

Self-Assembly in Model Magnetic Inks

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Abstract— We have studied the stability of ordered structures in simulated suspensions of magnetic particles similar to those used in the manufacture of magnetic tape. We previously reported[1] that a monodisperse colloidal suspension of acicular uniformly magnetized particles forms a smectic ordered phase consisting of planar layers within which the particles are oriented perpendicular to the plane. One reason why these structures have not been seen experimentally may be that real magnetic inks have a distribution of particle sizes. We have generalized the simulation to allow this, using a log-normal length distribution. We find that the smectic structure is stable against a small amount of polydispersity – a system of particles with a 10% length variation forms a smectic structure similar to the monodisperse system, whereas 25% variation is sufficient to suppress the ordering. Work is under way to quantitatively establish the phase boundaries for the smectic ordering.

I. INTRODUCTION

It has recently been shown[1] that simulated colloidal suspensions of acicular magnetic nanoparticles spontaneously self-assemble into a layered structure. Since self-assembly is of potential interest as a faster alternative to lithographically patterned or scanning-tip-deposited particulate arrays for high-density information storage, we have investigated the stability of these ordered states against polydispersity, which may be responsible for the fact that they are not observed experimentally.

II. COMPUTER MODEL OF MAGNETIC DISPERSION

We simulate a collection of acicular magnetic particles (cylinders with spherical caps) in a binder solution. All physically important forces are included: steric, hydrodynamic, magnetostatic, and Brownian. The steric interaction is modeled by a strongly repulsive quadratic interaction potential, as in previous simulations[2][3]. The hydrodynamic drag is taken to be linear in the velocity, as in Stokes' formula for the drag on a sphere. This sort of

simulation is often referred to as "Stokesian" although in the cylinder case there are distinct longitudinal and transverse drag coefficients, as well as a rotational drag coefficient. The Brownian forces and torques are implemented by a random number generator with a Gaussian distribution[3]. The magnetostatic forces are the most difficult and time-consuming to model. We use a Stoner-Wohlfarth model in which the magnetization vector (assumed uniform within a single particle) is computed by minimizing the Stoner-Wohlfarth energy (including anisotropy energy) of the particle. Thus the magnetization vector is not necessarily along the particle axis (the easy axis, as a result of shape anisotropy) and the resulting magnetic pole density (the outward component of magnetization at the surface) is not confined to the spherical ends of the particles. In a simulation in which the magnetization is always along the particle axis, it is quite accurate to model the magnetostatic field using a single north and south pole near the end of the particle[2][3][4]. In the present case, however, there is a strip of pole density along each flank of the particle, due to the transverse component of the magnetization. We model this by a series of six point poles along this flank, as shown in Fig. 1.

As a result of allowing transverse magnetization, we have a very large number of poles (14 per particle) and calculating all forces between pairs is very slow. We have instead used a particle-particle/particle-mesh (PPPM) method[5] together with a multipole expansion[6][7]. This method takes into account all periodic images of each pole in a manner similar to the Ewald summation method.

To construct an initial condition, we have used a method described previously[3] in which the particles are placed randomly in a very large periodic simulation box (so overlap is not a problem) and then the box is shrunk gradually (over 1500 time steps), allowing the particles to push each other out of the way as the density increases. Then the external magnetic field is increased linearly to 500 Oe over a period of 4000 time steps, where it remains for the rest of the simulation, while we wait for the appearance of a smectic phase.

III. MODELING POLYDISPERSITY

In previous simulations, all particles have been assumed to have a common length L . We have generalized this to a log-normal distribution of lengths:

$$L = L_0 e^{px} \quad (1)$$

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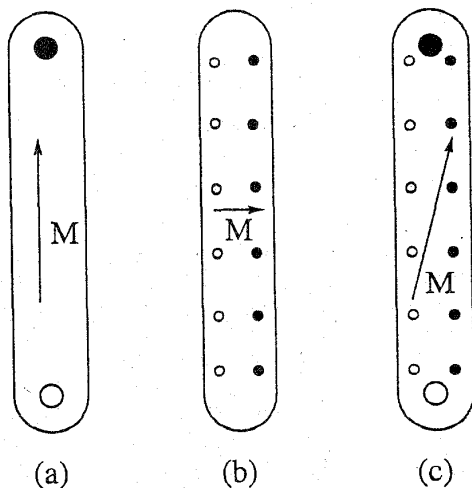


Fig. 1. (a) A particle with only longitudinal magnetization, modeled by a north (filled circle) and south (open circle) point pole. (b) A particle with only transverse magnetization, in the plane of the figure, showing the strings of poles that approximate it. They are equally spaced along a line determined by the center of mass of a cross-section of the north pole density in a plane perpendicular to the particle axis. (c) A general magnetization vector having both a longitudinal and a transverse component, showing the 14 poles that are used to represent it.

where L_0 is the nominal length, x is a Gaussian random variable with unit variance and zero mean, and p is a dimensionless polydispersity parameter. We will refer to the case with $p = 0.10$, for example, as "10% variation in length". For simplicity, we have assumed that the cylinder radius remains the same for all particles.

IV. SIMULATION PARAMETERS

In our simulations we used particles with a nominal aspect ratio (the ratio of the axial length to the diameter) of 6.5, with a radius of 4.6 nm and a magnetization of 148 emu/gm. Thus the nominal length is 30 nm; the actual lengths vary around this as specified by Eq. 1. We simulate 100 particles (but note that this involves 1400 poles), the effective binder viscosity is taken to be 1 poise, the integration time step is 5×10^{-7} s, and the temperature is 300K. In all the simulations reported here, the box was shrunk until the volume fraction was 6%. The simulations were carried out to 20,000 steps (0.01 s). Each simulation takes about 60 hours on a Silicon Graphics Indy workstation with a 132 MHz R4600 processor.

V. RESULTS

Figure 2 shows the smectic structure formed by a monodisperse system. Although the north poles of the particles in a given layer lie in the same plane, their repulsion is mitigated by the fact that the south poles of the particles in the next layer interpose themselves between them[1]. The sensitivity of this phase to the orientation

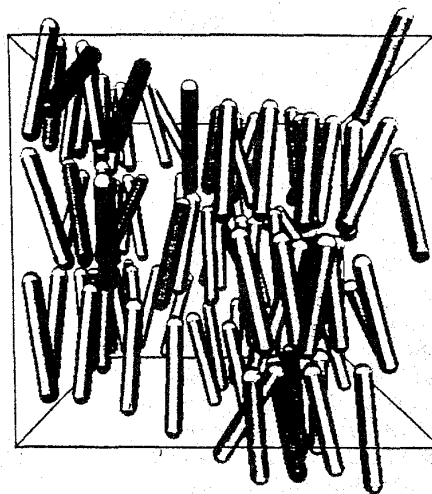


Fig. 2. The structure formed by a monodisperse magnetic colloid subjected to a 500 Oe vertical external field.

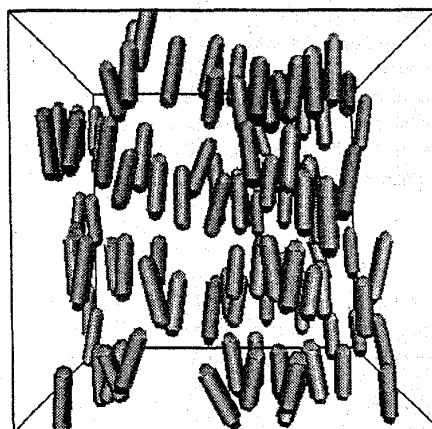


Fig. 3. The structure for the case of 10% length variation.

of the field relative to the sides of the periodic box, and hence with respect to the commensurability of the particle length and the box size, has been investigated to some extent previously[1] and found to be relatively insensitive. If we introduce a 10% polydispersity ($p = 0.1$ in Eq. 1), the final configuration is as shown in Fig. 3. Note that the layers are less well developed, but the system is still clearly an ordered one. In Figs. 4 and 5 (15% and 20% length variation) there is a weaker degree of ordering, and in Fig. 6 (25%) there appears to be only local ordering. At this level of polydispersity, there are significant numbers of particles that are 2 or 3 times the nominal length, which extend through more than one layer and disrupt the order.

VI. CONCLUSION

We have simulated colloidal suspensions with various degrees of polydispersity in an external field strong enough to cause smectic ordering in a monodisperse sys-

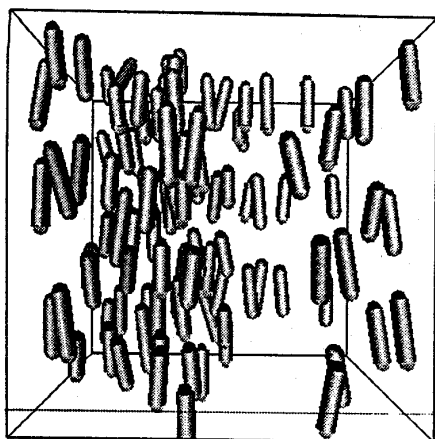


Fig. 4. The case of 15% length variation.

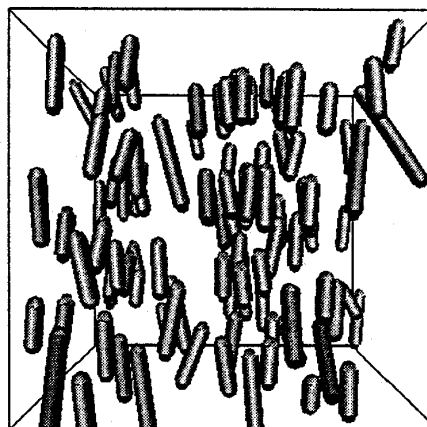


Fig. 6. The case of 25% length variation.

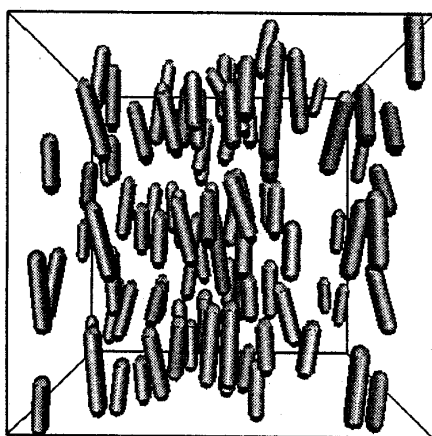


Fig. 5. The case of 20% length variation.

tem, and shown that 25% length variation is sufficient to suppress this ordering. Clearly a more quantitative measure of the ordering is desirable, for example the Fourier components of the density (of particle centers, not mass) for wavevectors along the magnetic field direction. The dependence of the ordering on volume fraction of solid also should be investigated, although because the system has a filamentary structure throughout a wide range of densities, and smectic structure seems to form within the filaments, the dependence on the density may not be strong.

Experimental investigation of possible smectic phases in magnetic colloids, perhaps by low-angle neutron scattering, would also be interesting and useful.

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- [7] All of these methods require first modeling the system by a set of point charges; work is under way on a hierarchical method that treats the continuum particle magnetization without this approximation.