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Physical, mathematical, and numerical derivations of the Cahn–Hilliard equation

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ABSTRACT

We review physical, mathematical, and numerical derivations of the binary Cahn–Hilliard equation (after John W. Cahn and John E. Hilliard). The phase separation is described by the equation whereby a binary mixture spontaneously separates into two domains rich in individual components. First, we describe the physical derivation from the basic thermodynamics. The free energy of the volume Ω of an isotropic system is given by $N_V \int_\Omega [F(c) + 0.5\epsilon^2|\nabla c|^2]d\mathbf{x}$, where N_V, c, $F(c)$, ϵ, and ∇c represent the number of molecules per unit volume, composition, free energy per molecule of a homogenous system, gradient energy coefficient related to the interfacial energy, and composition gradient, respectively. We define the chemical potential as the variational derivative of the total energy, and its flux as the minus gradient of the potential. Using the usual continuity equation, we obtain the Cahn–Hilliard equation. Second, we outline the mathematical derivation of the Cahn–Hilliard equation. The approach originates from the free energy functional and its justification of the functional in the Hilbert space. After calculating the gradient, we obtain the Cahn–Hilliard equation as a gradient flow. Third, various aspects are introduced using numerical methods such as the finite difference, finite element, and spectral methods. We also provide a short MATLAB program code for the Cahn–Hilliard equation using a pseudospectral method.

1. Introduction

In this paper, we review physical, mathematical, and numerical derivations for the binary Cahn–Hilliard (CH) equation, and we provide a short MATLAB program code for the equation using a pseudospectral method. The CH equation describes the temporal evolution of a conserved field that is a continuous, sufficiently differentiable function of position. The evolution of the phase separation is due to the non-Fickian diffusion driven by gradients in chemical potential. It was originally proposed to model the spinodal decomposition of a binary *A*–*B* system at a fixed temperature, for which an initially homogeneous system with a uniform composition of c, the mole fraction of component *B*, spontaneously decomposes into two phases with the same crystal structure, but with different compositions. In this case, the spatial distribution of the two phases during decomposition could be described by the composition field, $c(\mathbf{x}, t)$, which is a continuous, differentiable function of position ($\mathbf{x}$) and time (t) [1]. The temporal evolution of the spinodal decomposition in the system is governed by the CH equation [2]:

$$\frac{\partial c}{\partial t} = \nabla \cdot (M\nabla\mu) = M\Delta\mu, \tag{1}$$

where M is the constant mobility. In general, M is the tensor-valued variable mobility [3]. Here μ is the local chemical potential defined as

$$\mu = F'(c) - \kappa\Delta c. \tag{2}$$

In Eq. (2), $F(c)$ is the Helmholtz free energy density per molecule of the homogeneous system with composition c, and κ is a positive constant often called the gradient energy coefficient ($\kappa = \epsilon^2$), which is related to the interfacial energy.

The essential concept underlying the CH equation is that the interface between two phases, say α and β phases, is not sharp, but has a finite thickness in which the composition c changes gradually. For instance, when the binary system approaches near the equilibrium state composed of α phase with $c = c_\alpha^{eq}$ and β phase with $c = c_\beta^{eq} > c_\alpha^{eq}$, the domains where $c(\mathbf{x}, t) = c_\alpha^{eq}$ and $c(\mathbf{x}, t) = c_\beta^{eq}$ correspond to the α and β phases, respectively, whereas the region where $c(\mathbf{x}, t)$ varies gradually from c_α^{eq} to c_β^{eq} represents the interface between the α and β phases, as shown in Fig. 1.

One of the most striking advantages of using the CH equation for simulating microstructural evolution is the avoidance of explicit tracking of the interface. This concept of a diffuse interface has been adopted to model various physical phenomena involving

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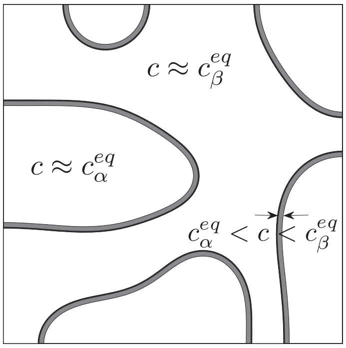

Fig. 1. Two phase microstructure with order parameter *c*.

moving interfaces, in which the order parameter, or phase field $\phi(\mathbf{x}, t)$, instead of the composition field $c(\mathbf{x}, t)$, is introduced to describe the spatial distribution of the entire microstructure of a system. If the overall phase fraction in the system is conserved during evolution, as in the coarsening phenomenon of a precipitate phase in a matrix phase, the governing equation for the temporal equation of $\phi(\mathbf{x}, t)$ is given by a CH-type equation similar to Eq. (1).

Some examples of applications of the CH equation are the phase separation of binary and ternary liquid mixture [4,5], multi-phase fluid flows [6–9], Taylor flow in mini/microchannels [10], two-layer flow in channels with sharp topographical features [11], spinodal decomposition with composition-dependent heat conductivities [12], phase decomposition and coarsening in solder balls [13], the thermal-induced phase separation phenomenon [14], the evolution of arbitrary morphologies and complex microstructures such as solidification, solid-state structural phase transformations [15–18], meta-stable chemical composition modulations in the spinodal region [19], modeling of martensitic phase transformation [20], grain growth [21], pore migration in a temperature gradient [22], image inpainting [23,24], and tumor growth [25,26].

The remainder of this paper is organized as follows. Section 2 describes a detailed physical derivation of the CH equation using basic thermodynamics. Section 3 reviews a mathematical derivation of the CH equation as a gradient flow and mathematical analysis of the equation. Section 4 presents several numerical methods up to now for solving the CH equation. Finally, Section 5 states the conclusions.

2. Physical derivation

In this section, the CH equation is derived along the lines of some previous studies [1,27,28] by using basic thermodynamics. Considering a binary, regular solid solution at constant temperature, we first derive the form of the Helmholtz free energy density, $F(c)$, for a homogeneous system. Then, we derive the local free energy density for a compositionally inhomogeneous system, so as to obtain the total free energy of an inhomogeneous system having volume V, with F as a functional of $c(\mathbf{x}, t)$. The local chemical potential, μ, which must be uniform throughout the system in equilibrium, is defined as the variational derivative of F and the mass flux $\mathcal{J}$ is proportional to the minus gradient of μ. Finally, the CH equation is obtained by substituting the constitutive equation between $\mathcal{J}$ and μ into the continuity equation for mass conservation. We denote the free energy of a domain bounded by Ω in $\mathbb{R}^d$ $(d = 1, 2, 3)$, as $N_V \int_\Omega [F(c) + 0.5\epsilon^2 |\nabla c|^2] d\mathbf{x}$. Using the usual continuity equation, we obtain the CH equation. A detailed descriptions is provided below. The following derivations have been obtained in previous studies [1,27,28]. First, we derive the form of $F(c)$, the free energy per molecule of a homogenous system.

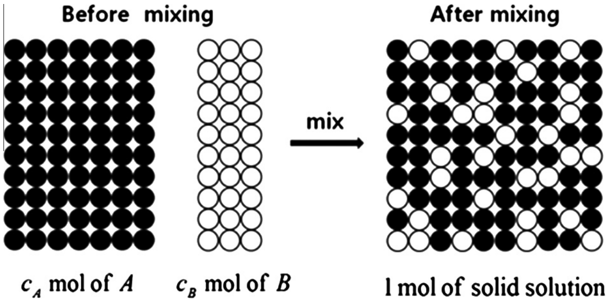

Fig. 2. Free energy of mixing. Before mixing: $F^0 = c_A F_A^0 + c_B F_B^0$, after mixing: $F_{\text{mix}} = F^0 + \Delta F_{\text{mix}}$.

2.1. Free energy of a homogeneous system

For a simple and closed system to be in equilibrium at fixed temperature (T) and volume (V), its Helmholtz free energy F must be minimized. By definition, the Helmholtz free energy of a system, F, is given by $F = E - TS$, where E and S are the internal energy and entropy of the system, respectively. In general, the thermodynamic properties of a solid solution will include a combination of its configurational, vibrational, electronic, and magnetic properties. For example, consider the process for preparing a binary *A*–*B* solid solution by mixing pure *A* and *B* at a fixed temperature. This mixing process will, in principle, result in not only configurational and vibrational changes, but also electronic and magnetic changes in each atom. For simplicity, by assuming that pure *A* and *B* have an equal molar volume and exhibit no changes in molar volume when mixed, only the configurational contributions will be taken into account for investigating the changes in thermodynamic properties during the mixing process.

Consider one mole of a binary solid system composed of N_A atoms of *A* and N_B atoms of *B*. The overall composition of the system is given by the mole fraction of component *B*, *c*, defined as $c = N_B/(N_A + N_B) = N_B/N_a$, where N_a is Avogadro's number (6.023×10^{23}). When the N_A atoms of *A* and N_B atoms of *B* are randomly mixed at a fixed temperature *T*, the binary solid mixture is a homogenous solid solution with a uniform composition *c*. Thus, we consider the homogenous solid solution as a regular solution, assuming random mixing of components *A* and *B* while accounting for the difference in the chemical affinity between *A* and *B* from those between atoms of the same type. In order to obtain the molar Helmholtz free energy of the regular solution, as shown in Fig. 2, consider the isothermal mixing process of $1 - c$ moles of pure *A* and *c* moles of pure *B*. The molar Helmholtz free energy of the system before mixing, F^0, is the weighted sum of those of the pure components, F_A^0 and F_B^0, and is given by $F^0 = E^0 - TS^0 = (1 - c)F_A^0 + cF_B^0$, as shown in Fig. 3. The mixing process alters the atomic configuration of *A* and *B* in the system, leading to changes in the internal energy and entropy, i.e., ΔE_{mix} and

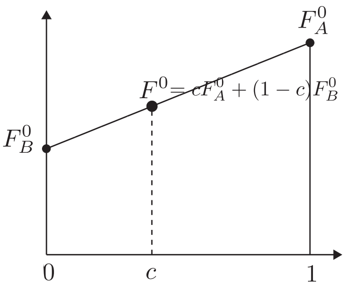

Fig. 3. Variation in the free energy F^0 before mixing with alloy composition *c*.