Phase Transitions Affected by Molecular Interconversion

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If a binary liquid mixture, composed of two alternative species with equal amounts, is quenched from a high temperature to a low temperature, below the critical point of demixing, then the mixture will phase separate through a process known as spinodal decomposition. However, if the two alternative species are allowed to interconvert, either naturally (e.g. the equilibrium interconversion of enantiomers) or forcefully (e.g. via an external source of energy or matter), then the process of phase separation may drastically change. In this case, depending on the nature of interconversion, two phenomena could be observed: either phase amplification, the growth of one phase at the expense of another stable phase, or microphase separation, the formation of nongrowing (steady-state) microphase domains. In this work, we generalize the Cahn-Hilliard theory of spinodal decomposition to include molecular interconversion of species and describe the physical properties of systems undergoing either phase amplification or microphase separation. We apply the developed theory to describe the simulation results of three atomistic models which demonstrate phase amplification and/or microphase separation. We also discuss the application of our approach to phase transitions in polyamorphic liquids. Lastly, we describe the effects of fluctuations of the order parameter in the critical region on phase amplification and microphase separation.

I. INTRODUCTION

Phase transitions play a crucial role in condensed-matter physics and chemistry, astrophysics, biology, and engineering applications. Examples include structural, superconductive, and ferromagnetic transitions in solids, superfluidity in helium, as well as various liquid-solid, liquid-liquid, and liquid-vapor phase transformations. While equilibrium phase transitions in simple systems are well-studied and understood, the description of phase transformations in the presence of interconversion between alternative molecular or supramolecular states, and in systems far from equilibrium, is much less developed.

Unlike separation of fluids and solids into phases of different densities and/or concentrations, which coexist in equilibrium, ferromagnetic and ferroelectric materials do not establish equilibrium coexistence between alternative magnetic or ferroelectric states. Yet, such materials often consist of metastable long-lived micro-domains. However, if a phase separating substance also exhibits interconversion of species, similar to the flipping of magnetic spins or electric dipoles, the thermodynamics and kinetics of phase separation will dramatically change.

In magnetic and ferroelectric materials, there is no restriction on the direction of magnetization or polarization, meaning that there is no conservation of the number of magnetic spins or electric dipoles with a particular orientation. As a result, the phase domain in such materials will grow with a preference to one magnetic- or electric-spin orientation at the expense of the other one, the phenomenon known as “phase amplification”. The phenomenon of phase amplification can also be observed in fluids with molecular interconversion of species due to the competition between the dynamics of diffusion, associated with a conserved property (the number of particles), and the dynamics of interconversion, associated with a nonconserved property. It has been shown by Shumovskyi et al. through the simulations of a hybrid binary-lattice/Ising model that by introducing even a small probability for the species to interconvert promotes phase amplification in binary mixtures.

If a binary mixture, initially containing equal amounts of molecules, is quenched from the one-phase homogeneous region at a high temperature into the unstable region, below the critical temperature of demixing, then the mixture will evolve towards phase separation at early stages through a process known as “spinodal decomposition”. In this work, we generalize Cahn-Hilliard’s theory of spinodal decomposition to include natural (equilibrium) and forceful (nonequilibrium) molecular interconversion of species. In particular, we quantitatively describe the phenomenon of phase amplification and the results obtained by Shumovskyi et al.

By introducing a dissipation of energy, which drives the system away from equilibrium, into the generalized Cahn-Hilliard theory, we demonstrate that a striking phenomenon of steady-state microphase separation may occur. We show that the formation of the microphase domain is controlled through the magnitude of the energy dissipation and its competition with interconversion and mutual diffusion.

The paper is organized as follows. In Sec. II, we generalize Cahn-Hilliard’s theory to include interconversion of species in equilibrium and dissipative systems. In Sec. III, we investigate the domain growth for a phase separating system exhibiting molecular interconversion through the time evolution of the structure factor. In Sec. IV, we compare our approach with the results of simulations of a hybrid binary-lattice/Ising model and a chiral-mixture model. In Sec. V, we consider a connection between our approach to phase transitions

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FIG. 1. A symmetric binary mixture is quenched along the critical concentration (where the order parameter \( \hat{c}_A = 0 \)) from its equilibrium value, \( \mu \) (which may be positive or negative) can be written in a variety of forms, but in this work, the case \( \pi < 0 \) (a “sink” of energy) is considered, which only affects the interconversion dynamics. Alternatively, the source could promote interconversion through the flux of matter such as in a system constrained to an adsorbing-desorbing layer\(^{30}\), or it could affect the diffusion dynamics to enhance or inhibit phase separation through the interactions between the molecules and external radiation\(^{31}\).

with molecular interconversion to liquid polyamorphism\(^{25,26}\), a striking phenomenon which could be a result of interconversion between molecular or supramolecular structures\(^{29,27}\). In Sec. VI, we provide scaling arguments to generalize our approach beyond the mean field approximation to account for the effects of critical fluctuations. In the conclusion, we provide suggestions for the extension of our approach to a broader range of phenomena.

II. SPINOdal DECOMPOSITION AFFECTED BY MOLECULAR INTERCONVERSION

Cahn-Hilliard’s theory of spinodal decomposition, in a binary mixture containing species A and B, can be generalized through the addition of two terms in the temporal evolution of the order parameter as

\[
\frac{\partial \hat{c}_A}{\partial t} = M \nabla^2 \hat{\mu} - L \hat{\mu} + \pi \tag{1}
\]

For this particular case, the order parameter, \( \hat{c}_A \), is uniquely linked to the concentration of species A as \( \hat{c}_A = 2(c_A - 1/2) \). The first term on the right hand side of Eq. (1) describes the mutual diffusion dynamics. In the classical Cahn-Hilliard theory, only this term exists\(^{20}\). The second term describes the interconversion dynamics\(^{28}\) and the third term is a source of energy (or matter), which drives the system to a nonequilibrium state. The prefactors \( M \) and \( L \) are the corresponding kinetic coefficients\(^{29}\), and \( \hat{\mu} = \mu / \rho_b k_B T_c \) is the reduced deviation of the chemical-potential difference in solution (\( \mu = \mu_A - \mu_B \)) from its equilibrium value, \( \mu = 0 \), where the critical density and temperature for liquid-liquid phase separation are \( \rho_c \) and \( T_c \), respectively. Depending on the model, the source term, \( \pi \) (which may be positive or negative) can be written in a variety of forms, but in this work, the case \( \pi < 0 \) (a “sink” of energy) is considered, which only affects the interconversion dynamics. Alternatively, the source could promote interconversion through the flux of matter such as in a system constrained to an adsorbing-desorbing layer\(^{30}\), or it could affect the diffusion dynamics to enhance or inhibit phase separation through the interactions between the molecules and external radiation\(^{31}\).

A. Chemical Potential for Equilibrium Molecular Interconversion

To understand the evolution of the concentration given by Eq. (1), we begin with deriving the chemical potential for a symmetric binary mixture. This system can be described by a Landau-Ginzburg free-energy functional with a single order parameter, \( \hat{c}_A \). This functional reads as

\[
F[\{\hat{c}_A\}] = \int_V \left( \hat{G} (\hat{c}_A, T, P) + \frac{1}{2} \kappa |\nabla \hat{c}_A|^2 \right) dV \tag{2}
\]

where the first term represents the thermodynamic “bulk” free energy and the second term is included to describe the contribution to the free energy due to inhomogeneities within the system. For an isotropic system, the coefficient \( \kappa \) is the square of the range of intermolecular interactions, on the order of the square of the molecular size. In the applications to the atomistic models (Sec. IV), we adopt \( \kappa = 1 \).

The bulk free energy density for the system, \( \hat{G} \), is the reduced Gibbs energy, \( \hat{G} = G / \rho_b k_B T_c \), as

\[
\hat{G} = \hat{G}_A + (1 - \hat{c}_A) \hat{G}_{BA} + \hat{G}_{\text{mix}} \tag{3}
\]

where \( \hat{G}_{BA} = \rho_b^0 - \rho_b^A \) is the difference between the Gibbs energies (chemical potentials) of pure species A and B, referred to as the Gibbs energy change of reaction. For the symmetric binary-lattice (“regular solution”) model, \( \hat{G}_{\text{mix}} \) is formulated through the order parameter, \( \hat{c}_A \), and in the mean field approximation, it reads as

\[
\hat{G}_{\text{mix}} = \hat{T} \left[ \frac{1 + \hat{c}_A}{2} \ln \left( \frac{1 + \hat{c}_A}{2} \right) + \frac{\vepsilon}{4} (1 - \hat{c}_A^2) \right] \tag{4}
\]

where \( \hat{T} = T / T_c \) and \( \vepsilon \) is a non-ideality interaction parameter, which generally depends on temperature and pressure. The conditions for liquid-liquid phase equilibrium is

\[
\frac{\partial \hat{G}_{\text{mix}}}{\partial \hat{c}_A} = \frac{\hat{T}}{2} \ln \left( \frac{1 + \hat{c}_A}{1 - \hat{c}_A} \right) - \frac{\vepsilon}{2} \hat{c}_A = 0 \tag{5}
\]

From the stability condition, \( \partial^2 \hat{G}_{\text{mix}} / \partial \hat{c}_A^2 = 0 \), the interaction parameter is \( \vepsilon = 2 \) in units of \( k_B T_c \), since \( T_c = \vepsilon / 2 k_B \).

In this work, we consider the interconversion between molecular states A and B through a reversible chemical reaction of the form

\[
A \xrightarrow{k_1} \frac{k_2}{k_1} \xrightarrow{B}
\]
where $k_1$ and $k_2$ are the forward and reverse reaction rates respectively. Since the order parameter could be considered as the reaction coordinate, the chemical reaction equilibrium condition reads
\[ \frac{\partial G}{\partial \hat{c}_A} \bigg|_{T,P} = \frac{\partial G_{\text{mix}}}{\partial \hat{c}_A} \bigg|_{T,P} - \frac{1}{2} G_{BA} = 0 \]  
(7)

This reaction-equilibrium condition constrains the number of thermodynamic degrees of freedom for the system. Consequently, the fraction of interconversion, given through the order parameter $\hat{c}_A$, is no longer an independent thermodynamic variable, but instead, becomes a function of temperature and pressure. The reduced Gibbs energy change of reaction, $\hat{G}_{BA}$, can be expressed through the reaction equilibrium constant $\mathcal{K}$, and given in the linear approximation as
\[ \hat{G}_{BA} = -\hat{T} \ln \mathcal{K} = \hat{e}_0 + \hat{P} - \hat{s} \]  
(8)

where $\hat{e} = e/k_BT_c$ is the reduced energy change of reaction, $\hat{0} = \hat{0}/k_BT_c$ is the reduced volume change of reaction, and $\hat{s} = s/k_BT$ is the entropy change of reaction.\(^9\)^\(^{27}\)

Next, we consider the chemical potential for a system undergoing spinodal decomposition towards both chemical-reaction and phase equilibrium. The reduced time-dependent chemical potential is found from the functional derivative of Eq. (2) as
\[ \hat{\mu} = \frac{\partial G}{\partial \hat{c}_A} - \kappa \nabla^2 \hat{c}_A \]  
(9)

where the order parameter depends on space and time, $\hat{c}_A = \hat{c}_A(r,t)$ and the first term is
\[ \frac{\partial G}{\partial \hat{c}_A} = \frac{\hat{T}}{2} \ln \left( \frac{1 + \hat{c}_A}{1 - \hat{c}_A} \right) - \frac{e}{2} \hat{c}_A - \frac{1}{2} \left( \hat{e} + \hat{0}P - \hat{s} \hat{T} \right) \]  
(10)

Expanding the first term to first order in $\hat{c}_A$ via a Taylor series around $\hat{c}_A = 0$ (the value of the order parameter at the initial time $t = 0$), gives $\partial G/\partial \hat{c}_A = \approx \hat{c}_A^{-1} \hat{c}_A$, where the inverse susceptibility in the limit of zero wavenumber is $\hat{\chi}^{-1}_{q=0} = \partial^2 G/\partial \hat{c}_A^2$. In the mean-field regular-solution model, the inverse susceptibility scales as $\hat{\chi}^{-1}_{q=0} \sim \Delta \hat{T}$, where $\Delta \hat{T} = T/T_c - 1$ is the reduced distance to the critical temperature. Therefore, the chemical potential defined in Eq. (9) in the first-order approximation becomes
\[ \hat{\mu} = \Delta \hat{T} \hat{c}_A - \frac{1}{2} \left( \hat{e} + \hat{0}P - \hat{s} \hat{T} \right) - \kappa \nabla^2 \hat{c}_A \]  
(11)

We emphasize that the reduced chemical potential, given by Eq. (11), when the term related to interconversion is absent, is the same as obtained in the classical Cahn-Hilliard theory.\(^{20}\)

### B. Four Scenarios of Phase Domain Growth

To illustrate the effects on the temporal evolution of the order parameter produced by the three terms in Eq. (1), we consider the simplest chemical reaction where the interconversion equilibrium constant $\mathcal{X} = k_1/k_2 = 1$, such that $\ln \mathcal{X} = 0$. Therefore, the Gibbs energy change of reaction, given by Eq. (8), is $\hat{G}_{BA} = 0$. In this approximation, the interconversion between $A$ and $B$ mirrors the flipping of spins in the Ising model, in which there is no heat or volume change of the reaction. Using the chemical potential defined by Eq. (11) along with this approximation, we consider the following four scenarios.

#### 1. Diffusion Dynamics Toward Equilibrium

When there is no natural and forceful interconversion ($\pi = 0$ and $L = 0$), Eq. (1) reduces to the classical Cahn-Hilliard equation\(^{20}\)
\[ \frac{\partial \hat{c}_A}{\partial t} = M \nabla^2 \hat{\mu} \]  
(12)

This equations describes the dynamics of a system where the total number of particles of each type is conserved, and as such, when quenched into the unstable region (under the spinodal), the system will evolve toward phase separation. This equation can be analytically solved with use of Fourier analysis to determine the phase domain growth rate (known as the “amplification factor”)\(^{20}\). In the Cahn-Hilliard theory, the amplification factor is given by
\[ \omega(q) = -Dq^2(1 - \xi^2q^2) \]  
(13)

where $\xi$ is the correlation length of concentration fluctuations and $D$ is the mutual diffusion coefficient; in the mean field approximation, $\xi^2 = \kappa/\hat{\chi}^{-1}_{q=0}$ and $D = M\hat{\chi}^{-1}_{q=0}$. In the unstable (under the spinodal) region, the susceptibility is negative, and consequently, the mutual diffusion coefficient is negative and is the driving force for phase separation through spinodal decomposition.\(^{20}\)

#### 2. Interconversion Dynamics Toward Equilibrium

In the absence of forceful interconversion and molecular mobility ($\pi = 0$ and $M = 0$), Eq. (1) reduces to the Cahn-Allen equation\(^{28}\)
\[ \frac{\partial \hat{c}_A}{\partial t} = -L\hat{\mu} \]  
(14)

This equation describes the dynamics of a system where the number of particles of a specific type (A or B) is not conserved due to the possibility of interconversion of species. Since there is no diffusion, but the species are allowed to interconvert, this equation describes the dynamics of an “Ising-like” system with a nonconserved order parameter where the flipping of spins mirrors the interconversion of species A and B. The growth rate for the system exhibiting phase amplification is
\[ \omega(q) = -L\hat{\chi}^{-1}_{q=0}(1 - \xi^2q^2) \]  
(15)
This equation is fundamentally different from the amplification factor in Cahn-Hilliard’s theory, Eq. (13), as it does not contain the wavenumber coupled with the susceptibility $\hat{\chi}^{-1}$, and thus, describes the relaxation dynamics of the nonconserved order parameter. In addition, the dynamics of such natural interconversion is conceptually different from a chemical reaction caused by the local interactions of particles. In our case, interconversion may be enhanced or diminished through the long-ranged interactions of species. Consequently, this interconversion is dependent on both the bulk and interfacial terms in the Landau-Ginzburg free energy functional, Eq. (2).

Therefore, if the mixture starts in a homogeneous state with an equal concentration of each species, then after infinite time, only one phase will survive. The competition and growth of one of the alternative stable phases at the expense of the other is known as phase amplification. We note that if interconversion is unbiased with respect to the formation of the order parameter, then the term, $L\hat{\mu}$, in Eq. (14) will not depend on the formation of the interface and the phenomenon of phase amplification will not occur. Consequently, $\hat{\mu}$ in this term will only contain the bulk part of the chemical potential.

We emphasize that the phase transition through phase amplification is fundamentally different from phase separation. Phase amplification occurs to avoid the formation of an energetically unfavorable interface between alternative stable phase domains. This phenomenon is only possible due to the conserved nature of the order parameter. In contrast, in a phase separating binary mixture the formation of an interface is required due to the conserved nature of the order parameter. However, we note that in macroscopic systems where the interfacial energy is much smaller than the bulk energy, a system with a nonconserved order parameter may enter a metastable state in which an interface forms between phases. Thus, the size of the system plays a crucial role in phase amplification. With increasing system size, the energy of the surface decreases when compared to the bulk energy, the conformational energy of the metastable interface becomes less unfavorable, and the possibility that the system will form an interface drastically increases.

3. Diffusion Dynamics in the Presence of a Racemizing Force Toward a Steady State

If we consider a source of forceful interconversion that is independent of the chemical potential in the equilibrium state, then it will drive the system towards a “racemized state” - a spatially homogeneous state with an equal amount of interconverting species. Thus, forceful interconversion may be viewed as a local chemical reaction for which the chemical potential difference depends only on the bulk concentration. For this reason, we will refer to such a source as a “racemizing” force. If we consider the effect of a racemizing force on a system with conserved order-parameter dynamics ($L = 0$), this corresponds to the model originally introduced by Glotzer et al. where in the first order approximation (valid only near thermodynamic equilibrium) the racemizing term has the form of $\pi = k_2c_B - k_1c_A$. Rearranging this reaction rate using the fact that the total number of particles in the system is conserved, $c_A + c_B = 1$ and $K = k_1 = k_2$, then the racemizing force may be written in terms of the order parameter ($\hat{c}_A$) as $\pi = -K\hat{c}_A(r, t)$. In this case, Eq. (1) is given by

$$\frac{\partial \hat{c}_A}{\partial t} = -K\hat{c}_A + M\nabla^2 \mu$$

Glotzer et al. found that the addition of such a specific type of a racemizing force causes the system to phase separate into microphase domains with a characteristic length scale less than the size of the simulation box. This model describes the formation of microphase domains in a nonequilibrium steady-state in the presence of a racemizing force.

4. Hybrid Diffusion and Interconversion Dynamics in the Presence of a Racemizing Force Toward a Steady State

Lastly, we consider a more general case in which diffusion, interconversion, and forceful racemization are present in the system together. Using the racemizing force considered by Glotzer et al., $\pi = -K\hat{c}_A$, and the chemical potential described by Eq. (11), we can express Eq. (1) in the form

$$\frac{\partial \hat{c}_A}{\partial t} = -(L + L\hat{\chi}_{q=0}^{-1})\hat{c}_A + (M\hat{\chi}_{q=0}^{-1} + L\kappa)\nabla^2 \hat{c}_A - M\kappa \nabla^4 \hat{c}_A - K\hat{c}_A$$

This differential equation has the following solution:

$$\hat{c}_A = \hat{c}_0 + \sum_i \hat{c}_i e^{\omega(q) t} \cos(q_i \cdot r)$$

where $\hat{c}_0$ and $\hat{c}_\infty$ are constants determined by the initial ($t = 0$) and steady-state ($t \to \infty$) conditions of the order parameter, respectively. Also, $\omega(q)$ is the generalized growth rate, (amplification factor), defined as

$$\omega(q) = -(L\hat{\chi}_{q=0}^{-1} + K) - (M\hat{\chi}_{q=0}^{-1} + \kappa L)q^2 - M\kappa q^4$$

We note that a conceptually similar equation for the growth rate in a system with an auto-catalytic reaction was also obtained by Lefever et al. Eq. (20) can also be expressed through the susceptibility, $\hat{\chi}_{q=0}$, and the correlation length, $\xi$, as

$$\omega(q) = -K - (M\xi^2 + L\kappa)(1 - \xi^2 q^2)$$

The generalized amplification factor describes the characteristics of phase domain growth for both phase amplification and microphase separation.
C. Phase Amplification vs. Microphase Separation

Whether phase amplification or microphase separation will occur depends on the interplay of the three dynamics in the system: diffusion, interconversion, and forceful racemization, as given through the amplification factor, Eq. (21). In the limiting cases when one of the rates dominates the system, complete phase separation, unrestricted phase amplification, or a homogeneous steady state will be observed. The results of these observations are summarized in Table I.

### Table I. Limiting cases of the interplay between diffusion, interconversion, and forceful racemization.

|       | $M = 0$ | $L = 0$ |
|-------|---------|---------|
| $M = 0$ | Homogeneous Steady State |
| $K = 0$ | Unrestricted Phase Amplification Separation |

* Without diffusion, the competition between natural and forceful interconversion will produce either phase amplification or a homogeneous steady state - see Fig. 2.

### Table II. Conditions for phase amplification and microphase separation as illustrated in Figure 2. The left column corresponds to the solid lines and the right column corresponds to the dashed lines.

| $M|\hat{\chi}_{q=0}^{-1}| > LK$ | $M|\hat{\chi}_{q=0}^{-1}| < LK$ |
|----------------------------------|----------------------------------|
| Restricted (Slow) Phase Amplification | Unrestricted (Fast) Phase Amplification |
| $L|\hat{\chi}_{q=0}^{-1}| > K$ | Microphase Separation Steady State |
| $L|\hat{\chi}_{q=0}^{-1}| < K$ | Homogeneous Separation |

In a system with mixed dynamics where diffusion, interconversion, and forceful racemization are present, the interplay between these three rates produces either phase amplification, microphase separation, or a homogeneous steady state with no domain growth. The resultant effect on the system may be determined through the shape and intercepts of the amplification factor. For instance, the competition between natural interconversion ($L\hat{\chi}_{q=0}^{-1}$) and forceful racemization ($K$), as follows from Eq. (20), shifts the intercept of $\omega(q = 0)$ up or down producing either phase amplification or microphase separation depending on their magnitude. Meanwhile, the competition between diffusion ($M\hat{\chi}_{q=0}^{-1}$) and natural interconversion ($LK$) dynamics is described by the concavity and convexity of the amplification factor around $q = 0$, which when combined with the position of the intercept determines whether restricted or unrestricted phase amplification will be observed or if the system will remain homogeneous instead of phase separating into microphase domains. Amplification factors for various relationships between $M$, $L$, and $K$ are shown in Figure 2 and summarized in Table II.

To achieve phase amplification, the racemizing rate must be slower than the natural interconversion rate, $K < L|\hat{\chi}_{q=0}^{-1}|$, such that the amplification factor is shifted up. Alternatively, microphase separation occurs when the racemizing rate and the diffusion rate is faster than the natural interconversion rate, such that $K > L|\hat{\chi}_{q=0}^{-1}|$ and $M|\hat{\chi}_{q=0}^{-1}| > \kappa L$, respectively. We note that in the case when forceful racemization overcomes natural interconversion (while the diffusion rate is slower than the interconversion rate) the system will be in a homogeneous state as the amplification factor is negative for all wavenumbers.

The conditions for whether the system will achieve complete macro phase separation, undergo microphase separation, or experience phase amplification can be determined from the characteristic wavenumbers of the amplification factor, Eq. (21), found from its two roots and maximum. These wavenumbers are: $q_m^0$, the wavenumber corresponding to the fastest growing inhomogeneities; $q_-$, the first root of $\omega(q)$; and $q_+$, the second root of $\omega(q)$. These three characteristic wavenumbers are related through $q_-^2 = 2(q_m^0)^2 - q_+^2$. As will be proven in Sec. III, the existence of a non-zero $q_-$ indicates steady-state microphase separation; such that, after infinite time, the size of the steady-state phase domain, $R_\infty$, will be described by $R_\infty \sim 1/q_-$, which in the lowest order approximation is given through $M$, $L$, and $K$ as

$$q_-^2 = \frac{K - L\hat{\chi}_{q=0}^{-1}}{M\hat{\chi}_{q=0}^{-1} - LK} = \frac{K - L\hat{\chi}_{q=0}^{-1}}{D_{\text{eff}}^0}$$

(22)

where $D_{\text{eff}}^0 = -\hat{\chi}_{q=0}^{-1}(M - L\hat{\chi}_{q=0}^{-2})$ is the effective diffusion coefficient modified by interconversion kinetics. Additionally,
solving Eq. (21) for \( q_m^0 \), gives

\[
(q_m^0)^2 = \frac{1}{\xi^2} \left( 1 - \frac{L}{M} \xi^2 \right)
\]

(23)

The maximum of the amplification factor is shifted in comparison to Cahn-Hilliard theory, \( q_m^0 = 1/\sqrt{2\xi} \),\(^{20}\) as shown in Figure 2. This shift is independent of the strength of the racemizing force.

III. STRUCTURE FACTOR: MANIFESTATION OF MICROPHASE SEPARATION

We have observed in atomistic models\(^{19,24,37,41}\) (discussed in Sec. IV.) and through computational calculations of the time-dependent structure factor for the system\(^{42}\) that the steady-state domain size may be predicted from the lower cut-off wave number, \( q_\infty \), determined, and when \( \omega(q, t) \) may be written in the form

\[
S(q, t) = S_\infty(q) \left( 1 - e^{2\omega(q, t)t} \right)
\]

(25)

which is valid from the initial stages of spinodal decomposition to the coarsening regime\(^{31,53}\). The steady-state (infinite time) structure factor is given by

\[
S(q, t \to \infty) = S_\infty(q) = \frac{Mq^2 + L\kappa}{\omega(q, t \to \infty)}
\]

(26)

It can be seen that in the absence of forceful interconversion \( (K = 0, \text{equilibrium conditions}) \) when either \( L = 0 \) or \( M = 0 \), then this equation reduces to the Ornstein-Zernike structure factor - \( S_\infty = \xi^2/(1 + \xi^2 q^2) \). To highlight the time-dependent effects on the amplification factor, it is most convenient to express Eq. (21) through the wavenumbers corresponding to

FIG. 3. Temporal evolution of the structure factor: a) for a system undergoing diffusion dynamics \( (M = 1) \) toward an equilibrium state in the absence of interconversion \( (L = 0) \) and forceful racemization \( (K = 0) \); b) for a system undergoing a hybrid of diffusion \( (M = 1) \) and interconversion \( (L = 0.01) \) dynamics in the presence of forceful racemization \( (K = 1.5 \times 10^{-3}) \) toward a steady state. The structure factor, given by Eq. (20), exhibits a crossover from spinodal decomposition to the nucleation regime. The dashed-black curves indicate the development of the maximum of the structure factor. The characteristic crossover time is defined in Eq. (28) and adopted as \( \tau = 100 \). In (a) the evolution of the maximum of the structure factor moves to \( q = 0 \) for infinite-size system and saturates at \( S_m(q = 0, t \to \infty) = 1/(2\xi^2) = 5 \) for \( \Delta T = -0.1 \). In contrast, in (b) the evolution of the maximum is interrupted at a characteristic cut-off wavenumber predicted by the amplification factor, \( q_m^0(t \to \infty) \propto q_\infty \), and it saturates at \( S_m(q_\infty, t \to \infty) = 417 \).
the maximum \( (q_m^0) \) and lower cut-off \( (q_-) \) of the amplification factor, Eqs. (22 and 23) respectively, as
\[
\omega(q,t) = M\kappa(q_m^0)^2(t)[(q_m^0)^2(t) - 2q_-] - M\kappa[q^2 - (q_m^0)^2(t)]^2 \tag{27}
\]
In this form, the amplification factor highlights the time dependence of \( q_m^0 = q_m^0(t) \), while illustrating that \( q_- \) is an intrinsic property of the system which determines the steady-state cut-off of the growing domain sizes, \( q_m^0(t \to \infty) \approx q_- \). The origin of the time dependence of \( q_m^0 \) is due to the change in concentration at constant temperature from the unstable \( (\xi_A = 0) \) to the stable \( (\xi_A > 0) \) regime present in the higher order terms of Eq. (10), \( \hat{S}^{-1}_{q=0} \approx \Delta T + \hat{C}_A(t) \). Based on observations in simulations,\(^{24,42} \) the time dependence of \( q_m^0(t) \), through \( \hat{S}^{-1}_{q=0} \), may be approximated by the interpolation between the two physical limits of \( q_m^0(t = 0) \) and \( q_m^0(t \to \infty) \) as
\[
q_m^0(t) = q_m^0(t = 0)e^{-t/\tau} + q_- (1 - e^{-t/\tau}) \tag{28}
\]
where \( \tau \) is a system-dependent parameter, which controls the crossover between spinodal decomposition and nucleation regimes.

To describe the crossover of the time-dependent structure factor, Eq. (25), between the two regimes, the appropriate scaling behavior must still be obeyed. As given by Lifshitz-Slyozov’s theory for Oswald ripening\(^{34,55} \), the nucleation regime is characterized by an Ornstein-Zernike structure factor that scales with time as \( S(q,t) \approx t \) and a phase domain size that grows as \( q \approx t^{1/3} \).\(^{50} \) We note that in the classical Cahn-Hilliard theory for the early stage of spinodal decomposition, the phase domain size grows as \( q \approx t^{1/4} \).\(^{53} \) To appropriately introduce the scaling crossover from \( q \approx t^{1/4} \) to \( q \approx t^{1/3} \), we adopt the scaling relation for the “crossover time” \( (t_x) \), suggested by Binder et al., that in the nucleation regime the exponential growth scales with time and wavenumber as \( \omega(q,t_x) = t_q \).\(^{50} \) Accordingly, we use the following Padé approximant in the exponential factor in Eq. (25), such that the time, \( t \), is replaced by the crossover time, \( t_x \), given by
\[
t_x = \frac{t(t + \tau)}{1 + t\tau} \tag{29}
\]
where \( \tau \) is the same crossover parameter used for \( q_m^0(t) \), Eq. (28). Lastly, to satisfy the infinite time (steady-state) limit that the structure becomes the Ornstein-Zernike structure factor, a simple crossover structure factor given by
\[
S(q,t_x) = a_0S_{OZ}(q) \left( \frac{S(q,t_x)}{S_{OZ}(q) + S(q,t_x)} \right) \tag{30}
\]
where \( S(q,t_x) = S_\infty(q)(1 - e^{\omega(q)t_x}) \) and \( a_0 \) is a system-dependent constant. In this form, Eq. (30) represents the full crossover time-dependent structure factor from the spinodal regime to the nucleation regime.

B. Cut-Off Length Scale in Microphase Separation

Using Eq. (30), we compare a system of diffusion dynamics to equilibrium with a system of diffusion dynamics in the presence of a racemizing force toward steady state. The behavior of these systems through all three regimes, namely spinodal decomposition, coarsening, and nucleation, is shown in Figs. (3a,b). It is observed that the introduction of a racemizing force causes the growth of the structure factor to be interrupted at the lower cut-off wavenumber, \( q_- \). In the first order approximation, the wavenumber corresponding to the maximum of structure factor, \( q_m^0 \), in the steady-state limit of \( q_m^0(t \to \infty) \) determined from \( \partial S(q,t \to \infty)/\partial q = 0 \) is given by
\[
q_m^0(t \to \infty) = 2^{1/4}q_\infty \propto \sqrt{\frac{K}{D_{eff}}} \tag{31}
\]
We note that the general scaling law \( q_m^0 \propto K^{1/2} \) was observed in simulations of a chiral model\(^{41} \) and a hybrid Ising/lattice-gas model\(^{12} \) to be discussed in detail in Sec. IV. This behavior differs from studies of the microphase domain formation in block copolymers where it was found that \( q_m^0 \propto K^{1/4} \).\(^{41,56} \) The difference in this behavior between our binary mixture and the block copolymers might be attributed to the difference in the nature of the order parameter for the two systems - our binary mixture being described by a single component order parameter and the block copolymers being described by an \( n \)-component order parameter.

The crossover behavior for the transition between spinodal decomposition and nucleation in a system with diffusion dynamics toward equilibrium is shown in Figure 4. The wavenumber corresponding to the maximum of the structure factor, given by Eq. (30), evolves according to \( q \approx t^{1/4} \) (short times, spinodal decomposition regime) and \( q \approx t^{1/3} \) (long times, nucleation regime). The crossover from one regime to the other is illustrated by the crossing of the orange and green dashed lines in Figure 4.
IV. APPLICATIONS TO ATOMIC MODELS

In this section, we apply the generalized theory of spinodal decomposition to the results of simulations of two atomic models, which were reported by Shumovskyi et al.\textsuperscript{19} and Uralcan et al.\textsuperscript{24} The first model is a hybrid Ising / binary-lattice model that exhibits unrestricted (fast) phase amplification, restricted (slow) phase amplification, or complete phase separation, depending on the conditions presented in Table (II)\textsuperscript{19}. The second model is a chiral-mixture considered in two formulations: a conservative-force formulation in which it exhibits phase amplification, and a dissipative-force formulation in which it demonstrates steady-state microphase separation\textsuperscript{24}.

A. Hybrid Binary-Lattice/Ising Model: Phase Amplification

In 1952, Lee and Yang showed that the Ising model for an anisotropic ferromagnet and the lattice-gas model for a fluid are mathematically equivalent\textsuperscript{57}. The lattice-gas model can also be formulated as an incompressible binary lattice liquid, which could be used to describe liquid-liquid phase transitions in binary mixtures\textsuperscript{58}. However, while the lattice-gas (or binary lattice-liquid) and Ising models are equivalent in thermodynamics, they are fundamentally different in dynamics. The order parameter in the lattice-gas model (the density or concentration) is conserved, while the order parameter in the Ising model (the magnetization) is not\textsuperscript{59}. As a result, the density (or concentration) relaxes to equilibrium by spatial-dependent diffusion, while the relaxation of the magnetization in the lowest approximation is not spatial-dependent. An important consequence of this contrast in dynamics is the difference in the equilibrium states. In the lattice gas, below the critical temperature, two equilibrium fluid phases must coexist to conserve the total number of particles (occupied cells), while in the Ising ferromagnet only one of the alternative magnetizations, positive or negative, will survive\textsuperscript{19}. Since the interface between the two alternative magnetic phases is energetically costly, eventually, one phase will win over the other - a process known as phase amplification\textsuperscript{19}.

The phenomenon of phase amplification was previously observed qualitatively in simulations of chiral models exhibiting interconversion of enantiomers and referred to as "phase bullying".\textsuperscript{22,60} Quantitatively, Shumovskyi et al.\textsuperscript{19} studied this phenomenon through Monte Carlo simulations of a hybrid model exhibiting diffusion (Kawasaki dynamics) and inter-conversion (Glauber dynamics). In this section, we compare the generalized theory of spinodal decomposition with the results of Shumovskyi et al.\textsuperscript{19}

We consider an Ising-like lattice system, which represents two species A and B equivalent to a mixture of two spin types, directed up and down. These species or spins may interconvert (flip up and down), but also, since their mixing is energetically unfavorable, they will mutually diffuse toward phase separation below the critical temperature. The growth-rate equation for such a hybrid system is characterized by a mixture of conserved and non-conserved order-parameter dynamics.

\begin{equation}
\omega(q) = -\hat{\chi}_{q=0}^{-1}(L\kappa + Mq^2)(1 - \hat{\xi}^2 q^2)
\end{equation}

where $\omega(q) = -\hat{\chi}_{q=0}^{-1}(L\kappa + Mq^2)(1 - \hat{\xi}^2 q^2)$ is the nonconserved order parameter grows according to Ising spin-interconversion dynamics\textsuperscript{28}, while when $M = 0$, the conserved order parameter grows according to lattice-gas molecular-diffusive dynamics\textsuperscript{50}. From Eq. (32), the probability that the system will exhibit Ising-model spin interconversion is defined as $p_r = L\kappa/(Mq^2 + L\kappa)$. If $p_r = 1$, the order parameter relaxes to equilibrium through unrestricted (fast) amplification to one of two alternative phases with either positive or negative order parameter. If $p_r = 0$, the order parameter exhibits complete phase separation, and if $0 < p_r < 1$, the rate of phase amplification is restricted by the interconversion probability, the distance to the critical temperature, and the system size.

Applying the generalized theory of spinodal decomposition, we quantify the evolution of the order parameter in the hybrid model through Eq. (19). In a system with pure Ising dynamics ($p_r = 1$), the wavenumber corresponding to the fastest growth is $q^0_m = 0$, hence the amplification factor is $\omega(q_m) = -L\hat{\chi}_{q=0}^{-1}$. During the later stages of spinodal decomposition, as the system evolves toward nucleation, the susceptibility, at constant temperature, changes due to the time evolution of the concentration. To account for the crossover to the nucleation regime, we consider the time-dependent susceptibility evolving through the two limits: $\hat{\chi}_{q=0}^{-1}(t \to 0) \propto -\Delta \hat{T}$ and $\hat{\chi}_{q=0}^{-1}(t \to \infty) \propto \Delta \hat{T}$. By interpolating between these two limits, we obtain the susceptibility in the form

\begin{equation}
\hat{\chi}_{q=0}^{-1}(t) = a\hat{\chi}_{q=0}^{-1}(t = 0) \left(2e^{-t/\tau} - 1\right)
\end{equation}

It can be characterized from Eq. (1), in the absence of forceful racemization ($\pi = 0$), as $\omega(q) = -\hat{\chi}_{q=0}^{-1}(L\kappa + Mq^2)(1 - \hat{\xi}^2 q^2)$.
where \( a \) is a constant depending on the temperature and \( b \) is an effective exponent which empirically was found to change between \( b = 1/3 \) to \( b = 1/2 \) in the interval of \( \Delta \hat{T} = 0.32 - 0.06 \). The temporal evolution of the order parameter as a result of phase amplification, for \( p_r = 1 \), is described as

\[
\hat{c}_A = \hat{c}_\infty \left(1 - e^{\omega(q_m^0 \mu)}\right) \tag{34}
\]

We note that to satisfy the boundary conditions that the order parameter is \( \hat{c}_A = 0 \) at \( t = 0 \), while also reaching its equilibrium value in the limit \( t \to \infty \), then \( \hat{c}_\infty = -\hat{c}_0 / \Delta \hat{T} \), in Eq. (19), where \( \hat{c}_\infty \) denotes the equilibrium value of the order parameter. As illustrated in Figure 5, the results of Shumovskiy et al. are in good agreement with this description.

We emphasize that phase amplification is manifested by the growth of the average order parameter from \( \hat{c}_A = 0 \) to its equilibrium value. In the case of pure diffusion dynamics, \( p_r = 0 \), the time evolution of the order parameter is described by a special form of Eq. (19), when the constant \( \hat{c}_0 = 0 \), corresponding to the Cahn-Hilliard theory:

\[
\hat{c}_A = \hat{c}_e e^{\omega(q_m^0 \mu)} \cos(q_m^0 \mu) \tag{35}
\]

In this case, \( q_m^0 = 1/(\sqrt{2} \xi) \), such that the average order parameter is given through the factor \( \langle \cos(q_m^0 \mu) \rangle = 0 \). In contrast, for Ising spin-interconversion dynamics, the cosine term is evaluated at \( q_m^0 = 0 \) corresponding to \( \langle \cos(q_m^0 = 0 \cdot \mu) \rangle = 1 \). Therefore, for pure diffusion dynamics \((p_r = 0)\), the average order parameter will remain at \( \hat{c}_A = 0 \), corresponding to complete phase separation into two symmetric phases of positive and negative order parameter with the same magnitude.

In a hybrid case, when both diffusion and interconversion are present \((0 < p_r < 1)\), the average of the general time evolution of the order parameter will no longer be zero, and phase amplification will be observed. This prediction is in agreement with the simulations of Shumovskiy et al., who demonstrated that even an extremely small probability of interconversion dynamics may result in phase amplification, although the number of corresponding realizations will be exponentially small.

### B. Conservative-Force Formulation of the Chiral Model: Phase Amplification

The chiral model is a series of works on a 4-site tetramer model based on the simplest chiral molecule existing in nature, hydrogen peroxide. Molecular Dynamics simulations of the interconversion between the two stable enantiomeric forms is controlled through rotations around the dihedral angle. The ease at which molecules may interconvert is given through a rigidity (“spring-like”) constant \( k_d \), which is related to the interconversion probability in the hybrid model through \( k_d \propto \sqrt{(1/p_r) - 1} \). In this model, the parameters \( k_d \) and \( T \) are represented in dimensionless form.

There are two formulations of the chiral model: a conservative-force formulation, in which all of the forces are balanced, and a dissipative-force formulation, in which an imbalance of intermolecular forces is imposed between substituents of opposite chirality.

The kinetics of diffusion and interconversion for both formulations of the chiral model have been reported by Uralcan et al. In the conservative formulation, for \( k_d = 10^{-3} \) (corresponding to \( p_r \approx 1 \) in the hybrid model), phase amplification has been observed. Figure 6 depicts snapshots of simulations of the chiral model above and below the critical temperature. Phase amplification to either A-type enantiomers, green, or B-type enantiomers, blue, will occur with equal probability.

#### C. Dissipative-Force Formulation of the Chiral Model: Microphase Separation

In this formulation of the chiral model, an imbalance of intermolecular forces produces an imbalance in chemical potential associated with the interconversion dynamics, such that the order parameter, instead of being described by Eq. (1) (with \( \pi = 0 \)), evolves according to

\[
\frac{\partial \hat{c}_A}{\partial t} = MV^2 \mu - L \hat{\mu} \tag{36}
\]

This imbalance corresponds to the compensation of the contribution from the enthalpy of mixing in the chemical potential coupled with the interconversion kinetic coefficient, \( L \). We note that the first term in Eq. (11) could also be written through the derivatives of the reduced entropy of mixing, \( \Delta S_{\text{mix}} = \Delta S_{\text{mix}} / \rho_c k_B T_c \), and the reduced enthalpy of mixing, \( \Delta H_{\text{mix}} = \Delta H_{\text{mix}} / \rho_c k_B T_c \), as

\[
\Delta T \frac{\partial \hat{c}_A}{\partial \hat{c}_A} + \frac{\partial (\Delta H_{\text{mix}})}{\partial \hat{c}_A} \approx \Delta T \hat{c}_A - \hat{c}_A \tag{37}
\]

Therefore, the interconversion of enantiomers is equivalent to forceful racemization driven only by the entropy of mixing as

\[
T > T_c \quad \text{A & B} \quad T < T_c \quad \text{A} \quad \text{B}
\]

**FIG. 6. Phase amplification as observed in the conservative force formulation of the chiral model.** Above the critical temperature, the system is homogeneous, where the only apparent inhomogeneities are attributed to the correlation length of concentration fluctuations, while below the critical temperature each phase, composed of either A-type (green) or B-type (blue) enantiomers, has an equal probability of growing at the expense of the other one.
seen through the comparison with Eq. (37). As a result, the “unbalanced” chemical potential, \( \bar{\mu} \), is given by
\[
\bar{\mu} \approx \hat{T} \hat{\epsilon}_A - \nu \hat{V}^2 \hat{\epsilon}_A
\]  
(38)
Alternatively, we may attribute the effect of the energy dissipation in this model to the racemizing force, \( \pi \), in Eq. (1). In this case, \( \pi \) has the form \( \pi = L(\mu - \bar{\mu}) = -(\varepsilon / 2) \hat{c}_A \).

The amplification factor for the dissipative chiral system with a chemical potential given by Eq. (38) reads
\[
\omega(q) = -L(\hat{T} + \kappa q^2) - M \Delta T q^2 (1 - \xi^2 q^2)
\]  
(39)
Solving Eq. (39) for \( \omega(q) = 0 \), we obtain the first root, \( q_- \), corresponding to the minimum wavenumber below which the amplification factor becomes negative and phase domain growth will not be possible. In the first approximation, it reads as
\[
q_-^2 = \frac{L}{D_{\text{eff}}}
\]  
(40)
where the effective mutual diffusion coefficient is defined as
\[
D_{\text{eff}} = -(\Delta \hat{T} / \hat{T})(M + L \xi^2)
\]  
in which \( \Delta \hat{T} / \hat{T} = (T - T_c) / T_c \). The effective mutual diffusion coefficient represents the diffusion of species affected by interconversion. Remarkably, forceful racemization of species enhances the translational molecular mobility \( M \), into the effective mobility, \( M_{\text{eff}} = M + L \xi^2 \). This is a novel phenomenon that was recently discovered.\(^{24}\)

As interconversion between enantiomers depends on the ease at which the substituents may rotate around the dihedral angle, the interconversion kinetic coefficient is assumed to be proportional to the mobility, \( M \), and, as observed by Uralcan et al.\(^ {24}\), has the following dependence on the rigidity parameter, \( k_d \),
\[
L = M \frac{T^2}{k_d} \left( 1 + \frac{T^2}{k_d} \right)
\]  
(41)
where \( a \) is constant. For the rigidity parameters in the range investigated by Uralcan et al.\(^ {24}\) (5 < \( k_d \) < 30), we consider the first order approximation, \( L \approx M T^2 / k_d^2 \). We predict that the effective mobility increases with lower values of \( k_d \), as \( M_{\text{eff}} = M(1 + T^2 / k_d^2 \Delta \hat{T}) \). This effect was indeed observed in simulations reported by Uralcan et al.\(^ {24}\).

Moreover, computational data on the effective diffusion rate and interconversion rate show quantitative agreement with the theoretical predictions for \( D_{\text{eff}} \) and \( L \).\(^ {24}\)

The phase domain growth for the dissipative-force formulation of the chiral model is illustrated in Figure 7 for four different dihedral force constants. The domain size is calculated from the inverse wavenumber corresponding to the maximum of the time-dependent structure factor, \( R(t) \sim 1 / q_m^\infty \), as given by Eq. (31). It was observed by Uralcan et al.\(^ {24}\) that the steady-state domain size is inversely proportional to \( k_d \), which agrees with the prediction given by Eq. (31) when \( k_d \) is large, \( L = M T^2 / k_d^2 \) and \( R_{\infty} \approx k_d / T \) as seen in Figure 7.

As a result, the characteristic size of the steady-state domains is presented in the first approximation of Eq. (40) by
\[
R_{\infty} \approx k_d \frac{T}{\sqrt{-\Delta \hat{T} / \hat{T}}}
\]  
(42)
In Figure 8, we demonstrate the agreement of the effect of forceful racemization on the effective diffusion coefficient, given by Eq. (40), with computational data\(^ {24}\).
FIG. 9. The effect of increasing racemization force on the amplification factor for $M = 100$, $L = 1$, and $\Delta T = -0.5$. The red dashed line corresponds to the inverse maximum size of the phase domain on the length scale of the simulation box, $q^*$. When $q_- > q^*$ microphase domains will form. Alternatively, when $q_- < q^*$, the size of the simulation box will cut-off the growing phase domains. The conditions where $\alpha(q) < 0$ (dashed-dot portions of the curves) correspond to non-growing wavenumbers. As the racemization force increases, the amplification factor is shifted down from the onset of phase separation where $q_- = q^*$ (red, $K = 1$), to the microphase region (green, $K = 3.75$), to the termination point of domain growth (blue, $K = 6.5$) where $q_- = q_{m}^{\infty} = q_+ = q^{**}$, and to the no growth regime for any wavenumber (orange, $K = 9.25$).

D. Dissipative-Force Formulation of the Chiral Model: Microphase Domain Growth Restricted by Finite Size

Within the dissipative-force formulation of the chiral model, the phase domain growth is restricted by the finite size of the system $l$. The event when the domain size reaches the size of the computational box, was defined as “complete” phase separation, $l \sim 1/q^*$. This phenomenon is illustrated by Figure 7. We used dashed curves to indicate the prediction for the unrestricted domain growth.

In this case, the line separating the apparent two phase region ($R_m > 1/q^*$) and the microphase region ($R_m \leq 1/q^*$) is found from the first root of the amplification factor - see Fig. 9 and Eq. (40). The line interpreted as the onset of microphase separation (where $R_m = 1/q^* \sim \ell$, $T = T^*$) is determined as

$$\frac{1}{k_d^2} = \frac{2}{\hat{T}^*} \left( -\Delta \hat{T}^* \right)^2 \left[ 1 - \left( \frac{q^*}{\Delta \hat{T}^*} \right)^2 \right]$$

Figure 10 illustrates the steady-state phase diagram for this system, showing the curve, $T = T^*$, that separates the apparent two phase region from the microphase region. The onset temperature $T^*$ could be viewed as the length-scale dependent critical temperature of microphase separation in the nonequilibrium system. In addition, the time of liquid-liquid phase separation can be quantitatively determined from the characteristic growth rate, $\tau_{LPS} \approx 1/\omega(q^*)$ given by Eq. (39) and evaluated at the onset of phase separation when $q_- \approx q^* \sim 1/\ell$. When the temperature is less than the onset temperature $T^*$ liquid-liquid phase separation will take place in the coarsening regime. However, when $T = T^*$, then the time of phase separation will become infinite.

In addition to the onset of microphase separation, another phenomenon takes place when the racemizing force shifts the entire amplification factor below zero. In this scenario, when the growth rate becomes negative for all wavenumbers, a homogeneous steady state exists, in which no phase domain growth will occur. The point at which the maximum of the amplification factor crosses zero, $\omega(q_{m}^{\infty}) = 0$, is characterized through the termination temperature, $T^{**}$. At this point, the three characteristic wavenumbers merge into a single point, $q_{m}^{\infty} = q_- = q_+ = q^{**}$ - see Figure 9. For the dissipative chiral model the termination probability is given in the first order approximation by

$$\frac{1}{k_d^2} = 2 \left( \frac{\Delta \hat{T}^{**}}{\hat{T}^{**}} \right)^2 \left[ \hat{T}^{**} + \Delta \hat{T}^{**} \right]^{-1}$$

The termination line, $T = T^{**}$ is also shown in Figure 10. The growth-termination temperature is restricted by the correlation length such that the microphase separation domain is constrained between the size of the computational box and the correlation length of the order-parameter fluctuations. Figure 11 shows the termination line along with three lines of constant domain size (wavenumber).
V. ACCOUNTING FOR THE HEAT AND VOLUME CHANGE OF REACTION: LIQUID POLYMORPHISM

The chiral model with interconversion of enantiomers is one of the simplest examples of liquid polymorphism, the existence of two liquid states in a single-component substance. Chemical-reaction equilibrium constraints the number of thermodynamic degrees of freedom, thus allowing the mixture to be considered as a single-component fluid. Liquid polymorphism has been found in multiple substances including hydrogen, isotopes of helium, liquid carbon, sulphur, phosphorous, and cerium. In addition, liquid and vitreous polymorphism has been supported by simulations of various atomistic models. It has been hypothesized that liquid polymorphism, via the existence of two alternative molecular or supramolecular structures, may explain the remarkable anomalies of the properties in supercooled water. The existence of the liquid-liquid transition in supercooled water has been demonstrated by simulations of water-like models and supported by experiment. Recently, simulations have confirmed the 3D Ising-model universality class of the liquid-liquid critical behavior in the TIP4P/2005 model of water.

The interconversion between two alternative molecular or supramolecular states in a single-component substance has been suggested to be a generic cause of liquid polymorphism. However, in the “Ising-like” models (such as the chiral model and the hybrid model considered so far in this work), the Gibbs energy change of the reaction, $\Delta G_{\text{BA}}$, does not depend on pressure or temperature; thus, the forward and reverse equilibrium reaction rates are always equivalent ($\mathcal{X} = 1$). Since, in this case, the enthalpy of reaction, given through the Gibbs-Helmholtz relation, $\Delta H_{\text{BA}} = T^2 \partial (\ln \mathcal{X}) / \partial T = 0$. Therefore, in the one phase region, the equilibrium interconversion between states A and B remains 50:50 being independent of temperature and pressure. However, generally, in most polyamorphic substances, the enthalpy and volume change of the reaction are non-zero, such that, the equilibrium fraction of interconversion depends on temperature and pressure. This effect may be incorporated into the time evolution of the order parameter using the complete equation for the reduced chemical potential, Eq. (11). In this case, the solution of Eq. (1) becomes

$$\hat{c}_A = \frac{L(\hat{\theta} + \hat{P} - s\hat{T})}{2(K + L\hat{K}_{q=0})} + \sum_r \hat{c}_e e^{\omega(q) \cdot \cos(q, \mathbf{r})}$$

where only the infinite time solution of the order parameter is affected by the Gibbs energy of reaction. The amplification factor, $\omega(q)$, remains unaffected and is described by Eq. (21).

In polyamorphic systems, in which the two alternative phases have the same density, the system has two characteristic energies, $\hat{\theta}$ and $\epsilon$. We consider the heat of reaction, $\Delta H_{\text{BA}} = \hat{\epsilon}$, which defines the temperature dependence of the equilibrium interconversion fraction, and the heat of mixing $\Delta H_{\text{mix}} \propto \epsilon$, given by Eq. (4), which defines the critical temperature of liquid-liquid demixing. Suppose that the $\hat{\theta} > 0$ such that cooling favors the formation of species B. Depending on the relation between the reference temperature of interconversion $T_{\text{BA}}$, at which $\ln \mathcal{X} = 0$ (corresponding to 50:50 interconversion), and the critical temperature of demixing one can observe different scenarios upon quenching below $T_c$. As shown in Figure 12. If $T_{\text{BA}} > T_c$, the liquid-liquid phase transition will not be observed. If $T_{\text{BA}} = T_c$, the system follows the interconversion fraction to the phase enriched with B without phase coexistence. If $T_{\text{BA}} < T_c$, the system crosses the first-order liquid-liquid phase transition at the point where the interconversion fraction of B is smaller than 50%. Depending on the final location of the quenching point, phase amplification will occur with a preference to the formation of a single A-rich or B-rich phase. When the final location of the quench is $\hat{\epsilon} = \hat{\epsilon}_A = 0$ (corresponding to a 50:50 interconversion rate) as shown in Figure 12, phase amplification will occur randomly without a preference to an alternative phase, as discussed in Sec. IV. However, due to the difference between bulk energies of species A and B, for one stable phase to grow at the expense of another phase, energy must be supplied or removed from the system. Therefore, this process must be conducted in a heat reservoir and the thermal conductivity of the system must be faster than the interconversion rate.

Next, we consider the case when the two alternative species have different molecular volumes. In this case, the volume change of the interconversion reaction is not zero. For example, we consider the hypothesized phase diagram of super-
Here, we illustrate a quench by compression to $P = 20\text{MPa}$ in the one phase region to $P = 120\text{MPa}$ below the critical temperature of demixing along the Widom line for water, where $\ln \chi = 0.9,76,80,82,85$. This condition is preserved along this path because the change in the temperature is compensated by the corresponding change in the pressure as predicted by Eq. (8). In this case, phase amplification may only occur in the presence of a specific “barostat” that supplies or removes molecules to compensate the volume change of the interconversion reaction. Without such a barostat, phase amplification would not be possible. Further elaboration of the developed approach accounting for both the heat and volume change of the interconversion reaction would be desirable.

We note that even though phase amplification may be predicted to occur if there is no volume change of interconversion, there are a variety of factors (like the size of the system, distance from the critical temperature, and the rate of interconversion) that may increase the probability of a metastable interface to form between phases$^{19}$. The effect of possible phase amplification has not been discussed in previous simulations of models for polyamorphic substances, but it could be a factor effecting the possibility of equilibrium phase separation to be observed in both experiment and simulations.

Cooled water suggested by Caupin and Anisimov$^{76}$ and shown in Figure 13. It has been suggested the liquid-liquid phase separation in supercooled water is caused by the interconversion between two alternative supramolecular structures$^{74,76,77}$. Here, we illustrate a quench by compression from $P_1 = 20\text{MPa}$ in the one phase region to $P_2 = 120\text{MPa}$ below the critical temperature of demixing along the Widom line for water, where $\ln \chi = 0.9,76,80,82,85$. This condition is preserved along this path because the change in the temperature is compensated by the corresponding change in the pressure as predicted by Eq. (8). In this case, phase amplification may only occur in the presence of a specific “barostat” that supplies or removes molecules to compensate the volume change of the interconversion reaction. Without such a barostat, phase amplification would not be possible. Further elaboration of the developed approach accounting for both the heat and volume change of the interconversion reaction would be desirable.

Since the order parameter in polyamorphic systems is a hybrid containing both conserved and nonconserved components, the coupling between these two components affects the phase domain growth in both nucleation and spinodal decomposition regimes$^{89}$. This important feature of the dynamics of liquid polyamorphism could also be elaborated within the framework of interconversion of molecular or supramolecular species.

VI. EFFECTS OF CRITICAL FLUCTUATIONS OF THE ORDER PARAMETER

As was emphasized in Sec. IV.A, the Ising and lattice-gas models are mathematically equivalent. It was later proven that all fluids exhibiting phase separation, whether simple or complex, belong to the same class of critical-point universality in thermodynamics as the Ising model$^{89}$. Within the same universality class, systems demonstrate the same critical singularities and the same critical equation of state, provided that the appropriately defined order parameter has the same symmetry. The one-component-vector order parameter (the magnetization of the Ising model) and the scalar order parameter (the density of fluids) possess the same $Z_2$ up-down symmetry$^{91,92}$.

According to Halperin and Hohenberg$^{89}$, the Ising and lattice-gas models belong to the different dynamic universality classes, A and H respectively. The relaxation of the conserved order-parameter (density) in the lattice-gas model is controlled by diffusion, while the relaxation of the noncon-
served order-parameter (the fraction of spins pointing up or down) in the Ising model is controlled by the flipping of spins (spin "interconversion"). In addition, the mobility, $M$, in fluids diverges near the critical point as described by the mode-coupling theory, while the interconversion kinetic coefficient, $L$, is constant.

The mean field approximation does not properly incorporate the effects of diverging fluctuations in the critical region. This part of the phase diagram is roughly defined by the region where the correlation length of the order-parameter fluctuations is significantly larger than the distance between molecules (the Ginzburg criterion). In practice, the region where physical properties of fluids are significantly modified by fluctuations can roughly be estimated as $\Delta T \lesssim 0.1$. Fluctuation-induced effects are described by the renormalization group (RG) theory and the scaling theory of critical phenomena. A comprehensive theory of phase transitions in the presence of molecular interconversion in the vicinity of the critical point has not yet been developed. In this section, we present simple scaling arguments on the behavior of such systems in the approximation of the first-order epsilon expansion of the RG theory in powers of $\varepsilon = 4 - d$, where $d$ is the system dimensionality. In this approximation, the Landau-Ginzburg free energy functional in the form of Eq. (2), used in the description of spinodal decomposition, corresponds to the Ornstein-Zernike correlation function, in which the susceptibility is proportional to the square of the correlation length, $\xi = \xi_0^2 / \kappa$.

As the system approaches the critical point, the susceptibility, $\hat{\chi}_{q=0} \sim (\partial^2 f_0 / \partial q^2)_q^{-1}$, diverges as $|\Delta T|^{-\gamma}$ and the correlation length diverges as $\xi \sim |\Delta T|^{-\nu}$, where in the first-order RG epsilon expansion for the 3d Ising-model universality class $\gamma = 1 + \varepsilon/6 = 7/6$ and $\nu = \gamma/2 = 1/2 + \varepsilon/12 = 7/12$. The actual theoretical and most accurate experimental values for the critical exponents differ from those given by the lowest approximation of the RG theory, such that $\gamma = 1.24$ and $\nu = 0.63$. The difference between $\gamma$ and $2\nu$ appears only in the second-order epsilon expansion, in which $\gamma = 3(2 - \varepsilon^2/54)$. However, these differences only marginally change the behavior of the amplification factor presented below.

There is another effect, the fluctuation induced divergence of the mobility, which is only relevant for the dynamic universality class H. In the vicinity of the critical point, the mode-coupling theory, strongly supported by accurate experimental studies, predicts the divergence of the molecular mobility:

$$M = M_0 \xi^{1-\eta_0} K(q\xi) \left[ 1 + \left( \frac{q\xi}{2} \right)^{-\eta_0/2} \right]$$

(46)

where $M_0 = k_B T / (6\pi \eta_0 \kappa)$ is the non-diverging mobility in the mean field approximation; $\eta_0$ is the amplitude of the dynamic viscosity, which weakly diverges as $\eta = \eta_0 \xi^{\eta_0}$ ($\eta_0 = 1/19$ in the first RG epsilon expansion); and $K(q\xi) = K(x) = (3/(4\pi^2)) [1 + x^2 + (3 - x^{-1}) \arctan(x)]$ is the Kawasaki function. The net effect is that the mutual diffusion coefficient asymptotically close to the critical point in the limit $q \to 0$ vanishes as $D_m = M \hat{\chi}_{q=0}^{-1} = |\Delta T|^{\nu-\eta_0/2}$ Therefore, the amplification factor given through Eq. (20) incorporates the form of $\hat{\chi}_{q=0}^{-1}$ from scaling theory and $M$ from mode coupling theory, Eq. (46).

The comparison between the prediction for the amplification factor, Eq. (20), in the mean field approximation and in scaling theory is shown in Figure 14a. This figure depicts a significant effect of critical fluctuations on the amplification factor. The wavenumber corresponding to the steady-state domain size is shifted toward smaller wavenumbers and the maximum of the amplification factor is much stronger, indicating that the domain size growth into steady-state microphase domains will be faster and result in larger domain sizes in the steady-state regime. The structure factor in the scaling regime is given by Eq. (30) with use of the scaling amplification factor and diverging inverse susceptibility, $\hat{\chi}_{q=0}^{-1} \sim |\Delta T|^{-\gamma}$ in Eq. (28).

FIG. 14. a) Amplification factor in the vicinity of the critical point ($\Delta T = -0.001$) for $M_0 = 1$, $L = 0.002$, and $K = 2.25 \times 10^{-5}$ calculated through Eq. (20), (red curve) with use of the diverging molecular mobility, Eq. (46), and scaling inverse susceptibility in the first order epsilon expansion, $\hat{\chi}_{q=0}^{-1} \sim |\Delta T|^{-\gamma}$ with $\gamma = 1 + \varepsilon/6 (\varepsilon = 4 - d)$. The mean field approximation is shown by the green curve, Eq. (20). b) The onset (red solid curves, Eq. (47)) and termination (red dashed curves, Eq. (48)) of microphase separation affected by critical fluctuations for $M = 1$, $L = 0.01$, $\ell = 100$, $\nu = 1/2 + \varepsilon/12$. The mean field approximation is shown by the green curves.
In addition, both the onset and termination of microphase separation are affected by critical fluctuations. In particular, from the amplification factor $\omega(q)$, it can be shown from Eq. (20) that

$$K(\hat{T}^*) = L\hat{T}^{-1}_{q=0} - (M\hat{T}^{-1}_{q=0} + L\kappa)(q^*)^2 - M\kappa(q^*)^4$$  \hspace{1cm} (47)

where $\hat{T}^* = T^*/T_c$ is the reduced temperature at the onset. Therefore, the magnitude of forceful racemization at the onset of microphase separation scales with proximity to the critical point as $K \propto L\hat{T}^{-1}_{q=0} \sim |\Delta\hat{T}^*|^2$. In contrast, in the mean field approximation, $K \propto |\Delta\hat{T}^*|$. In addition, the magnitude of forceful racemization at the termination of microphase separation ($\omega(q_m^0) = 0$) is given by

$$K(\hat{T}^{**}) = \frac{(-M\hat{T}^{-1}_{q=0} + L\kappa)^2}{4M\kappa}$$  \hspace{1cm} (48)

where $\hat{T}^{**} = T^{**}/T_c$ is the reduced temperature at the termination point, and thus, $K \propto D_m\hat{T}^{-1}_{q=0} \sim |\Delta\hat{T}^{**}|^3$, while in the mean field approximation, $K \propto |\Delta\hat{T}^{**}|^2$. As shown in Figure 14b, the effect of critical fluctuations lowers the amplitude of the onset and termination lines. Away from the critical point, these lines should converge with their mean field predictions. Lastly, we note that for the dissipative force formulation of the chiral model unlike the strong effect of the non-conserved dynamics, such as the Ising model for an anisotropic ferromagnet. We have presented a theory of phase transitions affected by both natural and forceful molecular interconversion. The theory is applicable to systems where the order parameter possesses both conserved and non-conserved dynamics, such as a hybrid of the incompressible binary-fluid lattice model and the Ising model for an anisotropic ferromagnet. We have shown that a source of forceful racemization may cause microphase separation, while in the absence of forceful racemization, the competition between diffusion and interconversion dynamics results in the phenomenon of phase amplification, when one phase grows at the expense of another stable phase.

The theory has promising applications to more complex systems with interconversion of molecules or supramolecular structures. For example, by incorporating the pressure and temperature dependent fraction of interconversion, the developed approach could be applied to the description of systems exhibiting liquid and vitreous polymorphism (Sec. V). In addition, the phenomenon of microphase separation could be used to clarify the formation of membraneless organelles. Just like molecular interconversion in the presence of an external energy source, the interconversion of proteins from a folded to an unfolded state in biological systems could be also considered using the developed approach.

Lastly, microphase structures caused by forceful racemization can be considered as an example of dissipative structures. It would be promising to connect the developed approach with the general theory of dissipative structures of Prigogine et al.$^2$ It could also have cross-disciplinary applications to other nonlinear phenomena like hydrodynamic instabilities,$^{108}$ bifurcations, and catastrophe theory.$^{109}$

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DATA AVAILABILITY

Data sharing is not applicable to this article as no unpublished data were created or analyzed in this study.

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