MECHANISMS WHICH CAN ACCELERATE THE GROWTH OF PHASE SEPARATING DOMAINS NEAR A WALL

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ABSTRACT

Though the dynamics of bulk phase separation during spinodal decomposition is fairly well understood nowadays, recent experiments have shown that the same process occuring near a wall introduces some surprisingly fast domain growth kinetics. Studies of both polymer mixtures and simple binary fluids at critical composition quenched into the unstable regime reveal the presence of a fast mode associated with domains coarsening at the wall. The scattering data indicates that while the bulk domains grow in time as $t^{1/3}$, as dictated by usual diffusion driven dynamics, the surface domains coarsen with exponents ranging from about 1.1 to 1.5 depending on the quench depth. We construct a model in which the average size of domains in a binary mixture undergoing spinodal decomposition near a wall can achieve growth exponents much larger than 1/3. The accelerated growth is associated with the domains of the non-wetting phase coarsening anisotropically against a wall coated with the wetting phase.The faster growth evolves from coupling Lifshitz-Slyozov type coarsening for critical volume fractions, modified to include the geometric constraint of growth near a wall, the process of domain coalescence. Included are some predictions for experimental tests of these ideas.

INTRODUCTION

Recent experiments on phase separation in different types of binary mixtures undergoing spinodal decomposition near a wall reveal surprisingly fast and as yet unexplained domain growth. In studies of the polymer blend polyisoprene–poly(ethylene–propylene) at critical composition confined to a thin cell and quenched into the unstable regime [1, 2], the growth of domains in the bulk of size L_B were found to coarsen with the usual diffusion driven dynamics leading to $L_B \sim t^{1/3}$. The domains growing parallel to the surfaces, however, coarsened at the accelerated rate of $L_S \sim t^{3/2}$. More recent experiments on the simpler fluid mixture of guaiacol and glycerine/water [3] have shown that the exponent associated with L_S is quench dependent with a range of about 1.1 to 1.5. Though the mechanism reponsible for this accelerated surface growth appears generic to binary mixtures in general, there has been no theoretical framework with which to interpret these results.

It remains an open experimental question as to whether the fast surface growth is associated with the non-wetting or the wetting phase. For the kinetics to achieve such large growth exponents through a single mechanism controlled mainly by diffusion is difficult to imagine. We instead propose a modelin which the fast surface growth stems from the coupling of two distinct processes. The first involves curvature driven Lifshitz-Slyozov (LS) coarsening in the presence of a wall and the second describes coalescence of three dimensional (3D) domains growing against a two-dimensional (2D) surface. Due to the constraint of growth near a 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 significantly increase this exponent. In particular, if the individual non-wetting domains near a wall coarsen as $L \sim t^{\alpha}$, then the process of coalescence can cause the *average* characteristic size of domains to grow as $L \sim t^{3\alpha}$. Predictions based on this coupled growth mechanism are calculated below and can easily be tested experimentally. We have also reviewed one of the earliest experiments [4] on a binary fluid mixture near the consolute critical point used to probe the connection between the growth of a wetting layer against a wall and bulk phase separation. Contrary to previous reports, we find that the exponents measured most recently [1, 2, 3] and those measured in the earlier works [4]

may all be consistent.

EXPERIMENTAL RESULTS

The experiments cited above, designed to investigate the effect of a nearby surface on the coarsening process, have uncovered the presence of two growth modes. The scattered intensities versus wavevector, q, reveal the evolution of two distinct peaks, differing in amplitude by an order of magnitude. Tracking these two peak positions as a function of time and intensity has uncovered a slow bulk mode evolving as $q_B \sim t^{-1/3}$ and a fast surface mode evolving as $q_S \sim t^{-\beta}$ with $1.1 \leq \beta \leq 1.5$. The model we construct below proposes two distinct but coupled mechanisms which can explain this quench dependent spectrum of exponents. Upon inspecting the experimental data, however, we note that the exponent associated with the slow mode shown in Fig. 2 of Ref. [1] and Fig. 13 of Ref. [2] does not scale neatly with a slope of -1/3 and appears also to depend on quench depth ΔT. The shallowest quenches show the larger absolute slope approaching 1/3 while the deeper quenches show progressively smaller slopes [5]. Although the quench depth dependence may be an artifact of the curve-fitting routines used to separate the two signals, this raises the question of whether the bulk of these systems has yet reached the later stages of phase separation since it is known that for finite times this effective exponent is less than 1/3 [6]. In what follows we assume that the exponent associated with the growth of the bulk domains is at most 1/3 but perhaps even smaller.

COARSENING OF BINARY MIXTURES AT CRITICAL VOLUME FRACTION NEAR A WALL

We review the origin of the power law $L_B \sim t^{1/3}$ for domains in the bulk. Lifshitz and Slyozov (LS) [8] first described the diffusion driven growth of 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 still 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 [6] has shown that the typical size of the growing domains still scales as $t^{1/3}$ at long times. Renormalization group arguments confirm this result for either critical or off-critical quenches [10].

Model Geometry

We draw attention to Fig.[1] where we have sketched the spinodal process for the case where the fast surface signal derives from the growth of the non-wetting domains near a wall. (In a separate work [11] we are investigating the alternative possibility where the signal derives from the growth of the wetting phase against the substrate.) The system is phase separating into an A phase (rich in A component) and a B phase (rich in B component) where the B component preferentially wets the wall. There exists an enriched B layer at the wall and a corresponding depletion of the A component in the vicinity of the wall. The tendency toward surface wetting and subsequent layering of the wetting and non-wetting phases has been seen in polymeric mixtures [12]. Since the wetting layer is depleted in the A component, the domains of A will be slowed down in the direction perpendicular to the wall and instead tend to grow laterally. There can also be a dynamic effect enhancing growth in the lateral direction within a thickness of the order of the wetting layer away from the wall since there can exist an enriched layer of the A phase (due to expulsion) which has not yet equilibrated with the bulk concentration . The A domains

which originally grew isotropically in the bulk are now confined to grow anisotropically along the wall. Such biased growth will create elongated domains of the A phase growing on top of the B rich wetting layer. The A/B interfaces which are growing in a direction parallel to the wall will tend to develop higher curvature as a result. We denote by R_S the average radius of curvature for interfaces A/B adjacent to the wetting layer and by R_B the average radius of curvature for interfaces closer to the bulk where $R_S \ll R_B$. This description of anisotropic growth parallels closely what has been seen in the optical micrographs taken by Guenoun et al [4] although the bulk liquid in their system has already evolved to the late stages where coarsening occurs by capillary flow [13].

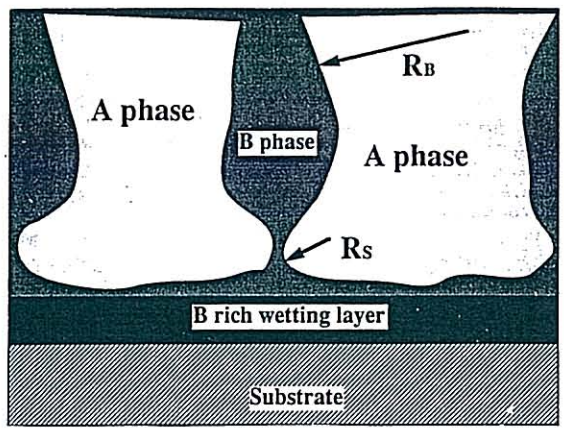

Figure 1: Schematic diagram for the anisotropic growth and incipient coalescence of non-wetting A phase domains during spinodal decomposition. The radii of curvature, R_B and R_S, denote the length scales appropriate to the bulk and surface interface growth, respectively

Lifshitz-Slyozov Argument Modified to Critical Volume Fractions In Bulk Systems

Huse's argument for the growth of diffusion-limited, interconnected domains relates the velocity of an interface to the gradient in the local curvature. The system is assumed to be near local equilibrium on length scales small compared to the radius 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, μ between the two species. For a portion of a curved interface to be in local equilibrium, the Laplace pressure, $\sigma/R_B(t)$ (where σ is the interfacial surface tension) must balance the pressure, μN, due to the local driving field. The local field, μ, is therefore of order $\sigma/[NR_B(t)]$ and, for an isotropic system with only one length scale, the local field gradient will be of order $\sigma/[NR^2{}_B(t)]$. The interfaces move with a velocity $dR_B(t)/dt$ in response to the local field gradients which induce a particle flux, j, 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

$$\frac{dR_B(t)}{dt} \sim \frac{\sigma}{R_B{}^2(t)}. \tag{1}$$

This curvature driven growth in isotropic systems leads to the growth law $R_B(t) \sim t^{1/3}$ [14].

Lifshitz-Slyzov Argument Modified to Critical Volume Fractions in Systems Near a Wall

Suppose that the A/B interfaces adjacent to the wetting layer are more highly curved than in the bulk because of the mechanics leading to biased lateral growth. There will then be two length scales to consider, namely the two radii of curvature, R_S and R_B, where $R_S \ll R_B$. The local chemical potential field near the wall scales as $\sigma/NR_S(t)$ but variations in this field occur over much longer distances, R_B, since gradients sample regions on order of the domain size. The lateral growth of domains near the surface should then scale as

$$\frac{dR_S(t)}{dt} \sim \frac{\sigma}{R_S(t)R_B(t)} \quad . \tag{2}$$

If we assume that on the time scale appropriate to the growth of the smaller scale features represented by R_S, the larger length scale R_B is growing slowly and, by comparison, is effectively frozen, then Eqn. (2) gives the power law growth $R_S(t) \sim t^{1/2}$ correct to order $\sigma/R_B(t)$. This different scaling law is simply a result of the geometric observation that during phase separation, the less wetting A phase will tend to form more elongated domains pressed up against the wetting B phase and this enhanced curvature will speed up the coarsening process. As we alluded earlier, the exponent measured for the slow bulk mode shown in Fig. 2 of Ref. 1 corresponding to R_B seems to be less than 1/3 except for the shallowest quench. If significant, this observation satisfies even better the condition that R_B is more slowly varying than R_S. It is not clear how one can experimentally measure this different power law near the surface. The scattering intensity is proportional to the scattering volume and in the systems so far studied, the surface to volume ratio is small which would make it very difficult to detect a slightly different power law near the surface. The process of coalescence to be described below may be an indirect measurement of this different power law near the surface.

The argument leading to $R_S(t) \sim t^{1/2}$ 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, since the phase separation process proceeds more slowly and the interfacial tension is lower, the surface curvature will not be as fully developed and the system should behave more isotropically, leading to a growth exponent closer to 1/3. On the other hand, for the deepest quenches, the phase separation occurs very quickly, the interfacial tension is higher and the A/B interfaces near the wall should be well developed and highly curved leading to an exponent for interface growth closer to 1/2. Monte Carlo simulations of the square lattice Ising model with a wall potential attracting one the phases can be useful in settling this issue of whether the bulk interface growth exponent of 1/3 can be increased to 1/2 in the case of the growth of non-wetting domains coarsening against a wetting layer.

EFFECT OF COALESCENCE ON DOMAIN GROWTH EXPONENT

Given that the *individual* non-wetting domain growth exponent is expected to scale as $R_S(t) \sim t^{\alpha}$ where $1/3 \leq \alpha \leq 1/2$, we now indicate how domain coalescence near the wall will increase this exponent by a factor of three. The pheonomenom of 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 [15, 16]. 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 three times as large as the individual growth radius. The relationship is strictly a consequence of the geometrical constraint imposed by having a 3D droplet growing on a 2D substrate.

The condensation problem involves liquid droplets bounded on one side by a solid and on the other by a supersaturated vapor. The system of interest to us involves instead the growth of two viscous interconnected structures. Coalescence of two A domains will involve squeezing fluid of phase B from the region inbetween the approaching domains. We expect this process to lead to a

slightly slower growth law than we predict below. Calculations paralleling those of Siggia [13] for hydrodynamic interactions like droplet deformation and ensuing internal circulations which can occur during coalescence can be performed but previous investigation of these retardation effects indicate that the hard sphere results capture the essential physics. Also, the convoluted domains undergoing coalescence do not resemble spherical droplets 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 nonethless since we are only interested in the temporal power laws derived from the similarity solution and all geometrical factors can be ignored.

We consider domains of the A phase with preferential growth parallel to the wall whose surfaces ever so often come into contact to merge and form a single larger domain. During this process, the average domain size increases while the number of domains decreases. We define the surface domain size distribution function, $\psi(R(t),t)$ to be the number density of domains of size $R(t)$ of phase A coarsening against the wetting layer of phase B. The domains parameterized by $R(t)$ need not have a circular cross-section but it is necessary that the domains retain a fixed three-dimensional shape during growth such that the size is defined by only one parameter. Two domains are assumed to fuse instantaneously upon contact since the time scale, $\tau_{fusion} \sim \eta R/\sigma$, is much shorter than the time scale for growth by diffusion $\tau_{diffusion} \sim R^2/D$, where η is the viscosity, D the cooperative diffusion constant and σ the interfacial tension [17]. In the simplest model, we consider only binary collisions with no domain correlations. Let $P(R_1,R_2)$ represent the probability for coalescence per unit area per unit time of two domains of size R_1 and R_2. The probability distribution function obeys a rate equation of the form

$$\begin{aligned}\frac{\partial\psi}{\partial t} &= -\frac{\partial\psi}{\partial R}\frac{dR}{dt} + \frac{1}{2}\int P(R_1,R_2)\delta[({R_1}^3+{R_2}^3)^{\frac{1}{3}} - R]dR_1dR_2 \\ &\quad -\int P(R_1,R)dR_1. \end{aligned} \tag{3}$$

where the first term represents a change in ψ due to individual domain growth, the second (gain) term for coalescences producing a domain of size R, and the third (loss) term for coalescence with a domain of size R. The probability of coalescence is defined as $P(R_1,R_2) = A(R_1,R_2)\psi(R_1)\psi(R_2)$ where the collision kernel, A, represents the number of encounters per unit area per unit time. We assume the domains are immobile and collisions are strictly caused by the increased surface area due to individual domain growth. For coalescence in a plane, we imagine a "circle" of radius r centered about a domain of size R_1 such that any other domain entering this region of coagulation will be instantly bonded to the first. The collision probability is therefore directly proportional to the perimeter associated with the distance of closest approach $r \approx R_1 + R_2$, as well as the flux of material crossing this perimeter, which for binary collisions is proportional to the relative velocity of approach $d(R_1+R_2)/dt$. This leads to

$$A(R_1,R_2) = (R_1+R_2)\frac{d}{dt}(R_1+R_2) \tag{4}$$

where for simplicity all geometrical factors are eliminated.

We introduce the n-th moment of the distribution function:

$$S_n = \int R^n\psi(R,t)dR \tag{5}$$

such that the total number of domains against the substrate is S_o, the average domain size is S_1/S_o, the total area is proportional to S_2 and the total volume to S_3. Recognizing that the collision integral is symmetric, we seek a similarity solution to the equation for dS_n/dt of the form

$$\psi(R(t),t) = t^{-\delta}\psi_o(z) \tag{6}$$

where the dimensionless variable $z = t^{-\gamma}R(t)$. The exponent γ reflects growth through coalescence so that by definition, the average domain size $< R(t) >$ scales as $t^{-\gamma}$. The self similar solution requires that $\delta = 3\gamma$.

The instantaneous coalescences are volume conserving and therefore the only increase in total volume of the A domains occurs through diffusion. We showed previously that the individual growth is governed by the power law $R \sim t^{\alpha}$. If the domains grow isotropically, so that the volume of the domains scales as $t^{3\alpha}$, then

$$\int R(t)^3\psi(R(t),t)dR(t) \sim t^{3\alpha}, \tag{7}$$

which gives the relation $\gamma = 3\alpha$. This relationship, which is independent of the particular mechanism governing individual growth, states that the process of coalescence leads to a power law for the *average* domain size which is three times the exponent associated with the *individual* growth law. In our case, the individual domains are expected to grow as t^{α} for $1/3 \le \alpha \le 1/2$ while the average domain growth including coalescence should therefore scale as $t^{3\alpha}$. Returning to our earlier notation, this gives an exponent, β, for the surface growth including coalescence with values ranging between 1 and 1.5, with the higher exponents associated with the deeper quenches. This range of values for the surface growth has recently been seen [3].

PREDICTIONS AND CONCLUSION

Based on this model, we predict the following behavior. The zeroth moment defines the number of non-wetting A domains, $N_A(t)$, growing along the 2D surface. Our scaling predicts that $N_A(t) \sim t^{-6\alpha}$ so that for shallow quenches we expect t^{-2} while for deeper quenches we expect t^{-3}. Our original scaling ansatz assumes that the coarsening morphology is self similar which implies that the surface area coverage (appropriately scaled by R_S) is constant, which seems verified experimentally. Our interpretation also 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 $I_{max} \sim {q_{max}}^{-2}$ as seen experimentally for the fast surface signal. Finally, the model applies to binary mixtures in general, be they simple binary fluids or polymer mixtures.

The appearance of the large exponent reflecting surface growth is in disagreement with the exponent measured in another observation [4] of phase separating domains growing near a surface. This discrepancy has been attributed [1] to the fact that earlier experiments were conducted at dimensionless times (i.e. time is rescaled by the correlation length derived from linear stability analysis and the effective diffusion constant) greater than 1000, while the later experiments were conducted for times between 50 and 1000. After reviewing the data by Guenoun et al we suggest another possible explanation for this discrepancy. Fig. 3 of Ref. [4] represents the scaled wavenumber, K_λ^*, as a function of dimensionless time corresponding to the distance between the centers of the domains constituting the less wetting phase and K_e^* corresponding to the thickness of the macroscopic wetting layer against the quartz substrate. The measured points, made from hand measurements off of video images, gave $K_\lambda^* \sim t^{0.64\pm0.15}$ and $K_e^* \sim t^{0.56\pm0.18}$. Our inspection of the data reveals some systematic oscillation in the curves.

There appears to exist two different power laws for each curve, one associated with a fast dropoff in the wavevector (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 -3/2 over the portions of the data that show the sharp dropoff. There is not enough data presented to fit the flatter portions of the two curves. The curve for K_e^* follows nicely the behavior shown in K_λ^*. It appears that each time there is a coalescence event, there is a corresponding increase in the thickness of the wetting layer. This behavior is to be expected since a coalescence event must involve squeezing fluid out from inbetween the non-wetting domains, and some of this expelled fluid must go into increasing the thickness of the wetting layer. We suggest that with more available data, the average slope would have been weighted more toward the exponent associated with coalescence, leading to a power much higher than 0.64, bringing the value in line with the more recent experiments [18].

Though the coupled mechanism proposed above seems to offer a consistent explanation for the range of quench dependent growth exponents measured experimentally, we have been exploring another model strictly based on growth by diffusion alone which also seems to be giving exponents larger than one [11]. As first published, Wiltzius and Cumming seemed to suggest that the fast growth signal is confined to a planar region whose thickness is on the order of 10 microns. Fig. 3 of Ref. [1] in which the peak position is plotted against the maximum intensity seems to suggest that the fast signal is associated with a three dimensional structure of constant thickness. The exponents one derives depend somewhat on the multiparameter fit used to deconvolute the bulk and surface signal and therefore, the separation in dimensions as plotted in Fig. 3 may be misleading. Nevertheless, it is an intriguing possibility.

To investigate the consequences of such two-dimensional growth, we have modelled the growth of an isolated wetting domain by considering an absorbing disk of constant thickness toward which species diffuse from a supersaturated liquid. Our analytic and numerical solutions show that when the concentration field can equilibrate faster than the disc grows laterally, the radius of the disc increases linearly in time. This is strictly a reflection of the geometric constraint restricting growth in the vertical direction (i.e. the thickness of the disc). At later times, the fully time dependent solution reveals that the concentration field cannot adjust as quickly as the disc grows, producing even faster radial growth with exponents in excess of one. Further work is needed to decide whether this conceptually simpler model is able to capture the essential physics as measured experimentally. In either case, the fact that a nearby substrate can enhance domain growth to such a degree is a problem not before considered and one in which experiments can help guide modelling efforts.

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