Solution of the Langevin equation for rare event rates using a path-integral formalism

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We present an approach to the problem of evaluating the rates of rare activated events by solving the Langevin equation through a path-integral formalism. At temperatures much lower than the activation barrier, we find that the minimal path approximation to the path integral yields excellent accuracy, and greatly simplifies numerical efforts in the solution of the Langevin equation. In addition, the extremal paths allow one to locate the saddle points without presuming any particular physical mechanisms for getting from one configuration to another. As a demonstration of this approach, we study the Brownian motion of a particle in a periodic potential subject to stochastic forces. This model has many applications in varied fields besides physics, such as chemistry and communication theory. We focus specifically in this paper on the application to the problem of surface adatom diffusion. For one dimension, the results we obtain with this approach are in full agreement with standard analytical and numerical methods. Furthermore, we have derived analytical formulas for the probability distribution of jump lengths. [S0163-1829(99)02248-1]

I. INTRODUCTION

A variety of phenomena in physics, chemistry, and other fields can be modeled as Brownian motion in a potential with local minima (stable or metastable states) separated by activation barriers.[1,2] Particles executing Brownian motion are subject to both regular forces resulting from the adiabatic potential and stochastic forces coming from coupling to the environment (a heat bath). The corresponding equation of motion describing this Brownian motion is the Langevin equation. At low temperatures, a typical trajectory of the system consists of a long period of localized motion about a local minimum, followed by a jump over a barrier, and then another long period of localized motion about another minimum, and so on. Activated processes over barriers are generally rare events, as the thermal energy k_BT is much less than the activation barrier V_b under typical conditions of practical importance. This makes a direct numerical simulation of the Langevin equation practically intractable, because most of the computation time would be ''wasted'' in the time interval between activated events, when the system is ''trapped'' in small oscillations in potential wells. Various schemes have been invented to speed up the processes and overcome this problem.[3] In this paper, we present an approach to the activated rare event problem by casting the Langevin equation into a path-integral formalism. We show that in the low-temperature regime, the contributions to the path integral are dominated by the extremal paths. These paths can be obtained by integrating a set of deterministic equations, and there is no ''wasted time'' in the potential well in this approach. It works well exactly in the regime where conventional numerical simulation methods are not feasible. As a demonstration of the approach, we apply the formalism to study the diffusion of adsorbed atoms (adatoms) on solid surfaces.[4] In this case, the problem can be described by a Langevin equation for the adatom in a periodic potential subject to stochastic forces. For one dimension, analytical results for the escape rate from a metastable state and the diffusion constant for a periodic potential in the high and low friction limits have been obtained through a direct solution of the Langevin equation or the equivalent Fokker-Planck equation.[5–10] However, a complete solution for an arbitrary friction value poses a considerable challenge. We show below that at low temperatures, the extremal path approximation to the path integral yields a result for the diffusion constant valid for all values of the friction. It agrees with the known results in the high and low friction limits. Analytical and numerical results on the jumping distance distribution are obtained within this approximation. Moreover, our approach can be easily applied to higher-dimensional cases, and for the inclusion of non-Markovian memory effects in the frictional damping.

The rest of this paper is organized as follows. In Sec. II, the path-integral formalism for the Langevin equation and the extremal path approximation is introduced. In Sec. III, we describe the application of this formalism to the study of the surface adatom diffusion problem. General formulas for the diffusion constant, jump distance distribution, and activation rate are obtained within the extremal path approximation, and numerical results for a wide range of friction values are presented. Analytical results for these observables in the underdamped and overdamped regimes are presented in Sec. IV. Section V contains discussions on the saddle points and extremal paths, and Sec. VI a summary.

II. PATH INTEGRAL FORMALISM FOR LANGEVIN EQUATION

The standard Langevin equation can be written in the following form:

$$m\ddot{x}(t) = -2\eta \int_{t_0}^{t} dt' s(t-t')\dot{x}(t') - \nabla V[x(t)] + \xi(t). \tag{1}$$

In the Langevin equation approach, there exists considerable flexibility in separating the explicit dynamical degrees of freedom represented by the vector coordinate $x(t)$ and the rest of the system representing the ''heat bath'' degrees of freedom, giving rise to the friction η and the random force ξ. For example, in the simplest type of surface diffusion mechanism involving the hopping motion of an adatom on the surface, the entire substrate degrees of freedom can be incorporated into the heat bath, and show up only implicitly in the friction η and the random force ξ. For more exotic mechanisms such as exchange or concerted motion, a larger dimension of explicit dynamical variable $x(t)$ is needed. Even for the simple hopping motion, the inclusion of all degrees of freedom explicitly in $x(t)$ is desirable, since the microscopic friction is then dynamically generated through the interaction of the particles rather than assumed in the Langevin equation as a parameter. When all the dynamical degrees of freedom are explicitly included, the role of the friction in Eq. (1) is then strictly just to provide a true heat bath. The numerical simulation of Eq. (1) then corresponds to doing molecular dynamics at a constant temperature for a canonical ensemble rather than a strict solution of Newton's equations that corresponds to a microcanonical ensemble. At this point, we are not restricting our discussion to any particular system, so $x(t)$ stands for a multicomponent vector with dimension ND, where N is the number of particles and D is the physical dimension of the system. $V(x)$ is a generalized potential including both external potential and interparticle interactions. The random force $\xi(t)$ characterizes the coupling to the heat bath. Its correlation can be written in the form $\langle \xi(t)\xi(t')\rangle = 2k_B T\eta s(t-t')$. Here η is the friction (damping) coefficient, and the function $s(t-t')$ has a correlation time τ. In general, the potential $V(x)$ has many local minima separated by activation barriers. To illustrate the nature of the path-integral approach clearly, in this paper we consider only the Markovian limit of the frictional damping. This is the limit where the random force correlation time $\tau \ll 1/\gamma$, so that $s(t-t')$ can be approximated by a delta function, namely, $s(t-t') \simeq \delta(t-t')$. Generalization to include memory effects is straightforward.

Unlike the case of a deterministic equation, there exists a whole distribution of solutions (paths) to the Langevin equation for a given boundary condition, and physical observables are obtained as averages over this distribution of paths. It has been shown that with regard to the solution of the Langevin equation (1), the joint probability $P[x(t)]$ for the system to take a particular path $x(t)$ starting at (x_i, v_i, t_i) and ending at (x,v,t) is given by the following expression:[11]

$$P[x(t)] = \frac{1}{\mathcal{N}} \exp\left\{ -\frac{1}{4\eta k_B T} \int_{t_i}^{t} dt [m\ddot{x} + \eta\dot{x} + \nabla V(x)]^2 \right\} \Bigg|_{\substack{\{x(t)=x,\dot{x}(t)=v\} \\ \{x(t_i)=x_i,\dot{x}(t_i)=v_i\}}} . \quad (2)$$

The total joint probability for the particle to be in (x_i, v_i) at $t=t_i$ and in (x,v) at $t=t$ is then given by the path (functional) integral[12]

$$P(x_i, v_i, t_i | x, v, t) = \int [\mathcal{D}x] P[x(t)]. \quad (3)$$

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 is much less than the activation barriers. Under this condition, there exist special paths whose contribution to the path integral in Eq. (3) dominates over all the other paths. To illustrate this more clearly, we introduce the typical length scale d, energy scale V_0, and time scale $\tau_0 \equiv \sqrt{md^2/V_0} \equiv 1/\omega_0$ for the system under consideration. Equation (3) can then be expressed in terms of dimensionless, scaled variables in the form

$$P(x_i, v_i, t_i | x, v, t) = \int [\mathcal{D}x] \exp\left\{ -\frac{1}{\lambda} I \right\}, \quad (4)$$

with the boundary conditions $\{x(t_i)=x_i, \dot{x}(t_i)=v_i\}$ and $\{x(t)=x, \dot{x}(t)=v\}$, and an effective action

$$I = \int_{t_i}^{t} dt \{\ddot{x}(t) + 2\gamma\dot{x}(t) + \nabla V[x(t)]\}^2, \quad (5)$$

where x, t, and V are all in their dimensionless form. The dimensionless friction parameter γ is defined as $\gamma \equiv \eta/m\omega_0$, and the dimensionless parameter λ appearing in the exponential of the functional integrand is $\lambda = 4\gamma k_B T/V_0$. Clearly, in the low-temperature and/or underdamped regime ($\gamma \ll 1$), $\lambda \ll 1$, the extremal 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 extremal path carry negligible contribution to the path integral in Eq. (4). The extremal path is determined from the condition that the functional derivative $\delta I/\delta x(t)$ vanishes. This leads to the standard Euler equation for the extremal path

$$\ddot{\zeta}(t) - \gamma\dot{\zeta}(t) + \zeta \cdot \nabla\nabla V[x(t)] = 0. \quad (6)$$

Here, $\zeta(t)$ stands for the combination $\ddot{x}(t) + \gamma\dot{x}(t) + \nabla V[x(t)]$. All quantities in Eq. (6) are in dimensionless form.

We note that Eq. (6) always allows a solution

$$\zeta = \ddot{x}(t) + \gamma\dot{x}(t) + \nabla V[x(t)] = 0. \quad (7)$$

This corresponds to the minimal path approximation (MPA) yielding the minimal value of the action $I=0$. The MPA is particularly useful for an actual evaluation of the rate processes as demonstrated in the sections below. Equation (7) is a deterministic equation that yields a final configuration $[x_f(x_i, v_i), v_f(x_i, v_i)]$ when integrated over time interval (t_i, t_f) for a given initial configuration (x_i, v_i). Expanding the action functional I up to second order in the deviation paths, and taking the limit $\lambda \to 0$, the joint probability in the MPA reduces to the form

$$P(x_i, v_i, t_i | x, v, t_f) = \delta[x - x_f(x_i, v_i)] \times \delta[v - v_f(x_i, v_i)] \exp(-I/\lambda), \quad (8)$$

where $I = \int_{t_i}^{t_f} dt \zeta(t)^2$ is evaluated along the minimal path solution satisfying Eq. (7). From this joint probability together with the initial (equilibrium) distribution $P(x_i, v_i)$, physical

observables can be evaluated conveniently. It should be pointed out that this path-integral formalism and the MPA are applicable to arbitrary interacting systems.

III. APPLICATION TO SURFACE ADATOM DIFFUSION

In order to illustrate the formalism described in Sec. II, we consider a model system describing the diffusive motion of a single particle on a substrate surface. The regular part of the interaction with the substrate is represented as a simple one-dimensional sinusoidal potential with period d and magnitude V_0. In the dimensionless form with d and V_0 as the length and energy scale, respectively, it can be expressed as

$$V(x)=[1-\cos(2\pi x)]. \tag{9}$$

The minima of this potential are located at integer values of $x=l$, with $l=0,1,2$, etc. The substrate vibrational (and electronic) degrees of freedom are incorporated in the friction and random force terms[13] in Eq. (1). We now consider the special solution $\zeta=0$ to Eq. (6) corresponding to the minimum of the action. This minimal path satisfies a simple Newtonian equation with friction:

$$\ddot{x}(t)+\gamma\dot{x}(t)+V'[x(t)]=0. \tag{10}$$

Integration of this minimal path equation produces a final configuration (x_f,v_f) from a given initial configuration (x_i,v_i). From Eq. (10), it follows easily that the scaled energy $e(x)=\dot{x}^2/2+V(x)$ decreases monotonously along the minimal path as

$$\frac{de(x)}{dt}=-\gamma\dot{x}^2=-2\gamma[e(x)-V(x)]. \tag{11}$$

So, starting from the initial location at x_i with initial energy $e_i=v_i^2/2+V(x_i)$, the energy $e(x)$ at a new location x following the minimal path is

$$e(x)-e_i=-\gamma\int_{x_i}^{x}dx(\pm)\sqrt{2[e(x)-V(x)]} \tag{12}$$

for $e_i\geq e(x)\geq 2$ (i.e., when the actual energy E is larger than or equal to the diffusion barrier $V_b=2V_0$). Here the $\pm$ sign corresponds to $\dot{x}>0$ or $\dot{x}<0$. Starting from x_i with $-1/2<x_i<1/2$ (with $v_i>0$), and following the minimal path $x(t)$, a point x_p will be reached where $e(x_p)=2$. After this point, the particle does not have enough energy to cross the next barrier. It will oscillate between two potential barriers with decreasing energy, and eventually settles down to the well bottom located at $x=l=[x_p+0.5]$. Here $[x_p+0.5]$ denotes the integral part of the real number $x_p+0.5$. Therefore, we conclude that the final position $x_f=l=[x_p+0.5]$ [i.e., $(l-1/2)<x_p<(l+1/2)$] with the final velocity $v_f=0$ (noting that we are interested in $t_f=\infty$). Thus we have

$$x_f=l, v_f=0 \quad \text{for } e_l(x_i)<e_i<e_{l+1}(x_i), \tag{13}$$

where the energy boundary

$$e_l=2+\gamma\int_{x_i}^{l-1/2+0}dx\sqrt{2[e(x)-V(x)]} \tag{14}$$

is determined by solving Eq. (12) for an $e(x)$ that satisfies the boundary conditions $e(x=x_i)=e_l$ and $e(x=l-1/2+0)=2$.

The solution of these minimal paths corresponds nicely to the physical picture that, at low temperatures, the actual motion of the adatom can be characterized by a series of uncorrelated jumps of variable lengths. We can define a jump length distribution p_l as the probability for the particle being activated from $[-1/2,1/2]$ and deactivated into $[(\pm l-1/2),(\pm l+1/2)]$ (jumping over l barriers with $l\geq 1$). This distribution function p_l does not directly follow from the joint probability in Eq. (8), but can be deduced from the raw jump probability P_l which is defined as the joint probability for a particle to be in the region $[-1/2,1/2]$ at t_i and to be deactivated in $[(\pm l-1/2),(\pm l+1/2)]$ at t_f. In this definition of P_l, jumps activated in $[(\mp k-1/2),(\mp k+1/2)]$ for an arbitrary nonnegative integer k, passing through the central region $[-1/2,1/2]$, and then deactivated in $[(\pm l-1/2),(\pm l+1/2)]$ are all included. The raw jump probability P_l can be directly evaluated within the minimal path approximation for the joint probability in Eq. (8) as

$$\begin{aligned}P_l&=\frac{1}{\mathcal{C}}\int\int dx_i dv_i\int\int dx dv P(x_i,v_i)\\&\quad\times\chi_0(x_i)\chi_l(x)P(x_i v_i,t_i|x,v,t_f)\\&=\frac{1}{\mathcal{C}}\int\int dx_i dv_i P(x_i,v_i)\chi_0(x_i)\chi_l[x_f(x_i,v_i)],\end{aligned} \tag{15}$$

where $x_f(x_i,v_i)$ is the solution of the deterministic equation (6) with $\zeta=0$. The characteristic function $\chi_l(x)=1$ when $(\pm l-1/2)<x<(\pm l+1/2)$, and $\chi_l(x)=0$ otherwise. $\mathcal{C}$ is a normalization constant chosen such that $\Sigma_{l=1}^{\infty}P_l=1$. Making use of the symmetry of the potential $V(x)$ and the minimal path solutions in Eqs. (13) and (14), we can simplify Eq. (15) to the form

$$P_l=\frac{2}{\mathcal{C}Z}\int_{-1/2}^{1/2}dx_i\int_{e_l}^{e_{l+1}}de_i\left|\frac{\partial v_i}{\partial e_i}\right|\exp\left(-\frac{V_0 e_i}{k_B T}\right), \tag{16}$$

which is for $l\geq 1$ and in terms of the dimensionless x_i,v_i, and e_i. Here the initial distribution $P(x_i,v_i)=\exp(-E_i/k_BT)/Z$ is made use of explicitly. Z is the dimensionless partition function given by the expression

$$Z=\int_{-1/2}^{1/2}dx_i\int_{-\infty}^{\infty}dv_i\exp\left(-\frac{V_0 e_i}{k_B T}\right), \tag{17}$$

and the normalization constant $\mathcal{C}$ is easily determined to be

$$\mathcal{C}=1-\frac{2}{Z}\int_{-1/2}^{1/2}dx_i\int_{0}^{e_1}de_i\left|\frac{\partial v_i}{\partial e_i}\right|\exp\left(-\frac{V_0 e_i}{k_B T}\right). \tag{18}$$

Considering the translational invariance at equilibrium, we have the relation $P_l=P_1\Sigma_{k=0}^{\infty}p_{l+k}$. Therefore, the true distribution p_l which measures the relative probabilities of jumps originating from particle at equilibrium in the central region is given by

$$p_l=(P_l-P_{l+1})/P_1 \quad \text{when } l=1,2,\ldots. \tag{19}$$

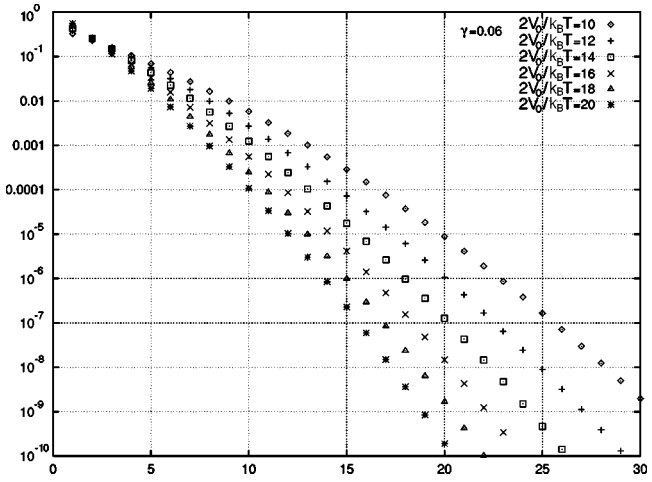

FIG. 1. The jumping distance distribution p_l vs l for various temperatures: $2V_0/k_BT=10$–20 in steps of 2. $\gamma=0.06$.

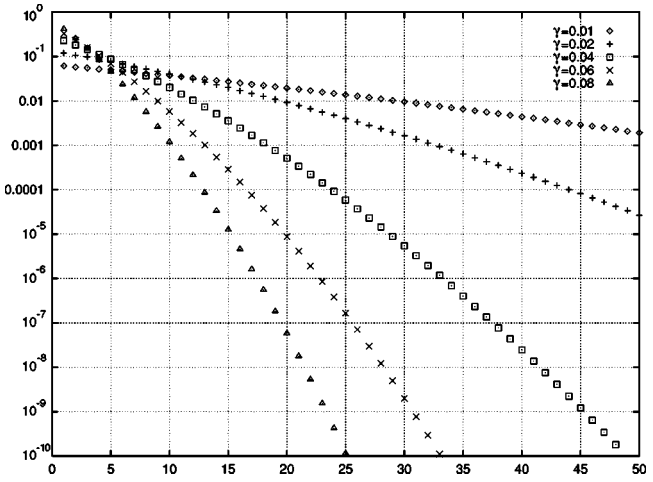

FIG. 2. The jumping distance distribution p_l vs l for various friction values: $\gamma=0.01$, 0.02, 0.04, 0.06, and 0.08. $2V_0/k_BT=10$.

The jump length distribution p_l defined in the above equation is properly normalized such that $\Sigma_{l=1}^{\infty}p_l=1$, provided that the raw jump probability P_l decreases with l. With the knowledge of the distribution function p_l for the various jump lengths, the diffusion constant D can now be expressed in the form

$$D=\nu d^2\langle l^2\rangle \quad \text{with } \langle l^2\rangle=\sum_{l=1}^{\infty} l^2 p_l . \tag{20}$$

Here ν is the activation rate which is equal to the deactivation rate from the detailed balance condition. The latter is equal to the product of the current flowing into region $[-1/2,1/2]$, and the probability to deactivate there. As the influx current comes from the nearest neighbors, the probability to deactivate in $[-1/2,1/2]$ is simply P_1. Therefore,

$$\nu=2\int_0^{\infty} dv_i P(x_i=-1/2,v_i)v_i P_1 . \tag{21}$$

The application of this formula requires a knowledge of the transition state boundaries which is trivial for the present case, corresponding to the two points $x=-1/2$ and 1/2.

In the minimal path approach, the diffusion constant D can also be directly evaluated through the velocity autocorrelation function as

$$\begin{aligned} D&=2\int_0^{\infty} dt\langle v(0)v(t)\rangle dt \\ &=2\langle v(0)[x(t_f)-x(0)]\rangle\big|_{t_f\to 0} \\ &=2\int dv_i \int dx_i P(x_i,v_i)v_i x(x_i,v_i,t_f)\big|_{t_f\to 0} . \end{aligned} \tag{22}$$

Applying the conclusion about the final configuration x_f for a given e_i in Eq. (13), we can decompose the expression for D in Eq. (22) into contributions from minimal paths of various jumping length l as

$$D=\frac{4d^2}{Z\tau_0}\int_{-1/2}^{1/2} dx_i \sum_{l=1}^{\infty} \int_{e_l}^{e_{l+1}} de_i \exp\left(-\frac{V_0 e_i}{k_B T}\right) l. \tag{23}$$

Here the initial position x_i, velocity v_i, and energy $e_i=v_i^2/2+V(x_i)$ are all in dimensionless form, while D carries its physical dimension. When the diffusion constant D and the mean-square jump distance $d^2\langle l^2\rangle$ have been evaluated independently through Eqs. (23) and (20), the activation rate ν can then be simply obtained from the ratio of these two quantities.

We have solved the equation for the minimal paths numerically for a full range of friction γ. The numerical results for the jump length distribution p_l vs l at low temperatures and various values of the friction parameter γ are plotted in Figs. 1–3. The near-exponential behavior of p_l upon l stems from the fact that longer jumps require higher initial energy, and an initial configuration of higher energy is exponentially less probable (initial equilibrium distribution $P(x_i,v_i)=\exp[-V_0 e_i/k_BT)]$. This interesting behavior becomes more explicit in the analytical result in the underdamped regime ($\gamma\ll 1$), as described in Sec. IV. It should be noted that for the one-dimensional model system considered here, some of the results presented here have been obtained by others, relying on numerical implementation of the matrix-continued-

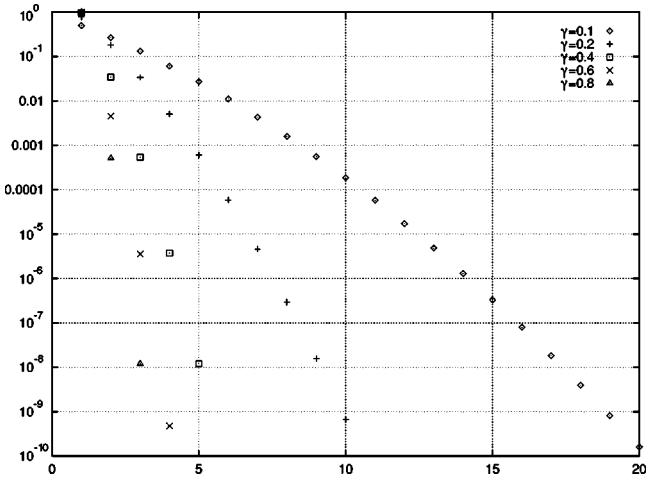

FIG. 3. The jumping distance distribution p_l vs l for various friction values: $\gamma=0.1$, 0.2, 0.4, 0.6, and 0.8. $2V_0/k_BT=10$.

fraction expansion (MCFE).[7,9] However, for higher dimensions and low friction regime, the MCFE is very difficult, if not impossible, to implement numerically.[15] On the other hand, the numerical demand of the present minimal path approach is modest, and the solution for higher-dimensional systems is quite feasible.

IV. ANALYTICAL RESULTS IN THE UNDERDAMPED AND OVERDAMPED REGIMES

In the underdamped and overdamped regimes corresponding to $\gamma \ll 1$ or $\gamma \gg 1$, analytical results can be obtained. First we examine the underdamped regime. In this region, the energy of the particle in transit differs only slightly from the threshold value of $e=2$ (i.e., $E=2V_0$). Thus, to lowest order in γ, we can replace the energy function $e(x)$ in the integrand of Eq. (14) by the constant value of 2, leading to the expression

$$e_l = 2 + \gamma \int_{x_i}^{l-1/2} dx \sqrt{2[1+\cos(2\pi x)]}. \tag{24}$$

For $l \geqslant 1$,

$$e_l = 2 + (l-1)\frac{4}{\pi}\gamma + \gamma\frac{2}{\pi}(1-\sin \pi x_i). \tag{25}$$

The diffusion constant can be evaluated through the substitution of the result for e_l in Eq. (25) into the expression for D in Eq. (23), yielding the following result valid for $\gamma \ll 1$:

$$D = \frac{4d^2 k_B T}{Z\tau_0 V_0} \int_{-1/2}^{1/2} dx_i \sum_{l=1}^{\infty} \left[\exp\left(-\frac{V_0 e_l}{k_B T} \right) - \exp\left(-\frac{V_0 e_{l+1}}{k_B T} \right) \right] l$$

$$= \frac{2d^2 k_B T}{Z\tau_0 V_0} \exp\left(-\frac{2V_0}{k_B T} \right) I_0\left(\frac{2V_0\gamma}{\pi k_B T} \right) \Big/ \sinh\left(\frac{2V_0\gamma}{\pi k_B T} \right). \tag{26}$$

Considering that $V_0 \gg k_B T$ and $e_1 \simeq 2$, the combination of Eqs. (25) and (16) yields the expressions for P_l to the first order of γ for $l=1,2,\ldots$ as

$$P_l = \left(\exp\left(\frac{\Delta E}{k_B T} \right) - 1 \right) \exp\left(-l\frac{\Delta E}{k_B T} \right), \quad l = 1,2,\ldots; \tag{27}$$

here $\Delta E = 4V_0\gamma/\pi$. Interestingly, in this limit the true jump length distribution p_l follows from Eq. (19) identically to P_l. This analytical formula for the jump length distribution clearly shows that there seems to be an energy ''barrier'' ΔE separating jumps over different distances. In the low-temperature regime where $V_0/k_B T \gg 1$, underdamping ($\gamma \ll 1$) does not necessarily imply the smallness of $\Delta E/k_B T$. Therefore, interesting behaviors of the jump distance distribution upon jump length and temperature can be observed.[9,14–19] In fact, in the appropriate temperature range, a jump over $l+1$ barriers has an additional barrier ΔE to overcome than a jump over l barriers. The dependence of jump length distribution p_l possesses the ''Arrhenius'' form, which was recently observed experimentally.[17]

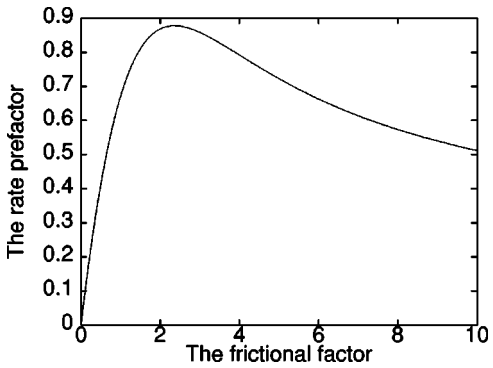

FIG. 4. The rate prefactor $[(\nu/\omega_0)\exp(2V_0/k_B T)]$ vs the frictional factor $(4V_0\gamma/\pi k_B T)$.

With the knowledge of the relative probability of jump lengths of l lattice constants p_l, we can obtain the second expression for D from Eq. (20) as

$$D = \nu d^2 [\exp(\Delta E/k_B T) - 1] \sum_{l=1}^{\infty} l^2 \exp(-l\Delta E/k_B T)$$

$$= \nu d^2 \coth(\Delta E/2k_B T)[1-\exp(-\Delta E/k_B T)]^{-1}. \tag{28}$$

The activation rate can be found through Eqs. (26) and (28):

$$\nu/\omega_0 = 4\exp(-2V_0/k_B T) I_0(\Delta E/2k_B T)/\cosh(\Delta E/2k_B T). \tag{29}$$

This result can also be derived through Eq. (21). Figure 4 shows the well known ''turnover'' behavior of the jump rate ν as a function of the friction γ. As γ rises from 0, so does the rate ν in proportion with γ. The rate ν rises to a maximum at $\gamma \sim k_B T/V_0$ before it decreases upon further increase of γ. We also note that in the ''low friction'' limit when we have $\gamma \ll k_B T/V_0$, Eq. (26) simplifies to

$$D = \frac{\pi k_B T}{m\gamma\omega_0} \exp\left(-\frac{2V_0}{k_B T} \right), \tag{30}$$

which coincides with the result derived by other means.[6] Note that in the low-temperature regime, $V_0 \gg k_B T$, the condition for the low friction limit required for the validity of Eq. (30) is much more stringent than the mere requirement of underdamping, i.e., $\gamma \ll 1$.

In the high friction regime, when $\gamma \gg 1$, the minimal path approximation again recovers the known analytical results. For $\gamma \gg 1$, energy dissipates rapidly along the minimal path at a rate $\sim \gamma$ [see Eq. (11)]. It is clear that $e_l \geqslant e_1 + O(\gamma)$ for $l=2,3,\ldots$, and, therefore, activated jumps are dominantly over one single barrier. Furthermore, considering a minimal path starting from $-1/2 < x_i < 1/2$ with $v_i > 0$, $e_1(x_i)$ even more strongly depends on initial position x_i and, in fact, the minimal path can reach the next well region $x > 1/2$ only when x_i is very close to the barrier $x=1/2$. So we approximate the potential around $x=1/2$ as $V(x) = 2 + 2\pi^2(x-1/2)^2$; the minimal path solution of Eq. (6) gives

$$e_1 = 2 + \frac{1}{2}\gamma^2 (x_i - 1/2)^2, \tag{31}$$

where the energy $e(x)$ (in the minimal path solution) satisfies the boundary conditions $e(x = x_i) = e_1$ and $e(x = 1/2 + 0) = 2$. In this, integrating Eq. (23), the diffusion constant is found:

$$D = (k_B T / 2m\gamma\omega_0) \exp(-2V_0 / k_B T); \tag{32}$$

this is in exact agreement with the known result derived through other means.[10] Carrying out the integrations in Eq. (16), the raw jump probabilities P_l are given as

$$P_1 = 1, \tag{33}$$

$$P_l = O\left[\exp\left(-\gamma \frac{V_0}{k_B T}\right)\right] \quad \text{for } l = 2,3,\ldots, \tag{34}$$

with which Eq. (19) delivers the jump length distribution as

$$p_1 = 1, \quad p_l \approx 0 \quad \text{for } l = 2,3,\ldots. \tag{35}$$

This leads to the mean-square average jumping distance $\sqrt{\langle l^2 \rangle} = 1$. The activation rate can then be obtained:

$$\nu = (k_B T / 2\eta d^2) \exp(-2V_0 / k_B T); \tag{36}$$

this is again identical to the result derived through other means.[10] It should be noted that the validity of the overdamped limit analytical results are rather limited because $\lambda = 4\gamma k_B T / V_0$ has to be $\ll 1$ for the minimal path approximation to be applicable, while the underdamped limit results have a wider range of applicability.

V. SADDLE POINTS AND EXTREMAL PATHS

In the last two sections, we demonstrated how the minimal path approximation in the path-integral formalism yields results for the diffusion constant and the jump rates for a model diffusion problem without the usual ''rare events'' trouble in the conventional approach of a direct simulation of the Langevin equation. As shown in Eq. (6), the minimal path is just a special case of the extremal path. In the MPA approach, the rare activation problem at low temperatures is avoided by starting at or above the threshold energy at the saddle point, and sampling the neighborhood of these starting points. Thus the MPA approach is similar to the transition-state theory (TST), including all the dynamical corrections.[20] The effects of ''recrossing'' or long jumps are automatically included in the minimal paths. These minimal paths also are similar to the ''transition paths'' discussed by Jacobsen and co-workers[18,21] in a different approach.

For the simple one-dimensional model studied in the last two sections, the threshold just corresponds to the top of the potential, and the application of the MPA is straightforward. For multidimensional systems where all the interacting particles are explicitly included instead of being allocated to the heat bath degrees of freedom, the saddle-point structures can be very complicated, and are usually not known *a priori*. Powerful methods have been introduced recently to locate the saddle points in such multidimensional systems.[22,23] However, they still require a knowledge of starting and ending configurations which is equivalent to assuming a particular physical mechanism for the transition between the two configurations. In this regard, the extremal paths discussed in Eq. (6) can be used as a powerful tool for locating the relevant saddle points near the starting configuration without preassuming the mechanism. To illustrate this, we have solved Eq. (6) for the Langevin dynamics of a particle in a two-dimensional potential,

$$V(x,y) = 1 - \exp[-4x^2 - (y-2)^2] - \exp[-(x-2)^2 - 4y^2], \tag{37}$$

which possesses two potential wells located at (0,2) and (2,0) respectively. There is a unique extremal path solution to Eq. (6), that starts from one well bottom, $(x_i, y_i) = (0,2)$ and $\mathbf{v}_i = (0,0)$, ascends to the saddle point located at (0.4,0.4), and descends into the other well bottom $(x_f, y_f) = (2,0)$ and $\mathbf{v}_f = (0,0)$. In terms of initial conditions, this corresponds to a definite choice for the initial values for ζ and $\dot{\zeta}$. The nature of this extremal path switches from activation to deactivation exactly at the saddle point when the value of ζ is precisely zero there. The deactivation part of this path actually obeys the minimal path equation $\zeta(t) = 0$. In practice, the precise values of this particular pair of initial values ζ and $\dot{\zeta}$ are unknown. However, we find that there is a range of choice of initial conditions such that the extremal path would still go through the saddle point, albeit with a nonvanishing value of ζ there. Thus numerical integration of Eq. (6) enables one to selectively simulate the activation-deactivation processes without ''wasting'' computing time on the long but fruitless oscillation part between two rare activated events. It is interesting to note that the extremal path searches for and locates the desired saddle points without requiring a knowledge of the final configuration. Moreover, it produces the true activation dynamics. Applications of this method to multidimensional systems will be published elsewhere.

VI. SUMMARY

In summary, we have presented an alternative to the direct simulation of the Langevin equation by casting it into a path-integral formalism. The formalism can be applied to multidimensional systems where all the degrees of freedom of interacting particle are explicitly included. In this case, the Langevin dynamics simply corresponds to a particular form of constant-temperature molecular dynamics. In the low-temperature regime where conventional simulation methods are not practical, the path-integral approach is particularly simple because contributions to the path integral in this regime are dominated by extremal paths. Among the extremal paths, the minimal path is particularly important since it directly yields results for the activation rate, diffusion constant, jumping distance distribution, etc., as demonstrated by the explicit calculation for a simple model. Since the tempera-

ture is not an explicit factor in the minimal path [Eq. (6)], this study does not require greater CPU time in lower temperatures. The results for activation rate and diffusion constant are in full agreement with the known results through other means. Furthermore, analytical and numerical results on the jumping distance distribution have been obtained. Finally, we demonstrate that besides the minimal path, other extremal paths are useful for finding threshold (saddle point) barriers without any presumption of the physical activation mechanism or intensive numerical efforts. This could be particularly useful for systems with complicated energy landscapes.

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[1] V. I. Mel'nikov, Phys. Rep. **209**, 1 (1991).
[2] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[3] See, e.g., A. F. Voter, Phys. Rev. Lett. **78**, 3908 (1997); J. Chem. Phys. **106**, 4665 (1997).
[4] R. Gomer, Rep. Prog. Phys. **53**, 917 (1990).
[5] H. A. Kramers, Physica (Amsterdam) **7**, 284 (1940).
[6] H. Risken, *The Fokker-Planck Equation* (Springer-Verlag, Berlin, 1989).
[7] R. Ferrando, R. Spadacini, and G. E. Tommei, Phys. Rev. E **48**, 2437 (1993).
[8] E. Pollak and P. Talkner, Phys. Rev. E **47**, 922 (1993).
[9] L. Y. Chen and S. C. Ying, Phys. Rev. Lett. **71**, 4361 (1993); Phys. Rev. B **49**, 13 838 (1994).
[10] S. C. Ying, Phys. Rev. B **41**, 7068 (1989); T. Ala-Nissila and S. C. Ying, Prog. Surf. Sci. **39**, 227 (1992).
[11] A. Schmid, J. Low Temp. Phys. **49**, 609 (1982).
[12] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
[13] M. Brandbyge, P. Hedegard, T. F. Heinz, J. A. Misewich, and D. M. Newns, Phys. Rev. B **52**, 6042 (1995).
[14] Yu. Georgievskii and E. Pollak, Phys. Rev. E **49**, 5098 (1994).
[15] L. Y. Chen, M. R. Baldan, and S. C. Ying, Phys. Rev. B **54**, 8856 (1996).
[16] S. Yu. Krylov, A. S. Prosyanov, and J. J. M. Beenhakker, J. Chem. Phys. **107**, 6970 (1997).
[17] T. R. Linderoth, S. Horch, E. Laegsgaard, I. Stensgaard, and F. Besenbacher, Phys. Rev. Lett. **78**, 4978 (1997).
[18] J. Jacobsen, K. W. Jacobsen, and J. P. Sethna, Phys. Rev. Lett. **79**, 2843 (1997).
[19] F. Montalenti and R. Ferrando, Phys. Rev. B **58**, 3617 (1998).
[20] For a review of dynamical corrections to TST, see J. B. Anderson, Adv. Chem. Phys. **71**, 381 (1995).
[21] K. W. Jacobsen (private communication).
[22] C. Dellago, P. G. Bolhuis, F. S. Csajka, and D. Chandler, J. Chem. Phys. **108**, 1964 (1998).
[23] H. Jonsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998), Chap. 16, and references therein.