## **Field-Induced Structures in Ferrofluid Emulsions**

Jing Liu,<sup>1</sup> E. M. Lawrence,<sup>1</sup> A. Wu,<sup>1</sup> M. L. Ivey,<sup>1</sup> G. A. Flores,<sup>1</sup> K. Javier,<sup>1</sup> J. Bibette,<sup>2</sup> and J. Richard<sup>3</sup>

<sup>1</sup>Department of Physics and Astronomy, California State University, Long Beach, California 90840

<sup>2</sup>Centre de Recherche Paul Pascal, Avenue A. Schweitzer, F-33600 Pessac, France

<sup>3</sup>*Rhone-Poulenc Recherches, 52 Rue de la Hale Coq, 93308 Aubervilliers, France* 

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The field-induced structure in a monodisperse ferrofluid emulsion is studied. An applied magnetic field induces a magnetic dipole moment in each droplet. When the dipole-dipole interaction energy exceeds the thermal energy, a phase transition occurs as the fluid of randomly dispersed droplets changes to a solid of nearly equally sized and spaced columns. Our results show that the column spacing follows a relation  $d = 1.33L^{0.37}$  for cell thickness  $3 \le L \le 800 \ \mu\text{m}$ . A new theory, which treats the column shape more realistically, is developed to account for the results.

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When an external electric or magnetic field is applied to a colloidal suspension comprised of particles with a dielectric constant or magnetic permeability different than the surrounding liquid, dipolar interactions are induced within the particles. If the induced dipolar interactions are sufficiently strong, the colloidal particles can undergo a phase transition, changing from a liquid to a solid. As a result, the particles develop a columnar structure. The development of a detailed understanding of this phase transition, and the resultant induced structures, present a formidable scientific challenge. The nature of this phase transition is also of considerable practical interest; these field-induced structures can dramatically modify the rheological properties of the suspension leading to many potential applications.

Suspensions which exhibit this sensitivity to externally applied electric and magnetic fields are called electrorheological (ER) and magnetorheological (MR) fluids. Perhaps because of their more immediate practical utility, ER fluids have received considerable attention in the past several years [1,2]. While detailed questions still remain, the phase behavior and field-induced structures of ER fluids are reasonably well understood [3–6].

By contrast, the behavior of particles interacting through induced magnetic dipoles is significantly more complex, and not nearly as well understood. Unlike ER fluids, the boundary conditions used for MR fluids typically preclude the presence of image dipoles. Thus, the long-range nature of the interaction can persist even when the particles form chains or columns. The range of the interaction between the chains depends very sensitively on their length. For example, in the limit of a single layer of particles, the long range of the repulsive interactions  $(\sim 1/r^3)$  between the induced magnetic dipoles causes the particles to crystallize into a two-dimensional hexagonal lattice [7]. By contrast, in the limit of no confinement, infinitely long chains form which result in an equilibrium structure as fully phase separated, similar to that in an ER fluid [3,4] due to chain fluctuations [6] and short-range interaction [ $\sim \exp(-r/a)$ , *a* is the particle radius] between chains.

The behavior of chains of intermediate length is considerably more complex, and has not been definitively studied experimentally. Theoretically, not like the two extreme cases mentioned above, it is very difficult to calculate exactly the interaction between finite chains and columns of dipoles. All published theoretical models attempt to predict the induced structures in this regime using series approximations; different approximations resulted in different structural relations. Because of the dearth of experimental data, these models have not been adequately tested. The few experimental studies that have been reported use polydisperse particles, masking the subtle behavior controlling the phase transition and the resultant structures [8-10]. Moreover, these studies were limited to a short range of cell thicknesses, making it difficult to measure an accurate relationship between the structure and the column length. Despite our lack of knowledge, it is chains of intermediate length that are of the greatest practical importance, making a definitive study of their behavior essential. In addition, there is great interest in using MR fluids to simulate the interaction and structure of magnetic flux in type-II superconductors [11].

In this Letter, we present the first detailed and definitive study of field-induced structures in a suspension of monodisperse particles interacting through induced magnetic dipoles. By varying the thickness of the sample cell over 2 orders of magnitude, we quantitatively determine the dependence of the equilibrium structure on the chain length. We find that the particles form chains which coalesce into thicker columns. Strong ordering, as shown by a characteristic spacing between the columns, is observed. This reflects the persistence of significant interactions between the columns. We find that the increase of the column width with the cell thickness can be described by a power law, but that the power-law exponent measured is significantly less than that predicted by any of the theoretical models proposed to date. To account for our data we offer a new cylindrical column model to describe more realistically the shape of the columns. Our model predicts a lower apparent exponent; in fact, it suggests a slight,

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but noticeable deviation from a simple power law. It is in excellent agreement with our data. We also find that the column spacing is essentially independent of the particle volume fraction  $\phi$ , suggesting that the column width increases with  $\phi$  while the column number remains unchanged. Our model also accounts for this behavior. Our work not only shows a completely new structural relation, newer than that observed in any existing dipolar media including the domain structure of ferrofluid and ferromagnetic materials, but also identifies the key interactions between finite columns which have been neglected by all the previous theories.

Our system is a ferrofluid emulsion consisting of oil droplets stabilized by surfactant and suspended in water [12,13]. Inside each droplet is a ferrofluid which contains small magnetic grains with permanent dipole moments. The droplets are highly monodisperse with a diameter of 0.5  $\mu$ m. In the absence of a magnetic field, Brownian motion randomly orients these grains and the droplets act as hard spheres. Upon application of a magnetic field, the moments of the grains are preferentially aligned, inducing a magnetic dipole moment in each droplet; the resultant dipolar interactions can be sufficiently large to cause phase transitions and induce the formation of the larger structures.

The strength of the dipolar interaction between droplets is usually described by a coupling constant  $\lambda$  defined as the ratio of the interaction energy of two parallel dipoles in contact and the thermal energy [1]

$$\lambda = \frac{E_d}{k_B T} = \frac{\pi \mu_0 a^3 \chi^2 H^2}{9k_B T}, \qquad (1)$$

where  $\mu_0$  is the magnetic permeability in a vacuum, *a* is the droplet radius,  $k_B$  is the Boltzmann constant, and *T* is the temperature. The droplet susceptibility is  $\chi = \chi_b/(1 + \chi_b/3)$ , with  $\chi_b$  the bulk ferrofluid susceptibility. All of the structures described in this Letter are formed at  $\lambda \gg 1$ ; however, the magnitude of the external field is increased sufficiently slowly to ensure that the structures reflect equilibrium behavior.

Figure 1 shows the structure formed when the applied magnetic field strength is 38 mT corresponding to  $\lambda =$ 166. The sample has  $\phi = 0.04$  and is held in a thin cell whose thickness in the field direction is  $L = 50 \ \mu m$ , or about 100 droplet diameters. Figure 1(a) shows a microscope image viewed normal to the field direction. The structure is clearly a solid as no apparent Brownian motion of droplets is observed. It consists of columns, many droplets thick, that span the thickness of the cell. The columns are roughly uniform in width, although there are short chains between the columns near both ends of columns. The ordering of the columns is evident. However, only local ordering is observed, rather than the hcp crystal structure exhibited by a single layer of dipoles. Therefore, as the length of column increases, the interaction between columns is partially screened compared to that between a single layer of dipoles. Notice that the



FIG. 1. (a) Microscope image showing the cross section of a column structure taken at  $\phi = 0.04$ ,  $L = 50 \ \mu$ m, and  $\lambda = 166$ ; (b) the corresponding light scattering pattern; (c) the correlation function obtained from (a); and (d) the light scattering intensity as a function of the scattering wave vector obtained from (b).

same structure is obtained as long as  $\lambda > 6$ . The observed columnal structure at  $\lambda \gg 1$  supports that fluctuations of chains due to Peierls-Landau instability can still exist and play an important role in column formation [6,14].

Figure 1(b) shows a momentum space representation of the same structure formed by light diffraction. Here the incident laser light, of wavelength 632.8 nm, is parallel to the magnetic field direction and is directed normal to the cell surface. A screen behind the sample displays the small angle scattering. When the applied magnetic field reaches  $\lambda > 1$ , an intense ring is observed; it becomes sharper with increasing  $\lambda$ . A typical scattering pattern contains three to four concentric rings; in some case seven rings are observed. The large number of rings observed reflects the strong ordering of the columns; however, the structure is not a perfect crystal lattice, as no distinct diffraction spots are observed.

The column spacing can be measured either from the real space images, by calculating the correlation function of the columns, or from the momentum space data, by measuring the diameter of the diffraction ring. We use both methods. The correlation function is shown in Fig. 1(c); the position of the highest peak directly measures the column spacing d. The angle averaged scattering is shown in Fig. 1(d); the peak position of the scattered light  $q_{\text{max}}$  yields the column spacing through  $d = 2\pi/q_{\text{max}}$ . The two methods yield identical values of d.

Figure 2 shows a log-log plot of the column spacing vs the cell thickness at a constant volume fraction  $\phi = 0.04$ and a constant magnetic field strength corresponding to  $\lambda = 166$ . The dependence of d on L is approximately linear, giving a power-law relation  $d = 1.33L^{0.37}$ , obtained by a least-squares fit, shown by the solid line. Despite the relatively good fit, a power-law dependence is only an approximation; there are slight deviations at



FIG. 2. Column spacing as a function of column length on a log-log scale. The triangles are the experimental data. The solid line is the least-squares fit of the data. The solid dots are the theoretical fit.

higher L. If we fitted only the data in the range of  $100 < L \le 800 \ \mu$ m, we would obtain a somewhat higher exponent 0.47. The exponent never goes beyond 0.5.

Several theories [3,8,15] have been developed to understand the length dependence of the field-induced structures of interacting dipolar colloids. All of them attempt to calculate the lowest free energy of a continuous system including either two or three of the dipolar interactions: (a) the dipole interaction between the droplets within a single column, which favors forming separate long and narrow columns to reduce the effects of demagnetization or dipolarization field from the ends; (b) the surface energy, which favors forming large columns to minimize the surface area, and which is a correction to the bulk energy calculated in (a) originating from the fact that surface droplets are subjected to a different local field compared to those inside; and (c) the interaction energy between neighboring columns, which is dominated by the interaction between the ends of the columns and is mainly repulsive, favoring a large column spacing and a smaller area at the ends of columns. For a given column length, minimizing the total interaction energy yields the column width and spacing. These theories apply only to equilibrium structures; in our experiments, this is ensured by increasing the external field sufficiently slowly. All of these theoretical models assume an ellipsoidal shape of the columns in calculating the structure. All predict a power-law dependence of d on L. Depending on the exact nature of the interaction, different exponents are predicted, ranging from 0.5 to 1. None of them agree with our experimental results.

We believe that the reason for this discrepancy is the assumption of ellipsoidal-shaped columns. The very narrow caps on the columns reduce the interaction between them and therefore underestimate this interaction energy. Our microscope images show that the shapes of the ends of each column are neither points with a radius of one droplet a nor disks of uniformly distributed droplets with the radius b of the column. The exact column shape depends on the cell thickness and the volume fraction. We

observed both tapered ends with a radius r in between a and b, and split-branch ends with r about the same as b. However, in both cases, just a few droplets away from the ends, the column is cylindrical in shape. Therefore, we modify the theories to incorporate a cylindrical shape for the columns [16].

In our cylindrical model, each disklike end of a column contains many uniformly distributed monopoles due to the induced dipoles within each column. In the case of an ellipsoidal column where only one monopole is assumed to be at each end, increasing d reduces the repulsive interaction between the neighboring columns at each end plane. Therefore minimizing the energy favors a larger column spacing, hence larger columns, when  $\phi$  is fixed. In the case of a cylindrical column, increasing d causes an increase in the number of surface monopoles at each end of the columns because  $2r \sim d\sqrt{\phi}$ , and hence an increase of the repulsive interaction between the monopoles. Therefore, by minimizing this repulsive energy, smaller columns result, which leads to a smaller d.

In our model, the free energy due to a magnetic interaction is

$$U = \int d\nu \left(\frac{H^2}{8\pi} + \frac{1}{2}\vec{H}\cdot\vec{M}\right)$$
(2a)

$$= \int d\nu \left( \frac{H_0^2}{8\pi} - \vec{H}_0 \cdot \vec{M} - \frac{1}{2}\vec{H}_m \cdot \vec{M} + \frac{M^2}{2\chi_m} \right),$$
(2b)

where H,  $H_0$ , and  $H_m$  are the total, external, and demagnetization field, M is the magnetization of the column and  $d\nu$  is the volume unit. The relations between them are  $\vec{H} = \vec{H}_0 + \vec{H}_m$  and  $M = \chi_m H$ , where  $\chi_m$  is the column susceptibility. All the information about the equilibrium structure of the medium is contained in  $\vec{H}_m$ . Only the third term contributes when the energy is minimized; therefore, we limit our consideration to it.

The third term is the demagnetization energy, which can be expressed in terms of a potential  $\Psi_m$ , due to the induced surface monopoles, and the monopole density  $\rho_m$ :

$$U_d = \int d\nu \left( -\frac{1}{2} \vec{H}_m \cdot \vec{M} \right) = \int d\nu \left( \frac{1}{2} \rho_m \psi_m \right) \quad (3)$$

$$= \left\lfloor \alpha_1 \left(\frac{d}{L}\right) - \alpha_2 \left(\frac{d}{L}\right)^2 \right\rfloor M^2 V, \qquad (4)$$

where  $\alpha_1$  and  $\alpha_2$  are constants that depend on the bulk material properties, and V is the total volume of the sample. The first term accounts for the repulsive interaction between the same type of monopoles within the same end plane, thus including the interaction within one end disk of a column, and between all the neighboring disks. The second term accounts for the attractive interaction of opposite monopoles between all the disks at the opposite planes. These potentials are all relative to constant backgrounds.

The surface energy  $U_s$  should also be included to account for the different local field experienced by the droplets at the surface and inside each column. Based

on Halsey's model [3] for the surface energy, the total interaction energy considered is

$$U = U_d + U_s = \left[ \alpha_1 \left(\frac{d}{L}\right) - \alpha_2 \left(\frac{d}{L}\right)^2 + \alpha_3 \left(\frac{\zeta}{d}\right) \right] M^2 V,$$
(5)

where  $\zeta$  is the surface depth of the columns within which droplets or part of the droplets are considered to be on the surface. By minimizing U, we can obtain a relation between d and L. In the large L limit, the second term in Eq. (5) can be neglected. We find that  $d \propto L^{0.5}$ . As L decreases, the contribution of the second term increases, which reduces the exponent of the power law below 0.5. The result of minimizing Eq. (5) is plotted in Fig. 2 as solid dots with the fitting parameters of  $(\alpha_1, \alpha_2, \alpha_3 \zeta) =$  $(1, 2.23, 0.33 \ \mu m)$ . As seen from the plot, the theory agrees with the experiment quite well even correctly predicting the slight deviation from the power law that is observed. For L below 60  $\mu$ m, the theory diverges, as the continuous-medium assumption fails since each column contains only a few droplets across the diameter. Further confidence in the validity of our model is obtained when we calculate  $\alpha_1$  exactly and determine the absolute value of  $\alpha_3 \zeta$  from the fit. Comparing with Halsey's model [17] for an fcc lattice,  $\zeta$  is then estimated to be 0.1  $\mu$ m of a/2.5. This result is in good agreement with the expected value a used in the calculation by Toor and Halsey for dipolar colloids [6]. The success of our cylindrical column model in explaining the observed dvs L relation, demonstrates that the interactions between monopoles within a disk at the end of each column are critical and cannot be neglected as was previously done.

We also explored the dependence of the field-induced structure on the droplet volume fraction; our results are shown in Fig. 3. We measured the column spacing d as a function of  $\phi$ , at a constant cell thickness  $L = 100 \ \mu m$ and a constant final field corresponding to  $\lambda = 166$ . Surprisingly, we do not find any obvious dependence of the measured d on  $\phi$  over the range of  $0.04 \le \phi \le 0.2$ . This result is confirmed for other L ranging from 10 to 100  $\mu$ m. These results are remarkable. As  $\phi$  increases, instead of forming more columns at reduced spacing, the column width increases as  $\sqrt{\phi}$  so as to maintain a constant column spacing. To compare these results with our theory, we neglect the small contribution of the second term in Eq. (5), and calculate the relative d as a function of  $\phi$ . The predicted behavior, scaled to the data at  $\phi \approx 0.1$  is shown by the solid line in Fig. 3. For a qualitative comparison, the agreement is quite satisfactory; our theory with approximation captures the essential point of the independence of d on  $\phi$  for a large range of  $\phi$  as well as the rise at low  $\phi$ .

In conclusion, we have studied the field-induced structure in an induced and confined dipolar colloids. The equilibrium structure consists of equally sized and locally ordered columns of dipoles. The column spacing increases



FIG. 3. Column spacing as a function of volume fraction. The data are measured for  $L = 100 \ \mu \text{m}$  and  $H = 38 \ \text{mT}$ .

with length approximately as a power law  $d = 1.33L^{0.37}$ . A new theory that models the column shape as cylinders is developed to explain this behavior; excellent agreement with the experimental results is obtained. It demonstrates that the interactions between monopoles within a disk at the end of each column are critical.

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FIG. 1. (a) Microscope image showing the cross section of a column structure taken at  $\phi = 0.04$ ,  $L = 50 \ \mu\text{m}$ , and  $\lambda = 166$ ; (b) the corresponding light scattering pattern; (c) the correlation function obtained from (a); and (d) the light scattering intensity as a function of the scattering wave vector obtained from (b).