SEGREGATION IN THE DIPOLAR HARD SPHERE SYSTEM: NUMERICAL SIMULATION

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Abstract: A series of Monte Carlo and molecular dynamics simulations have been performed to determine equilibrium concentration profiles of dipolar hard sphere system in a wide range of coupling constant values and in the presence of the strong gravitational field. These data have been used to estimate the diffusion coefficient of colloidal particles and to determine applicability limits of the most recent analytical models for this coefficient. No signs of the first order phase transition predicted by all the models were observed in the simulation.

1. Introduction

One of the most important problems that must be handled in order to create a highly stable magnetic fluid is the problem of concentration stratification. Its essence is that in the course of time an initially homogeneous fluid becomes spatially inhomogeneous with respect to the magnetic phase concentration due to the gravitational sedimentation and magnetophoresis (the motion of particles under the action of nonuniform magnetic field). The only mechanism that prevents stratification in the absence of convective motion is the gradient diffusion of magnetic particles in fluid. Generally, to obtain the concentration profile of the fluid in a cavity one must solve a boundary-value problem including Maxwell's equation for magnetic field and the dynamic mass transfer equation with consideration for terms responsible for magnetophoresis and sedimentation. The approximation of a dilute solution (when the volume fraction of particles is small compared to unity) makes it possible to separate the magnetic and diffusion parts of the boundary-value problem and to write the diffusion equation, which is linear in terms of the particle concentration and correctly considers magnetophoresis, sedimentation and gradient diffusion [1]. But in the case of concentrated fluids a description of the segregation process is a really challenging task due to the interparticle interactions. Today, there are quite a few works on mass transfer in magnetic fluids, which take into account steric, hydrodynamic and also magnetodipole interactions. For example, a formula for the chemical potential of magnetic fluid describing the excluded volume effect was derived by Cebers [2]. A large success in the problem of taking into account steric interactions was also achieved by Buevich et al. [3]. They derived a formula for the gradient diffusion coefficient in the framework of Carnahan–Starling approximation for the hard sphere fluid equation of state. Besides, they introduced the correction, linear in concentration, for the effective attraction of spherical dipoles. The theory of diffusion processes in magnetic fluid that takes into account both steric and magnetodipole interactions was developed by Morozov [4] and Bacry with coauthors [5]. The main drawback of this theory is the geometry limitation of an infinite flat layer. Perhaps one of the most complete mass transfer equations has been proposed in Ref. [6]. This equation describes the temporal and spatial variations of the volume fraction φ of single-domain colloidal particles and, in the absence of convective flows, can be written as follows:

$$\frac{\partial \varphi}{\partial t} = -div\left\{D_0 K(\varphi)\left(\varphi L(\xi_e)\nabla\xi_e + \varphi G_\gamma \boldsymbol{e} - \left[1 + \frac{2\varphi(4-\varphi)}{(1-\varphi)^4} - \varphi\frac{\partial^2(\varphi^2 G(\lambda,\varphi))}{\partial\varphi^2}\right]\nabla\varphi\right)\right\}. \quad (1)$$

Here, $K(\varphi) = b/b_0$, where b and b_0 are the particle mobility in the magnetic fluid and carrier fluid, respectively, $D_0 = b_0 kT$ is Einstein's value of the diffusion coefficient for a Brownian particle in dilute solution, $\mu_0 = 4\pi\times10^{-7}$H/m, $L(\xi) = \coth(\xi) - 1/\xi$ is the Langevin function, and

$\xi_e = \mu_0 m H_e/(kT)$ is the Langevin parameter, H_e is the effective magnetic field, which depends both on the applied field and the local concentration, $\lambda = \mu_0 m^2/(4\pi d^3 kT)$ is the coupling constant (the ratio of the magnetodipole interaction energy to the thermal energy), m and d are the magnetic moment and full diameter of the particle (including a protection shell), respectively, kT is the energy of the thermal motion, G_γ is the gravitational parameter, **e** is the unit vector in the direction of the gravitational field, and $G(\lambda,\varphi)$ is the contribution of magnetodipole interactions to the free energy density referred to the density of the thermal energy of the Brownian particle motion. The first term in the Eq. (1) represents magnetophoresis. The expression in square brackets can be considered as an effective diffusion coefficient of colloidal particles:

$$D = D_0 K(\varphi)\left[1 + \frac{2\varphi(4-\varphi)}{(1-\varphi)^4} - \varphi\frac{\partial^2(\varphi^2 G(\lambda,\varphi))}{\partial\varphi^2}\right]. \quad (2)$$

Here, the first term is responsible for the gradient diffusion, the second one – for the steric interactions (Carnahan–Starling approximation) and the last one takes into account magnetodipole interactions. The main practical difficulty associated with Eq. 1 is a need for $G(\lambda,\varphi)$ expression. Originally authors of Ref. [6] have used interpolation formula for the free energy virial expansion in terms of φ calculated up to φ^2:

$$D_1 = D_0 K(\varphi)\left[1 + \frac{2\varphi(4-\varphi)}{(1-\varphi)^4} - \varphi\frac{\partial^2(\varphi^2 G_1)}{\partial\varphi^2}\right],$$
$$G_1 = \frac{4}{3}\lambda^2\frac{(1+0.04\lambda^2)}{(1+0.308\lambda^2\varphi)}\frac{(1+1.28972\varphi+0.72543\varphi^2)}{(1+0.83333\lambda\varphi)}. \quad (3)$$

Another, more promising expression was recently introduced in Ref. [7]. By applying it to the case of diffusion coefficient we will get:

$$D_2 = D_0 K(\varphi)\left[1 + \frac{2\varphi(4-\varphi)}{(1-\varphi)^4} - \varphi\frac{\partial^2(\varphi^2 G_2)}{\partial\varphi^2}\right], \quad \varphi G_2 = \ln\left(1 + I_1\varphi + \frac{1}{2}I_2\varphi^2 + \frac{1}{3}I_3\varphi^3\right), \quad (4)$$
$$I_1 = \frac{4}{3}\lambda^2 + \frac{4}{75}\lambda^4 + \frac{116}{55125}\lambda^6, \quad I_2 = 2.901720\lambda^2,$$
$$I_3 = \left(4\ln 2 + \frac{2}{3}\right)\lambda^2 - \frac{20}{9}\lambda^3 + \left(\frac{661727}{9600} - \frac{1468}{15}\ln 2\right)\lambda^4 - 0.155\lambda^5 + 0.111\lambda^6 - 0.0143\lambda^7 + 0.0105\lambda^8 - 0.00$$

Finally, one more formula for D has been proposed in Ref. [8]. Instead of using free energy approach authors directly determine a magnetodipole term heuristically:

$$D_3 = D_0 K(\varphi)\left[1 + \frac{2\varphi(4-\varphi)}{(1-\varphi)^4} - \frac{8\lambda^2\varphi}{3(1+1.25\lambda\varphi)^2}\right]. \quad (5)$$

Obviously, the model is significantly less strict but it can be easily extended to the case of partially aggregated system. Eqs. (3), (4) and (5) work well in the area of moderate values of the interaction energy ($\lambda < 2$) and volume concentration ($\varphi < 0.4$). However, their extrapolation to the area of high energies and concentrations, which presents considerable interest for engineering applications, might be a risky step. The purpose of this work is to obtain reliable estimates for the diffusion coefficient of strongly coupled dipolar hard sphere system by means of the numerical simulation and to use these data in order to compare mentioned analytical models and determine their limits of applicability.

2. Simulation details

Simulated system is the finite-size circular cylinder filled with N dipolar spheres. The height of the cylinder is Z (in units of particle diameter d). Cylinder is vertically placed in the gravitational

field $G_\gamma \mathbf{e}$. Cylinder axis (z-axis) is directed against $\mathbf{e}$. Applied magnetic field is absent. In our work we use Monte Carlo (MC) and molecular dynamics (MD) methods to obtain equilibrium concetration distribution profiles of particles along z-axis at given λ and φ. In the case of MC simulation we use a standard Metropolis algorithm for the *NVT* ensemble. To get the *NVT* ensemble in MD simulation we use the Langevin dynamics approach. Potential energy of the i-th particle is given by expression:

$$\frac{U_i}{kT} = G_\gamma z_i + \frac{U_{i,boundaries}^{SR}}{kT} + \sum_{\substack{j=1 \\ j\neq i}}^{N} \left\{ \frac{U_{ij}^{SR}}{kT} - \lambda \left[\frac{3(\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} - \frac{3(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j)}{r_{ij}^3} \right] \right\}, \quad (6)$$

where $\boldsymbol{\mu}_i$ is the unit vector in the direction of particle magnetic moment, r_{ij} is the distance between centers of the i-th and the j-th particles (in units of d), U_{ij}^{SR} is a short-range interparticle potential, for MC this is hard-sphere potential $U^{HS}(r_{ij}) = \infty$ if $r_{ij} < 1$ and 0 otherwise, for MD this is truncated and shifted modified Lennard-Jones potential $U^{MLJ}(r_{ij}) = 4\varepsilon(1/r_{ij}^{48} - 1/r_{ij}^{24} + 1/4)$ if $r_{ij} < 2^{1/24}$ and 0 otherwise. Interaction with a cylinder boundary is considered as a short-range interaction with an image particle placed equidistantly on the other side of a boundary. The equations of motion for the i-th particle are:

$$m_0 \dot{\mathbf{v}}_i = \mathbf{F}_i - \gamma^T \mathbf{v}_i + \boldsymbol{\zeta}_i^T, \qquad I_0 \dot{\boldsymbol{\omega}}_i = \boldsymbol{\tau}_i - \gamma^R \boldsymbol{\omega}_i + \boldsymbol{\zeta}_i^R, \quad (7)$$

where m_0 is the mass of particle, $\mathbf{v}_i$ ($\boldsymbol{\omega}_i$) is the linear (angular) velocity, $\mathbf{F}_i = -\nabla U_i$ ($\boldsymbol{\tau}_i$) is the conservative force (torque) acting on particle, γ^T (γ^R) is the translation (rotational) friction coefficient, $\boldsymbol{\zeta}^T_i$ ($\boldsymbol{\zeta}^R_i$) is the random Brownian force (torque) acting on the particle, its component are drawn independently from Gaussian distribution with moments $\langle \boldsymbol{\zeta}^T_i \rangle = 0$, $\langle \boldsymbol{\zeta}^R_i \rangle = 0$, $\langle \boldsymbol{\zeta}^T_i(t) \boldsymbol{\zeta}^T_j(t') \rangle = 6kT\gamma^T \delta_{ij}\, \delta(t - t')$, $\langle \boldsymbol{\zeta}^R_i(t) \boldsymbol{\zeta}^R_j(t') \rangle = 6kT\gamma^R \delta_{ij} \delta(t - t')$. We determine the concentration profile of the system by dividing cylinder into equal horizontal layers with a height equals to one particle diameter and calculating average volume fraction for each layer. To find a link between profiles and the diffusion coefficient we use the equilibrium condition derived from Eq. (1): $\partial\varphi/\partial z = -\varphi G_\gamma/(D/D_0 K(\varphi))$. To ensure the system has reached equilibrium we perform every simulation with two types of initial states: 1) homogeneous particle distribution; 2) most of the particles are concentrated on the bottom of the cylinder in a thin layer four times lower than Z. Typical simulation parameters are: $N = 1000$ for MC and $N = 1024$, 8192 and 16384 for MD, $\varphi = 0.06$, $0 \le \lambda \le 8$, $Z = 20$, $G_\gamma Z = 5$, $\varepsilon/kT = 1$, MD time step $\Delta t = 0.002(m_0 d^2/\varepsilon)^{0.5}$, $\gamma^T = 10.0(m_0\varepsilon/d^2)^{0.5}$, $\gamma^R = 3.0(m_0\varepsilon d^2)^{0.5}$, number of simulation steps is 10^6 (both for MD and MC; the first 5×10^5 are rejected).

3. Results and discussion

The results achieved for the range $\lambda \le 5$ seem to be reliable. Equilibrium profiles here depend weakly on the initial state, number of particles and simulation method. Some examples of these profiles are shown in Fig. 1. To estimate the error between analytical theories and the numerical data we use the coefficient of determination R^2. If (y_i, x_i) are numerical data, $\bar{y}$ is their average and $y(x) = f(x)$ is the model function, R^2 might be written as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (y_i - [f(x)]_i)^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2}. \quad (8)$$

$R^2 = 1$ means that the match is perfect, $R^2 = 0$ means that model function describes data no better than a straight line $y(x) = \bar{y}$. The dependences of R^2 on λ for Eqs. (3), (4) and (5) are shown in Fig. 2. For D_1 and D_2 the error starts to arise after $\lambda \approx 3$ and for D_3 after $\lambda \approx 3.5$. But for the last

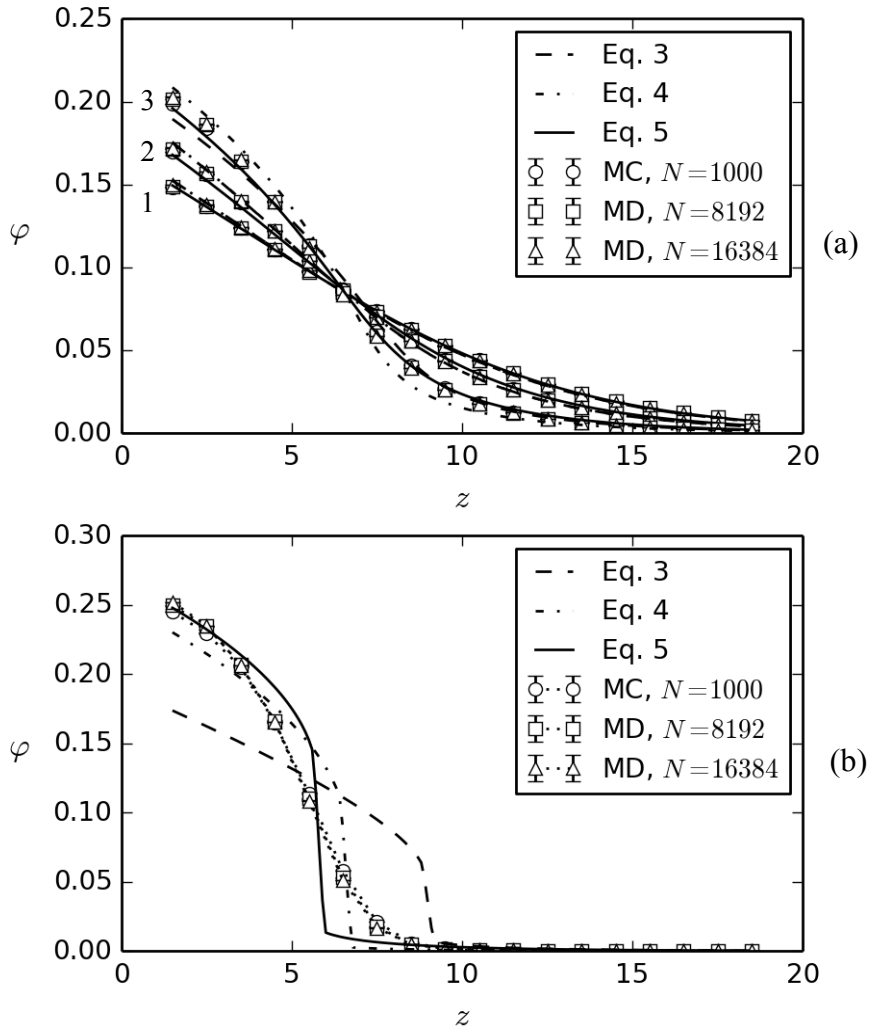

Figure 1: static concentration profiles in a vertical cylinder of finite height placed in the gravitational field. The magnetic field is absent. $<\varphi> = 0.06$. Curves correspond to analytical models and markers – to numerical results. In fig. (a): curves 1 correspond to $\lambda = 1$, curves 2 to $\lambda = 2$, curves 3 to $\lambda = 3$. In fig. (b) $\lambda = 5$.

two models the decline of R^2 is far less abrupt. Declines are obviously correlated with the critical areas where theoretical models predict the phase separation of the system. For every model there exist a critical point (λ^*, φ^*) after which the diffusion coefficient becomes negative. For Eq. (3) this is ($\lambda^* \approx 4.2$, $\varphi^* \approx 0.03$), for Eq. (4) ($\lambda^* \approx 3.5$, $\varphi^* \approx 0.05$), for Eq. (5) ($\lambda^* \approx 4.1$, $\varphi^* \approx 0.06$). After reaching this point the system becomes unstable and stratifies into two phases, weakly and strongly concentrated (phase transition "gas – liquid"). Fig. 1(b) shows examples of such a critical stratification. It also shows that at $\lambda = 5$ the agreement between D_3 and simulation results is good for sufficiently high local concentrations (outside the critical area). No signs of phase transition were observed in the numerical simulation for $6 \leq \lambda \leq 8$ as well. But it should be mentioned here that for this area of extremely strong magnetodipole interactions the equilibration time rises significantly and so does the simulation error. This issue is not so crucial in the case when initial state of the system is a concentrated layer. But still we believe that this range of coupling constant values should be investigated more accurately. Finally, we have performed some additional MC simulations for average concentrations larger than $\varphi = 0.06$ in order to directly estimate the diffusion coefficient of the colloidal particles from calculated profiles. Resulting coefficient for $\lambda = 5$ is shown in fig. 3 along with D_1, D_2 and D_3. Simulation points in figure are approximated with

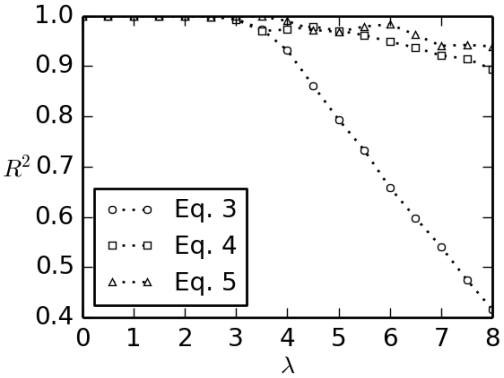

Figure 2: Coefficient of determination R^2 versus λ for different models. The closer R^2 to unity the better model approximates numerical data (MD, $<\varphi> = 0.06$, N = 8192).

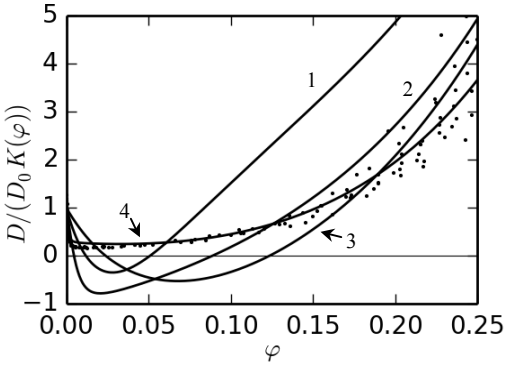

Figure 3: Diffusion coefficient versus local volume fraction for different models. $\lambda = 5$. Dots correspond to num. data (MC, N = 1000), curve 1 to Eq. (3), 2 to Eq. (4), 3 to Eq. (5), 4 to Eq. (9).

$$D_{approx} = D_0 K(\varphi)\left[1 + \frac{2\varphi(4-\varphi)}{(1-\varphi)^4} - \frac{8}{3}\lambda^2\varphi\frac{1 + [\exp(3\lambda)-1]\cdot(0.0007\lambda\varphi + 0.002\lambda^2\varphi^2)}{1 + 2.5\lambda\varphi + [\exp(3\lambda)-1]\cdot(0.254 - 0.1711\lambda + 0.0371\lambda^2)\varphi^2}\right]. \quad (9)$$

4. Conclusion

In this work we have performed a series of Monte Carlo and molecular dynamics simulations to determine equilibrium concentration profiles of strongly coupled hard sphere system in the gravitational field and in the absence of magnetic field. For $\lambda \leq 5$ we have achieved sufficiently accurate results and have used them to analyze three theoretical expressions for the diffusion coefficient of interacting magnetic particles (D_1, D_2 and D_3). Model D_1 doesn't match the numerical data at $\lambda > 3$. Model D_3 works well even at $\lambda = 5$ for high local volume fractions $\varphi > 0.22$, but for the lesser concentrations, where model predicts a negative diffusion coefficient and the "gas – liquid" phase transition, the agreement is poor. Theoretical curves for D_2 are also close to numerical results for sufficiently high local concentrations. No signs of the phase transition were observed in simulations. However, the precision of results for $6 \leq \lambda \leq 8$ is lower and this area should be the object of further investigations.

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6. References

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