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# Mathematical modeling and computational simulation of phase separation in ternary mixtures

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ABSTRACT

In this study, a phase field model for ternary partially miscible mixture is derived by extending an existing model for binary mixture. Particularly, a fourth-order free energy function for binary mixture is extended to a ternary model in such a way that the ternary model is dynamically and algebraically consistent with the binary model. The ternary model is employed to study the phase separation dynamics of ternary mixtures under initial still conditions. The scaling of domain size growth, $d \propto \tau^{1/3}$, is always obeyed, which appears at the late stage of the phase separation. The scaling law can appear relatively earlier if one phase is totally spreading between two other phases.



## 1. Introduction

Many industrial and biochemical processes involve mixtures of three liquids. For example, one can find three-phase flow of oil-gas-water mixtures in a pipeline in the petroleum industry [1]. In the chemical and biochemical processes, double emulsions, where the droplets of the dispersed phase contain even smaller dispersed droplets, have been a subject of interest due to a wide range of their applications [2,3]. More examples can be also found in the recent microfluidics area [3–5]. For example, Utada et al. [3] produced monodisperse double emulsions of three immiscible liquids by using a microcapillary device. In addition, various emulsions having more complex structures could be produced by phase separations of ternary mixtures in a microfluidic device [6,7].

As far as theoretical study on the mixture is concerned, Cahn and Hilliard achieved a pioneering work in 1959 [8]. In the thermodynamic theory by Cahn and Hilliard, the free energy of the mixture depends not only on the local composition but also on the local composition gradient, and it was originally developed to describe near-critical behavior of binary mixtures [8,9]. The model has been successfully employed to study phase separations of binary mixtures [10–13]. In addition, the model could be coupled with the hydrodynamic equations to study two-phase flow problems [14–16].

While the scope of Cahn–Hilliard model was not limited to the binary mixture, detailed studies on the ternary model began relatively later [17,18], because of the complexity of the system and the computational cost, presumably. Although significant progress has been made by several researchers until recently [19–22], practical implementation of the ternary model to industrial problems is still a challenging issue.

Regarding the increasing interests on the ternary mixture, this work aims to provide mathematical modeling of the ternary *partially miscible* mixture and computational study of the phase separation on the basis of the classical work by Cahn and Hilliard. As noted by Kim and Lowengrub [19], modeling the partial miscibility within ternary mixture is nontrivial. In this regard, motivation of the present work originates from a question if one can obtain a polynomial-based approximation

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function for the free energy of the ternary partially miscible mixture by noting that a fourth-order polynomial function has been successfully employed for binary mixtures [23]. This work is also motivated by the previous work by Boyer and Lapuerta [20] who derived a polynomial-based free energy function for ternary *immiscible* system by extending a fourth-order polynomial function of binary immiscible system.

In this study, we derive the free energy function for ternary *partially miscible* mixture by extending a fourth-order polynomial for the binary mixture, and the derivation procedure mostly follows the previous work on ternary *immiscible* mixture by Boyer and Lapuerta [20]. Particularly in the present model, partial miscibility between each species is allowed in a more general formula than the previous models [19,20]. In Section 2, fundamental equations of the phase field model are summarized, and binary model is briefly introduced in Section 3. Derivation procedure of the free energy for ternary partially miscible mixture is given in Section 4. Section 5 presents computational results of the phase separations. Finally, a summary and discussion is given in Section 6.

## 2. Phase field model

Fundamental equations of the phase field model is described here. The mixture consists of $N$ components of the same density and the mass fraction of $i$th component is denoted as $c_i(\mathbf{x}, t)$. The governing equation can be written as a diffusional model as follows

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (M_i \nabla \mu_i), \tag{1}$$

where $\mu_i$ is the chemical potential defined as

$$\mu_i = \frac{\delta f}{\delta c_i}. \tag{2}$$

$M_i$ is the mobility parameter, $\delta$ represents the variational derivative, and $f$ is the specific free energy. In this study, the mobility parameter is assumed to be constant.

According to Cahn and Hilliard [24], the free energy of mixture can be written as follows

$$f(\mathbf{c}, \nabla \mathbf{c}) = f_0(\mathbf{c}) + \sum_{i=1}^{N} \frac{1}{2} \varepsilon_i |\nabla c_i|^2 \tag{3}$$

where $\mathbf{c} = \lfloor c_1, c_2, \ldots, c_N \rfloor$, $f_0$ is homogeneous part of the free energy and $\varepsilon_i$ is the gradient energy parameter.

There is a constraint which $c_i$ should satisfy at any time as follows

$$\sum_{i=1}^{N} c_i = 1. \tag{4}$$

In other words, the diffusional flux $M_i \nabla \mu_i$ should satisfy $\sum_{i=1}^{N} M_i \nabla \mu_i = 0$. Therefore, the chemical potential is rewritten as follows

$$\mu_i = \frac{\delta f}{\delta c_i} + \lambda = \frac{\partial f_0}{\partial c_i} - \varepsilon_i \nabla^2 c_i + \lambda, \tag{5}$$

where $\lambda$ is a Lagrange multiplier [20]. Then the constraint is rewritten as

$$\sum_{i=1}^{N} M_i \nabla \left( \frac{\partial f_0}{\partial c_i} - \varepsilon_i \nabla^2 c_i + \lambda \right) = 0.$$

Assuming $M_i \varepsilon_i = M_0$, $i = 1, 2, \ldots, N$, the Lagrange multiplier is given as follows

$$\lambda = -\frac{1}{M_s} \left( \sum_{i=1}^{N} M_i \frac{\partial f_0}{\partial c_i} \right), \tag{6}$$

where $M_s = \sum_{i=1}^{N} M_i$.

## 3. Binary model

The free energy of binary mixture is written as follows

$$f(\mathbf{c}, \nabla \mathbf{c}) = f_0(c_1, c_2) + \frac{1}{2} \varepsilon_1 |\nabla c_1|^2 + \frac{1}{2} \varepsilon_2 |\nabla c_2|^2. \tag{7}$$