TOPICAL REVIEW

Dipolar fluids under external perturbations

Sabine H L Klapp

Stranski-Laboratorium für Physikalische und Theoretische Chemie Sekretariat TC7, Technische Universität Berlin, Straße des 17. Juni 124, D-10623 Berlin, Germany

E-mail: sabine.klapp@fluids.tu-berlin.de

Abstract
We discuss recent developments and present new findings on the structural and phase properties of dipolar model fluids influenced by various external perturbations. We concentrate on systems of spherical particles with permanent (point) dipole moments. Starting from what is known about the three-dimensional systems, particular emphasis is given to dipolar fluids in different confining situations involving both simple and complex (disordered) pore geometries. Further topics concern the effect of quenched positional disorder, the influence of external (electric or magnetic) fields, and the fluid–fluid phase behaviour of various dipolar mixtures. It is demonstrated that due to the translational–orientational coupling and due to the long range of dipolar interactions even simple perturbations such as hard walls can have a profound impact on the systems.

Contents

1. Introduction

In recent years, the physics of complex fluids such as colloidal dispersions, liquid crystals, polymers, biopolymers, and emulsions has attracted growing interest [1], stimulated partly by the important role of these materials in a variety of technological applications. The present topical review deals with class of complex fluids which we call 'dipolar fluids'. These consist of particles with an electric or magnetic dipole moment. The resulting dipole–dipole interactions are complex in the sense that they are strongly direction dependent and of long range. Recent theoretical and experimental research has demonstrated that fluids with dominant dipole–dipole interactions can display new, unexpected behaviour such as self-assembly of the particles into dipolar chains [2], and crystallization into novel structures [3, 4]. These developments have rejuvenated the interest in understanding dipolar fluids by statistical mechanical methods.

Historically, research on dipolar fluids was mainly motivated by the importance of dipolar forces in molecular liquids, the majority of which consist of polar molecules with permanent electric dipole moments [5–7]. Examples are, of course, water, but also chloroform, methanol, and acetonitrile. The dipolar interactions in these systems are important not only for the solvation properties; they also lead to a significant increase of the vapour–liquid critical temperature relative to typical non-polar fluids [7]. Dipolar interactions also have an impact on the phase behaviour of liquid crystals [8, 9] where they can stabilize or destabilize certain mesophases [9]. However, as far as structural properties are considered, dipolar interactions in *molecular* complex fluids are often less determinant than other factors such as van der Waals forces, anisotropic steric forces, or hydrogen bonding [7].

This is different in several colloidal systems where dipole–dipole interactions may indeed play a key role. An important example is ferrofluids [10–13], which are suspensions of single-domain ferromagnetic nano-particles in carrier liquids such as water or oil. Due to the large (permanent) magnetic dipole moments, ferrofluids are extremely sensitive to external magnetic fields. The accompanying structural and rheological effects [13] such as formation of long chains and the resulting dramatic increase of the viscosity have led to a broad variety of technical applications. On the other hand, some strongly coupled ferrocolloids self-assemble into chains even in the *absence* of an external field [14]. An example is given in the left part of figure 1.

In colloidal dispersions consisting of superparamagnetic particles, dipolar interactions between the particles can be induced by an external magnetic field. Particular attention has recently been given to two-dimensional realizations of magnetic colloids, with repulsive interactions generated by an out-of-plane magnetic field [15–17]. These systems have proven to be excellent experimental 'model systems' to study the two-dimensional freezing transition [18]. Further systems with induced dipoles are magnetorheological [19, 20] and electrorheological fluids [21–23] where the external magnetic/electrical fields can generate various patterns [24] and structural transitions accompanied by dramatic changes of the rheological behaviour [25]. In this context, an aspect receiving increasing interest is the *micromechanical* properties of the chains formed at intermediate field strength [26, 27, 29, 28, 30]. On the other hand, the solid structures formed in magnetorheological fluids at high field strengths are discussed as candidates for the generation of novel magnetic crystals [31–33]. We finally mention colloidal polarizable particles subject
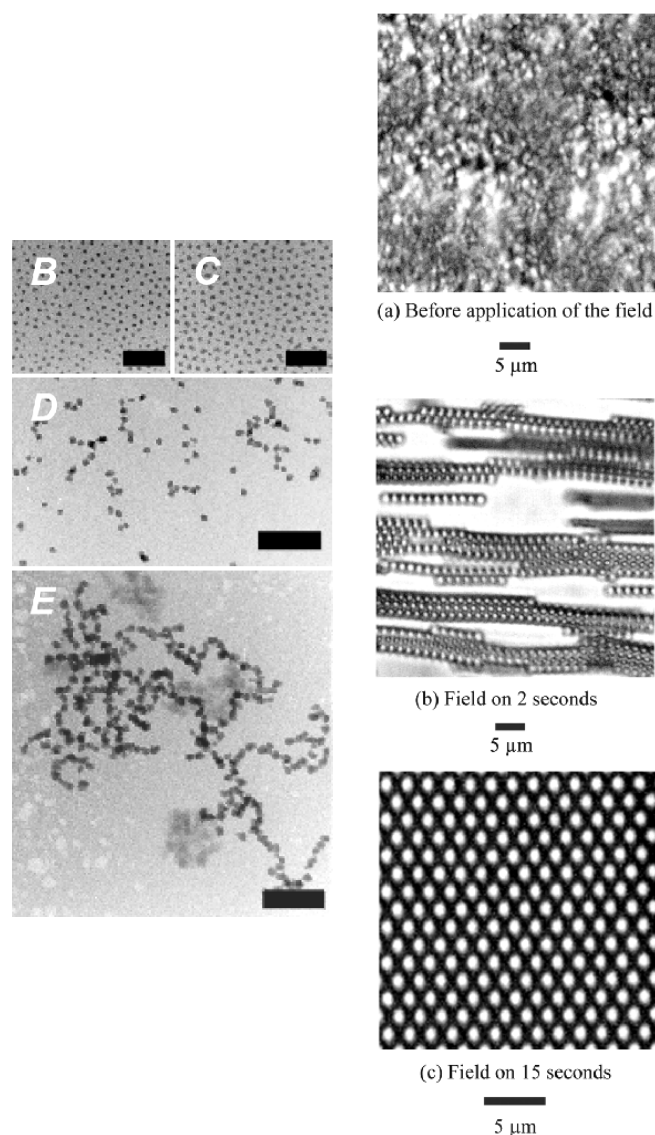
Figure 1. Left: cryo-transmission electron micrographs (TEMs) [14] of metallic iron particles suspended in decalin in the absence of an external magnetic field. The radius of the iron core of the particles gradually increases from ferrofluid B (6 nm) to ferrofluid E (8 nm), yielding an increase of the magnetic dipole moment and a corresponding increase of the dipolar coupling between the particles. Right: field-induced crystallization [34] of latex spheres (diameter 1.4 μm) on a glass surface with an in-plane electric field. (a) Homogeneous fluid phase before application of the field. (b) Formation of chains in field direction. (c) Formation of a two-dimensional crystal due to lateral interactions between the chains.

to spatially varying electric fields (dielectrophoresis) [34–37]. Figure 1 (right) illustrates the behaviour of such systems in two dimensions (with in-plane induced dipoles).

The above examples demonstrate the richness of phenomena induced by dipolar interactions. They also illustrate that, in many cases of practical interest, dipolar fluids are

subject to external perturbations such as confinement or magnetic (electric) external fields. Understanding the impact of such perturbations on the material properties of dipolar, and any complex, fluid thus becomes more and more important [38]. Only very recently, however, basic questions concerning simple *bulk* dipolar model fluids have been solved, and a deeper understanding of the impact of perturbations such as confinement is just starting to emerge.

The goal of the present topical review is to summarize and discuss recent theoretical progress concerning the structure and phase properties of dipolar fluids influenced by various *time-independent* perturbations. That is, we do not address here the properties of systems subject to shear flow [25] or other time-varying (e.g., rotating magnetic [39–41]) fields. Moreover, we concentrate on fluids of spherical particles and *permanent* (point) dipole moments, for which bulk behaviour has been intensely studied in the last decade [2]. Systems with induced dipoles are only briefly touched on. The same holds for quasi-two-dimensional dipolar fluids, which have been considered in a recent review of Weis [42]. We also note that the model fluids considered in this review are frequently used as model ferrofluids, for which equilibrium properties have been recently summarized by Huke and Lücke [43].

This topical review is organized as follows. In section 2 we present a summary of recent results concerning *bulk* dipolar model fluids. The subsequent sections are each devoted to a different type of perturbation. To begin with, we discuss in sections 3 and 4 the impact of spatial confinement realized in simple confining geometries and in disordered porous media, respectively. Further topics concern the effect of quenched positional disorder (section 5), the influence of external magnetic or electric fields (section 6), and the fluid–fluid phase behaviour of dipolar fluids with non-uniform dipole moments (section 7). Finally, some overall conclusions for dipolar fluids under external perturbations are drawn in section 8, where we also discuss open problems in this context and the theoretical and computational challenges that lie ahead.

2. The unperturbed system

The basic model underlying the following discussions is a three-dimensional, one-component dipolar fluid consisting of spherical particles (diameter σ) with permanent point dipole moments $\boldsymbol{\mu}_i$. The resulting pair potential has the form

$$u(12) = u_{\text{SR}}(r) + u_{\text{DD}}(12), \tag{2.1}$$

where $u_{\text{SR}}(r)$ is some short-range potential, which depends only on the interparticle separation $r = |\boldsymbol{r}| = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$, and the second term in (2.1) represents the dipole–dipole interaction

$$u_{\text{DD}}(12) = \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r^3} - 3\frac{(\boldsymbol{\mu}_1 \cdot \boldsymbol{r})(\boldsymbol{\mu}_2 \cdot \boldsymbol{r})}{r^5}. \tag{2.2}$$

One characteristic feature of u_{DD} is its long range: it decays only as r^{-3} and therefore much slower than, e.g., the van der Waals interactions between two molecules [5]. Secondly, the interaction is strongly anisotropic in the sense that it favours—depending on the spatial configuration of two particles—rather parallel or antiparallel alignment, or something in between. In particular, the energetically most favourable configuration of two dipolar spheres of diameter σ is a head-to-tail alignment, whereas two spheres lying side-by-side prefer to point *antiparallel* instead of parallel. Both features—range and anisotropy—are important to understand the complex structural and phase behaviour of such systems, as illustrated below. However, a further important factor, particularly for the low-density behaviour, is the character of the short-range potential $u_{\text{SR}}(r)$ supplementing the dipolar interaction [44, 2].

We start by considering systems where the short-range potential is purely repulsive. Common examples are so-called *dipolar hard spheres* (DHSs) or *dipolar soft spheres* (DSSs)
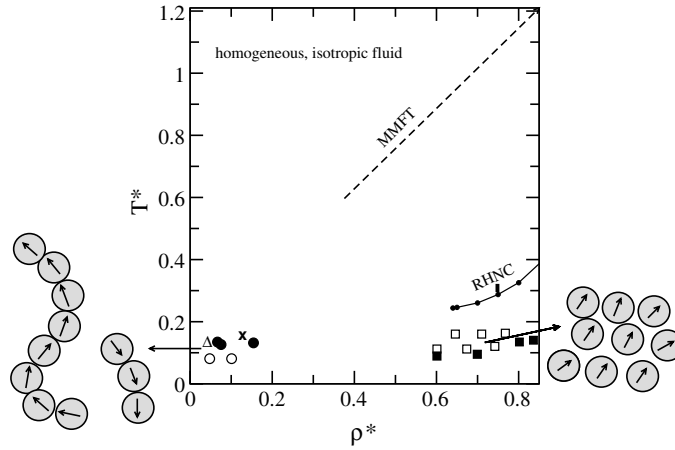
Figure 2. Sketch of the phase diagram of bulk DHS and DSS fluids in the plane spanned by the reduced density $\rho^* = \rho\sigma^3$ and the reduced temperature $T^* = k_B T \sigma^3/\mu^2$. The symbols in the low-density regime denote states where MC simulations reveal clustering and chain formation (solid, open, and grey circles and the triangle correspond to results from [44] (DSS), [45] (DHS), [46] (DHS), and [47] (DHS)). The cross indicates a critical point separating chained states as predicted in [46]. The boxes in the high-density regime denote states with long-range parallel ordering of the dipoles as predicted by MC simulations for DHS [48–50] (filled boxes) and MD simulations for DSS [51, 52] (open boxes). Corresponding integral equation (RHNC) results [53, 54] and modified mean-field theory (MMFT) results [55] for the phase transition between isotropic and ferromagnetic/ferroelectric fluid states in DHS systems are indicated by the rectangle [53], the solid line [54] (RHNC), and the dashed (MMFT) line [55].

defined by

$$u(12) = u_{HS}(r) + u_{DD}(12) \qquad \text{(DHS)}, \qquad\qquad (2.3)$$

$$u(12) = u_{SS}(r) + u_{DD}(12) \qquad \text{(DSS)}, \qquad\qquad (2.4)$$

where $u_{HS}(r) = \infty$ (0) for $r < \sigma$ ($r > \sigma$) and $u_{SS}(r) = 4\epsilon_0(\sigma/r)^{12}$ is the hard- and soft-sphere potential, respectively. Fluids of DHSs and DSSs display the same type of phase behaviour, which is illustrated in figure 2. The sketched phase diagram focuses on the fluid phase regime and contains results from a variety of recent studies based on Monte Carlo (MC) and molecular dynamics (MD) computer simulations, integral equation techniques, and density functional theory. We note that, even for the restricted density range considered in figure 2, a complete picture for the low-temperature phase behaviour (including precise location of the phase boundaries) still does not exist.

Chain formation

At high reduced temperatures $T^* = k_B T \sigma^3/\mu^2$ (with k_B being the Boltzmann constant), that is when the thermal energy dominates the dipolar interactions, DHS/DSS systems form an ordinary, homogeneous isotropic fluid state in the whole density range considered. This changes at low T^* and low densities, where the anisotropy of the interaction drives the particles to *self-assemble* into long clusters and chainlike structures. Interestingly, chain formation was predicted as early as 1970 by de Gennes and Pincus [56].

However, only in the 1990s were chainlike structures directly observed in a number of MC computer simulation studies of dilute DHSs/DSSs [44–47, 57]. These investigations suggest that the self-assembled chains are 'living polymers' [47] which frequently break and recombine,

rather than true chain 'molecules' with stable bonds. Moreover, the chain formation seems to *suppress* [44] the usual vapour–liquid transition, which was originally expected to occur since the orientationally averaged, Boltzmann-weighted dipolar interaction between two DHS/DSS particles is *attractive*. This discrepancy has stimulated a number of theoretical investigations based on concepts such as polymer theory [47, 58–61], Debye–Hückel theory [62] and other free energy approximations [63] (for a review, see [2]). These studies have helped to understand some characteristics of the 'chained state' (such as the length distribution) observed in the simulations, whereas the question as to *why* chain formation suppresses the vapour–liquid transition (at the temperatures investigated) remains unsettled [2]. A main argument brought up in this context is that as soon as the particles in the dilute gas have self-assembled into chains the interactions *between* the chains become very weak and short ranged, leaving no driving force for a condensation into a denser state [2]. We note, however, that more recent, large-scale simulations of Camp *et al* [46] yield again a different picture where a critical gas–liquid transition does indeed occur, but at extremely small values of the critical temperature and density as indicated by the cross in figure 2. Also, the structure of the coexisting phases is dominated by chains rather than by isotropic aggregates as in simple fluids. Based on these results, Tlusty and Safran [64] have proposed to consider the transition as a 'connectivity' transition separating an 'end-rich' gas consisting of isolated chains and a denser, 'junction-rich' liquid consisting of branched chains. We finally mention a recent study of strongly interacting, dilute DSS fluids [65] where it was demonstrated, based on MD and Brownian dynamics simulation, that chain formation is clearly reflected in the frequency-dependent dielectric (magnetic) response. These results may be relevant for the interpretation of future relaxation experiments on strongly interacting dipolar fluids [66].

Direct experimental observation of chain formation in the *absence* of external fields has been recently achieved in thin layers of ferrofluids with dominating (magnetic) dipole–dipole interactions [14, 67, 68] and other near-to-two-dimensional systems [42]. An illustration is given in the left part of figure 1.

Long-range orientational ordering and some theoretical approaches

We now turn to *dense*, strongly coupled DHS/DSS fluids. For such systems, computer simulations of the early 1990s [48–52] have revealed the occurrence of *spontaneous* polarization[1] within the *fluid* part of the phase diagram. The resulting state is characterized by long-range parallel order of the dipole moments, and consequently a non-vanishing order parameter $P_1 \equiv N^{-1} |\sum_{i=1}^{N} \hat{\boldsymbol{\mu}}_i \cdot \hat{\mathbf{d}}|$ (the caret denotes unit vectors) involving a global director $\hat{\mathbf{d}}$. At the same time, the translational structure is still short ranged. We note that in experiments of ferrofluids, which are closest to the DHS/DSS models considered here, long-range order has so far not been observed, possibly since the required density range (see figure 2) is beyond the density range currently accessible in ferrofluids. Nevertheless, what has been reported [66] is a strong increase of the magnetic susceptibility upon cooling a ferrofluid at $\rho^* \approx 0.3$, that is the precursor of long-range parallel ordering.

Even among theorists the detection of ferroelectric/ferromagnetic, yet *nematic*, states in simple dipolar fluids was quite a surprise in view of the anisotropic nature of the dipolar interactions. Subsequent investigations (based on simulations [49, 52] and various levels of density functional theory [69–73]) have indicated that the existence of such phases hangs on several factors. First of all, and this is a consequence of the long-range character of the interaction, parallel ordering of the *whole* system occurs only for appropriate boundary

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[1] To be consistent with the original literature on this phenomenon we use here the language appropriate for electric dipoles.

conditions, which do not result in any depolarizing fields. Examples are samples with the shape of a long needle (with the ordering direction parallel to the long axis of the needle) [69–71], and spherical samples immersed in a conducting medium. The latter situation is the one usually considered in computer simulations [49, 52]. In other situations (such as spherical samples in a vacuum) one expects the system to break off into polarized domains. The thermodynamic conditions under which ordering occurs within one (macroscopically large) domain should then be comparable to that of the whole system with 'tin-foil' boundary conditions [72, 73].

Each particle in the polarized fluid (or domain) feels not only the local field E^{local} stemming from its immediate neighbours, but also a mean field [74] generated by the parallel order of the dipoles outside the local correlation sphere. This mean field is given by

$$E^{\text{MF}} = (4\pi/3)P = (4\pi/3)\rho\mu P_1\hat{\mathbf{d}}, \tag{2.5}$$

yielding an energy contribution $U^{\text{MF}}/V = -1/2\, P \cdot E^{\text{MF}} = -(2\pi/3)\rho^2\mu^2 P_1^2$ to the total energy per volume V [75, 76]. The mean field thus *favours* parallel ordering, especially at high densities.

The second reason for the existence of ferroelectric fluid phases is that the particles can develop suitable short-range spatial correlations, which minimize the frustration stemming from the anisotropy of the dipolar interaction in the local environment of a particle, and thereby optimize the field E^{local}. Specifically, the particles form long, parallel chains which tend to align relative to each other such that neighbouring chains are out of registry [51, 52, 49]. Due to this arrangement, neighbouring chains indeed *attract* rather than repel each other, as was first shown by Tao and Sun [3, 4] in the context of electrorheological fluids (where the dipoles point parallel *a priori*). Clearly, the optimization of E^{local} works even better within polarized *solid* states and such states have indeed been found in computer simulations at densities beyond those considered in figure 2. Several crystalline structures have been observed, such as body-centred tetragonal [49, 51, 52], face-centred cubic [49], and body-centred orthorhombic [49, 77]. However, the true (ground-state) structure of dense DHS/DSS systems is still an open problem.

Given the complex interplay between long- and short-range correlations, it is clear that theoretical predictions of the ferroelectric transition are rather challenging, even when only fluid states are considered. In figure 2 we have included results from two different approaches. The first one is density functional theory in the modified mean-field approximation (MMFT) [55] (for more details, see section 7.1), which approach was established for dipolar fluids by Groh and Dietrich [70, 71]. The MMFT locates the phase transition between the isotropic and the ferroelectric liquid within the same density range predicted by the computer simulation results, but the temperatures related to the onset of parallel ordering are much too high. This is since the MMFT focuses on the mean field (2.5) as the driving force for spontaneous ordering, whereas the competing short-range correlations are strongly underestimated. This aspect is somewhat better taken into account by integral equation theory [78], which is the basis for the theoretical predictions of Wei *et al* [53] and Klapp and Forstmann [54] included in figure 2. These authors have numerically solved the exact Ornstein–Zernike (OZ) equation [79]

$$h(12) = c(12) + \rho \int \mathrm{d}3\, h(13)\, c(32) \tag{2.6}$$

with $h(12) = g(12) - 1$ and $c(12)$ being the total and the direct correlation function, respectively, in combination with the reference hypernetted chain (RHNC) approximation [80, 81]

$$g(12) = \exp[-\beta\, u(12) + h(12) - c(12) + B^{\text{HS}}(12)], \tag{2.7}$$

with the hard-sphere Bridge function $B^{\text{HS}}(12)$ [80, 81] (the choice $B^{\text{HS}}(12) = 0$ corresponds to the conventional HNC approximation [78]). The results in figure 2 are based on the RHNC

correlation functions for the *isotropic* fluid phase [82, 54], implying that ferroelectric phase transitions are detected only via a divergence of the dielectric constant (and, respectively, by a density functional estimate based on the isotropic correlations [53]). The corresponding temperatures (see figure 2) significantly improve the predictions for the onset of long-range parallel ordering compared to the MMFT. We finally mention two very recent theoretical studies [83, 84] dealing with the onset of long-range ordering on the basis of exact expressions for the singlet density combined with approximate correlation functions. The results [83, 84] question again the very *existence* of spontaneous ordering, which is in contradiction to the computer simulation results. Nevertheless, this discrepancy does illustrate the persisting difficulties in understanding the low-temperature behaviour of DHS/DSS fluids, including features such as the boundaries (and the nature of the related phase transition) between isotropic and ordered phases.

2.1. The impact of attractive interactions

The model fluids discussed so far are suitable for the description of some sterically stabilized dipolar colloids [85, 86], but not when polar molecular fluids [5–7] or dipolar colloidal systems with *dispersive* interactions are considered. A common model incorporating dispersive, i.e. isotropic attractive interactions is the so-called *Stockmayer* fluid defined by

$$u(12) = u_{\text{LJ}}(r) + u_{\text{DD}}(12), \tag{2.8}$$

where the first term is the conventional Lennard-Jones (LJ) potential given by $u_{\text{LJ}}(r) = 4\epsilon_0((\sigma/r)^{12} - (\sigma/r)^6)$. The ratio of dipolar relative to dispersive interactions can be measured by the parameter $m^{*2} = \mu^2/\epsilon_0\sigma^3$. In the limit $m^{*2} \to \infty$ (at fixed ϵ_0 and σ), the dipolar interactions dominate, and the phase behaviour of Stockmayer fluids reduces to that of DSS fluids discussed in the preceding paragraph. Upon decreasing m^{*2}, the main effect of the dispersive interactions is the re-appearance of the vapour–liquid transition (within the isotropic phase). Gibbs-ensemble Monte Carlo (GEMC) results for the corresponding coexistence curves of systems up to $m^{*2} = 6.0$ have been obtained by Neumann [87] and van Leeuwen [7]. Theoretical approaches such as MMFT [70, 71] and RHNC also predict an (isotropic) vapour–liquid coexistence, e.g. at $m^{*2} = 4.0$, with the RHNC critical temperature being very close to that predicted by the GEMC simulations [54]. At higher densities Stockmayer fluids display ferroelectric liquid and solid phases in analogy to the DHS/DSS systems. An exemplary phase diagram has been recently obtained by Gao *et al* [77] on the basis of constant-pressure MC simulations.

3. Confinement by slit-pore geometries

Understanding the material properties of fluids confined to nanoscopic spaces plays a central role in many applications involving porous materials [88, 89], in micro- and nanofluidics [90, 91], in nanotribology [92–94], and in electrochemical applications [95]. The investigation of simple [96] and complex (such as dipolar) fluids in confinement is thus a very active field of research [88]. In this section we focus on situations where a dipolar fluid is confined to one single 'pore' space, specifically a slit pore defined by two plane-parallel, infinitely extended walls. Though somewhat idealized, the slit-pore model does have relevance in the context of well characterized materials such as activated carbon fibres or MCM-41 [88, 89], in lubrication experiments [97], and, obviously, in situations where the fluid is trapped between two planar surfaces such as electrodes.

Indeed, most of the earlier studies on confined dipolar fluids have focused on electrochemical problems [95] involving the structure and ordering of polar solvents in the vicinity of one or two planar electrodes. In these studies, the solvent is typically modelled

as a system of pure DHS (see, e.g., [98–101]) or Stockmayer [102, 103] particles, but more complex solvents such as binary dipolar mixtures [104, 105] and ion–dipole mixtures [106] have been investigated as well. The latter systems display particularly interesting effects such as a surface-induced *demixing* transition [106]. Many of these investigations have been performed on the basis of (HNC-like) integral equation theories [99, 106] and density-functional approaches [101, 104, 105, 107], which are approximate but computationally much less expensive than computer simulations of confined dipolar fluids [98, 102, 103, 107–109]. Indeed, for simulations the combination of long-range dipolar interactions and reduced spatial symmetry is still a challenge. In particular, well established *bulk* techniques such as the three-dimensional Ewald summation [110, 111] have to be significantly modified [42], yielding generally an increase in computational time (as compared to the bulk). Some simplifications arise for confined fluids with *induced* dipoles such as electrorheological fluids between two charged electrodes [112]. The experimentally observed complex structure formation [23] in electrorheological fluids, involving self-assembly of the particles into chains, columns, and sheets, has been partly reproduced in simulation studies [112, 39].

In the limit of vanishing surface separation the slit-pore geometry degenerates into a planar confinement. Over the last five years, the resulting *two-dimensional* (2D) dipolar fluids have been intensely studied, mostly by computer simulations (for a review, see [42]). Interest in 2D systems (or thin dipolar films) has been triggered, on one hand, by recent experimental studies involving dipole-coupled *colloidal* films containing very few or even only one layer of particles. Examples are the systems illustrated in figure 1, Fe_2O_3-doped colloidal particles arranged on water–air interfaces [15–17], which have turn out to be excellent model systems to study 2D crystallization, and coated magnetic micro-spheres floating on a glycerin surface [31, 113]. Further motivation has been supplied by the behaviour of thin magnetic (solid) films [114, 115], in which the interplay of dipolar, exchange, and surface interactions leads to a complex phase behaviour (for a summary of corresponding simulation results see [42]).

Computer simulations of 2D *fluids* with *permanent* dipoles have so far focused on dilute states. Results for 2D versions of DHS and DSS fluids (with three-dimensional dipole moments) suggest that these systems do not condense but display chain formation [116–121] in close analogy to what is observed in the bulk (see figure 2). Characteristic features of the 2D chains have been investigated in [119, 120] on the basis of polymer theory. Finally, by adding dispersive interaction one recovers again an ordinary vapour–liquid transition, as demonstrated in GEMC simulations of 2D Stockmayer fluids [122].

Compared to the large number of data for 2D dipolar fluids, little is known about the phase behaviour of dipolar fluid films with *finite* thickness. In the following we summarize recent simulation results [123, 124] on strongly coupled DSS squeezed between smooth, non-conducting walls.

3.1. Local and global ordering in strongly coupled confined fluids

Given the appearance of an orientationally ordered, yet liquid-like phase in bulk dipolar fluids (see figure 2), a main question addressed by Klapp and Schoen [123, 124] was whether or not spontaneous ordering of this type exists in nanoscopic slit pores. To this end they performed MC simulations in a constant-parallel-pressure ($P_\parallel$) ensemble, fixing temperature and dipole moment at values where dense bulk DSS fluids are ferromagnetic.

It turns out that spontaneous ordering does indeed occur in certain ranges of the wall separation L_z. Exemplary configurations of a system with $L_z = 7\sigma$ are given in figure 3, where the left and right parts correspond to the isotropic (low $P_\parallel$) and ferromagnetic (high $P_\parallel$) phases, respectively. The displayed particles are those within one of the contact layers,
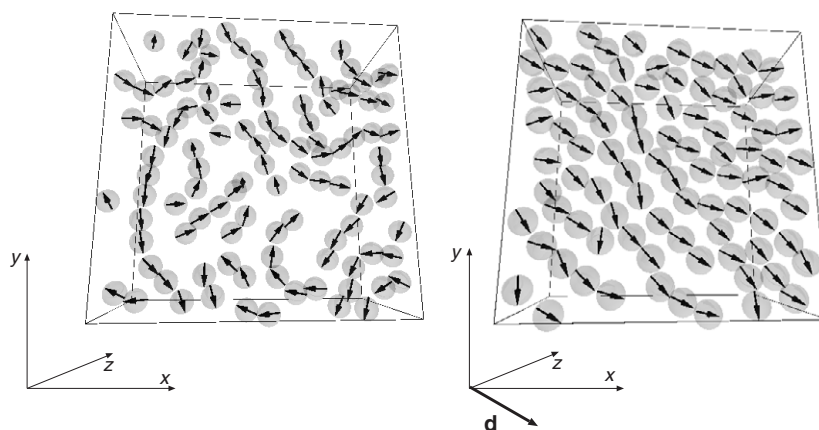
Figure 3. Two configurations of DSS particles in the contact layer of confined DSS fluids ($k_BT/\epsilon_0 = 1.35$ and $\mu/\sqrt{\epsilon_0\sigma^3} = 3.0$). Left: isotropic phase ($P_\parallel^* = 1.0$). Right: ferromagnetic phase ($P_\parallel^* = 5.0$). The thick arrow labelled by 'd' denotes the direction of the global director in the x–y plane. From [124].

that is the layers closest to the walls (note that layer formation, six layers in the present case, is a generic effect in slit-pore confined systems [89]). The isotropic state is characterized by the appearance of clusters and chains of particles with essentially random directions, as expected for a dilute, strongly coupled dipolar fluid (see figure 2). In this regard, a main effect of the spatial confinement is that the dipolar particles tend to form chains with *in-plane* rather than *out-of-plane* orientation. This is reminiscent of the chain formation in true 2D dipolar fluids [42]. The orientationally ordered state (right part of figure 3) of the confined fluid is characterized by long, essentially straight chains aligned into a direction within the plane parallel to the walls. The in-plane structure perpendicular to the chains is generally more open, and inspection of the corresponding in-plane correlation functions [123] shows that the ordered system is still *liquid-like* within the layers.

Comparing the confined fluid with its bulk counterpart, it turns out that the walls *promote* rather than suppress spontaneous orientational order. This can be explained by the fact that the director $\hat{\mathbf{d}}$ in the confined system is forced to point along an (arbitrary) direction *parallel* to the walls (ordering in the normal direction would lead to surface charges, generating, in turn, a demagnetizing/depolarizing field). Due to this restriction, which is absent in the bulk, orientational fluctuations are constrained even in the isotropic phase and the ferromagnetic transition occurs at significantly lower pressures/densities [123].

In view of the MC results at $L_z = 7\sigma$ it is tempting to ask whether long-range parallel ordering becomes even more promoted (relative to the bulk) when the wall separation further decreases. However, the very *existence* of ferromagnetic liquid ordering in systems near 2D is unclear at present [42]. Indeed, Klapp and Schoen [123] were not able to reach definite conclusions on ferromagnetic ordering at wall separations $L_z \leqslant 6\sigma$, due to a strong increase of equilibration time. We note that the structure of the *solid* phases of 2D dipolar fluids is also unknown. Ground-state lattice calculations for 2D dipolar (magnetic) spin systems have revealed various types of orientational ordering depending on the lattice structure, which is expected due to the strong positional–orientational coupling of the dipolar interactions. In particular, square lattices [125] and honeycomb lattices [126] display *antiferromagnetic* ordering characterized by two or several sublattices. On the other hand, hexagonal lattices support *ferromagnetic* ordering, as demonstrated by recent simulations of Russier [127].

4. Confinement by disordered porous media

So far we have considered only situations where the fluid is confined to one single pore space. However, real porous solids most often contain an interconnected network of pores of various sizes and shapes [88]. Prominent examples for such *disordered* porous materials are mesoporous glasses such as Vycor and CPG (controlled pore glass), which are typically characterized by a relatively low porosity (i.e., the volume fraction of the space available for the adsorbed fluid) of 30–60%, and (silica) aerogels, which are formed by extremely dilute disordered networks of microscopic particles (porosity 95–98%). Aerogels are important in many technological contexts such as in catalysis, gas separation, oil recovery, and purification [128]. An example of particular relevance in the present context is liquid chromatography, where aerogels composed of molecules with polar headgroups are employed for the purification of (polar) mixtures [129].

From a theoretical point of view, investigation of a dipolar—or any—model fluid adsorbed to an aerogel is significantly more complicated than in the bulk. This is due to the *quenched disorder* realized by the nearly random aerogel network. Only in the 1990s were statistical–mechanical tools to deal with this problem established, in particular a replica-integral equation formalism pioneered by Given and Stell [130–132]. These developments, as well as the first applications on 'simple' systems with spherical interactions, have been reviewed by Rosinberg [133] and Pizio [134]. In the following we focus on recent replica-integral equation studies [135–141] and computer simulations [137, 138] of confined dipolar fluids.

4.1. Models and theoretical treatment

All investigations of disordered adsorbed dipolar systems employ the concept of a *quenched-annealed* (QA) mixture [133, 134] where the dipolar fluid molecules equilibrate in a solid 'matrix' of particles frozen (quenched) in a disordered configuration. The latter is chosen according to a distribution $P(\{Q\})$ (with $\{Q\} = Q_1, \ldots, Q_{N_m}$ being the set of matrix particle coordinates which is typically assumed to be an equilibrium (canonical) distribution established at some inverse temperature β_0. In the simplest case, the matrix particles are just neutral (hard) spheres [137, 139]), but more complicated situations such as charged matrices [138] or matrices consisting of anisotropic particles [136, 140, 141] have also been considered.

The adsorbed dipolar fluids investigated so far are DHS fluids [137, 138], Stockmayer fluids [139–141], and, in one case, a more realistic polar liquid composed of molecules with several sites [136]. In order to compute structural and thermodynamic properties of these annealed, yet perturbed, fluids, one needs to note that thermal averages $\langle \cdots \rangle$ involving the fluid's microscopic variables, still depend on the specific realization of the matrix. Thus, an additional average over different matrix configurations is required, yielding $[\langle \cdots \rangle_Q] = \int d\{Q\} \langle \cdots \rangle_Q P(\{Q\})$. For example, the total correlation function between two fluid particles with coordinates $q = (r, \omega)$ and $q' = (r, \omega)$ (in an macroscopically homogeneous and isotropic system) is defined as

$$\left(\frac{\rho}{4\pi}\right)^2 h_{\mathrm{ff}}(\bar{r}, \omega, \omega') \equiv \left[\left\langle \sum_{i \neq j}^{N} \delta(q - q_i)\delta(q' - q_j) \right\rangle_Q\right] - \left(\frac{\rho}{4\pi}\right)^2, \qquad (4.1)$$

where $\bar{r} = r - r'$. In computer simulations of adsorbed fluids, the double average (4.1) has to be performed explicitly by evaluating the thermal averages for several (e.g., six [137, 138]) different matrix configurations.

The idea of the replica approach is to circumvent the double average by relating the original QA system to a completely artificial, but fully annealed system. This is done by introducing, on

the basis of a simple mathematical identity [142], n copies $\alpha = 1, \ldots, n$ of the fluid variables. The resulting 'replicated' system is a $(n + 1)$-component fluid mixture [132] defined by the Hamiltonian

$$H^{\text{rep}} = \frac{\beta_0}{\beta} H^{\text{mm}}(\{Q\}) + \sum_{\alpha=1}^{n} \left(H^{\text{ff}}(\{q^\alpha\}) + H^{\text{fm}}(\{q^\alpha\}, \{Q\}) \right), \tag{4.2}$$

where the sub-Hamiltonians $H^{\text{mm(ff,fm)}}$ contain the interactions between the (former) matrix and the fluid particles. All particles in the multicomponent replicated system are *mobile*, with the implication that this system can be treated by standard liquid state approaches such as integral equation theories [78]. However, corresponding physical quantities are related to those of the original QA system only in the limit $n \to 0$, e.g.

$$h_{\text{ff}}(\bar{r}, \omega, \omega') = \lim_{n \to 0} h_{\alpha\alpha}^{\text{rep}}(\bar{r}, \omega, \omega'), \tag{4.3}$$

where $h_{\alpha\alpha}^{\text{rep}}$ is the total correlation function between two fluid particles of the same copy. The standard way to deal with this problem is to start from the integral equations for the $(n + 1)$-component replicated system (for an integer n) and to assume permutation symmetry between the replicas, which then allows us to perform the $n \to 0$ limit [130–132]. The resulting *replica-symmetric Ornstein–Zernike* (RSOZ) equations, which were originally derived for spherical systems, can be easily generalized to anisotropic systems [143], and can be numerically solved with the same techniques as developed for bulk fluids. This is described in detail in [137–140]; the corresponding interaction site formulation can be found in [136]. What is important to note is that the RSOZ equations are *exact* relationships, as are the OZ equations for bulk (dipolar) fluids. The approximate character of replica-integral equations is introduced through the closure expression relating the correlation functions to the pair potentials. The investigations on adsorbed DHS [137, 138] and Stockmayer fluids [139–141] are based on variants of the HNC equation introduced in (2.7).

4.2. Properties of dipolar model fluids in disordered media

The simplest disordered medium is realized by a hard-sphere (HS) matrix, resulting in purely repulsive fluid–matrix interactions. Their influence on the structure and thermodynamics of adsorbed DHS fluids (in the isotropic high-temperature phase) has been studied by Fernaud *et al* [137], who employed both replica-HNC theory and grand-canonical MC simulations. The HNC theory proved to be quite accurate at temperatures above the phase transition regime. The results also indicate that the presence of the matrix *facilitates* the transition into ferroelectric states. Similar observations were made by Spöler and Klapp [139] who employed an RHNC approximation to investigate the phase behaviour of an adsorbed Stockmayer fluid. Based on investigation of the dielectric constant, these authors found the ferroelectric transition temperatures to *increase* with increasing matrix density. A further main finding from [139] was that the vapour–liquid (VL) transition occurring in bulk Stockmayer fluids (see section 2.1) still takes place in matrices with sufficiently high porosity, such as 95%. This is a value typical for real silica aerogel, where VL transitions have indeed been observed experimentally [144, 145]. The VL critical point of the Stockmayer model system is shifted towards a lower temperature and density, in agreement with previous results on simpler fluids in HS matrices [146, 147]. Shifts towards lower temperature and *higher* densities, which is the situation encountered in experiments [144, 145], are only observed in the presence of additional attractive fluid–matrix interactions [139]. Spöler and Klapp also showed that the effects of HS matrices on the VL transition can be reproduced when the dipolar model fluid is approximated by a fluid with angle- (Boltzmann-) averaged dipolar interactions [141].

More dramatic effects arise when the perturbation induced by the disordered matrix couples directly to the dipole moments of the fluid particles. An example are *charges* on the matrix particles, for which the influence on a DHS fluid has been studied by Fernaud *et al* [137]. They report a significant decrease of the dielectric constant, and an enhanced tendency for dipole association at low densities. Finally, Spöler and Klapp [140] have considered *dipolar* disordered matrices, using again replica-RHNC theory. Similar to charges, dipolar fluid–matrix interactions play a central role in liquid chromatography where polar liquids are adsorbed to disordered materials composed of molecules with polar headgroups [129]. Concerning the VL transition of the adsorbed Stockmayer fluid, the dipolar fields generated by the matrix act effectively as an *attractive isotropic* interaction between the fluid and the matrix [140]. The anisotropic nature of the dipolar interactions plays a more dominant role at high fluid densities where one observes a pronounced decrease of the dielectric constant, and a strong degree of local orientational ordering of the fluid particles along the local fields generated by the matrix [140]. Moreover, an instability of the dielectric constant, that is a precursor of ferroelectric ordering occurring both in bulk Stockmayer fluids [54, 214] and in fluids in non-polar matrices [139], is observed only for very small dipolar fluid–matrix couplings [140].

This suggests that larger fields destroy the ferroelectric ordering as one might indeed expect on physical grounds. However, even for the weakly disturbed systems it seems likely that the frozen dipolar matrix fields influence the structure *inside* the low-temperature ferroelectric state. Based on work on related systems such as nematic liquid crystals in disordered silica matrices (which have been intensely studied both experimentally [148, 149] and theoretically [150–152]) one could imagine that the *long-range* ferroelectric ordering typical for bulk fluids is replaced by some type of short-range or 'quasi'-long-range ordering. In our opinion, a closer investigation of the nature of the low-temperature states in disordered dipolar systems is currently beyond the replica-integral equation approach. This is partly because of technical factors (specifically, the increasing complexity of the Ornstein–Zernike equations in ordered states), but also because more simulation data are required in order to test and improve the closure approximations (including a discussion of replica-symmetry breaking [142]) under strongly coupled conditions.

5. Positional disorder

Another type of quenched disorder occurs in systems of dipolar particles with the positions being *frozen* in an irregular configuration. Examples for such systems, which seem better described as *amorphous solids* rather than as liquids, are mixed crystals with polar impurities (e.g., $K_{1-x}Li_xTaO_3$) [153, 154], diluted dipolar-coupled magnets (e.g., $LiHo_xY_{1-x}F_4$) [155, 156], assemblies of ultrafine ferromagnetic particles [157, 158], and 'frozen ferrofluids' [159–162]. The latter systems result from a quench of an equilibrated ferrofluid into a state below the freezing temperature of the non-magnetic solvent. This fixes the positions of the magnetic particles, whereas their dipole moments are still relatively free to rotate (except of random anisotropies generated by the frozen easy axes of the particles).

A common feature of the systems mentioned above is that the frozen positional structure is more or less random. Under these conditions, the anisotropy of the dipolar interaction necessarily introduces *competition* between ferromagnetic and antiferromagnetic interactions, with which the frozen system (in contrast to a dipolar fluid) cannot deal by developing suitable spatial arrangements. Moreover, the long-range nature of the dipolar coupling implies that many competing interactions can simultaneously influence the local field on a particular dipole. From this point of view, positionally frozen dipolar systems are often highly *frustrated* systems, which is consistent with the spin-glass-like behaviour detected in experiments of several mixed

crystals [153, 154] and frozen ferrofluids [159]. The observed glassy behaviour (such as irreversibilities in polarization/magnetization measurements) seems to be restricted to very small dipole concentrations, that is, conditions where positional randomness is expected to play a dominant role. Some of the experimental observations have been explained by local mean-field theories [163–166] and computer simulations [167].

Another fundamental question on positionally frozen dipolar systems, especially when it comes to denser systems, concerns the existence of long-range orientational ordering. Interestingly, the answer appears to depend on the dimension of the dipolar degrees of freedom. Specifically, long-range order has been detected experimentally—and reproduced theoretically [165]—in diluted dipole-coupled magnets [155, 156], where the magnetic degrees of freedom are essentially 'Ising dipoles' (due to strong crystal anisotropies). On the other hand, frozen ferrofluids, where the dipoles are three dimensional, do not display any global ordering [159].

Theoretical results on three-dimensional, positionally dipolar systems are contradictory. In particular, a mean-field approach (MFT) [154] put forward by Zhang and Widom [168] suggests that quenched positional disorder simply reduces the range of the ordered phase in the temperature–density phase diagram (compared to fully coupled 3D dipolar fluids). On the other hand, subsequent results based on MD calculations by Ayton *et al* [75, 76] indicated that the systems rather freeze orientationally into a glass-like state as the temperature is decreased. As discussed by Ayton *et al* [75, 76], one may interpret this discrepancy either as a failure of the MFT (which tends to underestimates frustration) or as a failure of the simulations (which might not have reached equilibrium). Subsequent theoretical results by Klapp and Patey [169] have shed some new light on this question. Their approach, which was later extended to Heisenberg systems by Lomba *et al* [170, 171], is a variant of the replica theory employed for disordered confined fluids (section 4).

5.1. Replica approach and the occurrence of global ferroelectric ordering

The simplest model for a positionally frozen dipolar system consists of spherical particles with the positions fixed according to a distribution $P(\{r\}) = P(r_1, \ldots, r_N)$, and with freely rotating dipole moments. Thus, thermal averages $\langle \ldots \rangle_r$ over the orientational degrees of freedom depend on the spatial configuration $\{r\}$ and need to be supplemented by an average over $P(\{r\})$. The resulting double averages can be circumvented [169] by means of the replica method, in analogy to the corresponding procedure for partly quenched mixtures (see section 4.1). The only difference is that for the latter systems quenched and annealed variables belong to *different* particles, while for the present system *one* particle involves both a quenched variable (its position) and an annealed degree of freedom (its orientation). As a consequence, the 'replicated' system corresponding to the positionally frozen dipolar system (in the limit $n \to 0$) is nothing else than a special, one-component dipolar fluid, where each (spherical) particle carries $1 + n$ degrees of freedom: the particle's position and the orientation of n dipole moments within the particle. Choosing a canonical distribution (at inverse temperature β_0) for $P(\{r\})$, the corresponding replicated Hamiltonian is given as [169]

$$H^{\text{rep}} = \frac{\beta_0}{\beta} \sum_{i>j} u^{\text{SR}}(r_{ij}) + \sum_{\alpha=1}^{n} \sum_{i>j} u^{\text{DD}}(r_{ij}, \omega_i^{\alpha}, \omega_j^{\alpha}). \tag{5.1}$$

Based on (5.1), a set of replica-integral equations in the HNC approximation was derived [169]. Numerical solutions were obtained for systems in globally isotropic states, with the consequence that long-range ferroelectric ordering could only be detected via a divergence of the dielectric constant ϵ. Results are shown in figure 4. Based on the behaviour of ϵ,
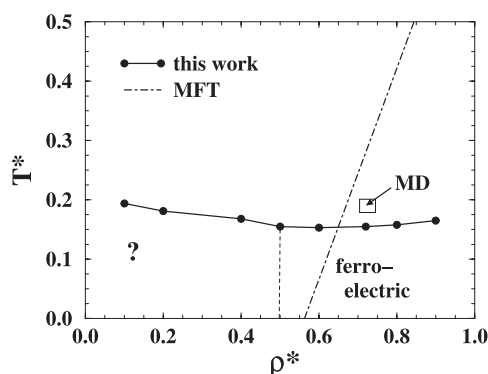
Figure 4. Overview of the replica-HNC results for a frozen dipolar system with randomly distributed positions in the temperature–density plane. The filled circles indicate the lowest temperatures where numerical solutions could be obtained; the solid line is simply to guide the eye. The theory predicts ferroelectric order for densities above the dashed line. Also shown is the boundary of the ferroelectric phase according to mean-field theory (MFT) [168]. The square indicates the density and the lowest temperature investigated in MD simulations [75, 76]. From [169].

ferroelectric order was found to occur at low temperatures and densities beyond a threshold density ($\rho^*_{min} \approx 0.5$), indicating that the long-range dipolar interactions (which favour ordering) may indeed overcome the short-range frustration induced by positional disorder.

The existence of a threshold density is consistent with the experimental results for frozen ferrofluids [159, 161] where the dipole density was typically rather small ($\rho^* < 0.1$) and no spontaneous polarization was found. At high densities, the HNC predictions for the ferroelectric transition temperatures depend strongly on the degree of spatial correlation in the underlying system of frozen spheres [169]. For a randomly frozen system (i.e., $g(r) = 1$), the transition temperatures are found to be much lower than that those predicted by the MFT [168], and also considerably lower than the temperature where the MD simulations [75, 76] (lacking evidence for ferroelectric order) have been performed. Moreover, the HNC predicts a gradual local freezing of the dipole axes upon decreasing temperature (induced by inhomogeneities in the spatial structure). The HNC results thus supplement rather than contradict the MD results, which also indicate some sort of orientational freezing [75, 76]. On the other hand, strong positional correlations can push the transition towards temperatures even higher than those in equilibrated dipolar fluids. This is consistent with subsequent results for positionally frozen Heisenberg fluids by Lomba *et al* [170, 171].

6. Field-induced structural effects

External magnetic or electric fields are one of the most obvious perturbations for fluids with permanent dipole moments, since these fields couple directly to the particles via the (external) one-body potential

$$\Phi^{ext}(1) = -\boldsymbol{\mu}_1 \cdot \boldsymbol{H}_0(1). \tag{6.1}$$

External fields are particularly important in the context of ferrofluids [10–12]: in these systems, the permanent magnetic dipole moments of the colloidal particles are typically so large that even small field strengths $H_0 = |\boldsymbol{H}_0|$ yield a magnetic field energy comparable to the thermal energy, i.e., $\mu H_0 / k_B T \approx 1$. Therefore, ferrofluids respond much more strongly to external

fields than polar molecular fluids, where the individual (electric) dipole moments are generally small [5]. The resulting excellent possibilities to control the material properties of ferrofluids by external fields have led to a broad variety of technical applications [10–12], many of which concern the hydrodynamic [12] and rheological behaviour (in particular, the viscosity), and the related microstructure. Theoretical approaches towards a description of these phenomena have been recently summarized by Hess [13] and Kröger *et al* [25]. In the following we focus on recent progress in describing the *equilibrium* behaviour of ferro- (and other dipolar) fluids in external fields.

Most of the theoretical studies in this context concentrate on calculating averaged quantities such as the magnetization $M(H_0)$. At very low concentrations, ferrofluids display ideal gas behaviour, that is (for monodisperse systems), $M = M_{sat}\mathcal{L}(\alpha)$ with M_{sat} being the saturation magnetization, $\mathcal{L}(\alpha) = \coth(\alpha) - \alpha^{-1}$ is the Langevin function, and $\alpha = \mu H_0/k_B T$. In order to investigate systems at higher concentrations, various semi-analytical approaches have been proposed, including thermodynamic perturbation theory [172] and a theory based on Mayer expansions of the interparticle correlations [173, 174]. These approaches, which have been very recently reviewed by Huke and Lücke [43] perform well in quite dilute ferrofluids (magnetic volume fractions up to ∼10–12%) with moderate coupling strengths ($\mu^2/k_B T\sigma^3 \leqslant 1$), but break down when denser systems or more strongly coupled ferrofluids are considered [175]. Clearly, these drawbacks are due to the increasing importance of interparticle correlations [43].

The most important correlational effect of an external field on a ferrofluid (and any strongly coupled dipolar fluid) is the self-assembly of particles into chain-like structures parallel to the field direction, an effect which was theoretically predicted as early as the 1970s by de Gennes and Pincus [56] together with their work on spontaneous chain formation (see section 2). The practical importance of field-induced chain formation results from the accompanying strong modifications of the ferrofluids rheological behaviour [25], particularly the abrupt increase of viscosity [11]. Field-induced chain formation has been directly observed and analysed in computer simulations of dipolar model fluids [57, 176, 177]. Experimental visualization of the self-assembly has been achieved in two-dimensional ferrofluids [67, 68] and other dipolar colloidal systems [36, 34] where the external field points along a direction *within* the plane to which the particles are confined. In particular, Velev and co-workers [36, 34] have shown that sufficiently large fields drive the chains (formed already at smaller fields) to coalesce into novel two-dimensional crystal structures (see figure 1). A summary of computer simulation results concerning 2D dipolar fluids in a field is given in the review of Weis [42].

Coming back to three-dimensional systems, we note that scattering experiments (see, e.g., [178–181]) indicate the field-induced aggregation into chains by a strong anisotropy of the scattering intensity, i.e. the structure factor $S(\mathbf{k})$ of the colloidal magnetic particles, which in turn reflects a strongly anisotropic pair correlation function $g(12)$. These anisotropies have been recently analysed by MC [182] and Brownian dynamic [183] computer simulations. The latter reproduced the experimentally observed increase (decrease) of the scattering intensity in the direction perpendicular (parallel) to the field.

Theoretically, the natural framework to investigate the anisotropic correlations induced by external fields is the integral equation approach. Recent progress in this direction is summarized below in section 6.1. We close this brief overview by noting that external fields also have, naturally, an effect on the overall *phase behaviour* of dipolar model fluids. Most studies in this context concern the vapour–liquid transition of Stockmayer fluids. In particular, Stevens and Grest have shown via GEMC simulations that the external field generally increases the critical temperature [184]. Similar findings emerge from density functional theory [70] and other theoretical studies based on (approximate) free energy ansatzes [172, 69]. The behaviour of

dipolar mixtures in external fields is briefly discussed at the end of section 7. Experimentally, evidence for a stabilization of the condensation transition of ferrofluids by an external magnetic fields has been reported in [185, 186].

6.1. Integral equations for dipolar fluids with fluctuating orientational order

The first integral equation studies on dipolar fluids in external fields were performed in the 1980s and were based on highly idealized models where the dipoles are constrained to be *perfectly* aligned. Structural and thermodynamic properties of these systems have been investigated both within the mean-spherical approximation (MSA) [187, 188] and by RHNC theory [189, 190]. For finite external fields, however, one would expect the orientational order to be non-perfect or *fluctuating*. The development of appropriate integral equation techniques started only in the late 1990s, beginning with a series of studies on simpler orientable fluids such as the Heisenberg spin fluid [191–193] and other models with separable interactions [194]. The first (and so far, the only) applications to the more complicated dipolar case concern two-dimensional DHSs in the presence of an out-of-plane field [117], three-dimensional DHS systems [195], and systems of dipolar ellipsoids [196]. All of these studies consider homogeneous external fields yielding singlet densities of the form

$$\rho(1) = \rho(\omega_1) = \frac{\rho}{2\pi}\,\alpha(x_1), \tag{6.2}$$

where $\alpha(x_1) = \alpha(\cos\theta_1)$ is a normalized orientational distribution function and $\cos\theta_1$ describes the orientation of dipole 1 with respect to the field direction. In the *absence* of a field, the distribution $\alpha(x_1)$ is just a constant, whereas *perfect* orientational order corresponds to $\alpha^{\text{perfect}}(x) = \delta(x-1)$. At finite field strengths, $\alpha(x)$ has to be determined *self-consistently* along with the two-body correlations describing the structure of the ordered fluid. This means that the usual integral equations consisting of the Ornstein–Zernike relation plus a closure relation have to be supplemented by a third equation relating two-body correlations, the distribution $\alpha(x)$ and the external potential (6.1). References [195] and [196] are based on the exact Lovett–Mou–Buff–Wertheim (LMBW) equation [197, 198]

$$i\boldsymbol{L}_1 \ln\rho(1) + i\boldsymbol{L}_1\beta\Phi^{\text{ext}}(1) = \frac{1}{\mathcal{V}}\int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \int \mathrm{d}\omega_2 c(12)i\boldsymbol{L}_2\rho(2), \tag{6.3}$$

where $\mathcal{V}$ is the (fixed) volume and $\mathbf{L} = -i(\boldsymbol{r} \times \nabla)$ is the angular momentum operator. An alternative is to use the—likewise exact—first member of the Born–Green–Yvon (BGY) hierarchy [78], which involves the pair correlation function and the gradient of the interaction potential [117]. We note that both single-particle equations are capable of generating a non-trivial distribution even in the absence of a field (spontaneous ordering). From a technical point of view, the necessity to solve simultaneously three instead of two integral equations renders the approach somewhat more involved compared to the isotropic case. A further increase of the numerical effort arises through the reduced symmetry (cylindrical versus spherical), which implies that the orthogonal angle expansions for the two-body correlations become more complicated as well [195, 196].

Results obtained so far indicate that integral equation theories for ordered dipolar fluids are similarly accurate as in the isotropic case. Explicit comparison with computer simulation results has been made by Lomba *et al* [117] who considered DHS monolayers with an out-of-plane external field. It is shown that the integral equation method (HNC approximation) provides an accurate description both of the structure and of the thermodynamic quantities for moderate dipolar coupling strengths $\mu^{*2} \approx 1$. Klapp and Patey [169] have studied orientationally ordered three-dimensional DHS fluids. As in the isotropic case [5], the MSA

and the RHNC closure predict quite different results both for correlation functions and for the dielectric behaviour, with the RHNC results appearing more reliable in terms of internal consistency. Based on the RHNC approximation, it is also possible to study the isotropic–to–ferroelectric transition. This is done [195] by stabilizing the numerical calculations with an infinitesimal external field (in a true zero-field situation, the restoring force for a rotation of the global director is identically zero, yielding infinite perpendicular fluctuations). The integral equation results obtained *within* the ferroelectric phase reveal a strongly anisotropic dielectric response, and chain formation along the global director. This is consistent with computer simulation results for ferroelectric and field-ordered liquid phases [57, 176, 177].

Finally, the RHNC description of the ferroelectric liquid phase has also been employed as a *reference* in a second-order perturbation density functional study [199] for crystallization. Besides predictions for the preferred ferroelectric lattice structures, the theory also indicates that ferroelectric 'reference' liquid is indeed stable in a small range of densities. This finding contradicts earlier density functional studies [200, 201] based on isotropic reference states, but agrees with computer simulation results (see figure 2).

7. Size heterogeneities

Throughout this article we have considered *pure* dipolar fluids consisting of identical particles. This assumption, however, is not fulfilled in many real dipolar systems which are typically characterized by some sort of *non-uniformity*. In ferrofluids, for instance, non-uniformity is naturally introduced by the essentially omnipresent polydispersity. In typical ferrofluids, the sizes σ_i of the magnetic particles are distributed according to a log-normal or gamma distribution (with a mean diameter of about 10 nm) [43]. The magnetic dipole moments are coupled to the sizes through the relation

$$m_i = m \, \mathcal{V}_i = m \, \pi \sigma_i^3 / 6 \tag{7.1}$$

with m being the specific magnetization. Size polydispersity therefore yields automatically a non-uniformity in the distribution of dipole moments and the resulting interaction strengths. Recent experimental work (for a review, see [11]), as well as theoretical [83, 172, 174] and computer simulation studies [182, 202–204], has shown that the dipolar non-uniformities can indeed have a profound influence on the material properties of ferrofluids. For example, the presence of some larger particles in a system of predominantly smaller particles yields a significant increase of the field-induced magnetization and the initial susceptibility [204, 174]. Regarding the microstructure in strongly coupled systems, the computer simulations [182, 204] demonstrate that the self-assembled chains mostly consist of larger particles, whereas the majority (but not all) of the smaller particles remains non-aggregated. These observations can be reproduced by theory based on a free energy model, where the system is treated as a collection of non-interacting chains of different sizes [83]. The initial susceptibility of polydisperse systems has been recently considered by various free-energy approaches (for a summary, see [43]). An alternative approach was provided, as early as the 1970s and 1980s, by generalizations of integral equation techniques for one-component (isotropic) dipolar fluids to the mixture case (see [205–207] and [208] for applications of the MSA and the RHNC theory, respectively).

Further interesting effects of polydispersity appear when it comes to the phase behaviour. In particular, there is experimental evidence [86, 185, 209] that the vapour–liquid transition of polydisperse ferrofluids is accompanied by a saturation of larger (i.e., more strongly interacting) particles in the denser (liquid) phase. This phenomenon, which is of great importance as a method to *size-separate* the system [185], has been reproduced in a recent computer simulation

study [210] of the condensation of a polydisperse ferrocolloid. It also indicates that in polydisperse ferrofluids, which may be regarded as multicomponent mixtures, condensation transitions are always—at least to some degree—coupled with *demixing* phase transitions. However, a profound understanding of the appearance of these phase transitions and their dependence on external conditions (thermodynamic states, external fields) is still missing. The same is true for fluid–fluid phase transitions in *molecular* polar mixtures. The latter systems are intrinsically interesting since their polarities, and thereby their solvation properties, can be tuned by varying the composition [211, 212]. In order to make use of these properties, however, it is vital to know under which thermodynamic conditions these mixtures demix and/or condense. Again this is a topic which is so far not well understood, partly because computer simulations of model dipolar mixtures [213–215] are necessarily restricted to small portions of the parameter space.

In the following we summarize recent density functional and RHNC integral equation studies of Range and Klapp [216–219] for the fluid–fluid phase behaviour of the first approximation of polydisperse ferrofluids, that is *binary dipolar mixtures*. The same simplification has been made in most of the previous theoretical and simulation studies of ferrofluids (see, e.g., [83, 204, 220, 221]). The work of Range and Klapp goes beyond earlier theoretical studies in that the full interplay of condensation, demixing, and ferromagnetic ordering is considered.

7.1. Phase behaviour of binary dipolar mixtures

The investigations [216–219] are mainly based on modified mean-field density functional theory (MMFT), which has also been employed by Dietrich and co-workers [55, 70–72, 222] to study one-component dipolar fluids and related anisotropic systems such as Heisenberg spin fluids [223]. Within this framework, phase diagrams are determined by minimizing an approximate grand-canonical free energy functional $\Omega[\rho]$. Isotropic and spatially homogeneous ferromagnetic phases are included by considering singlet densities of the form $\rho_a(\mathbf{r}_1, \omega_1) = \rho_a(2\pi)^{-1}\bar{\alpha}_a(\cos\theta)$ where the subscripts a and b denote the components considered, and $\bar{\alpha}_a(\cos\theta)$ are orientational distribution functions of the form already introduced in section 6.1. The resulting MMF functional of a mixture of DHS is given by [216, 218]

$$\frac{\Omega}{\mathcal{V}} = \sum_a \frac{\rho_a}{\beta}\Big[\ln(\rho_a\Lambda_a^3) - 1\Big] + \sum_a \frac{\rho_a}{\beta}\int_{-1}^{1} dx\, \bar{\alpha}_a(x)\, \ln(2\bar{\alpha}_a(x)) - \sum_a \mu_a\rho_a$$
$$- H_0 \sum_a m_a\rho_a \int_{-1}^{1} dx\, \bar{\alpha}_a(x)\, x + \frac{F_{\mathrm{HS}}^{\mathrm{ex}}}{\mathcal{V}} + \frac{F_{\mathrm{DD}}^{\mathrm{ex}}}{\mathcal{V}}, \qquad (7.2)$$

where the first two terms on the right-hand side of (7.2) correspond to the ideal (translational and orientational) part of the free energy, μ_a are the chemical potentials, H_0 is the strength of a homogeneous external field, and $F_{\mathrm{HS}}^{\mathrm{ex}}$ is the excess free energy of the underlying mixture of mono- or bidisperse hard spheres [224–226]. The MMF approximation [70, 222] enters the dipolar contribution to the excess free energy, $F_{\mathrm{DD}}^{\mathrm{ex}}$, and consists in setting the pair distribution function $g_{ab}(12)$ involved in the *exact* expression for $F_{\mathrm{DD}}^{\mathrm{ex}}$ equal to its low density limit, i.e., $g_{ab}(12) \to \exp[-\beta u_{ab}(12)]$ (see [216, 217] for details). Minimization of the functional (7.2) with respect to ρ_a and $\alpha_a(x)$ then yields the equilibrium densities at given $(\mu_a, T, \mathcal{V})$.

Based on the functional (7.2), Range and Klapp have investigated binary dipolar mixtures of increasing complexity, starting from the most basic model where the two components differ only in their dipole moments (i.e., $m_A \neq m_B$) and the external field H_0 is zero [216, 217]. Despite these restrictions, the results reveal complex fluid–fluid phase behaviour involving
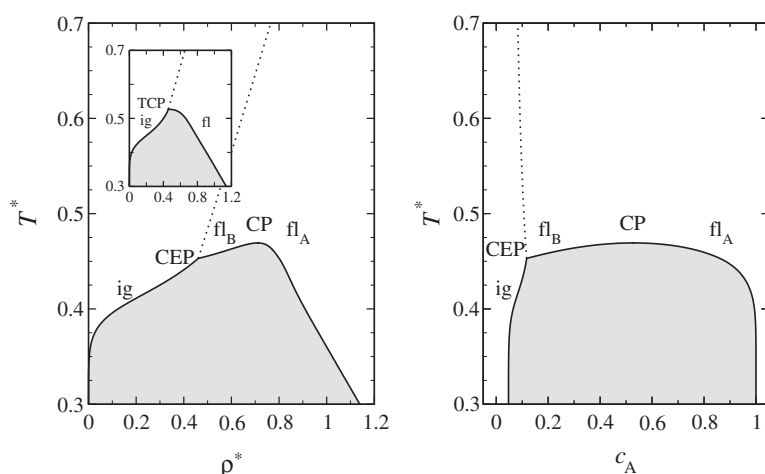
Figure 5. MMFT phase diagrams in the density–temperature plane (left) and the concentration–temperature plane (right) for monodisperse DHS mixtures at $\Gamma = m_B^2/m_A^2 = 0.60$ and $\Delta\mu^* = \mu_B - \mu_A = 3.0$ ($T^* = k_B T \sigma^3/m_A^2$, $\rho^* = (\rho_A + \rho_B)\sigma^3$, $c_A = \rho_A/\rho$). Dashed lines are lines of critical points separating the isotropic gas (ig) from ferromagnetic fluid (fl) phases, CEP and TCP denote critical end points and tricritical points, respectively, and CP corresponds to a demixing critical point between two ferromagnetic fluids with different compositions. The inset on the left-hand side additionally contains the density–temperature diagram at $\Delta\mu^* = 1.3$. From [216].

both isotropic-to-ferromagnetic phase transitions (which also occur in the pure system) and—particularly at small values of the parameter $\Gamma = m_B^2/m_A^2$—demixing phase transitions. Exemplary phase diagrams are given in figure 5. The demixing transition separates a fluid saturated with less strongly coupled B particles and a denser fluid with strongly coupled A particles. This is, in principle, consistent with the condensation/demixing behaviour observed in real ferrofluids (see, e.g., [185]). Contrary to reality, however, the MMFT predicts demixing only at quite high packing fractions corresponding to the *ferromagnetically* ordered region of the phase diagram. The same is true for *bidisperse* mixtures [218], where the two species of DHSs differ not only in their dipole moments, but also in their sizes. On the other hand, more sophisticated approaches such as the RHNC theory [227, 228, 217] (and simulations for the limiting case $\Gamma = 0$ [229]) do indeed already predict demixing in the isotropic phase. This discrepancy underlines the relevance of correlational effects for the existence of demixing transitions in dipolar systems *without* dispersive interactions. Indeed, considering *Stockmayer* instead of DHS mixtures the MMFT yields isotropic demixing transitions in close agreement to the RHNC predictions [217].

A generic finding from both the MMFT studies [216–218] and an accompanying RHNC investigation [217] is that the ferromagnetic transition in dipolar mixtures is generally shifted towards significantly lower temperatures and/or higher densities compared to the one-component case, indicating that spontaneous parallel ordering in dipolar systems is generally strongly *destabilized* by non-uniformity in the dipole moments. This is consistent with a recent MC study of binary DHSs [202].

Finally, the case $H_0 \neq 0$ has also been studied within the MMFT [219]. For mixtures dominated by one of the components, MMFT predicts the tricritical point of the transition between an isotropic gas and a ferromagnetic liquid occurring at $H_0 = 0$ to be changed into a critical point separating two magnetically ordered phases of different densities. The corresponding critical temperature increases with H_0. Completely different behaviour is found in the context of the demixing phase transitions, where the corresponding critical temperature

is found to decrease with H_0. This sensitivity suggests that external magnetic fields can indeed be efficiently used to control the mixture's phase behaviour over a large temperature interval.

8. Summary and perspectives

To summarize, we have demonstrated that fluids interacting by long-ranged, direction-dependent dipolar interactions are strongly affected even by the most simple perturbations which do not couple directly to the dipole moments. Key examples are insulating walls or purely repulsive, disordered confining media: Both *promote* the tendency of dense dipolar fluids to develop orientational ordering (although the reasons in the two cases are quite different).

The theoretical progress in treating perturbed dipolar fluids on the basis of methods previously established for bulk systems is substantial. In this topical review we have discussed several approaches such as replica-integral equations for dipolar fluids in the presence of disordered confinement and positional quenched disorder. Both types of disorder have a significant influence on phase transition temperatures, and can give rise to interesting structural phenomena such as local freezing of the dipole axes in systems with positional disorder. From a technical point of view, it appears that replica-integral equations yield reasonable results at small degrees of perturbation but become inconsistent (or numerically too complex to solve) under strongly coupled conditions. As a result, several important questions such as the nature of the disordered (possibly glassy) low-temperature ferroelectric states remain to be answered. An additional problem is the lack of simulation results for strongly coupled, disordered dipolar systems to test the theoretical predictions.

We have also discussed recent integral equation methods to investigate dipolar fluids with field-induced or spontaneous orientational order. First applications have focused on quite dense dipolar fluids. The increasing interest in ferrocolloids may stimulate further studies of more dilute systems, for which a large number of experimental and simulation data concerning the field-induced magnetization, susceptibility, and the anisotropic structure factor already exist. Given a positive evaluation, integral equation methods for ordered dipolar fluids could be established as an accurate, and computationally less expensive alternative to computer simulations, similar to the role of conventional integral equations for the investigation of bulk dipolar fluids.

Finally, there are many open questions concerning the behaviour of confined dipolar fluid *films*. Indeed, only recently efficient techniques to handle the long-range interactions in computer simulations of dipolar films have been developed [42]. As a consequence, the overall phase behaviour of dipolar fluid films is at present unclear. The investigations discussed in this review may provide the basis for further studies concerning the influence of boundary conditions, and in particular the impact of dielectric or conducting versus the non-conducting walls considered in section 3.1. Indeed, conducting walls are most important in experimental situations such as AFM experiments involving polar solvents, and in biological contexts [230, 231]. Moreover, in many of these situations, the polar fluid is subject to an additional external field, the influence of which has so far only been studied for very specific systems. Another open question concerns the structure, both in the ground state and at non-zero temperatures, of dense dipolar systems at very small wall separations. This topic is relevant not only from a fundamental point of view, but also in the context of the search for novel magnetic crystals [32, 127]. Another problem receiving growing interest is the behaviour of planar or near-to-two-dimensional magnetic and electric systems with *field-induced* dipoles [33, 38, 232].

In conclusion, the statistical mechanics of dipolar model fluids under external perturbations raises many interesting questions, the solution of which is important not only from a

fundamental point of view, but also for future applications of these fascinating fluids. In the present topical review we have focused on *equilibrium* problems and on systems with permanent dipoles. One may expect, however, that the results and tools developed within this context will serve a basis for future, more general investigations including dynamic properties and non-equilibrium phenomena such as shear-flow or transport through complex geometries.

Acknowledgments

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