

Stochastic-Difference-Equation Method for Long Time-scale Molecular Dynamics Simulations

Atsushi UCHIDA, Chieko TOTSUJI, Kenji TSURUTA, and Hiroo TOTSUJI
 Graduate School of Natural Science and Technology, Okayama University
 Tsushima-naka 3-1-1, Okayama 700-8530, JAPAN

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We present a Stochastic-Difference-Equation (SDE) approach to long time-scale molecular dynamics (MD) simulations, which are required for nanosecond-scale phenomena. In this method, the MD trajectory in a fixed time period is obtained as a stationary solution of an action functional based on an error accumulation of the equation of motion along the path, thus reducing the problem to a boundary-value problem, instead of an initial-value problem in the ordinary MD method. We apply the method to formation processes of Cu thin film via nanocluster deposition onto a substrate. The applicability of the SDE algorithm to the problem and the effects of the choice of SDE parameters on the optimization processes of configuration pathway are examined.

I. INTRODUCTION

Molecular Dynamics(MD) simulation plays important roles as a powerful tool for studying the complex many-body problems found not only in basic science but also in various engineering fields. Despite its usefulness, the MD method has been suffered from a limitation on timescale, especially in the cases for nanometer-scale phenomena. The short time step, such as on the order of femtosecond, is necessary to stabilize the numerical integration in many of MD simulations on materials. On the other hand, there are the fundamental processes that evolve as slowly as over hundreds of nanosecond. In such cases, unaffordable computation time for the simulations is required.

To overcome this limitation, numerous improvements are suggested[1][2]. In this paper, we employ the Stochastic-Difference-Equation (SDE[2][3][4]) method for a long time-scale simulation, and examine its applicability to a thin-film formation process which is a nanosecond-scale phenomenon.

II. BASIC FORMALISM

In the ordinary MD method, the Newton's equation-of-motion is solved numerically by the time discretization, as an initial value problem. The time step, Δt , has to be small enough to approximate the

differentiation in the equation-of-motion by a finite difference. The error vector, $\varepsilon(\varepsilon^x, \varepsilon^y, \varepsilon^z)$, involved in the estimation of time evolution of the coordinates is defined as

$$M_i \frac{\mathbf{R}_{i,k-1} + \mathbf{R}_{i,k+1} - 2\mathbf{R}_{i,k}}{\Delta t^2} + \frac{dU_k}{d\mathbf{R}_{i,k}} = \varepsilon_{i,k} \quad (1)$$

where M_i and $\mathbf{R}_i(R_i^x, R_i^y, R_i^z)$ are the mass and the coordinates of i th particle, respectively. k denotes an index of the time frame, and U represents the potential energy.

We define an action along a pathway as

$$S_c = \int_0^T dt \sum_{i=1}^n \left(M_i \frac{d^2 \mathbf{R}_i}{dt^2} + \frac{dU}{d\mathbf{R}_i} \right) \cdot \left(M_i \frac{d^2 \mathbf{R}_i}{dt^2} + \frac{dU}{d\mathbf{R}_i} \right), \quad (2)$$

where n is the number of particles. Here the two boundary points $\mathbf{R}_i(0)$ and $\mathbf{R}_i(T)$ are fixed.

In the discrete representation of the time integration in Eq. (2), the action can be written as

$$S = \sum_{k=1}^N \sum_{i=1}^n (\varepsilon_{i,k} \cdot \varepsilon_{i,k}), \quad (3)$$

where $N \equiv T/\Delta t$ is the total number of time steps. The essence of the SDE algorithm is based on the fact that in the limit of $N \rightarrow \infty$ the true trajectory can be obtained by minimizing the functional S with respect to the trajectory $\mathbf{Y}_i (= \{\mathbf{R}_{i,k}\}_{k=1}^N)$, and, therefore, we

may extend the idea to the cases in the finite values of N . The question is then reduced to how small N can be taken without loss of gross feature of the true trajectory.

To minimize the action efficiently, we solve the equation-of-motion for fictitious dynamics,

$$\frac{d^2 \mathbf{Y}_i}{d\tau^2} = -\nabla_{\mathbf{Y}_i} S, \quad (4)$$

where τ is a fictitious time of optimization process in the SDE method.

Table. I shows the procedure of the optimization process in the SDE method. In the simulated-annealing process, the fictitious kinetic energy, defined with the fictitious velocity $dY/d\tau$, is scaled to be constant as

$$\lambda^2 \sum_{i=1}^n \left(\frac{d\mathbf{Y}_i}{d\tau} \right) \cdot \left(\frac{d\mathbf{Y}_i}{d\tau} \right) = NnT_{\text{eff}} \quad (5)$$

where λ denotes a scaling parameter and T_{eff} defines the fictitious temperature in the SDE simulation, which has the dimension of (energy/length)². The actual unit (eV/Å)² for T_{eff} is omitted in the following descriptions.

TABLE I: Flow of the SDE algorithm

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- (1) Set a presumed reaction path (initial, intermediate, and final states).
 - (2) Calculate the action S and its gradient on the path.
 - (3) Perform a simulated annealing by solving Eq. (4) numerically.
 - (4) Minimize the action S by finding that the system reached a stationary state.
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For systems where atoms interact with each other via a spherically symmetric pair potential $V(r)$, that is a function of distance r_{ij} between atoms i and j , the total potential energy is written by

$$E_{\text{tot}} = \frac{1}{2} \sum_i \sum_{j \neq i} V(r_{ij}), \quad (6)$$

and the force exerted on atom i is

$$\begin{aligned} \mathbf{F}_i &= -\frac{\partial E_{\text{tot}}}{\partial \mathbf{R}_i} \\ &= -\sum_{j \neq i} \frac{dV(r_{ij})}{dr_{ij}} \frac{\partial r_{ij}}{\partial \mathbf{R}_i}, \end{aligned} \quad (7)$$

where

$$\frac{\partial r_{ij}}{\partial \mathbf{R}_i} = \frac{\mathbf{R}_i - \mathbf{R}_j}{r_{ij}}. \quad (8)$$

From Eqs. (1), (3), and (4), the driving force on atom i in the fictitious dynamics of SDE process is written by

$$\begin{aligned} \mathbf{G}_{i,k} &= -\frac{\partial S}{\partial \mathbf{R}_{i,k}} \\ &= 2 \left[M_1 + M_2 - \frac{(\varepsilon_{i,k+1} + \varepsilon_{i,k-1} - 2\varepsilon_{i,k})}{\Delta t^2} \right], \end{aligned} \quad (9)$$

where

$$\begin{aligned} M_1 &= \frac{\partial F_{i,k}^x}{\partial \mathbf{R}_{i,k}} \varepsilon_{i,k}^x + \frac{\partial F_{i,k}^y}{\partial \mathbf{R}_{i,k}} \varepsilon_{i,k}^y + \frac{\partial F_{i,k}^z}{\partial \mathbf{R}_{i,k}} \varepsilon_{i,k}^z = \\ &- \sum_{j \neq i} \left[\frac{V'}{r_{ij}} \varepsilon_{i,k} + \alpha(i) \left(\frac{V''}{r_{ij}^2} - \frac{V'}{r_{ij}^3} \right) (\mathbf{R}_{i,k} - \mathbf{R}_{j,k}) \right] \end{aligned} \quad (10)$$

$$\begin{aligned} M_2 &= \sum_{j \neq i} \left(\frac{\partial F_{j,k}^x}{\partial \mathbf{R}_{i,k}} \varepsilon_{j,k}^x + \frac{\partial F_{j,k}^y}{\partial \mathbf{R}_{i,k}} \varepsilon_{j,k}^y + \frac{\partial F_{j,k}^z}{\partial \mathbf{R}_{i,k}} \varepsilon_{j,k}^z \right) = \\ &\sum_{j \neq i} \left[\frac{V'}{r_{ij}} \varepsilon_{j,k} + \alpha(j) \left(\frac{V''}{r_{ij}^2} - \frac{V'}{r_{ij}^3} \right) (\mathbf{R}_{i,k} - \mathbf{R}_{j,k}) \right], \end{aligned} \quad (11)$$

and

$$\begin{aligned} \alpha(l) &= (\mathbf{R}_{i,k} - \mathbf{R}_{j,k}) \cdot \varepsilon_{l,k}, \\ V'(r) &= \frac{dV(r)}{dr}, \\ V''(r) &= \frac{d^2V(r)}{dr^2}. \end{aligned} \quad (12)$$

III. LENNARD-JONES POTENTIAL

The Lennard-Jones (LJ) potential is well known as one of the simplest model for spherically symmetric interatomic potentials. In a normalized form, the potential is represented by

$$V(r) = \frac{1}{12} \left(\frac{1}{r^{12}} - \frac{1}{r^6} \right), \quad (13)$$

and the first and the second derivatives of the potential are

$$V' = \frac{dV(r)}{dr} = \left(-\frac{1}{r^{13}} + \frac{1}{2r^7} \right), \quad (14)$$

$$V'' = \frac{d^2V(r)}{dr^2} = \left(\frac{13}{r^{14}} - \frac{7}{2r^8} \right). \quad (15)$$

From these equations, the SDE driving force with LJ potential can be written explicitly by

$$\mathbf{G}_{i,k} = 2 \left[\sum_{j \neq i} \left\{ \left(\frac{1}{r_{ij}^{14}} - \frac{1}{2r_{ij}^8} \right) (\varepsilon_i - \varepsilon_j) \right. \right.$$

$$-\beta \left(\frac{14}{r_{ij}^{16}} - \frac{4}{r_{ij}^{10}} \right) (\mathbf{R}_{i,k} - \mathbf{R}_{j,k}) \left. \vphantom{\frac{14}{r_{ij}^{16}}} \right\} - \frac{(\varepsilon_{i,k+1} + \varepsilon_{i,k-1} - 2\varepsilon_{i,k})}{\Delta t^2} \right], \quad (16)$$

where $\beta = \alpha(i) - \alpha(j) = (\mathbf{R}_i - \mathbf{R}_j) \cdot (\varepsilon_i - \varepsilon_j)$.

IV. MODEL

We simulate a long time process of Cu thin film formation via deposition of Cu clusters onto a substrate. The substrate with Cu(001) surface has 128 atoms per atomic layer and consists of 16 layers (2048 atoms). Atomic positions in the lower half of the substrate are fixed, and the periodic boundary conditions are imposed in the two directions parallel to the surface plane. Initially, two Cu clusters with 55 atoms each are deposited on the upper side of the surface. The parameters of the LJ potential model for Cu, used in the present study, are listed in Table II [5].

TABLE II: Parameters for LJ potential model of Cu [5].

| Energy unit (ϵ) [eV] | Length unit (σ) [\AA] |
|---------------------------------|---|
| 0.4093 | 2.338 |

In the SDE method, a presumed reaction path has to be guessed before the simulation is started. Figure 2 shows the initial (after the two clusters are deposited) and the final states in the presumed path. Additionally, we prepared the two intermediate states, *i.e.*, a sequential set of the systems with 4 and 3 atomic layers on the surface. Seven identical configurations are cloned for each state, and thus total of 28 states are prepared as the presumed path. The time step between each state is about 134[ps] and the total time simulated is 3.6[ns].

The fictitious temperature T_{eff} , defined in Eq. (5), is set to be 2.69×10^{-5} or 4.03×10^{-5} .

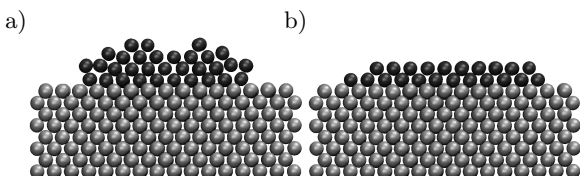


FIG. 1: Atomic positions of (a) the initial and (b) the final state. Gray balls represent Cu atoms of the substrate and black balls are deposited atoms.

V. RESULTS

In the SDE simulations, we run 20000 SDE steps to optimize the path. Figure 2 depicts the change of the action S for the first 400 SDE steps with $T_{\text{eff}} = 4.03 \times 10^{-5}$. The S decreases rapidly to the value which corresponds to the fictitious kinetic energy in Eq. (5).

Figure 3 shows the distribution of ε , defined in Eq. (1), after the SDE run for $T_{\text{eff}} = 4.03 \times 10^{-5}$. The dispersion of the distribution is approximately $\sqrt{T_{\text{eff}}/2} = 4.49 \times 10^{-3}$.

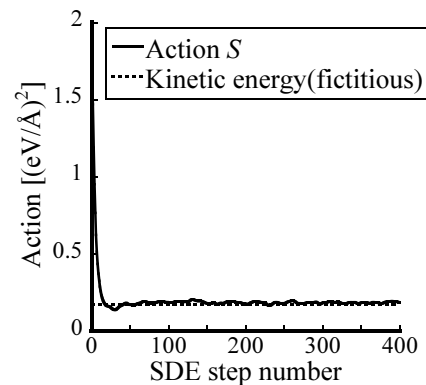


FIG. 2: Change of S in SDE process

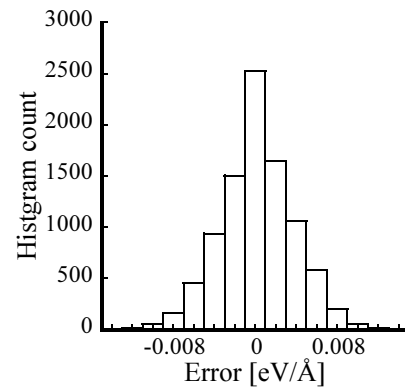


FIG. 3: Error distribution

Figure 4 shows time evolutions of the potential energy in the presumed path and that after the SDE optimization with different T_{eff} . In Fig. 4(b), with higher T_{eff} , high potential barriers can be found around $16-20 \times 134$ [ps]. Since the barriers are quite high, it will take extremely long time in the ordinary MD at low temperatures to observe that the system evolves to the final state. It is thus demonstrated that such a rare event can be explored by using the SDE method with an appropriate choice of fictitious temperature.

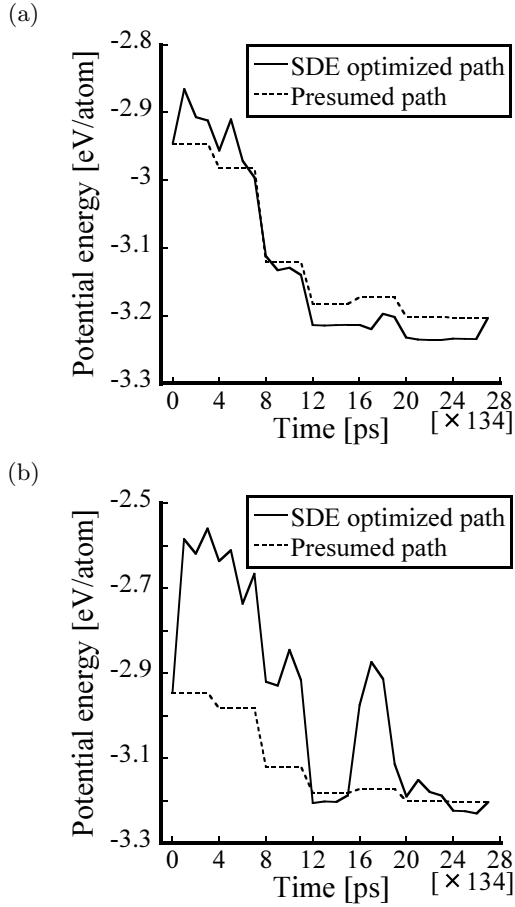


FIG. 4: Potential energy vs. time in the presumed and SDE optimized path for (a) $T_{\text{eff}} = 2.69 \times 10^{-5}$ and for (b) $T_{\text{eff}} = 4.03 \times 10^{-5}$.

We also calculate mean distances between the surface of substrate and atoms in the clusters in order to characterize the evolution of the film formation. Figure 5 depicts the time evolution of the mean distance in the SDE optimized paths with different T_{eff} , as well as that in the presumed one.

As shown in Fig. 5, the ranges in the SDE search for optimum path are relatively small in the case of low T_{eff} , whereas it undergoes wide range for the search in the case of higher T_{eff} .

VI. CONCLUSION

In this paper, we have presented basic methodology of the SDE method, and have applied it to a long time process of the Cu thin-film formation on substrate. It is shown that using SDE approach a system evolution for a few nanoseconds can be simulated with Δt of as large as 134[ps]. We have also demonstrated that the rare event, which may be hardly found by an ordinary MD, can be traced by choosing appropriate values of the fictitious temperature T_{eff} .

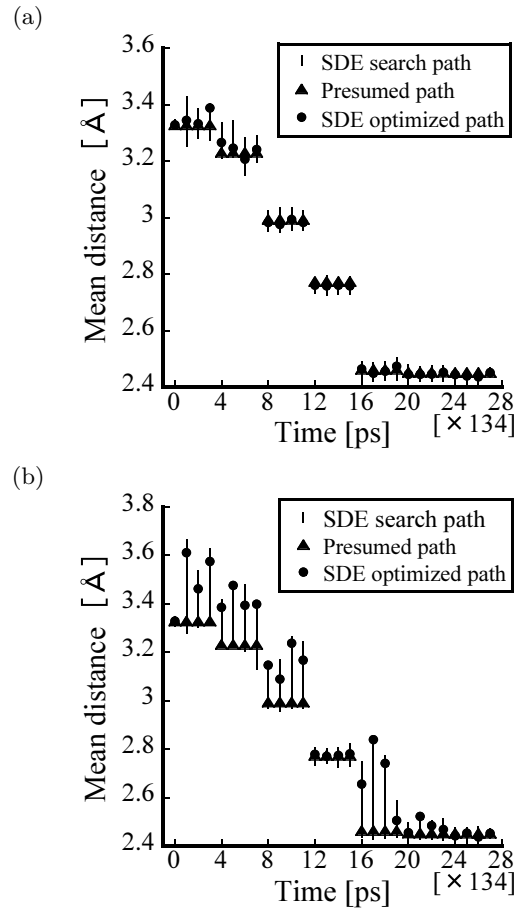


FIG. 5: Mean distance between surface and deposited atoms vs. time for (a) $T_{\text{eff}} = 2.69 \times 10^{-5}$ and for (b) $T_{\text{eff}} = 4.03 \times 10^{-5}$.

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