

# Kinetic Monte Carlo Study on the Role of Heterogeneity in the Dissolution Kinetics of Glasses

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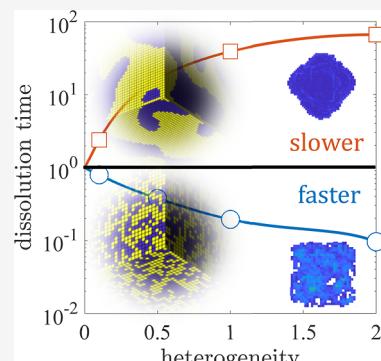
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**ABSTRACT:** The dissolution of silicate and other oxide glasses regulates many natural processes and plays an important role in many technological applications. Despite the fact that these glasses are inherently heterogeneous, current theories of glass dissolution exclusively rely on average descriptors of the structure or chemistry of the glass. The effect that spatial fluctuations in the local structure and chemical composition of a glass has on its dissolution kinetics is not well understood. Here, we use kinetic Monte Carlo (KMC) simulations to elucidate the role that heterogeneity plays in the dissolution kinetics of a glass model system. In single-phase particles, we find that heterogeneity, far from having a monotonic effect, can slow down or speed up the dissolution depending on the average extent of disorder of the glass. In two-phase particles, we find that the dissolution kinetics of phase-separated systems is governed by the less-soluble phase, while for well-mixed systems, the dissolution can be faster than that of the equivalent single-phase system because as the more soluble phase dissolves, it leaves behind a sparse structure of the less soluble phase which can then dissolve faster. We explain our findings based on both the mechanisms of dissolution observed in the KMC simulations and theoretical arguments.



## INTRODUCTION

Silicates and other oxide glasses, which consist of a non-equilibrium, disordered network of polyhedral units made of oxygen-coordinated ions, such as silicon or boron (network formers), depolymerized by cations such as calcium, sodium, or potassium (network modifiers), are intrinsically heterogeneous.<sup>1,2</sup> The weathering and dissolution of oxide glasses far from equilibrium are fundamentally regulated by the activation energy that the network-forming ions need to overcome to transition from the glass into solution.<sup>3</sup> Such phenomena play an essential role in natural processes such as carbon sequestration,<sup>4</sup> and its understanding is essential to advance technological applications such as the search for low-carbon alternatives to ordinary Portland cement.<sup>5</sup> Compositional relationships and simple structural descriptors of the glass, such as the ratio of non-bridging to bridging oxygens, have been shown to correlate poorly, or not at all, with the dissolution rate of silicates.<sup>6,7</sup> On the other hand, topological descriptors of the glass network, such as the average number of topological constraints per atom, have been shown to correlate better with the initial dissolution rate of silicates<sup>6</sup> and have recently been incorporated in machine learning frameworks to predict dissolution with some success.<sup>8,9</sup> Yet, current models of glass dissolution still rely on average descriptors which neglect the chemical and structural spatial fluctuations inherent to real glasses.

Kinetic Monte Carlo (KMC) is an event-driven simulation technique which, as such, is not limited by the timescale of individual events.<sup>10</sup> In the context of glass or mineral

dissolution, events typically consist of the removal of sites representing network-former units or atoms from the glass or mineral surface, respectively. KMC simulations have therefore been extensively employed to study the dissolution of minerals<sup>11,12</sup> and glasses under simplifying assumptions about their amorphous structure and the kinetics of single events.<sup>13,14</sup> In a recent study, Kerisit and Du mapped the connectivity of the KMC model from glass configurations obtained using molecular dynamics simulations,<sup>15</sup> which constitutes a first step toward the dissolution of realistic glass structures. Besides structural simplifications, most previous KMC studies of glass dissolution<sup>13–15</sup> have assumed constant probabilities of dissolution for sites with the same number of neighbors (the probability of dissolution typically scales linearly with the number of neighbors), thus neglecting the structural and chemical heterogeneity of real glasses. The recent work by Jan et al. is an exception to this practice, where a normal distribution of dissolution probabilities was used in an effort to account for the variability in the strength of the linkages between network-former units in real glasses.<sup>16</sup> Currently, the main bottleneck toward the realistic simulation of glass

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dissolution is the impossibility of calculating and cataloguing all the activation energies to dissolution of each of the network-former units in each of the myriad the different local environments found in the glass.

Here, we carry out KMC simulations of dissolution far from equilibrium of glass particles in order to investigate the role of heterogeneity in their dissolution kinetics. In our model, the disordered and heterogeneous character of the glass is captured by the stochastic nature of the activation energies to dissolution assigned to each site, which are drawn from a statistical distribution with controlled average and standard deviation. The average of the distribution of activation energies represents an average descriptor of the glass structure and therefore should be correlated with quantities in dissolution models such as the average number of topological constraints per atom. On the other hand, the standard deviation of the distribution of activation energies captures the extent of the spatial fluctuations in the glass structure and/or chemical composition, which we refer to as heterogeneity in the disorder. For multiphase glass particles, there are two potential sources of heterogeneity: the heterogeneity in the disorder of each individual phase and the heterogeneity induced by the spatial distribution of the phases, which depends on the degree of phase separation. While our model system is inspired by oxide glasses, it does not capture the realistic molecular structure of such glasses, and therefore, the predictions made here are not intended to be quantitative. Our model, however, offers a simple, controllable framework to systematically evaluate the role of heterogeneity in the dissolution kinetics of multiphase disordered systems. Our findings demonstrate that heterogeneity has a non-trivial effect on the dissolution kinetics of glasses, which emphasize the need for new theories of glass dissolution that transcend the use of just average descriptors, an issue that has begun to be recognized across fields.<sup>17</sup>

## ■ COMPUTATIONAL METHODS

We carry out KMC simulations of the dissolution of finite-size 3D particles consisting of a regular lattice of sites with von Neumann neighborhoods of range 1 (i.e., the neighbors of a certain site are orthogonally adjacent to it). In 3D, the maximum number of von Neumann neighbors of a site is 6. We simulate the dissolution process far from equilibrium (i.e., under dilute conditions), which implies that once a site is removed or dissolved, it cannot redeposit on the reacting surface of the particle. A limitation of this assumption is that alteration or passivation layers cannot be simulated. All the results reported in this paper were obtained for cubic particles with 125,000 sites ( $50 \times 50 \times 50$ ). As shown in Figure S1, the size of the system only affects the overall dissolution timescale but not the mechanism of dissolution.

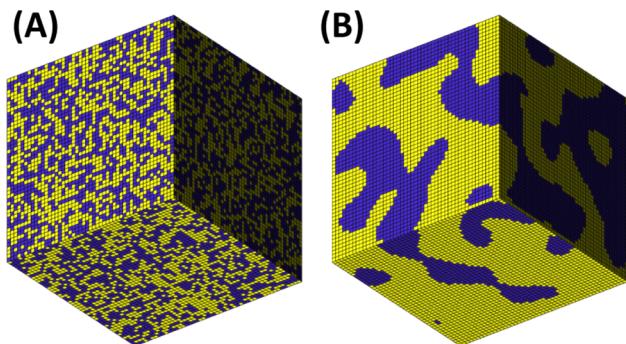
The dissolution of the particle proceeds through the removal of a surface site from the system at each step of the simulation. The removal of a surface site represents the dissolution of a single network-former unit from the glass particle, and only sites on the surface of the particle are considered to be in contact with the solution and thus dissolvable. The selection of the site to be removed at each step and the calculation of the time step are carried out using the Bortz–Kalos–Liebowitz algorithm. Each step of the simulation, a dissolution rate is assigned to each surface site in the system calculated using  $r_i = \omega_0 e^{-E_a^i/k_B T}$ , where  $E_a^i$  is the activation energy to the

dissolution site  $i$ ,  $k_B T$  is the thermal energy, and  $\omega_0$  is an attempt frequency. We assume  $\omega_0$  to be the same for all sites and therefore use  $\omega_0^{-1}$  as our time unit. Site  $i$  is removed from the system if it satisfies  $R_{i-1} < u_1 R_N < R_i$ , where  $u_1 \in [0,1]$  is a uniform random number,  $R_i = \sum_{j=1}^i r_j$  is the function of cumulative rates for each event  $i = 1, 2, \dots, N$ , where  $N$  is the total number of transitions, and  $R_N = \sum_{j=1}^N r_j$  is the sum of the rates of all transitions. The time step assigned to the event is given by  $\Delta t = -\log u_2 / R_N$ , where  $u_2 \in [0,1]$  is another uniform random number.

The activation energy to dissolution of a site  $i$  is given by  $E_a^i = nn_i \bullet E_0^i$ , where  $nn_i$  is the number of von Neumann neighbors of site  $i$  and  $E_0^i$  is a stochastic base activation energy  $E_0^i = X(\bar{E}_0, \sigma_{E_0})$ , where  $X$  is a log-normal random variable with mean  $\bar{E}_0$  and standard deviation  $\sigma_{E_0}$ . We associate  $\bar{E}_0$  with the overall disorder or degree of polymerization of the glass (or in the context of topological constraint theory, to the average number of topological constraints per atom). Therefore, lower values of  $\bar{E}_0$ , correspond to more soluble glasses. The standard deviation of the distribution,  $\sigma_{E_0}$ , captures the heterogeneity in the disorder in the glass. The specific function of the statistical distribution of the base activation energies does not affect the trends reported here (Figure S2).

We simulate single-phase systems with  $\bar{E}_0 = 2, 4, 6, 8$ , or  $12 k_B T$  and  $\sigma_{E_0} = 0, 0.1, 0.5, 1$ , or  $2 k_B T$ . We refer to single-phase systems with  $\sigma_{E_0} = 0$  as homogeneous. We also simulate two-phase systems, where each phase A and B is characterized by a different distribution of the base activation energies:  $E_{0,A}^i = X(\bar{E}_0^A, \sigma_{E_0}^A)$  and  $E_{0,B}^i = X(\bar{E}_0^B, \sigma_{E_0}^B)$ . We only simulate systems where the fraction of sites of each phase is the same. The spatial distribution of the phases is generated by numerically simulating, on the system lattice, the spinodal decomposition process of a binary fluid using the Cahn–Hilliard equation  $\partial c / \partial t = D \nabla^2 (c^3 - c - \gamma \nabla^2 c)$ , where  $c = \pm 1$  indicates the phase,  $D$  is a diffusion coefficient, and  $\gamma$  is a parameter that governs the length scale of the transition regions between domains of different phases.<sup>18</sup> We generate the different phase morphologies by adjusting the parameter  $\gamma$ . We quantify the degree of phase separation using the order parameter  $\Phi = n_{AB} / (n_{AA} + n_{BB}) \in [0,1]$ , where  $n_{IJ}$  is the number of von Neumann neighbors between phases I and J. For a system where the phase identity of the sites is selected at random,  $\Phi = 1$ , and in a system where the phases are separated into just two large domains,  $\Phi \rightarrow 0$ . Here, we compare the dissolution behavior of two-phase morphologies: well-mixed ( $\Phi = 0.74$ ) and phase-separated ( $\Phi = 0.09$ ) (Figure 1). The average base activation in the system is  $\bar{E}_0 = (\bar{E}_0^A + \bar{E}_0^B) / 2 = 6$  or  $12 k_B T$ , the difference in the average base activation energy between the two phases is  $\Delta \bar{E}_0 = \bar{E}_0^A - \bar{E}_0^B = 2, 4$ , or  $6 k_B T$ , and the standard deviation of the distribution of base activation energies is the same for both phases:  $\sigma_{E_0}^A = \sigma_{E_0}^B = \sigma_{E_0} = 0, 0.5, 1$ , or  $1.5 k_B T$ . The chosen values for the different parameters are intended to cover a broad range of the parameter space and thus a variety of system behaviors.

For each combination of parameters, we perform four independent runs. The values shown in the figures of this paper correspond to the average values among those



**Figure 1.** Snapshots of the two-phase systems with different degrees of phase separation. (A) Well-mixed ( $\Phi = 0.74$ ). (B) Phase-separated ( $\Phi = 0.09$ ).

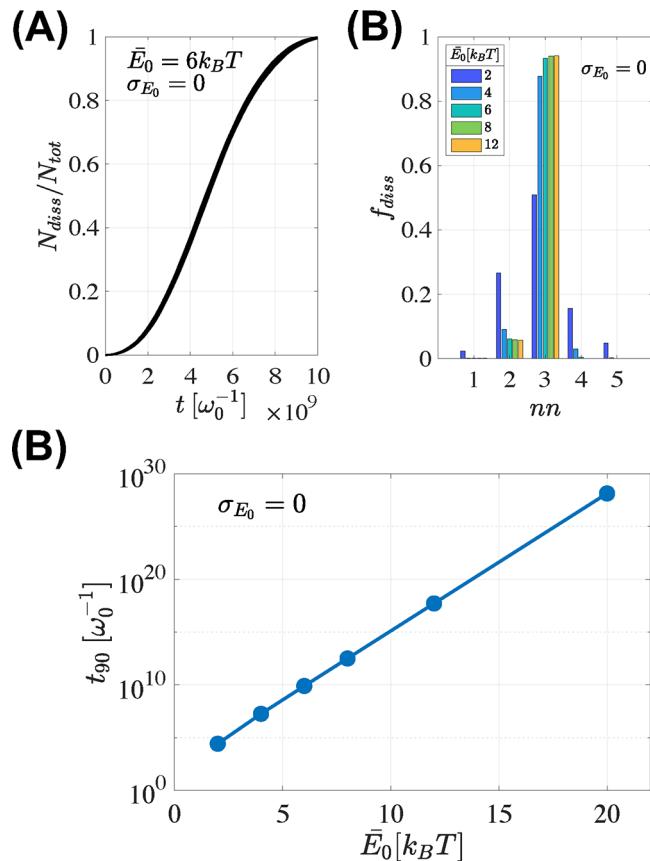
independent runs. The error bars in the figures are not shown when the errors are smaller than the size of the symbols, which is the case for most of the analyzed quantities.

All the simulations and numerical analysis have been carried out using our own scripts and the program MATLAB.<sup>19</sup>

## RESULTS AND DISCUSSION

In this section, we first explain the kinetics and mechanism of dissolution of single-phase homogeneous systems. We follow up by characterizing the effect of heterogeneous disorder on the dissolution of single-phase systems and explain the fundamental mechanisms that are responsible for speeding up or slowing down the process. Finally, we elucidate the role that multiphase morphology and heterogeneous disorder have in the dissolution kinetics of two-phase heterogeneous systems.

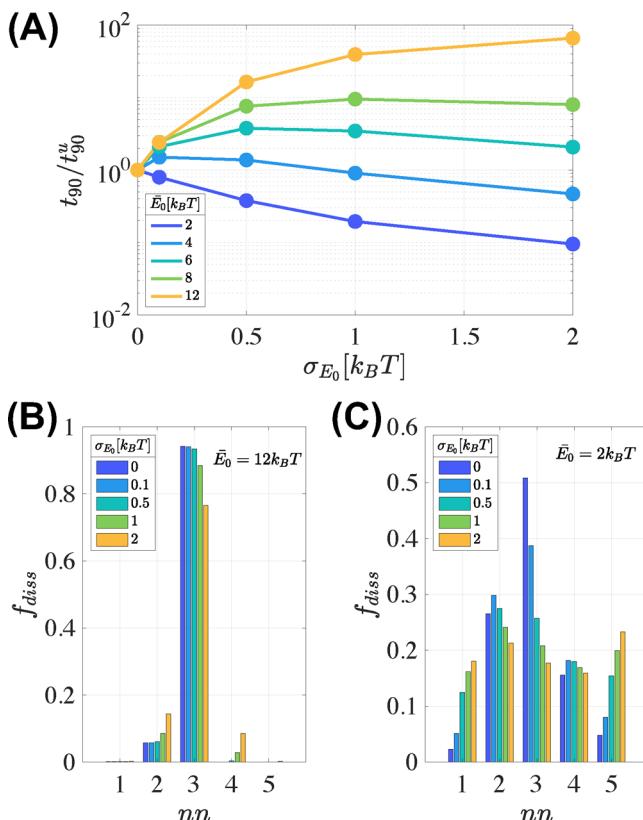
**Single-Phase Homogeneous Systems.** The degree of dissolution over time,  $N_{\text{diss}}/N_{\text{tot}} \in [0,1]$ , where  $N_{\text{diss}}$  is the number of dissolved sites at a given time (i.e., the number of sites removed from the system since the start of the simulation up to a given time) and  $N_{\text{tot}}$  is the total number of sites in the system, displays a sigmoidal shape for homogeneous systems ( $\sigma_{E_0} = 0$ ) (Figure 2A). Initially, dissolution proceeds at the corners of the cubic particle, which increases the number of sites exposed on the surface with three von Neumann neighbors (i.e., kink sites), which in turn increases the dissolution rate. Once the particle becomes roughly spherical, the number of kink sites on the surface of the system monotonically decreases as the system dissolves and becomes smaller, which slows down the dissolution. The distribution of the number of neighbors that sites had at the time of dissolution quantitatively supports the mechanism of dissolution by kink site desolvation (Figure 2B). Only for very low base activation energies (e.g.,  $\bar{E}_0 = 2 k_B T$ ) which would correspond to a highly depolymerized, highly soluble glass, we find a non-negligible fraction of sites that dissolved having two or four neighbors. A homogeneous system dissolving through a barrierless process,  $\bar{E}_0 = 0$ , would show a roughly uniform distribution of the number of neighbors of dissolved sites. As shown in Figure 2C, the time that it takes to dissolve 90% of the sites of a particle,  $t_{90}$ , depends exponentially on the average base activation energy,  $t_{90} \propto e^{\bar{E}_0/k_B T}$ . This Arrhenius behavior has been experimentally observed for the initial dissolution rate (where the far-from-equilibrium assumption made here should be suitable) of glasses<sup>20,21</sup> for a broad range of pH values. Our results are also qualitatively consistent with the abundant



**Figure 2.** Dissolution of homogeneous systems ( $\sigma_{E_0} = 0$ ). (A) Degree of dissolution,  $N_{\text{diss}}/N_{\text{tot}}$ , as a function of time for the homogeneous system with  $\bar{E}_0 = 6 k_B T$ . The lines corresponding to the different independent runs largely overlap in this plot. (B) Distribution of the number of neighbors that sites had at the time of dissolution. (C) Time that it takes to dissolve 90% of the sites of the particle,  $t_{90}$ , as a function of the average base activation energy,  $\bar{E}_0$ .

experimental evidence that increasing the structural disorder of a glass (equivalent to decreasing  $\bar{E}_0$  here) speeds up its dissolution rate exponentially.<sup>22</sup>

**Single-Phase Heterogeneous Systems.** The dissolution time of single-phase heterogeneous systems normalized by that of the homogeneous systems with the same average base activation energy is shown in Figure 3A. The simulations reveal that the effect of heterogeneity on the dissolution kinetics, whether it slows down or speeds up the process, depends on the average base activation energy  $\bar{E}_0$ . For systems with low  $\bar{E}_0$ , corresponding to highly soluble glasses, increasing the heterogeneity in the disorder (i.e., the standard deviation of the base activation energies,  $\sigma_{E_0}$ ) speeds up the dissolution. On the other hand, intriguingly, increasing  $\sigma_{E_0}$  slows down the dissolution of systems with high  $\bar{E}_0$ . For example, the dissolution of the most heterogeneous system ( $\sigma_{E_0} = 2 k_B T$ ) with the lowest average base activation energy ( $\bar{E}_0 = 2 k_B T$ ) simulated here dissolves about 10 times faster than its homogeneous counterpart, while the most heterogeneous system ( $\sigma_{E_0} = 2 k_B T$ ) with the highest average base activation energy ( $\bar{E}_0 = 12 k_B T$ ) dissolves around 100 times slower than the homogeneous counterpart. For systems with intermediate values of  $\bar{E}_0$ , the effect of heterogeneity on the dissolution



**Figure 3.** Dissolution of single-phase heterogeneous systems. (A) Time that it takes to dissolve 90% of the sites of the particle,  $t_{90}$ , normalized by the dissolution time of the homogeneous system with the same  $\bar{E}_0$ ,  $t_{90}^u$ , as a function of  $\sigma_{E_0}$  for systems with different  $\bar{E}_0$ . Panels (B,C) show the distribution of the number of neighbors that sites had at the time of dissolution for heterogeneous systems with  $\bar{E}_0 = 12 k_B T$  and  $\bar{E}_0 = 2 k_B T$ , respectively.

kinetics can be non-monotonic (Figure 3A). For example, for the system with  $\bar{E}_0 = 4 k_B T$ , increasing the heterogeneity slightly slows down the dissolution initially, but for  $\sigma_{E_0} > k_B T$ , the trend is reversed, and dissolution is sped up with respect to the homogeneous system.

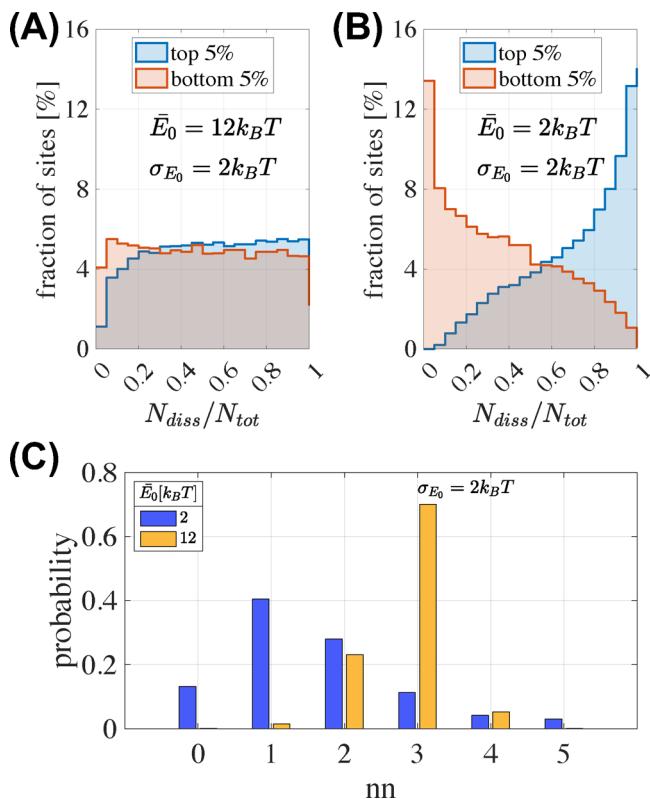
In regard to the mechanism of dissolution of single-phase heterogeneous systems, we find that systems with high  $\bar{E}_0$  primarily dissolve through kink site removal regardless of the level of heterogeneity, analogous to the dissolution mechanism of homogeneous systems (Figure 3B). Highly heterogeneous systems with low  $\bar{E}_0$ , on the other hand, dissolve through near-random site removal, as evidenced by the fact that the distribution of the number of neighbors of dissolved sites is nearly uniform (Figure 3C).

We can theoretically show that the heterogeneity in the base activation energies unequivocally leads to slower dissolution with respect to an equivalent homogeneous system as long as the dissolution pathway for both homogeneous and heterogeneous systems is deterministic. In our model (see the Computational Methods section), the activation energy associated with the site dissolved at some step  $i$  is  $E_a^i = nn_i \bar{E}_0$ , where  $nn_i$  is the number of neighbors of the site and  $E_0^i = X(\bar{E}_0, \sigma_{E_0})$  is the stochastic base activation energy assigned to the site, where  $X$  is a random variable drawn from a statistical distribution with mean  $\bar{E}_0$  and standard

deviation  $\sigma_{E_0}$ . The dissolution time of the system,  $T$ , can be written as  $T = \sum_{i=1}^N \Delta t_i$ , where  $\Delta t_i$  is the time step associated with such activated event which is proportional (not equal) to the activation energy:  $\Delta t_i \propto e^{E_a^i/k_B T}$ . Therefore, for a homogeneous system, where  $E_a^i = nn_i \bar{E}_0$ , the timescale of dissolution can be written as  $T_u \propto \sum_{i=1}^N e^{nn_i \bar{E}_0/k_B T}$ . For a heterogeneous system, if we assume for the sake of simplicity that the base activation energy can be expressed as the sum of a constant plus a stochastic term with zero mean,  $E_0^i \approx \bar{E}_0 + X(0, \sigma_{E_0})$ , the timescale of dissolution can then be written as  $T_h \propto \sum_{i=1}^N e^{nn_i [\bar{E}_0 + X(0, \sigma_{E_0})]/k_B T}$ . If we further assume that the pathway to dissolution is deterministic, which means that the sequence of  $nn_i$  is the same for both homogeneous and heterogeneous systems, then it follows that  $T_h/T_u > 1$ . In conclusion, under the assumption that the dissolution pathway is deterministic, the heterogeneity will slow down the dissolution with respect to a homogeneous system. Although the exact dissolution pathway (i.e., the sequence of  $nn_i$ ) will be in principle different, even between two realizations of the dissolution of the same system, our simulations show that systems with high  $\bar{E}_0$  primarily dissolve through kink site desolvation regardless of  $\sigma_{E_0}$  (Figure 3B), which is the same dissolution pathway observed for the homogeneous systems (i.e.,  $nn_i = 3$  for most steps). Consequently, systems with high  $\bar{E}_0$  fulfill, approximately, the assumption of the deterministic pathway made in the theoretical argument above, and, in fact, we observe that the heterogeneity slows down the dissolution of these systems (Figure 3A). An alternative perhaps more intuitive way to think about this mechanism is as follows. If one envisions the sequential dissolution of kink sites as a one-dimensional path, eventually, sites with high base activation energies must be dissolved, which will disproportionately slow down the dissolution kinetics due to the exponential dependence of the dissolution rate on the activation energy to dissolution.

The question remains of how heterogeneity is able to speed up the dissolution of systems with low  $\bar{E}_0$ . In heterogeneous systems with high  $\bar{E}_0$ , dissolution is primarily controlled by the number of neighbors of dissolvable sites, and only the sites with the lowest number of neighbors (typically kink sites) have a reasonable probability of dissolving. The noise induced by the heterogeneity in the disorder cannot significantly offset this effect in those cases. In contrast, in systems with low  $\bar{E}_0$  and high  $\sigma_{E_0}$ , it is not only statistically possible but likely that non-kink sites dissolve before kink sites do, if such sites have a low stochastic base activation energy which can offset the energetic cost of having more neighbors. This mechanism of dissolution would lead to an incongruent dissolution pattern, where the probability of dissolving sites with any number of neighbors is roughly the same, which is exactly what we observe in our simulations (Figure 3C), where the distribution of the number of neighbors of dissolved sites is nearly uniform for  $\bar{E}_0 = 2 k_B T$  and  $\sigma_{E_0} = 2 k_B T$ .

To further illustrate how the fundamental mechanisms explained above arise in our simulations, we analyze the time of dissolution of sites with the top and bottom 5% base activation energies (Figure 4). For  $\bar{E}_0 = 12 k_B T$  and  $\sigma_{E_0} = 2 k_B T$ , save for the early stages of dissolution, all sites, regardless of



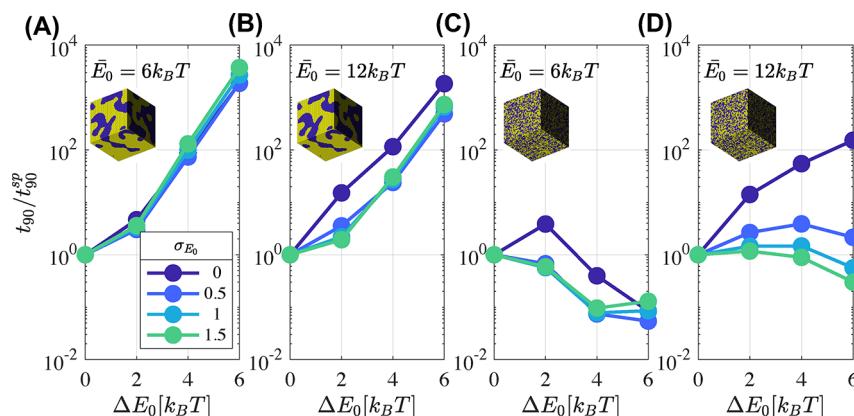
**Figure 4.** Dissolution mechanism of single-phase heterogeneous systems. (A,B) show the percentage of sites with the top and bottom 5% base activation energies dissolved at different times during the simulation. (C) Distribution of the number of neighbors at the time of dissolution of sites with the top 5% base activation energies for systems with  $\bar{E}_0 = 2 k_B T$  and  $12 k_B T$ .

whether their base activation energy is on the top or bottom 5% of the distribution, dissolve at roughly the same rate during the span of the simulation (Figure 4A). On the other hand, for the system with  $\bar{E}_0 = 2 k_B T$  and  $\sigma_{E_0} = 2 k_B T$ , we find that sites with base activation energies in the top 5% are primarily dissolved toward the end of the simulation, while sites with base activation energies in the bottom 5% mostly dissolve at earlier times (Figure 4B). If we look at the distribution of the

number of neighbors at the time of dissolution of sites with the top 5% base activation energies for both  $\bar{E}_0 = 2 k_B T$  and  $\bar{E}_0 = 12 k_B T$  systems (Figure 4C), we see that, for  $\bar{E}_0 = 2 k_B T$ , the distribution is shifted toward fewer numbers of neighbors compared to that of the system with  $\bar{E}_0 = 12 k_B T$ . Therefore, we find that in systems with low  $\bar{E}_0$ , the heterogeneity enables the dissolution of sites with high base activation energies at later times when their number of neighbors is small, which speeds up the dissolution kinetics. In other words, the sites with high base energies do not affect the dissolution kinetics of systems with low  $\bar{E}_0$ , as it was the case for systems with high  $\bar{E}_0$ , where they were unavoidable.

**Two-Phase Heterogeneous Systems.** We first analyze the effect on the dissolution kinetics of the difference in the average base activation energy between of the two phases,  $\Delta\bar{E}_0$ . For phase-separated systems (Figure 5A,B), increasing  $\Delta\bar{E}_0$  leads to an exponential slowdown of dissolution with respect to the equivalent, single-phase system with the same  $\bar{E}_0$  and  $\Delta\bar{E}_0 = 0$ . For example, a two-phase particle with  $\bar{E}_0 = 6 k_B T$  and  $\Delta\bar{E}_0 = 6 k_B T$ , thus  $\bar{E}_0^A = 3 k_B T$  and  $\bar{E}_0^B = 9 k_B T$ , dissolves about 4000 times slower than the equivalent single-phase particle. This result indicates that the dissolution of phase-separated systems is primarily governed by the dissolution of the less-soluble phase. The heterogeneous disorder of each phase,  $\sigma_{E_0}$  (the different series plotted in Figure 5A and 5B), or the overall average base activation energy of the system,  $\bar{E}_0$  (Figure 5A vs Figure 5B), seem to play a minor role in comparison.

In well-mixed, two-phase systems, the effect of  $\Delta\bar{E}_0$  is more nuanced (Figure 5C,D). For systems with moderate average base activation energies, e.g.,  $\bar{E}_0 = 6 k_B T$ , increasing  $\Delta\bar{E}_0$  speeds up the dissolution (Figure 5C), although the accelerating effect is more modest than the decelerating effect of  $\Delta\bar{E}_0$  on phase-separated systems. This behavior can be explained by the fact that, in a well-mixed system, the dissolution of the more soluble phase leaves behind a sparse, solid structure of the less-soluble one, which dissolves much faster than if it would be in a compact, dense shape as is the case in phase-separated systems (Figure 5C). As the average base activation energy in the system increases to  $\bar{E}_0 = 12 k_B T$ ,



**Figure 5.** Dissolution time of heterogeneous two-phase systems. The different colors stand for different values of the heterogeneity in the disorder of the phases  $\sigma_{E_0}$ . The dissolution times of the two-phase systems are normalized by the dissolution time of the equivalent single-phase system (same  $\bar{E}_0$  and  $\Delta\bar{E}_0 = 0$ ),  $t_{90}^{sp}$ . (A) Phase-separated and  $\bar{E}_0 = 6 k_B T$ . (B) Phase-separated and  $\bar{E}_0 = 12 k_B T$ . (C) Well-mixed and  $\bar{E}_0 = 6 k_B T$ . (D) Well-mixed and  $\bar{E}_0 = 12 k_B T$ .

the heterogeneity in the disorder of the phases plays a significant role (Figure 5D). For systems made of homogeneous phases, increasing  $\Delta\bar{E}_0$  leads to slightly slower dissolution, but as  $\sigma_{E_0}$  increases, the trend reverts, although the speed-up effect is very modest. Well-mixed, two-phase systems with higher base activation energies and heterogeneous disorder (e.g.,  $\Phi = 0.74$ ,  $\bar{E}_0 = 12 k_B T$ , and  $\sigma_{E_0} = 1.5 k_B T$ ) resemble single-phase systems more closely than other multiphase systems, and as a result, their dissolution kinetics is very close to that of the single-phase systems.

## CONCLUSIONS

Here, we have used KCM simulations of the far-from-equilibrium dissolution kinetics of glass model systems to elucidate the effect of heterogeneity in the disorder of single phase and multiphase systems. In our model, each site in the system is associated to a stochastic base activation energy,  $E_0$ , drawn from a log-normal distribution,  $E_0 = X(\bar{E}_0, \sigma_{E_0})$ , where the average base activation energy,  $\bar{E}_0$ , captures the overall level of disorder in the glass (e.g., degree of depolymerization), and the standard deviation of the distribution,  $\sigma_{E_0}$ , accounts for the heterogeneity of that disorder (spatial fluctuations in the structure and chemical composition).

We found from the KMC simulations that, when compared to homogeneous systems ( $\sigma_{E_0} = 0$ ), increasing the heterogeneity in the disorder slowed down the dissolution of systems with high  $\bar{E}_0$  but sped up the dissolution of systems with low  $\bar{E}_0$ . Using a theoretical argument, we explained the slow-down effect of heterogeneity on systems with high  $\bar{E}_0$ , which is expected when the dissolution pathway is deterministic. We found that the accelerating effect of heterogeneity on systems characterized by low  $\bar{E}_0$  was due to the fact that, in such systems, it becomes statistically likely to dissolve sites with low base activation energies early on during the simulation, which allows for sites with high base activation energies to be dissolved at later times, when their number of neighbors is reduced, and thus, the time step incurred to dissolve them is much shorter. In other words, the sites in the system with high base activation energies, whose presence becomes more likely as the heterogeneity increases, limit the dissolution kinetics of systems with high  $\bar{E}_0$ , but not those with low  $\bar{E}_0$ , where the dissolution of such sites occurs later during the dissolution process, when the average number of neighbors of those sites is reduced.

In binary systems, we found that the dissolution kinetics of particles where the phases are separated in large domains is governed by the less-soluble phase, and as a result, these systems dissolve much more slowly than single-phase systems with an equivalent average base activation energy. In the case of particles with well-mixed phase morphologies, the dissolution is faster than that of the equivalent single-phase system because as the more soluble phase dissolves, it leaves behind a sparse structure of the less-soluble phase where the coordination of the sites is much lower than in a uniform bulk system.

Based on previous experimental studies of the activation energies to dissolution in glasses,<sup>21,23</sup> it is likely that most real glasses will behave closely to what we have referred to here as high  $\bar{E}_0$  systems, for which increasing heterogeneity slows down the dissolution kinetics. Direct comparison of our results

with experimental studies is challenging mainly due to the generic chemical nature of our model, and the fact that the effect of the overall level of disorder in the glass and that of its heterogeneity are convoluted in experimental studies. Moreover, quantitative measurements of the spatial distribution of structural disorder in glasses are lacking. It is also possible, perhaps even likely, that the average level of disorder is correlated with its heterogeneity in real glasses, which would imply that both factors cannot be tuned independently. For example, Angeli et al. showed that borosilicate glasses with higher overall structural disorder displayed broader distributions of T–O–T' bridge angles (where T and T' are network-formers), which is a descriptor that could be correlated with the degree of heterogeneity that we use here.<sup>22</sup> In that study, the most disordered (and presumably more heterogeneous) glasses were found to dissolve faster than the less disordered systems,<sup>22</sup> which is consistent with the role of  $\bar{E}_0$  in our simulations. In an attempt to isolate compositional effects from structural effects, several studies have compared the dissolution kinetics between crystals and glasses with equivalent chemical compositions. However, elucidating the role of disorder based on the results from such studies is challenging. For example, while amorphous silica dissolves about an order of magnitude faster than quartz,<sup>21</sup> the dissolution kinetics of albite glass and crystal are similar.<sup>24</sup> Other studies have also highlighted the mechanistic differences in the dissolution of crystals and glasses, making it harder to isolate the effect of just structural disorder on the dissolution kinetics.<sup>25,26</sup> Some studies have also aimed at understanding the chemical durability (inversely related to solubility) of multiphase, heterogeneous, borosilicate glasses.<sup>27,28</sup> In such studies, the addition of molybdenum oxide was observed to polymerize the silicate network of the surrounding vitreous phase and make it more durable (equivalent to increasing the  $\bar{E}_0$  of the more soluble phase).<sup>27</sup> Crystalline domains promoted by rare-earth elements were also observed to promote the polymerization of the surrounding silicate network.<sup>28</sup> It is worth noting that the phase morphologies in those studies are the product of nucleation and growth processes (not spinodal decomposition) and that both phases are not always found in equal proportions.

In summary, our work highlights the non-trivial (possibly counterintuitive) effect of heterogeneity on the dissolution kinetics of glass model systems and the need to incorporate in theories of glass dissolution, not only the overall level of disorder but also a description of the fluctuations in the chemical composition and molecular structure found in real glasses.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c01123>.

Size effects of the kinetics of dissolution of single-phase systems and effect on the dissolution kinetics of the statistical distribution of base activation energies (PDF)

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## Notes

The authors declare no competing financial interest.

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