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Lifetime of undercooled wetting layers

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The recently observed large hysteresis effects in undercooling or overheating of wetting layers in systems with a prewetting transition are shown to be a simple consequence of the geometry of the phase diagram. In order to estimate quantitatively the lifetime of such metastable layers, one has to calculate the excess free energy E_c of the corresponding critical nuclei. For the case of undercooling we determine E_c as a function of chemical potential μ for a fixed temperature T well below the wetting transition point T_w. For overheating E_c is known from previous calculations as a function of T at bulk coexistence $\mu=\mu_c$.

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The adsorption of ^{4}He on a cesium substrate has recently been studied by Taborek and Rutledge [1,2] in the neighborhood of the prewetting transition. In their experiment it turned out to be much easier to nucleate a thick film by overheating a thin film than to nucleate a thin film by undercooling a thick film [2]. The same hysteresis effect has also been seen in the cyclohexane-methanol mixture [3].

To explain this observation, Schick and Taborek [4] considered the nucleation of two-dimensional droplets on the wall of the system, leading to the usual hysteresis effects of three-dimensional homogeneous nucleation theory. According to them, the hysteresis in the two-dimensional case is enhanced by the singular behavior of the line tension as the wetting transition point is approached along the prewetting line [5]. Their approach obviously rests on the assumption that the droplets have a cylindrical shape so that the free energy is a sum of terms linear and quadratic in the cylinder radius. However, this is only true in a narrow region enclosing the prewetting line [6] where the two competing phases have approximate Ising symmetry, while Fig. 1 shows that a typical path of overheating or undercooling mainly stays outside of this region.

In the following we will demonstrate that the hysteresis effects along the path of Fig. 1 are much stronger than those described in [4]. We have already shown previously [7] that the critical droplets for overheating have qualitatively an ellipsoidlike profile in the region $T>T_w$, $\mu=\mu_c$. Their free energy μ decreases from infinity at $T=T_w$ to zero at some spinodal temperature $T_s>T_w$. Below, we will show that the critical nuclei for undercooling into the region $T<T_w$, $\mu\lesssim\mu_c$ are funnel-shaped dents in the wetting layer, and calculate their depth and excess free energy as a function of μ at some temperature T well below T_w. It turns out that both quantities diverge in the limit $\mu\to\mu_c-0$ where the path of undercooling is located. This, to our belief, is the reason for the observed long lifetime $\tau\sim\exp(-E_c/T)$ of the undercooled metastable wetting layer.

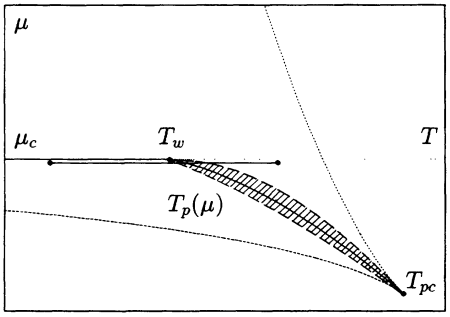

FIG. 1. The wetting phase diagram with the prewetting line $T_p(\mu)$, the two surface spinodals (dotted lines) and a path of undercooling (or overheating) close to bulk coexistence $\mu=\mu_c$. The shaded region schematically indicates where critical nuclei have a cylindrical shape.

Before entering the calculations we present a qualitative argument for the divergent behavior of the critical nuclei for undercooling near bulk coexistence. Above T_w the equilibrium states are homogeneous wetting layers, and their thickness continuously goes to infinity when the coexistence line $\mu=\mu_c$ is approached from negative μ. On the other hand, below T_w there is a jump of the layer thickness from a microscopic value at $\mu=\mu_c-0$ to infinity at $\mu=\mu_c+0$. Therefore the partial wetting line $T<T_w$, $\mu=\mu_c$, is a line of first-order surface transitions where also nonwet regions can coexist with droplets or with a liquid wedge [5]. Now, contrary to the case of overheating, the path of undercooling always stays close to a first-order line where generally critical nuclei diverge in size and free energy. As a side remark we mention that the smooth behavior of the layer thickness at $T\geq T_w$, $\mu\leq\mu_c$ is in accordance with the interpretation of the wetting transition point as a critical end point by Robledo and Indekeu [8].

The quantitative discussion of the excess free energy of critical nuclei starts from an effective interface model with the Hamiltonian [9]

$$H[f]=\int d^2x\left[\frac{\gamma}{2}(\nabla f)^2+V(f)-(\mu-\mu_c)f\right], \qquad (1)$$

where $f(x)$ is the local thickness of the wetting layer on the two-dimensional surface of the wall. The gradient term comes from the interface between the two fluids with the surface tension γ. For $\mu<\mu_c$ the potential $\phi(f)\equiv V(f)$

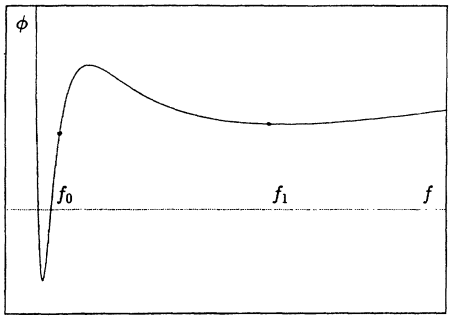

FIG. 2. The potential $\phi(f)\equiv V(f)-(\mu-\mu_c)f$ for $T<T_w$, $\mu<\mu_c$.

$-(\mu-\mu_c)f$ is of the form shown in Fig. 2. The repulsive core of $V(f)$ simulates the wall, and the relative height of the minima of the thin and the thick film can be changed by variation of temperature and chemical potential. In a mean-field picture the prewetting transition occurs when both minima of $\phi(f)$ have equal height.

The shape of a critical nucleus follows from the saddle-point equation $\delta H/\delta f=0$. Under the assumption of rotational symmetry of the nucleus around the normal to the wall the equation for its radial profile reads

$$f''(r)+(1/r)f'(r)=\gamma^{-1}\partial\phi/\partial f. \tag{2}$$

Adequate boundary conditions for a critical dent are $f'(0)=0$, $f(\infty)=f_1$, where f_1 is the thickness of the undercooled layer. The profile of the dent can be identified with the trajectory of a fictitious particle with position f moving in time r according to the equation of motion (2). Figure 3 shows the numerically calculated profile $f(r)$ of the critical dent corresponding to the potential shown in Fig. 2.

In order to determine the divergent behavior of the excess free energy of the critical dent $E_c\equiv H[f]-H[f_1]$ on a path $\mu\to\mu_c$ well below T_w, we first consider the central depth $F_c\equiv f_1-f_0$ where f_0 is the lower turning point in the dent profile (see Fig. 2). Close to coexistence $\mu=\mu_c$ we have $F_c\approx f_1\gg f_0$ so that $V'(F_c)=\mu-\mu_c$. Here, only the behavior $V(f)\sim f^{1-\sigma}$ for large f with $\sigma>1$ is relevant, which yields

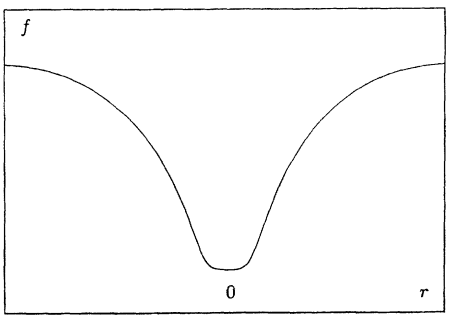

FIG. 3. The critical dent profile corresponding to the potential of Fig. 2.

$$F_c\sim(\mu_c-\mu)^{-1/\sigma}. \tag{3}$$

For retarded and nonretarded van der Waals forces $\sigma=4$ and $\sigma=3$, respectively.

It is now convenient to change from the differential equation (2) to an integral equation for the slope of the inverted dent profile $s(f)\equiv f'(r(f))$ which incorporates the boundary conditions for the dent. After the substitutions $\varphi\equiv f/F_c$, $\tau(\varphi)\equiv s(f)/F_c^{(\sigma-1)/2}$, and $\varrho(\varphi)\equiv r(f)/F_c^{(\sigma+1)/2}$ one finds

$$\tfrac{1}{2}\tau^2(\varphi)+\int_{\varphi_0}^{\varphi}d\tilde{\varphi}\,\frac{\tau(\tilde{\varphi})}{\varrho(\tilde{\varphi})}=\gamma^{-1}[\phi(\varphi)-\phi(\varphi_0)], \tag{4}$$

where

$$\varrho(\varphi)=\int_{\varphi_0}^{\varphi}\frac{d\tilde{\varphi}}{\tau(\tilde{\varphi})}. \tag{5}$$

In terms of these quantities the excess free energy of the critical dent reads

$$E_c=2\pi F_c^2\int_{\varphi_0}^{1}d\varphi\,\frac{\varrho(\varphi)}{\tau(\varphi)}\left[\frac{\gamma}{2}\,\tau^2(\varphi)+\phi(\varphi)-\phi(1)\right]. \tag{6}$$

All the integrals in (4)–(6) are finite in the limit $F_c\to\infty$ for temperatures well below T_w. There $\phi(\varphi)$ has a finite slope near $\varphi_0=f_0/F_c$ which implies $\tau(\varphi)\sim\varrho(\varphi)\sim(\varphi-\varphi_0)^{1/2}$ so that the integrals are well behaved near the lower limit of integration which then can be put to zero. Thus from (3) and (6) we obtain for the excess free energy of a critical dent well below T_w the dependence

$$E_c\sim(\mu_c-\mu)^{-2/\sigma}. \tag{7}$$

The case of nonretarded van der Waals forces, $\sigma=3$, is relevant for the experiments published in [2] for which the largest thickness of the helium films on cesium is around 100 Å. Retarded van der Waals forces where $\sigma=4$ are relevant for helium films of thicknesses larger than 800 Å [10]. The prediction (7) can in principle be checked in a sequence of undercooling experiments at different values of the chemical potential asymptotically close to the surface coexistence line.

The excess free energy of critical droplets for overheating has been calculated previously [7]. For $\sigma\geq 3$ the result is

$$E_c\sim[T-T_p(\mu)]^{-1} \tag{8}$$

with an additional factor $\ln(T-T_w)$ in the special case $\sigma=3$, $\mu=\mu_c$. The behavior (8) can only be seen within a spinodal region, the boundaries of which also might be detected in an experiment [3].

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