Hydrodynamic interaction and wetting near the critical point

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Analysis of the hydrodynamic correlations in a film of a simple liquid reveals a new result: There is a region of incomplete wetting near the critical point T_c. The steric interaction of the fluctuations of the film-substrate boundary leads to a divergence of the film thickness h and to the vanishing of the wetting edge angle θ in the limit $T \to T_c$.

A substrate (S) is known[1] to be wetted completely by one of the components (F_1) of a liquid mixture $F_1 + F_2$ or by the condensate of saturated vapor at a temperature T below the critical temperature of the mixture, T_c. The description of this wetting transition by a quadratic-gradient Landau functional,[1] however, ignores the long-range electrodynamic and hydrodynamic correlations and the associated size corrections $V(h)$ to the free energy of the film.[2-4] As a rule, the van der Waals (electrodynamic) forces[2] expand the region of complete wetting, since the energy $V_{VW} = A/2h^2 > 0$ is at a minimum in the limit $h \to \infty$: The film boundary is repelled from the substrate. The constant $A \lesssim 50$ K depends on the nature of the film and the substrate. The contribution of acoustic and capillary waves, on the other hand, is universal[3]:

$$V_{ac} + V_{cap} = -\zeta(3)T / 16\pi h^2 = -0.024\, T/h^2 . \tag{1}$$

This contribution determines the attraction of the boundary to the substrate. At low temperatures the relation $V_{ac} + V_{cap} \ll V_{VW}$, would usually hold. In the limit $t = (T_c - T)/T_c \to 0$ the constant A exhibits the behavior $A \sim \Delta\epsilon \sim t^{\beta} \to 0$, where $\Delta\epsilon$ is the difference between the dielectric constants of the components at the characteristic absorption frequency,[2] and $\beta \approx 0.34$ (Ref. 5).

In this letter we will show that Eq. (1) also holds in the limit $T \to T_c$ for $h \gg \xi_b$, where ξ_b is the correlation length of the volume. Near T_c the free surface energy of a substrate covered by a film F_1 of a large but finite thickness $h_0 \gg \xi_b$ is therefore given by $\sigma_{SF_2} = \sigma_{SF_1} + \sigma + V(h_0) < \sigma_{SF_1} + \sigma$, and we have $\cos\theta = (\sigma_{SF_2} - \sigma_{SF_1})/\sigma = 1 - |V(h_0)|/\sigma < 1$; i.e., the wetting is incomplete, but not far from being complete. Here the σ_{ij} refer to the boundary between semi-infinite media $i, j, = S, F_1, F_2$; and $\sigma \equiv \sigma_{F_1F_2}$. In the limit $T \to T_c$, the entropic repulsion of the boundary from the substrate, which limits the amplitude of the capillary fluctuations (which grow anomalously by virtue of the relation $\sigma \approx T_c/\xi_b^2 \to 0$), becomes important. The equilibrium thickness increases more rapidly than ξ_b in this case: $h \sim \xi_b \ln \xi_b$. Correspondingly, we have $\theta \sim |V(h_0)/\sigma|^{1/2} \sim \ln^{-1}\xi_b \to 0$, and we can say that there is a coalescence of the wetting transition with the critical point.

The classification of hydrodynamic waves as either acoustic or capillary is also

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valid in the limit $T\to T_c$, since the ratio of characteristic energies is $\chi^{-1}k^2/\sigma k^3 \approx (\Lambda/k)(\Lambda\xi_b)^\eta \gg 1$ under the condition $k \ll \Lambda$ (the atomic scale in k space). Here we have made use of the relation $\chi \sim \xi_b^{-2+\eta}$, where $\eta = 0.05 > 0$, for the compressibility.[5] It was actually shown in Ref. 4 that we have $V_{ac}h^2 \sim t^\beta \to 0$, by analogy with V_{VW}. For the frequency of a capillary wave at the boundary of film F_1 with the bulk liquid F_2 we find (cf. Ref. 6)

$$\omega_h^2 = \sigma k^3/[\rho_{F_1} \coth(kh) + \rho_{F_2}] \approx [1-\exp(-2kh)]\,\sigma k^3/2\rho \ ,$$

where the bulk densities are described by $\rho_{F_1} \approx \rho_{F_2} = \rho$ in the limit $T\to T_c$. Subtracting from the free energy of a long wave $T\ln(\hbar\omega_h/T)$ the corresponding expression for $h=\infty$ ($\omega_\infty^2 = \sigma k^3/2\rho$), and integrating over the values of the wave vector in the plane of the substrate,

$$V_{cap} = T\int \ln[1-\exp(-2kh)]d^2k/(2\pi)^2 \ , \qquad (2)$$

we find (1). Integral (2) is determined by waves with $k\sim h^{-1}$. The condition under which these waves can be treated hydrodynamically is $\xi_b \ll h \ll \xi_\parallel$, where the correlation length of the capillary fluctuations is $\xi_\parallel \approx [V''(h_0)/\sigma]^{-1/2}$. Since we have $V''(h) = O(h^{-4})$, we can write $\xi_\parallel \gtrsim h^2/\xi_b$; i.e., the inequality on the right follows from that on the left. A more stringent requirement is the requirement that the viscous damping coefficient be small[6]: $2\eta k^2/\rho \ll \omega_h(k)$. This requirement limits the applicability of our derivation to thicknesses $h \gg \eta^2/\rho\sigma \sim \xi_b^{2(1+x_\eta)} \gg \xi_b$. The shear viscosity is $\eta \sim \xi_b^{x_\eta}$, where $x_\eta \approx 0.04$. According to the scaling hypothesis, however, the static value of $V(h)$ could not be any larger in scale than ξ_b. Consequently, expression (1), which holds at $h \gg \eta^2/\rho\sigma$, also holds at all $h \gg \xi_b$.

To study the role played by the entropic repulsion of the boundary from the substrate, we renormalize the potential of the solid wall, $W(h) = +\infty$, $h<0$, by means of the nonlinear transformation of Ref. 7. For the first derivative, we find

$$W_l(h) = -\ \mathrm{const}\ T\Lambda^2 a^{-1} l^{-1} \exp[2l - h^2/2la^2] + O(e^{-h^2/a^2 l}),$$

where the scale of the cutoff of the configuration integral in k space is $\Lambda \to \Lambda e^{-l}$, and $\alpha = T/2\pi\sigma$. The capillary potential is renormalized in a trivial way[8]: $V_l = Ve^{2l}$. At scales larger than the correlation length $\xi_\parallel = \Lambda^{-1}e^{l^*}$, found from the condition $\partial_h^2(V_{\rm cap}+W)_{l^*} \approx \sigma\Lambda^2$, the fluctuations are suppressed, and the equilibrium thickness is determined by minimizing $(V_{\rm cap}+W)_{l^*}$. We find

$$h = (T_c/2\pi\sigma)^{1/2}[\ln(T_c\Lambda^2/\sigma) + (11/4)\ln\ln(T_c\Lambda^2/\sigma)] , \qquad (3)$$

$$\xi_\parallel \sim (T_c/\sigma)^{1/2}\ln^{3/2}(T_c\Lambda^2/\sigma) . \qquad (4)$$

Using $T_c/\sigma \approx \xi_b^2$, we find $\xi_b \ll h \ll \xi_\parallel$, justifying the use of (1). It is easy to show that we have $V(h) \approx V_{\rm cap}(h)$ and thus $\theta \approx |V(h)/\sigma|^{1/2} \sim \ln^{-1}(T_c\Lambda^2/\sigma) \to 0$. We actually assumed above that the steric interaction outweighs the repulsion of the Landau model[1] $V(h) \approx (T_c/\xi_b^2)\exp(-h/\xi_b)$. The opposite assumption leads to $h \approx \omega_c\xi_b\ln(\Lambda\xi_b)$, where $\omega_c = \lim_{T\to T_c} T/4\pi\sigma(T)\xi_b^2(T)$. Comparing it with (3), we see that the steric interaction is stronger at $\omega_c < 8$; this condition would apparently always hold in liquid systems.

Assuming $A(T) \approx A(O) t^{1/3}$, $A(O) \approx 50$ K, and $T_c \approx 300$ K, we find from the condition $A(T) < 0.048 T_c$ the width of the interval of incomplete wetting: $\Delta T \gtrsim 10$ K. Substituting $\sigma \approx t^{1.28} \times 67.7$ erg/cm^2, $T_c \approx 283$ K, and $T_c - T \approx 10$ K for CCl_4 into (3), we find $h \lesssim 70$ Å. The effects which have been discussed here would thus be amenable to ellipsometric study.

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