EQUILIBRIUM SUSCEPTIBILITY OF CONCENTRATED FERROCOLLOIDS: MONTE CARLO SIMULATION

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The Monte Carlo method is used to study the influence of the magneto-dipole interaction on a highly concentrated system of solid spheres (magnetic fluids). Some analogous works predict the occurrence of long-range magnetic ordering in such a system. Their common feature is the use of periodic boundary conditions. In this work, the periodic boundary conditions are not imposed on the system. Instead, a model of the permeameter is proposed to exclude demagnetizing fields. The results of simulation with moderate values of the dipole-dipole interaction energy and particle concentration are in good agreement with the reliable analytical models. In the region of highly intensive dipole-dipole interactions, which is the subject of the discussions, the “ferromagnetic” ordering is really possible, but only in the case when the diameter of the simulated cylindrical cell is less than four diameters of the dipole sphere. Since this particular nearly-one-dimensional case is obviously far from any practical use and the moment ordering does not occur at larger cell diameters, it is concluded that the periodic boundary conditions are able to produce the simulation artifact of the second-order “paramagnetic–ferromagnetic” phase transition.

Introduction. It is a well known fact that interparticle interactions (steric, dipole-dipole, hydrodynamic and Van der Waals) are responsible for a wide variety of effects in magnetic fluids (MF), such as the non-linear dependence of susceptibility on the particle concentration, the temperature dependence of susceptibility, which is distinct from the Curie’s law, intensification of magnetophoresis, nanoscale aggregation and the first-order “gas–liquid” phase transition [1–6]. Some problems dealing with the interparticle interactions in MF are still unsolved. One of them is the possibility of the second-order “paramagnetic–ferromagnetic” phase transition, and our work is a new attempt to clarify it. Here we take into consideration only steric and dipole-dipole interactions. This assumption seems reasonable, as hydrodynamic interactions have no effect on the equilibrium properties of the system, and Van der Waals interactions are inhibited in MF by surfactants. In this case, the system behaviour is determined by the sample geometry (due to demagnetizing fields), the particle volume fraction $\varphi$ and by the dipolar coupling constant $\lambda$, which relates the dipole-dipole interaction energy of two contacting particles to the thermal energy $kT$:

$$\lambda = \frac{\mu_0 m^2}{4\pi d^3 k_B T},$$

where $\mu_0 = 4\pi \times 10^7$ H/m, $m$ is the magnetic moment, $d$ is the particle diameter, $k$ is the Boltzmann’s constant, and $T$ is the temperature.

Small and moderate values of the dipole-dipole interaction intensity ($\lambda \leq 2$) are well-studied. Results of theoretical and numerical investigations of this region are in good agreement with experiment and denote the absence of long-range orientational order in MF. On the contrary, there is almost no reliable information about the region of strong dipole-dipole interactions ($\lambda \geq 3$), which conceivably
lead to the “ferromagnetic” transition. At present, a laboratory examination is impossible because of the technical difficulties of high-λ ferrocolloid production. As for analytical researches, their results at high λ critically depend on the applied approach. The Weiss effective field model predicts the appearance of the “paramagnetic–ferromagnetic” phase transition in dipolar fluids [6], and so does the density-functional self-consistent-field theory [7]. A general approach within the framework of the direct correlation function formalism casts doubt on the occurrence of transition [8]. The mean-spherical approximation [8, 9] and the modified effective field model [4, 10] do not predict the transition. We suppose that the reason of the disagreements is that the region of the potential “ferromagnetic” ordering (λ ≥ 3) is outside the applicability domain of conventional analytical models. Although the Weiss effective field model, the mean-spherical approximation and the modified effective field model agree well with experimental data for moderate values of λ and ϕ [9, 11, 12], their extrapolation to λ ≥ 3 should be made with a great caution.

Monte Carlo and molecular-dynamic simulations do not impose any formal restrictions on the dipole-dipole interaction energy. Nevertheless, the simulation data are also inconsistent. The second-order “ferromagnetic” phase transition was observed in [13–15], but not found in [16–18]. The most obvious reason for these discrepancies is the difference between the simulation algorithms. Here, one should mention two well recognized fundamental problems, which are inseparably related to the numerical simulation of dipolar systems [18]. The first is the finite number of particles in numerical experiment. If the system is far from the thermodynamic limit, its properties depend on the number of particles. The second problem is demagnetizing fields created by the interactive dipoles themselves. These fields reduce the internal magnetic field and, in the general case, are strongly dependent on the sample shape. The most common way to solve the above mentioned problems is the Ewald summation and the periodic boundary conditions. These techniques really allow simulation of an effectively limitless system, which is free from demagnetizing fields, although potentially they may introduce undesired features into the simulation algorithm: the periodic boundary conditions suggest a quasi-crystalline structure of the system. The Ewald summation and periodic boundary conditions were used in all studies, in which the “ferromagnetic” phase transition was observed. The influence of the Ewald summation on the numerical experiment has already been analyzed in [19]. To depart from the Ewald technique, a new approach to the thermodynamic limit has been proposed. It is based on the application of non-typical one-dimensional periodic boundary conditions. Nevertheless, the phase transition was observed at λ ≃ 3. It favours the views that the Ewald technique is not a necessary condition of the “ferromagnetic” phase transition.

The purpose of this work is to investigate numerically the finite-size dipolar system and gain clear understanding of the role of the periodic boundary conditions in the phenomenon of magnetic ordering.

1. Details of the simulation method. A possible way to reduce demagnetizing fields is to place a MF cell between the poles of a massive electromagnet. In laboratory practice, the most suitable instrument for this purpose is the permeameter, which is widely used for rapid measurements of permeability of ferromagnetic samples. The permeameter electromagnet is a rectangular frame, inside which an examined sample is placed. The lines of the sample demagnetizing field converge at the iron core rather than in the space near the sample boundaries. The demagnetizing field inside the sample becomes negligible. To simulate this situation numerically, we assume that the MF cell is clamped between two semi-infinite
parallel walls made of soft magnetic material with $\mu \to \infty$. These boundary conditions can be easily taken into account, for which purpose it is necessary to add one extra term to the expression for the dipole full energy.

The simulated system is shown schematically in Fig. 1. The MF cell is a circular hard-boundary cylinder, and MF particles are hard spheres of equal diameter $d$ and magnetic moment $m$. The number of particles $N$, the relative cylinder length $L$ (which relates the cylinder height $Z_{\text{max}}$ to its diameter $D$) and the volume fraction of the particles $\varphi$ are taken as the main parameters of the sample. The equilibrium state of the system is determined by the dimensionless parameters $\varphi$, $\lambda$ and the Langevin parameter $\xi$, which relates the dipole energy in the applied field to the thermal energy $kT$:

$$
\xi = \frac{\mu_0 m H_0}{k_b T}.
$$

The difference between the $H_0$ and the internal $H$ fields is negligible due to the influence of the permeameter.

Applying the simulation algorithm yields the expression for the magnetization of the equilibrium system

$$
M = M_\infty \langle \cos \vartheta \rangle,
$$

where $M_\infty = mn$ is the saturation magnetization, $n$ is the particle number density, and $\vartheta$ is the angle between the direction of the particle moment and the direction of the applied field; the brackets denote both the particle ensemble and the time averaging.

The full reduced magnetostatic energy of the $i$-th particle in the sample is given by the equation:

$$
\frac{U_i}{k_b T} = -\xi \cos \vartheta_i - \sum_{j \neq i}^N \lambda \left( \frac{3(e_i \cdot r_{ij})(e_j \cdot r_{ij})}{r_{ij}^3} - \frac{e_i \cdot e_j}{r_{ij}} \right) + \frac{U_i^p}{k_b T},
$$

where $e_i$ is the unit vector along the dipole moment, $r_{ij}$ is a vector between the centers of the $i$-th and $j$-th particles. The first term in Eq. (4) is the dipole energy in the applied field, the second term is the total dipole-dipole interaction energy, and the third term is the energy of the interaction with the permeameter yoke.
Fig. 2. On the problem of interaction between the dipole and the permeameter yoke.

The latter can be determined from the standard magnetostatic problem of dipole placed near the boundary between two half-spaces with permeabilities $\mu_1$ and $\mu_2$ (Fig. 2). The result is

$$\frac{U^p}{k_B T} = -\frac{\lambda}{8l^3} \frac{\mu_2 - \mu_1}{\mu_2 + \mu_1} \left(1 + \cos^2 \vartheta \right),$$

where $l$ is the distance between the dipole center and the boundary. With reference to the permeameter model (Fig. 1), an additional term to Eq. (4) is given by

$$\frac{U^p_i}{k_B T} = -\frac{\lambda}{8} \frac{Z_{\text{max}}^3 - 3z_i Z_{\text{max}}(Z_{\text{max}} - z_i)}{z_i^3 (Z_{\text{max}} - z_i)^3} \left(1 + \cos^2 \vartheta_i \right). \quad (5)$$

In this work, we use the standard Metropolis algorithm [20]. In order to simulate steric interactions of particles, it is assumed that the particles and the cell boundaries are impermeable. The initial coordinates and the moment orientation of each particle are random. The number of Monte Carlo steps is always quite sufficient to make calculations with less than 1% mean squared error.

2. Initial susceptibility and indication of the “paramagnetic-ferromagnetic” phase transition. If the dependence $M(H)$ is known, we can easily find the initial susceptibility of the sample $\chi = M/H|_{H \to 0}$. The Langevin theory describes fairly well the behaviour of dilute MF, where the dipole-dipole interaction energy is much less than the thermal energy, and gives the exact expression $\chi \equiv \chi_L = 8\lambda \varphi$, where $\chi_L$ is the Langevin susceptibility. A conventional tool for estimating the effect of the magneto-dipole interaction on the MF is the dependence $\chi(\chi_L)$.

In the simplest Weiss model, this relation is obtained from

$$\chi = \frac{\chi_L}{1 - \kappa \chi_L}, \quad (6)$$

where $\kappa$ is the constant of the effective field. This model describes a real MF only in the case of low particle concentration.

The modified model of the effective field [4] combines $\chi$ and $\chi_L$ as

$$\chi = \chi_L \left(1 + \frac{\chi_L}{3} + \frac{\chi_L^2}{144} \right). \quad (7)$$

Eq. (7) agrees well with most experimental and numerical results for the moderate coupling constants $\lambda \leq 2$ and moderate particle concentrations $\varphi \leq 0.3$. The results of numerical and experimental investigations in the region of higher
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values of the dimensionless parameters are inconsistent with Eq. (7). Apparently, this is due to the fact that \( \lambda \) and \( \varphi \) are taken into consideration only as a product. The parameter \( \lambda \) determines the possibility of local aggregation in the MF. For low or mean values of \( \lambda \) this possibility is also low, and the system can be well described in terms of one parameter \( \chi_L \). But for the intensive dipole-dipole interactions, we should use two independent dimensionless parameters \( \lambda \) and \( \chi_L \) (or, equivalently, \( \lambda \) and \( \varphi \)). In [5], the experimental values of the susceptibility of highly concentrated MF for \( \lambda \leq 2.5 \) have been successfully approximated by a semi-empirical equation
\[
\chi = \chi_L \left( 1 + \frac{\chi_L}{3} g(\lambda) + (17I(\rho^*) - 16) \frac{\chi_L^2}{144} \right).
\] (8)
Eq. (8) adds two correction factors to Eq. (7). The first one allows for the value of \( \lambda \) [21]:
\[
g(\lambda) = 1 + \frac{\lambda^2}{25} + \frac{4\lambda^4}{1225} + \frac{\lambda^6}{6615} + \frac{37\lambda^8}{8004150} + \cdots.
\]
It becomes essential at \( \lambda > 2 \). The second one allows for the particle volume fraction \( \varphi \) [22]:
\[
I(\rho^*) = \frac{1 - 0.93952\rho^* + 0.36714\rho^{*2}}{1 - 0.92398\rho^* + 0.23323\rho^{*2}}, \quad \rho^* = \frac{6}{\pi}\varphi.
\]
It becomes essential at \( \varphi > 0.2 \).

The relation \( \chi(\chi_L) \) must diverge fast while tending to the phase transition point. For instance, the transition point in the Weiss theory is \( \chi_L = \kappa^{-1} \). If \( \kappa = 1/3 \) (in this case, Eq. (6) coincides with Eq. (7) at \( \chi_L \to 0 \)), the transition point is \( \chi_L = 3 \). But real magnetic fluids never show signs of magnetic ordering at such values of the Langevin susceptibility. One more attribute of any second-order phase transition is a nonzero order parameter. In case of MF, the order parameter is magnetization. So, in the “ferromagnetic” state the fluid has a nonzero average magnetic moment even in the absence of the applied magnetic field (spontaneous magnetization).

3. Results and their analysis. First of all it is necessary to understand how the sample finite sizes and the finite number of particles affect the system without periodic boundary conditions. Two series of dependences have been calculated:

\[ \frac{\chi}{3\chi_L} \]

Fig. 3. Initial susceptibility vs. particle number. \( \varphi = 0.2; L = 40. \square - \lambda = 2.6; \circ - 2.0; \triangle - 1.0. \]
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Fig. 4. Initial susceptibility vs. cylinder relative length. \( \varphi = 0.2; N = 1500 \). \( \Box - \lambda = 2.0; \circ - 1.0 \).

the dependences of the susceptibility on the particle number \( N \) (some examples are illustrated in Fig. (3)) and the dependence of the susceptibility on the relative cylinder length \( L = Z_{\text{max}}/D \) (Fig. 4). At \( \lambda \geq 2 \), these dependences are essentially different from straight lines. A possible explanation is a surface effect. With an increase of \( L \) (at \( \varphi, N = \text{const} \)) and a decrease of \( N \) (at \( \varphi, L = \text{const} \)), the percentage of particles contacting with the sample boundaries grows. For these “surface” particles the possibility of changing their coordinates is much less than

Fig. 5. Fluctuations of magnetization in zero applied field. \( \varphi = 0.28 \). (a) \( L = 85 \), (b) 100, (c) 110, (d) 120.
for the particles located deep inside the sample. Their ability to move is restricted, and it is natural to expect that their contribution to the system susceptibility is greater.

The fact that the initial susceptibility increases rapidly with $L$ has led us to another series of simulations, which showed how the fluctuations of the magnetization $z$-projection in zero applied field occur at different values of $L$. Every 300 steps of the Monte Carlo simulation the dipolar coupling constant $\lambda$ was changed stepwise. Fig. 5 displays examples of these fluctuations. The result of experiments is that the spontaneous magnetization appears in the system at $L > 100$ and $\lambda \geq 3$. The magnetization is stable and saves the value and the sign at least during $2 \times 10^6$ Monte Carlo steps.

In Fig. 6, the calculated initial susceptibility is plotted versus the Langevin susceptibility for two different volume fractions: $\varphi = 0.4$ (Fig. 6a) and $\varphi = 0.28$ (Fig. 6b). $N = 1500$. In the first case, $L = 25$ and no signs of spontaneous magnetization are observed. At $\chi_L < 5$ (or for this concentration at $\lambda < 1.6$), the experimental values agree with Eq. (7), which confirms the validity of our model. Furthermore, up to $\chi_L = 8$, the results also well agree with Eq. (8). It is quite possible that increasing the particle number will improve the agreement with Eq. (8). Fig. 6b displays two experimental curves. The lower one corresponds to $L = 55$ and spontaneous magnetization is absent. The upper one corresponds to $L = 120$ and spontaneous magnetization in the system appears at $\lambda = 3.1$ (or at $\chi_L = 7.94$ and $\varphi = 0.28$). For comparison, the dotted line in Fig. 6b corresponds.
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to the Weiss model (6) with \( \kappa = 7.94^{-1} \). One can see that the dependence \( \chi(\chi_L) \)
for the sample, in which magnetic ordering is possible, grows much faster than
Eq. (8) predicts, but it is not consistent with the hyperbolic dependence predicted by the Weiss theory.

4. Conclusion. The Monte Carlo method was used to simulate the behaviour of the highly concentrated dipolar system in wide ranges of the dipole-dipole interaction energy and particle concentration. A model of the permeameter, which does not impose periodic boundary condition on the system, was used to eliminate demagnetizing fields. Predictions in the range of small and moderate interactions agree with the results of reliable analytical models, which lend support to the reliability of our numerical scheme.

In the region of strong dipole-dipole interactions (\( \lambda \geq 3 \)), the system behaviour critically depends on the percentage of particles, coming in contact with the sample boundaries. To change this percentage, we varied the relative length \( L \) of the MF cell. At \( L > 100 \), a stable long-range magnetic ordering indicative of the “ferromagnetic” phase transition is really possible in the system. To make things clear, it should be noted that the critical relative length matches the cell diameter, which is only four times as big as the particle diameter \( d \). Hence, the phase transition occurs only in the nearly one-dimensional system. Of course, this condition could hardly be used in practices. For bigger diameters, the calculated values of the initial susceptibility are close to the semi-empirical Eq. (8).

The obtained results suggest that the periodic boundary conditions imposed on a highly concentrated dipolar system can produce a simulation artifact – the false second-order “paramagnetic–ferromagnetic” phase transition.

REFERENCES


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