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Three-Body Problem in the Theory of the Dielectric Constant

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We study the corrections to the Clausius–Mossotti formula for the dielectric constant of a disordered system of polarizable spherical particles. Previously we have derived an exact cluster expansion for the correction terms. Here we study the three-body correction in detail. We derive an explicit expression for the integrand of the three-body cluster integral for a system of polarizable point dipoles.

KEY WORDS: Dielectric constant; cluster expansion; three-body problem.

1. INTRODUCTION

In this paper we study nonpolar dielectrics consisting of a disordered array of identical spherical particles immersed in a uniform background with dielectric constant ε_1. The particles may be inclusions with a spherically symmetric dielectric profile, or they may be spheres with a polarizable point dipole at their center. In a previous article,[(1)] referred to as I, we have shown, following earlier work by Felderhof *et al.*,[(2–4)] that the effective dielectric constant ε^* of such a system may be written in the form

$$\frac{\varepsilon^* - \varepsilon_1}{\varepsilon^* + 2\varepsilon_1} = \frac{4\pi n\alpha/3\varepsilon_1}{1 - (4\pi n\alpha/3\varepsilon_1)(\lambda + \mu)} \tag{1.1}$$

where n is the number density and α is the dipole polarizability of a particle. The denominator on the right-hand side represents the correction

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to the Clausius–Mossotti formula. In I we have derived exact cluster expansions for the dimensionless coefficients λ and μ of the form

$$\lambda = \sum_{s=2}^{\infty} \lambda_s, \qquad \mu = \sum_{s=2}^{\infty} \mu_s \tag{1.2}$$

where λ_s and μ_s are given by absolutely convergent cluster integrals over the solution of a dielectric problem involving s spheres. In this paper we study the three-body terms λ_3 and μ_3 in detail.

In Sections 2–4 we describe the model and summarize our previous results. In Section 5 we give detailed expressions for the so-called nodal connectors appearing in the two- and three-body cluster integrals. In Section 6 we derive the explicit expressions for the integrands of the three-body cluster integrals for the case of the polarizable point dipole model. The paper is concluded with a discussion.

2. MICROSCOPIC DESCRIPTION

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 are characterized by a spherically symmetric dielectric constant. For a fixed configuration of inclusions in which they are centered at $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N$, the dielectric constant at a field point $\mathbf{r}$ is then

$$\varepsilon(1,\ldots, N; \mathbf{r}) = \begin{cases} \varepsilon_1, & |\mathbf{r} - \mathbf{R}_j| > a \\ \varepsilon(|\mathbf{r} - \mathbf{R}_j|), & |\mathbf{r} - \mathbf{R}_j| < a \end{cases} \qquad (j = 1,\ldots, N) \tag{2.1}$$

The basic equations for the electric field $\mathbf{E}$ and the dielectric displacement $\mathbf{D}$ are Maxwell's electrostatic equations

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

where $\rho_0 = \rho_0(\mathbf{r})$ is a fixed charge distribution, independent of the configuration of the inclusions. The applied field $\mathbf{E}_0(\mathbf{r})$ is the solution of Eqs. (2.2) with ε a uniform dielectric constant ε_1. We define the induced polarization, relative to the medium in the absence of inclusions, via the relation

$$\mathbf{D} = \varepsilon_1 \mathbf{E} + 4\pi\mathbf{P} \tag{2.3}$$

We define the scattering operator $\mathsf{M}(1)$ for a single inclusion, isolated in the uniform medium and centered at $\mathbf{R}_1$, from the equation

$$\mathbf{P}(\mathbf{r}) = \int \mathsf{M}(\mathbf{R}_1; \mathbf{r}, \mathbf{r}') \cdot \mathbf{E}_0(\mathbf{r}')\, d\mathbf{r}' \tag{2.4}$$

where $\mathbf{E}_0(\mathbf{r})$ is an arbitrary applied field. We note that the operator $\mathsf{M}(1)$ is localized about $\mathbf{R}_1$ in the following sense:

$$M_{jk}(1; \mathbf{r}, \mathbf{r}') = 0 \qquad \text{if} \quad |\mathbf{r} - \mathbf{R}_1| > a \quad \text{or} \quad |\mathbf{r}' - \mathbf{R}_1| > a \tag{2.5}$$

It can be shown that the kernel is symmetric,

$$M_{jk}(1; \mathbf{r}, \mathbf{r}') = M_{kj}(1; \mathbf{r}', \mathbf{r}) \tag{2.6}$$

The localization property (2.5) follows from the fact that for a single inclusion the induced polarization is nonvanishing only within a sphere of radius a about $\mathbf{R}_1$, and from the symmetry (2.6). The dipole polarization of the inclusion is given by

$$\alpha \mathsf{1} = \iint \mathsf{M}(1; \mathbf{r}, \mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' = (0 | \mathsf{M}(1) | 0) \tag{2.7}$$

where the second equality defines a useful shorthand notation.

It is often convenient to consider a simplified model of polarizable point dipoles. In this model the dielectric constant is ε_1 everywhere, but each inclusion has a polarizable point dipole with polarizability α at its center. In this case the induced polarization is defined by

$$\mathbf{P}(\mathbf{r}) = \sum_{j=1}^{N} \mathbf{p}_j\, \delta(\mathbf{r} - \mathbf{R}_j) \tag{2.8}$$

where $\mathbf{p}_j$ is the dipole moment at the center of inclusion j, and the dielectric displacement $\mathbf{D}$ is defined by (2.3). The scattering operator for a single inclusion is given by

$$\mathsf{M}(1; \mathbf{r}, \mathbf{r}') = \alpha \mathsf{1}\; \delta(\mathbf{r} - \mathbf{R}_1)\, \delta(\mathbf{r}' - \mathbf{R}_1) \tag{2.9}$$

For N inclusions the dipole moment $\mathbf{p}_j$ is proportional to the field acting at $\mathbf{R}_j$, so that the N dipole moments are given by the set of coupled equations

$$\mathbf{p}_j = \alpha \left[\mathbf{E}_0(\mathbf{R}_j) + \sum_{k \neq j} \mathsf{T}_{jk} \cdot \mathbf{p}_k \right], \qquad j = 1, \ldots, N \tag{2.10}$$

where $\mathsf{T}_{jk} = \mathsf{T}(\mathbf{R}_j - \mathbf{R}_k)$ is the dipole tensor defined from the tensor field

$$\mathsf{T}(\mathbf{r}) = \frac{-\mathsf{1} + 3\hat{r}\hat{r}}{\varepsilon_1 r^3} \tag{2.11}$$

Our explicit calculation in this paper will be limited to the point dipole model.

3. EFFECTIVE DIELECTRIC CONSTANT

In this section we recall the definition of the effective dielectric constant ε^* of a macroscopically large system of randomly distributed inclusions. Moreover, we recall the exact expressions for the coefficients λ and μ occurring in (1.1).

We describe the disordered system of inclusions by a distribution function $W(1,..., N)$. The probability distribution is assumed normalized to unity and symmetric in the labels $1,..., N$. The partial distribution functions are defined by

$$n(1,..., s)=\frac{N!}{(N-s)!}\int\cdots\int d\mathbf{R}_{s+1}\cdots d\mathbf{R}_N\, W(1,..., N) \tag{3.1}$$

We assume that on average the inclusions are distributed uniformly and isotropically in a volume Ω with density $n=N/\Omega$. In our final expressions we take the thermodynamic limit $N\to\infty$, $\Omega\to\infty$ at constant $n=N/\Omega$.

Averaging over the probability distribution $W(1,..., N)$, we obtain the average polarization $\langle\mathbf{P}\rangle$ and the average electric field $\langle\mathbf{E}\rangle$. These average fields vary only on a length scale large compared to the average distance between inclusions. Eliminating the applied field $\mathbf{E}_0(\mathbf{r})$, we find that the averages are related by

$$\langle\mathbf{P}(\mathbf{r})\rangle=\int \mathsf{X}(\mathbf{r},\mathbf{r}')\cdot\langle\mathbf{E}(\mathbf{r}')\rangle\, d\mathbf{r}' \tag{3.2}$$

with a linear susceptibility kernel $\mathsf{X}(\mathbf{r},\mathbf{r}')$. In the bulk of the system this kernel becomes translationally invariant in the thermodynamic limit, and dependent only on the difference $\mathbf{r}-\mathbf{r}'$. For a macroscopic field $\langle\mathbf{E}(\mathbf{r})\rangle$ which varies slowly over the range of the kernel we may then replace (3.2) by the local relationship

$$\langle\mathbf{P}\rangle=\chi^*\langle\mathbf{E}\rangle \tag{3.3}$$

where the effective susceptibility χ^* is given by the integral of the susceptibility kernel $\mathsf{X}(\mathbf{r}-\mathbf{r}')$. The effective dielectric constant is given by

$$\varepsilon^*=\varepsilon_1+4\pi\chi^* \tag{3.4}$$

In I we have shown that ε^* may be expressed exactly by a generalization of the Clausius–Mossotti formula, as given by (1.1), with dimensionless coefficients λ and μ which each may be expressed in terms of a cluster expansion, as written in (1.2). The coefficient λ is given by

$$\lambda=\frac{\varepsilon_1}{4\pi n\alpha^2}\mathrm{Tr}(0\,|\,\mathsf{M}(1)\,\mathsf{S}(1)\,\mathsf{M}(1)\,|\,0) \tag{3.5}$$

where we have used the notation of (2.7) and the trace is taken with respect to the Cartesian components of the tensor. The reaction field operator S(1) is given by the cluster expansion[1]

$$\mathsf{S}(1) = \sum_{s=2}^{\infty} \mathsf{S}_s(1) \tag{3.6}$$

where $\mathsf{S}_s(1)$ is defined as an average scattering operator for s inclusions. Similarly, the coefficient μ is given by

$$\mu = \frac{\varepsilon_1}{4\pi\alpha^2} \operatorname{Tr} \int d\mathbf{R}_2 \, (0 \,|\, \mathsf{M}(1) \, \mathsf{S}_{\text{no}}(1, 2) \, \mathsf{M}(2) \,|\, 0) \tag{3.7}$$

where the operator $\mathsf{S}_{\text{no}}(1, 2)$ is the nonoverlap contribution to the short-range connector S(1, 2). The latter has again a cluster expansion[1]

$$\mathsf{S}(1, 2) = \sum_{s=2}^{\infty} \mathsf{S}_s(1, 2) \tag{3.8}$$

and may be written

$$\mathsf{S}(1, 2) = \mathsf{S}_{\text{no}}(1, 2) - \theta(2a - |\mathbf{R}_1 - \mathbf{R}_2|)\mathsf{G}_0 \tag{3.9}$$

where $\theta(x)$ is the step function and G_0 is the Green function for the uniform medium with dielectric constant ε_1. The explicit form for G_0 acting on a given vector field $\mathbf{V}(\mathbf{r})$ is

$$[\mathsf{G}_0 \cdot \mathbf{V}](\mathbf{r}) = -\frac{4\pi}{3\varepsilon_1} \mathbf{V}(\mathbf{r}) + \int_\delta d\mathbf{r}' \, \frac{3(\mathbf{r} - \mathbf{r}') \cdot \mathbf{V}(\mathbf{r}')(\mathbf{r} - \mathbf{r}') - (\mathbf{r} - \mathbf{r}')^2 \, \mathbf{V}(\mathbf{r}')}{\varepsilon_1 \, |\mathbf{r} - \mathbf{r}'|^5} \tag{3.10}$$

where the subscript δ on the integral indicates that the integral is carried out with the exclusion of an infinitesimally small sphere centered at **r**. In (3.5) and (3.7) the center $\mathbf{R}_1$ of inclusion 1 may be taken to be at the origin without loss of generality.

4. TWO- AND THREE-BODY CONTRIBUTIONS

In this section we specify the two- and three-body contributions to the coefficients λ and μ in more detail. First we recall the explicit expressions for the two- and three-body contributions to the reaction field operator S(1) and the short-range connector S(1, 2).

The two-body contribution to $\mathsf{S}(1)$ is given by

$$\mathsf{S}_2(1)=\int d2\, n(2)\, k(1,2)\, \mathsf{N}_{11}(1,2) \tag{4.1}$$

where $k(1,2)=g(1,2)$ is simply the normalized two-particle distribution function defined by $n(1,2)=n(1)\,n(2)\,g(1,2)$, and $\mathsf{N}_{11}(1,2)$ is a two-body nodal connector defined in terms of the two-body dielectric problem. The three-body contribution to $\mathsf{S}(1)$ is given by

$$\begin{aligned}\mathsf{S}_3(1)=\int d2\, d3\, n(2)\, n(3)[&k(1,2,3)\, \mathsf{N}_{11}(1,2,3)\\ &+k(1,2\mid 1,3)\, \mathsf{N}_{11}(1,2\mid 1,3)]\end{aligned} \tag{4.2}$$

with the chain correlation functions

$$k(1,2,3)=g(1,2,3), \qquad k(1,2\mid 1,3)=g(1,2,3)-g(1,2)\,g(1,3) \tag{4.3}$$

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 in (4.2) are defined in terms of the three-body dielectric problem and will be described in more detail in the next section. We merely note that they correspond to scattering sequences involving three inclusions in which the first and the last scatterer have the label 1.

Similarly, the two-body contribution to the short-range connector $\mathsf{S}(1,2)$ is given by

$$\mathsf{S}_2(1,2)=g(1,2)[\mathsf{N}_{12}(1,2)-\mathsf{G}_0]+h(1,2)\mathsf{G}_0 \tag{4.4}$$

where $h(1,2)=g(1,2)-1$. The three-body contribution to $\mathsf{S}(1,2)$ is given by

$$\begin{aligned}\mathsf{S}_3(1,2)=\int d3\, n(3)[&k(1,2,3)\, \mathsf{N}_{12}(1,2,3)+k(1,2\mid 2,3)\, \mathsf{N}_{12}(1,2\mid 2,3)\\ &+k(1,2,3)\, \mathsf{N}_{12}(1,3,2)+k(1,3\mid 1,2)\, \mathsf{N}_{12}(1,3\mid 1,2)\\ &+k(1,3\mid 2,3)\, \mathsf{N}_{12}(1,3\mid 3,2)]\end{aligned} \tag{4.5}$$

The chain correlation functions k are defined in analogy to (4.3) and the operators N_{12} are again various nodal connectors.

The two- and three-body contributions to the coefficients λ and μ may now be found by substitution of the above expressions into (3.5) and (3.7). The two-body contributions are combined conveniently in the form $\lambda_2+\mu_2$. This contribution has been studied in detail by several authors[3,5] and will not be discussed further here. The three-body contribution λ_3 may be written as

$$\lambda_3 = \lambda_3(1, 2, 3) + \lambda_3(1, 2 \mid 1, 3) \tag{4.6}$$

corresponding to the two terms in (4.2). Similarly, the three-body contribution μ_3 may be written as a sum of five terms

$$\begin{aligned}\mu_3 = \mu_3(1, 2, 3) + \mu_3(1, 2 \mid 2, 3) + \mu_3(1, 3, 2) \\ + \mu_3(1, 3 \mid 1, 2) + \mu_3(1, 3 \mid 3, 2)\end{aligned} \tag{4.7}$$

corresponding to the decomposition in (4.5).

In (1.1) we need the sum $\lambda_3 + \mu_3$ and it is convenient to divide the terms in (4.6) and (4.7) into two groups. From (3.5), (3.7), (4.2), and (4.5) we find

$$\begin{aligned}&\lambda_3(1, 2, 3) + \mu_3(1, 2, 3) + \mu_3(1, 3, 2) \\ &\quad = \frac{\varepsilon_1}{4\pi\alpha^2} n \int d\mathbf{R}_2\, d\mathbf{R}_3\, g(1, 2, 3) \operatorname{Tr}(0 \mid \mathsf{M}(1)[\mathsf{N}_{11}(1, 2, 3)\, \mathsf{M}(1) \\ &\qquad + \mathsf{N}_{12}(1, 2, 3)\, \mathsf{M}(2) + \mathsf{N}_{13}(1, 2, 3)\, \mathsf{M}(3)] \mid 0)\end{aligned} \tag{4.8}$$

In the last term we have used the symmetry of $g(1, 2, 3)$ to perform an interchange of labels. Similarly, we find

$$\begin{aligned}&\lambda_3(1, 2 \mid 1, 3) + \mu_3(1, 2 \mid 2, 3) + \mu_3(1, 3 \mid 1, 2) + \mu_3(1, 3 \mid 3, 2) \\ &\quad = \frac{\varepsilon_1}{4\pi\alpha^2} n \int d\mathbf{R}_2\, d\mathbf{R}_3\, k(1, 2 \mid 1, 3) \\ &\qquad \times \operatorname{Tr}(0 \mid [\mathsf{M}(1)\, \mathsf{N}_{11}(1, 2) + \mathsf{M}(2)\, \mathsf{N}_{21}(2, 1)]\, \mathsf{M}(1) \\ &\qquad \times [\mathsf{N}_{11}(1, 3)\, \mathsf{M}(1) + \mathsf{N}_{13}(1, 3)\, \mathsf{M}(3)] \mid 0)\end{aligned} \tag{4.9}$$

Here we have used that a three-body nodal connector with a slash factorizes into a product of two-body nodal connectors with an intermediate scatterer. For example,

$$\mathsf{N}_{12}(1, 2 \mid 2, 3) = \mathsf{N}_{12}(1, 2)\, \mathsf{M}(2)\, \mathsf{N}_{22}(2, 3) \tag{4.10}$$

The integral in (4.8) is the more difficult to evaluate, since the nodal connectors appearing there involve the solution of a three-body scattering problem. In the next section we investigate the three-body nodal connectors in more detail.

5. NODAL CONNECTORS

In this section we describe the nodal connectors which have appeared in the expressions of the preceding section. We consider first the nodal connector $\mathsf{N}_{11}(1, 2)$. It is associated with the sum of scattering sequences $[1\,2\,1] + [1\,2\,1\,2\,1] + \cdots$ describing repeated scatterings between the two inclusions 1, 2, with the condition that the first and last scatterer be 1. Explicitly the connector is

$$\mathsf{N}_{11}(1, 2) = \theta(1)\, \mathsf{G}_0 \mathsf{M}(2)[\mathsf{I} - \mathsf{G}_0 \mathsf{M}(1)\, \mathsf{G}_0 \mathsf{M}(2)]^{-1}\, \mathsf{G}_0 \theta(1) \qquad (5.1)$$

where the θ operator is defined by

$$\theta(1; \mathbf{r}, \mathbf{r}') = \theta(a - |\mathbf{r} - \mathbf{R}_1|)\, \delta(\mathbf{r} - \mathbf{r}') \qquad (5.2)$$

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

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

$$\mathsf{N}_{12}(1, 2) = \theta(1)\, \mathsf{G}_0[\mathsf{I} - \mathsf{M}(2)\, \mathsf{G}_0 \mathsf{M}(1) \mathsf{G}_0]^{-1}\, \theta(2) \qquad (5.3)$$

Next we consider the three-body connectors. Some of these have a slash indicating a nodal point. A label j is a nodal point of the scattering sequence $[1\,2 \cdots]$, if at that point the label j may be replaced by $j|j$ such that all labels to the left of the slash have only the label j in common with those on the right. The three-body connectors with a nodal point factorize as in (4.10). The nodal connectors $\mathsf{N}_{11}(1, 2, 3)$, $\mathsf{N}_{12}(1, 2, 3)$, and $\mathsf{N}_{13}(1, 2, 3)$ correspond to scattering sequences without nodal points. In particular, the connector $\mathsf{N}_{11}(1, 2, 3)$ corresponds to the sum of scattering sequences $[1\,2\,3\,1] + [1\,2\,3\,2\,1] + \cdots$, 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 first appear in this order. Similarly, the connector $\mathsf{N}_{12}(1, 2, 3)$ corresponds to the sum of scattering sequences $[1\,2\,3\,1\,2] + [1\,2\,1\,3\,1\,2] + \cdots$, with the same conditions as before, except that now the last scatterer must be 2. Finally, the connector $\mathsf{N}_{13}(1, 2, 3)$ corresponds to the sum of scattering sequences $[1\,2\,3\,1\,3] + [1\,2\,1\,3\,2\,3] + \cdots$ with the same conditions as before, except that the last scatterer must be 3.

In I we have expressed the connectors $\mathsf{N}_{1j}(1, 2, 3)$ in terms of a sum of sequences 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.[6,7] However, we have found in explicit calculations that a different expression, in which no resummation is carried out, is to be preferred.

Quite generally, for N scatterers we may write the N-body T-matrix[8] in the form

$$T(1,..., N) = \sum_{j,k} T_{jk}(1,..., N) \tag{5.4}$$

where $T_{jk}(1,..., N)$ may be represented by a sum of scattering sequences with the condition that the first scatterer be j and the last one be k. This may be expressed by the relation

$$T_{jk}(1,..., N) = \theta(j)\, T(1,..., N)\, \theta(k) \tag{5.5}$$

It is convenient to introduce a connection operator $V(1,..., N)$ by the equation[9]

$$T(1,..., N) = M_0(1,..., N) + M_0(1, ..., N)\, V(1,..., N)\, M_0(1,..., N) \tag{5.6}$$

where $M_0(1,..., N)$ represents the sum of isolated scatterers

$$M_0(1,..., N) = \sum_{j=1}^{N} M(j) \tag{5.7}$$

with $M(j) = T(j)$. In analogy to (5.4) we may write $V(1,..., N)$ as a sum of connectors

$$V(1,..., N) = \sum_{jm} V_{jm}(1,..., N) \tag{5.8}$$

The separate terms are given by

$$V_{jm}(1,..., N) = \theta(j)\, G_0 \theta(m)(1 - \delta_{jm}) + \theta(j) G_0 \sum_{\substack{k \neq j \\ l \neq m}} T_{kl} G_0 \theta(m) \tag{5.9}$$

The operators $T_{jk}(1,..., N)$ and $V_{jk}(1,..., N)$ may be regarded as elements of an $N \times N$ matrix. We introduce the $N \times N$ operator matrix

$$\mathscr{M}^{(N)} = \begin{pmatrix} M(1) & & & 0 \\ & M(2) & & \\ & & \ddots & \\ 0 & & & M(N) \end{pmatrix} \tag{5.10}$$

and similarly

$$\mathscr{G}^{(N)} = \begin{pmatrix} 0 & \theta(1)\, G_0\theta(2) & \theta(1)\, G_0\theta(3) & \cdots & \theta(1)\, G_0\theta(N) \\ \theta(2)\, G_0\theta(1) & 0 & & & \vdots \\ \vdots & & & 0 & \theta(N-1)\, G_0\theta(N) \\ \theta(N)\, G_0\theta(1) & & \cdots & \theta(N)\, G_0\theta(N-1) & 0 \end{pmatrix} \tag{5.11}$$

The corresponding operator matrix $\mathscr{T}^{(N)}$ is defined by

$$\mathscr{T}^{(N)} = \mathscr{M}^{(N)}[I^{(N)} - \mathscr{G}^{(N)}\mathscr{M}^{(N)}]^{-1} \tag{5.12}$$

The operator $T_{jk}(1,..., N)$ is the jk element of this matrix. In analogy to (5.6), we also introduce the $N \times N$ operator matrix $\mathscr{V}^{(N)}$ by

$$\mathscr{T}^{(N)} = \mathscr{M}^{(N)} + \mathscr{M}^{(N)}\mathscr{V}^{(N)}\mathscr{M}^{(N)} \tag{5.13}$$

From (5.12) we find

$$\mathscr{V}^{(N)} = \mathscr{G}^{(N)}[I^{(N)} - \mathscr{M}^{(N)}\mathscr{G}^{(N)}]^{-1} \tag{5.14}$$

The connector $V_{jk}(1,..., N)$ is the jk element of this matrix.

The two-body nodal connectors may be identified as

$$\mathsf{N}_{11}(1, 2) = \mathsf{V}_{11}(1, 2), \qquad \mathsf{N}_{12}(1, 2) = \mathsf{V}_{12}(1, 2) \tag{5.15}$$

where the boldface notation emphasizes the Cartesian tensor character. The three-body nodal connectors may be expressed in two alternative ways. In the first formulation we simply sum all scattering sequences which contribute and find

$$\begin{aligned}
\mathsf{N}_{11}(1, 2, 3) = {} & \mathsf{N}_{11}(1, 2)\, \mathsf{M}(1)[\mathsf{N}_{11}(1, 3)\, \mathsf{M}(1) \\
& + \mathsf{N}_{13}(1, 3)\, \mathsf{M}(3)]\, \mathsf{G}_0 \mathsf{M}(2)\, \mathsf{V}_{21}(1, 2, 3) \\
& + \mathsf{N}_{12}(1, 2)\, \mathsf{M}(2)[\mathsf{N}_{22}(2, 3)\, \mathsf{M}(2)\, \mathsf{V}_{21}(1, 2, 3) \\
& + \mathsf{N}_{23}(2, 3)\, \mathsf{M}(3)\, \mathsf{V}_{31}(1, 2, 3)] \\
\mathsf{N}_{12}(1, 2, 3) = {} & \mathsf{N}_{11}(1, 2)\, \mathsf{M}(1)[\mathsf{N}_{11}(1, 3)\, \mathsf{M}(1)\, \mathsf{V}_{12}(1, 2, 3) \\
& + \mathsf{N}_{13}(1, 2, 3)\, \mathsf{M}(3)\, \mathsf{V}_{32}(1, 2, 3)] \\
& + \mathsf{N}_{12}(1, 2)\, \mathsf{M}(2)[\mathsf{N}_{22}(2, 3)\, \mathsf{M}(2) \\
& + \mathsf{N}_{23}(2, 3)\, \mathsf{M}(3)]\, \mathsf{G}_0 \mathsf{M}(1)\, \mathsf{V}_{12}(1, 2, 3) \\
\mathsf{N}_{13}(1, 2, 3) = {} & \mathsf{N}_{11}(1, 2)\, \mathsf{M}(1)[\mathsf{N}_{11}(1, 3)\, \mathsf{M}(1) \\
& + \mathsf{N}_{13}(1, 3)\, \mathsf{M}(3)]\, \mathsf{G}_0 \mathsf{M}(2)\, \mathsf{V}_{23}(1, 2, 3) \\
& + \mathsf{N}_{12}(1, 2)\, \mathsf{M}(2)[\mathsf{N}_{22}(2, 3)\, \mathsf{M}(2) \\
& + \mathsf{N}_{23}(2, 3)\, \mathsf{M}(3)]\, \mathsf{G}_0 \mathsf{M}(1)\, \mathsf{V}_{13}(1, 2, 3)
\end{aligned} \tag{5.16}$$

In the second formulation we first sum over arbitrary scattering sequences and then exclude those specified by the definition of the nodal connectors. Thus, we obtain

$$
\begin{aligned}
N_{11}(1,2,3) &= V_{11}(1,2,3) - N_{11}(1,2) - N_{11}(1,3) - N_{11}(1,2)\,M(1)\,N_{11}(1,3) \\
&\quad - [N_{11}(1,3)\,M(1) + N_{13}(1,3)\,M(3)]\,G_0 M(2)\,V_{21}(1,2,3) \\
N_{12}(1,2,3) &= V_{12}(1,2,3) - N_{12}(1,2) - N_{12}(1,2)\,M(2)\,N_{22}(2,3) \\
&\quad - [N_{11}(1,3)\,M(1) + N_{13}(1,3)\,M(3)]\,G_0[\theta(2) \\
&\quad + M(2)\,V_{22}(1,2,3)] \\
N_{13}(1,2,3) &= V_{13}(1,2,3) - N_{13}(1,3) \\
&\quad - N_{11}(1,2)\,M(1)\,N_{13}(1,3) - N_{12}(1,2)\,M(2)\,N_{23}(2,3) \\
&\quad - [N_{11}(1,3)\,M(1) + N_{13}(1,3)\,M(3)]\,G_0 M(2)\,V_{23}(1,2,3)
\end{aligned}
\tag{5.17}
$$

Summing and symmetrizing with respect to the labels 2 and 3 we find

$$
\begin{aligned}
&N_{11}(1,2,3) + N_{11}(1,3,2) + N_{12}(1,2,3) \\
&\quad + N_{12}(1,3,2) + N_{13}(1,2,3) + N_{13}(1,3,2) \\
&= V_{11}(1,2,3) + V_{12}(1,2,3) + V_{13}(1,2,3) \\
&\quad - V_{11}(1,2) - V_{11}(1,3) - V_{12}(1,2) - V_{13}(1,3) \\
&\quad - V_{11}(1,2)\,M(1)[V_{11}(1,3) + V_{13}(1,3)] \\
&\quad - V_{11}(1,3)\,M(1)[V_{11}(1,2) + V_{12}(1,2)] \\
&\quad - V_{12}(1,2)\,M(2)[V_{22}(2,3) + V_{23}(2,3)] \\
&\quad - V_{13}(1,3)\,M(3)[V_{32}(2,3) + V_{33}(2,3)]
\end{aligned}
\tag{5.18}
$$

This last expression will be used in the following.

6. POLARIZABLE POINT DIPOLE MODEL

The expressions for the nodal connectors derived in the preceding section may in principle be used to evaluate the integrals in (4.8) and (4.9). Here we specify the integrals in more detail for the polarizable point dipole model. For this model the two-body nodal connectors have been given explicitly in (I.8.2) and (I.8.3).

We consider first the integral in (4.9). To express the result in a concise way, we introduce the dimensionless variables

$$
p = \frac{a^3}{R_{12}^3}, \qquad q = \frac{a^3}{R_{23}^3}, \qquad r = \frac{a^3}{R_{13}^3}, \qquad z = \frac{\varepsilon_1 a^3}{\alpha} \tag{6.1}
$$

By straightforward calculation we find that the integral in (4.9) is given by

$$\lambda_3(1, 2 | 1, 3) + \mu_3(1, 2 | 2, 3) + \mu_3(1, 3 | 1, 2) + \mu_3(1, 3 | 3, 2)$$
$$= \frac{n}{4\pi a^3} z \int d\mathbf{R}_2 \, d\mathbf{R}_3 \, k(1, 2 | 1, 3) \, F(p, r, \theta_1; z) \qquad (6.2)$$

Here θ_1 is the angle between the vectors $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$, and the function $F(p, r, \theta_1; z)$ is given by

$$F(p, r, \theta_1; z) = 3pr \frac{(3 \cos^2 \theta_1 - 1) z^2 + 4pr}{(z + p)(z - 2p)(z + r)(z - 2r)} \qquad (6.3)$$

In the limit of large z, corresponding to small α, the integral in (6.2) reduces to the three-body integral of Kirkwood[10] and Yvon.[11]

The integral in (4.8) is of the form

$$J = \int d\mathbf{R}_2 \, d\mathbf{R}_3 \, g(1, 2, 3) \, f(1, 2, 3) \qquad (6.4)$$

where by isotropy and translational invariance the functions $g(1, 2, 3)$ and $f(1, 2, 3)$ depend only on the variables R_{12}, R_{13}, and $\cos \theta_1$. We may therefore transform to

$$J = 8\pi^2 \int_{2a}^{\infty} \int_{2a}^{\infty} \int_{-1}^{1} g(1, 2, 3) \, f(1, 2, 3) \, R_{12}^2 R_{13}^2 \, dR_{12} \, dR_{13} \, d(\cos \theta_1) \qquad (6.5)$$

The integrand may be symmetrized with respect to the labels 2 and 3. Of course, the distribution function is already symmetric, so that we may use the symmetrized sum of nodal connectors given in (5.18). The integral in (6.5) may be cast in the form

$$J = 8\pi^2 \int_{2a}^{\infty} \int_{2a}^{\infty} \int_{2a}^{\infty} g(1, 2, 3) \, f(1, 2, 3) \, R_{12} R_{13} R_{23} \, dR_{12} \, dR_{13} \, dR_{23} \qquad (6.6)$$

with the convention that $g(1, 2, 3)$ vanishes when the triangle condition on the variables R_{12}, R_{13}, and R_{23} is not satisfied. Hence, we may also symmetrize the integrand with respect to the labels 1, 2, and 3. This completely symmetrized form is of advantage in the polarizable point dipole model.

To find the matrix element appearing in (4.8) for the polarizable point dipole model, it suffices to solve the problem of three coupled induced dipoles in a uniform applied field. That is, we must solve the set of coupled equations

$$\mathbf{p}_1 = \alpha[\mathbf{E}_0 + \mathsf{T}_{12} \cdot \mathbf{p}_2 + \mathsf{T}_{13} \cdot \mathbf{p}_3]$$
$$\mathbf{p}_2 = \alpha[\mathbf{E}_0 + \mathsf{T}_{21} \cdot \mathbf{p}_1 + \mathsf{T}_{23} \cdot \mathbf{p}_3] \qquad (6.7)$$
$$\mathbf{p}_3 = \alpha[\mathbf{E}_0 + \mathsf{T}_{31} \cdot \mathbf{p}_1 + \mathsf{T}_{32} \cdot \mathbf{p}_2]$$

where the dipole tensor is given by (2.11). We may solve the last two equations for $\mathbf{p}_2$ and $\mathbf{p}_3$ in terms of $\mathbf{E}_0$ and $\mathbf{p}_1$, and substitute into the first equation. We may simplify the problem further by choosing the z axis perpendicular to the plane containing the three centers. We are then left with two coupled equations for the components p_{1x} and p_{1y}, and with one equation for p_{1z}. The solution allows us to find the matrix elements of the operators $\mathsf{V}_{1j}(1, 2, 3)$ in (5.18).

As a final result, we find

$$\begin{aligned}&\lambda_3(1, 2, 3) + \mu_3(1, 2, 3) + \mu_3(1, 3, 2)\\ &\quad = \frac{2\pi n}{3a^3} z \int_{2a}^{\infty} \int_{2a}^{\infty} \int_{2a}^{\infty} g(1, 2, 3)[G_{xy}(1, 2, 3) + G_z(1, 2, 3)\\ &\qquad - F(p, r, \theta_1; z) - F(q, p, \theta_2; z) - F(r, q, \theta_3; z)\\ &\qquad - H(p, z) - H(q, z) - H(r, z) - 3]\, R_{12} R_{13} R_{23}\, dR_{12}\, dR_{13}\, dR_{23} \qquad (6.8)\end{aligned}$$

with dimensionless functions G_{xy}, G_z, F, and H. The function $G_z(1, 2, 3)$ is given by

$$G_z(1, 2, 3) = N_1/D_1 \qquad (6.9)$$

with the abbreviations

$$\begin{aligned}N_1 &= (z-p)(z-q)(z-r)\\ D_1 &= z^3 - (p^2+q^2+r^2)z + 2pqr\end{aligned} \qquad (6.10)$$

The function $G_{xy}(1, 2, 3)$ is more complicated and is given by

$$G_{xy}(1, 2, 3) = \frac{9(zP - Q) + N_1 D_2 + N_2 D_1}{9Q + D_1 D_2} \qquad (6.11)$$

with the abbreviations

$$\begin{aligned}N_2 &= (z+2p)(z+2q)(z+2r)\\ D_2 &= z^3 - 4(p^2+q^2+r^2)z - 16pqr\\ P &= Az^3 + Bz^2 + Cz + D\\ Q &= Rz^3 + Sz^2 + Tz + U\end{aligned} \qquad (6.12)$$

where in turn

$$\begin{aligned}
A &= -(s_1+s_2+s_3)\\
B &= 3s_{123}-(p+r)s_1-(q+p)s_2-(r+q)s_3\\
C &= (2p^2+pr+2r^2)s_1+(2q^2+qp+2p^2)s_2\\
&\quad +(2r^2+rq+2q^2)s_3-2(p+q+r)s_{123}\\
&\quad +pc_{3,12}+qc_{1,23}+rc_{2,31} \qquad (6.13)\\
D &= (9s_1-2q^2)c_{1,23}+(9s_2-2r^2)c_{2,31}+(9s_3-2p^2)c_{3.12}\\
R &= 2s_{123}\\
S &= prs_1+qps_2+rqs_3\\
T &= -4(p^2c_{3,12}+q^2c_{1,23}+r^2c_{2,31})\\
U &= -9s_{123}^2
\end{aligned}$$

In the latter expressions we have used the abbreviations

$$\begin{aligned}
s_1 = pr\sin^2\theta_1, \qquad s_2 = qp\sin^2\theta_2, \qquad s_3 = rq\sin^2\theta_3\\
s_{123} = \tfrac{1}{2}pqr(\sin^2\theta_1+\sin^2\theta_2+\sin^2\theta_3)\\
c_{i,jk} = \tfrac{1}{2}pqr(\sin^2\theta_j+\sin^2\theta_k-\sin^2\theta_i) \qquad (6.14)
\end{aligned}$$

Here θ_2 is the angle between $\mathbf{R}_{21}$ and $\mathbf{R}_{23}$, and θ_3 is the angle between $\mathbf{R}_{31}$ and $\mathbf{R}_{32}$. Finally, the functions H in (6.8) are given by

$$H(p,z)=\frac{6p^2}{(z+p)(z-2p)} \qquad (6.15)$$

These functions arise from the two-body nodal connectors in the form

$$\mathrm{Tr}(0\,|\,\mathsf{M}(1)[\mathsf{N}_{11}(1,2)\,\mathsf{M}(1)+\mathsf{N}_{12}(1,2)\,\mathsf{M}(2)]\,|\,0)=\alpha H(p,z) \qquad (6.16)$$

We note that the subtracted terms in (6.8) make the integral absolutely convergent.

7. DISCUSSION

We have studied the three-body cluster integrals λ_3 and μ_3, as defined in (1.1) and (1.2). Our final results for the polarizable point dipole model are given in (6.2) and (6.8). Even for this simple model the expressions are complicated and the final integrals can be evaluated only numerically. It would be of interest to compare the theoretical results with the electrostatic spectra we have obtained in a computer experiment for a hard-sphere fluid with polarizable point dipoles.[12]

For more realistic models, say uniform spherical inclusions with a dielectric constant ε_2, the calculation of the three-body integrals will be considerably more difficult. As a first step beyond the polarizable point dipole model one might attempt to include quadrupoles. The quadrupole contribution to the two-body cluster integrals has already been studied by Felderhof and Jones.[13]

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