Diverging length scales at first-order wetting transitions

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The singular behavior of the equilibrium line tension at first-order wetting transitions can be understood as a critical phenomenon with diverging length scales. Also, near the wetting transition the decay of a metastable nonwet state is accompanied by the divergent length scales of the unstable critical droplet. We discuss the relationship between these two sets of diverging lengths and verify a scaling hypothesis for the singular part of the line tension and a generalized Laplace equation for critical droplets. For sufficiently long-ranged forces the equilibrium and nonequilibrium lengths are governed by the same universal laws, whereas for short-ranged forces the results indicate a distinct nonequilibrium universality class.

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I. INTRODUCTION AND MOTIVATION

Recent studies of the first-order wetting transition have provided evidence that a critical phenomenon is taking place. The line tension τ between a thin film and a thick wetting layer displays singular behavior when the wetting temperature T_w is approached in equilibrium [1]. The singular behavior of τ has been shown to display the universal features of a critical end point [2]. Associated with the singularity of the line tension at wetting are diverging lengths: the parallel and perpendicular correlation lengths $\xi_\parallel$ and $\xi_\perp$, and the film thickness l. All these quantities diverge as functions of the temperature "distance" $t \equiv (T - T_w)/T_w$ with universal exponents [1,2].

A first-order wetting transition can also be brought about by a nonequilibrium process involving a quench from temperatures $T < T_w$ to $T > T_w$. If the quench is performed sufficiently fast, the nonwet surface state persists as a metastable state which subsequently decays by the formation of droplets. The properties of the critical droplets associated with this decay process have also recently been studied [3]. If the quench to the complete wetting regime at bulk coexistence is performed such that the final temperature is only slightly above T_w, then the height F and the contact radius R of the critical droplet are large. In fact, these lengths diverge as the final temperature approaches T_w. Thus, near T_w, two *additional* divergent length scales appear.

Now the question arises as to how these nonequilibrium lengths relate to the critical behavior associated with the equilibrium transition. Specifically, one might wonder whether the universal exponents characterizing the divergence of $\xi_\parallel$, $\xi_\perp$, and l as functions of t are identical to those of R and F. If they are, one might conclude that the equilibrium and nonequilibrium lengths are governed by the same universality principle. It turns out that for sufficiently long-ranged forces this *strong* universality indeed applies, whereas for sufficiently short-ranged forces the nonequilibrium lengths display different universal behavior. These facts follow from purely thermodynamic arguments, as we shall discuss.

The parallel correlation length $\xi_\parallel$ associated with the interface fluctuations parallel to the film surface obeys a scaling relation proposed for the singular part of the line tension [1,2]

$$\gamma_{\text{sing}} \propto \frac{\tau_{\text{sing}}}{\xi_\parallel}, \qquad (1)$$

where γ_{sing} is the singular part of the surface free energy. In the partial wetting regime $t < 0$, one has $\gamma_{\text{sing}} = S \equiv \gamma_{sg} - \gamma_{sl} - \gamma_{lg}$, where s, g, l denote the bulk phases solid, liquid and gas, respectively. The quantity S is the *equilibrium* spreading coefficient. Below T_w, $S < 0$, and near T_w, $S \propto t$. In the complete wetting regime $t > 0$, where $S = 0$ (equilibrium), γ_{sing} pertains to the surface free energy associated with the approach to bulk coexistence from the gas phase. In Eq. (1), the correlation length $\xi_\parallel$ diverges according to $\xi_\parallel \propto |t|^{-\nu_\parallel}$, where it is understood that for $t < 0$ the wetting transition is approached along partial wetting in the presence of the contact line between a thin film and bulk liquid, and for $t > 0$ along the prewetting line $t_p \equiv t_p(h)$. Asymptotically close to $t = 0$ the prewetting line satisfies $t_p \propto h^{(\sigma-1)/\sigma}$, where h is the chemical potential difference between the bulk liquid and gas phases. In Fig. 1 the different paths along partial wetting (I), prewetting (II), and complete wetting (III) are shown schematically.

In the complete wetting regime along path III of Fig. 1, the contact radius of the critical droplet R satisfies a surface analog of the Laplace equation which generally governs the pressure difference across a curved interface,

$$S^* \propto \frac{\tau_{\text{CD}}}{R}. \qquad (2)$$

Here τ_{CD} is the line tension of the contact circle where the critical droplet meets the substrate. $S^* > 0$ is the *nonequilibrum* spreading coefficient. It is of the same form as S defined earlier, but with γ_{sg} replaced by the value γ_{sg}^* for the metastable surface state. Above and near T_w, $S^* \propto t$. S can be interpreted as a "surface" pressure difference across the contact line, since it represents
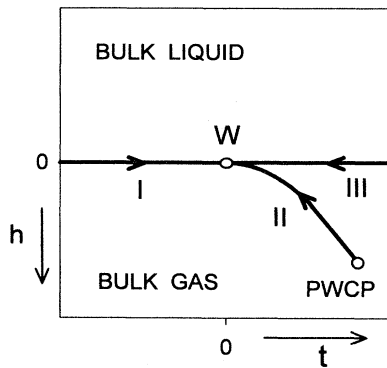
FIG. 1. The wetting phase diagram in the parameters temperature difference from the wetting temperature t and chemical potential difference h. The first-order wetting transition point is indicated by W, and the prewetting critical point by PWCP. The numbers and arrows refer to the paths discussed in the text; I: partial wetting, II: prewetting transition, III: complete wetting. Along I the transition zone or contact line between a thin film and bulk liquid is monitored. Along II the properties of the boundary between the thin and the thick film are examined. Along III the critical droplet of nucleation is studied.

a force per unit length.

Note the formal similarity between Eqs. (1) and (2). However, while Eq. (1) represents a scaling hypothesis, Eq. (2) can be expected to hold on general thermodynamic grounds. An expression similar to Eq. (2) near prewetting has recently been discussed on the basis of a phenomenological expression for the excess free energy of a *cylindrical* droplet [4–6]. In that case, τ_{CD} assumes a finite positive value, the "boundary tension," at the prewetting transition [1]. Furthermore, the possible validity of Eq. (2) in the complete wetting regime at bulk coexistence has been discussed for van der Waals and short-range forces [4,6,7].

We now turn to the discussion of the various divergent lengths that appear when the wetting point is approached along the paths I–III of Fig. 1. Depending on the path, Eq. (1) or (2) is relevant, and its validity will be verified. The equilibrium paths (I and II) are addressed first.

II. EQUILIBRIUM LENGTHS

In [2] it was shown that the line tension τ can be written as $\tau(t)=\tau(0)+\tau_{\text{sing}}(t)=\tau(0)+\tau_{\pm}|t|^{2-\alpha_l}$ near $t=0$. In this expression, τ_+ and τ_- are the amplitudes of the singular part $\tau_{\text{sing}}(t)$ for $t>0$ and $t<0$, respectively, and α_l is the universal line specific-heat exponent. If the substrate-adsorbate forces are sufficiently short ranged, $\tau \to \tau(0)>0$ at T_w. This finite positive limit arises for intermolecular interaction potentials in d dimensions of the form $\phi(r) \propto r^{-(d+\sigma)}$, with $\sigma>3$. On the other hand, if $\sigma \leq 3$, e.g., for van der Waals or longer-ranged potentials in $d=3$, $\tau_{\text{sing}}(t)$ diverges at wetting and hence dominates in the behavior of τ near T_w. If d is greater than the so-called upper critical dimension d_0, mean-field theory is valid, whereas fluctuation effects are important below d_0.

For first-order wetting, $d_0(\sigma)=3-4/(\sigma+1)$, as discussed in [1,2].

In the mean-field regime the critical exponents depend on σ, whereas in the fluctuation regime they depend on d. At $d_0(\sigma)$ their values coincide. The actual interfacial correlation lengths $\xi_\parallel$ and $\xi_\perp$ are always characterized by the d-dependent exponents, even for $d>d_0$. However, in the latter regime two analogous lengths characterized by the σ-dependent exponents become more important [8]. These lengths are of thermodynamic nature, and must be distinguished from the correlation lengths. In order to keep the notation uniform, we use again ξ to denote these lengths, but attach the superscript MF, as was also done in [8]. The same superscript is used for the exponents, whenever the σ-dependent expressions apply.

A. Mean-field regimes

1. $d>d_0$ and $\sigma>3$

Here it was found that $2-\alpha_l=(\sigma-3)/[2(\sigma-1)]$ $=1-\nu_\parallel^{MF}$ [1,2], so that Eq. (1) indeed holds. The wetting layer thickness l at a distance $\xi_\parallel^{MF}$ from the contact line (and parallel to the substrate) diverges along path I according to

$$l \propto \xi_\perp^{MF} \propto (\xi_\parallel^{MF})^{\zeta^{MF}} \propto (-t)^{-1/(\sigma-1)}, \qquad (3)$$

where the anisotropy exponent ζ^{MF} is given by $\zeta^{MF}=2/(\sigma+1)$ [8,9]. Along path II, the thickness of the thick film satisfies $l \propto h^{-1/\sigma}$, which can be rewritten as $l \propto t^{-1/(\sigma-1)}$, using the asymptotic behavior of the prewetting curve. Furthermore, $\xi_\perp^{MF}$ and $\xi_\parallel^{MF}$ are characterized by the same critical exponents as along path I when expressed as functions of t. Thus, on both paths we have $l \propto \xi_\perp^{MF}$, and the representative exponent is $1/(\sigma-1)$.

2. $d>d_0$ and $\sigma<3$

Here, $2-\alpha_l<0$ and τ diverges. A detailed analysis shows that $\tau=\infty$ for $\sigma \leq 2$ in the thermodynamic limit, even for $t \neq 0$ [8,9]. For $2<\sigma<3$, Eq. (1) holds as in Sec. II A 1, and the same scaling behavior is found, with critical exponent $1/(\sigma-1)$.

3. $d>d_0$ and $\sigma=3$

In this marginal case $\tau_{\text{sing}} \propto \ln(|t|^{-1})$ [9], which is consistent with Eq. (1), since $\nu_\parallel^{MF}=1$, but the logarithm is not predicted by the scaling hypothesis.

B. Fluctuation regime

$2<d<d_0$

In the fluctuation regime, $\xi_\parallel$ and $\xi_\perp \equiv \xi_\parallel^\zeta$ are actual correlation lengths related by the roughness exponent $\zeta=(3-d)/2$. Universality is stronger in this regime, since both $2-\alpha_l=(d-2)/(d-1)$ and $\nu_\parallel=1/(d-1)$ do not depend on the range of forces, i.e., on σ [1]. We thus have

$$l \propto \xi_\perp \propto |t|^{-(3-d)/2(d-1)} . \tag{4}$$

III. NONEQUILIBRIUM LENGTHS

We now turn to the divergent length scales associated with the critical droplet along path III. If $\tau(0)$ is finite, τ and τ_{CD} become identical at the wetting transition. Furthermore, the singular parts of τ and τ_{CD} have the same scaling properties, so that no distinction between τ and τ_{CD} will be made in the following. In [3] it was shown how the radius R, the height F, and the excess free energy E of the critical droplet depend on the temperature distance t from the wetting point. We will now make use of these results, and check if they satisfy the surface Laplace equation (2).

A. Mean-field regimes

1. $d > d_0$ and $\sigma > 3$

For $t \to 0+$, $\tau(0) = \tau_{\mathrm{CD}}$ is finite, and $R \propto t^{-1}$ [3], so that (2) is valid. The height F of the critical droplet scales generally according to $F \propto R^{\zeta^{\mathrm{MF}}}$ [3], so that

$$F \propto R^{\zeta^{\mathrm{MF}}} \propto (S^*)^{-\zeta^{\mathrm{MF}}} \propto t^{-2/(\sigma+1)} . \tag{5}$$

Comparing this with Eq. (3), we conclude that the equilibrium wetting layer thickness l and the height of the critical droplet F diverge with *different* exponents. The former is characterized by $1/(\sigma-1)$ and the latter by $2/(\sigma+1)$.

2. $d > d_0$ and $\sigma < 3$

Here, τ diverges according to $\tau_{\mathrm{sing}} \propto t^{2-\alpha_l}$. In this case, the number of independent length scales is significantly reduced because $\xi_\parallel^{\mathrm{MF}} \propto R$, and $\xi_\perp^{\mathrm{MF}} \propto l \propto F$. The common exponent of l and F is $1/(\sigma-1)$. This implies that the universality is *stronger* when τ diverges at wetting.

This result is in accord with the observation first made by Joanny and de Gennes that for $\sigma < 3$ the expression for τ is independent of microscopic length scales [10]. The same holds true for the excess free energy E of the critical droplet [3], and is the reason for the difference in the scaling behavior of R for $\sigma < 3$ and $\sigma > 3$. This implies that a nonuniversal background contribution to τ and E appears for $\sigma > 3$. This background reflects the existence of a microscopic length scale associated with the decay of the interface displacement profile towards the thin film [1].

3. $d > d_0$ and $\sigma = 3$

In this borderline case, the logarithmic behavior $\tau_{\mathrm{CD}} \propto \ln(t^{-1})$ and the result $R \propto t^{-1}\ln(t^{-1})$ [3,4] imply that Eq. (2) is again valid. Note also that the exponents $1/(\sigma-1)$ and $2/(\sigma+1)$ coincide for $\sigma = 3$.

B. Fluctuation regime

$2 < d < d_0$

The existence of a critical droplet in the fluctuation regime has not yet been demonstrated. Therefore, we have no results for checking the validity of Eq. (2). However, presupposing that the critical droplet exists, we speculate that τ_{CD} remains finite for $t \to 0+$, since $2 - \alpha_l = (d-2)/(d-1) > 0$. Equation (2) can then be satisfied on path III *provided* $R \propto (S^*)^{-1} \propto t^{-1}$. In this case we expect

$$F \propto R^{\zeta} \propto (S^*)^{-(3-d)/2} \propto t^{-(3-d)/2} . \tag{6}$$

Note that the correlation lengths $\xi_\parallel |t|^{-1/(d-1)}$ and $\xi_\perp \propto |t|^{-(3-d)/2(d-1)}$ on paths I and II then scale differently from R and F, respectively, on path III.

IV. CONCLUSIONS AND CONSEQUENCES

We have shown that, in the mean-field regime, the divergence of the equilibrium and nonequilibrium lengths associated with the first-order wetting transition is represented by a single critical exponent $1/(\sigma-1)$, for sufficiently long-ranged forces, $\sigma \leq 3$. In contrast, for $\sigma > 3$ two representative critical exponents apply, $1/(\sigma-1)$ for the (perpendicular) equilibrium lengths, and $2/(\sigma+1)$ for the (perpendicular) nonequilibrium lengths. Furthermore, in the fluctuation regime we argue, assuming the existence of a critical droplet, that also two different exponents apply.

We have proposed to explain this in terms of two distinct universality principles. One is associated with the singular part of the line tension at wetting, and embodied in the scaling hypothesis Eq. (1). The other is connected with the line tension itself, and is incorporated in the surface thermodynamical relation Eq. (2). In all cases in which τ can be separated into a finite regular part and a vanishing singular contribution at wetting, the two universalities are different, each carrying its proper exponents. In contrast, whenever τ diverges at wetting, its singular part dominates, and the universality contained in the scaling relation also governs the thermodynamic aspects.

The consequences of this are twofold.

(i) The cases in which two distinct critical exponents for the equilibrium wetting layer thickness l and the critical droplet height F are found, suggest the existence of a separate universality class for the nonequilibrium quantities associated with nucleation of wetting layers, near the equilibrium transition point at T_w.

(ii) The interpretation of the first-order wetting transition as a genuine critical phenomenon acquires further significance. Indeed, there are now three reasons for putting forward this interpretation. The first is that the diverging lengths at complete wetting are also found at first-order wetting [1,2]. The second is that first-order wetting is actually an interface critical end point, implying universal amplitude ratios [1,2]. The third, and new reason, is that, in general, a second set of critical exponents must be added to those that were already identified to play a role at a first-order wetting transition. This second set pertains to the nonequilibrium lengths associated with the critical droplet of nucleation.

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