Published in final edited form as:

J Chem Phys. 2007 June 14; 126(22): 224103. doi:10.1063/1.2737454.

An exact formulation of hyperdynamics simulations

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Abstract

We introduce a new formula for the acceleration weight factor in the hyperdynamics simulation method, the use of which correctly provides an exact simulation of the true dynamics of a system. This new form of hyperdynamics is valid and applicable where the transition state theory (TST) is applicable and also where the TST is not applicable. To illustrate this new formulation, we perform hyperdynamics simulations for four systems ranging from one degree of freedom to 591 degrees of freedom: (1) We first analyze free diffusion having one degree of freedom. This system does not have a transition state. The TST and the original form of hyperdynamics are not applicable. Using the new form of hyperdynamics, we compute mean square displacement for a range of time. The results obtained agree perfectly with the analytical formula. (2) Then we examine the classical Kramers escape rate problem. The rate computed is in perfect agreement with the Kramers formula over a broad range of temperature. (3) We also study another classical problem: Computing the rate of effusion out of a cubic box through a tiny hole. This problem does not involve an energy barrier. Thus, the original form of hyperdynamics excludes the possibility of using a nonzero bias and is inappropriate. However, with the new weight factor formula, our new form of hyperdynamics can be easily implemented and it produces the exact results. (4) To illustrate applicability to systems of many degrees of freedom, we analyze diffusion of an atom adsorbed on the (001) surface of an fcc crystal. The system is modeled by an atom on top of a slab of six atomic layers. Each layer has 49 atoms. With the bottom two layers of atoms fixed, this system has 591 degrees of freedom. With very modest computing effort, we are able to characterize its diffusion pathways in the exchange-with-the-substrate and hop-over-the-bridge mechanisms.

1. Introduction

Since its introduction about a decade ago, the hyper molecular dynamics or hyperdynamics (HD) method^{1–9} has been applied to a wide range of problems involving thermally activated rare events. To illustrate the range of its applications, we list, in Refs. 10–27, a number of 2006 papers that cited the original papers of Voter. Based on the transition state theory (TST), the rate of simulated HD events in a boosted potential, $V_b(\mathbf{r}) = V(\mathbf{r}) + V_b(\mathbf{r})$, is related to the rate of physical processes in the physical potential, $V(\mathbf{r})$, by¹

$$k_{A \rightarrow}^{\text{TST}} = \frac{n_{\text{esc}}}{\sum_{i=1}^{n_{\text{tot}}} \Delta t e^{\beta \Delta V_b[\mathbf{r}(t_i)]}} \quad (1)$$

Here $k_{A \rightarrow}^{\text{TST}}$ is the rate of transition out of the initial state A represented by $\mathbf{r}_A$ that is in the vicinity of a local minimum of $V(\mathbf{r})$. $\mathbf{r}$ is the state vector. It is the set of atomic position vectors for an atomistic system. $\beta = 1/k_B T$ with k_B being the Boltzmann constant and T being the temperature. Δt is the HD simulation time step. n_{esc} is the number of escape attempts. n_{tot} is the total number of HD steps and t_i is the time at the i th HD step. Naturally, the HD method is valid wherever the TST is applicable.

While the TST has a wide range of applicability, there are a great many important “rare” events such as the entropic barrier problems, which are beyond the reach of the TST. Moreover, the original form of hyperdynamics is very effective for rare events limited by an energy barrier that is much higher than $k_B T$ but it is not so for systems that do not have a high energy barrier. Therefore, it is desirable to extend the efficient HD method to cases in which the TST is inapplicable and where rare events are not limited by an energy barrier. This paper presents such an attempt by introducing an exact formula, in parallel to Eq. (1), for the rate of transition out of the initial state, A .

In general, the rate of transition out of an initial state A is given by

$$k_{A \rightarrow} = \frac{dP_{A \rightarrow}(t)}{dt}. \quad (2)$$

Here, $P_{A \rightarrow}(t)$ is the probability for the system to transition out of state A during the time interval $(0, t)$. Considering the stochastic dynamics of the system in a boosted potential, the transition probability can be evaluated as the following weighted statistical average over stochastically sampled trajectories²⁸

$$P_{A \rightarrow}(t) = \frac{1}{\mathcal{N}} \sum_{\xi} e^{-\beta I_{\xi}(t)}. \quad (3)$$

Here, $\mathcal{N}$ is the normalization factor. The summation is over all samples of the random force. The effective action functional $I(t)$ is a time integral along the trajectory for a given sample of .

$$\begin{aligned} I_{\xi}(t) &= \frac{1}{4m\gamma} \int_0^t d\tau \nabla \Delta V_b(\mathbf{r}(\tau)) \cdot [\nabla \Delta V_b(\mathbf{r}(\tau)) - 2\xi(\tau)] d\tau \\ &= \frac{1}{4m\gamma} \sum_i \nabla \Delta V_b(\mathbf{r}(t_i)) \cdot [\nabla \Delta V_b(\mathbf{r}(t_i)) - 2\xi(t_i)] \Delta t. \end{aligned} \quad (4)$$

$\xi(t)$ is Gaussian with the following characteristics:

$$\langle \xi_i(t) \rangle = 0, \quad \langle \xi_i(t) \xi_j(t') \rangle = 2mk_B T \gamma \delta(t - t') \delta_{ij}, \quad (5)$$

where $i, j = 1, 2, \dots, D$, with D being the number of degrees of freedom of the system. m is the mass of a particle (atom) of the system, and γ is the damping constant (frictional coefficient). The Dirac δ -function and the Kronecker Delta are used in Eq. (5). The state vector $\mathbf{r}(t)$ at a given time t is obtained by numerically integrating the Langevin equation

$$m\ddot{\mathbf{r}}(t) + m\gamma\dot{\mathbf{r}}(t) + \nabla V(\mathbf{r}(t)) + \nabla \Delta V_b(\mathbf{r}(t)) = \xi(t), \quad (6)$$

with the initial condition $\mathbf{r}(0) = \mathbf{r}_A$. Throughout this paper we employ scales of convenience for energy, ϵ_0 , and time, τ_0 . Accordingly, $\mathbf{r}$ has units of $d_0 = \tau_0 \sqrt{\epsilon_0/m}$, and I has units of ϵ_0 .

The derivation of Eq. (3) can be achieved in three steps:²⁸ (1) Express the transition probability as a path integral $P_{A \rightarrow}(t) = (1/\mathcal{N}) \int [\mathcal{D}\mathbf{r}] e^{-\beta I}$ Where

$I = (1/4m\gamma) \int_0^t d\tau [m\ddot{\mathbf{r}} + m\gamma\dot{\mathbf{r}} + \nabla V]^2$. This corresponds to the Langevin dynamics in the physical potential V . (2) Express the action functional as $I = I_b + I$ where I_b is identical to I except for V being replaced by $V + V_b$. I is equal to $I - I_b$ of course. Then

$P_{A \rightarrow}(t) = (1/\mathcal{N}) \int [\mathcal{D}\mathbf{r}] e^{-\beta I_b} e^{-\beta I}$. (3) Cast the path integral back to trajectory sampling, we now have Eq. (3) and the Langevin dynamics in the boosted potential $V + V_b$ in Eq. (6). And I takes the form of Eq. (4).

Equation (6) governs the Langevin stochastic dynamics of a system subject to the boosted potential $V_b = V + V_b$. With an appropriate boost, V_b stochastic processes corresponding to rare events occurring in the original physical potential, $V(\mathbf{r})$, are accelerated to take place in short time scales. However, the exponential weight factor in Eq. (3) correctly takes full account of the dynamical effects. Therefore, this new formulation of HD is valid quite generally. It should be pointed out that the boost does not have to be in the form of a conservative force. A nonconservative boost force $\mathbf{F}_b$ can be used in place of $-V_b$ in this formulation without compromising its validity.

The rest of this paper is devoted to applications of the new formulation of hyperdynamics to four systems having degrees of freedom numbering from one to 591. It is organized as follows. In Sec. II a study of free diffusion is presented. In Sec. III we examine the Kramers escape rate problem. In Sec. IV we analyze effusion out of a box. In Sec. V an atomistic model of surface diffusion is studied. The results for these four systems show that our new form of hyperdynamics is valid where the TST is valid, and also where the TST is not valid, and that it is applicable to both simple systems and complex systems. Concluding remarks are presented in Sec. VI.

II. Free Diffusion

Stochastic dynamics in a free space of high dimensions, $V(\mathbf{r})=0$, is a simple superposition of one-dimensional dynamics. Therefore, without loss of generality, we consider here free diffusion in one dimension. This is an analytically solvable problem, for which an exact solution is available. We have examined this system of one degree of freedom with hyperdynamics simulation and with regular Langevin dynamics simulation.

The hyperdynamics (biased Langevin dynamics) simulation is done by numerically integrating Eq. (6) with the following bias potential:

$$\Delta V_b(x) = c_0 |x|/d_0. \quad (7)$$

Here, x is the coordinate of the system. The dimensionless parameter is taken as $c_0 = 0.2$. For each sample of the random force $(\dot{\mathbf{r}})$, a stochastic trajectory is obtained for the time interval from 0 to $5\tau_0$. The mean square displacement is computed as a statistical average over all the trajectories so sampled, with the statistical weight factor e^{-I} given in Eq. (3).

The unbiased Langevin dynamics simulation is done by numerically integrating Eq. (6) with $V_b=0$ and the mean square displacement is computed as the unbiased statistical average over all the trajectories sampled, with equal statistical weights. Note that unbiased Langevin

dynamics can be viewed as a special case of hyperdynamics. Namely, when $V_b=0$, $I=0$, and thus, $e^{-I}=1$.

In Fig. 1, the results from the unbiased Langevin dynamics simulation and from the hyperdynamics simulation are plotted against the known analytical solution

$$\langle (x(t) - x(0))^2 \rangle = \frac{2k_B T}{m\gamma} \left[t + \frac{1}{\gamma} (e^{-\gamma t} - 1) \right]. \quad (8)$$

Needless to say that the TST is inapplicable for this system as there is no saddle point involved in the problem. And the bias potential used here clearly violates the rules of Ref. 1. Nevertheless, the hyperdynamics simulation is in perfect agreement with the exact solution, even better than the unbiased Langevin dynamics simulation.

III. The Kramers Rate Problem

In this section, we perform a hyperdynamics study of the classical Kramers rate problem. The physical system consists of a particle in a meta-stable state of the potential given by

$$V(x) = \varepsilon_0 \left[3 \left(\frac{x}{d_0} \right)^2 - 2 \left(\frac{x}{d_0} \right)^3 \right], \quad (9)$$

as exhibited in Fig. 2. This potential has a local minimum at $x=0$ and a saddle point (transition state) at $x=d_0$ with a barrier $E_b = \varepsilon_0$. If the initial state, A , is in the vicinity of the minimum, the stochastic process of escape over the barrier takes a very long time at low temperature $k_B T / \varepsilon_0 \ll 1$. In this situation, an unbiased Langevin dynamics simulation is impractical. For this system, the TST is valid at an intermediate point of the damping constant $\sim 1/\tau_0$.²⁹ From the overdamped regime to the intermediate damping regime, Kramers provided an analytical formula that involves the damping constant in the prefactor³⁰

$$k_{A \rightarrow} = \left[\sqrt{(4/\tau_0^2 + \gamma^2)} - \gamma \right] e^{-\beta E_b} \text{ for } \beta E_b \gg 1 \text{ and } \gamma \tau_0 > 1. \quad (10)$$

We have carried out hyperdynamics simulations for this system using a bias potential $V_b(x)$ that fills the potential well all the way up to the barrier level, as shown in Fig. 2. Even with this rather crude choice of bias, the hyperdynamics simulation agrees perfectly with the Kramers formula over a wide range of temperature (Fig. 3). Therefore, with our new form of hyperdynamics, the boost potential is much less restricted than what was prescribed in Ref. 1.

IV. Effusion Out of a Box

In this section, we consider a system of noninteracting particles confined in a cubic box that extends in three dimensions ($0 \leq x/d_0 \leq 1, 0 \leq y/d_0 \leq 1, 0 \leq z/d_0 \leq 1$). The physical potential, $V(x,y,z) = 0$, vanishes both inside and outside the box. The particles are subject to random forces $\vec{f}(t) = (f_x(t), f_y(t), f_z(t))$. They are also subject to perfect reflections by the six walls of the box. There is a $2h \times 2h$ opening on one side of the box located at $x=0$, $|y/d_0 - 1/2| < h$, $|z/d_0 - 1/2| < h$ with $h=0.01$. This is another classical problem on statistical mechanics. The rate of effusion per particle can be approximated as³¹

$$k_{A \rightarrow} = \frac{4h^2}{d_0^3 \sqrt{2\pi}} \sqrt{\frac{k_B T}{m}}, \quad (11)$$

when recrossing events induced by random forces are neglected.

We have performed unbiased Langevin dynamics simulations for the effusion events. Out of the 10^5 trajectories over a time interval $(0, 2\tau_0)$, there are three events of escape out of the box. The probability of effusion as a function of time is computed from these trajectories and are shown in Fig. 4 for $\tau = 1/\tau_0$ and $\tau = 10/\tau_0$.

For the same system, we have also carried out hyperdynamics simulations with the bias potential $V_b = |\mathbf{r} - \mathbf{r}_h|$, corresponding to the following bias force

$$\mathbf{F}_b = -\frac{\mathbf{r} - \mathbf{r}_h}{|\mathbf{r} - \mathbf{r}_h|}, \quad (12)$$

where $\mathbf{r}_h = (0, d_0/2, d_0/2)$ is the position vector of the small hole. Out of the 10^5 trajectories over a time interval $(0, 2\tau_0)$, there are thousands of events of escaping out of the box. The probability of effusion as a function of time is computed as a weighted statistical average over those trajectories using Eq. (3). The result is a nearly continuous curve shown in Fig. 4. Taking the slope of the curve, our hyperdynamics study predicts an effusion rate of $4.7 \times 10^{-5}/\tau_0$ for $\tau = 1/\tau_0$ and $\tau = 10/\tau_0$. This compares very well with the analytical prediction ($5.0 \times 10^{-5}/\tau_0$) from Eq. (11). The small difference does not indicate an inaccuracy of hyperdynamics, but, rather, it reflects an error in the analytical formula that does not include the effect of recrossing events.

It should be pointed out that this system does not have an energy barrier. For effusion, the original form of hyperdynamics would be no different than the regular molecular dynamics because the bias potential can only be zero. Our new form of hyperdynamics does not have such a restriction on the bias potential/force. It works perfectly well even with a rather crude choice of bias force such as in Eq. (12).

V. Adatom Diffusion on an FCC (001) Crystal Surface

To illustrate the applicability of our new formulation of hyperdynamics to systems of many degrees of freedom, we consider an atomistic model of surface diffusion. The system is shown in the left illustration of Fig. 5. It consists of 294 substrate atoms (blue) in six monolayers and one adatom (red) above the top layer near its center. Each substrate layer has 7×7 atoms. Periodic boundary conditions are imposed on the x - and y -directions. The atoms in the bottom two layers are fixed in their equilibrium positions. Correspondingly, this system has 591 degrees of freedom. The 885 components of the state vector $\mathbf{r}$ are arranged as the x -, y -, and z -coordinates of the first atom at the origin, and then the next atom in the same row, and so on. In this scheme of labeling, the coordinates of the atom at the center of the top layer are the 808th to the 810th components of $\mathbf{r}$. The coordinates of the adatom are the 883th to the 885th components of $\mathbf{r}$. The first through the 294th components of $\mathbf{r}$ are fixed.

The interactions between the atoms are modeled by the multibody Sutton-Chen potential for Ni crystal^{32,33}

$$V(\mathbf{r}) = \varepsilon_0 \sum_{i=1}^{295} \left[\frac{1}{2} \sum_{j \neq i} \left(\frac{a}{r_{ij}} \right)^n - c \sqrt{\rho_i} \right], \quad (13)$$

where the multibody function ρ_i is given by

$$\rho_i = \sum_{j \neq i} \left(\frac{a}{r_{ij}} \right)^m. \quad (14)$$

Here, r_{ij} is the distance between the i th and the j th atoms. The parameters suitable for Ni crystal are $\varepsilon_0 = 1.5707 \times 10^{-2}$ eV, $c = 39.432$, $n = 9$, $m = 6$, and the lattice constant is $a = 0.352$ nm. We choose $d_0 = a$ and, accordingly, the time scale is $\tau_0 = 2.19058$ ps. For this system at $T = 300$ K ($\beta = 0.607/\varepsilon_0$) with a damping constant $\gamma = 1/\tau_0$, we have performed hyperdynamics simulations to search for diffusion pathways. Starting from the initial state shown in Fig. 5 that is a minimum of $V(\mathbf{r})$, we run the unbiased Langevin dynamics (with $\mathbf{F}_b = 0$) until the system reaches thermal equilibrium. Then we run the hyperdynamics for a few hundred steps using one of the two sets of bias force components stated below. After that, we run a few hundred steps of unbiased Langevin dynamics again for the system to settle back to equilibrium.

Using a bias force whose components are

$$\begin{aligned} F_{bi} &= 200.1\varepsilon_0/d_0 + \nabla_i V(\mathbf{r}) \text{ for } i = 808, 809, \\ F_{bi} &= 300.1\varepsilon_0/d_0 + \nabla_i V(\mathbf{r}) \text{ for } i = 810, \\ F_{bi} &= 200.1\varepsilon_0/d_0 + \nabla_i V(\mathbf{r}) \text{ for } i = 883, 884, \\ F_{bi} &= -300.1\varepsilon_0/d_0 + \nabla_i V(\mathbf{r}) \text{ for } i = 885, \\ F_{bi} &= 0 \text{ for all other values of } i, \end{aligned} \quad (15)$$

we found the exchange-with-the-substrate pathway³⁴ of diffusion shown in Fig. 5. Along the pathway, we computed the potential energy and the effective action defined in Eq. (4). The results are plotted in Fig. 6. Noting the exponential dependence of the transition probability upon the inverse temperature in Eq. (3), the numerical value of I along the diffusion pathway produces a diffusion activation barrier given by $E_{bex} = 0.76$ eV.

Using another bias force whose components are

$$F_{bi} = 400.1\varepsilon_0/d_0 + \nabla_i V(\mathbf{r}) \text{ for } i = 883, F_{bi} = 0 \text{ for } i \neq 883. \quad (16)$$

we found the hop-over-the-bridge pathway of diffusion shown in Fig. 7. Along this pathway, the potential energy and the effective action defined in Eq. (4) are plotted in Fig. 8. For this diffusion mechanism, the numerical value of I along the pathway produces a diffusion barrier given by $E_{bbr} = 0.87$ eV.

We note that the exchange-with-the-substrate diffusion pathway has a significantly lower barrier than the hop-over-the-bridge pathway. We also note that the Sutton-Chen potential may not be very accurate for characterizing surface diffusion. But the energy barriers we found for both diffusion pathways are in good agreement with the results of a recent *ab initio* computation for the Ni/Ni(001) system.³⁵

It should be pointed out that the bias force fields in Eqs. (15) and (16) are not the best choice. Yet, we were able to use them to derive the correct physics. Of course, better bias potentials/forces can be implemented to sample both hopover-the-bridge and exchange-with-the-substrate diffusion events. The nature and characteristics of the representative transition paths sampled with better bias potentials such those in Refs. 1, 8, and 9 are in fact identical to those obtained with our crude choice of bias force field. We emphasize that our new form of hyperdynamics works with our crude choice of bias forces in Eqs. (15) and (16) and it works with other bias potentials in the literature as well.

VI. Summary

In summary, we have introduced a new form of Voter's hyperdynamics simulation method. This new form is valid and applicable where TST is applicable and where the TST is not applicable. We have performed hyperdynamics simulations for four systems ranging from one degree of freedom to 591 degrees of freedom: (1) We have analyzed free diffusion and found that our new form of hyperdynamics agrees perfectly with the analytical solution. (2) We have also examined the classical Kramers escape rate problem. The rate computed from hyperdynamics simulations is in perfect agreement with the Kramers formula over a broad range of temperature. (3) We have studied another classical problem: effusion out of a cubic box through a tiny hole. This entropic barrier problem does not have an energy barrier and thus is beyond the reach of the original form of hyperdynamics. Using the new form of hyperdynamics, our study once again produced perfect agreement with the known exact solution. (4) The last system we analyzed is diffusion of an atom adsorbed on the (001) surface of an fcc crystal. The system is modeled by an atom on top of a slab of six atomic layers. Each layer has 49 atoms. For this system of 591 degrees of freedom, with very modest computing effort, we were able to characterize its diffusion pathways in exchange-with-the-substrate and hop-over-the-bridge mechanisms. It is expected that our new version of hyperdynamics will facilitate studies of many systems that are beyond the reach of the TST.

Acknowledgments

This work has been supported in part by an NIH/MBRS/SCORE grant (Grant No. GM008194), by an NCSA/TeraGrid grant (Grant No. TG-MCB060002T) and by the U.S. Department of Defense (DAAD No. 19-01-1-0592) through the DURINT program of the Army Research Office.

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Fig. 1.

Mean square displacement (unit: $\epsilon_0 \tau_0^2 / m$) vs time (unit: τ_0) for free diffusion. The solid line is the analytical solution. The dashed line that completely overlaps the solid line is the result of the hyperdynamics simulation. The dotted line is the result of the Langevin dynamics simulation. The inverse temperature is $\beta = 10 / \epsilon_0$ and the damping constant is $\gamma = 2.5 / \tau_0$.

Fig. 2. The Kramers potential $V(x)$ (solid) and the boosted potential $V_B(x)$ (dashed). The unit of potential is ϵ_0 and the unit of x is $d_0 = \tau_0 \sqrt{\epsilon_0/m}$.

Fig. 3. Kramers rate $\times 10^3$ (unit: $1/\tau_0$) vs inverse temperature (unit: $1/\tau_0$). The line is the Kramers formula and the points are the results of the present hyperdynamics study. The damping constant is taken as $\gamma = 2.5/\tau_0$.

Fig. 4. Probability ($\times 10^5$) for a particle to escape the box as a function of time (unit: τ_0). The solid curve is the result of our hyperdynamics study and the dashed one is from the unbiased Langevin dynamics simulation for 10^5 paths sampled. $\tau = 1/\tau_0$ and $\tau = 10/\tau_0$.

Fig. 5.
(Color) Ni on Ni(001) surface before (left), at transition state (center), and after (right) an exchange-with-the-substrate event.

FIG. 6. Potential energy $V(t)$ (left) and action functional $I(t)$ (right) along the diffusion pathway for an exchange-with-the-substrate event. The hyperdynamics simulation is executed during the time interval shown. Outside this time interval, regular Langevin dynamics prevail.

Fig. 7. (Color) Ni on Ni(001) surface before (left), at transition state (center), and after (right) a hop-over-the-bridge event.

Fig. 8. Potential energy $V(t)$ (left) and action functional $I(t)$ (right) along the diffusion pathway for a hop-over-the-bridge event. The hyperdynamics simulation is executed during the time interval shown. Outside this time interval, regular Langevin dynamics prevail.