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Phase separation of binary systems[☆]

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ABSTRACT

In this paper, three physical predictions on the phase separation of binary systems are derived based on a dynamic transition theory developed recently by the authors. First, the order of phase transitions is precisely determined by the sign of a nondimensional parameter K such that if $K > 0$, the transition is first order with latent heat and if $K < 0$, the transition is second order. Here the parameter K is defined in terms of the coefficients in the quadratic and cubic nonlinear terms of the Cahn–Hilliard equation and the typical length scale of the container. Second, a phase diagram is derived, characterizing the order of phase transitions, and leading in particular to a prediction that there is only a second-order transition for molar fraction near $1/2$. This is different from the prediction made by the classical phase diagram. Third, a TL-phase diagram is derived, characterizing the regions of both homogeneous and separation phases and their transitions.

1. Introduction

Materials consisting of two components A and B, such as binary alloys, binary solutions and polymers, are called binary systems. Sufficient cooling of a binary system may lead to phase separations, i.e., at the critical temperature, the concentrations of both components A and B with homogeneous distribution undergo changes, leading to heterogeneous spatial distributions. There have been many studies on this; see among others [1–8].

The main objective of this paper is to precisely describe the phase separation mechanism and to make a few physical predictions. The main results obtained are based on the rigorous mathematical analysis of the Cahn–Hilliard equation in Ref. [9]. The study presented here and in Ref. [9] is based on a dynamic transition theory developed recently by the authors. Our main philosophy of the theory is to search for the full set of transition states, giving a complete characterization on stability and transition. The set of transition states – physical "reality" – is represented by a local attractor. For equilibrium phase transition problems, this local attractor may include both equilibria and some transients represented by a homoclinic orbit. Following this philosophy, the dynamic transition theory is developed to identify the transition states and to classify them both dynamically and physically [10–12]. Using this theory, a few typical and important equilibrium phase transition problems are addressed, including the physical vapor transport (PVT) system [13], ferromagnetism [14], binary system (Cahn–Hilliard equation) [9], and superfluidity of the liquid helium (helium-3 [12], helium-4 [15], and their mixture [16]), leading to a number of physical predictions.

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As mentioned earlier, this paper focuses on the physical implications of the rigorous mathematical results obtained in Ref. [9] for the Cahn–Hilliard equation in both general and rectangular domains supplemented with either the Neumann or the periodic boundary conditions. For simplicity of the presentation, in this paper, we consider only the case where the spatial domain is a rectangular domain with the Neumann boundary condition. The main mathematical theorems are given by Theorems 4.1 and 4.2 in Ref. [9], and the physical conclusions in this paper are obtained by carefully examining these two theorems, and by deriving phase diagrams in different phase planes. The main points presented in this paper are as follows:

First, we give a physical interpretation of these two theorems by introducing a nondimensional parameter K and its associated dimensional parameter K_d, depending on the coefficients of the quadratic and cubic terms in the Cahn–Hilliard equation and the typical length scale. The two mathematical theorems are then translated into a precise criteria to determine the type of phase transitions for the binary system by the sign of the parameter K (or K_d).

Second, we use the Landau mean field theory to make connections of the coefficients in the Cahn–Hilliard equation to the temperature T and the average molar fraction u_0. Using this connection, we are able to derive two precise formulas. The first one is obtained by solving $K_d = 0$, and is for the critical length scale L_d in terms of the critical temperature T_c and u_0. By definition of K_d and Theorems 4.1 and 4.2 in Ref. [9], this formula determines the phase transition types. The second formula is derived by solving the $\beta_1 = 0$, where β_1 is the first eigenvalue of the linearized equation. The resulting formula characterizes the critical control parameters where the phase transition occurs.

Third, with the above formulas, we are able to derive precise phase diagrams in the Lu_0-plane, Tu_0-plane, and TL-plane respectively, leading to Physical Conclusions II and III. Here u_0 is mol fraction of the component B in the homogeneous state.

Fourth, we focus in this paper on the case where the spatial domain is a rectangular region, leading to Type-I and Type-II transitions in the dynamical sense. For general domains, however, it is shown in Ref. [9] that the dynamic transition of the Cahn–Hilliard equation is generically Type-III (mixed type) in the sense of dynamic classification of phase transitions [9,12]. This leads to either first- or second-order transitions, depending on the initial fluctuations.

Finally, the Cahn–Hilliard model we use is classical, and has been studied by many authors. The model retains only up to cubic order nonlinear terms, and can be derived by the expansion near the critical points of phase transitions, following the idea of the Landau mean field theory. It is worth mentioning that the analysis in Ref. [9] and consequently the physical conclusions given in this paper is valid if we retain more or all the higher order terms in the mean field expansion, and the results are exactly the same as in Ref. [9] and in this paper. In other words, the main results will still be true if we work on the logarithmic nonlinearity as given in (2) below. Also, we remark that part of the results in Ref. [9] and in this paper can be generalized to nonlocal Cahn–Hilliard models, and we shall report this study in a forthcoming article.

2. Cahn–Hilliard equation

Consider a binary system, and let u_A and u_B be the concentrations of components A and B respectively, then $u_B = 1 - u_A$. The Helmholtz free energy is given by

$$F(u) = F_0 + \int_\Omega \left[\frac{\mu}{2}|\nabla u_B|^2 + f(u_B)\right] \mathrm{d}x. \tag{1}$$

Here according to the Hildebrand theory (see Reichl [17,18]), we have

$$f = \mu_A(1-u_B) + \mu_B u + RT(1-u_B)\ln(1-u_B) + RTu_B \ln u_B + au_B(1-u_B), \tag{2}$$

where μ_A, μ_B are the chemical potentials of A and B respectively, R is the molar gas constant, $a > 0$ the measure of repulsion action between A and B, and T is the temperature parameter.

In a homogeneous state, u_B is a constant in space and is equal to its mean value, i.e., $u_B = \bar{u}_B$. Let

$$u = u_B - \bar{u}_B, \qquad u_0 = \bar{u}_B.$$

Using the Landau mean field theory, we have the following Cahn–Hilliard equation

$$\frac{\partial u}{\partial t} = -k\Delta^2 u + \Delta[b_1 u^1 + b_2 u^2 + b_3 u^3], \tag{3}$$

where the coefficients k, b_1, b_2 and b_3 are given by

$$\begin{aligned}
&k = \mu D,\\
&b_1 = \frac{D}{2}\frac{\mathrm{d}^2 f(u_0)}{\mathrm{d}u^2} = \left[\frac{RT}{u_0(1-u_0)} - 2a\right]\frac{D}{2}\\
&b_2 = \frac{D}{3!}\frac{\mathrm{d}^3 f(u_0)}{\mathrm{d}u^3} = \frac{2u_0 - 1}{6u_0^2(1-u_0)^2} DRT,\\
&b_3 = \frac{D}{4!}\frac{\mathrm{d}^4 f(u_0)}{\mathrm{d}u^4} = \frac{1 - 3u_0 + 3u_0^2}{12u_0^3(1-u_0)^3} DRT,
\end{aligned} \tag{4}$$

where D is the diffusion coefficient.