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Abstract
The influence of polydispersity on the magnetization of two-dimensional dipolar discs with
short-range repulsive interaction is studied by means of Monte Carlo simulations and a high
field approximation perturbation theory. Within the framework of perturbation theory an
analytical expression is derived for the magnetization of monodisperse and polydisperse
systems. The theoretical predictions are in good agreement with the corresponding Monte Carlo
simulation data.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Monolayers of dipolar particles play a prominent role in
experimental situations and liquid-state theories. The physical
properties of these systems are frequently described by the
quasi-two-dimensional (q2D) dipolar fluid models [1–3]. In
a q2D dipolar fluid the particles and the centres of the dipole
moments are constrained to lie on the same plane while the
dipole vectors can freely rotate in three dimensions (3D).
In such confined systems the orientational entropy of the
system is generally restricted, and thus new properties without
any bulk analogue may emerge. In q2D ferrofluids, e.g.,
an external magnetic field perpendicular to the surface (or
confinement walls) can be used to induce tunable repulsive
interactions between the particles. The long-ranged nature
of the dipole–dipole interaction in both 2D and 3D means
that special techniques are required in theories and computer
simulations of polar fluids. Sometimes, in lower dimensions,
these techniques are less time-consuming and therefore it is
worthwhile to study 2D models from both theoretical and
simulation points of view. In true 2D the dipole vectors are
allowed to rotate only in the plane of the dipole centres. It
has to be emphasized that the fluids under discussion here
are strictly two-dimensional ones and, in particular, that none
of our results apply to monolayers of a real, i.e. 3D, fluid.
However, today's nanotechnology is able to produce platelet-
shaped magnetic nanoparticles [4], and this work would be a
first step in studying the restricted monolayers of such kinds

of particles. The literature for 2D dipolar fluids in not so
huge as that for the corresponding q2D and 3D ones. Among
others, Bossis *et al* [5–7] have performed molecular dynamics
(MD) simulations of the dielectric constant, distribution and
autocorrelation functions, and thermodynamic properties. The
second and third pressure and dielectric virial coefficients of
2D dipolar hard discs were calculated by Joslin [8]. The
mean spherical approximation (MSA) has been obtained for
dipolar hard discs by Isbister and Freasier [9]. Multipole
expansions for 2D dipolar systems have been worked out
by Joslin and Gray [10]. Recently Vargas *et al* [11] have
studied the thermodynamics of 2D magnetic particles. In
one of our earlier publications [12] we studied the magnetic
properties of polydisperse monolayers, where the susceptibility
of 2D fluids is also investigated. As a continuation, in
this work we deduce, on the basis of first-order perturbation
theory [13], an equation for the magnetization of polydisperse
2D ferrofluids. In order to verify the predictions of our theory
we carried out Monte Carlo simulations for the determination
of magnetization curves of 2D monodisperse and polydisperse
magnetic fluids.

2. Model

The system consists of soft discs of diameter σ_i, which have
permanent magnetic point dipole moments m_i. The short-
range repulsive interactions between particles i and j are

modelled by a shifted and truncated Lennard-Jones (soft disc) pair potential:

$$
u_{ij}^{\mathrm{sd}} =
\begin{cases}
4\epsilon \left[\left(\dfrac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\dfrac{\sigma_{ij}}{r_{ij}} \right)^{6} - \left(\dfrac{\sigma_{ij}}{\sigma_{\mathrm{c}}} \right)^{12} + \left(\dfrac{\sigma_{ij}}{\sigma_{\mathrm{c}}} \right)^{6} \right], \\
\qquad\qquad\qquad r \leqslant \sigma_{\mathrm{c}} \\
0, \qquad\quad r > \sigma_{\mathrm{c}}
\end{cases}
\tag{1}
$$

where ϵ is the energy parameter, r_{ij} is the interparticle distance, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and σ_{c} is the cut-off parameter. This form of soft disc repulsion takes into account the fact that the particle size in fluids exceeds the magnetic core diameter σ_i. In 2D the dipole vectors are allowed to rotate only in the plane of the dipole centres and the dipole–dipole potential can be written as

$$
u_{ij}^{\mathrm{dd}} = -m_i m_j D(i, j)/r_{ij}^2,
\tag{2}
$$

where

$$
D(i, j) = 2(\widehat{\mathbf{m}}_i \widehat{\mathbf{r}}_{ij})(\widehat{\mathbf{m}}_j \widehat{\mathbf{r}}_{ij}) - (\widehat{\mathbf{m}}_i \widehat{\mathbf{m}}_j) = \cos(\theta_i + \theta_j - 2\theta_{ij}).
\tag{3}
$$

Here the hat denotes a unit vector, θ_i, θ_j and θ_{ij} specify the orientation of $\mathbf{m}_i$, $\mathbf{m}_j$ and the interparticle vector $\mathbf{r}_{ij}$, respectively, with respect to some arbitrarily chosen space-fixed axis. The interaction of dipoles with an external magnetic field $\mathbf{H}$ is

$$
u_i^{\mathrm{ex}} = -\mathbf{H}\mathbf{m}_i.
\tag{4}
$$

The particle polydispersity is described by the gamma distribution [14],

$$
p(x) = \frac{x^{\ominus}}{x_0} \left(\frac{x}{x_0} \right) \frac{\exp(-x/x_0)}{\Gamma(a+1)},
\tag{5}
$$

where x is the magnetic core diameter of particles, x_0 and a are the parameters of the distribution, Γ denotes the Gamma function, and $x^{\ominus} = 1$ nm is taken as the unit length. For the disc-shaped particles, $\sigma = x$, and the magnetic moment reads

$$
m(x) = M_{\mathrm{d}} \pi x^2/4,
\tag{6}
$$

where M_{d} represents the bulk magnetization of discs.

3. Magnetization of the ideal system

Using the concept of components we consider the mixture of dipolar soft discs as a system of $N = \sum_{\kappa=1}^{c} N_{\kappa}$ particles with point dipoles at the centres of m_{κ} (where c is the number of components and N_{κ} is the number of particles of component κ). The fluid is constrained to a 2D volume V at temperature T and placed in an external magnetic field. The direction of the field is irrelevant, so we can safely fix it in the direction of the x axis, $\mathbf{H} = H\mathbf{e}_x$. In the case of the ideal system it is obvious that the potential energy of particles, which arises from the presence of the external field, depends upon the orientations of the dipoles with respect to the direction of the field and thus the partition function of the system is given by

$$
Q_0 = \prod_{i=1}^{N} \int_0^{2\pi} \mathrm{d}\theta_i \exp\left(\frac{m_i H}{k_{\mathrm{B}} T} \cos\theta_i \right) = \prod_{\kappa=1}^{c} [I_0(\alpha_{\kappa})]^{N_{\kappa}}, \tag{7}
$$

where $I_0(x)$ is the modified Bessel function of the first kind of zero order, and $\alpha_{\kappa} = m_{\kappa} H/(k_{\mathrm{B}} T)$. The magnetization of the system will indeed be in the direction of the field, and for its magnitude one has

$$
M = -\frac{1}{V}\left(\frac{\partial F}{\partial H} \right)_{N,V,T} = \frac{k_{\mathrm{B}} T}{V} \left(\frac{\partial \ln Q}{\partial H} \right)_{N,V,T}, \tag{8}
$$

where $F = -k_{\mathrm{B}} T \ln Q$ is the free energy of the system. For the mixture of non-interacting dipoles this yields

$$
M_0 = \rho \sum_{\kappa=1}^{c} \frac{N_{\kappa}}{N} m_{\kappa} \frac{I_1(\alpha_{\kappa})}{I_0(\alpha_{\kappa})}, \tag{9}
$$

where $\rho = N/V$ is the particle number density, and $I_1(x)$ is the modified Bessel function of the first kind of first order. Assuming continuous polydispersity in dipole moment, the magnetization can be expressed with the help of an integral containing the particle distribution function of equation (5):

$$
M_0 = \rho \int_0^{\infty} \mathrm{d}x \, p(x) m(x) \frac{I_1[\alpha(x)]}{I_0[\alpha(x)]}, \tag{10}
$$

where $m(x)$ is given by equation (6) and $\alpha(x) = m(x)H/(k_{\mathrm{B}} T)$. In the following we calculate the magnetization of the polydisperse system on the basis of this equation.

4. Perturbation theory

The present calculation is based on the high field perturbation approximation originally introduced by Buyevich and Ivanov [13] for 3D systems. In the framework of this theory we assume that the orientation of magnetic dipoles is governed mainly by the external magnetic field and the dipole–dipole interaction can be considered as a perturbation. Therefore the reference system is described by the following interaction energy:

$$
U_r = \sum_{i<j} u_{ij}^{\mathrm{sd}} + \sum_{i} u_i^{\mathrm{ex}}. \tag{11}
$$

The pair distribution function of the reference system reads

$$
g_{ij}^{r}(r_{12}, \theta_1, \theta_2) = f_i(\theta_1) g_{ij}^{\mathrm{sd}}(r_{12}) f_j(\theta_2), \tag{12}
$$

where g_{ij}^{sd} is the pair correlation function of the soft disc fluids and $f_i(\theta_i)$ is the single-particle orientation distribution function in the external magnetic field. On the basis of the preceding section it is obvious that

$$
f_i(\theta_i) = \exp(\alpha_i \cos\theta_i)/I_0(\alpha_i). \tag{13}
$$

The configurational integral of the reference system is given as

$$
Q_r = Q_{\mathrm{sd}} \prod_{\kappa=1}^{c} [I_0(\alpha_{\kappa})]^{N_{\kappa}}. \tag{14}
$$

In this approximation, knowledge of the configurational integral Q_{sd} is not necessary for the calculation of the magnetization (since it does not depend on the magnetic field strength); therefore we do not specify the corresponding formula. The long-ranged dipole–dipole interaction in

equation (2) is considered as a perturbation and, on the basis of an expansion of the total configurational integral (Q) with respect to the Mayer function $f_{\kappa,\lambda}^{M}$, we obtain

$$\ln \frac{Q}{Q_r} = \frac{1}{2}\rho \sum_{\kappa,\lambda} N_\kappa N_\lambda \int \int \int \int d^2 r_1 \, d^2 r_2 \, d\theta_1 \, d\theta_2$$

$$\times f_\kappa(\theta_1) f_\lambda(\theta_2) f_{\kappa,\lambda}^{M}(r_{12},\theta_1,\theta_2) g_{\kappa,\lambda}^{sd}(r_{12}) \qquad (15)$$

with

$$f_{\kappa,\lambda}^{M}(\mathbf{r}_{12},\theta_1,\theta_2) = \exp\left(-u_{\kappa,\lambda}^{dd}(\mathbf{r}_{12},\theta_1,\theta_2)/(k_B T)\right) - 1. \quad (16)$$

To calculate the integrals in equation (15) a further approximation is necessary. We expand the Mayer function into a first-order Taylor series with respect to the dipole–dipole interaction. After the series expansion the integration with respect to θ_1 and θ_2 can be performed analytically according to the following equation:

$$\int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \, f_\kappa(\theta_1) D(\theta_1,\theta_2,\theta_{12}) f_\lambda(\theta_2)$$

$$= \frac{I_1(\alpha_\kappa)}{I_0(\alpha_\kappa)} \frac{I_1(\alpha_\lambda)}{I_0(\alpha_\lambda)} (2\cos^2\theta_{12} - 1). \qquad (17)$$

The remaining integration in equation (15) is

$$\int d^2 r_{12} \frac{g_{\kappa,\lambda}^{sd}(r_{12})}{r_{12}^2} (2\cos^2\theta_{12} - 1) = \pi, \qquad (18)$$

where, to avoid the depolarization, the integration is carried out on an infinitely prolate ellipsis, and we used that the asymptotic value of $g_{\kappa,\lambda}^{sd}(r_{12})$ is 1. Using equations (17) and (18) for the first-order perturbation free energy term we obtain

$$F_1 = -\frac{\pi}{2V} \sum_{\kappa,\lambda} N_\kappa N_\lambda m_\kappa m_\lambda \frac{I_1(\alpha_\kappa)}{I_0(\alpha_\kappa)} \frac{I_1(\alpha_\lambda)}{I_0(\alpha_\lambda)}$$

$$= -\frac{\pi \rho N}{2} \left(\sum_\kappa \frac{N_\kappa}{N} m_\kappa \frac{I_1(\alpha_\kappa)}{I_0(\alpha_\kappa)} \right)^2. \qquad (19)$$

Taking into account the continuous polydispersity in dipole moment, the first-order perturbation term can also be expressed as an integral containing the particle distribution function:

$$F_1 = -\frac{\pi \rho N}{2} \left(\int_0^\infty dx \, p(x) m(x) \frac{I_1[\alpha(x)]}{I_0[\alpha(x)]} \right)^2. \qquad (20)$$

The corresponding first-order term for the magnetization is

$$M_1 = \rho \left(\int_0^\infty dx \, p(x) m(x) \frac{I_1[\alpha(x)]}{I_0[\alpha(x)]} \right)$$

$$\times \left(\frac{\pi \rho}{k_B T} \int_0^\infty dx \, p(x) m^2(x) \right.$$

$$\times \left[1 - \frac{1}{\alpha(x)} \frac{I_1[\alpha(x)]}{I_0[\alpha(x)]} - \left(\frac{I_1[\alpha(x)]}{I_0[\alpha(x)]} \right)^2 \right] \right). \qquad (21)$$

The total magnetization is the sum of the contribution of the ideal gas term (equation (10)) and the first-order perturbation term (equation (21)):
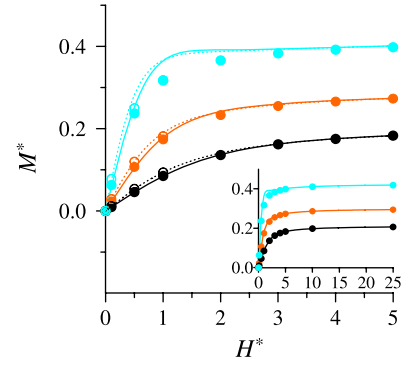
$$M = M_0 + M_1. \qquad (22)$$

Figure 1. Magnetization as a function of the external magnetic field for the monodisperse (full lines and full circles) and for the polydisperse (dotted lines and open circles) fluids at $T^* = 1.0$ and $\rho^* = 0.3$. Symbols represent the simulation results and lines are the theoretical predictions. From bottom to top, the curves with different colours correspond to magnetizations at $m^{*2} = 0.5$, 1.0 and 2.0, respectively. The statistical uncertainties of the simulation results are less than the symbol size. The total magnetization curves for the monodisperse fluids are displayed in the inset.

5. Monte Carlo simulation

Constant volume and temperature Monte Carlo calculations have been performed using translational–orientational and resizing moves of the particles (semigrand ensemble). In our recent work [12] a simple scheme was constructed to produce appropriate distribution functions for the trial moves responsible for generating the possible configurations of particle sizes. In this method, the underlying (sampling) particle distribution density $p_u(x)$ for the resizing moves is dynamically updated during the first period of the simulation in such a way as to minimize the deviation of the instantaneous particle distribution density from the target distribution density $p(x)$. In the second period of the simulation we take the final $p_u(x)$ as the input of a normal semigrand ensemble simulation in order to obtain the exact equilibrium results for the properties of interest. In all simulations $N = 500$ particles were employed. The frequency of attempting resizing moves was equal to that of the translational and orientational moves and, likewise, the acceptance criterion of the resizing moves was the same as that used for the translational and orientational moves. The long-ranged dipolar interactions were treated using the Ewald summation with a conducting boundary condition; see [15].

6. Results and discussion

The results for the (magnetic) dipolar fluids are presented in reduced units, where the mean magnetic core diameter $\langle x \rangle$ is used for σ: $\rho^* = N\sigma^2/V$ is the reduced density, $T^* = k_B T/\epsilon$ is the reduced temperature, $m^{*2} = m^2/(\epsilon\sigma^2)$ is the reduced squared magnetic dipole moment, $H^* = H\sqrt{\sigma^2/\epsilon}$ is the reduced magnetic field strength, and $M^* = M\sqrt{\sigma^2/\epsilon}$ is the reduced magnetization. For the magnetic coupling, $\lambda = m^{*2}/T^* = 0.5$, 1 and 2 were adopted at $T^* = 1$. This choice implies that the average reduced magnetic dipole moments were $\sqrt{0.5}$, 1 and $\sqrt{2}$ in all calculations. The
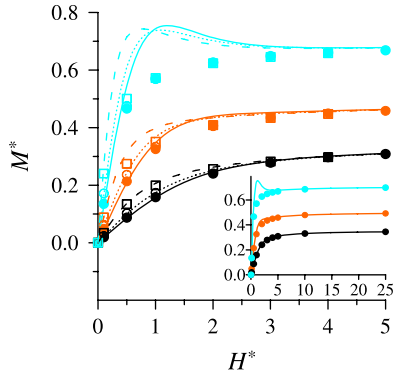
Figure 2. Magnetization as a function of the external magnetic field for the monodisperse (full lines and full circles) and for the polydisperse (dotted and dashed lines and open circles and squares) fluids at $T^* = 1.0$ and $\rho^* = 0.5$. Symbols represent the simulation results and lines are the theoretical predictions. The dashed lines and the squares are the results obtained with a higher degree of polydispersity ($x_0/x^{\ominus} = 1$, $a = 6$, see text). From bottom to top, the curves with different colours correspond to magnetizations at $m^{*2} = 0.5$, 1.0 and 2.0, respectively. The statistical uncertainties of the simulation results are less than the symbol size.
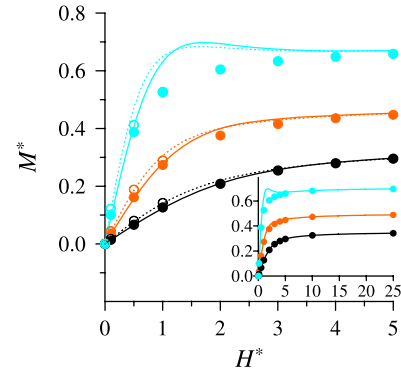

Figure 4. Magnetization as a function of the external magnetic field for the monodisperse (full lines and full circles) and for the polydisperse (dotted and dashed lines and open circles) fluids at $T^* = 1.25$ and $\rho^* = 0.5$. Symbols represent the simulation results and lines are the theoretical predictions. From bottom to top, the curves with different colours correspond to magnetizations at $m^{*2} = 0.5$, 1.0 and 2.0, respectively. The statistical uncertainties of the simulation results are less than the symbol size. The total magnetization curves for the monodisperse fluids are displayed in the inset.
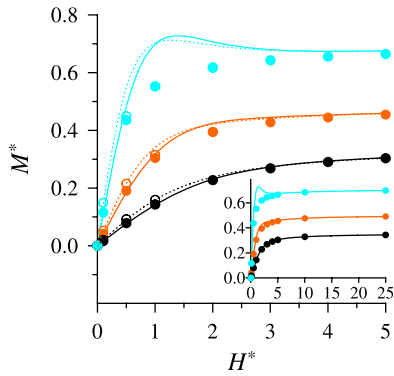

Figure 3. Magnetization as a function of the external magnetic field for the monodisperse (full lines and full circles) and for the polydisperse (dotted and dashed lines and open circles) fluids at $T^* = 1.1$ and $\rho^* = 0.5$. Symbols represent the simulation results and lines are the theoretical predictions. From bottom to top, the curves with different colours correspond to magnetizations at $m^{*2} = 0.5$, 1.0 and 2.0, respectively. The statistical uncertainties of the simulation results are less than the symbol size. The total magnetization curves for the monodisperse fluids are displayed in the inset.
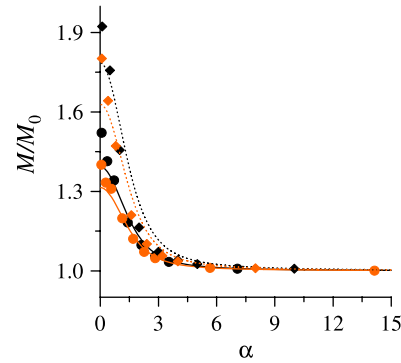

Figure 5. Calculated magnetization relative to the magnetization of the ideal ferrocolloid gas as a function of the Langevin parameter for the monodisperse fluids at $T^* = 1.0$ (black) and $T^* = 1.25$ (orange) and at $\rho^* = 0.5$. Circles and full lines and diamonds and dotted lines correspond to results at $m^{*2} = 0.5$ and $m^{*2} = 1.0$, respectively.

monodisperse fluid is characterized by uniform σ and m, with the additional specification that $m^{*2} = 0.5$, 1 and 2. Due to the fact that $\langle m \rangle \propto \langle x^2 \rangle$ and $\langle x^2 \rangle \neq \langle x \rangle^2$ for the polydisperse fluid, the monodisperse fluid can be considered to have either a different mean core diameter or different bulk magnetization to those of the polydisperse fluid. For the parameters of the gamma distribution, $x_0/x^{\ominus} = 0.3$ and $a = 24$ were taken. In our case, essentially zero net magnetizations were detected in the directions perpendicular to the applied field direction. Figure 1 shows the reduced dipole moment dependence of the magnetization curves at $T^* = 1$ and $\rho^* = 0.3$ for monodisperse and polydisperse dipolar fluids. For the dipole moments $m^{*2} = 0.5$ and 1 we find both the perturbation theoretical and the MC results to be in excellent quantitative agreement for practically all field strengths. For $m^{*2} = 2$

the level of quantitative agreement reduces significantly for the field strengths $1 \lesssim H \lesssim 3$. The difference between the magnetization curves of the monodisperse and polydisperse fluids is very small for the density $\rho^* = 0.3$. The magnetization curves at $\rho^* = 0.5$ for several temperatures are displayed in figures 2–4. We can see that the agreement between the simulations and the present theory deteriorates mainly at the highest reduced dipole moments, but this weakness of the theory will be compensated to some extent as the temperature increases. Since deviations from equation (10) clearly reflect the variations in the interparticle interactions, finally we present the calculated magnetizations relative to those of the corresponding ideal system for two monodisperse systems. In figure 5 we can emphasize how well the theory works also in the low field region for $m^{*2} = 0.5$ and 1.0 and that the influence of temperature on the net interaction between the particles is significant here.

In summary, on the basis of the comparison between the first-order perturbation theoretical and MC simulation results

we can conclude that the proposed equations (equations (10) and (21)) seem to predict reliably the magnetic properties of 2D dipolar fluids for the dipole moments $m^* \lesssim 1$.

Acknowledgment

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