

A Dipolar Fluid in an External Field:
Dielectric Properties in the Bulk

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Abstract

The dielectric properties of a system of rigid dipolar particles in the presence of an external electric field are investigated. A general expression in terms of microscopic correlations is obtained for the dielectric susceptibility of the fluid expressed as the ratio of polarization to Maxwell field, in the low-field limit, via the use of the orientational one-particle density function. The expression is found to be identical to one recently derived from the two-particle density function in a field-free system of the same particles. Use of the method is extended to a consideration of several approximations which incorporate non-linear effects. In particular, results for dielectric saturation and electrostriction effect are derived and compared with other theories.

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I. INTRODUCTION

Over the past few years there has appeared a substantial body of new theoretical work concerning the distribution functions and dielectric constant of polar fluids aimed at both a deeper understanding of those quantities and the establishment of more accurate means of computing them from first principles.¹⁻³ Almost all recent analysis of the dielectric constant has exploited the fact that each dipolar particle can be viewed as a field source acting on all the rest of the particles. As a result, for simple polar fluids the dielectric constant given by the ratio of polarization to Maxwell field strength in the low-field limit can alternatively be computed from the pair distribution function in the absence of an external field. This alternative approach however has only marginally increased our understanding of how to directly extend the well-known results of Debye for a system of non-interacting polar particles in the presence of a field⁴ to the case of a dense fluid of interacting particles.

In this paper we study the dielectric properties of a polar non-polarizable fluid in the presence of an external field by considering the field-free dielectric susceptibility computed as a ratio of the polarization \vec{P} to the Maxwell field \vec{E} in the limit of vanishing field:

$$\frac{\epsilon-1}{4\pi} = \lim_{\vec{E} \rightarrow 0} \frac{\vec{P}}{\vec{E}} \quad (1.1)$$

where ϵ is the dielectric constant. The polarization can be obtained from the orientational one-particle density function $\rho(\vec{\Omega}, \vec{E}_0)$ that gives the probability of finding a particle with orientation $\vec{\Omega}$ in the presence of an external field \vec{E}_0 . Thus, \vec{P} is given by

$$\vec{P} = \int \vec{m}(\vec{\Omega}) \rho(\vec{\Omega}, \vec{E}_0) d\vec{\Omega}, \quad (1.2)$$

where $\vec{m}(\vec{\Omega})$ is the dipole moment of a particle having orientation Ω .

Although the orientational density has already been calculated within the context of modern approximate theories^{5,6} the results as yet remain to be utilized in obtaining ϵ via Eqs. (1.1) and (1.2). Here we shall use these equations and then go on to study via Eq. (1.2) some non-linear phenomena such as dielectric saturation and electrostriction. To compute $\rho(\vec{\Omega}, \vec{E}_0)$ and, from it, the dielectric properties of a fluid of rigid dipolar particles in the presence of a field of arbitrary strength we shall first consider the more general problem of computing a spatially dependent one-particle density function $\rho(\vec{r}, \vec{\Omega}, \vec{E}_0)$ in the presence of a smooth impenetrable macroscopic sphere of radius R_2 through which an external field is passing. The macrosphere serves to define a surface (of curvature R_2^{-1} , which is zero on the microscale set by the diameter R of a typical fluid particle) from which we can conveniently measure the perpendicular distance z to a particle center. In the double limit $R_2 \rightarrow \infty$, then $z \rightarrow \infty$, $\rho(\vec{r}, \vec{\Omega}, \vec{E}_0)$ becomes $\rho(\vec{\Omega}, \vec{E}_0)$ independent of z . For $R_2 \rightarrow \infty$ but small z/R_2 , on the other hand, $\rho(\vec{r}, \vec{\Omega}, \vec{E}_0)$ depends non-trivially upon both z and $\vec{\Omega}$ (as well as \vec{E}_0) and describes how the mean orientation of the fluid particle is affected by the proximity of the surface.

In section II we review some of the general statistical-mechanical results for the correlation function of a hard spherical-core dipolar fluid in the presence of an external field and a smooth surface. This model can also represent a ferromagnetic colloid

in an external magnetic field.⁷ We pay special attention to the results that hold far from the wall where $\rho(\vec{\Omega}, \vec{E}_0)$ does not depend on the distance to the wall.

In section III, the linear case (low electric field) is discussed. The polarization is calculated in terms of \vec{E}_0 and by establishing a relation between \vec{E}_0 and the Maxwell field \vec{E} in the fluid, a general expression for the dielectric constant is obtained. When $\rho(\vec{\Omega}, \vec{E}_0)$ is computed in the Mean Spherical Approximation (MSA), ϵ coincides with Wertheim's result⁸ for the dielectric constant in terms of the field-free $g(1,2)$. We also note that our result for $\rho(\vec{\Omega}, \vec{E}_0)$ for a fluid characterized by the exact field-free $g(1,2)$ will yield the exact field-independent ϵ .

In section IV we study the Γ -ordered cluster expansion. In particular, the EXP approximation serves to study electrostriction, the change in density when an external field is applied. The result when compared with the thermodynamic expression¹⁰ and other statistical theories⁹ show that the EXP does not correlate translational and orientational degrees of freedom adequately in the liquid state but is useful at gaseous densities.

We study saturation effects in section V. Explicit formulas for the excess dielectric constant are presented both in the EXP and the Quadratic Hypernetted Chain approximation (QHNC). The latter approximation more adequately couples translational and orientational correlations.

In a companion paper¹¹ to this one, we treat the closely related problem of a configurationally disordered spin system in the presence

of a magnetic field using the same techniques. In work with Rasaiah and Isbister, one of us¹² further considers in detail electrostriction in a higher-order approximation. Our results here and in refs. [9] and [12] complement and extend the recent work of Høye and Stell¹³ who consider polar fluids in the presence of external fields from a somewhat different standpoint.

II. PRELIMINARY THEORY

The results in this section were independently derived by Isbister and Freasier (IF),⁵ within the context of the MSA. As we shall see, they are valid in a more general context. Isbister and Freasier exploit the fact that a by-now standard method of producing a fluid in the presence of a wall can be extended to introduce a field coming out of the wall as follows: If we consider a polar binary mixture (with densities ρ_1 and ρ_2 and radii R_1 and R_2 , $R_{ij} = R_i + R_j$) the dipole-dipole potential between 1 and 2 can be written as

$$u_{21}^D(r, \vec{\Omega}_1, \vec{\Omega}_2) = -\frac{m_1 m_2}{r^3} D(12), \quad r > R_{12} \quad (2.1)$$

where $D(12) = \hat{s}_1 \cdot (3\hat{r}_{12}\hat{r}_{12} - \mathbf{I}) \cdot \hat{s}_2$ is the dipolar tensor. In the limit $R_2 \rightarrow \infty$ this becomes

$$u_{21}^D(r, \vec{\Omega}_1, \vec{\Omega}_2) = -m_1 \hat{s}_1 \cdot \vec{E}_0, \quad (2.2)$$

when the limit has been taken in such a way that

$$\lim_{R_2 \rightarrow \infty} m_2 / R_{21}^3 = E_0 = \text{constant}. \quad (2.3)$$

Here \hat{s}_1 and \hat{s}_2 are the unit vectors in the directions of \vec{m}_1 and \vec{m}_2 , the

dipole moments, $\hat{r}_{12} = \vec{r}_{12}/|\vec{r}_{12}|$ and $R_{12} = R_1 + R_2$. The external field \vec{E}_0 can be written as⁹

$$\vec{E}_0 = E_0 (3 \cos^2 \theta_2 + 1)^{1/2} \hat{e}_0, \quad (2.4)$$

where $\cos \theta_2 = \hat{s}_2 \cdot \hat{r}_{12}$, and \hat{e}_0 is a unit vector in the direction of \vec{E}_0 . The electric field makes an angle α_1 with respect to the normal to the wall given by

$$\cos \alpha_1 = \hat{e}_0 \cdot \hat{r}_{12} = \frac{2 \cos \theta_2}{(3 \cos^2 \theta_2 + 1)^{1/2}}. \quad (2.5)$$

When the limit $\rho_2 \rightarrow 0$ is also taken such that $\rho_2 R_2^3 \rightarrow 0$ we have a polar fluid with a short-ranged interaction (which can be any potential with cylindrical symmetry) in the presence of a wall and of an external electric field. The density profile $\rho(z, \vec{\Omega}, \vec{E}_0)$ of dipolar molecules at a distance z from the wall and with an orientation $\vec{\Omega}$ with respect to \vec{E}_0 is related to $h_0(z, \vec{\Omega}, \vec{E}_0)$, the wall-particle correlation function, by the expression

$$\rho(z, \vec{\Omega}, \vec{E}_0) = \frac{\rho}{4\pi} [h_0(z, \vec{\Omega}, \vec{E}_0) + 1]. \quad (2.6)$$

The wall-particle correlation function can be obtained from the Ornstein-Zernike (OZ) equation with closure conditions for a polar fluid, after the limit $\rho_2 \rightarrow 0$ and the limit $R_2 \rightarrow \infty$ have been taken. We write the results which are well known in the context of the MSA, but which do not appear to have been made explicit heretofore, although they follow directly from the work of Wertheim⁸ and Isbister and coworkers^{5,6} and are used in ref. [9].

Before any limit is taken the total and direct correlation functions $h_{12}(r, \vec{\Omega}_1, \vec{\Omega}_2)$ and $c_{12}(r, \vec{\Omega}_1, \vec{\Omega}_2)$, respectively, can be expanded as

$$h_{12}(r, \vec{\Omega}_1, \vec{\Omega}_2) = h_{12}^S(r) + h_{12}^\Delta(r)\Delta(12) + h_{12}^D(r)D(12) + \dots \quad (2.7a)$$

$$c_{12}(r, \vec{\Omega}_1, \vec{\Omega}_2) = c_{12}^S(r) + c_{12}^\Delta(r)\Delta(12) + c_{12}^D(r)D(12) + \dots \quad (2.7b)$$

In the MSA, and Linearized and Quadratic HNC, only the first three terms contribute to the dielectric properties but the expansion cannot be truncated in the general case. When Eqs. (2.7a) and (2.7b) are substituted in the OZ relation for a mixture, (with $\rho_2 = 0$) one obtains an infinite number of coupled equations for the different terms in the expansion. When the limit $R_2 \rightarrow \infty$ is taken we transform the correlation functions h_{12} and c_{12} to the wall-particle $h_0(z, \vec{\Omega}, \vec{E}_0)$ and $c_0(z, \vec{\Omega}, \vec{E}_0)$. There is no guarantee that taking the limit $R_2 \rightarrow \infty$ will permit us to truncate the expansion of h_0 and c_0 and therefore to decouple the system of OZ equations. However in the double limit $R_2 \rightarrow \infty$, then $z \rightarrow \infty$, the OZ equations are decoupled in the sense that the spherically symmetric terms h_0^S and c_0^S satisfy an OZ equation that decouples from the orientational terms h_0^Δ , h_0^D , c_0^Δ and c_0^D exactly through order \vec{E}_0 .

When $z \rightarrow \infty$ the effect of the wall vanishes on the microscale set by R_{11} . The only orientational function which has a long-range part, in a theory exact through order \vec{E}_0 (or in the truncated approximations mentioned above), is h_0^D , which can be written as

$$h_0^D(z, \vec{\Omega}, \vec{E}_0) = \hat{h}_0(z, \vec{\Omega}, \vec{E}_0) + 3K_0, \quad (2.8)$$

where $\hat{h}_0(z, \vec{\Omega}, \vec{E}_0)$ is a short-range function which goes to zero as $z \rightarrow \infty$. K_0 is determined by the expression⁹

$$3K_0 \left(1 - \frac{1}{1+K_h} + \dots \right) = -\frac{m_1 E_0}{kT} + K_0 [2q_+ (2K_{11} \rho_1 R_{11}^3) + q_1 (-K_{11} \rho_1 R_{11}^3)]. \quad (2.9)$$

Here

$$K_h = \frac{\rho - \rho_1}{\rho_1} \quad (2.10)$$

is the relative change in density when the external field is turned on (electrostriction effect). The $q_+(x)$ and $q_-(x)$ are quantities related to the bulk correlation functions $c_{11}^\Delta(r)$ and $c_{11}^D(r)$ by

$$q_+ = 1 - \frac{\rho_1 [\tilde{c}_\Delta(0) + 2\tilde{c}_D(0)]}{3} = 1 - 2K_{11}\rho_1 \tilde{c}^+(0), \quad (2.11a)$$

$$q_- = 1 - \frac{\rho_1 [\tilde{c}_\Delta(0) - \tilde{c}_D(0)]}{3} = 1 - (-K_{11})\rho_1 \tilde{c}^-(0), \quad (2.11b)$$

where $\tilde{c}_\Delta(0)$ and $\tilde{c}_D(0)$ are the Fourier and Hankel transforms at $k = 0$ of c_{11}^Δ and c_{11}^D , respectively. The functions q_+ and q_- are different in general and only in linear approximations such as the MSA do they have the same functional form. The function K_{11} is given by

$$\frac{4\pi m_1^2 \rho_1}{3kT} = q_+(2K_{11}\rho_1 R_{11}^3) - q_-(-K_{11}\rho_1 R_{11}^3). \quad (2.12)$$

The general form of the left-hand side (l.h.s.) of Eq. (2.9) is not known for an arbitrary approximation. In the MSA and LHNC, $K_h = 0$. In the QHNC only the first two terms shown in the l.h.s. of Eq. (2.9) survive. It is important to note that Eq. (2.9) is derived from the asymptotic behavior of $c_{12}^D(r)$ when $R_2 \rightarrow \infty$, then $z \rightarrow \infty$.

From Eq. (2.9) it is clear that non-linear effects are sensitive to which approximation is used.^{9,12} In the linear case however an exact relation for any closure can be obtained. The function K_h is of order $O(E_0^2)$. Thus, only the last term in the l.h.s. of Eq. (2.9) is going to be of $O(E_0)$. Hence in the linear case

$$\frac{m_1 \vec{E}_0}{kT} = K_0 [2q_+ + q_-]. \quad (2.13)$$

From Eqs. (2.8) and (2.13) the asymptotic form of the orientational part of the total correlation function is given by

$$h_0(\vec{\Omega}, \vec{E}_0) = \frac{\vec{m}_1 \cdot \vec{E}_0}{kTf} \quad (2.14)$$

where

$$f = \frac{2q_+ + q_-}{3} \quad (2.15)$$

and Eqs. (2.2) and (2.4) have been used. This result is independent of the orientation of \vec{E}_0 with respect to the wall. It is an exact result that can be expected to be satisfied in any good approximation. The knowledge of the bulk properties is of course necessary to calculate f in Eq. (2.16). The orientational one-particle density function $\rho(\vec{\Omega}, \vec{E}_0)$ is, through $O(E_0)$, exactly given by

$$\rho(\vec{\Omega}, \vec{E}_0) = \frac{\rho_1}{4\pi} \left(1 + \frac{m_1 E_0 \cos \theta_1}{kTf} \right) \quad (2.16)$$

where $\cos \theta_1 = \hat{s}_1 \cdot \hat{e}_0$ is the angle a dipole makes with the external field. The general normalization condition

$$\int \rho(\vec{\Omega}, \vec{E}_0) d\vec{\Omega} = \rho \quad (2.17)$$

yields $\rho = \rho_1$ in the linear case [i.e., through $O(E_0)$].

III. POLARIZATION AND DIELECTRIC CONSTANT

The one-particle density function $\rho(\vec{\Omega}, \vec{E}_0)$ serves to define the polarization P of the dielectric via (1.2). In magnitude, P is given by

$$P = \int m_1 \rho(\vec{\Omega}, \vec{E}_0) \cos \theta_1 d\vec{\Omega} \quad (3.1)$$

which can also be written as

$$P = \langle m_1 \rangle \rho \quad (3.2)$$

where

$$\langle m_1 \rangle = \frac{\int m_1 \cos \theta_1 \rho(\vec{\Omega}, \vec{E}_0) d\vec{\Omega}}{\int \rho(\vec{\Omega}, \vec{E}_0) d\vec{\Omega}} \quad (3.3)$$

is the average value of m_1 , and use has been made of Eq. (2.17).

Substituting Eq. (2.16) in Eq. (3.1) gives

$$\vec{P} = \frac{m_1 \rho_1}{3kTf} \vec{E}_0 . \quad (3.4)$$

It is interesting to point out that when $f = 1$ Eq. (3.4) reduces to the expression for the polarization of an ideal polar gas.⁴ This is because then $q_+ = q_- = 1$ and there are no correlations between particles in the bulk.

It is known that the relationship between \vec{P} and \vec{E}_0 depends on the boundaries of the system. However, at small external fields the polarization and the Maxwell field \vec{E} inside the dielectric are linearly related by the dielectric susceptibility χ independently of the boundaries, i.e.

$$\vec{P} = \chi \vec{E} = \frac{\epsilon - 1}{4\pi} \vec{E} \quad (3.5)$$

where ϵ is the dielectric constant. This can be considered a definition of ϵ . If we have the relation between \vec{E}_0 and \vec{E} , the dielectric constant can be expressed in terms of the density, temperature and the molecular quantities which appear in Eq. (3.4). Because the interactions in a dipolar system are long-ranged this relation depends on the boundary conditions.

The limit $R_2/R_1 \rightarrow \infty$ that we consider here, where R_1 is the radius of a particle of species 1, 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 \vec{E}_0 to the macroscopic field. The subsequent large- z limit that we consider 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 $R_2/R_1 \rightarrow \infty$ limit) even though on the molecular scale of R_1 one moves arbitrarily far from the flat wall, as $z/R_1 \rightarrow \infty$.

The potential ψ outside the macrocavity, i.e. in the dielectric, is¹⁴

$$\psi = \frac{3}{2\epsilon+1} \frac{m_2 \hat{S}_2 \cdot \vec{R}_{12}}{R_{12}^3}. \quad (3.6)$$

The field \vec{E} is given by $\vec{E} = -\nabla\psi$. Then

$$\vec{E} = \frac{3}{2\epsilon+1} (3 \cos^2 \theta_2 + 1)^{1/2} E_0 \hat{e}_0 = \frac{3}{2\epsilon+1} \vec{E}_0, \quad (3.7)$$

which is the relation between \vec{E} and \vec{E}_0 appropriated for our boundary conditions. From Eqs. (3.4), (3.5) and (3.7) one obtains

$$\frac{\epsilon-1}{2\epsilon+1} = \frac{3y}{2q_+ + q_-} = \frac{y}{f}, \quad (3.8)$$

with $y = \frac{4\pi}{9} \beta m_1^2 \rho_1$. But in the bulk

$$3y = q_+ - q_- \quad (3.9)$$

and we are left with the result

$$\varepsilon = q_+/q_- . \quad (3.10)$$

Thus, we have arrived at a formula for the dielectric constant that is completely general and is in perfect agreement with previous results.^{1,3}

When some particular approximation is used for q_+ and q_- (e.g. the MSA) then Eq. (3.10) gives the ε appropriate to that approximation.

The whole procedure described above can be checked using a general formula for $\rho(\vec{\Omega}, \vec{E}_0)$ obtained by Nienhuis and Deutch¹⁵

$$\rho(\vec{\Omega}, \vec{E}_0) = \frac{\rho_1}{4\pi} [1 + \beta \vec{m}_{\text{eff}}(\vec{\Omega}) \cdot \vec{E}], \quad (3.11)$$

where

$$\vec{m}_{\text{eff}}(\vec{\Omega}) = \frac{\varepsilon-1}{3y} m_1 \hat{s}_1 . \quad (3.12)$$

Comparing with Eq. (2.16) we obtain

$$\vec{E}_0 = \frac{\varepsilon-1}{3} \frac{2q_+ + q_-}{q_+ - q_-} \vec{E} \quad (3.13)$$

which gives Eq. (3.10) if Eq. (3.7) is used or *vice versa*.

IV. NON-LINEAR APPROXIMATIONS

The results derived in the last sections are general when the dielectric constant is independent of the field. It is clear from Eq. (2.9) however that if one considers non-linear effects, the truncation of the series on the l.h.s. of the equation involves an approximation. Thus in ref. [9] electrostriction has been studied using the QHNC approximation which keeps only the first two terms in the l.h.s. of Eq. (2.9). In this section we present an alternative way to extend our

calculations to higher orders in the electric field, the Γ -ordered cluster expansion. In particular we study the EXP approximation¹⁶ and compare its predictions with those of the QHNC.

The MSA closures for the OZ equations⁸

$$c_0^{\pm\text{MSA}}(z) = 0 \quad z > 0, \quad (4.1a)$$

$$c_{11}^{\text{MSA}}(12) = \frac{-m_1^2 D(12)}{r^3} \quad r > R_{11} \quad (4.1b)$$

define the first in a well-defined sequence of approximations.¹⁷ If one replaced Eq. (4.1) by

$$c_0^{\pm}(z) = c_0^{\pm\text{REF}}(z) \quad z > 0, \quad (4.2a)$$

$$c_{11}(12) = c_{11}^{\text{REF}}(12) - \frac{m_1^2 D(12)}{r^3} \quad r > R_{11} \quad (4.2b)$$

as closures for the wall-particle and bulk OZ relations, respectively, one defines the Lowest-Order Gamma-ordered Approximation (LOGA).¹⁷ Here $c_0^{\pm\text{REF}}(z)$ is the direct correlation function of the reference system in the wall-particle problem. The correlation function for the LOGA can be written as

$$h_0^{\text{LOGA}}(z, \vec{\Omega}, \vec{E}_0) = h_0^{\text{REF}}(z, \vec{\Omega}) + c_0(z, \vec{\Omega}, \vec{E}_0) \quad (4.3)$$

so that when $z \rightarrow \infty$

$$h_0^{\text{LOGA}}(\vec{\Omega}, \vec{E}_0) = c_0(\vec{\Omega}, \vec{E}_0), \quad (4.4)$$

where

$$c_0(\vec{\Omega}, \vec{E}_0) = \frac{m_1 \hat{s}_1 \cdot \vec{E}_0}{kTf}. \quad (4.5)$$

It should be pointed out that the functional form of $h_0^{\text{LOGA}}(z, \vec{\Omega}, \vec{E}_0)$ is the same as that of $h_0^{\text{MSA}}(z, \vec{\Omega}, \vec{E}_0)$. In the LOGA, however, the

contribution of the reference system to C_0 is treated exactly, not in the Percus-Yevick approximation as in the MSA. The Γ -ordered expansion can then be extended to treat the situation of a dipolar fluid in an external field. The expansion of $h_0(z, \vec{\Omega}, \vec{E}_0)$ in terms of h_0^{REF} and C_0 can be written as

$$\ln(g_0/g_0^{\text{REF}}) = C_0(z, \vec{\Omega}, \vec{E}_0) + H_0 * S^B + S_0 * H^B + S_0 * S_0^B + F \quad (4.6)$$

where $g_0 = h_0 + 1$, the notation $A * B$ denotes a convolution and

$$H_0 = h_0^{\text{LOGA}} \quad (4.7)$$

$$S_0 = g_0^{\text{REF}} \exp C_0 - C_0 - g_0^{\text{REF}}, \quad (4.8)$$

with the same definitions for the bulk quantities. The function F is of order ρ_1^2 and is described elsewhere.¹⁷ When the limit $z \rightarrow \infty$ is taken, $g_0^{\text{REF}} \rightarrow 1$, $h_0^{\text{REF}} \rightarrow 0$ and Eq. (4.6) becomes

$$\begin{aligned} \ln g_0(\vec{\Omega}, \vec{E}_0) &= C_0(\vec{\Omega}, \vec{E}_0) + C_0(\vec{\Omega}, \vec{E}_0) * S^B + S_0(\vec{\Omega}, \vec{E}_0) * H^B \\ &+ S_0(\vec{\Omega}, \vec{E}_0) * S^B + F^\infty, \end{aligned} \quad (4.9)$$

where

$$S_0(\vec{\Omega}, \vec{E}_0) = \exp C_0(\vec{\Omega}, \vec{E}_0) - C_0(\vec{\Omega}, \vec{E}_0) - 1. \quad (4.10)$$

The terms on the r.h.s. of Eq. (4.9) except $C_0(\vec{\Omega}, \vec{E}_0)$ and F^∞ involve the correlation of the wall and two particles. F^∞ involves simultaneous correlations of the wall and at least three particles.

If we neglect all terms but $C_0(\vec{\Omega}, \vec{E}_0)$ in the Γ expansion we obtain the well-known EXP approximation^{16,17}

$$g_0^{\text{EXP}}(\vec{\Omega}, \vec{E}_0) = \exp C_0(\vec{\Omega}, \vec{E}_0). \quad (4.11)$$

As we shall see this approximation gives poor results except at low densities where it lends itself to the study of non-linear effects in a dielectric in which a high electric field is present. The one-particle distribution function is given by

$$\rho^{\text{EXP}}(\vec{\Omega}, \vec{E}_0) = \frac{\rho_1}{\Omega} \exp c_0(\vec{\Omega}, \vec{E}_0). \quad (4.12)$$

From Eq. (2.17) we find that

$$\rho = \rho_1 \frac{\sinh x}{x} \quad (4.13)$$

where $x = \frac{m_1 E_0}{kTf}$. This means that the density ρ in the presence of the field is greater than ρ_1 , the density in the absence of the field, i.e. there is an electrostriction effect. To $O(E_0^2)$ the change in density is

$$K_h^{\text{EXP}} = \frac{1}{6} \left(\frac{m_1 E_0}{kTf} \right)^2 = \frac{(\epsilon-1)^2 \beta}{24\pi y \rho_1} E^2 \quad (4.14)$$

where use has been made of Eq. (3.8). If we compare Eq. (4.14) with the thermodynamic formula for electrostriction¹⁰

$$K_h = \frac{1}{8\pi} \frac{1}{kT} \left(\frac{\partial \epsilon}{\partial \rho} \right)_{E,T,N} \frac{E^2}{Q} \quad (4.15)$$

where

$$Q = \frac{1}{\rho_1 k T \kappa_T} \quad (4.16)$$

and κ_T is the isothermal compressibility, we conclude that the EXP

is fully consistent with K_h only when $Q = 1$ and ϵ is given by the Clausius-Mossotti equation

$$\frac{\epsilon-1}{\epsilon+2} = y. \quad (4.17)$$

Thus the EXP gives poor results for

electrostriction except at low densities where $\rho_1 kT \kappa_T$ approaches one, and Eqs. (3.10) and (4.17) give similar results. The QHNC result for electrostriction⁹

$$K_h^{\text{QHNC}} = \frac{\beta}{24\pi\rho_1\gamma} \frac{(\epsilon-1)^2 E^2}{Q} \quad (4.18)$$

improves the situation because it contains the correct factor Q . Thus it couples the orientational and translational degrees of freedom in a better way than the EXP even if it is not able to go beyond Eq. (4.17) when consistency with the thermodynamic formula Eq. (4.15) is required.

V. DIELECTRIC SATURATION

The approximations discussed in the last section allow us to calculate the change in dielectric constant when high fields are applied. In an open system the polarization can be expanded in terms of the external field \vec{E}_0 and the Maxwell field \vec{E} , to include non-linear terms¹⁸

$$\vec{P} = \chi\vec{E} + \eta E^2\vec{E} + \dots, \quad (5.1)$$

$$\vec{P} = b\vec{E}_0 + cE_0^2\vec{E} + \dots, \quad (5.2)$$

where χ is the susceptibility and η is the quantity of interest in describing dielectric saturation. Usually the non-linear behavior is expressed in terms of

$$\frac{\Delta\epsilon}{E^2} = \frac{\epsilon_E - \epsilon}{E^2} \quad (5.3)$$

where ϵ is the linear dielectric constant and $\epsilon_E = \partial D / \partial E$ is the quantity which measures the deviation from ϵ at high fields. The electric induction \vec{D} can be written as

$$\vec{D} = \epsilon \vec{E} + 4\pi\eta E^2 \vec{E} \quad (5.4)$$

using (5.1). Then¹⁸

$$\frac{\Delta\epsilon}{E^2} = 12\pi\eta. \quad (5.5)$$

When $\eta < 0$ one has normal saturation, when $\eta > 0$ there is anomalous saturation.¹⁸

The EXP polarization is obtained substituting Eqs. (4.12) in Eq. (3.2). Then

$$P = m_1 \rho L(x), \quad (5.6)$$

where $L(x) = \coth x - 1/x$ is the Langevin function and $x = \frac{m_1 E_0}{kTf}$. When $f = 1$ we recover Debye's classic ideal-gas result.⁴ When $x \ll 1$, i.e. at small field or high temperature, the polarization is linear in the field.

If we expand the Langevin function to $O(E_0^3)$ we have

$$\vec{P} = \frac{m_1 \rho}{3kTf} \vec{E}_0 - \frac{m_1 \rho}{45} \frac{1}{(kTf)^3} E_0^2 \vec{E}_0 + \dots \quad (5.7)$$

Substituting Eq. (4.14) in Eq. (5.7) to take electrostriction into account we get

$$\vec{P} = \frac{m_1 \rho_1}{3kTf} \vec{E}_0 + \frac{m_1 \rho_1}{30} \frac{1}{(kTf)^3} E_0^2 \vec{E}_0 + \dots \quad (5.8)$$

Now the polarization is written in terms of ρ_1 , the density in the absence of the field.

A relation between \vec{E} and \vec{E}_0 is necessary to calculate $\Delta\epsilon$. We cannot use Eq. (3.7) because when non-linear terms are present, the Laplace equation does not hold. Thus we write \vec{E} in terms of \vec{E}_0 as

$$\vec{E} = \frac{3}{2\epsilon+1} \vec{E}_0 + B E_0^2 \vec{E}_0 + \dots \quad (5.9)$$

where B should be calculated solving the electrostatic problem for the non-linear case. An approximation considered by Böttcher¹⁸ relating \vec{E} and \vec{E}_0 is to take Eq. (3.7) but instead of ϵ , to use an ϵ' defined by

$$\epsilon' = D/E = \epsilon + 4\pi\eta E^2. \quad (5.10)$$

Using this approximation we have

$$\vec{E} = \frac{3}{2\epsilon' + 1} \vec{E}_0 \quad (5.11)$$

and consequently

$$B = -\frac{216 \pi \eta}{(2\epsilon+1)^4}. \quad (5.12)$$

Using Eqs. (5.1), (5.8) and (5.9) with Eq. (5.12) we obtain

$$\frac{\Delta\epsilon^{\text{EXP}}}{E^2} = 12\pi\eta = \frac{2\pi}{5} m_1^4 \rho_1 \frac{1}{(kT)^3} \left(\frac{\epsilon-1}{3\gamma}\right)^3 \left(\frac{2\epsilon+1}{3}\right). \quad (5.13)$$

Hence, the EXP predicts an increase of ϵ at high fields. It is clear from Eqs. (5.7) and (5.8) that electrostriction is responsible for producing this result. (In the literature¹⁸ it is customary not to include the effect of electrostriction in discussing saturation, on the grounds that experimentally it is usually found to be a negligible contribution. In the simple Hamiltonian model we treat here, however, it appears to be a major contribution to the dependence of ϵ upon field, at least for small ρ and all \vec{E} , where the EXP is reliable. We expect that approximations like QHNC should give better overall results than EXP as discussed in the preceding section. To calculate $\Delta\epsilon^{\text{QHNC}}/E^2$ we first obtain the polarization via Eq. (3.1). The one-particle density function $\rho^{\text{QHNC}}(\vec{\Omega}, \vec{E}_0)$ is given by [cf. Eqs. (2.6) and (2.9)]

$$\rho^{\text{QHNC}}(\vec{\Omega}, \vec{E}_0) = \frac{\rho_1}{4\pi} \left[1 + h_0^S(E_0) + \frac{m_1 E_0 \cos \theta_1}{kT \left(f - \frac{K_h}{1+K_h} \right)} \right]. \quad (5.14)$$

where $h_0^S(\vec{E}_0) = \lim_{z \rightarrow \infty} \int h_0(z, \vec{\Omega}, \vec{E}_0) d\vec{\Omega} / 4\pi$.

Therefore, the polarization to $O(E_0^2)$ is

$$\vec{P} = \frac{m_1^2 \rho_1 \beta \vec{E}_0}{3f} \left(1 + \frac{K_h}{f} \right). \quad (5.15)$$

But K_h is given by⁹

$$K_h = \frac{1}{6} \frac{\beta^2 m_1^2}{f^2} \frac{E_0^2}{Q}, \quad (5.16)$$

and \vec{P} can be written as

$$\vec{P} = \frac{m_1^2 \rho_1 \beta \vec{E}_0}{3f} + \frac{m_1^4 \rho_1}{18} \frac{1}{(kTf)^3} \frac{E_0^2 \vec{E}_0}{fQ} \quad (5.17)$$

where f is given by the QHNC approximation for the bulk. Using Eqs. (5.1), (5.9) and (5.17) with (Eq. (5.12)) we arrive at the expression

$$\frac{\Delta \epsilon^{\text{QHNC}}}{E^2} = 12\pi\eta = \frac{2\pi}{3} \frac{m_1^4 \rho_1}{(kT)^3} \left(\frac{\epsilon-1}{3y} \right)^4 \left(\frac{3}{2\epsilon+1} \right) Q^{-1} \quad (5.18)$$

If we compare Eq. (5.18) with Eq. (5.13) we note that both predict an increase of ϵ at high field. In Eq. (5.18) however, the isothermal compressibility is not the ideal-gas one due to the more adequate way in which the QHNC couples translational and orientational correlations.

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