Field-induced smectic ordering in model magnetic inks

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We have performed Brownian dynamics simulations of model colloids of acicular (cigar-shaped) magnetic particles with aspect ratio 6.5, similar to Toda F ceramic-coated metal particles. In the absence of a magnetic field, these have a gel-like structure. We have investigated the effect of a magnetic field on this structure. At very low volume fractions the particles (after orienting along the field) form chains in the field direction. At more realistic volume fractions (3%–9%), we find a unique filamentary structure, in which the filaments themselves are smectically ordered. That is, the particles are stacked side-by-side with their poles in a common plane. The net effect of the orienting field is to promote aggregation into filaments. © *1997 American Institute of Physics.* [S0021-8979(97)79308-3]

I. INTRODUCTION

Most previous analytic and simulation[1] studies of the phase behavior of dipolar systems have modeled the particle moment as a point dipole at the center of a spherical particle. For colloidal suspensions of acicular magnetic particles, we have used a more realistic model, a cylindrical particle with spherical end caps, with point magnetic poles at the sphere centers. In zero external field, this model forms gel-like aggregates[2] at volume fraction 6.5%, consistently with rheological and magnetic measurements on such colloids. In this article we investigate the unique structures formed in the presence of a magnetic field. These structures depend critically on the acicular shape of the particles; they are not found in point–dipole simulations.

II. THE PHYSICAL SYSTEM AND THE SIMULATION METHOD

The physical system we study is a collection of acicular magnetic particles in a solvent. The large number of solvent molecules are omitted from the simulation, and their effects on the magnetic particles are represented by a combination of random forces and frictional terms. This in effect replaces Newton's equations of motion by some kind of Langevin equation. We use Ermak's algorithm[3] to numerically evaluate the equations of translational motion. Previous simulations of acicular magnetic particles[4] have taken into account damping of translational motions, but not rotational ones. Using the quaternion representation of rigid body rotations,[5] we developed a new algorithm to numerically integrate the equations of rotational motion.

In a simulation only a finite number of particles can be accommodated. We define a main simulation box in which a finite number of particles is placed, and the problem of surface effects is overcome by implementing periodic boundary conditions: the main simulation box is replicated throughout space to form an infinite lattice and image particles are placed in each box.

We have used a method developed previously[2] for initializing the particle positions. Particles are placed randomly in a large box at low volume fraction (0.6%) and the box is gradually compressed to the desired final volume fraction, in the presence of the magnetic field.

A. Interactions

The long-ranged magnetic interaction and the short-ranged steric repulsion due to the polymer coating on particles are the two types of interactions between particles that we consider.

The long-ranged magnetic interaction is modeled as a pole-to-pole force, poles being placed at the sphere centers. The potential energy due to the interaction of two poles of strength P and P' is PP'/r where r is the distance between the poles. The total magnetic force on a particle has an infinite number of contributions coming from image particles under periodic boundary conditions. The traditional Ewald rule to do this sum is CPU intensive. Instead we have used the particle-particle particle-mesh method (PPPM)[6] combined with a multipole expansion (MPE).[7]

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

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

where $r_{ij}^{\min}$ is the distance of closest approach[4] 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.)

B. Simulation parameters

In our simulations we used particles with an 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/g. The magnetization direction is taken to be fixed in the particle, along the cylinder axis. The number of particles in the main simulation box is 100, the viscosity is 1 poise, the time step for the numerical integration of the equations of motion is 5×10^{-7} s, and the temperature is 300 K.

III. ORDERING PHENOMENA

Ordered phases are usually found in fairly dense systems, because they require strong interparticle interaction. When we first found a smectic ordered phase at 6.5% volume

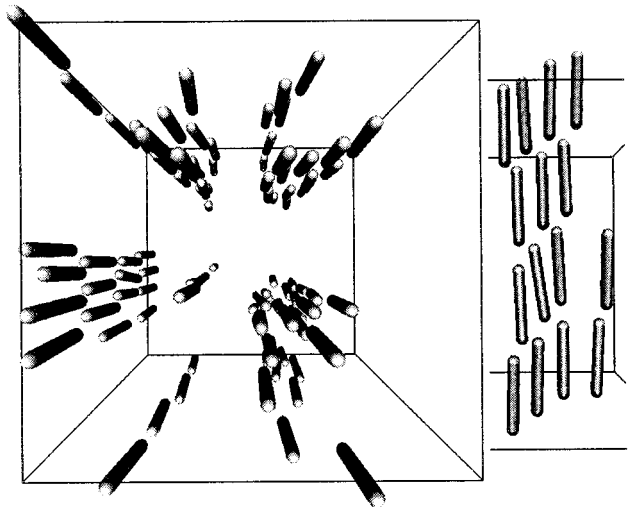

FIG. 1. End-on view (along the field) of the chains and ''sheets'' of particles in a dilute colloid (2% volume fraction). Detail at right shows only the particles in a thin slice (of thickness 30 nm, half a particle length) perpendicular to the paper.

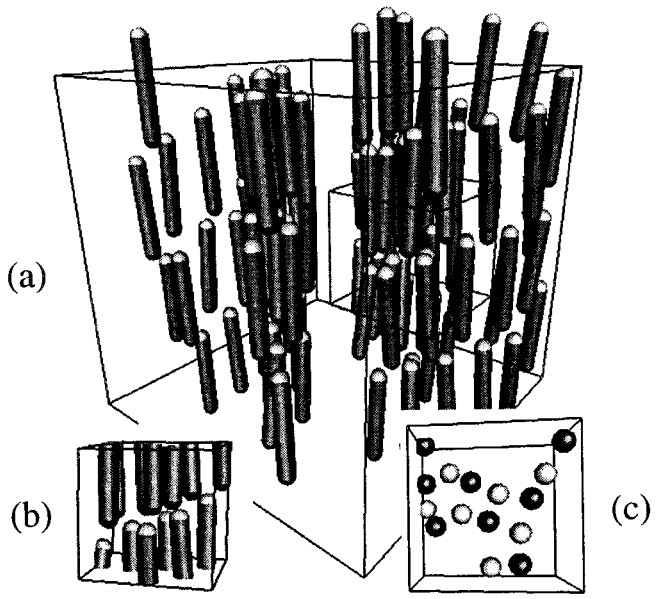

FIG. 2. (a) A colloid with 6% volume fraction, with a small box surrounding a piece of interface between two filament segments. (b) Expanded view of the interface region. (c) Top view (along the field) of the interface region. The cylindrical parts of the particles are omitted, so we see only the north and south poles (as dark and light shaded spheres).

fraction and 400 Oe field, we assumed it would disappear at lower volume fraction and become more pronounced at higher volume fraction. As we see below, the opposite appears to be true. At very low volume fractions, it is intuitively plausible that chains of particles form, like paper clips hanging from a magnet, and indeed this is what initially occurs at our lowest volume fraction of 2%. One might expect these chains to then drift toward each other and aggregate into sheets or filaments, as indeed they do (Fig. 1).

It is not hard to convince one's self that two registered chains (with the north poles at the same height on both) will repel, so a sheet cannot consist of a regular array of chains. One might think that the poles would be randomly displaced from one chain to the next, so the poles would not lie on a line. However, it turns out that the poles *do* lie nearly on a line, which is almost perpendicular to the field, as seen in Fig. 1. Two particles do approach each other at the same height, so their north poles repel, but this repulsive energy is more than compensated for by a south pole that positions itself between the two north poles.

As the volume fraction increases, this same pattern persists but the 2D sheets become 3D filaments along the field direction. The north poles lie on a plane perpendicular to the field. This resembles the structure of a smectic liquid crystal. The filament is composed of cylindrical segments, each composed of many particles stacked side-by-side. The structure of the interface between the segments is interesting—if each north pole had a south pole directly above it (as though the structure were constructed by packing chains) the system would be magnetostatically unstable. The south poles must interpose between the north poles, as in the 2D ''sheet'' case, to stabilize the interface. Such an interface is shown in Fig. 2.

In any molecular-dynamics study of structure, one must be concerned with the effect of boundary conditions on the structure. We have done some simulations with the magnetic field along different axes, and find similar filamentary structures. Figure 3 shows a configuration produced by a field in the (111) direction; the (011) direction produces similar results.

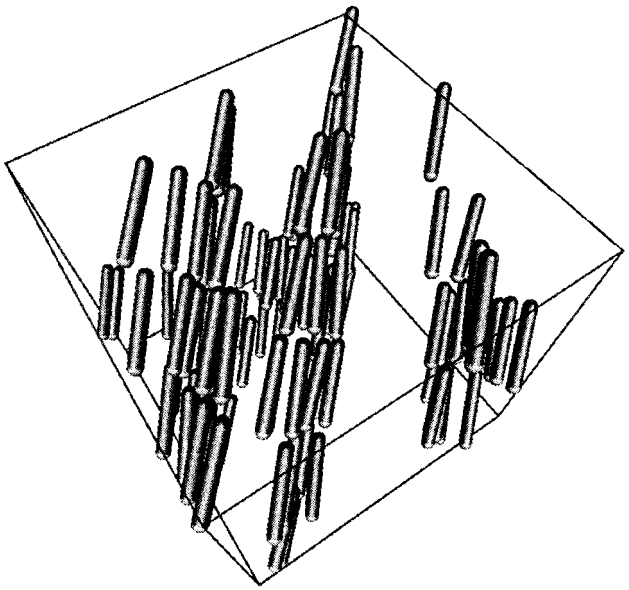

FIG. 3. Filaments in a colloid at 3% volume fraction produced by a 1500 Oe field in the (111) direction.

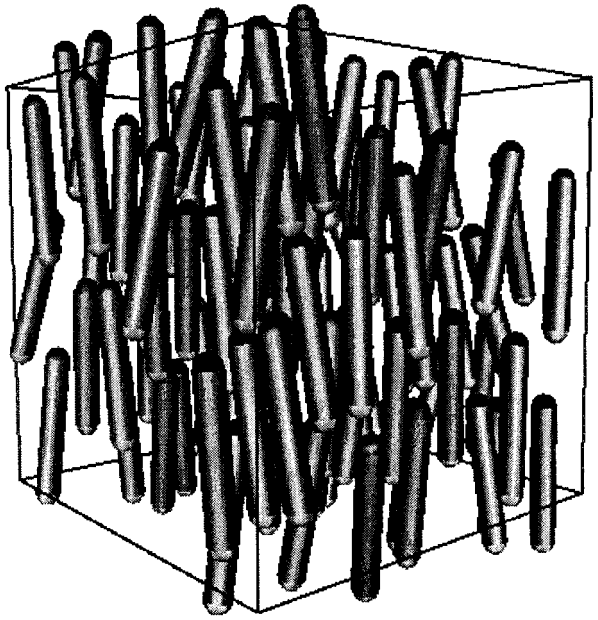

FIG. 4. Typical configuration of a dense colloidal suspension (12% volume fraction).

As the density of particles increases, the tendency to smectic ordering seems to decrease, as shown in Fig. 4 at 12% volume fraction. The absence of a layered phase could be a result of a glasslike transition which prevents rearrangement into a smectic phase, or could be related to changes in the box length—clearly the commensurability of the box length and the particle length is an important factor. All of our simulations have 100 particles and start with the same size box at low volume fraction. Thus after compression, the higher volume fractions end up in shorter boxes. We intend to do simulations in which the volume fraction and the box/particle length ratio are varied independently.

IV. CONCLUSION

We have shown that complex segmented filamentary structures arise spontaneously in simulations of colloids of acicular magnetic particles in the presence of a magnetic field. These simulations raise the question whether the smectic structures might be experimentally detectable, for example by neutron scattering. Calculations of the static structure factor would be useful for comparison with scattering results. It is also important to determine the effect of polydispersity on the layering, by doing simulations with a distribution of particle lengths.

ACKNOWLEDGMENT

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