The Kramers problem revisited: A minimal path approximation
to the Langevin equation

L. Y. Chen

Department of Physics, University of Texas at San Antonio, San Antonio, TX 78249

Abstract

Applying the minimal path approximation to the Langevin equation, we re-
visit the well-known Kramers problem, noise-activated escape of a particle
out of a meta-stable well and present a new technique to evaluate the activa-
tion rate. This new technique is valid for low to intermediate friction and is
accurate for low temperatures. For low friction, analytical solution is derived.
For intermediate friction, numerical results are obtained with minimal com-
putational effort and the numerical effort required does not increase going for
lower temperature.
I. INTRODUCTION

Noise-activated escape from a meta-stable state was investigated in a historic pioneering paper by Kramers. [1] Since then the Kramers problem has been elaborated and extended in many ways, see, for example, references [2–8]. In particular, Kramers calculated the activation (or escape) rate in the very low friction limit and the high friction limit. The crossover from the low friction to the high friction limit has been of much interest but substantial improvements upon Kramers’ original analytical results have only been obtained rather recently. Matrix-continued-fraction-expansion solution [2,6] to the Fokker-Planck equation and direct simulation [5,8] of the Langevin equations, among other methods, have produced accurate results for the activation rate in a range of friction values. Both methods are only feasible for not very low temperatures and not very low friction. In this paper, we apply a recently developed approximation, the minimal path approximation [9] to the Langevin equation and present a formulation for solving the Kramers problem. This new technique is valid for low to intermediate friction and is accurate for low temperatures. For intermediate friction, numerical results are obtained with minimal computational effort and the numerical effort required does not increase going for lower temperature. For low friction (i.e., when the friction coefficient $\eta/m \ll \omega_0$, the oscillation frequency around the meta-stable state), analytical solution will be derived. It is interesting to note that the crossover from the very low friction behavior to “high” friction behavior can even occur in the low friction regime when the temperature $T$ is low enough. Our analytical solution will explicitly show that the crossover actually occurs when the friction parameter $\eta/m\omega_0$ moves from the $\ll k_BT/V_0$ limit to the $\gg k_BT/V_0$ limit ($V_0$, relevant potential energy scale and $k_B$, the Boltzmann constant). This whole range can fall within the low friction $\eta/m\omega_0 \ll 1$ regime if the temperature is low enough $k_BT/V_0 \ll 1$.

In section II, the minimal path approximation is adapted into a form appropriate for the Kramers problem. In section III, the evaluation of activation (or escape) rate and the numerical result. In section IV, the analytical result and a discussion on the crossover. In
II. THE MINIMAL PATH APPROXIMATION

We start with the standard Langevin equation in its dimensionless form,

\[ \ddot{x}(t) = -\gamma \dot{x}(t) - V'(x(t)) + \xi(t) \tag{1} \]

where \( x(t) \), scaled by \( d \), is the coordinate and

\[ V(x) = x^2 (1 - x/2) \tag{2} \]

shown in Fig.1, is the potential, \( V(x) = V_0 (x/d)^2 (1 - x/2d) \), scaled by \( V_0 \). \( \xi(t) \), scaled by \( m d \omega_0^2 \), is the random force that characterizes the coupling of the system to its environment (a heat bath). Its correlation can be written in the form \( \langle \xi(t) \xi(t') \rangle = 2(\gamma/\beta) \delta(t - t') \) in the Markovian limit. Dimensionless inverse temperature \( \beta = V_0/k_B T \). Dimensionless frictional (damping) parameter \( \gamma = \eta/m \omega_0 \) where \( \eta \) is the frictional coefficient. \( \omega_0 = \sqrt{2V_0/md^2} \), and \( m \) is the mass of the particle. Energy \( E \) is scaled by \( V_0 \), and time \( t \), by \( \tau_0 \equiv 1/\omega_0 \) etc. Here and through the end of this paper, we work in dimensionless forms. The frequency of local vibration in the well is 1 in its dimensionless form (i.e., \( \omega_0 \) if not scaled).

In the path integral formalism, [10–12] the 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 given by the following path (functional) integral

\[ P(x_1, v_1, t_1|x_2, v_2, t_2) = \int [\mathcal{D}x] \exp \left\{ -\frac{1}{\lambda} I[x(t)] \right\} \bigg|_{\{x(t_1)=x_1, \dot{x}(t_1)=v_1\}}^{\{x(t_2)=x_2, \dot{x}(t_2)=v_2\}} \tag{3} \]

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

\[ I[x(t)] = \int_{t_1}^{t_2} dt [\ddot{x}(t) + \gamma \dot{x}(t) + V'(x(t))]^2 \tag{4} \]

is positive-definite. Clearly, in the low temperature \( (k_B T \ll V_0) \) and/or under damped regime \( (\gamma \ll 1) \), \( \lambda = 4\gamma k_B T/V_0 \ll 1 \), the minimal path of functional \( I[x(t)] \) carries the
dominant weight in the path integration of Eq. (3) and any deviations from the minimal path carry negligible contribution to the path integral in Eq. (3).

There are two types of minimal paths for the action functional in Eq. (4). First the deactivation path $x_d(t)$ that satisfies

$$\ddot{x}_d(t) + \gamma \dot{x}_d(t) + V'(x_d(t)) = 0. \tag{5}$$

Integrating Eq. (5) forward with boundary conditions $x_d(t_M) = x_M, \dot{x}_d(t_M) = v_M$, from time $t_M$ to $t_f > t_M$, 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 path $x_d(t)$ the energy of the system decreases monotonously and the action $I[x_d(t)]$ assumes its minimal value $I_d = 0$. The activation path that is a minimum of action functional $I[x(t)]$ with a different set of boundary condition satisfies

$$\ddot{x}_a(t) - \gamma \dot{x}_a(t) + V'(x_a(t)) = 0. \tag{6}$$

Integrating Eq. (6) backward with boundary conditions $x_a(t_M) = x_M, \dot{x}_a(t_M) = v_M$, from time $t_M$ to $t_i < t_M$, 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 path $x_a(t)$, from $t_i$ to $t_M$, the energy of the system increases monotonously and the action $I[x_a(t)]$ assumes its minimal value $I_a = 4 \gamma (E_M - E_i)$ where $E_M = v_M^2/2 + V(x_M)$ and $E_i = v_i^2/2 + V(x_i)$ are the energies at times $t_i$ and $t_M$ respectively.

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,

$$P(x_i, v_i, t_i | x_M, v_M, t_M | x_f, v_f, t_f) = \delta(x_i - x_a(t_i | M)) \delta(v_i - \dot{x}_a(t_i | M)) \exp[-\beta (E_M - E_i)] \delta(x_f - x_d(t_f | M)) \delta(v_f - \dot{x}_d(t_f | M)). \tag{7}$$

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.
III. ACTIVATION RATE

For the potential in Eq.(2), there is a meta-stable well located at \( x_w = 0 \) where \( V_w = 0 \). The barrier is located at \( x_B = 4/3 \) where \( V_B = 16/27 \). In order to evaluate the activation (or escape) rate \( r \), we define the well region as \( x \leq x_B \) and introduce a characteristic function \( h_w(x) \) which is equal to 1 when \( x \leq x_B \) and is equal to 0 otherwise. Then the rate of activation out of the well can be expressed as [13]

\[
r = \frac{d}{dt_M} \langle h_w(x(t_i))h_{\bar{w}}(x(t_M))h_{\bar{w}}(x(t_f)) \rangle
\]

(8)

where \( h_{\bar{w}}(x) \) is the characteristic function of the out-of-the-well region \( x \geq x_2 \) (\( x_2 \) should be \( \geq x_B \)). This formula in conjunction with the joint probability in Eq.(7) produces a result independent of time \( t_M \) that is valid for low temperatures where \( t_f - t_i << 1/r \). The ensemble average

\[
< \cdot > = \int \int dx_idv_i \int \int dx_Mdv_M \int \int dx_fdv_f(\cdot)P(x_i, v_i)P(x_i, v_i|x_M, v_M|x_f, v_f)
\]

(9)

is with respect to the joint probability in Eq.(7). It is interesting to point out that the choice of \( x_2 \) in the definition of the out-of-the-well region is not absolute. The physical results is insensitive to \( x_2 \) as long as \( x_2 \geq x_B \) and the \( h_w(x_i) \) and \( h_{\bar{w}}(x(t_f)) \) factors are in force.

Carrying out the time derivative in Eq.(8), we have

\[
r = \langle h_w(x_i)\delta(x_M - x_2)v_Mh_{\bar{w}}(x_f) \rangle.
\]

(10)

Take the initial distribution function in the well region as equilibrium

\[
P(x_i, v_i) = \frac{1}{Z}\exp(-\beta E_i)
\]

(11)

with the partition function

\[
Z = \int_{-\infty}^{x_W}dx_i \int_{-\infty}^{\infty}dv_i \exp(-\beta E_i).
\]

(12)

Employing Eq.(7), Eq.(10) can be manipulated into
\[ r = \frac{1}{Z} \int dE_M \int dx_M d\nu_M \exp(-\beta E_M) h_w(x_a(t_1\!|M)) \delta(x_M - x_2) \nu_M h_{\bar{w}}(x_d(t_f\!|M)). \] (13)

Here \( x_a(t_i\!|M) \) is obtained by integrating the activation equation (6) backward from \( t_M \) to \( t_i \) and \( x_d(t_f\!|M) \) by integrating the deactivation equation (5) forward from \( t_M \) to \( t_f \). Eq.(13) can be readily implemented numerically. The numerical results for \( r \) are presented in Fig.2 to Fig.4. The temperature dependence is the expected Arrhenius form with a slope of 0.59 in the \( r \) vs. \( \beta \) plot which is exactly the potential barrier \( V_B \). It’s interesting to note the dependence of rate \( r \) upon the damping parameter \( \gamma \) in Figs.3 and 4. At low friction, we have \( r \propto \gamma \), identical to Kramers’ original derivation. [1] Increasing \( \gamma \), \( r \) crosses over to the intermediate damping transition state theory result. The crossover occurs at a friction value that depends on the temperature.

**IV. ANALYTICAL RESULT**

In the low friction regime, \( \gamma \ll 1 \), the deactivation path \( x_d(t\!|M) \) and the activation path \( x_a(t\!|M) \) (Eqs.(5) and (6)) can be manipulated to analytically determine the characteristic function \( h_w(x_a(t_1\!|M)) \) and \( h_{\bar{w}}(x_d(t_f\!|M)) \) in Eq.(13). This leads to analytical solution for the activation rate \( r \).

Carrying out the integration with respect to \( x_M \) and converting the \( \nu_M\)-integral into the \( E_M\)-integral, we have, from Eq.(13),

\[ r = \frac{1}{Z} \int dE_M \exp(-\beta E_M) h_w(x_a(t_1\!|M)) h_{\bar{w}}(x_d(t_f\!|M)) \bigg|_{x_M=x_2}. \] (14)

First consider the case when \( \nu_M > 0 \). We see that energy \( E = [\dot{x}_d(t)]^2/2 + V(x_d(t)) \) decreases along the deactivation path \( x_d(t) \) from \( t_M \) to \( t_f \). From Eq.(5),

\[ \frac{d}{dt}E(x_d(t)) = -\gamma[\dot{x}_d(t)]^2. \] (15)

If \( \nu_M \geq 0 \) and \( E_M > V_B \), path \( x_d(t) \) will end up to be out of the meta-stable well, i.e., the characteristic function in Eq.(14) \( h_{\bar{w}}(x(t_f\!|M)) = 1 \). For other characteristic function
Consider how the energy $E = [\dot{x}_a(t)]^2/2 + V(x_a(t))$ decreases with going backward in time from $t_M$ to $t_i$. Eq.(6) leads to

$$\frac{d}{dt}E(x_a(t)) = \gamma [\dot{x}_a(t)]^2.$$  \hspace{1cm} (16)

In this, for a given $v_M > 0$, path $x_a(t)$ falls into the well region if $V_B < E_M < V_B + 2\gamma S$ and falls into the out-of-the-well region otherwise. Namely, we have $h_w(x_a(t_i|M)) = 1$ when $V_B < E_M < V_B + 2\gamma S$ and $h_w(x_a(t_i|M)) = 0$ when $E_M > V_B + 2\gamma S$. Here $S$ is the mechanical action along the activation path $x_a(t)$ from the turning point $x_L$ left to the well to the barrier top $x_B$,

$$S = \int dt[\dot{x}_a(t)]^2 = \int_{x_L}^{x_B} dx \sqrt{2(V_B - V(x))} = \frac{16\sqrt{2}}{15}$$  \hspace{1cm} (17)

with $x_L = -2/3$ being the root of $V(x_L) = V_B$.

Now consider the case when $v_M < 0$. Analysis similar to the above leads to the conclusion that a state with $v_M < 0$ at the top of the barrier can only be activated into from the right to the barrier, i.e., $h_w(x_a(t_i|M)) = 0$ if $v_M < 0$.

Putting the characteristic functions determined above into Eq.(14), we have

$$r = \frac{1}{Z} \int_{V_B}^{V_B+2\gamma S} dE_M \exp(-\beta E_M)$$

$$= \frac{1}{2\pi} \exp(-\beta V_B)[1 - \exp(-2\beta \gamma S)].$$  \hspace{1cm} (18)

Clearly Eq.(18) gives us the Kramers low friction result

$$r = \frac{\beta \gamma S}{\pi} \exp(-\beta V_B)$$  \hspace{1cm} (19)

when $\gamma \ll 1/\beta S$. Note that the $r \propto \gamma$ behavior requires more than $\gamma \ll 1$ because $1/\beta \ll 1$ for low temperatures. We also observe the crossover behavior in Eq.(18) from the $\gamma \ll 1/\beta S$ regime to the $\gamma \gg 1/\beta S$ regime. The crossover value of damping $\gamma$ depends upon the temperature $1/\beta$. 

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V. SUMMARY

We have applied the minimal path approximation to the Langevin equation to studying the rare events of thermal activation out of a meta-stable potential well. A three-configuration joint 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 a minimal “action” and connecting \((x_M, v_M)\) to \((x_f, v_f)\) with a deactivation path also having a minimal “action”. Revisiting the well-known Kramers problem, we derive a smooth crossover from Kramers’ analytical result in the low damping limit to his intermediate friction formula. Finally, this minimal path approach is accurate and convenient at low temperatures and thus complements the existing methods that work better at higher temperatures.

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REFERENCES


FIG. 1. The potential with a meta-stable well. The well is located at $x_w = 0$ where $V_w = V(0) = 0$ and barrier at $x_B = 4/3$ where $V_B = V(4/3) = 16/27$.

FIG. 2. Activation rate $r$ vs. inverse temperature $\beta$. Friction $\gamma = 0.1$

FIG. 3. Activation rate $r$ vs. friction $\gamma$. Inverse temperature $\beta = 10$
FIG. 4. Activation rate $r$ vs. friction $\gamma$. Inverse temperature $\beta = 20$