

Power Laws and Crossovers in Off-Critical Surface-Directed Spinodal Decomposition

Sanjay Puri^{1,2} and Kurt Binder¹

¹*Institut für Physik, Johannes-Gutenberg-Universität Mainz, Staudinger Weg 7, 55099 Mainz, Germany*

²*School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India*

(Received 18 September 2000)

We study the dynamics of phase separation in binary mixtures near a surface with a preferential attraction for one of the components of the mixture. We obtain detailed numerical results for a range of mixture compositions. In the case where the minority component is attracted to the surface, wetting layer growth is characterized by a crossover from a surface-potential-dependent growth law to a universal law. We formulate a simple phenomenological model to explain our numerical results.

DOI: 10.1103/PhysRevLett.86.1797

PACS numbers: 68.05.-n, 64.75.+g, 68.08.Bc

When a binary mixture (AB) is quenched from the one-phase region inside the miscibility gap, the unstable homogeneous state decays via nucleation or spinodal decomposition and the subsequent growth of A - and B -rich domains [1,2]. Much effort has focused on understanding the growth law for the domain size, $R(\tau) \propto \tau^\phi$, where τ is the time after the quench [2]. It is now well-established that $\phi = \frac{1}{3}$ for solid binary mixtures due to a droplet evaporation-condensation mechanism, irrespective of the composition of the mixture. This growth law is referred to as the Lifshitz-Slyozov or LS law [3]. In the case of fluid mixtures, on the other hand, droplet diffusion and coagulation [4] also yields $\phi = \frac{1}{3}$ in $d = 3$, and may be the dominant mechanism when the morphology is not bicontinuous. However, if the phase-separated structure has an interconnected morphology, hydrodynamic flows yield an exponent $\phi = 1$ [2,5].

For many materials, it is of great experimental interest to consider phase separation in a thin-film geometry or near surfaces (see reviews in [6–8]). Typically, one component (say, A) may be preferentially attracted to the surface. After segregation has started via surface-directed spinodal decomposition [9–11], competition sets in between the growth of a wetting layer at the surface and usual domain growth in the bulk. This problem has been the subject of intense experimental investigation, particularly in the context of polymer and fluid mixtures [9,10]. While various exponents x for the growth of the thickness $R_1(\tau)$ of the wetting layer [$R_1(\tau) \propto \tau^x$] were observed in simulations [11–16] and experiments [6–10], a comprehensive theoretical understanding of these observations was mostly lacking. For a quench onto the coexistence curve, where no phase separation occurs in the bulk, an attractive potential $V(z) \propto z^{-n}$ (z being the distance from the surface) results in a wetting-layer growth with $x = 1/[2(n+1)]$ [17], but this scenario does not apply in the present context.

In this Letter, we provide a fresh perspective on this problem through extensive numerical calculations using the Cahn-Hilliard-Cook (CHC) model with appropriate boundary conditions [7,8]. We will focus on the case where domain growth is driven by diffusive processes only [18]; and the system is quenched deep into the coexistence

region so that mean-field arguments are applicable. In particular, we present a phenomenological explanation of our results which constitutes a reasonable understanding of the exponents which characterize surface-directed spinodal decomposition for arbitrary surface fields and mixture composition.

The order parameter field $\phi(\vec{x}, \tau) \equiv \phi(\vec{\rho}, z, \tau)$, which measures the local composition, satisfies the standard CHC equation [7,8]:

$$\frac{\partial \phi}{\partial \tau} = -\nabla^2[\phi - \phi^3 + \frac{1}{2}\nabla^2\phi + V(z)] + \vec{\nabla} \cdot \vec{\xi}. \quad (1)$$

In Eq. (1), $\vec{\rho}$ is a coordinate parallel to the surface located at $z = 0$; $\vec{\xi}$ is a Gaussian random force; and all variables have been rescaled into dimensionless units. Thus, $\phi = +1(-1)$ corresponds to the A -rich (B -rich) phase. The Gaussian white noise $\xi(\vec{x}, \tau)$ satisfies the fluctuation-dissipation relation:

$$\langle \xi_i(\vec{x}, \tau) \xi_j(\vec{x}', \tau') \rangle = \epsilon \delta_{ij} \delta(\vec{x} - \vec{x}') \delta(\tau - \tau'), \quad (2)$$

where ϵ measures the strength of the noise ($\epsilon \propto T$ at low temperature T). To avoid problems due to a singularity of the potential $V(z)$ at the surface ($z = 0$), we choose $V(z) = H_1$ for $z \leq 1$ and $V(z) = H_1 z^{-n}$ for $z > 1$. Equation (1) needs to be supplemented by boundary conditions [7,8]:

$$\frac{\partial \phi(\vec{\rho}, z=0, \tau)}{\partial \tau} = V(0) + g\phi + \gamma \frac{\partial \phi}{\partial z} \Big|_{z=0}, \quad (3)$$

$$0 = \frac{\partial}{\partial z} [\phi - \phi^3 + \frac{1}{2}\nabla^2\phi + V(z) + \text{noise}] \Big|_{z=0}. \quad (4)$$

In Eq. (3), the parameters $V(0)$, g , γ essentially characterize the static surface phase diagram (we consider here only a choice where the surface is completely wetted by the A -rich phase in equilibrium); and Eq. (4) corresponds to zero current across the plane $z = 0$.

Figures 1 and 2 exhibit typical evolution pictures obtained from Eqs. (1)–(4) for the domains formed in $d = 2$ from a homogeneous initial condition with average order parameter ϕ_0 . We consider a surface potential with exponent $n = 4$, which corresponds to nonretarded van der

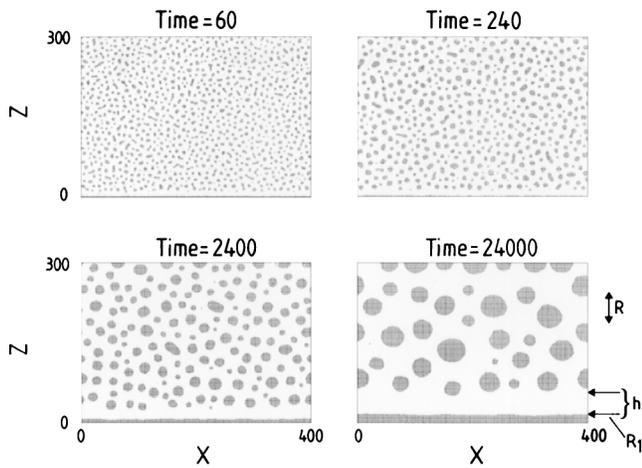


FIG. 1. Evolution pictures obtained from a simulation of the model in Eqs. (1)–(4). The initial condition consisted of small-amplitude order parameter fluctuations about an average value $\phi_0 = -0.4$. The simulations were done on two-dimensional lattices of size $N_x \times N_z$ ($N_x = 400, N_z = 300$), with discretization mesh sizes of $\Delta x = 1, \Delta \tau = 0.03$. Lattice sites with $\phi > 0$ (i.e., A-rich) are marked in black, and lattice sites with $\phi < 0$ are unmarked. The surface (located at $z = 0$) is completely wetted by the A-rich phase. In the picture at $\tau = 24\,000$, we have schematically indicated the various length scales, i.e., $R(\tau), R_1(\tau)$, and $h(\tau)$. The numerical values for wetting layer length scales at $\tau = 24\,000$ are $R_1 \approx 17.4, h \approx 39.5$.

Waals' interactions in $d = 2$. The other parameter values were $H_1 = 0.8, g = -0.4$, and $\gamma = 0.4$ corresponding to complete wetting in equilibrium [7,8]. The noise amplitude was taken to be $\epsilon = 0.0817$. The choice of parameters will be discussed in an extended publication [19]. If the phase attracted to the surface is the minority component (Fig. 1), we see that both a surface enrichment (or wetting) layer of thickness $R_1(\tau)$ and a depletion zone of thickness $h(\tau)$ are formed. It is reasonable to assume that the wetting and depletion layers have an average composition comparable to ϕ_0 , suggesting that $R_1(\tau)$ and $h(\tau)$

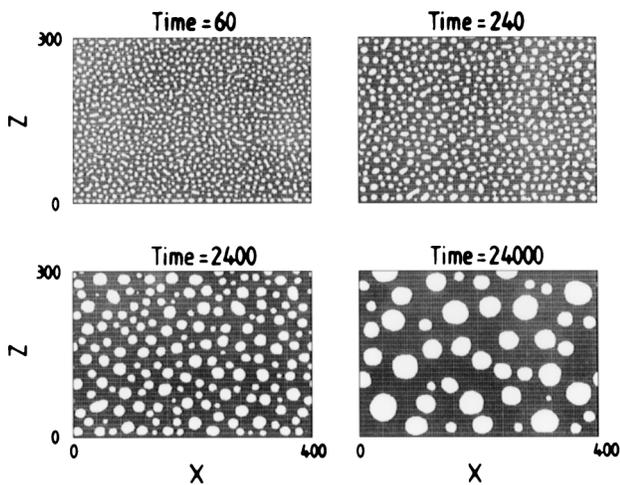


FIG. 2. Analogous to Fig. 1, but for $\phi_0 = +0.4$.

exhibit the same time dependence. (We have confirmed this numerically.) For the opposite case, where the majority component is attracted to the surface (Fig. 2), this layered structure of enrichment/depletion layers is obviously absent.

The asymmetry of the local structure near the surface leads to pronounced differences for the growth law of the wetting layer. For $\phi_0 > 0$, one finds an exponent compatible with $x = \frac{1}{6}$, independent of ϕ_0 [Fig. 3(a)]. For the case $\phi_0 < 0$, the situation is more complicated [Fig. 3(b)]. There is an initial slow growth regime where the exponent is compatible with $x = \frac{1}{6}$. However, this crosses over to a faster growth with an exponent compatible with $x = \frac{1}{3}$ [14,15]. The crossover time is later for higher surface

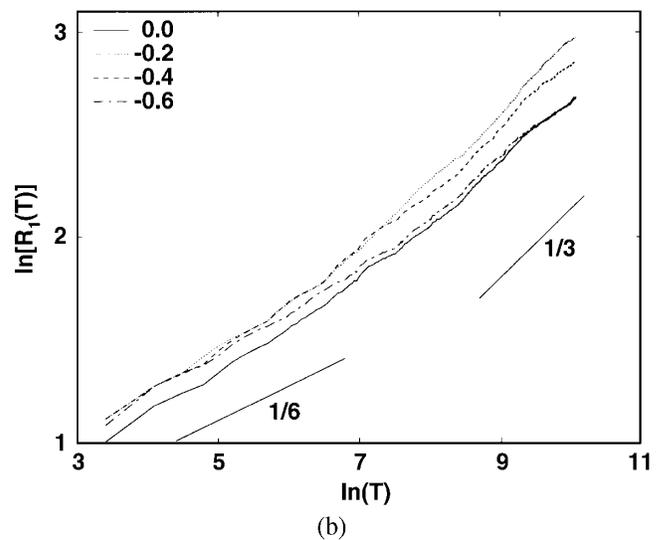
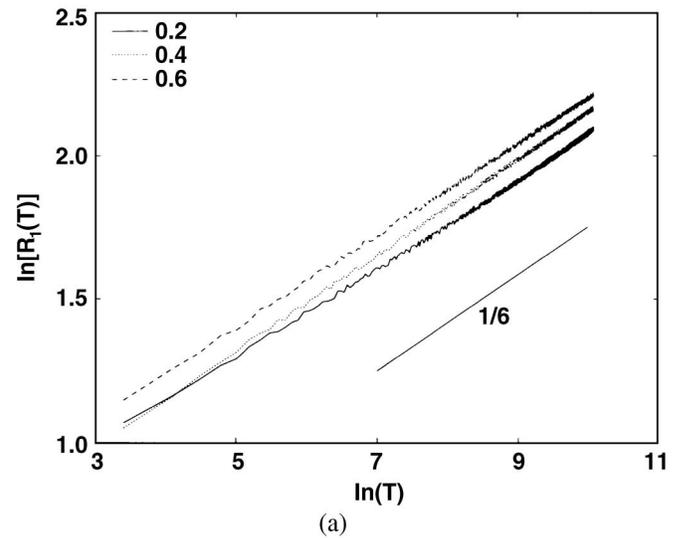


FIG. 3. Log-log plot of the first zero of laterally averaged order parameter profiles, $R_1(\tau)$ versus time τ . We present results for (a) three choices of $\phi_0 > 0$, as indicated, and (b) four choices of $\phi_0 \leq 0$, as indicated. All data sets were obtained from averages over 200 independent runs.

field strengths; and the initial growth exponent is potential dependent [12].

How can one understand all these results? An examination of Fig. 1 suggests the growth mechanism of the wetting layer for $\phi_0 < 0$. The bulk droplets [of length scale $R(\tau)$] must feed the wetting layer [of thickness $R_1(\tau)$], and this requires diffusion through the depletion zone [of thickness $h(\tau)$] [15]. We need to estimate the current at $z = R_1$, which consists of two pieces,

$$J_z = \left. \frac{dV(z)}{dz} \right|_{z=R_1} - \frac{\sigma}{Rh} \approx -\frac{nH_1}{R_1^{n+1}} - \frac{\sigma}{RR_1} \left(\frac{1 + \phi_0}{1 - \phi_0} \right), \quad (5)$$

σ being the surface tension. While the first term of the current is an obvious consequence of the surface potential, the second is due to the fact that there is a gradient of chemical potential from $\mu \approx \sigma/R$ (at the surface of the droplets) to $\mu \approx 0$ (at the interface between the enrichment and depletion layer, a distance h apart).

Our assumption that overall composition is approximately fixed at ϕ_0 in the wetting plus depletion layers yields $h \approx R_1(1 - \phi_0)/(1 + \phi_0)$, which we have verified numerically [19]. For domain growth in the bulk, we have the LS growth law $R(\tau) = f(\phi_0)(\sigma\tau)^{1/3}$, where the function $f(\phi_0)$ is analytically understood in the limit $\phi_0 \rightarrow \pm 1$, and numerically studied only for intermediate values of ϕ_0 [1,2].

Using this result, we find that, for $\tau \rightarrow \infty$, the second term on the right-hand side of Eq. (5) always dominates, yielding the universal domain growth law [14,15]:

$$R_1(\tau) \approx \sqrt{\frac{3}{f(\phi_0)} \frac{(1 + \phi_0)}{(1 - \phi_0)}} (\sigma\tau)^{1/3}, \quad \tau \rightarrow \infty, \quad \text{if } \phi_0 < 0. \quad (6)$$

However, for early times the first term dominates, yielding the potential-dependent growth law

$$R_1(\tau) \approx [n(n + 2)H_1]^{1/(n+2)} \tau^{1/(n+2)}, \quad \tau < \tau_c, \quad \text{if } \phi_0 < 0, \quad (7)$$

with a crossover time scale obtained by equating Eqs. (6) and (7),

$$\tau_c \approx [n(n + 2)H_1]^{3/(n-1)} \left[\frac{f(\phi_0)}{3} \frac{1 - \phi_0}{1 + \phi_0} \right]^{[3(n+2)]/2(n-1)} \times \sigma^{-(n+2)/(n-1)}, \quad n > 1. \quad (8)$$

Clearly, the crossover can be extremely delayed—depending on the surface-field strength and the range of the potential. The above arguments should clarify the observation of a range of growth exponents in simulations [11–16] and experiments [6–10, 20–22].

Next, let us consider the case $\phi_0 > 0$, where the majority component is preferred by the surface (Fig. 2). Pre-

liminary numerical results for this case have been reported by Brown *et al.* [16]. Notice that the second term on the right-hand side of Eq. (5) is not present for $\phi_0 > 0$, as the droplets are of the nonpreferred phase, and the chemical potential at the droplet surface is negative, i.e., they do not feed the preferred species to the wetting layer. Thus, the growth law in Eq. (7) holds for arbitrary times. As a matter of fact, the droplets in Fig. 2 actually attract the preferred component and should slow down the growth in Eq. (7), though we have not seen this in our simulations.

When one considers a short-range surface potential, one has to consider the limit $n \rightarrow \infty$ in the above treatment. It is straightforward to see that this yields a logarithmic growth law, $R_1(\tau) \propto \ln\tau$, for the potential-dependent regime.

Interestingly, a logarithmically slow growth law would also result from the second term in Eq. (5) if bulk domains grow in fluid mixtures according to the Siggia mechanism [5], $R(\tau) \propto \tau$, yielding $d[R_1^2(\tau)]/d\tau \propto \tau^{-1}$ and, hence, $R_1^2(\tau) \propto \ln\tau$. Essentially, if droplets in the bulk grow very fast, they fail to feed the growing surface layer sufficiently. In that case, Eq. (7) would dominate growth even for $\phi_0 < 0$, provided diffusive mechanisms still apply. Of course, there are a variety of other mechanisms for fast wetting-layer growth in phase-separating fluids, e.g., hydrodynamic draining through bulk tubes which establish contact with the wetting layer [18,23].

In conclusion, we have demonstrated by numerical calculations supported by phenomenological arguments that, at the surface of deep-quenched phase-separating binary mixtures, there exists a length scale that grows with time as $R_1(\tau) \propto \tau^{1/(n+2)}$, when the surface attracts a component with a potential $V(z) \propto z^{-n}$ [24]. If the preferred component is the majority component, this growth law is the asymptotic behavior for $\tau \rightarrow \infty$; otherwise, a crossover to the LS law $R_1(\tau) \propto \tau^{1/3}$ occurs after a crossover time τ_c . The present Letter elucidates the simple laws governing morphology evolution in surface-directed spinodal decomposition. Experiments [6–10, 20–22] and earlier numerical simulations [11–16] should be interpreted in the context of the framework discussed here. At the same time, we hope that our results will provoke fresh experiments on these problems—especially for off-critical morphologies in both polymer blends and binary fluid mixtures.

We are grateful to H.L. Frisch for stimulating discussions and a fruitful collaboration in earlier related papers [12,13]. S.P. thanks H.W. Diehl for useful discussions regarding these problems. One of us (S.P.) acknowledges partial support from the Deutsche Forschungsgemeinschaft under Sonderforschungsbereich 262.

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