Kinetic Monte Carlo Perturbation Analysis for Adsorption Dynamics

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1. Introduction

The kinetic Monte Carlo (KMC) method can provide the exact dynamical evolution of a system over large timescale by simulating the individual transition events with incrementing time intervals appropriately.[1,2] Since Beeler's simulation of radiation damage annealing [3], KMC has been widely applied for analyses of material irradiation, gas surface interactions, statistical physics, etc. In the KMC simulations, the accuracy of numerical result depends on the reliability of transition data. The sensitivity analyses are useful to enhance the accuracy by ordering the transition data by importance and quantify the uncertainty of the KMC output and

The Monte Carlo (MC) perturbation methods [4] such as the differential operator sampling (DOS) and the correlated sampling have been successfully applied for the sensitivity calculations [5,6] in the MC particle transport analyses. In this paper, I derive the Neumann series formulation corresponding to the KMC solution and then the DOS formulations for the KMC perturbation calculations. The effectiveness of the developed formulations is investigated for the Langmuirian adsorption dynamics problem [7].

2. Derivation of KMC Perturbation Formulations

2.1 Mathematical Derivation of KMC Algorithm

Fichthorn and Weinberg [2] expressed a Master equation for KMC as

$$\frac{\partial P(\mathbf{X},t)}{\partial t} + k_{\mathbf{X}} P(\mathbf{X},t) = \sum_{\mathbf{X}'} k_{\mathbf{X}'\to\mathbf{X}} P(\mathbf{X}',t)\,; \qquad (1)$$

$$k_{\mathbf{X}} = \sum_{\mathbf{X}'} k_{\mathbf{X}\to\mathbf{X}'}\,, \qquad (2)$$

$$S(\mathbf{X},t) = \sum_{\mathbf{X}'} k_{\mathbf{X}'\to\mathbf{X}} P(\mathbf{X}',t)\,. \qquad (3)$$

$P(\mathbf{X},t)$ denotes the probability that a system is in state $\mathbf{X}$ at time t. $k_{\mathbf{X}'\to\mathbf{X}}$ means the probability per unit time that the system will undergo a transition from state $\mathbf{X}'$ to state $\mathbf{X}$ where $\mathbf{X}$ and $\mathbf{X}'$ are successive states of the system. An initial condition at t=0 can be given by

$$Q(\mathbf{X}) \equiv P(\mathbf{X},0) \qquad (4)$$

Then the solution of Eq. (1) with the initial condition of Eq. (4) can be expressed by

$$P(\mathbf{X},t) = e^{-k_{\mathbf{X}}t} Q(\mathbf{X}) + \int_0^t e^{-k_{\mathbf{X}}(t-t')} \cdot S(\mathbf{X},t')dt'\,. \qquad (5)$$

For the transition probability, Ψ, defined by

$$\Psi(\mathbf{X},t) \equiv k_{\mathbf{X}} P(\mathbf{X},t)\,, \qquad (6)$$

Eq. (5) can be written as

$$\Psi(\mathbf{X},t) = k_{\mathbf{X}} e^{-k_{\mathbf{X}}t} Q(\mathbf{X}) + \int_0^t k_{\mathbf{X}} e^{-k_{\mathbf{X}}(t-t')} \cdot S(\mathbf{X},t')dt'\,. \qquad (7)$$

By introducing the time-flight kernel, T, and the event kernel, C, defined by

$$T(t' \to t \mid \mathbf{X}) = k_{\mathbf{X}} e^{-k_{\mathbf{X}}(t-t')}\,, \qquad (8)$$

$$C(\mathbf{X}' \to \mathbf{X}) = \frac{k_{\mathbf{X}'\to\mathbf{X}}}{k_{\mathbf{X}'}}\,, \qquad (9)$$

Eq. (7) can be expressed as

$$\Psi(\mathbf{X},t) = \hat{Q}(\mathbf{X},t) + \int_0^t \sum_{\mathbf{X}'} K(\mathbf{X}',t' \to \mathbf{X},t)\Psi(\mathbf{X}',t')dt'; \qquad (10)$$

$$\hat{Q}(\mathbf{X},t) = T(0 \to t \mid \mathbf{X})Q(\mathbf{X})\,, \qquad (11)$$

$$K(\mathbf{X}',t' \to \mathbf{X},t) = T(t' \to t \mid \mathbf{X}) \cdot C(\mathbf{X}' \to \mathbf{X})\,. \qquad (12)$$

The solution of Eq. (10) can be expressed by the Neumann series solution [8]:

$$\Psi(\mathbf{X},t) = \sum_{j=0}^{\infty} \psi_j(\mathbf{X},t)\,; \qquad (13)$$

$$\psi_j(\mathbf{X},t) = \int_0^t dt_0 \sum_{\mathbf{X}_0} K_j(\mathbf{X}_0,t_0 \to \mathbf{X},t)\hat{Q}(\mathbf{X}_0,t_0)\,, \qquad (14)$$

$$\begin{aligned}
&K_0(\mathbf{X}_0,t_0 \to \mathbf{X},t) = \delta(\mathbf{X}_0 - \mathbf{X})\delta(t_0 - t),\\
&K_1(\mathbf{X}_0,t_0 \to \mathbf{X},t) = K(\mathbf{X}_0,t_0 \to \mathbf{X},t),\\
&K_2(\mathbf{X}_0,t_0 \to \mathbf{X},t) = \int_{t_0}^t dt_1 \sum_{\mathbf{X}_1} K(\mathbf{X}_1,t_1 \to \mathbf{X},t)K(\mathbf{X}_0,t_0 \to \mathbf{X}_1,t_1),\\
&\qquad\vdots\\
&K_j(\mathbf{X}_0,t_0 \to \mathbf{X},t) = \int dt_1 \sum_{\mathbf{X}_1} \cdots \int dt_{j-1} \sum_{\mathbf{X}_{j-1}}\\
&\quad \times K(\mathbf{X}_{j-1},t_{j-1} \to \mathbf{X},t)K(\mathbf{X}_{j-2},t_{j-2} \to \mathbf{X}_{j-1},t_{j-1}) \cdots K(\mathbf{X}_0,t_0 \to \mathbf{X}_1,t_1).
\end{aligned} \qquad (15)$$

From Eqs. (13) and (14), we can clearly see that the KMC algorithm is an sequence of samplings from the

probability distribution functions given by the time-flight kernel of Eq. (8) and the event kernel of Eq. (9).

2.2 DOS Formulation of KMC

In the KMC simulations, a system parameter to be analyzed, R, can be expressed as

$$R = \int \sum_{\mathbf{X}} r(\mathbf{X},t)\Psi(\mathbf{X},t)dt\,, \tag{16}$$

where $r(\mathbf{X},t)$ denotes the response function to R from the state $\mathbf{X}$ at t.

The insertion of the Neumann series solution of Eq. (13) into Eq. (16) gives

$$R = \sum_{j=0}^{\infty} \int \sum_{\mathbf{X}} r(\mathbf{X},t)\psi_j(\mathbf{X},t)dt\,. \tag{17}$$

From Eq. (17), the first order sensitivity of R to a input parameter α can be calculated by

$$U_1 = \frac{dR}{d\alpha} = \sum_j U_{1,j}\,; \tag{18}$$

$$\begin{aligned} U_{1,j} &= \frac{d}{d\alpha}\left[\int \sum_{\mathbf{X}} r(\mathbf{X},t)\psi_j(\mathbf{X},t)dt\right] \\ &= \int dt \sum_{\mathbf{X}} \cdot \int dt_0 \sum_{\mathbf{X}_0} \cdots \int dt_{j-1} \sum_{\mathbf{X}_{j-1}} u_{1,j}^{\mathrm{DOS}}(\mathbf{X}_0,t_0 \to \mathbf{X},t) \\ &\quad \times r(\mathbf{X},t)K(\mathbf{X}_{j-1},t_{j-1} \to \mathbf{X},t)\cdots K(\mathbf{X}_0,t_0 \to \mathbf{X}_1,t_1)\hat{Q}(\mathbf{X}_0,t_0), \end{aligned} \tag{19}$$

$$\begin{aligned} & u_{1,j}^{\mathrm{DOS}}(\mathbf{X}_0,t_0 \to \mathbf{X},t) \\ &= \frac{1}{r(\mathbf{X},t)}\frac{\partial r(\mathbf{X},t)}{\partial \alpha} \\ &\quad + \sum_{k=1}^{j} \frac{1}{K(\mathbf{X}_{k-1},t_{k-1} \to \mathbf{X}_k,t_k)} \frac{\partial K(\mathbf{X}_{k-1},t_{k-1} \to \mathbf{X}_k,t_k)}{\partial \alpha} \\ &\quad + \frac{1}{\hat{Q}(\mathbf{X}_0,t_0)}\frac{\partial \hat{Q}(\mathbf{X}_0,t_0)}{\partial \alpha}. \end{aligned} \tag{20}$$

By using the sensitivity calculated by Eq. (18), the variation of R due to a deviation of α, $\Delta\alpha$, can be estimated by

$$\Delta R \equiv R(\alpha+\Delta\alpha) - R(\alpha) \cong U_1 \cdot \Delta\alpha\,. \tag{21}$$

3. Numerical Results

The simplest adsorption scenario assumes direct, non-activated, random, and non-dissociative adsorption of non-interacting particles. Therefore the particle adsorbs only on free adsorption sites with a probability of S_0. This type of adsorption is called Langmuirian adsorption dynamics (LD) [7]. The flux of the impinging particles is assumed to be 1/sec for a 50×50 lattice area. In this LD problem with S_0 of 0.7, the change of the time-dependent adsorbed particle number, $\Delta N(t)$, due to a 20% change of S_0 is estimated by the derived DOS formulation for KMC.

Figure 1 shows the comparison between $N(t)$'s estimated by the perturbation method and the direct simulations with (S_0+ΔS_0) of 0.84. From the figure, we can see that the developed KMC perturbation method can remarkably well predict $N(t)$ for the perturbed system.

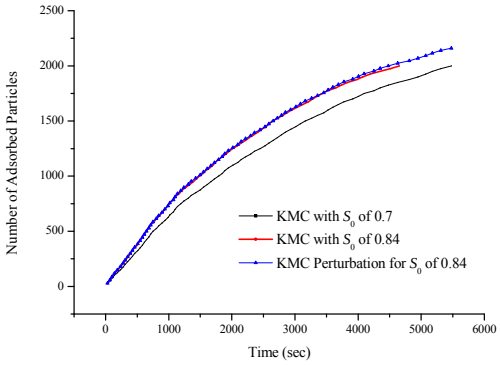

Fig. 1. Comparison of the numbers of adsorbed particles estimated by the KMC perturbation and the direct KMC

4. Conclusions

I have derived the mathematical formulation which governs the KMC simulations. Based on the derived Neumann series solution, I have developed the KMC perturbation method which can efficiently and accurately estimate the changes of design parameters due to the transition data changes. The developed KMC perturbation method can be applied for the sensitivity and uncertainty analyses for various KMC simulations.

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