Kinetic complete wetting of a planar defect close to a bulk tricritical point

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The nucleation of a new phase at a moving planar defect is considered in the high-symmetry phase of a bulk tricritical point. In the first-order regime a kinetic complete-wetting transition is found where the thickness of the nucleation layer diverges, inducing a change of the drag coefficient of the defect. When the tricritical point is approached, the complete-wetting transition disappears, and, in the adjacent second-order regime, the layer thickness is finite in the full nucleation region.

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The heterogeneous nucleation of a new phase at extended defects in a crystal generally occurs in the high-symmetry regime of some bulk phase transition. Various examples of such situations are quoted in Ref. [1] where, with regard to plastic behavior, the driven motion of a planar defect, coated by the layer of a new phase, has been discussed. In a reinvestigation of the problem, we have recently observed that, in case of a first-order bulk transition, the moving nucleation layer displays a kinetic complete-wetting transition [2]. In fact, if some temperature-dependent critical velocity is approached from below, the layer thickness shows a logarithmic divergence and stays infinite in the adjacent complete-wetting regime. We have also pointed out that this transition should be detectable by a shift of the drag coefficient of the defect.

The analysis in Ref. [2] was based on a model with a piecewise parabolic free-energy density which only allowed to consider the case of a strong first-order bulk transition. In order to describe the behavior close to a tricritical point, we here use instead the standard polynomial form of the local free energy. This complements our previous paper [2] where more details and references, concerning the general context of the problem, can be found.

Although the approach in the present paper prevents a complete analytic description of the moving nucleation layer, the most important attributes of the complete-wetting transition can be determined exactly within a mean-field approach. This applies to the location of the complete-wetting regime, and to the shift of the drag coefficient which both turn out to disappear at the tricritical point.

Access to these quantities is opened up on account of the following observations. With increasing velocity the trail of the nucleus profile develops a shoulder where the order parameter is captured by one of the metastable minima of the free energy [2]. For subcritical velocities this shoulder is limited by a kink which tries to release the metastable state by moving towards the defect, and, in a steady state, this motion is just balanced by the defect motion. Asymptotically close to the critical velocity the kink is so far from the defect that its velocity is essentially determined by the well-studied free-kink motion, induced by appropriate boundary conditions [3]. The result for the critical velocity and the value of the free energy at the metastable state eventually fix the shift of the drag coefficient in the way outlined in Ref. [2].

Following Ref. [3], we describe the bulk phase transition by a scalar order parameter η, entering the free-energy density

$$f(\eta) = \frac{A}{2}\eta^2 - \frac{B}{4}\eta^4 + \frac{C}{6}\eta^6. \tag{1}$$

The stability of the system generally requires $C>0$, whereas $B>0$, $B=0$, $B<0$ for first-order, tricritical, and normal-critical transitions, respectively. $A=\alpha(T-T_0)$ is a linear function of temperature T where, in the first-order regime, T_0 means the lower spinodal temperature. The upper spinodal temperature $T^*(B)$ is defined by the relation $A-B^2/(4C) \equiv \alpha(T-T^*(B))$ which follows from the identity $\eta_1^2 \equiv [B/(2C)][1+\sqrt{1-4AC/B^2}]$ for the nonzero minima $\pm\eta_1$ of $f(\eta)$. Finally, the condition $f(0)=f(\pm\eta_1)$ fixes the transition temperature $T_c(B)$ via the definition $A-3B^2/(16C) \equiv \alpha(T-T_c(B))$. At the tricritical point, $A=\alpha(T-T_c(0))$ which also applies to the normal-critical regime.

A one-dimensional kink profile $\eta(x)$ only exists in the hysteresis temperature range $T_0<T<T^*(B)$. In order to find its explicit form, one should add to Eq. (1) a term $K(\partial_x\eta)^2/2$ with $K>0$, and solve the resulting saddle-point equations with boundary conditions $\eta(\infty)=\eta_1$ and $\eta(-\infty)=0$. Since the latter is more stable in the presently interesting high-symmetry phase, the kink will propagate in the positive x direction. As demonstrated in Ref. [3], the time-dependent Ginzburg-Landau equation

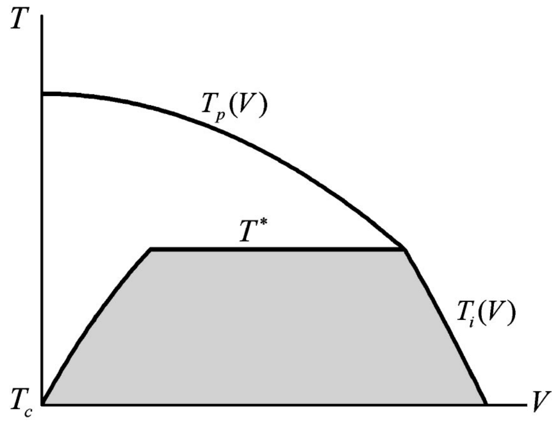

FIG. 1. Nucleation region in the T,V plane, bounded by the prewetting and incomplete-wetting lines $T=T_p(V)$ and $T=T_i(V)$. The shaded region is the complete-wetting regime $T_c(B)<T<T^*(B)$, $v(T)<V<V_i(T)$, where $V_i(T)$ is the inverse of $T_i(V)$.

$$\partial_t \eta = \Gamma[K\partial_x^2 \eta - f'(\eta)], \tag{2}$$

involving a damping coefficient Γ, has, in the comoving system, the stationary solution $\eta(x-vt)$, where the result for the kink velocity v can be written in the form

$$v(T) = \Gamma \sqrt{\frac{K}{3C}} \left\{ B - \sqrt{B^2 + \frac{16\alpha C}{3}[T_c(B) - T]} \right\}. \tag{3}$$

In the plane, spanned by the defect velocity V and by temperature T, the function $V=v(T)$ is represented by the left branch of a downward parabola which runs through the origin $V=0, T=T_c(B)$. As argued in the introduction, the strip $V>v(T), T_c(B)<T<T^*(B)$, shown in Fig. 1, represents the complete-wetting regime. In the strong first-order situation, considered in Ref. [2], the upper spinodal temperature T^* was located outside of the nucleation region. In the present case, however, one finds $T^*(B)-T_c(B)=B^2/(16\alpha C)$, so that the complete-wetting region vanishes in the tricritical limit $B\rightarrow 0$. This completes our analysis, concerning the behavior of the kinetic complete-wetting transition within the model (1) and (2).

Regrettably, we cannot offer an analytic expression for the boundary of the nucleation regime in the presently used model. From Ref. [2] it is known, however, that in the first-order regime of the bulk transition, this boundary has two branches, $T=T_p(V)$, and $T=T_i(V)$ which are lines of kinetic prewetting and incomplete-wetting transitions, respectively. Whereas these lines have been included in Fig. 1 in a schematic way only, the character of the related surface transitions can be determined quantitatively in both cases.

Concerning the kinetic prewetting transition, it seems natural to assume that its character is the same as that at zero velocity. There, the Cahn theory of wetting transitions [4] easily allows to locate a stability limit $T=T_p(B)$, up to which a nucleation layer can exist at least in a metastable state. This theory is based on the free-energy expression

$$F = \int dx \left[\frac{K}{2}(\partial_x \eta)^2 + f(\eta) - \frac{\kappa}{2}\eta^2 \delta(x-X) \right], \tag{4}$$

where the integral runs over $-\infty<x<+\infty$, and X denotes the defect position. The coupling term to the defect is the same as in Ref. [2], again assuming $\kappa>0$ for the coupling constant.

From the saddle-point equation $\delta_\eta F=0$ we obtain the jump condition

$$\eta'(X-0) - \eta'(X+0) = \eta(X)\kappa/K, \tag{5}$$

and from its first integral

$$\eta'(X\pm 0) = \mp \sqrt{2f(\eta(X))/K}. \tag{6}$$

These equations allow to establish for the surface-order parameter $\phi \equiv \eta(X)$ the closed equation

$$\phi^2 \left[\phi^4 - \frac{3B}{2C}\phi^2 - \frac{3}{C}\left(A - \frac{\kappa^2}{4K} \right) \right] = 0. \tag{7}$$

Within the interval

$$T_c(B) < T < T_p(B) \equiv T_c(B) + \frac{\kappa^2}{4\alpha K}, \tag{8}$$

Eq. (7) has the solutions

$$\phi^2 = \frac{3B}{4C} + \sqrt{\frac{3\alpha}{C}[T_p(B) - T]} \tag{9}$$

in the first-order regime $B>0$,

$$\phi^2 = \sqrt{\frac{3\alpha}{C}[T_p(0) - T]} \tag{10}$$

in the tricritical regime $B=0$, and

$$\phi^2 \approx \frac{2\alpha}{\langle B \rangle}[T_p(0) - T] \tag{11}$$

in the normal-critical regime $B<0$, whereas $\phi=0$ for $T>T_p(B)$.

According to Eq. (9) ϕ has a finite jump at $T=T_p(B)$, so that, following the behavior in the bulk, the nucleus appears via a first-order transition. Since, moreover, the point $V=0, T=T_p(B)$ clearly lies outside the complete-wetting region, the nucleation process has the character of a prewetting transition. From Eqs. (10) and (11) it is seen that, in the related regimes, the surface-order parameter ϕ just has the same mean-field critical behavior near the nucleation threshold $T_p(0)$ as the bulk order parameter η near $T_c(0)$.

Next, we consider the incomplete-wetting transition which only exists in the first-order regime of the bulk phase transition. From Ref. [2] it is known that, below the incomplete-wetting line, the wetting layer has a constant order-parameter value, extending up to the defect plane. Since the layer is captured by the metastable minimum of the free-energy density at say $+\eta_1$, this value just can be identified as a jump of the surface-order parameter across the incomplete-wetting line. Sufficiently close to the tricritical point the incomplete-wetting line will cut the horizontal branch of the complete-wetting line. As a result, the surface-order parameter then has the value $\phi=\sqrt{B/(2C)}$ at the intersection point. Amazingly, the common value $\phi=\sqrt{3B/(4C)}$ is found at the end points $T=T_p(0)$ and $T=T_c$ of the full nucleation boundary.

We now turn to the second major topic of our present investigation which concerns the critical behavior of the drag coefficient along isotherms close to the complete-wetting transition. The friction force per unit area of the defect plane is defined by $G=-\partial_X F$ which, by use of the equation of motion $\partial_t \eta=-\Gamma\ \delta_\eta F$, can be written as

$$G = \int dx[\Gamma^{-1}(\partial_t \eta)(\partial_x \eta) + \partial_x f(\eta)]. \tag{12}$$

For stationary solutions in the comoving frame, we have $\partial_t \eta=-V\partial_x \eta$, so that

$$G(V) = -D(T,V)V - \Theta(V-v(T))\ f(\eta(x=-\infty)), \tag{13}$$

where $\Theta(V-v(T))$ means the Heaviside step function. As observed in Ref. [2], there exists a regime where $\approx D(T,V) = D(T)+\Theta(V-v(T))\ d(T)$ with a drag coefficient $D(T)$ and a shift $d(T)$ of this coefficient. Since, furthermore, $f(\eta(x=-\infty))=f(\eta_1)$ in the complete-wetting region $V>v(T)$, we obtain, in terms of known quantities,

$$d(T) = -f(\eta_1(T))/v(T), \tag{14}$$

which is valid on all isotherms with $T_c(B)<T<T^*(B)$, and represents the second main result of the present note.

The fact that most displacive phase transitions occur close to tricritical points [5] should allow to verify our predictions experimentally. Moreover, these predictions complement and partly correct previous work on a similar subject [6].

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