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Kinetic Monte Carlo method for simulating reactions in solutions

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We present an off-lattice kinetic Monte Carlo method, which is useful to simulate reactions in solutions. We derive the method from first-principles. We assume that diffusion leads to a Gaussian distribution for the position of the particles. This allows us to deal with the diffusion analytically, and we only need to simulate the reactive processes. The rate constants of these reactions can be computed before a simulation is started, and need not be computed on-the-fly as in other off-lattice kinetic Monte Carlo methods. We show how solvent molecules can be removed from the simulations, which minimizes the number of particles that have to be simulated explicitly. We present the relation with the customary macroscopic rate equations, and compare the results of these equations and our method on a variation of the Lotka model.

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I. INTRODUCTION

Kinetic Monte Carlo (kMC) simulations are increasingly being used to study the kinetics of catalytic processes. They do not have the drawbacks of the older macroscopic equations that are based on a mean-field approximation, which assumes a homogeneous distribution of the reactants and an absence of fluctuations. In fact, kMC can be derived from first principles and give for a given model practically exact results; the few assumptions in the derivations are usually correct [1,2]. Of course, computational costs of kMC are higher than those for macroscopic equations, but they are only modest compared to for example electronic structure calculations.

Many kMC simulations use a lattice-gas model. The translational symmetry allows for a drastic simplification of the models that one uses; the number of processes becomes limited because of the symmetry, and their kinetic parameters can be determined independently from the simulation itself. This means that kMC simulations require generally only very modest computer resources, and they can be applied to quite large systems [3].

The remarks above certainly apply to many KMC simulations used for studying reactions on surfaces. A more general approach in which no *a priori* assumption on the processes and the symmetry of the system are made (in particular no lattice-gas model) has been used as well [4–6]. The drawback of that approach is that the determination of the processes and their rate constants become part of the simulations. This slows down the simulations by many orders of magnitude. If electronic structure calculations are used for this, then it is no longer possible to study kinetics properly, although it can reveal unusual mechanisms for some processes. [4]. Kinetics can still be studied with a force field, but this has only been done with kMC for few systems [7–9].

In this paper, we take the general approach and apply it to reactions in solutions. We will show that we can simplify the

kMC simulations in such a way that the reactions can be determined independently from the simulations, just as for the lattice-gas kMC. We treat the diffusion of molecules in the solution analytically. Because we then only need to simulate the reactions explicitly, the time that a simulation takes is drastically reduced. We call the resulting kMC method continuum kMC. It has the same advantage with respect to macroscopic rate equations as lattice-gas kMC.

This paper is structured as follows. Section II presents the theory of continuum kMC. Section II A gives the derivation of the master equation for the most general case. The equation forms the basis for kMC. In Section II B, we present process-type reduction, which is a coarse-graining method that eliminates the explicit handling of diffusion in continuum kMC. Sections II C and II D derive expressions for the kMC rate constants of uni- and bimolecular reactions, respectively. Section II E generalizes the derivation from pointlike particles to real molecules. Section II F relates continuum kMC to rate equations, and shows how solvent molecules that may appear as reactants in reactions can be eliminated from the formalism. Section III describes our algorithm for continuum kMC. It consists of the algorithm itself (Sec. III A), the method to determine the time when (Sec. III B), and the place where a reaction takes place (Sec. III C). Section IV presents simulations of an adaptation of the Lotka model. It shows that continuum kMC gives clearly different results from rate equations for the model, and discusses the reasons for that. Finally, Sec. V gives a brief summary.

II. THEORY

A. Master equation

The derivation of the master equation is usually based on the observation that there is a separation between the time scale on which reactions take place and the time scale of much faster motions like vibrations [10,11]. The longer time scale of reactions defines states, in which the system is localized in configuration space, and the transitions between them can be described by a master equation. The rates of the

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FIG. 1. A sketch of a potential-energy surface of an arbitrary system and its corresponding graph. The points are minima. The edges in the graph connect minima that have catchment regions that border on each other. They correspond to reactions or other activated processes. The thin lines on the left depict the borders of the catchment regions.

individual transitions can each be computed separately by one of the methods of chemical kinetics; e.g., transition state theory (TST) [10–12]. We present here a different derivation that incorporates all process at the same time. It has only been outlined in the literature yet, so we give it here in some detail [2,13,14]. It is a generalization of the derivation of variational TST (VTST); i.e., we partition phase space in more than two regions [15–17], and it is an alternative to the derivation using projection operators [18,19].

In line with the idea of different time scales mentioned above, we start with identifying the regions in configuration space where the fast motions take place. We will comment however at the end of this section on how to generalize the approach. Figure 1 shows a sketch of a potential-energy surface (PES) of an arbitrary system. We assume that only the electronic ground state is relevant, so that the PES is a single-valued function of the positions of all the atoms in the system. The points in the figure indicate the minima of the PES. Each minimum of the PES has a catchment region. This is the set of all points that lead to the minimum if one follows the gradient of the PES downhill [20].

We now partition phase space into these catchment regions and then extend each catchment region with the conjugate momenta. Let's call $\mathcal{C}$ the configuration space of a system and $\mathcal{P}$ its phase space [21,22]. The minima of the PES are points in configuration space. We define C_α to be the catchment region of minimum α . This catchment region is a subset of configuration space $\mathcal{C}$, and all catchment regions form a partitioning of the configuration space.

$$\mathcal{C} = \bigcup_{\alpha} C_{\alpha}. \quad (1)$$

(There is a small difficulty with those points of configuration space that do not lead to minima, but to saddle points, and with maxima. These points are irrelevant because the number of such points is vanishing small with respect to the other points. They are found where two or more catchment regions meet, and we can arbitrarily assign them to one of these catchment regions.) With $\mathbf{q}$ the set of all coordinates and $\mathbf{p}$ the set of all conjugate momenta we can extend the catch-

ment region C_α to a corresponding region in phase space R_α as follows:

$$R_\alpha = \{(\mathbf{q}, \mathbf{p}) \in \mathcal{P} | \mathbf{q} \in C_\alpha\}. \quad (2)$$

We then have for phase space

$$\mathcal{P} = \bigcup_{\alpha} R_{\alpha}. \quad (3)$$

If we use the regions R_α , we can derive the master equation exactly as for the lattice-gas model.

The probability to find the system in region R_α is given by

$$P_\alpha(t) = \int_{R_\alpha} \frac{d\mathbf{q}d\mathbf{p}}{h^D} \rho(\mathbf{q}, \mathbf{p}, t), \quad (4)$$

where h is Planck's constant, D is the number of degrees of freedom, and ρ is the phase space density. The denominator h^D is not needed for a purely classical description of the kinetics. However, it makes the transition from a classical to a quantum mechanical description easier [21].

The master equation tells us how these probabilities P_α change in time. Differentiating Eq. (4) yields

$$\frac{dP_\alpha}{dt} = \int_{R_\alpha} \frac{d\mathbf{q}d\mathbf{p}}{h^D} \frac{\partial \rho}{\partial t}(\mathbf{q}, \mathbf{p}, t). \quad (5)$$

This can be transformed using the Liouville-equation into [22]

$$\frac{dP_\alpha}{dt} = \int_{R_\alpha} \frac{d\mathbf{q}d\mathbf{p}}{h^D} \sum_{i=1}^D \left[\frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} \right], \quad (6)$$

where H is the system's Hamiltonian, which we assume to have the form

$$H = \sum_{i=1}^D \frac{p_i^2}{2m_i} + V(\mathbf{q}), \quad (7)$$

with V the PES. The integrals over the conjugate momenta can be done for the terms with derivatives of the Hamiltonian with respect to the coordinates. This shows that these terms become zero, because ρ goes to zero for any of its variables going to $\pm\infty$. (Otherwise it would not be integrable). The integrals over the coordinates of the terms with derivatives of the Hamiltonian with respect to the momenta can be converted to a surface integral using the divergence theorem [23]. This yields

$$\frac{dP_\alpha}{dt} = - \int_{S_\alpha} dS \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \sum_{i=1}^D n_i \frac{p_i}{m_i} \rho, \quad (8)$$

where the first integration is a surface integral over the surface of R_α , and n_i are the components of the outward pointing normal of that surface. As $p_i/m_i = \dot{q}_i$, we see that the summation in the last expression is the flux through S_α in the direction of the outward pointing normal (see Fig. 2).

The final step is now to decompose this flux in two ways. First, we split the surface S_α into sections $S_\alpha = \bigcup_{\beta} S_{\beta\alpha}$, where $S_{\beta\alpha}$ is the surface separating R_α from R_β . Second, we distinguish between an outward flux, $\sum_i n_i p_i / m_i > 0$, and an inward flux, $\sum_i n_i p_i / m_i < 0$. This gives then the master equation

FIG. 2. Schematic of the partitioning of phase space into regions R , each of which corresponds to some catchment region of the potential-energy surface. The process that changes α into β corresponds to a flow from R_α to R_β . The transition probability $W_{\beta\alpha}$ for this process equals the flux through the surface $S_{\beta\alpha}$, separating R_α from R_β , divided by the probability to find the system in R_α .

$$\frac{dP_\alpha}{dt} = \sum_\beta [W_{\alpha\beta}P_\beta - W_{\beta\alpha}P_\alpha], \quad (9)$$

with transition probabilities for the process $\alpha \rightarrow \beta$ defined by

$$W_{\beta\alpha} = \frac{\int_{S_{\beta\alpha}} dS \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \left[\sum_{i=1}^D n_i \frac{p_i}{m_i} \right] \Theta \left[\sum_{i=1}^D n_i \frac{p_i}{m_i} \right] \rho}{\int_{R_\alpha} d\mathbf{q} \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \rho}. \quad (10)$$

The function Θ is the Heaviside step function [24].

Although we will use Eq. (10) in what follows, we want to show here also a more familiar form in which the transition probabilities can be written. We assume that ρ can locally be approximated by a Boltzmann-distribution

$$\rho \propto \exp \left[-\frac{H}{k_B T} \right], \quad (11)$$

where T is the temperature and k_B is the Boltzmann constant. We also assume that we can define $S_{\beta\alpha}$ and the coordinates in such a way that $n_i=0$, except for one coordinate i , called the reaction coordinate, for which $n_i=1$. These assumptions make the derivation easier, but are not essential. The integral of the momentum corresponding to the reaction coordinate can then be done and the result is

$$W_{\beta\alpha} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q}, \quad (12)$$

with

$$Q^\ddagger \equiv \int_{S_{\beta\alpha}} dS \int_{-\infty}^{\infty} \frac{dp_1 \dots dp_{i-1} dp_{i+1} \dots dp_D}{h^{D-1}} \times \exp \left[-\frac{H}{k_B T} \right], \quad (13)$$

$$Q \equiv \int_{R_\alpha} d\mathbf{q} \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \exp \left[-\frac{H}{k_B T} \right]. \quad (14)$$

We see that this is an expression that is formally identical to the TST expression for rate constants [25]. There are differences in the definition of the partition functions Q and $Q^\ddagger$, but they can generally be neglected. For example, it is quite common that the PES has a well-defined minimum in R_α and on $S_{\beta\alpha}$, and that it can be replaced by a quadratic form in the integrals above. The borders of the integrals can then be extended to infinity and the normal partition functions for vibrations are obtained. This is sometimes called harmonic TST [26].

The W 's indicate how fast the system moves from (the catchment region of) one minimum to another. We will often call them therefore rate constants. The system can only move from minimum α to minimum β if the catchment region of these minima border on each other. Only in such a case we have $W_{\beta\alpha} \neq 0$. The right-hand-side of Fig. 1 shows the minima of the PES as points. Two minima are connected if their catchment regions border on each other, and the system can move from one to the other without having to go through a third catchment region. The result is the graph in Fig. 1. The vertices of the graph are the minima of the PES and the edges indicate how the system can move from one minimum to another.

Although we have presented the partitioning of phase space based on the catchment regions of the PES, this is formally not required. In fact, we have not used this particular partitioning in the derivation up to Eq. (10) anywhere. One can in principle partition phase space in any way one likes and derive a master equation. It is the partitioning that then defines the processes that the master equation describes. Of course, most partitionings lead to processes that are hard to interpret physically, but there are variations in the partitioning above that are useful. For example, by taking the union of catchment regions separated only by low barriers, as in Sec. II B, Eqs. (17) and (19) follow immediately.

The surface $S_{\beta\alpha}$ was split to distinguish fluxes in opposite directions. If there is a trajectory of the system that crosses the surface and then recrosses it, then no reaction has occurred, but both crossings contribute to the rate constants of $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$. The idea of VTST is to move $S_{\beta\alpha}$ to remove recrossings and to minimize the rate constants [12,15–17]. It can be shown that when we have a canonical ensemble, this is equivalent to locating $S_{\beta\alpha}$ at a maximum of the Gibbs energy along the reaction coordinate [27,28]. In this paper we assume that the effect of such variations can be neglected. As our derivation is a generalization of VTST, it has the same limitations and possible ways to deal with them. We refer to Chapter 4 of [12] for a fuller discussion.

B. Process-type reduction

The changes that correspond to edges of the graph in Fig. 1 correspond to a number of different types of processes. The most important changes for us are chemical reactions, but different minima can also arise from diffusion of atoms or molecules, reorientations of molecules, and conformational

FIG. 3. The fat lines in these plots partition the minima of the potential-energy surface into groups that are separated by reactions. Minima within a group are connected by diffusion, reorientations, or conformational changes. The trajectory on the left shows two reactions, AB and CD, with low-barrier processes in between. In process-type reduction these intermediate processes are replaced by one step (dashed arrows) that is done analytically.

changes of a molecule. In fact most changes will not be reactions, because they normally have high activation barriers (small rate constants W) relatively to other possible changes. Consequently, most computer time in a kMC simulation will be spent on other changes than reactions. This is undesirable. In this subsection we introduce an idea of a kMC method that does only reactions.

To separate the chemical reactions from the low-barrier processes we partition the minima of the PES (see Fig. 3). All minima within one group are connected by low-barrier process, and to get from one group to another at least one chemical reaction has to take place. We adapt our notation by replacing α by (a, r) with a indicating the various groups, and r the various minima within a group. The master equation in terms of these new labels becomes

$$\frac{dP_{(a,r)}}{dt} = \sum_{(b,s)} [W_{(a,r)(b,s)}P_{(b,s)} - W_{(b,s)(a,r)}P_{(a,r)}]. \quad (15)$$

This master equation still has low-barrier processes, which are characterized by rate constants $W_{(a,r)(b,s)} \neq 0$ with $a=b$. There are also reactions; i.e., $a \neq b$. To identify the high-barrier processes with chemical reactions is correct if all molecules are “point-like” and the density is not too large, but it may not be correct if we are dealing with large molecules or high densities. In that case the partition should not only be based on chemical reactions, but on other high-barrier processes as well.

Instead of $P_{(a,r)}$ we introduce

$$\pi_a \equiv \sum_r P_{(a,r)}. \quad (16)$$

It is possible to write down a master equation for π_a .

$$\begin{aligned} \frac{d\pi_a}{dt} &= \sum_r \frac{dP_{(a,r)}}{dt} = \sum_r \sum_{(b,s)} [W_{(a,r)(b,s)}P_{(b,s)} - W_{(b,s)(a,r)}P_{(a,r)}] \\ &= \sum_b [\omega_{ab}\pi_b - \omega_{ba}\pi_a] \end{aligned} \quad (17)$$

with

$$\omega_{ab} = \sum_{r,s} W_{(a,r)(b,s)} \frac{P_{(b,s)}}{\pi_b}. \quad (18)$$

The ratio $P_{(b,s)}/\pi_b$ is a conditional probability that the system is at minimum (b, s) if we know that the system is in one minimum belonging to group b . The rate constant ω_{ab} is then the sum of the rate constants of all reactions from group b to group a weighted with this conditional probability.

The rate constants in the master Eq. (15) are given by Eq. (10) with the appropriate change in notation. Because the denominator for $W_{(a,r)(b,s)}$ is equal to $P_{(b,s)}$ we get

$$\omega_{ab} = \frac{\int_{S_{ab}} dS \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \left[\sum_{i=1}^D n_i \frac{p_i}{m_i} \right] \Theta \left[\sum_{i=1}^D n_i \frac{p_i}{m_i} \right] \rho}{\int_{R_b} d\mathbf{q} \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \rho}. \quad (19)$$

$R_b = \sum_s R_{(b,s)}$, S_{ab} is the surface bordering on R_a and R_b , and n_i is component i of the outward-pointing surface normal of R_b . (Actually, we could have gotten this expression and master Eq. (17) directly by partitioning phase space in regions R_a .)

Because the approach here reduces the number of types of processes that we have to handle explicitly in the kMC simulations, we call it process-type reduction. It is useful if we can easily compute the new rate constants ω_{ab} . This is possible if we can determine the rate constants $W_{(a,r)(b,s)}$ with $a \neq b$ before a kMC simulation and if it is easy to compute $P_{(b,s)}/\pi_b$ during the simulation. We can determine the rate constants $W_{(a,r)(b,s)}$ if, for example, the reaction rates $W_{(a,r)(b,s)}$ do not depend, at least approximately, on r and s . If the reaction takes place in the gas phase or in a solvent, then its rate constant may depend only little on the precise position of all the atoms and molecules. For the ratio $P_{(b,s)}/\pi_b$ it may be possible to derive analytical expressions based on simple models of diffusion, reorientation, and conformational changes. Alternatively, we might be able to work with Eq. (19) directly.

C. Unimolecular reactions

To make progress we need to specify our system in more detail. We assume that our system consists of atoms and molecules that can react with each other and a larger number of inert atoms and molecules. We also assume that all these atoms and molecules can be regarded as “pointlike” particles. An extension of our method to particles with an internal structure is possible, but at first we want to deal with this simpler case. We are only interested in the reacting atoms and molecules, but the other atoms and molecules are important for the diffusion of the reacting particles. Such a system as we are describing here could be a solution or a gas mixture. In such a system the groups are defined by the number of particles.

The simplest reaction to deal with is a unimolecular reaction of the type $A \rightarrow B$. Such a reaction allows us to give a simple expression for ω_{ab} starting from Eq. (18). We first note that when a reaction takes place at minimum (b, s) there is only one minimum (a, r) that the system can go to. If there

would be another minimum (a, r') with $r \neq r'$ that the system might be able to go to, then this would be not a simple reaction but a reaction combined with some diffusion. We are excluding this. As a consequence the summation over r in Eq. (18) has just one term for which $W_{(a,r)(b,s)} \neq 0$.

The second observation is that such a reaction can take place everywhere, at any time, and always with the same rate constant. This means that $W_{(a,r)(b,s)} \neq 0$ has always the same nonzero value. If we call that value W_{uni} , then we have

$$\omega_{ab} = \sum_{r,s} W_{(a,r)(b,s)} \frac{P_{(b,s)}}{\pi_b} = W_{\text{uni}} \sum_s \frac{P_{(b,s)}}{\pi_b} = W_{\text{uni}}. \quad (20)$$

D. Bimolecular reactions

For bimolecular reactions $A+B \rightarrow C$ the reasoning for unimolecular reactions does not work. A bimolecular reaction is not possible in most of the minima in a group, because they correspond to situations where the particles are too far apart to be able to react. These minima are the ones that have been removed in Fig. 3 when going from the left to the right part. The particles have to get together first before they can react. This means that we have to work with Eq. (19).

The first step is to get an expression for $\rho(\mathbf{q}, \mathbf{p}, t)$. We can split off the momenta as follows [21,22]:

$$\rho = \rho(\mathbf{q}, \mathbf{p}, t) \propto \rho(\mathbf{q}, t) \prod_i \exp\left[-\frac{p_i^2}{2m_i k_B T}\right]. \quad (21)$$

As long as the particles stay apart so that they don't interact, they only diffuse. We can then take

$$\rho(\mathbf{q}, t) \propto \prod_i \exp\left[-\frac{(q_i - q_i^{(0)})^2}{2\sigma_i^2}\right] \quad (22)$$

with

$$\sigma_i^2 = 2D_i t \quad (23)$$

and D_i the diffusion constant of the particle of coordinate q_i . This expression holds for diffusing particle that have coordinates $q_i^{(0)}$ at time $t=0$. For particles to react they have to get close to each other. This will increase the energy, because there will be an activation barrier. The configuration space density will have to be modified in the region where the particles are close together. We assume that when the particles approach each other the change in $\rho(\mathbf{q}, t)$ can be given by a Boltzmann factor so that

$$\rho(\mathbf{q}, t) \propto \exp\left[-\frac{V(\mathbf{q})}{k_B T}\right] \prod_i \exp\left[-\frac{(q_i - q_i^{(0)})^2}{2\sigma_i^2}\right]. \quad (24)$$

The normalization constants that are missing in these expressions can be ignored, because they cancel in Eq. (19).

To evaluate ω_{ab} we can assume that we have only one particle A and one particle B. If there are more particles, then we get a rate constant for the reaction of each A-B pair that is the same. By looking at just two particles the mathematics is simplified substantially. With two particles the surface S_{ab} depends only on the distance between the particles. In fact, it

is defined as the set of points in phase space for which the distance between the particles is the distance in the transition state of the reaction.

The integrals are easiest to evaluate if we transform to center-of-mass and relative coordinates. The integrals over the momenta of the center-of-mass in numerator and denominator of Eq. (19) cancel. For relative coordinates it is best to transform to spherical coordinates. The difference in the integrals over the conjugate momenta is that in the denominator the integral over the conjugate momentum p_r of the distance between the particles is from $-\infty$ to ∞ . In the numerator however it is from $-\infty$ to 0. This is because the particles have to get closer together to react. After integration of the momenta we are left with

$$\omega_{ab} = \left(\frac{k_B T}{2\pi\mu}\right)^{1/2} \frac{\int_{S_{ab}} d\mathbf{X} dr d\theta d\varphi r^2 \sin\theta \rho(\mathbf{X}, r, \theta, \varphi, t)}{\int_{C_b} d\mathbf{X} dr d\theta d\varphi r^2 \sin\theta \rho(\mathbf{X}, r, \theta, \varphi, t)}. \quad (25)$$

with $\mathbf{X}$ the center-of-mass coordinates, and (r, θ, φ) the relative coordinates in spherical form. As explained above, for the relative coordinates S_{ab} is a sphere with a radius that is equal to the distance between the particles in the transition state. C_b is the interior of that sphere.

The integrals over the center-of-mass coordinates in Eq. (25) also cancel. For the remaining integrals we need Eq. (24). For the denominator we assume that the PES is constant over the integration area. This is not the case for the area where the particles get close to each other, but the contribution of that region to the integral can be ignored. For the numerator the PES has the value corresponding to the energy of the transition state of the reaction. The final result is then

$$\omega_{ab} = \left(\frac{k_B T}{2\pi\mu}\right)^{1/2} \exp\left[-\frac{E_{\text{bar}}}{k_B T}\right] \times \frac{4R_{\text{TS}}^2}{\sqrt{16\pi(D_A + D_B)^3 t^3}} \exp\left(-\frac{|\mathbf{x}_B^{(0)} - \mathbf{x}_A^{(0)}|^2}{4(D_A + D_B)t}\right) \quad (26)$$

when we assume that R_{TS} is small compared to $|\mathbf{x}_B^{(0)} - \mathbf{x}_A^{(0)}|$. E_{bar} is the height of the barrier for the reaction, and R_{TS} the distance between the particles at the transition state.

E. Composite particles

Suppose A and B are again point-like, but that the diffusion has led to an equilibrium situation. This changes the configuration space density $\rho(\mathbf{q}, t)$ because the exponent of the diffusion in Eq. (24) becomes a constant. In the derivation above we still get Eq. (25), because nothing changes for the conjugate momenta. The integrals over the coordinates do change. In fact they become much simpler. We get

$$\omega_{ab}^{(\text{eq})} = \left(\frac{k_B T}{2\pi\mu}\right)^{1/2} \frac{4\pi R_{\text{TS}}^2}{L^3} \exp\left[-\frac{E_{\text{bar}}}{k_B T}\right] \quad (27)$$

when we assume that the particles move in a cubic box with sides of length L . If we compare this to the expression in Eq.

(26) we see that the effect of the diffusion is to change the rate constant by a factor

$$f_{\text{diff}} = \frac{L^3}{[4\pi(D_A + D_B)t]^{3/2}} \exp\left(-\frac{|\mathbf{x}_B^{(0)} - \mathbf{x}_A^{(0)}|^2}{4(D_A + D_B)t}\right). \quad (28)$$

The important point now is that we assume that the rate constant when the system is not yet at equilibrium is

$$\omega_{ab} = k_{\text{rx}} f_{\text{diff}} \quad (29)$$

with k_{rx} the rate constant at equilibrium for any type of particle. Indeed, if we use the normal TST expression

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q} \exp\left[-\frac{E_{\text{bar}}}{k_B T}\right] \quad (30)$$

and evaluate it for a reaction $A+B \rightarrow C$ of “pointlike” particles, then we get back Eq. (25).

F. Rate equations

If we look at $\omega_{ab}^{(\text{eq})}$, Eq. (27), it seems that as the box in which the particles move becomes bigger, the particles react more slowly. This is indeed the case, and as it should be. If we change the size of the box then the number of reactions that actually occurs per unit time scales with the box's volume L^3 . The number of pairs of A and B that can react, however, scales with the square of the volume of the box L^6 . As a consequence the rate constant has to scale with L^{-3} , as it does. This may not be immediately apparent if we look at Eq. (29). However, the rate constant k_{rx} contains partition functions for translations which does lead to a L^{-3} dependence of ω_{ab} .

The necessity of such dependence can also be shown by deriving the rate equations in terms of concentrations. These should have rate constants that do not have this L dependence. To see that this is indeed so we first write the rate equations in terms of numbers of particles.

$$\frac{dN_A}{dt} = -\omega N_A N_B, \quad (31)$$

with ω the rate equation that we have derived in the previous sections. To get concentrations we have to divide by L^3 .

$$\frac{d[A]}{dt} = \frac{1}{L^3} \frac{dN_A}{dt} = -(L^3 \omega) \frac{N_A}{L^3} \frac{N_B}{L^3} = -(L^3 \omega) [A][B]. \quad (32)$$

We see that the L dependence of ω that we have in the rate equation in terms of numbers of particles cancels against a L^3 factor.

The factor f_{diff} shows a L^3 dependence in Eq. (28), but for long times this factor has to go to 1, because the results for the rate constant should go to the equilibrium expression k_{rx} . It is clear that the exponent in the expression for f_{diff} goes to 1. This does not hold for the ratio. The problem here is that we have assumed a Gaussian dependence of the configuration space density $\rho(\mathbf{q}, t)$. This is correct as long as the diffusion length is small compared to the size of the box. The expressions above should therefore only be used when $L \gg \sqrt{4\pi(D_A + D_B)t}$.

If the solvent is only a spectator in the reactions, then we can practically ignore it. The presence of a solvent may change the rate constants, but that effect can be taken into account by simply modifying the intrinsic rate constant k_{rx} in Eq. (29). If the solvent actually takes place in the reaction, but we do not want to include it explicitly in our simulations, then the expressions for the rate constants above need to be modified. There are two cases.

To focus our minds let's deal with water that participates in acid-base reactions. We assume that there is a particle Zp that can donate a proton to H_2O (or OH^-). The particle Zp is then transformed into Z. There is also a reverse reactions where Z gets back a proton from H_2O (or H_3O^+). I assume that there is an equilibrium

with S either H_2O (Sp is then H_3O^+) or OH^- (Sp is then H_2O). The different possibilities for S mean that there are really two different equilibria.

We can write a macroscopic rate equations for this equilibrium.

$$\frac{d[\text{Zp}]}{dt} = -k_1[\text{Zp}][\text{S}] + k_{-1}[\text{Z}][\text{Sp}]. \quad (34)$$

Here k_1 and k_{-1} are macroscopic rate constants. They are related to the rate constants for a kMC simulation via $k_n = \omega_n V$ with ω_n the kMC rate constant and V the volume of a simulation box [see Eq. (32)]. In a kMC simulation we work with discrete particles Z and Zp. For the number of particles we have

$$\frac{dN_{\text{Zp}}}{dt} = -k_1 N_{\text{Zp}}[\text{S}] + k_{-1} N_{\text{Z}}[\text{Sp}]. \quad (35)$$

We do not want to include the particles S and Sp explicitly in the simulation. The expression above shows that we can accomplish this by replacing the (two) equilibria above by

with rate constants $k_1[\text{S}] = \omega_1 N_{\text{S}}$ and $k_{-1}[\text{Sp}] = \omega_{-1} N_{\text{Sp}}$ with N_{S} (N_{Sp}) the number of S (Sp) in the simulation box if we would include them in the simulation explicitly. (Note that we still have two equilibria or four reactions because of different possibilities for S.) Multiplying $\omega_{\pm 1}$ by the number of solvent particles N_{S} or N_{Sp} means that the rate constant no longer depends on the size of the simulation box. The number of particles combines with the volume of the simulation box (L^3 in the rate constant k_{rx}) to give a density. This is appropriate, because the reaction effectively has become a unimolecular reaction.

Solvent molecules can also be formed by a reaction (e.g., if we have a condensation reaction), or be reacted away by the reverse of such a reaction. We can write this as

with S the solvent molecule. We can again write a macroscopic rate equations for this equilibrium.

$$\frac{d[X]}{dt} = -k_1[X] + k_{-1}[Y][S]. \quad (38)$$

For the number of particles we have

$$\frac{dN_X}{dt} = -k_1N_X + k_{-1}N_Y[S]. \quad (39)$$

Again we do not want to include the particles S explicitly in the simulation. The expression above shows that we can accomplish this by replacing the equilibrium above by

with rate constants $k_1 = \omega_1$ and $k_{-1}[S] = \omega_{-1}N_S$. The rate constant of the first reaction does not change, because it is a unimolecular reaction (i.e., of the type $A \rightarrow \dots$).

Note that because we have derived the expressions here using concentrations, we have implicitly assumed that our system is homogeneous; i.e., both our particles of interest and the solvent molecules are randomly distributed. This means we have taken $f_{\text{diff}} = 1$. An alternative derivation that only assumes that the solvent molecules are homogeneously distributed can also be given. Suppose we have a reaction $X + S$, with S a solvent molecule. The rate constant for a particular molecule X with a particular molecule S is given by $\omega = k_{\text{rx}}f_{\text{diff}}$. We can get the rate constant for a particular molecule X with all molecules S by summing ω over all molecules S. This summation does not affect the rate constant k_{rx} , but summing f_{diff} gives us

$$\frac{L^3}{[4\pi(D_X + D_S)t]^{3/2}} \sum_n \exp\left[-\frac{|\mathbf{r}_X - \mathbf{r}_{S,n}|^2}{4(D_X + D_S)t}\right] \quad (41)$$

with $\mathbf{r}_{S,n}$ the position of solvent molecule n just after a reaction. We now assume that the solvent molecules are randomly distributed. We can then replace the summation by an integral. The result is

$$\frac{L^3}{[4\pi(D_X + D_S)t]^{3/2}} \int d\mathbf{r}_S \rho_S \exp\left[-\frac{|\mathbf{r}_X - \mathbf{r}_S|^2}{4(D_X + D_S)t}\right] \quad (42)$$

$$= L^3 \rho_S = N_S. \quad (43)$$

Here ρ_S is the density of the solvent molecules. We see that we get the same result as above; we have to multiply the rate constant by the number of solvent molecules and set $f_{\text{diff}} = 1$.

III. KMC ALGORITHMS

Because the rate constants depend on time, we need to use the first-reaction method (FRM) [13,29,30], but the method needs to be adapted from the lattice-gas version. There are two possibilities. The first is to make a list of all reactions, determine which reaction occurs first, do that reaction, update the position of all particles that did not react, and then repeat this procedure. Because of the updating of the particle positions, we have to deal with the diffusion of the particles explicitly. We do not want to do this. It is also not necessary. If we store when and where each particle is created, then

updating the position of the particles after each reaction can be avoided as explained in the next section.

A. Asynchronous updating of particle positions

Suppose that we only know the positions of the particles at the time they were created; i.e., at the beginning of a simulation and when they were formed. The FRM algorithm then looks as follows.

- (1) Initialize the simulation.
- (2) Determine the next reaction to occur.
- (3) Update the system, and repeat at 2, unless the end of the simulation is reached (e.g., no more reactions, or no more time).

Initializing the simulation consists of the following steps.

- (1.1) Generate initial positions $\mathbf{r}_{i,0}$ of the particles.
- (1.2) Set the time t to some initial value t_0 .
- (1.3) Choose conditions when to stop the simulation.
- (1.4) Make a list L_{part} of particle positions and times when the particles were at the corresponding positions.
- (1.5) Make a list L_{rx} containing all reactions and times when the reaction will take place (see the end of this section and Sec. III B).

Determining the next reaction to occur involves looking in L_{rx} for the reaction that occurs first. We define t_n as the time of the n^{th} reaction to take place. We have $t_i > t_j$ if and only if $i > j$.

Updating the system when a reaction (say number n) takes place involves the next series of steps.

- (3.1) Determine the position where the reaction takes place (see the end of this Section and Sec. III C).
- (3.2) Remove the reacting particles from L_{part} and their reactions from L_{rx} .
- (3.3) Add the particles that are formed to L_{part} and their reactions to L_{rx} . (This involves mainly determining when the new reactions take place. This is explained at the end of this section and Sec. III B.)
- (3.4) Change time to $t = t_n$.

In this algorithm it is only known where the particles are at the beginning of the simulation, when they are created, and when they react. The list L_{part} consists of pairs $(\mathbf{r}_i, \tau_i)$ that indicate the particle i was at position $\mathbf{r}_i$ at time τ_i . This list and also L_{rx} is not computed anew after each reaction, but both are updated. This should make this algorithm faster. L_{rx} is implemented as a binary tree of reactions and the times when they will occur [31]. It is ordered based on these times. When a new particle is created all its reactions are determined and added to L_{rx} . As is standard in FRM [30], a reaction is only removed when it is about to occur and a check reveals that a particle in the reaction no longer exists.

The determination of the place where a bimolecular reaction takes place changes a bit. Let's call the reacting particles again 1 and 2. If they are at position $\mathbf{r}_1$ at time τ_1 and position $\mathbf{r}_2$ at time τ_2 , respectively, then diffusion will bring them to position $\mathbf{r}$ at a time t with $t > \tau_i$ with probability

$$\frac{1}{[4\pi D_i(t - \tau_i)]^{3/2}} \exp\left[-\frac{|\mathbf{r} - \mathbf{r}_i|^2}{4D_i(t - \tau_i)}\right]. \quad (44)$$

So they will both be at position $\mathbf{r}$ with a probability proportional to

$$\exp\left[-\frac{|\mathbf{r}-\mathbf{r}_1|^2}{4D_1(t-\tau_1)}\right]\exp\left[-\frac{|\mathbf{r}-\mathbf{r}_2|^2}{4D_2(t-\tau_2)}\right]. \quad (45)$$

This is a probability distribution centered at

$$\frac{D_2(t-\tau_2)\mathbf{r}_{1,n-1}+D_1(t-\tau_1)\mathbf{r}_{2,n-1}}{D_1(t-\tau_1)+D_2(t-\tau_2)} \quad (46)$$

with a width

$$\sqrt{\frac{2D_1(t-\tau_1)D_2(t-\tau_2)}{D_1(t-\tau_1)+D_2(t-\tau_2)}} \quad (47)$$

in all directions.

For the rate constant of a bimolecular reaction we get instead of Eqs. (28) and (29)

$$\omega = k_{\text{rx}} \frac{L^3}{\{4\pi[D_1(t-\tau_1)+D_2(t-\tau_2)]\}^{3/2}} \times \exp\left\{-\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{4[D_1(t-\tau_1)+D_2(t-\tau_2)]}\right\} \quad (48)$$

for $t > \tau_1, \tau_2$. The reaction time is given by

$$\int_{\tau_2}^{t_{\text{rx}}} dt \omega = -\ln r \quad (49)$$

assuming $\tau_2 > \tau_1$ and with r a random number from the interval $[0, 1]$. Substitutions of the expression for ω gives us for the integral

$$\int_{\tau_2}^{t_{\text{rx}}} dt \omega = \frac{k_{\text{rx}} L^3}{4\pi(D_1+D_2)|\mathbf{r}_2-\mathbf{r}_1|} \left[\text{erf}\left(\frac{|\mathbf{r}_2-\mathbf{r}_1|}{2\sqrt{D_1(\tau_2-\tau_1)}}\right) - \text{erf}\left(\frac{|\mathbf{r}_2-\mathbf{r}_1|}{2\sqrt{(D_1+D_2)t_{\text{rx}}-D_1\tau_1-D_2\tau_2}}\right) \right] \quad (50)$$

with erf the error function [32]. This integral is limited to

$$0 \leq \int_{\tau_2}^{t_{\text{rx}}} dt \omega \leq \frac{k_{\text{rx}} L^3}{4\pi(D_1+D_2)|\mathbf{r}_2-\mathbf{r}_1|} \text{erf}\left(\frac{|\mathbf{r}_2-\mathbf{r}_1|}{2\sqrt{D_1(\tau_2-\tau_1)}}\right). \quad (51)$$

We see that there is a probability that the reaction will never take place.

B. Determining reaction times

The reaction time of a unimolecular reaction is given by the usual expression [30]

$$\Delta t = -\frac{1}{k_{\text{rx}}} \ln r \quad (52)$$

with Δt the time between the beginning of the simulation or the time that the particle was formed, r a random number from the interval $[0, 1]$, and k_{rx} the rate constant of the reaction.

To get the reaction times for bimolecular reactions we have to solve Eq. (49). We can write this equation as

$$\text{erfc}\left(\frac{\alpha}{\sqrt{\Delta t}}\right) = \beta \quad (53)$$

with

$$\beta = -\frac{4\pi(D_1+D_2)|\mathbf{r}_2-\mathbf{r}_1|\ln r}{k_{\text{rx}}L^3} + \text{erfc}\left(\frac{|\mathbf{r}_2-\mathbf{r}_1|}{2\sqrt{D_1(\tau_2-\tau_1)}}\right) \quad (54)$$

and

$$\Delta t = t_{\text{rx}} - \frac{D_1\tau_1 + D_2\tau_2}{D_1 + D_2}. \quad (55)$$

The function erfc is the error function complement [32]. It equals one minus the error function. We have $\alpha, \beta > 0$ so that $0 \leq \text{erfc}(\alpha/\sqrt{\Delta t}) \leq 1$ for $\Delta t > 0$. This means that Eq. (53) has no solution if $\beta > 1$. This is something that we have already seen.

We don't know an analytical solution of Eq. (53), so we will look at numerical methods. The function $\text{erfc}(\alpha/\sqrt{\Delta t})$ is a monotonically increasing function of non-negative Δt from 0 to 1. We would prefer to use Newton-Raphson to get the solution, because it converges very rapidly to the solution [33]. Unfortunately, that is not always possible. The derivative is a monotonically increasing function for $0 \leq \Delta t \leq 2\alpha^2/3$. This means that on that interval Newton-Raphson can be used. If we are on this interval, but above the solution, then Newton-Raphson will approach the solution from above. If we are on this interval, but below the solution, then the first step Newton-Raphson will bring us above the solution. This may bring us outside the interval, which should be checked. If we are outside the interval, then we should bracket and use bisection [33]. The whole procedure then looks as follows. We start by bracketing the solution, then do Newton-Raphson if we have $0 \leq \Delta t \leq 2\alpha^2/3$, or a bisection if not.

C. Determining the position of the reaction

For a unimolecular reaction this is quite easy. The particle simply diffuses and then reacts at whatever place it will be. So if a particle is at position $\mathbf{r}'$ at time τ , then diffusion will bring it to position $\mathbf{r}$ at a time t with $t > \tau$ with probability

$$\frac{1}{[4\pi D(t-\tau)]^{3/2}} \exp\left[-\frac{|\mathbf{r}-\mathbf{r}'|^2}{4D(t-\tau)}\right], \quad (56)$$

where D is its diffusion constant.

For a bimolecular reaction it becomes a bit more difficult. Let's call the reacting particles again 1 and 2. If they are at position $\mathbf{r}_1$ at time τ_1 and position $\mathbf{r}_2$ at time τ_2 , respectively, then diffusion will bring them to position $\mathbf{r}$ at a time t with $t > \tau_i$ with probability

$$\frac{1}{[4\pi D_i(t-\tau_i)]^{3/2}} \exp\left[-\frac{|\mathbf{r}-\mathbf{r}_i|^2}{4D_i(t-\tau_i)}\right]. \quad (57)$$

So they will both be at position $\mathbf{r}$ with a probability proportional to

$$\exp\left[-\frac{|\mathbf{r}-\mathbf{r}_1|^2}{4D_1(t-\tau_1)}\right]\exp\left[-\frac{|\mathbf{r}-\mathbf{r}_2|^2}{4D_2(t-\tau_2)}\right]. \quad (58)$$

This is a probability distribution centered at

$$\frac{D_2(t-\tau_2)\mathbf{r}_{1,n-1} + D_1(t-\tau_1)\mathbf{r}_{2,n-1}}{D_1(t-\tau_1) + D_2(t-\tau_2)} \quad (59)$$

with a width

$$\sqrt{\frac{2D_1(t-\tau_1)D_2(t-\tau_2)}{D_1(t-\tau_1) + D_2(t-\tau_2)}} \quad (60)$$

in all directions. (We have seen this already in Sec. III A.)

IV. ILLUSTRATIVE EXAMPLE

We present here results for a variation of the Lotka model to illustrate the method described in the previous sections [34]. In the original two-dimensional lattice-gas version there are two types of particles; A and B. The A's adsorb with rate constant ξ , the B's desorb with rate constant $1-\xi$, and when there is an A next to a B then it is immediately transformed into a B as well. The rate equations for this model show a steady state with probability that a site is occupied by an A equal to 0 and by a B equal to ξ . (The probability for A goes to 0 as the rate constant for the transformation of A to B goes to infinity.) If the parameter ξ is small however, a kMC simulation shows very well defined oscillation.

We have here no lattice with sites, so we have adapted the model. We have three reactions

Here the particle S has the same function as a vacant site. We have given it therefore also a very small diffusion constant of $1.25 \times 10^{-11} \text{ Å}^2/\text{s}$. The A's and B's have been given a diffusion constant of $1.25 \times 10^{-2} \text{ Å}^2/\text{s}$. This is still quite a small diffusion constant. The idea is to try to mimic the behavior of the two-dimensional lattice-gas model. That model has avalanches in which clusters of A's are converted into B's at the same time. A fast diffusion mixes up the system and destroys such clusters before they have been able to convert. The rate constants for the reactions are 0.005 s^{-1} , 0.995 s^{-1} , and 158 s^{-1} , respectively. The last one is not infinite, but still much faster than the others.

Figure 4 shows how the concentrations change as a function of time. Initially there are only B's; 262 144 B particles in a cubic box of size $160 \times 160 \times 160 \text{ Å}^3$. The rate equations predict a steady state with concentrations $[A]=1.54 \times 10^{-9}/\text{Å}^3$ and $[B]=3.2 \times 10^{-4}/\text{Å}^3$. We see that the concentration of B is close to this value, but that the concentration of A is much larger. There are also quite large fluctuations. In fact, if we Fourier-transform the steady state part of Fig. 4 we get a peak around 0.07 s^{-1} (see Fig. 5), which indicates that we may have oscillations. They are

FIG. 4. Concentration of A and B for the Lotka model as a function of time. The initial concentration of B's is $6.4 \times 10^{-2} \text{ particles}/\text{Å}^3$.

however much less well-defined as in the two-dimensional lattice-gas model, but comparable to the three-dimensional lattice-gas model [34].

The oscillations have the same origin as oscillations in the two-dimensional lattice-gas model. In the lattice-gas model most $A+B \rightarrow 2B$ reactions occur in the form of avalanches; i.e., an A next to a B is converted into a B, another A next to that first A is then also transformed into a B, etc. The number of A's that are transformed in one go can become quite large [34], but here they remain much smaller. We define the size of an avalanche as the number of $A+B \rightarrow 2B$ reactions between consecutive formations of an A. Figure 6 shows the probability distribution of the size of these avalanches. The reason why they are so much smaller than those in the original lattice-gas model is that it takes some time for each $A+B \rightarrow 2B$ reaction to occur in the continuum kMC simulations, mainly because the particles have to diffuse to each other to react, whereas in the lattice-gas model they start as neighbors and react immediately. The avalanches form clusters of B's and a clear segregation of A's and B's as can be seen in Fig. 7.

The difference between the lattice-gas and the continuum kMC simulations can be made smaller by using a larger grid with lattice points closer together. The drawback is that the

FIG. 5. Power spectrum (in arbitrary units) of the steady state concentration of A.

FIG. 6. Probability distribution $P(s)$ as a function of the size s of the $A + B \rightarrow 2B$ avalanches.

computer time increases. The reason is that the number of diffusional hops that need to be simulated in the lattice-gas model is inverse proportional to the square of the distance between the lattice points [1,2].

It may be that the oscillations in the continuum kMC simulations become better defined when the system size is increased. When we decrease the size of the system, all properties remain the same, except that the power spectrum becomes noisier. Unfortunately, we could not increase the size substantially as the simulation times would become too large. Decreasing the parameter ξ , which gave better defined oscillations in the two-dimensional lattice-gas model, shifted the peak in the power spectrum to smaller values, but did not make it less noisy. This is similar to the three-dimensional lattice-gas model.

V. SUMMARY

We have presented here a form of kMC simulations, which we call continuum kMC, that should be useful to simulate reactions in solution. As for lattice-gas kMC, the rate constants of the reactions can be determined prior to the simulation, so that the simulation itself takes little computer time, or can be done on large systems.

We have derived the method from the master equation that described the evolution of the system as hops from one minimum of the potential-energy surface to a neighboring one. This master equation is coarse grained by using an analytical approach to the diffusion of the particles. This leads to a new master equation that describes only the chemical reactions, and no other processes. The diffusion is incorporated

FIG. 7. Snapshot of a simulation of the Lotka model showing the clusters of A's (light spheres) and B's (dark spheres) that are formed.

in the expression for the rate constants. Solvent molecules need not be included explicitly in the simulations. Their effect can be incorporated in the rate constants as well.

The algorithm that we have used is an adaptation of the first-reaction method. The positions of the particles are not updated. At most two positions of each particle are generated during a simulation; the position where the particle is formed, and the position where it reacts and ceases to exist. For both positions there is a corresponding time.

We have illustrated the method using a Lotka model. This model shows kinetics that is clearly different from that obtained from the rate equations. The reason for that is that the system is not homogeneous. There are clusters of particles, and all particles in one cluster react at about the same time.

We think that continuum kMC will be useful for many other systems. We are currently using it to simulate the formation of small silicate oligomers from $\text{Si}(\text{OH})_4$ [35–37]. This is the initial stage of the formation of zeolites. An important aspect is the effect of template molecules, other cations, pH, and temperature. All this can easily be included in our method.

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