Dielectric Constant of Polarizable, Nonpolar Fluids and Suspensions

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We study the dielectric constant of a polarizable, nonpolar fluid or suspension of spherical particles by use of a renormalized cluster expansion. The particles may have induced multipole moments of any order. We show that the Clausius–Mossotti formula results from a virtual overlap contribution. The corrections to the Clausius–Mossotti formula are expressed with the aid of a cluster expansion. The integrands of the cluster integrals are expressed in terms of two-body nodal connectors which incorporate all reflections between a pair of particles. We study the two- and three-body cluster integrals in some detail and show how these are related to the dielectric virial expansion and to the first term of the Kirkwood–Yvon expansion.

KEY WORDS: Dielectric constant; nonpolar liquids; suspensions; renormalized cluster expansion.

1. INTRODUCTION

The theory of nonpolar dielectrics has a long and distinguished history, but has not yet settled to a final state. Although major advances have been made, there is no agreement on the best way of calculating the dielectric constant of a dense system of polarizable, nonpolar particles. Several review articles in which various approaches are discussed have appeared recently.[1–4]

Most of the attention has focused on a simplified model in which spherical particles possess only a polarizable point dipole moment at their center. We·assume for generality that the point dipoles are immersed in a

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uniform background of dielectric constant ε_1. The effective dielectric constant ε^* of this polarizable point dipole model may be written in the form

$$\frac{\varepsilon^* - \varepsilon_1}{\varepsilon^* + 2\varepsilon_1} = \frac{4\pi}{3\varepsilon_1} n\alpha[1 + S] \tag{1.1}$$

where n is the number density and α the dipole polarizability. For $S = 0$ this is the Clausius–Mossotti formula, which may be derived by the Lorentz local field argument.[5] The term S describes the deviation from the Clausius–Mossotti formula arising from corrections to the Lorentz local field due to the microscopic structure of the system. Long ago Kirkwood[6] and Yvon[7] derived an expansion for S in powers of the polarizability α. For real liquids the dimensionless parameter $n\alpha$ is sufficiently small that only the term S_2 of order α^2 is significant.[8] Kirkwood and Yvon expressed S_2 as an integral over two- and three-particle correlation functions. The comparison with experiment is not very good due to quantum mechanial effects which affect the pair polarizability.[9,10] Alternatively, one may expand S in powers of the density. This leads to the dielectric virial expansion for a nonpolar gas.[11]

A new approach to the polarizable point dipole model was developed by Wertheim,[12] who performed a graph-theoretic analysis of the dipole moments induced by an applied field and detected an Ornstein–Zernike type structure. The theory leads to integral equations similar to those studied in the theory of liquids. Wertheim proposed an approximation analogous to the mean spherical approximation. The theory was further developed by Høye and Stell.[13] Logan[14] extended Wertheim's approach to fluids of molecules with polarizable point dipoles and quadrupoles.

As a more general model, one may study a suspension of spherical inclusions with a radially symmetric dielectric profile. Such inclusions possess polarizable multipole moments of all orders. For this model Felderhof et al.[15] developed a cluster expansion in which the effective dielectric constant ε^* is expressed as a sum of absolutely convergent integrals. This is in contrast to the Kirkwood–Yvon expansion, in which the integrals are not absolutely convergent and must be specified to run over a spherical sample. Felderhof et al.[16] also showed which parts of the cluster integrals give rise to the Clausius–Mossotti formula. The terms correspond to virtual overlap configurations of the inclusions.

Recently we have extended Wertheim's approach and have derived a renormalized cluster expansion for the related problem of wave propagation in a disordered system of scatterers.[17] Here we apply the renormalized cluster expansion to a dielectric suspension of spherical

inclusions. A modification of Wertheim's theory allows us to find a relatively simple expression for the electric susceptibility kernel. We show that the effective dielectric constant ε^* may be written in the form (1.1) with

$$1 + S = \left[1 - \frac{4\pi}{3\varepsilon_1} n\alpha(\lambda + \mu) \right]^{-1} \tag{1.2}$$

where the coefficients λ and μ are each given by a sum of absolutely convergent cluster integrals. We study the low-order integrals in some detail. All multipole orders may occur, but of course the theory simplifies for the polarizable point dipole model.

For a special class of dielectric suspensions, in which the dielectric profile of the inclusions is uniform and equal to a constant ε_2, exact upper and lower bounds on the effective dielectric constant ε^* have been derived.[18,19] The bounds are tight when ε_2 differs little from the background value ε_1. A generalization to penetrable inclusions and a different calculation of the bounds has been proposed by Torquato.[20] It would be of interest to compare the predictions of the renormalized cluster expansion, when approximated by the lower order terms, with the exact bounds.

For the polarizable point dipole model Bedeaux and Mazur[21] have derived an expression for S in (1.1) based on the idea that fluctuations of the density are small. Felderhof discussed this type of expansion in a different formalism.[22] The theory has been compared with Wertheim's approach by Høye and Bedeaux[23] and was extended to include higher order multipoles by Geigenmüller and Mazur.[24] Although in principle exact, when carried to infinite order, the theory has the disadvantage that in any finite order there are contributions from the nonphysical overlap region where the propagator between different particles may be chosen arbitrarily. This point was first emphasized by Sullivan and Deutch.[25] In our view this is an unattractive feature, since it is difficult to motivate the choice of propagator in the nonphysical region. In our expansion there also occur contributions from a virtual overlap region, but we do not have the freedom of modifying the propagator there.

Here we first develop the theory for dielectric suspensions, closely following the work of Felderhof et al.[15] We then apply the renormalized cluster expansion and derive (1.2). The low-order cluster integrals are discussed in some detail. Finally, we compare with the Kirkwood–Yvon expansion and the dielectric virial expansion for the polarizable point dipole model.

2. EXPRESSION FOR THE WAVEVECTOR-DEPENDENT SUSCEPTIBILITY TENSOR

We consider a dielectric system consisting of N nonoverlapping spherical inclusions embedded in a uniform background of dielectric constant ε_1. The inclusions are identical, each of radius a and characterized by a spherically symmetric dielectric constant. For a fixed configuration of inclusions in which they are centered at $R_1, R_2,..., R_N$, the dielectric constant at a field point r is then $(j = 1,..., N)$

$$\varepsilon(1,..., N; r) = \begin{cases} \varepsilon_1, & |r - R_j| > a \\ \varepsilon(|r - R_j|), & |r - R_j| < a \end{cases} \tag{2.1}$$

The basic equations for the electric field E and the dielectric displacement D are Maxwell's electrostatic equations

$$\nabla \cdot D = 4\pi\rho_0, \qquad \nabla \times E = 0, \qquad D = \varepsilon E \tag{2.2}$$

where $\rho_0 = \rho_0(r)$ is a fixed charge distribution, independent of the configuration of the inclusions. The applied field $E_0(r)$ is the solution of Eqs. (2.2) with ε a uniform dielectric constant ε_1. The electric field $E(r)$ in the presence of the inclusions is related to the applied field by

$$E(1,..., N) = \underset{\approx}{K}(1,..., N) \cdot E_0 \tag{2.3}$$

where $\underset{\approx}{K}(1,..., N)$ is a linear operator which depends parametrically on the positions of the inclusions. We define the induced polarization, relative to the medium in the absence of inclusions, via the relation

$$D = \varepsilon_1 E + 4\pi P \tag{2.4}$$

The polarization is also related linearly to the applied field

$$P(1,..., N) = \chi(1,..., N) \underset{\approx}{K}(1,..., N) \cdot E_0 \tag{2.5}$$

where

$$\chi(1,..., N) = \frac{\varepsilon(1,..., N) - \varepsilon_1}{4\pi} \tag{2.6}$$

is the relative dielectric susceptibility. It follows from (2.1) and the assumption that the inclusions do not overlap that the susceptibility is a sum of one-body terms

$$\chi(1,..., N) = \sum_{j=1}^{N} \chi(j), \qquad \chi(j) = \frac{\varepsilon(j) - \varepsilon_1}{4\pi} \theta(j) \tag{2.7}$$

where the step function $\theta(j) = \theta(a - |\mathbf{r} - \mathbf{R}_j|)$ localizes the field point $\mathbf{r}$ to lie within the inclusion j.

The inclusions are randomly distributed as described by a probability distribution $W(1,..., N)$. The distribution is assumed normalized to unity and symmetric in the labels $1,..., N$. The partial distribution functions are defined by

$$n(1,..., s) = \frac{N!}{(N-s)!} \int \cdots \int d\mathbf{R}_{s+1} \cdots d\mathbf{R}_N \, W(1,..., N) \tag{2.8}$$

The average electric field in the presence of the inclusions is

$$\langle \mathbf{E} \rangle = \int \cdots \int d\mathbf{R}_1 \cdots d\mathbf{R}_N \, W(1,..., N) \, \mathbf{E}(1,..., N) \tag{2.9}$$

and the average polarization $\langle \mathbf{P} \rangle$ is defined similarly. From (2.3) and (2.5) we find

$$\langle \mathbf{E} \rangle = \langle \underset{\approx}{\mathbf{K}} \rangle \cdot \mathbf{E}_0, \qquad \langle \mathbf{P} \rangle = \langle \chi \underset{\approx}{\mathbf{K}} \rangle \cdot \mathbf{E}_0 \tag{2.10}$$

Eliminating the aplied field $\mathbf{E}_0$, we find that the averages are related by

$$\langle \mathbf{P} \rangle = \underset{\approx}{\mathbf{X}} \cdot \langle \mathbf{E} \rangle \tag{2.11}$$

with the linear susceptibility kernel $\underset{\approx}{\mathbf{X}}(\mathbf{r}, \mathbf{r}')$ given by

$$\underset{\approx}{\mathbf{X}} = \langle \chi \underset{\approx}{\mathbf{K}} \rangle \cdot \langle \underset{\approx}{\mathbf{K}} \rangle^{-1} \tag{2.12}$$

We cast this in a more familiar form by defining the T operator by

$$\underset{\approx}{\mathbf{T}}(1,..., N) = \chi(1,..., N) \underset{\approx}{\mathbf{K}}(1,..., N) \tag{2.13}$$

The operator $\underset{\approx}{\mathbf{K}}(1,..., N)$ may be written alternatively

$$\underset{\approx}{\mathbf{K}}(1,..., N) = \underset{\approx}{\mathbf{I}} + \underset{\approx}{\mathbf{G}}_0 \underset{\approx}{\mathbf{T}}(1,..., N) \tag{2.14}$$

where $\underset{\approx}{\mathbf{G}}_0$ is the Green function for the uniform medium with dielectric constant ε_1. The explicit form for $\underset{\approx}{\mathbf{G}}_0$ acting on a given vector field $\mathbf{V}(\mathbf{r})$ is $[\underset{\approx}{\mathbf{G}}_0 \cdot \mathbf{V}](\mathbf{r})$

$$= -\frac{4\pi}{3\varepsilon_1} \mathbf{V}(\mathbf{r}) + \int_\delta d\mathbf{r}' \frac{3(\mathbf{r} - \mathbf{r}') \cdot \mathbf{V}(\mathbf{r}')(\mathbf{r} - \mathbf{r}') - (\mathbf{r} - \mathbf{r}')^2 \, \mathbf{V}(\mathbf{r}')}{\varepsilon_1 |\mathbf{r} - \mathbf{r}'|^5} \tag{2.15}$$

where the subscript δ on the integral indicates that the integral is carried out with the exclusion of an infinitesimally small sphere centered at $\mathbf{r}$. Using (2.13) and (2.14), we may write (2.12) in the form

$$\underset{\approx}{\mathbf{X}} = \langle \underset{\approx}{\mathbf{T}} \rangle \langle \underset{\approx}{\mathbf{I}} + \underset{\approx}{\mathbf{G}}_0 \underset{\approx}{\mathbf{T}} \rangle^{-1} \tag{2.16}$$

This expression is identical to that obtained for the self-energy operator in many-body scattering theory.

The analogue of (2.7) in many-body scattering theory is the statement that the scattering potential is a sum of one-body potentials. This circumstance together with the expression (2.16) is at the basis of the renormalized cluster expansion which we have developed recently.[17] Therefore we can immediately apply this expansion in the present case. The susceptibility kernel is given by

$$\underset{\approx}{X} = \int d1 \, n(1) \, \underset{\approx}{B}(1) + \int d1 \, d2 \, n(1) \, n(2) \, \underset{\approx}{B}(1) \, \underset{\approx}{F}(1, 2) \, \underset{\approx}{B}(2) \qquad (2.17)$$

where the integrations are over the positions $\mathbf{R}_1$ and $\mathbf{R}_2$ of two spheres, $n(1)$ is the number density of spheres, $\underset{\approx}{B}(1)$ is the so-called bridge operator, and $\underset{\approx}{F}(1, 2)$ is the pair connector. In the next two sections we shall give the cluster expansion expressions for these operators.

We assume that the system has a proper thermodynamic limit $N \to \infty$, volume $\Omega \to \infty$, at constant $n = N/\Omega$, in which it becomes spatially homogeneous. In the thermodynamic limit the density $n(1)$ becomes a constant n, the operator $\underset{\approx}{B}(1)$ depends only on the variables $\mathbf{r} - \mathbf{R}_1$ and $\mathbf{r}' - \mathbf{R}_1$, and the operator $\underset{\approx}{F}(1, 2)$ depends only on $\mathbf{r} - \mathbf{R}_1$, $\mathbf{r}' - \mathbf{R}_2$, and $\mathbf{R}_1 - \mathbf{R}_2$. Hence in this limit the susceptibility operator $\underset{\approx}{X}(\mathbf{r}, \mathbf{r}')$ becomes translationally invariant and depends only on $\mathbf{r} - \mathbf{r}'$. Its plane wave matrix elements defined by

$$(\mathbf{q} \,|\underset{\approx}{X}|\, \mathbf{q}') \equiv \int d\mathbf{r} \int d\mathbf{r}' \exp(-i\mathbf{q} \cdot \mathbf{r}) \, \underset{\approx}{X}(\mathbf{r}, \mathbf{r}') \exp(i\mathbf{q}' \cdot \mathbf{r}') \qquad (2.18)$$

acquire delta-function behavior and take the form

$$(\mathbf{q} \,|\underset{\approx}{X}|\, \mathbf{q}') = 8\pi^3 \, \chi^*(\mathbf{q}) \, \delta(\mathbf{q} - \mathbf{q}') \qquad (2.19)$$

where $\chi^*(\mathbf{q})$ is the effective susceptibility tensor which relates the Fourier components of the average fields

$$\langle \mathbf{E_q} \rangle = \frac{1}{8\pi^3} \int \exp(-i\mathbf{q} \cdot \mathbf{r}) \, \langle \mathbf{E}(\mathbf{r}) \rangle \, d\mathbf{r}$$

$$\langle \mathbf{P_q} \rangle = \frac{1}{8\pi^3} \int \exp(-i\mathbf{q} \cdot \mathbf{r}) \, \langle \mathbf{P}(\mathbf{r}) \rangle \, d\mathbf{r} \qquad (2.20)$$

according to

$$\langle \mathbf{P_q} \rangle = \chi^*(\mathbf{q}) \cdot \langle \mathbf{E_q} \rangle \qquad (2.21)$$

The effective dielectric tensor is given by

$$\epsilon^*(\mathbf{q}) = \varepsilon_1 1 + 4\pi\chi^*(\mathbf{q}) \tag{2.22}$$

It follows from (2.17) and (2.19) that the susceptibility tensor may be expressed as

$$\chi^*(\mathbf{q}) = n(\mathbf{q}|\underset{\approx}{B}(1)|\mathbf{q}) + n^2 \int d\mathbf{R}\ (\mathbf{q}|\underset{\approx}{B}(1)\ \underset{\approx}{F}(1, 2)\ \underset{\approx}{B}(2)|\mathbf{q}) \tag{2.23}$$

where the center of sphere 1 may be taken to be at the origin and where $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$ is the position of sphere 2 relative to sphere 1. In the following we shall particularly interested in the $\mathbf{q} \to 0$ limit.

3. BRIDGE OPERATOR

In this section we study first the bridge operator $\underset{\approx}{B}(1)$ occurring in the expression (2.23) for the susceptibility tensor. We recall that the bridge operator $\underset{\approx}{B}(1)$ is defined by[17]

$$\underset{\approx}{B}(1) = \underset{\approx}{M}(1)[\underset{\approx}{I} - \underset{\approx}{S}(1)\ \underset{\approx}{M}(1)]^{-1} \tag{3.1}$$

where $\underset{\approx}{M}(1) \equiv \underset{\approx}{T}(1)$ is the T operator for a single particle centered at $\mathbf{R}_1$, and $\underset{\approx}{S}(1)$ is the so-called reaction field operator.

We note that the operator $\underset{\approx}{M}(1)$ is localized about $\mathbf{R}_1$ in the following sense. The operator acts as an integral kernel on a vector field $\mathbf{E}(\mathbf{r})$ such that

$$[\underset{\approx}{M}(1)\mathbf{E}]_j(\mathbf{r}) = \int d\mathbf{r}'\ M_{jk}(1; \mathbf{r}, \mathbf{r}') \cdot E_k(\mathbf{r}') \tag{3.2}$$

The localized property of $\underset{\approx}{M}(1)$ is that

$$M_{jk}(1; \mathbf{r}, \mathbf{r}') = 0 \quad \text{if} \quad |\mathbf{r} - \mathbf{R}_1| > a \quad \text{or} \quad |\mathbf{r}' - \mathbf{R}_1| > a \tag{3.3}$$

It may be shown from the basic equations that the kernel is symmetric

$$M_{jk}(1; \mathbf{r}, \mathbf{r}') = M_{kj}(1; \mathbf{r}', \mathbf{r}) \tag{3.4}$$

The localization property (3.3) follows from (2.7), (2.13), and the symmetry (3.4).

The reaction field operator $\underset{\approx}{S}(1)$ is given by a cluster expansion

$$\underset{\approx}{S}(1) = \sum_{s=2}^{\infty} \underset{\approx}{S}_s(1) \tag{3.5}$$

where $\underset{\approx}{S}_s(1)$ is defined as an average scattering operator for s particles. Explicitly, the s-particle operator is given by

$$\underset{\approx}{S}_s(1) = \sum_C \int d2 \cdots ds \, n(2) \cdots n(s) \, k(C) \, \underset{\approx}{N}_{11}(C) \qquad (3.6)$$

where the sum is over all connected ordered partitions of s labels, $k(C)$ is a corresponding chain correlation function, and $\underset{\approx}{N}_{11}(C)$ is a corresponding nodal connector. The precise definitions of these quantities have been given in ref. 17. By way of example, we write the lowest order terms in more explicit form. Thus, the two-particle term in (3.5) is given by

$$\underset{\approx}{S}_2(1) = \int d2 \, n(2) \, k(1, 2) \, \underset{\approx}{N}_{11}(1, 2) \qquad (3.7)$$

where $k(1, 2) = g(1, 2)$ is simply the normalized two-particle distribution function defined by $n(1, 2) = n(1) \, n(2) \, g(1, 2)$. The three-particle term is given by

$$\underset{\approx}{S}_3(1) = \int d2 \, d3 \, n(2) \, n(3) [k(1, 2, 3) \, \underset{\approx}{N}_{11}(1, 2, 3)$$

$$+ k(1, 2 \,|\, 1, 3) \, \underset{\approx}{N}_{11}(1, 2 \,|\, 1, 3)] \qquad (3.8)$$

with the chain correlation functions

$$k(1, 2, 3) = g(1, 2, 3), \qquad k(1, 2 \,|\, 1, 3) = g(1, 2, 3) - g(1, 2) \, g(1, 3) \qquad (3.9)$$

where $g(1, 2, 3)$ is defined by $n(1, 2, 3) = n(1) \, n(2) \, n(3) \, g(1, 2, 3)$. The nodal connectors $\underset{\approx}{N}_{11}(C)$ will be discussed more fully at a later stage. We merely note that they correspond to scattering sequences in which the first and the last scatterer have the label 1. It follows from the symmetry (3.4), the symmetry of the Green function (2.15), and the definition of the nodal connectors that they are symmetric kernels. As a consequence, the reaction field operator also possesses the symmetry property (3.4). Hence, the bridge operator $\underset{\approx}{B}(1)$ given by (3.1) has the same symmetry.

In the calculation of the effective dielectric constant corresponding to the $q \to 0$ limit in (2.23) we must consider the matrix element $(0 \,|\, \underset{\approx}{B}(1) \,|\, 0)$, where we employ the notation (2.18). We note that the corresponding matrix element of $\underset{\approx}{M}(1)$ is given by

$$(0 \,|\, \underset{\approx}{M}(1) \,|\, 0) = \alpha \mathbf{1} \qquad (3.10)$$

where α is the polarizability of a sphere, since $(0 \,|\, \underset{\approx}{M}(1) \,|\, 0) \cdot \mathbf{E}_0$ is just the total dipole moment of sphere 1 by itself in a uniform applied field $\mathbf{E}_0$.

Next we consider $\underset{\approx}{S}(1)\,\underset{\approx}{M}(1)|0)$ as a function of the field variable $\mathbf{r}$. It follows from the equations of electrostatics and the assumed isotropy of the system that this has the remarkable property

$$[\underset{\approx}{S}(1)\,\underset{\approx}{M}(1)|0)](\mathbf{r}) = \frac{4\pi}{3\varepsilon_1}\,\lambda n\alpha \mathbf{1} \qquad \text{for} \quad |\mathbf{r} - \mathbf{R}_1| \leqslant a \qquad (3.11)$$

where λ is a dimensionless coefficient. To show this property, we note that in a uniform applied field $\mathbf{E}_0$

$$[\underset{\approx}{S}(1)\,\underset{\approx}{M}(1)|0)\cdot\mathbf{E}_0](\mathbf{r}) = \int G_0(\mathbf{r} - \mathbf{r}')\cdot F(\mathbf{r}')\cdot\mathbf{E}_0\,d\mathbf{r}' \qquad (3.12)$$

where $G_0(\mathbf{r} - \mathbf{r}')$ is the kernel of the Green function $\underset{\sim}{G}_0$ defined in (2.15) and $F(\mathbf{r}')\cdot\mathbf{E}_0$ is a polarization field surrounding sphere 1, which vanishes identically for $|\mathbf{r}' - \mathbf{R}_1| \leqslant a$. Hence the right-hand side of (3.12) satisfies Laplace's equation and by symmetry it represents a field which is uniform for $|\mathbf{r} - \mathbf{R}_1| \leqslant a$, parallel to $\mathbf{E}_0$, and which we may put equal to $\mathbf{E} = (4\pi\lambda n\alpha/3\varepsilon_1)\mathbf{E}_0$.

By repeated application of (3.11) in the expanded form of (3.1), we find that the matrix element $(0|\underset{\approx}{B}(1)|0)$ is given by

$$(0|\underset{\approx}{B}(1)|0) = \frac{\alpha}{1 - 4\pi\lambda n\alpha/3\varepsilon_1}\,\mathbf{1} \qquad (3.13)$$

It is natural to use this expression to define a dressed polarizability α' by

$$\alpha' = \alpha[1 - (4\pi\lambda n\alpha/3\varepsilon_1)]^{-1} \qquad (3.14)$$

We may calculate the reaction field constant λ from (3.11) by approximating the reaction field operator $\underset{\approx}{S}(1)$ by the first few terms (3.7) and (3.8) of its cluster expansion. Before turning to that task, we first study the second term in (2.23).

4. PAIR CONNECTOR

In this section we study the second matrix element in (2.23), again in the limit $\mathbf{q} \to 0$. The pair connector $\underset{\approx}{F}(1, 2)$ is related by an integral equation of Ornstein–Zernike type

$$\underset{\approx}{F}(1, 2) = \underset{\approx}{S}(1, 2) + \int d3\,n(3)\,\underset{\approx}{S}(1, 3)\,\underset{\approx}{B}(3)\,\underset{\approx}{F}(3, 2) \qquad (4.1)$$

to the so-called short-range connector $\underset{\approx}{S}(1, 2)$. The latter has a cluster expansion of the form

$$\underset{\approx}{S}(1, 2) = \sum_{s=2}^{\infty} \underset{\approx}{S}_s(1, 2) \tag{4.2}$$

where $\underset{\approx}{S}_s(1, 2)$ is an average scattering operator involving s particles. For $s = 2$ the operator is given by

$$\underset{\approx}{S}_2(1, 2) = g(1, 2)[\underset{\approx}{N}_{12}(1, 2) - \underset{\approx}{G}_0] + h(1, 2)\underset{\approx}{G}_0 \tag{4.3}$$

where $h(1, 2) = g(1, 2) - 1$. For $s \geqslant 3$ the operators are expressed conveniently with the aid of an auxiliary label d in the form

$$\underset{\approx}{S}_s(1, d) = \sum_C \sum_{l=2}^{s} \int d2 \cdots ds$$
$$\times \delta(\mathbf{R}_d - \mathbf{R}_l)[n(2) \cdots n(s)/n(l)] \, k(C) \, \underset{\approx}{N}_{1l}(C) \tag{4.4}$$

Here we have taken note of the fact that 2 in (2.23) plays the role of a generic label different from 1. By a renaming of labels we may obtain an expression for $\underset{\approx}{S}_s(1, 2)$. For example, for $s = 3$

$$\underset{\approx}{S}_3(1, 2) = \int d3 \, n(3)[k(1, 2, 3) \, \underset{\approx}{N}_{12}(1, 2, 3)$$

$$+ k(1, 2 | 2, 3) \, \underset{\approx}{N}_{12}(1, 2 | 2, 3)$$

$$+ k(1, 2, 3) \, \underset{\approx}{N}_{12}(1, 3, 2) + k(1, 3 | 1, 2) \, \underset{\approx}{N}_{12}(1, 3 | 1, 2)$$

$$+ k(1, 3 | 2, 3) \, \underset{\approx}{N}_{12}(1, 3 | 3, 2)] \tag{4.5}$$

The chain correlation functions k are defined in analogy to (3.9). The nodal connectors $\underset{\approx}{N}_{12}$ have been defined in detail in ref. 17. At a later stage we shall be concerned with the explicit expressions.

We must study the matrix element $(0 | \underset{\approx}{B}(1) \, \underset{\approx}{F}(1, 2) \, \underset{\approx}{B}(2) | 0)$. We iterate the integral equation (4.1) and consider first the ket $\underset{\approx}{S}(k, 2) \, \underset{\approx}{B}(2) | 0)$ as a function of the field variable $\mathbf{r}$. It is convenient to write the short-range connector as a sum of two contributions

$$\underset{\approx}{S}(1, 2) = \underset{\approx}{S}_{ov}(1, 2) + \underset{\approx}{S}_{no}(1, 2) \tag{4.6}$$

where $\underset{\approx}{S}_{ov}(1, 2)$ is defined by the virtual overlap contribution to the last term in (4.3),

$$\underset{\approx}{S}_{ov}(1, 2) = -\theta(2a - |\mathbf{R}_1 - \mathbf{R}_2|)\underset{\approx}{G}_0 \tag{4.7}$$

This is the only term in $\underset{\approx}{S}(1, 2)$ in which the Green function acts between overlapping inclusions, as may be seen from the multiple scattering expansion of the nodal connectors and the expression of the chain correlation functions k in terms of normalized distribution functions g. Although the inclusions cannot overlap physically, nonetheless the overlap contribution (4.7) appears as a consequence of the fact that the susceptibility kernel is a ratio of two averages, as may be seen from (2.12). In earlier work[16] it has been shown that the virtual overlap configurations make an important contribution and are responsible for the Clausius–Mossotti approximation to the effective dielectric constant.

Therefore we first consider the ket $\underset{\approx}{S}_{ov}(k, 2)\,\underset{\approx}{B}(2)|0\rangle \cdot \mathbf{E}_0$ as a function of the field variable $\mathbf{r}$, or equivalently $-\underset{\approx}{G}_0\underset{\approx}{B}(2)|0\rangle \cdot \mathbf{E}_0$ with the condition that the inclusions k and 2 must overlap. The latter ket is related to

$$\mathbf{E}_{ind}(2) = \underset{\approx}{G}_0\underset{\approx}{M}(2)|0\rangle \cdot \mathbf{E}_0 = \underset{\approx}{K}(2) \cdot \mathbf{E}_0 - \mathbf{E}_0 \qquad (4.8)$$

which is the induced field, within and without the inclusion 2, when placed in the uniform field $\mathbf{E}_0$. It follows from (3.1) and (3.11) that the ket $\underset{\approx}{G}_0\underset{\approx}{B}(2)|0\rangle \cdot \mathbf{E}_0$ is given by

$$\underset{\approx}{G}_0\underset{\approx}{B}(2)|0\rangle \cdot \mathbf{E}_0 = E'_{ind}(2) = (1 - 4\pi\lambda n\alpha/3\varepsilon_1)^{-1}\, E_{ind}(2) \qquad (4.9)$$

It was shown in ref. 16 that within the inclusion centered at $\mathbf{R}_k$ the induced field corresponding to an inclusion centered at $\mathbf{R}_2$ when integrated over all overlapping configurations is just the uniform field

$$\int_{|\mathbf{R}_k - \mathbf{R}_2| < 2a} d\mathbf{R}_2\, \mathbf{E}_{ind}(2; \mathbf{r}) = -\frac{4\pi\alpha}{3\varepsilon_1}\mathbf{E}_0 \qquad \text{for} \quad |\mathbf{r} - \mathbf{R}_k| < a \quad (4.10)$$

Combining this with (4.9), we therefore find

$$\int_{|\mathbf{R}_k - \mathbf{R}_2| < 2a} d\mathbf{R}_2\, [\underset{\approx}{G}_0\underset{\approx}{B}(2)|0\rangle \cdot \mathbf{E}_0](\mathbf{r}) = -\frac{4\pi\alpha'}{3\varepsilon_1}\mathbf{E}_0 \qquad \text{for} \quad |\mathbf{r} - \mathbf{R}_k| < a$$
$$(4.11)$$

where the dressed polarizability α' is given by (3.14). If the bridge operator $\underset{\approx}{B}(2)$ is approximated by the bare operator $\underset{\approx}{M}(2)$, then $\alpha' = \alpha$ in (4.11). We show in the next section that if in addition $\underset{\approx}{S}(1, 2)$ is approximated by $\underset{\approx}{S}_{ov}(1, 2)$, then (4.11) leads to the Clausius–Mossotti formula.

Next we consider the ket $\underset{\approx}{S}_{no}(k, 2)\,\underset{\approx}{B}(2)|0\rangle \cdot \mathbf{E}_0$ as a function of the field variable $\mathbf{r}$. In analogy to (3.12), the integral of this ket over the non-overlap positions of sphere 2 is given by

$$\int d\mathbf{R}_2\, [\underset{\approx}{S}_{no}(k, 2)\,\underset{\approx}{B}(2)|0\rangle \cdot \mathbf{E}_0](\mathbf{r}) = \int G_0(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}'(\mathbf{r}') \cdot \mathbf{E}_0\, d\mathbf{r}' \qquad (4.12)$$

where $F'(\mathbf{r}') \cdot \mathbf{E}_0$ is a polarization field surrounding sphere k which vanishes identically for $|\mathbf{r}' - \mathbf{R}_k| \leq a$. Hence, the right-hand side of (4.11) satisfies Laplace's equation and by symmetry it represents a field which is uniform for $|\mathbf{r}' - \mathbf{R}_k| \leq a$ and which we may put equal to

$$\int d\mathbf{R}_2 \left[\underset{\approx}{S}_{no}(k, 2) \underset{\approx}{B}(2) | 0) \cdot \mathbf{E}_0 \right](\mathbf{r}) = \frac{4\pi}{3\varepsilon_1} \mu \alpha' \mathbf{E}_0 \qquad \text{for} \quad |\mathbf{r} - \mathbf{R}_k| < a \qquad (4.13)$$

with a dimensionless coefficient μ. Adding (4.11) and (4.13) and making use of (4.6) and (4.7), we therefore find

$$\int d\mathbf{R}_2 \left[\underset{\approx}{S}(k, 2) \underset{\approx}{B}(2) | 0) \cdot \mathbf{E}_0 \right](\mathbf{r}) = \frac{4\pi}{3\varepsilon_1} (1 + \mu) \alpha' \mathbf{E}_0 \qquad \text{for} \quad |\mathbf{r} - \mathbf{R}_k| < a$$

$$(4.14)$$

We may now repeat the above argument in the iterated form of (4.1). For each pair of factors $\underset{\approx}{S}(j-1, j) \underset{\approx}{B}(j)$ we obtain upon integration over $\mathbf{R}_j$ a uniform field acting on the next inclusion. Hence we find

$$\int d\mathbf{R}_2 \left[\underset{\approx}{F}(1, 2) \underset{\approx}{B}(2) | 0) \right](\mathbf{r})$$

$$= \frac{4\pi}{3\varepsilon_1} (1 + \mu) \alpha' \left[1 - \frac{4\pi}{3\varepsilon_1} (1 + \mu) n\alpha' \right]^{-1} 1, \qquad \text{for} \quad |\mathbf{r} - \mathbf{R}_1| < a \qquad (4.15)$$

Finally, this yields, with use of (3.13) and (3.14),

$$n^2 \int d\mathbf{R} \, (0 | \underset{\approx}{B}(1) \underset{\approx}{F}(1, 2) \underset{\approx}{B}(2) | 0)$$

$$= \frac{4\pi}{3\varepsilon_1} (1 + \mu)(n\alpha')^2 \left[1 - \frac{4\pi}{3\varepsilon_1} (1 + \mu) n\alpha' \right]^{-1} 1 \qquad (4.16)$$

Together with (3.13), this yields a simple expression for the effective dielectric constant, which we shall discuss in the next section.

To conclude this section, we note that the definition (4.13) may be simplified by replacing the operator $\underset{\approx}{B}(2)$ by the single-particle operator $\underset{\approx}{M}(2)$, namely

$$\int d\mathbf{R}_2 \left[\underset{\approx}{S}_{no}(1, 2) \underset{\approx}{M}(2) | 0) \right](\mathbf{r}) = \frac{4\pi}{3\varepsilon_1} \mu \alpha 1 \qquad \text{for} \quad |\mathbf{r} - \mathbf{R}_1| < a \qquad (4.17)$$

since in both (4.13) and (4.17) a uniform applied field $\mathbf{E}_0$ first induces a dipole moment in inclusion 2.

5. EXACT EXPRESSION FOR THE EFFECTIVE DIELECTRIC CONSTANT

We may use the results obtained in the last sections to derive an exact expression for the effective dielectric constant in terms of the density n, the dipole polarizability α, and the coefficients λ and μ defined by (3.11) and (4.17). In the $\mathbf{q} \to 0$ limit the effective dielectric tensor defined by (2.22) becomes a scalar

$$\epsilon^*(0) = \epsilon^* \mathbf{1} \tag{5.1}$$

From (2.23), (3.13), and (4.16) we find the exact expression

$$\varepsilon^* = \varepsilon_1 + 4\pi n\alpha' \left[1 - \frac{4\pi}{3\varepsilon_1}(1+\mu)\,n\alpha' \right]^{-1} \tag{5.2}$$

By use of (3.14) this may also be written

$$\varepsilon^* = \varepsilon_1 + 4\pi n\alpha \left[1 - \frac{4\pi}{3\varepsilon_1}(1+\lambda+\mu)\,n\alpha \right]^{-1} \tag{5.3}$$

or equivalently

$$\varepsilon^* = \varepsilon_1 + 4\pi n\alpha'' \tag{5.4}$$

with the doubly dressed polarizability

$$\alpha'' = \alpha \left[1 - \frac{4\pi}{3\varepsilon_1}(1+\lambda+\mu)\,n\alpha \right]^{-1} \tag{5.5}$$

Alternatively, we may cast (5.3) in the Clausius–Mossotti form

$$\frac{\varepsilon^* - \varepsilon_1}{\varepsilon^* + 2\varepsilon_1} = \frac{4\pi}{3\varepsilon_1} n\alpha^* \tag{5.6}$$

with the effective polarizability

$$\alpha^* = \alpha \left[1 - \frac{4\pi}{3\varepsilon_1}(\lambda+\mu)\,n\alpha \right]^{-1} \tag{5.7}$$

In many cases α^* will be close to α and then the usual Clausius–Mossotti formula provides a good approximation to the effective dielectric constant. Inverting (5.6), we obtain

$$\frac{\varepsilon^* + 2\varepsilon_1}{\varepsilon^* - \varepsilon_1} = \frac{3\varepsilon_1}{4\pi n\alpha} - \lambda - \mu \tag{5.8}$$

which is related to Wertheim's[12] Eq. (26).

The above equations are exact. The remaining task is to evaluate the coefficients λ and μ, which can be achieved only in approximation. The Clausius–Mossotti form (5.6) together with (5.7) provides a convenient starting point for comparison with results obtained in the literature.

6. COEFFICIENTS λ AND μ

In this section we consider the approximate calculation of the coefficients λ and μ defined by (3.11) and (4.17). For both coefficients we may write a cluster expansion

$$\lambda = \sum_{s=2}^{\infty} \lambda_s, \qquad \mu = \sum_{s=2}^{\infty} \mu_s \tag{6.1}$$

corresponding to (3.5) and (4.2). We choose the origin in the center of inclusion 1 and for each of the connected partitions occurring in (3.6) and (4.4) we define two tensors by the equations

$$\mathsf{F}_{11}(C) = \frac{3\varepsilon_1}{4\pi\alpha} \left[\underset{\approx}{\mathsf{N}}_{11}(C) \, \underset{\approx}{\mathsf{M}}(1) \,|\, 0 \right](\mathbf{0})$$

$$\mathsf{F}_{12}(C') = \frac{3\varepsilon_1}{4\pi\alpha} \left[\underset{\approx}{\mathsf{N}}_{12}(C') \, \underset{\approx}{\mathsf{M}}(2) \,|\, 0 \right](\mathbf{0}) \tag{6.2}$$

where C' corresponds to C by a reordering of labels as in (4.5). It then follows from (3.7) and (3.11) that the two-particle coefficient λ_2 is given explicitly by

$$\lambda_2 \mathbf{1} = \int d\mathbf{R}_2 \, g(1, 2) \, \mathsf{F}_{11}(1, 2) \tag{6.3}$$

Similarly, we find from (3.8) and (3.11) for the three-particle coefficient

$$\lambda_3 = \lambda_3(1, 2, 3) + \lambda_3(1, 2 \,|\, 1, 3) \tag{6.4}$$

with the two contributions

$$\lambda_3(1, 2, 3)\mathbf{1} = n \int d\mathbf{R}_2 \, d\mathbf{R}_3 \, k(1, 2, 3) \, \mathsf{F}_{11}(1, 2, 3)$$

$$\lambda_3(1, 2 \,|\, 1, 3)\mathbf{1} = n \int d\mathbf{R}_2 \, d\mathbf{R}_3 \, k(1, 2 \,|\, 1, 3) \, \mathsf{F}_{11}(1, 2 \,|\, 1, 3) \tag{6.5}$$

We find from (4.3), (4.6), (4.7), and (4.17) for the two-particle coefficient μ_2

$$\mu_2 \mathbf{1} = \int d\mathbf{R}_2 \, g(1, 2) \left[\mathsf{F}_{12}(1, 2) - \frac{3\varepsilon_1}{4\pi} \, \mathsf{G}_0(\mathbf{R}_2) \right] \tag{6.6}$$

Here we have used the explicit form of the Green function defined by (2.15) to show that the last term in (4.3) does not contribute in the nonoverlap region due to angular integration. From (4.5), (4.17), and (6.2) we obtain a sum of five contributions for the coefficient μ_3

$$\mu_3 = \mu_3(1, 2, 3) + \mu_3(1, 2 \,|\, 2, 3) + \mu_3(1, 3, 2)$$
$$+ \mu_3(1, 3 \,|\, 1, 2) + \mu_3(1, 3 \,|\, 3, 2) \qquad (6.7)$$

where explicitly

$$\mu_3(1, 2, 3)\mathbf{1} = n \int d\mathbf{R}_2\, d\mathbf{R}_3\, k(1, 2, 3)\, \mathsf{F}_{12}(1, 2, 3)$$

$$\mu_3(1, 2 \,|\, 2, 3)\mathbf{1} = n \int d\mathbf{R}_2\, d\mathbf{R}_3\, k(1, 2 \,|\, 2, 3)\, \mathsf{F}_{12}(1, 2 \,|\, 2, 3)$$

$$\mu_3(1, 3, 2)\mathbf{1} = n \int d\mathbf{R}_2\, d\mathbf{R}_3\, k(1, 2, 3)\, \mathsf{F}_{12}(1, 3, 2) \qquad (6.8)$$

$$\mu_3(1, 3 \,|\, 1, 2)\mathbf{1} = n \int d\mathbf{R}_2\, d\mathbf{R}_3\, k(1, 3 \,|\, 1, 2)\, \mathsf{F}_{12}(1, 3 \,|\, 1, 2)$$

$$\mu_3(1, 3 \,|\, 3, 2)\mathbf{1} = n \int d\mathbf{R}_2\, d\mathbf{R}_3\, k(1, 3 \,|\, 2, 3)\, \mathsf{F}_{12}(1, 3 \,|\, 3, 2)$$

The two coefficients μ_3 $(1, 2, 3)$ and $\mu_3(1, 3, 2)$ differ not just by an interchange of labels, since an ordering is implied in the definition of the nodal connectors $\underset{\sim}{N}_{12}(C)$ which enter the definition (6.2) of the tensors $\underset{\approx}{F}_{12}$.

We presume that the low-order contributions $\lambda_2 + \lambda_3$ and $\mu_2 + \mu_3$ yield a good approximation to the coefficients λ and μ. In the following we first give a more detailed description of the nodal connectors entering the calculation. Then we show on the example of the point dipole model how the coefficients $\lambda_2,..., \mu_3$ may be calculated.

7. NODAL CONNECTORS

In this section we describe the nodal connectors entering the calculation of the low-order coefficients $\lambda_2,..., \mu_3$. Consider first the nodal connector $\underset{\sim}{N}_{11}(1, 2)$. It is associated with the sum of scattering sequences $[121] + [12121] + \cdots$, describing repeated scatterings between the two inclusions $1, 2$, with the condition that the first and last scatterer be 1. Explicitly the connector is

$$\underset{\sim}{N}_{11}(1, 2) = \theta(1)\, \underset{\approx}{G}_0 \underset{\approx}{M}(2)\, \underset{\approx}{G}_0 \theta(1)$$
$$+ \theta(1)\, \underset{\approx}{G}_0 \underset{\approx}{M}(2)\, \underset{\approx}{G}_0 \underset{\approx}{M}(1)\, \underset{\approx}{G}_0 \underset{\approx}{M}(2)\, \underset{\approx}{G}_0 \theta(1) + \cdots$$
$$= \theta(1)\, \underset{\approx}{G}_0 \underset{\approx}{M}(2)[\underset{\approx}{I} - \underset{\approx}{G}_0 \underset{\approx}{M}(1)\, \underset{\approx}{G}_0 \underset{\approx}{M}(2)]^{-1}\, \underset{\approx}{G}_0 \theta(1) \qquad (7.1)$$

where the θ operator is defined by

$$\theta(1; \mathbf{r}, \mathbf{r}') = \theta(a - |\mathbf{r} - \mathbf{R}_1|)\,\delta(\mathbf{r} - \mathbf{r}') \tag{7.2}$$

It localizes the field points $\mathbf{r}$ and $\mathbf{r}'$ to the volume of inclusion 1.

Similarly, the connector $\underset{\approx}{\mathrm{N}}_{12}(1, 2)$ corresponds to the sum of scattering sequences $[12] + [1212] + \cdots$, and is given explicitly by

$$\underset{\approx}{\mathrm{N}}_{12}(1, 2) = \theta(1)\,\underset{\approx}{\mathrm{G}}_0\,\theta(2) + \theta(1)\,\underset{\approx}{\mathrm{G}}_0\,\underset{\approx}{\mathrm{M}}(2)\,\underset{\approx}{\mathrm{G}}_0\,\underset{\approx}{\mathrm{M}}(1)\,\underset{\approx}{\mathrm{G}}_0\,\theta(2) + \cdots$$

$$= \theta(1)\,\underset{\approx}{\mathrm{G}}_0[\underset{\approx}{\mathrm{I}} - \underset{\approx}{\mathrm{M}}(2)\,\underset{\approx}{\mathrm{G}}_0\,\underset{\approx}{\mathrm{M}}(1)\,\underset{\approx}{\mathrm{G}}_0]^{-1}\,\theta(2) \tag{7.3}$$

Next we consider the three-body connectors. Some of these have a slash indicating a nodal point. Such connectors can be decomposed into a product of two-body connectors separated by a one-body scattering operator, namely

$$\underset{\approx}{\mathrm{N}}_{11}(1, 2\,|\,1, 3) = \underset{\approx}{\mathrm{N}}_{11}(1, 2)\,\underset{\approx}{\mathrm{M}}(1)\,\underset{\approx}{\mathrm{N}}_{11}(1, 3)$$

$$\underset{\approx}{\mathrm{N}}_{12}(1, 2\,|\,2, 3) = \underset{\approx}{\mathrm{N}}_{12}(1, 2)\,\underset{\approx}{\mathrm{M}}(2)\,\underset{\approx}{\mathrm{N}}_{22}(2, 3)$$

$$\underset{\approx}{\mathrm{N}}_{12}(1, 3\,|\,1, 2) = \underset{\approx}{\mathrm{N}}_{11}(1, 3)\,\underset{\approx}{\mathrm{M}}(1)\,\underset{\approx}{\mathrm{N}}_{12}(1, 2)$$

$$\underset{\approx}{\mathrm{N}}_{12}(1, 3\,|\,2, 3) = \underset{\approx}{\mathrm{N}}_{13}(1, 3)\,\underset{\approx}{\mathrm{M}}(3)\,\underset{\approx}{\mathrm{N}}_{32}(2, 3) \tag{7.4}$$

We introduce a short-hand notation which will be helpful in the study of the remaining three-body connectors. We indicate the pairs $(1, 2)$, $(2, 3)$, and $(3, 1)$ by the letters A, B, and C, respectively. Then the right-hand side of (7.4) is fully specified by the following abbreviated notation:

$$\underset{\approx}{\mathrm{N}}_{11}(1, 2\,|\,1, 3) = [AC]_{11}, \qquad \underset{\approx}{\mathrm{N}}_{12}(1, 2\,|\,2, 3) = [AB]_{12}$$

$$\underset{\approx}{\mathrm{N}}_{12}(1, 3\,|\,1, 2) = [CA]_{12}, \qquad \underset{\approx}{\mathrm{N}}_{12}(1, 3\,|\,2, 3) = [CB]_{12} \tag{7.5}$$

In each case the two letters specify both the two nodal connectors and the intermediate one-body scattering operator. The subscripts specify the first and last subscript of each product.

The nodal connectors $\underset{\approx}{\mathrm{N}}_{11}(1, 2, 3)$, $\underset{\approx}{\mathrm{N}}_{12}(1, 2, 3)$, and $\underset{\approx}{\mathrm{N}}_{12}(1, 3, 2)$ correspond to scattering sequences without nodal points. In particular, the connector $\underset{\approx}{\mathrm{N}}_{11}(1, 2, 3)$ corresponds to the sum of scattering sequences $[1231] + [12321] + \cdots$, the conditions being that, reading from left to right, the first and last scatterer be 1, that the scattering sequence contain no nodal point, and that the labels $1, 2, 3$ must first appear in this order. Similarly, the connector $\underset{\approx}{\mathrm{N}}_{12}(1, 2, 3)$ corresponds to the sum of scattering sequences $[12312] + [121312] + \cdots$, with the same conditions as before, except that now the first scatterer must be 1 and the last scatterer be 2.

Finally, the connector $\underset{\approx}{N}_{12}(1, 3, 2)$ corresponds to the sum of scattering sequences $[13212] + [131232] + \cdots$, with the same conditions as before, except that the first scatterer must be 1, the last scatterer must be 2, and the labels 1, 3, 2 must first appear in this order.

The nodal connectors $\underset{\approx}{N}_{11}(1, 2, 3)$, $\underset{\approx}{N}_{12}(1, 2, 3)$, and $\underset{\approx}{N}_{12}(1, 3, 2)$ may be evaluated explicitly by expressing them in terms of two-body connectors. This corresponds to a resummation of scattering sequences similar to the binary collision expansion familiar from the kinetic theory of gases.[26,27] Employing the abbreviated notation introduced in (7.5), we may write the connector $\underset{\approx}{N}_{11}(1, 2, 3)$ in the form

$$\underset{\approx}{N}_{11}(1, 2, 3) = [ABA + ABC + ACA + ABAC + ABCA$$
$$+ ACAC + ACBA + ACBC + \cdots]_{11} \qquad (7.6)$$

The complete sum may be characterized as the sum of all words formed from the letters A, B, C with the conditions that each word contain at least three letters, that no two successive letters are the same, that the first letter be A, and the last one be A or C. Similarly, the connector $\underset{\approx}{N}_{12}(1, 2, 3)$ is given by

$$\underset{\approx}{N}_{12}(1, 2, 3) = [ABA + ACA + ACB + ABAB + ABCA$$
$$+ ABCB + ACAB + ACBA + \cdots]_{12} \qquad (7.7)$$

The complete sum may be characterized as the sum of all words formed from the letter A, B, C with the conditions that each word contain at least three letters, that no two successive letters are the same, that the first letter be A, and the last one be A or B. Similarly the connector $\underset{\approx}{N}_{12}(1, 3, 2)$ is given by

$$\underset{\approx}{N}_{12}(1, 3, 2) = [CAB + CBA + CABA + CACA + CACB$$
$$+ CBAB + CBCA + CBCB + \cdots]_{12} \qquad (7.8)$$

The complete sum may be characterized as the sum of all words formed from the letters A, B, C with the conditions that each word contain at least three letters, that no two successive letters are the same, that the first letter be C, and the last one be A or B.

We may find more concise expressions for the connectors in (7.6)–(7.8) by use of a matrix formalism. We arrange the two-body nodal connectors and the one-body scattering operators in 6×6 matrices. We consider first the matrix operator

$$\underset{\approx}{\mathscr{N}} = \begin{pmatrix} \underset{\approx}{N}(1, 2) & 0 & 0 \\ 0 & \underset{\approx}{N}(2, 3) & 0 \\ 0 & 0 & \underset{\approx}{N}(3, 1) \end{pmatrix} \qquad (7.9)$$

where the first diagonal element is a short-hand notation for the 2×2 matrix

$$\underset{\approx}{N}(1, 2) = \begin{pmatrix} \underset{\approx}{N}_{11}(1, 2) & \underset{\approx}{N}_{12}(1, 2) \\ \underset{\approx}{N}_{21}(1, 2) & \underset{\approx}{N}_{22}(1, 2) \end{pmatrix} \tag{7.10}$$

and the other two are found by cyclic permutation of the labels $(1, 2, 3)$. Further, we define the matrix

$$\underset{\approx}{\mathscr{M}} = \begin{pmatrix} 0 & \underset{\approx}{M}^{-}(2) & \underset{\approx}{M}^{+}(1) \\ \underset{\approx}{M}^{+}(2) & 0 & \underset{\approx}{M}^{-}(3) \\ \underset{\approx}{M}^{-}(1) & \underset{\approx}{M}^{+}(3) & 0 \end{pmatrix} \tag{7.11}$$

with the 2×2 matrices

$$\underset{\approx}{M}^{+}(i) = \begin{pmatrix} 0 & \underset{\approx}{M}(i) \\ 0 & 0 \end{pmatrix}, \qquad \underset{\approx}{M}^{-}(i) = \begin{pmatrix} 0 & 0 \\ \underset{\approx}{M}^{-}(i) & 0 \end{pmatrix} \tag{7.12}$$

Now one has, for example,

$$\underset{\approx}{N}(1, 2) \underset{\approx}{M}^{-}(2) \underset{\approx}{N}(2, 3)$$

$$= \begin{pmatrix} \underset{\approx}{N}_{12}(1, 2) \underset{\approx}{M}(2) \underset{\approx}{N}_{22}(2, 3) & \underset{\approx}{N}_{12}(1, 2) \underset{\approx}{M}(2) \underset{\approx}{N}_{23}(2, 3) \\ \underset{\approx}{N}_{22}(1, 2) \underset{\approx}{M}(2) \underset{\approx}{N}_{22}(2, 3) & \underset{\approx}{N}_{22}(1, 2) \underset{\approx}{M}(2) \underset{\approx}{N}_{23}(2, 3) \end{pmatrix} \tag{7.13}$$

Each of the matrices $\underset{\approx}{\mathscr{N}}, \underset{\approx}{\mathscr{M}}$ has 36 elements which may be labeled as $[P\sigma, P'\sigma']$, where P and P' denote one of the three pairs $(1, 2)$, $(2, 3)$, and $(3, 1)$, and the indices σ and σ' take the values $\pm$.

The matrix

$$\underset{\approx}{\mathscr{Z}} = \underset{\approx}{\mathscr{N}} \underset{\approx}{\mathscr{M}} \underset{\approx}{\mathscr{N}} \underset{\approx}{\mathscr{M}} \underset{\approx}{\mathscr{N}} [\underset{\approx}{I} - \underset{\approx}{\mathscr{M}} \underset{\approx}{\mathscr{N}}]^{-1} \tag{7.14}$$

comprises the sum of all binary collision sequences starting and ending with one of the 12 two-body nodal connectors $\underset{\approx}{N}_{kl}(i, j)$, consisting of an alternation of one-body scattering operators and two-body nodal connectors, with the conditions that no two successive connectors are the same and that the sequence contain at least two one-body scattering operators.

The nodal connector $\underset{\approx}{N}_{11}(1, 2, 3)$ may now be characterized as the sum of matrix elements,

$$\underset{\approx}{N}_{11}(1, 2, 3) = \underset{\approx}{\mathscr{Z}}[(1, 2) + ; (1, 2) +] + \underset{\approx}{\mathscr{Z}}[(1, 2) + ; (3, 1) -] \tag{7.15}$$

Similarly, the nodal connector $\underset{\approx}{N}_{12}(1, 2, 3)$ is given by

$$\underset{\approx}{N}_{12}(1, 2, 3) = \underset{\approx}{\mathscr{Z}}[(1, 2) + ; (1, 2) -] + \underset{\approx}{\mathscr{Z}}[(1, 2) + ; (2, 3) +] \tag{7.16}$$

The nodal connector $\underset{\approx}{N}_{13}(1, 2, 3)$ is given by

$$\underset{\approx}{N}_{13}(1, 2, 3) = \underset{\approx}{\mathscr{L}}[(1, 2) + ; (3, 1) +] + \underset{\approx}{\mathscr{L}}[(1, 2) + ; (2, 3) -] \quad (7.17)$$

One obtains the nodal connector $\underset{\approx}{N}_{12}(1, 3, 2)$ by interchanging the labels 2 and 3 in (7.17).

Clearly the above procedure may be extended to nodal connectors containing more than three labels. All the higher order nodal connectors may be expressed in terms of two-body connectors by use of the binary collision expansion.

8. POLARIZABLE POINT DIPOLE MODEL

The simplest model to be studied is a system of spherical particles with a polarizable point dipole at the center. Although strictly speaking this does not fit into the scheme developed in Section 2, the subsequent developments are valid nonetheless with the simple one-body T operator

$$\underset{\approx}{M}(1) \equiv M(1; \mathbf{r}, \mathbf{r}') = \alpha 1 \delta(\mathbf{r} - \mathbf{R}_1) \, \delta(\mathbf{r}' - \mathbf{R}_1) \quad (8.1)$$

The two-body nodal connectors given by (7.1) and (7.3) may be found explicitly for this model. For the nodal connector $\underset{\approx}{N}_{11}(1, 2)$ we find

$$\underset{\approx}{N}_{11}(1, 2; \mathbf{r}, \mathbf{r}') = \theta(a - |\mathbf{r} - \mathbf{R}_1|) \, G_0(\mathbf{r} - \mathbf{R}_2)$$

$$\times \alpha \left[\frac{\varepsilon_1^2 R^6}{\varepsilon_1^2 R^6 - 4\alpha^2} \hat{R}\hat{R} + \frac{\varepsilon_1^2 R^6}{\varepsilon_1^2 R^6 - \alpha^2} (1 - \hat{R}\hat{R}) \right]$$

$$\times G_0(\mathbf{r}' - \mathbf{R}_2) \, \theta(a - |\mathbf{r}' - \mathbf{R}_1|) \quad (8.2)$$

where $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$. Similarly, we find for the nodal connector $\underset{\approx}{N}_{12}(1, 2)$

$$\underset{\approx}{N}_{12}(1, 2; \mathbf{r}, \mathbf{r}') = \theta(a - |\mathbf{r} - \mathbf{R}_1|) \left\{ G_0(\mathbf{r} - \mathbf{r}') \right.$$

$$+ G_0(\mathbf{r} - \mathbf{R}_2)\alpha \left[\frac{2\alpha\varepsilon_1 R^3}{\varepsilon_1^2 R^6 - 4\alpha^2} \hat{R}\hat{R} \right.$$

$$\left. - \frac{\alpha\varepsilon_1 R^3}{\varepsilon_1^2 R^6 - \alpha^2} (1 - \hat{R}\hat{R}) \right] G_0(\mathbf{r}' - \mathbf{R}_1) \Big\} \, \theta(a - |\mathbf{r}' - \mathbf{R}_2|) \quad (8.3)$$

The three-body connectors given by (7.15)–(7.17) may also be found explicitly. We present the complete expressions in a separate article.

With the aid of the 2-body and 3-body nodal connectors, we may evaluate the coefficients $\lambda_2,...,\mu_3$ as shown in Section 6. In particular we find from (6.2) and (8.2)

$$\mathsf{F}_{11}(1,2) = \frac{3\varepsilon_1\alpha}{4\pi}\left[\frac{4}{\varepsilon_1^2 R^6 - 4\alpha^2}\hat{R}\hat{R} + \frac{1}{\varepsilon_1^2 R^6 - \alpha^2}(1-\hat{R}\hat{R})\right] \qquad (8.4)$$

and from (6.2) and (8.3)

$$\mathsf{F}_{12}(1,2) = \frac{3\varepsilon_1}{4\pi}\mathsf{G}_0(\mathbf{R}) + \frac{3\alpha^2}{4\pi R^3}\left[\frac{8}{\varepsilon_1^2 R^6 - 4\alpha^2}\hat{R}\hat{R} - \frac{1}{\varepsilon_1^2 R^6 - \alpha^2}(1-\hat{R}\hat{R})\right] \qquad (8.5)$$

Hence we obtain by use of (6.3) and (6.6)

$$\lambda_2 + \mu_2 = 6\varepsilon_1\int_{2a}^{\infty}dR\, R^2 g(R)\frac{\alpha}{(\varepsilon_1 R^3 - 2\alpha)(\varepsilon_1 R^3 + \alpha)} \qquad (8.6)$$

If this expression is expanded in powers of α, then the lowest order term is

$$\lambda_2^{(1)} + \mu_2^{(1)} = \frac{6\alpha}{\varepsilon_1}\int_{2a}^{\infty}dR\,\frac{g(R)}{R^4} \qquad (8.7)$$

We shall consider only the corresponding lowest order contribution to the 3-body terms λ_3, μ_3. It is easily seen that the only contribution of order α comes from the term $\mu_3(1,3\,|\,3,2)$ in (6.8). It yields

$$\mu_3^{(1)}\mathbf{1} = \frac{3\varepsilon_1}{4\pi}n\alpha\int d\mathbf{R}_2\, d\mathbf{R}_3\, k(1,3\,|\,2,3)\,\mathsf{G}_0(\mathbf{R}_{13})\cdot\mathsf{G}_0(\mathbf{R}_{32}) \qquad (8.8)$$

or equivalently

$$\mu_3^{(1)} = \frac{3}{2\pi\varepsilon_1}n\alpha\int d\mathbf{R}_2\, d\mathbf{R}_3\,[g(1,2,3) - g(1,3)\,g(2,3)]\frac{P_2(\cos\theta)}{R_{13}^3 R_{23}^3} \qquad (8.9)$$

where θ is the angle between $\mathbf{R}_{13}$ and $\mathbf{R}_{23}$ and P_2 is the second Legendre polynomial.

Conventionally, one writes the renormalized polarizability defined by (5.6) in the form

$$\alpha^* = \alpha[1 + S(n,\alpha)] \qquad (8.10)$$

where $S(n,\alpha)$ gives the deviations from the Clausius–Mossotti formula. An expansion of $S(n,\alpha)$ in powers of α starts with α^2 and one denotes this first term by S_2:

$$S(n,\alpha) = S_2 + O(\alpha^3) \qquad (8.11)$$

Expanding the denominator in (5.7) in powers of α, we find

$$S_2 = \frac{4\pi}{3\varepsilon_1} (\lambda_2^{(1)} + \mu_2^{(1)} + \mu_3^{(1)}) \, n\alpha \tag{8.12}$$

Substituting from (8.7) and (8.9), we recover the result of Kirkwood[6] and Yvon.[7] It was pointed out by Nijboer[28] that the two-particle contributions to the function $S(n, \alpha)$, as given by its Kirkwood–Yvon expansion in powers of α, may be summed exactly and expressed in terms of the radial distribution function $g(R)$. The sum is given by

$$S^{(2)}(n, \alpha) = \frac{4\pi}{3\varepsilon_1} (\lambda_2 + \mu_2) \, n\alpha$$

$$= 8\pi n\alpha^2 \int_{2a}^{\infty} dR \, g(R) \frac{R^2}{(\varepsilon_1 R^3 - 2\alpha)(\varepsilon_1 R^3 + \alpha)} \tag{8.13}$$

in agreement with (5.7) and (8.6).

   Alternatively, one may expand $S(n, \alpha))$ in powers of the density. This yields the so-called dielectric virial expansion[11,29,30]

$$S(n, \alpha) = Bn + Cn^2 + \cdots \tag{8.14}$$

It is clear that only two-particle terms can contribute to the second virial coefficient B. From (8.6) we find

$$B = 8\pi\alpha^2 \int_{2a}^{\infty} dR \, e^{-\beta\phi(R)} \frac{R^2}{(\varepsilon_1 R^3 - 2\alpha)(\varepsilon_1 R^3 + \alpha)} \tag{8.15}$$

where $\phi(R)$ is the pair interaction potential. The above result was found by Buckingham and Pople.[11] It was derived by Isihara[31,32] from the virial expansion of the pressure. Isihara's derivation contained an error which was corrected by Bose et al.[33]

   In this section we have discussed the relation of our theory to the expansion of Kirkwood–Yvon and the dielectric virial expansion for the polarizable point dipole model. We wish to emphasize that not only is our theory more general in that it includes all higher multipoles, there is an important difference with the Kirkwood–Yvon theory even for the polarizable point dipole model. The higher order correction terms in the KY theory are expressed as integrals with long-range integrands which are to be calculated for a volume of spherical shape. In contrast, our cluster integrals have short-range integrands and are absolutely convergent. The reason for this difference was explained in some detail in ref. 15 for the unrenormalized cluster expansion.

9. CONCLUSION

We have derived an exact expression for the correction S to the Clausius–Mossotti formula, as defined in (1.1). The expression is given by (1.2), where the coefficients λ and μ are defined by (3.11) and (4.17). Each of these coefficients has a cluster expansion of the form (6.1), where the coefficients λ_s and μ_s may in principle be found by averaging the result of an s-body problem over an s-body correlation function. In practice, we cannot expect to go much beyond $s = 2, 3$. But it is clear that even a calculation of $\lambda_2, ..., \mu_3$ goes far beyond the results (8.12)–(8.14). This is of no importance for real liquids, since for real liquids the product $n\alpha$ is sufficiently small that the Kirkwood–Yvon expression (8.12) should be a good approximation. Experimental deviations from this result are due to additional quantum mechanial effects,[9,10] However, in computer simulations we may study the idealized system of polarizable point dipoles with values of the parameter $n\alpha$ of order unity. It would be of interest to perform such simulations and obtain values of the function $S(n, \alpha)$. These could then be compared with theoretical values, as given by (1.2) with λ and μ replaced by the first few terms of their cluster expansion. In future work we hope to study the two- and three-body coefficients $\lambda_2, ..., \mu_3$ in more detail. In addition, we may calculate selected contributions to the higher order cluster integrals, for example, the ring diagrams. These are known to be important for the rate constant of diffusion-controlled reactions.[34]

In our opinion, for a reliable prediction of the dielectric constant at high density one cannot avoid dealing with at least the two- and three-body cluster integrals. It has been suggested for the density fluctuation expansion of Bedeaux and Mazur[21] that already a two-body integral might yield good results.[24] However, in this rearranged expansion the two-body integral includes the nonphysical overlap region, where the integrand may be chosen at will. The contribution from the nonphysical region cancels again in higher order of the expansion. The mechanism is explained in some detail by Geigenmüller and Mazur[24] for the Kirkwood–Yvon term S_2. It is suggested that the nonphysical contributions may be chosen such as to improve the convergence of the expansion. However, any particular choice cannot be justified without a detailed investigation of the higher order terms. It seems simpler not to introduce the nonphysical contributions at all and study the cluster integrals directly.

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