Density-amplitude formulation of the phase-field crystal model for two-phase coexistence in two and three dimensions

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The phase-field crystal approach describes the dynamics of the local atomic probability density on atomic length and diffusive time scales. However, the small grid spacing required to resolve the atomic length scale restricts the applicability to relatively small systems. We present a new amplitude-equation formulation that can be applied to model the evolution of a two-phase system by building upon the multiple-scale approach developed for the phase-field crystal model that explicitly incorporates a miscibility gap in the atomic density field. The new set of equations are less stiff by two orders in the spatial derivative and are found to retain acceptable accuracy even with a significantly larger grid size. Furthermore, the proposed model provides insight into the link between the phase-field-crystal model and a phase-field model in which conserved and nonconserved dynamics are coupled to describe a solid–liquid system. Models and simulation results are presented for two-dimensional hexagonal and three-dimensional body-centered cubic structures. Validation of the two-dimensional model is carried out by examining the Gibbs–Thomson effect. Simulations of growth and coarsening are performed to demonstrate the model’s potential for large-scale simulations.

Keywords: computer simulation; mathematical modeling; phase-field crystal model; crystal growth; microstructure; solidification

1. Introduction

Understanding the evolution of nano- and micro-scale structures of materials is crucial for the optimization of many important materials processing phenomena. Unfortunately, obtaining such an understanding is complicated by the wide range of length and time scales that are often involved. A number of computational approaches have been applied to address this challenge, including quantum-mechanical density functional theory, molecular dynamics or Monte Carlo methods for atomistic simulations and dislocation dynamics or continuum modeling for mesoscale phenomena. In nanotechnology, the atomic length scale is of particular importance as the electronic, magnetic, optical or other properties become strongly
dependent on the atomic configuration and atomic-level processes. However, many processes still involve a wide range of time scales.

In recent decades, the phase-field (PF) method has led to a rapid growth in the computational modeling of micro/nanostructural evolution in materials science, particularly in light of the development of asymptotic analyses that provide explicit relationships between PF models and sharp interface descriptions [1–6]. PF models have become important tools used in the study of structural evolution and have been successful in describing dendritic solidification in pure materials and binary or multicomponent alloys [2,3,7–15], precipitation growth [16–18], surface corrugation of elastically stressed films [19–22], dislocation dynamics [23–26] and grain growth [27–29]. There have been several reviews on this method [30,31] as well as microstructure evolution [32]. Most PF models effectively solve complex moving-boundary problems by describing the dynamics of phase fields that are spatially uniform inside the bulk phases and rapidly changing in interfacial regions through relaxation toward lower total free energy.

Despite the great success of PF methods, such approaches have limitations. The standard PF models use spatially uniform fields in equilibrium and fail to capture many features that are due to the periodic atomic ordering, such as multiple crystal orientations, defects, and elastic and plastic deformations. In order to integrate these effects into PF models, other auxiliary fields such as atomic displacement field [16–21,23], dislocation density [20,23–26] or multiple phase-fields [27,29] must be introduced. These fields are then coupled with the appropriate phase fields. However, these models do not explicitly include the effects of atomic structures, and therefore only approximately include the features of the crystal structures such as the anisotropic interfacial energies and defects.

Recently, a similar, but alternative methodology, was proposed [33,35] that incorporates atomic structure by modeling the atomic number density, which in the crystalline phase varies periodically in space. This model is referred to as the phase-field crystal (PFC) model and is similar in form to the model proposed by Jin and Khachaturyan [36]. The periodic nature of the atomic density field in the PFC model naturally gives rise to elastic effects, multiple crystal orientations and the nucleation and migration of dislocations. The method has been applied to a wide range of problems such as grain growth [33,35], liquid-epitaxial growth [33–35], stress–strain relationship of nanocrystalline solids [33], crack propagation [33], transition from the liquid to the amorphous state [36,40], commensurate/incommensurate transitions [37,38], glide, climb and annihilation of the edge dislocation [39], and pre-melting at grain boundaries and dislocations [41]. The main advantage of the PFC method over standard atomic modeling is that larger time scales can be simulated. For example, classical molecular dynamics simulations, which solve Newton’s equation of motion for a collection of atoms, are limited by time scale of the lattice vibrations (~ps) and the spatial scale of lattice constant (~Å). While the PFC time scale is much larger than such an approach, the method is still unsuitable for modeling systems with large length scales (~μm) because of the high computational cost required to resolve atomic length scales.

Very recently, Goldenfeld and collaborators have extended the accessible length scales of PFC models up to mesoscales by using a renormalization-group approach to derive equations of motion for the amplitudes of the periodic atomic density
field [42–45]. These amplitudes vary only near dislocations and within interfacial regions and are thus suitable for adaptive mesh techniques. Combining the amplitude-equation formalism with adaptive mesh techniques can reduce the computational cost and provides a unified multiple-scale approach from the atomic scale up to continuum mechanics. However, the originally developed amplitude equations describe only the evolution of the amplitude fields and do not include the miscibility gap in density between the liquid and crystal phases. Therefore, the original equations cannot be applied to many phase-transformation phenomena, such as crystal growth and coarsening, in which two or more phases coexist.

In this paper, we present a density-amplitude formulation for the PFC model that can be applied to phase transformations in the two-phase coexistence region of the phase diagram in both two and three dimensions. Our improved amplitude-equation formulation allows for two-phase coexistence by coupling the amplitudes to the average atomic density field. Furthermore, the formulation is shown to be much more computationally efficient than the standard PFC model. We compare the computational efficiency and stability of numerical simulations of two choices of density-amplitude formulations and the standard PFC model. Finally, numerical simulations are performed for the polycrystalline growth of two-dimensional (2D) hexagonal and three-dimensional (3D) BCC structures.

2. Models

2.1. Phase-field-crystal modeling

In the standard PFC model of a pure material, the free energy functional is described in terms of one scalar field, \( \psi(x, t) \) that represents the scaled local atomic density [33,35,39,50,51]. The form of the free energy varies, but is typically of the form:

\[
\mathcal{F} = \int \mathrm{d}r \left[ \frac{a_0}{2} \psi (\nabla^2 + q_o)^2 \psi + \frac{a_2}{2} \psi^2 + \frac{a_3}{3} \psi^3 + \frac{a_4}{4} \psi^4 \right],
\]

(1)

where \( a_0, a_2, a_3, a_4 \) and \( q_o \) are determined by material properties such as the lattice constant, the liquid phase isothermal compressibility and the elastic constants of the crystal [33,35,51,52]. The field \( \psi \) is uniform in the liquid phase and periodically varying in the crystalline phase. As shown recently [51], this free energy functional can be connected to the classical density functional theory of freezing. The evolution equation of the atomic density \( \psi \) is given by

\[
\frac{\partial \psi}{\partial t} = \Gamma \nabla^2 \frac{\delta \mathcal{F}}{\delta \psi} = \nabla^2 \left[ a_0 (\nabla^2 + 1)^2 \psi + a_2 \psi + a_3 \psi^2 + a_4 \psi^3 \right],
\]

(2)

where, for simplicity, the constants \( \Gamma \) and \( q_o \), which set the mobility and the length scale of the oscillatory behavior, were taken to be unity, and stochastic thermal fluctuations are ignored.

In two dimensions, the free energy functional \( \mathcal{F} \) given in Equation (1) is minimized by a periodic \( \psi \) with hexagonal symmetry in the crystal phase and by a constant \( \psi \) in the liquid phase. In the single-mode approximation (where atomic density is expressed by a sinusoidal function whose period corresponds to the atomic spacing), the atomic densities of the crystal \( \psi_c \) and the liquid phase \( \psi_l \) are given by
\[ \psi_s = \bar{\psi}_s + A_h \left[ \cos(qy)/2 - \cos(q\sqrt{3}x/2) \cos(qy/2) \right] \] and \( \psi_I = \bar{\psi}_I \), respectively. Here, the bar denotes the average of the quantity and \( A_h \) represents the amplitude of the periodic variations of the 2D hexagonal crystal structure. Minimizing Equation (1) with these substitutions gives the free energy densities of the solid (crystal) and liquid, \( f^s \) and \( f^l \):

\[
f^s = \frac{a_0 + a_2}{2} \bar{\psi}_s^2 + \frac{a_3}{3} \bar{\psi}_s^3 + \frac{a_4}{4} \bar{\psi}_s^4 + \frac{3}{16} \left( a_2 + 2a_3 \bar{\psi}_s + 3a_4 \bar{\psi}_s^2 \right) A_h^2
+ \frac{1}{16} \left( a_3 + 3a_4 \bar{\psi}_s \right) A_h^3 + \frac{45}{512} a_4 A_h^4, \tag{3a}
\]

and

\[
f^l = \frac{a_0 + a_2}{2} \bar{\psi}_I^2 + \frac{a_3}{3} \bar{\psi}_I^3 + \frac{a_4}{4} \bar{\psi}_I^4, \tag{3b}
\]

respectively, where the equilibrium amplitude and wavevector are given by [33,35]

\[
A_h = \frac{4}{15a_4} \left\{ a_3 + 3a_4 \bar{\psi}_s - \left( a_3^2 - 15a_2a_4 - 24a_3a_4 \bar{\psi}_s - 36a_4 \bar{\psi}_s^2 \right)^{1/2} \right\}, \tag{4}
\]

and \( q = 1 \), respectively.

An example plot of the free energy densities of both phases is presented in Figure 1. The liquid and the crystal are stable for the high and low average density, respectively, and the two-phase coexistence region exists between two single-phase stable regions. The equilibrium liquidus and solidus densities (\( \bar{\psi}^{eq}_l \) and \( \bar{\psi}^{eq}_s \)) in the two-phase coexistence region can be obtained using a common tangent construction.

2.2. Renormalization-group approach for PFC equation

Although the PFC model accurately reproduces the nonequilibrium dynamics of phase transitions, a fine computational grid is needed to resolve the variation of \( \psi \) on

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Free energy densities of the liquid and solid phases as a function of the corresponding average density (\( \bar{\psi}_l \) or \( \bar{\psi}_s \)) and the common tangent construction for the equilibrium liquidus and solidus densities, \( \bar{\psi}^{eq}_l \) and \( \bar{\psi}^{eq}_s \), in two-phase coexistence region. The parameters \( a_0 = 1.0, a_2 = 0.03, a_3 = -1/2, a_4 = 1/3 \) and \( q_o = 1 \) are used.
atomic scales, which makes the method computationally expensive. As mentioned earlier, Goldenfeld et al. [42–45] have recently derived amplitude equations for the PFC model based on a renormalization-group approach. To derive the amplitude equations from Equation (2), a two-dimensional hexagonal atomic arrangement is described in the single-mode approximation with three amplitudes $A_j$ by:

$$
\psi = \bar{\psi} + \sum_{j=1}^{3} \left( A_j e^{i k_j \cdot x} + A_j^* e^{-i k_j \cdot x} \right),
$$

(5)

where the superscript asterisk is used to denote the complex conjugate. The basis vectors $k_j$ for hexagonal atomic structure are the reciprocal lattice vectors and are given by

$$
k_1 = -\frac{\sqrt{3}}{2} \hat{i} - \frac{1}{2} \hat{j},$$

$$
k_2 = \hat{j},$$

$$
k_3 = \frac{\sqrt{3}}{2} \hat{i} - \frac{1}{2} \hat{j},$$

(6)

where $\hat{i}$ and $\hat{j}$ are the unit vectors in the $x$- and $y$-directions, respectively.

To obtain equations of motion for the complex amplitudes, Goldenfeld et al. used a so-called “quick and dirty Renormalization Group” (QDRG) method, which gives [42–45]

$$
\frac{\partial A_j}{\partial t} = \left( \mathcal{L}_{k_j} - 1 \right) \left\{ a_0 \mathcal{L}_{k_j}^2 A_j + \left( a_2 + 2a_3 \bar{\psi} + 3a_4 \bar{\psi}^2 \right) A_j \right\} - 2(a_3 + 3a_4 \bar{\psi}) \prod_{i \neq j}^{3} A_i^* \left( 2 \sum_{i=1}^{3} |A_i|^2 - |A_j|^2 \right),
$$

(7)

where $\mathcal{L}_{k_j} \equiv \nabla^2 + 2k_j \cdot \nabla$. The model represented by Equation (7) was termed the PFC-RG method [45]. Although the QDRG approach can be used to derive these amplitude equations with less effort, it yields amplitude equations that are slightly different from those derived using the classical multiple-scale analysis [44], which provides the full and rigorous expressions for the amplitude equations as follows:

$$
\frac{\partial A_j}{\partial t} = \left( \mathcal{L}_{k_j} - 1 \right) \left\{ a_0 \mathcal{L}_{k_j}^2 A_j + \left( a_2 + 2a_3 \bar{\psi} + 3a_4 \bar{\psi}^2 \right) A_j + 2(a_3 + 3a_4 \bar{\psi}) \prod_{i \neq j}^{3} A_i^* \right\} + 3a_4 A_j \left( 2 \sum_{i=1}^{3} |A_i|^2 - |A_j|^2 \right).
$$

(8)

Note that the QDRG derivation of Equation (7) does not contain the contribution of higher-order derivatives of nonlinear terms. Detailed descriptions and comparisons of various derivations can be found in Ref. [44].
2.3. Amplitude equations coupled with spatially varying average density field

The main advantage of the PFC-RG model described in the previous section over the PFC model is computational efficiency. A simulation of the standard PFC model typically requires a minimum of 8–10 grid points per atomic spacing, while the PFC-RG model can simulate the system with four or less grid points since the amplitudes vary more slowly in space than the atomic density, resulting in increased computational efficiency. However, the basic assumption of the constant average density over the entire system restricts the application of the PFC-RG model to single-phase systems. In this section, we present the amplitude equations including the change of the average density using the multiple-scale analysis. Coupling of periodic amplitudes and field averages has also been considered by Matthews and Cox [49] in one dimension.

The basic premise of the multiple-scale analysis is that, while the atomic density varies on the scale of the atomic spacing, the average density and amplitudes vary on much larger length and time scales. For this analysis a small parameter $\epsilon$ is used to introduce the scaled arguments $(X, T) = (\epsilon x, \epsilon^2 t)$ for the slowly varying amplitude fields $A_j(X, T)$ [44]. In this study, we also treat the average density as the slowly varying field $\bar{\psi}(X, T)$ instead of the constant average density, and follow the standard process of multiple-scale analysis (see e.g. Ref. [54]). The multiple-scale derivation for the model below is outlined in Appendix A. Using this approach, we obtain the evolution equation for the average density field:

$$\frac{\partial \bar{\psi}}{\partial t} = \nabla^2 \left[ a_0 (\nabla^2 + 1)^2 \bar{\psi} + (a_2 \bar{\psi} + a_3 \bar{\psi}^2 + a_4 \bar{\psi}^3) + 2(a_3 + 3a_4 \bar{\psi}) \sum_{i=1}^{3} |A_i|^2 \right]$$

$$+ 6a_4 \left( \prod_{i=1}^{3} A_i + \prod_{i=1}^{3} A_i^* \right).$$

We will refer to this model as the full PFC-MS (FPFC-MS) model, which describes the dynamics of the amplitude and average density fields with Equations (8) and (9), respectively. Note that “MS” denotes the multiple-scale analysis employed in the derivation, which yields results similar to those of the RG method.

An unfortunate aspect of the multiple-scale analysis result given in Equation (9) is that it is only numerically stable when the computational grid spacing is the same as or smaller than that used in standard PFC simulations. Larger grid spacings (i.e. four or less grid points per atomic spacing), lead to periodic patterns in $\bar{\psi}$. Generally this numerical instability initiates near interfaces and quickly propagates into bulk liquid and crystalline phases. Since the FPFC-MS method requires more equations to be solved, this method not only lacks an advantage over the standard PFC model, but is in fact less computationally efficient. Direct quantitative comparisons will be presented in Section 3.2. More importantly, as will be detailed in Section 3.1, under certain conditions this FPFC-MS model would be linearly unstable at finite wavenumbers, leading to short-wavelength oscillations of amplitudes $A_j$ in the solid phase which are inconsistent with the original PFC model.
2.4. Modified density-amplitude formulation for PFC

To overcome the limitations of the FPFC-MS model, it is useful to note that the numerical instability arises from the terms involving higher- (fourth and sixth) order spatial derivatives in Equation (9). For computational efficiency, we propose to eliminate terms involving fourth- and sixth-order derivatives in Equation (9). A justification can be given by noting that the contribution of such terms to the free energy is zero in both the equilibrium liquid and solid phases. In essence, these terms only serve to slightly modify the surface tension. More importantly, elimination of these terms removes the unnecessary linear instability of $\psi$ to form oscillations that can occur in the FPFC-MS model for some initial conditions. This instability is already included in the amplitudes.

While this proposed change provides a remedy for resolution limitation described earlier, the amplitude equation, Equation (8), remains numerically stiff. Without loss of accuracy, $L_k$ in the operator $(L_k - 1)$ appearing in Equation (8) can be ignored. Eliminating this term greatly decreases the stiffness of the equation and consequently increases the computational efficiency. This, combined with the elimination of higher-order terms in the average density equation, constitutes the modified density-amplitude formulation, which we will term the modified PFC-MS (MPFC-MS) model. Both of these approximations will be justified by direct comparisons of the FPFC-MS and MPFC-MS models in Section 3.

The approximations used for the MPFC-MS model result in the following coupled equations:

\[
\frac{\partial \tilde{\psi}}{\partial t} = \nabla^2 \left[ (a_0 + a_2)\tilde{\psi} + a_3\tilde{\psi}^3 + 2(a_3 + 3a_4\tilde{\psi}) \sum_{i=1}^3 |A_i|^2 \right.
\]

\[
+ 6a_4 \left( \sum_{i=1}^3 A_i + \sum_{i=1}^3 A_i^* \right) \right],
\]

(10a)

and

\[
\frac{\partial A_j}{\partial t} = -\left\{ a_0 L_k^2 A_j + (a_2 + 2a_3\tilde{\psi} + 3a_4\tilde{\psi}^2) A_j + 2(a_3 + 3a_4\tilde{\psi}) \prod_{i=1}^3 A_i^* \right.
\]

\[
+ 3a_4 A_j \left( 2 \sum_{i=1}^3 |A_i|^2 - |A_j|^2 \right) \right\}.
\]

(10b)

Note that Equation (10b) contains $L_k^2$, rather than a lower-order operator. In Appendix B, we show that this is necessary in order to recover the linear elasticity behavior in the presence of small deformation. The MPFC-MS model satisfies the original assumption that the average atomic density is relatively constant. Furthermore, it allows much higher computational efficiency due to a larger grid size and a larger time step. The direct comparisons of simulation results using the PFC, FPFC-MS and MPFC-MS models will be presented in Section 3.
Up to this point, the physical basis of the MPFC-MS equations, Equations (10a) and (10b), is unclear. To obtain a more physical interpretation of these equations, we provide below an alternative derivation and then make analogies with classical PF modeling. To this end, we apply the variational approach with the free energy functional based on the single-mode approximation given by Equation (5); the justification for this approximation is provided below. The resulting free energy functional, $F'$, is given by

$$
F' \approx \int dr \left\{ \frac{a_0}{2} \sum_{j=1}^{3} \left( A_j (\nabla^2 - 2ik_j \cdot \nabla)^2 A_j^* + A_j^* (\nabla^2 + 2ik_j \cdot \nabla)^2 A_j \right) + \frac{a_0 + a_2}{2} \bar{\psi}^2 
+ \frac{a_3}{3} \bar{\psi}^3 + \frac{a_4}{4} \bar{\psi}^4 + (a_2 + 2a_3 \bar{\psi} + 3a_4 \bar{\psi}^2) \sum_{j=1}^{3} |A_j|^2
+ 2(a_3 + 3a_4 \bar{\psi}) \left( \prod_{j=1}^{3} A_j + \prod_{j=1}^{3} A_j^* \right) + 6a_4 \sum_{i=1}^{3} \sum_{j=i+1}^{3} |A_i|^2 |A_j|^2 + \frac{3a_4}{2} \sum_{j=1}^{3} |A_j|^4 \right\}. 
$$ (11)

The MPFC-MS model can be obtained from the variational derivatives of $F'$ via

$$
\frac{\partial \bar{\psi}}{\partial t} = \nabla^2 \frac{\delta F'}{\delta \bar{\psi}},
$$ (12a)

and

$$
\frac{\partial A_j}{\partial t} = - \frac{\delta F'}{\delta A_j},
$$ (12b)

where the average density and the amplitude fields are treated as conserved and nonconserved properties, respectively. Detailed derivation of Equation (11) and the MPFC-MS model using the variational approach are discussed in Appendix C.

In the above analysis, we assumed that the terms related to modes other than the one corresponding to the equilibrium atomic lattice and higher-order derivatives can be neglected. The $n$-th-order derivative of the amplitude will be inversely proportional to $(kw)^n$, where $k$ is the magnitude of the wavevector and $w$ is the characteristic width of the solid–liquid interface [46]. The characteristic width $w$ is greater than the atomistic length scale $1/k_{\text{min}}$, where $k_{\text{min}}$ is the smallest magnitude of the wavevectors considered. Therefore, one may assume that $kw \gg 1$, in which case the terms related to higher-order derivatives are small and can be neglected [46].

We also note that the mobility $\Gamma$ would in general vary for different modes, but with a single-mode approximation, the mobility is restricted to one value, taken to be unity. This can be justified following the argument found in Refs. [47,48] for liquid–solid transition. $\Gamma$ is inversely proportional to the relaxation time of density fluctuations, $\tau$, which is related to the bulk liquid structure factor $S(k)$. In solid–liquid transition, $\tau$ exhibits a sharp maximum at the position of the first peak in $S(k)$, and thus the rate-limiting slowest relaxation time occurs at that value of $k$. Therefore, the single-mode approximation with a single value of $\Gamma$ is applicable in describing the evolution of such systems.
The dynamics of the MPFC-MS model is analogous to typical phase field models with two types of order parameters, one conserved (cf. Equation (12a)) and the other nonconserved (cf. Equation (12b)) [2,3,7–15]. This type of dynamics was termed model C by P.C. Hohenberg and B.I. Halperin [53]. The average density field and the amplitude fields in the MPFC-MS model are thus analogous to the diffusion field and the order parameter field in PF models, respectively. Furthermore, it is evident that the negative second-order derivative and the fourth-order polynomials of the amplitudes $A_j$ in $\mathcal{F}'$ are analogous to the gradient energies and the double-well potentials commonly used in the PF models. The only differences are the three complex amplitudes that are used to describe the atomic configuration and the higher-order derivatives that assure consistency with linear elasticity. Such a comparison will lead to the linkage between the classical PF models and the PFC models.

3. Comparison among PFC, FPFC-MS and MPFC-MS models

3.1. Linear stability analysis

We start from the FPFC-MS model, i.e. Equations (9) and (8). If assuming perturbations around the homogeneous (liquid) state with $A_j=0$ and $\bar{\psi} = \bar{\psi}_l$, i.e.

$$A_j = 0 + \sum_k \hat{A}_j e^{ikr}, \quad \bar{\psi} = \bar{\psi}_l + \sum_k \hat{\psi} e^{ikr},$$

and substituting them into Equations (8) and (9), we can obtain the linearized, first-order equations governing the perturbed quantities $\hat{A}_j$ and $\hat{\psi}$ as well as the corresponding perturbation growth rates. The perturbation growth rate of $\hat{A}_1$ is given by

$$\sigma_{A_1} = \left( k_x^2 + k_y^2 - \sqrt{3} k_x - k_y + 1 \right) \left[ a_l - a_0 \left( k_x^2 + k_y^2 - \sqrt{3} k_x - k_y \right) \right],$$

where

$$a_l = -(a_2 + 2a_3 \bar{\psi}_l + 3a_4 \bar{\psi}_l^2).$$

Similar results can be obtained for $\hat{A}_2$ and $\hat{A}_3$.

In the solid phase with $a_l>0$ (as given from the original PFC Equation (2)), we have $\text{max}(\sigma_{A_j})>0$, showing the instability of the liquid phase. However, it can be found that the maximum perturbation growth rate does not lie at $k_x = k_y = 0$, but at some finite wavenumbers. For simplicity, we consider the example of 1D case with only $y$-dependent amplitudes. Thus, by setting $q_x = 0$ in Equation (15) we find the maximum $\sigma_{A_1}$ appearing at wavenumbers

$$k_y^\pm = \frac{1}{2} \left[ 1 \pm \sqrt{\left( 4\sqrt{3} a_l/a_0 + 1 - 1 \right) / 3} \right],$$

with the corresponding maximum growth rate being
\[
\sigma_{A_1}(k_y = k^\pm_y) = \frac{2}{27} \left[ (3a_1/a_0 + 1)^{3/2} + 9a_1/a_0 - 1 \right].
\] (18)

Therefore, the amplitude of short-wavelength oscillations are expected to grow in time, in disagreement with the original PFC model. Therefore, beyond the initial instability stage, short-wavelength oscillations with nonzero wavenumbers \(k^\pm_y\) are expected to develop in the solution of amplitudes, disagreeing with the original PFC model. This inconsistency can be attributed to the fact that during the derivation of FPFC-MS equations, we neglect the contributions from higher harmonics which would play an important role in the selection of instability mode for amplitudes.

On the other hand, for the MPFC-MS model (Equations (10a) and (10b)) the perturbation growth rate is given by
\[
\sigma_{A_1} = \left[ a_1 - a_0 \left( k_x^2 + k_y^2 - \sqrt{3}k_x - k_y \right)^2 \right],
\] (19)
different from Equation (15). Thus, the maximum value of \(\sigma_{A_1}\) can only be \(a_1\), occurring at wavenumbers \(k_x = k_y = 0\) and some other values such as \((k_x = 0, k_y = 1)\) for 1D case. The selection among these wavenumbers depends on details of nonlinearities and evolution at later time, for which our numerical calculations of this MPFC-MS model indicate the dominance of the \(k_x = k_y = 0\) mode. The oscillation of amplitudes is then absent, consistent with the original PFC model.

3.2. Numerical comparison

In this section, we present a detailed numerical comparison of the PFC, FPFC-MS and MPFC-MS models. Before presenting comparisons of the simulation results, we first discuss the computational efficiency of each model. In all numerical implementations, a simple explicit Euler scheme for the time integration and a spherical approximation for the spatial derivatives [33,45] is used. Periodic boundary conditions are imposed at the computational domain boundaries. Following Ref. [51], we use: \(a_0 = B_s\), \(a_2 = B_l - B_s\), \(a_3 = -1/2\), and \(a_4 = 1/3\) (with \(q_o = 1\) as before, which sets the equilibrium interatomic spacing to be \(4\pi/\sqrt{3}\)), where \(B_s\) and \(B_l\) are the crystal bulk modulus and the liquid isothermal compressibility, respectively. The maximum grid spacing and time step size, based on the stability and accuracy in a simulation with planar geometry, are determined by trial and error (using \(\Delta x\) of \(\pi/4\), \(\pi/2\), and \(\pi\) for each model) and are summarized in Table 1.

<table>
<thead>
<tr>
<th>(\Delta x)</th>
<th>PFC (\Delta t_{\text{max}} = 0.008)</th>
<th>FPFC-MS (\Delta t_{\text{max}} = 0.0048)</th>
<th>MPFC-MS (\Delta t_{\text{max}} = 0.039)</th>
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</thead>
<tbody>
<tr>
<td>(\pi/4)</td>
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<tr>
<td>(\pi/2)</td>
<td>Insufficient resolution</td>
<td>Unstable</td>
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<tr>
<td>(\pi)</td>
<td>Not tested</td>
<td>Not tested</td>
<td>(\Delta t_{\text{max}} = 0.360)</td>
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Table 1. The allowable grid-spacings and the maximum time steps for the PFC, FPFC-MS and MPFC-MS models.
The average density field of the FPFC-MS model is stable only for $\Delta x = \pi/4$, and the allowable time steps are less than that of the PFC model. For $\Delta x = \pi/2$, the FPFC-MS model $\psi$ develops periodic oscillations. The 2D FPFC-MS model employs four variables (one scalar and three complex variables), and it requires calculation time approximately 7–8 times more than the standard PFC model at the same grid and time step. Therefore, the FPFC-MS model is least efficient computationally. On the other hand, the MPFC-MS model retains stability even at $\Delta x = \pi$. However, the practical limit of $\Delta x$ is $\pi/2$ to ensure sufficient accuracy to resolve complex morphologies of microstructures and relatively fast varying complex amplitudes. At this resolution, the MPFC-MS model is 14–15 times faster computationally than the PFC model for a 2D hexagonal crystal structure, and therefore it can be a powerful alternative for large-scale simulations.

Now we compare the simulation results from the three models, mainly to quantify the effects of the approximation made in the MPFC-MS model and to validate its applicability. First, we compare the results of the MPFC-MS model with the FPFC-MS model for planar crystal growth starting from an initial thin solid plate placed at the center of the computational domain. The parameters used in the simulations are $(B_c, B_l) = (0.988, 1.0)$. For the given parameters, the equilibrium solidus and liquidus densities are $(\bar{\psi}_s, \bar{\psi}_l) = (0.0067, -0.0713)$, respectively. Note that the densities are measured in a relative manner such that they can be positive or negative (see Ref. [51]). The initial overall average density is set as $-0.030$, and only the central quarter region has the equilibrium amplitudes for $\bar{\psi} = -0.03$, as shown in Figure 2a. The grid spacings of $\Delta x = \pi/4$ and $\pi/2$ are used for the FPFC-MS and MPFC-MS simulations, respectively.

Simulation results of the FPFC-MS and MPFC-MS models are shown in Figures 2b and c. The results from the FPFC-MS model are shown with a solid line, and those from the MPFC-MS are noted with squares (the average density, $\bar{\psi}$) and circles (the norm of the amplitude, $|A_1|$). The figure clearly demonstrates that the results of the two models are nearly identical. To examine the differences more carefully, the average density and amplitude fields around the interface at $t = 4000$

![Figure 2](https://example.com/figure2.png)

Figure 2. The evolution of the average density $\bar{\psi}$ and the absolute value of the amplitude $|A_1|$ at (a) $t = 0$, (b) $t = 2000$ (c) $t = 20000$. Circles and squares represent $|A_1|$ and $\bar{\psi}$ obtained by the MPFC-MS model and the lines represent those obtained using the FPFC-MS model. The circles and squares are plotted at every four grid points.
are magnified in Figure 3. The differences in the average density $\bar{\psi}$, the amplitude $|A_i|$, and the reconstructed atomic density $\psi$ around a planar interface resulting from the FPFC-MS and MPFC-MS models at $t=4000$. The data are taken from a cross-section through the center of an atomic layer.

We also compared simulation of the PFC model with that of the MPFC-MS model for the system with the same input parameters and initial conditions. Figure 4 shows the equilibrium atomic densities of the MPFC-MS and PFC models. It is evident that the equilibrium state produced by the MPFC-MS model is slightly different from that by the PFC model, as seen in the small changes of the solid volume fractions and their average densities.

In order to investigate the equilibrium states, the phase diagrams, constructed using two models and using the single-mode approximation, are presented.
in Figure 5. The values of the bulk moduli were chosen to be \( B_s = 1.0 \) and \( B_l \) varying from 0.9 to 1.0. Note that \( a_2 = \Delta B = B_l - B_s \) is linearly related to \( \Delta T = T - T_m \) for a small \( \Delta B \), where \( T_m \) is the melting temperature \([33,51]\). The overall density of the system is set as the average of the equilibrium liquidus and solidus densities predicted from the single-mode approximation, and thus the equilibrium solid volume fraction is 50% when the single-mode approximation is met. Thus, the deviation of the solid volume fraction from this value is a measure of the departure from the single-mode approximation. The equilibrium liquidus and solidus densities are obtained from the MPFC-MS and PFC simulations after the system relaxes to the equilibrium state. In PFC simulations, the liquidus densities are measured in the liquid phase at the midpoint between two solid–liquid interfaces, and the solidus densities are calculated from the volume fractions of two phases. In order to obtain the volume fractions, the interface positions are taken where the density has the average of the liquid density and the maximum value of the solid density from the function obtained by connecting the maxima of the atomic density shown in Figure 4b. The errors in determining volume fractions are less than about 2% and thus the errors in the solidus densities are acceptable.

As shown in Figure 5, the equilibrium densities calculated by the MPFC-MS model are nearly identical to the prediction of the single-mode approximation. This is because the MPFC-MS model is based on the single-mode approximation. On the other hand, the PFC results deviate from those of the single-mode approximation, demonstrating that the atomic density cannot be represented fully by the single mode having a wavelength of the atomic spacing. While the single-mode approximation is commonly used to relate the equilibrium properties or elastic constants with the PFC models \([33,35]\), this will lead to errors especially when the difference between \( B_l \) and \( B_s \) is large. For the same reason, the MPFC-MS results will differ from those of the PFC model in the same regime. This may lead to different anisotropies in the interfacial energy and elasticity compared to the corresponding the PFC model, depending on the system parameters. Thus, it is necessary to evaluate such resulting material properties for each set of system parameters in simulations.
4. Multidimensional numerical simulations

4.1. Gibbs–Thomson effect of the MPFC-MS model

In this section, we examine the Gibbs–Thomson effects in the MPFC-MS model. To this end, the interfacial free energy and the effect of a curved interface on the free energy are evaluated. To obtain the interfacial energy, the total free energy per unit length, $F'$ of a planar interface in a system with 50% solid-volume fraction is calculated numerically as given by Equation (11). The interfacial free energy, $\gamma$ is then given by $\gamma = F' - (1/2)(F_s^{eq} + F_l^{eq})$ for a system with 50% solid-volume fraction, where $F_s^{eq}$ and $F_l^{eq}$ are total free energies of pure liquid and solid systems at equilibrium, respectively, and $L$ is the total interfacial length in the system. For $(B_s, B_l) = (1.0, 1.0)$, the interfacial free energy was found to be $\gamma \approx 1.82 \times 10^{-2}$. In this chosen system, the anisotropy of the interfacial energy is sufficiently small to be negligible.

To evaluate the effect of curvature on the free energy, we simulate a two-dimensional circular solid in equilibrium with a liquid at a solid volume fraction of 35% in the absence of curvature. The excess energy associated with a solid–liquid interface is illustrated schematically in Figure 6a. A gray-scale plot of $\psi$ in equilibrium is shown in Figure 6b. The radius of this crystal was measured to be $R_c \approx 130.0$ by defining the interface position at points where the number density is the average of the solid and liquid densities. The Gibbs–Thomson effect shifts the solid average density, $\bar{\psi}_s$, from the equilibrium solidus density, $\bar{\psi}_s^{eq}$, in the absence of curvature effects. Based on the measured interfacial free energy $\gamma$ and the equilibrium radius $R_c$ of the crystal, the shift of average densities, $(\Delta \bar{\psi}_l, \Delta \bar{\psi}_s)$ from $(\bar{\psi}_l, \bar{\psi}_s) = (-0.08686, -0.00359)$, can be predicted by the common-tangent construction, as shown in Figure 6c, which were found to be $(\Delta \bar{\psi}_l, \Delta \bar{\psi}_s) = (0.00162, -0.00205)$. The values of $(\Delta \bar{\psi}_l, \Delta \bar{\psi}_s)$ calculated by the MPFC-MS simulation by sampling from the points furthest from the solid–liquid interface are $(\bar{\psi}_l, \bar{\psi}_s) = (0.00153, -0.00212)$. Thus, the differences from the common-tangent predictions are 5.6% in the liquid and 3.4% in the solid, and therefore we conclude that the MPFC-MS model implicitly includes the Gibbs–Thomson effect with acceptable accuracy.

4.2. Two-dimensional numerical simulations of growth of the hexagonal crystal structure

Using the MPFC-MS model, numerical simulations were performed for polycrystalline growth from randomly distributed nuclei. The parameters used in the simulations were $(B_s, B_l) = (1.0, 0.97)$ and the equilibrium liquidus and solidus densities were $(\bar{\psi}_l^{eq}, \bar{\psi}_s^{eq}) = (-0.1259, -0.0263)$, respectively. In the simulations, $512 \times 512$ grid points were used with $(\Delta x, \Delta t) = (\pi/4, 0.35)$. The computational domain is initially seeded by 50 circular nuclei, each having a radius of $5\Delta x$, average density $\bar{\psi}_s^{eq}$, and randomly chosen orientations. The initial supersaturated liquid density is determined to satisfy the overall average density of the system, corresponding to the given solid volume fraction.

Figure 7 shows the process of crystal growth for a 90% solid-volume-fraction system, whose overall average density is $0.1\bar{\psi}_l^{eq} + 0.9\bar{\psi}_s^{eq}$. The atomic densities at $t = 0, 875, 4375$ and 17,500 are presented. The solid nuclei grow toward the
supersaturated liquid phase and create grain boundaries (e.g. consisting of dislocations) in many cases due to the high volume fraction. The evolution then proceeds by grain growth except for regions with remaining liquid. Note that the liquid coexists with the solids in this system, and the liquid volume fraction does not change significantly after reaching the near-equilibrium solid volume fraction.

The defects or grain boundaries can be seen very clearly in the plots of $\sum_{C22}$ and $|A|^2$ (Figures 8b and d, respectively). Also, in Figure 8b, the Gibbs–Thomson effect is clearly seen as the average density field inside the crystal phase is not uniform, especially near regions of high curvature. In contrast, $|A|$ (see Figure 8d) is relatively constant, showing uniformity in the degree of crystalline order within crystals. The different patterns of the real part of the amplitude $A$ inside grains in Figure 8c represent the different grain orientations.
While we have not implemented an adaptive mesh technique (such as that found in Refs. [43,45]), the MPFC-MS model is amendable to adaptive mesh and will greatly benefit by such implementation. In the MPFC-MS model, the average density $\tilde{\rho}$ and the absolute value of the amplitude fields $|A_j|$ indeed change slowly. However, the amplitudes $A_j$ can still have rapid spatial variation in crystals, depending on the crystalline orientation, which needs to be resolved. The amplitude $A_j^0$ for a specific grain can be written as [45]

$$A_j^0 = |A_j^0| e^{i\delta k_j(\theta) \cdot x} \tag{20}$$

where $\delta k_j(\theta) = k_j'(\theta) - k_j$ and $k_j'(\theta)$ is the hexagonal lattice basis vectors rotated by angle $\theta$ from the basis vectors $k_j$ in Equation (6). Initial orientations of nuclei are set using Equation (20) with randomly chosen $\theta$ from the range $[-\pi/6, \pi/6]$ based on the six-fold symmetry of the hexagonal structure. The periodicity of the amplitude $A_j$ are

Figure 7. Polycrystalline growth and coarsening for a 90% solid-volume-fraction system at (a) $t=0$, (b) $t=875$, (c) $t=4375$ and (d) $t=17500$. 
determined by $|\delta k'(\theta)|$. The wavelength of the highest fluctuating periodicity ($\theta = \pm \pi/6$, $|\delta k'(\pm \pi/6)| = 0.518$) is $2\pi/|\delta k'(\pm \pi/6)| = 3.86\pi$, which is equivalent to $15.5\Delta x$. Thus, during the simulations, at least about 11 grids are located on one period of $A_j$ having the highest frequency. However, the spatial profiles of the amplitudes $A_j$ inside the crystal still give the restriction on an adaptive mesh technique. Therefore, an adaptive mesh technique requires other spatially uniform fields irrespective of crystal orientations. Goldenfeld et al. used the amplitude moduli $\Psi_j = |A_j|$ and the phase angles $\Phi_j = \arctan [\Im\{A_j]/\Re\{A_j\}]$, instead of the complex amplitude fields $A_j$, where $\Im\{A_j\}$ and $\Re\{A_j\}$ represent the real and imaginary components of $A_j$, respectively [43,45]. When using $\Psi_j$ and $\Phi_j$ instead of $A_j$, the grid spacing is constrained by the solid–liquid interface width, which is governed by

Figure 8. (a) The reconstructed atomic density, $\psi$, (b) the average density, $\bar{\psi}$, (c) the real component of the amplitude, $\Re\{A_j\}$ and (d) the absolute value of the amplitude, $|A_j|$, at $t = 17500$ for a 90% solid-volume-fraction system.
model parameters (rather than the periodicity in $A_j$ arising from the orientation of the crystal lattice).

Figure 9 shows the process of crystal growth in a 50% solid volume fraction system with the same initial condition as the 90% solid volume fraction system except for the lower liquid supersaturation. Due to the lower supersaturation, the interface velocities are slower than those for the 90% solid system. After the volume fraction reaches the near-equilibrium value, coarsening is observed; large crystals become larger at the expense of small ones, which results in a reduction of the system’s interfacial energy. The number of defects in the crystals is small in comparison with those for the 90% system, because two merging crystals can rotate with respect to each other during the coalescence process.

Figure 9. Polycrystalline growth and coarsening for a 50% solid-volume-fraction system at (a) $t=0$, (b) $t=875$, (c) $t=4375$ and (d) $t=17500$. 
4.3. Three-dimensional MPFC-MS model for BCC structure

The MPFC-MS model can easily be extended to three dimensions. Here, we take the body-centered cubic (BCC) structure as an example. The equilibrium atomic density for the BCC crystal structure, \( \psi_B \), can be approximated by

\[ \psi_B = \psi + A_B \cos(qx) \cos(qy) + \cos(qy) \cos(qz) + \cos(qz) \cos(qx), \]  

(21)

where \( q = R/\sqrt{2} = 1/\sqrt{2} \) (with \( q_0 = 1 \)), and thus the single-mode approximation is given by

\[ \psi = \tilde{\psi} + \sum_{j=1}^{6} (A_j e^{i k_j x} + A_j^* e^{-i k_j x}). \]  

(22)

The six basis vectors in Equation (22) are \( k_1 = (i+j)/\sqrt{2}, \ k_2 = (i+k)/\sqrt{2}, \ k_3 = (j+k)/\sqrt{2}, \ k_4 = (j-k)/\sqrt{2}, \ k_5 = (i-j)/\sqrt{2} \) and \( k_6 = (-i+k)/\sqrt{2} \). The density-amplitude formulation based on the variational approach, as described earlier and in Appendix C, was used to derive the evolution equations for the average density and amplitudes due to the enormous complexity involved in rigorous multiple-scale analysis for the 3D case. The results are as follows: the evolution equation for \( \psi \) is given by

\[ \frac{\partial \psi}{\partial t} = \nabla^2 \left[ (a_0 + a_2) \psi \psi^* + \sum_{i=1}^{6} |A_i|^2 \right] \]

\[ + 6a_4 \left( A_4 A_5 A_6 + A_1^* A_2 A_4 + A_2^* A_3 A_5 + A_3^* A_4 A_6 \right) \]

\[ + \left( A_4^* A_5^* A_6^* + A_4 A_5 A_6^* + A_2 A_5^* A_6^* + A_3 A_4^* A_6^* \right) \],

(23a)

and the evolution equations for the amplitudes \( A_j \) for \( j = 1, 2, 3 \) are given by

\[ \frac{\partial A_j}{\partial t} = -\left\{ a_0 |k_j|^2 A_j + (a_2 + 2a_3 \psi + 3a_4 \psi^2) A_j + 2(a_3 + 3a_4 \psi) (A_k A_l + A_l A_k^*) \right. \]

\[ + 6a_4 \left( A_i A_l A_m + A_m^* A_l A_i^* \right) + 3a_4 A_j \left( \sum_{p=1}^{6} |A_p|^2 - |A_j|^2 \right) \}, \]

(23b)

where the index \( (i,j,k) \) and \( (l,m,n) \) are cyclic permutations of \( (1,2,3) \) and \( (4,5,6) \), respectively, starting from \( (i,j,k,l,m,n) = (1,2,3,4,5,6) \). The equations for the other amplitudes \( A_m \) for \( m = 4, 5, 6 \) are

\[ \frac{\partial A_m}{\partial t} = -\left\{ a_0 |k_m|^2 A_m + (a_2 + 2a_3 \psi + 3a_4 \psi^2) A_m + 2(a_3 + 3a_4 \psi) (A_j A_k^* + A_k A_j^*) \right. \]

\[ + 6a_4 \left( A_k^* A_i A_m^* + A_j A_k^* A_i^* \right) + 3a_4 A_m \left( \sum_{p=1}^{6} |A_p|^2 - |A_m|^2 \right) \}, \]

(23c)

and the cyclic permutations rules are the same as those for Equation (23b).

A MPFC-MS simulation of the growth of BCC crystals was performed. The parameters in the simulation are \( (B_x, B_z) = (1.0, 1.0) \) and other parameters appearing in Equation (1) are the same as before. The equilibrium densities of the liquid and the
BCC crystal are \((\bar{\psi}_i^{eq}, \bar{\psi}_s^{eq}) = (-0.1008, -0.0386)\), respectively, and the overall average density is set so that the equilibrium solid volume fraction is 90\%. Figure 10 presents evolution of the BCC crystal from the 25 randomly oriented nuclei of radius \(5\Delta x\) and average density \(\bar{\psi}_s^{eq}\) at \(t = 0, 100, 300, 500, 1000\) and 3000. It shows BCC crystal growth and grain boundary formation. At the late stage of the simulation, the growth of the crystal stops due to the depletion of the liquid density supersaturation, and the grain growth is observed.

In this three-dimensional simulation, \(128 \times 128 \times 128\) grid points are used with \((\Delta x, \Delta t) = (\pi/\sqrt{2}, 1.0)\). This grid spacing guarantees four grid points per lattice parameter, which provides sufficient accuracy in this model. The volume of the computational domain is equivalent to 32,768 BCC unit cells and contains 65,536 atoms when fully crystallized. The CPU time for this simulation was about 18.5 hours on a single AMD Opteron 252-2.6GHz processor, demonstrating that the three-dimensional MPFC-MS model greatly enhances the computational efficiency. By comparing this model and the current standard PFC model in which \(\Delta x \sim \pi/4\) and \(\Delta t \sim 10^{-2}\) are used, we found that the MPFC-MS model is about two orders of magnitude faster than the standard PFC model.

5. Discussion and conclusion

In this paper, we presented the density-amplitude formulation that can be applied to dynamics of two-phase systems by building upon the multiple-scale approach for the

![Figure 10](image-url)
The modified phase-field-crystal model based on the multiple-scale approach (the MPFC-MS model) includes the change of the average density field, and thus it can be applied to investigate phenomena in systems in which liquid and crystalline phases coexist, making it more widely applicable in micro/nanostructural evolution simulations than the existing amplitude formulations \cite{42-45}. Furthermore, the new set of equations is less numerically stiff by two orders in the spatial derivative, and is thus more computationally efficient. By examining the similarities and differences between the two density-amplitude formulations proposed and the standard phase-field-crystal model, insights were gained into the physical interpretations of the MPFC-MS model. In particular, it was shown that the model is equivalent to a Cahn–Hilliard-type (conserved) dynamics for the average density field and to an Allen–Cahn-type (nonconserved) dynamics for the amplitudes with the free energy functional given by the single-mode approximation to the standard PFC free energy functional. Thus, the approach presented here may provide the link between the standard phase-field model and the phase-field-crystal model. The models and simulation results were presented for the two-dimensional hexagonal structure and for the three-dimensional body-centered cubic structure. Model validation was carried out by examining the interfacial energy and the associated Gibbs–Thomson effect. The MPFC-MS model was found to retain acceptable accuracy even with a significantly larger grid size. Along with less stiffness of the equation, the MPFC-MS was found to be about two orders of magnitude faster in computing the evolution of a system with 65,356 atomic positions, even without the use of an adaptive mesh technique. Therefore, it will allow simulations spanning a much larger length and time scale than previously possible using the standard phase-field-crystal model. Simulations of growth and coarsening are performed to demonstrate its potential for large-scale simulations.

Whether the new model presented above is computationally superior to other atomistic models such as kinetic Monte Carlo (KMC) depends on the details of the system being simulated and algorithms employed. Thus, we simply highlight the advantages of this PFC-based method. Since the PFC model does not require a fixed atomic lattice, it is quite simple and natural to simulate defects such as dislocations and grain boundaries by actually describing atomic positions. The model also allows co-existing liquid. Describing these phenomena based on individual atomic positions in the crystalline phase would require an off-lattice treatment in KMC, which can be computationally expensive. In addition, as demonstrated in Refs. \cite{33,35}, PFC models naturally incorporate elasticity, and we have shown that the density-amplitude formulation retains linear elasticity properly. While elastic effects can be accounted for in KMC, they must be included as an additional sub-model.

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References

Appendix A: Multiple-scale derivation for the FPFC-MS model

In this appendix, we outline the derivation of amplitude equations for the PFC equation, Equation (2), based on the multiple-scale analysis. We first introduce the small parameter $\epsilon$ and scale the coefficients $a_2 = \epsilon^2 \tilde{a}_2$ and $a_3 = \epsilon^3 \tilde{a}_3$. The other coefficients, $a_0$ and $a_4$ in Equation (2), are assumed to be of $O(1)$. We also introduce the slowly varying spatial and temporal scales as $(X, Y) = (x, \epsilon y)$ and $T = \epsilon^2 t$. Thus, the derivatives and the operator are scaled as follows:

$$
\frac{\partial}{\partial t} \rightarrow \epsilon^2 \frac{\partial}{\partial T}, \quad \frac{\partial}{\partial x} \rightarrow \epsilon \frac{\partial}{\partial X} + \frac{\partial}{\partial x}, \quad \frac{\partial}{\partial y} \rightarrow \frac{\partial}{\partial Y} + \epsilon \frac{\partial}{\partial Y}, \quad \nabla^2 \rightarrow \nabla^2_{xy} = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + 2\epsilon \left( \frac{\partial^2}{\partial x \partial X} + \frac{\partial^2}{\partial Y \partial Y} \right) + \epsilon^2 \left( \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} \right).
$$

Then we expand $\psi$ in a powers of $\epsilon$, noting that the leading order of $\psi$ is of $O(1)$:

$$
\psi \simeq \tilde{\psi} + \sum_{j=1}^{3} \left( A_j e^{iK x} + A_j^* e^{-iK x} \right) + \text{other harmonics} = \left( \epsilon \tilde{\psi}(0) + \epsilon^2 \tilde{\psi}(1) + \epsilon^3 \tilde{\psi}(2) + \cdots \right) + \sum_{j=1}^{3} \left[ \left( \epsilon A_j(0) + \epsilon^2 A_j(1) + \cdots \right) e^{iK x} + \left( \epsilon A_j^*(0) + \epsilon^2 A_j^*(1) + \cdots \right) e^{-iK x} \right] + \text{other harmonics}.
$$

Substituting Equation (24) into Equation (2) and using the solvability condition [54], we obtain the evolution equations for the average density and the amplitudes at each order in $\epsilon$; i.e. $\partial \tilde{\psi}(0) \partial T$, $\partial \tilde{\psi}(1) \partial T$, $\partial A_j(0) \partial T$, $\partial A_j(1) \partial T$, $\partial A_j^*(0) \partial T$, $\partial A_j^*(1) \partial T$, … For example, the lowest-order evolution equations for the average density $\psi$ and the amplitude $A_1$ are given by

$$
\frac{\partial \tilde{\psi}(0)}{\partial T} = a_0 \left( \frac{\partial^2 \tilde{\psi}(0)}{\partial X^2} + \frac{\partial^2 \tilde{\psi}(0)}{\partial Y^2} \right),
$$

(25a)
where \( \bar{a} \) is a constant. For this specific deformation the contribution to the free energy given in this term gives (i.e. in the continuum elasticity limit). For a hexagonal lattice (i.e. using the basis vectors in \( \mathbf{k} \)), the last approximation is valid for small displacements in the long wavelength limit.

To illustrate the elastic energy contained in the free energies presented in the text it is useful to consider a small deformation of the form \( \mathbf{A}_i = \mathbf{A} \mathbf{e}^{\mathbf{k}_i \mathbf{u}} \), where \( \mathbf{u} \) is the displacement vector and \( \mathbf{A} \) is a constant. For this specific deformation the contribution to the free energy given in Equation (11) is due to the term \( a_0 \sum_j \int d\mathbf{r} (\mathbf{A}_j \mathbf{L}_k^2 \mathbf{A}_j + A_j (\mathbf{L}_k^2 \mathbf{A}_j)^2)/2 = a_0 \sum_j \int d\mathbf{r} |\mathbf{L}_k \mathbf{A}_j|^2 \), where \( \mathbf{L}_k \) is defined below Equation (8). Substituting the deformed configuration into this term gives

\[
a_0 |\mathbf{L}_k \mathbf{A}_j|^2 = a_0 \left( |\nabla^2 (\mathbf{k}_j \cdot \mathbf{u})|^2 + 4 \left[ \frac{1}{2} |\nabla (\mathbf{k}_j \cdot \mathbf{u})|^2 + (\mathbf{k}_j \cdot \nabla)(\mathbf{k}_j \cdot \mathbf{u}) \right] \right) A^2 \\
\approx 4a_0 |\mathbf{k}_j \cdot \nabla (\mathbf{k}_j \cdot \mathbf{u})|^2 A^2, \tag{27}
\]

where the last approximation is valid for small displacements in the long wavelength limit (i.e. in the continuum elasticity limit). For a hexagonal lattice (i.e. using the basis vectors in Equation (6)) the elastic contribution of this deformation is then

\[
4a_0 \sum_j |\mathbf{k}_j \cdot \nabla (\mathbf{k}_j \cdot \mathbf{u})|^2 A^2 = 3 a_0 \left( \frac{3}{2} (u_{xx}^2 + u_{yy}^2) + u_{xx} u_{yy} + 2 u_{xy}^2 \right) A^2, \tag{28}
\]

where \( u_{ij} \) is the linear strain tensor, \( u_{ij} = (\partial u_i + \partial u_j)/2 \). Using standard notation, the following relationships between the elastic constants can be established: \( C_{11} = C_{22}, \)
where \( C_{12} = C_{21} = C_{66} = C_{11}/3 \), as expected for a hexagonal lattice. The same calculations can be repeated for the BCC crystal (i.e. using the basis vectors given below Equation (22)) to obtain

\[
4a_0 \sum_j (k_j \cdot \nabla(k_j \cdot \mathbf{u}))^2 = 4a_0 \left[ \left( u_{xx}^2 + u_{yy}^2 + u_{zz}^2 \right) + 2 \left( u_{xy}^2 + u_{xz}^2 + u_{yz}^2 \right) \right] + [u_{xx}u_{yy} + u_{xx}u_{zz} + u_{yy}u_{zz}] A^2, \tag{29}
\]

which implies \( C_{11} = C_{22} = C_{33}, C_{44} = C_{55} = C_{66} = C_{11}/2 \) and \( C_{12} = C_{13} = C_{23} = C_{11}/2 \), consistent with BCC symmetry. Thus this appendix explicitly shows that for hexagonal and BCC symmetry the term \(|\mathcal{L}_k, A_j|^2\) correctly incorporates linear elasticity.

**Appendix C: Derivation of FPFC-MS and MPFC-MS models using the variational approach**

### C.1. FPFC-MS model

In this appendix, the FPFC-MS and MPFC-MS models will be derived using the variational approach based on free energy functionals obtained by applying the single-mode approximation to the PFC functional, Equation (1). For simplicity, we take the two-dimensional hexagonal structure as an example. In this approximation, the atomic density \( \psi \) is approximated by the sum of the average density field \( \tilde{\psi} \) and the periodic functions \( \psi_j = A_j \exp(\mathbf{k}_j \cdot \mathbf{x}) \):

\[
\psi \simeq \tilde{\psi} + \sum_{j=1}^3 \left( \hat{\psi}_j^* + \hat{\psi}_j \right), \tag{30}
\]

where \( \hat{\psi}_j^* \) is a complex conjugate of \( \hat{\psi}_j \).

Substituting Equation (30) into the free energy functional \( \mathcal{F} \) in Equation (1) gives the approximate functional \( \mathcal{F}_F \):

\[
\mathcal{F}_F \simeq \int d\mathbf{r} \left\{ \frac{a_0}{2} \sum_{j=1}^3 \left[ \hat{\psi}_j (\nabla^2 + 1)^2 \tilde{\psi} + \hat{\psi}_j^* (\nabla^2 + 1)^2 \tilde{\psi} \right] + \frac{a_0}{2} \tilde{\psi} (\nabla^2 + 1)^2 \tilde{\psi} + \frac{a_2}{2} \tilde{\psi}^2 \right. \\

\left. + \frac{a_3}{3} \tilde{\psi}^3 + \frac{a_4}{4} \tilde{\psi}^4 + (a_2 + 2a_3 \tilde{\psi} + 3a_4 \tilde{\psi}^3) \sum_{j=1}^3 |\hat{\psi}_j|^2 \right. \\

\left. + 2(a_3 + 3a_4 \tilde{\psi}) \left( \sum_{j=1}^3 \hat{\psi}_j^* + 3 \hat{\psi}_j \right) + 6a_4 \sum_{j=1}^3 \sum_{j'\neq j}^3 |\hat{\psi}_j|^2 |\hat{\psi}_j'|^2 + \frac{3a_4}{2} \sum_{j=1}^3 |\hat{\psi}_j|^4 \right\}. \tag{31}
\]

In the above approximation, the contributions of the periodic terms to the integration, such as those containing \( \hat{\psi}_1, \hat{\psi}_2^* \) and \( \hat{\psi}_1 \hat{\psi}_2 \), are ignored because these contributions would be negligible after integrating over the unit cell. For this approximation to be valid, it has been implicitly assumed that the amplitudes \( A_j \) vary on length scales much larger than the atomic spacing. This assumption also applies to all of the following derivations.

The evolution equations for the average density \( \tilde{\psi} \) and the periodic functions \( \hat{\psi}_j \) can be obtained by applying the variational approach for conserved properties, \( \partial_t \psi = \nabla^2 \delta \mathcal{F}_F / \delta \tilde{\psi} \) and \( \partial_t \hat{\psi}_j = \nabla^2 \delta \mathcal{F}_F / \delta \hat{\psi}_j^* \):

\[
\frac{\partial \tilde{\psi}}{\partial t} = \nabla^2 \left[ a_0 (\nabla^2 + 1)^2 \tilde{\psi} + (a_2 \tilde{\psi} + a_3 \tilde{\psi}^2 + a_4 \tilde{\psi}^3) + 2(a_3 + 3a_4 \tilde{\psi}) \sum_{j=1}^3 |\hat{\psi}_j|^2 \right. \\

\left. + 6a_4 \left( \sum_{j=1}^3 \hat{\psi}_j^* + \sum_{j=1}^3 \hat{\psi}_j \right) \right], \tag{32a}
\]
Applying the variational approaches for the conserved field MS model:

Using Equation (34), the free energy functional respectively. Writing Equations (32a) and (32b) in terms of the amplitude $A_j$ gives the FPFC-MS model:

In particular, we assume that the average density varies slowly in space compared to the atomic density. Now we apply the separation of these length scales.

C.2. MPFC-MS model

In the above derivation, no assumptions for the length scales of the varying average density and of the atomic density have been made. Now we apply the separation of these length scales. In particular, we assume that the average density varies slowly in space compared to the atomic density. Introducing the small parameter $\varepsilon$ and slowly varying argument $X = \varepsilon x$ and rewriting Equation (30) give:

Using Equation (34), the free energy functional $\mathcal{F}$ can be approximated to the zeroth-order in $\varepsilon$ as:

As in the FPFC-MS model, the average density $\bar{\psi}$ should be considered as a conserved order parameter due to mass conservation. However, since $\bar{\psi}_j$ contains only the information of the atomic configuration, we regard $\psi_j$ as a nonconserved order parameter. Nevertheless, the mass conservation of $\bar{\psi}_j$ is automatically satisfied due to their functional form $\sim e^{k_j x}$. Applying the variational approaches for the conserved field $\bar{\psi}$ and the nonconserved field

and

\[
\frac{\partial \hat{\psi}_j}{\partial t} = \nabla^2 \left[ a_0 (\nabla^2 + 1)^2 \hat{\psi}_j + \left( a_2 + 2a_3 \bar{\psi} + 3a_4 \bar{\psi}^2 \right) \hat{\psi}_j \right]
\]

\[
+ 2(a_3 + 3a_4 \bar{\psi}) \sum_{i=1}^{3} \left( \hat{\psi}_i^* + 3a_4 \hat{\psi}_j \left( 2 \sum_{i=1}^{3} \hat{\psi}_i - |\hat{\psi}_j|^2 \right) \right] .
\]
\[
\dot{\psi}_j (\partial_j \psi = \nabla^2 \delta F_M / \delta \psi \text{ and } \partial_j \dot{\psi}_j = -\delta F_M / \delta \psi^*) \text{ and rewriting } \dot{\psi}_j \text{ in terms of the amplitudes } A_j \text{ give the MPFC-MS model:}
\]
\[
\frac{\partial \hat{\psi}}{\partial t} = \nabla^2 \left[ (a_0 + a_2) \hat{\psi} + a_3 \hat{\psi}^2 + a_4 \hat{\psi}^3 + 2(a_3 + 3a_4 \bar{\psi}) \sum_{i=1}^3 |A_i|^2 + 6a_4 \left( \prod_{i=1}^3 A_i + \prod_{i=1}^3 A_i^* \right) \right], \tag{36a}
\]
and
\[
\frac{\partial A_i}{\partial t} = -\left\{ a_0 \omega_k^2 A_j + (a_2 + 2a_3 \bar{\psi} + 3a_4 \bar{\psi}^2) A_j + 2(a_3 + 3a_4 \bar{\psi}) \prod_{i \neq j}^3 A_i^* \right.
\]
\[
+ 3a_4 A_j \left( 2 \sum_{i=1}^3 |A_i|^2 - |A_j|^2 \right) \} \tag{36b}.
\]