A hierarchy of generalized kinetic equations

An efficient hierarchy of generalized kinetic equation approximations to the chemical master equation applied to surface catalysis

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We develop an efficient hierarchy of methods that approximate the chemical master equation for systems that are assumed to be translationally invariant and have finite spatial correlations. The system size of each method within the hierarchy scales with the range of spatial correlations. In principle, this hierarchy will converge to the master equation as the system size grows, and we demonstrate this in one- and two-dimensional numerical examples. In the one-dimensional system, we demonstrate that lower levels within the hierarchy are both significantly faster than tradition kinetic Monte Carlo (KMC) methods, by as much as three orders of magnitude for one-dimensional systems, and predict identical system dynamics and steady states as KMC methods. We also test this methodology on the realistic test case of oxidation of CO on RuO$_2$(110). In the realistic example, it is observed that a relatively small system size within the hierarchy captures many of the important system dynamics. We note that in the current exposition, we have found no a priori method of determining the necessary system size of the method in the hierarchy needed to accurately approximate the master equation. The hierarchy may be thought of as a class of generalized phenomenological kinetic models since each element of the hierarchy approximates the master equation and the lowest level in the hierarchy is identical to simple existing phenomenological kinetic models. In addition to the hierarchy’s efficiency, it also provides a framework in which to test whether each individual method has converged to the correct system dynamics. We also discuss the utility of this hierarchy for predicting transition rates from experimental data in the discussion.

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I. INTRODUCTION

Computational modeling plays an increasingly important role in the characterization and understanding of a broad range of elementary chemical transformations relevant to catalytic processes. Such catalytic chemical reactions can be described by microscopic kinetic models such as the coarse-grained lattice kinetic Monte Carlo (KMC) method.

A computational simulation of the time evolution of some stochastic process. Typically, simulation of processes arising in catalytic chemistry are carried out based upon rates for adsorption, reaction, desorption, and diffusion that are obtained from experiments, density functional theory (DFT), and transition state theory (TST). If a system exhibits significant transport, hybrid methods for heterogeneous reaction kinetics can be constructed, which combine KMC for the chemical kinetics with finite difference methods for the continuum-level heat and mass transfer.

One class of computational methods for catalytic processes hypothesize ad hoc rate equations, derived by physical reasoning, to construct phenomenological kinetic (PK) models of surface processes. Such PK models start from an idealized surface geometry for binding sites and site connections. For example, on a (110) idealized surface, there one can define bridge and cus sites connected by a square lattice, as shown in Figure 1. The models track the probability of finding a site of given type bound to a particular molecule, and use a maximum-entropy/well-mixed assumption to reconstruct spatially correlated information. The well-mixed assumption on surfaces can often fail, and there are many examples in which a given kinetic model fits one set of data well, but fails with additional test data.

As a response to the deficiency of the PK models, and facilitated by advances in computational power and algorithm design, kinetic Monte Carlo (KMC) simulations are now often used to determine the surface dynamics and steady state values in surface catalysis problems. KMC algorithms are stochastic realizations of the surface dynamics, and are able to take into account spatial correlations that PK models fail to consider. The advantage of KMC algorithms is demonstrated in ref. where the authors demonstrate the breakdown of PK models when compared to KMC predictions. KMC simulations are, however, far more expensive than PK models, and rely on statistical averaging for predicting desired observable quantities.

Underlying both the PK and the KMC frameworks is the chemical master equation. The chemical master equation describes the evolution of a multivariate probability distribution function (PDF) for finding a surface in any given state. PK models may be thought of as an approximation to the chemical master equation in which we only examine the probability distribution of finding a single surface site in a particular state, i.e.,
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II. THE CHEMICAL MASTER EQUATION AND APPROXIMATION

A. Problem formulation

Consider a surface $\Omega$ made of $N \times N$ sites, each labeled as particular type from a set $T$. For example, on an idealized (100) surface there are atop, bridge, and 4-fold hollow sites and so $T = \{\text{atop, bridge, hollow}\}$, while as on a (110) crystal surface there are bridge and cus site types and so $T = \{\text{bridge, cus}\}$ (see Figure 1). Each site on the surface may be in a particular state and we will call the set of possible states $S$. For example, in the surface oxidation of CO, CO and $O_2$ adsorb and desorb on the surface. CO remains bonded upon adsorption where as $O_2$ dissociates, two adjacent sites will become occupied by a single O molecule. In this case the set of possible site states is $S = \{\emptyset, O, CO\}$, which corresponds to an unoccupied site, a site occupied by O, and a site occupied by CO, respectively.

Supposing that we start with an $N \times N$ surface, the chemical master equation is formulated with a known transition matrix, $A_{ij}$, which prescribes the rate at which one particular system state transitions to another and may be written as

$$\frac{dP(S_i)}{dt} = \sum_j A_{ij}P(S_j) - A_{ij}P(S_i), \quad (1)$$

where $P(S_i)$ is the probability of the surface being in state $S_i$, and a state $S_i \in S^{N \times N}$ is an $N \times N$ vector describing the state of each site (for example, refs. [8], [13] and [14]). In the discrete setting of surface reactions, each site may be in one of $|S|$ states, where $|\cdot|$ represents the cardinality of a set. The chemical master equation yields a system of $|S|^2$ ordinary differential equations (ODEs). In the limit of $N \to \infty$, the system kinetics are described by an infinite dimensional ODE system (so long as $|S| > 1$), an intractable problem that requires truncation along with periodic boundary conditions to become solvable. Even truncated systems, the size of state space is often intractably large for realistic choices of $N$, and thus instead of solving the chemical master equation directly, a stochastic realization of the surface dynamics is considered using kinetic Monte Carlo algorithms (see for example, ref. [1]).

In the present work, we develop and examine a method to efficiently approximate the analytic chemical master equation by a finite-dimensional system of ODEs which does not rely on stochastic realization. To approximate the master equation, we assume that the system is translationally invariant with finite length-scale correlations. For the current exposition and the remainder of the paper, we assume that the underlying lattice is rectangular, however we see no reason why the method described below cannot be generalized to other lattices. With this restriction in mind, we consider an arbitrary rectangular tile of size $(m \times n)$ that covers a block of $m \times n$ sites.
of the \(N^2\) sites making up the surface (see Figure 1 for an illustration). Any given \((m \times n)\) tile will be made of \(m \times n\) sites, each of which has a site type in \(T\). The collected space of all site types will be contained in the space \(T' \subset T^{m \times n}\). A given lattice structure, however, will constrain the \(m \times n\) site type tuples and we call this constrained space \(T' \subset T^{m \times n}\). Each tile with site types \(\tau \in T'\), may be in one of \(|S|^{m \times n} \ll |S|^N\) possible states, and we assume that \(m, n \ll N\). Finally, given a lattice, we assign the distinct \((m \times n)\) tiles as \(\xi \in \Xi\) where \(\Xi\) is the space of all distinct tilings. We denote the tile \(\xi\) as being in the state \(s\) as \(\xi(s)\). In the examples of the (110) and (100) surfaces above, the tiling types \(\xi\) will identify uniquely with the site types \(\tau\), however this is not generally true. For example, we may consider a 1D lattice with fundamental lattice block made up of sites with type \(A\), \(B\) and \(C\) and given as \(ABBBBC\). This surface has two distinct \(\tau = BB\), \((2 \times 1)\) tilings: one that is surrounded by sites with type \(A\) and a type \(B\), and the other by sites with type \(B\) and a type \(C\).

Having categorized each tile \(\xi\) in state \(s \in S^{m \times n}\) (denoted \(\xi(s)\)), with underlying site types \(\tau \in T'\), we may then assign a discrete PDF of finding tile \(\xi\) in state \(s\), and denote this probability as \(P_\xi(s) \equiv P(\xi(s))\). Due to the assumed translational invariance of the system, all tiles identified with tile type \(\xi\) in the lattice are assumed to have identical probability distributions throughout time. We seek to approximate these dynamics by assuming knowledge only up to a given \((m \times n)\) tiling on the system, which will hold information of the PDF’s \(\{P_\xi\}_{\xi \in \Xi}\). Each PDF has a domain of size \(|S|^{m \times n}\), there are \(|\Xi|\) PDF’s to track, and thus the goal is to reduce the large or infinite dimensional master equation (Equation 1) to a \(|\Xi| \times |S|^{m \times n}\) dimensional system of ordinary differential equations. Because \(|\Xi| = |T'|\) in many interesting cases (such as the (110) and (100) surfaces described above), the dimensionality of the system will often be equivalent to \(|T'| \times |S|^{m \times n}\).

To achieve this approximation, we first note that given an arbitrary \((m \times n)\) tile located on the \(N \times N\) surface with site type geometry \(\tau \in T'\) and lattice position described by \(\xi \in \Xi\), we may evaluate the dynamics of the discrete PDF over the state space on this tile based on the full description of the chemical master equation (Equation 1). Below we will refer to ‘the tile \(\xi\),’ by which we mean an arbitrary choice from all the similar tiles \(\xi\) from the full \(N \times N\) system. We reiterate that the reason we may choose any arbitrary \(\xi\) is due to the assumed translational invariance of the system. To approximate the dynamics of the PDF \(P_\xi\) on a reduced system, we decompose the transition matrix \(A\) into a sum of three matrices: a matrix that only changes site states within the tile \(\xi\), \(\bar{A}\), a matrix that changes site states both within the tile and exterior to the tile, \(\hat{A}\), and a matrix that does not change any of the site states within the tile, \(\delta\). Thus we write

\[
A = \bar{A} + \hat{A} + \delta.
\]  

(2)

The second matrix, \(\bar{A}\) is further decomposed by considering collections of sites that include an arbitrary number of exterior sites along with all of the sites in the tile \(\xi\), and in which the site states of \(\xi\) are specified. Any one of these collections will be denoted \(r_\xi(\sigma)\) where \(r_\xi\) is a collection of sites that includes the sites in \(\xi\), and \(\sigma\) represents the states of each site in the collection \(r_\xi\). We then define \(\bar{A}^{\xi(\sigma)}\) to be the matrix that encodes transitions such that (i) at least one site in the tile \(\xi\) changes state, (ii) every site exterior to the tile \(\xi\) in \(r_\xi\) is changed, and (iii) no site exterior to \(r_\xi\) changes state. Summing over all possible choices of \(r_\xi(\sigma)\), both in selection of \(r_\xi\) and the choice of states \(\sigma\), we then further decompose \(A\) to be

\[
A^{\xi} = \sum_{r_\xi(\sigma)} \bar{A}^{\xi(\sigma)}.
\]  

(3)

Because we are only interested in the local events, we
then average the rate of each transition type in the tile going from state $s_i$ to state $s_j$ (both states in $S^{m \times n}$). We describe these averaged transition rates as

$$\tilde{a}_{ij}^\xi = \sum_{b \in S(\Omega \setminus \xi)} \tilde{A}_{ij}^\xi(b) P(b|\xi(s_i), \{P_c\}|_{\xi \in \Xi}),$$

and

$$\tilde{a}_{ij}^{r(\sigma_i)} = \sum_{b \in S(\Omega \setminus \Omega_{r_i})} \tilde{A}_{ij}^{r(\sigma_i)}(b) P(b|\xi(s_i), \{P_c\}|_{\xi \in \Xi}),$$

where $S(\Theta)$ is the set of all possible states of the collection of sites $\Theta$, $\xi$ is the tile that may also be thought of as a set of sites on the surface $\Omega$ that comprise the tile, and $\sigma_i$ is a choice of $\sigma$ that is constrained so that the states on the tile are described by $s_i$. The matrix elements $B_{ij}^\xi(b)$ in the interior of each sum are the elements of the transition matrix that begin in state $s_i$ on the subset $\xi \subset \Omega$ and finish in state $s_j$ on $\xi$, and all exterior states in $\Omega \setminus \xi$ remain fixed in state $b$. The last condition will be trivially satisfied based on the definitions of the matrix decomposition above. Finally the sum is weighted by the conditional probability that the system will be in state $b$ given that we know either the state of the tile $\xi(s_i)$ or the state of tile and the external sites $r_\xi(\sigma_i)$, along with the discrete PDFs of all tiles.

We then define new transition matrices $\tilde{a}_i^\xi$ and $\tilde{a}_i^{r(\sigma_i)}$, all of which have dimension $|S^{m \times n}| \times |S^{m \times n}|$. Taken together, these matrices represent a mean field theory that accounts only for the changes that occur within the tilings, averaging the influences of the system states that do not change with a given transition; we note that in general, the reduced matrices will depend non-trivially on the PF’s of the tiling, however in the current work we will primarily focus on systems that have transition rates independent of the state of sites that do not change states. Therefore, having a fixed $i, j$ and $\Omega$, we assume that $B_{ij}^\xi(b_1) = B_{ij}^\xi(b_2)$ for all $b_1, b_2 \in S(\Omega \setminus \xi)$, which means that we may arbitrarily assign any of these elements to the reduced matrix:

$$\tilde{a}_{ij}^\xi = \tilde{A}_{ij}^\xi(b), \forall b \in S(\Omega \setminus \xi),$$

and

$$\tilde{a}_{ij}^{r(\sigma_i)} = \tilde{A}_{ij}^{r(\sigma_i)}(b), \forall b \in S(\Omega \setminus \Omega_{r_i}).$$

Having defined the transition rates on the reduced tiling system, we may now describe an approximated master equation to the tiling system, which we may write as

$$\frac{dP_\xi(s_i)}{dt} = \sum_{j=1}^{\left|S\right|^{m \times n}} \left(\tilde{a}_{ij} P_\xi(s_j) - \tilde{a}_{ij} P_\xi(s_i)\right)$$

$$+ \sum_{j=1}^{\left|S\right|^{m \times n}} \sum_{r_\xi(\sigma_j)} \tilde{a}_{ij}^{r(\sigma_j)} P_\xi(s_j) P(r_\xi(\sigma_j)|\xi(s_j), \{P_c\}|_{\xi \in \Xi})$$

$$- \sum_{j=1}^{\left|S\right|^{m \times n}} \sum_{r_\xi(\sigma_i)} \tilde{a}_{ij}^{r(\sigma_i)} P_\xi(s_i) P(r_\xi(\sigma_i)|\xi(s_i), \{P_c\}|_{\xi \in \Xi}).$$

The first summation on the right hand side represent state changes that occur entirely within tile. The second and third summation represents transitions that move into and out of state $s_i$ (respectively) on the tile due to transitions effecting both inner and outer sites.

To close the system of equations we must specify how to construct the conditional probabilities $P(r_\xi(\sigma)|\xi(s), \{P_c\}|_{\xi \in \Xi})$, which is to say that if we know the state of the tile is $s$, and we know the PDF’s of the full system, how can we reconstruct the probability of finding the exterior sites of $\xi^T$ in the states specified in $\sigma$. To do this we may use conditional probabilities. For example, if we simply track $(1 \times 1)$ tiles and have a transition that affects sites on two adjacent tiles $\xi$ and $\xi'$, we can assume that the local probabilities are independent. Thus if we examine a transition that affects the tile $\xi$ and an adjacent tile $\xi'$, we have $r_\xi = \{\xi, \xi'\}, \sigma = (s, s')$, and then

$$P(r_\xi(\sigma)|\xi(s), \{P_c\}|_{\xi \in \Xi}) = P(\xi'(s')|\xi(s), \{P_c\}|_{\xi \in \Xi}) = P_c(s').$$

Next suppose we have a $(2 \times 1)$ tiling with tiles $\xi$ and $\xi'$ and a transition that takes $\xi((a, b)) \rightarrow \xi((c, d))$. Suppose also that $\xi'$ has a first site in common with the second site of $\xi$. In this case the transition on $\xi$ is captured within the $\tilde{a}_i^\xi$ transition matrix, but the transition on $\xi'$ must take into account the possibility that the $\xi$ tile has transitioned which will effect the first site of $\xi'$. We therefore have a non-zero value for $\tilde{a}_i^{\xi'}$ and must determine $P(r_\xi(\sigma)|\xi'(b, c), \{P_c\}|_{\xi' \in \Xi})$ where $r_\xi$ is a collection of three sites, the first two sites of which represent a $\xi$ tile and the second to of which represent a $\xi'$ tile. We may reconstruct the conditional probability of finding $\xi((a, b))$ given $\xi'((b, c))$ as

$$P(r_\xi((a, b, c))|\xi'(b, c), \{P_c\}|_{\xi' \in \Xi})$$

$$= P(\xi((a, b))|\xi'(b, c), \{P_c\}|_{\xi' \in \Xi})$$

$$= \sum_{i \in S} P_c(i, b).$$

Conditional probabilities for finding exterior tiles that overlap at more than one site are determined similarly. The idea is always to minimize the uncertainty in the conditional probabilities with the known information of the PF’s on the tiling. We note and can readily see from the two examples above, that larger tilings take into account longer range spatial correlations. Thus, so long as the true solution to the full chemical master equation (Equation 1) has finite spatial correlations, increasing the tiling size will cause the approximated master equation (Equation 4) to converge to the correct dynamics.

Having established a reduced system of equations for arbitrary rectangular tilings, we next mention some simple ways in which we can take advantage of rotational symmetries on the lattice, and then introduce a generalization to a mixed tiling system. Following this exposition, to ensure both the system in written in equation 4 and the generalization presented below are self-consistent, we state two consistency criteria. From here,
we present a simple example, and then the concrete example of surface catalysis, which will be used below in numerical tests.

B. Rotational symmetry and mixed tilings

Up to this point, we have discussed tilings with fixed orientations. Certain lattices, however, contain symmetries that may be obtained to obtain higher range spatial correlations without increasing the dimension of the system. In the (100) crystal above, for example, there are four rotational symmetries of the lattice found by rotation of $\pi/2$ radians. Thus we expect that if for each $(m \times n)$ tile, there is a corresponding $(n \times m)$ tile with an equivalent PDF over site states under rotation. Therefore, in reconstructing the conditional probabilities used in conjunction with $\tilde{a}$, we assume that we have both $(m \times n)$ and $(n \times m)$ tiling types. The case in which $m \neq n$, this may lead to more detail in spatial correlations along both lattice directions, and thus a more accurate method with no additional cost.

We may also consider the (110) surface described above that only has two rotational symmetries found by rotation of $\pi$ radians. In this case, considering $(m \times 1)$ tiles would provide us with spatial correlations along cus-cus or bridge-bridge sites but we would be assuming independence in the cus-bridge direction. Similarly a $(1 \times n)$ tiling would retain spatially correlated data in the bridge-cus direction, but not along bridge-bridge or cus-cus networks. To get around this we could consider $(m \times n)$ tiling, however the system size would grow exponentially, and ($m \times n$) to a $|S|^{(m \times n)}$ dimensional system, where $\Xi = \{1, 2, \ldots, n\}$ is the tile set when considering a $(m \times n)$ tiling. In the case of the (110) surface $|\Xi| = 2$, $|\Xi| = 1$, and $|\Xi| = 1$ if $n$ is even and 2 if $n$ is odd. Instead we may consider mixed tilings, which is to say we consider the system constructed when considering the PDF’s on $(m \times 1)$ and $(1 \times n)$ tiles, which causes the system to grow from an $|\Xi| \times |S|$ to a $|\Xi| \times |S|$ dimensional system. If, however, the spatial correlations die off quickly in one direction

With all of these methods, we must ensure that several constraints are met to ensure the system is consistent. We expose these constraints in the following subsection.

C. Consistency and constraints on tiling dynamics

Care must be taken to ensure that certain constraints are obeyed by any of resulting systems described above. For one, a system must be initialized to have normalized PDF’s over each tile. Analytically, the PDF’s will trivially be normalized throughout all time, since what is added to one state is taken away from another. Next all lower dimensional projections must be well defined. By this we mean that lower dimensional projections must agree between (i) different tiles $\xi \in \Xi$ and (ii) within a given tiling. For example, suppose we have a mixed $(2 \times 1)$ and $(1 \times 2)$ tiling on a (110) surface as described above, suppose we have a bridge-bridge tile, $\xi$ and a bridge-cus tile $\xi'$. We note that in the $(1 \times 1)$ tiling system all bridge and cus sites are identical on the lattice and thus the probability of finding a bridge site in a particular state must be the same no matter how it is determined. This means that we must have

$$\sum_{s_i \in S} P_{\xi}((s, s_i)) = \sum_{s_i \in S} P_{\xi}((s, s_i)), \forall s \in S, \quad (9a)$$

$$\sum_{s_i \in S} P_{\xi}((s, s_i)) = \sum_{s_i \in S} P_{\xi}((s, s_i)), \forall s \in S. \quad (9b)$$

We conjecture that systems will be well behaved for rectangular $m \times n$ tiling systems and for mixed tiling systems. We note that we have numerically verified that all systems mentioned below satisfy the above criteria for a variety of test cases and projections. From this point on we will assume all tiling systems are mixed, i.e. saying that we are working with a $(2 \times 1)$ tiling system will mean that we are working with a mixed $(2 \times 1)$ and $(1 \times 2)$ tiling system.

In general, Equation (9) may be difficult to work with explicitly, however we will show that in several relevant problems it simplifies to a system that can be easily coded into a computational algorithm.

D. A simple example

We illustrate the above concepts with a simple example. Suppose that $\Omega$ is comprised of two sites each of which is identical, and each of which can be in states $S = \{0, 1\}$. The state space is then $\{00, 01, 10, 11\}$. The transition matrix is chosen as

$$A = \begin{pmatrix} -2r_1 & 0 & 0 & 0 \\ r_1 & -r_2 & 0 & 0 \\ r_1 & 0 & -r_2 & 0 \\ 0 & r_2 & r_2 & 0 \end{pmatrix}, \quad (10)$$

which states that a site in state 0 can transition to state 1, but not the other way around, and that the rate with which this happens depends on the state of the other site.

The four dimensional system may be written as

$$\dot{P}_{00}(t) = -2r_1 P_{00}, \quad \dot{P}_{01}(t) = r_1 P_{00} - r_2 P_{01}, \quad \dot{P}_{10}(t) = r_1 P_{00} - r_2 P_{10}, \quad \dot{P}_{11}(t) = r_2 P_{01} + r_2 P_{10}. \quad (11)$$

Suppose we choose a $(1 \times 1)$ tiling and wish to determine the reduced dynamics. There is only one type of tile as both sites share identical dynamics. We find that $\tilde{A} = 0$ (and hence $\tilde{a} = 0$) as there are no reactions effecting both sites and

$$\tilde{a} = \begin{pmatrix} -2r_1 P_0 - r_2 P_1 & 0 \\ r_1 P_0 + r_2 P_1 & 0 \end{pmatrix}, \quad (12)$$
corresponding to the state space \((0,1)^T\), which leads to dynamics given by
\[
\dot{P}_0(t) = -(r_1 P_0 + r_2 P_1) P_0, \quad \dot{P}_1(t) = (r_1 P_0 + r_2 P_1) P_0.
\]

\(13\)

\(E.\ A\ concrete\ example\ on\ an\ idealized\ (110)\ surface\)

We next demonstrate how to construct approximated systems with a more realistic example. To do this, we consider the \((110)\) surface made up of bridge and cus sites (see Figure 1). Each bridge site is connected to two other bridge sites and two cus sites. We suppose that we know a collection of surface transitions and each of their rates. In the following example we consider approximate descriptions of CO oxidation for \((1\times1)\) rates. In the limit as \(dt \to 0\), these terms will vanish leaving a simple transition matrix that only describes events that generate state changes on a site or two adjacent sites via the site and pair transitions listed above, respectively, with transition rates that are assumed to be independent of the sites that are not effected by the transition. This observation greatly reduces the space of possible choices \(r_\xi\), and allows us to use the reduction presented in equations \(15a\) and \(15b\). We note further that there are multiple choices for \(r_\xi\) that will lead to identical reactions. For example given a \((1 \times 1)\) tile covering a single bridge site, bridge-bridge pair transitions can effect the bridge tile either through the left or right bridge site. Based on the symmetry of the system, each transition rate will be identical, and thus instead of accounting for these distinct choices for \(r_\xi\), we combine and weight them with a weight function \(w(\xi'|\xi)\) which describes the number of adjacent tiles \(\xi'\) given that we are at the tile \(\xi\). This weight function has arisen naturally by summing over \(r_\xi(\sigma)\) and will appear in the \(\vec{a}_\xi\) terms of equation \(6\). We may write the resulting six-dimensional system explicitly as
\[
\frac{dP_\xi(CO)}{dt} = k_{\theta_1\rightarrow CO} P_\xi(\emptyset) - k_{\theta_1\rightarrow CO} P_\xi(CO), \quad \frac{dP_\xi(\emptyset)}{dt} = -k_{\theta_1\rightarrow CO} P_\xi(\emptyset) + k_{\theta_1\rightarrow CO} P_\xi(CO)
\]

\(15a\)

\(15b\)

\(15c\)

\(15d\)

\[\sum_{\xi'\in\Xi} w(\xi'|\xi) \left( k_{\theta_1\theta_2\rightarrow CO} P_\xi(\emptyset) P_{\xi'}(O) P_{\xi'}(O) \right) \]

The weight function \(w(\xi'|\xi)\) is computed from the geometry of the system. In the current geometry, each cus has two bridge and two cus neighbors, so that \(w([b]|c]) = \frac{1}{2}\). A similar calculation is performed over all pairings. This system is identical to the PK model found in ref. \([6]\).

\(2.\ (2\times1)\ tilings\)

We continue with a \((2 \times 1)\) tiling. We note that in the given geometry there is a one-to-one mapping between \(\xi\) and its site types \(\tau = (\tau_1, \tau_2) \in \mathcal{T}'\), and thus denote \(\xi\) by it’s pair of site types. In this case, there...
are three possible tilings (up to symmetry and assuming a mixed tiling system) based on the given geometry, given as $\Xi = \mathcal{T} = \{\emptyset, b, b, c, c\}$. We wish to determine an approximation of the master equation describing the probability of finding each particular pair in a certain state. Note that all of the listed transitions may occur within the interior of the listed tiles and thus contribute to $\tilde{a}$. In the current setting we now have a $|\Xi| \times |\mathcal{S}|^2 = 3 \times 3^2 = 27$ dimensional system. Let $p_{ij}^\emptyset$ denote the probability of finding tiling $[i, j]$ in state $s = (l, m)$. We demonstrate the system construction by writing the dynamics for $p_{ij}^\emptyset$. We again take advantage of the fact that the transition matrix will only account for local transitions, and that multiple choices of $\xi$ will lead to identical contributions and so again introduce weight functions. Using Equation 5 to reconstruct the neighbor probabilities. We obtain the system

$$
\begin{align*}
\frac{dp_{ij}^\emptyset}{dt} &= -k_{0,\emptyset,\rightarrow CO} p_{ij}^\emptyset - k_{0,j,\rightarrow CO} p_{ij}^\emptyset + k_{CO,\rightarrow \emptyset} p_{ij}^{\emptyset CO} + k_{CO,\rightarrow j} p_{ij}^{\emptyset CO} - k_{0,\emptyset,\rightarrow O,CO} p_{ij}^{\emptyset O} + k_{O,\emptyset,\rightarrow j} p_{ij}^{\emptyset O} - k_{0,j,\rightarrow O,CO} p_{ij}^{\emptyset O} + k_{O,j,\rightarrow j} p_{ij}^{\emptyset O} - \sum_{i \text{ s.t. } [i,j] \cup [i,j] \in \mathcal{T'}} w([i,i])[i,j] k_{0,\emptyset,\rightarrow O,O} p_{ij}^{\emptyset O} \frac{p_{ij}^{\emptyset O}}{\sum_{n} p_{in}^{\emptyset O}} - \sum_{i \text{ s.t. } [j,i] \cup [j,i] \in \mathcal{T'}} w([i,i])[j,i] k_{0,\emptyset,\rightarrow O,O} p_{ij}^{\emptyset O} \frac{p_{ij}^{\emptyset O}}{\sum_{n} p_{in}^{\emptyset O}} + \sum_{i \text{ s.t. } [i,i] \cup [j,j] \in \mathcal{T'}} w([i,i])[i,j] k_{CO,O,\rightarrow j} p_{ij}^{\emptyset O} \frac{p_{ij}^{\emptyset O}}{\sum_{n} p_{in}^{\emptyset O}} + \sum_{i \text{ s.t. } [i,i] \cup [j,j] \in \mathcal{T'}} w([i,i])[i,j] k_{O,O,\rightarrow j} p_{ij}^{\emptyset O} \frac{p_{ij}^{\emptyset O}}{\sum_{n} p_{in}^{\emptyset O}}.
\end{align*}
$$

where $w([i,i][i,j])$ is the weight function which gives the number of additional neighbors of type $i$ to site type $i$, given that we have already included a neighbor of type $j$. For example, $w([b,b][b,b]) = 1$ and $w([b,c][b,b]) = 2$. The first sum represents neighboring pairs that share site $i$ in state $\emptyset$, with second site type $\emptyset$ in state $\emptyset$; in other words this term represents oxygen adsorption that effects sites both inside and outside the tile. The remaining terms are analogous but for oxygen desorption (additive terms) and the other site of type $j$ (second and fourth terms).

Higher-order tilings, such as $(n \times 1)$ and $(n \times n)$ tilings may be constructed similarly. Note that in these higher-dimensional cases, the tiles will overlap on a greater number of sites and thus the conditional probability will account longer range spatial correlations.

F. Algorithm construction

The steps listed above may be generalized to a computational algorithm. However the weighting functions will change for each type of tiling. Given a lattice we may calculate the neighbor and conditional neighbor probabilities, we may construct the list of tiles $\xi$ along with their site types $\mathcal{T}$ and position on the lattice, and we may construct a list of state transitions $\mathcal{R}$ along with the transition rates which may be looped through and added in accordance with the above procedures. We construct this algorithm and test the convergence of the approximated master equation (Equation 6) in the proceeding section.

III. NUMERICAL EXAMPLES

A. CO oxidation on simplified (110) surfaces

We continue with the example above of oxidation of CO on the (110) surface, however we simplify the model in two ways. First, we treat the cus sites as being inactive which reduces the system to a one dimensional lattice. Next, we assume there is no difference between cus and bridge sites and set the transition rates accordingly. For both cases, we then have $\mathcal{S} = \{\emptyset, O, CO\}$ and $\mathcal{T} = \{a\}$ along with the transitions listed in Equations 14a, 14b. After analyzing these two test cases, we will then examine the system with differentiated bridge and cus sites and use the realistic parameters found in ref. 6 and 11.

For the test cases, we choose test parameters with ratios that are similar (in order of magnitude) to parameters found for the realistic system. In non-dimensional units of time, we set $k_{OO,\rightarrow \emptyset} = 1.0, k_{\emptyset,\rightarrow CO} = 10^{-3}, k_{CO,\rightarrow \emptyset} = 0.1, k_{CO,\rightarrow O} = 10^{-2},$ and vary $k_{\emptyset,\rightarrow CO} \in [0, 1]$.

1. Inactive cus sites

For the single dimensional (1D) lattice, we compare $(n \times 1)$ tiling approximations of the master equation for $n \in \{1, 2, 3, 4, 5\}$. We then compare the approximated master equation with a reaction-first KMC simulations on a 1024x1 periodic lattice. A $(n \times n)$ tiling approximation makes up a $3^n$ dimensional system. The ODE’s are integrated using the LSODA routine wrapped in the scipy package for python. Details of the KMC simulation can be found in ref. 1, however we note that we use a GPU to accelerate the computation of the overall system reaction rate.

With the results from the ODE systems, we use the information on the larger tiles to determine the probability of finding a CO on any given site, and plot the the steady state of this value for each system in Figure 2. Steady state values for the KMC simulations are found by approximating the time scale of system equilibration, $T$, predicted by the higher dimensional tilings, and then running the system for $10T$ and averaging the results from $t \in [5T, 10T]$. For $(4 \times 1)$ and larger tilings, the approximated chemical master equation dynamics fall less than
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FIG. 2. For the 1D system, steady states values of the probability of CO on a single site are shown as the CO adsorption rate is increased for four tiling types and KMC results. The $3 \times 1$ tiling approximation yields a solution that is within twice the standard deviation of the KMC mean statistics. The $4 \times 1$ tiling approximation lies within a quarter of a standard deviation of the KMC mean statistics.

(a)

(b)

FIG. 3. For the 1D system, the maximum of the absolute error between successive tilings over all parameter values is plotted (a). The total speed between an $i \times 1$ tiling and the KMC simulations over 10 different parameter runs is shown (b). The $5 \times 1$ tiling runs 43 times faster than the KMC simulations.

The total speed between an $i \times 1$ tiling and the KMC simulations over 10 different parameter values is increased for four tiling types and KMC results. The $3 \times 1$ tiling approximation yields a solution that is within twice the standard deviation of the KMC mean statistics. The $4 \times 1$ tiling approximation lies within a quarter of a standard deviation of the KMC mean statistics.

appear to match precisely for the higher dimensional tiles ($n > 3$) and the KMC simulations; a single KMC realization is compared to all of the tilings in Figure 4 for $k_{\theta \to CO} = 10^{-0.2}$. As expected, the execution times of the ODE's are far faster than KMC simulation (see Figure 5). In the case of the $(3 \times 1)$ tiling, the approximate system runs 1690 times faster than the KMC simulations, and in the more accurate case of the $(4 \times 1)$ tiling, the approximate system runs 352 times faster than the KMC simulations. We note that the tiling associated ODE systems are solved using serial CPU execution, whereas the KMC simulations exploit parallel capabilities of GPUs, and thus the true acceleration of our methods can be even greater than what we have presented (exact performance figures depend to a large extent on computer architecture; all tests were run on a standard early 2013 15” MacBook Pro).

2. Identical cus and bridge sites

Next, we analyze the two dimensional system in which bridge sites are treated identically to cus sites. In this case we run the KMC simulations for a $32 \times 32$ periodic grid, and compare $(1 \times 1)$, $(2 \times 1)$, $(2 \times 2)$ and $(3 \times 2)$ tilings which yield $3, 3^2, 3^4$ and $3^6$ dimensional systems respectively. We again compare the steady states of the tiling approximations with results from KMC simulations and find that only the $(3 \times 2)$ tiling approximation lies within two times the standard deviation of the KMC results for all parameters (see fig 5). The $(2 \times 2)$ tiling does not show significant improvement over the $(2 \times 1)$ tiling. Additionally we plot the speed up in Figure 5. The $(3 \times 2)$ tiling approximation runs 7.7 times faster than the KMC simulation.

We do not test larger tilings as the system matrices quickly become too large for the LSODA method to approximate the system Jacobian. We determine the spatial correlations where the approximations have maximal error ($k_{\theta \to CO} = 10^{-0.16}$; see Figure 5). We find that at steady state, the spatial correlations die down over four nearest neighbors, and determine that the fifth near-
zero (p in which we assume that the partial pressure of CO be 600K. Reaction rates are taken from ref. 6. We next test the tiling approximations for the catalysis problem described in refs. 6 and 11. In this system \( S = \{ \emptyset, O, CO \} \), \( T = \{ \text{bridge}, \text{cus} \} \). Using the formalism above, we compare \((1 \times 1)\) and \((2 \times 1)\) tiling approximations with results from KMC simulations. The tiling types \( \Xi \) may again be mapped directly to the site types which are \( T' = \{ [b], [c] \} \) for a \((1 \times 1)\) tiling and \( T'' = \{ [b,b],[b,c],[c,c] \} \) for a \((2 \times 1)\) tiling. These approximations result in \(2 \times 3\) and \(3 \times 3^2\) dimensional systems. We repeat one of the numerical experiments from ref. 6, in which we assume that the partial pressure of CO is zero \((p_{CO} = 0)\), fix the partial pressure of O\(_2\) to be 1 atm \((p_{O2} = 1 \text{ atm})\) and determine the system evolution for a variety of partial pressures of CO \((p_{CO})\), ranging from 0.5 to 50 atm (21 partial pressures evenly partitioned on a log scale). The temperature of the system is taken to be 600K. Reaction rates are taken from ref. 6.

To determine the accuracy of the \((1 \times 1)\) and \((2 \times 1)\) tilings, KMC simulations are performed on a \(60 \times 60\) grid and 98 runs are completed at each partial pressure. On the bridge sites the \((2 \times 1)\) tiling approximation falls within a standard deviation of the mean KMC results for site occupations (see Figure 7). On cus sites the \((2 \times 1)\) tiling approximation fails for partial pressures greater than 2 and less than 5 atm (see Figure 7). The \((2 \times 1)\) tiling approximation, however, demonstrates a vast improvement from the \((1 \times 1)\) tiling approximation (PK) model; far more so than the parameters of the previous section.

To determine the approximated size of a tiling that would lead to an accurate description of the system dynamics, we again examine the length scale correlations at steady state as a function of partial pressure. Within the KMC simulations at a partial pressure of \(p_{CO} = 3.15\text{atm}\), we find that the bridge-bridge correlations die off nearly completely after the nearest neighbor; the cus-bridge pairs, however, are significantly correlated up to many neighbors away, while the cus-cus pairs are significantly correlated beyond 8 neighbors away (see Figures 8 and 9). This data supports the observations that the predicted dynamics for bridge sites is accurate for a \((2 \times 1)\) tiling, where as the predicted dynamics for the cus sites is not. To accurately capture the system dynamics at this partial pressure, we would need either an unmixed \(9 \times 2\) tiling approximation which would result, at minimum, in a \(|S|^{9 \times 2} = 3.87 \times 10^8\) dimensional system. We could also potentially use a mixed \((9 \times 1)\) (and \((1 \times 9)\)) system which would lead to a \(|\Xi| \times |S|^{9} \approx 6 \times 10^4\) dimensional system which is far more tractable. Finally it is also possible to use a more complex mixed tiling system such that we use \((2 \times 1)\) tiles for bridge-bridge and bridge-cus connections and \((n \times 1)\) tiles in the cus-cus direction, which would

![FIG. 5. Steady states (a) and relative speed up (b) in the two-dimensional case in which bridge and cus sites are treated identically. The speed up is plotted based on the number of sites per tile. The \((3 \times 2)\) (6 tile sites) approximation has the slowest speed up and runs 7.7 times faster than the KMC simulation over all 10 data runs.](image)

![FIG. 6. Correlation of the \(i,j\) neighbor with the labeled site. The correlations are taken at steady state and \(k_{O + CO} = 10^{-0.16}\). The correlations die down slowly in this regime; distant correlations are at 10% of nearest neighbor correlations at a distance of 5 nearest neighbors.](image)
FIG. 7. We plot the probability that bridge (a) and cus (b) sites will be occupied by CO. Notice that the $(2 \times 1)$ tiling approximation equation fits with in the error bars of the KMC simulation for the bridge sites, but does not for some regions of the cus sites. The traditional $(1 \times 1)$ tiling predicts values and behavior with large error.

FIG. 8. The maximum covariance as a function of distance from a site is given for $p_{CO} = 5\text{ atm}$ and $3.15\text{ atm}$. The former value shows low correlations beyond nearest neighbors which corresponds to the accurate model prediction. The latter value demonstrates high correlations even up to eight neighbors away.

FIG. 9. The correlation for a cus site is decomposed based on the system geometry. The horizontal axis shows a line of constant cus sites and the high correlation that persists in this line. In the vertical direction, the first bridge and cus site away show non-negligible correlation to the cus site at the origin.

lead to a $2 \times |S|^3 + |S|^n$ dimensional system; for $n = 9$, this gives a $\sim 2 \times 10^4$ dimensional system, which is far more tractable still. The first method leads to a system which is intractably large. The second system is numerically tractable and the typical system we have been using in the present work. The third system is yet a new tiling structure which we begin to explore with $n = \{2, 3, 4, 5\}$, the $n = 2$ case being equivalent to the $2 \times 1$ scheme that we have examined above. We check for consistency over all single site projections of the probability of finding CO on cus sites for each case and verify that the consistency criteria is satisfied in these test cases. We plot the results found at steady state in figure [11]. We find an improvement in the mixed tiling scheme, however note that we do not see full convergence having only gone up to a $(5 \times 1)$ tiling scheme in the cus-cus direction. As in the previous section, we compare the speed up of the generalized PK models with a single KMC run and determine the average speed up over all examined partial pressures. We note that we have taken 98 KMC simulations and thus the actual average speed up in our computations is 98 times greater than what is presented. We display the speed up in figure [11] and find that the $(2 \times 1)$ tiling scheme runs 4500 times faster than a single KMC realization. The $(5 \times 1)$ mixed tiling scheme yields a speed up of 4.5 for a single KMC simulation run.

With the two tiling systems that we have presented, we have confirmed that the hierarchy of systems leads to improved predictions for realistic surface dynamics and have shown that this occurs even with small improvements within the hierarchy. We have also introduced the idea of mixed tiling systems and shown how they may be used to introduce improvements in the accuracy of the dynamics.

IV. DISCUSSION

We have developed a method of approximating the chemical master equation for systems that are assumed to be translationally invariant with finite spatial corre-
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2x1 tiling
3x1 tiling
4x1 tiling
5x1 tiling
kMC

Partial pressure of CO (atm)

FIG. 10. Adding a mixed tiling scheme that accounts only for the spatial correlations in the cusc-cus direction shows an improvement from the (2\times1) tiling scheme, however we do not see convergence when the partial pressure of CO is 3.15.

2 3 4 5
0 500 1000 1500 2000 2500 3000 3500 4000 4500

Mixed tile size

Speed up from KMC

FIG. 11. We present the speed up of the (n \times 1) mixed tiling scheme when compared to a single KMC realization with speed ups averaged over all partial pressure runs. We find a speed up of 4.5 for the largest case when mixing (5 \times 1) tilings.

lations. In principle, this system will always converge to the master equation and we have shown this in one- and two-dimensional examples. In the current exposition, there is no a priori method of determining the necessary tilings needed to approximate the master equation, and such a method would be useful to determine whether or not it is worth using a tiling system or a traditional KMC approach to solving the master equation. The speed up of the developed method has been explored and demonstrated on the test examples and we find that for smaller systems, we see significant reductions in computational time. We have also shown that the methods quickly lead improvements on a realistic example of oxidation of CO on RuO\textsubscript{2}(110), and have observed that a modest improvement to (2 \times 1) tilings captures many of the important system dynamics within the parameters considered.

The ability to extend models to larger tilings also provides a means to hypothesis test PK models on smaller tiles. In any pursuit in which one hypothesizes that a generalized PK model provides a suitable model, the current methodology provides a fast method to justify this choice of model by testing this hypothesis with extended tiling systems. Should the dynamics change significantly between the smaller and larger tilings, we can reject the method. Although this provides a sufficient tool for hypothesis rejection, it is an open and interesting question to ask that if we do not see improvement between a smaller and larger tiling system, does this mean that the method has converged or are their local plateaus (i.e. is the condition necessary)?

This hierarchy of generalized PK models may also be used to fit parameters from observed experimental data. These parameter estimates can be similarly tested by examining larger tilings. If the parameters change, we can conclude that longer range spatial correlations play a significant role in the surface dynamics, however if the parameter estimates do not change it is still an open question as to whether or not we can conclude these are accurate surface parameters. If this question can be answered in the affirmative, we can then use transition state theory (TST) to predict energy barriers and energy differences between bound and unbound site states, and also predict transition rates over all temperatures. The two open questions presented in this and the above paragraph will be the subject of a future investigation.

The methodology here has been tested in the context of constant rate coefficients so that Equations 4a and 4b may be simplified to Equations 5a and 5b. In many interesting catalysis reactions, rate reactions will change based on local spatial correlations. Although we have not investigated such mechanisms in the current work, it will be interesting to examine methods to reconstruct longer range spatial correlations that may be used to predict variable rate equations based on the current state of the tilings. Again, we must ensure that this more complex models will be consistent based on the ideas presented in section II C. In the current work we have not attempted to prove several natural propositions that have arisen, such as finding conditions for when a tiling scheme will be consistent. We save this pursuit for future work as well.

Another potentially intriguing application of this work is to use successive tilings as a predictor scheme for a KMC system state, to then instantiate the KMC model based on the largest calculated tiling, and then to correct the system by determining the direction in phase space based on the KMC instantiation and short time dynamics. We are looking into the possibility of such a multi scale algorithm and believe that this extended framework may aid in speeding up KMC algorithms due to the fact that it eliminates well-mixed assumptions.
Finally, we have presented a generalized framework in terms of surface kinetics on square lattices. The work immediately extends to three dimensional reaction networks and may extend to more general lattices and tiling structures. There are many other models that take the same form of PK models such as SIR models and other ecological model; indeed, pairwise models corresponding to $(2 \times 1)$ tilings have been examined and it will be interesting to examine whether the more generic framework presented in the current work will lead to more accurate modeling while retaining efficiency. We remark that the current methodology may have extensions to more irregular networks and we note that this is a promising continuation of the present work.

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