Segregation disrupts the Arrhenius behavior of an isomerization reaction

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Coexistence of segregation and interconversion or isomerization reaction among molecular species leads to fascinating structure formation in the biological and chemical worlds. Using Monte Carlo simulations of the prototype Ising model, we explore the chemical kinetics of such a system consisting of a binary mixture of isomers. Our results reveal that even though the two concerned processes are individually Arrhenius in nature, the Arrhenius behavior of the isomerization reaction gets significantly disrupted due to an interplay of the nonconserved dynamics of the reaction and the conserved diffusive dynamics of segregation. The approach used here can be potentially adapted to understand reaction kinetics of more complex reactions.

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I. INTRODUCTION

The phenomenon of the existence of two or more molecular species having the same chemical formula but different properties is referred to as isomerism [1]. Structural chirality is one of the reasons behind such isomerism, giving rise to optical isomers or enantiomers [1,2]. For instance, L Glucose, unlike its enantiomer D glucose, is not an energy source for living organisms, as it cannot be phosphorylated during glycolysis. The final product of synthesis of such molecular species is often comprised of a mixture of its enantiomers. Depending on the kind of interactions among themselves the enantiomeric components of such mixtures can spontaneously or inductively segregate from each other [3,4]. Simultaneously, either naturally or owing to an external drive, the enantiomers may undergo an isomerization or interconversion reaction leading to an enantio-selective production or amplification of one of them [5–12]. Such enantio-selective processes are ubiquitous in nature as well, e.g., amino acid residues of naturally occurring proteins are mostly L enantiomers [13]. In the light of the above discussion, it is crucial to have a microscopic understanding of the physical laws governing such a phenomenon of segregation of molecular species simultaneously undergoing an isomerization reaction [14-26].

Segregation in enantiomeric mixtures can be easily understood by simply translating the concepts of kinetics of phase segregation, which has been extensively studied in the past [27,28] and recently developed further in more complex and realistic scenarios [29–31]. Similarly, the interconversion reaction among isomers can be captured under the essence of phase ordering of ferromagnets [32]. In phase ordering, typically one ends up in a state where a majority of the magnetic dipoles point in the same direction, following a quench from high-temperature disordered state to a temperature below the Curie point. Both kinetics of phase segregation in a binary mixture and phase ordering can essentially be modeled by using simple lattice models, e.g., the nearestneighbor Ising model. Although both adaptations of the model produce equivalent thermodynamics, fundamentally their dynamics are different. Combining the two approaches results in an appropriate model for exploring the effect of isomerization reaction during enantiomeric phase segregation in solids using state-of-the-art Monte Carlo (MC) simulations [14,16,23].

In solid phase, according to Hohenberg-Halperin nomenclature [33], the segregation dynamics belongs to Model B, whereas the phase ordering belongs to Model A. In the past, combining these two types of dynamics were motivated more from a technical point of view. In this regard, the first study was by Glotzer et al. [14], where they focused on the steadystate pattern formation and scaling of the characteristic length scale, i.e., the average domain size, with the reaction probability. Alongside, there were quite a few studies that, instead of using MC simulations, modified the Cahn-Hilliard equation to include the nonconserved dynamics for a theoretical description of such systems [15–19,21,34]. Recent interests in this regard have shifted toward modeling reactions in solutions using molecular dynamics (MD) simulations [35,36]. These attempts have successfully explored novel mesoscopic steady-state structures mimicking microphase segregation observed in the chemical and biological worlds. In a nutshell, all these previous studies where a combination of conserved and nonconserved dynamics were used, the primary focus has always been on either pattern formation or the scaling of the characteristic length scale. However, answers to some of the fundamental questions such as the effect of segregation on the reaction kinetics, are still unexplored. Particularly, how the rate of the interconversion reaction changes as a function of temperature has rarely been explored to date. In this work, we focus on this particular aspect of the competing dynamics.

$$A_1 \rightleftharpoons A_2, \tag{1}$$

We study the kinetics of an isomerization reaction of the following type:

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where the two isomers A_1 and A_2 are also undergoing segregation from each other. The reaction is a unimolecular elementary reaction, e.g., interconversion of cyclopropane and propene. The mechanism of such a reaction can easily be understood using the transition-state theory, always yielding an Arrhenius-type relation between the rate constant k and the temperature T [37]. In the present case too, if there is no segregation, k as a function of T obeys the Arrhenius behavior given as

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T}\right),\tag{2}$$

where A is a preexponential constant, E_a is the activation energy, and R is the universal gas constant. Our results from MC simulations of the prototype Ising model mimicking the system described above reveal that at high reaction probability the Arrhenius behavior is maintained. However, as the reaction probability decreases and segregation dominates, a significant deviation from the Arrhenius behavior is observed.

The rest of the paper is divided into three different sections. In Sec. II, we describe in detail the model and method of simulation. Following that in Sec. III, we present the results and analyses. Finally, we put forward our conclusion in Sec. IV.

II. MODEL AND SIMULATION METHOD

We choose a square lattice system where on each site *i* there sits an Ising spin $S_i = +1(\text{or } -1)$ that corresponds to species $A_1(\text{or } A_2)$. The interaction energy between the spins are given by the conventional Ising Hamiltonian

$$H = -J \sum_{\langle ij \rangle} S_i S_j, \tag{3}$$

where $\langle ij \rangle$ indicates that only nearest neighbors can interact with each other and J is the corresponding interaction strength. We apply periodic boundary conditions in all possible directions to eradicate any surface effects. The model exhibits an order-disorder transition with a critical temperature $T_c = 2J/k_B \ln(1 + \sqrt{2})$, where k_B is the Boltzmann constant [38]. From now onward the unit of temperature is J/k_B , and for convenience we have set $J = k_B = 1$. In order to capture the essence of a segregating mixture of isomers undergoing isomerization reaction, we have introduced both Kawasaki spin-exchange dynamics and Glauber spin-flip dynamics [39-42]. In Kawasaki exchange, interchange of positions between a randomly chosen pair of nearest-neighbor spins is attempted, facilitating segregation of species. Such an MC move replicates atomic diffusion, and the resultant dynamics is conserved as it keeps individual compositions of the species unaltered. On the other hand, in a Glauber spin-flip move, an attempt is made to flip a randomly chosen spin, thus mimicking the interconversion or isomerization reaction. We consider the forward and backward reactions in (1) to be equally likely. The spin-flip move is nonconserved as it changes the individual composition of the species. Both moves are accepted according to the standard Metropolis criterion [41,42].

We start with a racemic mixture of the isomers, i.e., equal proportions of A_1 and A_2 are uniformly distributed on the lattice, and then in the simulation we set the temperature to



FIG. 1. Pattern formation due to isomerization reaction and segregation. Typical snapshots depicting time evolution of a binary mixture of isomers, simultaneously undergoing isomerization reaction and segregation, following a quench from a homogeneous phase above T_c to a temperature $T = 0.6T_c$. The results are obtained from simulations on a square lattice of linear size L = 32. Different rows are for different values of the reaction probability p_r , as indicated. Contrasting colors correspond to different species.

 $T < T_c$. At each MC step, the Glauber move is attempted with a probability p_r , while the Kawasaki exchange attempt is executed with a probability $1 - p_r$. We choose one MC sweep (MCS) as the unit of time, which refers to L^2 attempted MC moves. We perform all our simulations on a square lattice of linear size L = 32 having $L^2 = 1024$ isomers, at different T for a range of $p_r \in [10^{-4}, 5 \times 10^{-1}]$. Note that the model and methodology described above are applicable to a reactive binary mixture of isomers in solid phase.

III. RESULTS

Segregation of molecular species in combination with the isomerization reaction leads to pattern formation, as pertinent to the individual dynamics associated with the two processes. Typical representative time-evolution snapshots at $T = 0.6T_c$ are presented in Fig. 1, for different p_r . For the highest $p_r = 10^{-1}$, the patterns are similar to what is observed for a system with purely nonconserved spin-flip dynamics, i.e., in phase ordering [43,44]. The isomerization reaction seems to have finished faster as p_r increases. This rationalizes the difference in the set of times for which the snapshots are presented for different p_r in Fig. 1. As p_r decreases, the snapshots at intermediate times appear to have more bicontinuous morphologies. For all cases, although at different times, the system finally approaches a morphology where one of the isomers survives as the majority. For $p_r = 10^{-4}$, such a stage



FIG. 2. Progress of the reaction. Linear-log plots for time dependence of the concentration difference $\chi(t)$ of the two isomers, at different temperatures for (a) $p_r = 10^{-1}$, (b) $p_r = 10^{-2}$, (c) $p_r = 10^{-3}$, and (d) $p_r = 10^{-4}$. The data presented are averaged over 80 independent time evolutions obtained by using different random number seeds in the MC simulations. The upper insets show the same plots on double-log scale. There the dashed black lines represent a power law $\sim t^{1/2}$. The red dashed line in (d) represents another power-law $\sim t^{1/3}$. The lower insets show representatives of histograms of the extracted reaction completion time τ_r , at $T = 0.8T_c$. In the lower insets of (a) and (b) the dashed lines represent a function of the form $f(\tau_r) = 100 \exp(-\lambda \tau_r)$, where $\lambda = 550$ and 60, respectively.

is reached at a much longer time $\approx 5 \times 10^7$ MCS, making it computationally expensive. Hence, we refrain ourselves from simulating larger lattices than L = 32. For evolution snapshots at other temperatures see Figs. S1 and S2 in the Supplemental Material (SM) [45]. From there it is apparent that at high temperature ($T = 0.8T_c$), for smaller p_r , at first the system segregates to a slablike morphology, and then evolves further due to the isomerization reaction. However, at low temperature ($T = 0.4T_c$), even for $p_r = 10^{-4}$, the morphologies resemble more of what is shown in Fig. 1.

Since the objective is to study the reaction kinetics, we have to extract the rate constant k. As a first step, we need to monitor the progress of the reaction until it finishes, i.e., when one of the molecular species becomes almost negligible compared to the other. For that we calculate the concentration difference of the two species

$$\chi(t) = \frac{|N_{A_1}(t) - N_{A_2}(t)|}{N_{A_1}(t) + N_{A_2}(t)},\tag{4}$$

where $N_{A_1}(t)$ and $N_{A_2}(t)$ are, respectively, the number of molecules of A_1 and A_2 , at a time *t*. The denominator in Eq. (4) $N_{A_1}(t) + N_{A_2}(t) = L^2$ is the total number of molecules present

in the system. By construction, at t = 0 for a racemic mixture $\chi(0) \approx 0$, and at large t when the reaction is completed $\chi(t) \approx 1$, thus making $\chi(t)$ a suitable parameter to capture the progress of the reaction. In the main frames of Figs. 2(a)-2(d), we present the corresponding data at different T for four choices of p_r , as indicated. Apparently, for all p_r the data show an initial transient regime where $\chi(t)$ remains almost constant, followed by a steep increase before finally settling at a value ≈ 1 indicating the completion of the reaction. However, one could notice that the transient regime broadens as p_r decreases, indicating a dominance of segregation over the reaction.

Also noticeable is the presence of a third regime where $\chi(t)$ again attains almost a plateau before finally approaching unity. The plateau is most prominent for $p_r = 10^{-1}$ (where nonconserved dynamics dominates) at low temperatures ($T < 0.6T_c$). For $p_r = 10^{-4}$, at high T this plateau vanishes (see Figs. S3–S6 in the SM [45] for individual plots at different T). This implies that the plateau signals a freezing in the dynamics due to low T. At a later time, it can come out of this metastable state via merging of interfaces leading to a rapid growth of domains, referred to as an avalanche. Such a behavior has



FIG. 3. Temperature dependence of the reaction rate constant k. Plots of $-\ln\langle k \rangle$ against 1/T to verify the presence of Arrhenius behavior for different p_r . The dashed straight lines in (a)–(c) are fits using Eq. (2), and the dashed lines in (d)–(f) are just connecting the data points. Here, the symbol $\langle \ldots \rangle$ indicates an average over 80 independent simulation runs.

been observed previously for the Ising model with purely nonconserved dynamics [43,46]. Of course, this can be interpreted as a finite-size effect. However, the primary finite-size effect comes into the picture after the avalanche when the growing domains become comparable with the system size.

The upper insets of Fig. 2 showing the same data on a double-log scale unravel significant differences in the time dependence of $\chi(t)$ for different p_r . For $p_r = 10^{-1}$ and 10^{-2} , data for all T is consistent with a power-law $\chi(t) \sim t^{1/2}$. In a ferromagnetic system $\chi(t) \equiv |m(t)|$. There, during phase ordering, the absolute magnetization |m(t)| obeys the same power-law $|m(t)| \sim t^{1/2}$ in space dimension d = 2 [44]. For lower p_r , particularly at high T, the dominance of segregation makes the growth of $\chi(t)$ much slower, roughly with a power-law exponent of 1/3. This early-time behavior is reminiscent of the Lifshitz-Slyozov growth [47], observed for the time dependence of the characteristic length $\ell(t)$ during phase segregation [48-50]. However, since the condition $\chi(t) \equiv |m(t)| \sim \ell(t)$ does not hold for conserved dynamics, the analogy is misleading. For nonconserved dynamics it has been shown that in two dimension, $m(t) \sim \ell(t) \sim t^{1/2}$. In the present case, even if one had plotted $\ell(t)$ for the modest value of p_r , the late-time data would always be following the behavior $\ell(t) \sim t^{1/2}$. This is because for modest p_r initially the segregation dominates over the reaction, thus the system quickly reaches a state where the two isomers are almost completely segregated from each other. Given the Hamiltonian of the nearest-neighbor Ising model, the system from there on can move further only via the nonconserved Glauber moves that mimic the interconversion reaction. Hence, at late time, $\chi(t)$ behaves similar to a purely nonconserved dynamics. For details on the behavior of $\ell(t)$ we refer to Ref. [51].

Next, we extract the reaction-completion time τ_r as

$$\chi(t=\tau_r)=h,\tag{5}$$

where we choose h = 0.9 [52]. Histogram of the extracted τ_r (see Figs. S7–S10 in the SM [45] for histograms at different T for four values of p_r) shows nonuniform localized patterns for $p_r \ge 10^{-2}$ with an exponential behavior at high T as presented in the lower insets of Figs. 2(a) and 2(b), respectively, for $p_r = 10^{-1}$ and 10^{-2} , at $T = 0.8T_c$. The dashed lines there represent best fits using $f(\tau_r) = 100 \exp(-\lambda \tau_r)$, with decay constants $\lambda = 550$ and 60, respectively, for $p_r = 10^{-1}$ and 10^{-2} , implying a slower decay as p_r decreases. For even lower p_r , the exponential nature is lost and the histogram appears to flatten out, as shown for $p_r = 10^{-4}$ in the lower inset of Fig. 2(d).

From the extracted τ_r we calculate the rate constant k of the isomerization reaction as $k = \tau_r^{-1}$. In Fig. 3 we show the temperature dependence of k, by plotting $-\ln\langle k \rangle$ as a function of 1/T. For $p_r \ge 10^{-2}$, the data show a linear nature confirming the Arrhenius behavior depicted in Eq. (2). The dashed lines in Figs. 3(a)–3(c) represent respective best fits obtained using the ansatz in Eq. (2). The obtained activation energies



FIG. 4. Interplay of segregation and reaction. Plots of the time evolution of the segregation order parameter $\psi(t)$ against the corresponding concentration difference $\chi(t)$, on a linear-log scale at different temperatures T for (a) $p_r = 10^{-1}$, (b) $p_r = 10^{-2}$, (c) $p_r = 10^{-3}$, and (d) $p_r = 10^{-4}$. The color bar represents the corresponding time. The snapshots at $T = 0.4T_c$ and $0.8T_c$ represent typical configurations having $\psi(t) \approx 0.85$. The green arrows in (c) and (d) are guides to show the trend in data with increasing T.

are $E_a \in [3.46, 3.75]$ with a mean of $\langle E_a \rangle = 3.65(18)$. For all $p_r \ge 10^{-2}$, fits using $E_a = 3.65$ in Eq. (2) also work reasonably well, indicating possibly a p_r -independent activation energy. For $p_r < 10^{-2}$, the data do not appear to be linear anymore, and, in fact, for $p_r = 10^{-4}$ it becomes almost flat. This implies that the dominance of diffusive segregation dynamics disrupts the Arrhenius behavior of the isomerization reaction, even though segregation itself is an Arrhenius process [53]. An apparent linear behavior of the data can be noticed in the large and small 1/T limit, respectively, for Figs. 3(d) and 3(f), for a very small range with only three data points. Since a fitting of Eq. (2) with two free parameters using only three data points is not justified, we abstain ourselves to pursue them as a possible Arrhenius behavior.

To investigate the phenomenon of an interplay of two Arrhenius processes leading to a non-Arrhenius behavior, we probe the segregation using the time evolution of the order parameter

$$\psi(t) = \frac{1}{L^2} \sum_{i} \frac{|n_{A_1}^{\square} - n_{A_2}^{\square}|}{n_{A_1}^{\square} + n_{A_2}^{\square}},$$
(6)

where the \sum is over all lattice sites and $n_{A_1}^{\square}$ (or $n_{A_2}^{\square}$) is the number of A_1 (or A_2) molecules in a sub lattice of size $\ell \times \ell$ with $\ell = 1$ around a site *i* of the parent square lattice.

By construction, ψ for a segregated system is higher (≈ 1) than a homogeneous one. For a purely segregating system, the time when ψ approaches unity, provides a measure of the associated relaxation time τ_s , and a plot of $-\ln\langle \tau_s^{-1} \rangle$ against 1/T confirms the Arrhenius behavior (see Fig. S11 in the SM).

For a system where reaction is happening along with segregation, time dependence of $\psi(t)$ alone will capture the effect of both processes. Hence, to understand the interplay between the segregation and the reaction, in Fig. 4 we plot the time dependence of $\psi(t)$, characterizing the segregation with $\chi(t)$ reflecting the temporal progress of the reaction at different T for four values of p_r . For $p_r = 10^{-1}$, shown in Fig. 4(a), $\psi(t)$ increases monotonously with $\chi(t)$, and the spread of data points over time for different T appear to be quite condensed, suggesting no trend as a function of T. Typical configurations having $\psi(t) \approx 0.85$, a value that corresponds to an almost completely segregated state for a purely segregating system, are also shown in Fig. 4(a) for a high and low T. None of them represent a completely segregated morphology, suggesting that both the dynamics affect the system concurrently. However, the reaction has progressed slightly further for $T = 0.8T_c$ with $\chi(t) = 0.1$ compared to $\chi(t) = 0.08$ at $T = 0.4T_c$. This difference eventually gets manifested in the form of an Arrhenius behavior, expected for a simple isomerization reaction.

As p_r decreases, the data for different T look more dispersed with a T-dependent trend, as guided by the green arrows in Figs. 4(c) and 4(d). There, one can notice that at the beginning $\psi(t)$ increases sharply while no significant change in $\chi(t)$ is observed, implying that initially during the evolution segregation dynamics dominate. The effect is more pronounced for $p_r = 10^{-4}$ at high T. This could be further appreciated from the almost completely segregated morphology of the configuration representing a system having $\psi(t) = 0.85$ at $T = 0.8T_c$, for $p_r = 10^{-4}$, shown in Fig. 4(d). The value of $\chi(t) = 0.02$ at this instance indicates that the progress of the reaction is negligible. Since segregation itself is an Arrhenius process, the system reaches such a state much faster at high T. However, after attaining such a morphology, not only the segregation dynamics almost seizes, but the activation energy E_a of the reaction also increases, temporarily halting the entire evolution of the system. This is analogous to the phenomenon of dynamic freezing due to emergence of metastable slablike configurations during phase ordering of a ferromagnet [43,46,54]. On the other hand, at $T = 0.4T_c$ the value of $\chi(t) = 0.06$ when $\psi(t) = 0.85$ suggests that the reaction has progressed further compared to $T = 0.8T_c$. Corresponding typical configuration at $T = 0.4T_c$, shown in Fig. 4(d), also does not represent a segregated morphology. Thus, in this case the reaction can easily proceed even further toward its completion. Hence, at low T and low p_r , although the system always encounters a simultaneous occurrence of segregation and reaction, it never gets trapped in a completely segregated state, making the reaction completion time comparable with the one at high T. Overall it implies that for low p_r , the activation energy E_a of the isomerization reaction is not T independent, and rather it depends irregularly on T, which in turn gets manifested in the form of a non-Arrhenius behavior of the isomerization reaction.

IV. CONCLUSION

To summarize, we have presented results on chemical kinetics of an elementary isomerization reaction when it competes with a segregation process among the isomers. Results from our MC simulations of a model constructed using the nearest-neighbor Ising model with two competing dynamics reveal that the Arrhenius behavior of the reaction gets disrupted as segregation dynamics dominates over the reaction dynamics, even though segregation itself is an Arrhenius process. Non-Arrhenius behavior is also observed in glass-forming materials around the glass-transition temperature [55,56]. However, there the system is intrinsically disordered, having a fairly complex energy landscape. In our case, the chosen Hamiltonian of the system lacks any sort of disorder, and hence, the observation of a non-Arrhenius behavior analogous to glass-forming materials is also not an obvious outcome. We have rationalized this observation by virtue of a phenomenological argument that, at high temperature and low reaction probability, the segregation of isomers reaches completion leading to an almost completely segregated morphology, and thereby raising the activation energy of the reaction making it difficult for the system to evolve further. These findings shall provoke an experimental verification, which to the best of our understanding can be done without much hassle.

As a next step it would be worth exploring aging and related dynamical scaling [57] in a system with mixed dynamics such as presented here. Note that the results presented here are for solid phase reactions. Thus, as a future endeavor, it would be intriguing to consider similar reactions in solution phase by performing MD simulations of a fluid system [58]. This would lead to a mixed dynamics of Model A and Model H of dynamic critical phenomenon [33]. Furthermore, based on the model presented here, one can construct similar models for reactions of higher complexity, and subsequently may also invoke the role of a catalyst. For that, use of a multispecies model like the Potts model is required [43,59].

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- A. D. McNaught, A. Wilkinson *et al.*, *Compendium of Chemical Terminology* (Blackwell Science Oxford, 1997), Vol. 1669.
- [2] M. Anne Fox and J. K. Whitesell, *Organic Chemistry* (Jones & Bartlett Learning, 2004).
- [3] W. H. Pirkle, J. M. Finn, J. L. Schreiner, and B. C. Hamper, A widely useful chiral stationary phase for the high-performance liquid chromatography separation of enantiomers, J. Am. Chem. Soc. 103, 3964 (1981).
- [4] W.- C. Shieh and J. A. Carlson, Asymmetric transformation of either enantiomer of narwedine via total spontaneous resolution process, a concise solution to the synthesis of (-)-galanthamine, J. Org. Chem. **59**, 5463 (1994).
- [5] K. Soai, T. Shibata, H. Morioka, and K. Choji, Asymmetric autocatalysis and amplification of enantiomeric excess of a chiral molecule, Nature (London) **378**, 767 (1995).

- [6] T. Shibata, K. Choji, T. Hayase, Y. Aizu, and K. Soai, Asymmetric autocatalytic reaction of 3-quinolylalkanol with amplification of enantiomeric excess, Chem. Commun. 10, 1235 (1996).
- [7] T. Shibata, H. Morioka, T. Hayase, K. Choji, and K. Soai, Highly enantioselective catalytic asymmetric automultiplication of chiral pyrimidyl alcohol, J. Am. Chem. Soc. 118, 471 (1996).
- [8] Q. Tran-Cong and A. Harada, Reaction-induced ordering phenomena in binary polymer mixtures, Phys. Rev. Lett. 76, 1162 (1996).
- [9] Q. Tran-Cong, T. Ohta, and O. Urakawa, Soft-mode suppression in the phase separation of binary polymer mixtures driven by a reversible chemical reaction, Phys. Rev. E 56, R59(R) (1997).

- [10] T. Ohta, O. Urakawa, and Q. Tran-Cong, Phase separation of binary polymer blends driven by photoisomerization: An example for a wavelength-selection process in polymers, Macromolecules **31**, 6845 (1998).
- [11] C. Viedma, Chiral symmetry breaking during crystallization: Complete chiral purity induced by nonlinear autocatalysis and recycling, Phys. Rev. Lett. 94, 065504 (2005).
- [12] T. G. Lombardo, F. H. Stillinger, and P. G. Debenedetti, Thermodynamic mechanism for solution phase chiral amplification via a lattice model, Proc. Natl. Acad. Sci. **106**, 15131 (2009).
- [13] A. L. Lehninger, D. L. Nelson, and M. M. Cox, *Lehninger Principles of Biochemistry* (Macmillan, 2005).
- [14] S. C. Glotzer, D. Stauffer, and N. Jan, Monte carlo simulations of phase separation in chemically reactive binary mixtures, Phys. Rev. Lett. 72, 4109 (1994).
- [15] S. Puri and H. L. Frisch, Segregation dynamics of binary mixtures with simple chemical reactions, J. Phys. A 27, 6027 (1994).
- [16] S. C. Glotzer, E. A. Di Marzio, and M. Muthukumar, Reactioncontrolled morphology of phase-separating mixtures, Phys. Rev. Lett. 74, 2034 (1995).
- [17] D. Carati and R. Lefever, Chemical freezing of phase separation in immiscible binary mixtures, Phys. Rev. E 56, 3127 (1997).
- [18] C. Tong, H. Zhang, and Y. Yang, Phase separation dynamics and reaction kinetics of ternary mixture coupled with interfacial chemical reaction, J. Phys. Chem. B 106, 7869 (2002).
- [19] O. Kuksenok, R. D. M. Travasso, and A. C. Balazs, Dynamics of ternary mixtures with photosensitive chemical reactions: Creating three-dimensionally ordered blends, Phys. Rev. E 74, 011502 (2006).
- [20] R. Krishnan and S. Puri, Molecular dynamics study of phase separation in fluids with chemical reactions, Phys. Rev. E 92, 052316 (2015).
- [21] A. Lamorgese and R. Mauri, Spinodal decomposition of chemically reactive binary mixtures, Phys. Rev. E 94, 022605 (2016).
- [22] M. A. Anisimov, M. Duška, F. Caupin, L. E. Amrhein, A. Rosenbaum, and R. J. Sadus, Thermodynamics of fluid polyamorphism, Phys. Rev. X 8, 011004 (2018).
- [23] N. A. Shumovskyi, T. J. Longo, S. V. Buldyrev, and M. A. Anisimov, Phase amplification in spinodal decomposition of immiscible fluids with interconversion of species, Phys. Rev. E 103, L060101 (2021).
- [24] B. Uralcan, T. J. Longo, M. A. Anisimov, F. H. Stillinger, and P. G. Debenedetti, Interconversion-controlled liquid–liquid phase separation in a molecular chiral model, J. Chem. Phys. 155, 204502 (2021).
- [25] N. D. Petsev, F. H. Stillinger, and P. G. Debenedetti, Effect of configuration-dependent multi-body forces on interconversion kinetics of a chiral tetramer model, J. Chem. Phys. 155, 084105 (2021).
- [26] J. Bauermann, S. Laha, P. M. McCall, F. Jülicher, and C. A. Weber, Chemical kinetics and mass action in coexisting phases, J. Am. Chem. Soc. 144, 19294 (2022).
- [27] K. Binder, Kinetic ising model study of phase separation in binary alloys, Z. Phys. 267, 313 (1974).
- [28] Kinetics of Phase Transitions, edited by S. Puri and V. Wadhawan (CRC Press, Boca Raton, 2009).
- [29] A. A. Hyman, C. A. Weber, and F. Jülicher, Liquid-liquid phase separation in biology, Annu. Rev. Cell Dev. Biol. 30, 39 (2014).

- [30] S. Basu, S. Majumder, S. Sutradhar, S. K. Das, and R. Paul, Phase segregation in a binary fluid confined inside a nanopore, Europhys. Lett. 116, 56003 (2016).
- [31] F. Müller, H. Christiansen, and W. Janke, Phase-separation kinetics in the two-dimensional long-range Ising model, Phys. Rev. Lett. **129**, 240601 (2022).
- [32] A. J. Bray, Theory of phase-ordering kinetics, Adv. Phys. 51, 481 (2002).
- [33] P. C. Hohenberg and B. I. Halperin, Theory of dynamic critical phenomena, Rev. Mod. Phys. 49, 435 (1977).
- [34] A. Singh, S. Puri, and C. Dasgupta, Growth kinetics of nanoclusters in solution, J. Phys. Chem. B 116, 4519 (2012).
- [35] T. J. Longo and M. A. Anisimov, Phase transitions affected by natural and forceful molecular interconversion, J. Chem. Phys. 156, 084502 (2022).
- [36] T. J. Longo, N. A. Shumovskyi, B. Uralcan, S. V. Buldyrev, M. A. Anisimov, and P. G. Debenedetti, Formation of dissipative structures in microscopic models of mixtures with species interconversion, Proc. Natl. Acad. Sci. **120**, e2215012120 (2023).
- [37] K. J. Laidler and M. C. King, The development of transitionstate theory, J. Phys. Chem. 87, 2657 (1983).
- [38] L. Onsager, Crystal statistics. I. A two-dimensional model with an order-disorder transition, Phys. Rev. 65, 117 (1944).
- [39] R. J. Glauber, Time-dependent statistics of the Ising model, J. Math. Phys. 4, 294 (1963).
- [40] K. Kawasaki, Diffusion constants near the critical point for time-dependent Ising models. I, Phys. Rev. 145, 224 (1966).
- [41] M. E. J. Newman and G. T. Barkema, *Monte Carlo Methods in Statistical Physics* (Oxford University Press, Oxford, 1999).
- [42] D. Landau and K. Binder, A Guide to Monte Carlo Simulations in Statistical Physics (Cambridge University Press, Cambridge, 2021).
- [43] S. Majumder, Disentangling growth and decay of domains during phase ordering, Phys. Rev. E 107, 034130 (2023).
- [44] W. Janke, H. Christiansen, and S. Majumder, The role of magnetization in phase-ordering kinetics of the short-range and long-range Ising model, Eur. Phys. J.: Spec. Top. 232, 1693 (2023).
- [45] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevE.109.034119 for evolution snapshots at other *T*, individual plots for progress of the reaction at different *T*, histograms of τ_r at different *T* and p_r , and the time evolution of $\psi(t)$ for a purely segregating system and its corresponding Arrhenius behavior.
- [46] J. Olejarz, P. L. Krapivsky, and S. Redner, Zero-temperature coarsening in the 2D Potts model, J. Stat. Mech. (2013) P06018.
- [47] I. M. Lifshitz and V. V. Slyozov, The kinetics of precipitation from supersaturated solid solutions, J. Phys. Chem. Solids 19, 35 (1961).
- [48] S. Majumder and S. K. Das, Domain coarsening in two dimensions: Conserved dynamics and finite-size scaling, Phys. Rev. E 81, 050102(R) (2010).
- [49] S. Majumder and S. K. Das, Diffusive domain coarsening: Early time dynamics and finite-size effects, Phys. Rev. E 84, 021110 (2011).
- [50] S. Majumder, S. K. Das, and W. Janke, Universal finite-size scaling function for kinetics of phase separation in mixtures with varying number of components, Phys. Rev. E 98, 042142 (2018).

- [51] S. Thwal and S. Majumder, Interplay of phase segregation and chemical reaction: Crossover and effect on growth laws, arXiv:2311.10464.
- [52] The overall qualitative behavior of all the subsequent results are insensitive to any choice of h > 0.6.
- [53] See Fig. S11 in the SM to check how the segregation order parameter $\psi(t)$ captures the kinetics of a purely phase segregating system, and the corresponding Arrhenius behavior of the relaxation time τ_s .
- [54] J. Viñals and J. D. Gunton, Fixed points and domain growth for the Potts model, Phys. Rev. B 33, 7795 (1986).

- [55] J. C. Dyre, *Colloquium:* The glass transition and elastic models of glass-forming liquids, Rev. Mod. Phys. 78, 953 (2006).
- [56] L. Berthier and G. Biroli, Theoretical perspective on the glass transition and amorphous materials, Rev. Mod. Phys. 83, 587 (2011).
- [57] M. Henkel and M. Pleimling, Non-Equilibrium Phase Transitions: Ageing and Dynamical Scaling far from Equilibrium (Springer, Heidelberg, 2010), Vol. 2.
- [58] S. Majumder and S. K. Das, Effects of density conservation and hydrodynamics on aging in nonequilibrium processes, Phys. Rev. Lett. 111, 055503 (2013).
- [59] F. Y. Wu, The Potts model, Rev. Mod. Phys. 54, 235 (1982).