Mixing of viscous liquid mixtures
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Abstract

When a quiescent binary mixture is instantaneously brought from two- to one-phase region of its phase diagram, the resulting mixing process is driven both by diffusion and by convection. Applying the diffusion interface model, here we show by numerical simulation that the bulk motion that is induced during phase transition effectively slows down the mixing process. In fact, in our model convection is induced by a non-equilibrium body force that is proportional to the chemical potential gradients, expressing the tendency of the demixing system to minimize its free energy. In liquid systems, as this driving force induces a material flux which is much larger than that due to pure molecular diffusion, drops tend to coalesce and form larger domains which eventually must dissolve by diffusion. Therefore, in the absence of any external agitation, mixing is slower in mixtures with larger viscosities, contrary to common thinking. In addition, as expected, the mixing rate decreases as the Margules parameter $\Psi$ increases, where $\Psi$ describes the relative weight of enthalpic versus entropic forces.

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1. Introduction

In most of the previous numerical studies on mixing, mixing of two fluids $A$ and $B$ has been considered as the result of the chaotic advection of one fluid into the other, assuming that the instantaneous velocity of a fluid particle (of either $A$ or $B$ type) is the solution of the Navier–Stokes equation for a single-phase fluid (see Aref, 1984; Ottino, 1990; Wiggins, 1991; Fountain et al., 1999, with references therein). Clearly, this is rigorously true only in the dilute limit and when the fluid mixture is ideal, which means that the enthalpic properties of the fluid mixture are neglected, assuming that the interparticle forces between $A$ and $A$ are equal to those between $B$ and $B$ and those between $A$ and $B$ (Sandler, 1999). This approximation seems to be justified when the flow is turbulent, so that convection dominates any diffusive process resulting from the thermodynamic properties of the system. In general, however, at low Reynolds numbers this approximation ceases to be valid and the physico-chemical properties of the fluid mixture have to be taken into account.

In this work, we present a series of simulations of the mixing process occurring after heating a quiescent and initially phase-separated liquid mixture to a temperature $T$ well above its critical point of miscibility, showing that the process is strongly influenced by the interplay between convection and diffusion. The latter is induced by the velocity fluctuations of the molecules that compose the system at thermal equilibrium and consists of their incoherent, random motion, with no specific preferential direction. On the contrary, convection, when it is not imposed from the outside, can exist only for a system far from equilibrium, as it consists of the collective, coherent motion of its molecules, and is therefore a much faster process than diffusion. As explained by the so-called diffuse interface model (otherwise called model H, in the taxonomy of Hohenberg and Halperin, 1977), convection arises as the system tends to minimize its free energy and, in fact, is induced by a (non equilibrium) body force that is proportional to the gradient of the chemical potential (Anderson et al., 1998; Lowengrub and Truskinovsky, 1998). At the late stages of phase
separation, after the system has developed well-defined phase interfaces, this body force reduces to the more conventional surface tension, as shown by Jasnow and Viñals (1996), so that the driving force can be thought of as a non-equilibrium attractive force among drops.

The diffuse interface model provides a description of two-phase systems that is alternative to the classical fluid-mechanical approach, where phase interfaces are modeled as free boundaries that evolve in time. In fact, Jacqmin (2000), performing a careful matched asymptotic expansion, showed that the motion of sharp interfaces between immiscible fluids, obtained as the outer expansion of the velocity field calculated using the diffuse interface approach, satisfies the usual Marangoni-type boundary conditions at the interfaces.

Applying the diffuse interface model, Valls and Farrell (1993), Tanaka and Araki (1998) and Vladimirova et al. (1999a,b) showed by numerical simulation that spinodal decomposition of fluid mixtures strongly depends on the relative importance of convection and diffusion, and that the enhanced coarsening rate is due to the strong coupling between concentration and velocity fields.

In this article, we illustrate in Section 2 how the diffuse interface model predicts that the mixing process of two miscible liquids is driven by the convection induced by a non-equilibrium body force, which is proportional to the chemical potential gradients. Then, in Section 3, after describing the numerical method employed in our simulations, we present the results obtained.

2. Theory

The motion of an incompressible binary fluid mixture composed of two species A and B is described here through a modification of the diffuse interface model, which is described in detail by Vladimirova et al. (2000). Here, A and B are assumed to have equal viscosities, $\eta$, densities, $\rho$, and molecular weights, $M_w$, with the composition of the system uniquely determined through the molar fraction $\phi$ of, say, species A, as a function of position $\mathbf{r}$ and time $t$.

If the flow is assumed to be slow enough to neglect the inertial terms in the Navier–Stokes equation, conservation of mass and momentum lead to the following system of equation,

$$\frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = -\frac{1}{\rho} \nabla \cdot \mathbf{J}, \quad (1)$$

$$\eta \nabla^2 v - \nabla p = \mathbf{F}_f, \quad \nabla \cdot v = 0, \quad (2)$$

where $v$ is the average local fluid velocity, $\mathbf{J}$ is the diffusion flux and $\mathbf{F}_f$ is a body force. As shown by Mauri et al. (1996), $\mathbf{J}$ is proportional to the gradient of the chemical potential through the relation,

$$\mathbf{J} = -\rho \phi (1 - \phi) D \nabla \tilde{\mu}, \quad (3)$$

where $D$ is the molecular diffusivity, and $\tilde{\mu} = \mu_A - \mu_B$ is the generalized (non-dimensional) chemical potential difference between the two species defined as (Landau and Lifshitz, 1953) $\tilde{\mu} = (\Delta g/RT)/\partial \phi$. Here $\Delta g$ denotes the molar free energy of mixing, defined as (see Van der Waals, 1979; Cahn and Hilliard, 1959),

$$\Delta g = RT \left[ \phi \ln \phi + (1 - \phi) \ln (1 - \phi) \right] + \Psi(1 - \phi) + \frac{1}{2} \sigma^2 (\nabla \phi)^2, \quad (4)$$

where $R$ is the gas constant, $a$ is a characteristic microscopic length and $\Psi$ is the Margules parameter, which describes the relative weight of enthalpic versus entropic forces.

Phase separation occurs whenever the temperature of the system $T$ is lower than the critical temperature $T_c$. Imposing that at the critical point $d^2 g/d\phi^2 = 0$ and $\phi = \frac{1}{2}$, we find that $T_c = 2$ is the critical value of $\Psi$. Therefore, the single-phase region of the phase diagram corresponds to values $\Psi < 2$, while the two-phase region has $\Psi > 2$. At the end of the phase segregation process, a surface tension $\sigma$ can be measured at the interface and from that, as shown by Van der Waals (1979), $a$ can be determined as

$$a \sim \frac{1}{\sqrt{\tau}} \frac{\sigma M_w}{\rho R T}, \quad (5)$$

where $\tau = (\Psi - 2)/2$, while $(\Delta \phi)_{eq}$ is the composition difference between the two phases at equilibrium. This relation can be easily derived considering that $\sigma \sim \rho (\Delta g)_{eq}/M_w$, where $(\Delta g)_{eq}$ is the jump in free energy across an interface at equilibrium, which can be estimated from Eq. (4) and $\tau \sim a/\sqrt{\tau}$ is the characteristic interface thickness (Van der Waals, 1979). In the following, we will assume that $\tau = O(1)$.

The body force $\mathbf{F}_f$ appearing in Eq. (2) equals the generalized gradient of the free energy, and therefore it is driven by the chemical potential gradients within the mixture (see Anderson et al., 1998; Vladimirova et al., 2000):

$$\mathbf{F}_f = \frac{\rho}{M_w} \frac{\partial \Delta g}{\partial \mathbf{r}} = \left( \frac{\rho R T}{M_w} \right) \tilde{p} \nabla \phi$$

$$= \left( \frac{\rho R T}{M_w} \right) \left[ \nabla \tilde{p} - \phi \nabla \tilde{\mu} \right], \quad (6)$$

where $\tilde{p} = \phi \tilde{\mu}$ is a pressure term which does not play any role. In particular, when the system presents well-defined phase interfaces, such as at the late stages of phase separation, this body force reduces to the more conventional surface tension, as shown by Jasnow and Viñals (1996) and by Jacqmin (2000). Therefore, being proportional to $\tilde{\mu}$, which is identically zero at local equilibrium, $\mathbf{F}_f$ can be thought of as a non-equilibrium interfacial force.

Since $\mathbf{F}_f$ is driven by surface energy, it tends to minimize the energy stored at the interface driving, say, $A$-rich drops towards $A$-rich regions. The resulting non-equilibrium
attractive force $f_A$ between two isolated drops of radius $R$ separated by a thin film of thickness $d$ can be easily evaluated as $f_A \sim F_\phi R^2 d \sim R^2 \sigma / a$, where $F_\phi \sim \sigma / d^2$ can be obtained through Eqs. (5) and (6). The magnitude of this attractive force is much larger than that of any repulsive interaction among drops due to the presence of surface-active compounds, thus explaining why the rate of phase separation in deeply quenched liquid mixtures is almost independent of the presence of surfactants (see the experimental results by Gupta et al., 1996, 1999).

The ratio between convective and diffusive mass fluxes defines the Peclet number, $N_{Pe} = V a / D$, where $V$ is a characteristic velocity, which can be estimated through Eqs. (2) and (6) as $V \sim F_\phi a^2 / \eta$, with $F_\phi \sim \rho R T / (a M_w)$. Finally we obtain,

\[ N_{Pe} = \frac{a^2}{D} \frac{\rho RT}{\eta M_w} \approx \frac{\sigma a}{\eta D^3} \]

which coincides with the “fluidity” parameter defined by Tanaka and Araki (1998). For systems with very large viscosities, $N_{Pe}$ is small and the model describes a diffusion-driven separation process, as in polymer melts and alloys. For most liquids, however, $N_{Pe}$ is very large, typically $N_{Pe} > 10^3$, showing that diffusion is important only in the vicinity of local equilibrium, when the body force $F_\phi$ is negligible. In general, therefore, for fluid mixtures that are in conditions of non-equilibrium, either phase-separating or mixing, convection dominates diffusion.

Although this approach has been developed for very idealized systems, it seems to capture the main features of real mixtures, at least during the phase separation process. This is why we did not add further terms to generalize our model, although they can be derived rather easily (see Vladimirova et al., 1998, 2000).

### 3. Numerical results

Now we restrict our analysis to two-dimensional systems, so that the velocity $v$ can be expressed in terms of a stream function $\psi$, i.e. $v_1 = \partial \psi / \partial r_2$ and $v_2 = - \partial \psi / \partial r_1$. Consequently, the equations of motion become (see Vladimirova et al., 1999a,b, 2000):

\[
\frac{\partial \tilde{\psi}}{\partial t} = N_{Pe} \nabla \tilde{\psi} \times \nabla \psi + \nabla \cdot (\nabla \phi - \phi (1 - \phi)) \times [2 \Psi + \nabla^2 \tilde{\psi}],
\]

\[
\nabla^4 \tilde{\psi} = - \nabla (\nabla^2 \phi) \times \nabla \psi.
\]

This system of differential equations has been time-integrated on a $L = 1000a$ square domain with periodic boundary conditions using the finite difference scheme described in Vladimirova et al. (2000).

First, we simulated the mixing process between two fluids which are initially quiescent and separated by a plane interface, $r_1 = L/2$. In this case, the RHS of Eq. (12), i.e. the body force, is identically zero, so that $v = 0$ and therefore the process does not depend on the Peclet number. In fact, Eq. (11) (in its dimensional form) is well approximated by the following equation:

\[
\frac{\partial \tilde{\psi}}{\partial t} = D^* \frac{\partial^2 \tilde{\psi}}{\partial r_1^2},
\]

with

\[
D^*(\tilde{\phi}) = D [1 - 2 \Psi \tilde{\phi} (1 - \tilde{\phi})],
\]

where $\tilde{\phi}$ represents the mean value of $\phi$, as the neglected terms play a role only at the very beginning of the mixing process, when the interface is still sharp. As shown in Fig. 1, the results of our simulations are in perfect agreement with Eq. (13), confirming that the mixing process...
of two fluids separated by an initially plane sharp interface remains one-dimensional, does not depend on the Peclet number and is a purely diffusive process, with an effective diffusivity $D^*$ that depends on the thermodynamic properties of the mixture, i.e. the value of the Margules parameter $\Psi$. The same result is obtained whenever the initial configuration is one-dimensional, as in the case of an isolated drop.

When we simulate the mixing process of a collection of drops immersed in a background field, we have already shown in Vladimirova et al. (1999a) that, while a single drop remains still as it is absorbed, two drops tend to attract each other and even coalesce, provided that the Peclet number is large enough and the drops are initially very close to each other. This effect is further investigated in the simulations shown in Fig. 2, representing the evolution of two identical drops with $\Psi = 1.9$ and radius $40a$, that are placed within the quiescent bulk fluid at a distance of $120a$ from each other.

Fig. 2. Snapshots of the evolution of two identical drops with $N_{Pe} = 0$ (left) and $N_{Pe} = 10^4$ (right) at time $t = 0, 1, 2, 3, 4$ and $5 \times 10^3 a^2/D$. The drops have $\Psi = 1.9$, an initial radius of $40a$ and are placed within the bulk fluid at a distance of $120a$ from each other.

When $N_{Pe} = 0$, the drops do not move and are reabsorbed by diffusion, while when $N_{Pe} = 10^4$, they rapidly coalesce and form a larger isolated single drop. This latter, though, has to be reabsorbed by diffusion, too, and, being larger than the original drops, will take approximately twice as long to disappear. Consequently, mixing appears to be faster in the absence of convection.

This result is confirmed by the series of simulations shown in Fig. 3, where the initial concentration field is that resulting from a random distribution of 250 drops with radii between

Fig. 3. Snapshots of the evolution of a random collection of 250 drops with $N_{Pe} = 0$ (left) and $N_{Pe} = 10^4$ (right), at time $t = 0, 1, 2$ and $4 \times 10^3 a^2/D$. The drops have $\Psi = 1.9$ and initial radii between $5a$ and $20a$. 
Fig. 4. Time evolution of the degree of mixing [cf. Eq. (15)] with \( \text{Pe} = 0 \) and \( 10^4 \).

5a and 20a and with \( \Psi = 1.9 \). The results of these simulations are summarized in Fig. 4 in terms of the degree of mixing \( \delta_m \), defined as

\[
\delta_m(t) = \frac{\langle |\phi(r,t) - \phi_{av}|^2 \rangle}{\langle |\phi_0(r) - \phi_{av}|^2 \rangle} = \frac{\phi_{rms}^2(t)}{\phi_{rms}^2(0)},
\]

(15)

where the brackets indicate volume average. Comparing the behavior for \( \text{Pe} = 0 \) with that for \( \text{Pe} = 10^4 \), we see that \( \delta_m \) decays exponentially as

\[
\delta_m(t) = \exp\left(-10^3 \frac{Dt}{\alpha^2} \right),
\]

(16)

where \( \alpha \approx 0.8 \) when \( \text{Pe} = 0 \) and \( \alpha = 2.1 \) when \( \text{Pe} = 10^4 \). This result shows that indeed \( \delta_m \) decays faster in the absence of the convection that is induced by non-equilibrium interfacial forces, i.e. for very viscous liquids.

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References


