

## Two-Particle Cluster Integral in the Expansion of the Dielectric Constant

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*Received January 26, 1982*

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We study in detail the two-particle cluster integral in the cluster expansion for the effective dielectric constant of a suspension of spherically symmetric polarizable inclusions embedded in a uniform medium. Although our form for the integrand differs from that derived earlier by Finkel'berg and by Jeffrey, we show that the integral is equivalent. The two-body dielectric problem for particles with an arbitrary radial dependence of the dielectric constant is solved by an expansion in spherical harmonics. Numerical results for some special models illustrate the importance of multipole contributions to the effective dielectric constant.

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**KEY WORDS:** Effective dielectric constant; cluster integral; two-sphere problem; random media; Clausius-Mossotti formula.

### 1. INTRODUCTION

In a preceding paper (hereafter referred to as I) we developed a cluster expansion for the effective dielectric constant  $\epsilon^*$  of a collection of spherically symmetric inclusions embedded in a uniform dielectric medium.<sup>(1)</sup> The expansion consists of a sum of cluster integrals involving many-body polarizability kernels and distribution functions describing the statistics of the inclusions. The expansion is ordered according to the number of inclusions involved in each term. In the present paper we consider in detail the first- and second-order cluster integrals.

The first-order term was already derived by Maxwell as the contribution to  $\epsilon^*$  linear in the density. The second-order cluster integral involves

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the two-inclusion distribution function and therefore reflects the local structure of a liquid or solid suspension. Previously an expression for the two-inclusion cluster integral was derived by Finkel'berg<sup>(2)</sup> and by Jeffrey.<sup>(3)</sup> Jeffrey also found an exact solution of the electrostatic problem for two inclusions in a uniform external electric field for the case of uniform dielectric spheres. The integrand in Finkel'berg's and Jeffrey's expression differs from ours in a nontrivial manner, but we shall show that the value of the integral is the same. In his calculations Jeffrey assumed that the spheres were statistically distributed like a low-density hard-sphere gas, i.e., the spheres do not overlap but are otherwise uncorrelated. This corresponds to an expansion of the two-particle distribution function to second order in the density. In this way the second-order density contribution to the dielectric constant is obtained. Within the framework of a statistical mechanical virial expansion the second-order density correction was calculated by Buckingham and Pople<sup>(4)</sup> in dipole approximation. Their result is easily recovered from our more general expression.

In Section 2 we recall the basic equations of the cluster expansion for the effective dielectric constant, giving prescriptions for the first- and second-order cluster integrals. We also quote the corresponding prescription of Finkel'berg and Jeffrey. These prescriptions involve the solution of electrostatic problems in the presence of a single inclusion in first order, of two inclusions in second order, etc. In Section 3 we discuss the second-order term. We first present a general solution of the two-inclusion problem, introducing multipole polarizabilities to characterize the electrical response of the inclusions. The solution is expressed in terms of the ratio of two infinite determinants with the multipole polarizabilities as parameters. We next solve the remaining electrostatic problem associated with the second-order terms and show the equivalence with the form given by Finkel'berg and Jeffrey. The section is concluded with the evaluation of the second-order cluster integral in terms of the solution of these electrostatic problems. In Section 4 we discuss the calculation of the multipole polarizabilities for various models of the inclusions. In Section 5 we present numerical results for some of these models. Finally, in Section 6 we briefly discuss the application of our results to the case of a gas of nonpolar molecules.

## 2. BASIC EQUATIONS

We consider a system of identical spherical polarizable inclusions embedded in a uniform background with dielectric constant  $\epsilon_1$ . The inclusions are assumed to be statistically distributed with a probability distribution which is spatially homogeneous, isotropic, and independent of the

applied external field. In addition, the inclusions are not allowed to overlap, i.e., the probability distribution vanishes if the separation of the centers of any pair of inclusions is less than their diameter. We have shown in I that the effective dielectric constant  $\epsilon^*$  of the system can be expressed in the form of an irreducible cluster expansion. The terms through second order in this expansion are [cf. I, Eq. (7.16)]

$$\epsilon^* = \epsilon_1 + \epsilon^*(1) + [\epsilon^*(1,2) + \epsilon^*(1|2)] + \dots \quad (2.1)$$

where, in the notation of I, the first-order term is given by

$$\epsilon^*(1)\vec{\mathbb{I}} = 4\pi n(0|\vec{M}(1)|0) \quad (2.2)$$

and the two second-order terms by

$$\begin{aligned} \epsilon^*(1,2)\vec{\mathbb{I}} &= 4\pi \int d\mathbf{R}_2 n(1,2) (0|\vec{M}(1,2) - \vec{M}(1) \cdot \vec{L}(2)|0) \\ \epsilon^*(1|2)\vec{\mathbb{I}} &= 4\pi \int d\mathbf{R}_2 [n(1,2) - n^2] (0|\vec{M}(1) \cdot \vec{L}(2)|0) \end{aligned} \quad (2.3)$$

Here  $\vec{\mathbb{I}}$  is the unit dyadic and the various quantities are defined as follows. The quantity  $n$  is the number density of inclusions and  $n(1,2)$  is the pair distribution function, defined such that  $n(1,2)d\mathbf{R}_1 d\mathbf{R}_2$  is the number of pairs of inclusions in which one is centered in volume  $d\mathbf{R}_1$  about the position  $\mathbf{R}_1$  and the other in volume  $d\mathbf{R}_2$  about the position  $\mathbf{R}_2$ . The dyadic operators  $\vec{M}$  and  $\vec{L}$  are in turn expressed in terms of a dyadic operator  $\vec{K}$ , defined by the relation

$$\mathbf{E}(1,2,\dots,s) = \vec{K}(1,2,\dots,s) \cdot \mathbf{E}_0 \quad (2.4)$$

where  $\mathbf{E}(1,2,\dots,s)$  is the electric field which results when exactly  $s$  inclusions, centered at  $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s$ , are placed in an applied external field  $\mathbf{E}_0$ . The operator  $\vec{L}(1)$  is then

$$\vec{L}(1) = \vec{K}(1) - \vec{\mathbb{I}} \quad (2.5)$$

The operators  $\vec{M}$  are given by

$$\begin{aligned} \vec{M}(1) &= \chi(1)\vec{K}(1), \\ \vec{M}(1;2) &= \chi(1)\vec{K}(1,2) - \chi(1)\vec{K}(1) \end{aligned} \quad (2.6)$$

where  $\chi(1)$  is the relative dielectric susceptibility of an inclusion centered at  $\mathbf{R}_1$ , i.e., if  $\mathbf{E}$  is the electric field within the inclusion then  $\chi(1)\mathbf{E}$  is the induced polarization (dipole moment per unit volume) within the inclusion and relative to the background. More explicitly, in the case where the

inclusions are uniform spheres of radius  $a$  and dielectric constant  $\epsilon_2$ ,

$$\chi(1; \mathbf{r}) = \begin{cases} 0, & |\mathbf{r} - \mathbf{R}_1| > a \\ \frac{\epsilon_2 - \epsilon_1}{4\pi}, & |\mathbf{r} - \mathbf{R}_1| < a \end{cases} \quad (2.7)$$

Finally, the dyadic operators may be formally expressed as integral operators. Thus, in an expanded notation, (2.4) can be written

$$\mathbf{E}(1, 2, \dots, s; \mathbf{r}) = \int d\mathbf{r}' \vec{K}(1, 2, \dots, s; \mathbf{r}, \mathbf{r}') \cdot \mathbf{E}_0(\mathbf{r}') \quad (2.8)$$

The bracket notation in (2.2) and (2.3) corresponds to

$$(0|\vec{K}(1, 2, \dots, s)|0) \equiv \int d\mathbf{r} \int d\mathbf{r}' \vec{K}(1, 2, \dots, s; \mathbf{r}, \mathbf{r}') \quad (2.9)$$

and similarly for the other operators. Note that, because of our assumption of spatial homogeneity and the resulting translation invariance of the problem, the expressions (2.2) and (2.3) are independent of the coordinate  $\mathbf{R}_1$ . Furthermore, for the purpose of this paper we can confine ourselves to a uniform applied electric field.

The evaluation of the first-order term (2.2) is straightforward and consists only in putting the formal operator expression into more familiar language. We proceed as follows. For a uniform applied field  $\mathbf{E}_0$  the electric field in the presence of a single inclusion centered at  $\mathbf{R}_1$  is given by

$$\mathbf{E}(1; \mathbf{r}) = \int d\mathbf{r}' \vec{K}(1; \mathbf{r}, \mathbf{r}') \cdot \mathbf{E}_0 \quad (2.10)$$

The polarization induced within the inclusion is  $\mathbf{P}(1) = \chi(1)\mathbf{E}(1)$  and integrating this over the interior of the inclusion we get the electric dipole moment induced in the inclusion

$$\mathbf{p}(1) = \int d\mathbf{r} \int d\mathbf{r}' \chi(1; \mathbf{r}) \vec{K}(1; \mathbf{r}, \mathbf{r}') \cdot \mathbf{E}_0 \quad (2.11)$$

With (2.6) and (2.9) this can be written

$$\mathbf{p}(1) = (0|\vec{M}(1)|0) \cdot \mathbf{E}_0 \quad (2.12)$$

But, the dipole polarizability  $\alpha$  of an inclusion is defined by the relation

$$\mathbf{p}(1) = \alpha \mathbf{E}_0 \quad (2.13)$$

(independent of  $\mathbf{R}_1$ ). Thus from (2.12) we see that

$$\alpha \hat{1} = (0|\vec{M}(1)|0) \quad (2.14)$$

As remarked above the expression on the right is in fact independent of  $\mathbf{R}_1$  and its proportionality to the unit dyadic follows from our assumption of

spherical symmetry of the inclusions. With (2.14) we see that the first-order term (2.2) is given by

$$\epsilon^*(1) = 4\pi n\alpha \quad (2.15)$$

a well known result first obtained by Maxwell.<sup>(5)</sup>

By entirely similar arguments we can also interpret the quantities occurring in the second-order terms (2.3) in more familiar language. Thus, for a uniform applied field  $\mathbf{E}_0$ ,

$$\left(0|\vec{M}(1;2)|0\right) \cdot \mathbf{E}_0 = \mathbf{p}(1;2) - \mathbf{p}(1) \quad (2.16)$$

where, as above,  $\mathbf{p}(1)$  is the dipole moment induced in an isolated inclusion centered at  $\mathbf{R}_1$ , while  $\mathbf{p}(1;2)$  is the dipole moment induced in an inclusion centered at  $\mathbf{R}_1$  in the presence of a second inclusion centered at  $\mathbf{R}_2$ . On the other hand, still for a uniform field  $\mathbf{E}_0$ ,

$$\left(0|\vec{M}(1) \cdot \vec{L}(2)|0\right) \cdot \mathbf{E}_0 = \mathbf{p}(1|2) - \mathbf{p}(1) \quad (2.17)$$

Here  $\mathbf{p}(1|2)$  is the dipole moment induced in an inclusion centered at  $\mathbf{R}_1$  when it is subject to the (nonuniform) field  $\mathbf{E}(2) = \vec{K}(2) \cdot \mathbf{E}_0$  which results when a single inclusion is placed with its center at  $\mathbf{R}_2$  in the uniform applied field  $\mathbf{E}_0$ . With the interpretations (2.16) and (2.17), the second-order terms (2.3) are given by

$$\begin{aligned} \epsilon^*(1,2)\mathbf{E}_0 &= 4\pi \int d\mathbf{R}_2 n(1,2) [\mathbf{p}(1;2) - \mathbf{p}(1|2)] \\ \epsilon^*(1|2)\mathbf{E}_0 &= 4\pi \int d\mathbf{R}_2 [n(1,2) - n^2] [\mathbf{p}(1|2) - \mathbf{p}(1)] \end{aligned} \quad (2.18)$$

These interpretations of the second-order terms will be useful when we come to their explicit evaluation in the next sections.

The expression [Ref. 3, Eq. (3.13)] given by Jeffrey for the two-body contribution corresponds in (2.3) to making the replacement

$$\left(0|\vec{M}(1) \cdot \vec{L}(2)|0\right) \rightarrow \left(0|\vec{M}(1)|0\right) \cdot \left(0|\delta(\mathbf{r} - \mathbf{R}_1)\vec{L}(2)|0\right) \quad (2.19)$$

This in turn corresponds in (2.17) and (2.18) with replacing  $\mathbf{p}(1|2)$  by the dipole moment induced in the inclusion centered at  $\mathbf{R}_1$  when it is subject to a *uniform* electric field which is equal to the (nonuniform) field  $\mathbf{E}(2)$  evaluated at  $\mathbf{R}_1$ . Nevertheless, as we shall show in Section 3, the result of the integration in (2.3) is the same as our expression.

### 3. EVALUATION OF THE SECOND-ORDER TERM

We in general restrict our discussion to inclusions which have a finite "electrical" radius  $a$ , outside which the susceptibility  $\chi$  vanishes, as in (2.7).

In the integrals appearing in the second-order terms, given in (2.3) or (2.18), we can therefore distinguish two regions of integration and their corresponding contributions: overlapping ( $|\mathbf{R}_2 - \mathbf{R}_1| < 2a$ ) and nonoverlapping ( $|\mathbf{R}_2 - \mathbf{R}_1| > 2a$ ). We assume that the distribution of inclusions is such that they never overlap, which in particular implies

$$n(1, 2) = 0, \quad |\mathbf{R}_2 - \mathbf{R}_1| < 2a \quad (3.1)$$

The overlap contribution comes therefore only from  $\epsilon^*(1|2)$ , which involves the solution of the electrostatic equations in the presence of a single isolated inclusion. This contribution corresponds to a correction for contributions which were overcounted in the first-order term. It is analogous to the imaginary (or virtual) scattering contributions which occur in the density expansion of the Boltzmann equation.<sup>(6)</sup> The solution of the electrostatic equations in the presence of two inclusions occurs only in the nonoverlap contribution. We consider that problem first.

### 3.1. Solution of the Two-Inclusion Problem

Our aim here will be to calculate  $\mathbf{p}(1; 2)$ , the electric dipole moment induced in an inclusion centered at  $\mathbf{R}_1$  in the presence of a second inclusion centered at  $\mathbf{R}_2$ . The two inclusions are to be nonoverlapping and subject to a uniform applied field  $\mathbf{E}_0$ . Our method of solution is a generalization of that used by Jeffrey to solve the problem for the case where the inclusions are uniform dielectric spheres.<sup>(3)</sup>

We introduce coordinates as indicated in Fig. 1, with the polar axis along the line joining the two centers. As indicated,  $\mathbf{r}_1 = \mathbf{r} - \mathbf{R}_1$  and  $\mathbf{r}_2 = \mathbf{r} - \mathbf{R}_2$  are the coordinates of the field point with respect to the centers  $\mathbf{R}_1$  and  $\mathbf{R}_2$ , respectively, and  $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$ . The azimuthal angle  $\phi$  is the angle between the planes determined by the vectors  $\mathbf{E}_0, \mathbf{R}$  and  $\mathbf{r}_1, \mathbf{R}$ . The nonoverlap condition requires  $R > 2a$ . We write the electric field in the presence of the inclusions as

$$\mathbf{E}(1, 2) = -\text{grad } \Phi(1, 2) \quad (3.2)$$

where  $\Phi(1, 2)$  is the electrostatic potential.

Now, in the region *outside* the inclusions the potential must be harmonic and can be written as the sum of the potential of the applied field plus that due to the induced polarizations within the inclusions. This is expressed by the twin expansion:

$$\begin{aligned} \Phi(1, 2; \mathbf{r}) = -\mathbf{E}_0 \cdot \mathbf{r} + \sum_{l=1}^{\infty} \sum_{m=0}^l \left[ A_{lm}^{(1)} r_1^{-l-1} P_l^m(\cos \theta_1) \right. \\ \left. + A_{lm}^{(2)} r_2^{-l-1} P_l^m(\cos \theta_2) \right] \cos m\phi \quad (3.3) \end{aligned}$$

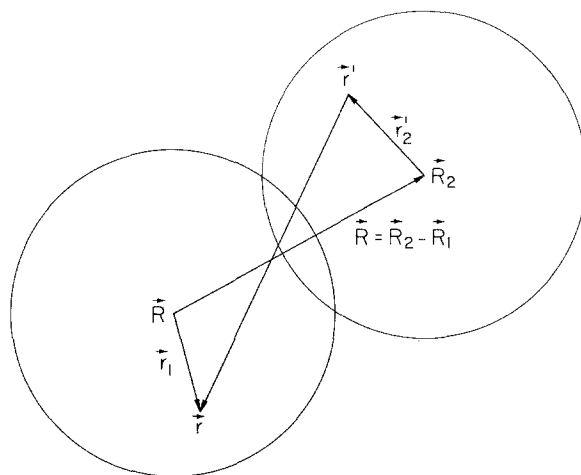


Fig. 1. Coordinates for the problem of two nonoverlapping inclusions.

where  $P_l^m$  is the associated Legendre function.<sup>(7)</sup> The two terms within the sum correspond to induced  $2^l$  poles within either inclusion. The monopole terms are absent since the inclusions are uncharged. In the usual method of solving such electrostatic problems one would make corresponding expansions of the potential *inside* the inclusions and match at the surfaces to determine the coefficients.<sup>(3)</sup> We will use instead a more general method which will be applicable to inclusions, e.g., molecules, which are not dielectric spheres. In our method the coefficients  $A_{lm}^{(1)}$  and  $A_{lm}^{(2)}$  in the expansion are determined by conditions *just outside* either inclusion. We describe this condition in the following paragraph.

Because of the spherical symmetry of an inclusion, its electrostatic properties are completely characterized by its multipole polarizabilities. These quantities are defined in terms of the response to an applied multipole field, supplied by sources outside the inclusion. For an inclusion centered at the origin, the electrostatic potential in the region outside the inclusion, but within a sphere which excludes the sources of the applied multipole field, must be of the form<sup>(8)</sup>

$$\Phi_{lm} \propto \left( -r^l + \frac{\alpha_l}{\epsilon_1} r^{-l-1} \right) P_l^m(\cos \theta) \cos m\phi \quad (3.4)$$

where  $\theta$  and  $\phi$  are the polar angles of  $\mathbf{r}$ . Here the first term is the potential of the applied  $2^l$ -pole field and the second term is that of the induced  $2^l$ -pole moment. The coefficient  $\alpha_l$  is the  $2^l$ -pole polarizability of the inclusion. These multipole polarizabilities are generalizations of the familiar

dipole polarizability, which corresponds to the case  $l = 1, \alpha_1 = \alpha$ . From our present point of view we consider the  $\alpha_l$  as given, characterizing the inclusions. We discuss their calculation for various models of the inclusions in the following section. Our condition at the surface of the inclusion is therefore that the potential must be a superposition of potentials of the form (3.4).

To determine the coefficients  $A_{lm}^{(1)}$  and  $A_{lm}^{(2)}$  in (3.3) we require that just outside the inclusion centered at  $\mathbf{R}_1$  the potential must be expressible as a superposition of potentials of the form (3.4) with  $(r, \theta) \rightarrow (r_1, \theta_1)$ , and similarly just outside the inclusion centered at  $\mathbf{R}_2$ . To accomplish this we must expand the multipole potentials centered at one sphere in terms of those centered at the other, which we do with the pair of formulas<sup>(9), 4</sup>

$$r_2^{-l-1} P_l^m(\cos \theta_2) = (-)^{l+m} \sum_{l'=m}^{\infty} \binom{l+l'}{l'+m} \frac{r_1^{l'}}{R^{l+l'+1}} P_{l'}^m(\cos \theta_1) \quad (3.5)$$

which is valid for  $r_1 < R$ , and

$$r_1^{-l-1} P_l^m(\cos \theta_1) = \sum_{l'=m}^{\infty} (-)^{l'+m} \binom{l+l'}{l'+m} \frac{r_2^{l'}}{R^{l+l'+1}} P_{l'}^m(\cos \theta_2) \quad (3.6)$$

which is valid for  $r_2 < R$ . We need also the formulas

$$\begin{aligned} \mathbf{E} \cdot \mathbf{r} &= \mathbf{E}_0 \cdot \mathbf{R}_1 + E_{\parallel} r_1 P_1^0(\cos \theta_1) + E_{\perp} r_1 P_1^1(\cos \theta_1) \cos \phi \\ &= \mathbf{E}_0 \cdot \mathbf{R}_2 + E_{\parallel} r_2 P_1^0(\cos \theta_2) + E_{\perp} r_2 P_1^1(\cos \theta_2) \cos \phi \end{aligned} \quad (3.7)$$

where  $E_{\parallel}$  and  $E_{\perp}$  are, respectively, the components of  $\mathbf{E}_0$  parallel and perpendicular to  $\mathbf{R}$ . Using (3.5) and the first of the formulas (3.7), the condition just outside the surface of the inclusion centered at  $\mathbf{R}_1$  gives the relation

$$\frac{\epsilon_1}{\alpha_l} A_{lm}^{(1)} = (E_{\parallel} \delta_{m,0} + E_{\perp} \delta_{m,1}) \delta_{l,1} - \sum_{l'=m}^{\infty} (-)^{l'+m} \binom{l+l'}{l+m} \frac{A_{l'm}^{(2)}}{R^{l+l'+1}} \quad (3.8)$$

In the same way, using (3.6) and the second of the formulas (3.7), the condition just outside the inclusion centered at  $\mathbf{R}_2$  gives

$$\frac{\epsilon_1}{\alpha_l} A_{lm}^{(2)} = (E_{\parallel} \delta_{m,0} + E_{\perp} \delta_{m,1}) \delta_{l,1} - (-)^{l+m} \sum_{l'=m}^{\infty} \binom{l+l'}{l+m} \frac{A_{l'm}^{(1)}}{R^{l+l'+1}} \quad (3.9)$$

For each  $m$  the equations (3.8) and (3.9) are an infinite set of coupled linear equations for the coefficients  $A_{lm}^{(1)}$  and  $A_{lm}^{(2)}$ . The solution vanishes unless  $m = 0, 1$ , since otherwise the inhomogeneous term is zero. Moreover, be-

<sup>4</sup> We note that the expansion (3.6) is given incorrectly by Hobson.



cause of the symmetry of the equations we can put

$$A_{lm}^{(1)} = (-)^{l-1} A_{lm}^{(2)} = (E_{\parallel} \delta_{m,0} + E_{\perp} \delta_{m,1}) a^{l+2} a_{lm} \quad (3.10)$$

in which case Eqs. (3.8) and (3.9) both take the same form and can be written

$$\sum_{l'=1}^{\infty} M_{ll'}^m a_{l'm} = \delta_{l,1}, \quad l = 1, 2, \dots \quad (3.11)$$

where

$$M_{ll'}^m = \frac{\epsilon_1 a^{2l+1}}{\alpha_l} \delta_{ll'} - (-)^m \binom{l+l'}{l+m} \left(\frac{a}{R}\right)^{l+l'+1} \quad (3.12)$$

The solution of the equations (3.11) can now be obtained using the rule of Cramer,<sup>(10)</sup>

$$a_{lm} = \frac{\text{cof}(M_{ll}^m)}{\det(M^m)} \quad (3.13)$$

where the denominator is the determinant of the infinite matrix whose elements are the  $M_{ll'}^m$  and the numerator is the cofactor of the  $ll$  element in  $M^m$ . The operational meaning of (3.13) is the limit as  $n \rightarrow \infty$  of the corresponding ratio formed with the  $n$ th truncation, i.e., the  $n \times n$  matrix in the upper left-hand corner of  $M^m$ .

The  $l = 1$  terms in the sum (3.3) give the potential due to the induced dipole moment in either inclusion. In particular the potential due to  $\mathbf{p}(1; 2)$ , the dipole moment induced in the inclusion centered at  $\mathbf{R}_1$ , is

$$\frac{\mathbf{p}(1; 2) \cdot \mathbf{r}}{\epsilon_1 r_1^3} = \sum_{m=0}^1 A_{1m}^{(1)} \frac{1}{r_1^2} P_1^m(\cos \theta_1) \cos m\phi \quad (3.14)$$

Using (3.10) and making the identification

$$E_{\parallel} r_1 P_1^0(\cos \theta_1) = \mathbf{E}_0 \cdot \hat{\mathbf{R}} \hat{\mathbf{R}} \cdot \mathbf{r}_1, \quad E_{\perp} r_1 P_1^1(\cos \theta_1) \cos \phi = (\mathbf{E}_0 - \hat{\mathbf{R}} \cdot \mathbf{E}_0 \hat{\mathbf{R}}) \cdot \mathbf{r} \quad (3.15)$$

where  $\hat{\mathbf{R}} = \mathbf{R}/R$ , we get the result

$$\mathbf{p}(1; 2) = \epsilon_1 a^3 [a_{10}(R) \hat{\mathbf{R}} \cdot \mathbf{E}_0 \hat{\mathbf{R}} + a_{11}(R) (\mathbf{E}_0 - \hat{\mathbf{R}} \cdot \mathbf{E}_0 \hat{\mathbf{R}})] \quad (3.16)$$

This result, with  $a_{1m}(R)$  given by (3.13), is our desired expression for  $\mathbf{p}(1; 2)$ .

### 3.2. Solution of the $\mathbf{p}(1|2)$ Problem

The problem we consider is the following. A single inclusion is placed with its center at  $\mathbf{R}_2$  in a uniform applied field  $\mathbf{E}_0$ . The resulting field, inside

as well as outside the inclusion, is  $\mathbf{E}(2)$ . This nonuniform field is now treated as an external field in which a second inclusion is placed with its center at  $\mathbf{R}_1$ . The dipole moment induced in this second inclusion is  $\mathbf{p}(1|2)$ , and our problem is to calculate this quantity. It is clear from (2.18) and (3.1) that  $\mathbf{p}(1|2)$  occurs in both nonoverlapping and overlapping configurations, so we must discuss both cases.

Consider first the nonoverlapping case. Again we use coordinates as indicated in Fig. 1. The inclusion centered at  $\mathbf{R}_1$  is then subject to the field  $\mathbf{E}(2)$  *outside* the inclusion centered at  $\mathbf{R}_2$ . But, when a spherical inclusion is placed in a uniform field the field outside the inclusion is the uniform field plus the field due to the induced dipole moment. Hence,

$$\mathbf{E}(2; \mathbf{r}) = \mathbf{E}_0 + \frac{3\mathbf{p}(2) \cdot \mathbf{r}_2 \mathbf{r}_2 - r_2^2 \mathbf{p}(2)}{\epsilon_1 r_2^5}, \quad r_2 > a \quad (3.17)$$

The dipole moment induced in an inclusion placed in this field with center at  $\mathbf{R}_1$  is obtained from a theorem, sometimes termed Faxén's law,<sup>(11)</sup> for which we give a proof in Appendix A. This theorem states that when a spherical inclusion is placed in a nonuniform external field whose *source is outside the inclusion*, the induced dipole moment is the dipole polarizability times the external field evaluated at the center of the inclusion. Thus (see Fig. 1 for definition of the coordinates)

$$\begin{aligned} \mathbf{p}(1|2) &= \alpha \mathbf{E}(2; \mathbf{R}_1) \\ &= \alpha \mathbf{E}_0 + \alpha \frac{3\mathbf{p}(2) \cdot \hat{\mathbf{R}}\hat{\mathbf{R}} - \mathbf{p}(2)}{\epsilon_1 R^3}, \quad R > 2a \end{aligned} \quad (3.18)$$

Since, as in (2.13),  $\mathbf{p}(2) = \alpha \mathbf{E}_0$ , we can write this in the form

$$\mathbf{p}(1|2) = \alpha \mathbf{E}_0 + \alpha^2 \frac{3\mathbf{E}_0 \cdot \hat{\mathbf{R}}\hat{\mathbf{R}} - \mathbf{E}_0}{\epsilon_1 R^3}, \quad R > 2a \quad (3.19)$$

which is our desired expression for  $\mathbf{p}(1|2)$  in the nonoverlap case.

Next consider the overlapping case. In this case the source density of the field  $\mathbf{E}(2)$  partly lies within the inclusion centered at  $\mathbf{R}_1$ , so that it appears that the response of this inclusion cannot be expressed in terms of the multipole polarizabilities defined above. Nevertheless, we will now show that the integral of  $\mathbf{p}(1|2)$  over the overlap region which is all we need in the second of the equations (2.18), is expressible in terms of the dipole polarizability of the inclusions. To proceed we first write

$$\mathbf{E}(2) = \mathbf{E}_0 + \mathbf{E}_{\text{ind}}(2) \quad (3.20)$$

where  $\mathbf{E}_{\text{ind}}(2)$  is the induced field which results when an inclusion is placed

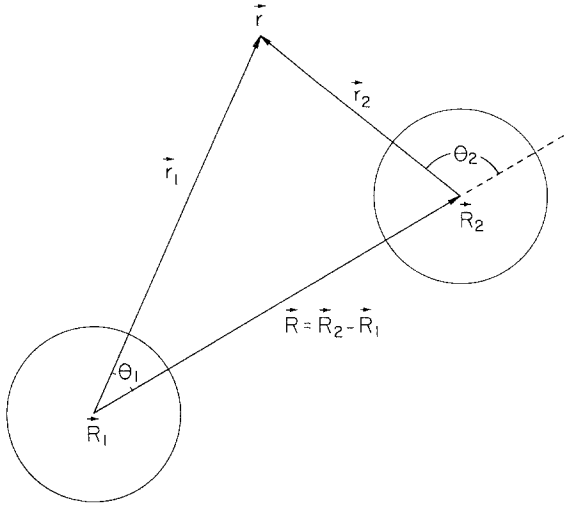


Fig. 2. Coordinates for the problem of two overlapping inclusions.

with its center at  $\mathbf{R}_2$  in the field  $\mathbf{E}_0$ . The source of  $\mathbf{E}_{ind}(2)$  is  $\mathbf{P}(2)$ , the induced polarization in the inclusion. We can therefore write

$$\mathbf{E}_{ind}(2; \mathbf{r}) = \frac{\partial}{\partial \mathbf{r}} \int d\mathbf{r}' \frac{\partial}{\partial \mathbf{r}} \cdot \frac{\mathbf{P}(2; \mathbf{r}')}{\epsilon_1 |\mathbf{r} - \mathbf{r}'|} \tag{3.21}$$

Because the applied field  $\mathbf{E}_0$  is uniform the polarization  $\mathbf{P}(2)$  depends only upon  $\mathbf{r}_2$ , the coordinate of the field point relative to  $\mathbf{R}_2$ . Keeping this in mind and using the coordinates indicated in Fig. 2, we can write

$$\mathbf{E}_{ind}(2; \mathbf{r}) = - \frac{\partial}{\partial \mathbf{r}_1} \int d\mathbf{r}'_2 \frac{\partial}{\partial \mathbf{R}} \cdot \frac{\mathbf{P}(2; \mathbf{r}'_2)}{\epsilon_1 |\mathbf{r}_1 - \mathbf{r}'_2 - \mathbf{R}|} \tag{3.22}$$

Now we integrate both sides of this equation over  $\mathbf{R}_2$  in the overlap region, which for fixed  $\mathbf{R}_1$  corresponds to integrating over  $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$  in a sphere of radius  $2a$ . We then get

$$\int_{R < 2a} d\mathbf{R}_2 \mathbf{E}_{ind}(2; \mathbf{r}) = - \frac{\partial}{\partial \mathbf{r}_1} \int d\mathbf{r}'_2 \int d\Omega (2a)^2 \frac{\hat{\mathbf{R}} \cdot \mathbf{P}(2; \mathbf{r}'_2)}{\epsilon_1 |\mathbf{r}_1 - \mathbf{r}'_2 - 2a\hat{\mathbf{R}}|} \tag{3.23}$$

where on the right-hand side we have used Gauss's theorem and  $d\Omega$  is the element of solid angle of the direction of  $\hat{\mathbf{R}}$ . The polarization  $\mathbf{P}(2)$  vanishes except within the inclusion centered at  $\mathbf{R}_2$ , so in the integral on the right in (3.23)  $r'_2 < a$ . On the other hand, we need the integral only for points within the inclusion centered at  $\mathbf{R}_1$ , so we take  $r_1 < a$ . Since  $r_1 < a$  and  $r'_2 < a$

then, referring to Fig. 2,  $|\mathbf{r}_1 - \mathbf{r}'_2| < 2a$  and we can use the familiar expansion<sup>(12)</sup>

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}'_2 - 2a\hat{\mathbf{R}}|} = \sum_{l=0}^{\infty} \frac{|\mathbf{r}_1 - \mathbf{r}'_2|^l}{(2a)^{l+1}} P_l\left(\hat{\mathbf{R}} \cdot \frac{\mathbf{r}_1 - \mathbf{r}'_2}{|\mathbf{r}_1 - \mathbf{r}'_2|}\right) \quad (3.24)$$

Putting this expansion in the integrand of (3.23) and using the orthogonality of the Legendre polynomials, which yields

$$\int d\Omega \hat{\mathbf{R}} \cdot \mathbf{A} P_l(\hat{\mathbf{R}} \cdot \hat{\mathbf{n}}) = \frac{4\pi}{3} \hat{\mathbf{n}} \cdot \mathbf{A} \delta_{l,1} \quad (3.25)$$

for arbitrary  $\hat{\mathbf{n}}$  and  $\mathbf{A}$ , we find

$$\int_{R < 2a} d\mathbf{R}_2 \mathbf{E}_{\text{ind}}(2; \mathbf{r}) = -\frac{4\pi}{3\epsilon_1} \int d\mathbf{r}'_2 \mathbf{P}(2; \mathbf{r}'_2), \quad r_1 < a \quad (3.26)$$

Since the  $\mathbf{P}(2)$  is the induced dipole moment per unit volume, the integral on the right is just  $\mathbf{p}(2)$ , the total induced dipole moment in the inclusion. Hence we have

$$\int_{R < 2a} d\mathbf{R}_2 \mathbf{E}_{\text{ind}}(2; \mathbf{r}) = -\frac{4\pi}{3\epsilon_1} \mathbf{p}(2), \quad r_1 < a \quad (3.27)$$

This result is independent of the field point  $\mathbf{r}$ , i.e., within the inclusion centered at  $\mathbf{R}_1$  the integral over the overlap region of the induced field due to the inclusion centered at  $\mathbf{R}_2$  is uniform. Since  $[\mathbf{p}(1|2) - \mathbf{p}(1)]$  is the dipole moment induced in the inclusion centered at  $\mathbf{R}_1$  due to the field  $\mathbf{E}_{\text{ind}}(2)$ , and since the dipole moment induced in an inclusion by a uniform field is the dipole polarizability  $\alpha$  times the field, we have from (3.27)

$$\int_{R < 2a} d\mathbf{R}_2 [\mathbf{p}(1|2) - \mathbf{p}(1)] = -\frac{4\pi\alpha}{3\epsilon_1} \mathbf{p}(2) = -\frac{4\pi\alpha^2}{3\epsilon_1} \mathbf{E}_0 \quad (3.28)$$

This is our desired result for the overlap region.

Before we proceed to the evaluation of the second-order terms we remark that at this point we can see the equivalence of our expression for these terms with that of Finkel'berg and of Jeffrey. As we noted in Section 2, their expression corresponds to the replacement (2.19) or, in the notation of this present section,

$$\mathbf{E}_{\text{ind}}(2; \mathbf{r}) \rightarrow \mathbf{E}_{\text{ind}}(2; \mathbf{R}_1) \quad (3.29)$$

For the nonoverlap case this is exactly the prescription resulting from the Faxén theorem and which yields (3.18). For the overlap case, as we have just seen, the integral (3.27) is independent of the field point  $\mathbf{r}$ , provided only that  $\mathbf{r}$  is within the inclusion centered at  $\mathbf{R}_1$ . Placing the field point at the center of that inclusion therefore gives the identical result. This equivalence with Finkel'berg and Jeffrey does not persist, however, for higher-

order terms. This will be discussed in more detail in the next article in this series.

### 3.3. Evaluation of the Second-Order Terms

We consider first the evaluation of the integral in the second expression in (2.18). Using (2.13), (3.19), (3.28), and the nonoverlap condition (3.1) we can write

$$\epsilon^*(1|2)\mathbf{E}_0 = \frac{(4\pi n\alpha)^2}{3\epsilon_1} \mathbf{E}_0 + \frac{4\pi\alpha^2}{\epsilon_1} \int_{R>2a} d\mathbf{R}_2 [n(1,2) - n^2] \frac{3\mathbf{E}_0 \cdot \hat{\mathbf{R}}\hat{\mathbf{R}} - \mathbf{E}_0}{R^3} \tag{3.30}$$

where in the remaining integral we have used the notation indicated in Fig. 1 with  $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$  and  $\hat{\mathbf{R}} = \mathbf{R}/R$ . We assume the usual product property of the pair distribution function,

$$n(1,2) \sim n^2, \quad R \rightarrow \infty \tag{3.31}$$

and therefore the integral in (3.30) is absolutely convergent. Because of this absolute convergence we may introduce spherical coordinates centered at  $\mathbf{R}_1$ , writing  $d\mathbf{R}_2 = R^2 dR d\Omega$ , and perform the integral over solid angles first. Since, on account of our assumption of spatial isotropy,  $n(1,2)$  depends only upon  $R$ , we can use the familiar result

$$\int d\Omega \hat{\mathbf{R}}\hat{\mathbf{R}} = \frac{4\pi}{3} \mathbf{1} \tag{3.32}$$

to conclude that the integral in (3.30) vanishes. The only contribution to  $\epsilon^*(1|2)$  comes therefore from the overlap region of the integral in (2.18) and we have the result

$$\epsilon^*(1|2) = \frac{(4\pi n\alpha)^2}{3\epsilon_1} \tag{3.33}$$

We now consider the integral in the first expression in (2.18). Here, on account of (3.1), only the nonoverlap region occurs and, using (3.16) and (3.19), we can write

$$\begin{aligned} \epsilon^*(1,2)\mathbf{E}_0 = 4\pi \int_{R>2a} d\mathbf{R}_2 n(1,2) & \left\{ \left[ \epsilon_1 a^3 a_{10}(R) - \alpha - \frac{2\alpha^2}{\epsilon_1 R^3} \right] \hat{\mathbf{R}} \cdot \mathbf{E}_0 \hat{\mathbf{R}} \right. \\ & \left. + \left\{ \left[ \epsilon_1 a^3 a_{11}(R) - \alpha + \frac{\alpha^2}{\epsilon_1 R^3} \right] (\mathbf{E}_0 - \hat{\mathbf{R}} \cdot \mathbf{E}_0 \hat{\mathbf{R}}) \right\} \right. \end{aligned} \tag{3.34}$$

As one can readily see from the expression (3.13) for  $a_{lm}$ , and as we shall see explicitly in the next section, the quantities within the square brackets in

(3.34) are of order  $R^{-6}$  for large  $R$ . Therefore we again have an absolutely convergent integral in accordance with the general proof given in I. We may therefore introduce spherical coordinates and perform the integration over solid angles using (3.32), extending the integration over  $R$  to  $\infty$ . In this way we find the following expression for  $\epsilon^*(1, 2)$ :

$$\epsilon^*(1, 2) = \frac{(4\pi)^2}{3} \int_{2a}^{\infty} dR R^2 n(1, 2) \left\{ \left[ \epsilon_1 a^3 a_{10}(R) - \alpha - \frac{2\alpha^2}{\epsilon_1 R^3} \right] + 2 \left[ \epsilon_1 a^3 a_{11}(R) - \alpha + \frac{\alpha^2}{\epsilon_1 R^3} \right] \right\} \quad (3.35)$$

Note that the terms  $\propto R^{-3}$  cancel between the two square brackets in the integrand. We keep these terms because for large  $R$  they cancel *within* the square bracket and we want to integrate over the expressions in the two square brackets separately.

Together with the expression (2.15) for the first-order term in the expansion (2.1) for the effective dielectric constant, the results (3.33) and (3.35) are a complete prescription for  $\epsilon^*$  including two-inclusion effects. In order to proceed to the evaluation of the integral in (3.35) we must have a model for the distribution of the inclusions, which leads to a form for  $n(1, 2)$ , and a model for the inclusions themselves, which leads to a prescription for the  $\alpha_l$  and then through (3.13) to forms for  $a_{10}(R)$  and  $a_{11}(R)$ . We discuss the calculation of the  $\alpha_l$  in the next section.

#### 4. MULTIPOLE POLARIZABILITIES

Here we discuss the calculation of the multipole polarizabilities for a number of simple models of the inclusions.

These quantities are defined through (3.4) in terms of the (linear) response of the inclusion to an applied multipole field. For a uniform sphere of dielectric constant  $\epsilon_2$  straightforward application of the electrostatic boundary conditions (continuity of the potential and of  $\epsilon$  times the normal derivative) yields for the  $2^l$ -pole polarizability

$$\alpha_l = \frac{l\epsilon_1(\epsilon_2 - \epsilon_1)}{l\epsilon_2 + (l + 1)\epsilon_1} a^{2l+1} \quad (\text{dielectric sphere}) \quad (4.1)$$

This is the model considered by Jeffrey.<sup>(3)</sup>

In the case of dielectric spheres with an arbitrary radial dependence of their dielectric constant, we determine  $\alpha_l$  by solving the radial equation

$$\frac{d}{dr} \epsilon(r)r^2 \frac{df_l}{dr} - l(l + 1)\epsilon(r)f_l = 0 \quad (4.2)$$

with the condition that  $f_l(r)$ , the radial potential function, be regular at

$r = 0$  and have the form [see (3.4)]

$$f_l(r) = -r^l + \frac{\alpha_l}{\epsilon_1 r^{l+1}}, \quad r > a \quad (4.3)$$

outside the sphere. As an example, consider a spherical shell with inner radius  $b$  and outer radius  $a$ , with dielectric constant  $\epsilon_2$  for  $b < r < a$  and  $\epsilon_1$  for  $0 < r < b$ . In this case one finds by this method

$$\alpha_l = \frac{l\epsilon_1(\epsilon_2 - \epsilon_1)[(l+1)\epsilon_2 + l\epsilon_1](a^{2l+1} - b^{2l+1})a^{2l+1}}{[l\epsilon_2 + (l+1)\epsilon_1][(l+1)\epsilon_2 + l\epsilon_1]a^{2l+1} - l(l+1)(\epsilon_2 - \epsilon_1)^2 b^{2l+1}} \quad (4.4)$$

It is of interest to consider a thin, highly polarizable spherical shell. Thus we define

$$\gamma = \lim_{\substack{\epsilon_2 \rightarrow \infty \\ a-b \rightarrow 0}} \frac{\epsilon_2}{\epsilon_1} \frac{a-b}{a} \quad (4.5)$$

and obtain in this limit

$$\alpha_l = \epsilon_1 \frac{l(l+1)\gamma}{2l+1+l(l+1)\gamma} a^{2l+1} \quad (\text{thin spherical shell}) \quad (4.6)$$

Note that both for the uniform sphere and for the thin spherical shell the coefficients  $\epsilon_1 a^{2l+1}/\alpha_l$ , which occur in the matrix elements (3.12), tend to a constant for large  $l$ . In the limit of large  $\gamma$  in the case of the thin spherical shell and in the limit of large  $\epsilon_2$  for the case of a uniform dielectric sphere the multipole polarizabilities become identical with those for a conducting sphere,

$$\alpha_l = \epsilon_1 a^{2l+1} \quad (\text{conducting sphere}) \quad (4.7)$$

It is convenient to express the multipole polarizabilities using the dipole polarizability  $\alpha_1 = \alpha$  as a parameter. If we do this the results (4.1) and (4.16) can be summarized in the form

$$\alpha_l = \alpha \times \begin{cases} \frac{3l\epsilon_1 a^{2l+1}}{(l-1)\alpha + (2l+1)\epsilon_1 a^3} & (\text{dielectric sphere}) \\ \frac{3l(l+1)\epsilon_1 a^{2l+1}}{(3l+2)(l-1)\alpha + 2(2l+1)\epsilon_1 a^3} & (\text{spherical shell}) \end{cases} \quad (4.8)$$

## 5. NUMERICAL RESULTS

In this section we discuss the calculation of the two-body cluster integral (3.35) for  $\epsilon^*(1,2)$ , using the models discussed in Section 4 for

determining the multipole polarizabilities. We first consider the case of inclusions which behave electrically like polarizable points, with only dipolar interactions. For this case one obtains simple closed-form expressions for the quantities  $a_{10}(R)$  and  $a_{11}(R)$  in the integrand of (3.35). We discuss the integral, which depends upon the form of the pair distribution function  $n(1,2)$ , and give the exact result for the dilute hard-sphere case. We then go on to discuss more general models, showing how the exact results obtained for the polarizable point case can be used as the basis of an efficient method for the numerical evaluation of the expression (3.13). We then give tables of selected numerical results.

### 5.1. Polarizable Point Inclusions

Here we consider the case of inclusions which have only a dipolar polarizability, i.e., for which the  $2^l$ -pole polarizability is given by

$$\alpha_l = \begin{cases} \alpha, & l = 1 \\ 0, & l = 2, 3, \dots \end{cases} \quad (5.1)$$

This can be considered as a limiting case of the dielectric sphere model by taking in Eq. (4.8) the limit  $a \rightarrow 0$ , while keeping  $\alpha$  fixed. However, for the statistical properties of the inclusions we keep a fixed nonzero radius  $a$  to ensure nonoverlapping spheres. We call this the polarizable point model since it corresponds to a zero-radius polarizable sphere at the center of a sphere of radius  $a$ .

For this case the expression (3.13) can be evaluated by a straightforward limiting process, although it is simpler to go back to the equation (3.11) for  $a_{lm}$ . The result is that  $a_{1m}$  is the reciprocal of the 11 element of the matrix  $M^m$ ,

$$a_{1m} = (M_{11}^m)^{-1} \quad (5.2)$$

and  $a_{lm}$  vanishes for  $l = 2, 3, \dots$ . Using the expression (3.12) for  $M_{11}^m$  we find

$$a^3 a_{10} = \frac{\alpha}{\epsilon_1 - 2\alpha/R^3}, \quad a^3 a_{11} = \frac{\alpha}{\epsilon_1 + \alpha/R^3} \quad (5.3)$$

Putting these expressions in (3.35) we can write, after some rearrangement,

$$\epsilon^*(1,2) = 2(4\pi\alpha)^2 \int_{2a}^{\infty} dR R^2 n(1,2) \frac{\alpha}{(\epsilon_1 R^3 - 2\alpha)(\epsilon_1 R^3 + \alpha)} \quad (5.4)$$

As an example we consider the integral (5.4) for the case where the pair distribution function  $n(1,2)$  is that corresponding to a dilute system of hard spheres of radius  $a$ ,

$$n(1,2) = \begin{cases} 0, & R < 2a \\ n^2, & R > 2a \end{cases} \quad (5.5)$$



Then we find

$$\epsilon^*(1,2) = 2 \left( \frac{4\pi n\alpha}{3\epsilon_1} \right)^2 \log \frac{8\epsilon_1 a^3 + \alpha}{8\epsilon_1 a^3 - 2\alpha} \quad (5.6)$$

Combining this result with (3.33) and (2.15), the expansion (2.1) for the effective dielectric constant becomes

$$\epsilon^* = \epsilon_1 + 4\pi n\alpha + \epsilon_1 \left( \frac{4\pi n\alpha}{3\epsilon_1} \right)^2 \left( 3 + 2 \log \frac{8\epsilon_1 a^3 + \alpha}{8\epsilon_1 a^3 - 2\alpha} \right) \quad (5.7)$$

which we repeat is an expression for  $\epsilon^*$  for the case of polarizable point inclusions distributed according to the law for a dilute hard-sphere gas.

## 5.2. Other Models

There is a difficulty associated with the numerical evaluation of the integral (3.35) for  $\epsilon^*(1,2)$  arising from the cancellation among the terms within square brackets. As we see explicitly in the above case of polarizable point inclusions, this cancellation is nearly complete, especially for large  $R$  where it leads to the absolute convergence of the integral. This means that when we use (3.13) to calculate  $a_{1m}$  to a given accuracy, most of this accuracy is lost in the cancellation. We must, therefore, find a method to evaluate (3.35) which allows us to calculate with acceptable numerical accuracy.

What we do is to write

$$a_{1m} = (M_{11}^m)^{-1} + b_{1m} \quad (5.8)$$

Here the first term on the right is exactly what one would have for the case of polarizable point inclusions with the same dipole polarizability as that of the model we are considering. For this case the cancellation within the integrand of (3.33) is exact and leads to the integral (5.4) for which numerical accuracy is no problem. For  $b_{1m}$  we have the formula

$$b_{1m} = -(M_{11}^m)^{-1} \frac{\det(\tilde{M}^m)}{\det(M^m)} \quad (5.9)$$

where  $M^m$  is the matrix whose elements are given by (3.12), and  $\tilde{M}^m$  is the same matrix but with the 11 elements set equal to zero. That is, the matrix elements of  $\tilde{M}^m$  are given by

$$\tilde{M}_{i'j'}^m = (1 - \delta_{i,1}\delta_{j',1})M_{i'j'}^m \quad (5.10)$$

The formula (5.9) follows from (5.8) and (3.13) with the observation

$$\det(M^m) = M_{11}^m \text{cof}(M_{11}^m) + \det(\tilde{M}^m) \quad (5.11)$$

As in the case of the formula (3.13), the operational meaning of the ratio of

infinite determinants in (5.9) is the limit at  $n \rightarrow \infty$  of the corresponding ratio formed with the  $n$ th truncation.

This then is our prescription for the evaluation of (3.35), given a model which allows us to calculate the multipole polarizabilities. First we form (5.4) with  $\alpha = \alpha_1$ , the dipole polarizability. Then we add to that an integral of the form (3.35) but with  $a_{1m}$  replaced by  $b_{1m}$ , given by (5.9). We evaluate the integrals numerically and evaluate  $b_{1m}$  using a sufficiently large truncation of the determinants in (5.9). In practice this is a rapid and effective scheme.

### 5.3. Results

Numerical results for the two-body cluster integrals for the case of inclusions distributed according to the dilute hard-sphere case (5.5) are presented in Table I for several models of the inclusions. For various values of  $\alpha/\epsilon_1 a^3$ , where  $\alpha$  is the dipole polarizability and  $a$  the radius of the inclusion, we list the values of the two-body integrals divided by  $\epsilon_1 c^2$ , where the volume fraction  $c = 4\pi n a^3/3$ . Using (3.33) we see that the overlap contribution is

$$\epsilon^*(1|2)/\epsilon_1 c^2 = 3(\alpha/\epsilon_1 a^3)^2 \quad (5.12)$$

independent of the model. On the other hand, from inspection of (3.35), we see that the dependence of the nonoverlap contribution  $\epsilon^*(1,2)/\epsilon_1 c^2$  upon the model is only through the quantities  $\alpha_l/\epsilon_1 a^{2l+1}$ , and from inspection of (4.8) we see that for the models considered these quantities depend only upon  $\alpha/\epsilon_1 a^3$ . In this sense the entries in Table I depend only upon the model. In Table I we list first the overlap contribution  $\epsilon^*(1|2)/\epsilon_1 c^2$  and then for each model the nonoverlap contribution  $\epsilon^*(1,2)/\epsilon_1 c^2$  together with the total second-order contribution  $(\epsilon_2^*)_2/\epsilon_1 c^2$ , where

$$(\epsilon_2^*)_2 = \epsilon^*(1|2) + \epsilon^*(1,2) \quad (5.13)$$

In general the overlap contribution is larger than the nonoverlap contribution although for larger values of  $\alpha/\epsilon_1 a^3$ , the difference is not so great. The effect of the multipole polarizabilities is seen in the difference between the nonoverlap contributions of the polarizable point model and that of the other models. A qualitative explanation as to why the effects of the multipole polarizabilities for the spherical shell model are larger than those for the dielectric sphere model is that the higher multipole polarizabilities depend upon the dielectric response near  $r = a$ . (The apparent discrepancy for  $\alpha/\epsilon_1 a^3 = 1.1$  is because  $\epsilon_2 < 0$  for this value.)

Note that the overlap contribution (5.12) corresponds to the term of second order in the density in  $\epsilon_{CM}$ , where  $\epsilon_{CM}$  is the dielectric constant

**Table 1. Reduced Two-Inclusion Contributions to the Effective Dielectric Constant  $\epsilon^*$  as a Function of the Reduced Dipole Polarizability  $\alpha/\epsilon_1 a^3$  for Three Models Discussed in the Text. The Overlap Contribution  $\epsilon^{*(1|2)}$  Is Defined in Eq. (3.33) and Is Independent of the Model. The Nonoverlap Contribution  $\epsilon^{*(1,2)}$  Is Defined in Eq. (3.35) and Is Evaluated for the Dilute Hard-Sphere Case (5.5). The Total Second-Order Contribution  $(\epsilon^*)_2 = \epsilon^{*(1|2)} + \epsilon^{*(1,2)}$ . The Volume Fraction  $c = 4\pi n a^3/3$ . For the Dielectric-Sphere Model These Results Duplicate Those of Jeffrey (Ref. 3).**

$\alpha/\epsilon_1 a^3$	Overlap		Polarizable point		Dielectric Sphere		Spherical Shell	
	$\epsilon^{*(1 2)}/\epsilon_1 c^2$	$\epsilon^{*(1,2)}/\epsilon_1 c^2$	Total	Nonoverlap	Total	Nonoverlap	Total	Nonoverlap
-0.5	0.75	-0.091	0.660	-0.162	0.588	-0.247	0.503	-0.247
-0.4	0.48	-0.047	0.433	-0.082	0.399	-0.138	0.341	-0.138
-0.3	0.27	-0.020	0.250	-0.034	0.236	-0.101	0.169	-0.101
-0.2	0.12	-0.006	0.114	-0.010	0.110	-0.018	0.102	-0.018
-0.1	0.03	-0.001	0.029	-0.001	0.029	-0.002	0.028	-0.002
0.	0.	0.	0.	0.	0.	0.	0.	0.
0.2	0.12	0.006	0.126	0.010	0.130	0.012	0.132	0.012
0.4	0.48	0.049	0.529	0.083	0.563	0.095	0.575	0.095
0.6	1.08	0.169	1.249	0.290	1.370	0.316	1.396	0.316
0.8	1.92	0.408	2.328	0.718	2.638	0.754	2.674	0.754
0.9	2.43	0.586	3.016	1.055	3.485	1.083	3.513	1.083
1.0	3.	0.811	3.811	1.506	4.506	1.506	4.506	1.506
1.1	3.63	1.090	4.720	2.121	5.751	2.041	5.671	2.041

given by the Clausius–Mossotti formula:

$$\frac{\epsilon_{\text{CM}} - \epsilon_1}{\epsilon_{\text{CM}} + 2\epsilon_1} = \frac{4\pi n\alpha}{3\epsilon_1} \quad (5.14)$$

The nonoverlap contribution, therefore, represents a correction to the Clausius–Mossotti result. For all cases the sign of the nonoverlap contribution  $\epsilon^*(1,2)$  is the same as that of the polarizability  $\alpha$ . For the dielectric sphere case this follows from the Hashin–Shtrikman theorem,<sup>(13)</sup> which states that for an isotropic two-phase (i.e., with only two values of  $\epsilon$ ) dielectric medium the Clausius–Mossotti value  $\epsilon_{\text{CM}}$  is a lower bound for the effective dielectric constant when  $\epsilon_2 > \epsilon_1$  and an upper bound with  $\epsilon_2 < \epsilon_1$ . We can get a measure of the deviation,  $S$ , from the Clausius–Mossotti result by forming the quantity<sup>(14)</sup>

$$S = \frac{\epsilon^* - \epsilon_1}{\epsilon^* + 2\epsilon_1} \cdot \frac{3\epsilon_1}{4\pi n\alpha} - 1 \quad (5.15)$$

which has the value zero for  $\epsilon^* = \epsilon_{\text{CM}}$ . Inserting our expansion (2.1), and using (2.15) and (3.33), we find through second-order terms

$$S/c = \frac{1}{3} \frac{\epsilon^*(1,2)}{\epsilon_1 c^2} \cdot \frac{\epsilon_1 a^3}{\alpha} \quad (5.16)$$

In Table II we list this quantity for the various models as calculated from

**Table II. Corrections to the Clausius–Mossotti Formula for Three Models of the Inclusions. For Each Model the Reduced Deviation  $S/c$  Defined in Eq. (5.16) Is Given as a Function of the Reduced Dipole Polarizability  $\alpha/\epsilon_1 a^3$ , Using the Results from Table I.**

$\alpha/\epsilon_1 a^3$	Polarizable point	Dielectric sphere	Spherical shell
– 0.5	0.061	0.108	0.165
– 0.4	0.039	0.068	0.115
– 0.3	0.022	0.038	0.112
– 0.2	0.010	0.017	0.030
– 0.1	0.003	0.003	0.007
0.	0.	0.	0.
0.2	0.010	0.017	0.020
0.4	0.041	0.069	0.079
0.6	0.094	0.161	0.176
0.8	0.170	0.299	0.314
0.9	0.217	0.391	0.401
1.0	0.270	0.502	0.502
1.1	0.330	0.643	0.618

the data in Table I. The deviations from Clausius–Mossotti are small but nevertheless significant, again in particular for the larger values of  $\alpha/\epsilon_1 a^3$ . We should emphasize also that the deviations are about a factor of 2 larger for the dielectric sphere and spherical shell than for the polarizable point model. This shows that the contributions from the higher-order multipoles can be appreciable and that the polarizable point (dipole–induced dipole) approximation must be used with caution in practical situations.

## 6. APPLICATION TO NONPOLAR MOLECULES

So far in our discussion we have had in mind the application to a suspension of macroscopic spheres. In this section we make some remarks on the application to a gas of nonpolar molecules.

We first note that (with  $\epsilon_1 = 1$ ) the result (5.4) is equivalent with that obtained by Buckingham and Pople<sup>(4)</sup> and by Isihara<sup>(15)</sup> in their discussions of the virial expansion of the Clausius–Mossotti function  $(\epsilon^* - 1)/(\epsilon^* + 2)$ . We have commented on this expansion in paper I. Nijboer<sup>(16)</sup> found the same result by a resummation of the Kirkwood–Yvon series expansion. We remark incidentally that the statement by Buckingham and Pople that the singularity in the integral (5.4) at  $R^3 = 2\alpha/\epsilon_1$  is artificial is not correct. This singularity corresponds to what in another context is called the image enhancement effect.<sup>(17)</sup> It will be significant, however, only for highly polarizable inclusions, for which  $\alpha \geq 4\epsilon_1 a^3$ , and we assume here that this is not the case. We hope to return to this interesting point in a later publication.

Next we remark that in the application of our results to the case of nonpolar molecules as opposed to macroscopic objects a number of important differences must be recognized. The first is the nonoverlap condition (3.1). Molecules can overlap despite the strong short-range repulsive forces, and when they do overlap there is evidence that their polarizability is much reduced.<sup>(18)</sup> Another difference arises from the long-range van der Waals forces, which have their origin in the fluctuating multipole moments in the molecule. These fluctuations, which are quantum mechanical in origin, induce a polarization of the electron cloud in nearby molecules which, in addition to giving rise to an attractive force, causes changes in their polarizability.<sup>(19)</sup> This appears as a quantum mechanical correction to  $\mathbf{p}(1; 2)$ , the dipole moment in 1 in the presence of 2, which in some cases can be as large as the effect we calculate.<sup>(18)</sup> Our general formalism can be extended to take into account these differences, but that is beyond the scope of this present work. Nevertheless, it is of interest to apply our calculation to the molecular case, primarily to show the magnitude of the

effect due to higher multipole polarizabilities, which have in general been neglected in previous calculations. We consider the monoatomic gases He and Ar at low densities. We treat the molecule as a dielectric sphere for purposes of calculating the higher multipole polarizabilities, fitting the form (4.8) with the experimentally determined polarizability  $\alpha$  and Lennard–Jones diameter  $\sigma = 2a$ . We take into account the attractive intermolecular force by replacing the hard-sphere form (5.5) of the pair distribution function with the form

$$n(1,2) = \begin{cases} 0, & R < 2a \\ n^2 \exp \left[ \frac{4\epsilon}{kT} \left( \frac{2a}{R} \right)^6 \right], & R > 2a \end{cases} \quad (6.1)$$

where  $\epsilon$  is the experimentally determined Lennard–Jones parameter. For He we take  $\alpha = 0.2052 \text{ \AA}^3$ ,  $a = 1.278 \text{ \AA}$ , and  $\epsilon = 0.86 \text{ meV}$ . We find at  $T = 300 \text{ K}$

$$\frac{S}{c} = \begin{cases} 0.00431, & \text{dielectric sphere} \\ 0.00244, & \text{polarizable point (DID)} \end{cases} \quad (6.2)$$

For Ar we take  $\alpha = 1.643 \text{ \AA}^3$ ,  $a = 1.702 \text{ \AA}$ , and  $\epsilon = 10 \text{ meV}$ . We find at  $T = 300 \text{ K}$

$$\frac{S}{c} = \begin{cases} 0.104, & \text{dielectric sphere} \\ 0.055, & \text{polarizable point (DID)} \end{cases} \quad (6.3)$$

Thus we see that inclusion of the higher multipole polarizabilities corresponds to about a factor of 2 increase in the predicted corrections to the Clausius–Mossotti result. Despite the crudity of our calculation this conclusion is significant. There are quantitatively important corrections to the dipole-induced-dipole approximation which is customarily employed in the theory of nonpolar liquids.

## ACKNOWLEDGMENT

We are indebted to the NATO Research Grants Programme, Grant No. 1945, for support for this work.

## APPENDIX A. THE FAXÉN LAW

Consider a spherically symmetric inclusion which is placed in a non-uniform external field  $E_0(\mathbf{r})$  whose sources are fixed and outside the inclusion. The theorem we here demonstrate states that the induced dipole moment is the dipole polarizability times the external field at the center of

the inclusion, i.e., the same as if the inclusion were placed in a uniform field with that value.

To show this we can take the center of the inclusion to be the origin. Let  $a$  be the radius of the inclusion and  $b > a$  the radius of a sphere centered at the origin which excludes the sources of the applied field. Then within the sphere of radius  $b$  the external field must be derivable from a harmonic potential  $\Phi_0$  of the form

$$\Phi_0(\mathbf{r}) = - \sum_{l=1}^{\infty} \sum_{m=-l}^l B_{lm} r^l Y_{lm}(\theta, \phi), \quad 0 < r < b \quad (\text{A1})$$

where  $\theta$  and  $\phi$  are the polar angles of  $\mathbf{r}$  and  $Y_{lm}$  is the spherical harmonic.<sup>(7)</sup> When the inclusion is placed in the field  $\mathbf{E}_0$  the resulting field will be of the form  $\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_{\text{ind}}$ , where  $\mathbf{E}_{\text{ind}}$  is the field due to the polarization induced in the inclusion. Because of the spherical symmetry of the inclusion the field  $\mathbf{E}$  in the region outside the inclusion but inside the sphere of radius  $b$  must be derivable from a potential  $\Phi$  which is a superposition of potentials of the form (3.4) with  $Y_{lm}(\theta, \phi)$  replacing  $P_l^m(\cos \theta)\cos m\phi$ . Hence

$$\Phi_0(\mathbf{r}) = \sum_{l=1}^{\infty} \sum_{m=-l}^l B_{lm} \left( -r^l + \frac{\alpha_l}{\epsilon_1 r^{l+1}} \right) Y_{lm}(\theta, \phi) \quad (\text{A2})$$

From the  $l = 1$  terms in this sum we identify the induced dipole moment  $\mathbf{p}$ , as in (3.14). Thus

$$\frac{\mathbf{p} \cdot \mathbf{r}}{\epsilon_1 r^3} = \frac{\alpha_1}{\epsilon_1 r^2} \sum_{m=-1}^1 B_{1m} Y_{1m}(\theta, \phi) \quad (\text{A3})$$

or, multiplying both sides by  $\epsilon_1 r^3$  and forming the gradient,

$$\mathbf{p} = \alpha_1 \text{grad} \sum_{m=-1}^1 B_{1m} r Y_{1m}(\theta, \phi) \quad (\text{A4})$$

But, using (A1), the applied field at the origin is

$$\begin{aligned} \mathbf{E}_0(0) &= - \{ \text{grad} \Phi_0(\mathbf{r}) \}_{r=0} \\ &= \text{grad} \sum_{m=-1}^1 B_{1m} r Y_{1m}(\theta, \phi) \end{aligned} \quad (\text{A5})$$

where we have used the fact that  $r^l Y_{lm}(\theta, \phi)$  is a homogeneous polynomial of degree  $l$  in the Cartesian components of  $\mathbf{r}$ . Comparing (A4) and (A5) and writing  $\alpha_1 = \alpha$ , the dipole polarizability, we have

$$\mathbf{p} = \alpha \mathbf{E}_0(0) \quad (\text{A6})$$

which is the Faxén law.

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