

## Bubbles and stripes in dipolar fluids

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Dipolar fluids exhibit phase behavior as a function of the dimensionless magnetic energy  $N_B$  ("magnetic Bond number") and concentration. I propose a phase diagram for such fluids, in an infinite-aspect-ratio cell, for large Bond numbers. For concentrations  $\phi \ll N_B^{-1/2}$ , a two-dimensional lattice of magnetic bubbles should appear, while for higher concentrations, a striped phase has a lower energy. The aspect ratio of the stripes, while asymptotically constant at high concentrations or Bond numbers, shows significant variation near the transition. I expect these results to be relevant to pattern formation in magnetorheological fluids, and possibly to ferrofluids as well.

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Perhaps the most common frustration-inducing interaction in nature is the dipolar interaction. In most microscopic contexts, dipolar interactions arising from electrical or magnetic polarizations are quite weak compared with thermal energy scales, and are thus largely irrelevant to the physics. On mesoscopic or macroscopic length scales, on the other hand, dipolar interactions can be quite strong compared to competing energy scales, and can dominate pattern formation on these larger length scales, as in the domain structure of a ferromagnet.

Of course, the domain structure of a ferromagnet is largely determined by kinetic effects, due to the ease with which Bloch walls separating domains of differing magnetization may be pinned by impurities. Pattern formation in dipolar systems is thus more easily studied in liquid systems, of which a variety have been recently explored.

(1) Electrorheological (ER) fluids consist of suspensions of electrically polarizable particles of size  $0.1-100 \mu\text{m}$  in insulating solvents [1]. These fluids develop fibrillated and columnar structures parallel to a sufficiently strong electric field. However, the long-range repulsive part of the dipolar interaction is suppressed by the presence of constant potential boundary conditions, which lead to significant image forces [2]. I will not consider this system further in this paper.

(2) Monolayer domains of polar amphiphiles at an air-water interface show patterns that are determined by the long-ranged dipolar repulsion [3]. Recent studies have shown that the phase diagram of these systems is predominantly determined by amphiphile concentration [4]. At low concentrations, the lowest-energy state consists of a lattice of "bubbles," while at higher concentrations, the lowest-energy state is a striped state. Finally, at high concentrations, an "inverted bubble" phase, in which vacancy regions form a lattice, is expected to have the lowest energy.

(3) Ferrofluids are suspensions of small ( $\sim 100 \text{ \AA}$ ) permanently magnetized particles in a nonmagnetic solvent. These fluids are different from the ER fluids mentioned above in that the magnetic moments are permanent, and thus thermal energies must always be at least of the order of magnitude, if not greater, than magnetic energies, in

order to prevent flocculation of the suspension [5]. In a sufficiently strong field, the magnetic moments rotate in the direction of the field, leading to a largely field-independent macroscopic magnetization. These fluids show a dynamical transition in which a bubble of fluid confined between glass plates evolves into a "labyrinthine" pattern [6].

(4) Magnetorheological (MR) fluids are a close analogue to ER fluids. If a ferrofluid is dispersed, using a surfactant, in a third phase, then one has small approximately micrometer-scale micelles of magnetizable fluid suspended in a nonmagnetizable fluid [7,8]. The interaction energy between these bubbles may be very much larger than  $k_B T$ , since the magnetic moment of these micelles is induced by the external field. A way of quantifying the distinction between cases (2), (3), and (4) is by using the "magnetic Bond number,"

$$N_B = \frac{M^2 L}{\sigma}, \quad (1)$$

where  $M$  is the magnetization (or polarization for amphiphiles) per unit volume,  $L$  is the extent of the system in the direction parallel to the field, and  $\sigma$  is the surface tension of the dipolar fluid. In the monolayer systems,  $L$  is on the order of molecular dimensions, and one expects  $N_B \ll 1$ . For the ferrofluid systems, one typically has  $N_B \sim 1$ . In the magnetorheological fluids, the magnetic interaction between the micrometer-scale micelles is typically much larger than any other interaction scale. This implies that the surface energy will be of the order of magnitude of  $M^2 r_d$ , where  $r_d \sim 1 \mu\text{m}$  is the micelle radius [2,9]. Thus in the MR fluids we expect  $N_B \sim L/r_d \gg 1$ .

In this Rapid Communication I shall be concerned with the lowest energy structure of a dipolar fluid in the low-concentration limit. The approximations that I will use are valid, provided that the concentration  $\phi \ll 1$  and that the aspect ratio of the dipolar domains  $\beta = 2r_\perp/L$  is small. Here  $2r_\perp$  is the size of the domain in the direction perpendicular to the field. This latter criterion restricts us to the case of high magnetic Bond number, although I expect that my results can be qualitatively extended to

$N_B \sim 1$ . I shall also suppose that the cell aspect ratio is infinite; i.e., the extent of the cell in the direction parallel to the field will be taken as  $L$ , while the two-dimensional extent will be taken as unbounded.

My principal result is that, for low concentrations, the preferred state is a hexagonal lattice of bubbles, while for high concentrations, the preferred state is striped. Qualitatively, this agrees with the results for  $N_B \ll 1$  reported by Hurley and Singer [4]. However, the phase boundary between these two regions goes to zero concentration as  $N_B^{-1/2}$  for large magnetic Bond number. In practice, this probably means that labyrinthine patterns, which are disordered striped patterns, will be seen in equilibrium MR fluids over almost the entire range of concentrations.

We will suppose that the domains of dipolar fluids may be modeled either as spheroids with their axis of symmetry parallel to the field direction (bubbles), or as columns of elliptical cross section perpendicular to the field (stripes). In the former case, the radius of the spheroid parallel to the field is  $c = L/2$ , and its radius perpendicular to the field is  $r_\perp$ . In the latter case, we take the elliptical radius parallel to the field to be  $c = L/2$ , and its radius perpendicular to the field to be  $r_\perp$ . In each case, we define the aspect ratio of that domain as  $\beta = r_\perp/c$ . By restricting the domain shape to be ellipsoidal, we insure that the demagnetizing field of a single domain is constant within that domain. We expect this restriction to work, provided that  $\beta < 1$ , especially if the dipolar fluid does not wet the walls of the cell. For  $\beta > 1$ , this approximation misses logarithmic terms in the demagnetization factor, which are crucial in the pattern formation [4].

Besides this restriction of the shape of the domains, we also approximate the interaction of neighboring domains by supposing that they simply add constant fields at one another's respective positions. This should be valid at low concentrations, where the typical distance between domains  $r \gg r_\perp$ .

The surface energy per domain is simply  $E_S = \sigma S$ , where  $\sigma$  is the surface energy per unit area and  $S$  is the surface of the domain. The demagnetization energy  $E_M$  is more subtle. If the magnetization is in the linear regime, with  $\mathbf{M} = [(\mu - 1)/4\pi]\mathbf{H}$ , then

$$E_M = - \frac{(\mu - 1)V\mathcal{H}^2}{8\pi\{1 + (\mu - 1)n_\parallel + [(\mu - 1)/4\pi]\Gamma\}}, \quad (2)$$

where  $V$  is the volume of the domain,  $n_\parallel(\beta)$  is the demagnetization factor of the domain,  $\mathcal{H}$  is the applied magnetic field, and the term proportional to a lattice dependent factor  $\Gamma(\beta, \phi)$  includes the demagnetizing effect of neighboring domains. On the other hand, if the magnetization is saturated, with  $|\mathbf{M}| = M_s$ , then

$$E_M = 4\pi M^2 \left[ n_\parallel(\beta) + \frac{\Gamma}{4\pi} \right], \quad (3)$$

where I have omitted constant terms, and  $\Gamma$  is again a function of  $\beta$  and  $\phi$ . To lowest order in  $\chi = (\mu - 1)/4\pi$ , these two energies are identical up to overall constants [10]. At higher orders, Eq. (2) is explicitly dependent upon  $\chi$ ; thus, for simplicity, I only study Eq. (3).

One can easily estimate the energies of a two-dimensional lattice of bubbles or of stripes, in the limit of small aspect ratio  $\beta$ . The demagnetization arising from neighboring domains contributes an energy per unit fluid volume  $\varepsilon \sim M^2 V/r^3 \sim M^2 \phi^{3/2}/\beta$  for a bubble lattice, and an energy per unit volume  $\varepsilon \sim M^2 A/r^2 \sim M^2 \phi^2/\beta$  for a stripe lattice, where  $r$  is the lattice spacing and  $A$  is the cross-sectional area (or volume per unit length) of the stripes. The surface energy per unit volume is also inversely proportional to  $\beta$ . For the striped lattice, we thus expect the surface energy to be dominant in determining the shape of the structure for  $\phi \ll N_B^{-1/2}$ , while for the bubble lattices, we expect the surface energy to be dominant for  $\phi \ll N_B^{-2/3}$ .

For both of these cases, the energy at larger concentrations is  $\sim M^2$ , so a more precise calculation is necessary in order to determine which of the two structures has a lower energy. However, on the low concentration side of this boundary, it is clear that for stripes,  $\beta \sim N_B^{-1/2}$  and  $\varepsilon \sim M^2 N_B^{-1/2}$ , while for the bubbles,  $\beta \sim N_B^{-1/3}$  and  $\varepsilon \sim M^2 N_B^{-2/3}$ , where I have balanced surface energy with the demagnetization of a single domain. Thus we expect that for  $\phi \ll N_B^{-1/2}$ , the lowest-energy state will be a bubble lattice.

When one must take into account the demagnetizing field of neighboring domains, the calculation is somewhat more involved. I have computed energies and aspect ratios  $\beta$  for both the striped lattice and also for square and hexagonal bubble lattices. I used the well-known sums [4]

$$(4)r^3 \sum_S \frac{1}{r_n^3} = 9.033\ 621$$

for a square lattice with spacing  $r$ , where the sum is over all points  $r_n$  of the lattice and

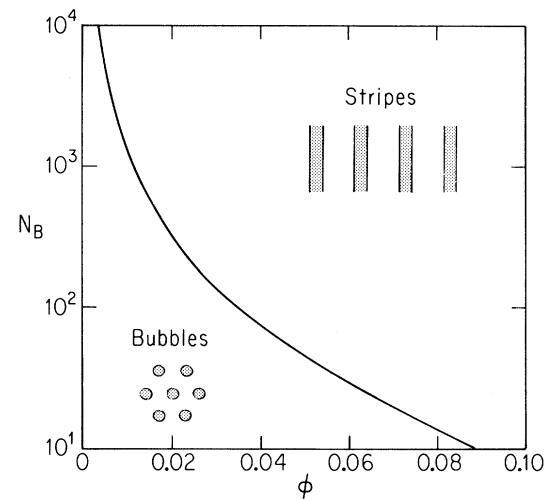


FIG. 1. The zero-temperature phase diagram of a dipolar liquid, as a function of concentration  $\phi$  and magnetic Bond number  $N_B$ . At low concentrations, a hexagonal lattice of magnetic bubbles has the lowest energy. At higher concentrations, the preferred state is a striped phase. At high Bond numbers, the critical concentration  $\phi_c \propto N_B^{-1/2}$ .

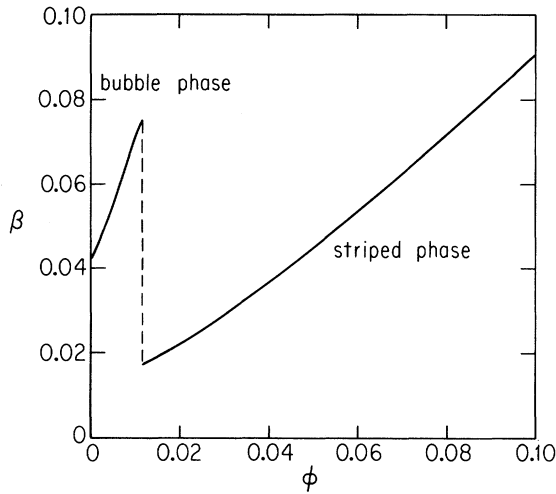


FIG. 2. Aspect ratio  $\beta$  vs concentration  $\phi$  for Bond number  $N_B=1000$ . On the left is the aspect ratio in the bubble phase; on the right is the aspect ratio in the striped phase.

$$r^3 \sum_H \frac{1}{r_n^3} = 11.034 175 \quad (5)$$

for a hexagonal lattice with spacing  $r$ , where the sum is over all points of the lattice.

For the striped lattice of spacing  $r$ , we have

$$r^2 \sum_{St} \frac{1}{r_n^2} = 3.289 868 . \quad (6)$$

It was also necessary to use standard formulas for the demagnetization factors of spheroids and elliptical cylinders, and for their surface areas [11].

The phase diagram is shown in Fig. 1. The striped phase is preferred at concentrations higher than  $\phi_c(N_B) \sim N_B^{-1/2}$ . Below this concentration, the hexagonal lattice of magnetic bubbles is preferred. Actually, at Bond numbers  $N_B \sim 1$ , this approximation predicts that the phase boundary turns around, so that the striped phase persists to low concentrations. However, in this regime, the aspect ratio  $\beta \sim 1$ , so the approximations used in computing the demagnetization factors are breaking down.

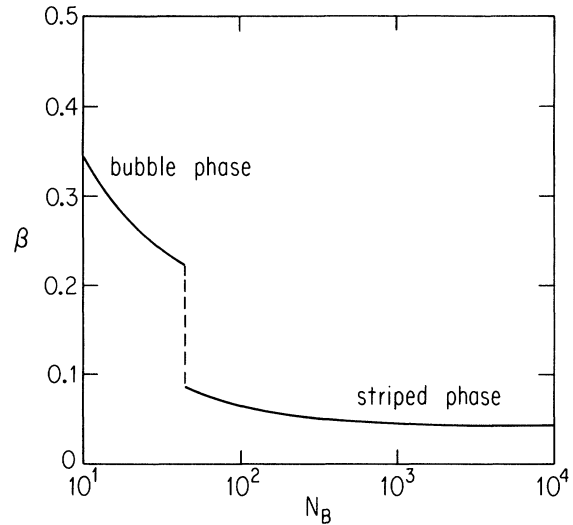


FIG. 3. Aspect ratio  $\beta$  vs Bond number  $N_B$  for concentration  $\phi=0.05$ . On the left is the aspect ratio in the bubble phase; on the right is the aspect ratio in the striped phase. The transition value of the striped aspect ratio is roughly twice its asymptotic, high-Bond-number, value.

In Fig. 2, the aspect ratio as a function of  $\phi$  is shown for  $N_B=1000$ . In Fig. 3, a complementary display of the aspect ratio as a function of  $N_B$  is shown for fixed  $\phi=0.05$ . The reader should note that although the asymptotic aspect ratio in the striped phase is constant, as predicted by Lemaire, Grasselli, and Bossis [8] the aspect ratio still shows a residual dependence on  $N_B$  quite deep into the striped phase; the transition value of  $\beta$  is approximately twice the asymptotic value. Thus surface-energy effects may be observable, even in relatively concentrated suspensions, or at relatively high magnetic Bond numbers.

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