Escape rate for a Brownian particle in a potential well*

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An improved calculation of the rate of escape of a Brownian particle from a one-dimensional potential well is presented for the low-friction case. This problem is important in the calculation of catalytic reaction rates at solid surfaces. The rate is found to have a nearly Arrhenius exponential dependence on barrier height, but to be surprisingly insensitive to barrier shape and injection energy distribution.

This paper presents an improved solution to the problem of escape of a classical Brownian particle from a potential well. This is a problem of current interest in the study of surface catalysis.[1-5] The problem of computing the rate of a reaction catalyzed by a solid surface may often be approximately reduced to the problem of calculating the rate of escape from a one-dimensional potential well. The arguments for this reduction have been given in detail elsewhere.[1-3,6-8] Basically the "particle" in the well represents a point in the configuration space of a reacting cluster of atoms. A chemical reaction corresponds to motion of this point from the potential well corresponding to the reactant configuration to that corresponding to the product. This motion is confined for energetic reasons to the vicinity of the minimum energy path. Considering only motion along this one-dimensional path, the energy of the system might resemble the solid line in Fig. 1; to escape from the reactant well A the particle must surmount a barrier C. The escape is governed by a Langevin equation [Eq. (1)] incorporating a stochastic frictional force (arising physically from interactions with internal motions of the solid surface[7,8]) described by a friction coefficient η.

The escape problem was first investigated by Kramers.[9] The problem has been solved numerically[6] for the case where η is not too low. This paper is therefore concerned with the case of very low friction, which is much harder but of importance because of indications[10] that η is indeed small in various situations. When η is much less than the oscillation frequency in the well, the particle oscillates many times before the stochastic force causes a significant fractional change in its energy. This case should be thought of as a process of slow diffusion in energy, as was first observed by Kramers, who suggested an equation to describe steady-state diffusion. My approach differs from Kramers's in that I formulate the problem including a source term describing the injection of particles to replace those escaping. This gives two advantages over previous approaches. First, it is possible to derive an energy-diffusion equation (5) in a much more convincing way. Second, the equation is nonsingular and can be straightforwardly solved; whereas, as we show below, Kramers's method essentially assumes that all the particles are injected exactly at zero energy, a mathematically singular case whose solution Kramers did not obtain.

This new equation makes it possible to study the effects of the various factors which influence the rate (the friction coefficient, the injection energy distribution, and the height and shape of the potential barrier). This paper presents an analysis of these effects and gives an improved formula [Eq. (14)] for the rate. In the high-friction limit[6] the rate depended very little on the injection energy because the friction brought the energy into equilibrium quickly. For low friction this is not true, and one might expect strong dependence on the injection energy; a surprising result of my calculation is that this dependence is quite small, for injection energies well below the barrier (see Fig. 3).

In the Brownian-motion model, we consider a particle in a potential $V(x)$ subject to the Langevin equation

$$\frac{dv}{dt} = F(x) - \eta v + A(t) \ , \tag{1}$$

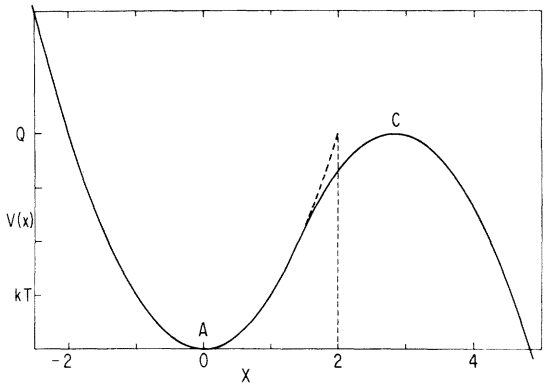

FIG. 1. Two potentials used for explicit calculations, with smooth (solid curve) and sharp (broken curve) barriers, respectively. Here $Q = 4kT$ and $\omega_A = \omega_C$ in Eq. (7) [so $\alpha = 2^{1/2}$, $d = 2^{3/2}$ in units with $(2kT/m)^{1/2} = \omega_A = 1$].

where $F(x) = -(1/m)dV/dx$, m is the mass, η is the friction coefficient, and $A(t)$ is a Markovian random force. It can then be shown[11] that the distribution function $f(x, v, t)$ of an ensemble of systems changes with time according to the Fokker-Planck equation

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} + F\frac{\partial f}{\partial v} = \eta\frac{\partial}{\partial v}\left(vf + \frac{kT}{m}\frac{\partial f}{\partial v}\right). \tag{2}$$

For low η, we describe the process as a diffusion in energy by transforming from the coordinates x, v to the "energy-epoch" canonical coordinates E, τ, where $E(x, v) = \frac{1}{2}mv^2 + V(x)$ and τ is the time variable along a trajectory (starting at an arbitrary point). To allow a steady-state solution of (2), escaping particles must be replaced; we assume $\lambda(x, v)\,dx\,dv$ particles are injected per unit time in the phase volume $dx\,dv(= dE\,d\tau)$. [In an application to catalysis, $\lambda(x, v)$ would be given by the phase space distribution of reactants as they adsorb on the surface.]

The Fokker-Planck equation then becomes

$$0 = \frac{\partial f}{\partial t}(E, \tau; t) = \lambda(E, \tau) + \eta\left[f + kT\frac{\partial f}{\partial E} + mv^2(E, \tau)\left(\frac{\partial f}{\partial E} + kT\frac{\partial^2 f}{\partial E^2}\right)\right] + \cdots, \tag{3}$$

where we have omitted several terms involving $\partial f/\partial\tau$ because we seek solutions $f(E)$ independent of τ. For general $\lambda(E, \tau)$ such solutions do not exist and determining $f(E, \tau)$ is extremely difficult. But it turns out that for any desired λ, we can find a slightly different source function λ', for which a solution $f(E)$ *does* exist, where λ' is physically equivalent to λ in the sense that the trajectory average

$$\bar{\lambda}(E) \equiv \frac{1}{T(E)}\int_0^{T(E)} d\tau\,\lambda(E, \tau) \tag{4}$$

[here $T(E)$ is the period of the trajectory of energy E within the well] is the same for λ and λ'. These two sources are practically equivalent because η is assumed small: for η much smaller than the oscillation frequency, particles are carried around the trajectory in a time short compared to that ($\sim \eta^{-1}$) required for diffusion in energy away from the trajectory. What matters is the total number of particles injected on a trajectory [i.e., $\bar{\lambda}(E)$], not their detailed distribution in τ. To find such a solution $f(E)$, given $\lambda(E, \tau)$ [and hence $\bar{\lambda}(E)$], average Eq. (3) over a trajectory:

$$0 = \bar{\lambda}(E) + \eta\left[f(E) + kT\frac{\partial f}{\partial E} + \langle mv^2\rangle\left(\frac{\partial f}{\partial E} + kT\frac{\partial^2 f}{\partial E^2}\right)\right]. \tag{5}$$

For each E, we define

$$\langle mv^2\rangle \equiv \frac{1}{T(E)}\int_0^{T(E)} mv^2(E, \tau)\,d\tau\,.$$

This second-order differential equation, with the requirement of regularity at $E = 0$ (the bottom of the well) and the boundary condition $f(Q) = 0$ at the top of the barrier, determines $f(E)$ uniquely.

The escape rate is defined as the ratio of the number of particles escaping per unit time (equal, in a steady state, to the number injected) to the total number in the well

$$r = \int\lambda(E, \tau)\,d\tau\,dE \Big/ \iint f(E)\,d\tau\,dE = \int\bar{\lambda}(E)T(E)\,dE \Big/ \int f(E)T(E)\,dE\,. \tag{6}$$

Equations (5) and (6) make it possible to compute the energy distribution $f(E)$ and the escape rate r, for any potential $V(x)$ and source distribution $\bar{\lambda}(E)$.

To study the effect of changing the barrier shape, we consider two different potentials shown in Fig. 1. They share the same harmonic oscillator well on the left, of frequency ω_A and the same barrier height Q, but differ in barrier shape. The smooth barrier (solid line) is an inverted quadratic well of "frequency" ω_C, i.e.,

$$V(x) = \begin{cases} \frac{1}{2}m\omega_A^2 x^2, & x < \alpha, \\ Q - \frac{1}{2}m\omega_C^2(x - d)^2, & x > \alpha \end{cases} \tag{7}$$

(d and α are uniquely determined by Q, ω_A, ω_C).

The sharp barrier (broken line in Fig. 1) is obtained by abruptly cutting off the quadratic when $V(x) = Q$ at $x = 2$.

For the sharp barrier computing the trajectories is trivial; for the smooth one

$$T(E) = \begin{cases} 2\pi/\omega_A & [E < V(\alpha)], \\ \dfrac{2}{\omega_A}\left[\sin^{-1}\left(\dfrac{V(\alpha)}{E}\right)^{1/2} + \dfrac{\pi}{2} + \dfrac{\omega_A}{\omega_C}\cosh^{-1}\left(\dfrac{Q - V(\alpha)}{Q - E}\right)^{1/2}\right] & [E > V(\alpha)]; \end{cases} \tag{8}$$

$$\langle mv^2\rangle = \begin{cases} E & [E < V(\alpha)], \\ E - Q + 2\left\{Q\left[\dfrac{\pi}{2} + \sin^{-1}\left(\dfrac{V(\alpha)}{E}\right)^{1/2}\right]\Big/\omega_A + \left(\dfrac{m}{2}\right)^{1/2} d[E - V(\alpha)]^{1/2}\right\}\Big/T(E) & [E > V(\alpha)]. \end{cases} \tag{9}$$

Having $\langle mv^2\rangle$ we can integrate Eq. (5) numerically. A particular example is shown in Fig. 2, obtained for the smooth barrier [Eq. (9)] and a thermal equilibrium source

$$\bar{\lambda}(E) = e^{-E/kT}\,, \tag{10}$$

which is most reasonable for catalytic rate theory

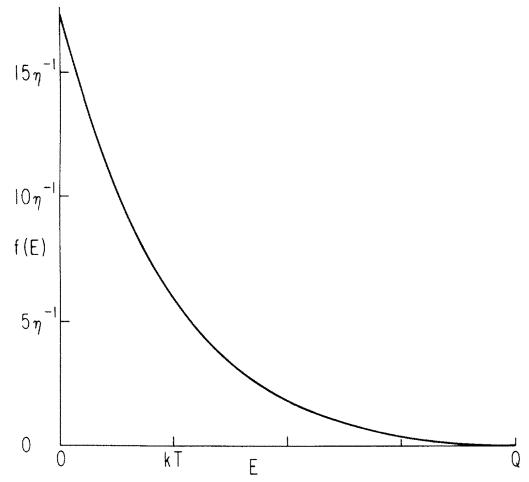

FIG. 2. Energy distribution function computed numerically for smooth barrier and equilibrium source [Eq. (10)]. [$f(E)$ scales with η^{-1} when the source is held fixed.]

applications. The numerical integration starts at $E=Q$ with $f(Q)=0$; the initial derivative $(\partial f/\partial E)_{E=Q}$ was varied to find the unique value for which the solution did not diverge at $E=0$.

To establish the general dependence of the rate on injection energy distribution, it is convenient to consider monoenergetic distributions

$$\bar{\lambda}(E)=\delta(E-E_0) \tag{11}$$

and calculate their rates $r(E_0)$. Then the rate r (more precisely, its reciprocal r^{-1}) for an arbitrary distribution $\bar{\lambda}(E)$ is simply a weighted average

$$r^{-1}=\int r^{-1}(E_0)\bar{\lambda}(E_0)T(E_0)\,dE_0\Big/\int\bar{\lambda}(E_0)T(E_0)\,dE_0\ . \tag{12}$$

The distribution function $f(E)$ for the monoenergetic source (11) has a discontinuous derivative at $E=E_0$, but otherwise resembles Fig. 2. It was calculated numerically for the smooth barrier, but for the sharp barrier (pure quadratic potential) it is obtainable analytically: $f(E)$ is $\exp(-E/kT)$ for $E<E_0$, and a linear combination of this with $\exp(-E/kT)\mathrm{Ei}(E/kT)$ for $E>E_0$ (Ei is the exponential integral). The rate $r(E_0)$ is given by

$$\eta r^{-1}(E_0)=\mathrm{Ei}\left(\frac{Q}{kT}\right)-\ln\left(\frac{Q}{kT}\right)-\mathrm{Ei}\left(\frac{E_0}{kT}\right)-\ln\left(\frac{E_0}{kT}\right), \tag{13}$$

which is plotted against injection energy E_0 in Fig. 3, along with the numerical result for the smooth barrier.

Note in Fig. 3 that the dependence on barrier shape is very slight, about 2%, even though the barriers represent opposite extremes of sharpness and smoothness. Very likely Eq. (13) for the sharp barrier is quite adequate for intermediate barriers as well. Also, the first term of (13) dominates the others exponentially for $Q/kT\gg1$. Thus the dependence on E_0 is very weak (this is already apparent in our $Q/kT=4$ example, Fig. 3, for small E_0) so the rate (12) is insensitive to the injection distribution $\bar{\lambda}(E_0)$, as long as injection is predominantly near the bottom of the well (as it is in rate theory applications). Due to these fortunate circumstances, we can write an analytic expression, independent of barrier shape and injection distribution, which closely approximates the rate

$$\eta r^{-1}\simeq\mathrm{Ei}\left(\frac{Q}{kT}\right)=e^{Q/kT}\left[\frac{kT}{Q}+\left(\frac{kT}{Q}\right)^2+\left(\frac{kT}{Q}\right)^3+\cdots\right]\ . \tag{14}$$

Making a relative error kT/Q we may reduce this to

$$\eta r^{-1}\approx(kT/Q)\exp(Q/kT)\ , \tag{15}$$

which is precisely the result originally given by Kramers.[9] This is not accidental; in fact, Kramers's sourceless differential equation is equivalent to (5) and (11) for $E_0=0$ and the pure quadratic well. The exact solution diverges logarithmically with Ei at $E=0$, but gives the correct, finite, rate [Eq. (13)]. Kramers got (15) rather than (13) because he did not obtain the exact solution, but expoited a first integral of the differential equation and made some approximations to get the rate. Kramers's solution to the sourceless differential equation has been improved and extended by Brenig, Müller, and Sedlmeier.[5] They calculated the rate r for the sharp parabolic well treated exactly here, as well as for square and Morse wells. For the parabolic well they obtained the Kramers result (15), which has relative error kT/Q. Their method (in which r is assumed small) therefore also requires kT/Q

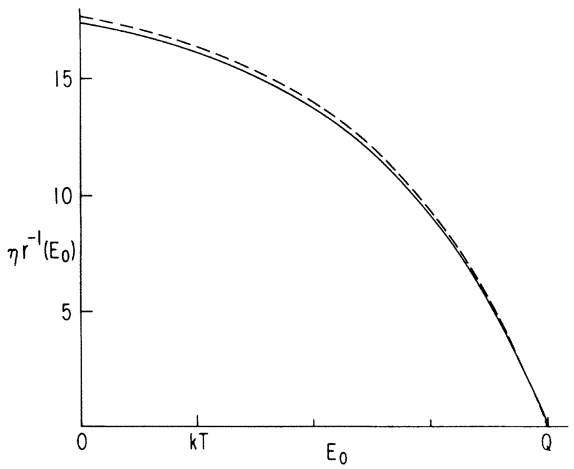

FIG. 3. Reciprocal rate for monoenergetic source as a function of source energy E_0, for smooth (solid curve) and sharp (broken curve) barriers.

to be small.

Their results for the extreme cases of square and Morse wells (effectively zero-width and infinite-width barriers, even "sharper" and "smoother," respectively, than the "sharp" and "smooth" barriers considered here) reinforce a conclusion which is already apparent from Fig. 3: smooth barriers have larger escape rates than sharp ones. This contradicts what one might expect intuitively; whether it is a true consequence of the Fokker-Planck equation (2) or an artifact of the approximations leading to (5) is impossible at present to determine. In any case, it is a very small effect for physically plausible barriers, and does not affect our general conclusions.

The results of the present calculation (giving r proportional to η) can only be valid for very small η. It can be shown that r cannot exceed the absolute-rate-theory[3] value $(\omega_A/2\pi)\exp(-Q/kT)$, which places an upper limit of $(\omega_A/2\pi)(kT/Q)$ on the η's for which the present approach can be correct [using Eq. (15)]. Numerical work[6] at larger η suggests that the coefficient of η^2 is roughly $(\pi/\omega_A)\times(Q/kT)^2$, so that r is proportional to η within 10% for η less than $(\omega_A/10\pi)(kT/Q)$.

In summary, I have given a well-defined numerical method which [assuming the validity of the argument leading to Eq. (5)] gives the correct rate of escape from a well for a Brownian particle in the low-friction limit. I have also given an approximate formula (14) for this rate which is an improvement of a previous result of Kramers's, and which is correct within a relative error $\sim\exp(-Q/kT)$ for the pure quadratic well (sharp barrier) and within a few percent for smooth barriers. It is a function only of barrier height and friction coefficient, and not of barrier shape or injection energy.

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