What Controls the Thickness of Wetting Layers near Bulk Criticality?

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We study the thickness of wetting layers in the binary-liquid mixture cyclohexane methanol. Far from the bulk critical point, the wetting layer thickness is independent of temperature, resulting from the competition between van der Waals and gravitational forces. Upon approaching the bulk critical temperature $[t = (T_c - T)/T_c \rightarrow 0]$, we observe that the wetting layer thickness diverges as $t^{-\hat{\beta}}$ with effective critical exponent $\hat{\beta} = 0.23 \pm 0.06$. This is characteristic of a broad, intermediate scaling regime for the crossover from van der Waals wetting to critical scaling. We predict $\hat{\beta} = \beta/3 \approx 0.11$, with β the usual bulk-order parameter critical exponent, showing a small but significant difference with experiment.

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When a liquid drop is placed on a substrate, two scenarios arise depending on the contact angle. If the contact angle is zero, the drop spreads across the surface corresponding to complete wetting. For all other values of the contact angle, the drop does not spread and only partial wetting of the substrate results. The surface phase transition from partial to complete wetting is called the wetting transition and has been extensively studied theoretically and experimentally over the last few decades [1].

Much less well understood is the behavior of wetting films near the bulk critical point. Here the temperature dependence of the wetting layer thickness is additionally complicated due to effects related to the increase of the bulk correlation length [2]. It has long been anticipated that near the bulk critical point the influence of long-ranged dispersion forces diminishes and that interfacial fluctuation effects are amplified due to the vanishing of the surface tension [3]. However, a proper quantitative assessment of this has not been previously possible leaving the behavior of wetting films near bulk criticality a matter of some debate.

In the present Letter we study gravity-thinned wetting layers in binary-liquid mixtures in which we probe the critical region much closer than in previous experiments. Our data unambiguously show the divergence of the film thickness on approaching the bulk critical temperature characterized by a critical exponent that is distinct from the critical exponent for the bulk correlation length. Scaling arguments are forwarded which show the observed exponent is consistent with a crossover regime for van der Waals dominated wetting to critical scaling of the wetting film thickness. We also show the presence of an effective short-ranged or fluctuation-induced correction to the leading order direct, intermolecular (van der Waals) dominated contribution.

Wetting films, on a substrate or at the interface between coexisting bulk fluid phases, most often have a mass density different from that of the bulk phase(s) supporting the film [1,4,5]. As a result, there is a gravitational cost to the formation of the wetting layer at some height (H) above its bulk reservoir, leading to finite, gravity-thinned complete wetting layers since the gravitational cost is equivalent to a shift off true bulk existence. At a theoretical level this behavior may be modeled using an effective interfacial binding potential $V(\ell)$ which takes into account the gravitational cost, direct influence of intermolecular forces, and also possible fluctuation-induced contributions from the thermal wandering of the unbinding interface [6]. The equilibrium wetting film thickness ℓ then simply corresponds to the minimum of the effective binding potential. For systems with short-ranged forces [1,7],

$$V(\ell) = \sigma_0 e^{-\ell/\xi} + \Delta\rho g H \ell, \tag{1}$$

where ξ is the bulk correlation length, σ_0 has the dimensions of a surface tension, $\Delta\rho$ is the density difference, and we have assumed that $H \gg \ell$. Strictly speaking (1) is the bare or mean-field binding potential which does not take into account the influence of thermal fluctuation effects. However, for the experimentally relevant case of dimensions $d = 3$, renormalization effects do not significantly alter the form of the binding potential and merely change the numerical factor of the ℓ/ξ argument of the exponential (for very thick films). This expansion for the binding potential is valid even for relatively thin complete wetting films [8] where ℓ is of order ξ. Similarly near the bulk critical point we expect that (1) is valid even for thin wetting films with $\ell \approx \xi$ since the correlation length is much greater than the molecular size. Minimization then yields $\ell = \xi \ln(\sigma/\Delta\rho g H \xi)$ so that for fixed H, and up to unimportant logarithmic corrections, ℓ will remain comparable to the bulk correlation length.

The situation for complete wetting in systems with long-ranged van der Waals dispersion forces, as pertinent to most physical systems, is quite different. For distances ℓ much larger than the bulk correlation length [1],

$$V(\ell) = A/\ell^2 + \Delta\rho g H \ell, \tag{2}$$

where A is the (positive) Hamaker constant and, again, we have neglected higher order terms. For $\ell \gg \xi$ the binding potential is dominated by the direct influence of long-ranged intermolecular forces: exponential contributions similar to (1) arising from bulklike fluctuations are negligible. Similarly the fluctuation-induced repulsion for systems with long-range forces decays very quickly (as a Gaussian) for $\ell \gg \xi$ and is also unimportant. Thus the equilibrium film thickness is $\ell = (2A/\Delta\rho g H)^{1/3}$, leading to quite different behavior for the wetting film as the temperature is increased towards criticality [9]. The Hamaker constant depends on the reduced temperature in the same way as the difference in density $\Delta\rho$ so that (2) predicts that the wetting layer thickness should be independent of temperature. Clearly this argument is valid only if $\ell \gg \xi$, and we must anticipate some crossover scaling to $\ell \approx \xi$ closer to the critical temperature.

Previous experimental results for binary-liquid mixtures show that the wetting film thickness is indeed constant up to film thickness close to the bulk critical point [1]. There are, however, also indications from measurements close to bulk criticality [10,11] that indicate a potential crossover to a divergent film thickness.

In the present experiment we study complete wetting in two examples of a demixed binary-liquid system of cyclohexane and methanol at the critical composition. The upper consolute point T_c was determined to 0.005 °C accuracy. Previous studies [5] demonstrated that upon approaching the upper consolute temperature from below, a wetting layer of the heavier methanol-rich phase intrudes between the cyclohexane-rich phase and the vapor. We use here two different kinds of methanol, which differ in their degree of deuteration: one is normal methanol (CH_3OH) and one is deuterated (CD_3OD). For normal methanol, the two liquid phases are almost density matched. By deuteration, we can subsequently reach density differences characteristic of those for other binary-liquid systems [12]. The other parameters, notably the Hamaker constant A, remain virtually unchanged [5].

Brewster angle ellipsometry [13] is used to study the thickness of the wetting layer. The measured total ellipticity is the sum of two terms: one related to the film thickness and one to the interfacial roughness. Explicit calculation of the latter [14] shows that the roughness term does not contribute significantly to the ellipticity. Then, using the Drude equation [15] considering the intruding wetting layer as a slab, the ellipticity is directly proportional to the thickness of the wetting layer.

Thermostating was done with a water bath; when carefully insulating the system, the long-time temperature stability is better than a few mK. Equilibration of the sample is followed by continuous measurement of the ellipticity in time. Typically, after a temperature step of 0.2 K, the measured ellipticity fluctuates wildly for half an hour, after which it evolves slowly (on a period of a day or so) to a stable value. We then wait for at least 3 d before taking the data point; close to T_c we wait for a week in order to avoid spurious effects due to critical slowing down.

Measuring much closer to the critical point than in previous experiments, we observe a significant increase and apparent continuous divergence of the wetting layer thickness as $T \to T_c$ (Fig. 1). Away from T_c the wetting layer thickness for both deuterated and nondeuterated methanol mixtures is approximately constant with $\ell \approx 307 \pm 50$ A for CH_3OH and $\ell \approx 128 \pm 30$ A for CD_3OD; the smaller film thickness for the deuterated sample is consistent with the larger gravity thinning. For $T \to T_c$, for the deuterated sample we observe that over nearly four decades the apparent divergence of ℓ is very well described by the power law with a power $\hat{\beta} = 0.23 \pm 0.06$ (Fig. 2, error is 2σ). We refer to $\hat{\beta}$ as an effective critical exponent since the observed power-law behavior of ℓ clearly cannot extend down to $t = 0$. Similar behavior occurs for the nondeuterated methanol mixture, although the deviation from the constant film thickness regime does not happen until $t \approx 5 \times 10^{-3}$ (Fig. 1).

The roughly constant thickness of the wetting layers away from bulk criticality is consistent with Eq. (2).

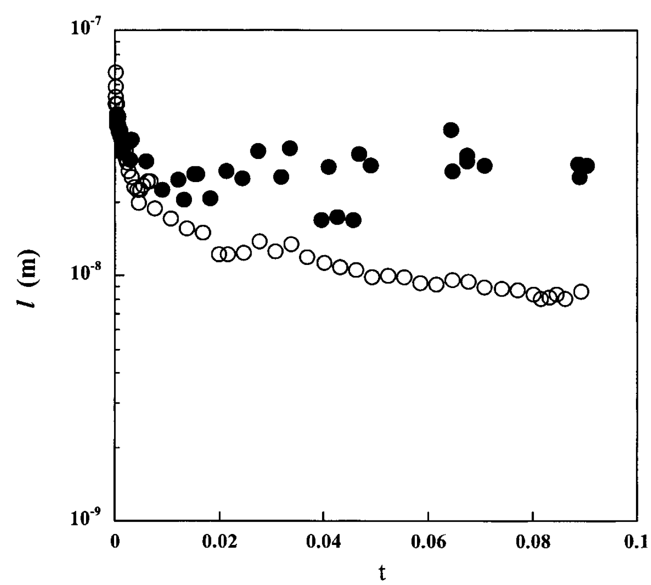

FIG. 1. Film thickness ℓ as a function of the temperature t for C_6H_{12}/CH_3OH samples (open circles) and for C_6H_{12}/CD_3OD samples (filled circles).

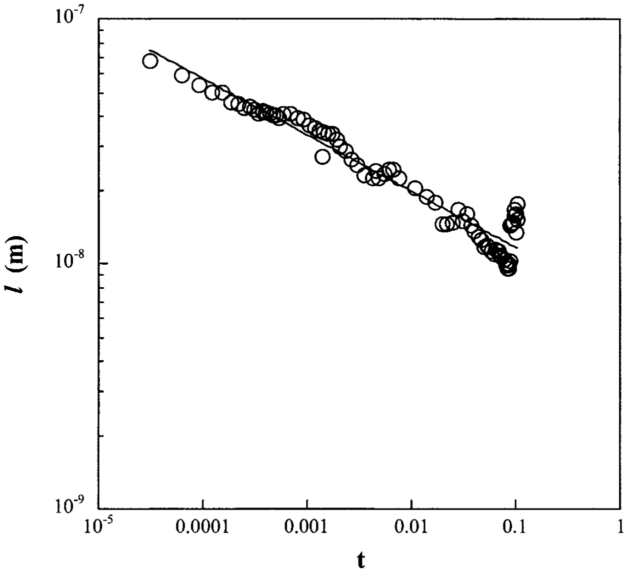

FIG. 2. Film thickness ℓ as a function of the temperature t for the C_6H_{12}/CD_3OD sample. The straight line gives $\hat{\beta} = -0.23$.

However, this clearly breaks down as $T \rightarrow T_c$ and we are forced to conclude that Eq. (2) does not contain all the essential physics. On the other hand, the observed divergence of ℓ is *not* of the expected form for short-ranged forces [Eq. (1)]. If this were the case the film would diverge like the bulk correlation length with critical exponent $\nu \approx 0.63$ compared to the much smaller power law $\hat{\beta} = 0.23$. This poses two related problems: (i) What controls the apparent divergence of the wetting film thickness ℓ outside the van der Waals dominated regime? In particular, how is the effective critical exponent $\hat{\beta}$ related to other bulk critical, surface critical, and wetting critical exponents? (ii) What form does the effective binding potential $V(\ell)$ take in the power-law regime and how does this compare with expressions (1) and (2) discussed above?

For $\hat{\beta}$, we forward a simple crossover scaling argument showing that the observed power-law increase in ℓ is associated with a broad, intermediate regime with $\hat{\beta}$ determined by standard bulk critical and complete wetting exponents. For systems showing complete wetting, with "normal" surface criticality (corresponding to nonvanishing surface field), single variable scaling holds.

As a result we can expect the scaled film thickness ℓ/ξ to be described by a scaling function of the variable $y = \Delta\mu/t^{\Delta}$, $\Delta \approx 1.53$ being the gap exponent. Similarly, the bulk correlation length, which remains finite off coexistence, can be written [2,11] $\xi = \xi_0 t^{-\nu} f(y)$, where $f(y \rightarrow 0) = \text{const}$ and $f(y \rightarrow \infty) \propto y^{-\nu/\Delta}$. The first limit applies when $\Delta\mu \ll t^{\Delta}$, i.e., close to bulk coexistence, and the second when $\Delta\mu \gg t^{\Delta}$, in the critical adsorption regime [2].

However, as we have seen above, the van der Waals forces may also intervene, which allows for a third regime where the long-range forces are relevant because $\ell \gg \xi$ but the correlation length is close to its coexistence value. Since $\ell \propto \Delta\mu^{-1/3}$ and $\xi = \xi_0 t^{-\nu}$, this works out as $\Delta\mu \ll t^{3\nu}$. In summary we must distinguish three regimes [2]: (i) van der Waals wetting, $\Delta\mu \ll t^{3\nu}$: ℓ is determined by Eq. (2) and is independent of t; (ii) critical scaling at coexistence, $t^{3\nu} \ll \Delta\mu \ll t^{\Delta}$: the wetting layer grows as the bulk correlation length at coexistence: this is the regime where Eq. (1) holds; (iii) critical adsorption, $\Delta\mu \gg t^{\Delta}$: the wetting layer thickness ℓ is proportional [2] to $\Delta\mu^{-\nu/\Delta}$. The final regime is not relevant for us, as it holds only extremely close to bulk criticality.

The experiments show that at low temperatures the van der Waals regime is retrieved. Upon approaching T_c, the chemical potential difference, $\Delta\mu \propto gH = \text{const}$, however, crosses the line separating regimes (i) and (ii), $\Delta\mu = t^{3\nu}$. Thus it is clear that the experimental path crosses over from van der Waals to critical scaling at coexistence.

The observed divergence of the film thickness can consequently be understood as a crossover between regimes (i) and (ii). In order to quantitatively describe the finite film thickness off coexistence, we write $\ell = \xi(y)g(y)$, where $g(y)$ is again a scaling function that may depend on the interactions [11]. If $\ell \ll \xi$, [regime (ii)] long-range forces are irrelevant and $g(y)$ is constant. Regime (i) imposes [11] that $g(y) \sim y^{-1/3}$, for $y < t^{3\nu-\Delta}$, consistent with van der Waals wetting.

The value of the effective critical exponent $\hat{\beta}$ then follows directly from the scaling assumption $g(y) \sim y^{-1/3}$. On approaching T_c, the effective chemical potential difference due to gravity thinning is $\Delta\mu = \text{const}$. The scaling assumption then yields $\ell \sim t^{-\nu}(\Delta\mu/t^{\Delta})^{-1/3}$ so that by our definition $\ell \sim t^{-\hat{\beta}}$ it follows that $\hat{\beta} = \nu - \Delta/3$. On using the standard bulk critical exponent relation $\Delta = 2 - \alpha - \beta$ together with the hyperscaling relation $2 - \alpha = 3\nu$ pertinent to the present three-dimensional system, this reduces to $\hat{\beta} = \beta/3$. Using the well-known result $\beta \approx 0.325$ this predicts $\hat{\beta} \approx 0.11$ in broad agreement with the experimentally determined value of 0.23 ± 0.06. However, taking also the error bar on the experimental value into account, there remains a small but significant difference between theory and experiment that merits further investigation in the future.

Finally we turn our attention to the form of the effective potential in the crossover regime where we observe the power-law divergence of ℓ. It is tempting to speculate that the form of the potential in this regime is indicative of a crossover from long-ranged to short-ranged-like behavior where the latter contributions arise from bulklike fluctuations and the influence of interfacial wandering. Both these effects are believed to give rise to an exponentially decaying term in the effective potential (for short-ranged forces in three dimensions) [6]. To our knowledge there has been no quantitative experimental assessment of this and to this end we suppose that the binding potential for our binary-liquid mixture can be written $V(\ell) = A/\ell^2 + \Delta\rho g H \ell + V_{fl}(\ell)$, where $V_{fl}(\ell)$ is an effective fluctuation or crossover

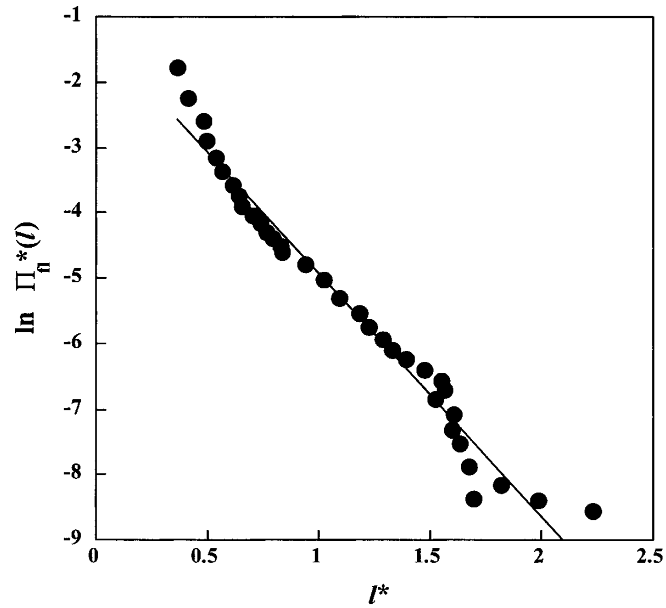

FIG. 3. Reduced disjoining pressure $\Pi^*_{\mathrm{fl}}(\ell)$ versus reduced film thickness ℓ^* for the deuterated sample.

term. Assuming that the potential has this form we can extract information on $V_{\mathrm{fl}}(\ell)$ from the condition for equilibrium $dV(\ell)/d\ell = 0$. This is conveniently expressed in terms of the corresponding disjoining pressure $\Pi(\ell) = -dV(\ell)/d\ell$; from the equilibrium condition it follows that $\Pi_{\mathrm{fl}}(\ell) = 2A/\ell^3 - \Delta\rho g H$, which can therefore be obtained from the observed temperature dependence of the wetting film thickness together with the (temperature dependent) fluid density difference and Hamaker constant. The latter quantity is found from the experimental results obtained at low temperatures. The resulting fluctuation disjoining pressure is shown in a semilog plot in Fig. 3 using appropriate dimensionless units $\Pi^*_{\mathrm{fl}}(\ell) = \xi^3 \Pi_{\mathrm{fl}}(\ell)/k_B T$ and $\ell^* = \ell/\xi$. For values of ℓ/ξ of order unity there is a reasonable fit to a straight line consistent with $V_{\mathrm{fl}}(\ell) \approx \sigma e^{-(\ell/\xi)}$ with the coefficient $\sigma \sim \xi^2$ having the correct critical singularity of the (near critical) fluid interfacial tension. The observed behavior of $V_{\mathrm{fl}}(\ell)$ is therefore at least in semiquantitative agreement with theoretical expectations concerning the increasing influence of effective short-ranged forces for wetting in the critical region [6]. This exponential dependence is very different from what was found for surfactant-laden interfaces. Here, the excursions of the interface are limited by the bending rigidity rather than the surface tension, leading to an algebraic repulsion [16].

In conclusion, we studied the thickness of wetting layers in the binary-liquid mixture of cyclohexane and methanol, upon approaching the bulk critical temperature T_c. Far from T_c the film thickness is approximately constant, resulting from the balance between van der Waals intermolecular forces and the gravitational cost of maintaining a (heavy) wetting layer above the bulk reservoir. On approaching T_c we observe that the film thickness appears to diverge and is very well described by a power law with effective critical exponent $\hat{\beta} = 0.23$. The value of this can be understood using a crossover scaling argument. Finally, we have shown that the divergence of ℓ is consistent with the influence of a fluctuation-induced correction term to the direct intermolecular contribution to the disjoining pressure, which for short distances comparable with the bulk correlation length decays exponentially with film thickness.

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