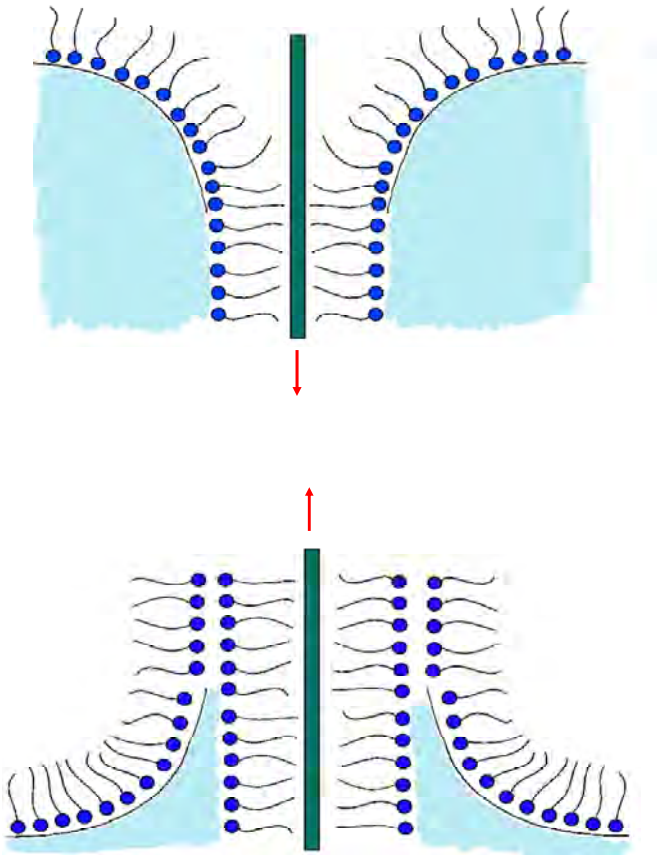
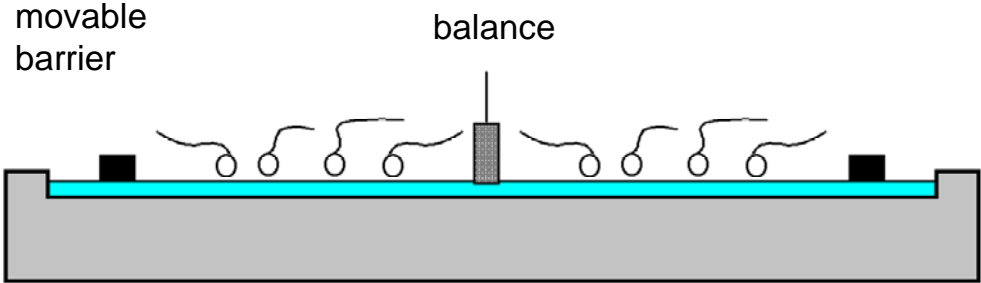


Langmuir-Blodgett Films



Surface energy / Surface tension

$$dE = \delta q + \delta w$$

$$dS = \frac{\delta q}{T} \quad \delta q = TdS$$

$$\delta w = -PdV + \gamma dA$$

$$dE = TdS - PdV + \gamma dA$$

$$H = E + PV$$

$$dH = dE + PdV + VdP \quad dE = dH - PdV - VdP$$

$$dH - PdV - VdP = TdS - PdV + \gamma dA \quad dH = TdS + VdP + \gamma dA$$

$$G = H - TS$$

$$dG = dH - TdS - SdT \quad dH = dG + TdS + SdT$$

$$dG + TdS + SdT = TdS + VdP + \gamma dA$$

$$dG = VdP - SdT + \gamma dA$$

$$G = f(P, T, A)$$

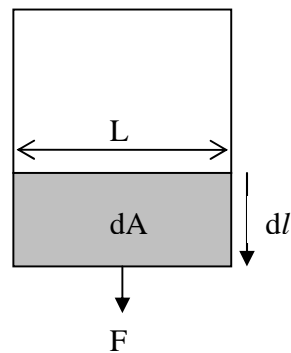
$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,A} dT + \left(\frac{\partial G}{\partial P} \right)_{T,A} dP + \left(\frac{\partial G}{\partial A} \right)_{T,P} dA$$

$$\left(\frac{\partial G}{\partial T} \right)_{P,A} = -S \quad \left(\frac{\partial G}{\partial P} \right)_{T,A} = V \quad \boxed{\left(\frac{\partial G}{\partial A} \right)_{T,P} = \gamma}$$

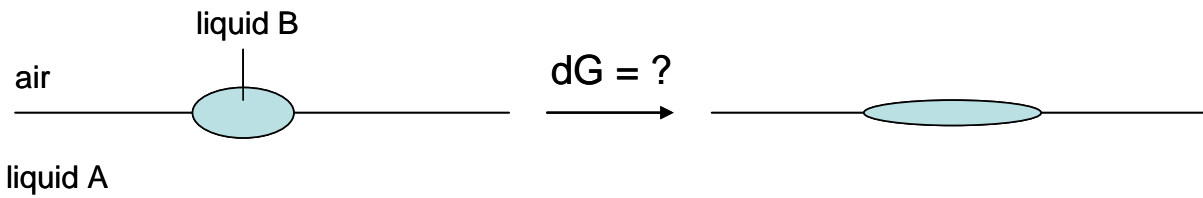
$$\delta w = \gamma dA \quad dA = Ldl \quad \delta w = \gamma Ldl$$

$$\delta w = Fdl$$

$$\gamma = \frac{F}{L}$$



Spreading of one liquid on another



$$dG = \left(\frac{\partial G}{\partial A_A} \right) dA_A + \left(\frac{\partial G}{\partial A_B} \right) dA_B + \left(\frac{\partial G}{\partial A_{A,B}} \right) dA_{A,B}$$

$$dA_B = -dA_A = dA_{A,B}$$

$$dG = \left(\frac{\partial G}{\partial A_A} \right) (-dA_B) + \left(\frac{\partial G}{\partial A_B} \right) dA_B + \left(\frac{\partial G}{\partial A_{A,B}} \right) dA_B$$

$$dG = -\gamma_A dA_B + \gamma_B dA_B + \gamma_{A,B} dA_B$$

$$\left(\frac{dG}{dA_B} \right) = \gamma_B + \gamma_{A,B} - \gamma_A$$

Liquid B spreads on liquid A for $\left(\frac{dG}{dA_B} \right) < 0$

Wilhelmy plate

$$F_{surface} = \gamma P$$

$$\cos \theta = \frac{F_{surface,\perp}}{F_{surface}}$$

$$F_{surface,\perp} = \gamma P \cos \theta$$

$$F_{total} = W_{plate} - Buoyancy + F_{surface,\perp}$$

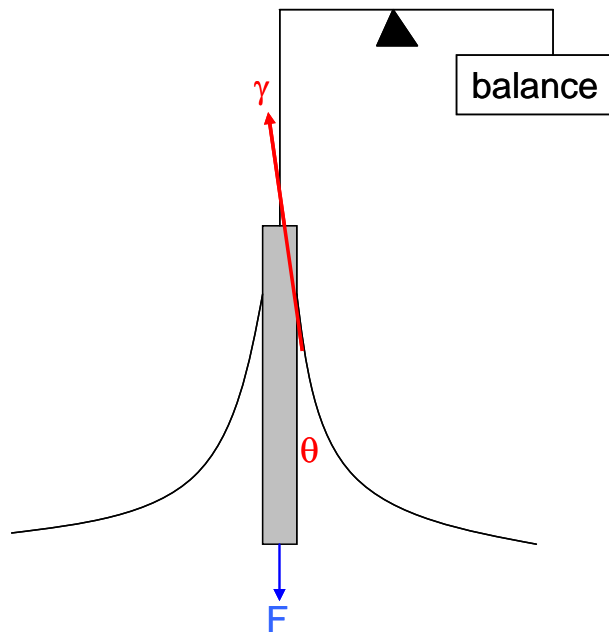
$$F_{total}^o = W_{plate} - Buoyancy + \gamma_o P \cos \theta$$

$$F_{total} = W_{plate} - Buoyancy + \gamma P \cos \theta$$

$$F^o - F = (\gamma_o - \gamma) P \cos \theta$$

Surface pressure :

$$\Pi = \gamma_o - \gamma$$



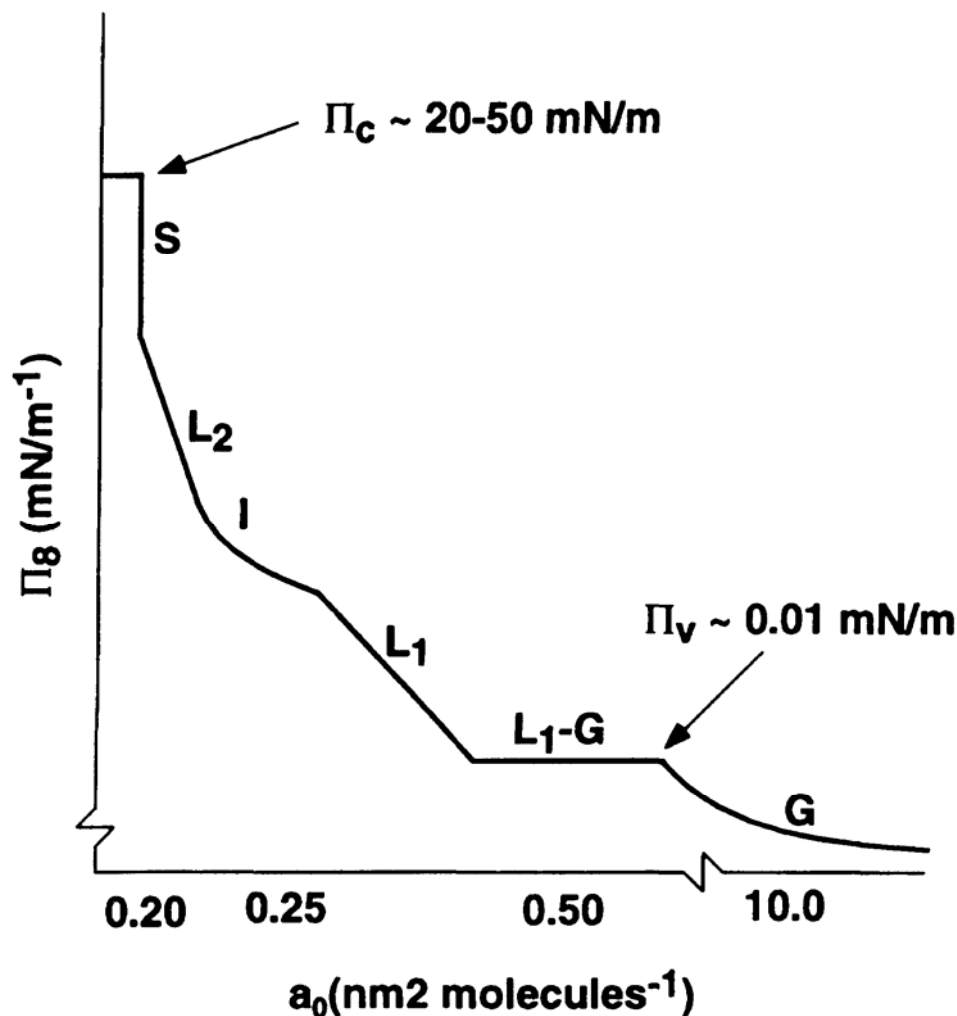


Figure 2.13
 Composite two-dimensional pressure (Π_s)-area (a_0) isotherm, which includes a wide assortment of gaslike, liquidlike, and solidlike monolayer phenomena. To permit all features to be included on one set of coordinates, the scale of the figure is not uniform. Π_v is the highest pressure of the gaslike film. Π_c is the collapse pressure of the film. (P.C. Hiemenz, *Principles of Colloid and Surface Chemistry*, 2nd ed., Dekker, New York, 1986, p. 364.)

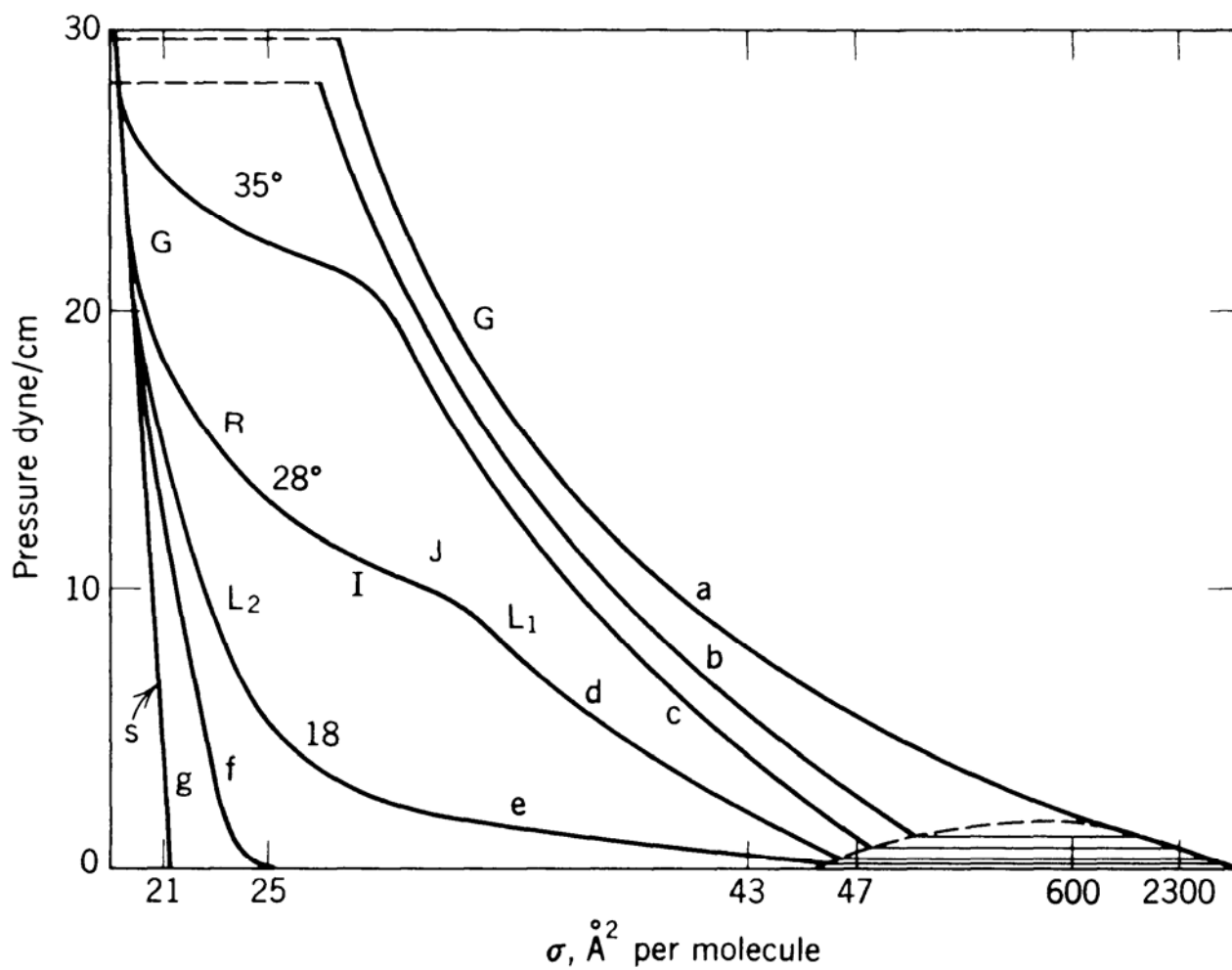


Fig. IV-15. States of monolayers (schematic).

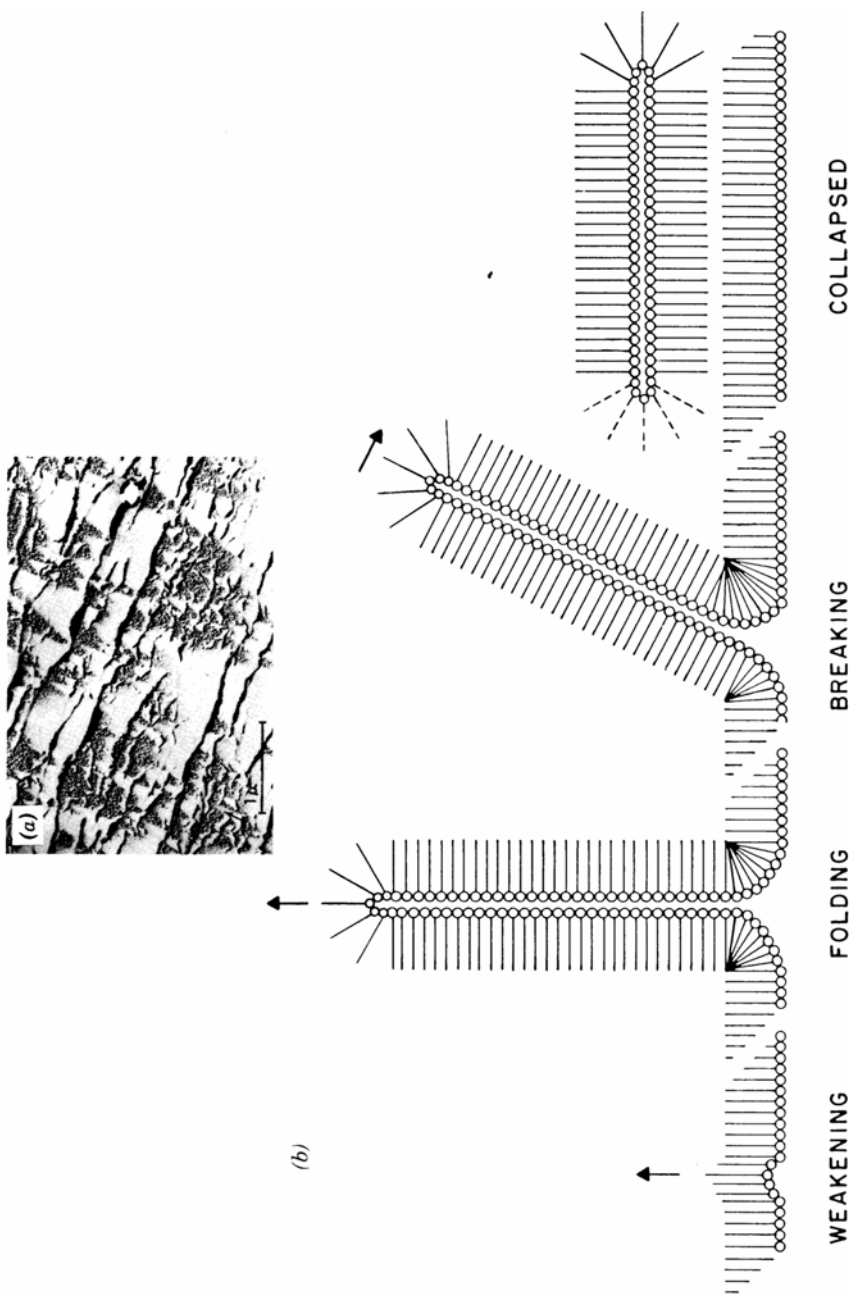


Fig. IV-20. (a) Electron micrograph of a collapsing film of 2-hydroxytetraacosanoic acid. Scale bar: 1. [From H. E. Ries, Jr., *Nature*, **281**, 287 (1979).] (b) Possible collapse mechanism. Reprinted with permission from H. E. Ries, Jr. and H. Swift, *Langmuir*, **3**, 853 (1987) (Ref. 130). Copyright 1987, American Chemical Society.

Monolayer phase transitions

The first law of thermodynamics states that $dE = \delta q + \delta w$. At equilibrium, $\delta q = TdS$ and, if both mechanical and surface work are allowed, $\delta w = -PdV + \gamma dA$. The exact differential for the internal energy can thus be written as

$$dE = TdS - PdV + \gamma dA. \quad [A1]$$

The enthalpy, H , can be obtained from the energy function by performing two successive Legendre transformations, replacing V by P and A by γ , respectively.

Since $\left(\frac{\partial E}{\partial V}\right)_{S,A} = -P$ and $\left(\frac{\partial E}{\partial A}\right)_{S,P} = \gamma$, the double Legendre transformation yields the enthalpy as

$$H = E + PV - \gamma A \quad [A2]$$

and thus $dH = dE + PdV + VdP - \gamma dA - Ad\gamma$.

The free energy, G , is defined by $G = H - TS$. Therefore $dG = dH - TdS - SdT$ and when combined with equation [A1] and the differentiated form of equation [A2], we obtain

$$dG = VdP - SdT - Ad\gamma. \quad [A3]$$

As pointed out by Bromberg¹ many authors simply add the surface work directly to the free energy expression, leading to $dG = VdP - SdT + \gamma dA$. While not incorrect, this approach lacks uniformity in that the PV work term is transformed while surface work term is not. Use of the consistent system, in which all work terms are transformed, is required to obtain the desired form of the modified Clapeyron equation. Furthermore, the enthalpy change thus evaluated must include the surface work term as given by equation [A2].

¹ Bromberg, J.P. *Physical Chemistry*, 2nd ed.; Allyn and Bacon, Toronto, 1984; p 379.

Consider a single component system composed of two surface phases, α and β . At equilibrium at temperature T , the molar free energies of the two phases are equal: $\bar{G}_\alpha(T) = \bar{G}_\beta(T)$. The system is then subjected to a temperature change, dT , at constant pressure. At equilibrium, at the new temperature, $\bar{G}_\alpha(T + dT) = \bar{G}_\beta(T + dT)$. Therefore $d\bar{G}_\alpha = d\bar{G}_\beta$. Substitution of the free energies changes by equation [A3] (with $dP = 0$) yields:

$$-\bar{S}_\alpha dT - \bar{A}_\alpha d\gamma = -\bar{S}_\beta dT - \bar{A}_\beta d\gamma$$

or

$$\frac{d\gamma}{dT} = -\frac{\Delta\bar{S}_{\alpha\rightarrow\beta}}{\Delta\bar{A}_{\alpha\rightarrow\beta}} \quad [\text{A4}]$$

Since $\Pi = \gamma_o - \gamma$,

$$\frac{d\Pi}{dT} - \frac{d\gamma_o}{dT} = \frac{\Delta\bar{S}_{\alpha\rightarrow\beta}}{\Delta\bar{A}_{\alpha\rightarrow\beta}}. \quad [\text{A5}]$$

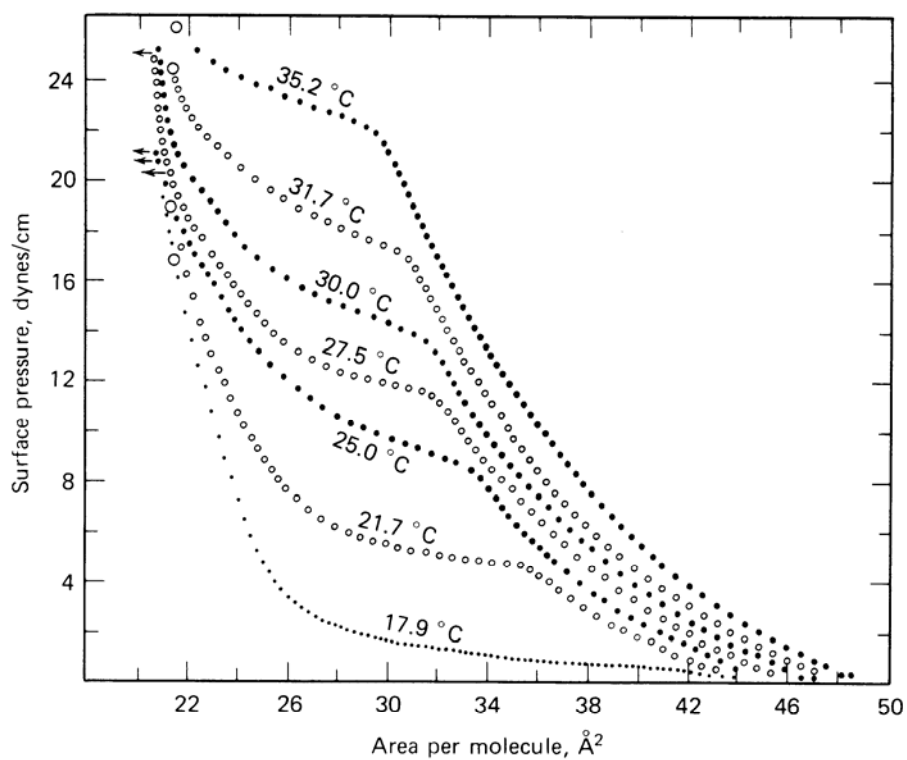


Fig. IV-18. Pressure–area relations for monolayers of pentadecylic acid at pH 2. (From Ref. 149.)

Self-Assembly in Two Dimensions: Surface Micelles and Domain Formation in Monolayers

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The thermodynamics of small systems, together with simple molecular packing and energetic considerations, previously applied to self-assembling surfactant aggregates in bulk solutions, is here extended to two-dimensional aggregates such as "surface micelles" or domains in monolayers. A new pressure-area (π - A) isotherm—the "surface micelle isotherm"—is derived that displays features typically exhibited by many surfactant monolayers on the water-air surface. This equation clarifies the nature of continuous-phase transitions in monolayers and allows for the determination of various 2D micellar properties, including aggregation numbers, from the shapes of π - A curves. Comparison with experiment is currently limited because of the absence of direct methods for observing small 2D micelles or nanometer-sized domains on surfaces. However, on the basis of the shapes of many measured π - A curves, it is concluded that nanodomains with aggregation numbers in the tens or hundreds must exist if these curves represent the true equilibrium states of the monolayers.

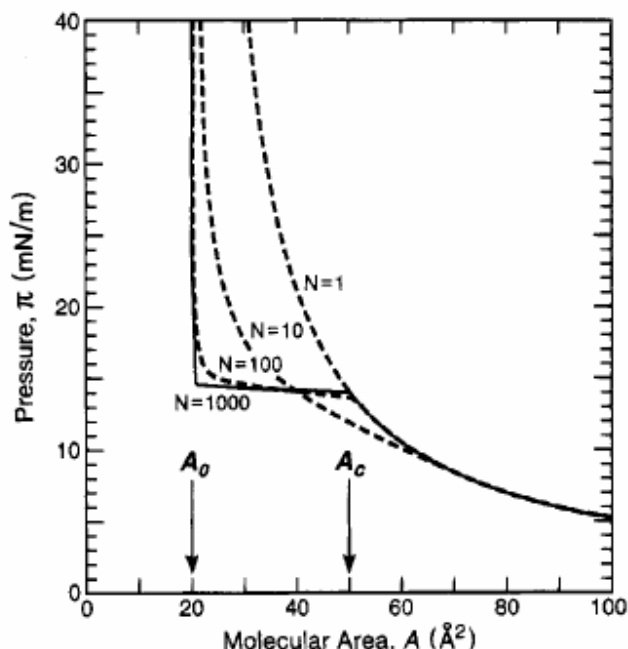


Figure 3. Theoretical π - A curves for domains of aggregation number N varying from $N = 1$ (no domains, no phase transition) to $N = 1000$ (large domains, approaching a first-order phase transition). The curves are based on the "surface micelle isotherm", eq 21, using A_c (critical area) = 50 \AA^2 , A_0 (excluded area per molecule) = 20 \AA^2 , and $T = 300 \text{ K}$.

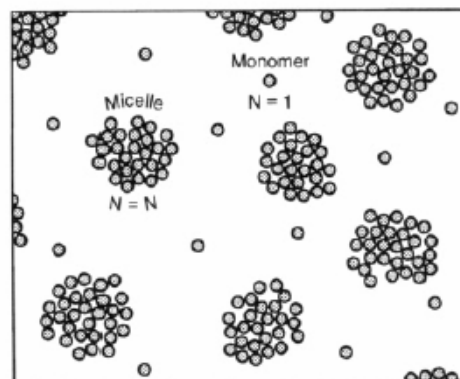


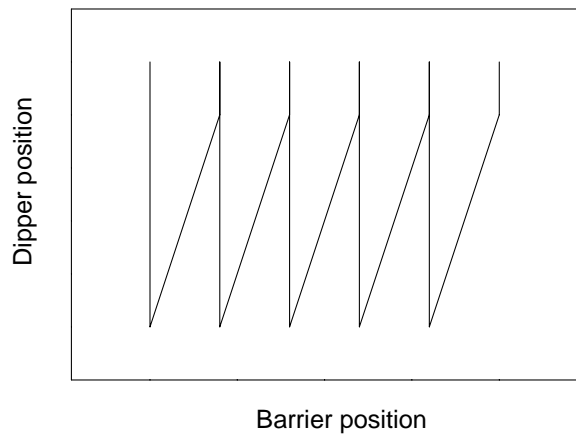
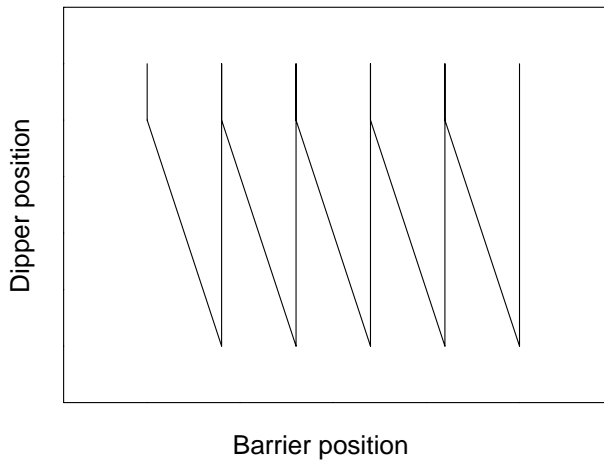
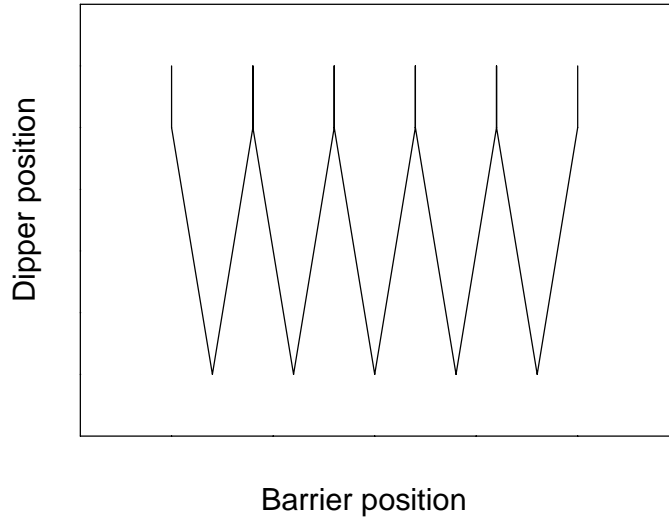
Figure 2. Two-dimensional circular micelles (domains) of aggregation number $N \approx 25$ on a liquid or solid surface.

$$\pi = \frac{kT}{N} \left[\frac{1}{(A - A_0)} + \frac{(N - 1)}{(A_1 - A_0)} \right] \quad (21)$$

Transfer to solid substrates

Transfer ratio:

$$\tau = \frac{\text{Substrate area}}{\Delta \text{ monolayer area}}$$



A New Series of Amphiphilic Molecules Forming Stable Z-Type (Polar) Langmuir–Blodgett Films

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Received August 14, 1989

Chart I

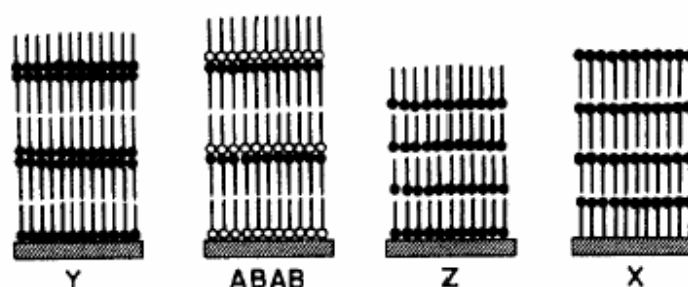
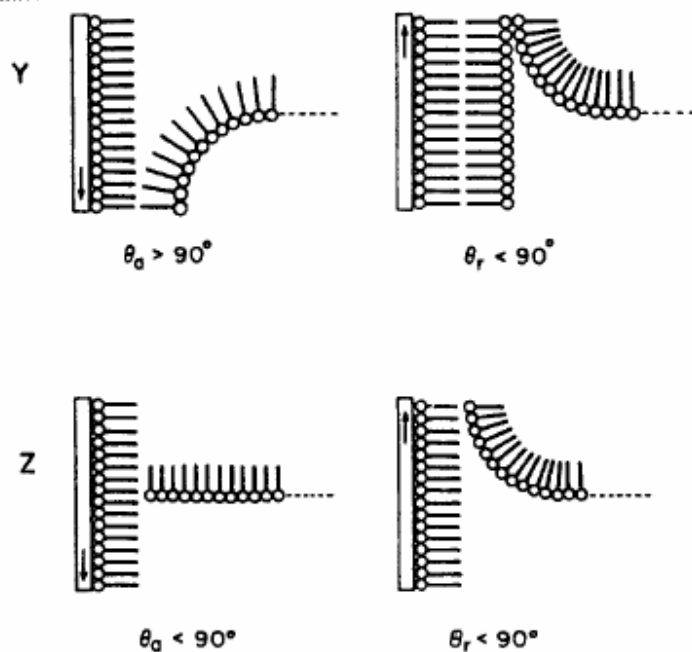


Chart II



Experimental Analysis of the Thermodynamic Mechanism of Langmuir-Blodgett Film Transfer

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(Received: December 6, 1988; In Final Form: October 12, 1989)

An experimental investigation was made on the mechanism for the transfer of a Langmuir-Blodgett (LB) film. The transfer ratio (ρ) and the interfacial force (f) were observed for stearyl alcohol and cadmium stearate monolayers on silicon substrates, by systematically varying both the surface pressures (π) of the monolayer and the hydrophilicities of the substrate characterized by contact angle (θ_0). It was found that the ratios ρ observed both for up- and down-stroke depositions changed discretely within zero and unity, divided at the critical values of π and θ_0 . To examine the film-transfer characteristics, on the basis of thermodynamics, the interfacial forces applied to the moving substrate were measured during the deposition process. In the case of $\rho = 0$, the force showed little dependence upon π . On the contrary, in the case of $\rho = 1$, the forces applied to the hydrophilic substrates in the up stroke linearly increased with increasing π , while those applied to hydrophobic substrates in the down stroke decreased with increasing π . These results reveal that the dynamic interfacial force is a substantial factor in the LB film transfer. The force is ascribable to the changes in the surface energies caused by the vertical displacement of the related interfaces. The mechanism of the LB film transfer is consequently considered as a subject of thermodynamics, and the success or failure in the monolayer transfer can be quantitatively interpreted by taking account of the dynamic force changes during the processes.

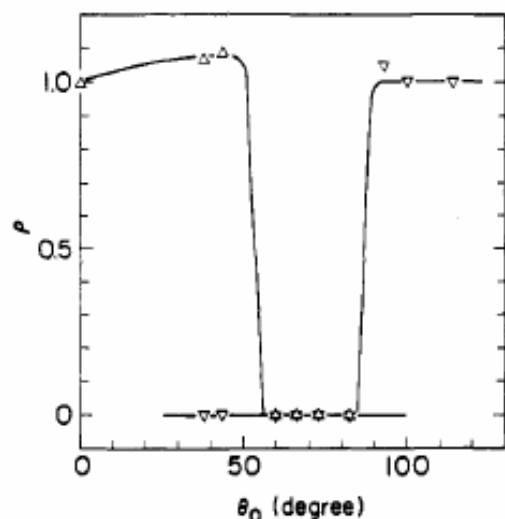


Figure 1. Transfer ratios (ρ) of stearyl alcohol monolayers for the up-stroke (Δ) and down-stroke (∇) transfer onto the substrates with various hydrophobicities (θ_0). The surface pressure (π) was 30 dyn/cm.

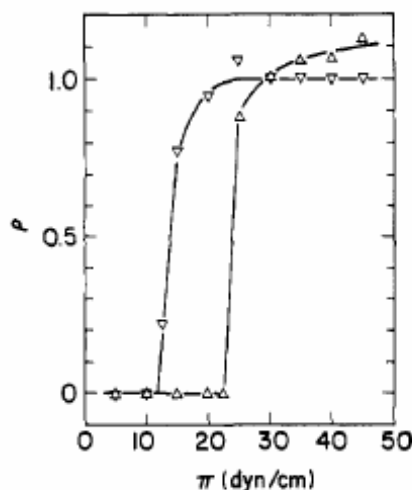


Figure 2. Transfer ratios (ρ) of stearyl alcohol monolayers at various surface pressures (π) for the up-stroke (Δ) transfer onto the substrate with $\theta_0 = 60^\circ$, and down-stroke (∇) transfer onto the substrate with $\theta_0 = 90^\circ$.

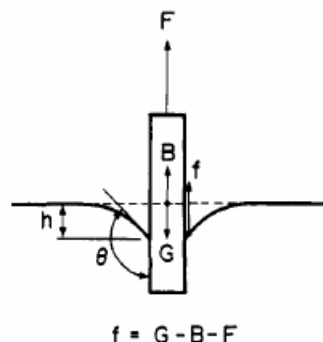


Figure 3. Schematic representation of a force balance applied to the substrate at the meniscus: F , total force; B , buoyancy; G , gravitational force; f , interfacial force at contact line; h , meniscus height; θ , contact angle.

Molecular-Hydrodynamic Description of Langmuir–Blodgett Deposition

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The molecular-hydrodynamic description of Langmuir–Blodgett deposition presented in this study relates the velocity of deposition to the activation free energy of adsorption occurring along the three-phase contact line, the density of the hydrophilic headgroups (considered as adsorption centers), and the viscosity, density, and surface tension of the liquid phase. It introduces rigorously defined dynamic contact angles that can be easily determined in the experiment. It is shown that the pure molecular-kinetic and hydrodynamic theories do not adequately describe the experimental relationship between velocity of deposition and dynamic contact angles while the molecular-hydrodynamic one fits the experimental data up to the maximal velocity, U_{\max} , at which a liquid film is entrained during the upstroke stage of deposition. Comparison between this theory and experiment points out that the hydrodynamic deformation of the fluid interface is negligible when deposition is performed from dilute aqueous subsolutions but can become important for viscous subsolutions and deposition at high surface pressure. Analysis of energy dissipation in the three-phase zone and in the bulk of the moving meniscus shows that the nonhydrodynamic dissipation in the three-phase contact zone prevails in the whole velocity range up to U_{\max} . This dissipation depends on the nature of the hydrophilic headgroups, and their modification via counterion adsorption significantly changes its value. It is shown that substitution of the carboxylic groups by barium-carboxylate ones decreases this dissipation and causes an increase of U_{\max} , probably due to facilitated dehydration of the heads.

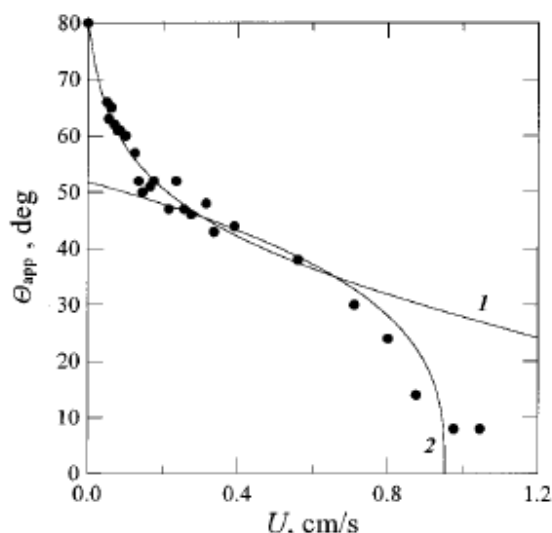


Figure 3. Experimental dependence of the apparent dynamic contact angle, Θ_{app} , on solid substrate velocity, U , during deposition of arachidic acid from 1×10^{-2} M HCl subsolution at 30 mN/m. Data from ref 2. Curve 1 is plotted according to the molecular-kinetic theory (eq 2) with $K = 9.4 \times 10^4 \text{ s}^{-1}$ and $\lambda = 11.1 \text{ \AA}$ and curve 2 represents the hydrodynamic description (eqs 7 and 11) assuming that Θ_c is a constant determined as a free parameter.