

Quantitative nondiagonal phase field modeling of pearlite growth involving multi-diffusion paths

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Despite extensive research on pearlite formation, the rate-controlling mechanisms of pearlite growth remain under debate. Phase field modeling has become a key tool for investigating such transformations; however, in solid-state systems where diffusion occurs both within individual phases and along their interfaces, the commonly assumed local-equilibrium boundary conditions are rarely satisfied, leading to artificial interface effects in conventional diagonal formulations. Here, we present a thermodynamically consistent nondiagonal three-phase field model formulated within the grand-potential framework to investigate pearlite growth. By introducing an Onsager-symmetric cross-coupling term between conserved and nonconserved order parameters, the model inherently recovers the correct equilibrium boundary conditions regardless of the active diffusion pathways, including bulk diffusion and interfacial diffusion. We systematically analyze four diffusion scenarios: (i) diffusion in austenite; (ii) diffusion in austenite, ferrite, and cementite; (iii) diffusion in austenite and ferrite; and (iv) diffusion in austenite combined with interfacial diffusion along austenite/ferrite and austenite/cementite boundaries. The model's quantitative performance is benchmarked against available analytical solutions for each case. Overall, the proposed framework provides a robust and thermodynamically sound approach for elucidating how different diffusion pathways control pearlite growth kinetics.

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I. INTRODUCTION

Pearlite is a potential structure for industrial application due to its excellent mechanical performances [1,2]. The pearlitic structure consists of alternating lamellae of ferrite (α) and cementite (θ) phases which generally form cooperatively via the decomposition of austenite (γ) phase during the eutectoid transformation [3,4]. Since cementite is rich in carbon, while the carbon concentration in ferrite is much lower, the carbon redistribution plays a crucial role in the pearlite transformation. Numerous investigations have been conducted in the past decades regarding the mechanisms of pearlite growth. The pioneering theoretic work of Zener and Hillert explains

the growth kinetics of the pearlite transformation [5,6]. For specific undercooling and lamellar spacing, the Zener-Hillert (Z-H) model can be expressed as

$$V_{\gamma}^{\text{ZH}} = \frac{2D_{\gamma}}{\eta^{\alpha}\eta^{\theta}} \left(\frac{c_e^{\gamma\alpha} - c_e^{\gamma\theta}}{c^{\theta} - c^{\alpha}} \right) \frac{1}{S_i} \left(1 - \frac{S_c}{S_i} \right), \quad (1)$$

where V_{γ}^{ZH} is the growth velocity of pearlite, D_{γ} is the diffusivity of carbon in austenite, η^{α} and η^{θ} are the fractions of ferrite and cementite phases, respectively. $c_e^{\gamma\alpha}$, $c_e^{\gamma\theta}$, c^{θ} , and c^{α} are the extrapolated equilibrium concentrations (see Fig. 2). S_i is the specified lamellar spacing, while S_c is the lamellar spacing for which curvature and undercooling exactly compensate and the growth velocity of pearlite is zero. The Z-H model predicts the stable growth velocities of pearlite during isothermal transformation with the consideration of carbon transport through the γ phase (volume diffusion) under the assumption of flat γ/α and γ/θ interfaces. Based on the same assumptions, Jackson and Hunt [7] have adopted the Z-H model and found a steady-state solution that gives an analytical expression of the average undercooling of the growth front

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(J-H theory), depending on the growth velocity V_γ^{JH} and the lamellar spacing

$$V_\gamma^{\text{JH}} = \frac{K_1^{\text{JH}}}{S_i} \left(\Delta T - \frac{K_2^{\text{JH}}}{S_i} \right), \quad (2)$$

where K_1^{JH} and K_2^{JH} are constants that depend on the thermodynamic properties of the mother and growing phases. Although many attempts have been carried out to reevaluate the carbon diffusivity of γ phase, the predictions of Z-H model still exhibit a large discrepancy to the experimental observations [8,9].

In order to explain the faster growth velocities of pearlite observed in the experiments, diffusion in the growing phases (bulk diffusion) is proposed as a possible diffusion path for carbon transport. Nakajima *et al.* [10] suggested that the growth rate of pearlite is enhanced by the diffusion of carbon through the α phase in view of the fact that the diffusivity in α is approximately two orders of magnitude larger than that in γ . After turning on the bulk diffusion, the growth velocities of pearlite are four times larger than the predictions of the Z-H theory but still lower than the experimental observations. Afterward, Ankit *et al.* [11] investigated the situation in which the diffusion in α and θ phases occur. They obtained a linear relation to predicting the pearlite growth velocity, which is given by

$$V_{\gamma+\alpha+\theta}^{\text{Ankit}} = V_\gamma (1 + t_\alpha \mu_\alpha \eta_\alpha + t_\theta \mu_\theta \eta_\theta), \quad (3)$$

where V_γ is calculated by Eqs. (1) or (2). μ_α and μ_θ are the diffusivity ratios of α and θ phases to γ phase, i.e., $\mu_\alpha = D_\alpha/D_\gamma$ and $\mu_\theta = D_\theta/D_\gamma$, with D_α and D_θ being the diffusivities in α and θ phases. t_α and t_θ are constants, which are given by $t_\alpha = m^{\gamma/\alpha}/m^\alpha$ and $t_\theta = m^{\gamma/\theta}/m^\theta$, with $m^{\gamma/\alpha}$ ($m^{\gamma/\theta}$) being the slope of the coexistence line when α (θ) phase is in equilibrium with γ phase and m^α (m^θ) being the slope of the coexistence line of the γ phase in equilibrium with α (θ) phase. However, an unsatisfactory deviation between the experimental data and the enlarged pearlite growth velocity when considering the bulk diffusion remains.

Interface diffusion is another possible path to elucidate the pearlite growth [12]. To avoid confusion, we clarify that interface diffusion in the present work means diffusion along γ/α and γ/θ interfaces. An early interface boundary controlled growth prediction for pearlite was obtained by substituting $D_{\text{int}}\delta_{\text{int}}/S_i$ for D_γ in the Z-H model [13,14], where D_{int} is the interface diffusivity and δ_{int} is the interface thickness. Hillert [15,16] considered the balance of the surface tensions at the growth front and derived the growth rate of pearlite only involving interface diffusion,

$$V_{\text{int}}^{\text{Hillert}} = \left(\frac{12KD_{\text{int}}\delta_{\text{int}}}{S_i} \right) \frac{1}{\eta^\alpha \eta^\theta} \left(\frac{c_e^{\gamma\alpha} - c_e^{\gamma\theta}}{c^\theta - c^\alpha} \right) \frac{1}{S_i} \left(1 - \frac{S_c}{S_i} \right), \quad (4)$$

where K is the boundary segregation coefficient. Pandit and Bhadeshia [17] presented a growth model of pearlite by accounting for the diffusion fluxes through the γ phase and the interface region simultaneously without the consideration of mechanical equilibrium at the phase junctions, which

leads to

$$V_{\gamma+\text{int}}^{\text{Pandit}} = \left(\frac{12D_{\text{int}}\delta_{\text{int}}}{S_i} + 2D_\gamma \right) \frac{1}{\eta^\alpha \eta^\theta} \left(\frac{c_e^{\gamma\alpha} - c_e^{\gamma\theta}}{c^\theta - c^\alpha} \right) \frac{1}{S_i} \left(1 - \frac{S_c}{S_i} \right). \quad (5)$$

Yan *et al.* [18] investigated pearlite growth by considering interface formation, bulk diffusion, interface diffusion, and the solute drag effect. This model predicts the growth rate, lamellar spacing, and the partitioning of elements between ferrite and cementite of pearlite. Consequently, combining the various diffusion paths is a promising way to reveal the main carbon transport mechanisms during pearlite transformation. In most research, the integration of the volume and interface diffusion has attracted plenty of attention. However, Verhoeven [19] pointed out that even though the concentration difference in the α phase is much smaller than in the austenite, the much larger diffusivity in α phase elicits a larger diffusion flux into the α phase than γ phase by a ratio of 3.2. Therefore, to our knowledge, the influence of the bulk diffusion on the pearlite growth is still doubtful and the explanation of the pearlite growth mechanisms is not entirely consistent.

In the past decades, due to the significant progress in numerical simulations of microstructure evolution, the phase field (PF) method has become a powerful tool to obtain novel insights into the diffusion controlled moving boundary problems, including dendritic growth [20,21,31], peritectic reaction [22,23], eutectic solidification [24,25,33], as well as the eutectoid transformations [10,11,26–30]. The characteristic feature of this diffuse interface approach is that tracking of the interface position is explicitly avoided. To distinguish different phases, the PF variable ϕ is introduced, which exhibits spatial variations inside the interface on the scale of the interface thickness W . The interface thickness is a purely numerical parameter and is artificially enhanced to be orders of magnitude larger than the atomistic scale, in order to be able to simulate appreciable length scales with less computational effort. This enhancement of the interface thickness gives rise to undesired anomalous interface effects. Karma and Rappel [31] proposed the thin-interface limit to eliminate the abnormal interface effects by linking the classical PF model to the free boundary problem for equal diffusivities in the solid and liquid phase (symmetric model) during the pure substance solidification. This pioneering work made it possible to remove all the abnormal interface effects and achieve local equilibrium boundary conditions by choosing the appropriate PF kinetic parameters (quantitative model). Subsequently, this quantitative PF model was extended to binary alloys solidification with negligible diffusivity (one-sided model) in the growing phase [32]. The equilibrium boundary conditions are achieved by introducing a correction term called antitrapping current that is proportional to the interface velocity. For three-phase transformations, such as the eutectic solidification, Folch and Plapp [33] developed a quantitative PF model with the antitrapping current in the one-sided case by proposing a fifth-order interpolation function to ensure the disappearance of spurious third phases in the two-phase interface. However, for general phase transformations, such as the pearlite growth,

where the diffusivities in the growing phases are comparable to the one in the parent phase (two-sided model), the discontinuities of chemical potentials at the interface are proportional to the interface thickness and incapable to be fully eliminated by the velocity dependent antitrapping current [34]. Additionally, the tangential interface diffusion significantly contributes the solute transport, in particular along a solid/solid interface, and consequently modifies the interface dissipation when the interface thickness is artificially enhanced. Moreover, most of the existing PF simulations for pearlite transformation mainly focus on the morphology features of pearlite. A systematical investigation of the influence of the different diffusion paths on the pearlite growth by using the PF method is still missing, which is likely due to a lack of quantitative PF models when different diffusion paths are taken into account.

As mentioned above, the reproduction of the desired boundary conditions with various activated diffusion paths is a prerequisite for quantitative PF modeling of pearlite growth. Recently, a crossing coupling term was introduced between the conserved and nonconserved fields in the PF equations according to the Onsager's relation, named nondiagonal phase field (NPF) model [35–39]. Compared with the classical PF model, where the time derivatives of the phase field ϕ and concentration field C are $-\delta G/\delta\phi = \tau\dot{\phi}$ and $-\nabla\delta G/\delta C = \mathbf{J}/D$, these relations become $-\delta G/\delta\phi = \tau\dot{\phi} + (MW\nabla\phi) \cdot \mathbf{J}$ and $-\nabla\delta G/\delta C = \mathbf{J}/D + (MW\nabla\phi)\dot{\phi}$ in the NPF model. The cross-coupling term $MW\nabla\phi$, that has to be the same in both equations according to Onsager symmetry, exists only at the interface region and vanishes in the bulk phase. The NPF model's advantages are that (i) the antitrapping current naturally appears in a thermodynamically consistent way; (ii) it provides a new degree of freedom to reproduce the equilibrium boundary conditions in the symmetric, one-sided and two-sided cases; (iii) it offers the ability to flexibly achieve the desired boundary conditions, such as the reproduction of surface diffusion. The capabilities of the NPF model were examined, and the necessity of the kinetic cross-coupling term was demonstrated in simulations of dendritic solidification of pure substances exhibiting diffusional contrast between the solid and liquid phases [40]. Furthermore, for multiphase transformations, the binary NPF model was extended to the nondiagonal three-phase field model for eutectic and eutectoid transformations [41]. In both one- and two-sided cases, the necessity of using the cross-coupling term was verified for quantitative simulations. However, the developed NPF method was derived from a free energy functional, which prohibits an accurate thermodynamic description of the pearlite transformation in the binary Fe-C alloy.

For the quantitative reproduction of isothermal pearlite growth in Fe-C binary alloys, we develop a grand-potential-based nondiagonal three-phase field model following the approach of Plapp [42] and determine the NPF parameters by performing a thin-interface-limit analysis. Subsequently, we simulate four benchmark cases involving (i) diffusion in the γ phase; (ii) diffusion in the γ , α , and θ phases; (iii) diffusion in the γ and α phases; and (iv) diffusion in the γ phase and along the γ/α and γ/θ interfaces. The purpose of the present paper is to establish and validate the quantitative NPF framework by comparison with the corresponding analytical descriptions for these diffusion scenarios. The identification of the dominant

diffusion paths in real Fe-C pearlite, together with quantitative comparisons against experimentally measured growth velocities, constitutes a separate application of the model and will be addressed in a subsequent study.

II. GRAND-POTENTIAL-BASED NONDIAGONAL PHASE FIELD MODEL

A. Grand-potential functional

The free energy based nondiagonal phase field model developed in Ref. [41] is restricted to simple symmetric phase diagrams. In the spirit of Ref. [42] we formulate a grand-potential-based NPF model to investigate the pearlite transformation ($\gamma \rightarrow \alpha + \theta$). To distinguish different phase state of the system α , θ , and γ , the phase field vector is notated as $\vec{\phi} = (\phi_\gamma, \phi_\alpha, \phi_\theta)$. Then, the Fe-C binary alloy is a mixture of two pure substances iron and carbon, where iron is considered as the solvent. The number density of carbon atoms is defined as ρ , which is related to the local concentration of carbon atoms, and is given by $\rho = c/V_A$, where c is the dimensionless concentration of carbon atoms, i.e., $c = (C - C_E)/(C_\theta - C_\alpha)$ with C_E , C_θ , and C_α being the equilibrium concentrations of the parent phase (γ) and the growing phases (α and θ) at the eutectoid temperature T_E . V_A is the dimensionless atomic volume in the crystal, that we consider independent of the carbon content within the unit cell, i.e., whether considering the presence of interstitial carbon atoms or considering the Fe_3C cementite. Hence, the number density is a conserved field, which obeys $\dot{\rho} = -\nabla \cdot \mathbf{J}$, with $\mathbf{J}$ being the mass flux. Under the assumption of constant atomic volume, composition changes in a binary alloy are governed by the difference between the chemical potentials of the two components. The relevant thermodynamic driving force is therefore the diffusion chemical potential $\mu \equiv \mu_B - \mu_A$, rather than the individual chemical potentials μ_A and μ_B separately [42]. For simplicity, this diffusion chemical potential is referred to as the chemical potential in the following. The grand potential, $\Omega[\vec{\phi}, \mu]$, of the pearlite system is defined as the Legendre transformation of the free Gibbs energy and ρ takes the form $\rho = -\delta\Omega[\vec{\phi}, \mu]/\delta\mu$. In analogy to the free energy functional, the grand-potential functional is given by

$$\begin{aligned} \Omega[\vec{\phi}, \mu] &= \int_V [\omega_{\text{grad}}(\nabla\phi) + \omega_{\text{tw}}(\vec{\phi}) + \omega_{\text{chem}}(\vec{\phi}, \mu)] dV \\ &= \int_V \left[\frac{HW^2}{2} \sum_{i=\alpha, \theta, \gamma} (\nabla\phi_i)^2 + H \sum_{i=\alpha, \theta, \gamma} \phi_i^2 (1 - \phi_i)^2 \right. \\ &\quad \left. + \sum_{i=\alpha, \theta, \gamma} g_i(\vec{\phi}) \omega_i(\mu) \right] dV, \end{aligned} \quad (6)$$

where W is the interface thickness and H denotes the height of the triple well potential. Here, all three isotropic interface energies between γ , α , and θ are identical, which is reasonable for the pearlite transformation, yielding a constant capillary length $d_0 = \psi HW$, where $\psi = W \int_{-\infty}^{\infty} [\phi'_{\text{eq}}(x)]^2 dx = \sqrt{2}/6$. $\omega_i(\mu)$ indicates the grand-potential density of phase i and can be written as $\omega_i(\mu) = f_i - \mu\rho$, where f_i is the Gibbs free energy density of phase i . In this work, parabolic free

energy functions are utilized for constructing f_i , i.e., $f_i = \epsilon_i(c - c_i)^2/2 + f_i^0$, with c_i and f_i^0 being respectively the equilibrium dimensionless concentration for phase i at the eutectoid temperature and the temperature-dependent minimum of the parabolic free energy function, that vanishes at T_E by convention. The parabolic coefficients ϵ_i are the curvature of the parabolae with units of energy density. They prescribe the boundaries of the two-phase regions. For the pearlite transformation, we have $\epsilon_\theta \gg \epsilon_\alpha \gg \epsilon_\gamma$. Subsequently, the dimensionless chemical potential is expressed as $\mu = \partial f_i / \partial \rho = v_A \epsilon_i (c - c_i)$ and the dimensionless concentration has the form $c = \mu / (v_A \epsilon_i) + c_i$. Then, $\omega_i(\mu)$ can be obtained, i.e., $\omega_i(\mu) = -\mu^2 / (2v_A^2 \epsilon_i) - \mu c_i / v_A + f_i^0$. Furthermore, $g_i(\phi)$ in the last term of the grand-potential functional is defined as a fifth-order interpolation function to avoid the appearance of spurious third-phase contributions in a two-phase interface [33], which can be written as $g_i(\vec{\phi}) = \frac{\phi_i^2}{4} \{15(1 - \phi_i)[1 + \phi_i - (\phi_k - \phi_j)^2] + \phi_i(9\phi_i^2 - 5)\}$ ($i \neq j \neq k$). For a binary i/j interface for which $\phi_i = \phi$, $\phi_j = 1 - \phi$ and $\phi_k = 0$, this polynomial reduces to $p(\phi) = \phi^3(10 - 15\phi + 6\phi^2)$.

B. Evolution equations

The three phase fields obey, at any time and any position, a normalization rule $\sum_{i=\gamma,\alpha,\theta} \phi_i = 1$, requiring $\sum_{i=\gamma,\alpha,\theta} \dot{\phi}_i = 0$. In order to impose such a constraint to the PF model, a Lagrange multiplier λ is introduced into the evolution equation. For example, the constrained phase-field evolution can be written schematically as $\tau \dot{\phi}_i = -\delta \Omega / \delta \phi_i + \lambda$, ($i = \alpha, \gamma, \theta$). The phase-field constraint $\sum_i \dot{\phi}_i = 0$ gives $\lambda = 1/3 \sum_i \delta \Omega / \delta \phi_i$. The same projection can be applied to the phase-field gradients. Then, we use the operators

$$\left. \frac{\delta \Omega}{\delta \phi_i} \right|_{\sum \phi_n=1} = (2/3) \frac{\delta \Omega}{\delta \phi_i} - (1/3) \frac{\delta \Omega}{\delta \phi_j} - (1/3) \frac{\delta \Omega}{\delta \phi_k} \quad (7)$$

$$\nabla \phi_i|_{\sum \phi_n=1} = (2/3) \nabla \phi_i - (1/3) \nabla \phi_j - (1/3) \nabla \phi_k, \quad (8)$$

where i, j, k are different and ϕ_i, ϕ_j , and ϕ_k are considered independent on the right-hand side. Then, in accordance with Onsager symmetry, we write down the grand-potential-based nondiagonal PF equations in the following variational form,

$$-\left. \frac{\delta \Omega}{\delta \phi_i} \right|_{\sum \phi_n=1} = \tau \dot{\phi}_i + (MW \nabla \phi_i|_{\sum \phi_n=1}) \cdot \mathbf{J}, \quad (9)$$

$$-\nabla \mu = \sum_{i=\gamma,\alpha,\theta} (MW \nabla \phi_i|_{\sum \phi_n=1}) \dot{\phi}_i + \frac{\mathbf{J}}{D}, \quad (10)$$

where $\tau = \tau(\vec{\phi})$, $M = M(\vec{\phi})$, and $D = D(\vec{\phi})$ are respectively the relaxation time, the coefficient parametrizing the cross-coupling term, and the diffusivity. $\tau(\vec{\phi})$ and $M(\vec{\phi})$ are given by

$$\tau(\vec{\phi}) = \frac{\tau_{\gamma\alpha}\phi_\gamma\phi_\alpha + \tau_{\gamma\theta}\phi_\gamma\phi_\theta + \tau_{\alpha\theta}\phi_\alpha\phi_\theta}{\phi_\gamma\phi_\alpha + \phi_\gamma\phi_\theta + \phi_\alpha\phi_\theta}, \quad (11)$$

$$M(\vec{\phi}) = \frac{M_{\gamma\alpha}\phi_\gamma\phi_\alpha + M_{\gamma\theta}\phi_\gamma\phi_\theta + M_{\alpha\theta}\phi_\alpha\phi_\theta}{\phi_\gamma\phi_\alpha + \phi_\gamma\phi_\theta + \phi_\alpha\phi_\theta}, \quad (12)$$

giving for a binary i/j interface $\tau(\phi_i = \phi, \phi_j = 1 - \phi, \phi_k = 0) = \tau_{ij}$ and the same for M . For the diffusion coefficient $D(\phi)$, one shall not only reproduce constant diffusivities in various bulks but also provide the flexibility to tune interface

diffusion. Thus, different activated diffusion paths demand different diffusivity functions.

With the intention of eliminating all the abnormal interface effects, a thermodynamically consistent nondiagonal phase field model is established in the spirit of Onsager's relation via introducing a kinetic cross-coupling term between the phase field ϕ and number density field ρ . The aforementioned coefficients of the nondiagonal PF model can be considered as elements of a 4×4 matrix constituting Eqs. (9) and (10). To ensure a positive dissipation (second law of thermodynamics), the determinant of the Onsager's matrix has to be positive in the entire simulation domain, which demands

$$\text{Det}_{\text{PF}} = \frac{\tau}{D} - (MW)^2 \sum_{i=\gamma,\alpha,\theta} (\nabla \phi_i|_{\sum \phi_n=1})^2 > 0. \quad (13)$$

In the present simulations, this positivity condition is taken into account during the calibration of the NPF parameters. The relaxation time τ and the cross-coupling coefficient M are not selected independently; they are determined from the thin-interface analysis so that the desired sharp-interface boundary conditions are reproduced while the Onsager matrix remains positive definite. In Cases 2–4, where diffusivity contrasts and cross-coupling terms are active, only parameter sets satisfying Eq. (13) throughout the relevant diffuse-interface profiles are retained, ensuring positive entropy production for all simulations reported below.

C. Link with the free boundary description: Thin-interface limit

In the macroscopic description of a moving two-phase i/j interface with negligible interface thickness (sharp interface), mass conservation associated with solute transport should of course be obeyed, and it possibly includes the effect of interface diffusion. On the other hand, local equilibrium is assumed at the interface when the driving force for its motion is low enough, meaning that the equilibrium concentrations on both sides of the i/j interface are generalized by the Gibbs-Thomson condition. However, the unrealistic interface thickness W chosen in the PF method brings undesired alterations of the boundary conditions that are reproduced by the PF model, such as a chemical potential discontinuity at the interface. We thus perform the thin-interface limit on an assumed binary interface, i.e., i/j interface, that provides the relation between the kinetic parameters in the PF model and the sharp interface boundary conditions that the latter reproduces. This allows the former to be chosen in order to achieve the desired sharp interface boundary conditions, and especially local equilibrium.

At a moving i/j interface with negligible interface diffusion, such as a typical solid/liquid interface, the conservation laws for atoms A and B are expressed in terms of J_B as [46]

$$D_i \nabla \rho|_i \cdot \mathbf{n} + V \rho_{ij}^0 = D_j \nabla \rho|_j \cdot \mathbf{n} + V \rho_{ji}^0 = J_B, \quad (14)$$

where D_i and D_j are the diffusivities in phase i and phase j , respectively. $\nabla \rho|_i$ ($\nabla \rho|_j$) indicates the concentration gradient at the interface on the side of phase i (phase j). $\mathbf{n}$ is the unit normal vector to the interface. V is the normal velocity of the interface and, according to our assumption of constant atomic volume, equals the total flux of atoms through the interface. If J_B is the flux of B atoms through the interface, the flux of

A atoms is then $J_A = V - J_B$. ρ_{ij}^0 and ρ_{ji}^0 are the equilibrium number densities in phase i and j respectively, that are linked through V_A to the equilibrium concentrations obtained via the common tangent construction (see Sec. II A).

While Eq. (14) yields the well-known Stefan condition

$$V(\rho_{ij}^0 - \rho_{ji}^0) = -(D_i \nabla \rho|_i - D_j \nabla \rho|_j) \cdot \mathbf{n}, \quad (15)$$

the latter becomes

$$V(\rho_{ij}^0 - \rho_{ji}^0) = -(D_i \nabla \rho|_i - D_j \nabla \rho|_j) \cdot \mathbf{n} - D_{\text{int,SI}}^{ij} \nabla_S^2 \mu_{\text{int}} \quad (16)$$

when the interface diffusion is non-negligible at the i/j solid/solid interface. Here ∇_S^2 is the surface Laplacian and $D_{\text{int,SI}}^{ij}$ is the interface diffusion coefficient in the present sharp interface method. μ_{int} is the chemical potential at the interface, which is here assumed to be equal on both sides of the interface (the case $\bar{B} = 0, \bar{C} = 0$, see below). In the PF model, the ϕ -dependent diffusivity varies smoothly across the interface and Almgren has shown [47] that Eq. (16) is reproduced with

$$D_{\text{int,PF}}^{ij} = (D_{\text{int,SI}}^{ij} - D_i/2 - D_j/2) \delta_{\text{int}}/W \\ = \int_{-\infty}^{\infty} \left[D(\phi) - \frac{1}{2} D_i - \frac{1}{2} D_j \right] \frac{dx}{W}, \quad (17)$$

that represents the total excess diffusivity at the solid-solid interface, whose width is δ_{int} and normal direction is x .

Concerning the kinetic boundary conditions, one defines them in accordance with the Onsager's principle [45]. We consider a flat interface across which a grand potential and a chemical potential jumps, $\delta\Omega_{\text{SI}}$ and $\delta\mu_{\text{SI}}$, are linearly related to the aforementioned fluxes V and J_B . Additionally, V is the flux conjugated to $\delta\Omega_{\text{SI}}$ while J_B is the flux conjugated to $\delta\mu_{\text{SI}}$. Then, the kinetic boundary conditions are expressed as

$$\delta\Omega_{\text{SI}} = \bar{A}V + \bar{B}J_B + d_0\kappa, \quad (18)$$

$$\delta\mu_{\text{SI}} = \bar{B}V + \bar{C}J_B, \quad (19)$$

where d_0 and κ are the capillary length and the interface curvature, respectively. $\bar{A}$, $\bar{B}$, $\bar{C}$ are the three independent kinetic coefficients of the 2×2 Onsager matrix. For a positive energy dissipation at the interface

$$\mathcal{R}_{\text{SI}}^{\text{int}} = (\delta\Omega_{\text{SI}}V + \delta\mu_{\text{SI}}J_B) = \bar{A}V^2/2 + \bar{C}J_B^2/2 + \bar{B}VJ_B, \quad (20)$$

the Onsager matrix must be positive definite, i.e., $\bar{A} > 0, \bar{C} > 0$ and the determinant $\bar{A}\bar{C} - \bar{B}^2 > 0$.

Thereafter, for the same binary i/j interface, the sharp interface dissipation $\mathcal{R}_{\text{SI}}^{\text{int}}$ is identified with the interface dissipation within the NPF model. This yields expressions for $\bar{A}$, $\bar{B}$, and $\bar{C}$ in terms of the equilibrium profiles

$$\phi_{\text{eq}}(x) = \frac{1}{2} \left\{ 1 - \tanh \left[\frac{x}{\sqrt{2}W} \right] \right\}$$

and

$$\rho_{\text{eq}}(x) = (\rho_{ij}^0 + \rho_{ji}^0)/2 + (\rho_{ij}^0 - \rho_{ji}^0)\{2p[\phi_{\text{eq}}(x)] - 1\}/2.$$

Here, the equilibrium profile $\rho_{\text{eq}}(x)$ is obtained for an equilibrium i/j interface, i.e., $\omega_i = \omega_j$, following the same construction as Eq. (42) in Ref. [42].

Then, for the three-phase model, they read [41]

$$\bar{A} = 2 \int_{-\infty}^{\infty} \tau [\phi'_{\text{eq}}(x)]^2 dx - 4 \int_{-\infty}^{\infty} \{ MW [\phi'_{\text{eq}}(x)]^2 \rho_{\text{eq}}(x) \} dx \\ + \int_{-\infty}^{\infty} \left\{ \frac{\rho_{\text{eq}}^2(x)}{D} - \frac{(\rho_{ij}^0)^2}{2D_i} - \frac{(\rho_{ji}^0)^2}{2D_j} \right\} dx, \quad (21)$$

$$\bar{B} = 2 \int_{-\infty}^{\infty} \{ MW [\phi'_{\text{eq}}(x)]^2 \} dx \\ - \int_{-\infty}^{\infty} \left\{ \frac{\rho_{\text{eq}}(x)}{D} - \frac{\rho_{ij}^0}{2D_i} - \frac{\rho_{ji}^0}{2D_j} \right\} dx, \quad (22)$$

$$\bar{C} = \int_{-\infty}^{\infty} \left\{ \frac{1}{D} - \frac{1}{2D_i} - \frac{1}{2D_j} \right\} dx. \quad (23)$$

The dissipation at the interface vanishes when the latter is at local equilibrium. This means that, for arbitrary V and J_B , each kinetic coefficient must vanish, i.e., $\bar{A} = 0, \bar{B} = 0$, and $\bar{C} = 0$. This provides constraints that allow us to determine the appropriate functions $\tau(\phi)$, $M(\phi)$, and $D(\phi)$.

Before going into the details of this procedure, let us make a short remark. When interface dissipation vanishes, we have $\delta\Omega_{\text{SI}} = d_0\kappa$ and $\delta\mu_{\text{SI}} = 0$. For weakly out-of-equilibrium conditions, we can linearize the expressions for $\delta\Omega_{\text{SI}}$ and $\delta\mu_{\text{SI}}$, i.e.,

$$\delta\Omega_{\text{SI}} = f_j''(c_{ji}^0)c_{ji}^0(c_{ji} - c_{ji}^0) - f_i''(c_{ij}^0)c_{ij}^0(c_{ij} - c_{ij}^0), \quad (24)$$

$$\delta\mu_{\text{SI}} = f_i''(c_{ij}^0)(c_{ij} - c_{ij}^0) - f_j''(c_{ji}^0)(c_{ji} - c_{ji}^0), \quad (25)$$

where c_{ij}^0 and c_{ji}^0 are equilibrium concentrations (see Sec. II A), which can be obtained from the phase diagram at specific temperature. $f_i''(c_{ij}^0)$ and $f_j''(c_{ji}^0)$ are the second derivatives of the bulk free energy of phase i and j , i.e., $f_i''(c_{ij}^0) = \epsilon_i$ and $f_j''(c_{ji}^0) = \epsilon_j$ here. The Gibbs-Thomson relation thus becomes $c_{ij} - c_{ij}^0 = (c_{ji} - c_{ji}^0)\epsilon_j/\epsilon_i = -\tilde{d}\kappa$, where $\tilde{d} = d_0/[(c_{ij}^0 - c_{ji}^0)\epsilon_i] = d_0/[V_a(\rho_{ij}^0 - \rho_{ji}^0)\epsilon_i]$.

D. Determination of the NPF model parameters

In the present work, we make a number of simplifying assumptions: (i) Local equilibrium at the γ/α , γ/θ , and α/θ binary interfaces is achieved during isothermal pearlite transformation; (ii) Diffusivity is equal along the γ/α and γ/θ interfaces, whereas the diffusion along an α/θ interface is omitted; (iii) Solute drag effects are not considered. In addition, elastic and plastic effects are not included in the present model. This simplification is consistent with the analytical benchmark models used here and allows us to isolate the role of bulk and interfacial diffusion pathways. Elastic stresses associated with coherent interfaces and plastic relaxation near incoherent interfaces or dislocation structures may modify the local driving force and interface mobility, and their coupling to the present quantitative NPF formulation is left for future work. The simulations are also performed in two dimensions. For the steady-state lamellar growth considered here, the third dimension is assumed to be translationally invariant, as in classical Zener-Hillert and Jackson-Hunt type descriptions. A fully three-dimensional treatment may introduce additional effects associated with interface curvature, lamellar

stability, and diffusion along a second tangential direction of the interface.

Moreover, for the diffusion coefficient $D(\vec{\phi})$, one shall not only reproduce the constant diffusivities in various bulk phases but also provide the flexibility to tune the interface diffusion in Eq. (17). Turning on or off the diffusion in the bulk phases or along interfaces may lead to different expressions for $D(\vec{\phi})$. As mentioned in the Introduction, we investigate in this article four different cases with various activated diffusion mechanisms, and in the following we therefore provide the corresponding choices for the coefficients τ_{ij} , M_{ij} in Eqs. (11) and (12) and for $D(\vec{\phi})$.

1. Case 1: Diffusion in γ phase

First of all, we are interested in the “volume diffusion” case where diffusion only appears in the bulk mother phase γ . The diffusion coefficient in the growing phases α and θ is negligible, i.e., $D_\gamma \gg D_\alpha, D_\theta$, and we set $D_\alpha = D_\theta = 0$. In the NPF method, we therefore set $\tau_{\alpha\theta} = M_{\alpha\theta} = 0$. The diffusivity function D_{c1} for Case 1 is one-sided

$$D(\vec{\phi}) = D_{c1}(\vec{\phi}) = D_\gamma(1 - \phi_\alpha - \phi_\theta), \quad (26)$$

and it vanishes for $\phi_\alpha = 1$ or $\phi_\theta = 1$. For an interface, oriented perpendicularly to the x axis, between γ and one growing phase j ($j = \alpha, \theta$), the interface diffusion is automatically eliminated, i.e., $\int_{-\infty}^{\infty} [D_{c1}(\vec{\phi}) - D_\gamma/2] dx = 0$.

According to the mass conservation in Eq. (14), the suppression of the diffusivity in the growing phase j yields a relation between V and J_B , i.e., $J_B = V\rho_{j\gamma}^0$. The boundary conditions in Eqs. (18) and (19) then become $\delta\Omega_{SI} = (\bar{\mathcal{A}} + \rho_{j\gamma}^0 \bar{\mathcal{B}})V + d_0\kappa$ and $\delta\mu_{SI} = (\bar{\mathcal{B}} + \rho_{j\gamma}^0 \bar{\mathcal{C}})V$. Since the two fluxes V and J_B are not linearly independent, $\delta\Omega_{SI}$ and $\delta\mu_{SI}$ are related to a single flux, and the Onsager symmetry becomes irrelevant. According to Eqs. (21), (22), and (23), we have

$$\bar{\mathcal{A}} + \rho_{j\gamma}^0 \bar{\mathcal{B}} = \frac{2\psi\tau_{j\gamma}}{W} - \frac{\xi_{c1}(\rho_{j\gamma}^0 - \rho_{j\gamma}^0)^2 W}{4D_\gamma}, \quad (27)$$

$$\bar{\mathcal{B}} + \rho_{j\gamma}^0 \bar{\mathcal{C}} = 2\psi M_{j\gamma} - \frac{\mathcal{K}_{c1}(\rho_{j\gamma}^0 - \rho_{j\gamma}^0)W}{2D_\gamma}, \quad (28)$$

where

$$\psi = W \int_{-\infty}^{\infty} [\partial_x \phi_{eq}(x)]^2 dx = \sqrt{2}/6, \quad (29)$$

$$\xi_{c1} = \frac{1}{W} \int_{-\infty}^{\infty} \frac{1 - (2p[\phi_{eq}(x)] - 1)^2}{1 - \phi_{eq}(x)} dx \approx 3.42778, \quad (30)$$

$$\mathcal{K}_{c1} = \frac{1}{W} \int_{-\infty}^{\infty} \frac{\phi_{eq}(x) + 1 - 2p[\phi_{eq}(x)]}{1 - \phi_{eq}(x)} dx \approx 2.12132. \quad (31)$$

Local equilibrium requires $\bar{\mathcal{A}} + \rho_{j\gamma}^0 \bar{\mathcal{B}} = 0$ and $\bar{\mathcal{B}} + \rho_{j\gamma}^0 \bar{\mathcal{C}} = 0$. Therefore, we set

$$\tau_{j\gamma} = \frac{(\rho_{j\gamma}^0 - \rho_{j\gamma}^0)^2 W^2 \xi_{c1}}{8\psi D_\gamma}, \quad (32)$$

$$M_{j\gamma} = \frac{(\rho_{j\gamma}^0 - \rho_{j\gamma}^0)W \mathcal{K}_{c1}}{4\psi D_\gamma}. \quad (33)$$

Here, the antitrapping current naturally appears in the evolution equation for the conserved field. However, an extra term also appears for the nonconserved field due to the force-flux relations that are obeying Onsager symmetry in the NPF model. Therefore, the NPF simulations show a slight discrepancy to the PF model in which only the antitrapping current is present [41].

2. Case 2: Diffusion in γ , α , and θ phases

In Case 2, we consider the case where the diffusion in bulk γ , α and θ phases is turned on. The corresponding diffusivity coefficient D_{c2} is defined by its inverse in order to automatically obtain $\bar{\mathcal{C}} = 0$ (see below):

$$\frac{1}{D(\vec{\phi})} = \frac{1}{D_{c2}(\vec{\phi})} = \frac{1}{3} \sum_{i=\alpha,\theta,\gamma} \left\{ \frac{1}{D_i} + h_i(\vec{\phi}) \times \left(\frac{1}{D_i} - \frac{1}{2D_j} - \frac{1}{2D_k} \right) \right\}, \quad (34)$$

where

$$h_i(\vec{\phi}) = (2\phi_i - 1)(1 + 4a_{c2}^{ij}\phi_j + 4a_{c2}^{ik}\phi_k), \quad (35)$$

for $(i, j, k) = (\alpha, \theta, \gamma)$ and permutations. The diffusivities in the α , θ , and γ bulk phases are rigorously reproduced, i.e., $D_{c2}(\phi_i = 1, \phi_j = 0, \phi_k = 0) = D_i$. Three additional parameters a_{c2}^{ij} , a_{c2}^{ik} , and a_{c2}^{jk} are introduced to tune the interface diffusion coefficient in Eq. (17).

For a binary i/j interface for which $(\phi_i = \phi, \phi_j = 1 - \phi, \phi_k = 0)$, the diffusivity coefficient in Eq. (34) becomes

$$\frac{1}{D_{c2}(\phi_i = \phi, \phi_j = 1 - \phi, \phi_k = 0)} = \frac{1}{D_{c2}^{i/j}(\phi)} = \frac{1}{2D_i} + \frac{1}{2D_j} + h_{i/j}(\phi) \left(\frac{1}{2D_i} - \frac{1}{2D_j} \right), \quad (36)$$

where

$$h_{i/j}(\phi) = (2\phi - 1)[1 + 4a_{ij}\phi(1 - \phi)], \quad (37)$$

with $h_{i/j}(\phi) = -h_{i/j}(1 - \phi)$ and $h_{i/j}(\phi = 1) = 1$. Returning to the calculations of kinetic boundary conditions in Eqs. (21)–(23), we obtain the following expressions for the kinetic coefficients:

$$\bar{\mathcal{A}} = \frac{2\psi\tau_{ij}}{W} - \frac{\zeta(\rho_{ij}^0 - \rho_{ji}^0)^2}{4} \left(\frac{W}{2D_i} + \frac{W}{2D_j} \right), \quad (38)$$

$$\bar{\mathcal{B}} = 2\psi M_{ij} - \frac{\varrho_{c2}^{ij}(\rho_{ji}^0 - \rho_{ij}^0)}{2} \left(\frac{W}{2D_i} - \frac{W}{2D_j} \right), \quad (39)$$

$$\bar{\mathcal{C}} = 0, \quad (40)$$

where

$$\zeta = \frac{1}{W} \int_{-\infty}^{\infty} dx \{1 - [2p(\phi_{eq}) - 1]^2\} \approx 1.40748, \quad (41)$$

$$\varrho_{c2}^{ij} = \frac{1}{W} \int_{-\infty}^{\infty} dx \{1 - [2p(\phi_{eq}) - 1]h_{i/j}(\phi_{eq})\}. \quad (42)$$

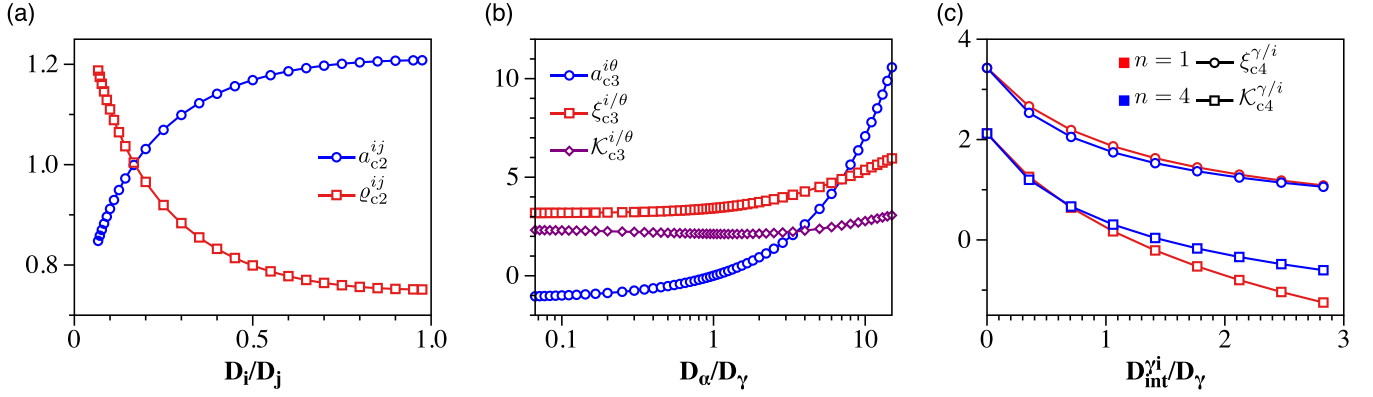


FIG. 1. (a) Demonstration of the parameters a_{c2}^{ij} and ϱ_{c2}^{ij} as a function of diffusivity ratio D_i/D_j without interface diffusion when the diffusion in γ , α , and θ phases are turned on. (b) Demonstration of the parameters of $a_{c3}^{i\theta}$, $\xi_{c3}^{i/\theta}$, and $\mathcal{K}_{c3}^{i/\theta}$ as a function of D_α/D_γ with vanished surface diffusion when diffusion in γ and θ are considered. (c) Demonstration of the parameters of $\xi_{c4}^{\gamma/i}$ and $\mathcal{K}_{c4}^{\gamma/i}$ as a function of surface diffusion with different parameter n in Eq. (50) when diffusion in γ phase and along the γ/α and γ/θ interfaces are considered. (d) Demonstration of the parameters of a_{ij} and $\varrho_{\gamma+\alpha+\theta+\text{surf}}^{ij}$ as a function of diffusivity ratio D_i/D_j with finite surface diffusion, such as $D_{\text{surf}}/(D_i + D_j) = 0.5$.

$\bar{C}$ vanishes automatically due to the oddness of the function $h_{i/j}(\phi)$. Local equilibrium boundary conditions at i/j interface demand also $\bar{A} = 0$ and $\bar{B} = 0$, that is provided by

$$\tau_{ij} = \frac{\zeta W^2 (\rho_{ij}^0 - \rho_{ji}^0)^2}{8\psi} \left(\frac{1}{2D_i} + \frac{1}{2D_j} \right), \quad (43)$$

$$M_{ij} = \frac{\varrho_{c2}^{ij} (\rho_{ji}^0 - \rho_{ij}^0) W}{4\psi} \left(\frac{1}{2D_i} - \frac{1}{2D_j} \right). \quad (44)$$

Let us first note that the expression for τ_{ij} is much simpler than in Ref. [41] owing to a more appropriate general definition of the function $\tau(\phi)$ (compare Eq. (42) in Ref. [41] with Eq. (11) above). Second, it is clear that ϱ_{c2}^{ij} depends on a_{c2}^{ij} . The determination of a_{c2}^{ij} involves the diffusivity contrast D_i/D_j and the interface diffusion coefficient D_{int}^{ij} in Eq. (17). In Fig. 1(a), we present, as a function of diffusivity ratio D_i/D_j , the value of a_{c2}^{ij} providing $D_{\text{int}}^{ij} = 0$, and the corresponding value for ϱ_{ij} . Here we focus on $0 < D_i/D_j < 1$ because a_{c2}^{ij} for D_i/D_j is equal to a_{c2}^{ij} for D_j/D_i . It is important to notice that, under the condition of vanishing interface diffusion, the positiveness of the interface dissipation, i.e., here the inequality $2\tau_{ij}/D_{c2}^{i/j}(\phi_{\text{eq}}) - 4M_{ij}^2 W^2 \phi_{\text{eq}}^2 > 0$, sets a upper bound and a lower bound, $1/17 < D_i/D_j < 17$, for the diffusivity ratio [39].

Moreover, one should note that the two-sided case presented just above reduces to the so-called symmetric case when $D_i = D_j$. Then, according to Eq. (44), $M_{ij} = 0$ and the cross-coupling term vanishes in the NPF equations (9) and (10).

3. Case 3: Diffusion in γ and α phases

For the case where the diffusivity vanishes in the bulk θ phase ($D_\theta = 0$), the diffusivity coefficient is defined as

$$\begin{aligned} D(\vec{\phi}) &= D_{c3}(\vec{\phi}) \\ &= \frac{2D_\gamma D_\alpha (1 - \phi_\theta) (1 + a_{c3}^{\gamma\theta} \phi_\theta \phi_\gamma) (1 + a_{c3}^{\alpha\theta} \phi_\theta \phi_\alpha)}{D_\gamma + D_\alpha + (\phi_\gamma - \phi_\alpha) (1 + 4a_{c3}^{\gamma\alpha} \phi_\gamma \phi_\alpha) (D_\alpha - D_\gamma)}. \end{aligned} \quad (45)$$

The parameters $a_{c3}^{\gamma\theta}$, $a_{c3}^{\alpha\theta}$, and $a_{c3}^{\gamma\alpha}$ allow to suppress interface diffusion at the θ/γ , θ/α , and γ/α interfaces, respectively.

The two-sided γ/α interface. For the binary γ/α interface with $\phi_\gamma = \phi = 1 - \phi_\alpha$, we recover the diffusivity in Eq. (36) as expected. Thus, local equilibrium at the γ/α interface is provided by $\tau_{\gamma\alpha}$ and $M_{\gamma\alpha}$ given by Eqs. (43) and (44), respectively. Furthermore, the absence of interface diffusion at the γ/α interface is ensured by the same procedure relating $a_{c3}^{\gamma\alpha}$ to D_γ/D_α and $\varrho_{c3}^{\gamma\alpha}$ as in Case 2.

The one-sided i/θ interface. For a binary i/θ interface ($i = \alpha, \gamma$) for which diffusivity vanishes in the bulk θ phase, we obtain the one-sided diffusivity

$$\begin{aligned} D_{c3}(\phi_i = \phi, \phi_j = 0, \phi_\theta = 1 - \phi) \\ = D_{c3}^{i/\theta}(\phi) = \frac{2D_\gamma D_\alpha \phi [1 + a_{c3}^{i\theta} \phi (1 - \phi)]}{D_\gamma + D_\alpha + \phi (D_j - D_i)}, \end{aligned}$$

that yields $D_{c3}^{i/\theta} = D_i$ when $\phi = 1$ and $D_{c3}^{i/\theta} = 0$ when $\phi = 0$ as expected, but in which D_j ($j = \alpha$ if $i = \gamma$ and vice versa) plays a role.

In analogy to Eqs. (32) and (33), local equilibrium requires

$$\tau_{i\theta} = \frac{(\rho_{i\theta}^0 - \rho_{\theta i}^0)^2 W^2 \xi_{c3}^{i/\theta}}{8\psi D_i}, \quad (46)$$

$$M_{i\theta} = \frac{(\rho_{i\theta}^0 - \rho_{\theta i}^0) W \mathcal{K}_{c3}^{i/\theta}}{4\psi D_i}, \quad (47)$$

with

$$\xi_{c3}^{i/\theta} = \frac{1}{W} \int_{-\infty}^{\infty} \frac{1 - (2p[\phi_{\text{eq}}(x)] - 1)^2}{D_{c3}^{i/\theta}(\phi)/D_i} dx, \quad (48)$$

$$\mathcal{K}_{c3}^{i/\theta} = \frac{1}{W} \int_{-\infty}^{\infty} \left\{ \frac{2 - 2p[\phi_{\text{eq}}(x)]}{D_{c3}^{i/\theta}(\phi)/D_i} - 1 \right\} dx, \quad (49)$$

where $\xi_{c3}^{i/\theta}$ and $\mathcal{K}_{c3}^{i/\theta}$ depend on $a_{c3}^{i\theta}$ and on the diffusivity ratio D_γ/D_α .

For $D_{c3}^{i/\theta}$, interface diffusion is not automatically eliminated as in Case 1, and $a_{c3}^{i\theta}$ has to be chosen such that $D_{\text{int}}^{i\theta} =$

$W^{-1} \int_{-\infty}^{\infty} dx \{D_{c3}^{i/\theta} [\phi_{\text{eq}}(x)] - D_i/2\} = 0$, thereby determining $\xi_{c3}^{i/\theta}$ and $\mathcal{K}_{c3}^{i/\theta}$. In Fig. 1(b), we present the parameter $a_{c3}^{i/\theta}$ for which $D_{\text{int}}^{i/\theta} = 0$ together with the corresponding $\xi_{c3}^{i/\theta}$ and $\mathcal{K}_{c3}^{i/\theta}$, in the range $1/15 < D_i/D_j < 15$. As compared to Case 2 in Fig. 1(a) for which the interval $0 < D_i/D_j < 1$ suffices [see the discussion after Eq. (44)], the value of $a_{c3}^{i/\theta}$ that leads to $D_{\text{int}}^{i/\theta} = 0$ is different for D_i/D_j and D_j/D_i , and thus in Fig. 1(b), D_i/D_j takes also values larger than 1.

4. Case 4: Diffusion in γ and along the γ/α and γ/θ interfaces

Until now, we have presented the procedure for the determination of the NPF parameters in Cases 1–3 for which the interface diffusion is eliminated. However, the influence of interface diffusion is typically not negligible during the pearlite transformation. Therefore now, we explain how to tune the interface diffusion in the NPF model without altering the equilibrium boundary conditions.

In Case 4, we consider a one-sided diffusion in γ phase only and the diffusion along the γ/α and γ/θ interfaces. Extra terms that contribute to the interface diffusion coefficient and only exist at the interface region are added into Eq. (26). The diffusivity is formulated as

$$D(\vec{\phi}) = D_{c4}(\vec{\phi}) = D_\gamma(1 - \phi_\alpha - \phi_\theta) + k_{\text{int}}[D_{\text{int}}^{\gamma\alpha}\phi_\gamma^n\phi_\alpha^n + D_{\text{int}}^{\gamma\theta}\phi_\gamma^n\phi_\theta^n], \quad (50)$$

where $k_{\text{int}}^{-1} = W^{-1} \int_{-\infty}^{\infty} dx \phi_{\text{eq}}(x)^n [1 - \phi_{\text{eq}}(x)]^n$. The exponent n is physically meaningless but controls the width of the interface diffusion zone. A larger exponent n yields drastic reduction of this width. The influence of the parameter n on the growth velocity of pearlite is investigated in the following section.

For a binary γ/i interface ($i = \alpha, \theta$), the diffusivity becomes

$$D_{c4}(\phi_i = \phi, \phi_j = 0, \phi_\gamma = 1 - \phi) = D_{c4}^{\gamma/i}(\phi) = D_\gamma(1 - \phi) + k_{\text{int}}D_{\text{int}}^{\gamma/i}\phi^n(1 - \phi)^n,$$

with the interface diffusion coefficient $D_{\text{int}}^{\gamma/i} = W^{-1} \int_{-\infty}^{\infty} dx \{D_{c4}^{\gamma/i}[\phi_{\text{eq}}(x)] - D_\gamma/2\}$ being explicitly incorporated into the diffusivity function. Repeating the procedures in Sec. IID 1, the reproduction of equilibrium boundary conditions demands

$$\tau_{\gamma i} = \frac{(\rho_{\gamma i}^0 - \rho_{i\gamma}^0)^2 W^2 \xi_{c4}^{\gamma/i}}{8\psi D_\gamma}, \quad (51)$$

$$M_{\gamma i} = \frac{(\rho_{\gamma i}^0 - \rho_{i\gamma}^0) W \mathcal{K}_{c4}^{\gamma/i}}{4\psi D_\gamma}, \quad (52)$$

where

$$\xi_{c4}^{\gamma/i} = \frac{1}{W} \int_{-\infty}^{\infty} \frac{1 - (2p[\phi_{\text{eq}}(x)] - 1)^2}{D_{c4}^{\gamma/i}(\phi)/D_\gamma} dx, \quad (53)$$

$$\mathcal{K}_{c4}^{\gamma/i} = \frac{1}{W} \int_{-\infty}^{\infty} \left\{ \frac{2 - 2p[\phi_{\text{eq}}(x)]}{D_{c4}^{\gamma/i}(\phi)/D_\gamma} - 1 \right\} dx. \quad (54)$$

In Fig. 1(c), we present the parameters $\xi_{c4}^{\gamma/i}$ and $\mathcal{K}_{c4}^{\gamma/i}$ as a function of $D_{\text{int}}^{\gamma/i}/D_\gamma$ and for an exponent $n = 1$ and $n = 4$.

The parameter $\xi_{c4}^{\gamma/i}$ is not sensitive to n , whereas the parameter $\mathcal{K}_{c4}^{\gamma/i}$ increases with n .

III. SIMULATION PARAMETERS

In this study, the isothermal pearlite growth is investigated by means of the presented grand-potential-based nondiagonal PF model, with two-dimensional simulations at the eutectoid composition, Fe-3.44at.%C. To reproduce the thermodynamic properties, a linearized Fe-C phase diagram is reconstructed, as illustrated in Fig. 2(a). According to this phase diagram, the γ phase decomposes into α and θ phases when the temperature T is below the eutectoid temperature T_E . The undercooling $\Delta T = T_E - T$ in the simulations is chosen from 10 to 50 K. The dimensionless equilibrium concentration of phase i in contact with phase j at a specific temperature is defined as c_{ij}^0 , with $i, j = \gamma, \alpha, \theta$ and $i \neq j$. In Fig. 2(b), we also show the dimensionless free energy densities with parabolic formulations, i.e., $f_i = \epsilon_i(c - c_i)^2/2 + f_i^0$, as mentioned in Sec. II A. Here, the γ phase is defined as the reference phase. We then have $c_\gamma = 0$, $f_\gamma^0 = 0$, and $\epsilon_\gamma = 1$. While $\epsilon_\alpha/\epsilon_\gamma$ is assumed to be 50.213 in line with Ref. [10], the fact that the θ phase is stoichiometric requires that ϵ_θ is large enough. We use $\epsilon_\theta/\epsilon_\gamma = 1000$. The corresponding average capillary length is $\tilde{d}/W = [1/(c_{\gamma\alpha}^0 - c_{\alpha\gamma}^0) + 1/(c_{\gamma\theta}^0 - c_{\theta\gamma}^0)]d_0/[2\epsilon_\gamma W]$ with $d_0/W = 0.21696(\Delta T/10 \text{ K})$ to obtain a constant lamellar spacing of pearlite at the largest growth velocity, i.e., $S_e = 96W$, during the isothermal transformation to ensure a sufficient scale separation between the lamellar spacing and the interface thickness [41]. The temperature dependence of the equilibrium concentrations c_{ij}^0 determines, through the common tangent construction, the curvature ϵ_i of the free energy curves. At the beginning of each simulation, a pair of ferrite (α) and cementite (θ) lamellae is embedded in the parent austenite (γ) phase in a rectangular simulation box of total size $n_x \times n_y$, with grid spacing $\Delta x = \Delta y = 0.4W$. The initial widths of the α and θ lamellae are chosen according to their equilibrium phase fractions, whereas the remaining simulation domain is occupied by the γ phase with the initial austenite composition. During the simulation, the α and θ lamellae grow into the surrounding γ phase and eventually reach a steady-state growth regime. The length n_y is chosen sufficiently large so that diffusion perpendicular to the growth front is not hindered. During the simulations, different diffusion paths are activated from Case 1 to Case 4 as shown in Fig. 2(c), with interface diffusion activated only in Case 4. The physical and thermodynamic properties of pearlite growth are summarized in Table I. The interface width δ_{int} in the sharp interface description of interface diffusion is chosen as 0.5 nm, which is a commonly used estimation in metals [43]. To save computational efforts, periodic boundary conditions are prescribed at the boundaries parallel to the growth direction, whereas no-flux boundary conditions are used at the boundaries perpendicular to the growth direction. Additionally, a moving-frame method and GPU acceleration are applied in the simulations [44]. In the moving-frame procedure, the average growth-front position, defined by the $\phi_\gamma = 0.5$ contour, is checked every 100 time steps. If the front advances by more than five grid spacings ($5\Delta x$), all phase-field and

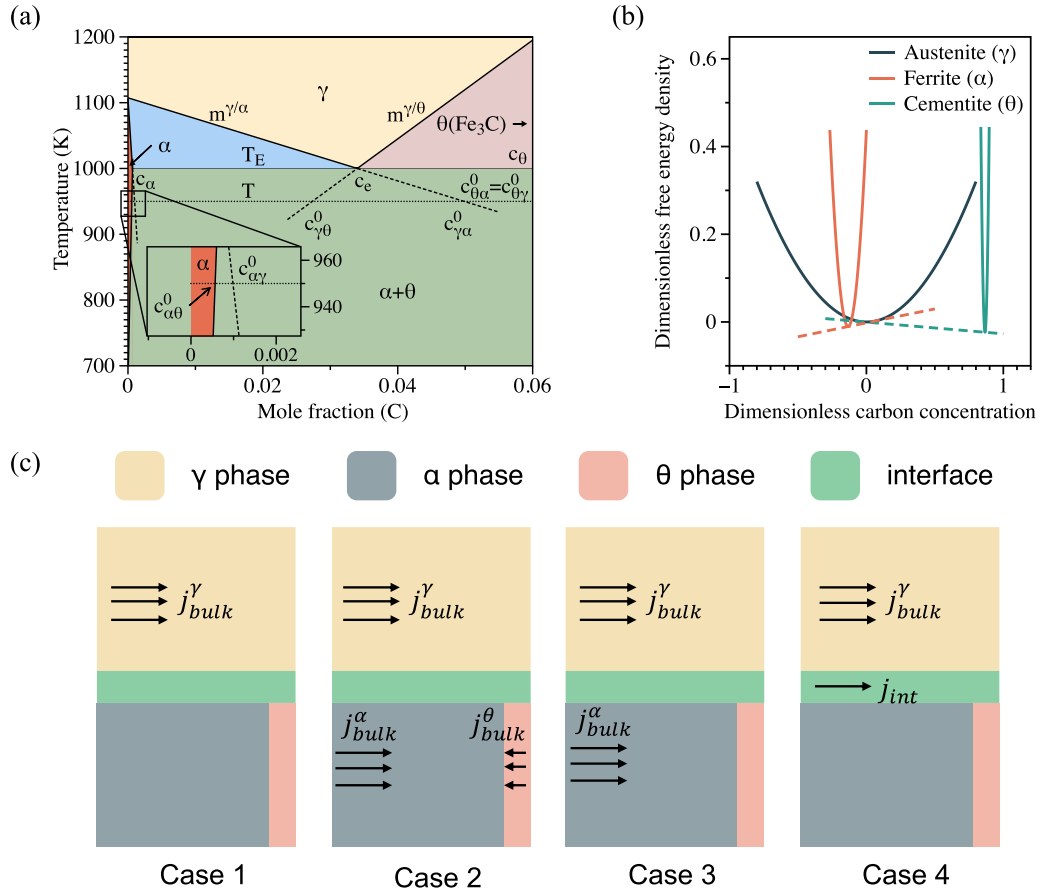


FIG. 2. (a) Linearized phase diagram of pearlite in Fe-C binary alloy. (b) The dimensionless free energy densities of γ , α , and θ phases with parabolic formulations at 950 K, in which the dashed lines depict the common tangent constructions. (c) Demonstration of simulation scenarios with the consideration of (i) diffusion in γ phase; (ii) diffusion in γ , α , and θ phases; (iii) diffusion in γ and α phases; (iv) diffusion in γ phase and along γ/α , γ/θ interfaces.

concentration fields are shifted backward by the corresponding number of grid points. The newly created region ahead of the growth front is filled with the parent γ phase and the initial austenite composition. The pearlite growth velocity is

evaluated every 10 000 time steps from the temporal evolution of the total front displacement, which is the sum of the instantaneous front position within the computational domain and the cumulative displacement introduced by the moving-frame

TABLE I. The simulation parameters used in the present work for pearlite transformation.

Symbol	Description	Value
W	Dimensionless interface width in the PF simulations	1
d_0	Capillary length	1.41×10^{-9} m
V_A	Dimensionless average atomic volume	1
R	Gas constant	8.314 J/(mol K)
T_E	Temperature at eutectoid point	1000 K [10]
C_E	Eutectoid composition	0.034 mol [10]
C_α	Composition of α phase at the eutectoid point	0.000 677 mol [10]
C_θ	Composition of θ phase at the eutectoid point	0.25 mol [10]
η_α	Volume fraction of α phase	0.1337
η_θ	Volume fraction of θ phase	0.8663
$m^{\gamma/\alpha}$	Slope of γ/α transformation line	-3155 K/mol [10]
$m^{\gamma/\theta}$	Slope of γ/θ transformation line	7503 K/mol [10]
D_γ^{exp}	Diffusion coefficient in γ phase	$1.5 \times 10^{-5} \exp[-142\,100(\text{J/mol})/(RT)]$ m ² /s [10]
D_α^{exp}	Diffusion coefficient in α phase	$2.2 \times 10^{-4} \exp[-122\,500(\text{J/mol})/(RT)]$ m ² /s [10]
$D_{\text{int}}^{\text{exp}}$	Diffusion coefficient in interface region	$8.51 \times 10^{-5} \exp[-96\,851(\text{J/mol})/(RT)]$ m ² /s [17]
δ_{int}	Interface width	5×10^{-10} m [43]

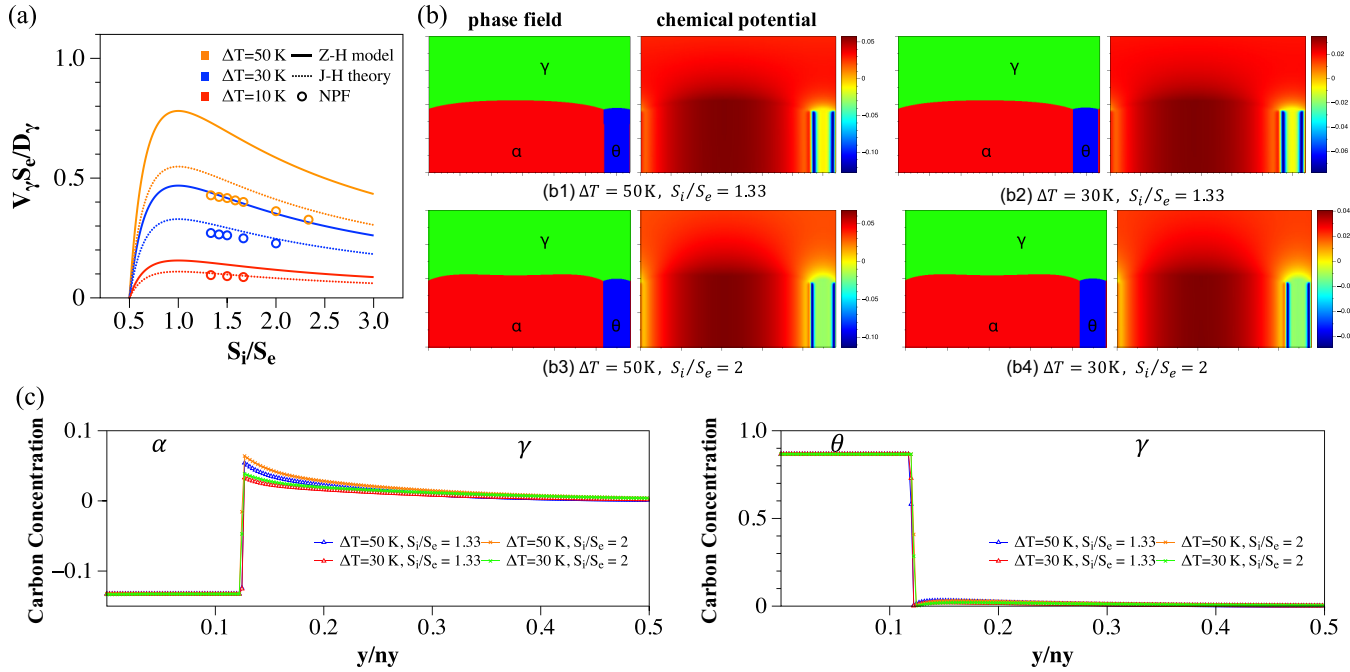


FIG. 3. (a) Comparison of the nondiagonal PF (NPF) results and the analytical predictions (Z-H model and J-H theory) for $\Delta T = 10, 30$, and 50 K in Case 1. The NPF results agree well with the J-H theory, but have larger discrepancy with the calculations of the Z-H model. In (a), the colored squares in the legend identify the different temperatures, whereas the plotted circular symbols and lines represent the PF simulation data and analytical predictions, respectively. (b) The steady-state microstructure of the pearlite in the vicinity of the growth front presented by phase field (left) and chemical potential field (right) for (b1) $\Delta T = 50$ K, $S_i/S_e = 1.33$, (b2) $\Delta T = 30$ K, $S_i/S_e = 1.33$, (b3) $\Delta T = 50$ K, $S_i/S_e = 2$ and (b4) $\Delta T = 30$ K, $S_i/S_e = 2$. (c) Demonstration of the dimensionless concentration profiles of carbon along the lines that intersect the center of γ/α and γ/θ interfaces in the y direction in the case of (b1)–(b4).

procedure. After the initial transient, this total front displacement varies linearly with time, and the steady-state growth velocity is obtained from the slope of the linear regime.

Moreover, the two-dimensional simulations are performed in the present work, hence, assuming translation invariance in the third direction. Under this assumption, the diffusion problem reduces to a two-dimensional one, which is consistent with classical analytical descriptions such as the Zener-Hillert and Jackson-Hunt type approaches. Therefore, the two-dimensional simulations are expected to capture the essential diffusion mechanisms governing pearlite growth. Nevertheless, a fully three-dimensional treatment may introduce additional effects associated with interface curvature, lamellar stability, and diffusion along a second tangential direction of the interface. The quantitative influence of these effects on the competition between bulk diffusion and interface diffusion remains an open question and deserves further investigation.

IV. SIMULATION RESULTS AND DISCUSSION

In order to investigate the growth mechanisms of pearlite, we simulate the isothermal pearlitic transformation of the Fe-C alloy with the assumptions proposed in Sec. II D by using the present nondiagonal PF model in 2-D domains for (i) diffusion in the γ phase only; (ii) diffusion in γ , α , and θ phases; (iii) diffusion in γ and α phases; and (iv) diffusion in the γ phase and along the γ/α and γ/θ interfaces.

A. Case 1: Diffusion in γ phase

First, we investigate the kinetics of pearlite growth for various undercooling and lamellar spacings when the diffusion in the growing phases and along the interfaces are inhibited. In Fig. 3, the points, solid and dashed lines indicate the dimensionless growth velocities of the pearlite growth at steady state obtained via the nondiagonal PF simulations, predictions of Z-H model in Eq. (1) and J-H theory in Eq. (2), respectively. We find that the nondiagonal PF results exhibit a similar relation between the growth velocity and lamellar spacing as Z-H model and J-H theory predicts. With an increase in undercooling, i.e., from 10 to 50 K, the deviation between the nondiagonal PF results and the predictions of Z-H model increases from 18% to 39%. However, the discrepancy between PF results and the predictions of J-H theory is significantly decreased. As elucidated in Ref. [41], the deviation is caused by the simplifications of the theoretical models rather than the present nondiagonal PF model. Overall, the quantitative capabilities of nondiagonal PF model for pearlite transformation in the one-sided case are demonstrated. Figure 3(b) portrays the phase profiles and the corresponding chemical potentials of the pearlite at the steady state near the interesting growth front region for (b1) $\Delta T = 50$ K, $S_i/S_e = 1.33$, (b2) $\Delta T = 30$ K, $S_i/S_e = 1.33$, (b3) $\Delta T = 50$ K, $S_i/S_e = 2$ and (b4) $\Delta T = 30$ K, $S_i/S_e = 2$. As expected, the α/θ interfaces are parallel to the growth direction and a decrement in the interface curvatures at the center of the α and θ phases is observed when the lamellar spacing increases.

However, for a given lamellar spacing, the interface curvature shows no noticeable change when the undercooling varies [see Figs. 3(b1) vs 3(b2) and 3(b3) vs 3(b4)]. Figure 3(c) plots the rescaled dimensionless composition profiles of carbon along the lines that intersect the center of γ/α and γ/θ interfaces in the y direction in the case of Figs. 3(b1)–3(b4). The increase in undercooling and lamellar spacing results in higher carbon concentration in the γ phase near the γ/α interface.

B. Case 2: Diffusion in γ , α , and θ phases

In this section, we investigate the pearlite growth in the two-sided case where the diffusion in γ , α , and θ are all activated. The diffusivity ratios of the growing phases to the mother phase are prescribed as $\mu_\alpha = D_\alpha/D_\gamma$ and $\mu_\theta = D_\theta/D_\gamma$. With respect to the predictions of growth velocity of pearlite in the two-sided case, Ankit *et al.* [11] formulates the growth rate of pearlite ($V_{\gamma+\alpha+\theta}$) as a linear function of μ_α and μ_θ , through adding the diffusion fluxes in the growing phases into the mass conservation equations. With the assumption $\mu_\alpha = \mu_\theta = \mu$, this linear relation in Eq. (3) can be rewritten as

$$\tilde{V}_{\gamma+\alpha+\theta} = \frac{V_{\gamma+\alpha+\theta} - V_\gamma}{\mu V_\gamma} = t_\alpha \eta_\alpha + t_\theta \eta_\theta = \text{const.} \quad (55)$$

Aiming at exploring the dependence of growth velocities obtained by the NPF simulations on the choice of the interface width, we perform a convergence study with respect to the interface width at 970 and 950 K. In these simulations, the ratio S_i/S_e remains constant, i.e., $S_i/S_e = 1.33$. Figure 4(a) presents the rescaled dimensionless growth velocity $\tilde{V}_{\gamma+\alpha+\theta} S_e/D_\gamma$ as a function of S_e/W for $\mu_\alpha = \mu_\theta = 5$. With an increase in S_e/W , the dimensionless growth velocity converges. For the interface width used in the present work (see the filled symbol), i.e., $S_e/W = 96$, the errors are smaller than 0.5%, which is quite satisfactory. This confirms that the NPF results do not depend on the interface width.

Figure 4(b) illustrates the dimensionless growth velocity $\tilde{V}_{\gamma+\alpha+\theta}$ as a function of diffusivity ratios. The black dashed lines indicate the analytical model as defined in Eq. (55). The blue, green, and red solid lines correspond to the NPF results with the lamellar spacing ratio S_i/S_e of 1.33, 1.67, and 2, respectively. We clearly observe a good agreement from the comparison between the NPF results and the predictions of analytical model. The deviation of the NPF results from the analytical predictions is due to the assumption that the interface is flat in the Ankit's model. It is noteworthy that for smaller lamellar spacings, such as $S_i/S_e = 1.33$, the NPF results exhibit a slight decrease with increasing diffusivity ratio before eventually converging to a constant value. As the lamellar spacing increases, this tendency diminishes, resulting in an almost constant dimensionless growth velocity, especially for $S_i/S_e = 2$.

To clarify the influence of the diffusion in the growing phases under Case 2 conditions, we define j_i as the product $D_i \Delta c_i$ where Δc_i is the concentration difference in phase i given by the phase diagram. Thus, j_i is a measure of the diffusion flux in phase i . From the linear phase diagram in Fig. 2(a), the concentration difference ratios

of the growing phases to the mother phase $\Delta c_\alpha/\Delta c_\gamma$ and $\Delta c_\theta/\Delta c_\gamma$ are temperature-independent and are respectively 0.0199 and 0.001. For the maximum diffusivity ratios used in Case 2, i.e., $\mu_\alpha = \mu_\theta = 15$, the diffusion flux ratios of the growing phases to the mother phase, j_α/j_γ and j_θ/j_γ , are respectively 0.2985 and 0.015. The stability constraint in our NPF model prohibits simulations at more realistic diffusivity ratios such as $\mu_\alpha = 175$ for $\Delta T = 50$ K and $\mu_\alpha = 167$ for $\Delta T = 30$ K provided in Table I. We may however use Ankit's model to predict the velocity ratio $V_{\gamma+\alpha+\theta}/V_\gamma$, and we find 4.04 for $\Delta T = 50$ K and 3.90 for $\Delta T = 30$ K. This indicates a very significant contribution of the diffusion fluxes in the growing phases to the growth velocity.

Moreover, the blue, green, and red dashed lines present the classical PF (CPF) results in which the coefficient of the cross-coupling term vanishes, i.e., $M(\vec{\phi}) = 0$, for different lamellar spacing. The larger discrepancy between CPF results and analytical predictions indicates the importance of the cross-coupling term.

The steady-state pearlitic microstructure at $\Delta T = 50$ K in the vicinity of the growth front region are portrayed by the phase field and the chemical potential field in Fig. 4(c) for (c1) $S_i/S_e = 1.33$, $\mu_\alpha = \mu_\theta = 1$; (c2) $S_i/S_e = 1.33$, $\mu_\alpha = \mu_\theta = 10$; (c3) $S_i/S_e = 2$, $\mu_\alpha = \mu_\theta = 1$; (c4) $S_i/S_e = 2$, $\mu_\alpha = \mu_\theta = 10$. Since the diffusion in α and θ phases are turned on, a chemical potential gradient appears in the growing phases. In contrast to Case 1 (diffusion only in γ phase), the solute transport that occurs from high chemical potential region (γ/α interface) to low chemical potential region (γ/θ interface) in the growing phases facilitates the transformation of θ towards α phase. On the one hand, this results in the thickening of the θ phase behind the growth front at the expense of the α phase. For same lamellar spacing, a larger diffusivity ratio, such as $\mu_\alpha = \mu_\theta = 10$, significantly accentuates this thickening behavior. On the other hand, the concentration of carbon in the γ phase near the γ/α interface reduces with an increase in diffusivity ratios, whereas it increases near the γ/θ interface. Figure 4(d) illustrates the dimensionless carbon concentration profiles along the center lines of α and θ phases for the four cases presented in Fig. 4(c). The maximum carbon concentration near the γ/α interface at $S_i/S_e = 1.33$ ($S_i/S_e = 2$) decreases from 0.0535 (0.0642) for $\mu_\alpha = \mu_\theta = 1$ to 0.0507 (0.0623) for $\mu_\alpha = \mu_\theta = 10$. Conversely, the minimum carbon concentration near the γ/θ interface increases from 0.001 07 (−0.008 41) to 0.002 65 (−0.005 88).

Overall, the good agreement between the numerical results and the analytical predictions indicates the quantitative capabilities of the nondiagonal PF model with the consideration of the diffusion in γ , α , and θ phases. Through comparing the nondiagonal PF results with the CPF results, the importance of the cross-coupling term is also evidenced. Furthermore, when the diffusion in the growing phases is present, a thickening of θ phase behind the growth front is observed.

C. Case 3: Diffusion in γ and α phases

In this section, we investigate the pearlite growth with the consideration of the diffusion in γ and α phases.

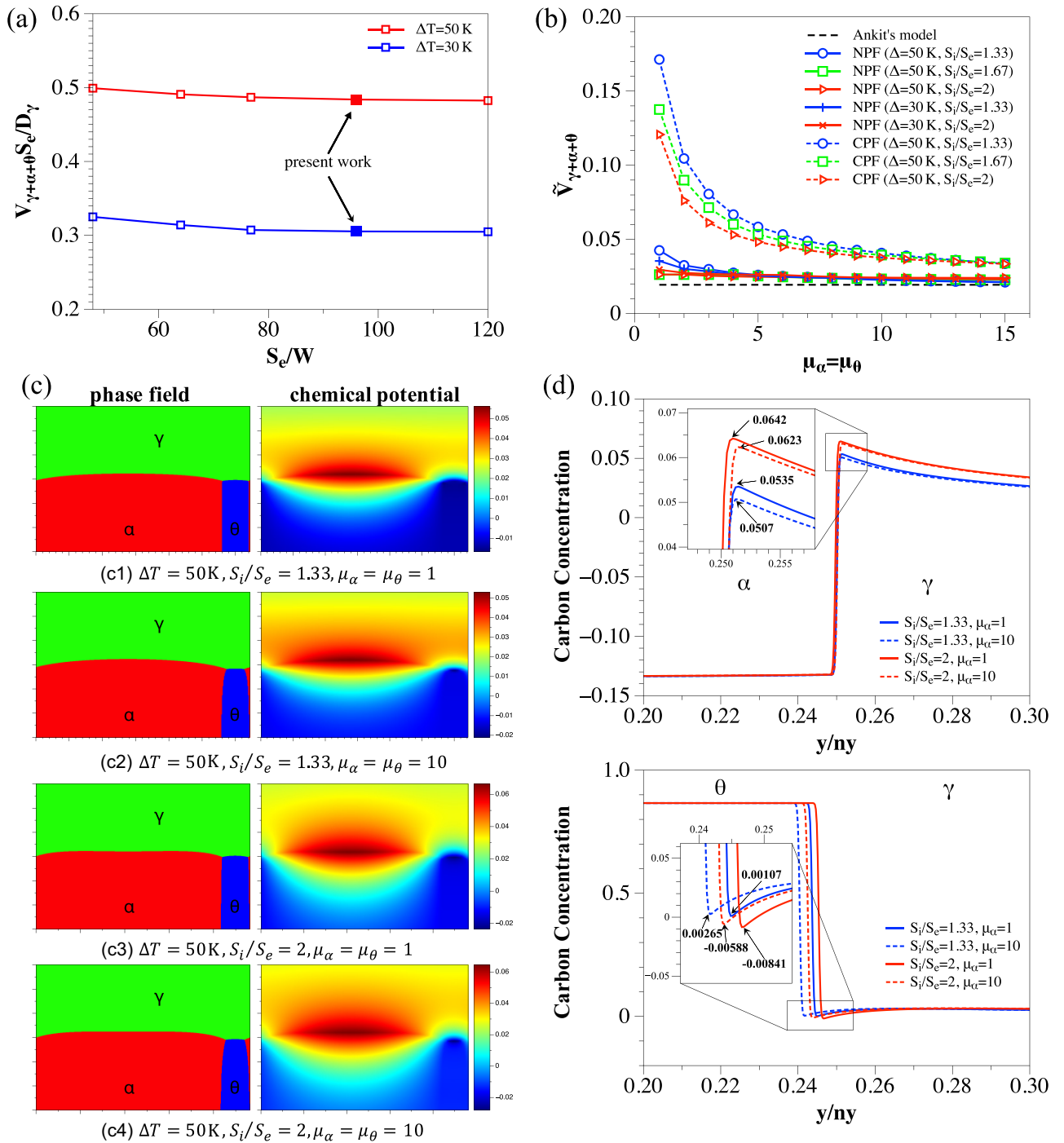


FIG. 4. (a) The dimensionless growth velocity $V_{\gamma+\alpha+\theta} S_e / D_\gamma$ as a function of diffuse interface width S_e / W for the given lamellar spacing $S_i / S_e = 1.33$ in Case 2. (b) Comparison of the nondiagonal PF (NPF) results and the predictions of Ankit's model in Case 3. NPF results agree well with the predictions of Ankit's model while classical PF (CPF) results exhibit much larger discrepancy. (c) The steady-state microstructure of the pearlite near the growth front presented by phase field (left) and chemical potential field (right) for (c1) $S_i / S_e = 1.33$, $\mu_\alpha = \mu_\theta = 1$; (c2) $S_i / S_e = 1.33$, $\mu_\alpha = \mu_\theta = 10$; (c3) $S_i / S_e = 2$, $\mu_\alpha = \mu_\theta = 1$; (c4) $S_i / S_e = 2$, $\mu_\alpha = \mu_\theta = 10$. (d) The dimensionless carbon concentration profiles along the center lines of α and θ phases for the four cases presented in Fig. 4(c).

Equation (45) is used as the diffusivity equation in the PF simulations and the diffusivity ratio of γ phase to α phase is defined as $\mu_\alpha = D_\alpha / D_\gamma$. Due to the fact that θ phase

is stoichiometric, the diffusion in θ phase is negligible. We omit the diffusivity ratio of θ phase to γ phase, i.e., $\mu_\theta = 0$, in Eq. (3), the growth velocity of pearlite $V_{\gamma+\alpha}$ therefore

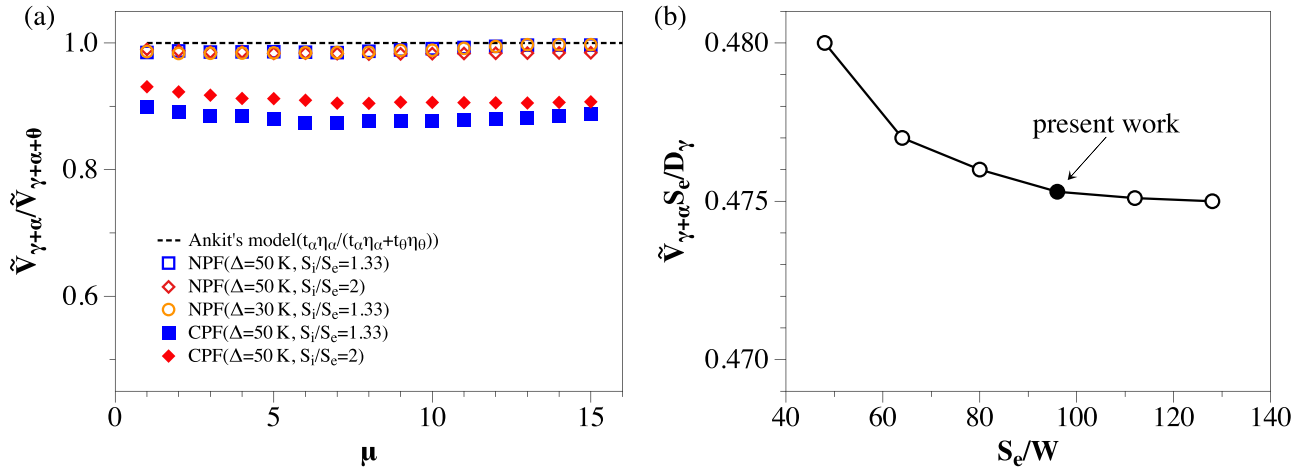


FIG. 5. (a) Comparison of the growth velocity ratio ($\tilde{V}_{\gamma+\alpha}/\tilde{V}_{\gamma+\alpha+\theta}$) obtained by NPF, CPF simulations and the predictions of Ankit's model. (b) The dimensionless growth velocity $\tilde{V}_{\gamma+\alpha}S_e/W$ as a function of diffuse interface width S_e/W for $\Delta T = 50$ K, $\mu_\alpha = 5$, and $S_i/S_e = 1.33$.

becomes proportional to μ_α . In analogy to Eq. (55), we have

$$\tilde{V}_{\gamma+\alpha} = \frac{V_{\gamma+\alpha} - V_\gamma}{\mu_\alpha V_\gamma} = t_\alpha \eta_\alpha = \text{const.} \quad (56)$$

Aiming to investigate the influence of the diffusion in θ phase on the pearlite growth velocity, we depict the growth velocity ratio, i.e., $\tilde{V}_{\gamma+\alpha}/\tilde{V}_{\gamma+\alpha+\theta}$, as a function of μ_α in Fig. 5(a). The open symbols indicate the NPF simulation results, while the filled symbols are CPF simulation results without the contribution of cross-coupling term. The NPF results exhibit good agreement with the predictions of Ankit's model and distribute in the range of 0.982 to 0.997, which implies that pearlite growth is insensitive to diffusion in theta phase. However, the CPF results are much lower than the predictions of Ankit's model. In Fig. 5(b), we present the dimensionless growth velocity of pearlite with the diffusion in γ and α phases obtained by NPF simulations as a function of interface width for $\Delta T = 50$ K, $\mu_\alpha = 5$, and $S_i/S_e = 1.33$. With an increase in S_e/W , the pearlite growth velocity converges. The deviation between the growth velocity at $S_e/W = 96$ used in the present work and the converged value is within 0.1%.

Hence, in Case 3, we not only extend the NPF model to the situation in which one of the three diffusivities vanishes but also verify the NPF simulation results are independent of the choice of the interface thickness. The NPF results and predictions of Ankit's model clarify that the influence of diffusion in θ phase does not influence pearlite growth. Finally, the inaccurate CPF results indicate the significance of the cross-coupling term.

D. Case 4: Diffusion in γ phase and along the γ/α and γ/θ interfaces

Interface diffusion along the γ/α and γ/θ interfaces, which is an important diffusion path in pearlite growth, is not considered in the previous cases. In this section, we investigate the situation in which both diffusion in the γ phase and diffusion along these interfaces are considered. Pandit *et al.* [17] formulate Eq. (5) to predict the pearlitic growth velocity by combining the diffusion fluxes in the γ phase and along the

interfaces. Through rewriting Eq. (5), we have

$$\tilde{V}_{\gamma+\text{surf}} = \frac{V_{\gamma+\text{surf}}}{V_\gamma} - 1 = \frac{6D_{gb}\delta_{gb}}{D_\gamma S_i}, \quad (57)$$

where $D_{gb}\delta_{gb}$ is equivalent to the surface diffusion coefficient. The match of the surface diffusion in the sharp interface method with the PF method is presented in Eq. (17). For given D_γ and S_i , the dimensionless velocity $\tilde{V}_{\gamma+\text{surf}}$ is proportional to the surface diffusion coefficient. Moreover, to describe the diffusion in the mother phase and along the γ/α and γ/θ interfaces, Eq. (50) is used as the diffusivity equation in the nondiagonal PF simulations.

Figure 6(a) demonstrates the dimensionless growth velocity $\tilde{V}_{\gamma+\text{surf}}$ for $S_i/S_e = 1.33$ as a function of surface diffusion coefficient obtained by the nondiagonal PF and classical PF simulations. The red and blue solid (dashed) lines indicate the nondiagonal PF (classical PF) results with $\Delta T = 50$ and 30 K. With an increase in surface diffusion coefficient, perfect linear relations are reproduced by the nondiagonal PF simulations in agreement with the predictions of Pandit's model, whereas the slopes of the dashed lines are obviously dependent on the surface diffusion. In addition, the comparison between the PF results and the analytical predictions shows that the classical PF results are much higher than analytical predictions and the deviation between nondiagonal PF results and analytical predictions is significant. For the sake of reducing the discrepancy, Fig. 6(b) displays the influence of the lamellar spacing on $\tilde{V}_{\gamma+\text{surf}}$ for a given surface diffusion coefficient, i.e., $D_{\text{surf}}W = 2.121$. As depicted in Fig. 6(b), with an increase in the lamellar spacing, the rescaled growth velocity of pearlite decreases both in nondiagonal PF and classical PF simulations and the nondiagonal PF results become closer and closer to analytical predictions, which corresponds to a significant reduction of the discrepancy. Nevertheless, the deviation is not negligible. To figure out the reason for this discrepancy, Figs. 6(c) and 6(d) illustrate the dimensionless growth velocity $V_{\gamma+\text{surf}}S_e/D_\gamma$ as a function of the interface thickness and the exponent n introduced in Eq. (50), respectively. In Fig. 6(c), we clearly observe that the growth velocity reaches constant with a decrease in interface thickness for different undercooling and surface diffusion. The deviations

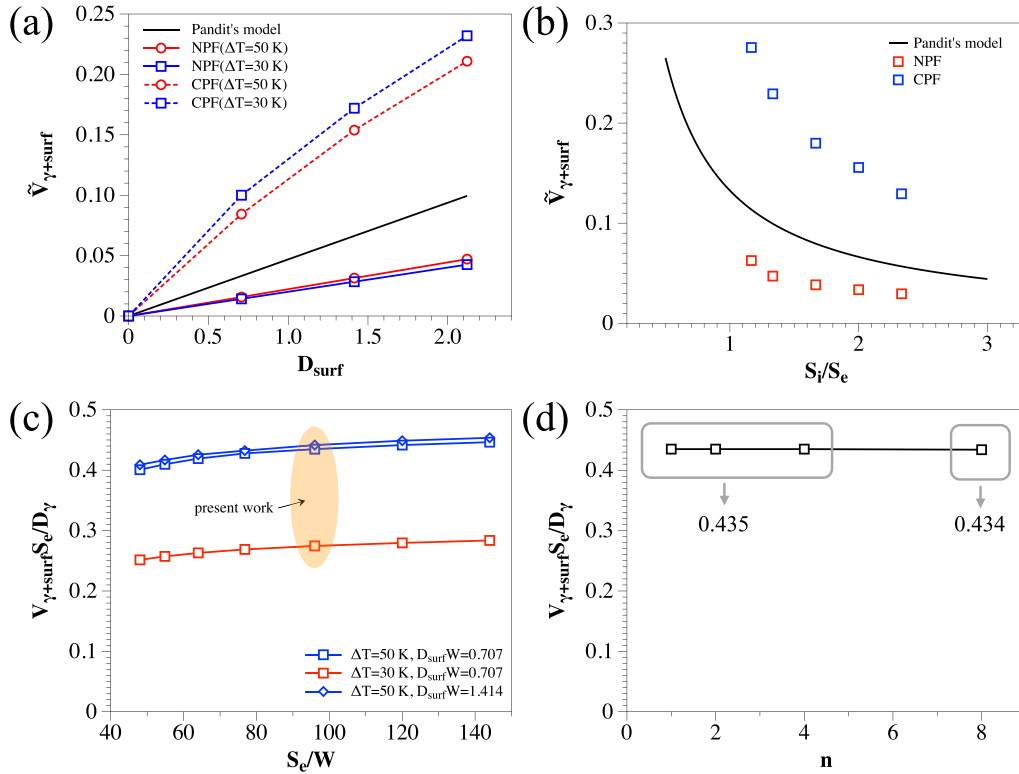


FIG. 6. (a) The comparison of nondiagonal PF (NPF) results and the predictions of Pandit's model for $S_i/S_e = 1.33$ in Case 4. NPF results indicate the dimensionless growth velocity $\tilde{V}_{\gamma+\text{surf}}$ is perfectly proportional to the surface diffusion, whereas the classical PF (CPF) results is nonlinear. (b) The dimensionless growth velocities $\tilde{V}_{\gamma+\text{surf}}$ obtained from Ankit's model, NPF and CPF as a function of lamellar spacing S_i/S_e for $D_{\text{surf}} W = 2.1213$ and $\Delta T = 50$ K. (c) The dimensionless growth velocity $V_{\gamma+\text{surf}} S_e/D_\gamma$ as a function of diffuse interface width S_e/W . (d) The dimensionless growth velocity $V_{\gamma+\text{surf}} S_e/D_\gamma$ as a function of parameter n in Eq. (50). The result shows that the velocity is independent of parameter n .

between the NPF results for $S_e/W = 96$ and the convergent values are smaller than 3.5%. Similarly, in Fig. 6(d), the influence of the parameter n on the growth velocity of pearlite is less than 0.1%. Consequently, our nondiagonal PF results are independent of the interface width and of the exponent n in the diffusivity equation. The discrepancy between the nondiagonal PF results and the analytical predictions may be caused by two factors: (i) Pandit's model assumes the γ/α and γ/θ interfaces to be flat and simply combines the diffusion fluxes in the mother phase and along the γ/α and γ/θ interfaces; and (ii) the scalar diffusivity used in the nondiagonal PF simulations also contributes to diffusion parallel to the pearlite growth direction within the interface region, which cannot fully reproduce purely tangential surface diffusion.

In summary, we have investigated pearlite growth when diffusion in the γ phase and along the γ/α and γ/θ interfaces are considered. The nondiagonal PF results imply that the dimensionless growth velocity $\tilde{V}_{\gamma+\text{surf}}$ is proportional to the surface diffusion coefficient, in agreement with Pandit's model. Additionally, we verify that the nondiagonal PF results are insensitive to the interface width and to the exponent n . The remaining discrepancy between the nondiagonal PF results and analytical predictions may originate from the simplifying assumptions of Pandit's model and from the use of a scalar diffusivity in the diffuse-interface region.

V. CONCLUSIONS

In this work, we have addressed the challenge of reproducing the correct equilibrium boundary conditions during phase transformations involving finite diffusivities in multiple phases and along interfaces, such as the pearlite transformation. By developing a grand-potential-based nondiagonal three-phase field model consistent with Onsager's relations, we demonstrated that introducing kinetic cross-coupling between conserved and nonconserved fields enables the determination of nondiagonal PF parameters through thin-interface analysis, and consequently restores the desired local equilibrium at interfaces. The main conclusions are summarized as follows:

(1) Four diffusion scenarios were systematically examined, including (i) diffusion in γ bulk phase, (ii) diffusion in γ , α and θ bulk phases, (iii) diffusion in γ and α bulk phases, (iv) diffusion in γ bulk phase and along γ/α , γ/θ interfaces. In all cases, the proposed nondiagonal formulation successfully eliminates the abnormal interface effects and recovers the physically consistent equilibrium boundary conditions.

(2) Quantitative assessments against analytical solutions confirm the accuracy and robustness of the nondiagonal phase field model. The roles of bulk and interfacial diffusion pathways are clearly distinguished. In contrast, classical phase-field (CPF) simulations exhibit significant deviations from analytical predictions without the cross-coupling term.

(3) The proposed model provides a powerful and versatile framework for studying coupled diffusion-controlled phase transformations. Its ability to treat multiple diffusional pathways and kinetic cross-coupling makes it well suited for investigating complex microstructure evolution in eutectoid steels and other multicomponent, multiphase systems where interface thermodynamics and kinetics are tightly coupled.

The present work should be viewed as a central development and validation study for the quantitative NPF framework, as a step towards the full identification of the dominant diffusion paths in pearlite. Modeling the latter requires the use of experimentally determined diffusivities and direct comparison with measured pearlite growth velocities. Such an application will make it possible to assess combinations of ferrite bulk diffusion, cementite bulk diffusion, and diffusion along the γ/α and γ/θ interfaces, and thereby to determine which diffusion pathways provide the most representative description of pearlite growth kinetics in real Fe-C alloys.

Several limitations of the present work should be noted. First, the model is validated under the assumptions of local equilibrium at the binary interfaces, equal diffusivity along the γ/α and γ/θ interfaces, negligible diffusion along the α/θ interface, and no solute-drag effect. Second, elastic and plastic effects are not included, although coherency stresses, dislocation structures, and plastic relaxation may modify the local driving force and interface mobility in real pearlitic microstructures. Third, the nu-

merical demonstrations are restricted to two-dimensional lamellar growth with translational invariance along the third direction; fully three-dimensional simulations may introduce additional curvature effects, lamellar-instability mechanisms, and interface-diffusion pathways. These aspects will be important targets for future extensions of the present quantitative NPF framework.

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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