Phase Separation Dynamics in a Concentration Gradient

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Abstract

Phase separation dynamics with an initially non-uniform concentration are studied. Critical and off-critical behavior is observed simultaneously. A mechanism for an expanding phase separated region is demonstrated and the time dependence of the concentration is determined. The final equilibrium state consists of a planar interface separating one phase from the other. The evolution to this state is characterized by an experimentally observable flux, $j$, crossing this interface. We find that $j \sim t^{-2/3}$ if patterns are formed in the bulk and $j \sim t^{-1/2}$ if the bulk remains homogeneous. The results are explained in terms of scaling arguments which are confirmed numerically.
Phase separation dynamics of a binary mixture is a prototype nonequilibrium process exhibiting features such as domain growth, front propagation, pattern formation and pattern selection [1–3]. In a typical experiment, a binary mixture in the homogeneous phase is rapidly quenched to inside the coexistence curve. For a near critical quench convoluted domains of each component are formed, while in an off-critical quench, droplets of the minority phase form within the majority phase background. The phase separation process exhibits dynamical scaling and the characteristic domain size, $R$, usually grows as a power law in time. If the dynamics conserves the order parameter and hydrodynamics is irrelevant, $R(t)$ grows as $t^{1/3}$ at late times [4,5].

Usually critical and off-critical quenches occur separately. However, if the initial state is inhomogeneous, these processes can be concurrent. For example, in the binary liquid experiments of Jayalakshmi et al., the fluid was prepared with a linear gradient concentration profile [6]. A spinodal decomposition region was observed in the middle of the cell with slowly expanding nucleation regions on either side of the central region [7]. Kolb et al. performed simulations of the kinetic Ising model using both a linear gradient profile and a step function profile as the initial states [8]. Their results were interpreted using gradient percolation theory and they concluded that the concentration profile does not change with time.

In this letter we study phase separation with inhomogeneous initial conditions via a numerical integration of the time-dependent Ginzburg-Landau equation for a conserved field (the Cahn-Hilliard equation) [9]. We discuss an additional mechanism for the expansion, with time, of the area in which phase separation has occurred. We show that the kinetic Ising model simulations [8] describe early time behavior and follow the change in the concentration profile with time. However, since our method is very effective in obtaining the long time behavior [9], our emphasis, will be on the late stage dynamics not discussed previously. To reach the final equilibrium configuration of the two co-existing phases separated by a planar interface, mass must be transferred from one side of the system to the other. We find that the mass current density, $j$, behaves as $j \sim t^{-2/3}$ if patterns are formed in the bulk after the
quench and \( j \sim t^{-1/2} \) if the bulk remains homogeneous. The results are explained in terms of scaling arguments based on, in the first case, the formation of droplets, and, in the latter case, diffusion. We confirm the scaling assumptions numerically.

We describe the phase separation dynamics using the Cahn-Hilliard equation,

\[
\frac{\partial}{\partial t} c(\mathbf{r}, t) = \nabla^2 \frac{\delta F(\{c\})}{\delta c(\mathbf{r}, t)} = \nabla^2 \mu(\mathbf{r}, t),
\]

(1)

where \( c(\mathbf{r}, t) \) is the deviation of the concentration from its critical value, \( F[c] \) is the Ginzburg-Landau \( c^4 \) free energy. The local chemical potential, \( \mu \), is then

\[
\mu(\mathbf{r}, t) = \frac{\delta F(\{c\})}{\delta c(\mathbf{r}, t)} = -c(\mathbf{r}, t) + c(\mathbf{r}, t)^3 - \nabla^2 c(\mathbf{r}, t).
\]

(2)

Here \( c, \mathbf{r} \) and \( t \) are scaled to set all coefficients to unity \[10\]. We assume a deep quench so that an additive noise term in Eq. (1) can be discarded. Therefore, any phase separation must be triggered by randomness in the initial condition \[5\].

We numerically integrated Eq. (1) using an Euler discretization on an \( L_x \times L_y \) lattice with mesh size \( \Delta x = \Delta y = 1.0 \) and time step \( \Delta t = 0.01 \). Periodic boundary conditions are used in the \( x \)-direction and reflecting b.c. in the \( y \)-direction (‘cylindrical symmetry’) \[11\]. Two types of initial conditions are examined. We consider a linear gradient profile,

\[
\frac{\mathbf{r}}{L_y} + \xi(\mathbf{r}),
\]

(3)

where \( \mathbf{r} \equiv (x, y) \), \( c_0 \) is the absolute maximum of \( c \) and \( \xi(\mathbf{r}) \) is an uncorrelated random variable with standard deviation \( \Delta(y) \). In addition, we also consider a step function for the initial condition, i.e.,

\[
\frac{\mathbf{r}}{L_y} \theta(y - \frac{L_y}{2}) - \frac{c_0 \theta(y - \frac{L_y}{2}) + \xi(\mathbf{r})},
\]

(4)

where \( \theta \) is the step function. Such an initial condition would be appropriate if the system is allowed to phase separate and equilibrate and then quenched to another point inside the coexistence curve.

In Refs. \[6\] and \[8\], it was assumed that the only effect of the concentration gradient was to change the local average concentration, \( \bar{c}(y) \). The fact that the region in which phase
separation has occurred grows with time was interpreted to be because the timescale for phase separation increases with increasing deviation from the critical concentration \( [6] \). That is, inside the spinodal, the linear growth timescale diverges as \( \bar{c}(y) \) approaches the mean field spinodal while, outside the spinodal, the nucleation timescale diverges as \( \bar{c}(y) \) approaches the coexistence value. However, there is also a second possibility. Phase separation in the region where \( \bar{c}(y) \approx 0 \) (near the critical concentration) may serve as a seed for phase separation in the rest of the system. That is, the time at which phase separation occurs is not determined by the local \( \bar{c} \) but by the fact that phase separation has occurred in an adjoining region. To test for this possibility we used a linear gradient profile (Eq. (3)) with the initial randomness restricted to a small strip in the middle of the system. Specifically, \( \Delta(y) = 0.01 \) for \( 0.45L_y < y < 0.55L_y \) and \( \Delta(y) = 0 \) otherwise. Any phase separation outside the middle strip is therefore initiated from this strip.

Figure 1 shows the patterns formed after such a quench with \( c_0 = 0.8 \). Immediately after the quench a convoluted structure similar to that for a critical quench is formed in the central region. There are well-defined boundaries within which phase separation has occurred and outside which it has not. The phase separated region grows leaving behind a droplet-like structure \([12]\). This zone continues to grow until it reaches where the local concentration is of order the mean field spinodal, \( c \approx c_{sp} = \pm 1/\sqrt{3} \). For intermediate times, a convoluted interface exists in the middle, separating regions of majority plus phase from that of majority minus phase. This interface becomes smoother with time but does not become planar during our simulations. Even at \( t = 6400 \), it has some curvature correlated with the remaining droplets.

We repeated the experiment with initial randomness over the whole system. Very similar behavior was found with the phase separated region expanding at about the same rate as before. Therefore we conclude that, even for uniform randomness, the time at which phase separation occurs is determined by phase separation in a neighboring region rather than there being uniform phase separation (based on the local concentration) over the entire system \([13]\). Which of these two mechanisms dominate depends on the relative magnitudes.
of the initial concentration gradient, the initial randomness and thermal noise. Elucidating this dependence should prove interesting but will not be done here.

Figure 2 shows the concentration profile averaged in the $x$ direction, $\bar{c}(y, t) = L_x^{-1} \int_0^{L_x} dx \ c(r, t)$. There is no change in the profile at early times. However, with increasing time, $\bar{c}(y, t)$ approaches its bulk equilibrium values of $\pm 1$ first at the boundaries of the system (where $\bar{c}(y, 0)$ is in the nucleation regime). This equilibrium region invades the phase separated regions very slowly since the invasion requires the elimination of droplets. The Ising model simulations did not observe this slow change in $\bar{c}(y, t)$ due to the smaller systems and times used [8].

Significantly different behavior was found for the step function initial condition (Eq. (4)). Figure 3 shows the patterns obtained with $c_0 = 0.5$ and $\Delta(y) = 0.1$ for all $y$. Although the central interface is unstable at very early times due to the flux across it (the Mullins-Sekerka instability) [14], it rapidly becomes planar since the flux decreases rapidly with time. Droplets then emerge everywhere except in a ‘depletion’ region near the central interface. Both the droplet size $R(t)$ and depletion region thickness, $L_D(t)$, grow in time. A plot of $\bar{c}(y, t)$ (Fig. 4) also show the substantial difference between the two initial conditions. Here $\bar{c}(y, t)$ first approaches the equilibrium interface profile in the central region. The region in which $\bar{c}(y, t)$ is $\pm 1$ grows around the central interface and is precisely the depletion region seen in the patterns. Simulations with $c_0 = 0.65 > c_{sp}$ and $\Delta(y) = 0.01$ were also performed. In this case, no droplets were formed because fluctuations are not strong enough and one only observes the planar central interface.

Therefore, for $c_0 < c_{sp}$, one of the dominant late stage processes is the growth of droplets. However, since the final equilibrium state is the two coexisting phases separated by a planar interface, therefore there must also be a macroscopic flux transferring mass across the central interface. (In fact, the total area occupied by the droplets decreases even though the characteristic size is increasing.) Therefore a measure of the approach to the final equilibrium is the total mass transferred per length, $m(t)$. 
\[ m(t) = \frac{1}{L_x} \left( \int_{L_y/2}^{L_y} dy - \int_0^{L_y/2} dy \right) \int_0^{L_x} dx \left[ c(r, t) - c(r, 0) \right], \]
\[ = 2 \int_0^t dt' \, j(t'), \quad (5) \]

where \( j(t) \) is the average current density across the middle of the system,
\[ j(t) = -\frac{1}{L_x} \int dx \, \frac{\partial}{\partial y} \mu(r, t) \bigg|_{y=L_y/2}. \quad (6) \]

This quantity can be measured directly. However, it may be experimentally simpler to examine a first order transition in which the motion of the domains are determined by the rate at which heat is removed. In this case the thermal current is analogous to \( j(t) \) discussed above.

Figure 5 shows \( j(t) \) for step function initial conditions with \( c_0 = 0.5 \) and \( c_0 = 0.65 \). For \( c_0 = 0.65 \) we find \( j(t) \sim t^{-1/2} \) for all times. At early times, \( j(t) \) for \( c_0 = 0.5 \) is very similar. However, at \( t \approx 100 \), droplets begin to appear and there is a rapid decrease in the current density. There is a crossover to the late time behavior, \( j(t) \sim t^{-2/3} \), which seems to begin when the local equilibrium is established. For finite \( L_y \), there is a further drop in the current density when the last bubble disappears. This last time depends on \( L_y \), for \( L_y = 64 \), the final regime begins at \( t \approx 3000 \).

To understand the behavior of \( j(t) \), we consider the chemical potential \( \mu \) which, in contrast to \( c(r, t) \), is continuous on all lengthscales. If \( c_0 > c_{sp} + \Delta \) no phase separation occurs in the bulk phases. The dynamics are effectively one-dimensional (see Fig. 3). Except at the central interface, we can expand \( \mu \) as \( \mu = 2\delta c + \mathcal{O}(\delta c^2) \) where \( c = \pm 1 + \delta c \). (The sign depends on the which side of the interface one is on.) The change in \( c(y, t) \) occurs first near \( y = 0 \) so the appropriate boundary conditions are \( \mu(y = \pm \infty, t) = \pm \mu_{\infty} \equiv \mp c_0(1 - c_0^2) \) while, local equilibrium gives \( \mu(y = 0, t) = 0 \). Substituting \( \delta c \approx \mu/2 \) into the Cahn-Hilliard equation gives,
\[ \frac{\partial \mu}{\partial t} = 2 \frac{\partial^2 \mu}{\partial y^2}. \quad (7) \]

Therefore this regime is diffusion controlled [15]. The asymptotic current density, \( j(t) = \)
\[- \partial \mu(y, t)/\partial y|_{y=0}, \text{ is then } j(t) = -\mu_\infty/\sqrt{2\pi t} \text{ in agreement with our numerical results (for } c_0 \text{ near 1).} \]

The above analysis no longer holds if patterns are present. The dynamics are no longer one-dimensional and the droplets are important (see Fig. 3). Figure 4 shows that most of the variation in \(\bar{c}(y, t)\) occurs within the depletion width, \(L_D(t)\), while in the bulk, the patterns are independent of \(y\). The growth of the droplets in the bulk phases is that of an off-critical quench [12] with \(R \sim t^{1/3}\) [4, 5, 12]. Therefore, \(\mu_\infty\) must be time dependent with local equilibrium giving \(\mu_\infty \sim 1/R \sim \mp t^{-1/3}\) [16]. To complete the picture we need the behavior of \(L_D(t)\). In principle, \(L_D(t)\) may grow with a dynamic exponent different from \(R(t)\). However, results for the Cahn-Hilliard equation near a wall shows the exponents are the same in both parallel and perpendicular directions [17]. Therefore we assume that \(L_D(t) \sim R(t) \sim t^{1/3}\) and the asymptotic current density becomes

\[ j(t) \sim \frac{|\mu|}{L_D(t)} \sim t^{-2/3}, \tag{8} \]

in agreement with our numerical results.

If our assumptions hold, the chemical potential averaged over \(x\) has the scaling form

\[ \mu(y, t) = t^{-1/3} g(y/t^{1/3}). \tag{9} \]

Figure 6 shows the scaling function, \(g(z)\), for times from \(t = 400\) to \(t = 6400\). In agreement with our discussion, most of the variation in \(\mu(y, t)\) is in the depletion region and approaches time-dependent bulk values outside it. The collapse of \(g(z)\) is reasonable indicating that the scaling form of \(\mu(y, t)\) is correct and that our arguments for \(j(t) \sim t^{-2/3}\) are valid.

In summary, we examine phase ordering dynamics for constant gradient and step function initial conditions. We demonstrate an additional mechanism for the expanding phase separated region observed in experiments. We discuss how the concentration profile changes with time. We measure the flux characterizing the evolution to the final equilibrium state. Its asymptotic behavior is obtained and understood in terms of scaling arguments.
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FIGURES

FIG. 1. Concentration patterns for a constant gradient initial condition with $c_0 = 0.8$, $L_x = 256$, $L_y = 512$ and $\Delta(y) = 0.01$ for $0.45L_y < y < 0.55L_y$.

FIG. 2. The concentration profiles for parameters in Fig. 1 (averaged over five configurations). The equilibrium values $\bar{c}(y, t) = \pm 1$ are first reached at the boundaries. The oscillations at late times are because the bubbles arrange in rows next to the line where $\bar{c}(y, 0) = c_{sp}$.

FIG. 3. Concentration patterns for a step function initial condition with $c_0 = 0.5$, $\Delta(y) = 0.1$ and $L_x = L_y = 512$.

FIG. 4. The concentration profiles for the parameters in Fig. 3 (averaged over 5 configurations).

FIG. 5. $j(t)$ vs. $t$ in one and two dimensions for step function initial conditions. The solid line is $j(t) \sim t^{-2/3}$. For $c_0 = 0.65$, $j(t) \sim t^{-1/2}$.

FIG. 6. Scaled chemical potential, $g(z) = t^{1/3} \mu(zt^{1/3}, t)$, for the parameters in Fig. 4. The unscaled $\mu$ is shown in the inset.