Statistical mechanics of dipolar fluids: dielectric constant and sample shape

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Abstract

We give a new proof that the constitutive relation of macroscopic electrostatics holds in a dipolar fluid with a sample shape independent dielectric constant. Our approach is based on a BGY-like hierarchy equation which allows us to calculate the canonical one-body density function up to linear order in the electric field, in the thermodynamic limit. The dielectric constant comes out as an integral over a 3-point correlation function of the infinite unperturbed (unpolarized) system, from which one can recover the well-known formula for ε in terms of the 2-point direct correlation function. © 2000 Elsevier Science B.V. All rights reserved.

In honor of Joel Lebowitz on the occasion of his 70 birthday

1. Introduction

Since the last century, it is known that the phenomenology of linear, homogeneous and isotropic dielectrics in static fields is well described by the constitutive relation of macroscopic electrostatics $\boldsymbol{P}(\boldsymbol{r}) = (\varepsilon - 1)/(4\pi)\boldsymbol{E}(\boldsymbol{r})$. The dielectric constant ε is assumed to be an intrinsic quantity of the infinite unperturbed (without any external field applied) system, that depends only on its thermodynamical state, while on the contrary the average polarization $\boldsymbol{P}(\boldsymbol{r})$ and the average electric field $\boldsymbol{E}(\boldsymbol{r})$ depend on the shape of the finite system considered. The phenomenology of linear dielectrics is based on the physical insight that the response of the system is a local phenomenon, the molecules responding to the ambient electric field. The latter is given by the macroscopic field $\boldsymbol{E}(\boldsymbol{r})$ which, contrary to the external field $\boldsymbol{E}_0(\boldsymbol{r})$, includes the contribution of the charge density induced on the surface of the sample. These charges make the macroscopic field

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(as well as the polarization) shape-dependent because of the long range of the Coulomb potential. Two (related) basic questions then naturally arise:

(a) *How do we calculate the dielectric constant of a substance?*

(b) *For a given material, is the macroscopic relation indeed satisfied, with the same and unique dielectric constant, irrespective of the sample shape and of the applied external field?*

These questions can only be answered on the basis of a particular model for the dielectric. The first one was studied even before the underlying microscopic structure of dielectrics was clearly understood. An approximate formula for ε was obtained by Mossotti [1] and Clausius [2] (the corresponding formula for the index of refraction was given by Lorenz [3] and Lorentz [4,5]) and other approximate results were later proposed by Debye [6] and Onsager [7]. Except for Debye's formula, which is an exact low-density asymptotic behavior, these formulae are not really satisfactory because they are based on uncontrolled approximations, such as the use of macroscopic electrostatics on a microscopic scale. Kirkwood [8] initiated the modern theory of dielectrics by using the tools of statistical mechanics. Let us consider a particularly simple model of a dielectric which is a fluid made of N identical molecules carrying an ideal dipole moment $\boldsymbol{p}$, in a volume V at temperature T. This model presents the necessary ingredients to behave as a dielectric and should obey the phenomenological law. It has already been much studied in the literature, as well as more elaborate models. We refer the reader to a few books [9–12] and review articles [13,14] where a complete list of references can be found. In this context, the two questions already found an answer. Several exact and equivalent formulae for the dielectric constant were proposed by different authors, in particular [15–18]. We point out in Section 3 that these formulae can in fact be very easily obtained by specifying the constitutive relation to the case of an external field created by an external charge localized inside the sample. The question (b) was studied in the pioneering work of Nienhuis and Deutch [19] and received a complete solution by Ramshaw [20] (it was later studied again by Martina and Stell [21]). Ramshaw's approach is based on an integral equation, involving the direct correlation function, for the linear variation of the one-body density due to an external electric field. If we isolate a purely dipolar contribution in the direct correlation function, we can make the macroscopic field appear on one hand, while no other finite size effect survives in the infinite volume limit on the other hand. This approach provides a complete answer to question (b), but unfortunately relies on a diagrammatic argument for the control of the thermodynamic limit (see Section 3.4).

The purpose of this article is to give an alternative to Ramshaw's proof which does not use diagrammatic arguments. Our approach is based on the equilibrium hierarchy equations for the correlation functions of the finite system in the presence of an external field $\boldsymbol{E}_0(\boldsymbol{r})$, obtained by considering an infinitesimal dipole orientation change $\boldsymbol{p} \to \boldsymbol{p} + \delta \boldsymbol{p}$. We show, in a diagrammatic-free way, that in the thermodynamic limit the boundary effects on the one-body density function up to linear order in the electric field are entirely contained in the macroscopic field $\boldsymbol{E}(\boldsymbol{r})$. This function, written in terms of $\boldsymbol{E}(\boldsymbol{r})$, involves only intrinsic quantities specific to the infinite unpolarized system. This

approach yields a new formula for the dielectric constant which involves an integral over a three-point correlation function. Using the hierarchy equations of the infinite unperturbed system, we show that this formula is in fact equivalent to the well-known expression for ε in terms of the direct correlation function.

The paper is organized as follows. Since the already vast literature on the subject may be somewhat overwhelming, we present synthetically in the first few sections how the two questions can be most simply answered. We start by defining in Section 2 the classical rigid-dipole fluid model and consider its thermodynamic limit (whose existence is implicitly assumed in the phenomenology). The equilibrium quantities (pressure, correlations, ...) are indeed well defined and independent of the shape of the sample used in the limit, although the dipolar potential is at the border of integrability. A few simple results on the asymptotic decay of the correlations are also given in Section 2.2, for later use. In Section 3, we consider the linear response of the system to an external electric field. After recalling in Section 3.1 a subtlety in the definition of the macroscopic field, we point out in Section 3.2 that a straightforward linear response calculation of the induced polarization is not sufficient to establish the constitutive relation because of the appearance of a rather delicate shape-dependent integral. In Section 3.3, we show that the well-known formulae for ε can be obtained by specifying the constitutive relation to the special case of an external field created by an external charge localized inside the sample. The infinite volume limits of the fields $\boldsymbol{P}_V(\boldsymbol{r})$ and $\boldsymbol{E}_V(\boldsymbol{r})$ are then easily calculated from their expressions obtained by standard linear response theory, because no boundary effect occurs. We finish the introductory part in Section 3.4 with an outline of Ramshaw's approach to question (b). The Section 4 contains then the detailed presentation of our hierarchy approach and we conclude in Section 5.

2. The unpolarized infinite system

2.1. Definition of the model

We consider a simple model of a dielectric which is a classical dipolar fluid made of N identical molecules in a volume V at temperature T. The molecules are assumed to carry an ideal unpolarizable dipole moment $\boldsymbol{p}_i$ and we denote the position and the dipole moment of the ith molecule by $i = (\boldsymbol{r}_i, \boldsymbol{p}_i)$. An average over the angle of $\boldsymbol{p}$ will be written as $\langle \ldots \rangle_{\boldsymbol{p}} := 1/4\pi \int \ldots \, \mathrm{d}\Omega_{\boldsymbol{p}}$ and the condensed notation $\int_V \mathrm{d}1$ stands for $\int \mathrm{d}\Omega_1 \int_V \mathrm{d}^3\boldsymbol{r}_1$. The molecules interact via the dipolar potential and have a hard core of radius σ:

$$u_{\text{int}}(1,2) = \begin{cases} -\boldsymbol{p}_1 \cdot \boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|2) & \text{if } |\boldsymbol{r}_1 - \boldsymbol{r}_2| > 2\sigma, \\ \infty & \text{otherwise}, \end{cases} \tag{1}$$

where $\boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|2) = -\boldsymbol{\nabla}_1 (\boldsymbol{p}_2 \cdot \boldsymbol{\nabla}_2) \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$ is the electric field at $\boldsymbol{r}_1$ created by a dipole $\boldsymbol{p}_2$ at $\boldsymbol{r}_2$. (The choice of this particular short-ranged regularization does not play an

essential role.) This model presents three independent parameters: the volume V, the density $\rho = N/V$ and the inverse temperature $\beta = 1/(k_B T)$. The excess (non-ideal) quantities depend on two independent dimensionless parameters: $\rho\sigma^3$, a measure of the density of the system, and $\beta p^2/\sigma^3$, a parameter which compare the maximum dipolar interaction energy (two spheres in contact) to the thermal energy. We shall also use the dimensionless quantity $y = 4\pi\beta\rho p^2/9$, which is proportional to the product of the two parameters.

2.2. The thermodynamic limit and bulk correlations

To our knowledge, there does not exist a rigorous proof of the existence of the thermodynamic limit for the rigid-dipole fluid model in the absence of an external field. However, the existence of this limit is strongly suggested by the observation that all the graphs in the Mayer expansions of the correlation functions are finite owing to a first integration over the angles of the dipoles. This integration kills by parity all the dangerous logarithmic divergent terms which could arise from the slow decay of the dipolar potential. Note also that Froehlich and Park [22] have rigorously proved the existence of the thermodynamic limit for a similar model with another short-range regularization of the dipolar potential. We shall attach a subscript V to a quantity calculated in the finite system and none for its value in the thermodynamic limit, since it is shape independent. At small enough density and high enough temperature, the phase should be fluid and unpolarized, so the one-body density becomes $\rho^{(1)}(\boldsymbol{r},\boldsymbol{p}) = \rho^{(1)} = \rho/4\pi$ in the thermodynamic limit. All the higher order correlations become invariant under global translations and rotations of their arguments. On the contrary, note that when the system in submitted to an external field, the quantities still depend in general on the sample shape in the thermodynamic limit and therefore receive a subscript ∂V.

We denote the two-point density function by $\rho^{(2)}(1,2) = \rho^{(1)}\rho^{(1)}[1 + h(1,2)]$, where $h(1,2)$ is the Ursell function. The direct correlation function $c(1,2)$ is defined by the Ornstein–Zernike equation

$$h(1,2) = c(1,2) + \rho^{(1)} \int d3 \; c(1,3)h(3,2) \,. \tag{2}$$

As suggested by its diagrammatic Mayer representation, the direct correlation function is expected to behave asymptotically as $-\beta$ times the dipolar potential at large distances. It is useful to isolate in this function the asymptotic dipolar part, and this can be done by decomposing for example $c(1,2)$ as $c(1,2) = c_{\text{sr},\sigma}(1,2) + c_{\text{dip},\sigma}(1,2)$ where $c_{\text{sr},\sigma}(1,2)$ is a short-ranged function (decaying faster than $|\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-3}$) and $c_{\text{dip},\sigma}(1,2)$ is equal to $-\beta(\boldsymbol{p}_1 \cdot \boldsymbol{\nabla}_1)(\boldsymbol{p}_2 \cdot \boldsymbol{\nabla}_2)1/|\boldsymbol{r}_1 - \boldsymbol{r}_2|$ if $|\boldsymbol{r}_1 - \boldsymbol{r}_2| > 2\sigma$ and to 0 otherwise. However, this decomposition is not the most appropriate one for our purpose, because it leads to unnecessarily complicated formulae. For instance, the Fourier transform of this last function is

$$\tilde{c}_{\text{dip},\sigma}(\boldsymbol{k};\boldsymbol{p}_1,\boldsymbol{p}_2) = -4\pi\beta\frac{j_1(2k\sigma)}{2k\sigma}[3(\boldsymbol{p}_1 \cdot \hat{\boldsymbol{k}})(\boldsymbol{p}_2 \cdot \hat{\boldsymbol{k}}) - \boldsymbol{p}_1 \cdot \boldsymbol{p}_2] \,, \tag{3}$$

where $j_1(x) = -\cos(x)/x + \sin(x)/x^2$ is a modified Bessel function. In order to work with simpler expressions, we let

$$c(1,2) = c_{sr}(1,2) + c_{dip}(1,2),$$ (4)

where $c_{sr}(1,2)$ is again a short-ranged function and

$$c_{dip}(1,2) = -\beta \lim_{d \to 0} \begin{cases} (\boldsymbol{p}_1 \cdot \boldsymbol{\nabla}_1)(\boldsymbol{p}_2 \cdot \boldsymbol{\nabla}_2)\dfrac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} & \text{if } |\boldsymbol{r}_1 - \boldsymbol{r}_2| > 2d, \\ \dfrac{4\pi}{3}\boldsymbol{p}_1 \cdot \boldsymbol{p}_2 \, \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) & \text{otherwise}. \end{cases}$$ (5)

The limit $d \to 0$ is understood to be taken after the spatial integrations over the variables $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. The Fourier transform of this function reads $\tilde{c}_{dip}(\boldsymbol{k}; \boldsymbol{p}_1, \boldsymbol{p}_2) = -4\pi\beta$ $(\boldsymbol{p}_1 \cdot \hat{\boldsymbol{k}})(\boldsymbol{p}_2 \cdot \hat{\boldsymbol{k}})$ since $\lim_{x \to 0} j_1(x)/x = 1/3$. The definition (5) may seem artificial, but it corresponds to defining $c_{dip}(1,2)$ as $-\beta$ times the dipolar potential at all distances, with a delta function singularity at the origin. This delta singularity appears naturally in the definition of the macroscopic field (see Section 3.1) and it should be noted that $-4\pi\beta(\boldsymbol{p}_1 \cdot \hat{\boldsymbol{k}})(\boldsymbol{p}_2 \cdot \hat{\boldsymbol{k}})$ is the result expected from a calculation in the sense of distributions of the Fourier transform of the full dipolar potential. In the limit $k \to 0$ at fixed $\hat{\boldsymbol{k}}$, the Fourier transform of $c(1,2)$ becomes

$$\lim_{k \to 0} \tilde{c}(\boldsymbol{k}; \boldsymbol{p}_1, \boldsymbol{p}_2) = -4\pi\beta(\boldsymbol{p}_1 \cdot \hat{\boldsymbol{k}})(\boldsymbol{p}_2 \cdot \hat{\boldsymbol{k}}) + \tilde{c}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2),$$

$$\tilde{c}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2) = \tilde{c}_{sr}(\boldsymbol{k} = \boldsymbol{0}, \boldsymbol{p}_1, \boldsymbol{p}_2).$$ (6)

The first singular term that still depends on $\hat{\boldsymbol{k}}$ arises from the slow $1/r_{12}^3$-tail in $c(1,2)$ and the second term $\tilde{c}_{sr}(\boldsymbol{k}=0; \boldsymbol{p}_1, \boldsymbol{p}_2)$ is necessarily, by rotational invariance, a function of the relative angle between $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$. Substituting the decomposition (4) in the Ornstein–Zernike equation (2) gives [15]

$$h(1,2) = h_{sr}(1,2) + h_{lr}(1,2)$$ (7)

with

$$h_{sr}(1,2) = c_{sr}(1,2) + \rho^{(1)} \int d3 \, c_{sr}(1,2) h_{sr}(3,2),$$ (8)

$$h_{lr}(1,2) = \int d3 \, d4 [\delta(1,3) + \rho^{(1)} h_{sr}(1,3)] c_{dip}(3,4)[\delta(4,2)$$

$$+ \rho^{(1)} h_{sr}(4,2) + \rho^{(1)} h_{lr}(4,2)].$$ (9)

Inserting the result (6) in these equations shows that the Fourier transform of the Ursell function takes the following form in the limit $k \to 0$:

$$\lim_{k \to 0} \tilde{h}(\boldsymbol{k}; \boldsymbol{p}_1, \boldsymbol{p}_2) = \alpha(\boldsymbol{p}_1 \cdot \hat{\boldsymbol{k}})(\boldsymbol{p}_2 \cdot \hat{\boldsymbol{k}}) + \tilde{h}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2),$$

$$\tilde{h}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2) = h_{sr}(\boldsymbol{k} = \boldsymbol{0}, \boldsymbol{p}_1, \boldsymbol{p}_2),$$ (10)

where α is a coefficient that depends on the thermodynamic parameters. The form (10) shows that $h(1,2)$ also decays as $1/r_{12}^3$ at large distances, like $c(1,2)$. This simple

consequence of the Ornstein–Zernike equation (and of the $1/r_{12}^3$-decay of $c(1,2)$) is compatible with an analysis order by order in density of the Mayer graphs that represent $h(1,2)$. This diagrammatic analysis also suggests that the next terms in the large-r asymptotic expansions of $h(1,2)$ and $c(1,2)$ decay as $1/r_{12}^6$. Notice that the Ornstein–Zernike equation, combined with (6) and (10), implies that

$$\tilde{h}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2) = \tilde{c}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2) + \rho^{(1)} \int d\Omega_3 \, \tilde{c}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_3)\tilde{h}_0(\boldsymbol{p}_3 \cdot \boldsymbol{p}_2) \,. \tag{11}$$

In particular, we have

$$b = a + \rho b a \quad \text{with} \quad a = \langle \tilde{c}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2)(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{p}}_2) \rangle_{\boldsymbol{p}_1, \boldsymbol{p}_2} \,,$$

$$b = \langle \tilde{h}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2)(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{p}}_2) \rangle_{\boldsymbol{p}_1, \boldsymbol{p}_2} \,. \tag{12}$$

Similar considerations can also be made for higher-order correlations. For example, the Fourier transform over $\boldsymbol{r}_3$ of the truncated three-point density is also the sum of a singular term (depending on the non-analytic function $\hat{\boldsymbol{k}}$) and of a regular (at $\boldsymbol{k} = \boldsymbol{0}$) term:

$$\lim_{k \to 0} \tilde{\rho}^{(3,\mathrm{T})}(1,2;\boldsymbol{p}_3,\boldsymbol{k}) = \tilde{\rho}_{\mathrm{sing}}^{(3,\mathrm{T})}(1,2;\boldsymbol{p}_3,\hat{\boldsymbol{k}}) + \tilde{\rho}_0^{(3,\mathrm{T})}(1,2;\boldsymbol{p}_3) \,. \tag{13}$$

3. The system in the presence of an external field

3.1. The macroscopic field

When a finite sample of the dipolar fluid is submitted to an external field $\boldsymbol{E}_0(\boldsymbol{r})$, an induced polarization

$$\boldsymbol{P}_V(\boldsymbol{r}_1) = \int d\Omega_1 \, \boldsymbol{p}_1 \rho_{V,E_0}^{(1)}(1) \tag{14}$$

appears and the macroscopic field $\boldsymbol{E}_V(\boldsymbol{r})$ is given by

$$\boldsymbol{E}_V(\boldsymbol{r}_1) = \boldsymbol{E}_0(\boldsymbol{r}_1) - \boldsymbol{\nabla}_1 \int_V \boldsymbol{P}_V(\boldsymbol{r}_2) \cdot \boldsymbol{\nabla}_2 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d^3 r_2 \tag{15}$$

$$= \boldsymbol{E}_0(\boldsymbol{r}_1) - \int_{\partial V} \left(\boldsymbol{\nabla}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right) \boldsymbol{P}_V(\boldsymbol{r}_2) \, d\boldsymbol{S}_2$$

$$+ \int_V \boldsymbol{\nabla}_2 \boldsymbol{P}_V(\boldsymbol{r}_2) \left(\boldsymbol{\nabla}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right) d^3 r_2. \tag{16}$$

These integrals are well defined because the volume element $d^3 r_2$ makes the singularity of the integrand integrable at $\boldsymbol{r}_1 = \boldsymbol{r}_2$. Let us recall a subtlety in the definition of the macroscopic field, related to the singularity of the dipolar potential at the origin. If we call $B(\boldsymbol{r}_1, d)$ a ball of radius d centered on $\boldsymbol{r}_1$, we have

$$\lim_{d \to 0} \int_{V \setminus B(\boldsymbol{r}_1, d)} (\boldsymbol{P}_V(\boldsymbol{r}_2) \cdot \boldsymbol{\nabla}_2) \left(-\boldsymbol{\nabla}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right) d^3 r_2$$

$$= \int_{\partial V} \left(-\boldsymbol{\nabla}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right) \boldsymbol{P}_V(\boldsymbol{r}_2) \, \mathrm{d}\boldsymbol{S}_2$$

$$- \lim_{d \to 0} \int_{\partial B(\boldsymbol{r}_1, d)} \left(-\boldsymbol{\nabla}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right) \boldsymbol{P}_V(\boldsymbol{r}_2) \, \mathrm{d}\boldsymbol{S}_2$$

$$+ \int_V \boldsymbol{\nabla}_2 \cdot \boldsymbol{P}_V(\boldsymbol{r}_2) \left(\boldsymbol{\nabla}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right) \, \mathrm{d}^3 \boldsymbol{r}_2 \,. \tag{17}$$

The integral on the surface $\partial B(\boldsymbol{r}_1, d)$ of the ball gives $-4\pi/3\boldsymbol{P}(\boldsymbol{r}_1)$ in the limit $d \to 0$. Combining the last two equations, we find

$$\boldsymbol{E}_V(\boldsymbol{r}_1) = \boldsymbol{E}_0(\boldsymbol{r}_1) + \lim_{d \to 0} \int_{V \backslash B(\boldsymbol{r}_1, d)} (\boldsymbol{P}_V(\boldsymbol{r}_2) \cdot \boldsymbol{\nabla}_2) \left(-\boldsymbol{\nabla}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right) \, \mathrm{d}^3 \boldsymbol{r}_2 - \frac{4\pi}{3} \boldsymbol{P}_V(\boldsymbol{r}_1) \,. \tag{18}$$

If we agree to define $\lim_{d \to 0} \int_{B(\boldsymbol{r}_1, d)} (\boldsymbol{P}_V(\boldsymbol{r}_2) \cdot \boldsymbol{\nabla}_2)(-\boldsymbol{\nabla}_1 1/|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \, \mathrm{d}^3 \boldsymbol{r}_2 = -4\pi/3\boldsymbol{P}_V(\boldsymbol{r}_1)$, which is the result suggested by a calculation in the sense of distributions, we can then write the following formula for the macroscopic field

$$\boldsymbol{E}_V(\boldsymbol{r}_1) = \boldsymbol{E}_0(\boldsymbol{r}_1) - \int_V (\boldsymbol{P}_V(\boldsymbol{r}_2) \cdot \boldsymbol{\nabla}_2) \boldsymbol{\nabla}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \, \mathrm{d}^3 \boldsymbol{r}_2 \,. \tag{19}$$

If we had inverted carelessly the integral and the gradient in Eq. (15), we would have obtained this formula directly, but would then not know how to treat the singularity of the dipolar potential at $\boldsymbol{r}_1 = \boldsymbol{r}_2$. The previous calculation shows that it should be handled as the delta function $4\pi/3\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)$ [23].

3.2. Linear response and thermodynamic limit

An elementary linear response calculation of the induced polarization results in the Kirkwood expression

$$\boldsymbol{P}_V(\boldsymbol{r}_1) = \beta \int \mathrm{d}\Omega_1 \int_V \mathrm{d}2[\rho_V^{(1)}(1)\delta(1,2) + \rho_V^{(1)}(1)\rho_V^{(1)}(2)h_V(1,2)]\boldsymbol{p}_1(\boldsymbol{p}_2 \cdot \boldsymbol{E}_0(\boldsymbol{r}_2)) \,. \tag{20}$$

This formula shows in particular that the infinite volume limit of $\boldsymbol{P}_V(\boldsymbol{r})$ depends in the general case on the shape of the sample, as expected. Such a dependence is produced by two different mechanisms: the integral $\int_V \mathrm{d}^3 \boldsymbol{r}_2 \dots$ depends on the shape because $h(1,2) \sim |\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-3}$ and also the finite volume dependent part of the Ursell function, $\Delta h_V(1,2) = h_V(1,2) - h(1,2)$, gives a non-vanishing shape-dependent contribution in the limit $V \to \infty$, as first pointed out by Jepsen [24]. These intricate boundary effects make Kirkwood's formula not useful in answering question (b) but it is valuable for question (a). Namely, if we consider the special case of an external field created by an external charge localized inside the sample, all these complicated boundary effects disappear, because of the decay of the external field $\boldsymbol{E}_0(\boldsymbol{r}_2)$ at increasing distances.

However, in this situation, the electric field varies over microscopic distances and it is appropriate to generalize the constitutive relation to

$$P(r) = \int_{\mathbb{R}^3} \chi(r-r')E(r')\,d^3r' = \int_{\mathbb{R}^3} \frac{\varepsilon(r-r') - \delta(r-r')}{4\pi} E(r')\,d^3r' \tag{21}$$

or, in Fourier transform,

$$\tilde{P}(k) = \frac{\varepsilon(k) - 1}{4\pi} \tilde{E}(k). \tag{22}$$

[We do not write a tilde on $\varepsilon(k)$ and rely on the argument to recognize $\varepsilon(r)$ from its Fourier transform $\varepsilon(k)$.] The (longitudinal) static dielectric function $\varepsilon(k)$ depends only on the modulus of k because of the isotropy of the unpolarized system. If we approximate in (21) the kernel $\varepsilon(r-r')$ by the local kernel $\varepsilon(k=0)\delta(r-r')$, we recover the usual form of the constitutive relation $P(r) = (\varepsilon - 1)/(4\pi)E(r)$, with a dielectric constant ε equal to $\varepsilon(k=0)$.

3.3. Expressions for ε in terms of two-body bulk correlations

We consider the special case of an external charge density localized inside the sample, where, as already stated, all boundary effects become out of play in the thermodynamic limit. In this limit, the macroscopic field does not depend on the shape of the sample and is given by

$$E(r_1) = -\nabla_1 \left[\int [\rho^{\text{ext}}(r_2) + \rho^{\text{ind}}(r_2)] \frac{1}{|r_1 - r_2|} \right] d^3r_2, \tag{23}$$

where $\rho^{\text{ind}}(r) = -\nabla \cdot P(r)$ is the charge density induced by the external charge $\rho^{\text{ext}}(r)$. From (22) and (23), the dielectric constant is related to these charge densities by

$$\varepsilon^{-1}(k) = 1 + \lim_{\rho^{\text{ext}} \to 0} \frac{\tilde{\rho}^{\text{ind}}(k)}{\tilde{\rho}^{\text{ext}}(k)}. \tag{24}$$

[The limit $\rho^{\text{ext}} \to 0$ is necessary to capture only the linear response.] At $k = 0$, the fraction $\tilde{\rho}^{\text{ind}}(0)/\tilde{\rho}^{\text{ext}}(0)$ measures the (incomplete) dielectric screening of the external charge. The thermodynamic limit of Kirkwood's expression (20) becomes trivially

$$P(r_1) = \beta \int d\Omega_1 \int_{\mathbb{R}^3} d2 [\rho^{(1)}\delta(1,2) + \rho^{(1)}\rho^{(1)}h(1,2)] p_1(p_2 \cdot E_0(r_2)). \tag{25}$$

The integral over r_2 is a convolution. Therefore, we obtain by using $\tilde{\rho}^{\text{ind}}(k) = -ik \cdot \tilde{P}(k)$ and $\tilde{E}_0(k) = -ik\tilde{\rho}^{\text{ext}}(k)4\pi/k^2$,

$$\frac{\tilde{\rho}^{\text{ind}}(k)}{\tilde{\rho}^{\text{ext}}(k)} = -4\pi\beta \left[\frac{1}{3}\rho p^2 + \rho^2 \langle \tilde{h}(k; p_1, p_2)(p_1 \cdot \hat{k})(p_2 \cdot \hat{k}) \rangle_{p_1, p_2} \right]. \tag{26}$$

Substituting this result in (24), we see that the dielectric constant of the dipolar fluid is given in terms of the Ursell function $h(1,2)$ by [12]

$$\varepsilon^{-1}(k) = 1 - 3y - 9y\rho \langle \tilde{h}(k; p_2, p_2)(\hat{p}_1 \cdot \hat{k})(\hat{p}_2 \cdot \hat{k}) \rangle_{p_1, p_2}. \tag{27}$$

Recall from (10) that $\lim_{k\to 0} \tilde{h}(k;\boldsymbol{p}_1,\boldsymbol{p}_2)$ still depends on the direction of $\hat{\boldsymbol{k}}$, so that we cannot merely infer a formula for $\varepsilon(0)$ in terms of $\lim_{k\to 0}\langle \tilde{h}(k;\boldsymbol{p}_1,\boldsymbol{p}_2)\boldsymbol{p}_1 \cdot \boldsymbol{p}_2\rangle_{\boldsymbol{p}_1\cdot\boldsymbol{p}_2}$. Nevertheless, we can express ε in terms of quantities that decay faster than $h(1,2)$, so that the final result does not involve $\hat{\boldsymbol{k}}$ explicitly. By using (7) and by applying the convolution theorem to the infinite series generated by (9), we find

$$\langle \rho^2 \tilde{h}(k;\boldsymbol{p}_1,\boldsymbol{p}_2)(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{k}})(\hat{\boldsymbol{p}}_2 \cdot \hat{\boldsymbol{k}})\rangle_{\boldsymbol{p}_1,\boldsymbol{p}_2} = \rho^2 \langle \tilde{h}_{\mathrm{sr}}(k;\boldsymbol{p}_1,\boldsymbol{p}_2)(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{k}})(\hat{\boldsymbol{p}}_2 \cdot \hat{\boldsymbol{k}})\rangle_{\boldsymbol{p}_1,\boldsymbol{p}_2}$$

$$+ \sum_{n=1}^{\infty} (-4\pi\beta p^2)^n (\rho\langle [\delta(\boldsymbol{p}_1,\boldsymbol{p}_2) + \rho\tilde{h}_{\mathrm{sr}}(k;\boldsymbol{p}_1,\boldsymbol{p}_2)](\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{k}})(\hat{\boldsymbol{p}}_2 \cdot \hat{\boldsymbol{k}})\rangle_{\boldsymbol{p}_1,\boldsymbol{p}_2})^{n+1} .$$

(28)

After little algebra, it follows from (27) and (28) that

$$\varepsilon(k) = 1 + 3y + 9y\rho\langle h_{\mathrm{sr}}(k;\boldsymbol{p}_1,\boldsymbol{p}_2)(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{k}})(\hat{\boldsymbol{p}}_2 \cdot \hat{\boldsymbol{k}})\rangle_{\boldsymbol{p}_1,\boldsymbol{p}_2} . \tag{29}$$

Since the function $h_{\mathrm{sr}}(1,2)$ decays faster than $|\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-3}$, we obtain in the limit $k \to 0$

$$\varepsilon = 1 + 3y(1 + \rho b) = 1 + \frac{3y}{1 - \rho a} , \tag{30}$$

where the second equality follows from (12). We stress that according to the decomposition (4) and the corresponding $c_{\mathrm{sr}}(1,2)$, a reduces to the regular (analytical) part of $\tilde{c}(k;\boldsymbol{p}_1,\boldsymbol{p}_2)$ at $\boldsymbol{k}=0$, namely $a=\langle\lim_{k\to 0}[\tilde{c}(k;\boldsymbol{p}_1,\boldsymbol{p}_2)+4\pi\beta(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{k}})(\hat{\boldsymbol{p}}_2 \cdot \hat{\boldsymbol{k}})](\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{p}}_2)\rangle_{\boldsymbol{p}_1,\boldsymbol{p}_2}$. If another decomposition of $c(1,2)$ is used, we obtain of course the same expression for ε in terms of the previous intrinsic a, but the relation between a and the new short-ranged part of $c(1,2)$ is modified. For instance, for $c(1,2) = c_{\mathrm{sr},\sigma}(1,2) + c_{\mathrm{dip},\sigma}(1,2)$, we have $a = \langle \tilde{c}_{\mathrm{sr},\sigma}(\boldsymbol{k}=0;\boldsymbol{p}_1,\boldsymbol{p}_2)(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{p}}_2)\rangle_{\boldsymbol{p}_1,\boldsymbol{p}_2} + 4\pi\beta p^2/9$ and the formula (30) can therefore also be written in the quite different looking form

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{y}{1 - \rho\langle \tilde{c}_{\mathrm{sr},\sigma}(\boldsymbol{k}=0;\boldsymbol{p}_1,\boldsymbol{p}_2)(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{p}}_2)\rangle_{\boldsymbol{p}_1,\boldsymbol{p}_2}} . \tag{31}$$

The present formula for the dielectric constant (in its various forms) is well known [15–17], but is derived here in a very simple way. In particular, we did not resort to intricate diagrammatic analysis nor expansions for the orientational dependence of the correlations. A similar approach for obtaining the dielectric constant can also be used in more general classical models of polar fluids, where the molecules do not carry only a purely dipolar electric moment. Instead of calculating the induced charge density $\rho^{\mathrm{ind}}(\boldsymbol{r}) = -\nabla \cdot \boldsymbol{P}(\boldsymbol{r})$ from Kirkwood's expression, one can use the standard linear response result $\tilde{\rho}^{\mathrm{ind}}(k) = -\beta\tilde{S}(k)\tilde{\rho}^{\mathrm{ext}}(k)4\pi/k^2$ that leads to

$$\varepsilon^{-1}(k) = 1 - 4\pi\beta\frac{\tilde{S}(k)}{k^2} , \tag{32}$$

where $\tilde{S}(k)$ is the Fourier transform of the charge–charge correlation function of the infinite unperturbed system. The latter formula for $\varepsilon(k)$ has been used by Chandler to give an exact expression for the dielectric constant of a classical fluid composed of polarizable and deformable molecules [18]. It is interesting to note that the result (27) for the dielectric constant of the rigid-dipole fluid model can also be obtained from

(32) by considering the dipoles to be constituted of two opposite charges $\pm|\boldsymbol{p}|/d$, a distance $d \to 0$ apart.

3.4. General validity of the constitutive relation

The formula for $\varepsilon(k)$ obtained in the previous section is derived under the assumption that the external charge density $\rho^{\text{ext}}(\boldsymbol{r})$ is localized inside the sample. Now, we want to outline Ramshaw's approach [20,25] which establishes the validity of the constitutive relation (22) in the general case, with the same expression for ε.

Ramshaw's approach is based on the following integral equation for the linear variation $\delta\rho_{V,E_0}^{(1)}(1)$ of the one-body density due to an external potential $\phi(1) = -\boldsymbol{p}_1 \cdot \boldsymbol{E}_0(\boldsymbol{r}_1)$:

$$\delta\rho_{V,E_0}^{(1)}(1) = \rho_V^{(1)}(1)(-\beta\phi(1)) + \rho_V^{(1)}(1)\int_V d2\, c_V(1,2)\delta\rho_{V,E_0}^{(1)}(2)\,. \tag{33}$$

This equation is a direct, though not immediately obvious, consequence of the definition of the direct correlation function, see [20]. Let us consider the thermodynamic limit of this equation and introduce for this purpose the decomposition $c_V(1,2) = c(1,2) + \Delta c_V(1,2)$. The Mayer density expansion of the function $\Delta c_V(1,2)$ involves connected diagrams which have neither nodal nor articulation points and in which at least one black point is integrated over the region $\mathbb{R}^3 \setminus V$ (i.e., outside V) [12]. Because of the asymptotic dipolar character of the bonds and of the topological structure of the graphs, the function $\Delta c_V(1,2)$ is expected to behave as

$$\Delta c_V(1,2) = O\left(\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|^3}\right)O\left(\frac{1}{V}\right) + O\left(\frac{1}{V^2}\right)\,, \tag{34}$$

with $\boldsymbol{r}_1$ a point inside the sample far from the boundaries. From (34), we conclude that the term $\rho_V^{(1)}(1)\int_V d2\,\Delta c_V(1,2)\delta\rho_{V,E_0}^{(1)}(2)$ in (33) is dominated by a constant times $\int_V d2\,\Delta c_V(1,2)$ and vanishes therefore in the thermodynamic limit. This provides

$$\delta\rho_{\partial V,E_0}^{(1)}(1) = \frac{\beta\rho}{4\pi}(\boldsymbol{p}_1 \cdot \boldsymbol{E}_0(\boldsymbol{r}_1)) + \frac{\rho}{4\pi}\lim_{V\to\infty}\int_V d2\, c(1,2)\delta\rho_{V,E_0}^{(1)}(2)\,, \tag{35}$$

where now only the direct correlation function associated to the infinite system enters. If we introduce the decomposition (4), we make the macroscopic field (19) appear

$$\delta\rho_{\partial V,E_0}^{(1)}(1) = \frac{\beta\rho}{4\pi}\boldsymbol{p}_1 \cdot \lim_{V\to\infty}\left[\boldsymbol{E}_0(\boldsymbol{r}_1) - \int_V \boldsymbol{\nabla}_1(\boldsymbol{P}(\boldsymbol{r}_2) \cdot \boldsymbol{\nabla}_2)\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}d^3r_2\right]$$

$$+ \frac{\rho}{4\pi}\lim_{V\to\infty}\int_V d2\, c_{\text{sr}}(1,2)\delta\rho_{\partial V,E_0}^{(1)}(2)\,. \tag{36}$$

Because of the integrable decay (faster than $|\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-3}$) of the function $c_{\text{sr}}(1,2)$, the integral in the last term can be extended to the whole space:

$$\delta\rho_{\partial V,E_0}^{(1)}(1) = \frac{\beta\rho}{4\pi}(\boldsymbol{p}_1 \cdot \boldsymbol{E}(\boldsymbol{r}_1)) + \frac{\rho}{4\pi}\int_{\mathbb{R}^3} d2\, c_{\text{sr}}(1,2)\delta\rho_{\partial V,E_0}^{(1)}(2)\,. \tag{37}$$

This integral equation implies that $\delta\rho^{(1)}_{\partial V, E_0}(1)$ depends on the shape of the sample only through the macroscopic field E. Multiplying the previous equation by p_1, integrating over the angles of p_1, and using Eq. (8), we obtain

$$P(r_1) = \frac{3y}{4\pi}E(r_1) + \beta\frac{\rho^2}{(4\pi)^2}\int d\Omega_1 \int d2\, h_{sr}(1,2)p_1(p_2 \cdot E(r_2)) \tag{38}$$

which relates $P(r)$ to the macroscopic field $E(r)$. Taking a Fourier transform and using the longitudinality $\tilde{E}(k) = E(k)\hat{k}$ of the electrostatic field, eventually lead us to conclude that (22) indeed holds in general, with the same dielectric function (29) as that found in Section 3.3.

4. Microscopic foundation of the local dielectric law

4.1. The hierarchy equations for the one-body density

We turn now to our main point, i.e., giving a new proof that the constitutive relation $P(r) = (\varepsilon - 1)/(4\pi)E(r)$ is satisfied in the rigid-dipole fluid model with the dielectric constant (30), in the general case where induced charges appear on the surface of the dielectric (thereby making the macroscopic field and the polarization shape-dependent). The central quantity of interest is the canonical one-body density up to linear order in the external field $E_0(r)$, in the thermodynamic limit. We consider the case where the external charge density (the source of the external field) is localized outside the considered finite dielectric sample. Then, $E_0(r)$, as well as all the other macroscopic fields, varies on macroscopic scales controlled by the size of the sample. The contributions of eventual external charges localized inside the sample can be treated separately (like in Section 3.3) by the virtue of the superposition principle. Therefore, they can be omitted in the present analysis. The thermodynamic limit will be taken by scaling all the distances by a common multiplicative factor λ and setting $\lambda \to \infty$. A point s_1 inside the sample (not on the boundaries) will be transformed into $r_1 = \lambda s_1$ which stays far away from the boundaries in the thermodynamic limit. The one-body density $\rho^{(1)}_{\partial V, E_0}(1)$ is then expected to become homogeneous in a microscopic neighborhood of r_1. This can be checked from a BGY-like equation, that also ultimately provides the required polarization $P(r_1)$ in terms of the macroscopic field $E(r_1)$.

Let us consider an infinitesimal change δp_1 of the orientation of the dipole p_1. Similarly to the first BGY hierarchy equation, the corresponding variation of the one-body density in the previous thermodynamic limit can be expressed as

$$\Delta_{\delta p_1}\rho^{(1)}_{\partial V, E_0}(1) := \rho^{(1)}_{\partial V, E_0}(r_1, p_1 + \delta p_1) - \rho^{(1)}_{\partial V, E_0}(r_1, p_1) \tag{39}$$

$$= \beta\rho^{(1)}_{\partial V, E_0}(1)(\delta p_1 \cdot E_0(r_1))$$

$$+ \beta\lim_{V\to\infty}\int_V d2\, \rho^{(2)}_{V, E_0}(1,2)(\delta p_1 \cdot E_{dip}(r_1|2)) \,. \tag{40}$$

The choice of the hard sphere regularization simplified somewhat this equation, but short-ranged regularizations which depend on the orientations of the dipoles can also be considered, at the expense of an additional term which does not involve any sample shape subtlety. Note that the integral in (39) depends on the contrary non-trivially on the sample shape in the infinite volume limit, because not only the function $\rho^{(2)}_{\partial V, E_0}(1,2)$ is shape-dependent, but, more importantly, because the integrand decays only as $|\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-3}$ since $\rho^{(2)}_{V, E_0}(1,2)$ is asymptotically equal to $\rho^{(1)}_{V, E_0}(1)\rho^{(1)}_{V, E_0}(2)$. Now the obvious but main step is to free ourselves from this last delicate shape dependence by expressing the two-body density in terms of the corresponding truncated quantity (i.e., the correlation). Employing the notation convention introduced after Eq. (18), we can write

$$\Delta_{\delta \boldsymbol{p}_1} \rho^{(1)}_{\partial V, E_0}(1) = \beta \rho^{(1)}_{\partial V, E_0}(1) \delta \boldsymbol{p}_1 \cdot \lim_{V \to \infty} \left[\boldsymbol{E}_0(\boldsymbol{r}_1) - \int_V (\boldsymbol{P}(\boldsymbol{r}_2) \cdot \boldsymbol{\nabla}_2) \boldsymbol{\nabla}_1 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d^3 \boldsymbol{r}_2 \right]$$

$$+ \beta \lim_{V \to \infty} \int_V d2 \, \rho^{(2,T)}_{V, E_0}(1,2)(\delta \boldsymbol{p}_1 \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1 | 2)) \,. \tag{41}$$

We recognize in the square brackets the macroscopic field (19) while the integral in the last term can now without harm be extended to the whole space because of the fast decay of the integrand (at least as $|\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-6}$):

$$\Delta_{\delta \boldsymbol{p}_1} \rho^{(1)}_{\partial V, E_0}(1) = \beta \rho^{(1)}_{\partial V, E_0}(1)(\delta \boldsymbol{p}_1 \cdot \boldsymbol{E}(\boldsymbol{r}_1)) + \beta \int_{\mathbb{R}^3} d2 \, \rho^{(2,T)}_{\partial V, E_0}(1,2)(\delta \boldsymbol{p}_1 \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1 | 2)) \,.$$
$$\tag{42}$$

Let us linearize this expression with respect to the electric field. Since the truncated two-body density $\rho^{(2,T)}_{\partial V, E_0}(1,2)$ may be viewed as a functional of the one-body density $\rho^{(1)}_{\partial V, E_0}(1)$, we have

$$\rho^{(2,T)}_{\partial V, E_0}(1,2) = \rho^{(2,T)}(1,2) + \int d3 \, G(1,2,3) \delta \rho^{(1)}_{\partial V, E_0}(3) + O(E_0^2) \,, \tag{43}$$

where $\delta \rho^{(1)}_{\partial V, E_0}(1)$ is the linear variation of the one-body density due to the external field (as in Section 3.3) and

$$G(1,2,3) = \frac{\delta \rho^{(2,T)}(1,2)}{\delta \rho^{(1)}(3)} = \rho^{(1)} h(1,2)[\delta(1,3) + \delta(2,3)] + \rho^{(1)} \rho^{(1)} \frac{\delta h(1,2)}{\delta \rho^{(1)}(3)} \,.$$
$$\tag{44}$$

Both $\rho^{(2,T)}(1,2)$ and $G(1,2,3)$ refer to the infinite unperturbed system, and consequently no longer depend on the shape of the genuine finite sample. The integral over $\boldsymbol{r}_3$ can be extended to the whole space because of the fast decay of $G(1,2,3)$ with respect to $\boldsymbol{r}_3$ (cf. Appendix A). The linearization of Eq. (42) therefore results in the following integro-variational equation for $\delta \rho^{(1)}_{\partial V, E_0}(1)$

$$\Delta_{\delta \boldsymbol{p}_1} \rho^{(1)}_{\partial V, E_0}(1) = \beta \rho^{(1)}(\delta \boldsymbol{p}_1 \cdot \boldsymbol{E}(\boldsymbol{r}_1)) + \beta \int_{\mathbb{R}^6} d2 \, d3 \, G(1,2,3) \delta \rho^{(1)}_{\partial V, E_0}(\boldsymbol{r}_1, \boldsymbol{p}_3)$$

$$\times (\delta \boldsymbol{p}_1 \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1 | 2)) + O(E^2) \,. \tag{45}$$

In the integral on the right-hand side of (45), $\delta\rho^{(1)}_{\partial V,E_0}(r_3,p_3)$ has been replaced by $\delta\rho^{(1)}_{\partial V,E_0}(r_1,p_3)$ because the integrand decays on a finite microscopic scale while $\delta\rho^{(1)}_{\partial V,E_0}(r_3,p_3)$ varies on the same macroscopic scale as $E(r_1)$. The first term of (43) did not give any contribution to this equation because $\int d2\rho^{(2,T)}(1,2)E_{dip}(r_1|2)$ is collinear to p_1 and $\delta p_1 \cdot p_1 = 0$ (this contribution had to vanish since it is of order zero in the electric field and $\rho^{(1)}(r,p) = \rho^{(1)}$ does not depend on the orientation of p). The structure on the right-hand side of (45) has a very simple physical interpretation that justifies the implicit assumptions of the phenomenological construction of the constitutive relation. Indeed, the first term, which is of the mean-field-type, clearly shows that the dipoles at r_1 feel the macroscopic field $E(r_1)$ rather than the external field $E_0(r_1)$. Moreover, the second term involves the contributions of intrinsic correlations of the unperturbed system, that decay on a finite microscopic scale. Thus, the response $\delta\rho^{(1)}_{\partial V,E_0}(1)$ to the external field is proportional to the macroscopic field, i.e., $\delta\rho^{(1)}_{\partial V,E_0}(1) \sim \alpha_x E_x(r_1) + \alpha_y E_y(r_1) + \alpha_z E_z(r_1)$, where the coefficients α_μ only depend on p_1 and on the intrinsic quantities of the homogeneous unperturbed infinite system, in perfect agreement with the phenomenological statement. In other words, Eq. (45) explicits the microscopic foundation of the macroscopic approach. From the previous considerations, we conclude that $\delta\rho^{(1)}_{\partial V,E_0}(r,p)$ depends on the sample shape and on r only through the macroscopic field $E(r)$. Because of the rotational invariance of the fluid phase considered, this function is necessarily of the form

$$\rho^{(1)}_{\partial V,E_0}(r,p) = \rho^{(1)} + \beta\rho^{(1)}A\,p \cdot E(r) + O(E^2)\,. \tag{46}$$

A constant times $p \cdot E(r)$ is namely the only rotational invariant scalar expression linear in $E(r)$ which can be built with the two vectors p and $E(r)$. Here A is a dimensionless quantity which, from (14), is related to the dielectric constant by $\varepsilon = 1 + 3yA$.

The result (46), together with (14), answers to question (b) and shows that the polarization $P(r)$ is indeed proportional to the macroscopic field $E(r)$, the constant of proportionality being an intrinsic quantity of the infinite unperturbed system. It is interesting to note the similarity between our Eq. (45) and Ramshaw's Eq. (37). They have the same structure and lead to the same conclusion. Ramshaw's equation looks somewhat simpler than ours, but relies on not so trivial properties of the direct correlation function while our equation is based merely on the large-distance decay of the two-body correlations which is a rather weak assumption.

4.2. A new intrinsic expression for the dielectric constant

Our hierarchy approach leads to a new explicit formula for the dielectric constant. If we substitute (46) into (45), we obtain an equation for A:

$$A\beta(\delta p_1 \cdot E) = \beta(\delta p_1 \cdot E) + A \int d2\,d3\,G(1,2,3)(\beta p_3 \cdot E)\beta(\delta p_1 \cdot E_{dip}(r_1|2))\,. \tag{47}$$

The r dependence of the electric field $E(r)$ can be omitted since it does not intervene in the calculation of A. The dielectric constant is therefore given by the following formula, letting $p_\perp = \delta p_1$,

$$\varepsilon = 1 + \frac{3y}{1-I}$$

where

$$I = \frac{1}{(p_\perp \cdot E)} \beta \int d2 \, d3 \, G(1,2,3)(p_3 \cdot E)(p_\perp \cdot E_{dip}(r_1|2)) \,. \tag{48}$$

Because of its structure and of the rotational invariance of the infinite system, $\int d2 \, d3$ $G(1,2,3)(p_3 \cdot A)(B \cdot E_{dip}(r_1|2))$ is necessarily of the form $\alpha(A \cdot p_1)(B \cdot p_1) + \gamma(A \cdot B)$. Since in our case $p_\perp \cdot p_1 = 0$, the factors $(p_\perp \cdot E)$ cancel out and I is independent of E and $p_\perp$, as expected. The integral I does not necessarily depend either on p_1 or on r_1, so that we obtained a well-defined intrinsic expression for the dielectric constant.

4.3. Uniqueness of the dielectric constant

The question (b) is now fully answered but we would like to show explicitely that the formula (48) for the dielectric constant is indeed equivalent to the result (30) (it has to be so).

The first step in this proof is to rewrite (48) in terms of the two- and three-point density functions. We start by studying the function $G(1,2,3)$. From the chain rule, we have

$$G(1,2,3) = \int d4 \, \frac{\delta\phi(4)}{\delta\rho^{(1)}(3)} \, \frac{\delta\rho^{(2,\mathrm{T})}(1,2)}{\delta\phi(4)} \,. \tag{49}$$

Since

$$\frac{\delta\phi(4)}{\delta\rho^{(1)}(3)} = \frac{1}{\beta} c(4,3) - \frac{1}{\beta\rho^{(1)}} \delta(4,3) \tag{50}$$

and

$$\frac{\delta\rho^{(2,\mathrm{T})}(1,2)}{\delta\phi(4)} = -\beta\rho^{(3,\mathrm{T})}(1,2,4) - \beta\rho^{(2,\mathrm{T})}(1,2)[\delta(1,4) + \delta(2,4)] \tag{51}$$

we find

$$G(1,2,3) = \rho^{(1)}h(1,2)[\delta(1,3) + \delta(2,3)] + \frac{1}{\rho^{(1)}} K(1,2,3) \,, \tag{52}$$

where

$$K(1,2,3) = \rho^{(3,\mathrm{T})}(1,2,3) - \rho^{(1)}$$
$$\times \int d4 \, (\rho^{(3,\mathrm{T})}(1,2,4) + \rho^{(2,\mathrm{T})}(1,2)[\delta(4,1) + \delta(4,2)])c(4,3) \,. \tag{53}$$

The reader can find a simple diagrammatic interpretation of $K(1,2,3)$ in the Appendix A. Both K and G decay faster than r_3^{-3} when r_3 is sent to infinity with $1, 2$ and p_3 fixed.

Thus the Fourier transform $\tilde{G}(1,2;\boldsymbol{p}_3,\boldsymbol{k})$ of G with respect to $\boldsymbol{r}_3$ is regular at $\boldsymbol{k} = 0$, and reduces to $\tilde{G}_0(1,2;\boldsymbol{p}_3)$. Then, according to (48), I can be rewritten as

$$I = \frac{1}{(\boldsymbol{p}_\perp \cdot \boldsymbol{E})} \beta \int d\Omega_3 \int d2 (\boldsymbol{E} \cdot \boldsymbol{p}_3)(\boldsymbol{p}_\perp \cdot \boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|2)) \tilde{G}_0(1,2;\boldsymbol{p}_3) \,. \tag{54}$$

In order to express (54) in terms of the Fourier transforms of correlation functions, we first calculate $\tilde{K}(1,2;\boldsymbol{p}_3,\boldsymbol{k})$:

$$\tilde{K}(1,2;\boldsymbol{p}_3,\boldsymbol{k}) = \tilde{\rho}^{(3,\text{T})}(1,2;\boldsymbol{p}_3,\boldsymbol{k}) - \rho^{(1)}\langle \tilde{\rho}^{(3,\text{T})}(1,2;\boldsymbol{p}_4,\boldsymbol{k})\tilde{c}(\boldsymbol{k};\boldsymbol{p}_4,\boldsymbol{p}_3)\rangle_{\boldsymbol{p}_4}$$

$$- \rho^{(1)}\rho^{(2,\text{T})}(1,2)[\tilde{c}(\boldsymbol{k};\boldsymbol{p}_1,\boldsymbol{p}_3) + \tilde{c}(\boldsymbol{k};\boldsymbol{p}_2,\boldsymbol{p}_3)] \,. \tag{55}$$

Substituting (6) and (13) in (55) gives, since the singular terms necessarily cancel out,

$$\tilde{K}_0(1,2;\boldsymbol{p}_3) = \tilde{\rho}_0^{(3,\text{T})}(1,2;\boldsymbol{p}_3) - \rho^{(1)}\langle \tilde{\rho}_0^{(3,\text{T})}(1,2;\boldsymbol{p}_4)\tilde{c}_{\text{sr}}(\boldsymbol{p}_4 \cdot \boldsymbol{p}_3)\rangle_{\boldsymbol{p}_4}$$

$$- \rho^{(1)}\rho^{(2,\text{T})}(1,2)[\tilde{c}_{\text{sr}}(\boldsymbol{p}_1 \cdot \boldsymbol{p}_3) + \tilde{c}_{\text{sr}}(\boldsymbol{p}_2 \cdot \boldsymbol{p}_3)] \,. \tag{56}$$

Let us now insert (52) and (56) into (54). Using $\int d\Omega_3 (\boldsymbol{E} \cdot \boldsymbol{p}_3)\tilde{c}_{\text{sr}}(\boldsymbol{p}_1 \cdot \boldsymbol{p}_3) = a(\boldsymbol{E} \cdot \boldsymbol{p}_1)$ where a is defined in (12), we obtain

$$I = \frac{\beta(1 - a\rho)}{\rho^{(1)}(\boldsymbol{E} \cdot \boldsymbol{p}_\perp)} \left\{ \int d2 (\boldsymbol{E} \cdot \boldsymbol{p}_1)(\boldsymbol{p}_\perp \cdot \boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|2))\rho^{(2,\text{T})}(1,2) \right.$$

$$+ \int d2 (\boldsymbol{E} \cdot \boldsymbol{p}_2)(\boldsymbol{p}_\perp \cdot \boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|2))\rho^{(2,\text{T})}(1,2)$$

$$\left. + \int d\Omega_3 (\boldsymbol{E} \cdot \boldsymbol{p}_3) \int d2 (\boldsymbol{p}_\perp \cdot \boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|2))\tilde{\rho}_0^{(3,\text{T})}(1,2;\boldsymbol{p}_3) \right\} \,. \tag{57}$$

Since I is independent of $\boldsymbol{E}$, we can evaluate the previous equation in the special case where $\boldsymbol{E}$ is collinear to $\boldsymbol{p}_\perp$. The first term then disappears and we are left with

$$I = \frac{\beta(1 - a\rho)}{\rho^{(1)}} \left\{ \int d2 (\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{p}_2)(\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|2))\rho^{(2,\text{T})}(1,2) \right.$$

$$\left. + \int d\Omega_3 \int d2 (\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{p}_3)(\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|2))\tilde{\rho}_0^{(3,\text{T})}(1,2;\boldsymbol{p}_3) \right\} \,. \tag{58}$$

We completed the first step: the integral I is now expressed in terms of two- and three-point density correlations.

The next step is to relate the integral over the three-point density in (58) to a similar integral over a two-point correlation. This relation is obtained by considering the hierarchy equations of the infinite system in the absence of an external field. The variation $\Delta_{\delta\boldsymbol{p}_1}\rho^{(2,\text{T})}(1,2)$ produced by an infinitesimal dipole orientation change $\boldsymbol{p}_1 \to \boldsymbol{p}_1 + \delta\boldsymbol{p}_1$ is given by the second BGY-like equation

$$\Delta_{\delta\boldsymbol{p}_1}\rho^{(2,\text{T})}(1,2) = \beta\delta\boldsymbol{p}_1 \cdot \boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|2)\rho^{(2)}(1,2) + \int d3 \,\rho^{(3)}(1,2,3)\beta\delta\boldsymbol{p}_1 \cdot \boldsymbol{E}_{\text{dip}}(\boldsymbol{r}_1|3) \,. \tag{59}$$

In order to relate the integral in the last term to the one which appears in (58), we start by expressing the two- and three-point density functions in terms of the corresponding

fully truncated quantities $[\rho^{(3,\mathrm{T})}(1,2,3) = \rho^{(3)}(1,2,3) - \rho^{(1)}(\rho^{(2,\mathrm{T})}(2,3) + \rho^{(2,\mathrm{T})}(1,3) + \rho^{(2,\mathrm{T})}(1,2)) - \rho^{(1)}\rho^{(1)}\rho^{(1)}]$:

$$\Delta_{\delta\boldsymbol{p}_1}\rho^{(2,\mathrm{T})}(1,2) = \beta\delta\boldsymbol{p}_1 \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1|2)\rho^{(2,\mathrm{T})}(1,2) + \int \mathrm{d}3[\rho^{(1)}\{\rho^{(1)}\delta(2,3)$$

$$+ \rho^{(2,\mathrm{T})}(2,3)\} + \rho^{(3,\mathrm{T})}(1,2,3)]\beta\delta\boldsymbol{p}_1 \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1|3) \,. \tag{60}$$

The terms involving $\rho^{(1)}\rho^{(2,\mathrm{T})}(1,2)$ and $\rho^{(1)}\rho^{(1)}\rho^{(1)}$ vanish indeed by parity, while $\rho^{(1)}\int \mathrm{d}3\rho^{(2,\mathrm{T})}(1,3)\beta\delta\boldsymbol{p}_1 \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1|3) = 0$ because it is proportional by rotational invariance to $\delta\boldsymbol{p}_1 \cdot \boldsymbol{p}_1 = 0$. We take the Fourier transform $\int \mathrm{d}^3r_2 \exp[-i\boldsymbol{k}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)]\ldots$ of the last equation, evaluated in the limit $k \to 0$ at fixed $\hat{\boldsymbol{k}}$. On the left-hand side, we find from (10)

$$\lim_{k\to 0} \Delta_{\delta\boldsymbol{p}_1}\tilde{\boldsymbol{p}}^{(2,\mathrm{T})}(\boldsymbol{k};\boldsymbol{p}_1,\boldsymbol{p}_2) = (\rho^{(1)})^2[\alpha(\delta\boldsymbol{p}_1 \cdot \hat{\boldsymbol{k}})(\boldsymbol{p}_2 \cdot k) + (\delta\boldsymbol{p}_1 \cdot \boldsymbol{p}_2)\tilde{h}_0'(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2)]$$

$$\tag{61}$$

with $\tilde{h}_0'(x) = \mathrm{d}\tilde{h}_0(x)/\,\mathrm{d}x$. Let us consider successively the Fourier transform of the three terms on the right-hand side of (60). The first term is integrable ($\sim r_{12}^{-6}$) and gives the regular contribution $\beta \int \mathrm{d}^3r_2\delta\boldsymbol{p}_1 \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1|2)\rho^{(2,\mathrm{T})}(1,2)$ at $\boldsymbol{k} = 0$. The second term can be evaluated with the convolution theorem and the result (10) on the Fourier transform $\rho^{(2,\mathrm{T})}(\boldsymbol{k};\boldsymbol{p}_1,\boldsymbol{p}_2)$. Its contribution is entirely singular because $\tilde{\boldsymbol{E}}_{\mathrm{dip}}(\boldsymbol{k};\boldsymbol{p}_3) = -4\pi\hat{\boldsymbol{k}}(\hat{\boldsymbol{k}} \cdot \boldsymbol{p}_3)$. From (13), the third term is equal in the limit $k \to 0$ to the sum of the regular term $\beta \int \mathrm{d}3\delta\boldsymbol{p}_1 \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1|3)\tilde{\rho}_0^{(3,\mathrm{T})}(1,3;\boldsymbol{p}_2)$ and of a singular term. The identification of the regular terms of the Fourier transform of Eq. (60), followed by a multiplication by $(\boldsymbol{p}_\perp \cdot \boldsymbol{p}_2)$ and an integration over the angles of $\boldsymbol{p}_2$ yields

$$(\rho^{(1)})^2 \int \mathrm{d}\Omega_2(\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{p}_2)^2\tilde{h}_0'(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2) = \beta \int \mathrm{d}2(\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{p}_2)(\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1|2))\rho^{(2,\mathrm{T})}(1,2)$$

$$+ \beta \int \mathrm{d}\Omega_2 \int \mathrm{d}3(\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{p}_2)(\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{E}_{\mathrm{dip}}(\boldsymbol{r}_1|3))$$

$$\times \tilde{\rho}_0^{(3,\mathrm{T})}(1,3;\boldsymbol{p}_2) \,. \tag{62}$$

We completed the second step and, wonderfully enough, the right-hand side of this equation is precisely what appears in the braces of Eq. (58)! We obtain therefore the simple result $I = (1 - a\rho)\rho^{(1)} \int \mathrm{d}\Omega_2(\hat{\boldsymbol{p}}_\perp \cdot \boldsymbol{p}_2)^2\tilde{h}_0'(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2)$. An integration by parts shows furthermore that $I = (1 - a\rho)\rho^{(1)} \int \mathrm{d}\Omega_2(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{p}}_2)\tilde{h}_0(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2)$. Using the relation (12) between a and b, the formula (48) for the dielectric constant reduces eventually to

$$\varepsilon = 1 + \frac{3y}{1 - a\rho} \,, \tag{63}$$

which is indeed identical to (30).

5. Conclusion

We have established, in a diagrammatic free way, that the constitutive relation of macroscopic electrostatics holds in the rigid-dipole fluid model. Our approach, based on

hierarchy equations, leads to the new formula (48) for the dielectric constant and we showed that it is equivalent to the well-known formula in terms of the direct correlation function. We stress that the present study, like Ramshaw's approach, does not give a complete answer to the microscopic validation of macroscopic electrostatics. Indeed, it remains to show that $E(r)$ can be computed from the macroscopic equations. This requires the analysis at a microscopic level of the surface charge density induced by $E_0(r)$ on the boundaries.

The rigid-dipole fluid model displays very rich physics and the present analysis focuses only on a narrow part of it. A complete theory of this model would have to discuss the crystalline phase, non-linear effects, time-dependent phenomena, etc.... . More complicated models of dielectrics can also be (and has also been) studied, such as fluids with polarizable molecules and higher multipole moments. In our opinion, a very interesting development would be to carry the classical theory of linear dielectrics to the quantum case. The molecules would then be described by quantum mechan- ically bound charges, so that no arbitrary modelization of the molecules would be necessary anymore. A major conceptual difficulty appears however from the fact that the quantum system cannot be appropriately described as a collection of interacting neutral molecules because of the inevitable presence of a tiny amount of free charges. Although the total dipole moment of the system is still well defined, the concept of the local polarization $P(r)$, defined as the average dipole moment of a small cell, is challenged because formally always equal to zero! It appears to us that the question (b) should be rephrased in the quantum mechanical case to become: Do the micro- scopic surface charge densities induced in a (quantum) dielectric indeed display, in the appropriate regime, the macroscopic behavior predicted by classical electrostatics? The dielectric properties of quantum matter is under current study by the authors and Ph.A. Martin.

Acknowledgements

Appendix A

We show in this appendix how Eq. (53) can be obtained from diagrammatic con- siderations. In complete similarity with the Ursell function, the truncated three-body density is given by the sum of all topologically different irreducible graphs with 3 white points numbered $1, 2, 3$ and any number of black points, linked together by at most one Mayer link $f(i, j) = \exp[-\beta u_{\mathrm{int}}(i, j)] - 1$. An irreducible graph has no articulation point, i.e. no point such that when removed, the graphs splits in several parts, one of them consisting of only black points.

The truncated three-body density therefore satisfies the equation

$$(A.1)$$

where $K(1,2,3)$ is the sum of all graphs without any nodal point (black or white) between the point 3 and the points 1, 2 (3 can be a nodal point) and $c(1,2)$ is the direct correlation function (whose graphs do not contain nodal points). The last two terms are necessary to take into account the case where 1 (resp. 2) is a nodal point and 3 is connected to it with a graph without any nodal point. For example, $\circ_3$— $\circ_1$ —$\circ_2$ is included in the one but last term while $\circ_1$— $\circ_3$ —$\circ_2$ belongs to $K(1,2,3)$. The decomposition (A.1) is indeed the graphical equivalent of Eq. (53). Notice that $K(1,2,3)$ is also given by $(\rho^{(1)})^3 \delta h(1,2)/\delta \rho^{(1)}(3)$ because taking this functional derivative corresponds to whitening successively the black points of the Ursell function. Moreover, the previous topological analysis implies that $K(1,2,3)$ should decay with r_3 at least as $|r_1 - r_3|^{-3}|r_2 - r_3|^{-3}$.

References

[1] P.F. Mossotti, Bibl. Univ. Modena 6 (1847).
[2] R. Clausius, Die Mechanische Wärmetheorie, Vol. II, Braunschweich, 1879.
[3] L. Lorentz, Ann. Phys. Chem. 11 (1880) 70.
[4] H.A. Lorentz, Ann. Phys. 9 (1880) 641.
[5] H.A. Lorentz, Theory of Electrons, Dover, New York, 1952.
[6] P. Debye, Phys. Z. 13 (1912) 97.
[7] L. Onsager, J. Am. Chem. Soc. 58 (1936) 1486.
[8] J.G. Kirkwood, The dielectric polarization of polar liquids, J. Chem. Phys. 7 (1939) 911–919.
[9] H. Fröhlich, Theory of Dielectrics, 2nd Edition, Oxford University Press, Oxford, 1958.
[10] C. Böttcher, Theory of Electric Polarization, Vol. 1, Elsevier Scientific Publishing Company, Amsterdam, 1973.
[11] B.K.P. Scaife, Principles of Dielectrics, Clarendon Press, Oxford, 1989.
[12] J.-P. Hansen, I. MacDonald, Theory of Simple Fluids, 2nd Edition, Academic Press, New York, 1986.
[13] M.S. Wertheim, Equilibrium statistical mechanics of polar fluids, Ann. Rev. Phys. Chem. 30 (1979) 471–501.
[14] G. Stell, G.N. Patey, J.S. Høye, Dielectric constants of fluid models: statistical mechanical theory and its quantitative implementation, Adv. Chem. Phys. 48 (1981) 183–328.
[15] S.A. Adelman, J.M. Deutch, The structure of polar fluids, Adv. Chem. Phys. 31 (1975) 4213–4229.
[16] J.D. Ramshaw, Existence of the dielectric constant in rigid-dipole fluids: the direct correlation function, J. Chem. Phys. 57 (1972) 2684–2690.
[17] J.S. Høye, G. Stell, Statistical mechanics of polar systems: Dielectric constant for dipolar fluids, J. Chem. Phys. 61 (1974) 562–572.
[18] D. Chandler, The dielectric constant and related equilibrium properties of molecular fluids: interaction site cluster theory analysis, J. Chem. Phys. 67 (3) (1977) 1113–1124.

[19] G. Nienhuis, J.M. Deutch, Structure of dielectric fluids. I. The two-particle distribution function of polar fluids, J. Chem. Phys. 55 (1971) 4213–4229.

[20] J.D. Ramshaw, Existence of the dielectric constant in rigid-dipole fluids: the functional-derivative approach, J. Chem. Phys. 66 (1977) 3134–3138.

[21] E. Martina, G. Stell, Dipolar fluid in an external field: dielectric properties in the bulk, Phys. Rev. A 24 (1981) 2765–2772.

[22] J. Froehlich, Y.M. Park, Correlation inequalities and the thermodynamic limit for classical and quantum continuous systems, Commun. Math. Phys. 59 (1978) 235–266.

[23] J.D. Ramshaw, Comments on the theory of dipolar fluids, J. Chem. Phys. 70 (1979) 1577.

[24] D.W. Jepsen, Calculation of the dielectric constant of a fluid by cluster expansion methods, J. Chem. Phys. 44 (1965) 774–781.

[25] D. Chan, D. Mitchell, B. Ninham, B. Pailthorpe, On the theory of dipolar fluids and ion-dipole mixtures, J. Chem. Phys. 69 (1978) 691–696.