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Citation: *The Journal of Chemical Physics* **82**, 394 (1985); doi: 10.1063/1.448758

View online: <http://dx.doi.org/10.1063/1.448758>

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# On the effective interaction of test multipoles in polar fluids. II. Finite-volume spherical geometry

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(Received 30 August 1984; accepted 19 September 1984)

The effective interaction energy of two test particles immersed in a molecular fluid of finite volume is defined and expressed in terms of the molecular pair correlation function. The specific problem of electric multipoles immersed in a fluid of polar nonpolarizable molecules filling a spherical volume is then analyzed in detail. The long-range part of the effective interaction of the test multipoles is obtained to leading order in  $1/V$ . A comparison is made with similar results obtained in the case of infinite volume.

## I. INTRODUCTION

Two electric probes, when immersed in a dielectric fluid, do not interact the way they would were the fluid not present. A macroscopic calculation of this interaction can be done through classical electrostatics, supplemented with boundary conditions appropriate to the probe-fluid interface. A microscopic calculation, on the other hand, rests upon statistical mechanics, as elucidated in the important work of Jepsen and Friedman,<sup>1,2</sup> Neinhuis and Deutch,<sup>3,4</sup> and Høye and Stell.<sup>5,6</sup>

Of all types of electric probes, particularly simple ones are test multipoles. They are electric multipoles of arbitrary order and very small moments, so that their potential energy of interaction with fluid molecules is much smaller than the intermolecular potential energy. An exact calculation of the long-range part of the effective interaction energy of two test multipoles immersed in an infinite sea of dielectric fluid was carried in a previous paper,<sup>7</sup> hereafter referred to as I.

The present paper is concerned with a similar calculation, but for a system contained in a finite volume. In such a situation, small but complicated surface effects and inhomogeneities are expected to occur. Thus our calculation of the long-range part of the effective interaction energy of two test multipoles will no longer be exact. Nevertheless, it will be correct to leading order in  $1/V$ , where  $V$  is the total volume of the system. And these contributions will reveal rather significant features.

Apart from the fact that all real systems are bounded some way or other, there are several reasons why the study of finite-volume systems is of importance. Thus it is particularly interesting to see what happens when the thermodynamic limit is taken at the very end of a given calculation, rather than at some intermediate step. Furthermore, there are systems whose volumes are not only finite but definitely small, namely, the ones studied in computer simulations. Their proper understanding is impossible without taking into account finite-volume effects.

Our paper is organized as follows: In Sec. II, we define the effective interaction energy  $\Phi_{LM}^V$  of two particles  $L$  and  $M$  immersed in a molecular fluid of volume  $V$ .

We then obtain a formula for  $\Phi_{LM}^V$  in terms of the molecular pair correlation function. In Sec. III, we particularize our system to test multipoles immersed in a fluid of polar nonpolarizable molecules contained in a spherical volume. All leading contributions (in  $1/V$ ) to the long-range part of  $\Phi_{LM}^V$  are computed. Our results are analyzed in Sec. IV where a comparison is made with the case of infinite volume considered in paper I.

## II. EFFECTIVE INTERACTION BETWEEN TEST PARTICLES IN A FINITE VOLUME

We consider two test particles, of type  $L$  and  $M$  respectively, immersed in a fluid of  $(N-2)$  identical molecules of type  $F$ . The full system is contained in some finite volume  $V$ . Let the coordinates (both spatial and orientational) of the test particles be denoted by (1) and (2), and those of the molecules by (3), (4),  $\dots$ ,  $(N)$ . The potential energy of the system can be written as

$$\begin{aligned} U(1, 2, 3, \dots, N) &= \phi_{LM}(1, 2) + \sum_{i=3}^N \{ \phi_{LF}(1, i) + \phi_{MF}(2, i) \} \\ &+ \sum_{i>j>2}^N \phi_{FF}(i, j). \end{aligned} \quad (2.1)$$

The probability density of the molecules and test particles is proportional to

$$\exp\{-\beta U(1, 2, \dots, N)\},$$

where  $\beta = (kT)^{-1}$ . Furthermore, the reduced probability density of the two test particles, denoted by  $\rho_{LM}^V(1, 2)$  and obtained by averaging over all molecular coordinates, is given by

$$\begin{aligned} \rho_{LM}^V(1, 2) &= \frac{\int d(3) \dots d(N) \exp\{-\beta U(1, 2, \dots, N)\}}{\int d(1) d(2) \dots d(N) \exp\{-\beta U(1, 2, \dots, N)\}}. \end{aligned} \quad (2.2)$$

All spatial integrations in Eq. (2.2) are restricted to  $V$ . The denominator is simply a normalization constant.

As the full probability density of the system is proportional to the exponential of  $-\beta$  times its energy, the reduced probability density of the test particles is proportional to the exponential of  $-\beta$  times their effective energy. This effective energy is made up of three separate contributions. Two of them, which we denote by  $f_L^V(1)$  and  $f_M^V(2)$ , depend on the coordinates of each test particle separately.  $f_L^V(1)$  would remain and contribute, for instance, even if the second particle was altogether absent. The presence of  $f_L^V(1)$  and  $f_M^V(2)$  comes from the fact that the system, being restricted to a finite volume, lacks translational invariance. The third contribution is denoted by  $\Phi_{LM}^V(1, 2)$ . It is the effective interaction energy of the two test particles, and it vanishes unless both particles are present. Thus we can write

$$\rho_{LM}^V(1, 2) = C \exp\{-\beta[f_L^V(1) + f_M^V(2) + \Phi_{LM}^V(1, 2)]\}. \quad (2.3)$$

Here  $C$  is a normalization constant having the dimensions of  $V^{-2}$ .

As explained in paper I, the specification that particles (1) and (2) are test particles means that their interaction with fluid molecules is weak. Formally, this can be expressed by introducing a small parameter, say  $\lambda$ , such that  $\phi_{FF}$  is of zeroth order,  $\phi_{LF}$  and  $\phi_{MF}$  of first order, and  $\phi_{LM}$  of second order in  $\lambda$ . One then assumes that quantities of interest relating to the test particles [e.g.,  $\Phi_{LM}^V(1, 2)$ ] can be expanded in a power series in  $\lambda$ . This means that for sufficiently small  $\lambda$ , i.e., for genuine test particles, only the first nonvanishing term of the series contributes substantially. Accordingly, we shall be interested in computing the leading term of  $\Phi_{LM}^V$ , the effective interaction energy, in the small parameter  $\lambda$ . Note that the small parameter is understood to be included in the definition of  $\phi_{LM}$ , etc., so that it will not be displayed explicitly.

The formula we want to derive for  $\Phi_{LM}^V(1, 2)$  can now be obtained in the following way. In the numerator on the right-hand side of Eq. (2.2) the exponential is expanded up to second order in the small parameter. The various terms are then rearranged to put  $\rho_{LM}^V(1, 2)$  in the form of Eq. (2.3). Since the calculation has much in common with the corresponding one in paper I, we will skip directly to the results. It is useful to introduce the following definitions:

$$\mathcal{J} = \int d(3) \cdots d(N) \exp\left[-\beta \sum_{i>j>2}^N \phi_{FF}(i, j)\right], \quad (2.4)$$

$$\rho_F^V(3) = \frac{N-2}{\mathcal{J}} \int d(4) \cdots d(N) \times \exp\left[-\beta \sum_{i>j>2}^N \phi_{FF}(i, j)\right], \quad (2.5)$$

$$\rho_{FF}^V(3, 4) = \frac{(N-2)(N-3)}{\mathcal{J}} \int d(5) \cdots d(N)$$

$$\times \exp\left[-\beta \sum_{i>j>2}^N \phi_{FF}(i, j)\right], \quad (2.6)$$

$$\rho_{FF}^V(3, 4) = \rho_F^V(3)\rho_F^V(4)\{1 + h_{FF}^V(3, 4)\}. \quad (2.7)$$

Here  $\rho_F^V(3)$  and  $\rho_{FF}^V(3, 4)$  are the reduced probability densities for one and two fluid molecules, respectively.  $h_{FF}^V(3, 4)$  is the molecular pair correlation function. The formula obtained for the effective interaction energy of the two test particles can be written as

$$\begin{aligned} \Phi_{LM}^V(1, 2) = & \phi_{LM}(1, 2) - \beta \int d(3) \rho_F^V(3) \phi_{LF}(1, 3) \\ & \times \phi_{FM}(3, 2) - \beta \int d(3) d(4) \rho_F^V(3) \rho_F^V(4) \\ & \times \phi_{LF}(1, 3) h_{FF}^V(3, 4) \phi_{FM}(4, 2). \end{aligned} \quad (2.8)$$

Here  $\phi_{FM}(3, 2) \equiv \phi_{MF}(2, 3)$ . All spatial integrations are restricted to  $V$ . The calculation of  $\Phi_{LM}^V(1, 2)$  also yields formulas for  $f_L^V(1)$  and  $f_M^V(2)$ , namely,

$$\begin{aligned} f_L^V(1) = & \int d(3) \rho_F^V(3) \left\{ \phi_{LF}(1, 3) - \frac{\beta}{2} [\phi_{LF}(1, 3)]^2 \right. \\ & - \frac{\beta}{2} \int d(4) \rho_F^V(4) h_{FF}^V(3, 4) \\ & \left. \times \phi_{LF}(1, 3) \phi_{LF}(1, 4) \right\}, \end{aligned} \quad (2.9)$$

$$\begin{aligned} f_M^V(2) = & \int d(3) \rho_F^V(3) \left\{ \phi_{MF}(2, 3) - \frac{\beta}{2} [\phi_{MF}(2, 3)]^2 \right. \\ & - \frac{\beta}{2} \int d(4) \rho_F^V(4) h_{FF}^V(3, 4) \\ & \left. \times \phi_{MF}(2, 3) \phi_{MF}(2, 4) \right\}. \end{aligned} \quad (2.10)$$

It is interesting to see how Eqs. (2.8)–(2.10) reduce to the results of paper I in the case of infinite volume (and infinite  $N$ ). Let  $\phi_{LM}$ ,  $\phi_{LF}$ ,  $\phi_{MF}$ , and  $\phi_{FF}$  be rotationally and translationally invariant. That is, let  $\phi_{LF}(1, 3)$ , for instance, depend not on (1) and (3) separately, but only on relative position and orientation. Then, in the limit of infinite  $V$ , Eqs. (2.5)–(2.7) imply that  $\rho_F^V(3)$  becomes a constant, and  $\rho_{FF}^V(3, 4)$  and  $h_{FF}^V(3, 4)$  only depend on relative coordinates. Moreover,  $f_L^V(1)$  and  $f_M^V(2)$  also become constants. This means that Eq. (2.3) reduces to

$$\rho_{LM}^V(1, 2) = C' \exp[-\beta \Phi_{LM}^V(1, 2)],$$

where  $C'$  is a constant and  $\Phi_{LM}^V$  is given by Eq. (2.8) in the limit of infinite volume. This coincides with the results of paper I.

### III. TEST MULTIPOLES IN A SPHERICAL DIELECTRIC

The considerations of Sec. II will now be applied to the case of electric multipoles in a dielectric fluid. We consider a system of  $N-2$  identical molecules contained in a spherical volume  $V$ . The molecules are assumed to be polar and nonpolarizable, i.e., they carry permanent

dipole moments of fixed magnitude  $\mu$ . Thus molecular interactions come from long-range dipole-dipole forces in addition to complicated short-range forces. We also assume that the molecules share the cylindrical symmetry of their dipole moments. A given molecule is then fully specified by its position and moment orientation.

Let two point-like electric test multipoles of order  $L$  and  $M$ , respectively, be immersed in the fluid. We recall the parameterization used in Appendix A of paper I. The multipole  $L$ , for instance, is specified by a completely symmetric three-dimensional  $L$ th rank tensor  $L_{\alpha_1 \dots \alpha_L}$ , whose components are real and satisfy the constraints

$$L_{\alpha\alpha\alpha_3 \dots \alpha_L} = 0. \quad (3.1)$$

Summation over repeated indices is understood. Furthermore, for any vector  $\mathbf{v}$  we define  $(L \cdot \mathbf{v})$  and  $(L \cdot \mathbf{v})_\alpha$  as

$$(L \cdot \mathbf{v}) = L_{\alpha_1 \dots \alpha_L} v_{\alpha_1} \dots v_{\alpha_L},$$

$$(L \cdot \mathbf{v})_\alpha = L_{\alpha\alpha_2 \dots \alpha_L} v_{\alpha_2} \dots v_{\alpha_L}. \quad (3.2)$$

Similarly, the multipole  $M$  is specified by an  $M$ th rank tensor  $M_{\beta_1 \dots \beta_M}$ .

If multipole  $L$  is at  $\mathbf{r}_1$  and multipole  $M$  is at  $\mathbf{r}_2$ , their potential energy of interaction is given by

$$\phi_{LM}(1, 2) = \frac{1}{(2L-1)!!} \frac{1}{(2M-1)!!}$$

$$\times (L \cdot \nabla^{(1)})(M \cdot \nabla^{(2)}) \frac{1}{r_{12}}. \quad (3.3)$$

Here  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$  and  $\nabla^{(1)}$ , for instance, is the gradient operator with respect to  $\mathbf{r}_1$ .

If molecule (3) has position  $\mathbf{r}_3$  and dipole moment parallel to the unit vector  $\hat{\mathbf{s}}$ , the interaction between the dipole and multipole  $L$  is given by

$$\phi_{L\mu}(1, 3) = \frac{\mu}{(2L-1)!!} \left\{ (L \cdot \nabla^{(1)})(\hat{\mathbf{s}} \cdot \nabla^{(3)}) \frac{1}{r_{13}} \right.$$

$$\left. - \frac{4\pi L}{2L+1} \eta_L \hat{\mathbf{s}}_\alpha (L \cdot \nabla^{(1)})_\alpha \delta(\mathbf{r}_{13}) \right\}. \quad (3.4)$$

As explained in paper I,  $\eta_L$  is a real constant which specifies the singularity of  $\phi_{L\mu}(1, 3)$  at  $r_{13} = 0$ .<sup>8</sup> Similarly, the interaction between multipole  $M$  and the dipole moment  $\mu\hat{\mathbf{l}}$  of molecule (4) at  $\mathbf{r}_4$  is

$$\phi_{M\mu}(2, 4) = \frac{\mu}{(2M-1)!!} \left\{ (M \cdot \nabla^{(2)})(\hat{\mathbf{l}} \cdot \nabla^{(4)}) \frac{1}{r_{24}} \right.$$

$$\left. - \frac{4\pi M}{2M+1} \eta_M \hat{\mathbf{l}}_\beta (M \cdot \nabla^{(2)})_\beta \delta(\mathbf{r}_{24}) \right\}. \quad (3.5)$$

We want to compute the long-range part of  $\Phi_{LM}^V(1, 2)$ , the effective interaction energy of the two test multipoles. Looking at Eq. (2.8) we see that it involves, among other things, the multipole-molecule potential energy  $\phi_{LF}(1, 3)$ . Included in  $\phi_{LF}(1, 3)$  is the multipole-dipole term  $\phi_{L\mu}(1, 3)$ , given in Eq. (3.4). In general,  $\phi_{LF}(1, 3)$  will also include other terms, if for instance the molecule has a quadrupole moment, etc. These other terms, however, all have range shorter than  $\phi_{L\mu}(1, 3)$ . It was shown

in paper I that such short-range terms do not contribute to the long-range part of  $\Phi_{LM}^V$ . For the case of finite volume, a similar argument establishes the same result to leading order in  $1/V$ . Thus we shall use Eq. (2.8), with  $\phi_{LF}$  and  $\phi_{FM}$  given by Eqs. (3.4) and (3.5).

The pair correlation function  $h_{FF}^V$  for a system of polar molecules in a finite volume has been investigated by Nienhuis and Deutch.<sup>3</sup> They have shown that  $h_{FF}^V(3, 4)$  can be approximated by a sum of two terms, which we write as<sup>9</sup>

$$h_{FF}^V(3, 4) = h_{FF}^0(3, 4) + h_{FF}^1(3, 4). \quad (3.6)$$

$h_{FF}^0(3, 4)$  is of microscopic range and, except very near the boundary of the system, it depends only on the relative position and orientation of molecules (3) and (4). Following Nienhuis and Deutch, we shall neglect boundary effects.<sup>10</sup> In particular, this means that the one-particle reduced probability density  $\rho_F^V(3)$  will be set equal to  $\rho$ , a constant, as it is in the limit of infinite volume.

With the help of  $h_{FF}^0(3, 4)$ , one can define a vector  $\kappa$  (3) as

$$\kappa(\mathbf{r}_3, \hat{\mathbf{s}}) = \rho \int_V d\mathbf{r}_4 D(\hat{\mathbf{i}}) h_{FF}^0(\mathbf{r}_3, \hat{\mathbf{s}}; \mathbf{r}_4, \hat{\mathbf{i}}) \mu \hat{\mathbf{i}}. \quad (3.7)$$

Here  $D(\hat{\mathbf{i}})$  is the volume element in the angular space of molecule (4). We normalize  $D(\hat{\mathbf{i}})$  so that its integral is one, i.e.,

$$D(\hat{\mathbf{i}}) = \frac{1}{4\pi} d\Omega_{\hat{\mathbf{i}}}. \quad (3.8)$$

Owing to the properties of  $h_{FF}^0$  and the cylindrical symmetry of the molecules,  $\kappa(\mathbf{r}_3, \hat{\mathbf{s}})$  does not depend on  $\mathbf{r}_3$  and is parallel to  $\hat{\mathbf{s}}$ . Thus we can write

$$\kappa(\mathbf{r}_3, \hat{\mathbf{s}}) = \kappa \hat{\mathbf{s}}, \quad (3.9)$$

where  $\kappa$  is the constant magnitude of  $\kappa$ . It is related to the dielectric constant of the fluid through the equation<sup>3</sup>

$$\frac{\epsilon - 1}{4\pi} = \frac{1}{3} \beta \rho \mu (\mu + \kappa). \quad (3.10)$$

The other term in  $h_{FF}^V$ , namely,  $h_{FF}^1(3, 4)$ , can be written as

$$h_{FF}^1(3, 4) = \frac{\beta}{\epsilon} (\mu + \kappa)^2 \{ T(3, 4) + R^*(3, 4) \}, \quad (3.11)$$

where

$$T(3, 4) = -(\hat{\mathbf{s}} \cdot \nabla^{(3)})(\hat{\mathbf{l}} \cdot \nabla^{(4)}) \frac{1}{r_{34}}, \quad (3.12)$$

$$R^*(3, 4) = -(\hat{\mathbf{s}} \cdot \nabla^{(3)})(\hat{\mathbf{l}} \cdot \nabla^{(4)})$$

$$\times \sum_{l=0}^{\infty} \frac{(\epsilon - 1)(l + 1)}{\epsilon l + l + 1} \frac{r_3^l r_4^l}{R^{2l+1}} P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4). \quad (3.13)$$

Here  $\hat{\mathbf{r}}_3$  is a unit vector parallel to  $\mathbf{r}_3$ ,  $P_l$  is a Legendre polynomial, and  $R$  is the radius of the sphere whose volume is  $V$ . Note that  $T(3, 4)$  is singular at  $r_{34} = 0$ . The singularity is handled according to the rule

$$\int_{r_{34} < \delta} d\mathbf{r}_4 T(3, 4) = \frac{-4\pi}{3} \hat{s} \cdot \hat{i}, \quad (3.14)$$

where  $\delta$  is any positive number.

How good an approximation to the true  $h_{FF}^V(3, 4)$  is the sum  $h_{FF}^0(3, 4) + h_{FF}^1(3, 4)$ ? Nienhuis and Deutch have shown that for microscopic  $r_{34}$  the sum includes all contributions of order  $V^0$  to  $h_{FF}^V$  and, for large  $r_{34}$ , it includes all contributions of order  $V^{-1}$ . A contribution of order  $V^{-1}$ , when integrated over the whole volume, results in a term of order  $V^0$ . Thus the sum  $h_{FF}^0 + h_{FF}^1$ , when used instead of the true  $h_{FF}^V$ , is expected to yield the correct leading order in  $1/V$  of any quantity computed by integrating  $h_{FF}^V$ .

We now have everything we need to compute, to leading order in  $1/V$ , the long-range part of the effective interaction energy of the two test multipoles. From the previous discussion the right-hand side of Eq. (2.8) can be written as

$$\begin{aligned} \phi_{LM}(1, 2) - \beta\rho \int d\mathbf{r}_3 D(\hat{s}) \phi_{LM}(1, 3) \phi_{\mu M}(3, 2) \\ - \beta\rho^2 \int d\mathbf{r}_3 D(\hat{s}) d\mathbf{r}_4 D(\hat{i}) \phi_{LM}(1, 3) \{h_{FF}^0(3, 4) \\ + h_{FF}^1(3, 4)\} \phi_{\mu M}(4, 2). \end{aligned} \quad (3.15)$$

For simplicity, we shall first do the computation for the case where the parameters  $\eta_L$  and  $\eta_M$  in Eqs. (3.4) and (3.5) vanish. Since the combination of operators appearing in Eq. (3.3) for  $\phi_{LM}(1, 2)$  will occur repeatedly, we introduce the simplified notation

$$\Delta_{LM} = \frac{1}{(2L-1)!!} \frac{1}{(2M-1)!!} (L \cdot \nabla^{(1)}) (M \cdot \nabla^{(2)}), \quad (3.16)$$

so that

$$\phi_{LM}(1, 2) = \Delta_{LM} \frac{1}{r_{12}}. \quad (3.17)$$

Let us now consider the second term in Eq. (3.15), which we denote by  $Y_2$ . Substituting Eqs. (3.4) and (3.5) (with  $\eta_L = 0 = \eta_M$ ), we see that it becomes

$$\begin{aligned} Y_2 = -\beta\rho \int d\mathbf{r}_3 D(\hat{s}) \left[ \frac{\mu}{(2L-1)!!} (L \cdot \nabla^{(1)}) (\hat{s} \cdot \nabla^{(3)}) \frac{1}{r_{13}} \right] \\ \times \left[ \frac{\mu}{(2M-1)!!} (M \cdot \nabla^{(2)}) (\hat{s} \cdot \nabla^{(3)}) \frac{1}{r_{13}} \right] \\ = -\beta\rho\mu^2 \Delta_{LM} \int d\mathbf{r}_3 D(\hat{s}) (\hat{s} \cdot \nabla^{(3)}) \frac{1}{r_{13}} (\hat{s} \cdot \nabla^{(3)}) \frac{1}{r_{23}}. \end{aligned} \quad (3.18)$$

The integral over  $D(\hat{s})$  can be done using the relation

$$\int D(\hat{s}) s_\alpha s_\beta = \frac{1}{3} \delta_{\alpha\beta}, \quad (3.19)$$

where  $\delta_{\alpha\beta}$  is the Kronecker symbol. Thus we obtain

$$Y_2 = -\frac{1}{3} \beta\rho\mu^2 \Delta_{LM} \int_V d\mathbf{r}_3 \left( \nabla^{(3)} \frac{1}{r_{13}} \right) \cdot \left( \nabla^{(3)} \frac{1}{r_{23}} \right). \quad (3.20)$$

The integral over  $d\mathbf{r}_3$  is calculated in the Appendix, and the result is given in Eq. (A6). So we get

$$Y_2 = -\frac{4\pi}{3} \beta\rho\mu^2 \Delta_{LM} \times \left\{ \frac{1}{r_{12}} - \frac{1}{R} \sum_{l=0}^{\infty} \frac{l+1}{2l+1} \left( \frac{r_1 r_2}{R^2} \right)^l P_l(\hat{r}_1 \cdot \hat{r}_2) \right\}. \quad (3.21)$$

Next we turn to the third term in Eq. (3.15), more specifically to the contribution coming from  $h_{FF}^0$ . We call this contribution  $Y_{30}$ . Upon substitution of Eqs. (3.4) and (3.5) we obtain, after rearranging

$$\begin{aligned} Y_{30} = -\beta\rho^2 \Delta_{LM} \int d\mathbf{r}_3 D(\hat{s}) (\mu \hat{s} \cdot \nabla^{(3)}) \frac{1}{r_{13}} \\ \times \int d\mathbf{r}_4 D(\hat{i}) h_{FF}^0(\mathbf{r}_3, \hat{s}; \mathbf{r}_4, \hat{i}) (\mu \hat{i} \cdot \nabla^{(4)}) \frac{1}{r_{42}}. \end{aligned} \quad (3.22)$$

Since  $h_{FF}^0$  is of microscopic range, we can replace  $\nabla^{(4)}(r_{42})^{-1}$  by  $\nabla^{(3)}(r_{32})^{-1}$  without affecting the long-range part of  $Y_{30}$ . Taking  $\nabla^{(3)}(r_{32})^{-1}$  outside the  $d\mathbf{r}_4$  integral and making use of Eqs. (3.7) and (3.9), we get

$$\begin{aligned} Y_{30} = -\beta\rho \Delta_{LM} \int d\mathbf{r}_3 D(\hat{s}) \\ \times (\mu \hat{s} \cdot \nabla^{(3)}) \frac{1}{r_{13}} (\kappa \hat{s} \cdot \nabla^{(3)}) \frac{1}{r_{32}}. \end{aligned} \quad (3.23)$$

Comparing Eqs. (3.23) and (3.18), we see that  $Y_{30}$  is equal to  $(\kappa/\mu)Y_2$ . Equations (3.21) and (3.10) therefore yield

$$\begin{aligned} Y_2 + Y_{30} = -(\epsilon - 1) \Delta_{LM} \\ \times \left\{ \frac{1}{r_{12}} - \frac{1}{R} \sum_{l=0}^{\infty} \frac{l+1}{2l+1} \left( \frac{r_1 r_2}{R^2} \right)^l P_l(\hat{r}_1 \cdot \hat{r}_2) \right\}. \end{aligned} \quad (3.24)$$

There remains to calculate the  $h_{FF}^1$  contribution to the third term in Eq. (3.15), which we denote by  $Y_{31}$ . Making use of Eqs. (3.4), (3.5), (3.11), (3.12), and (3.13) we obtain, after rearranging

$$\begin{aligned} Y_{31} = \frac{1}{\epsilon} \beta^2 \rho^2 \mu^2 (\mu + \kappa)^2 \Delta_{LM} \int d\mathbf{r}_3 D(\hat{s}) d\mathbf{r}_4 \\ \times D(\hat{i}) (\hat{s} \cdot \nabla^{(3)}) \frac{1}{r_{13}} (\hat{s} \cdot \nabla^{(3)}) (\hat{i} \cdot \nabla^{(4)}) \\ \times \left\{ \frac{1}{r_{34}} + \sum_{l=0}^{\infty} \frac{(\epsilon - 1)(l+1)}{\epsilon l + l + 1} \frac{r_3^l r_4^l}{R^{2l+1}} P_l(\hat{r}_3 \cdot \hat{r}_4) \right\} \\ \times (\hat{i} \cdot \nabla^{(4)}) \frac{1}{r_{42}}. \end{aligned} \quad (3.25)$$

The integrals over  $D(\hat{s})$  and  $D(\hat{i})$  are easily done with the help of Eq. (3.19). Thus we get, using Eq. (3.10),

$$\begin{aligned} Y_{31} = \frac{1}{\epsilon} \left( \frac{\epsilon - 1}{4\pi} \right)^2 \Delta_{LM} \int_V d\mathbf{r}_3 d\mathbf{r}_4 \left( \nabla^{(3)} \frac{1}{r_{13}} \right) \cdot \nabla^{(3)} \nabla^{(4)} \\ \times \left\{ \frac{1}{r_{34}} + \sum_{l=0}^{\infty} \frac{(\epsilon - 1)(l+1)}{\epsilon l + l + 1} \frac{r_3^l r_4^l}{R^{2l+1}} P_l(\hat{r}_3 \cdot \hat{r}_4) \right\} \\ \times \nabla^{(4)} \frac{1}{r_{42}}. \end{aligned} \quad (3.26)$$

The integral over  $dr_3 dr_4$  is calculated in the Appendix, and the result is given in Eq. (A9). Hence  $Y_{31}$  becomes

$$Y_{31} = \frac{1}{\epsilon} (\epsilon - 1)^2 \Delta_{LM} \left\{ \frac{1}{r_{12}} - \frac{1}{R} \sum_{l=0}^{\infty} \left[ 1 + \frac{l}{\epsilon l + l + 1} \right] \times \frac{l+1}{(2l+1)} \left( \frac{r_1 r_2}{R^2} \right)^l P_l(\hat{r}_1 \cdot \hat{r}_2) \right\}. \quad (3.27)$$

The long-range part of  $\Phi_{LM}^V$  is now obtained, to leading order in  $1/V$ , by adding the various terms in Eq. (3.15), namely, Eqs. (3.17), (3.24), and (3.27). The remarkably simple result is

$$\Phi_{LM}^V(1, 2) \rightarrow \Delta_{LM} \frac{1}{\epsilon} \left\{ \frac{1}{r_{12}} + \frac{\epsilon - 1}{R} \times \sum_{l=0}^{\infty} \frac{l+1}{\epsilon l + l + 1} \left( \frac{r_1 r_2}{R^2} \right)^l P_l(\hat{r}_1 \cdot \hat{r}_2) \right\}. \quad (3.28)$$

Equation (3.28) gives the leading long-range part of  $\Phi_{LM}^V(1, 2)$  for the special case where the parameters  $\eta_L$  and  $\eta_M$ , in Eqs. (3.4) and (3.5), vanish. For  $\eta_L \neq 0 \neq \eta_M$ , the integrals in Eq. (3.15) involve additional terms. They can be calculated and, again, the final result is rather simple. Equation (3.28) still holds, except that the factor  $\epsilon^{-1}$  in front of the curly bracket is replaced by a constant  $c_{LM}(\epsilon)$  given by

$$c_{LM}(\epsilon) = \left[ 1 + (\epsilon - 1) \frac{L\eta_L}{2L+1} \right] \times \frac{1}{\epsilon} \left[ 1 + (\epsilon - 1) \frac{M\eta_M}{2M+1} \right]. \quad (3.29)$$

Thus the general result is

$$\Phi_{LM}^V(1, 2) \rightarrow \Delta_{LM} c_{LM}(\epsilon) \times \left\{ \frac{1}{r_{12}} + \frac{\epsilon - 1}{R} \sum_{l=0}^{\infty} \frac{l+1}{\epsilon l + l + 1} \left( \frac{r_1 r_2}{R^2} \right)^l P_l(\hat{r}_1 \cdot \hat{r}_2) \right\}. \quad (3.30)$$

#### IV. DISCUSSION

The leading long-range part of  $\Phi_{LM}^V(1, 2)$ , given by Eq. (3.30), can be expressed simply in terms of  $\Phi_{00}^V(1, 2)$ . For  $L = M = 0$ , i.e., for test charges, the operator  $\Delta_{LM}$  defined in Eq. (3.16) reduces to the product  $qq'$  of the two charges, and  $c_{LM}(\epsilon)$  in Eq. (3.29) becomes  $\epsilon^{-1}$ . Thus we have

$$\Phi_{00}^V(1, 2) \rightarrow \frac{qq'}{\epsilon} \times \left\{ \frac{1}{r_{12}} + \frac{\epsilon - 1}{R} \sum_{l=0}^{\infty} \frac{l+1}{\epsilon l + l + 1} \left( \frac{r_1 r_2}{R^2} \right)^l P_l(\hat{r}_1 \cdot \hat{r}_2) \right\}. \quad (4.1)$$

But this means that

$$\Phi_{LM}^V(1, 2) \sim \Delta_{LM} \Phi_{00}^V(1, 2), \quad (4.2)$$

which should be compared with Eq. (3.17). The same operator  $\Delta_{LM}$  which relates multipole-multipole to charge-charge potential energies in empty space also relates, to

within a constant, their leading long-range effective interactions in a dielectric fluid.

The expression inside curly brackets in Eq. (3.30) consists of two terms: the inverse distance  $(r_{12})^{-1}$  and an expansion in Legendre polynomials and powers of  $r_1 r_2 / R^2$ . It is interesting to assess the relative contribution of these two terms as  $R$  grows large. For  $r_1$  and  $r_2$  fixed, the second term becomes negligible compared with  $(r_{12})^{-1}$ . If, on the other hand,  $r_1$ ,  $r_2$ , and  $R$  are of comparable magnitude, then  $r_{12} \sim R$  and  $r_1 r_2 / R^2 \sim 1$ . Therefore, both terms contribute more or less equally to Eq. (3.30).

It was shown in paper I that the long-range part of the effective interaction energy of two test multipoles immersed in an infinite volume of dielectric fluid is given by<sup>11</sup>

$$\Phi_{LM}^{\infty}(1, 2) \rightarrow \Delta_{LM} c_{LM}(\epsilon) \frac{1}{r_{12}}. \quad (4.3)$$

The right-hand side of Eq. (4.3) coincides with the first term on the right-hand side of Eq. (3.30). This means that, as  $R \rightarrow \infty$ ,  $\Phi_{LM}^V$  goes to  $\Phi_{LM}^{\infty}$  only if  $r_1/R$  and  $r_2/R$  go to zero. If, on the other hand,  $r_1 \sim r_2 \sim R$ , then no matter how large  $R$  is,  $\Phi_{LM}^{\infty}$  is not a good approximation to  $\Phi_{LM}^V$ .

It is interesting to compare our results with those obtained by Neinhuis and Deutch in Ref. 4. The system they considered consists of multipolar impurities immersed in a dielectric fluid of finite volume and arbitrary shape. They have obtained general relations for the long-range part of the potential of mean force between impurities, whose definition in terms of the reduced probability density essentially coincides with the long-range part of our effective interaction energy. The impurities, however, were not assumed to interact weakly with the fluid molecules. The potential of mean force between such impurities contains more terms than the effective interaction between test multipoles. It turns out that our results and those of Neinhuis and Deutch essentially agree for charges and dipoles. For higher-order multipolar impurities, however, they find a long-range contribution which has no counterpart in the case of test multipoles.

Although Neinhuis and Deutch have not obtained detailed formulas for specific geometries, they have shown that the potential of mean force between two charges, for instance, agrees with the potential energy computed from macroscopic electrostatics. This is illustrated in our case by Eq. (4.1). Indeed one can show that the right-hand side of Eq. (4.1) precisely corresponds to the potential energy of a charge  $q$  at  $r_1$  and a charge  $q'$  at  $r_2$ , immersed in a spherical dielectric of permittivity  $\epsilon$ .

As discussed in paper I, the parameters  $\eta_L$  and  $\eta_M$  in Eqs. (3.4) and (3.5) specify the singularity of the multipole-dipole interaction. Physically, they correspond to the way the interaction behaves at short distances. One sees from Eq. (3.30) that  $\eta_L$  and  $\eta_M$  directly enter the final result for  $\Phi_{LM}^V(1, 2)$  through the constant  $c_{LM}(\epsilon)$ . A macroscopic calculation of the potential energy of two multipoles must make assumptions on the coupling between the multipole and the continuum. The explicit

form of  $c_{LM}(\epsilon)$ , given in Eq. (3.29), shows how a macroscopic coupling originates from a specific microscopic interaction.<sup>12</sup>

The effective interaction energy  $\Phi_{LM}^V$  of two test multipoles in a dielectric fluid of finite volume is related to their reduced probability density  $\rho_{LM}^V$  through Eq. (2.3). Given the form of the microscopic potentials  $\phi_{LM}$ ,  $\phi_{LF}$ ,  $\phi_{MF}$ , and  $\phi_{FF}$ , the reduced probability density is a quantity which can be calculated by computer simulation. The effective interaction energy of the multipoles can then be extracted, at least in principle, from  $\rho_{LM}^V$ . If the leading long-range part of  $\Phi_{LM}^V$  obtained in Eq. (3.30) is a good approximation to the true effective interaction for reasonable volumes, a comparison of Eq. (3.30) with the result of the computer simulation would yield a value of  $\epsilon$  for the molecular fluid considered.<sup>13</sup> Whether a scheme like this one is practical remains to be investigated.

## ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada, and by the Government of Québec through the FCAC fund.

## APPENDIX

To do the integrals in Eqs. (3.20) and (3.26), we will need the following identities<sup>14</sup>:

$$\nabla^{(j)} \cdot \nabla^{(i)} \frac{1}{r_{ij}} = -4\pi\delta(\mathbf{r}_{ij}), \quad (A1)$$

$$\frac{1}{r_{ij}} = \sum_{l=0}^{\infty} \frac{r_i^l}{r_j^{l+1}} P_l(\hat{\mathbf{r}}_i \cdot \hat{\mathbf{r}}_j), \quad r_i < r_j, \quad (A2)$$

$$P_l(\hat{\mathbf{r}}_i \cdot \hat{\mathbf{r}}_j) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}(\hat{\mathbf{r}}_i) Y_{lm}^*(\hat{\mathbf{r}}_j), \quad (A3)$$

$$\int d\Omega_{\hat{\mathbf{r}}_i} Y_{lm}(\hat{\mathbf{r}}_i) Y_{lm}^*(\hat{\mathbf{r}}_i) = \delta_{ll'} \delta_{mm'}. \quad (A4)$$

Let us first consider the integral in Eq. (3.20). Making use of Eq. (A1) and of Gauss's theorem, we can write

$$\begin{aligned} & \int_V d\mathbf{r}_3 \left( \nabla^{(3)} \frac{1}{r_{13}} \right) \cdot \left( \nabla^{(3)} \frac{1}{r_{32}} \right) \\ &= \int_V d\mathbf{r}_3 \left\{ - \left[ \nabla^{(3)} \cdot \nabla^{(3)} \frac{1}{r_{13}} \right] \frac{1}{r_{32}} + \nabla^{(3)} \cdot \left[ \left( \nabla^{(3)} \frac{1}{r_{13}} \right) \frac{1}{r_{32}} \right] \right\} \\ &= \int_V d\mathbf{r}_3 4\pi\delta(\mathbf{r}_{13}) \frac{1}{r_{32}} + \int_{r_3=R} (r_3)^2 d\Omega_{\hat{\mathbf{r}}_3} \left( \hat{\mathbf{r}}_3 \cdot \nabla^{(3)} \frac{1}{r_{13}} \right) \frac{1}{r_{32}} \\ &= 4\pi \frac{1}{r_{12}} + R^2 \int_{r_3=R} d\Omega_{\hat{\mathbf{r}}_3} \left( \frac{\partial}{\partial r_3} \frac{1}{r_{13}} \right) \frac{1}{r_{32}}. \end{aligned} \quad (A5)$$

In the remaining integral,  $r_1$  and  $r_2$  are always smaller than  $r_3$ , so that Eq. (A2) can be used. With the help of Eqs. (A3) and (A4) we get the result

$$\begin{aligned} & \int_V d\mathbf{r}_3 \left( \nabla^{(3)} \frac{1}{r_{13}} \right) \cdot \left( \nabla^{(3)} \frac{1}{r_{32}} \right) \\ &= 4\pi \frac{1}{r_{12}} - \frac{4\pi}{R} \sum_{l=0}^{\infty} \frac{l+1}{2l+1} \left( \frac{r_1 r_2}{R^2} \right)^l P_l(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2). \end{aligned} \quad (A6)$$

Before we turn to Eq. (3.26), it will be useful to obtain an intermediate result. Using Gauss's theorem and the fact that  $r_4^l P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4)$  solves Laplace's equation, we can write

$$\begin{aligned} & \int_V d\mathbf{r}_4 \nabla^{(4)} [r_4^l P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4)] \cdot \nabla^{(4)} \frac{1}{r_{42}} \\ &= \int_V d\mathbf{r}_4 \left\{ \nabla^{(4)} \cdot \left[ \left( \nabla^{(4)} r_4^l P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4) \right) \frac{1}{r_{42}} \right] \right. \\ &\quad \left. - \frac{1}{r_{42}} \nabla^{(4)} \cdot \nabla^{(4)} [r_4^l P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4)] \right\} \\ &= \int_{r_4=R} (r_4)^2 d\Omega_{\hat{\mathbf{r}}_4} \frac{\partial}{\partial r_4} [r_4^l P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4)] \frac{1}{r_{42}} \\ &= lR^{l+1} \int_{r_4=R} d\Omega_{\hat{\mathbf{r}}_4} P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4) \frac{1}{r_{42}}. \end{aligned} \quad (A7)$$

We note that  $r_2 < r_4$ . We substitute Eq. (A2) for  $(r_{42})^{-1}$  and use Eqs. (A3) and (A4) to obtain

$$\begin{aligned} & \int_V d\mathbf{r}_4 \nabla^{(4)} [r_4^l P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4)] \cdot \nabla^{(4)} \frac{1}{r_{42}} \\ &= \frac{4\pi l}{2l+1} r_2^l P_l(\hat{\mathbf{r}}_2 \cdot \hat{\mathbf{r}}_3). \end{aligned} \quad (A8)$$

The integral in Eq. (3.26) can now be done by using Eqs. (A6) and (A8) twice as follows:

$$\begin{aligned} & \int_V d\mathbf{r}_3 d\mathbf{r}_4 \left( \nabla^{(3)} \frac{1}{r_{13}} \right) \cdot \nabla^{(3)} \nabla^{(4)} \\ &\quad \times \left\{ \frac{1}{r_{34}} + \sum_{l=0}^{\infty} \frac{(\epsilon-1)(l+1)}{\epsilon l + l + 1} \frac{r_3^l r_4^l}{R^{2l+1}} P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4) \right\} \cdot \nabla^{(4)} \frac{1}{r_{42}} \\ &= \int_V d\mathbf{r}_3 \left( \nabla^{(3)} \frac{1}{r_{13}} \right) \cdot \nabla^{(3)} \left\{ \int_V d\mathbf{r}_4 \left( \nabla^{(4)} \frac{1}{r_{34}} \right) \cdot \left( \nabla^{(4)} \frac{1}{r_{42}} \right) \right. \\ &\quad \left. + \sum_{l=0}^{\infty} \frac{(\epsilon-1)(l+1)}{\epsilon l + l + 1} \frac{r_3^l}{R^{2l+1}} \int_V d\mathbf{r}_4 \nabla^{(4)} \right. \\ &\quad \left. \times [r_4^l P_l(\hat{\mathbf{r}}_3 \cdot \hat{\mathbf{r}}_4)] \cdot \nabla^{(4)} \frac{1}{r_{42}} \right\} \\ &= \int_V d\mathbf{r}_3 \left( \nabla^{(3)} \frac{1}{r_{13}} \right) \cdot \nabla^{(3)} \\ &\quad \times \left\{ 4\pi \frac{1}{r_{32}} - 4\pi \sum_{l=0}^{\infty} \frac{l+1}{\epsilon l + l + 1} \frac{r_2^l r_3^l}{R^{2l+1}} P_l(\hat{\mathbf{r}}_2 \cdot \hat{\mathbf{r}}_3) \right\} \\ &= (4\pi)^2 \left\{ \frac{1}{r_{12}} - \frac{1}{R} \sum_{l=0}^{\infty} \left[ 1 + \frac{l}{\epsilon l + l + 1} \right] \right. \\ &\quad \left. \times \frac{l+1}{2l+1} \left( \frac{r_1 r_2}{R^2} \right)^l P_l(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2) \right\}. \end{aligned} \quad (A9)$$

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- <sup>5</sup> J. S. Høye and G. Stell, *J. Chem. Phys.* **61**, 562 (1974).
- <sup>6</sup> J. S. Høye and G. Stell, *J. Chem. Phys.* **64**, 1952 (1976).
- <sup>7</sup> L. Marchildon, *J. Chem. Phys.* **80**, 449 (1984).
- <sup>8</sup> It is not necessary to specify the singularity of  $\phi_{LM}(1, 2)$  in Eq. (3.3), since we are only interested in its long-range behavior. Indeed  $\phi_{LM}$  contributes directly (i.e., without being integrated) to the effective interaction  $\Phi_{LM}^V$ .
- <sup>9</sup> Our  $h_{FF}^0$  and  $h_{FF}^1$  correspond to what Nienhuis and Deutch call  $\rho^{-2}G_2^{(0)}$  and  $\rho^{-2}G_2^{(1)}$ .
- <sup>10</sup> Boundary effects are expected to introduce contributions of order  $V^{-1/3}$  relative to volume effects. Neglecting them should not affect the computation of the leading term in  $\Phi_{LM}^V$ .
- <sup>11</sup> In Ref. 7,  $c_{LM}(\epsilon)$  was denoted by  $\lambda[(L, M, (\epsilon - 1)/(\epsilon + 2))]$ .
- <sup>12</sup> In the expression (3.29) for  $c_{LM}(\epsilon)$ , the two factors inside brackets can be viewed as the average coupling of each multipole with the surrounding molecules, and  $\epsilon^{-1}$  governs the propagation of the interaction through the fluid. All three factors are independent of the volume of the system.
- <sup>13</sup> For a discussion of the computer simulation of polar fluids, see M. S. Wertheim, *Annu. Rev. Phys. Chem.* **30**, 471 (1979); G. Stell, G. N. Patey, and J. S. Høye, *Adv. Chem. Phys.* **48**, 183 (1981).
- <sup>14</sup> E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, 4th ed. (Cambridge, London, 1927); P. Dennery and A. Krzywicki, *Mathematics for Physicists* (Harper and Row, New York, 1967). Note that Eq. (A1) is consistent with Eq. (3.14).