Dynamics of Phase Separation under Shear: A Soluble Model

N. P. Rapapa and A. J. Bray
Department of Physics and Astronomy, The University, Manchester M13 9PL, UK
(March 24, 2022)

The dynamics of phase separation for a binary fluid subjected to a uniform shear are solved exactly for a model in which the order parameter is generalized to a $n$-component vector and the large-$n$ limit taken. Characteristic length scales in directions parallel and perpendicular to the flow increase as $(t^2/\ln t)^{1/4}$ and $(t/\ln t)^{1/4}$ respectively. The structure factor in the shear-flow plane exhibits two parallel ridges as observed in experiment.

The dynamics of phase separation under shear has attracted considerable theoretical, experimental and simulational attention in recent years. In the absence of shear, the dynamics of phase separation is now quite well understood. Domains of the two equilibrium phases are formed, and coarsen with time in a manner well-described by a dynamical scaling phenomenology with a single growing length scale $L(t)$ which generally grows as a power law in time, $L(t) \sim t^a$. The structure factor is spherically symmetric, with a maximum at wavevector $k_m \sim L^{-1}$. For binary fluids, the exponent $a$ takes different values depending on the dynamical regime under study. In order of increasing time, there are ‘diffusive’ ($a = 1/3$), ‘viscous hydrodynamic’ ($a = 1$) and the ‘inertial hydrodynamic’ ($a = 2/3$) regimes. The crossover between these regimes is determined by the fluid properties (viscosity, density). Here we will focus on the diffusive regime, in which hydrodynamic effects can be neglected. In the absence of shear, phase separation is described by the Cahn-Hilliard equation for the order-parameter field $\phi(r, t)$, namely

$$\partial_t \phi = -\nabla^2 (\nabla^2 \phi + \phi - \phi^3).$$

(1)

For a critical mixture quenched into the two-phase region from the homogeneous phase, an appropriate initial condition is a Gaussian random field with zero mean and short-range correlations: $\langle \phi_i(r, 0) \phi_j(r', 0) \rangle = \Delta \delta_{ij, \delta} \delta(r - r')$.

This Letter we present the first exact solution for a system phase-separating under shear, by solving (1) in the limit $n \to \infty$. We obtain characteristic length scales $L_x \sim k_m^{-1} \sim (t^2/\ln t)^{1/4}$, $L_y \sim k_m^{-1} \sim (t/\ln t)^{1/4}$, and $L_z \sim k_m^{-1} \sim (t^3/\ln t)^{1/4}$. These are extracted from the structure factor, $S(k, t)$ which has four maxima, located at $k = \pm(k_{mx}, -k_{my}, \pm k_{mz})$. Thus the rotational symmetry of the zero-shear limit is completely broken. In the $k_z = 0$ plane there are two maxima terminating two long parallel ridges as observed in experiment. The structure factor exhibits multiscaling, rather than simple scaling, but this is presumably an artifact of the large-$n$ limit, as in the zero-shear case. At the end of the paper we conjecture how the results will be modified for the scalar order parameter appropriate to binary mixtures.

In the limit $n \to \infty$, one can replace $(\phi')^2/n$ in (1) by its mean in the usual way, leading to a self-consistent linear equation. After Fourier transformation this reads

$$\frac{\partial \phi_k}{\partial t} - \gamma_k \nabla_x \phi_k = -k^2 \gamma_k - a(t) \phi_k,$$

(2)

where $\phi$ is (any) one component of $\phi$, and $a(t) = 1 - (\phi')^2$.

The same equation was studied in a recent Letter by Corberi et al. [14], where it was regarded as a ‘self-consistent one-loop’ approximation to the scalar version of (1). These authors, however, did not solve the equation analytically, but rather integrated it numerically (in two space dimensions). As a result they were unable to access the asymptotic ($t \to \infty$) behavior which is the main focus of the present work. In particular we do not find the oscillatory large-time behavior that Corberi et al. conjectured from their numerical results.

Equation (2) can be solved via the change of variables $(k_x, k_y, k_z, t) \rightarrow (k_x, \sigma, k_z, \tau)$, where $\sigma = k_y + \gamma k_z t$. The left-hand side of (2) then becomes $\partial \phi_k / \partial \tau$, and the equation can be integrated directly to give, after transforming back to the original variables, $\phi_k(t) = \phi_k(0) \exp(b(t), k)$, where

$$f(k, t) = -\frac{k_x^2 + k_z^2}{3} \frac{2(k_x^2 + k_z^2)}{3\gamma k_x} ((k_y + \gamma k_z t)^3 - k_y^3)$$

$$- \frac{1}{5\gamma k_x} ((k_y + \gamma k_z t)^3 - k_y^3)$$

$$+ (k_x^2 + k_z^2 + (k_y + \gamma k_z t)^2) b(t)$$

$$- 2\gamma k_x(k_y + \gamma k_z t) \epsilon(t) + \epsilon^2 k_z^2 \epsilon(t),$$

(3)

with $b(t) = f_0^t dt' a(t'), c(t) = f_0^t dt' t a(t'),$ and $c(t) = f_0^t dt' t^2 a(t').$

The next step is to determine $a(t)$ self-consistently, using its definition: $a(t) = 1 - (\phi')^2 = 1 - \sum_k S(k, t)$, where $S(k, t) = \langle \phi_k(t) \phi_{-k}(t) \rangle$ is the structure factor. The momentum sum can be evaluated for large $t$ using the
method of steepest descents. To simplify the analysis we make the following ansatz, which will be justified a posteriori. Naive power counting applied to (3) suggests characteristic length scales \(L_y \sim t^{1/4}\), and \(L_x \sim t^{5/4}\), where the dominant \(k_x\)-dependence comes from the shear term, and that \(a(t) \sim t^{-1/2}\). This suggests that only the \(k_x\) terms multiplied by \(\gamma\) in (3) survive in the ‘scaling’ limit. In fact we will find that the naive power counting result is modified by logarithms, but the above conclusion still holds. Guided by the \(\gamma = 0\) result, we make the ansatz \(a(t) \sim (\ln t/t)^{1/2}\) for \(t \to \infty\). Then, to leading logarithmic accuracy, \(b(t) \sim (t \ln t)^{1/2}\), \(c(t) \to t b(t)/3\), and \(c(t) \to t^2 b(t)/5\). Inserting these results in (3), and making the change of variable

\[
\gamma k_x = \sqrt{\frac{b}{t}} u, \quad \gamma k_y = \sqrt{\frac{b}{t}} v, \quad \gamma k_z = \sqrt{\frac{b}{t}} w
\]

(4) gives

\[
S(k, t) = \Delta \exp \left(2 \frac{b^2}{t} F(u, v, w)\right)
\]

(5)

\[
F(u, v, w) = \frac{1}{5u} ((u + v)^5 - v^5) + \frac{8}{15} u^2 + \frac{4}{3} u v + v^2
\]

\[
- \frac{2}{3} w^2(u^2 + 3u v + 3v^2) + u^2 - w^2, w
\]

(6)

where contributions to \(F\) which vanish as \(t \to \infty\) (at fixed \(u, v, w\)) have been dropped.

The self-consistency equation for \(a(t)\) reads

\[
1 - a(t) = \int \frac{d^3k}{(2\pi)^3} S(k, t)
\]

and \(\Delta = \Delta b^{3/2}

\[
= \frac{\Delta b^{3/2}}{(2\pi)^3} \gamma t^{5/2}
\]

\[
\times \int du dv dw \exp \left(2 \frac{b^2}{t} F(u, v, w)\right).
\]

(7)

Since \(b^2/t\) grows like \(\ln t\) by assumption, the triple integral can be evaluated by steepest descents for large \(t\). The complete set of stationary points \((u, v, w)\) is listed in Table 1, together with their type (maximum, minimum, saddle point) and the corresponding values of \(F\). The stationary points with \(w = 0\) are also stationary points of the two-dimensional (2D) theory, and their types in the \((u, v)\) plane are listed separately. The \(w = 0\) structure of \(S(k, t)\) is relevant for light scattering with the incident beam normal to the \(xy\)-plane.

The maximum value of \(F\), \(F_m = 23/60\), occurs at four points in \(uvw\)-space (labeled \(f\) in Table 1), corresponding, via (4), to four points in momentum space. The integral in (6) can now be evaluated by steepest descents. Since \(a(t)\) in (4) vanishes (like \((\ln t/t)^{1/2}\)) for \(t \to \infty\), it can be dropped to give

\[
1 = \text{const.} \frac{\Delta \gamma t b^{3/2}}{F_m b^2} \exp \left(2 \frac{F_m b^2}{t}\right),
\]

(8)

whence, to leading logarithmic accuracy,

\[
b(t) = \left(\frac{7}{8F_m} \ln t\right)^{1/2},
\]

(9)

finally justifying our original ansatz.

| Label | Position | Number | \(F\) | Value | Type (3D) | Type (2D) |
|-------|----------|--------|------|-------|-----------|-----------|
| a     | (0, 0, 0) | 1      | 0    | 0     | Min       | Min       |
| b     | \(±(2/\sqrt{3}, 0, 0)\) | 2      | 16/45 | .35556 | IS        | IMax      |
| c     | \(±(\sqrt{2} - 1/\sqrt{3}, -1/\sqrt{2}, 0)\) | 2      | (37 - 12\(\sqrt{6}\))/180 | .04225 | S2        | S         |
| d     | \(±(\sqrt{2} + 1/\sqrt{3}, -1/\sqrt{2}, 0)\) | 2      | (37 + 12\(\sqrt{6}\))/180 | .36885 | S1        | Max       |
| e     | \(±(0, 0, 1/\sqrt{2})\) | 2      | 1/4  | .25   | S1        | -         |
| f     | \(±(\sqrt{3}, -1/\sqrt{3}, 1/6)\) | 4      | 23/60 | .38333 | Max       | -         |

Table 1. Stationary points of \(F(u, v, w)\): Max = maximum, Min = minimum, S = saddle point (2D), Sn = saddle point of type \(n\) (the matrix of second derivatives has \(n\) positive eigenvalues), IS = ‘inflection saddle point’ (one positive, one zero, one negative eigenvalue), IMax = ‘inflection maximum’ (one zero, one negative eigenvalue).

From equation (3) we can define characteristic length scales for the three directions: \(L_x = \gamma (t^3/b)^{1/2} \sim \gamma (t^5/\ln t)^{1/4}\), and \(L_y = L_z = (t/b)^{1/2} \sim (t/\ln t)^{1/4}\), by setting \(u = k_x L_z\), \(v = k_y L_y\), and \(w = k_z L_z\). Finally the structure factor is given by \(S(k, t) = \Delta \exp[(2b^2/t)F(u, v, w)]\). Using (4) this can be recast as

\[
S(k, t) = \text{const.} (\ln V_s)^{3/2} V_s^{F(q)/F_m},
\]

(10)

where \(V_s(t) = L_x L_y L_z \sim \gamma t^{7/4}/(\ln t)^{3/4}\) is the ‘scale volume’ at time \(t\), and \(q = (k_x L_x, k_y L_y, k_z L_z)\) is the scaled momentum. The corresponding result for zero shear (in space dimension \(d\)) is \(S(k, t) = \text{const.} (\ln L)^{1/2} L^{d_0(q)}\), where \(L = (8t/\ln t)^{1/4}\), \(q = kL\), and \(d_0(q) = 2q^2 - q^4\). Equation (10) does not have a form consistent with conventional scaling, \(S(k, t) = V_s(t)f(q)\), but rather a form of ‘multiscaling’, as in the zero-shear case, where the power of the scaling volume \(V_s\) depends on the scaling variables. As in the zero-shear case, how-
ever, we anticipate that simple scaling will be recovered asymptotically for any finite $n$, and that the $\ln t$ terms will disappear from the length scales $[3]$. 

For the beam in the $y$ direction, the scattering intensity, $S(k_x,0,k_y,t)$, is determined by $F(u,0,w)$. Figure 2 is a contour plot of this function with the positions of the stationary points $(u,w)$ indicated. These are a minimum (labeled $a$) with $F = 0$, at $(0,0)$, a pair of saddle points $(b)$, with $F = 16/45$, at $(\pm 2/\sqrt{3},0)$, a second pair of saddle points $(c)$, with $F = 1/4$, at $(0,\pm 1/\sqrt{2})$, and four maxima $(d)$, with $F = 29/80$, at $(\pm 3, \pm 1)/2\sqrt{2}$. Currently available experimental data cannot resolve this structure. Instead a broadly elliptical scattering pattern is seen in the $(k_x,k_z)$ plane $[3]$, with the major axis along the $k_z$ direction, and the eccentricity increasing in time, as expected from the different growth rates (by a factor $t$) of $L_x$ and $L_z$. 

Finally, if the beam is parallel to the flow ($k_x = 0$), the shear term drops out of $[2]$. The scattering intensity then has full circular symmetry in the $(k_y,k_z)$ plane. 

From the asymptotic solution, the expressions derived by Onuki $[1]$ for the shear-induced contributions to the viscosity, $\Delta \eta = -(1/\gamma) \int [d^3 k/(2\pi)^3] k_z k_y S(k,t)$, and to the normal stress differences $\Delta N_1 = \int [d^3 k/(2\pi)^3] (k_y^2 - k_z^2) S(k,t)$, and $\Delta N_2 = \int [d^3 k/(2\pi)^3] (k_x^2 - k_y^2) S(k,t)$ may be easily evaluated. Since $S(k,t)$ is a sharply peaked function, the factors involving $k_x, k_y, k_z$ in the integrands can be replaced by their values at the peaks ($f$ in Table 1). Using also $\int [d^3 k/(2\pi)^3] S(k,t) = 1$ gives, asymptotically, $\Delta \eta \sim (b/\gamma^2 t^2) \sim (\ln t/t^3)^{1/2} \eta_0^{-2}$, $\Delta N_1 = (b/3t) \sim (\ln t/t)^{1/2}$, and $\Delta N_2 = (b/6t) = \Delta N_1/2$. 

FIG. 1. Contour plot of $F(u,v,0)$ showing approximate locations of the stationary points $a, b, c, d$ from Table 1. Contour lines for $F < -0.1$ are not shown.

FIG. 2. Contour plot of $F(u,0,w)$ showing approximate locations of the stationary points $a, b, c, d$ (see text). Contour lines for $F < -0.1$ are not shown.
We now compare our analytical results with the numerical solution of \( \frac{3}{2} \) by Corberi et al. \( \frac{4}{10} \) in two dimensions (the shear-flow, i.e. \( xy \) plane). Repeating our analysis for \( d = 2 \) is straightforward. The dominant stationary points are the two maxima labeled \( d \) in Table 1 and Figure 1. A two-dimensional steepest descent integration over the scaling variables \( u \) and \( v \) yields the self-consistency condition

\[
1 = \text{const.} \frac{\Delta}{\gamma t^d} \exp \left( \frac{2F_{m}^2 / t^2}{t} \right), \tag{11}
\]

instead of \( \frac{3}{2} \), where (from Table 1) \( F_{m}^2 (37 + 12\sqrt{6})/180 \), giving \( b(t) = (3t \ln t / 4F_{m}^2 )^{1/2} \) (to leading logarithmic accuracy) instead of \( \frac{3}{2} \). The structure factor is given by \( S(k, t) = \text{const.} (\ln A_s) A_s^{2D}(q) / V_{m}^{2D} \), where \( A_s = L_x L_y \) is the ‘scale area’, \( L_x = (t^3 / b)^{1/2} \sim \gamma (t^3 / \ln t)^{1/4} \), \( L_y = (t / b)^{1/2} \sim (t / \ln t)^{1/4} \), \( q = (k_2 L_x, k_3 L_y) \) is the scaled momentum, and \( F_{m}^{2D}(q) \) means \( F(u, v, 0) \), with \( u = k_{2} L_{x} \) and \( v = k_{3} L_{y} \). In other words, the 2D structure factor has an identical shape (shown in Figure 1) to the 3D structure factor with \( k_{3} = 0 \). The main difference is that the numerical values of \( F_{m} \) (0.38333...) and \( F_{m}^{2D} \) (0.35555...) are (slightly) different.

In their numerical results, Corberi et al. also find two ridge-like structures, but the ridges are terminated by two peaks whose relative heights oscillate in time, such that first one peak, then the other is the higher. They further speculate that these oscillations persist to late times and ‘characterize the steady state’. Since no oscillatory behaviour is found in the asymptotics of our analytical solution, we believe that the observed oscillations are slowly-decaying presymptomatic transients.

We conclude with some conjectures about the physically realistic case (for binary fluids in the diffusive regime) of a scalar order parameter. These are informed by our exact solution for \( n = \infty \), and by the way the \( n = \infty \) solution is known to be modified for scalar fields in the unsheared case \( \frac{3}{2} \). First we expect that, for any finite \( n \), the structure factor will exhibit asymptotic scaling of the form \( S(k, t) = V_{s} g(q) \), with \( V_{s} = \Pi_{i=1} L_{i} \) \( (i = x, y, z) \) and \( q_{i} = k_{i} L_{i} \), instead of the multiscaling form \( \frac{3}{2} \). As in the \( n = \infty \) case, we expect the growth of the characteristic scales for directions normal to the flow to obey the same power laws as in the unsheared case, i.e. for scalar fields, \( L_{y} \sim L_{z} \sim t^{1/3} \). The growth in the \( x \)-direction can then be deduced from the assumed scaling form for the structure factor; if we multiply the two terms on the left-hand side of \( \frac{3}{2} \) by \( \phi_{-k}(t) \), and average, the result \( L_{x} \sim \gamma t L_{y} \) follows immediately if we insert the scaling form for \( S(k, t) \) and assume both terms are of the same order in the scaling limit. This leads to the prediction \( L_{x} \sim \gamma t^{4/3} \). The shear-induced viscosity and normal stresses then scale as \( \Delta \eta \sim (\gamma L_{x} L_{y})^{-1} \sim \gamma^{-2} t^{-5/3} \), and \( \Delta N_{1,2} \sim 1 / L_{y}^{2} \sim t^{-2/3} \).

In the viscous hydrodynamic regime, where without shear \( L(t) \sim t \), the same heuristics suggest \( L_{y} \sim L_{z} \sim t \), \( L_{x} \sim \gamma t^{2} \) (with corresponding modifications to \( \Delta \eta \) and \( \Delta N_{1,2} \)). The predictions for the length scales are consistent with data on polymer blends \( \frac{3}{2} \), though it has been suggested \( \frac{3}{2} \) that a stationary state eventually develops for \( \gamma t \gg 1 \) due to a competition between stretching and breaking of domains.

As far as the shape of the structure factor is concerned, we expect the scaling function \( g(q) \) to be described, in broad terms, by \( \ln g(q) \sim F(q_{x}, q_{y}, q_{z}) \), where \( F(u, v, w) \) is given by \( \frac{3}{2} \), i.e. rather like the large-\( n \) theory but without the \( \ln V_{s} \sim \ln t \) factor multiplying \( F \). In particular, a contour plot of \( \ln g(q_{x}, q_{y}, 0) \) should look very similar to Figure 1. (However, the behaviour near \( q = 0 \) would be modified by the requirement that \( g(0) = 0 \), imposed by the conservation of the order parameter). We hope that these predictions will act as a spur to further experimental work.

We thank Caroline Emmott for useful interactions in the early stages of this work. This work was supported by EPSRC under grant GR/L97698 (AB), and by the Commonwealth Scholarship Commission (NR).

References:

1. A. Omuk, J. Phys.: Condens. Matter 9, 6119 (1997), and references therein.
2. C. K. Chan, F. Perrot, and D. Beysens, Phys. Rev. A 43, 1826 (1991).
3. A. H. Krall, J. V. Sengers, and K. Hamano, Phys. Rev. Lett. 69, 1963 (1992).
4. T. Hashimoto, K. Matsuzaka, E. Moses, and A. Onuki, Phys. Rev. Lett. 74, 126 (1995).
5. J. Gäger, C. Laubner, and W. Gronski, Phys. Rev. Lett. 75, 3576 (1995).
6. D. H. Rothman, Phys. Rev. Lett. 65, 3305 (1990).
7. P. Padilla and S. Toxvaerd, J. Chem. Phys. 106, 2342 (1997).
8. A. J. Wagner and J. M. Yeomans, preprint cond-mat/9904033.
9. A. J. Bray, Adv. Phys. 43, 357 (1994).
10. E. D. Sigia, Phys. Rev. A 20, 595 (1979).
11. H. Furukawa, Phys. Rev. A 31, 1103 (1985).
12. A. Coniglio and M. Zannetti, Europhys. Lett. 10, 575 (1989).
13. A. J. Bray and K. Humayun, Phys. Rev. Lett. 68, 1559 (1992).
14. F. Corberi, G. Gonnella, and A. Lamura, Phys. Rev. Lett. 81, 3852 (1998).