Phase separation of viscous ternary liquid mixtures

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HIGHLIGHTS

▶ We study the phase separation of ternary liquid mixtures.
▶ Our theoretical model follows the standard diffuse-interface model.
▶ Hydrodynamics is coupled with thermodynamics of ternary phase field variables.
▶ Two examples are studied using a second-order finite element method.
▶ We discuss the morphology development and domain growth during the phase separation.

ARTICLE INFO

ABSTRACT

In this work we study the demixing of ternary liquid mixtures, following an initial quench to an unstable state of their phase diagram. Our theoretical model follows the standard diffuse interface model, where convection and diffusion are coupled via a body force, expressing the tendency of the mixture to minimize its free energy. Here we model the behavior of a very viscous polymer melt, so that the Peclet number, expressing the ratio between convective and diffusive mass fluxes, is small. Two examples are presented, describing the phase separation of ternary mixtures in two and three phases, respectively. In the first case, as expected, we see that the growth of the domain size follows the well known diffusion-driven scaling, $R(t) \propto t^{1/3}$. On the other hand, in the second example, the domain size growth follows the usual $t^{1/3}$ scaling only until the symmetry among the three phases breaks down and the domain size of two of the three phases decrease sharply. After that point, the morphology of the system becomes more regular, almost crystal-like, and the three phases start to grow again, with the same growth rate $R(t) \propto t^n$, with $n=0.11$.

1. Introduction

The diffuse interface model was developed originally to describe near-critical behavior of single-component fluids and partially miscible binary mixtures (Cahn and Hilliard, 1958, 1959; Hohenberg and Halperin, 1977; Lowengrub and Truskinovsky, 1998; Vladimirova et al., 1999), and it has been widely used to study many kinds of physical phenomena of binary mixtures such as mixing of viscous liquids (Vladimirova and Mauri, 2004), droplet dynamics (Yue et al., 2004) and structure development of polymer blends (Prusty et al., 2007; Keestra et al., 2011).

Despite many industrial and biochemical processes involve mixtures with three or more components, only a few theoretical and numerical works have studied these systems. In particular,

Huang et al. (1995) analyzed numerically the dynamics of phase separation of ternary alloys (i.e. where convective effects can be neglected) into two and three phases by solving the nonlinear spinodal decomposition equations in two dimensions. Examining the dynamical scaling and the growth laws for the late stages of separation, they saw that the growth law $R(t) \propto t^{1/3}$ is always obeyed, despite the fact that the self-similar regime is achieved very slowly in ternary systems. Later, Kim and Lowengrub (2004, 2005) developed a full Navier–Stokes/Cahn–Hilliard code to model the phase mixing/demixing and the Rayleigh instability of ternary mixtures using a diffuse interface model in the low Reynolds number regime. There, applying boundary integral methods, the effects of surfactants on drop dynamics, tip-streaming and drop deformation have been investigated. Phase-field ternary mixture models have also been of interest for modeling many different physical phenomena, for example, solidification and microstructure evolution in ternary alloy systems (Kobayashi et al., 2003), mutual diffusion effects in partially miscible polymer

blends (Tufano et al., 2010), and surfactant-induced emulsion coarsening (Lamorgese and Banerjee, 2011).

In this work, starting from the already existent results for two component systems (Lamorgese and Mauri, 2005), we develop a general model of ternary mixtures, in which the Navier–Stokes equation is coupled to generalized Cahn–Hilliard equations for the phase variables. Compared to previous models (Kobayashi et al., 2003; Lamorgese and Banerjee, 2011), the present one has the advantage of simplicity and thermodynamic consistency, without employing any *ad hoc* term that cannot be directly related to macroscopic, easily measured parameters.

2. The governing equations

2.1. Multi-component mixtures at equilibrium

Consider a homogeneous mixture of N species A_k ($k = 1, 2 \ldots N$), with molar fractions x_k, kept at temperature T and pressure P. For sake of simplicity, in our model we assume that the molecular weights, specific volumes and viscosities of all species are the same, namely $M_k = M_w$, $\overline{V}_k = \overline{V}$ and $\eta_k = \eta$, for all species k, so that molar, volumetric and mass fractions are all equal to each other, and the mixture viscosity is composition-independent. The equilibrium state of this system is described by the "coarse-grained" free energy functional, that is the molar Gibbs energy of mixing:

$$\Delta g^{th} = g^{th} - \sum_{k=1}^{N} g_k x_k, \tag{1}$$

where g^{th} is the energy of the mixture at equilibrium, while g_k is the molar free energy of pure species A_k at temperature T and pressure P. The free energy Δg^{th} is the sum of an ideal part Δg^{id} and a so-called excess part g^{ex}, with

$$\Delta g^{id} = RT \sum_{k=1}^{N} x_k \log x_k, \tag{2}$$

where R is the gas constant, while the excess molar free energy can be expressed as

$$g^{ex} = \frac{1}{2} RT \sum_{i,k=1}^{N} \Psi_{ik} x_i x_k, \tag{3}$$

where Ψ_{ik} are functions of T and P, with $\Psi_{ik} = \Psi_{ki}$ and $\Psi_{ii} = 0$. This expression can be generally derived by considering the molecular interactions between nearest neighbors or summing all pairwise interactions throughout the whole system (Lifshitz and Pitaevskii, 1984). As shown by Mauri et al. (1996), Eq. (3) can also be derived from first principles, assuming that the pairwise forces between identical molecules, $F_{i,i}$ are all equal to each other and larger than the pairwise forces among unequal molecules, $F_{i,j}$ (with $i \neq j$), i.e. $F_{i,i} = F_{j,j} > F_{i,j}$, obtaining an expression for Ψ_{ij} which depends on ($F_{i,i} - F_{i,j}$). In the following, we shall assume that P is fixed, so that the physical state of the mixture at equilibrium depends only on T and x_i.

Now, it is well known that any variation of the molar free energy can be written as (Prausnitz et al., 1986)

$$dg^{th} = RT \sum_{i=1}^{N} \mu_i^{th} dx_i, \tag{4}$$

where μ_i^{th} denotes the chemical potential of species A_i in solution, i.e.

$$\mu_i^{th} = \frac{1}{RT} \frac{\partial(c g^{th})}{\partial c_i}, \tag{5}$$

with $c_i = c x_i$ denoting the mole densities, that is the number of moles per unit volume, of species A_i, and $c = \sum c_i$ is the total mole density.

In our case, by using Eqs. (1)–(3), we obtain

$$\mu_i^{th} = \frac{g_i}{RT} + \log x_i + \sum_{k=1}^{N} \Psi_{ik}(1 - x_i)x_k - \sum_{j,k \neq i=1}^{N} \Psi_{jk} x_j x_k. \tag{6}$$

Since free energy is an extensive quantity, it is easy to show that chemical potentials represent the amount of free energy due to each species, i.e.

$$g^{th} = RT \sum_{i=1}^{N} \mu_i^{th} x_i. \tag{7}$$

Therefore, comparing Eqs. (4) and (7), we obtain the Gibbs–Duhem relation:

$$\sum_{i=1}^{N} x_i \, d\mu_i^{th} = 0. \tag{8}$$

Considering that $\sum_{i=1}^{N} x_i = 1$, we see that Eq. (4) can be rewritten as

$$dg^{th} = RT \sum_{i=1}^{N-1} \mu_{iN}^{th} \, dx_i, \tag{9}$$

where $\mu_{ij}^{th} \equiv \mu_i^{th} - \mu_j^{th}$. Accordingly, we see that the quantities x_i and $RT\mu_{iN}^{th}$ are thermodynamically conjugated, i.e. $RT\mu_{iN}^{th} = \partial g_{eq}/\partial x_i$. In fact, applying this expression, we obtain

$$\mu_{ij}^{th} = \ln \frac{x_i}{x_j} + \Psi_{ij}(x_j - x_i) + \sum_{k \neq i,j=1}^{N} (\Psi_{ik} - \Psi_{jk})x_k, \tag{10}$$

where, by definition, $\mu_{ij}^{th} \equiv \mu_{ik}^{th} - \mu_{jk}^{th}$ and $\mu_{ij}^{th} = -\mu_{ji}^{th}$. The same result could be obtained directly from Eq. (6).

2.2. Non-local terms

In order to take into account the effects of spatial inhomogeneities, following Cahn and Hilliard (1958, 1959), we assume that the total, or generalized, free energy $\tilde{g}$ is the sum of an equilibrium part and a non-local part:

$$\tilde{g} = g^{th} + g^{nl}, \tag{11}$$

where the latter is given by the following expression:

$$g^{nl} = \frac{1}{4} RT a^2 \sum_{i=1}^{N} (\nabla x_i)^2. \tag{12}$$

Here a represents typical length of spatial inhomogeneities in the composition which, as shown by van der Waals (1893), is proportional to the surface tension between the two phases. Note that, considering that $\sum_{i=1}^{N} x_i = 1$, this expression can also be written as

$$g^{nl} = -\frac{1}{2} RT a^2 \sum_{i \neq j=1}^{N} \nabla x_i \nabla x_j = \frac{1}{2} RT a^2 \sum_{i=1}^{N-1} \left(\nabla x_i \sum_{j \geq i}^{N-1} \nabla x_j \right). \tag{13}$$

Now, chemical potentials can be generalized as follows:

$$\tilde{\mu}_i = \frac{1}{RT} \frac{\delta(c\tilde{g})}{\delta c_i} = \mu_i^{th} + \mu_i^{nl}, \tag{14}$$

where μ_i^{th} is defined in Eq. (5), while,

$$\mu_i^{nl} = -\frac{1}{RT} \nabla \cdot \left(\frac{\partial(c g^{nl})}{\partial \nabla c_i} \right). \tag{15}$$

Consequently we obtain

$$\mu_i^{nl} = \frac{a^2}{2} \nabla \cdot \left[-(1 - x_i) \nabla x_i + \sum_{j \neq i=1}^{N} x_j \nabla x_j \right]. \tag{16}$$