Kramers-Like Turnover in Activationless Rate Processes

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The activationless escape of a free Brownian particle from a unit interval is analyzed over the entire range of friction coefficient γ. Approximate analytic expressions that compare favorably with simulations are derived for the effective and asymptotic rate constants k and Γ that describe the escape kinetics. Both rate constants show a turnover behavior as functions of γ, qualitatively similar to the rate constant in the Kramers theory of activated rate processes. It is found that $k \sim 1/\ln(1/\gamma)$ and $\Gamma \sim \gamma^{1/3}$ as $\gamma \to 0$ while both rate constants vanish as γ^{-1} as $\gamma \to \infty$.

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In the Kramers description of activated rate processes, the rate of escape of a Brownian particle from a potential well over a high barrier has a turnover as a function of the friction coefficient [1,2]. In this paper we show that turnover can also occur for activationless rate processes, albeit for different physical reasons. There is a fundamental distinction between these two processes. The kinetics of activated escape is exponential in time for any value of the friction, while for activationless processes the kinetics is generally nonexponential. Therefore, we will use two rate constants to characterize the activationless escape. One of these, the asymptotic rate constant, denoted by Γ, describes the long time decay of the survival probability. The second, the effective rate constant, denoted by k, is defined as the inverse of the mean lifetime of the particle. In activated rate processes the two rate constants are equal. In what follows we study the dependence of k and Γ on the friction coefficient γ for the activationless escape of a free Brownian particle in one dimension from a unit interval. It is found that when the friction coefficient approaches infinity both rate constants go to zero as γ^{-1} just like the rate constant in the Kramers theory. However, when $\gamma \to 0$ the rate constants k and Γ approach zero in different ways. In contrast to the Kramers rate constant which tends to zero as γ, we find that Γ goes to zero as $\gamma^{1/3}$, while k approaches zero as $1/\ln(1/\gamma)$. An immediate consequence of our theory is that the steady-state rate constant of the trapping problem in one dimension also exhibits a turnover behavior.

We consider the escape of a Brownian particle from the unit interval $[0,1]$. The particle motion is assumed to be governed by the Langevin equation. Then the joint density in phase space, $p(x,v,t)$, satisfies the Klein-Kramers equation, which, in dimensionless variables ($m = k_B T = 1$), is

$$\frac{\partial p}{\partial t} = -v\frac{\partial p}{\partial x} + \gamma \frac{\partial}{\partial v}\left(\frac{\partial p}{\partial v} + v p\right), \tag{1}$$

where γ is the dimensionless friction coefficient. Equation (1) is supplemented by the initial conditions that the particle position is uniformly distributed over the interval $0 \le x \le 1$ and that the density of velocity is Maxwellian, so that $p(x,v,0) = f_{\mathrm{eq}}(v) = (2\pi)^{-1/2}\exp(-v^2/2)$. The boundary conditions that guarantee that an escaping particle never returns to the interval are $p(0,v,t)|_{v>0} = p(1,v,t)|_{v<0} = 0$. It is worthwhile to note that the problem we are dealing with is closely related to the one of the survival of a particle moving in phase space in the presence of a trap, first posed by Wang and Uhlenbeck [3]. This problem is trivial for a diffusing particle but is extremely complicated in phase space. A discussion of the source of this complexity and a list of key references is to be found in Refs. [4,5].

The solution to Eq. (1) allows one to calculate the survival probability $S(t)$ of the particle on the interval,

$$S(t) = \int_0^1 dx \int_{-\infty}^{\infty} p(x,v,t)\, dv\,. \tag{2}$$

The two rate constants characterizing the escape kinetics are the effective rate constant $k = 1/\langle t \rangle$, where the mean lifetime $\langle t \rangle$ of the particle is given by

$$\langle t \rangle = \frac{1}{k} = \int_0^{\infty} S(t)\, dt\,, \tag{3}$$

and the asymptotic rate constant Γ determined from $S(t)$ by

$$\Gamma = -\lim_{t\to\infty} \frac{d}{dt} \ln[S(t)]\,. \tag{4}$$

The latter is the least (in magnitude) eigenvalue of the Klein-Kramers operator on the right-hand side of Eq. (1) with appropriate boundary conditions. When the survival probability is a single exponential, k coincides with Γ; more generally it does not.

Since a solution for $p(x,v,t)$ is unknown we first derive approximate expressions for $k(\gamma)$ and $\Gamma(\gamma)$ for

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both the large and small γ regimes. In the large γ regime our analysis is based on the ordinary diffusion equation along the position x with radiation boundary conditions. In the small γ regime the two rate constants are determined by solving the diffusion equation in velocity space in the presence of a sink term. Finally, an heuristic interpolation formula, originally suggested in Ref. [6], is used to obtain expressions for the two rate constants that cover the entire range in γ.

High friction regime.—When $\gamma \to \infty$, the problem reduces approximately to diffusion on a line with radiation boundary conditions imposed at its end points. That is, the reduced density, $q(x,t) = \int_{-\infty}^{\infty} p(x,v,t)\,dv$, satisfies

$$\frac{\partial q}{\partial t} = D\frac{\partial^2 q}{\partial x^2}; \qquad D = \frac{1}{\gamma}, \tag{5}$$

which is to be solved subject to the boundary conditions

$$D\frac{\partial q(x,t)}{\partial x}\bigg|_{x=0} = \kappa q(0,t) \quad \text{and} \quad -D\frac{\partial q(x,t)}{\partial x}\bigg|_{x=1} = \kappa q(1,t), \tag{6}$$

where

$$\kappa = \langle |v| \rangle = \int_{-\infty}^{\infty} |v| f_{\rm eq}(v)\,dv = (2/\pi)^{1/2}. \tag{7}$$

This problem can be solved using standard techniques which lead to the following expression for $k_{\rm high}$ (where the subscript indicates the high friction regime),

$$\frac{1}{k_{\rm high}(\gamma)} = \frac{1}{k_{\rm PT}} + \frac{1}{k_{\rm FP}(\gamma)} = \frac{1}{2\kappa} + \frac{1}{12D} = \left(\frac{\pi}{8}\right)^{1/2} + \frac{\gamma}{12}. \tag{8}$$

When $\gamma \to \infty$ so that $D \to 0$, the effective rate constant is given by the inverse mean first-passage (FP) time to $x = 0$ or 1 and $k_{\rm high} \approx k_{\rm FP} = 12D = 12/\gamma$. In the opposite limit, $\gamma \to 0$, since the diffusion constant approaches infinity, the particles remain uniformly distributed in the interval and the escape rate is given by perturbation theory (PT) as $k_{\rm high} \approx k_{\rm PT} = 2\kappa$.

The asymptotic rate constant $\Gamma_{\rm high}$ can also be found using standard techniques. The eigenvalue problem that determines $\Gamma_{\rm high}$ reduces to solving the transcendental equation

$$(D\Gamma_{\rm high})^{1/2}\tan\left[\left(\frac{\Gamma_{\rm high}}{4D}\right)^{1/2}\right] = \kappa. \tag{9}$$

When $D \to \infty$ ($\gamma \to 0$), we have $\Gamma_{\rm high} \approx \Gamma_{\rm PT} = 2\kappa = k_{\rm PT}$ as it should be since in this case the escape kinetics is single-exponential. When $D \to 0$ ($\gamma \to \infty$) the asymptotic rate constant goes to zero as $\Gamma_{\rm high} \approx \Gamma_\infty = \pi^2 D = \pi^2/\gamma$. In order to bridge the gap between these two regimes we use an interpolation formula of the form [suggested by the exact expression in Eq. (8)]

$$\frac{1}{\Gamma_{\rm high}(\gamma)} = \frac{1}{\Gamma_{\rm PT}} + \frac{1}{\Gamma_\infty(\gamma)} = \frac{1}{2\kappa} + \frac{1}{\pi^2 D} = \left(\frac{\pi}{8}\right)^{1/2} + \frac{\gamma}{\pi^2}. \tag{10}$$

This has been compared with the numerical solution of Eq. (9) and has been found to fit the data to within a relative error of 2% or less. Thus, we have shown that in the high friction regime both $k_{\rm high}$ and $\Gamma_{\rm high}$ decrease monotonically with the friction coefficient and approach zero as γ^{-1}. They have the same maximum value at $\gamma = 0$ given by 2κ.

Low friction regime.—To analyze the escape in the low friction regime ($\gamma \to 0$) we consider the velocity density, $f(v,t) = \int_0^1 p(x,v,t)\,dx$, which approximately satisfies the equation

$$\frac{\partial f}{\partial t} = \gamma\frac{\partial}{\partial v}\left(\frac{\partial f}{\partial v} + vf\right) - K(v)f, \tag{11}$$

where the sink term $K(v)$ is chosen so as to match the exact mean lifetime in the unit interval at $\gamma = 0$. For $\gamma = 0$, the survival probability of a particle with initial velocity v, found from Eq. (11), is $e^{-K(v)t}$, and the lifetime of the particle is therefore $1/K(v)$. For the ballistic dynamics [i.e., $\gamma = 0$ in Eq. (1)], this lifetime can be found exactly as follows: If a particle is initially at x, the time to reach the boundary is $(1-x)/v$ when v is positive and $x/|v|$ when v is negative. Averaging this time with respect to the uniform distribution of x results in the mean lifetime given by $1/(2|v|)$. Thus, matching these lifetimes leads to $K(v) = 2|v|$. Averaging the survival probability $e^{-K(v)t} = e^{-2|v|t}$ with respect to the Maxwell distribution of initial velocity gives $S_{\rm approx}(t) = \int_{-\infty}^{\infty} e^{-2|v|t} f_{\rm eq}(v)\,dv = e^{2t^2}\,{\rm erfc}(\sqrt{2}\,t)$. On the other hand, the exact survival probability $S(t)$ calculated from Eq. (1) with $\gamma = 0$ is $S(t) = {\rm erf}[1/(\sqrt{2}\,t)] - \sqrt{2t^2/\pi}\,[1 - e^{-1/(2t^2)}]$. These survival probabilities have identical asymptotic behavior and, in fact, essentially coincide except at short times.

We now use Eq. (11) to analyze how the mean lifetime, and hence k, depends on γ in the low friction regime. To find the behavior of $k_{\rm low}$ when $\gamma \to 0$, we first determine the mean lifetime $\langle t(v) \rangle$ of a particle with initial velocity v by solving the equation

$$\gamma\left[\frac{d^2\langle t(v)\rangle}{dv^2} - v\frac{d\langle t(v)\rangle}{dv}\right] - 2|v|\langle t(v)\rangle = -1. \tag{12}$$

Using the singular perturbation theory we find

$$\langle t(v) \rangle \simeq \begin{cases} 1/(4\gamma)^{1/3} + [(\gamma/2)^{2/3} - v^2]/(2\gamma); & 0 \le |v| \le (\gamma/2)^{1/3}, \\ 1/(2|v|); & (\gamma/2)^{1/3} \le |v| < \infty. \end{cases} \tag{13}$$

Averaging $\langle t(v)\rangle$ in Eq. (13) with respect to $f_{\rm eq}(v)$, we find that the limiting behavior of $k_{\rm low}(\gamma)$ when $\gamma \to 0$ is given by

$$k_{\rm low}(\gamma) \approx 3\sqrt{2\pi}\left[\ln\!\left(\frac{1}{\gamma}\right)\right]^{-1} = \frac{3\pi}{2}\left[\ln\!\left(\frac{1}{\gamma}\right)\right]^{-1} k_{\rm PT}\,. \tag{14}$$

It is worth emphasizing that this result is *exact* and can be derived directly from Eq. (1) together with the initial and boundary conditions indicated in the text below Eq. (1). In the opposite limiting case when $\gamma \to \infty$, rapid diffusion along the velocity coordinate permanently maintains the Maxwell distribution of velocities and the sink can be regarded as a small perturbation. From this it follows that the survival probability decays exponentially with the rate constant given by perturbation theory, $k_{\rm low} \approx k_{\rm PT} = \langle K(v)\rangle = 2\kappa$. Surprisingly, this rate constant is exactly the same as that found in the high friction regime when $\gamma \to 0$. The following heuristic formula accurately interpolates the dependence of $k_{\rm low}$ on γ between $k_{\rm PT}$ when $\gamma \to \infty$ and that given in Eq. (14) when $\gamma \to 0$:

$$k_{\rm low}(\gamma) = k_{\rm PT}\left\{1 + \frac{2}{3\pi}\ln\!\left[1 + \frac{A}{\gamma}\right]\right\}^{-1}, \tag{15}$$

in which $A = 1.45$ is a constant determined by fitting exact results [obtained by solving Eq. (12) numerically] with Eq. (15).

We next turn to finding an approximate solution for the least eigenvalue of the operator on the right-hand side of Eq. (11) with $K(v) = 2|v|$, i.e., calculating the asymptotic rate constant $\Gamma_{\rm low}$. Let $\varphi(v)$ be the eigenfunction associated with the eigenvalue λ. By representing the eigenfunction as $\varphi(v) = e^{-v^2/4}\psi(v)$, the eigenvalue problem takes the Schrödinger-like form

$$-\frac{d^2\psi}{dv^2} + \left[\frac{v^2}{4} + \frac{2|v|}{\gamma}\right]\psi = \left(\frac{\lambda}{\gamma} + \frac{1}{2}\right)\psi = E\psi\,. \tag{16}$$

When $\gamma \to \infty$, a solution for the least eigenvalue can be found by perturbation theory, leading to $\Gamma_{\rm low} \approx \Gamma_{\rm PT} = 2\langle |v|\rangle = 2\kappa$ which is equal to $k_{\rm PT}$. One can attempt to find an approximate solution for $\Gamma_{\rm low}(\gamma)$ valid for the entire range of γ by applying the WKB method. The equation for E, which can be regarded as a ground state energy, is

$$\int_0^{v_{\max}(E)} \sqrt{E - \frac{v^2}{4} - \frac{2v}{\gamma}}\, dv = \frac{\pi}{4}\,, \tag{17}$$

where $v_{\max}(E)$ is the positive root of the quadratic equation $v^2/4 + 2v/\gamma - E = 0$. The integration can be carried out exactly leading to the transcendental equation for E,

$$\left(\frac{1}{\gamma^2} + \frac{E}{4}\right)\times \left\{1 - \frac{2}{\pi}\sin^{-1}\!\left[\left(1 + \frac{\gamma^2 E}{4}\right)^{-1/2}\right]\right\} - \frac{\sqrt{E}}{\pi\gamma} = \frac{1}{8}\,. \tag{18}$$

The WKB solution for the asymptotic rate constant is therefore $\Gamma_{\rm WKB} = \gamma(E - 1/2)$, where E is the root of Eq. (18). It is known that the WKB method does not lead to a very good approximation for the ground state energy. In the present case the use of the WKB formalism gives $\Gamma_{\rm WKB} = 4\sqrt{2}/\pi$ when $\gamma \to \infty$ rather than the correct value $(8/\pi)^{1/2}$. Nevertheless, $\Gamma_{\rm WKB}(\gamma)$ does appear to have the right functional dependence on γ as compared with a numerical solution of the eigenvalue problem in Eq. (16). If $\Gamma_{\rm WKB}$ is multiplied by a factor $\sqrt{\pi}/2$ to guarantee the correct value of $\Gamma_{\rm low}$ in the large-γ limit, one arrives at an expression

$$\Gamma_{\rm low}(\gamma) = \frac{\sqrt{\pi}}{2}\,\Gamma_{\rm WKB}(\gamma)\,, \tag{19}$$

which deviates from the numerically obtained results by no more than 3% over the entire range of γ. The value of $\Gamma_{\rm low}(\gamma)$ as calculated from Eq. (19) increases monotonically with γ from zero to $\Gamma_{\rm PT}$. At small γ, $\Gamma_{\rm low}$ is approximated as $\Gamma_{\rm low}(\gamma) \approx 3^{2/3}(\pi/4)^{7/6}\gamma^{1/3}$.

Bridging à la Visscher-Mel'nikov-Meshkov.—Now that we know expressions for $k_{\rm low}$ and $k_{\rm high}$, $\Gamma_{\rm low}$ and $\Gamma_{\rm high}$, as functions of γ, we complete this analysis by providing approximate analytic expressions for k and Γ that cover the entire range of γ. First of all, we note that $k_{\rm PT} = \Gamma_{\rm PT}$ is an upper limit for $k_{\rm low}(\gamma)$ and $\Gamma_{\rm low}(\gamma)$ when $\gamma \to \infty$ and for $k_{\rm high}(\gamma)$ and $\Gamma_{\rm high}(\gamma)$ when $\gamma \to 0$. This

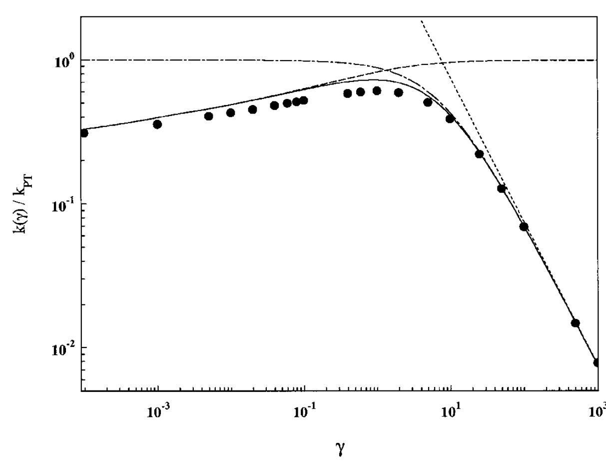

FIG. 1. Reduced effective rate constant $k(\gamma)/k_{\rm PT}$ as a function of the friction γ. The data (closed circles) are obtained from Langevin dynamics simulations, the dash-dotted line corresponds to $k_{\rm high}(\gamma)$ given in Eq. (8), the long-dashed line to $k_{\rm low}(\gamma)$ given in Eq. (15), and the solid line represents the Visscher-Mel'nikov-Meshkov interpolation in Eq. (20). The dotted line corresponds to $k_{\rm FP}(\gamma)/k_{\rm PT}$.

suggests making use of the Visscher-Mel'nikov-Meshkov interpolation formula [2,6] to cover the entire range of γ. For the effective rate constant, this leads to

$$\frac{k(\gamma)}{k_{\mathrm{PT}}} = \frac{k_{\mathrm{low}}(\gamma)k_{\mathrm{high}}(\gamma)}{k_{\mathrm{PT}}^2} = \left\{\left[1 + \frac{2}{3\pi}\ln\left(1 + \frac{A}{\gamma}\right)\right]\left[1 + \frac{\gamma}{\sqrt{18\pi}}\right]\right\}^{-1}. \tag{20}$$

As shown in Fig. 1, this compares favorably with results of Langevin dynamics simulations. The function $k(\gamma)$ in Eq. (20) has a turnover qualitatively similar to that in the Kramers theory of activated rate processes. Both the present theory for activationless escape and the theory of activated rate processes predict that the rate constants go to zero as $1/\gamma$ in the limit $\gamma \rightarrow \infty$. In the small-$\gamma$ limit, however, $k(\gamma)$ goes to zero as $1/\ln(1/\gamma)$ while the Kramers rate constant is proportional to γ.

Similarly, we find for the asymptotic rate constant

$$\frac{\Gamma(\gamma)}{\Gamma_{\mathrm{PT}}} = \frac{\Gamma_{\mathrm{high}}(\gamma)\Gamma_{\mathrm{low}}(\gamma)}{\Gamma_{\mathrm{PT}}^2} = \left[1 + \left(\frac{2}{\pi}\right)^{3/2}\frac{\gamma}{\pi}\right]^{-1}\frac{\sqrt{\pi}}{2}\,\Gamma_{\mathrm{WKB}}(\gamma). \tag{21}$$

Figure 2 compares the results of simulations to those produced by this formula, indicating a good fit to the numerical results. Figure 2 also shows a turnover behavior of the asymptotic rate constant as γ is varied. When $\gamma \rightarrow \infty$ the asymptotic rate constant goes to zero as $1/\gamma$ like k and the Kramers rate constant, whereas it decreases as $\gamma^{1/3}$ for $\gamma \rightarrow 0$.

In conclusion, we have derived approximate analytic expressions for the effective and asymptotic rate constants describing the escape of a Brownian particle from a unit interval. These rate constants are given in Eqs. (20) and (21), respectively. In the high friction limit, all three (i.e., the Kramers rate constant, k, and Γ) go to zero as $1/\gamma$ simply because the diffusion coefficient vanishes as $1/\gamma$. If the particle does not move, it cannot escape. In the low friction limit, the physics of activated and activationless escape is different. For activated escape, the rate constant goes to zero as $\gamma \rightarrow 0$ because the particle does not have sufficient energy to surmount the barrier. For activationless processes, even in the inertial limit, the particle will always escape and hence the survival probability tends to zero at long times. However, if it tends to zero sufficiently slowly, then the mean lifetime diverges (i.e., the effective rate constant becomes zero). Since the rate goes to zero in both limits, it must exhibit a turnover behavior as a function of the friction coefficient.

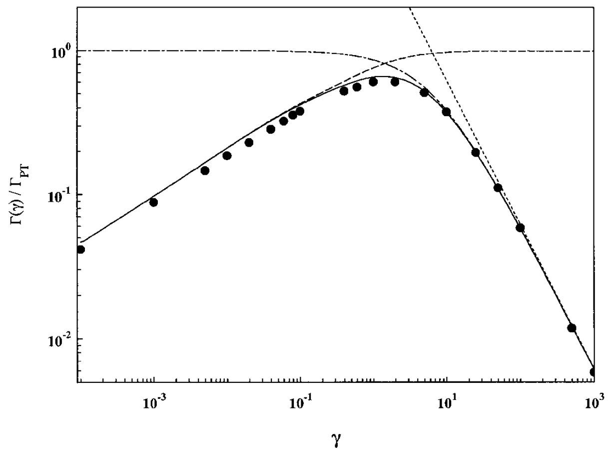

FIG. 2. Reduced asymptotic rate constant $\Gamma(\gamma)/\Gamma_{\mathrm{PT}}$ as a function of the friction γ. The data (closed circles) are obtained from Langevin dynamics simulations, the dash-dotted line corresponds to $\Gamma_{\mathrm{high}}(\gamma)$ given in Eq. (10), the long-dashed line to $\Gamma_{\mathrm{low}}(\gamma)$ given in Eq. (19), and the solid line represents the Visscher-Mel'nikov-Meshkov approximation in Eq. (21). The dotted line corresponds to $\Gamma_{\infty}(\gamma)/\Gamma_{\mathrm{PT}}$.

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[1] H. A. Kramers, Physica **7**, 284 (1940); P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[2] V. I. Mel'nikov and S. V. Meshkov, J. Chem. Phys. **85**, 1018 (1986); V. I. Mel'nikov, Phys. Rep. **209**, 1 (1991).
[3] M. S. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945).
[4] T. W. Marshal and E. J. Watson, J. Phys. A **18**, 3531 (1985); **20**, 1345 (1987).
[5] C. R. Doering in *Unsolved Problems of Noise,* edited by C. R. Doering, L. B. Kiss, and M. F. Shlesinger (World Scientific, Singapore, 1997), p. 11; J. Masoliver and J. M. Porrà, Phys. Rev. E **53**, 2243 (1996).
[6] P. B. Visscher, Phys. Rev. B **13**, 3272 (1976).