Competing Interactions and Domain-Shape Instabilities in a Monomolecular Film at an Air-Water Interface

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Domain-shape instabilites are investigated in a two-dimensional binary mixture of near-critical composition, a monomolecular film confined to an air-water interface and composed of a phospholipid and cholesterol. We apply the methodology of spectral analysis to the quantitative description of domain-wall configurations. This permits us to identify an elliptic instability and a branching instability leading into a "melted" stripe phase in the vicinity of the consolute point. In between, a regime exists in which domain-wall fluctuations exhibit a capillary-wave spectrum.

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Competing interactions give rise to a variety of complex phases in condensed matter.[1] A realization of this principle is afforded by systems whose constituents simultaneously experience mutual magnetostatic or electrostatic repulsion and an attractive interaction of short range. This scenario has been invoked to account for the formation of domains in uniaxial ferromagnets,[2–5] in ferrofluids,[6] and in ferroelectrics[7] by predicting periodic modulations of the magnetization and polarization, respectively. The competition of demagnetizing and domain-wall contributions to the free energy also leads to instabilities of individual domain and droplet shapes and governs the dynamics of their fluctuations.[4,8] Recently, the formation of domains has been discovered during phase coexistence in monomolecular films of phospholipids confined to an air-water interface.[9] Theoretical analyses[10,11] assume the complete equivalence, at the level of mean-field theory, of this phenomenon in two-dimensional amphiphilic films to domain formation in the aforementioned magnetic systems. Specifically, they invoke the van der Waals attraction between aliphatic chains as the source of a domain-wall energy which is balanced by a depolarizing term arising from repulsive electrostatic interactions between the polar moieties of these compounds. Consequently, the predicted phase diagram contains a coexistence region marked by the appearance of periodic intralayer density or composition modulations.[10]

In contrast to the rich diversity of domain morphologies and patterns documented to date in amphiphilic monolayers,[9,12] one notes the relative scarcity of quantitative analysis. In this Letter we introduce the methodology of spectral analysis, based on digital image-processing techniques, to the quantitative description of domain-wall configurations and their excitations. Its application to the study of binary mixed monomolecular films containing cholesterol and dimyristoylphosphatidylcholine (DMPC) (Ref. 13) permits us to identify several distinct regimes of domain-shape stability which are encountered as a film of near-critical composition approaches the upper consolute point terminating a fluid-fluid coexistence region.[14] In particular, we document the existence of an elliptic and of a branching instability of the domain walls. The latter manifests itself in the immediate vicinity of the critical point and represents the precursor for the formation of a disordered or "melted" stripe phase. This stripe liquid gives way to a homogeneous mixture as the coexistence curve is crossed near the critical point.[14] In contrast to the situation in magnetic systems, fluctuations are revealed to play a fundamental role in the amphiphilic monolayers under investigation here.

Experiments were performed on a small trough whose design relies on the property of a rhombus to maintain a constant perimeter during compression along one diagonal. Trough, compression mechanism, and an X-Y positioning stage were placed into a sealed enclosure, permitting optical access to the air-water interface via a 40×, NA0.65 objective. The fluorescence of a phospholipid analog, labeled on one aliphatic chain with a fluorophore and included in the layer at a concentration of 1 mol%, was excited using the 457.9-nm line of a 5-W argon-ion laser.[14] Images were collected by a SIT video camera (Cohu 5150, Cohu, San Diego, CA) during film compression and recorded on videotape under computer control.[15] The observation of a single domain undergoing the various shape instabilities to be described required the illumination and tracking of a given field of view of ~ 180 μm diam over extended periods of time ($\gtrsim 30$ min). The analysis of individual video frames involved a series of steps to extract normalized Fourier descriptors[16] and moments of domain shapes, and is described elsewhere in greater detail.[15]

In the course of compression along a near-critical isotherm,[14] shown in the bottom panel of Fig. 1, circular domain shapes [Fig. 3(a)] first undergo an elliptic instability [see Figs. 1(a) and 1(b)]. Our analysis, summarized in Fig. 2, demonstrates that the circular ground state becomes unstable to elliptic perturbations. In complete analogy to a soft-mode structural phase transition,

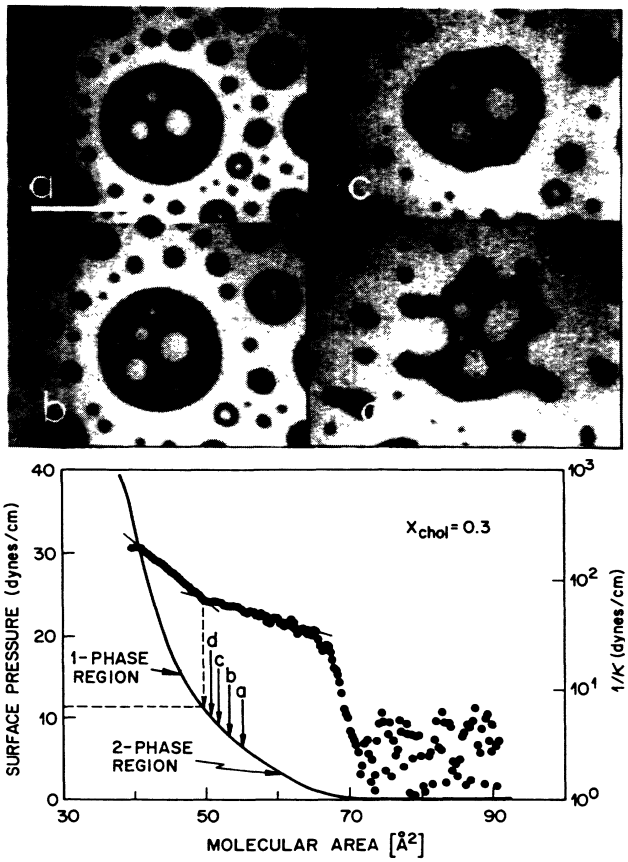

FIG. 1. Regimes of domain-shape stability. Sequence of micrographs of an individual domain in a mixed DMPC-cholesterol monomolecular film ($X_{chol}=0.3$) undergoing shape instabilities during isothermal compression. Snapshots depict the domain in the regime of stability of (a) a circular ground state and (b) of an elliptic ground state, (c) in the regime of capillary-wave scaling, and (d) near the branching instability. The corresponding isotherm (solid line) and the bulk modulus curve (individual dots) derived from it are shown in the bottom panel. The break in the plot of $1/\kappa$ near a mean molecular area of 50 Å^2, marked by dashed lines, indicates the transition into the one-phase region (see Ref. 14). The bar in (a) marks 50 μm.

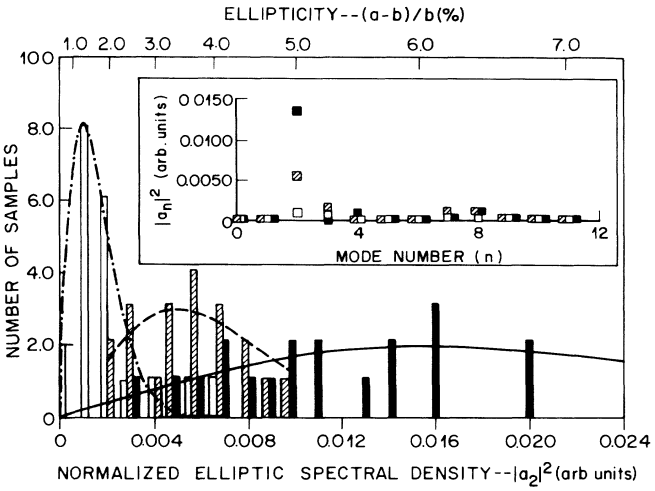

FIG. 2. Elliptic shape instability. Temporal distributions of (normalized) instantaneous elliptic spectral densities in the power spectra of domain-wall excitations, derived from ~30-sec sequences for a domain of ~70 μm diam, and based on twenty samples in each case. During monolayer compression [see Figs. 1(a) and 1(b)] a stable elliptic ground state (solid histogram) evolves from the original circular ground state (open histogram) via intermediates (hatched histogram) as shown. Fits to the respective distributions are discussed in the text. Inset: Typical samples of power spectra corresponding to the three distributions. The ellipticity is given in terms of the semiaxes a and b of an ideal ellipse.

the time-averaged spectral weight, $\langle a_2\rangle$, associated with the elliptic excitations may be regarded as the order parameter of this instability. It is readily extracted from a series of power spectra of instantaneous domain-wall configurations. Histograms of the resulting temporal distribution of momentary elliptic mode amplitudes, a_2, collected to average over shape fluctuations, clearly document the evolution of a small but permanent elliptic distortion marking the appearance of a new stable ground state. The functional form $f(z)\sim\exp[-(z+\eta^2)/2\sigma^2]I_0(\sqrt{z}\,\eta/\sigma^2)$ describes the distribution of a random variable $z\equiv x^2+y^2$, $z>0$, if x and y are independent, Gaussian random variables of equal variance, σ^2, and mean η_x,η_y, respectively; $\eta\equiv(\eta_x^2+\eta_y^2)^{1/2}$, and I_0 denotes the modified Bessel function of order zero.[17] Fits by this expression, shown in Fig. 2, yield for the three examples $\sigma^2=0.0002$ (open histogram), 0.0005 (hatched histogram), and 0.0020 (solid histogram), and $\langle|a_2|^2\rangle\equiv\eta^2=0.0012$ (open), 0.0055 (hatched), and 0.0176 (solid), suggesting a continuous transition. Examples in the inset of Fig. 2 illustrate the effect by comparing spectra obtained for a circular domain (open squares) exhibiting a small elliptic fluctuation and elliptically deformed domains (hatched squares and solid squares). This is the first confirmation of a recent theoretical prediction of such an elliptic instability,[18] in accordance with the expectation of linear stability analysis.[4,8]

Further compression results in the shift of significant spectral weight to modes of higher rotation symmetry implying a persistence length $\xi\sim\lambda_n$, where λ_n is the wavelength of the nth mode. In domains of 50 to 100 μm diam significant spectral weight accumulates in modes of symmetry up to $n\simeq 10$, giving rise to distorted shapes such as the one shown in Fig. 1(c). Concomittantly, long-lived ($\gtrsim 20$ sec) excitations into ground states of different symmetry occur. That is, the largest spectal amplitude fluctuates slowly between states of, say, twofold (elliptic), threefold, and fourfold symmetry, while higher modes appear and decay on a shorter time scale (~1 sec). This situation is strongly reminiscent of

very similar observations made in Monte Carlo simulations of two-dimensional "vesicles."[19]

To extract the static aspects of the fluctuation spectrum we average over a sufficient number of uncorrelated samples (typically 10–20) of the domain-wall fluctuations. This procedure reveals that the mode spectral densities scale according to $\langle |a_n|^2 \rangle \propto 1/(n-1)^2$, where n (≥ 2) denotes the rotational symmetry of successive modes. That is, spectral densities are distributed in accordance with equipartition, as expected in a harmonic approximation of the domain-wall energy,[20] the system no longer retaining a memory of the elliptic instability. This observation implies a surprisingly simple picture: Fluctuations, in this regime, are governed by a capillary-wave Hamiltonian and an effective surface or line tension. Consequently, the nonlocal dipolar kernel appears to be well approximated here by the leading term of its expansion for a dipolar sheet, shown by Milner[21] to have the form of a (local) negative surface tension.

The scaling regime terminates in an interfacial instability giving rise to the formation of "branches." This branching instability is marked by the appearance of a new length scale [here of order 10 μm; see Fig. 1(d)] and, for an isolated domain, generates a ramified domain morphology. This observation is again reminiscent of findings in the aforementioned simulations of two-dimensional vesicles, where "crumpled" shapes appear in a "deflated" regime.[19] This latter aspect of the instability is captured by a precipitous increase in the global shape parameter s, defined as a normalized ratio of perimeter (L) and area (A): $s \equiv L^2/4\pi A$. The relevant values for s in Fig. 1 are (a) 1.00, (b) 1.00, (c) 1.04, and (d) 2.48. We may also establish a correspondence to an elongation instability predicted for ferrofluids:[8] In the present system, domains of sufficiently small size in fact undergo, instead of the branching instability, a permanent elongation into a short strip of the required width.

The interaction with neighboring domains favors the complete transformation of domains into stripes (of finite length) which exhibit undulation fluctuations of large amplitude, while also rupturing and branching. One may regard the observed branching as a manifestation of a "labyrinthine,"[7] "serpentine,"[8] or "undulation"[22] instability of stripe domains. The striplike objects condense into a disordered, fluctuating stripe phase, shown in Fig. 3(b). Its residual order may be characterized by an intraplanar nearest-neighbor spacing and manifests itself in the form of a diffuse ring in the (static) two-dimensional Fourier spectrum computed from the pattern [inset of Fig. 3(b)], essentially that of a fluid. The discovery of the stripe phase in the monolayer systems qualitatively confirms the expectation of mean-field theory.[5,10] However, at finite temperatures dislocation unbinding destroys long-range positional order.[5] In fact, a finite density, n_D, of free dislocations is predicted[23] to

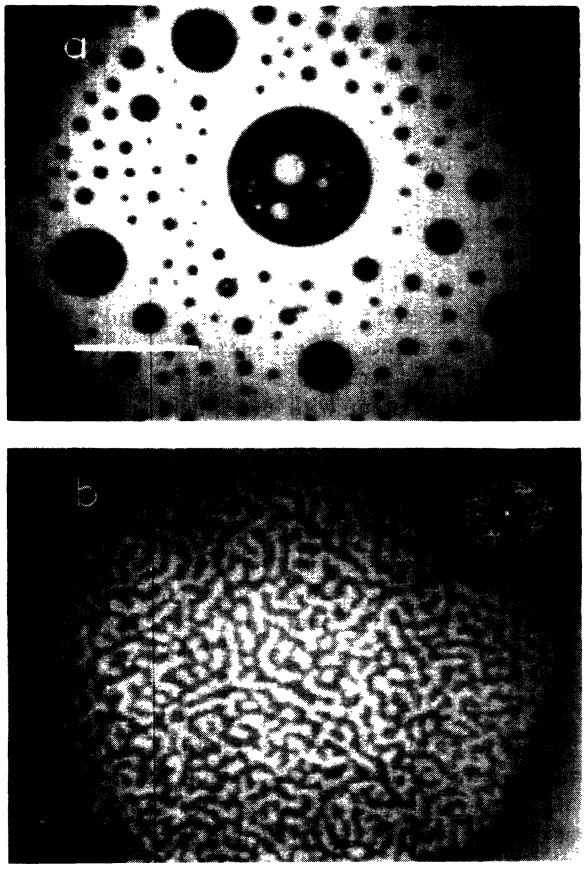

FIG. 3. Circular droplets and melted stripe phase. In a mixed film of near-critical composition ($X_{chol}=0.3$) a disordered stripe phase (b) emerges near the consolute point from the original phase of circular droplets (a) immediately following a branching instability [Fig. 1(d)]. Inset in (b): A weak diffuse ring in the two-dimensional (logarithmically scaled) Fourier transform of the stripe phase. The bar in (a) marks 50 μm.

transform a layered material into a two-dimensional "nematic" at length scales $\xi_D \simeq n_D^{-1/2}$. Upon further approach of the critical point the period of the stripe pattern decreases continuously until contrast in the images is lost at our resolution limit of ~ 1 μm, yielding a homogeneously fluorescent phase,[14] the analog of the paramagnetic phase in magnetic systems.

The sequence of domain-wall instabilities reported here arises from the competition of a repulsive dipolar interaction and attractive van der Waals forces manifesting themselves in the form of a finite domain-wall energy. As the upper consolute point of a binary mixed monolayer is approached under isothermal compression, the domain-wall energy continually decreases. As a result, the balance of the competing interactions is altered in favor of the dipolar repulsion. At the critical point, the domain-wall energy must vanish. Consequently,

fluctuations of large amplitude arise in the critical region, resulting in the formation of a "stripe liquid" phase. The qualitative similarities to analogous phases reported in magnetic systems[5,6,8] unequivocally implicate electrostatic interactions between polar moieties of phospholipids in the formation and mutual interaction of domains during phase coexistence. Their effective range in the monolayer films remains to be determined.

Furthermore, our analysis reveals the prominent role of shape fluctuations which goven the dynamics of domain-wall motion. By their very nature, the cited mean-field treatments neglect these effects. Thus, while the formation of a stripe phase near the critical point is qualitatively consistent with mean-field predictions, the treatment of the fluctuation-induced "melting" of the stripe or 2D smectic phase[22] exceeds the scope of current theories.

The hydrodynamics of shape fluctuations have recently been considered for phospholipid vesicles and erythrocytes[24] and for bicontinuous microemulsions.[25] Both systems are generally thought to be described by a curvature elastic energy. In contrast, the behavior of the present, two-dimensional system appears to be governed, over a certain range of lateral density, by an effective capillary-wave Hamiltonian. Among the intriguing open questions remains the analysis of the fluctuations dynamics in the various regimes of stability and in the disordered stripe phase. The approach to this problem, and to others of its nature, will rely on the application of the type of extensive image-analysis techniques introduced here which represent an essential tool to identify and determine the quantities of physical significance.

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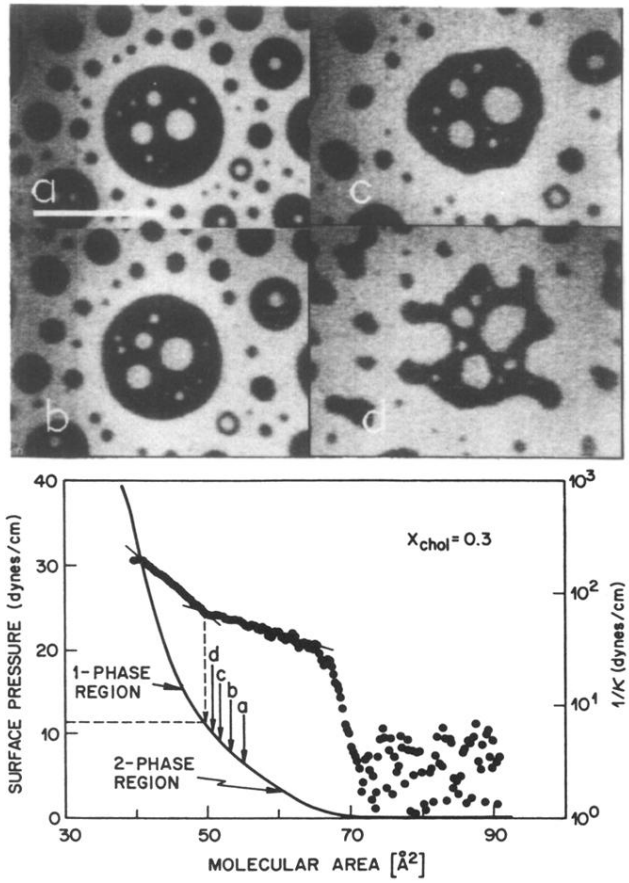

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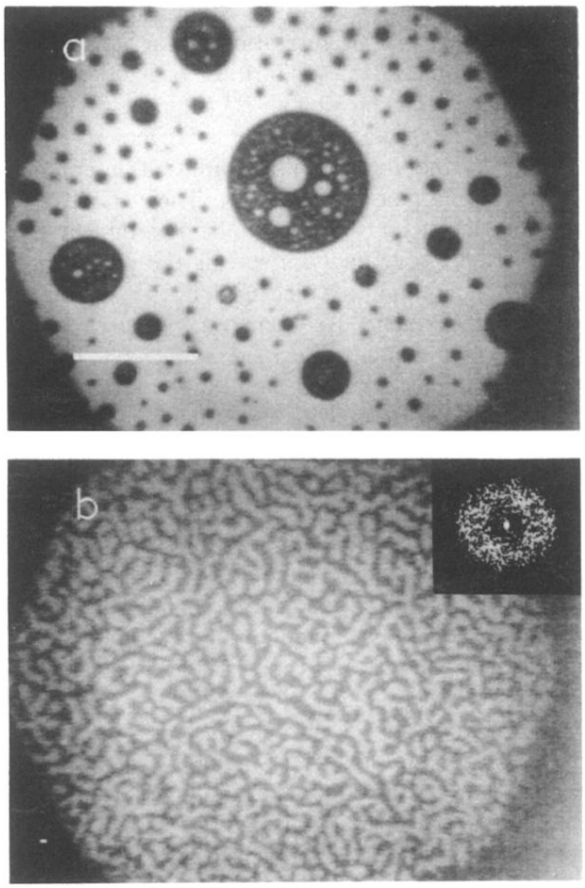

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