One- and Two-Dimensional Crystallization of Magnetic Holes

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Holes are produced inside a thin layer of magnetic fluid with use of monodisperse polystyrene spheres with diameters in the micrometer range. With an external magnetic field an apparent magnetic dipole will be associated with each hole as a result of the displaced fluid. The apparent dipolar interactions between the spheres may be made attractive or repulsive. This Letter presents the first direct microscopic observations of the crystallization of magnetic holes forming a variety of different lattices.

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Dispersions of colloidal magnetic particles in a nonmagnetic liquid solvent have been studied for a long time in regard to various crystallization phenomena.[1,4] The reverse situation with nonmagnetic particles in a magnetic fluid or ferrofluid has only been studied for application purposes like material separation.[5] The use of highly monodisperse polystyrene spheres of diameters in the micrometer range dispersed in a magnetic fluid represents a new concept for model studies of phase transitions. The basis for this is that the holes created by the spheres appear to possess a magnetic moment as a result of the magnetization of the surrounding fluid. The purpose of this Letter is to report the first direct microscopic observation of the collective behavior of holes in a magnetized fluid.

A magnetic fluid consists typically of a colloidal suspension of monodomain ferromagnetic particles like magnetite (diameter about 0.01 μm) in a nonmagnetic carrier fluid like water or kerosene.[5] A surfactant covering the particles prevents agglomeration, and because of the small size, Browian motion prevents sedimentation in a gravitational field. The particles behave as classical dipoles and the fluid is ideally paramagnetic in that it only becomes magnetic in an external field. Such fluids have many technical applications.[6]

A thin layer of magnetic fluid containing a monolayer of monodisperse spheres has several unique features. The apparent magnetic dipolar interactions between the spheres may be made attractive or repulsive by an external field H parallel or perpendicular to the layer, respectively. The interaction energy between two spheres is to first order proportional to H^2 and may easily be made comparable to the thermal energy. This offers a wide range of model systems for experimental studies of phase-transition phenomena. These include (1) a two-dimensional system of repulsive dipoles forming a triangular lattice for melting studies; (2) systems of attractive dipoles forming "gaslike," "liquidlike," and "solidlike" structures depending on the density of the spheres and the external field; (3) systems with mixtures of different-sized spheres forming a variety of crystalline and amorphous configurations. Only a few selected systems will be discussed in this Letter, while other studies will be presented elsewhere.

The experimental setup is shown schematically in Fig. 1. The thin layer of magnetic fluid containing the spheres was confined between two plane glass plates. The observations were made with either an ordinary microscope in transmitted-light illumination mode or an inverted metallurgical microscope. The lattices could be photographed or recorded on tape with a video camera attachment. Uniform magnetic fields could be produced both normal ($H_\perp$) and parallel ($H_\parallel$) to the layer with use of Helmholtz coils.

The experiments reported here were made with polystyrene spheres[7] of diameter $D = 1.9$ μm at concentrations typically $N = 10^7$ spheres/cm^2. A kerosene-based magnetic fluid was used[8] with saturation magnetization $M_s = 400$ G and initial susceptibility $\chi = 0.17$.[9] The layer thickness was approximately $h = 5$ μm which could be fixed by using a low concentration of 5-μm-diam spheres as spacers.

Figures 2(a) and 2(b) show typical ordered

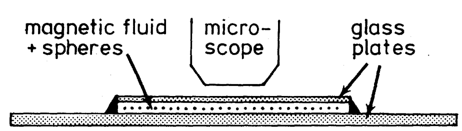

FIG. 1. Schematic of the experimental setup where the magnetic fields are produced by two pairs of Helmholtz coils which are not shown.

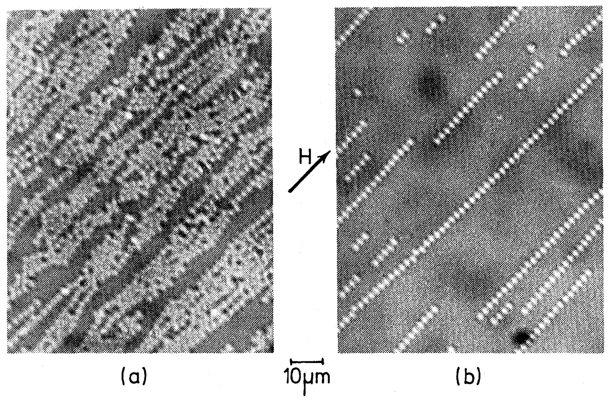

FIG. 2. Photographs of polystyrene spheres in a magnetic-fluid film with an external field $H_{\parallel} = 120$ Oe parallel to the film. (a) High sphere concentration; (b) low sphere concentration.

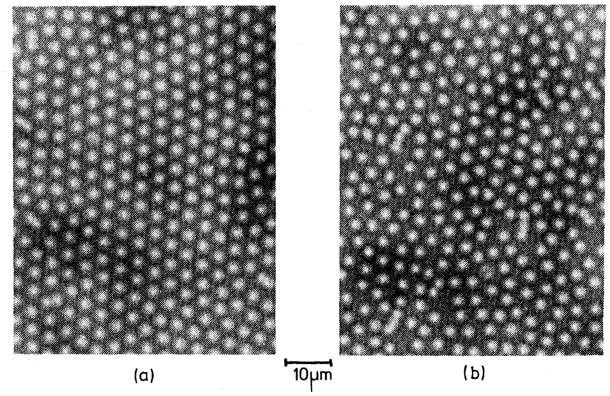

FIG. 3. Photographs of polystyrene spheres in a magnetic-fluid film with fields normal to the film. (a) Crystalline structure for $H_{\perp} = 75$ Oe; (b) amorphous structure for $H_{\perp} = 20$ Oe.

structures with a field $H_{\parallel} = 120$ Oe parallel to the layer with different sphere concentrations. There are qualitatively three different phases: (1) a low-density or "gaslike" phase with isolated spheres and dimers; (2) a medium-density or "liquidlike" phase with chain formation signifying attractive interactions between spheres and repulsive interaction between chains; and (3) a high-density or "solidlike" phase signified by hard-sphere-like packing. By reducing the field $H_{\parallel}$, the chains were eventually seen to break up into smaller pieces as a result of Browian motion. This already suggests an interesting model system for stuides of a rich phase diagram involving the sphere concentration and interactions characterized by H as will be discussed below. These investigations will be presented elsewhere.

In Fig. 3(a), a field $H_{\perp} = 75$ Oe is applied normal to the layer producing a fairly regular two-dimensional triangular structure with an average lattice constant $a = 4.5$ μm. This signifies apparent long-range repulsive interactions between the spheres. It may be noted that there are a few dislocations which are due to impurities or spheres sticking together. More careful preparation of the samples than for the present experiments would certainly reduce the dislocation density. In Fig. 3(b), a smaller field $H_{\perp} = 20$ Oe is applied and the structure is now disordered because of dominant thermal fluctuations. The nature of such a melting transition is of considerable fundamental interest and will be discussed in more detail below.

We shall first take a closer look at the dominant interaction producing the lattices just pictured. Figure 4(a) shows the situation for an isolated sphere inside the magnetic fluid. The apparent magnetic moment associated with the sphere is to first order given by

$$M_v(\theta) = -\chi_{\mathrm{eff}}(\theta) V H(\theta). \tag{1}$$

Here, θ is the angle between the field direction and the layer and $V = \pi D^3/6$, the volume of the sphere. A linear medium is assumed and $\chi_{\mathrm{eff}}(\theta)$ is the effective volume susceptibility of the fluid and given to first order by

$$\chi_{\mathrm{eff}}(\theta) = \chi / \{1 + [N_c(\theta) - 4\pi/3]\chi\}. \tag{2}$$

Here, χ is the bulk susceptibility, $N_c(\theta)$ is the demagnetizing factor of the container, and $4\pi/3$ represents the demagnetizing factor for a sphere.

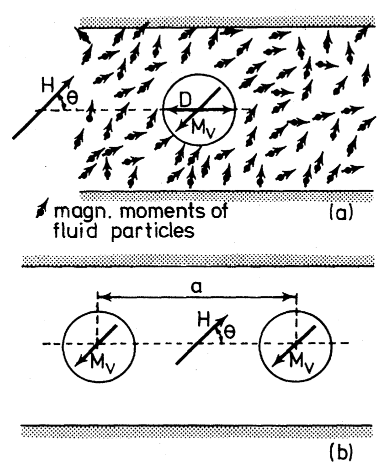

FIG. 4. The situation for (a) one isolated sphere in a magnetic fluid; (b) two interacting spheres.

For a field normal to the layer, $N_c(\theta)=N_c(90^\circ)=4\pi$, whereas a parallel field gives $N_c(\theta)=N_c(0^\circ)=0$.

For two spheres separated by distance a as shown in Fig. 4(b), there will be to first order an apparent dipolar interaction given by

$$E_{dd}(\theta)=[M_v(\theta)]^2(1-3\cos^2\theta)/a^3. \quad (3)$$

For fields parallel ($\theta=0^\circ$) and perpendicular ($\theta=90^\circ$) to the layer, the interactions are thus attractive and repulsive, respectively, consistent with the observations in Figs. 2 and 3.

It appears that the spheres are self-positioned midway between the two glass boundaries although this could not be determined precisely. This indicates that the spheres are trapped in an energy well deeper than the thermal energy k_BT, where k_B is Boltzmann's constant and T is the absolute temperature. This effect is apparently due to the formation of dipolar layers of magnetic particles along the glass boundaries.

It should be noted that electrostatic interactions are of minor importance for the present system. The kerosene-based magnetic fluid contains very few free electric charges. In addition, electrostatic repulsive interactions for the immersed spheres are only of short range with a factor $\exp(-a/\lambda_D)$, where λ_D is the Debye length. This was also borne out from direct observations in zero external field. The lattices were completely random and Brownian motion could bring two spheres almost into contact.

In contrast, earlier phase-transition studies of polystyrene spheres in aqueous solutions are based on electrostatic repulsive interactions.[10] However, it appears to be difficult to vary the interactions in a continuous and controlled manner for such systems as it involves elaborate adjustments of the ionic strength of the solutions. The present system governed by magnetic interactions therefore appears to be more tractable, as it only involves the use of external magnetic fields.

Because of the ideal paramagnetic behavior of the fluid, there is also no remanent magnetic interactions between the spheres with no external field. This is a distinct advantage over electrostatic-controlled systems as well as a system of magnetic particles with domain effects and remanence.

As demonstrated in the order-disorder transition of the triangular lattice in Fig. 3, two-dimensional melting may be studied with the present system. In particular, the Kosterlitz-Thouless[11] and Halperin-Nelson[12] theories of melting may be tested. It is thus of interest to determine whether the melting transition is first order, involving a region of coexistence between crystalline and amorphous phases, or whether there are two second-order transitions with a hexatic phase existing between them.

The relevant parameter in the melting studies of the present system is the dimensionless coupling constant given as the ratio between the dipolar energy and the thermal energy:

$$\Gamma=[M_v(90^\circ)]^2/a^3k_BT. \quad (4)$$

For the lattice shown in Fig. 3, $a=4.3$ μm and $T=300$ K, giving $\Gamma\simeq 8$ and 110 for $H_\perp=20$ and 75 Oe, respectively. This already indicates that the melting of the dipolar-coupled lattices takes place between these two values for Γ.

There are two recent molecular-dynamics simulations for melting in a two-dimensional system with dipolar interactions. They both indicate that the transition is first order, occurring at $\Gamma=62\pm3$,[13] and $\Gamma=59-65$.[14] This is therefore consistent with the qualitative observations in Fig. 3.

To proceed with a more quantitative analysis of our system, calculations of the positional and directional correlation functions will be needed.[11,12] An extensive analysis along these lines is in progress, and will be presented in a forthcoming publication.

Observations were also made by rotating a constant field from a parallel to a normal direction relative to the layer with a medium density of spheres. This produced a transition from a quasi one-dimensional to a two-dimensional lattice, which suggests another interesting phase diagram involving the parameters Γ, $H_\perp/H_\parallel$, and N.[15]

The analysis of the dominant magnetic interactions presented here clearly involves various approximations. In more precise calculations one should also consider the size effects of the magnetized fluid around the spheres, uneven dipole layers along the boundaries, as well as concentration-dependent effective demagnetizing factors. However, the present Letter is intended to give a first qualitative description of the observations and those other refinements would not add to the basic understanding.

There are many interesting extensions of the new concept of interacting magnetic holes. The use of anisotropic, nonmagnetic bodies will thus introduce additional rotational and anisotropic forces reminiscent of liquid crystals. There is also the possibility of using monodisperse gas or liquid bubbles to create interacting deformable magnetic holes in a magnetized fluid. These are all examples of new model systems for fundamental studies of collective phonomena. In addition, numerous applications like gratings, filters, polarizers, circulators, etc. for acoustic and electromagnetic waves are also evident.

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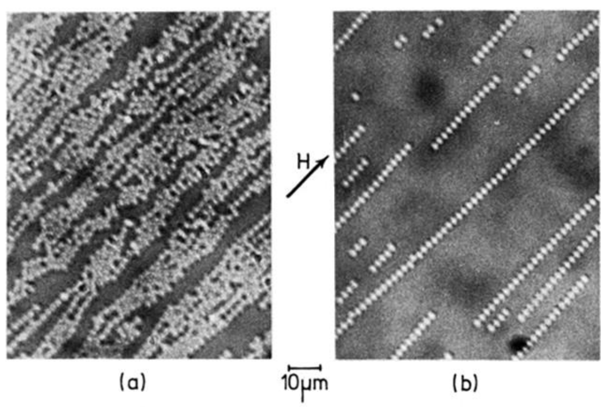

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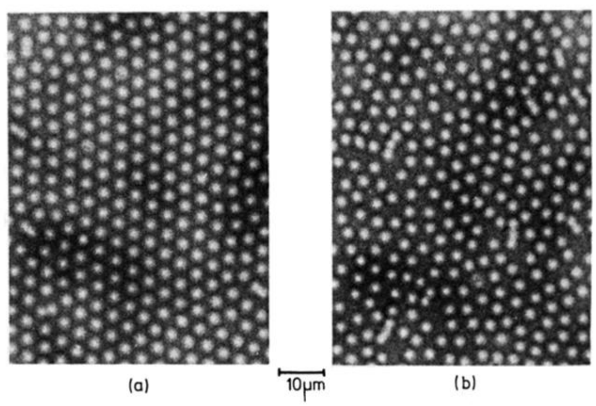

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