PAPER

Partial structure factors derived from coarse-grained phase-separation dynamics on a disordered lattice with density fluctuations

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Abstract

The simplest and most time-efficient phase-separation dynamics simulations are carried out on a disordered lattice to calculate the partial structure factors of coarse-grained A-B binary mixtures. The typical coarse-grained phase-separation models use regular lattices and can describe the local concentrations but cannot describe both local density and concentration fluctuations. To introduce fluctuation for local density in the model, the particle positions from a hard sphere fluid model are determined as disordered lattice points for the model. Then we place the local order parameter as the difference of the concentrations of A and B components on each lattice point. The concentration at each lattice point is time-evolved by discrete equations derived from the Cahn-Hilliard equation. From both fluctuations, Bhatia and Thornton’s structure factor can be accurately calculated. The structure factor for concentration fluctuations at the large wavenumber region gives us the correct mean concentrations of the components. Using the mean concentrations, partial structure factors can be converted from three of Bhatia and Thornton’s structure factors. The present model and procedures can provide a means of analysing the structural properties of many materials that exhibit complex morphological changes.

1. Introduction

There are many different objects in the world, and we can see the diversity of their shapes—for example, some are beautiful, some are complex—and these shapes fascinate us. Some objects, like crystalline materials, maintain their stable and regular shape for a long time, while others, like clouds in the sky, easily change their shape [1]. Others, like galaxies, which are made up of many stars, form slowly over a long period of time [2]. Binary mixtures of two elements are the simplest systems in which phase separation occurs, but they also exhibit diverse and fascinating morphological changes during the phase-separation process [3]. For ease of understanding, we will focus on the morphological changes in phase-separation phenomena and discuss their structural characteristics, but those changes can be applied to other general physical phenomena as well.

The phenomenon of phase separation in two-component systems consisting of A and B appears in systems with interactions where for the three pairs of nearest neighbors, AA, BB, and AB, the AA and BB pairs occupy more configurations than the AB pair. In other word, assuming that the interaction energy of each pair is $\epsilon_{\text{AA}}$, $\epsilon_{\text{BB}}$, and $\epsilon_{\text{AB}}$ respectively, this phenomenon is mainly observed in systems where the interaction energy decreases when atoms of the same species are placed next to each other, i.e., $\epsilon_{\text{AB}} > (\epsilon_{\text{AA}} + \epsilon_{\text{BB}}) / 2$. This system is an order-disorder transition in which a homogeneous mixture phase at a higher temperature, upon quenching to a lower temperature, separates into two different heterogeneous mixture phases through an irreversible non-equilibrium process. During this process, various forms appear and disappear depending on the conditions.
For example, when the local concentration is taken as a variable and the thermodynamic free energy function of the entire system monotonically decreases, which is often the case for compositions near 50%. In this case, the phase separations develop spontaneously over the entire system. This type of phase separation is known as spinodal decomposition. In the case where there is a large difference in composition, the free energy function initially rises, but once the energy barrier is crossed, the free energy decreases. When the energy barrier is crossed, nucleation occurs in a localized region and the second phase (the nucleus) grows in size while changing the number and radius of the nucleus. This is called the nucleation and growth process. The morphological changes that emerge over a long period of time are drastically different when spinodal decomposition finally leads to phase separation and when the system separates into two phases with the nucleation and growth process. However, they can be described by the same phenomenological equations. In order to observe the complex structural behaviour of such systems, the size of the system and the length of the time evolution are important (figure 1).

Attempts to understand the alluring morphological changes in terms of the structural properties of the constituents have long been made [4, 5]. In particular, many studies have concentrated on whether there is a scaling law for structural changes related to spinodal decomposition. At the same time, they have described what the exponent $\phi$ of the power laws of the nucleus radius growth is for the evolution time, $R(t) \sim t^\phi$ [6–12]. The structure that has appeared in the phase-separation process has been discussed using structure functions or structure factors. A structure factor is a one-dimensional function that describes the correlations of the three-dimensional spatial arrangement of the constituents; in crystal materials, it gives the Bragg peaks [13]. Structure factors in non-crystal materials are also well-defined [14, 15] and have been the most commonly used analytical method for a long time because of their high relevance to scattering experiments and thermodynamic properties [13, 16]. In general, for a one-component system, they can be obtained by dividing the scattering intensity by the scattering factor of one of the constituent atoms.

For example, in X-ray diffraction measurements, the coherent scattering intensity for an X-ray, $I_{\text{coh}}(q)$, is, as a sum of contributions from individual atoms, given by

$$I_{\text{coh}}(q) = \left\langle \sum_j \sum_k f_j(q) f_k(q) \exp(-i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)) \right\rangle,$$  

(1)

where $\mathbf{r}$ is the atomic position, $\mathbf{q}$ is the reciprocal lattice vector, $f_j(q)$ is the atomic scattering factor for a single atom, $k$, which accounts for the shape of the atom. Here the brackets $\langle \rangle$ denote the statistical average. For a one-component system, the above equation is reduced to the form

\[ I_{\text{coh}}(q) = \sum_j f_j(q) \exp(-i\mathbf{q} \cdot \mathbf{r}_j) \]

Figure 1. The 3D plots of order parameters (local concentration differences) $\psi_j$ for all sites of the results obtained from the phase-separation model used in the present paper. The different clusters of sites where $\psi_j > 0$ are drawn in different colours. Model descriptions and initial conditions of these results are explained in the following sections. Typical spinodal decomposition is shown in (a). Nucleation and growth and spinodal decomposition process seem to be going on at the same time in (b).
\[
I^{\text{coh}}(q) = f^2(q) \left\{ \sum_{j=1}^{N_1} \exp(-i\mathbf{q} \cdot \mathbf{r}_j) \right\}^2 + f_2^2(q) \left\{ \sum_{k=1}^{N_2} \exp(-i\mathbf{q} \cdot \mathbf{r}_k) \right\}^2 + 2f_1(q)f_2(q) \left\{ \sum_{j=1=1}^{N_1N_2} \exp(-i\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{r}_{jk})) \right\}.
\]

Therefore, the structure factor \( S(q) \) can be defined as
\[
I^{\text{coh}}(q) = NF^2(q)S(q).
\]
If \( S(q) \) is inferred from the observed intensity, the inverse Fourier transformation of \( S(q) \) gives pair distribution function
\[
g(r) = 1 + \frac{1}{(2\pi)^3} \int (S(q) - 1) \sin(qr) q^4 dq ,
\]
which represents the distribution of distances between pairs of atoms.

In a two-component system, however, it is not so easy to specify the atomic arrangements of the constituent elements from one measured diffraction experiment. The coherent scattering intensity for a two-component system can be written as
\[
I^{\text{coh}}(q) = f_1^2(q) \left\{ \sum_{j=1}^{N_1} \exp(-i\mathbf{q} \cdot \mathbf{r}_j) \right\}^2 + f_2^2(q) \left\{ \sum_{k=1}^{N_2} \exp(-i\mathbf{q} \cdot \mathbf{r}_k) \right\}^2 + 2f_1(q)f_2(q) \left\{ \sum_{j,k=1=1}^{N_1N_2} \exp(-i\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{r}_{jk})) \right\}.
\]

The three terms in equation (5) correspond to the partial structure factors of respective atom pairs 1–1, 2–2 and 1–2. However, the definitions of the partial structure factors are not unique. Ashcroft and Langreth (AL) proposed the following definition for the partial structure factors, \( S_{ij}(q) \) [17]:
\[
S_{ij}(q) = \frac{1}{\sqrt{N_1N_2}} \left\{ \sum_{j=1=1}^{N_1N_2} \exp(-i\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{r}_{jk})) \right\} = \sqrt{N_1N_2} \delta_{ij} \delta_{kl}.
\]

Then
\[
I^{\text{coh}}(q) = N_1f_1^2(q)S_{11}(q) + N_2f_2^2(q)S_{22}(q) + 2\sqrt{N_1N_2}f_1(q)f_2(q)S_{12}(q).
\]

These partial structure factors are directly related with Fourier transforms of direct correlation functions or partial pair distribution functions for the two-component mixtures.

In many research papers on morphological changes during phase separation, these are discussed as structure functions rather than exact structure factors [4]. Even in those cases that are treated as structure factors, the structure is treated as a single component of the matter. The major reason that might be expected is that most phase-separation models are treated as crystal systems or systems without density fluctuations. If there is no distinction between density and concentration, then it may be a one-component system. Performing phase-separation simulations as a two-component system in the manner of microscopic approaches like the Ising model and others [c] is very inefficient. In order to reduce the cost of those calculations, in many cases, the model becomes coarse-grained. As a result, accurate structure factors cannot be obtained, and it is difficult to make comparisons with structure factors determined from the experiments with sufficient accuracy.

In the coarse-grained binary system, three structure factors constructed from the Fourier transforms of two local fluctuations of number density, \( n_1(r, t) \) and concentration \( c_1(r, t) \) are formalized by Bhatia and Thornton (BT) [18]. The definitions of the BT structure factors are described later in detail. It should be briefly mentioned at this point that these structure factors are explicitly related to AL partial structure factors through the mean concentrations [14] as follows:

Let \( S_{NN}(q) \), \( S_{CC}(q) \), and \( S_{NC}(q) \) be the structure factors for number density fluctuation, concentration fluctuation, and the correlation between these two local fluctuations, respectively. AL partial structure factors \( S_{11}(q) \), \( S_{22}(q) \), \( S_{12}(q) \) are given by
\[
S_{11}(q) = c_1 S_{NN}(q) + S_{CC}(q)/c_1 + 2 S_{NC}(q),
\]
\[
S_{22}(q) = c_2 S_{NN}(q) + S_{CC}(q)/c_2 - 2 S_{NC}(q),
\]
\[
S_{12}(q) = \sqrt{c_1c_2} S_{NN}(q) - S_{CC}(q)/\sqrt{c_1c_2} + \{\sqrt{c_1}/\sqrt{c_2} - \sqrt{c_2}/\sqrt{c_1}\} S_{NC}(q),
\]
where \( c_1 \) and \( c_2 \) are the mean concentrations of the type 1 and 2 components, respectively. These relations hold even in a long-wavelength region and therefore make a comparison with small-angle scattering experiments in the phase transition possible [19]. To obtain AL partial structure factors from BT structure factors, we need accurate \( c_1 \) and \( c_2 \) values in the coarse-grained system.
In a more general model, the density and concentration fluctuations simultaneously exist; however, the variable in the typical model is the concentration fluctuation, $\tilde{c} - c(r, t)$, or the difference of the local concentrations, $c_B(r, t) - c_A(r, t)$. In order to get partial structure factors, we need introduce the density fluctuation in the model. To do so, we find that, instead of assigning both $c(r, t)$ and $n(r, t)$ to each site, we can introduce density fluctuations into the site arrangement itself. In the present model, to decrease the computational cost, the density fluctuations do not change with time and are kept fixed. To construct such a dynamical system, we modify the well-known cell-dynamical-system (CDS) model proposed by Oono and Puri [20–22] with the help of the hard sphere fluid model. Because, although their model is quite efficient at computation, it is based on square or cubic lattices.

If the local density, $n(r)$, is determined at all points in the coarse-grained system, then accurate partial structure factors can be estimated. From the knowledge of the main structural analysis techniques, they will lead to fruitful comparisons with experimental data. For example, for the phase separation of liquids and amorphous materials, the density fluctuations will not be small. In these systems, it is very difficult to distinguish between fluctuations due to density and those due to concentration. Therefore, it is worthwhile to specifically evaluate the partial structure factors of coarse-grained phase-separated models with density fluctuations.

In this paper, we show how to accurately evaluate three types of partial structure factors from concentration fields or concentration differences obtained from general phase-separation models. The model is expected to be applied to the phase separation in metallic glasses [23]. It seems that the lack of a satisfactory theory for the form of the scaling law for the structure factors [22] remains one of the major unsolvable problems in the field of phase-order dynamics [4]. This method might be a tool that can contribute greatly to addressing this problem and the analysis of the structural properties of many materials that exhibit complex morphological changes.

2. Model

2.1. Disordered lattice model

As most coarse-graining models divide the system into uniform cells (on a regular lattice), the cells or lattice sites do not have local density fluctuations. Figure 2(a) illustrates such a situation. Sites 1 and 2 in the image on the left have a constant local density, $4/V$. But both sites in the image on the right have different densities. To calculate the mean concentration over the system from the average of the local concentrations, we need local density information. In the coarse-graining stage, most of the approximations consider the density to be constant and only deal with the concentration changes. However, the scattering intensities and structure factors obtained from diffraction experiments contain both local density and local concentration information. This has led to discrepancies between the model and the experiment. Especially in the phase-separation model, this difference needs to be rigorously incorporated. We use the disordered particle positions of a hard sphere fluid model to introduce the local density fluctuation in lattice itself. One can call it off-lattice, but the random atomic configuration is fixed through the dynamic process.

![Figure 2. Schematic pictures of concentration fluctuations in a square lattice (a) and those on a disordered lattice with density fluctuations (b). Both images (a) and (b) have the same total number density, $8/V_0$, and the same mean concentration over the system, 0.5. The local densities of two sites are different in image (b). The local concentrations of the filled circles on sites 1 and 2 of the square lattice have values of 3/4 and 1/4, respectively. The local concentrations for sites 1 and 2 of the disordered lattice are 2/3 and 2/5, respectively. Therefore, the average of the local concentrations does not match the concentration over the system for the case with density fluctuations.](image-url)
2.2. Dynamics model for phase separation

Figure 3 is a typical phase diagram of an isomorphous system, represented by Cu-Ni alloys. In the system, from the state of homogeneous mixture of A and B at a higher temperature with some component, \( c_0 \), by quenching to a lower temperature, \( T_1 \), the alloy gradually separates into a heterogeneous mixture of A-rich and B-rich phases with an arbitrary composition, and finally two phases have the concentrations \( c_1 \) and \( c_2 \). The binodal line on a solid solution is determined by searching the two-phase area while changing the temperature and composition conditions. The area surrounding the line is called an immiscibility gap. To get to such a diagram, Gibbs’s free energy, \( G \), needs to be a double well curve, shown in figure 3(b). The binodal line is the curve connecting the points determined by the condition \( \frac{dG}{dc_B} = 0 \), and the spinodal line is the curve determined by the condition \( \frac{d^2G}{dc_B^2} = 0 \).

![Figure 3. A phase diagram of a complete solid solution or isomorphous system. The horizontal axis is the composition or concentration of component B, \( c_B \), common for (a) and (b). The vertical axes are (a) temperature, \( T \), and (b) Gibbs’s free energy, \( G \). The uppermost line in (a) is the liquidus line and the solidus line follows. The area between the two lines is a liquid and solid coexisting phase. The area below the solidus line is one phase of homogeneous mixture of the components.](image)
As the variable of the phase transition dynamics for binary alloys is usually the concentration, we need to use a continuum model or coarse-grained model. Therefore, the local concentration difference of A and B atoms, \( \psi_j(r, t) = c_{ij} - c_{jk} = \psi_j(t) \), is chosen as the local order parameter of the system, where, since the amount of atoms is constant, the average order parameter, \( 1/N \int \psi(r, t) \, dr = \bar{\psi} \) (const.), is kept constant.

In almost all analytical approaches of phase-separation phenomena of binary alloys, the starting point is a partial differential equation,\n\[
\frac{\partial \psi(r, t)}{\partial t} = -L(\nabla \psi)^2 \frac{\delta H[\psi(r, t)]}{\delta \psi(r, t)},
\]
where \( \psi(r, t) \) is the order parameter field at position \( r \) and at time \( t \); \( L \) is a phenomenological parameter; \( \beta = 1 \) for the conserved-order parameter case, that is, the Cahn Hilliard (CH) equation [24–26]; and \( \beta = 0 \) for the non-conserved case, the so-called time-dependent Ginzburg–Landau (TDGL) equation [27, 28]. \( H[\psi(r, t)] \) is usually the coarse-grained free-energy functional,\n\[
H[\psi(r, t)] = \int dr \left\{ \frac{1}{2} (\nabla \psi)^2 - \frac{\tau}{2} \psi^2 + \frac{g}{2} \psi^4 \right\},
\]
with \( \tau \) and \( g \) being phenomenological parameters greater than zero. The parameter \( \tau \) measures the depth of the quench. In the conserved-order-parameter case, \( \int \psi(r, t) \, dr \) is kept constant.

It is very hard to directly solve the CH equation by numerical calculation. Instead of directly solving the differential equation, the corresponding difference equation with the form
\[
x_{n+1} = f(x_n)
\]
can be quickly and stably solved, albeit approximately. One can think that the function, \( f \), is a one-dimensional one-to-one map like a logistic injection. The shape of the local free-energy functional for a cell is sketched in figure 4(a). The behaviour of the time evolution of the order parameter in every time step can be mimicked by repeating the injection of \( \psi \). The same process describes the time evolution of the order parameters at all sites on the lattice. As this model is a discretized model, we might have to use the word 'site,' however, as each site or lattice point is randomly placed. Here, we write the order parameter, density and concentration at site \( j \), respectively. We define the order parameter as concentration difference \( \psi_j(r, t) = c_{ij}(r, t) - c_{jk}(r, t) \), which takes values from \(-1\) to \(1\), and \( \psi = 0 \) corresponds to the composition 50 at% B.

We choose \( f(x) = 1.3 \tanh(x) \) for the present model, as Ono and Puri did before. Their CDS model is a so-called cellular automaton (CA) and corresponds to one of the difference schemes of the CH equation.

The model can be described as follows:

\[
\psi_j(r, t+1) = F[\psi_j(r, t)] \quad \text{with} \quad F[\psi_j(r, t)] = f(\psi_j(r, t) + D[\langle\psi_j(r, t)\rangle]).
\]

\[
\langle\psi_j(r, t)\rangle = \omega_{ji,1} \sum_{j,1-\text{shell}} N_{ji,1} \psi_j(r, t) + \omega_{ji,2} \sum_{j,2-\text{shell}} N_{ji,2} \psi_j(r, t),
\]

\[
\omega_{ji,1} N_{ji,1} + \omega_{ji,2} N_{ji,2} = 1,
\]
where \( \psi_j(r, t) \) is the order parameter field at position \( r \) and at time \( t \), and \( D \) is a parameter proportional to the phenomenological diffusion constant, \( f(x) = 1.3 \tanh(x) \). \( \ll \) denotes the isotropic local average of order parameters on the disordered lattice. We introduce the softness parameter \( \omega_{ji,1}/\omega_{ji,2} \), which means the isotropic average in a disordered lattice, in a similar way to how Mouritsen introduced it in his domain-growth kinetics [29], where \( \omega_{ji,1} \) is the factor for the sum of the first shell of site \( j \), and \( \omega_{ji,2} \) is for the second shell of site \( j \). \( N_{ji,1} \) and \( N_{ji,2} \) are the number of atoms within the first shell around site \( j \) and within the second shell around site \( j \), respectively. Also \( \omega_{ji,1} \) and \( \omega_{ji,2} \) should satisfy equation (16). Usually, on a disordered lattice, each site has a different number of neighbours. Using this definition, the softness of Ono and Puri’s CDS model is 2. In the present model, we also set the softness as 2 for all sites on the disordered lattice.

To concretely construct a three-dimensional disordered lattice with local density fluctuations, we use the hard sphere (HS) fluid model. The particle positions obtained from the HS model can be regarded as a disordered lattice [13]. Concretely, we prepared the HS model with the number of particles \( N = 800000 \) and the packing fraction \( \eta = 0.45 \) (hard sphere diameter \( \sigma = 0.010242 \)), so as to observe the characteristic structure of phase separation. The structure factor, \( S(q) \), and the corresponding pair distribution function, \( g(r/\sigma) \), of the lattice points are shown in figures 5(a) and (b). \( D_1 \) and \( D_2 \) in figure 5(a) represent the first minimum after the first peak and the second minimum positions after the second peak, respectively. In a system with small-scale local density fluctuations, the values of the structure factor gradually converge to some small non-zero value as \( q \).
approaches zero. The large value for the low $q$ region in figure 5(a) illustrates the existence of large density fluctuations.

This density fluctuation comes from the coordination number distribution $D(N_C)$ of this disordered lattice site. Figures 6(a) and (b) shows $D(N_C)$ is in the first-shell and second-shell, respectively, where the first shell means particles within $D_1$ and the second shell represents particles between $D_1$ and $D_2$. The average coordination numbers were about 12.3 and 43.7 for the first and second shells, respectively. Thus, we constructed a disordered lattice with the local density fluctuations. The existence of the local density fluctuations
can be clearly viewed from the fact that the structure factor in the low-wavenumber $q$ region becomes larger with decreasing $q$.

But this is just a one-component disordered lattice model with local density fluctuations. We can put real numbers with values from $-1.0$ to $1.0$ for the local order parameter, $\psi(r,t)$, on the disordered lattice points instead of the particle itself. In this paper we call this model random-cell-dynamics CA (RCDCA).

3. Results

3.1. Time evolution of order parameters

To demonstrate, we select the condition $\Psi = -0.6$ ($c_a = 0.2$ in figure 3). This condition lies between the binodal and spinodal lines in the phase diagram, so that nucleation growth takes place. In order to build this condition up at the initial time, 800 sites are randomly selected and those sites and the first-shell sites around them are given the order parameter value of $+0.98$ as an embryo. The other sites have random values between $-0.6 + / -0.125$.

Then the following $\Delta \psi$ is added to all sites so that the average of all sites becomes $-0.6$:

$$\psi_k = \psi_j + \Delta \psi, \quad \Psi = \frac{1}{N} \sum_{k=1}^{N} \psi_k = -0.6$$

Although $\Psi = -0.6$ represents the composition 20 at% B, in this initial state ($t = 0$), there are actually 790, 242 sites with negative values near $-0.6$ and 9,758 sites with positive values near $+0.9$ on the random lattice, and a total of 800 embryos.

The order parameters after some simulation time steps of RCDCA are drawn as 3D density plots in figures 7(a) and (b). In these pictures, sites with a $\psi_k$ large value are drawn half-translucently. Although it looks like there are many nuclei, the initial 800 embryos came 18 nuclei containing 159 positive value sites after $t = 80$.

3.2. Derivation of BT structure factors

First, we derive the correct Bhatia-Thornton (BT) structure factors $[18], S_{NN}(q), S_{CC}(q), S_{NC}(q)$, from the local order parameters. On a system with $N$ atoms ($N_1$ A atoms and $N_2$ B atoms) in a volume $V$, the local density fluctuation for species $\alpha$ ($\alpha = 1, 2$) at position $r$ and time $t$ is described, using the mean number density of $\alpha$ ions $\bar{n}_\alpha = N_\alpha / V$, as follows:

$$\Delta n_\alpha(r, t) = n_\alpha(r, t) - \bar{n}_\alpha = -\bar{n}_\alpha + \sum_{j} N_\alpha \delta(r - \mathbf{R}_j(t)),$$

where $n_\alpha(r, t)$ denotes the local density of type $\alpha$ at position $r$ and time $t$, and $\delta$ is Kronecker’s $\delta$, $\mathbf{R}_j(t)$ position of the atom $j$ at time $t$, making the Fourier expansion

$$\Delta n_\alpha(r, t) = \frac{1}{V} \sum_{q} \tilde{N}_\alpha(q, t) e^{-iq \cdot r},$$

$$\tilde{N}_\alpha(q, t) = \int \Delta n_\alpha(r, t) e^{iq \cdot r} d^3r$$
Similarly, Fourier transformation of the local fluctuation $\Delta n(r, t)$ in the total number density $n(r, t) = n_1(r, t) + n_2(r, t)$ is defined by

$$\tilde{N}(q, t) = \tilde{N}_1(q, t) + \tilde{N}_2(q, t).$$

If $\bar{c} = N_1/N$ denotes the mean concentration, the local concentration fluctuation at position $r$ and time $t$,

$$\Delta c(r, t) = \frac{V}{N}[(1 - \bar{c}) \Delta n_1(r, t) - \bar{c} \Delta n_2(r, t)].$$

If $\tilde{C}(q, t)$ denotes the Fourier transformation of the local concentration fluctuation $\Delta c(r, t)$, then

$$\tilde{C}(q, t) = \frac{1}{V} \int \Delta c(r, t) e^{iqr} dr.$$

From equations (21) and (23), three structure factors are defined as

$$S_{NN}(q, t) = \frac{1}{N} \langle \tilde{N}^*(q, t) \tilde{N}(q, t) \rangle,$$

$$S_{CC}(q, t) = N \bar{c}^* \langle (q, t) \tilde{C}(q, t) \rangle,$$

$$S_{NC}(q, t) = \text{Re} \langle \tilde{N}^*(q, t) \tilde{C}(q, t) \rangle.$$

We have to modify the expression of local fluctuations for our model as follows: as lattice site $j$ has position $R_j$ and order parameter $\psi_j(R)$ in our model, site $j$ simultaneously includes both A and B atoms at the rate of $c_1(r, t)$ and $c_2(r, t)$, respectively. Therefore, the local density of species $\alpha$ for all lattice sites is expressed by

$$n_\alpha(r, t) = \sum_j c_\alpha(r, t) \delta(r - R_j).$$

Using equations (27), (18) is written as

$$\Delta n_\alpha(r, t) = -\bar{n}_\alpha + \sum_j c_\alpha(r, t) \delta(r - R_j).$$

As always, $c_1(r, t) + c_2(r, t) = 1$, and the expression for $\tilde{N}(q, t)$ is the same as the original. That is, as for density fluctuations, we do not need to distinguish A atoms from B atoms at each site.

Figure 7. The 3D density plots of order parameters $\psi_k$ for all sites at times (a) $t = 80$ and (b) $t = 2000$. The colours in the plots show the different values of $\psi_k$; the blue sites are occupied by negative values and the red are positive.
Recalling the definition of the local order parameter,

\[ \psi(r, t) = c_2(r, t) - c_1(r, t) = 1 - 2 \, \bar{q}(r, t), \]

Equation (22) can be rewritten as

\[
\Delta c(r, t) = \frac{V}{N} \left[ \Delta n_1(r, t) - \bar{\varepsilon} \, \Delta n_2(r, t) - \bar{\tau} \, \Delta n_2(r, t) \right]
\]

\[
= \frac{V}{N} \left[ n_1(r, t) - \bar{\varepsilon} \, n_1(r, t) - (\bar{\tau} + \bar{\varepsilon}) \right]
\]

\[
= \frac{V}{N} \left[ \bar{q}(r, t) - \bar{\varepsilon} \, n(r, t) \right]
\]

\[
= \frac{V}{N} \left[ q_1(r, t) - \bar{\varepsilon} \, n(r, t) \right]. \tag{29}
\]

Although \( \bar{\varepsilon} = N_1 / N \), no one knows the value of \( N_1 \) in a coarse-grained model. If the mean concentration can be estimated from the average of the order parameters, that is, \( \bar{\varepsilon} = (1 - \bar{\psi}) / 2 \), we can rewrite equation (29) as

\[
\Delta c(r, t) = \frac{V}{N} \left[ \bar{\psi} - \bar{\psi}(r, t) \right] \, n(r, t) \tag{30}
\]

Although \( \bar{\varepsilon} = N_1 / N \), no one knows the value of \( N_1 \) in a coarse-grained model. If the mean concentration can be estimated from the average of the order parameters, that is, \( \bar{\varepsilon} = (1 - \bar{\psi}) / 2 \), we can rewrite equation (29) as

\[
\Delta c(r, t) = \frac{V}{N} \left[ \bar{\psi} - \bar{\psi}(r, t) \right] \, n(r, t) \tag{30}
\]

Note that the average of all order parameters in the system changes to a small degree, even with conserved-order-parameter dynamics. The difference in parentheses in equation (30) should be calculated with great accuracy.

Using equation (30) and the definitions of BT structure factors, we directly calculated \( S_{NN}(q\sigma) \), \( S_{CC}(q\sigma) \), \( S_{NC}(q\sigma) \) from the order parameters of the two states shown in figure 7. Figures 8 and 9 are the whole drawings in the range of \( 0.06 \times \sigma < 70 \) for \( t = 80 \) and 2000.

It is easily found that the behaviour of the three structure factors in a large \( q\sigma \) is consistent with the basic profile suggested from equations (24)–(26), that is, taking \( q \to \infty \), \( S_{NN}(q\sigma) \to 1 \), \( S_{CC}(q\sigma) \to q_2 \), and \( S_{NC}(q\sigma) \to 0 \). The result, that \( S_{NC}(q\sigma) \) oscillates around zero and gradually disappears toward the limit of infinity wave number, is responsible for the correct structure factors due to the density fluctuations and concentration fluctuations of BT. \( S_{NN}(q\sigma) \) also corresponds to the structure factor of the one-component system of a random lattice point shown in figure 5(b).
Note that \(c_1\) and \(c_2\) are mean concentrations of A and B atoms regarded as an atomistic system, not the concentrations as the continuous media. We calculated structure factors until \(q\sigma = 80\), to estimate the \(c_1c_2\) with great accuracy. Figure 10 shows the degree of convergence.

From the results of the fitting, we get \(c_1c_2\) is \(-0.000415 \pm 5 \times 10^{-6}\) for \(t = 80\) and \(c_1c_2\) is \(-0.00364 \pm 1 \times 10^{-4}\) for \(t = 2000\). Therefore, at \(t = 80\), approximately \(c_1 = 0.9995847\) (\(c_2 = 0.0004153\)) and \(c_1 = 0.9963436\) (\(c_2 = 0.0036564\)) at \(t = 2000\). The value for \(c_1c_2\) obtained here corresponds to the fraction of the \(\alpha(\beta)\) phase during the separation process. That is, the lattice points occupied by the \(\alpha(\beta)\) phase were 799,668 (332) for the case at \(t = 80\), and 797,075 (2925) for \(t = 2000\). Substituting these \(c_1\) and \(c_2\) into equations (7)–(9), partial structure factors for AL can be exactly estimated. We show the complete figures of the partial structure factors in figures 11 and 12.

We can see that the characteristic domain structure in the morphological changing appears in the region where \(q\sigma\) is less than one.
The general profile of the AL partial structure factors is that $S_{11}(q) > 0$, $S_{22}(q\sigma) > 0$, and $S_{12}(q\sigma) > 0$ are always true and when $q \to \infty$, $S_{11}(q\sigma) \to 1$, $S_{22}(q\sigma) \to 1$, and $S_{12}(q\sigma) \to 0$. From the figures, one can see that these profiles are sufficiently satisfactory. As mentioned above, the result that $S_{12}(q\sigma)$ oscillates around zero and gradually disappears toward the limit of infinity wavenumber is responsible for the correct values of $c_1$ and $c_2$.

These results can be regarded as the structure factors of the atomistic model derived from a coarse-grained system and can be compared directly with diffraction experimental data. Especially, the partials from AL can be directly double-logarithmic plotted. For example, for $S_{22}(q\sigma)$ at $t = 2000$ in figure 7, using small-angle scattering techniques (the formalism of the form factor of the sphere with radius $R_0 = 1$ [30]), the average radius of nucleus $R_0/\sigma$ was estimated to be 7.81 ± 0.01. If we estimate the radius as the distance for which the radial average of the order parameters around the nucleus is zero, then $R_0/\sigma = 7.55$ [31]. There seems to be at least 5% uncertainty. Moreover, the time evolution of the nucleus radius and partial structure factors from the nucleation process to the equilibrium state will reveal the correct power laws for the morphology of the domain growth.

Figure 1 shows the results for the number of sites $N = 1000000$. Typical morphology of spinodal decomposition shown in (a) appeared in the condition of the average order parameter $\bar{\Psi} = 0.0$, the time step $t = 150$, and starting without embryo. The complex morphology in figure 1 (b) observed in the condition of the average order parameter $\bar{\Psi} = -0.1$, the time step $t = 150$, and starting at one embryo. This condition lies on the region where spinodal decomposition occurs. But the embryo grows until some hundreds of time steps have been taken. The spinodal decomposition starts later.

4. Conclusions

In this paper, we demonstrated three Bhatia-Thornton-type structure factors are exactly estimated from the order parameter field of the coarse-grained phase-separation model, and we gave the exact exchange procedures for the partial structure factors to the corresponding atomistic model. We confirmed that Ashcroft-Langreth-type partial structure factors are correctly produced. The present analytical method is not specific to this model; by using a backbone lattice with density fluctuations, this method could be used in many other simulations. The present model and procedures can provide a means of analysing the structural properties of many materials that exhibit complex morphological changes.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
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