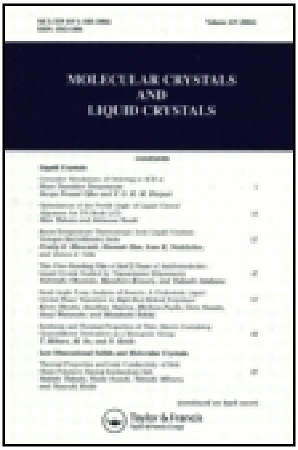

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MONOMOLECULAR FILMS AND LONG-RANGE DIPOLE FORCES

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Abstract Domain structures of ferromagnetic substances and lipid monolayers at the air-water interface are compared. It will be seen that there are some remarkable qualitative similarities between these seemingly unrelated systems. These similarities arise from the effects of long-range dipole forces.

INTRODUCTION

Many of the familiar properties of ferromagnetic substances depend on long-range magnetic fields due to electron spin magnetic moments. Recent work has shown that long-range electric fields play an important role in certain properties of molecular films at the air-water interface. Thus one can anticipate that these seemingly disparate states of matter may share a number of common properties. The purpose of the present note is to enumerate briefly some of these common properties.

Domain Shapes

Fluorescence microscopy can be used to study lipid monolayers at the air-water interface when the monolayers are doped with low concentrations of a fluorescent lipid probe.[1-4] Differential solubility of the probe in solid, liquid and gas phases permits the visualization of co-existing domains, such as gas and liquid, and liquid and solid. Recently, co-existing, immiscible liquid phases have been discovered in binary mixtures of phosphatidylcholines and cholesterol.[5] The shapes of co-existing fluid domains (liquid and gas, or two liquids) are the simplest to discuss.

Consider two immiscible monolayer fluid phases, A and B, and a single, isolated domain of A surrounded by B, as sketched in Fig. 1. When this system is maintained under conditions of constant area, and the free energy minimized with respect to domain <u>shape</u>, one obtains a simple circular domain as in Figure 1 when the A-B interfacial line tension is the only domain shape-dependent contribution to the free energy. When the calculation includes long-range repulsions between the vertical components of the molecular dipole moment (perpendicular to the surface of the air-water interface) the circular shape remains the shape of minimum free energy as the dipole density difference $\mu_A - \mu_B = \Delta$ in the fluid phases is increased, until one

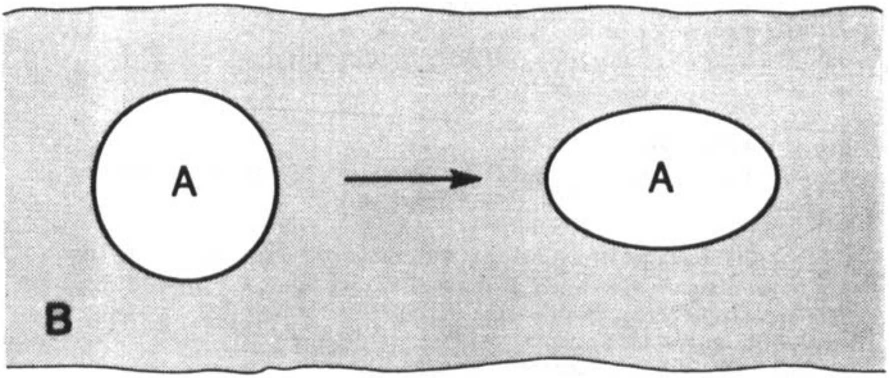

FIGURE 1. Lipid domains A and B. On the left the domain of one liquid lipid A is circular and is surrounded by the second liquid lipid B. The circular shape becomes unstable when the difference in dipole density $\mu_A - \mu_B = \Delta$ is increased, leading to a shape transition in which the circle changes to an ellipse or other shape of lower symmetry. A ferromagnetic analogue is discussed in the text.

reaches a critical value for this density difference, Δ_c, above which the circular shape becomes unstable, and the A domain undergoes a <u>shape transition</u>, to a distorted shape such as an ellipse.[6,7] Such shape transitions have been observed in binary mixtures of phosphatidylcholine and cholesterol.[5] In this latter case the transition is brought about by increasing the monolayer pressure, which results in a change in both Δ and the line tension.

The closest ferromagnetic analogue we have found to the above shape transition in monolayers is the deformation of spherical ferrofluid droplets in a magnetic field. When a magnetic field is applied to spherical droplets of ferrofluid, these droplets elongate into ellipsoids, the shapes of which depend on the strength of the applied field.[8]

The monolayer and this ferrofluid system differ in symmetry. In the monolayer problem mentioned above the electric dipole moments are perpendicular to the monolayer surface and thus the Hamiltonian itself does not break the circular symmetry, whereas the magnetic field that induces polarization in a spherical drop of ferrofluid does break the spherical symmetry.

A closer similarity exists between the stripe phases of monolayers and the stripe (or labyrinthine) phases of magnetic fluids. Figure 2 illustrates a

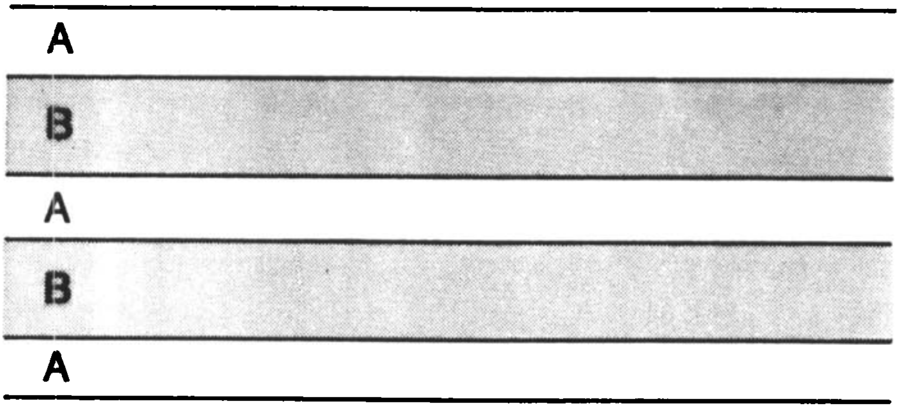

FIGURE 2. The stripe phase of lipid monolayers is closely analogous to the stripe or labyrinthine phase of thin ferromagnetic films.

stripe phase. Such phases are seen in lipid monolayers where the stripes arise from periodic, alternating domains of solid and fluid lipid. In the ferromagnetic case, a mixture of ferromagnetic fluid (colloidal magnetic particles in a hydrocarbon carrier) and water is contained between two thin, flat horizontal plates in a magnetic field. Under appropriate conditions this system develops a labyrinthine pattern that closely approximates the array of parallel stripes.[9] In the electrostatic as well as ferromagnetic case the relative widths of the stripe domains is determined by the experimental conditions (relative amounts of fluid and solid lipid, or relative amounts of ferrofluid and water) and the absolute values of the widths are determined by a completion between the line tensions separating the phases, and the dipole-dipole repulsions.

Related phenomena can be observed with thin magnetic films of ferromagnetic $BaFe_{12}O_{19}$. In these thin films the direction of easy magnetization is in the direction of the hexagonal c-axis, and the domain structure can be shown by optical means to be a regular array of parallel stripes of equal width[10]. Here the competition is between the dipolar interactions and the Bloch wall exchange energies (line or surface tension energy). Applying a magnetic field to this system parallel to the c-axis changes the ratio of the areas of the parallel to antiparallel orientations. This corresponds to compressing a lipid monolayer, changing the ratio for example of solid and fluid phases. At high magnetic fields, the antiparallel domain stripes first become well separated, then contract eventually to cylindrical domains. This is qualitatively similar to the shape transition mentioned above for isolated domains of lipid. The collapsed cylindrical domains form a hexagonal lattice, in which case one has a stripe to hexagonal ("bubble") phase transition that has been discussed theoretically for both ferromagnetic[11] systems and lipid monolayers.[12-13]

Chiral Domain Shapes

Solid lipid domains of optical isomers of phospholipid molecules frequently have strongly chiral shapes;[14,15] one is sketched in Fig. 3. These shapes may be understood as follows. It has been shown that in monolayer domains of some lipids, there is long range molecular orientational order.[16] This can be thought of as a molecular tilt order. When optically active molecules in a crystalline solid monolayer are tilted in one direction, the line tension around the crystal perimeter has no symmetry. This gives rise to chiral shapes by Wulf's theorem. The long-range dipole forces enhance the effects of line tension anisotropy, giving rise to the observed pronounced chiral shapes.[17] It has been pointed out that in chiral smetic liquid crystals the tendency of chiral molecules to twist can be represented by a free energy density of the form $-2qK(\vec{\nabla} \times \vec{\mu}_{\|}) \cdot \vec{k}$ where $\vec{k}$ is a unit vector perpendicular to the flat surface of the film.[18] The integral of this interaction over a two-dimensional

FIGURE 3. The chiral shape of this triskelion is related to the chiral structure of the lipid molecule, dipalmitoylphosphatidylcholine. The solid (dark) region is solid lipid, and the surrounding region is fluid lipid. The drawing is taken from a fluorescence microphotograph taken by H. Gaub and V. Moy in this laboratory. (Unpublished).

area can be transformed to a line integral around the perimeter, which scales like an anisotropic line tension.

There is also a relation between chiral lipid domains and the weak ferromagnetism discussed by Moriga.[19] In solids of suitable symmetry an anisotropic (antisymmetric) spin exchange interaction of the form $\vec{k} \cdot \vec{S}_i \times \vec{S}_j$ can give rise to a weak ferromagnetism in a system where the spins are otherwise to a first approximation coupled in an antiferromagnetic array. (For a related anisotropic spin-spin interaction in molecules such as the ferrocenes, see ref. 20). A theoretical calculation has used this model of weak ferromagnetism to describe certain chiral lipid domains.[21] A simple way to see this is to imagine that the spins $\vec{S}_i$ and $\vec{S}_j$ on adjacent atoms in weak ferromagnetic solids tend to twist relative to one another in the same way that chiral molecules tend to twist relative to one another. If the degree of twisting in a substance is low, then the interaction $(\vec{S}_i \times \vec{S}_j) \cdot \vec{k}$ can be replaced by a term such as $(\vec{\nabla} \times \vec{S}(r)) \cdot \vec{k}$, which then leads to the same picture of an anisotropic line tension mentioned above.

CONCLUSIONS

While none of the ferromagnetic systems cited in the present note are physically or mathematically strictly equivalent to the monolayer sytstems, there are clearly strong qualitative resemblances. Similarities of the lipid monolayers to ferroelectric systems are also to be expected, especially when free charges play a role in affecting domain structure and closure.

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Note added 31 March 1989. A publication (22) dealing with shape instabilities of isolated thin liquid domains of ferromagnetic fluids in magnetic fields perpendicular to the domains is closely related to our calculations on monolayer domain shapes (6, 17).

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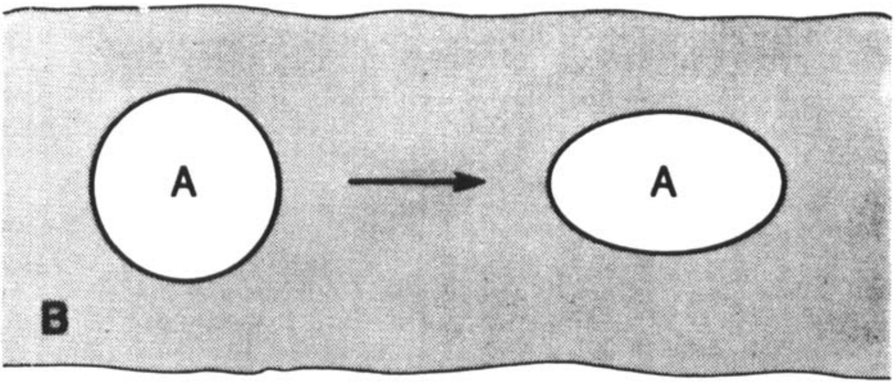

Fig. 1

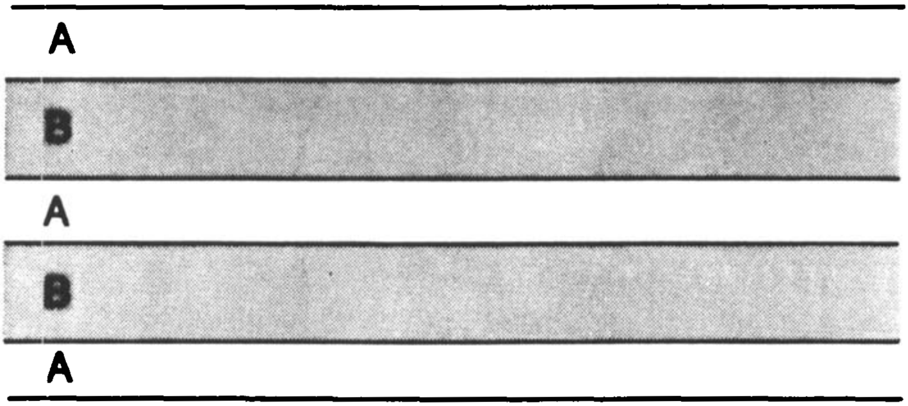

Fig. 2

Fig. 3