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Critical droplets on a wall near a first-order wetting transition

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For critical droplets on a wall near a first-order wetting transition we discuss the crossover behavior from the partial wetting to the prewetting regime. The droplet shape changes smoothly from a spherical cap in the former to a flat cylinder in the latter regime. For sufficiently long-ranged molecular interactions the crossover behavior can be described by scaling forms which in a number of special cases reduce to results previously obtained by de Gennes and co-workers. van der Waals forces form a limiting case in which we recover logarithmic anomalies. For interactions of shorter range we present some mean-field results, although fluctuations might be important in this case.

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I. INTRODUCTION

Wetting transitions occur at the coexistence of two fluid phases in the presence of a wall which prefers one of these phases [1]. Above the transition temperature T_w, a macroscopic layer of the preferred phase forms on the wall through a first- or second-order phase transition. In the case of a first-order transition the nonwet wall can exist above T_w in a metastable state. The decay of this state starts with the nucleation and growth of supercritical droplets sitting on the wall. In the description of the nucleation process, the critical droplet plays a crucial role [2], which for wetting has recently been discussed theoretically [3–5] as well as experimentally [6].

In our work [5] we have discussed the temperature dependence of the height, radius, and excess free energy of the critical droplet. We now want to determine the dependence of these quantities on temperature T and chemical potential μ. This allows us to move off bulk coexistence $\mu=\mu_c$ and to approach the partial-wetting regime $T<T_w, \mu \gtrsim \mu_c$ as well as the regime $T>T_w$, $\mu \gtrsim \mu_p(T)$ near the prewetting line $\mu=\mu_p(T)$. The behavior of droplets in these regimes has been discussed before in some detail by de Gennes and co-workers [7].

In Sec. II, we discuss qualitatively the phase diagram and the properties of the droplets in different regions near the wetting transition point. This discussion is made quantitative in Sec. III, where, within mean-field theory, we consider the partial-wetting regime, the prewetting regime, and the crossover behavior between both. In our conclusions, we briefly comment on the possible influence of fluctuations. We also discuss qualitatively the stability of a macroscopic film against undercooling and the appearance of critical nuclei in that case. Finally, we mention some dynamic effects in the growth of supercritical droplets.

II. QUALITATIVE PICTURE

Our discussion will be based on the effective Hamiltonian [8]

$$H[f]=\int d^{d-1}x \left[\frac{\gamma}{2}(\nabla f)^2+V(f)-hf\right], \tag{2.1}$$

where the field $f(x)$ refers to the local thickness of the wetting layer on the $(d-1)$-dimensional surface of the wall. The first term in (2.1) is the area of the interface (to lowest order in ∇f) multiplied by the surface tension γ between the two bulk phases. In the last term, $h \equiv \mu-\mu_c$ measures the distance from coexistence of these phases. For a first-order wetting transition, the effective potential $V(f)$ is of the form shown in Fig. 1. In a mean-field picture, the two minima at $f=f_0$ and $f=\infty$ represent the nonwet state of the wall, and the state with an infinite (macroscopic) layer on the wall. At the transition, $h=0$ and $V(f_0)=V(\infty)\equiv 0$, which for the spreading coefficient

$$S \equiv V(f_0) \tag{2.2}$$

implies the behavior $S \sim T-T_w$ near the transition temperature T_w [1].

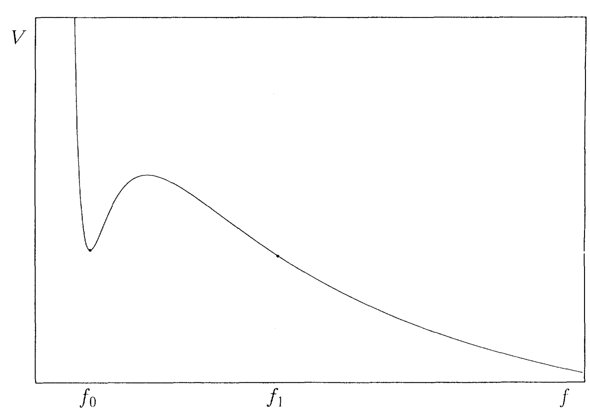

FIG. 1. The effective potential $V(f)$ in the case of a first-order wetting transition with minima at the nonwet state $f=f_0$, and the wet state at $f=\infty$. Also shown is the height f_1 of a critical droplet.

If $h>0$, an infinite layer on the wall is stable even below T_w, since the full potential $\phi(f)\equiv V(f)-hf$ then inevitably goes to minus infinity for $f\to\infty$ (see Fig. 2). In the region $h<0, T<T_w$, a thin layer corresponding to the lower minimum of $\phi(f)$ is stable, so that the coexistence line $h=0$ between the two bulk phases simultaneously is a coexistence line of a surface transition up to point $T=T_w$. From here (as a kind of continuation of this line) a line of first-order prewetting transitions $h=h_p(S)$ [1] extends into the region $h<0, T>T_w$, ending in a prewetting critical point at T_{pc}, h_{pc} (see Fig. 3). Along the prewetting line the two minima of $\phi(f)$ have equal height, and the transition is between layers of thickness f_{p0} and f_{p1}, which are the locations of the two minima.

Above the full first-order line, there is a region of metastability where $\phi(f)$ still has a local minimum at $f_0(T,h)$ corresponding to a metastable thin layer (as in Fig. 4). This region is enclosed by an upper classical spinodal line $h_s(S)$ determined by $\phi'(f_0)=\phi''(f_0)=0$ (see Fig. 3). In our conclusions, we will briefly discuss the appearance of an additional region below the first-order line, where a thick layer is metastable against dewetting.

We now want to discuss the appearance of critical droplets on the wall of the system in the upper metastable region. In mean-field theory, the shape of such a droplet follows from the saddle-point equation $\delta H/\delta f=0$ supplemented by suitable boundary conditions. Assuming rotational symmetry around the normal of the wall, we find, for model (2.1),

$$f''(r)+\frac{d-2}{r}f'(r)=\gamma^{-1}\left[\frac{\partial V(f(r))}{\partial f(r)}-h\right] \tag{2.3}$$

with boundary conditions $f'(0)=0$, $f(\infty)=f_0$, and $r=|x|$. In an often-used analogy [4], the droplet profile is identified as the trajectory of a fictitious particle which, according to (2.3), moves in the potential $-\phi(f)/\gamma$ from the top of the hill at f_0 up to f_1 and back to f_0. The shape of the droplet profile is illustrated by Fig. 5 for $S>0, h=0$ and Fig. 6 for $S>0, h>h_p$.

It is also well known [4] that a linear stability analysis

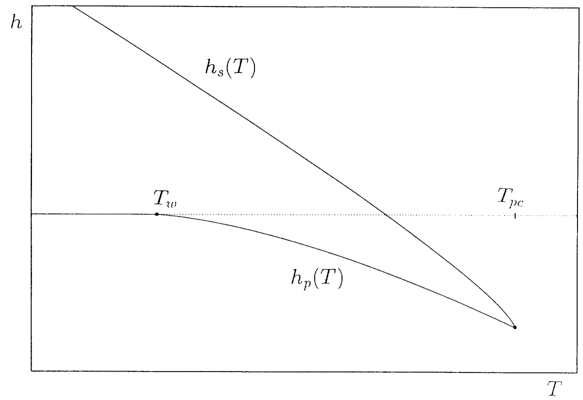

FIG. 3. The phase diagram in the (T,h) plane.

of the profile $f(r)$ leads to a Schrödinger-type equation for the fluctuations $\delta f(x)$, and that $\delta f(x)\sim f'(r)$ is a $(d-1)$-fold degenerate marginal mode which describes translations of the droplet on the wall. For $d=2$, it then follows that there is only a single unstable mode corresponding to the ground state of the Schrödinger problem, since $f'(r)$ obviously has only one node. For $d>2$, the arguments of Ref. [4] show that the rotational symmetry of a critical droplet is linearly stable. However, the existence of only one rotational-symmetric unstable mode can presently only be stated as a conjecture. The unstable mode leads to growth of a supercritical and shrinkage of a subcritical droplet, and consequently can be suppressed by fixing the volume of the droplet. In this case h has to be considered as a Lagrange parameter determined by the fixed-volume condition.

When, in the metastable region of Fig. 3, the classical spinodal is approached, the critical droplet and, accordingly, $F_c\equiv f_1-f_0$ shrinks to zero. On the other hand, from Fig. 2 one can conclude that F_2 goes to infinity when the section $T\le T_w, h=0$ of the coexistence line is approached. Along the prewetting line, F_c decreases from infinity at T_w to zero at T_{pc}. Although the maximal height of a critical droplet thus stays finite close to an interior point of the prewetting line, the size of the droplet

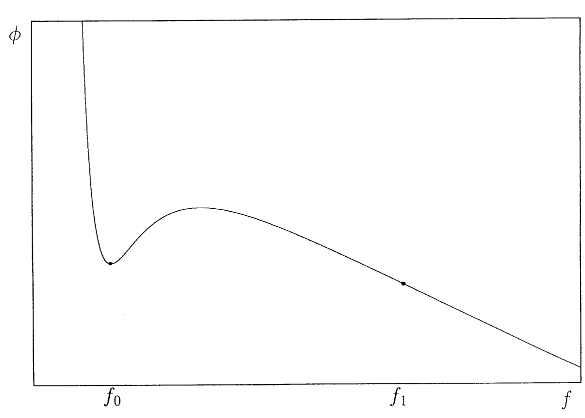

FIG. 2. The potential $\phi(f)=V(f)-hf$ in the partial-wetting regime.

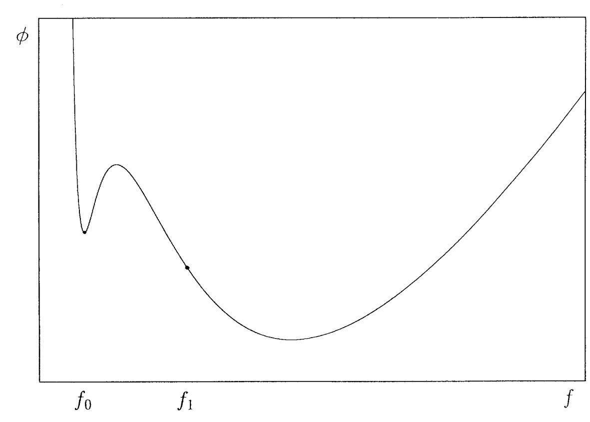

FIG. 4. The potential $\phi(f)$ in the prewetting regime.

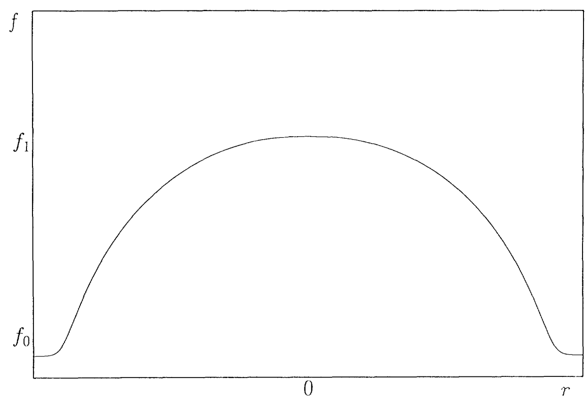

FIG. 5. The critical droplet for $S>0, h=0$.

diverges because its radius grows to infinity (see below).

It has been pointed out by de Gennes and co-workers [7] that the macroscopic form of a droplet is very different in various regimes near the coexistence line. In the partial-wetting regime $T<T_w, h \gtrsim 0$, the macroscopic portion (sufficiently far from the wall) of a droplet is dominated by the field term $-hf$ in $\phi(f)$. If only this term is taken into account, and if $(\nabla f)^2/2$ in H is replaced by the exact expression $\sqrt{1+(\nabla f)^2}$ of the capillary energy [9], then the condition $\delta H/\delta f=0$ means that the droplet surface has constant mean curvature and therefore the form of a spherical cap. Of course, this also stays true approximately for model (2.1), which is designed to describe the behavior near the wetting transition and correspondingly assumes $(\nabla f)^2 \ll 1$.

Near the prewetting line, a droplet has the form of a flat cylinder (called a pancake droplet by de Gennes *et al.*) which resembles the superposition of a kink and an antikink of a Ginzburg-Landau model. In accordance with that, the curvature of the profile at the center of the droplet vanishes due to (2.3) and the obvious relation

$$V'(f_1(T,h_p(S)))=h_p(S) \ . \tag{2.4}$$

In the region $T \gtrsim T_w, h=0$, the droplet is neither a spherical cap nor a cylinder, and has previously been described [5] by a scaling behavior for the height and the radius.

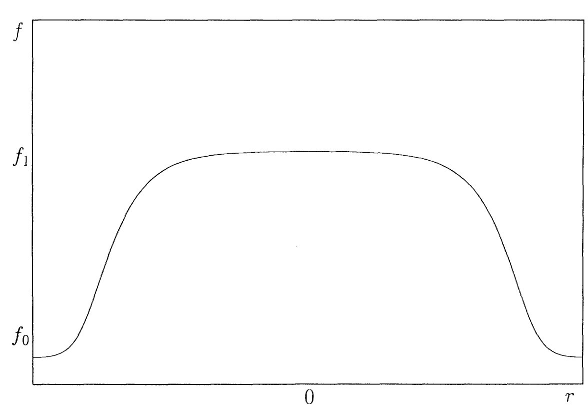

FIG. 6. The critical droplet for $S>0, 0>h>h_p$.

Again, one may replace $\phi(f)$ by that part which dominates the large-f behavior and for nonretarded van der Waals forces is proportional to f^{-2} [1]. For $d=2$, Eq. (2.3) then can be solved exactly and yields the upper half of an ellipse.

III. QUANTITATIVE BEHAVIOR

We now want to determine the crossover behavior of the critical droplet between the different near-coexistence regimes of the upper metastable region. For this purpose, we change from the differential equation (2.3) with the boundary condition $f'(0)=0$, and with $f(0)\equiv f_1$, to the integral equation

$$\frac{\gamma}{2}s^2(f)=V(f)-V(f_1)+h(f_1-f) -(d-2)\gamma\int_f^{f_1} d\tilde{f}\frac{s(\tilde{f})}{r(\tilde{f})} \ , \tag{3.1}$$

$$r(f)=\int_f^{f_1}\frac{d\tilde{f}}{s(\tilde{f})} \tag{3.2}$$

for the (inverted) droplet profile and its slope $s(f)\equiv -f'(r(f))$.

Since the second boundary condition $r(f_0)=\infty$ implies $s(f_0)=0$, we find, from (3.1) and (2.2),

$$V(f_1)-h(f_1-f_0)+(d-2)\gamma\int_{f_0}^{f_1} df\frac{s(f)}{r(f)}=V(f_0) =S+O(h^2) \ . \tag{3.3}$$

As in [5], we define the height and the radius of the critical droplet (here marked with subscripts c) by

$$F_c \equiv f_1-f_0, \quad R_c \equiv \int_{f_2}^{f_1}\frac{df}{s(f)} \ , \tag{3.4}$$

with f_2 chosen as the turning point of the droplet profile, i.e., $f_2=f(R_c), f''(R_c)=0$. The excess free energy of the critical droplet is given by

$$E_c=\Omega_{d-1}\int_{f_0}^{f_1} df\frac{r(f)^{d-2}}{s(f)}\left[\frac{\gamma}{2}s^2(f)+V(f)-V(f_0) -h(f-f_0)\right] , \tag{3.5}$$

where Ω_{d-1} is the surface of the $(d-1)$-dimensional unit sphere.

Near the wetting transition point $S=h=0$, we may ignore the term $O(h^2)$ in (3.3), and we expect $F_c \approx f_1 \gg f_0, f_2$, so that the large-$f$ behavior of $V(f)$ will dominate in (3.1)–(3.5). In the following, we assume

$$V(f)=A/f^{\sigma-1} \quad \text{for } f\to\infty, \ \sigma>1 \ , \tag{3.6}$$

which corresponds to a molecular interaction potential $W(r)\sim r^{-d-\sigma}$ [1].

We now apply these formulas to the partial-wetting regime and consider a droplet at constant $S<0$ in the limit $h\to 0$. Then for sufficiently large f, the potential terms in

(3.1) can be neglected compared to the field term. This yields

$$s^2(f)=\frac{2}{\gamma(d-1)}h(F_c-f)\ , \tag{3.7}$$

and via (3.2) a parabolic profile near the center of the droplet. If this is extrapolated down to $f=0$, one obtains

$$\frac{f}{F_c}+\frac{r^2}{R_c^2}=1\ , \tag{3.8}$$

with

$$F_c=(d-1)|S|h^{-1},\quad R_c=\sqrt{2\gamma}(d-1)|S|^{1/2}h^{-1}\ , \tag{3.9}$$

$$E_c=\Omega_{d-1}2^{(d+1)/2}\gamma^{(d-1)/2}\frac{(d-1)^{d-2}}{d+1}\times|S|^{(d+1)/2}h^{1-d}\ . \tag{3.10}$$

Not unexpectedly, the h dependence of (3.9) and (3.10) resembles the behavior of a critical droplet in the bulk. From (3.7) and the first Eq. (3.9) we recover Young's relation for the contact angle

$$\cos\theta\approx1-\tfrac{1}{2}s^2(f=0)=1+S/\gamma\ . \tag{3.11}$$

For not-too-long-ranged interactions, a line tension

$$\tau\equiv\frac{\Delta E_c}{\Omega_{d-2}R_c^{d-2}} \tag{3.12}$$

can be defined, where ΔE_c is the difference in excess free energy of the exact droplet and a parabolic droplet of the same curvature at $f=f_1$. The latter requires the replacement $h-V'(F_c)$ for h in Eqs. (3.7)–(3.10) which does not affect the asymptotic behavior for $h\to0$. In this limit, τ is finite provided the interactions decay with an exponent $\sigma>2$ [7,10]. This can be seen by expanding the integrand of ΔE_c in powers of $v(f)\equiv[V(f)-V(f_1)-V'(f_1)(f-f_1)]/[V(f_1)+V'(f_1)(f-f_1)]$ followed by the substitution $\varphi\equiv f/f_1$. Then the term $\varphi^{1-\sigma}$ dominates near the lower limit of the integration, and ΔE_c thus diverges for $\sigma\le2$. The dependence of τ on S at $h=0$ will be discussed below.

Next we consider the behavior of droplets near the prewetting line $h=h_p(S)$, which follows from Eqs. (2.4) and (3.3) by eliminating f_1. When the prewetting line is approached at constant $S>0$, the droplet height F_c stays finite, whereas R_c and E_c diverge according to

$$R_c\sim[h-h_p(S)]^{-1}\ , \tag{3.13}$$

$$E_c\sim[h-h_p(S)]^{2-d}\ , \tag{3.14}$$

which agrees with previous results by Joanny and de Gennes [7] (for $d=3$). (3.13) follows from the saddle-point equation which at $r=R_c$ reduces to $(d-2)\gamma s(f_2)/R_c=-\phi'(f_2)$. From (3.1), it can be seen that $s(f_2)$ has a finite limit for $h\to h_p(S)$, while $\phi'(f_2)$ vanishes linearly in $h-h_p(S)$. E_c essentially consists of two parts which both show the behavior (3.14). One contribution comes from the top and bottom surfaces of the cylindrical droplet and therefore may be defined as $E_c^0\equiv[\phi(f_1)-\phi(f_0)]R_c^{d-1}\Omega_{d-1}/(d-1)$, with $\phi(f_1)-\phi(f_0)\sim h-h_p(S)$ and R_c as given by Eq. (3.13). The other is the difference $E_c-E_c^0$, and is proportional to ξR_c^{d-2}, where ξ is a finite length for $h_p(S)>h_{pc}$. In fact, by expanding the saddle-point equation in $f-f_2$, one finds $\xi=\sqrt{\gamma/\phi''(f_2)}$.

Equations (3.13) and (3.14) show that the prewetting critical droplets behave as spherical droplets in dimension $d-1$. The expression $\tau\equiv[E_c-E_c^0]/[R_c^{d-2}\Omega_{d-2}]$ can be regarded as a boundary tension, as introduced by Widom and Clarke [11]. Its behavior close to the prewetting line will be described below.

We now consider the crossover behavior of the critical droplet from the partial-wetting to the prewetting regimes. If, in Eqs. (3.1)–(3.5), we substitute $\varphi\equiv f/f_1$, $\tau(\varphi)\equiv s(f)/f_1^{(1-\sigma)/2}$, and $\rho(\varphi)=r(f)/f_1^{(1+\sigma)/2}$, the integrals in (3.3) and (3.5) converge near the lower limit of integration f_0/f_1 for $f_1\to\infty$, provided $\sigma<3$. In this case, from (3.3)–(3.5) we obtain the asymptotic scaling forms

$$F_c=|S|^{-1/(\sigma-1)}\mathcal{F}(h|S|^{-\sigma/(\sigma-1)})\ , \tag{3.15}$$

$$R_c=|S|^{-(\sigma+1)/[2(\sigma-1)]}\mathcal{R}(h|S|^{-\sigma/(\sigma-1)})\ , \tag{3.16}$$

$$E_c=|S|^{-[d-d_0(\sigma)](\sigma+1)/[2(\sigma-1)]}\mathcal{E}(h|S|^{-\sigma/(\sigma-1)})\ , \tag{3.17}$$

$$d_0(\sigma)=\frac{3\sigma-1}{\sigma+1} \tag{3.18}$$

for $S,h\to0$. From (3.9), (3.10), (3.13), and (3.14), we conclude that the scaling functions in Eqs. (3.15)–(3.17) have the form

$$\mathcal{F}(x)\sim x^{-1},\quad \mathcal{R}(x)\sim x^{-1/2},\quad \mathcal{E}(x)\sim x^{1-d} \tag{3.19}$$

in the partial-wetting regime and

$$\mathcal{R}(x)\sim(x-x_p)^{-1},\quad \mathcal{E}(x)\sim(x-x_p)^{2-d}\ , \tag{3.20}$$

with $x_p\equiv x(h_p(S))$ in the prewetting regime. When the wetting transition point is approached from above at $h=0$, all scaling functions reduce to constants [5]. On a path $S=0,h\ge0$, the S dependence in Eqs. (3.15)–(3.17) should cancel everywhere, which yields the behavior

$$\mathcal{F}(x)\sim x^{-1/\sigma},\quad \mathcal{R}(x)\sim x^{-(\sigma+1)/2\sigma}\ ,\quad \mathcal{E}(x)\sim x^{-[d-d_0(\sigma)](\sigma+1)/2\sigma}\ . \tag{3.21}$$

This agrees with results by Joanny and de Gennes on what they call small droplets [7].

The divergences which show up for $\sigma\ge3$ lead to modifications of F_c, R_c, and E_c, which we now discuss along the paths $S>0,h=0$ and $S=0,h>0$. The divergences do not affect the integral in (3.4) and generally imply

$$R_c\sim F_c^{(\sigma+1)/2}\ . \tag{3.22}$$

The excess free energy behaves according to

$$E_c\sim\begin{cases}R_c^{d-2}\ln R_c & \text{for } \sigma=3 & (3.23)\\ R_c^{d-2} & \text{for } \sigma>3\ , & (3.24)\end{cases}$$

which comes from the lower limit of integration in (3.5). From Eq. (3.3), the connection between F_c and S at $h=0$ and between F_c and h at $S=0$, respectively, follow as

$$S \sim \begin{cases} F_c^{-2}\ln F_c , \quad h \sim F_c^{-3}\ln F_c \quad \text{for } \sigma=3 & (3.25) \\ F_c^{-(\sigma+1)/2}, \quad h \sim F_c^{-(\sigma+3)/2} \quad \text{for } \sigma>3 \; . & (3.26) \end{cases}$$

According to (2.4) and (3.6), the prewetting line has the asymptotic form

$$h \sim [F_c(S)]^{-\sigma} \qquad (3.27)$$

close to the wetting transition point. Due to (3.15) and (3.27), the relation between F_c and S is $F_c \sim S^{-1/(\sigma-1)}$ for $\sigma<3$, and for $\sigma \geq 3$ again is given by (3.25) and (3.26). We finally point out the behavior of the line tension (3.12) along the path $h=0, S<0$. From (3.16) and (3.17), we recover the scaling behavior [10]

$$\tau \sim \begin{cases} |S|^{(\sigma-3)/[2(\sigma-1)]} \quad \text{for } 2<\sigma<3 & (3.28) \\ \ln|S| \quad \text{for } \sigma=3 & (3.29) \\ \text{const} \quad \text{for } \sigma>3 \; . & (3.30) \end{cases}$$

The same behavior is found for the boundary tension along the prewetting line $h_p(S)$ without the restriction $\sigma>2$. Although the introduction of a line tension for $h=0, S>0$ seems to be somewhat arbitrary, we mention that in this regime the ratio E_c/R_c^{d-2} also scales according to (3.28)–(3.30).

IV. DISCUSSION

The whole discussion of the crossover behavior of critical droplets in the nucleation regime near the wetting transition has been based on mean-field theory. Although we are dealing with a first-order transition, fluctuations may be important and lead to modifications of the droplet properties. The reason is that, near the wetting transition point, the effective interface potential develops a broad minimum at infinity. In fact, it has been conjectured by Kroll, Zia, and Lipowsky [12] that fluctuations may drive the wetting transition from first to second order in the strong-fluctuation regime $d<d_0(\sigma)$. More recent renormalization-group calculations [13], however, seem to allow the existence of first-order wetting transitions in this regime above $d \approx 2.4$. In $d=2$, the effect of fluctuations has been discussed by transfer-matrix techniques [14]. Fluctuation effects on the line tension near first-order wetting transitions have recently been pointed out by Indekeu and Robledo [15].

Another aspect of nucleation phenomena at wetting is the existence of a metastable region below the first-order line in the phase diagram bounded by another spinodal line. A macroscopic film can be undercooled into this region and will decay via the formation of critical nuclei which appear as dents in the film. When a macroscopic layer is undercooled at $h \lesssim 0$, one always stays close to the coexistence line so that critical nuclei will be very large. Therefore, we expect an unusually long lifetime of the metastable thick film, which recently seems to have been observed experimentally [16] (and supported by a different interpretation [17]).

Concerning dynamical properties of critical droplets, one naturally expects that for supercritical droplets the central height $F(t)$ and the radius $R(t)$ grow in different ways. Within a purely relaxational model introduced by Lipowsky [18], one finds $F(t) \sim t^{1/(\sigma+1)}$ and $R(t) \sim t^{1/2}$ for $t \to \infty$ [19]. For fluid systems, a model with a conserved bulk order parameter (which we currently investigate) is more relevant. The asymptotic growth of the droplet will still be anisotropic, but in addition we expect the occurrence of a dynamical instability of the Mullins-Sekerka type [20].

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