Isotherms and isobars for the crystal-liquid transition in a two-dimensional monolayer

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An attempt is made to explain the many experimental anomalies observed in first-order "crystal-liquid" transitions in monolayers of surface-active materials, including hysteresis, slope of isotherms in the stratification region, and so on. It is suggested that the freezing of the liquid monolayer is accompanied by the emergence of a structure in the form of a solid ring around the liquid spot. The surface pressure, i.e., the pressure on the boundary of the monolayer, is then determined not only by the conditions of equilibrium between the liquid and the solid phases, but also by elastic stresses that appear in the solid ring. These stresses can be determined in the axially symmetric case when the entire monolayer and the liquid phase take the form of concentric rings. The isotherms (isobars) for compression (cooling) and subsequent expansion (heating) of the monolayer are determined. It is found that existing experimental data can be interpreted by assuming that the plastic threshold of the monolayer is low and plastic strains appear when it is compressed. Their irreversibility is responsible for the observed well-defined hysteresis.

INTRODUCTION

The experimental isotherms of surface pressure against area for a monolayer of surface-active material (SAM) in the neighborhood of the crystal-liquid phase transition exhibits a behavior that is not in accordance with generally accepted ideas about phase transitions.[1,2] Whilst calorimetric measurements show that there is a discontinuity in enthalpy and a relatively high latent heat of the transition at the transition point, compression isotherms obtained for a monolayer of this kind do not have a segment corresponding to constant pressure, but they do show a "knee." Thus, calorimetric data and compression isotherms indicate the presence of first-order and second-order transitions, respectively. Monolayer expansion isotherms exhibit appreciable hysteresis, which again indicates the presence of first-order transitions. Area against temperature isobars also exhibit hysteresis: two different transition temperatures are observed at constant pressure when the monolayer is heated and cooled, respectively (see Fig. 1).

Attempts have been made to explain these phenomena by introducing artificial assumptions about transitions of intermediate (one and a half) order,[3] independent cooperative units,[2] and so on. The suggestion that experimental results were distorted by impurities present in the monolayer and in water have not been confirmed. The authors of Ref. 2 carried out repeated purification of water and the SAM. Although, initially, impurities did, in fact, have an effect on the monolayer isotherms, purification beyond a certain point had no effect on the final results. Moreover, results reported by different authors, using different equipment, are found to be in agreement even though the composition and influence of impurities could hardly be the same.

X-ray scattering data show that, in the more dense low-temperature phase, monolayers of many SAMs such as lipids, fatty acids, and their derivatives form a regular triangular lattice without long-range order. The nature of the Bragg peaks indicates that the monolayer takes the form of a two-dimensional crystal on a smooth substrate in which, again, there is no long-range order. The hysteresis attending the phase transitions also indicates that there is a crystal phase in which the shear modulus differs from zero.

The aim of the present work was to explain the shape of isotherms and isobars of SAM monolayers on the basis of the assumption that hysteresis and other anomalies are due to the appearance of elastic stresses in the crystal phase. The crystal phase is not then in a state of equilibrium from the standpoint of conventional thermodynamics, but the corresponding relaxation (recrystallization) time is much longer than the time of the experiment. This approach was successfully used many years ago by Gibbs[4] to describe the melting of a three-dimensional crystal. The appearance of elastic stresses is due to the different densities of the liquid and solid phases and to nonzero shear modulus, at least in one of the phases.[5,6] So far, experimental data have been obtained both

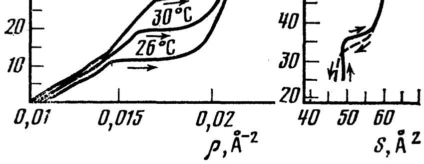

FIG. 1. Isotherms and isobars obtained for monolayers of L-α-dipalmitoyllecithin (from Ref. 2: a—surface pressure Π as a function of the concentration ρ of molecules when a monolayer was compressed at constant temperature; b—isobar of temperature versus area per molecule, recorded in two directions—with increasing and decreasing temperature, respectively. Surface pressure 30 dyn/cm. The curves recorded when the monolayer was respectively heated and cooled were very different from one another and yielded different values for the transition temperature.

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for monolayers of circular shape[7,8] and for a cylinder-piston type systems. In this paper, we shall give a quantitative analysis of the phase transition in the axially symmetric case alone: the monolayer will be assumed to be circular in shape and its radius will be a function of the external (two-dimensional) pressure Π_e. This model will also provide a qualitative explanation of experimental data obtained with the usual rectangular Langmuir balance. The monolayer then has the shape of a rectangle and the external pressure is applied to one of its sides so that compression and expansion occur in only one direction.

Our main hypothesis on which all subsequent discussion is based is as follows. We assume that crystallization begins on the boundary of the monolayer, and the crystallization front subsequently moves from the boundary to the center of the monolayer. The solid phase then always takes the form of a ring surrounding the liquid phase. We assume that crystallization occurs infinitely slowly (adiabatically), so that there are no instabilities due to the propagation of the crystallization front. These assumptions are based on the analogy with the three-dimensional situation where the boundary is the natural crystallization center. The walls of the container, made from teflon, can also facilitate the formation of solid-phase nuclei, since the van der Waals and hydrophobic interactions of the SAM molecules with teflon give rise to an increase in the local SAM density on the boundary of the monolayer. Moreover, in contrast to the gas-crystal situation in which the formation of the solid phase nuclei occurs all over the monolayer surface, the compression isotherms have a completely different shape:[1] the stratification region has a horizontal portion which acquires a constant slope when the monolayer density reaches a critical value. This situation is also characterized by a large density discontinuity accompanying the transition, and will not be examined here.

Compression of the monolayer is accompanied not only by the crystallization of the liquid phase, but also by the deformation of the solid phase already present along the boundary of the monolayer. Since experiments have recorded not the pressure on the phase separation boundary, but the radial stress in the solid phase on the boundary of the monolayer, this explains the increase in external pressure in the phase stratification region (see Figs. 1 and 2). The axially symmetric shape of the monolayer enables us to obtain the external pressure as a function of the monolayer radius in an analytic form. We have used the approximation of an elastic isotropic medium and have retained only terms that were linear in stress and strain. This approximation is valid if the relative discontinuity in the monolayer area in the course of transition is small and can subsequently be regarded as a small parameter. Since the phase diagram of the monolayer usually has a tricritical point, at which the discontinuity in area is zero, our results are valid at least in its neighborhood.

We have found that plastic strain has to be taken into account to explain the experimental data. Moreover, analysis of experimental data has shown that, as a rule, these strains play a determining role. It was assumed in calculation of plastic strains that the plastic threshold of the monolayer, ε, is independent of pressure. Plastic deformation arises when the sum of the squares of the components of the deviator of the stress tensor reaches $2\varepsilon^2$. It is assumed that, when plastic strain occurs, this sum is constant and equal to $2\varepsilon^2$. This means that the solid monolayer begins to flow when a pressure ε is applied along one axis and a tensile stress $-\varepsilon$ along another. Further increase in the shear stress results in flow (similar to that of a liquid) until the shear stresses fall to ε.

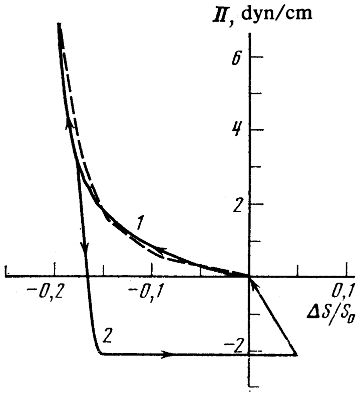

FIG. 2. Theoretical dependence of surface pressure Π on relative change in the area of the monolayer $\Delta S/S_0$ on compression at constant temperature (curve 1). Broken line shows the experimental isotherm for a monolayer of egg lecithin at 30 °C. The parameters γ and K for the monolayer used in constructing the theoretical graph of $\Pi(\Delta S/S_0)$ were taken to be those for the egg lecithin monolayer at 30 °C, as reported in Ref. 2. The plastic threshold ε was chosen so as to ensure that the two curves were identical for large values of Π (the pressure is measured from Π_c). The graph also shows the theoretical dependence of Π on $\Delta S/S_0$ during the stretching of the monolayer that was first compressed to a pressure $\Pi_0 = 3$ dyn/cm (downward portion of curve 2).

Section 1 exploits this approach to calculate compression isotherms and cooling isobars for a monolayer in the phase stratification region. Figure 2 shows that experimental and theoretical (curve 1) compression isotherms for a particular case (the data are taken from Ref. 2).

The same model is used in Sec. 2 to examine hysteresis under compression and expansion of a monolayer in the phase stratification region. The origin of this can be traced to irreversible plastic strain that appears on compression and extension of the monolayer. The work expended on plastic deformation is equal to the area of the hysteresis loop on the pressure-area plane.

It is important to note that only dense monolayer phases (solid and liquid) can be looked upon as two-dimensional systems. Despite the negligible solubility, the number of SAM molecules in the bath of the Langmuir balance can be greater by an order of magnitude than in the monolayer itself. However, it has now been shown[1] that the dense phase contains a barrier formed by the self-consistent field of the monolayer molecules, which prevents the exchange of dissolved molecules between the monolayer and the tenuous gas, so that the number of molecules in the monolayer may be looked upon as constant.

§ 1. FREEZING OF A LIQUID MONOLAYER

Consider the freezing of a liquid monolayer at constant temperature T, and let us determine the shape of the isotherms in the phase stratification region. We shall assume that the monolayer is in the form of a circle and that the freezing of the liquid monolayer begins on its boundary, i.e., on the walls of the container. The onset of the phase transition as the pressure increases on the pressure area plane corresponds to a surface pressure $\Pi_c = \Pi_c(T)$, which is equal to the equilibrium pressure in homogeneous phases at temperature T. Let S_1 and S_2 be the monolayer areas per molecule in the uniform solid and liquid phase at $\Pi = \Pi_c$, respectively. As already noted, the relative area discontinuity $\gamma = (S_2 - S_1)/S_2$ may be looked upon as small, which enables us to use the linear theory of elasticity. The main parameters that are measured in practice are the surface pressure Π_e applied to the monolayer from outside and the monolayer area per molecules S. Let the radius of the monolayer for $\Pi_e = \Pi_c$ (when it is still in the liquid phase) be denoted by R_0. The monolayer radius for a given running value of Π_e will be denoted by L, which is also the external radius of the solid phase. The inner radius of the solid phase will be denoted by R; the region $r < R$ will remain liquid. For simplicity, pressures will be measured from Π_c, i.e., we shall suppose that $\Pi_c = 0$. Our aim is to determine the shape of the functions $L(\Pi_e)$ and $R(\Pi_e)$.

In the axially symmetric case, the two-dimensional stress tensor is determined by the two functions $\Pi(r)$ and $\tau(r)$:

$$\sigma_{ik}(r) = -\Pi(r)\delta_{ik} + \tau(r)(\delta_{ik} - 2n_i n_k). \tag{1}$$

The first term describes the hydrostatic pressure and the second the pure shear stress. The quantity $\sigma_{rr} = -\Pi - \tau$ must be continuous across separation boundaries. To obtain a further boundary condition, we must consider the freezing of the successive particles of the liquid phase. The resulting solid-phase particle must have the minimum possible thermodynamic potential under the given conditions. Since elastic stresses appear in the expression for the thermodynamic potential in the form of a positive-definite quadratic form, the resulting solid phase does not contain them, i.e., $\tau(R) = 0, \Pi(R) = 0$. A more detailed quantitative derivation of this condition is given in Sec. 2.

Consider a monolayer under external pressure $\Pi_e > 0$ such that all the strains are puely elastic. When the external pressure increases by the small amount $d\Pi_e$, the solid-phase particles receive radial displacements $du(r)$ and a certain number dn of the molecules transfer from the liquid to the solid phase. The area of the liquid spot changes by the amount

$$S_2 dn = -2\pi R dR.$$

The same dn molecules occupy the area $S_1 dn$ in the solid state. The condition of continuity across the solid-liquid interface enables us to relate dn to the displacement $du(r)$ of the solid phase at $r = R$:

$$2\pi R du(R) = (S_2 - S_1) dn.$$

Eliminating dn, we obtain $du(R) = -\gamma dR$.

We must now determine the elastic stresses in the solid phase. The equation $\partial\sigma_{ik}/\partial x_k = 0$ imposes the following condition on Π and τ:

$$\Pi'(r) + \tau'(r) + \frac{2\tau(r)}{r} = 0. \tag{2}$$

Instead of the displacements $du(r)$, we now have the increments $d\sigma_{ik}(r, R)$ in the stress tensor. In linear theory of elasticity, these increments do not depend on stresses already present in the solid (this is the Colonetti theorem). It follows that $d\Pi(r, R)$ and $d\tau(r, R)$ are related to du by Hooke's law and obey Eq. (2). To find the boundary conditions for $d\Pi$ and $d\tau$, we write the complete stress tensor σ_{ik} as a function of r and R. We then find that $\sigma_{rr}(R, R) \equiv 0$ since the pressure in the liquid phase is constant and equal to Π_c, whereas $\tau(R, R) = 0$ in accordance with the preceding discussion. Hence,

$$\begin{gathered} -d\Pi(R, R) - d\tau(R, R) = d\sigma_{rr}(R, R) = \sigma_{rr}(R, R) \\ -\sigma_{rr}(R, R - dR) = -\partial\sigma_{rr}/\partial r(R, R)\, dR = 0, \end{gathered} \tag{3}$$

since, according to (2),

$$\partial\sigma_{rr}/\partial r(R, R) = 2\tau(R, R)/R = 0.$$

Using the second boundary condition

$$d\sigma_{rr}(L, R) = -d\Pi_e$$

we obtain

$$\begin{gathered} d\Pi(r, R) = d\Pi_{\text{в}}/(1 - R^2/L^2), \\ d\tau(r, R) = -d\Pi_e (R/r)^2 (1 - R^2/L^2), \\ du(r, R) = -{}^1\!/_2 d\Pi_e [1/K + (R/r)^2/\mu] R/(1 - R^2/L^2), \end{gathered} \tag{4}$$

where K is the bulk modulus of the solid phase and μ is its shear modulus. We have already shown that

$$du(r, R)|_{r=R} = -\gamma dR,$$

so that

$$d\Pi_e = -2\gamma K'(1 - R^2/L^2)\, dR/R, \qquad K' \equiv K\mu/(K + \mu).$$

Integration of (4) with respect to R between r and R yields

$$\begin{gathered} \tau(r, R) = \gamma K'(1 - R^2/r^2), \qquad \Pi(r, R) = 2\gamma K' \ln(r/R), \\ u(r, R) = r[\gamma K' K^{-1} \ln(R/r) + {}^1\!/_2 \gamma (K'/K - 1)(1 - R^2/r^2)]. \end{gathered} \tag{5}$$

The two measured quantities are then given by

$$\begin{gathered} \Pi_e = -\sigma_{rr}(R_0) = 2\gamma K' \ln(R_0/R) - \gamma K'(1 - R^2/R_0^2), \\ S = S_2(1 + 2\gamma K' K^{-1} \ln(R/R_0) - \gamma K'(1 - R^2/R_0^2). \end{gathered} \tag{6}$$

These two equations determine the dependence of S on Π_e in parametric form. If we suppose that $1 - R/R_0$ is small, we may write

$$\Pi_e = 2\gamma K'(1 - R/R_0)^2, \qquad S = S_2[1 - 2\gamma(\Pi_e/2\gamma K')^{1/2}].$$

The first equation in (5) shows that, as Π_e increases (and R decreases), the shear stresses will also increase, reaching their maximum on the outer boundary of the monolayer. However, the modulus of the quantity $\tau(r)$ cannot exceed ε—the plastic threshold for the monolayer. This means that (5) and (6) are valid for $\Pi_e \leqslant \varepsilon^2/2\gamma k'$.

As an example, let us consider the data reported in Ref. 2 on egg lecithin monolayers: At $T = 303$ K, we have $\gamma = 0.18, S_1 = 51\ \text{Å}^2, K = 330$ dyn/cm. The quantities ε and

μ were not measured, but μ can be estimated from the shear modulus obtained by Nelson and Halperin[9] for a two-dimensional crystal with a triangular lattice on a smooth substrate at the melting point. The transition examined by Nelson and Halperin was due to the breaking of dislocation pairs and the appearance in the crystal of single free dislocations. It is readily seen that the value of the shear modulus of the crystal at the melting point is then the minimum possible at a given temperature. For low shear moduli, the bonding energy of the dislocation pair will also be lower and its decay will be thermodynamically convenient. Since the SAM molecules have a large number of conformations, this result is only an order of magnitude estimate, yielding $\mu \sim 100$ dyn/cm for the egg lecithin monolayer. The quantity ε can be estimated by comparing our calculations with experimental data (see below) for the concluding stage of monolayer compression, when the fraction of the liquid phase is small and the shape of the boundary has no significance. We have found that ε is small: $\varepsilon = 1.1$ dyn/cm. Substituting numerical values, we find that the pure elastic compression of the monolayer occurs only for $\Pi_e < 0.1$ dyn/cm. Currently available experimental precision means that this region is not accessible to experimental investigation.

Further increase in the pressure $\Pi_e > \varepsilon^2/2\gamma K'$ ensures that a plastic strain zone with an inner radius R' appears near the outer edge of the solid phase. For $r \leqslant R'$ the formulas given by (5) and obtained for elastic stresses and displacements are valid. The condition $|\tau(r)| = \varepsilon$ should be satisfied at $r = R'$ and hence

$$R'^2=R^2/(1-\varepsilon/\gamma K'). \qquad (7)$$

In the plastic deformation zone, we have Eq. (2) as before, but the theory of elasticity is not valid. We shall use the condition $|\tau| \equiv \varepsilon$, i.e., $\tau \equiv -\varepsilon$ as the second equation for Π and τ. Solving Eq. (2) subject to $\sigma_{rr}(R_0) = -\Pi_e$, we then obtain for $r \geqslant R'$

$$\Pi(r)=2\varepsilon \ln(r/R_0)+\Pi_e+\varepsilon.$$

The pressure $\Pi(r)$ should be continuous at $r = R'$ therefore

$$2\gamma K' \ln(R'/R)=2\varepsilon \ln(R'/R_0)+\Pi_e+\varepsilon.$$

The dimensionless plastic deformation parameter $\varepsilon/\gamma K'$ is small (it is of the order of 0.1) and the retention of terms of the order of ε^2 within the framework of the linear theory of elasticity would take us outside attainable precision. In view of this, we find from (7) that

$$R'=R_0 \exp(-\Pi_e/2\varepsilon), \qquad R=(1-\varepsilon/2\gamma K')\exp(-\Pi_e/2\varepsilon). \quad (8)$$

In the absence of stresses, the areas of the ring $R' < r < R_0$ should be $\pi(R_0^2 - R'^2)(1-\gamma)$. Because of deformation, this area is equal to $\pi[L^2 - R'^2 - 2R'u(R')]$. The variation in the area is described by

$$\pi[L^2-R_0^2+\gamma R_0^2-\gamma R'^2-2R'u(R')]=-\int_{R'}^{R_0} 2\pi K^{-1}\Pi(r)\,r\,dr.$$

Solving this for L^2, we obtain

$$L^2=R_0^2(1-\gamma)+R_0^2[\gamma \exp(-\Pi_e/\varepsilon)-\Pi_e/K]. \qquad (9)$$

The dependence of the area S on the applied pressure Π_e is

$$S=S_2[1-\gamma+\gamma \exp(-\Pi_e/\varepsilon)-\Pi_e/K]. \qquad (10)$$

Figure 2 (curve 1) shows a graph of this function together with the experimental curve (taken from Ref. 2). Figure 1 shows the measured function $S(\Pi_e)$ for different temperatures. Since the experiments were performed on rectangular monolayers, quantitative comparison is possible only for $\exp(\Pi_e/\varepsilon) \gg 1$ when the liquid phase is well away from the monolayer boundary and the shape of the boundary is immaterial. It is also important to note that compression of the monolayer is not all-sided and occurs in only one direction. The theoretical function $S(\Pi_e)$ was constructed for $T = 303$ K.

Let us now examine the freezing of the monolayer at constant pressure $\Pi_e = \Pi_c$. When the monolayer temperature is reduced to $T - \delta T$, the pressure corresponding to equilibrium between homogeneous liquid and solid phases changes in accordance with the Clausius-Clapeyron equation by the amount

$$\delta\Pi=-\varkappa\delta T/\gamma S_2 T,$$

where $\varkappa$ is the heat of transition per molecule. We thus arrive at a problem that has already been solved, in which the external pressure exceeds the pressure of equlibrium between homogeneous phases in the monolayer by a given amount. Consequently, the equation for the monolayer cooling isobar is obtained from (10) by substituting $\delta\Pi$ for Π_e.

§ 2. HYSTERESIS DURING COMPRESSION AND EXPANSION OF A MONOLAYER

Consider a monolayer compressed to the pressure $\Pi_0 > 0$ (the pressure is measured from Π_c) and let us begin to stretch slowly, gradually reducing the pressure. The monolayer temperature is constant and equal to T.

Plastic deformations described in Sec. 1 occur when the monolayer is compressed. They are irreversible and the heat expended in producing them is dissipated into heat. Because of plastic deformations, the monolayer relaxes partially to a new radius $L(\Pi_0)$ so that to stretch it to its initial radius R_0, we must supply energy to produce the reverse deformation. Hence, compression and stretching of the monolayer to the same area corresponds to different stresses inside the monolayer and different values of the liquid-phase radius. The area of the hysteresis loop on the (Π_e, S) plane is equal to the energy expended in plastic deformation of the monolayer and dissipated into heat.

Let us now take the state of the monolayer for $\Pi_e = \Pi_0$ as the undeformed state, so that the stretching of the monolayer may be looked upon as a consequence of an externally applied negative pressure $\Pi = \Pi_e - \Pi_0$, where Π_e is the current external pressure. Since we are neglecting the dependence of elastic moduli on stress and the terms that are quadratic in strains, the presence of stresses and strains at $\Pi_e = \Pi_0$ has no effect on the response of the system to the external agency (Colonetti's theorem). In calculations of the change in monolayer area, they can be neglected when the equations of the theory of elasticity are written down, and they appear only in the initial conditions for these equations.

Let us examine in detail the conditions on the boundary between the liquid and solid phases. In equilibrium, the change in the thermodynamic potentials of the two phases during the transition of one particle from the liquid to the solid phase and back again must be zero. In this situation the quantity ${}^4f + \Pi' S$ plays the role of the thermodynamic potential in calculations per molecule, where f is the free energy per molecule and Π' is the liquid phase pressure. The free energy f includes the shear stress energy (in the solid phase).

Shear stresses vanish when one particle undergoes a transition from the solid to the liquid phase. As a result, the change in the thermodynamic potential on melting turns out to be

$$\Delta\varphi_{12}=\varphi_1(\Pi_c)-\varphi_2(\Pi_c)+S_1[-(\Pi')^2/2K_1+\tau^2(R)/2K'-\gamma\Pi'+(\Pi')^2/2K_2], \tag{11}$$

where $\Pi(R)$ and $\tau(R)$ are, respectively, the pressure and shear stress in the solid phase on the boundary with the liquid, and we are using the boundary condition $\Pi' = \Pi(R) + \tau(R)$; φ_2 and φ_1 are the chemical potentials of the homogeneous liquid and solid phases, respectively. At the same time, $\Delta\varphi_{12}$ is the change in the thermodynamic potential when the liquid freezes with a given $\Pi(R)$ and $\tau(R)$. Hence, it is clear that the formation of the solid phase with $\tau \neq 0$ is thermodynamically inconvenient.

When the liquid freezes, shear stresses in the newly frozen layer are initially zero. Consequently, the change in the thermodynamic potential on freezing is

$$\Delta\varphi_{21}=\varphi_2(\Pi_c)-\varphi_1(\Pi_c)+S_1[\gamma\Pi'+(\Pi')^2/2K_1-(\Pi')^2/2K_2],$$

where K_1 and K_2 are the bulk moduli of the solid and liquid phases.

From the condition $\Delta\varphi_{12} = \Delta\varphi_{21} = 0$, and since $\varphi_1(\Pi_c) = \varphi_2(\Pi_c)$ at temperature T, we find that $\tau(R) = 0$, $\Pi(R) = 0$ on the boundary between the solid and liquid phases under the conditions of equilibrium. Hence, if, as a result of some process, the stress τ on the phase separation boundary is not zero, this will be followed by freezing or recrystallization of the solid ring in which τ will smoothly fall to zero. The stresses and strains in this ring are described by the equations (5) of Sec. 1.

The problem reduces to the determination of the stretching of the monolayer under the action of the negative external pressure $\Pi_1 = \Pi_e - \Pi_0$. The true stress tensor will then be equal to the sum of the stress tensor that arises on stretching and the stress tensor prior to stretching. New plastic deformation will arise if the resultant shear stress parameter $\tau(r)$ reaches ε. Let the running radius of the liquid phase be ρ (we have introduced a different symbol in order to avoid confusion in the formulas of Sec. 1). The radius of the liquid monolayer for $\Pi_e = \Pi_c$ will, as before, be represented by R_0. We recall once again that the state of the monolayer for $\Pi_e = \Pi_0$ is taken to be undeformed, i.e., all the stresses and strains to be calculated are increments on existing stresses and strains. All the quantities referring to the monolayer state at $\Pi_e = \Pi_0$ will therefore be labeled with the superscript (0) and quantities referring to the stretching of the monolayer will be indicated by the superscript (1).

A gradual increase in the radius of the liquid phase will occur as Π_e is reduced. Melting can be divided into three segments, described in general by different equations. The elastic stress zone present at $\Pi_e = \Pi_0$ melts on the first segment. The plastic deformation zone remains unaltered during this process and there is no recrystallization of the solid ring mentioned above. The resulting deformation is purely elastic. The plastic deformation zone melts on the second segment, but the resulting additional deformation remains purely elastic. The width of the recrystallized ring gradually increases from zero during this process. New plastic deformation appears in the solid phase on the third segment.

In the first approximation in $\varepsilon/\gamma K'$, the first and second segments of melting can be examined together, since melting can then be neglected. In fact, it is readily shown that the change in the radius of the liquid phase and in the width of the recrystallized ring is, in both cases, of the order of $R^{(0)}\varepsilon/\gamma K'$, and can be neglected. The problem reduces to the determination of the stretching of the ring with given inner and outer radii. The change in the area of the monolayer per molecule is

$$\Delta S=S_2(\Pi_0-\Pi_e)\,[e^{-\Pi_0/\varepsilon}(K')^{-1}/(1-e^{-\Pi_0/\varepsilon})+1/K_1]. \tag{12}$$

This formula is valid for

$$\Pi_0-\Pi_e<2\varepsilon\,[1-\exp(-\Pi_0/\varepsilon)],$$

and the first segment of melting ends at

$$\Pi_0-\Pi_e=\varepsilon\,[1-\exp(-\Pi_0/\varepsilon)].$$

Let us now consider the third segment of melting when new plastic deformations arise as the monolayer is stretched. The plastic deformation zone occupies the region $r<\rho'$, since shear stresses now increase from the boundary toward the monolayer center. It is surrounded by the recrystallized ring in which the shear stresses fall to zero in accordance with (5). The displacement vector $u^{(1)}(r)$ is determined only for $r>\rho'$, i.e., in the elastic strain zone, where

$$\sigma_{ik}^{(1)}=-\Pi^{(1)}\delta_{ik}+2\mu b r^{-2}(\delta_{ik}-2n_i n_k),$$
$$u^{(1)}(r)=-\Pi^{(1)}r/2K+b/r,$$

as is usual for planar problems in the theory of elasticity. In the plastic deformation zone, $r<\rho'$, we can readily show that

$$\Pi^{(1)}(r)=\Pi^{(1)}-4\varepsilon\ln(r/\rho'),\qquad \tau^{(1)}(r)=2\varepsilon.$$

It follows from (5) that $\sigma_{rr} \sim \varepsilon^2/\gamma K'$, $u(r) \sim r\varepsilon/K'$ on the outer boundary of the recrystallized ring, i.e., these quantities can be neglected. This leads to the following three boundary conditions for stresses and displacements on the inner and outer boundaries of the solid phase:

$$\sigma_{rr}^{(1)}(R_0)=-\Pi_1,\qquad \sigma_{rr}^{(1)}(\rho)+\sigma_{rr}^{(0)}(\rho)=0,\qquad \delta\rho^{(1)}+\delta\rho^{(0)}=0, \tag{13}$$

where $\delta\rho^{(0)}$ and $\delta\rho^{(1)}$ are the changes, respectively, for $\Pi_e = \Pi_0$ and for the running value of Π_e in the radius of the circle containing particles with $r<\rho$ for $\Pi_e = \Pi_c$ (i.e., in the liquid state). The equation for $\delta\rho^{(1)}$ can be written in the same way as for δR_0 in the derivation of (9) in Sec 1:

$$2\pi[\rho' u^{(1)}(\rho')-\rho\,\delta\rho^{(1)}]=-K^{-1}\int_\rho^{\rho'}\Pi^{(1)}(r)\cdot 2\pi r\,dr.$$

An analogous equation can be written down for $\delta\rho^{(0)}$ if we use the results of Sec. 1. The result is that the equations given by (13) reduce to two equations:

$$\Pi^{(1)}-\Pi_1=2\varepsilon \exp[-(\Pi^{(1)}+\Pi_0+2\varepsilon)/2\varepsilon]\rho/R_0,$$
$$(\Pi^{(1)}-\Pi_1)/K'+\gamma \exp(-\Pi_0/\varepsilon)-\gamma\rho^2/2R_0^2=0.$$

The change in the monolayer area per molecule is

$$\Delta S^{(1)}=S_2[2u^{(1)}(R_0)/R_0].$$

Let us represent $\Pi_1-\Pi^{(1)}$ by y, so that the dependence of $\Delta S^{(1)}$ on Π_e is given in the following parametric form:

$$\begin{aligned}\Delta S^{(1)}&=S_2[(\Pi_0-\Pi_{\text{B}})/K_1+y/K'],\\ \Pi_e&=2\varepsilon[\ln(2\varepsilon/y)+{}^1/_2\ln(y/\gamma K'+e^{-\Pi_0/\varepsilon})]+y-2\varepsilon,\end{aligned} \tag{14}$$

The minimum of Π_e occurs for the value of y given by

$$y_0={}^1/_2\varepsilon[1-\nu+(1+6\nu+\nu^2)^{1/2}],\quad \nu=\gamma K'\varepsilon^{-1}e^{-\Pi_0/\varepsilon}. \tag{15}$$

The minimum value of Π_e is negative. When $\Pi_e<\Pi_e(y_0)$, the liquid and solid phases cannot coexist in the monolayer and still remain at rest. From the point of view of the theory of elasticity, this corresponds to the disintegration of the solid-phase ring under large stretching loads. After this, the monolayer assumes complete equilibrium under the given Π_e, i.e., it assumes the homogeneous liquid state.

When (14) and (15) are compared with experiment, it must be remembered that intensive formation of nuclei on dislocations and other crystal-lattice defects occurs for negative Π_e. These nuclei reduce the elastic moduli of the solid phase and its plastic threshold.

The ideas developed in Sec. 1 can readily be used to obtain the temperature dependence of the area for a monolayer cooled down to temperature $T_0<T_c$ and subsequently gradually heated: all that needs to be done is to replace Π_e in (14) and (15) with $\varkappa(T_c-T)/\gamma S_2 T_c$ and Π_0 with $\varkappa(T_c-T_0)/\gamma S_2 T_c$.

There is very little published experimental information on hysteresis in monolayers. The functions $S(\Pi_e)$ reported in Ref. 10 for monomolecular layers of insoluble polymers are in quantitative agreement with our results.

§ 3. DISCUSSION

To facilitate calculations, we have introduced a relatively stringent limitation on the structure of the freezing monolayer. The true structure may differ from that assumed in our axially symmetric model. It can be determined by observing under a microscope the Brownian motion of fine impurity particles deposited on the monolayer, or by following the distribution of radioactive traces added to the SAM. Both methods can be used to identify regions occupied by the liquid and solid phases, since the mobility of the Brownian particles in the solid is much smaller than in the liquid, and the density of the radioactive tracer is proportional to the local density of the monolayer. The structure of a monolayer consisting of several spots of liquid phase can lead to a change in the coefficients in (6), (12), and (14), which give the monolayer area as a function of external pressure. This also applies to the change in the geometry of the experimental situation.

The interphase tension energy was neglected in our calculations. The consequence of this was that, as indicated by (8) and (10), an infinite pressure has to be applied to achieve complete freezing of the monolayer. It must, however, be remembered that inclusion of interphase tension in the case of a sufficiently small liquid spot will make it unstable with respect to a transition to the liquid phase.

The results of Sec. 1 show that a frozen monolayer has a nonuniform distribution of elastic stresses over its area which remains even after all the liquid-phase spots have disappeared. This nonuniformity should be observable.

We have not considered the melting of a uniform solid monolayer. Work on the melting of three-dimensional crystals[4–6] has shown that, to produce a liquid-phase nucleus, the crystal must be heated to a temperature $T'>T$ or the pressure must be reduced to $\Pi_c'<\Pi_c$. This hysteresis is due to the loss of a certain amount of free energy that is incurred in forming the deformations surrounding the liquid-phase nucleus in the crystal. It would have been possible to develop a theory analogous to the three-dimensional treatment, but quantitative results are impossible to obtain because the formation of these nuclei is sensitive to the presence of impurities, dislocations, and to the interaction between them.

Before a quantitative comparison of our results with experimental data can be made, it will be necessary to give the monolayer a circular shape and to apply pressure to its entire perimeter. This problem was solved in Refs. 7 and 8. However, the method used there to measure the surface pressure (by measuring the velocity of capillary waves and using the Rayleigh formula) does not seem to be fully justified. The Rayleigh formula was derived for waves on the surface of a uniform medium and may not be valid in the case of the monolayer water system.

It may be possible to obtain a quantitative confirmation of the above results by investigating SAM films on the surface of an expanding sphere or even the usual soap bubbles. The quantities ε and μ can be measured directly by a slightly modified form of the Langmuir balance. However, such experiments have not as yet been performed.

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