Effect of Viscosity Ratio on Structure Evolution during Mixing/Demixing of Regular Binary Mixtures

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We simulate the mixing (demixing) process of a quiescent binary mixture with a composition-dependent viscosity which is instantaneously brought from the two-phase (resp. one-phase) to the one-phase (resp. two-phase) region of its phase diagram. Our theoretical approach follows a standard diffuse-interface model of partially miscible regular binary mixtures wherein convection and diffusion are coupled via a nonequilibrium capillary force, expressing the tendency of the phase-separating system to minimize its free energy. Based on 2D simulation results, we discuss the influence of viscosity ratio on basic statistics of the mixing (segregation) process triggered by a rapid heating (quench), assuming that the ratio of capillary to viscous forces (a.k.a. the fluidity coefficient) is large. We show that, for a phase-separating system, at a fixed value of the fluidity coefficient (with the continuous phase viscosity taken as a reference), the separation depth and the characteristic length scale of single-phase microdomains increase monotonically for increasing values of viscosity ratio; however, for a mixing system the attainment of a single-phase equilibrium state by coalescence and diffusion is retarded by an increase in viscosity ratio at a fixed fluidity for the dispersed phase.

1. Introduction

We investigate numerically the influence of a composition-dependent mixture viscosity on the mixing (resp. phase segregation) process occurring after heating (resp. quenching) a regular binary fluid mixture to a temperature above (resp. below) its critical point, as a function of the viscosity ratio between its component fluids. In fact, the liquid mixtures of interest in our previous works (Lamorgese and Mauri, 2002, 2005, 2006; Lamorgese *et al.*, 2011) had been assumed to have components with equal viscosities, densities, and molecular weights (i.e., an ideally perfectly symmetric binary system). Herein, although we still keep the assumption of equal densities and molecular weights, we consider Newtonian mixtures with component species having different dynamic viscosities, such as, e.g., aqueous solutions of organic solvents (Lalibertè, 2007). In fact, over the past two decades, a phase-separating binary fluid mixture with a viscosity asymmetry in its pure components has been addressed in a number of numerical works, mostly focused on morphology and rheology, with and without an imposed shear flow (Onuki, 1994; Tanaka, 1999; Zhang *et al.,* 2001; Luo *et al.*, 2004). However, even in the presence of a viscosity asymmetry, the results of those previous investigations only lend partial support to convection-driven coalescence as the dominant mechanism of segregation after spinodal decomposition of a low-viscosity binary fluid system. On the other hand, much less attention has been paid in the literature to the influence of viscosity ratio on basic statistics of the mixing process of an initially phase-separated binary fluid mixture triggered by a rapid heating across its coexistence curve, since a large number of numerical and experimental works have been focused on the mixing of miscible fluids in microfluidic devices (Orsi *et al.,* 2013; Galletti *et al.*, 2015). Therefore, herein we intend to further address a viscosity asymmetry in the components of a binary fluid mixture having a large fluidity coefficient [i.e., of order $O(10^3)$] as it mixes (phase separates) after a rapid heating (quench) across its coexistence curve, by means of a diffuse-interface model of phase transition in liquid mixtures with a composition-dependent viscosity. Note that, in general, considering that viscosity represents the resistance against the diffusive transport of momentum, and that in fluid mixtures those resistances are in parallel (Ottino and Chella, 1983), the viscosity of a binary mixture can be related to those of its pure components *A* and *B* via

$$\frac{1}{\eta(\phi)} = \frac{\phi}{\eta_A} + \frac{1-\phi}{\eta_B} + \Delta f_{mix}(\phi), \tag{1}$$

where $x_A \equiv \phi$ is the mass fraction of, say, the minority species, while Δf_{mix} represents the fluidity of mixing, which accounts for a nonideal mixture. However, in what follows we further restrict attention to the viscosity of an ideal mixture, as given by Eq. (1) with the last term on the RHS set to zero.

In remainder of this paper, the governing equations and numerical methods are briefly outlined in Sects. 2 and 3, respectively. Then, we discuss the influence of viscosity ratio on basic statistics of the segregation and mixing processes from phase-field simulations of phase transition in liquid mixtures triggered by a thermal quench. Conclusions are then presented.

2. The governing equations

The derivation of the equations of motion for a strictly isopycnic, regular binary mixture having partially miscible components at low Reynolds number within a diffuse-interface description has been presented elsewhere (Lamorgese *et al.*, 2011; Lamorgese and Mauri, 2016). Restricting attention to 2D systems, so that the velocity can be expressed in terms of a streamfunction, ψ, the governing equations can be rewritten as follows:

$$(\partial_t - \nabla^2)\phi = -\nabla^2 \left\{ \phi(1-\phi)[2\Psi\phi + (a/L)^2 \nabla^2\phi] \right\}$$
$$+ \partial_x \left\{ [2\Psi\phi + (a/L)^2 \nabla^2\phi](1-2\phi)\phi_x - \alpha_r \phi\psi_y \right\} \tag{2}$$
$$+ \partial_y \left\{ [2\Psi\phi + (a/L)^2 \nabla^2\phi](1-2\phi)\phi_y + \alpha_r \phi\psi_x \right\},$$

$$0 = \partial_{xy}^2 \left\{ \phi_x^2 - \phi_y^2 - 4\theta\psi_{xy} \right\} + (\partial_y^2 - \partial_x^2)\left\{ \phi_x\phi_y + \theta(\psi_{xx} - \psi_{yy}) \right\}, \tag{3}$$

where Ψ and a denote the Margules parameter and a sub-micron-scale length (representing the typical interface thickness at equilibrium), respectively. Furthermore, lengths and times have ben scaled based on L and L^2/D, respectively, with L denoting a macroscale length, which in our case coincides with the periodicity length of the computational domain. Taking the curl of the Stokes equation yields Eq. (3), which can be seen as a static constraint on the streamfunction field, meaning that at each instant in time the streamfunction can be determined once the concentration field is known. In Eq. (3), the dependence $\theta(\phi) \equiv \eta(\phi)/\eta_r$ (with η_r chosen as the smaller pure species viscosity) interpolates between the viscosities of the pure components according to Eq. (1). Note that α_r in Eq. (2) denotes the fluidity coefficient (Tanaka and Araki, 1998) with the smaller pure species kinematic viscosity taken as a reference, i.e.,

$$\alpha_r \equiv \frac{RTa^2}{M_W \nu_r D} \quad (r = A,\ B). \tag{4}$$

Obviously, one more fluidity coefficient can be introduced (based on the larger pure species viscosity), which can be simply obtained after dividing α_r by the viscosity ratio $\Theta \equiv \max\theta$. Note that $\Theta > 1$ in all cases since, as previously noted, the smaller pure species viscosity has been taken as a reference for defining the (dimensionless) viscosity in Eq. (3); so, to circumvent this difficulty, in what follows we take $\xi \equiv \eta_A/\eta_B$ as our definition of viscosity ratio. Herein, we will assume that both fluidity coefficients are large, as one can easily see from Eq. (4) (see Lamorgese *et al.*, 2011).

In the first set of simulations reported herein, spinodal decomposition in liquid mixtures is studied numerically by perturbing unstable mixtures of van der Waals fluids with delocalized (random) concentration fluctuations. In such simulations, we assume $\Psi = 2.1$, corresponding to an instantaneous quench (at the initial time) from the homogeneous composition at a stable state above the critical point to an unstable state within the spinodal range of the phase diagram (at a temperature T corresponding to $\Psi = 2T_c/T$, with T_c denoting the critical temperature). In practice, for a low-viscosity system such as the acetone-hexadecane mixture (with a critical temperature of $T_c = 27\,°C$, as reported by Santonicola *et al.*, 2001), this would correspond (after a thorough homogenization at a temperature above the critical point) to the system being brought to 12 °C, using a large quenching rate.

We also present simulations of the influence of viscosity ratio on the mixing process of an initially phase-separated binary mixture at equilibrium after a rapid heating, with the mixture initially consisting of a

monodisperse array of drops of the minority phase embedded in a continuous phase (with both phases at equilibrium). In these simulations, we assume $\Psi = 1.9$, corresponding to an instantaneous heating (at the initial
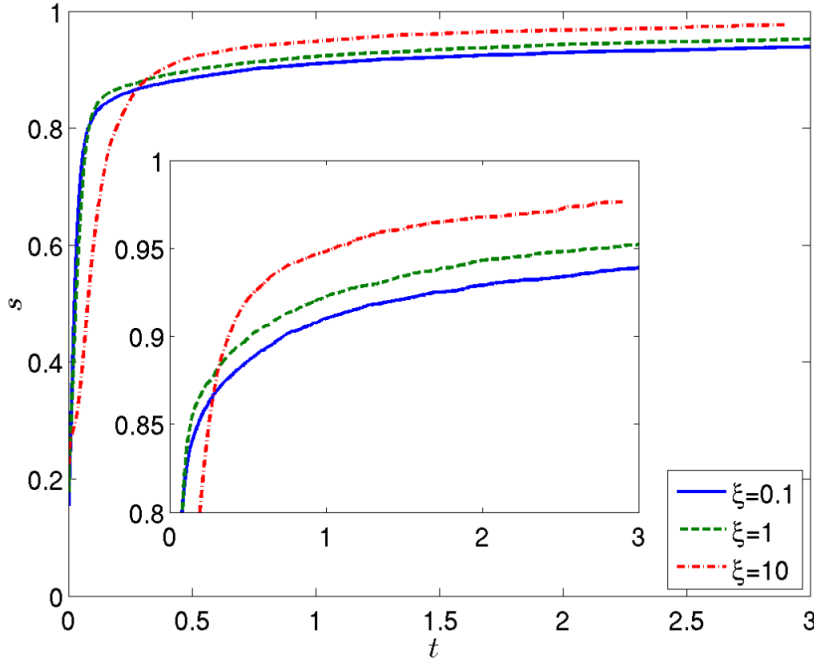

Figure 1: Separation depth vs. time (diffusive time units) from phase-field simulations of a binary mixture with $\Psi = 2.1$, $\alpha_A = 1000$, on a 512^2 grid and different values of viscosity ratio $\xi = 0.1, 1, 10$ (solid, dashed, and dot-dashed).

time) from a two-phase local equilibrium state below the critical point to a stable state within the one-phase region. Again, for the above-mentioned acetone-hexadecane system, this would correspond to rapidly heating the mixture to 42 °C, starting with the mixture in its phase-separated state below the critical point.

3. Numerical results

Numerical methods are the same as in our previous works (Lamorgese and Mauri, 2002, 2005, 2006). We only summarize below the necessary changes to our numerical procedures that allow for a composition-dependent viscosity in the Stokes equation, along with an adaptive time-stepping scheme for the Cahn-Hilliard equation. At each instant in time, Eq. (3) is solved for the streamfunction field using a fixed-point (Picard) iteration with relaxation (Ramière and Helfer, 2015). In fact, we noticed that the number of iterations per step for solving Eq. (3) stays constant in time when the chosen temporal scheme is a standard 4th-order Runge-Kutta; however, we found that fewer iterations per step are necessary if we chose instead the Cash-Karp Runge-Kutta method (Press *et al.*, 1992) as the temporal scheme.

Numerical results from 2D spinodal decomposition simulations of a regular binary mixture having a composition-dependent viscosity are now described. Simulations were run for different values of the viscosity ratio, $\xi = \frac{1}{10}, \frac{1}{3}, 3, 10$, at a fixed fluidity coefficient ($\alpha_A = 1000$). We took the initial system location at $\langle \phi \rangle = 0.45$,

corresponding to a slightly off-critical quench. For each value $\xi = \frac{1}{10}, \frac{1}{3}, 3, 10$, we found spinodal patterns that

look very similar to those for a binary system with no viscosity contrast between the pure components (Lamorgese and Mauri, 2002), namely, we saw the formation and temporal growth of *A*-rich nuclei within a *B*-rich continuous phase. To elucidate the influence of viscosity ratio on the average phase composition of the nuclei, we show in Fig. 1 the temporal evolution of the separation depth (Vladimirova *et al.*, 1998; Lamorgese and Mauri, 2002)
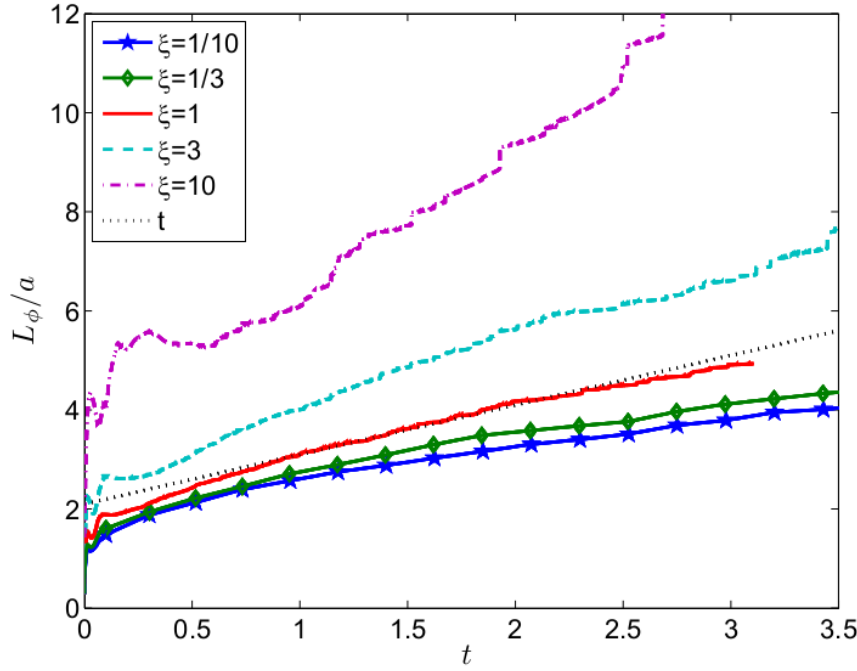
Figure 2: Characteristic length scale vs. time (diffusive time units) from phase-field simulations of a binary mixture with $\Psi = 2.1,\ \alpha_A = 1000,$ *on a 512^2 grid and different values of viscosity ratio.*

$$s = \left\langle \frac{\phi(\mathbf{r}) - \phi_0}{\phi_{eq}(\mathbf{r}) - \phi_0} \right\rangle,$$ (5)

expressing the distance of the mean composition of the nuclei from their local equilibrium state, for different values (above) of the viscosity ratio. As can be seen, the separation depth has a monotonic dependence on the viscosity ratio, particularly for times in the linear growth regime, corresponding to convection-driven coalescence. In fact, in view of our assumption of isothermal conditions, a fixed value of α_A translates into a fixed value of ν_α, meaning that as ξ increases from $\frac{1}{10}$ to 10, the viscosity of the continuous phase monotonically decreases from $10\nu_\alpha$ to $\frac{1}{10}\nu_\alpha$. In turn, this means that $\xi = 10$ (resp. 1/10) corresponds to a smaller (resp. larger) resistance to coalescence as compared to that for a unit viscosity ratio, thereby explaining the strictly monotonic dependence of the separation depth on viscosity ratio. We also checked that in the case with fixed α_B (corresponding to a fixed ν_β), since increasing values of ξ can only be realized via monotonically increasing values of ν_α, the separation depth has a monotonically decreasing dependence on viscosity ratio, since (other parameters the same) an increasing viscosity of the dispersed phase translates into an increased resistance to coalescence.

We also looked at the temporal evolution of the characteristic length scale of single-phase microdomains defined as

$$L_\phi(t) = \frac{1}{\phi_{rms}^2} \sum_{\mathbf{k}} \frac{\left|\hat{\phi}_{\mathbf{k}}\right|^2}{\left|\mathbf{k}\right|}.$$ (6)
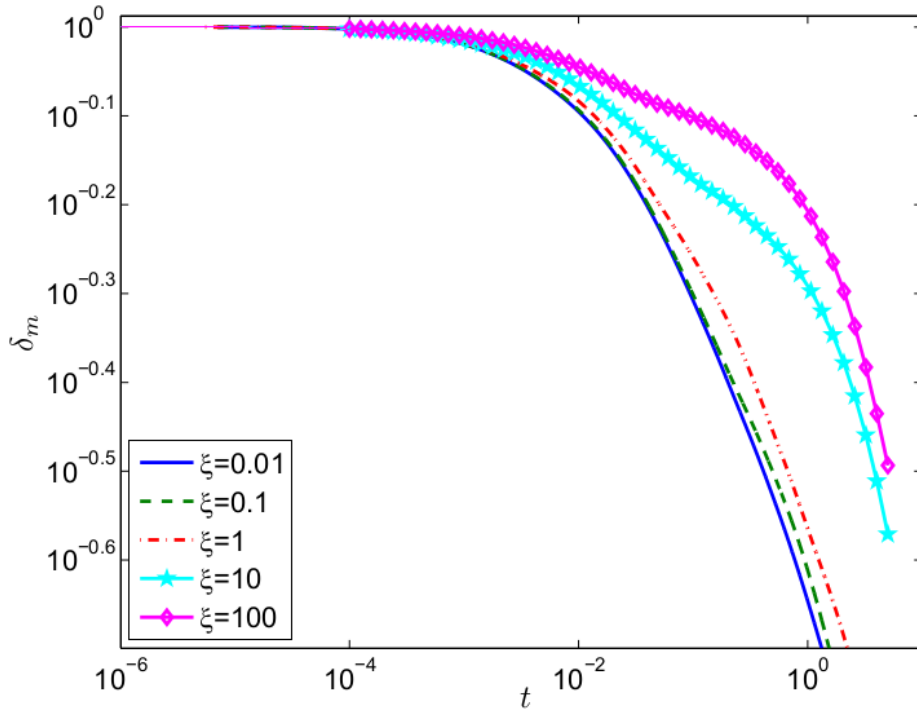
Figure 3: Degree of mixing vs. time (diffusive time units) from phase-field simulations of a binary mixture with $\Psi = 1.9$, $\alpha_A = 1000$, on a 512^2 grid and different values of viscosity ratio.

As can be seen, Figure 2 (which corresponds to a fixed α_A) shows the same monotonic dependence with respect to viscosity ratio as that shown in Figure 1. On the other hand, we checked that in the case corresponding to a fixed α_B, the characteristic length scale has a monotonically decreasing behavior with respect to viscosity ratio.

Finally, regarding the mixing process of an initially phase-separated mixture at local equilibrium, consisting of a monodisperse array of 150 drops (each having a radius of $8a$) of the minority phase, embedded in a continuous phase (such that $\langle\phi\rangle = 0.486$), we show in Fig. 3 the temporal evolution of the degree of mixing (Vladimirova and Mauri, 2004; Lamorgese and Mauri, 2006)

$$\delta_m(t) = \frac{\left\langle (\phi(\mathbf{r},t) - \langle\phi\rangle)^2 \right\rangle}{\left\langle (\phi(\mathbf{r},0) - \langle\phi\rangle)^2 \right\rangle} \tag{7}$$

as a function of viscosity ratio, at a fixed fluidity coefficient ($\alpha_A = 1000$). In this circumstance, an increasing viscosity ratio corresponds to a decreasing viscosity of the continuous phase, and this in turn translates into a decreased resistance to coalescence. In fact, in previous works on the mixing of regular binary mixtures (Vladimirova and Mauri, 2004; Lamorgese and Mauri, 2006), we showed that (counter to common intuition) in a low-viscosity binary system convection-driven coalescence among drops leads to an effective additional delay for the mixing process to complete (as compared to the case with no convection), since the larger drops that result from coalescence events take longer to be reabsorbed by diffusion. In other words, since the degree of mixing has a strictly increasing dependence on the coalescence rate among drops, this then explains why the degree of mixing increases for increasing values of viscosity ratio (Fig. 3). Incidentally, we also checked that, as expected, at a fixed α_B (corresponding to a fixed viscosity of the continuous phase), the degree of mixing has a strictly decreasing dependence on viscosity ratio.

4. Conclusions

We have discussed basic statistics of the convection-driven demixing (resp. mixing) process occurring after a regular binary liquid mixture is instantaneously quenched (resp. heated) to a temperature below (resp. above)

its critical point, as a function of the viscosity ratio between its component fluids. In particular, for a phase-separating system we showed that, at a fixed fluidity coefficient for the dispersed phase, an increasing ratio between the dispersed and continuous phase viscosities (viscosity ratio) leads to a faster phase separation (as compared to the case with no viscosity contrast), which is reflected in a monotonically increasing dependence of both the separation depth and the characteristic length scale of single-phase microdomains on viscosity ratio. On the other hand, at a fixed fluidity coefficient based on the continuous phase viscosity, an increasing viscosity ratio leads to a slower phase separation. In both cases, our numerical results support a linear growth regime, corresponding to convection-driven coalescence. Finally, as regards the mixing process of a binary mixture initially consisting of a monodisperse array of drops of the minority phase embedded in a continuous phase (with both phases at equilibrium), at a fixed viscosity of the dispersed (resp. continuous) phase the degree of mixing is monotonically increasing (resp. decreasing) with respect to viscosity ratio. This result can be readily explained based on our previous numerical findings on the mixing process of a binary mixture with no viscosity contrast between its component fluids.

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