Metastable States and Nucleation near First-Order Wetting Transitions

Daniel Bonn,[1] Hamid Kellay,[2] and Jacques Meunier[1]
[1]*Laboratoire de Physique Statistique, Ecole Normale Superieure, 24, Rue Lhomond, 75231 Paris Cedex 05 France*
[2]*Department of Physics and Astronomy, Allen Hall University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

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Ellipsometry experiments on wetting in a binary liquid mixture show that the thick wetting film can be undercooled below the first-order transition temperature and has an anomalously long lifetime. Also, a metastable thin film can be observed in the experiments with a much shorter lifetime. We employ a simple theory to calculate the wetting and prewetting phase diagram, including the spinodals of the first-order surface transition. The location of the spinodals in the phase diagram provides us with qualitative information on the lifetimes of metastable states, which agrees with the experiments.

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Sufficiently close to the upper consolute point of a demixed binary fluid system, a wetting layer of one of the two fluid phases can intrude between the other fluid and any third phase that happens to be present [1,2]. Very recently, a number of experiments have shown convincingly that the character of this surface phase transition, called the wetting transition, is first order. Three groups have shown [3–5] independently that in different systems the first-order transition is accompanied by hysteresis. For nucleation in bulk, hysteresis is usually found on only one side of the transition point. For the nucleation of surface phases, we show here that hysteresis can be observed on either side of the transition.

Rutledge and Taborek [3] (RT) have detected a very long-lived *metastable thick film* for the wetting at coexistence of (superfluid) helium on cesium substrates. On the other hand, the present authors [4] and Law [5] have detected, in two different binary liquid systems, a *metastable thin film* for the wetting at coexistence.

The observation of metastable states has given rise to a number of discussions on the nucleation of wetting layers. Schick and Taborek [6] and Law [7], starting from heterogeneous nucleation theory, invoke a possible divergence of the *line tension* [8] to account for the lifetime of metastable states. Bausch and Blossey [9], on the other hand, argue that the line tension is not very important and that it is mainly the topology of the wetting and prewetting phase diagram and the location of the spinodals which determines the lifetimes.

The purposes of this Letter are (i) to present experimental evidence that also in binary liquid mixtures a very long-lived *metastable thick film* can exist, (ii) to calculate explicitly the entire wetting and prewetting phase diagram, including the spinodals of the first-order transition and show that this provides a satisfactory explanation for the experimental observations, and (iii) to show that the height difference between the thick and the thin films also affects the lifetime of the metastable states.

The system we consider is the demixed binary liquid system of cyclohexane (C_6H_{12}) and methanol (CH_3OH) at the critical composition. The methanol-rich phase is the heavier phase and is favored at the liquid-vapor interface. The adsorption of methanol at the liquid-vapor interface is studied by means of ellipsometry. In these experiments one probes the integral over the dielectric constant profile which can be related, through the Drude formula [10], to the adsorption of methanol at the interface. The measured quantity, the coefficient of ellipticity $\bar{\rho}$, is then directly proportional to the adsorption, or equivalently [2], the thickness of the adsorbed film.

In a recent Letter [4] we have shown that, starting from a temperature below the wetting temperature T_w, and increasing T in small steps, over a rather large temperature interval either the equilibrium (macroscopic) wetting layer or a microscopically thin adsorbed film could be found at the same temperature. The hysteresis we observed is depicted in Fig. 1 (closed symbols), where we plot the results of a number of experimental runs in the same figure. The important observation is that the transitions from the thin film to the thick film may take place anywhere between 22.3 and 38 °C. Also, it is observed that the thin film-thick film transitions occur more frequently at higher temperatures. As these measurements were performed by *increasing* the temperature in small steps, the lower limit of the hysteresis interval, 22.3 °C, in fact, constitutes an upper bound for the real first-order wetting temperature T_w. We believe T_w to be very close to this temperature, since the duration of the experiment, typically days, largely exceeds the lifetime of the observed metastable state (typically a few hours). Moreover, in our recent determination of the prewetting line in this system [11], T_w was found to be 23 ± 1 °C, in agreement with this identification. Then, we observe a *metastable thin film* for all temperatures between 22.3 and 38 °C. The upper limit of the hysteresis interval, 38 °C, then has to be identified as the *metastability limit* of the thin film: For $T > 38$ °C only the thick equilibrium wetting layer could be found in the experiment.

The open symbols in Fig. 1 depict the result of a similar series of measurements performed on a slightly

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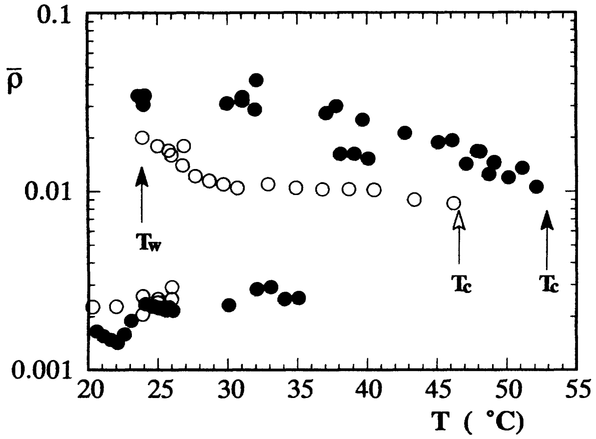

FIG. 1. Ellipticity vs temperature when heating the system in small steps; for the cyclohexane-methanol system (closed symbols) and for the cyclohexane-deuterated methanol system (open symbols). For temperatures exceeding $T_w = 22.3\,^{\circ}\mathrm{C}$, either the large or the small ellipticity state is observed in both systems.

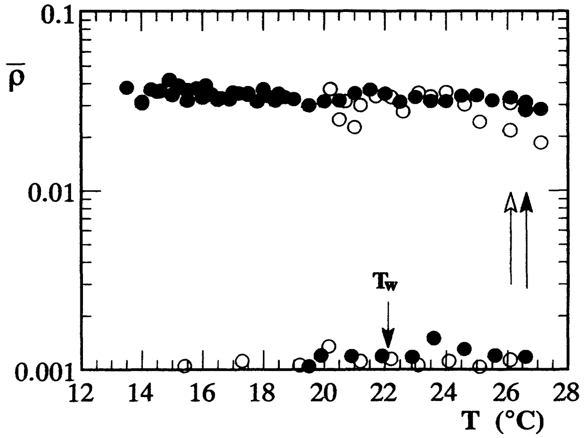

FIG. 2. Ellipticity vs temperature for the cyclohexane-methanol system. The open and closed symbols represent two different experimental runs. The open and closed arrows indicate the temperature for which in the two experiments the transition from the thin to the thick films took place.

different system, the mixture cyclohexane-deuterated methanol (CH_3OD). Two striking differences can be observed between the two systems. First, the equilibrium wetting layer is significantly thinner for the deuterated system. This is a consequence of the deuteration: The density difference with the cyclohexane is a factor of 3 larger for the deuterated alcohol. Because the wetting layer results from a competition between van der Waals forces and gravity, this results in a thinner layer [12]. A more surprising observation is that the hysteresis is limited to a much smaller temperature interval: The two different adsorption states can only be found for $T_w = 22.3\,^{\circ}\mathrm{C} < T < 27\,^{\circ}\mathrm{C}$.

In order to see if also a *metastable thick film* state could be found, we attempted to undercool the thick wetting layer in the system cyclohexane-methanol. The results of two different experimental runs are shown in Fig. 2. Starting again from the partial wetting state below T_w and increasing the temperature, the transition to the thick film state occurs for an arbitrary temperature above T_w and below 38 °C. Then, if the temperature is decreased in very small steps (0.1 °C), the *thick film persists at the surface for temperatures below* T_w. The experimental observation is that, regardless of the temperature or waiting time, no transition to the thin film state takes place. Even if the cell is allowed to rest for a week at the lowest temperature that we reached (13 °C), the metastable thick film still persists at the surface. Moreover, this branch is completely reversible: We could detect no difference between heating and cooling cycles on the thick film branch. The biggest experimental difficulty we encountered here (and before [4]) is that the system is very sensitive to temperature gradients [13]. In fact, we find the system to be even more sensitive when decreasing the temperature than when increasing T. If too large temperature steps are taken, the system is destabilized completely; the ellipticity then fluctuates heavily over a period of several hours. With the thick wetting film present and for very large temperature jumps to below T_w, we have shown [4] that after typically 12 h, the thin film state can be found again. Once the thick wetting film is present, this is the only way we found to return to the thin film state. The long lifetime of the metastable states may well have influenced earlier measurements on binary liquid mixtures [13,14]: In addition to temperature gradients [4,13], the slowness of bulk diffusion and the effect of stirring [14], nonequilibrium states may also result from the first-order character of the wetting transition.

In summary, *both the thick film and the thin film* in our system *have metastable extensions* below and above T_w, respectively. Also, the lifetime of the metastable thick film (more than a week) is much longer than that of the metastable thin film (typically a few hours). Then, for both the helium/cesium experiment and in our system a very long-lived metastable thick film can be observed. The only difference is the observation that in the binary liquid mixture also a metastable thin film can be observed. In the helium-cesium system, the lifetime of the metastable thin film could be too short to be observable experimentally. Also, for the prewetting transition [11] we observed hysteresis in our system, whereas RT did not. Therefore, there may be a difference in the *dynamics* of the nucleation process for the two systems, for which the transport properties will be important [15]: these differ greatly between the two systems.

One may wonder why a metastable thick film has a longer lifetime than a metastable thin film. To address this question, we will calculate the entire wetting and prewetting phase diagram, including the spinodals of the first-order surface transition, for the binary liquid mixture under study. To do so, we employ the simple Cahn theory [1] of wetting together with an expression for the bulk free energy that is appropriate for this mixture.

Consider the grand potential difference $\Delta\Omega$ needed to create a unit volume of a certain composition x when the bulk is at a different composition x_b, where $\Omega = F - \sum_i \mu_i N_i$ with F the bulk free energy; μ_i and N_i are the chemical potential and the number of particles of species i, respectively. To a first approximation, $\Delta\Omega$ can be written [1]

$$\Delta\Omega_m = 1/V[\Omega_m(x_b,T) - (x - x_b)\partial\Omega_m(x = x_b)/\partial x], \tag{1}$$

where $\Omega_m(x,T)$ the molar grand potential as a function of composition and temperature and V the molar volume (95 cm^3/mole for our system). For the molar bulk free energy F_m, we use the expression [16]

$$F_m(x_1,x_2,T) = RTx_1 \log x_1 + RTx_2 \log x_2 + x_1x_2(A + Bx_1^2), \tag{2}$$

where x is the mole fraction, the subscript 1 denotes the methanol and 2 the cyclohexane; R is the gas constant; A and B are (temperature dependent) parameters that are adjusted to describe the coexistence curve correctly [16]. The reason for the use of this parametrization is that it is the simplest one capable of describing both the coexistence curve and the heat of mixing correctly.

In the usual squared-gradient theory, the difference between the surface free energies before and after the wetting transition (i.e., the spreading coefficient) can be written [1]

$$\sqrt{\kappa}\int_{x'}^{x''} dx[\phi/2\sqrt{\kappa} + \sqrt{\Delta\Omega_m}], \tag{3}$$

where x' and x'' denote the *surface compositions* for which the surface free energy exhibits a minimum; this happens at the zero crossings of the integrand. The two coupling constants ϕ (an effective short-range interaction that describes the wall preference) and κ (the usual coupling constant for the squared-gradient term) are assumed independent of both temperature and concentration. Then, the value of the quotient $\phi/2\sqrt{\kappa}$ can be found by noting that the integral must be zero at the wetting temperature. Adjusting the value of $\phi/2\sqrt{\kappa}$ at the wetting temperature until this condition is satisfied [647 (J/m^3)$^{1/2}$ for our system], with this value the entire wetting and prewetting phase diagram can be calculated [17]. One striking observation from this calculation is that, at two-phase coexistence, the free-energy minimum corresponding to the *metastable thin film* ceases to exist at a temperature between T_w and the upper consolute point T_c [18]. This occurs at a temperature of 33 °C. Above this temperature, the thick equilibrium wetting layer is the only stable solution for the free energy. Conversely, this does not happen for the metastable thick film: The free energy minimum corresponding to this state is found to exist for *all temperatures* below T_c, including those below T_w.

The location of the prewetting line in the composition-temperature plane of the phase diagram can be obtained by adjusting the temperature until the integral in Eq. (3) is zero for an arbitrary bulk composition x_b. To obtain the phase diagram in the chemical potential-temperature plane, the distance from two-phase coexistence has to be calculated. The chemical potential difference $\Delta\mu = \mu_{pw} - \mu_0$, where μ_0 is the chemical potential at bulk coexistence and μ_{pw} the chemical potential at the prewetting line, can be calculated using Eq. (2) for the free energy. Then [16],

$$\mu_1 = RT \ln x_1 + x_2^2(A + 3Bx_1^2), \tag{4}$$

the difference $\Delta\mu$ is then evaluated by calculation of the chemical potentials for the coexistence curve and the prewetting line compositions at the same temperature. An important observation is that, if one moves off coexistence, *metastability limits can be found for both the thick and the thin film.* It seems plausible to identify these metastability limits with the (classical) spinodals of this first-order phase transition [19].

The final result of the calculation is shown in Fig. 3, where the thick solid line represents the bulk coexistence line, the thin line is the prewetting line, and the two dashed lines are the metastability limits of the thick and thin films. The central question is now if this can account for the experimental observations. The points shown in Fig. 3 are deduced from our previous determination of the prewetting line in this system [11], with the chemical potentials calculated from Eq. (4). Although the agreement is not spectacular, this simple calculation gives a reasonable indication for the chemical potential difference between the prewetting line and the coexistence

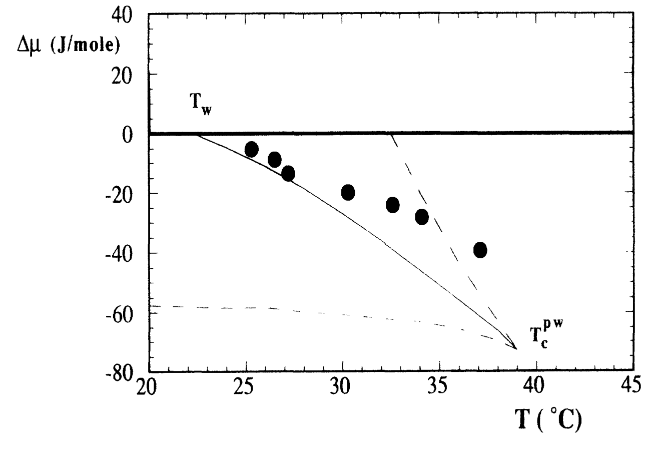

FIG. 3. Representation of the phase diagram in the chemical potential-temperature plane. The thick line represents the bulk coexistence line, the thin line is the prewetting line, and the dashed lines are the spinodals. The upper curve and lower curve are the metastability limits of the thin and the thick films, respectively. The data points were taken from our previous determination of the prewetting line in this system.

curve. We believe the main reason for the discrepancy between these results to be that the calculated chemical potential is rather sensitive to the details of the model, i.e., the precise values for the parameters A and B. Moreover, the *length* of the prewetting line is well described by this theory: From both the experiments [11] and the calculation one finds $T_c^{pw} = 39\,^{\circ}\mathrm{C}$ for the prewetting critical point.

It can be observed from the phase diagram that the upper "spinodal" (the metastability limit of the thin film) intersects the bulk coexistence line at a temperature of 33 °C. This is consistent with the experimental observation that the thin film ceases to exist at a temperature between T_w and T_c. This happens at 38 and at 27 °C for the normal and the deuterated system, respectively; the model thus gives a very reasonable indication of the metastability limit temperature. As the nucleation probability will be larger in the vicinity of the spinodal, this also provides an explanation for the observation that the thin-thick transitions occur more frequently at higher temperatures.

Because all interactions remain virtually unaffected by the deuteration of the methanol [12], the only difference between the two systems considered here is the thickness of the equilibrium wetting layer. The observation that the nucleation process occurs more readily for the deuterated system must then be attributed to the difference in thickness, a factor that is possibly also important for the nucleation near the prewetting transition.

The final question is then why the nucleation probability is not symmetrical with respect to T_w, i.e., why a metastable thick film is longer lived than a metastable thin one. Schick and Taborek [6] have shown that from classical nucleation theory such an asymmetry could be expected for small undercooling or superheating. A somewhat different viewpoint was taken by Bausch and Blossey [9] who argue that the location of the spinodals matters most. In the classical picture of nucleation, the critical droplet is infinitely large if the two phases coexist. Consequently, the nucleation probability is zero. Moving off coexistence, the nucleation probability is determined by the energy necessary to form a critical droplet. At the spinodal line, even further from coexistence, the size of the critical droplet is zero, and the nucleation probability is unity. Considering the phase diagram of Fig. 3, it is evident that this provides an alternative explanation for our observations. Namely, if one *overheats a thin film*, one is always relatively close to the spinodal. This in turn means that the critical droplets for the nucleation will be small and the nucleation probability large. Conversely, if one *undercools a thick film*, one is always very far from the spinodal, since it does not intersect the bulk coexistence line. Consequently, the nucleation will be very difficult, which was indeed observed in the experiment of RT and the present experiment.

In conclusion, we have shown that in the binary liquid mixture we studied both the thin film and the thick film have metastable extensions. We also show that it is feasible to calculate the phase diagram and to locate the classical spinodals of the first-order surface transition. Then, the experimental observation of very long-lived metastable thick films, as well as the behavior of the thin film, can be understood as a consequence of the location of the spinodals. Finally, we provide experimental evidence that the height difference between the thick and the thin films should also be taken into account for a complete understanding of the nucleation of wetting films near first-order wetting transitions.

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