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ELECTROSTRICTION AND DIPOLAR ORDERING AT AN ELECTRIFIED WALL

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A theory of electrostriction which follows from studies of dipolar ordering at an electrified wall is discussed in the quadratic hypernetted chain approximation. Bridge diagrams for the wall–particle correlation functions contribute significantly to electrostriction even to lowest order in the electric field. The form of the constitutive relation between the polarization density and the field in strong fields is discussed.

1. Introduction

The ordering of dipoles at a wall from which an electric field emerges has been studied in the mean spherical (MS) [1] and linearized hypernetted chain (LHNC) [2] approximations. We report here that electrostriction appears as an added feature when the theory is carried beyond the LHNC approximation for the wall–particle correlation functions, leading to a molecular theory of this phenomenon in which graphical analysis and integral equation approximations that are ubiquitous in the theory of fluids may be exploited. Of the hierarchy of approximations generated by the hypernetted chain equation (HNC), we find that the quadratic hypernetted chain (QHNC) approximation is the first to predict electrostriction. The leading term in the relative change in density an *infinite distance* away from a flat wall is of $O(E^2)$, where E is the magnitude of the local field. Approximations beyond the QHNC theory systematically generate terms of higher order, so that the QHNC approximation also contains within it the complete electrostriction term of $O(E^2)$ in the HNC approximation.

All of the theories of electrostriction which have their genesis in the HNC approximation ignore the bridge diagrams, but we find, by comparing the QHNC theory with the thermodynamics of electrostriction [3], that these diagrams must contribute significantly even to lowest order in E. This leads us to believe that they play an equally important role in determining the local density when the dipoles are closer to the wall.

We report here the barest outline of our molecular theory for an open system [4] in which contributions from the QHNC approximation to $O(E^2)$ and from the bridge diagrams to the same order in the electric field and to lowest order in the density and the dipole moment are evaluated analytically. Our theory can also be extended to higher order in E but this will not be pursued here. The thermodynamic discussion of Kirkwood and Oppenheim [3] however is limited to deriving the electrostriction term of $O(E^2)$, since it is based on a thermodynamic perturbation theory of first order in E^2, that uses as reference-state input the linear constitutive relation between the polarization density $\boldsymbol{P}(\infty)$ and the local electric field $\boldsymbol{E}$ for a field-independent ϵ,

$$P(\infty) = (\epsilon - 1)\, E(\infty)/4\pi \tag{1}$$

Further details of our work and extensions to it will be presented elsewhere [4] but we remark that our study yields the constitutive relation with the same value of ϵ as that obtained from from relating ϵ to the two-particle orientational correlation function in the absence of a field, and also provides a basis for determining non-linear terms in the electric field for the polarization density

2. Electrostriction in an open system

We employ the technique discussed in refs [1,2] to generate an electric field by taking a mixture of dipolar hard spheres to the zero-density limit of species 2 with an attendant increase in the radius R_2 to infinity, under the constraint that its dipole moment m_2 divided by the cube of the radius of the excluded volume $R_{21} = R_2 + R_1$ is a constant E_0 The electric field E_2 emerging from the wall is related to E_0 by [1,2]

$$\boldsymbol{E}_2 = E_0 (3 \cos^2\theta_2 + 1)^{1/2}\, \hat{\boldsymbol{e}}_2, \tag{2}$$

where $\boldsymbol{e}_2$ is a unit vector dependent upon θ_2 [1,2], the angle which the wall dipole makes with the wall normal $\hat{\boldsymbol{n}}$ Note that E_2 is constant when the wall dipole orientation θ_2 is fixed The relationship between $\boldsymbol{E}_2$ and the Maxwell field $\boldsymbol{E}$ in the fluid is of the form

$$\boldsymbol{E} = [3/(2\epsilon + 1)]\, \boldsymbol{E}_2 + \text{terms non-linear in } \boldsymbol{E}_2 \tag{3}$$

Here the non-linear terms are of magnitude const E_2^3 + when $\theta_2 = 0$, and ϵ is the dielectric constant of the fluid at zero field In the notation of ref [2], the wall–particle correlation function has the invariant expansion

$$h_{21}(z, E_2, \boldsymbol{\Omega}_1) = h^{s}_{21}(z) + h^{D}_{21}(z)\, D(2,1)$$

$$+\, h^{\Delta}_{21}(z)\, \Delta(2,1) + \quad , \tag{4}$$

where $\Delta(2,1) = \hat{\boldsymbol{s}}_2 \cdot \hat{\boldsymbol{s}}_1$ and $D(2,1) = \hat{\boldsymbol{s}}_2 \cdot (3\hat{\boldsymbol{n}}\hat{\boldsymbol{n}} - \mathbf{U}) \cdot \hat{\boldsymbol{s}}_1$ in which $\hat{\boldsymbol{s}}_2$ and $\hat{\boldsymbol{s}}_1$ are unit vectors in the directions of the wall dipole and fluid dipole respectively, z is the distance of a fluid dipole (of orientation $\boldsymbol{\Omega}_1$) from the wall, and $\mathbf{U}$ is the unit tensor In this wall limit, $R_2 \to \infty$,

$$h^{D}_{21}(z) = \bar{h}^{D}_{21}(z) + 3K_{21}, \tag{5}$$

where $\bar{h}^{D}_{21}(z)$ is short-ranged and K_{21} is a constant related to the electric field E_2 (see section 3) Hence

$$\lim_{z \to \infty} h^{D}_{21}(z) = 3K_{21} \tag{6}$$

The coefficients $h^{\Delta}_{21}(z)$ and those beyond it in (4) are short-ranged The origin of electrostriction in our theory is the coupling that can exist between $h^{D}_{21}(z)$ and $h^{s}_{21}(z)$, this feedback begins with the QHNC approximation

We define the electrostriction effect K_h as the relative change in density of the bulk fluid when the electric field is switched on, so that

$$K_h \equiv \Delta\rho/\rho^0_1 = h^{*}_{21}(\infty, E_2), \tag{7}$$

where

$$h^{*}_{21}(z, E_2) = \Omega^{-1} \int h_{21}(z, E_2, \boldsymbol{\Omega}_1)\, \mathrm{d}\boldsymbol{\Omega}_1 \tag{8}$$

$\Omega = 4\pi$ for dipolar hard spheres and ρ^0_1 is the density of the bulk fluid when $E_2 = 0$ If K_c is the corresponding asymptotic limit of the angularly averaged direct correlation function $c_{21}(z, E_2, \boldsymbol{\Omega}_1)$, we find [4] that, in the absence of molecular polarizability

$$K_h = K_c/Q, \tag{9}$$

where Q is the inverse compressibility of the fluid,

$$Q = 1 - (\rho^0_1/\Omega^2) \int c_{11}(r, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_3)\, \mathrm{d}\boldsymbol{\Omega}_1\, \mathrm{d}\boldsymbol{\Omega}_3\, \mathrm{d}\boldsymbol{r} \tag{10}$$

and $c_{11}(r, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_3)$ is the direct correlation function of the bulk fluid The thermodynamic theory of electrostriction [3] for an open system gives K_h to $O(E^2)$ as

$$K^{(2)}_h = (\beta/8\pi)\,(\partial\epsilon/\partial\rho^0_1)\, E^2/Q, \tag{11}$$

where $\beta = 1/kT$, k is Boltzmann's constant, T is the absolute temperature and the superscript (2) means the term of $O(E^2)$

3. The QHNC approximation for electrostriction

By considering the asymptotic limit of $c^{D}_{21}(z)$ in the invariant expansion for the wall–particle direct correlation function $c_{21}(z, E_2, \boldsymbol{\Omega}_1)$ we find [4] that K_{21} is related to E_2 in the QHNC approximation by

$$\beta m_1 E_2/(3\cos^2\theta_2+1)^{1/2} = K_{21}[2Q_+(2K_{11}\rho_1^0 R_{11}^3) + Q_-(-K_{11}\rho_1^0R_{11}^3) - 3K_h/(1+K_h)], \qquad (12)$$

where the $Q_\pm(\ )$ functions are defined in ref [2], and the constant K_{11} is related quite generally (i e. not just in the QHNC theory) to the fluid dipole moment m_1 by [4–6]

$$3y = Q_+(2K_{11}\rho_1^0R_{11}^3) - Q_-(-K_{11}\rho_1^0R_{11}^3), \qquad (13)$$

where $y = 4\pi m_1^2\rho_1^0\beta/9$. The dielectric constant ϵ of the fluid is also quite generally given by [6]

$$\epsilon = Q_+(2K_{11}\rho_1^0R_{11}^3)/Q_-(-K_{11}\rho_1^0R_{11}^3) \qquad (14)$$

We also find from the $z\to\infty$ limit of the QHNC approximation for $c_{21}(z, E_2, \mathbf{\Omega}_1)$ that

$$K_c^{(2)} = \tfrac{3}{2}K_{21}^2(3\cos^2\theta_2+1) \qquad (15)$$

and on using (2), (3), (9) and (12)–(14) we have

$$K_h^{(2)} = (\beta/24\pi\rho_1^0 y)(\epsilon-1)^2 E^2/Q, \qquad (16)$$

where the superscript (2) means again the term of $O(E^2)$ Note that in (16) $K_h^{(2)}$ is independent of the inclination θ_2 of the wall dipole Consistency with the thermodynamic theory (11) demands that

$$\rho_1^0\,\partial\epsilon/\partial\rho_1^0 = (\epsilon-1)^2/3y \qquad (17)$$

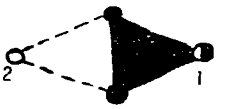
This relation is indeed satisfied by the simple Debye equation $(\epsilon-1)/(\epsilon+2) = y$, but the more exact expression [7,8] (for arbitrary y and $\rho_1^0\to 0$)

$$(\epsilon-1)/(\epsilon+2) = y - \tfrac{15}{16}y^3 + \qquad (18)$$

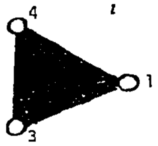
introduces a discrepancy of $O(y^2)$ in (17). Since higher order approximations derived from the HNC equation do not produce additional contributions to K_h of $O(E^2)$, the apparent inconsistency lies in ignoring the bridge diagrams.

4. Bridge diagrams of $O(E^2)$

The bridge diagram of $O(E^2)$ and to lowest order in the fluid density can be represented graphically, when $z\to\infty$, by

$B^*(2,1) =$  , (19)

where $\underset{2}{\circ}- - - -\underset{i}{\circ} \equiv 3K_{21}D(2,i)$, and



is the three-particle direct correlation function $c_3(X_1, X_3, X_4)$ for the fluid with $X_i \equiv (r_i, \mathbf{\Omega}_i)$ $B^*(2,1)$ contributes to the wall–particle direct correlation function In (19) the open circle 2 is the wall dipole root point, the half black circle ◑ signifies angular integration over the orientations of the bulk fluid dipole 1 and the black circles (field points) represent spatial and angular integrations of fluid dipoles To evaluate (19) to lowest order in ρ_1^0 and m_1 we use the low-density limit in terms of Mayer f functions

$$c_3(X_1, X_3, X_4) \simeq f(X_1, X_3)\, f(X_3, X_4)\, f(X_4, X_1) \qquad (20)$$

and retain only the $n = 1$ term in the perturbation expansion [8,9]

$$f(X_i, X_j) = f_0(r_{ij}) + [1 + f_0(r_{ij})]\sum_{n=1}^{\infty}[\beta m_1^2 D(i,j)/r_{ij}^3]^n \qquad (21)$$

for the Mayer f function, where $f_0(r_{ij})$ is the corresponding Mayer function for the reference hard-sphere system The bridge diagram is now evaluated analytically using Hankel transforms and we find eventually that when $z\to\infty$,

$$B^{(2)*}(\infty) \simeq -\tfrac{5}{128}(\epsilon-1)^2\,\beta y E^2/\pi\rho_1^0, \qquad (22)$$

in which the contribution from the three-particle correlation function appears as the third virial coefficient for hard spheres! Adding this to (16), after using (9), we have

$$K_h^{(2)} \simeq \left[\frac{\beta(\epsilon-1)^2}{24\pi\rho_1^0 y} - \frac{5(\epsilon-1)^2\beta y}{128\pi\rho_1^0}\right]\frac{E^2}{Q}, \qquad (23)$$

where $\simeq$ emphasizes that our calculation of the bridge diagram of $O(E^2)$ is correct only to lowest order in ρ_1^0 and m_1. This is sufficient however to test the molecular theory against thermodynamics using (18) for the dielectric constant. Instead of (17) we now need

$$\rho_1^0\,\partial\epsilon/\partial\rho_1^0 \simeq (\epsilon-1)^2/3y - \tfrac{5}{16}(\epsilon-1)^2 y, \qquad (24)$$

which is consistent with (18) to $O(y^2)$. We have thus shown that the bridge diagrams make significant contributions to the density when $z \to \infty$, and it appears likely that they affect the density profiles also when the dipoles are closer to the wall Theoretical studies of the ordering of dipoles and ions at a wall that have appeared so far ignore these bridge diagrams

5. The polarization density $P(\infty, E_2)$ in an open system

From the definition of $P(z, E_2)$ in the grand ensemble [6] we have

$$P(z,E_2) = (m_1\rho_1^0/\Omega)\int h_{21}(z,E_2,\Omega_1)\hat{s}_1(\Omega_1)\,\mathrm{d}\boldsymbol{\Omega} \quad (25)$$

In our discussion E_2 is independent of z [see (2)] Using the invariant expansion for $h_{21}(z, E_2, \Omega_1)$, we find, after doing the necessary angular integrations, that

$$P(\infty, E_2) = m_1\rho_1^0 K_{21}(3\cos^2\theta_2 + 1)^{1/2}\,\hat{e}_2, \quad (26)$$

which is independent of any approximation for the wall–particle correlation function' Employing the QHNC approximation for K_{21} given in (12),

$$P(\infty, E_2) = \beta\rho_1^0 m_1^2 E_2[2Q_+(2K_{11}\rho_1^0 R_{11}^3)$$

$$+ Q_-(-K_{11}\rho_1^0 R_{11}^3) - 3K_h/(1+K_h)]^{-1} \quad (27)$$

$$= [(\epsilon - 1)/4\pi][3E_2/(2\epsilon + 1)]$$

$$\times \left[1 - \frac{K_h}{y(1+K_h)}\,\frac{\epsilon - 1}{2\epsilon + 1}\right]^{-1} \quad (28)$$

When $K_h = 0$ (i.e in the absence of electrostriction as in the MS and LHNC approximation) and when all the higher coefficients of E_2^n $(n \geqslant 3)$ in (3) are assumed zero, we recover the constitutive relation (1) Conversely when K_h and the higher coefficients in (3) are not zero, non-linear terms in the polarization density will appear. Substitution of (15) and (9) in (28) followed by expansion of the denominator draws out the term of $O(E_2^3)$ in the QHNC approximation for the polarization density which is

$$P_{\mathrm{QHNC}}(\infty, E) = [(\epsilon - 1)/4\pi][3E_2/(2\epsilon + 1)]$$

$$\times \left[1 + \frac{3\beta}{8\pi\rho_1^0 y^2}\left(\frac{\epsilon - 1}{2\epsilon + 1}\right)^3 \frac{E_2^2}{Q}\right] + O(E_2^5). \quad (29)$$

If the non-linear terms in (3) are neglected

$$P_{\mathrm{QHNC}}(\infty, E) = [(\epsilon - 1)/4\pi]E$$

$$\times \left[1 + \frac{\beta}{24\pi\rho_1^0 y^2}\,\frac{(\epsilon - 1)^3}{2\epsilon + 1}\,\frac{E^2}{Q}\right] + O(E^5) \quad (30)$$

A more complete calculation of this term in the QHNC approximation would require the determination of the coefficient of the E_2^3 term in (3) when $\theta_2 = 0$ An exact calculation of the term of $O(E^3)$ would require in addition that the contributions of the bridge diagrams to electrostriction [see (22)] and to the relationship between K_{21} and E_2 be included

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