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Surface-induced nucleation

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When a two-component mixture with an off-critical composition is quenched into the metastable region of its phase diagram, the nucleation barriers may be reduced or eliminated near a substrate that wets the majority phase. The appearance of nuclei and the subsequent domain growth of the nonwetting minority phase can thus occur near such a surface, long before the nucleation and the growth can occur in the bulk. We characterize this *surface-induced nucleation* process by a numerical study of a model system, and address the issue of experimentally observing it.

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The dynamics of phase ordering of liquid mixtures [1,2] near a substrate that attracts (either partially or completely wets [3]) one of the ordering phases has proven to be a fascinating subject [4–9]. The surface breaks the rotational and translational symmetry present in the isotropic bulk systems and affects domain formation from the earliest times. Previously, the case where the mixture is quenched into the unstable region of its phase diagram, or surface-directed spinodal decomposition, has been studied. In this case, ordering begins immediately following a quench, and the surface organizes domains in its vicinity.

In this paper, we examine a striking effect that occurs near a wetting substrate when a mixture is quenched into the metastable region of the bulk phase diagram, a situation encountered for sufficiently off-critical compositions. In this case, the bulk does not immediately begin to order after the quench because there is a nucleation barrier [1]: one must either wait for stable thermally excited nuclei of the minority phase to appear, or else depend on impurities or strong initial inhomogeneities to "seed" nuclei. We consider such a mixture near a substrate that attracts the majority phase. We argue that minority droplets may rapidly form near the wall, long before nucleation can occur in the bulk, as a result of reduction or elimination of the local nucleation barrier for the minority phase above the substrate. This occurs because of the local increase in minority phase concentration, at a distance of about one thermal correlation length above the substrate, following concentration of the majority phase at the wall. We characterize this *surface-induced nucleation* process by a numerical study of a model system and address the issue of observing such a phenomenon in experimental situations.

A prototype model system of nucleation and growth processes in the presence of surface interactions is the Cahn-Hilliard-Cook (CHC) model [1,10] with surface interactions [7–9]. There are no hydrodynamic effects in this model: domain growth proceeds via diffusion, leading to a bulk domain size R which grows with time after the quench t as $R \sim t^{1/3}$, reflecting the evaporation-condensation mechanism originally discussed by Lifshitz and Slyozov [1]. The CHC model may be used to describe the early-time dynamics of phase separation of viscous liquids, before domain walls can be advected by fluid flows. We add a surface interaction and appropriate boundary conditions [8] to the CHC model to study the effect of a surface which preferentially attracts one of the components. After rescaling time, distance, and local concentration, the CHC equation for the order parameter $\psi(\mathbf{r},t)$ (proportional to the deviation of the local composition from critical concentration) after a quench to zero temperature is [12]

$$\partial\psi(\mathbf{r}t)/\partial t=\tfrac{1}{2}\nabla^2[-\psi+\psi^3-\nabla^2\psi+v(\mathbf{r})]\ , \qquad (1)$$

where $v(\mathbf{r})$ is the long-range wall potential. After rescaling, $\psi=\pm 1$ are the binodals (coexisting phases) and distances are in units of the thermal correlation length, which is the equilibrium domain wall width.

A wall that attracts the majority component of the mixture ($\psi=+1$) is placed at $z=0$ and another confining noninteracting wall is placed at $z=255$. The system has dimensions $L_x=L_z=256$ with periodic boundary conditions in the x direction. No diffusive flux is allowed to pass through the surfaces $z=0$ and $z=255$. We have used a power-law wall potential

$$u(z)=\begin{cases} -\dfrac{\sigma}{z^{p+1}}\ , & z>0 \\ -\sigma, & z=0\ . \end{cases} \qquad (2)$$

For the two-dimensional results discussed here we have taken $p=1$ and $\sigma=0.4$. We have considered two area fractions of the minority phase: $\phi=0.1$ and $\phi=0.2$. The average value of the order parameter is $\psi_0=1-2\phi$, and is thus 0.8 and 0.6. In each case we are between the binodal ($\psi_b=1$) and spinodal ($\psi_s=1/\sqrt{3}$) and thus we expect metastability of the bulk following the quench. We have considered zero temperature quenches, so that the bulk nucleation is due only to remnant fluctuations in the initial state. Nucleation and growth of droplets, in a two-dimensional bulk off-critical system with area fractions $\phi\approx 0.2$, have been well characterized recently [13] for zero temperature quenches.

In the present study, for the two area fractions, we consider two initial conditions: (a) a narrow uniform distribution between $\psi_0 \pm 0.1$ and (b) a wide Gaussian distribution centered at ψ_0 with a variance of unity. We then carry out numerical integration of Eq. (1) up to a maximum time $t_{\max}=2000$, with a time step $dt=0.01$. We have averaged our results over ten realizations for each type of initial condition.

In Fig. 1. we show a gray-scale plot of the evolution of the system after quenches for $\phi=0.2$ and uniform-distribution initial condition. In this situation, the initial fluctuation of the order parameter is not strong enough to lead to the nucleation of bulk domains. However, as the majority component forms a wetting layer near the attractive wall, a depletion layer next to the wetting layer is formed. With time, this depletion layer ceases to be metastable (the local concentration actually drops below ψ_s in a region a few correlation lengths thick), and minority droplets appear in this region. An important feature of these droplets is that *they are of similar size,* due to the well-defined structure of the depletion layer organized by the substrate. The dominant process of subsequent droplet growth is a combination of condensation of dissolved minority phase and droplet coalescence. As the wetting layer grows, the distance of the droplets from the wall increases with time.

Now we compare the evolution of the system with the same area fraction with a different initial condition, namely a Gaussian distribution with a variance of unity. For $\phi=0.2$, the strong fluctuations provided by the initial Gaussian distribution were able to nucleate *bulk* minority droplets as shown in Fig. 2. There is still a wetting layer and a depletion zone next to the wetting layer where surface-induced droplets are formed, but the bulk droplets are comparable in density to those near the surface [14].

To characterize the evolution of the system near the wall, we have measured the time variation of the density profile function $n(z,t)$:

$$n(z,t)=\frac{1}{L_x}\sum_{x=1}^{L_x}\psi(\mathbf{r}=(x,z),t)\ . \tag{3}$$

This profile is directly observable in ion-beam scattering experiments carried out on polymer blends [5,15]. A density $n=1$ corresponds to the majority phase and $n=-1$ to the minority phase. We define the thickness of the wetting layer $l(t)$ to be the first solution of $n(l(t),t)=\psi_0$. We define the second solution to be $l_2(t)$, which is a measure of the height of the droplet layer.

In Fig. 3 we show $n(z,t)$ for $\phi=0.2$, for the two initial conditions. For the uniform initial distribution (a), which yields surface-induced nucleation, the density profile shows a depletion layer dominated by the minority phase [Fig. 3(a)], which is coarsening with time. We note that at early times ($t=20$) the depletion layer crosses the spinodal, and thus in a narrow region the mixture is actually unstable. For the Gaussian initial distribution (b), the depletion layer is not dominated by minority phase and the density there never reaches a negative value [Fig. 3(b)]. In this case, bulk nucleation dominates, leading to more even dispersal of the minority phase throughout the system.

In Fig. 4 we plot the thickness of the wetting layer perpendicular to the surface $l(t)$ and the height of the top of

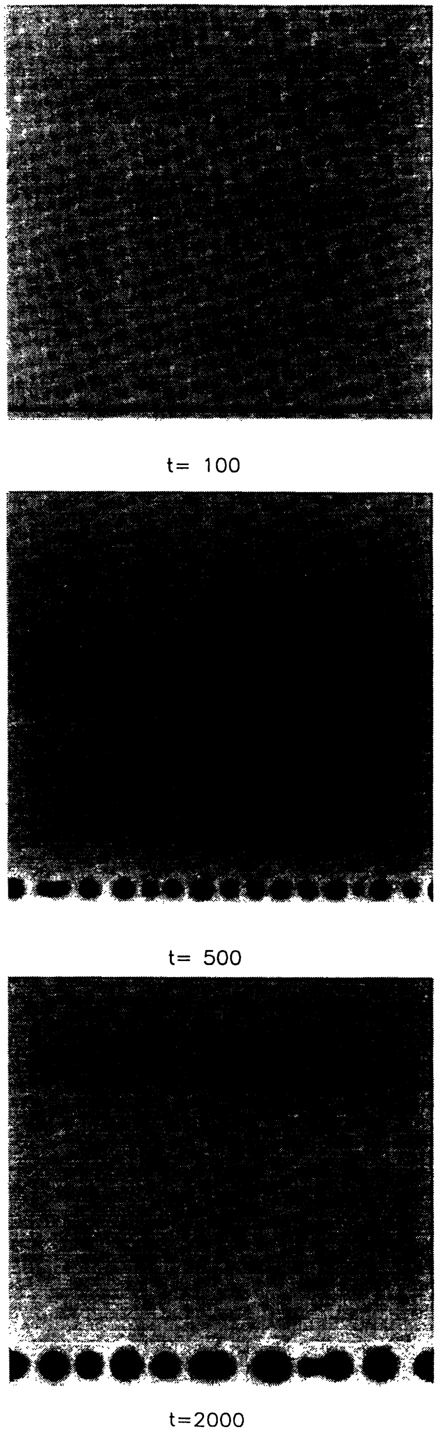

FIG. 1. Time evolution of order parameter during two-dimensional phase separation near a substrate that attracts the majority phase. Minority phase area fraction is $\phi=0.2$. A random initial configuration with a narrow uniform distribution (see text) is used. At the bottom of the frames is the wetting substrate $z=0$; at the top is $z=255$. Droplets appear only above the wetting layer and subsequently grow via condensation of the dissolved minority phase from the upper region of the sample.

the droplet layer $l_2(t)$ for $\phi=0.2$ and uniform initial condition. We see that the wetting layer thickness initially grows as $t^{1/3}$, but once minority droplets nucleate and start growing, $l(t)$ roughly follows a slower power law $l \sim t^{1/6}$, possibly due to the *screening* effect of the droplet layer. However, we note that $l_2(t)$ increases much more quickly at late times: $l_2(t) \sim t^{1/3}$. Thus, the droplets are increasing in size roughly as $t^{1/3}$.

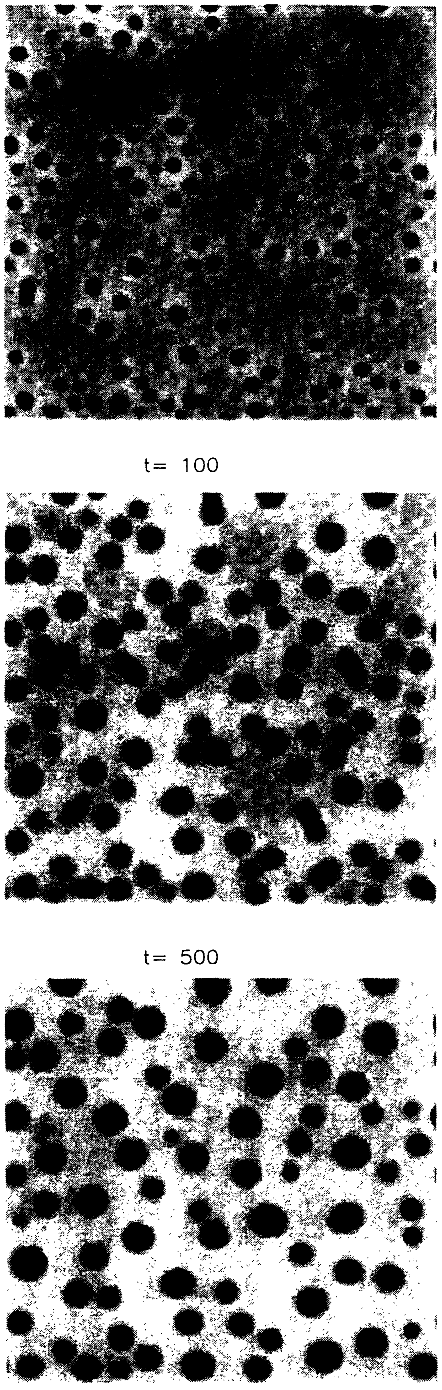

FIG. 2. As in Fig. 1, but with the random initial configuration distributed with a wide Gaussian distribution (see text). Initial fluctuations are sufficient to cause nearly immediate nucleation of stable droplets throughout the bulk, which then grow by a conventional condensation-evaporation mechanism.

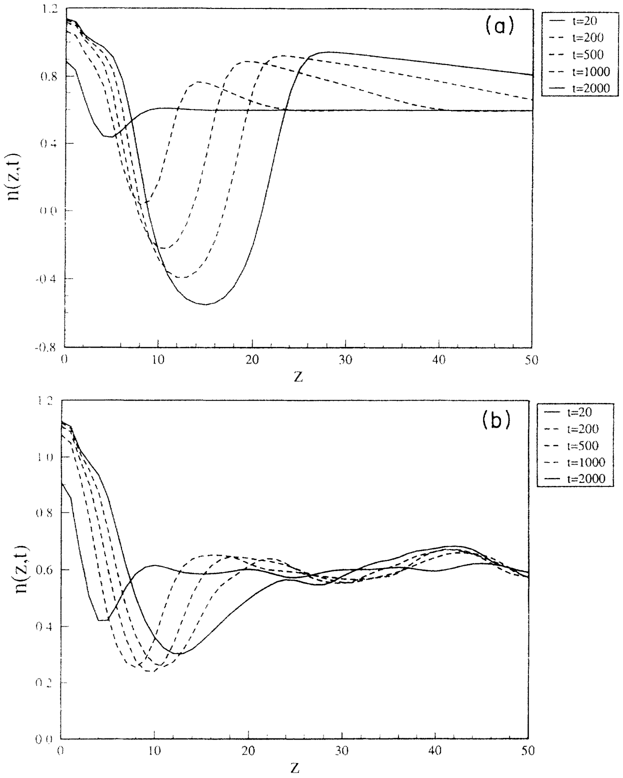

FIG. 3. Density profile evolution $n(z,t)$ for minority phase area fraction $\phi=0.2$. (a) Narrow uniform distribution initial condition. At early times ($t=20$) the density above the surface is pulled beneath the spinodal value $n=0.5773$; subsequent droplet formation is observed. (b) Wide Gaussian distribution initial condition. A less deep minimum followed by a more rapid decay to the average concentration $n \approx 0.6$ arises than in (a), due to the many randomly distributed droplets.

The $t^{1/3}$ growth law has been shown to apply to bulk domains which exchange material by diffusion and also describes wetting layer thickening during surface-directed spinodal decomposition [7–9], it can be justified if it is assumed that there is a single length characterizing the domain pattern [9]. It is remarkable that $l_2 \sim t^{1/3}$ describes the growth of the isolated surface-induced nuclei,

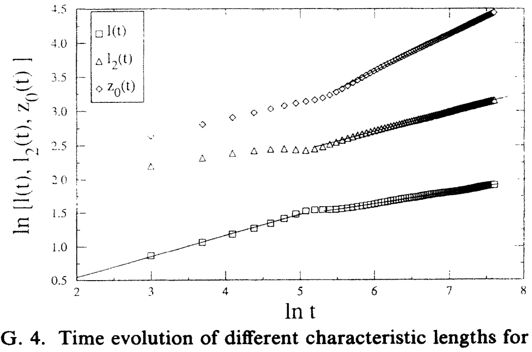

FIG. 4. Time evolution of different characteristic lengths for $\phi=0.2$ with a uniform initial distribution. The best fit to the data indicates that the wetting layer thickness $l(t)$ initially grows as $t^{0.31 \pm 0.01}$, but after the minority droplets nucleate and start growing, $l(t)$ follows a slower power law $l \sim t^{0.17 \pm 0.01}$ possibly due to the *screening* effect of the droplet layer. The height of the droplet layer $l_2(t)$ increases as $l_2(t) \sim t^{0.30 \pm 0.01}$ at late times. The other length scale $z_0(t)$ (see text) grows roughly as $t^{0.55 \pm 0.02}$.

since growth at late times proceeds mainly by removal of the minority phase from the large region above the droplet layer. One can see in Fig. 3(a) a long "enrichment tail" extending above the droplets, reflecting this condensation process. The concentration profile above the droplet layer has an almost linear decay over a rapidly increasing distance. Extrapolation of the linear decay to where it reaches the bulk value of ψ_0 yields a length z_0 (also plotted in Fig. 4) which grows roughly as $z_0 \sim t^{0.55}$. We note that a roughly linear decay is what is needed to provide transfer of the order parameter with constant flux from the undepleted bulk to the droplet layer, the flux will scale with the slope of this linear decay. We need a flux of order dl_2/dt, indicating that the point z_0 where $n(z_0,t)=\psi_0$ should behave as $z_0 \sim (dl_2/dt)^{-1}$. For $l_2 \sim t^{1/3}$, this suggests $z_0 \sim t^{2/3}$, roughly consistent with what we observe. This is distinct from the growth of domains distributed throughout space [note the rapid decay of the profile in Fig. 3(b)], where the minority phase is transferred by evaporation of small droplets and condensation of the minority phase onto larger ones, with the interdroplet distances scaling with droplet size. We thus see that there are several different characteristic length scales describing the late-time growth of surface-induced nuclei. Rescaling of z by any of these lengths thus cannot lead to a universal density profile, again in contrast to the situation encountered for surface-directed spinodal decomposition [7–9].

We have also carried out simulations in three dimensions using a cell-dynamical system [16]. In these simulations we used a short-ranged surface interaction (i.e., a symmetry-breaking boundary condition at the substrate) and dynamical noise (finite temperature) in both the initial and final states. The interactions and initial and final temperatures were chosen to resemble those in recent experiments on isotopic polymer blends [5,15]. We have found the same basic phenomena, namely that in cases where bulk growth will occur only after nucleation, droplets form preferentially near the surfaces. Again, we observe roughly $t^{1/3}$ growth of the wetting layer and of the droplets. The lowering of nucleation barriers and subsequent preferential nucleation of minority phase droplets near a surface that attracts the majority phase thus occurs independent of (i) the exact nature of the surface interaction, (ii) dimensionality, and (iii) choice of annealing temperature. This is to be expected since the basic effect is due to the conservation law, which forces the formation of a minority-phase-rich layer if the minority phase is concentrated at the substrate.

These phenomena should be observable in experiments on isotopic polymer blends at sufficiently off-critical composition for the bulk to be metastable, but close enough to the spinodal that the nucleation barrier above the substrate can be substantially modified by the expelled minority phase. Isotopic blends are well described by mean-field theories and have well-defined spinodals; for entangled polymers (degree of polymerization $N \gg 100$) the viscosities can be so large that the early-time diffusive evolution may be carefully studied. Experiments of Krausch *et al.* [5,15] on $N=2300$ polystyrene–deuterated polystyrene blends undergoing spinodal decomposition near surfaces should show these effects, if concentrations are used that show nucleation in the bulk. The depth profiling techniques used in those experiments should show a layer of minority-phase bubbles forming near the surface long before any stable nuclei are excited in the bulk. A long enrichment tail on the profile as observed in our simulations is another signature of this process.

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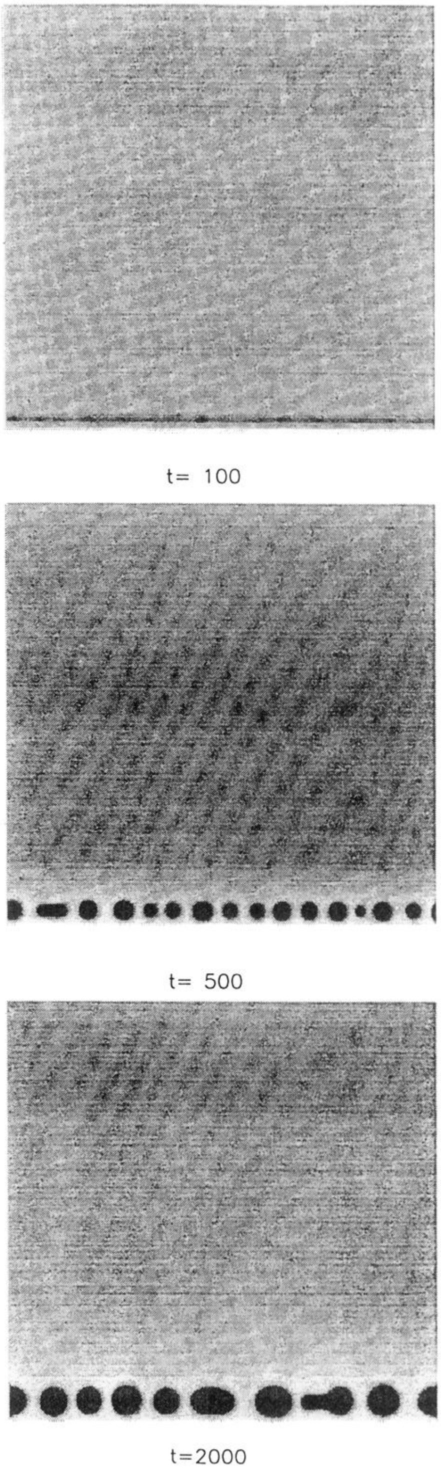

t= 100

t= 500

t=2000

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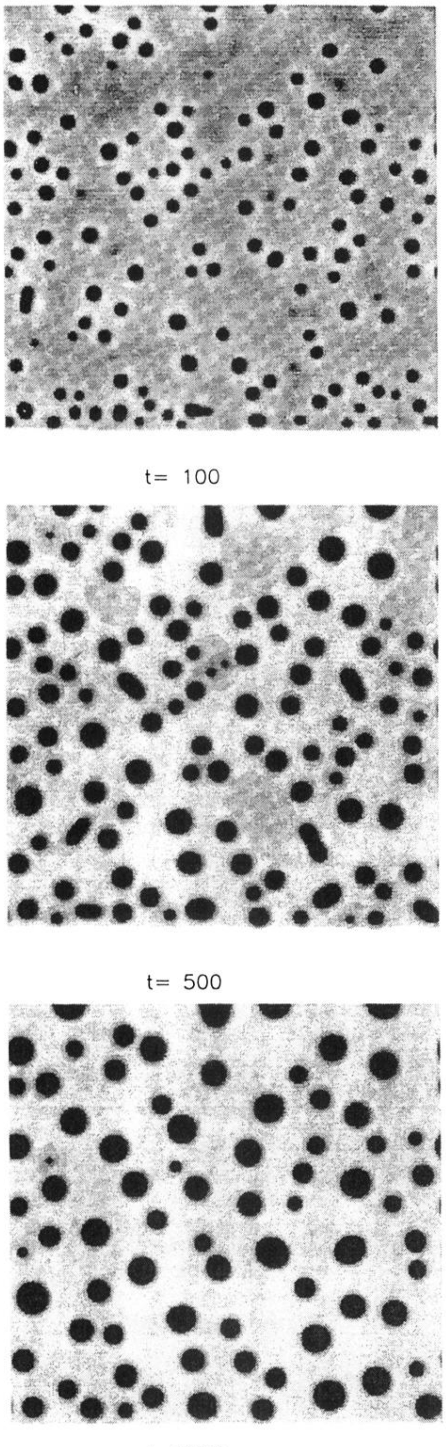

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