Theoretical foundations of dynamical Monte Carlo simulations

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Monte Carlo methods are utilized as computational tools in many areas of chemical physics. In this paper, we present the theoretical basis for a dynamical Monte Carlo method in terms of the theory of Poisson processes. We show that if: (1) a "dynamical hierarchy" of transition probabilities is created which also satisfy the detailed-balance criterion; (2) time increments upon successful events are calculated appropriately; and (3) the effective independence of various events comprising the system can be achieved, then Monte Carlo methods may be utilized to simulate the Poisson process and both static and dynamic properties of model Hamiltonian systems may be obtained and interpreted consistently.

I. INTRODUCTION

Monte Carlo methods are utilized as computational tools in many areas of chemical physics.[1,2] Although this technique has been largely associated with obtaining static, or equilibrium properties of model systems, Monte Carlo methods may also be utilized to study dynamical phenomena. Often, the dynamics and cooperativity leading to certain structural or configurational properties of matter are not completely amenable to a macroscopic continuum description. On the other hand, molecular dynamics simulations describing the trajectories of individual atoms or molecules on potential energy hypersurfaces are not computationally capable of probing large systems of interacting particles at long times. Thus, in a dynamical capacity, Monte Carlo methods are capable of bridging the ostensibly large gap existing between these two well-established dynamical approaches, since the "dynamics" of individual atoms and molecules are modeled in this technique, but only in a coarse-grained way representing average features which would arise from a lower-level result.

The application of the Monte Carlo method to the study of dynamical phenomena requires a self-consistent dynamical interpretation of the technique and a set of criteria under which this interpretation may be practically extended. In recent publications,[3,4] certain inconsistencies have been identified which arise when the dynamical interpretation of the Monte Carlo method is loosely applied. These studies have emphasized that, unlike static properties, which must be identical for systems having identical model Hamiltonians, dynamical properties are sensitive to the manner in which the time series of events characterizing the evolution of a system is constructed. In particular, Monte Carlo studies comparing dynamical properties simulated away from thermal equilibrium have revealed differences among various sampling algorithms.[3–6] These studies have underscored the importance of utilizing a Monte Carlo sampling procedure in which transition probabilities are based on a reasonable dynamical model of a particular physical phenomenon under consideration, in addition to satisfying the usual criteria for thermal equilibrium. Unless transition probabilities can be formulated in this way, a relationship between Monte Carlo time and real time cannot be clearly demonstrated. In many Monte Carlo studies of time-dependent phenomena, results are reported in terms of integral Monte Carlo steps, which obfuscate a definitive role of time. Ambiguities surrounding the relationship of Monte Carlo time to real time preclude rigorous comparison of simulated results to theory and experiment, needlessly restricting the technique. Within the past few years, the idea that Monte Carlo methods can be utilized to simulate the Poisson process has been advanced in a few publications[6–8] and some Monte Carlo algorithms which are implicitly based on this assumption have been utilized.[1,4] This is an attractive prospect, since within the theory of Poisson processes, the relationship between Monte Carlo time and real time can be clearly established.

In this paper, we shall focus on dynamical interpretation of the Monte Carlo method. We shall show that if three criteria are met, namely, that transition probabilities reflect a "dynamical hierarchy" in addition to satisfying the detailed-balance criterion, that time increments upon successful events are formulated correctly in terms of the microscopic kinetics of the system, and that the effective independence of various events can be achieved, then the Monte Carlo method may be utilized to simulate effectively a Poisson process. Within the theory of Poisson processes, both static and dynamic properties of Hamiltonian systems may be consistently simulated with the benefit that an exact correspondence between Monte Carlo time and real time can be established in terms of the dynamics of individual species comprising the ensemble. We shall demonstrate the formalism by considering the approach to and the attainment of Langmuir adsorption–desorption equilibrium in a lattice–gas system. We shall also discuss straightforward extension of the methodology to more complicated systems of interacting particles.

II. DYNAMICAL INTERPRETATION OF THE MONTE CARLO METHOD

Under a dynamical interpretation,[1] the Monte Carlo method provides a numerical solution to the Master equation

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$$\frac{\partial P(\sigma,t)}{\partial t} = \sum_{\sigma'} W(\sigma' \to \sigma) P(\sigma',t) - \sum_{\sigma'} W(\sigma \to \sigma') P(\sigma,t), \tag{1}$$

where σ and σ' are successive states of the system, $P(\sigma,t)$ is the probability that the system is in state σ at time t, and $W(\sigma' \to \sigma)$ is the probability per unit time that the system will undergo a transition from state σ' to state σ. The solution of the Master equation is achieved computationally by choosing randomly among various possible transitions to a model system and accepting particular transitions with appropriate probabilities. Upon each successful transition (or, in some instances, each attempted transition), time is typically incremented in integral units of Monte Carlo steps which are related to some unit time τ. At steady state, the time derivative of Eq. (1) is zero and the sum of all transitions into a particular state σ equals the sum of all transitions out of state σ. In addition, the detailed-balance criterion

$$W(\sigma' \to \sigma) P(\sigma',eq) = W(\sigma \to \sigma') P(\sigma,eq), \tag{2}$$

in which

$$P(\sigma,eq) = Z^{-1} e^{-H(\sigma)/k_B T}, \tag{3}$$

must be imposed for each pair of exchanges, so that the Monte Carlo transition probabilities can be constructed to guarantee that the system will attain a thermal equilibrium consistent with the model Hamiltonian. In Eq. (3), Z is the partition function and H is the Hamiltonian of the system. The detailed-balance criterion does not, however, uniquely specify these probabilities. When static properties of model Hamiltonian systems are sought, Eqs. (2) and (3) are the only standards which must be met in addition to the necessity of a sampling procedure which is sufficiently random to prevent statistical bias. Dynamical properties require that a more definite relationship between the Monte Carlo time step and the transition probabilities is established. We shall show that this relationship can be established and implemented, once transition probabilities are formulated as rates with physical meaning, through the theory of Poisson processes.

In a dynamical interpretation of the Monte Carlo method, it can be assumed that time resolution is accomplished on a scale at which no two events occur simultaneously. Once this perspective has been adopted, the task of the Monte Carlo algorithm is to create a chronological sequence of distinct events separated by certain interevent times. Since the microscopic dynamics yielding the exact times of various events are not modeled in this approach, the chain of events and corresponding interevent times must be constructed from probability distributions weighting appropriately all possible outcomes. The distributions governing transitions and interevent times available to a system at any time t can be developed from considerations fully consistent with the mesoscopic genre. On a course-grained, mesoscopic level, it must be assumed that the totality of microscopic influences underlying various transitions of a system dictate certain distinctive events $\mathbf{E} \equiv \{e_1,e_2,...,e_n\}$, which can be characterized by average transition rates $\mathbf{R} \equiv \{r_1,r_2,...,r_n\}$. In the absence of microscopic detail, it can be held that any particular transition which becomes possible at time t can potentially occur at any later time $t + \Delta t$ with a uniform probability which is based on its rate and is independent of the events before time t. Let us consider the ramifications of these premises for a stationary process with two states representing "forward" and "reverse" transitions. This process may correspond, e.g., to the time-dependent occupancy or vacancy of one "site" among many in the adsorption–desorption equilibrium of a gas-phase molecule with a solid, single-crystalline surface. Adopting a frequency definition of probability, the average rate r of, say, the forward transition (which becomes intermittently available via the reverse transition) can be interpreted as a time density of events. Sampling small, identical time intervals δ of a larger time increment, $t = n\delta$, the average rate is the ratio of the number of time intervals containing events n_δ to the total number of intervals sampled n per unit time δ in the limit $\delta \to 0$ and $n \to \infty$,

$$r = \lim_{\delta \to 0, t \to \infty} \frac{n_\delta}{t}. \tag{4}$$

In the limit $\delta \to 0$, each interval will contain, at most, one event. Also, consistent with our premise is that each time interval has an equal probability $r\delta$ of containing an event. Let $N_{e,t}$ be a random variable counting the number of events which have occurred within a time t. Then, the probability that n_e events will occur in time t is

$$P(N_{e,t} = n_e) = \binom{n}{n_e} (r\delta)^{n_e} (1 - r\delta)^{n - n_e}, \tag{5}$$

and in the limit $\delta \to 0$,

$$P(N_{e,t} = n_e) = \frac{(rt)^{n_e}}{n_e!} e^{-rt}. \tag{6}$$

From Eq. (6), the expected number of events occurring within a time t is $\langle N_{e,t} \rangle = rt$, from which the rate is recovered through division by t. In Eqs. (4)–(6), it is seen that a mathematical adaption of these very basic assumptions leads to the characterization of a stationary series of random, independent events occurring with an average rate r in terms of a Poisson process.[9,10] It can be shown that a Poisson process is consistent with the Master equation.[11] Additional features are attributable to the Poisson process and the most significant of these for the purpose at hand is characterization of the probability density of times t_e between successive events[10]

$$f_{t_e}(t) = re^{-rt}. \tag{7}$$

From the probability density, the mean time period between successive events is calculated as $\langle t_e \rangle = 1/r$.

A particularly useful feature of the Poisson process is that an ensemble of independent Poisson processes will behave as one, large Poisson process such that statistical properties of the ensemble can be formulated in terms of the dynamics of individual processes. Considering N-independent forward–reverse Poisson processes (or, keeping with the previous analogy, the adsorption–desorption equilibrium of an entire system of independent molecules), each with some arbitrary, but finite rate r_i, let $N_{e0,t}$ be a random variable counting the overall number of events in the ensemble which have occurred within a time interval t. The quantity $N_{e0,t}$ is then the sum of random variables counting the number of

events which have occurred in each of the individual processes, i.e.,

$$N_{e0,t} = \sum_{i=1}^{N} N_{ei,t}. \tag{8}$$

The overall probability of n_e events in time t is given by the convolution of the individual probability mass functions characterizing each of the individual processes

$$P(N_{e0,t} = n_e) = P(N_{e1,t}) * P(N_{e2,t}) * \cdots * P(N_{eN,t}), \tag{9}$$

and the probability mass function characterizing the overall distribution of events is obtainable by the method of characteristic functions[12]

$$P(N_{e0,t} = n_e) = \frac{(\lambda t)^{n_e}}{n_e!} e^{-\lambda t}, \tag{10}$$

where

$$\lambda = \sum_{i=1}^{N} r_i. \tag{11}$$

A final point which should be emphasized is that the basic premises leading to Eqs. (6), (7), and (10) are equally applicable to systems which are nonstationary and evolving toward equilibrium. In the nonstationary Poisson process, the overall rate simply becomes a function of time. Thus, if the Monte Carlo algorithm can be made to simulate the Poisson process, then the relationship between Monte Carlo time and real time can be given a firm basis in both static and dynamic situations. In the following section, we shall demonstrate, through an example of the approach to the attainment of Langmuirian adsorption equilibrium, the criteria which must be applied so that the Poisson process may be effectively simulated with Monte Carlo methods.

III. ADSORPTION–DESORPTION EQUILIBRIUM

Adsorption equilibrium of a gas-phase species A with a solid, single-crystalline surface occurs when the chemical potentials of gas-phase and chemisorbed A are equal. From a kinetic point of view, adsorption equilibrium (steady state) is established when the net rate of chemisorption of gas-phase A is equal to the net rate of desorption of chemisorbed A to the gas phase. Within the context of a lattice–gas model in which adsorption is unactivated, each chemisorbed A molecule requires one adsorption site. We assume that chemisorbed A molecules do not interact appreciably with one another and envision a collection of gas-phase molecules whose temperature, pressure, and intrinsic partition functions dictate a series of independent arrivals of molecules to a surface containing a uniform and periodic array of adsites. The arrivals occur at random, uncorrelated times and can be characterized by an average rate r_A. A similar scenario is applicable to molecules chemisorbed on the surface—the totality of microscopic influences (e.g., surface phonons and electron–hole pair creation) acting on an ensemble of chemisorbed molecules induces desorption events which occur with an average rate r_D. The appropriate kinetic expression for this balance is

$$\frac{d\theta}{dt} = r_A(1-\theta) - r_D\theta. \tag{12}$$

Here, θ is the fractional surface coverage of A. The absence of adsorbate–adsorbate interactions in our example allows Eq. (12) to be solved readily for the approach to and the attainment of adsorption–desorption equilibrium once r_A and r_D are known in terms of the intensive and extensive properties of the system. With the initial condition $\theta(t=0) = 0$,

$$\theta(t) = \frac{r_A}{r_A + r_D}(1 - e^{-(r_A + r_D)t}) \tag{13}$$

and, in the limit as $t \to \infty$,

$$\theta_e = \frac{r_A}{r_A + r_D}. \tag{14}$$

Equation (14) reflects the detailed balance of the simple adsorption–desorption model. If the rates are cast in terms of appropriate partition functions,[13–15] then both the desired kinetics and thermal equilibrium of the system are ensured. To maintain generality, we shall retain generic rate expressions for the elementary steps. It should be stressed, however, that both kinetic and equilibrium behavior can and should be incorporated in the rates of elementary steps indigenous to a particular system, so that both aspects of the system can be modeled consistently.

Figure 1 depicts the general features of one algorithm for simulating as a Poisson process the adsorption equilibrium of a gas-phase species A with a two-dimensional lattice containing N sites. A trial in this algorithm begins when one of the N sites is selected randomly. If the site is vacant, adsorption occurs with probability W_A; and desorption occurs with probability W_D if the site is occupied. Time is advanced by an increment τ_i upon successful realization of an event at trial i and, for illustrative purposes, we shall also count the overall number of trials T, which accumulate over repetition of the algorithm. We shall show that through a proper definition of W_A and W_D, the utilization of an appropriate τ_i, and the random selection process, the Monte Carlo algorithm of Fig. 1 simulates the Poisson process and provides the correct

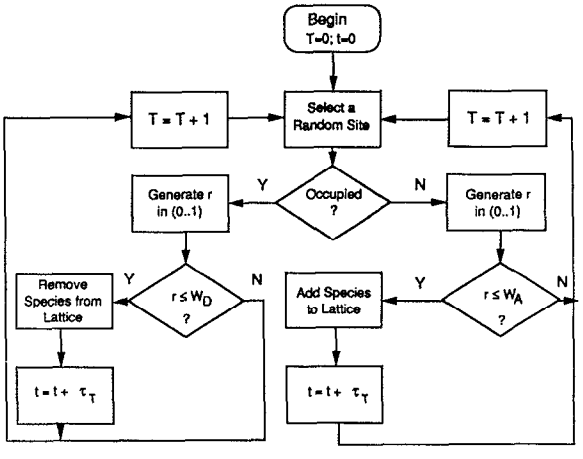

FIG. 1. A flow diagram for simulating as a Poisson process the approach to and the attainment of Langmuirian adsorption equilibrium. T is the (integral) number of trials, t represents real time, r is a uniform random number between 0 and 1, W_i is the transition probability for event i [$i = A$ (adsorption) or D (desorption)], and τ_T is the real time increment at trial T.

solution to Eq. (12) for the N-site ensemble.

The first criterion which must be met to simulate effectively the Poisson process is that the transition probabilities W_A and W_D must be chosen so that the Monte Carlo simulation obeys detailed balance, as specified, e.g., by Eq. (14). To demonstrate the manner in which this is achieved, let us first consider the discrete stochastic process of the Monte Carlo algorithm of Fig. 1. By performing this algorithm, we simulate a sequence of independent Bernoulli trials in which the probability per trial of a successful adsorption event is $W_A(1-\theta_i)$, the probability per trial of a successful desorption event is $W_D\theta_i$ and the total probability of success per trial is $W_A(1-\theta_i)+W_D\theta_i \leqslant 1$. Here, θ_i is the fractional coverage of A at trial i, which for M_i occupied lattice sites is given by $\theta_i = M_i/N$. When the system has reached steady state, $\langle\theta_i\rangle \to \theta_s$ the simulated equilibrium fractional surface coverage of A. In general, θ_s will be different from θ_e the continuum equilibrium fractional surface coverage, since the continuum coverage should arise from time-weighted (and not trial-weighted) θ_i. However, in systems which are sufficiently large, θ_s should approach θ_e (*vide infra*). The statistics of the equilibrium system may be obtained readily. Let $N_{A,T}$ be a random variable counting the number of successful adsorption events in T trials. Then the average probability of n_A successful adsorption events in T trials is given by

$$P(N_{A,T}=n_A) = (T/n_A)[W_A(1-\theta_s)]^{n_A} \times [1-W_A(1-\theta_s)]^{T-n_A}, \quad (15)$$

for $0 \leqslant n_A \leqslant T$. From Eq. (15), the expected number of adsorption events in T trials is given by

$$\langle N_{A,T}\rangle = W_A(1-\theta_s)T. \quad (16)$$

Similar results may be obtained for desorption events and the overall statistics of both adsorption and desorption.

When steady state has occurred in the simulation, the average rate of adsorption [obtained from Eq. (16)] is equal to the average rate of desorption, i.e.,

$$W_A(1-\theta_s) = W_D\theta_s. \quad (17)$$

Detailed balance is satisfied at equilibrium (steady state) if W_A and W_D are defined in a way which allows the physical model represented by Eq. (14) to be recovered from Eq. (17). The transition probabilities satisfying this relationship are not unique and, as noted previously, in the traditional equilibrium application of the Monte Carlo method, these probabilities are often formulated without regard for the behavior of the system away from equilibrium. To simulate dynamical phenomena, an additional criterion is necessary so that transition probabilities reflect unique transition rates (and, hence, simulate dynamics). These probabilities should be formulated so that a dynamical hierarchy of transition rates is established in terms of appropriate models for the rates of microscopic events comprising the overall process. Generally stated, a dynamical hierarchy of transition probabilities is created when these probabilities are defined, for a transition i, as

$$W_i = r_i/\xi_{\max}, \quad (18)$$

where r_i is the rate at which event i occurs and $\xi_{\max} \geqslant \sup\{r_i\}$. A dynamical hierarchy is not achieved, e.g., in the standard Metropolis algorithm[16] applied to systems approaching equilibrium, because all transitions of the system to lower or equivalent energy states are considered to have a probability of unity. The Kawasaki transition probabilities,[17–19] on the other hand, create a dynamical hierarchy among transition rates. However, it has been pointed out[3,4] that this hierarchy is not appropriate for most physical processes. In the algorithm of Fig. 1, e.g., the transition probabilities could be constructed through normalization of the rates of adsorption and desorption by the larger of the two. If, say, $r_A > r_D$, then transition probabilities could be defined

$$W_A = 1 \quad \text{and} \quad W_D = \frac{r_D}{r_A}, \quad (19)$$

(i.e., $\xi_{\max} = r_A$). With these definitions, the relative frequencies of adsorption and desorption events in the Monte Carlo simulation will satisfy the detailed-balance criterion [Eq. (14)] with $\theta_s \to \theta_e$ (*vide infra*). Furthermore, with this choice of transition probabilities, the success-to-trial ratio will be optimized for an algorithm such as the one depicted in Fig. 1. It should be noted, however, that while this particular algorithm is reasonably effective if the time scales of various processes in the system are similar, its efficiency declines as the stiffness of the system increases. In stiff systems, where the majority of events are generally confined to a minority of sites, many trials will have to be attempted before a successful event is selected. Other, more efficient algorithms are available[1,20,21] and should be utilized to simulate these systems. Regardless of the implementation, the relative frequencies with which various events are performed must comply with the detailed-balance condition for both the dynamics and the equilibrium of the physical system if any meaningful comparison of the simulation of a physical system is intended.

A second criterion which must be satisfied to simulate the Poisson process is proper correspondence of Monte Carlo time to real time. To this end, it should be noted that the Poisson process is, in actuality, a continuous-time version of the discrete Bernoulli process which is simulated by the Monte Carlo algorithm when time is measured in terms of trials. By replacing the discrete interevent times with appropriate continuous values, the Monte Carlo algorithm produces a chain of events which is a Poisson process. The continuous interevent times are constructed through the developments leading to Eqs. (7)–(11). Upon each trial i at which an adsorption or desorption event is realized, time should be advanced with an increment τ_i selected from an exponential distribution with parameter

$$r_i = (N-M_i)r_A + M_i r_D. \quad (20)$$

Here, M_i is the number of sites occupied at trial i (i.e., $\theta_i = M_i/N$). The selection of a time increment in this way yields consistency with Eq. (7), which provides the distribution of interevent times for the Poisson process. Over many successful trials at steady state, the average time between successive events is

$$\langle t_0\rangle = \sum_i \frac{f_i}{(N-M_i)r_A + M_i r_D}. \quad (21)$$

Here, f_i is the fraction of successful trials at which M_i sites

are occupied. Equation (21) represents a time weighting of various configurations of the simulated N-site ensemble which is consistent with that dictated by the detailed-balance criterion for the equilibrium ensemble. A finite-size lattice can approximate the continuum ensemble to the extent that its size allows resolution of the ensemble. In general, the simulated ensemble at a particular point in time [characterized, in our simple example, by $\theta_s(t)$] could fluctuate about the true continuum ensemble at that time [$\theta(t)$, in our example] without ever achieving exactly the continuum value. Thus, time-weighted averages (which correspond to thermodynamic averages at equilibrium if the detailed-balance criterion for thermal equilbrium is fulfilled) must be computed to estimate the true continuum ensemble at any point in time to within the desired degree of accuracy.

When time is incremented according to the procedure delineated above and transition probabilities are chosen to satisfy the detailed-balance criterion, the correct macroscopic rates of adsorption and desorption can be measured from the simulation at steady state. Let us consider, e.g., the rate of adsorption. Over S successful trials resulting in either adsorption or desorption, $\langle N_{A,S} \rangle$ adsorption events will have occurred, on the average, where

$$\langle N_{A,S} \rangle = \left[\frac{W_A(1-\theta_s)}{W_A(1-\theta_s)+W_D\theta_s} \right] S = \left[\sum_i \frac{f_i W_A(1-\theta_i)}{W_A(1-\theta_i)+W_D\theta_i} \right] S. \quad (22)$$

The corresponding amount of time which has passed during the S successes Δt is

$$\Delta t = \left[\sum_i \frac{f_i}{r_A(N-M_i)+r_D M_i} \right] S. \quad (23)$$

Defining the rate of adsorption as the number of adsorption events occurring per site per unit time and utilizing the definition of W_A and W_D in Eq. (19) [or any definition satisfying Eq. (18)], the simulated rate of adsorption $\langle R_A \rangle$ becomes

$$\langle R_A \rangle = \sum_i r_A(1-\theta_i)\phi_i = r_A(1-\theta_e), \quad (24)$$

where

$$\phi_i = \frac{f_i/[r_A(N-M_i)+r_D M_i]}{\Sigma_j f_j/[r_A(N-M_j)+r_D M_j]} = \frac{f_i \tau_i}{\langle t_0 \rangle} \quad (25)$$

provides the time weighting of each configuration characterized, in this simple system, by θ_i. A similar result can be obtained for the desorption events.

A final and perhaps more subtle criterion which must be fulfilled for the Poisson process to be simulated effectively is that independence of events comprising the time sequence of the process is achieved. Strictly speaking, the formalism which we have presented is valid only when independent events are simulated. In general, the independence of successive trials is ensured both by utilization of a system which is sufficiently large that single site and intersite correlations are lost, and by random selection of sites on which potential events may occur. The former condition is not always possible to achieve, particularly if the system is stiff. In such systems, it may not always be feasible computationally to define a lattice sufficiently large to represent the full system ensemble and to simulate independent events. Nevertheless, if transition probabilities are chosen to satisfy the detailed-balance criterion and if time is incremented in a procedure analogous to that outlined in Eqs. (20) and (21) in these situations, the time series can be interpreted in terms of a Poisson process of one of the events (analogous to the continuum rate-limiting step approximation), and accurate ensemble averages can be obtained through time averaging. For example, in the single-site adsorption–desorption process introduced previously, successive adsorptions and desorptions are correlated. Nevertheless, a Poisson process can be constructed consisting of one of the events, e.g., adsorption occurring with a rate $r_A(1-\theta)$. The criterion of a random selection of lattice sites for potential events prevents correlations from developing among specific sites and is usually achieved by utilization of an adequate random number generator. In certain applications, the intersite correlations induced by an inadequate random number generator may lead to erroneous results.[22] The selection of an appropriate random number generator is, therefore, an issue requiring careful consideration.

Thus, through the example of the lattice gas, we have outlined the basic elements comprising a formalism through which Monte Carlo simulations may be utilized to simulate dynamical phenomena within the context of the lattice-gas model. We have utilized this methodology to simulate the adsorption–desorption algorithm of Fig. 1. Simulations were run on 128×128 square lattices with $r_A = 1.0$ (site s)$^{-1}$ and $r_D = 2.0$ (site s)$^{-1}$. Transition probabilities were defined by normalization of each rate by the rate of desorption (i.e., $W_A = 1/2$, $W_D = 1.0$). Figure 2 depicts the fractional surface coverage of adsorbate as a function of time for an initially empty surface for both the transient analytical (exact) solution of Eq. (13) and the Monte Carlo simulation. The Monte Carlo curve is the result of one run

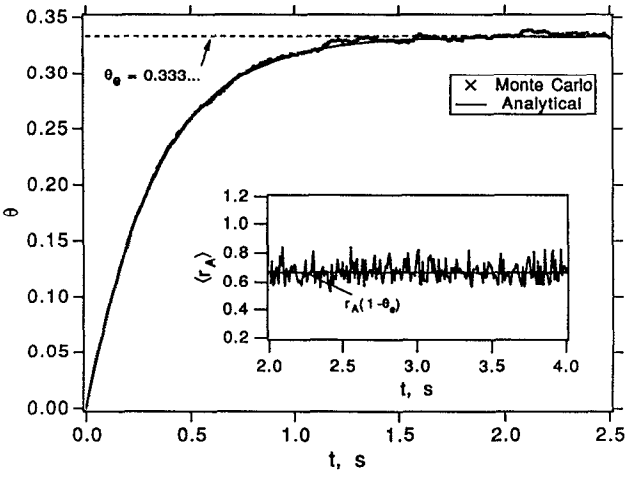

FIG. 2. The transient solution of Eq. (12) for the initial condition of an empty surface [$\theta(t=0)=0$] provided by both the analytical form of Eq. (13) and the Monte Carlo algorithm of Fig. 1 with $r_A = 1.0$ (site s)$^{-1}$ and $r_D = 2.0$ (site s)$^{-1}$ ($W_A = 1/2$ and $W_D = 1$). The inset depicts the rate of adsorption measured from the Monte Carlo simulation at steady-state and the continuum steady-state rate.

only. There is excellent agreement between the two solutions in the approach to equilibrium and the steady-state fractional surface coverage. The inset of Fig. 2 depicts both the analytical (exact) and Monte Carlo steady-state rate of adsorption (desorption). The rate of adsorption on a per site basis was measured as the reciprocal of the variable amount of time Δt required for 50 adsorption events (i.e., $r_A = 50/N\Delta t$, and N is the size of the lattice). It can be seen that this rate fluctuates about the predicted continuum rate of $r_A = 0.666...(\text{site s})^{-1}$. Of course, the amplitude of the fluctuation depends on the number of events averaged. The mean rate measured from the simulation over the depicted time interval of 2.0 s was 0.67 ± 0.06 adsorptions/site/s.

IV. GENERAL APPLICABILITY OF THE FORMALISM

Monte Carlo simulations are preferable to macroscopic continuum approaches whenever structural or configurational properties of a system arise which cannot be approximated analytically with a reasonable degree of accuracy. Such spatial organization occurs in a surprising number of simple systems[2,23–27] in which molecules may be considered effectively to be hard spheres and potential energy surfaces are otherwise uniform. In systems such as these, the identification of characteristic time scales and their incorporation into a dynamical Monte Carlo algorithm is accomplished through a straightforward extension of the methodology. Hence, direct and unambiguous comparison of simulation results to theory is possible. Perhaps dynamical Monte Carlo simulations will be of the greatest utility when they are linked in a hierarchy with *ab initio* quantum mechanics and molecular dynamics to model the dynamics of systems of molecules which interact with one another. When concentration-dependent potential energy surfaces have been delineated, events can be defined as a molecule's crossing the saddle point between two potential energy minima and the subsequent redefinition of the potential energy surface (due to the local shift in concentration) which existed prior to barrier crossing. Average rate coefficients for barrier crossing of molecules in all possible configurations of the system can be calculated (for a lattice gas with localized interactions extending only a few molecular diameters, the number of distinct transitions will be limited) and incorporated into a dynamical Monte Carlo simulation aimed at discernment of global characteristics of the full system. Such calculations involving semiempirical assumptions regarding the dependence of the rate of barrier crossing on local concentration through localized interactions have been of utility in the insight they have provided to thermal desorption,[28–32] the dynamics of surface reactions,[28,33–39] and diffusion.[1–4,6,7,28,40,41]

The methodology may now be generalized. Let us consider a system comprised of N species which, considering all possible spatial arrangements of the system and corresponding changes in the distribution of transition rates, are capable of undergoing k transition events. The k transition events are characterized by rates $\mathbf{R} \equiv \{r_1, r_2, ..., r_k\}$, which are formulated to be consistent with average dynamics of barrier crossing on some form of potential energy surface. The N species can be partitioned among the various possible transition events as $\mathbf{N} \equiv \{n_1, n_2, ..., n_k\}$, where n_i is the number of species capable of undergoing a transition with a rate r_i and

$$N = \sum_{i=1}^{k} n_i. \tag{26}$$

Thus, a particular configuration of the system at a particular time can be characterized by the distribution of $\mathbf{N}$ over $\mathbf{R}$. This distribution is constructed by a Monte Carlo algorithm which selects randomly among various possible events available at each time step and which effects the events with appropriate transition probabilities $\mathbf{W} \equiv \{w_1, w_2, ..., w_k\}$. The transition probabilities should be constructed in terms of $\mathbf{R}$ so that detailed balance is achieved at thermal equilibrium *and* a "dynamical hierarchy," as expressed in Eq. (18), of transition rates is preserved away from equilibrium. If a sufficiently large system is utilized to assure that the independence of various events is achieved, then the Monte Carlo algorithm effectively simulates the Poisson process, and the passage of real time can be maintained in terms of $\mathbf{R}$ and $\mathbf{N}$. To accomplish this, at each trial i at which an event is realized, time should be updated with an increment τ_i selected from an exponential distribution, i.e.,

$$\tau_i = -\frac{1}{\sum_i n_i r_i} \ln (U), \tag{27}$$

where U is a uniform random number between 0 and 1. This procedure should ensure that a direct and unambiguous relationship between Monte Carlo time and real time is established.

V. CONCLUSIONS

In conclusion, we have outlined the basic elements comprising a self-consistent dynamical interpretation of the Monte Carlo method. We have shown that if three criteria are met, namely, if (1) a dynamical hierarchy of transition probabilities is created which also satisfies the detailed-balance criterion; (2) time increments upon successful events are calculated appropriately; and (3) the effective independence of various events comprising the system can be achieved, then Monte Carlo methods simulate a Poisson process, and both static and dynamic properties of model Hamiltonian systems may be obtained and interpreted consistently. We have demonstrated the methodology through the example of the approach to and the attainment of Langmuirian adsorption equilibrium and discussed extension of the methodology to systems of interacting species. We anticipate that dynamical Monte Carlo simulations will continue to be a valuable tool in the development of statistical mechanical theory and in modeling applications. The formalism which we have proposed should, henceforth, eliminate any ambiguity surrounding the conduction and the interpretation of dynamical Monte Carlo simulations.

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