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Modulated structures and competing interactions in amphiphilic monolayers

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ABSTRACT We investigate the effects of electrostatic interactions on the phase behavior and structure of insoluble Langmuir monolayers at the liquid/air interface. Both for charged and neutral monolayers, the competition between such repulsive long-range and attractive short-range interactions of the monolayer tends to stabilize modulated phases. Phase diagrams are obtained in two limits: (i) close to the liquid–gas critical point and (ii) at low temperatures.

Monolayers of insoluble amphiphilic molecules, such as surfactants, fatty acids, and phospholipids at the liquid/air interface (Langmuir monolayers), have been studied quite extensively over the last 60 years (for a general review, see refs. 1 and 2). They are of fundamental interest because of their variety of two-dimensional phase transitions. In addition, these monolayers are studied as simple models for biological membranes of phospholipids.

Measurements of surface pressure versus area per molecule show that monolayers undergo a two-dimensional liquid–gas transition at very low surface pressure (<0.1 dyne/cm; 1 dyne = 10 μ N) (3–5). At higher surface pressures, a peculiar “kink” in the isotherms is seen in many experiments. The origin of this singularity is not clear and is a matter of dispute [refs. 6 and 7; see, for instance, ref. 8 and ref. 9 (and references therein)]. It has been interpreted as either a second-order transition between two liquid phases (termed “liquid-condensed” and “liquid-expanded”) or as a first-order liquid–solid transition under poorly controlled conditions: presence of impurities, undersaturated water vapor pressure, retention of the spreading solvent, or non-equilibrium determination of the isotherms (6, 7).

Recently, other experimental techniques have been developed and applied to the study of structural properties of monolayers. Among others they include electric surface potential (10–12) and viscoelastic measurements (13), nonlinear optics (14), epifluorescence microscopy (15–18), and x-ray diffraction (19, 20) from a synchrotron source. The epifluorescence microscopy, for example, allows a direct visualization of monolayers on length scales of micrometers. In lipid monolayers, an organization of liquid-like and solid-like regions that repeat periodically is seen and is shown schematically in Fig. 1.

In this paper, we address the interesting question of the physical origin of such modulated structures. We briefly present theoretical calculations (21–23) that explain such modulated structures as the result of a competition between dipolar and short-range interactions of the monolayer. We also draw the analogy with other systems (magnetic films and

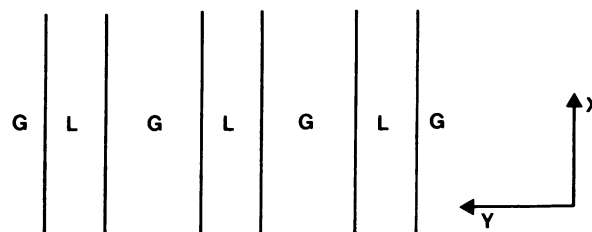


FIG. 1. The stripe phase is shown schematically, where the stripes are chosen to be in the x direction. Domain walls (which are sharp only at low temperatures) separate denser liquid (L) from dilute gas (G).

ferrofluids) where similar competition gives rise to modulated structure on different length scales.

Many neutral amphiphilic molecules carry a permanent dipole. Dipole–dipole interaction between two dipoles varies as r^{-3} , where r is the distance between the two dipoles. In two dimensions, we can estimate the dipolar energy of a monolayer, which has a concentration modulation with wave vector q , to be (21–22)

$$F_{el} = -\frac{1}{2} |q| \mu^2 \Phi_q^2, \quad [1]$$

where Φ_q is the q -component of the inplane monolayer concentration, and μ is the strength of the dipole moment assumed to be perpendicular to the liquid/air interface. For charged monolayers, the role of the dipole is played by an induced dipole that depends on the ionic strength of the aqueous solution.

Close to a critical point (e.g., at the liquid–gas critical point of the monolayer), it is convenient to express the free energy in terms of a Ginzburg–Landau expansion. This expansion is in powers of both the order parameter (the two-dimensional monolayer concentration) and its gradient. Since the lowest power in the gradient is quadratic, $(\nabla\Phi)^2$, and since this term is positive because of the energy cost to create an interface, the equilibrium state of the system depends on the competition between the dipolar energy, Eq. 1, and this interfacial energy. A detailed study of the complete free energy was carried out within a Ginzburg–Landau expansion (21, 22), and Fig. 2 shows the calculated phase diagram. Depending on the temperature and the monolayer concentration, the stable phase is either a homogeneous dilute (gas) or a denser (liquid) phase. Modulated phases exist as well with either stripe or hexagonal symmetry. All of the phase-transition lines are found to be first order. In addition, we find a magnetic analogy between dipolar monolayers and thin uniaxial magnetic films (24, 25) subject to a perpendicular magnetic field. Experiments on the magnetic systems (24) show the existence of modulated magnetic phases on the scale of a few dozen micrometers.

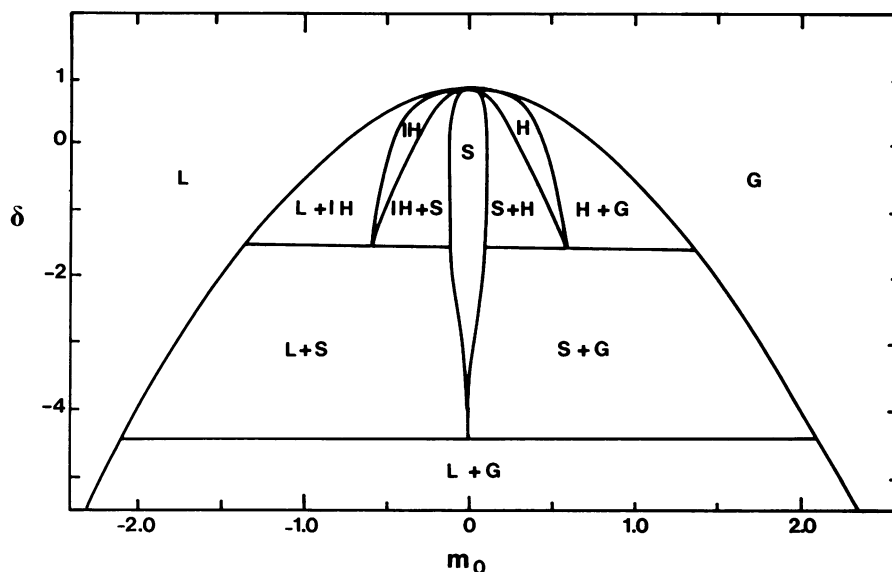


FIG. 2. Phase diagram in the (m_0, δ) plane where $\delta \sim T - T_c$ is the reduced temperature and $m_0 \sim \langle \Phi \rangle - \Phi_c$ is the reduced concentration. The two isotropic phases, liquid (L) and gas (G), are separated by the hexagonal (H), stripe (S), and inverted-hexagonal (IH) phases. Two-phase coexistence regions are also indicated.

At low temperatures, modulated structures have sharp domain walls. Thus, the expansion that was used to describe the dipolar monolayer in the vicinity of a critical point is inappropriate at low temperatures. Alternatively, we calculated the dipolar energy for stripe and hexagonal structures with sharp domain walls at low temperatures, assuming they have a perfect periodicity—i.e., neglecting possible defects such as lines of dislocation. We find that dipole energy density of modulated two-dimensional structures scales as $\log(D)/D$, where D is the periodicity of the structure. This can be understood as the contribution of electric “fringe” fields, which are important in two dimensions. The total energy density is written as the sum of the dipolar contribution and the interfacial one, $2\gamma/D$:

$$f = -T \frac{\text{const}}{D} \log(D/a) + 2\gamma/D. \quad [2]$$

By minimizing this energy, we obtain an optimum periodicity that scales exponentially with the ratio between the surface tension and the dipole energy strength. Similar results were obtained independently by Keller *et al.* (23). Our results and theirs are of importance in interpreting recent epifluorescence experiments (15–18). There, stripes (and in some conditions other structures) of liquid-like and solid-like domains coexist.

An analogy can also be made with ferrofluids (ref. 26; for a review on ferrofluids, see ref. 27) for which thermal fluctuations are of no importance. Hence, ferrofluids simulate the low temperature limit of monolayers on a completely different length scale, which is in the millimeter range.

In conclusion, the model presented in this paper suggests that long-range dipolar interactions stabilize modulated structures in amphiphilic monolayers at thermodynamic equilibrium. From an experimental point of view, these structures may result, at least in some cases, from nonequilibrium procedures. Thus, the inclusion of dipolar forces in the kinetic of domain growth and spinodal decomposition is of relevance and is addressed separately (28).

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