SELECTIVE ACTIVATION DYNAMICS: A MINIMAL PATH APPROACH

L. Y. CHEN AND P. L. NASH
Program of Physics, University of Texas at San Antonio, San Antonio, TX 78249, USA
AND
S. C. YING
Department of Physics, Brown University, Providence, RI 02912, USA

1. Introduction

Surface diffusion[1] or transition between stable (or metastable) states presents well known computational difficulties, particularly when the dynamical bottlenecks separating the initial and final (stable or metastable) states are not known. Conventional methods for studying rare event activations are based on transition state theory.[2, 3, 4] The application of this approach requires prior knowledge of the mechanism or pathway for the activation process. For multidimensional systems, it is a challenging problem to determine the transition state numerically without assuming any particular configurations.[5] Various innovations have been put forward to improve or go beyond the transition state theory. Examples are the accelerated dynamics approach[6] and the transition path approach.[7, 8, 9] In reference [10], we have proposed a novel approach to the calculation of the rate for activated processes based on the path integral solution of Langevin equation. In this paper, we pursue further the idea proposed there and fully establish the minimal path approximation. According to the path integral formulation of the Langevin equation, the probability for an arbitrary path connecting the initial and the final configurations is determined by a positive-definite “action” functional. It is shown that the paths having the minimal action dominate over all others for low temperatures. Taking advantage of this fact, the expectation value of a physical observable is computed as weighted average of its values along the minimal paths. The minimal paths
are found through integrating an activation equation and a deactivation
equation (both second order differential equations). This minimal path
approach does not require prior knowledge of the “transition states” or that
of the stable/metastable states. Instead, through sampling of intermediate
states and integrations along the minimal activation/deactivation paths,
both can be found by a numerical effort on the level of Monte-Carlo sam-
pling in the phase space. It is important to note that not only is the prior
knowledge of the transition state not necessary, the implementation of the
minimal path method also avoids the usual approximations involved in the
transition state theory which becomes increasingly inaccurate in the limit
of low frictional damping.

2. The Minimal Path Approximation

We start with the standard Langevin equation,

\[ m\ddot{x}(t) = -\eta \dot{x}(t) - \nabla V(x(t)) + \xi(t) \]  \hspace{1cm} (1)

that has a wide variety of applications \cite{11, 12, 13} and has been the basis
for study of surface diffusion in references \cite{14, 15, 16}. Here \( x(t) \) stands
for a multicomponent vector with dimension \( ND \), where \( N \) is the num-
ber of particles and \( D \) is the physical dimension of the system. \( V(x) \) is a
general potential including both external potential and interparticle inter-
actions. The random force \( \xi(t) \) characterizes the coupling of this system
to its environtment (a heat bath). Its correlation can be written in the form
\( \langle \xi(t)\xi(t') \rangle = 2k_B T \eta \delta(t-t') \) as we consider in this paper only the Markovian
limit. \( \eta \) is the frictional (damping) coefficient. In general, potential \( V(x) \)
has many local minima separated by activation barriers.

Due to the stochastic nature of the Langevin equation, there exists a
whole distribution of solutions (paths) to Eq.(1) for a given set of bound-
ary conditions, and physical observables are obtained as averages over this
distribution of paths. It has been shown that, with regards to the solution
of the Langevin equation Eq.(1), the probability functional \( P[x(t)] \) for the
system to take a particular path \( x(t) \) starting at \( (x_1, v_1, t_1) \) and ending at
\( (x_2, v_2, t_2) \) is given by the following expression \cite{17}

\[
P[x(t)] = \frac{1}{N} \exp \left\{ -\int_{t_1}^{t_2} \frac{dt}{4\eta k_B T} \left[ m\ddot{x} + \eta \dot{x} + \nabla V(x) \right]^2 \right\} \left| \begin{array}{c}
x(t_2) = x_2, \dot{x}(t_2) = v_2 \\
x(t_1) = x_1, \dot{x}(t_1) = v_1 \\
\end{array} \right| . \hspace{1cm} (2)
\]

The total joint probability for the particle to be in \( (x_1, v_1) \) at \( t = t_1 \) and in
\( (x_2, v_2) \) at \( t = t_2 \) is then given by the path (functional) integral \cite{18, 19}

\[
P(x_1, v_1, t_1 | x_2, v_2, t_2) = \int [Dx] P[x(t)]. \hspace{1cm} (3)
\]
The functional integrand in Eq.(3), though complicated, is positive-definite, and thus, the numerical implementation of the path integral in Eq.(3) is well-defined. The physically interesting regime usually corresponds to the situation such that the thermal energy \(k_B T\) is much less than the activation barriers. Under this condition, there exist some special paths whose contribution to the path integral in Eq.(3) dominates over all the other paths. To illustrate this more clearly, we introduce a length scale \(d\), an energy scale \(V_0\) and a time scale \(\tau_0 \equiv \sqrt{md^2/V_0} \equiv 1/\omega_0\) for the system under consideration. The Eq.(3) can then be expressed in terms of dimensionless, scaled variables in the form,

\[
P(x_1, v_1, t_1|x_2, v_2, t_2) = \int [Dx] \exp \left\{ -\frac{1}{\lambda} I[x(t)] \right\}
\]

with the boundary conditions \(\{x(t_1) = x_1, \dot{x}(t_1) = v_1\}\) and \(\{x(t_2) = x_2, \dot{x}(t_2) = v_2\}\). The effective action

\[
I[x(t)] = \int_{t_1}^{t_2} dt \zeta^2
\]

where

\[
\zeta(t) = \ddot{x}(t) + \gamma \dot{x}(t) + \nabla V(x(t))
\]

and \(x, t, V\) are all in their dimensionless form. The dimensionless friction parameter \(\gamma\) is defined as \(\gamma \equiv \eta/m\omega_0\), and the dimensionless parameter \(\lambda\) appearing in the exponential of the functional integrand is \(\lambda = 4\gamma k_B T/V_0\).

Clearly, in the low temperature \((k_B T \ll V_0)\) and/or underdamped regime \((\gamma \ll 1)\), \(\lambda \ll 1\), the minimal path of functional \(I[x(t)]\) carries the dominant weight in the path integration of Eq.(4). Since the action functional \(I\) is positive-definite, deviations from the minimal path carry negligible contribution to the path integral in Eq.(4). The minimal path is determined from the condition that the functional derivative \(\delta I/\delta x(t)\) vanishes. This leads to the standard Euler-Lagrange equation for the minimal path

\[
\ddot{\zeta}(t) - \gamma \dot{\zeta}(t) + \zeta \cdot \nabla \nabla V(x(t)) = 0.
\]

Note again that all quantities are in dimensionless form.

An obvious solution to Eq.(7) is \(\zeta = 0\), i.e.,

\[
\ddot{x}_d(t) + \gamma \dot{x}_d(t) + \nabla V(x_d(t)) = 0.
\]

Integrating Eq.(8) forward with boundary conditions \(x_d(t_M) = x_M, \dot{x}_d(t_M) = v_M\), for \(t_f > t_M\), a minimal path \(x_d(t)\) is obtained that characterizes deactivation from state \((x_M, v_M)\) at \(t_M\) to state \((x_f = x_d(t_f), v_f = \dot{x}_d(t_f))\) at
$t_f$. Along this path $x_d(t)$ the energy of the system decreases monotonously and the action $I = \int_{t_M}^{t_f} dt \zeta(t)^2$ assumes its minimal value $I_d = 0$.

A less obvious solution to the minimal path equation (7) is that $\zeta = 2\gamma \dot{x}_a$, i.e.,

$$\ddot{x}_a(t) - \gamma \dot{x}_a(t) + \nabla V(x_a(t)) = 0. \quad \text{(9)}$$

Integrating Eq. (9) backward with boundary conditions $x_a(t_M) = x_M, \dot{x}_a(t_M) = v_M$, for $t_i < t_M$, a minimal path $x_a(t)$ is obtained that characterizes activation from $(x_i = x_a(t_i), v_i = \dot{x}_a(t_i))$ at $t_i$ to $(x_M, v_M)$ at $t_M$. Along this path $x_a(t)$, from $t_i$ to $t_f$, the energy of the system increases monotonously and the action $I = \int_{t_i}^{t_f} dt \zeta(t)^2$ assumes its minimal value $I_a = 4\gamma (E_M - E_i)$ where $E_M = v_M^2/2 + V(x_M)$ are $E_i = v_i^2/2 + V(x_i)$ are the energies in dimensionless form at times $t_i$ and $t_M$ respectively.

It is worth noting that the deactivation path $x_d(t)$ is a minimum (not maximum) of the action functional $I[x(t)]$ and that so is the activation path $x_a(t)$. While it is straightforward to see $x_d(t)$ being a minimum, the fact $x_a(t)$ being a minimum can be verified by expanding $I[x(t)]$ to the second order in an infinitesimal deviation $\delta x(t)$ from $x_a(t)$, i.e.,

$$I[x_a(t) + \delta x(t)] = I[x_a(t)] + \delta^{(1)} I + \delta^{(2)} I. \quad \text{(10)}$$

Here the first order term $\delta^{(1)} I = 0$ by virtue of the Euler-Lagrange equation (7) and the second order term can be manipulated into the following form

$$\delta^{(2)} I = \int_{t_i}^{t_f} dt \left[ \delta \dot{x}(t) - \gamma \delta x(t) + \nabla \nabla V(x_a(t)) \delta x(t) \right]^2 \quad \text{(11)}$$

which is positive definite.

Sewing the activation path $x_a(t)$ and deactivation path $x_d(t)$ together, we obtain the following three-configuration joint probability, within the minimal path approximation,

$$P(x_i, v_i, t_i | x_M, v_M, t_M | x_f, v_f, t_f) = \delta(x_i - x_a(t_i | M)) \delta(v_i - \dot{x}_a(t_i | M)) \exp \left[ -(I_a + I_d)/\lambda \right] \delta(x_f - x_d(t_f | M)) \delta(v_f - \dot{x}_d(t_f | M)). \quad \text{(12)}$$

Here $(\cdot | M)$ indicates that the activation path $x_a(t)$ and the deactivation path $x_d(t)$ are joined at $t_M$, i.e., $x_a(t_M) = x_d(t_M) = x_M$ and $\dot{x}_a(t_M) = \dot{x}_d(t_M) = v_M$. This three-configuration joint probability can be used, together with the initial (equilibrium or nonequilibrium) distribution $P(x_i, v_i)$, to conveniently evaluate the expectation values of physical observables.

It should be pointed out that sewing the activation path and the deactivation path at $t_M$ brings in a discontinuity in $\zeta(t)$ of Eq. (6) and thus in the integrand of $I[x(t)] = \int_{t_i}^{t_f} dt \zeta(t)^2$. However, both $x(t)$ and $\dot{x}(t)$ are continuous
at $t_M$ and the $I[x(t)]$ integral is well defined for such a discontinuity where $\zeta(t)$ experiences a finite jump from $2\gamma \dot{x}_a(t_M)$ to 0. Therefore it should not bring any artificial error into the evaluation of physical observables.

3. Three Lennard-Jones particles in an external potential

To illustrate the application of the minimal path approximation, we consider a cluster of three particles ($N = 3$) in two dimension ($D = 2$) interacting with one another in the form of Lennard-Jones potential, in its dimensionless form,

$$V_{L,J}(i,j) = 4 \left( \frac{1}{r_{ij}^6} - \frac{1}{r_{ij}^2} \right)$$

(13)

where $r_{ij}$ is the distance between the $i$-th particle and the $j$-th particle. This cluster is subject to an external potential

$$V_{ex}(x, y) = \left( 1 - \left( \frac{x}{4} \right)^2 \right)^2 + \left( 4 + 100 \exp(-y^2) \right) \left( y/4 \right)^2.$$ (14)

This external potential has two minima located at $(-4,0)$ and $(4,0)$ that are separated by a narrow passage located around the saddle point $(0,0)$ as shown in the equipotential contour plot in figure 1. Relative to the two minima where $V_{ex}(-4,0) = 0$, the saddle point has a potential $V_{ex}(0,0) = 1$. The configuration of lowest energy is when three particles form an equilateral triangle and reside in one of the two potential wells, i.e., the left or the right configuration in figure 2.
Figure 2. The initial (left), intermediate (center), and final (right) configurations of the cluster along the minimal path.

Considering activation of the cluster initially in the well located around \((-4,0)\) into the other well located around \((4,0)\), the minimal path of successful activation can be found by the following scheme. Choose an intermediate state \((x_M, v_M)\), then integrate the activation path equation (9) backward from \(t_M\) to \(t_i\), arriving at the initial state \((x_i, v_i)\), and integrate the deactivation path equation (8) forward from \(t_M\) to \(t_f\), arriving at the final state \((x_f, v_f)\). If the initial and final states thus obtained are distinctively different (i.e., in different wells), a successful activation path is found. And the probability for this path is \(\exp(-I_a/\lambda)\) (noting that \(I_d = 0\)). Thus, the dynamics information is obtained for each chosen intermediate state. The integration of equations (8) and (9) need to be performed only for short durations in the presence of finite friction (damping) \(\gamma\). The numerical effort required can be further reduced through random Monte-Carlo sampling of the intermediate points \((x_M, v_M)\) in the \((x, v)\) phase space. It is interesting to pay close attention to one minimal path of this three cluster activation whose action \(I_a\) is the smallest among all paths of successful activation that corresponds to the lowest value of energy \(E_M\) at the intermediate state \((x_M, v_M)\) (note that \(I_a = 4\gamma(E_M - E_i)\)). The energy and the \(x\)-coordinate of the center of mass of the cluster along this path are plotted in figure 3 and figure 4 respectively. In order to go along this minimal path, the cluster breaks one of the three “bonds” in the initial state and squeezes through the narrow passage located around \(x = 0\) as shown in the center configuration in figure 2. This aspect is clearly seen in figure 5: The area of the triangle is diminished as the cluster comes into the narrow passage (in the intermediate state) and is recovered afterward when it deactivates into the potential well in the right.

4. Summary

We have proposed an approximate solution to the Langevin equation for processes when a system initially in a stable/metastable state being activated out of it and deactivating into another. A three-configuration joint
Figure 3. Energy of the cluster along the minimal path.

Figure 4. X-coordinate of the center of mass of the cluster along the minimal path of activation.
probability, for the system being in the initial state \((x_i, v_i)\) at time \(t_i\), final state \((x_f, v_f)\) at time \(t_f\), and, an intermediate state \((x_M, v_M)\) at time \(t_M\), is obtained by connecting \((x_i, v_i)\) to \((x_M, v_M)\) with an activation path having the minimal “action” and connecting \((x_M, v_M)\) to \((x_f, v_f)\) with a deactivation path also having minimal “action”. This minimal path approach is accurate at low temperatures and thus complements the existing methods that work better at higher temperatures. For a temperature not low enough, fluctuations around the minimal paths can be sampled numerically to improve the computation. As an example, we have studied the activation of a cluster of three Lennard-Jones particles over a narrow passage from one stable state to another in a two dimensional external potential. With moderate numerical efforts, we are able to identify the relevant activation mechanism and to locate new stable/metastable states.

5. acknowledgments

Thanks are due to Professors Tapio Ala-Nissila and Karsten W. Jacobsen for helpful discussions.

References