Phase ordering of two-dimensional symmetric binary fluids: a droplet scaling state

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The late-stage phase ordering, in \( d = 2 \) dimensions, of symmetric fluid mixtures violates dynamical scaling. We show however that, even at 50/50 volume fractions, if an asymmetric droplet morphology is initially present then this sustains itself, throughout the viscous hydrodynamic regime, by a ‘coalescence-induced coalescence’ mechanism. Scaling is recovered (with length scale \( t \sim t \)), as in \( d = 3 \)). The crossover to the inertial hydrodynamic regime is delayed even longer than in \( d = 3 \); on entering it, full symmetry is finally restored and we find \( l \sim t^{2/3} \), regardless of the initial state.

When a symmetric binary fluid is quenched below its critical temperature it will phase separate into domains. This initial stage of phase separation is diffusive; but in this letter we are concerned with the hydrodynamic stage of the process, which follows afterwards. The evolution equations can be taken [1] as the Navier-Stokes and the advective diffusion equations:

\[
\rho D_t \mathbf{u} = -\nabla P - \phi \nabla \mu_\phi + \eta \nabla^2 \mathbf{u} \tag{1}
\]
\[
D_t \phi = \nabla (M \nabla \mu_\phi) \tag{2}
\]

Here \( \mathbf{u} \) is the fluid velocity, \( D_t \) the material derivative, \( P \) pressure, \( \mu_\phi \) the chemical potential for the order parameter \( \phi \), \( \eta \) the viscosity, \( \rho \) the density and \( M \) an Onsager coefficient. As usual, \( \mu_\phi = \delta F/\delta \phi \) with \( F[\phi] \) a (symmetric) free energy functional; once the interfaces are sharp, the source term \( \sim \phi \nabla \mu_\phi \) in Eq. (2) is just the Laplace pressure of interfacial curvature [1].

These equations are nonlinear, but deterministic; thermal noise should be irrelevant at late times. The only source of noise is then in the initial condition, and it is often assumed that the physics is the same for all conditions without long-range correlations [1,2]. But we find below that the nonlinear dynamics are more subtle: for two dimensional 50/50 binary fluid mixtures of equal viscosity, the hydrodynamic coarsening depends very strongly on the topology of the sharp interfaces formed by the early time (short length-scale) physics, previously assumed irrelevant. Specifically, droplet morphologies evolve quite unlike bicontinuous ones: dynamical scaling, absent for bicontinuous states in \( d = 2 \) dimensions [3], is recovered for a new, self-sustaining droplet state. Such scaling requires that any averaged property of the system is invariant if all lengths are scaled by a single length scale \( L(t) \). Whereas at early times diffusive phase-ordering leads to \( L \propto t^{1/3} \) in both \( d = 2 \) and \( d = 3 \), scaling of interfacial curvatures with \( L \) implies that at later times the chemical potential obeys \( \mu_\phi \sim \sigma/L(t) \) where \( \sigma \) is the surface tension (computable from \( F[\phi] \)). Dimensional analysis of Eqs.1,2 then identifies two subsequent regimes, the viscous hydrodynamic (VH [4]) and the inertial hydrodynamic (IH [4]) in which the driving force is balanced by viscosity and inertia respectively [5].

There is good numerical evidence for this behavior in bicontinuous \( d = 3 \) mixtures [6]: allowing for a nonuniversal early time diffusive offset, and choosing the reduced unit of time as \( t_0 = \eta^3/\rho \sigma^2 = 1 \), one finds a universal scaling curve \( l(t) \) where \( l(t) = L(t) \rho \sigma/\eta^2 \) is the reduced coarsening length. Choosing \( L \equiv 2\pi \int S(k)dk / \int kS(k)dk \) with \( S(k) \) the density autocorrelator, one then finds that the viscous and inertial asymptotes are \( l = 0.07t \) and \( l = 0.9t^{2/3} \); these cross at \( t^* \approx 10^3 \), a large value (though formally still \( O(1) \) [7]).

In two dimensions, in contrast, the VH regime was recently found to violate scaling altogether [8]. Starting from a 50/50 bicontinuous state, a cascade of small droplets is left behind by the large connected domains as they coarsen; these droplets, which must coalesce in order to grow, evolve more slowly than the larger domains around them. Length measures defined \( (\ldots) \) from different moments of the structure factor do not scale. Furukawa [9] found, however, that the size of the largest domains does scale as \( l \sim t \) throughout VH; and that, in the IH regime, full scaling is recovered with \( l \sim t^{2/3} \).

For symmetric binary fluids, droplet morphologies usually arise for an asymmetric composition. Until recently these morphologies were held to give non-hydrodynamic phase ordering by either the evaporation-condensation mechanism or the Brownian coalescence of droplets, each of which has \( t^{1/3} \) growth [10,11]. But Tanaka [12] discovered that such droplet states can coarsen via a ‘coalescence induced coalescence’ (CIC) mechanism; Nicolaev et al. [13] considered this for some simplified \( d = 3 \) geometries, and predicted the recovery of a VH \( (l \sim t) \) growth regime mediated by CIC for \( \phi > 0.26 \) in \( d = 3 \).

In \( d = 2 \), droplet morphologies can, however, also arise in symmetric \( (50/50) \) quenches whenever there is asymmetry in the dynamics. This occurs, \( \ldots \), when the two components have different diffusivities so that \( M \) is strongly \( \phi \)-dependent [14]; or when one phase is viscoelastic [15]. In the first case, the evolution equation should approach that of a fully symmetric mixture on entering VH. In the second case (since the mean shear rate is of order \( \bar{l}/t \sim 1/t \)), one must wait until \( t \) exceeds the Maxwell time; this could still be early in VH [14]. In either case the dynamic asymmetry is then forgotten, \( \ldots \) that it has instilled local correlations in the “initial” condition for subsequent events. It is usual to argue that these correlations cannot influence the late time scaling states once the domain scale \( L(t) \) is larger than the original cor-
relation length; indeed, Bhattacharya et al. [3] thereby argued that viscoelastic phase separation could not lead to new scaling states. We now show that, in contrast to such expectations, a distinct CIC droplet scaling state does exist for a 50/50 quench, and survives throughout the VH regime.

We use a well-established lattice Boltzmann method [15] to simulate Eqs. 1, 2. We initialize each simulation with a droplet morphology, at 50/50 volume fraction, generated from a white-noise initial state using a separate viscoelastic lattice Boltzmann model [13]. (The initial droplets are at rest.) Thereafter the evolution equations are fully symmetric: the two fluids are Newtonian and have equal mobilities and viscosities. We choose parameters such that the phase ordering is dominantly hydrodynamic, ensuring that residual diffusion is negligible at the < 1% level [2]. The algorithm shows good isotropy for the shape of an equilibrium droplet [16], but some dynamic anisotropy is noticeable in the IH regime (visible in Figure 2). Reduced physical units \( l, t \) are defined as above, and nonuniversal (diffusive) time offsets for each simulation run calculated [2]. All the simulations shown here were performed on a 1024 \( ^2 \) lattice, but terminated at \( L \leq 256 \) to minimize finite size artifacts [2]. The surface tension is \( 10^{-2} \), the density is 2, and we varied the viscosity from 0.5 to 0.001 (all in lattice units).

We used three different length-scale measures \[ L^\# \, L^\circ \, L^\partial \], derived from the number of domains \( N \), the interface length \( L_I \) and the derivatives of the order-parameter \( \phi \):

\[
L^\# = \sqrt{\frac{\Lambda_x \Lambda_y}{N}} \quad L^\circ = \sqrt{2\pi \frac{\Lambda_x \Lambda_y}{L_I}} \quad L^\partial = \frac{2 \sum_x \phi^2}{\text{Tr} \left( \sum_x \partial_x \phi \partial_x \phi \right)}
\]

where \( \lambda \) is the average of the eigenvalues of the derivative matrix \( \partial_x \phi \partial_x \phi \), and \( \Lambda_x, y \) are the sample dimensions. The lengths \( L^\#, L^\circ \) and \( L^\partial \) are normalized such that each gives the unit cell spacing for a square lattice of droplets of 50% volume fraction. For bicontinuous morphologies in \( d = 3 \), all are comparable to \( L(t) \) as defined previously; for example, \( L^\partial \approx 1.2L \).

We show in Fig. 1 the evolution of the droplet morphology for a simulation run that lies wholly within the VH regime. After a brief transient (leading to the first coalescence) the coarsening mechanism is CIC, as first seen in experiments by Tanaka [10]. The results are reminiscent of the predictions for CIC in \( d = 3 \) [11], where it was predicted that the droplets that just underwent a coalescence would be the next to coalesce. Instead we observe that in \( d = 2 \) the coalescence of two droplets usually induces a coalescence elsewhere. (This is especially clear in animations [15].) Perhaps for this reason, the CIC process does not (in \( d = 2 \)) lead rapidly to percolation of the droplets as was suggested for \( d = 3 \) [11]. Such percolation would cause a rapid crossover to bicontinuity. Instead, the system achieves a self-sustaining droplet state that, in contrast to the bicontinuous analogue [3], shows good dynamical scaling (Fig.1). This behavior is seen for all runs that lie within the VH regime as identified from the universal scaling plot found below (Fig.3).

![Fig. 1](image1)

**FIG. 1.** (a) The droplet scaling state for \( \eta = 0.22 \) (VH regime) for reduced times \( t = 1100, 1500 \) and 2400 respectively. (b) A section scaled by \( l(t) \) is shown; note the scale invariance. (c) The evolution of \( L^\#, L^\partial \) and \( L^\circ \) with time (where \( L^\# < L^\partial < L^\circ \)). All three length-scales agree well with each other and approach \( L \sim t \) (grey line).

This behavior is quite unexpected [3] and only partly explicable. On one hand, while only local rearrangements (of order parameter or interface) are needed to transform
one to the other, droplet and bicontinuous morphologies are very different: the largest connected domains present are small in one case, and percolate in the other. The issue is whether the ‘chain-reaction’ of CIC is fast enough to percolate the droplets [1]: we find it is not fast enough. On the other hand, it is just fast enough to keep going indefinitely, whereas it might equally have stopped in finite time, leaving classical, non-hydrodynamic coarsening processes to take over. Note that under the CIC process, large domains can no longer coarsen simply by deforming their tortuous boundaries, but have to coalesce. This explains why scaling is recovered: all domains are droplets and coarsen via the same mechanism.

In Fig.2 we see the counterpart of Fig.1 for a run that lies wholly in IH. Here the initial droplet morphology (not shown) crosses over rapidly to a bicontinuous scaling state seen previously for the IH regime in two dimensions [13]. The mechanism for the rapid morphological transition is fluid inertia: two coalescing droplets wobble violently as they fuse together, causing local as well as distant coalescence events and rapid percolation of the initial droplet structure. In the IH scaling state, the difference between droplet or bicontinuous initial conditions has thus been lost and local correlations inherited from early-time asymmetry do not have any long-term effect. The observed coarsening mechanism, in which the local topology is constantly being ruptured and reconnected by underdamped interfacial oscillations, is somewhat reminiscent of the ‘turbulent remixing’ process hypothesized in [14] (see also [20]). (This is somewhat hard to ascertain from the still pictures in Figure 2 but is easily seen in our animations [13].) But in contrast to the prediction [14] that $l \sim O(t^{1/3})$, we see (as in [8]) a simple $l \sim t^{2/3}$ scaling throughout the accessible IH regime.

Just as in $d = 3$, we cannot rule out a further crossover to a regime where the viscosity is so low that the growth rate is not limited by the input of energy from the surface tension, so that the primary balance in Eqs. [4] is between inertial and viscous effects. Kendon [8] considered this case in $d = 3$ and argued that $l \sim t^{2/3}$ might survive for the structural length scale, so long as other lengths (describing the velocity field) do not scale the same way. It would be interesting to pursue this suggestion in $d = 2$, although the properties of $d = 2$ and $d = 3$ turbulence [21] are very different.

To establish scaling with confidence, Figure 1(c) and 2(c) are not sufficient; we must combine several simulations with different viscosities to span many decades on the $l(t)$ curve [2]. As shown in Fig.3, this yields very good data collapse onto a universal scaling curve for all three length measures. A prefactor deviation appears between $L^\#$ and the others in the IH regime, but this results from the change in morphology (Fig.2), not a violation of scaling. The asymptotes are (for lengths defined via $L^\#$ and $L^\dagger$) $l = 0.02t$ and $l = 0.9t^{2/3}$. These cross at $t = t^* \simeq 2 \times 10^6$, a value even larger than the $d = 3$ case, whose asymptotes (using $L = 2\pi \int S(k)dk/\int kS(k)dk$) are also shown for comparison.

FIG. 2. Recovery of bicontinuous scaling state for $\eta = 0.0044$ (IH regime). (a) The symmetric scaling state that rapidly evolved from the initial droplet morphology for $t = 2 \times 10^5$, $4.2 \times 10^7$ and $9.3 \times 10^7$. (b) Images scaled by $l(t)$, showing dynamic scaling. (c) $L^\#$, $L^\dagger$ and $L^\#$ all scale as $t^{2/3}$ but $L^\#$ is now larger that the other two measures, indicating the change in morphology.

In comparable units, our VH droplet growth is significantly slower than for the $d = 3$ bicontinuous VH scaling morphology. This is reasonable: the amount of interface actually driving the coarsening is much smaller since only droplets undergoing coalescence contribute to the flow at any time, while in the bicontinuous case the entire in-
terface is in motion. Once the IH regime is entered the $d=2,3$ structures are both bicontinuous and the coefficients of $t^{2/3}$ become much more similar.

It would be interesting to see whether $d=3$ systems close to percolation show similar anomalies, and whether a self-sustaining CIC droplet scaling is again recovered for compositions in that region.

This work was funded in part by grant EPSRC (UK) GR/M56234. We thank I. Pagonabarraga for discussions.

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