Applications of sum rules and the contact value theorem to dipolar fluids

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Applications of the contact value theorem and two sum rules to a dipolar fluid adjacent to a charged wall are considered. Statistical mechanical formulas for electrostriction, changes with the field of the singlet density at contact with the wall and changes in the distribution functions at contact with the wall are derived.

I. INTRODUCTION

In this note we discuss applications of the contact value theorem[1,2] and two sum rules[3] to dipolar ordering near a charged wall. Expressions which relate the singlet density $\rho(i, \mathbf{E})$ and molecular correlation functions [e.g., $h(1,2;\mathbf{E})$] to changes in the bulk pressure $p(\mathbf{E})$ and bulk density $\rho(\infty, \mathbf{E})$ are obtained. These changes can be related by thermodynamic arguments to the Maxwell field $\mathbf{E}$, the dielectric constant ϵ, and its derivative with respect to the bulk density. The particular relationships obtained are found to be critically dependent on whether the system is open or closed.

The two sum rules considered are

$$\frac{\partial \ln \rho(1,\mathbf{E})}{\partial E_0} = \beta\left[\mu(1)\cdot\hat{n} + \int d\mathbf{2}\,\mu(2)\cdot\hat{n}\rho(2,\mathbf{E})\,h(1,2;\mathbf{E})\right] \tag{1.1}$$

and

$$-\frac{\partial}{\partial z_1}\rho(1,\mathbf{E}) = \int dx_2\,dy_2\,d\Omega_2\rho_{12}^T(1,2;\mathbf{E})\,|_{z_2=d/2} \tag{1.2}$$

and the contact theorem is

$$p(\mathbf{E}) = kT\rho\left(\frac{d}{2},\mathbf{E}\right) - \frac{E_0^2}{8\pi}. \tag{1.3}$$

In these Eqs. $\rho(i,\mathbf{E})$ is the singlet density of dipoles of diameter d and dipole moment $\mu(i)$ at "position" i characterized by the spatial and orientation coordinates $(\mathbf{r}_i, \Omega_i)$, where $\mathbf{r}_i = (x_i, y_i, z_i)$ and the z coordinate denotes the distance from the wall. In Eq. (1.2), $\rho_{12}^T(1,2;\mathbf{E})$ is the truncated pair-correlation function related to $h(1,2;\mathbf{E})$ of Eq. (1.1) by

$$\rho_{12}^T(1,2;\mathbf{E}) = \rho(1,\mathbf{E})\,\rho(2,\mathbf{E})\,h(1,2;\mathbf{E}). \tag{1.4}$$

All of these functions as well as the bulk pressure $p(\mathbf{E})$ depend on the electric (Maxwell) field $\mathbf{E}$. The external field, denoted by E_0, is assumed to be perpendicular to the wall. Finally $\beta = (kT)^{-1}$, where k is Boltzmann's constant and T is the absolute temperature.

II. APPLICATION OF THE SUM RULE EQ. (1.1)

Equation (1.1) can be written as

$$\frac{\partial \rho(1,\mathbf{E})}{\partial E_0} = \beta\mu\rho(1,\mathbf{E}) \times\left[\left(\cos\theta_1 + \int d\Omega_2\,d\mathbf{r}_2\cos\theta_2\rho(2,\mathbf{E})h(1,2;\mathbf{E})\right)\right], \tag{2.1}$$

where $\mu = |\boldsymbol{\mu}|$ and θ_i is the angle which the dipole at "position" i makes with the unit normal $\hat{n}$. Since the field is perpendicular to the wall, the singlet density $\rho(i,\mathbf{E})$ can be expanded in Legendre polynomials $[P_n(\cos\theta_i)]$:

$$\rho(i,E) = \sum_{n=0}^{\infty}\rho_n(z_i,E)\,P_n(\cos\theta_i), \tag{2.2}$$

where, using the orthogonality property of the Legendre polynomials,

$$\int_{-1}^{+1}P_n(\cos\theta_i)\,P_m(\cos\theta_i)\,d(\cos\theta_i) = \delta_{nm}\frac{2}{2n+1} \tag{2.3}$$

we have

$$\rho_n(z_i,\mathbf{E}) = \frac{2n+1}{2}\int\rho(i,\mathbf{E})\,P_n(\cos\theta_i)\,d(\cos\theta_i). \tag{2.4}$$

In particular, $\rho_0(z,\mathbf{E})$ is the angularly averaged singlet density and

$$\rho_1(z,\mathbf{E}) = \frac{3}{\mu}\mathcal{P}(z,\mathbf{E}) \tag{2.5}$$

is related to the polarization density per unit volume defined by

$$\mathcal{P}(z,\mathbf{E}) = \frac{\mu}{2}\int\rho(z,\mathbf{E})\,P_1(\cos\theta_i)\,d(\cos\theta_i). \tag{2.6}$$

Since E_0 is normal to the wall, $\mathcal{P}(z,\mathbf{E})$ is also perpendicular to the wall.[4] Substituting Eq. (2.2) in Eq. (2.1) and making use of the relation[5]

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$$\int_{-1}^{+1} P_n(\cos\theta_i)\,P_1(\cos\theta_i)\,P_{n_1}(\cos\theta_i)\,d(\cos\theta_i) = 2\begin{pmatrix} n & 1 & n_1 \\ 0 & 0 & 0 \end{pmatrix}^2 , \tag{2.7}$$

where the expression in parenthesis is the Wigner 3-j symbol, we have

$$\frac{\partial\rho_n(z,\mathbf{E})}{\partial E_0} = \frac{(2n+1)}{2}\beta\mu\Bigg[2\sum_{n_1}\begin{pmatrix} n & 1 & n_1 \\ 0 & 0 & 0 \end{pmatrix}^2 \rho_{n_1}(z,\mathbf{E}) + \int d\mathbf{r}_2 \sum_{n_1,n_2} \rho_{n_1}(z,\mathbf{E})\varphi_{n_2}(z,\mathbf{E})\,d\Omega_1\,d\Omega_2\,P_{n_1}(\cos\theta_1)\,P_n(\cos\theta_1)$$
$$\times h(1,2;\mathbf{E})\,P_1(\cos\theta_2)\,P_{n_2}(\cos\theta_2)\Bigg]. \tag{2.8}$$

The products of Legendre polynomials can be written as[5]

$$P_{n_1}(\cos\theta_1)\,P_n(\cos\theta_1) = \sum_{m_1=|n_2-n_1|}^{n_2+n_1} P_{m_1}(\cos\theta_1((2m_1+1)\begin{pmatrix} n_1 & n & m_1 \\ 0 & 0 & 0 \end{pmatrix}^2 , \tag{2.9}$$

$$P_1(\cos\theta_2)\,P_{n_2}(\cos\theta_2) = \sum_{m_2=|n_2-1|}^{n_2+1} P_{m_2}(\cos\theta_2)\,(2m_2+1)\begin{pmatrix} 1 & n_2 & m_2 \\ 0 & 0 & 0 \end{pmatrix}^2 . \tag{2.10}$$

Using Eqs. (2.9) and (2.10) in Eq. (2.8), one finds

$$\frac{\partial\rho_n(z,\mathbf{E})}{\partial E_0} = \frac{(2n+1)}{2}\beta\mu\Bigg[2\sum_{n_1}\begin{pmatrix} n & 1 & n_1 \\ 0 & 0 & 0 \end{pmatrix}^2 \rho_{n_1}(z,\mathbf{E}) + \sum_{\substack{n_1,n_2 \\ m_1,m_2}} (2m_1+1)\,(2m_2+1)\begin{pmatrix} 1 & n_2 & m_2 \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} n_1 & n & m_1 \\ 0 & 0 & 0 \end{pmatrix}^2 \rho_{n_1}(z,\mathbf{E})$$
$$\times \int d\mathbf{r}_2\rho_{n_2}(z,\mathbf{E})\,\langle h(z,2;\mathbf{E})\rangle_{m_1,m_2}\Bigg], \tag{2.11}$$

where

$$\langle h(1,2;\mathbf{E})\rangle_{m_1,m_2} = \int d\Omega_1\,d\Omega_2\,P_{m_1}(\cos\theta_1)\,P_{m_2}(\cos\theta_2)\,h(1,2;\mathbf{E}). \tag{2.12}$$

In particular for $n=0$, we have from the properties of the 3-j symbols that $n_1=1$ in the first term of Eq. (2.11) and $n_1=m_1$ in the second term. Therefore,

$$\frac{\partial\rho_0(z,\mathbf{E})}{\partial E_0} = \beta\Bigg[\wp(z,\mathbf{E}) + \frac{\mu}{2}\sum_{n_2=0}^{\infty}\sum_{m_1=0}^{\infty}\sum_{m_2=|n_2-1|}^{n_2+1}(2m_2+1)\begin{pmatrix} 1 & n_2 & m_2 \\ 0 & 0 & 0 \end{pmatrix}^2 \rho_{m_1}(z,\mathbf{E})\int d\mathbf{r}_2\,\rho_{n_2}(z,\mathbf{E})\,\langle h(1,2;\mathbf{E})\rangle_{m_1,m_2}\Bigg]. \tag{2.13}$$

This is an exact expression for the external field dependence of the angularly averaged singlet density. When $z\to\infty$, we get the corresponding expression for for the change in bulk density with the external field electrostriction.[6] The distribution functions $h(1,2;\mathbf{E})$ are essentially three-body correlation functions involving the planar charged surface and two particles in the fluid where we consider the "electrode" as an infinitely large charged sphere.

The most general expansion of a triplet of molecules is

$$g(1,2,3) = \sum_{\substack{m,n,s,l \\ \mu,\mu',\nu,\nu' \\ \sigma,\sigma',\lambda,\lambda'}} g^{mnsl}_{\mu\mu'\nu\nu'\sigma\sigma'\lambda\lambda'}(r_{12},r_{13},r_{23})$$
$$\times D^m_{\mu\mu'}(\Omega_1)\,D^n_{\nu\nu'}(\Omega_2)\,D^s_{\sigma\sigma'}(\Omega_3)\,D^l_{\lambda\lambda'}(\Omega_\Delta), \tag{2.14}$$

where we consider the triangle (Δ) formed by the centers of the molecules as just another "molecule." The coefficients in Eq. (2.14) must be invariant under rigid rotation of the whole assembly which means that we can rotate it rigidly through an angle $\Omega=(\alpha,\beta,\delta)$ and get the totally symmetric representation.[7] The rotations are given by[5]

$$D^m_{\mu\mu'}(\Omega_1) = \sum_{\mu''} D^m_{\mu\mu''}(\Omega)\,D^m_{\mu''\mu'}(\Omega'_1) \tag{2.15}$$

and the totally symmetric representation is obtained using

$$\frac{1}{8\pi^2}\int d\Omega\,D^m_{\mu\mu''}(\Omega)\,D^n_{\nu\nu''}(\Omega)D^S_{\sigma\sigma''}(\Omega)\,D^l_{\lambda\lambda''}(\Omega)$$
$$= \sum_{j,z,z'}(2j+1)(-)^{z+z'}\begin{pmatrix} m & n & j \\ \mu & \nu & -z \end{pmatrix}\begin{pmatrix} j & s & l \\ z & \sigma & \lambda \end{pmatrix}\begin{pmatrix} m & n & j \\ \mu'' & \nu'' & -z'' \end{pmatrix}\begin{pmatrix} j & s & l \\ z'' & \sigma'' & \lambda'' \end{pmatrix} \tag{2.16}$$

from which, after some straightforward algebra, we get

$$g(1,2,3)=\sum_{\substack{mnsl\,j\\ \mu\nu\sigma\lambda}}(2j+1)\,g^{mn;sl;j}_{\mu\nu\sigma\lambda}(r_{12},r_{13},r_{23})\times\Phi^{mn;sl;j}_{\mu\nu\sigma\lambda}(\Omega_1,\Omega_2,\Omega_3,\Omega_\Delta) \tag{2.17}$$

with

$$\Phi^{mn;sl;j}_{\mu\nu\sigma\lambda}(\Omega_1,\Omega_2,\Omega_3,\Omega_\Delta)=\sum_{\mu'\nu'\sigma'\lambda'}(-)^{s''}\begin{pmatrix}m&n&j\\ \mu''&\nu''&-z''\end{pmatrix}\begin{pmatrix}j&s&l\\ z''&\sigma''&\lambda''\end{pmatrix}\times D^{m}_{\mu'',\mu}(\Omega_1)\,D^{n}_{\nu'',\nu}(\Omega_2)\,D^{s}_{\sigma'',\sigma}(\Omega_3)\,D^{l}_{\lambda'',\lambda}(\Omega_\Delta)\ . \tag{2.18}$$

Now if we take the electrode as the limit of a big charged sphere (particle 3) then

$$s=\sigma=\sigma''=0\ , \tag{2.19}$$

$$\begin{pmatrix}j&0&l\\ z''&0&\lambda''\end{pmatrix}=\delta_{jl}\,\delta_{z'',-\lambda''}(-)^{j-\lambda''}\frac{1}{\sqrt{2j+1}}\ , \tag{2.20}$$

and

$$g(1,2;w)=\sum_{\substack{mnl\\ \mu\nu\lambda}}g^{mnl}_{\mu\nu0}(12;w)\,\Phi^{mnl}_{\mu\nu\lambda}(\Omega_1\Omega_2\Omega_\Delta) \tag{2.21}$$

with

$$\Phi^{mnl}_{\mu\nu\lambda}(\Omega_1\Omega_2\Omega_\Delta)=\sum_{\mu'\nu'\lambda'}\begin{pmatrix}m&n&l\\ \mu'&\nu'&\lambda'\end{pmatrix}D^{m}_{\mu',\mu}(\Omega_1)\,D^{n}_{\nu',\nu}(\Omega_2)D^{l}_{\lambda',\lambda}(\Omega_\Delta)\ , \tag{2.22}$$

where w stands for the wall.

Consider now as a further restriction the case in which we select a particular reference frame such that the z axis is parallel to $\mathbf{r}_{12}$. Then the Euler angles of the triangle $\Delta(1,2,3)$ are $\Omega_\Delta=(0,0,0)$ and

$$D^{l}_{\lambda\lambda'}(\Omega_\Delta)=\delta_{0\lambda}\,\delta_{0\lambda'} \tag{2.23}$$

and we immediately have

$$g(1,2;w)=\sum_{l}g^{mnl}_{\mu\nu0}(1,2;w)\sum_{\kappa}D^{m}_{\kappa\mu}(\Omega_1^\Delta)\,D^{n}_{-\kappa\nu}(\Omega_2^\Delta)\begin{pmatrix}m&n&l\\ z&-z&0\end{pmatrix}, \tag{2.24}$$

$$=\sum_{\kappa}g^{mnl}_{\mu\nu;\kappa}(1,2;w)\,D^{m}_{\kappa\mu}(\Omega_1^\Delta)\,D^{n}_{-\kappa\nu}(\Omega_2^\Delta)\ , \tag{2.25}$$

with

$$g^{mnl}_{\mu\nu;\kappa}(1,2;w)=\sum_{l}\begin{pmatrix}m&n&l\\ z&-z&0\end{pmatrix}g^{mnl}_{\mu\nu0}(1,2;w) \tag{2.26}$$

and $h(1,2;\mathbf{E})=1+g(1,2;w)$.[8]

The averages of the correlation functions $h(1,2;\mathbf{E})$ defined in Eq. (2.12) can be written in terms of the three-body correlation functions.

$$\langle h(1,2;\mathbf{E})\rangle_{m_1m_2}=\frac{1}{64\pi^4}\int d\Omega_1\,d\Omega_2\,D^{m_1}_{00}(\Omega_1)\,D^{m_2}_{00}(\Omega_2)\,h(1,2;\mathbf{E}) \tag{2.27}$$

$$=\frac{1}{(2m_1+1)(2m_2+1)}\,g^{m_1m_2}_{00;0}(1,2;w)\ . \tag{2.28}$$

Substituting in Eq. (2.13), we have

$$\frac{\partial\rho_0(z,\mathbf{E})}{\partial E_0}=\beta\left[\mathcal{P}(z,\mathbf{E})+\frac{\mu}{2}\sum_{n_2=0}^{\infty}\sum_{m_1=0}^{\infty}\sum_{m_2=|n_2-1|}^{n_2+1}\begin{pmatrix}1&n_2&m_2\\ 0&0&0\end{pmatrix}^2\times(2m_1+1)^{-1}\rho_{m_1}(z,\mathbf{E})\int dr_2\rho_{n_2}(z,\mathbf{E})\,g^{m_1m_2}_{00;0}(1,2;w)\right]\ . \tag{2.29}$$

Corresponding expressions for the external field dependence of the polarization density

$$\frac{\mu}{3}\rho_1(z,\mathbf{E})$$

and the other coefficients ($n>1$) in the expansion of Eq. (2.2) can be readily obtained from Eq. (2.11) by analogous methods. The resolution of Eq. (1.1) into its components immediately invites the construction of approximate theories which use only a few terms of expansion in Eq. (2.29).

III. APPLICATION OF THE CONTACT THEOREM EQ. (1.2) AND THE SUM RULE EQ. (1.3)

To obtain the contact theorem for a pure dipole fluid against a charged wall requires only a slight extension of the argument for an ion–dipole mixture.[9] For such a mixture it has already been shown by Blum and Henderson that

$$p(\mathrm{mix})=kT\sum_{\alpha}\rho_\alpha\left(\frac{d_\alpha}{2},\ \mathbf{E}\right)-\frac{E_0^2}{8\pi}\ , \tag{3.1}$$

where $p(\mathrm{mix})$ is the pressure of the ion–dipole mixture, $\rho_\alpha(z,\mathbf{E})$ is the singlet density of species α, and d_α is the hard-core diameter. Now consider the case when all the ions are condensed on one wall. Then we have the contact theorem for hard dipoles[10]

$$p(E)=kT\rho\left(\frac{d}{2},\ E\right)-\frac{E_0^2}{8\pi}\ . \tag{3.2}$$

Subtracting the result at zero field, we have

$$p(E)-p(0)+\frac{E_0^2}{8\pi}=kT\left[\rho\left(\frac{d}{2},\ E\right)-\rho\left(\frac{d}{2},\ 0\right)\right]\ . \tag{3.3}$$

Thermodynamic expressions for the change in pressure with the electric (Maxwell) field E are discussed in the literature.[11,12] The relevant relations (dropping the ∞ and E in parentheses) are (see Appendix)

$$\frac{1}{\rho\kappa_T}\left(\frac{\partial\rho}{\partial E}\right)_{N,\rho,T}=-\left(\frac{\partial p}{\partial E}\right)_{N,V,T}=\rho\left(\frac{\partial\mathcal{P}}{\partial\rho}\right)_{N,E,T}-\mathcal{P}\ , \tag{3.4}$$

$$\frac{1}{\rho\kappa_T}\left(\frac{\partial\rho}{\partial E}\right)_{\mu,T}=\rho\left(\frac{\partial\mathcal{P}}{\partial\rho}\right)_{E,T}\ , \tag{3.5}$$

$$\left(\frac{\partial p}{\partial E}\right)_{\mu,T}=\mathcal{P}\ , \tag{3.6}$$

where μ is now the chemical potential and κ_T is the compressibility defined by

$$\kappa_T=\frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)_{E,T}\ . \tag{3.7}$$

In the linear regime,

$$\mathcal{P}=\frac{\epsilon-1}{4\pi}E \tag{3.8}$$

and Eq. (3.5) can be integrated to give[13]

$$\rho(E) - \rho(0) = \frac{\kappa_T^0 \rho(0)^2}{8\pi} \frac{\partial \epsilon}{\partial \rho(0)} E^2 \ , \tag{3.9}$$

where κ_T^0 is the compressibility at zero field.

In this linear approximation, we have from Eqs. (3.3) and (3.4) to Eq. (3.5):

(a) for a closed (N, V, T) system,

$$kT\left[\rho\left(\frac{d}{2}, E\right) - \rho\left(\frac{d}{2}, 0\right)\right] = \frac{E_0^2}{8\pi} + \frac{E^2}{8\pi}\left[(\epsilon - 1) - \rho(0)\frac{\partial \epsilon}{\partial \rho(0)}\right], \tag{3.10}$$

(b) for an open (μ, V, T) system,

$$kT\left[\rho\left(\frac{d}{2}, E\right) - \rho\left(\frac{d}{2}, 0\right)\right] = \frac{E_0^2}{8\pi} + \frac{E^2}{8\pi}(\epsilon - 1) \ . \tag{3.11}$$

Finally we consider an application of the sum rule given in Eq. (1.2). Integrating

$$\rho(\infty, \mathbf{E}) - \rho\left(\frac{d}{2}, \mathbf{E}\right) = \int d\mathbf{r}_1 d\Omega_1 d\Omega_2 \rho_{12}^T(1, 2; \mathbf{E})\big|_{z_2 = d/2} \ . \tag{3.12}$$

Multiplying by kT and subtracting the corresponding result at zero field, produces a result for electrostriction:

$$kT[\rho(\infty, E) - \rho(\infty, 0)] = kT\left[\rho\left(\frac{d}{2}, E\right) - \rho\left(\frac{d}{2}, 0\right)\right] + \int d\mathbf{r}_1 d\Omega_1 d\Omega_2 [\rho_{12}^T(1, 2; \mathbf{E})\big|_{z_2 = d/2} - \rho_{12}^T(1, 2; 0)\big|_{z_2 = d/2}] \ . \tag{3.13}$$

If we use Eqs. (3.9) and (3.11) for an open system we have

$$\int d\mathbf{r}_1 d\Omega_1 d\Omega_2 [\rho_{12}^T(1, 2; \mathbf{E})\big|_{z_2 = d/2} - \rho_{12}^T(1, 2; 0)\big|_{z_2 = d/2}] = \left[\kappa_T^0 \rho(0)^2 \frac{\partial \epsilon}{\partial \rho(0)} - (\epsilon - 1)\right] \frac{E^2}{8\pi} - \frac{E_0^2}{8\pi} \ . \tag{3.14}$$

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APPENDIX: THERMODYNAMICS OF A DIPOLAR FLUID IN AN ELECTRIC FIELD

We summarize the basic thermodynamic results used in this paper by following the discussion due to Frank, except that the linear constitutive relation between the polarization density $\mathbf{P}(\infty, \mathbf{E})$ and the Maxwell field:

$$\mathcal{P} = \frac{\epsilon - 1}{4\pi} \mathbf{E} \tag{A1}$$

is not assumed in deriving the general relations, although our equations may be specialized to this case. We make a careful distinction between properties derived in an open system of fixed volume V, temperature T, and chemical potential $\mu = \{\mu_1, \mu_2, \ldots, \mu_\sigma\}$ of each species and a closed system in which V, T, and the numbers of moles $\mathbf{N} \equiv \{n_1, n_2, \ldots, n_\sigma\}$ of each species is held constant. We also discuss a system of fixed $(T, \mathbf{p}, \mathbf{N})$. All of these systems which are subjected to an electric field can be realized through the thought experiment described by Frank.[11]

The fundamental thermodynamic relation for an open system in an electric field is

$$dU = TdS - pdV + \mathbf{E} \cdot d(V\mathcal{P}) + \sum_{i=1}^{\sigma} \mu_i \, dn_i \ , \tag{A2}$$

where the symbols have their customary meaning and the pressure p has the operational definition discussed by Frank.

Defining

$$G^* = U + pV - TS - \mathbf{E} \cdot (V\mathcal{P}) \ , \tag{A3}$$

we have

$$dG^* = -SdT + Vdp - (V\mathcal{P}) \cdot d\mathbf{E} + \sum_i \mu_i \, dn_i \ . \tag{A4}$$

(a) System at constant $\mathbf{N}, p, T$—the bulk density ρ and chemical potentials μ are functions of E.

From the Maxwell relation

$$\left(\frac{\partial V}{\partial \mathbf{E}}\right)_{\mathbf{N},p,T} = -\left(\frac{\partial (V\mathcal{P})}{\partial p}\right)_{\mathbf{E},\mathbf{N},T} \tag{A5}$$

$$= -\mathcal{P}\left(\frac{\partial V}{\partial p}\right)_{\mathbf{E},\mathbf{N},T} - V\left(\frac{\partial \mathcal{P}}{\partial p}\right)_{\mathbf{E},\mathbf{N},T} \tag{A6}$$

we have

$$-\frac{1}{\rho}\left(\frac{\partial \rho}{\partial \mathbf{E}}\right)_{\mathbf{N},p,T} = -\kappa_T \mathcal{P} + \left(\frac{\partial \mathcal{P}}{\partial \rho}\right)_{\mathbf{E},\mathbf{N},T}\left(\frac{\partial \rho}{\partial p}\right)_{\mathbf{E},\mathbf{N},T} \tag{A7}$$

$$= \kappa_T\left[\rho\left(\frac{\partial \mathcal{P}}{\partial \rho}\right)_{\mathbf{E},\mathbf{N},T} - \mathcal{P}\right] \ , \tag{A8}$$

where the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{\mathbf{E},\mathbf{N},T} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_{\mathbf{E},\mathbf{N},T} \ . \tag{A9}$$

For a system consisting n moles of one component whose chemical potential is μ,

$$\left(\frac{\partial \mu}{\partial \mathbf{E}}\right)_{\mathbf{N},p,T} = -\left(\frac{\partial (V\mathcal{P})}{\partial n}\right)_{\mathbf{E},p,T} = -\bar{V}\mathcal{P} \ , \tag{A10}$$

where $\bar{V}$ is the molar volume. Equations (A8) and (A10) are the basic results for this system.

(b) System at constant $\mathbf{N}, V, T$—the pressure p and chemical potential change with $\mathbf{E}$. The bulk density ρ is independent of $\mathbf{E}$.

$$\left(\frac{\partial p}{\partial \mathbf{E}}\right)_{\mathbf{N},V,T} = -\left(\frac{\partial p}{\partial V}\right)_{\mathbf{E},\mathbf{N},T}\left(\frac{\partial V}{\partial \mathbf{E}}\right)_{\mathbf{N},\rho,T} \tag{A11}$$

$$= \mathcal{P} + V\left(\frac{\partial \mathcal{P}}{\partial V}\right)_{\mathbf{E},\mathbf{N},T} \ , \tag{A12}$$

where we have made use of Eq. (A6):

$$\left(\frac{\partial p}{\partial \mathbf{E}}\right)_{\mathbf{N},V,T} = \mathcal{P} - \rho\left(\frac{\partial \mathcal{P}}{\partial \rho}\right)_{\mathbf{E},\mathbf{N},T} \ . \tag{A13}$$

Likewise it is easy to show that

$$\left(\frac{\partial \mu}{\partial \mathbf{E}}\right)_{\mathbf{N},V,T} = -\bar{V}\rho\left(\frac{\partial \mathcal{P}}{\partial \rho}\right)_{\mathbf{E},\mathbf{N},T} \ . \tag{A14}$$

(c) System at constant μ, V, T—the density and pressure change with $\mathbf{E}$. We have

$$\left(\frac{\partial p}{\partial \mathbf{E}}\right)_{\mu,T} = -\left(\frac{\partial p}{\partial \mu}\right)_{\mathbf{E},T}\left(\frac{\partial \mu}{\partial \mathbf{E}}\right)_{\mathbf{N},p,T} = -\frac{1}{\overline{V}}(\overline{V}\mathcal{P}) = \mathcal{P} \ , \tag{A15}$$

where $\overline{V} = -(\partial\mu/\partial p)_{\mathbf{E},T}$ and Eq. (A10) have been used in the last step. To obtain the change in volume with $\mathbf{E}$ [since $V = V(T, P, \mathbf{E}, \mathbf{N})$] we have,

$$\left(\frac{\partial V}{\partial E}\right)_{T,\mu} = \left(\frac{\partial V}{\partial \mathbf{E}}\right)_{\mathbf{N},p,T} + \left(\frac{\partial V}{\partial p}\right)_{T,\mathbf{E},\mathbf{N}}\left(\frac{\partial p}{\partial \mathbf{E}}\right)_{T,\mu} \ , \tag{A16}$$

$$= -V\left(\frac{\partial \mathcal{P}}{\partial p}\right)_{\mathbf{E},\mathbf{N},T} = -V\left(\frac{\partial \mathcal{P}}{\partial \rho}\right)_{\mathbf{E},\mathbf{N},T}\left(\frac{\partial \rho}{\partial \mathcal{P}}\right)_{\mathbf{E},\mathbf{N},T} , \tag{A17}$$

where we have used Eqs. (A6) and (A15) in the first step of Eq. (A17):

$$\frac{1}{\rho}\left(\frac{\partial \rho}{\partial \mathbf{E}}\right)_{T,\mu} = \kappa_T \rho\left(\frac{\partial \mathcal{P}}{\partial \rho}\right)_{\mathbf{E},\mathbf{N},T} \ . \tag{A18}$$

To summarize, our basic results are Eqs. (A8) and (A18) for electrostriction, Eqs. (A13) and (A15) for the change in pressure with electric field, and Eqs. (A10) and (A14) for the change in chemical potential with electric field. Note that each of these quantities depends crucially on the variables that are held constant in an open and closed system. If the linear constitutive relation is assumed, we get the relations discussed by Frank. In particular,

$$\frac{1}{\rho\kappa_T}\left(\frac{\partial \rho}{\partial E}\right)_{p,T} = -\left(\frac{\partial p}{\partial E}\right)_{p,T} = \frac{E}{4\pi}\left[\rho\left(\frac{\partial \epsilon}{\partial \rho}\right)_{E,T} - (\epsilon - 1)\right] \ , \tag{A19}$$

$$\frac{1}{\rho\kappa_T}\left(\frac{\partial \rho}{\partial E}\right)_{\mu,T} = \frac{E}{4\pi}\rho\left(\frac{\partial \epsilon}{\partial \rho}\right)_{E,T} \ , \tag{A20}$$

$$\left(\frac{\partial p}{\partial E}\right)_{\mu,T} = \frac{E}{4\pi}(\epsilon - 1) \ . \tag{A21}$$

To obtain the thermodynamic formula for electrostriction in an open system we integrate Eq. (A20) assuming

$$\kappa_T = \kappa_T^0 + O(E^2) \ , \tag{A22}$$

$$\frac{\partial \epsilon}{\partial \rho} = \frac{\partial \epsilon}{\partial \rho(0)} + O(E^2) \ , \tag{A23}$$

and obtain,

$$\rho(E) - \rho(0) = \frac{\kappa_T^0 \rho(0)^2}{8\pi}\frac{\partial \epsilon}{\partial \rho(0)}E^2 \ , \tag{A24}$$

which is Eq. (3.9) of the text. Since $\kappa_T^0 = \beta/\rho(0)Q$, where Q is the inverse compressibility,

$$\rho(E) - \rho(0) = \frac{\beta\rho(0)}{8\pi}\left(\frac{\partial \epsilon}{\partial \rho(0)}\right)\frac{E^2}{Q} \ . \tag{A25}$$

This is the thermodynamic formula for electrostriction which is compared with the statistical mechanical calculation in Ref. 6. Microscopic derivations of Eq. (A25) follow from the work of Høye and Stell[14] and Carnie and Stell.[15]

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