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# Mean Field Treatment of Heterogeneous Steady State Kinetics

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## Abstract

We propose a method to quickly compute steady state populations of species undergoing a set of chemical reactions whose rate constants are heterogeneous. Using an average environment in place of an explicit nearest neighbor configuration, we obtain a set of equations describing a single fluctuating active site in the presence of an averaged bath. We apply this Mean Field Steady State (MFSS) method to a model of  $H_2$  production on a disordered surface for which the activation energy for the reaction varies from site to site. The MFSS populations quantitatively reproduce the KMC results across the range of rate parameters considered.

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## Introduction

Beneath the ensemble average common to macroscopic observations, heterogeneity plays an astonishing role in chemical kinetics. From light harvesting [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15] to chemical catalysis [16, 17, 18, 19, 20, 21, 22, 23, 24] to signaling [25, 26, 27, 28, 29, 30] to enzyme function [31, 32, 33, 34] there is a common theme: chemical function is not determined by the typical or average member of the ensemble. Rather, the rate of a given

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process can be strongly influenced by outliers.

Stochastic approaches have proven indispensable in the theoretical understanding of how this kind of molecule-by-molecule heterogeneity governs the dynamics. Kinetic Monte Carlo (KMC) provides an in principle exact method for dealing with both spatial and temporal fluctuations in rate constants.[35, 36, 37, 38, 39, 40, 41, 42] Meanwhile, stochastic master equations provide a powerful tool for simulating systems in which the rate constant is spatially uniform but fluctuates in time. This kind of purely dynamic disorder is, for example, thought to be widespread in cooperative or allosteric interactions.[43, 44, 45, 46] The challenge of using any of these techniques is that they are often frustratingly slow, either because of the range of timescales involved [47, 39, 48] or because of the influence of long-range forces on the rates. [36, 47, 49, 50] The time-consuming nature of these methods can sometimes prevent systematic study of the importance of individual rates on the dynamics, since such exploration requires running dozens or hundreds of already time consuming simulations.

In this article, we report the development of a new method, the Mean Field Steady State (MFSS) approximation, that retains the speed and simplicity of ensemble kinetics while also accounting in an averaged sense for the static disorder that is evident in so many chemical situations. MFSS makes a different use of the mean field approximation than the Langmuir-Hinshelwood[51, 52, 53] or Bragg-Williams[54, 55] theories employed in the modeling of catalytic surfaces. Indeed, these techniques assume a perfect species mixing by relying on a uniform distribution of catalytic sites. As a result, they quickly fail for inherently heterogeneous phenomena as considered here. To circumvent this issue, other groups have introduced an inhomogeneity factor, effectively allowing for local variations in species occupancy probabilities within the mean field approximation.[56, 57, 58, 59, 60] However, this approach also differs from our MFSS that finds self consistent steady state populations of species subject to inhomogeneous chemical activity.

The general MFSS scheme is illustrated in Figure 1. Envisioning each reaction as occurring at a fixed lattice position, static disorder induces changes in

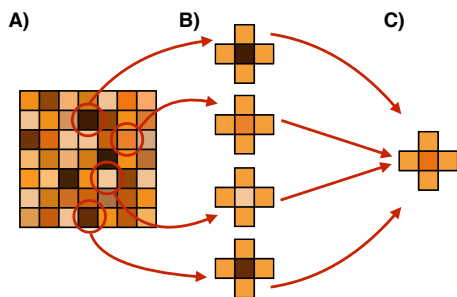


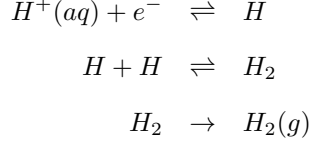
Figure 1: Illustration of the mean field steady state idea. Beginning with a set of sites with different rates (A) one simulates steady state for each site in the presence of a set of averaged neighbors (B). The average of these steady states (C) then self-consistently defines the average neighbor used to obtain steady state.

the underlying rates at individual sites. Focusing on one active site we can approximately replace the neighboring sites by their ensemble averages (the mean field approximation). We can then examine the influence of fluctuations in the rate constants at the active site in the presence of the averaged neighbors to approximately describe the influence of local heterogeneity on the overall kinetics. We finally make the entire simulation self consistent by forcing the average neighbor state to match the computed average over fluctuations at the active site. We should emphasize that here we use the word *heterogeneity* to refer to variations in chemical activity (disorder in chemical rates) as distinguished from heterogeneous catalysis, where *heterogeneity* refers to the phase of the catalyst as compared to the substrate. While self-consistent mean field methods like this are quite common in a variety of fields, for instance in electronic structure, [61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71] and statistical mechanics [72, 73, 74] the analogous formalism does not appear to be widely used in the study of rate equations. This work begins to remedy that situation.

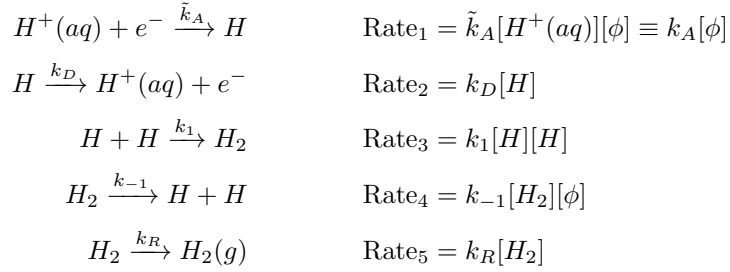
### Working example

It is perhaps easiest to explain how these ideas function by using an example. Toward that end, consider the following hypothetical mechanism for the

catalytic hydrogen evolution ( $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$ ) at a metal surface in aqueous solution:



where  $\text{H}$  and  $\text{H}_2$  refer to chemisorbed species at the surface. For a given chemical system, this may or may not be the appropriate mechanism, but for the purposes of illustration this example is sufficient. If these are the elementary steps in our reaction then at an ensemble level these steps imply a steady state rate expression in the following familiar way. Using  $([\phi], [\text{H}], [\text{H}_2])$  to refer to the fraction of surface sites that are vacant, occupied by an H atom and occupied by  $\text{H}_2$ , respectively, the rate expressions for each step are:



where, for simplicity, we assume that the reaction occurs at constant pH and electrical potential so that  $[\text{H}^+]$  can be absorbed into the rate constant  $k_A$ . We intentionally build a model as simple as possible, for example ignoring the diffusion of adsorbed  $\text{H}_2$ , as is commonly done in method development studies of chemical kinetics.[56, 58, 60] The diffusion of adsorbed hydrogen is effectively accounted for by the sequence of desorption and adsorption steps (slow diffusion limit). At steady state, these macroscopic rate expressions imply that the rate of production of  $\text{H}_2$  gas would be

$$\begin{aligned} &\frac{2k_1k_A(k_A + 2k_R) + (k_A + k_D)(k_Dk_{-1} + k_Dk_R + k_A(k_{-1} + k_R) + \sqrt{\xi})}{2k_1(k_A + 2k_R)^2} \\ &\xi \equiv (k_{-1} + k_R)((k_A + k_D)^2(k_{-1} + k_R) + 4k_1k_A(k_A + 2k_R)). \end{aligned} \quad (1)$$

Now, the steady-state rate (Eq. 1) has the clear weakness that it assumes that the system is homogeneous: every potential absorption site possesses the same catalytic rate  $k_1$  as every other. However, in reality each site might have its own rate as a result of point defects, doping, surface reconstruction, charging, grain boundaries, etc. A specific example in the context of heterogeneous catalysis would be bimetallic surfaces, where the random distribution in the nearest neighbor shell gives rise to non-uniform rates. Alternatively, disorder in catalytic rates can arise from weak adsorbate-adsorbate interactions that does not allow for a significant ordering of the adsorbed layer. Assuming that the activation energy of the bimolecular chemical step is normally distributed, we will vary the rate  $k_1$  (proportional to the exponential of the activation energy) from site to site according to a log-normal distribution:[47]

$$P(\ln(k_1)) = \frac{1}{\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(\ln(k_1) - \overline{\ln(k)})^2}{2\sigma^2}\right), \quad (2)$$

where  $\overline{\ln(k)}$  and  $\sigma$  are the mean and standard deviation respectively. Note then, that  $\sigma$  takes the units of  $k_B T$  such that a value of  $\sigma=5 k_B T$  corresponds to a standard deviation of  $5 k_B T$  in activation energy.

A log-normal distribution is also used in the popular Gaussian disorder model (GDM). [75, 76, 77] In GDM, site energies are distributed in an uncorrelated fashion according to a normal distribution. In our case, we assume that the activation barrier fluctuates in this manner, which would seem a particularly interesting case for kinetics. This distribution might arise, for example, in the presence of randomly distributed point defects near the active site. While physically reasonable, this choice of probability distribution is arbitrary. The method presented here can, in principle, deal with any distribution that is dictated by the underlying chemistry (e.g. a binomial distribution arising from terrace and ledge sites or a logistic distribution representing the cumulative effect of sub-surface defects).

Note that by detailed balance, the variations in  $k_1$  imply similar variations in  $k_{-1}$  because  $k_1 = K_{eq} k_{-1}$  where  $K_{eq}$  is the equilibrium constant for the overall

reaction at the given conditions. For the purpose of this paper, we focus on introducing disorder in the bimolecular rate. Therefore, we will assume that the rate constants for all other steps -  $k_A$ ,  $k_D$  and  $k_R$  - are homogeneous, as also seen elsewhere.[56, 58, 59]

We should also note that the method described here would be perfectly capable of accounting for disorder in all variables. We have performed a single study of disorder in all rates (Figure 4 in the SI), and note that disorder improved the  $H_2$  generation. For simplicity, in the rest of this letter we restrict our attention to disorder in a single variable, but further explorations of simultaneous disorder in multiple variables could be illuminating.

### The self consistent mean field approach

In this situation, the typical solution is to employ KMC [35, 36] to simulate the kinetics: one generates a large lattice of sites with rates  $k_1$  drawn from Eq. 2 (as in Figure 1A) and then monitors the dynamics of all species at all sites until steady state is established. For example, the rate of change of  $H_2$  at site  $i$  at any given instant would be:

$$\frac{d[H_2]_i}{dt} = -k_R[H_2]_i + \sum_j k_1^i [HH]_{ij} - k_{-1}^i [H_2\phi]_{ij}, \quad (3)$$

where  $k_1^i$  and  $k_{-1}^i$  are the catalytic rates at site  $i$ ,  $[H_2]_i$  refers to the probability that site  $i$  is occupied by  $H_2$  and  $[AB]_{ij}$  refers to the probability of  $A$  being at site  $i$  while  $B$  occupies the neighboring site  $j$ . Note that we assume that when  $H_2$  forms or dissociates on a given site, it is the value of  $k_1$  or  $k_{-1}$  at that site that determines the reaction rate.

Clearly, the difficult things to obtain in Eq. 3 are the joint probabilities  $[HH]_{ij}$  and  $[H_2\phi]_{ij}$ . We can simplify these terms by assuming the populations on neighbor sites are independent:

$$[HH]_{ij} \approx [H]_i [H]_j \quad [H_2\phi]_{ij} \approx [H_2]_i [\phi]_j \quad (4)$$

in which case Eq. 3 becomes

$$\begin{aligned}\frac{d[H_2]_i}{dt} &= -k_R[H_2]_i + k_1^i[H]_i \sum_j [H]_j - k_{-1}^i[H_2]_i \sum_j [\phi]_j \\ &\approx -k_R[H_2]_i + k_1^i[H]_i d \bar{H} - k_{-1}^i[H_2]_i d \bar{\phi}\end{aligned}\quad (5)$$

where in the second line, we have made the mean field approximation, replacing the sum over  $d$  neighbor sites ( $\sum_j$ ) with  $d$  times the equilibrium average over all sites. Like most mean field approaches, we expect this approximation to be more accurate when there are many neighbors, [78, 63] because then the sum over neighbors will more closely reflect the ensemble average. We also note that this mean field approximation may fail if there is strong spatial correlation between the heterogeneities, such as those occurring at a step edge. In this case, the model would need to be extended to address such correlations.

Applying the same mean field approximation to the other two absorbed species gives:

$$\begin{aligned}\frac{d[H]_i}{dt} &= k_A[\phi]_i - k_D[H]_i - d (k_1^i \bar{H} + \overline{Hk_1})[H]_i \\ &\quad + d \overline{H_2k_{-1}}[\phi]_i + d k_{-1}^i \bar{\phi}[H_2]_i, \\ \frac{d[\phi]_i}{dt} &= -k_A[\phi]_i + k_D[H]_i + d \overline{Hk_1}[H]_i \\ &\quad - d \overline{H_2k_{-1}}[\phi]_i + k_R[H_2]_i.\end{aligned}\quad (6)$$

Here, in addition to  $\bar{H}$ ,  $\bar{H}_2$  and  $\bar{\phi}$  the joint averages  $\overline{Hk_1}$  and  $\overline{H_2k_{-1}}$  appear. These arise from reactions that can occur at a neighbor site but either produce or consume a species at the active site. For example,  $H_i + H_j \rightarrow H_2 + \phi$  gives a contribution to  $\frac{d[H]_i}{dt}$  of

$$\begin{aligned}d \sum_j (k_1^i + k_1^j)[H]_i[H]_j &= d k_1^i[H]_i \sum_j [H]_j \\ &\quad + d [H]_i \sum_j k_1^j[H]_j \\ &\approx d k_1^i[H]_i \bar{H} + d [H]_i \overline{k_1[H]}\end{aligned}$$

where the first term corresponds to the formation of  $H_2$  at site  $i$  and the second term corresponds to the formation of  $H_2$  at a neighbor site. Note that the mean



field approximation converts the non-linear ensemble rate expressions into a set of *linear* equations for  $[H_2]_i$ ,  $[H]_i$  and  $[\phi]_i$ .

Setting Eqs 5 and 6 to zero to enforce steady state gives the populations

$$\begin{aligned}\alpha[H_2]_i &= d k_1^i \bar{H} (d \overline{H_2 k_{-1}} + k_A) \\ \alpha[H]_i &= (d \overline{H_2 k_{-1}} + k_A) (k_{-1}^i \bar{\phi} + k_R) \\ \alpha[\phi]_i &= k_R (d \overline{H k_1} + d k_1^i \bar{H} + k_D) + k_{-1}^i \bar{\phi} (d \overline{H k_1} + k_D)\end{aligned}\tag{7}$$

where  $\alpha$  is an arbitrary constant. For simplicity we will choose  $\alpha$  so that  $[H_2]_i + [H]_i + [\phi]_i = 1$ .

Eqn. 8 predicts the steady state behavior given a set of known rate constants  $k_1^i, k_{-1}^i, k_A, k_D$  and  $k_R$  and a set of averages  $\bar{H}_2, \bar{H}, \bar{\phi}, \overline{H k_1}$  and  $\overline{H_2 k_{-1}}$ , which we don't know *a priori*. However, Eqn. 8 suggests a means of obtaining these averages. By solving for the mean field steady state of each potential active site in the lattice, one can compute the averages as

$$\begin{aligned}\bar{H}_2 &= \frac{1}{N} \sum_i [H_2]_i \\ \overline{H k_1} &= \frac{1}{N} \sum_i k_1^i [H]_i\end{aligned}\tag{8}$$

and similarly for  $\bar{H}$ ,  $\bar{\phi}$  and  $\overline{H_2 k_{-1}}$ . Note that these averages can equivalently (and perhaps more conveniently) be computed as integrals over the probability distribution of  $k_1$ . For example

$$\bar{H}_2 = \int [H_2](k) P(k) dk\tag{9}$$

where  $[H_2](k)$  is given by Eq. 5 with  $k \equiv k_1^i$ .

No matter how the averages are computed numerically, the key point is that the steady state equations (Eqs. 5 and 6) need to be solved self-consistently with the ensemble average relationship (Eq. 8). In practice we have found that a simple iterative approach of solving one set of equations and then feeding the results into the other converges quickly for this example. In more difficult MFSS equations, it might be necessary to use a convergence acceleration technique similar to the Direct Inversion in the Iterative Subspace (DIIS). [79, 80, 81]

Taken together, Eqs. 5,6 and 8 provide a simple, approximate means of accounting for static fluctuations in the rate constant that might occur in the catalytic production of  $H_2$  at a disordered surface. For the key catalytic step, each site interacts with a set of neighbors that are representative of the steady state distribution averaged over the whole system. Within that average environment, the steady state at each site fluctuates according to its local catalytic rate. The resulting MFSS solution should give at least a reasonable estimate of the effects of heterogeneity on the rate of  $H_2$  production. We should note that similar approaches have been used occasionally in treating metal alloys [82, 83] but overall this kind of approximation appears to be seldom used in chemical kinetics.

## Results

To validate our approach we solved the MFSS equations (Eq. 8) self-consistently until convergence of the average populations. These were computed by quadrature using Eq. 9 with a log normal distribution of rates. Figure 2 shows the resulting steady state  $\phi$ ,  $H$  and  $H_2$  populations for an increasing heterogeneity in the catalytic rates (increasing  $\sigma$ ).

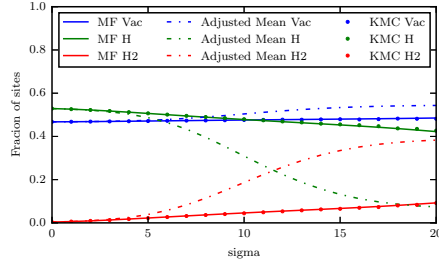


Figure 2: Steady state  $\phi$  (blue),  $H$  (green) and  $H_2$  (red) populations calculated with KMC (dots) and MFSS (solid lines) as a function of the standard deviation of the log normal distribution of the catalytic rates  $k_1$ . At ambient temperature, the upper limit  $\sigma = 20 k_B T \sim 0.5$  eV sets a realistic range of expected disorder in real systems. Also shown are the MFSS populations for a null standard deviation but a mean adjusted to  $\overline{\ln(k)} + \sigma/2$  (dotted lines). The homogeneous rates were:  $k_r = 0.1$ ,  $k_d = 0.1$ ,  $k_a = 0.1$

Comparing with the KMC populations (details of the KMC algorithm can be found in the Supporting Information), we observe that the two methods give essentially identical results. When scanning over the disorder in the bimolecular rate, as measured by the value of  $\sigma$ , KMC and MF are within  $10^{-3}$  of each other in the range tested. Clearly the MFSS approach gives an accurate and yet highly efficient description of the heterogeneous kinetics of this system. Most notably, the surface fraction of  $H_2$ , which is proportional to the rate of production ( $\text{rate}_{\text{prod}} \propto k_r[H_2]$ ), increases from  $3 \times 10^{-3}k_r$  (at  $\sigma = 0 k_B T$ ) to  $0.11k_r$  (at  $\sigma = 20 k_B T$ ), vividly illustrating the simple truth that the average of the rates is not the same as the rate of the average site. It is somewhat shocking that something as simple as MFSS can capture this kind of significant change. As a point of comparison, it should be noted that because of the asymmetry of the log normal distribution, changing  $\sigma$  as we have done leaves the mode of  $k$  fixed, but adjusts the mean to  $\overline{\ln(k)} + \sigma/2$ . One might then suspect that using this adjusted mean in the ensemble SS expression (Eq. 1) might also give good agreement with KMC. As illustrated in Figure 2, this approach vastly overestimates the effect of heterogeneity, emphasizing that MFSS is doing something non-trivial here. To check that these results hold when the diffusion of adsorbed hydrogen is fast, we ran the same calculations only adding an explicit diffusion step with independent rate constant (see Supporting Information). We observe that fast diffusion does not affect the results in the parameter space considered here.

As an alternative test, we show in Figure 3 the MFSS and KMC steady state populations when tuning the log average rate  $\overline{\ln(k)}$ , at fixed disorder ( $\sigma = 10 k_B T$  in the Figure). Because  $\overline{\ln(k)} \approx \frac{\bar{E}_a}{k_B T}$  one can change the log rate either by adjusting the mean activation energy or the overall temperature. Thus, this scheme corresponds to the other, more “conventional” way one could increase  $H_2$  production: tuning the average activation energy. Here again we observe quantitative agreement between the two methods. When scanning the typical mean of the bimolecular rate, KMC and MF are on average within  $10^{-2}$  of one another, with the result being qualitatively different than predicted by the

ensemble SS with the average rate.

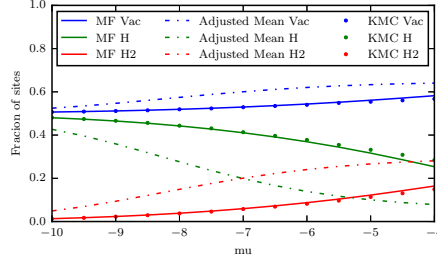


Figure 3: Steady state  $\phi$  (blue),  $H$  (green) and  $H_2$  (red) populations calculated with KMC (dots) and MFSS (solid lines) for a range of the mean log of the catalytic rates  $\overline{\ln(k)}$ . The homogeneous rates were:  $k_r = 0.01$ ,  $k_d = 0.16$ ,  $k_a = 0.14$

Having worked through one example, it is now fairly clear how MFSS could be applied to a general heterogeneous system:

**Step 1** Write out the elementary steps of the reaction and determine (either by experiment, computation or estimation) the rate constants, including the probability distribution of any rate(s) that are heterogeneous.

**Step 2** Guess approximate ensemble average populations for all species ( $\bar{X}$ ). For example, these might be the values obtained from the average rate constants.

**Step 3** Solve the pseudo-first order rate equations (e.g. Eqs. 5 and 6) to obtain an expression for the steady state populations for each site ( $[X]_i$ ) or equivalently for every rate constant ( $[X](k)$ ). Because the equations will be linear, this should be feasible for mechanisms involving as many as several thousand distinct reactions.

**Step 4** Integrate over the probability distribution  $P(k)$  to obtain new steady state values:

$$\bar{X} = \int [X](k)P(k)dk$$

Equivalently, one could sum over all sites to obtain the averages (e.g. Eq. 8). For simple mechanisms this might be done analytically, but other cases this integral can be evaluated to high accuracy by quadrature as long as there are not too many rate constants that vary independently.

**Step 5** Compare the new  $\bar{X}$  to the old  $\bar{X}$ . If the two agree, the calculation is complete. If they differ significantly, return to the second step with the new averages replacing the old.

It seems likely that this scheme could be useful for describing the effect of disorder on the rates of numerous chemical systems. For example, catalytic processes like methanol oxidation [84, 85, 86], oxygen evolution [87, 88, 89], and the hydrogenation of olefins [90, 91] could all potentially be described using a formulation similar to the one discussed here. In a somewhat different context, the generation and destruction of charges in OLEDs [92, 93] and OPVs [94, 95, 96] could also benefit from an analysis like this one. At a basic level, in any system where the rate constants have some static disorder and where one of the steps is bimolecular (so that the active site interacts with sites around it) MFSS provides an attractive means to quickly approximate the ensemble averaged kinetics.

## Conclusion

The resulting methodology thus seems like a worthwhile tool for chemical kinetics quite generally. It is extremely easy to apply, involving only some algebraic manipulations and a modest amount of numerical integration. To put it another way, MFSS allows us to study heterogeneity without being limited by the speed of the computer on which we run the simulation.

Of course, as with any inexpensive method, MFSS is highly approximate. For the simple example we have discussed here ( $H_2$  formation) it is rather difficult to find situations where it fails, but it is not hard to imagine what these would be. In cases where there are not many near neighbors (e.g. in low dimensional

systems) the assumption that the average over neighbors approximates the ensemble average is likely to be poor. Alternatively, when the mechanism involves multiple bimolecular steps, it seems likely that the populations of neighboring sites will actually be correlated: the presence of  $A$  on one site might appreciably reduce the probability that  $B$  appears on a neighbor site. The severity of these limitations is not immediately clear, but they create an obvious area for future study.

There are a number of other clear directions to extend this work. Beyond the above-mentioned applications, it would be interesting to try to build correlated fluctuations into MFSS theory in much the same way that correlation is built into other mean field theories. [97] In this case, the most obvious steps are to either include self-consistent fluctuations in the neighbor sites (as opposed to just a self-consistent mean) and/or simply including more than one active site in the MFSS kinetics. It would also be interesting to go beyond the steady state situation and apply these kinds of approximations to examine the average *time evolution* of heterogeneous reaction networks. Finally, in addition to being able to treat static disorder in this way, it would also be useful to have a simple mean field picture for dynamic disorder in the rate constant.

## Supplementary Material

See supplementary material for the details of the kinetic Monte Carlo algorithm and quantitative comparison with the MFSS scheme for a range of parameters.

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