

Brownian Dynamics Simulation of Magnetic Colloid Aggregation

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Abstract—We have done simulations of aggregation of magnetic colloids at relatively high solids fraction, using new high-efficiency algorithms to deal with the long-range magnetic forces. We have included the effects of viscous damping on both translational and rotational motions. We have calculated bond-angle statistics that give information about the short-range structure of flocculated dispersions which will influence the rheological and magnetic properties.

I. INTRODUCTION

We have developed a program for the particle-level simulation of magnetic inks. Although our ultimate objective is to study the magnetic and rheological response, we have begun by developing methods for constructing realistic model colloids (necessarily somewhat aggregated, at realistic volume fractions) to use as initial conditions for such simulations. We have studied the aggregation of acicular (cigar-shaped) particles of two different aspect ratios, 6.5 (similar to that of Toda F ceramic-coated metal particles) and 1.5 (nearly spherical).

Various statistical measures can be used to characterize the aggregation behavior. At low volume fractions of solids, the particles initially form well-defined finite clusters which have been characterized by a "compactness" parameter [1]. However, at fractions above the percolation threshold (or at low volume fractions after a long time) the clusters become very large and this is not so useful. We have found that useful summary information about suspensions at technologically useful volume fractions is given by a histogram of the "hinge angle" θ . This angle is computed for each pair of particles whose (opposite) poles are close together, and is just the angle between the magnetization vectors. In a magnetically oriented (saturated) suspension, the distribution peaks around $\theta = 0$; its behavior in other cases will be described below (see Figs. 2 and 3).

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To generate an initial condition for a simulation by randomly placing particles, it is necessary to use a relatively low volume fraction – otherwise particles will almost always overlap other particles. Previous dynamical simulations [2] have used volume fractions of order 0.84%, for example. The structures formed at low volume fraction will tend to be rather filamentary, perhaps not characteristic of those at typical volume fractions for real dispersed paints, not to mention the even higher volume fractions obtained after drying the paint. To address this problem, we have developed a technique for achieving realistic volume fractions, in effect by simulating the drying process. This is done by starting with a low volume fraction and gradually shrinking the periodic simulation box. (A similar idea has been used in Monte Carlo simulation[3]; instead of shrinking the box, the particles were initially assumed very small and allowed to grow.)

II. SIMULATION TECHNIQUE

Molecular-dynamics (MD) simulation of molecular fluids is a well-developed field, in which one follows particle trajectories by finite difference solution of their Newtonian equations of motion. However, the realistic simulation of magnetic colloids presents severe additional problems. As with any colloid, the effects of the solvent (which we take to include the dissolved binder as well) must be taken into account. This has previously been done [2] by Stokesian simulations, meaning that the forces exerted on colloid particles by solvent molecules are modeled by a viscous drag force. This is very time-consuming when the solvent viscosity is high, because the characteristic time for a moving particle to slow down is extremely short (inversely proportional to the viscosity) and the computational time step Δt must be taken to be even smaller. In this "Brownian" limit, it can be shown [4] that it is not necessary to follow the velocity in detail, and that an algorithm in which the displacement of a particle is proportional to the force on it (plus a random Brownian force) gives the correct dynamics. We have used such a Brownian dynamics algorithm.

Previous simulations of acicular magnetic particles [2] have taken into account damping of translational motions, but not rotational ones. Rotational damping is critical, for example, in the formation of a tightly bound dimer

from an "L" shaped hinge configuration of two particles attached to each other at one pole – when magnetic attraction causes the hinge to close, in the absence of rotational drag the hinge can bounce open again. We have developed a new algorithm for the simulation of rotational as well as translational Brownian motion.

A. Particles

We model the magnetic particles as cylinders with spherical caps (spherocylinders). In the simulations reported in Section III we have used particles with an aspect ratio (the ratio of the axial length to the diameter) of 6.5 and 1.5, a radius of $a = 4.6$ nm and a magnetization of 1154 emu/cm³. The magnetization direction is taken to be fixed in the particle, along the cylinder axis.

B. Interactions

There are two types of interactions between particles: the long-ranged magnetic interaction and the short-ranged steric repulsion due to the polymer coating on the particles.

We model the magnetic force between particles as a pole-to-pole force. Because of the long range nature of the interaction, demagnetization effects due to images under the periodic boundary conditions are important, and have not previously been included in such simulations. The traditional Ewald sum rule to include the forces from the image charges is quite CPU intensive; we have used instead the particle-particle and particle-mesh (PPPM) method[5] combined with a multipole expansion (MPE) [6] [7] [8] [9]. The force on a particle has two contributions: a direct sum of forces due to neighboring particles (PP part), and a slowly varying force evaluated in terms of the multipole moments of magnetic pole charges of distant particles (PM part).

We model the short-ranged steric interaction due to the coating on the surface of the particles by a parabolic potential of the form

$$U_{steric}(ij) = U(r_0 - r_{ij}^{min})^2$$

where r_{ij}^{min} is the distance of closest approach [2] between the axes of particles i and j , the range r_0 of the interaction is taken to be $2.6a$, and U is chosen such that the equilibrium distance between two side-by-side particles is equal to $2.3a$. (This is equivalent to assuming a thickness of $0.15a$ for the polymer coating on the particles.)

C. Box shrinking (solvent evaporation)

We have used the simplest possible protocol to shrink the simulation box. The length L of the box is decreased by a fixed fraction at each time step Δt , determined by a volume strain rate $\dot{\gamma}$:

$$\frac{dL}{dt} = -\dot{\gamma}L$$

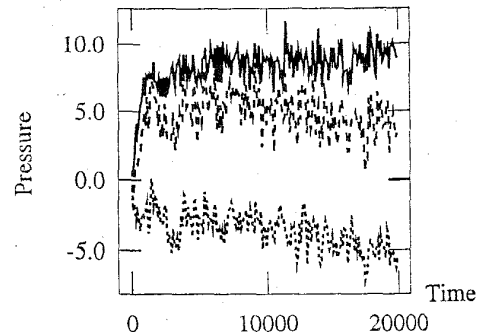


Fig. 1. Pressure as a function of time, for aspect ratio 6.5. The cell was shrunk during the first 400 time steps, then kept at constant size for the remainder of the simulation. The part of the pressure due to magnetic forces (lowest curve) and that due to steric repulsion (highest curve) are shown, as well as the total particle pressure (middle curve). Fluid pressure is not included. The shrinkage rate $\dot{\gamma}$ is $1/2000\Delta t = 10^3$ s⁻¹.

We begin with 100 particles in a cube of length $L = 60a$, where a is the radius of a sphero-cylindrical particle, corresponding to a volume fraction of about 1.8%. Figure 1 shows the increase in pressure as the box is compressed.

At low volume fraction the particle pressure is negative because of the magnetic attraction (the total pressure, which includes the fluid pressure as well, is of course positive). The particle pressure becomes positive when the steric repulsion takes over at high volume fraction, at which point the pressure increases very rapidly with further contraction.

In these runs we have used $\Delta t = 5 \times 10^{-7}$ s for aspect ratio 6.5 and 1×10^{-7} s for aspect ratio 1.5. We assumed a viscosity of 1 poise, and calculated the translational and rotational drag by modeling the cylinder as a string of spheres and using Stokes' law.

We save the particle configuration at two volume fractions, and anneal each such configuration at constant volume fraction. The results are described in the next section.

III. AGGREGATION SIMULATION RESULTS

In Figs. 2 and 3 we show the hinge angle distribution. Note the peak at $\theta = 180^\circ$ ($\cos \theta = -1$). This represents clusters of parallel particles (mostly dimers and trimers) that are held together at both ends by the attraction between opposite magnetic poles. There is a marked dip at around $\cos \theta = -0.75$ (about $\theta = 140^\circ$), probably due to the fact that pairs with this hinge angle can quickly jackknife into the parallel configuration. 4.

We have also simulated aggregation in the presence of a constant magnetic field. In this case particles tend to align themselves in the direction of the magnetic field such that chains of particles are formed; the hinge an-

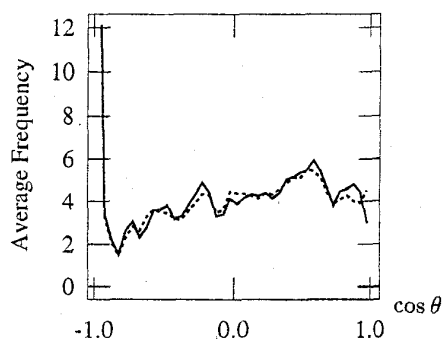


Fig. 2. Histogram of hinge angle distribution, for aspect ratio 6.5 and volume fractions 3.25% (dashed line) and 6.5% (solid line). If the particles were randomly oriented the frequency would be independent of $\cos \theta$.

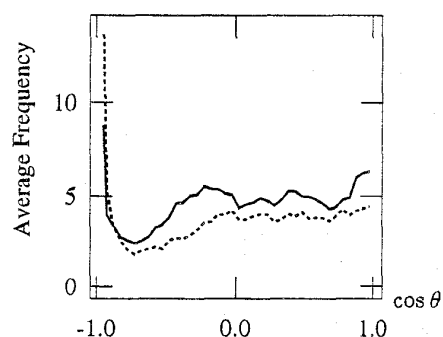


Fig. 3. Like Fig. 2 but for aspect ratio 1.5.

gle is strongly peaked at $\theta = 0^\circ$. Consistently with the results of Coverdale et al. [1], the magnetization remains nearly saturated even after annealing in zero field.

In the future, we hope to calculate the susceptibility (transverse and longitudinal) of the present model. By subjecting it to oscillatory shear, we will calculate its rheological properties. We will try to correlate magnetic measures of interaction, such as the α parameter [10] with the geometric statistics we have calculated.

Our present form for the steric potential is a function only of the nearest distance between points of the spherocylinders. That is, the energy is the same for an end-to-end configuration as for side-by-side. Clearly it would be more realistic to allow these energies to be different. Less obviously, this potential causes the torque on a particle in a side-by-side dimer to be a discontinuous function of orientation, which causes severe numerical problems. Also, TEM images suggest that metal nanoparticle shapes might be better modeled as ellipsoids rather than spherocylinders. We have developed a simple potential model for ellipsoidal particles and will use it for further simulations.

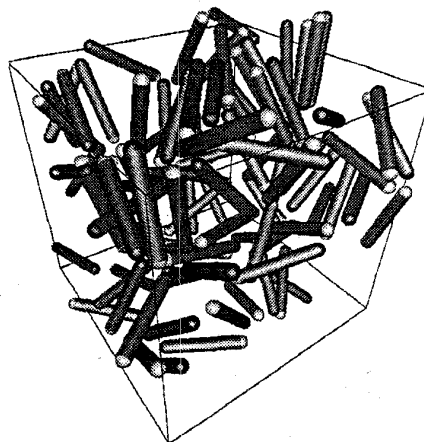


Fig. 4. Snapshot of a suspension, for the case of aspect ratio 6.5 and volume fraction 6.5%.

IV. CONCLUSION

We have developed a method for generating realistic initial conditions for simulation of magnetic ink, and used it to calculate the hinge angle distribution. This distribution is sensitive to differences in flocculation structure, for example between colloids aggregated with and without an applied magnetic field.

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