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Study of Cahn-Hilliard Equation to Simulate Phase Separation

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***Abstract*—**An investigation into Cahn-Hilliard equation was carried out through numerical simulation to identify a possible phase separation for one and two dimensional domains. It was observed that this equation can reproduce important mass fluxes necessary for phase separation within the miscibility gap and for coalescence of particles.

***Keywords*—**Cahn-Hilliard equation, miscibility gap, phase separation.

I. Introduction

THE Cahn-Hilliard equation was originally proposed in 1958 as a mathematical model to describe phase separation in binary alloys [1]. This equation has been adopted to model many other physical systems [2], [3]. In order to solve it, many algorithms have been proposed using a variety of discretization methods including finite element, finite volume and finite difference [2], [4], [5].

Its dynamics can be roughly explained with phase diagrams within the framework of classical thermodynamics [6]. An example for spinodal decomposition is given in Fig. 1.

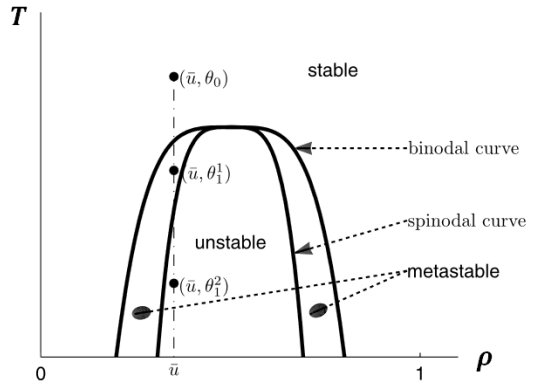

Fig. 1 Phase diagram given in temperature versus composition with a miscibility gap (adapted [6])

According to Fig. 1, compositions in the spinodal region are unstable, because small fluctuations can produce phase separation. On the other hand, compositions outside the spinodal, but under the binodal curve, are metastable. In this case, phase separation would also decrease the free energy of the system, but it can only occur if nuclei of the phases form, since small fluctuations are not sufficiently to promote the separation [6], [7].

This study aims to evaluate the response of the Cahn-Hilliard equation in one and two dimensions, with or without the energy gradient term, subjected to conditions in which the composition is above the binodal curve, between the binodal and spinodal curves or below the spinodal curve.

II. Cahn-Hilliard Equation

The Cahn-Hilliard differential equation can be written as

$$\frac{\partial \rho}{\partial t} = \vec{\nabla} \cdot \left[\left(M \frac{\partial^2 f_0}{\partial \rho^2} \right) \vec{\nabla} \rho - M \vec{\nabla} \left(K_p \nabla^2 \rho \right) \right] \tag{1}$$

where ρ is composition, f_0 is the free energy density, and K_p is the gradient energy coefficient.

It can be rewritten in two dimensions and Cartesian coordinates as

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{\partial}{\partial x} \left\{ M \frac{\partial}{\partial x} \left[\frac{\partial f_0}{\partial \rho} - K_p \left(\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} \right) \right] \right\} \\ &+ \frac{\partial}{\partial y} \left\{ M \frac{\partial}{\partial y} \left[\frac{\partial f_0}{\partial \rho} - K_p \left(\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} \right) \right] \right\} \end{aligned} \tag{2}$$

This equation was discretized using the finite volume method with explicit formulation.

III. Numerical Results

A. Evolution to Steady State - Adjustment of Phase Quantity and Composition

This study was carried out to analyze how Cahn-Hilliard equation predicts the time evolution of a one-dimensional system in an initial condition as

$$\begin{cases} p = 0.5 & \rightarrow \quad 0 \le x \le L \\ p = 3.0 & \rightarrow \quad a.L \le x \le b.L \end{cases}$$

where L is the length of the domain, and a, b are variables that are adjusted to give the average composition according to Table I.

TABLE I
Coefficients to Give the Initial Composition in the One Dimensional System

Average composition	a	b
0.9	0.42	0.58
1.1	0.38	0.62
1.5	0.30	0.70

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In Fig. 2 the curves for the free energy density functions and the average compositions are shown

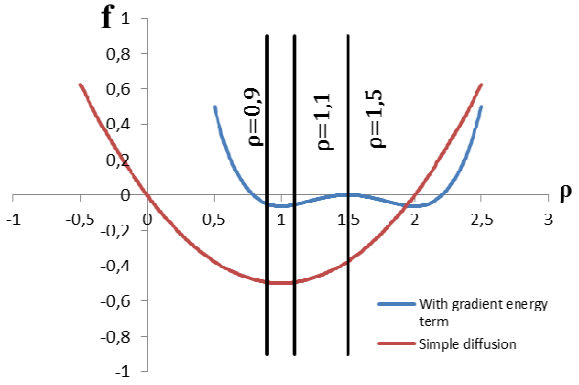
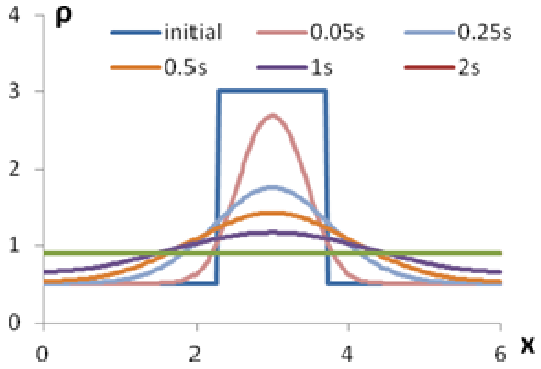
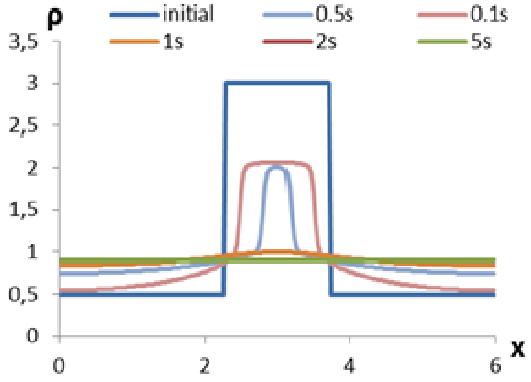


Fig. 2 Free energy density function and mean composition (ρ) indicated

The average composition value of 0.9 is placed outside the miscibility gap and its behavior, regardless of the presence or not of the gradient energy term, corresponds to the homogenization of the system composition. The evolution of the profile with time can be seen and compared in Figs. 3 (a) and (b).



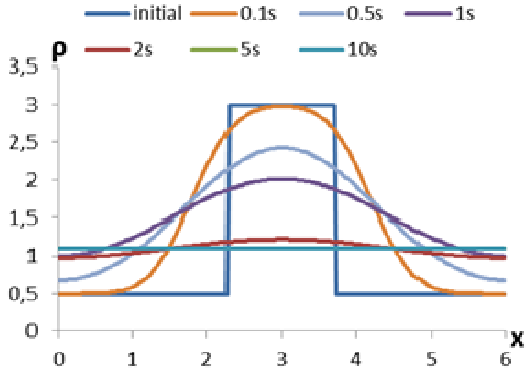
(a)



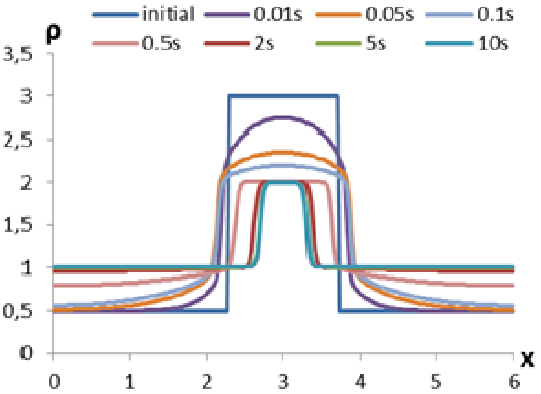
(b)

Fig. 3 Mean composition value ρ = 0.9 (a) without the gradient energy term (b) with the gradient energy term

When the average composition is 1.1 or 1.5, the presence of the gradient energy term changes the final steady-state of the system. Figs. 4 and 5 (a) represent a simple diffusion problem and the result is the homogenization of the system at the average value. In contrast, when the gradient energy term is included there is phase separation and the composition is adjusted to keep constant its average value Figs. 4 and 5 (b).

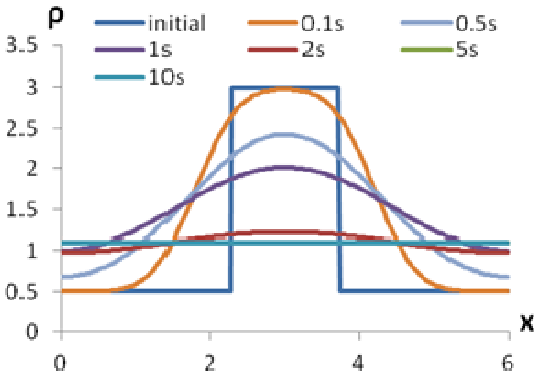


(a)

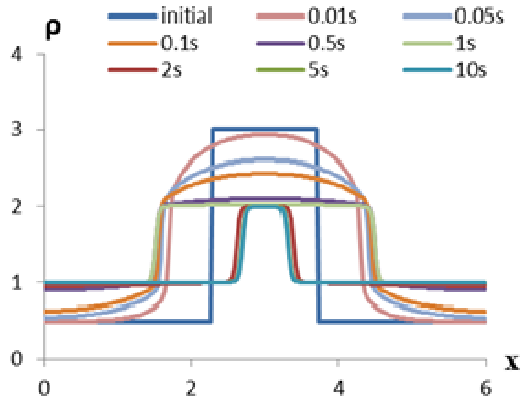


(b)

Fig. 4 Mean composition value 1.1 (a) without the gradient energy term, (b) with the gradient energy term.



(a)



(b)

Fig. 5 Mean composition value 1.5 (a) without the gradient energy term, (b) with the gradient energy term

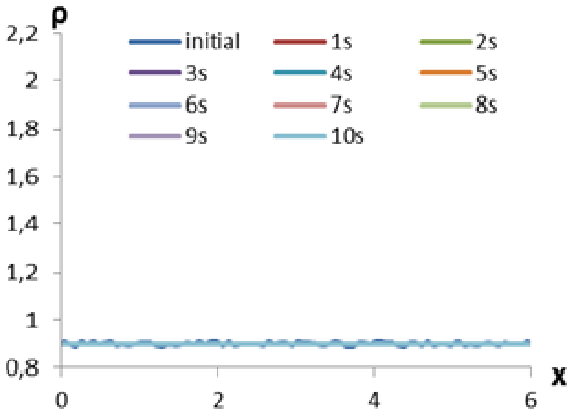


Fig. 6 Initial profile for ρ = 0.9

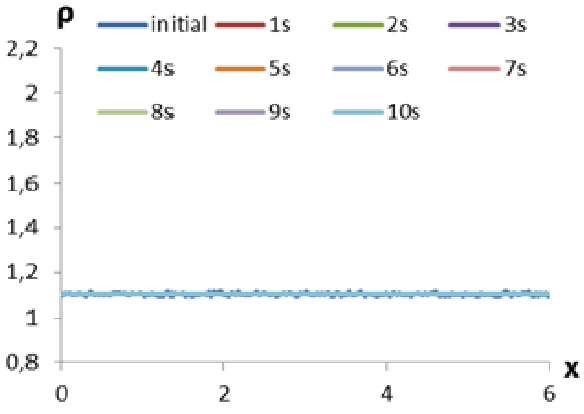


Fig. 7 Initial profile for ρ = 1.1

B. Phase Separation

Phase separation was examined with Cahn-Hilliard equation. The initial condition was a uniform composition with the superposition of a 1% random fluctuation in composition. Without the term derived from the gradient energy, the fluctuation was eliminated by simple diffusion, reaching a final state of uniform composition. In the presence of the term derived from gradient energy, the behavior of the system depends on the average composition. For ρ = 0.9 there is no phase separation, because it is outside the miscibility gap. For ρ = 1.1, the composition is in the meta-stable region (Fig. 1) and the 1% fluctuation was not sufficient to cause phase separation. When ρ = 1.5, phase separation occurred, because the composition is in the unstable region and the initial small fluctuations were sufficient to trigger the separation. Figs. 6-8 show these simulations.

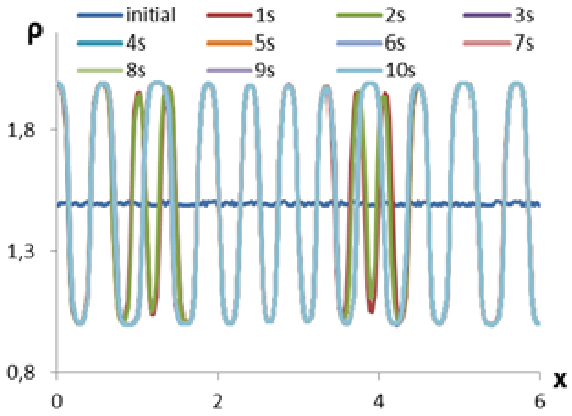


Fig. 8 Initial profile for ρ = 1.5.

C. Coarsening Effect

Cahn-Hilliard equation was solved in a two dimensional domain. An initial composition is given by

$$\begin{cases} p = 0.5 & \rightarrow \quad 0 \le x, y \le L \\ p = 3.0 & \rightarrow \quad a.L \le x, y \le b.L \end{cases}$$

where L is the length of the domain, and a, b are adjusted to give the average composition according to Table II.

TABLE II
DIMENSIONS FOR THE INITIAL DOMAIN ACCORDING TO THE MEAN COMPOSITION FOR TWO DIMENSION ANALYSIS

Mean composition	a	b
0.9	0.30	0.70
1.1	0.255	0.745
1.5	0.18	0.82

A mesh of 80x80 nodes and the free energy density functions presented in Fig. 2 were used. The composition ρ = 0.9, which is located outside the miscibility gap, leads to simple homogenization of the composition by a diffusion mechanism (Fig. 9). When the average composition is within the miscibility gap (ρ= 1.1), the initial square profile becomes a circle by a diffusion mechanism that causes mass transport from the vertices to the edges, but a complete homogenization does not occur, as seen in Fig. 10. The same behavior is observed when ρ = 1.5 (Fig. 11), but the central square/circle is larger. This phenomenon is similar to coarsening, which occurs for precipitated particles in a matrix. In this case, mass is transferred from regions of larger to smaller curvatures of the interface between precipitate and matrix.

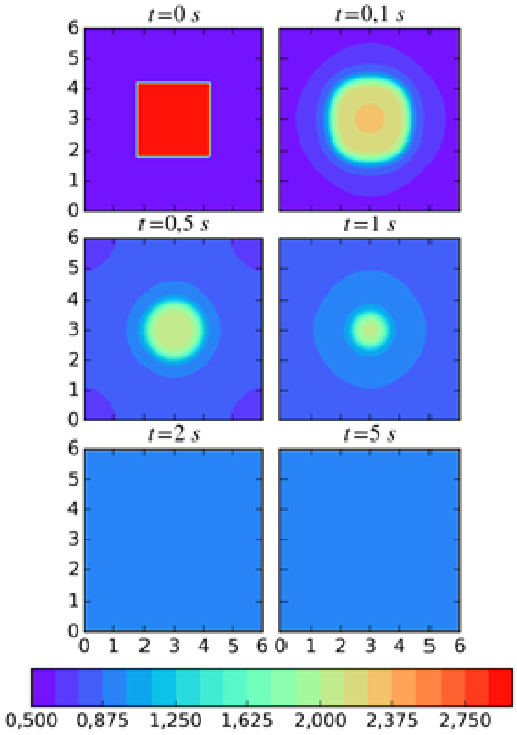


Fig. 9 Mean composition 0.9

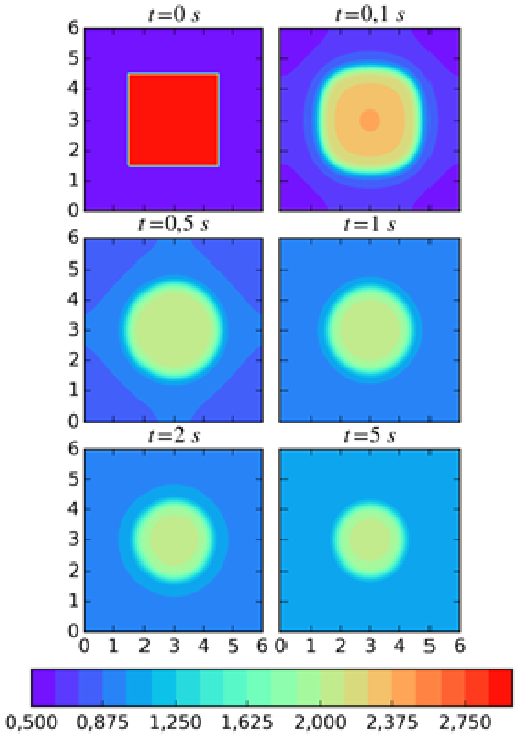


Fig. 10 Mean composition 1.1

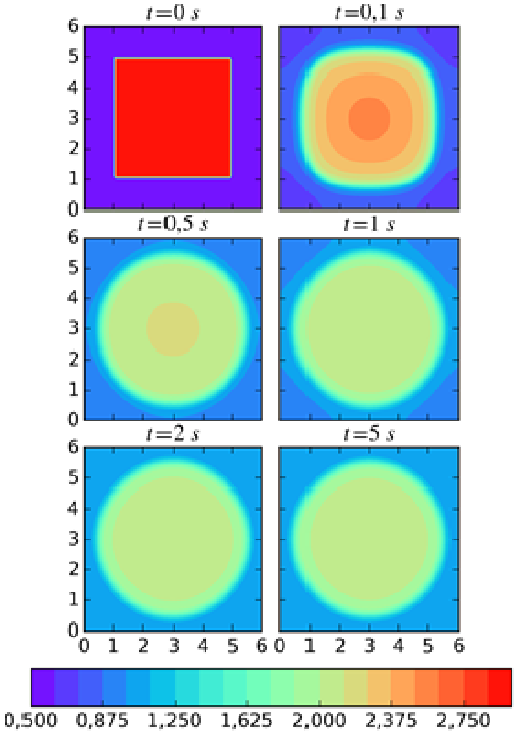


Fig. 11 Mean composition 1.5

IV. Conclusion

An explicit finite volume method (FVM) solution for Cahn-Hilliard equation was implemented for one and two dimensional domains. In the one-dimensional problem, the solution was consistent with the expected thermodynamic behavior for the following simulated processes: (a) homogenization of the system composition, when its average value is placed outside the miscibility gap; (b) adjustment to the amount of phases and composition when the average composition is within the miscibility gap; (c) meta-stability of one phase system, when the average composition is inside the miscibility gap but outside the spinodal region; (d) instability of a system of one phase when its average composition lies within the spinodal composition for one and two-dimensional problems.

The Cahn-Hilliard equation indicated a time evolution of the system consistent with thermodynamics, promoting mass fluxes from the regions with larger to smaller curvatures, i.e. edges, transforming a square area into a circular one. This mechanism is responsible for particle coalescence.

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