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Instability in a system of two interacting liquid films: Formation of liquid bridges between solid surfaces

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A theoretical study of systems composed of two solid-supported liquid films that are subject to a mutual attractive interaction reveals the existence of a mechanical instability: for distances closer than a certain threshold value, the system composed by two separate liquid films has no stable equilibrium configurations, and the system collapses to form a single liquid body. The sudden condensation of a connecting liquid bridge when two solid surfaces are brought to close proximity inside an undersaturated medium has been observed experimentally using the surface-force apparatus [see, e.g., Christenson *et al.*, Phys. Rev. B **39**, 11750 (1989)]. In this paper, these results are explained as follows: first, liquid films condense on the surfaces; then, if the distance is short enough, the films jump to contact, because of a mechanical instability due to attractive interactions.

I. INTRODUCTION

When two condensed-matter bodies interact attractively with each other, it may happen that, at distances below a given threshold, no stable-equilibrium configurations are available to the separated system; when this happens, the two interacting parts "jump together" and form a single, connected body.

The analytical calculations of Pethica and Sutton[1] and the molecular simulations and experiments of Landman *et al.*[2] have shown that such an instability exists for a solid tip (such as an atomic-force or scanning tunneling microscopy tip) in front of a flat solid. Taylor *et al.*[3] have studied the instability of two atomically flat solid surfaces as they approach each other.

The experimental results of Mate *et al.*,[4] in which the thickness obtained by dipping an atomic-force microscopy tip into a solid-supported liquid film appears to be larger than the optically determined thickness of the film, have been explained in terms of the instability of the liquid surface under the attraction of the tip:[5–8] for distances shorter than a given threshold, the liquid film becomes unstable and jumps into contact with the tip, and a neck or bridge forms between the tip and the liquid film.

There is extensive experimental evidence for the sudden condensation of liquid bridges between two molecularly flat solid surfaces brought to close proximity inside an undersaturated medium, as observed using the surface-force apparatus.[9–12] The undersaturated medium is either nitrogen gas containing the vapor of a hydrocarbon, or an organic liquid containing traces of water. The formation of the bridges will be explained here in terms of a mechanical instability of thin precursor liquid films that condense on the surfaces; this instability causes the liquid films to jump into contact and form a bridge. The geometry of this bridge is then determined by the interplay of capillary and intermolecular forces. If the surfaces are then pulled apart, the variation of the total energy of the bridge with distance gives rise to an adhesive force.

The mechanism for the initiation of capillary condensation proposed here is therefore relevant to the study of a variety of phenomena, many of which have important technological applications: adhesion of surfaces and powders, friction of surfaces, etc.

This paper deals with a linear study of the instabilities that develop in the interaction of two liquid films for systems of very low curvature, in which the liquid surfaces may be treated as planar. The linearized interaction of two liquid bodies via van der Waals forces has also been the subject of a quantum-many body study by Garcia-Molina *et al.*,[13] but these authors did not consider the existence of instability at short distances.

This report is organized as follows: Sec. II describes the theoretical model used; Sec. III applies this model to the case of van der Waals interactions; Sec. IV compares the predictions of the theory with the available experimental data; and finally, some concluding remarks are given in Sec. V.

II. THEORETICAL MODEL

The model system that will be studied in this paper is shown in Fig. 1. Two laterally infinite liquid films L_1 and L_2, both with average thickness t, are bound to planar solid substrates S_1 and S_2. The film–solid systems face each other across an intervening medium I that may be vacuum, gas, or another liquid, containing an undersaturated concentration of the liquid that forms the films. The symbol d will be used for the solid–solid distance. The solids, the films, and the intervening medium are modeled as continuous, incompressible media with sharp interfaces. All interactions in the system will be assumed to be additive.

The mechanism leading to the formation of the bridges is proposed to be the following.

(i) First, liquid films form at the solid surfaces by condensation of the undersaturated vapor (or solute) from the intervening medium. The thickness of the

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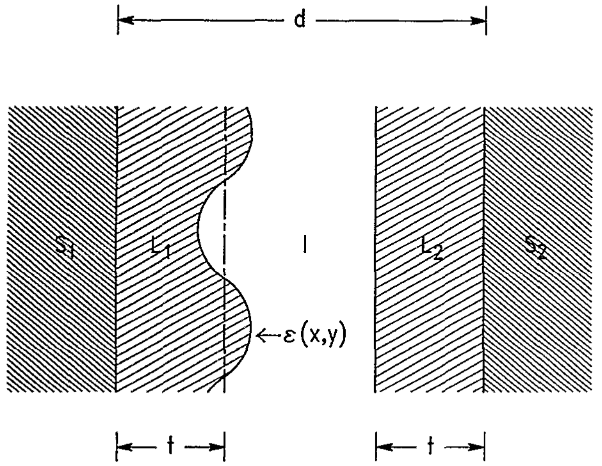

FIG. 1. The model system: two parallel, solid-supported planar liquid films.

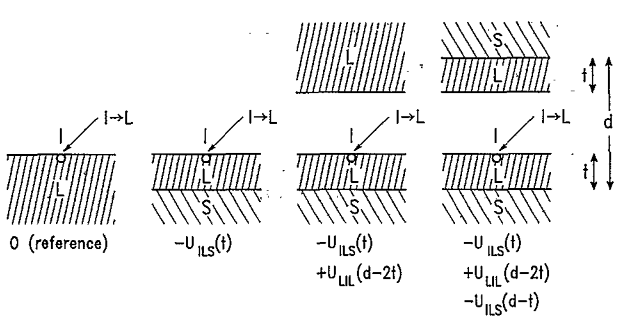

FIG. 2. Origin of the excess free energy leading to enhanced condensation, Eq. (1). For the systems studied in this work, $U_{\rm ILS}>0$ and $U_{\rm LIL}<0$ (see text).

films is determined by the activity of the liquid in the intervening medium and by the interactions with the solid surfaces. In fact, for a given activity, the films will grow as the solid surfaces approach (enhanced condensation), because of the increase of the attractive interactions across the gap.

(ii) After the films have formed, the fate of a random fluctuation of the thickness of one of the films depends on the way the fluctuation changes the total potential energy of the system. If the surfaces are close enough, the change in energy may be negative; the fluctuation will then grow at a rate determined by the viscosity of the liquid and induce a fluctuation in the facing film, which will also grow. When the films eventually come into contact, surface tension forces will drag liquid toward the junction and a bridge or neck will form as the new equilibrium configuration.

The mechanism proposed here is sequential: first, the films form from the vapor (or solute), and then, instability causes the fluctuations in film thickness to grow hydrodynamically. The decoupling of film formation and fluctuations is pertinent to the linear treatment that will be used in this paper. But, in addition, fluctuations in film thickness during formation of the film may be large enough to cause further condensation in the low-energy areas of the film; a possible result of the coupling of condensation and fluctuations is an earlier onset of the instability that leads to the formation of bridges, as suggested by one referee.

A. Formation of the liquid films: Enhanced condensation

The condensation of liquid on a solid surface from an undersaturated vapor or solution of the liquid is due to the fact that the free energy of the liquid at the surface of the solid-supported film has been lowered by the attraction toward the solid. If the liquid film is assumed to be structurally identical to the uppermost layers of a body of bulk liquid [the Frenkel–Halsey–Hill (FHH) approximation[14]], the lowering of free energy at the liquid surface with respect to the bulk free energy is equal to the change in potential energy due to the substitution of liquid by solid. Consequently, a liquid film may condense on a solid at activities smaller than one. This approximation is only valid if the film is thicker than a couple of monolayers, as below this thickness the FHH approximation breaks down due to entropic effects.[14]

If we have two such solid-supported liquid films facing each other, such as in Fig. 1, the attractive interactions across the gap induce an additional lowering of the free energy of the liquid at the film surface, due to the substitution of vapor (or solution)by the facing system. Accordingly, for two identical solid surfaces at a given distance d and an activity a at the intervening medium, the equilibrium thickness of the films, t, is determined by

$$\frac{RT}{V_m}\ln a=-U_{\rm ILS}(t)+U_{\rm LIL}(d-2t)-U_{\rm ILS}(d-t), \qquad (1)$$

where V_m is the molar volume, R is the gas constant, T is the temperature, and

$$U_{\rm ABC}(z)=u_{\rm AC}(z)+u_{\rm BB}(z)-u_{\rm AB}(z)-u_{\rm BC}(z), \qquad (2)$$

where $u_{\rm AB}(z)=u_{\rm BA}(z)$ represent the potential energy for the interaction of a unit volume of A with a semi-infinite volume of B at a distance z, and A, B, and C may be liquid (L), solid (S), or intervening medium (I).

Figure 2 illustrates the meaning of the terms to the right of Eq. (1). These terms represent the change in the energy that is needed to substitute a unit volume of I by a unit volume of L at the L–I interface (represented by a small circle in Fig. 2), when the system changes from two semi-infinite masses of I and L ($t,d\rightarrow\infty$, the reference state) to the system studied here. Each term represents one of the stepwise substitutions described in Fig. 2: the change of semi-infinite liquid to solid at a distance t under the interface; the change of intervening medium to liquid at a distance $d-2t$ above the interface; and the change of liquid to solid at a distance $d-t$ above the interface.

The necessary condition for the existence of a condensed, spreading film of liquid L of thickness t on a solid S immersed in medium I is $U_{\rm ILS}(t)>0$.

B. Development of the instability

Once the films have formed, their surfaces may be unstable to a small perturbation. To study the stability of the system to small perturbations of the film surfaces, a linear approach will be used. A perturbation of film 1 will be studied (the choice of which film is perturbed is immaterial in a symmetrical system). The local thickness of film 1 at a position (x,y) along the surface is $t+\epsilon(x,y)$, where t is the average thickness and ϵ is the extent of the local deformation. The deformations ϵ will conserve the average thickness (no liquid is added to the films).

The change in total energy of the system in Fig. 1, from the unperturbed state (both films have uniform thickness) to the state in which film 1 has been perturbed with a perturbation ϵ may be shown to be

$$\begin{aligned} E[\epsilon]-E[0] &= \gamma_{\mathrm{LI}} \int dx \int dy \left\{ \left[1+\left(\frac{\partial \epsilon}{\partial x}\right)^2+\left(\frac{\partial \epsilon}{\partial y}\right)^2 \right]^{1/2} -1 \right\} \\ &\quad + \int dx \int dy \left[\int_{d-2t-\epsilon}^{d-2t} dz\, U_{\mathrm{LIL}}(z) \right. \\ &\quad \left. - \int_{d-t-\epsilon}^{d-t} dz\, U_{\mathrm{ILS}}(z) + \int_{t+\epsilon}^{t} dz\, U_{\mathrm{ILS}}(z) \right], \qquad (3) \end{aligned}$$

where γ_{LI} is the interfacial tension between the film and the intervening medium, and the terms $U_{\mathrm{ABC}}(z)$ have been defined in Eq. (2).

For a small perturbation of the film thickness of the form

$$\epsilon=\hat{\epsilon}\cos(kx), \qquad (4)$$

such that its amplitude $\hat{\epsilon}$, is small compared to t, d, and its wavelength $2\pi/k$, the first-order change in energy per unity area is

$$\Delta e=\frac{\hat{\epsilon}^2}{4}\left(\gamma_{\mathrm{LI}}k^2-f\right), \qquad (5)$$

where

$$f=U'_{\mathrm{LIL}}(d-2t)-U'_{\mathrm{ILS}}(d-t)+U'_{\mathrm{ILS}}(t) \qquad (6)$$

and

$$U'_{\mathrm{ABC}}(z)=\frac{dU_{\mathrm{ABC}}}{dz}. \qquad (7)$$

If the value of Δe is negative, the system is unstable to the perturbation, which will grow exponentially at a rate controlled by the viscosity of the liquid film.

Instability may only happen if the value of f is positive and when the wave number k of the perturbation is smaller than k_c, where k_c is the value of k that gives $\Delta e=0$,

$$k_c=\sqrt{\frac{f}{\gamma_{\mathrm{LI}}}}. \qquad (8)$$

Jain and Ruckenstein[15] have shown that the lifetime τ of a single, solid-supported unstable film is

$$\tau \simeq \frac{12\eta\gamma}{t^3 f^2}, \qquad (9)$$

where η and γ are the dynamic viscosity and surface tension of the liquid, respectively, t is the thickness and f is given to Eq. (6). For typical ideal liquids and nanometer-sized unstable films under nonpolar interactions, τ is of the order of 1 μs. In our system, the viscosity of the intervening medium and the boundary conditions imposed by the facing system may increase the lifetime of the unstable film considerably.

This is a Rayleigh–Taylor instability,[16,17] such as the one that appears when a liquid is held upside down in the Earth's gravitational field.

According to Eqs. (1), (6), and (8), for a given activity a, one may compute a critical distance d_c below which instabilities start to be possible. The distance d_c corresponds to the value of d that reduces f to zero in Eq. (6). This sets an upper bound to the jump-into-contact distance. Actual jump-into-contact distances will be smaller because the finite size of the real system will define a minimum wave number k_c [Eq. (8)]. In a real experiment, the solid surfaces will be slowly brought together at a certain rate; if the growth rate of the instability is comparable to the speed of approach, the jump-into-contact distances may be even smaller; indeed, a dependence of the jump-into-contact distance on the speed of approach was observed by Christenson.[11]

III. APPLICATION TO VAN DER WAALS INTERACTIONS

If all forces in the system are assumed to be nonretarded, unscreened van der Waals interactions (as in Ref. 13), then the basic interaction terms have the form

$$u_{\mathrm{AB}}(z)=-\frac{A_{\mathrm{AB}}}{6\pi z^3}, \qquad (10)$$

where A_{AB} is the Hamaker constant for the van der Waals interaction between medium A and medium B.[18]

An expression for f, Eq. (6), may be obtained by substituting Eq. (10) into Eq. (2) and differentiating,

$$f=\frac{A_{\mathrm{LIL}}}{2\pi(d-2t)^4}+\frac{A_{\mathrm{ILS}}}{2\pi}\left(\frac{1}{t^4}-\frac{1}{(d-t)^4}\right), \qquad (11)$$

where

$$A_{\mathrm{ABC}}=A_{\mathrm{AC}}+A_{\mathrm{BB}}-A_{\mathrm{AB}}-A_{\mathrm{AC}}. \qquad (12)$$

Instabilities are only possible if $A_{\mathrm{LIL}}>0$.

The value of the thickness t for a given distance d and activity a is, from Eqs. (1), (2), and (10),

$$\frac{RT}{V_m}\ln a=\frac{A_{\mathrm{ILS}}}{6\pi t^3}-\frac{A_{\mathrm{LIL}}}{6\pi(d-2t)^3}+\frac{A_{\mathrm{ILS}}}{6\pi(d-t)^3}. \qquad (13)$$

The condition for the condensation of preexisting films is $A_{\mathrm{ILS}}<0$.

With Eq. (13), and setting f to zero in Eq. (11), the upper bound d_c for the jump-into-contact distance is ob-

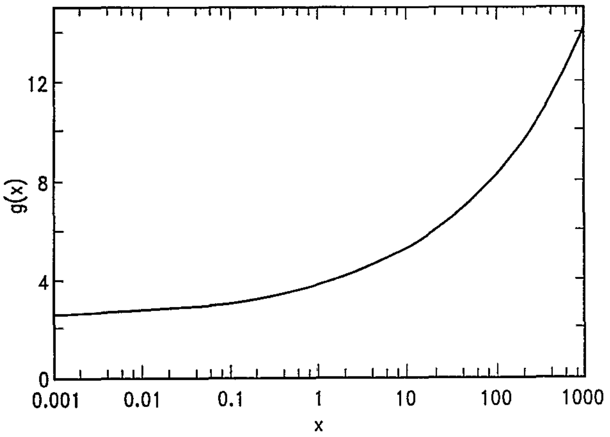

FIG. 3. The dimensionless function $g(x)$, Eq. (15).

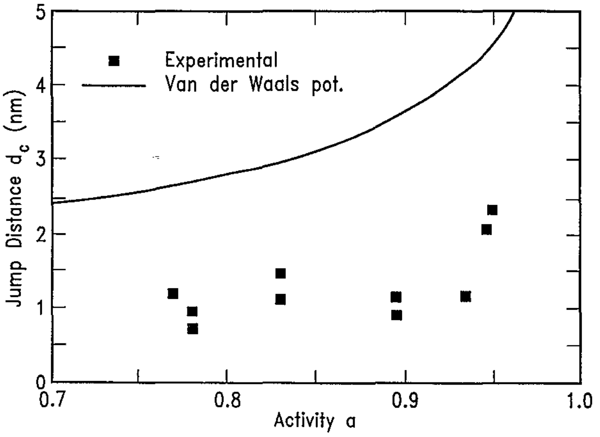

FIG. 4. The distance for bridge formation d_c as a function of cyclohexane activity in the vapor phase: squares, experimental data by Fisher and Israelachvili (Ref. 9); solid line, van der Waals calculation.

tained. In this case, it may be shown that the instability distance and the activity are related through the simple expression

$$a=\exp\left(-\frac{d_0^3}{d_c^3}\right), \tag{14}$$

where

$$d_0=\left(-\frac{A_{\mathrm{ILS}}V_m}{6\pi RT}\right)^{1/3} g\left(-\frac{A_{\mathrm{LIL}}}{A_{\mathrm{ILS}}}\right) \tag{15}$$

is a typical distance and $g(x)$ is a rather smoothly increasing function of x that has to be computed numerically, and is shown in Fig. 3; the limiting behavior of g is $g(0)=16^{1/3}$, $\lim_{x\to\infty}g(x)=x^{1/3}$, and $g(x)>\max(16^{1/3}, x^{1/3})$.

For typical values of Hamaker constants, d_0 is of the order of 1 nm. This means that instability distances are very short in the case of van der Waals interactions; indeed, the validity of the continuum model used here is in question for such short distances. However, the basics of the model (enhanced adsorption due to the facing system, mechanical instability below a given distance) may still be valid in a molecular representation.

IV. COMPARISON WITH EXPERIMENT

A. Cyclohexane bridges

Fisher and Israelachvili[9] used the surface-force apparatus to study the properties of bridges of hydrocarbons between two mica surfaces. In particular, they studied cyclohexane bridges formed from vapor-containing nitrogen. They observed contact distances of the order of twice the thickness of a monolayer of cyclohexane for low activities ($a<0.94$), and longer distances for higher activities (a monolayer of cyclohexane is roughly 0.5 nm thick). These authors made the assumption that the contact distance was equal to twice the thickness of the cyclohexane films.

The value of d_0 (the typical instability distance) for the mica-cyclohexane-nitrogen system is 1.7 nm at 21 °C, using the following data: Hamaker constants for van der Waals interactions, $A_{\mathrm{II}}\cong 0$ (nitrogen), $A_{\mathrm{LL}}=5.2\times10^{-20}$ J, $A_{\mathrm{SS}}=13.5\times10^{-20}$ J, $A_{\mathrm{AB}}\cong A_{\mathrm{AA}}^{1/2}A_{\mathrm{BB}}^{1/2}$;[18] molar volume of cyclohexane, $V_m=1.08\times10^{-4}$ m^3. This value of d_0 leads to a large overestimate of the jump-to-contact distance observed, as shown in Fig. 4, where the theoretical result is compared to the experimental data of Ref. 9.

In addition to the possible inadequacy of a simplified van der Waals treatment, as pointed by Beaglehole *et al.*[19], there are two more reasons for the discrepancy shown in Fig. 4: first, the films are too thin for a continuum description such as the one used in the present theory; second, the dynamics of the film may be too slow, and its lifetime may be much longer than the time for the approach of the surfaces.

It has to be commented that the geometry used in the surface-force apparatus is not exactly planar. The mica surfaces are cylindrical and crossed, which simplifies the alignment process; however, due to the large radii of the cylinders and the short distances involved, they may be treated as planes to a very good approximation (this is usually called the Deryagin approximation[18]).

B. Water bridges

1. van der Waals treatment

As a first approximation, the formation of water bridges between two mica surfaces immersed in an undersaturated solution of water in octamethylcyclotetrasiloxane, reported in Refs. 10 and 11 may be analyzed using the van der Waals approximation of Sec. III.

The following Hamaker constants will be used, together with the relation $A_{\mathrm{AB}}\cong A_{\mathrm{AA}}^{1/2}A_{\mathrm{BB}}^{1/2}$. $A_{\mathrm{SS}}=13.5\times10^{-20}$ J;[18] $A_{\mathrm{LL}}=4.8\times10^{-20}$ J (from A_{SS} and $A_{\mathrm{SLS}}=2.2\times10^{-20}$ J);[18] $A_{\mathrm{II}}=4.4\times10^{-20}$ J (estimated from the surface tension of the liquid, $\gamma=0.0216$ J).[18] Using these constants and the molar volume of water, 1.8×10^{-5} m^3, the value of d_0 [Eq. (15)] at 21 °C is very small, 0.236 nm. Figure 5 shows the experimental data of Christenson *et al.*,[10] together with the van der Waals results (dashed line). As can be seen, the van der Waals approximation underesti-

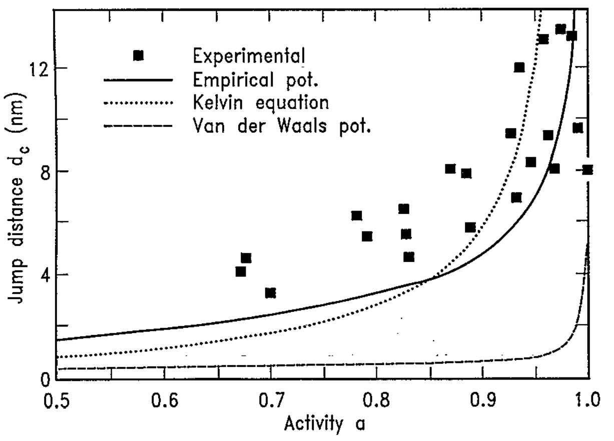

FIG. 5. The distance for bridge formation d_c as a function of water activity in the intervening medium: squares, experimental data by Christenson *et al.* (Ref. 10); dashed line, van der Waals calculation; solid line, results of empirical treatment based on the experiments of Beaglehole *et al.* (Ref. 19) (see text); dotted line, results using the Kelvin equation (Ref. 10).

mates the distance in most cases. This is an expected result, since polar effects are very important both for water–water and water–mica interactions.

2. Empirical treatment

In the absence of a suitable theory for water–water and water–mica interactions, an empirical potential can be derived from experimental data to try to get a better agreement.

Beaglehole *et al.*[19] have recently measured the thickness of water films adsorbed on mica as a function of the activity of water vapor. Their results show the inadequacy of Lifshitz theory (an exact continuum theory[18] that reduces in some limits to the simple van der Waals treatment used in this paper) for this system. For water thicknesses larger than two or three monolayers, one may use the FHH approximation used in Sec. II A for a single water film on mica, neglecting the interactions with the vapor,

$$\frac{RT}{V_m}\ln a = u_{\rm LS}(t) - u_{\rm LL}(t). \tag{16}$$

Then, a fit of one of the sets the experimental data of Ref. 19, yields

$$u_{\rm LS}(t) - u_{\rm LL}(t) \cong -At^{-2}, \tag{17}$$

with $A = 1.02 \times 10^{-11}$ J m^2. The values of $u_{\rm LL}$ and $u_{\rm LS}$ can be estimated to be proportional to the surface tension of water, 0.073 J/m^2,[18] and to the geometric mean of the surface tension of water and an estimate of the surface energy of mica, 0.120 J/m^2,[20] respectively. For the interactions with octamethylcyclotetrasiloxane, the van der Waals potentials are used, since the liquid is almost nonpolar.

This, in conjunction with Eq. (1) and $f=0$ in Eq. (6), was used to obtain numerically the instability distance d_c corresponding to each activity. The results obtained in this way are in much better agreement with the experimental data of Ref. 10, which suggests that the mechanism proposed here may be the one responsible for the formation of the water bridges.

Christenson *et al.*[10] compared their experimental results to those that may be obtained by a simple analysis of the bridge once it has formed, using Kelvin's equation for capillary condensation,

$$\frac{RT}{V_m}\ln a = \gamma_{\rm LI}(R_1^{-1} + R_2^{-1}), \tag{18}$$

where R_1 and R_2 are the radii of curvature of the interface between the liquid and the intervening medium. For a bridge geometry, these authors used $R_2 \ll R_1 \cong d/2$, neglecting the thickness of the liquid outside the bridge area, and assuming a zero contact angle. (The results of this equation are shown in Fig. 5). As may be seen, they are similar to the results obtained with the empirical binding potential (long-dash line). However, Kelvin's equation, only valid once the bridge has formed (since it refers to a single liquid body), assumes that intermolecular interactions are not important. This is not the case here, as, when the bridges form, the separation between the surfaces is very small; a correct description of the bridge, once formed, should include both capillary and interaction terms.

V. CONCLUDING REMARKS

This paper reports a theoretical study of systems that are composed of two facing planar, solid-supported liquid films. The study shows the existence of a mechanical instability due to the mutual attractive interaction, that appears when the solid–solid distance is shorter than a certain threshold, and leads to collapse of the liquid films and subsequent adhesion of the solid surfaces. It is shown that this threshold distance depends on the thickness of the films, which in turn is related to the activity of the film molecules in the medium between the films.

The theory has been used to model the sudden formation of a connecting liquid bridge between two solid surfaces, when they are brought together inside an undersaturated medium, as observed by various researchers[9–12] with the surface-force apparatus. These calculations provide an explanation for the phenomenon; a mechanism of bridge formation is proposed which involves the instability and collapse of *preexisting* liquid films, rather than the sudden phase separation suggested by Christenson *et al.*[10]

For cyclohexane bridges,[9] a model based on the interplay of nonretarded, unscreened van der Waals interactions leads to an overestimation of the jump-to-contact distance. This discrepancy may be due to the breakdown of the continuum description, as well as to a very slow dynamics of the instability.

For water,[10] as would be expected, the van der Waals model leads to a gross underestimation of the distance at which collapse occurs; however, a much better agreement is obtained by using an empirical expression for the interaction of water films with mica surfaces, based on the adsorption measurements by Beaglehole *et al.*[19]

The results in this paper suggest that, in general, the mechanical instability of solid-supported liquid films interacting at short distances may be responsible for the initiation of liquid bridges that lead to the adhesion of solid surfaces immersed in undersaturated media.

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