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Two and Three Dimensional Monte Carlo Simulation of Magnetite Nanoparticle Based Ferrofluids

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ABSTRACT

We have simulated a magnetite nanoparticle based ferrofluid using Monte Carlo method. Two and three dimensional Monte Carlo simulations have been done using parallel computing technique. The aggregation and rearrangement of nanoparticles embedded in a liquid carrier have been studied in various particle volume fractions. Our simulation results are in complete agreement with the reported experimental observations. We have also checked the accuracy of our results with the prediction of theoretical expressions. In addition, we have applied the distributed computing method to reduce the run time of the program.

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1. INTRODUCTION

Ferrofluids are stable colloidal dispersions of single domain ferromagnetic nanoparticles of about 10 nanometers embedded by nonmagnetic liquid carrier [1]. Stabilization is one of the most important characters of the colloids. The interactions between these particles are mainly the magnetic dipole-dipole and attractive van der Waals forces. The outcome of these forces usually arranges the particles such that clusters form in ferrofluids. These aggregations lead to sedimentation of particles and is not desirable for most applications. To solve the problem, particles are usually stabilized against agglomeration by coating them with long chain molecules, applying mechanical repulsive forces between particles, called Steric stabilization or decorating them with charged groups, applying electrostatic repulsive forces between particles, called electrostatic stabilization. However, after these treatments, aggregation formation has been observed by cryogenic electron microscopy [2]. It seems that simulation of particle configuration is one of the best ways to predict ferrofluid properties.

The main purpose of this paper is to investigate how the variation of particle volume fraction affects the mean number of particles in clusters. It is shown that for low values of particle volume fraction, there are very good agreement in simulation results, experimental observation and theoretical expressions. But, the analogy of simulation results and experimental observation decreases by the increment of particle volume fraction.

This paper is organized as follow, in the next section, the theoretical expressions which describe the mean number of particles in clusters is introduced, Monte Carlo method is explained, the mathematical formula of particle interactions are nominated, simulation procedure is characterized and the distributed computing method is introduced. In section 3, the simulation results are exhibited and the effects of increasing the particle volume fraction on clusters mean number are inspected. The main results and conclusions are presented in section 4.

2. THEORY AND SIMULATION

2. 1. Theory Theoretical approach that deals with correlation phenomena in the colloidal magnetic particles in a uniform magnetic field have been developed by de Gennes, Pincus and Jordan [1-4]. They considered the magnetic force between particles as the

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most effective force and neglected the other probable interactions. They obtained two important expressions for the mean number of particles per cluster and chain in the absence and presence of external magnetic field. In their model, the mean number of particles per chain in the presence of strong external magnetic field is [1]:

$$n_{\infty} = [1 - 2/3(\varphi/\lambda^2)\exp(2\lambda)]^{-1} \quad (1)$$

where φ is the particle volume fraction and λ is the coupling coefficient which is defined in the following equation:

$$\lambda = \mu_0 M_d^2 V / 24\, kT \quad (2)$$

where μ_0 is the permeability of free space, M_d is the magnetization of ferromagnetic nanoparticles, V is the volume of each particle, k is Boltzmann constant and T is the absolute temperature in degrees Kelvin. It should be noticed that based on the theoretical assumptions, just the values $\lambda>1$ have the physical significance [1].

In the case of zero external fields, the mean number of particles associated with each cluster can be calculated by Eq. (3):

$$n_0 = [1 - 2/3(\varphi/\lambda^3)\exp(2\lambda)]^{-1} \quad (3)$$

As $\lambda>1$ it is obvious that $n_0<n_\infty$. Eqs. (1)-(3) are used in the sections (3.1 and 3.2) to validate the simulation results.

2. 2. Simulation Metropolis Monte Carlo simulation method has been used for simulation in this work. Monte Carlo simulation is a computational method to solve a model for which, change or growth does not proceed in some rigorously predefined method (like Newton's equation of motion), but rather use random numbers which generate during the simulation [5,6]. It is suited for calculation by a computer and tend to be used when it is infeasible to compute an exact result with a deterministic algorithm. Monte Carlo methods are especially useful for simulating systems with many coupled degrees of freedom, such as fluids. The Metropolis method consists of repeatedly trying to make a perturbation in system and then deciding whether to accept the new configuration or to retain the previous one [7]. Each Monte Carlo step or each perturbation in system will be accepted if the system total energy decreases or $\Delta E<0$. Otherwise, it will be accepted with probability exp $(-\Delta E/kT)$.

We define the ferrofluid as a gas which is consisted of N dipolar hard sphere with a magnetic moment m and diameter d dispersed in a cubic box of side length L with periodic boundary condition. Different volume fractions are obtained by varying the box size. The particles have translational and rotational degrees of freedom. Each particle is coated with a surfactant layer of thickness δ and the number of molecules adsorbed on the nanoparticle surface is ζ. Total inter-particle potential energy consists of E_d; the magnetic dipole-dipole energy, E_w; van der Waals attractive energy and E_s; the steric repulsion energy all with the following definitions:

$$E_d^{ij} = \frac{1}{4\pi\mu_0}\left[\frac{\vec{m}_i.\vec{m}_j}{r_{ij}^3} - 3\frac{(\vec{m}_i.\vec{r}_{ij})(\vec{m}_j.\vec{r}_{ij})}{r_{ij}^5}\right] \quad (4)$$

where $r_{i,j}$ is the centre to centre particle distance [8]:

$$E_w^{ij} = -\frac{A}{12}\left[\frac{d_{ij}^2}{r_{ij}^2} + \frac{d_{ij}^2}{r_{ij}^2 - d_{ij}^2} + 2\ln\left(\frac{r_{ij}^2 - d_{ij}^2}{r_{ij}^2}\right)\right] \quad (5)$$

where $d_{ij}=(d_i+d_j)/2$ is the average diameter of particles i and j [9]:

$$E_s^{ij} = \frac{\pi d_{ij}^2 \zeta kT}{2}\left[2 - \frac{l_{ij}+2}{t_{ij}}\ln\left(\frac{1+t_{ij}}{1+l_{ij}/2}\right) - \frac{l_{ij}}{t_{ij}}\right] \quad (6)$$

$L_{ij}=2s_{ij}/d_{ij}$ and $t_{ij}=2s_{ij}/\delta$ where s_{ij} is the surface to surface distance between particles i and j [10]. We have also considered the external magnetic field potential, E_m and gravitational field potential energy, E_g:

$$E_m^i = \vec{m}_i.\vec{H} \quad (7)$$

$$E_g^i = mass_i.g.\Delta h \quad (8)$$

where H is the external magnetic field intensity [8] and $mass_i$ is the mass of i^{th} particle, g is the gravitational acceleration of earth and Δh is the difference of height between the primary and secondary position of the particle.

2. 3. Distributed Computing Method One of the challenges faced in Monte Carlo simulation is the low speed of available computers. So, the process time and statistical errors are two significant problems in Monte Carlo simulation. Parallel computing toolbox and distributed computing server in Matlab software, have provided the possibility of parallel computing. Thereby, to reach a faster process, the calculations related to independent operators can be done in a network of connected computers. In this method, a set of few large operators is called one job and each job is divided to some sections called tasks. Making decision about how to divide a job to tasks is optional. But, by a smart choice, it is possible to select the most effective way for sooner implementation. Job manager is a part of distributed computing server which is responsible for distributed computing. Duties of this section are queuing the jobs, transfering the tasks to workers or computing centres and receiving and analyzing the results. Each worker receives one task from a running job by job manager and does the calculations related to that task, returns the results to the job manager and receives another task. When the tasks of one job ran out,

job manager repeats the same operation for another job and pursue this process until all the desired calculations finish [12].

We have used the distributed calculation method for calculating the energy in each step of Metropolis algorithm. To check the accuracy of results, we have calculated the total energy of the system consists of 200 nanoparticles by both sequential and distributed methods. In sequential method, the run time was 211 second and the process time reduced to 116 second when we used distributed computing with two workers.

3. RESULTS AND DISCUSSION

In this section, the simulation results are presented and they are validated with the theoretical predications. As we could predict, for a system which consists of Fe_3O_4 particles with the diameter of 10 nm, Monte Carlo simulation results exhibit a proper agreement with theoretical calculations in low particle volume fraction values. In section 3.1 the simulation results are presented in the absence of external magnetic field and section 3.2 is dedicated to the state which there is a strong external magnetic field.

3. 1. Simulation Results in the Absence of External Magnetic Field Figure 1 demonstrates some snapshots of particles configuration for various particle volume fraction values in the absence of external magnetic field. Aggregation of particles is seen obviousely by incresing the particle volume fraction. Quantitative reaults for these aggregation are presented in Figure 2 and Table 1. In Figure 2, different aggregation percent histograms such as monomer, dimer, trimers, tetramer, etc are shown for various values of particle volume fractions in the absence of external magnetic field and the mean number of particles per cluster achieved by Monte Carlo simulation and theoretical expressions are presented in Table 1. Percentage of larger aggregates increases by increasing the particle volume fraction.

To validate simulation results, mean number of particles per cluster in various volume fractions are calculated using both simulation and theoretical expersions. very good agreement between theory and simulation is clearly seen in Table 1.

TABLE 1. Very good agreement can be seen between simulation results and theoretical values for mean number of particles per cluster (n_0) for iron oxide nanoparticles in the absence of external magnetic field and in various volume fractions.

Concentration (%)	0.5	2	4	8	16
n_0 (theory)	1.02	1.09	1.19	1.48	2.58
n_0 (simulation)	1.03	1.16	1.35	1.75	2.13

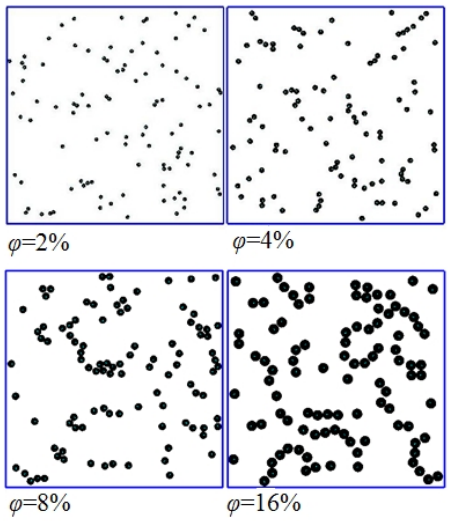

Figure 1. Snapshots of equilibrium configuration of iron oxide nanoparticles (10 nm diameter) at various volume fractions, in the absence of external magnetic field. Larger and more clusters appear by increasing particle volume fraction.

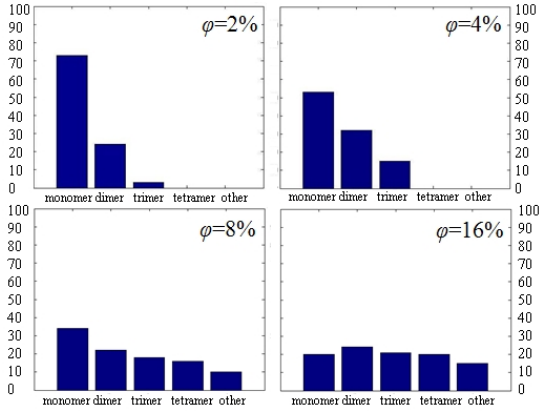

Figure 2. Percentage of various aggregations such as monomer, dimer, etc for iron oxide nanoparticles of 10 nm diameter in the absence of external magnetic field at various particle volume fractions. Percentage of larger clusters increse by incresing particle volume fraction.

3. 2. Simulation Results in the Presence of External Magnetic Field Figure 3 demonstrates some snapshots of particle configuration for various particle volume fraction values in the presence of external magnetic field. Long chains of particles formed along the external magnetic field and increaed by incresing particle volume fraction. Different aggregation percent histograms such as monomers, dimers, trimers, tetramers, etc are shown in Figure 4 for various values of particle volume fractions in the absence of external magnetic field.

The mean number of particles per cluster gained from Monte Carlo simulation and theoretical expressions are presented in Table 2.

By comprising the Monte Carlo simulation results and the values coming from theoretical expressions, it can be understood that the simulation results are in a good agreement with the theoretical predictions.

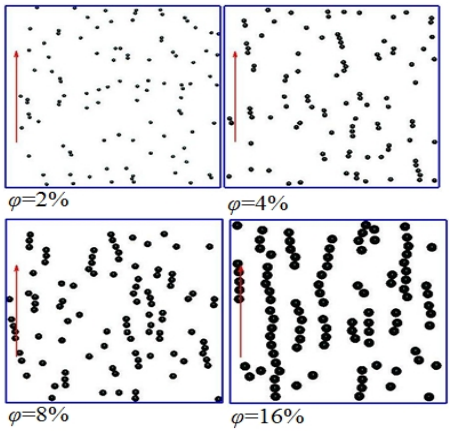

Figure 3. Snapshots of equilibrium configuration of iron oxide nanoparticles (10 nm diameter) at various values of particle volume fraction in the presence of external magnetic field. Long chain of particles appears along the external magnetic field and increases by increasing particle volume fraction.

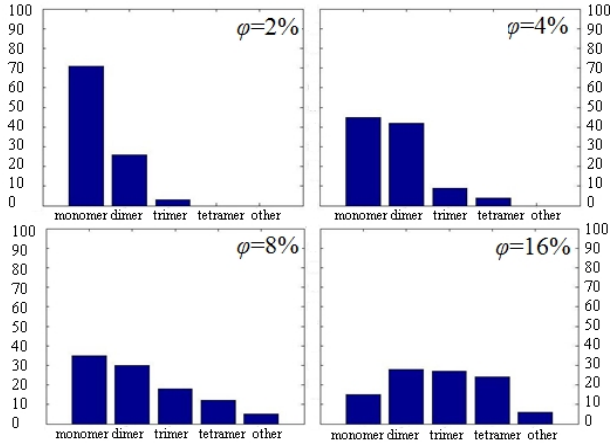

Figure 4. Concentration of various aggregates such as monomer, dimmer, etc, for iron oxide nanoparticles of 10 nm diameter in the presence of external magnetic field and at various volume fractions. Percentage of larger clusters increse by incresing particle volume fraction.

TABLE 2. Very good agreement can be seen between simulation results and theoretical values for mean number of particles per chain (n_z) for iron oxide nanoparticles in the presence of external magnetic field and at various volume fractions.

Concentration (%)	0.5	2	4	8	16
n_z(theory)	1.03	1.12	1.27	1.76	7.16
n_z(simulation)	1.04	1.19	1.42	1.67	2.22

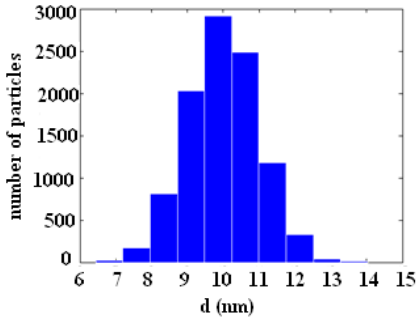

Figure 5. Particle diameter histogram by Gaussian distribution functions for particles of 10 nm mean diameter.

3. 3. Comparison between Simulation Results and Experimental Observations The distribution of particle diameters is an important issue in simulating the particles behavior. The Gaussian distribution function is used in this simulation. Figure 5 shows a typical distribution of particle diameters for 10000 nanoparticles.

Three dimensional Monte Carlo simulations of Fe_3O_4 nano particles was done by Castro and his coworkers in 2005 [11]. They calculated the percent of monomers in ferrofluids and made a comparison between simulation results and experimental observations. Their report shows a fair resemblance in low values of particle volume fraction. But, for values of particle volume fractions above 4%, significant inequality emerges between simulation results and experimental observations. In addition to calculate the percent of monomers, we have calculated the percent of other kinds of aggregation like dimer, trimers, tetramer, etc. Our simulation is based on the Fe_3O_4 nanoparticles with the diameter of 8.9 nm which are covered by dodecanicacids surfactants with 1.2 nm thickness. The number of molecules that are absorbed in a unit of surface is 1×10^{18}. The calculated Hamaker constant for these particles is 3×10^{-19}. Figure 6 shows a snapshot of particle configuration at the concentrations of 0.29 % and 3.7%

The qualitative results are presented in Figure 6. Figure 7 shows the histogram of each kind of aggregations. Percentage of larger aggregates increases by incresing particle volume fraction. The percentage of monomers achieved by simulation and experimental measurements are also compared in Table 3.

It can be seen in Table 3 that at low values of particle volume fraction, the percent of monomers gained from simulation is in a good agreement with experimental observation. The differences between experimental observation and simulation results increase when the particle volume fraction increases. This disparity can be attributed to not considering the reduction of magnetic diameters of particle due to interaction with surfactant and carrier liquid.

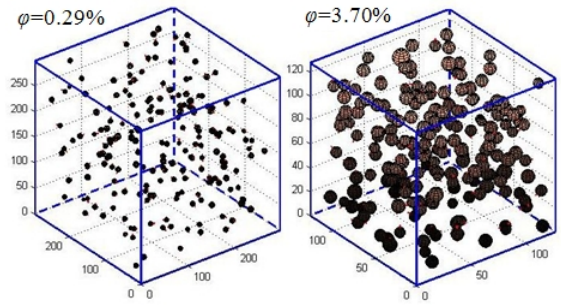

Figure 6. Snapshots of equilibrium configuration of polydisperse iron oxide nanoparticles wih mean diameter of 8.9 nm coated by dodecanoic acid in the absence of external magnetic field.

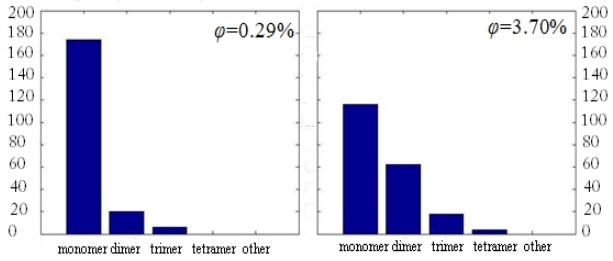

Figure 7. Concentration of various aggregates such as monomer, dimer, etc. for polydispersed iron oxide nanoparticles with mean diameter of 8.9 nm coated by dodecanoic acid in the absence of external magnetic field. Percentage of larger aggregetes increse by incresing particle volume fraction.

TABLE 3. Comparison between simulation results and experimental values for the concentration of monomers for polydispersed iron oxide nanoparticles with mean diameter of 8.9 nm coated by dodecanoic acid in the absence of external magnetic field.

Concentration (%)	Monomer (simulation) (%)	Monomer (experimental) (%)
0.29	87.0	84.0
3.70	58.0	60.1
10.0	18.0	58.9

4. CONCLUSION

In this work, Monte Carlo method, Metropolis algorithm and method for distributed computing were used to investigate the configuration of magnetic nanoparticles in magnetic fluids. The mean number of particles in each cluster structure and chain system consisting of iron oxide nanoparticles of 10 nm in diameter obtained at various particle volume fractions. Interaction between particles in the system is only magnetic dipole interaction. Comparing the results of this simulation with the values calculated using theoretical expressions, show that the Monte Carlo simulations using the Metropolis algorithm, could correctly describe the configuration of magnetic nanoparticles. In addition, using this simulation method, the configuration of system consisting of iron oxide nanoparticles with average diameter of 8.9 nm has been obtained. In this system, particles are covered with a surfactant layer of 1.2 nm thickness. Interactions between the particles are magnetic interaction, van der Waals attraction and Steric repulsion. Simulation results of calculating the percentage of single particle mass and other gatherings at various volume fractions showed that in low values of particle volume fractions, the only binary type aggregation can be seen that is in complete agreement with empirical observations. The percentage of single particles in low-volume fraction values shows a good agreement with experimental observations. But in high values of particle volume fraction, the difference between the experimental observations and simulation results became higher, because the reduction of particle's magnetic diameter during the reaction with the surfactant and carrier fluid was not considered. Moreover, to calculate the total system energy in each Metropolis algorithm steps, to reach a lower runtime, distributed computing method and computer networks were used.

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چکیده

شبیه سازی نانوذرات مغناطیسی در سیالات مغناطیسی با استفاده از روش مونت کارلوانجام شده است. این شبیه سازی در دو و سه بعد و با از روش محاسبات موازی استفاده شده است. تجمع و باز سازی نانو ذرات معلق در یک سیال حامل در نسبت های حجمی متفاوت مورد بررسی قرار گرفته است. نتایج شبیه سازی با گزارشات مشاهدات تجربی در توافق کامل است. همچنین درستی نتایج با استفاده از معادلا نظری امتحان شده است. به علاوه، برای کاهش دادن زمان اجرای برنامه، روش محاسبات توزیع شده مورد استفاده قرار گرفته است

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