MODULATED PHASES IN AMPHIPHILIC MONOLAYERS AT THE WATER/AIR INTERFACE

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ABSTRACT

Recently, modulated phases of insoluble monolayers of fatty acids and phospholipids spread on the water/air interface have been observed by fluorescence microscopy experiments. We propose a theoretical explanation of this observation by including electrostatic (dipolar) interactions in the total free energy calculation for the monolayer. Dipoles can originate from two sources: neutral amphiphiles have a permanent dipole and charged amphiphiles have an induced one. Modulated phases are found to be stable in two different limits: close to the liquid-gas transition and at low temperatures. Several phases with stripe and hexagonal symmetry are predicted and the phase transitions between them are calculated.

INTRODUCTION

Most of the research on insoluble amphiphilic monolayers at the water/air interface [1-2] has been conducted either on fatty acids such as pentadecanoic, myristic, oleic, arachidic and stearic acids, or on phospholipids such as DPPC and DPMA. Insoluble monolayers (so-called Langmuir monolayers) have been studied using several experimental techniques such as: isothermal measurements of surface pressure as a function of area per molecule [3-13], surface potential [14-16], reflection and diffraction methods of X-rays from a synchrotron source [17-19], spectroscopic methods like second harmonic generation [20], viscoelastic measurements [21], and fluorescence microscopy [22-26]. Several reviews on the experimental situation exist in the literature [3-7, 27].

Except for being studied as simple but realistic models for natural biological cell membranes (phospholipids), Langmuir monolayers have several appealing advantages as models for two-dimensional systems: (i) unlike other quasi two-dimensional systems, they are composed of only one molecular layer bounded on the flat water surface. (ii) The interaction with the liquid subphase is quite homogeneous since there are no preferred adsorption sites as on solid surfaces such as graphite. (iii) Lateral movement and diffusion are possible. (iv) By changing the surface pressure, various phase transitions can be induced in analogy with the gas-liquid-solid transitions in the bulk.

On the other hand, the main disadvantage of amphiphiles as two-dimensional models has to do with their molecular complexity. Unlike simple spherical molecules, amphiphiles have a flexible hydrocarbon tail and a polar head and thus, ordering can occur also in the perpendicular direction.

ELECTROSTATIC INTERACTIONS IN LANGMUIR MONOLAYERS

Neutral Monolayers

Recently, it has been shown [14, 28-31] that electrostatic interactions are of importance in neutral and charged monolayers. For neutral amphiphiles, we consider [29-30] only the case where the average dipolar moment points along the perpendicular $\vec{z}$-direction, $<\vec{\mu}>=\mu_z$. The dipole-dipole interaction is long-range and repulsive (all dipoles are forced to have their polar head in the water) . Since the dipoles are restricted to stay on the flat water/air interface, an inplane density wave of the dipoles will reduce the overall repulsive dipolar interaction, $F_{\rm el}$:

$$F_{\rm el} = -\frac{1}{2}\int \vec{P}(\rho)\cdot\vec{E}(\rho)\; d^2\rho = -\frac{1}{2}\frac{\varepsilon_0}{\varepsilon(\varepsilon+\varepsilon_0)}|q|\mu^2\phi_q^2 \tag{1}$$

where $\vec{P}(\rho)=\vec{\mu}\phi(\vec{\rho})$ is the two-dimensional polarization, $\phi(\rho)=\phi_0+\phi_q\cos(\vec{q}\cdot\vec{\rho})$ is the amphiphile density, and ε (ε_0) is the water (air) dielectric constant.

In (1), the dipoles are assumed to be immersed in the water and the interaction is screened by approximately ε^2 for $\varepsilon >> \varepsilon_0$. However, since the polar moieties lie very close to the water surface, the effective dielectric constant, ε^*, felt by the dipoles is expected to be smaller than the bulk value, $\varepsilon = 80$. In addition, if the aliphatic tail of the molecules also contributes to the molecular dipole moment, then some of the dipolar interactions are not screened. The linear dependence of $F_{\rm el}$ in (1) on the modulation wavevector $|q|$ is a consequence of the long-range character of the dipolar forces. In general, an algebraically decaying interaction, $F_{\rm el}\sim 1/r^{(d+\sigma)}$, where d is the spacial dimension, will have a Fourier component with a $|q|^\sigma$ dependence. For dipoles, $d+\sigma=3$, $d=2$, hence, $\sigma=1$.

Charged Monolayers

If the amphiphiles are charged and an electrolyte is added to the water, the electric potential can be obtained from the Poisson-Boltzmann (PB) equation. Here, we restrict ourselves to the linearized version of the PB equation.

$$\begin{aligned} &\nabla^2 V(\vec{r}) = \kappa^2 V(\vec{r}) && z<0 \\ &\nabla^2 V(\vec{r}) = 0 && z>0 \end{aligned} \tag{2}$$

where κ^{-1} is the Debye-Hückel screening length. We solve the electrostatic problem (2) for a modulation in the surface charge density $e\phi(\vec{\rho})=e\phi_0+e\phi_q\cos(\vec{q}\cdot\vec{\rho})$, with the appropriate boundary conditions at $z=0$.

The electrostatic energy is then given by

$$F_{\rm el} = \frac{1}{2}\int \sigma V(z=0)\; d^2\rho \;\; = \;\; \frac{e^2\phi_q^2}{2(\varepsilon\kappa_1+\varepsilon_0|q|)} \tag{3}$$

where in (3) we omit the average electrostatic contribution depending on ϕ_0 and $\kappa_1^2 = \kappa^2+q^2$ is the effective screening length for the q-mode. For strong ionic solutions, the Debye-Hückel screening length is small, $\kappa >> q$. Expanding (3) in powers of q/κ, equation (1) is recovered. In this case, the counter ions together with the surface charges form effective dipoles at the water surface with a moment

$$\mu = \frac{e}{\kappa}\sqrt{1+\varepsilon_0/\varepsilon} \;\; \simeq \;\; e/\kappa \quad \text{for} \quad \varepsilon >> \varepsilon_0 \tag{4}$$

Strong dipoles can be obtained by changing the ionic strength in the solution and reaching $\kappa^{-1} \simeq 10\mathring{A}$

In the opposite limit of weak electrolytes, $q >> \kappa$, the electrostatic interactions are almost unscreened and the interaction is Coulombic $\sim 1/r$. We will not discuss further this case but note that similar two-dimensional colloidal systems tend to form Wigner crystals [32].

MODULATED PHASES AND PHASE TRANSITIONS

Simple models of condensation (e.g., van der Waals models) predict a condensation from a more expanded phase (gas or liquid-expanded) to a more condensed phase (liquid or liquid-condensed) [2, 5, 33]. The condensation occurs as the attractive interaction between molecules starts to dominate over the entropy of mixing. In a Langmuir trough, the transition is induced by increasing the surface pressure. For a range of temperatures, a first-order transition characterized by a jump in the surface area per molecule occurs. This is nothing else but a direct analog to the bulk liquid-gas transition. The first-order coexistence curve in the temperature – density plane terminates with a critical point. For temperatures higher than the critical one, there is no discontinuous jump as a dilute gas condenses at constant temperature.

Electrostatic interactions modify the above mentioned liquid-gas transition. They tend to stabilize phases with modulated density. Phase diagrams incorporating the possibility of modulated phases were calculated within the frame of the mean-field approximation in two cases: (i) Close to a critical point where only the most dominant q-mode is considered, and (ii) at low-temperatures where entropy is neglected.

Landau Theory Close to T_c

Close to the critical point $T = T_c$, the free-energy can be written phenomenologically [28-29] as an expansion in the order parameter,

$$\psi(\vec{\rho}) = \phi(\vec{\rho}) - \phi_c \tag{5}$$

The expansion contains only even terms in ψ

$$\Delta F_0/k_BT = \frac{1}{2}\alpha(T-T_c)\psi^2(\vec{\rho}) + \frac{1}{4}u\psi^4(\vec{\rho}) \tag{6}$$

where the coefficients, $\alpha \sim T - T_c$ and $u > 0$, can be obtained from an expansion of the monolayer free-energy of mixing. Since the electrostatic interactions prefer spacial modulations, we have to consider also the energy gain and loss as an inplane modulation of the two-dimensional concentration is created. The gain will be in the electrostatic energy

$$F_{\rm el}/k_BT = -\frac{1}{2}\int \vec{P}\cdot\vec{E}\ d^2\rho = \frac{1}{2}\int \psi(\vec{\rho})g(\vec{\rho}-\vec{\rho}')\psi(\vec{\rho}')\ d^2\rho d^2\rho' \tag{7}$$

where $g(\rho) = k_BTb^3/2\pi\rho^3$ and $b^3 = \mu^2\varepsilon_0/[\varepsilon(\varepsilon+\varepsilon_0)k_BT]$.

The modulation energy loss is the interfacial line energy between domains in a two-dimensional geometry. For small density variations, the line energy is written as the lowest order in a gradient expansion

$$F_I/k_BT = \frac{1}{2}\Sigma_0^2 \int (\nabla\psi)^2 \; d^2\rho \tag{8}$$

with Σ_0 being the compact area per molecule. In Fourier space, eqs. (7)-(8) can be expressed as

$$(F_{\rm el} + F_I)/k_BT = \frac{1}{2}\sum_q (\Sigma_0^2 q^2 - b^3|q|)\psi_q^2 \tag{9}$$

where $\psi(\vec{\rho}) = \psi_0 + \sum_q \psi_q \cos\vec{q}\cdot\vec{\rho}$. The most dominant q-mode is the one minimizing the ψ_q^2 coefficient in (9).

$$|\vec{q}|^* = b^3/2\Sigma_0^2 \tag{10}$$

Close to a critical point, it is a good approximation to consider only modulations with magnitude q^* in addition to the homogeneous ($q = 0$) solutions: $\psi(\vec{\rho}) = \psi_0$ and $\psi(\vec{\rho}) = -\psi_0$ for the dilute and condensed phases, respectively.

Two types of spacial modulation of the two-dimensional density are considered [29, 34-35]

(i) a stripe-like phase, $\psi_S(\vec{\rho}) = \psi_0 + \psi_q \cos q^* x$ (see Fig. 1)
(ii) a hexagonal phase, $\psi_H(\vec{\rho}) = \psi_0 + \sum_{i=1}^{3} \psi_q \cos(\vec{k}_i \cdot \vec{\rho}_i)$, with $|\vec{k}_i| = q^*$ and $\sum_{i=1}^{3} \vec{k}_i = 0$.

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).

The phase diagram can be calculated by comparing the homogeous with the tripe and hexagonal solutions.

$$
\begin{aligned}
F_S &= \frac{\delta}{2}M_0^2 + \frac{1}{4}M_0^4 + M_q^2(\delta - 1 + 3M_0^2) + \frac{3}{2}M_q^4 \\
F_H &= \frac{\delta}{2}M_0^2 + \frac{1}{4}M_0^4 + M_q^2(3\delta - 3 + 9M_0^2 + 12M_0M_q) + \frac{45}{2}M_q^4 \\
F_0 &= \frac{\delta}{2}M_0^2 + \frac{1}{4}M_0^4
\end{aligned}
\tag{11}
$$

where,

$$
\delta = 4\alpha/\eta^2, \quad M_0^2 = (4u/\eta^2)\psi_0^2, \quad M_q^2 = (u/\eta^2)\psi_q^2, \quad \text{and} \quad \eta^2 = b^6/\Sigma_0^3 \tag{12}
$$

FIG. 2. Phase diagram in the (M_0, δ) plane where $\delta \sim T - T_c$ is the reduced temperature and $M_0 \sim <\phi> - \phi_c$ 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-phases coexistence regions are also indicated.

In Fig. 2, the phase diagram in the reduced temperature δ – reduced average concentration, $M_0 \sim <\phi> - \phi_c$ plane is shown. The usual coexistence region between liquid and gas regions, $M_0^2 = \delta$ is largely modified. A novel critical point at $M_0^* = 0, \delta^* = 1$, is the termination point of five distinct phases: gas (G), stripe (S), hexagonal (H), inverted hexagonal (IH), and liquid (L). The gas and liquid phases are two isotropic dilute and dense phases, respectively. All the transition lines below the critical point (M_0^*, δ^*) are first order. Consequently, four regions of two-phase coexistence exist between the phases. At low enough temperatures below δ^*, the stripe (S) and the hexagonal phases (H, IH) disappear, as seen in Fig. 2. We believe that this is a defect of the single mode Landau-Ginzburg expansion employed here. In the next section, a direct calculation of the free energy of the modulated phase at low temperatures will show that these phases are expected to be stable even at low temperatures over a range of concentrations.

Modulated Phases at Low Temperatures

It is of interest to compare the relative stability of the modulated and homogeneous phases at low temperatures [29, 31] since our treatment of the previous section is valid only close to T_c. For simplicity, only the stripe phase with sharp domain walls is considered. The stripe phase is formed from a periodic arrangement of stripes of the dilute phase of size D_G and dense phase of size D_L. The electrostatic free energy of the stripe phase is

$$F_{\rm el}/k_BT = \frac{b^3}{\pi a}[x\phi_L^2 + (1-x)\phi_G^2] - \frac{b^3}{\pi D}(\phi_L - \phi_G)^2 \log\left(\frac{D\sin\pi x}{\pi a}\right) \tag{13}$$

where $x = D_L/D = D_L/(D_L + D_G)$ and $a \simeq \sqrt{\Sigma_0}$ is a microscopic cutoff. The first two terms in (13) represent the overall average contribution to the electrostatic energy and are independent of the periodicity D. The third term is an exact summation of the intra- and inter-stripe electrostatic interactions [36]. An additional contribution to the free energy difference ΔF between the stripe and the homogeneous phases with the same concentration comes from the line tension γ associated with every domain wall separating a G domain from an L one. The total free energy difference is thus

$$\Delta F = -\frac{k_BTb^3}{\pi D}(\phi_L - \phi_G)^2 \log\left(\frac{D}{a}\frac{\sin\pi x}{\pi}\right) + \frac{2\gamma}{D} \tag{14}$$

The equilibrium periodicity D^* of the stripe structure is given by minimizing (14) with respect to D

$$D^* = a(\frac{\pi}{\sin\pi x})\exp\beta \tag{15}$$

where

$$\beta = \frac{2\pi\gamma}{k_BTb^3(\phi_L - \phi_G)^2} + 1 \tag{16}$$

The exponential dependence of the periodicity D^* on the ratio between the line tension γ and the dipole interaction coefficient $b^3(\phi_L - \phi_G)^2$ makes it difficult to give an accurate estimate of D^* since neither γ nor b are known accurately from experiments. However, b can be changed in a controlled way by tunning the electrolyte strength for a charged monolayer and (15) can be verified experimentally. In addition, it has been found that cholesterol [22-25, 31] reduces the line tension γ causing thinning of the domains in accord with the theoretical predictions [29-31].

CONCLUSIONS

At thermodynamic equilibrium, dipolar interactions tend to stabilize modulated phases. Here we studied two such phases: a stripe-like and a hexagonal one, and show that close to a critical point as well as at low temperatures the modulated phases are stable. In experiments, the stable domains that are seen close to the liquid expanded – liquid condensed or the liquid-solid transitions may also arise from out of equilibrium growth. Hence, spinodal decomposition and nucleation in presence of dipolar interactions may be of relevance and has been studied separately [37].

One promising possibility of checking quantitatively the effects of electrostatic interactions is to consider the charged monolayer. The strength of the effective dipoles can be tuned by changing the amounts of the added electrolyte in the aqueous solution.

Finally, in addition to the perpendicular component of the electric dipole, the inplane component may also induce shape transitions and has been studied experimentally and theoretically [37-40]. Of particular interest will be to find an explanation to the spiral-like shape of domains formed as a condensation of *chiral* phospholipids occurs [22-25, 37-40].

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