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Equivalence of on-Lattice Stochastic Chemical Kinetics with the Well-Mixed Chemical Master Equation in the Limit of Fast Diffusion

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Abstract

Well-mixed and lattice-based descriptions of stochastic chemical kinetics have been extensively used in the literature. Realizations of the corresponding stochastic processes are obtained by the Gillespie stochastic simulation algorithm and lattice kinetic Monte Carlo algorithms, respectively. However, the two frameworks have remained disconnected. We show the equivalence of these frameworks whereby the stochastic lattice kinetics reduces to effective well-mixed kinetics in the limit of fast diffusion. In the latter, the lattice structure appears implicitly, as the lumped rate of bimolecular reactions depends on the number of neighbors of a site on the lattice. Moreover, we propose a mapping between the stochastic propensities and the deterministic rates of the well-mixed vessel and lattice dynamics that illustrates the hierarchy of models and the key parameters that enable model reduction.

Keywords

Master equation; time scale separation; stiffness; kinetic Monte Carlo; Gillespie algorithm; chemical kinetics

1. Introduction

Stochasticity in the occurrence of chemical reactions has recently attracted significant interest in different research areas, such as biology and catalysis. In biology, the small sizes of the cellular compartments and the low numbers of molecules participating in biochemical reactions result in appreciable noise in gene expression and regulatory functions of the cell (Maheshri and O'Shea, 2007; McAdams and Arkin, 1997, 1999). This noise modulates the behavior of genetic circuits and can induce novel expression patterns, such as enhancement of cellular variability and creation or destruction of bistability (Blake et al., 2003; Hasty et al., 2000; Kepler and Elston, 2001; Raser and O'Shea, 2005; Stamatakis and Mantzaris, 2009) that have been linked to cell fate decisions (Maamar et al., 2007; Raser and O'Shea, 2005; Süel et al., 2007). In catalysis, the small sizes of systems, such as supported nanoparticle catalysts (Jacobs et al., 1997; Johánek et al., 2004; Zhdanov and Kasemo, 1998) or facets of field emitter tips (Suchorski et al., 2001; Suchorski et al., 1999), result in fluctuations in the coverages and reactivity, which have profound effects on the observed

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behavior. Complex phenomena, such as loss of bistability, noise-induced transitions or oscillations have been predicted by theory and confirmed by experiment (Liu and Evans, 2002; Pineda et al., 2006; Pineda et al., 2007; Vlachos et al., 1991; Zhdanov and Kasemo, 1994, 1998, 2000).

Such phenomena can be analyzed by probabilistic descriptions of chemical kinetics, which have been used for many decades to model both well-mixed and spatially-distributed systems. Well-mixed systems are described by the chemical master equation (Gardiner, 2004; McQuarrie, 1967; Nicolis and Prigogine, 1977; van Kampen, 1992), realizations of which can be obtained by an exact stochastic simulation algorithm (SSA), also known as the Gillespie kinetic Monte Carlo (KMC) algorithm (Gibson and Bruck, 2000; Gillespie, 1976, 1977). For spatially distributed systems, the lattice gas model (Kreuzer and Zhang, 1990) and the Ising spin model (Kawasaki, 1972) are used. Kinetic Monte Carlo (KMC) methods have been developed for simulating the dynamic behavior of these models (Chatterjee and Vlachos, 2007). The method is often attributed to Bortz et al. (1975).

From a theoretical standpoint, the two stochastic simulation methods, namely lattice KMC and the Gillespie SSA, remain disconnected, even though similar computational schemes are used in the simulation of lattice and well-mixed systems. Thus, in this work we are concerned with bridging the stochastic descriptions of spatially-distributed and well-mixed chemical systems. We apply singular perturbation analysis under the assumption of fast diffusion dynamics without closure assumptions or coarse-graining. We thus show that a master equation for the dynamics of a single species on the lattice reduces to a birth-death master equation that pertains to a well-mixed chemical system. This procedure elucidates the mapping between the microscopic lattice propensities and those of the well-mixed stochastic model. We further demonstrate that the error of the approximation drops linearly with the inverse of the diffusion rate. Moreover, we investigate the thermodynamic limit of large system sizes and derive deterministic models that can accurately capture the dynamics.

2. Methods

Several methods have appeared in the literature for the treatment of time scale separation in chemical kinetics of well-mixed systems (Cao et al., 2005a; 2005b; E et al., 2005; Haseltine and Rawlings, 2002, 2005; Hill et al., 2008; Mastny et al., 2006, 2007; Peles et al., 2006; Rao and Arkin, 2003; Salis and Kaznessis, 2005a; 2005b; Salis et al., 2006; Samant et al., 2007; Samant and Vlachos, 2005; Weinan et al., 2007). We have extended these ideas to any type of discrete master equation by explicitly partitioning of the state space into sets within which the dynamics evolves rapidly and subsequently indexing of these sets. This procedure is essentially a coordinate transformation through which the state space is mapped to the index sets of the partition and each element of the partition. Through this mapping, conveniently chosen variables are introduced, thereby making possible the treatment of complex processes, such as the chemical kinetics of a fast diffusing species on a lattice. Previous methods can be viewed as a special case of our derivation when this mapping is linear. In the following, we summarize the key result of this derivation, the details of which appear in section 1 of the Supplementary Material along with a detailed review of previous methods.

We start from a discrete master equation of the type:

$$\frac{\partial P(\mathbf{w};t)}{\partial t} = \sum_{\mathbf{w}' \in W} [\alpha_{\mathbf{w}'}(\mathbf{w}) \cdot P(\mathbf{w}';t) - \alpha_{\mathbf{w}}(\mathbf{w}') \cdot P(\mathbf{w};t)] \quad (1)$$

where $\mathbf{w}$ and $\mathbf{w}'$ denote states belonging to W , the state space of the system whose evolution is governed by equation (1). The latter equation is a balance for $P(\mathbf{w};t)$, the probability that the system is in state $\mathbf{w}$ at time t . The transition probability for going from state $\mathbf{w}'$ to state $\mathbf{w}$ is denoted as $\alpha_{\mathbf{w}'}(\mathbf{w})$. Thus, the positive terms of the right hand side of equation (1) express probability influx from states $\mathbf{w}'$ to state $\mathbf{w}$, and the negative terms express probability efflux from state $\mathbf{w}$ to state $\mathbf{w}'$.

We subsequently introduce a partitioning in W :

$$\begin{aligned} P &= \{P_v\}_{v \in V} \\ P_v &\subseteq W \quad \forall v \in V \\ P_v \cap P_{v'} &= \emptyset \quad \forall v \in V \quad \forall v' \in V \\ \bigcup_{v \in V} P_v &= W \end{aligned} \quad (2)$$

This partitioning is essentially a change of coordinates which maps every state $\mathbf{w}$ to a pair of elements $(\mathbf{u}, \mathbf{v})$, where $\mathbf{v} \in V$, with V being an index set for P , and $\mathbf{u} \in U_v$, with U_v being an index set for P_v . Figure 1 illustrates this mapping in a simple case where a state space consisting of 16 discrete states is partitioned to 7 disjointed sets.

If the transition probabilities of equation (1) involve large parameters that are on the order of ε^{-1} , ε being a small parameter, one can construct a partitioning that satisfies the following condition:

$$\alpha_{\mathbf{u}', \mathbf{v}'}(\mathbf{u}, \mathbf{v}) = \begin{cases} \frac{1}{\varepsilon} \cdot \bar{\alpha}_{\mathbf{u}', \mathbf{v}}(\mathbf{u}, \mathbf{v}) & \text{if } \mathbf{v}' = \mathbf{v} \\ \bar{\alpha}_{\mathbf{u}', \mathbf{v}}(\mathbf{u}, \mathbf{v}) & \text{otherwise} \end{cases} \quad (3)$$

Then, equation (1) can be decomposed to the following two equations which become exact in the limit $\varepsilon \rightarrow 0$:

$$0 = \sum_{\mathbf{u}' \in U_v} [\bar{\alpha}_{\mathbf{u}', \mathbf{v}}(\mathbf{u}, \mathbf{v}) \cdot P(\mathbf{u}' | \mathbf{v}; t) - \bar{\alpha}_{\mathbf{u}, \mathbf{v}}(\mathbf{u}', \mathbf{v}) \cdot P(\mathbf{u} | \mathbf{v}; t)] \quad \forall \mathbf{v} \in V \quad (4)$$

$$\frac{\partial P(\mathbf{v}; t)}{\partial t} = \sum_{\substack{\mathbf{v}' \in V \\ \mathbf{v}' \neq \mathbf{v}}} \left\{ \left(\sum_{\mathbf{u}' \in U_{\mathbf{v}'}} \sum_{\mathbf{u} \in U_{\mathbf{v}}} [\alpha_{\mathbf{u}', \mathbf{v}'}(\mathbf{u}, \mathbf{v}) \cdot P(\mathbf{u}' | \mathbf{v}'; t)] \right) \cdot P(\mathbf{v}'; t) - \left(\sum_{\mathbf{u}' \in U_{\mathbf{v}'}} \sum_{\mathbf{u} \in U_{\mathbf{v}}} [\alpha_{\mathbf{u}, \mathbf{v}}(\mathbf{u}', \mathbf{v}') \cdot P(\mathbf{u} | \mathbf{v}; t)] \right) \cdot P(\mathbf{v}; t) \right\} \quad (5)$$

Equation (4) expresses the quasi-steady-state approximation and (5) captures the slow dynamics onto which the fast ones have been projected.

3. Theory

3.1. Model Formulation

In this section we develop a master equation for the dynamics of adsorption, desorption, diffusion and reaction on a lattice (see Table I for the reaction network), involving a single species, and subsequently reduce this equation using the methodology of the previous section. The difference between the current work and that of Mastny et al. (2006) lies in the analytical formulation of exact and approximate mathematical models for single species

lattice dynamics, whereas Mastny et al. (2006) focus on developing a numerical simulation strategy based on quasi-equilibrium arguments.

The last process appearing in Table I is the diffusional hopping of a particle to an unoccupied neighboring site, and the kinetic constant for this process is denoted as k_{dif} . We assume that this parameter assumes values that are much larger than any other kinetic constant. Thus, we can introduce a small parameter ε and write this kinetic constant as:

$$k_{\text{dif}} = \frac{\kappa_{\text{dif}}}{\varepsilon} \quad (6)$$

where κ_{dif} is the normalized diffusion constant, which is of the order of 1. Since k_{dif} is now expressed as a parameter of order of ε^{-1} , it is possible to apply singular perturbation analysis.

The assumption of fast diffusion is usually valid for catalytic surfaces, for example CO diffusion is much faster than other processes on Pt surfaces (Raimondeau and Vlachos, 2002; Zhdanov and Kasemo, 1994). This, however, may not be the case when dealing with diffusion-limited processes for example those occurring in zeolites (Coppens et al., 1998; Iyengar and Coppens, 2004).

Since diffusion conserves the number of particles on a lattice, we can partition the state space into subsets in which the number of adparticles is constant (see equations 2, 3). The state of the system can then be represented as a vector of integers $(v, x_1, x_2, \dots, x_v)$, where v denotes the number of adparticles that exist on the lattice, and $x_1, \dots, x_v$ denote the sites that these particles occupy in an ascending order, so that we avoid double-counting of configurations. The corresponding master equation can be written as (see section 2 of the Supplementary Material):

$$\begin{aligned} \frac{\partial P(v, x_1, \dots, x_v; t)}{\partial t} = & \sum_{\xi=1}^v k_{\text{ads}} \cdot P(v-1, x_1, \dots, x_{\xi-1}, x_{\xi+1}, \dots, x_v; t) - \sum_{\substack{q=1, \dots, N_L \\ q \neq x_i \forall i=1, \dots, v}} k_{\text{ads}} \cdot P(v, x_1, \dots, x_v; t) + \\ & \sum_{\substack{q=1, \dots, N_L \\ q \neq x_i \forall i=1, \dots, v}} k_{\text{des}} \cdot P(v+1, x_1, \dots, q, \dots, x_v; t) - \sum_{\xi=1}^v k_{\text{des}} \cdot P(v, x_1, \dots, x_v; t) + \\ & \sum_{\substack{q=1, \dots, N_L \\ q \neq x_i \forall i=1, \dots, v}} k_{\text{rxn1}} \cdot P(v+1, x_1, \dots, q, \dots, x_v; t) - \sum_{\xi=1}^v k_{\text{rxn1}} \cdot P(v, x_1, \dots, x_v; t) + \\ & \sum_{\substack{p=1, \dots, N_L \\ p \neq x_i \forall i=1, \dots, v}} \sum_{\substack{q=p+1, \dots, N_L \\ q \neq x_i \forall i=1, \dots, v}} k_{\text{rxn2}} \cdot \mathbf{1}_{\{p \text{ neighbors } q\}} \cdot P(v+2, x_1, \dots, p, \dots, q, \dots, x_v; t) + \\ & - \sum_{\xi=1}^{v-1} \sum_{\zeta=\xi+1}^v k_{\text{rxn2}} \cdot \mathbf{1}_{\{x_\xi \text{ neighbors } x_\zeta\}} \cdot P(v, x_1, \dots, x_\xi, x_\zeta, \dots, x_v; t) + \\ & \sum_{\xi=1}^v \sum_{\substack{q=1, \dots, N_L \\ q \neq x_i \forall i=1, \dots, v}} k_{\text{dif}} \cdot \mathbf{1}_{\{x_\xi \text{ neighbors } q\}} \cdot P(v, x_1, \dots, x_{\xi-1}, x_{\xi+1}, \dots, q, \dots, x_v; t) + \\ & - \sum_{\xi=1}^v \sum_{\substack{q=1, \dots, N_L \\ q \neq x_i \forall i=1, \dots, v}} k_{\text{dif}} \cdot \mathbf{1}_{\{x_\xi \text{ neighbors } q\}} \cdot P(v, x_1, \dots, x_\xi, \dots, x_v; t) \end{aligned} \quad (7)$$

Here k_{ads} , k_{des} , k_{rxn1} , k_{rxn2} , and k_{dif} refer to the kinetic rates for the occurrence of each microscopic event, namely adsorption, desorption, single-site reaction, two-site reaction and diffusion, shown in Table I. Moreover, the indicator $\mathbf{I}_{\{x_i \text{ neighbors } x_j\}}$ evaluates to 1 if the two sites x_i and x_j are neighbors, otherwise it returns 0. State $(v, x_1, \dots, x_v)$ may have resulted from adsorption of a particle to site $x_\xi \neq x_i$, $i = 1, \dots, v$. Thus, state $(v, x_1, \dots, x_v)$ receives probability influxes due to adsorption from all possible states containing $v - 1$ particles in sites $x_1, \dots, x_{\xi-1}, x_{\xi+1}, \dots, x_v$ (excluding site x_ξ). The propensity for site x_ξ to become occupied in the next dt is k_{ads} , and x_ξ may be any one of the sites $(x_1, \dots, x_v)$; hence, the overall contribution of probability influxes due to adsorption events is given by the first sum of the right hand side.

Furthermore, configuration $(v, x_1, \dots, x_v)$ has empty sites $q = 1, \dots, N_L$ provided that $q \neq x_i$, $\forall i = 1, \dots, v$. Thus, adsorption to any of these sites can change the configuration, thereby generating the probability efflux term (the second sum in equation 7). The counter q over which summation is performed does not appear in the summand, since the probability is written for the occupied sites. However, q implicitly enters the calculation, in this case as a multiplication factor (the number of empty sites).

For the desorption and single site reaction processes, state $(v, x_1, \dots, x_v)$ receives probability influx from states which have an additional adparticle at site q . The latter may take any value different from $x_1, \dots, x_v$, thereby justifying the expression used in the summation over q .

The probability efflux term is justified as follows: any one of the adparticles existing in sites $x_1, \dots, x_v$ can desorb giving rise to a different configuration. Thus, the probability efflux is the sum over all sites of the single site desorption terms.

For the probability influx terms due to two-site reaction events, similar arguments can be applied to derive the terms that appear in equation (7), with the only difference that we now have two additional adparticles that need to be neighboring in order to react. Thus, we sum over the possible sites that the two particles can occupy, using the indicator for sites p and q being neighbors, $\mathbf{I}_{\{p \text{ neighbors } q\}}$.

For the diffusion process, a particle jumps from site q to site x_ξ . Consequently, state $(v, x_1, \dots, x_v)$ receives contributions from states in which site x_ξ is unoccupied and site q is an occupied neighbor of site x_ξ . In a similar way, efflux terms for diffusion and reaction are calculated on the basis of the events that are allowed to happen when the system is in state $(v, x_1, \dots, x_v)$.

3.2. Model Reduction

Since diffusion does not change the number of particles on the lattice, let us introduce the marginal probability for the number of adparticles as $P(v; t)$ and the conditional probability for their positions $P(x_1, \dots, x_v | v; t)$. It follows that:

$$P(v, x_1, \dots, x_v; t) = P(x_1, \dots, x_v | v; t) \cdot P(v; t) \quad (8)$$

and thus, by applying the singular perturbation methodology we reduce equation (7) to the following:

$$O(\epsilon^{-1}):$$

$$P_0(x_1, \dots, x_v | v; t) = \binom{N_L}{v}^{-1} = \frac{v! (N_L - v)!}{N_L!} \quad (9)$$

$$O(1):$$

$$\frac{\partial P_0(v; t)}{\partial t} =$$

$$k_{\text{ads}} \cdot (N_L - v + 1) \cdot P_0(v - 1; t) - k_{\text{ads}} \cdot (N_L - v) \cdot P_0(v; t) +$$

$$k_{\text{des}} \cdot (v + 1) \cdot P_0(v + 1; t) - k_{\text{des}} \cdot v \cdot P_0(v; t) +$$

$$k_{\text{rxn1}} \cdot (v + 1) \cdot P_0(v + 1; t) - k_{\text{rxn1}} \cdot v \cdot P_0(v; t) +$$

$$\frac{k_{\text{rxn2}} \cdot v_{\text{coord}}}{2(N_L - 1)} \cdot (v + 2) \cdot (v + 1) \cdot P_0(v + 2; t) - \frac{k_{\text{rxn2}} \cdot v_{\text{coord}}}{2(N_L - 1)} \cdot v \cdot (v - 1) \cdot P_0(v; t) \quad (10)$$

where v_{coord} is the coordination number of the lattice, namely the number of the nearest neighbors of a site. For our purposes we consider a 2D regular lattice, and thus, the coordination number can take one of the following values: 3 for a honeycomb-type lattice, 4 for a rectangular lattice, and 6 for a hexagonal lattice.

3.3. Deterministic Model in the Thermodynamic Limit

By taking the limit for large system size in the birth-death master equation (10), we can formulate an ordinary differential equation (ODE) for the processes of adsorption, desorption, and reaction, which we will refer to as the thermodynamic-limit deterministic model (TL-deterministic model). Such deterministic models have been previously formulated (Mastny *et al.*, 2006). However, those were based on the chemical master equation, whereas ours are derived from the well-mixed lattice master equation (10), thereby being capable of revealing the effects of lattice connectivity and adparticle localization. Starting from equation (10) we multiply both sides with v/N_L and sum over v :

$$\sum_{v=0}^{N_L} \frac{v}{N_L} \cdot \frac{\partial P_0(v; t)}{\partial t} =$$

$$\sum_{v=1}^{N_L} k_{\text{ads}} \cdot \frac{v}{N_L} \cdot (N_L - v + 1) \cdot P_0(v - 1; t) - \sum_{v=0}^{N_L-1} k_{\text{ads}} \cdot \frac{v}{N_L} \cdot (N_L - v) \cdot P_0(v; t) +$$

$$\sum_{v=0}^{N_L-1} k_{\text{des}} \cdot \frac{v}{N_L} \cdot (v + 1) \cdot P_0(v + 1; t) - \sum_{v=1}^{N_L} k_{\text{des}} \cdot \frac{v}{N_L} \cdot v \cdot P_0(v; t) +$$

$$\sum_{v=0}^{N_L-1} k_{\text{rxn1}} \cdot \frac{v}{N_L} \cdot (v + 1) \cdot P_0(v + 1; t) - \sum_{v=1}^{N_L} k_{\text{rxn1}} \cdot \frac{v}{N_L} \cdot v \cdot P_0(v; t) +$$

$$\sum_{v=0}^{N_L-2} \frac{k_{\text{rxn2}} \cdot v_{\text{coord}}}{2(N_L - 1)} \cdot \frac{v}{N_L} \cdot (v + 2) \cdot (v + 1) \cdot P_0(v + 2; t) - \sum_{v=2}^{N_L} \frac{k_{\text{rxn2}} \cdot v_{\text{coord}}}{2(N_L - 1)} \cdot \frac{v}{N_L} \cdot v \cdot (v - 1) \cdot P_0(v; t) \quad (11)$$

Subsequently, we change the summation limits of the positive terms, for instance for the 2-site reaction term:

$$\sum_{v=0}^{N_L-2} \frac{k_{\text{rxn2}} \cdot v_{\text{coord}}}{2 \cdot (N_L - 1)} \cdot \frac{v}{N_L} \cdot (v + 2) \cdot (v + 1) \cdot P_0(v + 2; t) = \sum_{v=2}^{N_L} \frac{k_{\text{rxn2}} \cdot v_{\text{coord}}}{2 \cdot (N_L - 1)} \cdot \frac{v - 2}{N_L} \cdot v \cdot (v - 1) \cdot P_0(v; t) \quad (12)$$

and thus:

$$\begin{aligned}
 & \sum_{\nu=0}^{N_L-2} \frac{k_{rxn2} \cdot \nu_{coord}}{2 \cdot (N_L - 1)} \cdot \frac{\nu}{N_L} \cdot (\nu+2) \cdot (\nu+1) \cdot P_0(\nu+2;t) \\
 & - \sum_{\nu=2}^{N_L} \frac{k_{rxn2} \cdot \nu_{coord}}{2 \cdot (N_L - 1)} \cdot \frac{\nu}{N_L} \cdot \nu \cdot (\nu-1) \cdot P_0(\nu;t) \\
 & = -2 \cdot \frac{k_{rxn2} \cdot \nu_{coord}}{2} \cdot \sum_{\nu=2}^{N_L} \frac{\nu \cdot (\nu-1)}{N_L \cdot (N_L - 1)} \cdot P_0(\nu;t) \\
 & = -k_{rxn2} \cdot \nu_{coord} \cdot \left\langle \frac{\nu}{N_L} \cdot \frac{\nu-1}{N_L - 1} \right\rangle
 \end{aligned} \tag{13}$$

In the thermodynamic limit $N_L \rightarrow \infty$, correlations and fluctuations are suppressed:

$$\left\langle \frac{\nu}{N_L} \cdot \frac{\nu-1}{N_L - 1} \right\rangle = \theta^2 \tag{14}$$

Applying the same reasoning to the rest of the terms in equation (11), one derives the following deterministic model:

$$\frac{d\theta}{dt} = r_{ads}(\theta) - r_{des}(\theta) - r_{rxn1}(\theta) - 2 \cdot r_{rxn2}(\theta) \tag{15}$$

where the intensive propensity functions are given as:

$$r_{ads}(\theta) = k_{ads} \cdot (1 - \theta) \tag{16}$$

$$r_{rxn1}(\theta) = k_{rxn1} \cdot \theta \tag{17}$$

$$r_{rxn2}(\theta) = \frac{k_{rxn2}}{2} \cdot \nu_{coord} \cdot \theta^2 \tag{18}$$

$$r_{des}(\theta) = k_{des} \cdot \theta \tag{19}$$

Therefore, the TL-deterministic model is written as:

$$\frac{d\theta}{dt} = k_{ads} \cdot (1 - \theta) - k_{des} \cdot \theta - r_{rxn1} \cdot \theta - k_{rxn2} \cdot \nu_{coord} \cdot \theta^2 \tag{20}$$

Note that this model is identical to the mean-field models derived using the law of action kinetics (Lutsevich *et al.*, 1991). Here, equation (20) was derived using singular perturbation assuming fast Fickian diffusion and a subsequent system size expansion.

4. Results and Discussion

4.1. Comparison of Microscopic Lattice KMC with Well Mixed Stochastic Kinetics

In order to compare the full master equation (7) with the birth-death master equation (10), realizations of the corresponding stochastic processes were obtained through KMC simulations for fast diffusion dynamics. To simulate equation (7), we developed a lattice KMC code in FORTRAN 95. The code incorporates a binary tree structure for storing the partial sums of the propensities, thereby allowing for efficient $O(\log_2(P))$ search and update, where P is the number of microscopic processes considered, i.e., the number of microscopic processes per site times the number of lattice sites. Note that P scales linearly with the number of lattice sites, N_L . On the other hand, well mixed stochastic kinetics was simulated with Gillespie's SSA algorithm, using the propensity functions appearing in equation (10). The stationary probability density was also obtained by direct solution of a system of N_L+1 algebraic equations, obtained by writing equation (10) at steady state for $v = 1, \dots, N_L-1$, along with the following relations for $v = 0$ and N_L :

$$0 = -k_{\text{ads}} \cdot N_L \cdot P_0(0;t) + k_{\text{des}} \cdot P_0(1;t) + k_{\text{rxn1}} \cdot P_0(v+1;t) + \frac{k_{\text{rxn2}} \cdot v_{\text{coord}}}{(N_L - 1)} \cdot P_0(2;t) \quad (21)$$

$$0 = k_{\text{ads}} \cdot P_0(N_L - 1;t) - k_{\text{des}} \cdot N_L \cdot P_0(N_L;t) - k_{\text{rxn1}} \cdot N_L \cdot P_0(N_L;t) - \frac{k_{\text{rxn2}} \cdot v_{\text{coord}}}{2 \cdot (N_L - 1)} \cdot N_L \cdot (N_L - 1) \cdot P_0(N_L;t) \quad (22)$$

Figure 2 summarizes the results of these comparisons. Panel (a) shows transients of the number of adparticles on the lattice and panel (b) the corresponding stationary probability mass functions (PMFs), revealing an excellent agreement between the full and reduced model. At stationary conditions, the number of adparticles on the lattice can be viewed as a random variable that converges weakly (in distribution) to the random number of particles predicted by equation (10). The error of the approximation is on the order of ε as computationally shown in panel (c). For this plot, the stationary distribution $P^s(v)$ was obtained through lattice KMC simulation, the approximate distribution $P_0^s(v)$ was obtained by solving equation (10) at steady state along with equations (21, 22) and the error was calculated as the Euclidean norm of the difference $P^s(v) - P_0^s(v)$ (see equation 13 of Supplementary Material, section 1). Furthermore, the quality of the approximation is not affected by the presence of "boundaries": excellent agreement is also observed for parameter sets for which the probability accumulates to the minimum ($v = 0$) or the maximum ($v = N_L$) number of particles as shown in Figure 2(d) and Figure 2(e).

The results obtained with the birth-death master equation (10) and the full model (7) should also agree in non-stationary conditions. To show this agreement we can solve a linear system of N_L+1 ordinary differential equations obtained by writing expression (10) for $v = 0, \dots, N_L$ thereby computing $P_0(v;t)$. Subsequently, the latter can be compared to the probability distributions obtained through KMC simulations. The results of these comparisons are shown in Figure 3a, b in which the system is initialized with an empty lattice ($P(v,0) = \delta_{v,0}$) and the two probability densities are compared at two different times. In order to perform a convergence analysis, we evaluate the two distributions at 16 time instances from 0 to $1.5 \cdot 10^{-6}$ and calculate the error as:

$$\text{Error} = \sqrt{\sum_{i=0}^{N_t} \sum_{v=0}^{N_L} (P(v; i \cdot \Delta t) - P_0(v; i \cdot \Delta t))^2} \quad (23)$$

Figure 3c portrays the average v of the birth-death equation as well as the time instances $0, \Delta t, 2 \cdot \Delta t, \dots$ used in the calculation of the error (equation 23), showing that the non-stationary solution is being sampled correctly. The convergence plot of Figure 3d shows that the error drops linearly with ε (see equation 6).

It is interesting to observe that the bimolecular reaction propensity that appears in equation (10) depends on the coordination number of the lattice v_{coord} , which is the number of neighbors of a site. The maximum value of v_{coord} is $N_L - 1$ and occurs when all lattice sites are treated as neighbors. For 1st-nearest neighbors in regular 2-dimensional lattices, the possible values of the coordination number are 3, 4 or 6 (triangular, rectangular and hexagonal lattices, respectively). Figure 4 shows the effect of lattice type on the stationary PMF for the number of adparticles. For the more connected hexagonal lattice (panels c, d), the rate of bimolecular reactions is higher, resulting in lower numbers of particles on the lattice at stationary state. If one rescales the reaction rate constant for lattices at different coordination numbers, so that the $k_{\text{rxn}2} \cdot v_{\text{coord}}$ is the same for these lattices, identical results are obtained (results not shown).

4.2. Comparison of Microscopic Lattice KMC with TL-Deterministic Model

Figure 5 compares of the TL-deterministic model (20) with lattice KMC simulations for fast diffusion and relatively large numbers of sites. Two different lattice configurations were used, namely triangular and hexagonal lattice, in both of which the agreement between the KMC and the TL-deterministic results is excellent. Fast (Fickian) diffusion homogenizes the adsorbates on the lattice thereby rendering the approximation accurate. Our derivation and the observations just noted are in line with previously published computations comparing KMC simulation results with those obtained by ideal models employing mean-field arguments (Araya et al., 1989; Lutsevich et al., 1991; Meakin and Scalapino, 1987). For example, Lutsevich et al. (1991) observe progressively better agreement between the KMC simulations and a deterministic ideal adsorbed layer model as the coordination number of the lattice increases (maximum number of reaction partners as noted in the cited paper). Inspection of equation (20) elucidates this observation: if all sites were treated as neighbors, the coordination number would be $v_{\text{coord}} = N_L - 1$. For this case, the intensive reaction rate entering the mean-field model ($k_{\text{rxn}2} \cdot v_{\text{coord}}$) is approximately equal to the microscopic one scaled by the number of sites ($k_{\text{rxn}2} \cdot N_L$), and thus the KMC simulation and the deterministic mean-field model are in excellent agreement.

4.3. Computational Savings

It is important to note that simulating the approximate models (10) or (15) is much faster than performing the full lattice KMC simulation with fast diffusion. Depending on the value of the diffusion coefficient, the required computational time for the lattice KMC can vary from several minutes to hours. On the contrary, the corresponding simulations of the birth-death master equation typically take less than a minute and the TL-deterministic model can be simulated in a few seconds. Specifically, for fast diffusion, the computational time of the KMC increases linearly with the value of the diffusion coefficient, whereas the computational times of the approximate models remain constant. Thus, one can achieve computational speedup at least proportional to $1/\varepsilon$, namely, linear with respect k_{dif} (see equation 6). This argument assumes that $O(1)$ search and update algorithms are used in the

lattice KMC (Chatterjee and Vlachos, 2007). In reality, the search and update algorithms are more expensive making the computational savings even larger.

4.4. Comparison with Chemical Master Equation and Deterministic Mass Action Law Model

It is interesting to compare the birth-death master equation (10) and the TL-deterministic model (20) with the following chemical master equation and the corresponding deterministic model, which is based on the mass action law, respectively:

$$\begin{aligned} \frac{\partial P(v;t)}{\partial t} = & k_{in}^{wm} \cdot (N_{max} - v + 1) \cdot P(v - 1;t) - k_{in}^{wm} \cdot (N_{max} - v) \cdot P(v;t) + \\ & k_{rxn1}^{wm} \cdot (v + 1) \cdot P(v + 1;t) - k_{rxn1}^{wm} \cdot v \cdot P(v;t) + \\ & \frac{k_{rxn2}^{wm}}{2 \cdot V \cdot N_A} \cdot (v + 2) \cdot (v + 1) \cdot P(v + 2;t) - \frac{k_{rxn2}^{wm}}{2 \cdot V \cdot N_A} \cdot v \cdot (v - 1) \cdot P(v;t) \end{aligned} \quad (24)$$

$$\frac{dC}{dt} = k_{in}^{wm} \cdot (C_{max} - C) - k_{rxn1}^{wm} \cdot C - k_{rxn2}^{wm} \cdot C^2 \quad (25)$$

where N_{max} is the maximum possible number of particles in the vessel, $C = v/(N_A \cdot V)$ is the concentration of particles, with N_A denoting the Avogadro's number and V the volume of the vessel, and $C_{max} = N_{max}/(N_A \cdot V)$. Moreover, k_{in}^{wm} , k_{rxn1}^{wm} , and k_{rxn2}^{wm} are the kinetic constants for the species inflow, and the 1st- and 2nd-order reactions, respectively (note that desorption has been omitted here for simplicity since it is a 1st-order process, in our example, like a reaction).

Furthermore, by introducing the normalized concentration:

$$\chi = \frac{C}{C_{max}} \quad (26)$$

which is analogous to the coverage fraction θ of the lattice, equation (25) becomes:

$$\frac{d\chi}{dt} = k_{in}^{wm} \cdot (1 - \chi) - k_{rxn1}^{wm} \cdot \chi - k_{rxn2}^{wm} \cdot C_{max} \cdot \chi^2 \quad (27)$$

Note that the processes described by equations (24) and (25) are different from those of equations (10) and (20), since in the former, the molecules can be located anywhere in the continuous space of the vessel, whereas in the latter the molecules are localized to discrete lattice sites. Thus, the extensive reaction rates in the well-mixed vessel are affected by the volume, whereas in the lattice they are affected by the site density and neighboring structure. In the case of a vessel, bimolecular reactions occur between colliding molecules. Consequently, localization of particles in small volumes will result in more frequent collisions, and thus, higher reaction rates. For the lattice, however, bimolecular reactions occur only between neighboring molecules, and that is why the coordination number v_{coord} appears in the 2-site reaction propensity and deterministic rate.

Despite these differences, the mathematical formalisms of equations (10, 24) and (20, 27) are analogous, thereby making possible a comparison between the two frameworks of well-mixed versus lattice-based stochastic kinetics. The differences just noted are manifested as proportionality factors in the kinetic constants found in the models. Table II reveals the mapping between the stochastic propensities and the deterministic rates of the well-mixed vessel and lattice equations. Specifically, if one wants to use a well-mixed KMC (such as the

Gillespie algorithm) for capturing lattice dynamics, one would have to use the propensities appearing in the 4th column (Stochastic Well-Mixed Propensity) and the rows of Table II marked as “Vessel”, with the following rate constants for the well-mixed case:

$$\begin{aligned} N_{\max} &= N_L \\ k_{\text{in}}^{\text{wm}} &= k_{\text{ads}} \\ k_{\text{rxn1}}^{\text{wm}} &= k_{\text{rxn1}} \\ k_{\text{rxn2}}^{\text{wm}} &= k_{\text{rxn2}} \cdot \frac{v_{\text{coord}} \cdot V \cdot N_A}{(N_L - 1)} \end{aligned} \quad (28)$$

Similarly, simulation of a well-mixed vessel using the deterministic mass-action law equation (27) would yield identical results with the TL-deterministic model if equalities (28) hold and additionally:

$$N_L \rightarrow \infty \Rightarrow k_{\text{rxn2}}^{\text{wm}} = k_{\text{rxn2}} \cdot \frac{v_{\text{coord}}}{C_{\max}} \quad (29)$$

5. Conclusions

Motivated by the challenge of bridging the stochastic descriptions of spatially distributed and well-mixed chemical systems, we studied the stochastic on-lattice kinetics of a single species and showed the equivalence of the two formulations in the fast diffusion limit.

Starting from a master equation for the processes of adsorption, desorption, diffusion and reaction of a single species on a lattice, we applied singular perturbation for fast Fickian diffusion, thereby deriving a stochastic birth-death model pertaining to a well-mixed system. This model can be simulated with the Gillespie algorithm and was found to be in excellent agreement with the full lattice model. The quality of the approximation becomes progressively better for higher values of the diffusion coefficient and the computational savings from simulating the reduced models can be tremendous.

We further derived the deterministic model in the thermodynamic limit (TL) of large system sizes (infinite number of lattice sites). Our TL-deterministic model is identical to the Bragg-Williams mean-field formulation, when the lattice coordination number is taken into account in the kinetic constant of the two-site reaction. This reduction procedure naturally led to a mapping of the parameters of the different models in the hierarchy, thereby bridging the different levels of approximation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Illustration of the mapping $w \rightarrow (u,v)$. A set of 16 discrete states labeled $w = 1, 2, \dots, 16$ (left schematic) can be partitioned to 7 disjoint sets P_v , for $v \in V = \{1, 2, \dots, 7\}$ (right schematic), each of which contains a different number of states. Each of the states belonging to the same set P_v is assigned a “local number” u , so that the state is now specified by the ordered pair (u,v) . For instance, the set P_v for $v = 3$ contains the states $w = 5, 10$ and 15 ; thus, $P_3 = \{5, 10, 15\}$. The corresponding index set is $U_3 = \{1, 2, 3\}$ and therefore the state $w = 10$ is now denoted as $(u,v) = (2, 3)$.

Figure 2.

(a): Comparison of the transients obtained with the lattice KMC and the simulation of the birth-death master equation (10). (b): Histograms corresponding to the transients of panel (a). Parameter values for panels (a, b): rectangular periodic 5×5 mesh ($N_L = 25$), $v_{\text{coord}} = 4$, $k_{\text{ads}} = 8.5 \times 10^5$, $k_{\text{des}} = 4.0 \times 10^5$, $k_{\text{dif}} = 10^9$, $k_{\text{rxn2}} = 10^6$, $t_{\text{final}} = 4 \times 10^{-4}$; sampling of the stochastic path was performed at time intervals $\Delta t_{\text{sample}} = 10^{-8}$. (c): The points connected with lines show the error of the approximation with respect to ϵ . The error was calculated as the Euclidean norm of $P^s(\nu) - P_0^s(\nu)$, in which the stationary distribution $P^s(\nu)$ is obtained through lattice KMC and the approximate one $P_0^s(\nu)$ from solving steady state equations (10-22). The straight line indicates the scaling relation $C \cdot \epsilon$ where ϵ was evaluated as $\epsilon = k_{\text{ads}}/k_{\text{dif}}$. (d): As in panel (b) with $k_{\text{ads}} = 8.5 \times 10^7$, $t_{\text{final}} = 4 \times 10^{-4}$. (e): As in panel (b) with $k_{\text{ads}} = 5 \times 10^4$, $t_{\text{final}} = 10^{-3}$.

Figure 3.

(a, b): Comparison of probability distributions for the number of particles obtained with the lattice KMC and the simulation of the birth-death master equation (10) in the non-stationary regime. Multiple trajectories were run and sampled at $t = 10^{-7}$ (panel a) and 5×10^{-7} (panel b). Kinetic constants as in Figure 2a. (c): The mean number of particles on the lattice as a function of time. The triangles mark the time instances used for evaluating the error in equation (23). (d): Convergence plot (similar to Figure 2c) but for the non-stationary regime. Multiple KMC trajectories were run and sampled at the times $0, 10^{-7}, 2 \times 10^{-7}, \dots$ marked in panel (c). The error was calculated from equation (23). Parameters as in panels (a, b).

Figure 4.

(a): A 6×6 triangular lattice ($v_{\text{coord}} = 3$). (b): Histograms obtained from lattice and birth-death simulations of adsorption, desorption and reaction dynamics for the lattice of panel (a). Parameter values except mesh size and coordination number as in Figure 2(a). (c): A 6×6 hexagonal periodic lattice ($v_{\text{coord}} = 6$). (d): As in panel (b) for the lattice of panel (a).

Figure 5.

Comparison of lattice KMC transients with mean-field results (ODE model 20). (a): Triangular periodic 30×30 mesh ($N_L = 900$), $v_{\text{coord}} = 3$. (b): Hexagonal periodic 30×30 mesh ($N_L = 900$), $v_{\text{coord}} = 6$. Other parameters: $k_{\text{ads}} = 8.5 \times 10^5$, $k_{\text{des}} = 4.0 \times 10^5$, $k_{\text{dif}} = 10^9$, $k_{\text{rxn1}} = 0$, $k_{\text{rxn2}} = 10^6$.

Table I

Single Species Elementary Steps for Lattice Kinetics

Reaction ^{1,2}	Description
$*_{(s)} \xrightarrow{k_{\text{ads}}} A_{(s)}$	Adsorption
$A_{(s)} \xrightarrow{k_{\text{des}}} *_{(s)}$	1 st -order Desorption
$A_{(s)} \xrightarrow{k_{\text{rxn1}}} *_{(s)}$	1-Site, 1 st -order Reaction
$A_{(s)} + A_{(n)} \xrightarrow{k_{\text{rxn2}}} *_{(s)} + *_{(n)}$	2-Site, 2 nd -order Reaction
$A_{(s)} + *_{(n)} \xrightarrow{k_{\text{dif}}} *_{(s)} + A_{(n)}$	Diffusion

¹: microscopic kinetic constants are shown.

²: subscripts (s) and (n) denote a site and its neighbor, respectively.

Table II

Comparison of rate expressions in various frameworks

Process	System	Microscopic Propensity	Stochastic (Well-Mixed) Propensity	Deterministic Rate
Species Inflow	Lattice	$k_{\text{ads}} \cdot (1 - \sigma_i)$	$k_{\text{ads}} \cdot (N_L - \nu)$	$k_{\text{ads}} \cdot (1 - \theta)$
	Vessel	–	$k_{\text{in}}^{\text{wm}} \cdot (N_{\text{max}} - \nu)$	$k_{\text{in}}^{\text{wm}} \cdot (1 - \chi)$
1 st -order	Lattice	$K_{\text{rxn1}} \cdot \sigma_i$	$K_{\text{rxn1}} \cdot \nu$	$K_{\text{rxn1}} \cdot \theta$
	Vessel	–	$k_{\text{rxn1}}^{\text{wm}} \cdot \nu$	$k_{\text{rxn1}}^{\text{wm}} \cdot \chi$
2 nd -order	Lattice	$K_{\text{rxn2}} \cdot \sigma_i \cdot \sigma_j$	$\frac{k_{\text{rxn2}} \cdot \nu_{\text{coord}}}{2 \cdot (N_L - 1)} \cdot \nu \cdot (\nu - 1)$	$K_{\text{rxn2}} \cdot \nu_{\text{coord}} \cdot \theta^2$
	Vessel	–	$\frac{k_{\text{rxn2}}^{\text{wm}}}{2 \cdot V \cdot N_A} \cdot \nu \cdot (\nu - 1)$	$k_{\text{rxn2}}^{\text{wm}} \cdot C_{\text{max}} \cdot \chi^2$