

## Coalescence Induced Domain Growth near a Wall During Spinodal Decomposition

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We propose a model whereby the average size of domains in a binary mixture undergoing spinodal decomposition near a wall can achieve growth exponents much larger than the usual bulk value of  $1/3$ . The accelerated growth is associated with the nonwetting phase coarsening anisotropically against a wall coated with the wetting phase. The larger exponents arise from the coupling of domain coalescence with Lifshitz-Slyozov type growth, modified to include the geometric constraint of growth near a wall. We include experimental tests of these ideas.

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Recent experiments designed to probe the effect of a nearby surface on the kinetics of spinodal decomposition have uncovered unusually large structures and accelerated domain growth near the walls. In studies of binary mixtures at critical composition quenched into the unstable regime [1–3], the domains growing at the surfaces have been shown to coarsen with an exponent ranging between 1.1 to 1.5 depending on quench depth, while the bulk domains coarsen with the usual diffusion driven exponent of  $1/3$ . The mechanism responsible for this accelerated surface growth appears universal since the fast signal has appeared both in polymer mixtures [1,2] and in a simple binary fluid [3]. There has so far been no theoretical treatment of this enhanced growth.

Whether the fast surface growth is associated with the nonwetting or the wetting phase remains an open question. In this Letter we propose a mechanism whereby the domains of the nonwetting phase can experience accelerated growth near a wall. We describe a model in which the fast surface growth arises from the coupling of two distinct processes. The first process is curvature driven Lifshitz-Slyozov (LS) growth modified to include two length scales reflecting the bulk and surface properties, and the second process describes coalescence of three-dimensional (3D) domains along a two-dimensional (2D) surface. Because of the geometric constraint of a nearby wall, we argue that *individual* domains growing by an LS type mechanism can exhibit power law exponents ranging from  $1/3$  to  $1/2$ . We then indicate how coalescence of domains can effectively triple this exponent by using an argument first developed in the context of heterogeneous vapor condensation [4]. Predictions based on this coupled growth mechanism can be tested directly. We have also reviewed earlier work [5] on phase separation occurring near a wall. Contrary to previous reports, we find that the exponents measured in Refs. [1–3] and [5] may in fact all be consistent.

The experimental plots of the scattered intensity versus wave vector,  $q$ , reveal the evolution of two distinct peaks, differing in amplitude by an order of magnitude: a slow *bulk* mode coarsening as  $q_B \sim t^{-1/3}$  and a fast *surface* mode evolving as  $q_S \sim t^{-\beta}$  with  $1.1 \leq \beta \leq 1.5$ .

We have inspected the published data for the slow mode shown in Fig. 2 of Ref. [1] and Fig. 13 of Ref. [2] and note that  $q_B$  does not scale neatly with a slope of  $-1/3$  as reported. The slope depends on the quench depth with the deeper the quench, the smaller the slope [6]. Although the quench depth dependence may be an artifact of the curve-fitting routines used to separate the two peaks, we emphasize that the fast signal scaling as  $q_S \sim t^{-\beta}$  appears *before* the bulk has reached the asymptotic scaling of  $q_B \sim t^{-1/3}$ . (It is well known that at finite times the bulk exponent is less than  $1/3$  [7].) In the numerical results we present later, we have found that the enhanced surface growth appears before the bulk domains have reached their asymptotic long time scaling of  $1/3$ . Our results indicate that the two length scales merge into one precisely when the value  $1/3$  is achieved.

We first review the origin of the  $1/3$  power law for domains in the bulk. Lifshitz and Slyozov [8] first described the diffusion driven growth process for isolated droplets coarsening in a matrix of a second continuous phase and showed that the average droplet radius scales asymptotically as  $R \sim t^{1/3}$ . Voorhees and Glicksman [9] later numerically solved the multidroplet diffusion problem for volume fractions of the coarsening phase up to 95%. Their conclusion was that the  $t^{1/3}$  kinetics is preserved at late times for all volume fractions. The usual LS equation holds strictly for vanishingly small volume fractions of the minority phase and cannot be used to study systems above the percolation threshold. In the case where the volumes of the two demixing phases are comparable and the morphology resembles interconnected domains, Huse [7] has shown that the typical size of the growing domains scales as  $t^{1/3}$  with finite time corrections. Renormalization group arguments confirm this result for either critical or off-critical quenches [10].

Before presenting the Huse argument, we describe our model as depicted in Fig. 1 where the fast surface signal derives from the growth of the nonwetting  $A$  rich domains against a wall. (In a separate work [11] we have studied the second possibility where the signal derives from the growth of the wetting phase against the substrate.) The binary system consisting of  $A$  and  $B$  species

is phase separating into an  $A$  rich and a  $B$  rich phase where the  $B$  component preferentially wets the wall and thereby establishes a  $B$  enriched wetting layer different in composition than the bulk  $B$  rich domains. This tendency towards surface wetting has been seen in polymeric mixtures [12]. Since the wetting layer is poor in the  $A$  component, the  $A$  rich nonwetting domains near the wall will have their growth substantially slowed in the direction perpendicular to the wall and will therefore assume an elongated shape as they grow in the horizontal direction. (There can also exist a dynamic effect enhancing growth in the horizontal direction since, due to expulsion, there may exist a thin enriched layer of the  $A$  phase which has not yet equilibrated with the bulk concentration.) The  $A$  rich domains which originally grew isotropically in the bulk are now confined to grow anisotropically along the wall. These domains are expected to develop higher curvature because they are rich in the nonwetting component. We have labeled the average radius of curvature for interfaces  $A/B$  adjacent to the wetting layer,  $R_S$ , and for interfaces within the bulk,  $R_B$ , where  $R_S \ll R_B$ . This description of anisotropic growth parallels closely what has been observed in the optical micrographs published by Guenoun *et al.* [5].

Huse's original argument for the growth of diffusion-limited, interconnected domains relates the velocity of an interface to the gradient in the local principal radii of curvature. The system is assumed to be near local equilibrium on length scales small compared to the radii of curvature. The difference between the local and critical concentration of one of the diffusing species defines the order parameter  $N$ , whose growth is driven by the local gradient in the chemical potential difference of this species,  $\mu$ , in the two different phases. For a portion of a curved interface to be in local equilibrium, the Laplace pressure,  $\sigma(1/R_1 + 1/R_2)$  (where  $\sigma$  is the interfacial tension), must balance the pressure of the local driving field,  $\mu N$ . This local field  $\mu$  is therefore of order  $\sigma(1/R_1 + 1/R_2)/N$  and for isotropic systems with only one length scale, i.e.,

$R_1 = R_2 = R_B$ , the local field gradient will be of order  $2\sigma/NR_B^2(t)$ . The interfaces move with a velocity  $dR_B/dt$  in response to the local field gradients which induce a particle flux proportional to  $D\nabla\mu/(\partial\mu/\partial N)_{T,p}$  where  $D$  is the mutual diffusion constant and  $(\partial\mu/\partial N)_{T,p}$  is the osmotic susceptibility. The domains are then expected to coarsen at the rate

$$\frac{dR_B(t)}{dt} = \frac{D}{\left(\frac{\partial\mu}{\partial N}\right)_{T,p}} \frac{2\sigma}{NR_B^2(t)}. \quad (1)$$

This curvature driven growth in isotropic bulk systems leads to the growth law  $R_B(t) \sim t^{1/3}$  [13].

Now suppose that the  $A/B$  interfaces adjacent to the wetting layer are more highly curved than in the bulk due to the biased lateral growth. There will then be two length scales to consider, namely,  $R_S$  and  $R_B$ , where  $R_S \ll R_B$ . For a piece of interface with its normal parallel to the wall, the local curvature will be  $1/R_S + 1/R_B$ . The local chemical potential field near the wall therefore scales as  $\sigma(1/R_S + 1/R_B)/N$ . Variations in this chemical potential field will occur over distances scaling with  $R_B$ , not  $R_S$ , since the appropriate gradients are sampling regions on the order of the domain size or spacing. The lateral growth of domains near the surface will therefore scale as

$$\frac{dR_S(t)}{dt} = \frac{D}{\left(\frac{\partial\mu}{\partial N}\right)_{T,p}} \frac{\sigma}{NR_B(t)} \left(\frac{1}{R_S} + \frac{1}{R_B}\right). \quad (2)$$

If we assume that on the time scale appropriate to the growth of the smaller scale  $R_S$ , the larger length scale  $R_B$  is growing slowly and, by comparison, is effectively frozen, then Eq. (2) gives the power law growth  $R_S(t) \sim t^{1/2}$  correct to order  $\sigma/R_B(t)$ .

To examine the time dependent scaling which can result in the case of two length scales, we have numerically integrated the coupled Eqs. (1) and (2), representing the growth of bulk and surface domains, respectively. For convenience we have set  $D\sigma/[N(\partial\mu/\partial N)_{T,p}]$  equal to 1. The initial condition specifying the ratio  $R_S/R_B$  at  $t = 0$  sets the time scale for the problem. In Fig. 2 is shown

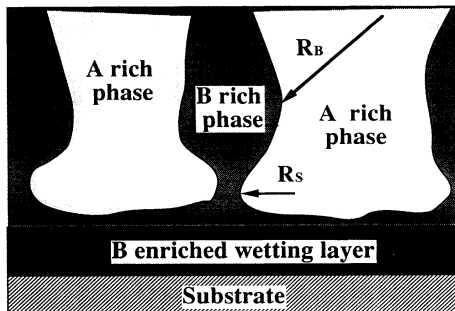


FIG. 1. Schematic diagram for the anisotropic growth and incipient coalescence of nonwetting  $A$  rich domains during spinodal decomposition. The radii of curvature,  $R_B$  and  $R_S$ , denote the length scales appropriate to the bulk and surface interface growth, respectively.

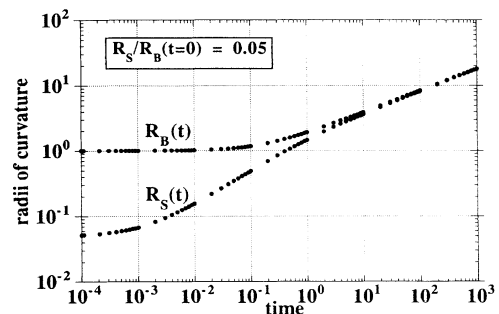


FIG. 2. Temporal growth of the two radii of curvature,  $R_S$  and  $R_B$ , for an initial ratio of 1:20.

the growth of both length scales for an initial ratio of  $R_S/R_B = 1/20$ .  $R_S$  grows rapidly while  $R_B$  is frozen for the first 3 decades in time. At late times, when the surface and bulk length scales become comparable, both length scales achieve power law growth with an exponent of  $1/3$ . By measuring the local slope of the surface growth curve  $R_S(t)$  on log-log axes, we find that for 1.5 decades in time after  $t = 10^{-2}$ ,  $R_S$  actually scales with an exponent of  $1/2$ . To show this more clearly, we have plotted in Fig. 3 the value of the surface exponent for six different starting ratios of  $R_S/R_B$  including the ratio 1:20 whose growth is shown in Fig. 2. The dotted line drawn across the upper part of the plot indicates a slope equal to  $1/2$ . The data in curve *a* represent the case of isotropic growth; the exponent asymptotes to  $1/3$  only after  $t = 10$ . Before that time, the numerical results clearly show that depending on the initial condition, there can exist for up to several decades in time a regime where the surface exponent equals  $1/2$  as most clearly demonstrated in *f*. The results for curves *a-c* show no extended flat regime except for the value  $1/3$  at late times. In Fig. 3, curves *d-f*, on the other hand, the exponent remains very close to  $1/2$  for at least a decade in time before finally settling to a value of  $1/3$  at late times. For initial ratios  $R_S/R_B$  smaller than 0.1, there therefore exists a time interval for power law growth different than  $1/3$  and close to  $1/2$ .

This different scaling exponent simply derives from the fact that during phase separation, the less wetting *A* rich phase will tend to form more elongated domains pressed up against the wetting *B* rich phase and this enhanced curvature will speed up the coarsening process. This enhanced growth, with a surface exponent  $1/3 \leq \alpha_S \leq 1/2$  occurs *before* the bulk has reached its asymptotic exponent of  $1/3$ , consistent with experimental data.

The previous argument requires that there be a separation in length scales in the system. How will this separation in scales be affected by the quench depth? We expect that for shallow quenches in which both the gradients in chemical potential and the interfacial tension are small, the surface curvature will not be as fully developed and the system should behave more isotropically leading

to an exponent close to  $1/3$ . For deeper quenches, one expects a time interval in which the surface exponent is close to  $1/2$ . This relation between quench depth and surface exponent is born out by the results of Fig. 3 in Ref. [3].

Given that the *individual* nonwetting domains are expected to scale as  $R_S(t) \sim t^{\alpha_S}$  where  $1/3 \leq \alpha_S \leq 1/2$ , we now indicate how domain coalescence near the wall can triple this exponent. Coalescence and the consequent increase in the growth exponent associated with the average domain size has previously been studied for the case of droplet growth during heterogeneous vapor condensation onto a partially wetting surface [4,14]. Scaling analysis of this system reveals that irrespective of the particular transport mechanism governing the growth of individual droplets, the average drop radius grows with an exponent 3 times as large as the individual growth radius. This result is strictly a consequence of the geometrical constraint imposed by having a 3D droplet growing on a 2D substrate. There is no such increase in exponent for the case of a 2D object growing and coalescing on a 2D surface. We describe below how one can apply the original argument, which was developed in a very different context, to model the process of coalescence of phase separating domains near a wall.

For the sake of brevity, we refer the reader to Refs. [4,14] for the original argument. We focus instead on how the calculation applies equally well to the system shown in Fig. 1 and interpret the results and implications for our system. One might argue that the condensation problem described in Refs. [4,14] refers to liquid droplets growing and coalescing amidst a vapor whose viscosity can be ignored. We are instead modeling coalescence of *A* rich viscous domains highly interconnected with the bulk and moving in a background of viscous *B* rich phase. Coalescence of two *A* rich domains will involve squeezing fluid of the *B* rich phase from the region in between the approaching domains. We expect this process to modify only slightly the growth law predicted below. In fact calculations by Siggia [15] for hydrodynamic interactions like droplet deformation and internal fluid circulation which can occur during coalescence have shown that such flow retardation effects do not strongly affect the basic scaling results. One might also argue that the elongated domains undergoing coalescence do not resemble spherical droplets, as in the condensation problem, unless the high curvature near the base of a domain causes the elongated part to pinch off and detach from the "tube" extending into the bulk. The derivation below holds, nonetheless, since we are only interested in the temporal power growth laws derived from the similarity solution—geometrical factors describing the shapes of the domains will only change the magnitudes, not the temporal scaling results. In order for the original calculation to hold, it is necessary, though, that the domains be parametrized by one length scale  $R(t)$ ; they need not have a circular cross section but their overall volume must

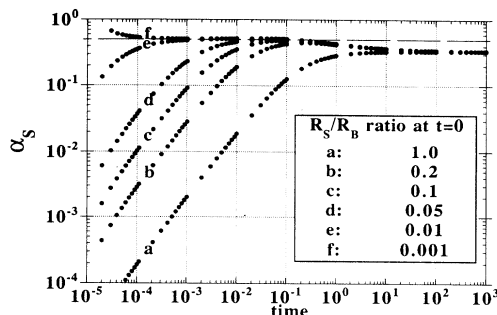


FIG. 3. Surface exponent,  $\alpha_S$ , for different initial ratios,  $R_S/R_B$ , including the isotropic case (1:1) shown in curve *a*.

be defined by only one parameter. The original calculation requires that two domains fuse quickly upon contact in comparison to the time scale set by the individual growth mechanism. Our estimates show that even for such viscous liquids as used in the experiments cited, the time scale for fusion of two domains,  $\tau_{\text{fusion}} \sim \eta R/\sigma$ , is much shorter than the time scale governing growth by diffusion  $\tau_{\text{diffusion}} \sim R^2/D$ , where  $\eta$  is the viscosity and  $D$  the cooperative diffusion constant [16]. In the simplest model, only binary collisions are allowed, the domain centers are pinned, and there exist no domain correlations. Collisions are strictly caused by the increased surface area due to individual domain growth.

As constructed, the Smoluchowski type equation for the domain size distribution function allows a self-similar solution in the case of a symmetric collision integral. The results show that for a 3D object subject to coalescence on a 2D surface, the *average* domain size grows with an exponent 3 times as large as the exponent associated with the *individual* growth law. As we showed earlier, the individual domains grow as  $t^{\alpha_S}$  for  $1/3 \leq \alpha_S \leq 1/2$  and so the average domain growth including coalescence will therefore scale as  $t^{3\alpha_S}$ . This gives an effective surface exponent (including coalescence) with values ranging between 1 and 1.5, with the higher exponents associated with the deeper quenches. This is exactly the range of values recently measured for the surface exponent [3].

Our coupled model predicts the following results. The total number of domains,  $N_A(t)$ , against the wall scales as  $N_A(t) \sim t^{-6\alpha_S}$ ; shallow quenches give  $t^{-2}$  while deeper quenches give  $t^{-3}$ . The self-similar solution automatically implies that the surface area coverage (appropriately scaled by  $R_S$ ) is constant, which also seems verified experimentally. Our interpretation gives rise to domain shapes with large length to height aspect ratios where the growth appears more and more 2D-like. According to dynamic scaling, these 2D structures would give  $I_{\text{max}} \sim q_{\text{max}}^{-2}$  as seen experimentally for the fast surface signal. Finally, our simple model applies to binary mixtures in general, be they simple binary fluids or polymer mixtures. The fast signal has been measured in both types of fluids [1–3].

In conclusion, we would like to point out that our model possibly also resolves a discrepancy between the exponents previously measured by Guenoun *et al.* and those of Cumming *et al.* This discrepancy has been attributed to the fact that the bulk domains in the earlier experiments have already evolved to the very late stages where the growth exponent is 1. We suggest another possibility. Figure 3 of Ref. [5] represents the scaled wave number  $K_\lambda^*$  as a function of dimensionless time corresponding to the distance between the centers of the domains constituting the less wetting phase. These mea-

surements were made manually from video images and the data when averaged over the limited set of measurements gave  $K_\lambda^* \sim t^{0.64 \pm 0.15}$ , nowhere near the values measured by Cumming *et al.* Our inspection of the data in Ref. [5] reveals the presence of two apparent power laws, one associated with a fast dropoff in the wave vector (presumably reflecting coalescence) and the other with a much more slowly varying growth (presumably reflecting individual growth between coalescence events). For the different quench depths shown, we find we can easily fit a line with a slope close to  $-1.5$  over the portions of the data with the sharp dropoff. We suggest that with more numerous measurements, the average slope would have been weighted more toward the exponent associated with coalescence, leading to a power much higher than 0.64, bringing this value in line with the exponents measured in the more recent experiments.

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