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Dynamics of Phase Transitions in Langmuir Monolayers of Polar Molecules

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Insoluble monolayers in the presence of dipolar forces have been predicted to form lamellar and hexagonal supercrystal phases at the liquid-gas or liquid-expanded - liquid-condensed transition. We study here the dynamics of the initial stages of the formation of these supercrystal phases including the flow induced in the supporting liquid in three different geometries a) free films b) films on a solid c) film on a bulk liquid phase.

INTRODUCTION

Electrostatic dipolar interactions have recently been shown to be of major importance in Langmuir monolayers of polar molecules /1/2/3/ : they may change drastically the phase diagram of the monolayer. In insoluble monolayers of amphiphilic molecules, dipolar forces may have two origins :

i) neutral molecules carry a permanent electrostatic dipole of the order of a few millidebye with a preferential orientation perpendicular to the interface ;

ii) charged monolayers build up an electrical double layer which can be considered as a layer of dipoles at sufficiently high ionic strength.

At the liquid-gas or liquid-expanded - liquid-condensed phase transition, the repulsive long-range interactions between the dipole ($\sim 1/r^3$) give rise to spatially periodic arrangement of the molecules (sometimes called supercrystals) in a significant part of the coexistence region /1/2/.

Our aim here is to study the dynamics of formation of the supercrystal phases of a monolayer initially in a one-phase isotropic region of the phase diagram, which has been rapidly quenched into the coexistence region either in a two-phase region or in a one-phase region corresponding to a spatially periodic, supercrystal phase, by changing either the temperature of the surface pressure.

If in the final state the homogeneous isotropic phase is metastable, the new equilibrium phase grows first by a nucleation process, which requires an activation energy to initiate the phase separation. If the isotropic phase is unstable after the quench, the equilibrium state forms by amplification of the local fluctuations of concentration which in monolayers corresponds to a divergence of the longitudinal Lucassen modes.

We study here this process known as spinodal decomposition. The nucleation process and the kinetics of domain growth (Ostwald Ripening) will be addressed in a separate study. In addition to the role of long-range forces, spinodal decomposition in Langmuir monolayers is interesting and different from usual spinodal decomposition in three-dimensional liquid systems /9/ for the following reasons :

a. as in any two-dimensional system, gravity plays no role : this is thus an example of phase separation in zero-gravity ;

b. although the static phase diagram is purely two-dimensional, motions in the monolayer induce a backflow in the water substrate. We will show that dissipation is dominated by the viscous dissipation in the substrate and has thus a three-dimensional character ;

c. the first unstable mode (the spinodal line) does not occur at zero-wave vector as in systems with short-range forces but at a finite wave vector q^* . This situation is also found in other systems such as block copolymers /4/ (in three dimensions) or ferrofluids /5/ (in two dimensions) ;

d. contrary to usual liquid-liquid phase separations where the soft mode (critical mode) is diffusive, thus overdamped, outside the spinodal region, the "LUCASSEN" modes /6/ are propagating ; we show that in the unstable spinodal regions, the propagation disappears and the unstable fluctuations grow exponentially without any oscillations.

We first quickly recall the complex diagram of Langmuir monolayers of polar molecules. The amplification of the Lucassen mode is then studied in different geometries : films on a thin liquid slab above a solid substrate for which viscous dissipation is the dominant effect and the more common case of a monolayer on an infinite bulk water phase for which both inertia and viscous dissipation play a role.

1. SUPERCRYSTAL PHASES of POLAR MONOLAYERS

We call μ the mean value (vertically oriented) of the permanent dipoles of the amphiphilic molecules. If Σ is the area per polar head, the dipole $P = \mu \Sigma^{-1}$ is derived from the contact potential V

$$V = \frac{P}{\epsilon} = \frac{\mu}{\epsilon \Sigma_0} \phi, \quad (1)$$

where Σ_0 is the area corresponding to close packing, ϕ the surface fraction occupied by molecules and ϵ the dielectric constant seen by the dipoles at the interface (which might be different from the water bulk value). Equation (1) is valid both for neutral and charged monolayers at high ionic strength, the equivalent dipole in this case is $\mu = e \kappa^{-1}$, where e is the elementary charge and κ^{-1} the Debye-Hückel screening length.

In the supercrystal phases the surface fraction varies periodically on the surface. Close to a liquid-gas or liquid-expanded - liquid-condensed critical point, it is sufficient to describe this variation by a one-mode expansion

$$\phi(r) = \phi_0 + \phi_q(\vec{r}),$$

the undulation ϕ_q being periodic with a period $2\pi/q$.

The electrostatic free energy associated with the undulation ϕ_q is

$$F_D = -\frac{1}{2} |q| \frac{\mu^2}{\Sigma_0^2} \phi_q^2 \frac{\epsilon_0}{(\epsilon + \epsilon_0)}. \quad (2)$$

The phase diagram of the monolayer may thus be deduced from a Landau-Ginzburg expansion of the free energy :

$$\frac{F_S - F_0}{kT} = \frac{1}{2} \Delta \psi^2 + \frac{1}{4} B \psi^4 + \Sigma_0 \phi_c^2 \Sigma_q \left[-K |q| + \frac{1}{2} L q^2 \right] \psi_q^2, \quad (3)$$

where $\psi = \frac{\phi - \phi_c}{\phi_c}$ is the order parameter, $\Delta = \alpha \frac{T - T_0}{T_0}$ vanishes at T_0 . L is related to the attractive short-range interaction and K to the long-range repulsion

$$\left[K = \frac{1}{2kT} \frac{\mu^2}{\Sigma_0^2} \frac{\epsilon_0}{(\epsilon + \epsilon_0)} = \frac{\lambda}{\Sigma_0^{1/2}}, \text{ where } \lambda \text{ is a small parameter measuring the strength of dipolar interactions } (\lambda \sim 10^{-3}) \right].$$

The functional (3) is optimal for a wave vector q^*

$$q^* = \frac{K}{L} \quad (4)$$

of the order of 1000 \AA for $\lambda \sim 10^{-3}$. Setting $q = q^*$ in (3) leads to a renormalization of the mean field critical temperature ($T_c = T_0 \left[1 + \frac{1}{\alpha} \frac{K^2}{L} \tau_0 \phi_c^2 \right]$).

The phase diagram deduced from (3) is shown on fig.1.

a) Near the critical point, the monolayer builds up a supercrystalline phase spatially modulated, of period $2\pi/q^*$. The order may be smectic or triangular. Near the axis $\psi = 0$, the smectic phase is always stable. Near the isotropic phase coexistence line, one finds a triangular phase made of a network of circular islands /2/.

b) At lower temperatures, all wavevectors contribute to the surface fraction ϕ and the one-mode approximation breaks down : the period is not any more related to q^* and increases exponentially /2/.

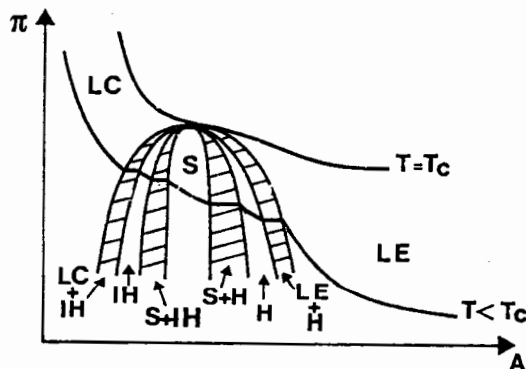


Fig. 1 : Phase diagram and $\pi - A$ curves of a Langmuir monolayer of polar molecules : the two isotropic phases liquid-condensed - liquid expanded are separated by the hexagonal (H), stripe (S) and inverted hexagonal (IH) phases.

2. SPINODAL DECOMPOSITION of POLAR MONOLAYERS

The monolayer, in an isotropic homogeneous phase, is suddenly quenched into the coexistence region (see fig. 1). The critical mode is the longitudinal mode (fig. 2) first discussed by LUCASSEN /6/, and in more details by KRAMER /7/. The monolayer acts as an elastic membrane : we call $u_q = u_0 e^{iqx} e^{-i\omega t}$ the displacement of the monolayer in the direction x of the wavevector q . The fluctuation of the surface density ψ_q is related to u_q by a conservation equation $\psi_q = -\partial u_q / \partial x$.

For any concentration fluctuations ψ_q , there is an elastic force F_{el} opposing the displacement u_q which can be calculated from the free energy(3)

$$F_{el} = E(q) \frac{\partial^2 u}{\partial x^2} \quad (5)$$

b. Thin Liquid Slab on a Solid

The monolayer bounds a very thin water film deposited on a solid plane. Any fluctuation in the monolayer induces a shear in the film. In the limit $qd \ll 1$, the lubrication approximation /8/ holds and the equation of motion, given by a balance between the elastic and the viscous forces, can be written as :

$$E \frac{\partial^2 u}{\partial x^2} = \frac{\eta}{d} \frac{\partial u}{\partial t}, \quad (8)$$

η is the film viscosity.

This leads to a diffusive mode with a relaxation time

$$\frac{1}{\tau} = E \frac{d}{\eta} q^2. \quad (9)$$

The fluctuation is amplified for negative membrane elasticity E . If the quenching temperature is close to T_C , the amplified modes are the modes around q^* [$q_1 < q < q_2$] as shown on fig.3. As T decreases, the threshold q_1 of instability goes to zero and the wave vector q_M of the fastest mode increases. q_M varies from q^* at T_C to a large value at low temperature :

$$q_M^2 \approx \Delta \Sigma_0^{-1} \phi_c^{-2} L^{-1}. \quad (10)$$

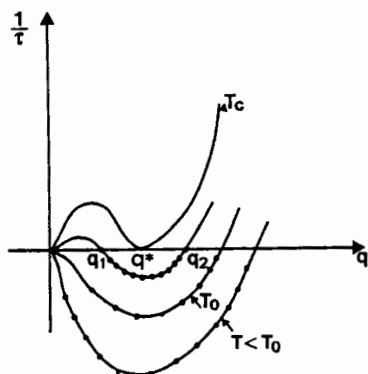


Fig. 3 : Relaxation time of the longitudinal mode of a polar Langmuir monolayer deposited on a thin liquid film. The first instability ($1/\tau < 0$) arises for a mode of wave length equal to the period of the supercrystal.

c. Monolayer on a Bulk Liquid

The longitudinal modes of a monolayer on a bulk liquid have been studied in detail by LUCASSEN /6/. Taking into account the coupling between longitudinal and transversal modes (capillary waves), the dispersion relations are given by the roots of the following equation :

$$(x'^2 + 2x' + Q_\gamma) (x'^2 + 2x' + Q_E \sqrt{1+x'}) = (2x' + Q_E) (2x' \sqrt{1+x'} + Q_\gamma), \quad (11)$$

where $x' = \frac{i\omega\rho}{nq^2}$, $Q_\gamma = \frac{\gamma\rho}{n^2|q|}$ and $Q_E = \frac{E(q)\rho}{n^2|q|}$.

$\sqrt{\quad}$ means that the real part of the square root is positive ; γ is the surface tension ($\gamma = \gamma_0 - \pi$, where γ_0 is the pure water surface tension ($\gamma_0 \approx 70$ dynes cm^{-1}) and π the surface pressure). In (11), we have neglected gravity ($q\kappa^{-1} > 1$, where κ^{-1} is the Laplace capillary length). We study the roots of (11) as a function of the quenching temperature T .

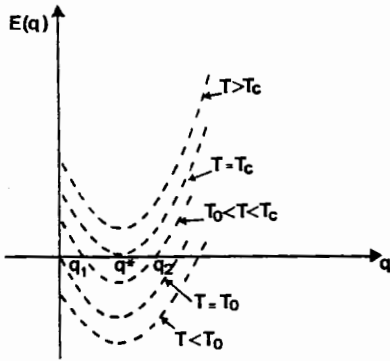


Fig. 2 : Elastic modulus E of a polar Langmuir monolayer as a function of wave vector q for several temperatures ; because of the dipolar repulsions, the sign of E is reversed at finite q value ($q = q^*$) corresponding to the period ($2\pi/q^*$) of the supercrystal.

$E(q)$ is the monolayer membrane elasticity :

$$\frac{E(q)}{kT} = \frac{\Delta}{\Sigma_0} + 2\phi_c^2 \left[-K |q| + \frac{1}{2} L q^2 \right].$$

Whenever the elasticity is positive, the elastic force is a restoring force and the monolayer is stable with respect to the fluctuation ψ_q .

If the elasticity $E(q)$ is negative, the elastic force increases the fluctuation and the membrane is unstable.

The condition $E(q) = 0$ thus defines the spinodal line.

The variation of $E(q)$ is sketched on fig. 2 for several temperatures ; the first unstable mode arises for $T = T_c$, $q = q^*$.

In order to describe the dynamics of the Lucassen mode, one must include the motion of the liquid driven by the fluctuations of the monolayer. Before studying the case of a monolayer on a bulk liquid phase, we first look at two limiting cases in order to show the relative role of viscous and inertial forces.

a. "Free" Film

A water film of thickness d is bounded on its two surfaces by monolayers. We study the limit $qd \ll 1$ where the liquid follows adiabatically the fluctuations of the membrane. In soap films, the two monolayers have dipoles with opposite direction. The dipolar interactions may thus be strongly reduced if $q^*d < 1$ and the expression of $E(q)$ may be different from (6). The problem is purely inertial. The equation of motion is :

$$2E(q) \frac{\partial^2 u}{\partial x^2} = d\rho \frac{\partial^2 u}{\partial t^2}, \quad (6)$$

ρ is the density of the film.

The dispersion relation of the longitudinal modes is then

$$w^2 = \frac{2E}{d\rho} q^2. \quad (7)$$

When the elasticity E is positive, we find two sound waves ($w = \pm \sqrt{\frac{2E}{d\rho}} q$). The sound velocity goes to zero for $E = 0$. For negative E , the two modes become non propagative ($iw = \frac{1}{\tau} = \pm \sqrt{\frac{2|E|}{d\rho}} q$), one diverges and the other one is overdamped. We shall now look at the opposite limit of viscous dissipation in the liquid.

1° Shallow Quench ($T > T_c$)

If T is close to T_c , $E(q)$ is very small compared to γ . In this limit, one can assume that the water surface remains flat as the monolayer fluctuates.

The dispersion relation for the longitudinal mode can be deduced from (11) by taking the limit $C_V/Q_E \rightarrow \infty$:

$$\frac{x'}{\sqrt{1+x'} - 1} = -\frac{E\rho}{\eta^2|q|} = -Q_E. \quad (12)$$

The roots of (12) depend upon the sign and the amplitude of Q_E .

a) $|Q_E| \gg 1$

If Q_E is large and positive, the roots of (12) are

$$x' = e \pm 2i\pi/3 |Q_E|^{2/3} \quad (13)$$

$$\text{or } \frac{1}{\tau} = \frac{E(q)}{\eta^{1/3} \rho^{1/3}} q^{4/3} e^{\pm 2i\pi/3}. \quad (13')$$

The modes are propagative and involve both inertia (ρ) and viscosity (η). One can check that the elastic energy is balanced by the kinetic energy of a slab of liquid

of thickness l ($l^{-1} = \sqrt{q^2 + i\rho\eta}$).

If Q_E is negative, (12) has only one root :

$$x' = |Q_E|^{2/3} \quad (14)$$

or a negative relaxation time :

$$\frac{1}{\tau} = - |E(q)|^{2/3} q^{4/3} / \eta^{1/3} \rho^{1/3}. \quad (14')$$

This mode is amplified exponentially, without any oscillation.

b) $|Q_E| \ll 1$

In this limit, (12) reduces to

$$x' = -\frac{E\rho}{2\eta^2|q|}. \quad (15)$$

The relaxation time is :

$$\frac{1}{\tau} = \frac{E(q)}{2\eta} |q|. \quad (15')$$

If E is positive, the mode is overdamped.

If E is negative, the mode is amplified exponentially.

For a clear shallow quench near T_c , the most unstable wave vector q_M is very close to q^* and $Q_E \ll 1$. The characteristic time for the divergence of the fluctuation is then given by (15') with $q = q^*$

$$\frac{1}{\tau} = - |E(q^*)| \frac{q^*}{\eta} = - \left| \frac{\Delta}{\Sigma_0} - \phi_c \frac{K^2}{L} \right| \frac{q^* kT}{2\eta} . \quad (16)$$

The amplified mode is purely viscous. This regime is similar to the case of a liquid slab of thickness $d = q^{-1}/2$ deposited on a solid (see (9)).

2° Deep Quench ($T \ll T_c$)

Far from T_c , the elastic modulus E is usually much larger than the surface tension γ . We assume now $Q_E \gg Q_\gamma$ in (11).

If $|Q_E| \gg 1$, we find here also that $x'^{3/2} = -Q_E$, and the dispersion relation is given by (13') if $E > 0$ and by (14') for negative E .

If $|Q_E| \ll 1$, one finds $x' = -\frac{Q_E}{2}$.

For a deep quench, $|E|$ is large, and for the most unstable mode, $|Q_E| \gg 1$; the dispersion relation is then given by (14'). For a deep quench, we have a viscous inertial behaviour. The wave vector q_M is given by (10). It is much larger than q^* and dipolar interactions are negligible in the small time regime of the spinodal decomposition.

3 . CONCLUSIONS

We have studied spinodal decomposition in a Langmuir monolayer of polar molecules in the coexistence region between the liquid and gas or liquid-expanded and liquid-condensed phases where periodic supercrystal phases form. We summarize here the most important results :

- The unstable critical mode of the monolayer is the longitudinal Lucassen mode.
- The spinodal line where the elastic modulus vanishes does not occur at zero wave-vector but at the equilibrium wave-vector at the critical point q^* resulting from a competition between dipolar and short-range forces.
- A deep quench at a low temperature leads to a quite classical spinodal behaviour, long-range forces play no role, and the only important feature is the flow induced in the water substrate.
- After a shallow quench, close to the critical point, the diverging fluctuation has the equilibrium wave-vector q^* . At longer time, the growth of the equilibrium periodic phase will require only a variation in the amplitude of the modulation of the surface concentration.

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