The effect of dipolar forces on the structure and thermodynamics of classical fluids

REVIEW ARTICLE

The effect of dipolar forces on the structure and thermodynamics of classical fluids

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Abstract. The present understanding of how dipolar forces affect the structure and phase behaviour of classical fluids is reviewed. We focus mainly on the apparent absence of a liquid–vapour phase transition for strongly polar spherical particles, and discuss how the same can be recovered. By concentrating on theoretical and simulation studies of simple models, the roles and interplay of dipolar and Van der Waals interactions and molecular shape can be clearly discerned. Connection is made with experimental work on ferrofluids. Finally, we discuss the theoretical and computational challenges that lie ahead.

1. Introduction

Electric charge is present in the building blocks of most types of matter, spanning the whole spectrum of length scales from the molecular level (nanometres) to colloids (microns) and on to plasmas as are now used in everyday applications (centimetres or metres). A distribution of discrete charges is described, in classical electromagnetism, by multipole moments. The lowest non-zero moment of an overall neutral body is the dipole moment, which measures the asymmetry in the spatial distribution of charges. It is defined as a vector directed from the centre of negative charges to the centre of positive charges, with magnitude equal to the common absolute value of those charges multiplied by the distance between their centres. If this asymmetry is permanent and caused by the particular equilibrium geometry of the body, as in, e.g., a hydrogen fluoride molecule, we have a *permanent dipole*. An *instantaneous dipole*, on the other hand, results from a fluctuation in the position of the charge carriers, e.g., a sudden deformation of the electron cloud surrounding an otherwise non-polar molecule such as carbon dioxide. Finally, an *induced dipole* is induced by some outside field, whether externally imposed or due to the neighbouring particles. All three types are important; in this review we shall restrict ourselves to permanent dipoles.

Dipolar interactions are not only ubiquitous in nature, they also occur and play a prominent role in many artificial systems, such as ferrofluids and electro-rheological fluids. Ferrofluids are stable colloidal dispersions of ferromagnetic particles, such as cobalt, iron, iron oxide (Fe_3O_4) or nickel, coated with stabilizing surfactant or silica layers and dispersed in a host liquid, such as water or paraffin (Rosensweig 1985, Donselaar 1998). They are interesting by virtue of their high magnetic susceptibility. Applications include floppy disks, credit cards, video tapes, loudspeakers, rotating shaft seals (as in computer hard disk drives) and exclusion

seals (Pankhurst and Pollard 1993). Electro-rheological fluids, on the other hand, are colloidal dispersions of highly polarizable particles in solvents with low dielectric constant, whose rheological and mechanical properties change dramatically when an electric field is applied (Halsey 1992).

Model systems are the key to understanding the effect of dipolar forces on the structure and thermodynamics of classical fluids. Although widely studied in statistical mechanics (Deutch 1973, Groh and Dietrich 1999), the phase diagrams of dipolar fluids in general, and of *strongly* dipolar fluids in particular, have remained largely uncharted. However, starting from the early 1990s a large number of works have appeared, and many important new insights have emerged. Our purpose here is to collect, systematize and critically discuss existing results, at present scattered over a huge literature that has grown by about ten publications a year over the past couple of years. We identify the key issues and the questions that remain to be answered by future research, concentrating mainly on positionally disordered *bulk* phases of monodisperse particles in zero external field.

This review is organized as follows. In section 2 we critically discuss early (mostly 1970s) theoretical and simulation work on the phase diagrams of model dipolar fluids. Then in section 3 we enter the 'modern era', starting about 1992. The key feature is the totally unexpected behaviour of dipolar soft and hard spheres, and in particular their failure to exhibit a liquid–vapour critical point (section 3.1). We next enquire how 'conventional' behaviour can be recovered: stretching the spheres into rods (section 3.2) and the consequences this may have for liquid crystalline phase transitions, where shape is crucial (section 3.3); adding dispersive (Van der Waals) interactions to the intermolecular potential (section 3.4) or switching on an external field (section 3.5). Finally, in section 4 we summarize what has been learnt so far and list a number of outstanding issues which are, in our opinion, essential for a full understanding of these systems.

2. Early theory and simulation

The dipole–dipole potential is highly anisotropic. It couples not only the relative orientations of dipoles $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, but also the orientation of each of these with the interdipole vector $\boldsymbol{r}_{12}$ (see figure 1):

$$\phi_{DHS}(12) = -\frac{\mu^2}{r_{12}^3} \left[3 \left(\hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{r}}_{12} \right) \left(\hat{\boldsymbol{\mu}}_2 \cdot \hat{\boldsymbol{r}}_{12} \right) - \hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2 \right] \qquad r_{12} > \sigma \qquad (1)$$

where μ is the common strength of the dipole moments, $\hat{\boldsymbol{\mu}}_i = \boldsymbol{\mu}_i / \mu$, and we have assumed that the interaction is cut off inside some spherical 'hard core' of diameter σ. Equation (1) defines the model dipolar hard-sphere fluid (DHS): the lowest-energy minimum corresponds
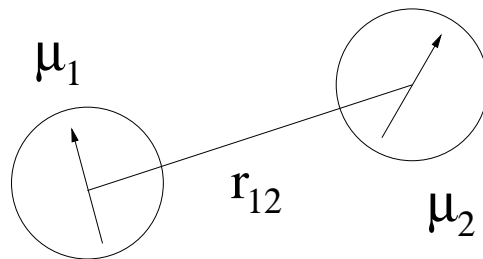

Figure 1. Two interacting dipoles, $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, connected by $\boldsymbol{r}_{12}$.

to two spheres in contact and aligned head-to-tail, with a secondary minimum if they touch but are anti-parallel. Because of its complexity, $\phi_{DHS}(12)$ is difficult to treat theoretically, which led Keesom (1921) to derive the angle-averaged dipole–dipole potential:

$$\overline{\phi}_{DHS}(r_{12}) = \langle e^{-\beta\phi_{DHS}(12)}\phi_{DHS}(12)\rangle_{\omega_1\omega_2} = -\frac{2}{3}\frac{\beta\mu^4}{r_{12}^6} + \mathcal{O}\left(\frac{\beta^3\mu^8}{r_{12}^{12}}\right) \qquad (2)$$

where $\langle A\rangle_{\omega_1\omega_2} = \int A\, d\omega_1 d\omega_2$ and $\beta = 1/(k_B T)$. This is the interaction energy between two dipoles that are able to rotate about their axes much faster than the characteristic timescale of their mutual interactions. $\overline{\phi}_{DHS}(r_{12})$ is useful at high temperatures (relative to the energy scale set by μ), or at large interdipole separations; importantly, it allows us to define the dimensionless parameter $\mu^* = (\beta\mu^2/\sigma^3)^{1/2}$ as a measure of the relative importance of dipolar interactions and thermal agitation. Woodward and Nordholm (1984) and Dietrich and co-workers (Frodl and Dietrich 1992, 1993a, b, Frodl *et al* 1994) gave an alternative definition of the effective isotropic dipole–dipole potential which incorporates an entropic, as well as an energetic, contribution:

$$\begin{aligned}\overline{\phi}_{DHS}(r_{12}) &= -\beta^{-1}\log\langle e^{-\beta\phi_{DHS}(12)}\rangle_{\omega_1\omega_2}\\ &= -\frac{1}{3}\frac{\beta\mu^4}{r_{12}^6} + \frac{7}{450}\frac{\beta^3\mu^8}{r_{12}^{12}} - \frac{163}{99225}\frac{\beta^5\mu^{12}}{r_{12}^{18}} + \cdots.\end{aligned} \qquad (3)$$

Note that the leading term on the right-hand side of equations (2) and (3) is attractive and has the same distance dependence as, e.g., the long-range part of the popular Lennard–Jones (LJ) potential. On the basis of this fact, de Gennes and Pincus (1970) conjectured that the phase diagram of the DHS fluid should be similar to that of a Van der Waals fluid, with vapour, liquid and solid phases. And indeed Woodward and Nordholm (1984) found standard liquid–vapour (L–V) coexistence using both generalized Van der Waals (GVdW) theory with equation (3) and Wertheim's (1971) solution of the mean-spherical approximation (MSA). Qualitatively the same phase diagram has been obtained in various studies: by Rushbrooke *et al* (1973) from perturbation theory to orders μ^{*4} and μ^{*6}, with and without Padé resummation of the free energy expansion; by Sutherland *et al* (1974) from their Onsager model; by Winkelmann (1979) from a different theromodynamic perturbation theory, to order μ^{*6}; by Morozov *et al* (1987) again from Wertheim's (1971) MSA; by Kalikmanov (1992) employing a cell theory combined with a perturbative expansion or with MSA†; by Buyevich and Ivanov (1992) from perturbation theory to order μ^{*2}, for a fluid in a cylindrical container; by Russier and Douzi (1994) within the second-order virial expansion combined with simulation data for the reference HS system; and by Boda *et al* (1995) from Gubbins–Pople–Stell perturbation theory with Padé resummation, applied to the closely related dipolar *soft* spheres (DSSs). Other treatments yielded the possibility of a first-order transition between a vapour and a ferroelectrically ordered liquid: the mean-field (MF) theories of Tsebers (1982), and of Sano and Doi (1983); the GVdW theory of Zhang and Widom (1993, 1994) and the modified MF theory of Groh and Dietrich (1997a).

   In all the above approaches that predict bulk phase separation into a liquid and a vapour phase in zero external field, this separation is due exclusively to dipolar interactions. Prior to 1992, the only test of this state of affairs was a Monte Carlo (MC) simulation of just 32 DHSs by Ng *et al* (1979): the configurational energy was computed along six (umbrella sampling) or seven (Boltzmann sampling) isochores for $\mu^{*2} = 0.5 - 4.0$, and fitted to a fourth-degree polynomial in the density; no long-range corrections were applied. The standard double-tangent construction bore out the expected result: isotropic L–V coexistence of the LJ type,

† This paper only estimates the L–V critical point.

ending at a critical point at high temperatures. Such a comforting picture lay undisturbed for well over a decade.

3. The modern era of dipolar fluids

3.1. Spherical particles

Interest in simple models of dipolar fluids was revived by Wei and Patey (1992a, b). They showed, by molecular dynamics (MD) simulation, that on compression DSSs exhibit a continuous (or weakly first-order (Wei, 1994)) transition into a ferroelectric liquid (FL) phase. At high densities the FL phase is characterized by nematic and polar order parameters $S \sim 0.4 - 0.7$ and $P \sim 0.7 - 0.9$, respectively, where S is the largest eigenvalue of the second rank nematic tensor and P is the average polarization in the direction of the (nematic) director. These results were obtained for periodic systems with conducting boundaries, which suppress the depolarization field. In large systems surrounded by a vacuum, the simulation cell broke up into two or more ferroelectric domains, each with essentially the same properties as the single domain of the conducting boundary case. This is to be expected if the thermodynamic limit applies to polarized liquids, which indeed has been proved recently (Banerjee *et al* 1998). A similar picture has emerged from MC work on DHSs (Weis and Levesque 1993a), suggesting that more complex phases of strongly dipolar *spherical* particles than an isotropic liquid are possible. It was not until somewhat later that experimental evidence for spontaneous ferromagnetism was reported in undercooled liquid CoPd alloys (Platzek *et al* 1994, Reske *et al* 1995, Albrecht *et al* 1997) and in small droplets of a FeCoSiB amorphous compound (Grigorenko *et al* 1998a, b). Costa Cabral (2000), however, has shown by MC simulation that polar order can be significantly reduced by size or dipole moment polydispersity, which will be present in most experimental situations.

Shortly after their MC work on DHSs Weis and Levesque (1993b) ran canonical ensemble (NVT) simulations of 500 DHSs in a cubic box repeated periodically in space, for reduced densities $\rho^* = \rho\sigma^3$ and temperatures $T^* = 1/\mu^{*2}$ in the ranges $0.02 \leqslant \rho^* \leqslant 0.3$ and $0.082 \leqslant T^* \leqslant 0.25$. The surrounding medium was taken to be a conductor, and the long range of the dipolar interactions was accounted for by means of the Ewald summation method. Most surprisingly, no L–V transition was found: visual inspection of snapshots of equilibrium configurations revealed that the spheres had aggregated into linear, chain-like, structures. To quantify these results, an energy criterion, rather than a geometric one, was proposed: two spheres were considered to be bonded if their potential energy was less than a certain value, E_c. Using this algorithm, the mean chain length of each equilibrium configuration was measured and the development of structure was followed during a simulation: chains grew, broke and recombined, but the mean chain length remained constant during each run. This established that each point (ρ^*, T^*) of the phase diagram could be characterized by a chain length distribution of mean value $\bar{N}$. $\bar{N}$ increased with decreasing temperature (at fixed density). Variations with density (for fixed temperature) were not so regular: no chains would form above $T^* \approx 0.15$, coinciding with a sharp drop in the internal energy (which is an increasing function of the temperature). The average persistence length of long chains was also measured: chains seemed stiffer for higher densities and lower temperatures. Later, the same authors (Levesque and Weis 1994) carried out a more detailed MC study for $0.005 \leqslant \rho^* \leqslant 0.8$ and confirmed that there is chaining, and no condensation, at low densities ($\rho^* \leqslant 0.2$), while at high densities ($\rho^* > 0.6$) the fluid does indeed become polarized, with $P \sim 0.8$. No conclusions could be drawn concerning the intermediate density range, where the simulations appeared unable to equilibrate. Finally, Weis (1998) reported extensive chaining (and no L–V

transition) in an MC NVT probe of 400 DHSs with centres of mass and dipole moments confined to a plane, for densities $0.05 \leqslant \rho^* \leqslant 0.8$ and $\mu^* = 2$ or 3. Many rings were seen, and, at the highest density vortex-like structures were observed, but no ferroelectric ordering. It is appropriate to note that the ground state of low-density dipolar fluids is composed of rings and not chains (Jacobs and Bean 1955, de Gennes and Pincus 1970, Clarke and Patey 1994)†, so some rings should be present also in 3D; yet to our knowledge this only occurs in simulations of dipolar clusters, presumably owing to the additional geometrical constraint of particle proximity (Clarke and Patey 1994, Lavender *et al* 1994, Lu and Singer 1995).

The above-mentioned failure to find L–V condensation led Caillol (1993) to perform systematic NpT MC simulations along two isotherms ($T^* = 0.222\ldots, 0.1818\ldots$) below the critical temperature estimated by Ng *et al* (1979). $N = 256$ dipolar spheres were used, with long-range interactions taken into account by employing as a simulation cell the 3D surface of a 4D hypersphere. In spite of some technical difficulties related to finite-size effects and to convergence problems, the corresponding density histograms revealed no 'loops' in the pressure, and thus no sign of an L–V transition. These results were confirmed through a finite size scaling analysis and through simulations in the Gibbs ensemble (GEMC). Caillol concluded that, if there exists L–V condensation in the DHS fluid, the corresponding critical temperature is lower than $T^* = 0.1818\ldots$ (and/or the critical density lower than $\rho^* = 0.1$). Although no structural analysis was done in this work, the technical difficulties encountered— low acceptance ratios for particle insertion, unreasonably low pressures for reasonably low values of the density—are very similar to those experienced by other authors and attributed to chain formation.

The pioneering research of Levesque and Weis (1993b, 1994) has been extended by Tavares *et al* (1999), who carried out NVT simulations for a fixed reduced density $\rho^* = 0.05$ and three values of the reduced temperature (see figure 2). $N = 1024$ spheres were utilized to reduce the finite-size effects, together with longer runs to improve the statistics and guarantee equilibration (in particular, it is important to ensure that there are always monomers—chains of unit length—present in the simulation cell). Several quantities (mean chain length, number of *free* monomers, number of chains, etc) were computed as functions of E_c, in order to study the influence of this parameter on the final results. It was found that for each simulation these quantities do depend on the choice of E_c (e.g., $\bar{N}$ increases as E_c increases), but that qualitatively, the structure, a polydisperse mixture of self-assembled linear chains of dipolar spheres, is preserved. Distributions of chain lengths were collected for two values of E_c in the three simulations performed. This, and the earlier works by Levesque and Weis, and Stevens and Grest (1995a), confirmed the mechanical stability of the chains and established that analysis of their statistics can overcome, in a first approximation, the difficulty of describing the structure of dipolar fluids at low densities, which involves many-body, short-range anisotropic correlations.

In what may be a dramatic twist of the story, Camp *et al* (2000) have reported NpT, GCMC and NVT simulations of 256 DHSs. The $T^* = 0.1322$ isotherm appears to exhibit *three* distinct branches (obtained for different starting densities and pressures) in the range $0.05 \lesssim \rho^* \lesssim 0.2$, pointing towards the existence of at least one phase transition between isotropic liquid phases. Consistently, the Helmholtz free energy, calculated as a function of ρ^* for $T^* = 0.1333, 0.1429, 0.1538, 0.1667, 0.1818$ and 0.2000, seems to have two minima at the two lowest temperatures. This led the authors to conjecture that one of the branches of the equation of state is a line of metastable points, and to estimate an L–V critical temperature of

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† We thank P J Camp for bringing this to our attention. See also Wen *et al* (1999) for related experimental and simulation work.
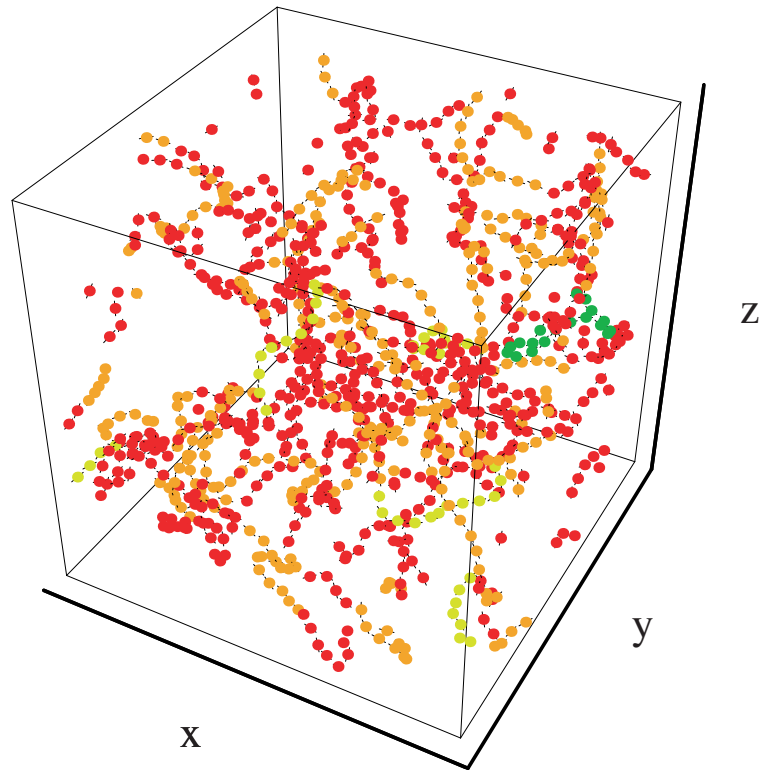
Figure 2. Snapshot of a configuration of 1024 DHSs for $\rho^* = 0.05$ and $\mu^* = 2.5$, from the NVT simulations of Tavares *et al* (1999). The chains are coloured according to the number of spheres they contain. Red: 1–5; orange: 5–10; yellow: 10–15; green: 15–20.

$T_c^* \simeq 0.15 - 0.16$.

All theoretical attempts at explaining the striking behaviour of strongly dipolar fluids treat them as a mixture of self-assembled chains of spheres in 'chemical' equilibrium. Within this assumption, the free energy density (FED) is approximated by the sum of the entropy of an ideal mixture with excess terms coming from interactions between the chains:

$$f = k_{\mathrm{B}} T \sum_{i=1}^{\infty} \rho_i (\ln \rho_i - 1 - \ln \tilde{q}_i) + f_{exc}(\rho, \{\rho_i\}) \equiv f_{id}(\{\rho_i\}) + f_{exc}(\rho, \{\rho_i\}). \tag{4}$$

Here ρ_i is the density of chains of length i and $\tilde{q}_i$ is the partition function (divided by the total volume V) of a chain of length i. The densities are constrained by conservation of the total number of dipolar spheres

$$\rho = \sum_{i=1}^{\infty} i \rho_i \tag{5}$$

or, equivalently, the 'chemical reactions' between chains—where they break and re-form— must conserve the total number of dipolar spheres, whence the chemical potential of chains of length i, μ_i, is

$$\mu_i = i \mu_1. \tag{6}$$

Equation (6) can be transformed, with the aid of equation (4), into

$$\left(\frac{\rho_1}{\tilde{q}_1}\right)^i \exp(i\tilde{\mu}_1) = \frac{\rho_i}{\tilde{q}_i}\exp(\tilde{\mu}_i) \tag{7}$$

where $\tilde{\mu}_i$ is the (reduced) excess chemical potential of chains of length i, $\tilde{\mu}_i = \beta\partial f_{exc}/\partial\rho_i$. Thus, for a dipolar fluid of density ρ at temperature T, the distribution of chain lengths $\{\rho_i\}$ can be calculated using equations (5) and (7). Substitution of this distribution into equation (4) gives the equilibrium free energy of the system, which determines its thermodynamic behaviour. However, approximations are still needed for the partition function, $\tilde{q}_i$, and for the excess free energy, $f_{exc}(\rho, \{\rho_i\})$.

The partition function of a chain of length i can be generally written as the product of a kinetic part, q_i^K, and a configurational part, q_i^C:

$$q_i = q_i^K \times q_i^C. \tag{8}$$

The kinetic part is simply

$$q_i^K = \frac{1}{h^{3i}}\int \mathrm{d}p^{3i}\exp\left(-\beta\sum_{k=1}^{3i}\frac{p_k^2}{2m}\right) = \Lambda^{-3i} \tag{9}$$

where Λ is the de Broglie wavelength of a dipolar sphere. It can easily be seen, by inserting equation (9) into equation (7), that q_i^K has no effect on the structure. Furthermore, from equation (4) it follows that q_i^K contributes to the FED a term proportional to ρ, which does not affect the thermodynamics of the system. The configurational partition function of an *ordered* DHS chain is (Osipov *et al* 1996)

$$q_i^C = \int \mathrm{d}\vec{r}_1\dots\mathrm{d}\vec{r}_i\mathrm{d}\omega_1\dots\mathrm{d}\omega_i$$
$$\exp\left[-\beta\phi_{DHS}(\vec{r}_1 - \vec{r}_2, \omega_1, \omega_2) - \dots - \beta\phi_{DHS}(\vec{r}_{i-1} - \vec{r}_i, \omega_{i-1}, \omega_i)\right] \tag{10}$$

with $\vec{r}_k$ the position vector of the kth dipole and ω_k the set of Euler angles that describe its orientation. In writing equation (10) it has been assumed that interactions between consecutive monomers are dominant, and all others are neglected. This is consistent with a chain that is rigid on the length scale of a few σ: such rigidity is a short-range effect, as dipoles like to sit in the minima of their pairwise potential.

Osipov and co-workers then used the theory of semi-flexible polymers (Khokhlov and Semenov 1981, 1982) to obtain

$$q_i^C = V\exp\left[(i-1)S_0\right] \tag{11}$$

with S_0 given by

$$S_0 = 2\mu^{*2} + \ln\left(\frac{\pi\sigma^3}{18\mu^{*6}}\right) - \frac{3}{2\mu^{*2}}. \tag{12}$$

The first two terms on the right-hand side (rhs) of this equation are the asymptotic ($\mu^* \to \infty$) value of

$$\ln\left[\int \mathrm{d}\omega_1\mathrm{d}\omega_2\int_{|\vec{r}|>\sigma}\mathrm{d}\vec{r}\exp\left(-\beta\phi_{DHS}(\vec{r}, \omega_1, \omega_2)\right)\right] \tag{13}$$

and have simple interpretations: the first term, which dominates at large μ^*, is the energy of two head-to-tail dipolar spheres in contact, and thus corresponds to a configuration where all dipoles are aligned head-to-tail; the second term is a correction coming from fluctuations around this configuration. Finally, the third term is an approximation to the conformational entropy of the chain, enforcing the correct behaviour when $\mu^* \to 0$. Very similar approximations for the

partition function of a DHS chain have been made by Van Roij (1996) and Levin (1999), and in studies of lattice models of living polymers (Milchev and Landau 1995). In view of the above, $-k_B T S_0$ can be interpreted as the mean free energy of each bond. Moreover, it reflects the ordered nature of the chain, with dipolar spheres in fixed relative positions. However, we know from simulations that the chains are not such well defined aggregates, since the spheres diffuse through all chains in the course of equilibrium runs. Hence the configurational partition function of a DHS chain can be written as

$$q_i^C = \frac{1}{i!} \int d\vec{r}_1 \ldots d\vec{r}_i d\omega_1 \ldots d\omega_i \exp\left[-\beta \Phi_{DHS}(\vec{r}_1, \ldots \vec{r}_i, \omega_1, \ldots \omega_i)\right] \quad (14)$$

where Φ_{DHS} is the sum of the DHS interactions between all pairs of particles. Using for the integral in equation (14) the same approximation as led to equation (11), Tavares *et al* (1999) found:

$$q_i^C = \frac{1}{i!} \exp\left[(i - 1)S_0\right] \quad (15)$$

which amounts to assuming that the spheres in a given chain are indistinguishable†. These approximations can be viewed as two opposite limits of the structure of a chain: a solid with a mean free energy per bond given by $-k_B T S_0$, and a gas with energy equal to $-(i - 1)k_B T S_0$.

The excess FED $f_{exc}(\rho, \rho_i)$ is expected to be small in the low density regime. Osipov *et al* (1996) estimated the steric and dipolar interactions between chains. They treated separately 'free' monomers and 'semi-flexible' chains of length L, persistence length ℓ and breadth σ. The chains were viewed as a concatenation of linear rigid segments of length ℓ, each containing ℓ/σ spheres whose dipoles are aligned head-to-tail; in the limit of strong dipoles, $L \gg \ell \gg \sigma$. Within this picture, interactions between the N_{ch} dipolar spheres that belong to chains are equivalent to those between $N_{ch}\sigma/\ell$ segments. Then, at the level of a second-virial approximation, the contribution of steric interactions between chains to the excess free energy of the isotropic phase is proportional to $(N_{ch}/V)^2 \equiv \rho_{ch}^2$. As for the contribution of dipolar interactions between chains, in a uniform system it separates into two parts. The first part is just the energy of the electrostatic field of the fluid, and vanishes when the average field is zero (i.e., when the surrounding medium is a conductor, which is the case in most simulations of dipolar fluids). The second part is proportional to ρ_{ch}^2, to the square of the polarization of the system, and to the integral of the dipole–dipole interaction between two chains over their excluded volume. This last integral is approximately the depolarization factor $\mathcal{D}$ of a disc of thickness σ and area $\propto \ell^2$, with polarization in the plane of the disc. In the limit $\ell \gg \sigma$, $\mathcal{D}$ vanishes, and thus the contribution to the free energy of dipolar interactions between long chains in uniform polarized phases is expected to be small. Furthermore, that same contribution will vanish, to a first approximation, in unpolarized phases, because of the symmetry of the dipole–dipole potential.

It is therefore not unreasonable to regard the chains as non-interacting. Following Osipov *et al* (1996) and Tavares *et al* (1999), we derive expressions for the structure of the system neglecting the excess FED. The chemical potentials μ_i are then trivially obtained from equation (4), as $\mu_i = \ln \frac{\rho_i}{q_i}$. Insertion of this expression into equation (7) using either equation (11) or equation (15) yields the results of Osipov and co-workers or Tavares and co-workers, respectively. Remarkably, both approximations give rise to analytic expressions for several properties such as the mean chain length, the most probable chain length and the chain length

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† As a consequence, S_0 as derived by Tavares *et al* (1999) is different from that of Osipov *et al* (1996): the factor 1/18 in equation (12) is, in Tavares *et al*, 1/24. Tavares and co-workers accounted for fluctuations of the distance between spheres around the minimum, $r = \sigma$, while Osipov and co-workers (and also Levin (1999)) have taken that distance to be fixed. We do not discuss this discrepancy here, as it only slightly changes results quantitatively.

distribution, equation (7), which will be directly compared with simulation data for the low-density regime.

Equation (11) enables us to express all relevant quantities as functions of ρ and μ^* (or S_0). The mean chain length is found to be

$$\bar{N} \equiv \frac{\sum_{i=1}^{\infty} i\rho_i}{\sum_{i=1}^{\infty} \rho_i} = \frac{1}{2} + \sqrt{\frac{1}{4} + \rho \exp(S_0)} \tag{16}$$

leading to the scaling $\bar{N} \sim \sqrt{\rho} e^{\mu^{*2}}$ for large dipole moments. Within this approximation the density of *free* monomers ρ_1 is $\rho_1 = \rho \bar{N}^{-2}$, the most probable chain length N_0 of the distribution $i\rho_i$ is the integer in the interval $(\bar{N} - 1, \bar{N})$ and the density of monomers in chains of length i is $i \left[\frac{\rho \exp(S_0)}{N^2} \right]^i$.

From the other approximation, equation (15), it is also possible to calculate the same quantities, but only as implicit functions of ρ and S_0. Equations (5), (7) and (15) now yield, for ρ_1,

$$\rho = \rho_1 \exp\left(\rho_1 e^{S_0}\right) \tag{17}$$

and for the mean chain length

$$\bar{N} = \frac{\rho e^{S_0}}{\exp\left(\rho_1 e^{S_0}\right) - 1} \tag{18}$$

while the large-μ^* scaling is now $\bar{N} \simeq \ln \rho + 2\mu^{*2}$.

Table 1. Mean values of the number of free monomers, N_m, and chain length, $\bar{N}$, obtained in the simulations of Tavares *et al* (1999) for different choices of E_c. Theoretical values calculated according to Tavares *et al* (1999), Osipov *et al* (1996) and Sear (1996).

	$\mu^* = 2.25$		$\mu^* = 2.5$		$\mu^* = 2.75$	
	N_m	$\bar{N}$	N_m	$\bar{N}$	N_m	$\bar{N}$
Simulations						
$E_c = -1.4\mu^{*2}$	410	1.61	155	2.7	50	4.8
$E_c = -1.5\mu^{*2}$	523	1.41	249	2.08	104	3.23
$E_c = -1.6\mu^{*2}$	656	1.25	393	1.62	213	2.22
$E_c = -1.7\mu^{*2}$	800	1.13	591	1.32	407	1.59
Tavares (1999)	594	1.30	253	1.86	62	2.98
Osipov (1996)	405	1.59	275	2.93	25.8	7.3
Sear (1996)	86	4.12	16	10.25	2	29.01

In table 1 and figure 3, these two approximations are tested against the simulations of Tavares *et al* (1999). We can easily see that the growth of chains with increasing dipole strength, and the existence of a distribution of chain lengths, are qualitatively explained by both approximations. For the two weakest dipoles it is possible to have quantitative agreement between the mean chain lengths and the numbers of free monomers from theories and simulation. However, compared to simulation the distribution obtained from equation (11) is broader, and peaked at a larger N, while that from equation (15) is narrower and peaked at a smaller N (see figure 3): equation (11) overestimates the number of long chains and equation (15) underestimates it. The only difference between the two approximations is the indistinguishability factor, i.e., whether each chain is a solid or a gas. In fact, we know from
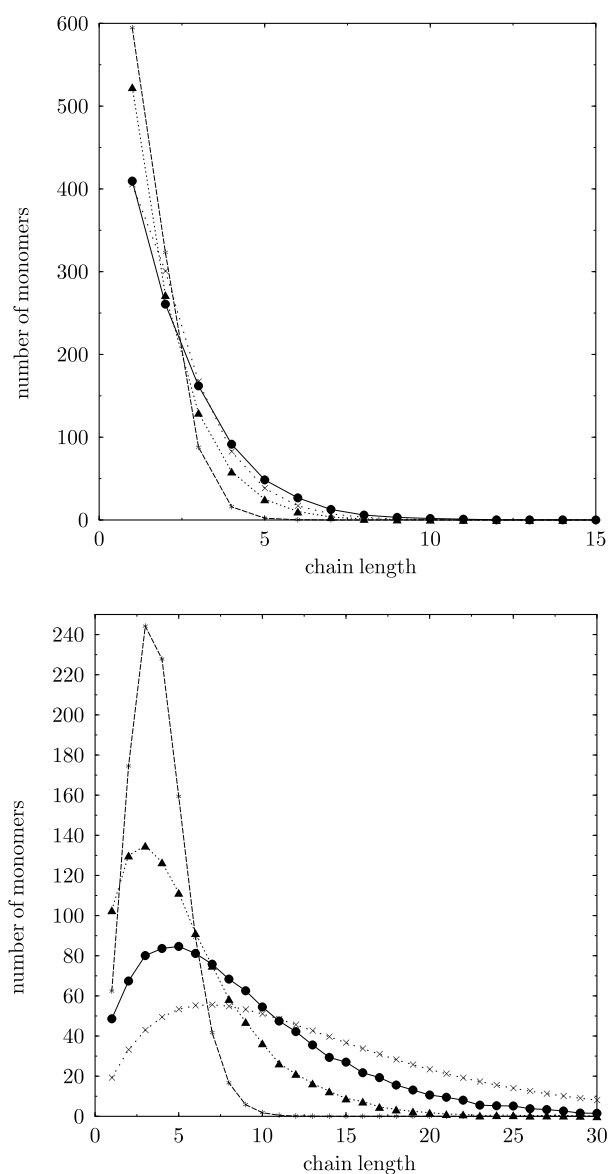
Figure 3. Mean number of monomers against chain length in a DHS fluid for $\mu^* = 2.25$ (top) and $\mu^* = 2.75$ (bottom). Circles and triangles: simulations of Tavares *et al* (1999) with $E_c = -1.4\mu^{*2}$ and $E_c = -1.5\mu^{*2}$. Crosses and asterisks: theories of Osipov *et al* (1996) and Tavares *et al* (1999), respectively.

simulations that they are neither: on the one hand, chains are similar to solids in the sense that they are structures with some stability, but on the other hand, these structures are not well defined, since monomers diffuse through chains. So equations (11) and (15) represent two opposite limiting cases and, accordingly, the simulation results lie in between.

We have included in tables 1 and 2 the mean chain lengths due to Sear (1996). He started by considering the expansion of the pressure, p, in powers of the activity, z (Hansen and

Table 2. Mean chain length: comparison between the theoretical results of Osipov *et al* (1996), Sear (1996) and Tavares *et al* (1999), and the simulations of Weis and Levesque (1993b).

ρ^*	μ^*	$\bar{N}_{sim}$ (Weis and Levesque 1993)	$\bar{N}$ (Sear 1996)	$\bar{N}$ (Osipov 1996)	$\bar{N}$ (Tavares 1997)
0.3	2.0	2.7	4.63	1.94	1.36
0.3	2.5	5.2	10.25	7.09	2.79
0.3	3.0	16.5	222.15	59.97	6.19
0.3	3.5	27.0	2445.12	966.4	11.2
0.2	3.5	24.6	1814.19	789.15	10.84
0.1	2.0	2.6	2.7	1.43	1.16
0.1	2.5	6.7	14.61	4.36	2.18
0.1	3.0	24.5	128.07	34.84	5.27
0.1	3.5	24.2	1475.4	558.16	10.20
0.05	3.5	30.4	914.02	394.8	9.57
0.02	2.0	2.3	1.43	1.11	1.04
0.02	3.5	8.4	620.93	249.9	8.75

McDonald 1986):

$$\beta p = \sum_{i=1}^{\infty} b_i z^i \tag{19}$$

and assumed that the only diagrams that pertain to a fluid of non-interacting chains of particles with only nearest-neighbour interactions are linear chain graphs. Therefore, it follows, for $i \geqslant 2$,

$$b_i = \frac{1}{2} \left(-2B_2 \right)^{i-1} \tag{20}$$

where $B_2 \equiv -b_2$ is the second virial coefficient of the DHS fluid. Substitution of equation (20) into equation (19) gives the pressure as a function of the activity

$$\beta p = z - \frac{z^2 B_2}{1 + 2z B_2}. \tag{21}$$

By means of the approximate equation (20) and the exact relation for homogeneous systems $\rho = \sum_{i=1}^{\infty} i b_i z^i$, it is possible to relate the activity to the density:

$$\rho = z - \frac{2z^2 B_2 + 2z^3 B_2^2}{(1 + 2z B_2)^2}. \tag{22}$$

This equation, together with an expression for $B_2(\mu^*)$ (Sear used Joslin's (1981)), enables us to calculate the activity z for given ρ and μ^*. Once this is known, the pressure (and all the thermodynamics) can be found from equation (21). Mean chain lengths, obtained via $\bar{N} = \rho/\beta p$ (valid for *ideal* chains), are gross overestimations (see tables 1 and 2), although the asymptotic behaviour when $\mu^* \to \infty$ is the same as in Osipov *et al* (1996).

Direct comparison between Sear's approach and the approaches of Osipov and co-workers and Tavares and co-workers is possible if we make the (reasonable) following identifications: (i) $z = \rho_1$, because the activity is the exponential of the chemical potential which, for the present ideal mixture, equals $\ln \rho_1$; (ii) $B_2 = -2 \exp(S_0)$, as $\exp(S_0)$ is in fact the asymptotic value of the second virial coefficient (see equation (13)). We conclude that the coefficients b_i of Osipov *et al* (1996) are twice as large as those of Sear (1996). Finally, it can be seen that Sear's approximation is equivalent to retaining only the terms that account for correlations between neighbouring spheres in the integral of equation (14). Sear's theory yields extremely large

chain lengths when compared with simulations even if we use as input our $B_2 = -2\exp(S_0)$ (with S_0 given by equation (12)) instead of using Joslin's B_2.

   None of the above theories can address the question of whether there is L–V condensation in the DHS fluid, since these theories describe the DHS fluid as an ideal mixture of chains, i.e., they do not include attractive interactions that can stabilize the liquid. However, they do suggest that once chains are formed they are very stable, and there is little energy to be gained from their aggregation. In fact, the internal configurational energy of the system within these approximations can be written as the product of the number of bonds by the mean energy of a bond. It is clear that this mean energy is just $-k_B T S_0$ (or $-k_B T \ln(-2B_2)$ in Sear's theory). Thus the mean internal energy per particle u is

$$\beta u = -\left(1 - \frac{1}{\bar{N}}\right) S_0. \tag{23}$$
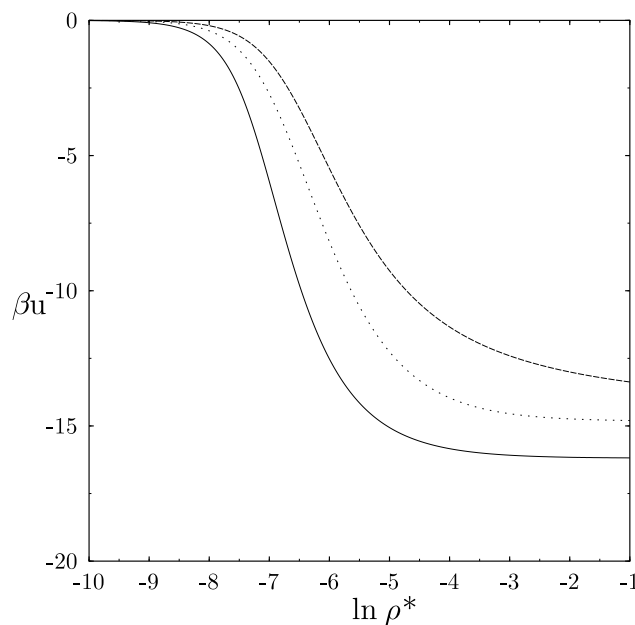

Figure 4. Internal energy per particle against $\ln \rho^*$ for $\mu^* = 3.5$. Solid line: Sear (1996); dotted line: Osipov *et al* (1996); dashed line: Tavares *et al* (1999).

In figure 4 we plot this quantity as a function of ρ^* for $\mu^* = 3.5$, in the three approximations, and conclude that there exists a broad region of densities, 10^{-4} or $10^{-5} \leqslant \rho^* \leqslant 0.1$, where it changes very little, i.e., at a fixed temperature, the internal energy saturates at very low densities. This same behaviour is encountered in simulations: for example, for $\mu^* = 3.5$ and $\rho^* = 0.2$ and 0.02 βu is, respectively, -25.84 and -24.0 (Weis and Levesque, 1993a), whereas for $\mu^* = 2.75$ it is practically constant, at -14.6, over the range $0.049 \leqslant \rho^* \leqslant 0.33$ (Camp *et al* 2000). These saturation values can be compared with the energy of the most stable DHS solid, a bct lattice composed of two sublattices of aligned dipoles (the dipoles have opposite orientations in each sublattice). The internal energy per particle of this solid can be estimated using the results of Tao and Sun (1991) and of Jund *et al* (1995), as $\beta u \approx -2.8\mu^{*2}$. For $\mu^* = 3.5$ we have $\beta u = -34.3$, which is only 2 to 3 times greater than theories predict for fluids of dipolar chains at saturation, and about 1.5 times greater than the value obtained through

simulations. Such small differences in internal energy between extremely-low-density and close-packed phases suggest that formation of an ordinary liquid phase may be unfavourable.

However, this is a very qualitative argument. Attempts have been made to prove that, even if interactions are included in the FED through $f_{exc}(\rho, \{\rho_i\})$, the L–V transition is absent in the DHS fluid, and some minimum amount of dispersive energy is needed to induce it. Tavares and co-workers (Tavares *et al* 1997) used the FED of equation (4) with the approximations of Osipov *et al* (1996) and of Tavares (1999) for the partition function of a chain. In the spirit of Osipov *et al* (1996), the system was regarded as consisting of 'free' monomers and long semi-flexible chains with a large persistence length, and dipolar interactions between chains were neglected. Unlike in previous work (Osipov *et al*, 1996), steric interactions between chains and between monomers were treated in the Parsons–Lee scheme of McGrother *et al* (1996b); we denote the corresponding FED by f^{hc}. Most problematic was the estimation of the contribution of dipolar interactions between 'free' monomers to the FED, since these interactions are not given by equation (1), but by some effective potential that does not include the strong anisotropy that is the cause of chain formation (already accounted for in the free energy through association). This was first accomplished in Tavares *et al* (1997), by considering a residual potential obtained by subtracting from the dipole–dipole potential the part that contains its absolute minimum (see equation (6) of Tavares *et al* 1997)). From angular integration of this residual potential ϕ_{DHS}^{res}, an effective radial potential was constructed (equation (3) with ϕ_{DHS} replaced by ϕ_{DHS}^{res}) and its contribution to the free energy calculated within the MF approximation. A simpler approach (Tavares 1999), leading to similar results, consists of evaluating this contribution in a low-density approximation, i.e.,

$$\beta f_m^{dd} = \frac{1}{2} \rho_1^2 \int d\hat{r} \int_\sigma^\infty r^2 dr \int \frac{d\omega_1}{4\pi} \int \frac{d\omega_2}{4\pi} \left[1 - \exp(-\beta \phi_{DHS}^{eff}) \right]. \tag{24}$$

In Tavares (1999) two estimates of this integral were made, one by choosing as effective potential the residual potential of Tavares *et al* (1997), and the other one by restricting the angular and radial integrations in equation (24) to limits that do not allow chain formation. Either route yields an expression of the form

$$\beta f_m^{dd} = \frac{1}{2} \rho_1^2 \sigma^3 \frac{A}{T^{*2}} \tag{25}$$

where the value of A depends on the particular approximation employed. Tavares (1999) carried out a study of the thermodynamic properties of the DHS fluid as described by the FED of equation (4) with $f_{exc} = f^{hc} + f_m^{dd}$, as a function of A, for $0 \leqslant A \leqslant 0.65$. Results confirm a possibility raised by the work of Van Roij (1996) (discussed in more detail in the following section) that there is a threshold value of A ($A_{co} = 0.284$) separating two very different regimes: for $A > A_{co}$ there exists an L–V critical point and the associated coexistence between phases rich in 'free' monomers, whereas for $A < A_{co}$ L–V coexistence is absent and the behaviour of the system is similar to that of non-interacting DHS chains. Which approximations for f_m^{dd} are correct can then be decided by simulating the DHS fluid.

More recently, Levin (1999) approached this problem using methods originally developed for the restricted primitive model of charged hard spheres. Levin considered an FED of the form

$$\beta f = \beta f_{id}(\{\rho_i\}) + \beta f_{el}(\rho_1). \tag{26}$$

The ideal term is calculated by means of an approximation for the partition function of a chain that is similar to Osipov *et al*'s (1996). The excess term is electrostatic; the Laplace equation, supplemented by appropriate boundary conditions, is integrated by the Debye charging process and the Onsager reaction field theory, to extract the renormalized dielectric constant of the

medium that contains the dipolar spheres. Equation (26) gives the density of 'free monomers' and the chain length distribution for each ρ. As the excess free energy depends solely on ρ_1, the chains are still ideal, and the criticality of the system is determined by the 'free' monomers only. Consequently, it is possible to get from equation (26) the critical density of 'free' monomers and the critical temperature. What Levin has shown is that, for the critical parameters thus obtained, there is no ρ that satisfies equation (5), and therefore, within the present approximations, DHSs do not have a critical point. Levin also proposed a way of calculating the free energy contributions of electrostatic interactions between chains and between chains and 'free' monomers, and remarked that, after a preliminary analysis, he again found no signature of a L–V transition.

In the high-density region, the question of which mechanisms stabilize the polar liquid is still open (indeed it has even been argued (Lagerwall 1996) that such a liquid should not exist at all). There are indications that the short-range structure of the FL phase is rather complex and may be the cause of the polar ordering (Gingras and Holdsworth 1995), although contributions from the long-range character of the dipolar interactions cannot be discounted. Indeed, in theoretical calculations of the MF type, ferroelectric order is exclusively a consequence of the long-range nature of the interactions (Tsebers 1982, Sano and Doi 1983, Zhang and Widom 1993, 1994). A more sophisticated variant of MF corroborates these results (Osipov *et al* 1997, Groh and Dietrich 1996b, 1997a). In these studies the IL–FL transition may be first-order or continuous, and the topology of the various phase diagrams is similar to those of the simpler Heisenberg fluid (Hemmer and Imbro 1977, Tavares *et al* 1995). However, a shortcoming of the above theories is that they completely ignore the short-range anisotropic correlations leading to self-assembly of dipolar chains in the low-density regime, thus casting serious doubts on the nature and/or mechanisms they propose as driving forces of the polarization transition.

Short-range correlations can also be taken into account within the framework of integral equation theories. There have been several studies based on the hypernetted chain (HNC) equation, supplemented with a stability analysis and/or density functional theory, to pinpoint the phase boundaries (Wei *et al* 1993, Klapp and Forstmann 1997a, 1997b, 1998, 1999). The shortcomings of the HNC route to a self-consistent thermodynamics are well documented in the literature and prevent definite conclusions from being drawn at this stage. More recently the mean spherical approximation (MSA) was applied to a fluid of dipolar Yukawa particles, but the phase diagrams obtained do not exhibit FL phases (Szalai *et al* 1999). Further indication of the role that short-range structure may play is provided by the fact that the reference HNC shows a transition from an isotropic to an FL phase whereas the MSA does not (Klapp and Patey 2000a).

Although there are indications that the phase of chains (at low densities) and the FL phase (at high densities) are (at least mechanically) stable with respect to the solid, and various solid phases of DSSs as well as DHSs have been investigated, the solid-liquid phase boundary has only just begun to be established by computer simulation. A detailed MC study of DHSs (Weis and Levesque 1993a) was carried out for $\mu^* = 2.5$, covering the density range $\rho^* = 0.7 - 1.2$, from the dense fluid to the solid, but no attempt was made to calculate the free energy of the different phases. There are strong indications from second-order density-functional theory that the FL may be stable, but results are highly sensitive to the choice of reference state (Klapp and Patey 2000b). For the Stockmayer fluid, an NpT MC evaluation of the Gibbs free energy (Gao and Zeng 2000) demonstrated that, near the triple point, the stable solid phase is a body-centred orthorhombic ferroelectric crystal coexisting with a stable FL. This agrees with the scenario proposed by Groh and Dietrich (1996b) for intermediate dipole strengths. Finally, the phase boundary between polarized and isotropic (low- or high-density) liquids is also unknown. The original simulations of Wei and Patey (1992a, b) appeared to show a continuous transition

from a dense isotropic liquid to the FL phase, but subsequent analysis (Levesque and Weis 1994) suggests that the isotropic fluid phase is at best metastable.

In conclusion, it is fair to say that a theory is not yet available that is capable of describing dipolar fluids over the whole range of densities and dipole strengths. Moreover, the mechanisms driving the phase transitions (as well as the location of the phase boundaries) remain unclear. In the following sections we address different ways in which 'conventional' behaviour can be recovered for this class of systems.

3.2. What happens when you stretch your spheres?

At this stage it is natural to ask ourselves whether it is possible to recover 'conventional' phase behaviour by slightly modifying the models. The simplest way to inhibit chain formation while retaining the basic features of a repulsive hard or soft core + dipolar interaction is to make the two competing energy minima less different by stretching the sphere into a rod along the direction of the dipole moment. McGrother and Jackson (1996) simulated by GEMC a fluid of hard spherocylinders (HSCs) with central dipoles directed parallel to their long axes, and found an island of L–V coexistence when the two minima are nearly equal, i.e., for length-to-breadth ratios $0.19 \lesssim L/D \lesssim 0.27$ (they are equal for $L/D = 2^{1/3} - 1 \approx 0.26$)†. Longer spherocylinders than this form 'ribbons', where nearest neighbours are now approximately antiparallel. So it would seem that, once chaining is suppressed by 'reducing the anisotropy' of the interaction potential, phase separation comes into play.

However, very recent GEMC and GCMC simulations of both dipolar hard dumbbells and dipolar HSCs by Shelley *et al* (1999) yielded L–V coexistence for aspect ratios as small as 0.1, with the critical temperature decreasing with increasing aspect ratio. Severe sampling problems were experienced for $L/D \lesssim 0.1$; because at low aspect ratios the particles are (strongly) associated into chains, the probability of achieving successful insertion or deletion moves becomes very small. This is particularly serious in the case of GEMC, where a deletion and an insertion must be performed simultaneously. Furthermore, a particle in a chain sits very close to its nearest neighbours, and for that reason Shelley *et al* have argued that such a system effectively behaves as if it were much denser. This renders GEMC even less reliable by decreasing the likelihood of successful volume exchanges between simulation cells. In practice, GEMC results begin to depend on the initial conditions, or appear to 'converge' to different states.

Shelley *et al* 's investigation casts serious doubts on the usefulness of either GEMC or GCMC to study associating fluids in general, and suggests that the possibility (or not) of L–V coexistence in the DHS fluid is still very much an open question. Extrapolation to $L/D = 0$ led Shelley *et al* to predict that if such coexistence exists it should terminate at a critical temperature of about 0.18 and a very low critical density (compare with Camp *et al* 's (2000) estimate of $T^* \simeq 0.15 - 0.16$).

Thus far we have restricted ourselves to weakly anisometric particles, which cannot order orientationally. In the next section we discuss the effect of dipolar forces on the stability of various mesophases

3.3. Impact of dipolar forces on phase transitions in liquid crystals

It is worth mentioning here an early suggestion by Born (1916, 1918) that liquid crystalline (LC) phases would result from dipolar interactions between molecules. This is now known to be incorrect: the main driving force for mesophase formation has since been identified as

† Following the usual convention, L is the length of the cylindrical part of the molecule.

deviations from a spherical particle shape. However, many nematogens do possess strong dipole moments, e.g. 4.77 D for 5CB (Sharma 1993), and it makes sense to ask what influence these may exert on LC transitions.

There is a wealth of theoretical work concerning nematic (N) ordering. Solution of the HNC approximation for dipolar hard ellipsoids (HEs) (Perera and Patey 1989) yielded stabilization of the N-phase if the particles are prolate, and little effect if they are oblate. Vega and Lago (1994) reached qualitatively the same conclusion regarding HSCs with central dipoles, on the basis of an Onsager-type theory. Vanakaras and Photinos (1995) found from variational cluster theory that central longitudinal dipoles stabilize the N-phase of HSCs, but off-central ones can de-stabilize it over a range of dipole moments, leading to the possibility of N–I–N re-entrance. In all cases there is strong antiparallel association of the molecular dipoles which is only weakly affected by their position along the particle axis. Strong enhancement of N-order and antiparallel orientation of nearest-neighbour molecules likewise follow from application of the method of conditional distribution functions to the (truncated) dipolar Gay–Berne (GB) fluid (Zakharov *et al* 1999). The above approaches all fail to predict a ferroelectric nematic (FN) phase, perhaps because they do not treat the long-range part of the dipolar interaction correctly. Indeed, FN phases are obtained in density-functional theories of HEs which do not suffer from this deficiency (Baus and Colot 1989, Groh and Dietrich 1997a). In Baus and Colot's study, the dipole has no effect on the N–I transition, whereas in Groh and Dietrich's the N–I transition is driven to lower densities.

At this point it would seem that a central longitudinal dipole can at best stabilize the N relative to the I phase. However, more recent work, which employed more accurate liquid correlation functions, suggests that the opposite may be true: McGrother *et al* (1997) took the non-polar reference structure from MC simulations as input to their thermodynamic perturbation theory, while Williamson and del Rio (1997) used Onsager perturbation theory including explicit expressions for the two- and three-body terms. In a separate development, Emelyanenko and Osipov (1999) have shown, in the context of a simple generalization of Maier–Saupe theory, that the N–I transition temperature exhibits a maximum as a function of dipole strength. The decrease at large dipoles is due to the pairing of molecules into dimers which then possess a smaller length-to-breadth ratio. The presence of two competing tendencies, dipolar forces favouring ordering on the one hand, and the effective unfavourable change in molecular geometry on the other, may help explain why T_{NI} does not appear very sensitive to dipole moment. Below we shall see that this scenario is also supported by simulations.

There are, to our knowledge, no theories of dipolar non-spherical objects that allow for smectic (Sm) or other more complex types of LC order. None the less, a coherent picture emerges from the many simulations already carried out. Almost all Sm phases of dipolar prolate particles encountered so far in simulations are monolayered and unpolarized. A central, longitudinal dipole is seen to favour antiparallel arrangements of HEs (Zarragoicoechea *et al* 1991) and to stabilize the Sm-A phase of both HSCs (McGrother *et al* 1996a, Gil-Villegas *et al* 1997a, McGrother *et al* 1998) and GB particles (Satoh *et al* 1996b, Houssa *et al* 1998a, b). Strong dipoles can suppress the N phase altogether, leading to a I–N–SmA triple point. A destabilization of the N relative to the I phase occurs in HSCs, but not in GB systems. These results can be understood by noting that the number of antiparallel side-by-side pairs can be maximized by forming layers (unpolarized in all cases), while at the same time the effective particle aspect ratio, which drives the I–N transition of HSCs, is reduced. On the other hand, the I–N transition of GB particles is unaffected, perhaps because the (roughly ellipsoidal) shape of the soft GB core does not favour dimerization. Finally, Camp and Patey (1999) simulated hard spheres each carrying two point dipoles a distance *l* apart and found stable orientationally

ordered phases at high density: FN for dipole separations $l/\sigma \lesssim 0.3$, and antiferroelectric (N) otherwise.

Central *transverse* dipoles also stabilize the SmA phase of HSCs (Gil-Villegas *et al* 1997, 1998), by associating head-to-tail in the smectic planes, which is reminiscent of the 'Kosterlitz–Thouless' chain structures seen by Weis (1998) for 2D discs with 3D dipoles. If, however, the HSCs are replaced by GB particles, the effect is absent (Gwóźdź *et al* 1997), although this may be a consequence of an incorrect treatment of the long-range dipolar interaction. In either case the location of the N–I equilibrium does not change. By contrast, a terminal longitudinal dipole can lead to total suppression of the Sm-phase in favour of the N-phase (McGrother *et al* 1996a, Satoh *et al* 1996c, 1997).

There have been fewer studies of disc-like particles, in spite of an earlier prediction by Palffy-Muhoray *et al* (1988) that they should be a better vehicle for the realization of FN phases. This is indeed observed for dipolar oblate ellipsoids, with a transition to an antiferroelectric columnar phase as the temperature is lowered (Ayton *et al* 1996, 1997). Moreover, columns of cut spheres with central dipoles become polarized at high densities, whereupon they adopt an antiferroelectric arrangement (Zarragoicoechea *et al* 1993). Lastly, polar domains form inside columns of discotic GB particles with central axial dipoles (Berardi *et al* 1997), whereas transverse dipoles give rise to local biaxial order (Berardi *et al* 2000).

3.4. Adding dispersive attractions

In order to investigate the impact of dispersion (Van der Waals) forces on the phase behaviour of dipolar fluids, Van Leeuwen and Smit considered a generalized Stockmayer fluid, whose spherical particles of diameter σ interact via the potential

$$\phi(12) = 4\epsilon \left[\left(\frac{\sigma}{r_{12}} \right)^{12} - \lambda \left(\frac{\sigma}{r_{12}} \right)^6 \right] - \phi_{DHS}(12) \qquad (27)$$

where $\phi_{DHS}(12)$ is given by equation (1) and λ is the non-dimensional parameter that controls the strength of the isotropic attractive interactions, included so as to mimic the dispersive interactions of real polar molecules. $\lambda = 1$ corresponds to the Stockmayer fluid and $\lambda = 0$ to the DSS fluid, which is expected to behave like DHSs†. Van Leeuwen and Smit then performed GEMC simulations over the whole range of λ. For $0.3 \leqslant \lambda \leqslant 1$, L–V coexistence could be detected, and critical densities and temperatures were estimated (figure 5). No chains were present, either in the vapour or liquid phases, at the simulated temperatures. The reduced critical temperature, T_c^*, decreased with λ as expected, but the drop in the reduced critical density, ρ_c^*, by a factor of 2 when λ was varied from 1 to 0.35 was unexpected. Also surprisingly, attempts to find coexistence for $\lambda < 0.3$ failed completely; very stable chains formed and the system did not phase separate. Technically, chain formation led to low acceptance ratios of volume and particle exchanges. The authors concluded with two possible interpretations of their results: either condensation exists in the DHS fluid and then, as extrapolation to $\lambda = 0$ of ρ_c^* and T_c^* shows, the critical parameters are much smaller than those predicted by the theories described in section 2 here; or condensation of the generalized Stockmayer fluid requires a minimum amount of dispersive interactions (and thus is absent in DHSs). Another GEMC simulation of the same model, equation (27), but where the centres-of-mass of particles are confined to a plane (Gao *et al* 1997), likewise reported a drop in T_c^* as λ was reduced from 1 to 0.5, below which the success rate of particle exchanges became too low.

The question of whether there can be an L–V transition of DHSs without isotropic attractions, was first addressed theoretically by Van Roij (1996). Van Roij approximated

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† The potential of equation (27) can be mapped onto the Stockmayer fluid (Stevens and Grest 1995b).

the internal partition function as in Osipov *et al* (1996), but took the 'bond' energy as a free parameter, U, unrelated to the dipolar potential. Steric interactions were accounted for in a free-volume approximation. Next, Van Roij assumed, without detailed justification, that interchain interactions would be screened and only those between monomers would be relevant. This contribution was approximated by a MF form, $-a\rho_1^2$, where a was again a free parameter, unrelated to the underlying potentials (dipolar or dispersive). Van Roij then showed that it was possible to eliminate condensation by decreasing a/U. For two values of a/U, it was verified that condensation was present when the most stable solution of equation (5) was rich in free monomers, and absent when it was rich in chains.

A more detailed investigation was conducted by Tavares and co-workers (Tavares *et al* 1997, Tavares 1999), who wrote down the free energy of a DHS fluid with added LJ attractions as

$$\beta f = \beta f_{id}(\{\rho_i\}) + \beta f_1(\lambda, A, \rho_1) + \beta f_2(\lambda, \rho) \qquad (28)$$

where $\beta f_1(\rho_1)$ and $\beta f_2(\rho)$, are, respectively, the contributions from interactions between monomers and between chains. These were estimated in an MF fashion. Note that the interaction potential is cut off inside the excluded volume of a pair of objects, which is different for spheres and chains; a chain was again assimilated to a string of rods of length ℓ. In order to make direct comparison with Van Leeuwen and Smit's results, the phase diagram was studied for $0 < \lambda \leqslant 1$. For $\lambda > 0.28$ there is, as in the simulations, coexistence between two 'free'-monomer–rich phases ($\bar{N}$ at the critical point, N_c, is always less than 2 in this range), and the steep drop in the critical density, ρ_c with decreasing λ, is also reproduced (see figure 5). This latter feature does not appear to be captured by any of the earlier theories for the Stockmayer fluid, which do not allow for association (Stell *et al* 1972, 1974, Frodl and Dietrich 1992, 1993a, b, Frodl *et al* 1994, Russier and Douzi 1994). Although these theories have not been extended to as small λ (or, equivalently (Stevens and Grest 1995b), to as large μ^* as in the simulations), their perturbative character leads one to suspect that they would fail in that limit. However, Tavares and co-workers still found coexistence for $\lambda < 0.3$, but now between phases rich in *chains*: when $\lambda \to 0$, N_c diverges and ρ_c vanishes, both exponentially. This is compatible with the numerical evidence, since conventional simulation techniques cannot deal with long 'self-assembled' chains.

Despite the presence of polydispersity, the situation for $\lambda < 0.3$ is reminiscent of polymers in a poor solvent, both experimentally and as described by Flory–Huggins theory. Below a critical temperature†, these can separate into a polymer-rich ('liquid') and a polymer-poor ('vapour') phase. The critical density is a decreasing function of the polymer molecular weight (or length, N_p); in Flory–Huggins theory, it scales with N_p in the same way as ρ_c of DHSs scales with $\bar{N}_c$ when λ is decreased.

A recent MC probe of the dipolar Yukawa fluid (Szalai *et al* 1999) revealed the same qualitative behaviour: chain formation at low densities and high dipole moments; L–V coexistence only above a threshold value of the ratio of Yukawa to dipolar interaction strengths; and a drop in ρ_c as this ratio is made smaller. Although the MSA (Henderson *et al* 1999) yields such a trend for ρ_c, it is not clear within this approximation what its relation is to chain formation.

It should be also noted that the above scenarios are very similar to those found by Jackson *et al* (1988) and Chapman *et al* (1988), who mapped out the phase diagram of a fluid of hard spheres with two bonding (diametrically opposed) sites and LJ attractions, using MC simulations and a perturbative approximation to the general theory of associating fluids of Wertheim (1984a, b, 1986a, b). When the strength of the directional energy that promotes

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† For simplicity, we consider only systems characterized by an upper critical solution temperature.
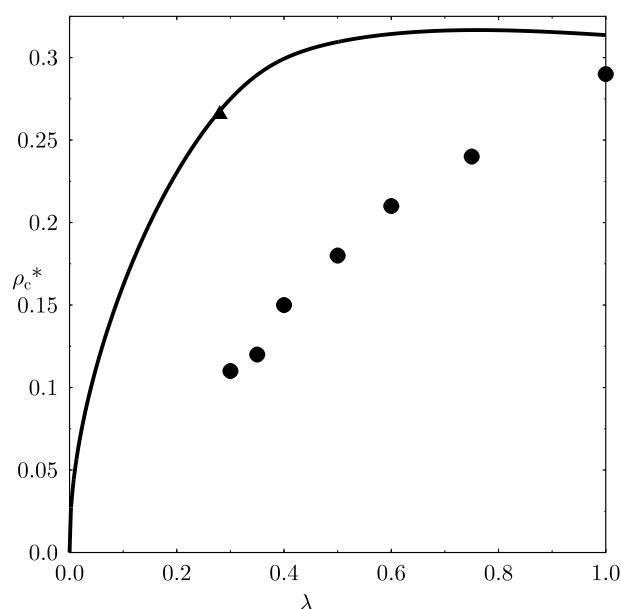
Figure 5. Generalized Stockmayer fluid: critical density against λ from simulation (circles) (Van Leeuwen and Smit 1993) and theory (solid line) (Tavares *et al* 1997, Tavares 1999). The triangle at λ = 0.28 is where theory predicts a mean chain length of 2 at the critical point; this is the boundary between monomer condensation (λ > 0.28) and chain condensation (λ < 0.28) regimes.

bonding is increased relative to the LJ attractions, the critical density drops and the mean chain length of aggregates increases exponentially. The same two regimes of coexistence (monomer–monomer and chain–chain) are observed, and the critical point is absent when no LJ attractions are included. This comparison emphasizes that strongly dipolar fluids behave like a system of particles with highly directional interactions, which cannot be replaced by an effective isotropic attraction.

The chain-rich phase appears to play an important role in the nucleation of the liquid phase of polar fluids. In a very exciting development, Ten Wolde *et al* (1998, 1999) simulated the formation of liquid droplets in a supersaturated Stockmayer vapour. They calculated the nucleation barrier and the size of the critical nucleus at a temperature 30% lower than the critical temperature and for a range of supersaturations. They found that clusters with size less than ≈ 30 are chain-like, whereas bigger clusters are spherical (as seen previously by Stevens and Grest (1995a)), but have chains on their surfaces. If the supersaturation is sufficiently increased, the size of the critical nucleus decreases and reaches a value of ≈ 30. For larger supersaturations, the critical clusters become chain-like, and the predictions of classical nucleation theory fail: the nucleation barrier becomes flat (independent of the supersaturation), and the linear variation of the critical cluster size has a discontinuity where it changes slope. These two features show that a small change in supersaturation can result in a jump in the critical cluster size. The simulations did not extend to larger dipoles, so we can only speculate on what happens if the tendency towards chaining is even more pronounced. One expects (Ten Wolde *et al* 1998) that in such a case the length for which chain clusters collapse will be pushed even higher, meaning that condensation will be preceded (or pre-empted) by the growth of polymer-like chains. An analogy can be made with crystal nucleation in the LJ fluid (Ten Wolde *et al* 1995, 1996), where nuclei of the thermodynamically most stable phase are

wetted by a shell of the metastable solid phase, which is the structure of the smaller clusters. Likewise, the chain phase might be metastable in weakly dipolar fluids, but the most stable phase when dipolar interactions dominate the thermodynamics.

Finally, for completeness we mention that FL order in the Stockmayer fluid has been theorized (Groh and Dietrich 1994a, b) and simulated (Stevens and Grest, 1995b).

3.5. Switching on an external field

Stevens and Grest (1994) performed GEMC simulations of DSSs in an applied magnetic field, and reported coexistence between two phases of chains, each consisting of dipoles aligned head-to-tail and directed along the field. They obtained critical temperatures and densities for several values of the applied field; extrapolation of these to the zero-field limit yielded a very low critical density and temperature. Owing to the same problems experienced in the simulations described before, it was not possible to find coexistence below a threshold field strength. Teixeira *et al* (1998) proposed a partial interpretation of this result in terms of the residual attraction between nearly parallel, rod-like dipolar objects of *finite* extension.

4. Discussion and conclusions

In this final section we briefly summarize the successes achieved so far in the understanding of how dipolar interactions impact on the structure of uniform bulk fluid phases, and point out what still needs to be done. We have only briefly touched on a number of other issues, such as: the effects of applied fields; interchain interactions due to the discrete nature of the chains, or to fluctuations on length scales much shorter than their persistence length; solid phases and the spatial configurations that dipoles actually adopt within a sample of a given shape, and bounded by a given surrounding medium. Indeed, both theory (Zhang and Widom 1995, Groh and Dietrich 1995, 1996a, Banerjee *et al* 1998, Banerjee and Widom 2000) and recent numerical work (Groh and Dietrich 1997b, 1998) imply that complex domain formation may be substantial. We have also left out most studies on mixtures with DHSs as one of their components.

We start by noting that the DHS and DSS fluids provide the most stringent tests possible of theories of liquid structure; because all multipolar contributions to the free energy vanish at the MF level, any effects will come from beyond MF. In this connection it must be stressed that there exist at the moment no reliable theoretical methods for computing the free energies—and hence the phase boundaries—of *strongly* polar fluids. On the other hand, few such calculations have been performed in simulations, and it is indeed doubtful that the simulation techniques employed so far are at all applicable to strongly associating fluids. One suitable candidate might be a cluster-moving MC algorithm, such as those already used to investigate DHSs in a field (Satoh *et al* 1996a, and references therein) or in dilute thin films (Davis *et al* 1999). The upshot of this is that it is difficult to directly test theories for strongly dipolar fluids, and whether they exhibit condensation or not remains an open question. However, chaining due to dipolar interactions in a *molecular* system was recently observed by Nauta and Miller (1999), who dispersed hydrogen cyanide (HCN) in superfluid helium at 0.37 K. The HCN molecule has a very large dipole moment (3D), but, because of their origin in quantum fluctuations, dispersive interactions are always present, and only at these low temperatures do dipole–dipole interactions become dominant. Nauta and Miller reported the formation of a distribution of chain lengths, and comparisons are feasible with the results of theories for the DHS fluid.

Weakly dipolar fluids are easier to tackle. Most importantly, even when not dominant, the dipolar interactions manifest themselves indirectly, via: a lowering of the L–V critical
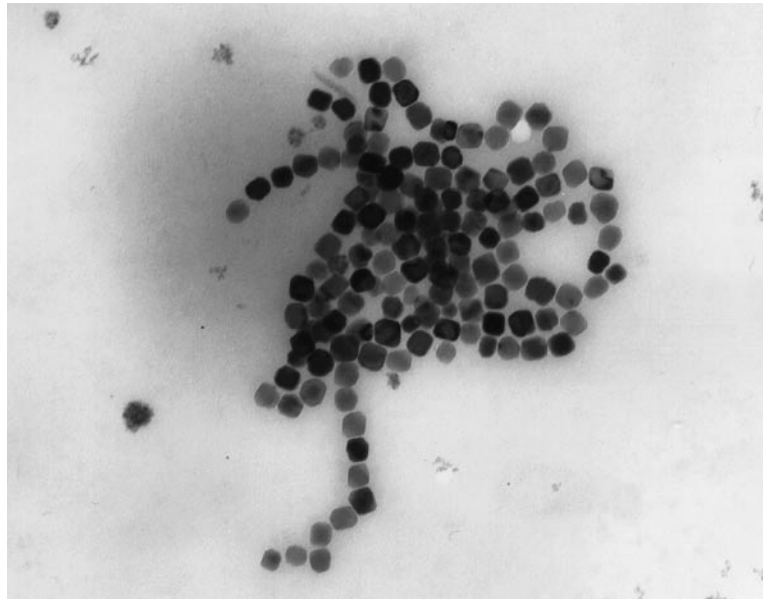
Figure 6. Transmission electron micrograph of single-domain magnetite (Fe_3O_4) particles (diameter $\sim$ 50 nm) made by magnetotactic bacteria (Philipse and Maas, 2000). The sample was prepared by dipping a grid in an aqueous solution of the particles and then drying it, so the image is actually that of a 2D system (courtesy of A P Philipse).

density; the near-constancy of the pressure as a function of the density in dilute systems and the irregular shapes of nucleation clusters. All these effects are predicted, qualitatively and sometimes semi-quantitatively, by the above-mentioned theories for strongly dipolar fluids that take association into account. This reassures us that they contain the correct physical ingredients, even though better quantitative approximations are required in the weak-dipole regime.

Finally, chain formation in zero field at low densities is perhaps not so surprising after all. Indeed, it was observed in a cobalt-based ferrofluid more than 30 years ago (Thomas 1966). Even more significantly, nature has known about it for millions of years: magnetotactic bacteria have backbones consisting of short, fairly stiff chains of *monodomain* magnetite grains (interaction energy at contact of the order of $50k_BT$), which enable them to swim along the lines of the Earth's magnetic field (Blakemore 1975). These bacteria can be 'farmed' to produce fairly monodisperse magnetic cores of the maximum size that will not break up into domains (Philipse and Maas 2000): an example is shown in figure 6. Recall that, in a real ferrofluid, Van der Waals forces can never be completely neglected in comparison to dipolar forces, the latter being weak owing to the small particle size. The magnetic grains in figure 6 are large enough for dipolar interactions to dominate; note the remarkable similarity between this structure and that of a Stockmayer nucleation cluster with chains on its surface.

Acknowledgments

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