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Contribution to Statistical Mechanics*

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The method of the grand partition function may be used to calculate distribution functions $F_n(z, \{\mathbf{n}\})$ proportional to the probability that n molecules in a system of fugacity z , and fixed temperature, occupy the position of their coordinates symbolized by $\{\mathbf{n}\}$. The method makes use of the distribution functions $F_n(0, \{\mathbf{n}\})$ at zero fugacity. The distribution functions may be written $F_n(z, \{\mathbf{n}\}) = \exp[-W_n(z, \{\mathbf{n}\})/kT]$, in which $W_n(z, \{\mathbf{n}\})$ is the potential of average force of n molecules at the fugacity z , which becomes equal to the ordinary potential energy at zero fugacity. The equations may be generalized to permit the calculation of the distribution functions at

any fugacity assuming a knowledge of them at any other fugacity. Using methods previously employed for imperfect gases, the pressure, and also the density in molecules per unit volume, may be developed in a power series of difference of fugacity around any arbitrary fugacity. The coefficients of these developments are calculable at all fugacities by the same equations always employing the potentials of average force at the fugacity around which the development is made. The power series obtained represent functions which are regular on the real positive axis of fugacity except at the points characteristic of the phase transitions in the system.

INTRODUCTION

WE consider only systems of infinite extent in the volume space, the temperatures of which are fixed at T . The systems are one component systems, containing only one kind of molecule. Instead of using pressure P or density ρ for the independent variable of the system we shall find it convenient to use the fugacity, normalized in density units, for which the symbol z or y will be used. The definition of this fugacity may be written:

$$z = \lim_{\rho \rightarrow 0} [\rho_0 \exp(\mu - \mu_0)/kT], \quad (1)$$

in which μ is the chemical potential of the system, and μ_0 is the chemical potential at the density ρ_0 . The density is expressed in molecules per unit volume, $\rho = \lim (N/V)$. According to this definition of z , as the fugacity is reduced to such a value that the system becomes a perfect gas the fugacity and density become equal:

$$\lim_{z \rightarrow 0} \left[\frac{z}{\rho} \right] = 1. \quad (2)$$

The individual molecule requires f coordinates for the description of its configuration, and three of these may always be chosen as the three cartesian coordinates, x, y, z , of the center of mass. The $f-3$ internal coordinates are either bounded between limits such as 0 and 2π , or the

internal energy of the molecule is assumed to approach infinity as the value of the coordinate becomes large. The coordinates of the molecule i will be symbolized by

$$(i) = x_i, y_i, z_i, q_{1i}, \dots, q_{(f-3)i}, \quad (3)$$

and the volume element, calculated in the f dimensional cartesian space by

$$d(i) = dx_i dy_i dz_i J \left[\frac{x}{q} \right] dq_{1i} \dots dq_{(f-3)i}, \quad (4)$$

in which J is the Jacobian. The coordinates of n molecules will be indicated by

$$\{\mathbf{n}\} = (1), (2), \dots, (i), \dots, (n), \quad (5)$$

and the volume element by

$$d\{\mathbf{n}\} = d(1)d(2) \dots d(i) \dots d(n). \quad (6)$$

The distribution function $F_n(z, \{\mathbf{n}\})$, a function of the coordinates of n molecules, is defined by the statement that in an infinite system of fugacity z the probability that n molecules be at the position symbolized by $\{\mathbf{n}\}$, and in the element of configuration space $d\{\mathbf{n}\}$ is proportional to $F_n(z, \{\mathbf{n}\})d\{\mathbf{n}\}$:

$F_n(z, \{\mathbf{n}\})$ is proportional to probability of the configuration $\{\mathbf{n}\}$, (7)

and the normalization is so chosen that

$$\lim_{V \rightarrow \infty} \left[\frac{1}{V^n} \int \int \dots \int F_n(z, \{\mathbf{n}\}) d\{\mathbf{n}\} \right] = 1; \quad (8)$$

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the average value of the function F_n integrated over the internal coordinates of the molecules is unity in the $3n$ -dimensional cartesian space of the coordinates of the centers of mass.

Functions $W_n(z, \{\mathbf{n}\})$ of the coordinates of n molecules in a system of fugacity z may be defined by the equation

$$-W_n(z, \{\mathbf{n}\})/kT = \ln F_n(z, \{\mathbf{n}\}). \quad (9)$$

These functions are actually the potentials of the average forces between n molecules in an infinite system of the fugacity z .

At zero fugacity the density is zero, and the n molecules are isolated in space. In a classical system the distribution function at zero density is proportional to the exponent of minus the potential energy divided by kT . We see, then, that for a classical system

$$W_n(0, \{\mathbf{n}\}) = U_n\{\mathbf{n}\} \quad (\text{classical}). \quad (10)$$

If the deviations due to quantization from the classical equations are large the function $W_n(0, \{\mathbf{n}\})$ is generally a function of the temperature, but will still have such properties of the potential energy as will be made use of in this article. For convenience we shall refer to W_n at zero fugacity as the potential energy, but the use of the equations of this article is in no way restricted to classical systems.¹ For a quantum mechanical system the function $W_n(0, \{\mathbf{n}\})$ must be calculated by means of a Slater sum. An alternative and probably more satisfactory method of handling the case of a system of molecules having internal quantized degrees of freedom would be to replace the internal coordinates by the corresponding set of quantum numbers and replacing integration in the equations of this article by summation over the discrete values of the internal quantum numbers. In general the functions of the coordinates of the centers of mass may be handled as classical, but the functions would be different for different values of the internal quantum numbers.

In the succeeding section we shall construct an equation relating the distribution functions at two different fugacities, z and $y+z$.

¹ See, for instance, the analogous treatment of quantum mechanical systems by B. Kahn and G. E. Uhlenbeck, *Physica* 5, 237 (1938), and by J. de Boer, *Dissertation*, Amsterdam (1940).

GENERALIZATION OF THE GRAND PARTITION FUNCTION

For reasons of brevity we introduce the symbol

$$\varphi(z) = P(z)/kT, \quad (11)$$

with $P(z)$ the pressure.

The probability $P_n(V, z, \{\mathbf{n}\})d\{\mathbf{n}\}$ that in an infinite system of fugacity z , there will be within the finite volume V exactly n and no more molecules, located at the position indicated by the symbol $\{\mathbf{n}\}$ (for which all n centers of mass are within V), and within the element $d\{\mathbf{n}\}$ of the configuration space, is known, from the theory of the grand partition function, to be given by

$$P_n(V, z, \{\mathbf{n}\}) = [\exp - V\varphi(z)] z^n F_n(0, \{\mathbf{n}\}). \quad (12)$$

The probability that there be exactly n molecules within V , without reference to their positions, is obtained by dividing the integral of this function over the volume V by $n!$, since integration covers $n!$ equivalent positions differing only in permutations of the identical molecules. The probability of having no molecules in V is $\exp - V\varphi(z)$. The sum of these probabilities over all n values, 0 to ∞ , is unity. It follows that

$$\exp V\varphi(z) = \sum_{n=0}^{\infty} \frac{z^n}{n!} \int \cdots \int_V F_n(0, \{\mathbf{n}\}) d\{\mathbf{n}\}, \quad (13)$$

which is one of the usual forms of the grand partition function.

The volume V must be macroscopically large so that the influence of surface effects is negligible. It is to be noted that the normalization of Eq. (8) applies only to the limit of infinite volume, and the integral of F_n over the finite volume V is not, in general, V^n .

For finite volumes V and real systems with short range repulsive forces the sum in (13) always converges, since the repulsive energy at short distances assures us that for sufficiently large values of n the integrand F_n approaches zero over the whole range of integration. Since the series is regular to infinite values of the fugacity, singularities in the pressure, indicative of phase transitions, appear only by going to the limit of infinite volume.¹

The probability that in an infinite system of fugacity z , there be at the n points $\{\mathbf{n}\}$, in the element $d\{\mathbf{n}\}$, one molecule at each point, irrespective of the positions of other molecules in the system, is $[\rho(z)]^n F_n(z, \{\mathbf{n}\}) d\{\mathbf{n}\}$. This probability will be equal to the sum of probabilities constructed in the following way. We enclose the n points by a singly connected volume V . The probability that there be a molecule at each of the n points, $\{\mathbf{n}\}$, and exactly m other molecules somewhere in V will be the integral of $P_{n+m}(V, z, \{\{\mathbf{n}\} + \{\mathbf{m}\}\}) d\{\mathbf{n} + \mathbf{m}\}$ over all positions $\{\mathbf{m}\}$ within V divided by $m!$. The probability desired is the sum of these probabilities over all values of m :

$$[\rho(z)]^n F_n(z, \{\mathbf{n}\}) = \sum_{m=0}^{\infty} \int_V \cdots \times \int P_{n+m}(V, z, \{\mathbf{n} + \mathbf{m}\}) d\{\mathbf{m}\}. \quad (14)$$

In order to obtain somewhat simpler appearing equations later we introduce

$$Q_n(z, \{\mathbf{n}\}) = \left[\frac{\rho(z)}{z} \right]^n F_n(z, \{\mathbf{n}\}), \quad (15)$$

and note that in view of Eq. (2),

$$Q_n(0, \{\mathbf{n}\}) = F_n(0, \{\mathbf{n}\}). \quad (15')$$

Introducing (15') in (14), and using (15) and (12), one finds, with the completely arbitrary introduction of $\exp V\varphi(0) = 1$, since $\varphi(0) = 0$,

$$[\exp V\varphi(z)] Q_n(z, \{\mathbf{n}\}) = \sum_{m=0}^{\infty} \frac{z^m}{m!} [\exp V\varphi(0)] \times \int_V \cdots \int Q_{n+m}(0, \{\mathbf{n} + \mathbf{m}\}) d\{\mathbf{m}\}. \quad (16)$$

The convention

$$Q_0(z) = 1 \quad (16')$$

is used. With (16') Eq. (13) is seen to be a special case of (16).

For all finite values of V , and for real systems of molecules with short range forces and repulsion

at short distances, the sum of (16) converges for the same reason discussed in connection with (13). Furthermore, for finite values of V , the functions $Q_n(z, \{\mathbf{n}\})$ for sufficiently large values of n are seen to approach zero in value for all values of the argument $\{\mathbf{n}\}$ within the volume V .

We form the permanently convergent sum

$$I_n\{\mathbf{n}\} = \sum_{m=0}^{\infty} \frac{(-z)^m}{m!} [\exp V\varphi(z)] \times \int_V \cdots \int Q_{n+m}(z, \{\mathbf{n} + \mathbf{m}\}) d\{\mathbf{m}\}. \quad (17)$$

Into this the expression (16) for $Q_{n+m}(z, \{\mathbf{n} + \mathbf{m}\})$ is inserted:

$$I_n\{\mathbf{n}\} = \sum_{m=0}^{\infty} \sum_{k=0}^{\infty} \frac{z^{m+k} (-)^m}{m! k!} [\exp V\varphi(0)] \times \int_V \cdots \int Q_{n+m+k}(0, \{\mathbf{n} + \mathbf{m} + \mathbf{k}\}) d\{\mathbf{m} + \mathbf{k}\}.$$

It is seen that for any given value of $m+k$ the sum of the coefficients is $(1-1)^{m+k}$ so that only the term $m=0, k=0$, remains. It follows that $I_n\{\mathbf{n}\} = [\exp V\varphi(0)] Q_n(0, \{\mathbf{n}\})$. One may write

$$[\exp V\varphi(0)] Q_n(0, \{\mathbf{n}\}) = \sum_{m=0}^{\infty} \frac{(-z)^m}{m!} [\exp V\varphi(z)] \times \int_V \cdots \int Q_{n+m}(z, \{\mathbf{n} + \mathbf{m}\}) d\{\mathbf{m}\}. \quad (18)$$

Let us now form $[\exp V\varphi(y+z)] Q_n(y+z, \{\mathbf{n}\})$, for the fugacity $y+z$, by inserting $y+z$ instead of z in the right-hand side of Eq. (16). Into this expression Eq. (18) for $[\exp V\varphi(0)] Q_{n+m}(0, \{\mathbf{n} + \mathbf{m}\})$ may be inserted. The resulting expression gives an explicit equation for the functions at the fugacity $y+z$ in terms of a double summation over numbers m and k of integrals of the functions at the fugacity z of $n+m+k$ molecules. For constant value of $m+k$ the coefficient is the sum of $(y+z)^m (-z)^k / m! k!$ over all values m with $m+k$ constant. The value of this sum is

$y^{m+k}/(m+k)!$. One obtains

$$[\exp V\varphi(y+z)]Q_n(y+z, \{\mathbf{n}\}) \\ = \sum_{m=0}^{\infty} \frac{y^m}{m!} [\exp V\varphi(z)] \\ \times \int_V \cdots \int_V Q_{n+m}(z, \{\mathbf{n}+\mathbf{m}\}) d\{\mathbf{m}\}. \quad (19)$$

Equation (19) might be regarded as a generalization of the equation of the grand partition function. The special case $z=0$ leads to Eq. (16). The case $y=-z$ leads to Eq. (18). The case $n=0$, with the convention (17) leads to an equation for the pressure $P=kT\varphi$, Eq. (11). In the usual formulation of the theory of the grand partition function the potential energy $U_n\{\mathbf{n}\}$ of n isolated molecules plays a singular role. In the formulation of Eq. (19) the fugacity zero, for which $W_n=U_n$, Eq. (10), is not singled out as exceptional, but the potentials of average force at any two different fugacities are connected.

For finite values of V , and for real systems with short range forces and repulsion on close approach, the sum of Eq. (19) is permanently convergent for all values of y . There are, consequently, no singularities in the functions φ or Q if these are calculated by using finite V values. There will, however, be enormously sharp breaks in the plot of these functions against y if macroscopic volumes are used. The equation implicitly assumes that the limit of infinite volume is used.

Equation (19) is entirely unsuitable, without transformation, for numerical solution, and for the same reason that the sharp breaks in the functions of y occur at large values of V , namely because for finite y and macroscopic values of V numerical convergence only sets in at enormously high terms: the largest term in the sum is that for which m is about 10^{23} . In the next section we shall show one method, of limited value, by which numerical computations may be attempted.

THE DEVELOPMENT OF Q_n AS A SUM OF SEPARABLE FUNCTIONS

The equations of the last section have been derived almost without reference to the form of the functions $Q_n(z, \{\mathbf{n}\})$ for different values of n .

It was only necessary to assume the absolute convergence of the various sums appearing, which was assured by the assumption of a repulsive energy of sufficient magnitude.

In view of their definition in terms of probabilities, all the functions $Q_n(z, \{\mathbf{n}\})$ must be positive. It is seen from (19) that if the $Q_n(0, \{\mathbf{n}\})$ are all positive, then the $Q_n(z, \{\mathbf{n}\})$ will all be positive for real positive values of the fugacity. The functions at zero fugacity are generally regarded as defining the system, being themselves defined in terms of the potential energy $U_n\{\mathbf{n}\}$ by (10), (9), and (15'). As long as the potential energy is real the functions at zero fugacity are positive.

Most methods of attempting to obtain the properties of systems in the liquid state make implicit use of the assumption that the potentials of average force, $W_n(z\{\mathbf{n}\})$, and the distribution functions Q_n , at the fugacity z can undergo arbitrary small variations away from the equilibrium values, without leading to geometrical inconsistencies in their definitions as probabilities.

Some light may be shed on whether this is justifiable by a consideration of Eq. (19). Arbitrary functions $Q_n(z, \{\mathbf{n}\})$ could only represent a conceivable geometrical configuration of molecules at the fugacity z if the functions themselves were positive, and if the functions $Q_n(0, \{\mathbf{n}\})$, calculated from (19) with $y=-z$ were also positive. This condition is necessary and sufficient.

Now it can be independently shown that an arbitrary set of functions $F_n\{\mathbf{n}\}$ obeying conditions which will be set forth in the latter part of this section (namely, Eqs. (25), (26), and (27)) represents geometrically possible distribution functions of any finite numbers of molecules in an infinite system, provided the total density in the system is less than some value ρ_0 , but are geometrically inconceivable as distribution functions if the density is assumed to exceed this value. The proof follows somewhat later.

The experimental functions $Q_n(z, \{\mathbf{n}\})$ in a real system obey Eq. (19) leading to functions $Q_n(0, \{\mathbf{n}\})$ of the real system, which are, of course, positive. Now suppose that we were to use Eq. (19) to calculate certain hypothetical functions, $Q_n(-\epsilon, \{\mathbf{n}\})$, $\epsilon > 0$, for which ρ would have the negative value, $-\alpha$. As long as ϵ

remains small (but not necessarily infinitesimal), the functions $Q_n(-\epsilon, \{\mathbf{n}\})$ will remain positive; indeed, this will presumably be the case at least up to values of ϵ equal to the fugacity at which condensation occurs if the temperature is below the critical point. The functions $Q_n(z, \{\mathbf{n}\})$ of this system would then represent the distribution functions in another system for which the fugacity is $z+\epsilon$, and for which the distribution functions at zero fugacity were $Q(-\epsilon)$, and which would have a higher density than the first. It follows that the distribution functions of a real system are permissible geometrical representations of the distribution of molecules at a higher density than the real density of the system.

If we now only assume that the limiting density ρ_0 , characteristic of the distribution functions, is a continuous function of the form of the functions $F_n\{\mathbf{n}\}$, then an arbitrary infinitesimal variation in the form of the actual distribution functions of a real system will not lead to functions which are geometrically unrealizable as probability functions for the distribution of molecules at the density of the system.

It remains necessary to prove that there is one limiting density ρ_0 for a given assumed set of distribution functions, $F_n\{\mathbf{n}\}$.

Such an assumed set of distribution functions must first obey the conditions imposed on any probability functions, that

$$\lim_{V \rightarrow \infty} \left[\frac{1}{V} \int \int \cdots \int F_n\{\mathbf{n}\} d(i) \right] = F_{n-1}\{\{\mathbf{n}\} - (i)\}, \quad (20)$$

in which the division of the integral by V is required by the normalization of Eq. (8). The set of functions will obey (20) if

$$\lim_{r_{ni} \rightarrow \infty} [F_{n+1}\{\{\mathbf{n}\} + (i)\}] = F_n\{\mathbf{n}\} F_1(i), \quad (21)$$

and the approach F_{n+1} to the product $F_n F_1$ is sufficiently rapid as the distance r_{ni} between the molecule i and the nearest member of the set $\{\mathbf{n}\}$ increases. This condition will be satisfied for finite values of n if the functions are constructed according to (25) and (26), as discussed later. If (27) is also satisfied we have a self-

consistent scheme of constructing functions $F_n\{\mathbf{n}\}$, up to any finite value of n , which represent possible geometrical distributions of n molecules in an infinite space, and therefore at zero density.

We now ask whether such a set of functions, defined up to some given n , can represent the distribution of a set of n molecules in a system of volume V (n/V negligibly small) in which there are a total of N molecules with $N/V = \rho$. The question is equivalent to asking whether there exists a positive function $F_N\{\mathbf{N}\}$ of the coordinates $\{\mathbf{N}\}$ of all the molecules in the system for which

$$\frac{1}{V^{N-n}} \int \int \cdots \int_V F_N\{\mathbf{N}\} d\{\mathbf{N} - \mathbf{n}\} = F_n\{\mathbf{n}\}.$$

But if such a positive function does exist for N molecules there also exists one for $N-k$ molecules, namely, that obtained by integrating $F_N\{\mathbf{N}\}$ over the coordinates of k molecules, and dividing by V^k . Conversely if no such function exists for N , then no such function exists for a number of molecules greater than N . It is also trivial to see that for the type of distribution functions occurring in nature, namely, those for which repulsion between molecules exists, and $F_n\{\mathbf{n}\}$ approaches zero if two molecules are too close together, the upper limit N_0 , for which such a positive distribution function can be found, is not, in general, infinity. It follows that for any arbitrarily defined set of distribution functions obeying (20), there exists a density $N_0/V = \rho_0$ such that the distribution functions represent a conceivable geometrical distribution of molecules in any system of density equal to or less than ρ_0 , but not at higher densities.

We propose to seek solutions for the set of Eqs. (19) for which the distribution functions $Q_n(z, \{\mathbf{n}\})$ obey certain restricting conditions. The conditions themselves will be discussed first, and secondly whether the limitations are to be expected to be applicable to real systems.

We wish to seek only solutions for which the distribution functions of two distant subsets of molecules $\{\mathbf{n}\}$ and $\{\mathbf{m}\}$ are equal to the product of the distribution functions of the two subsets separately. If r_{nm} is used to signify the distance, in the three-dimensional cartesian space of the

centers of mass of the molecules, of the two nearest molecules belonging to different sets $\{\mathbf{m}\}$ and $\{\mathbf{n}\}$, then we wish to assume that always,

$$\lim_{r_{nm} \rightarrow \infty} [Q_{n+m}(z, \{\mathbf{n}+\mathbf{m}\})] = Q_n(z, \{\mathbf{n}\})Q_m(z, \{\mathbf{m}\}). \quad (22)$$

We shall use the symbol $\{\mathbf{v}\}_n$ to indicate the coordinates of a set of ν molecules, all of which are members of the set $\{\mathbf{n}\}$, and $\sum \{\mathbf{v}\}_n$ to indicate summation over all possible subsets of the set $\{\mathbf{n}\}$ including the improper subset $\{\mathbf{v}\}_n = \{\mathbf{n}\}$. Using the functions $W_n(z, \{\mathbf{n}\})$ defined by (9) we may formally define functions $w_\nu(z, \{\mathbf{v}\})$ by the equation

$$w_\nu(z, \{\mathbf{v}\}) = \sum \{\mathbf{n}\}_\nu (-)^{\nu-n} W_n(z, \{\mathbf{n}\}), \quad (23)$$

for which the inverse is

$$W_n(z, \{\mathbf{n}\}) = \sum \{\mathbf{v}\}_n w_\nu(z, \{\mathbf{v}\}), \quad (24)$$

in which the functions w_ν will be referred to as the component potentials of average force.

Taking the logarithm of (22), using (15) and (9), one sees that the assumption of Eq. (22) is equivalent to the assumption that

$$\lim_{r_{\nu\mu} \rightarrow \infty} [w_{\nu+\mu}(z, \{\mathbf{v}+\mathbf{u}\})] = 0, \quad (25)$$

namely, that the component potentials of average force approach zero in value if any one of the molecules of the set is far distant from all the other molecules of the set, or more generally, if the set breaks naturally into two or more distant subsets of molecules.

The use of Eq. (24) to represent the total potential of n molecules as a sum of terms each depending on the coordinates of a subset of the molecules alone, is usual at zero fugacity, for which the potential of average force is the true potential of the isolated molecules. For systems with van der Waals forces it is usually written with the drastic assumption that the total potential is the sum of the potentials of the single molecules $w_1(0, (i))$, plus the sum over all pairs of the mutual pair potentials $w_2(0, \{(i)+(j)\})$, which in our terminology would be assuming that $w_\nu = 0$, $\nu \geq 3$. The assumption of Eq. (25) is essentially only that all forces fall to zero between distant molecules.

We wish, however, to make a more restrictive assumption than (25), namely, that the approach to zero is sufficiently rapid so that the integral

$$\lim_{V \rightarrow \infty} \left[\int \int \cdots \int_V [\exp -w_\nu(z, \{\mathbf{v}\})/kT - 1] \times \prod_{i=1}^{\nu} [\exp -w_1(z, (i))/kT] d\{\mathbf{v}-1\}, \quad (26)$$

remains finite even if the volume V over which the range of integration is extended approaches infinite limits. The assumption of finite values for (26) will not be valid for $w_2(0, \{(i)+(j)\})$ if the molecules i and j are charged. In all other cases of physical significance it appears to be likely that the assumption is justified.

We wish actually to assume that the terms w_ν of Eq. (24) converge very rapidly, and that terms with $\nu \geq 3$ are sufficiently unimportant that useful results may be obtained with their neglect. This assumption is in no way formally required, but any numerical computation involving the higher terms must necessarily be tedious, at least. Formally, however we shall have to assume that

$$\lim_{\nu \rightarrow \infty} [w_\nu(z, \{\mathbf{v}\})] = 0 \quad (\text{for all configurations } \{\mathbf{v}\}). \quad (27)$$

The assumptions of Eqs. (25), (26), and (27), will presumably be accepted as reasonable assumptions for systems composed of uncharged molecules at such temperatures and fugacities for which the liquid or gaseous phases are stable. The validity of the assumptions in the case that the crystalline phase is stable requires special consideration.

For a single crystal of fixed direction of the crystal axes, and with fixed phase of the lattice points along the axes, it appears to be natural to accept all three assumptions as valid for the distribution function. Such a crystal will be referred to as a fixed crystal. The function $w_1(z, (i))$ will be triply periodic in the coordinates of the center of mass of the molecule i . The periodicity of this function alone determines the long range order in the crystal. The function $w_2(z, \{(i)+(j)\})$ would also be expected to be triply periodic, with the same periodicity of the

lattice, in a rigid translation of the two centers of mass of the two molecules i and j together. (It might, however, conceivably be accidentally invariant under such a translation.) The function w_2 determines the extent of the correlation between the positions of the two molecules, and must, in a real system, approach zero for large distances between the two molecules. It must also, in a real system, approach positively infinite values as the distance between the two molecules becomes small, assuring zero probability for the two molecules to be at the same position.

There seems, however, to be no simple way to insert boundary conditions into the grand ensemble upon which Eq. (19) is based, in such a way as to assure us that the solutions obtained would correspond to those of a fixed crystal. It is true that Kirkwood and Monroe² in their theory of fusion have obtained periodic solutions for w_1 by a method which is not essentially dissimilar to that which can be based on (19). However, the absence of satisfactory existence theorems for the type of non-linear integral equation which they were forced to solve, and the necessity which they faced of making several assumptions, may still leave possible doubt as to the validity of the result.

It might seem at first sight as though there were no difficulty. The solution expected from such an equation as (19) would correspond to the distribution functions for an ensemble of randomly oriented crystals with random phase of the lattice points for each orientation. Such a distribution function will be a linear combination of those corresponding to the fixed crystals. The solution of an integral equation derived by operating on (19) may well be expected to correspond to that of a fixed crystal with fixed but arbitrary axes and phase, so that the general solution would be a linear combination of these with all axes and phases. The difficulty arises in that the equations lead directly to the potentials of average force, and under the assumptions which we have made in Eqs. (25), (26), and (27).

The linear combination of *distribution functions* corresponding to an ensemble of fixed crystals will not correspond to a linear combination of

potentials of average force, and the potentials of average force of such a linear combination will most certainly *not* obey the condition (22). None of the assumptions (25), (26), or (27) will be valid for the potentials of average force obtained from the distribution functions for an ensemble of crystals by Eq. (9).

We propose to show, however, that solutions corresponding to one single fixed crystal would be expected, if a system is assumed whose characteristics go over in the limit to those of the real system. It appears therefore to be probable, even aside from the success of Kirkwood and Monroe, that distribution functions corresponding to one fixed crystal, and obeying (25), (26), and (27), would be solutions to equations based on (19) and solved with the usual limits of accuracy in the treatment of the grand partition function.

Consider a real system, characterized by its component potentials $w_v(0, \{\mathbf{v}\})$ at zero fugacity, for which the solutions of Eq. (19) at T and \mathbf{z} would be expected to be functions corresponding to an ensemble of crystals with randomly oriented axes. The component potential $w_1(0, (i))$ of molecule i of this system is independent of the coordinates of the center of mass. Consider, now, a second system, consisting of a finite number N of molecules, but otherwise differing from the first only in an additive triply periodic term $w'_1(0, (i))$ in the component potentials of each of the single molecules, which has the periodicity of one of the fixed crystals of the equilibrium ensemble of the first system at T and \mathbf{z} . The average value of w'_1 may be chosen as zero, and its amplitude as proportional to $N^{-1} \ln N$. The equilibrium configuration of this system will be that of a single fixed crystal, the orientation of which will be determined by the periodic external field, and the relative probability of this orientation to a random one will be proportional to some power of N , approaching infinity as the size of the system becomes infinite. Similarly the equilibrium configuration of a finite portion of volume V of this infinite system will be that of a single fixed crystal. But as the number N of molecules in the ensemble approaches infinity, the functions $Q_n(0, \{\mathbf{n}\})$ of any finite number n of molecules approach the same value as the corresponding functions of the

² John G. Kirkwood and Elizabeth Monroe, J. Chem. Phys. 9, 514 (1941).

first system without the periodic external field. For solutions of (19) at finite values of V only functions Q_n with n finite enter. We must expect functions $Q_n(z, \{\mathbf{n}\})$ corresponding to a single fixed crystal to be *also* solutions of (19) for the original system, without the periodic field, as well as those not obeying the conditions (25), (26), and (27), corresponding to an ensemble of randomly oriented crystals.

The apparent contradiction of postulating two different solutions to (19), which in the form $z=0$, consists of a set of completely solved equations for the different $Q_n(y, \{\mathbf{n}\})$ functions of different n values, is resolved by the fact that the equation must always be solved by one of a number of various approximation methods. It is assumed that as V becomes large the influence of the surface is immaterial, and the "true" solutions are obtained without reference to the surface conditions.

Condition (27) assumes that the functions

$Q_n(z, \{\mathbf{n}\})$ for large but finite values of n are completely determined in their functional dependence on the coordinates $\{\mathbf{n}\}$ by a finite (and numerically to a good approximation by a small) number of functions $w_\nu(z, \{\mathbf{v}\})$.

Functions $Q_n(z, \{\mathbf{n}\})$ obeying condition (22), and therefore also (25), may be conveniently written in various ways as sums of products of functions which are separable in the coordinates of subsets $\{\mathbf{v}\}_n$ of the set of molecules $\{\mathbf{n}\}$.

Condition (26) is required in order that the integral over the functions of the subsets converge.

For instance, we may write Q_n as the sum, $\sum \{k\{\mathbf{v}_i\}_n\}_u$, over all possible sets, $\{k\{\mathbf{v}_i\}_n\}_u$, for various k values, of k unconnected subsets $\{\mathbf{v}_i\}_n$ of the set $\{\mathbf{n}\}$, of products of functions of these subsets $\{\mathbf{v}_i\}_n$. By unconnected subsets we mean that no member occurs in more than one subset, but every member of the set $\{\mathbf{n}\}$ occurs in one of the k subsets of every set of subsets. We write

$$Q_n(z, \{\mathbf{n}\}) = \sum \{k\{\mathbf{v}_i\}_n\}_u \prod_{i=1}^{i=k} [\rho(z)/z]^v g_\nu(z, \{\mathbf{v}_i\}_n), \quad (28)$$

for which the inverse is

$$g_\nu(z, \{\mathbf{v}\}) = [z/\rho(z)]^v \sum \{k\{\mathbf{n}_i\}_\nu\}_u (-)^{k-1} (k-1)! \prod_{i=1}^{i=k} Q_n(z, \{\mathbf{n}_i\}_\nu). \quad (29)$$

We define the cluster integrals as

$$b_\nu(z) = \frac{1}{V_\nu!} \int \int \cdots \int_V g_\nu(z, \{\mathbf{v}\}) d\{\mathbf{v}\}, \quad (30)$$

which are, in the limit of infinite V , finite and independent of V for all finite values of ν , in view of (26).

Using (30) in (28) one finds

$$\int \int \cdots \int_V Q_n(z, \{\mathbf{n}\}) d\{\mathbf{n}\} = n! \sum_{n_\nu \geq 0} (\sum n_\nu = n) \prod_{\nu \geq 1} \frac{1}{n_\nu!} \{V b_\nu(z) [\rho(z)/z]^v\}^{n_\nu}, \quad (31)$$

since the number of ways that one can arrange n numbered objects in piles, n_ν piles of ν objects each, is $n!/\prod n_\nu! (\nu!)^{n_\nu}$ with $\sum n_\nu = n$. The normalization (8) of F_n , with (15), shows that

$$\lim_{V \rightarrow \infty} \left\{ \frac{1}{V^n} \int \int \cdots \int_V \left[\frac{z}{\rho(z)} \right]^n Q_n(z, \{\mathbf{n}\}) d\{\mathbf{n}\} \right\} = [b_1(z)]^n = 1, \quad (32)$$

or

$$b_1(z) = 1, \quad (32')$$

which fixes the arbitrary constant in $w_1(z, (i))$ so that the normalization (8) is valid.

We must also be able to integrate the function $Q_{n+m}(z, \{\mathbf{n}+\mathbf{m}\})$ over the limited number of coordinates of the set $\{\mathbf{m}\}$. It is somewhat more convenient to write our definitions in terms of the functions $F_n(z, \{\mathbf{n}\})$, related to the Q_n 's by the simple proportionality of Eq. (15). We define functions $G_{n\mu}(z, \{\mathbf{n}\}, \{\mathbf{u}_i\}_m)$ by

$$F_{n+m}(z, \{\mathbf{n}+\mathbf{m}\}) = F_n(z, \{\mathbf{n}\}) \sum \{k\{\mathbf{u}_i\}_m\}_u \prod_{i=1}^{i=k} G_{n\mu}(z, \{\mathbf{n}\}, \{\mathbf{u}_i\}_m), \quad (33)$$

for which the inverse is

$$G_{n\mu}(z, \{\mathbf{n}\}, \{\mathbf{u}\}) = \sum \{k\{\mathbf{m}_i\}_\mu\}_u (-)^{k-1} (k-1)! \prod_{i=1}^{i=k} [F_{n+m}(z, \{\{\mathbf{n}\} + \{\mathbf{n}\mathbf{m}_i\}_\mu\}) / F_n(z, \{\mathbf{n}\})]. \quad (34)$$

If the molecules of the set $\{\mathbf{u}\}$ and those of the set $\{\mathbf{n}\}$ are all distant in the three-dimensional space of the centers of mass, the functions $G_{n\mu}(z, \{\mathbf{n}\}, \{\mathbf{u}\})$ approach the functions $g_\mu(z, \{\mathbf{u}\})$ in value.

We make use of this latter fact and write

$$G_{n\mu}(z, \{\mathbf{n}\}, \{\mathbf{u}\}) = g_\mu(z, \{\mathbf{u}\}) + \sum \{\mathbf{v}\}_n g_{v\mu}(z, \{\mathbf{v}\}_n, \{\mathbf{u}\}), \quad (35)$$

for which the inverse is

$$\begin{aligned} g_{v\mu}(z, \{\mathbf{v}\}, \{\mathbf{u}\}) &= \sum \{\mathbf{n}\}_v (-)^{v-n} [G_{n\mu}(z, \{\mathbf{n}\}_v, \{\mathbf{n}\}) - g_\mu(z, \{\mathbf{u}\})] \\ &= (-)^v g_\mu(z, \{\mathbf{u}\}) + \sum \{\mathbf{n}\}_v (-)^{v-n} G_{n\mu}(z, \{\mathbf{n}\}_v, \{\mathbf{u}\}). \end{aligned} \quad (36)$$

The functions $g_{v\mu}$ approach zero in value if any one of the molecules of the set $\{\mathbf{u}\}$ is sufficiently distant from all members of the set $\{\mathbf{v}\}$.

We may substitute (34) for $G_{n\mu}$ in (36) and obtain

$$\begin{aligned} g_{v\mu}(z, \{\mathbf{v}\}, \{\mathbf{u}\}) &= \sum \{\mathbf{n}\}_v \sum \{k\{\mathbf{m}_i\}_\mu\}_u (-1)^{v-n+k-1} (k-1)! \\ &\quad \left\{ \prod_{i=1}^{i=k} F_{n+m}(z, \{\{\mathbf{n}\}_v + \{\mathbf{m}_i\}_\mu\}) / F_n(z, \{\mathbf{n}\}_v) - \prod_{i=1}^{i=k} F_m(z, \{\mathbf{m}_i\}_\mu) \right\}, \end{aligned} \quad (37)$$

or with (35) in (33) one finds

$$F_{n+m}(z, \{\mathbf{n}+\mathbf{m}\}) = F_n(z, \{\mathbf{n}\}) \sum \{k\{\mathbf{u}_i\}_m\}_u \prod_{i=1}^{i=k} \{g_\mu(z, \{\mathbf{u}_i\}_m) + \sum \{\mathbf{v}\}_n g_{v\mu}(z, \{\mathbf{v}\}_n, \{\mathbf{u}_i\}_m)\}. \quad (38)$$

In terms of the functions Q , using (15), this becomes

$$\begin{aligned} Q_{n+m}(z, \{\mathbf{n}+\mathbf{m}\}) &= Q_n(z, \{\mathbf{n}\}) \sum \{k\{\mathbf{u}_i\}_m\}_u \prod_{i=1}^{i=k} \{[\rho(z)/z]^\mu g_\mu(z, \{\mathbf{u}_i\}_m) \\ &\quad + \sum \{\mathbf{v}\}_n [\rho(z)/z]^\mu g_{v\mu}(z, \{\mathbf{v}\}_n, \{\mathbf{u}_i\}_m)\}. \end{aligned} \quad (38')$$

It is seen that with $Q_0=1$, Eq. (28) is the special case of (38') with $n=0$.

We define

$$b_{v\mu}(z, \{\mathbf{v}\}) = \frac{1}{v!} \int \int \cdots \int g_{v\mu}(z, \{\mathbf{v}\}, \{\mathbf{u}\}) d\{\mathbf{u}\}, \quad (39)$$

analogously to the cluster integrals of Eq. (30). Using (39) in (38') one finds

$$\begin{aligned} \int \int \cdots \int Q_{n+m}(z, \{\mathbf{n}+\mathbf{m}\}) d\{\mathbf{m}\} &= Q_n(z, \{\mathbf{n}\}) m! \sum_{m_\mu \geq 0} (\sum \mu m_\mu = m) \prod_{\mu \geq 1} \frac{1}{m_\mu!} \{ V b_\mu(z) [\rho(z)/z]^\mu \\ &\quad + \sum \{\mathbf{v}\}_n b_{v\mu}(z, \{\mathbf{v}\}_n) [\rho(z)/z]^\mu \}^{m_\mu}. \end{aligned} \quad (40)$$

It is seen again that (31) is a special case of (40) when $n=0$.

DEVELOPMENT IN POWERS OF THE DIFFERENCE OF FUGACITY

Equation (40), if inserted in (19), leads immediately to expressions for the pressure, $P(y+z) = kT\varphi(y+z)$, and the component potentials of average force $w_\nu(y+z, \{\nu\})$ at the fugacity $y+z$, in terms of a power series in y , the coefficients of which are the functions $b_\mu(z)$ and $b_{\nu\mu}(z, \{\nu\})$ at the fugacity z .

Multiplication of Q_{n+m} by y^m in (40) may be accomplished by multiplication of each term $\rho(z)/z$ by y . Division by $m!$ and summation over m (Eq. (19)), removes the restriction on the m_μ 's. One finds

$$\begin{aligned} [\exp V\varphi(y+z)]Q_n(y+z, \{\mathbf{n}\}) &= [\exp V\varphi(z)]Q_n(z, \{\mathbf{n}\}) \sum_{m_\mu \geq 1} \prod_{\mu \geq 1} \frac{1}{m_\mu!} \{Vb_\mu(z)[y\rho(z)/z]^\mu \\ &+ \sum \{\mathbf{v}\}_n b_{\nu\mu}(z, \{\mathbf{v}\})_n [y\rho(z)/z]^\mu\}^{m_\mu} = [\exp V\varphi(z)]Q_n(z, \{\mathbf{n}\}) \\ &\times \exp \left\{ \sum_{\mu \geq 1} Vb_\mu(z)[y\rho(z)/z]^\mu + \sum \{\mathbf{v}\}_n \sum_{\mu \geq 1} b_{\nu\mu}(z, \{\mathbf{v}\})_n [y\rho(z)/z]^\mu \right\}, \quad (41) \end{aligned}$$

for all values of y smaller than the radius of convergence of the series occurring in the last expression. Using (15) and the Eqs. (9) and (13) defining the component potentials of average force, taking the logarithm of (41) and collecting the terms on both sides of the equation that are the same power of V and functions of the coordinates of the same molecules, one finds:

$$\varphi(y+z) = \varphi(z) + \sum_{\mu \geq 1} b_\mu(z)[y\rho(z)/z]^\mu, \quad (42)$$

$$w_1(y+z, (i))/kT + \ln [\rho(y+z)/(y+z)] = w_1(z, (i))/kT + \ln [\rho(z)/z] + \sum_{\mu \geq 1} b_{1\mu}(z, (i))[y\rho(z)/z]^\mu, \quad (43)$$

$$w_\nu(y+z, \{\nu\})/kT = w_\nu(z, \{\nu\})/kT + \sum_{\mu \geq 1} b_{\nu\mu}(z, \{\nu\})[y\rho(z)/z]^\mu. \quad (44)$$

For the special case $z=0$, $\rho(z)/z=1$, Eq. (2), with $y+z=y$, and $\varphi(z)=0$, Eq. (42) becomes the usual equation for the pressure expressed as a power series of the fugacity in an imperfect gas.³ Under the same conditions Eqs. (43) and (44) permit the calculation of the component potentials of average force in an imperfect gas in terms of a power series in the fugacity. The equations are essentially similar to those derived previously⁴ although the form corresponding to (43) and (44) has not been published previously.

As with the special case that $z=0$, the singularities on the real axis of the series (42) correspond to the singularities in the function $\varphi(y+z)$ in the real system.⁵

However, singularities off the real axis of y , or on the real axis with opposite sign, may cause divergence of the series (42) at values of y for which no singularity in $\varphi(y+z)$ exists. Equations (43) and (44) present feasible methods of calculation to extend the evaluation of $\varphi(y+z)$ beyond such radii of convergence. One may use (43) and (44) to evaluate $w_\nu(y'+z, \{\nu\})$ for some value y' inside the radius of convergence. With these functions known, the coefficients $b_\mu(y'+z)$ for the development around the new point $y'+z$ may be evaluated. This may be repeated until a singularity of φ on the real axis is reached.

One might, of course, attempt to calculate around the singularity on the real axis by following this procedure into the complex plane.

Some interesting equations may be obtained by differentiation of (42). We differentiate with respect to y , ν times, and let y approach zero. One finds

$$[\partial^\nu \varphi(y+z)/\partial y^\nu]_{y=0} = \partial^\nu \varphi(z)/\partial z^\nu = (\partial/\partial y)_{y=0} \sum b_\mu(z)[y\rho(z)/z]^\mu = \nu! b_\nu(z)[\rho(z)/z]^\nu.$$

³ Joseph E. Mayer and S. F. Harrison, J. Chem. Phys. **6**, 87 (1938).

⁴ Joseph E. Mayer and Elliott Montroll, J. Chem. Phys. **9**, 2 (1941).

⁵ See the discussion of Max Born and Klaus Fuchs, Proc. Roy. Soc. **A166**, 391 (1938).

This may be rewritten as

$$\partial^{\nu} \varphi(y+z) / \partial y^{\nu} = \nu! b_{\nu}(y+z) [\rho(y+z)/(y+z)]^{\nu}. \quad (45)$$

For the particular case that $\nu=1$ this reduces to a readily obtained thermodynamic equation, in view of (32') that $b_1=1$,

$$\partial \varphi(y+z) / \partial y = \rho(y+z)/(y+z). \quad (46)$$

We may equate the expression on the right of (45) to that obtained by differentiation of (42) without having y approach zero, obtaining

$$b_{\nu}(y+z) [\rho(y+z)/(y+z)]^{\nu} = \sum_{\mu \geq 1} \frac{\mu!}{(\mu-\nu)! \nu!} b_{\mu}(z) [\rho(z)/z]^{\mu}. \quad (47)$$

For the case $\nu=1$ we obtain

$$\rho(y+z)/(y+z) = \sum_{\mu \geq 1} \mu b_{\mu}(z) [\rho(z)/z]^{\mu}, \quad (48)$$

which permits the calculation of the density at the fugacity $y+z$ from the properties of the system at the fugacity z .

In the treatment of the monatomic imperfect gas^{3,4} it was found to be advisable to make use of the fact that the integrals b_{μ} could be expressed as a sum of products of what were there called irreducible integrals β_k . This led to an expansion in a power series in the density ρ as an expression for the pressure, the coefficients of which involved these irreducible integrals. The transformation had several advantages. In the first place, it is convenient to have density rather than fugacity as independent variable. Secondly, the calculation of the cluster integrals would actually be performed by primary evaluation of the irreducible integrals, and it seems natural to attempt to express the properties of the system in terms of these integrals.

A third result was more complex in nature. It is possible that the power series in fugacity diverge while those in the density remain convergent, the criterion for the phase transition (divergence of the fugacity series on the real axis) being either that the density series become singular, or that one of them ($\sum k \beta_k \rho^k$) becomes unity in value. The type of transition would be ordinary first order in the former case, and anomalous first order in the second case. It was claimed that the disappearance of the phase transition with rising temperature at the critical point must be preceded by a temperature range in which the anomalous transition is present.⁶ The conclusion has been criticized¹ on the justifiable grounds that the physical nature of the coefficients, the irreducible integrals β_k , were not made use of. The criticism, in this form, may be answered, at least partially. The β_k 's may be defined as integrals over the coordinates of $k+1$ molecules (divided by the volume) of an integrand which is a function of the potential energy and of T . Especially if component potentials $w_{\nu}(0, \{\nu\})$ with $\nu \geq 3$ are assumed to exist (which was not assumed in the previous paper) there seems to be no reason why physical systems should not exist in which a wide variety of ratios would occur between the numerical values of the β_k 's for different k 's.

As the parameter T increases a singularity on the real axis of ρ in the series $\sum k \beta_k \rho^k$ may well disappear into the complex plane at $T=T_c$, and the series remain regular (represent a regular function) to high values of ρ on the real axis above this temperature. If the series approaches a value less than unity when the singularity is approached on the real axis for all $T \leq T_c$ then the density $\rho_0(T)$ at which the singularity occurs will be the density of condensation. T_c will be the upper limit of the temperature at which condensation occurs.

However, if the series approaches a value less than unity at the singularity as T approaches T_c , then $(\partial P / \partial V)_T = -(RT/V^2)(1 - \sum k \beta_k \rho^k)$ will not be zero at the critical point. This state of affairs would represent a strange type of critical phenomenon not found in nature. In order to have a critical point of the van der Waals type it is necessary that the value of the function represented

⁶ S. F. Harrison and J. E. Mayer, J. Chem. Phys. **6**, 101 (1938).

by $\sum k\beta_k\rho^k$ (approached along the real axis from small ρ values) at the singularity become exactly unity as T approaches T_c , and that the value of the derivative $\sum k^2\beta_k\rho^k$ become zero at this point. These criteria can be fulfilled, if at all, only by very special types of potential energy functions, and it appears hardly possible that all critical phenomena are of this type.

The actual state of affairs in real systems seems to be that the value of $\sum k\beta_k\rho^k$ at the singularity increases with T to unity at some temperature T_m lower than the temperature at which the singularity moves into the complex plane. Above T_m an anomalous first-order transition occurs. The experimental evidence is certainly not in contradiction to this view.

Since the critical phenomena in binary liquid mixtures appear to show the same anomalous first-order transition region that is evidenced in the one component gas liquid critical region,⁷ it is tempting to try the same introduction of the $\beta_k(z)$'s in the equations derived here, in the prospect of eventually treating two or more component systems.

In order to make the development general, it is necessary to define the new quantities introduced, $\beta_m(z)$ and $h_{nm}(z, \{n\})$, in terms of the $b_\mu(z)$ and $b_{\nu\mu}(z, \{\nu\})$, in which case the development is purely formal and any conclusions drawn about the nature of the approach to singularities would be open to the criticism previously raised. However, in the case that $w_1(z, (i))$ is invariant under translation in the three-dimensional space of the center of mass of the molecule i , which is the case in the liquid and gas, and that $w_\nu(z, \{\nu\})$ for $\nu \geq 2$ is independent of the internal coordinates, then the functions $\beta_m(z)$ and $h_{nm}(z, \{n\})$ are calculable as direct integrals of relatively simple functions of the potentials of average force and temperature. In this case the definitions of these functions are given for $\beta_k(0)$ in Eq. (18), reference 3 and for $h_{\mu n}(0, \{\mathbf{u}\})$ in Eq. (53), reference 4. The definitions given in these articles assume that w_2 alone differs from zero, but the generalization for other cases is fairly obvious. In the general case we may use the definitions:

$$\beta_m(z) = \sum_{m_\mu \geq 0} [\sum (\nu-1)m_\mu = m] (-)^{\sum m_\mu} \frac{(m-1+\sum m_\mu)!}{m!} \prod_{\mu \geq 2} \frac{[\mu b_\mu(z)]^{m_\mu}}{m_\mu!}, \quad (49)$$

for which the inverse is

$$b_\mu(z) = \frac{1}{\mu^2} \sum_{m_\mu \geq 0} (\sum m_\mu = \mu - 1) \prod_{m \geq 1} \frac{[\mu \beta_m]^{m_\mu}}{\mu_m!}, \quad (50)$$

and

$$b_{\nu\mu}(z, \{\nu\}) = \mu b_\mu(z) h_{\nu 1}(z, \{\nu\}) + \sum_{\substack{m_\mu = \mu \\ m_{\nu \geq 2}}} m h_{\nu m}(z, \{\nu\}) [\partial b_\mu(z) / \partial \beta_{m-1}(z)]. \quad (51)$$

With these definitions the method used in references 3 and 4 may be readily generalized to apply to the Eqs. (42), (43), and (44). Equation (49) shows that $m\beta_m(z)$ is the negative of the coefficient of y^m in

$$[1 + \sum_{\mu \geq 2} \mu b_\mu(z) y^{\mu-1}]^{-m} = y^m [\sum_{\mu \geq 1} \mu b_\mu(z) y^\mu]^{-m}$$

so that

$$\begin{aligned} \sum_{m \geq 1} m \beta_m(z) x^m &= -\frac{1}{2\pi i} \oint \frac{1}{y} \sum_{m \geq 1} x^{-1} [\sum_{\mu \geq 1} \mu b_\mu(z) y^\mu]^{-m} dy \\ &= \frac{1}{2\pi i} \oint x \{y[x - \sum_{\mu \geq 1} \mu b_\mu(z) y^\mu]\}^{-1} dy, \end{aligned} \quad (52)$$

where the path of integration must enclose the origin of y , and, in order to permit the second expression, must be just outside the curve along which the absolute value of the sum, $\sum \mu b_\mu(z) y^\mu$, exceeds x in value. The integrand has two poles enclosed by this path: one at $y=0$ with residue

⁷ Louis D. Roberts and J. E. Mayer, J. Chem. Phys. 9, 852 (1941).

unity, and the other when the sum equals x , that is at y_0 determined by

$$\sum_{\mu \geq 1} \mu b_{\mu}(z) y_0^{\mu} = x, \quad (53)$$

the residue of which is found by inserting the derivative of the denominator for the denominator to be $-x[\sum \mu^2 b_{\mu}(z) y_0^{\mu}]^{-1}$. Comparing (53) and (48) we may set $x = y\rho(y+z)/(y+z)$ and find that

$$\begin{aligned} \sum_{m \geq 1} m \beta_m(z) [y\rho(y+z)/(y+z)]^m &= 1 - \left\{ \sum_{\mu \geq 1} \mu^2 b_{\mu}(z) [y\rho(z)/z]^{\mu} \right\}^{-1} [y\rho(y+z)/(y+z)], \\ \sum_{\mu \geq 1} \mu^2 b_{\mu}(z) [y\rho(z)/z]^{\mu} &= [y\rho(y+z)/(y+z)] \left\{ 1 - \sum_{m \geq 1} m \beta_m(z) [y\rho(y+z)/(y+z)]^m \right\}^{-1}. \end{aligned} \quad (54)$$

Equation (54) is valid up to values of y for which the function $\varphi(y+z)$ becomes singular, and this y is determined by

$$\sum_{m \geq 1} m \beta_m(z) [y\rho(y+z)/(y+z)]^m = 1, \quad (55a)$$

$$\sum_{m \geq 1} m \beta_m(z) [y\rho(y+z)/(y+z)]^m \text{ singular.} \quad (55b)$$

For the not too trivial proof that the case (55b) as well as (55a) determines the singularity in $\varphi(y+z)$ the reader is referred elsewhere.^{5,8}

To proceed we note that from (53)

$$d \ln y_0 / dx = \sum_{\mu \geq 1} \mu^2 b_{\mu}(z) y_0^{\mu-1} = x^{-1} - \sum_{m \geq 1} m \beta_m(z) x^{m-1}.$$

Integrating and substituting we find

$$\ln [y\rho(y+z)/(y+z)] = \ln [y\rho(z)/z] + \sum_{m \geq 1} \beta_m(z) [y\rho(y+z)/(y+z)]^m. \quad (56)$$

Similarly, using (53) again, we find

$$(d/dx) \sum_{\mu \geq 1} b_{\mu}(z) y_0^{\mu} = x(d \ln y_0 / dx) = 1 - \sum_{m \geq 1} m \beta_m(z) x^m$$

which can be integrated and substituted to yield

$$\begin{aligned} \varphi(y+z) &= \varphi(z) + \sum_{\mu \geq 1} b_{\mu}(z) [y\rho(z)/z]^{\mu} \\ &= \varphi(z) + [y\rho(y+z)/(y+z)] \left\{ 1 - \sum_{m \geq 1} \frac{m}{m+1} \beta_m(z) [y\rho(y+z)/(y+z)]^m \right\}. \end{aligned} \quad (57)$$

We shall now show that Eqs. (43) and (44) may be transformed into a power series in $y\rho(y+z)/(y+z)$, the coefficients of which are the functions $h_{\nu m}(z, \{\nu\})$. To do this the symbol x is again used for $y\rho(y+z)/(y+z)$ and y_0 for $y\rho(z)/z$. From Eq. (57) it is seen that

$$(\partial/\partial \beta_{m-1})_z \sum b_{\mu} y_0^{\mu} = (\partial/\partial \beta_{m-1})_x (x - \sum (k/k+1) \beta_k x^{k+1}) = -(m-1)x^m/m.$$

One may, instead, use (53) and (56) to find

$$\begin{aligned} (\partial/\partial \beta_{m-1})_x \sum b_{\mu} y_0^{\mu} &= \sum (\partial b_{\mu}/\partial \beta_{m-1}) y_0^{\mu} + (\partial \ln y_0 / \partial \beta_{m-1})_x \sum \mu b_{\mu} y_0^{\mu} \\ &= \sum (\partial b_{\mu}/\partial \beta_{m-1}) y_0^{\mu} - x^m, \end{aligned}$$

and comparing this with the previous equation, one finds

$$\sum [\partial \beta_{\mu}(z)/\partial \beta_{m-1}(z)] [y\rho(z)/z]^{\mu} = [y\rho(y+z)/(y+z)]^m / m. \quad (58)$$

⁸ Mayer and Mayer, *Statistical Mechanics* (J. Wiley and Sons, 1940), p. 465.

If (48) and (58) are used with (51) in Eqs. (43) and (44) one obtains immediately

$$w_1(y+z, (i))/kT + \ln [\rho(y+z)/(y+z)] = w_1(z, (i))/kT + \ln [\rho(z)/z] + \sum_{m \geq 1} h_{1m}(z, (i)) [y\rho(y+z)/(y+z)]^m, \quad (59)$$

$$w_r(y+z, \{\mathbf{v}\})/kT = w_r(z, \{\mathbf{v}\})/kT + \sum_{m \geq 1} h_{rm}(z, \{\mathbf{v}\}) [y\rho(y+z)/(y+z)]^m. \quad (60)$$

For the special case that $z=0$, $y+z=y$, $y\rho(y+z)/(y+z)=\rho(y)$, and $\rho(z)/z=1$, Eqs. (54) to (57) reduce to those derived in reference 3, and (59) and (60) reduce to equations derived in reference 4.

SUMMARY AND CONCLUSION

Let us, for brevity, adopt the symbol

$$J_n(z, V) = [\exp V\varphi(z)] \int \int \cdots \int_V Q_n(z, \{\mathbf{n}\}) d\{\mathbf{n}\}, \quad (61)$$

in which z is the fugacity, Eq. (1), $\varphi(z) = P(z)/kT$ is proportional to the pressure P , and the Q_n 's, Eqs. (15) and (7), are proportional to the distribution functions at the fugacity z . At zero fugacity $\varphi(0)=0$ and in view of (2), and (9) and (10),

$$J_n(0, V) = J_n(V) = \int \int \cdots \int_V \exp(-U_n\{\mathbf{n}\}/kT) d\{\mathbf{n}\}, \quad (61')$$

in which $U_n\{\mathbf{n}\}$ is the potential energy of n molecules as a function of their coordinates $\{\mathbf{n}\}$ of position.

The normal use of the grand partition function leads to Eq. (13) that

$$\exp V\varphi(z) = \sum_{n=0}^{\infty} J_n(V) z^n / n!, \quad (62)$$

a power series in z with positive coefficients that for real systems with molecules having short range repulsion is absolutely convergent to $z=\infty$ for all finite values of the volume V . The first term in the series, J_0 , is unity.

Differentiation of (62) leads to an equation for the density ρ in molecules per unit volume,

$$\rho(z) = z(\partial\varphi/\partial z) = \sum_{n=0}^{\infty} n J_n(V) z^n / n! / \sum_{n=0}^{\infty} J_n(V) z^n / n!, \quad (63)$$

and

$$\frac{\partial\rho}{\partial z} = \frac{\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (m-n)^2 J_n(V) J_m(V) z^{n+m} / n! m!}{2Vz \left[\sum_{n=0}^{\infty} J_n(V) z^n / n! \right]^2}, \quad (64)$$

which shows, in view of the positivity of the coefficients, that neither ρ nor $\partial\rho/\partial z$ can take negative values on the real positive axis of z , which alone is of physical significance.

The first result of this paper is that if the function $\exp [V\varphi(y+z)]$ is developed around the point z as a power series in y the coefficients are the $J_n(z, V)/n!$ of Eq. (61) (compare Eq. (19) with $n=0$) in which the distribution functions of the integrand are proportional to $\exp [-W_n(z, \{\mathbf{n}\})/kT]$, with $W_n(z, \{\mathbf{n}\})$ the potential of average force at the fugacity z ; and the normalization of the distribution functions are so chosen that their average value in an infinite volume are $[\rho(z)/z]^n \exp [V\varphi(z)]$.

The function $\varphi(z)$ may be expressed as a power series in z , the ν 'th coefficient of which, $b_\nu(0)$, is an integral of an integrand which depends only on the potential energy of ν molecules, and the temperature (Eqs. (29) and (30) with $z=0$). The quantities $b_\nu(0)$ depend on the volume V over which the integration is extended, but for finite values of ν they approach finite limits as $V \rightarrow \infty$, provided the mutual potentials of the molecules converge rapidly enough to zero at infinite distance.

The quantities $b_\nu(0, V)$ could be defined using any macroscopic but finite V , and the series

$$\varphi_V(z) = \sum_{\nu \geq 1} b_\nu(0, V) z^\nu, \quad (65)$$

used to determine the $\varphi(z)$ defined by (62) at this value of V . The coefficients $b_\nu(0, V)$ of this series would have the value $b_\nu(0)$ of the limit $V = \infty$ except for very large values of ν . Since (62) is absolutely convergent for all z 's, if V is finite, it follows that (65) determines a function which is regular except at the zeros of (62), and that (65) is convergent out to the absolute value of z of the zero of (62) nearest to the origin. This zero of course cannot occur on the positive real axis of z .

The function $\varphi_V(z)$ determined by (65) is then regular along the positive real axis of z , as long as V remains finite. If for each ν we extend the range of integration of Eq. (30) to infinity, the coefficient approaches the limiting value $b_\nu(0)$, and the resulting series

$$\varphi(z) = \sum_{\nu \geq 1} b_\nu(0) z^\nu \quad (66)$$

expresses the pressure $P(z) = kT\varphi(z)$ of an infinite thermodynamic system, having singularities on the real positive axis at the values of the fugacity characteristic of the phase transitions. At all these singularities for real positive finite z 's, the function $\varphi(z)$ represented by the series (66) approaches the same (positive finite) value as the singularity is approached from either above or below along the real axis.

The slope $\partial\varphi/\partial z = \rho(z)/z$ may approach a higher (positive finite) value if the singularity is approached along the positive real axis from above than if approached from below. In this case the transition is first order. If $\partial\rho/\partial z$ approaches finite values as the singularity is approached either way the transition is normal, if infinite values are approached the transition is anomalous first order.

If the slope of φ , namely, ρ/z , approaches the same value as the singularity is approached from either above or below, then the singularity corresponds to a phase transition of second or higher order, the order depending on which derivative of φ undergoes a discontinuity.

It has been shown that if the function $\varphi(y+z)$ is developed around the point z as a power series in y , and the ν 'th coefficient is written $[\rho(z)/z]^\nu b_\nu(z)$, then $b_\nu(z)$ is calculable by the same equation as $b_\nu(0)$, with only the replacement of the potential energy appearing in the expression for the latter by the potential of average force at the fugacity z .

The component potentials of average force, $w_\nu(z, \{\mathbf{v}\})$, Eq. (23), may also be developed as a power series in the fugacity around any arbitrary fugacity. The coefficients of the developments around different fugacities differ only that in each case the potentials of average force at the fugacity around which the development is made enter into the equations. In the special case of zero fugacity the potentials of average force are the potential energies of the molecules.