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Dynamic scaling of phase separation in CuCo alloys

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The Langer–Bar–Miller (LBM) theory and the non-linear Cahn theory on phase separation dynamics in alloys have been reviewed briefly and applied to calculate dynamics of phase separation of homogenized CuCo alloys. The three-parameter technique of the LBM theory for evaluating compositional fluctuations is applicable only in a narrow range of alloy composition. In this narrow range, the as-calculated equal time structure function $S(k,t)$, where k is the wave vector and t is time, does not follow the universal scaling hypothesis in the late stage of phase separation: $k_m^3\, S(k,t) = f(k/k_m)$, where f is a scaling function and k_m is the peak position of $S(k,t)$. The kinetic growth exponent, defined by k_m as a power function of time, does not agree with prediction of the scaling analysis. The non-linear Cahn approach has been applied to evaluate the profile and amplitude spectra of the compositional fluctuations during phase separation in both meta-stable and non-stable regions. Overall range of alloy composition, the structure function $S(k,t)$ in the late stage of phase separation shows scaling behaviours quite well consistent with the universal scaling hypothesis. The kinetic growth exponent equals to 0.22 in the non-stable region, well consistent with prediction of the scaling analysis. In the meta-stable region, this exponent increases up to 0.28 as the alloy composition decreases down to 0.01, exhibiting good agreement with theory of coarsening kinetics.

1. Introduction

The problem of phase separation in homogenized alloys has been of interest in last decades, not only from the point of view of technological application but also as a representative example of the first order phase transitions [1–3]. Since Cahn [4–6] published the first linearized dynamic theory on this problem, many studies on improving this theory from different points of view and applying it to explain a series of experimental phenomena observed in processing of different materials (metals, glasses, polymers and biological materials etc.) have been reported. Our understanding of phase separation dynamics has been considerably advanced. For progress in this field, we refer to the excellent reviewing articles of Binder [2, 7], and Wagner and Kampmann [8]. It is now well believed that the linearized Cahn theory is only successful in the very early stage of spinodal decomposition, one of the two mechanisms responsible for phase separation in alloys. Afterwards, the non-linear effect becomes critical [7]. For precipitation of alloys in the metastable region, the classical nucleation model which actually results from the reaction kinetic concept and has gradually been improved seems to be satisfactory [8]. However, besides the cluster expansion approach of Binder *et al.* [9, 10], which successfully describes dynamic behaviours of phase separation in both metastable and non-stable regions, a phenomenological dynamic aproach applicable in both regions is still open to us.

Almost twenty years ago, Langer *et al.* [11–14] proposed the well known Langer–Bar–Miller (LBM) theory of spinodal decomposition, which reveals the dynamic characters but also predicts the universal scaling property of phase separation in alloys exhibiting a Landau-type character of thermodynamics. This theory may still represent one of the best models on phase separation dynamics. The wide generality of the proposed equation for dynamic evolution and the performed scaling analysis in this theory has been recognized. However, this theory has rarely been applied to real alloy systems. The main difficulty is involved in an evaluation of the time-dependent compositional fluctuations which exhibit strong non-linear characters. Langer *et al.* [14] pre-assumed a single-point correlation of compositional fluctuations which follows the Gaussian distribution and developed a three-parameter technique to numerically evaluate the compositional fluctuations. What should be pointed out here is that this technique shows a lower stability of numerical iteration if the free energy of the system as a function of alloy composition is required to be expanded to a higher order. For a model system exhibiting a Landau-type form of thermodynamics ($\Delta G = a\phi^2 - b\phi^4$, where a and b are positive constants, ΔG and ϕ are the free energy and order parameter of the system, respectively), a checking of validity of this technique by comparison with the Monte-Carlo simulations was performed [14].

Recently, Miyazaki *et al.* [15–17] developed a Fourier-transforming scheme of the non-linear Cahn diffusion equation and updated the Cahn theory into a non-linear approach. This makes it possible to directly calculate compositional fluctuations during phase separation without imposing any pre-assumption. Previous studies on one-dimensional calculations showed that the dynamic behaviours of phase separation in the non-stable region and around the spinodal boundary are quite well described by the non-linear Cahn approach [18–20]. As the metastable region is entered, a reasonable approach requires involving thermal noises and then the dynamic characters can no longer be identified [21, 22]. A systematic calculation of phase separation dynamics in at least a two-dimensional case is necessary to understand these characters. In addition, a surprising similarity of the non-linear Cahn approach with the LBM theory is revealed by performing a comparison between them.

CuCo system is an excellent model alloy for study of phase separation as its thermodynamics is well established and its phase diagram exhibits a broad miscibility gap and no intermediate phase exists. The two products of phase separation are both f.c.c.-type, characterized by coherency and small lattice mismatch. The giant magnetoresistance (GMR) recently observed in decomposed CuCo alloys [23, 24] has also stimulated intense investigations of phase separation kinetics of this system because the GMR depends strongly on the microstructure.

In this paper, we will apply the LBM theory and the non-linear Cahn theory to calculate phase separation dynamics of CuCo alloys and perform a checking of their validity. Firstly, we will briefly review both theories and present the thermodynamic description of CuCo alloys. Then, the calculated results based on the two models will be given. We will show that the three-parameter technique of the LBM theory is applicable only in a narrow range of alloy composition. As the non-linear Cahn theory has been used to evaluate the compositional fluctuations, the as-calculated structure function and kinetic growth exponent have been approved by a detailed comparison with the scaling hypothesis and coarsening theory.

2. Theoretical background

2.1. Motion equation for structure function

A derivation of this equation can be found in Langer's papers [11, 14]. Here, we will only give a concise description in order to fix notation. By the master equation approach, Langer *et al.* gave following equation of motion for the structure function $S(k, t)$ which is defined as the Fourier transform of the two-point correlation function of composition fluctuations in space

$$\frac{\partial S(k,t)}{\partial t} = -2Mk^2[Kk^2 + A(u)]S(k,t) + 2MRTk^2 \tag{1}$$

where M is the atomic mobility, K is the coefficient of gradient energy, R is the general gaseous constant, T is temperature, $u = u(r, t) = C(r, t) - C_0$, $C(r, t)$ is the alloy composition at position r and time t and C_0 is its average value. The symbol $A(u)$ in Equation 1 represents a non-linear feedback term from compositional fluctuations which exhibit strong time dependence. The right second term of Equation 1 involves a contribution of thermal noises and should be much weaker than the right first term. Denoting by ΔG the Gibbs free energy of the system, we have [14]

$$A(u) = \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \frac{\partial^{n+2}(\Delta G)}{\partial C_0^{n+2}} \frac{\langle u^{n+2} \rangle}{\langle u^2 \rangle} \tag{2}$$

where $\langle u^i \rangle$ represents the average of the self-correlation u^i over the real space as considered, which can be directly derived from the compositional profile if it is available. Comparing Equation 1 with the linearized Cahn theory [6], only has an additional term $A(u)$ been included. However, evaluation of this term seemed to be so difficult in mathematics that only recently has a precise solution of it become available, i.e. the non-linear Cahn theory to be described below. Besides this, the three-parameter technique of the LBM theory also represents a well known approximation of it.

2.2. Langer–Bar–Miller theory

In the LBM theory, the compositional fluctuations were assumed to exhibit a Gaussian type single point distribution. The correlation function $\rho(u)$ is approached as:

$$\rho = \frac{b_2}{\sqrt{2\pi}\sigma(b_1 + b_2)} \exp\left[-\frac{(u - b_1)^2}{2\sigma^2}\right] + \frac{b_1}{\sqrt{2\pi}\sigma(b_1 + b_2)} \exp\left[-\frac{(u + b_2)^2}{2\sigma^2}\right] \tag{3}$$

where b_1, b_2 and σ are three parameters which define uniquely the character of the distribution. Here it is required that $b_1 > 0$, $b_2 > 0$ and $\sigma > 0$.

Due to limited space here, we directly write the equations of motion for the self-correlation $\langle u^i \rangle$ [14]

$$\frac{\mathrm{d}\langle u^2 \rangle}{\mathrm{d}t} = 2M[-W + RT(\Delta/a^3)] \tag{4a}$$

$$\frac{\mathrm{d}\langle u^3 \rangle}{\mathrm{d}t} = -3M\left[\frac{W\langle u^3 \rangle}{\langle u^2 \rangle} + \Delta \sum_{n=3}^{\infty} \frac{1}{(n-1)!} \frac{\partial^n(\Delta G)}{\partial C_0^n} \times \left(\langle u^{n+1} \rangle - \langle u^2 \rangle\langle u^{n-1} \rangle - \frac{\langle u^3 \rangle\langle u^n \rangle}{\langle u^2 \rangle}\right)\right] \tag{4b}$$

$$\frac{\mathrm{d}\langle u^4 \rangle_c}{\mathrm{d}t} = 4M\left[-\frac{W\langle u^4 \rangle_c}{\langle u^2 \rangle} + \Delta \sum_{n=3}^{\infty} \frac{1}{(n-1)!} \frac{\partial^n(\Delta G)}{\partial C_0^n} \times \left(\langle u^{n+2} \rangle - \langle u^3 \rangle\langle u^{n-1} \rangle - \frac{\langle u^4 \rangle\langle u^n \rangle}{\langle u^2 \rangle}\right)\right] \tag{4c}$$

where a is the coarse-graining length which normally takes a few atomic spacings for those systems of short range interaction, such as metallic CuCo alloys to be considered here, $k_{\max} = \sqrt[3]{6\pi^2/a^3}$, $\Delta = 0.6k_{\max}^2$, $W = \frac{1}{2\pi^2}\int_0^{k_{\max}} k^4[K\,k^2 + A(u)]\,S(k,t)\mathrm{d}k$ and $\langle u^4\rangle_c \equiv \langle u^4\rangle - 3\langle u^2\rangle^2$.

As in Equation 3 $\rho(u)$ is assumed to be a sum of displaced Gaussians, any term $\langle u^i\rangle$ can be expressed as a function of the three parameters b_1, b_2 and σ, for instance

$$\begin{aligned}
\langle u^2\rangle &= \sigma^2 + b_1b_2\\
\langle u^3\rangle &= b_1b_2(b_1 - b_2)\\
\langle u^4\rangle_c &= b_1b_2[(b_1 - b_2)^2 - 2b_1b_2]\\
\langle u^5\rangle &= b_1b_2(b_1 - b_2)[10\sigma^2 + b_1^2 + b_2^2]\\
\langle u^6\rangle &= 15\sigma^6 + 45\sigma^4b_1b_2\\
&\quad + 15\sigma^2b_1b_2(b_1^2 - b_1b_2 + b_2^2) + b_1b_2\\
&\quad \times(b_1^4 - b_1^3b_2 + b_1^2b_2^2 - b_1b_2^3 + b_2^4) \qquad (5)
\end{aligned}$$

This is the well known three-parameter technique of the LBM theory. A finite-difference scheme of evaluating $\langle u^i\rangle$ is: at $t = 0$, b_1, b_2 and σ are imposed suitable values and $S(k, 0) = 0$; at time t, term $\langle u^i\rangle$ is calculated by Equation 5 and $A(u)$ is obtained from Equation 2, then $S(k, t + \Delta t)$ are calculated by Equation 1 through

$$S(k, t + \Delta t) = S(k, t) + \Delta t\frac{\partial S(k, t)}{\partial t} \qquad (6)$$

Finally, term $\langle u^i\rangle$ at time $t + \Delta t$ are obtained from Equation 4 and new values of the three parameters are determined by solving Equation 5. This procedure is repeated and $S(k, t)$ as a function of time can be numerically evaluated.

Note that from Equation 5 we can find a cubic equation for term (b_1b_2)

$$(b_1b_2)^3 + \tfrac{1}{2}(b_1b_2)\langle u^4\rangle_c - \tfrac{1}{2}\langle u^3\rangle^2 = 0 \qquad (7)$$

it is obvious that a positive root of this equation always exists. However, as $(b_1b_2) > \langle u^2\rangle$, σ^2 must be negative, which has no physical meaning. We will show in following sections that for CuCo system, this three-parameter technique may only be used in a very narrow range of alloy composition, beyond which the case of $(b_1b_2) > \langle u^2\rangle$ occurs.

2.3. Non-linear Cahn theory

The term $\langle u^i\rangle$ can be evaluated by the non-linear Cahn theory, and so a direct calculation of the structure function $S(k, t)$ becomes possible. This theory is based on an analytical solution of the following Cahn equation

$$\frac{\partial u}{\partial t} = \nabla(D(u)\nabla u) - 2MK\nabla^4 u \qquad (8)$$

where $D(u)$ is the inter-diffusion coefficient which is dependent of compositional fluctuations. In the Fourier transform scheme of Equation 8, $D(C)$ is formulated as [15–17]

$$\begin{aligned}
D(C) &= \sum_{n=0}^{\infty} D_nu^n = M\frac{\partial^2(\Delta G)}{\partial C}\\
&= M\sum_{n=0}^{\infty}\frac{1}{n!}\frac{d^{n+2}(\Delta G)}{dC_0^{n+2}}u^n \qquad (9a)
\end{aligned}$$

Considering phase separation in two-dimensional space, by Fourier transforming, we have

$$u = \sum_{m,n}^{\infty} Q(m, n, t)\exp[i\beta(mx + ny)] \qquad (9b)$$

where β is the reciprocal of length of the region considered here, m and n are the wave numbers of Fourier fluctuations and x and y are the co-ordinates in the real space. Substituting Equations 9a and 9b into the two-dimensional Cahn equation, we obtain the motion equation for the amplitude $Q(m, n, t)$ of the Fourier waves:

$$\begin{aligned}
\frac{\partial Q(m, n, t)}{\partial t} = -\beta^2(m^2 + n^2)\Bigg[&2MK\beta^2(m^2 + n^2)\\
&\times Q(m, n, t) + \sum_{i=0}^{\infty}\frac{M}{(i + 1)!}\frac{\partial^{i+2}(\Delta G)}{\partial C_0^{i+2}}\\
&\times R_j(m, n, t)\Bigg] \qquad (10)
\end{aligned}$$

where $R_j(j = 1 \ldots \infty)$ is the jth order two-point correlation of compositional fluctuations in Fourier space:

$$R_0(m, n, t) = Q(m, n, t) \qquad (11a)$$

$$R_1(m, n, t) = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} Q(k_1, k_2, t)Q(m - k_1, n - k_2, t) \qquad (11b)$$

$$\begin{aligned}
R_j(m, n, t) = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} &R_{j-1}(k_1, k_2, t)\\
&\times Q(m - k_1, n - k_2, t), \qquad j \geqslant 2 \qquad (11c)
\end{aligned}$$

The numerical scheme for evaluating the compositional fluctuations is very simple: for a suitable choice of the initial parameters: β and $[m, n]$, $Q(m, n, 0)$ is generated by a standard stochastic technique within a range with its upper and lower boundaries being determined by the fluctuation-dissipative theorem

$$|Q(m, n, 0)|/\Delta t \leqslant 2MRT\,\beta^2(m_{\max}^2 + n_{\max}^2),$$
$$\text{here } \Delta t = 1.0\text{ s} \qquad (12)$$

with m: $[-m_{\max}, m_{\max}]$ and n: $[-n_{\max}, n_{\max}]$; then for available $Q(m, n, t)$, $Q(m, n, t + \Delta t)$ is obtained from Equations 10 and 11 by a finite difference scheme

$$Q(m, n, t + \Delta t) = Q(m, n, t) + \frac{\partial Q(m, n, t)}{\partial t}\Delta t \qquad (13)$$

For the case of CuCo alloys, that $m_{\max} = n_{\max} = 128$ and $\beta = 50\ \mu\mathrm{m}^{-1}$ is chosen.

2.4. Scaling hypothesis and kinetic growth exponent

It is well known that there are two different mechanisms responsible for phase separation, i.e. spinodal decomposition in the non-stable region and nucleation and growth in the metastable. However, it is now recognized that these mechanisms can be identified only in the early stage of phase separation, whereas towards the late stage coarsening becomes dominant. No matter what the mechanism initiating the phase separation, the late stage of phase separation always follows the well-known dynamic scaling hypothesis [25–27] as follows

$$S(k, t) = k_m^{-3} f(k/k_m) \tag{13}$$

where $f(x)$ is a scaling function which is time independent. Another common character of phase separation is coarsening behaviour in the late stage [28–30], which is characterized by motion of the peak position of $S(k, t)$, k_m. This kinetics is found to satisfy a power law as plotted against time t

$$k_m \propto t^{-n} \tag{14}$$

where n is the kinetic growth exponent. Different values of n were proposed by different theories applicable for different situations. In the non-stable region, Binder proposed $n = 1/4$ [28], and the scaling analysis of Langer *et al.* [14] gave $n = 0.212$. For the case of domain growth, $n = 1/3$ from the LSW theory [31, 32] which is essentially a mean-field theory valid in the case of very low volume fraction χ of the new phase (which should fall into the metastable region). Therefore, we can at least conclude that n in the non-stable region should be smaller than that in the metastable region where χ is lower. Equations 13 and 14 will be the critical measures of the validity of the two theories described above. Especially, a general dynamic approach applicable in both non-stable and metastable regions should be able to predict a reasonable value for the kinetic growth exponent as applied to different regions.

2.5. Free energy and diffusion data of CuCo alloys

We have briefly reviewed the LBM theory and the non-linear Cahn theory. An application of both theories requires data of the diffusion coefficient and the Gibbs free energy of the alloy as a function of alloy composition and temperature. For CuCo alloys, these data are already available from measurements and calculations. Between 673–873 K, ΔG can be written as [33, 34]

$$\Delta G(C_0) = (1 - C_0)G^0_{\mathrm{Cu}} + C_0 G^0_{\mathrm{Co}} - TS^{\mathrm{mix}} + \Delta G^{\mathrm{ex}} \tag{15}$$

with

$$S^{\mathrm{mix}} = -R[(1 - C_0)\ln(1 - C_0) + C_0 \ln(C_0)] \tag{16a}$$

$$\begin{aligned}\Delta G^{\mathrm{ex}} = {} & A_1 C_0(1 - C_0) + A_2 C_0(1 - C_0)(1 - 2C_0) \\ & + A_3 C_0(1 - C_0)(1 - 2C_0)^2 \\ & + TB_1 C_0(1 - C_0)\end{aligned} \tag{16b}$$

where G^0_{Cu} and G^0_{Co} are the free energies of the two pure components, S^{mix} is the ideal entropy of mixing, ΔG^{ex} is the excess free energy, T is temperature (K), R is the general gas constant (8.31 J mol^{-1}), A_1, A_2, A_3 and B_1 are the coefficients of the free energy function (for an f.c.c. solid solution, $A_1 = 37\,100$, $A_2 = 2829$, $A_3 = 3251$ and $B_1 = -5.194$; the unit of ΔG^{ex} is J mol^{-1}). Although the Curie point of Co is 1396 K, much higher than the temperature of interest here, the magnetic contribution of cobalt to the free energy should be included, but this contribution can be omitted as a good approximation since in the present case $C_0 \ll 0.1$. The elastic energy contribution can also be neglected because the contribution of this term is estimated to be less than 5%.

The diffusion data of Co in Cu has been obtained by impurity diffusion method, from which the temperature dependent mobility of atoms in CuCo alloys was evaluated [19, 35]

$$M = 0.000172 \exp(24829.3/T)/RT \quad (\text{unit: cm}^2\,\text{s}^{-1}). \tag{17}$$

A reasonable estimation of the coarse-graining length a for CuCo system is a few times the lattice spacing r_0. Here, we take $a = 3r_0$ where $r_0 = 0.368$ nm [34]. The gradient energy coefficient K can be written as $K = \Delta H_0\, a^2/2$, where $\Delta H_0 = 12$ kJ mol^{-1} [34] is the maximum mixing enthalpy.

3. Numerical results

All of the calculation has been focused on the phase separation of homogenized CuCo alloys annealed at $T = 773$ K. We will present the calculated results from the LBM model and the non-linear Cahn approach, respectively.

As $C_0 = 0.5$ and 0.35, the calculated structure function $S(k, t)$ for different times is shown in Fig. 1(a) and Fig. 2(a), where the time scales are inserted inside. A plotting of the single point distribution $\rho(u)$ for several times is presented in Fig. 1(b) and Fig. 2(b), respectively. As $C_0 = 0.5$, $S(k, t)$ shows a rapidly leftwardly shifting peak k_{m} in the early stage of phase separation and is then remarkably decelerated, accompanying an accelerating increase of $S(k_{\mathrm{m}}, t)$ in the late stage, which is physically unreasonable and indicates a worse convergence of the numerical iteration. Two peaks of $\rho(u)$ can be clearly identified at $t = 50$ s, afterwards they exhibit a further growth. In the late stage an abnormal leftwardly shifting of both peaks is found, which is, unfortunately, due to instability of numerical iteration. For the case of $C_0 = 0.35$, considerable motion for the peak of $S(k, t)$ even in the late stage is achieved and the distribution function $\rho(u)$ exhibits two-peak pattern after 70 s. The stability of numerical iteration at $C_0 = 0.35$ is considerably improved comparing to the case of $C_0 = 0.5$, due to the fact that a locally symmetrical shape of $\Delta G(C_0)$ around this value is shown. For both cases, no crossover phenomenon as identified by Langer *et al.* can be observed, the other features remaining similar to those as revealed.

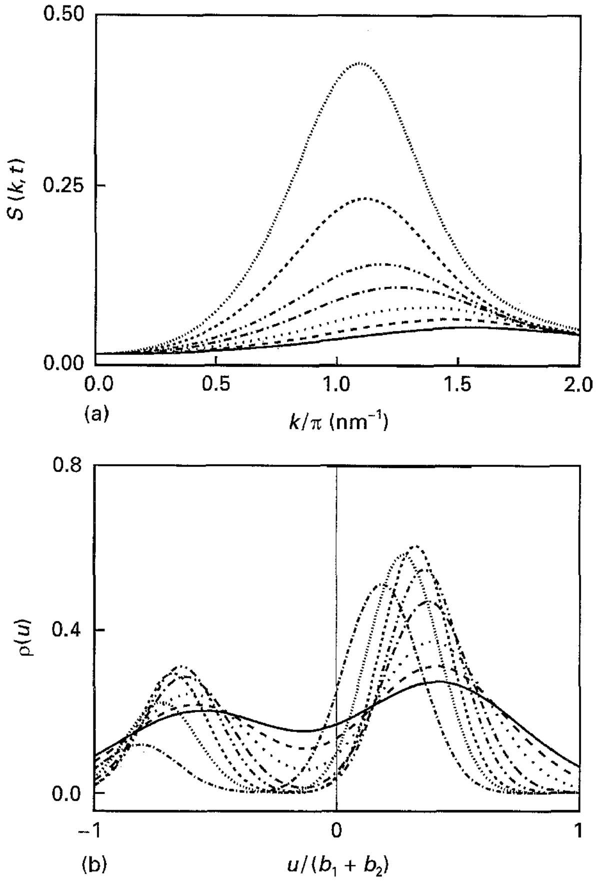


Figure 1 The calculated structure function $S(k, t)$ (a) and single point distribution $\rho(u)$ (b) from the LBM theory for CuCo alloy of $C_0 = 0.5$ annealed at $T = 773$ K for different times. —— 50 s; – – – 70 s; - - - 100 s; – · – · 150 s; – · · – · · 200 s; ·· ·· ·· 300 s; ··· 400 s; – · – · – · – · 500 s.

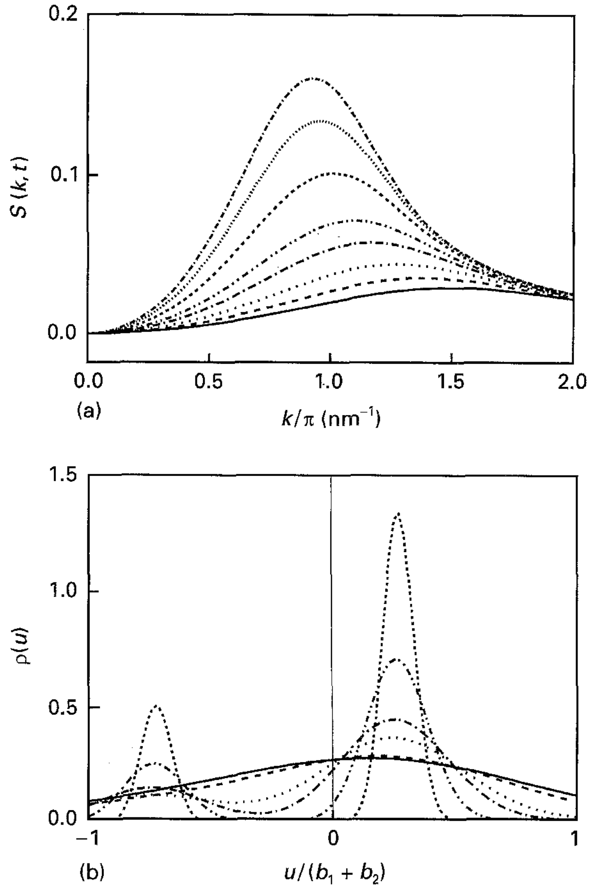


Figure 2 The calculated structure function $S(k, t)$ (a) and single point distribution $\rho(u)$ (b) from the LBM theory for CuCo alloy of $C_0 = 0.35$ annealed at $T = 773$ K for different times. See Fig. 1 caption for key.

Note here that ΔG as a function of alloy composition at a fixed temperature shows a maximum at $C_0 = 0.35$ but not 0.5. A faster kinetics of phase separation at $C_0 = 0.35$ than that at $C_0 = 0.5$ is demonstrated from the distribution function $\rho(u)$ as shown in Figs 1(b) and 2(b), however, the structure function at $C_0 = 0.35$ shows a slower growth compared with the case of $C_0 = 0.5$ because of a worse convergence of the numerical iteration in the latter case. Unfortunately, as $C_0 \leqslant 0.32$ and $C_0 \geqslant 0.55$, non-negative values of the three parameters b_1, b_2 and σ can no longer be achieved after ten seconds, apart from the initial state regardless of effort of improving the numerical stability, indicating that the three-parameter technique becomes no longer valid. The calculated structure function from the LBM theory is in doubt then, except in the very narrow range of alloy composition around 0.35. As a further checking, rescaling of $S(k, t)$ by $k_m^3 S(k, t)$ and k by k/k_m from Figs 1(a) and 2(a), following the scaling hypothesis, is made and the output is shown in Fig. 3. For both cases, only after 50 s, has the scaling hypothesis been well followed, but the points again deviate away from the scaling curve in the late stages (after 200 s) where the scaling hypothesis should be satisfied in a better way. This indicates that at least in the late stage of phase separation (where coarsening dynamics is dominant), the three-parameter technique of LBM theory becomes invalid. In addition, the

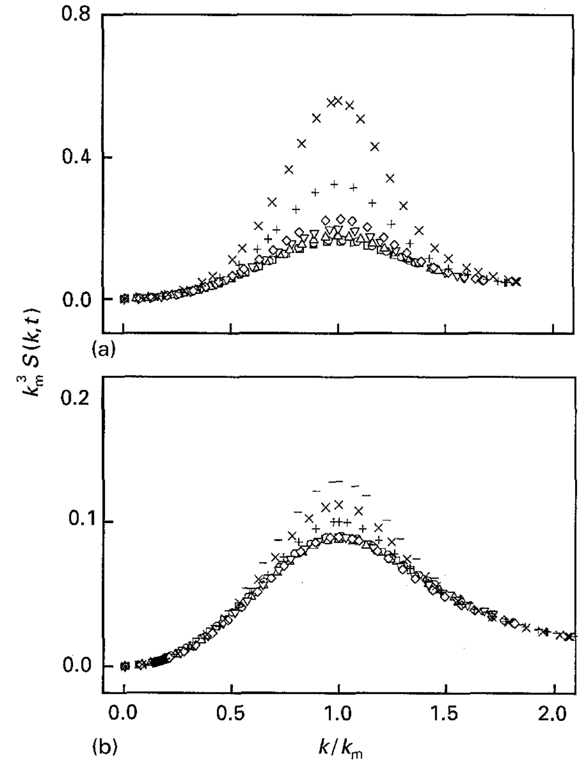


Figure 3 Rescaling of the structure function $S(k, t)$ as shown in Figs 1 and 2, following the scaling hypothesis. (a) for $C_0 = 0.5$ and (b) for $C_0 = 0.35$. □ 50 s; ○ 70 s; △ 100 s; ▽ 150 s; ◇ 200 s; + 300 s; × 400 s; — 500 s.

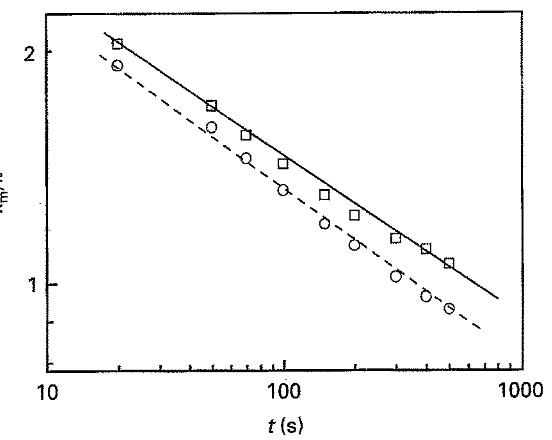


Figure 4 A plot of k_m/π against time t for CuCo alloys phase separating at $T = 773$ K, as calculated by the LBM theory, for evaluating the kinetic growth exponent n. □ $C_0 = 0.50$, $n = 0.178$; ○ $C_0 = 0.35$, $n = 0.705$.

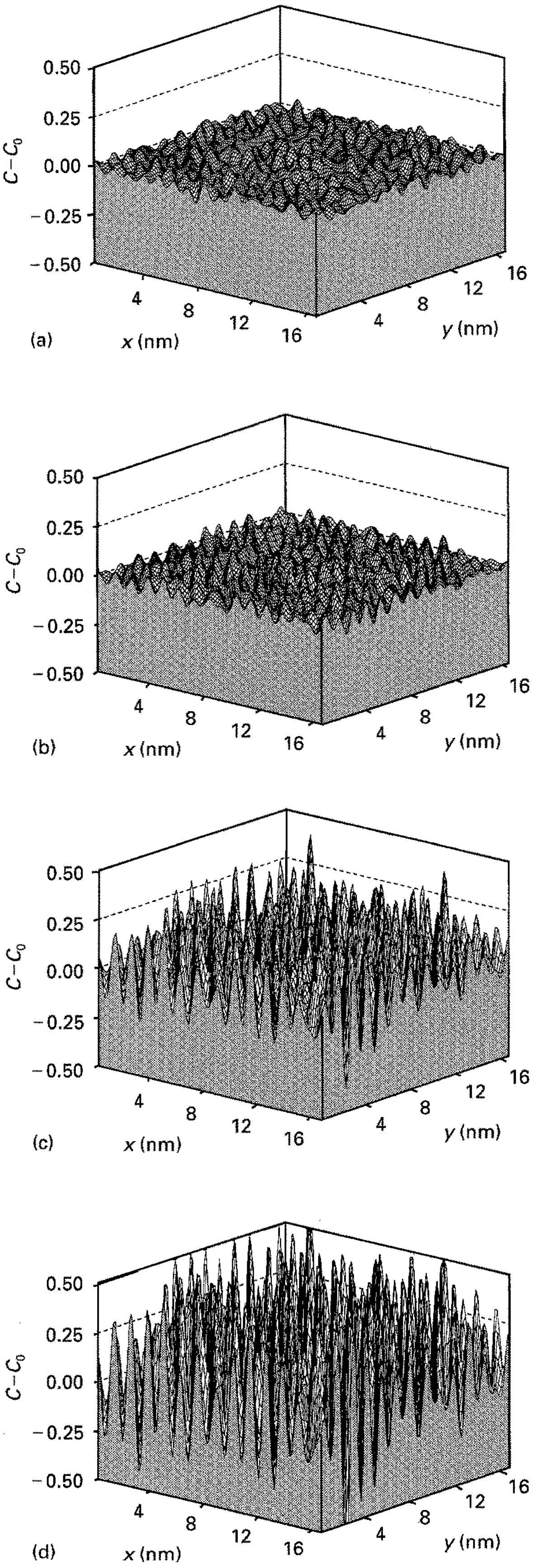
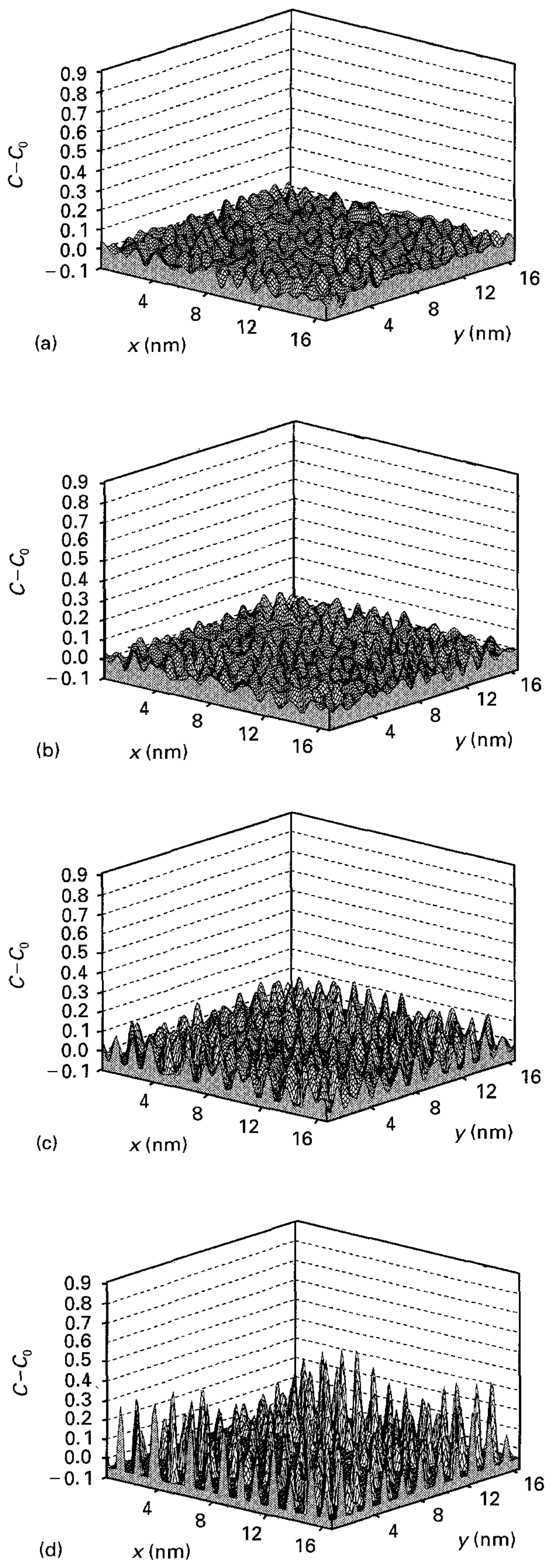


Figure 5 The compositional profiles at several times for CuCo alloy of $C_0 = 0.50$ phase separating at $T = 773$ K, as calculated by the non-linear Cahn theory. (a) $t = 0$; (b) $t = 50$ s; (c) $t = 200$ s; (d) $t = 300$ s.

kinetics growth exponent n obtained by plotting k_m against time t as shown in Fig. 4 is 0.18 as $C_0 = 0.5$ and 0.71 as $C_0 = 0.35$, showing big differences from 0.21, the exponent predicted by the scaling analysis. We conclude that the three-parameter technique in the LBM theory for calculating compositional fluctuations may be applicable only in a very narrow range of composition regardless of its validity, at least for CuCo system.

Therefore, we have to search for a new technique of evaluating compositional fluctuations during phase separation. An updated approach is the non-linear Cahn theory as described above. A systematical evaluation of compositional profile and amplitude spectra of the Fourier waves has been made, as presented below.

The two dimensional composition profiles for several times of annealing as $C_0 = 0.5$ and 0.05 are presented in Figs 5 and 6, respectively. As $C_0 = 0.5$, weak modulating of the wavenumbers in the early stage can be observed. With time, the profile develops from an initially stochastic pattern (Fig. 5(a)) into a regular one of pseudo-periodicity along both axes (Fig. 5(b)). As shown in Fig. 5(c) and (d), inter-connected structure has formed in the late stage. In addition, we can identify that some peaks of the profile grow at a higher rate than other ones, whereas the other peaks remain unchanged or even decayed with time. Advancing of those peaks of higher growth rate, balanced by decaying of those peaks which fall behind, contributes to the so-called "coarsening process". As $C_0 = 0.05$, strong modulating of wavenumbers takes place in the very early stage (Fig. 6(a) and (b)), followed by a rapid developing of the Co-rich regions (Fig. 6(c) and (d)). These regions exhibit a very sharp interface with the matrix. Note here that at $C_0 = 0.05$ and $T = 773$ K the system is already inside the metastable region. From the point of view of classic nucleation concept, it may be allowed to say that some nuclei have already formed in the matrix at $t = 200$ s. As $t = 400$ s, equilibrium composition has been achieved in most Co-rich regions, indicating that the kinetics of nucleation and growth is very rapid. Afterwards, considerable coarsening of the microstructure is demonstrated by a comparison of Fig. 6(e) with Fig. 6(f), where some Co-rich particles are widened and the other Co-rich phases disappear. From these results it seems to be



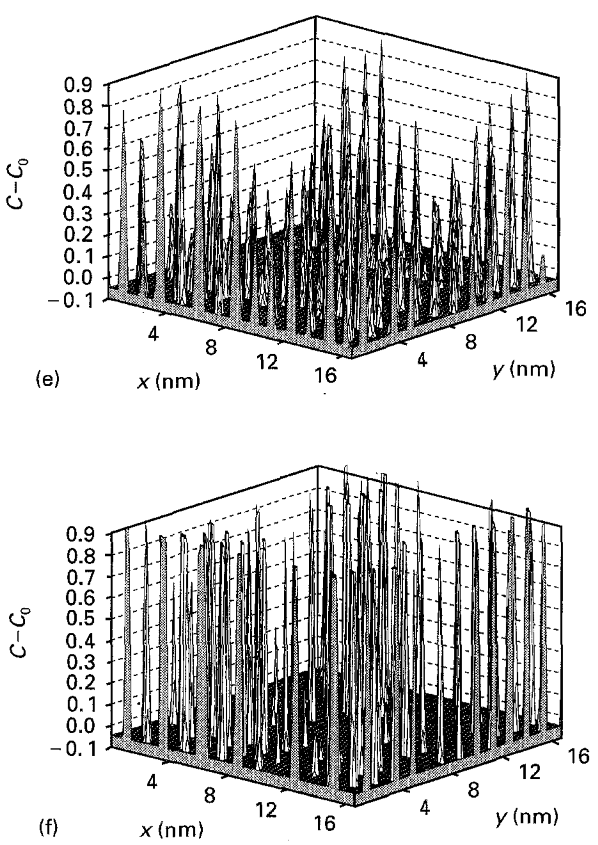


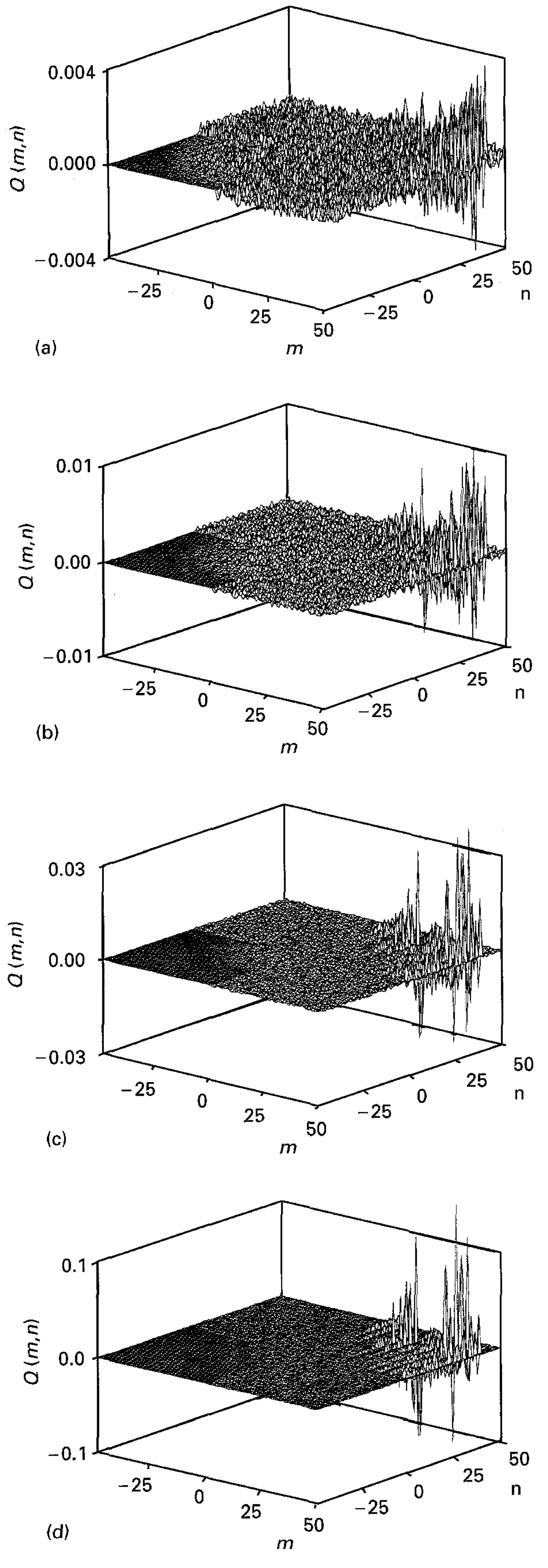
Figure 6 The compositional profiles at several times for CuCo alloy of $C_0 = 0.05$ phase separating at $T = 773$ K, as calculated by the non-linear Cahn theory. Note here the system is inside the metastable region, but the as-shown profile grows with time, indicating that phase separation (nucleation in the early stage) is taking place. (a) $t = 0$; (b) $t = 50$ s; (c) $t = 100$ s; (d) $t = 200$ s; (e) $t = 400$ s; (f) $t = 1000$ s.

allowed for such an argument that the non-linear Cahn theory can also give a reasonable description of phase separation in the metastable region, besides its successful modelling of spinodal phenomenon in the non-stable region.

It should be useful to give an insight of evolution of the amplitude spectrum of the Fourier waves, in order to understand the mechanism for modulating compositional profile. As a representative example, in Fig. 7 the spectra of several times for the case of $C_0 = 0.05$ are given. Starting from the initial state, the Fourier waves of negative numbers ($m < 0$ and $n < 0$) rapidly decay and those waves of positive numbers grow gradually, whereas the other waves in co-ordinate spaces of ($m > 0$, $n < 0$) and ($m < 0$, $n > 0$) remain roughly unchanged (Fig. 7(a) and (b)). Apart from the early stage, there are two local sections in the wavenumber space ($m > 0$, $n > 0$) in which the amplitudes of some wavenumbers show faster growth compared to other spaces (Fig. 7(c–f)). Obviously, one of the sections (with smaller values of m and n) contributes to wavelength modulating of the compositional profile and late stage coarsening of the microstructure, the other (with larger values of m and n) configures the shape of the profile, resulting in sharper and sharper interface of Co-rich phases with the matrix (see Fig. 6(e) and (f)). From these spectra, the non-linear characters of phase separation, even forward to the late stage where phase separation proceeds via coarsening of the microstructure, can be clearly revealed.

4. Structure function and dynamic scaling

The above results demonstrate that the non-linear Cahn theory describes in a better way the dynamic



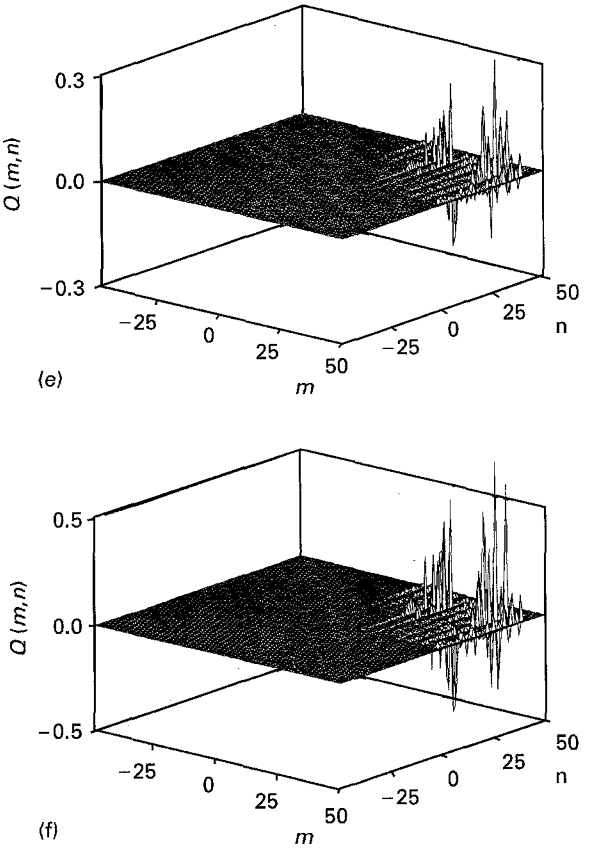


Figure 7 The amplitude spectra at several times for CuCo alloy of $C_0 = 0.05$ phase separating at $T = 773$ K, as calculated by the non-linear Cahn theory. For details, see text. (a) $t = 50$ s; (b) $t = 100$ s; (c) $t = 200$ s; (d) $t = 400$ s; (e) $t = 600$ s; (f) $t = 1000$ s.

characters of phase separation of CuCo alloys. More importantly, this theory presents a numerical technique from which the compositional fluctuations can be directly calculated without imposing any assumption. A convincing approvement of this theory should be after a favourable checking of the universal scaling behaviour in the late stage and the kinetic growth exponent as calculated from this theory. Unfortunately, in this theory an analytical expression of the structure function is not given. In fact, a surprising similarity of Equation 1 with Equation 10 can be found if Equation 1 is rewritten as

$$\frac{\partial S(k,t)}{\partial t} = -k^2\left[2MKk^2S(k,t) + \sum_{n=0}^{\infty}\frac{M}{(n+1)!}\times\frac{\partial^{n+2}(\Delta G)}{\partial C_0^{n+2}}\,\frac{2\langle u^{n+2}\rangle S(k,t)}{\langle u^2\rangle}\right] \qquad (18)$$

If only the contribution of a single Fourier wave of wavenumber (m, n) to the compositional fluctuation in real space is considered, a comparison of Equation 10 with Equation 17 directly yields

$$\frac{2\langle u^{i+2}\rangle}{\langle u^2\rangle} = \frac{R_i(m,n,t)}{R_0(m,n,t)}, \qquad i \geqslant 0 \qquad (19)$$

here R_i (m, n, t) $(i \neq 0)$ actually represents the two-point correlation function of compositional fluctuations in Fourier space, which has one-to-one correspondence to the fluctuations in real space. Therefore, Equation 19 seems to be qualitatively true. As term u in Equation 19 is a summation of Fourier waves of wavenumbers occupying over the Fourier space, a reasonable approach of Equation 19 is performed by replacing $R_i(m, n, t)$ by the average of the two-point

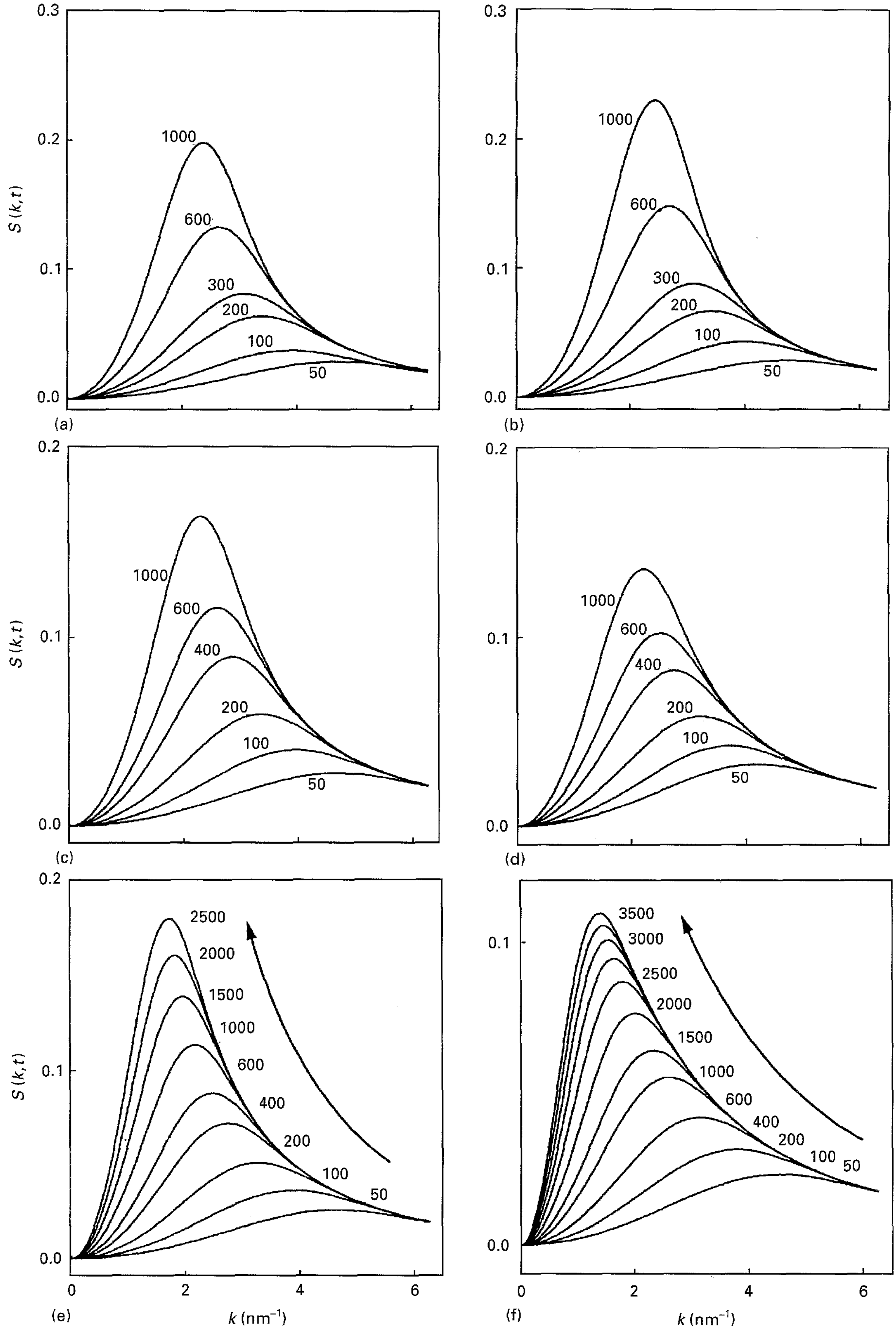


Figure 8 The calculated structure function $S(k, t)$ from the non-linear Cahn theory, for CuCo alloys annealed at $T = 773$ K. The time scales are inserted in the figures. C_0 = (a) 0.5, (b) 0.3, (c) 0.1, (d) 0.07, (e) 0.05, (f) 0.01.

correlation functions over all the Fourier space

$$\frac{R_i(m,n,t)}{R_0(m,n,t)} \Rightarrow \frac{\sum\limits_{k_1,k_2} R_i(m,n,t)\,Q(m-k_1,n-k_2,t)}{\sum\limits_{k_1,k_2} Q(m,n,t)\,Q(m-k_1,n-k_2,t)}$$

$$\Rightarrow \frac{\sum\limits_{m,n} R_{i+1}(m,n,t)}{\sum\limits_{m,n} R_1(m,n,t)} \qquad (20)$$

Unfortunately, here we could not provide a mathematically strict derivation of Equation 20, where the sign of equality has been replaced by an arrow.

As a good approximation, Equations 1 and 2 can then be rewritten as

$$\frac{\partial S(k,t)}{\partial t} = -2Mk^2[(Kk^2 + A(u)]S(k,t) + 2MRTk^2 \qquad (21)$$

$$A(u) = \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \frac{\partial^{n+2}(\Delta G)}{\partial C_0^{n+2}} \frac{\sum\limits_{m,n} R_{n+1}(m,n,t)}{\sum\limits_{m,n} R_1(m,n,t)} \qquad (22)$$

No visible difference between Equations 2 and 22 was revealed by a previous calculation, which demonstrates that Equation 20 is indeed a reasonable formulation. However, from a consideration of reliability, we have still applied the following procedure: $S(k, 0)$ for all k is imposed zero and $Q(m, n, 0)$ is generated by the standard stochastic method as described above. Here, $\Delta t \ll a^2/D$ is chosen, where D is the diffusion coefficient of Co in pure copper. Starting from $S(k, t)$ and $Q(m, n, t)$, $u(x, y, t)$ is calculated from Equation 9 and then $\langle u^i \rangle$ is obtained by taking the average of twenty compositional profiles over a real space of 32×32 nm^2. These profiles are evaluated by imposing different random seeds for creating $Q(m, n, 0)$. From Equation 2 $A(u)$ is calculated and $\partial S(k, t)/\partial t$ and then $S(k, t + \Delta t)$ are obtained from Equation 1 and $S(k, t + \Delta t) = S(k, t) + \Delta t \partial S(k, t)/\partial t$. $\partial Q(m, n, t)/\partial t$ and then $Q(m, n, t + \Delta t)$ are calculated from Equations 10 and 12. Finally, $u(x, y, t + \Delta t)$ was recomputed and thus completing the iteration cycle.

By applying this improved technique of numerical iteration, dynamics of phase separation of CuCo alloys over all the range of composition ($C_0 = 0.50$, 0.30, 0.10, 0.07, 0.05, 0.01) has been calculated. The results are presented in Figs 8 to 10. Fig. 8 gives the calculated $S(k, t)$ for different times, where the time scales are inserted in the figures, respectively. For all cases, gradual growth and peak shifting leftwardly of $S(k, t)$ are achieved. The lower the composition is, the slower the growth is and the more considerably the peak shifts. A roughly constant decelerating growth of $S(k_m, t)$ until a stage where $S(k, t)$ tends to be saturated with time can be identified for each of the cases. As an example, at $C_0 = 0.05$, the average wavelength of about 3.0 nm for the profile at $t = 1000$ s, as shown in Fig. 6(f), agrees very well with an estimation from Fig. 8(e) where $k_m = 2.2\,\text{nm}^{-1}$ at $t = 1000$ s. After $t > 5000$ s, leftwardly shifting and increasing of $S(k_m, t)$ is not so easy to be distinguished, indicating coarsening of the microstructure is very slow. For all cases, no cross-over phenomenon of $S(k, t)$ from different times is observed.

A plotting of $\ln(k_m)$ against $\ln(t)$ for all the cases demonstrates that the linear law is very well followed, as shown in Fig. 9. The kinetic growth exponent n, i.e. absolute value of the slope of $\ln(k_m)$ against $\ln(t)$, as a function of alloy composition, is also inserted in the figure. In the non-stable region which has a boundary with the metastable one at $C_0 \approx 0.08$, $n = 0.22 \sim 0.23$, exhibiting a very weak dependence of C_0 due to the fact that in this composition range the microstructure consists of inter-connected new phases embedded in the matrix. This value agrees quite well with that (0.25) predicted by Binder *et al.* [28] and the scaling exponent (0.212) obtained by Langer *et al.* [14]. Very interestingly, as C_0 decreases further and thus the system enters the metastable region, n increases rapidly until $n = 0.28$ as $C_0 = 0.01$ where the LSW theory, we argue, should be roughly valid. This value indeed deviates not so far from the predicted 0.33 by the LSW theory. In fact, many experiments and simulations on coarsening kinetics in those systems of short range interaction (such as metallic systems) have demonstrated that n always falls between 1/3 and 1/4.

Finally, we come to check the dynamic scaling of the calculated structure function. A rescaling of $S(k, t)$ by $k_m^3 \times S(k, t)$ and k by k/k_m for all the cases is shown in Fig. 10(a) to (f), respectively. Without exception, the scaling hypothesis is very well satisfied in the late stage of phase separation for all the cases. Due to the kinetic reason, as $C_0 = 0.5$, $S(k, t)$ falls in the scaling curve at $t > 100$ s, whereas the scaling state has not been reached until $t = 1000$ s as $C_0 = 0.01$. However, a further checking of Fig. 10 reveals that the early stage of phase separation in the metastable region exhibits a much more remarkable positive deviation from the scaling function compared to the cases of $C_0 = 0.5$ and 0.3. This positive deviation should be attributed

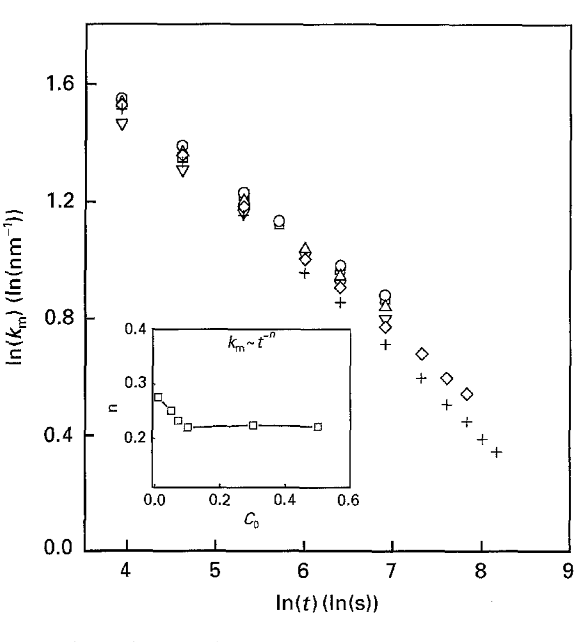
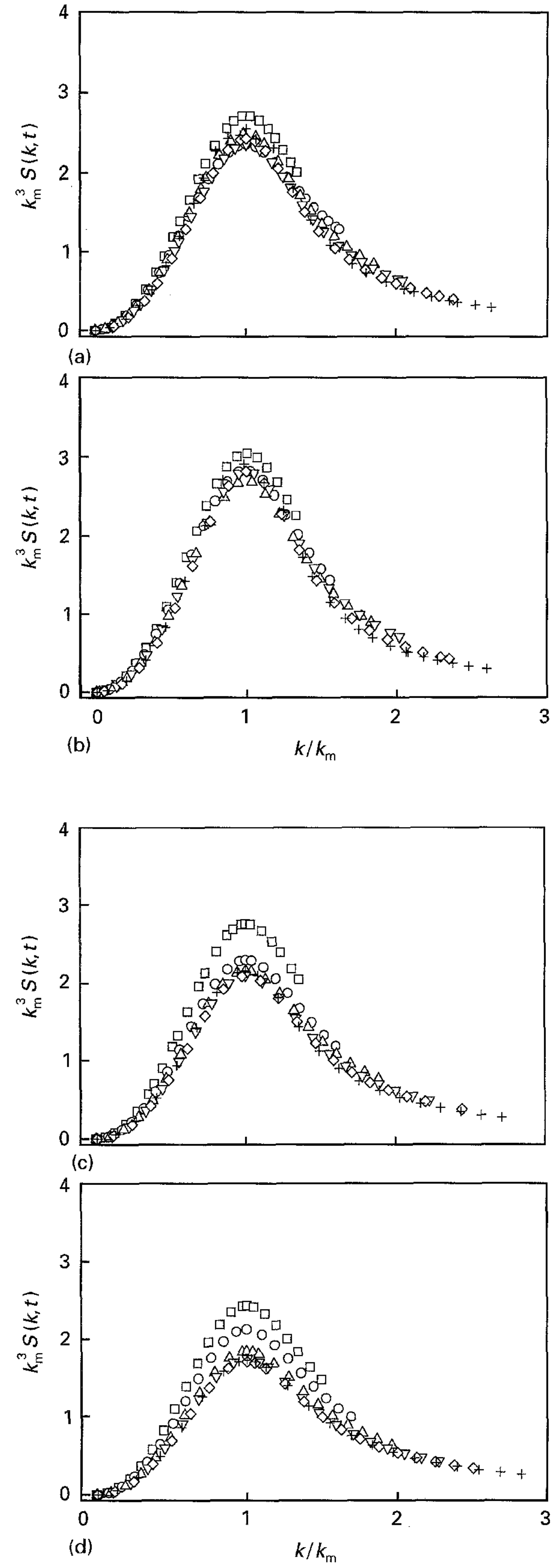


Figure 9 A plotting of $\ln(k_m)$ against $\ln(t)$ for CuCo alloys annealed at $T = 773$ K, as calculated by the non-linear Cahn theory. C_0 = □ 0.5, ○ 0.3, △ 0.1, ▽ 0.07, ◇ 0.05, + 0.01.



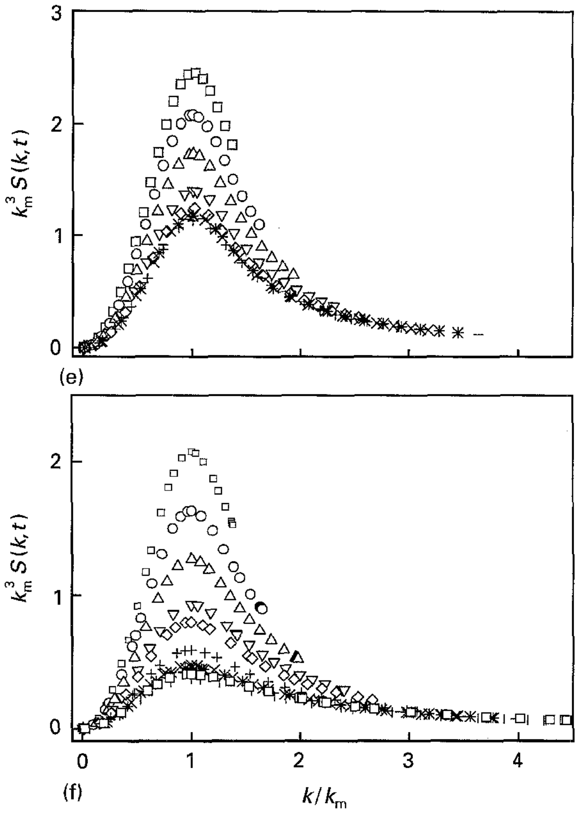


Figure 10 Rescaling of the structure function $S(k, t)$ as shown in Fig. 8, following the scaling hypothesis. C_0 = (a) 0.5, (b) 0.3, (c) 0.1, (d) 0.07, (e) 0.05, (f) 0.01. □ 50 s; ○ 100 s; △ 200 s; ▽ 300 s; ◇ 600 s; + 1000 s; × 1500 s; * 2000 s; — 2500 s; | 3000 s; ● 3500 s.

to the fact that nucleation is a rapid event and the nucleus reaches its equilibrium composition in a short time which results in a rapid growth of $S(k_m, t)$. Contrarily, the spinodal decomposition is characterized by a gradual growth of the compositional fluctuations. Therefore, it is reasonable that a large positive deviation from the scaling function is achieved for phase separation proceeded via nucleation mechanism.

5. Conclusions

In conclusion, we have studied the dynamics of phase separation of CuCo alloys at $T = 773$ K by applying the LBM theory and the non-linear Cahn theory. The three-parameter technique of the LBM theory for evaluating compositional fluctuations during phase separation has been proved to be applicable only in a very narrow range of alloy composition around $C_0 = 0.35$, and the as-calculated structure function $S(k, t)$ in the late stage of phase separation and the kinetic growth exponent do not agree with the universal dynamic scaling hypothesis and the theory of coarsening kinetics, respectively.

The compositional profile and its amplitude spectrum in the Fourier space of CuCo alloys phase-separating in both non-stable and metastable regions have been calculated by applying the non-linear Cahn theory. By coupling the Cahn theory into the motion equation for structure function, an improved technique of numerical calculation of the structure function has been proposed. Over all the range of alloy composition, the structure function $S(k, t)$ in the late stage of phase separation shows dynamic scaling behaviours quite well consistent with the universal scaling hypothesis. The kinetic growth exponent obtained for the non-stable region, is quite well consistent with prediction of the scaling analysis, whereas phase separation in the metastable region exhibits a composition dependent exponent of kinetic growth, which shows good agreement with theories of coarsening kinetics.

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