Non-uniqueness of late-time scaling states in spinodal decomposition

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Abstract

In this letter we show that the late-time scaling state in spinodal decomposition is not unique. We performed lattice Boltzmann simulations of the phase-ordering of a 50%-50% binary mixture using as initial conditions for the phase-ordering both a symmetric morphology that was created by symmetric spinodal decomposition and a morphology of one phase dispersed in the other, created by viscoelastic spinodal decomposition. We found two different growth laws at late times, although both simulations differ only in the early time dynamics. The new scaling state consists of dispersed droplets. The growth law associated with this scaling state is consistent with a \( L \sim t^{1/2} \) scaling law.

I. INTRODUCTION

The phase-ordering in binary fluids following spinodal decomposition has been the focus of considerable interest in the recent past. A number of different scaling regimes with different growth laws have been identified with the help of scaling arguments, but little emphasis has been placed on morphological effects. Unusual asymmetric morphologies are often seen in the early stages of viscoelastic spinodal decomposition, but it has been argued that viscoelastic effects are unimportant at late times and therefore only one true late-time phase-ordering scaling state exists. The concept remains useful to understanding phase-ordering dynamics in binary fluids.

The argument of the unimportance of viscoelasticity in the late-stage growth, as well as many of the scaling arguments, rely on an assumption that is often implicitly made: for the phase-ordering of symmetric binary fluid mixtures only one universal late-time scaling state exists. In this letter, however, we show that this assumption is not valid, and that therefore the early time dynamics are very important in selecting the late-time scaling state. The possibility of the non-uniqueness of the scaling state was first suggested by A. Rutenberg, although at the time no persuasive numerical evidence could be found.

II. NUMERICAL METHOD

For the simulations we use the viscoelastic two-component lattice Boltzmann simulation introduced in an earlier paper. Briefly, in lattice Boltzmann simulations densities \( f_i \) that are associated with velocities \( v_i \) are streamed on a lattice according to the lattice Boltzmann equation

\[
 f_i(x + v_i \Delta t, t + \Delta t) = f_i(x, t) + \Delta t \sum_j \Lambda_{ij} [f_j^0(x, t) - f_j(x, t)]
\]

where \( f_i^0 \) is an equilibrium distribution, \( \Lambda_{ij} \) is a collision matrix, and \( v_i \Delta t \) is a lattice vector. The velocity set for our simulation consists of 17 velocities given by \( \{(0,0), (1,0), (0,1), (-1,0), (0,-1), (1,1), (-1,1), (-1,-1), (1,-1), (1,0), (0,1), (-1,0), (0,-1), (1,1), (-1,1), (1,-1), (1,1), (-1,-1), (1,-1)\} \). Note that the last 8 velocities are the same as the previous eight velocities. This duplicity allows the simulation to have two independent stresses which represent a viscoelastic and a purely viscous contribution to the total stress tensor. The two contributions are used to produce a Jeffrey’s model for the stress (see eqn. (3)). The algorithm is required to conserve mass and momentum, but not energy. Energy conservation is replaced by a condition of constant temperature. The macroscopic density \( \rho \) and velocity \( \mathbf{u} \) are defined as

\[
 \rho = \sum_i f_i, \quad \rho \mathbf{u} = \sum_i f_i \mathbf{v}_i.
\]

To simulate a two-component mixture we introduce a second lattice Boltzmann equation for densities \( g_i \)

\[
 g_i(x + v_i \Delta t, t + \Delta t) = g_i(x, t) + \frac{\Delta t}{\tau} [g_i^0(x, t) - g_i(x, t)]
\]
where we choose a diagonal collision matrix with a single relaxation time \( \tau \). These densities are only defined on the first nine velocities \( v_i \). The density difference \( \phi = \rho_1 - \rho_2 \) of the two components is given by
\[
\phi = \sum_i g_i
\]
and the total density is given by \( \rho = \rho_1 + \rho_2 \). By choosing appropriate equilibrium distributions and an appropriate collision matrix, we ensure that the following partial differential equations are being simulated up to second order in the derivatives but assuming that the relaxation of the viscoelastic stress \( \sigma \) is slow (\( \theta \sim 1/\sqrt{\tau} \)):
\[
\begin{align*}
\partial_t \rho + \partial_x (\rho u) &= 0 \quad (5) \\
\rho \partial_t u + \rho u \nabla u &= -\partial_x P + \partial_x (\sigma_v + \sigma) \quad (6) \\
\sigma_v &= \nu_{\infty} (\nabla (\rho u) + (\nabla (\rho u))^T - \nabla \cdot u \delta) \\
\sigma + \theta(\phi) \sigma_{(1)} &= -(\nu_{\infty} (\nabla (\rho u) + (\nabla (\rho u))^T) \\
\partial_t \phi + \partial_x (\phi u) &= D \Delta^2 \mu + \nabla . (\phi / \rho \nabla . (P - \sigma)) \quad (9)
\end{align*}
\]
where \( \delta \) is the identity matrix, \( \sigma \) is the viscoelastic stress tensor, \( \sigma_{(1)} = \partial_t \sigma + u \nabla \sigma - \sigma . (\nabla u - (\nabla u)^T) \sigma \) is its upper convected derivative, \( P = 0.5 \rho + 0.007(\nabla \phi \nabla \phi - 0.5 \nabla \phi \cdot \nabla \phi \cdot \delta - \phi \nabla^2 \phi \delta) \) is the pressure tensor, and \( \mu = -0.54 \phi / \rho + 0.25 \ln((\rho + \phi) / (\rho - \phi)) - 0.007 \nabla^2 \phi \) is the chemical potential. The parameters \( \nu_{\infty}, \xi_{\infty} \), and \( \theta \) are determined by the eigenvalues of the collision matrix. The values for the parameters were \( \Delta t = 1, \tau = 1, D = 0.5, \xi_{\infty} = 0.31, \) and \( \nu_{\infty} = 0.01 \). For the low-viscosity phase we used \( \theta = 0.055, \nu_0 = 0.013 \) and for the viscoelastic phase \( \theta = 39.5 \) and \( \nu_0 = 1.97 \). For the symmetric simulations of Figure 1 we used \( \theta = 0.055 \) and \( \nu_0 \approx \nu_{\infty} = 0.075 \).

III. SIMULATIONS

We performed simulations of critical spinodal decomposition of a viscoelastic binary mixture in two dimensions where one component is much more viscoelastic than the other. These simulations lead to the usual morphologies in which the viscoelastic phase is connected and the less viscoelastic phase is dispersed. We performed our simulations on a 256\(^2\) lattice and after about 1000 iterations the less viscoelastic phase is completely dispersed, although the domains are still highly deformed. We used this morphology as an initial condition for a simulation where we make both components purely viscous to examine the effects of initial conditions that are not symmetric on symmetric binary fluid mixtures. This allows us to distinguish the effect that the morphology created by viscoelastic phase separation has from the effect of viscoelasticity itself in the late-time phase-ordering process.

FIG. 1. A comparison of the phase-ordering of two identical symmetric binary mixtures after different early time spinodal decomposition. In (a) a phase-ordering is seen from an initial morphology generated by viscoelastic phase separation in which the light component is dispersed (the originally low-viscous component). In (b) we see the usual symmetric phase separation. Fig. (c) shows the length scales \( L(t) \) for (a) \( L \sim t^{1/2} \) and (b) \( L \sim t^{2/3} \).
It is usual to assume that the phase-ordering process is independent of the details of the early time spinodal decomposition, although this assertion has, to our knowledge, only been tested with respect to different random initial conditions. If this assumption were true we would expect the domain growth to lead to a reconnection of the dispersed domains that would lead to a morphology and a growth law that are identical to a system which started with the same viscosities for both components.

In Figure 1 we see a comparison of the phase-ordering from an initially dispersed phase (a) and a symmetric initial condition (b). The morphologies for both systems are shown after 1000, 2000, 4000, and 8000 iterations. We see that the phase-ordering of the morphology with a dispersed phase leads to an even more pronounced dispersed phase where almost all domains are circular at late times. We see that droplet coalescence occurs frequently with only few domains vanishing due to the evaporation-condensation mechanism underlying Oswald ripening. The droplet coalescence, however, is not frequent enough to change the connectivity of the domains. Instead, we observe that domains become more circular on average, suggesting that even for very long times we do not expect a transition to a bi-continuous morphology. In Figure 1(c) we see that the growth law for the droplet phase is \( L(t) \sim t^{1/2} \) and is smaller than the \( L(t) \sim t^{2/3} \) seen for the symmetric phase-ordering shown in Figure 1(b), but also faster than the \( L(t) \sim t^{1/3} \) usually seen in the coarsening of off-critical droplet morphologies of symmetric binary mixtures. (The data for the well established scaling law of \( L \sim t^{2/3} \) for the symmetric phase-ordering in Figure 1(c) is more noisy since it relies on a single simulation on a 256\(^2\) lattice where as the data for the droplet morphology has been obtained by simulation on a 1024\(^2\) lattice.) We suggest that the high density of droplets enhances the droplet coalescence and leads to a faster growth of \( L \sim t^{1/2} \). We measure \( L(t) \) as the inverse of the length of the interface. We should also point out that a length scale derived as \( L \sim 1/\sqrt{N} \), where \( N \) is the number of domains, scales as \( L \sim t^{1/2} \) well, suggesting that it may be a true scaling state.

The existence of this second scaling state, distinct from the bi-continuous scaling state, is important to understanding the late-time regime of viscoelastic phase separation because, even in the absence of viscoelastic effects, we observe a droplet-morphology evolving from the initial morphology created by viscoelastic phase separation. This result is also important for practical reasons in processes where late-time morphologies need to be controlled. It is well known that mixing of high-viscosity and low-viscosity components by means of mechanical agitation leads to morphologies where the high-viscosity phase is dispersed in droplets for volume fractions of the low-viscosity component of much less than 50%. This effect is enhanced if the high-viscous phase is viscoelastic. This leads us to consider what the late-time morphology of a phase-ordering system with an early morphology created by mechanical mixing would be.

![Figure 2](image.png)

**FIG. 2.** The phase-ordering of a binary mixture of a viscoelastic phase (dark color) and a low viscosity Newtonian phase (light color) is shown in (a) and (b). (a) corresponds to a usual viscoelastic phase separation of a 50%-50% mixture and (b) shows the phase-ordering after the viscoelastic and low-viscosity domains have been interchanged. Morphologies are shown after 2000, 4000, 8000, and 16000 iterations. The scaling behavior of the two mixtures is shown in (c) where for (a) \( L \sim t^{0.2} \) and for (b) \( L \sim 0.4 \).
In order to answer this question we performed a simulation of viscoelastic phase separation and after a droplet morphology had been formed at 1000 time-steps, we inverted the properties of the two components. We used this state as a model for the morphologies of dispersed droplets of the viscoelastic phase in a matrix of the low viscosity Newtonian phase that is typical of mechanically mixed morphologies. We then continued the simulations and observed the phase-ordering behavior of the new morphology. The results of these simulations are shown in Figure 2. In Figure 2(a) the morphology for a viscoelastic phase separation of a 50%-50% mixture is shown. We should emphasize that the phase-ordering (see eqn. (9)) does not have a composition-dependent diffusion constant and therefore no domain shrinkage is observed in these simulations. Domain shrinkage can be a very slow process in viscoelastic phase separation that prolongs the spinodal decomposition process and makes it more difficult to differentiate the early-stage decomposition and the late-time phase-ordering processes. This does not reduce the validity of our results, however, since we are only interested in the late-time behavior when the domain shrinkage is completed.

The morphologies shown in Figure 2(b) are of a simulation where at 1000 iterations, after the dispersion was achieved, the viscoelastic and the low viscosity components were exchanged. We see that the morphology remains a droplet morphology, albeit now of the viscoelastic phase. Comparing Figures 2(a) and (b) we see that the most important factor in determining the final morphology is the early stage dynamics, and that phase-ordering scaling morphologies of both dispersed viscoelastic and dispersed low viscosity domains exist.

From Figure 2(c) we see that each scaling state has a different growth law. The morphology of dispersed viscoelastic domains grows as \( L \sim t^{0.4} \) whereas the morphology of dispersed low viscosity domains grows as \( L \sim t^{0.2} \) after near circular droplets have been formed. An anomalously slow growth in viscoelastic phase separation has first been observed experimentally by Tanaka who found \( L \sim t^{0.15} \) for a system of high molecular-weight polystyrene/diethyl malonate (4.0 wt.%).

These simulations also emphasize the difference between a morphology after spinodal decomposition and after mechanical mixing. The morphology after spinodal decomposition is a dispersed low viscosity phase, whereas the state after mechanical mixing has a dispersed viscoelastic phase. Subsequent phase-ordering does not change the connectivity of these states, in agreement with the conventional wisdom that there is a profound difference in states produced by spinodal decomposition and mechanical mixing.

IV. CONCLUSIONS

In this letter we have shown that more than one scaling state exists for late-time spinodal decomposition and that the early time behavior of a phase-separating binary mixture is very important in selecting one of these scaling states. We have also explained the difference between viscoelastic phase-ordering states after spinodal decomposition and mechanical mixing. Our results show that the volume fraction and the physical properties of a mixture do not select a morphology by themselves, but that the morphology of the initial state is of paramount importance. This is why viscoelastic phase separation can lead to unusual late-time scaling states even when viscoelasticity is no longer important at large length scales.

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1. A.J. Bray, Adv. Phys. 43, 357 (1994)
2. A.J. Wagner and J.M. Yeomans, Phys. Rev. Lett. 80, 1429 (1998)
3. V.M. Kendon, J.C. Desplat, P. Bladon, M.E. Cates, Phys. Rev. Lett. 83, 576 (1999)
4. V.M. Kendon, electronic preprint, cond-mat/9910287 (1999)
5. K.R. Mecke and V. Sofonea V, Phys. Rev. E 56, R3761 (1997)
6. A. Bhattacharya, S.D. Mahanti, and A. Chakrabarti, Phys. Rev. Lett. 80, 333 (1998)
7. C. Haas and J.M. Torkelson, Phys. Rev. E 55, 3191 (1997)
8. A. Onuki and T. Taniguchi, J. Chem. Phys. 106, 5761 (1996)
9. M. Grant and K.R. Elder Phys. Rev. Lett. 82, 14 (1999)
10. A.D. Rutenberg and A.J. Wagner, unpublished, (1997)
11. A.J. Wagner, L. Giraud, and C.E. Scott, submitted to Phys. Fluids, (1999)
12. A.J. Wagner and C.E. Scott, in preparation, (1999)
13. L.A. Utracki, J. Rheol 35, 1615 (1991)
14. H. Vanoene, J. Colloid Interface Sci. 40, 448 (1971)
15. H. Tanaka, Phys. Rev. Lett. 71, 3158 (1993)