Experimental Observation of Hysteresis in a Wetting Transition

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An ellipsometric study of the cyclohexane-methanol mixture shows that in the wetting regime, either a very thin or a thick film is formed at the liquid/vapor interface. The observed hysteresis is consistent with the assumption that the wetting transition is first order. The thick layer can be accounted for by the stabilization of the wetting layer by long-range van der Waals forces. In agreement with this, the equilibrium wetting layer thickness shows no dependence on the temperature. The thin film is shown to be governed by short-range forces.

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Sufficiently close to the upper consolute point T_c of a demixed binary fluid system, a wetting layer of the heavy phase can intrude between the lighter phase and the vapor [1,2]. The equilibrium thickness of these layers is commonly assumed to be given by the Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) theory of dispersion forces [3,4]. However, this theory has been confirmed only for two unique cases of a fluid that wets a solid surface [5,6]. In the study of binary liquid mixtures, only a few experiments have been reported [2,7-9], with results that were not only difficult to reconcile with the DLP theory [4] but also seemed contradictory. It has been recognized that the long equilibration times in these systems [4] and their sensitivity to temperature gradients [6] pose a serious problem. Closely related to the questions of the layer thickness and the equilibration is that of the order of the wetting transition [10,11]. The available evidence seems to point in the direction of a first-order (discontinuous) phase transition [11], but again, the experimental situation is not very clear [10]. In this Letter we present measurements of both equilibrium and nonequilibrium wetting layers in the binary liquid mixture of cyclohexane and methanol. From the measured equilibrium values, it is inferred that we observe hysteresis in the wetting regime and thus that the wetting transition is a first-order phase transition. Also, the measured equilibrium wetting layer thickness and its temperature dependence are in reasonable agreement with theoretical predictions.

Our measurements are obtained by ellipsometry. The ellipticity $\bar{\rho}$ is the imaginary part of the reflectivity ratio r_p/r_s. Here r_p and r_s are the reflectivity coefficients for the amplitude of the electric field for parallel and perpendicular polarizations, respectively. Measurements were performed with a HeNe laser ($\lambda = 632.8$ nm) incident at the Brewster angle. A simple slab model is used to interpret the ellipticity in terms of a layer thickness: Under the assumptions that the wetting film has the same index of refraction as the bulk phase of the wetting liquid and that its boundaries are sharp, the ellipticity is proportional to the difference in refractive indices of the two liquid phases and the layer thickness [7]. The ellipsometer is a phase-modulated apparatus [12] coupled to a personal computer, which allows us to monitor the ellipticity continuously with time. Typically, every 2 min a new measurement is taken. This allows us to follow the system as it changes with time, and to record all stable and unstable values for the ellipticity.

In Fig. 1 the measured stable values of the ellipticity are depicted as a function of the temperature. The surprising result is that, above a certain temperature, two different values for the ellipticity can be found at the same temperature. We monitored the ellipticity for either of the two states for periods of over 20 h; no variation with time could be detected. Moreover, after several days, the same value is found. The lowest temperature for which two different values for $\bar{\rho}$ can be observed, presumably T_w, is 22.3 °C; in earlier experiments [7,8] the wetting temperature was found to be $T_w \cong 22$ °C. Then, below T_w the ellipticity of the cyclohexane/vapor interface is measured. Raising the temperature in small steps of 0.1–0.5 K, in the range $T_w < T < T_c$, either up to 10% larger values for the ellipticity are observed, or values are found that are 2 orders of magnitude larger than those measured for the cyclohexane/vapor interface. Coming from below the wetting temperature it is not a
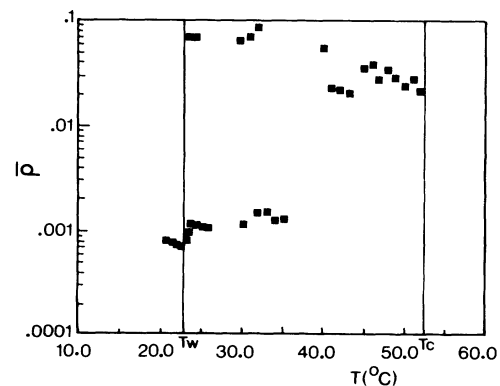

FIG. 1. The measured ellipticity vs the temperature. For temperatures exceeding $T_w = 22.3$ °C, either the large- or the small-ellipticity state is observed. The critical temperature for this sample is 53.3 °C.

priori clear what value will be found for $T > T_w$; both states seem to have an almost equal probability of occurrence. However, if different experimental runs are plotted together as in Fig. 1, a clear physical picture emerges. First, the large values for $\bar{\rho}$ persist over the entire interval $T_w < T < T_c$. The small-ellipticity state is observed only in the interval $T_w < T < 38\,°C$. Second, when increasing the temperature, only transitions from the small to the large values for the ellipticity are observed. These transitions can take place anywhere between T_w and $38\,°C$, but seem to be more likely at higher temperatures. Third, we find the small values to be sensitive to mechanical perturbation; if the experimental setup is touched, often a transition to the large values occurs. Then, the thin film we observe for $T_w < T < 38\,°C$ is most likely to be a metastable state, reaching its metastability limit at $T = 38\,°C$, and the thick film is the equilibrium wetting layer. The apparent existence of two real roots as for a van der Waals adsorption isotherm, in combination with the observed hysteresis, strongly indicates that we observe a first-order wetting transition.

These findings support those of Schmidt and Moldover [9] that the wetting transition is first order. In a different system they found that, due to the first-order character of the transition, a hysteresis can be observed. However, they found evidence for a hysteresis in only a very small temperature interval below T_w. Their data indicate a wetting layer for $T = T_w - 0.015$ K. Our data clearly indicate that a hysteresis can be observed over a large temperature interval, $22\,°C < T < 38\,°C$.

To prove that the measured values are indeed the equilibrium values, one has to show that the time of measurement is much longer than the equilibration time. This is done by measuring the thickness of a nonequilibrium draining film as a function of time. Lowering the temperature from a value well above the wetting temperature $(30\,°C)$ to $2°$ below T_w, a thick layer is formed at the liquid/vapor interface by condensation of the vapor. This thick layer exhibits interference patterns when illuminated with white light, implying that the layer is about 5000 Å thick. The interference fringes disappear within a few minutes, after which the thinning of this layer is followed by continuous measurement of the ellipticity. The result is shown in Fig. 2, together with measurements of the two equilibrium states for $T > T_w$. The thick, nonequilibrium wetting layer disappears in a roughly exponential fashion with a time constant on the order of 2 h. The equilibrium thickness for the high-ellipticity state is about 450 Å, whereas the small values for $\bar{\rho}$ correspond to a thickness of about 10 Å. As stated before, the ellipticity for either of the two equilibrium states remains constant over a period of several days. Since the time of measurement for the stable values of the ellipticity is much longer than the equilibration time, we conclude that these are, in fact, the equilibrium values.

The cause of this relatively fast equilibration may be found in the specific geometry in which the experiment
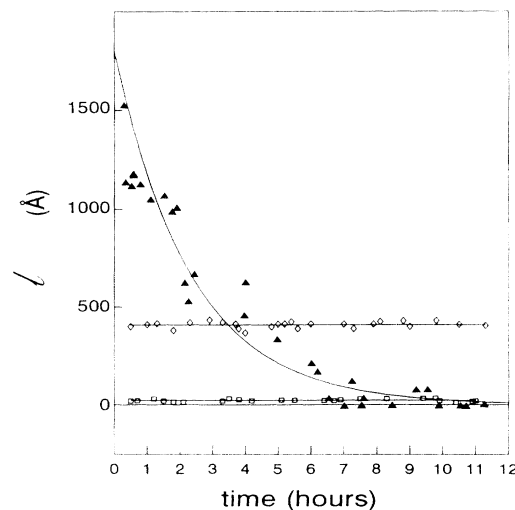

FIG. 2. The layer thickness as a function of time for the equilibrium and nonequilibrium states. The open symbols represent the measurements of the two equilibrium states at $T = 30.1\,°C$. The closed symbols represent the measurements for the nonequilibrium state measured at $T = 20.2\,°C$.

was carried out. The measuring cell is a glass cylinder with a diameter of 2.2 cm and a height of 7 cm. In this system the methanol-rich phase also intrudes between the cyclohexane-rich phase and the walls of the measuring cell. This allows equilibration to take place by hydrodynamic flow rather than by the diffusion process [4] which is much slower. The importance of the presence of this vertical wetting layer for the equilibration of the horizontal layer can be illustrated as follows. If the equilibrium thickness of this vertical wetting layer is calculated from DLP theory [13], one finds an average thickness $l_v = 2000$ Å, 5 times as thick as was found for the horizontal wetting layer. In Ref. [4], it was suggested that the thinning of the horizontal layer can be a factor $(l_v/l_h)^3$ faster than that of the vertical one. In equilibrium $l_v/l_h = 5$; taking this as a guideline, a process that would take one month for the vertical layer would take only 6 h for a horizontal wetting layer. Thus, it may be that the presence of a thick vertical wetting layer is important for the equilibration. In the study of Beaglehole [8], this vertical wetting layer was probably not present since he made the walls nonwetting to the methanol-rich phase.

To investigate the sensitivity of the wetting layer to the presence of thermal gradients, we examined the dependence of the wetting layer thickness on the heating or cooling rate. In our setup, the measuring cell is inserted in a copper block and held in place with Teflon rings. Water from a large temperature-stabilized water bath flows through the block; the temperature of the water could be changed in steps of 100 mK. Using slow heating rates of 0.1–2 K/h, inducing a maximum temperature gradient of 20 mK/cm, we find that the ellipticity

changes rather smoothly from one value to another. However, using higher heating rates, or upon cooling at 2 K/h, the ellipticity starts fluctuating rapidly and no layer thickness can be deduced from the measurements. Thus, we find thermal gradients to be important, but not as crucial as in the case where a fluid wets a vertical wall near its critical point [10].

To account for the variation of the layer thickness with temperature for the two equilibrium states, in Fig. 3 we have plotted the ellipticity against the reduced temperature $t = (T_c - T)/T_c$ on a log-log scale. As the presence of trace amounts of water is believed to be an important parameter in this system [8], we studied samples with two different water concentrations, 0.1 and 0.5 wt% with critical temperatures $T_c = 49.5\,°C$ and $53.3\,°C$, respectively. In Fig. 3(a) the results are shown for the high-ellipticity state. As is clear from the figure, no effect of the water concentration is detected. A least-squares fit to the data shows that the ellipticity varies as $\bar{\rho} \sim t^{(0.380 \pm 0.062)}$. In the slab model, the ellipticity is proportional to the layer thickness l and the refractive index difference Δn. Knowing the variation of the refractive index [14], $\Delta n \sim t^{0.328}$, we can conclude that, within the experimental resolution, the layer thickness is independent of the temperature. In Fig. 3(b) we see that, for the small-ellipticity state, the ellipticity decreases with increasing distance from the critical point. Keeping in mind that the data do not even cover a decade in the reduced temperature, because there were no data for $T > 38\,°C$, they can be fitted by a line. The line drawn in Fig. 3(b) has a slope -0.375 ± 0.09, which implies that the thickness probed for the small-ellipticity state varies as $t^{-(0.703 \pm 0.09)}$.

The latter findings can easily be accounted for if we assume an interface potential $V(l)$ of the general form [11,15,16]

$$V(l) = \sigma_0 \exp(-l/\xi) + W/l^2 + \Delta \rho g H l , \qquad (1)$$

where the first term on the right-hand side represents the exponentially decaying short-range interactions (ξ is the bulk correlation length and σ_0 a characteristic surface tension). The second term accounts for the algebraically decaying nonretarded van der Waals forces, and the third term is the gravity contribution. Here W is the Hamaker constant, $\Delta \rho$ the density difference (both proportional to $t^{1/3}$), g the gravitational acceleration, and H the height of the wetting layer above the bulk phase. For the observed thin layer, only the short-range interactions should be important. Minimizing the potential with respect to the thickness then leads to the expression $l = \xi \ln(\sigma_0/\Delta \rho g H \xi)$. Neglecting the weak divergence of the logarithmic term, we see that the thickness diverges as the bulk correlation length, $l \sim \xi \sim t^{-\nu}$, with $\nu = 0.63$, in agreement with the least-squares fit to the data in Fig. 3(b). On the other hand, we expect only the long-range forces to be important for the thick layer. First proposed by de Gennes [15], this leads to a layer thickness $l = (2W/\Delta \rho g H)^{1/3}$.
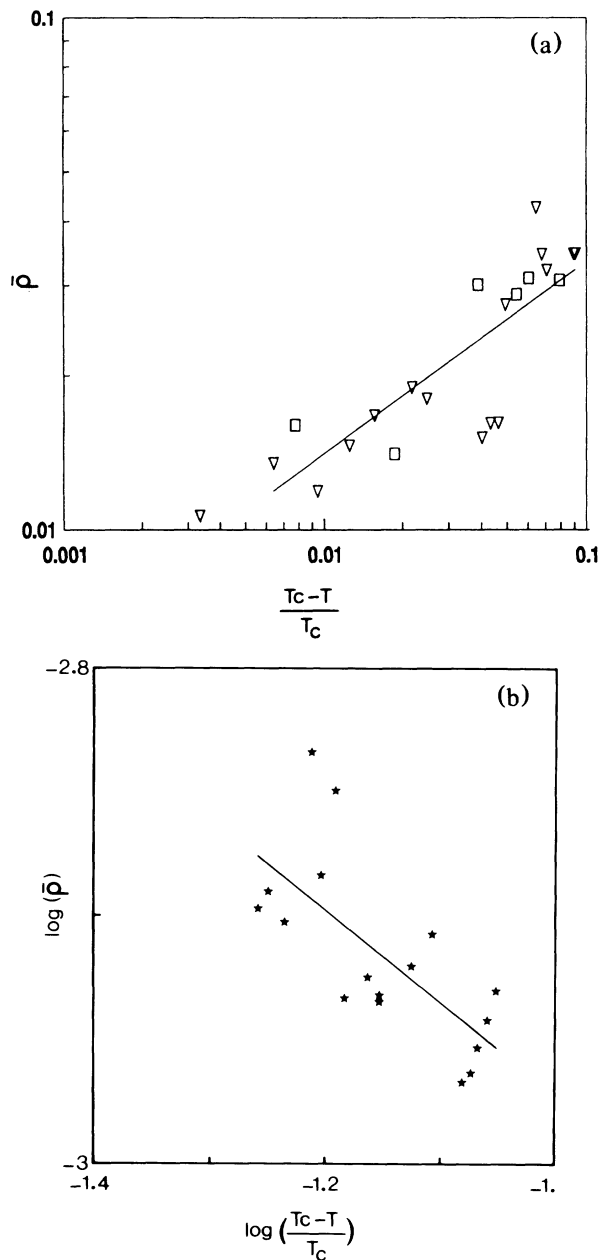

FIG. 3. (a) Variation of the ellipticity for the large-ellipticity state with the reduced temperature for two different water concentrations. Triangles: water concentration 0.5 wt%, critical temperature $T_c = 53.3\,°C$. Squares: 0.1 wt% water, $T_c = 49.5\,°C$. The fitted line has a slope 0.380 ± 0.062. (b) Ellipticity for the small-ellipticity state vs the reduced temperature for a water concentration of 0.5 wt%. The line has a slope -0.375 ± 0.09.

As both the Hamaker constant and the density difference have the same critical exponent, the layer thickness is expected to be independent of temperature. This agrees with the data of Fig. 3(a), where the ellipticity shows the same temperature dependence as the difference in refrac-

tive indices. The equilibrium wetting layer thickness is found to be 450 Å; no influence of either the water concentration or the temperature could be detected. Taking $l \cong 450$ Å, the calculated Hamaker constant is $W = 1.6 \times 10^{-15}$ erg ($T = 25\,°C$), or equivalently, $W/\Delta\rho = 25 \times 10^{-24}$ m^{5}s^{-2}, in reasonable agreement with the theory of dispersion forces of Ref. [4], where $W/\Delta\rho$ is estimated to be 200×10^{-24} m^{5}s^{-2}.

We studied the quasibinary liquid mixture of cyclohexane and methanol with and without the addition of water. The main conclusions are the following: (i) We observe hysteresis in the wetting regime; the wetting transition is a first-order phase transition in this system. (ii) Our findings are well described using a simple model which incorporates both long- and short-range interactions. (ii) The measured equilibrium wetting layer thickness calculated from the slab model is 450 Å, independent of either water concentration or temperature.

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