

Magnetic properties of colloidal suspensions of interacting magnetic particles

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Abstract

We review equilibrium thermodynamic properties of systems of magnetic particles like ferrofluids in which dipolar interactions play an important role. The review is focused on two phenomena: (i) magnetization with the initial magnetic susceptibility as a special case and (ii) the phase transition behaviour. Here, the condensation ('gas/liquid') transition in the subsystem of the suspended particles is treated as well as the isotropic/ferromagnetic transition to a state with spontaneously generated long-range magnetic order.

Contents

	Page
1. Introduction	1733
2. Statistical mechanical description	1734
2.1. Ideal paramagnetism	1736
2.2. Weiss and Onsager model	1736
2.3. Short-range potentials	1737
3. Initial susceptibility	1739
3.1. Cluster expansion methods	1740
3.2. HNC and related approaches	1742
3.3. Numerical simulations	1744
3.4. A comparison	1745
3.5. Other potentials	1746
3.6. Polydisperse theories	1746
3.7. Applications to ferrofluids	1747
4. Magnetization	1748
5. Nonspherical potentials and higher-order magnetic moments	1752
6. Phase transitions	1753
6.1. Dilute/dense phase transitions	1753
6.2. Ferromagnetic phases	1757
7. Conclusion	1759
Acknowledgments	1761
References	1761

1. Introduction

Ferrofluids [1] are suspensions of ferromagnetic or ferrimagnetic particles with diameters of the order of 10 nm in a liquid carrier. A common combination is magnetite (Fe_3O_4) in hydrocarbons. The volume fraction of the magnetic material is typically a few per cent. The particles are monodomain. They are too small for the build-up of domain walls [2,3]. Thus, the quantum-mechanical exchange interaction between the electronic spins can keep all the atomic magnetic moments aligned so that the total magnetic moment, m , of the particles is of the order of about $10^4 \mu_{\text{B}}$. Hence, to describe the equilibrium magnetic properties of the ferrofluid one can take each particle i to have a magnetic moment $\mathbf{m}_i(t)$ that fluctuates in time, but with its magnitude $m_i = |\mathbf{m}_i(t)|$ fixed. Thus, we do not address here the magnetic properties of the ferrofluid system on the nanometre scale, i.e. of the magnetic particles themselves: questions related to the size and form of the magnetocrystalline anisotropy, to magnetostrictive effects, to shape anisotropy, to dead layers, etc of the particles [2–5] are not addressed here.

Whether the magnetic moment $\mathbf{m}_i(t)$ fluctuates only as a result of the rotational diffusion of the particle in the carrier liquid (Brownian relaxation) or also because the temperature is sufficiently high to stimulate $\mathbf{m}_i(t)$ itself to move in the potential landscape over the anisotropy energy barriers of the particle's lattice structure (Néel relaxation) does not influence the *long-time equilibrium* magnetic properties of the suspension but only its dynamics. In any case, the magnetic particles cause the ferrofluid to display the equilibrium thermodynamics of a paramagnetic liquid—if one postpones for the moment the currently debated question of whether spontaneous long-range magnetic order is possible or not. The initial susceptibility can easily reach values of $\chi \approx 1$ and higher. Being orders of magnitude larger than for ordinary (molecular) paramagnetic liquids, one thus speaks of a 'superparamagnetic' liquid.

Ferrofluid particles are small enough to avoid segregation caused by gravity or customary magnetic gradient fields. But the strong van der Waals attraction between the nanoscale particles would lead to irreversible agglomeration. To prevent this, they are either coated with polymer surfactants of about 2 nm length whose entropic repulsion counteracts the van der Waals forces, or with ionic groups that prevent agglomeration due to their electrostatic repulsion. In the latter case the carrier is a polar liquid like water, containing the necessary counterions.

In a sufficiently diluted ferrofluid the magnetic particles can be thought of as noninteracting, and the equilibrium magnetic properties of such a ferrofluid are those of an ideal paramagnetic gas. Still, there is an important difference for a molecular paramagnetic fluid like, say, oxygen: the ferrofluid particles are not identical, they differ both in size and magnetic moment. This polydispersity has an influence on the properties of the ferrofluid, in particular also on the equilibrium magnetization.

At higher concentrations the ideal gas approximation fails to reproduce the equilibrium magnetization curve of ferrofluids. This is already the case for susceptibilities of the order of unity. Then, the particle interaction—and first of all the dipolar interaction—has to be taken into account. Since there exists a perfect analogy between magnetic and electric dipoles, the large number of theories developed for the latter case are directly applicable to this problem.

The thermodynamics of dipolar interacting particles is not only of interest because of the applicability to (electric) polar fluids and ferrofluids. It is also of great theoretical interest because the dipole–dipole interaction shows at least two interesting features: (i) it is attractive and/or repulsive, depending on the orientation of the particles and (ii) it is of long-range nature.

Because the dipolar interaction is neither always attractive nor always repulsive it is not trivially clear how the magnetic moments of the particles affect e.g. the condensation phase

transition of the suspended particles and especially whether the dipole–dipole interaction can cause such a transition in a system of particles without additional attractive interactions. This question is still being discussed in the literature. An externally applied magnetic field can be expected to further modify the phase transition behaviour.

Another example of a phase transition where the magnetic moments play an important role is the isotropic/ferromagnetic transition, i.e. a spontaneous breaking of the rotational symmetry resulting in a nonvanishing magnetization without an applied magnetic field. Also, the question of whether the dipolar interaction alone can trigger such a phase transition is not yet settled.

There is quite an extensive literature on ferrofluids. The references to it are accumulated in the special issues of the *Journal of Magnetism and Magnetic Materials* that cover the International Conferences on Magnetic Fluids. Odenbach *et al* [6] show in the latest issue that by 2002 the total number of papers on ferrofluids had grown to well above 6000 with about 1000 being published in the period 1998–2001 [7]. The research topics cover problems as varied as fluid dynamics and the modifications in classical pattern formation experiments by using ferrofluids, pattern formation processes genuine to ferrofluids, such as the Rosensweig instability or the labyrinth instability, magnetorheological properties, dynamical magnetic susceptibility, medical and engineering applications [8–12].

We restrict ourselves, here, to the topics where the dipolar interaction between the magnetic particles is of major importance, namely the already mentioned equilibrium magnetization and initial susceptibility, on the one hand, and phase transitions, on the other hand.

This review is organized as follows. Following this introduction we discuss in section 2 the basic statistical mechanics of systems of dipolar particles. In section 3 the influence of the dipolar interaction on the initial susceptibility of systems of otherwise spherically symmetric particles is reviewed, mainly for dipolar hard spheres (DHSs) and Lennard–Jones particles with an additional magnetic moment (Stockmayer particles). This question has already been discussed for the electrical case before ferrofluids became an active research area. The more general question of the equilibrium magnetization, on the other hand, was mainly investigated with regard to the application to ferrofluids. The literature concerning the equilibrium magnetization is reviewed in section 4. In section 5 the effect of additional nonspherical interactions other than the dipolar one are briefly discussed. Phase transitions of the gas/liquid and isotropic/ferromagnetic type are reviewed in section 6. We conclude in section 7.

Because of the analogy between systems of magnetically and electrically polar particles and for reasons of simplicity, we will always use the magnetic terminology when reviewing the literature, even when only the electric case is considered. This is mostly the case in the earlier literature.

2. Statistical mechanical description

A complete description of ferrofluids within the framework of statistical mechanics would have to include all the components of a ferrofluid: magnetic particles, carrier liquid, polymer surfactants, etc. But theoretical approaches to explain the thermodynamic properties connected to magnetism, generally, concentrate quite successfully on the magnetic component. Since the magnetic properties of the carrier liquid can be neglected, it is clear that it can only have an indirect influence on the magnetization. A more elaborate model of a ferrofluid describing both the magnetic particles and the carrier fluid is discussed by Kalikmanov [13], who shows that under some assumptions the carrier fluid has no influence on the equilibrium magnetic properties of the ferrofluid as a whole.

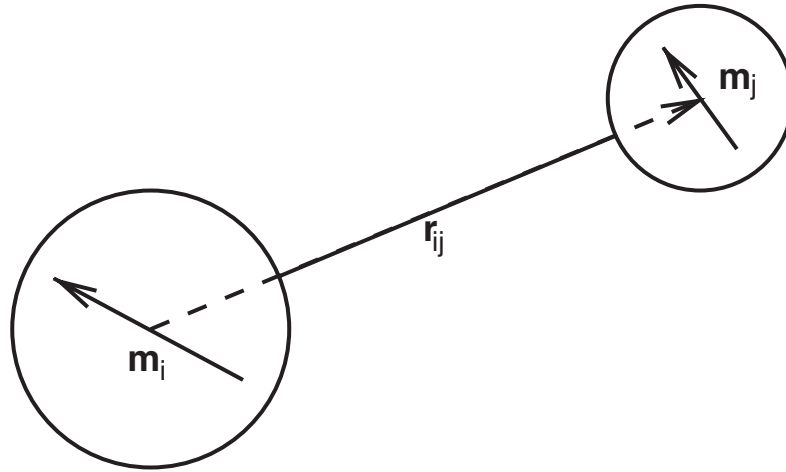


Figure 1. Spheres i and j carrying dipole moments \mathbf{m}_i and \mathbf{m}_j , respectively, that interact via the potential (2.2).

Ignoring the carrier, the ferrofluid can be described as a system of particles, $i = 1, \dots, N$, each carrying a magnetic moment \mathbf{m}_i and thus interacting with an external magnetic field \mathbf{H}_e via the potential

$$V_i = -\mathbf{m}_i \cdot \mathbf{H}_e. \quad (2.1)$$

The magnetic moments as used here include the vacuum permeability μ_0 (see, e.g. equation (2.4)). The absolute values $|\mathbf{m}_i|$ are fixed; but in general they are different from each other. These magnetic particles interact pairwise with each other via the dipole–dipole interaction potential

$$V_{ij}^{\text{DD}} = -\frac{3(\mathbf{m}_i \cdot \hat{\mathbf{r}}_{ij})(\mathbf{m}_j \cdot \hat{\mathbf{r}}_{ij}) - \mathbf{m}_i \cdot \mathbf{m}_j}{4\pi\mu_0 r_{ij}^3}. \quad (2.2)$$

Here, $\mathbf{r}_{ij} = r_{ij}\hat{\mathbf{r}}_{ij}$ is the distance vector between particles i and j (see figure 1). Since this potential decreases radially only as r^{-3} the dipolar interaction is of long-range nature.

In addition to (2.2) there, generally, exist also some short-range interactions between the particles that we capture by the potential V_{ij}^{SR} . It might include nonmagnetic components and in general also short-range magnetic interactions involving quadrupolar or higher-order magnetic moments. For later use we define the dimensionless potentials

$$v_i = \frac{V_i}{k_B T}, \quad v_{ij}^{\text{DD}} = \frac{V_{ij}^{\text{DD}}}{k_B T}, \quad v_{ij}^{\text{SR}} = \frac{V_{ij}^{\text{SR}}}{k_B T}. \quad (2.3)$$

The long-range nature of the magnetic interaction requires some care in statistical mechanical considerations. The local magnetic field acting on a particle is the sum of the external field and the dipolar fields of the other particles. The dipolar contribution depends on the distribution of the particles on a macroscopic scale, i.e. in particular also on the probe geometry. In macroscopic magnetostatics this property translates into the fact that the equilibrium magnetization \mathbf{M} of a magnetic medium depends on the internal field \mathbf{H} . This macroscopic field itself depends on \mathbf{H}_e , \mathbf{M} , and the geometry. The difference between \mathbf{H} and \mathbf{H}_e can, therefore, be interpreted as an effect of the dipolar interaction.

2.1. Ideal paramagnetism

If all dipolar interactions are discarded, then, the magnetic particles of the ferrofluid feel only the external magnetic field, i.e. $H = H_e$. This is a useful approximation if $M \ll H_e$ such that $H \approx H_e$. Assuming, in addition, that all particles are identical—the monodisperse case—with common magnetic moment $|m_i| = m$, then the equilibrium magnetization is given by

$$M = M_L = \frac{mN}{\mu_0 V} \mathcal{L} \left(\frac{mH}{k_B T} \right) = M_{\text{sat}} \mathcal{L}(\alpha) \quad (2.4)$$

with $H = H_e$. Here, N/V is the particle density and \mathcal{L} is the Langevin function, $\mathcal{L}(\alpha) = \coth(\alpha) - 1/\alpha$. Its argument $\alpha = mH/k_B T$ measures the energy of the moment m in the field $H = H_e$ in units of the thermal energy $k_B T$. The saturation magnetization $M_{\text{sat}} = mN/\mu_0 V$ of the ferrofluid corresponds to the case of parallel dipoles.

One might think that using in equation (2.4) the real internal field H in the ferrofluid instead of H_e would be an improvement of the ideal paramagnetic model by itself. However, such a replacement does not incorporate the effect of dipolar interactions in a systematic and controlled manner since they additionally modify the simple functional relation (2.4) between the equilibrium magnetization M and internal field H in various ways that are of the same order as the replacement of H_e by H in equation (2.4).

In a polydisperse extension of the above-described ideal, noninteracting monodisperse model the magnetic moments of the particles are allowed to be different. Then, the magnetization is given by

$$M = M_L = \sum_i \frac{m_i}{\mu_0 V} \mathcal{L} \left(\frac{m_i H}{k_B T} \right). \quad (2.5)$$

Here, the sum extends over all magnetic particles, $i = 1, \dots, N$. Using the mean magnetic moment $\bar{m} = (1/N) \sum m_i$ to introduce the reduced moment $\mu_i = m_i/\bar{m}$ of particle i we can write more conveniently

$$M = \frac{\bar{m}}{\mu_0 V} \sum_i \mu_i \mathcal{L} \left(\frac{\mu_i \bar{m} H}{k_B T} \right) = M_{\text{sat}} \mathcal{L}^{\text{poly}}(\bar{\alpha}), \quad (2.6)$$

where

$$M_{\text{sat}} = \frac{\bar{m}N}{\mu_0 V}, \quad \mathcal{L}^{\text{poly}}(\bar{\alpha}) = \frac{1}{N} \sum_i \mu_i \mathcal{L}(\mu_i \bar{\alpha}), \quad \bar{\alpha} = \frac{\bar{m}H}{k_B T}. \quad (2.7)$$

2.2. Weiss and Onsager model

The earliest model of a self-interacting magnetic medium is the mean-field Weiss model [14]. In this monodisperse model every particle is thought to be located at the centre of an empty spherical cavity, which is surrounded by a magnetic continuum with an internal field H and magnetization M . In thermal equilibrium, the magnetization is given by a Langevin function into which enters the local field $H_{\text{local}} = H + M/3$ within the spherical cavity. This leads to the implicit relation

$$M = M_{\text{sat}} \mathcal{L} \left[\frac{m}{k_B T} \left(H + \frac{M}{3} \right) \right], \quad (2.8)$$

which can be solved numerically to give the sought for equilibrium magnetization $M(H)$.

The initial susceptibility of the Weiss model

$$\chi = \frac{\partial M}{\partial H}(H = 0) = \frac{\chi_L}{1 - \chi_L/3} \quad (2.9)$$

is equivalent to the well known Clausius–Mosotti relation. Here,

$$\chi_L = \frac{\partial M_L}{\partial H}(H = 0) = \frac{1}{3} M_{\text{sat}} \frac{m}{k_B T} \quad (2.10)$$

is the Langevin initial susceptibility of the ideal monodisperse paramagnetism (2.4).

The Weiss model works well for weakly interacting ferrofluids but strongly overestimates the magnetization of concentrated magnetic fluids. It predicts ferromagnetic solutions, i.e. a spontaneous magnetization $M(H = 0) \neq 0$ whenever $\chi_L > 3$. While this criterion is at odds with experiments the possible existence of ferromagnetic phases in systems of DHSs cannot be ruled out for stronger interactions (cf section 6.2).

A similar early approach to the problem of a self-interacting magnetic medium is the Onsager theory [15] originally conceived for polarizable molecules. Therein, say, spherical molecules occupy a cavity in a polarizable continuum with susceptibility χ . The field acting on the molecule is the sum of a cavity field plus a reaction field that is parallel to the actual total (permanent and induced) moment of the molecule. Here, the resulting equation between χ_L and χ reads

$$\frac{\chi(3 + 2\chi)}{3(1 + \chi)} = \chi_L. \quad (2.11)$$

While the Weiss model overestimates the initial susceptibility of concentrated ferrofluids, the Onsager model generally underestimates it. It is instructive to write χ according to (2.9) and (2.11) for small χ_L as power series in χ_L

$$\chi = \chi_L + \frac{1}{3}\chi_L^2 \pm \frac{1}{9}\chi_L^3 + \dots \quad (2.12)$$

Here, the positive sign refers to the Weiss model and the negative one to the Onsager model. The first and second terms agree with a systematic expansion of χ in terms of dipolar coupling strength and magnetic volume fraction (cf section 3.1). However, the third order term of this expansion reads $+\frac{1}{144}\chi_L^3$ (see equation (3.8)). Thus, both the Onsager as well as the Weiss model strongly overestimate the influence of this term.

2.3. Short-range potentials

If one wants to go beyond the mean field models of section 2.2 one has to specify the potential with which the magnetic particles interact besides the long-range dipolar one.

Rosensweig [1] has proposed quite an elaborate potential for the short-range interaction, V^{SR} , of sterically stabilized magnetic particles. It consists of the sum of the van der Waals attraction between spherical magnetic particles and the sterical repulsion of their surfactants, i.e. $V^{\text{SR}} = V^{\text{vdW}} + V^{\text{ster}}$. The van der Waals attraction between the spheres is given by

$$V_{ij}^{\text{vdW}}(r_{ij}) = -\frac{A}{6} \left[\frac{2}{l^2 + 4l} + \frac{2}{(l+2)^2} + \ln \frac{l^2 + 4l}{(l+2)^2} \right]. \quad (2.13)$$

Here, A is the Hamaker constant. The quantity

$$l = \frac{2s}{D_{\text{core}}} = \frac{2r_{ij}}{D_{\text{core}}} - 2 \quad (2.14)$$

is given by twice the surface-to-surface distance s of the particles reduced by the diameter D_{core} of the magnetic particles while r_{ij} is the distance between their centres. The sterical repulsion of the surfactants is described by

$$V_{ij}^{\text{ster}}(r_{ij}) = \frac{\pi D_{\text{core}}^2 \xi k_B T}{2} \left[2 - \frac{l+2}{t} \ln \left(\frac{1+t}{1+l/2} \right) - \frac{l}{t} \right] \quad 0 < l < 2t. \quad (2.15)$$

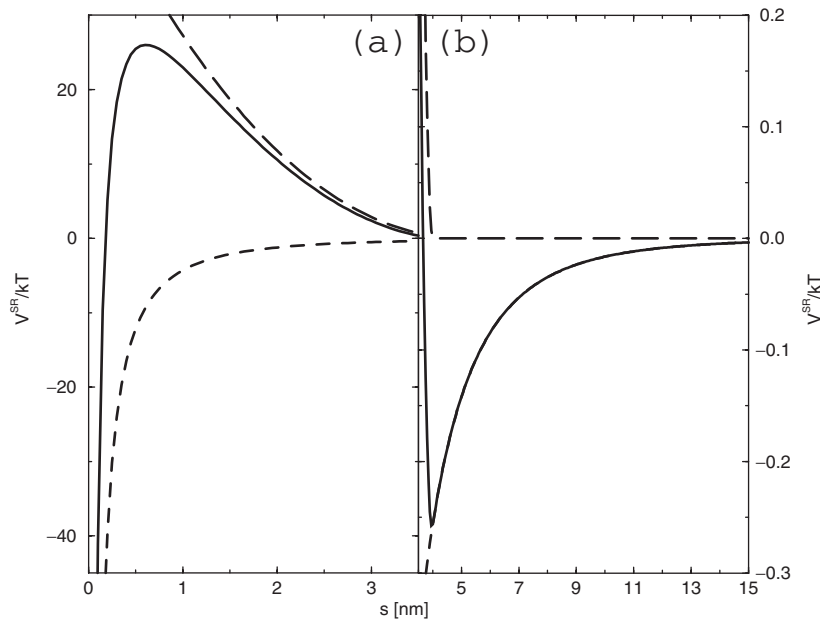


Figure 2. Nonmagnetic interaction potential for sterically stabilized ferrofluid particles as a function of the surface-to-surface distance s . - - -: van der Waals attraction, - · - · -: steric repulsion, —: combined potential. Note that the scales of both separation and energy are different in (a) and (b).

Here, ξ is the surface density of the polymers and

$$t = \frac{2\delta_{\text{polymer}}}{D_{\text{core}}} \quad (2.16)$$

is given by twice the length, δ_{polymer} , of the surfactant polymers. In the Rosensweig potential the carrier liquid component is not completely ignored but rather taken into account on a continuum level via the electric permeability of the liquid that enters into the Hamaker constant A .

Figure 2 shows the interaction potential $V^{\text{SR}} = V^{\text{vdW}} + V^{\text{ster}}$ [(2.13) and (2.15)] for typical values given by Rosensweig: $A = 10^{-19} \text{ J}$, $\xi = 1 \text{ nm}^{-2}$, $D_{\text{core}} = 10 \text{ nm}$, and $\delta_{\text{polymer}} = 2 \text{ nm}$. The need for sterical stabilization becomes apparent in this plot. The van der Waals interaction is strongly attractive for small particle separations—it even diverges in this simple model. The sterical potential modifies the interaction for distances less than 4 nm, such that only a small attractive tail at larger distances remains in the combined potential. At very small surface-to-surface separations the potential still diverges, but this inner attractive region is effectively shielded by a potential barrier with a height of about $25k_{\text{B}}T$.

To obtain an equivalent model potential for electrostatically stabilized ferrofluids, V^{ster} is replaced (see, e.g. [16]) by the interaction potential

$$V_{ij}^{\text{Debye}}(r_{ij}) = \frac{Q_{\text{eff}}^2}{4\pi\epsilon r_{ij}} e^{-(r_{ij}-D_{\text{core}})/\lambda_{\text{d}}} \quad (2.17)$$

of charged spheres in ionic solutions. Here, λ_{d} is the Debye length, ϵ is the dielectric constant of the carrier liquid, and Q_{eff} is an effective charge of the particles. The combined potential shows the same qualitative features as in the sterical case.

Another important model potential for describing dipolar particles is the Stockmayer potential in which the short-range interaction is given by the Lennard–Jones function for the

van der Waals interaction of point-like particles

$$v_{ij}^{\text{SR}} = 4v_0 \left[\left(\frac{D}{r_{ij}} \right)^{12} - \left(\frac{D}{r_{ij}} \right)^6 \right]. \quad (2.18)$$

Here, D is the collision parameter marked by the zero of this potential and v_0 is the depth of the potential well.

However, most often the effects of particle interaction are discussed within the simpler model of DHSs. Here, the short-range part of the interaction is given by the hard sphere repulsion potential

$$v_{ij}^{\text{SR}} = v_{ij}^{\text{HC}} = \begin{cases} \infty & \text{for } r_{ij} < D, \\ 0 & \text{for } r_{ij} > D \end{cases} \quad (2.19)$$

with D being the common hard sphere diameter in the monodisperse case. In the polydisperse case with different hard sphere diameters, D_i , one has to replace D by $(D_i + D_j)/2$ in the above equation. The only other interaction in this model is the long-range dipolar potential.

Some aspects of the sterical interaction (2.15) can also be incorporated into the DHS model. Since the magnetic field of a perfect, homogeneously magnetized sphere is exactly dipolar one can introduce into the DHS model particles that consist of two concentric spheres: an outer hard sphere with diameter D and a magnetized spherical core of diameter $D_{\text{core}} < D$. The latter is the source of the dipole field. The nonmagnetic layer models the surfactants, i.e. $D - D_{\text{core}} \approx 2\delta_{\text{polymer}}$. A nonmagnetic dead layer [17] on the particle can also be modelled.

The DHS model system was initially introduced to describe the electric polarizability of fluids of polar molecules. However, in reality, deviations from the spherical shape, particle polarizability, and higher-order moments have an important influence. Ferrofluids, on the other hand, resemble the model system much better. That the hard sphere repulsion is a good approximation to the Rosensweig potential becomes apparent when looking at the quantity $\exp(-v^{\text{SR}})$, which is more relevant for the equilibrium properties than v^{SR} itself. In figure 3 $\exp[-v^{\text{SR}}(r)]$ is plotted for the Rosensweig potential (solid line) ignoring the irrelevant inner attractive region. As can be seen, $\exp(-v^{\text{SR}})$ resembles quite well the unit step function $\exp(-v^{\text{HC}})$ of the hard sphere potential that goes from 0 to 1 at contact distance.

The long dashed line for the best fitting hard sphere potential and the short dashed line for the van der Waals potential are included in figure 3 for comparison. Although the Rosensweig potential resembles more with the van der Waals potential since both have an attractive part, the hard sphere potential fits the Rosensweig potential even a little bit better.

3. Initial susceptibility

Most of the older approaches to the magnetic or electric properties of polar fluids deal with the linear response problem, i.e. the initial susceptibility. The nonlinear behaviour was of lesser interest in common atomic polar fluids since the available electromagnetic fields were not strong enough to reach saturation. However, with the advent of superparamagnetic ferrofluids with large magnetic moments of the particles the linear and also the nonlinear magnetization behaviour of interacting dipoles again became a more active research area.

Most of the approaches to calculating the initial susceptibility can roughly be classified into cluster expansion, hypernetted chain (HNC), and numerical simulation methods. In this section, we will mainly address the results for DHSs.

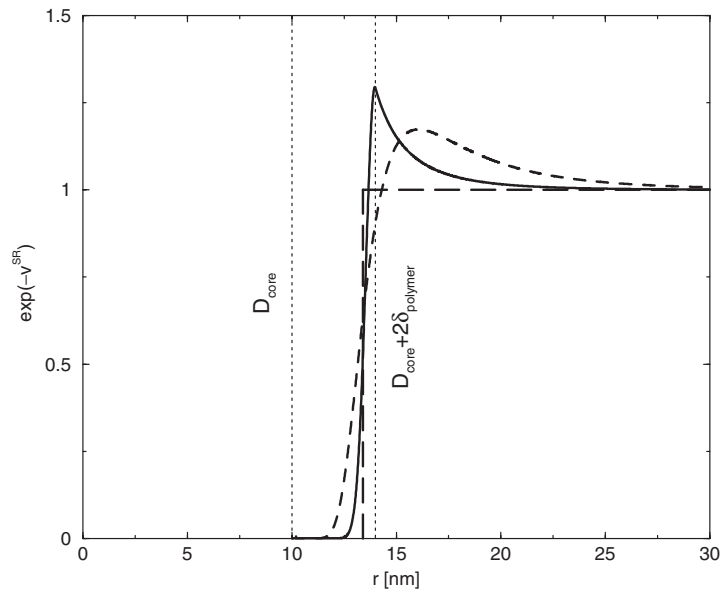


Figure 3. The quantity $\exp(-v^{\text{SR}})$ as function of particle distance for the potential of figure 2 (—). The contribution from the divergent part of the potential at very small surface-to-surface distances is suppressed in this plot. The short dashed and long dashed lines show $\exp(-v^{\text{SR}}(r))$ for best fitting hard sphere and van der Waals potentials, respectively.

3.1. Cluster expansion methods

Consider a system of N particles interacting with each other via a pair potential v_{ij} and with an external potential v_i . Then, the canonical partition function is given by

$$Z = \int \exp\left(-\sum_i v_i - \sum_{i<j} v_{ij}\right) d\Gamma. \quad (3.1)$$

Here, $d\Gamma$ indicates the integration over the configuration space spanned by the positions and magnetic moments of the particles. The ideal-gas factor contained in the canonical partition function that comes from the momentum degrees of freedom is not indicated here.

The key point of the cluster expansion method is to introduce into (3.1) the functions

$$f_{ij} = \exp(-v_{ij}) - 1 \quad (3.2)$$

which are small when the interaction is weak. Thus, one inserts $\exp(-v_{ij}) = 1 + f_{ij}$ into (3.1) and expands the integrand in terms of f_{ij} .

Then, (3.1), reads, up to first order, e.g.

$$Z = Z_N^0 + Z_{N-2}^0 \sum_{i<j} \int f_{ij} d(i) d(j), \quad (3.3)$$

where Z_N^0 is the partition function of the ideal noninteracting N -particle system. These approximations to Z then allow us to calculate the thermodynamic quantities of interest. The advantage of this expansion is that, in contrast to (3.1), the approximations to Z such as (3.3), and higher orders require only low-dimensional integrations, which can be performed at least numerically.

In the case of DHS the calculation of the leading terms can be done even analytically if one performs another series expansion, namely the expansion of (3.2) in terms of the dipolar

interaction potential v_{ij}^{DD} that enters via $v_{ij} = v_{ij}^{\text{DD}} + v_{ij}^{\text{HC}}$. The two expansions then translate into a power series for Z and thus for M or χ in two dimensionless parameters, namely the volume fraction

$$\phi = \frac{N\pi D^3}{6V} \quad (3.4)$$

of the particles, and a dipolar coupling constant

$$\lambda = \frac{m^2}{4\pi\mu_0 D^3 k_B T}. \quad (3.5)$$

It is also common to choose $\rho^* = ND^3/V$ and $y = 8\phi\lambda/3$ as parameters. These parameters fully characterize the system for $H = 0$. To make a comparison with Stockmayer particles easier, we will use these parameters here also. In the case of Stockmayer particles one also has to specify the potential strength v_0 entering into equation (2.18). It should be noted that in the literature a system of Stockmayer particles is normally characterized by giving values for $1/v_0$ and λ/v_0 .

In ordinary ferrofluids, ϕ is of the order of 10^{-2} . For magnetite ferrofluids with 10 nm particle diameters and an additional polymer layer of 2 nm, λ is less than one. In this case, higher orders in the (ϕ, λ) -expansion have only a minor influence on χ . But it is also possible to produce much stronger interacting ferrofluids. For example, van Ewijk, Vroege, and Philipse [18] report the production of ferrofluids with values for λ up to 2.7 and volume fractions up to 0.5. Even higher λ could be realized by Mamiya *et al* [19].

The long-range nature of the dipolar interaction causes some cluster integrals to be geometry dependent and mathematically ambiguous if the thermodynamic limit is naively performed. This problem is circumvented by dealing with a macroscopic but finite spherical geometry. In that case the initial susceptibility with respect to the external field $\chi_e = \partial M / \partial H_e$ ($H_e = 0$) can be calculated unambiguously and is related to the geometry-independent quantity χ via

$$\frac{\chi}{3 + \chi} = \frac{1}{3} \chi_e. \quad (3.6)$$

In 1966 Jepsen [20] performs a cluster expansion to obtain

$$\frac{\chi}{3 + \chi} = \frac{1}{3} \chi_L - \frac{5}{144} \chi_L^3 \quad (3.7)$$

for DHS. χ is then given up to the calculated order by

$$\chi = \chi_L + \frac{1}{3} \chi_L^2 + \frac{1}{144} \chi_L^3. \quad (3.8)$$

This equation can also be understood as a (ϕ, λ) -expansion, since $\chi_L = M_{\text{sat}} m / 3k_B T = Nm^2 / 3\mu_0 k_B T V$ can be written as

$$\chi_L = 8\phi\lambda. \quad (3.9)$$

The fact that both the Weiss and the Onsager model correctly predict the prefactor of the χ_L^2 term shows that this term has a mean-field origin that is independent of the type of short-range interaction.

Rushbrooke [21] calculated more terms in 1979. His result, as corrected later by Joslin [22], reads

$$\begin{aligned} \frac{\chi}{3 + \chi} &= \frac{8}{3} \phi\lambda + \frac{64}{225} \phi^2 \lambda^4 - \frac{160}{9} \phi^3 \lambda^3 - \frac{8(1187 - 600 \ln 2)}{3375} \phi^3 \lambda^4 + 1.13358 \phi^4 \lambda^3 \\ &= 2.66667 \phi\lambda + 0.284444 \phi^2 \lambda^4 - 17.7778 \phi^3 \lambda^3 \\ &\quad - 1.82782 \phi^3 \lambda^4 + 1.13358 \phi^4 \lambda^3. \end{aligned} \quad (3.10)$$

The $\phi\lambda$ and $\phi^3\lambda^3$ terms agree with the χ_L and χ_L^3 terms of Jepsen. The last term requires a numerical integration. Rushbrookes error affected the $\phi^3\lambda^4$ term. Buckingham and Joslin [23] calculate the second dielectric virial coefficient, i.e. the $\phi^2\lambda^n$ terms in the above expansion:

$$\frac{\chi}{3 + \chi} = \dots + \sum_{n=1}^{\infty} \frac{64}{3n[(2n+3)!!]^2} \sum_{k=0}^n (3k-n) \binom{2k}{k} \phi^2 \lambda^{2n+2} + \dots \quad (3.11)$$

Joslin [22] also presents, besides the aforementioned correction to the result of Rushbrooke, the term

$$\frac{32(315 \ln 2 - 218)}{3375} \phi^3 \lambda^5 = 0.003\,236\,62 \phi^3 \lambda^5. \quad (3.12)$$

Thereafter, Rushbrooke and Shrubbsall [24] calculate, in addition, the term

$$\left[\frac{105\,133\,619}{4\,042\,500} - \frac{298\,976}{7875} \ln 2 \right] \phi^3 \lambda^6 = -0.308\,396 \phi^3 \lambda^6. \quad (3.13)$$

A numerical calculation of the ϕ^3 term as a function of λ using Monte Carlo methods was reported by Joslin and Goldman in 1993 [25].

Tani *et al* [26] take a slightly different route to calculate χ using the system of (nonpolar) hard spheres as the reference system. They get

$$\chi = 8\phi\lambda + \frac{64}{3}\phi^2\lambda^2 + f(\phi)\lambda^2, \quad (3.14)$$

where the last term is a numerical expression based on approximate expressions for the two- and three-particle correlation functions for hard spheres as found in Monte Carlo simulations. For small ϕ this result reduces to (3.8). Goldman [27] compares results of this theory very successfully to Monte Carlo data for systems of hard spheres and Stockmayer particles.

3.2. HNC and related approaches

Using the HNC approach the initial susceptibility is calculated via the two-particle correlation functions $g(1, 2)$ and $h(1, 2) = g(1, 2) - 1$ of the polar particles [28]. The HNC is based on the Ornstein–Zernike relation

$$h(1, 2) = c(1, 2) + \frac{N}{4\pi V} \int c(1, 3)h(3, 2) d(3), \quad (3.15)$$

defining the direct correlation function $c(1, 2)$ and a closure relation, the HNC approximation reading

$$c(1, 2) = h(1, 2) - \ln[g(1, 2)] - v_{12}, \quad r_{12} > D, \quad (3.16)$$

$$g(1, 2) = 0, \quad r_{12} < D, \quad (3.17)$$

in the case of hard spheres. It can be shown [28] that this approximation is equivalent to a cluster expansion using an infinite number of f -integrals, neglecting only a certain class, the so-called bridge diagrams that appear only in higher orders.

Wertheim [29] and Nienhuis and Deutch [30] used the so-called mean spherical approximation (MSA) [31] to calculate the initial susceptibility of DHS. In the MSA (3.16) is replaced by

$$c(1, 2) = -v_{12} \quad \text{for } r_{12} > D, \quad (3.18)$$

effectively using the approximation $\ln[g(1, 2)] = \ln[1 + h(1, 2)] \approx h(1, 2)$, which is correct for large distances, where $h(1, 2)$ is small. Wertheim showed that this equation together with (3.15) allows a simple ansatz, representing the dependence of the correlation functions on \mathbf{m}_1 and \mathbf{m}_2 as linear combinations of three functions. He sets

$$h(1, 2) = h_S(r_{12}) + h_D(r_{12})f_D(\hat{\mathbf{m}}_1, \hat{\mathbf{m}}_2) + h_\Delta(r_{12})f_\Delta(\hat{\mathbf{m}}_1, \hat{\mathbf{m}}_2) \quad (3.19)$$

with

$$f_{\Delta}(\hat{\mathbf{m}}_1, \hat{\mathbf{m}}_2) = \hat{\mathbf{m}}_1 \cdot \hat{\mathbf{m}}_2, \quad (3.20)$$

$$f_{\text{D}}(\hat{\mathbf{m}}_1, \hat{\mathbf{m}}_2) = 3(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{m}}_1)(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{m}}_2) - \hat{\mathbf{m}}_1 \cdot \hat{\mathbf{m}}_2. \quad (3.21)$$

$g(1, 2)$ and $c(1, 2)$ have a similar representation with the same f_{D} and f_{Δ} . The MSA then provides an implicit solution for χ that is given by the three equations

$$\chi = \frac{\chi_{\text{L}}}{q(-x)}, \quad \chi_{\text{L}} = q(2x) - q(-x), \quad q(x) = \frac{(1+2x)^2}{(1-x)^4}. \quad (3.22)$$

Here, χ depends only on $\chi_{\text{L}} = 8\phi\lambda$ but not on ϕ and λ separately. Expanding χ in powers of χ_{L} yields (3.8) again for the leading terms.

In 1974, Verlet and Weis [32] proposed an improved theory. Therein they replace the term $h_{\text{S}}(r)$, which does not depend on the dipolar character of the fluid, by a better result for nonpolar hard spheres. Stell and Weis [33] calculate the initial susceptibility of DHS using this modification and a further improved version. They get larger values for χ that agree better with the Monte Carlo data.

Patey [34] improves the theory of Wertheim by retaining the ansatz (3.19) but expanding the full relation (3.16) linear in f_{D} and f_{Δ} . This approach is known as linear HNC (LHNC), although it was pointed out later that an equivalent theory was proposed already in 1973 by Wertheim [35] himself, called the single-superchain theory. In contrast to the MSA, the LHNC requires a numerical calculation of the correlation functions $h_{\text{S}}(r)$, $h_{\text{D}}(r)$, etc to find the initial susceptibility. Within the LHNC χ depends on both ϕ and λ independently. Patey did not apply the ‘pure’ HNC but uses again h_{S} and c_{S} from the system of nonpolar hard spheres as a system of reference (known as reference LHNC or RLHNC).

The RLHNC was followed by the reference quadratic HNC (RQHNC) proposed by Patey *et al.* In [36] this approach is applied to DHS. In the RQHNC (3.16) is expanded up to quadratic terms in f_{D} and f_{Δ} . Differences in χ between RQHNC and RLHNC amount only to a few per cent for $\lambda < 2$ and relatively large $\phi \approx 0.4$. But they are more significant for larger λ . However, later on it turned out in Monte Carlo simulations (see section 3.3) that both theories overestimate χ here—the apparently better RQHNC even more so than the RLHNC.

These authors also considered Stockmayer particles, using DHS as a reference system. They argue that a Stockmayer system with $\phi = 0.8\pi/6$ and $1/v_0 = 1.35$ should be similar to a system of DHS with the same ϕ for not too large a λ . Indeed, the results for the susceptibility do not differ very much for $\lambda < 2$. For higher coupling constants the RQHNC now gives smaller values for χ than the RLHNC.

Agrafonov *et al* [37] expand the full HNC equation in terms of λ and obtain the result

$$\frac{\chi^2}{\chi + 1} = 64\phi^2\lambda^2 \left(1 - \frac{8}{3}\phi\lambda\right) \quad (3.23)$$

for DHS. This expression yields after solving for χ the correct terms in $\phi\lambda$ and $\phi^2\lambda^2$. However, the next term is already incorrect. Chan and Walker [38] propose to expand the HNC approximation (3.16) given in the form

$$g(1, 2) = \exp[h(1, 2) - c(1, 2) - v_{12}], \quad (3.24)$$

in terms of rotational invariants for the orientational distribution of $\hat{\mathbf{m}}_1$ and $\hat{\mathbf{m}}_2$, truncating the expansion after a sufficient number of terms. They take into account, however, only three terms, namely the functions already used in the MSA, RLHNC, and RQHNC. Using this truncated HNC ansatz (THNC) they obtain even higher values for the susceptibility of DHS than predicted by the RQHNC.

In 1985 Fries and Patey [39] finally extend the ansatz (3.19) by adding more terms. They also use (3.16) in a form differentiated with respect to r_{12} eliminating the logarithmic term. Solving numerically the full RHNC approximation for DHS in that way they come to results for χ that are in much better agreement with Monte Carlo calculations. In the same year Lee *et al* [40] also investigate the Stockmayer system. As in the case of DHS the results agree better with numerical data than those of RLHNC and RQHNC. Finally, in 1986, Fries and Patey [41] apply the similar Percus–Yevick approximation to DHS finding it less well suited to predict the susceptibility than the RHNC and even the MSA.

Another modification is done by Lado [42], who varies the diameter of the nonpolar hard spheres in the system of reference to minimize the free energy. Lomba *et al* [43] solve the pure HNC, and find an even better agreement for the correlation functions with Monte Carlo calculations than for the RHNC.

3.3. Numerical simulations

Numerical simulations for calculating the susceptibility are mostly based on Monte Carlo methods. χ is either determined from the magnetization fluctuations $\langle M^2 \rangle$ in the absence of an external field or more directly from the magnetization in small fields. Calculating the susceptibility from the simulation results for $h(1, 2)$ is less appropriate since χ depends on the long-range behaviour of $h(1, 2)$, which cannot be determined accurately in finite simulation cells [36].

The influence of the distant dipoles can be incorporated by cutting off the dipolar interaction at a finite distance R_s and replacing the dipoles beyond R_s by a magnetic continuum of given χ (reaction field method). This susceptibility is either adjusted to the susceptibility of the simulated system or set to an arbitrary value (usually to $\chi = 0$). The chosen value then enters into the determination of the system's susceptibility.

Another method that is the most commonly used today is the Ewald summation based on a periodic continuation of the system together with an effective method for calculating the resulting total dipolar field. A discussion of the different methods can be found, e.g. in [44, 45]. The Ewald summation is described in [46].

Monte Carlo calculations of the free energy and other thermodynamical quantities that depend less strongly on the long-range nature of the dipolar forces were already performed in the seventies of the last century [32, 47–49]. Patey *et al* [34, 36, 50] calculate the correlation function $h(1, 2)$ and compare with the predictions of the LHNC and QHNC. An indirect comparison for the susceptibility, demonstrating the superiority of the MSA over the Onsager model can be found already in [49].

An early Monte Carlo calculation of χ is done by Adams and McDonald [46] in 1976. The authors, however, do not consider a fluid but fcc and sc lattices. They compare the Ewald sum and reaction field results for interaction strengths up to $\phi\lambda \approx 2$. Levesque *et al* [50] calculate χ for $\phi = 0.8\pi/6$ and $\lambda \leq 1$. They compare different methods and system sizes, and in 1982 they also studied the case $\lambda = 2$ [51]. In 1980, Adams [44] already considered $\lambda = 2.75$. Lado [52] uses a combination of a Monte Carlo calculation and RHNC for the long-range part of the potential.

Susceptibility calculations for Stockmayer particles were mainly performed for the values $\phi = 0.8\pi/6$ and $v_0 = 1/1.35$ as already considered by Patey *et al* [36]. Pollock and Alder [53] consider values for λ up to 3 while Adams and Adams [45] study different values for v_0 . Levesque and Weis [54] calculate χ for $\lambda = 2$, and Evans and Morriss [55] do so for $\lambda \leq 1.7$. Neumann *et al* [56] consider the parameter combination $v_0 = 1/1.15$, $\phi \approx 0.43$, and $\lambda = 2.6$. In 1984, Hesse-Bezot *et al* [57] used molecular dynamic methods to investigate $\lambda = 2$.

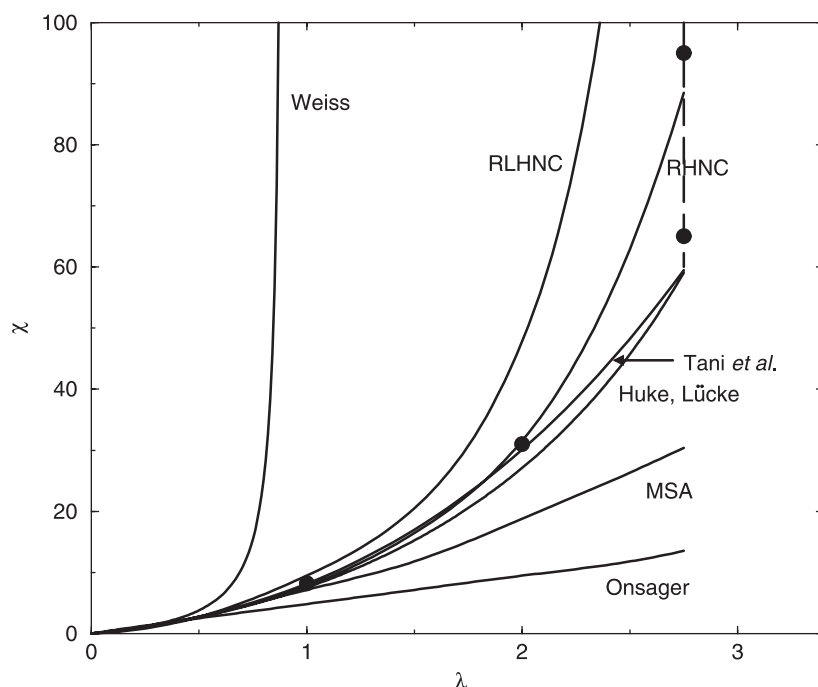


Figure 4. Comparison of theoretical results for the initial susceptibility of DHSs for $\phi = 0.8\pi/6$: Weiss [14] and Onsager [15] models, MSA by Wertheim [29], RLHNC results by Patey [34], RHNC results by Fries and Patey [39], cluster expansion result by Huke and Lücke [64], and the theory by Tani *et al* [26]. Full circles denote Monte Carlo data taken from a similar figure in [28].

Some of the works cited above treat the long-range nature of the dipolar interaction incorrectly (see the discussion by Neumann [58], Neumann and Steinhauser [59, 60] and Gray *et al* [61]). These papers also discuss the relationship between the reaction field and the Ewald sum approach. Further discussions of the Ewald summation and of other techniques used for dipolar systems were given recently by Wang *et al* [62, 63].

3.4. A comparison

Unfortunately, most of the earlier studies deal with systems with large volume fractions: a typical value is $\phi = 0.8\pi/6 = 0.419$. This is reasonable for customary polar liquids but it is very high for ferrofluids. Figure 4 shows a comparison of the most important theories discussed above for the case of DHS. In this figure χ is plotted as a function of λ for fixed $\phi = 0.419$. The Monte Carlo data (denoted by circles) and the results for RLHNC and RHNC were taken from [39] and a similar plot in [28]. Onsager theory and MSA clearly underestimate the Monte Carlo data while Weiss theory and RLHNC overestimate them. The RHNC works much better, as does the numerically much less complicated result by Tani *et al* [26]. The curve denoted as 'Huke and Lücke' refers to a cluster expansion theory [64] for the full magnetization curve. In the linear case considered here in this section, this theory [64] yields equation (3.8) and in addition also the $\phi^2\lambda^n$ terms given by equation (3.11).

The large scatter of the Monte Carlo results for $\lambda = 2.75$ is indicated in figure 4 as well. Surprisingly, there seems to be no final conclusion in the literature concerning the appropriate

value of χ for $\lambda = 2.75$ despite the fact that these different Monte Carlo results have been in the literature for quite a while. The different predictions for χ at $\lambda = 2.75$ are discussed in [60] where preference is given to a relatively low value of $\chi \approx 64$.

3.5. Other potentials

The susceptibility of some variants of the DHS and Stockmayer particle systems were also investigated. The system of dipolar sticky hard spheres, where the short-range potential contains an additional δ -function term, were investigated by Chapela and Martina [65] using integral theories like MSA and RLHNC to calculate χ . The authors come to contradictory results concerning the effect of the additional term in the potential on χ . Joslin and Gray [66] show that the second dielectric virial coefficient of dipolar sticky hard spheres is positive.

In 1989 and the following years, Kusalik [67–69] investigated dipolar soft spheres, i.e. Stockmayer particles without the attractive r^{-6} term in the short-range part of the potential using the RLHNC and the RHNC as well as Monte Carlo calculations. The Monte Carlo results for $v_0 = 1/1.35$, $\phi = 0.8\pi/6$, and $\lambda = 2$ are very similar to those for Stockmayer particles. But RLHNC and RHNC overestimate χ somewhat more.

Henderson *et al* [70, 71] apply the MSA, the theory by Tani *et al* [26], and Monte Carlo calculations to dipolar Yukawa particles with a hard core. Again, the results are found to be similar to those for DHSs and Stockmayer particles. The Monte Carlo data for χ at $\phi = 0.8\pi/6$ and $\lambda = 1, 2$ depend little on the strength of the Yukawa potential and they agree well with the Monte Carlo data for DHSs. The perturbation theory by Tani *et al* is found to reproduce the Monte Carlo data better than the MSA.

To summarize, the nature of the short-range interaction seems to have a rather weak influence on the susceptibility, even for relatively high densities.

3.6. Polydisperse theories

Normally, in real ferrofluids, the influence of polydispersity cannot be neglected. In the case of ideal paramagnetism discussed in section 2.1 the initial susceptibility is given by

$$\chi_L = \sum_i \frac{m_i^2}{3\mu_0 V k_B T}, \quad (3.25)$$

as follows from (2.5). Therefore, χ_L is proportional to the second moment of the distribution of the magnetic moments and larger than in the monodisperse case if the average particle volume is kept constant. When particle interactions are taken into account even higher moments of the distribution enter into the initial susceptibility.

Several of the theories discussed above were also extended to the system of polydisperse or at least bidisperse DHS, where the particles have different hard sphere diameters and/or carry different magnetic moments. In 1973, the MSA of Wertheim was applied to the polydisperse case by Adelman and Deutch [72], although restricted to particles with a common diameter. The authors defined an equivalent monodisperse system having the same thermodynamical properties.

Isbister and Bearman [73] generalize the MSA to mixtures with arbitrary diameters. The susceptibility predicted by this theory is calculated by Freasier *et al* [74]. The authors also describe a comparable monodisperse system giving at least approximately the same results. Ramshaw and Hamer simplify the evaluation [75]. Cummings and Blum [76] compare results of the MSA to Monte Carlo results for the bidisperse case.

Lee and Ladanyi [77] present an RLHNC extension and generalizations [78] of the RHNC and the cluster expansion by Tani *et al* [26]. They compare with the Monte Carlo data from [76],

coming to similar conclusions about the quality of the different theories as in the monodisperse case discussed above (section 3.4).

3.7. Applications to ferrofluids

With the preparation of highly concentrated ferrofluids, real physical systems became available that have much more in common with the simple model system of DHS than the ordinary polar fluids. Ferrofluids, thus, allowed not only more reliable experimental tests but they also initiated new theoretical investigations.

Two-dimensional Monte Carlo simulations on the initial susceptibility of ferrofluids were performed by Menear and co-workers in the early 1980s [79–83]. Here, the particles are not modelled as pure hard spheres but the sterical repulsion of the surfactants according to Rosensweig (2.15) is also taken into account. In [83] a polydisperse ferrofluid is simulated. In particular, the temperature dependence of the susceptibility entering via $\lambda \sim 1/T$ is investigated. A Curie–Weiss law $1/\chi \sim T - T_0$ is found, as is to be expected from simple mean field models, e.g. the Weiss model.

Bradbury and co-workers [84, 85] also perform full three-dimensional simulations for DHS with additional sterical repulsion and obtain good agreement with RHNC calculations. The authors again find a Curie–Weiss law for $\chi(T)$ but less pronounced than for the 2D calculations. The calculations are done for a small value of ϕ , $\phi = 0.01$, and very high λ up to 7.21. These values refer to the real hard sphere diameter. However, the dipolar coupling would be better characterized by using the total diameter of the particles, i.e. that of the core plus polymer layer. That would reduce λ to maximal values of 2.63. In this λ -range much simpler cluster expansion theories still work and reproduce the result. It should be mentioned that although $1/\chi = c(T - T_0)$ is a very good approximation in that range, the Weiss model already fails since it predicts significantly different values for c and T_0 .

A behaviour of $1/\chi \sim T - T_0$ is also found in experiments [79, 86]. The results in [79], however, rely on data in a narrow range of temperatures extending over an interval of about 60 K where only very strongly interacting ferrofluids should exhibit a pronounced nonlinear behaviour. In [86] a negative value for T_0 was found, i.e. a Néel behaviour that was not predicted by the theories. A more comprehensive experimental investigation of the initial susceptibility was published in 1990 by Holmes *et al* [87]. Inspecting a broader range of temperatures the authors show deviations from the Curie–Weiss law for ferrofluids based on magnetite. They also argue that the Néel behaviour found in [86] may result from measurements for too large fields, i.e. already in the nonlinear range of the magnetization curve. They find a linear and a quadratic term in the concentration dependence of the susceptibility. The nonlinear behaviour of $1/\chi(T)$ was confirmed by Williams *et al* [88] in 1993.

Morozov *et al* [89, 90] apply the MSA to ferrofluids. Further results can be found in [91]. The authors demonstrate good agreement with experiments concerning the concentration and temperature dependence of χ . As discussed above in section 3.4, the MSA does not seem to be a good theory for strongly interacting systems. The ferrofluids investigated ($\phi \leq 0.172$, $\chi \leq 10$), however, fall in a range where the difference in χ between MSA and cluster expansions [26, 64] is only a few per cent. Applying the formula (3.8) shows that the χ_L^3 term which is correctly predicted by the MSA gives only minor contributions to χ .

Pshenichnikov [93] compares several theories, namely the Onsager model, the Weiss model, the MSA and a theory by Ivanov *et al* [94] with experimental data in a similar range of ϕ and λ . The latter theory [94] deals with the equilibrium magnetization for arbitrary fields, and is explained in the next section. For the initial susceptibility this theory gives $\chi = \chi_L + \chi_L^2/3$, i.e. equation (3.8) up to second order. Pshenichnikov shows good agreement with both Ivanov's

theory and the MSA, thereby also indirectly demonstrating the small influence of the χ_L^3 term that is present in the MSA but not in Ivanov's theory. Both theories, however, fail to adequately describe the temperature dependence of ferrofluids with $\chi(T)$ lying in the range between ≈ 20 and 80.

Kalikmanov [92] proposes in 1999 the so-called algebraic perturbation theory that is corrected by Szalai *et al* [95] and found to be identical to the cluster expansion theory of Tani *et al* [26].

Van Ewijk *et al* [18] perform susceptibility measurements on highly concentrated ferrofluids and compare with different theories. For a ferrofluid with $\lambda \approx 2.7$ and $\chi_L \leq 6$, they find a surprisingly low susceptibility of $\chi \leq 10$, best described by the Onsager theory or the MSA. These results seem to contradict the data presented in figure 4, although ϕ is slightly higher there. Some theoretical support for these findings can, however, be found in a paper by Pshenichnikov and Mekhonoshin [96], who presented in 2000 Monte Carlo data in the same range of χ_L . For $\lambda = 3$ and $\lambda = 4$, they find similar low values for the susceptibility. They explain the low susceptibility with aggregates of particles that have a small combined magnetic moment and interact with the field only weakly.

4. Magnetization

The equilibrium magnetization of a ferrofluid cannot be described in general by a simple Langevin ansatz or its polydisperse generalization. Experimental hints to this fact can already be found in a paper published in 1979 by Tari *et al* [97], where a comparison of a magnetization curve with a theoretical curve based on an independently measured size distribution is made. However, the theories for the magnetization of, say, DHSs in arbitrary fields are less advanced than for the special case of the initial susceptibility. Most of the theories discussed below have been devised with regard to the application to ferrofluids. For this reason, many of them were directly or shortly thereafter extended to include the effects of polydispersity as well.

When comparing a polydisperse ferrofluid with a monodisperse one with the same average magnetic moment of the particles and the same volume fraction, the equilibrium magnetization curve will be steeper for small fields in the polydisperse case since the initial susceptibility is higher. The asymptotic behaviour for high fields will, however, be the same. This results in a maximal difference between the magnetization curves for medium fields $\alpha \approx 1$.

Pollock and Alder [53] and Adams and Adams [45] perform Monte Carlo calculations for the equilibrium magnetization of Stockmayer particles. In 1981 Høye and Stell [98] propose a mean field model based on general thermodynamic considerations and compare their results with the data from [53]. The magnetization in this model is given by

$$M = M_{\text{sat}} \mathcal{L} \left(\frac{m}{k_B T} H_{\text{eff}} \right), \quad (4.1)$$

where H_{eff} is an effective field,

$$H_{\text{eff}} = H + \frac{1}{3}(1 - \Theta)M. \quad (4.2)$$

Here, Θ is to be taken from the results for the initial susceptibility. For $\Theta = 0$ the formula reduces to that of the Weiss theory. Dikanskii [99] proposes a concentration dependent term for an effective field calculated from a fit to susceptibility data. Sano and Doi [100] investigate phase transitions in ferrofluids using a model of a randomly filled cubic lattice. As an additional result they obtain the Weiss expression for the equilibrium magnetization.

Woodward and Nordholm [101] propose an effective potential for the dipolar interaction that results from averaging over the orientations of the dipoles according to

$$\exp\left(\frac{-V_{12}^{\text{eff}}}{k_B T}\right) = \left\langle \exp\left(\frac{-V_{12}^{\text{DD}}}{k_B T}\right) \right\rangle_{\hat{m}_1, \hat{m}_2}. \quad (4.3)$$

The so-defined V^{eff} is then a function of particle separation and temperature. It vanishes for large distances as r_{12}^{-6} . In 1986 [102], these authors extended their ansatz to a theory for the equilibrium magnetization. They propose a functional for the free energy F of a magnetic continuum in a magnetic field. Minimized with respect to the orientational distribution of the dipoles it gives for zero field an expression for F that contains V^{eff} as the interaction potential. Including the external field, the dipolar interaction is described by a long-range part as in the Weiss model and a short-range part that is a generalization of V^{eff} which, however, depends also on the magnetic field. The magnetization has the form (4.1) and (4.2) with a function $\Theta(M, T)$ that can be calculated numerically. The authors compare the resulting initial susceptibility with the RLHNC predictions. The results are, however, not convincing: they are larger than in the RLHNC already for $\phi \approx 0.3$ and diverge for $\phi \approx 0.4$. Comparisons for DHS with the magnetization results of Høye and Stell can be found in [103].

Kalikmanov [13] and Berkovsky *et al* [104, 105] developed between 1985 and 1992 a thermodynamical theory for ferrofluids. Based on cluster expansion methods they calculate the magnetization in two special cases. They derive expressions for spherical geometries where $H = H_e - M/3$. For small fields, $\alpha \ll 1$, the authors obtain the following expression for the susceptibility with respect to the external field H_e :

$$\chi_e = \frac{\partial M}{\partial H_e} = 8\lambda\phi - \frac{160}{3}\lambda^3\phi^3. \quad (4.4)$$

If one restates this expression as a result for χ , a missing $\phi^2\lambda^2$ term appears and one obtains (3.8). For stronger fields they get

$$M = M_{\text{sat}}[\mathcal{L}(\alpha_e) + L_{1,2}(\alpha_e)\phi\lambda^2 f(\phi)]. \quad (4.5)$$

Here, $L_{1,2}(\alpha_e)$ is an analytic expression and $f(\phi)$ depends on the correlation function $g(1, 2)$ of nonpolar hard spheres that is used as a reference system. Again, by restating the expression in a form $M = M(H)$ an additional term of order $\phi\lambda$ shows up. Here, one has to note that M/M_{sat} is independent of ϕ and λ in leading order, whereas χ starts with a $O(\phi\lambda)$ term. Likewise, terms of order $\phi^m\lambda^n$ in M/M_{sat} always correspond to $O(\phi^{m+1}\lambda^{n+1})$ terms in χ .

Between 1990 and 1992 also Ivanov *et al* [94, 106–109] developed a thermodynamical theory of ferrofluids also using cluster expansion techniques. For a needle-shaped geometry in which $H_e = H$ they obtain the correct result in $O(\phi\lambda)$,

$$M = M_{\text{sat}}[\mathcal{L}(\alpha) + 8\phi\lambda\mathcal{L}(\alpha)\mathcal{L}'(\alpha)]. \quad (4.6)$$

A correct polydisperse generalization, replacing $\mathcal{L}(\alpha)$ by $\mathcal{L}^{\text{poly}}(\bar{\alpha})$ (2.7), is also given.

Lebedev [110] suggests applying the MSA to finite magnetic fields also. To that end, he replaces the equations (3.22) by

$$M(H) = \frac{M_L(H)}{q(-x)}, \quad \frac{dM(H)}{dH} = \frac{q(2x) - q(-x)}{q(-x)} \quad (4.7)$$

with $q(x)$ given as before by the third equation in (3.22). Thus, χ and χ_L in the first equation of (3.22) are replaced in (4.7) by M and M_L , respectively. The second equation of (4.7) can be derived by combining the first two equations in (3.22) and replacing the initial susceptibility χ by the susceptibility $dM(H)/dH$ for finite fields. Hence, the equations (4.7) reduce to the MSA for small fields.

In 1990, Morozov *et al* [91, 111] presented a real extension of the MSA aimed at predicting the magnetization for arbitrary fields. They use the so-called Lovett–Mou–Buff–Gubbins equation [112, 113] to relate the one-particle probability density $\rho(\mathbf{r}, \mathbf{m})$ in the presence of an external field to the direct correlation function $c(1, 2)$ taken in the MSA form of equation (3.18). With Wertheim’s method [29] they then derive from the Ornstein–Zernike equation two independent Percus–Yevick like equations for a hard-sphere fluid with renormalized densities. As a result of this approximation scheme they present M given by the Langevin magnetization for an effective field $C\alpha$:

$$M = M_{\text{sat}} \mathcal{L}(C\alpha). \quad (4.8)$$

Here, C has to be calculated as follows: let

$$A = \frac{\partial \ln M}{\partial \ln(CH)} \quad \text{and} \quad 35x^2 - 5(10 - 3A)x - 7(7 + 3A) = 0. \quad (4.9)$$

With x_1 and x_2 being two solutions of the quadratic equations, C must be given self-consistently by

$$C = \left[1 + \frac{4\pi}{3}(1 + x_1) \frac{M}{H} \right] \frac{1}{q(x_1 y)} = \left[1 + \frac{4\pi}{3}(1 + x_2) \frac{M}{H} \right] \frac{1}{q(x_2 y)}. \quad (4.10)$$

Here, y is defined via the second equality and $q(x)$ is still given by the expression in (3.22). The authors also propose a polydisperse generalization. Comparisons with experiments can be found in [91, 111]: the MSA reproduces well the magnetization curves of polydisperse ferrofluids with saturation magnetizations up to 87 kA m^{-1} .

Based on preliminary work [114] concerning the two-dimensional case Bradbury and Martin [115] and independently Ayoub *et al* [116] develop the so-called dimer model of dipolar interaction. The partition function for N particles is written as the $(N/2)$ th power of a two-particle partition function calculated via a cluster expansion assuming that the two particles are closer than a typical next-neighbour distance. This model has several shortcomings. The long-range character of the forces is not taken into account leading to an expression for M in which the $\phi\lambda$ term is missing. Also the calculated $O(\phi\lambda^2)$ terms are wrong in both cases and moreover they do not agree with each other¹. Even the corrected calculation leads to a wrong result by a constant factor due to the somewhat arbitrary assumption of using the next-neighbour distance as a cutoff.

Zubarev and Iskakova [117] present a magnetization equation relying on a model of noninteracting magnetic clusters (chains). They derive the equilibrium distribution of chain lengths based on a simple expression for the free energy of a system of such chains. The magnetization is then formally the equilibrium magnetization of a polydisperse ideal paramagnetic gas where the chains are the fundamental constituents. The chain length distribution is, however, a function of the magnetic field and furthermore of ϕ and λ . Abu-Aljarayesh and Migdadi [118] investigate this theory further, calculating the entropy and some equilibrium magnetization curves.

Pshenichnikov *et al* [119] suggest an equation for the equilibrium magnetization that reads

$$M = M_{\text{sat}} \mathcal{L} \left[\alpha + \frac{m M_{\text{sat}}}{3k_{\text{B}} T} \mathcal{L}(\alpha) \right]. \quad (4.11)$$

It agrees better with their experiments in the range of medium fields than the expression (4.6) that gives the same initial susceptibility. Furthermore, it gives more consistent results for the

¹ In [115] the last term in equation (44) must read $32(\sinh \alpha/\alpha - 2 \cosh \alpha/\alpha^2 + 2 \sinh \alpha/\alpha^3)^2$. In [116] the last term in equation (12) must read $3i_2^2(\alpha)/\alpha^2$.

diameter distribution of polydisperse ferrofluids at different stages of dilution. Also, their earlier result (4.6) can be derived from equation (4.11) by expanding the latter up to first order in ϕ and λ since $mM_{\text{sat}}/3k_{\text{B}}T = 8\phi\lambda$. On the other hand, equation (4.11) can be obtained from the Weiss formula (2.8) by iterating and stopping after the first step. However, equation (4.11) has the advantage over equation (4.6) that it always produces physically sound magnetization curves with M being a monotonic function of H with $0 \leq M < M_{\text{sat}}$. This is not the case for equation (4.6) when $\phi\lambda$ becomes too large.

In 2000, the authors of this review [64] perform a cluster expansion calculation to derive some of the terms in the sum

$$M = M_{\text{sat}} \left[\mathcal{L}(\alpha) + \sum_{a,b} L_{a,b}(\alpha) \phi^a \lambda^b \right], \quad (4.12)$$

namely a number of $L_{1,b}$ terms and the leading term, $L_{2,2}$, in $O(\phi^2)$. All the calculated terms are given as analytic expressions. The first one, $L_{1,1}(\alpha) = 8\mathcal{L}(\alpha)\mathcal{L}'(\alpha)$, yields the result (4.6) of Ivanov *et al* and $L_{1,2}$ is the same as in the expression (4.5). A generalization to the polydisperse case is given in [120].

In the same year, Klapp and Patey [121] present results obtained from two different integral equation approximation schemes that use either the MSA or the RHNC as two-particle closures. The singlet density ρ and the external field are related in formally exact ways either via the first BGY hierarchy equations [28] to the pair correlation function $g(1, 2)$ or via the Lovett–Mou–Buff–Wertheim equations [112, 122] to the direct correlation function $c(1, 2)$. The results turn out to be strongly dependent on the form of the closure used. For example, the authors find in zero field, ferromagnetic behaviour using the RHNC closure that is absent in case of the MSA closure [121].

Pshenichnikov and Mekhonoshin [96] present Monte Carlo results for a finite system giving χ as a function of χ_{L} for fixed $\lambda = 1, 3$, and 4. They also calculate the equilibrium magnetization for a volume fraction $\phi = 0.226$ and $\lambda = 1$ and 4. The results for $\lambda = 1$ can be quite well described by equation (4.11). The equilibrium magnetization for $\lambda = 4$ is, however, smaller than that predicted by any theory for interacting particles and is explained as being due to the formation of clusters with a small total magnetic moment.

Ivanov and Kuznetsova [123] perform a cluster expansion calculating the $O(\phi^2\lambda^2)$ term in M/M_{sat} . While their results are not given explicitly they seem to reproduce [124] the result of [64]. The authors of [123] suggest an extension of equation (4.11) that reads

$$M = M_{\text{sat}} \mathcal{L} \left(\frac{mH_{\text{eff}}}{k_{\text{B}}T} \right), \quad H_{\text{eff}} = H + \frac{1}{3} M_{\text{sat}} \mathcal{L}(\alpha) + \frac{1}{144} M_{\text{sat}}^2 \mathcal{L}(\alpha) \frac{\text{d}}{\text{d}H} \mathcal{L}(\alpha). \quad (4.13)$$

A polydisperse generalization, replacing \mathcal{L} by $\mathcal{L}_{\text{poly}}$ is also given. The formula (4.13) produces sound magnetization curves for arbitrary ϕ, λ as in the case of equation (4.11). When comparing the results of [123] with those of the cluster expansion [64] one has to be aware that in [123] some calculated terms that do not contribute to the initial susceptibility were discarded in order to be able to write the result in the form (4.13). Thus, when this equation is expanded in $\phi\lambda$ one does not recover the general $O(\phi^2\lambda^2)$ term of (4.12), while it is reproduced in the expression for the initial susceptibility.

Molecular dynamics simulations of monodisperse dipolar systems were performed in 2002 by Wang *et al* [125] for several combinations of ϕ and λ . They use a modified Stockmayer potential with a shifted and truncated Lennard–Jones potential. Comparing with the theory of Ivanov and Kuznetsova [123] they find good agreement for $\lambda \leq 2$, but with deviations for higher λ , both for the magnetization curve and the initial susceptibility. The authors also demonstrate that M and χ are not functions of the product $\phi\lambda$ alone as predicted in [123] and

that the theory [123] becomes less applicable for large λ and small ϕ . Furthermore, they analyse the microstructure of the simulated fluid and determine the length distribution of chains. They show that the susceptibility can be better explained by replacing the Langevin susceptibility in (3.8) by the susceptibility of a system of ideal dipolar chains with a length distribution found in the simulations. In 2004 Ivanov *et al* [126] use a variant of the chain formation model of [117] to obtain a length distribution independent of the simulation results. In 2003, Wang and Holm published simulation results on bidisperse dipolar systems [127]. For a system containing particles with $\lambda = 1.3$ and $\lambda = 5.32$ and a total volume fraction of $\phi = 0.07$ they report that the theory of Ivanov and Kuznetsova [123] works well for volume fractions $\phi_L \leq 0.02$ of the large particles. However, differences become apparent for larger fractions of the large particles, say, $\phi_L = 0.05$ and even more so in the limiting case, $\phi_L = 0.07$, without any small ones, i.e. for a monodisperse fluid containing only large particles. Kristóf and Szalai [128] performed, in the same year, Monte Carlo simulations for two polydisperse ferrofluids with realistically chosen parameters. They find good agreement with the polydisperse version of (4.6).

Raşa *et al* [129] measure in 2002 the initial susceptibility and the magnetization of ferrofluids at various stages of dilution. The susceptibility is found to be best described by Ivanov's theory [94] and the MSA [111].

5. Nonspherical potentials and higher-order magnetic moments

Real ferrofluid particles can be expected to have small deviations from a perfectly spherical shape. Such deviations affect not only the form of the nonmagnetic part of the interparticle potential, but the magnetic interaction potential will also be changed since the magnetic field of a nonspherical magnetized particle will contain higher magnetic moments beyond the dipolar one as well. Both features will have some influence on the susceptibility and the magnetization. The susceptibility of systems of simple nonspherical dipolar particles and particles with dipolar *and* quadrupolar particles were also investigated on some occasions.

A straightforward generalization of the system of DHS is the system of dipolar hard ellipsoids. Joslin calculates [130] numerically the second dielectric virial coefficient for this system for different λ and axis ratios. For spheres, this coefficient is positive, see equation (3.11). However, it depends strongly on the axis ratio: it grows with growing prolateness but it becomes negative even for slightly oblate particles. Perera and Patey [131] investigate this system by means of the HNC, finding the same trend.

Dimer ferrofluid particles were modelled by dipolar fused spheres (dumbbells). A Monte Carlo simulation of Stockmayer dimers can be found in a paper of de Leeuw and Quirke [132]. χ is found to decrease with growing sphere separation. Dimers of DHSs are simulated by Lomba *et al* [133]. They study the density dependence of the susceptibility for fixed dipolar strength and find a decrease of χ at high densities due to the hindrance of particle rotation.

Dipolar particles of spherical shape that carry, however, an additional quadrupolar moment are investigated with respect to their susceptibility by Patey *et al* [134] and Carnie and Patey [135] for different choices of the quadrupolar tensor using integral theories. The susceptibility is shown to decrease with growing quadrupolar moment.

In view of the fact that the average shape of a ferrofluid particle is roughly spherical it seems to us that systems of identical nonspherical or multipolar particles that have been considered in the literature are probably less applicable to the description of real ferrofluids than systems of DHS or Stockmayer particles. To improve upon monodisperse models of identical particles one would have to consider at least binary mixtures of particles of different nature, e.g. of prolate and oblate ellipsoids or of monomers and dimers.

6. Phase transitions

Two different kinds of phase transitions are addressed in this section. The first one is the condensation of magnetic particles into a denser phase. The second one is the transition from an isotropic nonmagnetic phase to a state with spontaneous long-range magnetic order.

There are other, less intensively investigated transitions in systems of dipolar particles such as fluid/solid transitions [136–138] or the demixing of particle species in bidisperse systems [139]. Another example of a phase transition, which we do not touch on here, is the emergence of a dipole glass state at low temperatures for systems of dipoles in a solid matrix, like frozen ferrofluids [140–142]. The existence of such a state in liquid ferrofluids has been reported, e.g. in [143]. But then it was shown that the observed temperature behaviour of the susceptibility can be explained as an effect of the temperature dependence of the viscosity of the carrier liquid [144]. A review of this subject for the electrical case can be found in [145].

6.1. Dilute/dense phase transitions

Ferrofluid particles possess an isotropic attractive potential: the outer tail of the van der Waals attraction that is not shielded by the steric or electrostatic repulsion. This can result in the creation of small clusters, as seen by Donselaar *et al* [146] in cryo-TEM images.

When the attractive potential has a strength of about $k_B T$ a dilute/dense phase transition should occur. It is possible to weaken the repulsive shielding of the ferrofluid particles enough to allow such a reversible phase transition without reducing it so much that an irreversible agglomeration takes place as observed in experiments with ionic ferrofluids [147–150]. This reversible transition is a kind of gas/liquid transition. It affects, however, only the magnetic subsystem of the ferrofluid—the carrier system always remains a liquid. We will use the term ‘dilute/dense’ instead of ‘gas/liquid’ phase transition also when referring to the common model systems without any carrier liquid to avoid a confusion of terms. The dense phase exists in the form of (mesoscopic) droplets.

In a typical ferrofluid the isotropic interaction is rather weak. In figure 3, e.g. the best fitting Lennard–Jones potential has a depth of $v_0 = 0.16$. Since a dilute/dense transition does not occur in pure Lennard–Jones systems when $v_0 < 0.76$ [151] one concludes that such a phase transition might possibly occur in ferrofluids with smaller v_0 only if the dipolar interactions have a net supporting, i.e. attractive effect.

A dilute/dense transition observed in experiments, which might be caused mainly by dipolar interactions, was reported by Mamiya *et al* [19]. These authors investigate a ferrofluid consisting of iron-nitride in kerosene with $3 \lesssim \lambda \lesssim 10$. They find a hysteresis in χ as a function of temperature when ϕ is roughly between 0.002 and 0.06. For larger ϕ the hysteresis vanishes. Furthermore, $\chi(T)$ is larger when cooled than when reheated in the hysteresis region. The authors explain this with the presence of closed rings or drops of particles with mostly vanishing total magnetic moment in the low-temperature phase.

When studying phase transitions of DHSs, the dipolar coupling constant $\lambda \sim 1/T$ serves as the dimensionless inverse temperature. Likewise, ϕ serves as the dimensionless density. In the case of Stockmayer particles both λ and v_0 provide an inverse temperature scale and, in general, the latter is used. The other quantity or the temperature independent quantity λ/v_0 serves as an additional parameter.

Considering these main model potentials, it is clear that a system of Stockmayer particles will exhibit a dilute/dense phase transition below some critical T_c since it contains the Lennard–Jones potential as a special case. The additional dipole–dipole interaction raises T_c (see later) — an effect that cannot be explained trivially, since this interaction can be both repulsive and

attractive and its orientational mean is zero. However, an averaging procedure as in (4.3) that takes into account the fact that attracting configurations are preferred yields an attracting mean dipolar contribution.

In the case of DHSs and also soft spheres it is even more unclear *a priori* whether such systems show a dilute/dense phase transition since here the dipolar interaction is the only one that could cause such a behaviour. As we will discuss below, the question whether this phase transition exists or not in pure DHS systems is still being debated.

In systems of Stockmayer particles with small v_0 strong dipolar couplings seem to be necessary in order to raise the critical temperature enough to observe a dilute/dense transition. For example, Frodl and Dietrich [152] find, using a density-functional theory, that already a dipolar coupling constant of $\lambda \approx 1.5$ is necessary to lower the critical point to about $v_0 \approx 0.4$. According to Monte Carlo calculations by Smit *et al* [153] and van Leeuwen *et al* [154, 155] done between 1989 and 1994 it is $\lambda \approx 2.35$ for $v_0 \approx 0.4$. Monte Carlo calculations of Stevens and Grest [156] from 1995 give a very similar value here. This means that common ferrofluid particles with small v_0 will not show a dilute/dense phase transition within a reasonable temperature range except in systems where the dipolar interaction is the by-far dominating contribution. It may seem that, in such a case, the short-range attraction should play no role any more and that Stockmayer particles with high λ should behave similar to DHSs. However, as mentioned already this does not seem to be the case.

In the 1970s and 1980s the dilute/dense phase transition of DHSs was studied by using mainly analytical and semianalytical theories that were conceived to investigate the equilibrium magnetization or initial susceptibility. A usual kind of (V, T) phase diagram was found with a roughly parabolic coexistence curve and no phase transition above some critical T_c (i.e. below some critical λ_c). However, the calculated critical values differed somewhat.

Rushbrooke *et al* [157] present in 1973 the coexistence curve based on the MSA and a perturbation expansion ansatz by Stell *et al* [158]. An early Monte Carlo calculation was undertaken by Ng *et al* in 1979 [159] using only $N = 32$ particles. Woodward and Nordholm [101] use three similar expressions for the free energy based on their effective potential (4.3) to calculate the coexistence curve. Kalikmanov and co-workers [13, 105] use the same effective potential and replace it by a related Lennard–Jones potential to find the critical point. Joslin and Goldman [25], finally, calculate in 1993 the critical point by using second and third virial coefficients obtained from numerically calculated cluster integrals. The approximate results for the critical point (ϕ_c, λ_c) are summarized in the following table:

Work	[157](MSA)	[157](SRN)	[159]	[101]a	[101]b	[101]c	[13]	[25]
ϕ_c	0.056	0.083	0.15	0.17	0.14	0.13	0.16	0.028
λ_c	4.4	3.6	4.0	2.3	2.9	2.9	1.5	3.8

Despite the different predictions for the critical point, there was a general belief at that time in the existence of a first-order dilute/dense phase transition. This changed when a couple of new Monte Carlo simulations failed to detect such a transition.

Caillol [160] performs a Monte Carlo simulation with up to 512 particles and does not find a phase transition for the two coupling constants $\lambda = 4.5$ and $\lambda = 5.55$ and volume fractions $0.08(\pi/6) < \phi < 0.38(\pi/6)$. Furthermore, Monte Carlo calculations by Weis and Levesque [136, 161] done for systems of similar size do not show a dilute/dense transition at low densities, $0.01 < \phi < 0.16$, even for couplings as strong as $\lambda = 12.25$. Instead association of particles into chains is observed.

Van Leeuwen and Smit [162] consider a dipolar fluid with a modified Lennard–Jones short-range potential of the form

$$v_{ij}^{\text{SR}} = 4v_0 \left[\left(\frac{D}{r_{ij}} \right)^{12} - c \left(\frac{D}{r_{ij}} \right)^6 \right]. \quad (6.1)$$

The introduction of the parameter c allows a smooth transition from dipolar soft spheres ($c = 0$) to Stockmayer particles ($c = 1$)². For a fixed v_0 the authors do not find a dense–dilute phase transition if $c < 0.3$ and conclude that the dipolar soft and hard sphere fluid will not exhibit such a transition. They observe chain formation instead.

Levesque and Weis [163] investigate the system of DHS with a dipolar coupling $\lambda = 12.25$ in an even larger range of volume fractions, $0.005(\pi/6) < \phi < 0.8(\pi/6)$, and in addition the range $4 < \lambda < 12.25$ for $\phi = 0.01(\pi/6)$ and $\phi = 0.3(\pi/6)$. For $\lambda = 12.25$ they find long chains when $\phi < 0.2(\pi/6)$. For higher volume fractions the situation is less clear. Shorter chains can still be found applying an energetic criterion, but these chains are not directly visible in the configuration snapshots. At $\phi = 0.6(\pi/6)$ and higher they find a ferroelectric state (see later). They observe a continuous association of monomers into chains when increasing λ for fixed volume fraction.

In 1994 and 1995, Stevens and Grest [156, 164] performed Monte Carlo calculations for dipolar soft spheres both with and without an applied magnetic field. They do not find a phase transition for the zero field case. Instead, they also observe, in this system, chain formation similar to that of DHS. However, still in 1995, the same authors [151] report a dilute/dense phase transition for Monte Carlo simulated Stockmayer fluids, where the critical temperature measured in $1/v_0$ and the critical density depend linearly on λ/v_0 . The critical parameters agree well with those found by Hendriks and co-workers [153, 154], Leeuwen [155] who had already considered a smaller range of λ/v_0 between 1989 and 1994.

The association of ferrofluid particles into chains for $\lambda \gg 1$ and low densities is a natural consequence of the highly directional dipolar potential [165, 166]. The magnetic moments should be oriented in these chains in the energetically most favourable head-to-tail configuration with energy $-2\lambda k_B T$ for a pair of them. The numerical observation of chain formation instead of a homogeneous dilute/dense transition leads to a number of papers considering simple thermodynamic models of chains of DHSs of similar particles. Small-angle neutron scattering experiments [167] have provided experimental support for the existence of such chain structures. Recently, a direct visual confirmation of the existence of chain structures in cryo-TEM images was achieved by Butter *et al* [168].

Sear [169] argues that the chains should interact with each other only weakly and so he considers a model of only nearest-neighbour interacting particles, forming ideal chains. He compares the results with those obtained in simulations in [163] and [160]. Van Roij [170] investigates the competition between condensation due to isotropic interactions and chain formation due to dipolar forces.

The most detailed model was proposed by Telo da Gama and co-workers [171, 172] who also take into account chain–chain interactions. They compare them with results from [160] and [161]. These authors find semi-quantitative agreement concerning the critical points with the results of [162] for Stockmayer-like potentials. They predict a dilute/dense phase transition to appear also for particles with weak isotropic attraction (but not for DHS) where, in both phases, chaining should be observed. However, they also note that finite-size effects may make it difficult to observe this kind of transition in simulations. In 1999, Tavares *et al* [173] improved

² It should be noted however that the potential for $c \neq 0$ can still be written as Stockmayer potential with different v_0 and D .

the theory and performed their own Monte Carlo calculations at low densities $\phi = 0.05(\pi/6)$ and $5 \lesssim \lambda \lesssim 7.6$. Also, in 1999, Levin [174] used the Debye–Hückel–Bjerrum theory to show that the clustering of particles into chains in the system of DHS should always reduce the density of free particles below the density necessary for a phase transition.

Klapp and Forstmann [175, 176] investigate Stockmayer and DHS fluids using the RHNC. There exists a parameter region of low temperatures where the RHNC fails to provide solutions. The boundary of this region is believed to be connected with phase transitions. At small densities the authors find growing fluctuations near this boundary that seem to represent the appearance of chains. There are analogous hints for a dilute/dense phase transition in the case of Stockmayer particles but not for DHS.

By the end of the 1990s there was thus a kind of consensus reached that DHS do not show a dilute/dense phase transition because of the competing process of chaining. But then Shelley *et al* [177], in 1999, performed Monte Carlo simulations for dipolar hard dumbbells and spherocylinders. They find a dense/dilute phase coexistence even for almost spherical particles and observe, however, increasing sampling problems. They suggest that these sampling problems may have prevented the discovery of such a coexistence for DHS. Camp *et al* [178], therefore, reinvestigate, in 2000, the system of DHS with Monte Carlo simulations. For $\lambda = 7.56$ they indeed find evidence for one or even two isotropic dense/dilute phase transitions. In the same year, Camp and Patey [179] studied the evolution of a system with $0.001(\pi/6) \leq \phi \leq 0.6(\pi/6)$. The simulation shows ring structures for the smallest ϕ , chain structures for intermediate densities ($0.06(\pi/6) < \phi < 0.35(\pi/6)$), where the phase transitions reported in [178] take place, and a structureless dense liquid for still larger ϕ .

Pshenichnikov and Mekhonoshin [180, 181] also perform Monte Carlo simulations of DHS using a finite system. They find an ordinary dilute/dense transition with a critical point already at $\lambda_c \approx 3$ and $\phi_c = 0.034$. This result is at odds with previous ones, possibly because the authors of [180, 181] use, instead of the generally preferred Ewald summation technique, finite cylindrical and spherical systems with 1000 particles. They remark that periodic boundary conditions may cause errors in the case of long-range forces. However, a finite system with $N = 2046$ particles was previously used by Levesque and Weis [163] for a volume fraction near ϕ_c and much higher λ without finding a phase separation.

Morozov and Shliomis [182] study the intrachain correlations of chains of DHS for large λ by performing a $1/\lambda$ -expansion of the required statistical integrals. They find a persistence length of $\lambda/2$ for $\lambda \rightarrow \infty$. Considering nonideal chains, they predict a transition from chain to globule structures at $\lambda = 3.2$.

As discussed above, chaining in monodisperse systems has a strong influence on the dilute/dense phase transition. When comparing with experiments done on real ferrofluids it should, therefore, also be noted that polydispersity affects the lengths of chains as theoretically predicted by Kantorovich and Ivanov [183], and demonstrated in simulations by Wang and Holm [127].

The phase behaviour of DHS and similar systems is further complicated when taking into account a nonvanishing magnetic field. Sano and Doi [100] investigate the dilute–dense phase transition in the presence of a magnetic field in a randomly filled lattice of dipolar particles. In zero field they find a rather small critical λ and a rather large critical concentration in this system. In general, a magnetic field makes a phase transition more likely and increases the density differences of coexisting phases. But there is a λ -interval near the zero-field λ_c where a phase transition occurs for small and large fields but not for intermediate fields.

Stevens and Grest [151, 156, 164], who failed to find a dilute–dense transition for dipolar soft spheres in zero field, demonstrate the existence of such a transition in Monte Carlo simulations with applied fields. However, the two phases cannot be described as simple

homogeneous gas and liquid phases since long chains are present in both of them. For both dipolar soft spheres and Stockmayer particles they show that λ_c becomes smaller in applied fields whereas the value $\phi_c \approx 0.017$ remains mainly unchanged. In [171], however, it is argued that this observed phase transition for soft spheres may just be an artefact of the insufficient system size.

Kusalik [184] does not find a phase separation in the system of dipolar soft spheres at high fields. However, his value of $\lambda \approx 3$ is smaller than those considered by Stevens and Grest, who show that $\lambda_c > 5$ even for infinite fields. The field dependence of λ_c and ϕ_c in the case of Stockmayer particles is also studied with Monte Carlo techniques by Boda *et al* [185]. The authors find very similar results to those of Stevens and Grest. Szalai *et al* [186] find also the same qualitative behaviour when they study dipolar Yukawa particles using the MSA.

Klapp and Forstmann [187] investigate perfectly aligned DHS, i.e. the infinite-field limit within the framework of the RHNC. They also do not find a dilute/dense phase transition up to $\lambda \approx 5$.

Zubarev and Iskakova [188, 189] investigate an interacting variant of their chain model that has already been used to calculate the equilibrium magnetization in [117, 118, 126] and show that, in this model, chain formation prevents a dilute/dense transition in the infinite field limit.

Morozov and Shliomis [182] find that nonideal chains gain stability against the transition to a globular cluster in applied fields.

6.2. Ferromagnetic phases

Here, we review papers that have addressed the question of whether the classical dipolar interaction between the nanoscale particles in a ferrofluid suffices to induce long-range orientational order of the magnetic dipoles in a liquid state without positional order, i.e. with homogeneously distributed particle positions.

Already, the oldest model for the equilibrium magnetization of dipolar interacting particles, namely the Weiss model allows ferromagnetic solutions, i.e. a spontaneously generated equilibrium magnetization $M \neq 0$ for $H = 0$: equation (2.8) reads, in a needle-shaped probe geometry, for which $H = H_e$,

$$M = M_{\text{sat}} \mathcal{L} \left(\frac{mM}{3k_B T} \right) \quad (6.2)$$

when $H = H_e = 0$. This equation has solutions with $M \neq 0$ when $M_{\text{sat}} m / 3k_B T = \chi_L = 8\phi\lambda$ exceeds 3. Approaching this critical value, $\chi_L = 3$, of the Langevin susceptibility the initial susceptibility (2.9) of the Weiss model undergoes a divergence. While the existence of a ferromagnetic state for such a rather large range, $\phi\lambda > \frac{3}{8}$, of parameters can be ruled out experimentally there are experimental hints for a ferromagnetic phase in the paper by Mamiya *et al* in 2000 [19], where they find growing ferromagnetic fluctuations in their iron-nitride ferrofluid, at low temperatures, for $\phi \approx 0.15$.

It should be noted that the above mentioned divergence of χ disappears when the next diagonal term in the (ϕ, λ) expansion, i.e. the $\phi^2 \lambda^2$ term is included in the expression for the equilibrium magnetization [64]. In this extended Weiss model, one has

$$M = M_{\text{sat}} \left[\frac{1}{3} \alpha_{\text{eff}} - \frac{20}{9} \phi^2 \lambda^2 \alpha_{\text{eff}} - \dots \alpha_{\text{eff}}^3 + O(\alpha_{\text{eff}}^5) \right], \quad (6.3)$$

where $\alpha_{\text{eff}} = (m/k_B T)(H + (M/3))$ is the Weiss mean field. In this case, the additional $\phi^2 \lambda^2$ term prevents the existence of ferromagnetic solutions for $H = 0$.

Zhang and Widom [190] extend the Weiss mean field theory, describing the local field as a stochastic variable and find that ferromagnetic phases do not exist for any value of λ if the volume fraction ϕ is smaller than some critical value 0.295.

At the end of the 1980s theoretical investigations based on model Hamiltonians [191] or model distribution functions [192] led to the prediction of ferromagnetic states only for particles with sufficient prolateness or oblateness. Nematic ferro- or antiferromagnetic phases were investigated using different methods in systems of dipolar ellipsoids and spherocylinders, e.g. in [131, 193–195].

But in 1992, MD calculations by Wei and Patey [196, 197] show the existence of ferromagnetic states in the system of dipolar soft spheres for $v_0 = 1/1.35$ and $\lambda/v_0 = 9$ for volume fractions above $\phi \approx 0.65(\pi/6)$. Since both the soft and the hard sphere potential, are not only spherically symmetric but also purely repulsive both should behave in a very similar manner. In 1992, Weis *et al* [198] did indeed find in Monte Carlo simulations ferromagnetic fluid and solid phases in the system of DHS in their investigated range $0.8(\pi/6) < \phi < 1.2(\pi/6)$ and $\lambda = 6.25$. More results for this range were reported 1993 in [136]. Weis and Levesque [161] find ferromagnetic states also at lower volume fractions $\phi \approx 0.3(\pi/6)$.

Wei *et al* [199] use density-functional methods to investigate the transition to ferroelectric phases in systems of dipolar hard and soft spheres reproducing the numerical results qualitatively but not quantitatively. More systematic investigations of the phase diagrams of Stockmayer particles are undertaken by Groh and Dietrich [200–202] also using density-functional methods. The critical temperatures are high. For $v_0 \approx 0.3$, e.g. they find a transition between a dilute, isotropic fluid and a dense, ferroelectric fluid already for $\lambda/v_0 = 4$ or $\lambda \approx 1.3$.

Zhang and Widom [203] investigate the phase diagram starting with the expression for the free energy of a van der Waals fluid with two additional terms modelling the magnetic properties. The authors find qualitatively similar phase diagrams: for high temperatures there is a continuous transition from a dilute isotropic to a dense ferromagnetic liquid that becomes first order at smaller temperatures. If the short-range interaction energy is small enough compared to the dipolar interaction energy, then there exists a temperature interval where the isotropic/ferromagnetic phase transition is preceded at smaller densities by a first-order transition between two isotropic phases having different densities.

Levesque and Weis [163] find ferromagnetic states for $\lambda = 12.25$ and $\phi > 0.6(\pi/6)$. They, however, now argue that the ferromagnetic phase reported in [161] for smaller ϕ was probably just a slowly decaying nonequilibrium state. Stevens and Grest [151, 156] find spontaneously magnetized fluid phases of Stockmayer particles for $\lambda = 4$ and $\phi > 0.47$. For soft spheres, they find such magnetic fluid phases for the investigated values $4 < \lambda < 9$ when ϕ is greater than a value that depends linearly on λ . They see hints for a hysteresis in the magnetic-isotropic transition for $\lambda = 16$.

Groh and Dietrich [204] study the phase transition properties of nonspherical dipolar hard particles using a density functional ansatz. In the special case of DHS they find no dilute/dense transition between isotropic phases but an isotropic/ferromagnetic transition that becomes noncontinuous at $\lambda > 1.33$ and $\phi \approx 0.2$. The authors admit that the stability of the ferromagnetic phase is overestimated with respect to the simulations. That density functional methods are probably not useful for quantitative investigations of the phase behaviour is also pointed out by Osipov *et al* [205] and in a different context by Ivanov [206] and Morozov [207].

Klapp and Forstmann [175, 176] find fluctuations at the high density boundary of the region of existence of isotropic RHNC solutions for the DHS and Stockmayer systems. They also find ferromagnetic solutions beyond that boundary.

In 2000, Camp and Patey [179] reported that they found in their Monte Carlo simulations ferromagnetic phases at $\lambda \approx 7.5$ for $\phi > 0.5(\pi/6)$. A Monte Carlo simulation of a DHS fluid with dipolar polydispersity, one with a bidisperse diameter distribution, and a binary mixture

of dipolar and neutral hard spheres was undertaken by Cabral [208] for $\phi = 0.8(\pi/6)$ and $\lambda = 6.25$. He showed that the polydispersity reduces the ferromagnetic order.

In 2003, Ivanov [206] investigated the BBGKY equation relating the one-particle distribution function $\rho(\mathbf{r}, \mathbf{m})$ to the pair correlation function $g(1, 2)$. He employs for the latter the self-consistent expression used in density functional approaches [187, 199, 200, 202]. When expanding it up to second order in the dipolar interaction the so-approximated BBGKY equation shows a bifurcation to a solution with spontaneously generated *ferrimagnetic* long-range order for $\chi_L > 12(\sqrt{5} - 2) \simeq 2.83$, i.e. slightly below the bifurcation threshold for ferromagnetism in the Weiss model. Ivanov [206] argues that this peculiar ferrimagnetic behaviour is an artefact that is ultimately due to the mean-field character of the density functional ansatz for the pair correlation function.

Then, in 2003, Morozov [207] investigates the bifurcation properties of the so-called Lovett–Mou–Buff–Gubbins integral equation [112, 113] that relates the one-particle probability distribution function to the direct correlation function $c(1, 2)$ and that is equivalent to the above-mentioned first BBGKY equation. He establishes criteria for the bifurcation of solutions with long-range magnetic order in ellipsoidal and spherical sample shapes in vacuum and compares with mean-field predictions, density function theory, and MSA results. Using a generalized MSA type of expression for $c(1, 2)$ he finds that the strength of short-range correlations plays a decisive role in the appearance of spontaneous long-range magnetic order—the susceptibility diverges when the former exceed a critical strength. More qualitative arguments then show that the short-range correlations are most likely to be antiferromagnetic. He also shows that approximating $c(1, 2)$ by the two lowest orders in its diagram expansion always gives rise to liquid ferromagnetic solutions.

At the end of this section on phase transitions in ferrofluids, we would like to quote Teixeira and co-workers [209]. They presented, in 2000, a fairly extensive review on the effect of dipolar forces on the structure and thermodynamics of classical fluids, which covers many aspects of the problems related to gas/liquid condensation phase transitions in various dipolar systems. Since their summary of the state of research on these problems still gives in our opinion an adequate picture of today's state of the art—also concerning the problem of liquid ferromagnetism—we provide two quotes [209]:

'Although widely studied in statistical mechanics, the phase diagrams of dipolar fluids in general, and of strongly dipolar fluids in particular, have remained largely uncharted' and '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.'

7. Conclusion

Ferrofluids, i.e. suspensions of magnetic nano-particles in liquid carriers are not only of technological interest but they continue to also be the object of many basic research projects. Among those, the effect of dipolar interactions that are important in ferrofluids attracted considerable interest for two reasons: first, dipolar forces are long-range so that e.g. the equilibrium magnetization (or polarization) is geometry dependent. Second, dipolar forces are attractive or repulsive depending on the relative orientation of the particles and their dipole moments with the orientational mean being zero. A realistic theoretical description of the colloidal suspension will also take into account other interactions between the particles and in addition the dispersion of particle diameters and magnetic moments in ferrofluids that is absent

in molecular systems. The dipolar interaction naturally affects the equilibrium magnetization, and also the phase transition behaviour. These two subjects were reviewed here.

The question of how dipolar interactions influence the initial susceptibility χ was studied for electrically polar systems long before the advent of ferrofluids. The oldest models, the Weiss and Onsager models, to capture this influence with mean-field approaches were already proposed in the first half of the 20th century. Only after 1970 were other theoretical methods used intensively to investigate χ by cluster expansions, integral equations, and Monte Carlo and molecular dynamics simulations. Here, mainly DHSs and Stockmayer particles were investigated. While both represent only poorly polar molecules like water they are much better approximations to the nanoscale magnetic particles of ferrofluids. In fact, the latter seem to be very good realizations of these two model systems. Many of the earlier analytical and semi-analytical theories that were originally conceived for molecular systems were also extended to account for polydispersity in ferrofluids.

When comparing cluster expansion methods and integral equation methods with numerical simulations it seems that the RHNC theory and the simpler perturbation theory by Tani *et al* [26] agree best with the Monte Carlo results for χ , at least for relatively high densities. The second theory has also been applied to explain experimental data for a highly concentrated ferrofluid, as has a related cluster expansion result by Ivanov and Kuznetsova [123].

With the synthetization of ferrofluids, i.e. dipolar systems in which saturation could easily be reached, not only χ but also the full magnetization curve $M(H)$ became of interest. Here, the main theoretical results date from 1985 onwards. The proposed theories were mostly extensions of those already used to describe χ . For example, the one by Ivanov and Kuznetsova [123] compares well with experimental data. However, recent numerical simulations by Wang and co-workers [125, 127] for χ and $M(H)$ are not well described by this theory when the volume fraction of the magnetic particles is small and the dipolar coupling is strong: they are better explained by a model of small noninteracting chains of different lengths.

An ever increasing analytical, numerical, and experimental research activity has been devoted to phase transition phenomena in dipolar systems, namely, (i) the separation into dilute and dense phases and (ii) the appearance of spontaneous (ferromagnetic) long-range order in zero magnetic field. Both phenomena refer in the case of ferrofluids solely to the subsystem of the magnetic particles without positional long-range order.

Dilute/dense transitions occur in Lennard–Jones systems and, more generally, whenever the attractive part of the interaction is sufficiently strong. In fact, simulations have shown that switching on an additional dipolar interaction in such systems favours the transition and increases the critical temperature. However, the question as to whether such a phase transition occurs also for purely DHSs without any isotropic attraction is more difficult to answer. The fact that such a phase separation has been observed experimentally in real ferrofluids does not help much in solving the above theoretical problem when (strong) isotropic interactions cannot be excluded to be present in the ferrofluid.

In the 1970s and 1980s a variety of semi-analytical theories was applied to investigate the dilute/dense phase transition behaviour of DHSs. They all found the usual phase diagram with a roughly parabolic coexistence curve. However, there was no agreement about the location of the critical point. But Monte Carlo simulations in the 1990s did not find such phase transitions for DHSs. For strong enough dipolar couplings or, equivalently, low enough temperatures a formation of head-to-tail dipolar chains was observed instead. They are caused by the highly directional character of the dipolar pair potential. Thus, new models were developed to explain the observed behaviour by means of polymer theory. According to these models the assembly of chains prevent a usual dilute/dense transition or mask it and make its observation in simulations difficult due to finite-size effects.

Another turning point was reached in 2000 when Camp *et al* [178] found evidence for one or even two phase transitions between chain-dominated states in Monte Carlo simulations. Pshenichnikov and Mekhonoshin [180, 181] even observed the common dilute/dense transition already at quite low dipolar couplings where chain formation is not very effective. They explain the differences from other studies as being due to their choice of a finite system instead of one with periodic boundary conditions. The differences between both simulation methods remain to be investigated further.

The phase transition behaviour is complicated further by the presence of a magnetic field. In the case of Stockmayer particles the field supports the phase separation, i.e. it enlarges the coexistence region. The question as to whether a field can trigger such a phase separation also for DHSs is not yet settled.

In comparison to the question of a dilute/dense transition, the research results concerning the possibility of having a phase with spontaneous (ferromagnetic) long-range order in zero magnetic field seem to be more coherent—albeit only at first sight: experimental hints for such a phase were found by Mamiya *et al* [19] and the simulations performed since the 1990s generally agree that there exist ferromagnetic phases for DHSs and similar systems in regions of high densities and strong couplings. This behaviour was also found in density functional theories although they seem to be less suited to explaining the phase behaviour, and the results differ quantitatively. The conditions for the appearance of spontaneous long-range magnetic order were recently investigated by Morozov [207] and Ivanov [206] using integral equation methods. They conclude that mean-field type approximations that are also the core of density functional approaches tend to generate artificially long-range magnetic order.

So, all in all, we think that a lot of questions/problems related to the equilibrium behaviour of ferrofluids and dipolarly interacting particles remain to be addressed.

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