Spinodal decomposition in an order-disorder transition: Effect of interfacial properties

Andres M. Somoza[1] and Celeste Sagui[2]

[1]*Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, Universidad Autónoma (C-XII),
Madrid E-28049, Spain*

[2]*Department of Physics, McGill University, Montréal, Québec, Canada H3A 2T8*

(Received 11 May 1995)

A model C system is defined by the presence of a nonconserved order parameter coupled to a conserved concentration. When such a system is quenched from the disordered state into the order-disorder coexistence region of its phase diagram, two different types of interfaces, an order-order and an order-disorder interface, form. We discuss how changes in the associated wetting properties of the interfaces modify the morphology of the growing domains. The ratio between the surface tensions is therefore an important parameter in determining the universality classes at late times.

PACS number(s): 68.10.−m, 64.60.Cn

I. INTRODUCTION

When a system is quenched from the disordered, high-temperature, single-phase region of its phase diagram to a point inside of the coexistence curve, it orders kinetically. A long-wavelength instability amplifies the fluctuations present in the initial conditions, leading to the formation of domains which grow with time. At late times, this growth is often characterized by a single, time-dependent length scale, the average domain size $R(t)$ [1–4]. The growth of the average domain size often follows a power law $R(t) \sim t^n$, with growth exponent n. At late times $R(t)$ becomes much larger than all the microscopic lengths and the system exhibits scaling behavior. For example, the nonequilibrium correlation function takes the simple scaling form $C(r,t) = G(x)$, with $x = r/R(t)$. Quantities like the scaling function $G(x)$ and the growth exponent n are used to classify different dynamical systems into a small set of universality classes. It is accepted that a given universality class is also determined by the symmetry of the order parameter, the space dimensionality, and the relevant hydrodynamic modes and conservation laws present in the system. At late times, the motion of the relevant defects of the system dominates the kinetics.

When considering topological defects, one wants to identify the key properties relevant to the dynamical aspects of the problem. For a system with a scalar order parameter, it is the interface or domain walls separating the ordered phases that is the characteristic topological defect. Thus, we want to determine which interfacial properties could be relevant to the characterization of the dynamical behavior of a system. In this paper, we show that in systems with more than one type of interface, the ratio of surface tensions plays an important role in determining the system morphology. We consider a model system with a disordered and two degenerate ordered stable states. A quench takes the system from the high-temperature disordered state into the order-disorder coexistence region. Three types of domains are formed, belonging to the two ordered and the disordered phases. Thus two types of interfaces (order-order and order-disorder) exist and wetting phenomena can play a role. In particular, an order-order interface at equilibrium can display a wetting transition, as the disordered-phase layer at the interface

thickens to a macroscopic dimension. Our numerical simulations show that small changes in the free energy involving only the interfacial properties dramatically change the domain morphology. These results suggest that, in some cases, interfacial properties must be considered explicitly when studying a dynamical universality class. These properties have largely been ignored in previous studies of this system [5–7].

After a temperature quench into the coexistence region, a model C system is characterized by a stable disordered and two degenerate ordered phases. This is in contrast with a system described by model A or model B, where the disordered minimum of the energy before the quench becomes completely unstable after the quench. Thus, the system is driven to the equilibrium ordered states with less symmetry in model A, or to phase separation in model B. In a model C system, the disordered state is still stable after the quench, therefore the order parameter alone cannot take the system out of that state, unless there are very large fluctuations. However, the coupling of the order parameter to a concentration makes the single phase unstable in the associated spinodal region, and transitions to the ordered states become allowed. Here we consider the simplest case of a model C system: a *scalar* order parameter and no hydrodynamic modes (other than the coupled conserved quantity). Possible physical realizations of this system might include metal alloys below the tricritical point [8,9].

The paper is structured as follows. In Sec. II we introduce the model and the details of the simulation. In Sec. III we discuss the results and we reserve Sec. IV for the conclusions.

II. MODEL

We begin with the Ginzburg-Landau free energy:

$$F[\phi,\psi] = \int d\mathbf{r}\left[\frac{1}{2}l_\psi^2(\boldsymbol{\nabla}\psi(\mathbf{r}))^2 + \frac{1}{2}l_\phi^2(\boldsymbol{\nabla}\phi(\mathbf{r}))^2 + f(\phi,\psi)\right],$$

(1)

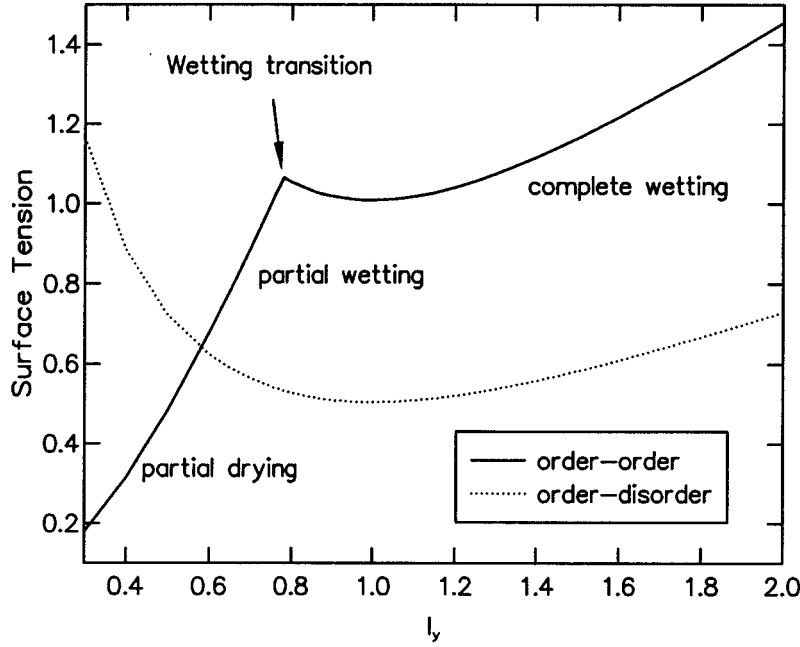where $f(\phi,\psi)$ is the bulk free energy density,

FIG. 1. Surface tension of interfaces in a model C system as a function of the parameter l_y. A surface layer of the disordered phase may exist at the interface between two ordered phases. Three different regimes are possible: (i) partial drying: $\gamma_{oo} < \gamma_{od}$; (ii) partial wetting: $\gamma_{od} < \gamma_{oo} < 2\gamma_{od}$; and (iii) complete wetting: $2\gamma_{od} \lesssim \gamma_{oo}$.

$$f(\phi,\psi) = \frac{1}{2}r\psi^2 + u\psi^4 + v\psi^6 + \frac{1}{2}\chi_n^{-1}\phi^2 + \gamma\phi\psi^2 - \Delta\phi. \tag{2}$$

Here ψ is the nonconserved order parameter, ϕ is the coupled conserved concentration, $r, u, v, \chi_n, \gamma, l_\psi$, and l_ϕ are system parameters ($v, \chi_n, l_\psi, l_\phi > 0$), and Δ is the chemical potential related to the concentration. A mean-field analysis reveals that the system has a line of first-order phase transitions at

$$\tilde{r} \equiv r + 2\Delta\gamma\chi_n = 0, \tag{3}$$

$$\tilde{u} \equiv u - \frac{1}{2}\gamma^2\chi_n > 0. \tag{4}$$

This line ends in a tricritical point at $\tilde{r}=0$, $\tilde{u}=0$. There is also a line of second-order phase transitions at $\tilde{r} = \tilde{r}_0 \equiv \tilde{u}^2/2v$ and $\tilde{u}<0$. We are interested in studying a quench from the disordered phase ($\tilde{r}>0$, $\tilde{u}>0$) into the coexisting region, where the units of energy, concentration, and order parameter can be rescaled to give a dimensionless free energy density [9]:

$$f(c,y) = y^2(1-y^2)^2 + \alpha(c+y^2-1)^2 + \frac{l_c^2}{2}(\nabla c)^2 + \frac{l_y^2}{2}(\nabla y)^2. \tag{5}$$

Here y and c are the rescaled order parameter and concentration, respectively. There are three positive arbitrary constants: α, l_c, and l_y. We fix $\alpha=4$ and select the unit of length such that $l_c l_y = 1$, but we allow for variations in l_y. The local free energy has three coexisting minima in the (c,y) plane located at $(1,0)$ (disordered phase) and $(0,\pm 1)$ (ordered phase). Thus there are three interfaces: two equivalent interfaces between the ordered and disordered phases and one interface between ordered domains of opposite sign. The relationship between the corresponding surface tensions,

γ_{od} and γ_{oo}, depends on l_y. The surface phase diagram for the discrete version of the model as described below is shown in Fig. 1. Three different regimes are observed: (i) *partial drying*: ordered domains of opposite sign prefer to be in contact, $\gamma_{oo} < \gamma_{od}$; (ii) *partial wetting*: an ordered domain prefers to be in contact with a disordered one, $\gamma_{od} < \gamma_{oo} < 2\gamma_{od}$; and (iii) *complete wetting*: there is always a disordered wetting layer between ordered domains ($2\gamma_{od} \lesssim \gamma_{oo}$). We study the growth and ordering processes for systems in these three regimes.

The dynamics of the phase separation process is described by the coupled Langevin equations:

$$\frac{\partial c}{\partial t} = \Gamma_c \nabla^2 \left[\frac{\partial f(c,y)}{\partial c} - l_c^2 \nabla^2 c \right] + \xi_c, \tag{6}$$

$$\frac{\partial y}{\partial t} = -\Gamma_y \left[\frac{\partial f(c,y)}{\partial y} - l_y^2 \nabla^2 y \right] + \xi_y, \tag{7}$$

where ξ_c and ξ_y are stochastic variables obeying the fluctuation-dissipation relation. In this study, we neglect the thermal noise and set the mobilities $\Gamma_c = \Gamma_y = 1$.

The Langevin equations were solved numerically using Euler's method on a two-dimensional grid of linear size $L=256$ with a finite difference scheme. Periodic boundary conditions were used throughout. The spatial mesh size was taken to be $\Delta x = 1.0$ and the time mesh size was chosen as $\Delta t = 0.01$. Further reduction of the mesh sizes gave essentially the same results. Our initial distribution of y's was specified by a random uniform distribution in the range $(-0.1, 0.1)$, while the initial distribution of c's, for a particular mean concentration c_0, was specified by a similar random distribution in the range $(c_0 - 0.1, c_0 + 0.1)$. We probed different system sizes and found that a size $L=256$ provides good enough self-averaging in the correlation functions for our purposes. For this system size, to obtain reasonable statistics, 15 independent runs were performed for each of the

cases specified below. For systems in the wetting regime, the equations were iterated to $t=1500$ for $c_0=1/3$ and $t=2000$ for $c_0=2/3$. For systems in the partial wetting and partial drying regimes, the mean concentration was kept at $c_0=1/3$ and the equations were iterated to $t=3000$ and $t=5000$, respectively. For each case we computed the non-equilibrium pair correlation function for both the conserved variable c and the nonconserved order parameter y, defined as $C_c(\mathbf{r},t)=\langle[c(0,t)-c_0][c(\mathbf{r},t)-c_0]\rangle$ and $C_y(\mathbf{r},t)=\langle y(0,t)y(\mathbf{r},t)\rangle$, where the brackets indicate an ensemble average. We also computed their circular average and the typical length scales $R_c(t)$, associated with domains of c, and $R_y(t)$, associated with domains of the variable y. $R_c(t)$ is defined as the smallest value of r for which $C_c(r,t)=0$ at time t; $R_y(t)$ is defined as the value of r at time t for which $C_y(r,t)$ takes one-half of its value at the origin in the scaling regime.

III. RESULTS AND DISCUSSION

A. Morphology

In model B systems, it is assumed that the morphology of the growing domains depends only on the mean concentration. Specifically, interconnected domains are observed for critical quenches and isolated droplets are observed for off-critical ones. For a model C system, on the other hand, it is necessary to know whether the minority phase is ordered or disordered, as well as the wetting properties of the interfaces. For $c_0>1/2$, the minority phase is the ordered one and forms isolated droplets. Inside each droplet complete order is obtained, the order parameter takes either a positive or a negative value, and the order-order interfaces rapidly disappear from the system. An isolated domain is not affected by the value of the order parameter of other domains. In this case the degeneracy of the ordered state does not play a qualitatively important role in the growth process. For the same reason, changes in the wetting regime are not dramatic. A completely different situation arises when the minority phase is the disordered one ($c_0<1/2$). In this case an ordered domain can grow to an infinite size, percolating through the system. Now, long-range order is never reached in a finite time and, thus, order-order interfaces can remain in the system even at late times. The presence of these interfaces in the system depends on the interfacial wetting properties.

Next, we study the effect of varying both c_0 and l_y on the domain morphology. The complete wetting regime occurs for $l_y>0.79$: two ordered domains with a different sign in the order parameter are separated by a macroscopic disordered wetting layer. The disordered domains tend to surround the ordered domains and percolate through the system, see Fig. 2. This figure shows two different off-critical quenches, for $c_0=1/3$ and $c_0=2/3$, both with $l_y=1$. Figure 2(a) ($c_0=1/3$) shows that, in the complete wetting regime, the disordered-phase morphology corresponds to elongated stripes (with a few shrinking droplets) instead of the isolated droplets that would correspond to a standard model B with an equivalent concentration. However, a morphology similar to that of model B is recovered when the minority phase is the ordered one, as shown in Fig. 2(b).

The partial drying regime occurs for $l_y<0.60$: an ordered domain prefers to be in contact with another ordered domain
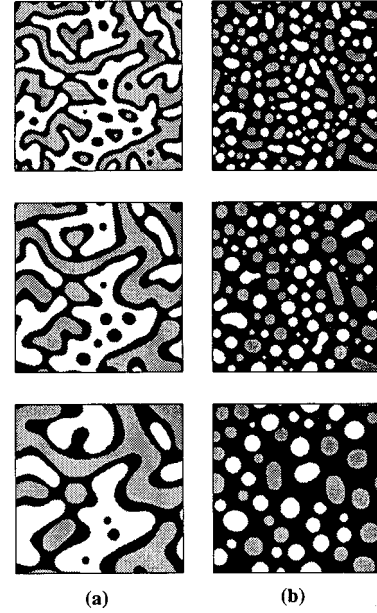

(a)   **(b)**

FIG. 2. Typical configurations for a model C system quenched into the order-disorder coexistence region in the complete wetting regime. Three different times are shown for the following mean concentrations: (a) $c_0=1/3$ (normalized concentration $\chi=-1/3$), (b) $c_0=2/3$ ($\chi=+1/3$). The black regions correspond to the disordered phase, the white and gray regions correspond to ordered domains with positive and negative order parameter, respectively.

instead of a disordered one. The disordered domains no longer surround the ordered domains and, instead, adopt compact shapes, as shown in Fig. 3(a). Nevertheless, the disordered domains tend to be located at the order-order interface instead of being fully surrounded by one single ordered domain. The intermediate case, for $0.6<l_y<0.79$, corresponds to the partial wetting regime, and is illustrated in Fig. 3(b).

B. Correlation functions

Clearly, as shown in Figs. 2 and 3, changes in interfacial properties lead to changes in morphology. The question then arises: how are these changes reflected in the correlation function and how do they affect the universality classes? To answer these questions we have examined the characteristic growth exponent n and the correlation function $C_c(\mathbf{r},t)$.

In the model C system considered, y is a nonconserved quantity that evolves faster than the conserved concentration. Thus for late times, growth is driven by diffusion of the conserved variable and the order parameter becomes slaved to the concentration. In fact, we observe numerically that at late times both $R_y(t)$ and $R_c(t)$ are consistent with a growth law t^n with $n=1/3$ for all cases.

Regarding the correlation functions, we center our attention on $C_c(\mathbf{r},t)$, for which the statistics are better due to reduced finite-size effects. Also, this quantity allows a direct comparison with the correlation function of a model B system. For all the runs, the data are consistent with the scaling hypothesis: $C_c(\mathbf{r},t)=G_c(r/R(t))$. Superposition of the data at different times is certainly excellent for the two cases in the complete wetting regime with $l_y=1.0$ (shown in Fig. 2),
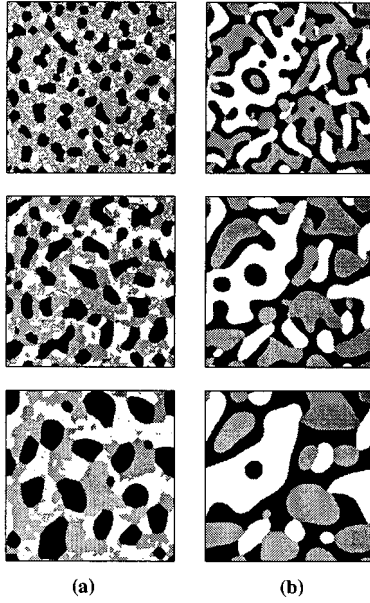
FIG. 3. Typical configurations for two model C systems quenched into the order-disorder coexistence region with mean concentration $c_0 = 1/3$. The systems are in (a) the partial drying regime ($l_y = 0.5$), (b) the partial wetting regime ($l_y = 0.7$). The black regions correspond to the disordered phase, the white and gray regions correspond to ordered domains with positive and negative order parameter, respectively.
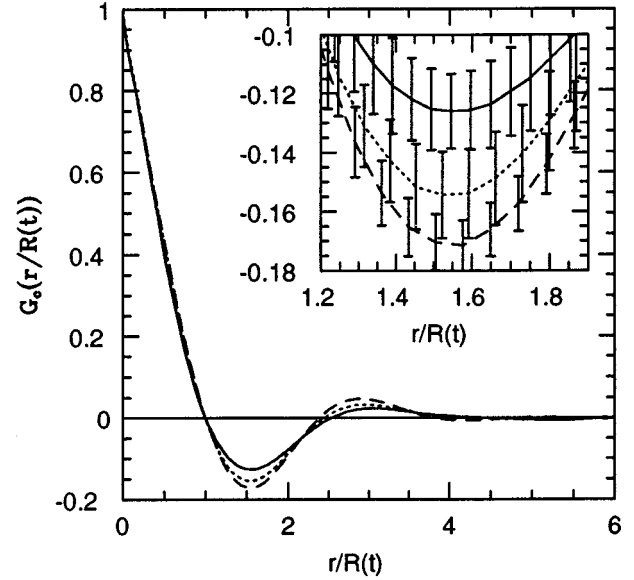

FIG. 4. Concentration-concentration correlation functions near the scaling regime. The solid line corresponds to a model C system with normalized concentration $\chi = -1/3$ [$c_0 = 1/3$, Fig. 2(a)], the dotted line corresponds to the same system with $\chi = +1/3$ [$c_0 = 2/3$, Fig. 2(b)], and the dashed line corresponds to a model B system with $\chi = \pm 1/3$. The inset shows the first minimum and the error bars, which are the typical deviations of the data after an average over 15 runs.

but it worsens slightly as l_y is reduced through the partial wetting and partial drying regimes (Fig. 3). The possibility that scaling breaks down in these last two cases cannot be ultimately discarded.

At late times the nonconserved order parameter y becomes slaved to the concentration. It is natural to suppose that it can be eliminated through an adiabatic approximation ($\partial y/\partial t \approx 0$) in the scaling regime. Also, previous simulations of a model C system showed scaling functions consistent with the model B universality class [7]. Here we try to quantify the effects of the morphology on the correlation functions and we show that model B and model C actually present different scaling functions.

In the presence of a conserved concentration, the correlation function depends on the mean concentration c_0. If the concentrations of the two phases are c_a and c_b, we can define a normalized concentration:

$$\chi = \frac{2c_0 - (c_a + c_b)}{c_b - c_a}, \tag{8}$$

so that the scaled correlation function is a function of both χ and $x = r/R(t)$; i.e., $G(\chi, x)$. Two systems in the same universality class with the same value of χ should display the same scaling function for any value of x. The function $G(\chi, x)$ is universal, and its dependence on χ, as well as on x, is shared by the whole universality class. In order to demonstrate that two systems correspond to different universality classes, it is enough to show that their scaling functions have a different dependence in χ. For model B and any local free energy with two minima, the scaling function does not depend on the sign of χ. However, we do not expect this in-

variance of $G(\chi, r/R(t))$ with the sign of χ to hold in model C due to the differences in morphology, as depicted in Fig. 2 for the wetting regime and normalized concentrations $\chi = -1/3$ ($c_0 = 1/3$) and $\chi = +1/3$ ($c_0 = 2/3$).

Although correlation functions are very insensitive to morphology [10,11], the differences between the scaling functions of the two quenches and of a model B system can be quantified. Figure 4 shows the corresponding concentration-concentration correlation functions. These functions have been rescaled by the theoretical value in the scaling limit: $G_c(0) = c_0(1 - c_0)$. The simulations have not reached this value because the width of the interfaces ϵ, although small, is still not completely negligible compared to the typical length $R(t)$. By construction, all scaling functions agree at $r = 0$ and $r/R(t) = 1$, and for r much larger that $R(t)$, they rapidly tend to zero. Thus, the major differences are expected near the first minimum. This region is amplified in the inset, where the error bars correspond to ± 1 typical deviation. The real statistical error is the typical deviation divided by $\sqrt{(nr-1)}$, where nr is the number of runs (15 in our case). At least for $c_0 = 1/3$ ($\chi = -1/3$), the model C scaling function displays differences from the model B scaling function (obtained for $\chi = \pm 1/3$). Naturally, for $c_0 = 2/3$ ($\chi = +1/3$) the differences with model B are smaller, but even in this case the effective repulsion between opposite-signed ordered domains affects the correlation function: this repulsion forbids coalescence between opposite domains, which are slightly less circular than in model B, and thus it reduces the depth of the minimum in the correlation function. Only in the limit $c_0 \rightarrow 1$ are the correlation functions of model B and model C expected to overlap rigorously. To

further assess the existence of these differences in the correlation functions, the data have been improved by *hardening* the profile $c(\mathbf{r},t)$, i.e., by taking the integer part of $c(\mathbf{r},t)$ (0 or 1) before calculating the correlation functions. As pointed out by Shinozaki and Oono [12], the correlation function based on the hardened data becomes time independent and the resultant universal function is the asymptotic form. The *hardened* correlation functions overlap with those of Fig. 4 for $r > R(t)/2$, indicating that near the first minimum, the correlation functions are not affected by the finite ratio $\epsilon/R(t)$. In other words, the asymptotic correlation functions for model B and model C are different.

Since the morphology of the disordered domains in the partial drying regime is completely different from that in the complete wetting regime, the corresponding scaling functions must be different, indicating a change in the universality class. Thus l_y (or the ratio between surface tensions) is not an irrelevant parameter in the renormalization group sense. The parameter l_y is either relevant or marginal. If there are two different universality classes (one for the complete wetting regime and the other for the partial drying regime) and the system always flows to one of these, then l_y is relevant. If, on the other hand, the system does not flow to any of these points, l_y is marginal. In the wetting regime the system has reached its asymptotic behavior. In the drying regime, although self-similarity is very clear in the figures and scaling is good, this flow can unfortunately be a very slow process. Thus, it is very difficult to unequivocally differentiate between a marginal and a relevant parameter through a simulation [13].

IV. CONCLUSIONS

We have studied the effect of wetting between bulk phases during phase separation. The functional dependence of the scaled correlation function $G(\chi,x)$ on the normalized concentration χ for any value of $x = r/R(t)$ should be shared by all the members of the same universality class. We have shown that the concentration correlation function in a model C system has a different χ dependence than that in a model B system. Moreover, for a model C system, the correlation function for a fixed value of χ changes according to the value of the ratio between surface tensions, and thus is not uniquely determined by χ and x. Thus, for a model C system the ratio between surface tensions is not an irrelevant parameter, but rather plays an important role in determining the domain morphology and the scaling function. This behavior should be common to systems with three or more asymmetric coexisting minima. Experimentally, this could be tested in, for instance, phase-separating three component systems.

ACKNOWLEDGMENTS

[1] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8.

[2] H. Furukawa, Adv. Phys. **34**, 703 (1985).

[3] K. Binder, Rep. Prog. Phys. **50**, 783 (1987).

[4] A. J. Bray, Adv. Phys. **43**, 357 (1994).

[5] P. S. Sahni and J. D. Gunton, Phys. Rev. Lett. **45**, 369 (1980).

[6] T. Ohta, K. Kawasaki, A. Sato, and Y. Enomoto, Phys. Lett. A **126**, 93 (1987); Y. Enomoto and T. Watanabe, *ibid.* **133**, 497 (1988); T. Ohta, Y. Enomoto, K. Kawasaki, and A. Sato, in *Dynamics of Ordering Processes in Condensed Matter* (Plenum, New York, 1988), p. 127.

[7] A. Chakrabarti, J. B. Collins, and J. D. Gunton, Phys. Rev. B **38**, 6894 (1988).

[8] S. M. Allen and J. C. Cahn, Acta Metall. **24**, 425 (1976).

[9] C. Sagui, A.M. Somoza, and R.C. Desai, Phys. Rev. E **50**, 4865 (1994).

[10] R. Toral, A. Chakrabarti, and J. D. Gunton, Phys. Rev. B **39**, 901 (1989).

[11] P. Fratzl, J.L. Lebowitz, O. Penrose, and J. Amar, Phys. Rev. B **44**, 4794 (1991).

[12] A. Shinozaki and Y. Oono, Phys. Rev. Lett. **66**, 173 (1991); Phys. Rev. E **48**, 2622 (1993).

[13] The partial wetting pictures seem to indicate that the system is not flowing to any of the other two cases (for example, the ratio between the lengths of the two kinds of interfaces remains approximately constant).