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2007 J. Phys.: Condens. Matter 19 072201

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Stochastic method for accommodation of equilibrating basins in kinetic Monte Carlo simulations

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Received 19 October 2006, in final form 27 November 2006

Published 2 February 2007

Online at stacks.iop.org/JPhysCM/19/072201

Abstract

A computationally simple way to accommodate ‘basins’ of trapping states in standard kinetic Monte Carlo simulations is presented. By assuming that the system is effectively equilibrated in the basin, the residence time (time spent in the basin before escape) and the probabilities for transitions to states outside the basin may be calculated. This is demonstrated for point defect diffusion over a periodic grid of sites containing a complex basin.

The kinetic Monte Carlo (kMC) method is used to evolve atomistic systems *dynamically* from state to state over timescales much longer than can be achieved in molecular dynamics simulations [1, 2]. The method utilizes a catalogue of state-to-state transition rates obtained from atomistic (dynamic or static) calculations, to determine probabilistically a sequence of states (and their residence times) that closely resembles the actual system dynamics. The computational efficiency of the kMC method is due to the neglect of details: the system is simply moved from one distinct state to another, and the time clock is advanced accordingly. However, it may be that the set of transition rates is such as to equilibrate the system in a subset of mutually accessible states, from which escape is a very rare event. This situation of course reduces the efficiency of the method greatly. Here we present a simple means to accommodate such equilibrating basins in the standard kMC approach for the case of defect diffusion in solids or on surfaces. In fact the basin is regarded as just another accessible defect site with a characteristic residence time. This is only possible when the defect is considered to have equilibrated in the basin (that is, all sites in the basin have been visited many times), so its entry and exit points are uncorrelated. This treatment of equilibrating basins will be particularly useful for kMC simulations of defect diffusion in nanocrystalline materials, where the diffusion coefficients for the defect in the grain boundaries and the crystalline grains may differ by many orders of magnitude [3], and of radiation damage in solids, where microstructure evolution (driven by defect diffusion) over very long timescales is of interest.

In a kMC simulation of defect diffusion, the defect moves over a regular or irregular grid of sites (representing the potential wells that can accommodate the defect) according

to probabilistic rules. The diffusion coefficient D is then obtained in the usual way: $D = \langle x^2 \rangle / (2dt)$, where x is the defect displacement over the time t , and d is the dimension of the space. Typically, the residence times associated with moves from visited sites are summed until the required time interval t is completed. But for purposes of this derivation, it is necessary also to regard t as the sum of the *accrued* residence times at the visited sites. This is because those accrued times, for sites in the basin, are proportional to the equilibrium defect concentrations there. Also, for purposes of the derivation, it is convenient to use the term ‘periphery site’ for those sites in the basin from which the defect can move out of the basin. With this terminology set, we obtain expressions for the probability p_i of escape from the basin via the particular periphery site i , and for the residence time t_{basin} associated with a visit by the defect to the basin.

Consider a defect at periphery site i . With each move from site i , the accrued residence time for that site increases by an (average) amount $\tau_i = (\sum_{b(i)} k_{i \rightarrow b(i)} + \sum_{q(i)} k_{i \rightarrow q(i)})^{-1}$, where the two sums are over all transition rates from site i to accessible sites $b(i)$ within the basin and to accessible sites $q(i)$ outside the basin, respectively. The probability that it will escape the basin on that move is $\epsilon_i = (\sum_{q(i)} k_{i \rightarrow q(i)}) \tau_i$; thus on average one of every ϵ_i^{-1} visits by the defect to site i will result in an escape. In that event, the residence time $t_i^e \equiv \tau_i \epsilon_i^{-1} = (\sum_{q(i)} k_{i \rightarrow q(i)})^{-1}$, on average, has accrued to site i . It is noteworthy that t_i^e is a function only of the rates $k_{i \rightarrow q(i)}$ out of the basin.

Of course, the basin may contain many periphery and interior sites. As the defect moves within the basin, it produces an increasingly accurate set $\{t_k / \langle t_k \rangle\}$ of *relative* residence times, where the sites k are in the basin (periphery and interior) and the average (indicated by the angle brackets) is taken over all sites in the basin. In fact the elements $t_k / \langle t_k \rangle$ approach the values $c_k / \langle c_k \rangle$, where c_k is the equilibrium defect concentration at site k that is routinely obtained in molecular dynamics and statics calculations (c_k is an exponential function of the defect formation energy at site k). During the time $T = \sum_k t_k$, the number of visits by the defect to site i is t_i / τ_i . Since the probability that a particular visit will *not* lead to an escape from the basin is $(1 - \epsilon_i)$, the *a priori* probability that the defect does *not* escape from the basin via site i during the time interval T is $(1 - \epsilon_i)^{t_i / \tau_i}$. Then the *a priori* probability that the defect *does* escape the basin via site i during the time interval T is $1 - (1 - \epsilon_i)^{t_i / \tau_i} \approx (t_i / \tau_i) \epsilon_i$ for $\epsilon_i \ll 1$. This equals t_i / t_i^e when the definition $t_i^e \equiv \tau_i \epsilon_i^{-1}$ is used. Thus the probability p_i that the defect escapes the basin from periphery site i rather than from another periphery site is given by

$$p_i = (t_i / t_i^e) \left(\sum_j (t_j / t_j^e) \right)^{-1} \quad (1)$$

where the sum is over all periphery sites j . Substituting into equation (1) the expression for t_i^e gives

$$p_i = t_i \sum_{q(i)} k_{i \rightarrow q(i)} \left[\sum_j \left(t_j \sum_{q(j)} k_{j \rightarrow q(j)} \right) \right]^{-1}. \quad (2)$$

As is evident from this last equation, the escape from periphery site i out of the basin would be to site q' with probability $p_{i \rightarrow q'} = k_{i \rightarrow q'} (\sum_{q(i)} k_{i \rightarrow q(i)})^{-1}$, where site q' is one of the set $\{q(i)\}$. That is, a defect trapped in the basin will escape via periphery site i to site q' (outside the basin) with probability $P_{i \rightarrow q'} = p_i p_{i \rightarrow q'}$.

The long-term, average behaviour of the defect is thus reproduced by the standard kMC method, with the addition that, if the defect enters the basin, on its next move it escapes the basin from a periphery site chosen in accordance with the probability distribution implied by

equation (2). The residence time t_{basin} associated with this move is given by the relation

$$t_{\text{basin}} = \sum_j t_j^e p_j + \sum_k t_k (t_j^e p_j / t_j) \quad (3)$$

where the first sum is over all *periphery* sites j , and the second sum is over all basin *interior* sites k . The second sum accounts for the time the defect spends at interior sites, which in the case of a particular interior site k equals the ratio t_k/t_j of time spent by the defect at site k to time spent at an arbitrarily chosen periphery site j , multiplied by the average time $t_j^e p_j$ spent at site j during a visit by the defect to the basin (note that the ratio $t_j^e p_j / t_j$ is identical for all periphery sites j). The simplest example demonstrating equation (3) is that of a basin comprised of n *identical* periphery sites (that is, the probability p_j of escaping the basin via a particular periphery site is $1/n$, and all t_j^e equal the ‘lifetime’ t^e) and no interior sites. Clearly the average residence time in the basin per visit by the defect is t^e , so the average residence time in each periphery site per visit to the basin must be t^e/n , which equals $t_j^e p_j$ as expected.

By use of equation (2) for p_j , equation (3) may be rewritten as

$$t_{\text{basin}} = \sum_k t_k \left[\sum_j \left(t_j \sum_{q(j)} k_{j \rightarrow q(j)} \right) \right]^{-1} \quad (4)$$

where now the sum is over *all* (periphery *and* interior) basin sites k . As discussed above, the ratio t_k/t_j may be replaced by c_k/c_j . Thus the equilibrating basin is accommodated by addition of the set $\{P_{i \rightarrow q(i)}\}$ of probabilities for moves out of the basin, and the residence time t_{basin} , to the kMC catalogue of transition rates.

It may be noted that the derivation of equation (1) relies on the use of the *average* value (called τ above) for the time that accrues to a basin site with each visit by the defect prior to escape. In conventional kMC simulations, the time may alternatively be advanced by an amount Δt taken randomly from the exponential distribution $\tau^{-1} \exp(-\Delta t/\tau)$; that is, by the amount $\Delta t = \tau(-\ln z)$ where z is chosen randomly from the interval (0, 1]. Thus it is possible in the latter case to calculate the higher moments of the escape time from the basin as well as the average time t_{basin} . Of course, the method developed here for handling deep basins in kMC simulations presupposes that calculation of an accurate distribution of basin escape times (whether desired or not) is not computationally feasible. In this event, it is recommended (for consistency) that *average* values τ , rather than variable values Δt , be used to accrue time to sites outside the basin. This should not affect the average value $\langle x^2 \rangle$ obtained for a specified diffusion time t , that is needed to calculate the defect diffusion coefficient D .

This method of handling a set of connected states may be contrasted with that of Novotny [4], who applies the finite Markov chain formalism [5]. The basin sites are therefore *transient* states, and the sites to which the defect moves out of the basin are *absorbing* states. All transition probabilities connecting transient states, and connecting transient states with absorbing states, are elements in the Markov transition matrix \mathbf{M} . Then the formalism gives, for the defect in a specified initial transient state, (1) the mean number of times in each of the transient states before absorption, and (2) the probabilities for absorption in each of the absorbing states. (See [6] for a detailed example of how to use finite Markov chain theory to model stochastic physical systems.) The correlation between the entrance and exit points at the basin periphery is thus preserved at the expense of considerable mathematical and computational complication (e.g., a different matrix \mathbf{M} is needed for each of the possible initial states). That virtue is minor when the defect is essentially equilibrated in the basin before its escape, and in any event may be negated by the various sources of error (e.g., inaccurate transition rates) and the stochastic nature of the simulation. It should be emphasized that the

Markov approach requires that all transition rates between basin sites be available, while the present approach can alternatively use equilibrium defect concentrations.

Before applying the method to sample systems with complex basins, it is interesting to consider a very simple, one-dimensional system that can be solved analytically. This is a linear arrangement of four sites, labelled (in order) 1 through 4, where the transition rates $k_{2 \rightarrow 3}$ and $k_{3 \rightarrow 2}$ are much faster than the rates $k_{2 \rightarrow 1}$ and $k_{3 \rightarrow 4}$. Thus a defect will ‘flicker’ between sites 2 and 3 many times before escaping to site 1 or 4 [7]. The average behaviour of the defect in this system is easily calculated by use of the Markov formalism when sites 1 and 4 are regarded as absorbing states. In the event that the defect is initially at site 2, the analytic calculation produces the row vector

$$\beta = \frac{1}{p_{2 \rightarrow 1} + p_{2 \rightarrow 3}p_{3 \rightarrow 4}} (p_{2 \rightarrow 1} \quad p_{2 \rightarrow 3}p_{3 \rightarrow 4} \quad 1 \quad p_{2 \rightarrow 3})$$

where $p_{i \rightarrow j}$ is the probability for the defect at site i to move to site j (so, for example, $p_{2 \rightarrow 1} = k_{2 \rightarrow 1}/(k_{2 \rightarrow 1} + k_{2 \rightarrow 3})$); the elements β_1 and β_2 are the probabilities for absorption at site 1 and site 4, respectively; and the elements β_3 and β_4 are the mean number of times at sites 2 and 3, respectively, before absorption. The expressions for β_1 and β_2 have been obtained previously by Mason *et al* [7], by accounting for all possible numbers of flickers prior to escape from sites 2 and 3: for example, the probability that a defect initially at site 2 will escape to site 1 is $\sum_{n=0}^{\infty} (p_{2 \rightarrow 3}p_{3 \rightarrow 2})^n p_{2 \rightarrow 1} = p_{2 \rightarrow 1}/(1 - p_{2 \rightarrow 3}p_{3 \rightarrow 2})$, which equals β_1 .

In the event that the defect is initially at site 3, the corresponding calculation produces the row vector

$$\beta' = \frac{1}{p_{2 \rightarrow 1} + p_{2 \rightarrow 3}p_{3 \rightarrow 4}} (p_{3 \rightarrow 2}p_{2 \rightarrow 1} \quad p_{3 \rightarrow 4} \quad p_{3 \rightarrow 2} \quad 1).$$

Then the ‘averaged’ results are given by the row vector $\bar{\beta} = \chi_2\beta + \chi_3\beta'$, where χ_2 and χ_3 are relative concentrations at sites 2 and 3 that satisfy $\chi_2 + \chi_3 = 1$ and detailed balance, $\chi_2k_{2 \rightarrow 3} = \chi_3k_{3 \rightarrow 2}$. Note that this averaging removes any memory of the ‘initial’ defect site (that is, whether the defect entered from site 1 or from site 4). The averaged vector is

$$\bar{\beta} = \frac{1}{p_{2 \rightarrow 1} + p_{2 \rightarrow 3}p_{3 \rightarrow 4}} (\gamma_1 p_{3 \rightarrow 2}p_{2 \rightarrow 1} \quad \gamma_2 p_{2 \rightarrow 3}p_{3 \rightarrow 4} \quad \gamma_1 p_{3 \rightarrow 2} \quad \gamma_2 p_{2 \rightarrow 3})$$

where $\gamma_1 = 1 + k_{3 \rightarrow 4}(k_{2 \rightarrow 3} + k_{3 \rightarrow 2})^{-1}$ and $\gamma_2 = 1 + k_{2 \rightarrow 1}(k_{2 \rightarrow 3} + k_{3 \rightarrow 2})^{-1}$. This may be compared with the equivalent row vector \mathbf{B} constructed from the stochastic quantities derived above for an equilibrated basin:

$$\begin{aligned} \mathbf{B} &= \left(p_2 \quad p_3 \quad \frac{\chi_2 t_{\text{basin}}}{\tau_2} \quad \frac{\chi_3 t_{\text{basin}}}{\tau_3} \right) \\ &= \frac{1}{p_{3 \rightarrow 2}p_{2 \rightarrow 1} + p_{2 \rightarrow 3}p_{3 \rightarrow 4}} (p_{3 \rightarrow 2}p_{2 \rightarrow 1} \quad p_{2 \rightarrow 3}p_{3 \rightarrow 4} \quad p_{3 \rightarrow 2} \quad p_{2 \rightarrow 3}) \end{aligned}$$

which very closely resembles $\bar{\beta}$ when $p_{2 \rightarrow 3} \gg p_{2 \rightarrow 1}$ and $p_{3 \rightarrow 2} \gg p_{3 \rightarrow 4}$.

A more complex basin is represented in figure 1. This system is a periodically repeated (in both dimensions) 10×10 regular network of nodes (defect-accessible sites) connected by bonds (diffusion paths), where the ‘equilibrating basin’ is the subset of 34 nodes connected by the 40 thick bonds. Given the transition rates associated with each bond, it is a straightforward matter to obtain the defect diffusion coefficient by a kMC simulation.

Table 1 presents the diffusion coefficients calculated by the standard method (‘Exact’) and by the ‘basin’ method (‘Approximate’), and an estimate of the relative computation time needed in each case, for three different sets of transition rates. The first set (row 1) has $k_{i \rightarrow j} = 10 \exp(-(\mu_i - \mu_j))$ for the thick bonds and $k_{i \rightarrow j} = \exp(-(\mu_i - \mu_j))$ for the thin

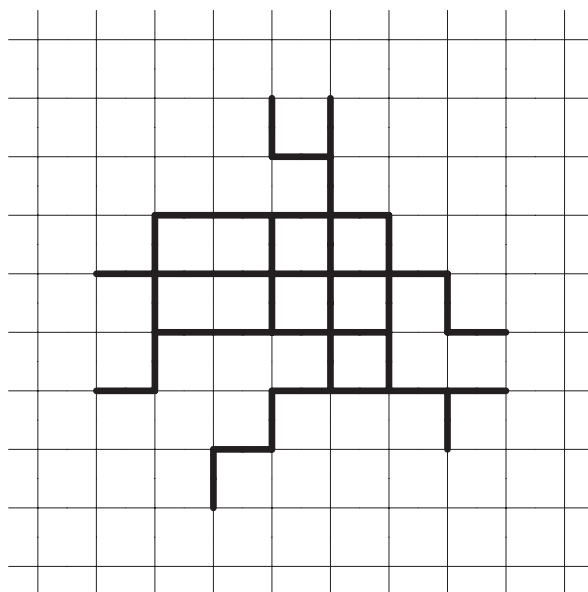


Figure 1. Representation of a system of trapping and non-trapping sites. Those sites (nodes) connected by the thick bonds comprise the ‘equilibrating basin’ in which the defect may be trapped for very long periods of time.

bonds, where the $\{\mu_i\}$ are chemical potentials assigned to the nodes with values taken randomly from the interval $[0, 1]$. The second set (row 2) is similar to the first set, but with the difference that the μ_i for nodes belonging to the basin are taken from the interval $[3, 4]$, so that the defect will segregate to the basin. The third set (row 3) is similar to the first set, but with the rates $k_{i \rightarrow j}$ for the thick bonds having the prefactor 1000 (instead of 10). With these transition rates, detailed balance is satisfied: $c_i k_{i \rightarrow j} = c_j k_{j \rightarrow i}$. The set $\{c_i\}$ is needed to calculate the probabilities $\{p_i\}$ and the residence time t_{basin} , and furthermore provides a nice check on the calculations (namely, the accrued residence time t_i at node i should be proportional to c_i). The values for the diffusion coefficient D are believed to be accurate to ± 1 in the last digit. In the last column, the ‘speed-up factor’ (due to use of the basin method) refers to the computational time needed to accomplish a given defect diffusion time t , not to the computational time needed to achieve a particular accuracy.

The large difference in D values in the first row of table 1 shows that the basin method does a poor job when the defect cannot equilibrate before escaping; that is, when there is a significant spatial correlation between the entry and exit points (in this case due to the small diffusivity contrast between regions, which does not sufficiently confine the defect to the basin). Otherwise, the diffusion coefficients obtained by assuming the defect to equilibrate in the basin are seen to be very comparable to the ‘exact’ values, while costing (potentially) orders-of-magnitude less computer time. Furthermore, the accrued residence times at the nodes (both inside and outside the basin) are in every case extremely close to their exact values (proportional to the $\{c_i\}$).

The results in table 1 give a general indication of the utility of the basin method. In particular, the method is accurate when the defect is essentially equilibrated in the basin. The extent to which this is the case may be determined by a conventional kMC simulation (where the basin method is not used): the set $\{t_k / \langle t_k \rangle\}$ of relative residence times for sites in the basin,

Table 1. Comparison of diffusion coefficients calculated by the kinetic Monte Carlo method. The transition rates for the paths represented by thick and thin bonds in figure 1 are given by $k_{i \rightarrow j}^{(\text{thick})}$ and $k_{i \rightarrow j}^{(\text{thin})}$, respectively. The μ_i are chemical potentials associated with the nodes that, for the purposes of this work, ensure that detailed balance is obeyed. The ‘Exact’ and ‘Approximate’ D are diffusion coefficients calculated in the standard manner, and with the set of trapping states treated as an equilibrating basin, respectively. The speed-up factor shows the computational advantage of the latter approach.

Transition rates	Exact D	Approximate D	Speed-up factor
$k_{i \rightarrow j}^{(\text{thick})} = 10 \exp[-(\mu_i - \mu_j)]$ $k_{i \rightarrow j}^{(\text{thin})} = \exp[-(\mu_i - \mu_j)]$ $\mu_i \in [0, 1]$	1.373	1.799	1.2
$k_{i \rightarrow j}^{(\text{thick})} = 10 \exp[-(\mu_i - \mu_j)]$ $k_{i \rightarrow j}^{(\text{thin})} = \exp[-(\mu_i - \mu_j)]$ $\mu_i^{(\text{basin})} \in [3, 4]$ $\mu_i^{(\text{non-basin})} \in [0, 1]$	0.0285	0.0287	3.1
$k_{i \rightarrow j}^{(\text{thick})} = 1000 \exp[-(\mu_i - \mu_j)]$ $k_{i \rightarrow j}^{(\text{thin})} = \exp[-(\mu_i - \mu_j)]$ $\mu_i \in [0, 1]$	1.79	1.799	81.0

obtained for a *single* visit by the defect to the basin, is compared with the set $\{c_k/\langle c_k \rangle\}$. The two sets are more or less identical for a defect that is more or less equilibrated in the basin.

In general the basin method gives an upper bound for the actual diffusion coefficient. This is due to its neglect of any spatial correlation between the entry and exit points at the basin periphery: the distance between these points is, on average, less when they are spatially correlated than when they are not. In either case the time spent in the basin per visit has average value t_{basin} (calculated according to the analytic expression above), so a higher value for the diffusion coefficient is obtained in the latter case. (That the average time spent in the basin per visit is t_{basin} in *both* cases is evident from the fact that a kMC simulation will produce a set $\{t_m/\langle t_m \rangle\} \approx \{c_m/\langle c_m \rangle\}$ (where now *all* sites m in the system—those outside the basin as well as those inside—are included), whether the basin method is incorporated in the kMC code or not.) A comparison of rows 1 and 3 in table 1 illustrates this point. The two systems with different sets of transition rates nonetheless possess (by design) identical sets $\{c_m\}$, $\{p_j\}$, and $\{k_{j \rightarrow q(j)}\}$, and identical basin residence time t_{basin} : this is the reason the two systems produce the same ‘Approximate’ value for the diffusion coefficient (1.799). But the defect in the first system (row 1) is not well equilibrated in the basin, causing an ‘Approximate’ value for D that is too high in that case.

As a final comment, it should be emphasized that this approach to accommodating such trapping basins (created by, for example, segregation or orders-of-magnitude differences in transition rates as considered in table 1) in kMC simulations gives increasingly accurate results as the degree of confinement increases, which is precisely the situation where kMC simulations are, in the absence of this approach, increasingly inefficient and inaccurate.

This work was supported in part by the INL Laboratory Directed Research and Development Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

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