

## Buckling of Polymerized Monomolecular Films

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The buckling of a two-dimensional polymer network at the air-water interface has been evidenced by grazing incidence x-ray scattering. A comprehensive description of the inhomogeneous octadecyltrichlorosilane polymerized film was obtained by atomic force microscopy and x-ray scattering measurements. The buckling occurs with a characteristic wavelength  $\simeq 10 \mu\text{m}$ .

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The statistical mechanics of two-dimensional polymer networks has recently attracted considerable attention [1]. The distinctive property of noncrumpled, free polymeric films is the lack of intrinsic tension [2]. Their fluctuations are therefore dominated by bending rigidity. The differences in the elastic properties of tethered and fluid films are dramatically revealed by the theoretical finding of a low temperature "flat phase" of tethered membranes. This phase exhibits a long range order of membrane normals caused by the divergence of the bending modulus  $K$  at large scales due to coupling with in-plane phonons. Under constrained boundary conditions, an additional buckling transition is expected [3]. Buckling is not restricted to films possessing in-plane elasticity, and was also predicted for fluid films [4]. For monolayers at the air-water interface, buckling can only occur for a slightly negative surface tension, i.e., for a surface pressure  $\Pi \geq \gamma_{\text{H}_2\text{O}}$  ( $\Pi = \gamma_{\text{H}_2\text{O}} - \gamma$ , where  $\gamma_{\text{H}_2\text{O}}$  and  $\gamma$  are the surface tensions of pure water and of the monolayer). The system is then governed by bending rigidity. However, buckling was never observed in fluid monolayers, probably because they collapse through the growth of bulk multilayered domains before attaining the high pressure required for buckling [5]. Since the growth of such domains must be impeded in polymerized monolay-

ers, which moreover possess no intrinsic tension, buckling should be observable in this case.

Until recently, monolayers of insoluble amphiphiles adsorbed at the air-water interface have been mainly studied through isotherm  $\Pi(A_0)$  measurements using the film balance technique [6], i.e., by recording the surface pressure, as a function of the projected area  $A_0$ . In principle  $A_0$  is different from the actual surface  $A$  of the fluctuating film. Beyond the in-plane structure of the two-dimensional interface [7], the morphology and the fluctuations of the surface into the third dimension are just beginning to be studied in greater detail, in particular owing to the development of grazing incidence x-ray scattering methods [8-11]. Surface scattering of x rays [10,11] allows the study of in-plane modes ranging from tens of nm to  $\sim 10 \mu\text{m}$ , the limitations being only due to the brilliance of the currently available sources and to the angular resolution [8]. The intensity scattered by interfaces located at  $z_i(x, y)$ , limiting layers of indices  $n_{i-1}$  and  $n_i$ , results from correlated height fluctuations within an interface or between different conformal interfaces. Using a linear fine focus x-ray source (along the  $y$  axis normal to the plane of incidence), only the  $q_x$  longitudinal in-plane dependence of the scattered intensity can be measured:

$$\Sigma_{ij}(q_x) = \frac{\Delta q_x}{\sqrt{2\pi}} e^{-\frac{1}{2}[q_{iz}^2(z_i^2) + q_{jz}^2(z_j^2)]} \int dx (e^{iq_{iz}z_i(z_i(0)z_j(x))} - 1) e^{iq_x x} e^{-\frac{1}{2}\Delta q_x^2 x^2}, \quad (1)$$

where  $q_{iz}$  is the  $z$  (vertical) component of the wave-vector transfer in medium  $i$ , assuming a Gaussian resolution function of half width at half maximum  $\sqrt{2 \ln 2} \Delta q_x$ . The  $q_z$  normal dependence, which results from interferences between beams scattered at different interfaces, is similar to that of the reflected intensity which follows the Fresnel laws of optics [12], except that the contrast of the interference pattern is modulated by  $\Sigma_{ij}$  (1). In the limit of small  $q_z$  wave-vector transfer Eq. (1) reduces to the Fourier transform of the correlation function, i.e., the spectrum of surface modes, convoluted with the resolution function. For liquids, due to the logarithmic divergence of the height-height correlation functions

[13], the existence of a true specular component arises only due to finite size effects [14], and  $\Sigma_{ij}$  is strongly peaked at  $q_x = 0$ . An important consequence is that the ratio of diffusely scattered to reflected intensity in the specular  $q_x = 0$  direction becomes larger than 1 when  $e^{\frac{1}{2}[q_{iz}^2(z_i^2) + q_{jz}^2(z_j^2)]} \Sigma_{ij}(q_x = 0) > 1$ . The so-called reflectivity technique, which consists in measuring the reflection coefficient of an interface as a function of the wave-vector transfer  $q_z$ , can therefore only be safely applied when diffuse scattering is carefully taken into account [11].

Among an increasing number of systems capable of two-dimensional polymerization, it has been demon-

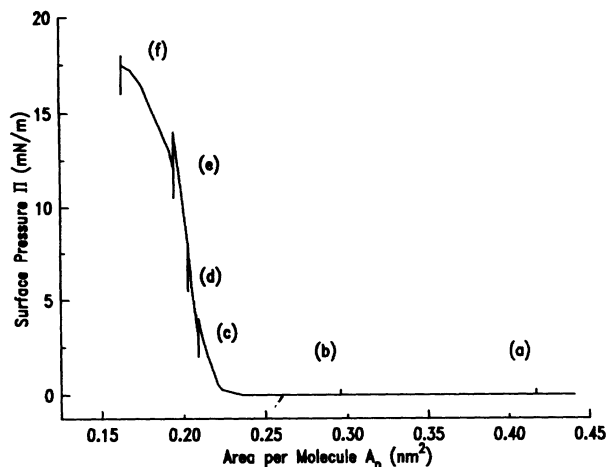


FIG. 1. Isotherm of the  $C_{18}H_{37}SiCl_3$  chlorosilane at  $T = 20^\circ C$ . The surface pressure relaxes as soon as the compression is stopped [points (c)–(f)].

strated that chlorosilane molecules ( $C_nH_{2n+1}SiCl_3$ ) may build large connected domains at the water surface [15,16]. A strong evidence for this is that, in contrast to, e.g., fatty acids in the solid phase, talcum deposited onto the monolayer surface remains perfectly motionless under a stream of air [16]. The polymerization reaction proceeds by hydrolysis of the Si–Cl bonds and further elimination of a water molecule to build a Si–O–Si–backbone [17]. The ordering of the aliphatic tails has been demonstrated by grazing incidence synchrotron x-ray diffraction [16]. However, the exact two-dimensional structure remains unknown. In the present experiments,  $100 \mu l$  of a  $1 \text{ gl}^{-1}$  chloroform solution of  $C_{18}H_{37} - SiCl_3$  silane purchased from ABCR, Karlsruhe, were deposited on the surface of fresh water from a Millipore MilliQ system acidified to  $pH = 2$  (HCl). The surface pressure was measured using either a Langmuir or a Wilhelmy balance, and the experiments were carried out at  $T = 20 \pm 1^\circ C$ . After deposition, the film was slowly compressed ( $< 10^{-2} \text{ nm}^2/\text{min molecule}$ ), and the isotherm  $\Pi(A_0)$  was recorded (Fig. 1). A Langmuir trough could be inserted in the diffractometer described in Ref. [18] for x-ray measurements. Using the  $Cu K\alpha_1$  radiation ( $\lambda = 0.154 \text{ nm}$ ) and a Si(111) monochromator, our in-plane resolution coherence length  $2\pi/\Delta q_x \simeq 4\pi/q_z\Delta\theta \simeq 50 \mu m$  for  $q_z = 0.5 \text{ nm}^{-1}$ .

Fluorescence microscopy experiments (using NBD stearic acid as probe) showed that the layer in the flat  $\Pi \simeq 0$  region of the isotherm is inhomogeneous, with large ( $\sim 1 \text{ mm}$ ) polymerized domains in coexistence with a gas phase, reminiscent of the gas to liquid-condensed phase transition of conventional amphiphiles. The pressure rises when these domains come into contact. At higher magnification, the domains appear to be composed of smaller subdomains which are best observed by atomic force microscopy (AFM) on films deposited onto

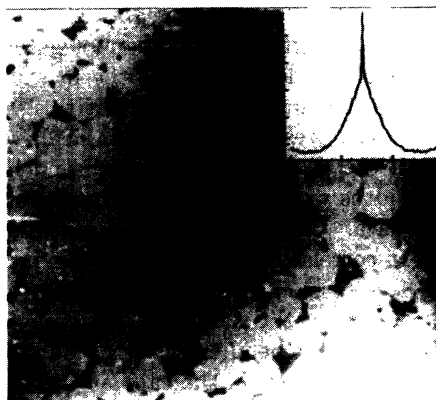


FIG. 2. AFM image of the polymerized silane monolayer deposited on a silicon wafer. The image size is  $80 \mu m \times 80 \mu m$ . Inset: corresponding height-height correlation function; 1 graduation =  $4 \mu m$ .

silicon wafer substrates (Fig. 2). AFM experiments were performed with a Nanoscope II microscope from Digital Instruments operated in the constant force mode [19]. Large scans ( $100 \mu m \times 100 \mu m$ ) were performed, and the forces used in these experiments were typically  $10^{-8} \text{ N}$ . The film is composed of small round-shaped polymerized domains, approximately  $\sim 7 \mu m$  in diameter welded together. The size of these small domains as well as the mechanical properties of the film critically depends on the silane sample purity and all the results presented in this Letter were obtained with freshly distilled silane maintained under a dry nitrogen atmosphere.

The normal structure of the film can be obtained from  $q_z$  reflectivity measurements (Fig. 3). As mentioned above, reflectivity measurements require a careful interpretation in terms of surface scattering. More precisely, the reflectivity curve is determined by both the

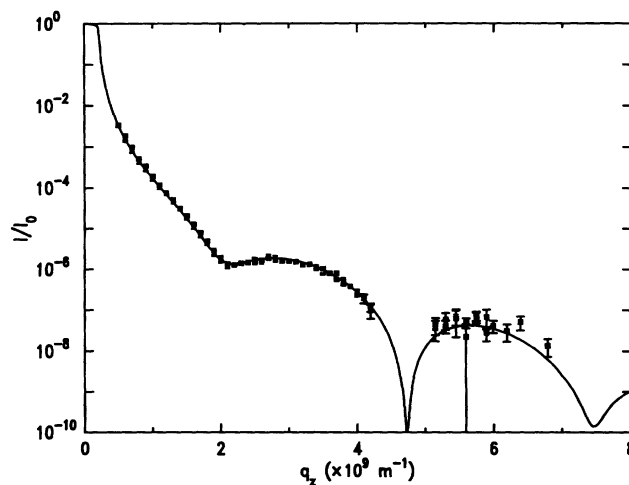


FIG. 3. X-ray reflectivity curve of  $C_{18}H_{37}SiCl_3$  at  $\Pi = 5 \text{ mN/m}$ .

film structure and the actual height-height correlation function [11]. In particular, one cannot assume a simple "Debye-Waller" dependence of the measured intensity to include the interface width. If this were to be attempted in the present case, nonphysical, very different values of the air-chain, chain head, and head-water interfacial widths would have been inferred from the experimental data. On the contrary, a realistic model of height-height correlation functions, taking into account gravity, surface tension, and bending rigidity, gives a remarkable account of the data with only one adjustable elastic parameter, the bending rigidity modulus  $K$  which plays the role of a cutoff in the capillary wave spectrum [13]. Using the method of Ref. [11] with the model correlation function [13] and two optically different layers for the description of the film (one for the chains, and one for the heads), one can obtain a very accurate description of the polymerized monolayer. The electron densities of the chains and the heads are found to be, respectively,  $\rho_c = (0.96 \pm 0.03) \times \rho_{\text{H}_2\text{O}}$  and  $\rho_h = (1.7 \pm 0.25) \times \rho_{\text{H}_2\text{O}}$ . The headgroup and chain layers are  $0.24 \pm 0.06$  nm and  $2.15 \pm 0.1$  nm thick, 0.24 nm being the covalent diameter of a Si atom and 2.3 nm the length of completely extended  $\text{C}_{18}\text{H}_{37}$  chains. Finally, the fit ( $\chi^2 = 1.6$ ) was obtained with  $\gamma = 68$  mN/m (the measured value), and  $K = 30k_B T$  ( $5k_B T < K < 100k_B T$ ). An additional, intrinsic roughness of the chain-air interface (0.15 nm) was included in the model [20]. It should be noted that the experimental curve for the  $\text{C}_{22}\text{H}_{43}\text{SiCl}_3$  chlorosilane could be fitted with identical parameters, except a greater chain length.

The intensity scattered in the incidence plane ( $x, z$ ) is presented in Fig. 4 as a function of the longitudinal wave-vector transfer  $q_x$  at  $q_z = 0.5 \text{ nm}^{-1}$  for different stages of the compression. The central peak at  $q_x = 0$  corresponds to the specular condition and the peaks at  $q_x = \pm 1.73 \times 10^6 \text{ m}^{-1}$ , the so-called Yoneda wings, correspond to critical scattering for which the incident and scattered fields are in phase at the surface. Most interesting is the peak at  $q_x \simeq \pm 5 \times 10^5 \text{ m}^{-1}$ . Its sharpness, comparable to that of the specular peak reveals a well defined wavelength in the system ( $\lambda_b = 2\pi/q_b = 10 \mu\text{m}$ ). This strong scattering can be attributed either to height fluctuations or to density inhomogeneities within the film corresponding to the size of polymerized domains in coexistence with a gas phase. In order to check this crucial point, domain-domain correlation functions were calculated from a great number of large scale ( $100 \mu\text{m} \times 100 \mu\text{m}$ ) atomic force microscopy images, comprising more than 100 domains. The subdomains appear to be quite polydisperse (their size ranging from 4 to 9  $\mu\text{m}$ ), and the correlation function decreases rapidly, no diffuse ring being obtained by Fourier analysis of the images. This implies that the scattering is not due to density inhomogeneities within the film but to its buckling into the third dimension. Further evidence is provided by the fact that the scattering intensity increases by ap-

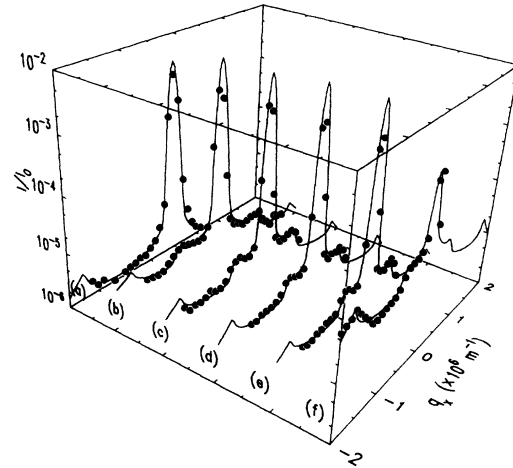


FIG. 4. Intensity scattered by the film at points (a)–(f) as a function of the longitudinal in-plane wave-vector transfer  $q_x$  and best fits for the polymerized film of Figs. 1 and 2 on water.  $q_z = 0.5 \text{ nm}^{-1}$ .

proximately 1 order of magnitude under a small compression [ $\simeq 10\%$  between (e) and (f) in Fig. 4] which is clearly inconsistent with a scattering due to inhomogeneities within the film. In this case, the structure factor, and thus the intensity, should be maximum when the total area of polymerized domains is half the total area [(a) in Fig. 4], and then decreases upon compression. A very simple model for the buckled surface profile  $z(x, y) = h_0 \sin(2\pi/\lambda_b [x \sin \theta + y \cos \theta] + \phi)$ , yielding a height-height correlation function  $\langle z(0)z(x, y) \rangle = h_0^2 \cos(2\pi/\lambda_b [x \sin \theta + y \cos \theta])$  can account for the experimental data. Using this correlation function in Eq. (1) in addition to the capillary wave correlation function [13], and averaging over  $\theta$ , one obtains a very good fit to the scattered intensity. Values for the wave amplitude  $h_0$  range between 0.25 nm [(c) in Fig. 4] and 2 nm (f). Of course such values are only indicative of the overall degree of buckling, and a more realistic model should involve the size and the density of buckled regions. It should nevertheless be noticed that such amplitudes only yield small differences ( $\simeq 10^{-3}$ ) between the real area  $A$  and the projected area  $A_0$ , and that the instability gives ultimately rise to the collapse of the monolayer [in particular in case (f)], with collapsed lines  $\approx 10 \mu\text{m}$  from each other.

A theoretical study of the buckling of monomolecular films has been recently performed by Milner, Joanny, and Pincus [4]. Though qualitative differences are expected in the behavior of liquid and polymerized films due to in-plane elasticity, the main lines of their argument should apply in a more general case. Buckling can only occur with a vanishing surface tension (in fact a slightly negative one because the monolayer is stabilized by the bending energy). The interface is therefore only submitted to curvature stiffness and gravity. The wavelength  $\lambda_b$  of the instability is the only length available in the system, obtained by balancing the gravity and curva-

ture energies [4],  $2\pi/\lambda_b = q_b = (\Delta\rho g/K)^{1/4}$  where  $K$  is the bending rigidity modulus. Using this equation, one can estimate the overall bending rigidity of the film to be  $K = (15 \pm 5) \times k_B T$ , consistent with reflectivity measurements. This value is slightly smaller than estimations for conventional amphiphilic materials of comparable chain length [21]. However, the wavelength  $\lambda_b$  is comparable to the size of the subdomains. This suggests the need of an alternative description taking better account of the film inhomogeneity. Since the buckling instability is expected to occur at zero tension, the question arises as to the meaning of the measured surface tension. There is no energy associated to the area of polymerized domains which is constant. However, at thermodynamic equilibrium, the polymerized domains are submitted to a tension  $\gamma \simeq \gamma_{H_2O}$  exerted at their edges by the dilute phase in coexistence with them; this is the measured surface tension. Upon compression, this tension vanishes along certain directions when the domains get connected, hence the possibility of buckling. It should be noted that, accordingly, the layer does not withstand high pressures: the pressure relaxes as soon as the compression is stopped (Fig. 1), and the maximum surface pressure that can be attained is no more than 15 mN/m, much less than  $\simeq 50$  mN/m for fatty acids of comparable chain length. If the compression goes on, the monolayer collapses, with the characteristic wavelength  $\lambda_b$ . However, the addition of  $\simeq 5\%$  stearic acid, which decreases the degree of polymerization of the film, is sufficient to give a much better stability to the layer, and to prevent buckling.

Evidence for the buckling of a two-dimensional polymer film into the third dimension is reported in this Letter from combined x-ray surface scattering and AFM measurements. Further investigation into the buckling mechanism should pay much attention to the inhomogeneous structure of the film. In any case, a characteristic property of two-dimensional polymer networks has been evidenced, which opens the way to future investigations of the statistical properties of these fascinating systems.

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- $$\Sigma_{ij}(q_x = 0, q_z) = \pi^{-1/2} \Gamma \left[ \frac{1}{2} - \frac{k_B T q_z^2}{4\pi\gamma}, \frac{1}{2} \Delta q_x^2 \frac{K}{\gamma} \right] \times \exp - \left[ \frac{q_z^2 k_B T}{2\pi\gamma} \ln \left( \frac{e^{\gamma_E} \sqrt{\gamma/K}}{\sqrt{2} \Delta q_x} \right) \right],$$
- where  $\Gamma$  is the incomplete  $\Gamma$  function, and  $\gamma_E$  Euler's constant (see also [11,21]).
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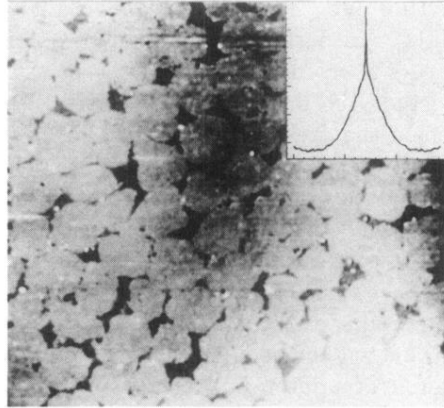


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