X) means the algebraic sign of X & (22) has been used again.

Suppose now that $T<T_c$. When $|\sigma| > \frac{2}{3}$, f_1, f_2 are complex conjugates of each other & hence, by (28) & the reality of f_p, each has real part $(-\frac{1}{2}f_p)$. When $\frac{2}{3} > |\sigma| > 0$, so that all the roots of (8) are real & nonvanishing, (30) implies that f_1, f_2 have the same sign — opposite to that of f_p — & we have the inequalities

$$|f_p| = |f_1| + |f_2| > |f_r|$$

for r = 1 or 2.

Consequently, we have the conditions:

$$3\sigma f_p(\sigma) > 3\,\text{Rl}[\sigma f_r(\sigma)] \qquad \text{VI(32)}$$

$$\text{Rl}[f_p^2 - f_r^2] = f_p^2 - \text{Rl}[f_r^2] > f_p^2 - (\text{Rl}[f_r])^2 > 0 \qquad \text{VI(33)}$$

which hold for all bounded $|\sigma|$ (>0) when $T<T_c$.

Using (29), (32) & (33) in (25) & (26), we conclude that both d_1 & d_2 are positive for all bounded $|\sigma|>0$ & $T<T_c$.

At the point $\sigma = 0$, we have, using (19) & the definition of $f_1(\sigma)$ for $T<T_c$,

$$d_1(0) > 0$$

$$\lim_{\sigma \to 0\pm} d_2(\sigma) = 0$$

so that the pressure is continuous across $\sigma = 0$, while f_p & f_2 "change places". It is just this interchange that produces the first order phase transition (discontinuity in the first derivative of $\overline{\Pi}(z)$) associated with van der Waals' equation of state.
When $T>T_c$, we use (21) - (23) in (25) & (27), obtaining

$$d_1(\sigma) = d_2(\sigma) = 6\text{shvsh}3v - 6\text{sh}^2v - 3 \equiv 3\ (\text{ch}4v - 2\text{ch}2v) \qquad \text{VI(34)}$$

in cases A & B; & in <u>case C</u>,

$$d_1(\sigma) = d_2(\sigma) = 2\text{shvsh}3v - 2\text{sh}^2v - 3 + o(1) = o(1) - 3.... \qquad \text{VI(35)}$$

where we are using the fact that $\sigma \approx 0$ (case C) implies that shv is o(1). If we define the numbers $\pm v_o$ to be the solutions of the equation $\text{ch}4v = 2\text{ch}2v$, & write

$$J \equiv \left|\tfrac{2}{3} \text{ sh } 3\ v_o\right| \qquad \text{VI(36)}$$

then we can summarize the behaviour of the functions d_1, d_2 for $T>T_c$, by

$$d_1(\sigma) = d_2(\sigma) \begin{cases} <0, & <|\sigma|<J \\ =0, & |\sigma| = J \\ >0, & J<|\sigma|<\infty \end{cases} \qquad \text{VI(37)}$$

as we anticipated.
To study the situation near the points $\sigma = \pm iJ$, we set

$$v = v_o + \lambda \ (|\lambda| << 1) \qquad \text{VI(38)}$$

which defines λ, & we suppose, also, that $|u| << 1$, so that

$$\left.\begin{aligned} \sin u &= u + O(u^3) \\ \cos u &= 1 + O(u^2) \end{aligned}\right\} \qquad \text{VI(39)}$$

We wish to characterize the set of points $\{\sigma\}$ such that one of the conditions

$$Rl[h_o - h_+] = 0, \quad Rl[h_o - h_-] = 0 \qquad VI(40)$$

holds, where h is given by (18) in cases A,B & is $o(1)$ in case C, & the subscripts o , +, -, indicate that we take u equal to O , $+\frac{2\pi}{3}$, $-\frac{2\pi}{3}$, respectively in (20). We denote these sets of points by C +, C- respectively. We note, first, that near the points $\sigma = \pm iJ$, case A applies to all of the roots of (8), so that, by combining (18) & (20), we obtain $h = 2\cos 4w - 4\cos 2w + 2$. VI(41).

On using (20), (38) & (39) in (41), we find that, to lowest order u, λ, the points of $C_{\pm}$ must satisfy the conditions.

$$12\lambda(\mathrm{sh}\,2v_o - \mathrm{sh}\,4v_o) = \pm 4\,3u(\mathrm{ch}2v_o + \mathrm{ch}4v_o) \qquad VI(42)$$

$$12\lambda(\mathrm{sh}\,4v_o - \mathrm{sh}\,2v_o) = \pm 4\,3u(\mathrm{ch}2v_o + \mathrm{ch}4v_o) \qquad VI(43)$$

where (42) applies to the point $\sigma = -iJ$ & (43) to the point $\sigma = +iJ$.

If we define the function B(t) by

$$B(t) \equiv \frac{\mathrm{sh}4t - \mathrm{sh}2t}{3(\mathrm{ch}4t + \mathrm{ch}2t)} \qquad VI(44)$$

where t is real, then we find that C_+ comprizes a straight line of gradient $+B^{-1}(|v_o|)$ through the point $\sigma = +iJ$ & a straight line of gradient $-B^{-1}(|v_o|)$ through the point $= -iJ$, while C_- consists of lines of gradients $-B^{-1}(|v_o|) + B^{-1}(|v_o|)$, respectively, through the same pair of points. We note from (44) that B(t) is an odd function of t & is positive when $t > O$. This specification of C_+, C_- is valid only near the points $\sigma = \pm iJ$, in accordance with (38) & (39).

To complete our description of the sets of points at which two branches of Π have LRP, we must consider $Rl[h_+ - h_-]$ for $|u| \ll 1$. Using (41), we obtain

$$Rl[h_+ - h_-] = -2\sqrt{3}\sin 2u\,(2\cos 2u \operatorname{ch} 4v + \operatorname{ch} 2v). \qquad \text{VI(45)}$$

Since $|u| \ll 1$, by assumption, cos u is always positive, while ch2v, ch4v are intrinsically positive. Further, (21) gives

$$Rl[\sigma] = -\frac{2}{3}\sin 3u \operatorname{ch} 3v. \qquad \text{VI(46)}$$

Combining (45) & (46), we obtain

$$Rl[h_+ - h_-] \gtrless 0 \iff Rl[\sigma] \gtrless 0 \qquad \text{VI(47)}$$

When $|u| \ll 1$.

(In fact (47) holds for a larger range of values of $|u|$, but this is irrelevant in the present calculation, in which only values of σ with real part near σ_c are important).

Finally, by (6), σ becomes imaginary with $\hat{z} + \frac{27}{4} k^2$ when $T < T_c$, so that the set of curves at whose points two branches of π have LRP for $T < T_c$ is obtained from the set for $T > T_c$ by an anticlockwise rotation through an angle $\frac{\pi}{2}$ about $\sigma = 0$. The corresponding sets of curves in the complex z-plane are sketched in Figure 1.

It only remains to treat the Case K = 0, which has already been studied by Hemmer & Hauge (1964).

On multiplying (6) by $\frac{27}{2} k^3$ and then setting K = 0, we obtain

$$\hat{z} = \frac{9}{2}\theta^3 - \frac{9}{4}\theta^4 + o(\theta^4) \qquad \text{VI(48)}$$

while (5) gives at once

$$\hat{\pi} = 12\,(\theta^3 + \theta^4) + o(\theta^4) \qquad \text{VI(49)}$$

in agreement with the expressions obtained by Hemmer & Hauge. (But note that our $\hat{\pi}$ is $\pi_c^{-1}(\pi-\pi_c)$, and Hemmer's is simply $\pi-\pi_c$).

To solve (48) for θ we write

$$\theta = (\frac{2}{9}\hat{z})^{\frac{1}{3}} + \alpha \qquad \text{VI(50)}$$

(which defines α). Substituting (50) into the right number of (49), we obtain to lowest order in $\hat{z}$:

$$\alpha = \frac{1}{6}(\frac{2}{9}\hat{z})^{2/3} . \qquad \text{VI(51)}$$

Using (50) & (51) in (49) we find that

$$\frac{1}{12}\hat{\pi}(\hat{z}) = \frac{2}{9}\hat{z} + \frac{3}{2}(\frac{2}{9}\hat{z})^{4/3} + o(\hat{z}^{4/3}), \qquad \text{VI(52)}$$

in agreement with our neglect of $o(\theta^4)$ in (48) & (49).

Let us write $\frac{2}{9}\hat{z} \equiv r_e^{i\varphi}$, where $-\pi \leq \varphi < \pi$

Then the tree possible values of $(2\hat{z}/9)^{4/3}$ for given $\hat{z}$ are

$$(\frac{2}{9}\hat{z})^{4/3} = r^{4/3} \exp\left[i(\frac{4}{3}\varphi + \frac{2s\pi}{3})\right] \qquad \text{VI(53)}$$

for S = 0,1,2.

When $\hat{z}$ is positive, we must take $\varphi = 0$. When $\hat{z}$ approaches a negative value through the lower half-plane, we take $\varphi = -\pi$; while, if $\hat{z}$ approaches a negative value through the upper half plane, we consider the limit process in which φ tends to $+\pi$ through positive values.

If we number the branches of $\hat{\pi}$ corresponding to S = 0,1,2 as I, II, III, respectively, we obtain the "lines of LRP" as shown in Figure 1. It may be verified from (53) that the branches II, III are equal on the real, negative $\hat{z}$ - axis, so that there is no discontinuity in the pressure across this line. We conclude that the LRP criterion is valid at $T = T_c$. For the physically meaningful values of $\hat{z}$ ($\hat{z}$ real) our results for the pressure agree with those obtained by Hemmer & Hauge (1964) using another criterion

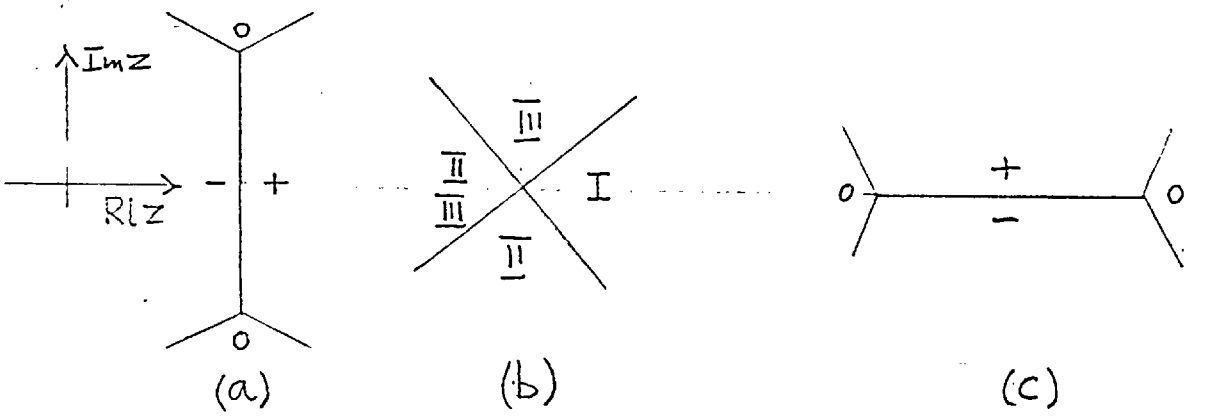

Figure 1. "Lines of L.R.P." in the complex Z - plane for (a) $T < T_c$ (b) $T = T_c$ (c) $T > T_c$.
The lines cut the real Z-axis at the point where $z = z_c(1-\frac{27}{4}k^2)$.

REFERENCES

Hemmer and Hauge (1964) Phys. Rev. 133, A. 1010

Acknowledgement

The General scheme of this proof is due to Penrose, who obtained similar results (in an unpublished calculation) by choosing from the outset a plausible form for $Z(\rho, \beta)$.