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New Method for Generating Density Expansions

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Citation Details
The calculus of finite differences is used to develop a new method for expressing the thermodynamic limit of a reasonably arbitrary statistical–mechanical average as a power series in the number density $\rho$. The method is simple, straightforward, and purely analytic: it involves no intermediate expansion in powers of the activity and it avoids the use of graph theory. Moreover, the method is developed independently of the prescription for computing the statistical average, a fact which lends to the results an especially wide range of applicability. In particular, these results may be used in classical or quantum statistical mechanics, for intermolecular potentials which are not spherically symmetric or pairwise additive, for molecules of arbitrary internal structure and complexity, and for polar molecules. A general formula is obtained for the coefficient of $\rho^k$ in the series; as usual, the most difficult problem one need solve in order to compute this coefficient is the evaluation of a $k$-molecule average. It is shown that if all the coefficients exist and if the density is less than a certain well-defined critical density, then the series converges to the thermodynamic limit of the average in question. The practical use of the method is clarified by examples.

I. INTRODUCTION

This article is concerned with the derivation of a new method for generating the power-series density expansion of a general canonical statistical–mechanical average $F(N, V, T)$, corresponding to some observable property $F$ of an equilibrium system of $N$ molecules in a volume $V$ at absolute temperature $T$. We assume that $F(N, V, T)$ has been defined to be intensive for large $N$ and $V$. To provide a framework for our introductory discussion, we will summarize here our principal results. Let $F(\rho, T) = \lim_{N \to \infty} F(N, V, T)$, where $\lim$ denotes the thermodynamic limit ($N \to \infty$, $N/V = \rho =$ const), and define

$$A_k(T) = (-1)^k \lim_{V \to \infty} \left[ \sum_{j=0}^k \frac{(-1)^j}{j!(k-j)!} F(j, V, T) \right]. \quad (1)$$

Under the assumption that all the $A_k(T)$ exist, we show that

$$F(\rho, T) = \sum_{k=0}^\infty A_k(T) \rho^k \quad \text{if } \rho < \rho_m(T). \quad (2)$$

The quantity $\rho_m(T)$ is defined in Appendix A; it is always less than or equal to the radius of convergence of the series in Eq. (2). The quantity $F(j, V, T)$ appearing in Eq. (1) is just the result of evaluating the statistical average in question for a system containing only $j$ molecules in the volume $V$. According to Eq. (1), $A_k(T)$ depends only upon the $F(j, V, T)$ with $j \leq k$. The evaluation of a $k$-molecule average is therefore the hardest problem one need solve in order to determine $A_k(T)$.

The quantity $F$ can be any physical quantity of interest, so long as all the corresponding $A_k(T)$ exist and $\rho_m(T)$ is nonzero [enabling the condition $\rho < \rho_m(T)$ to be satisfied]. Typical quantities of interest are the excess Helmholtz free energy per molecule, the pressure, the generic molecular distribution functions, the dielectric constant, the Kerr constant, the depolarization ratio for Rayleigh scattering of light, and so on. In order to clarify the way in which Eqs. (1) and (2) are applied in practice, we use them in Sec. IV to generate the density expansions of the pressure and the dielectric constant.

The distinctive features of the present method, in respect to which it differs from the various well-known density-expansion methods which already exist, are as follows: (a) The method generates directly an expansion in powers of the density, making the usual intermediate expansion in powers of the activity unnecessary. (b) The method is systematic and purely analytic; in particular, it uses no graph theory. (c) It is not necessary to specify the prescription for computing the statistical average $F(N, V, T)$ in order to derive the general formula (1) for the coefficients in the expansion. This fact allows the method to retain a good deal of generality, and means in particular that Eqs. (1) and (2) may be used in both classical and quantum statistical mechanics (even if Fermi–Dirac or Bose–Einstein statistics need to be taken into account), regardless of whether or not the $N$-molecule potential energy is pairwise or otherwise additive, and regardless of the existence of rotational, vibrational, electronic, or other “internal” molecular coordinates (and momenta), and any corresponding dependence on them of the potential energy or other dynamical variables. (d) Equations (1) and (2) are derived without specifying what observable quantity $F$ is being considered. The quantities most commonly density-expanded in other methods are the pressure (or the logarithm of the partition function) and the generic distribution functions, and the present method can also be applied to these quantities. In addition, however, it may be applied directly to quantities which cannot simply or conveniently be expressed in terms of derivatives of the partition function (such as the Kerr constant and...
the depolarization ratio), without the necessity of first re-expressing such quantities in terms of the generic distribution functions. (e) No explicit restriction to short-range intermolecular potentials is adopted. In most cases our assumption that all the $A_k(T)$ exist is equivalent to such a restriction, since the $A_k(T)$ are not ordinarily expected to exist unless the potential energy of a pair of interacting molecules goes to zero more rapidly than $r^{-3}$ as their intermolecular separation $r$ is increased. An important exception to this equivalence, however, is provided by polar substances, for which the $A_k(T)$ do not exist, in spite of the long-range $r^{-3}$ radial dependence of the permanent dipole–dipole interaction, because of the fact that this interaction is in many contexts rendered effectively short ranged by its angular dependence. Thus the present method may be applied to polar substances, whereas the applicability of other methods to such substances is somewhat questionable in view of their common restriction to short-range potentials.

The long-range nature of the dipole–dipole potential implies that the physical properties of polar substances cannot, in general, be expected to be independent of sample shape in the thermodynamic limit. Examples of such shape dependence are familiar from the theory of dielectrics. In such cases, the virial coefficients $A_k(T)$ will, of course, also depend upon the sample shape. The present method will automatically take such shape dependence into account if one takes the limit as $V \rightarrow \infty$ in Eq. (1) [and in the definition of $p_n(T)$—see Appendix A] with the shape held fixed in correspondence to the experimental geometry of interest. We have used Eqs. (1) and (2) to obtain the first two nonvanishing terms in the density expansion of the pair distribution function for a classical system composed of rigid polar molecules. For this case it was found that, although $A_3(T)$ is not explicitly shape dependent, $A_3(T)$ exhibits a nonzero (although negligible) dependence on the shape of the volume $V$, even though the infinite-volume limit has been taken. Such shape dependence will doubtless constitute only a negligible correction to the low-order virial coefficients, except possibly in cases where a cancellation causes it to become important by default. One suspects that higher-order coefficients would exhibit progressively stronger shape dependences.

For concreteness, and because it is the most common case of interest, we are restricting our attention to statistical–mechanical averages in the canonical ensemble. However, our results may be taken over to the microcanonical ensemble by the trivial modification of replacing the temperature $T$ by the mean thermodynamic internal energy per molecule $e$ everywhere in Eqs. (1) and (2). The validity of our derivation and results is unchanged by this replacement, since $T$ is simply carried along as a constant parameter throughout the derivation. The method does not appear to be directly applicable in the grand canonical ensemble, since in this ensemble the averages are not performed with $N$ held constant.

Although the method fails if some or all of the $A_k(T)$ do not exist, it may be possible in such cases to use Eqs. (1) and (2) as a starting point for a resummation scheme which removes the divergences. We are currently exploring this possibility.

II. INTUITIVE APPROACH

Before presenting the rigorous derivation of Eqs. (1) and (2), we describe a heuristic method, due to Zwanzig, of obtaining the same result for the coefficients $A_k(T)$. We assume that the quantity $F(N, V, T)$ can be expressed as the sum of a contribution independent of $N$ and contributions proportional to the number of singlets, pairs, triplets, etc., in the $N$-molecule system. That is, we write

$$F(N, V, T) = b_0(V, T) + Nb_1(V, T)$$

$$+ \frac{1}{2} N(N-1)b_2(V, T) + \cdots$$

$$= \sum_{k=0}^{N} b_k(V, T) \left( \begin{array}{c} N \\ k \end{array} \right),$$

(3)

where

$$\left( \begin{array}{c} N \\ k \end{array} \right)$$

is a binomial coefficient, defined by $N!/[k!(N-k)!]$. The coefficients $b_k(V, T)$ may simply be determined by varying $N$. Setting $N=0$ in Eq. (3) yields

$$b_0(V, T) = F(0, V, T).$$

(4a)

Setting $N=1$ in Eq. (3) and making use of Eq. (4a) yields

$$b_1(V, T) = F(1, V, T) - F(0, V, T).$$

(4b)

Setting $N=2$ in Eq. (3) and making use of Eqs. (4a) and (4b) yields

$$b_2(V, T) = F(2, V, T) - 2F(1, V, T) + F(0, V, T),$$

(4c)

and so on. In this way each $b_k(V, T)$ can be expressed in terms of the quantities $F(0, V, T), \ldots, F(k, V, T)$.

Now for large $N$ the binomial coefficient

$$\left( \begin{array}{c} N \\ k \end{array} \right)$$

differs negligibly from $N^k/k! = (V^k/k!)(N/V)^k$. In the
thermodynamic limit, therefore, Eq. (3) probably becomes
\[
F(\rho, T) = \lim_{N \to \infty} F(N, V, T) = \lim_{N \to \infty} \sum_{k=0}^{N} b_k(V, T) \binom{N}{k}
\]
\[
= \sum_{k=0}^{\infty} \left[ \lim_{N \to \infty} \frac{V^k}{k!} b_k(V, T) \right] \rho^k = \sum_{k=0}^{\infty} A_k(T) \rho^k, (5)
\]
where
\[
A_k(T) = \lim_{N \to \infty} \left[ \frac{(V^k/k!)}{b_k(V, T)} \right]. \quad (6)
\]
It is easily verified that Eq. (6), combined with Eqs. (4), is consistent with Eq. (1) for \( k = 0, 1, \) and 2. One can verify by induction that Eqs. (6) and (1) are consistent (equivalent) for all \( k \).

The above derivation is certainly plausible, but the following two objections to it can be raised: (a) It makes the assumption that an arbitrary function \( F(N, V, T) \) can be expanded in terms of binomial coefficients without remainder. This assumption has not been justified. (b) The thermodynamic limit in Eq. (5) was handled very carelessly, and the derivation consequently sheds no light on the conditions, if any, under which \( F(\rho, T) \) is rigorously equal to the infinite series on the right-hand side of Eq. (5).

Neither of these objections is of a serious nature and both of them could be disposed of at this point, but we shall find it more convenient to do so within the framework of the derivation given in the next section.

### III. Finite-Differences Approach

A more systematic approach to the density-expansion problem than that of the preceding section can be based upon the calculus of finite differences. The finite-differences approach proves fruitful in the present context simply because the number of molecules \( N \) is inherently a discrete variable: it takes on only non-negative integral values. One therefore cannot properly deal with \( N \) by the methods of the infinitesimal calculus (for example, one cannot differentiate with respect to \( N \)), and it is natural to resort instead to the methods of the finite calculus. The discrete character of the variable \( N \) is especially significant in a finite system, which is what we must deal with prior to taking the thermodynamic limit. The familiar binomial coefficients, which were introduced on an intuitive basis in the preceding section, will be seen to emerge somewhat more naturally in the finite-differences approach.

Although the intuitive approach of the preceding section and the finite-differences approach are basically complementary to one another, the latter has the advantage of being the more systematic. In particular, the general validity of the expansion (3) is evident from the beginning in the finite-differences approach, and the significance and appropriateness of this expansion are perhaps clearer. Moreover, the general formula (1) for the coefficients emerges automatically, whereas it would have to be arrived at by induction in the intuitive approach.

Two standard and useful treatises on the calculus of finite differences are the books by Milne-Thomson and Jordan. For our purposes, however, the brief (and somewhat more modern) introductory account of Apostol is a more appropriate reference, since we shall require only the most basic ideas of the subject.

We begin by summarizing the definitions and formulae from the finite calculus which we will make use of. In what follows \( F(N) \) is an arbitrary function of the discrete argument \( N \) \( (N=0, 1, 2, \cdots) \). The difference operator \( \Delta \) is defined by
\[
\Delta F(N) = F(N+1) - F(N), \quad (7)
\]
which implies that
\[
\Delta^2 F(N) = \Delta [\Delta F(N)] = F(N+2) - 2F(N+1) + F(N),
\]
and so on, according to the recursive definition
\[
\Delta^k F(N) = \Delta [\Delta^{k-1} F(N)].
\]

The factorial polynomial \( N^{(k)} \) (also called the factorial \( k \)th power of \( N \)) is defined by
\[
N^{(k)} = N!/(N-k)! \quad \text{if} \quad 0 \leq k \leq N,
\]
\[
= 0 \quad \text{if} \quad k > N, \quad (8)
\]
where \( k \) is an integer. Notice that the factorial polynomial \( N^{(k)} \) differs from the binomial coefficient
\[
\binom{N}{k}
\]
only by a factor of \( k! \) ! Its main significance in the finite calculus, however, is due to the relation
\[
\Delta N^{(k)} = kN^{(k-1)}, \quad (9)
\]
which can easily be verified from the definitions.

Equation (9) is the finite-differences formula analogous to \( d(x^k)/dx = kx^{k-1} \), and indicates that the factorial polynomial \( N^{(k)} \) is the finite-differences analog of the power function \( x^k \) of a continuous variable \( x \). Since
\[
N^{(k)} = k! \binom{N}{k},
\]
we see that the intuitive Eq. (3) is just the discrete equivalent of a power series in \( N \).

Next we need Newton's interpolation formula for the "interpolation polynomial" \( P_N(x) \) of degree \( \leq N \) which agrees with a function \( f(x) \) at the \( N+1 \) points \( x = 0, 1, \cdots, N \). When written in terms of the difference operator and factorial polynomials, Newton's
formula takes the form
\[ P_N(x) = \sum_{k=0}^{N} (k!)^{-1} [\Delta^k f(x')]_{x=x^{(k)}}. \] (10)

Here
\[ x^{(k)} = \prod_{j=0}^{k-1} (x-j) \] (11)
is the definition of the factorial polynomial which is used when \( x \) may be nonintegral; it clearly reduces to Eq. (8) when \( x \) is a nonnegative integer. Since \( P_N(x) \) is by definition exactly equal to \( f(x) \) when \( x = N \), we have from Eq. (10) that
\[ f(N) = P_N(N) = \sum_{k=0}^{N} (k!)^{-1} [\Delta^k f(N')]_{x'=0}. \] (12)

Since only the values \( f(0), f(1), \cdots, f(N) \) enter into Eq. (12), this equation is valid regardless of how (or whether) the arbitrary function \( f(x) \) is defined for nonintegral \( x \). Therefore
\[ F(N) = \sum_{k=0}^{N} (k!)^{-1} [\Delta^k F(N')]_{x'=0}N^{(k)} \] (13)
is an identity, rigorously valid for an arbitrary function \( F(N) \) of the discrete argument \( N \).

Equation (13) is the basic starting equation of our method. This equation may be regarded as the finite-differences analog of an ordinary Taylor series, to which it bears an obvious formal and structural resemblance. There are two important differences, however, between Eq. (13) and a Taylor series: (a) For finite \( N \) the summation in Eq. (13) is finite, whereas that in a Taylor series is infinite. (b) Equation (13) is valid for an arbitrary function \( F(N) \) of the discrete variable \( N \). In contrast, we know that even if all the derivatives of a function \( f(x) \) exist the corresponding infinite Taylor series without remainder does not necessarily represent \( f(x) \).

Because of the simple relation between \( N^{(k)} \) and
\[ \binom{N}{k}, \]
Eq. (13) is equivalent to Eq. (3). It is therefore now completely clear that no remainder term was omitted from Eq. (3). We also see that the coefficients \( b_k(V, T) \) in this equation can be obtained simply by taking the \( k \)th difference of \( F(N, V, T) \), which is considerably more convenient than the pedestrian procedure outlined in the preceding section. In fact, even the small amount of labor involved in taking the \( k \)th difference has already been performed for us. It is clear that \( [\Delta^k F(N')]_{x'=0} \) is a linear combination of the quantities \( F(0), F(1), \cdots, F(k) \), and the general relation is well known in the finite calculus; it is
\[ [\Delta^k F(N')]_{x'=0} = (-1)^k \sum_{j=0}^{k} \binom{k}{j} F(j). \] (14)

Incidentally, the general validity of Eq. (13) can be verified by substituting Eq. (14) into it and rearranging the resulting double summation. Equation (13) then reduces, after a little algebra, to the identity \( F(N) = F(N) \).

Now since Eqs. (13) and (14) are valid for an arbitrary function \( F(N) \), they are valid for \( F(N, V, T) \). Therefore
\[ F(N, V, T) = \sum_{k=0}^{N} a_k(V, T)N^{(k)}, \] (15)
where
\[ a_k(V, T) = (k!)^{-1} [\Delta^k F(N, V, T)]_{x'=0} = (-1)^k \sum_{j=0}^{k} \binom{k}{j} F(j, V, T). \] (16)

Equation (15) can be rewritten in the form
\[ F(N, V, T) = \sum_{k=0}^{N} A_k(V, T) \binom{N^{(k)}}{N^k}, \] (17)
where
\[ A_k(V, T) = V^k a_k(V, T). \] (18)

We have replaced \( N \) by infinity as the upper limit to the sum in Eq. (17), but this changes nothing since the factor \( N^{(k)} \) in the summand makes all terms with \( k > N \) zero.

We are interested in the quantity \( F(\rho, T) = \lim_{N, V \to \infty} F(N, V, T) \). Using Eq. (17), we can write this quantity as
\[ F(\rho, T) = \lim_{N, V \to \infty} F(N, V, T) = \lim_{N, V \to \infty} F(N, N/\rho, T) \]
\[ = \lim_{N, V \to \infty} \sum_{k=0}^{\infty} A_k(N/\rho, T) \binom{N^{(k)}}{N^k} \rho^k. \] (19)

We now define \( A_k(T) \) by
\[ A_k(T) = \lim_{V \to \infty} A_k(V, T), \] (20)
and we shall assume that \( A_k(T) \) exists for any \( k \). The explicit formula for \( A_k(T) \), obtained by combining Eqs. (20), (18), and (16), is given by Eq. (1). By virtue of Eq. (20) and a fundamental limit theorem, we have that
\[ \lim_{N \to \infty} \binom{A_k(N/\rho, T)N^{(k)}}{N^k} \]
\[ = \lim_{N \to \infty} A_k(N/\rho, T) \binom{N^{(k)}}{N^k} = A_k(T), \] (21)
where we have used the easily verified fact that
\[ \lim_{N \to \infty} \binom{N^{(k)}}{N^k} = 1 \]
for all $k$. From Eq. (19) we see that the desired result obtains immediately if the limit in Eq. (19) is taken inside the summation. We can therefore write

$$F(\rho, T) = \sum_{k=0}^{\infty} A_k(T) \rho^k$$

(22)

if $X$ is satisfied, where $X$ denotes any condition which is sufficient to guarantee the validity of taking the limit inside the summation. In Appendix A we show that such a condition is that $\rho$ be less than a certain well-defined critical value $\rho_0(T)$. Using this condition for $X$, we obtain Eq. (2); this completes the derivation.

**IV. EXAMPLES**

**A. The Pressure**

As our first example, we will use Eqs. (1) and (2) to obtain the second and third virial coefficients of the pressure of a classical system of spherically symmetric point particles interacting through nonadditive short-range forces. These results are well known and hence can be used as a test of the method. We shall identify $F(N, V, T)$ with $p/kT$, where $p$ is the pressure and $k$ is Boltzmann’s constant. Thus

$$F(N, V, T) = \frac{\partial}{\partial V} \log \int \prod_{i=1}^{N} dR_i W_N(R_1, R_2, \cdots, R_N),$$

(23)

where

$$W_N(R_1, R_2, \cdots, R_N) = \exp \{-U_N(R_1, R_2, \cdots, R_N)/kT\}$$

and

$$U_N(R_1, R_2, \cdots, R_N)$$

is the potential energy of the $N$-molecule system in the configuration $(R_1, R_2, \cdots, R_N)$. To go out to third order in the density, Eqs. (1) and (2) tell us that we need $F(j, V, T)$ with $j=0, 1, 2,$ and 3. Equation (23) is meaningless when $N=0$, but the pressure vanishes when there are no molecules in the system; therefore

$$F(0, V, T) = 0.$$  

(24)

We obtain $F(1, V, T)$, $F(2, V, T)$, and $F(3, V, T)$ by setting $N=1, 2,$ and 3, respectively, in Eq. (23):

$$F(1, V, T) = (\partial/\partial V) \log \int dR_1 W_1(R_1) \log V = V^{-1},$$

(25a)

$$F(2, V, T) = (\partial/\partial V) \log \int dR_1 dR_2 W_2(R_1, R_2),$$

(25b)

$$F(3, V, T) = (\partial/\partial V) \log \int dR_1 dR_2 dR_3 W_3(R_1, R_2, R_3).$$

(25c)

It is now necessary to re-express the integrals in Eqs. (25b) and (25c) in such a way their $V$ dependence is explicitly displayed. By performing manipulations of a standard nature, which exploit the short-ranged nature of $U_N(R_1, R_2)$ and the fact that it depends only upon $|R_i - R_j| = r$, the integral in Eq. (25b) can be put into the form

$$\int dR_1 dR_2 dR_3 W_2(r) = \int dR_1 dR_2 [1 + [W_2(r) - 1]] = V^2 - 2BV,$$

(26)

where

$$B = 2\pi \int_0^{\infty} r^2 dr \left[1 - W_2(r) \right]$$

(27)

and we have assumed $V^{1/2}$ to be much larger than the range of $U_2(r)$. Equation (25b) now becomes

$$F(2, V, T) = (\partial/\partial V) \log (V^2 - 2BV) = (2/V) (V^2 - 2B)^{-1} (V - B).$$

(28)

The integral in Eq. (25c) is dealt with in the same way:

$$\int dR_1 dR_2 dR_3 W_3(R_1, R_2, R_3) \int [1 + [W_2(R_1, R_2) - 1] + [W_3(R_1, R_2, R_3) - W_2(R_1, R_2) - W_2(R_2, R_3) + W_3(R_1, R_2, R_3) - W_2(R_1, R_3)]$$

$$= V^3 - 6BV^2 + 6rV,$$

(29)

where $\Gamma$ is just the familiar three-particle reducible cluster integral:

$$\Gamma = \frac{1}{6} \int dR_1 dR_2 dR_3 W_3(R_1, R_2, R_3) - W_3(|R_1 - R_2|) - W_2(|R_1 - R_3|) - W_2(|R_2 - R_3|) + 2]$$

(30)

We have made use of the fact that $U_3(R_1, R_2, R_3)$ (and hence $W_3(R_1, R_2, R_3)$ as well) depends only upon $R_{12} = (R_1 - R_2)$ and $R_{13} = (R_1 - R_3)$, and have assumed $V^{1/2}$ to be much larger than the range of $U_2$ and $U_3$. Equation (25c) now becomes

$$F(3, V, T) = (\partial/\partial V) \log (V^3 - 6BV^2 + 6rV) = (3/V) (V^2 - 6BV + 6rV)^{-1}$$

$$\times (V^2 - 4BV + 2r).$$

(31)

Next we must form the $A_k(V, T)$ from the $F(j, V, T)$ in accordance with Eqs. (18) and (16). From Eqs. (24), (25a), (28), and (31) we obtain

$$A_0(V, T) = F(0, V, T) = 0;$$

(32a)

$$A_1(V, T) = V[F(1, V, T) - F(0, V, T)] = 1;$$

(32b)

$$A_2(V, T) = \frac{1}{2} V^2 [F(2, V, T) - 2F(1, V, T)]$$

$$= B(1 - 2B/V)^{-1};$$

(32c)

$$A_3(V, T) = \frac{1}{6} V^3 [F(3, V, T) - 3F(2, V, T)$$

$$+ 3F(1, V, T)]$$

$$= [1 - (2B/V)]^{-1} [1 - (6B/V + (6r/V))^{-1}]$$

$$\times [4B^2 - 2(1 + (B/V))],$$

(32d)

$$= \frac{1}{6} V^3 [F(3, V, T) - 3F(2, V, T)$$

$$+ 3F(1, V, T)]$$

$$= [1 - (2B/V)]^{-1} [1 - (6B/V + (6r/V))^{-1}]$$

$$\times [4B^2 - 2(1 + (B/V))],$$

(32d)
where some algebra has been omitted. As instructed by Eq. (20) or Eq. (1), we now take the limit as $V \to \infty$ of the $A_k(V, T)$ given by Eqs. (32). The result is

\begin{align*}
A_0(T) &= 0; \\
A_1(T) &= 1; \\
A_2(T) &= B; \\
A_4(T) &= 4B^2 - 2T.
\end{align*}

Combining Eqs. (33) with Eq. (2) yields $p/kT$ in the thermodynamic limit:

$$p/kT = \rho + B\rho^2 + (4B^2 - 2T)\rho^3 + \mathcal{O}(\rho^4).$$

We see that our expressions for the second and third virial coefficients $A_2(T)$ and $A_4(T)$ are the same as the well-known results obtained by other methods.\(^12\)

**B. The Dielectric Constant**

As our second example, we will consider the low-density behavior of the dielectric constant of a classical nonpolar fluid. For simplicity, we will stop at second order in the density. In order to circumvent the usual assumption that the dielectric constant of an isotropic fluid is independent of position and sample geometry,\(^13\) we will focus attention directly on the "experimental" dielectric constant, namely the ratio of the capacitance of a parallel-plate capacitor filled with the dielectric to the capacitance of the empty capacitor. This ratio will be denoted by $D$. We shall assume that the capacitor behaves ideally; that is, that fringe effects may be neglected. It is then easy to show that\(^2\)

$$(D-1)/D = (4\pi/e)V \mathcal{E} \cdot \mathcal{E} = \left[ \langle \partial/\partial \mathcal{E} \rangle \mathbf{M}(\mathbf{E}; \mathcal{E}) \right]_{\mathcal{E}=0},$$

where $\mathcal{E}$ is the electric field due to the real charges on the capacitor plates, $\mathbf{e}$ is a unit vector normal to the plates, $\mathbf{M}(\mathbf{E}; \mathcal{E})$ is the total electric dipole moment of the dielectric for a given molecular configuration $\mathbf{r}$ in the presence of $\mathcal{E}$, and the angle brackets $\langle \cdots \rangle$ denote an average over configurations $\mathbf{r}$ weighted by the Boltzmann factor appropriate to equilibrium in the presence of $\mathcal{E}$. Although $\langle \mathbf{M} \rangle$ can be expressed in terms of the partition function $Q_B(N, V, T)$ in the presence of $\mathcal{E}$, the most workers have found it more convenient to express $\langle \mathbf{M} \rangle$ in terms of averages taken in zero applied field. Buckingham and Pople,\(^14\) in particular, find that

$$\left[ \langle \partial/\partial \mathcal{E} \rangle \mathbf{M}(\mathbf{E}; \mathcal{E}) \right]_{\mathcal{E}=0} = \langle \partial \mathbf{M}(\mathbf{E}; \mathcal{E})/\partial \mathcal{E} \rangle_{\mathcal{E}=0} + (kT)^{-1} \left[ \mathbf{M}(\mathbf{E}; 0) \mathbf{M}(\mathbf{E}; 0) \right]_{\mathcal{E}=0},$$

where the angle brackets with subscript "0" denote an average over $\mathbf{r}$ taken in zero applied field ($\mathcal{E}=0$).

That is

$$\langle A(\mathbf{r}) \rangle_0 = \int d\tau A(\mathbf{r}) W_N(\tau)/\int d\tau W_N(\tau),$$

where $W_N(\tau) = \exp[-U_N(\tau)/kT]$, and $U_N(\tau)$ is the $N$-molecule potential energy in zero applied field. We do not assume that $U_N(\tau)$ is additive.

The molecular configuration $\mathbf{r}$, written without a subscript, will be considered to consist of the set of all positional and orientational coordinates of the $N$ molecules in the sample. Molecular vibration will be neglected, although its inclusion (especially classically) would present no particular difficulty beyond making the description somewhat more complicated. Thus we have $\mathbf{r} = (\mathbf{R}_N, \mathbf{\omega})$, where $\mathbf{R}_N = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$ is the set of all molecular positions and $\mathbf{\omega} = (\omega_1, \omega_2, \ldots, \omega_N)$ the set of all orientation angles. The coordinates $(\mathbf{R}_i, \omega_i)$ of molecule $i$ will be designated by $\tau_i$.

The total dipole moment of the sample, $\mathbf{M}(\mathbf{r}; \mathcal{E}_0)$, is just the sum of the moments of the individual molecules. Thus

$$\mathbf{M}(\mathbf{r}; \mathcal{E}_0) = \sum_{k=1}^N \mu_k(\mathbf{r}; \mathcal{E}_0),$$

where $\mu_k(\mathbf{r}; \mathcal{E}_0)$ is the dipole moment of molecule $k$ for fixed configuration $\mathbf{r}$ and in the presence of $\mathcal{E}_0$. Since the molecules are polarizable, $\mu_k$ will in general depend not just on the coordinates $\tau_k$ of molecule $k$ itself, but on the coordinates of all the other molecules as well; this is why it must be written as $\mu_k(\mathbf{r}; \mathcal{E}_0)$ rather than $\mu_k(\tau_k; \mathcal{E}_0)$.

We shall identify $F(N, V, T)$ with $(D-1)/(4\pi D)$. Comparing Eqs. (35), (36), and (38), and making use of the fact that all the molecules are identical, we obtain

$$F(N, V, T) = \left( N/V \right) \left\{ \partial \mu_1(\mathbf{r}; \mathcal{E}_0)/\partial \mathcal{E} \right|_{\mathcal{E}=0} \right\} + (kT)^{-1} \left[ \mathbf{M}(\mathbf{r}; 0) \mathbf{M}(\mathbf{r}; 0) \right]_{\mathcal{E}=0} \times \left[ \langle \mu_1(\tau; 0) \cdot \mathbf{e} \rangle_0 \left[ \langle N(1/kT) \right] \right]_{\mathcal{E}=0}.$$  

To go out to second order in $\rho$, we need $F(0, V, T)$, $F(1, V, T)$, and $F(2, V, T)$. Setting $N=0$ in Eq. (39) yields

$$F(0, V, T) = 0,$$

Setting $N=1$ in Eq. (39) and using Eq. (37), we obtain

$$F(1, V, T) = \bar{\alpha}/V,$$

where

$$\bar{\alpha} = \Omega^{-1} \int d\omega \left[ \partial \mu_1(\omega; \mathcal{E}_0)/\partial \mathcal{E} \right]_{\mathcal{E}=0} \mathcal{E},$$

and $\Omega = \int d\omega$ is an angular normalization constant. The quantity $\bar{\alpha}$ is, of course, just the mean polarizability of the isolated molecule 1. The second term on the right-hand side of Eq. (39) does not contribute to $F(1, V, T)$, because the dipole moment $\mu_1(\tau; 0)$ of an isolated nonpolar molecule in zero field is zero.

Setting $N=2$ in Eq. (39) and using Eq. (37), we
obtain

\[ F(2, V, T) = \frac{2}{V} \int d\tau_1 d\tau_2 W_2(\tau_1, \tau_2) \left( \frac{\partial \mu_1(\tau_1, \tau_2; E_0)}{\partial E_0} \right)_{E_0=0} : \epsilon \epsilon \epsilon \epsilon \]  

\[ + (kT)^{-1} \left[ \mu_1(\tau_1, \tau_2; 0) \cdot \epsilon \right] \times \left[ \left( \mu_2(\tau_1, \tau_2; 0) + \mu_3(\tau_1, \tau_2; 0) \right) \cdot \epsilon \right] \}. \]  

(43)

Now \( W_2(\tau_1, \tau_2) \), \( \mu_1(\tau_1, \tau_2; 0) \), \( \mu_2(\tau_1, \tau_2; 0) \), and \( \left[ \mu_2^2(\tau_1, \tau_2; E_0)/\partial E_0 \right]_{E_0=0} \) depend only on \( |r_1 - r_2| = r \), \( \omega_1 \), and \( \omega_2 \), where \( \omega_1 \) and \( \omega_2 \) specify the orientations of molecules 1 and 2 relative to their intermolecular axis (the unprimed angles \( \omega \) specify orientations relative to a fixed laboratory frame). Because the molecules are nonpolar, the functions \( W_2(\tau_1, \tau_2) \) and \( \mu_1(\tau_1, \tau_2; 0) \) (i.e., both \( W_2(\tau_1, \tau_2) - 1 \) and \( \mu_1(\tau_1, \tau_2; 0) \)) go to zero with increasing \( r \) faster than \( r^{-2} \). The quantity \( \left[ \mu_2^2(\tau_1, \tau_2; E_0)/\partial E_0 \right]_{E_0=0} \) has a long-ranged part and requires special attention; it is dealt with in Appendix B. The foregoing considerations, and the equivalence of molecules 1 and 2, permit us to rewrite Eq. (43) in the form

\[ F(2, V, T) = \frac{2}{V^2 - 2BV} \frac{1}{V} \left( \Phi + (1/3kT) I_1 \right), \]  

(44)

where

\[ B = \frac{2\pi}{\Omega_0} \int_0^\infty r^2 dr d\omega_1 d\omega_2 \left[ 1 - W_2(r, \omega_1, \omega_2) \right] \]  

(45)

is, of course, just the second virial coefficient of the pressure of the system;

\[ I_1 = \frac{2\pi}{\Omega_0} \int_0^\infty r^2 dr d\omega_1 d\omega_2 W_2(\tau_1, \tau_2) \left[ \mu_1 + \mu_2 \right]^3, \]  

(46)

in which the arguments \( (r, \omega_1, \omega_2) \) of \( W_2, \mu_1, \) and \( \mu_2 \) have been suppressed; and

\[ \Phi = \frac{1}{V} \int d\tau_1 d\tau_2 W_2(\tau_1, \tau_2) \times \left[ \partial \mu_1(\tau_1, \tau_2; E_0)/\partial E_0 \right]_{E_0=0} : \epsilon \epsilon \epsilon \epsilon \]  

(47)

In Appendix B it is shown that

\[ \Phi = 2I_2 + \bar{\alpha}(V - 2B) - \frac{8\pi}{3} \bar{\alpha}^2, \]  

(48)

where \( I_2 \) is given by Eq. (B5) of Appendix B.

We next form the \( A_s(V, T) \) as before. From Eqs. (40) and (41) we find

\[ A_0(V, T) = F(0, V, T) = 0; \]  

(49a)

\[ A_1(V, T) = V[F(1, V, T) - F(0, V, T)] = \bar{\alpha}. \]  

(49b)

By combining Eqs. (40), (41), (44), and (48), we find for \( A_2(V, T) \) that

\[ A_2(V, T) = \frac{1}{2} F^2[F(2, V, T) - 2F(1, V, T) + F(0, V, T)] \]  

\[ = \left[ 1 - \frac{2B}{V} \right]^{-1} \left[ 2I_2 + (3kT)^{-1} I_1 - \frac{8\pi}{3} \bar{\alpha}^2 \right]. \]  

(49c)

Taking the limit as \( V \to \infty \) of Eqs. (49) then yields

\[ A_0(T) = 0; \]  

(50a)

\[ A_1(T) = \bar{\alpha}; \]  

(50b)

\[ A_2(T) = 2I_2 + (3kT)^{-1} I_1 - \frac{8\pi}{3} \bar{\alpha}^2. \]  

(50c)

In the thermodynamic limit, therefore, we have

\[ (D-1)/(4\pi D) = A_1(T) + A_2(T) \rho^2 + \theta(\rho'), \]  

(51)

with \( A_1(T) \) and \( A_2(T) \) given by Eqs. (50b) and (50c).

By comparing Eq. (51) with the results of Buckingham and Pople, which they obtained by a semiintuitive density-expansion method, we find that at least to within terms of order \( \rho^2 \) the quantity \( D \) is the same as the quantity \( e \) which they calculate. At least to second order in the density, therefore, the static dielectric constant calculated in a spherical geometry under the assumptions of position independence and geometry independence is indeed equal to the experimentally measured capacitance ratio for a parallel-plate capacitor.

In deriving Eqs. (50) and (51), we have assumed only that the molecules are nonpolar and that vibration may be neglected. Beyond this, we have left the molecular model arbitrary, so our expressions for \( A_1(T) \) and \( A_2(T) \) are still possessed of considerable generality. In particular, they automatically include such effects as those of quadrupole-induced dipoles and density-dependent molecular polarizabilities. This illustrates another important feature of our method: it frequently allows one to avoid specifying the molecular model and hence reducing the generality of the starting expression for \( F(N, V, T) \) until after general expressions for the virial coefficients \( A_s(T) \) have been obtained. The present example also illustrates a case in which it would be very inconvenient to proceed by first expressing \( F(N, V, T) \) in terms of the reduced generic distribution functions and then making use of the known density expansions of these latter quantities. Not only would this require one to adopt a molecular model at the beginning, but one would find that the averages in Eq. (39) involve the latter quantities. Not only would this require one to adopt a molecular model at the beginning, but one would find that the averages in Eq. (39) involve the latter quantities.

Although the two examples we have considered do not convey a full appreciation of the generality of the method (we have not, for example, considered quantum phenomena), they do contain many features of general importance, and should at least serve to make it clear how to apply the method to any particular case in which one may be interested.
V. CONCLUDING REMARKS

We have seen that the techniques of finite-difference calculus can be used to develop a method of generating density expansions. The method is straightforward in the sense that it consists, in essence, simply in expressing the quantity \( F(N, V, T) \) of interest as an expansion in the discrete equivalent of powers of \( N \). Finite-difference methods are really the natural ones to use in a problem involving a discrete variable (such as \( N \)), and we believe that they lend some new insight into the fundamental nature of density expansions in general. Although the density is a continuous variable in the thermodynamic limit, it has its origin in a purely discrete problem, and the virial coefficients \( A_k(T) \) retain something of this discrete character even in the thermodynamic limit. By tracing the coefficients back to their discrete beginnings, one sees, for example, more clearly why the determination of the \( k \)th coefficient \( A_k(T) \) is always associated with the solution of a problem involving only \( k \) (and fewer) molecules.

Although we have focused our attention on results valid in the limit of an infinite system, we remark parenthetically that Eq. (17) may be applied directly to finite systems, and provides a means of obtaining the correction terms which characterize the deviation of the virial coefficients from their infinite-system values. For macroscopic systems these deviations are ordinarily exceedingly negligible, but for some purposes they can be of crucial importance. To obtain these correction terms, one first replaces \( N \) and \( \rho \) (rather than \( N \) and \( V \)) may be considered as independent variables. One next expands \( N^k/N \) in powers of \( 1/N \) and \( A_k(N, \rho, T) \) in powers of \( \rho/N \). The first expansion is well known; the coefficients are called Stirling numbers of the first kind. The second expansion will depend upon the prescription for computing the statistical averages. One then substitutes these expansions into the expression for \( F(N, N/\rho, T) \) and collects the coefficients of equal powers of \( \rho \); the result is a power series in \( \rho \), each of whose coefficients is a power series in \( 1/N \).

From the examples given in the preceding section, it is clear that in any particular application it will be necessary to perform a certain amount of additional algebraic labor in order to put the \( A_k(T) \), as given by Eq. (1), into optimal form. This is, of course, the price one pays for the generality of the result. The important point is that Eq. (1) reduces the calculation of the \( A_k(T) \), for practically any conceivable situation, to the problem of performing the possibly tedious but essentially mechanical manipulations necessary to specialize Eq. (1) to the physical situation of interest and simplify the resulting expressions. In connection with such manipulations, we emphasize that the limit in Eq. (1) cannot ordinarily be taken inside the summation, for

\[
\lim_{V \to \infty} \left[ V^k F(j, V, T) \right]
\]

will not in general exist.

A final point of practical concern is that one will not ordinarily be able to determine whether all the \( A_k(T) \) in fact exist, or, if they do, whether \( \rho_n(T) \) is nonzero. He will probably know only [as a result of direct calculation from Eq. (1)] that the first few \( A_k(T) \) corresponding to a particular \( F(N, V, T) \) exist. In such a case, the degree of approximation to which \( F(\rho, T) \) is represented, at low density, by truncating the series in Eq. (2) at some low-order term is not at present known; one must simply assume it to be negligible, or attempt to settle the question by careful comparison with experiment.

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APPENDIX A

We want here to obtain a sufficient condition for the validity of taking the limit in Eq. (19) inside the summation. To this end, we define

\[
M_k(V, T) = \text{l.u.b. } \left| A_k(V', T) \right|,
\]

where l.u.b. stands for "least upper bound." In words, Eq. (A1) states that \( M_k(V, T) \) is the least upper bound of the values taken on by \( |A_k(V', T)| \) as \( V' \) takes on all values greater than or equal to \( V \). It is clear from this definition that \( M_k(V, T) \) decreases monotonically as \( V \) increases; that is,

\[
M_k(V_2, T) \leq M_k(V_1, T) \quad \text{if } V_2 > V_1.
\]

It is equally clear that the following are true statements:

\[
M_k(V, T) \geq |A_k(V, T)|; \quad M_k(V, T) \geq |A_k(T)| \quad \text{for all } V; \quad \lim_{V \to \infty} M_k(V, T) = |A_k(T)|.
\]

We next let \( \rho_n(V, T) \) denote the radius of convergence of the auxiliary series

\[
\sum_{k=0}^{\infty} M_k(V, T) \rho^k,
\]

and let \( \rho_u(T) \) denote the radius of convergence of the series

\[
\sum_{k=0}^{\infty} |A_k(T)| \rho^k.
\]

Since a power series converges absolutely over its
interval of convergence, the radius of convergence of the series
\[ \sum_{k=0}^{\infty} |A_k(T)| \rho^k \]
(A8)
is also \( \rho_0(T) \). By means of the comparison test, it is easy to see that Eq. (A4) implies
\[ \rho_m(V, T) \leq \rho_0(T) \quad \text{for all } V \]
(A9)
and that Eq. (A2) implies
\[ \rho_m(V_2, T) \geq \rho_m(V_1, T) \quad \text{if } V_2 > V_1; \]
(A10)
that is, \( \rho_m(V, T) \) increases monotonically as \( V \) increases. We may therefore define a quantity \( \rho_m(T) \) by
\[ \rho_m(T) = \lim_{V \to \infty} \rho_m(V, T). \]
(A11)
The quantity \( \rho_m(T) \) thus defined may be infinity, but this is all right; the important point is that \( \rho_m(T) \) is well defined, since the monotonic nature of \( \rho_m(V, T) \) means that the limit does not oscillate. In spite of Eq. (A5), \( \rho_m(T) \) need not be equal to \( \rho_0(T) \). The most that can be said in general is that
\[ \rho_m(T) \leq \rho_0(T), \]
(A12)
which follows from Eq. (A9). A sufficient condition for \( \rho_m(T) \) to equal \( \rho_0(T) \) is that there exist a \( V_* < \infty \) such that \( |A_k(V, T)| \leq |A_k(T)| \) for all \( k \) if \( V > V_* \), since in this case \( M_k(V, T) = |A_k(T)| \) for all \( k \) if \( V \geq V_* \).

Now notice that the summand in Eq. (19) satisfies the following inequality:
\[ |A_k(N/\rho, T)[N^{(k)}/N^k]| \rho^k \leq M_k(V_0, T) \rho^k \]
if \( N \geq \rho V_0 \)
(A13)
for any \( k \), where \( V_0 \) is an arbitrary finite volume. The inequality (A13) follows immediately from Eqs. (A3) and (A2), and the fact that \( N^{(k)}/N^k \leq 1 \) for all \( k \) and \( N \). But by the Weierstrass M test,\(^{17} \) Eq. (A13) implies that if \( \rho < \rho_m(V_0, T) \) [so that the auxiliary series (A6), with \( V \) replaced by \( V_0 \), converges], then the series in Eq. (19) converges uniformly in \( N \) for all \( N \geq \rho V_0 \). By a well-known theorem,\(^{17} \) this uniform convergence is sufficient to guarantee the validity of taking the limit in Eq. (19) inside the summation. Therefore the condition \( \rho < \rho_m(V_0, T) \) may be used for \( X \) in Eq. (22). But \( V_0 \) is an arbitrary finite volume, which we are free to choose in any convenient manner. The condition \( \rho < \rho_m(V_0, T) \) becomes least restrictive if we use this freedom to make \( \rho_m(V_0, T) \) as large as possible. Since \( \rho_m(V_0, T) \) increases monotonically with increasing \( V_0 \), this can be done by sending \( V_0 \) to infinity; \( \rho_m(V_0, T) \) then becomes equal to \( \rho_m(T) \). More precisely, Eq. (A11) implies that \( \rho_m(V_0, T) \) can be made arbitrarily close to \( \rho_m(T) \) (or arbitrarily large if \( \rho_m(T) \) is infinity) by choosing \( V_0 \) large enough. Therefore by choosing \( V_0 \) large enough we can make \( \rho_m(V_0, T) \) greater than any value of \( \rho \) which is less than \( \rho_m(T) \). For any such \( \rho \), then, we can take the limit in Eq. (19) inside the summation; therefore the condition \( \rho < \rho_m(T) \) may be used for \( X \) in Eq. (22).

It can be shown that \( \rho_m(T) \) is equal to the smaller of \( \rho_0(T) \) and
\[ \lim_{V \to \infty} \rho_m(V, T), \]
where \( \rho_m(V, T) \) denotes the radius of convergence of the series
\[ \sum_{k=0}^{\infty} \left[ \left| A_k(V', T) - A_k(T) \right| \right]^k. \]
(A14)
This provides an alternative but equivalent method of determining \( \rho_m(T) \), which may in some cases be more convenient.

From Eq. (A12) we see that the series (A7) may continue to converge for \( \rho \geq \rho_m(T) \), but for such \( \rho \) one has no guarantee that it represents \( F(\rho, T) \) any more. In the unfavorable case when \( \rho_m(T) = 0 \), one has no guarantee that the series represents \( F(\rho, T) \) for any \( \rho > 0 \), regardless of how large \( \rho_0(T) \) is.

In order to assess the extent of the applicability of Eq. (2) in any particular case, it is necessary to evaluate \( \rho_m(T) \). To do so, one needs to be able to determine the radius of convergence of an arbitrary power series. This can frequently be done by the ratio test,\(^{18} \) but this method sometimes fails. A general formula which always works is the Cauchy–Hadamard formula,\(^{18} \) although in practice it may be difficult or impossible to apply. In many cases it may be wiser to seek a lower bound on \( \rho_m(T) \) than to try to actually evaluate it. Even this limited goal may not be practically attainable except in unusually simple or favorable cases, for it requires information about the way in which the \( A_k(V, T) \) approach their limiting values \( A_k(T) \) for all \( k \). Ordinarily, one will probably not even know whether or not all the \( A_k(T) \) exist, as has been assumed. Thus the practical value of the condition \( \rho < \rho_m(T) \) is liable to be extremely limited. It is, however, of psychological value: it assures us that there at least exists a reasonable condition, which is doubtless satisfied at least some of the time, under which the density expansion is rigorously valid. We know in particular that the expansion is valid if the density is “low enough,” except in the pathological case when \( \rho_m(T) = 0 \).

**APPENDIX B**

We wish to consider the quantity \( \Phi \) defined by Eq. (47). For large \( |R_{12}| \approx r \), one has in general that
\[ \left[ \partial \mu_1(r_1, r_2; E_0) / \partial E_0 \right]_{E_0 = 0} = \alpha_1 + \alpha_1 \cdot \tau(R_{12}) \cdot \alpha_2 + S, \quad (B1) \]
where \( \alpha_1 \) and \( \alpha_2 \) are the polarizability tensors of the isolated molecules 1 and 2, \( R_{12} = (R_1 - R_2) \), \( \tau(r) = \ldots \)
\[ \Phi = 2I_2 + \bar{\alpha}(V - 2B) + \bar{\alpha}VT:ee, \]  
\[ (B2) \]

where

\[ 2I_2 = \Omega^{-2} \int dR_{12} d\omega_1 d\omega_2 W_2(\tau_1, \tau_2) \]
\[ \times \left[ \partial \mu_1(\tau_1, \tau_2; \varepsilon_0) / \partial \varepsilon_0 \right]_{\varepsilon_0 = 0} \epsilon:ee \]
\[ - \bar{\alpha} - \bar{\alpha} \theta(\tau) T(R_{12}):ee \]  
\[ (B3) \]

and

\[ T'(r) = (1/V^2) \int dR_{12} d\theta(r) T(R_{12}). \]  
\[ (B4) \]

The function \( \theta(r) \) is defined to be zero if \( r < \sigma \) and unity otherwise, where \( \sigma \) is a distance large enough that \( W_2 \) differs negligibly from unity if \( |R_{12}| > \sigma \), but much smaller than any macroscopic length. But \( T(R_{12}) \) averages to zero over an isotropic distribution of directions of \( R_{12} \), so that the last term in braces in the integrand in Eq. (B3) makes no contribution to the integral. Therefore

\[ I_2 = \frac{2\pi}{\Omega^2} \int_0^\infty r^2 dr d\omega d\omega' W_2^{(2)} \left[ \frac{\partial \mu_1}{\partial \varepsilon_0} \right]_{\varepsilon_0 = 0} :ee - \bar{\alpha}. \]  
\[ (B5) \]

Kirkwood has evaluated \( T' \) for the parallel-plate geometry, with the result

\[ T' = (4\pi/V) \left[ (1/3)U - e e \right]. \]  
\[ (B6) \]

Equation (B2) therefore becomes

\[ \Phi = 2I_2 + \bar{\alpha}(V - 2B) - (8\pi/3)\bar{\alpha}^2, \]  
\[ (B7) \]

with \( I_2 \) now given by Eq. (B5).

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5 In this connection, see, e.g., (a) J. E. Mayer, J. Chem. Phys. 18, 1426 (1950); (b) R. W. Zwanzig, Phys. Rev. 129, 486 (1963); (c) K. Kawasaki and I. Oppenheim, *ibid.* 139, A1763 (1965); (d) M. H. Ernst, L. K. Haines, and J. R. Dorfman, Rev. Mod. Phys. 41, 296 (1969); (e) E. G. D. Cohen and T. J. Murphy, Phys. Fluids 12, 1404 (1969).

6 R. W. Zwanzig (private communication).


10 Reference 9, Vol. 1, Chap. 9.


12 Reference 11, p. 144.

13 This assumption is discussed in detail in Ref. 2, and in J. D. Ramshaw, J. Chem. Phys. 55, 1763 (1971).

14 A. D. Buckingham and J. A. Pople, Trans. Faraday Soc. 51, 1029 (1955). Although these authors consider a spherical sample and make the usual assumption concerning the position and geometry independence of the dielectric constant, their derivation of Eq. (36) does not depend on these restrictions. We may therefore use Eq. (36) in the present context, keeping in mind that the averages \( \langle \cdots \rangle \) in it are to be performed over the interior of our parallel-plate capacitor instead of over a spherical region. (We also remark that Buckingham and Pople's expression for the energy of interaction between the sample and the applied field, \( -\mathbf{M}(r, \varepsilon_0) \cdot \mathbf{E}_0 \), is only correct to first order in \( \mathbf{E}_0 \), but this is all that is necessary since we are concerned with a linear effect.)


