Chapter 1

Considerations about universality in phase-ordering of binary liquids

Alexander J. Wagner
Department of Physics and Astronomy
The University of Edinburgh
awagner@ph.ed.ac.uk

In this article we show that the phase-ordering scaling state for binary fluids is not necessarily unique and that local correlations in the initial conditions can be responsible for selecting the scaling state. We describe a new scaling state for symmetric volume fractions that consists of drops of the one component suspended in a matrix of the other. The underlying reason for the existence of the newly observed scaling state is that the main coarsening mechanism of binary fluids which is the deformation of interfaces by flow is not acting, and this leads to a new scaling law. An initial droplet state can be formed by a number of physical phenomena. In a unified description this can be understood as local correlations in the initial conditions. Local correlations with length $\xi$ are believed to be irrelevant when the typical length scale $L$ of the system is large ($L \gg \xi$). Our result shows that these initial correlations, contrary to current thinking, can be important even at late times.

1.1 Introduction

Phase-ordering is observed in many spatial systems, including ones that underwent spinodal decomposition or mechanical mixing. Examples include a wide
variety of systems including magnetic systems, binary alloys, binary fluids, but also some reaction diffusion systems\([1]\) and some models of gene evolution\([2]\).

In a seminal paper Hohenberg and Halperin showed that most of these systems can be categorized to belong to a small number of categories, and each member of a category shows the same universal phase-ordering behavior. In particular they distinguished between systems in which the order parameter is not conserved, \(e.g.\) magnetic systems or genetic systems, and systems in which the order parameter is conserved, \(e.g.\) binary alloys or binary fluids. Liquid systems, such as binary fluids and magnetic fluids, can phase-order not only by diffusion but also via flow and therefore they are in a universality class of their own.

The phase-ordering process has been conjectured to observe scaling, \(i.e.\) the systems are characterized by a single length-scale \(L(t)\) such that the morphologies of the system scaled but that length-scale are statistically self-similar. The time dependence of this length-scale is then known as the scaling law. The scaling laws can be deduced by dimensional analysis from the equations of motion. For systems without hydrodynamics \(L(t)\) scales as \(t^{1/2}\) for systems with non-conserved order parameter and as \(t^{1/3}\) for systems with a conserved order parameter.

Because binary fluids have more that one mechanism for domain coarsening there is more that one growth law. Off-critical quenches that contain a much smaller volume fraction of one component form droplets and this morphology grows mostly via diffusion leading to a \(L(t) \sim t^{1/3}\) growth law. Most studies, however, deal with critical quenches with equal volume fractions for both components. Because of this symmetry bi-continuous morphologies are typically formed and both diffusion and hydrodynamic growth mechanisms operate.

There are, however, exceptions to this general rule. Sometimes dynamical asymmetries in the diffusion constant of the two phases or their viscoelastic properties can lead to droplet morphologies. A stationary morphology that consists of circular droplets has no hydrodynamic pathway of coarsening. Once two droplets coalesce they can induce a flow that can induce further coalescence. The central idea of this paper is that one of the main hydrodynamics pathways of coarsening can be suppressed if the morphology consists of droplets leading to a new 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\([12]\).

The droplet morphologies that we require are not unusual and can often seen in the early stages of viscoelastic spinodal decomposition \([8, 9, 10]\) as well as in systems with an order-parameter dependent mobility. We will use a viscoelastic lattice Boltzmann method to create the initial droplet morphology and then use a symmetric Newtonian lattice Boltzmann method to evolve the initial droplet morphology to verify that this new scaling state exists.

In viscoelastic phase-separation the droplet morphology consists of low-viscosity droplets suspended in the viscoelastic matrix. The opposite morphology is observed in mechanical mixing where the low viscosity material will form
Universality in phase-ordering

the matrix phase. We show that both droplet morphologies are stable under
phase-ordering, in agreement with experimental results.

1.2 Numerical method

For the simulations we use the viscoelastic two-component lattice Boltzmann
simulation introduced in an earlier paper [13]. Briefly, in lattice Boltzmann sim-
ulations densities $f_i$ that are associated with velocities $v_i$ are streamed on a
lattice according to the lattice Boltzmann equation

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

(1.1)

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 velo-
cities 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)\}. 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. (1.8)). 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 $u$ are defined as

$$\rho = \sum_i f_i, \quad \rho u = \sum_i f_i v_i.$$  \hspace{1cm} (1.2)

To simulate a two-component mixture we now have to consider the densities of
the two fluids $\rho_1$ and $\rho_2$. The first lattice Boltzmann equation (1.1) is now an
equation for the total density $\rho = \rho_1 + \rho_2$ and we introduce a second lattice
Boltzmann equation for $g_i$ to describe the evolution of the density difference
$\phi = \rho_1 - \rho_2$:

$$g_i(x + v_i \Delta t, t + \Delta t) =$$

$$g_i(x, t) + \frac{\Delta t}{\tau} [g_i^0(x, t) - g_i(x, t)]$$

(1.3)

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 $\phi$ is given by

$$\phi = \sum_i g_i.$$  \hspace{1cm} (1.4)

By choosing appropriate equilibrium distributions and an appropriate collision
matrix, we ensure that the following partial differential equations are being sim-
ulated up to second order in the derivatives but assuming that the relaxation of
the viscoelastic stress $\sigma$ is slow ($\theta \sim 1/\sqrt{\epsilon}$):

\[
\begin{align*}
\partial_t \rho + \partial_x (\rho u) &= 0 \quad (1.5) \\
\rho \partial_t u + \rho u \cdot \nabla u &= -\partial_x P + \partial_x (\sigma_v + \sigma) \quad (1.6) \\
\sigma_v &= \nu_{\infty} (\nabla (\rho u) + (\nabla (\rho u))^T - \nabla u \delta) + \xi_{\infty} \nabla \cdot u \delta \quad (1.7) \\
\sigma + \theta(\phi) \sigma_{(1)} &= -(\nu_0(\phi) - \nu_{\infty})(\nabla (\rho u) + (\nabla (\rho u))^T) \quad (1.8) \\
\partial_t \phi + \partial_x (\phi u) &= D \nabla^2 \mu + \nabla . ((\phi/\rho) \nabla (P - \sigma)) \quad (1.9)
\end{align*}
\]

where $\delta$ is the identity matrix, $\sigma$ is the viscoelastic stress tensor, $\sigma_{(1)} = \partial_t \sigma + u \cdot \nabla \sigma - \sigma.(\nabla u) - (\nabla u)^T \sigma$ is its upper convected derivative, $P = 0.5 \rho + 0.007(\nabla \phi \nabla \phi - 0.5 \nabla \phi \cdot \nabla \phi - \phi \nabla^2 \phi \delta$ is the pressure tensor, and $\mu = -0.55 \phi/\rho + 0.25 \ln((\rho + \phi)/(\rho - \phi)) - 0.007 \nabla^2 \phi$ 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 1.1 we used $\theta = 0.055$ and $\nu_0 \approx \nu_{\infty} = 0.075$.

### 1.3 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\[14\]. We performed our simulations on a $256^2$ and a $1024^2$ 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. We choose the viscosity such that a system started with a random initial condition will be in the viscous scaling state. 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.

In Figure 1.1 we see a comparison of the phase-ordering from a droplet morphology (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
Figure 1.1: 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) $L \sim t^{2/3}$. The apparent growth law in (a) is misleading. A more detailed study that examines the growth of the droplet morphology over several decades in length shows that the growth-law is $L \sim t$ (see [18]).
transition to a bi-continuous morphology. (This is no longer true when we leave viscous regime and enter into the inertial regime. Here a return to the inertial scaling state is observed [18]. In Figure 1.1(c) we see that the growth law for the droplet phase appears to be $L(t) \sim t^{1/2}$ and is smaller than the $L(t) \sim t^{2/3}$ seen for the symmetric phase-ordering shown in Figure 1.1(b). More recent simulations of the droplet morphology, however, establish scaling over several orders of magnitude and find that the actual growth-law is $L \sim t$ [18]. This emphasizes the fact that dynamic scaling analysis that does not cover several decades can be misleading. Unfortunately such studies are very computationally demanding and exist only in few studies.

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 [15] for volume fractions of the low-viscosity component of much less than 50%. This effect is enhanced if the high-viscous phase is viscoelastic [16]. 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.

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 1.2. In Figure 1.2(a) the morphology for a viscoelastic phase-separation of a 50%-50% mixture is shown. We should emphasize that the phase-ordering (see eqn. (1.9)) 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 1.2(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 1.2(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
Figure 1.2: 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) $L \sim 0.4$. As in Fig. 1.1 these power-laws have not been established for several decades and should therefore not be taken too literally.
dispersed viscoelastic and dispersed low viscosity domains exist.

From Figure 1.2(c) we see that each scaling state appears to have 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 \( \sim t^{0.2} \) after near circular droplets have been formed. An anomalous slow growth in viscoelastic phase-separation has first been observed experimentally by Tanaka\[17\] who found \( L \sim t^{0.15} \) for a system of high molecular-weight polystyrene/diethyl malonate (4.0 wt.%). It must, however, be emphasized that it is impossible to conclusively determine scaling exponents from such a short run. It is conceivable that a more extensive scaling analysis could lead to different exponents.

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.

### 1.4 Conclusions

In this article we have shown that more than one scaling state exists for late-time spinodal decomposition of two-dimensional binary fluids and that local correlations in the initial conditions or the early time behavior of a phase-separating binary mixture can be 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.

### Acknowledgments

The authors acknowledge the financial support of DuPont Chemical Company. A.W. acknowledges the support of EPSRC Grant GR/M56234 and would like to thank Craig Carter for the generous permission to use his Origin2000 computer.

### Bibliography

[1] Irv Epstein showed examples of oscillating chemical reactions during his presentation at the ICCS3 that clearly exhibited some phase-ordering behavior.
Universality in phase-ordering

[2] H. Sajama and Y. Bar-Yam, *InterJournal* Complex systems, 417.

[3] A.J. Bray, Adv. Phys. **43**, 357 (1994).

[4] A.J. Wagner and J.M. Yeomans, Phys. Rev. Lett. **80**, 1429 (1998).

[5] V.M. Kendon, J.C. Desplat, P. Bladon, M.E. Cates, Phys. Rev. Lett. **83**, 576 (1999).

[6] V.M. Kendon, electronic preprint, cond-mat/9910287 (1999).

[7] K.R. Mecke and V. Sofonea V, Phys. Rev. E **56**, R3761 (1997).

[8] A. Bhattacharya, S.D. Mahanti, and A. Chakrabarti, Phys. Rev. Lett. **80**, 333 (1998).

[9] C. Haas and J.M. Torkelson, Phys. Rev. E **55**, 3191 (1997).

[10] A. Onuki and T. Taniguchi, J. Chem. Phys. **106**, 5761 (1996).

[11] M. Grant and K.R. Elder Phys. Rev. Lett. **82**, 14 (1999).

[12] A.D. Rutenberg and A.J. Wagner, unpublished, (1997).

[13] A.J. Wagner, L. Giraud, and C.E. Scott, submitted to Phys. Fluids, (1999).

[14] A.J. Wagner and C.E. Scott, in preparation, (1999).

[15] L.A. Utracki, J. Rheol **35**, 1615 (1991).

[16] H. Vanoeene, J. Colloid Interface Sci. **40**, 448 (1971).

[17] H. Tanaka, Phys. Rev. Lett. **71**, 3158 (1993).

[18] A.J. Wagner and M. Cates, Euro. Phys. Lett. **56**, 556 (2001).