Dynamics of Wetting Layer Formation

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(Received 28 December 1999)

We study the formation and growth of wetting layers in the binary liquid mixture cyclohexane-methanol. By progressively deuterating the methanol we can tune the equilibrium wetting layer thickness. Hysteresis of the transition is observed for large thicknesses and is absent for thinner ones. This can be understood by calculating the activation energy for wetting layer nucleation as a function of the film thickness. We also show that the late-stage growth of the wetting layer after the nucleation process follows a power law in time, in agreement with a diffusion-limited growth mechanism proposed theoretically.

PACS numbers: 68.45.Gd, 68.10.–m

When a liquid droplet is put onto a surface, two situations (distinguishable by the contact angle) may result [1]. If the contact angle is zero, the droplet spreads across the surface, a situation referred to as complete wetting. Second, if the contact angle is between zero and 180°, the droplet does not spread, a situation called partial wetting. A wetting transition is a surface phase transition from partial wetting to complete wetting.

The wetting transition is generally first order (discontinuous), implying a discontinuity in the first derivative of the surface free energy [1]. Two key observations demonstrate this: the observation of metastable states and of prewetting transitions away from bulk two-phase coexistence [2]. Although the latter has been confirmed for a number of systems, the situation for the metastable states is less clear. In some systems, a clear hysteresis is observed [2], whereas in others no such observation is made [3]. This obviously results from a difference in the *dynamics* of these wetting phase transitions, i.e., the nucleation and growth of the stable phase. Although detailed theories of wetting dynamics exist [4,5], few experiments have been performed. The formation of wetting films after a quench [6] was shown to agree quantitatively with a theory of droplet nucleation [7]. However, since for this system the equilibrium wetting behavior is not known, the dynamics cannot be related to the phase behavior.

It is the purpose of the present Letter to study the dynamics of wetting in a system whose equilibrium wetting properties are well known. We show, by studying different binary liquid systems, that there is a simple explanation for the observation or not of hysteresis in experiment, which is due to the presence of gravity. Although in theory the equilibrium wetting layer thickness is infinite, due to the repulsive van der Waals forces, in practice it is large but finite, due to the attractive gravitational potential [8]. Studying systems with varying density differences, we observe a hysteresis for large wetting film thickness (small density difference), but not for small thicknesses. Calculating the nucleation probability for the thick film, it turns out that the nucleation probability decreases rapidly with increasing film thickness so that in some cases long-lived metastable states can indeed be observed, whereas in other cases they cannot. We also show that the growth of the wetting layer towards its final equilibrium state is driven by the long-range van der Waals forces and limited by diffusion. Thus we arrive at a complete characterization of the dynamics of this first-order surface phase transition.

We study the demixed binary liquid system of cyclohexane and methanol at the critical composition. Previous studies [2,9] demonstrated that upon approaching the upper consolute temperature T_c from below, a wetting layer of the heavier methanol-rich phase intrudes between the cyclohexane-rich phase and the vapor. Three different kinds of methanol are used, which differ in their degree of deuteration: one is normal methanol (CH_3OH), one is partly deuterated (CH_3OD), and one is completely deuterated (CD_3OD). This specific system is used because for normal methanol, the two liquid phases are almost density matched. By progressive deuteration, we can subsequently reach density differences characteristic of those for other binary liquid systems [3]. The main effect of the deuteration is a change in the density difference. The other parameters, notably the Hamaker constant A, remain virtually unchanged. Explicit calculation, following the method outlined by Israelachvili [10], yields $A = 8.5 \pm 0.5 \times 10^{-23}$ J for the three systems ($T = 25\,°C$).

Ellipsometry [11] is used to study the thickness of the wetting layer. The measured quantity is the ellipticity at the Brewster angle; using the Drude equation [12], the ellipticity can be related to the integral of the dielectric constant profile in the interfacial region. Considering the intruding wetting layer as a slab, the ellipticity is directly proportional to the thickness of the wetting layer.

Here, we are interested only in the formation of the equilibrium wetting layer, starting out from a thin film. We consequently discuss the dynamics of wetting and do not consider the inverse dewetting problem, which may be very different [13]. In a typical experiment we start at a low temperature, and increase T in small steps. The results for the different systems (Fig. 1) show that below the wetting temperature T_w, the ellipticity corresponds to that of a cyclohexane/vapor interface with a small amount of methanol adsorbed: A microscopic film is present, and we are consequently in the partial wetting state. Above T_w, either values for the layer thickness are found that are almost 2 orders of magnitude larger, or we find values that are indistinguishable from those below T_w. The large values persist over the entire interval $T_w < T < T_c$. For the cyclohexane-methanol system, the small values are observed only in an interval $T_w < T < T_{\mathrm{ML}}$ with T_{ML} (the metastability limit of the thin film) ≈ 35 °C. For cyclohexane-CH_3OD [Fig. 1(b)], the interesting observation is that the hysteresis is limited to a much smaller temperature interval: T_w is approximately equal for both systems, but $T_{\mathrm{ML}} \approx 26\,^{\circ}\mathrm{C}$ is much smaller. For cyclohexane-CD_3OD [Fig. 1(c)] *the hysteresis temperature range disappears completely:* T_w and T_{ML} coincide.

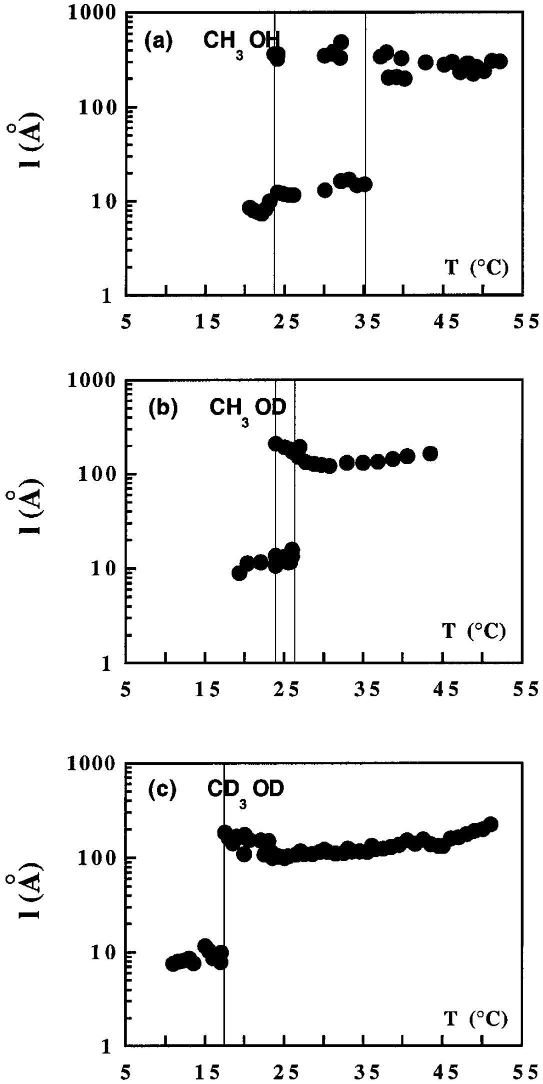

FIG. 1. Measured thickness of the wetting layer as a function of temperature for the three different degrees of deuteration: (a) CH_3OH, (b) CH_3OD, and (c) CD_3OD. The hysteresis disappears completely for the last system. The difference in critical temperature is due to the presence of trace amounts of water; see Ref. [9].

These experiments are all performed in different experimental runs. At the beginning of each run, we start out with a thin film; we found it necessary each time to create large temperature gradients in the sample to recover the thin film once a thick film had formed. The data of Fig. 1 result from the superposition of a number of experimental runs; in each run, for the systems for which a hysteresis was observed, the transition to a thick film occurred at a different temperature.

The thickness of the thick film also depends on the deuteration. The average layer thicknesses obtained are 307 ± 50, 154 ± 40, and 129 ± 30 Å for CH_3OH, CH_3OD, and CD_3OD, respectively. This can be explained by noting that the thickness of the wetting layer results from a competition between the long-range van der Waals forces embodied in the Hamaker constant A that favor the formation of an infinitely thick wetting layer, and the gravitational energy cost of maintaining the wetting layer above its bulk phase. This leads to a layer thickness [8] $l_{\mathrm{eq}} = (2A/\Delta\rho g H)^{1/3}$, with H the height of the layer above its bulk. As both A and $\Delta\rho$ have the same critical exponent, the layer thickness should be independent of temperature, which is indeed found in the experiment. For the pure components, the ratio of the density differences is approximately 9:3:1 (CD_3OD:CH_3OD:CH_3OH), leading to a theoretical ratio of layer thicknesses 1:1.4:2.0, in fair agreements with the experimental result of 1:1.2:2.4.

Since the deuteration does not affect the interaction potentials, the observed change in the hysteretic behavior must be due to the kinetics of nucleation of the thick film. Upon overheating the thin film to temperatures $T > T_w$, the buildup of the thick film will be initiated by the formation of droplets of the wetting phase at the liquid-vapor interface. The energy barrier for droplet nucleation is the excess free energy E_c of the critical droplet. The droplet nucleation rate is given by $\Gamma = \Gamma_0 \exp(-E_c/k_B T)$, where Γ_0 is an attempt frequency [5]. We will show that the equilibrium wetting film thickness intervenes in both the activation energy and in the prefactor in such a way that it provides an explanation for the observed differences.

The excess free energy of a droplet of radius R to form by thermal fluctuations is approximately given by [4]

$$E = 2\pi R\tau + \pi R^2 \tilde{S}\,, \tag{1}$$

where τ is the line (boundary) tension of a droplet, and $\tilde{S}$ the (nonequilibrium) spreading coefficient [4]:

$$\tilde{S} = S - \frac{A}{l^2} - \Delta\rho g H l\,. \tag{2}$$

$\tilde{S}$ differs slightly from the spreading coefficient S at two-phase coexistence, because the transition is formally a prewetting transition (i.e., a wetting transition off coexistence) due to the presence of gravity. Minimization of E with respect to R yields the excess free energy of the critical droplet as

$$E_c = \pi\tau^2/\tilde{S}\,. \tag{3}$$

For $T \approx T_w$, $S \approx 0$ and it follows that the off-coexistence spreading coefficient $\tilde{S} \propto l_{\mathrm{eq}}^{-2}$. The line tension τ contributes an additional dependence on the film thickness which grows logarithmically with the layer thickness l_{eq}. Within an interface displacement model, the line tension can be calculated from [4,14]

$$\tau = \sqrt{\sigma}\int_{l_1}^{l_{\mathrm{eq}}}\sqrt{V(l')}\,dl'\,, \tag{4}$$

where l_1 is the equilibrium thickness of the thin film, and σ is the liquid-vapor interfacial tension; $V(l) = A/l^2$ is the effective interface potential. Extrapolating $V(l)$ down to film thicknesses on the order of the thin film, we obtain

$$\tau = \sqrt{2\sigma A}\,\ln(l_{\mathrm{eq}}/l_1) \tag{5}$$

which depends only logarithmically on the thickness of the thin film. That the extrapolation indeed yields a good estimate for the order of magnitude of the line tension was verified by numerical calculation.

In total, the excess free energy of the droplet thus depends on film thickness via [4,5]

$$E_c \propto l_{\mathrm{eq}}^2\,\ln^2(l_{\mathrm{eq}}/l_0)\,, \tag{6}$$

where l_0 is some microscopic distance. Although logarithmic, the divergence of the line tension for large film thicknesses does contribute significantly to the activation energy; see Fig. 2.

In addition, the nucleation probability is proportional to the prefactor of the nucleation rate, a measure of the attempt frequency for the system to overcome the nucleation barrier. This further reduces the nucleation probability of thick films; it consists of a dynamical and a static contribution, $\Gamma_0 = \Gamma_d \cdot \Gamma_s$. The static part is determined by the fluctuation modes of the critical droplet which depend on its size; it is dominated by the unstable radial growth mode which scales with the film thickness as $\Gamma_s \propto l_{\mathrm{eq}}^{-2}$ [15]. Under the reasonable assumption that the differences in the dynamical prefactors in the three different systems can be neglected, we find for the ratios of the attempt frequencies: $\Gamma_{s,\mathrm{CH_3OH}}/\Gamma_{s,\mathrm{CH_3OD}} \approx 0.2$, $\Gamma_{s,\mathrm{CH_3OD}}/\Gamma_{s,\mathrm{CD_3OD}} \approx 0.4$, and $\Gamma_{s,\mathrm{CH_3OH}}/\Gamma_{s,\mathrm{CD_3OD}} \approx 0.1$. Thus, in the system with the thickest film, the attempt frequency is reduced by about 1 order of magnitude as compared to the thinnest film.

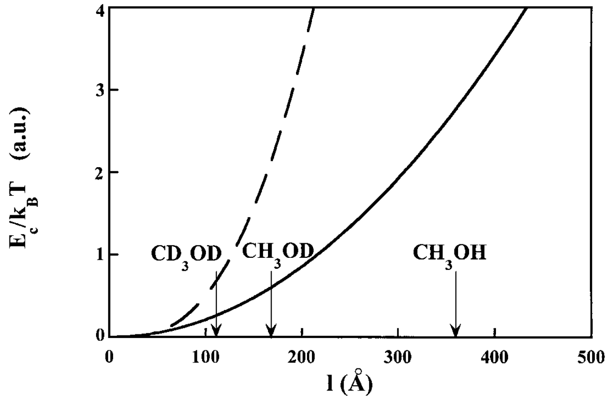

FIG. 2. Difference in energy of the critical nucleus due to the line tension. Solid line: without line tension effects. Dashed line: with inclusion of the logarithmic corrections. The equilibrium film thickness for the three systems is indicated.

In combination with the result for the droplet energy: $E_{c,\mathrm{CH_3OH}}/E_{c,\mathrm{CH_3OD}} \approx 8$, $E_{c,\mathrm{CH_3OD}}/E_{c,\mathrm{CD_3OD}} \approx 4$, and $E_{c,\mathrm{CH_3OH}}/E_{c,\mathrm{CD_3OD}} \approx 28$; this leads naturally to the conclusion that for thin films, the nucleation barrier between the thin and thick film states should be much easier to overcome by the thermal fluctuations than for thick films. Experimentally, the metastability limit temperature T_{ML} can be defined as the point at which the formation of the thick film takes less than 1 h, the time for the system to come to thermal equilibrium. Supposing that the energy barrier at T_{ML} is on the order of $0.1k_BT$, at the metastability limit temperature of the thinnest film ($\mathrm{CD_3OD}$), the above calculation teaches us that, supposing that the waiting time is 1 h for $\mathrm{CD_3OD}$, one has to wait half a day in order for the $\mathrm{CD_3OD}$ and six days for the $\mathrm{CD_3OH}$ films to nucleate. Even more dramatically, for $E_c = 0.25k_BT$, these times become one day and a whole year, respectively. We therefore conclude that due to the difference in equilibrium layer thickness in some wetting experiments hysteresis is observed and in other cases not.

In addition, these considerations allow us to obtain values for the line tension. From Eq. (5), we find $\tau_{\mathrm{CH_3OH}} \approx 7.2 \times 10^{-12}$ N, $\tau_{\mathrm{CH_3OD}} \approx 5.7 \times 10^{-12}$ N, and $\tau_{\mathrm{CD_3OD}} \approx 4.8 \times 10^{-12}$ N. These values differ from that reported by Wang *et al.* [16], which is 3 orders of magnitude larger. They are, however, close to recently calculated values: $\tau \approx 4 \times 10^{-12}$ N [17]. The liquid "substrates" we employ here prevent problems due to the anchoring of the contact line that might be the cause for this discrepancy.

The final question is in what way the wetting layer goes to its equilibrium thickness. We have measured the growth of the wetting layer after the nucleation and find that it approaches its equilibrium value very slowly in time (Fig. 3). Lipowsky and Huse (LH) [18] studied the growth problem and found three different regimes. After a transient period, the growth of the wetting layer should follow a scaling: $l(t) \approx ct^{1/8}$. The constant $c \approx (D^{1/2}AL_c/\sigma)^{1/4}$, with D the diffusion coefficient, L_c the capillary length, and σ the interfacial tension. In this regime the wetting layer thickness grows by a diffusion-limited process, in which its thickness increase is determined by the supply

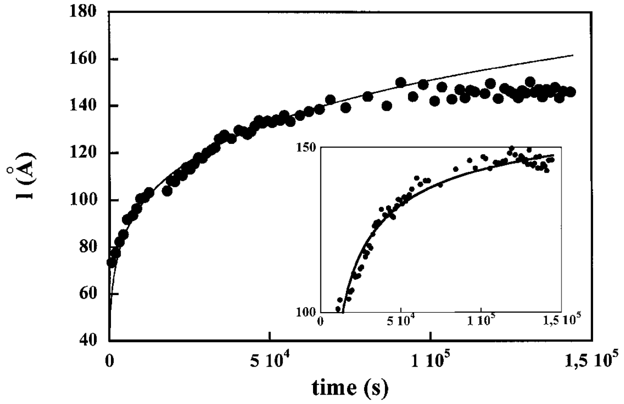

FIG. 3. Growth of the wetting layer as a function of time for the CD_3OH system at 43.5 °C. Drawn line is a fit to a power-law growth. Inset: the late time behavior. The fit is to an inverse diffusion behavior discussed in the text.

of molecules from the bottom reservoir. The diffusion process is driven by the van der Waals forces, leading to the unusually slow growth exponent $\frac{1}{8}$, instead of the more usual $l(t) \approx \sqrt{Dt}$. This growth regime is followed by a regime in which the equilibrium value l_{eq} is attained with an inverse diffusive behavior, $l_{\mathrm{eq}} - l(t) \approx [l_{\mathrm{eq}} - l(0)]/\sqrt{\omega t}$. We find that our system closely follows this scenario.

If we fit the data at early times to a power law (Fig. 3), we find a value for the power of 0.165 ± 0.05, which not only compares favorably to the theoretical prediction of $\frac{1}{8}$, but is also very different from that of a normal diffusion-limited process. Comparing measurements for the CD_3OD system at different temperatures in the range $T_w < T < T_c$, it is found that the exponent does not depend on temperature within the experimental error. From data at 20°, 30°, and 50°, combined with the data shown in Fig. 3(a) we obtain an average power of 0.17 ± 0.07, in agreement with the prediction that this power does not depend on the specific details of the system under study. The data on CH_3OH and CH_3OD show similar behavior, although the noise in the data is significantly larger because the forces maintaining the wetting layer are smaller.

Moreover, the prefactor c is also found to agree with the predictions: imposing the $\frac{1}{8}$ power law, we find $c \approx 30\ \text{Å}/\text{s}^{1/8}$, whereas LH, taking typical values, estimate $100\ \text{Å}/\text{s}^{1/8}$. Again, comparing data at different temperatures, this value is not found to depend sensitively on T. The saturation of the wetting layer thickness towards its equilibrium value is also well described by an inverse diffusion behavior (Fig. 3, inset). We therefore conclude that the growth of the wetting layer is in excellent agreement with the theoretical expectations.

In conclusion, we studied the dynamics of nucleation and growth of wetting layers in binary liquid mixtures of cyclohexane and methanol. We show that the larger the equilibrium film thickness is, the larger the barrier to nucleation becomes. This leads to pronounced hysteresis effects when the equilibrium film thickness is large. In addition, the growth of the wetting layer following the nucleation regime is diffusion limited and agrees quantitatively with theoretical predictions.

LPS de l'ENS is UMR 8550 of the CNRS, associated with universities P6 and P7. This work was supported by CNES Contract No. 793/CNES/99/7831 and EC, Contract No. FMRX-CT98-0171. R. B. thanks the Flemish government [Grant (No. VIS/97/01)] and the DFG (Grant No. He2016/5-3); E. B. thanks the Institut Français du Pétrole for financial support.

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