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KINETIC MONTE CARLO SIMULATION OF NON-EQUILIBRIUM LATTICE-GAS MODELS: BASIC AND REFINED ALGORITHMS APPLIED TO SURFACE ADSORPTION PROCESSES

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For many growth, transport, or reaction processes occurring on the surfaces or in the bulk of crystalline solids, atoms reside primarily at a discrete periodic array or lattice of sites, actually vibrating about such sites. These atoms make occasional "sudden" transitions between nearby sites due to diffusive hopping, or may populate or depopulate sites due to adsorption and desorption, possibly involving reaction. Most of these microscopic processes are thermally activated, the rates having an Arrhenius form reliably determined by transition state theory [1]. In general, these rates will depend on the local environment (i.e., the occupancy of nearby sites) thus introducing cooperativity into the process, and they may vary over many orders of magnitude.

Such systems are naturally described by lattice-gas (LG) models wherein the sites of a periodic lattice are designated as either occupied (perhaps by various types of particles) or vacant. A specification of all possible transitions between different configurations of particles, together with the associated rates, completely prescribes the evolution of the LG model for the process of interest. Such models are called Interacting Particle Systems (IPS) in the mathematical statistics community [2]. They correspond to stochastic Markov processes for evolution between different possible configurations of the system, and their evolution is rigorously described by appropriate master equations [3]. Since it is typically not possible to precisely determine the behavior of the solutions of these equations with analytic methods, Kinetic Monte Carlo (KMC) simulation is the most common tool for analysis. This approach, described below, implements on computer the "typical" evolution of the LG model

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through a specific sequence configurations using a random number generator to select processes with the appropriate weights [4]. The great advantage of KMC is that usually it can treat these processes on the physically relevant time and length scales, contrasting conventional Molecular Dynamics. Another advantage of KMC is its versatility with respect to model modification, allowing systematic testing of the effect of various processes on behavior.

The focus here is on simulation of non-equilibrium processes, hence the "kinetic" in KMC. This contrasts conventional Monte Carlo (MC) simulation for equilibrium (Gibbs) states of Hamiltonian systems. For the latter, the independence of the equilibrium state on the history or dynamics of the system provides considerable flexibility in optimizing the simulation procedure [4]. For example, to speed up the simulation, one can use artificial dynamics provided that is consistent with detailed-balance. Also, other tools are available for analysis of simulation data, e.g., histogram re-weighting, based on the features of the Gibbs distribution. These techniques are not available for non-equilibrium systems, where the simulation must incorporate the physical dynamics to correctly predict the possibly non-trivial competition between various kinetic pathways. This requirement was fully not appreciated in earlier studies of the approach to equilibrium where generic rules for rates were often used.

The philosophy adopted here is that the atomistic LG model should first be clearly defined, as distinct from the simulation algorithm used to analyze the model. Thus, below we first give a general description of non-equilibrium LG models, together with the master equations which describe their evolution, and only then describe the two types of generic KMC simulation algorithms. It is most instructive to illustrate these basic algorithms and various refinements to them in the context of specific classes of examples. We choose models for evolution of *homoepitaxial thin film systems* and for *catalytic surface reactions*.

1. Evolution of Stochastic Lattice-Gas Models: Master Equations

The basic master equation formulation described below applies to the case of finite systems, i.e., lattices with L^d sites where d is the spatial dimension. Any simulation is of course also restricted to such finite systems. Usually, finite-size effects are minimized by choosing periodic boundary conditions. Below, we let n_j denote the occupancy of site j, $\{n_j\}$ the configuration of the entire system, and $P(\{n_j\}, t)$ the probability for the system to be in this configuration at time t. Implicitly, these probabilities involve ensemble averaging which, in the context of KMC simulation, may correspond to averaging over a large number of simulation trials. Then, evolution is described exactly by the master equations [3]

$$\begin{aligned} \mathrm{d}/\mathrm{d}t\, P(\{n_j\}, t) = &\sum_{\{nj'\}} W(\{n_j'\} \to \{n_j\}) P(\{n_j'\}, t) \\ &- \sum_{\{nj'\}} W(\{n_j\} \to \{n_j'\}) P(\{n_j\}, t), \end{aligned} \tag{1}$$

where $W(\{n_j'\}{\to}\{n_j\})$ denotes the prescribed rate of transitions from configuration $\{n_j'\}$ to $\{n_j\}$. These two configurations will differ only in the occupancy of a single site for adsorption or desorption, but in the occupancy of a pair of sites for diffusion. On the right hand side of (1), the first (second) term reflects gain (loss) in the population of configuration $\{n_j\}$. As an aside, we note that for a Markov process, specifying a rate for each microscopic process actually means there is an exponential waiting-time distribution between events associated with this process, with the mean waiting-time between consecutive events given by the inverse of the rate.

The solutions of the master equations satisfy conservation of probability, positivity, etc. The eigenvalues of the evolution matrix associated with these linear equations have non-positive real parts to avoid blow-up of probabilities, but they can in general be complex-valued. The latter scenario corresponds to time-oscillatory solutions which can occur in open non-equilibrium systems. In cases where the energy of configuration $\{n_j\}$ is described by a Hamiltonian, $H(\{n_j\})$, selecting rates to satisfy the detailed-balance condition (Landau and Binder, 2000)

$$\begin{aligned} &W(\{n_j'\} \to \{n_j\}) \exp(-H(\{n_j'\})/kT) \\ &\quad = W(\{n_j\} \to \{n_j'\}) \exp(-H(\{n_j\})/kT), \end{aligned} \tag{2}$$

guarantees that the solution will evolve to the Gibbs equilibrium state $P_{\mathrm{eq}}(\{n_j\}) \propto \exp(-H\{n_j\}/kT)$. In this case, one can also show that the evolution matrix has only real (non-positive) eigenvalues, so solutions of (1) exhibit only decay in time, not oscillatory behavior [3].

In both analytic and simulation studies, the $P(\{n_j\}, t)$ typically contain too much information to be manageable. It is thus common to focus on reduced quantities such as the probability that a single site k is occupied, $P(n_k, t) = \sum_{nj \neq k} P(\{n_j\}, t)$, and higher-order quantities such as spatial pair-correlations. From (1), one can obtain a hierarchy of rate equations for these, which can be analyzed using approximate factorization relations to truncate the hierarchy at some low order, or by exact Taylor series expansions for short-time behavior [5]. Often, one has translational invariance due to periodic boundary conditions, so site quantities are independent of location, and pair-correlations depend only on separation of the pair of sites. Furthermore, behavior in the limit of infinite system size, $L \to \infty$, is of primary interest. Then, in the context of KMC simulation, such reduced quantities can be obtained precisely from a single simulation for a sufficiently large system, rather than by averaging over several trials.

2. Generic Kinetic Monte Carlo Simulation Algorithms

We first describe the two types of generic KMC algorithms applied to LG models. We then compare features of the two algorithms, and give an example of their application to a simple deposition process. Finally, we discuss some issues associated with the finite size of the simulation system. Below, we assume that these models incorporate a variety of distinct atomistic processes, which we label by α (e.g., α = adsorption, desorption, diffusion, reaction, etc.). Furthermore, we suppose that each process, α, occurs with only a *finite* number of microscopic rates, $W_\alpha(m)$, for $m = 1, 2, \ldots$, depending on the local environment.

2.1. Basic Algorithm

Here, we let $W_\alpha(\max)$ denote the maximum of the $W_\alpha(m)$, for each α. We then set $W_{\mathrm{tot}} = \Sigma_\alpha\, W_\alpha(\max)$, and define $p_\alpha = W_\alpha(\max)/W_{\mathrm{tot}}$, so that $\Sigma_\alpha\, p_\alpha = 1$. In the basic algorithm, one first randomly selects a site, then, selects a process, α, with probability, p_α, reflecting the maximum rate for that process α. Finally, one implements this process (if allowed) with a probability, $q_\alpha = W_\alpha/W_\alpha(\max) \leq 1$, where W_α is the actual rate for process α at site j. This means that W_α is one of the $W_\alpha(m)$, with m determined by the local environment of site j. It is also essential to connect the "simulation time," i.e., the number of times a site is chosen, with the "physical time" in the stochastic LG model. On each occasion a site is chosen, we increment the physical time by δt, where $L^d W_{\mathrm{tot}} \delta t = 1$. Thus, after one attempt per site, the physical time has increased by $1/W_{\mathrm{tot}}$.

2.2. Bortz Algorithm

Here, we let $N_\alpha(m)$ denote the (finite) number of particles which can partake in process α with the mth rate, $W_\alpha(m)$. Then, the total rate for all particles in the system associated with this process α occurring at the mth rate is $R_\alpha(m) = W_\alpha(m) N_\alpha(m)$, and the total rate for all processes is $R_{\mathrm{tot}} = \Sigma_\beta\, \Sigma_n\, R_\beta(n)$. The Bortz (or Bortz–Kalos–Lebowitz) simulation algorithm [6] maintains a list of these particles for each α and m. The simulation proceeds by selecting a sub-process (α, m) with probability $p_\alpha(m) = R_\alpha(m)/R_{\mathrm{tot}}$, then randomly selecting one of the $N_\alpha(m)$ particles capable of making this move from the corresponding list, and then implementing the process (after which lists have to be updated). Again, one must connect the "simulation time," i.e., the number of times a process is chosen, with the "physical time" in the stochastic LG model. On each occasion when a process is implemented, one increments the physical time by $\delta t = 1/R_{tot}$.

2.3. Comparison of Algorithms

In comparing standard and Bortz algorithms, it is appropriate to first note that often the rates $W_\alpha(m)$, described above, vary over many orders of magnitude. Furthermore, processes with high rates often have a low population of available particles, a feature which can apply not just under quasi-equilibrium conditions, but more generally. Thus, in the basic algorithm, after selecting a site, usually one selects a process α with a large $W_\alpha(\max)$, but then typically fails to implement this process due to the small population of particles in this class. Thus, the basic algorithm is simple, but possibly inefficient due to the large fraction of failed attempts. In contrast, in the Bortz algorithm, one always implements the chosen process, so in this sense the algorithm has optimal efficiency. However, there is a substantial "book keeping" penalty in that one must maintain and continually update lists of length $N_\alpha(m)$ of particles for each sub-process (labeled by α and m). In practice, for complex models where processes have many rates, one may compromise between the two approaches accepting some fraction of failed attempts to avoid substantial additional complexity or cost in book-keeping.

2.4. A Simple Example

To illustrate these features, consider irreversible island formation during submonolayer deposition [7]. Here, atoms deposit randomly at rate F per unit time at the adsorption sites on the surface represented by an $L \times L$ site square lattice (so $d = 2$) with coordination number $z = 4$, and with periodic boundary conditions. Adsorbed atoms (adatoms) then hop randomly to adjacent sites at rate h per unit time (in each of $z = 4$ directions) until meeting other diffusing atoms and irreversibly nucleating new (immobile) islands, or until irreversibly aggregating with existing islands. We assume some simple rule for incorporating into islands adatoms which land on top of islands, or which diffuse to island edges, where this rule does not involve additional processes with finite rates. Thus, the model is characterized by just two rates. Typically, $F \sim 10^{-2}$/s, but $h \sim 10^5 - 10^7$/s is many orders of magnitude higher, and this leads to a very low density of diffusing adatoms on the surface ($\sim 10^{-5} - 10^{-7}$ atoms per site).

For this deposition model, we write $\alpha =$ "dep" (deposition), or "hop" (diffusive hopping), where each process is described by a single rate. In the *basic algorithm*, one has $p_{dep} = F/(F + zh) \ll 1$, and $p_{hop} = zh/(F + zh) \approx 1$. Thus, after choosing a site, typically one attempts to hop, but fails due to the very low probability of that site being occupied by a diffusing adatom. Also, one increments time by $\delta t = (F + zh)^{-1} L^{-2}$. In the *Bortz algorithm*, one maintains a list of the N_{hop} diffusing adatoms and their positions. Then, one has $R_{dep} = FL^2$ (as all sites are adsorption sites) and $R_{hop} = zhN_{hop}$. Thus, at each Monte Carlo step, one chooses either to deposit with probability $p_{dep} = FL^2/(FL^2 + zhN_{hop})$, or to hop with probability $p_{hop} = zhN_{hop}/(FL^2 + zhN_{hop})$. For deposition, one randomly chooses a lattice site and deposits. For hopping, one randomly chooses one of the N_{hop} diffusing atoms from the list, and then implements the hop in a randomly chosen direction. After either event, the list of diffusing adatoms is updated. In particular, one must check for incorporation into an island, which leads to removal of the adatom from the list.

2.5. Finite Size Effects

For large systems, the time increments δt described above are small. Thus, the above algorithms accurately represent the continuous-time dynamics of the stochastic lattice gas models. These algorithms also automatically produce an exponential waiting-time distribution between consecutive events for each particle. However, for small systems, the increments δt become significant on the time scale of the slowest process. To recover an accurate description of continuous kinetics and waiting-time distributions, in the basic algorithm, one could simply reduce all the p_α by some factor $\varepsilon \ll 1$, and correspondingly reduce all the δt by the same factor. Analogous refinements are possible in the Bortz algorithm. Instead, one can recover the exponential waiting-time distribution by setting $\delta t = -\ln(x) L^{-d}/W_{tot}$ (basic algorithm), or $\delta t = -\ln(x)/R_{tot}$ (Bortz algorithm), where x is a random number chosen uniformly in [0,1].

For KMC simulation (in finite systems), there are fluctuations between different runs or trials in predictions of quantities at some specific time. Simplistically, fluctuations in some number, N (e.g., of adsorbed particles, of islands, etc.) should vary like the square root of the number, $\surd N$. Such numbers typically scale linearly with the system size (i.e., the number of sites $= L^d$), so the corresponding densities $\rho = N/L^d$ are roughly size-independent. Thus, it follows that uncertainties in numbers (densities) should scale like $L^{d/2}$ ($L^{-d/2}$). A more sophisticated analysis comes from applying general fluctuation-correlation relations (the presentation in Landau and Binder, 2000, for equilibrium systems is readily generalized): $\langle(\delta N)^2\rangle = L^d\, C_{tot}$, or equivalently that $\langle(\delta\rho)^2\rangle = L^{-d}\, C_{tot}$, where C_{tot} represents the pair-correlations for the quantity of interest (e.g., adsorbed atoms, islands, etc.) summed over all separations.

Finally, we discuss the effects of finite system size on mean behavior of quantities of interest. Usually, the choice of periodic boundary conditions is motivated by the desire to minimize such effects, and specifically to remove "edge effects". In general, one expects finite size effects to be negligible when the linear system size, L, significantly exceeds the relevant spatial correlation length, L_c. This condition is violated near "critical points" where $L_c \to \infty$.

3. Simulation of Homoepitaxial Thin Film Growth and Relaxation

Homoepitaxial growth [8] involves random deposition of adatoms on a surface, and their subsequent diffusion. Adatom diffusion mediates nucleation of new islands, when suitable number of adatoms meet, in competition with growth of existing islands, when adatoms aggregate with island edges. In addition, the details of interlayer transport are critical in determining multilayer morphologies. Post-deposition relaxation often occurs on a much longer time-scale than growth, and different processes may dominate, e.g., 2D evaporation-condensation at island edges.

3.1. Tailored Models and Algorithms

Rather than developing generic models which might handle both growth and relaxation, often a more effective strategy is to develop "tailored" models. These focus on the essential atomistic processes (for the conditions of interest) which are described by a few key parameters. As an example, we describe a simple but effective model for metal(100) homoepitaxial growth with irreversible island formation [9]. As in the simple example used above, deposition occurs at rate F and subsequent hopping to adjacent sites at rate h. Diffusing adatoms irreversibly nucleate new islands upon meeting, and irreversibly aggregate with existing islands. Islands have compact near-square shapes in these systems due to efficient edge diffusion and kink rounding. Thus, once a diffusing atom reaches an island edge, it is immediately moved to a nearby doubly-coordinated kink site. This produces near-square individual islands, and describes reasonably growth coalescence shapes for impinging islands. Atoms landing on top of islands diffuse until nucleating new islands in higher layers, or until reaching island edges. In the latter case, adatoms can hop down to lower layers also with rate h if the step edge is kinked, but with reduced rate $h' < h$, for a straight close-packed step edge. Finally, we incorporate "downward funneling" of atoms deposited right at step edges to adsorption sites in lower layers. See Fig. 1 for a schematic of these processes.

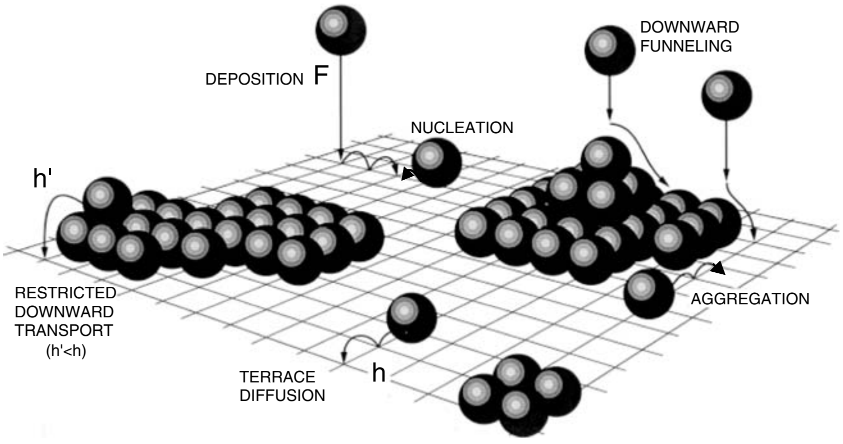

Figure 1. Schematic of metal(100) homoepitaxy with irreversible island formation. The square grid represents the lattice of substrate adsorption sites. Adatoms reaching island edges are moved immediately to nearby kink sites [9].

Thus, the model has only three rates, h, h', and F. One would naturally apply a Bortz-type algorithm maintaining a list of all hopping atoms in all layers. Rather than maintain a separate list of atoms just above close-packed step edges which can hop down at a distinct reduced rate h', it is easier to include them in a single list of "hoppers", but if hopping down is selected, then implement this process with probability $p_{\mathrm{down}} = h'/h < 1$. One can determine h by matching the observed submonolayer island density, and h' by matching, e.g., the second layer population after deposition of 1 ml. Corresponding activation barriers come from assuming an Arrhenius form with a prefactor of $\sim 10^{13}$/s. Then, matching F to experiment, the model has no free parameters. How does it do? For Ag/Ag(100) homoepitaxy at 300 K, a purported classic case of smooth quasi-layer-by-layer growth, it predicts initial smooth growth up to ∼30 ml, but then extremely rapid roughening up to ∼1500 ml. For lower temperatures, initial growth is rougher (as expected), but growth of thicker films is smoother than at 300 K (contrasting expectations). These predictions are supported by recent experiments, i.e., the tailored model works!

3.2. Classically Exact Models and Algorithms (with Look-up Tables for Rates)

In contrast to tailored models, one could attempt to describe exactly adatom diffusion in all possible local environments during or after growth. Typically, the barrier for intra-layer diffusion will depend only on the occupancy of sites which are neighbors or next-neighbors to either the initial or final site of the hopping particle. For metal(100) surfaces represented by a square lattice of adsorption sites, there are 10 such sites. Then, one should specify rates or barriers for 2^{10}=1024 possible local environments, ignoring symmetries [10, 11]. Thus, in the simulation algorithm, if hopping is chosen, one must assess the local environment of the selected adatom, and determine the relevant rate which will be stored in a large look-up table. It is not possible to precisely determine so many barriers, and in fact film morphology may not be sensitive to the precise values of many of these: too low means the process is essentially instantaneous, too high means inoperative on the relevant time scale. For efficiency in simulation with look-up tables, it is reasonable to not implement processes with barriers above a certain threshold value, and perhaps to divide up all diffusing particles into a few classes (fast, medium, slow diffusers) for Bortz-type treatment [11].

This approach was introduced by Voter [10] to treat post-deposition diffusion of 2D islands in metal(100) homoepitaxial systems, and then adapted to treat film growth [11]. Originally, the values of barriers for rates were determined from Lennard–Jones or semi-empirical many-body potentials. Effort has been made to decompose this large set of diffusion processes into a few basic classes (which can aid simulation, as indicated above), and to develop reliable approximate formulae for barriers in various environments. Recently, at least a subset of key rates have been extracted from higher-level DFT calculations. However, we caution that even DFT may not have the accuracy to allow quantitative prediction of film morphologies.

3.3. Self-Teaching or On-the-Fly Algorithms

There are a vast number of possible local configurations and rates for diffusing adatoms, but how many of these are practically important? Usually, most of these processes are associated with diffusion and detachment of adatoms at step edges, and one has some idea as to which are the most dominant processes. Thus, one strategy is to start with a smaller look-up table containing these key rates. Then, run the simulation using these rates, and any time a new local environment is generated in which an atom attempts to hop, stop the simulation, calculate the rate, insert the configuration and barrier value into the table, and continue the simulation [12, 13]. This approach could even be utilized to search for possible many-atom concerted moves in addition to probing single-atom hops.

3.4. Hybrid Algorithms

Many thin film deposition systems exhibit large characteristic lateral lengths (e.g., large island separations). Consequently, rather than atomistic simulation of deposition and diffusion-mediated aggregation at island edges, it makes sense to adopt a continuum PDE description of the adatom density [14, 15]. The local nucleation rate can be determined from this density, and the nucleation process implemented stochastically with this rate. This approach has a significant advantage for reversible island formation with a high density of diffusing adatoms, as it is computationally expensive to follow all these particles in KMC. However, a continuum description of island growth can be problematic. Growth shapes are very sensitive to noise in the aggregation process for inefficient shape relaxation (the Mullins–Sekerka or DLA instability), and reliable continuum formulations are lacking for compact growth shapes due to efficient shape relaxation. Thus, it is natural to combine a continuum description of deposition, diffusion, and aggregation with an atomistic description of island shape evolution [16]. To grow islands, one tracks the cumulative total aggregation flux, and adds an atom when this reaches unity at a location chosen with a probability reflecting the local aggregation flux. Treatment of detachment from island edges is similar. Edge diffusion is treated atomistically as in a standard simulation.

3.5. Other Algorithms

For island formation during deposition, island growth rates can be characterized precisely in terms of the areas of "capture zones" (CZs) which surround islands [14]. Combining this CZ-based formulation of island growth, together with a reliable characterization of the spatial aspects of nucleation, e.g., as primarily along CZ boundaries, one could imagine implementing a purely Geometry-Based Simulation (GBS) algorithm for island formation. As in the above hybrid approach, here one retains a stochastic component to the prescription of island nucleation [17]. Finally, we discuss tailored simulation algorithms for post-deposition coarsening of submonolayer island distributions in metal(100) homoepitaxial systems, where coarsening is mediated by the diffusion and coalescence of islands. Given the diffusion rates versus island size, one could develop the following simulation algorithm [18]: adopt a simple characterization of islands as squares with various sizes; let these undergo random walks with the appropriate diffusion rates; after each collision, replace two islands by a single island so as to preserve size.

4. Simulation of Catalytic Surface Reactions

In catalytic surface reaction systems, the reactants are continually introduced as a gas above the surface. They adsorb (sometimes reversibly), usually diffuse across the surface, and react with coadsorbed species, producing product(s) which desorb. The reactant and product species are continually removed from the system by pumping. Thus, one has an open system which might achieve a time-independent steady-state, but this is not a Gibbs state. In simple models, it may also be possible to develop absorbing (or poisoned) states where the surface is completely covered by some non-desorbing species [19]. In more complex models, one may develop oscillatory states, although fluctuations preclude perfect periodic behavior.

4.1. Basic Algorithms

If adsorption, desorption, diffusion, and reaction rates are comparable, then the basic KMC algorithm is effective. Consider the canonical monomer (A)–dimer (B_2) reaction [19–21], which mimics CO-oxidation (A=CO and B_2=O_2): A adsorbs reversibly at single empty sites; B_2 adsorbs dissociatively and irreversibly at nearby pairs of empty sites; A may diffuse on the surface; adjacent A and B react to produce the product AB (=CO_2) which immediately desorbs. For limited (non-reactive) desorption of A, upon increasing the adsorption rate of A relative to B_2, one finds a discontinuous non-equilibrium phase transition from a reactive steady state with low A-coverage, θ_A^-, to a nearly A-poisoned steady state with high θ_A^+. This discontinuous transition disappears at a non-equilibrium critical point upon increasing the A desorption rate. See Fig. 2 for a schematic of the monomer-dimer reaction model and its steady-state behavior.

As an aside, in the absence of desorption of A, this model exhibits a completely A-poisoned absorbing state [19]. From the general properties of finite-state Markov processes, any finite system must eventually evolve to such a state [3], while infinite systems can avoid such states indefinitely by remaining in other non-trivial steady states. Thus, KMC simulation must eventually reach such absorbing states (there are no true non-trivial steady states). However, in practice, this can take an immense amount of time, and the system resides in a pseudo-steady state which accurately reflects the true steady state of the corresponding infinite system.

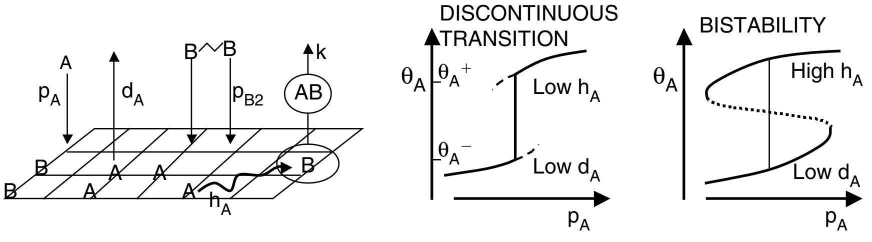

Figure 2. Schematic of the monomer (A)–dimer (B_2) surface reaction model which mimics CO-oxidation. Also shown is the variation of the steady-state coverage of A with adsorption rate, p_A. Note the emergence of bistability with increasing hop rate, h_A, of A.

The above example illustrates that non-equilibrium steady states can exhibit phase transitions analogous to classic equilibrium systems. One cannot apply thermodynamic concepts geared to Hamiltonian systems, but KMC simulation combined with finite-size-scaling ideas borrowed from equilibrium theory is an effective tool to analyze their behavior. This remains true for more a realistic reaction model which incorporate rapid diffusion of CO, and interactions between adsorbed CO and O, although refined algorithms are needed for efficient simulation [20].

4.2. "Constant-Coverage" Simulation Algorithms

In the conventional "constant-adsorption-rate" simulations of the above monomer-dimer model, if adsorption is selected as the process to be implemented, one chooses between attempting deposition of A or of B_2 with probabilities reflecting their adsorption rates. A distinct "constant-coverage" simulation approach was suggested by Ziff and Brosilow [22]. Here, the structure of the conventional simulation algorithm is retained, except that now if adsorption is selected, one attempts to adsorb A (B_2) if the current coverage is below (above) some prescribed target "constant-coverage" value, θ_A^*, say. Furthermore, during the simulation, one tracks the fraction of attempts to adsorb A (rather than B_2). The long-time value of this fraction determines the A adsorption rate corresponding to the prescribed coverage θ_A^*. Thus, it determines the adsorption rate exactly at the discontinuous transition if one chooses $\theta_A^- < \theta_A^* < \theta_A^+$. In summary, in conventional simulations of steady state behavior, one prescribes the A adsorption rate, and extracts the A coverage. In constant-coverage simulations, one prescribes the A coverage and extracts the A adsorption rate. Other variations are possible.

Are the constant-adsorption-rate and constant-coverage simulations entirely consistent? Clearly, for conventional simulations in a small finite system, there are significant fluctuations in the steady-state A coverage. Such fluctuations are "artificially" removed in the constant-coverage simulation approach, so one also should expect some differences in mean values of various quantities. However, in the limit of large system size where fluctuations in conventional simulations diminish, the two simulation approaches should converge.

4.3. Hybrid Algorithms

In "real" CO-oxidation or related reactions, the surface diffusion or hop rate for CO is often many orders of magnitude above other rates. Also, since removal of CO from the surface is not diffusion-limited, but reaction-limited, there is a significant build-up of rapidly hopping CO molecules. This makes conventional simulation inefficient. However, rapid mobility and reaction-limited removal of CO also mean that the CO should be quasi-equilibrated within the complex geometry of the relatively immobile coadsorbed reactant O. This suggests a hybrid approach wherein the distribution of CO is described by some simple analytic equilibrium procedure, and the O distribution is described by conventional LG KMC simulations [20, 23]. Here, reaction of a specific O to form CO_2 is determined from the equilibrium probability of finding an adjacent CO.

Next, we discuss application of the hybrid approach to the monomer–dimer reaction with infinitely mobile adsorbed A, which does not interact with other adsorbed A or B (other than through reaction with B). Now A will be randomly distributed on sites not occupied by B. Thus, in our hybrid simulation procedure, we track the location of all adsorbed Bs with a LG simulation, but just the total number of adsorbed A. From this number, one can readily determine the (spatially uniform) probability that any non-B site is occupied by A, and thus determine reaction rates, etc. The most dramatic consequence of replacing finite mobility of A with infinite mobility is that the discontinuous transition described above is replaced by bistability, i.e., stable reactive and near-poisoned states coexist for a range of A adsorption rates [24].

Bistability is also obtained from a mean-field rate equation treatment of the chemical kinetics. This is not surprising since mean-field equations apply to a well-stirred system (i.e., rapid surface diffusion). In this mean-field treatment, the two stable steady states are smoothly joined by a coexisting unstable state, all of which are readily determined from a steady-state rate equation analysis. In our hybrid model, one expects that an unstable steady state may exist. However, it will have a non-trivial distribution of adsorbed O, and cannot be readily analyzed by conventional (constant-adsorption-rate) simulations for which the system will always evolve away from the unstable state. However, efficient analysis of the non-trivial unstable state behavior is possible by simply implementing a constant-coverage version of the hybrid simulation code [20, 24]. By varying the target θ_A^*, one maps out both stable and unstable steady states.

5. Outlook

KMC simulation has proved a tremendously successful tool for analyzing and elucidating the evolution of non-equilibrium LG models for a broad variety of cooperative phenomena (not just in physical sciences). This approach will continue to be applied effectively to analyze more complex and realistic models in traditional areas of investigation, as well as in new areas of cooperative phenomena. Recent variations and hybrid algorithms show great promise not only in more efficiently connecting atomistic processes with resulting behavior on far larger length scales, but just as significantly in providing fundamental insight into the key physics.

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