Mode Expansion in Equilibrium Statistical Mechanics. I. General Theory and Application to the Classical Electron Gas

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A new expansion for the Helmholtz free energy of a classical system is presented. The potential energy of the system is assumed to be composed of two parts: a "reference system" potential energy and a perturbation potential, which is the sum of two-particle potentials. The two-particle perturbation potential energy is assumed to have a Fourier transform. Collective variables, which are the Fourier transforms of the single-particle density, are introduced, and the canonical ensemble partition function is expressed as an infinite series. The first term in the result for the Helmholtz free energy is the reference system free energy. The second is a mean field term, and the third is the random phase approximation. Subsequent terms involve correlations among the collective variables in the reference system. The general results are applied to the special case in which the reference system is the ideal gas. A density and temperature dependent renormalized potential arises from the analysis in a straightforward way. When the results are specialized to the case of the Coulomb potential, agreement with the ionic cluster theory is obtained, and the renormalized potential is the usual Debye–Hückel potential. Further applications of the technique are mentioned.

I. INTRODUCTION

This is the first of a series of papers in which we present a new expansion technique for classical equilibrium statistical mechanics. Research in this field is often directed toward the discovery of theories which give good approximations for the thermodynamic properties of a many-particle system. Many theories center attention on the particles and their interactions, assuming that in some sense the interactions are weak or infrequent. Outstanding examples are the Mayer cluster theory and its generalization to systems with long-range forces. The theory we introduce in this paper is based on an alternative point of view. We focus our attention on the Fourier components of the density and the correlations among them. These components are often called collective coordinates or collective variables since they depend on the positions of all the particles in the system.

Collective variables have been used by many authors to discuss many-particle systems. There are two different reasons for using collective coordinates. The first reason is to perform a canonical transformation of the dynamical variables in order to reduce the Hamiltonian to a more tractable form. Bohm and Pines used this method for the electron gas and obtained a dynamical description in terms of plasma waves. Percus and Yevick applied this technique in the original derivation of their equation for the pair correlation function of a classical fluid. Eisenschitz and Wilfred also used this method to discuss time-dependent processes in classical liquids. The second reason for using collective variables is to facilitate the computation of the classical configuration integral or other many-particle integrals. Techniques of this type were applied by Iukhnovskii, Kelbg, and Eisenhal and McMillan to calculate the configuration integral for ionic solutions and plasmas. A similar technique was used by Broyles and Hooper in the calculation of the distribution of electric microfields in a plasma. Brout used this method in discussing various phase transitions. In the present work, we are concerned only with the second use of collective variables.

Except for a few instances, the collective coordinate method for the evaluation of many-particle integrals has only been used in its simplest approximation, which is often called the random phase approximation. When applied to a system with Coulomb interactions, the random phase approximation leads to Debye–Hückel theory, a fact which has been known for some time. In order to extend the method it is necessary to find corrections to this approximation. The first correction for Coulomb forces was obtained by Iukhnovskii and Kelbg, but from their work it is not obvious that subsequent corrections can be found or that their method can be extended to other physical systems. The analogous first correction in the problem of the distribution of electric fields in a plasma was obtained by Broyles.

In this paper we present a systematic way of obtaining a sequence of corrections to the random phase approximation. The sequence is generated in a way similar to the way van Kampen derived the usual cluster theory. We apply the method to the case of spherically symmetric molecules whose intermolecular potential has a Fourier transform. The results are equivalent to the results of the ionic cluster expansion and contain no divergences for long-range forces, even for Coulomb potentials. There are two important advantages of our method of obtaining a sequence of approximations. The first advantage is that the first few terms in the sequence can be obtained rather easily.
and simply without the need for diagrammatic and combinatorial analyses of the type usually used to obtain and extend the Debye–Hückel results in the theory of ionic solutions. The second advantage is that the sequence has a form which suggests how to apply the same method to other physical problems.

The method gives a relatively simple way of calculating approximations to the configuration integral for systems in which large numbers of molecules interact simultaneously. In addition, the method can be modified in order to calculate the distribution functions and other useful quantities.

In Sec. II we express the configuration integral for a monatomic gas in terms of collective variables. The expansion procedure, which we call the mode expansion, is derived in Sec. III. In Sec. IV, the mode expansion is applied to a gas whose intermolecular potential has a Fourier transform, and in Sec. V the results are applied to the classical electron gas and compared with the results of the ionic cluster expansion. Section VI contains a discussion of the method and possible future applications.

II. REFORMULATION OF THE CONFIGURATION INTEGRAL IN TERMS OF COLLECTIVE VARIABLES

Throughout this paper we shall assume that the total potential energy of an \( N \)-particle system can be written as

\[
W(\mathbf{r}^N) = U_0(\mathbf{r}^N) + U(\mathbf{r}^N),
\]

where \( \mathbf{r}^N \) denotes the positions of the \( N \) particles. The potential \( U_0(\mathbf{r}^N) \) will be called the reference system potential energy and \( U(\mathbf{r}^N) \) the perturbation potential energy. We shall assume that the equilibrium properties (the free energy and reduced distribution functions) of the reference system are known. The methods we propose describe the effect of the perturbation on the equilibrium properties.

Since all the equilibrium properties of a system can be obtained directly from the Helmholtz free energy, we concern ourselves with the evaluation of the configuration partition function:

\[
\exp(-\beta \Delta A) = Q = V^{-N} \int d\mathbf{r}^N \exp[-\beta W(\mathbf{r}^N)].
\]

Here \( \beta \) is the reciprocal of Boltzmann’s constant times the temperature, and \( \Delta A \) is the Helmholtz free energy of the \( N \)-particle system in a volume \( V \) minus the ideal gas Helmholtz free energy at the same volume, density, and temperature. (\( \Delta A \) is often called the excess free energy.) By inserting Eq. (2.1) into (2.2) and factorizing, we obtain

\[
Q = Q_0 \exp[-\beta U(\mathbf{r}^N)],
\]

where \( Q_0 \) is the reference system configuration partition function,

\[
Q_0 = \exp(-\beta \Delta A_0) = V^{-N} \int d\mathbf{r}^N \exp[-\beta U_0(\mathbf{r}^N)].
\]

and the brackets \( \langle \cdots \rangle \) denote the configurational average in the reference system canonical ensemble

\[
\langle \cdots \rangle = \int \mathbf{r}^N \exp[-\beta U_0(\mathbf{r}^N)]/\int \mathbf{r}^N \exp[-\beta U_0(\mathbf{r}^N)].
\]

Equation (2.3) is the convenient starting point for equilibrium perturbation theories. The simplest is the high-temperature expansion of the Boltzmann factor \( \exp(-\beta U) \). A cluster expansion can also be obtained. One way to do this is to apply van Kampen’s method. In particular, assume that \( U_0 \) is zero and that the \( N \)-particle potential is a sum of two-particle potentials:

\[
W(\mathbf{r}^N) = U(\mathbf{r}^N) = \sum_{i<j=1}^N u(r_{ij}),
\]

where \( u(r_{ij}) \) is the two-particle potential. Then, the average in Eq. (2.3) becomes an average of a product. Van Kampen has expanded the resulting averaged product as a product of averages and obtained the familiar Mayer cluster expansion for \( Q \). His method is closely related to Kubo’s cumulant-cluster theory. It is in the spirit of van Kampen’s work that we propose a new expansion. But instead of being primarily concerned with the interactions between particles, as is done in the cluster theory, we consider the correlations among Fourier components of the particle density. To do this, the perturbation must be expressed in terms of the Fourier components.

We assume that the total perturbation potential energy is a sum of radially symmetric two-particle potentials, \( u(r_{ij}) \). Furthermore, we require that the two-particle perturbation potential have a Fourier transform. Then by imposing periodic boundary conditions on the \( N \)-particle system in a cubic box of volume \( V \), we obtain

\[
U(\mathbf{r}^N) = (1/2V) \sum_k \hat{u}(k)[q(k)q(-k) - N],
\]

where

\[
\hat{u}(k) = \int d\mathbf{r}u(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r})
\]

and \( q(k) \) is the Fourier transform of the particle density,

\[
q(k) = \sum_{j=1}^N \exp(-i\mathbf{k} \cdot \mathbf{r}_j).
\]

Since the summand in Eq. (2.7) is symmetric on inversion of \( \mathbf{k} \) through the origin, we can write

\[
U(\mathbf{r}^N) = \hat{u}(0)N(N - 1)/2V + V^{-1} \sum_k \hat{u}(k)[q(k)q(-k) - N],
\]

where \( \sum_{k'} \) denotes a sum over half of \( \mathbf{k} \) space with \( \mathbf{k} = 0 \) omitted. (Imagine dividing \( \mathbf{k} \) space into two regions with a plane through the origin. The sum is to be taken over the wave vectors on one side of the plane.)
By combining Eqs. (2.10) and (2.3), the configurational partition function can be expressed as

\[ Q = \Theta_0 \left[ \exp \left[ -\left( \frac{1}{2} \beta \right) N C \left( 1 - N^{-1} \right) \delta(0) \right] \right] \times \left[ \prod_k \exp \left[ \beta \delta(k) \right] \right] \left( \prod_k s(k) \right), \tag{2.11} \]

where

\[ s(k) = \exp \left[ -\left( \frac{1}{2} \beta \delta(k) / V \right) q(k) q(-k) \right] \tag{2.12} \]

is called the \( k \)th mode and \( \epsilon \) is the mean (thermodynamic) particle density,

\[ \epsilon = N/V. \tag{2.13} \]

The notation \( \prod_k' \) denotes a product over half of \( k \) space with \( k = 0 \) omitted. The first bracketed term in Eq. (2.11) is the “mean field” (van der Waals) contribution to \( Q \). The remaining terms express the effects of density fluctuations. Equation (2.11) is the reformulation of the configurational integral which we use as the starting point for our theory.

III. THE MODE EXPANSION

As written in Eq. (2.11), \( Q \) contains a reference system average of an infinite product. In this section, we introduce an expansion which systematically expresses \( Q \) in terms of a product of averages of products of a finite number of modes. The expansion is valid when the density Fourier components, and thus the modes, are weakly correlated in the reference system. In fact, our first approximation is the “random phase” approximation:

\[ \left( \prod_k' s(k) \right) \approx \prod_k \langle s(k) \rangle. \tag{3.1} \]

An important feature of our work is that we develop a systematic method to obtain better and better corrections to this popular approximation.

It should be noticed that if there were only one \( k \) vector in half of \( k \) space, Eq. (3.1) would be exact. Thus one way to improve the “random phase” approximation is to write

\[ \left( \prod_k' s(k) \right) \approx \left[ \prod_k' \langle s(k) \rangle \right] \left( \prod_k \frac{\langle s(k_1) s(k_2) \rangle}{\langle s(k_1) \rangle \langle s(k_2) \rangle} \right)^{1/2}, \]

which would be exact if \( k \) space contained only two \( k \) vectors. Clearly this procedure can be continued indefinitely, the prescription being that truncation at the \( n \)th factor should be exact if \( k \) space contained only \( n \) \( k \) vectors. Thus, we have the general expansion

\[ \left( \prod_k' s(k) \right) = \left[ \prod_k' \langle s(k) \rangle \right] \left[ \prod_k' \langle s_1 s_2 \rangle / \langle s_1 \rangle \langle s_2 \rangle \right]^{1/2} \times \left( \prod_{k_1 \neq k_2} \frac{\langle s_1 s_2 s_3 s_4 \rangle \langle s_1 \rangle \langle s_2 \rangle}{\langle s_3 s_4 \rangle \langle s_1 \rangle \langle s_2 \rangle} \right)^{1/2} \ldots, \tag{3.2} \]

where we have abbreviated \( s(k_n) \) by \( s_n \). When carried to infinite order, Eq. (3.2) is formally exact. The expansion is analogous to one discussed by Kubo in his paper on cumulant expansion.14

By taking the logarithm of the partition function as expressed in Eq. (2.11), and using Eq. (3.2), we obtain the mode expansion for the excess free energy:

\[ -\frac{\beta \Delta A}{V} = \alpha = \alpha_0 - \left( \frac{1}{2} \beta \right) \epsilon \left( 1 - \frac{1}{N} \right) \delta(0) + \sum_{n=1}^{\infty} a_n, \tag{3.3a} \]

where

\[ a_1 = (1/V) \sum_k \left[ c \beta \delta(k) + \ln B_1(k) \right], \tag{3.3b} \]

and

\[ B_1(k) = \langle s(k) \rangle, \]

\[ B_2(k) = \langle s_1 s_2 \rangle / \langle s_1 \rangle \langle s_2 \rangle, \]

\[ B_3(k) = \langle s_1 s_2 s_3 \rangle / \langle s_1 \rangle \langle s_2 \rangle \langle s_3 \rangle / \langle s_1 s_3 \rangle \langle s_2 s_3 \rangle, \]

\[ B_4(k) = \left( \langle s_1 s_2 s_3 s_4 \rangle / \langle s_1 \rangle \langle s_2 \rangle \langle s_3 \rangle \langle s_4 \rangle \right)^{1/4} \]

etc., and \( \alpha_0 \) is minus \( \beta \) times the excess free energy per unit volume of the reference system. The notation

\[ \sum_k' \]

denotes the \( n \)-fold vector sum

\[ \sum'_{k_1} \cdots \sum'_{k_n}, \]

subject to the constraint that no two \( k \) vectors in a particular term can be equal. (The sum \( \sum' \) is over all ordered sets of \( n \) distinct \( k \) vectors in half of \( k \) space with \( k = 0 \) omitted.) The quantity \( a_n \) gives the contribution to \( \alpha = V^{-1} \ln Q \) due to the correlations among \( n \) modes.

At this point in the development we could specialize our discussion to particular systems. However, to emphasize the generality of the theory, we shall perform a factorization procedure which greatly facilitates the calculation of terms in the mode expansion and which is valid for the most general system under discussion. The factorization we have in mind is analogous to the Mayer trick of introducing the \( f \) function in the derivation of the cluster expansions.1 To evaluate the \( B_n \)'s in Eqs. (3.3), we must first be able to calculate \( \langle s_1 s_2 \cdots s_n \rangle \). This quantity can be factored in the following way:

\[ \left( \prod_{a=1}^{n} s(k_a) \right) = \left( \prod_{a=1}^{n} \langle s(k_a) \rangle \right) \left( \prod_{a=1}^{n} (1 + C_a) \right), \tag{3.4} \]

where

\[ C_a = \left[ s(k_a) - \langle s(k_a) \rangle \right] / \langle s(k_a) \rangle. \tag{3.5} \]
By noting that $\langle C_n \rangle = 0$, Eq. (3.4) can be written as

$$
(\prod_{a=1}^{n} s(k_a)) = \prod_{a=1}^{n} s(k_a) \left[ 1 + \sum_{a < a'} \langle C_a C_{a'} \rangle + \sum_{a < a' < a''} \langle C_a C_{a'} C_{a''} \rangle + \cdots + \langle C_1 \cdots C_n \rangle \right].
$$

(3.6)

Inserting Eq. (3.6) into Eqs. (3.3c), we obtain

$$
B_{e}(k^2) = 1 + \langle C_1 C_2 \rangle,
$$

$$
B_{i}(k^2) = \frac{1 + \langle C_1 C_2 \rangle + \langle C_1 C_3 \rangle + \langle C_1 C_4 \rangle}{[1 + \langle C_1 C_2 \rangle][1 + \langle C_1 C_3 \rangle][1 + \langle C_1 C_4 \rangle]},
$$

$$
B_{i}(k^r) = (1 + \sum_{i<j} \langle C_1 C_j \rangle + \sum_{i<j<k} \langle C_1 C_j C_k \rangle + \langle C_1 C_2 C_3 C_4 \rangle)[\prod_{i<j} (1 + \langle C_1 C_j \rangle)]
$$

$$
\times \left[ \prod_{i<j} (1 + \langle C_1 C_j \rangle + \langle C_1 C_i \rangle + \langle C_1 C_i C_j \rangle + \langle C_1 C_i C_j C_k \rangle) \right]^{-1},
$$

(3.7)

etc. In later sections of this paper we show that $\langle C_j C_j \cdots \rangle$ is generally very small in the thermodynamic limit ($N, V \to \infty, N/V = c$ is finite). Thus the immediate simplification afforded by the factorization procedure is that in the thermodynamic limit the fractions in Eqs. (3.7) can be expanded and only a few simple terms need be retained.

IV. THE IDEAL GAS REFERENCE SYSTEM

In the remainder of this paper we specialize much of our development to the particularly simple case where the perturbation potential energy is the total potential energy. Thus, the reference system is the ideal gas. The case in which the reference system potential energy is non-zero will be discussed in the second paper of this series. Since we consider here the case where $U(r^N)$ is the total potential energy, the total two-particle interaction must have a Fourier transform. Of course, this is usually not the case for classical systems of experimental interest. However, the Coulomb potential has a Fourier transform. Thus, the theory developed in the remainder of this paper can be used to describe a classical electron gas, which is often used as a model for plasmas. As shown in the next section, the results of the mode expansion for the electron gas are the same as those of the ionic cluster expansions for the same system.

A. Evaluation of $a_1$

In order to calculate $a_1$ we must first be able to perform the configurational average $\langle s(k) \rangle$. One convenient way of accomplishing this, which is also applicable to an arbitrary reference system, is to express $s(k)$ in terms of a Gaussian integral:

$$s(k) = \exp\left\{ - \frac{\beta \alpha(k)}{V} q(k) q(-k) \right\},
$$

$$= \sum_{n=0}^{\infty} \left[ -\frac{\beta \alpha(k)}{V} \right]^n \frac{n!}{n!} [q(k) q(-k)]^n,
$$

$$= \int_0^\infty dz \frac{N}{2 \rho(k)} \exp \left\{ - \frac{N z^2}{4 \rho(k)} \sum_{n=0}^{\infty} \frac{(-1)^n}{(n!)^2} [q(k) q(-k)]^n \right\},
$$

(4.1)

where $\rho(k)$ is given by

$$\rho(k) = \frac{\beta \alpha(k)}{\gamma}.
$$

Next, note the identity

$$(2\pi)^{-1} \int_0^{2\pi} \sum_{j=1}^{K} \sin(k \cdot r_j + \phi) \prod_{j=1}^{\infty} d\phi
$$

$$= \frac{1}{2} \sum_{n=0}^{\infty} \frac{\beta \alpha(k)}{\gamma} [q(k) q(-k)]^n.
$$

(4.3)

Inserting Eq. (4.3) into (4.1) it is found that

$$s(k) = \int_0^\infty dz \frac{N}{2 \rho(k)} \exp \left\{ - \frac{\beta \alpha(k)}{\gamma} \right\}
$$

$$\times \int_0^{2\pi} d\phi \left[ \sum_{n=0}^{\infty} \frac{\beta \alpha(k)}{\gamma} \exp[i \sin(k \cdot r_j + \phi)] \right].
$$

(4.4)

By applying the integer Bessel function identity

$$\exp(i x \sin y) = \sum_{n=-\infty}^{\infty} J_n(x) \exp[i n y],
$$

(4.5)

the $\phi$ integration is easily performed to obtain

$$s(k) = \int_0^\infty dz \frac{N}{2 \rho(k)} \exp \left\{ - \frac{\beta \alpha(k)}{\gamma} \right\}
$$

$$\times \sum_{n=0}^{\infty} \cdots \sum_{n=0}^{\infty} \prod_{j=1}^{\infty} J_n(z) \exp[i k \cdot r_m(j)],
$$

such that $\sum_{n=0}^{\infty} n(i) = 0$.

(4.6)
We now perform the unweighted (ideal gas) configurational average of Eq. (4.6) to obtain
\[
\langle s(k) \rangle = \int_0^\infty dz \frac{N}{2p(k)} \exp \left( - \frac{Nz^2}{4p(k)} \right) [J_0(z)]^N \tag{4.7}
\]
for \( k \neq 0 \).

In the thermodynamic limit \((N, V \to \infty, N/V = \epsilon)\) is finite), the integrand in Eq. (4.7) is sharply peaked at \( z = 0 \). Thus, we expand \([J_0(z)]^N\) about \( z = 0 \). An elementary calculation gives
\[
[J_0(z)]^N = \exp \left( - \frac{1}{2} Nz^2 \right) \left[ 1 + O(Nz^2) \right]. \tag{4.8}
\]
Inserting Eq. (4.8) into (4.7), and performing the \( z \) integration, we obtain
\[
\langle s(k) \rangle = \left[ 1 + p(k) \right]^{-1} \left[ 1 + O(N^{-1}) \right]. \tag{4.9}
\]

With this result we can now calculate the first contribution to \( V^{-1} \ln Q \) in the mode expansion. Combining Eqs. (4.9) and (3.3c) yields
\[
a_1 = V^{-1} \sum_k \left[ p(k) - \ln [1 + p(k)] [1 + O(N^{-1})] \right]
= (2V)^{-1} \sum_{k \neq 0} \left[ p(k) - \ln [1 + p(k)] [1 + O(N^{-1})] \right], \tag{4.10}
\]
where the second equality is obtained from the symmetry of the summand as a function of \( k \). In the thermodynamic limit, the sum over \( k \) can be converted to an integral:
\[
\sum_{k} \left[ V/(2\pi)^2 \right] j dk. \tag{4.11}
\]
Thus, taking the thermodynamic limit we obtain
\[
a_1 = \frac{1}{2} (2\pi)^{-2} \int dk \left[ p(k) - \ln [1 + p(k)] \right]. \tag{4.12}
\]

In the remaining portion of this section we generalize the methods developed above and calculate the first few corrections to the "random phase" contribution \( a_1 \).

**B. Analysis of Higher-Order Terms**

It was shown in Sec. III that the calculation of \( a_n \) for \( n \geq 2 \) can be based on the evaluation of the functions \( \langle C_1 C_2 \cdots \rangle \). These quantities yield \( B_n(k) \), the logarithm of which is then summed to give \( a_n \). The summations are restricted in such a way that we need \( \langle C_1 C_2 \cdots \rangle \) for \( \mathbf{k}_1 \neq \pm \mathbf{k}_2 (i \neq j) \) and \( \mathbf{k}_1 \neq 0 \).

The definition of \( C_n \), Eq. (3.5), together with Eqs. (4.6) and (4.7), can be used to obtain
\[
C_n = \left\langle \sum_{n(1), n(2), \ldots, n(N) = 0} \left( \prod_{j=1}^N \frac{J_n(z_j)}{J_0(z_j)} \exp [i \mathbf{k}_j \cdot \mathbf{r}_j n(j)] \right) \right\rangle_a, \tag{4.13}
\]
where the brackets \( \langle \cdots \rangle_a \) denote the average
\[
\langle \cdots \rangle_a = \int_0^\infty dz \frac{N}{2p(k)} \exp \left( - \frac{Nz^2}{4p(k)} \right) [J_0(z)]^{-1}, \tag{4.14}
\]
which should not be confused with the configurational average represented by \( \langle \cdots \rangle \). The notation
\[
\sum_{n(1), \ldots, n(N)}^r \tag{4.15}
\]
denotes the \( N \)-fold sum over integers from \( -\infty \) to \( \infty \) and each term in the sum must satisfy the conditions that
\[
\sum_{j=1}^N n(j) = 0 \quad \text{and at least two of the } n(j)'s \text{ are nonzero.}
\]

The actual quantity of interest is \( \langle C_1 C_2 \cdots \rangle \), which can be obtained in the thermodynamic limit by expanding the quantity in curly brackets in Eq. (4.13) in powers of \( z \). This is true since in the averaging denoted by \( \langle \cdots \rangle_a \) each power of \( z \) can be regarded as a power of \( N^{-1/2} \) (for purposes of estimating orders of magnitude in the thermodynamic limit). Performing such an expansion in powers of \( z \) and calculating the unweighted configurational average, we obtain
\[
\langle C_1 C_2 \rangle = O(N^{-2}),
\]
\[
\langle C_1 C_2 C_3 \rangle = \frac{1}{2} N^2 \left( \prod_{a=1}^4 \langle - \frac{1}{2} z_a^2 \rangle \right)
\times \sum_{n_1, n_2, n_3, n_4 = \pm 1} \Delta(n_1 \mathbf{k}_1 + n_2 \mathbf{k}_2 + n_3 \mathbf{k}_3 + n_4 \mathbf{k}_4) + O(N^{-3}),
\]
\[
\langle C_1 C_2 C_3 C_4 \rangle = \frac{1}{2} N^3 \left( \prod_{a=1}^4 \langle - \frac{1}{2} z_a^2 \rangle \right)
\times \sum_{n_1, n_2, n_3, n_4, n_5 = \pm 1} \Delta(n_1 \mathbf{k}_1 + n_2 \mathbf{k}_2 + n_3 \mathbf{k}_3 + n_4 \mathbf{k}_4 + n_5 \mathbf{k}_5) + O(N^{-4}).
\]

Here \( \Delta(k) \) is the Kronecker delta function
\[
\Delta(k) = V^{-1} \int dk \exp (i \mathbf{k} \cdot \mathbf{r}) = 0, \quad \mathbf{k} \neq 0
= 1, \quad \mathbf{k} = 0. \tag{4.16}
\]

[The second equality in Eq. (4.16) follows from the use of periodic boundary conditions.] The effect of such a delta function (for purposes of estimating orders of magnitude) is to remove a summation over \( k \) and thereby remove a power of \( V \) [see Eq. (4.11)]. That is, the delta function is of order \( V^{-1} \). In the expression for \( \langle C_1 C_2 \rangle \) there would be a term of order \( N^{-1} \) were it not for the restriction that \( k \neq \pm k_2 \) [the term of order \( N^{-1} \) contains \( \Delta(k_1 \pm k_2) \) which is always zero]. The averaging denoted by \( \langle \cdots \rangle_a \) is performed with the aid
of Eqs. (4.14) and (4.8). The results are

\[
\langle C_0 C_2 \rangle = O(N^{-2}),
\]

\[
\langle C_0 C_2 C_3 \rangle = (2N)^{-1} \left( \prod_{n=1}^{3} \frac{-\rho(k_n)}{1 + \rho(k_n)} \right) \sum_{n_1, n_2, n_3 = \pm 1} \Delta(n_1 k_1 + n_2 k_2 + n_3 k_3) + O(N^{-4}),
\]

\[
\langle C_0 C_2 C_3 C_4 \rangle = \frac{1}{2N^2} \left( \prod_{n=1}^{4} \frac{-\rho(k_n)}{1 + \rho(k_n)} \right) \sum_{n_1, n_2, n_3, n_4 = \pm 1} \Delta(n_1 k_1 + n_2 k_2 + n_3 k_3 + n_4 k_4) + O(N^{-4}).
\]  

(4.17)

Inserting Eqs. (4.17) into (3.7) and collecting terms of the same order of magnitude, we obtain

\[
B_2(k^2) = 1 + O(N^{-2}),
\]

\[
B_3(k^2) = 1 + \langle C_0 C_2 C_3 \rangle + O(N^{-3}),
\]

\[
O(N^{-2})
\]

\[
B_4(k^2) = 1 + \langle C_0 C_2 C_3 C_4 \rangle + O(N^{-4})
\]

or

\[
\ln B_2(k^2) \sim O(N^{-2}),
\]

\[
\ln B_3(k^2) = (2N)^{-1} \left( \prod_{n=1}^{3} \frac{-\rho(k_n)}{1 + \rho(k_n)} \right) \sum_{n_1, n_2, n_3 = \pm 1} \Delta(n_1 k_1 + n_2 k_2 + n_3 k_3) + O(N^{-2}),
\]

\[
\ln B_4(k^2) = \frac{1}{2N^2} \left( \prod_{n=1}^{4} \frac{-\rho(k_n)}{1 + \rho(k_n)} \right) \sum_{n_1, n_2, n_3, n_4 = \pm 1} \Delta(n_1 k_1 + n_2 k_2 + n_3 k_3 + n_4 k_4) + O(N^{-4}).
\]  

(4.18)

Note that \( \ln B_3 \) and \( \ln B_4 \) are invariant under inversion of any \( k_i \) through the origin. This fact can be used to remove the restrictions from the summations over the \( k_i \) in Eqs. (3.3c). Consequently, inserting Eqs. (4.18) into (3.3) and taking the thermodynamic limit with the aid of Eq. (4.11), we obtain

\[
a_3 = \left[ \frac{c^4}{(2\pi)^8} \right] \int dk \left[ -\beta \hat{v}(k_1) \right] \left[ -\beta \hat{v}(k_2) \right] \left[ -\beta \hat{v}(k_3) \right] \hat{\delta}(k_1 + k_2 + k_3),
\]

\[
a_4 = \left[ \frac{c^4}{(2\pi)^8} \right] \int dk \left[ -\beta \hat{v}(k_1) \right] \left[ -\beta \hat{v}(k_2) \right] \left[ -\beta \hat{v}(k_3) \right] \left[ -\beta \hat{v}(k_4) \right] \hat{\delta}(k_1 + k_2 + k_3 + k_4),
\]

where \( \hat{\delta}(k) \) is the three-dimensional Dirac delta function, and

\[
\hat{v}(k) = (\beta \epsilon)^{-1} \left( \frac{\rho(k)}{1 + \rho(k)} \right) = \frac{\hat{\delta}(k)}{1 + \epsilon \beta \hat{\delta}(k)}.
\]  

(4.20)

The notation \( \int dk \) denotes \( \int dk_1 \int dk_2 \cdots \int dk_n \).

Using the same procedures, we obtain

\[
a_6 = \frac{c^4}{240(2\pi)^2} \left[ \prod_{n=1}^{8} -\beta \hat{v}(k_n) \right] \hat{\delta}(k_1 + k_2 + k_3 + k_4 + k_5 + k_6) + \frac{c^6}{8(2\pi)^2} \left[ \prod_{n=1}^{6} -\beta \hat{v}(k_n) \right] \hat{\delta}(k_1 + k_2 + k_3 + k_4 + k_5 + k_6) + \frac{c^6}{16(2\pi)^2} \int dk \left[ -\beta \hat{v}(k_1) \right] \left[ \prod_{n=2}^{6} -\beta \hat{v}(k_n) \right] \hat{\delta}(k_1 + k_2 + k_3 + k_4 + k_5 + k_6).
\]  

(4.19d)

Higher-order terms in the mode expansion can be obtained in an analogous fashion.

V. COMPARISON WITH THE IONIC CLUSTER THEORY AND APPLICATION TO THE CLASSICAL ELECTRON GAS

The results of the mode expansion, which are given in the previous section, are equivalent to those obtained from the Mayer cluster theory\(^4\) and from the cluster theory for ionic forces.\(^3\) In this section we establish this correspondence.

To facilitate the comparison of these theories, we will first transform the expressions for \( a_3 \), \( a_4 \), and \( a_6 \) into integrals over particle coordinates. In Eq. (4.12) for \( a_5 \) we substitute

\[
\delta(k_1 + k_2 + k_3) = (2\pi)^{-3} V^{-1} \int dr_x dr_y dr_z
\]

\[
\times \exp[i(k_1 + k_2 + k_3) \cdot r_x]
\]

to obtain

\[
a_3 = (c^2/2V) \int dr_x dr_y dr_z (2\pi)^{3} \left[ -\beta \nu(r_{12}) \right]^3,
\]

(5.1)

where

\[
\nu(r) = (2\pi)^{-3} \int dk \exp(ik \cdot r) \hat{\delta}(k)
\]

(5.2)
is the temperature and density dependent “potential” whose Fourier transform is $\tilde{v}(k)$. For Coulombic forces this potential is equal to the shielded Debye–Hückel potential, as we shall see below. By making similar substitutions for the Dirac delta functions in Eqs. (4.19b) and (4.19c) for $a_4$ and $a_6$, we obtain

$$a_4 = (\epsilon^4/24V)\int dr_1 dr_2 (41)^{-1}[-\beta v(r_{12})]^4,$$  \hspace{1cm} (5.3)

$$a_6 = (\epsilon^6/48V)\int dr_1 dr_2 (51)^{-1}[-\beta v(r_{12})]^5$$
$$+3(\epsilon^6/128V)\int dr_1 dr_2 dr_3 [-\beta v(r_{12})][21)^{-1}[-\beta v(r_{12})]^2$$
$$\times (21)^{-1}[-\beta v(r_{12})]^3$$
$$+6(\epsilon^8/48V)\int dr_1 dr_2 dr_3 dx [-\beta v(r_{12})][21)^{-1}[-\beta v(r_{12})]^2$$
$$\times (21)^{-1}[-\beta v(r_{12})][21)^{-1}[-\beta v(r_{12})]^2].$$  \hspace{1cm} (5.4)

Expressed in this way, the results are suggestive of the cluster integrals appearing in the theory of ionic solutions.

To establish the connection with cluster theory, let us apply the mode expansion to a classical electron gas. The internuclear potential is

$$u(r) = e^2/r,$$

where $-e$ is the electronic charge. The Fourier transform of this potential is found in the usual way, and we obtain

$$p(k) = e^2\delta\mu(k) = k^2/k^2,$$  \hspace{1cm} (5.5)

where $\kappa$ is the inverse of the Debye screening length defined by

$$\kappa^2 = 4\pi\beta e^2 c.$$

Applying Eq. (5.2), we find that the potential $v(r)$ is the Debye potential

$$v(r) = e^2e^{-\kappa r}/r.$$  \hspace{1cm} (5.6)

To insure stability of the system, we assume

$$\mu(0) = 0,$$

which is equivalent to adding a uniform continuous background of neutralizing charge. Then the mean field term in Eq. (3.3a) is zero. The single-mode term is obtained by substituting (5.5) into (4.12), which yields an integral which can be evaluated by integration by parts. The result is

$$a_4 = e^2/12\pi,$$

which is the usual Debye–Hückel result for the free energy. This result is obtained from the cluster theory by summing all ring diagrams, which are the most divergent diagrams resulting when the $f$ functions of the usual cluster theory are expanded in powers of $\beta$. The quantity $-\beta v(r)$ is equal to the function $q_0(r)$ used by Friedman.\(^2\) Thus the integrals in Eqs. (5.1), (5.3), and (5.4) for $a_4$, $a_6$, and $a_8$ are exactly the same as cluster integrals appearing in ionic cluster theory. The coefficients appearing in these equations are the same as the corresponding coefficients in the cluster theory.

Thus each of the terms appearing in $a_4$ to $a_6$ is equal to a term in the cluster theory for ionic systems. With the present analysis of the mode expansion, it is difficult to prove the exact equivalence of the two theories. (A more sophisticated analysis and proof will be the subject of a future paper in this series.) At this stage in the development, the most one can conclude is that the results of the mode expansion are consistent with those of the cluster theory.

Equations (5.1), (5.3), and (5.4), when applied to the Coulomb potential, lead to divergent integrals. The divergences occur for small $r$, and similar divergences occur in other theories of ionic solutions and plasmas. There are two ways in which these divergences are overcome in other theories, and these same two ways can be used in the mode expansion. The first way of overcoming the difficulty is to note that for real ionic solutions, there are short-range repulsions which keep charged particles from coming too close to one another. This effectively would apply a small $r$ cutoff to the integrals. Mathematically this cutoff arises in the following way: For each divergent integral similar to those in Eqs. (5.1), (5.3), and (5.4), there appears another integral with the same divergence but with an opposite sign. Thus the total result is convergent. In the mode expansion, the divergences also disappear when the short-range repulsions are taken into account by using a reference system which is not the ideal gas. The second way of overcoming the divergences in the cluster theory is to sum an infinite number of divergent integrals to obtain a convergent result. This was done by Abe\(^8\) for the so-called “watermelon” diagrams. Our expressions $a_4$ and $a_6$ and the first term in $a_8$ are watermelon contributions. The general watermelon term is

$$(\epsilon^2/24V)\int dr_1 dr_2 [-\beta v(r_{12})]^4.$$

When these contributions for $n \geq 3$ are summed, the result is

$$(\epsilon^2/24V)\int dr_1 dr_2 \left[\exp[-\beta v(r_{12})] - 1 + \beta v(r_{12}) - \frac{1}{2} [\beta v(r_{12})]^2] \right],$$

which is a convergent integral. In Friedman’s notation, this is

$$(\epsilon^2/24V)\int dr_1 dr_2 \delta'''(r_{12}).$$

Although the general term in the mode expansion is difficult to obtain, it can be shown that one of the terms in $a_8$ for $n \geq 3$ is precisely the expression in (5.6).

Thus, the results obtained in the mode expansion contain removable singularities for small $r$ if the intermolecular potential contains a singularity for small $r$. However, the mode expansion results have no divergence for large $r$ even though the original potential may be long ranged. The absence of long-range divergences in the mode expansion follows from the use of collective coordinates rather than particle coordinates.

VI. DISCUSSION

The mode expansion is a procedure for obtaining the free energy of a system in terms of the free energy and...
distribution functions of a reference system. The three important properties of the expansion are that it is simple, it is systematic, and it contains no divergences due to long range intermolecular potentials.

The simplicity of the expansion arises mainly from the use of van Kampen's method for obtaining the average value of a product. A series for \( \ln Q \) is obtained directly, without the need for performing a linked cluster analysis of an infinite series for \( Q \). Quantities analogous to unlinked clusters appear in the mode expansion only in the numerator and denominator of equations like (3.7), and they cancel when the quotient is calculated just as disconnected and reducible diagrams cancel in van Kampen's derivation of the cluster expansion. It should also be noted that only very simple mathematical techniques, such as the calculus and long division, are needed. Diagrammatic analysis and the solution of formidable combinatorial problems are not required. It is hoped that this simplicity will result in the mode expansion being useful for various other problems in statistical mechanics.

The second virtue of the mode expansion is that it provides a systematic way of calculating higher and higher order approximations. The \( n \)th contribution to the free energy, for small \( n \), can be obtained with a finite amount of labor. For an arbitrary reference system, the amount of work needed is prohibitively large for large \( n \). This is not a serious drawback, however, since for practical calculations the series for \( \alpha \) is only useful when it converges rapidly.

The third virtue of the mode expansion is that it contains no long-range divergences even for the Coulomb potential. This follows from the use of collective coordinates rather than particle coordinates. The basic physical quantity appearing in \( a_n \) for \( n \geq 2 \) is \( \tilde{v}(k) \). This is the Fourier transform of a density- and temperature-dependent renormalized potential which is of shorter range than \( \nu(\tau) \).

The major drawback of the mode expansion is that although the first few terms are easy to obtain it is difficult to find explicit expressions for the general term in the expansion. A consideration related to this is that the fact that the mode expansion does not automatically provide a rapidly convergent expansion in powers of some small parameter. The contribution of higher-order terms in the series depends in general on many factors, including the nature of the reference system, the perturbation potential, the temperature, and the density, and must be investigated and estimated separately for each specific problem.

The only specific application of the mode expansion which is presented in this paper is for the ideal gas reference case and spherically symmetric intermolecular potential-energy functions. The agreement between the mode expansion results and those of ionic cluster theory is an indication of the basic soundness of the method. Preliminary calculations indicate that the mode expansion also gives useful accurate results for other physical problems such as a dense monatomic liquid and electrolyte solutions. In addition, there is a class of theoretical problems for which graphical analysis has as yet made limited progress, such as the properties of fluids of polarizable molecules and the effects of ionic forces on the configuration of a polyelectrolyte molecule in solution. It is hoped that the mode expansion may prove useful for solution of these problems, as a result of its simplicity and the ease with which it deals with long-range forces. Further applications of the mode expansion will be discussed in future papers.

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