Derivation of the residence time for kinetic Monte Carlo simulations

Clinton DeW. Van Siclen
Idaho National Laboratory, Idaho Falls, Idaho 83415, USA
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I. INTRODUCTION

In a kinetic Monte Carlo (kMC) simulation, a model system is moved from state to state according to probabilistic rules. A nice example is adatom diffusion on a surface: in this case the “system” is the adatom plus surface, and a “state” has the adatom at a particular surface site. The probabilistic rules for moving the adatom from one site to another (i.e., the jump rates) are obtained from molecular dynamics (MD) calculations, which give the energy barriers over which the moves occur. Subsequently, a separate kMC simulation moves the adatom from site to site over the surface, and thereby enables calculation of the adatom diffusion coefficient, \( D \), from distance \( x \) traveled by the adatom over the time interval \( t \).

This example is typical in that the kMC simulation gives a macro- or mesoscopic quantity of interest (in this case the adatom diffusion coefficient), using information obtained from the microscopic or atomic scale. In fact, molecular dynamics calculations alone are impractical for simulating adatom diffusion over a surface: the adatom at room temperature attempts a jump every \( 10^{-13} \) seconds, while it is successful once every \( 10^{-5} \) seconds (so in MD simulations it is the numerous unsuccessful attempts at many sites, rather than the rare successful one, that enables the energy landscape to be mapped and jump rates determined).

The great virtue of the kMC method is that it enables simulation of physical processes that involve very disparate time scales. It is then essential that the actual time in the physical system be correctly reproduced by the residence times in the states of the model system, or equivalently, by the time between events in the model system.

While equivalent statements, the different semantics suggests the ability of the kMC method to obtain properties of an equilibrium system as well as to model the dynamic evolution of a non-equilibrium system. In the case of equilibrium systems, each state may be visited many times, so that the residence times in the states are proportional to the equilibrium populations of the physical states (for example, the adatom on a finite surface may be found at sites in proportion to the residence times at the corresponding states in the model system).

More generally the kMC method is used to model the evolution of a non-equilibrium system (that is, where a state once left can never be returned to), so this case will motivate the derivation of the residence time presented below. However, the mathematics apply to equilibrium systems as well, as will be made apparent at the end of the derivation.

II. DERIVATION OF THE RESIDENCE TIME

Consider a collection \( \{j\} \) of elements, where each element \( j \) has an expected lifetime \( \tau_j \). The kMC method follows from the assumption that the values \( \{\tau_j\} \) are time-independent (i.e., that the transition rates \( \{\tau_j^{-1}\} \) from the current state to accessible states are time-independent). Then the probability \( p_j(t)dt \) that the particular element \( j \) will fail during the infinitesimal time interval \( [t, t + dt] \) is given by the probability that element \( j \) will not fail prior to time \( t \), multiplied by the probability \( \tau_j^{-1}dt \) that it will fail during the subsequent time interval \( dt \); that is,

\[
p_j(t)dt = \left[ 1 - \int_0^t p_j(t')dt' \right] \frac{dt}{\tau_j}. \tag{1}
\]

This equation simplifies to

\[
p_j(t) = \left[ 1 - \int_0^t p_j(t')dt' \right] \frac{1}{\tau_j}. \tag{2}
\]

Taking the derivative of each side of Eq. (2) with respect to \( t \) and integrating produces the exponential probability density function (PDF)

\[
p_j(t) = \frac{1}{\tau_j} \exp \left[ -\frac{t}{\tau_j} \right]. \tag{3}
\]

Specifically, \( p_j(t) \) is the distribution of failure times for element \( j \); the average value of the failure time is \( \langle t_j \rangle = \int_0^\infty t p_j(t)dt = \tau_j \).

To perform a simulation, we need to randomly select a time \( t \) from this distribution. The formula for converting
a random number $x$ taken from the uniform probability distribution $P(x) = 1$ (such $x$ values are produced by the standard random number generators) to the corresponding $t$ value is derived as follows. The probabilities $p(t) \, dt$ and $P(x) \, dx$ must be equal, so $p(t) \, dt = dx$. Thus

$$x(t) = \int_0^t p(t') \, dt' = 1 - \exp \left[ -\frac{t}{\tau_j} \right]. \quad (4)$$

Inverting this expression then gives the desired relation between $x$ and $t$,

$$t = \tau_j [-\ln(1 - x)] \quad (5)$$

with $x$ randomly chosen from the interval $[0, 1]$.

In this way we get the set $\{t_j\}$ of element failure times. If the elements $\{j\}$ are completely independent of one another, they fail according to the time ordering of the set $\{t_j\}$.

If, however, the elements are not independent, the remaining values $\{\tau_j\}$ are altered with each failure. Consider that the smallest member of the set $\{t_j\}$ is $T_1$, so the first element to fail does so at time $T_1$. Which is the next element to fail, and when does that occur? If element $j$ is still functioning at time $T_1$, the PDF

$$p_j(t - T_1) = \frac{1}{\tau_j} \exp \left[ -\frac{(t - T_1)}{\tau_j} \right] \quad (6)$$

where $\tau_j'$ is the new lifetime of element $j$ for time $t > T_1$.

Equation (6) gives the distribution of times $t > T_1$ at which element $j$ fails, or equivalently, the distribution of time intervals $\Delta t \equiv t - T_1$ at the end of which element $j$ fails. As above, a value $\Delta t$ may be randomly chosen from this distribution by use of the relation

$$\Delta t = \tau_j' [-\ln(1 - x)] \quad (7)$$

where $x \in [0, 1)$. Thus the next element to fail is that producing the smallest member of the set $\{\Delta t_j\}$.

An alternative approach to simulating the system evolution is to randomly choose the next element to fail according to the set of probabilities $\{\tau^{-1}_k / \sum_j (\tau^{-1}_j)\}$, where element $k$ is one of the set $\{j\}$, $\tau^{-1}_k / \sum_j (\tau^{-1}_j)$ is the probability that element $k$ is the next to fail, and the sum is over all $N$ currently surviving elements $j$ (remember that the values $\{\tau_j\}$ may change after every failure). This failure occurs at the end of the time increment $\Delta t$, that may be taken to be the average value of the smallest innumerable member of the set $\{\Delta t_j\}$ (were the set to be calculated innumerable times),

$$\Delta t = \left\langle \Delta t_k \frac{\tau^{-1}_k}{\sum_j \tau^{-1}_j} \right\rangle = \frac{1}{N} \sum_{k=1}^N \Delta t_k \frac{\tau^{-1}_k}{\sum_j \tau^{-1}_j}$$

$$= \frac{1}{N} \sum_k \left[ -\ln(1 - x_k) \right] \left[ -\ln(1 - x_k) \right] \frac{\tau^{-1}_k}{\sum_j \tau^{-1}_j}$$

$$= \frac{1}{\sum_j \tau^{-1}_j}. \quad (8)$$

A different expression for $\Delta t$ may be found by noting that the probability $p(\Delta t) \, dt$ that the next element to fail will do so during the infinitesimal time interval $[\Delta t, \Delta t + dt]$ is

$$p(\Delta t) \, dt = \sum_{j=1}^N \left\{ p_j(\Delta t) \, dt \prod_{k(\neq j) = 1}^N \left[ 1 - p_k(\Delta t) \right] \right\} \quad (9)$$

where the content of the curly brackets is the probability that element $j$ will fail during the infinitesimal time interval $[\Delta t, \Delta t + dt]$, multiplied by the probability that no other element will fail during $\Delta t$. Then

$$p(\Delta t) = \sum_{j=1}^N \left\{ \frac{1}{\tau_j} \exp \left[ -\frac{\Delta t}{\tau_j} \right] \prod_{k(\neq j) = 1}^N \exp \left[ -\frac{\Delta t}{\tau_k} \right] \right\}$$

$$= \sum_{j=1}^N \left\{ \frac{1}{\tau_j} \exp \left[ -\Delta t \sum_{k=1}^N \tau^{-1}_k \right] \right\}$$

$$= \left( \sum_{j=1}^N \tau^{-1}_j \right) \exp \left[ -\Delta t \sum_{j=1}^N \tau^{-1}_j \right]. \quad (10)$$

As above, a value $\Delta t$ may be randomly chosen from this distribution by use of the relation

$$\Delta t = -\ln(1 - x) \frac{1}{\sum_j \tau^{-1}_j} \quad (11)$$

where $x \in [0, 1)$. The average value is given by Eq. (8), as expected.

The evolution of the system of elements is thus accomplished by selecting an element to fail, and incrementing time accordingly. With each failure the system enters a new state; obviously it cannot return to any old states. For this reason it has been convenient to use the set of “lifetimes” $\{\tau_j\}$ corresponding to the surviving elements $j$, rather than the set of transition rates $\{k_{i\to j}\}$ for transitions from the current state $i$ to the accessible states $j$ (the system will enter state $j$ if element $j$ is the next to fail). The connection between the sets is made by noting that $\sum_j \tau^{-1}_j = \sum_j k_{i\to j}$, where the system is currently in state $i$ in either case.

By making this replacement in the denominators of Eqs. (8) and (11), those equations for $\Delta t$ may be used for equilibrium systems (where the set of states and transition rates between states don’t change) as well. More generally, $\tau_j$ in the equations above may be replaced by $k^{-1}_{i\to j}$ when it is understood that the system is currently in state $i$.

For computational efficiency, it is most typical for a simulation to select the transition from current state $i$ according to the set of probabilities $\{k_{i\to j} / \sum_j k_{i\to j}\}$ and calculate the transition time interval $\Delta t$ using either Eq. (8) or (11), rather than to calculate the set $\{\Delta t_j\}$ from the relation $\Delta t_j = k^{-1}_{i\to j} [-\ln(1 - x)]$ and choose the destination state $j'$ from the smallest of those values. When
the distribution of simulation completion times is desired (for example, the time at which all elements have failed), it is necessary to perform a large number of nominally identical simulations, using Eq. (11) rather than Eq. (8) for every transition time interval $\Delta t$. (Note that this distribution will converge to a Gaussian distribution, according to the central limit theorem.)

Moreover, evolution of a dynamic system is not described by a set $\{k_{i\rightarrow j}\}$ of time-independent rate constants. In this case there is no set of probabilities $\{k_{i\rightarrow j'}/\sum_j k_{i\rightarrow j}\}$ from which to select the destination state $j'$. However, a set $\{t_j\}$ of transition times can still be calculated from a PDF, giving the sequence of events from an initial time. For example, consider that the distribution of failure times for element $j$ is given by the two-parameter ($\gamma$ and $\tau$) Weibull distribution

$$p(t) = \gamma t^{\gamma-1} \exp\left[-\left(\frac{t}{\tau}\right)^\gamma\right]$$  \hspace{1cm} (12)

rather than by Eq. (3). For $\gamma > 1$ this PDF decays faster than exponentially and so might be appropriate for an element that “ages”, or accumulates damage over time. (Indeed, the probability $\pi(t)dt$ that the element, having survived to time $t$, will immediately fail is $\gamma(t^{-1}/\tau)dt$, meaning that the probability of immediate failure increases with time.) The first and second moments of this distribution are, respectively,  

$$\langle t \rangle = \tau \frac{1}{\gamma} \Gamma \left(\frac{1}{\gamma}\right)$$  \hspace{1cm} (13)

and

$$\langle t^2 \rangle = \tau^2 \frac{2}{\gamma} \Gamma \left(\frac{2}{\gamma}\right)$$  \hspace{1cm} (14)

where $\Gamma$ is the Gamma function. The counterpart to Eq. (8) is

$$x(t) = \int_0^t p(t')dt' = 1 - \exp\left[-\left(\frac{t}{\tau}\right)^\gamma\right],$$  \hspace{1cm} (15)

so the failure time for element $j$ is

$$t_j = \tau_j \left[-\ln(1-x)\right]^{1/\gamma_j}$$  \hspace{1cm} (16)

where $x \in [0,1]$. If the parameter values $\{\gamma_j, \tau_j\}$ change with each element failure (reflecting, say, more rapid aging), the PDFs $\{p_j(t)\}$ given by Eq. (12) change accordingly. To calculate a new set $\{t_j\}$ of transition times following an element failure at time $T$, we note that $x$ and $t$ must be related by

$$\int_{x(T)}^x dx' = \int_0^t p(t')dt'$$  \hspace{1cm} (17)

where the lower limit $x(T) = 1 - \exp[-(T/\tau')^{\gamma'}]$ is obtained from Eq. (15), and $\gamma'$ and $\tau'$ are the parameter values for $t > T$. Then the counterpart to Eq. (11) is

$$x(t) = x(T) + \exp\left[-\left(\frac{T}{\tau'}\right)^{\gamma'}\right] - \exp\left[-\left(\frac{t}{\tau'}\right)^{\gamma'}\right]$$

$$= 1 - \exp\left[-\left(\frac{t}{\tau'}\right)^{\gamma'}\right]$$  \hspace{1cm} (18)

so the failure time for element $j$ is

$$t_j = \tau_j \left[-\ln(1-x)\right]^{1/\gamma_j}$$  \hspace{1cm} (19)

where $x \in [x(T), 1)$.

III. DISCUSSION

In physics and materials research, the kMC method is most often used for simulation of non-deterministic, thermally activated processes, as these give time-independent rate constants (time-independent probabilities) for transitions between states. A similar, but more complex, example to the adatom diffusion calculation mentioned in the Introduction is diffusion of vacancies and interstitial atoms in a grain boundary \[3\], where the transitions between states may occur by very complex mechanisms (for example, by concerted motion of atoms). However the rates $k$ are of the simple form

$$k_{i\rightarrow j} = \nu \exp\left[-\frac{E_m}{k_B T}\right]$$  \hspace{1cm} (20)

where $E_m$ is the energy barrier between the initial state $i$ and the final state $j$ (which the system may overcome with thermal energy supplied by local temperature fluctuations), $k_B$ is the Boltzmann constant, $T$ is the average temperature of the system, and $\nu$ is the frequency with which the system attempts to make the transition. The latter quantity gives the time scale for the microscopic process, that is needed for the kMC simulation.

Besides its natural application to atomic-scale processes, the kMC method has been used to simulate the time-dependent damage and failure of material under stress. For example, Curtin et al. \[2\] considered a spring network model where the rate $r$ of failure at site $j$ is

$$r_j(t) = A\sigma_j(t)^\eta$$  \hspace{1cm} (21)

where $\sigma_j(t)$ is the local stress at time $t$, and the exponent $\eta > 1$ ensures a nonlinear relationship between damage rate and stress as is the case for creep. The time between failures was calculated by Eq. (8), after which all the local stresses $\{\sigma_j\}$ and failure rates $\{r_j\}$ were recalculated. In contrast, Harlow et al. \[3\] considered a polycrystal under stress, and randomly chose, from a probability distribution that included the local stress as a parameter, a time-to-failure $t_j$ for each grain boundary facet $j$. Then
time was advanced by the amount of the smallest member of the set \( \{t_j\} \), the load supported by that failed facet was redistributed to adjacent facets, and a new set \( \{t_j\} \) was obtained from new distributions. In a similar way Andersen and Sornette [4] considered a fiber rupture model where failure of each fiber affected the failure-time probability distributions for the remaining fibers.

Effective use of the kMC method obviously requires that all important states of the system, and all important transitions between them, be identified. How to ensure this, and other technical and computational (i.e., practical) issues are addressed in a review by Voter [5]. Another problem is presented by “basins” of states, which are subsets of mutually accessible states from which escape is a very rare event. This of course defeats the purpose of the kMC method. However Van Siclen [6] has recently shown how to calculate the residence time for a system trapped in a basin, under the assumption that the system has equilibrated in the basin (which is to say, there is no correlation between the entry and exit states).

To conclude, the kinetic Monte Carlo method is a powerful technique for simulating the dynamics or evolution of non-deterministic systems. Thus it should have applications beyond the physical sciences, for example to biology, ecology, risk assessment, and finance.

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