Electrostriction and the dielectric constant of a simple polar fluid

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An exact statistical mechanical expression for electrostriction in an open system to $O(E^2)$ (where E is the electric field) is obtained by adding the appropriate bridge diagrams to the hypernetted chain (HNC) approximation for the wall-particle interactions between a dipolar fluid and an electrified wall. The expression for the relative change in bulk density is found to be independent of the inclination of the electric field (or the orientation of the "wall-dipole" which creates the field). Comparison with the thermodynamics of electrostriction leads to a differential equation for the dielectric constant ϵ whose solution is an equation first proposed by Ramshaw. The significance of the bridge diagram contributions to electrostriction suggests that they play an important role in determining the structure and properties of dipoles and ions near a charged wall.

I. INTRODUCTION

A molecular theory of electrostriction and polarization density which follows from the study of dipolar ordering near an electrified wall has been described recently.[1] The relative change in density $\Delta\rho/\rho_1^0$ at an infinite distance $(z\to\infty)$ away from the wall is initially of $O(E^2)$ where E is the electric field. The electrostriction effect of $O(E^2)$ can be calculated analytically when the quadratic hypernetted chain (QHNC) approximation is employed for the wall particle correlation function $h_{21}(z, \mathbf{E}, \mathbf{\Omega}_1)$. In the notation of Ref. 1,

$$K_h=\frac{\Delta\rho}{\rho_1^0}=\frac{\beta}{24\pi\rho_1^0 y}(\epsilon-1)^2\frac{E^2}{Q}\quad \text{(HNC)}, \tag{1.1}$$

where we recall that ϵ is the dielectric constant of the fluid in the limit of zero field, ρ_1^0 and Q are the density and inverse compressibility of the bulk fluid in the absence of the field, and

$$y=\frac{4\pi}{9}\beta m_1^2\rho_1^0, \tag{1.2}$$

in which m_1 is the dipole moment and $\beta=(kT)^{-1}$ where k is Boltzmann's constant and T is the absolute temperature. Equation (1.1) is characterized as the hypernetted chain (HNC) result for electrostriction because the term of $O(E^2)$ in the QHNC approximation is also the HNC approximation for electrostriction to the same order in the electric field.[1]

Comparison of Eq. (1.1) with the corresponding thermodynamic formula[2] for electrostriction to $O(E^2)$,

$$\frac{\Delta\rho}{\rho_1^0}=\frac{\beta}{8\pi}\left(\frac{\partial\epsilon}{\partial\rho_1^0}\right)\frac{E^2}{Q} \tag{1.3}$$

leads to the following differential equation[1]:

$$\rho_1^0\frac{\partial\epsilon}{\partial\rho_1^0}=\frac{(\epsilon-1)^2}{3y}, \tag{1.4}$$

whose solution, assuming an integration constant of 1/3, is the simple and well-known Debye relation

$$\frac{\epsilon-1}{\epsilon+2}=y. \tag{1.5}$$

It is known that Eq. (1.5) embodies only the leading term in the exact expression for the dielectric constant. Jepsen[3] and Rushbrooke[4] have calculated the term of $O(y^3)$ in the corresponding expression for the dielectric constant of dipolar hard spheres which is in agreement with Wertheim's solution of the mean spherical approximation.[5] The implication of Eq. (1.5) as the solution to Eq. (1.4) is that the HNC approximation does not even lead to the correct formula for electrostriction to lowest order in the electric field. This in turn implies that the bridge diagrams that are omitted in this approximation must play a significant role in determining electrostriction and dipolar ordering near an electrified wall.

The contributions of the bridge diagrams to electrostriction of $O(E^2)$ and to lowest order in the density ρ_1^0 and dipolar moment m_1 have already been evaluated in Ref. 1. Here we derive an exact expression for this term for arbitrary ρ_1^0 and m_1 and for an *arbitrary inclination of the electric field.* This leads to an exact statistical mechanical expression for electrostriction to $O(E^2)$ which is found to be independent of the field angle. Comparison with the thermodynamic theory enables us to derive an exact differential equation for the dielectric constant ϵ in terms of an integral of the projection of the direct correlation function for dipolar molecules in the absence of the field. The solution to this differential equation is found to be an expression first derived by Ramshaw[6] for the dielectric constant of dipolar molecules with cylindrical symmetry which is also the case considered by us.

Although Eq. (1.3) has long been known on purely thermodynamic grounds, we should note that its microscopic derivation immediately follows from the work of Høye and Stell.[7(a)] It was also subsequently rederived, in a microscopic analysis, by Carnie and Stell.[7(b)]

II. ELECTROSTRICTION TO $O(E^2)$—EXACT RESULTS

As discussed elsewhere,[1] the origin of electrostriction in our theory is the coupling that exists between the coeffi-

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cients $h_{21}^D(z)$ and $h_{21}^s(z)$ in the expansion for the wall particle indirect correlation function

$$h_{21}(z, \mathbf{E}_2, \mathbf{\Omega}_1) = h_{21}^s(z) + h_{21}^D(z)D(2,1) + h_{21}^\Delta(2)\Delta(2,1) + \cdots . \tag{2.1}$$

This feedback begins with the QHNC approximation and leads to a change in density at an infinite distance away from the wall because the asymptotic value of $h_{21}^D(z)$ is a constant $(3K_{21})$ related to the electric field by[8-10]

$$K_{21}(3\cos^2\theta_2 + 1)^{1/2} = \frac{\beta m_1(\epsilon - 1)E}{9y} + O(E^2) , \tag{2.2}$$

where θ_2 is the angle between the normal to the wall and the "wall dipole" which creates the electric field. Only the leading term in the relationship between K_{21} and the Maxwell field E is known exactly and required in our discussion of electrostriction to $O(E^2)$.

It follows from Eqs. (2.1) and (2.2) that the bridge diagram contributions of $O(E^2)$ to K_c, which is an angular average of the wall particle direct correlation function defined in Ref. 1, can have only two wall-dipole h_{21} bonds. The sum of these contributions [see Eq. (4.4) of Ref. 1(b)] written out explicitly is

$$B^*(2,1) = \frac{(3K_{21})^2\rho_1^{02}}{2\Omega^2}\int D(2,3)D(2,4) \times \frac{\delta}{\delta\rho(1)} c(3,4) d\Omega_1\, d\mathbf{r}_3\, d\mathbf{\Omega}_3\, d\mathbf{r}_4\, d\Omega_4 , \tag{2.3}$$

where $\Omega = 4\pi$,

$$D(2,i) = \hat{s}_2 \cdot (3\hat{n}\hat{n} - \mathbf{U}) \cdot \hat{s}_i , \tag{2.4}$$

with $\hat{n}$ the unit normal and i representing particle 3 or 4 and

$$c(3,4,1) = \frac{\delta c(3,4)}{\delta\rho(1)} , \tag{2.5}$$

in which $c(3,4,1)$ and $c(3,4)$ are the three and two-particle direct correlation fnnctions respectively in the absence of the field. If θ_2 is the inclination of the wall-dipole, Eq. (2.4) can also be written as

$$D(2,i) = (3\cos\theta_2\hat{n} - \hat{s}_2) \cdot \hat{s}_i \tag{2.6}$$

$$= (3\cos^2\theta_2 + 1)^{1/2}(\hat{e}_2 \cdot \hat{s}_i) , \tag{2.7}$$

where $\hat{e}_2$ is a unit vector in the direction of the electric field. From Eqs. (2.2), (2.3), and (2.7) one has to $O(E^2)$,

$$B^{*(2)} = \frac{\beta(\epsilon-1)^2 E^2 \rho_1^0 J(\rho_1^0, y)}{24\pi y} , \tag{2.8}$$

with

$$J(\rho_1^0, y) = \frac{3}{\Omega^3}\hat{e}_2 \cdot \left[\int d\mathbf{\Omega}_1\, d\mathbf{r}_3\, d\mathbf{\Omega}_3\, d\mathbf{r}_4\, d\mathbf{\Omega}_4 \hat{s}_3 \frac{\delta}{\delta\rho(1)} c(3,4)\hat{s}_4\right] \cdot \hat{e}_2 \tag{2.9}$$

$$= \frac{3}{\Omega^2}\hat{e}_2 \cdot \left[\frac{\partial}{\partial\rho_1^0}\int d\mathbf{r}_{34}\, d\Omega_3\, d\mathbf{\Omega}_4\, \hat{s}_3 c(3,4)\hat{s}_4\right] \cdot \hat{e}_2 . \tag{2.10}$$

By expanding $c(3,4)$ as

$$c(3,4) = c^s(r_{34}) + c^D(r_{34})D(3,4) + c^\Delta(r_{34})\Delta(3,4) + \cdots , \tag{2.11}$$

where the terms beyond $c^\Delta(r_{34})\Delta(3,4)$ are of shorter range than r_{34}^{-3} and $c(3,4)$ is finite as $r \to 0$ and making use of the relations

$$\int \hat{s}_i\, d\mathbf{\Omega}_i = 0, \tag{2.12}$$

$$\int \hat{s}_i\hat{s}_i\, d\Omega_i = \frac{4\pi}{3}\mathbf{U} , \tag{2.13}$$

$$\int d\mathbf{r}_{34} = \int_0^\infty r_{34}^2 dr_{34} \int d\hat{r}_{34} , \tag{2.14}$$

$$\int (3\hat{r}_{34}\hat{r}_{34} - \mathbf{U}) d\mathbf{r}_{34} = 0 , \tag{2.15}$$

and

$$\frac{1}{\Omega^2}\int \Delta(3,4)^2 d\mathbf{\Omega}_3 d\mathbf{\Omega}_4 = \tfrac{1}{3} , \tag{2.16}$$

we have

$$J(\rho_1^0, y) = \frac{\partial}{\partial\rho_1^0} I(\rho_1^0, y) , \tag{2.17}$$

where

$$I(\rho_1^0, y) = \frac{1}{\Omega^2}\int d\mathbf{r}_{34}\, d\mathbf{\Omega}_3\, d\mathbf{\Omega}_4 c(3,4)\Delta(3,4) . \tag{2.18}$$

Thus, the contribution of $O(E^2)$ to K_c from the bridge diagram is given by

$$B^{*(2)} = \frac{\beta(\epsilon-1)^2}{24\pi y} E^2 \rho_1^0 \frac{\partial I(\rho_1^0, y)}{\partial\rho_1^0} . \tag{2.19}$$

Note that the orientation of the wall dipole (θ_2) and hence the inclination α of the electric field to which it is related by[8,9]

$$\cos\alpha = \frac{2\cos\theta_2}{(3\cos^2\theta_2 + 1)^{1/2}} \tag{2.20}$$

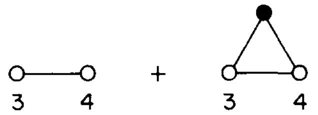
has completely disappeared from the bridge diagram contributions to electrostriction of $O(E^2)$. Using the relation $K_h = K_c/Q$, where Q is the inverse compressibility of the fluid, to get the contribution of the bridge diagrams to electrostriction, and adding this to the HNC relation (1.1), we obtain the exact relation for electrostriction to $O(E^2)$ in an open system:

$$\frac{\Delta\rho}{\rho_1^0} = \frac{\beta(\epsilon-1)^2}{24\pi\rho_1^0 y}\left[1 + \rho_1^{02}\frac{\partial I(\rho_1^0, y)}{\partial\rho_1^0}\right]\frac{E^2}{Q} . \tag{2.21}$$

In Eq. (2.19) and (2.21) the effect of the bridge diagrams has been factored into the product of two terms, one of which includes $\beta(\epsilon-1)^2E^2$ and the other involves the density derivative of integral $I(\rho_1^0, y)$, which contains the direct correlation function $c(3,4)$ *in the absence of the field*. We consider this briefly.

The graphical expansion of the direct correlation function is

$c(3,4) =$



$+ \quad O(\rho^2)$ (2.22)

where ○—○ is the Mayer f function and the field points are ρ vertices. The leading term in Eq. (2.22) contributes nothing to electrostriction since its density derivative is zero. The first contribution to $J(\rho_1^0, y)$ comes from

$$\frac{1}{\Omega^3}\int f(3,1)f(1,4)f(3,4)\Delta(3,4)d\Omega_3 d\Omega_4 d\mathbf{r}_{34} d\Omega_1 d\mathbf{r}_1 \qquad (2.23)$$

Using only the first two terms in the expansion of the f bond in terms of the Mayer function $f_0(r_{ij})$ for the reference system and the sum of products of dipole–dipole bonds multiplied by $e_0(r_{ij}) = 1 + f_0(r_{ij})$:

$$f(X_i, X_j) = f_0(r_{ij}) + e_0(r_{ij})\frac{\beta m_1^2 D(i,j)}{r_{ij}^3} + \cdots , \qquad (2.24)$$

we obtain the following approximation for $I(\rho_1^0, y)$ to lowest order in the density and dipole moment m_1:

$$I_1 = \frac{\beta^2 m_1^4 \rho_1^0}{\Omega^3}\int f_0(r_{34})\left[\int \phi(r_{31})\phi(r_{14})D(3,1)D(1,4)d\mathbf{r}_{13}d\Omega_1\right]$$
$$\times \Delta(3,4)d\Omega_3\, d\Omega_4\, d\mathbf{r}_{34} , \qquad (2.25)$$

where $\phi(r_{ij}) = e_0(r_{ij})/r_{ij}^3$. In arriving at Eq. (2.25) the orthogonality properties of $D(i,j)$ and $\Delta(i,j)$ have been used.[5] The analysis now is similar to the discussion in Ref. 1 except that it is much simpler due to the factorization of the bridge diagrams. In the same notation

$$I_1 = \frac{\beta^2 m^4}{\Omega^2}\int f^0(r_{34})[H^D(r_{34})D(3,4) + H^\Delta(r_{34})\Delta(3,4)]$$
$$\times \Delta(3,4)\, d\Omega_3\, d\Omega_4\, d\mathbf{r}_{34} \qquad (2.26)$$

$$= \frac{\beta^2 m^4}{3}\int f^0(r_{34})H^\Delta(r_{34})d\mathbf{r}_{34} , \qquad (2.27)$$

where

$$2\hat{H}^D(r_{34}) = H^\Delta(r_{34}) = \frac{2\rho_1^0}{3}\int d\mathbf{r}_{13}\,\hat{\phi}(r_{31})\hat{\phi}(r_{14}) \qquad (2.28)$$

and $\hat{\phi}(r_{ij})$ is a step function for dipolar hard spheres

$$\hat{\phi}(r_{ij}) = f^0(r_{ij})/R_{11}^3 , \qquad (2.29)$$

where R_{11} is the sphere diameter. For this case, the integral in I_1 contains the third virial coefficient as a factor and is equal to $-5\rho_1^0\pi^2/9$. Hence,

$$\rho_1^{0^2}\frac{dI_1}{\partial\rho_1^0} = -\frac{5}{27}\beta^2 m^4\pi^2\rho_1^{0^2} = -\frac{15}{16}y^2 \qquad (2.30)$$

and

$$\frac{\Delta\rho}{\rho_1^0} \simeq \frac{\beta(\epsilon-1)^2}{24\pi\rho_1^0 y}\left[1 - \frac{15}{16}y^2\right]\frac{E^2}{Q} , \qquad (2.31)$$

which is Eq. (4.31) of Ref. 1. By considering the higher order terms in the expansion for $c(1,2)$ or better approximations to it, one can go considerably beyond Eq. (2.31).

Comparison of the thermodynamic and statistical mechanical expressions for electrostriction to $O(E^2)$ leads to the following differential equation for the dielectric constant:

$$\rho_1^0\frac{\partial\epsilon}{\partial\rho_1^0} = \frac{(\epsilon-1)^2}{3y}\left[1 + \rho_1^{0^2}\frac{\partial I(\rho_1^0, y)}{\partial\rho_1^0}\right] . \qquad (2.32)$$

The solution to Eq. (2.32), with the integration constant 1/3 chosen to yield to correct Debye limit is

$$\frac{\epsilon-1}{\epsilon+2} = \frac{y}{1 - \rho_1^0 I(\rho_1^0, y)} , \qquad (2.33)$$

which is Ramshaw's equation.[6] On substitution of the approximation (2.30) for $I(\rho_1^0, y)$ we have

$$\frac{\epsilon-1}{\epsilon+2} = \frac{y}{1 + 15y^2/16} , \qquad (2.34)$$

which yields Jepsen's result[3] to $O(y^3)$ on expansion.

III. DISCUSSION

The right-hand side of the differential Eq. (2.32) is derived from statistical mechanics whereas the left side of this equation comes from the thermodynamic treatment[2] of electrostriction in an open system to $O(E^2)$. The latter assumes that the polarization density $\mathbf{P}(\infty, \mathbf{E})$ in the bulk fluid is related to the Maxwell field $\mathbf{E}$ by the constitutive relation

$$\mathbf{P}(\infty, \mathbf{E}) = \frac{\epsilon-1}{4\pi}\mathbf{E} + O(E^3) . \qquad (3.1)$$

Equation (3.1) defines the dielectric constant ϵ which appears in the thermodynamic expression (1.3). It is not immediately clear that the ϵ appearing in the statistical mechanical expression for electrostriction is also defined by Eq. (3.1), since the original derivation[9,1] of Eq. (2.2), which is the source of the factor $(\epsilon - 1)$ in Eqs. (2.21) and (2.32), employed a different expression for the dielectric constant.[11-13] However, Eq. (2.2) for the relation between K_{21} and $\mathbf{E}$ can also be derived from statistical mechanics and the definition of ϵ implied by the constitutive relation (3.1). It has been shown in a previous statistical mechanical study,[1] that to lowest order in the field

$$\mathbf{P}(\infty, \mathbf{E}) = m_1\rho_1^0 K_{21}(3\cos^2\theta_{2+1})^{1/2}\hat{\epsilon}_2 , \qquad (3.2)$$

where $\hat{e}_2$ is a unit vector in the direction of the field. Combining Eqs. (3.1), (3.2), and (1.2) we immediately have the desired relation (2.2). Hence, the ϵ appearing in both sides of our differential Eq. (2.32) and in its solution (2.33) is the dielectric constant defined by the constitutive realtion (3.1).

That Eq. (3.1) leads to Eq. (2.33), an exact relation for the dielectric constant, is indirect support for our statistical mechanical theory of electrostriction and polarization density.[1,14] This includes the zero density ($\rho_2 \to 0$) and infinite radius ($R_2 \to \infty$) limit[8-10] employed in studying these phenomena at an infinite distance ($z \to \infty$) away from the electrified wall. The same limit, or the closely related one of a solitary charged spherical giant has been widely used in investigations of the electrical double layer and dipolar ordering near a charged wall.[15,16] All of these studies ignore the bridge diagrams which are seen to be essential in a self-consistent treatment of electrostriction to lowest order in the electric field. It seems likely that the same diagrams must play an important role in determining the structure of the electrical double layer and other equilibrium properties of ions and dipoles near a charged wall.

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