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A Unified Theory of Free Energy Functionals and Applications to Diffusion

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Abstract

Free energy functionals of Ginzburg-Landau type lie at the heart of a broad class of continuum dynamical models, such as the Cahn-Hilliard and Swift-Hohenberg equations. Despite the wide use of such models, the assumptions embodied in the free energy functionals are frequently either poorly justified or lead to physically opaque parameters. Here, we introduce a mathematically rigorous pathway for constructing free energy functionals that generalizes beyond the constraints of Ginzburg-Landau gradient expansions. We show that the new formalism unifies existing free energetic descriptions under a single umbrella by establishing the criteria under which the generalized free energy reduces to gradient-based representations. Consequently, we derive a precise physical interpretation of the gradient energy parameter in the Cahn-Hilliard model as the product of an interaction length scale and the free energy curvature. The practical impact of our approach is demonstrated using both a model free energy function and the silicon-germanium alloy system.

Significance Statement

The free energy functional is a central component of continuum dynamical models used to describe phase transitions, microstructural evolution, and pattern formation. However, despite the success of these models in many areas of physics, chemistry, and biology, the standard free energy frameworks are frequently characterized by physically opaque parameters and incorporate assumptions that are difficult to assess. Here, we introduce a mathematical formalism that provides a unifying umbrella for constructing free energy functionals. We show that Ginzburg-Landau framework is a special case of this umbrella and derive a generalization of the widely employed Cahn-Hilliard equation. More broadly, we expect that the new framework will also be useful for generalizing higher-order theories, establishing formal connections to microscopic physics, and coarse-graining.

Main Text

Introduction

The principal goal of classical field theories, such as Ginzburg-Landau (GL) type¹ and classical density functional theory (DFT)², is to mathematically describe a system's free energy in terms of some order parameter(s) and consequently drive a continuum dynamical model (e.g., Cahn-Hilliard (CH) equation, phase field³⁻⁵). These continuum models play a central role in our understanding and mathematical modeling of the natural world in a vast range of applications spanning nucleation⁶, dendritic growth⁷, self-assembly⁸, intracellular organization^{9,10}, and brain cortex dynamics¹¹; see Fig. 1. Moreover, they have become objects studied in their own right as distinct classes of stochastic PDEs¹². Even in situations where the underlying microscopic physics may be described explicitly at the atomistic scale (e.g., molecular dynamics¹³, Langevin dynamics¹⁴, or Glauber dynamics¹⁵ driven by interatomic potentials), the hydrodynamic/probabilistic limits of these descriptions are often described in terms of free energy gradient flows¹⁶. Consequently, constructing a free energetic description within a unified and physically comprehensive framework is a centrally important task for the continuum modeling of dynamical systems.

The broad success of GL modeling notwithstanding, physical interpretations of GL free energy parameters are variably ambiguous except in a few idealized cases^{17,18}. This difficulty arises principally from the phenomenological supposition that the free energy is expressible in terms of a sequence of gradients of one or more order parameters¹⁹. Some insightful attempts have been made to derive GL free energies with a more explicit physical basis, most notably classical DFT²⁰, which relies on a liquid reference state²¹. One example is the Giacomini-Lebowitz model of phase segregation¹⁵, which has gained much attention in recent years as a non-local GL type theory that is physically interpretable. In another instance, a simplified classical DFT formulation, which leads to Swift-Hohenberg free energies, has given rise to the popular phase-field crystal (PFC) approach^{21,22}. The PFC framework has been proposed as a bridge²³ between classical dynamical DFT and phase-field models, although the numerous simplifications embodied within it have been observed to lead to various unphysical predictions²¹.

Here, we propose a generalization of GL type theory that addresses the challenges discussed above. We show that the new formalism relaxes the locality assumption in GL theory by removing the constraint that the free energy be strictly defined in terms of gradients. We also demonstrate, using specific examples, how the generalization reduces to widely employed models, such as the Cahn-Hilliard free energy, and in so doing obtain explicit criteria for their validity. Perhaps most practically, we also show that the generalized approach naturally leads to physically interpretable parameters while at the same time retaining the inherent multiresolution nature of the GL type framework. In this paper, we limit our analysis to species diffusion (i.e., conserved gradient flow) to demonstrate these features but emphasize that the free energy construction itself is entirely general.

Continuum Modeling of Diffusion

The standard continuum diffusion equation for species i is given by

$$\frac{\partial c_i}{\partial t} = \sum_j \nabla \cdot (\mathbf{M}_{ij} \cdot \nabla \beta \mu_j) + \epsilon = \sum_j \nabla \cdot \left(\mathbf{M}_{ij} \cdot \nabla \beta \frac{\delta F}{\delta c_j} \right) + \epsilon, \quad (1)$$

where c_i is the concentration, $\mathbf{M}_{ij}$ is the mobility matrix^{24,25}, $\nabla \mu_j$ is the driving force due to a generalized chemical potential μ_i , and ϵ is a thermal noise term that satisfies the fluctuation-dissipation theorem²⁶. The generalized chemical potential, $\mu_i \equiv \frac{\delta F}{\delta c_i}$, is defined as the variational derivative of the free energy of the system, F . In the present analysis, we neglect the noise term and focus on the deterministic evolution for single and binary component cases and drop the indices i and j . However, an extension to multicomponent cases²⁷ is straightforward.

The free energy¹, $F[c] \equiv \int f([c], \mathbf{r}) dV$, is most generally assumed to be a functional of the composition/density profile $[c]$, where $f([c], \mathbf{r})$ is the position-dependent free energy density functional. Without loss of generality, F can be decomposed into ideal and excess contributions, i.e.,

$$F = F^{id} + F^{ex} = \int f^{id} dV + \int f^{ex} dV, \quad (2)$$

where f^{id} and f^{ex} are the corresponding free energy densities. We do not consider external fields explicitly as they contribute one-body terms that, along with f^{id} , do not modify the theory. Note that the separation of F into ideal and excess components is natural as they arise from different aspects of the Brownian motion that generates the diffusion equation. For example, classical DFT relates f^{ex} to the Ornstein-Zernike relation/direct correlation²⁸ function using the liquid/homogeneous state as a reference. GL type theories do not usually consider this separation explicitly and assume F can be expanded directly with respect to gradient terms²⁹. Below we present an alternative framework for constructing the functional f^{ex} in terms of a sequence of convolution kernels that are directly linkable to the microscopic physics. Importantly, this framework requires no inherent assumptions or constraints be placed on $F[c]$ and can be linked formally to both GL type and classical DFT theories.

Results

General Free Energy Functional

Consider a discretized compositional profile where f^{ex} is to be evaluated with respect to a reference position $\mathbf{r}_0$ and $\{c_n\} \equiv \{c(\mathbf{r}_0 + \Delta \mathbf{r}_n)\}$ is the set of compositions that are $\{\Delta \mathbf{r}_n\}$ away from $\mathbf{r}_0$ with $c_0 \equiv c(\mathbf{r}_0)$. For the special case where the discretization corresponds to a crystal lattice, c_n denotes the

probability of site n being occupied by an atom. Assuming that $f^{ex}(\{c_n\}, \mathbf{r}_0)$ is analytical with respect to variations in $\{c_n\}$, it is possible to carry out a Taylor expansion with respect to any reference compositional profile. Specifically, we seek an expression that relates $f^{ex}(\{c_n\}, \mathbf{r}_0)$ to the function $\hat{f}^{ex}(c)$ —the evaluation of $f^{ex}(\{c_n\}, \mathbf{r}_0)$ at constant composition c —whose information can be obtained from equilibrium thermodynamic state variables and phase diagrams.

First, we note that $f^{ex}(\{c_n\}, \mathbf{r}_0)$ at constant composition may be expressed in two ways, i.e.,

$$\hat{f}^{ex}(c_0) \equiv f^{ex}(\{c_n\}, \mathbf{r}_0)|_{\{c_n=c_0\}}, \quad (3)$$

where the l.h.s. is a single-variable function, and the r.h.s. is a multivariate function evaluated at $\{c_n\} = c_0$. A Taylor expansion of the l.h.s. of eq. (3) with respect to some uniform concentration perturbation δ gives

$$\hat{f}^{ex}(c_0 + \delta) - \hat{f}^{ex}(c_0) = \sum_m \frac{1}{m!} \delta^m \left. \frac{\partial^m \hat{f}^{ex}}{\partial c^m} \right|_{c_0}, \quad (4)$$

where $m \in \mathbb{N}^+$. Correspondingly, Taylor expansion of the r.h.s. of eq. (3) gives

$$f^{ex}(\{c_n = c_0 + \delta\}, \mathbf{r}_0) - f^{ex}(\{c_n = c_0\}, \mathbf{r}_0) = \sum_m \frac{1}{m!} \delta^m \left. \frac{\partial^m f^{ex}}{\partial c^m} \right|_{\{c_n=c_0\}}. \quad (5)$$

The equivalence of eqs. (4) and (5) implies that

$$\frac{\partial}{\partial c} = \sum_n \frac{\partial}{\partial c_n}, \quad (6)$$

and therefore

$$\frac{\partial^m}{\partial c^m} = \frac{\partial^{m-1}}{\partial c^{m-1}} \frac{\partial}{\partial c} = \sum_{\mathbf{m}} \left(\frac{\partial}{\partial c} \right)^{\mathbf{m}} \equiv \sum_{n_1} \dots \sum_{n_m} \left(\prod_{i=1}^m \frac{\partial}{\partial c_{n_i}} \right), \quad (7)$$

where the multi-index notation $\mathbf{m} = (n_1, n_2, \dots, n_m)$ has been introduced. The application of eq. (7) to eq. (5) then gives

$$\begin{aligned} f^{ex}(\{c_n = c_0 + \delta\}, \mathbf{r}_0) - f^{ex}(\{c_n = c_0\}, \mathbf{r}_0) &= \sum_m \frac{1}{m!} \delta^m \sum_{\mathbf{m}} \left(\frac{\partial}{\partial c} \right)^{\mathbf{m}} f^{ex} \Big|_{\{c_n=c_0\}} \\ &= \delta \sum_{n_1} \left. \frac{\partial f^{ex}}{\partial c_{n_1}} \right|_{\{c_{n_1}=c_0\}} + \frac{1}{2} \delta^2 \sum_{n_1} \sum_{n_2} \left. \frac{\partial^2 f^{ex}}{\partial c_{n_1} \partial c_{n_2}} \right|_{\{c_{n_1}=c_{n_2}=c_0\}} + \dots \end{aligned} \quad (8)$$

Next, combining eqs. (5) and (8) gives

$$\left. \frac{\partial^m \hat{f}^{ex}}{\partial c^m} \right|_{c_0} = \sum_{\mathbf{m}} \left(\frac{\partial}{\partial c} \right)^{\mathbf{m}} f^{ex} \Big|_{\{c_n=c_0\}} = \sum_{\mathbf{m}} \rho_{\mathbf{m}}(c_0), \quad (9)$$

where $\rho_{\mathbf{m}}(c_0) \equiv \left(\frac{\partial}{\partial c} \right)^{\mathbf{m}} f^{ex} \Big|_{\{c_n=c_0\}}$ is the m -site contribution to $\left. \frac{\partial^m \hat{f}^{ex}}{\partial c^m} \right|_{c_0}$ at combination of sites $\mathbf{m}$. Finally, generalizing the preceding analysis to non-uniform perturbations, i.e., $\{c_n = c_0 + \delta_n\}$, Taylor expansion of f^{ex} gives

$$f^{ex}(\{c_n = c_0 + \delta_n\}, \mathbf{r}_0) = \hat{f}^{ex}(c_0) + \sum_{\mathbf{m}} \frac{1}{m!} \left(\sum_{\mathbf{m}} \rho_{\mathbf{m}}(c_0) \prod_{i=1}^m (c_{n_i} - c_0) \right), \quad (10)$$

Note that eq. (10) holds for any number of spatial dimensions; in d -dimensions it is convenient to replace the sum over $\mathbf{m} = \{n_i\}$ by one over $\{\mathbf{n}_i\}$, where each $\mathbf{n}$ has d components.

The continuum limit of eq. (10) is now readily obtained as

$$f^{ex}([c], \mathbf{r}) = \hat{f}^{ex}(c) + \sum_{\mathbf{m}} \frac{1}{m!} \int \dots \int \rho_{\mathbf{m}}(c, \{\Delta \mathbf{r}_1, \dots, \Delta \mathbf{r}_m\}) \prod_{i=1}^m (c_i - c) dV_i, \quad (11)$$

where $c_i - c \equiv c(\mathbf{r}_i) - c(\mathbf{r})$ and the discrete site indices $\{\mathbf{n}_1, \dots, \mathbf{n}_m\}$ become continuous coordinates $\{\mathbf{r}_1, \dots, \mathbf{r}_m\}$. Note also that the “0” subscripts denoting the reference position/composition have been dropped in eq. (11) for notational brevity—we will employ this contraction in the remainder of the paper. The continuum analog of eq. (9) is now given by

$$\left. \frac{\partial^m \hat{f}^{ex}}{\partial c^m} \right|_c = \int \dots \int \rho_{\mathbf{m}}(c, \{\Delta \mathbf{r}_1, \dots, \Delta \mathbf{r}_m\}) \prod_{i=1}^m dV_i, \quad (12)$$

where each $\int dV_i$ is an integration over the entire system volume. The total free energy of the system is then given by

$$F[c] = \int \left[\hat{f}(c) + \sum_{\mathbf{m}} \frac{1}{m!} \int \rho_{\mathbf{m}}(c, \{\Delta \mathbf{r}_1, \dots, \Delta \mathbf{r}_m\}) \prod_{i=1}^m (c_i - c) dV_i \right] dV, \quad (13)$$

Equation (13), along with the constraints in eq. (12), is a key result of the present work and a powerful basis for unifying and assessing the validity of a broad range of existing free energetic descriptions. For example, as we show below, this construct provides a mathematically explicit interpretation of the locality assumption inherent in gradient expansion-based GL at any order. Consequently, we find that using eq. (13) as a starting point and then imposing the locality assumption leads to more generalized versions of commonly employed functionals. Moreover, as we show below, the imposition of locality reduces the information regarding $\{\rho_{\mathbf{m}}\}$ that must be specified. While, in principle, it

is possible to specify a complete description of $\{\rho_m\}$ directly from measurements without invoking the locality assumption, this is generally impractical except in special cases (e.g., ρ_2 is closely connected to the direct correlation function used in classical DFT). We defer further discussion of this possibility to future work. Finally, although not a focus of the present work, other formalisms may also be derived as special cases of eq. (13). For example, as shown in Supplementary A, the Giacomin-Lebowitz model of phase separation¹⁵, an example of a so-called ‘non-local’ GL theory that has recently gained much attention in the PDE community³⁰, can also be recovered as a special case of eq. (13). More generally, all non-local free energy formulations, such as those proposed in Refs.^{31,32}, must also satisfy eq. (13).

Relation to the Ginzburg-Landau Formalism

In the GL formalism, the free energy density is assumed to be analytical with respect to gradient terms^{8,17}, i.e.,

$$F[c] = \int (\hat{f}(c) + \nabla c \cdot \kappa(c) \cdot \nabla c + \dots) dV, \quad (14)$$

where $\kappa(c)$ is a symmetric matrix. The task at hand, therefore, is to determine the conditions under which eq. (13) may be stated in the form of eq. (14). Consider a Taylor expansion of each site composition, c_i , with respect to a reference $c = c(\mathbf{r})$, i.e., $c_i - c = \sum_j \frac{1}{j!} [\Delta \mathbf{r}_i \cdot \nabla]^j c|_{\mathbf{r}}$, which gives

$$F[c] = \int \left[\hat{f}(c) + \sum_m \frac{1}{m!} \int \rho_m(c, \{\Delta \mathbf{r}_1, \dots, \Delta \mathbf{r}_m\}) \sum_{\mathbf{j}} \frac{1}{\mathbf{j}!} (\Delta \mathbf{r} \cdot \nabla)^{\mathbf{j}} \left| \prod_{i=1}^m dV_i \right| \right] dV, \quad (15)$$

where $\mathbf{j} = (j_1, \dots, j_m)$ and $j_i \in \mathbb{N}^+$ (see Methods A). To establish a connection between eq. (15) and the GL formalism in eq. (14) we note that the latter is written explicitly in terms of gradients of composition at various orders. Consequently, the terms in eq. (15) must be rewritten as

$$F[c] = \int \left[\hat{f}(c) + \sum_m \sum_{\mathbf{j}} \chi_{m,\mathbf{j}} \left(\frac{\partial c}{\partial \mathbf{r}} \right)^{\mathbf{j}} \right] dV, \quad (16a)$$

where the coefficients $\chi_{m,\mathbf{j}}$ are

$$\chi_{m,\mathbf{j}} = \frac{1}{m!} \left(\frac{1}{j} \right)^{\mathbf{j}} \int \rho_m(c, \{\Delta \mathbf{r}_1, \dots, \Delta \mathbf{r}_m\}) (\Delta \mathbf{r})^{\mathbf{j}} \prod_{i=1}^m dV_i, \quad (16b)$$

and $\mathbf{J} = \{j_{i,\alpha}\}$, $j_{i,\alpha} \geq 1$ is a multi-index that runs over all possible gradient terms where $i \in \{1, \dots, m\}$ and α represents the contribution along the α coordinate. This rearrangement is necessary to obtain distinct coefficients for each gradient term such as $\mathbf{\kappa}$ in eq. (14). Critically, such rearrangements are only guaranteed to converge for absolutely convergent series (Fubini's Theorem). Therefore, equating eqs. (14) and (16) implies that the representation of a GL free energy through gradient expansions requires this nontrivial assumption to hold. A similar concern was raised in an attempt to derive a GL free energy from classical DFT²⁰.

Equation (16) contains all possible combinations of $\left(\frac{\partial c}{\partial r}\right)^{\mathbf{J}}$ that are allowed by symmetry, and it is therefore formally equivalent to eq. (14). But it also lays bare a known limitation of the GL framework^{20,31}—not all function moments of ρ_m are well defined (see Methods A). In other words, assumption of a gradient expansion, or equivalently the transformation of eq. (13) into eq. (16), places strong constraints, often referred to as *locality*³³, on the class of ρ_m that are allowable. Consequently, continuum models based on gradient expansions, such as those proposed in Refs. ^{29,34}, only include a subset of the most general free energies that can be proposed. Perhaps equally importantly, the equivalence between eqs. (14) and (16) provides a pathway for determining how the parameters of GL free energies are related to function moments of ρ_m , enabling the interpretation of GL parameters in terms of interatomic potentials, coarse-grained interaction models, or experimental phase diagram data. This point is demonstrated in the following section for the specific case of the Cahn-Hilliard free energy.

Square-Gradient Theories and the Cahn-Hilliard Equation

We now consider in detail the specific case of second-order gradient expansion, which is often referred to as a square-gradient/GL/CH free energy and is a common basis of continuum and phase-field modeling of critical phenomena¹, where $\mathbf{\kappa}$ is usually assumed to be constant (but not necessarily isotropic). The most general $\mathbf{\kappa}$ is given by eq. (16) and only depends on the $\sum j_{i,\alpha} = 2$ terms (see Methods B), i.e.,

$$\kappa_{\alpha,\beta} = \left[\chi_2(\alpha, \beta) - \frac{\partial \chi_1(\alpha, \beta)}{\partial c} \right], \quad (17)$$

where α and β are direction indices and $\chi_1(\alpha, \beta) \equiv \int \rho_1 \Delta r_{1,\alpha} \Delta r_{1,\beta} dV_1$ and $\chi_2(\alpha, \beta) \equiv \int \int \rho_2 (\Delta r_{1,\alpha} \Delta r_{2,\beta}) dV_1 dV_2$ are the second moments of ρ_1 and ρ_2 , respectively. Equation (17) may be rewritten as

$$\mathbf{\kappa} \equiv -\sigma^2 \frac{\partial^2 \hat{f}^{ex}}{\partial c^2}, \quad (18)$$

where $\mathbf{\kappa}$ and $\mathbf{\sigma}$ are the matrix forms of $\kappa_{\alpha,\beta}$ and $\sigma_{\alpha,\beta}$, respectively, $\sigma_{\alpha,\beta}^2 = \int \int [\delta(r_1 - r_2) - 1] \tilde{\rho}_2(\Delta r_{1,\alpha} \Delta r_{2,\beta}) dV_1 dV_2$, and $\tilde{\rho}_2 \equiv \rho_2 / \frac{\partial^2 \hat{f}^{ex}}{\partial c^2}$ (see Methods B).

Equation (18) is an illuminating result in several regards. First, it shows that the square-gradient GL formalism is *most generally* expressed in terms of the gradient of the excess chemical potential and only the second moments of ρ_1 and ρ_2 . In other words, the square-gradient approximation does not (and cannot) include a complete description of these kernels; higher-order gradient terms would be required to specify higher-order moments of ρ_m . Conversely, assuming that the conditions are met for the square-gradient picture to be valid, only the second moments need to be estimated from data. This is a significant simplification because $\mathbf{\sigma}$ represents a physically interpretable quantity—an effective interaction range between sites—that is generally straightforward to estimate. Moreover, while $\mathbf{\sigma}$ may be composition-dependent, in practice, it is likely to be only weakly so because of the explicit separation of the thermodynamic contribution, $\frac{\partial^2 \hat{f}^{ex}}{\partial c^2}$. Equation (18) also provides the necessary and sufficient conditions for the commonly-employed constant $\mathbf{\kappa}$ approximation¹⁷ in the Cahn-Hilliard picture. While Cahn and Hilliard proved in their original papers that the constant $\mathbf{\kappa}$ approximation is valid for a regular solution, there has been no rigorous proof of how it arises as the limit of general microscopic models^{15,30}. But perhaps more significantly, eq. (18) also proves that the forms of $\mathbf{\kappa}$ obtained previously for special cases of regular solution models^{17,18} may be rigorously extended to any solution thermodynamics at any length scale. Although we do not presently consider elasticity and coherency strain contributions^{35–42}, the decomposition of $\mathbf{\kappa}$ into an interaction distance and a thermodynamic contribution may also suggest a more self-consistent route for incorporating these effects.

With the preceding considerations in mind, it is natural to introduce the simplest generalization of the constant- $\mathbf{\kappa}$ Cahn-Hilliard picture in which only $\mathbf{\sigma}^2$ is assumed to be constant, while retaining the compositionally dependent thermodynamic contribution in eq. (18). The corresponding diffusion equation, which we refer to as the Generalized Square-Gradient (GSG) model, is given by (see Methods C)

$$\frac{\partial c}{\partial t} = \nabla \cdot \left\{ D \nabla \beta \left[\hat{\mu} + \frac{1}{2} \left(\nabla \cdot \mathbf{\sigma}^2 \cdot \nabla \hat{\mu}^{ex} + \frac{\partial \hat{\mu}^{ex}}{\partial c} \nabla \cdot \mathbf{\sigma}^2 \cdot \nabla c \right) \right] \right\}, \quad (19)$$

where $\hat{\mu} \equiv \mu_B - \mu_A$ and $\hat{\mu}^{ex} \equiv \mu_B^{ex} - \mu_A^{ex}$ are given by the differences of the two atomic species chemical potentials and excess chemical potentials respectively. Equation (19) shows explicitly how the chemical potential is modified by both compositional and chemical potential gradients. We note that a generalized GL theory by Gurtin³⁴, which has received considerable attention, is consistent with this picture. Finally, the Cahn-Hilliard equation may then be obtained from eq. (19) by assuming $\hat{\mu}^{ex} = -\eta_{CH} c + b$, where η_{CH} and b are constants, giving

$$\frac{\partial c}{\partial t} = \nabla \cdot \{D \nabla \beta [\hat{\mu} - \nabla \cdot \kappa \cdot \nabla c]\}, \quad (20)$$

where $\kappa = 2\eta_{CH}\sigma^2$.

Model Binary System Near a Tricritical Point

In this section, we use an analytical free energy model of a binary system to demonstrate how the generalizations embedded in the GSG model modify dynamical evolution relative to that predicted by the constant- κ Cahn-Hilliard model. For all comparisons, both the isotropic diffusion coefficient, D , and the isotropic interaction distance, σ , are chosen to be constant and the same across the two models, allowing us to precisely identify how the additional physics embodied in the GSG model modifies pattern evolution as a function of initial conditions and solution thermodynamics. The free energy model is given by

$$\hat{f} = \hat{f}^{id} + \hat{f}^{ex} = [c \log c + (1 - c) \log(1 - c)] + \left[\alpha c(1 - c) - \epsilon \exp\left(-\frac{(c - 0.5)^2}{\gamma}\right) \right], \quad (21)$$

where the second term in the square brackets, modulated by the adjustable parameter ϵ , reflects deviations from regular solution behavior and results in a tricritical point. Note that in eq. (21), the concentration is normalized to represent the atomic fraction. Below the tricritical point, the free energy model in eq. (21) exhibits two stable ‘phases’: ξ_1 and ξ_3 , where $c(\xi_1) = 0.07$ and $c(\xi_3) = 0.93$. Past the tricritical point, a third stable phase (ξ_2) emerges at $c(\xi_2) = 0.5$; see Supplementary C. We consider two distinct situations: (1) spinodal decomposition in initially homogeneous, subcritical systems ($\epsilon < 0.03$), and (2) pattern evolution in various supercritical settings ($\epsilon > 0.03$). The other parameters in the free energy model are fixed at $\alpha = 3.0$ and $\gamma = 0.03$. Connection to a ‘best-fit’ Cahn-Hilliard model for each value of ϵ is made by finding the value of the (constant) gradient energy parameter, η_{CH} , that minimizes the difference between $\hat{f}^{ex}(c)$ in eq. (21) and that of a regular solution, i.e., $\eta_{CH} = \underset{\eta_{CH}}{\text{Argmin}} \int [\hat{f}^{ex}(c) - \eta_{CH}c(1 - c)] dx$.

All simulations are conducted using a finite difference scheme (central difference) and periodic boundary condition on a 100×100 square grid, with uniform grid spacing fixed at $l_G = 5a_0$, where a_0 is the underlying lengthscale.

Spinodal Decomposition: Shown in Fig. 2 are three cases in which a noisy uniform initial compositional distribution ($c = 0.5 + N(0, 0.01)$) undergoes spinodal decomposition. For each combination of ϵ and η_{CH} , the top row corresponds to the Cahn-Hilliard (CH) model prediction with $\kappa = 2\eta_{CH}\sigma^2$, while the bottom row is the generalized square-gradient (GSG) prediction with $\sigma = 2a_0$. As expected, the CH and GSG models predict identical spinodal decomposition evolution for $\epsilon = 0$ (regular solution), Fig. 2(a). However, as the excess free energy becomes increasingly non-quadratic (i.e., increasing $|\epsilon|$), the onset of spinodal

decomposition predicted by the CH model is slowed considerably relative to the GSG model, Fig. 2(b,c). Moreover, there is an apparent difference in the dominant wavelength, with the CH model exhibiting a slightly finer pattern.

These observations may be quantitatively predicted in the context of a linear stability analysis (see Methods D). Specifically, the analysis shows that the dominant Fourier modes for the CH and GSG models diverge from each other as $\lambda_{GSG}^{max} - \lambda_{CH}^{max} \propto \sqrt{r}$ where $r \equiv \frac{\partial^2 \hat{f}^{ex}}{\partial c^2} / \frac{\partial^2 \hat{f}}{\partial c^2} \rightarrow \infty$ as the critical point is approached. The corresponding difference in spinodal decomposition timescale, $\tau_{GSG} - \tau_{CH} \propto r^2$, also diverges as the tricritical point is approached, as seen in Fig. 2.

Pattern Evolution: Motivated by the potential impact of thermal annealing on nanoscale devices, we next consider several supercritical systems with various initial compositional heterogeneities and several different parameter combinations. Shown in Fig. 3 is a situation in which a square region with area $100a_0^2$ and composition $c = 0.3$ is placed in the center of an otherwise homogeneous field at $c = 0.5$. In this set of simulations, we consider a supercritical system ($\epsilon = 0.075$ corresponding to $\eta_{CH} = 2.7$ for the best-fit CH model) with three different interaction ranges: (a) $\sigma = 2a_0$, (b) $2.3a_0$, and (c) $3.3a_0$. The GSG model results show a clear dependence on the interaction range parameter, σ . For a small interaction range, the gradient energy penalty is small, and the square region grows over time while maintaining a composition that corresponds to phase ξ_1 . As the interaction distance is increased to $\sigma = 2.3a_0$, the growing patch exhibits a more rounded shape. Beyond this point, further increases to the interaction range destabilize the patch and lead to dissolution due to the gradient energy penalty becoming dominant. The CH model, however, predicts qualitatively different behavior. At the lowest interaction energy, the patch is observed to remain static over the simulation timescale. The patch does begin to grow and become more rounded as the interaction range increases, but the final trend towards dissolution is missed entirely in the CH picture.

Finally, we consider a strongly supercritical situation ($\epsilon = 0.1$, $\eta_{CH} = 2.6$ for the best-fit CH model) where the excess free energy curvature turns slightly positive near $c = 0.5$, and with an interaction range $\sigma = 3a_0$. As shown in Fig. 4, we investigate three initial configurations with different compositional heterogeneity geometries. The first two cases exhibit spinodal decompositions within the compositional heterogeneities in both GSG and CH models. However, in both instances, the spatiotemporal evolution predicted by the GSG model appears to be qualitatively more ‘organized’ and appears to produce higher symmetry configurations by the end of the simulations. This observation may be explained by the stronger gradient energy effects in the GSG description, which effectively delay a complete spinodal decomposition at early times. The delay allows the patterns in the GSG simulation to evolve more easily at earlier times, leading to the ‘cleaner’ final configurations. The last case, shown in Fig. 4(c), highlights yet another potential failure mode of the CH model. Here, two adjacent heterogeneities with compositions near $c(\xi_1) = 0.07$ and $c(\xi_3) = 0.93$ are, in principle, able to grow without altering the composition of the surroundings,

which are initialized at $c(\xi_2) = 0.5$. The driving force for the growth of the heterogeneities is provided by the lower free energy of the ξ_1 and ξ_3 phases relative to ξ_2 . This is indeed observed in the GSG model while the CH model predicts an essentially static situation.

Compound Semiconductor (SiGe) Interdiffusion

Finally, we consider interdiffusion in SiGe, a highly studied phenomenon with broad technological importance^{43–48}. Our choice of this system as an additional case study is motivated by two characteristics. First, remarkably and somewhat uniquely, a large body of work^{44,45,49} has established reasonable estimates for both the equilibrium thermodynamic and diffusion properties relevant to SiGe interdiffusion, enabling quantitative and predictive modeling. Second, we use the very simple phase behavior of the Si-Ge solid solution to demonstrate that gradient energy contributions may be significant in unexpected situations—notably, most diffusion modeling in semiconductor systems assumes Fickian physics in which gradient energy contributions are neglected⁴³.

Literature data^{43,44} is used to fully parametrize the GSG model, including the chemical potential function, the self-diffusivity, and the coherency strain contribution^{17,43} (see Supplementary B). The only remaining parameter is the effective interaction range, σ , which we fix to be twice the lattice parameter, i.e., $2a_0 = 11.08\text{\AA}$ (see Supplementary C for additional results with $\sigma = a_0/2$ and $\sigma = a_0$). Interdiffusion is simulated in two QW-type configurations (denoted as ‘well’ and ‘anti-well’), Fig. 5. The time evolution of the ‘well’ concentration profile predicted by the Fickian and GSG models is similar, showing a gradual spreading of the initial Gaussian configuration. On the other hand, the ‘anti-well’ configuration leads to qualitatively different evolution across the two models. Here, the Fickian model predicts slow diffusion in the center (low Ge fraction), which results in persistently sharp concentration peaks. The inclusion of the gradient term in the GSG model leads to much faster evolution and broadening. The differences between the two cases arise from the self-diffusivity’s strong concentration dependence, which increases rapidly with increasing Ge fraction (see Supplementary B). In the ‘well’ configuration, diffusion is rapid in the center but becomes slower at the edges, effectively blocking the spread of Ge and reducing the impact of the gradient energy term. In contrast, the ‘anti-well’ configuration shifts the diffusion bottleneck to the center where the Ge fraction is lowest, and Fickian diffusion becomes very slow, resulting in the persistent peak. The addition of the gradient energy term, which enhances diffusion in the presence of large gradients, compensates for this effect in the GSG model. Given the ever-shrinking length scale (and potentially increasing sensitivity to interdiffusion-related degradation) of optoelectronic devices, we conclude that gradient energy effects may be necessary for modeling in these systems, even in the absence of apparent features such as phase separation.

Discussion

The phenomenological nature of the GL free energy formalism has long been recognized as an important limitation of continuum dynamical models. As a result, it has often been difficult to make direct connections between key model parameters and microscopic physical properties, establish the bounds of model validity, or generalize models across material systems or even operating conditions. In this paper, we have presented a mathematically rigorous framework that leads to the most general hierarchy of free energy functionals in terms of a sequence of convolution kernels. These kernels are only weakly constrained by derivatives of the excess free energy of the system and therefore require additional inputs either from experimental measurements of compositional evolution or from microscopic (e.g., atomistic) simulations. Importantly, we demonstrate that the general hierarchy developed here can be explicitly matched to the gradient-expansion framework of the GL formalism. This matching provides precise mathematical insight into the nature of the approximations embodied within the GL construct while also demonstrating one possible pathway for approximating the convolutional kernels in the hierarchy developed here.

Looking ahead, several potential avenues for future study are apparent. Most obviously, the present hierarchy also may be used to analyze higher-order gradient expansions, such as the 4th-order Swift-Hohenberg free energy⁵⁰, for which an analogous set of validity conditions may be obtained. The formalism developed here is also useful for establishing a rigorous connection to microscopic physics, most notably those represented by interatomic potential models^{51–53}. One possible pathway for accomplishing this connection is to proceed via the classical DFT framework, where the equilibrium liquid-state direct correlation function may be used to infer the relevant convolution kernels. More broadly, the hierarchy developed here provides a formal mechanism for constructing a dictionary between thermodynamic properties of the system at equilibrium, e.g., interface shapes between different phases, and the free energy functional.

Methods

Methods A: Connection to Ginzburg-Landau Type Theories

To establish a connection between eq. (13),

$$F[c] = \int \left[\hat{f}(c) + \sum_m \frac{1}{m!} \int \rho_m \prod_{i=1}^m (c_i - c) dV_i \right] dV, \quad (\text{A.1})$$

and the GL formalism,

$$F = \int (\hat{f}(c) + \nabla c \cdot \kappa(c) \cdot \nabla c + \dots) dV, \quad (\text{A.2})$$

note first that the composition on each site, c_i , can also be related to a reference site $\mathbf{r}$ with composition c , via an additional Taylor expansion, as

$$c_i - c = \sum_j \frac{1}{j!} [\Delta \mathbf{r}_i \cdot \nabla]^j c|_{\mathbf{r}}, \quad (\text{A.3})$$

where $\Delta \mathbf{r}_i \equiv \mathbf{r}_i - \mathbf{r}$. Substituting eq. (A.3) into the integral terms on the R.H.S. of eq. (A.1) gives

$$\begin{aligned} \sum_m \frac{1}{m!} \int \rho_m \prod_{i=1}^m (c_i - c) dV_i &= \sum_m \frac{1}{m!} \int \rho_m \prod_{i=1}^m \left(\sum_{j_i} \frac{1}{j_i!} (\Delta \mathbf{r}_i \cdot \nabla)^{j_i} c|_{\mathbf{r}} \right) dV_i \\ &= \sum_m \frac{1}{m!} \int \rho_m \sum_{\mathbf{j}} \frac{1}{\mathbf{j}!} (\Delta \mathbf{r} \cdot \nabla)^{\mathbf{j}} \Big|_{\mathbf{r}} dV_i. \end{aligned} \quad (\text{A.4})$$

where $\mathbf{j} = (j_1, \dots, j_m)$ and

$$\frac{1}{\mathbf{j}!} (\Delta \mathbf{r} \cdot \nabla)^{\mathbf{j}} \equiv \prod_{i=1}^m \left[\frac{1}{j_i!} (\Delta \mathbf{r}_i \cdot \nabla)^{j_i} c|_{\mathbf{r}} \right]. \quad (\text{A.5})$$

Consequently eq. (A.1) becomes

$$F = \int \left[\hat{f}(c) + \sum_m \frac{1}{m!} \int \rho_m \sum_{\mathbf{j}} \frac{1}{\mathbf{j}!} (\Delta \mathbf{r} \cdot \nabla)^{\mathbf{j}} \Big|_{\mathbf{r}} \prod_{i=1}^m dV_i \right] dV. \quad (\text{A.6})$$

In order to establish a connection between eq. (A.6) and the GL formalism in eq. (A.2), we note that the latter is written explicitly in terms of gradients of composition at various orders. Consequently, the terms in eq. (A.6) must be reordered according to

$$F = \int \left[\hat{f}(c) + \sum_m \sum_{\mathbf{j}} \frac{1}{\mathbf{j}!} \frac{1}{m!} \int \rho_m(\Delta \mathbf{r} \cdot \nabla c)^{\mathbf{j}} \Big|_{\mathbf{r}} \prod_{i=1}^m dV_i \right] dV. \quad (\text{A.7})$$

This rearrangement is necessary to obtain distinct coefficients for each gradient term such as $\mathbf{k}$ in eq. (14). Critically, such rearrangements are only guaranteed to converge for absolutely convergent series (Fubini's Theorem). Therefore, equating eqs. (A.2) and (A.7) implies that the representation of a GL free energy through gradient expansions requires this nontrivial assumption to hold. A similar concern was raised in an attempt to derive a GL free energy from classical DFT²⁰.

We illustrate the problem described above by considering the $m = 1$ case for eq. (A.7), i.e.,

$$F_1 = \int \left[\hat{f}(c) + \sum_{\mathbf{j}} \frac{1}{\mathbf{j}!} \int \rho_1(\Delta r_{1,\alpha})^{\mathbf{j}} \frac{\partial^{\mathbf{j}} c}{\partial r_{\alpha}^{\mathbf{j}}} \Big|_{\mathbf{r}} dV_1 \right] dV. \quad (\text{A.8})$$

Since $\frac{\partial^{\mathbf{j}} c}{\partial r_{\alpha}^{\mathbf{j}}} \Big|_{\mathbf{r}}$ is independent of $\mathbf{r}_1$, eq. (A.8) can be written as

$$F_1 = \int \left[\hat{f}(c) + \sum_{\mathbf{j}} \frac{1}{\mathbf{j}!} \int \rho_1(\Delta r_{1,\alpha})^{\mathbf{j}} dV_1 \frac{\partial^{\mathbf{j}} c}{\partial r_{\alpha}^{\mathbf{j}}} \Big|_{\mathbf{r}} \right] dV. \quad (\text{A.9})$$

However, eq. (A.9) is only valid if all $\int \rho_1(\Delta r_{1,\alpha})^{\mathbf{j}} dV_1$ are bounded, or equivalently that all j^{th} function moments of ρ_1 are finite. This necessarily fails if $\rho_1 \propto \frac{1}{|\mathbf{r}|^k}$ asymptotically, i.e., decays algebraically, because $(\Delta r_{1,\alpha})^{\mathbf{j}} \propto |\mathbf{r}|^{\mathbf{j}}$, and the integral term in eq. (A.9) becomes

$$\int \rho_1(\Delta r_{1,\alpha})^{\mathbf{j}} dV_1 \propto \int \frac{1}{|\mathbf{r}|^{k-\mathbf{j}}} dV_1, \quad (\text{A.10})$$

which will diverge for $k - j \leq (d - 1)$. Similar arguments hold for all ρ_m and higher-order gradient terms can only be included if the ρ_m have finite moments at corresponding orders. Note that for most stable distributions the variance is not well-defined, and for most Pareto distributions even the mean is not well-defined. Such distributions are of broad interest in physical and economic models based on Brownian motion, and diffusion on networks or general metric spaces may also readily have such dependencies in the form of heavy-tailed distributions.

For completeness, we also demonstrate explicitly how eq. (A.2) can be obtained from eq. (A.1) when the rearrangement from (A.6) to (A.7) is valid. To do so, recall that $\Delta \mathbf{r}_i = \{\Delta r_{i,\alpha}\}$, where $\alpha \in \{1, \dots, d\}$, and d is the spatial dimension of the system. $\Delta \mathbf{r}_i \cdot \nabla$ can therefore be written as

$$\Delta \mathbf{r}_i \cdot \nabla = \sum_{\alpha} \Delta r_{i,\alpha} \frac{\partial}{\partial r_{\alpha}}. \quad (\text{A. 11})$$

Using eq. (A.5),

$$\frac{1}{\mathbf{j}!} (\Delta \mathbf{r}_i \cdot \nabla c)^{\mathbf{j}} = \prod_{i=1}^m \left[\frac{1}{j_i!} \left(\sum_{\alpha} \Delta r_{i,\alpha} \frac{\partial}{\partial r_{\alpha}} \right)^{j_i} c \right], \quad (\text{A. 12})$$

so that

$$\sum_{\mathbf{j}} (\Delta \mathbf{r}_i \cdot \nabla c)^{\mathbf{j}} = \sum_{\mathbf{J}} \left(\Delta r \frac{\partial c}{\partial r} \right)^{\mathbf{J}}, \quad (\text{A. 13})$$

where the multi-index notation $\mathbf{J} \equiv \{j_{i,\alpha}\}$ is introduced such that

$$\left(\frac{1}{j} \Delta r \frac{\partial c}{\partial r} \right)^{\mathbf{J}} \equiv \prod_{i=1}^m \frac{1}{(\sum_{\alpha} j_{i,\alpha})!} \prod_{\alpha=1}^d \left[\left(\Delta r_{i,\alpha} \frac{\partial}{\partial r_{\alpha}} \right)^{j_{i,\alpha}} c \right]. \quad (\text{A. 14})$$

Substituting eq. (A.14) into eq. (A.7) then gives

$$F = \int \left[\hat{f}(c) + \sum_m \frac{1}{m!} \int \rho_m \sum_{\mathbf{J}} \left(\frac{1}{j} \Delta r \frac{\partial c}{\partial r} \right)^{\mathbf{J}} \right] \prod_{i=1}^m dV_i \, dV, \quad (\text{A. 15})$$

which may be written compactly as

$$F = \int \left[\hat{f}(c) + \sum_m \sum_{\mathbf{J}} \chi_{m,\mathbf{J}} \left(\frac{\partial c}{\partial r} \right)^{\mathbf{J}} \right] dV, \quad (\text{A. 16})$$

where the coefficients $\chi_{m,\mathbf{J}}$ are

$$\chi_{m,\mathbf{J}} = \frac{1}{m!} \left(\frac{1}{j} \right)^{\mathbf{J}} \int \rho_m (\Delta r)^{\mathbf{J}} \prod_{i=1}^m dV_i, \quad (\text{A. 17})$$

and the integrals are the function moments of ρ_m . Note that because the free energy is a scalar, all odd function moments of ρ_m must be zero. As such, eq (A.17) shows that the GL framework is equivalent to requiring that the function moments of ρ_m do not diverge at all orders or a truncation of higher-order terms, which is equivalent to neglecting or setting higher-order moments of ρ_m to be zero.

Methods B: Interpretation of the Square-Gradient Coefficient

By inversion symmetry, eq. (A.7) can be written as

$$F \approx \int \left[\hat{f}(c) + \frac{1}{2} \int \rho_1 (\Delta \mathbf{r}_1 \cdot \nabla)^2 c dV_1 + \frac{1}{2} \int \int \rho_2 (\Delta \mathbf{r}_1 \cdot \nabla c) dV_1 (\Delta \mathbf{r}_2 \cdot \nabla c) dV_2 \right] dV + \dots, \quad (\text{B.1})$$

or

$$F = \int \left[\hat{f}(c) + \frac{1}{2} \sum_{\alpha} \sum_{\beta} \left(\chi_1(\alpha, \beta) \frac{\partial^2 c}{\partial r_{\alpha} \partial r_{\beta}} + \chi_2(\alpha, \beta) \frac{\partial c}{\partial r_{\alpha}} \frac{\partial c}{\partial r_{\beta}} \right) \right] dV + \dots, \quad (\text{B.2})$$

where

$$\chi_1(\alpha, \beta) \equiv \int \rho_1 \Delta r_{1,\alpha} \Delta r_{1,\beta} dV_1 \quad (\text{B.3})$$

and

$$\chi_2(\alpha, \beta) \equiv \int \int \rho_2 \Delta r_{1,\alpha} \Delta r_{2,\beta} dV_1 dV_2 \quad (\text{B.4})$$

are the 2nd-order function moments of ρ_1 and ρ_2 respectively. By the divergence theorem, eq. (B.2) can be rewritten as

$$F = \int \left\{ \hat{f}(c) + \frac{1}{2} \sum_{\alpha} \sum_{\beta} \left[\chi_2(\alpha, \beta) - \frac{\partial \chi_1(\alpha, \beta)}{\partial c} \right] \frac{\partial c}{\partial r_{\alpha}} \frac{\partial c}{\partial r_{\beta}} \right\} dV + \dots. \quad (\text{B.5})$$

Defining

$$\kappa_{\alpha, \beta} \equiv \left[\chi_2(\alpha, \beta) - \frac{\partial \chi_1(\alpha, \beta)}{\partial c} \right] \quad (\text{B.6})$$

gives

$$F = \int \left\{ \hat{f}(c) + \frac{1}{2} \nabla c \cdot \boldsymbol{\kappa} \cdot \nabla c \right\} dV + \dots, \quad (\text{B.7})$$

recovering eq. (14) in the main text.

A more physically transparent expression for $\boldsymbol{\kappa}$ is derived below. Differentiating eq. (B.3) gives

$$\frac{\partial \chi_1(\alpha)}{\partial c} = \int \frac{\partial \rho_1}{\partial c} \Delta r_{1,\alpha} \Delta r_{1,\beta} dV_1. \quad (\text{B.8})$$

Using the recursive property of the convolutional kernels (eq. (12) in the main text)

$$\left. \frac{\partial^m \hat{f}^{ex}}{\partial c^m} \right|_c = \int \rho_m \prod_{i=1}^m dV_i, \quad (\text{B.9})$$

eq. (B.3) can be rewritten as

$$\frac{\partial \chi_1(\alpha, \beta)}{\partial c} = \int \left(\int \rho_2 dV_2 \right) \Delta r_{1,\alpha} \Delta r_{1,\beta} dV_1. \quad (\text{B.10})$$

Rearranging terms in eq. (B.10) gives

$$\frac{\partial \chi_1(\alpha, \beta)}{\partial c} = \int \int \delta(r_1 - r_2) \rho_2(\Delta r_{1,\alpha} \Delta r_{2,\beta}) dV_1 dV_2. \quad (\text{B.11})$$

Substituting eq. (B.11) into eq. (B.6) gives

$$\kappa_{\alpha,\beta} = \int \int [1 - \delta(r_1 - r_2)] \rho_2(\Delta r_{1,\alpha} \Delta r_{2,\beta}) dV_1 dV_2. \quad (\text{B.12})$$

Next, applying eq. (B.9) for $m = 2$, i.e.,

$$\frac{\partial^2 \hat{f}^{ex}}{\partial c^2} = \int \int \rho_2 dV_1 dV_2, \quad (\text{B.13})$$

and since $\frac{\partial^2 \hat{f}^{ex}}{\partial c^2}$ is independent of r_1 and r_2 , we obtain

$$\int \int \tilde{\rho}_2 dV_1 dV_2 \equiv \int \int \left(\frac{\partial^2 \hat{f}^{ex}}{\partial c^2} \right)^{-1} \rho_2 dV_1 dV_2 = 1. \quad (\text{B.14})$$

where $\tilde{\rho}_2 \equiv \left[\left(\frac{\partial^2 \hat{f}^{ex}}{\partial c^2} \right)^{-1} \rho_2 \right]$ is a convolution in the $V_1 \times V_2$ space. Using eq. (B.14), eq. (B.12) can now be written as

$$\kappa_{\alpha,\beta} = - \frac{\partial^2 \hat{f}^{ex}}{\partial c^2} \int \int [\delta(r_1 - r_2) - 1] \tilde{\rho}_2(\Delta r_{1,\alpha} \Delta r_{2,\beta}) dV_1 dV_2. \quad (\text{B.15})$$

Note that the negative sign and reordering in eq. (B.15) is introduced because the contribution from $\chi_1(\alpha, \beta)$ is usually larger than $\chi_2(\alpha, \beta)$ (in the original CH derivation¹⁷, $\chi_2 = 0$). The integral term in eq. (B.15) is a linear combination of the 2nd moments of $\tilde{\rho}_2$ and has units of length squared, and we define it as

$$\sigma_{\alpha,\beta}^2 \equiv \int \int [\delta(r_1 - r_2) - 1] \tilde{\rho}_2(\Delta r_{1,\alpha} \Delta r_{2,\beta}) dV_1 dV_2, \quad (\text{B.16})$$

leading to the final result

$$\kappa_{\alpha,\beta} = -\sigma_{\alpha,\beta}^2 \frac{\partial^2 \hat{f}^{ex}}{\partial c^2}. \quad (\text{B.17})$$

or in matrix form

$$\mathbf{\kappa} = -\boldsymbol{\sigma}^2 \frac{\partial^2 \hat{f}^{ex}}{\partial c^2}. \quad (\text{B. 18})$$

Methods C: Derivation of Generalized Square-Gradient (GSG) Model

Consider the GL formalism

$$F = \int (\hat{f}(c) + \nabla c \cdot \mathbf{\kappa}(c) \cdot \nabla c + \dots) dV, \quad (\text{C. 1})$$

with the gradient energy parameter derived in eq. (C.18) subject to constant $\boldsymbol{\sigma}$. The corresponding variational derivative is then given by

$$\begin{aligned} \frac{\delta F}{\delta c} &\approx \hat{\mu} + \frac{1}{2} \frac{\partial^3 \hat{f}^{ex}}{\partial c^3} \nabla c \cdot \boldsymbol{\sigma}^2 \cdot \nabla c - \nabla \cdot \left(\frac{\partial^2 \hat{f}^{ex}}{\partial c^2} \boldsymbol{\sigma}^2 \cdot \nabla c \right) \\ &= \hat{\mu} + \frac{1}{2} \frac{\partial^3 \hat{f}^{ex}}{\partial c^3} \nabla c \cdot \boldsymbol{\sigma}^2 \cdot \nabla c - \frac{\partial^3 \hat{f}^{ex}}{\partial c^3} \nabla c \cdot (\boldsymbol{\sigma}^2 \cdot \nabla c) - \frac{\partial^2 \hat{f}^{ex}}{\partial c^2} \nabla \cdot (\boldsymbol{\sigma}^2 \cdot \nabla c) \\ &= \hat{\mu} - \frac{1}{2} \frac{\partial^3 \hat{f}^{ex}}{\partial c^3} \nabla c \cdot \boldsymbol{\sigma}^2 \cdot \nabla c - \frac{\partial^2 \hat{f}^{ex}}{\partial c^2} \nabla \cdot (\boldsymbol{\sigma}^2 \cdot \nabla c). \end{aligned} \quad (\text{C. 2})$$

In the case of $\boldsymbol{\sigma}^2 = \sigma^2 \mathbf{I}$, eq. (C.2) reduces to

$$\frac{\delta F}{\delta c} \approx \hat{\mu} - \frac{1}{2} \frac{\partial^2 \hat{f}^{ex}}{\partial c^2} \sigma^2 (\nabla c)^2 - \frac{\partial^2 \hat{f}^{ex}}{\partial c^2} \sigma^2 \nabla^2 c, \quad (\text{C. 3})$$

or

$$\frac{\delta F}{\delta c} \approx \hat{\mu} - \sigma^2 \left[\frac{1}{2} \frac{\partial^2 \hat{\mu}^{ex}}{\partial c^2} (\nabla c)^2 + \frac{\partial \hat{\mu}^{ex}}{\partial c} \nabla^2 c \right]. \quad (\text{C. 4})$$

Finally noting that

$$\nabla^2 \hat{\mu}^{ex} = \nabla \cdot \left(\frac{\partial \hat{\mu}^{ex}}{\partial c} \nabla c \right) = \frac{\partial^2 \hat{\mu}^{ex}}{\partial c^2} (\nabla c)^2 + \frac{\partial \hat{\mu}^{ex}}{\partial c} \nabla^2 c. \quad (\text{C. 5})$$

allows us to rewrite eq. (C.4) as

$$\frac{\delta F}{\delta c} \approx \hat{\mu} - \frac{1}{2} \sigma^2 \left(\nabla^2 \hat{\mu}^{ex} + \frac{\partial \hat{\mu}^{ex}}{\partial c} \nabla^2 c \right). \quad (\text{C. 6})$$

Substituting eq. (C.6) into the diffusion equation finally gives

$$\frac{\partial c}{\partial t} = \nabla \cdot \left\{ D \nabla \beta \left[\hat{\mu} + \frac{1}{2} \left(\nabla \cdot \sigma^2 \cdot \nabla \hat{\mu}^{ex} + \frac{\partial \hat{\mu}^{ex}}{\partial c} \nabla \cdot \sigma^2 \cdot \nabla c \right) \right] \right\}. \quad (\text{C. 7})$$

Methods D: Linear Stability Analysis within the Square-Gradient Theory

Here we present linear stability analyses of CH and GSG free energy functionals,

$$F_{CH} \equiv \int \left[\hat{f} + \frac{1}{2} \kappa (\nabla c)^2 \right] dV, \quad (\text{D. 1})$$

And

$$F_{GSG} \equiv \int \left[\hat{f} - \sigma^2 \frac{\partial^2 \hat{f}^{ex}}{\partial c^2} (\nabla c)^2 \right] dV, \quad (\text{D. 2})$$

respectively, where both σ^2 and κ are assumed to be constant. Note that eqs. (D.1) and (D.2) are equivalent when $\frac{\partial^2 \hat{f}^{ex}}{\partial c^2} = -\kappa/2\sigma^2$. Consider a system at an initial composition $c(\mathbf{r}) = c_0 + \epsilon \cos(\mathbf{q} \cdot \mathbf{r})$, where $\epsilon \ll 1$. Taylor expanding $\hat{f}$ about x_0 up to 2nd-order gives

$$F_{CH} \approx \int \left[\hat{f}(c_0) + \frac{\partial \hat{f}}{\partial c} (c - c_0) + \frac{1}{2} \frac{\partial^2 \hat{f}}{\partial c^2} (c - c_0)^2 + \frac{1}{2} \kappa (\nabla c)^2 \right] dV, \quad (\text{D. 3})$$

and,

$$\delta F_{CH} = F_{CH} - \int \hat{f}(c_0) dV \approx \int \left[\frac{1}{2} \frac{\partial^2 \hat{f}}{\partial c^2} (\epsilon \cos(\mathbf{q} \cdot \mathbf{r}))^2 + \frac{1}{2} \kappa (\epsilon q^2 \sin(\mathbf{q} \cdot \mathbf{r}))^2 \right] dV, \quad (\text{D. 4})$$

where $q = |\mathbf{q}|$. For small perturbations the saddle-point approximation gives

$$\frac{\delta F_{CH}}{V}(q) \approx \frac{\epsilon^2 q^2}{4} \left[\frac{\partial^2 \hat{f}}{\partial c^2} + \kappa q^2 \right] \delta x, \quad (\text{D. 5})$$

where all quantities are evaluated at x_0 . Applying the standard linear stability analysis for the GSG model, the critical wavelengths are then given by

$$\lambda_{CH}^c = 2\pi \sqrt{-\kappa \left(\frac{\partial^2 \hat{f}}{\partial c^2} \right)^{-1}}, \quad (\text{D. 6})$$

and

$$\lambda_{GSG}^c = 2\pi \sigma \sqrt{2r}. \quad (\text{D. 7})$$

where $r \equiv \frac{\partial^2 \hat{f}^{ex}}{\partial c^2} / \frac{\partial^2 \hat{f}}{\partial c^2}$.

To obtain the fastest-growing Fourier modes among all the modes that do not decay, we consider the diffusion equation for each free energy (eqs. (D.1) and (D.2)). For F_{CH} ,

$$\frac{\partial c}{\partial t} \approx D \nabla^2 \frac{\delta F}{\delta c} \approx D \left[\frac{\partial^2 \hat{f}}{\partial c^2} \nabla^2 c - \kappa \nabla^4 c \right], \quad (\text{D.8})$$

where D is assumed to be constant for small fluctuations. Applying a time-varying perturbation of the form $\delta x = \epsilon \cos(\mathbf{q} \cdot \mathbf{r}) \exp(\omega t)$ into eq. (D.8) gives

$$\omega = -\frac{D}{4} \kappa q^2 \left[\frac{1}{\kappa} \frac{\partial^2 \hat{f}}{\partial c^2} + q^2 \right]. \quad (\text{D.9})$$

Solving for the q that maximizes ω gives the fastest growing Fourier mode wavelength as

$$\lambda_{CH}^{max} = 2\pi \sqrt{-\left(\frac{\partial^2 \hat{f}}{\partial c^2}\right)^{-1}} 2\kappa = 2\pi \sqrt{-\left(\frac{\partial^2 \hat{f}^{ex}}{\partial c^2}\right)^{-1}} 2\kappa r, \quad (\text{D.10})$$

for the CH free energy and

$$\lambda_{GSG}^{max} = 4\pi\sigma\sqrt{r}. \quad (\text{D.11})$$

The dominant Fourier modes for the CH and GSG models diverge from each other as the tricritical point is approached ($r \rightarrow \infty$) according to

$$\lambda_{GSG}^{max} - \lambda_{CH}^{max} = 2\pi\sqrt{r} \left(2\sigma - \sqrt{-2\kappa \left(\frac{\partial^2 \hat{f}^{ex}}{\partial c^2}\right)^{-1}} \right). \quad (\text{D.12})$$

The corresponding growth rates, ω_{CH}^{max} and ω_{GSG}^{max} , which scale as q^4 as the tricritical point is approached (see eq. (D.9)), tend to zero as

$$\omega_{GSG}^{max} - \omega_{CH}^{max} = -\frac{D}{8} \left[2\sigma^2 \frac{\partial^2 \hat{f}^{ex}}{\partial c^2} (q_{GSG}^{max})^4 - \kappa (q_{CH}^{max})^4 \right] \propto r^{-4}. \quad (\text{D.13})$$

Therefore, the spinodal decomposition timescales, $\tau_{CH}^{max} = 1/\omega_{CH}^{max}$ and $\tau_{GSG}^{max} = 1/\omega_{GSG}^{max}$, both tend towards infinity as

$$\tau_{GSG}^{max} - \tau_{CH}^{max} \propto \frac{1}{\omega_{GSG}^{max}} - \frac{1}{\omega_{CH}^{max}} \approx r^4. \quad (\text{D.14})$$

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Figures and Tables

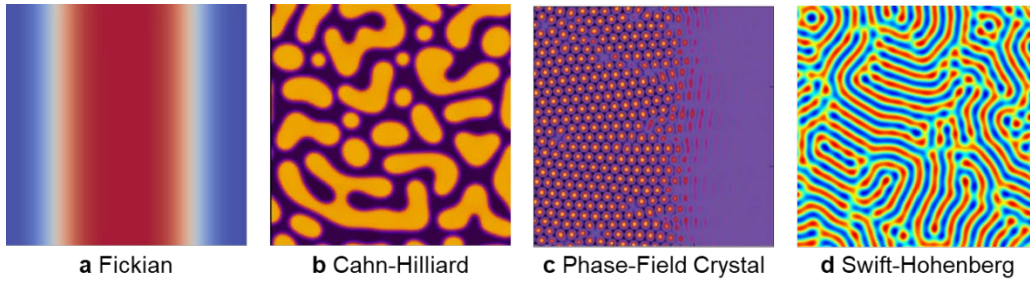


Figure 1. Representative pattern structures predicted by various free energy functional-based continuum models. a Fickian diffusion⁵⁴, **b** Cahn-Hilliard equation⁵⁵, **c** Phase-field crystal⁵⁶, and **d** Swift-Hohenberg equation⁵⁷.

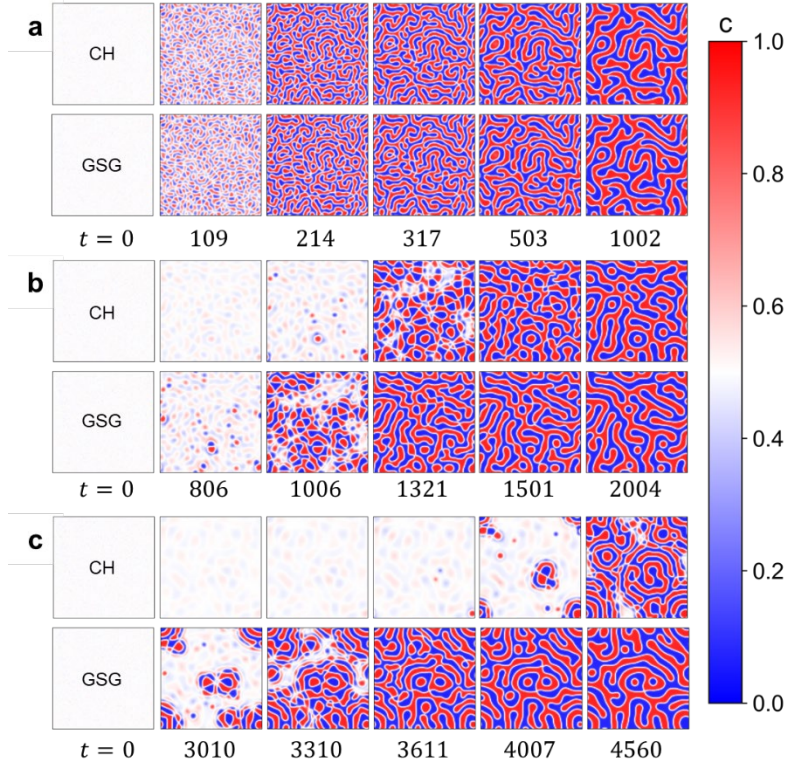


Figure 2. Spinodal decomposition behavior in an initially homogeneous, subcritical mixture predicted by CH (top) and GSG (bottom) models for three mixture free energies. **a** $\epsilon = 0$ and $\eta_{CH} = 3.0$, **b** $\epsilon = 0.022$ and $\eta_{CH} = 2.91$, and **c** $\epsilon = 0.026$ and $\eta_{CH} = 2.90$. In all cases **a, b, c**: $\sigma = 2a_0$ and time is scaled by the grid diffusion timescale, $\tau_D = 0.01(l_G)^2/D$.

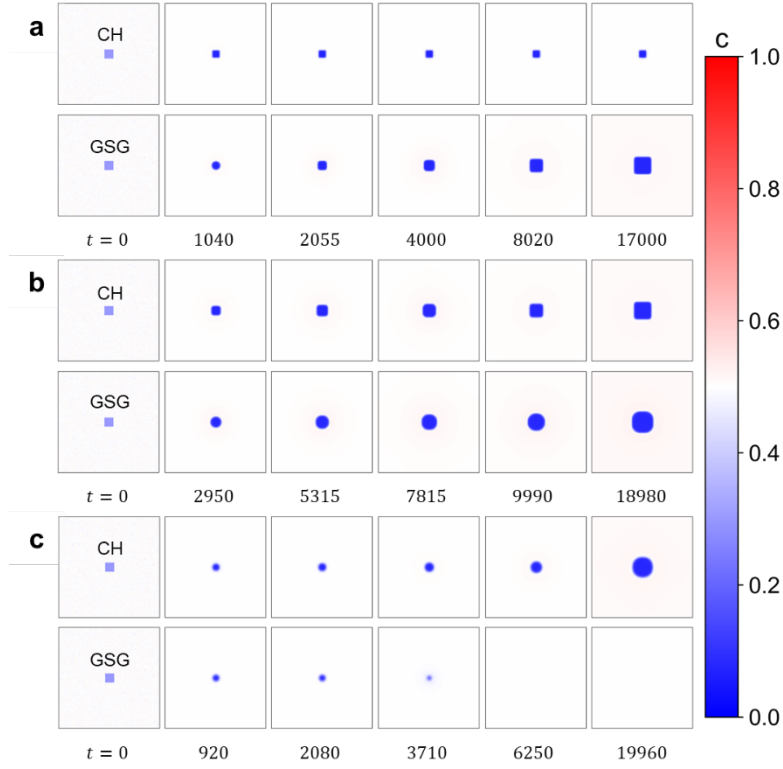


Figure 3. Growth behavior of a square compositional heterogeneity predicted by CH (top) and GSG (bottom) models as a function of interaction range for a supercritical mixture. **a** $\sigma = 2a_0$, **b** $\sigma = 2.3a_0$, **c** $\sigma = 3.3a_0$. For all cases **a**, **b**, **c**: $\epsilon = 0.075$, $\eta_{CH} = 2.70$, and time is scaled by the grid diffusion timescale, $\tau_D = 0.01(l_G)^2/D$.

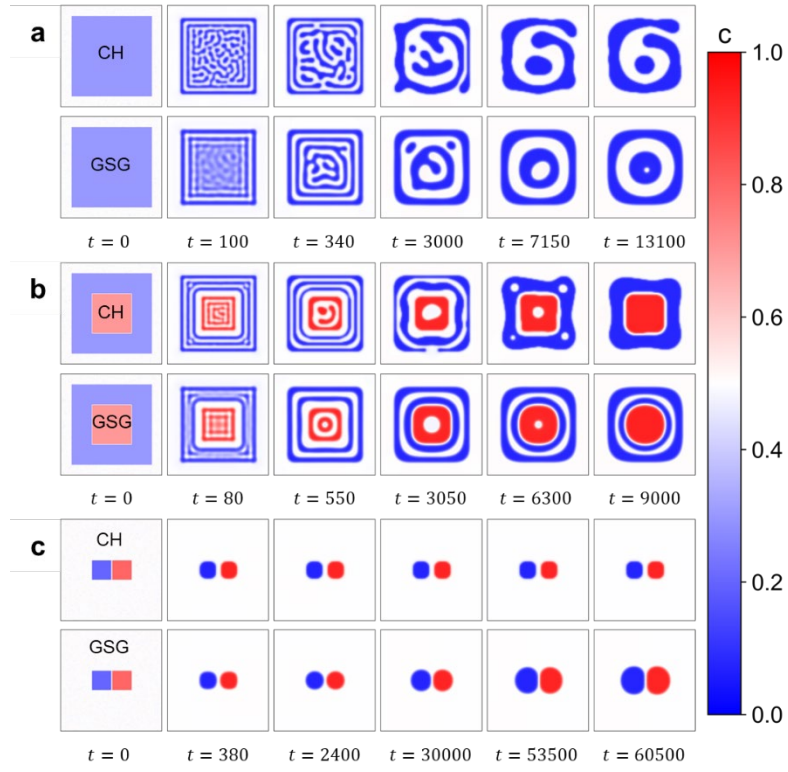


Figure 4. Pattern evolution due to different initial compositional heterogeneities predicted by CH (top) and GSG (bottom) models in a supercritical mixture. For all cases, **a, b, c:** $\epsilon = 0.1$, $\sigma = 3a_0$, and time is scaled by the grid diffusion timescale, $\tau_D = 0.01(l_G)^2/D$

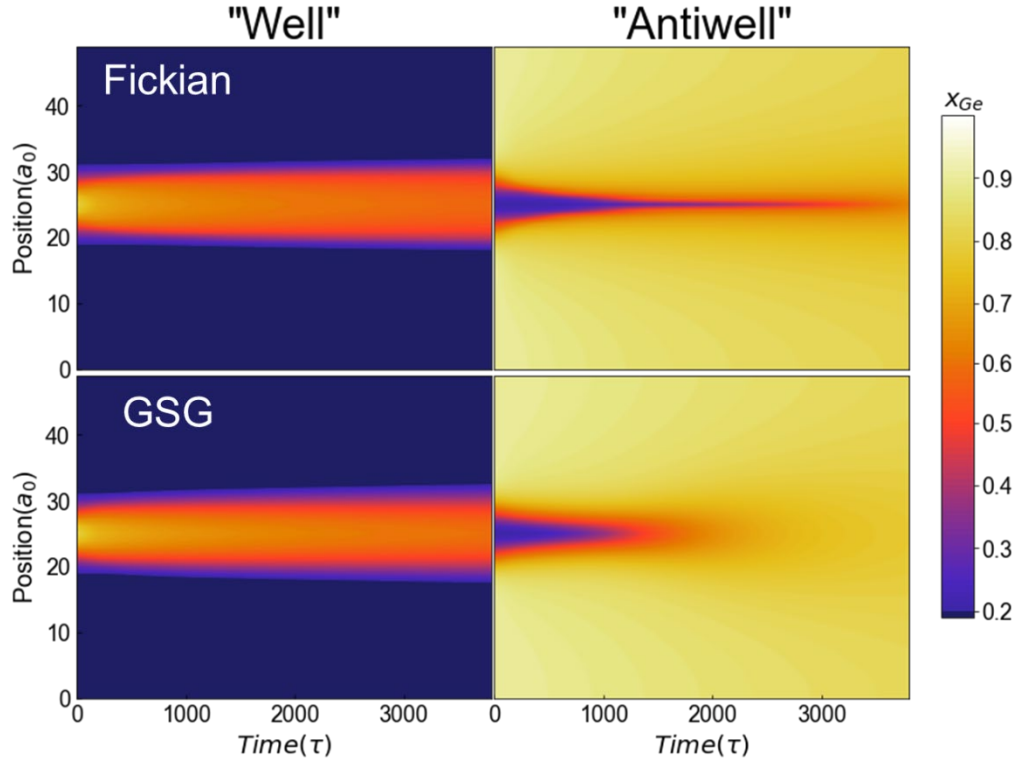


Figure 5. One-dimensional interdiffusion as a function of time around a Gaussian well in SiGe. Top row – Fickian, bottom row – GSG. ‘Well’ compositional profile (left) is given by $x_{Ge} = c_{Ge}/c_{tot} = 0.1 + 5.26 \cdot N(25, \sqrt{3})$, and ‘anti-well’ compositional profile (right) is $x_{Ge} = c_{Ge}/c_{tot} = 0.9 - 5.26 \cdot N(25, \sqrt{3})$. The quantity c_{tot} is the concentration of atomic sites. Position is scaled by a_0 . Time is scaled by the well variance diffusion timescale, $\tau = t/\tau_D$, with $\tau_D = 0.3/D_{max}$ and $D_{max} = D(x = 1)$. In all cases, $\sigma = 2a_0$.