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Capillary-rise study of nonequilibrium wetting by a binary liquid caused by temperature ramps

Niraj S. Desai and Carl Franck
Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

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A phase-separated mixture of cyclohexane and acetic anhydride was subjected to positive linear temperature ramps while the capillary rise of the acetic anhydride-rich phase against a glass substrate was measured. The ramps, which drove the system out of thermal equilibrium, had the effect of producing large nonlinear changes in capillary rise with respect to ramp rate. These changes may be explained in terms of the nonequilibrium behavior of the wetting-layer thickness, and depended only weakly on the size of the ramps. The deviation of the capillary rise from its equilibrium value was found to attain a steady state after the temperature had been raised by ≈ 0.6 K from the starting temperature of $T_c - T = 5.9$ K, independent of the ramp rate. This steady state may be indicative of the virtual disappearance of the wetting layer. Unlike recent direct observations of wetting-layer thickness [Dean Ripple and Carl Franck, Phys. Rev. A **44**, 8289 (1991)], our results could not be simply described as the "equilibrium" wetting behavior of a bulk nonequilibrium experiencing linear response to a weak temperature ramp.

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I. INTRODUCTION

Consider a binary liquid at coexistence composed of A and B molecules in contact with a solid wall. If the wall preferentially adsorbs one of the components—the B molecules for example—then sufficiently close to the critical solution temperature T_c of the bulk mixture, a thick layer of the B-rich phase may protrude between the wall and the A-rich phase. The structure and thermodynamics of this wetting layer depend on the detailed nature of the intermolecular forces and on the relative free energies of the bulk and adsorbed liquids. Dispersion forces [1], electrostatic forces [2], capillary waves [3], and the proximity of the critical point [4] may all play roles in determining the wetting structure. A variety of methods, including capillary rise and ellipsometry, have long been used to study wetting systems in equilibrium [5]. Such studies have greatly contributed to our understanding of the statics of wetting phenomena, including the equilibrium thicknesses of wetting layers.

Less well studied has been the response of wetting systems to being pushed out of thermal equilibrium. Recently researchers have examined the kinetics of wetting-layer formation and the response of layers to temperature perturbations [6–9]. Such experiments are motivated by questions of what determines the thickness of a wetting layer, how a layer attains its steady-state thickness (if it does so), and in what ways the nonequilibrium state differs from equilibrium. The answers to these questions also offer information about the nature of the wetting phase diagram and the details of the forces responsible for wetting. It has been suggested [9], for example, that by changing the temperature of a binary liquid mixture in a controlled fashion, one may move the system an arbitrary distance from coexistence and examine hitherto inaccessible regions of the phase diagram. Such an experimental method may be useful, among other things, in the search for prewetting transitions [10].

Another motivation for studying nonequilibrium wetting phenomena is to understand the role they play in practical equilibrium experiments. That temperature and concentration gradients can affect the thicknesses of wetting layers has been a source of concern for some time [11], but precisely what kind and how great an effect they have is for the most part unknown. Studies of wetting systems driven out of equilibrium provide some basis for evaluating these concerns.

In the present paper we are concerned with how capillary-rise phenomena are affected by spatially uniform changes in temperature. The particular system we study is a mixture of cyclohexane and acetic anhydride at the critical composition but below T_c. In equilibrium, the liquids are at two-phase coexistence and, when a narrow borosilicate glass tube penetrates the liquid-liquid interface, the glass is completely wet by the denser acetic anhydride-rich phase. The state of wetting and the surface tension are characterized by the capillary rise [12], the difference in height between the capillary meniscus and the bulk meniscus. Beginning with the system in such an initial state, we then subject it to positive linear temperature ramps ranging in strength between 14 mK/h and 3.3 K/h, and record changes in capillary rise as a function of time.

Summarizing our results, we find that the absolute value of the capillary rise drops dramatically, from several millimeters to almost zero as the temperature is increased a few kelvins. More interesting is the deviation of the capillary rise from its equilibrium value at a particular temperature as the temperature is ramped. For an infinitesimally slow ramp, the deviation would, of course, be zero. For these rather large ramps, however, the deviation initially increases substantially as the temperature increases and then levels off to a steady-state value. The size of this steady-state deviation depends very weakly (almost logarithmically) on the ramp rate.

This finding can be explained by considering how abruptly thinning the wetting layer—as driving the system out of equilibrium by increasing the temperature is wont to do—depresses capillary rise [8]. In particular, the observed steady state may be explained in terms of removing the wetting layer almost entirely; after the temperature ramp achieves this, no further changes are possible. Alternatively, it may be that the rate the linear ramp pushes the system off coexistence balances the relaxation of the mixture back towards equilibrium. The system would then be at a fixed thermodynamic distance from equilibrium, and the layer thickness would reflect that distance. It was this latter notion that motivated the experiments of Ripple and Franck [9] and their suggestion that the nonequilibrium technique of temperature ramping might be used to explore regions of the binary-liquid phase diagram off of coexistence. Explaining our results within this framework is problematic because we find that the linear-response theory used by Ripple and Franck to model the effect of a temperature ramp is not consistent with our data.

One particularly interesting aspect of our results is that the time for the capillary-rise deviation to achieve a steady state is inversely proportional to the ramp rate $\dot{T}$. That is, the steady state is achieved after the temperature is changed by a fixed amount from the starting temperature, regardless of the rate at which this is done. For a starting temperature of T=46.5 °C (5.9 K below the mixing temperature), this fixed amount was found to be $\Delta T \approx 0.6$ K. It may be that ΔT is the thermodynamic distance from two-phase coexistence (i.e., equilibrium) at which the wetting layer is almost entirely removed.

The outline of this paper is as follows. Section II details the sample preparation and experimental procedure. Section III presents the basic results and describes a control experiment that precludes thermal gradients as the source of the observed behavior. Section IV examines possible interpretations of the data. It is shown in that section that a linear-response model is not appropriate.

II. EXPERIMENTAL MATERIALS AND PROCEDURE

The sample cell used for these measurements is similar to those described in Ref. [13]. It consists of a 12-cm-long glass cylinder of inner diameter 0.9 cm. The bottom of the cylinder is fused shut and the top can be sealed with a Teflon stopcock. The cell was filled with a 9.5-ml mixture of cyclohexane and acetic anhydride at the critical composition of $\phi_c \approx 0.613$ volume fraction of cyclohexane. Soon after the sample preparation, the critical mixing temperature was measured to be $T_c \approx 52.41\,^\circ$C. This value of T_c was found to remain constant to within a few millikelvin over a period of three months.

The cell held six capillary tubes which had been cut from borosilicate glass micropipets. These tubes had inner radii of 0.134 or 0.190 mm and lengths of 4–6 cm. They were held and manipulated inside the sample cell by a cylindrical Teflon holder which contained a Teflon-encapsulated magnetic stir bar (see Fig. 2 of Ref. [13]). The cleaning process for the capillaries was meant to produce maximally clean, hydroxylated surfaces. It began with sonocation in several changes of acetone, methanol, and distilled water. The tubes were then exposed to chromic-sulfuric acid cleaning solution at 80 °C for 30 min, rinsed and boiled in distilled water, and dried in air. After the capillaries had been mounted in the sample cell, the cell was filled and sealed in an argon atmosphere.

Temperature control for the cell was provided by an insulated water bath. A Tronac temperature controller drove two aquarium heaters and the bath was stirred continuously by a pair of propellers mounted on a vertical shaft. The linear ramps in temperature used in this experiment were produced by adjusting the computer-operated controller. The fastest ramps remained linear to better than 5%, but an equipment problem superimposed a 7-mK oscillation of a 10-min period on the slower ramps. We are confident this problem did not affect our results because equilibrium measurements made with and without the oscillation proved to be the same.

The basic procedure was to fix the temperature at the starting value, normally $T_s = 46.5\,^\circ$C, and then to stir the liquid sample thoroughly by raising and lowering the capillary tubes and their holder repeatedly through the length of the cell. Sufficient time was then allowed to pass to ensure that the sample had equilibrated, that is, leaving two clear coexisting phases: the top phase rich in cyclohexane (the less dense liquid), the bottom phase rich in acetic anhydride. After this equilibrium had been established, the capillary tubes were slowly raised through the liquid-liquid interface; care was taken to make sure that the tubes were oriented vertically to within a few degrees. The rises of the capillary meniscii above the bulk meniscus attained their stationary values within a few minutes after the tubes were put in position, and a cathetometer of resolution 0.02 mm was used to measure these values.

Equilibrium measurements from 8 to 1 K below T_c all indicated complete wetting of the glass capillary walls by the acetic anhydride-rich phase. The equilibrium capillary rise $h_{\rm eq}$ in this temperature range was found to obey the expected power law in reduced temperature $t = (T_c - T)/T_c$, valid for $h \gg r$ [14],

$$h_{\rm eq} = \frac{a_0^2}{r}|t|^{\mu-\beta}, \tag{1}$$

with amplitude $a_0^2 \approx 15.5$ mm^2. In this equation, r is the capillary radius and the difference in critical exponents is known to be $\mu - \beta = 0.94$ [15].

Once equilibrium at the starting temperature ($|T_c - T_s| = 5.9$ K) had been established and measured, the temperature was increased linearly at a steady rate. Rates used in this study ranged between 14 mK/h and 3.3 K/h. The ramps had durations long enough typically to raise the temperature by a few degrees; some data runs lasted 1h, others several days. During a temperature ramp, the capillary rise in each tube was monitored and recorded periodically.

III. BASIC RESULTS

While equilibrium capillary-rise measurements proceed about linearly to zero as the critical temperature is approached, we found that, when the temperature is ramped, capillary rise drops even more sharply. A graph showing the amount by which several ramped rises differ from equilibrium rise is given in Fig. 1 for a tube of a particular radius and position; data for tubes of other radii and positions have the same general features. We see that there are two distinct regions: Immediately after the start of a temperature ramp, the capillary rise begins to deviate from equilibrium in a dramatic fashion, but after T has changed by a few tenths of a degree, the rise deviation levels off, tending towards a steady-state value.

It is interesting to note that, in the first region, the rise deviation increases in the same linear fashion with increasing temperature for all ramp rates studied. This suggests that it is the change in temperature, rather than the time lapsed, that most determines the system's response to a temperature ramp. We can make this statement somewhat more concrete by examining the dependence on the ramp rate of the time t_{SS} it takes the deviation to approach steady-state behavior. As our operational definition of t_{SS} we adopt the time after the beginning of a ramp at which the rise deviation is two-thirds of its final value. Figure 2 shows that this time is almost inversely proportional to $\dot{T}$. In other words, the deviation stops growing after the temperature has been changed from the starting temperature by $\Delta T = t_{SS}\dot{T} \approx$ const, independent of the ramp rate. We found that this constant was $\Delta T \approx 0.6$ K. Changing the position of the tubes with respect to the bulk meniscus did not affect the value of ΔT obtained, nor was any difference in ΔT detected between the two capillary radii we examined.

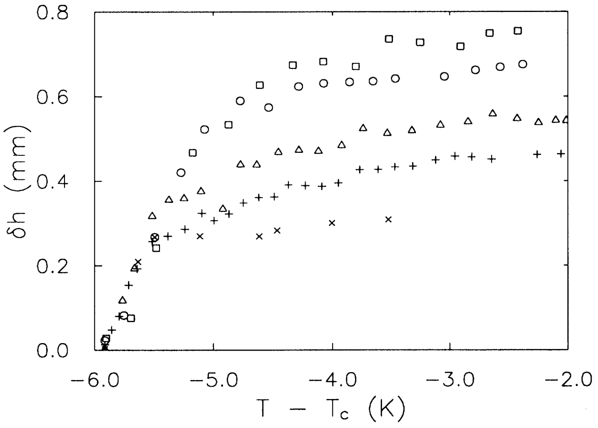

FIG. 1. Deviation of ramped capillary rise from equilibrium rise, $\delta h = h_{\mathrm{eq}} - h_{\mathrm{ramped}}$. Data are for a tube of radius 0.134 mm extending ~ 3.2 cm into the nonwetting phase. All temperature ramps began at $T - T_c = -5.9$ K. Results for five ramp rates are shown: 3.3 K/h (□), 2.6 K/h (○), 1.6 K/h (△), 0.8 K/h (+), 55 mK/h (×).

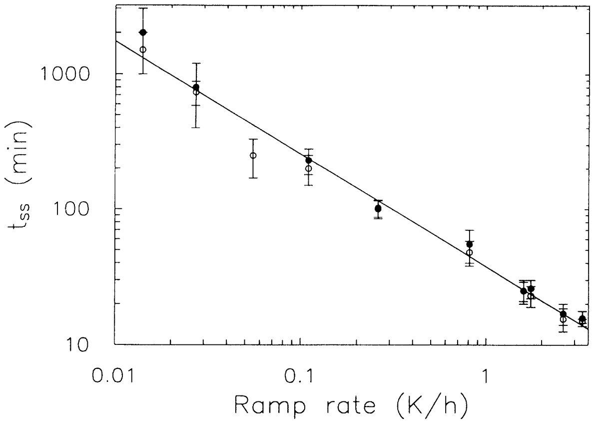

FIG. 2. Time to steady state t_{SS} as a function of ramp rate $\dot{T}$. Open circles are data for a capillary of inner radius $r = 0.134$ mm extending $l \approx 3.2$ mm above the bulk meniscus. Solid circles are for a capillary of $r = 0.190$ mm and $l \approx 2.2$ cm. The least-squares fit indicates $t_{SS} \propto \dot{T}^{\alpha}$, where $\alpha = -0.83 \pm 0.05$. This means $\Delta T = t_{SS}\dot{T}$ is almost constant; the fit gives $\Delta T \approx 0.6$ K.

In the second region, observe that the value of the steady-state deviation toward which the system tends depends only weakly on the ramp rate. Figure 3 gives steady-state deviation versus ramp rate for tubes of the two radii used in this study; repeated measurements at a single rate indicate the significant scatter in the data. The dependence could well be described as logarithmic. Alternatively, one could fit the data for both radii into an equation of the form $\delta h_{SS} \propto \dot{T}^{a}$, with an exponent a $= 0.17 \pm 0.04$.

Before proceeding, it is important to note the changes in capillary rise that we have measured are products of the linear temperature ramps themselves and not artifacts of the method we used to create those ramps. Of most obvious concern are the thermal gradients that were set up in the sample cell as a result of our continuously increasing the temperature. Wetting layers are thought

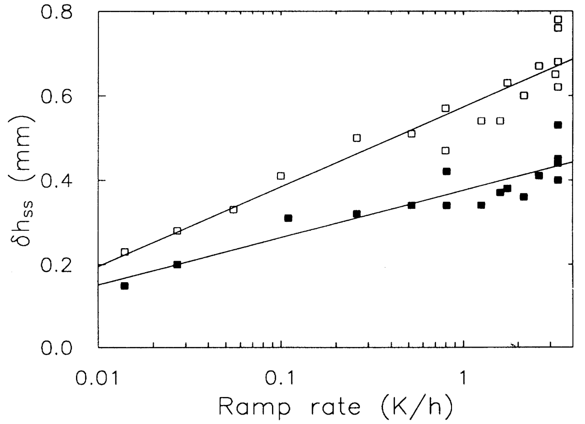

FIG. 3. Steady-state deviation vs ramp rate. Data for two capillaries are shown: one of radius 0.134 mm and extent $l \approx 3.2$ cm (open squares), the other of radius 0.190 mm and extent $l \approx 2.2$ cm (solid squares).

to be sensitive to the presence of thermal gradients [11], though no general theory yet exists for how large a gradient must be in order to have an important effect. To address this concern in the context of the present experiment, we used a thermocouple pair to measure directly the temperature difference between the inside and the outside of a capillary tube of inner radius 0.190 mm and wall thickness ≈ 0.3 mm while the sample cell was subjected to a 3-K/h ramp. We found this temperature difference, measured at the position of the capillary meniscus, was roughly 6 mK over the ≈ 0.5 mm distance spanned by the thermocouple pair. We then performed a control experiment in which we set up a somewhat larger temperature gradient near the meniscus position while the cell was at *fixed* overall temperature. This was done by attaching heating resistors to the side of the sample cell and keeping the water bath temperature constant. In the absence of temperature ramping, we found that this thermal gradient alone produced changes in capillary rise of less than 0.03 mm, slightly larger than the precision of our measurements but several times smaller than those produced in steady state by even the smallest linear ramp used in this study. Moreover, the very small changes we did see may have been caused by the process of establishing the gradient rather than by the gradient itself. This control experiment is not unassailable because the gradients produced by the heating resistors were not identical to those produced by ramping the water bath temperature. In particular, the latter would be expected to set up gradients uniform over the length of the capillary tube; the control experiment's resistors created the desired gradients in the vicinity of the capillary meniscus but not elsewhere along the tube. Nevertheless, this test does give us great confidence in thinking about our data in terms of a wetting system subject to spatially uniform changes in temperature.

IV. INTERPRETATION

We believe the explanation for our results rests primarily in the behavior of the wetting layer coating the inside of each capillary tube. Earlier work has found that wetting layers must decrease in thickness following a temperature burn or ramp [7, 8]. We would expect that, given the large ramp rates employed in this experiment, a particular capillary's wetting layer should thin substantially in the course of a ramp. Indeed, the layer may be removed entirely. Wetting layer material shed in this manner would diffuse into the interior of the capillary, changing the average density of the liquid inside the tube. Hydrostatic force balance, as a result, would then require a capillary rise markedly different from equilibrium rise.

This explanation is plausible because, absent convection, we would expect shedded layer material to remain trapped inside the capillary tube during a data run. Given a diffusion coefficient D of order 10^{-6} cm^2/sec [16], it would take only a few minutes for material to diffuse radially toward the center of the capillary, but roughly a week to move axially across, for example, half a typical tube extent—much longer than the times involved in this experiment (see Fig. 2). Also, the capillary rise should react very quickly to an unbalanced pressure because the characteristic relaxation time (the so-called Washburn time [17]) for this process is only of order 10 sec, in the temperature range studied, for all the capillaries in our sample cell [18].

Durian *et al.* [8] have considered the situation in which the layer thickness inside a capillary of radius r decreases by an average amount δ. The average is taken over the length l that the capillary extends into the nonwetting phase. The shedded material is assumed to change the density of the nonwetting phase inside the capillary to ρ'_N, while the density outside remains ρ_N ($\rho'_N > \rho_N$). The density of the wetting phase throughout is assumed unchanged and given by ρ_W. In such a situation, pressure balance indicates that, in steady state, the capillary rise should be

$$h \simeq \frac{2\sigma}{\Delta\rho g r} - \frac{2\delta l}{r}. \tag{2}$$

Here σ is the liquid-liquid interfacial tension, g is the gravitational acceleration, and $\Delta\rho = \rho_W - \rho_N$ is the equilibrium density difference. Two approximations have been made: the nonequilibrium density difference $\rho_W - \rho'_N$ is taken as equal to the equilibrium difference, and

$$\frac{\rho'_N - \rho_N}{\Delta\rho} \approx \frac{2\delta}{r}. \tag{3}$$

The first term in Eq. (2) is simply the usual capillary-rise formula, but the second indicates by how much the rise should be depressed because of the nonequilibrium density in the interior of the capillary. It is this second term that we believe produces most of the deviation from equilibrium that we have measured. Note that Eq. (2) indicates that the extent of the capillary tube above the liquid-liquid interface influences how much of an effect we should see. An obvious test of the validity of the second term is to measure the ramped capillary rise for various extents l. This is done in Fig. 4. Because Eq. (2) is a formula valid for *steady-state* behavior, only steady-state values of the capillary-rise deviation are shown. For the given ramp rate $\dot{T} = 3.3$ K/h, the time for the deviation to reach a steady state was ≈ 15 min for all extents.

Figure 4 does indicate a substantial dependence on l of the deviation from equilibrium, $\delta h_{\mathrm{SS}} = h_{\mathrm{eq}} - h_{\mathrm{ramped}}$. The dependence is reasonably linear—as Eq. (2) would seem to suggest it should be. This point is not at all clear, both because of the approximations employed and because the average thickness change δ should itself have some extent dependence. Nevertheless, we can attempt from a straight-line fit to Fig. 4 to extract a rough value for δ. Doing so, we find the curves for both size tubes give $\delta \approx 1$ μm. This number may signal the need for a more elaborate explanation of the effect of burning the wetting layer on capillary rise because direct measurements of layer thicknesses by others have so far found no wetting layers thicker than a few hundred nanometers [11]. On the other hand, these other measurements were made using other chemical systems in other geometries. Moreover, the temperature jump experiments of

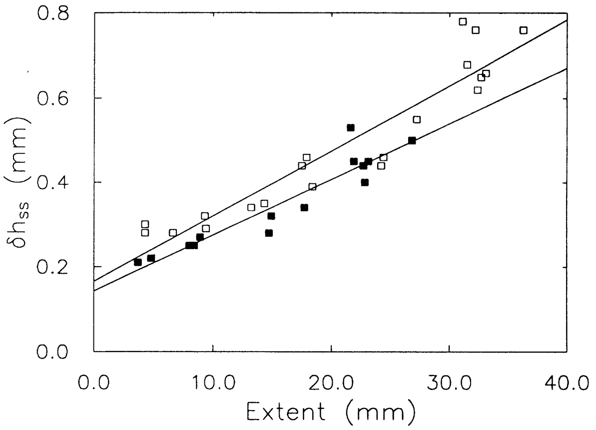

FIG. 4. Dependence of steady-state deviation on how far capillary extends above bulk meniscus. A ramp rate of 3.3 K/h was used for all data. One tube had radius 0.134 mm (open squares), the other tube had radius 0.190 mm (solid squares).

Durian *et al.* [8] also gave a value for the change in layer thickness of order 1 μm.

Another reason to suspect that our proffered explanation of the temperature ramp data is incomplete is the fact that neither line of Fig. 4 goes through the origin. That is, δh_{SS} does not go to zero when one tries to extrapolate to zero extent. This strongly suggests that ramping the temperature has other effects besides burning off parts of the wetting layer. To get at possible additional effects, consider the general capillary-rise formula [14], applicable in equilibrium

$$\begin{aligned} h &= \frac{2\sigma}{\Delta\rho g r}\cos\theta \\ &= \frac{2}{\Delta\rho g r}(\sigma_{NG}-\sigma_{WG}). \end{aligned} \tag{4}$$

Above, θ is the contact angle that the liquid-liquid interface makes with the glass wall. The second line of Eq. (4) defines two interfacial energies, σ_{NG} and σ_{WG}, which are associated with the interfaces between the glass substrate and the nonwetting and wetting liquid phases, respectively. We see immediately that forcing the bulk system out of equilibrium via temperature ramps can affect capillary rise in two ways other than by thinning the wetting layer. First, the average density difference of the bulk liquid phases may differ from the equilibrium difference at a given temperature. This was certainly the case in our experiment given the substantial and continuous temperature ramping. Second, the free-energy difference, $\Delta\sigma = \sigma_{NG} - \sigma_{WG}$, which depends on how the wall interacts with the liquids, may behave in some new manner if the system is forced off of two-phase coexistence and out of equilibrium. Indeed, it was the hope of detecting one such unusual behavior off of the coexistence curve, the prewetting transition, that originally motivated this experiment.

Three factors, therefore, seem most likely to have produced the measured deviations of capillary rise from equilibrium: thinning of the wetting layer by an amount δ, a nonequilibrium density difference $\Delta\rho$, and a nonequilibrium free-energy difference $\Delta\sigma$. Making a connection between these three factors and the temperature ramp rate $\dot{T}$ is the obvious next step, but it is one that has proven very difficult. To begin to see why, let us consider the steady-state behavior.

The first question to ask is, why does the capillary-rise deviation level off to a steady state? The simplest suggestion is that the wetting layer is eventually removed entirely by ramping the temperature at the rates we have used. In this view, the deviation from equilibrium grows after the start of a ramp because the wetting layer is being burned off piece by piece. After the temperature has been ramped by some amount ΔT—estimated earlier as 0.6 K independent of $\dot{T}$—the layer will essentially be gone. Once this has happened, the deviation stops growing and a steady state is reached in which the ramped capillary rise decreases at the same rate with increasing temperature as the equilibrium rise. This idea is plausible because Fig. 4 shows that layer thinning is the dominant effect of a ramp. One could then argue that the small dependence of the steady-state deviation δh_{SS} on $\dot{T}$ (Fig. 3) is caused, in part, by the other two factors—the nonequilibrium density and free-energy differences. Also, ramps at the smallest rates ($\sim$ 20 mK/h) take much longer to reach steady state than do the fastest ramps ($\sim$ 3 K/h), allowing material shed by the wetting layer more time to exit the nonwetting phase. The problem with this approach is that it alone does not contain any obvious framework for discussing the approach to steady state or the differences between ramp rates.

Another (and perhaps more interesting) explanation for the appearance of a steady state is that the rate at which a linear temperature ramp drives the mixture from two-phase coexistence is eventually balanced by the relaxation of the system back towards equilibrium [19]. The wetting-layer thickness, bulk density difference, and free-energy difference might then vary by fixed amounts from their equilibrium values at a particular temperature, producing the steady state observed. This notion is appealing because it suggests that it is possible to unambiguously characterize the effect of a linear ramp. Specifically, Ripple and Franck [9] have argued that weak linear ramps can be analyzed using the equilibrium phase diagram of a binary liquid mixture, which has as its coordinates the temperature and the chemical concentration of one of the mixture's components. The crucial ideas are that steadily increasing the temperature pushes the system off of coexistence somewhere into the single-phase region of the phase diagram, and that the system's wetting properties (including, in our case, the capillary-rise deviation) reflect this position, even though the bulk mixture itself is out of equilibrium. The question for us then is: Where in the single phase region does a particular ramp rate $\dot{T}$ move our system?

In trying to answer this question, it is worthwhile to go quickly through part of the Ripple-Franck argument (a more complete discussion is given in Ref. [9]). During a temperature ramp, the instantaneous chemical concentration $\phi(T)$ in the wetting phase (or in the adjacent spectator phase) differs from its coexistence value $\phi_{co}(T)$ at the instantaneous temperature T. This deviation forces a flux J of material across the liquid-liquid interface. The simplest relation we can imagine between this deviation and the flux is *linear response*, i.e., $J \sim \phi - \phi_{co}$. Mass conservation requires $J \sim \partial\phi/\partial t$, and so we have

$$\frac{\partial \phi}{\partial t} = -\frac{1}{\tau_0}(\phi - \phi_{co}), \tag{5}$$

where we have introduced a phenomenological time constant τ_0. If we introduce a new variable $\tilde{\phi} \equiv \phi - \phi_{co}$ and allow the temperature to vary at a constant rate $\dot{T}$, then Eq. (5) becomes

$$\frac{\partial \tilde{\phi}}{\partial t} = -\frac{\tilde{\phi}}{\tau_0} - \left[\frac{d\phi_{co}}{dT}\right]\dot{T}. \tag{6}$$

The solution of Eq. (6) is by inspection

$$\tilde{\phi} = Ae^{-t/\tau_0} - \tau_0 \dot{T}\left[\frac{d\phi_{co}}{dT}\right], \tag{7}$$

where $(d\phi_{co}/dT)$ is assumed to be constant. In the long-time limit, there exists a steady state in which the deviation from coexistence can be described in terms of a shift in chemical concentration:

$$\tilde{\phi}_{SS} = \phi_{SS} - \phi_{co} = -\tau_0 \dot{T}\left[\frac{d\phi_{co}}{dT}\right], \tag{8}$$

Alternatively, one could express this deviation as a shift in temperature, $T - T_{co} = \tau_0 \dot{T}$ [20], where T_{co} is the temperature at which ϕ_{SS} is at two-phase coexistence. The system may then be described as moving in the phase diagram, as the temperature is ramped, along a trajectory a fixed distance $\delta T = \tau_0 \dot{T}$ above the coexistence curve (see Fig. 2 of Ref. [9]).

We attempted to analyze our capillary-rise data within the Ripple-Franck linear-response model, but found this was not possible. The crucial difficulty was in identifying a single characteristic time τ_0. In principle, one can do so by turning on a linear ramp $\dot{T}$ and examining the temporal response. From Eq. (7) we see that the concentration deviation $\tilde{\phi}$ (or the temperature deviation δT) should reach a steady state exponentially with a time constant τ_0. To see how this idea might be applied to our data, first consider a graph of capillary-rise deviation δh versus time for the largest ramp rate [Fig. 5(a)]. We imagine that, in approaching the phase-diagram trajectory appropriate for that ramp rate, the system crosses over the trajectories appropriate for all lower rates, assuming momentarily the rise deviation of each those trajectories in turn. If this is a correct use of the phase diagram, then we can use Fig. 3 to convert specific values of δh into values of $\dot{T}$, which in turn are simply related to values of δT. The resulting curve should relax exponentially with time towards its final value. Figure 5(b) shows the result for the $\dot{T} = 3.3$ K/h data; the error bars were estimated by considering the scatter between the five data runs at that rate. The curve certainly does not have the desired exponential shape, and so no time constant τ_0 can be extracted.

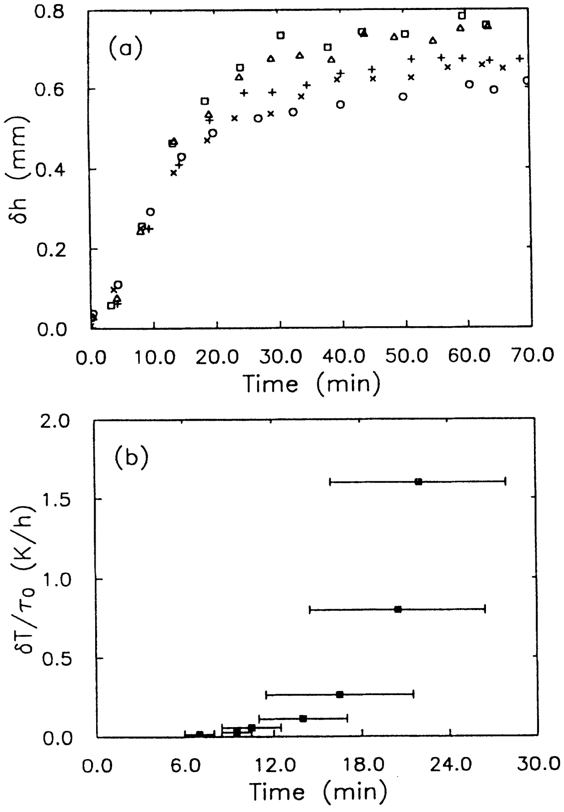

FIG. 5. (a) Capillary-rise deviation as a function of time. Data shown are for a tube of inner radius 0.134 mm and extent 3.2 cm; the ramp rate was 3.3 K/h. The same set of measurements was repeated five times; note significant scatter in data. (b) Temperature deviation vs time. Figure 3 was used to convert δh values of graph (a) into corresponding values of $\dot{T}$. These were then equated with temperature deviation $\delta T/\tau_0$ as per the linear-response model. Observe the nonexponential shape of the resulting graph.

Our attempt likely failed because the ramping rates were so large and the hydrodynamics so complicated that (1) linear response was inapplicable, and (2) it might not have been appropriate to use the equilibrium bulk phase diagram to characterize the nonequilibrium wetting phenomena. This is in contrast to the experiment of Ripple and Franck in which a direct observation of the wetting-layer thickness was used as a probe for the wetting-layer response to temperature ramps. The hydrodynamics of that experiment were sufficiently well understood that a successful estimate of τ_0 was made. Also, the ramping rates used were considerably smaller than in our work—25 mK/h was the largest rate. Whether this kind of linear-response model would work in our system for smaller ramp rates is an open question.

V. CONCLUSIONS

We have used a classic wetting experiment, capillary rise, to explore the behavior of a wetting system taken out of equilibrium by steadily increasing the system's temperature in a uniform manner. For sufficiently large temperature ramps, we find that capillary rise deviates significantly from equilibrium. In particular, we have witnessed a kind of steady-state behavior in the deviation after initial fast kinetics once a ramp is applied. We have also established that there is a characteristic temperature that signals the crossover from transient to steady-state response. The magnitude of the steady-state response is itself a weak function of the ramp rate. There is evidence to indicate that the nonequilibrium response found in this system is due, in part, to the effect on bulk hydrostatics of shedding wetting layers. We speculate that the observed steady-state behavior is indicative of the complete removal of wetting layers. All our results are ripe for theoretical investigation. The simplest approach of all, a linear-response theory based on a single phenomenological response coefficient—so successful in interpreting direct measurements of wetting-layer thickness subject to ramps—is apparently unsuitable. Whether such a linear-response regime in fact exists could be the object of future experiments. If attainable, it would provide an extremely useful means of extending capillary-rise investigations from off of coexistence and into the single-phase region. Future work examining the response of other chemical systems to temperature ramps might also be useful.

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