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Density-functional approach to the theory of dipolar fluids

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Abstract. We develop the formal density-functional theory of dipolar fluids allowing for bulk orientational (ferroelectric) order. The long-range character of the dipole–dipole interaction is treated by separating the direct correlation function of the fluid into short- and long-range parts. The contribution from the long-range part of the dipole–dipole interaction is shown to determine the energy of the macroscopic electric field, which depends on the sample shape and on boundary conditions. The short-range part of the direct correlation function can be used to calculate the regular contribution to the free energy, which is shape independent. An explanation is proposed for the failure of all existing density-functional theories to describe the behaviour of strongly dipolar fluids as observed in computer simulations.

1. Introduction

Despite much theoretical and simulation work extending over the past two decades, our understanding of the phase behaviour of dipolar fluids is still rudimentary. Recently, the phase diagrams of both dipolar hard spheres (DHSs) and dipolar soft spheres (DSSs) have been investigated in much greater detail than before by computer simulation, and it has been found that both model fluids can form orientationally-ordered phases at liquid densities [1–4]. Although several theories have been proposed for the true, long-range dipolar or Stockmayer fluids [5–31] as well as for the related Heisenberg fluid [32–36], considerable conceptual difficulties remain. Furthermore, the very strong anisotropy of these forces is reflected in the formation of chains in low-density strongly dipolar fluids, which pre-empts the usual liquid–vapour phase separation [37–40]. Finally, the need is felt for a study of the influence of dipolar forces on the structure of stable liquid crystalline phases and phase transitions [41–43], which would benefit from the more consistent treatment developed for the simpler systems described above.

The difficulties relating to the long-range character of the dipole–dipole interaction are well known in the dielectric theory of crystals [44]. The general strategy for overcoming these difficulties was proposed by Ewald long ago [45]. However, his particular method of lattice sums cannot be applied directly to dipolar fluids, which possess strong positional and orientational fluctuations. Instead, the separation between short- and long-range contributions in dipolar fluids must be formulated in terms of the corresponding correlation

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functions. At the same time, the general physical ideas of Ewald's theory remain valid in the case of polar fluids [30]. Here one has to split the interaction between a dipole and the local electric field in the medium into two parts. The first will be the interaction with the macroscopic electric field; this is long ranged because the macroscopic electric field is sensitive to the state of the system far from the given point, including the boundaries. The second part is the interaction with the fluctuations of the local field, which is short range. In this paper we perform the corresponding separation in the framework of the density-functional theory of fluids.

In a separate publication [46], we examined the behaviour of strongly dipolar fluids at low densities by assuming that the chains can be treated by the standard methods of polymer theory. This enabled us to derive a simple expression for the free energy of a system of (polydisperse) dipole chains, allowing for the possibility of orientational order. In this paper we address the formal problems of constructing a density-functional theory of dipolar fluids. We start by analysing the shape dependence of the free energy stemming from the long-range character of the dipole–dipole interaction and discuss how this can be consistently incorporated into a density-functional theory. Finally we consider the ferroelectric instability and explore the reasons for disagreement between the predictions of all currently available theories, and simulation results.

2. Theory

2.1. Shape dependence of the free energy

The long-range character of electrostatic, in this particular case dipolar, forces is a source of difficulties in the statistical mechanical theory of fluids. This has been discussed in detail by Groh and Dietrich [25, 27, 31], and can readily be seen in the following simple way. Let us consider the dipole–dipole interaction as a perturbation

$$\phi(\mathbf{x}_1, \mathbf{x}_2) = \phi_{\text{ref}}(\mathbf{x}_1, \mathbf{x}_2) + \phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) \quad (1)$$

where \mathbf{x}_i denotes the set of position \mathbf{r}_i and orientation \mathbf{a}_i coordinates of particle i , $\phi(\mathbf{x}_1, \mathbf{x}_2)$ is the total intermolecular potential, $\phi_{\text{ref}}(\mathbf{x}_1, \mathbf{x}_2)$ is some (usually short ranged) reference potential, and

$$\phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) = -\frac{\mu^2}{r_{12}^3} [3(\hat{\boldsymbol{\mu}}_1 \cdot \hat{\mathbf{r}}_{12})(\hat{\boldsymbol{\mu}}_2 \cdot \hat{\mathbf{r}}_{12}) - \hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2] + \frac{4\pi}{3} \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \delta(r_{12}) \quad (2)$$

is the dipole–dipole interaction [47]. In (2), $\hat{\boldsymbol{\mu}}_i = \boldsymbol{\mu}_i/\mu$ is a unit vector along the dipole moment $\boldsymbol{\mu}_i$ of particle i , $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/r_{12}$ is a unit vector along the intermolecular axis, and $\delta(r_{12})$ is a Dirac delta function. Then the free-energy functional of the fluid can be written as [48]

$$F[\rho(\mathbf{x})] = F_{\text{ref}}[\rho(\mathbf{x})] + \frac{1}{2} \int_0^1 d\alpha \int d\mathbf{x}_1 d\mathbf{x}_2 g(\mathbf{x}_1, \mathbf{x}_2, \alpha) \rho(\mathbf{x}_1) \rho(\mathbf{x}_2) \phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) \quad (3)$$

where $F_{\text{ref}}[\rho(\mathbf{x})]$ is the free energy of a fluid of density $\rho(\mathbf{x})$ characterized by the pair potential $\phi_{\text{ref}}(\mathbf{x}_1, \mathbf{x}_2)$ alone, and $g(\mathbf{x}_1, \mathbf{x}_2, \alpha)$ is the pairwise distribution function of a fluid in which molecules interact via

$$\phi(\mathbf{x}_1, \mathbf{x}_2, \alpha) = \phi_{\text{ref}}(\mathbf{x}_1, \mathbf{x}_2) + \alpha[\phi(\mathbf{x}_1, \mathbf{x}_2) - \phi_{\text{ref}}(\mathbf{x}_1, \mathbf{x}_2)]. \quad (4)$$

At large interparticle separation $r_{12} \gg \xi$, where ξ is the correlation length, $g(\mathbf{x}_1, \mathbf{x}_2, \alpha) \approx 1$ and (3) reduces to

$$F[\rho(\mathbf{x})] = F_{\text{short}}[\rho(\mathbf{x})] + \frac{1}{2} \int_{r_{12} > \xi} d\mathbf{x}_1 d\mathbf{x}_2 \rho(\mathbf{x}_1) \rho(\mathbf{x}_2) \phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) \quad (5)$$

where F_{short} contains F_{ref} and a part of the integral in (3). The second term on the right-hand side of (5) vanishes if the fluid has zero macroscopic polarization (whether the same is produced by an external field, or appears self-consistently, is immaterial), because the angular averages of the dipole moments vanish [52]. In other words, in a macroscopically non-polar fluid, the long-range dipolar contribution to the free energy vanishes owing to orientational averaging.

In a macroscopically polar fluid, however, the angular averages of the dipole moments are non-zero, and the free energy contains a shape-dependent contribution which is actually the energy of the macroscopic electrostatic field in the volume of the fluid, as will be shown in the next subsection. This macroscopic electrostatic field is determined by Maxwell's equations and depends not only on the spontaneous polarization (if any) of the fluid, but also on the boundary conditions and sample shape. It can be argued that a real sample with non-zero spontaneous polarization will split into domains, which will cause the average electrostatic field (and the shape-dependent contribution) to vanish. This, however, does not help avoid difficulties in the statistical theory, since one still requires a consistent procedure for cancelling all divergences. A similar problem arises in the dielectric theory of crystals, where the solution (the method of lattice sums) has been known since the work of Ewald in the 1920s [45]. Yet the same method cannot be directly applied to dipolar fluids, because the lattice is absent. Høye and Stell have proposed a consistent solution for a particular choice of the correlation function [11, 30]. More recently, Groh and Dietrich have separated short- and long-range contributions to the free energy of a dipolar fluid using the zero-density approximation of density-functional theory [25, 27, 31]. These authors have also considered the dependence of the free energy on sample shape and applied electric field. The same general problem has been addressed by Osipov and Sluckin [49] and by Terentjev *et al* [50], within the framework of mean-field theory. Here we propose a more general approach based on the long-range behaviour of the direct correlation function of a dipolar fluid, which is therefore valid regardless of the approximation one employs for this function.

2.2. Density-functional theory of dipolar fluids

In density-functional theory we can expand the free energy of the ferroelectric (polarized) phase (F) about that of the isotropic phase (I)

$$F_{\text{F}} = F_{\text{I}} + \rho k_{\text{B}} T \int d\mathbf{x} \hat{f}(\mathbf{x}) \log[4\pi \hat{f}(\mathbf{x})] - \frac{1}{2} \rho^2 k_{\text{B}} T \int d\mathbf{x}_1 d\mathbf{x}_2 c_2(\mathbf{x}_1, \mathbf{x}_2) \Delta \hat{f}(\mathbf{x}_1) \Delta \hat{f}(\mathbf{x}_2) + \dots \quad (6)$$

where $\hat{f}(\mathbf{x}) = \rho(\mathbf{x})/\rho$ is the orientational distribution function (ODF), $\Delta \hat{f}(\mathbf{x}) = \hat{f}(\mathbf{x}) - 4\pi^{-1}$, and $c_2(\mathbf{x}_1, \mathbf{x}_2)$ is the direct (pair) correlation function (DCF) of the isotropic fluid. This expansion can be used to calculate the limit of stability of the isotropic phase; this coincides with the phase transition boundary in the case of a continuous transition.

First, note that the integration over \mathbf{r}_{12} in the third term on the right-hand side of (6) creates the same problems as in (5). Indeed, the DCF behaves asymptotically as

$$c_2(\mathbf{x}_1, \mathbf{x}_2) \sim -\beta \phi(\mathbf{x}_1, \mathbf{x}_2) \quad (7)$$

where $\beta = (k_{\text{B}} T)^{-1}$, and in our case the long-range tail of the potential is the dipole-dipole interaction, (2). The important point is, however, that this is the *only* term in the whole expansion that causes problems. Higher-order terms, containing higher-order correlation functions, do not diverge. This can be readily seen, for example, by taking the virial

expansion of the DCF, which can be directly obtained from the Onsager virial expansion of the free energy. The leading-order term is the Mayer f -function,

$$c_2(\mathbf{x}_1, \mathbf{x}_2) = e^{-\beta\phi(\mathbf{x}_1, \mathbf{x}_2)} - 1 + \dots \quad (8)$$

whence at large r_{12} , $c_2(\mathbf{x}_1, \mathbf{x}_2)$ decays as $\phi(\mathbf{x}_1, \mathbf{x}_2)$ as stated above. By contrast, the expansion for the *triplet* DCF $c_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$ starts with the triangle graph,



whence the corresponding contribution to the free energy contains the integral

$$\int d\mathbf{r}_{12} d\mathbf{r}_{13} r_{12}^{-3} r_{13}^{-3} |r_{12} - r_{13}|^{-3} \quad (9)$$

which does not diverge. Thus we arrive at the general conclusion that the difficulties associated with the long-range nature of the dipolar interaction manifest themselves only at the level of the *pairwise* DCF, $c_2(\mathbf{x}_1, \mathbf{x}_2)$, which possesses a long-range tail.

Now the divergence in the third term on the right-hand side of (6) can be eliminated by a ‘renormalization’ of the pairwise DCF, similar to that performed on the pair potential in the mean-field theory [50]. Let us define the effective short-range pairwise DCF as

$$\tilde{c}_2(\mathbf{x}_1, \mathbf{x}_2) = c_2(\mathbf{x}_1, \mathbf{x}_2) + \beta\phi_{dd}(\mathbf{x}_1, \mathbf{x}_2). \quad (10)$$

Substituting (10) into (6), we obtain

$$F_F[\hat{f}(\mathbf{x})] = \tilde{F}[\hat{f}(\mathbf{x})] + U_{el} \quad (11)$$

where

$$\begin{aligned} \tilde{F}[\hat{f}(\mathbf{x})] &= F_1 + \rho k_B T \int d\mathbf{x} \hat{f}(\mathbf{x}) \log[4\pi \hat{f}(\mathbf{x})] \\ &\quad - \frac{1}{2} \rho^2 k_B T \int d\mathbf{x}_1 d\mathbf{x}_2 \tilde{c}_2(\mathbf{x}_1, \mathbf{x}_2) \Delta \hat{f}(\mathbf{x}_1) \Delta \hat{f}(\mathbf{x}_2) + \dots \end{aligned} \quad (12)$$

and U_{el} is the energy of the macroscopic electric field $\mathbf{E}(\mathbf{r})$:

$$\begin{aligned} U_{el} &= \frac{1}{2} \rho^2 \int d\mathbf{x}_1 d\mathbf{x}_2 \hat{f}(\mathbf{x}_1) \hat{f}(\mathbf{x}_2) \phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) \\ &= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 P_\alpha(\mathbf{r}_1) T_{\alpha\beta}(\mathbf{r}_{12}) P_\beta(\mathbf{r}_2) \\ &= -\frac{1}{2} \int d\mathbf{r} \mathbf{P}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}) \end{aligned} \quad (13)$$

where $\mathbf{P}(\mathbf{r}) = \rho \int d\omega \hat{f}(\mathbf{x}) \boldsymbol{\mu} = \rho \langle \boldsymbol{\mu} \rangle$ is the macroscopic polarization. In the absence of external fields this is related to the macroscopic electric field by

$$\mathbf{E}(\mathbf{r}) = - \int d\mathbf{r}' \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}') \quad (14)$$

where $\mathbf{T}(\mathbf{r})$ is the dipole–dipole tensor [51]. Consequently, the weighted average of the dipole–dipole interaction (without the hard-core cutoff) has been exactly transformed into the energy of the electrostatic field in the volume V of the fluid.

Thus we have split the total free energy of a polarized fluid into two parts. The first one is the usual free energy of a fluid characterized by the short-ranged pairwise DCF $\tilde{c}_2(\mathbf{x}_1, \mathbf{x}_2)$: this functional contains no shape dependence and behaves like the free energy of any system with short-range interactions. The second part is the energy of the electrostatic field. This

depends only on the macroscopic polarization and the macroscopic electric field. The relation between these two macroscopic quantities can now be determined solely within the framework of the macroscopic theory of dielectrics. In the particular case of an ellipsoidal sample, the polarization and the field are homogeneous and related by the depolarization factor, $\mathcal{D}(k)$, of the ellipsoid [53, 54]

$$\mathbf{E} = -4\pi\mathcal{D}(k)\mathbf{P} \quad (15)$$

where \mathbf{P} is assumed to be parallel to the major axis of the ellipsoid, and k is the aspect ratio. For a sphere, $k = 1$ and $\mathcal{D} = \frac{1}{3}$, whence

$$\mathbf{E}^{\text{sphere}} = -\frac{4}{3}\pi\mathbf{P}^{\text{sphere}} \quad (16)$$

$$U_{\text{el}}^{\text{sphere}}/V = \frac{2}{3}\pi(\mathbf{P}^{\text{sphere}})^2. \quad (17)$$

Formulae relating \mathbf{E} to \mathbf{P} can be found in the literature which take into account the dielectric constant of the surrounding medium, ϵ_{out} . The most important particular case is that of a conducting medium, for which $\epsilon_{\text{out}} = \infty$. This leads to $\mathbf{E} = 0$ and to the vanishing of the electrostatic energy. Therefore, the free energy of a polarized fluid surrounded by a conducting medium does not contain any shape-dependent contribution. This conclusion had already been reached by Groh and Dietrich [27], who presented a derivation of the general relations, (15)–(17).

Recall that the electrostatic energy is positive and therefore for $\epsilon_{\text{out}} = 1$ (sample in vacuum), the lowest-energy state is probably not homogeneous, but rather one where the system splits into domains, provided the resulting boundary free energy is less than the macroscopic electrostatic energy. The ideal domain structure would again correspond to zero average field [26, 31, 55].

Let us now return to the formal definition of the effective short-range DCF, (10). $\tilde{c}_2(\mathbf{x}_1, \mathbf{x}_2)$ thus defined has a singularity at the origin determined by the dipole–dipole potential and the limit at large r_{12} is not given explicitly. For every realistic intermolecular interaction, one can consider a sufficiently small ‘core’ of diameter σ , inside which the interaction potential is approximately isotropic [56]. Let us redefine the effective short-range DCF, taking into account that

$$\tilde{c}_2(\mathbf{x}_1, \mathbf{x}_2) = \lim_{R \rightarrow \infty} \tilde{c}_2(\mathbf{x}_1, \mathbf{x}_2, R) \quad (18)$$

where $R \gg \sigma$ is some (large) cutoff radius, and

$$\tilde{c}_2(\mathbf{x}_1, \mathbf{x}_2, R) = \begin{cases} c_2(\mathbf{x}_1, \mathbf{x}_2) + \beta\phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) & \text{if } r_{12} \leq R \\ 0 & \text{if } r_{12} > R \end{cases} \quad (19)$$

is the DCF with the long-range tail cutoff. Indeed, for sufficiently large separation $r_{12} > R$ the DCF is given by its asymptotic value, (7) and the two terms in (10) cancel each other. Thus the effective direct correlation function $\tilde{c}_2(\mathbf{x}_1, \mathbf{x}_2)$ does not possess a long-range tail and is expected to give a regular contribution to the free energy. On the other hand, the integral of the dipole–dipole potential within a sphere of finite diameter D is [57, pp 139–43]

$$\int_{r_{12} < D} d\mathbf{r}_{12} \phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) = \frac{4\pi}{3}\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2. \quad (20)$$

It is reasonable to assume that the DCF is also isotropic within the sphere $r_{12} < \sigma$, where the interaction potential is isotropic. We can then write the effective short-range DCF approximately as

$$\begin{aligned} \tilde{c}_2(\mathbf{x}_1, \mathbf{x}_2) \approx & \frac{4}{3}\pi\beta\delta(r_{12})\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 + c_2(\mathbf{x}_1, \mathbf{x}_2, R) \\ & + \beta H(\sigma - r_{12})H(r_{12} - R)\phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) \end{aligned} \quad (21)$$

where $H(x)$ is the step function ($H(x) = 1$ if $x < 0$ and zero otherwise), and

$$c_2(\mathbf{x}_1, \mathbf{x}_2, R) = \begin{cases} c_2(\mathbf{x}_1, \mathbf{x}_2) & \text{if } r_{12} \leq R \\ 0 & \text{if } r_{12} > R. \end{cases} \quad (22)$$

Equation (21) is asymptotically exact at $R \rightarrow \infty$ and $\sigma \rightarrow 0^+$; furthermore, both limits ($r_{12} \rightarrow 0$ and $r_{12} \rightarrow \infty$) are exhibited explicitly. Note that whereas the first term takes care of the discontinuity at the origin, the last term is the dipole–dipole potential cutoff at both ends of its range, and is therefore absolutely regular. This term does not contribute to the free energy of the *homogeneous* isotropic system because it vanishes on integration over r_{12} . It will, however, be non-zero in an inhomogeneous system (such as near a surface).

Insertion of (21) into the free-energy expansion, (11) and (12) and use of (13), yields

$$F_{\text{F}}[\hat{f}(\mathbf{x})] = F_0[\hat{f}(\mathbf{x})] - \frac{1}{2} \int d\mathbf{r} [\mathbf{P}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}) + \frac{4}{3}\pi \mathbf{P}^2(\mathbf{r})] \quad (23)$$

where the free energy F_0 is again given by (6), but with the full DCF $c_2(\mathbf{x}_1, \mathbf{x}_2)$ replaced by the short-ranged $c_2(\mathbf{x}_1, \mathbf{x}_2, R)$:

$$F_0 = F_1 + \rho k_{\text{B}} T \int d\mathbf{x} \hat{f}(\mathbf{x}) \log[4\pi \hat{f}(\mathbf{x})] - \frac{1}{2} \rho^2 k_{\text{B}} T \int d\mathbf{x}_1 d\mathbf{x}_2 c_2(\mathbf{x}_1, \mathbf{x}_2, R) \Delta \hat{f}(\mathbf{x}_1) \Delta \hat{f}(\mathbf{x}_2) + \dots \quad (24)$$

In (23) the terms in square brackets are the contributions from the long- and zero-range parts of the dipole–dipole interaction, (13) and (20), respectively. Now F_0 depends on the cutoff radius R and approaches the true free energy only in the limit $R \rightarrow \infty$. However, for sufficiently large $R \gg \sigma$ this dependence is very weak and can be neglected for practical purposes. At large intermolecular separation, $c(\mathbf{x}_1, \mathbf{x}_2)$ is given approximately by $f(\mathbf{x}_1, \mathbf{x}_2)$, the Mayer function (cf (8)). Now $f(\mathbf{x}_1, \mathbf{x}_2) \approx -\beta\phi_{dd}(\mathbf{x}_1, \mathbf{x}_2)$ if $|\beta\phi_{dd}(\mathbf{x}_1, \mathbf{x}_2)| \ll 1$, whence R must satisfy the strong inequality $(R/\sigma)^3 \gg \lambda$.

In the case of an ellipsoidal sample, the polarization of the sample in a homogeneous electric field is also homogeneous and if the polarization is along the major axis, (23) can be rewritten in a particularly simple form (using a generalization of (15))

$$F_{\text{F}}[\hat{f}(\mathbf{x})] = F_0[\hat{f}(\mathbf{x})] + 2\pi V [\mathcal{D}(k, \epsilon_{\text{out}}) - \frac{1}{3}] \mathbf{P}^2 \quad (25)$$

where $\mathcal{D}(k, \epsilon_{\text{out}})$ is the depolarization factor of an ellipsoid of aspect ratio k embedded in a medium of dielectric constant ϵ_{out} (an explicit expression for $\mathcal{D}(k, \epsilon_{\text{out}})$ can be found in, for example, [58]). In general, the equilibrium polarization and electric field will be inhomogeneous (for example, the spontaneously polarized ellipsoid in zero external field splits into domains). We do not discuss these effects here, but concentrate instead on the derivation of the free-energy functional $F[\mathbf{P}(\mathbf{r})]$. The spatial distribution of the polarization in a sample of a particular shape can then be found by minimizing this functional with appropriate boundary conditions. We are interested in some special cases.

(1) A spherical sample in a conducting medium, $\epsilon_{\text{out}} = \infty$. Here $\mathbf{E}(\mathbf{r}) = 0$ and $\mathcal{D}(1, \infty) = 0$, whence

$$F_{\text{F}}[\hat{f}(\mathbf{x})] = F_0[\hat{f}(\mathbf{x})] - \frac{2}{3}\pi V \mathbf{P}^2. \quad (26)$$

(2) A spherical sample in vacuum, $\epsilon_{\text{out}} = 1$. Now $\mathcal{D}(1, 1) = \frac{1}{3}$ and the second term on the right-hand side of (25) vanishes

$$F_{\text{F}}[\hat{f}(\mathbf{x})] = F_0[\hat{f}(\mathbf{x})]. \quad (27)$$

(3) A cylindrical sample in vacuum with polarization parallel to the axis. In this case $\mathcal{D}(\infty, 1) = 0$ and the free energy is given by (26).

(4) A thin layer in vacuum with polarization normal to the layer. Here $\mathcal{D}(0, 1) = 1$ and

$$F_{\text{F}}[\hat{f}(\mathbf{x})] = F_0[\hat{f}(\mathbf{x})] + \frac{4}{3}\pi V \mathbf{P}^2. \quad (28)$$

In conclusion, we have separated the long- and short-range contributions to the free energy of the polarized phase of a dipolar fluid in the most general case, simply by assuming the validity of the functional expansion, (6), and without resorting to any approximations for the DCF. The method described enables us, in principle, to apply the density-functional approach to any problem in the statistical physics of polar fluids.

The polarization-dependent term in the previous expressions for the total free energy, can be positive or negative depending on the sample shape and boundary conditions. The electrostatic energy (the first term in the square brackets in (25)) is always positive, but there is also a negative contribution coming from the molecular hard core. For a spherical sample in vacuum the two contributions cancel each other, whereas for a spherical sample in a conducting medium the total contribution is negative and thus in this case ferroelectric ordering is favoured. On the other hand, for a thin layer in vacuum this same contribution is positive and ferroelectricity is depressed. As mentioned in the introduction, ferroelectric ordering has been observed in computer simulations of a fluid of dipolar spheres (for a spherical sample). As far as we know, this is one of very few instances of a phase transition being so sensitive to sample shape and to the properties of the surrounding medium [59]. We shall discuss the ferroelectric phase transition in more detail in the next section.

2.3. Continuous ferroelectric phase transition in a weakly dipolar fluid

Let us assume that the transition to a homogeneous, uniaxial ferroelectric state, is continuous in some range of temperatures and densities. The ODF can then be expanded about its value in the isotropic phase,

$$\hat{f}(\mathbf{a} \cdot \mathbf{p}) = (4\pi)^{-1} [1 + 3(\mathbf{a} \cdot \mathbf{p}) + \dots] \quad (29)$$

where $\mathbf{p} = \int d\omega \hat{f}(\mathbf{x}) \mathbf{a} = \langle \hat{\boldsymbol{\mu}} \rangle$. Substitution of (29) into the expression for the free energy of a spherical ferroelectric sample in a conducting medium, (26), yields

$$F_{\text{F}} = F_{\text{I}} + \rho V k_{\text{B}} T \left(\frac{3}{2} - \frac{9}{2} \rho C_1 - \frac{2\pi}{3} \rho \frac{\mu^2}{k_{\text{B}} T} \right) \mathbf{p}^2 + \text{higher-order terms in } \mathbf{p} \quad (30)$$

where

$$C_1 = \int d\mathbf{r}_{12} \frac{d\mathbf{a}_1}{4\pi} \frac{d\mathbf{a}_2}{4\pi} c_2(\mathbf{x}_1, \mathbf{x}_2, R)(\mathbf{a}_1 \cdot \mathbf{a}_2) \quad (31)$$

is the contribution from the second term in the short-range DCF, (21), and we have used the fact that the macroscopic polarization is the dipole moment per unit volume, i.e. $\mathbf{P} = \rho \boldsymbol{\mu} \mathbf{p}$. The transition point is the limit of stability of the isotropic phase with respect to ferroelectric fluctuations. This is given by the vanishing of the coefficient of \mathbf{p}^2 ,

$$3\rho C_1 + \frac{4\pi}{9} \rho_{\text{inst}} \frac{\mu^2}{k_{\text{B}} T} = 1. \quad (32)$$

Let us compare the transition temperature/density thus obtained with that of Groh and Dietrich [27]. First, note that the present density-functional theory is more general than

theirs: indeed, their free-energy functional is recovered by retaining just the first two terms in our free-energy expansion and using the approximations

$$c_2(\mathbf{x}_1, \mathbf{x}_2) = e^{-\beta\phi(\mathbf{x}_1, \mathbf{x}_2)} - 1 \quad (33)$$

$$F_1 = F_{\text{hs}} - \frac{k_B T}{2} \rho^2 \int d\mathbf{x}_1 d\mathbf{x}_2 [e^{-\beta\phi(\mathbf{x}_1, \mathbf{x}_2)} - 1] \quad (34)$$

where F_{hs} is the free energy of the reference hard-sphere fluid. We shall see, however, that on a qualitative level the results of Groh and Dietrich for the continuous transition can be reproduced by treating the dipole–dipole potential as a perturbation (since they consider only relatively weak dipoles). In this spirit we further approximate $c_2(\mathbf{x}_1, \mathbf{x}_2)$ by

$$c_2(\mathbf{x}_1, \mathbf{x}_2) \approx e^{-\beta\phi_{\text{iso}}(r_{12})} - 1 - \beta\phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) e^{-\beta\phi_{\text{iso}}(r_{12})} \quad (35)$$

where $\phi_{\text{iso}}(r_{12})$ is some isotropic interaction (soft spheres, Lennard-Jones, etc). In this approximation, the quantity C_1 vanishes (cf (31)) and the ferroelectric instability occurs at

$$\rho_{\text{inst}}^* = \frac{9}{4\pi\lambda} \quad (36)$$

where $\rho^* = \rho\sigma^3$ and $\lambda = \mu^2/k_B T\sigma^3$. Let us now estimate the transition density for Groh and Dietrich's choice of parameters. Their reduced temperature and dipole moment are $T^* = k_B T/\epsilon$ and $(d^*)^2 = \mu^2/\epsilon\sigma^3 = \lambda T^*$, respectively, where ϵ is the depth of the Lennard-Jones potential well. In the region of continuous ferroelectric transitions, $T^* \sim 3.5$ for $d^* = 2$, whence $\lambda \sim 1.1$. This yields a ferroelectric instability at $\rho_{\text{inst}}^* \sim 0.7$, not too far from Groh and Dietrich's $\rho_{\text{inst}}^* \sim 0.6$. Equation (36) also predicts $\rho_{\text{inst}}^* \propto T^*$, which agrees with their quasilinear dependence [27, figure 15].

It follows from the foregoing discussion that the strongest dipole considered by Groh and Dietrich is only of order one in our reduced units. In the present context, λ is the relevant reduced dipole moment, since it is the ratio of the strength of the dipolar interaction at contact to the thermal energy, $k_B T$. Entropy dominates for $\lambda < 1$, and significant chain formation cannot be expected. Chains start to appear at $\lambda > 1$ (dimers first), and eventually dominate at $\lambda \gg 1$ [46].

Our simple approach yields results similar to the much more sophisticated theory of Groh and Dietrich. Furthermore, the instability condition, (36), does not depend on the particular form of the *isotropic* interaction potential, and therefore can be applied to both the Stockmayer and the dipolar soft- or hard-sphere fluids. This is because, in the present approximation, the transition is determined by the balance between the orientational entropy contribution, $\frac{3}{2}k_B T(\rho\mu^2)^{-1}\mathbf{P}^2$, and the second, long-range, term $-\frac{2}{3}\mathbf{P}^2$ in (26), which does not depend on the isotropic interaction.

The possibilities of the density-functional theory discussed above (of which Groh and Dietrich's is a special case) are, however, very limited. This can be readily seen from (36), which for $\lambda = 12.25$ as used by Levesque and Weis [4], yields $\rho_{\text{inst}}^* \approx 0.06$, one order of magnitude smaller than found by simulation. This strong discrepancy indicates that the present approach must be even qualitatively incorrect at large dipole moments. One might argue that such poor agreement is a consequence of the perturbative approximation, (35). This is obviously not valid at large λ , where higher powers of λ will dominate the expansion of $\exp[-\beta\phi_{dd}(\mathbf{x}_1, \mathbf{x}_2)]$. So a better approximation is required for the DCF in (31), but we shall show that this actually increases the discrepancy between theory and simulation, rather than decreasing it. Indeed, let us find C_1 in the zero-density approximation of Groh and Dietrich:

$$C_1 = \int d\mathbf{r}_{12} \frac{d\mathbf{a}_1}{4\pi} \frac{d\mathbf{a}_2}{4\pi} [e^{-\beta\phi_{\text{iso}}(r_{12}) - \beta\phi_{dd}(\mathbf{x}_1, \mathbf{x}_2)} - 1](\mathbf{a}_1 \cdot \mathbf{a}_2). \quad (37)$$

Now consider the case of strong dipoles, $\lambda \gg 1$, and evaluate the integral on the right-hand side of (37) taking into account that the integrand has a maximum for $r_{12} \sim \sigma$, $\mathbf{r}_{12} \parallel \mathbf{a}_1 \parallel \mathbf{a}_2$. For simplicity we take $\phi_{\text{iso}}(r_{12})$ to be the HS potential. The asymptotic expression for C_1 is then

$$C_1 \approx \frac{\pi \sigma^3}{18\lambda^3} e^{2\lambda} \quad (38)$$

and the condition for ferroelectric instability is now

$$\frac{\pi \rho_{\text{inst}}^*}{6\lambda^3} e^{2\lambda} + \frac{4\pi}{9} \rho_{\text{inst}}^* \lambda = 1. \quad (39)$$

For $\lambda = 9$ the first term on the left-hand side of (39) dominates and consequently the ferroelectric transition will take place at a vanishingly small density. Since this is obviously in contradiction with simulation, we are led to the conclusion that density-functional theory supplemented with the zero-density approximation for the DCF, is inappropriate for the study of strongly dipolar fluids. Indeed, Groh and Dietrich's theory underestimates the transition densities already at $\lambda \sim 1$ (i.e. $d^* = 2$), as noticed by Stevens and Grest [60]. In fact, the above strategy works well only for small dipole moments, $\lambda < 1$, as recognized also by Groh and Dietrich in their more recent work [27]. This is not surprising, because $\lambda \sim 1$ actually defines the boundary between 'weakly' and 'strongly' polar fluids. For $\lambda \ll 1$ the fluid is 'simple', whereas for $\lambda \gg 1$ long chains will form. At $\lambda = 1$ there is probably no significant chain formation, but there are already strong short-range dipolar correlations which are not taken into account completely by the existing theories.

From a qualitative, physical point of view, the situation is clear; our simplified treatment reveals that it is energetically very favourable for two molecules to have their dipoles parallel. This tendency already wins over entropic effects at very low densities. On the other hand, there exists another way of lowering the energy without aligning all dipoles. This is, of course, chain formation. Indeed, the quantity C_1 in (37) is determined by the minimum of the potential, which corresponds to two neighbouring spheres being part of a chain. As a result, chains form, even at low densities. However, as shown in [46], the interaction between chains appears to be weak, especially at low densities. Let us consider in more detail the dipole-dipole interaction between long chains, which can be responsible for ferroelectric ordering. In the case of strong dipoles the chains are rather stiff and interact locally like rigid rods of some effective length ℓ (see, for example, [61] for a discussion of the interchain interaction in semiflexible polymers). Now we can apply the general theory of the continuous ferroelectric phase transition already presented, to the system of dipolar rods of length ℓ and thickness σ . For simplicity we shall work in the mean-field approximation, where the short-range correlation function reads

$$c_2(\mathbf{x}_1, \mathbf{x}_2, R) = -\beta H(\xi_{12} - r_{12}) H(r_{12} - R) \phi_{dd}(\mathbf{x}_1, \mathbf{x}_2) \quad (40)$$

where the step function $H(\xi_{12} - r_{12})$ is zero when the two rods penetrate each other, and where the distance of minimum approach between the centres of two rods, ξ_{12} , is a function of the relative orientation of the two particles. Now (40) is to be substituted into the general equation (31). The corresponding integral of the dipole-dipole potential has been calculated numerically by Terentjev and Petschek [62], who have also given an interpolation formula. Using this formula, we obtain

$$C_1 = -\frac{4\pi \mu^2}{27k_B T} \left[\left(1 - \frac{\sigma}{\ell}\right)^{2/3} - \frac{2}{3} \frac{(\sigma/\ell)[1 - (\sigma/\ell)]}{[1 - (\sigma/\ell)]^2 + 6(\sigma/\ell)^2} \right]. \quad (41)$$

For sufficiently stiff chains, the length of the rigid segment $\ell \gg \sigma$. In this limit,

$$C_1 \approx -\frac{4\pi\mu^2}{27k_B T} \left(1 - \frac{4\sigma}{3\ell}\right). \quad (42)$$

Finally, insertion into (32) yields a ferroelectric instability at

$$\rho_{\text{inst}}^* = \frac{27\ell}{16\pi\lambda\sigma}. \quad (43)$$

Thus the density of the ferroelectric instability grows linearly with the anisotropy of the rod ℓ/σ , and can be much larger than the corresponding density for the system of dipolar spheres, cf (36). Assuming that the length ℓ can be of order 5σ – 10σ , we can fit (by order of magnitude) the transition density found in computer simulations. However, we know that the simulated ferroelectric phase does not contain any chains, unlike the low-density isotropic phase where very long, locally stiff, chains form which are essentially non-interacting [46], consistently with $\rho_{\text{inst}}^* \rightarrow \infty$ as $\ell/\sigma \rightarrow \infty$ from (43). Furthermore, it is even questionable whether the concept of chain is meaningful in the context of ferroelectric ordering [63]. We conclude that the actual strongly-dipolar fluid appears to be more complicated than expected and cannot be consistently described by the simple approach already presented. In fact a realistic theory must not only take into account chain formation at low densities, but also explain why the chains dissociate before the system becomes ferroelectric.

3. Discussion and conclusions

We have developed a density-functional theory of dipolar fluids, by taking into account the long-range character of the dipole–dipole interaction. In this context we have shown that the disagreement between theory and simulation as regards the ferroelectric transition, suggests that the formalism presented here is unsuitable for dealing with strongly directional forces.

Two mechanisms for the ferroelectric transition of DHSs were analysed in detail, namely ferroelectric ordering of an ordinary fluid and ferroelectric ordering of a fluid of chains. These were shown to yield results in disagreement with simulations performed in the strongly dipolar regime. The former mechanism predicts that the ferroelectric instability will occur at a density one order of magnitude lower than that obtained by simulation. By contrast, the latter yields a transition density of the right order of magnitude, but assumes that chains retain their integrity in the ordered phase, which is not borne out by simulations.

In an alternative scenario, proposed by Gingras and Holdsworth [63], the ferroelectric transition takes place from an intermediate phase characterized by local bond-orientational order, to the polarized phase characterized by long-range orientational order. It is indeed plausible that ferroelectric ordering in the dipolar fluid is qualitatively different from the magnetic-ordering transition in Heisenberg fluids [36, 64–66], in that it may be accompanied by important short-ranged spatial correlations owing to the strong anisotropy of the dipole–dipole potential. This anisotropy is responsible for the formation of long chains in the low-density phase and is likely to play an important role in driving the ferroelectric transition. Such spatial correlations constitute local-bond orientational order [67], analogous to that exhibited by hexactic smectic liquid-crystal phases [68] and the corresponding order parameter can be constructed from the eigenvalues of the rotationally-invariant tensors describing the orientation of the cage of neighbours [67]

$$B_{\alpha\beta} = \frac{1}{4\pi^2 V} \int (3\hat{r}_{12}^\alpha \hat{r}_{12}^\beta - \delta_{\alpha\beta}) g_2(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (44)$$

where $g_2(\mathbf{x}_1, \mathbf{x}_2)$ is the pair distribution function. This order parameter vanishes if the pair correlation function is completely isotropic, but along a chain it will decay exponentially on the scale of the persistence length. The principal axis of the uniaxial tensor \mathbf{B} will be along the local orientation of the chain. In the isotropic phase, however, the chains are randomly oriented and thus the order parameter \mathbf{B} vanishes after proper averaging. $B_{\alpha\beta}$ is non-zero (i.e. there is true long-range order) only if the correlation function $g_2(\mathbf{x}_1, \mathbf{x}_2)$ (or, equivalently, $h_2(\mathbf{x}_1, \mathbf{x}_2)$) approaches a constant value at large r_{12} . This value must depend on the unit vector $\hat{\mathbf{r}}_{12}$ and reflect the anisotropy of the bond-orientational order

$$h_2(\mathbf{x}_1, \mathbf{x}_2) \rightarrow \text{constant} \times n_\alpha n_\beta (3\hat{r}_{12}^\alpha \hat{r}_{12}^\beta - \delta_{\alpha\beta}). \quad (45)$$

Here \mathbf{n} is the unit vector that characterizes the macroscopic asymmetry of the system. It seems unlikely that bond-orientational order will appear self-consistently: most likely it will be induced by nematic or ferroelectric ordering. In the latter case \mathbf{n} is the unit vector along the direction of polarization.

We note that the order parameter $B_{\alpha\beta}$ has the same symmetry as the nematic order parameter $Q_{\alpha\beta}$. Indeed, the vector $\hat{\mathbf{r}}_{12}$ for consecutive particles within a rigid segment of a chain is a good definition of the local axis of the chain. Then $B_{\alpha\beta}$ is the nematic order parameter for chains, and thus local bond-orientational order is equivalent to local nematic order of the chains. By contrast, the order parameter that describes the broken symmetry in the ferroelectric phase is the macroscopic polarization, $\mathbf{P}(\mathbf{r})$, hence the bond-orientational order parameters are not the main order parameters of the ferroelectric transition. This fact notwithstanding, how does bond-orientational order affect this transition? The simplest Landau–Ginzburg free energy which takes into account the coupling between polarization and (uniaxial) bond-orientational order is

$$\Delta F = F_F - F_I = a(T - T_c)P^2 + bP^4 + \mathcal{A}B^2 - \mathcal{C}BP^2 + \dots \quad (46)$$

where $P = |\mathbf{P}(\mathbf{r})|$ (we restrict ourselves to the uniform, uniaxial ferromagnetic case), B is the largest eigenvalue of the traceless symmetric tensor \mathbf{B} , and a , b , \mathcal{A} and \mathcal{C} are positive coefficients which can be written in terms of the parameters of the dipole–dipole interaction. (The minus sign in front of the cross term, $-\mathcal{C}BP^2$, ensures that bond-orientational order—or, equivalently, nematic order of the chains—is along the direction of polarization.) After minimization with respect to B , one obtains $B = (\mathcal{C}/2\mathcal{A})P^2$, and the free energy becomes

$$\Delta F = a(T - T_c)P^2 + \left(b - \frac{\mathcal{C}^2}{4\mathcal{A}}\right)P^4 + \dots \quad (47)$$

Thus bond-orientational order renormalizes the coefficients of the free-energy expansion in powers of $\mathbf{P}(\mathbf{r})$ and can drive the continuous transition first-order, but it is important to realize that the instability temperature is unchanged. The actual first-order ferroelectric transition will nevertheless occur at a higher temperature, $T_{\text{IF}} > T_c$ (and therefore at an even lower density). This is not surprising, given that local bond-orientational order in the isotropic phase promotes all kinds of uniaxial orientational order and consequently does not shift the transition density in the desired direction.

In the simulations of Gingras *et al* [67] chains indeed appear due to a strongly-directional potential of the type dipole–dipole squared; however, once formed, they do not dissociate but only grow and arrange themselves in a two-dimensional (2D) pattern owing to emerging lateral bonds [67, figure 6]. That is, in this case the bond-orientational order does not destroy chains but rather orders them in a 2D biaxial structure which corresponds to a 2D crystal with numerous defects. In 3D this would be described by a state with a fourth-order bond orientational order parameter. Still, as pointed out by Gingras and Holdsworth [63], the

chain concept may not be useful in describing the build-up of correlations expected to occur in a dipolar system in the process of ordering ferroelectrically.

Apart from the accuracy of the present description, some questions remain unanswered. In particular, the nature of the crossover from the low-density regime, characterized by extensive chaining, to the fluid with local bond-orientational order, is not understood (at least quantitatively). At present we do not know of any general mechanism of chain dissociation other than strong monomer–monomer attraction [46, 69]. Despite the fact that simulations of the ferroelectric phase did not explicitly include the Van der Waals attraction between monomers, we can argue that such an attraction may be obtained from the weighted average of the dipole–dipole potential (i.e. from the second term in (34)). However, the very same attraction induces gas–liquid phase separation, which has not been found in the simulations of DHS fluids. Hence the relation between chain dissociation and ferroelectric ordering remains an unsettled issue, to be addressed by a more refined theory or by computer simulations. Finally, since the ferroelectric phase is a high-density fluid phase, the question arises of under what conditions the same is stable with respect to the solid [70]. Clearly much work remains to be done fully to elucidate the phase behaviour of strongly-dipolar fluids.

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