STRUCTURED MONOLAYERS OF CHARGED AND POLAR MOLECULES AT THE LIQUID/AIR INTERFACE

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ABSTRACT.   Effective dipoles in charged monolayers and permanent dipoles in neutral ones are shown to have a drastic effect on the structure and phase transitions of insoluble Langmuir monolayers. These long-range and repulsive dipolar interactions stabilize undulating phases in thermodynamic equilibrium. Results are presented for two cases: (i) Close to a liquid-gas critical point. (ii) At low temperatures. Possible implications of the former on the liquid-gas transition and of the latter to the liquid-solid and liquid expanded-liquid condensed transitions are discussed. In an ionic solution, the undulation periodicity can be controlled by the strength of the ionic solution.

1.   INTRODUCTION

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 sixty years. They are of fundamental interest because they exhibit a rich variety of (quasi-) two dimensional phase transitions. In addition, they are also of applied interest since they serve as a simple model for biological membranes.

Until recently, most of the experiments done on monolayers were isothermal measurements of the surface pressure as a function of the area per molecule [1]. For very low surface pressure (< 0.1 dynes/cm^2) the monolayer behaves like a two-dimensional gas. As the surface pressure increases, the area per molecule decreases monotonicaly and in some cases, e.g. pentadecanoic acid [2], a further increase in the pressure induces a first-order transition to a liquid state. In the coexistence region, the isotherm has a plateau and then, in the liquid, it starts to increase again. This two-dimensional liquid-gas coexistence region which ends with a critical point similar to a bulk liquid-gas transition, was observed for pontadecanoic acid around room temperature [2].

In the liquid state, many experiments [1] reported a peculiar "kink" in the isotherms. However, the origin of this singularity is not clear. Furthermore, it is not known whether it separates two phases (so called "liquid expanded" and "liquid condensed") which are in thermodynamic equilibrium. Such a kink in the isotherms can be interpreted as a signature of a second-order transition and was thus explained [3-5] as an orientational ordering of the molecular tails. On the other hand, quite recently Middleton et al [6] found a plateau instead of the kink in some amphiphic systems. Their claim is that a kink indicates presence of impurities, poor control of water vapor pressure, retention of the spreading solvent and nonequilibrium determination of the isotherms.

The controversy of the liquid expanded-liquid condensed transition could not be resolved without having some other structural information on the monolayer. Hence other experimental techniques such as: surface potential measurements [7-9], viscoelastic measurements [10], non linear optics [11], epifluorescence microscopy [12-13] and recently X-ray diffraction from a synchroton source [14-15] were used. The epifluorescence microscopy, for example, allows a direct visualization of the monolayer on length scales of microns. In lipid monolayers, an organization of liquid-like and solid-like regions that repeats periodically is seen for high concentrations. The same epifluorescence technique was also used to study the liquid-gas transition of fatty acid monolayers [16].

In this paper, theoretical calculations that take into account dipole interactions [17-18] are presented. The dipoles can be permanent in neutral monolayers or induced in charged monolayers where an electrical double layer is formed. The intensity of the dipoles can be varied in charged systems by changing the ionic strength of the aqueous solution or by changing the Debye-Huckel screening length. Experimentally, these electrostatic effects are measured by the so-called surface potential (or "zeta potential") [1,7].

2. ELECTROSTATIC INTERACTIONS IN LANGMUIR MONOLAYERS

2.1 Neutral Monolayers

Most neutral surfactant molecules carry a permanent dipole moment. Here we will assume that the dipoles μ are oriented perpendicular to the liquid/air interface and that they are immersed in the liquid close to its surface where locally the dielectric constant is ε (a quantity that is not well known close to the liquid/air interface). Such a dipole density will cause a jump, ΔV, in the electrostatic potential

$$\Delta V = \frac{\mu \phi}{\varepsilon} \ , \tag{1}$$

where ϕ is the inplane monolayer concentration. By using the appropriate boundary conditions, the electrostatic field $E(r)$ can be

calculated (details are found in Ref. [18]) for a monolayer
concentration that oscillates with wavevector q,
$\phi(x) = \phi_0 + \phi_q \exp(iqx)$. The electrostatic free energy of the
dipoles subject to this electrostatic field E(r) is

$$F_{el} = -\frac{1}{2} \int \phi \, \vec{\mu}.\vec{E} \, d^2\vec{r} = -\frac{1}{2} \frac{\varepsilon_0}{\varepsilon(\varepsilon+\varepsilon_0)} |q| \mu^2 \phi_q^2 \,. \qquad (2)$$

This result, Eq. (2), can also be obtained in terms of image dipoles
and is proportional to the Fourier transform in two dimensions of the
dipole-dipole interaction which varies as r^{-3}. A strong dielectric
constant, $\varepsilon \gg \varepsilon_0$, reduces the dipole interactions, Eq. (2). These
interactions are stronger if the dipoles are associated with the
molecular tails (above the liquid interface where the dielectric
constant is ε_0) rather than with the polar heads that are immersed
in the liquid.

2.2 Charged Monolayers

For charged monolayers, we calculate the electrostatic free energy
using a linearized Poisson-Boltzmann approximation. The surface
charge density is $\sigma = e\phi$, where e is the charge per molecule and the
ionic solution is characterized by the Debye-Huckel screening length
κ^{-1}. If the charge concentration of the monolayer oscillates with
wave vector q, $\delta\phi = \phi_q \exp(iqx)$, the effective screening length in
the solution is

$$\kappa'^2 = \kappa^2 + q^2, \qquad (3)$$

and the electrostatic energy of the amphiphilic molecules is [18]

$$F_{el} = \frac{e^2 \phi_q^2}{2(\varepsilon\kappa' + \varepsilon_0|q|)} \,. \qquad (4)$$

Two limits of Eq. (4) can be distinguished at this point:
(i) the limit of small wave vector, $|q| \ll \kappa$, where the charged
monolayer is described in terms of an effective dipole moment. This
is the limit applicable to strong ionic solutions where the
electrostatic free energy is very similar to Eq. (2)

$$F_{el} \simeq \frac{e^2 \phi_q^2}{2 \, \varepsilon \, \kappa} \left(1 - \frac{\varepsilon_0}{\varepsilon} \frac{|q|}{\kappa}\right) \,. \qquad (5)$$

This case will be employed throughout the remainder of this article.
(ii) In the limit of large wave vector, $|q| \gg \kappa$, the interactions

are Coulomb-like rather than dipole-like. This limit is relevant to low ionic strength solution and one can expect the formation of Wigner crystals similar to the two-dimensional colloidal crystals studied by Pieranski [19].

3. SUPERCRYSTAL STRUCTURE AND PHASE TRANSITIONS

3.1 Ginzburg-Landau Expansion close to a Critical Point

The dipole interactions discussed in the previous section have a drastic effect on the phase transition between two homogeneous phases (e.g. liquid and gas) that can be described close to the critical point by a Ginzburg-Landau expansion. We write an expansion in powers of the order parameter $\psi = \phi - \phi_c$, where ϕ_c is the critical value of the inplane concentration. Including the dipolar contribution, Eq (2), the total free energy is

$$\frac{F}{T} = \int \left\{ \frac{1}{2} \alpha \, \psi^2(\vec{r}) + \frac{1}{4} u\psi^4(\vec{r}) + \Sigma_0^2 \, (\nabla\psi)^2 \right\} d^2\vec{r} \; +$$

$$+ \frac{1}{2T} \int \psi(\vec{r}) \, g(|\vec{r}-\vec{r}'|) \, \psi(\vec{r}') \, d^2\vec{r} \, d^2\vec{r}' \; . \tag{6}$$

The first two terms are the usual Landau expansion with $\alpha \sim T-T_c$, and u being a constant. The third term is the lowest order gradient term and expresses the additional cost of inhomogeneity in ψ, where Σ_0 is the area per polar head. The last term is exactly the dipolar contribution calculated above with

$$g(r) = \frac{T}{2\pi} \left(\frac{b}{r} \right)^3 = \frac{\epsilon_0}{\epsilon(\epsilon+\epsilon_0)} \frac{\mu^2}{2\pi r^3} \; . \tag{7}$$

In Fourier space, $\psi(r) = \Sigma_q \phi_q \exp(i\vec{q}.\vec{r})$, and Eq. (6) can be written as

$$\frac{F}{T} = \int \left\{ \frac{1}{2} \alpha \, \psi^2(\vec{r}) + \frac{1}{4} u\psi^4(\vec{r}) \right\} d^2\vec{r} \; +$$

$$+ \frac{1}{2} \Sigma_q \, (\Sigma_0^2 \, q^2 - b^3|q|)\phi_q^2 \; , \tag{8}$$

where b is defined in Eq. (7). Due to the competition between the last two terms in Eq. (8), there is an optimum q-vector that minimizes the free energy. Its magnitude is

$$|q^*| = \frac{b^3}{2 \, \Sigma_0^2} \; . \tag{9}$$

Thus, in addition to the homogeneous phases (liquid and gas) we must consider these phases with undulations, Eq. (9). An approximation that can be justified close to a critical point [20-21], considers only the optimal q-vector, $|q| = |q^*|$, in Eq. (8).

Following Garel and Doniach [20] and Brozovskii [21], the two simplest solutions with undulations are:

(i)   the stripe (smectic) phase

$$\psi_s = \psi_0 + \phi_q \cos qx \tag{10a}$$

(ii)   the hexagonal phase

$$\psi_H = \psi_0 + \sum_{i=1}^{3} \phi_q \cos(\vec{k}_i \cdot \vec{r}_i) \ , \tag{10b}$$

$$\text{with } |\vec{k}_i| = q \quad , \quad \sum_{i=1}^{3} \vec{k}_i = 0 \ .$$

Substituting the two proposed solutions, Eqs. (10), into the free energy expansion (8), we get the following two rescaled free-energy densities

$$f_s = \frac{\delta}{2} M_0^2 + \frac{1}{4} M_0^4 + M_q^2 (\delta - 1 + 3M_0^2) + \frac{3}{2} M_q^4 \tag{11a}$$

$$f_H = \frac{\delta}{2} M_0^2 + \frac{1}{4} M_0^4 + M_q^2 (3\delta - 3 + 9M_0^2 + 12M_0 M_q) + \frac{45}{2} M_q^4 \tag{11b}$$

for the stripe and hexagonal phases respectively, where

$$\delta \equiv \frac{4\alpha}{\eta^2} \ , \ M_0^2 \equiv \frac{4u}{\eta^2} \psi_0^2 \ , \ M_q^2 \equiv \frac{u}{\eta^2} \phi_q^2 \ \text{and} \ \eta^2 \equiv \frac{b^6}{\Sigma_0^3} \ .$$

The free energy of these undulating phases is compared with the free energy of the homogeneous solution $f_I = \frac{\delta}{2} M_0^2 + \frac{1}{4} M_0^4$.

In Fig. 1, the phase diagram in the reduced temperature δ - reduced average concentration ($M_0 \sim \langle\phi\rangle - \phi_c$) plane is shown. The usual coexistence region between liquid and gas ($M_0^2 = \delta$) in the absence of dipolar interactions is largely modified. A novel critical point at $M_0^* = 0$, $\delta^* = 1$, is the termination point of five distinct phases: gas (G), dilute hexagonal (H) that consists of droplets of liquid in gas, stripe (S), inverted dense hexagonal (IH) and liquid (L). All the transition lines below the critical point (M_0^*, δ^*) are first-order, hence four regions of two-phase coexistence exist between the phases. At low enough temperatures, ($\delta < \delta^*$) the stripe (S) and the hexagonal (H, IH) phases disappear, as seen in Fig. 1. We believe that this is a defect of the single mode Ginzburg-Landau expansion that we used here. In the next section, a direct calculation of the free energy at low temperatures will show that the undulating phases

are expected to remain stable even at low temperatures over some
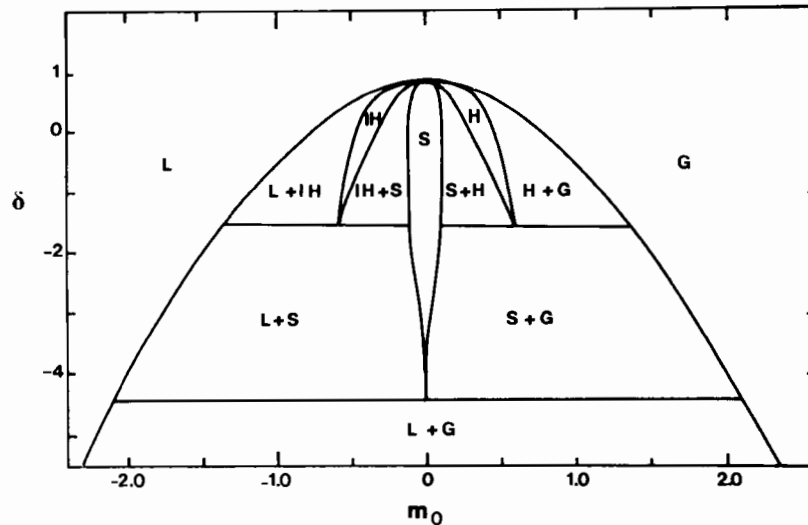range of concentrations.

Figure 1.   Phase diagram in the (M_o, δ) plane where $\delta \sim T-T_c$ is the
reduced temperature and $M_o \sim \langle\phi\rangle-\phi_c$ is the reduced concentration.
The two homogeneous 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. This phase diagram
was obtained from Eqs. (11) and is valid only close to
$(\delta^*=1, M_o^*=0)$.

3.2 Undulating Phases at Low Temperatures

It is of interest to compare the relative stability of the undulating
and the homogeneous phases at low temperatures; our treatment of the
previous section was valid only close to a critical point. In what
follows, we make few assumptions that simplifies the formulation; a
more detailed calculation can be found in Ref. [18].
     The undulating phase is assumed to be a stripe phase with sharp
domain boundaries where more condensed regions ("liquid") of size D_ℓ
and more dilute regions ("gas") of size D_g alternate, as is shown in
Fig. 2.   Thus the periodicity of the pattern is $D = D_\ell + D_g$.   In
principal, one should take into account both the concentration of the
liquid-like ϕ_ℓ, and the gas-like regions ϕ_g ; here we will
approximate $\phi_g = 0$.   (This assumption was not, however, made in Ref.
[18]).   The dipolar contribution to the total internal energy for
this structure is easily derived from Eq. (6)

$$\frac{f_{el}}{T} = \frac{b^3}{\pi a} x\phi_\ell^2 - \frac{b^3}{\pi D} \phi_\ell^2 \left\{ \ln \frac{D}{a} x - \sum_{p=1}^{\infty} \ln \frac{p^2}{p^2 - x^2} \right\}. \tag{12}$$

where $x \equiv D_\ell/(D_\ell + D_g) = D_\ell/D$ and $a \simeq \sqrt{\Sigma_0}$ is a molecular cutoff. The first term in Eq. (12) represents the average contribution of the dipole interactions and is independent of the periodicity D. The second and third terms represent the intra- and inter-stripes electrostatic interactions respectively. However, the leading contribution comes from the interactions within the same stripe; the effect of the inter-stripe interactions is to renormalize the line tension at the liquid/gas interface and following Ref. [22], this term can be summed analytically.
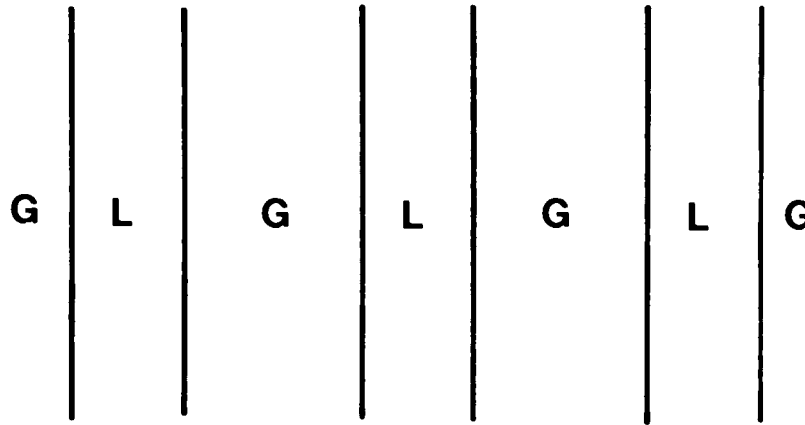

Figure 2. The stripe phase is shown schematically. Domain walls (which are sharp only at low temperatures) separate denser liquid (L) from dilute gas (G).

A further contribution to the free energy difference Δf between the stripe phase and the homogeneous phase comes from the line tension γ that accounts for the concentration variation at each liquid/gas interface. The total free energy difference between the stripe and homogeneous phase is thus

$$\Delta f = -T \frac{b^3}{\pi D} \phi_\ell^2 \left\{ \ln \frac{D}{a} x + \ln \frac{\sin \pi x}{\pi x} \right\} + \frac{2\gamma}{D}. \tag{13}$$

The equilibrium periodicity of the stripe structure is given by the minimum of Δf

$$D^* = \frac{a}{x} \frac{\pi x}{\sin \pi x} \exp\left(\frac{2\pi\gamma}{Tb^3 \phi_\ell^2} + 1\right) . \tag{14}$$

The exponential dependence of the periodicity D^* on the ratio between line tension γ and the dipolar interaction coefficient $b^3\phi_\ell^2$ makes it difficult to give accurate estimates of it since neither γ nor b (which depend on the local dielectric constant ϵ) are accurately known.

In a recent paper, Keller et al [22] presented calculations for the electrostatic free energy that are similar to ours [18] at low temperatures. In addition, they compared their predictions with epifluorescence experiments [23] done on phospholipid monolayers where stripe-like solid and liquid domains coexist. It was also observed that trace amounts of cholesterol can reduce the width of the stripe. Theoretically, this can be explained by a preferential binding of the cholesterol to the solid/liquid interface that reduces the line tension. The agreement between theory and experiments [23], for the predicted width of the domains as a function of the monolayer concentration, is good at high monolayer concentration.

4. CONCLUSIONS

We explored the effects of dipolar interactions in Langmuir monolayers. Their main effect is to stabilize supercrystal phases with an undulating inplane concentration. We studied stripe (smectic) phases and to some less extent hexagonal ("bubble") phases.

Experimentally, epifluorescence observations have shown the existence of undulating phases in a concentration range which corresponds to the liquid-solid transition. It seems that for such transitions, the undulating phase is probably due to the nucleation of two-dimensional solid regions in a liquid background and the observed hexagonal phases are, most likely, a non-equilibrium phenomenon. However, since the sizes of the solid domains depend strongly on the ionic strength of the solution, we believe that the electrostatic interactions play a major role in determining the structure of these undulating phases [17,22].

The theories proposed here both close to a critical point and for low temperatures are more applicable to fluid phases rather that to the solid-liquid region. This can be both in the liquid-gas or the liquid expanded-liquid condensed regions. Due to the low surface pressure and concentration in the former case, fewer effects can be measured (for neutral monolayers). The period of the undulations can be estimated from Eqs. (9) and (14); it varies from 1000Å to 1μm according to the precise magnitude of the dipoles on the surface (or equivalently the ζ potential). It also depends strongly on the local dielectric constant at the interface and the line tension γ which is not very well known.

For charged monolayers, the effective dipole can be tuned by

varying the ionic strength in the solution. Our theory gives an explicit dependence of the undulation period and the critical temperature as function of the screening length κ^{-1}. However, this does not represent the entire dependence on the ionic strength, since the charge per molecule e also depends strongly on the ionic strength. This must be taken into account when a comparison with experiments is done.

At the liquid expanded - liquid condensed transition, the model does not give a definite explanation for the kink observed in many experiments. It does, nevertheless, demonstrate the role played by an additional order parameter - in our case, the undulation amplitude. As was explained in the introduction, it is not clear if the experimental isotherms show a kink or a more complicated structure as proposed here. Moreover, the jump in the pressure between the two extreme transitions in Fig. 1 is of order of $\varepsilon\Delta V^2/D$, where ΔV is the potential jump across the monolayer and D is the period of the undulations. Estimating its magnitude we get a very small value of the order of 0.01 dynes/cm.

We also would like to point the connection between the dipolar monolayer and two other magnetic systems: a thin uniaxial magnetic film [24] and a thin layer of ferrofluid [25] both subject to a normal magnetic field. In these magnetic analogs, a competition between dipolar forces and domain wall energies or line tension also destabilizes the homogeneous state of the system. The ferrofluid is more like our system at zero temperature since thermal fluctuations do not play an important role, whereas for the thin magnetic film thermal fluctuations are important. These three systems are remarkably similar although the length scale of the undulations is very different; it can reach a few millimeters in the ferrofluid (subject to magnetic fields of only several hundred Gauss), whereas it can be as small as few hundred Å for the monolayer and in the intermediate micron range for the thin solid magnetic films.

In conclusion, it should be noted that the effect of the long-range dipolar forces is important for most of the monolayer properties and not only for the equilibrium phase diagram as was studied in this work. From an experimental point of view, non-equilibrium phenomena seem to be of particular importance in Langmuir monolayers. Thus, the inclusion of dipolar forces in the kinetics of domain growth is of relevance and will be addressed in a separate study.

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