# Blocking of metastable phase formation by an external field

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The influence of an external field on interfacial growth is analyzed within a Ginzburg-Landau model of front propagation. In the field-free case in a rapid temperature quench a metastable phase can be created by a dynamic instability that splits the front separating the stable high-temperature and low-temperature phases [J. Bechhoefer *et al.*, Phys. Rev. Lett. **67**, 1266 (1991)]. The external field blocks the production of the metastable phase. It is found that the thickness of the metastable phase is a *nonmonotonic* function of time. It first grows to mesoscopic size and then shrinks to a microscopic layer. Suggestions for observing this effect in real growth experiments are made.

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## I. INTRODUCTION

Metastable phases are usually produced by fast temperature quenches. The common picture is that due to kinetic obstacles the stable phase does not have enough time to form and a metastable phase can be created on a macroscopic scale. There are many concrete examples of metastable phases in physics and metallurgy [1] and for more than a century [2] experimental and technical experience on creating metastable crystalline structures and glasses from the melt has accumulated. It is, however, only recently that theoretical mechanisms have been studied. Two general mechanisms have been proposed [3]: First the *nucleation* rate of metastable germs may be larger than that of stable germs. Second, the *growth* rate of the metastable phase exceeds that of the stable phase.

Recently a simple Ginzburg-Landau model for interfacial growth with one nonconserved order parameter was investigated by Bechhoefer, Löwen, and Tuckerman [4]. They proposed a theory for the different growth velocities of the stable and metastable phases incorporating some quantities related to material parameters. An interesting dynamic splitting instability was found at the front separating the phase stable at high temperatures (phase 10) from the phase stable at low temperatures (phase 2). A macroscopic portion of a metastable phase (phase 1) intervenes dynamically between the two original phase 0 and 2 due to the different growth velocities of the 01 and 12 interfaces. The same picture also applies to two nonconserved order parameters [5], showing that the mechanism is quite universal and should be observable in many different experimental realizations.

In the Ginzburg-Landau model of Ref. [4] an *infinite* geometry with a planar system was assumed. In this case the growth of the metastable phase is not hindered by the finite size of the sample, and a macroscopic portion of the metastable phase forms. It is clear that the finite system size of the sample provides a natural limit to the growth of the metastable phase. Other circumstances that may hinder the growth of the split interface are external fields, such as walls or a gravitational field.

In this paper we address the influence of an external field on the dynamical creation of a metastable phase quantitatively within a suitable extension of the dynamical Ginzburg-Landau model. We do not include a finite system size but consider a semi-infinite system in an external (e.g., gravitational) field. We find that there are two different time regimes describing the growth of the 02 interface: For small times a metastable phase can be formed due to the splitting instability. This means that the 01-interface velocity is larger than the 12-interface velocity. Consequently the portion of the metastable phase increases and reaches mesoscopic or even macroscopic sizes depending on the strength of the external field. Then in a second (large) time regime the external field induces a *reduction* of the grown metastable phase. The width of the metastable phase now *decreases* with time. This is because the external field slows down the 01 interface motion much more than the 12-interface motion.

For very long times the interfacial profile approaches its equilibrium profile in the external field, consisting of a 02 interface with a microscopically small remnant of the metastable phase. Hence the width of the layer built up by the metastable phase is *nonmonotonic* in time. It first reaches mesoscopic or macroscopic sizes and then shrinks to microscopic dimensions. The dynamical nonmonotonicity in the portion of the created metastable phase should be observable in time-resolved growth experiments.

The paper is organized as follows. We first describe in Sec. II a simple model of Ginzburg-Landau dynamics for an interface in an external field. Numerical results for the interfacial motion and the dynamical creation of a metastable phase are presented in Sec. III. We finally conclude in Sec. IV.

## II. THE MODEL

To see the influence of an external field in its simplest setting, we study a semi-infinite spatial domain ($0 \leq x < \infty$). As in Ref. [4] we assume that the phase 0, 1,

 

and 2 may be described by a single nonconserved order parameter $q$. The order parameter is taken to be dimensionless and may be chosen to be a suitable scaled function of the bulk densities of the three different phases. For example, phase 0 may represent a disordered phase (e.g., a liquid) and phase 2 the stable low-temperature solid phase, whereas the metastable phase 1 may be a solid phase with different crystal structure, a quasicrystal, or a glass. For zero external field the bulk-free-energy density $F^{(0)}(q)$ has three local minima at $q_0^{(0)}$, $q_1^{(0)}$, and $q_2^{(0)}$. We choose $q_0^{(0)}<q_1^{(0)}<q_2^{(0)}$.

The Ginzburg-Landau dynamics model is defined in terms of the free-energy functional,

$$\mathcal{F}[q(x,t)]=\int_0^\infty dx\left[\frac{\epsilon\lambda}{2}\left(\frac{\partial q(x,t)}{\partial x}\right)^2+F[q(x,t),x]\right], \tag{1}$$

where $\lambda$ is a microscopic bulk correlation length which determines the length scale and $\epsilon$ sets the energy scale. The bulk free-energy density can be split into $F^{(0)}(q)$ and a field-dependent part as follows:

$$F(q,x)\equiv\epsilon f(q,x)=F^{(0)}(q)+\epsilon\alpha qx\ . \tag{2}$$

Here we consider a linear coupling of $q$ to the external field. The quantity $\alpha$ plays the role of a coupling constant. As a simple example, if the order parameter is proportional to the particle density, this linear coupling describes a homogeneous gravitational field. We assume the function $F^{(0)}(q)\equiv\epsilon f^{(0)}(q)$ to diverge as $q\to 0+$, which guarantees that phase 0 is stable for large $x$ and that the order-parameter profiles are bounded and positive. Since in all physical applications the order parameter stays finite, we are forced to introduce such a divergence into the functional. In our calculations we choose $f^{(0)}(q)$ to be a negative superposition of Gaussian peaks centered around the three local minima. For $q<q_0^{(0)}$ we add the term of the form $A+Bq+C/q$ that diverges as $\sim 1/q$ as $q\to 0+$. The parameters $A$, $B$, and $C$ are chosen such that the derivative $df^{(0)}(q)/dq$ is continuous at $q=q_0^{(0)}$. Two choices of $f^{(0)}(q)$ are given in Figs. 1(a) and 4(a), where the shape of $f(q,x)$ is shown for different $x$.

The dynamics of the nonconserved order-parameter profile $q(x,t)$ is defined by the relaxational equation

$$\frac{\partial q(x,t)}{\partial t}=-\Gamma\frac{\delta\mathcal{F}[q(x,t)]}{\delta q}\ . \tag{3}$$

The natural time scale for interfacial dynamics is given by $\tau_0=1/\Gamma\epsilon$. Henceforth we take $\tau_0$, $\epsilon$, and $\lambda$ as units for time, energy, and length. The solution of Eq. (3) is subject to the boundary conditions

$$q(x=0,t)=q_2^{(0)} \tag{4}$$

and

$$\lim_{x\to\infty} q(x,t)=0 \tag{5}$$

for all $t>0$. The latter boundary condition stems from the fact that the position of the left peak in $f(q,x)$ converges to zero as $x\to\infty$. The relaxation of the order-parameter profile was then studied using an arbitrary initial profile $q(x,t=0)$ as an input which obeys the boundary conditions (4) and (5).

Without an external field one may look for steady-state solutions where the 02 interface moves with constant velocity $v_{02}$. As has often been recognized [6], the equations of motion of the order-parameter profile are analogous to the classical mechanical equation of motion of a fictitious particle moving in the "potential"—$F^{(0)}(q)$, with a "velocity"-dependent friction with friction constant proportional to the interface velocity. This yields an analytical solution is some cases [7]. For a nonzero field the analogy breaks down. The influence of an external field may be viewed as a "time"-dependent force, but there are no steady-state solutions due to the breaking of the translational symmetry by the external field. Consequently, the equation of motion can only be solved numerically.

## III. RESULTS

We have calculated $q(x,t)$ numerically for three different parameter combinations (runs $A-C$) using the discretized version of the partial differential equation for the order-parameter profile. The numerical method is similar to that in Ref. [5]. In particular, a half-tahn mapping is used for the semi-infinite interval here. For run $A$ the form of $f^{(0)}(q)$ we chose is shown in Fig. 1(a). We have considered a coupling parameter $\alpha=0.8$ for run $A$. The parameters of run $A$ are in the regime where the metastable phase forms dynamically in the field-free case. This means that the splitting instability occurs, and there is no steady-state solution for the 02 interface. Order-parameter profiles for different times $t$ are shown in Fig. 1(b). Starting from an initial (left) profile the phase 2 grows at the expense of phase 0. For small times the metastable phase 1 appears and grows to a maximal width $w_{\max}$. Then further growth is blocked by the external field, and the profile reaches its equilibrium form for $t\to\infty$ with only a microscopic layer of phase 1 in between phase 2 and 0. We can define an interface position $x_{ij}(t)$ between two phases $i$ and $j$ by solving

$$q(x_{ij}(t),t)=\tfrac{1}{2}(q_i^{(0)}+q_j^{(0)})\ . \tag{6}$$

The time-dependent width $w(t)$ of the metastable phase is then defined via

$$w(t)=x_{01}(t)-x_{12}(t)\ . \tag{7}$$

A plot of $w(t)$ for run $A$ is shown in Fig. 2 (solid line). As can clearly be seen, $w(t)$ shows a nonmonotonic behavior and reaches a large value $w_{\max}$ for intermediate times. Then it decreases to its microscopic equilibrium value. In a second run $B$ we have chosen a stronger coupling $\alpha=2$ but did not change the other parameters. The width of the metastable phase for run $B$ is also shown in Fig. 2 (dashed line) exhibiting a smaller $w_{\max}$. The qualitative behavior of the interfacial growth was the same. With decreasing $\alpha$, $w_{\max}$ increases which implies that for small external fields $w_{\max}$ is macroscopic.

The nonmonotonic behavior of $w(t)$ stems from the different interfacial velocities $v_{01}(t) \equiv dx_{01}(t)/dt$ and $v_{12}(t) \equiv dx_{12}(t)/dt$. These velocities are shown in Fig. 3 for run $A$ on a normal [Fig. 3(a)] and a logarithmic scale [Fig. 3(b)]. For small times, $v_{01} > v_{12}$, whereas $v_{01} < v_{12}$ for intermediate times. If one looks at details of the interfacial velocity relaxation, there are *three* different time regimes in the decay of the interfacial velocities. *First*, there is relaxation from the initial profile towards a quasiequilibrated profile on a microscopic time scale. For run $A$ and the chosen initial profile this time regime is in the interval $0 \leq t \lesssim 0.1$. It is nonuniversal since it de-

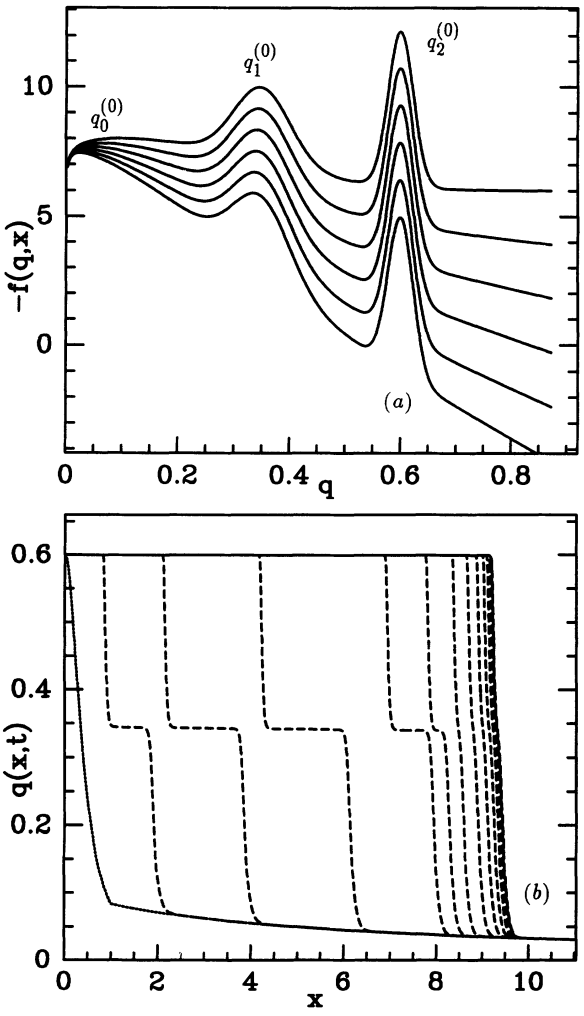


FIG. 1. (a) Form of $-f(q,x)$ versus $q$ for different $x$ for runs $A$ and $B$. $\alpha x$ is taken to be $\alpha x = 2.4n$, $n = 0,1,2,3,4,5$. The uppermost curve is $-f^{(0)}(q)$ where the positions of the three peaks, $q_0^{(0)}$, $q_1^{(0)}$, $q_2^{(0)}$, are also indicated. $-f(q,x)$ can be shifted by an arbitrary additive constant without changing the equations of motion. As $x$ increases, the left phase 0 becomes stable and the right phase 2 loses its stability. The middle phase 1 always remains metastable. (b) Order-parameter profiles $q(x,t)$ versus $x$ starting from an arbitrary initial profile $q(x,o)$ (left curve) in an external field for run $A$. The times for which $q(x,t)$ is shown are from left to right $t = 0.2n$ with $n = 1,2,3,7,15,19,23,\ldots$. The time is in units of $\tau_0$.

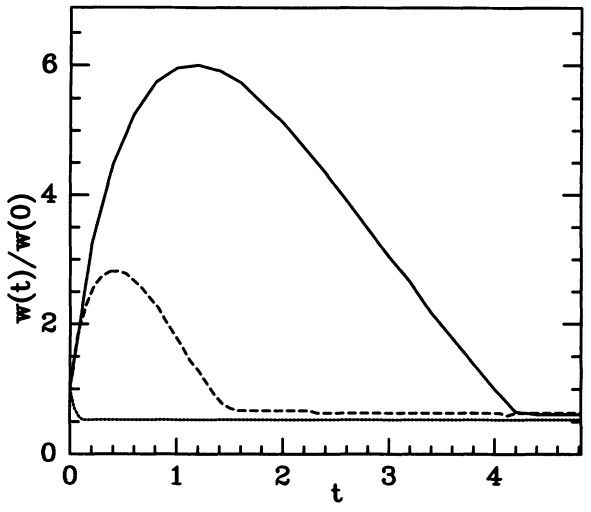


FIG. 2. Width of the layer of metastable phase, $w(t)$, versus time $t$ for runs $A$ (solid line), $B$ (dashed line), and $C$ (dotted line). The width is measured in terms of the width $w(0)$ of the arbitrarily chosen initial profile.

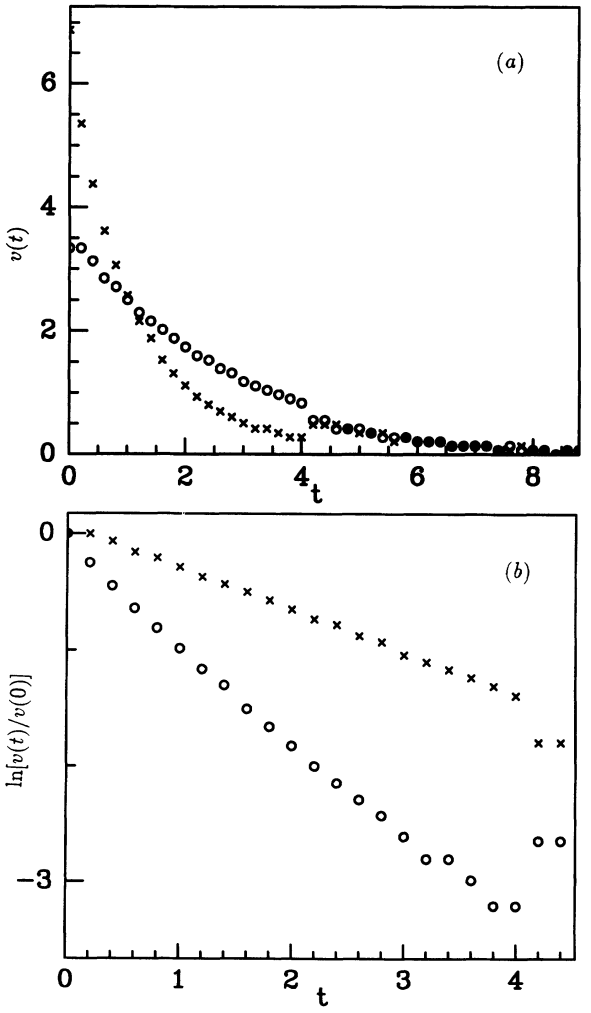


FIG. 3. (a) The different interfacial velocities $v_{01}$ (crosses) and $v_{12}$ (open circles) for run $A$ as a function of time. At $t \approx 4.2$ an abrupt change due to "interface fusion" is visible. (b) Interfacial velocities $v_{01}$ (open circles) and $v_{12}$ (crosses) from run $A$ on a logarithmic scale in the exponential regime. The velocities are scaled by their initial value $v(0)$ at $t = 0$.

pends on the explicit form of the initial profile. During this time the interface starts to split until practically two independent interfaces are formed.

Then in a *second* intermediate time regime the relaxation of both interfacial velocities falls on a straight line in the logarithmic plot of Fig. 3(b). This shows that it obeys an exponential law,

$$v_{ij}(t) \simeq \exp(-t/\tau_{ij}) , \quad ij=01,12 , \tag{8}$$

with a decay time $\tau_{ij}$.

This exponential law can also be proved by a simple *general argument*: Consider only one interface moving in an external field. The interface position is denoted by $\bar{x}$. For $t \to \infty$ the interface will approach its equilibrium position at $\bar{x}=\bar{x}_0$. The two maxima of the function $f(q,\bar{x}_0)$ are then of equal height. For $\bar{x} \neq \bar{x}_0$ the difference $\Delta$ in the height of the two peaks is a linear function of $\bar{x}-\bar{x}_0$ if $\bar{x}-\bar{x}_0$ is small. Now consider an interface without external field with $f(q,\bar{x})$ being the corresponding free energy. In this situation, steady-state motion with a steady-state velocity $v_s(\bar{x})$ is possible. For small $\Delta$, it is known [8] that $v_s$ is proportional to $\Delta$ which yields $v_s(\bar{x})=-c(\bar{x}-\bar{x}_0)$, where $c>0$ is a constant. We now assume that the external field is weak such that we can identify the steady-state velocity $v_s$ with the actual interface velocity $v=d\bar{x}/dt$. By solving the resulting differential equation $d\bar{x}/dt=-c(\bar{x}-\bar{x}_0)$ it turns out that the velocity changes exponentially in time $t$ with a decay constant $\tau=1/c$.

In our case we have two decoupled interfaces for intermediate times which both decay exponentially with different decay times $\tau_{01}$ resp. $\tau_{12}$ [see the different slopes in Fig. 3(b)]. Consequently the width of the metastable layer is a superposition of two exponentials for intermediate times.

Finally there is *third* time regime for $t \gtrsim 4.2$, where the velocities show a very abrupt change [see Fig. 3(a)]. Physically this interesting phenomenon occurs when the former decoupled 01 and 12 interfaces no longer exhibit independent motion but "fuse" into a single interface of microscopic thickness. The same abrupt change was detected in run *B* where the gravity was stronger showing that the phenomenon is quite general.

For the third parameter combination (run *C*), the form of $f_{(q)}^{(0)}$ we chose is given in Fig. 4(a). The coupling strength $\alpha$ is taken to be 1. For zero field there is now a steady-state solution for the interface, and no splitting instability occurs. In this case the interface initially moves with a weakly time-dependent velocity $v_{02}(t)$, which is close to the associated steady-state velocity. The velocity $v_{02}(t)$ then decreases, and the interfacial profile relaxes to its equilibrium value in the external field. The corresponding profiles $q(x,t)$ are shown in Fig. 4(b). For the sake of completeness we have also included the data for $w(t)$ of run *C* in Fig. 2 (dotted line). In this run $w(t)$ decreases monotonically towards its microscopic equilibrium value. This is due to the fact the width of the initial profiles was chosen to be relatively high. Following our general argument, the velocity of the 02 interface decays exponentially with time for large times.

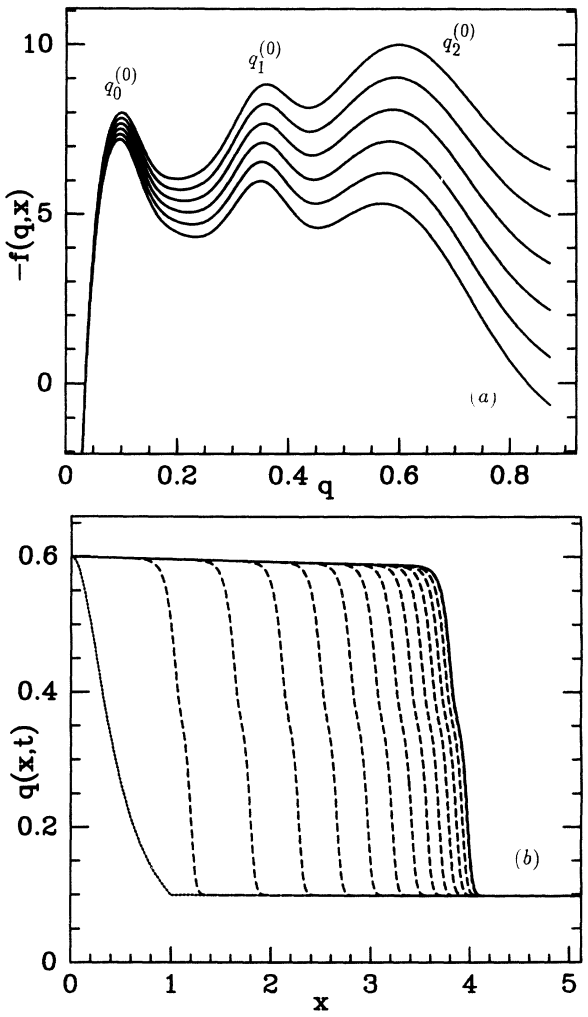


FIG. 4. Same as Fig. 1, but now for run *C*. (a) Form of $-f(q,x)$ versus $q$ for different $x$. $\alpha x$ is taken to be $\alpha x=2.4n$, $n=0,1,2,3,4,5$. The uppermost curve is $-f^{(0)}(q)$. As in Fig. 1(a), the middle phase 1 always remains metastable. (b) Order-parameter profiles $q(x,t)$ versus $x$ starting from an arbitrary initial profile $q(x,0)$ (left curve) in an external field. The scaled times for which $q(x,t)$ is shown are from left to right $t=0.04n$, where $n=0,7,15,23,27,\ldots$.

## IV. CONCLUSIONS

Since our Ginzburg-Landau model is constructed in a general way, the phenomenon of blocking of metastable phase formation may occur in quite a large number of different real physical systems. We thus conclude with some remarks on realizations of the nonmonotonic behavior of $w(t)$ in real physical situations and on possible experimental verifications.

One closely related phenomenon is surface melting, where the phases 0, 1, and 2 are the gas, liquid, and solid phase, respectively [9]. A minor difference here is that the intermediate phase 1 can also be a stable bulk phase. In surface melting in a gravitational field the equilibrium profile does not exhibit complete wetting of the solid but a liquid layer with finite thickness [10,11]. The dynamics of surface melting can also be described in a Ginzburg-Landau model as in this paper [12]. To see the effect of

the gravitational field, one can perform time-resolved scattering experiments on the solid-gas interface.

Another possible realization is in the growth of metastable phases of liquid crystals [13–15] in a centrifuge. There are different setups and the growth rates are slow enough to make an experimental resolution of the time scales.

At a growing solid-liquid interface an interfacial layer that may be related to a manifestation of a metastable phase was observed for ice [16], salol [17], and cyclohexane [18], by Bilgram and coworkers. If one performs these experiments in a gravitational field, a change in the layer thickness as a function of time should be detectable.

It may be difficult to resolve the time scale of the growing and shrinking of the metastable phase experimentally. Colloidal suspensions in a gravitational field may be more accessible experimentally since their dynamics are much slower. Colloids show different stable and metastable phases [19] and their sedimentation dynamics can be followed by depolarized light scattering [20]. The equilibrium density profiles of a colloidal suspension in a gravitational field have been extensively studied theoretically [21,22], also at two-phase coexistence, and it would be interesting to consider the dynamics of three phases near coexistence as well. The sedimentation dynamics of a colloidal suspension may exhibit unusual mesoscopic wetting layers of a metastable phase at intermediate time scales.

If the external field is a wall, different metastable crystalline phases which first grow and then disappear have been detected in the context of charge-stabilized colloidal suspensions [23]. It has yet to be checked whether this phenomenon is related to that proposed in the paper.

As a final comment, whereas there are a number of possible experimental realizations, it is very difficult to do a microscopic nonequilibrium computer simulation on the dynamics of interfacial motion. This is mainly due to the small system size accessible in a computer simulations.

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