The dielectric constant and related equilibrium properties of molecular fluids: Interaction site cluster theory analysis a)

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The interaction site formalism for molecular fluids is used to develop a microscopic theory for the dielectric constant \( \varepsilon \). A rigorous correlation function expression for \( \varepsilon \) is obtained from an elementary application of linear response theory. The formula is applicable to mixtures and fluids composed of polarizable and deformable molecules. The derivation shows that the correlation functions which determine \( \varepsilon \) are short ranged so that \( \varepsilon \) can be expected to be independent of sample shape or any other macroscopic boundary conditions. The theories for \( \varepsilon \) developed by Nienhuis and Deutch and by Høye and Stell are shown to be special cases of the formalism given herein. A cluster diagramatic analysis is presented to examine the origin and significance of the large distance behavior of the correlations between neutral polar molecules. The diagramatic analysis is also used to show that the large distance form for the potential of mean force between two microscopic ions at infinite dilution in a dielectric liquid solvent is \( z_A z_C/e_r \) where \( z_A \) and \( z_C \) are the charges of the two ions. This asymptotic form is independent of the short-ranged interactions between the ions and solvent molecules.

I. INTRODUCTION

During the last few years, we have developed a new statistical mechanical formalism for describing the equilibrium correlation functions of molecular fluids. 1-3 Our attention has focused on the description of the local structure in liquids composed of nonspherical molecules. 4,5 This work on molecular liquids as well as earlier studies by us 6,7 and by Verlet 8,9 on simple ionic liquids have documented that the local structures of dense fluids are dominated by the short-ranged, quickly varying intermolecular forces. Except for systems like water which have unusually large and specific attractive interactions (e.g., hydrogen bonds), these short-ranged interactions are the repulsive forces which define the shapes of molecules. Thus, until this publication, we have been concerned primarily with the description of the structural effects produced by harsh (essentially hard core) intermolecular interactions. However, a large class of experimental measurements probe dielectric properties of molecular systems. These are long wavelength properties which are obviously connected to relatively long-ranged interactions. Indeed, if molecules interacted with only short-ranged forces, the dielectric constant of even highly ordered systems would be unity. Thus, in this article, we consider the dielectric constant and related properties of molecular fluids.

Our general formalism is the interaction site cluster series. 1-3 The class of molecular models and the correlation functions which are treated with the formalism are discussed in Sec. II. A correlation function formula for the dielectric constant \( \varepsilon \) is derived in Sec. III. The formula is obtained from a simple application of linear response theory. It is applicable to deformable and polarizable molecules as well as to less realistic rigid models. The reader will note that our formula is a slight reworking of equations presented by Martin. 10

For the special case of rigid nonpolarizable "molecules," Høye and Stell 11 have shown that our equation for the dielectric constant can also be obtained from theories of Nienhuis and Deutch 12 and of Høye and Stell. 13

In Sec. IV, the interaction site cluster series is used to develop a perturbation expansion for the site-site correlation functions needed to calculate the dielectric constant. The expansion is arranged into a Dyson-like integral equation by methods of topological reduction. 14 The "self-energy" or hypervertex function in the integral equation is short ranged even when the molecular interactions are long ranged. In Sec. V another microscopic formula is derived which relates \( \varepsilon \) to the hypervertex function, and we derive the connection between this formula and the Nienhuis-Deutch equation for the dielectric constant. When developing the hypervertex formula for \( \varepsilon \), several properties of the hypervertex function and pair-correlation functions are derived. The origin and consequences of these properties are examined in Sec. VI. The article is concluded in Sec. VII.

II. INTERACTION SITE MODEL AND STATISTICAL MECHANICAL FUNCTIONS

When using the interaction site formalism for molecular fluids, 1-3 it is assumed that the total potential energy can be represented by a sum over all pairs of

\[
\tau_{\mu \nu'}(1_M, 2_M') = \sum_{\alpha} \sum_{\gamma} \tau_{\alpha \gamma M M'}(r_{1_M} - r_{1_M'}) .
\]  (2.1)

The vector \( r_{1_M}^{(a)} \) specifies the location of the \( a \)th interaction site in the \( M \)th molecule of type \( M \). There are \( \eta_M \) such sites per molecule. The function \( \tau_{\alpha \gamma M M'}(r) \) is the potential between the pair of sites \( \alpha M \) and \( \gamma M' \). In the simplest application of this model, the interaction sites would be located at the atomic nuclei, and the intramolecular geometry of each molecule would be fixed. But this simplification is not necessary, nor is it always accurate enough to be useful. In general, the interaction sites are not rigidly fixed within a molecule, and they need not be located at the nuclei. Thus, the model...
can describe deformable and polarizable molecules as well as hypothetical rigid polar particles. This generality of the interaction site model is important because condensed phase environments can have a strong effect on the conformations of nonrigid molecules.

The intramolecular distribution of interaction sites is described by $s$-functions

$$\rho_{\alpha M}^L(\mathbf{r}, \mathbf{r}, \ldots, \mathbf{r}^{(L)}) = \left\langle N_{\alpha M}^L(\mathbf{r} - \mathbf{r}^{(1)} - \cdots - \mathbf{r}^{(L)}) \rho_{\alpha}^{(1)}(\mathbf{r}^{(1)}, \cdots, \mathbf{r}^{(L-1)}) \delta(\mathbf{r}^{(L)} - \mathbf{r}) \right\rangle,$$  
(2.2)

where $\rho_{\alpha}$ is the average molecular density ($N_{\alpha M}/V$), and the pointed brackets denote the ensemble average. In the zero density limit, the $s$-function becomes $s_{\alpha M}^{(0)}(\mathbf{r}, \ldots, \mathbf{r}^{(L)})$ where the superscript 0 indicates that the ensemble average is performed as if the system was an ideal gas. In a previous article, we derived the exact cluster series from which the finite density $s$-function can be calculated as a functional of the $s_{\alpha M}^{(0)}$-functions and the site-site potentials.

When a system contains polar or/or polarizable molecules, the site-site interactions must be Coulombic at large $r$; that is

$$u_{\alpha M M'}(r) = e_{\alpha M} e_{M'} / r,$$  
(2.3)

where $e_{\alpha M}$ denotes the charge associated with the $\alpha$th site in molecules of type $M$. Provided the molecular species is neutral,

$$\sum_{\alpha} e_{\alpha M} = 0.$$  
(2.4)

It is physically reasonable to assume that except for the Coulombic tails, the site-site interactions are short ranged, dying off at least as fast as $r^{-6}$. As a result, it is convenient to factor the interactions according to

$$u_{\alpha M M'}(r) = u_{\alpha M M'}^{(0)}(r) + e_{\alpha M} e_{M'} / r,$$  
(2.5)

where $u_{\alpha M M'}^{(0)}(r)$ is a "short-ranged" potential.

To complete the definition of the interaction site model, a rule for calculating the microscopic instantaneous electric field must be specified. According to Eq. (2.3), a charge of $e_{\alpha M}$ is located at each $\alpha M$ site. By assuming enough sites are used to accurately represent the charge distribution, Coulomb's law gives

$$V_{\alpha M}(\mathbf{r}) = \sum_{\alpha M} e_{\alpha M} \int d\mathbf{r}' \rho_{\alpha M}(\mathbf{r}' - \mathbf{r})^{-1},$$  
(2.6)

where $V_{\alpha M}(\mathbf{r})$ is the instantaneous electric potential field at position $\mathbf{r}$ due to the charge distributions within the molecules, and

$$\rho_{\alpha M}(\mathbf{r}') = \sum_{\alpha} e_{\alpha M} \delta(\mathbf{r}' - \mathbf{r})$$  
(2.7)

is the density of sites of type $\alpha M$ at position $\mathbf{r}'$.

The dielectric constant formula derived in the next section does not depend explicitly on the full $n_{\alpha M}$-point intramolecular distribution function. Rather, only the two-point contractions appear. With the notation of Ref. 2, these functions are

$$s_{\alpha M}^{(2)}(\mathbf{r}, \mathbf{r}') = (1 - \beta_{\alpha M}) \int d\mathbf{r}_2 d\mathbf{r}_3^{(1)} d\mathbf{r}_4^{(1)} s_{\alpha M}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5).$$  
(2.8)

The one-point contraction,

$$s_{\alpha M}^{(1)}(\mathbf{r}) = \int d\mathbf{r}_2 d\mathbf{r}_3^{(1)} s_{\alpha M}(\mathbf{r}_2, \mathbf{r}_3),$$  
(2.9)

determines the ensemble average of the density of sites of type $\alpha M$

$$n_{\alpha M}(\mathbf{r}) = \sum_{\alpha M} \rho_{\alpha M}^L(\mathbf{r}^{(1)}).$$  
(2.10)

For a uniform system, $s_{\alpha M}^{(0)}(\mathbf{r}) = 1$, and $s_{\alpha M}^{(0)}(\mathbf{r}, \mathbf{r}) = s_{\alpha M}^{(0)}(1 - \mathbf{r} - \mathbf{r})$.

The dipole moment and polarizability of a molecule of type $M$ in a fluid are related to the second moment of $s_{\alpha M}^{(2)}(\mathbf{r})$. To show this, note that the instantaneous dipole moment of molecule $iM$ is

$$\mu_{i M} = \sum_{\alpha} e_{\alpha M} \mathbf{r}_{\alpha i}^{(i)}$$  
(2.11)

so that

$$|\mu_{i M}|^2 = \sum_{\alpha} e_{\alpha M}^2 |\mathbf{r}_{\alpha i}^{(i)}|^2,$$  
(2.12)

where the second equality follows from neutrality. Thus, for a uniform system,

$$|\mu_{i M}|^2 = \int d\mathbf{r} \frac{1}{2} \sum_{\alpha} e_{\alpha M}^2 z_{\alpha M}^2 s_{\alpha M}^{(2)}(\mathbf{r}).$$  
(2.13)

The average of the square can be factored as

$$|\langle \mu_{i M} \rangle|^2 = \mu_{\alpha M}^2 + \langle \delta \mu_{i M} \rangle^2,$$  
(2.14)

where $\mu_{\alpha M} = \langle |\mu_{i M}| \rangle$, and $\delta \mu_{i M} = |\mu_{i M}| - \mu_{\alpha M}$. The quantity $\mu_{\alpha M}$ is the "permanent" dipole moment for a molecule of type $M$. The fluctuation term in Eq. (2.14) is related to the polarizability by the standard arguments that relate induced properties to fluctuations. The result is

$$\langle \delta \mu_{i M} \rangle^2 = 3\beta^2 \alpha_{\alpha M},$$  
(2.15)

where $\beta^2 = k_B T$ is Boltzmann's constant times the temperature and $3\alpha_{\alpha M}$ is the trace of the polarizability tensor for a molecule of type $M$. Thus, according to Eqs. (2.13)-(2.15),

$$\sum_{\alpha} e_{\alpha M}^2 \int d\mathbf{r} \frac{1}{2} z_{\alpha M}^2 s_{\alpha M}^{(2)}(\mathbf{r}) = \sum_{\alpha} e_{\alpha M}^2 [ \mu_{\alpha M}^2 + 3\beta^2 \alpha_{\alpha M} ].$$  
(2.16)

If it were possible to measure the average dipole moment and polarizability of a single molecule in a condensed phase, these quantities would be $\mu_{\alpha M}$ and $\alpha_{\alpha M}$, respectively. In a dilute gas phase, $\mu_{\alpha M}$ and $\alpha_{\alpha M}$ become $\mu_{\alpha M}^{(0)}$ and $\alpha_{\alpha M}^{(0)}$, the permanent dipole moment and polarizability, respectively, of an isolated molecule. They are given by

$$\mu_{\alpha M}^{(0)} = V^{-1} \int d\mathbf{r} s_{\alpha M}^{(0)}(1, \mathbf{r}) \left[ \sum_{\alpha} e_{\alpha M} \mathbf{r}_{\alpha i}^{(i)} \right],$$  

$$\alpha_{\alpha M}^{(0)} = \frac{1}{3} \left[ V^{-1} \int d\mathbf{r} s_{\alpha M}^{(0)}(1, \mathbf{r}) \left( \sum_{\alpha} e_{\alpha M} \mathbf{r}_{\alpha i}^{(i)} \right)^2 - \left( \mu_{\alpha M}^{(0)} \right)^2 \right].$$  

Since molecules are, in general, polarizable and de-
formable, \( s_{\mu}(1_{\mu}) \) at finite densities is not necessarily the same as \( s_{\mu}^{(0)}(1_{\mu}) \). As a result, \( \mu_{\mu} \) and \( \alpha_{\mu} \) are not necessarily the same as \( \mu_{\mu}^{0} \) and \( \alpha_{\mu}^{0} \). Liquid 1,2-dichloroethane provides a physical example of where the difference between \( \mu_{\mu} \) and \( \mu_{\mu}^{0} \) is of outstanding importance. When this molecule is in the trans conformation, \( \mu_{\mu} \) is zero. In the gauche conformation, \( \mu_{\mu} \) is a few debyes. While the trans conformation is most favorable in the gas phase, the gauche conformations are more probable in the liquid phase. The physical origin of this phenomenon is twofold. First, condensed phases tend to stabilize polar species relative to gas phases. Second, the packing of a condensed phase favors the compressed (gauche) species (see Ref. 2). Thus, for liquids composed of nonrigid molecules, \( \mu_{\mu} \) can be dramatically different than \( \mu_{\mu}^{0} \).

Our theory for the dielectric constant requires the knowledge of the distribution functions between pairs of sites on different molecules as well as the intramolecular correlation functions. For a uniform system the site-site intermolecular correlation function is

\[
h_{\alpha H r' H'}(r) = g_{\alpha H r' H'}(r) - 1,
\]

where

\[
r_{\alpha H r' H'}(r) = (\langle N_{H}(N_{H' - \delta_{H H'}}) \delta(r_{12}^{(2)}) \delta(r_{23}^{(r)}) - r \rangle).
\]

The density-density correlation function is thus

\[
\chi_{\alpha H r' H'}(r, r') = (\langle \rho_{\alpha H}(r) \rho_{H H'}(r') \rangle - (\rho_{\alpha H}(r)) (\rho_{H H'}(r'))),
\]

\[
\chi_{\alpha H r' H'}(r, r') = \rho_{\alpha H} \delta_{\mu \mu'} \omega_{\alpha H}(r, r') + \rho_{\alpha H} \rho_{H H'} h_{\alpha H r' H'}(r, r'),
\]

where

\[
\omega_{\alpha H}(r, r') = \delta_{\alpha H}(r, r') + s_{\alpha H}(r, r').
\]

The functions \( \chi_{\alpha H r' H'}(r, r') \) form a matrix which we refer to as the susceptibility.

## III. GENERAL CORRELATION FUNCTION FORMULA FOR \( \epsilon \)

In this section, the indirect Kubo method is applied to find a formula for the dielectric constant. In particular, a simple microscopic calculation of the electric potential field due to an arbitrarily small change placed in the dielectric medium is compared with the phenomenological electrostatics result for the field. The comparison yields a correlation function expression for \( \epsilon \).

Imagine creating a test charge \( Q \) at some point within the dielectric fluid. For notational simplicity, assume that the fluid is isotropic when \( Q = 0 \). The location of the test charge is taken as the origin. According to phenomenological electrostatics, the electric potential field, \( V(r) \), satisfies

\[
V(r) = Q/r, \quad \text{for large } r.
\]

(3.1)

The indirect Kubo method makes no pretense at deriving Eq. (3.1). Rather, it is assumed that the classical macroscopic theory of dielectrics is valid.

According to Eq. (2.6), the microscopic formula for \( V(r) \) is

\[
V(r) = (Q/r) + \int V_{\alpha H r' H'}(r') dV_{\alpha H r' H'}(r'),
\]

\[
= (Q/r) + \sum_{\alpha H} z_{\alpha H} \int dV_{\alpha H r' H'}(r') \left| r - r' \right|^{-1},
\]

(3.2)

where the subscript \( Q \) indicates that the ensemble average is performed with the charge \( Q \) at the origin. For arbitrarily small \( Q \), the average can be evaluated perturbatively:

\[
\langle \rho_{\alpha H}(r') \rangle = \langle \rho_{\alpha H}(r') \rangle_{0} + \sum_{\alpha H} \beta \chi_{\alpha H H'}(r' - r') \partial_{\alpha H} \left[ \psi_{\alpha H}(r') \right]_{0} + 0(Q^2),
\]

(3.3)

where the functional derivative gives the rate of change of \( \langle \rho_{\alpha H}(r') \rangle \) due to an infinitesimal potential energy field \( \psi_{\alpha H}(r') \). That derivative is \( -\beta \chi_{\alpha H H'}(r' - r') \). Further, \( \langle \rho_{\alpha H}(r') \rangle_{0} = \rho_{\alpha H} \). Thus, by combining Eqs. (3.2) and (3.3) and applying the condition of neutrality, one finds

\[
V(r) = Q \left[ \frac{1}{r} - \beta \sum_{\alpha H} r_{\alpha H} \int dV_{\alpha H r' H'}(r') \int dV_{\alpha H r' H'}(r') \right] + 0(Q^2).
\]

(3.4)

The comparison of Eqs. (3.4) and (3.1) is most easily carried out by taking Fourier transforms. Let

\[
\hat{V}(k) = \int dV_{\alpha H r' H'}(r) \exp(-i\mathbf{k} \cdot \mathbf{r}) \left[ \frac{1}{r} - \beta \sum_{\alpha H} r_{\alpha H} \int dV_{\alpha H r' H'}(r') \int dV_{\alpha H r' H'}(r') \right] + 0(Q^2).
\]

(3.5)

The phenomenological result, Eq. (3.1), is equivalent to

\[
\hat{V}(k) = \frac{4\pi Q}{k^2}, \quad \text{for small } k.
\]

(3.6)

The microscopic result, Eq. (3.4), gives

\[
\hat{V}(k) = \frac{4\pi Q}{k^2} \left( 1 - \frac{4\pi \beta}{k^2} \sum_{\alpha H} r_{\alpha H} \chi_{\alpha H H'}(k) \right) + 0(Q^2),
\]

(3.7)

where

\[
\chi_{\alpha H H'}(k) = \rho_{\mu} \delta_{\mu H} \omega_{\alpha H}(k) + \rho_{\mu} \rho_{H H'} h_{\alpha H r' H'}(k).
\]

(3.8)

is the Fourier transform of \( \chi_{\alpha H r' H'}(r, r') \). The comparison of Eq. (3.6) (the assumed macroscopic formula) with Eq. (3.7) (the microscopic result) yields

\[
\left( \frac{1}{\epsilon} - 1 \right) = \lim_{h \to 0} \frac{4\pi \beta}{k^2} \sum_{\alpha H} r_{\alpha H} \chi_{\alpha H H'}(k).
\]

(3.9)

This equation for \( \epsilon \) is a generalization of a formula presented by Martin.\( ^{10} \) It can be further simplified by analyzing the behavior of \( \chi_{\alpha H H'}(k) \) at small \( k \).

The compressibility theorem states that

\[
\lim_{h \to 0} \chi_{\alpha H H'}(k) = (\partial_{\mu H} / \partial \mu_{\alpha}),
\]

(3.10)

where in this equation, and nowhere else, \( \mu_{\mu} \) denotes the chemical potential for molecules of type \( M \). Thus in the \( k \to 0 \) limit, \( \chi_{\alpha H H'}(k) \) is independent of \( \alpha \) and \( \gamma \) so that neutrality implies

\[
\sum_{\alpha H} z_{\alpha H} \chi_{\alpha H H'}(k) = k^2 \sum_{\alpha H} z_{\alpha H} \chi_{\alpha H H'}(k) + \cdots,
\]

(3.11)

where the subsequent terms in Eq. (3.11) are of higher order in \( k \) than \( k^3 \), and
\[
\chi_{\alpha,\mu'N'}^{(2)} = -\frac{1}{\epsilon} \int d\tau \tau^2 \chi_{\alpha,\mu'N'}(r). \tag{3.12}
\]

It is assumed when writing Eq. (3.12) that \(\chi_{\alpha,\mu'N'}(r)\) decays at large \(r\) faster than \(r^{-6}\). The single-molecule part, \(\omega_{\alpha,\mu'N'}(r)\) is intrinsically short ranged so that \(\tilde{\omega}_{\alpha,\mu'N'}(k)\) is clearly analytic at small \(k\). Indeed,

\[
\tilde{\omega}_{\alpha,\mu'N'}(k) = 1 + k^2 \omega_{\alpha,\mu'N'}^{(2)}(k^4), \tag{3.13}
\]

where according to Eq. (2.16),

\[
\sum_{\gamma} \tilde{z}_{\alpha,\gamma} \tilde{z}_{\gamma,\mu'N'}^{(2)} = \frac{1}{2} \mu N + \mu^{(2)} \rho. \tag{3.14}
\]

However, it is less clear that the small \(k\) behavior of \(\tilde{h}_{\alpha,\mu'N'}(k)\) can be expressed as

\[
\tilde{h}_{\alpha,\mu'N'}(k) = h^{(0)}_{\alpha,\mu'N'} + k^2 h^{(2)}_{\alpha,\mu'N'} + \cdots. \tag{3.15}
\]

[According to the compressibility theorem, the \(k = 0\) term, \(h^{(0)}_{\alpha,\mu'N'}\), is independent of \(\alpha\) and \(\gamma\). We believe (see Sec. V) that \(h_{\alpha,\mu'N'}(r)\) does decay as fast as \(r^{-6}\) at large \(r\). Such behavior will guarantee the existence of \(\tilde{h}_{\alpha,\mu'N'}(r)\). But all that is needed for the dielectric constant is

\[
\sum_{\alpha,\gamma} z_{\alpha,\gamma} \tilde{z}_{\gamma,\mu'N'}^{(2)} \tilde{h}_{\alpha,\mu'N'}(r) = -\frac{1}{\epsilon} \int d\tau \tau^2 \left[ \sum_{\alpha,\gamma} z_{\alpha,\gamma} \tilde{z}_{\gamma,\mu'N'} \tilde{h}_{\alpha,\mu'N'}(r) \right]. \tag{3.16}
\]

In view of Eq. (3.9) it is seen that the existence of \((\epsilon - 1)\)-1 guarantees that the right hand side of Eq. (3.16) is finite so that

\[
\sum_{\alpha,\gamma} z_{\alpha,\gamma} \tilde{z}_{\gamma,\mu'N'} \tilde{h}_{\alpha,\mu'N'}(r) \text{ must decay faster than } r^6.
\]

By combining Eqs. (3.8)–(3.16) we find

\[
- (1/\epsilon - 1) = 3 \sum_{\mu} \left[ 4 \beta_{\mu} \rho_{\mu} \frac{1}{3} + 4 \beta_{\mu} \omega_{\mu} \right] + 4 \beta \sum_{\mu'} \tilde{h}_{\alpha,\mu'} \tilde{h}_{\alpha,\mu'}^{(2)} \rho_{\mu} \tilde{h}_{\mu'N'}^{(2)}. \tag{3.17}
\]

This formula is our general result for the dielectric constant. In deriving it we have assumed only the correctness of macroscopic dielectric theory, i.e., Eq. (3.1), or equivalently

\[
\nabla V(r) = - (4\pi/\epsilon) \rho_{\nu}(r), \tag{3.18}
\]

where \(\rho_{\nu}(r)\) is the density of free charge. Assuming \(\epsilon\) does exist, the correlation functions which determine it must decay faster than \(r^{-6}\). Hence, it is reasonable to conclude that the \(\epsilon\) given in Eq. (3.14) is the dielectric constant for a macroscopic system. It is independent of macroscopic boundary conditions.

For the special case of a one-component fluid composed of rigid nonpolarizable molecules, Eq. (3.17) reduces to

\[
(\epsilon - 1)/\epsilon = \frac{3}{2} \pi \beta \mu^2 + 4 \pi \beta \sum_{\alpha,\gamma} z_{\alpha,\gamma} \tilde{h}_{\alpha,\mu'N'}^{(2)}, \tag{3.19}
\]

where

\[
\mu = \sum_{\alpha} z_{\alpha} \tilde{h}_{\alpha}^{(2)}. \tag{3.20}
\]

is the magnitude of the permanent dipole moment on each rigid molecule. Equation (3.19) is the formula derived by H"{o}ye and Stell.11

IV. PERTURBATION SERIES FOR LONG RANGED FORCES

Equation (3.17) shows that the dielectric constant is determined from a linear combination of second moments of the intra- and intermolecular pair-correlation functions, \(s_{\alpha,\mu'N'}^{(2)}(r)\) and \(h_{\alpha,\mu'N'}(r)\), respectively. In this section we discuss the interaction site cluster diagrammatic analysis of these correlation functions.

The cluster series for \(h_{\alpha,\mu'N'}(r)\) is given in Eq. (4.3) of Ref. 2, and in Eq. (4.4) of Ref. 1 for the special case of a one-component system. We shall follow the notational conventions established in Ref. 2. For the sake of brevity, it is assumed that the reader is familiar with that earlier work. Equation (4.3) of Ref. 2 states

\[
\rho_{\mu} \rho_{\nu} \tilde{h}_{\nu,\alpha,\mu'N'}(r, r^\prime) = \text{the sum of all simple connected }
\]

graphs with two white circles labeled \(\alpha M\) and \(\gamma M\), any number of black circles, \(\overline{s}\)-vertices, one or more \(\phi\)-bonds connecting circles of different vertices, no circle is associated with more than one vertex, no articulation vertices, and all black circles must be intersected by at least one \(\phi\)-bond.

\[
(4.1)
\]

The intermolecular interactions are contained in the \(\phi\)-bonds which represent the cluster function

\[
f_{\alpha,\mu'N'}(r) = \exp[-\beta h_{\alpha,\mu'N'}(r)] - 1
\]

\[
= f_{\alpha,\mu'N'}^{(s)}(r) \left[ 1 + f_{\alpha,\mu'N'}^{(s)}(r) \sum_{\nu} \frac{1}{\rho_{\nu}} \phi_{\alpha,\mu'N'}^{(s)}(r) \right]. \tag{4.2}
\]

In the second equality, \(f_{\alpha,\mu'N'}^{(s)}(r)\) is the cluster function associated with the short-ranged site-site potential \(u_{\alpha,\mu'N'}^{(s)}(r)\) and

\[
\phi_{\alpha,\mu'N'}^{(s)}(r) = - \epsilon \tilde{r}_{\alpha,\mu'N'}^{(s)} \rho_{\nu}(r).
\]

is the long-ranged perturbation interaction (in units of \(-k_B T\)). Equations (4.1) and (4.2) can be combined to yield a cluster series for \(h_{\alpha,\mu'N'}(r)\) which is a functional of \(f_{\alpha,\mu'N'}^{(s)}(r)\) and \(\phi_{\alpha,\mu'N'}^{(s)}(r)\). The description of the new series is the same as that in Eq. (4.1) except that "\(\phi\)-bonds" is replaced by "\(f^{(s)}\)-bonds and/or \(\phi\)-bonds," and the graphs are no longer "simple" with respect to the \(\phi\)-bonds. Rather, any number of \(\phi\)-bonds can connect two circles directly. Since they are no longer necessarily simple, the symmetry numbers of the graphs must account for the topological equivalency of different bonds as well as different black circles. Several diagrams in perturbation series with \(f^{(s)}\)-bonds and \(\phi\)-bonds are shown in Fig. 1. The solid lines refer to \(\phi\)-bonds; the dashed denote \(f^{(s)}\)-bonds. The value of the twelfth (third to last) graph is

\[
\sum_{\alpha,\mu'} \sum_{n=1}^{s_{\mu'}} \frac{1}{2} \int dx \, dx^\prime \rho_{\mu} f_{\alpha,\mu'N'}^{(s)}(|x - x^\prime|) \times [\phi_{\alpha,\mu'N'}^{(s)}(|x - x'|)]^2 \rho_{\nu} \tilde{z}_{\nu} \tilde{h}_{\alpha,\mu'N'}(r, r^\prime, r^\prime') \rho_{\mu', \nu}. \tag{4.3}
\]
The sum of all the graphs with no $\phi$-bonds yields $h_{\alpha M \gamma M}(r, r')$, the intermolecular pair correlation function for the fluid with short-ranged site-site interactions $u_{\alpha M \gamma M}(r, r')$. The remaining graphs can be divided into two infinite classes of diagrams. One class is the set of diagrams with one or more black circles which can be disconnected by removing only one $\phi$-bond. The seventh, twelfth, and thirteenth diagrams in Fig. 1 are members of this set. The second class of graphs are those which cannot be disconnected by removing only one $\phi$-bond. It seems reasonable to assume that the sum of graphs in the second infinite set form a short-ranged function while the graphs in the first set are long ranged. We let

$$\Omega_{\alpha M \gamma M}(r, r') = \delta_{\alpha M} + \rho_M \omega_M(r - r') + \rho_M \rho_M h_{\alpha M \gamma M}(r, r')$$

+ the sum of all diagrams in $h_{\alpha M \gamma M}(r, r')$

with one or more $\phi$-bonds which cannot be disconnected by removing only one $\phi$-bond,

$$\Omega_{\alpha M \gamma M}(r, r') = \sum_{\delta_{\alpha M} \rho_M \omega_M(r - r') + \rho_M \rho_M h_{\alpha M \gamma M}(r, r') + \text{the sum of all diagrams in } h_{\alpha M \gamma M}(r, r')}$$

which is apparently a short-ranged function. It is analogous to the hypervertex function introduced into the theory of simple fluids by Lebowitz, Stell, and Baer. A few terms in the cluster series for $\Omega_{\alpha M \gamma M}(r, r')$ are drawn out in Fig. 2.

Graphs which contribute to $h_{\alpha M \gamma M}(r, r')$ and are not summed in Eq. (4.4) can be expressed as simple chains involving $\phi$-bonds and $\Omega$-vertices. This fact follows from the topological requirement that the remaining graphs can be disconnected by simply removing one $\phi$-bond. Hence,

$$\rho_M \rho_M h_{\alpha M \gamma M}(r, r') = \rho_M \rho_M h^{(s)}_{\alpha M \gamma M}(r, r') + \text{the sum of all simple connected chains with } \Omega \text{-vertices and one or more } \phi \text{-bonds}$$

These diagrams are shown in Fig. 3. When summed to infinite order they yield

$$\rho_M \rho_M h_{\alpha M \gamma M}(r, r') = \rho_M \rho_M h^{(s)}_{\alpha M \gamma M}(r, r') + \left(\Omega_{\alpha M \gamma M}(r, r') \right) \rho_M \rho_M h^{(s)}_{\alpha M \gamma M}(r, r')$$

(4.5)

FIG. 1. Interaction site cluster series for the intermolecular site-site correlation functions. Site $\alpha M$ is fixed at position $r$, while site $\gamma M'$ is at $r'$. The dashed lines represent $\phi$-bonds. The solid lines represent the long-ranged $\phi$-bonds. The vertices are $s$-vertices (see Ref. 2).

FIG. 2. Interaction site cluster series for the hypervertex function, $\Omega_{\alpha M \gamma M}(r, r')$. The bonds are defined in Fig. 1.
refers to the site–site density correlation function (or susceptibility) defined in Eq. (2.18). Note that when \( \phi = 0 \), \( \mathcal{Q} = \chi^{(sr)} \), where \( \chi^{(sr)} \) is the susceptibility of the system in the absence of the long-ranged forces.

Equations (4.6) are completely general and exact (provided some arrangement of the interaction site cluster series converges). While we have in mind that \( \phi \) represents a matrix of Coulomb potentials, this particular division of the potential into long- and short-ranged portions is not unique. The topological reduction which leads to Eqs. (4.6) is valid for any division of the site–site interactions.

In closing this section it is instructive to note one important difference between the graphs involved in the usual simple fluid cluster series and the interaction site cluster diagrams and herein. The interaction site expansion for molecular fluids contains \( s \)-vertices, while the simple fluid expansion does not. The \( s \)-vertices describe correlations associated with intramolecular bonding. For obvious physical reasons, no diagram can have circles associated with more than one \( s \)-vertex. Due to this restriction, certain topological rearrangements are not possible in the interaction cluster series even though the analogous rearrangements are valid in the simple atomic fluids problem. For example, when there are no \( s \)-vertices in the expansion, one may show that

\[
\mathcal{Q} = \left[1 - \chi^{(sr)}(\phi + \phi')^{-1}\chi^{(sr)}\right],
\]

where \( \phi' \) represents the matrix of functions formed by summing those diagrams in Eq. (4.4) which are nodeless graphs. This result leads to the equation

\[
\chi = \left[1 - \chi^{(sr)}(\phi + \phi')^{-1}\chi^{(sr)}\right],
\]

which is like a random phase approximation except that the actual perturbation \( \phi \) is replaced by \( \phi + \phi' \). This equation, which is exact in the absence of intramolecular correlations, cannot be derived for the molecular fluids problem. The reason is that unallowed diagrams would be summed. In particular, one would be adding up graphs in which \( s \)-vertices were intersected by other \( s \)-vertices.

V. PROPERTIES OF THE HYPERVERTEX AND PAIR CORRELATION FUNCTIONS, AND ANOTHER FORMULA FOR \( \epsilon \)

In the previous section, we introduced the hypervertex function and stated our belief that the function is short ranged. We now give the arguments supporting this belief.

A. Large \( r \) and small \( k \) behavior of the hypervertex function

The cluster series for \( \Omega_{\alpha\beta\gamma\delta}(r_1 - r_2) \) is given in Eq. (4.4) and depicted in Fig. 2. It seems that the longest ranged contributions have portions with two \( \phi \)-bonds in parallel. The first diagram in Fig. 2 is the simplest such graph. Since \( \phi_{\alpha\beta\gamma\delta}(r) \propto r^{-1} \), the presence of these graphs might seem to imply a \( r^{-2} \) decay of \( \Omega_{\alpha\beta\gamma\delta}(r) \). However, in addition to these contributions, there are additional graphs of nearly the same structure except that the circles which the parallel \( \phi \)-bonds intersect are different circles in the same molecule. These graphs also decay as \( r^{-2} \). When they are all added together, the condition of neutrality makes the resulting sum decay as \( r^{-6} \) (the magnitude of the square of the dipole–dipole interaction). This behavior is exemplified by the addition of the first ten graphs in Fig. 2. It can be shown that this cancellation is a general property not peculiar to the simple graphs in Fig. 2. Thus, provided some arrangement of the cluster series for \( \Omega_{\alpha\beta\gamma\delta}(r) \) converges, this hypervertex function will decay at least as fast as \( r^{-6} \). Another fact is also apparent. The coefficients of \( r^{-6} \) and \( r^{-7} \) terms in the asymptotic expansion of \( \Omega_{\alpha\beta\gamma\delta}(r) \) will be independent of the indices \( \alpha \) and \( \gamma \). This independence follows from the symmetry of the hypervertex function and the fact that the dipole moment of a neutral distribution of charge is independent of the choice of the center of charge.

When a function \( f(|r|) \) decays as \( r^{-6} \) for large \( r \), the first two terms in the small \( k \) expansion of its Fourier transform, \( \tilde{f}(k) \), are analytic going as \( k^6 \) and \( k^8 \). Similarly, when the function decays as \( r^{-8} \), the first three terms in the small \( k \) expansion of \( f(k) \) are analytic. Thus, introducing \( \tilde{G}(k) \) which denotes the matrix with elements

\[
\tilde{G}_{\alpha\beta\gamma\delta}(k) = \int d\mathbf{r} \Omega_{\alpha\beta\gamma\delta}(r) \exp(-ik\cdot r),
\]

and the matrix \( \Phi \) which has elements

\[
\Phi_{\alpha\beta\gamma\delta} = -4\pi\beta\epsilon_{\alpha\beta\gamma\delta} r^{-4},
\]

the properties assigned to \( \Omega_{\alpha\beta\gamma\delta}(r) \) together with neutrality imply the existence of the coefficients in the small \( k \) expansions

\[
\tilde{G}(k) = G^{(0)} + k^2 G^{(2)} + \cdots,
\]

and

\[
\Phi(k) = \Phi^{(0)} + k^2 \Phi^{(2)} + k^4 \Phi^{(4)} + \cdots.
\]

The terms omitted in Eqs. (5.3) and (5.4) are higher order in \( k \) but not analytic.
B. Formula relating ε and the hypervertex function

Now consider the connection between $\tilde{\Phi}(k)$ and $\tilde{\chi}_\mu$, $\tilde{\chi}_{\mu'}(k)$. According to Eq. (4.6'),

$$\tilde{\Phi}(k) = \tilde{\Phi}(k)[1 + k^2 \tilde{\Phi}(k)]^{-1}$$

$$= \tilde{\Phi}(k)[1 + k^2 \tilde{\Phi}(k)]^{-1},$$

(5.5)

where the second equality makes use of the $k$-space representation of the $\phi$ bond,

$$\tilde{\phi}(k) = k^2 \tilde{\phi}.$$

(5.6)

The discussion in Sec. III concerning neutrality and the compressibility theorem yields

$$\lim_{k \to 0} \tilde{\Phi}(k) = 0.$$

(5.7)

Further, according to Eq. (3.17) or (3.9),

$$\text{Tr} \tilde{\Phi}(k) = (1/\varepsilon) - 1,$$

(5.8)

where $\text{Tr}$ denotes the trace of a matrix. The small $k$ expansion of Eq. (5.5) together with Eq. (5.7) gives

$$\tilde{\Phi}(k) = 0,$$

(5.9)

and

$$\tilde{\Phi}(k) = \tilde{\Phi}(k)[1 + \tilde{\Phi}(k)]^{-1},$$

(5.10)

so that

$$\text{Tr} \tilde{\Phi}(k) = \text{Tr} \tilde{\Phi}(k)[1 + \tilde{\Phi}(k)]^{-1}$$

$$= (\text{Tr} \tilde{\Phi}(k))[1 + (\text{Tr} \tilde{\Phi}(k))^{-1}].$$

(5.11)

The use of (5.8) with Eq. (5.11) gives

$$\varepsilon - 1 = -\frac{4\pi}{\varepsilon} \sum_{\alpha,\beta} x_{\alpha,\beta} \Omega_\alpha(\kappa) \Omega_\beta(\kappa'),$$

(5.12)

which is a new correlation function formula for $\varepsilon$.

C. Large r behavior of site–site pair correlation functions

Equation (4.6') can also be used to obtain

$$\tilde{\chi}(k) = \tilde{\Phi}(k)[1 + k^2 \tilde{\Phi}(k)]^{-1}.$$

(5.13)

By inserting Eqs. (5.3), (5.4), and (5.9) in (5.13), it is found that

$$\tilde{\chi}(k) = \tilde{\chi}(k) + k^2 \tilde{\chi}(k) + \cdots,$$

(5.14)

with, for example,

$$\tilde{\chi}(k) = \tilde{\Phi}(k)[1 - \tilde{\Phi}(k)]^{-1}.$$

(5.15)

The existence of $\tilde{\chi}(k)$ is thus verified. It is a direct consequence of the large $r$ behavior of $\Omega_{\alpha,\beta}(r)$.

D. Connection with Nienhuis–Deutsch theory

Equation (5.12) is a principal result of this article. It bears a striking resemblance to an equation for $\varepsilon$ developed by Nienhuis and Deutsch. In fact, their result is a special case of ours. To demonstrate the correspondence, consider a one-component fluid of rigid molecules which is the class of systems studied by Nienhuis and Deutsch. Equation (5.12) becomes

$$\varepsilon - 1 = -\frac{4\pi}{\varepsilon} \int d\mathbf{r} \sum_{\alpha,\beta} x_{\alpha,\beta} \Omega_\alpha(\mathbf{r}) \cdot \Omega_\beta(\mathbf{r}).$$

(5.15)

[The subscripts $M$ and $M'$ are dropped when considering a one-component system.] The Nienhuis–Deutsch formula is

$$\varepsilon - 1 = \frac{\varepsilon}{\mu^2} \int d\mathbf{r} d\mathbf{r} \sum_{\alpha,\beta} x_{\alpha,\beta} \Omega_\alpha(\mathbf{r}) \cdot \Omega_\beta(\mathbf{r}),$$

(5.16)

where, with our notation,

$$G_2^{(\alpha,\beta)} = \text{the sum of all the diagrams generated from the diagrams in Eq. (4.1) of Ref. 2 by expanding the f-bonds in terms of f}\alpha\beta\text{-bonds and } \phi\text{-bonds and neglecting those which can be disconnected by removing only one } \phi\text{-bond.}$$

(5.17)

[Note that 1 and 2 denote the collection of all the coordinates for the sites in molecules 1 and 2; respectively, e.g., $1 = (r_1^{(1)}, \ldots, r_1^{(n)}).$ Thus, $G_2^{(\alpha,\beta)}(1, 2)$ is a 2n-point function.] By comparing Eqs. (5.17) and (4.4) and applying the methods of Ref. 1 or 2, we find

$$\Omega_\alpha(\mathbf{r}_1^{(1)}, \mathbf{r}_2^{(1)})$$

$$= \rho \omega_\alpha(\mathbf{r}_1^{(1)}, \mathbf{r}_2^{(1)}) + \int \frac{d\mathbf{r}}{d\mathbf{r}^{(2)}} \int \frac{d\mathbf{r}}{d\mathbf{r}^{(2)}} G_2^{(\alpha,\beta)}(1, 2).$$

(5.18)

This result can be used with Eq. (5.16) and

$$\mu_1 \cdot \mu_2 = \frac{1}{2} \sum_{\alpha,\beta} x_{\alpha,\beta} |r_1^{(1)} - r_2^{(1)}|^2,$$

(5.19)

to reduce the Nienhuis–Deutsch result as follows:

$$\varepsilon - 1 = \frac{\varepsilon}{\mu^2} \int d\mathbf{r} d\mathbf{r} \sum_{\alpha,\beta} x_{\alpha,\beta} |r_1^{(1)} - r_2^{(1)}|^2$$

$$\times \int \frac{d\mathbf{r}}{d\mathbf{r}^{(2)}} \int \frac{d\mathbf{r}}{d\mathbf{r}^{(2)}} G_2^{(\alpha,\beta)}(1, 2).$$

(5.20)

where the last equality comes from Eq. (2.16) or equivalently Eq. (3.14). Equation (5.15) is identical to (5.20). Thus, our formula for $\varepsilon$ reduces to the Nienhuis–Deutsch expression for the special class of systems they considered.

The derivation of the correspondence between Eqs. (5.15) and (5.16), involves a subtlety that is worthy of examination. When writing the first equality of Eq. (5.20), it is assumed that the range of $G_2^{(\alpha,\beta)}(1, 2)$ is short enough so that the orders of integrations and summations can be manipulated freely. The assumption is valid because $G_2^{(\alpha,\beta)}(1, 2)$ decays as $r^{-6}$ for large $r$ where $r$ is the distance between molecules 1 and 2. But there are situations where the manipulations carried out in Eq.
such a simple alteration in convention. There will be much more said about this point in Sec. VI.

E. Pair-potential of mean force at infinite dilution between two ions in a dielectric fluid

A standard assumption in ionic solution theory is that the infinite dilution potential of mean force between two ionic solutes is $z_A z_A^/e V$ for large $r$. Here, $z_A$ and $z_A^/$ denote the charges on the two ions, $A$ and $A^/$. Equation (5.12) can be used to derive this asymptotic form irrespective of the short-ranged interactions between the ions and the solvent molecules.

In the limit of low solute concentrations, $\rho_A$ and $\rho_A^/$, the hypersurface function formalism gives

$$\hat{h}_{AA^/}(k) = \left[ \text{Fourier transform of a short-ranged function} \right]$$

$$+ \hat{\phi}_{AA^/}(k) + \sum_{\mu, \mu', \nu, \nu'} \left[ \hat{g}_{AA^/}(k) \left( 1 - (1/k^2) \hat{G}(k) \right) \right]_{\nu, \nu'}$$

$$\times \left( \hat{\phi}_{AA^/}(k) + \rho_A^/ \hat{g}_{AA^/}(k) \left[ (1 - (1/k^2) \hat{G}(k) \right) \right]_{\nu, \nu'}$$

$$\times \left[ (1/k^2) \hat{G}(k) \right]_{\nu, \nu'}$$

where $\hat{h}_{AA^/}(k)$ is the Fourier transform of the ion-ion pair correlation function, $g_{AA^/}(r) = 1 + \hat{g}_{AA^/}(k)$ is $-4\pi \rho_A \rho_A^/ k^2$, $\hat{G}(k)$ is $-4\pi \rho_A \rho_A^/ k^2$, and $\hat{G}(k)$ is the Fourier transform part of the part of the hypervortex function which connects an ion $A$ to site $\alpha$ in a molecular type $M$. The compressibility term and electroneutrality imply

$$\delta_{AA^/}(0) = \sum_{\alpha, \alpha'} \hat{g}_{AA^/}(0) = 0 .$$

Thus, at small $k$, Eq. (5.26) gives

$$\hat{h}_{AA^/}(k) = \left[ -4\pi \rho_A \rho_A^/ k^2 \left( 1 + (1 + \epsilon - 1) \right) \right]$$

$$+ \left[ \text{terms noninfinite at } k = 0 \right]$$

$$= \left[ -4\pi \rho_A \rho_A^/ k^2 \left( 1 + (1 - \epsilon) \right) \right]$$

$$+ \left[ \text{terms noninfinite at } k = 0 \right] ,$$

where the second equality follows from Eq. (5.12).

Since a $4k^2$ singularity at $k = 0$ is equivalent to an $r^{-1}$ decay at large $r$, Eq. (5.28) implies that

$$\hat{h}_{AA^/}(r) \sim -\beta \rho_A \rho_A^/ e r$$

for large $r$. Thus, we have derived that the asymptotic form of the potential of mean force between two macroscopic ions in a dielectric fluid is the same as that for two macroscopic ions.

VI. ORIGIN AND SIGNIFICANCE OF THE DECAY OF CORRELATIONS AT LARGE SEPARATION

In the previous sections an exact and general theory for the dielectric constant has been developed. In the process, several properties associated with the site-site correlation functions have been derived. Perhaps the most striking of these properties is the fact that $\hat{h}_{AA^/}(r)$ decays as $r^{-2}$ for large $r$. This behavior seems significant because an $r^{-2}$ decay of $\hat{h}_{AA^/}(r)$ is much faster than that for the full two-molecule correlation function $\hat{h}_{WW}(1, 2, \omega)$. The latter decays at large inter-

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molecular separations, \( r \), as \( r^{-3} \). As a result, the calculation of \( \epsilon \) for finite computer simulated systems may be more easily performed by applying Eq. (3.17) than by applying Kirkwood’s formula, Eq. (5.21). This advantage has been noted earlier by Høye and Stell\(^{11}\) and (indirectly) by Watts.\(^{18}\)

The opposite way of viewing the asymptotic behavior is to note that an \( r^{-6} \) decay is significantly weaker than the exponential decay which is generally believed to characterize the asymptotic correlations between free charged particles in a fluid of charged particles. For free charge systems, such as a model electrolyte solution, the long-ranged Coulombic interactions can be renormalized by systematically summing cluster graphs to form screened potentials. The screened potentials decay exponentially. As a result, it is expected that the pair correlations between free charges decay exponentially. In light of this fact, the “slow” \( r^{-6} \) decay between sites in polar molecules is remarkable.

To understand the origin of this behavior it is convenient to first consider a system with free charges and investigate how the Coulomb interactions between the charges are renormalized (in \( k \) space) or screened (in \( r \) space). Let \( z_i \) and \( \rho_i \) denote the charge and average density, respectively, for free charged particles of type \( i \). The condition of electroneutrality, which must hold in the thermodynamic limit, is \( \sum_i z_i \rho_i = 0 \). The Fourier transforms of the bare Coulomb interactions between charges forms a matrix of perturbation functions

\[
\hat{\Phi}(k) = \left( \frac{1}{k^3} \right) C ,
\]

where the matrix \( C \) has elements \(-4\pi\beta z_i z_j\). The Coulomb perturbations diverge when \( k \to 0 \). A renormalization of these interactions would be

\[
\hat{\Phi}_r(k) = \left( \frac{1}{k^3} \right) \hat{F}(k) C ,
\]

where \( \hat{F}(k) C \) must vanish at least as fast as \( k^3 \) at small \( k \). If the \( k \to 0 \) divergence is to be removed from \( \hat{\Phi}_r(k) \). The matrix of functions \( \hat{F}(k) \) can be expressed as

\[
\hat{F}(k) = \left[ 1 - \left( \frac{1}{k^3} \right) C \hat{W}(k) \right]^{-1} ,
\]

where topological considerations lead to\(^{11,20}\)

\[
W_{ij}(r, r') = \rho_i \delta_{ij} \delta(r - r') + \rho_i \rho_j \text{[short-ranged function of } |r - r'|\] .
\]

The quantity \( W_{ij}(r, r') \) is a two-point hypervertex function. If the low density limit is used, i.e., \( W_{ij}(k) = \rho_i \delta_{ij} \), the Debye–Hückel potential is found

\[
\hat{\Phi}_r(k) = \left( k^2 + k^6 \right)^{-1} C ,
\]

where \( k^2 = 4\pi\beta \sum_i \rho_i z_i^2 \). It is clear from Eq. (6.4) that \( C \hat{W}(0) \) is nonzero except at zero density. Thus, at any nonzero density of free charge, the Coulomb potential between charges is screened. The renormalized potential is finite as \( k \to 0 \), and it decays exponentially at large \( r \).

The analogous behavior does not appear to hold for interactions between charges that are associated with neutral polar molecules. The reason is associated with the nature of the electroneutrality condition. For a system of free charges, the neutrality is a property of the whole macroscopic system. It does not have to hold locally within a single molecule. However, when charges are not free, the molecular species by themselves must be neutral. As a consequence,

\[
\hat{\Phi}(0) = 0 .
\]

The function \( \hat{\omega}_{\sigma \nu}(k) \) is the Fourier transform of the single-molecule part of the hypervertex function for molecular fluids. It is the molecular analog of \( \delta_{ij} \) in Eq. (6.4). The charge matrix \( \Phi \) is the analog of \( C \).

The topological methods employed in Sec. V can be used to show that the general renormalization of the Coulomb bonds in the polar fluid case is

\[
\hat{\Phi}_r(k) = \left( \frac{1}{k^3} \right) \left[ 1 - \left( \frac{1}{k^3} \right) \Phi \right]^{-1} \Phi ,
\]

where

\[
\Omega_{\sigma \nu}(r, r') = \rho_{\sigma \nu} \omega_{\sigma \nu}(r, r') + \rho_{\sigma} \rho_{\nu} \text{[short-ranged function obtained by summing some or all the graphs in } \Omega_{\sigma \nu}(r, r') \right] .
\]

It was shown in Sec. V that \( \Phi(0) = 0 \). Thus, unless one sums a class of graphs to form \( \Omega_{\sigma \nu}(r, r') \) and reasonably neglects another class which is of exactly the same size, \( \Phi(0) \) will satisfy a “local neutrality” property,

\[
\Phi(0) = 0 .
\]

Equations (6.7) and (6.9) imply that at small \( k \)

\[
\hat{\Phi}_r(k) = \left( \frac{1}{k^3} \right) \left[ 1 - \Phi \right]^{-1} \Phi ,
\]

or, after some matrix algebra,

\[
\hat{\Phi}_r(k) = \left( \frac{1}{k^6} \right) \Phi(1 - \Phi)^{-1} .
\]

In these equations,

\[
\Phi(1 - \Phi) = \lim_{k \to 0} \left( \frac{1}{k^3} \right) \Phi(0) .
\]

If all the graphs in \( \Omega_{\sigma \nu}(r, r') \) are summed, Eqs. (6.10) and (5.12) yield

\[
\hat{\Phi}_r(k) - \hat{\Phi}(k) / \epsilon .
\]

The right-hand side of Eq. (6.10) is always singular at \( k = 0 \). Thus, no renormalization of the Coulomb potentials between charges on different molecules will change the \( r^3 \) power law decay of these interactions. Only the amplitude of the decay can be altered. \( \hat{\Phi}_r(k) \) must always contain a \( k^3 \) singularity at \( k = 0 \). This behavior is a consequence of local neutrality: each microscopic molecule separately must be neutral. As a result, the total correlations between neutral polar molecules at large distances will decay as a function which is proportional to the interaction. It is this fact that leads directly to the properties attributed to \( \Phi(k) \) and thus the \( r^{-3} \) decay of \( h_{\sigma \nu}(r) \).

The inability to renormalize the long-ranged interac-
tions between polar molecules leads to fascinating statistical mechanical problems when one actually tries to create an approximate theory to calculate $\epsilon$. In particular, the asymptotic decay of correlations is strongly linked to the local small distance behavior of intermolecular correlations. The linkage makes approximate theories very sensitive to the methods used to describe short-ranged correlations. This point is addressed by Hoge and Stell in their discussion of a "core parameter," and by Ramshaw both in his work on mean field theories for $\epsilon$ and his discussion of conditions governing the existence of $\epsilon$. The following pair of simple calculations illustrate the nature of the problem.

The equilibrium statistical mechanics of systems with long-ranged forces is commonly studied by performing simple chain sums of the long-ranged perturbations. The most primitive approximation obtained from this procedure is

$$
\hat{h}_{aH'W'}(r_1^{(\alpha)} - r_{2H'}^{(\gamma)}) = \sum \phi_{W'}(1,2_H') \left\{ \phi_{W'}(1,2_H') + \sum_{3_H'} \phi_{W'}(1,2_H',3_H'') \phi_{W'}(1,3_H'',2_H') \right\},
$$

where $\phi_{W'}(1,2_H')$ is an abbreviation for $\Sigma_{a',1} \phi_{aW'W'}(r_1^{(\alpha)} - r_{2H'}^{(\gamma)})$. The interaction site cluster series representation of this approximation is

$$
\rho_{W'} h_{aH'W'}(r_1^{(\alpha)} - r_{2H'}^{(\gamma)}) = \text{the sum of all simple singly connected chains with two white circles, $s$ vertices, any number of black circles, and $\phi$-bonds,}
$$

which is equivalent to replacing $\Omega_{aW'W'}(r)$ with its low density limit, $\rho_{W'} \omega_{aW'W'}(r)$. [See Fig. 4(a).] Thus, the result of the sum is

$$
\hat{h}_{aH'W'}(r) = \omega(k)[1 - \hat{\phi}(k)] \rho_{W'} \omega_{aW'W'}(r).
$$

The calculation of $\epsilon$ from Eqs. (6.14') and (3.17) gives

$$
1 - (1/\epsilon) = y/(1 + y),
$$

or

$$
\epsilon = 1 + y,
$$

where

$$
y = \sum \rho_{W'} (\delta_0^W + \alpha_W).
$$

This equation is the well-known ideal gas formula for $\epsilon$.

Another approximation can be obtained by decorating the graphs in Eq. (6.13) with $f^{(sr)}$-bonds which represent

$$
f_{aH'W'}^{(sr)}(r, r') = \delta_{aW'} \delta_{1W'} f_d(1 - r),
$$

where

$$
f_d(r) = -1, \quad r < d,
$$

$$
= 0, \quad r > d.
$$

The decorations give

$$
\hat{h}_{aH'W'}(r_1^{(\alpha)} - r_{2H'}^{(\gamma)}) = \text{the series of integrals in Eq. (6.13) but with the $\phi_{W'}(1,2_H')$ functions replaced with the functions $\phi_{W'}(1,2_H') + (f) \phi_{W'}(1,2_H')$ where $(f) \phi_{W'}(1,2_H')$ represents $\Sigma_{a,W'} \phi^{(sr)}_{W'}(r_1^{(\alpha)} - r_{2H'}^{(\gamma)})$.
$$

The diagrammatic statement of this approximation is

$$
\rho_{W'} h_{aH'W'}(r_1^{(\alpha)} - r_{2H'}^{(\gamma)}) = \text{the sum of all connected chains with $\phi$-bonds and $f^{(sr)}$-bonds, two white circles, and $s$-vertices, which become disconnected when any $s$-vertex not associated with the white circles is removed, and two vertices can be connected directly by one $\phi$-bond, or one $\phi$-bond times one $f^{(sr)}$-bond.}
$$

(6.19')
The mathematical difference between the sums in Eqs. (6.13) and (6.19) is that the latter excludes site 1 in any molecule from approaching site 1 in an adjacent molecule by distances smaller than a core diameter \( d \). Some of the diagrams are shown in Fig. 4. Notice that the hypervertex function associated with Eq. (6.19) is now a sum of an infinite class of diagrams. The evaluation of these graphs can be performed (tediously) by applying the methods discussed in Ref. 1. But when \( d \) is much larger than any intramolecular site-site length, the diagrams are more easily studied by noting that

\[
[1 + f_0(|r_{12}^{(1)} - r_{12}^{(1)}|)] \sum_{\nu,w} \phi_{\nu,w} |r_{12}^{(1)} - r_{12}^{(1)}| \]

\[
= [1 + f_0(|r_{12}^{(1)} - r_{12}^{(1)}|)] \mu_{12} \cdot \nabla |r_{12}^{(1)} - r_{12}^{(1)}|^{-1} ,
\]

\[
+ \cdots ,
\]

(6.20)

where \( \nabla \) denotes the gradient with respect to \( r_{12}^{(1)} \). The terms omitted in Eq. (6.20) are negligible in the limit that \( d \) is very large compared to the intramolecular lengths. The right hand side of Eq. (6.20) is a step function times a dipole–dipole interaction. Chain sums of this type of intermolecular bond have been studied many times.\(^{13,24}\) With the application of Eq. (6.20) in (6.19), and a significant amount of algebra, one obtains from Eq. (3.17)

\[
(1 - 1/\epsilon) \approx y/(1 + \frac{1}{3}y) ,
\]

or

\[
\epsilon - 1 \approx y/(1 - \frac{1}{3}y) ,
\]

or

\[
(\epsilon - 1)/(%2 + \frac{1}{3}y) \approx \frac{1}{y} ,
\]

(6.21)

which is the famous Clausius–Mosotti–Debye relation. This approximation is a very different result than \( \epsilon - 1 \approx y \) which was obtained from Eq. (6.13). It is remarkable that such a significant difference is a consequence of a simple addition of a short-ranged bond.
VII. CONCLUSIONS

In this article, we have shown that the straightforward application of linear response theory leads to an unambiguous formula for the dielectric constant. The formula is valid when the molecular species are polarizable and deformable. The correlation functions which determine \( \epsilon \) are short-ranged functions decaying as \( r^{-6} \) for large \( r \). As a result, the dielectric constant can be expected to be independent of the shape of the dielectric medium or any other macroscopic boundary conditions.

Our formulas for \( \epsilon \), Eqs. (3.17) and (5.12), are generalizations of equations presented earlier by Høye and Stell\(^{11}\) and by Nienhuis–Deutch.\(^ {12}\) The correspondence between these earlier works and ours was readily established. We have used our formulas for \( \epsilon \) together with a topological reduction to show that the asymptotic form for the infinite dilution potential of mean force between microscopic ions in a dielectric solvent is \( \epsilon A^2 \rho / \epsilon r \) irrespective of the short-ranged forces between the ions and solvent molecules.

We have studied the origin of the \( r^{-6} \) decay of correlations between pairs of sites on different polar molecules. It was shown that the \( r^{-6} \) decay of site–site correlations is a consequence of the local molecular neutrality of a polar fluid (as opposed to the global neutrality of a fluid containing free charges). The inability to renormalize the Coulombic site–site interactions leads to a remarkable coupling between the long wavelength properties which determine \( \epsilon \) and the local small wavelength correlations.

These conclusions were derived entirely within the context of the interaction site formulation of the molecular fluids problem.\(^ {1-3} \) We believe the derivations were relatively free of the ubiquitous subtleties found in the study of dielectric properties. The simplicity is a consequence of the interaction site formalism which requires nothing more than the straightforward application of Coulomb’s law. It is reasonable to expect that other problems, such as local field effects, can be handled with similar ease.

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