Transition path sampling with a one point boundary scheme

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Abstract

Studying the motion of Lennard-Jones clusters in an external potential having a very narrow channel passage at the saddle point, we present a one point boundary scheme to numerically sample transition (reaction) paths. This scheme does not require knowledge of the transition states (saddle points) or that of the final states. A transition path within a given time interval $(0, t_f)$ consists of an activation path during $(0, t_M)$ and a deactivation path during $(t_M, t_f)$ ($0 < t_M < t_f$) joined at an intermediate time $t_M$. The activation path is a solution to a Langevin equation with negative friction while the deactivation path is that to a regular Langevin equation with positive friction. Each transition path so generated carries a determined statistical weight. Typical transition paths are found for two-particle and three-particle clusters. A two-particle cluster adjusts its orientation to the direction of the narrow channel and then slides through it. A three-particle cluster completes a transition by opening one of its three bonds, becoming linear, and sliding through the channel.

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Many transition events, such as diffusion and chemical reactions, are activated processes in which the system has to surmount an energy barrier $E_b$ that is many times over the thermal energy $k_B T$. There is generally a very long period of time, $t_{tr}$, in between two transition events during which the system executes small scale stochastic motion on a time scale $t_{loc}$ within the vicinity of a local equilibrium (energy minimum). Since $t_{tr} \sim \exp(E_b/k_B T)t_{loc}$, a meaningful but straightforward simulation, that has to be run for a time much longer than $t_{tr}$, with a time step much less than $t_{loc}$, would take unrealistically long computing time. To overcome this bottleneck difficulty, the transition state theory (TST) [1] starts the system at a transition state (saddle point) and takes into account the dynamic processes from there. The TST approximation greatly shortens the required computing time but its application requires locating the transition state and determining the minimum energy path (MEP) along which the potential energy reaches its maximum at the saddle point. Many different methods have been developed for finding MEP and saddle points. [2–9] A one point boundary scheme does not require knowing, a priori, the final state for the search of saddle point. [3–6] It starts the system at a local minimum on the potential energy surface (the initial state) and then trace stepwise, in a sequential manner, to the saddle point. Also starting from the initial state (without knowing the final state) but doing the dynamics are the hyperdynamics method [10] and the temperature accelerated dynamics method. [11] A two point boundary scheme requires the knowledge of the final state and involves fixing the two ends of a trial path at the initial and final states. [7–9] In this category, the nudged elastic band method (NEB) has been very successful for systems with smooth potential energy surfaces. [9]

While TST has been fairly successful in various applications, the approximation is known to break down in the high and low friction regimes. [12–15] One of the formulations going beyond the TST approximation is the transition path approach. [16–19] This approach carries a significant benefit in its capability to survey multiple saddle points and irregular potential energy surfaces. Sampling transition paths with two point boundary schemes, this approach has been successfully applied to various systems whose initial and final states are both known. [19]

In this paper, we present a one point boundary scheme to sample transition paths, employing the negative friction technique. [20] A transition path within a given time interval $(0, t_f)$ consists of an activation path during $(0, t_M)$ and a deactivation path during $(t_M, t_f)$
(0 < t_M < t_f) joined at an intermediate time t_M. The activation path is a solution to a Langevin equation with negative friction while the deactivation path is that to a regular Langevin equation with positive friction. This scheme gives a simple way to search for a final state. For systems with smooth potential energy surfaces, the transition path so generated can be refined into accurate MEP using the two point boundary NEB method. For systems with irregular potential energy surfaces, this scheme provides a way to locate final states for employing the more sophisticated two-point boundary transition path sampling schemes.

We study the dynamics of a cluster of N particles, interacting with one another with Lennard-Jones interaction,

$$V_{LJ}(r_{ij}) = 1 + 4 \left( \frac{1}{r_{ij}^{12}} - \frac{1}{r_{ij}^{6}} \right)$$

where the distance between the i-th particle and the j-th particles $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, $i,j = 1,2,\cdots,N$. Here and in the rest of this paper, dimensionless form is assumed for physical quantities. The Lennard-Jones potential $V_{LJ}(r)$ has a minimum at $r = 2^{1/6}$ where $V_{LJ} = 0$.

The cluster is subject to a two dimensional potential

$$V(x, y) = \left( 1 - \left( \frac{x}{4} \right)^2 \right)^2 + (4 + 100e^{-x^2}) \left( \frac{y}{4} \right)^2$$

that has two wells located at $(x = \pm 4, y = 0)$ and a very narrow channel passage between two wells as shown in Fig.1. $V(\pm 4, 0) = 0$ at the two stable states and $V(0, 0) = 1$ at the saddle point.

In a straightforward simulation, a transition path $\mathbf{r}_\xi(t)$ is generated by integrating the standard Langevin equation for a given sample of the random force $\xi(t)$, starting from the initial state at $t = 0$ to a final state at $t = t_f$. Hereafter $\mathbf{r}$ is used to stand for collection of the particles’ positions \{\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N\} and $\mathbf{v}$ for collection of their velocities \{\mathbf{\dot{r}}_1, \mathbf{\dot{r}}_2, \cdots, \mathbf{\dot{r}}_N\}. And $\xi$ stands for \{\xi_1, \xi_2, \cdots, \xi_N\}. The standard Langevin equation in its dimensionless form for the particle is

$$\mathbf{\dot{r}}_i(t) + \gamma \mathbf{\dot{r}}_i(t) + \nabla V(\mathbf{r}_i(t)) + \sum_{j \neq i} \nabla V_{LJ}(r_{ij}(t)) = \xi_i(t).$$

$\xi_i(t)$ is the white noise Gaussian random force having zero mean and the following correlation

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

where $I$ is a 2 \times 2 unity matrix. $\beta = 1/k_B T$ is dimensionless inverse temperature and $\gamma$, dimensionless frictional (damping) coefficient. It is well known that the presence of the
friction term $\gamma \mathbf{r}_i(t)$ in Eq.(3) drives a particle’s energy, if far above $k_B T$, to decrease to around $k_B T$. Therefore it’s extremely rare at low temperature for a path so generated to go from a stable state, over the saddle point, to another stable state. The corresponding probability is $e^{-\beta E_b}$ with $E_b$ being the activation energy barrier.

Changing the sign of friction, the negative friction Langevin equation

$$\dot{\mathbf{r}}_i(t) - \gamma \mathbf{r}_i(t) + \nabla V(\mathbf{r}_i(t)) + \sum_{j \neq i} \nabla V_{LJ}(r_{ij}(t)) = \xi_i(t)$$

(5)

produces paths with increasing energy since the negative friction term $-\gamma \mathbf{r}_i(t)$ drives the particles farther and farther away from equilibrium.

Now, let’s start from a stable state $(\mathbf{r}_0, \mathbf{v}_0)$ at $t = 0$ and integrate the negative Langevin equation (5) to an intermediate time $t_M$. The path so generated is $\mathbf{r}_{-\xi}(t)$. From there, integrating the regular Langevin equation (3) produces path $\mathbf{r}_{+\xi}(t)$ for time $t$ from $t_M$ to $t_f$. One can be convinced that along an activation path $\mathbf{r}_{-\xi}(t)$ energy generally increases and that along a deactivation path $\mathbf{r}_{+\xi}(t)$ energy generally decreases. Therefore the joined path

$$\mathbf{r}_\xi(t) = \begin{cases} \mathbf{r}_{-\xi}(t) & 0 < t < t_M \\ \mathbf{r}_{+\xi}(t) & t_M < t < t_f \end{cases}$$

(6)

should be efficient in describing activation events, transition from a stable state, over a saddle point, to another stable state.

The statistical weight for this joined transition path is $e^{2N\gamma t_M - \beta(E_M - E_0)}$ with $E_M$ and $E_0$ being energy at $t_M$ and $t_0$, respectively. In this, the probability for transition from state $(\mathbf{r}_0, \mathbf{v}_0)$ at $t_0 = 0$ to state $(\mathbf{r}_f, \mathbf{v}_f)$ at $t_f$,

$$P(\mathbf{r}_0, \mathbf{v}_0, 0|\mathbf{r}_f, \mathbf{v}_f, t_f) = \int [\mathcal{D}\xi] P[\xi(t)] \delta(\mathbf{r}_\xi(t_f) - \mathbf{r}_f) \delta(\dot{\mathbf{r}}_\xi(t_f) - \mathbf{v}_f) e^{2N\gamma t_M - \beta(E_M - E_0)}.\quad (7)$$

Here the functional integral means summing over all possible samples of the random force $\xi(t)$ according its probability functional $P[\xi(t)]$. For each sample of the random force $\xi(t)$, integrating the negative friction Langevin equation (5) from time 0 to $t_M$ and integrating the regular (positive friction) Langevin equation (3) from $t = t_M$ to the final time $t = t_f$. Note that the intermediate state energy $E_M$ depends on the path generated for a given sample of $\xi(t)$ and therefore the corresponding exponential factor can not be moved out of the $\xi$-functional integral.

Using the afore-stated negative friction technique, we have studied the two and three particle clusters. A typical transition path for the two particle cluster ($N = 2$) is represented
in Fig. 2 to Fig. 4. The center of mass coordinates of the two particle cluster are plotted in Fig. 2. It is seen clearly that the cluster transfers from the left potential well located at \((-4, 0)\) through the narrow channel and relaxes down into the right potential well located at \((4, 0)\). The corresponding energy histogram in Fig. 3 shows the activation part with energy rising up and the deactivation part with energy falling down. From Fig. 4, we see that the distance between the two particles oscillates around the equilibrium value of \(2^{1/6}\) with a small amplitude. The orientation of the cluster “bond” adjusts roughly to the direction of the channel and the cluster moves up and through it to the other side.

An even more interesting transition path shows up for the three particle cluster \((N = 3)\). A typical transition event is described in Fig. 5 to Fig. 7. Fig. 5 shows the center of mass of the cluster transfers from left well at \((-4, 0)\) to the right well at \((4, 0)\). The corresponding energy histogram in Fig. 6 shows the energy rising up while activation out of the left well and the energy falling down while relaxation into the right well. Since a three cluster in the well region or in the absence of an external potential is about an equilateral triangle with each side equals \(2^{1/6}\) and the channel is much narrower than that size, it takes a very large energy for the cluster to go through the channel without drastically changing its shape. Fig. 7 shows the three bond lengths (distances between any two of the three particles). When the cluster is the left well, the three bonds are nearly equal to each other and it is near the equilibrium configuration. When it moves into the channel region, two bonds are still close to the equilibrium value but the third is approximately equal to the sum of the other two. Evidently, one of the three bonds breaks up and the cluster becomes linear when it activates up through the narrow channel into the other well on the right. During the relaxation into the right well, the three bonds again become approximately equal to one another and close to the equilibrium value as the energy falls down.

In summary, studying the motion of Lennard-Jones clusters in an external potential having a very narrow passage at the saddle point, we have presented a one point boundary scheme to numerically sample transition paths. This scheme does not require knowledge of the transition states (saddle points) or that of the final states. A transition path within a given time interval \((0, t_f)\) consists of an activation path during \((0, t_M)\) and a deactivation path during \((t_M, t_f)\) \((0 < t_M < t_f)\) joined at an intermediate time \(t_M\). The activation path is a solution to a Langevin equation with negative friction while the deactivation path is that to a regular Langevin equation with positive friction. For systems with smooth
potential energy surfaces, a final state can be located as where the transition path ends and the transition path so generated can be refined into accurate MEP using the two point boundary NEB method. For systems with irregular potential energy surfaces, this scheme provides a way to locate final states that are necessary for employing the more sophisticated two-point boundary transition path sampling schemes.


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FIG. 1: Contour plot of the two-dimensional potential in Eq.(2) that has a very narrow passage at saddle point. The potential well 1 is located around (-4,0) and well 2 at about (4,0). The saddle point is located at (0,0).

FIG. 2: A typical transition path of the two particle cluster. The x- (solid) and y- (dashed) coordinates of the center of mass of the cluster. The inverse temperature $\beta = 10.$ and friction $\gamma = 0.4.$

FIG. 3: Energy vs. time along the transition path in Fig.2.
FIG. 4: Bond length (solid) and orientation angle (dashed) (in radians) vs. time along the transition path in Fig.2.

FIG. 5: A typical transition path of the three particle cluster. The x- (solid) and y- (dashed) coordinates of the center of mass of the cluster. The inverse temperature $\beta = 5.0$ and friction $\gamma = 0.4$.

FIG. 6: Energy vs. time along the transition path in Fig.5.
FIG. 7: “Bond” lengths vs. time along the transition path in Fig.5: Distance between particles 1 and 2 (solid), distance between 2 and 3 (dashed), and distance between 1 and 3 (double dashed).