Finding transition paths and rate coefficients through accelerated Langevin dynamics

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(Received 21 August 2001; published 10 April 2002)

We present a technique to resolve the rare event problem for a Langevin equation describing a system with thermally activated transitions. A transition event within a given time interval $(0,t_f)$ can be described by a transition path that has an activation part during $(0,t_M)$ and a deactivation part during $(t_M,t_f)(0<t_M<t_f)$. The activation path is governed by a Langevin equation with negative friction while the deactivation path by the standard Langevin equation with positive friction. Each transition path carries a given statistical weight from which rate constants and related physical quantities can be obtained as averages over all possible paths. We demonstrate how this technique can be used to calculate activation rates of a particle in a two dimensional potential for a wide range of temperatures where standard molecular dynamics techniques are inefficient.

DOI: 10.1103/PhysRevE.65.042101 PACS number(s): 82.20.Uv, 05.10.Gg, 02.50.−r, 05.60.−k

The calculation of activation and transition rates of dynamical processes dominated by rare events is one of the most important problems in physics, chemistry, and many other fields. Various approximation schemes have been employed in the past to overcome this problem. The prevalent approximation for evaluating the rate of rare activation processes is the transition state theory (TST) [1]. Of central importance in the application of TST is the identification of the so-called transition state. For complicated systems, the determination of the transition state alone is a daunting task and many different methods have been developed for this purpose [2–4]. Based on the fundamental assumptions of TST, the hypermolecular dynamics (MD) scheme by Voter [5] boosts dynamical processes over the saddle points by modifying the potential. There are also other acceleration schemes such as temperature accelerated MD [6] that is based on the harmonic TST. While TST has been fairly successful in various applications, the approximation is known to break down in the high and low friction regimes [7]. Beyond TST, perhaps the most ambitious method is the transition path approach [4,8,9] with which the rates are determined as an average of correlations along the transition paths. This approach carries a significant benefit in its capability to survey multiple saddle points and rugged potential energy surfaces. The success of this approach, of course, depends upon efficient path sampling algorithms [4]. In this paper, we present a simple and efficient method to generate (sample) transition paths. It is also an efficient method for solving the Langevin equation (LE) describing the stochastic dynamics of a given system. This accelerated Langevin dynamics (ALD) method starts from an initial stable state. It does not require any prior knowledge of the saddle point or the final state. Thus it is a one-point boundary scheme in contrast to two-point boundary schemes such as the nudged elastic band [3], or those of Ref. [4]. ALD provides for a simple way to *simultaneously* survey the potential energy surface, to find the saddle points, and to evaluate the corresponding rates. It works even in the case of multiple saddle points and final stable or metastable states, and makes *no approximations* on the dynamical evolution of the system. It also allows one to compute rates at low temperatures where standard MD methods are impractical, thus overcoming the rare event problem.

The ALD method is based on the idea that the physical quantities obtained from the solution of the LE can be expressed as averages over relevant transition paths [10,11]. In an earlier work [11] we showed that taking into account only the most probable (minimal action) path, a transition event can be described in a manner of accelerated dynamics by sewing an activation path to a deactivation path, forming a joined path. The activation path is generated by a (deterministic) Newtonian equation with negative friction while the deactivation path by a regular Newtonian equation with positive friction. The joined path thus generated is very efficient for describing transitions over a barrier, tracing only the active part of the process without waiting for the long period of small oscillations in the minima. Here we show that this idea is not limited to only the most probable path but is generally valid for all the paths. We show that negative and positive friction in the corresponding stochastic LE's can be used to generate *all* possible transition paths with their proper statistical weights, without any approximations such as TST.

To illustrate the ALD technique, we study the dynamics of a particle in a two-dimensional (2D) potential obeying standard Langevin dynamics. The potential chosen here is the one that has been thoroughly examined in Ref. [3]. The contour plot of the potential $V(x,y)$ is shown in Fig. 1. The shape of the wells and the location of the saddle point make methods such as the slowest ascent path fail [3].

The standard Langevin equation in its dimensionless form for the particle is

$$\ddot{r}(t)+\gamma\dot{r}(t)+\nabla V(r(t))=\xi(t), \tag{1}$$

where $r=(x,y)$, and $\xi(t)=(\xi_1(t),\xi_2(t))$ is white noise with zero mean and correlations

$$\langle\xi_i(t)\xi_j(t')\rangle=2(\gamma/\beta)\delta_{ij}\delta(t-t'), \tag{2}$$

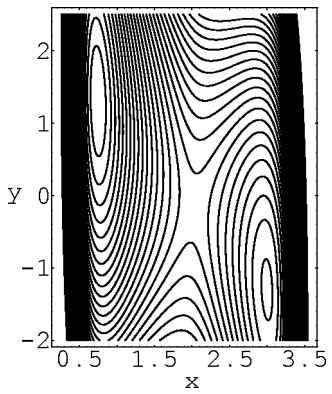

FIG. 1. Contour plot of $V(x,y)$. The potential well 1 is located at $x=3.00, y=-1.30$, well 2 at $x=0.741, y=1.30$, and the saddle point at $x=2.02, y=-0.173$.

with $\beta=1/k_BT$ and γ being the dimensionless frictional (damping) coefficient. For simplicity, here and in the rest of the paper we omit the vector notations. The transition probability $P(0|f)\equiv P(r_0,v_0,t_0|r_f,v_f,t_f)$ for a transition from state (r_0,v_0) at t_0 to state (r_f,v_f) at t_f can be built via intermediate states at $t_M (0<t_M<t_f)$ as

$$P\begin{pmatrix} r_0 & r_f \\ v_0 & v_f \\ t_0 & t_f \end{pmatrix} = \int\int dr_M dv_M P\begin{pmatrix} r_0 & r_M \\ v_0 & v_M \\ t_0 & t_M \end{pmatrix} \times P\begin{pmatrix} r_M & r_f \\ v_M & v_f \\ t_M & t_f \end{pmatrix}. \tag{3}$$

This formal decomposition is useful for evaluating the transition rate if the first part $P(0|M)$ describes activation towards or close to the saddle point, and the second part $P(M|f)$ deactivation to the next minimum. However, the activation part occurs with a very small probability, so the direct sampling of the paths through the solution of the regular LE poses the same problem as encountered in standard MD techniques. One way to overcome this problem is to solve a LE that has negative instead of positive friction. It can be shown through path integral manipulations [12] that the activation part $P(0|M)$ can be obtained by sampling paths $r_{-\gamma}(t)$ that are solutions to the LE with *negative* friction $-\gamma$,

$$\ddot{r}(t)-\gamma\dot{r}(t)+\nabla V(r(t))=\xi(t). \tag{4}$$

This yields the expression

$$P\begin{pmatrix} r_0 & r_M \\ v_0 & v_M \\ t_0 & t_M \end{pmatrix} = \exp[2\gamma t_M-\beta(E_M-E_0)]\int [\mathcal{D}\xi]P[\xi(t)] \times \delta[r_{-\gamma}(t_M)-r_M]\delta[\dot{r}_{-\gamma}(t_M)-v_M]. \tag{5}$$

In this expression, the Gaussian random force $\xi(t)$ is generated with its statistical weight functional $P[\xi(t)]$, in accordance with the correlations of $\xi(t)$ as defined in Eq. (2). The unusual feature is that along the path $r_{-\gamma}(t)$, the system *gains* energy through the negative friction and is thus able to escape the well into the saddle-point region without spending time performing oscillations in the minimum. The rare nature of the event is explicitly accounted for by the factor $\exp[2\gamma t_M-\beta(E_M-E_0)]$ in Eq. (5). The deactivation part $P(M|f)$ can be obtained by sampling paths $r_{+\gamma}(t)$ that are solutions to the standard LE of Eq. (1) with the initial condition $[r(t_M)=r_M,\dot{r}(t_M)=v_M]$, for various realizations of $\xi(t)$,

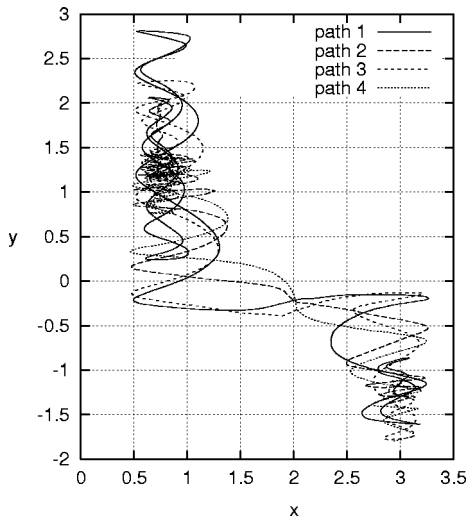

FIG. 2. Four typical transition paths for $V(x,y)$ using the ALD method. The inverse temperature $\beta=20$ and friction $\gamma=0.3$.

$$P\begin{pmatrix} r_M & r_f \\ v_M & v_f \\ t_M & t_f \end{pmatrix} = \int [\mathcal{D}\xi]P[\xi(t)]\delta[r_{+\gamma}(t_f)-r_f] \times \delta[\dot{r}_{+\gamma}(t_f)-v_f]. \tag{6}$$

Thus we have a one-point boundary scheme to sample transition paths. Each sampled path is $r_{-\gamma}(t)$ for $t_0\leq t\leq t_M$ joined to $r_{+\gamma}(t)$ for $t_M\leq t\leq t_f$. The first part $r_{-\gamma}(t)$ is obtained by integrating activation LE of Eq. (4) from the initial condition (x_0,v_0) at t_0 to t_M while $r_{+\gamma}(t)$ is obtained by integrating the standard LE from (x_M,v_M) at t_M to t_f. Because of the sampling of the first path from the negative friction LE, the rare event problem is resolved. It is also clear from the formalism that the ALD provides true dynamics with no approximations involved.

We have applied the ALD to the model potential of Fig. 1, and some typical transition paths are shown in Fig. 2. As expected, with a sensible choice of t_M most of the paths pass very close to the saddle point. In fact, ALD is exact for any $t_0<t_M<t_f$ but it is naturally most efficient if t_M roughly corresponds to a typical activation time to the saddle point, since high-energy paths have an exponentially decreasing weight as can be seen from Eq. (5). This time can be easily estimated if the saddle point is known, or by integrating the activation LE and checking for a transition, e.g., by simple

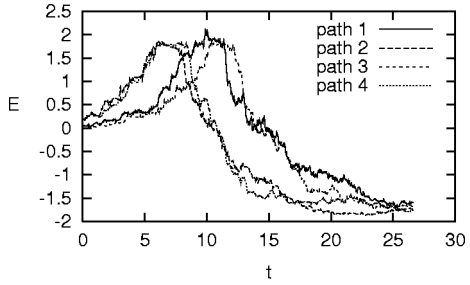

FIG. 3. Total energy E vs time t along the paths 1–4 corresponding to Fig. 2. E has been measured relative to the minimum 1.

minimization [6]. In Fig. 3 we show the time dependence of the total energy corresponding to the four paths that reveal the activated and deactivated nature of the two sections of the paths.

To calculate the transition rate $k_{1\to 2}$ we follow Ref. [4] and relate it to microcopic correlations as

$$k_{1\to 2} \simeq \frac{1}{\langle h_1(r(t_0))\rangle} \frac{d}{dt_f} \langle h_1(r(t_0)) h_2(r(t_f))\rangle, \qquad (7)$$

for $1/\gamma \ll t_f \ll (k_{1\to 2}+k_{2\to 1})^{-1}$, where $h_i(r)(i=1,2)$ is the characteristic function for the low-energy states in well i [4]. The correlator is computed with the transition probability formulated in Eq. (3), with Eqs. (5) and (6). The time derivative in Eq. (7) has a well-defined plateau as long as $1/\gamma \ll (k_{1\to 2}+k_{2\to 1})^{-1}$. The rate constant $k_{1\to 2}$ has been evaluated for inverse temperatures from $\beta=8$ to $\beta=20$ and is shown in Fig. 4. To obtain each point in the figure, 50 initial states (r_0, v_0) were sampled and for each initial state 20 000 joined paths were taken into account. The slope of the Arrhenius plot yields a value of 1.8 ± 0.1 for the activation barrier that agrees within the error bars with the exact value of $E_A=1.75$.

In summary, we have presented an accelerated dynamics technique to numerically solve LE's describing thermally activated transitions. A transition event within a given time interval (t_0, t_f) is conveniently described by a path that has an activation part during (t_0, t_M), joined together with a deactivation part during (t_M, t_f). The activation path is governed by a LE with a *negative* friction while the deactivation path by a regular LE. Each such joined path carries a given statistical weight given exactly by the path integral form. The problem of activating rare events is resolved due to the activation by negative friction in the first part of the path. Physical quantities such as transition rates can be calculated exactly as weighted averages over all possible paths, without invoking the TST approximation. As an illustration of this formalism, it has been applied to study the activation rate of a particle in a 2D model potential for a wide range of temperatures.

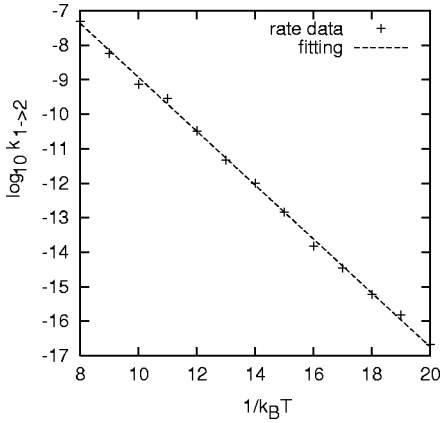

FIG. 4. An Arrhenius plot of the activation rate $k_{1\to 2}$ from well 1 to well 2 vs the inverse temperature $\beta=1/k_BT$. The dashed line is fit to the data giving $E_A=1.8\pm 0.1$.

In a system with many degrees of freedom with strong interactions, the rare transition events one is interested in generally correspond to a few active degrees of freedom gaining high enough energy. Again, direct simulations at low temperatures are often intractable. However, we can apply the negative friction LE selectively to the active degrees of freedom and simulate the other degrees of freedom using the regular LE. Details and applications of this generalization of the method will be published elsewhere.

This work has been supported, in part, by a UTSA faculty research program and by the Academy of Finland through its Center of Excellence program. We wish to thank F. Montalenti, O. Trushin, and P. Salo for useful discussions.

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