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Buckling of a Bidimensional Solid.

A. SAINT-JALMES (*), F. GRANER (*) (§), F. GALLET (*)
and B. HOUCHMANDZADEH (**)

(*) *Laboratoire de Physique Statistique de l'Ecole Normale Supérieure*
(URA 1306 associée au CNRS et aux Universités Paris 6 et Paris 7)
24, rue Lhomond, 75231 Paris Cedex 05, France
(**) *CNRS URA 8, Laboratoire de Spectrométrie Physique, Université Joseph Fourier*
BP 87, 38042 Saint-Martin d'Hères Cedex, France

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Abstract. – We observe buckling, without collapsing, of a solid Langmuir film under uniaxial compression, like an usual elastic plate. The preliminary characterization of this instability shows that, at the threshold, surface tension is strictly positive, amplitude is continuous and wavelength is $\lambda_c \sim 6\ \mu\text{m}$. Without adjustable parameter, we interpret these results as a second-order transition due to dipolar interactions between amphiphilic molecules.

Introduction. – When applying an external surface pressure Π to an insoluble monolayer of amphiphilic molecules deposited at the air-water interface, the surface tension decreases as $\gamma = \gamma_0 - \Pi$. A fluid film should become unstable against buckling when γ becomes negative [1]: such permanent undulation, with nanometer amplitude, has been observed on a polymerized monolayer [2]. We take advantage of the low γ_0 of a formamide subphase and its high stability against film collapse [3], and report the buckling of a solid film at strictly positive γ.

Dipolar interactions between molecules [4] can explain the interplane buckling of a thin separation line between two 2D bubbles [5]. We show that such interactions also lead to out-of-plane buckling of a two-dimensional film.

Experiments. – The experimental set-up is presented elsewhere, as well as a detailed characterization of the film phase diagram [3]. Briefly, our home-made thermostated Langmuir trough undergoes a symmetrical compression by two teflon barriers, varying the area from 260 cm^2 to 45 cm^2 with a typical compression rate of 4 to 10 Å^2 per molecule per minute (fig. 1). A 3 mm wide piece of filter paper, hanging on a Wilhelmy balance (Riegler

(§) Present address: CNRS URA 8, Laboratoire de Spectrométrie Physique, Université Joseph Fourier, BP 87, 38042 Saint-Martin d'Hères Cedex, France.

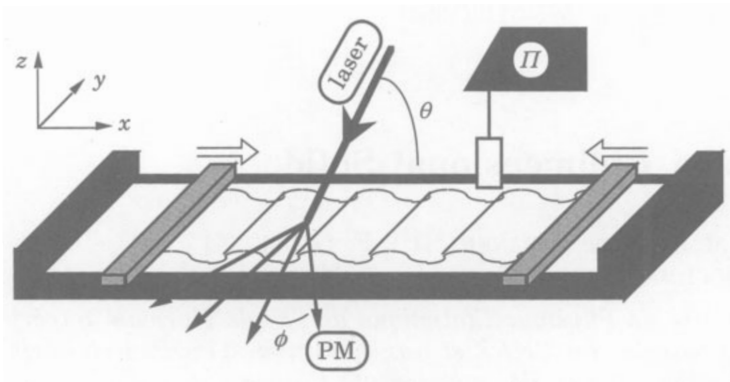

Fig. 1. – Sketch of the experimental set-up. Π = pressure measurement with a Wilhelmy balance and a piece of filter paper here spontaneously aligned with the x-axis; PM = photomultiplier to detect the laser light scattered horizontally at an angle φ.

and Kirstein, sensitivity $mN \cdot m^{-1}$), records surface isotherms. We deposit on the surface of formamide a phospholipid with two 18-carbons chains, the 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC, Avanti).

At 10 °C and finite pressure, the film is in a solid phase [3]; uniaxial compression stronger than $\Pi_c = 18\, mN \cdot m^{-1}$ along the x-axis creates a stable and permanent undulation of the surface roughly parallel to the y-axis (fig. 2; we denote z the vertical axis, y the orientation of barriers, and x their direction of compression, as defined in fig. 1). Surprisingly, it is directly visible with an intensified camera (SIT 68, Dage-MTI) and a standard $\times$ 20 or $\times$ 40 objective! Wavelength, as estimated by eye or by a Fourier transform of the digitized image, is around 6 μm. The roughly periodic deformation of the horizontal surface acts as a series of alternate convergent and divergent dioptres (shadowgraphy). Defocalising the objective of $\pm$ a few μm shows an inversion of contrast minima and maxima of light intensity: the amplitude along z is submicrometric ($\sim 10^{-7}$ m).

To measure the spectrum of the undulation, we use it as a grating to scatter a 35 mW argon laser beam. The beam, driven through a monomode optical fibre, arrives at the (y, z)-plane ($\phi = 0°$) at $\theta = 30°$ from the horizontal (x, y)-plane. We detect the signal scattered by the monolayer with a photomultiplier placed off the specular reflection, at $\theta' = 30°$ and $\phi \neq 0$ (fig. 1).

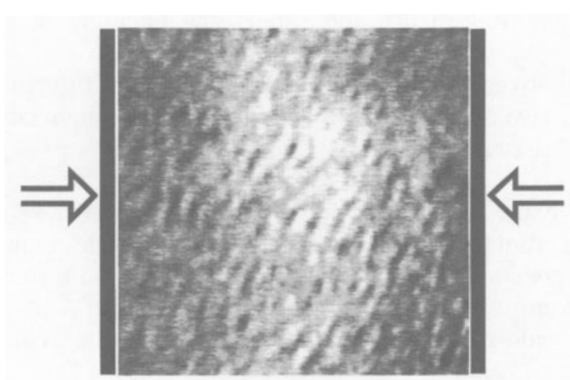

Fig. 2. – Visual observation of buckling. Field = (100×100) μm. Arrows indicate the direction of compression.

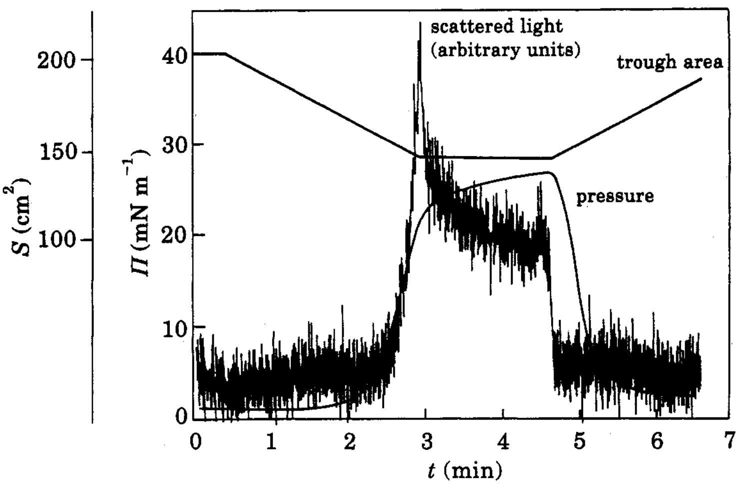

Fig. 3. – Recording of the pressure $\Pi(t)$, the scattered light intensity $I_{\rm scat}$ and the total trough surface S *vs.* time t. The lowest value of S corresponds roughly to 50 Å^2 per molecule.

At a fixed position $\phi = 15°$, we expect a scattered intensity $I_{\rm scat}$ proportional to the square of the deformation amplitude ξ^2 [6-8]. We exert slow compression steps and observe that $I_{\rm scat}$ increases during compression. When compression stops, $I_{\rm scat}$ decreases over a few tens of seconds, maybe due to rearrangement of solid domains, or even partial collapse (fig. 3). For Π less than $\Pi_{\rm c} = 18\ {\rm mN \cdot m^{-1}}$ but greater than $\Pi_{\rm c}' = 15\ {\rm mN \cdot m^{-1}}$, $I_{\rm scat}$ relaxes towards zero. For $\Pi > \Pi_{\rm c}$, $I_{\rm scat}$ reaches a plateau, which increases continuously with Π (fig. 4). On decompression, $I_{\rm scat}$ vanishes; on recompression, the apparition threshold $\Pi_{\rm c}'$ is smaller (down to $9\ {\rm mN \cdot m^{-1}}$). On very long time scales (~ 15 hours), we observe that $I_{\rm scat}$ always decreases towards zero: flux probably relaxes the stresses.

Theory. – We note that buckling lowers the energy cost needed to maintain two vertical dipoles side by side [4,5]. Thus the equation of state of the 2D film depends not only on its area A per molecule, but also on its possible extension in the third dimension. The free energy F of the film varies with the buckling amplitude ξ, introducing a term $\partial F(A, \xi)/\partial \xi$ which does not appear in eq. (7) of ref. [1]. Gravitational energy $\rho g z^2/2$ and surface tension γ stabilize the interface. Note that the bending modulus κ is negligible here (see appendix).

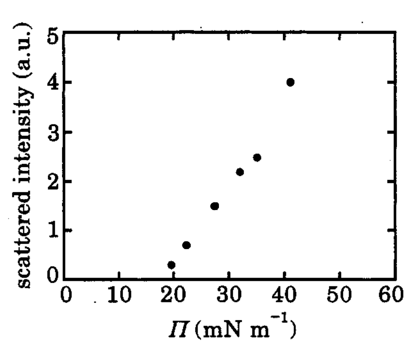

Fig. 4. – Light intensity (arbitrary units) scattered by the surface one minute after applying a uniaxial compression Π. Note that ξ_q is expected to scale like $\sqrt{I_{\rm scat}}$.

We assume here

i) polar subphase screens the interactions between xy components of dipoles, and not between z components [9]; for simplicity, we thus consider molecules which keep a fixed angle with the vertical, *i.e.* the z-component of dipoles is constant;

ii) for dipolar interactions, the sum over molecule positions can be computed as a continuous integral; the cut-off is of order $a \sim A^{1/2} \sim 7$ Å, so that $qa \ll 1$;

iii) the instability is linear and involves a single mode $z = \xi(x) = \xi_q \sin(qx)$ of small amplitude, *i.e.* $q\xi_q \ll 1$.

Then, without further assumptions, dipolar energy is fully described by a single parameter e_{dip}, namely the energy (per unit surface) of a plane horizontal monolayer of vertical dipoles [10, 11]:

$$e_{\mathrm{dip}} = \frac{2(\Delta V)^2 \varepsilon\varepsilon_0}{4\pi(\varepsilon + \varepsilon_0)} \iint_{\text{plane}} \frac{\mathrm{d}^2 r}{r^3} = \frac{\varepsilon\varepsilon_0}{\varepsilon + \varepsilon_0} \frac{(\Delta V)^2}{a}, \tag{1}$$

where the integral is dominated by the short-distance cut-off a. Here ΔV is the surface potential of the monolayer, ε_0 and ε the permittivities of air and solvent. An advantage is that the experimental value of ΔV can be used without any hypothesis on the permittivity of the intermediate phase of aliphatic chains, on A or even on the number of layers [12, 13], provided their interfaces appear flat over the dipole interaction distance.

For egg phosphocholines on water, $\Delta V = 328$ mV for $A = 50$ Å^2 [14]. If we assume the value on formamide is the same, we obtain $a \cdot e_{\mathrm{dip}} \approx 10^{-12}$ N, yielding $e_{\mathrm{dip}} = 1.34\ \mathrm{mN \cdot m^{-1}}$; it is likely a slight overestimate, since $\varepsilon = 109.5$ is higher than in water (and thus probably the fraction of molecule in the solvent is higher too), and since the cut-off a is probably greater than $\sqrt{A}$ by an unknown geometrical factor. On the other hand, Taylor and Bayes [13] note that eq. (1) needs a correction at short distance and obtain a 7% increase in the integral.

The free energy E per projected surface S of a buckled two-dimensional monolayer is then (see appendix)

$$\frac{E}{S} \approx \frac{E_0}{S} + [\rho g + (\gamma - 4.5 e_{\mathrm{dip}}) q^2 + 2a e_{\mathrm{dip}} |q|^3] \left(\frac{\xi_q}{2}\right)^2 + (21.1 e_{\mathrm{dip}} - 0.75\gamma) q^4 \left(\frac{\xi_q}{2}\right)^4. \tag{2}$$

The ξ^4-term becomes negative when $\gamma > 21.1 e_{\mathrm{dip}}/0.75 \sim 38\ \mathrm{mN \cdot m^{-1}}$, but no first-order transition is observed, since each mode sees a macroscopic energy barrier of order $\gamma S \gg k_{\mathrm{B}} T$. Buckling thus appears as a second-order transition when γ is lower than the positive threshold $\gamma_{\mathrm{c}} = 4.5 e_{\mathrm{dip}} - 3(\rho g a^2 e_{\mathrm{dip}}^2)^{1/3} \approx 4.5 e_{\mathrm{dip}}$. The most unstable mode has a finite wave vector q independent of γ, and an amplitude $\xi_q \sim (\gamma_{\mathrm{c}} - \gamma)^{1/2}$:

$$q^3 = \frac{\rho g}{a e_{\mathrm{dip}}} \quad \text{and} \quad q^2 \xi_q^2 = \frac{8}{3} \frac{\gamma_{\mathrm{c}} - \gamma}{6.25\gamma_{\mathrm{c}} - \gamma}. \tag{3}$$

Numerically, we obtain $\gamma_{\mathrm{c}} = 6\ \mathrm{mN \cdot m^{-1}}$, $q = 2.3 \cdot 10^5\ \mathrm{m^{-1}}$ and ξ_q submicrometric, with no adjustable parameter.

Discussion. – These predictions agree with experimental orders of magnitude, but deserve discussion. The predicted wavelength $\lambda = 2\pi/q$ is 4 times bigger than observed. A complete theory should take into account the presence of different solid domains with various orientations (see below). This could explain why the component q_y of the wave vector, which we neglected, is experimentally non-zero (fig. 2). Due to non-linear coupling between all unstable modes, the wave vector which is selected can be different from the linearly most unstable wave vector.

Concerning the surface tension, let us first remark that it is no longer isotropic under uniaxial constraint (stress $\sigma_{xx} < 0$ in compression [15]). Instead, in analogy with the surface stress tensor of a 3D solid [16], we define the surface stress tensor of a solid Langmuir film: $\bar{\bar{\gamma}} = \gamma_0 + \bar{\bar{\sigma}}$. If boundaries are fixed in the y-direction, there is an anisotropy of stresses in the plate [15]:

$$0 < \frac{\sigma_{yy}}{\sigma_{xx}} = \frac{\sigma_{\text{Poisson}}}{1 - \sigma_{\text{Poisson}}} < 1\,, \tag{4}$$

while $\sigma_{xy} = \sigma_{yx} = 0$; the Poisson coefficient is between 0 and 1/2 ($\sigma_{\text{Poisson}} = 1/2$ only for a fluid).

We should thus compare the theoretical and experimental thresholds:

$$|\sigma_{xx_c}^{\text{theo}}| = \gamma_0 - \gamma_c^{\text{theo}} \approx 52\ \text{mN}\cdot\text{m}^{-1}\,, \tag{5}$$

$$\Pi_c^{\text{exp}} \approx 20\ \text{mN}\cdot\text{m}^{-1}\,. \tag{6}$$

These values could be reconciled only if Π^{exp} does not measure $|\sigma_{xx}|$. In fact, the filter paper of our Wilhelmy balance is free to rotate, and we have observed that it orientates parallel to x (fig. 1): its free energy is minimum when its flat face (which feels the surface tension) is normal to the direction of the higher surface tension (lower pressure). We thus probably measure the lower pressure $\Pi^{\text{exp}} = |\sigma_{yy}|$. Compatibility between eq. (5) and (6) necessitates $\sigma_{yy}/\sigma_{xx} = 20/52$, *i.e.* $\sigma_{\text{Poisson}} = 0.3$, a reasonable value.

To look for such anisotropy, we use two Wilhelmy balances, calibrated together. The first one has a freely rotating paper (Π_1 measured mainly along y), the second has a paper fixed parallel to y (Π_2 measured mainly along x). In fluid phases (liquid and mesophase), we detect no buckling and no anisotropy ($\Pi_1/\Pi_2 = 1$). On the opposite, under the solidification temperature of 20 °C [3], we detect anisotropy ($\Pi_1/\Pi_2 \neq 1$) at all finite pressures, and buckling above the threshold.

However, while Π_1/Π_2 is constant within one compression, it is not reproducible from one experiment to another. During the first compression, we find Π_1/Π_2 between 1/3 and 3; during successive compression-decompression cycles, Π_1/Π_2 gets closer to 1. Fluorescence microscopy observations provide a possible explanation. At deposition, a monolayer is on the coexistence between gas and solid, at low pressure. On first compression, solid domains coalesce and at high pressure form a single plate. On decompression, at low pressure the solid phase breaks into large plates, greater than the vision field (600 μm at magnification × 20). Compression-decompression cycles show a progressive decrease in the size of solid domains, which form smaller and smaller grains, down to ≈ 100 μm. Thus the solid progressively turns into a bidimensional granular material, where macroscopic shear vanishes.

Failing to check whether $\Pi^{\text{exp}} = |\sigma_{yy}|$, we can at least turn to an indirect argument. Our teflon-coated trough has two barriers along x; on the y-direction the formamide level is higher than the trough sides by ~ 0.5 mm, *i.e.* less than the capillary length $\lambda \approx \sqrt{\gamma_0/\rho g} = 2.3$ mm. We thus expect that this positive meniscus should become unstable when γ_{yy} becomes less than about 2 mN·m^{-1}, *i.e.* $|\sigma_{yy}| > \approx 56$ mN·m^{-1}. In fact, we systematically see the formamide overflowing towards y when Π^{exp} approaches 58 mN·m^{-1}.

Conclusion. – i) We observe the buckling of a Langmuir film without collapsing, since formamide anchors well the polar heads of amphiphilic molecules and has a lower surface tension than water. At the threshold, the surface tension is strictly positive, the wavelength is of order 6 μm, and the amplitude is continuous. Above the threshold, the buckled state is stable, and the amplitude is submicrometric.

ii) We show that the dipolar interactions between molecules make a solid film buckle under uniaxial compression. Gravity and surface tension stabilize the film and determine the finite wave vector q. The amplitude is submicrometric, scaling like $\sqrt{(\Pi - \Pi_c)/\Pi_c}$ over a few $\mathrm{mN \cdot m^{-1}}$.

iii) Current experiments are aimed at measuring the spectrum of the deformation ξ, and the Poisson coefficient $\sigma_{\mathrm{Poisson}}$, to compare them with the theoretical predictions.

Additional Remark.

Since we first submitted this paper, we observed unambiguously by X-ray diffraction experiments [18] that the solid phase is crystalline, with a distorded triangular chain lattice. We also measure a chain tilt of about 35°. When pressure is increased from 1 to 40 $\mathrm{mN \cdot m^{-1}}$, the area per molecule decreases from 46.2 Å^2 to 45.7 Å^2, but the structure undergoes no phase transition which may interfere with the buckling instability. We also verify that the buckling instability does not occur for DSPC spread on pure water. We detect no specific signals either by shadowgraphy or by light diffusion.

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Appendix

If the film undergoes a slight deformation $z = \xi(x, y) = \xi_q \sin(qx)$, its dipolar energy per unit of projected surface decreases and becomes

$$\frac{E_{\mathrm{dip}}}{S} = \frac{a e_{\mathrm{dip}}}{2\pi} \int\int \mathrm{d}^2 r \frac{(1 - 3\sin^2\theta)}{[r^2 + \xi^2]^{3/2}}, \tag{A.1}$$

where $\mathrm{tg}\,\theta = \xi/r$. A development in ξ yields

$$\frac{E_{\mathrm{dip}}}{S} = \frac{a e_{\mathrm{dip}}}{2\pi} \int\int \mathrm{d}^2 r \left[r^{-3} - \frac{9}{2} r^{-5} \xi^2 + \frac{75}{8} r^{-7} \xi^4 + O(\xi^6) \right]. \tag{A.2}$$

Integration is on the whole plane, except for the small disk $r < a$. The exact development in the small parameters qa and $q\xi$ is

$$\frac{E_{\mathrm{dip}}}{S} = e_{\mathrm{dip}} \left[1 + \left(-\frac{9}{8} q^2 + \frac{1}{2} |q|^3 a \right) \xi_q^2 + \frac{675}{512} q^4 \xi_q^4 \right], \tag{A.3}$$

with higher-order terms in $q^4 a^2 \xi_q^2$, $q^5 a \xi_q^4$, $q^6 \xi_q^6$, which we neglect since $aq < 10^{-4}$. If, instead of hypothesis iii), molecules were to keep a constant angle with the normal of the buckled monolayer, only numerical factors would change. If we take a film with a bending modulus $\kappa \approx 10^{-21}$–10^{-20} J, *e.g.* 20 kT as measured on egg phosphocholine vesicules [17], we can also neglect $\kappa q / a e_{\mathrm{dip}} < 10^{-2}$.

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