Evaporation and instabilities of microscopic capillary bridges

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The formation and disappearance of liquid bridges between two surfaces can occur either through equilibrium or nonequilibrium processes. In the first instance, the bridge molecules are in thermodynamic equilibrium with the surrounding vapor medium. In the second, chemical potential gradients result in material transfer; mechanical instabilities, because of van der Waals force jumps on approach or a Rayleigh instability on rapid separation, may trigger irreversible film coalescence or bridge snapping. We have studied the growth and disappearance mechanisms of laterally microscopic liquid bridges of three hydrocarbon liquids in slit-like pores. At rapid slit-opening rates, the bridges rupture by means of a mechanical instability described by the Young–Laplace equation. Noncontinuum but apparently reversible behavior is observed when a bridge is held at nanoscopic surface separations H close to the thermodynamic equilibrium Kelvin length, $2r_K \cos \theta$, where r_K is the Kelvin radius and θ is the contact angle. During the course of slow evaporation (at $H > 2r_K \cos \theta$) and subsequent regrowth by capillary condensation (at $H < 2r_K \cos \theta$), the refractive index of the bridge may vary continuously and reversibly between that of the bulk liquid and vapor. The evaporation process becomes irreversible only at the very final stage of evaporation, when the refractive index of the fluid attains virtually that of the vapor. Measured refractive index profiles and the time-dependence of evaporating neck diameters also seem to differ from predictions based on a continuum picture of bridge evaporation far from the critical point. We discuss these findings in terms of the probable density profiles in evolving liquid bridges.

The equilibrium and dynamic aspects of phase changes are often influenced by the presence of surfaces and interfaces. For example, in the case of homogeneous nucleation of a liquid phase, a significant supersaturation must be reached before vapor starts to condense to form droplets because of the activation barrier in the free energy that hinders the nucleation of clusters smaller than a certain size. Interfaces can lower this activation barrier and speed up the nucleation process. From a practical point of view, the nucleation, condensation, and evaporation of fluids in confined geometries play a major role in adhesion, the behavior of moist granular materials, and the transport of fluids through porous media.

Much less attention has been paid to the process of evaporation or disappearance of capillary-held liquids than to their formation (condensation or nucleation). The surface force apparatus (SFA; refs. 1–3) provides a powerful means with which to study the behavior of highly confined fluids and has been used to study various aspects of capillary condensed liquids. Recently, we reported some preliminary results on the evaporation of microscopic cyclohexane bridges (4). The major result from this study was the observation of lateral refractive index gradients across the evaporating bridges once they shrink below a certain size (figure 2 of ref. 4), which were interpreted as reflecting a gradient in the mean density of the liquid across the bridges. In addition, it was observed that during the final stages of evaporation and subsequent regrowth by condensation, the refractive index at the center of the bridge could take values between those of bulk liquid and those of vapor. As discussed in ref. 4, one

possible interpretation of the results is that an evaporating capillary bridge develops a diffuse liquid–vapor interface. However, these gradients were measured over microscopic, rather than nanoscopic, dimensions. This interpretation would therefore differ significantly from the “conventional” picture of liquid bridges and vapor cavities (5), although a recent computer simulation (6) seems to have reproduced what was observed in these experiments, albeit for significantly smaller bridges.

Fig. 1 illustrates some of the important concepts associated with the formation and disappearance of liquid bridges. The equilibrium states depicted in Fig. 1 *A* and *B* are uniquely determined by the Kelvin length $2r_K \cos \theta$. However, thermodynamics alone does not tell us how long it will take for transitions to occur between two equilibrium states. Such transitions typically occur by means of nonequilibrium processes involving material transfer. In the limit of very rapid processes, mechanical instabilities may occur at constant liquid volume V , as depicted in Fig. 1 *C–E*. Neither the theoretical nor experimental aspects of these transitions have been fully explained, especially at the nano-scale.

In this paper, we report the results of a more extensive and detailed study of the slow evaporation and rupture (Fig. 1 *A* and *B*) of bridges of two liquids of relatively low vapor pressure, *n*-hexadecane and *n*-dodecane, and discuss them in the light of the results obtained with the more volatile liquid, cyclohexane (4). We also have studied the mechanical (as opposed to the thermodynamic) stability of liquid bridges (Fig. 1 *C–E*) and have extended our measurements to five orders of magnitude smaller V than previously studied.

Materials and Methods

The experimental set up is very similar to that used in previous SFA studies of capillary bridges (see refs. 1–3 for details). Briefly, the apparatus consists of two back-silvered mica surfaces mounted as crossed cylinders in a sealed, environmentally controlled chamber. The geometry of the gap between the surfaces is locally equivalent to that of a sphere of radius R near a flat surface, and the separation between the surfaces H can be precisely controlled and measured to within 0.2 nm. For contact angles $\theta < 90^\circ$, a liquid bridge is formed by capillary condensation in the gap between the surfaces when they are brought together in an atmosphere consisting of a mixture of inert (nitrogen) gas and the undersaturated vapor of the liquid. The vapor is produced by evaporation from a reservoir of excess bulk liquid inside the SFA chamber, and the undersaturation can be produced either from cooling the reservoir or heating the surfaces (see below), or by the addition of an involatile solute to the reservoir liquid.

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[†]In this paper, we use the terms “evaporation” and “condensation” to refer to the shrinkage and growth of liquid bridges, respectively. The actual mechanism of material transfer may involve evaporation/condensation and/or transport of material by flow of material along the pore surfaces.

Fig. 1. Liquid bridges between two surfaces. (A and B) The equilibrium state of a liquid bridge is determined by thermodynamics. At equilibrium, the mean curvature of the liquid-vapor interface of a bridge must equal the Kelvin radius r_K . For wide necks and small θ , we have $d \gg r$, so that $r \approx r_K$, as drawn here. Note that at true thermodynamic equilibrium in saturated vapor, a liquid bridge between two flat surfaces should be the lowest energy state for any value of H . (C–E) Transitions between the equilibrium states A and B usually occur via nonequilibrium processes. For example, because of the van der Waals force on approach or a Rayleigh instability on separation, fast mechanical instabilities may trigger bridge coalescence (C $\rightarrow$ D) or snapping (D $\rightarrow$ E). In such processes, the meniscus curvature is not determined by the Kelvin equation.

Information about the material in the gap between the mica surfaces is obtained optically by using multiple-beam interferometry (7, 8). The back-silvered mica surfaces form a symmetrical three-layer interferometer, and when white light is passed perpendicularly through the surfaces, a series of interference fringes, known as “fringes of equal chromatic order” (FECO; refs. 7 and 8), is produced. A microscope is used to focus the region of closest approach between the surfaces onto the slit of a grating spectrometer. Thus, the FECO which are observed at the exit slit of the spectrometer sample a crosssectional slice through the surfaces of lateral width $2d$ up to $500 \mu\text{m}$, with a resolution of $\approx 1 \mu\text{m}$ (Fig. 1B). Analysis of the FECO pattern enables one to determine the distance of closest approach H of the surfaces, their shape or profile $H(x)$, and the refractive index profile $n(x)$ of the intervening medium. Information about the height $H(x)$ and lateral size d of capillary bridges can thus be obtained from an analysis of the refractive index discontinuities which appear in the even-order and, to a much lesser extent, in the odd-order fringes (8).

In the measurements described here, $R \approx 2.5 \text{ cm}$, and the spring constant of the rigid support, estimated from the jump-out distance in an atmosphere of dry nitrogen gas (9), was $2 \times 10^5 \text{ Nm}^{-1}$. FECO were recorded by using a video camera (VE1000SIT, Dage-MTI, Michigan City, IN) and analyzed by using a video micrometer (model 305, Colorado Video, Chatsworth, CA). The nonlinearity of the video screen was calibrated by using the two standard emission lines of a mercury lamp (Pen-Ray lamp 90-0012-01, Ultraviolet Products, San Gabriel, CA). The volume of a given condensate was calculated by using the formula $V = \pi R h^2$ (10), where h is the measured surface separation at the liquid-vapor interface of the condensed liquid when the surfaces are in contact. In our geometry, the mean radius of curvature r of the liquid-vapor interface of a condensed liquid bridge is related to h by $h = 2r \cos \theta$. Thus, for liquids of small contact angles, such as those used in this study, $r \approx h/2$.

Both *n*-dodecane (99.7% pure) and *n*-hexadecane (99.7% pure) were purchased from Sigma and used without further

purification. Unlike in the previous study that used cyclohexane (4), the relative vapor pressure P/P_{sat} , where P is the vapor pressure in the chamber and P_{sat} is the saturated vapor pressure of the liquid at that temperature, was not controlled by using an involatile solute. For liquids with very low P_{sat} , such as *n*-hexadecane, evaporation from the liquid in the reservoir is very slow, and it takes many days to saturate fully the vapor inside the SFA chamber. This property allowed for measurements to be made during the approach to saturation, and, for the range of P/P_{sat} studied here, P can be regarded as virtually constant during a given experimental run, which typically lasted several minutes. Although true for *n*-hexadecane, this procedure was found to be a less reliable method for *n*-dodecane, particularly at low P/P_{sat} where the changes occur more rapidly. For *n*-dodecane, therefore, we concentrated only on the results obtained at high P/P_{sat} (near saturation).

All of the measurements were carried out in an atmosphere of nitrogen gas (at 1 atm) in the presence of P_2O_5 as drying agent. The temperature of the experimental room was controlled and monitored to within $\pm 0.1^\circ\text{C}$. All experiments were performed at temperatures in the range $23.0 \leq T \leq 25.0^\circ\text{C}$, which is well above the bulk and surface freezing (11) points of *n*-hexadecane. The range of P/P_{sat} studied was $0.75 \leq P/P_{\text{sat}} \leq 0.92$.

Results

Thermodynamic Transitions and Instabilities. We begin by describing the measured refractive index profiles of evaporating bridges, which, in this work, were performed only for *n*-hexadecane. A few notable differences in the results between cyclohexane (4) and *n*-hexadecane were observed. First, the necks of the evaporating bridges of cyclohexane in the final stages of evaporation showed a broad refractive index profile, whereas necks of *n*-hexadecane were much thinner, and their profiles were much sharper. This feature did not allow accurate measurements of their refractive index profiles, and, therefore, we concentrated here instead on the mean refractive index of the *n*-hexadecane bridges. This effect may be related to the large difference in the rates of evaporation of the two liquids (12–15). Second, the much slower rates of evaporation and condensation of *n*-hexadecane allowed for more accurate measurements to be made, especially during the final stages of evaporation, than was previously possible with cyclohexane. The principal result, which is shown in Figs. 2 and 3, is that the mean refractive index n measured at the center of the liquid bridge shows a continuous decrease from the bulk liquid value toward that of vapor as the evaporation proceeds. The evaporation process is reversible until the very final stage, consistent with the previous results for cyclohexane (4). Thus, the unusual behavior of the refractive index of an evaporating bridge is apparently not limited to liquids of high P .

The “limit cycle” or “hysteresis loop” of the refractive index n as a function of the bridge thickness H (defined by the shaded region and black arrows in Fig. 2) is not unique, but depends on V of the bridge and the time allowed for evaporation and condensation at any particular separation H ; i.e., it depends on the rate of change of V or H . For very rapid separations and reapproaches, even to distances much larger than $2r_K$, there is no time for the bridge to evaporate or snap, and the hypothetical path taken would be the horizontal line I $\rightarrow$ II $\rightarrow$ III $\rightarrow$ II $\rightarrow$ I in Fig. 2. In contrast, for very slow separations and reapproaches, the hypothetical path would be the loop I $\rightarrow$ II $\rightarrow$ IV $\rightarrow$ V $\rightarrow$ I, although the transition from IV to I may not go via V. All other cases apparently fall in between these two very different limits, including the actual data shown by the shaded region in Fig. 2.

It was difficult to accurately measure P/P_{sat} of *n*-hexadecane in these experiments because of the slow rate of material transfer between the condensates and the vapor in the chamber. Nevertheless, at low P/P_{sat} , where the equilibration time is still reasonably fast, we could estimate $2r_K$ from the value of H above

Fig. 2. Mean refractive index n of n -hexadecane bridge of neck diameter d between two mica surfaces at various surface separations H , which corresponds to the thickness of the bridge. (A–J) FCO images of the condensate as visualized at various stages of a cycle, from which the refractive index n and separation H were determined. The cycle shows the path taken at $P/P_{\text{sat}} = 0.88$ for a given separation and reapproach rate. With increasing H (A→B→C), the bridge diameter d shrinks by evaporation at constant (bulk) n until $H > 2r_K$ is reached, when the bridge totally disappears (to G). However, the final stages of disappearance at fixed H (D→G) occur via a continuous decrease in n rather than in d , which now remains roughly constant (compare with Fig. 3A). The disappearance can be reversed (at E or F) by decreasing H before the evaporation is complete, when the condensate can be made to regrow (to H).

which the liquid bridge is no longer stable and clearly starts to evaporate, essentially by means of a method we have used previously (1). Thus, at separations H greater than a certain value, the condensate diameter d is seen to shrink, whereas at smaller values of H , it is seen to grow (this phenomenon occurs before the refractive index of the bridge n begins to deviate from the bulk value). For small θ ($\cos\theta \approx 1$), the turning point in the value of H is simply $2r_K$. We have observed that, whereas the separation at which the condensate starts to evaporate depends only on H , its growth seems to depend both on H and on V of the condensate: the larger the value of V , the larger the value of H at which it begins to grow. In turn, V depends on the previous history of the system. In other words, the magnitude of the hysteresis loop can be varied by adjusting the rate at which the surfaces are separated, kept at a fixed separation, or brought together, all of which can be controlled *in situ* with appropriate feedback control. In the previous study using cyclohexane (4), the evaporation and condensation rates were so fast that it was not possible to control the hysteresis or to separate the surfaces far above $H = 2r_K$ without their snapping immediately.

Fig. 2 also shows that on separation (increasing H) the refractive index of the bridge at $H = 2r_K$ remains that of the bulk liquid, whereas at the point at which the condensate starts to regrow, it is significantly lower than that of the bulk yet also significantly higher than that of vapor.

We have also made observations of the time dependence of the lateral width or neck diameter d of evaporating liquid bridges. In the initial stages of evaporation (at $H \geq 2r_K$) of n -hexadecane and n -dodecane bridges, d shrinks at constant n , whereas in the final stages, n decreases while d remains almost constant (Figs. 2 and 3A). Fig. 3C shows d as a function of time

Fig. 3. Examples of the behavior of liquid bridges during the final stages of evaporation. (A) Time-lapse FCO image of an n -dodecane bridge during the final stages of evaporation corresponding to D→G in Fig. 2. The image was taken with a 35-mm camera with the shutter left open during the evaporation. In this sequence, H was kept constant, as can be seen from the lack of movement of the curved odd-order fringe during the exposure time. The horizontal line on the even-order fringe has a roughly constant thickness, which indicates that d remained roughly constant as n decreased (in time) from the bulk value to the value for vapor. The flattened fringes showing the two surfaces in contact are also shown superimposed on the noncontact fringes for comparison. (B) Liquid bridges of n -hexadecane during their final stages of evaporation (compare D→G in Fig. 2). The symbols refer to condensates at different P/P_{sat} , Kelvin radii r_K , and bridge volumes. (C) The lateral width d as a function of time t for an evaporating cyclohexane bridge. The white circles represent the experimental data. The solid straight line is included as a guide for the eye (see text).

for an evaporating bridge of cyclohexane (the diameters of the cyclohexane bridges were generally larger than those of n -hexadecane or n -dodecane and, therefore, easier to measure accurately). The bridge diameter continues to decrease in the final stages of evaporation but at a slower rate than in the initial stages. The change in rate occurs at approximately the point at which the refractive index begins to fall significantly below the bulk value (although it is difficult to define or measure d once the refractive index is no longer constant across the bridge, i.e., once the interface becomes diffuse).

The driving force for the disappearance of a bridge is the difference in the chemical potential between the liquid in the bridge and that in the vapor reservoir. This difference is simply related to the difference between the mean radius of curvature of the bridge meniscus and the Kelvin radius corresponding to

the chemical potential (P) of the reservoir. There are three possible modes of evaporation, each having different kinetics, which we refer to as “vapor diffusion,” “surface area,” and “film” modes. We have previously shown that, for relatively volatile liquids such as cyclohexane, the mode and kinetics of condensation is through vapor diffusion; i.e., the rate of growth of the liquid bridge is limited by the rate of diffusion of vapor through the narrow gap between the surfaces (12, 13). However, in the initial stages of rapid evaporation, the mode and kinetics of material transport may be determined by the exposed area of the liquid–vapor interface (“surface area” mode). For relatively involatile liquids such as *n*-hexadecane, we have previously shown that material transfer may occur primarily through the flow of liquid along the pore surfaces (“film” mode; refs. 12, 14, and 15).

Assuming that the evaporating bridge maintains a geometry such as the one depicted in Fig. 1*B*, it is relatively straightforward to calculate the expected time dependence of d for the first two modes of evaporation. For $R \gg H > 2r_K$, as we have here, the separation between the surfaces at the meniscus (and, hence, the mean radius of curvature of the liquid–vapor interface) does not change significantly as d decreases. Hence, we may assume that the driving force for evaporation does not depend on d . If one assumes that the evaporation is diffusion-limited, it follows rather simply that $d \approx (d_0^2 - Ct)^{1/2}$, where d_0 is the initial width of the bridge, and C is a constant determined by the relevant physicochemical properties of the bridge material and by the geometry of the gap between the surfaces (12, 13, 16). In the second scenario, the evaporation is limited by the rate at which material can leave the liquid–vapor interface. Because the liquid–vapor area is proportional to d , it follows that $d \approx d_0 - Kt$, where K is a (different) constant that can be calculated from the molecular kinetic theory of evaporation (17).

The shape of the cyclohexane evaporation curve is not consistent with either prediction. The experimental curve is a line of constant slope at large d ($>5 \mu\text{m}$), but deviates from it (decreasing less rapidly) at $d < 5 \mu\text{m}$. This behavior suggests that the initial evaporation rate is limited by the liquid–vapor interfacial area. However, the clear change in rate which occurs toward the final stages of evaporation is inconsistent with the simple picture of the evaporation process described above. Although we have not attempted to model the shrinkage of bridges of relatively involatile liquids such as *n*-hexadecane, the unusual final stages of evaporation of *n*-dodecane and *n*-hexadecane bridges, which are even more pronounced than for cyclohexane, also appear to be difficult to reconcile with a conventional picture of a shrinking bridge.

Mechanical Instabilities. When evaporation can be neglected, the behavior of a liquid bridge, upon increasing the surface separation, should be dominated by its mechanical stability, which is determined by its surface energy. To investigate this regime, we performed measurements of the rupture of liquid bridges of *n*-dodecane and *n*-hexadecane at relatively high rates of surface separation (typically $1 \mu\text{m/s}$). At sufficiently high P/P_{sat} , evaporation of these bridges occurs very slowly. Under such conditions, V of a bridge can be regarded as constant during the separation process. The volume of the bridges was varied by bringing the surfaces into contact and varying the “condensation” time t_c allowed for liquid to condense around the contact before separation (Figs. 2*A* and 4*A*). The minimum V (at $t_c \approx 0$) is determined by the thickness of the preexisting adsorbed films on the two surfaces (Fig. 1*A*) that are squeezed out from the contact zone as soon as the surfaces come into adhesive contact (13).

Under these conditions, liquid bridges were observed to rupture at a critical distance H_c , which increased with increasing V . This process was irreversible; i.e., a reduction of H to $H < H_c$

Fig. 4. Typical FECO images of the Rayleigh–Laplace instability (snapping or rupture) (*D* and *E*) of an *n*-hexadecane bridge when the surfaces are separated rapidly ($dH/dt > 1 \mu\text{m/s}$). The relative vapor pressure was the same here as in the measurements shown in Fig. 2. Note the much larger H after snapping (*E*–*J*) compared with Fig. 2, which can be seen from the much narrower fringe spacings.

did not lead to a continuous regrowth of the bridges (Fig. 4). The relationship between H_c and V , shown in Fig. 5, was found to be similar to that recently reported by Willett *et al.* (18) for macroscopic and microscopic bridges. Based on numerical solutions of the Young–Laplace equation, Willett *et al.* (18)

Fig. 5. The critical snapping distances H_c of *n*-hexadecane (●) and *n*-dodecane (○) bridges as a function of V at high P/P_{sat} . Data for *n*-hexadecane are limited to small V because of the slow growth rates of the condensates. The solid line is the theoretical curve obtained from Eq. 1.

derived the following relationship between a rescaled (dimensionless) rupture distance $H_c^* = H_c/R$ and volume $V^* = V/R^3$:

$$H_c^* = (1 + \theta/4)(V^{*1/3} - 2V^{*2/3}/5), \quad [1]$$

where θ is the contact angle in radians. For $R^3 \gg V$ and $\theta \approx 0$, as we have here, this reduces to

$$H_c^* \approx (1 + \theta/4)V^{*1/3} \approx V^{*1/3} \quad [2]$$

which is also the limit for a bridge between two flat surfaces.

Willett *et al.* (18) also tested their predictions experimentally for V larger than 10^{-11} m^3 and found good agreement with theory. The results shown in Fig. 5 provide support for the theoretical predictions down to five orders of magnitude smaller V than previously studied.

At intermediate P/P_{sat} (≈ 0.87), both reversible evaporation/condensation (Fig. 2) and irreversible Rayleigh–Laplace instabilities (Fig. 5) can be observed for the same condensate under different conditions solely by varying the rate at which the surfaces are moved. Thus, occurrence of both of these phenomena does not depend on V , P , or P_{sat} of the system.

Discussion

The results presented above and those reported earlier for cyclohexane (4) differ significantly from what one would expect from the conventional picture of a slowly evaporating liquid bridge, i.e., one whose curvature is close to the Kelvin radius and, therefore, close to the thermodynamic equilibrium state. Under such conditions, one would expect the lateral width (neck diameter d ; Fig. 1B) to decrease steadily with time at constant refractive index equal to that of the bulk liquid. This process should continue until d approaches the gap thickness H , when final detachment is expected to occur via a mechanical rupture, as described by Eq. 1. We note that for the typical values of H in this study, $H \approx 50 \text{ nm}$, V at which rupture should occur is predicted to be $\approx 10^{-22} \text{ m}^3$, i.e., $d \approx 50 \text{ nm}$. Such a bridge would be far too small to be resolved in our measurements. Thus, our observations should have been of a continually shrinking neck, manifested by a large and sharp discontinuity in the even-order FEKO fringe until it totally disappeared from view.

One possible interpretation of our results, suggested earlier (4) and illustrated in Fig. 6A, is that the evaporating bridge develops a density gradient, not only in the lateral direction but also in the normal direction, displaying a more liquid-like density at the mica walls and a more vapor-like density toward the middle of the gap. This kind of diffuse bridge could be composed of small clusters of molecules of varying cluster size and density. This interpretation is consistent with some recent computer simulations (6, 19) of vaporization and condensation of capillary bridges at the nanoscale. The liquid bridges in their final stages of evaporation may appear to behave like fluids above their critical points. However, we note that the Laplace pressure of the condensates is always negative and, therefore, far from the critical points of the liquids studied (4.08 MPa, 553.8 K for cyclohexane; 1.4 MPa, 723 K for hexadecane; ref. 20). Additionally, unlike the bulk fluid state where the entire phase is homogeneous, the system depicted in Fig. 6A exists only in the vicinity of interfaces, and its density is not uniform throughout. Thus, it is unlikely that the system depicted in Fig. 6A is related to the thermodynamic fluid state above the conventional critical point.

We now consider some other possibilities, illustrated in Fig. 6B–D. Fig. 6B shows how a liquid “bridge” could actually consist of a collection of submicroscopic bridges that are distributed in such a way as to give the observed refractive index profiles. Each individual bridge would be below the lateral resolution of the FEKO technique ($<1 \mu\text{m}$). The formation of numerous bridges

Fig. 6. Schematic pictures of the different possible scenarios describing the evaporation of capillary bridges of volatile and involatile liquids. (A) Diffuse liquid–vapor interface or bridge, exhibiting density gradients in both the normal and lateral directions (6), but less diffuse for involatile liquids. (B) The surfaces are connected by many submicroscopic bridges or “nano-bridges.” To account for the lateral density gradients observed with volatile liquids (4), the nano-bridges would need to be distributed strategically over an area of $10\text{--}1,000 \mu\text{m}^2$, with more or wider bridges near the center and fewer or thinner bridges near the edge. (C) Both surfaces have thick films with a nonuniform or uniform thickness profile. (D) Similar to C but with a submicroscopic neck connecting the two films.

would require the creation of a large liquid–vapor interfacial area which would be energetically very unfavorable. Also, a large number of such (sharp) interfaces would scatter light in such a way that would ultimately result in a smearing of the fringes, neither of which were observed. Such bridges are commonly seen during the detachment of viscoelastic polymer surfaces, a process that gives rise to “crazing,” “stringing,” or “tack” (21), although these are known to be nonequilibrium, rate-dependent processes, in contrast to the apparently equilibrated and reversible processes we observed here.

Another possibility is that the thinning “liquid bridge” actually corresponds to two thick liquid films on each surface, as illustrated in Fig. 6C. Each film would have a thickness profile that varies in a complicated way with time t and the gap thickness H . There is no simple way to explain how such films could be stable, nor why they should be formed (by bridge rupture) at a V many orders of magnitude larger than predicted. In addition, it is difficult to reconcile the reversible behavior of the mean refractive index of the bridges with observations on the coalescence of thin liquid films (22–24).

A more attractive explanation is based on postulating a shape such as that depicted in Fig. 6D, which is similar to the one in Fig. 6C but with a narrow neck connecting the two films that is below the lateral resolution of the FEKO optical technique. This shape would account both for the unusual behavior of the bridge refractive index and for the observed reversibility. In addition, a transition to such a highly convoluted bridge geometry could in principle be used to explain the unusual evaporation rate behavior. It is interesting to note that a shape very similar to that shown in Fig. 6D is indeed predicted by the equilibrium solution [$x = (d/2)\cosh(2y/d)$] of a sharp liquid–vapor interface having zero net curvature and zero contact angle in the limit of $d \rightarrow 0$ (25). However, this highly convoluted shape is not expected to arise until d approaches very close to H . For $d \gg H$, where all of the observations were made, the liquid bridge is expected to have a simple shape as shown in Fig. 1B or D, exhibiting the bulk refractive index both during evaporation and recondensation.

Although the shape of a liquid bridge under equilibrium conditions is expected to resemble that shown in Fig. 1*B*, it may be that a shape such as shown in Fig. 6*D* could arise under nonequilibrium conditions. Indeed, shapes similar to that depicted in Fig. 6*D* have been observed as transients in the “pinch-off” of liquid droplets (26–28). Images of an evaporating water meniscus obtained by using an environmental scanning electron microscope also suggest a convoluted geometry (29). Theoretical studies clearly show that the geometry of a liquid droplet or thin film can be influenced by mass and energy transfer processes occurring during evaporation (30, 31). We note, however, that by judicious feedback of H using the piezo-crystal distance control, we were able to maintain a bridge with a refractive index of 1.3 or even 1.2, apparently indefinitely (for timescales of minutes in the case of n -hexadecane). This observation would be difficult to explain if the geometry is to be attributed to a transient stage in the evaporation process, as shown in Fig. 6*D*.

In summary, to account for the experimental observations both qualitatively and quantitatively, we are unable to rule out the first scenario (Fig. 6*A*) in favor of any one of the more conventional explanations. Although a definitive conclusion is still lacking, future studies should focus on this possibility. If this interpretation is correct, it implies that a small volume of (confined) fluid in equilibrium with its saturated (or close to saturated) vapor may not be separated into a bulk-like liquid and vapor phase. This concept would have profound implications for our understanding of certain kinds of solvation forces. For example, a nonuniform distribution of condensed submicro-

scopic gas molecules between two hydrophobic surfaces in water (Fig. 6*A* but with the vapor and liquid phases reversed) has long been proposed as a possible explanation of the long-ranged attractive hydrophobic force (32, 33). It would also have enormous implications for other systems such as pore-filling mechanisms and wetting hysteresis, diffusion and fluid flow dynamics in confined geometries, small systems thermodynamics, and fluid mechanics. The surprising result is that V of fluid thus affected is unexpectedly large, of the order $10^{-18} \text{ m}^3 = 1 \text{ } \mu\text{m}^3 = 10^9 \text{ nm}^3$, which is of microscopic rather than nanoscopic dimensions. However, it is worth remembering that one of the dimensions of these liquid bridges (their thickness) is in the nanoscopic regime.

On the other hand, for rapidly stretched bridges that snap because of a conventional Rayleigh type of instability, our results are consistent with the classical explanation even for bridges having V as small as 10^{-16} m^3 , which is five orders of magnitude smaller than those previously studied. These results on snapping are clearly of importance in the study of adhesion between surfaces in the presence of liquid bridges. For example, the rupture distance of such bridges is an important parameter in describing the dynamic mechanical properties of moist granular materials (34).

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1. Fisher, L. R. & Israelachvili, J. N. (1981) *J. Colloid Interface Sci.* **80**, 528–541.
2. Christenson, H. K. (1997) *Colloids Surf.* **123–4**, A355–A367.
3. Christenson, H. K. (2001) *J. Phys. Condens. Mat.* **13**, R95–R133.
4. Maeda, N. & Israelachvili, J. N. (2002) *J. Phys. Chem.* **106**, B3534–B3537.
5. Rowlinson, J. S. & Widom, B. (1982) *Molecular Theory of Capillarity* (Clarendon, Oxford).
6. Stroud, W. J., Curry, J. E. & Cushman, J. H. (2001) *Langmuir* **17**, 688–698.
7. Tolansky, S. (1949) *Multiple-Beam Interferometry of Surfaces and Films* (Oxford Univ. Press, London).
8. Israelachvili, J. N. (1973) *J. Colloid Interface Sci.* **44**, 259–271.
9. Christenson, H. K. (1993) *J. Phys. Chem.* **97**, 12034–12041.
10. Maeda, N. & Christenson, H. K. (1999) *Colloids Surf.* **159**, A135–A148.
11. Maeda, N. & Yaminsky, V. V. (2001) *Int. J. Mod. Phys. B* **15**, 3055–3077.
12. Kohonen, M. M. (2001) Ph.D. thesis (Australian National University, Canberra).
13. Kohonen, M. M., Maeda, N. & Christenson, H. K. (1999) *Phys. Rev. Lett.* **82**, 4667–4670.
14. Maeda, N., Kohonen, M. M. & Christenson, H. K. (2000) *Phys. Rev. E Stat. Phys. Plasmas* **61**, 7239–7242.
15. Maeda, N., Kohonen, M. M. & Christenson, H. K. (2001) *J. Phys. Chem.* **105**, B5906–B5913.
16. Crank, J. (1975) *The Mathematics of Diffusion* (Oxford Univ. Press, London).
17. Cammenga, H. K. (1980) in *Current Topics in Materials Science*, ed. Kaldis, E. (North-Holland, Amsterdam), Vol. 5, pp. 335–446.
18. Willett, C. D., Adams, M. J., Johnson, S. A. & Seville, J. P. K. (2000) *Langmuir* **16**, 9396–9405.
19. Jang, J., Schatz, G. C. & Rantner, M. A. (2002) *J. Chem. Phys.* **116**, 3875–3886.
20. Lide, D. R., ed. (1999–2000) *CRC Handbook of Chemistry and Physics* (CRC, Boca Raton, FL).
21. Luengo, G., Pan, J., Heuberger, M. & Israelachvili, J. N. (1998) *Langmuir* **14**, 3873–3881.
22. Derjaguin, B. V. & Churaev, N. V. (1976) *J. Colloid Interface Sci.* **54**, 157–175.
23. Wanless, E. J. & Christenson, H. K. (1994) *J. Chem. Phys.* **101**, 4260–4267.
24. Christenson, H. K. (1994) *Phys. Rev. Lett.* **73**, 1821–1824.
25. Ducker, W. A., Xu, Z. & Israelachvili, J. N. (1994) *Langmuir* **10**, 3279–3289.
26. Padday, J. F., Petre, G., Rusu, C. G., Gamero, J. & Wozniak, G. (1997) *J. Fluid Mech.* **352**, 177–204.
27. Rothert, A., Richter, R. & Rehberg, I. (2001) *Phys. Rev. Lett.* **87**, 084501.
28. Chen, A. U., Notz, P. K. & Basaran, O. A. (2002) *Phys. Rev. Lett.* **88**, 174501.
29. Schenk, M., Futing, M. & Reichelt, R. (1998) *J. Appl. Phys.* **84**, 4880–4884.
30. Wayner, P. C., Jr. (1999) *AIChE J.* **45**, 2055–2068.
31. Oron, A., Davis, S. H. & Bankoff, S. G. (1997) *Rev. Mod. Phys.* **69**, 931–980.
32. Christenson, H. K. & Claesson, P. M. (2001) *Adv. Colloid Interface Sci.* **91**, 391–436.
33. Karaman, M., Ninham, B. W. & Pashley, R. M. (1996) *J. Phys. Chem.* **100**, 15503–15507.
34. Seville, J. P. K., Willett, C. D. & Knight, P. C. (2000) *Powder Technol.* **113**, 261–268.