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Layering transition in confined molecular thin films: Nucleation and growth

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When a fluid is confined between two molecularly smooth solid surfaces (e.g., mica surfaces) it tends to form layers of molecular thickness parallel to the surfaces. We study the process of the squeezing out of a monolayer as a function of an applied normal pressure. We estimate the pressure necessary to "nucleate" the thickness transition ($n \rightarrow n-1$, where n is the number of monolayers) and study the "growth" or "spreading" of the removal process after the nucleation has occurred.

I. INTRODUCTION

The properties of liquids confined within very small spaces, such as narrow pores or thin films, are generally quite different from their bulk properties. It has been found that the molecules become progressively more ordered in films with thickness less than about ten molecular diameters.[1-3]

The liquid density across molecular thin films is not uniform but has an oscillatory profile. The periodicity of the oscillations is close to the diameter of the liquid molecules and reflects the forced ordering of the liquid molecules into quasidiscrete layers between the two surfaces, see Fig. 1(a). The closer the two surfaces approach each other, the sharper these density oscillations become. Furthermore, for $n \sim 5-10$ layers and below, the fluid slab usually solidifies. This manifests itself through a finite shear stress τ necessary in order to slide the two surfaces relative to each other.

As a result of the layering of the molecular slab, many properties of the system exhibit "quantization". A classical example of layer-by-layer quantization is given by adsorption isotherms at temperatures below roughening. In the present case, if the normal load or pressure is varied, it is found that the thickness of the slab changes in a steplike manner, see Fig. 1(b). An increasingly strong pressure P is necessary to squeeze out layer after layer of the "fluid" from the interface and, in fact, it is often not possible to squeeze out the last layer or two of trapped molecules. During the transition from $n \rightarrow n-1$ layers, the film, or at least the layer being squeezed out, is believed to be in a melted or fluidized state.[2]

Another quantized property is the yield stress τ (the tangential stress necessary in order to initiate the sliding of the two surfaces relative to each other), which depends on the number of molecular layers in the film.[2] For more than $n \sim$ ten monolayers, the yield stress is usually zero, as expected for a fluid, but for thinner films a finite yield stress $\tau(n)$ is observed; furthermore, $\tau(n)$ increases monotonically as the number of monolayers n decreases and may be very high when $n=1$. The finite yield stress indicates that "inplane" ordering must occur in the monolayers, where, in particular, the molecules in contact with the solid surfaces "adjust" to the corrugated substrate potentials forming pinned solid adsorbate structures. (If ideally incommensurate solid adsorbate structures would be formed instead, they would experience a negligible

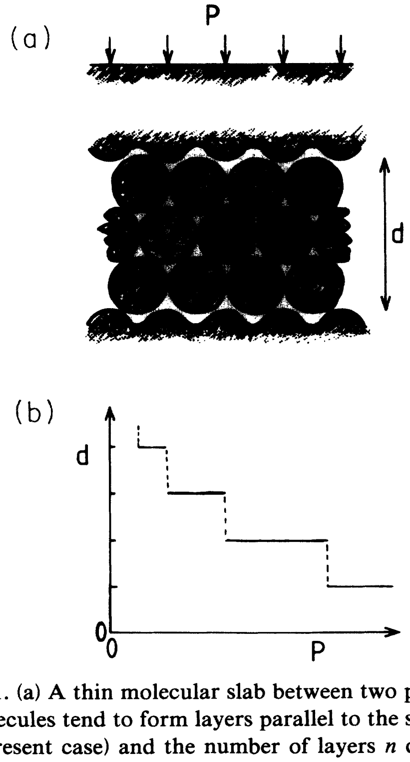

FIG. 1. (a) A thin molecular slab between two plane surfaces. The molecules tend to form layers parallel to the surfaces ($n=3$ in the present case) and the number of layers n depend on the external pressure P. (b) The variation in the thickness of the molecular film depends in a quantized manner on the pressure P.

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pinning potential[4] resulting in zero yield stress, contrary to experimental observations.)

As stated above, it is often not possible to squeeze out the last layer or two of trapped molecules. The reason for this is related to the solid nature of the adsorbate layers and to the fact that these are pinned by the substrate potential. But, if a large enough shear stress is applied the adsorbate layer may shear melt (in which case the two solid surfaces would move laterally relative to each other); in this case, it may be possible to squeeze out the last one or two monolayers as well. Furthermore, if a given normal pressure results in, say, n monolayers when the shear stress equals zero, then if the surfaces are forced to move laterally relative to each other, one or several further monolayers may be squeezed out as a result of the fluidization of the film during sliding.

The processes discussed above are likely to be of fundamental importance in boundary lubrication.[5,6] Since most macroscopic bodies have a rough surface, at least on a microscopic scale, when, say, a steel block is resting on a steel substrate, very high normal pressures will result in the "contact points" (junctions) between the two bodies. This will, in general, result in plastic deformation of the metals at the contact points in such a manner that each junction will be in a state of incipient plastic flow.[5] The normal pressure at a junction will, therefore, be close to the largest compressive stress σ_c (the penetration hardness) that the material can bear without plastic yielding. This, for steel, equals $\sigma_c \sim 10^9$ N/m^2. Now, if a lubricant is present between the two solid surfaces, the fundamental question is whether the very high local normal pressures will squeeze out the film completely (which would lead to a high sliding friction and large wear), or whether one monolayer (or more) of lubricant molecules will remain in the contact areas. For many lubricant molecules, the latter must be the case, since it is known that the presence of lubricant reduces the sliding friction at low sliding velocities (boundary lubrication) by a factor of 10 or so, while the wear may be reduced by several orders of magnitude.

In this paper, we study the nature of the film thickness transition $n \to n-1$ under the assumption that the layer to be squeezed out is in a two-dimensional fluid state. We calculate the "speed" of "squeezing out" and compare it with the experimental data of Gee, McGuiggan, and Israelachvili.[2] We also discuss the nature of the "nucleation" of the film thickness transition.

II. THEORY

We consider the layering transition $n=2 \to 1$ for which experimental information is available for, e.g., the liquid octamethylcyclotetrasiloxane (OMCTS) (a silicone liquid with approximately spherical molecules with diameter ~ 8.5 Å) between two flat mica surfaces.[2] We assume that the layer to be squeezed out is in a fluid state, which is the case if the two mica surfaces are in a relative parallel motion. Finally, we assume that the layering transition is initiated by a nucleation. A small circular region with $n=1$ is assumed to first nucleate somewhere in the contact region followed by a "spreading" or "growth" of the $n=1$ region and a corresponding decrease of the $n=2$ region so that the total area $A_{n=1}+A_{n=2}=A_0$ is a constant. We consider first the nucleation process and then the growth process.

A. Nucleation

We consider a perfect system with no imperfections, e.g., steps, on the two solid surfaces. The two confined molecular monolayers are laterally in a fluid state, but normally very well defined. Assume now that due to a thermal fluctuation a small circular hole is formed in the uppermost two-dimensional fluid layer. If R denotes the radius of the "hole" the adiabatic work to form the hole is the sum of three terms

$$U(R)=2\pi R\Gamma+\pi R^2 p_0-\alpha R^3 . \tag{1}$$

The first term $2\pi R\Gamma$ represent the free energy associated with the unsaturated bonds of the molecules at the periphery of the hole (Γ is a "line tension"). The second term $\pi R^2 p_0$ is the change in the interface free energy. If γ_s, γ_{lv} and γ_{sl} denote the solid-vacuum, liquid-vapor, and solid-liquid interface free energies, then $p_0=\gamma_s-\gamma_{\text{lv}}-\gamma_{\text{sl}}$. The two-dimensional pressure p_0 is usually called the spreading pressure.[7-9] For organic molecules on metal oxides, one has typically $p_0 \sim 4$ meV/Å^2. The third term in (1), $-\alpha R^3$, is an elastic relaxation energy, namely when a hole has been formed, the two solid confining materials will deform elastically as indicated in Fig. 2; this relaxation energy will tend to stabilize the hole. It will be shown below that the elastic relaxation energy scales with the radius of the hole as $\sim R^3$ and will, therefore, for a large enough hole, dominate over the interface energy term. Furthermore, we show below that $\alpha \sim P_0^2$ where P_0 is the (three-dimensional) pressure acting on the two solid bodies. The probability for a hole with the radius R to be formed by a thermal fluctuation is proportional to the Boltzmann factor

$$e^{-U(R)/k_B T} ,$$

where T is the temperature and k_B the Boltzmann constant. If R_c denote the critical radius, i.e., the radius for which $U(R)$ is maximal, the probability rate w of nucleation of the $n=1$ "phase" will be (see Appendix A)

$$w=w_0 e^{-U(R_c)/k_B T} . \tag{2}$$

From (1), we get

$$2\pi\Gamma+2\pi R_c p_0-3\alpha R_c^2=0 \tag{3}$$

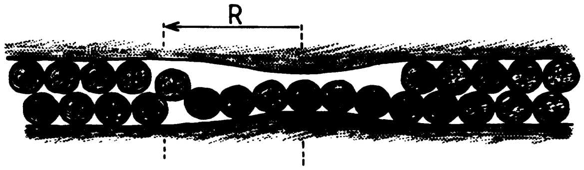

FIG. 2. A thermal fluctuation has created an $n=1$ nucleus (radius R) in an $n=2$ fluid layer. Because of the external pressure P, the surfaces of the elastic solids expand (relax) into the hole as indicated.

and

$$U(R_c)=\pi R_c^2 p_0/3+4\pi R_c\Gamma/3 \ . \tag{4}$$

In Appendix A, it is shown that in the present context $w_0\sim 10^{17}$ s^{-1}, and if we formally define nucleation to occur when $w\sim 0.01$ s^{-1} (i.e., about one nucleus per minute) then it follows from (2) that nucleation will occur when $U(R_c)/k_BT=\kappa$, where $\kappa\approx 44$.

Let us now evaluate the coefficient α in the elastic relaxation energy. We will treat the two solid bodies as isotropic elastic media, which certainly is not a good approximation for mica but a reasonable approximation for most "practical" cases, e.g., for most metals and metal oxides. Now, before the hole has been opened up, the $n=2$ monolayers must exert a normal pressure P_0 on the upper and lower elastic bodies. After the hole (radius R) has been opened up, the pressure on the solid bodies is assumed to be zero for $0<r<R$, where $r=0$ is the origin of the circular hole. For $r>R$, the normal pressure will be some function of r, $P=P(r)$ where $P(r)\to P_0$ as $r\to\infty$, and with

$$2\pi\int_R^\infty dr\, r[P(r)-P_0]=\pi R^2 P_0 \ ,$$

so that the total normal force (the "load") on the elastic body is unchanged. In principle, the function $P(r)$ (for $r>R$) can be determined from the theory of elasticity. The solution depends on the boundary conditions for $r>R$. In the literature, two limiting cases have been studied.[10] In the present context, we assume that the parallel (or tangential) stress vanishes everywhere on the elastic bodies. In this case, $P(r)$ is approximately given by[10]

$$P(r)=P_0+\tfrac{1}{2}P_0R[(r^2-R^2)^{-1/2}-r^{-1}] \tag{5}$$

for $r>R$. If u_0 and $u(\mathbf{x})$ denotes the normal displacement fields of the "upper" elastic solid at the surface contacting the $n=2$ layer, before and after opening up the hole, respectively, then the elastic relaxation energy associated with the upper solid body can be written as

$$U_{\mathrm{el}}=\tfrac{1}{2}\int d^2x[P(\mathbf{x})u(\mathbf{x})-P_0u_0] \ . \tag{6}$$

But for an isotropic elastic medium[11]

$$u(\mathbf{x})=\frac{1-\sigma^2}{\pi E}\int d^2x'\frac{P(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \ , \tag{7}$$

where E is Young's modulus and σ the Poisson's ratio. Substituting (7) in (6) gives

$$U_{\mathrm{el}}=-\frac{1-\sigma^2}{2\pi E}\int d^2x\, d^2x'\frac{1}{|\mathbf{x}-\mathbf{x}'|}[P_0^2-P(\mathbf{x})P(\mathbf{x}')] \ . \tag{8}$$

If we write $P(\mathbf{x})=P_0+P_0f(r/R)$ where

$$f(\xi)=-1 \quad \text{for} \quad \xi<1$$

and

$$f(\xi)=\tfrac{1}{2}[(\xi^2-1)^{-1/2}-\xi^{-1}] \quad \text{for} \quad \xi>1 \ ,$$

then it is easy to show that (8) reduces to

$$U_{\mathrm{el}}=(1-\sigma^2)P_0^2IR^3/E \ , \tag{9}$$

where I is a number,

$$I=\int_0^\infty d\xi\, d\xi'\int_0^{2\pi}d\phi\frac{\xi\xi' f(\xi)f(\xi')}{(\xi^2+\xi'^2-2\xi\xi'\cos\phi)^{1/2}}\approx 1.4 \ .$$

However, not only the upper elastic body will relax when the hole opens up, but so will the lower body. We can take this into account by doubling I; hence we will use $I=2.8$ below. Any other reasonable choice of $f(\xi)$ [i.e., of $P(r)$] would give a small numerical change of the integral I, but would not change the general form of (9). Using (9) we obtain

$$\alpha=(1-\sigma^2)P_0^2I/E \ . \tag{10}$$

In Fig. 3, we show the general form of $U(R)$ for two different external pressures P_1 and $P_0>P_1$. If P is increased, from some low value, both R_c and $U(R_c)$ decrease. The transition $n=2\to 1$ will nucleate when $U(R_c)/k_BT=\kappa$. In the present case, $\kappa\approx 44$ (see Appendix A).

Using (4) we get the nucleation condition

$$\pi R_c^2p_0/3+4\pi R_c\Gamma/3\approx\kappa k_BT$$

or

$$R_c\approx-\frac{2\Gamma}{p_0}\pm\left[\frac{4\Gamma^2}{p_0^2}+\frac{3\kappa k_BT}{\pi p_0}\right]^{1/2} \ , \tag{11}$$

where the $+$ and $-$ sign refer to $p_0>0$ and $p_0<0$, respectively. At room temperature ($k_BT\approx 25$ meV) and for organic molecules on mica ($p_0\approx 2$ meV/Å^2), $\Gamma\approx 10$ meV/Å (we estimate Γ from the product of the liquid-vapor surface free energy γ_l and the thickness of a molecular monolayer layer), we get $R_c\approx 15$ Å, which is large enough for the continuum approximation involved in the calculation of the elastic relaxation energy to be valid. Next, using (3) and (10) we get

$$P_0=\left[\frac{(2\pi\Gamma+2\pi R_cp_0)E}{3(1-\sigma^2)IR_c^2}\right]^{1/2} \ . \tag{12}$$

Let us tentatively apply this formula to OMCTS between two mica surfaces. The elastic properties of mica are

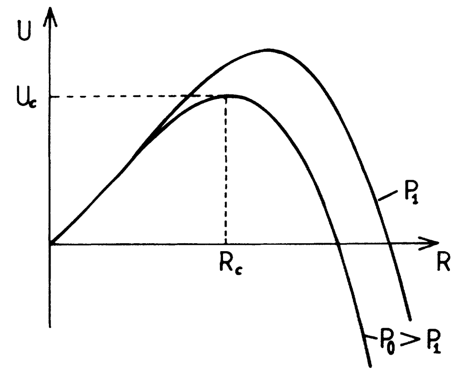

FIG. 3. The dependence of the energy of an $n-1$ nucleus on the radius R of the nucleus. As the pressure P increases ($P_0>P_1$), the "activation" energy U_c, which must be overcome in order to nucleate the layering transition $n\to n-1$, decreases.

highly anisotropic; the crystal is monoclinic quasihexagonal and has five independent elastic coefficients (in 10^{10} N/m^2)

$$C_{xx,xx}=17.8\ ,\quad C_{zz,zz}=5.5\ ,\quad C_{yz,yz}=1.2\ ,$$
$$C_{xx,zz}=1.5\ ,\quad C_{xx,yy}=4.2\ .$$

For the present problem, the most relevant of these are $C_{zz,zz}$ and $C_{yz,yz}$. We can choose the parameters E and σ to describe these elastic properties correctly; this gives $E=1.75\times10^{10}$ N/m^2 and $\sigma=0.44$. Using (12) we can now calculate the "critical" pressure necessary to nucleate the $n=1$ area; we get $P_0\approx7\times10^8$ N/m^2. This should be compared with the observed critical pressure,[2] $(2\pm1)\times10^7$ N/m^2, which is a factor of ~30 smaller than the theoretical estimate. This indicates that the actual nucleation may occur at some "weak" point between the mica surfaces where "imperfections", e.g., adsorbed water molecules or some organic contamination, may occur. This may locally reduce the spreading pressure (which may even become negative, i.e., nonwetting) and may reduce the elastic constant E, both effect of which would reduce the critical pressure P_0 (see below). The situation is obviously similar to that for three-dimensional systems, where the centers of formation of a new phase, e.g., solidification of an undercooled liquid, usually occur at various kinds of "impurities" (dust particles, ions, etc.).

As another application of (11) and (12), consider a metal block on a metal substrate with a lubricant fluid. Assuming that the spreading pressure $p_0\approx4$ meV as is typical for organic fluids on metal oxides,[9] Eq. (11) gives $R_c\approx12$ Å. For steel, $E\sim1\times10^{11}$ N/m^2, and (12) gives $P_0\approx2\times10^9$ N/m^2. This is similar to the pressure that occurs in the contact regions between the steel surfaces, which is of the order of the plastic yield stress (the penetration hardness), i.e., of order 10^9 N/m^2. Accounting for the imperfect nature of the real contact areas it is very likely that if the lubrication layer is in a fluid state it will be squeezed out from the contact areas. On the other hand, if the lubricant layer is in a solid state even this high pressure may not be able to remove the last layer or two of lubrication molecules from a junction region. But as the temperature increases, the lubrication film will finally melt (two-dimensional fluid) and the lubrication fluid can be squeezed out from the contact regions, as is indeed observed in many sliding systems. For example, Fig. 4 shows the temperature variation of the sliding friction coefficient f and the amount of metal transfer (the "pickup") from one metal surface to another, as a cadmium block is slid over a lubricated (palmic acid) cadmium substrate.[12] The metal transfer is measured by making the block radioactive and detecting the amount of radioactive metal transferred from the block to the substrate. Note that in a narrow temperature interval, from 110 to 130 °C, there is an abrupt increase in the sliding friction (by a factor of ~10) and an increase in the amount of metal transfer by almost a factor 10^5. This can be explained if it is assumed that the palmic-acid film melts in this temperature interval, and if the melted film is squeezed out from the contact regions between the two surfaces. In fact, since above ~130 °C the sliding friction and the metal transfer are essentially identical to those for clean surfaces, this is very likely the correct explanation.

It must be pointed out, however, that the squeezing out of a lubrication film may occur very slowly (see next section) so that, during sliding, if the transition $n=1\rightarrow0$ would nucleate somewhere in the contact region, the nucleus may not have enough time to grow before the two contact areas have passed each other. [The overall diameter of a contact area (junction) is not large, typically of order 0.01 mm.] This is also probably the reason why during sliding of lubricated surfaces the metal fragments transferred from one of the sliding surfaces to the other are usually very small compared with the case of unlubricated surfaces, where the metal fragments are of similar size as the contact area itself, as shown by radioactive tracer experiments.

In Fig. 5 we show the critical pressure P_0 and the criti-

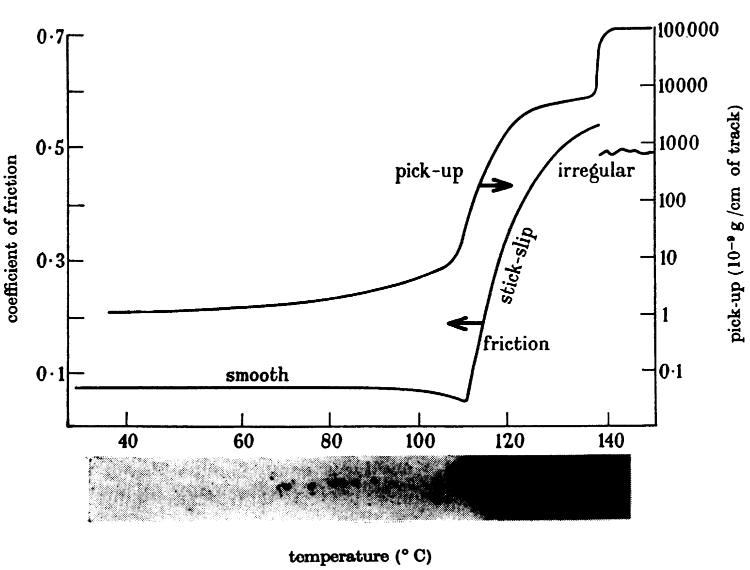

FIG. 4. The temperature dependence of the friction coefficient and of the metal transfer ("pickup") for cadmium surfaces lubricated with palmitic acid. The amount of pickup is deduced from the radiograph shown at the bottom (from Ref. 12).

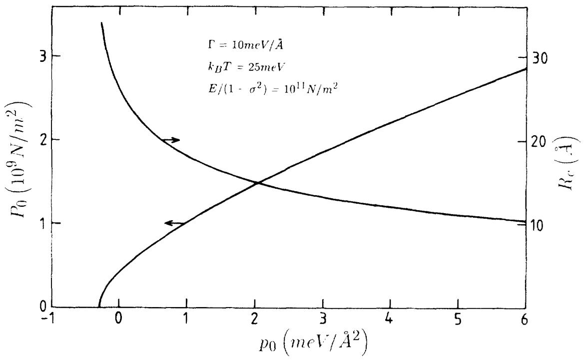

FIG. 5. The critical pressure P_0 and the critical radius R_c [Eqs. (11) and (12)] as a function of the spreading pressure p_0. In the calculation, $\Gamma=10$ meV, $k_BT=25$ meV, and $E/(1-\sigma^2)=10^{11}$ N/m^2, are assumed, as reasonable values for a generic situation.

cal radius R_c as a function of the spreading pressure p_0. In the calculation we have taken $\Gamma=10$ meV, $k_BT=25$ meV, $\kappa=44$, and the elastic constant $E_*=E/(1-\sigma^2)=10^{11}$ N/m^2. (The results for other values of E_* can be obtained from the fact that $P_0 \sim E_*^{1/2}$ while R_c is independent of E_*.) Note that P_0 vanishes for $p_0<-3\Gamma^2/(\pi\kappa k_BT)$, i.e., for $p_0<-0.3$ meV in the present case. Hence, if the spreading pressure is negative, the layering transition may nucleate spontaneously (i.e., without an external pressure). This may be the case, for example, for most fluids between two teflon surfaces, or between two metal-oxide surfaces covered by fatty acid monolayers.

B. Growth

We now study how the $n=1$ region will spread after the nucleation has occurred. Let $\mathbf{v}(\mathbf{x},t)$ be the two-dimensional velocity field of the monolayer being squeezed out. Assuming an incompressible two-dimensional fluid, the continuity equation and the (generalized) Navier-Stokes equations take the form

$$\nabla\cdot\mathbf{v}=0 \tag{13}$$

$$\frac{\partial\mathbf{v}}{\partial t}+\mathbf{v}\cdot\nabla\mathbf{v}=\frac{1}{mn_a}\nabla p+\nu\nabla^2\mathbf{v}-\bar{\eta}\mathbf{v} , \tag{14}$$

where p is the two-dimensional pressure and ν the kinematic viscosity. The last term in (14) describes the "drag force" by the substrate acting on the fluid.[13] Equation (14) has been studied earlier in the context of two-dimensional (2D) hydrodynamics by Ramaswamy and Mazenko[14] and a similar equation was used by de Gennes and Cazabat[15] in a study of the spreading of a wetting drop.

We assume that the contact area between the two solid surfaces has a circular shape with radius r_0. Assume first that the initial nucleation occurs at the center of the contact area. Hence, by symmetry the $n=1$ region has a circular shape with the radius $r_1(t)$ (see Fig. 6). Let p_1 be the two-dimensional pressure for $r=r_1$, which will be discussed below. At the boundary $r=r_0$, the two-dimensional pressure takes the value $p_0<p_1$, which is a constant (the spreading pressure) determined by local equilibrium between the fluid and the adsorbed molecules. Because of symmetry

$$\mathbf{v}=\hat{r}v(r,t) ,$$

$$p=p(r,t) .$$

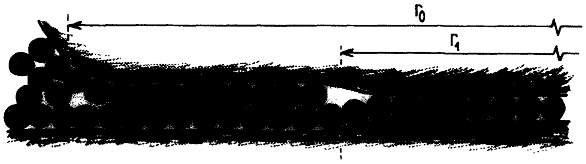

FIG. 6. Schematic picture of the layering transition $n=2\rightarrow1$. The lubrication film is assumed to be in a fluid state.

Substituting these Eqs. in (13) and (14) gives

$$\frac{\partial v}{\partial r}+\frac{v}{r}=0 , \tag{15}$$

$$\frac{\partial v}{\partial t}=-\frac{1}{mn_a}\frac{\partial p}{\partial r}+\nu\frac{\partial}{\partial r}\left[\frac{\partial v}{\partial r}+\frac{v}{r}\right]-\bar{\eta}v , \tag{16}$$

where we have dropped the nonlinear term in (14) since the velocity v is very small in the present applications. Note that because of the continuity Eq. (15), the viscosity term in (16) vanishes, i.e., the spreading does not depend on the two-dimensional viscosity. The relevant solution of (15) is of the form

$$v(r,t)=B(t)/r . \tag{17}$$

Substituting this in (16) gives

$$\partial p/\partial r=-mn_a[\dot{B}(t)+\bar{\eta}B(t)]/r ,$$

where $\dot{B}=dB/dt$. Using the boundary conditions $p(r_0)=p_0$, this equation has the solution

$$p(r)=p_0-mn_a[\dot{B}(t)+\bar{\eta}B(t)]\ln(r/r_0) . \tag{18}$$

Now, at the leading edge $r=r_1(t)$ of the $n=1$ region, the pressure $p=p_1$ so that from (18) we get

$$[\dot{B}(t)+\bar{\eta}B(t)]\ln(r_1/r_0)=-(p_1-p_0)/mn_a . \tag{19}$$

But we must also have

$$\dot{r}_1=v(r_1,t)=B(t)/r_1$$

so that (19) can be written as

$$\frac{d}{dt}\left[\frac{dr_1^2}{dt}+\bar{\eta}r_1^2\right]\ln(r_1/r_0)=-\frac{2(p_1-p_0)}{mn_a} . \tag{20}$$

For "large" times, r_1 varies slowly with time (see below), and we can neglect the second time derivative term in the expression above. Furthermore, if we introduce the area $A(t)=\pi r_1^2(t)$ Eq. (20) becomes

$$\frac{dA}{dt}\ln\left[\frac{A(t)}{A_0}\right]=-\frac{4\pi(p_1-p_0)}{\bar{\eta}mn_a} . \tag{21}$$

If we assume that p_1 is independent of r_1, i.e., of $A(t)$, then (21) can be integrated analytically.

$$\frac{A(t)}{A_0}\left[\ln\left[\frac{A(t)}{A_0}\right]-1\right]=-\frac{4\pi(p_1-p_0)t}{mn_a\bar{\eta}A_0} . \tag{22}$$

The time t^* it takes to completely squeeze out the layer is obtained from (22) by putting $A(t^*)=A_0$, which gives

$$t^*=\frac{mn_a\bar{\eta}A_0}{4\pi(p_1-p_0)} . \tag{23}$$

Let us now discuss the two-dimensional pressure p_1. We will show that $p_1=p_0+aP_0$, where a is the change of distance between the confining solid surfaces as one monolayer is squeezed out, i.e., roughly the diameter of a molecule. The easiest way to obtain p_1 is to evaluate the adiabatic work to squeeze out one monolayer, which must equal $(p_1-p_0)A$ where A is the surface area. But the adiabatic work is also equal to the change in free energy resulting from the squeeze out of the monolayer, which is given by $[(2\gamma_{\mathrm{sl}}+V_{11})-2\gamma_{\mathrm{sl}}+P_0a]A-V_{11}A$. In this expression, the term $[\dots]$ is the change in the free energy in the contact region, while the last term is the binding energy of the squeezed out layer material to the bulk of fluid outside the contact region ($V_{11}A$ describes the attractive van der Waals interaction, which occurs if we bring into contact two fluid slabs). Hence, we get $p_1=p_0+P_0a$. Since in a typical case $P_0\sim10^8$ N/m^2 and $a\sim10$ Å, the term $P_0a\sim6$ meV/Å^2, i.e., this term is of similar order of magnitude as p_0.

We can now use (23) to estimate the sliding friction $\bar{\eta}$ from the observed squeeze out time t^*. Using $p_1-p_0=P_0a$ gives

$$\bar{\eta}=\frac{4\pi t^*P_0a}{mn_aA_0} . \tag{24}$$

From the measurements of Gee, McGuiggan, and Israelachvili[2] for OMCTS between mica surfaces, $P_0=2\times10^7$ N/m^2, $t^*\approx120$ s, $a\approx10$ Å, and $A_0\approx7\times10^{-9}$ m^2 giving $\bar{\eta}=6\times10^{15}$ s^{-1}. This value is quite reasonable but not very accurate for the following reasons.

(a) The three-dimensional pressure in the contact area is unlikely to be constant but will instead take its highest value in the middle and vanish at the periphery. If we assume[11] that the pressure depends on r as $P(r)=(2P_0/3)[1-(r/r_0)^2]^{1/2}$, where P_0 is the average pressure, then (21) can no longer be solved analytically but a numerical integration shows that the expression (23) for t^* is increased by a factor 1.84 and $\bar{\eta}$ now takes the value 3×10^{15} s^{-1}.

(b) It is not obvious that the film to be squeezed out remains in a fluid configuration during the whole time period but may oscillate between a pinned solid state and the fluid state; this result is suggested by the stick-and-slip oscillations exhibited by the experimental friction force (see Ref. 2) even in the transition period from $n=2$ to $n=1$.

(c) In the calculation above it was assumed that the nucleation of the $n=1$ region occurred at the center of the contact region. If the pressure $P(r)$ were constant in the contact region, one would expect the nucleation to occur with equal probability anywhere within the contact region. But even if $P(r)$ varies with r as indicated above, the nucleation will, in general, occur some distance away from the origin; in fact a simple analysis based on (2) indicates that $\langle r\rangle\approx0.2r_0$, where $\langle\dots\rangle$ stands for averaging over the spatial probability distribution of nucleation. Taking this into account is unlikely to change t^* by more than a factor of 2 or so, but it has a drastic effect on the qualitative picture of how the monolayer removal occur, as we will now discuss.

We assume for simplicity that the pressure in the contact region is constant (equal to P_0); the qualitative picture presented below does not change if the pressure varies with r as discussed above. Neglecting the nonlinear and the viscosity terms in (14) and assuming that the velocity field change so slowly that the time derivative term can be neglected gives

$$-\frac{1}{mn_a}\nabla p-\bar{\eta}\mathbf{v}=0 . \tag{25}$$

From this equation it follows that

$$\mathbf{v}=\nabla\phi , \tag{26}$$

and the continuity Eq. (13) gives

$$\nabla^2\phi=0 . \tag{27}$$

Substituting (26) in (25) gives

$$\phi=-p/mn_a\bar{\eta} . \tag{28}$$

Now, from (27), we see that the velocity potential ϕ can be interpreted as an electrostatic potential. Furthermore, since the pressure p is constant at both the radius $r=r_0$ of the contact area as well as at the periphery of the transition region $n=2\rightarrow1$, the problem of finding ϕ is mathematically equivalent to finding the electrostatic potential between two conducting cylinders at different potentials, $\phi_0=-p_0/mn_a\bar{\eta}$ and $\phi_1=-p_1/mn_a\bar{\eta}$. The outer cylinder has a circular shape (radius r_0), and the inner cylinder an unknown (time dependent) shape to be determined. Now, suppose that the initial nucleation of the $n=1$ region occurs some distance away from the center of the contact region, as indicated by the small circle in Fig. 7(a). The lines between the two circular regions in this figure indicate the velocity field of the two-dimensional fluid at this moment in time, constructed by analogy to the electrostatic field lines between two cylinders at different potential. Now, a little later in time, this velocity field will result in a larger $n=1$ region (dotted area) as indicated in Fig. 7(b). Figures 7(c) and 7(d) show the further spreading of the $n=1$ region as time increases, constructed on the basis of the analogy with electrostatics.

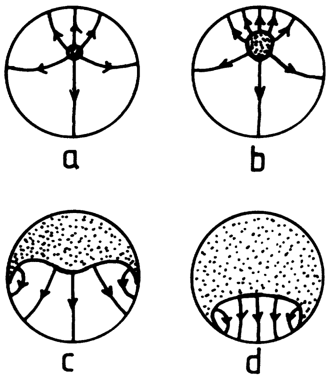

FIG. 7. Snapshot pictures (schematic) of the time evolution of the squeeze out of a monolayer, $n \rightarrow n-1$, in the slow (Laplacian) limit of Eqs. (25)–(28). The dotted area denotes the $n-1$ region. Lines of force coincide with the velocity field.

III. SUMMARY AND DISCUSSION

In this paper we have used the well-known fact that a liquid close to a rigid surface is strongly layered perpendicular to the surface, to explain the recent experimental observation of $n \rightarrow n-1$ layer transition of a thin fluid film between two flat solid surfaces, when pressure is applied between them. Nucleation theory is applied to calculate the critical pressure, while 2D hydrodynamics makes interesting predictions about the spreading dynamics of the $(n-1)$ "island." The predictions resulting from the present modeling will, hopefully, stimulate further experimental work.

A fundamental problem, which we have not addressed in the present paper, is how the layering transition occurs when the molecular layer between the mica surfaces is in a solid state rather than in fluid state. (In the present study we assumed that the two mica surfaces were in parallel motion relative to each other so that the molecular layer was in a fluidized state.) It is found experimentally that in this case a larger normal pressure is necessary in order to squeeze out one molecular layer $(n \rightarrow n-1)$; it has been suggested that the critical pressure may now be determined by the pressure necessary to induce the transition (solid layer → fluid layer). But, it is not obvious from theory how a pressure (i.e., *normal* force per unit area) can fluidize the molecular layer.

The class of phenomena involving liquid layering by proximity to a rigid substrate is very large.[16] For example, strong layering features in adsorption isotherms of fluids of inert atoms and molecules on substrates such as graphite have been the object of intense work for the last 40 years.[17] The spreading kinetics of a nucleation island in the $n \rightarrow n \pm 1$ transition caused by thermodynamic disequilibrium during adsorption and/or desorption may follow a similar 2D hydrodynamics to that described here.

Layering is also important for a fluid in contact with its own solid phase. In a bulk solid-liquid interface at thermodynamic coexistence, the layer structure of the solid is well known[18] to extend into the liquid according to $\exp(-z/l_0)$, with a decay length $l_0 \approx (\delta Q)^{-1}$, where δQ is the width of the main peak in the liquid structure factor, $S(Q)$. The advancing or retreating of the solid into the liquid caused by either thermodynamic interface fluctuations, or by an added external chemical potential imbalance, may be approached microscopically with some of the concepts elaborated above.

Close to the triple point T_c, also the solid-vapor coexistence interface (i.e., the ordinary solid surface) is in most cases wetted by a thin film of liquid (surface melting), which often is strongly layered, as shown, for example, by numerous simulations.[19] Chernov and Mikheev[20] pointed out that precisely this layering may be responsible for the nonwetting of the close-packed metal surfaces. Simulation work as well as further theory is in agreement with this idea, but also shows that the opposite is true for a poorly packed surface, where the liquid and the solid layering periodicities disagree.[21]

The process of advancing of the melting front from a solid surface inwards normally takes place *after* roughening, since the step energy can be argued to fall very steeply with temperature as the liquid film grows.[22] In this case, layering is destroyed by roughening. A more interesting case is, however, *incomplete* surface melting, which may occur without roughening. Here a thin strongly layered liquid film forms, and only grows to a finite thickness for $T \rightarrow T_c$. This process of limited growth in the absence of roughening may in the future be addressed with similar ideas to those developed here.

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APPENDIX A

In this appendix we derive the prefactor w_0 occurring in formula (2) for the nucleation rate. Assume that the contact area between the two solid surfaces has a circular shape with radius r_0 and that the initial nucleation occur at the center of the contact area. We consider only radial fluctuations of the hole [radius $R=R(t)$] and neglect the nonlinear term in the equation of motion for the two-dimensional fluid. For radial fluctuations the viscosity term vanishes (see Sec. II B) and we have

$$\nabla \cdot \mathbf{v} = 0 \, , \tag{A1}$$

$$\frac{\partial \mathbf{v}}{\partial t} = -\frac{1}{mn_a}\nabla p - \bar{\eta}\mathbf{v} + \frac{1}{m}\mathbf{f} \, , \tag{A2}$$

where $\mathbf{f}(x,t)$ is a stochastically fluctuating force, which is assumed to satisfy

$$\langle f_i(\mathbf{x},t) f_j(\mathbf{x}',t') \rangle = K\delta(\mathbf{x}-\mathbf{x}')\delta(t-t')\delta_{ij} \, , \tag{A3}$$

where, in order to satisfy the fluctuation-dissipation theorem,

$$K=2m\bar{\eta}k_BT/n_a \; . \tag{A4}$$

Now, if $f(\mathbf{x},t)=\mathbf{x}\cdot\mathbf{f}/r$ denote the radial component of $\mathbf{f}$, then (A3) gives

$$\langle f(\mathbf{x},t)f(\mathbf{x}',t')\rangle=K\delta(\mathbf{x}-\mathbf{x}')\delta(t-t') \; . \tag{A5}$$

Next, note that in polar coordinates

$$\delta(\mathbf{x}-\mathbf{x}')=\delta(r-r')\delta(\varphi-\varphi')/r \; .$$

Substituting this in (A5) and integrating over φ and φ' gives

$$\langle f(r,t)f(r',t')\rangle=\frac{K}{2\pi r}\delta(r-r')\delta(t-t') \; ,$$

where

$$f(r,t)=\frac{1}{2\pi}\int d\varphi f(\mathbf{x},t) \; .$$

Hence, using (A4),

$$\langle f(r,t)f(r',t')\rangle=\frac{m\bar{\eta}k_BT}{\pi n_a r}\delta(r-r')\delta(t-t') \; . \tag{A6}$$

Following Sec. II B, the solution to (A1) is of the form

$$v(r,t)=B(t)/r \; . \tag{A7}$$

The radial component of (A2) has the form

$$\frac{\partial v}{\partial t}=-\frac{1}{mn_a}\frac{\partial p}{\partial r}-\bar{\eta}v+\frac{1}{m}f$$

or, using (A7),

$$\frac{\partial p}{\partial r}=-mn_a\left[\frac{\dot{B}}{r}+\bar{\eta}\frac{B}{r}-\frac{1}{m}f\right] \; , \tag{A8}$$

where $\dot{B}=dB/dt$. Considering now a fluctuating hole with radius $R(t)$. Using (A8) we get

$$\begin{aligned}\int_R^{r_0}dr\frac{\partial p}{\partial r}&=p(r_0)-p(R)\\&=-mn_a(\dot{B}+\bar{\eta}B)\ln(r_0/R)+n_a\int_R^{r_0}dr\,f(r,t) \; ,\end{aligned} \tag{A9}$$

Now,

$$\dot{R}=v(R,t)=B(t)/R$$

and introducing $x=R^2/R_c^2$, we get

$$\dot{x}=2B/R_c^2 \; , \tag{A10}$$

and (A9) takes the form

$$\begin{aligned}\ddot{x}+\bar{\eta}\dot{x}=&-\frac{2[p(r_0)-p(R)]}{mn_aR_c^2\ln(r_0/R)}\\&+\frac{2}{mR_c^2\ln(r_0/R)}\int_R^{r_0}dr\,f(r,t) \; .\end{aligned} \tag{A11}$$

Let us multiply this equation with a constant M, to be determined below. This gives

$$M\ddot{x}+M\bar{\eta}\dot{x}=-U'(x)+F \; , \tag{A12}$$

where (with $R=R_c\sqrt{x}$)

$$U'(x)=\frac{2M[p(r_0)-p(R)]}{mn_aR_c^2\ln(r_0/R)} \tag{A13}$$

and

$$F=\frac{2M}{mR_c^2\ln(r_0/R)}\int_R^{r_0}dr\,f(r,t) \; .$$

In the present application the friction $\bar{\eta}$ is very large and it follows that $R(t)$ is a slowly varying quantity while $f(t)$ fluctuates rapidly. Averaging first over the rapid time variation we get, using (A6),

$$\langle F(t)F(t')\rangle=\frac{4M^2}{m}\frac{\bar{\eta}k_BT}{\pi n_aR_c^4}\frac{1}{\ln(r_0/R)}\delta(t-t') \; .$$

Now, although $R(t)$ is a fluctuating quantity, in the expression $\ln(r_0/R)$ we can neglect this fluctuation and replace $R(t)$ with the critical radius R_c. This is a good approximation since r_0/R is very large and $\ln(r_0/R)$ will, therefore, vary very little as $R(t)$ fluctuates. Next, let us choose M so that

$$\frac{4M^2\bar{\eta}k_BT}{m\pi n_aR_c^4\ln(r_0/R_c)}=2M\bar{\eta}k_BT \; .$$

This gives

$$M=mn_aR_c^4\frac{\pi}{2}\ln\left[\frac{r_0}{R_c}\right] \tag{A14}$$

and

$$\langle F(t)F(t')\rangle=2M\bar{\eta}k_BT\delta(t-t') \; . \tag{A15}$$

We can interpret (A12) as describing a point particle [at $x=x(t)$] with the mass M moving in an external potential $U(x)$, and under the influence of a friction force $-M\bar{\eta}\dot{x}$ and a fluctuating force $F(t)$, which is related to the friction $\bar{\eta}$ and the temperature T via the fluctuation-dissipation theorem (A15). The external force $-U'(x)$ is proportional to the pressure difference $p(r_0)-p(R)$ [see (A13)]. Now, $p(r_0)=p_0$ is the spreading pressure while $p(R)$ is the pressure exerted on the fluid at the periphery of the hole, by the elastic media and by the line tension. This quantity is easily obtained from the free energy $2\pi R\Gamma-\alpha R^3$ as follows. A small change in the radius R of the hole, $R\rightarrow R+\Delta R$, changes the free energy by $(2\pi\Gamma-3\alpha R^2)\Delta R$, which must be equal to the work $-p(R)2\pi R\Delta R$. Hence,

$$\begin{aligned}p(R)&=(3\alpha/2\pi)R-\Gamma/R\\&=(3\alpha R_c/2\pi)x^{1/2}-(\Gamma/R_c)x^{-1/2} \; .\end{aligned} \tag{A16}$$

Next, using (A13), (A14), and (A16),

$$U(x)=U_c(ax^{1/2}+bx-cx^{3/2}) \; , \tag{A17}$$

where

$$a=\frac{6\kappa}{1+4\kappa}\ ,\quad b=\frac{3}{1+4\kappa}\ ,\quad c=\frac{2+2\kappa}{1+4\kappa}\ , \tag{A18}$$

where $\kappa=\Gamma/p_0R_c$ and where R_c and U_c are given by (3) and (4). The effective potential (A17) is shown in Fig. 8. According to (A12) and (A15), the original problem of deriving the rate of nucleation of the layering transition is reduced to the calculation of the rate for a particle (with mass M) to be thermally excited over the potential barrier U_c in Fig. 8. But this is a standard problem, solved more than 50 years ago by Kramers.[23] In the present case we need his "large-friction" result where the chance per unit time for the particle, which originally was caught in the region $x<1$, to escape to $x>1$, is given by

$$\dot{n}=\frac{1}{M\beta\bar{\eta}}\left[\int_0^1 dx\, e^{-\beta[U(x)-U(0)]}\int_0^\infty dx\, e^{\beta U(x)}\right]^{-1} . \tag{A19}$$

With (A17) we get

$$\begin{aligned}\int_0^1 dx\, e^{-\beta[U(x)-U(0)]} &\approx \int_0^\infty dx\, e^{-\beta U_c a x^{1/2}}\\ &=2(\beta U_c a)^{-2}\end{aligned} \tag{A20}$$

and

$$\begin{aligned}\int_0^\infty dx\, e^{\beta U(x)} &\approx e^{\beta U_c}\int_{-\infty}^{\infty} e^{1/2\beta U''(1)(x-1)^2}\\ &=\left[\frac{2\pi}{-\beta U''(1)}\right]^{1/2} e^{\beta U_c}\ ,\end{aligned} \tag{A21}$$

where $U''(1)=-(3U_c/2)(1+2\kappa)/(1+4\kappa)$ from (A17).

Substituting (A20) and (A21) in (A19) gives

$$\dot{n}=\frac{9\kappa^2(1+2\kappa)^{1/2}}{(1+4\kappa)^{5/2}}\left[\frac{3}{\pi}\right]^{1/2}\frac{k_BT}{M\bar{\eta}}(\beta U_c)^{5/2}e^{-\beta U_c}$$

or, using (A14),

$$\dot{n}\approx\frac{\kappa^2(1+2\kappa)^{1/2}}{(1+4\kappa)^{5/2}}\,\frac{5.6(\beta U_c)^{5/2}}{n_aR_c^2\ln(r_0/R_c)}\,\frac{k_BT}{m\bar{\eta}R_c^2}e^{-\beta U_c} .$$

In the present applications $\beta U_c\approx 44$ (see below), $n_aR_c^2\sim 1$ (see Sec. II A), $\kappa\sim 0.5$, and $\ln(r_0/R_c)\sim 10$ so that

$$\frac{\kappa^2(1+2\kappa)^{1/2}}{(1+4\kappa)^{5/2}}\,\frac{5.6(\beta U_c)^{5/2}}{n_aR_c^2\ln(r_0/R_c)}\sim 160 .$$

Furthermore, with $\bar{\eta}\approx 3\times10^{15}\ \mathrm{s}^{-1}$ (see Sec. II B), $m\sim10^3$ u and $R_c\sim10^{-9}$ m we get at room temperature

$$\frac{k_BT}{m\bar{\eta}R_c^2}\sim 1\times10^{6}\ \mathrm{s}^{-1}\ ,$$

i.e.,

$$\dot{n}\sim(1\times10^{8}\ \mathrm{s}^{-1})e^{-\beta U_c} .$$

But the nucleation can occur at roughly $\pi r_0^2/\pi R_c^2$ different places in the contact region, so that the "total" nucleation rate will be

$$w\approx\dot{n}r_0^2/R_c^2\ ,$$

and with $R_c\sim10^{-9}$ m and (from experiment) $r_0\sim3\times10^{-5}$ m, we get finally

$$w\approx(1\times10^{17}\ \mathrm{s}^{-1})e^{-\beta U_c} .$$

If we somewhat arbitrarily "define" nucleation to occur when $w\sim10^{-2}\ \mathrm{s}^{-1}$ (i.e., about one nucleus per minute) then nucleation will occur when $\exp(-\beta U_c)\approx10^{-19}$ or $\beta U_c\approx 44$.

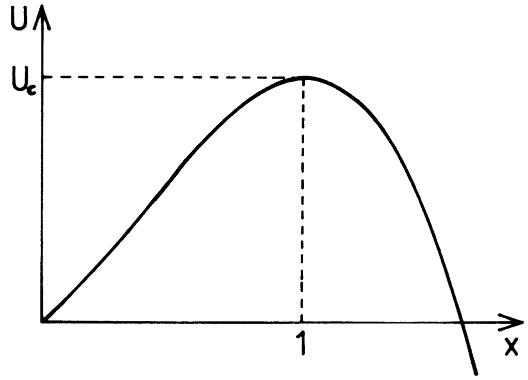

FIG. 8. The effective potential $U(x)$ as a function of the particle coordinate x.

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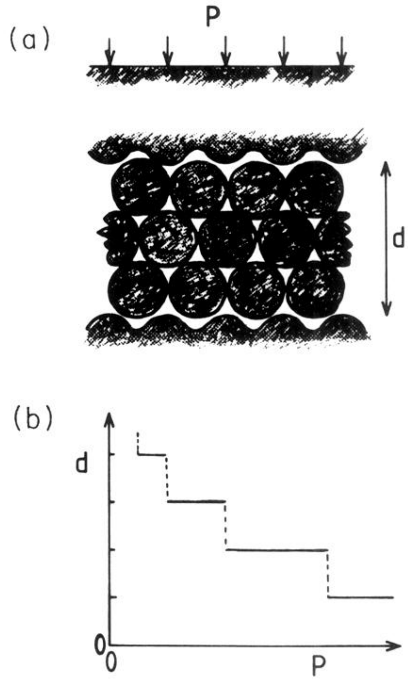

FIG. 1. (a) A thin molecular slab between two plane surfaces. The molecules tend to form layers parallel to the surfaces ($n=3$ in the present case) and the number of layers n depend on the external pressure P. (b) The variation in the thickness of the molecular film depends in a quantized manner on the pressure P.

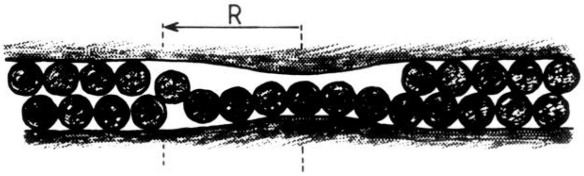

FIG. 2. A thermal fluctuation has created an $n=1$ nucleus (radius R) in an $n=2$ fluid layer. Because of the external pressure P, the surfaces of the elastic solids expand (relax) into the hole as indicated.

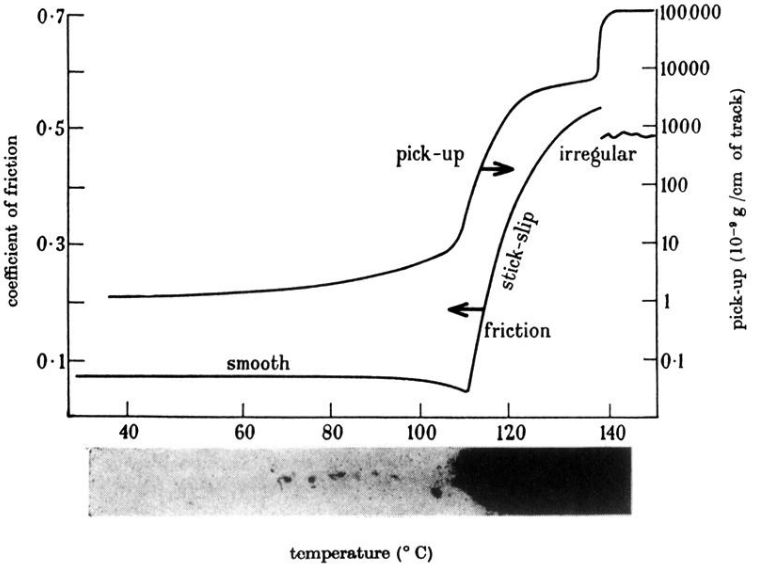

FIG. 4. The temperature dependence of the friction coefficient and of the metal transfer ("pickup") for cadmium surfaces lubricated with palmitic acid. The amount of pickup is deduced from the radiograph shown at the bottom (from Ref. 12).

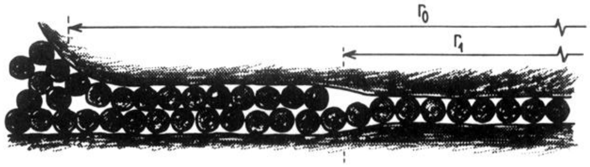

FIG. 6. Schematic picture of the layering transition $n=2\rightarrow1$. The lubrication film is assumed to be in a fluid state.