

Electrostatic Pressure and Line Tension in a Langmuir Monolayer

S. Rivière, S. Hénon, and J. Meunier

Laboratoire de Physique Statistique de l'Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris cedex 05, France

G. Albrecht, M. M. Boissonnade, and A. Baszkin

Laboratoire de Physicochimie des Surfaces, 5 rue Jean Baptiste Clément, 92236 Châtenay Malabry cedex, France

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We present a Brewster angle microscopy study of the domains of liquid condensed phase (L_2) in the liquid expanded phase (L_1) in a Langmuir monolayer of a long-chain fatty acid. A strong deformation of the domains is observed when they are close to each other, indicating the presence of long-range repulsive dipolar interactions between them. The line tension of the L_1/L_2 interface is deduced from the balance between the line tension and the electrostatic forces. The latter were deduced from surface potential measurements.

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In Langmuir films (monolayers of insoluble amphiphilic molecules at the air-water interface), first order phase transitions have been observed directly using fluorescence microscopy [1] and more recently Brewster angle microscopy [2]. A rich variety of domain shapes [3–7] and domain texture [6–9] has been observed in the coexistence regions. The equilibrium shape of the domains results from the competition between several interactions. The line tension of the interface between the two phases tends to make the domains circular, in order to minimize the perimeter of the boundary. On the other hand, the long-range repulsive electrostatic forces between the dipoles carried by the molecules tend to elongate the domains. Finally, for the case of tilted liquid condensed phases there is an anisotropic line tension that has to be considered.

Only a few estimates of the line tension λ of the interface between two coexisting phases have been made. Muller and Gallet [10] have estimated λ for a 2D solid-liquid interface by measuring the rate of nucleation of the domains as a function of the overpressure applied on the monolayer, supposing homogeneous nucleation. Stine, Knobler and Desai [11] take advantage of the observation of a buckling instability of the film to determine the ratio of λ for the 2D gas-liquid expanded interface to the relative dielectric constant ε in the monolayer. However, ε is in the range 1 (value for air) to 80 (value for water), but is unknown. Benvegnu and McConnell [12] measured λ for liquid domains in binary mixtures of lipid monolayers; they applied a shear stress to distort the domains and observed the relaxation of their shape with time. On the one hand, these authors supposed that the dipoles are located in a uniform medium, the air, to determine the strength of the repulsive interactions inside domains. On the other hand, the hydrodynamic problem is very complicated and needs assumptions on the film compressibilities and viscosities [13,14]. We propose a new method to determine λ that does not suffer from the

problems mentioned above. In contrast to the methods described above, which suppose that the domains are far from each other so that interactions between them can be neglected, we take advantage of the interactions between domains.

Using Brewster angle microscopy [2], we have studied the shape of domains of the L_2 or liquid condensed (LC) phase coexisting with the L_1 or liquid expanded (LE) phase in a Langmuir film of myristic acid spread on ultrapure water at pH 2, when the domains are close to each other. The shape results from the balance between the line tension and long-range dipolar repulsions, which induce a nonuniform surface pressure in the two different phases. We show here that the strength of the dipolar repulsions can be deduced directly from surface potential measurements, without involving any hypothesis on the structure of the interface.

The surface potential is defined as the difference between the electric potential through a clean water surface and that through the interface covered with a monolayer. For an un-ionized monolayer, the usual interpretation of ΔV is given by the generalized Helmholtz equation, based on an analogy with a multiple-layer parallel plate capacitor: $\Delta V = 1/[A\varepsilon_0](\rho_{n1}/\varepsilon_1 + \rho_{n2}/\varepsilon_2 + \dots)$. This equation means that ΔV results from different “layers” of dipoles in the monolayer. The contribution of each layer is $1/[A\varepsilon_0](\rho_{ni}/\varepsilon_i)$, where ε_i is the relative dielectric permittivity seen by the dipoles p_i , ρ_{ni} the mean value of the vertical component of p_i , A the mean area per molecule, and ε_0 the permittivity of the vacuum. This equation makes it possible to discern different contributions to the surface potential [15–17], such as the contribution of the different dipoles, p_i , borne by the amphiphilic molecules, the interactions between neighboring dipoles inducing a mutual depolarization, and the resulting reorientation of the water molecules near the monolayer. Surface potential measurement provides a direct measurement of the effective dipolar moment density, which is equal to $\varepsilon_0\Delta V$.

From x-ray diffraction experiments [18], it was concluded that the L_1 phase is a liquid and the L_2 phase a hexatic phase: The positional order of the molecules is short range, but the orientational order of the intermolecular directions is long range. Moreover, the molecules are tilted away from the surface normal towards a nearest neighbor, with the tilt angle fixed for a given surface pressure and temperature and the tilt azimuthal angle correlated over long distances [7–9]. Consequently, the average dipolar moment in the isotropic L_1 phase is vertical while it is tilted in the L_2 phase. The interaction between two vertical dipole components is dipolar and consequently long range, whereas the interaction between two horizontal ones is quadrupolar, i.e., short range, and can be included in the line tension. As a consequence, the only interactions that have to be considered are those between the vertical components, which can be obtained from surface potential measurements.

In all the models used to describe the interface [10,19,20], the dipolar interaction can be written as a function of the surface potential and is independent of both the dielectric constant of the medium in which the dipoles are embedded and of the number of dipoles in each molecule. Using the electrostatic image method and the generalized Helmholtz equation, it can be shown [20] that the interaction energy between two surface elements $d^2\mathbf{r}$ and $d^2\mathbf{r}_0$, located in \mathbf{r} and \mathbf{r}_0 , where the surface potentials are respectively $\Delta V(\mathbf{r})$ and $\Delta V(\mathbf{r}_0)$, is

$$\frac{1}{4\pi\epsilon_0\epsilon_1 + \epsilon_2} \frac{2\epsilon_1\epsilon_2}{|\mathbf{r} - \mathbf{r}_0|^3} [\epsilon_0\Delta V(\mathbf{r})d^2\mathbf{r}][\epsilon_0\Delta V(\mathbf{r}_0)d^2\mathbf{r}_0].$$

ϵ_1 and ϵ_2 are the relative dielectric constants of the air and the water. The potential energy per unit area $W_a(\mathbf{r})$ of this dipolar interaction is a result of a summation through the monolayer. $W_a(\mathbf{r}) = \Delta V_j[w_a(\mathbf{r}) + w_{aj}^0]$ for the phase j ($j = L_1$ or L_2), where w_{aj}^0 is a constant and

$$w_a(\mathbf{r}) = \frac{\epsilon_0}{2\pi} \frac{\epsilon_1\epsilon_2}{\epsilon_1 + \epsilon_2} \iint_{(S_{L_1} - C_a)} \frac{(\Delta V_{LE} - \Delta V_{LC})}{|\mathbf{r} - \mathbf{r}_0|^3} d^2\mathbf{r}_0. \quad (1)$$

The summation has been reduced to the L_1 phase using as an argument that, in a homogeneous monolayer, the electrostatic potential is constant. At low r , this integral diverges and a molecular cutoff a , approximately equal to the intermolecular distance, has to be introduced. The integration is performed over the surface $(S_{L_1} - C_a)$, i.e., over the L_1 phase, except for a circle of radius a with a center \mathbf{r} , where W is calculated.

The line tension is the excess free energy of a unit length of interface between two phases and is defined for short-range interactions. The Young-Laplace law $\Delta\Pi = \lambda/R$ gives the surface pressure difference (measured at a distance from the line larger than the range of the intermolecular forces) between the two sides of a domain boundary with a radius of curvature R and a line tension λ . The dipolar forces, on the other hand, are long ranged: The force between the two dipoles in the plane of the

interface decreases as $1/r^4$. In the presence of these forces, the pressure difference will thus depend on the whole configuration of the molecules in the monolayer. Also it will depend on the distance from the boundary. To avoid this difficulty, the long-range forces acting on a vertical dipole p_n can be divided arbitrarily into two components. The first one contains the contributions of the dipoles located at a distance smaller than b from p_n , i.e., in a circle (C_b) of radius b centered on p_n . If $b \ll R$ (radius curvature of the boundary), this short-range component can be included in the line tension. The Young-Laplace equation and the calculation to first order in b/R of the pressure difference between both sides of a curved boundary and of a straight line gives the expression of the line tension as a function of the arbitrary cutoff b :

$$\lambda_b = \lambda_0 - \frac{\epsilon_0(\Delta V_{LC} - \Delta V_{LE})^2}{2\pi} \frac{\epsilon_1\epsilon_2}{\epsilon_1 + \epsilon_2} \ln\left(\frac{b}{a}\right). \quad (2)$$

λ_0 includes the contribution of all the short-range interactions, which are, of course, independent of b . The negative sign in the second term of λ_b results from the repulsive character of the dipolar forces. Minimizing the free energy of a domain de Koker and McConnell [21] obtained a similar equation.

The second component includes the contribution of the dipoles acting over distances larger than b , which cannot be included in the line tension. This long-range component creates a pressure gradient $\nabla\Pi = \mathbf{f}$ in the monolayer, where \mathbf{f} is the surface density of the dipolar forces acting over distances larger than b . \mathbf{f} derives from a potential. At a point \mathbf{r} inside one of the two phases but at a distance larger than b from the border of this phase, this potential is given by Eq. (1) with $a = b$. This leads to $\Pi = -W_b(\mathbf{r})$. This equation is no longer valid at distances from a domain boundary smaller than b , because then the circle C_b intercepts this border. However, in the following we will use this equation close to the border of a domain. It can be shown that this introduces a negligible error ($\sim 1\%$) on the pressure difference between two sides of a border.

At a point A of a domain border where the radius of curvature is R_A , the pressure difference between the two sides of the border is $\Delta\Pi_A = \Pi_{A,L_2} - \Pi_{A,L_1} = \lambda_b/R_A$. Π_{A,L_2} (Π_{A,L_1}) is the surface on the L_2 (L_1) side of the line. Similarly at a point B of the line $\Delta\Pi_B = \lambda_b/R_B$. From these two equations and from (1), one obtains

$$\lambda_b \left(\frac{1}{R_A} - \frac{1}{R_B} \right) = (\Delta V_{L_1} - \Delta V_{L_2}) [w_b(A) - w_b(B)]. \quad (3)$$

This equation allows one to deduce the line tension λ_b from the shape of domains of the coexisting L_1/L_2 (LE/LC) phases and the measurement of the surface potential of the two phases.

For the experiments, myristic acid ($C_{13}H_{27}COOH$) (Sigma, 99% grade) was used without further purification.

A solution of this acid in chloroform (Merck, Pro Analyti grade) was spread on the free surface of the water of a Langmuir trough; the pH of the water was set as $pH = 2$ with HCl (Merck, Suprapur). In the L_1/L_2 coexistence region, the L_2 domains are observed to be circular when far away from each other, but are strongly distorted from their usual circular shape when close to each other (Fig. 1). The repulsive long-range interactions between the domains are so strong that just before they coalesce, the distance between them is still of the order of the microscope resolution ($1 \mu\text{m}$). The film collapses (i.e., three-dimensional objects appear) just after the coalescence of the domains. We have previously studied this phase transition in Gibbs films at $pH = 5.5$ [9]; the observations are the same in the present case of a Langmuir film at $pH = 2$. The tilt of the molecules in the L_2 domains creates an optical anisotropy: A striped texture is observed [9]. The line tension depends upon the orientation of molecules with respect to a domain boundary [8], which varies along this boundary. A simplification can be made by noting that there is no distortion from circular shape when the domains are far away from each other. This indicates that the anisotropic part of the line tension can be neglected with respect to the isotropic one.

The surface potential measurements were carried out by means of a differential method, using two radioactive americium (^{241}Am) electrodes [22,23]. The experimental setup consists of two cells communicating through a Teflon tap. One cell contains the monolayer and the other one pure water at the same pH . The electrodes are placed a few millimeters above the two surfaces. After a measurement of the potential difference between the

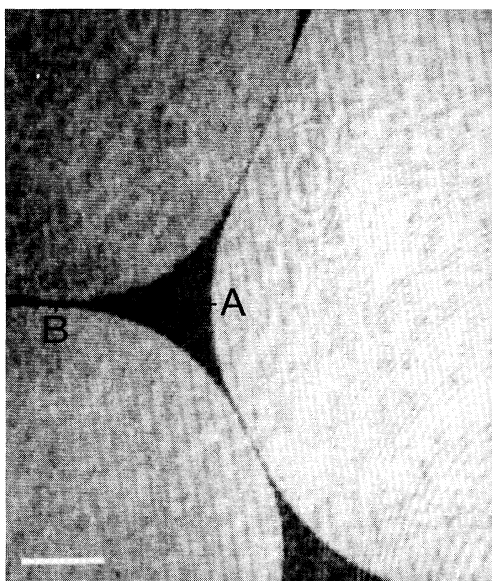


FIG. 1. Image of three liquid condensed domains (in bright) in the liquid expanded phase. A and B are the points where the surface pressure is calculated. The bar represents $50 \mu\text{m}$.

two surfaces, the electrodes are exchanged, and a new measurement is performed. The surface potential is taken as a mean of the two measurements. The error in the measured value that may result from the contamination of the surface of the electrodes is eliminated in this way. The area per molecule was varied by successive additions of myristic acid, after having verified by Brewster angle microscopy that the film texture obtained in this way was the same as that obtained by compression of the monolayer. The same values for the surface potential were found for $pH = 2.3$ and $pH = 1.3$, indicating that the monolayer was un-ionized. Figure 2 shows the surface potential ΔV as a function of the mean area per molecule A at $pH = 1.3$. For values of A between 300 and about $100 \text{ \AA}^2/\text{molecule}$, ΔV gradually increases from 20 to 50 mV, and then rises steeply when decreasing A . A kink appears at about 50 mN/m , a second one between 28 and $31 \text{ \AA}^2/\text{molecule}$, followed by a third one at about $20 \text{ \AA}^2/\text{molecule}$, where ΔV reaches a plateau value ($\Delta V \approx 370 \text{ mV}$). From the Brewster angle microscopy and from the areas per molecule at which the two first kinks are observed, we conclude that these two kinks correspond, respectively, to the end of the gas/ L_1 phase transition and the beginning of the L_1/L_2 phase transition, i.e., to the nucleation of the L_2 domains. The surface potential plateau corresponds to the collapse of the film. The location of the third kink depends upon the pH and the duration of the experiment. At $pH = 1.3$, the collapse appears more quickly and at higher area per molecule than at $pH = 2.3$.

In the L_1/L_2 coexistence region, the surface potentials of domains of the L_1 and L_2 phases are constant, namely, ΔV_{L1} and ΔV_{L2} . Since the surface potential ΔV is measured with electrodes much larger than the domains, it is equal to $x\Delta V_{L1} + (1-x)\Delta V_{L2}$, where x is the fraction of the plane occupied by the L_1 phase. The mean value of the area per molecule on the coexistence plateau is $A = xA_{L1} + (1-x)A_{L2}$, where A_{L1} and

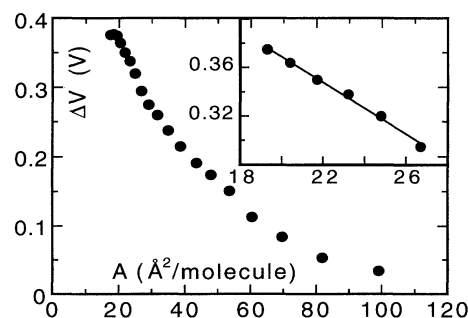


FIG. 2. Surface potential ΔV versus area per molecule A , at $pH = 1.3$. The inset shows the linear increase of the surface potential with A in the coexistence region. The two kinks, at about 50 and $30 \text{ \AA}^2/\text{molecule}$, correspond, respectively, to the end of the gas/LE transition and to the beginning of LE/LC one. The plateau at about 370 mV, corresponds to the collapse of the monolayer.

A_{L2} are, respectively, the areas per molecule of the L_1 and L_2 phases in coexistence. This leads to the linear dependence of ΔV on A in the coexistence region, which was indeed observed experimentally. ΔV_{L1} and ΔV_{L2} can then be deduced from A_{L1} and A_{L2} , and the corresponding linear part of the $\Delta V(A)$ curve. The determination of A_{L1} and A_{L2} from the surface $\Pi(A)$ curves is difficult since the end of the coexistence plateau is not well defined. However, the direct visualization of the film with either fluorescence or Brewster angle microscopy (BAM) allows determination of these areas precisely. Akamatsu [24] has studied this phase transition with fluorescence microscopy and obtains $A_{L1} = 27.5 \pm 1$ and $A_{L2} = 20.5 \pm 1 \text{ \AA}^2/\text{molecule}$ at room temperature. He also showed that the method of tangents yields the same value for A_{L2} . These values are in accordance with our observations using Brewster angle microscopy. From the slope of $\Delta V(A)$ in the coexistence region and $A_{L1} - A_{L2} = 7 \pm 2 \text{ \AA}^2/\text{molecule}$, we deduced $\varepsilon_0(\Delta V_{L2} - \Delta V_{L1}) = (0.65_{-0.25}^{+0.31}) \times 10^{-12} \text{ C m}^{-1}$. Moreover, $\Delta V_{L1} = 275 \pm 10 \text{ mV}$ for the L_1 phase and $\Delta V_{L2} = 360 \pm 20 \text{ mV}$ for the L_2 phase. The vertical components $\mu_N = p_N/\varepsilon$ of the effective molecular dipole moments for the two phases do not differ significantly: $205 \pm 15 \text{ mD}$ in the L_1 phase and $195 \pm 20 \text{ mD}$ in the L_2 phase.

Figure 1 shows an example of a configuration observed with BAM at the high Π end of the L_1/L_2 coexistence plateau. The L_2 domains are very close to each other and strongly distorted. The points A and B are chosen in such a way that the radii of curvature of the domain border in A and B , R_A and R_B , are very difficult. To calculate the potential in A and B , the distribution of the domains can be supposed to be isotropic at large distances from A and B . It thus suffices to consider only the L_1 domains in the vicinity of A and B . The curved portions of the borders of the domains were fitted with polynomial curves. The calculation of $w_b(A)$ and $w_b(B)$ was performed on seven Brewster angle microscopy images (where the minimum distance between two domains is in the range $2.5\text{--}3.5 \text{ \mu m}$) and led to $\lambda_b = \{(6.9\text{--}7.6) \times 10^{-2} \ln[b(\text{\AA})/5]_{-4.3}^{+8.1}\} \times 10^{-13} \text{ N}$. The uncertainty in determining the length of the coexistence plateau is the main source of error. For $b < 1000 \text{ \AA}$, the logarithmic dependence of λ_b can be neglected. This justifies the definition of the line tension we have given in the presence of long-range forces.

In conclusion, our result, $\lambda_0 = (6.9_{-4.3}^{+8.1}) \times 10^{-13} \text{ N}$, for the line tension of a hexatic-liquid interface is obtained without any assumption on the dielectric constant in the monolayer. As expected, λ_0 is somewhat smaller than the value found by Muller and Gallet [10] for a solid-

liquid interface ($5 \times 10^{-12} \text{ N}$), but is in the range of values measured in Ref. [9] ($\sim 10^{-13}$ to $2 \times 10^{-12} \text{ N}$). However, a comparison is difficult, since the systems under consideration are very different.

The Laboratoire de Physique Statistique de l'Ecole Normale Supérieure is URA CNRS 1306, associée aux Universités Paris VI et VII. The Laboratoire de Physicochimie des Surfaces of Université Paris XI is URA CNRS 1218.

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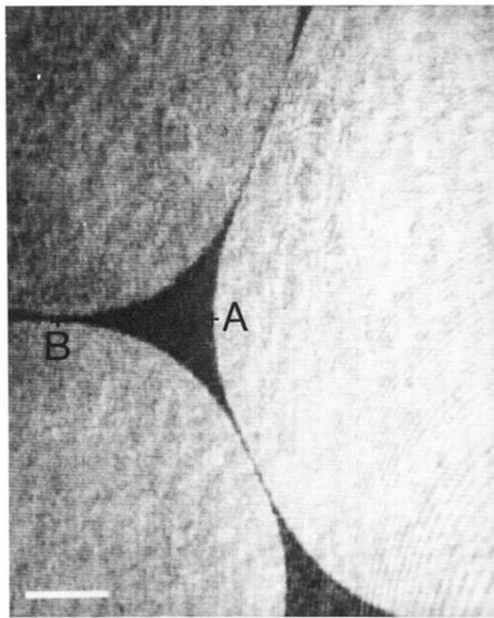


FIG. 1. Image of three liquid condensed domains (in bright) in the liquid expanded phase. *A* and *B* are the points where the surface pressure is calculated. The bar represents 50 μm .