# Buckling Instability in Monolayer Network Structures

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A buckling instability has been discovered in monolayer network structures. The instability, which can be seen by fluorescence microscopy, occurs when a network formed in the gas-liquid-expanded (LE) two-phase region is heated. It is interpreted as an Euler instability that arises because of constraints on the monolayer imposed by the network and by the interactions between domains of the LE phase. An analysis in terms of a Langevin equation with a Ginzburg-Landau free energy shows how the instability is related to the equilibrium and transport properties of the monolayer.

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Amphiphilic molecules such as long-chain fatty acids and phospholipids form insoluble monolayers at the air/water interface.[1] The phase diagrams of these systems exhibit coexistence regions between 2D condensed phases and a 2D gaseous (G) phase. The equilibrium between the gas and liquid-expanded (LE) phases of pentadecanoic acid has been investigated by detailed isotherm studies[2-4] and recently by fluorescence microscopy.[5] Although there has been some controversy about the shape of the coexistence curve and the location of the G-LE critical point,[5,6] there is no doubt about the character of the phases and the first-order nature of the transition.

The technique of fluorescence microscopy enables direct imaging of the morphology of monolayer domains. When such studies were performed on monolayers of stearic acid,[7] it was discovered that monolayers prepared in a two-phase region could have the form of a 2D random network structure that has the appearance of a soap foam. We have observed[8,9] such structures for monolayers of many other amphiphiles: lauric, myristic, and pentadecanoic acids and six different long-chain ethyl and methyl esters. A quantitative study of the evolution of 2D foams in monolayers of pentadecanoic acid has recently been reported.[10]

An example of such a network structure in a monolayer of ethyl heptadecanoate is shown in Fig. 1(a). The foam consists of cells in which the white LE phase, made visible by the probe nitrobenzoxadiazole-hexadecylamine, surrounds dark regions of the gaseous phase. The cell sides, which are typically 3 $\mu$m wide and 25–100 $\mu$m long, meet at threefold vertices. After the foam has been prepared by an expansion of the LE phase, at constant temperature the average cell area grows with time (primarily by so-called T1 and T2 processes[10]) but the network structure is maintained.

While studying the effect of temperature changes on the monolayer network structure, we have discovered a buckling instability in the cell sides. In this Letter we will describe the nature of the instability and propose a mechanism for it. As we shall demonstrate, the appearance of the instability provides information about the monolayer phase diagram and the nature of the LE phase.

The instability has been observed in fatty acid and ester monolayers. It is more easily studied in the esters, for which the phenomenon occurs at lower temperatures; we will focus on ethyl heptadecanoate, the system that we have studied in the most detail. The monolayers were prepared at 18 °C by depositing a chloroform solution of the amphiphile onto a subphase of Milli-*Q* purified water buffered to *p*H 7. The experiments were performed at constant areas, chosen to be in the G-LE coexistence region. Network structures are conveniently produced[10] by the addition of a small amount of chloroform to the surface, which rapidly compresses the monolayer. A rapid expansion then follows as the chloroform evaporates. The network shown in Fig. 1(a) was produced in this fashion at an area of 133 $\text{Å}^2\text{molecule}^{-1}$.

After a wait of 10–15 min to achieve temperature stability, the monolayer was heated at a constant rate. At the start the cell sides thicken slightly, but then, quite sharply, they begin to buckle with a roughly regular wavelength, Fig. 1(b). As the heating continues, the vertices of the network remain essentially fixed at their initial locations and the amplitude of the buckling increases, Fig. 1(c). The contrast between the LE and G regions diminishes as the sides pack together and fill the image, Fig. 1(d), which gradually becomes uniformly bright, i.e., all LE phase.

The buckling phenomenon has been observed in ethyl heptadecanoate at areas between 90 and 230 $\text{Å}^2\text{molecule}^{-1}$ and for heating rates varying from 0.2 to $1.0\,°\text{C}\,\text{min}^{-1}$; it does not appear at a rate of $0.1\,°\text{C}\,\text{min}^{-1}$. Buckling is not observed at higher areas. If the heating is stopped and the temperature held constant in the early stages of the buckling, the normal structure is

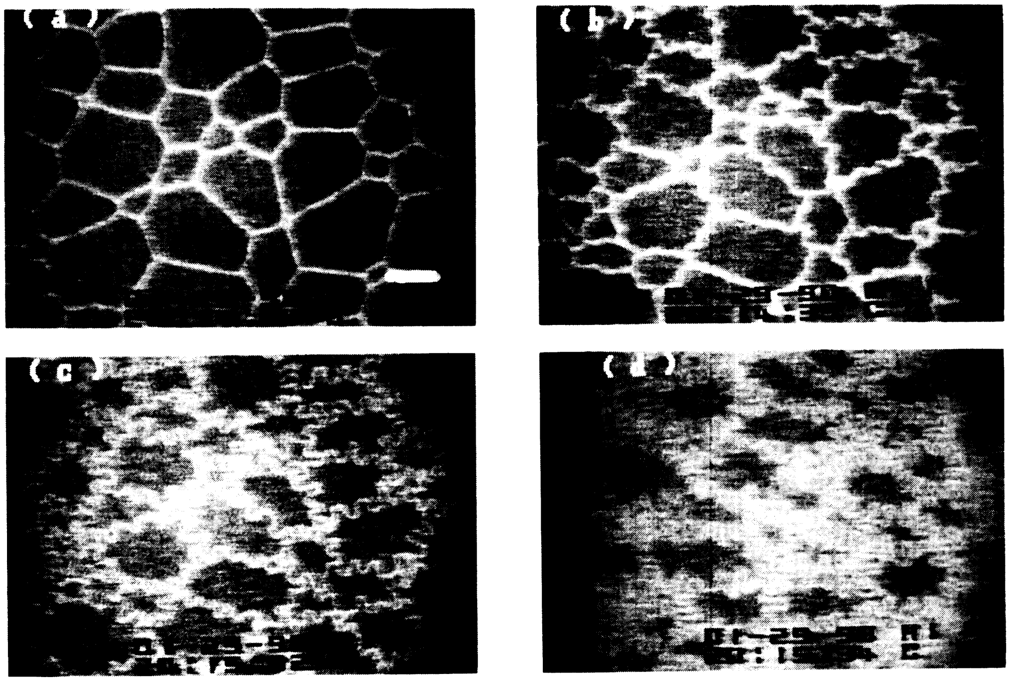

FIG. 1. Development of the buckling instability in an ethyl heptadecanoate monolayer. The monolayer was prepared at an area of 133 Å$^2$molecule$^{-1}$ at 18 °C, and then heated at constant area at a rate of 0.5 °C min$^{-1}$. The instability occurred at 19.0 °C (a); the temperature in (d) was 19.8 °C. The bar in (a) represents 100 $\mu$m.

regained, but if the amplitude is large, the buckled structure persists for long times.

We believe that the buckling instability appears because of four conditions that apply to the monolayer: (1) The monolayer density is greater than the critical density; (2) the width of the cell sides can change little with temperature; (3) the network structure pins the vertices thus fixing the topology; and (4) there are dipole-dipole repulsions between the cell sides.

If these conditions hold, then the instability can arise as follows. Since the density of the monolayer is greater than the critical density, the area of the LE phase must increase with increasing temperature as a result of condensation of the G phase. If the width of the sides is fixed, the increase in area can occur only as a change in the length of the cell sides, but if the vertices are pinned by the network structure, the sides can lengthen only if they buckle. (Note that foams can be observed in the monolayers even when on average the gap is a minority phase; the monolayer is then heterogeneous, with the foam constituting only a part of the monolayer.)

The G-LE coexistence curve of ethyl heptadecanoate has not been determined, but it is clear from the transition to the LE phase upon heating that the density is greater than the critical value for experiments in which the instability occurs. We have made a preliminary lever-rule analysis of the fluorescence images[5] in an attempt to determine the molecular areas of the coexisting phases. At 20 °C we find $A_{\mathrm{LE}}=81 \pm 8$ Å$^2$molecule$^{-1}$ for the area of the LE phase, which is consistent with the isotherm measurement by Harkins and Boyd,[11] but the uncertainties in the data are too large to allow us to determine the corresponding area for the gaseous phase. We are therefore unable to compute the diameter, which would be a reasonable approximation to the critical density. The observation that the instability disappears at large areas is consistent with our interpretation. For these areas we are unable to determine the phase boundary on heating because the contrast between the phases is lost before any transition to a one-phase region can be observed, in all probability because of proximity to the critical density.

Amphiphilic molecules are necessarily dipolar, and in monolayers the pinning of the head group at the water surface forces some degree of dipolar alignment when the molecules are in condensed phases.[1,5] Recent theories of monolayer phase morphology[12,13] have shown that structures observed arise from a balance between dipolar repulsions and line tension. There is a tendency for the condensed phases to form extended linear structures because these minimize the energy of the dipoles within the phase. The width of such lamellae is controlled only by the quantity $\exp(\sigma/\Delta\mu^2)$, where $\Delta\mu$ is the difference in dipole-moment surface density between the phases and $\sigma$ is the line tension.

We believe that the buckling can be seen as analogous to an Euler instability of a beam that is compressed axially in an elastic medium.[14] Such instabilities are also observed in cellular solids subjected to compression.[15] The stability can be determined by examining the solutions to the equation

$$EI(d^4X/dy^4)+|T|d^2X/dy^2+\alpha X=0\,, \tag{1}$$

where $I$ is the moment of inertia of the beam and $E$ is its Young's modulus, $T$ is the compressive force, which is along the $y$ axis, and $\alpha$ is the elastic modulus of the medium in which the beam is immersed. If the compressive force exceeds a critical value, $T_{\text{cr}}=2(\alpha EI)^{1/2}$, the beam will buckle with a wavelength given by

$$\lambda=2\pi(EI/\alpha)^{1/4}\,. \tag{2}$$

In the absence of the elastic medium, the wavelength is always twice the length of the beam. In the monolayer, the dipolar repulsion between the cell sides plays the role of the elastic medium.

As a first approximation, we can compute the properties of the effective elastic medium by considering the force between the cell sides to be that for an infinite number of parallel rows of dipoles with an inter-row separation distance $h$. In that case the force per unit length of the cell side is given by $F=C/3h^3$, so the effective $\alpha$ for the medium is $\alpha=C/h^4$. For our simple model, an array of parallel lines of dipoles, one finds $C=\alpha h^4=4.134\Delta\mu^2w^2\varepsilon_0/\varepsilon(\varepsilon+\varepsilon_0)$. In this expression $\varepsilon_0$ is the dielectric constant of air and $\varepsilon$ that of the subphase near the interface; $w$ is the width of the line. Substitution into Eq. (2) then gives

$$\lambda=2\pi(EI/C)^{1/4}h\,. \tag{3}$$

We therefore expect the buckling wavelength to increase linearly with the size of the cells. In Fig. 2 the wavelength at the onset of the buckling is plotted against the average cell diameter $D$, which is proportional to $h$ for a regular hexagonal array; the linear relationship predicted by the simple theory is observed.

The origins of the instability can also be explained in terms more appropriate to a monolayer by employing a time-dependent Ginzburg-Landau equation. The free energy can be written[16,17] as the sum of three terms: a "$\phi^4$" bulk free energy, a square-gradient term, and a nonlocal dipolar interaction. One then arrives at a linearized equation for the time evolution of the Fourier components of the local density $\rho(k,t)$:

$$\partial^2\rho/\partial t^2+[(\eta+\zeta)/\rho_0]k^2\partial\rho/\partial t+Bk^2\rho=0\,, \tag{4}$$

which is equivalent to expressions obtained by Brochard, Joanny, and Andelman.[18] In this equation, $\eta$ and $\zeta$ are the two-dimensional shear and bulk viscosities and $\rho_0$ is the mean density of the monolayer. An instability equivalent to the Euler instability arises when the coefficient $B$ becomes negative. There are three contributions to $B$,

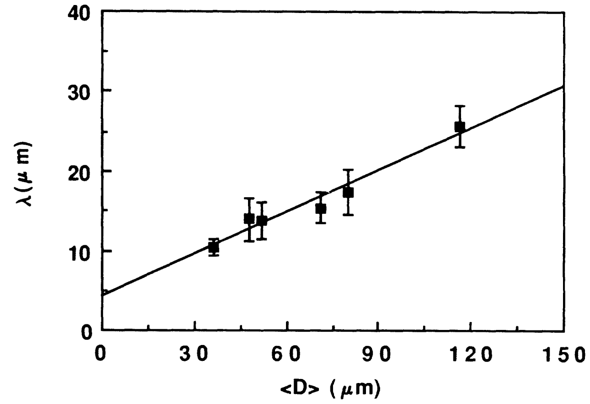

FIG. 2. Wavelength of the instability λ in μm as a function of the average cell diameter ⟨$D$⟩ in μm for an experiment carried out at an area of 120 Å$^2$molecule$^{-1}$. Each point represents an average of 16-30 cells. The wavelength was determined by measuring the distance between two vertices and counting the number of oscillations between them.

$$B=\Pi(T,\Delta\Phi)+\rho_0\kappa k^2-\rho_0b^3k_BT|k|\,, \tag{5}$$

which can be identified with the coefficients in the Euler equation by writing Eq. (1) in Fourier space and then equating terms of equal order in $k$. In this way we find that $\Pi$, the local contribution to the pressure augmented by the intracell dipolar contribution to the free energy, is equivalent to $T$, the compressive force. The product $EI$ is equivalent to the square-gradient contribution to the free energy, $\rho_0^2\kappa l$, where $l$ is the length of a cell side. In the van der Waals approximation the coefficient $\kappa$ can be expressed in terms of the line tension, the correlation length $\xi$, and the density difference between the phases $\Delta\rho$: $\kappa=\sigma\xi/\Delta\rho^2$. The third term in (5) can be seen as made up of two contributions: one arising from the dipolar interactions within a given cell side and another arising from the interactions of this cell side with all other sides; it is the latter that is equivalent to $\alpha$.

In order to calculate λ from (3) and the relations between $EI$, $\rho_0$, and $\kappa$, we need values for $\sigma$ and $\xi$, neither of which are as of yet known. We can, however, make rough estimates of these quantities. A value for $\sigma$ can be obtained from the relation $\sigma=(\Delta\mu^2/\varepsilon)[\ln(w/A_{\text{LE}}^{1/2})-0.577]$ derived by Keller, McConnell, and Moy,[19] where $w$ is the equilibrium strip width. The surface-potential measurements of Alexander and Schulman[20] give a value of $\mu\varepsilon_0/\varepsilon$ of 0.5 D, where $\mu$ is the dipole moment of an ethyl ester molecule in the LE phase. For $w=3$ μm, we find $\sigma\varepsilon_0/\varepsilon=3.4\times10^{-12}$ J m$^{-1}$. (Helm,[21] using another procedure, found $\sigma=1.4\times10^{-12}$ J m$^{-1}$ for the LE-liquid-condensed line tension in a phospholipid.) The area fraction of the LE phase for the pattern in Fig. 1(a) is 0.13; if we take $A_G=2000$ Å$^2$molecule$^{-1}$, a lever-rule calculation gives $\rho_0 = 0.0020$ molecule Å$^{-2}$. For $l = 25$ $\mu$m and $\xi = 100$ Å for the width of the LE-G interface, we obtain $\lambda = 1.4h$ for $\varepsilon = \varepsilon_0$ and $\lambda = 4.3h$ for $\varepsilon = 78\varepsilon_0$, values that are within an order of magnitude of the observed value. Given the many approximations and estimates, better agreement would be fortuitous.

The appearance of the buckling instability is a graphic demonstration of the important role that dipolar interactions play in determining the morphology of monolayer phases. Buckled structures have been observed as well in magnetic-bubble materials[17,22] in which there are long-range repulsive interactions. Such systems also exhibit labyrinthlike structures; we have seen similar morphologies in monolayers, but only as transient phenomena. While there are strong similarities between the magnet and monolayer systems, one should note that they differ in an important way: The order parameter is not conserved in magnets but is conserved in monolayers. The kinetics of the transitions may therefore be quite different.

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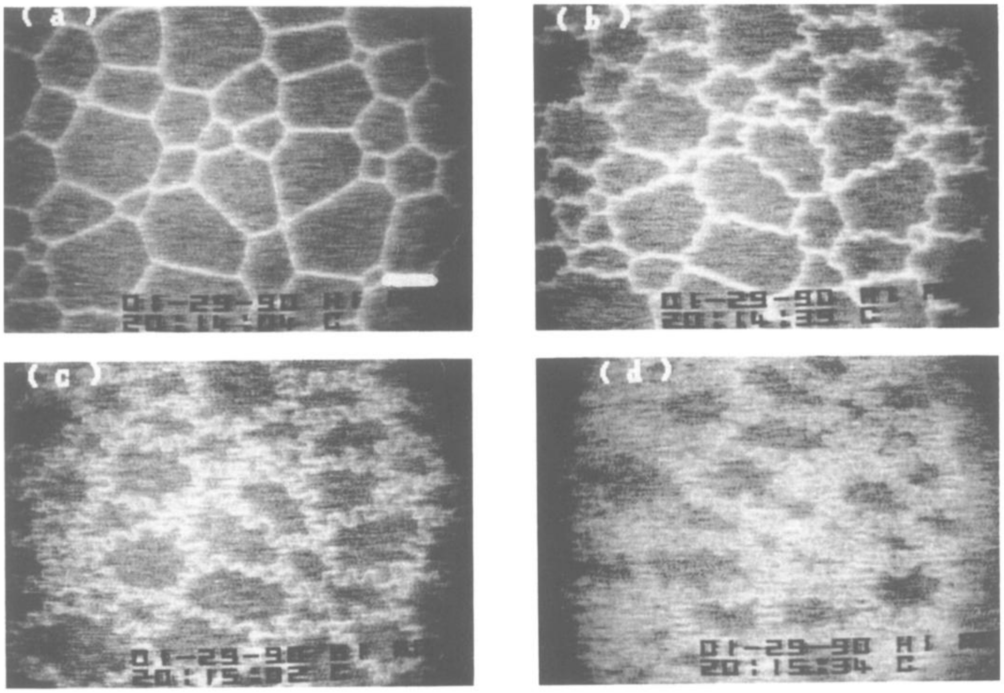

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