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Temperature-driven motion of a wetting layer

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The wetting layer formed by a phase-separated binary liquid mixture in contact with a glass substrate is observed to have a large nonequilibrium response in thickness to small temperature perturbations. An independent theoretical and physical picture is developed, which also provides a direct means of measuring the forces responsible for wetting and their effect on the dynamics of diffusion-limited interfacial motion. As an example, the curvature and anharmonicity of the minimum in the effective interface potential are found.

Consider a phase-separated binary liquid mixture in contact with the horizontal solid substrate constituting the bottom of its container. With suitable choice of liquids and substrate, a thick wetting layer of the upper phase can intrude between the lower phase and the substrate. The physics of wetting phenomena, such as this, is very rich and has attracted much attention in the past several years.[1] Questions motivating recent theoretical work include what determines the thickness of a wetting layer,[2,3] and how does a wetting layer attain its equilibrium thickness.[4,5] For the geometry under consideration, the answer to the former depends on the balance between the substrate-liquid interaction, which favors a thick layer, and gravity, which favors a thin layer. A construct known as the effective interface potential $V(l)$ includes both effects. It is the free energy per unit area for the configuration with wetting layer of thickness l; its minimum determines the equilibrium thickness. The issues raised in the latter question are familiar from diverse examples of interfacial dynamics.[6] Neither question has yet received a definitive, or even adequate, experimental attention. In this paper, we describe a striking method of perturbing the wetting layer, of interest in its own right, and develop a theoretical model to exploit it for experimental investigation of the above questions.

We studied a phase-separated critical-composition mixture of carbon disulfide plus nitromethane in contact with a borosilicate glass substrate using a reflectivity technique described earlier.[7] Since wetting behavior can be very sensitive to experimental detail, the following points are noteworthy. Our sample cell design follows Ref. 7, but with the thermistor can truncated above the mixture. Standard cleaning procedures were used for both stainless-steel[7] and glass[8] parts. The sample cell was assembled in air, vacuum baked, and filled with liquids in an Ar atmosphere, sealed with a stainless-steel gasket, then installed in a thermostat having rms thermal fluctuations of less than 0.3 mK, and no drift, over 2 h. The dimensions were such that each bulk phase had vertical height $L = 0.6$ cm, and the thermal relaxation time was less than 4 min. The critical temperature below which our liquid mixture phase separated was $T_c \simeq 63.6\,^{\circ}\mathrm{C}$ and had an initial drift of +15 mK/day. After one month, the drift settled to +5 mK/day and the liquids were slightly yellow. Reflectivity of an *s*-polarized He-Ne laser beam (0.5 mW, 1 mm diam. incident 74.1° from normal) was converted to wetting layer thickness by assuming that the layer is a homogeneous dielectric film between two bulk media, all with known[7] indices of refraction. The wetting layers were uniform as seen by eye and by measuring different portions of the surface. Because of the T_c drift and the unknown role of temperature gradients, we cannot be certain that the observed steady-state wetting-layer thickness represents true thermodynamic equilibrium.

Reference 7 showed that a thick wetting layer of the upper, nitromethane-rich, phase will intrude between the glass substrate and the heavier, carbon disulfide–rich, phase. To prepare a homogeneous layer, we raised the temperature to the desired point, stirred gently for several hours, stopped stirring, then waited more than 8 h until a steady-state thickness was established. This apparent equilibrium thickness was independent of temperature to within experimental resolution, ±0.5%, over the range studied here: 15.3 ± 0.2 K below T_c. Even so, a temperature increase (decrease) generally results in a *temporary* decrease (increase) in wetting-layer thickness; this has been known but not understood for some time.[7,9,10] Figure 1 shows how very sensitive the wetting layer is to temperature conditions: Tiny perturbations, as small as 2.5 mK at 15 K away from T_c, produce a response in wetting-layer thickness of several percent. Other data, not shown, indicate that the response to temperature jumps of opposite direction is symmetric for jumps smaller than about 1 mK; the perturbations of Fig. 1 can be called large in this sense. At the very least, we warn experimentalists wishing to measure equilibrium-wetting phenomena: Precise temperature control is crucial.

The following theoretical model can predict such sensitivity to small temperature perturbations. Lipowsky and Huse[4] (LH) studied the motion of a wetting layer when the system is otherwise equilibrated; here we consider the behavior of a wetting layer when the bulk liquids are *also* out of equilibrium. Suppose that the liquid mixture is

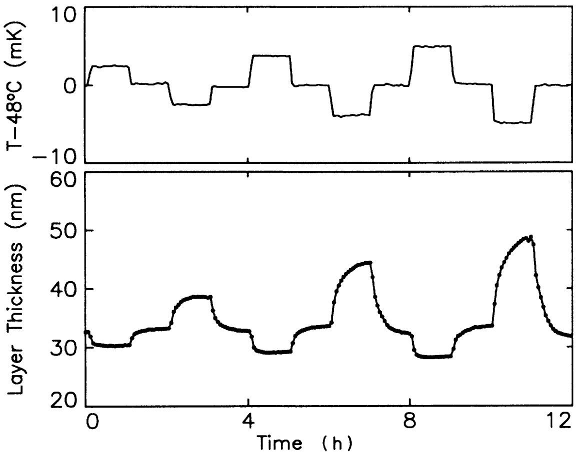

FIG. 1. Temperature-driven response of a wetting layer vs time at 15 K below T_c. A homogeneous wetting layer of steady-state thickness was prepared before the perturbations were applied at time zero. Note the striking sensitivity of the wetting-layer thickness to temperature conditions. The asymmetric response is due to the anharmonic effective interface potential. There is a ±40% uncertainty in the absolute thickness scale.

composed of A and B molecules such that the A-rich phase, a, forms a wetting layer between the B-rich phase, b, and the wall. Close enough to T_c, the equilibrium compositions obey $X_a - X_b \propto |T-T_c|^{\beta}$; X denotes number fraction of A molecules and $\beta \simeq 0.33$ is the order parameter exponent. LH adopt the approximation of "local equilibrium," which requires the wetting-layer interfacial motion to be slow compared with the characteristic time for diffusion throughout the wetting layer. For our experimental system, thought to be typical in this respect, these two time scales are very well separated. Figure 1 shows that measurable thickness changes occur on a time scale longer than several seconds. This is slow compared to the diffusion time scale for typical values of wetting layer thickness, $l = 35$ nm, and diffusion constant,[9] $D = 10^{-5}$ cm^2/s, $l^2/D \simeq 10^{-6}$ s: Therefore, LH's approximation should be very good and will also be adopted here.

Imagine that the bulk liquids are now brought out of equilibrium by a sudden temperature change to $T + \Delta T$. We denote the distance away from the substrate by z, and call the instantaneous position of the wetting layer interface z_i. The composition $X(z_i)$, just outside the wetting-layer interface, will instantly adjust to the chemical potential there. Including both the effect of temperature and of being away from the minimum in $V(l)$, we find

$$\frac{X(z_i)-X_b(T)}{X_a(T)-X_b(T)} = \frac{\beta \Delta T}{2|T-T_c|} + \frac{d_0}{\sigma}\left[\frac{\partial V}{\partial z}\right]_{z_i} . \tag{1}$$

The first term is the change in X_b upon equilibration after the temperature change, assuming the symmetric, noninverted, coexistence curve noted earlier. The second term is a result of LH; σ is the interfacial tension, and d_0 is a capillary length of order of the bulk correlation length ξ.[4,11] Each requires that ΔT be small compared to $|T-T_c|$.

To see what response is predicted by this picture, Fig. 2 shows the schematic composition profile very soon after a sudden change $\Delta T < 0$; the wetting layer has already attained its equilibrium composition but has not yet changed its thickness. At $z > z_i$ there is a composition gradient such that there will be a net diffusion of A molecules toward the wetting layer. Consequently the layer will become thicker and the interface will move out until it reaches $z_{\Delta T}$, where the composition at the interface is equal to that in the bulk. This is *not* the final thickness, however, because the bulk liquids are still out of equilibrium. In an experimental system, the mixture should equilibrate by diffusion within approximately a bulk diffusion time, L^2/D ($\simeq 10$ h for our sample). So as the composition ahead of the wetting layer relaxes to $X_a(T+\Delta T)$ over this third time scale, the thickness will return to equilibrium at the minimum of $V(l)$.

An exciting consequence of our model is that it suggests the following probe of $V(l)$ versus l. First, properly equilibrate the system and use, for example, reflectivity or ellipsometry to measure the wetting-layer thickness. Next, change the temperature by ΔT and measure $z_{\Delta T}$, how far the wetting layer moves before heading back toward equilibrium. If the system is large enough that the interface reaches $z_{\Delta T}$ well before a bulk diffusion time, then $z_{\Delta T}$ is found where Eq. (1) vanishes:

$$\left[\frac{\partial V}{\partial z}\right]_{z_{\Delta T}} = -\frac{\sigma}{d_0}\frac{\beta \Delta T}{2|T-T_c|} . \tag{2}$$

See Fig. 2 for a graphical interpretation of this condition. When all quantities on the right-hand side are known, this procedure can be repeated for various ΔT to map out $V(l)$. If the experimental system is too small, corrections to Eq. (2) will be required due to the continuously chang-

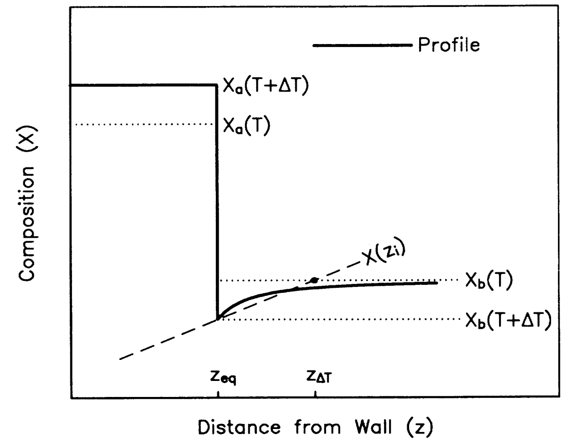

FIG. 2. Schematic composition profile soon after a small temperature jump ΔT away from T_c. $X_a(T)$ is the equilibrium composition of phase a at temperature T. $X(z_i)$ is the composition at the wetting-layer interface from Eq. (1). $z_{\Delta T}$ is the thickness achieved before relaxing back to the equilibrium value $z_{\rm eq}$.

ing bulk composition.[12] Note that there are no dynamical quantities in Eq. (2). This is analogous to locating the turning point in a one-dimensional mechanical system.

There has been much discussion of the nature of the substrate-liquid interaction in our system.[13–15] Experimental tests were previously limited to comparing the observed reflectivity to the value computed from the predicted wetting-layer structure. A direct measurement of $V(l)$, as proposed above, would permit a more detailed comparison with theory because it provides a natural description of the interaction. As a demonstration of our new technique, we present its application to preliminary observations.

At 15 K below T_c for our particular sample, the apparent equilibrium thickness was $z_{eq} \simeq 35$ nm; there is an estimated systematic error of ±40% from the reflectivity to thickness conversion.[9] This thickness steadily decreased over two months at a rate of -1%/day; such aging may be related to the T_c drift noted earlier, which indicates the increasing presence of impurities. This sample and level of systematic error are not ideal for a meaningful detailed measurement of $V(l)$. We can, however, make use of the $\simeq -1$ nm/mK linear response seen in Fig. 1, typical of all sample cells studied, to estimate the curvature of the minimum in $V(l)$; this is accomplished by expanding the left-hand side of Eq. (2). The result can be expressed naturally, and without reference to d_0/σ, by the inverse time constant for interfacial motion introduced in Eq. (10) of LH:

$$\omega_0 \equiv D\left[\frac{d_0}{\sigma}\left[\frac{\partial^2 V}{\partial z^2}\right]_{z_{eq}}\right]^2 = D\left[\frac{\beta}{2|T-T_c|}\frac{\Delta T}{\Delta Z}\right]^2 . \quad (3)$$

We find $\omega_0 = 0.07$/s with a factor of 5 uncertainty from the reflectivity to thickness conversion. Another result, also supported by all sample cells examined, is that the asymmetric response seen in Fig. 1 implies that outside the linear region, $V(l)$ more strongly resists decreasing than increasing the wetting-layer thickness.

These results can be compared with expectations based on a particular model of $V(l)$. It is now believed that the long-range substrate-liquid interaction in our system involves the preferential dissociation of surface hydroxyl groups and ionic impurities in the nitromethane-rich phase.[13–15] For the case of high-impurity concentration in the particular limit discussed by Kayser,[3] the effective interface potential simplifies to

$$V_{\text{ion}}(l) = A\exp(-2K_D l) + \Delta\rho g L l \ ;$$

K_D^{-1} is the Debye screening length, $\Delta\rho$ is the mass density difference between coexisting liquid phases, and g is gravitational acceleration. The sign of the asymmetry around the minimum of this form is consistent with our observations.[16] Direct calculation of Eq. (3) gives $\omega_0 = D(4d_0K_DL/a^2)^2$, where $a^2 = 2\sigma/\Delta\rho g$ is the gravitational capillary length squared. Taking $d_0 = \xi/6$, all quantities are known except K_D;[8,17] agreement with our value of ω_0 would require $K_D^{-1} \simeq 0.1$ nm. Up to this point, there is no major disagreement with our observations and the form $V_{\text{ion}}(l)$. Next, we solve Eq. (2) with $V = V_{\text{ion}}$ and find

$$z_{\Delta T} - z_{eq} = -\frac{1}{2K_D}\ln\left[1+\frac{a^2\beta}{4d_0 L}\frac{\Delta T}{|T-T_c|}\right] . \quad (4)$$

This predicts a much smaller linear region than could be supported by the data of Fig. 1; in fact Eq. (4) diverges for $\Delta T \lesssim -0.1$ mK. We conclude that the simple form $V_{\text{ion}}(l)$ does not adequately describe the substrate-liquid interaction in our particular sample. This demonstrates how our new technique may be applied; more realistic forms of $V(l)$ are available.[13–15]

Turning to the dynamics of temperature-driven wetting layers, we propose to measure the response versus frequency and amplitude of an applied sinusoidal temperature variation. This has the advantage over temperature-jump experiments that the dynamics are straightforward to model. Figure 3 demonstrates that such an experiment can be readily performed. Note that transients decay, leaving a steady-state oscillatory behavior which can be easily described. At 1.5 K below T_c, similar data showed that the same steady state was established whether the oscillations were applied to unequilibrated wetting layers which were initially very thick or very thin.

In these experiments, the composition far ahead of the wetting layer can be assumed constant because the system is driven faster than the bulk diffusion time. Therefore, of the three important time scales, only ω_0^{-1} remains of immediate concern. This simplification permits the dynamics to be modeled with nonlinear transport equations as follows. We denote the composition profile dimensionlessly by

$$m(z) \equiv [X(z) - X_b]/[X_a - X_b] \ ;$$

X_a and X_b refer to compositions at $\Delta T = 0$. Inside the wetting layer, $z < z_i$, the composition is constant by the

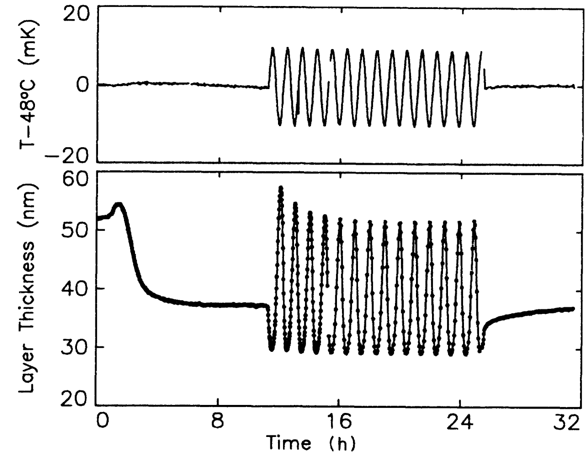

FIG. 3. Wetting-layer thickness vs time for 10 mK sinusoidal temperature oscillation at 15 K below T_c. At 1.0 h, the *in situ* stirring, which gives an artificially thick wetting layer as discussed in Ref. 9, was stopped. The temperature oscillation was started after the wetting layer had relaxed to a steady-state thickness. There is a ±40% uncertainty in the absolute thickness scale.

local equilibrium approximation. Elsewhere, behavior is governed by diffusion:

$$\frac{\partial m}{\partial t}=D\frac{\partial^2 m}{\partial z^2} \quad (z>z_i) , \tag{5}$$

$$\frac{dz_i}{dt}=D\left[\frac{\partial m}{\partial z}\right]_{z_i} , \tag{6}$$

$$m(z_i)=\frac{\beta\Delta T}{2|T-T_c|}+\frac{d_0}{\sigma}\left[\frac{\partial V}{\partial z}\right]_{z_i} . \tag{7}$$

Equation (6) is a conservation equation determining the change in wetting-layer thickness per unit time due to diffusion. The other boundary condition, Eq. (7), is Eq. (1) reproduced here for convenience. To compare with experiment, one must solve for the interfacial motion $z_i(t)$ when $\Delta T \propto \sin(\omega t)$.

For the simpler case $\Delta T=0$ we have obtained a numerical solution of Eqs. (5)–(7). We find support for earlier predictions[4,5] that the wetting layer approaches its equilibrium thickness as $(\omega_0 t)^{-1/2}$. Unfortunately, this *cannot* be tested by the relaxation data in Fig. 3, immediately after the stirring was stopped, because the bulk liquids, not just the wetting layer, are out of equilibrium. There, the approach is very well described by $\exp(-\sqrt{t/600\text{ s}})$; this stretched exponential form was observed in all such relaxations performed. We note that our numerical composition profiles are similar to a half-Gaussian and imply that it is *not appropriate* to employ the usual quasistatic approximation that the left-hand side of Eq. (5) is zero.

In conclusion, we have reported a striking, nonequilibrium, sensitivity of the wetting-layer thickness to small temperature perturbations. An independent theoretical model was proposed which also permits study of the substrate-liquid interaction to a degree not possible until now. To demonstrate this new technique, we have explored the nature of the minimum in the effective interface potential for a particular system. In addition to more detailed measurements of this potential, it would be interesting to explore other systems for secondary minima, such as are expected near certain wetting transitions. Finally, a specific program was outlined for further experimental and theoretical study of the interfacial dynamics of wetting layers. Further experimental and theoretical details are available.[18]

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[12] Temperature-jump experiments are, therefore, not ideal for studying dynamical questions: The size of the system enters nontrivially. The temperature-modulation experiment, proposed layer, avoids this complication.

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[16] Note that a van der Waals interaction, $V(l)=Al^{-p}+\Delta\rho gLl$ with $p=2$ or 3, also has a similarly asymmetric minimum.

[17] Footnote 7 of Ref. 9; ξ is deduced from turbidity measurements.

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