Nonlinear effects in polar fluids: A molecular theory of electrostriction

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A molecular theory of electrostriction arising from the study of dipolar adsorption at a wall in the presence of an electric field is described. The quadratic hypernetted chain (QHNC) approximation for the wall-particle closure is the first of the hierarchy of approximations generated by the hypernetted chain equation (HNC) to predict electrostriction; the mean spherical and linearized hypernetted chain fail to do so. It is found that the simplest bridge diagrams which are ignored in the HNC (and QHNC) approximations must be included if quantitative agreement with the thermodynamic theory for electrostriction as described by Kirkwood and Oppenheim is to be obtained. These bridge diagrams have been evaluated analytically resolving the above discrepancy in the term of $O(E^2)$, where E is the local electric field. The statistical mechanical approach has also been extended to evaluate a few of the contributions of $O(E^4)$ in electrostriction. Conditions under which the linear constitutive relation between the polarization density $\mathbf{P}(\infty,\mathbf{E})$ and the electric field $\mathbf{E}$ is recovered are discussed; its extension to include nonlinear terms in $\mathbf{E}$ is also considered.

I. INTRODUCTION

This paper discusses a molecular theory of electrostriction and polarization density which arises from a study of the adsorption of dipoles at a wall in the presence of an electric field. Isbister and Freasier[1] have considered the adsorption problem in their study of the mean spherical approximation (MSA) for the wall–particle and particle–particle interactions, and this has recently been extended by Eggebrecht, Isbister, and Rasaiah[2] to the linearized hypernetted chain approximation (LHNC). The electrostriction effects that we are about to discuss first arise when the next step in this hierarchy of approximations is taken for the direct and pair correlation functions; namely the quadratic hypernetted chain (QHNC) approximation. The leading term in the relative change in density $\Delta\rho/\rho_1^0$ is of order E^2, where E is the magnitude of the electric field. By considering the next few terms in the sequence of approximations generated by the hypernetted chain equation (HNC) one can systematically evaluate the terms of order E^4, E^6, etc. To make these calculations exact, however, one must also include the bridge diagrams of the appropriate order in E^2, E^4, etc. that are ignored in the HNC approximation. Our paper discusses the evaluation of the bridge diagrams to $O(E^2)$ and $O(E^4)$ in the electric field, and to the lowest order in the fluid density and dipole moment of the fluid molecules.

The change in density at an infinite distance away from a flat wall on the microscale set by the particle diameter is found to be independent of the inclination of the electric field to order E^2. The leading term of $O(E^2)$ can also be obtained from a thermodynamic argument, with respect to which our statistical mechanical answer is consistent. There is however no corresponding thermodynamic analysis of electrostriction to $O(E^4)$, which would require details of the nonlinear contribution of the electric field to the polarization density $\mathbf{P}$. An investigation of this problem has therefore also been initiated here.

In Sec. II of this paper we discuss the theoretical preliminaries which include a relation between $h_{21}^*(\infty)$ and $c_{21}^*(\infty)$, where $h_{21}^*(\infty)$ and $c_{21}^*(\infty)$ are the total and direct correlation functions for the wall–particle interactions at $r=\infty$ averaged over the angular coordinates of the fluid particles. Section III treats the closures at the QHNC level, and beyond, for the wall–particle interactions and in Sec. IV we consider the bridge diagrams of $O(E^2)$ and $O(E^4)$ which contribute to electrostriction. The polarization density in open systems is investigated in Sec. V and our conclusions are summarized in the last section. An appendix provides additional results on the statistical mechanics of these systems, a second discusses a relation for the electric field E_2 generated by the wall–dipole (2.32), and a third discusses the evaluation of a bridge diagram of $O(E_2^4)$. A summary of our principal results for open systems, without the detailed theoretical analysis in this paper, has been published elsewhere.[3]

II. THEORETICAL PRELIMINARIES

We employ the technique introduced by Isbister and Freasier[1] to generate an electric field at the wall by taking the following limit of a binary dipolar system:

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$$\lim_{R_2\to\infty}\lim_{\rho_2\to 0}\frac{m_2}{R_{21}^3}=E_0 . \qquad (2.1)$$

Here ρ_2, R_2, and m_2 are the density, radius, and dipole moment of species 2, with corresponding definitions for species 1, $R_{21}=R_2+R_1$ is the radius of the excluded volume and E_0 is related to the electric field $\mathbf{E}_2$ produced by the "wall–dipole", which resides at a distance $-\infty$ from the wall, through the equation[1,2]

$$\mathbf{E}_2=E_0(3\cos^2\Theta_2+1)^{1/2}\hat{e}_2 . \qquad (2.2)$$

In Eq. (2.2) Θ_2 is the angle which the wall–dipole makes with the normal to the wall; the inclination α of the electric field with this normal is related to Θ_2 by the equation[1,2]

$$\cos\alpha=(2\cos\Theta_2)/[(3\cos^2\Theta_2+1)^{1/2}] . \qquad (2.3)$$

The limit $R_2/R_1\to\infty$ that we consider here is a convenient device for generating, on the microscale set by the particle size R_1, a flat wall through which a spatially constant field is emanating. However, it is important to recognize that the limit can equally well be thought of as a shrinking of the fluid particles of species 1 as they become elements of a "continuum" fluid exterior to a spherical macrocavity of diameter R_2, at the center of which there is a macroscopic dipole. This is the way the limit would be perceived by an observer observing on the scale of R_2, which becomes the macroscale of continuum dielectric theory. It is this picture therefore that we must use in making contact with the equations of continuum theory in relating the applied field $\mathbf{E}_2$ to the macroscopic field. The subsequent large-z limit that we shall consider below (where z is the normal distance from the cavity wall into the fluid) defines a domain that macroscopically remains next to the outer surface of the spherical macrocavity (since $z/R_2=0$ for all z after taking the $R_2/R_1\to\infty$ limit) even though on the molecular scale of R_1 one moves arbitrarily far from the flat wall as $z/R_1\to\infty$. Once field dependence is expressed entirely in terms of the Maxwell field $\mathbf{E}$ rather than the applied field $\mathbf{E}_2$, one expects the dependence on details of the boundary geometry to be lost, for a prescribed $\mathbf{E}$, as one lets $z\to\infty$. In terms of prescribed $\mathbf{E}_2$, macroparticles of different shapes would give rise to different relations in the $z\to\infty$ limit, however. (This must be kept in mind in using the results of Refs. 1 and 2, which are given only in terms of $\mathbf{E}_2$.)

The density profile $\rho_1(z, \mathbf{E}_2, \Omega_1)$ of the fluid dipoles at a distance z from the wall is related to the limiting behavior of the total correlation function $h_{21}(r_{21}, \Omega_2, \Omega_1)$ as $\rho_2\to 0$ and $R_2\to\infty$. In terms of the distance $z=r_{21}-R_2$, the density profile is

$$\rho_1(z, \mathbf{E}_2, \Omega_1)=\rho_1^0[h_{21}(z, \mathbf{E}_2, \Omega_1)+1] , \qquad (2.4)$$

where our definition of $h_{21}(z, \mathbf{E}_2, \Omega_1)$ and its asymptotic properties requires ρ_1^0 to be the bulk density in the absence of an electric field. The bulk density in the presence of an electric field, averaged over the orientations of fluid molecules, is

$$\rho_1(\infty, \mathbf{E}_2)\equiv\frac{1}{\Omega}\int\rho_1(\infty, \mathbf{E}_2, \Omega_1)\,d\Omega_1 \qquad (2.5)$$

$$=\rho_1^0[h_{21}^*(\infty, \mathbf{E}_2)+1] , \qquad (2.6)$$

where

$$h_{21}^*(z, \mathbf{E}_2)\equiv\frac{1}{\Omega}\int h_{21}(z, \mathbf{E}_2, \Omega_1)\,d\Omega_1 , \qquad (2.7)$$

and $\Omega=4\pi$ for linear molecules and $8\pi^2$ for nonlinear molecules.

The relative change in bulk density, which measures the electrostriction effect, is our primary quantity of interest; from Eq. (2.6) this measure is given by

$$\Delta\rho/\rho_1^0=h_{21}^*(\infty, \mathbf{E}_2)=K_h , \qquad (2.8)$$

where K_h is zero when the MS and LHNC approximations are applied to wall–particle closures, but turns out to be a positive number beginning with the QHNC approximation. Our calculations, however, proceed through the corresponding asymptotic limit for the angularly averaged direct correlation function

$$c_{21}^*(z, \mathbf{E}_2)\equiv\frac{1}{\Omega}\int c_{21}(z, \mathbf{E}_2, \Omega_1)\,d\Omega_1 . \qquad (2.9)$$

Defining $K_c\equiv c_{21}^*(\infty, \mathbf{E}_2)$, we shall soon show that

$$K_h=K_c/Q , \qquad (2.10)$$

where Q is the inverse compressibility of the bulk fluid defined by

$$Q=1-\frac{\rho_1^0}{\Omega^2}\int c_{11}(r_{13}, \Omega_1, \Omega_3)\,d\mathbf{r}_{13}\,d\Omega_1\,d\Omega_3 . \qquad (2.11)$$

In Eq. (2.11), $c_{11}(r_{13}, \Omega_1, \Omega_3)$ is the direct correlation function for the bulk fluid, which has the invariant expansion,[4]

$$c_{11}(r_{13}, \Omega_1, \Omega_3)=c_{11}^s(r_{13})+c_{11}^D(r_{13})D(1, 3)+c_{11}^\Delta(r_{13})\Delta(1, 3)+\cdots , \qquad (2.12)$$

where only the first three terms are retained, in keeping with the definition of the QHNC approximation.[6]

The relation (2.10) may be derived starting with the Ornstein–Zernike relation for a binary nonpolarizable fluid in the limit $\rho_2\to 0$. On integrating this with respect to the orientations of the bulk dipolar particle 1, and after carrying out the angular convolution, we find for nonpolarizable molecules (see Appendix A) in the QHNCA

$$h_{21}^*(r_{21}, \Omega_2)=c_{21}^*(r_{21}, \Omega_2)+\rho_1^0\,h_{21}^*(r_{23}, \Omega_2)*c_{11}^s(r_{31}) , \qquad (2.13)$$

where

$$A*B\equiv\int AB\,d\mathbf{r}_3 . \qquad (2.14)$$

If the wall limit is taken, and bipolar coordinates are employed, we have

$$h_{21}^*(z, \mathbf{E}_2)=c_{21}^*(z, \mathbf{E}_2)+2\pi\rho_1^0\times\int_{-\infty}^{\infty}dy\,h_{21}^*(y, \mathbf{E}_2)\int_{|z-y|}^{\infty}ds\,s\,c_{11}^s(s) , \qquad (2.15)$$

where $c_{21}^*(z, \mathbf{E}_2)$ is a wall–particle direct correlation function, and $c_{11}^s(s)$ is the spherically symmetric part of the particle–particle direct correlation function. When

$z \geq 0$ and $y \leq 0$, $h_{21}^*(y) = -1$, and $|z-y| = z-y$, so that the integral from $-\infty$ to ∞ can be written as

$$\int_{-\infty}^{\infty} dy\, h_{21}^*(y, \mathbf{E}_2) \int_{|z-y|}^{\infty} ds\, s c_{11}^s(s) = \int_z^{\infty} ds\, c_{11}^s(s)(z-s)s + \int_0^{\infty} dy\, h_{21}^*(y, \mathbf{E}_2) \int_{|z-y|}^{\infty} ds\, s c_{11}^s(s) . \tag{2.16}$$

To proceed further, we anticipate the result derived in Sec. III which shows that $c_{21}^*(\infty, \mathbf{E}_2)$ is nonzero. This implies through Eqs. (2.8)–(2.10) that $h_{21}^*(\infty, \mathbf{E}_2)$ is also nonzero and allows us to partition $h_{21}^*(y, \mathbf{E}_2)$ as follows:

$$h_{21}^*(y, \mathbf{E}_2) = K_h + \Delta h_{21}(y, \mathbf{E}_2) , \tag{2.17}$$

where K_h is the asymptotic limit of $h_{21}^*(y, \mathbf{E}_2)$ and

$$\lim_{y \to \infty} \Delta h_{21}(y, \mathbf{E}_2) = 0 . \tag{2.18}$$

When $z \geq 0$,

$$h_{21}^*(z, \mathbf{E}_2) = c_{21}^*(z, \mathbf{E}_2) + 2\pi\rho_1^0 \int_z^{\infty} ds(z-s)\, c_{11}^s(s)s + 2\pi\rho_1^0 \times \left\{ \int_0^{\infty} [K_h + \Delta h_{21}(y, \mathbf{E}_2)]\, dy \int_{|z-y|}^{\infty} ds\, s c_{11}^s(s) \right\}. \tag{2.19}$$

By splitting the range of integration over y

$$\int_0^{\infty} dy \cdots = \int_0^z dy \cdots + \int_z^{\infty} dy \cdots , \tag{2.20}$$

and changing the order of integration, we find

$$2\pi\rho_1^0 K_h \int_0^{\infty} dy \int_{|z-y|}^{\infty} ds\, s c_{11}^s(s) = 2\pi\rho_1^0 K_h \left[\int_0^z ds\, s c_{11}^s(s) \left(\int_{z-s}^{z} dy + \int_z^{z+s} dy \right) + \int_z^{\infty} ds(z+s)s c_{11}^s(s) \right] \tag{2.21}$$

$$= 4\pi\rho_1^0 K_h \left[\int_0^{\infty} ds\, s^2 c_{11}^s(s) + \frac{1}{2} \int_z^{\infty} ds(z-s)s c_{11}^s(s) \right] \tag{2.22}$$

$$= K_h(1-Q) + 2\pi\rho_1^0 K_h \int_z^{\infty} ds(z-s)s c_{11}^s(s) . \tag{2.23}$$

Taking the limit $z \to \infty$ of Eq. (2.19), we have

$$K_h = K_c + K_h[1-Q] + \lim_{z\to\infty} 2\pi\rho_1^0 \left[\int_0^{\infty} \Delta h_{21}(y, \mathbf{E}_2)\, dy \times \int_{|z-y|}^{\infty} ds\, s c_{11}^s(s) + (1+K_h) \int_z^{\infty} ds(z-s)s c_{11}^s(s) \right] . \tag{2.24}$$

By splitting the range of integration again into two parts, and making use of Eq. (2.18) and the fact that $\lim_{s\to\infty} c_{11}^s(s) = 0$, one finds that the third term of Eq. (2.24) is zero. The vanishing of the last term in the limit of large z requires further details of the asymptotic behavior of $c_{11}^s(s)$. Taking[5] $c_{11}(12) \to -\beta u_{11}(12) + A_2 h_{11}^2(12) + \ldots$, we find $c_{11}^s(s) \to -\beta u_{11}^s(s) + A_2\{h_{11}^s(s) + \frac{1}{3}[h_{11}^{\Delta}(s)]^2 + \frac{2}{3}[h_{11}^D(s)]^2 + \ldots\}$. Since $h_{11}^s(s)$ and $h_{11}^{\Delta}(s)$ are both short ranged [of the form $e^{-\lambda s}s^{-1}\cos(\alpha s + \beta)$], the long ranged $h_{11}^D(s)$ contributes $\frac{2}{3}[h_{11}^D(s)]^2$ as $A_D s^{-6}$ to the limiting form of $c_{11}^s(s)$. Finally in the fourth term of Eq. (2.24)

$$\lim_{z\to\infty} \int_z^{\infty} ds(z-s) A_D s^{-5} = \lim_{z\to\infty} (-A_D/12z^3) = 0 .$$

Hence

$$K_h = K_c + K_h[1-Q] , \tag{2.25}$$

from which Eq. (2.10) follows.

The total and direct wall–particle correlation functions $h_{21}(z, \mathbf{E}_2, \Omega_1)$ and $c_{21}(z, \mathbf{E}_2, \Omega_1)$ are expanded as

$$h_{21}(z, \mathbf{E}_2, \Omega_1) = h_{21}^s(z) + h_{21}^D(z) D(2, 1) + h_{21}^{\Delta}(z)\Delta(2, 1) + \ldots , \tag{2.26}$$

$$c_{21}(z, \mathbf{E}_2, \Omega_1) = c_{21}^s(z) + c_{21}^D(z) D(2, 1) + c_{21}^{\Delta}(z)\Delta(2, 1) + \ldots , \tag{2.27}$$

where

$$D(2, 1) = \hat{s}_1 \cdot (3\hat{r}_{21}\hat{r}_{21} - \mathbf{U}) \cdot \hat{s}_2 , \tag{2.28}$$

$$\Delta(2, 1) = \hat{s}_1 \cdot \hat{s}_2 . \tag{2.29}$$

Here $\hat{s}_2$ and $\hat{s}_1$ are unit vectors in the same directions as $\mathbf{m}_2$ and $\mathbf{m}_1$, $\hat{\mathbf{r}}_{21}$ is a unit vector along the line joining the wall–particle 2 and the fluid particle 1, and $\mathbf{U}$ is the unit tensor. Since the wall dipole resides at a distance minus infinity from the surface of the wall, $\hat{r}_{21}$ coincides with the unit outward normal $\hat{n}$ to the wall. Again only the first three terms in the expansion for the wall–particle correlation functions are explicitly represented here, since the coefficients outside of $D(2,1)$ turn out to be not required in our investigation of electrostriction. A result of central importance to our discussion is that[1,2]

$$h_{21}^D(z) = \hat{h}_{21}^D(z) + 3K_{21} , \tag{2.30}$$

where $\hat{h}_{21}^D(z)$ is short ranged; hence

$$h_{21}^D(\infty) = 3K_{21} . \tag{2.31}$$

The constant K_{21} in the QHNC approximation is related to the electric field through the relation[2] (see Appendix B)

$$\frac{\beta m_1 E_2}{[3\cos^2\Theta_2 + 1]^{1/2}} = K_{21}\left[2Q_+(2K_{11}\rho_1^0 R_{11}^3) + Q_-(-K_{11}\rho_1^0 R_{11}^3) - \frac{3K_h}{(1+K_h)} \right] , \tag{2.32}$$

where $\beta = (k_B T)^{-1}$, k_B and T are the Boltzmann constant and temperature, respectively, and $Q_\pm$ are inverse compressibilities defined by (with $R_{11} = 2R_1$)

$$Q_+(2K_{11}\rho_1^0 R_{11}^3) = 1 - 2K_{11}\rho_1^0 \int_0^{\infty} c_{11}^+(r, 2K_{11}\rho_1^0)\, 4\pi r^2\, dr , \tag{2.33}$$

$$Q_-(-K_{11}\rho_1^0 R_{11}^3) = 1 + K_{11}\rho_1^0 \int_0^{\infty} c_{11}^-(r, -K_{11}\rho_1^0)\, 4\pi r^2\, dr , \tag{2.34}$$

in which the functions $c_{11}^{\pm}(r)$ are linear combinations defined[4(a)] through the relations

$$c_{11}^+(r) = [\hat{c}_{11}^D(r) + \tfrac{1}{2} c_{11}^{\Delta}(r)]/3K_{11} , \tag{2.35}$$

$$c_{11}^-(r) = [\hat{c}_{11}^D(r) - c_{11}^{\Delta}(r)]/3K_{11} , \tag{2.36}$$

where the "hatted" function is given by

$$\hat{c}_{11}^D(r) = c_{11}^D(r) - 3\int_r^\infty ds\, s^{-1} c_{11}^D(s) . \quad (2.37)$$

The inverse compressibilities $Q_\pm$ and the constant K_{11} also appear in the expression for the dipole moment of the fluid:

$$\frac{4\pi m_1^2 \rho_1^0}{3k_B T} = Q_+(2K_{11}\rho_1^0 R_{11}^3) - Q_-(-K_{11}\rho_1^0 R_{11}^3) . \quad (2.38)$$

Unlike Eq. (2.32), Eq. (2.38) is quite general[2] since it rests only on the asymptotic form of $c_{11}(r)$ in the absence of a field.

III. ELECTROSTRICTION

The HNC closure for the wall–particle correlation function is

$$c(2,\ 1) = h(2,\ 1) - \ln g(2,\ 1) - \beta U(2,\ 1) , \quad (3.1)$$

where we have abbreviated $c_{21}(z,\ \mathbf{E}_2,\ \Omega_1)$ by $c(2,\ 1)$ etc. and

$$U(2,\ 1) = U_{21}^s(z) - \mathbf{E}_2 \cdot m_1 \hat{s}_1 ,$$
$$g(2,\ 1) = h(2,\ 1) + 1 . \quad (3.2)$$

Using Eq. (2.26) in the logarithmic term, and expanding this up to the quadratic term, one finds in the QHNC approximation[6] that,

$$c(2,\ 1) = h_{21}^s(z) - \ln g_{21}^s(z) - \beta U_{21}^s(z) + h_{21}^D(z)(1 - g_{21}^s(z)^{-1}) D(2,\ 1) + \beta \mathbf{E}_2 \cdot m_1 \hat{s}_1 + h_{21}^\Delta(z)(1 - g_{21}^s(z)^{-1})\Delta(2,\ 1) + \cdots + \left[\frac{h_{21}^D(z)^2 D(2,\ 1)^2 + 2h_{21}^D(z) h_{21}^\Delta(z) D(2,\ 1)\Delta(2,\ 1) + h_{21}^\Delta(z)^2 \Delta(2,\ 1)^2}{2g_{21}^s(z)^2} + \cdots\right] . \quad (3.3)$$

On integrating over the angle Ω_1 and dividing by Ω, we have

$$c_{21}^*(z,\ \mathbf{E}_2) = h_{21}^s(z) - \ln g_{21}^s(z) - \beta U_{21}^s(z) + \frac{1}{6}\left\{\left[\frac{h_{21}^D(z)}{g_{21}^s(z)}\right]^2 (3\cos^2\Theta_2 + 1) + \left[\frac{h_{21}^\Delta(z)}{g_{21}^s(z)}\right]^2 + \frac{2h_{21}^\Delta(z)\, h_{21}^D(z)(3\cos^2\Theta_2 - 1)}{[g_{21}^s(z)]^2}\right\} + \cdots \quad (3.4)$$

In deriving Eq. (3.4) we have used the following results

$$\int \frac{d\Omega_1}{\Omega}[D(2,1)]^2 = \frac{(3\cos^2\Theta_2 + 1)}{3} , \quad (3.5)$$

$$\int \frac{d\Omega_1}{\Omega}[\Delta(2,1)]^2 = \tfrac{1}{3} , \quad (3.6)$$

$$\int \frac{d\Omega_1}{\Omega}\Delta(2,1) D(2,1) = \frac{(3\cos^2\Theta_2 - 1)}{3} . \quad (3.7)$$

For completeness we include a further integral which is required later

$$\int \frac{d\Omega_1}{\Omega}[D(2,1)]^4 = \frac{(3\cos^2\Theta_2 + 1)^2}{5} . \quad (3.8)$$

In the limit when $z \to \infty$, $h_{21}^\Delta(z)$ is zero, leaving the asymptotic form of c_{21}^* in the QHNC approximation as

$$c_{21}^*(\infty,\ \mathbf{E}_2) = K_h - \ln(1 + K_h) + \frac{3}{2}\frac{K_{21}^2}{(1 + K_h)^2}(3\cos^2\Theta_2 + 1)$$
$$= K_h - \ln(1 + K_h) + \tfrac{3}{2}\beta^2 m_1^2 E_2^2 / [(2Q_+ + Q_-) \times (1 + K_h) - 3K_h]^2 . \quad (3.9)$$

Using Eq. (2.10), the contribution of the term of order E_2^2 to electrostriction is

$$K_h^{(2)} = \frac{K_c^{(2)}}{Q} = \tfrac{3}{2} K_{21}^2 (3\cos^2\Theta_2 + 1)/Q = \frac{3/2\beta^2 m_1^2}{(2Q_+ + Q_-)^2}\frac{E_2^2}{Q} , \quad (3.10)$$

where the superscript (2) means the term of $O(E^2)$. It should be noted the electrostriction effect is independent of the direction of the electric field to the order E_2^2 considered in Eq. (3.10). In Eqs. (3.9) and (3.10) $Q(2K_{11}\rho_1^0 R_{11}^3)$ and $Q(-K_{11}\rho_1^0 R_{11}^3)$ are abbreviated by Q_+ and Q_- respectively.

It is convenient, as usual, to define[4(a)]

$$y = (4\pi/9)\rho_1^0 m_1^2 \beta , \quad (3.11)$$

and to rewrite Eq. (2.38) as

$$3y = Q_+(2K_{11}\rho_1^0 R_{11}^3) - Q_-(-K_{11}\rho_1^0 R_{11}^3) . \quad (3.12)$$

The dielectric constant ϵ is given by[7]

$$\epsilon = Q_+(2K_{11}\rho_1^0 R_{11}^3)/Q_-(-K_{11}\rho_1^0 R_{11}^3) . \quad (3.13)$$

The ϵ here is the $\mathbf{E}$-independent ϵ of linear theory. Making use of Eqs. (3.12) and (3.13), we have

$$3y[(2\epsilon + 1)/(\epsilon - 1)] = 2Q_+ + Q_- . \quad (3.14)$$

Finally the relation between the external field $\mathbf{E}_2$ and the Maxwell field $\mathbf{E}$ can be expected to be of the form, for $\Theta_2 = 0$,[8]

$$\mathbf{E} = [3/(2\epsilon + 1)]\mathbf{E}_2 + bE_2^2\mathbf{E}_2 + \cdots , \quad (3.15)$$

[where the contribution of $O(E_2)$ is independent of Θ_2] and our result for electrostriction to $O(E^2)$ (which is thus also independent of Θ_2) is

$$\frac{\Delta\rho}{\rho_1^0} = K_h^{(2)} = \left[\frac{\beta}{24\pi\rho_1^0 y}\frac{(\epsilon - 1)^2 E^2}{Q}\right] . \quad (3.16)$$

There are two contributions to electrostriction of $O(E^4)$: one from the term of $O(E_2^2)$ in Eq. (3.10) together with the b coefficient in Eq. (3.15), and a second from the contribution to K_h of $O(E_2^4)$ not shown in Eq. (3.10) together with the first term of Eq. (3.15). We restrict our attention here only to the second of these contributions but plan to return to the first after a more detailed study of the b coefficient for our problem.

To obtain the term of $O(E_2^4)$ to K_h, it is necessary to go *two* steps beyond the above QHNC approximation in a systematic expansion of the logarithmic term of Eq. (3.1); the first step beyond the QHNC approximation provides no additional information when $z \to \infty$ because $\int (d\Omega_1/\Omega)[D(21)]^3$ vanishes. From the next step we find

$$K_c = c_{21}^*(\infty,\ E_2) = K_h - \ln(1+K_h) + \frac{3K_{21}^2(3\cos^2\Theta_2+1)}{2(1+K_h)^2} + \frac{81K_{21}^4}{20(1+K_h)^4}(3\cos^2\Theta_2+1)^2\ , \qquad (3.17)$$

where we have made use of Eq. (3.8). The first two terms $K_h - \ln(1+K_h)$ arise from the spherically symmetric part of Eq. (3.3) when $z \to \infty$ $(h_{21}^s(z) \to K_h)$. From Eq. (2.32) the numerators of the remaining terms are of order E_2^2 and E_2^4, respectively.

For small values of the electric field, we can expand $\ln(1+K_h)$, $(1+K_h)^{-2}$, and $(1+K_h)^{-4}$. Retaining terms of $O(E_2^4)$, we have

$$K_c = K_h Q = K_h^2/2 + \tfrac{3}{2}K_{21}^2(3\cos^2\Theta_2+1)(1-2K_h+\dots) + (81K_{21}^4/20)(3\cos^2\Theta_2+1)^2\ . \qquad (3.18)$$

Solving Eq. (3.18) for K_h, we obtain for the electrostriction effect of order E_2^4 the expression

$$K_h^{(4)} = \frac{3x}{2Q} + \frac{81x^2}{20Q}\left(1 - \frac{10}{9Q} + \frac{5}{18Q^2}\right)\ , \qquad (3.19)$$

where $x = K_{21}^2(3\cos^2\Theta_2+1)$. Using Eqs. (3.11)–(3.15), we can recast this expression in terms of the dielectric constant as

$$\frac{\Delta\rho}{\rho_1^0} = K_h^{(4)} = \left[\frac{\beta}{24\pi\rho_1^0 y}(\epsilon-1)^2E^2 + \frac{\beta^2}{320\pi^2(\rho_1^0)^2y^2}(\epsilon-1)^4E^4 \times\left(1-\frac{10}{9Q}+\frac{5}{18Q^2}\right)\right]\frac{1}{Q}\ . \qquad (3.20)$$

These results arise from a systematic expansion of the HNC closure for the wall–particle correlation functions, which ignores the bridge diagrams in the wall–particle correlation functions. The inverse compressibility Q of the bulk dipolar fluid is however not restricted by any approximation, i.e., it is the exact result. In the rest of this section, we analyze the contribution of the term of $O(E^2)$ to electrostriction from the QHNC approximation.

Kirkwood and Oppenheim[9] discuss the thermodynamic derivation of electrostriction to $O(E^2)$ in an open system which leads to

$$\frac{\Delta\rho}{\rho_1^0} = \frac{\beta}{8\pi}\left(\frac{\partial\epsilon}{\partial\rho_1^0}\right)\frac{E^2}{Q}\ . \qquad (3.21)$$

The derivation of Eq. (3.21) assumes that the polarization density $\mathbf{P}(\mathbf{r})$ in an open system is linearly related to the electric field at $\mathbf{r}$ by the constitutive relation (ϵ independent of $\mathbf{E}$)

$$\mathbf{P}(\mathbf{r}) = (\epsilon-1)/4\pi\,\mathbf{E}(\mathbf{r})\ , \qquad (3.22)$$

which ignores nonlinear effects that are necessary to extend the thermodynamic theory to higher order in E. The thermodynamic approach to electrostriction can be compared with the results of statistical mechanics, for the term of $O(E^2)$. For our result of $O(E^2)$ to be consistent with Eq. (3.21) we must have

$$\rho_1^0[\partial\epsilon/\partial\rho_1^0] = (1/3y)(\epsilon-1)^2\ . \qquad (3.23)$$

This self-consistency test is indeed obeyed exactly by the simple Debye equation

$$(\epsilon-1)/(\epsilon+2) = y\ , \qquad (3.24)$$

but beyond that, if for example one uses for dipolar hard spheres

$$(\epsilon-1)/(\epsilon+2) = y - (15/16)y^3 + \dots\ , \qquad (3.25)$$

an inconsistency arises in the term of $O(y^2)$. To be specific

$$\rho_1^0\left(\frac{\partial\epsilon}{\partial\rho_1^0}\right) = \frac{(\epsilon+2)^2y}{3}\left(1-\frac{45y^2}{16}+\dots\right)\ , \qquad (3.26)$$

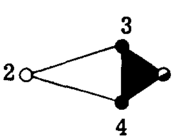
and

$$\frac{(\epsilon-1)^2}{3y} = \frac{(\epsilon+2)^2y}{3}\left(1-\frac{15y^2}{16}+\dots\right)^2 = \frac{(\epsilon+2)^2y}{3}\left(1-\frac{30y^2}{16}+\dots\right)\ . \qquad (3.27)$$

Jepsen's[10] derivation of Eq. (3.25) has been confirmed recently by Rushbrooke[11] as being exact through $O(y^3)$ in the $\rho_1^0 \to 0$ limit. Thus we are led to suspect that Eq. (3.23) is inconsistent because the bridge diagrams to $O(E^2)$, in the wall–particle correlation functions, have been ignored. A discussion of this follows.

IV. THE BRIDGE DIAGRAMS

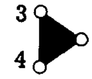
If we call the terms neglected in the HNC approximation [Eq. (3.1)] (i.e., the bridge diagrams) $B(2,\ 1)$, the leading contribution to c_{21}^* is

$B_1^*(2,\ 1) = 2$  1 , (4.1)

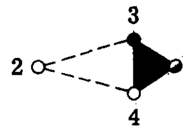
where

 $\equiv h(2,\ 1)$, (4.2)

and

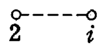
 $1 \equiv c(\mathbf{x}_1,\ \mathbf{x}_3,\ \mathbf{x}_4)$, (4.3)

in which $c(\mathbf{x}_1,\ \mathbf{x}_3,\ \mathbf{x}_4)$ is the three-particle direct correlation function for the bulk dipolar fluid and $\mathbf{x}_i = (\mathbf{r}_i,\ \Omega_i)$. The open circles ○ are root points, the half black circles ◑ indicate angular integration over the molecular orientations, and the full black circles (field points) ● indicate both spatial and angular integrations. The symmetry number of the graphs represented by Eqs. (4.1) and (4.4) is 2. When $z \to \infty$, $h(2,\ 1) \to K_h + 3K_{21}D(2,\ 1)$. Employing the wall limit, one sees that the term of $O(E^2)$ in $B_1^*(2,\ 1)$, when $z \to \infty$ is



(4.4)

where



$\equiv 3K_{21}D(2,\ i)$. (4.5)

The corresponding term of $O(E^4)$ in $B_1^*(2,\ 1)$ when $z\to\infty$ has a similar graphical representation, except that the bonds connecting the wall–dipole 2 to the field points 3 and 4 are $K_h^{(2)}$ bonds. We will evaluate analytically the contributions of these graphs to lowest order in the fluid density ρ_1^0 and dipole-moment squared m_1^2. To do this, we replace the three-particle direct correlation functions $c(\mathbf{x}_1\mathbf{x}_3\mathbf{x}_4)$ by the corresponding Mayer f bonds $f(\mathbf{x}_i,\ \mathbf{x}_j)$. The decomposition[12] of each f bond into reference f_0 bond and the sum of products of dipole bonds multiplied by $(1+f_0)$ is employed. In summary

$$c(\mathbf{x}_1,\ \mathbf{x}_3,\ \mathbf{x}_4)\simeq f(\mathbf{x}_1,\ \mathbf{x}_3)f(\mathbf{x}_3,\ \mathbf{x}_4)f(\mathbf{x}_4,\ \mathbf{x}_1)+O(\rho_1^0)\ , \tag{4.6}$$

where

$$f(\mathbf{x}_i,\ \mathbf{x}_j)=f_0(r_{ij})+[1+f_0(r_{ij})]\sum_{n=1}^{\infty}\frac{(\beta m_1^2D(i,\ j)/r_{ij}^3)^n}{n\,!}\ . \tag{4.7}$$

To the lowest order in the fluid dipole moment squared, it is necessary to retain only the first term in the sum. Denoting $[1+f_0(r_{ij})]$ by $e_0(r_{ij})$, we have

$$f(\mathbf{x}_i,\ \mathbf{x}_j)\simeq f_0(r_{ij})+e_0(r_{ij})\,\frac{\beta m_1^2D(ij)}{r_{ij}^3}\ . \tag{4.8}$$

The term of $O(E^2)$ derived from Eq. (4.4) will be considered first before discussing the term of $O(E^4)$.

A. The term of $O(E^2)$

Using Eqs. (4.8) and (4.6) in Eq. (4.4), and recognizing the fact that the angular integration of an odd number of D functions at a vertex is zero, we find that

$$B_1^{(2)*}(2,\ 1)=I_1^*(2,\ 1)+I_2^*(2,\ 1)\ , \tag{4.9}$$

where

$$I_1^*(2,\ 1)=A\int d\Omega_1\int d\mathbf{r}_3\,d\Omega_3\int d\mathbf{r}_4\,d\Omega_4D(2,\ 3)\times D(2,\ 4)f_0(r_{34})\,\phi(r_{31})\,\phi(r_{14})D(3,\ 1)D(1,\ 4) \tag{4.10}$$

$$=\frac{\Omega A}{\rho_1^0}\int d\mathbf{r}_{34}\,d\Omega_3\,d\Omega_4\,D(2,\ 4)D(2,\ 3)f_0(r_{34})H(3,\ 4)\ , \tag{4.11}$$

$$I_2^*(2,\ 1)=\frac{A}{\beta m_1^2}\int d\Omega_1\int d\mathbf{r}_3\,d\Omega_3\int d\mathbf{r}_4\,d\Omega_4D(2,\ 3)\times D(2,\ 4)\,\phi(r_{34})f_0(r_{31})f_0(r_{14})D(3,\ 4)\ , \tag{4.12}$$

where

$$H(3,\ 4)=\frac{\rho_1^0}{\Omega}\int d\Omega_1\int d\mathbf{r}_{13}\,\phi(r_{31})D(3,\ 1)\phi(r_{14})D(1,\ 4)\ , \tag{4.13}$$

$$A=9\beta^2m_1^4(\rho_1^0)^2K_{21}^2/2\Omega^3\ ,$$

and $\phi(r_{ij})=e_0(r_{ij})/r_{ij}^3$. Following the standard analysis of angular and spatial convolutions of dipolar bonds[3,11–13]

$$H(3,\ 4)=H_D(r_{34})D(3,\ 4)+H_\Delta(r_{34})\Delta(3,\ 4)\ . \tag{4.14}$$

From the work of Høye and Stell[13], and Rushbrooke[11]

$$2\hat{H}_D(r_{34})=H_\Delta(r_{34})=\frac{2\rho_1^0}{3}\int d\mathbf{r}_{13}\,\hat{\phi}(r_{31})\,\hat{\phi}(r_{14})\ , \tag{4.15}$$

where the hatted functions are defined by

$$\hat{h}(r)=h(r)-3\int_r^\infty h(s)\,s^{-1}\,ds\ , \tag{4.16}$$

and in particular, for dipolar hard spheres[13,11]

$$\hat{\phi}(r_{ij})=[f_0(r_{ij})/R_{11}^3]\ , \tag{4.17}$$

where R_{11} is the diameter $(=2R_1)$ of the spheres. We confine further analysis to the case of dipolar hard spheres with $\Omega=4\pi$, although the above treatment [excluding Eq. (4.17)] is quite general.

Distinguishing the term in Eq. (4.11) that arises from the Δ term of Eq. (4.14) by $I_{1\Delta}^*(2,\ 1)$ and the corresponding D term of Eq. (4.14) by $I_{1D}^*(2,\ 1)$, we have

$$I_{1\Delta}^*(2,\ 1)=\frac{A\Omega}{\rho_1^0}\int d\mathbf{r}_{34}\,H_\Delta(r_{34})f_0(r_{34})\times\int d\Omega_3\,d\Omega_4\,D(2,\ 3)D(2,\ 4)\Delta(3,\ 4)\ , \tag{4.18}$$

and

$$I_{1D}^*(2,\ 1)=\frac{A\Omega}{\rho_1^0}\int d\mathbf{r}_{34}\,H_D(r_{34})f_0(r_{34})\times\int d\Omega_3\,d\Omega_4\,D(2,\ 3)D(2,\ 4)D(3,\ 4)\ . \tag{4.19}$$

In Eq. (4.18),

$$\int d\mathbf{r}_{34}\,H_\Delta(r_{34})f_0(r_{34})=\frac{2\rho_1^0}{3R_{11}^6}\int d\mathbf{r}_{13}\int d\mathbf{r}_{34}\,f_0(r_{13})f_0(r_{34})f_0(r_{41})=\frac{2\rho_1^0}{3R_{11}^6}\left(-\frac{5\pi^2R_{11}^6}{6}\right)=\frac{-5\rho_1^0\,\pi^2}{9}\ , \tag{4.20}$$

where the double integral in the first line of the above is identified as the third virial coefficient for hard spheres. The remaining angular integrals in Eq. (4.18) can be reduced to

$$\int d\Omega_3\int d\Omega_4\,D(2,\ 3)D(2,\ 4)\Delta(3,\ 4)=\frac{\Omega^2}{9}(3\cos^2\Theta_2+1)\ . \tag{4.21}$$

Combining Eqs. (4.18), (4.20), and (4.21),

$$I_{1\Delta}^*(2,\ 1)=\frac{A\Omega}{\rho_1^0}\ \frac{-5\rho_1^0\pi^2}{9}\ \frac{\Omega^2(3\cos^2\Theta_2+1)}{9}=-\frac{5\pi^2}{18}\,\beta^2m_1^4(\rho_1^0)^2K_{21}^2(3\cos^2\Theta_2+1)\ , \tag{4.22}$$

wherein the value of A has been used. From Eq. (2.32), and Eqs. (3.11)–(3.15), we can reformulate $I^*_{1\Delta}(2,1)$ in terms of ϵ, E, and y as

$$I^*_{1\Delta}(2,\ 1)=-\frac{5}{128}\ \frac{(\epsilon-1)^2E^2\beta y}{\pi\rho_1^0}\ . \tag{4.23}$$

The analysis of Eq. (4.19) is similar with slight modifications. The angular integrals yield

$$\int d\Omega_3\int d\Omega_4 D(2,\ 3)D(2,\ 4)D(3,\ 4)$$
$$=\frac{\Omega^2}{9}\,\hat{s}_2\cdot(3\hat{n}\hat{n}-\mathbf{U})\cdot(3\hat{r}_{34}\hat{r}_{34}-\mathbf{U})\cdot(3\hat{n}\hat{n}+\mathbf{U})\cdot\hat{s}_2\ . \tag{4.24}$$

Substitution into Eq. (4.19) leads to

$$I^*_{1D}(2,\ 1)=\frac{A\Omega^3}{9\rho_1^0}\,\hat{s}_2(3\hat{n}\hat{n}-\mathbf{U})\cdot(3\hat{n}\hat{n}-\mathbf{U})\cdot\left[\int d\mathbf{r}_{34}H_D(r_{34})f_0\right.$$
$$\left.\times(r_{34})(3\hat{r}_{34}\hat{r}_{34}-\mathbf{U})\right]\cdot(3\hat{n}\hat{n}-\mathbf{U})\cdot\hat{s}_2\ . \tag{4.25}$$

Employing $\int d\mathbf{r}_{34}=\int_0^\infty dr_{34}\,r_{34}^2\int d\hat{r}_{34}$ and the identity

$$\int d\hat{r}_{34}(3\hat{r}_{34}\hat{r}_{34}-\mathbf{U})=0 \tag{4.26}$$

gives

$$I^*_{1D}(2,\ 1)=0\ . \tag{4.27}$$

The calculation of $I^*_2(2,\ 1)$ is very similar to that of $I^*_{1D}(2,\ 1)$ and will not be repeated. The result is

$$I^*_2(2,\ 1)=0\ . \tag{4.28}$$

Hence the only nonzero contribution to $R_1^{(2)*}(2,\ 1)$ comes from $I^*_{1\Delta}(2,\ 1)$ and

$$B_1^{(2)*}(2,\ 1)=-\frac{5}{128}\ \frac{(\epsilon-1)^2E^2\beta y}{\pi\rho_1^0}\ . \tag{4.29}$$

On adding this evaluation of the bridge diagram to the QHNC electrostriction term of $O(E^2)$ we have

$$K_h^{(2)}\cong\left[\frac{\beta(\epsilon-1)^2}{24\pi\rho_1^0 y}-\frac{5(\epsilon-1)^2\beta y}{128\pi\rho_1^0}\right]\frac{E^2}{Q}\ . \tag{4.30}$$

Agreement with the thermodynamic result to $O(E^2)$ at low densities requires that instead of Eq. (3.23) we have

$$\rho_1^0\left(\frac{\partial\epsilon}{\partial\rho}\right)=\frac{(\epsilon-1)^2}{3y}-\frac{5}{16}(\epsilon-1)^2y\ , \tag{4.31}$$

which is consistent with Eq. (3.25) to $O(y^2)$.

B. The term of $O(E^4)$ arising from the corresponding term of $O(E_2^4)$

The bridge diagram of $O(E_2^4)$ in the low density limit with $z\to\infty$ can be written as the sum of two terms as follows:

$$B_1^{(4)*}(2,\ 1)=J^*_1(2,\ 1)+J^*_2(2,\ 1)\ , \tag{4.32}$$

where

$$J^*_1(2,\ 1)=\frac{\rho_1^{0^2}(K_h^{(2)})^2}{2\Omega^3}\int d\Omega_1\int d\Omega_3\int d\Omega_4\int d\mathbf{r}_3\int d\mathbf{r}_4$$
$$\times f_0(r_{34})f_0(r_{41})f_0(r_{13}) \tag{4.33}$$
$$=-\frac{5\pi^2\rho_1^{0^2}R_{11}^6(K_h^{(2)})^2}{12}\ , \tag{4.34}$$

and

$$J^*_2(2,\ 1)=\frac{\rho_1^{0^2}(K_h^{(2)})^2}{2\Omega^3}(\beta m_1^2)^3\int d\Omega_1\int d\Omega_3\int d\Omega_4$$
$$\times\int d\mathbf{r}_3\int d\mathbf{r}_4\,\phi(r_{13})D(1,\ 3)\phi(r_{34})D(3,\ 4)$$
$$\times\phi(r_{41})D(4,\ 1)\ , \tag{4.35}$$

where we have again utilized the vanishing of the angular integration at any vertex of an odd number of D functions in reducing $B_1^{(4)*}(2,\ 1)$ to the sum of only two terms. By a straightforward (albeit lengthy) extension of the previous convolution techniques used in evaluating $I^*_{1\Delta}(2,\ 1)$ and $I^*_{1D}(2,\ 1)$, we found (see Appendix C)

$$J^*_2(2,\ 1)=-\frac{5}{54}\,\pi^2\rho_1^{0^2}R_{11}^6\left(\frac{\beta m_1^2}{R_{11}^3}\right)^3(K_h^{(2)})^2\ . \tag{4.36}$$

These results should be added to the term of $O(E^4)$ given in Eq. (3.20). To our knowledge, there is no available corresponding thermodynamic result of $O(E^4)$.

V. POLARIZATION

We shall consider the polarization in an open system described by chemical potential μ, volume V, and temperature T.

The polarization density $\mathbf{P}(\mathbf{r})$ is related to the partition function Ξ of the grand ensemble in an external field $\mathbf{E}_2$ by the functional derivative[7]

$$\mathbf{P}[\mathbf{r},\ \mathbf{E}_2(\mathbf{r})]=\beta^{-1}\frac{\delta\ln\Xi}{\delta\mathbf{E}_2(\mathbf{r})}=\frac{1}{\Omega}\int d\Omega_1$$
$$\times\rho_1(\mathbf{r},\ \mathbf{E}_2(\mathbf{r}),\ \Omega_1)\mathbf{m}_1(\Omega_1)\ . \tag{5.1}$$

For the adsorption of molecules at a wall, the position vector $\mathbf{r}$ is replaced by the scalar distance z from the wall. Also the external field created by the wall dipole is, in our investigation, constant and independent of position, i.e., $\mathbf{E}_2(\mathbf{r})=\mathbf{E}_2$. Therefore

$$\mathbf{P}(z,\ \mathbf{E}_2)=\frac{m_1}{\Omega}\int d\Omega_1\,\rho_1(z,\ \mathbf{E}_2,\ \Omega_1)\,\hat{s}_1(\Omega_1) \tag{5.2}$$
$$=\frac{m_1\rho_1^0}{\Omega}\int d\Omega_1\,h_{21}(z,\ \mathbf{E}_2,\ \Omega_1)\,\hat{s}_1(\Omega_1)\ , \tag{5.3}$$

where we have used Eq. (2.4) for the density function and employed the identity $\int\hat{s}_1(\Omega_1)\,d\Omega_1=0$. The polarization density profile is determined by wall–particle total correlation function, $h_{21}(z,\ \mathbf{E}_2,\ \Omega_1)$, which contains the effect of the external field and the effects of the correlations between the bulk molecules. Substituting the invariant expansion of Eq. (2.26) for h_{21} in Eq. (5.3) gives the polarization density profile as

$$\mathbf{P}(z,\ \mathbf{E}_2)=\frac{m_1\rho_1^0}{\Omega}\int d\Omega_1\,\hat{s}_1(\Omega_1)[h_{21}^D(z)D(2,\ 1)$$
$$+h_{21}^\Delta(z)\Delta(2,\ 1)+\ldots]\ . \tag{5.4}$$

Using the following identities

$$\frac{1}{\Omega}\int d\Omega_1\,\hat{s}_1(\Omega_1)\,\Delta(2,\ 1)=\tfrac{1}{3}\,\hat{s}_2\ , \tag{5.5}$$

$$\frac{1}{\Omega}\int d\Omega_1\,\hat{s}_1(\Omega_1)\,D(2,\ 1)=\tfrac{1}{3}(3\cos^2\Theta_2+1)^{1/2}\,\hat{e}_2\ , \tag{5.6}$$

and Eq. (2.30), reduces Eq. (5.4) to

$$P(z,\ E_2)=m_1\rho_1^0\left\{\left(K_{21}+\frac{\hat{h}_{21}^{D}(z)}{3}\right)(3\cos^2\Theta_2+1)^{1/2}\hat{e}_2+\frac{h_{21}^{\Delta}(z)\hat{s}_2}{3}+\ldots\right\} \tag{5.7}$$

As $z\to\infty$, $\hat{h}_{21}^{D}(z)$ and $h_{21}^{\Delta}(z)$ vanish. Hence,

$$P(\infty,\ E_2)=m_1\rho_1^0K_{21}(3\cos^2\Theta_2+1)^{1/2}\hat{e}_2 \tag{5.8a}$$

$$=\frac{\rho_1^0\beta m_1^2 E}{[2Q_+(2K_{11}\rho_1^0R_{11}^3)+Q_-(-K_{11}\rho_1^0R_{11}^3)-3K_h/(1+K_h)]}, \tag{5.8b}$$

where we have employed Eq. (2.32) in deriving the relation (5.8b) from (5.8a). The magnitude of $P(\infty, E_2)$ is independent of the inclination of the applied field, and its direction is parallel to it. Making use of Eq. (3.13), this can be rewritten as

$$P(\infty,\ E_2)=\frac{\epsilon-1}{4\pi}\ \frac{3E_2}{(2\epsilon+1)}\frac{1}{\{1-[K_h/y(1+K_h)](\epsilon-1)/(2\epsilon+1)\}}\ . \tag{5.9}$$

When $K_h=0$ as in the MS and LHNC approximations, and when b and higher coefficients in Eq. (3.15) are neglected, we recover the constitutive relation

$$P(\infty,\ E_2)=\frac{\epsilon-1}{4\pi}\ E(\infty,\ E_2)\ . \tag{5.10}$$

If b and the higher order coefficients in Eq. (3.15) are not ignored, nonlinear terms in E will be found even in the MS and LHNC approximations. In the QHNC and higher order approximations there are additional nonlinear effects which arise from electrostriction since K_h is no longer zero. In the QHNC approximation, $K_h^{(2)}$ is given by Eq. (3.10) and on using this with Eqs. (3.11) to (3.13) in Eq. (5.9) we have, after expanding the denominator,

$$P_{QHNC}(\infty,\ E_2)=\frac{\epsilon-1}{4\pi}\ \frac{3E_2}{(2\epsilon+1)}\left[1+\frac{3\beta}{8\pi\rho_1^0y^2}\times\left(\frac{\epsilon-1}{2\epsilon+1}\right)^3\frac{E_2^2}{Q}\right]+O(E_2^5)\ . \tag{5.11}$$

This gives the polarization density to $O(E_2^3)$ in the QHNC approximation where we recall that E_2 is the external field. Assuming that the relation between E_2 and the Maxwell field E is well approximated by Eq. (3.15) with b set equal to zero, we have to $O(E^3)$

$$P_{QHNC}(\infty,\ E)=\frac{\epsilon-1}{4\pi}E\left[1+\frac{\beta}{24\pi\rho_1^0y^2}\ \frac{(\epsilon-1)^3}{(2\epsilon+1)}\ \frac{E^2}{Q}\right]+O(E^5)\ . \tag{5.12}$$

An exact calculation of the term of $O(E^3)$ would require the determination of b of Eq. (3.15). In addition, the contributions of the bridge diagrams to electrostriction as given first in the form of Eq. (4.29) and second in the relationship between K_{21} and E_2 [c.f. Eq. (2.32)] must be determined (see Appendix B).

VI. DISCUSSION

Although several general treatments of dipolar systems in external fields have recently appeared[14] and a number of earlier molecular treatments of electrostriction already exist,[15] our treatment appears to be novel, complementing rather than overlapping earlier work on electrostriction and going considerably beyond it for fluids in the liquid regime.[16]

The discussion in the previous sections demonstrates the limitations of the MS and LHNC approximations for the wall–particle correlation functions, since they do not predict electrostriction. The QHNC approximation is the first member of the hierarchy of approximations which are derived from the hypernetted chain closure, to show this effect even qualitatively, but it is necessary to include the most elementary bridge diagrams as well, if quantitative agreement with the thermodynamic result of $O(E^2)$ is to be obtained. Thermodynamics thus provides a stringent test of our statistical mechanical approximation theory of dipoles in the presence of an electric field. Although our calculations deal only with electrostriction effects at an infinite distance away from the wall, it would be difficult to imagine that the simpler MS and LHNC approximations, which fail to predict electrostriction, can be trusted to provide accurate density profiles close to the wall.

Another result of our work has been a clarification of the deviations that can be expected in the linear relation between the polarization density $P(\infty)$ and local field $E(\infty)$. The QHNC approximation is found to generate nonlinear terms in E for the polarization density of an open system. It is clear that additional terms will appear when better approximations to the wall–particle correlation functions are employed.

We conclude with one other observation of the limitations of the MS and LHNC approximations. The surface excess Γ of dipolar molecules at the wall is given by

$$\Gamma=\frac{1}{\Omega}\iint[\rho(z,\ E_2,\ \Omega_1)-\rho(\infty,\ E_2,\ \Omega_1)]\,d\Omega_1\,dz \tag{6.1}$$

$$=\rho_1^0\int(h_{21}^{*}(z,\ E_2)-K_h)\,dz\ . \tag{6.2}$$

In the MS and LHNC approximations, $K_h=0$ and $h_{21}^{*}(z, E_2)$ is identically the total wall–particle correlation function for the reference system usually denoted by $h_{21}^{s}(z)$. The surface excess is therefore insensitive to the presence of an electric field when the MS and LHNC closures are employed. In the QHNC approximation and beyond, however, the interactions between the electric field and the dipolar molecules are coupled to $h_{21}^{*}(z, E_2)$ and lead to an increase in the surface excess over that which is found in the absence of an electric field.

APPENDIX A

This appendix gives the details of the derivation of Eq. (2.13). An alternative and more systematic form of Eq. (2.26) for $h_{21}(\mathbf{r}_{21}, \Omega_2, \Omega_1)$ is given by Blum and co-workers[4(b)] as

$$h_{21}(\mathbf{r}_{21},\ \Omega_2,\ \Omega_1)=\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\sum_{l=0}^{\infty}\sum_{|i|\le m}\sum_{|j|\le n} h^{mnl}_{ij,21}(r_{21})\times\phi^{mnl}_{ij}(\Omega_2,\ \Omega_1,\ \hat{r}_{21})\ , \tag{A1}$$

where

$$\phi^{mnl}_{ij}(\Omega_2,\ \Omega_1,\ \hat{r}_{21}) = \sum_{\mu,\nu,\lambda}\begin{pmatrix} m & n & l\\ \mu & \nu & \lambda\end{pmatrix} D^m_{i\mu}(\Omega_2)D^n_{j\nu}(\Omega_1)D^l_{0\lambda}(\hat{r}_{21})\ . \tag{A2}$$

Using the identity

$$\int\frac{d\Omega_1}{\Omega}D^n_{j\nu}(\Omega_1)=\delta_{n0}\,\delta_{j0}\,\delta_{\nu 0} \tag{A3}$$

gives the Ω_1 angle-averaged h^*_{21} at finite r_{21} as

$$h^*_{21}(\mathbf{r}_{21},\ \Omega_2)=\sum_{m,l,i} h^{mol}_{i0,21}(r_{21})\,\phi^{mol}_{io}(\Omega_2,\ 0,\ \hat{r}_{21}) \tag{A4}$$

$$=\sum_{m,i} h^{mom}_{io,21}(r_{21})\,\phi^{mom}_{io}(\Omega_2,\ 0,\ \hat{r}_{21})\ , \tag{A5}$$

since

$$\phi^{mol}_{io}=\sum_{\mu}\begin{pmatrix} m & o & l\\ \mu & o & -\mu\end{pmatrix}D^m_{i\mu}(\Omega_2)D^l_{o-\mu}(\hat{r}_{21})\,\delta_{ml} \tag{A6}$$

due to the symmetry properties of the $3j$ symbol. The Ornstein–Zernike equation for a binary mixture in which $\rho_2\to 0$ is (in k space)

$$\tilde{h}_{21}(\mathbf{k},\ \Omega_2,\ \Omega_1)=\tilde{c}_{21}(\mathbf{k},\ \Omega_2,\ \Omega_1)+\rho^0_1\int\frac{d\Omega_3}{\Omega}\tilde{h}_{21}(\mathbf{k},\ \Omega_2,\ \Omega_3)\tilde{c}_{11}(\mathbf{k},\ \Omega_3,\ \Omega_1)\ , \tag{A7}$$

where

$$\tilde{t}(\mathbf{k},\ \Omega_2,\ \Omega_1)=\int d\mathbf{r}\exp(-i\mathbf{k}\cdot\mathbf{r})\,t(\mathbf{r},\ \Omega_2,\ \Omega_1) \tag{A8}$$

for $t=h_{21}$, c_{21}, and c_{11}.

Applying $\int d\Omega_1/\Omega$ to Eq. (A7) gives

$$\tilde{h}^*_{21}(\mathbf{k},\ \Omega_2)=\tilde{c}^*_{21}(\mathbf{k},\ \Omega_2)+\rho^0_1\int\frac{d\Omega_3}{\Omega}\tilde{h}_{21}(\mathbf{k},\ \Omega_2,\ \Omega_3)\tilde{c}^*_{11}(\mathbf{k},\ \Omega_3)\ , \tag{A9}$$

where

$$\tilde{c}^*_{11}(\mathbf{k},\ \Omega_3)=\int\frac{d\Omega_1}{\Omega}\tilde{c}_{11}(\mathbf{k},\ \Omega_3,\ \Omega_1) \tag{A10}$$

along with similar definitions for $\tilde{h}^*_{21}$, $\tilde{c}^*_{21}$.

For nonpolarizable molecules the radial coefficients $c^{mom}_{io,11}$ are neglected for $m\ge 1$.[4(b)] Invariance of the c_{11} analog of Eq. (A1) to Fourier transform necessarily gives the vanishing of $\tilde{c}^{mom}_{io,11}(k)$ and by symmetry $\tilde{c}^{omm}_{io,11}(k)$ for $m=1,\ 2,\ 3,\ldots,\ \infty$, where

$$\tilde{c}^{mom}_{io,11}(k)=4\pi i^m\int_0^\infty dr\,r^2 j_m(kr)\,c^{mom}_{io,11}(r)\ . \tag{A11}$$

From Eq. (A8) with $t=c_{11}$, Eq. (A11) and the above comments, Eq. (A10) reduces to

$$\tilde{c}^*_{11}(\mathbf{k},\ \Omega_3)=c^{ooo}_{oo,11}(k)\ , \tag{A12}$$

and alternatively in r space

$$c^*_{11}(\mathbf{r},\ \Omega)=c^{ooo}_{oo,11}(r)\ . \tag{A13}$$

Use of Eq. (A12) for $\tilde{c}^*_{11}(\mathbf{k},\ \Omega_3)$ in Eq. (A9) gives

$$\tilde{h}^*_{21}(\mathbf{k},\ \Omega_2)=\tilde{c}^*_{21}(\mathbf{k},\ \Omega_2)+\rho^0_1\tilde{c}^{ooo}_{oo,11}(k)\int\frac{d\Omega_3}{\Omega}\tilde{h}_{21}(\mathbf{k},\ \Omega_2,\ \Omega_3)$$

$$=\tilde{c}^*_{21}(\mathbf{k},\ \Omega_2)+\rho^0_1\tilde{h}^*_{21}(\mathbf{k},\ \Omega_2)\tilde{c}^{ooo}_{oo,11}(k)\ . \tag{A14}$$

Identifying

$$\tilde{c}^{ooo}_{oo,11}(k)=\int\frac{d\Omega_1}{\Omega}\int\frac{d\Omega_2}{\Omega}\tilde{c}_{11}(\mathbf{k},\ \Omega_1,\ \Omega_2)=\tilde{c}^s_{11}(k)$$

gives

$$\tilde{h}^*_{21}(\mathbf{k},\ \Omega_2)=\tilde{c}^*_{21}(\mathbf{k},\ \Omega_2)+\rho^0_1\tilde{h}^*_{21}(\mathbf{k},\ \Omega_2)\tilde{c}^s_{11}(k)\ ,$$

which on inversion back to r space gives Eq. (2.13).

APPENDIX B: THE RELATIONSHIP BETWEEN K_{21} AND THE WALL-DIPOLE FIELD E_2

This discussion follows the derivation of the corresponding relation in the LHNC approximation[2] with the difference that electrostriction contributes additionally to the wall-particle correlation functions in the QHNC approximation and beyond. It would also become necessary, in an exact theory, to employ the complete invariant expansions for these correlation functions. However for us, this step produces nothing new since the higher-order terms beyond the coefficients of $D(2,1)$, are neglected in the QHNC approximations. We begin by considering the effect of electrostriction on the wall–dipole field starting with the HNC theory and specializing finally to the QHNC approximation which yields Eq. (2.32). The contributions of the simplest bridge diagrams to the wall–dipole field are also considered briefly.

In the HNC approximation for a binary dipolar fluid,

$$c(2,\ 1)=h(2,\ 1)-\ln g(2,\ 1)-\beta U(2,\ 1) \tag{B1}$$

$$=h^s_{21}(r)-\ln g^s_{21}(r)-\beta U^s_{21}(r)+\left[h^D_{21}(r)+\frac{\beta m_1 m_2}{r^3}\right]D(2,\ 1)+h^\Delta_{21}(r)\Delta(2,\ 1)-\ln\left[1+\frac{h^s_{21}(r)+h^D_{21}(r)D(2,\ 1)+h^\Delta_{21}(r)\Delta(2,\ 1)+\ldots}{g^s_{21}(r)}\right]+\ldots\ , \tag{B2}$$

where we use the complete invariant expansions for $h(2, 1)$ and $c(2, 1)$:

$$h(2, 1) = h_{21}^s(r) + h_{21}^D(r) D(2, 1) + h_{21}^\Delta(r) \Delta(2, 1) + \ldots , \tag{B3}$$

$$c(2, 1) = c_{21}^s(r) + c_{21}^D(r) D(2, 1) + c_{21}^\Delta(r) \Delta(2, 1) + \ldots . \tag{B4}$$

The projection of $c(2, 1)$ on $D(2, 1)$ is

$$c_{21}^D(r) = \int \frac{d\Omega_1 \, d\Omega_2}{\Omega^2} c(2, 1) D(2, 1) / \langle D(2, 1)^2 \rangle_{\Omega_1, \Omega_2} , \tag{B5}$$

where

$$\langle D(2, 1)^2 \rangle_{\Omega_1 \Omega_2} = \int \frac{d\Omega_1 \, d\Omega_2}{\Omega^2} D(2, 1)^2 = \frac{2}{3} . \tag{B6}$$

Substituting Eq. (B3) in Eq. (B1) we find the D-projected part of Eq. (B1) to be given by

$$c_{21}^D(r) = \frac{\beta m_1 m_2}{r^3} + h_{21}^D(r) - \tfrac{3}{2} \langle \{ \ln [1 + h_{21}^s(r) + h_{21}^D(r) D(2, 1) + h_{21}^\Delta(r) \Delta(2, 1) + \ldots] \} D(2, 1) \rangle_{\Omega_1 \Omega_2} , \tag{B7}$$

where in general

$$\langle \cdots \rangle_{\Omega_1, \Omega_2} = \int \frac{d\Omega_1 \, d\Omega_2}{\Omega^2} \ldots . \tag{B8}$$

On expanding the logarithmic term, recalling that angular integration of an odd power of $D(2, 1)$ is zero and that the terms beyond $h_{21}^D(r) D(2, 1)$ are neglected, we have

$$c_{21}^D(r) = \frac{\beta m_1 m_2}{r^3} + h_{21}^D(r) \{ 1 - [g_{21}^s(r)]^{-1} \} - \frac{3}{2} \left\{ \sum_{n=1}^{\infty} \left[\frac{h_{21}^D(r)}{g_{21}^s(r)} \right]^{2n+1} \frac{\langle D(2, 1)^{2n+2} \rangle_{\Omega_1 \Omega_2}}{(2n+1)} \right\} + \text{higher-order terms} , \tag{B9}$$

where $\langle D(2, 1)^2 \rangle_{\Omega_1 \Omega_2} = 2/3$ as in Eq. (B6), and

$$\langle D(2, 1)^4 \rangle_{\Omega_1 \Omega_2} = 24/25 , \tag{B10}$$

$$\langle D(2, 1)^6 \rangle_{\Omega_1 \Omega_2} = 464/245 . \tag{B11}$$

The general formula for $\langle D(2, 1)^{2n} \rangle_{\Omega_1 \Omega_2}$ is

$$\langle D(2, 1)^{2n} \rangle_{\Omega_1 \Omega_2} = \frac{4^n (n!)^2}{(2n+1)(2n+1)!} \sum_{k=0}^{n} \binom{2k}{k} . \tag{B12}$$

In the QHNC approximation we have

$$c_{21}^D(r) = \frac{\beta m_1 m_2}{r^3} + h_{21}^D(r) \{ 1 - [g_{21}^s(r)]^{-1} \} + \text{h.o.t} , \tag{B13}$$

where h.o.t stands for higher-order neglected terms. The first two terms of Eq. (B9) are just those obtained in the LHNC approximation. We now let $r = R_2 + z$ and consider the combined limits $\rho_2 \to 0$, $R_2 \to \infty$ followed by the limit $z \to \infty$, which gives the asymptotic form of the wall–particle correlation function. Using Eqs. (2.1), (2.8), and (2.30)

$$\lim_{\substack{R_2 \to \infty \\ z \to \infty}} c_{21}^D(r) = \lim_{z \to \infty} c_{21}^D(z) = \beta m_1 E_0 + 3K_{21} \left(\frac{K_h}{1 + K_h} \right) . \tag{B14}$$

In the LHNC and MS approximations, $K_h = 0$. The relationship between $c_{21}^D(r)$ and $\hat{c}_{21}^D(r)$ is[4(a)]

$$c_{21}^D(r) = \hat{c}_{21}^D(r) - \frac{3}{r^3} \int_0^r \hat{c}_{21}^D(s) \, s^2 ds , \tag{B15}$$

where in the QHNC approximation

$$\hat{c}_{21}^D(r) = \widehat{h_{21}^D(r) [1 - g_{21}^s(r)^{-1}]} . \tag{B16}$$

On taking the limits described earlier, we find that since $g_{21}^s(z)$ is bounded and $\hat{h}_{21}^D(z)$ is short ranged,

$$\lim_{\substack{R_2 \to \infty \\ z \to \infty}} \hat{c}_{21}^D(r) = 0 . \tag{B17}$$

Combining this with Eqs. (B14) and (B15)

$$3K_{21} \left(\frac{K_h}{1 + K_h} \right) + \beta m_1 E_0 = - \lim_{\substack{R_2 \to \infty \\ z \to \infty}} \left[\frac{3}{r^3} \int_0^r \hat{c}_{21}^D(s) \, s^2 ds \right] . \tag{B18}$$

To evaluate the integral, we proceed as for the LHNC approximation.[2] Substitution in the Ornstein–Zernike equation for a binary mixture followed by the limit $\rho_2 = 0$ yields an infinite number of equations as follows:

$$h_{21}^s(r) = c_{21}^s(r) + \rho_1 h_{21}^s * c_{11}^s + \text{h.o.t} , \tag{B19}$$

$$\hat{h}_{21}^D(r) = \hat{c}_{21}^D(r) + \frac{\rho_1}{3} (\hat{h}_{21}^D * \hat{c}_{11}^D + \hat{h}_{21}^D * c_{11}^\Delta + h_{21}^\Delta * \hat{c}_{11}^D) + \text{h.o.t} , \tag{B20}$$

$$h_{21}^\Delta(r) = c_{21}^\Delta(r) + \frac{\rho_1}{3} (2 \hat{h}_{21}^D * \hat{c}_{11}^D + h_{21}^\Delta * c_{11}^\Delta) + \text{h.o.t} , \tag{B21}$$

$$\vdots$$

In the limit $R_2 \to \infty$, the $z \to \infty$, the higher-order terms (h.o.t) are neglected in the QHNC approximation, and in this limit we are left with the three equations originally used by Wertheim for the bulk fluid in the MS approximation. In the same limit we may then take linear combinations of Eqs. (B20) and (B21) to get

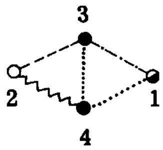
$$h_{21}^{\pm}(r) = c_{21}^{\pm}(r) + K_{11} \rho_1^{\pm} h_{21}^{\pm} * c_{11}^{\pm} , \tag{B22}$$

and our earlier argument[2] in the LHNC approximation for evaluating Eq. (B18) goes through unchanged. We then find

$$3K_{21} \left(\frac{K_h}{1 + K_h} \right) + \beta m_1 E_0 = K_{21} [2Q_+(2K_{11} \rho_1^0 R_{11}^3) - Q_-(-K_{11} \rho_1^0 R_{11}^3)] , \tag{B23}$$

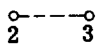
which when combined with Eq. (2.2) yields Eq. (2.32). Since K_h is of $O(E_2^2)$ in the QHNC approximation, Eq. (2.32) contains terms of $O(E_2^3)$, etc., which lie beyond the linear relation between K_{21} and E_2 obtained in the MS and LHNC approximations. There are bridge diagrams of the same order in the electric field which contribute to the relation between K_{21} and E_2. The simplest of these will now be examined.

None of the bridge diagrams that have been considered in our discussion of electrostriction [Eqs. (4.10), (4.12), (4.33), and (4.35)] can contribute to $c_{21}^D(z)$ and hence to the relation between K_{21} and E_2, since their projections along $D(2, 1)$ have an odd number of D functions at vertex 1 which vanishes on angular integration. The simplest bridge diagram of $O(E_2^3)$ when $z=\infty$ that does not have this liability is

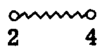
$B_3(2, 1) =$ 

$(z=\infty)$, (B24)

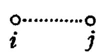
where



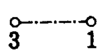
$\equiv 3K_{21}\,D(2, 3) \equiv 3K_{21}\,\hat{s}_2\cdot(3\hat{n}\hat{n}-\mathrm{U})\cdot\hat{s}_3$, (B25)



$\equiv K_h$, (B26)



$\equiv f_0(r_{ij})$, (B27)



$\equiv \phi(r_{31})D(3, 1)$. (B28)

The projection of this along $D(2, 1)$ is

$$B_3^D(2, 1) = \int \frac{d\Omega_1\,d\Omega_2}{\Omega^2}\,B_3(2, 1)D(2, 1) \tag{B29}$$

$$= \frac{3K_{21}\,K_h(\rho_1^0)^2\,\beta m_1^2}{\Omega^4}\int d\Omega_2\int d\Omega_1\int d\mathbf{r}_3\,d\Omega_3 \times \int d\mathbf{r}_4\,d\Omega_4\,D(2, 3)D(2, 1)D(3, 1) \times f_0(r_{34})f_0(r_{41})\phi(r_{31}) \tag{B30}$$

$$= \frac{3K_{21}K_h(\rho_1^0)^2\beta m_1^2}{\Omega^3}\int d\Omega_2\int d\Omega_1\int d\Omega_3\int d\mathbf{r}_{31}D(2, 3) \times D(2, 1)D(3, 1)\,g_1(r_{31})\,\phi(r_{31})\ , \tag{B31}$$

where

$$g_1(r_{31}) = \int d\mathbf{r}_{41}\,f_0(r_{34})f_0(r_{41})\ , \tag{B32}$$

but

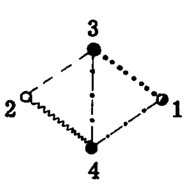
$$\int d\mathbf{r}_{31} = \int dr_{31}\,r_{31}^2\int d\hat{r}_{31}\ , \tag{B33}$$

and

$$\int d\hat{r}_{31}\,D(3, 1) = \int d\hat{r}_{31}(3\hat{r}_{31}\,\hat{r}_{31}-\mathrm{U}) = 0\ . \tag{B34}$$

Hence $B_3^D(2, 1)$ vanishes and Eq. (2.32) is valid beyond the QHNC approximation when the simplest bridge diagrams of $O(m_1^2E_2^3)$ as described above are also considered.

The simplest bridge diagram with a nonvanishing projection along $D(2,1)$ is

$B_{3,4}(2,1) =$ 

(B35)

which, to lowest order in the electric field, is of $O(m_1^4E_2^3)$. Our analysis below shows that the contribution of the bulk fluid to this projection, as depicted by the portion of the graph labeled 3 1 4, is essentially the third virial coefficient for the reference system. By a straightforward elaboration of our argument, it is apparent that all of the higher virial coefficients contribute to projections of bridge diagrams, of the same order, along $D(2, 1)$.

When $z\to\infty$, the projection of $B_{3,4}(2,1)$ along $D(2,1)$ is given by

$$\lim_{z\to\infty} B_{3,4}^D(2,1) = \frac{3K_{21}K_h(\rho_1^0)^2\beta^2m_1^4}{\Omega^4}\int d\Omega_2\int d\Omega_1\int d\mathbf{r}_3\,d\Omega_3\int d\mathbf{r}_4\,d\Omega_4 \times D(2,3)D(2,1)D(4,1)D(3,4)\phi(r_{34})\phi(r_{41})f_0(r_{31}) \tag{B36}$$

$$= \frac{3K_{21}K_h\rho_1^0\beta^2m_1^4}{\Omega^3}\int d\Omega_2\int d\Omega_1\int d\Omega_3\,D(2,3)D(2,1) \times\int d\mathbf{r}_{31}f_0(r_{31})[I_\Delta(r_{31})\Delta(3,1)+I_D(r_{31})D(3,1)]\ , \tag{B37}$$

where following our earlier analysis [see Eqs. (4.13) and (4.14)] of angular and spatial convolutions of dipolar bonds at vertex 4,

$$\frac{\rho_1^0}{\Omega}\int d\mathbf{r}_{41}\,d\Omega_4\,\phi(r_{34})D(3,4)\phi(r_{41})D(4,1) = I_\Delta(r_{31})\Delta(3,1)+I_D(r_{31})D(3,1) \tag{B38}$$

and

$$2\,\hat{I}_D(r_{31}) = I_\Delta(r_{31}) = \frac{2\rho_1^0}{3}\int d\mathbf{r}_{41}\,\hat{\phi}(r_{41})\,\hat{\phi}(r_{34})\ . \tag{B39}$$

The argument leading to Eq. (4.26), with 3 4 replaced by 3 1, ensures that the second term of Eq. (B37) vanishes. Likewise, using the same steps that lead to Eq. (4.21), we have in the first term of Eq. (B37) the following integral

$$\int d\Omega_2\int d\Omega_1\int d\Omega_3\,D(2,3)D(2,1)D(3,1) = \frac{2\Omega^3}{9}\ . \tag{B40}$$

Using Eqs. (B40) and (4.17) for $\hat{\phi}(r_{ij})$ in Eq. (B39), we find that

$$\lim_{z\to\infty} B_{3,4}^D(2,1) = \frac{4K_{21}K_h(\rho_1^0)^2\beta^2m_1^4}{9R_{11}^6} \times\int d\mathbf{r}_{31}\int d\mathbf{r}_{41}f_0(r_{41})f_0(r_{31})f_0(r_{34})\ , \tag{B41}$$

where the integral is the third virial coefficient equal to $-5\pi^2R_{11}^6/6$ for hard spheres.

$$\therefore \lim_{z\to\infty} B_{3,4}^D(2,1) = -\tfrac{15}{8}y^2K_{21}K_h\ ,$$

where y is defined in Eq. (3.11).

APPENDIX C: A BRIDGE DIAGRAM OF $O(E^4)$–CALCULATION OF EQ. (4.36)

We make use of the following lemma:

$$\int d\mathbf{r}f_1(r)f_2(r) = \frac{(-1)^l}{8\pi^3}\int d\mathbf{k}\bar{f}_2(k)\bar{f}_1(k) \tag{C1}$$

$$= (-1)^l\int d\mathbf{r}\hat{f}_1(r)\hat{f}_2(r)\ . \tag{C2}$$

The first equality is just Paserval's theorem in which the lth-order Hankel transforms $\bar{f}_n(k)$ of $f_n(k)$ ($n=1, 2$) are used.[4]

The Hankel transform of $f_n(r)$ is the Fourier transform of the corresponding hatted function $\hat{f}_n(r)$:

$$\bar{f}_n(k) = \tilde{\hat{f}}_n(k) = 4\pi \int_0^\infty dx x^2 j_0(kx) \hat{f}_n(x) , \qquad \text{(C3)}$$

where $j_0(kx)$ is a spherical Bessel function of order zero. Substituting Eq. (C3) in Eq. (C1), for $n=1$ and 2, and making use of

$$\int_0^\infty dk\, k^2 j_0(kx) j_0(ky) = \frac{\pi}{2xy}\, \delta(x-y) , \qquad \text{(C4)}$$

we arrive at Eq. (C2).

To derive Eq. (4.36), we start with Eq. (4.35) and do the spatial and angular integrations over vertex 3 to obtain

$$J_2^*(2, 1) = \frac{\rho_1^0 [K_h^{(2)}]^2 (\beta m_1^2)^3}{2\Omega^2} \int d\Omega_1 \int d\Omega_4\, d\mathbf{r}_4 \times [H_D(r_{14}) D(14) + H_\Delta(r_{14}) \Delta(14)]\, \phi(r_{14}) D(14) , \qquad \text{(C5)}$$

where $\Omega = 4\pi$ and Eq. (4.15) defines $H_\Delta(r_{14})$ and $\hat{H}_D(r_{14})$, with the $\hat{H}_D(r_{14})$ related to $H_D(r_{14})$ by Eq. (4.16). The second term in the sum of Eq. (C5) vanishes as a result of the orthogonality condition

$$\int d\Omega_1 \int d\Omega_4\, D(1, 4) \Delta(1, 4) = 0 . \qquad \text{(C6)}$$

For the first term in the sum we need,

$$\int d\Omega_1 \int d\Omega_4\, D(1, 4) D(1, 4) = \frac{4\pi}{3} \int d\Omega_1\, \hat{s}_1 \cdot (3\hat{r}_{14}\hat{r}_{14} - \mathrm{U}) \cdot (3\hat{r}_{14}\hat{r}_{14} - \mathrm{U}) \cdot \hat{s}_1 \qquad \text{(C7)}$$

$$= \frac{4\pi}{3} \int d\Omega_1 [3\hat{r}_{14} \cdot (\hat{s}_1 \hat{s}_1) \cdot \hat{r}_{14} + 1] = \frac{32\pi^2}{3} \qquad \text{(C8)}$$

$$\therefore J_2^*(2, 1) = \frac{\rho_1^0 [K_h^{(2)}]^2 (\beta m_1^2)^3}{3} \int d\mathbf{r}_4\, \phi(r_{14}) H_D(r_{14}) \qquad \text{(C9)}$$

$$= \frac{\rho_1^0 [K_h^{(2)}]^2 (\beta m_1^2)^3}{3} \int d\mathbf{r}_4\, \hat{\phi}(r_{14}) \hat{H}_D(r_{14}) , \qquad \text{(C10)}$$

where we have used Eq. (C2) with l necessarily 2 in the last step. Employing Eqs. (4.15) and (4.17) for $\hat{H}_D(r_{14})$ and $\hat{\phi}_D(r_{14})$, respectively, we find

$$J_2^*(2, 1) = \frac{\rho_1^{0^2} [K_h^{(2)}]^2}{9} \frac{(\beta m_1^2)^3}{R_{11}^9} \times \int d\mathbf{r}_4 \int d\mathbf{r}_3 f_0(r_{13}) f_0(r_{34}) f_0(r_{41}) . \qquad \text{(C11)}$$

The integral is related to the third virial coefficient for hard spheres and is equal to $-5\pi^2 R_{11}^6/6$. Substitution in Eq. (C11) leads to the final result quoted in Eq. (4.36).

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