

Uniform Expansion of the Transition Rate in Kramers' Problem

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Received September 7, 1983; revision received November 8, 1983

Kramers' model of diffusion over potential barriers, e.g., chemical reactions, based on the noise activated escape of a particle from a potential well, is considered. Kramers derived escape rates valid for intermediate and large damping, and in a separate analysis, for small damping. In the small damping limit, Kramers' intermediate result reduces to the transition state rate which does not agree with the small damping result. A new escape rate is derived that is uniformly valid for all values of the damping coefficient. The new rate reduces to Kramers' results in the appropriate limits and, in particular, connects Kramers' intermediate and small damping results.

KEY WORDS: First passage time; transition rate; Langevin equation; Kramers.

1. INTRODUCTION

In 1940, H. A. Kramers⁽¹⁾ introduced a diffusion model for chemical reactions, based on the Langevin equation of motion

$$\ddot{x} + \beta\dot{x} + U'(x) = \xi(t) \quad (1.1)$$

This work was partially supported by the Air Force Office of Scientific Research under Grant No. AFOSR-83-0086, U.S. Department of Energy under Grant No. DE-AC02-78ERO-4650, and the National Science Foundation under Grant No. MCS-83-00562. One of us (BJM) gratefully acknowledges the support of a John Simon Guggenheim Memorial Foundation Fellowship.

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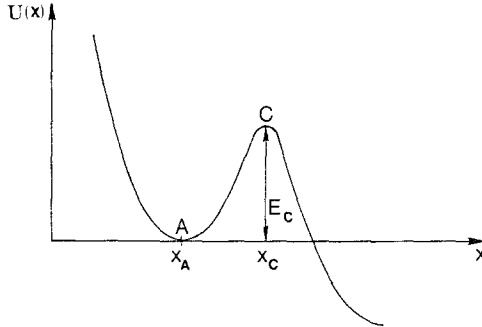


Fig. 1. Sketch of the potential well in which the particle is confined. Point A is a stable equilibrium, and point C is an unstable equilibrium.

for a particle in the potential field $U(x)$ depicted in Fig. 1, subject to the thermal noise force $\xi(t)$. Here $\xi(t)$ is Gaussian white noise with $\langle \xi(t) \rangle = 0$ and

$$\langle \xi(t)\xi(t') \rangle = 2\beta kT\delta(t-t') \quad (1.2)$$

where k is Boltzmann's constant. Kramers sought to calculate the reaction rate κ , which is the rate of escape of the particle from the potential well in which it is confined. In particular he sought to determine the dependence of κ on temperature T and on viscosity β , and to compare the values found with the results of the transition state method. It should be noted that Eqs. (1.1)–(1.2) serve as a model for many activated processes (cf. Ref. 2), for which the escape rate determines their time evolution.

The deterministic dynamics of the system, are governed by (1.1) with $\xi = 0$. Its phase space portrait is given in Fig. 2. The point x_A is a locally stable equilibrium, while the point x_C is an unstable equilibrium. The phase space $(x, y = \dot{x})$ is divided into the domain of attraction D , of the stable equilibrium, and the rest of phase space. They are separated by the curve Γ , called the separatrix (cf. Fig. 2). All deterministic trajectories starting in D , tend to the stable equilibrium point. The trajectory that starts on the separatrix tends to the unstable equilibrium point x_C . For $\xi \neq 0$, trajectories of (1.1) leave D in finite, though possibly large time. If T is small, a trajectory starting in D , spends a long time $\tau(A)$, fluctuating about x_A , but because of the random noise ξ , eventually reaches Γ and either leaves or returns to D , with equal probabilities.

Kramers considered the activation energy E_c (the depth of the potential well which the particle seeks to escape), to be large compared to the thermal energy kT , and in fact determined not one, but three different

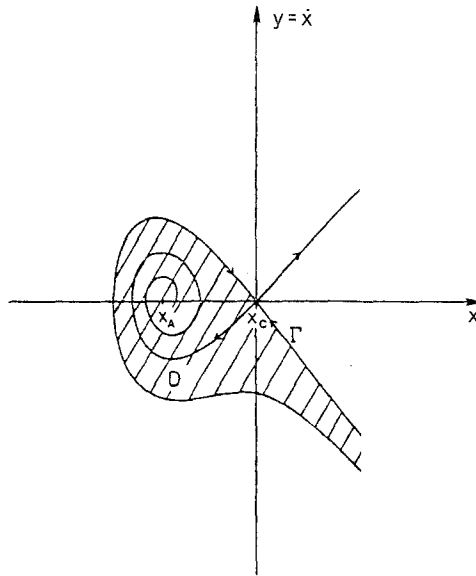


Fig. 2. Sketch of the domain of attraction D , in phase speed (x, \dot{x}) , of the stable equilibrium. The boundary of D is the separatrix Γ .

formulas for κ . In the Smoluchowski limit of β large, he obtained

$$\kappa_{Sm} = \frac{\omega_A \omega_c}{2\pi\beta} e^{-E_c/kT} \tag{1.3}$$

where $\omega_A = (U''(x_A))^{1/2}$ is the frequency of oscillation at the bottom of the well, $\omega_c = (-U''(x_c))^{1/2}$ is the imaginary frequency at the unstable equilibrium points x_c , and $E_c = U(x_c) - U(x_A)$ [assuming without loss of generality that $U(x_A) = 0$] is the depth of the well. For β very small, he obtained

$$\kappa_1 = \frac{\beta I_c \omega_A}{2\pi kT} e^{-E_c/kT} \tag{1.4}$$

where

$$I_c = \oint_{E=E_c} y_c(x) dx \tag{1.5}$$

is the action of the constant energy trajectory $E \equiv y^2/2 + U(x) = E_c$, whose equation is $y = y_c(x) = [2(E_c - U(x))]^{1/2}$ (see Fig. 3). Finally for intermediate $\beta = O(1)$ he obtained

$$\kappa_2 = \frac{\omega_A}{4\pi\omega_c} \left[(\beta^2 + 4\omega_c^2)^{1/2} - \beta \right] e^{-E_c/kT} \tag{1.6}$$

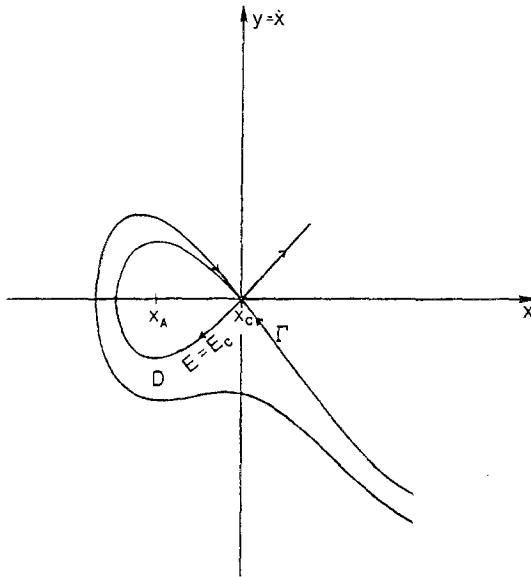


Fig. 3. Sketch of the separatrix Γ , and the energy curve $E = E_c$ in phase space.

We observe that the intermediate result (1.6) reduces to the Smoluchowski result (1.3) as $\beta \rightarrow \infty$. However, as $\beta \rightarrow 0$, Eq. (1.6) reduces to the transition state rate⁽³⁾ (TST)

$$\kappa_{\text{TST}} = \frac{\omega_A}{2\pi} e^{-E_c/kT} \quad (1.7)$$

which does not agree well with the small β result (1.5). Thus there is a gap in the description of κ , which is intermediate between the results (1.6) and (1.4). Several authors^(4,5) recently attempted to bridge this gap, and to connect (1.6) with (1.4). These are discussed below.

In this paper we derive a formula for κ that is uniformly valid for all $\beta > 0$. Our formula reduces to each of the results (1.3), (1.6) and (1.4) in the appropriate limits, and in particular it connects Kramers' results (1.6) and (1.4). Our formula is based on the observation that κ is the reciprocal of the mean time to escape the well.⁽⁶⁾ This time is the sum of the mean time $\tau_1(A)$ to reach energy level E_c , from the bottom of the well, and the mean time to proceed from E_c to Γ and then escape the well (see Fig. 3). The latter is twice the mean first passage time $\tau_2(E_c)$ from E_c to Γ , since trajectories that reach Γ are equally likely to leave or to return to $E = E_c$. Thus $\tau_2(E_c)$ must be counted twice. Our uniform formula for κ is therefore

given by

$$\kappa_{\text{unif}} = \frac{1}{\tau_1(A) + 2\tau_2(E_c)} \tag{1.8}$$

We show in Section 2, that $\tau_1(A)$ and $\tau_2(E_c)$ are, respectively, given by

$$\tau_1(A) = \frac{2\pi kT}{BI_c\omega_A} e^{E_c/kT} = \frac{1}{\kappa_1} \tag{1.9}$$

and

$$\tau_2(E_c) = \frac{2\pi\omega_c e^{E_c/kT} V}{\omega_A [(\beta^2 + 4\omega_c^2)^{1/2} - \beta]} \tag{1.10}$$

The result (1.9), derived by Kramers, and later by other authors (see, e.g., Refs. 7, 4, and the citations therein), under the assumption $\beta \ll 1$, is in fact uniformly valid for all $\beta > 0$, as we show below. The function V in (1.10) is a boundary layer function, as described in Ref. 7, and is given by [see (2.30) below]

$$V = \oint_{E=E_c} \frac{y_c(x)}{I_c} \operatorname{erf}[\rho\gamma/(2kT)^{1/2}] dx \tag{1.11}$$

The function V is included in order to account for the fact that the curve $E = E_c$ lies within the boundary layer near Γ , when β is small. Here ρ is the distance between Γ and the curve $E = E_c$, and γ is the solution of (2.25)–(2.26) below.

In the Appendix we show that for small β ,

$$\rho\gamma = O(\sqrt{\beta}) \tag{1.12}$$

so that for β small, $\tau_1(A) = O(1/\beta)$, while $\tau_2(E_c) = o(1)$, so that $\tau_1(A) \gg \tau_2(E_c)$, and (1.8) reduces to (1.4). In contrast for $\beta = O(1)$ or larger, $\rho\gamma$ is $O(1)$ or larger for any point on E_c away from x_c , so that for small kT , $\tau_2(E_c) \gg \tau_1(A)$ and (1.8) reduces to (1.6).

Buttiker, Harris, and Landauer⁽⁴⁾ connected (1.7) and (1.4) by employing the formula

$$\kappa_{\text{BHL}} = \frac{(1 + 4\alpha kT/\beta I_c)^{1/2} - 1}{(1 + 4\alpha kT/\beta I_c)^{1/2} + 1} \left(\frac{BI_c\omega_A}{2\pi kT} \right) e^{-E_c/kT} \tag{1.13}$$

where α is a parameter. This formula reduces to (1.4) as $\beta \rightarrow 0$, while in the limit $\beta \rightarrow \infty$, it reduces (for $\alpha = 1$) to (1.7). Carmeli and Nitzan⁽⁵⁾ bridged

the gap between (1.6) and (1.4), with the formula

$$\kappa_{\text{CN}} = \left[\frac{1 + \operatorname{erf} \left\{ \left[(\alpha + 1)(E_c - E_1)/kT \right]^{1/2} \right\}}{2\kappa_2} + \tau \right]^{-1} \quad (1.14)$$

where κ_2 is Kramers' result (1.6), α is given by

$$\alpha = \frac{1}{2} \left\{ \left[1 + \left(\frac{2\omega_c}{\beta} \right)^2 \right]^{1/2} - 1 \right\}$$

and E_1 is the energy at an intermediate point $x = x_1$ ($x_A < x_1 < x_c$), which is determined from the transcendental equation

$$\exp\left(\frac{-\alpha(E_c - E_1)}{kT}\right) = \frac{kT}{(\alpha + 1)\beta I_1} \left(\frac{\alpha(E_c - E_1)}{\pi kT}\right)^{1/2}$$

with I_1 denoting the action on the trajectory through x_1 . The quantity τ is the mean first passage time from $I = 0$ to $I = I_1$, for $\beta \ll 1$, given by

$$\tau = \frac{1}{\beta kT} \int_0^{I_1} dI \frac{\omega(I)}{I} \exp\left[\frac{E(I)}{kT}\right] \int_0^I \exp\left[-\frac{E(I')}{kT}\right] dI'$$

where

$$\omega(J) = \frac{dE}{dI}$$

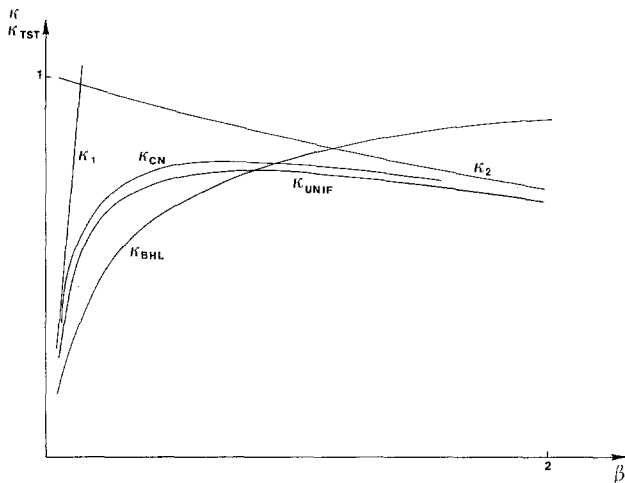


Fig. 4. Comparison of formulas for reaction rate κ as a function of β , for the potential $U(x) = x^2(x^2 - 16x/5 + 6)$ with $\epsilon = 0.5$. All rates are normalized by κ_{TST} .

In Fig. 4, we compare the various formulas for κ . These include Kramers' results (1.6) and (1.4), the results (1.13) and (1.14), and our result (1.8). Our result (1.8) agrees closely with the result of Ref. 5 (see κ_{UNIF} and κ_{CN} in Fig. 4). However (1.8) has the advantage that it is very simple to evaluate, in contrast to the result of Ref. 5. In addition, (1.8) was derived from mathematical considerations, whereas the result of Ref. 5 relies on physical intuition. The result of Ref. 4, which relies heavily on physical intuition, patches the curves κ_{BHL} and κ_2 in Fig. 4.

2. CALCULATION OF FIRST PASSAGE TIMES

To calculate the transition rate κ , we must calculate $\tau_1(A)$ and $\tau_2(E_c)$. To this end we introduce the mean first passage time $\tau_1(x, y)$ to reach the critical energy level $E = E_c$, starting at a point (x, y) in $E < E_c$, and then the mean first passage time $\tau_2(E_c)$ to proceed from there to the separatrix. We also find the distribution of exit points on $E = E_c$, which is necessary for the calculation of $\tau_2(E_c)$.

The mean passage time $\tau_1(x, y)$ from a starting point (x, y) in the domain $E < E_c$ is a solution of the equation

$$L\tau_1 \equiv \epsilon\beta \frac{\partial^2 \tau_1}{\partial y^2} + y \frac{\partial \tau_1}{\partial x} - [\beta y + U'(x)] \frac{\partial \tau_1}{\partial y} = -1, \quad \text{in } E < E_c \quad (2.1)$$

and the boundary condition

$$\tau_1 = 0, \quad \text{on } E = E_c \quad (2.2)$$

The mean first passage time τ_1 out of a domain \mathcal{D} is given by

$$\tau_1(x, y) = \int_0^\infty \int \int_{\mathcal{D}} p(x, y, t; \xi, \eta) d\xi d\eta dt \quad (2.3)$$

where $p(x, y, t, \xi, \eta)$ is the transition density function for the solution of the Langevin equation (1.1), with absorption at the boundary of \mathcal{D} , to go from (x, y) to (ξ, η) in time t . The transition density $p(x, y, t, \xi, \eta)$ is the solution of the Fokker–Planck equation with respect to the variables (ξ, η) and t , and of the backward Kolmogorov equation with respect to the variables (x, y) and t . Equation (2.1) is obtained by integrating the backward Kolmogorov equation for $p(x, y, t, \xi, \eta)$ with respect to (ξ, η) , over \mathcal{D} and t (see p. 118 of Ref. 8).

We assume that $kT \ll E_c$. Rather than nondimensionalizing the problem we set $\epsilon \equiv kT$ and assume $\epsilon \ll 1$. We now describe our method⁽⁶⁾ for solving the problem (2.1), (2.2) for small ϵ . As noted in Ref. 6, in the limit $\epsilon \rightarrow 0$, $\tau_1(x, y)$ has the form

$$\tau_1(x, y) = \tau_1(A)u(x, y) \quad (2.4)$$

where $\tau_1(A)$, which is exponentially large in ϵ , is to be determined below, and $\max_D u(x, y) = 1$. The function $u(x, y)$ is a solution of

$$Lu = \frac{-1}{\tau_1(A)}, \quad \text{in } E < E_c \quad (2.5)$$

$$u = 0, \quad \text{on } E = E_c \quad (2.6)$$

Since $1/\tau_1(A) \rightarrow 0$ as $\epsilon \rightarrow 0$, we consider the asymptotic solution of $Lu \cong 0$ for $E < E_c$. To leading order in ϵ , u is the solution of the reduced equation

$$y \frac{\partial u}{\partial x} - [\beta y + U'(x)] \frac{\partial u}{\partial y} = 0 \quad (2.7)$$

which can be written as

$$\frac{du}{dt}(x(t), y(t)) = 0 \quad (2.8)$$

where $(x(t), y(t))$ is any trajectory of (1.1) with $\xi = 0$. Thus u is constant on each trajectory. Since all trajectories converge to the stable equilibrium point A , and since u is continuous at A , u is constant for $E < E_c$. Hence by our normalization

$$u \equiv 1, \quad E < E_c \quad (2.9)$$

Since u must satisfy the boundary condition (2.6), (2.9) cannot be a valid approximation to u near $E = E_c$. Therefore we construct a boundary layer approximation to u , near $E = E_c$ by introducing the stretching transformation

$$\eta = \frac{E_c - E}{\epsilon} \quad (2.10)$$

and writing (2.5) in terms of η near $E = E_c$. The leading term of the boundary layer expansion is a solution of the boundary layer equation

$$\frac{\partial^2 u}{\partial \eta^2} + \frac{\partial u}{\partial \eta} = 0, \quad 0 < \eta < \infty \quad (2.11)$$

subject to the boundary condition

$$u = 0, \quad \eta = 0 \quad (2.12)$$

In addition, in order to match with the outer solution (2.9), u must satisfy the matching condition

$$u \rightarrow 1, \quad \eta \rightarrow \infty \quad (2.13)$$

The boundary layer solution of (2.11)–(2.13) is therefore given by

$$u = 1 - e^{-\eta} \quad (2.14)$$

In fact, (2.14) is the leading term of the uniform asymptotic expansion of (2.5), (2.6). To evaluate $\tau_1(A)$, we multiply (2.1) by $e^{-E(x, y)/\epsilon}$, which is a

solution of the adjoint equation $L^*Z = 0$, and integrate over the domain $E < E_c$, using the Green's or the Lagrange identity to obtain

$$\tau_1(A) = \frac{\int\int_{E < E_c} e^{-E/\epsilon} dx dy}{\oint_{E=E_c} e^{-E_c/\epsilon} \beta \nu_2 (\partial u / \partial y) ds} \tag{2.15}$$

where $\nu = (\nu_1, \nu_2)$ is the unit outer normal to $E = E_c$, and s denotes arclength on $E = E_c$. Employing (2.14) in (2.15) and evaluating the integrals in (2.15) asymptotically for small ϵ , we obtain

$$\tau_1(A) \sim \frac{2\pi\epsilon}{\beta I_c \omega_A} e^{E_c/\epsilon} \tag{2.16}$$

This agrees with Kramers' small β result given by (1.4), though we observe that (2.16) was derived for small ϵ with β arbitrary.

The time $\tau_2(E_c)$ to go from the curve $E = E_c$ to Γ is the time to go from a point $(x, y_c(x))$ on $E = E_c$, weighted by the density of starting points on $E = E_c$. The density $p(x)$ of points on $E = E_c$ that were reached by a trajectory starting in $E < E_c$, is Green's function $G(x, y, \xi, \eta)$ for the boundary value problem

$$\begin{aligned} Lw &= 0, & \text{for } E < E_c \\ w &= f, & \text{for } E = E_c \end{aligned} \tag{2.17}$$

where f is any smooth function defined on $E = E_c$. Then (see p. 120 of Ref. 8),

$$p(x) = G(x, y_c(x), x_A, 0) \tag{2.18}$$

The point $A \equiv (x_A, 0)$ in (2.18) can in fact be replaced by any point inside $E = E_c$, since $G(x, y, \xi, \eta)$ is independent of ξ and η , for (ξ, η) in the domain $E < E_c$, as shown below [cf. (2.19)–(2.21)]. To determine $G(x, y, \xi, \eta)$ we solve (2.17) for small ϵ . Setting $\epsilon = 0$ in (2.17) we find that the leading term in the asymptotic expansion of w , as $\epsilon \rightarrow 0$, is a constant, w_0 say. To match this leading term to the boundary value we construct a boundary layer function as above. After matching, we obtain the uniform expansion

$$w = \oint_{E=E_c} G(x, y, \xi, \eta) f(\xi, \eta) ds \sim w_0 + (f - w_0)e^{-\eta} \tag{2.19}$$

where η is given by (2.10). To determine the constant w_0 we multiply (2.17) by $e^{-E(x,y)/\epsilon}$, and use Green's or the Lagrange identity with w given by (2.19) to obtain

$$w_0 = \frac{\oint_{E=E_c} f(x, y) y dx}{\oint_{E=E_c} y dx} = \oint_{E=E_c} f(x, y) p(x) ds \tag{2.20}$$

Hence, to leading order in ϵ ,

$$p(x) ds = \frac{y_c(x) dx}{I_c} \tag{2.21}$$

We now calculate the mean first passage time $\tau_2(E_c)$, of trajectories to go from $E = E_c$, to the separatrix Γ . To this end we introduce the mean first passage time $\tau_2(x, y)$ to reach Γ , starting inside, or on, $E = E_c$. We will show that

$$\tau_2(x, y) = \tau_1(x, y) + \oint_{E=E_c} G(x, y, \xi, \eta) \tau_2(\xi, \eta) ds_{\xi\eta} \tag{2.22}$$

which holds for all points (x, y) in the domain $E \leq E_c$. The identity follows from the fact that both sides of (2.22) satisfy $L\tau = -1$ in $E < E_c$, and coincide on $E = E_c$. The function $\tau_2(x, y)$ is a solution of (2.1) subject to the boundary condition $\tau_2 = 0$ on Γ . We first write $\tau_2(x, y) = \tau_2(A)v(x, y)$ where $\max_D v(x, y) = 1$. As above, we construct the boundary layer function $v(x, y)$. We change the independent variables in (2.5) to (x, ρ) , where ρ denotes distance to Γ . We stretch ρ by setting

$$\zeta = \rho/\sqrt{\epsilon}$$

to obtain the leading order boundary layer equation

$$\beta \left(\frac{\partial \rho}{\partial y} \right)^2 (x, 0) \frac{\partial^2 v}{\partial \zeta^2} + \zeta b_0(x) \frac{\partial v}{\partial \zeta} + y_\Gamma(x) \frac{\partial v}{\partial x} = 0, \quad \zeta > 0, \quad x < x_c \tag{2.23}$$

where the function $y_\Gamma(x)$, which describes the separatrix, satisfies

$$y'_\Gamma(x) = -\beta - \frac{U'(x)}{y_\Gamma(x)}, \quad y_\Gamma(x_c) = 0 \tag{2.24}$$

Here we have used the representation of the flow vector

$$b(x, y) \equiv (y, -\beta y - U'(x)) = b_0(x)(\rho + O(\rho^2))\nu + (b_1(x) + o(1))\sigma$$

near $\rho = 0$, where $o(1) \rightarrow 0$ as $\rho \rightarrow 0$, and σ and ν are the unit tangent and unit exterior normal at Γ , respectively. The boundary condition for (2.23) is $v = 0$ for $\zeta = 0$ and the matching condition is $v \rightarrow 1$ as $\zeta \rightarrow \infty$.

We now change variables by defining

$$\mu = \gamma(x)\zeta$$

where $\gamma(x)$ is the solution of the Bernoulli equation

$$y_\Gamma(x)\gamma'(x) + b_0(x)\gamma(x) = \beta\rho_y^2(x, y_\Gamma(x))\gamma^3(x) \tag{2.25}$$

that satisfies the condition

$$\gamma(x_c) = \left[\frac{b_0(x_c)}{\beta \rho_y^2(x_c, 0)} \right]^{1/2} \tag{2.26}$$

Here the functions b_0 and ρ_y^2 are, respectively, given by

$$b_0(x) = \frac{y_\Gamma(x)U'(x)[1 - U''(x)] - \beta y_\Gamma(x)U''(x)}{y_\Gamma^2(x) + [\beta y_\Gamma(x) + U'(x)]^2} \tag{2.27}$$

and

$$\rho_y^2(x, y_\Gamma(x)) = \frac{y_\Gamma^2(x)}{y_\Gamma^2(x) + [\beta y_\Gamma(x) + U'(x)]^2} \tag{2.28}$$

Then (2.23) becomes

$$\frac{\partial^2 v}{\partial \mu^2} + \mu \frac{\partial v}{\partial \mu} + \frac{y_\Gamma(x)}{\beta(\partial \rho / \partial y)^2(x, 0)\gamma^2(x)} \frac{\partial v}{\partial x} = 0 \tag{2.29}$$

Equation (2.29) is a degenerate parabolic equation, whose unique solution is given by

$$v(x, y) = \left(\frac{2}{\pi} \right)^{1/2} \int_0^\mu e^{-s^2/2} ds = \text{erf}(\rho\gamma/\sqrt{2}\epsilon) \tag{2.30}$$

To determine $\tau_2(A)$ we again use the Lagrange identity as described above, to obtain

$$\tau_2(A) = \frac{- \int_D \int e^{-E/\epsilon} dx dy}{\epsilon \oint_\Gamma e^{-E/\epsilon} \beta \nu_2 (\partial v / \partial y) \{ 1 + [y_\Gamma(x)]^2 \}^{1/2} dx} \tag{2.31}$$

The integral in the denominator of (2.31) is evaluated asymptotically by Laplace's method. Since $E(x, y)$ achieves its minimum on Γ at $x = x_c$, it is only necessary to calculate $\partial v / \partial y$ in (2.31) at $\rho = 0$ and $x = x_c$. Employing (2.29) and (2.26), we find that

$$\frac{\partial v}{\partial y} \Big|_{\rho=0, x=x_c} = \left[\frac{2b_0(x_c)}{\epsilon\beta\pi} \right]^{1/2} \tag{2.32}$$

where

$$b_0(x_c) = \frac{1}{1 + \lambda^2} (\lambda\omega_c^2 + \lambda - \beta)$$

with

$$\lambda = \frac{\beta + (\beta^2 + 4\omega_c^2)^{1/2}}{2}$$

The integral in the denominator of (2.31) is thus asymptotically equal to

$$2\epsilon \left[\frac{\beta b_0(x_c)}{\lambda^2 + \omega_c^2} \right]^{1/2} e^{-E_c/\epsilon}$$

The integral in the numerator of (2.31) is also evaluated asymptotically by Laplace's method in which the major contribution comes from $(x_A, 0)$. Thus we obtain

$$\tau_2(A) \sim \frac{2\pi\omega_c e^{E_c/\epsilon}}{\omega_A \left[(\beta^2 + 4\omega_c^2)^{1/2} - \beta \right]} \tag{2.33}$$

This agrees with Kramers' $\beta = O(1)$ result (1.6) but does not agree with Kramers' small β result (1.4). It is clear that (2.33) cannot be a valid approximation to the mean first passage time for small β , since $E = E_c$ is contained within Γ , which implies that $\tau_2(A) > \tau_1(A)$. This contradiction is due to the fact that for small β , the curve $E = E_c$ lies within the boundary layer near Γ . To obtain the correct expression for $\tau_2(A)$, we iterate the identity (2.22) by writing

$$\tau_2^{(n+1)}(x, y) = \tau_1(x, y) + \oint_{E=E_c} G(\xi, \eta, x, y) \tau_2^{(n)}(\xi, \eta) ds_{\xi\eta} \tag{2.34}$$

As a first iterate, we use $\tau_2^0(\xi, \eta) = \tau_2(A)v(\xi, \eta)$, in the right-hand side of (2.34), with $\tau_2(A)$ and v , respectively, given by (2.33) and (2.30). We observe that the iteration procedure converges in one step, since

$$\begin{aligned} \tau_2^{(2)}(x, y) &= \tau_1(x, y) + \oint_{E=E_c} G(\xi, \eta, x, y) \tau_2^{(1)}(\xi, \eta) ds_{\xi\eta} \\ &= \tau_1(x, y) \\ &\quad + \oint_{E=E_c} G(\xi, \eta, x, y) \left[\tau_1(\xi, \eta) \right. \\ &\quad \quad \left. + \oint_{E=E_c} G(u, v, \xi, \eta) \tau_2^{(0)}(u, v) ds_{uv} \right] ds_{\xi\eta} \\ &= \tau_1(x, y) + \oint_{E=E_c} \oint_{E=E_c} G(\xi, \eta, x, y) G(u, v, \xi, \eta) \tau^{(0)}(u, v) ds_{\xi\eta} ds_{uv} \\ &= \tau_1(x, y) + \oint_{E=E_c} G(u, v, x, y) \tau^{(0)}(u, v) ds_{uv} = \tau_2^{(1)}(x, y) \end{aligned} \tag{2.35}$$

The last equation follows from the fact that $G(u, v, x, y)$ and $\phi_{E=E_c} G(\xi, \eta, x, y)G(u, v, \xi, \eta) ds_{\xi\eta}$ are both solutions of $LG = 0$ for (u, v) in $E < E_c$, and are equal on $E = E_c$. Setting $(x, y) = (x_A, 0)$, we observe that the right-hand side of (2.35) may be interpreted as the sum of the time $\tau_1(A)$ to go from $(x_A, 0)$ to $E = E_c$, plus the time to go from a point $(x, y_c(x))$ on $E = E_c$ to Γ , weighted by the density $p(x)$ of starting points on $E = E_c$ [given by (2.21)]. The weighted time from a point $(x, y_c(x))$ on $E = E_c$, is the time $\tau_2(E_c)$ to go from $E = E_c$ to Γ . Since trajectories that reach Γ are equally likely to cross or to return to $E = E_c$, the time $\tau_2(E_c)$ must be counted twice. Therefore the crossing rate is given by

$$\kappa = \frac{1}{\tau_1(A) + 2\tau_2(E_c)}$$

with $\tau_1(A)$ given by (1.9) and $\tau_2(E_c)$ given by (1.10).

ACKNOWLEDGMENT

We are pleased to acknowledge useful discussions of the problem with C. Knessl, A. Nitzan, B. Carmeli, and R. Landauer.

APPENDIX

In this appendix we show that $\rho\gamma$ in (1.11) is $O(\sqrt{\beta})$ for small β . In that case the curve $E = E_c$ is near Γ , so that we expand $y_\Gamma(x)$ about $y_c(x)$ as

$$y_\Gamma(x) = y_c(x) - \frac{\beta}{y_c(x)} \int_{x_c}^x y_c(x) dx + o(\beta)$$

Employing this expression in (2.28), we obtain

$$\rho(x, y_c(x)) = \frac{\beta}{y_c(x)} \int_{x_c}^x y_c(x) dx + o(\beta)$$

The function $\gamma(x)$ is estimated by setting $\gamma(x) = \gamma_0(x)/\sqrt{\beta}$, where $\gamma_0(x)$ satisfies the equation

$$y_c(x)\gamma_0'(x) + \omega_c\gamma_0(x) = \frac{\gamma_0^3(x)}{1 + \omega_c^2}$$

and the condition

$$\gamma_0(x_c) = [\omega_c(1 + \omega_c^2)]^{1/2}$$

Since the solution $\gamma_0(x)$ is bounded, independent of β , we see that

$$\rho(x, y_c(x))\gamma(x) = O(\sqrt{\beta})$$

Finally, we remark that to evaluate the function V in (1.11) we employ the expression

$$\rho\gamma = \frac{\sqrt{\beta} \gamma_0(x)}{[2(E_c - U(x))]^{1/2}} \int_{x_c}^x [2(E_c - U(x))]^{1/2}$$

for all β .

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