Domain Growth in Ternary Fluids: A Level Set Approach

K. A. Smith,[1] F. J. Solis,[2] L. Tao,[3] K. Thornton,[2] and M. Olvera de la Cruz[1,2]
[1]*Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60208*
[2]*Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208*
[3]*Department of Astronomy, Columbia University, New York, New York 10027*
(Received 2 July 1999)

We analyze phase separation in ternary systems in the asymptotic hydrodynamic regime when the volume fractions and concentrations are constant. The multiphase Navier-Stokes equations are solved using a level set method. A new projection method was developed to treat multiple junctions for systems with more than two phases. It is found that surface tension ratios can alter the growth mechanism of a minority phase in the presence of two majority phases. When the minority phase wets the interface of the majority phases the domain growth rate of all three phases is initially similar to that of a symmetric binary fluid but slows down at later times.

PACS numbers: 47.55.Kf, 47.20.Hw, 64.75.+g

Many systems of scientific and technological interest are multicomponent mixtures that undergo separation into multiple phases. The diffusion driven phase separation dynamics of *A*-*B*-*C* ternary mixtures decomposing into two and three phases was recently studied experimentally [1] and by numerically solving the nonlinear spinodal decomposition (NLSD) equations for the time evolution of a concentration field [2,3]. The decomposition into three phases leads to fascinating microstructures. Mixtures with a minority *C* component initially decompose into two unstable *A*-rich and *B*-rich majority phases. The minority *C* component segregates at the *A*-rich/*B*-rich interface as soon as the decomposition is initiated to decrease the *A*-*B* interfacial energy [4], in agreement with polymeric thin film experiments [1]. This adsorption results in higher concentration of *C* at the junction of multiple majority phase boundaries. Therefore, the coarsening of the metastable minority phase rich in *C* occurs at the vertices of majority phase boundaries in agreement with classical nucleation theory. Though the kinetic growth laws of diffusion induced separation are the same as in binary systems, the actual separation process was found to be considerably slower than in binary systems. Indeed, it is a common practice to add minority components to *A*-*B* mixtures to increase their miscibility and to slow down the phase separation kinetics [5]. We show here that in the later stages of the decomposition the coarsening kinetics of minority metastable phases in ternary incompatible fluids can actually be much faster than that of minority phases in binary fluids due to hydrodynamic flow. However, the growth of the majority *A* and *B* phases at long times can be slower when a minority *C* component is added if *C* wets the *A*-*B* interface.

In unstable binary fluid systems undergoing phase separation a fast hydrodynamic growth mode is possible during the late stages of the decomposition [6–8]. Recent work has focused on simulating hydrodynamic growth by a variety of methods including lattice-Boltzmann [9,10], time dependent Ginzburg-Landau [11,12], molecular dynamics [13], and dissipative particle dynamics [14]. To include hydrodynamic effects, these methods typically modify the equations that describe evolution of the local concentrations due to diffusion by coupling them to the fluid velocity. In the late stages, when the volume fractions and composition of the phases are constant, however, hydrodynamics is the dominant mechanism for coarsening. In this asymptotic hydrodynamic regime, all the dynamics are generated by sharp interfaces. Therefore, it is essential to determine the position and topology of the interfaces in numerical simulations accurately and efficiently. This is a major difficulty in the numerical modeling of multiphase fluid motion. In this Letter we, for the first time, study hydrodynamic coarsening by solving the multiphase Navier-Stokes equations directly, using a level set method for interface capturing. In our approach the relevant parameters in the late stages of the decomposition—viscosity, density, and surface tension—are specified macroscopically rather than being determined from another set of parameters. The level set method is designed to model sharp interfaces. Thus it can even be applied to strongly incompatible fluids that cannot mix at all on nano or microscopic length scales but can only be mixed mechanically up to certain length scales.

The level set method advances a function $\phi(\mathbf{x}, T)$, where $\mathbf{x}$ is position and T is time, defined such that the zero contour of $\phi(\mathbf{x}, T)$ specifies an interface. The correct interfacial motion can be modeled by advecting $\phi(\mathbf{x}, T)$:

$$\frac{\partial \phi}{\partial T} = -(\mathbf{v} \cdot \nabla)\phi \,. \tag{1}$$

The velocity $\mathbf{v}(\mathbf{x}, T)$ is obtained from the Navier-Stokes equation

$$\frac{\partial \mathbf{v}}{\partial T} + (\mathbf{v} \cdot \nabla)\mathbf{v} = \frac{\mathbf{F}}{\rho} - \frac{1}{\rho}\nabla P + \nu \nabla^2 \mathbf{v} \,, \tag{2}$$

where $\mathbf{F}(\mathbf{x}, T)$ is the force acting on the fluid, ρ is density, $P(\mathbf{x}, T)$ is pressure, and ν is kinematic viscosity. We

assume constant viscosity and density throughout the fluid. The force due to surface tension can be expressed as

$$\mathbf{F} = \sum_{i=A,B,C} \sigma_i' \delta(\phi_i) \kappa(\phi_i) \hat{\mathbf{n}}\,, \tag{3}$$

where $\delta(\phi_i)$ is the Dirac delta function of $\phi_i(\mathbf{x}, T)$, the zero level set of ϕ_i defines the phase i interface, $\kappa(\phi_i)$ is the local interfacial curvature, and $\hat{\mathbf{n}}$ is the normal to the interface. For the ternary case we have defined a separate level set function ϕ_i for each phase. The modified surface tension coefficients σ_i' are defined such that the standard surface tension coefficient for an interface between phases A and B is given by $\sigma_{AB} = \sigma_A' + \sigma_B'$. The motion of the interface is obtained from solving (1)–(3). Also a reinitialization of ϕ is done after every time step in order to maintain $|\nabla\phi| = 1$ without shifting the zero contour [15,16]. In two dimensions we solve the equations for the scalar vorticity ω obtained by taking the curl of (1), with $\omega\hat{\mathbf{z}} = \nabla \times \mathbf{v}$. This allows for the elimination of the pressure term.

The level set approach provides an efficient and accurate tool for modeling interfaces evolving under complex motion. A level set function $\phi_i(\mathbf{x}, T)$ is defined as the signed distance to the phase i interface. The magnitude of $\phi_i(\mathbf{x}, T)$ represents the shortest distance between the position $\mathbf{x}$ and the interface. The sign of $\phi_i(\mathbf{x}, T)$ is positive within phase i and negative outside of it.

For a binary fluid only one level set function is necessary to track the interface between the two phases. In general, $N - 1$ functions are needed to describe the morphology of an N phase system. Although it is simplest to evolve a set of $N - 1$ level set functions, $\{\phi_1 \cdots \phi_{N-1}\}$, this has the undesirable feature of not handling all N phases identically for $N > 2$. However, if each ϕ_i in the full set $\{\phi_1 \cdots \phi_N\}$ is evolved independently, numerical error can create overlaps (where two or more ϕ_i's are positive) and vacuums (where all ϕ_i's are negative), particularly at triple junctions. We have developed a novel mapping of $\{\phi_1 \cdots \phi_N\}$ onto a $N - 1$ dimensional space which maintains the desired symmetry between the phases. It can be shown that the set of allowed values for $\{\phi_1 \cdots \phi_N\}$ forms a $N - 1$ dimensional manifold M immersed in $\mathbf{R}^N$, made up of the union of $N(N - 1)/2$ pieces of hyperplanes. A one to one mapping from M to $\mathbf{R}^{N-1}$ is done by means of a simple Euclidean projection along the $(1, 1, \ldots, 1)$ direction into the $N - 1$ hyperplane $\sum_{i=1}^{N} \phi_i = 0$. This construction allows us to represent $\{\phi_1 \cdots \phi_N\}$ by $N - 1$ functions while treating all of the phases equally. Because M contains only the acceptable values of $\{\phi_1 \cdots \phi_N\}$ the creation of overlaps and vacuums is avoided. This method can be used in any number of dimensions and handles topological changes naturally.

We first consider a 50/50 binary fluid where both fluids have identical properties (polymer blends of similar degrees of polymerizations have very similar viscosities and densities [17–19]). For a system with no externally imposed length or time scales the Navier-Stokes equations can be nondimensionalized such that all physical parameters drop out. Domain length, L, and time, T, are scaled by the values

$$L_0 = \rho\nu^2/\sigma\,, \tag{4}$$

$$T_0 = \rho^2\nu^3/\sigma^2. \tag{5}$$

For 3D binary fluids a transition from viscous to inertial hydrodynamic growth has been predicted by scaling analysis [6,7,20]. The predicted growth rates are

$$l \sim t \quad \text{for } l \ll 1\,, \tag{6}$$

$$l \sim t^{2/3} \quad \text{for } l^{1/2} \gg 1\,, \tag{7}$$

where $l = L/L_0$ and $t = (T - T_i)/T_0$. T_i is a nonuniversal offset time which is needed for comparing different runs since L is nonzero at $T = 0$. Although the crossover length is $l_c = 1$, viscous effects decrease more slowly in the inertial regime than vice versa so that l_c can appear to be much larger. This effect can be seen in the crossover behavior reported by Kendon *et al.* [10] in 3D. In 2D it has been argued [7] that Eq. (7) should govern the entire coarsening process. Recently Wagner and Yeomans [9] have found a breakdown of scaling in 2D binary fluids due to creation of a hierarchy of small circular domains.

We briefly consider two scenarios for ternary systems with nonsymmetric volume fractions: (1) one majority phase and two dispersed minority phases, and (2) two majority phases and one minority phase, which could be continuous (if it wets the interface between the continuous majority phases) or dispersed. Case 1, where two of the phases exist only as isolated droplets, cannot be affected by hydrodynamic flow. The system may coarsen by a Lifschitz-Slyozov mechanism or by droplet collisions. This is analogous to the binary dispersed case, but collisions between different phase droplets must also be considered. If the continuous phase wets the droplet-droplet interface, then the droplet phases each coarsen separately, perhaps more slowly than in the binary case because movement is hampered by droplets of the other phase. If an equilibrium contact angle exists between the three phases, then collisions will create pairs of different phase droplets. This could lead to chains of alternating phase droplets like those seen in the solutions to the NLSD equations in the later stages [2]. If one droplet phase wets the interface between the other phases, then collisions could result in coated droplets.

For case 2 we label the minority phase C and the majority phases A and B. If C wets the A-B interface two situations may occur. If $\sigma_{AC} = \sigma_{BC} = 0$, then C acts similarly to a surfactant which eliminates surface tension between A and B [11]. Once C spreads, via hydrodynamics, across the A-B interface, the domains become frozen and cannot grow. In contrast, previous work [11] has modeled the diffusion of surfactant to the interface via a

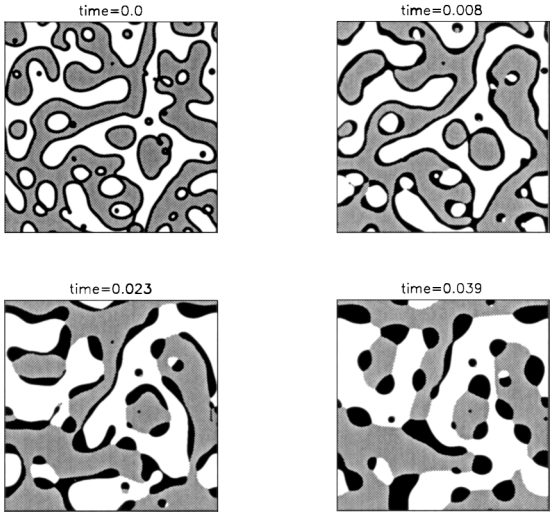

FIG. 1. Evolution of domains for ternary system with $\lambda = 1$, $\nu = 0.1$, $\sigma_{AC} = 5$, grid size $= 256^2$.

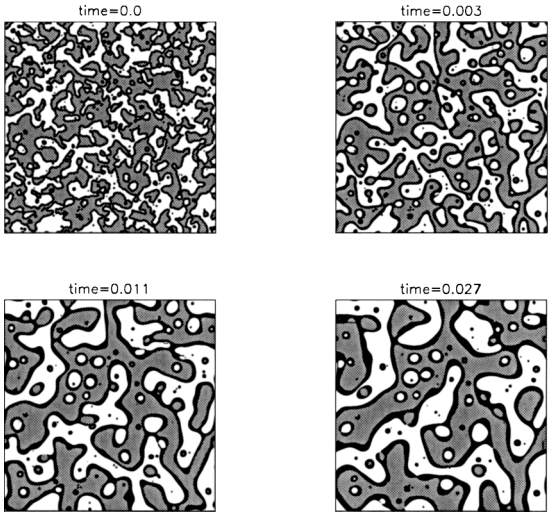

FIG. 2. Evolution of domains for ternary system with $\lambda = 1/2$, $\nu = 0.1$, $\sigma_{AC} = 5$, grid size $= 512^2$.

concentration field. If $\sigma_{AC} > 0$ or $\sigma_{BC} > 0$, then hydrodynamic growth occurs with C lying between the A and B domains. Because contact lines are not maintained, each phase is simply driven to minimize surface area.

We consider systems with majority phases A and B of equal volume fraction (41%) and minority phase C. The A-C and B-C surface tensions are equal, so that $\sigma_{AC} = \sigma_{BC} = \lambda\sigma_{AB}$. We examine domain growth for a system in which the C phase wets the A-B interface ($\lambda = 1/2$) and for a system with a nonwetting minority phase ($\lambda = 1$). For initial conditions in binary systems we use randomly generated patterns which are similar to the patterns seen by other groups [9,12] at the onset of hydrodynamic coarsening. For ternary systems we use similar initial conditions but insert a layer of minority phase at the interface between the two majority phases based on the structure seen in numerical [2,4] and experimental [1] studies of ternary systems. We use periodic boundary conditions in both directions.

A run for $\lambda > 1/2$ is shown in Fig. 1. We find that breakup of the minority phase occurs during the hydrodynamic growth process. In the resulting morphologies the A and B phases are continuous or semicontinuous while C is dispersed. Once breakup occurs, the minority domains grow through the slower process of random collisions. Thus one would expect the ratio l_C/l_A, where l_i is the dimensionless domain length of phase i ($l_A = l_B$ by symmetry), to decrease in time. This is similar to the breakdown in scaling found by Wagner and Yeomans [9] in binary systems as a nested hierarchy of circular domains forms. However, in the ternary case the C phase droplets are restricted to lie on the A-B interface which decreases with time according to the hydrodynamic growth rate. This increases the frequency of collisions and may lead to an enhanced growth rate for l_C. Thus, the growth of a dispersed phase is enhanced by hydrodynamic flow. The situation is quite different if, for example, $\sigma_{AC} \ll \sigma_{BC}$ so that the C phase droplets leave the interface to enter the A phase. Then the area (volume in 3D) in which the droplets lie stays constant in time.

We compare growth rates for $\lambda = 1/2$ (shown in Fig. 2) with a binary system. All runs are on a 512^2 grid. For the ternary system σ_{AC} is used in L_0 and T_0. The length, L, is measured by the inverse first moment of the circularly averaged structure factor. We compare the dimensionless length scales l_A and l_C, corresponding to the majority and minority phases, respectively, to that of a binary system, l_{bin}. Our results do not show a universal scaling law. In two of the ternary runs a sharp decrease in the growth rate appears (the third run was not long enough to observe this feature). A less abrupt decrease occurs for the binary run at largest l. This behavior occurs at $L < 0.2$ (where box length is 1) so it is unlikely that finite size effects play a role in slowing down the dynamics. The slowing down due to turbulence, as predicted by Grant and Elder [21], is not applicable here since 2D fluids cannot exhibit turbulence [22]. It appears that the coarsening mechanism leads to structures that are unable to continue growing at a constant rate.

TABLE I. Fitting Parameters ($\sigma = 5$ in all runs).

ν	T_i	z	a
Binary:			
0.5	0.028	0.598	0.522
0.2	0.013	0.558	1.170
0.1	0.0089	0.547	1.925
Ternary:			
0.5	0.017	0.582	0.739
0.2	0.0084	0.566	1.498
0.1	0.0062	0.563	2.238

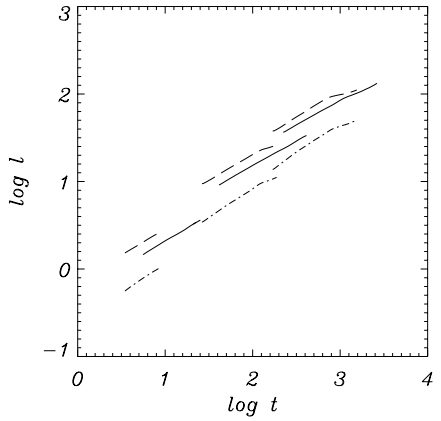

FIG. 3. Reduced data for domain growth. Results are for binary system (bold lines), ternary majority phase (dashed lines), and ternary minority phase (dash-dotted lines).

We determine growth rates for each data set, excluding the portions where the sharp decrease occurred, by fitting them to the form $L = A(T - T_i)^z$. This corresponds to a dimensionless growth law $l = at^z$, where $a = AT_0^z/L_0$. The values of ν, σ, T_i, z, and a for binary and ternary runs are listed in Table I. The results are plotted in Fig. 3. In all cases the growth exponent is in the range $0.55 \lesssim z \lesssim 0.6$. Binary and ternary results for the same parameters and similar initial conditions satisfy $L_A(T) \approx L_{\text{bin}}(1.6T)$. Motion is driven by surface tension of both the *A*-*C* and *B*-*C* interfaces. Thus, in the early stages, the ternary system behaves similar to a binary system with higher surface tension. However, disconnected domains are more likely to form in ternary systems. The reason is that the *C* phase can form a node separating two *A* domains and two *B* domains. This mechanism may disrupt self-similar growth and lead to a slowing down of the growth rate.

In conclusion, we have modeled the multiphase Navier-Stokes equations directly by a level set method and developed a projection method to handle any number of phases accurately. We find, for the binary case, a slower growth rate than previously reported. In the ternary case where a minority phase wets the *A*-*B* interface a similar growth rate is seen in the early stages with a sharp decrease occurring after a certain point. We attribute this decrease to the formation of disconnected domains.

We thank David Chopp, Julio Ottino, and Peter Voorhees for useful discussions. This work was supported by the National Science Foundation Grants No. DMR9807601 and No. DMR9632472.

[1] S. Walheim, M. Ramstein, and U. Steiner, Langmuir **15**, 4828 (1999).
[2] C. Huang, M. Olvera de la Cruz, and B. W. Swift, Macromolecules **28**, 7996 (1995).
[3] L. Q. Chen, Scr. Metall. Mater. **29**, 683 (1993); **42**, 3503 (1994).
[4] C. Huang and M. Olvera de la Cruz, Phys. Rev. E **53**, 812 (1996); Europhys. Lett. **34**, 171 (1996).
[5] V. Ginzburg, F. Qiu, M. Paniconi, G. Peng, D. Jasnow, and A. C. Balazs, Phys. Rev. Lett. **82**, 4026 (1999).
[6] E. D. Siggia, Phys. Rev. A **20**, 595 (1979).
[7] H. Furukawa, Phys. Rev. A **31**, 1103 (1985).
[8] A. J. Bray, Adv. Phys. **43**, 357 (1994).
[9] A. J. Wagner and J. M. Yeomans, Phys. Rev. Lett. **80**, 1429 (1998).
[10] V. M. Kendon, J-C. Desplat, P. Bladon, and M. E. Cates, Phys. Rev. Lett. **83**, 576 (1999).
[11] J-R Roan and E. I. Shakhnovich, Phys. Rev. E **59**, 2109 (1999).
[12] H. Tanaka and T. Araki, Phys. Rev. Lett. **81**, 389 (1998).
[13] M. Laradji, O. G. Mouritsen, and S. Toxvaerd, Phys. Rev. E **53**, 3673 (1996).
[14] S. I. Jury, P. Bladon, S. Krishna, and M. E. Cates, Phys. Rev. E **59**, 2535 (1999).
[15] Y. C. Chang, T. Y. Hou, B. Merriman, and S. Osher, J. Comput. Phys. **124**, 449 (1996).
[16] M. Sussman, E. Fatemi, P. Smereka, and S. Osher, Comput. Fluids **27**, 663 (1998).
[17] F. S. Bates and P. Wiltzius, J. Chem. Phys. **91**, 3258 (1989).
[18] T. Hashimoto, in *Polymer Structures and Properties*, edited by E. L. Thomas, Materials Science and Technology Vol. 12 (VCH, New York, 1993), pp. 251–300.
[19] L. Sung and C. C. Han, J. Polym. Sci. B, Polym. Phys. **33**, 2405 (1995).
[20] L. P. McMaster, Adv. Chem. Ser. **142**, 43 (1975).
[21] M. Grant and K. R. Elder, Phys. Rev. Lett. **82**, 14 (1999).
[22] H. Tennekes and J. L. Lumley, *A First Course in Turbulence* (MIT Press, Cambridge, MA, 1972).