Nucleated Wetting Layers

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We observe a new wetting layer growth mechanism at the liquid/vapor surface of the critical mixture acetone + hexadecane. After spinodal decomposition of the bulk liquid, a metastable surface state forms. This metastable state is consistent with critical adsorption and persists until a wetting film or droplets of the lower phase are nucleated at the surface. Film growth occurs for $\Delta T = T_c - T < 0.1\,°\mathrm{C}$ while droplet growth occurs for $\Delta T > 0.1\,°\mathrm{C}$. The droplet nucleation time is consistent with classical nucleation theory provided the droplet line tension, $\mathcal{L}$, is included in the surface free energy. We determine that $\mathcal{L} \sim t^{0.83}$ close to T_c where t is the reduced temperature.

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How does a wetting layer form at the liquid/vapor surface of a critical binary liquid mixture if the bulk phase undergoes a spinodal decomposition from the one-phase region into the two-phase region? There have been a few attempts at answering this question from both theorists [1,2] and experimentalists [3,4] in recent years; however, a definitive understanding of this problem has not been reached. The theoretical papers [1,2] consider the growth of a *uniform* wetting layer film via diffusion-limited growth from the upper liquid phase where initially a concentration gradient develops at the liquid/vapor surface [1]. At later times the wetting layer growth slows down because wetting molecules must diffuse over a distance $\delta(\tau) = (D\tau)^{1/2}$ in order to reach the wetting layer [2]. Here τ is time and D is the mutual diffusion coefficient.

In recent experiments [3,4] on critical liquid mixtures in contact with a glass surface the wetting layer has been observed to nucleate spontaneously as droplets on the glass surface. These droplets then grow and coalesce in a complicated manner due to the coupling between the droplet growth and the process of spinodal decomposition which is *simultaneously* occurring in the bulk; we call this growth mechanism spinodal wetting in this paper. The wetting droplets coarsen and grow at a faster rate than bulk growth [4]. A theoretical description of this complicated situation is at present unavailable.

In this Letter we study the critical liquid mixture acetone + hexadecane; this mixture is not density matched; therefore, for deep temperature quenches into the two-phase region the bulk phase separates very rapidly. We observe that, after an initial transient (which will be discussed later), the surface drops into a metastable state within ~15 min. This metastable state persists for many hours. The equilibrium wetting layer eventually develops from this metastable surface state either by nucleation, growth, and coalescence of wetting droplets (for $\Delta T = T_c - T > 0.1\,°\mathrm{C}$) or by continuous film growth (for $\Delta T < 0.1\,°\mathrm{C}$). We call this type of growth nucleated wetting—it occurs *a long time* after the bulk has phase separated and attained equilibrium. In this paper we will show that the metastable surface state is consistent with critical adsorption. We will also examine the nucleation time for droplet formation in the vicinity of the critical temperature, T_c. This nucleation time is well described by classical nucleation theory provided that the *droplet line tension*, $\mathcal{L}$, is included in the surface free energy. We determine that $\mathcal{L} \sim t^{0.83}$, where $t = |T_c - T|/T_c$ is the reduced temperature.

Our sample consisted of a critical mixture of acetone + hexadecane with critical volume fraction of hexadecane $\phi_c = 0.482$ and $T_c \approx 31.1\,°\mathrm{C}$. Pegg [5] has studied this mixture extensively and obtained $\phi_c = 0.4821$ and $T_c = 25.342\,°\mathrm{C}$. For this liquid mixture T_c is known to be very sensitive to any water impurities. A cylindrical glass ampoule approximately 1 in. in diameter and 2.5 in. long was half filled with a critical mixture and then flame sealed in air. In the experimental geometry the symmetry axis of the sample cell was horizontal. The heavier acetone-rich phase has *both* a lower liquid/vapor surface tension and a lower optical refractive index compared with the upper hexadecane-rich phase. Therefore we expect a thick acetone-rich wetting layer to form at the liquid/vapor surface of the mixture for temperatures sufficiently close to T_c. The equilibrium wetting layer thickness is stabilized by a competition between gravitational forces which thin the wetting layer and dispersion forces which thicken the layer [6].

A conventional phase-modulated ellipsometer, based upon the design of Beaglehole [7], was used to study the nucleation and growth of the wetting layer. The ellipsometer was used at the Brewster angle where the signal is given by $\bar{\rho} = \mathrm{Im}(r_p/r_s)$. Here r_p and r_s are the reflection amplitudes for the p and s polarizations, respectively. For the thin wetting layers observed (~25 nm) $\bar{\rho}$ can be interpreted using the Drude equation [8]. We find that for a uniform wetting film $\bar{\rho} = Ah$, where the proportionality constant $A = 0.002t^{\beta}\ \mathrm{nm}^{-1}$ with h in nm and β is a critical exponent. We have assumed that the wetting layer is well represented by a sharp slab model with refractive index equal to the bulk acetone-rich phase. The only new aspect to our experimental setup is the focusing of the laser beam to a beam diameter of either ~17 or ~100 μm at the liquid/vapor surface; the nucleation of a layer of droplets is indicated by a very noisy $\bar{\rho}$ signal. (An unfocused laser beam is less sensitive to droplet formation because the signal from the surface is spatially averaged.)

In a typical quench experiment the system was prepared in the one-phase region approximately 10 mK above T_c. The system was quenched to a temperature T in the two-phase region. The time to reach thermal equilibrium (measured using a thermistor in contact with the sample cell) was ~10–15 min because our thermostat was originally designed for equilibrium measurements. We do not believe that this relatively long time constant significantly affected our measurements because it is orders of magnitude shorter than the time to nucleate a film or a droplet, τ_0 (τ_0 is approximately many hours). In Figs. 1(a) and 1(b) we show $\bar{\rho}$ for two typical quenches as a function of time τ measured from the temperature quench at $\tau=0$. A characteristic behavior of most quenches was the appearance of a sharp peak in $\bar{\rho}$ near $\tau=0$ [Fig. 1(b), inset]. We attribute this peak to spinodal wetting [9] observed by others [3,4]. This wetting layer is removed (via the Marangoni effect [10]) and the system forms a metastable surface state within ~15 min. It remains in this metastable state until either film growth or droplet growth occurs at the nucleation time τ_0. Film growth is observed for $\Delta T < 0.1\,°\mathrm{C}$ [Fig. 1(a)] while droplet growth occurs for $\Delta T > 0.1\,°\mathrm{C}$, as can be observed by the unstable value of $\bar{\rho}$ [Fig. 1(b)]. Eventually the droplets grow and coalesce to a uniform film as indicated by the steady value of $\bar{\rho}$ for large τ.

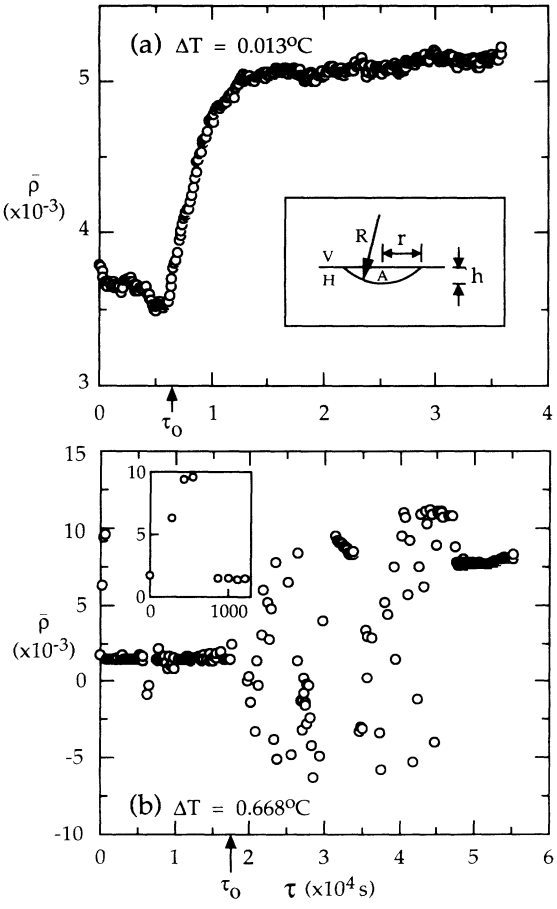

FIG. 1. Ellipsometric signal, $\bar{\rho}$, monitored as a function of time τ after a temperature quench into the two-phase region. The surface forms a metastable state until (a) film growth or (b) droplets are nucleated at the surface at time τ_0. Inset (a): Schematic diagram of an acetone-rich droplet, A, at the hexadecane/vapor, H/V, surface. Inset (b): Enhancement of the transient peak in $\bar{\rho}$ near $\tau=0$ where the vertical axis is $\bar{\rho}$ ($\times 10^{-3}$) and the horizontal axis is τ (s).

There are a number of features which one would like to interpret from the data: (i) What is the metastable state? (ii) What controls the nucleation time τ_0? (iii) Does the film growth regime obey a diffusion-limited growth model? This last question will be considered in a separate publication [11].

What is the metastable state? The most obvious suggestion is that the metastable state is the critical adsorption state. In a recent Letter [12] we have shown that for critical adsorption far from T_c,

$$\bar{\rho}_\pm \approx \bar{\rho}_{\mathrm{BG}} + \frac{\pi}{\lambda}\frac{(1+\varepsilon_L)^{1/2}}{\varepsilon_L} C m_{0\pm}\xi_{0\pm} t^{\beta-\nu}\int_0^\infty P_\pm(x)\,dx\,, \tag{1}$$

where the subscript + (−) applies in the one- (two-) phase region and the symbols have the same meaning as in [12]. The principal conclusions of [12] are that experimentally $\bar{\rho}\sim t^{\beta-\nu}$, where ν is another critical exponent, and that the surface amplitude ratio

$$R_{MA} = \frac{m_{0+}}{m_{0-}}\frac{\int P_+(x)\,dx}{\int P_-(x)\,dx} \tag{2}$$

is universal with an experimental value of $\sim 1.3 \pm 0.1$. Therefore, if we measure $m_{0+}\int P_+ dx$ in the one-phase region and use the experimental value for R_{MA} we can determine if Eq. (1) correctly describes the metastable data with the only adjustable parameter being the background $\bar{\rho}_{\mathrm{BG}}$. We find that Eq. (1) does describe the metastable state well for $t > 0.001$ as indicated by the solid line in Fig. 2. This provides strong evidence that the metastable state is indeed the critical adsorption state. Bonn, Kellay, and Wegdam [13] have recently also observed a metastable state for the liquid mixture cyclohexane+methanol; however, they have not demonstrated that it has properties similar to critical adsorption.

What controls the nucleation time τ_0 observed in Fig. 1? An idealized droplet of A at an H/V surface is shown in the inset of Fig. 1(a). If the lateral radius r is much less than the radius of curvature R (namely, droplets above the wetting transition should have a small contact angle) then, *to within a geometric factor of order unity*, the excess free energy for the droplet is

$$F \approx -S\pi r^2 + \mathcal{L}2\pi r + W\pi r^2/h^2 + \Delta\rho g L h \pi r^2\,, \tag{3}$$

where $S = \sigma_{\mathrm{HV}} - \sigma_{\mathrm{AV}} - \sigma_{\mathrm{HA}}$ is the spreading pressure with σ_{ij} the surface tension between phases i and j, $\mathcal{L}$ is

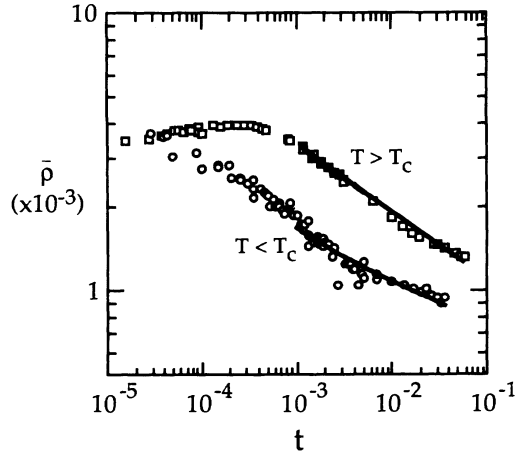

FIG. 2. Critical adsorption measurements as a function of reduced temperature t. Solid lines are nonlinear least-squares fits by (1) for $t \geq 10^{-3}$. For $T > T_c$ we have $Cm_{0+}\int P_{+}dx = 0.83 \pm 0.01$, $\bar{\rho}_{BG} = (3.8 \pm 0.3) \times 10^{-4}$, and $\chi^2 = 0.6$ while for $T < T_c$ (metastable state) we have $\bar{\rho}_{BG} = (5.0 \pm 0.2) \times 10^{-4}$, $\chi^2 = 0.8$, and $Cm_{0-}\int P_{-}dx$ is determined from (2). The quoted errors are for 1 standard deviation.

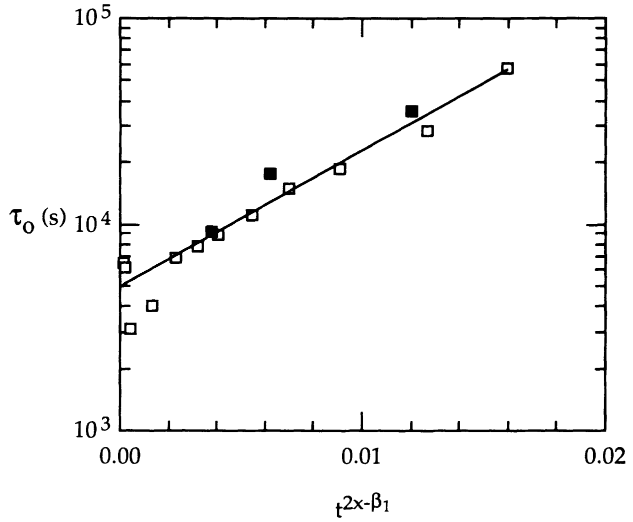

FIG. 3. Plot of nucleation time τ_0 as a function of $t^{2x-\beta_1}$, where $x = 0.83$. Open squares, 17-μm beam diameter; solid squares, 100-μm beam diameter. The solid line is a nonlinear least-squares fit to the data—see text for details.

the line tension which occurs at the junction of three bulk phases, W/h^2 the dispersion energy per unit area, and $\Delta\rho g L h$ the gravitational energy per unit area. Here $\Delta\rho$ is the mass density difference and L (~ 0.5 cm) the height of the bulk H phase.

The droplet thickness h at steady state is determined by the condition that

$$\left(\frac{\partial F}{\partial h}\right)_r = 0 \tag{4a}$$

which gives

$$h = (2W/\Delta\rho g L)^{1/3} . \tag{4b}$$

This expression is identical to the expression for the *equilibrium* wetting layer thickness [6] under the approximations assumed.

Above the wetting transition $S > 0$ and therefore the 2D Kelvin equation [14] implies that $\mathcal{L} > 0$. Therefore, according to classical nucleation theory, a droplet will grow provided that its lateral radius, r, is greater than the critical lateral radius, r_c, determined by

$$\left(\frac{\partial F}{\partial r}\right)_h = 0 \tag{5a}$$

hence

$$r_c = \mathcal{L}/S . \tag{5b}$$

In the derivation of r_c we have assumed that S (~ 0.1 erg/cm^2 [15]) is much greater than either the dispersion or gravitational terms which are typically $\sim 10^3$ erg/cm^2. Schmidt and Binder [16] have given a similar but more complicated analysis for the critical droplet size—they do not assume that $r \ll R$. The probability of a droplet nucleating is given by

$$p \sim \exp[-F(r_c)/kT], \quad F(r_c) \approx \pi\mathcal{L}^2/S , \tag{6}$$

where k is the Boltzmann constant and therefore the nucleation time

$$\tau_0 \sim 1/p \sim \exp(\pi\mathcal{L}^2/kTS) . \tag{7}$$

Close to T_c the spreading pressure $S \sim t^{\beta_1}$ [15]; therefore from (7) we have fitted the τ_0 data by an equation of the form $\tau_0 = B\exp[Ct^{2x-\beta_1}]$, where x is the critical exponent for the line tension. A nonlinear least-squares fit gives $x = 0.83 \pm 0.08$, $B = 5000 \pm 1300$ s, and $C = 150 \pm 100$ where the quoted errors represent 1 standard deviation. Equation (7) fits the data very well as demonstrated in Fig. 3 where we plot $\ln\tau_0$ vs $t^{2x-\beta_1}$ with $x = 0.83$. The straight line through the data is the best fit to the τ_0 data with x, B, and C given above.

In summary, we have observed a surface metastable state and a new wetting layer growth mechanism at the liquid/vapor surface of the critical mixture hexadecane + acetone. The metastable state is consistent with critical adsorption while, from classical nucleation theory, we determine that the droplet line tension $\mathcal{L} \sim t^{0.83}$ in the vicinity of the critical temperature.

We will report on light scattering and microscopy studies of droplet growth and coalescence in a future publication.

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[9] The following observations suggest that the transient peak near $\tau = 0$ is due to a wetting layer: (i) In Fig. 1(b) the magnitude of the peak, $\bar{\rho} \sim 9 \times 10^{-3}$, is similar to the $\bar{\rho}$ value for $\tau > 5 \times 10^4$ s when an equilibrium wetting layer is present. (ii) A similar transient peak was *not* observed for a 0.7 °C temperature quench from the one-phase into the two-phase region for a critical isobutyric acid + water mixture—this mixture does not possess a wetting layer at the liquid/vapor surface in equilibrium. This second observation excludes the possibility that the transient peak is an artifact of bulk spinodal decomposition.

[10] For our system the thermal equilibrium time ($\tau_T \sim 15$ min) was greater than the time for bulk phase separation (τ_P); therefore a surface tension gradient was still present at the liquid/vapor surface after a spinodal wetting layer had formed. For typical values of the temperature gradient at the liquid/vapor surface $\nabla T \sim 0.1$ °C/cm, surface tension derivative $d\sigma/dT \sim -0.1$ (erg/cm^2)/°C [5] and viscosity $\eta \sim 1$ cP we calculate a Marangoni flow velocity $v \sim 1$ mm/s [V. G. Levich, *Physicochemical Hydrodynamics* (Prentice-Hall, Englewood, 1962)] which is sufficient to remove the wetting layer. For the spinodal wetting growth observed in [3,4], $\tau_P \gg \tau_T$ and a surface tension gradient will *not* be present in the later stages of spinodal wetting.

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[14] For a spherical droplet of radius r in three dimensions Kelvin's equation connects the pressure difference ΔP with the surface tension σ, $\Delta P = 2\sigma/r$. Line tension theory [D. Platikanov, M. Nedyalkov, and A. Schedudko, J. Colloid Interface Sci. **75**, 612 (1980); D. Platikanov, M. Nedyalkov, and V. Nasteva, J. Colloid Interface Sci. **75**, 620 (1980); G. Navascues and P. Tarazona, J. Chem. Phys. **75**, 2441 (1981); G. Navascues and L. Mederos, J. Chem. Phys. **79**, 2006 (1983)] gives an equivalent equation for a "flat droplet" ($r \ll R$) at a surface, namely, $S = \mathcal{L}/r$. This equation correctly reduces to Antonow's rule [J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Oxford Univ. Press, London, 1982), Chap. 8] in the limit as $r \to \infty$. There has been considerable controversy concerning the sign of $\mathcal{L}$ (Rowlinson and Widom). The latest consensus is that $\mathcal{L}$ can be either positive or negative. The 2D Kelvin equation suggests that the sign of $\mathcal{L}$ is merely determined by the sign of S, namely, whether you are above ($S > 0$) or below ($S < 0$) the wetting transition.

[15] The spreading pressure $S = At^{\beta_1} - \sigma_0 t^{\mu}$ [D. E. Sullivan and M. M. Telo da Gama, in *Fluid Interfacial Phenomena,* edited by C. A. Croxton (Wiley, New York, 1985), p. 73; L. Sigl and W. Fenzl, Phys. Rev. Lett. **57**, 2191 (1986)], where A and σ_0 are constants while $\beta_1 = 0.83$ and $\mu = 1.24$ are critical exponents. For most critical liquid mixtures studied to date $T_c - T_w > 30$ °C [J. W. Schmidt, J. Colloid Interface Sci. **122**, 575 (1988), and references therein] and $\sigma_0 \sim 30$ ergs/cm^2 [M. R. Moldover, Phys. Rev. A **31**, 1022 (1985)]; therefore at the wetting transition, T_w, where $S = 0$ we obtain $A = \sigma_0 t^{\mu - \beta_1} \sim 12$ ergs/cm^2. For our experiment $T_c - T \sim 1$ °C and using the same values for A and σ_0 we find $S \sim 0.1$ erg/cm^2.

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