Does reaction path curvature play a role in the diffusion theory of multidimensional activated rate processes?

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The two-dimensional Kramers' barrier crossing problem in the overdamped (diffusion) limit is investigated with particular attention given to possible effects of the geometry of the potential surface on the rate. Previous work ascribes corrections to the two-dimensional Kramers' formula to curvature of the reaction path. In contrast, we find that these corrections are due to the anharmonicity of the potential surface at the saddle and may become appreciable for small window frequency, i.e., flat potential surface at the saddle in the direction perpendicular to the reaction path. A general formalism to calculate such corrections is described.

I. INTRODUCTION

Kramers' theory[1] of activated rate processes and its generalizations provides a general framework for the description of classical activated rate processes in condensed phases, a subject of long standing importance in many branches of science. Generalizations of the (one-dimensional) Kramers' theory to multidimensional systems, for the case of intermediate and high friction, have been known for a long time.[2–13] In such situations, the rate is determined by the dynamics near the saddle point where the motion along the reaction coordinate may be assumed to be essentially decoupled from the nonreactive modes. Under this assumption, the rate is obtained as a product of the one-dimensional rate and a ratio of equilibrium partition functions, which expresses the statistical weight of the transition state configuration and the initial reactant configuration:

$$k = k_{1D}\frac{Q^B}{Q^W}, \tag{1.1}$$

$$k_{1D} = \frac{\omega_r^B\,\omega_r^W}{2\pi\gamma}\,e^{-E_B/k_BT}. \tag{1.2}$$

Here ω_r^B and ω_r^W are the frequencies associated with the reaction coordinate on the barrier and in the well, respectively, E_B is the barrier height, i.e., the height of the saddle point above the bottom of the well in which the particle is initially confined, γ is the friction coefficient, k_B is Boltzmann's constant, and T is the temperature. The factors Q^B and Q^W are the partition functions of the subsystems of nonreactive modes associated with the barrier and the initial well configurations, respectively. In the classical limit $Q^B/Q^W = \Pi_n\,\omega_{\rm nr}^W/\omega_{\rm nr}^B$, where $\omega_{\rm nr}^B$ and $\omega_{\rm nr}^W$ are the frequencies associated with the nonreactive modes on the barrier and in the well, respectively, and where the product is taken over all such modes. More recently, a multidimensional version of the low friction limit was also derived, based on a generalized multidimensional energy diffusion equation.[14–16]

Equation (1.1) is based on the assumption that near the saddle point the reactive flux is one-dimensional; the nonreactive modes are assumed to be in thermal equilibrium. There have been several investigations in recent years of situations where this may not be the case.[17–19] Most notably it has been suggested that for curved reaction paths, the rate becomes dependent on the curvature of the reaction coordinate. Larson and Kostin[17] have calculated correction terms to the preexponential factor of the Kramers' rate expression for a particular model, and attributed these corrections to the effect of reaction path curvature. More recently, Larson[18] has used a variational formula for the optimal reaction coordinate of Berkowitz *et al.*,[19] to show that the actual reaction path in such a model deviates from the minimum energy path.

Aspects of reaction path curvature have been thoroughly investigated for reactions involving isolated molecules by Miller and his co-workers.[20] These theoretical studies clearly demonstrate the effect of this curvature on the reaction dynamics in the zero friction limit. In the high friction limit, where dynamical effects are expected only in the immediate vicinity of the barrier, it is less clear how reaction path curvature can affect the reaction rate. The high friction rate derived by Larson and Kostin for their model (described below) is[17]

$$k = k_0\left(1+\frac{1}{2p}+\cdots\right), \tag{1.3}$$

where k_0 is given by Eq. (1.1) and where

$$p = \frac{m\omega^2 r_0^2}{2k_BT}. \tag{1.4}$$

The factor ω is the frequency along the normal to the reaction path at the saddle point (denoted by ω_r in Ref. 17), r_0 is the radius of curvature of the reaction path, and m is the particle mass. This expression contains correction terms which are independent of friction, in contrast to the intuitive

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expectation that as the friction increases the dynamics is limited more and more to the neighborhood of the saddle point. Larson and Kostin interpret the correction term as the effect of reaction path curvature on the rate.

From the mathematical point of view, the high friction rate, given by Eqs. (1.1) and (1.2), is the first term in an expansion of the rate, in the small parameter $\epsilon = (E_B/k_BT)^{-1}$. Equations (1.1) and (1.2) are expected to be exact in the limits $\epsilon \to 0$ and $\gamma \gg \omega_r^W, \omega_r^B$, unless there are other dimensionless parameters in the problem which vanish as $\epsilon \to 0$. For example, the parameter p of Eq. (1.3) is potentially such a parameter. In addition, the frequencies $\omega_{\rm nr}^B$ of nonreactive modes at the barrier, nondimensionalized as $(h\omega_{\rm nr}^B/k_BT)^{-1} \equiv \epsilon_{\rm nr}$, are potentially such parameters. Their magnitudes measure the extent of the dynamical region about the saddle point, in directions perpendicular to the reaction coordinate. Thus, if some or all of the $\epsilon_{\rm nr}$ remain finite as $\epsilon \to 0$, deviations from Eqs. (1.1) and (1.2) are expected. In the discussion that follows we consider the two dimensional problem, with one parameter $\epsilon_{\rm nr}$.

In the present paper we discuss corrections to Kramers' rate expression resulting from the smallness of $\epsilon_{\rm nr}$, i.e., of $\omega_{\rm nr}^B$. We show that (a) such terms may lead to $O(1)$ corrections in the preexponential term of the Kramers' rate; (b) corrections in the model discussed by Larson and Kostin [Eqs. (3.1) and (3.2)] are due to the smallness of $\epsilon_{\rm nr}$; (c) such corrections are not associated with reaction path curvature; and (d) the reaction path, defined as the path of minimum energy, always goes through the saddle point on the potential energy surface. However, the distribution of exit points along the separatrix between the reactant and product domains of attraction, may peak at a slightly shifted position. This shift is again unrelated (in the high friction limit) to the reaction path curvature.

In addition to the effects discussed here, we note that in multidimensional situations, another dimensionless parameter may affect the reaction rate, namely the ratio between the friction coefficients (or diffusion constants) in different directions. Such effects were recently discussed by Agmon and Hopfield.[21] The application of the present formalism to such situations of nonisotropic diffusion will be described in a subsequent paper.

II. FORMALISM

We consider the Smoluchowski equation corresponding to overdamped motion in the plane (where tildes denote dimensional variables)

$$\dot{\tilde{x}}_1 = -\frac{1}{m\gamma}\frac{\partial \tilde{V}}{\partial \tilde{x}_1} + \sqrt{\frac{2mk_BT}{\gamma}}\,\dot{W}_1,$$
$$\dot{\tilde{x}}_2 = -\frac{1}{m\gamma}\frac{\partial \tilde{V}}{\partial \tilde{x}_2} + \sqrt{\frac{2mk_BT}{\gamma}}\,\dot{W}_2, \qquad (2.1)$$

where the friction coefficient γ is assumed large relative to all characteristic frequencies, and m denotes the particle mass. Here $\dot{W}_1$ and $\dot{W}_2$ are independent standard Gaussian white noises. The potential $\tilde{V}(\tilde{x}_1,\tilde{x}_2)$ is assumed to have two minima located at $\tilde{M}_a = (\tilde{x}_{1a},\tilde{x}_{2a})$ and $\tilde{M}_b = (\tilde{x}_{1b},\tilde{x}_{2b})$, whose domains of attraction in the plane are denoted by $\tilde{\mathscr{D}}_a$ and $\tilde{\mathscr{D}}_b$, respectively. The common boundary of $\tilde{\mathscr{D}}_a$ and $\tilde{\mathscr{D}}_b$ is the separatrix which we denote by $\tilde{\Gamma}$ (see Fig. 1). We assume that there is a single saddle point $\tilde{S} = (\tilde{x}_{10},\tilde{x}_{20})$ of $\tilde{V}(\tilde{x}_1,\tilde{x}_2)$ on $\tilde{\Gamma}$. The height of the potential barrier in $\tilde{\mathscr{D}}_i\,(i = a,b)$ is defined as $\Delta V_i = \tilde{V}(\tilde{x}_{10},\tilde{x}_{20}) - \tilde{V}(\tilde{x}_{1i},\tilde{x}_{2i})$. The Smoluchowski equation for the transition probability density $\rho(\tilde{x}_1,\tilde{x}_2,\tilde{t})$ of the process $[\tilde{x}_1(\tilde{t}),\tilde{x}_2,(\tilde{t})]$ defined by Eq. (2.1) is

$$\frac{\partial \rho}{\partial t} = \frac{1}{m\gamma}\tilde{\nabla}\cdot(\rho\tilde{\nabla}\tilde{V}) + \frac{k_BT}{m\gamma}\tilde{\nabla}^2\rho \equiv \mathscr{L}\rho, \qquad (2.2)$$

whose stationary solution is

$$\rho = \exp\{-\tilde{V}/k_BT\}. \qquad (2.3)$$

A trajectory $[\tilde{x}_1(\tilde{t}),\tilde{x}_2(\tilde{t})]$ that starts at a point $(\tilde{x}_1,\tilde{x}_2)$ in $\tilde{\mathscr{D}}_a$ say, hits $\tilde{\Gamma}$ for the first time at a random time $\tilde{\tau}^*$, at a point $\tilde{x}_1(\tilde{\tau}^*) = \tilde{\xi}_1, \tilde{x}_2(\tilde{\tau}^*) = \tilde{\xi}_2$. The probability density $\tilde{P}(\tilde{\xi}_1,\tilde{\xi}_2;\tilde{x}_1,\tilde{x}_2)$ for this exit point, given the initial point $(\tilde{x}_1,\tilde{x}_2)$, is Green's function for the boundary value problem

$$\mathscr{L}^*u \equiv \frac{K_BT}{m\gamma}\tilde{\nabla}^2u - \frac{1}{m\gamma}\tilde{\nabla}\tilde{V}\cdot\tilde{\nabla}u = 0 \text{ in } \tilde{\mathscr{D}}_a,$$
$$u = f \quad \text{on } \tilde{\Gamma}. \qquad (2.4)$$

Here the backward operator $\mathscr{L}^*$ is adjoint to $\mathscr{L}$, and f is an arbitrary function, prescribed on $\tilde{\Gamma}$.[8] We nondimensionalize Eq. (2.4) by setting

$$x_1 = \frac{\tilde{x}_1}{L}; \quad x_2 = \frac{\tilde{x}_2}{L}, \qquad (2.5a)$$
$$V = \frac{\tilde{V}}{\Delta V_a}; \quad \epsilon = \frac{k_BT}{\Delta V_a}, \qquad (2.5b)$$
$$\omega^2 = \frac{mL^2}{\Delta V_a}\,\tilde{\omega}^2 \qquad (2.5c)$$

where L is a characteristic length and where $\tilde{\omega}$ in Eq. (2.5c) represents any frequency in the problem. Depending on the shape of the well, we consider two choices for the characteristic length scale L.

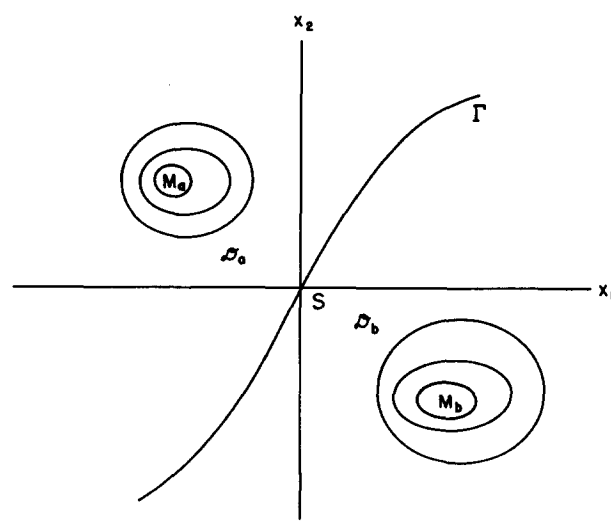

FIG. 1. Contour plot of a two-dimensional potential surface showing the reactant (a) and product (b) wells, the saddle point S, and the separatrix Γ.

A. Case I

As ΔV_a increases, the width $\tilde{r}_a$ of the well (the distance between $\tilde{M}_a$ and $\tilde{S}$) increases as $\sqrt{\Delta V_a}$ [Fig. 2(a)]. In this case we choose

$$L=\sqrt{\frac{\Delta V_a}{m\gamma^2}}$$

which implies that $r_a=\tilde{r}_a/L=O(1)$, and that the scaled frequency $\omega=\tilde{\omega}/\gamma$ does not change as ΔV_a increases.

B. Case II

As ΔV_a increases, $\tilde{r}_a$ remains constant, i.e., the well becomes effectively sharper [see Fig. 2b]. In this case we take $L=\tilde{r}_a$ so that $r_a=1$ by definition. The scaled frequencies are then given by Eq. (2.5c):

$$\omega^2=\frac{mr_a^2}{\Delta V_a}\tilde{\omega}^2,$$

so that for $\omega=O(1),\tilde{\omega}=O(\sqrt{\Delta V_a})$, expressing the increase in the sharpness of the well as ΔV_a increases. This holds for all frequencies but one. In the discussion below we are interested in the case where one of the barrier frequencies $\tilde{\omega}_t$ remains constant as ΔV_a increases, so that the corresponding dimensionless frequency ω_t is small $[O(1/\Delta V_a)]$.[22]

In the present work we will be mainly interested in case II, but for the time being we continue with the general scalings (2.5). Equation (2.4), rewritten in terms of the scaled variables, becomes

$$\epsilon\nabla^2 u-\nabla V\cdot\nabla u=0 \text{ in } \mathscr{D}_a,$$
$$u=f \quad \text{on } \Gamma, \tag{2.6}$$

where $\mathscr{D}_a$ and Γ are the scaled domain and separatrix, respectively. A method for treating the singularly perturbed boundary value problem (2.6) was introduced by Matkowsky and Schuss[7,13,23–26] (see also Ref. 27). Employing their method (briefly described in the Appendix), we find that the resulting function $P(\xi_1,\xi_2;x_1,x_2)$ is independent of the initial coordinates (x_1,x_2) except for those points (x_1,x_2) in an $O(\sqrt{\epsilon})$ neighborhood (boundary layer) of Γ. If Γ is parametrized by the arc length s measured from the saddle point S, then the solution u of Eq. (2.6) is given by $u=\int_\Gamma p(s)f(s)ds$, where the density $p(s)$ of hitting points is given by

$$p(s)\sim\frac{\exp\{-V[\xi_1(s),\xi_2(s)]/\epsilon\}g(s)}{\oint_\Gamma \exp\{-V[\xi_1(s),\xi_2(s)]/\epsilon\}g(s)ds}. \tag{2.7}$$

Here $g(s)$ is the solution to the Bernoulli equation $[g=g(s),g'=dg/ds]$

$$g^3+b_0(s)g+\frac{dV}{ds}[\xi_1(s),\xi_2(s)]g'=0 \tag{2.8}$$

with the initial condition

$$g(s=0)=\sqrt{-b_0(s=0)}. \tag{2.9}$$

In Eqs. (2.8) and (2.9), the function $b_0(s)$ is defined by the local expansion of ∇V near Γ. For a point (x_1,x_2) in D_a near the separatrix, and the corresponding nearest point s on Γ, this expansion is given by

$$\nabla V(x_1,x_2)\sim -b_0(s)l\hat{n}+\frac{dV}{ds}(s)\hat{\tau}+\cdots. \tag{2.10}$$

Here $\hat{n}$ and $\hat{\tau}$ are the unit outer normal and tangent to Γ, respectively, and l is the distance between (x_1,x_2) and s. More specifically,

$$b_0(s)=\frac{\partial}{\partial l}\nabla V\cdot\hat{n}\Big|_{l=0}=\frac{\partial^2 V}{\partial n^2}\Big|_\Gamma. \tag{2.11}$$

The most likely point of exit is the one at which $p(s)$ is maximal, i.e., the point s^* at which the numerator of Eq. (2.7) is maximal. Because of the s dependence of $g(s)$ on s, this point is not necessarily at the saddle point $S(s=0)$. For $\epsilon\ll 1$ it is given asymptotically by

$$s^*\sim\frac{\epsilon g'(0)}{g(0)V''(0)}, \tag{2.12}$$

where $g'(0)$ and $V''(0)$ are derivatives of g and V along Γ, evaluated at the saddle point. Equation (2.12) shows that for small ϵ, the most likely exit point s^* is close to the saddle point $s=0$, though shifted by $O(\epsilon)$. For problems in which the saddle is very flat, the asymptotic evaluation of Eq. (2.7), which leads to Eq. (2.12), is not valid. The maximum of $p(s)$ in Eq. (2.7) will be determined essentially by $g(s)$ alone, and s^* may be shifted from the saddle point $s=0$ by a distance that is determined by the flatness of the window.[27]

The mean time $\tilde{\tau}(\tilde{x}_1,\tilde{x}_2)$ for a trajectory that starts at $(\tilde{x}_1,\tilde{x}_2)$ in $\mathscr{D}_a$ to first hit $\tilde{\Gamma}$, is the solution of the boundary value problem[8]

$$\mathscr{L}^*\tilde{\tau}=-1 \text{ in } \tilde{\mathscr{D}}_a,$$
$$\tilde{\tau}=0 \quad \text{on } \tilde{\Gamma}. \tag{2.13a}$$

In scaled variables this becomes

$$\epsilon\nabla^2\tau-\nabla V\cdot\nabla\tau=-1 \text{ in } \mathscr{D}_a,$$
$$\tau=0 \quad \text{on } \Gamma, \tag{2.13b}$$

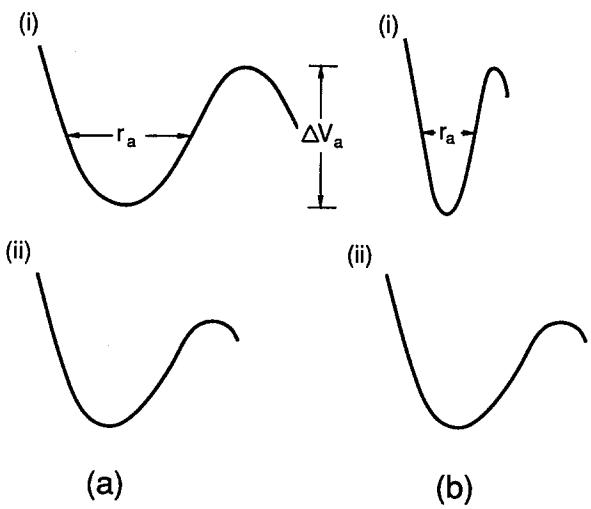

FIG. 2. Effect of scaling the well depth: in (a) ΔV_a increases together with the width of the attractive region, so that the well frequency remains unchanged, while in (b) ΔV_a increases, while the width of the attractive region (a) remains constant, thus effectively decreasing the well frequency. (i) is a sketch of the unscaled well, and (ii) is a sketch of the scaled well.

where all scalings are given by Eq. (2.5), and in addition

$$\tau = \tilde{\tau}\left(\frac{m\gamma L^2}{\Delta V_a}\right)^{-1}. \tag{2.14}$$

For $\epsilon \ll 1$, the time $\tilde{\tau}$ is given by[10–15]

$$\tilde{\tau} \sim \frac{m\gamma L^2}{\Delta V_a} \frac{\iint_{\mathscr{D}_a} dx_1\, dx_2 \exp\left[-V(x_1,x_2)/\epsilon\right]}{\sqrt{2\epsilon/\pi}\int_\Gamma ds \exp\left[-V(s)/\epsilon\right] g(s)}. \tag{2.15}$$

Equation (2.15) is the standard result used in all calculations pertaining to this problem. Under the assumptions described above, the numerator can be evaluated by the Laplace method[28] to give

$$\frac{2\pi}{H^{1/2}(M_a)} \exp\left(-V(M_a)/\epsilon\right), \tag{2.16}$$

where the Hessian H is defined by

$$H(M_a) = \begin{vmatrix} V_{x_1x_1}(M_a) & V_{x_1x_2}(M_a) \\ V_{x_1x_2}(M_a) & V_{x_2x_2}(M_a) \end{vmatrix} \equiv \omega_{a1}^2\, \omega_{a2}^2. \tag{2.17}$$

Here ω_{a1}^2 and ω_{a2}^2 are the eigenvalues of the Hessian matrix at M_a, so that ω_{a1} and ω_{a2} are the principal frequencies at the bottom of the potential well in $\mathscr{D}_a$.

The integral in the denominator of Eq. (2.15) can be expanded[28] as

$$\exp\left[-V(0)/\epsilon\right]\sqrt{\frac{2\pi\epsilon}{V^{(2)}(0)}}\, g(0) \times\left\{1+\frac{\epsilon}{V^{(2)}(0)}\left[\frac{5}{24}\left(\frac{V^{(3)}(0)}{V^{(2)}(0)}\right)^2 - \frac{V^{(4)}(0)}{24V^{(2)}(0)} - \frac{g'(0)}{2g(0)}\frac{V^{(3)}(0)}{V^{(2)}(0)} + \frac{g''(0)}{2g(0)}\right] + O(\epsilon)\right\}, \tag{2.18}$$

where $V^{(n)}(s)$ is the nth derivative of V with respect to s [in Eq. (2.18) all functions of s are evaluated at the saddle point].

The transition rate k, across Γ, is given by

$$k = \frac{1}{2\tau}, \tag{2.19}$$

where the factor 1/2 is due to the fact that trajectories reaching Γ from $\mathscr{D}_a$ are equally likely to cross Γ or to return to $\mathscr{D}_a$. Combining Eqs. (2.15)–(2.19) we obtain

$$k = k_0\left[1+\frac{A\epsilon}{\omega_t^2}+O(\epsilon)\right], \tag{2.20a}$$

$$k_0 = \frac{\omega_{a1}\omega_{a2}}{2\pi\gamma}\frac{\omega_n}{\omega_t}\exp\left(-1/\epsilon\right), \tag{2.20b}$$

where $\omega_n = \sqrt{-b_0(0)}$ and $\omega_t = \sqrt{V^{(2)}(0)}$ are the principal frequencies at the saddle point $s=0$, and where

$$A = \frac{5}{24}\left(\frac{V^{(3)}(0)}{V^{(2)}(0)}\right) - \frac{V^{(4)}(0)}{24V^{(2)}(0)} - \frac{g'(0)}{2g(0)}\frac{V^{(3)}(0)}{V^{(2)}(0)} + \frac{g^{(2)}(0)}{2g(0)}. \tag{2.21}$$

The squared frequencies ω_n^2 and ω_t^2 are proportional to the principal curvatures of the potential surface at the saddle point. They do not represent the curvature of the reaction path in the (x_1,x_2) plane. We note that the correction term $A\epsilon/\omega_t^2$ in Eq. (2.20) is small, unless ω_t is sufficiently small, i.e., $\omega_t^2 = O(\epsilon)$. In this case we have an $O(1)$ correction to the preexponential term, and Eq. (2.20a) must be modified (see discussion below). Mathematically, the orgin of this correction is the anharmonicity of the saddle.

Note that the rate k_0, given by Eq. (2.20b), is a generalization of the rate k_0 given by Eqs. (1.1) and (1.2). The difference lies in the fact that the form (2.20) does not require that the reactive mode (associated with the barrier frequency ω_n) and the nonreactive mode (associated with the frequency ω_t at the barrier) retain their identities in the well. In addition, the correction term $1+A(\epsilon/\omega_t^2)$ is similar to the correction term $1+1/2p$ in Eq. (1.3). Indeed, transforming back to dimensional variables, the factor ϵ/ω_t^2 is seen to be identical to $1/2p$, with p given by Eq. (1.4), provided we identify the characteristic length L [cf. Eq. (2.5c)] with the Larson–Kostin length parameter r_0 (see Sec. III).

Thus, in the notation of Ref. 17, the correction term is $A/2p$. Below we will show that for the model of Ref. 17, $A=1$.

It should be noted that other corrections to the expression (2.20), due to higher order terms in the boundary layer expansion, may also appear. In fact, they are of order $O(\epsilon^{1/2})$ and may dominate the $O(\epsilon)$ correction terms in Eq. (2.20). Such corrections, however, are independent of ω_t to leading order, and therefore do not become appreciable for very small ω_t.

Finally we note that as $\omega_t \to 0$ the expansion (2.20) must be modified (e.g., Ref. 7). For $\omega_t^2 = O(\epsilon)$, the contour integral in the denominator of Eq. (2.15) is no longer of Laplace type and cannot be expanded by approximating the exponent by a quadratic form. It may therefore have to be evaluated numerically. For $\omega_t^2 \ll \epsilon$, the dominant term in the expansion of the contour integral is associated with higher derivatives of the potential at the saddle point, which leads to corrections of a different order in ϵ in Eq. (2.20).

III. TWO EXAMPLES

We first apply the analysis of Sec. II to the model of Larson and Kostin.[17] In polar coordinates $(\tilde{r},\tilde{\theta})$, their potential is given by

$$\tilde{V}(\tilde{r},\tilde{\theta}) = \frac{V_0}{\tilde{a}^4}\left[(r_0\tilde{\theta})^2 - \tilde{a}^2\right]^2 + \frac{1}{2}m\tilde{\omega}^2(\tilde{r}-r_0)^2. \tag{3.1}$$

This potential is characterized by two wells, centered at $\tilde{r}=r_0, \tilde{\theta} = \pm(\tilde{a}/r_0)$, and a saddle point at $\tilde{r}=r_0, \tilde{\theta}=0$. The relevant part of the separatrix is the positive x axis ($\tilde{\theta}=0$), and the barrier height is V_0. Finally, $\tilde{\omega}$ in Eq. (3.1) is the barrier "window" frequency ($\tilde{\omega}_t$ of Sec. II). Measuring the curvature of the potential surface at the saddle, in the direction perpendicular to the reaction path, determines the degree to which the reactive trajectories are confined to the vicinity of the saddle point. The reaction (minimum energy) path from the reactant to the product well, is a circular arc of radius r_0, connecting the centers of the two wells.

In dimensionless (scaled) variables, Eq. (3.1) takes the form

$$V(r,\theta) = \left[\left(\frac{\theta}{a}\right)^2 - 1\right]^2 + \frac{1}{2}\omega^2(r-1)^2, \tag{3.2}$$

where

$$r=\frac{\tilde{r}}{r_0};\quad a=\frac{\tilde{a}}{r_0};\quad V=\frac{\tilde{V}}{V_0};\quad \theta=\tilde{\theta}, \tag{3.3}$$

and

$$\omega^2=\frac{mr_0^2}{V_0}\tilde{\omega}^2. \tag{3.4}$$

Note that the scaling employed in Eqs. (3.3) and (3.4) is of type II (see Sec. II). In Cartesian coordinates $x_1=r\cos\theta, x_2=r\sin\theta$ we have

$$V(x_1,x_2)=\left[\left(\frac{1}{a}\arctan\frac{x_2}{x_1}\right)^2-1\right]^2 + \frac{1}{2}\omega^2\left(\sqrt{x_1^2+x_2^2}-1\right)^2. \tag{3.5}$$

In order to evaluate the constant A in Eq. (2.21), we must compute the derivatives $V^{(j)}(0), (j=2,3,4)$ with respect to s (i.e., to x_1) at the saddle point $s=0$ (i.e., $x_1=1, x_2=0$). It is easily verified that

$$(\partial^3 V/\partial x_1^3)_{x_1=1,x_2=0}=(\partial^4 V/\partial x_1^4)_{x_1=1,x_2=0}=0,$$

so that Eq. (2.21) becomes

$$A=\frac{g''(0)}{2g(0)}, \tag{3.6}$$

where again differentiation is with respect to the coordinate x_1 and the functions are evaluated at the saddle point. The Bernoulli equation for $g(x_1)$ is

$$g^3+b_0(x_1)g+b(x_1)g'=0. \tag{3.7}$$

In the present case

$$b_0(x_1)=\left(\frac{d^2V}{dx_2^2}\right)_{x_2=0}=\omega^2\left(1-\frac{1}{x_1}\right)-\frac{4}{a^2x_1^2}, \tag{3.8}$$

and

$$b(x_1)=\left(\frac{dV}{dx_1}\right)_{x_2=0}=\omega^2(x_1-1). \tag{3.9}$$

Using Eqs. (3.8) and (3.9) in Eq. (3.7) at $x_1=1$, yields

$$g(0)=\frac{2}{a}. \tag{3.10}$$

To obtain $g''(0)$, we twice differentiate Eq. (3.7), and evaluate the results at the saddle point, to obtain

$$g'(0)=-\frac{2}{a};\quad g''(0)=\frac{4}{a} \tag{3.11}$$

so that [cf. Eq. (3.6)]

$$A=1. \tag{3.12}$$

This is exactly the Larson and Kostin result for their simple model. However, the interpretation of the origin of the correction term is different. We also note that for more general situations, Eq. (2.21) provides the full first order correction term.

To demonstrate that the correction term $A\epsilon/\omega_i^2$ is unrelated to reaction path curvation, we consider an example with a straight line reaction path, which nevertheless has such a correction term. Thus as a second example, we consider the potential

$$\tilde{V}(\tilde{x},\tilde{y})=\frac{V_0}{a^4}(\tilde{y}^2-a^2)^2+\frac{1}{2}m\tilde{\omega}^2\tilde{x}^2(1+\tilde{b}^2\tilde{y}^2)+\frac{V_0}{a^4}\tilde{x}^4. \tag{3.13}$$

This potential is again characterized by two minima, at $\tilde{x}=0;\tilde{y}=\pm a$. Here, however, the saddle point is at the origin $\tilde{x}=0,\tilde{y}=0$ and the minimum energy paths is a straight line connecting the centers of the two wells along the $\tilde{y}$ axis. The frequency $\tilde{\omega}$ here, as in Eq. (3.1), plays the role of a window frequency.

In dimensionless coordinates $[V=(\tilde{V}/V_0), x=\tilde{x}/a, y=\tilde{y}, b=\tilde{b}a]$, and $\omega^2=\omega^2 ma^2/V_0]$, we have

$$V(x,y)=(y^2-1)^2+\tfrac{1}{2}\omega^2x^2(1+b^2y^2)+x^4. \tag{3.14}$$

Repeating the analysis above, we find that $V^3(0)=0$, but $V^4(0)\neq 0$. Thus A is given by

$$A=-\frac{V^{(4)}(0)}{24V^{(2)}(0)}+\frac{g^{(2)}(0)}{2g(0)}, \tag{3.15}$$

where g is a solution of Eq. (3.7), with

$$b_0(x)=-4+\omega^2b^2x^2,$$
$$b(x)=\omega^2x. \tag{3.16}$$

At the saddle point,

$$g=2;\quad g'=0;\quad g''=-\frac{2\omega^2b^2}{\omega^2+4};\quad V^{(2)}=\omega^2;\quad V^{(4)}=24, \tag{3.17}$$

so that

$$A=-\frac{\omega^2b^2}{2(\omega^2+4)}-\frac{1}{\omega^2}. \tag{3.18}$$

Clearly the correction term $A\epsilon/\omega^2$ becomes appreciable for very small ω, even though the reaction path in this example is not curved.

IV. CONCLUSION

For transitions across a potential barrier in the overdamped (diffusion) limit, we have shown that the reaction rate does not depend on the reaction path curvature. Previously obtained corrections to the one-dimensional result that were attributed to the reaction path curvature, have been shown to be associated with anharmonicity of the potential, and to a small window frequency, namely a flat potential surface at the barrier, in the direction perpendicular to the reaction path.

Our result could have been anticipated on intuitive grounds. In the overdamped limit, the system is in thermal equilibrium everywhere but in a vanishingly small region at the saddle point, and the reaction path curvature, which by definition depends on the shape of the reaction path away from the barrier, is not expected to affect the dynamics of the reaction. The situation may be qualitatively different in the underdamped limit, when the reaction is affected and possibly even dominated by the dynamics away from the barrier. Such cases are currently under study.

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APPENDIX

In this Appendix we derive Eq. (2.7) from Eq. (2.6), and Eqs. (2.19) and (2.20) from Eq. (2.13b). First we consider Eq. (2.6):

$$\epsilon(u_{x_1x_1}+u_{x_2x_2})-V_{x_1}u_{x_1}-V_{x_2}u_{x_2}=0 \text{ in } \mathscr{D}_a, \quad (A1)$$

$$u=f \text{ on } \Gamma. \quad (A2)$$

The function $p(x_1,x_2,\xi_1,\xi_2)$, which is Green's function for Eqs. (A1) and (A2), is the probability density function of exit points (ξ_1,ξ_2) on Γ, given the initial state (x_1,x_2) in $\mathscr{D}_a$.[8] To find $p(x_1,x_2,\xi_1,\xi_2)$ we construct an asymptotic solution to Eqs. (A1) and (A2) for $\epsilon \ll 1$, by the method of Matkowsky and Schuss.[7,13,23–26]

The expansion of the solution in $\mathscr{D}_a$, for x_1,x_2 away from Γ, is given by

$$u \sim u^0+\epsilon u^1+\cdots \quad (A3)$$

with u^0 satisfying

$$\frac{du^0}{dt}\equiv -V_{x_1}u^0_{x_1}-V_{x_2}u^0_{x_2}=0. \quad (A4)$$

Here the total derivative in Eq. (A4) is taken along the trajectories

$$\dot{x}_1=-V_{x_1}, \quad \dot{x}_2=-V_{x_2}. \quad (A5)$$

Since all trajectories in $\mathscr{D}_a$ converge to (x_{1a},x_{2a}), we have $u_0=$ const. Thus,

$$\lim_{\epsilon\to 0} u=u_0=\text{const in } \mathscr{D}_a. \quad (A6)$$

To satisfy Eq. (A2), we correct the approximation (A3) by constructing a boundary layer function. The boundary layer equation is obtained by introducing the local variables (ρ,s), where ρ is the distance to Γ and s is arc length on Γ measured from the saddle point S. Stretching the distance ρ by setting

$$\eta=\rho/\sqrt{\epsilon},$$

and expanding the coefficients of Eq. (A1) in powers of $\sqrt{\epsilon}$ (after the change of variables) we obtain to leading order, the equation

$$u_{\eta\eta}-b_0(s)\eta u_\eta+b(s)u_s=0. \quad (A.7)$$

Here $b_0(s)$ is given in Eq. (2.11) and $b(s)=-dV/ds$ is the speed of the motion (A5) on Γ. The boundary conditions for Eq. (A7) are obtained from Eqs. (A2) and (A6) as

$$\lim_{\eta\to 0} u(\eta,s)=f(s), \quad (A8)$$

and

$$\lim_{\eta\to\infty} u(\eta,s)=u_0. \quad (A9)$$

An approximate solution of Eqs. (A7)–(A9) is given by[25]

$$u\sim f(s)+[u_0-f(s)]\sqrt{\frac{2}{\pi}}\int_0^{g(s)\rho/\sqrt{\epsilon}} e^{-s^2/2}\,ds, \quad (A10)$$

where $g(s)$ is given by Eqs. (2.8) and (2.9). To determine the constant u_0 we multiply Eq. (A1) by $e^{-V/\epsilon}$ and integrate over $\mathscr{D}_a$. Using Green's theorem we obtain

$$\int \exp(-V/\epsilon)\frac{\partial u}{\partial n}\,ds=0, \quad (A11)$$

where $\partial u/\partial n$ is the normal derivative of u on Γ. Using Eq. (A10) in Eq. (A11), we obtain

$$u_0\sim\frac{\int_\Gamma \exp(-V/\epsilon)g(s)f(s)ds}{\int_\Gamma \exp(-V/\epsilon)g(s)ds}, \quad (A12)$$

hence Eq. (2.7).

We now consider Eq. (2.13b). To obtain Eqs. (2.19) and (2.20), we note that $\tau\to\infty$ as $\epsilon\to 0$. Therefore, we set

$$\tau=C(\epsilon)q(x_1,x_2) \quad (A13)$$

in Eq. (2.13b), where

$$\max q(x_1,x_2)=1, \quad (A14)$$

and $C(\epsilon)\to\infty$ as $\epsilon\to 0$. Now, for $\epsilon\ll 1$, $q(x_1,x_2)$ satisfies Eq. (A1) with the boundary conditions

$$q=0 \text{ on } \Gamma \text{ [see Eq.(2.13b)]}, \quad (A15)$$

and Eq. (A14). Proceeding as above we obtain

$$q\sim\sqrt{\frac{2}{\pi}}\int_0^{g(s)\rho/\sqrt{\epsilon}} e^{-s^2/2}\,ds, \quad (A16)$$

and employing Green's theorem we obtain

$$C(\epsilon)\sim\frac{\iint_{\mathscr{D}_a}\exp(-V/\epsilon)dx_1\,dx_2}{\int_\Gamma\sqrt{(2\epsilon/\pi)}g(s)\exp(-V/\epsilon)ds}. \quad (A17)$$

Finally, Eqs. (2.19) and (2.20) are derived by asymptotically evaluating the integrals in Eq. (A17).

[1]H. A. Kramers, Physica (Utrecht) 7, 284 (1940).
[2]H. C. Brinkman, Physics 22, 149 (1956).
[3]G. H. Vineyard, J. Phys. Chem. Solids 3, 121 (1957).
[4]R. Landauer and J. A. Swanson, Phys. Rev. 121, 1668 (1961).
[5]H. R. Glyde, Rev. Mod. Phys. 39, 373 (1967).
[6]J. S. Langer, Phys. Rev. Lett. 21, 973 (1968); Ann Phys. (N.Y.)54, 258 (1969).
[7]Z. Schuss and B. J. Matkowsky, SIAM J. Appl. Math. 35, 604 (1979).
[8]Z. Schuss, *Theory and Application of Stochastic Differential Equations* (Wiley, New York, 1980).
[9]B. J. Matkowsky and Z. Schuss, SIAM J. Appl. Math. 40, 242 (1981).
[10]R. F. Grote and J. T. Hynes, J. Chem. Phys. 74, 4465 (1981); 75, 2191 (1981).
[11]B. J. Matkowsky, Z. Schuss, and E. Ben-Jacob, SIAM J. Appl. Math. 42, 835 (1982).
[12]G. van der Zwan and J. T. Hynes, J. Chem. Phys. 77, 1295 (1982).
[13]B. J. Matkowsky, Z. Schuss, and C. Tier, J. Stat. Phys. 35, 443 (1984).
[14]A. Nitzan, J. Chem. Phys. 82, 1614 (1985); 86, 2734 (1987).
[15]A. G. Zawadzki and J. T. Hynes, Chem. Phys. Lett. 113, 476 (1985).
[16]M. Borkovec and B. J. Berne, J. Chem. Phys. 82, 794 (1985).
[17]R. S. Larson and D. Kostin, J. Chem. Phys. 77, 5017 (1982).
[18]R. S. Larson, Physica A 137, 295 (1986).
[19]M. Berkowitz, J. D. Morgan, and J. A. McCammon, J. Chem. Phys. 79, 5563 (1983).
[20]W. H. Miller, N. C. Handy, and J. E. Adams, J. Chem. Phys. 72, 99 (1980).

[21]N. Agmon and J. J. Hopfield, J. Chem. Phys. **78**, 6947 (1983); **79**, 2042 (1983).
[22]We remark that the *physical* characteristics of the problem are determined by the *given* potential surface. We are interested in *physical situations* where ΔV_a is large, while a barrier frequency (in a direction different from the reaction coordinate) is small. This leads us to consider the *mathematical scaling* described here, according to which the scaled energies and frequencies are $O(1)$, except for the scaled inverse barrier height ϵ, and the scaled "window" frequency ω_t.
[23]B. J. Matkowsky and Z. Schuss, SIAM J. Appl. Math. **33**, 365 (1977).
[24]B. J. Matkowsky and Z. Schuss, Phys. Lett. A **95**, 213 (1983).
[25]B. J. Matkowsky and Z. Schuss, SIAM J. Appl. Math. **42**, 822 (1982).
[26]B. J. Matkowsky, Z. Schuss, and C. Tier, SIAM J. Appl. Math. **43**, 673 (1983).
[27]B. Z. Bobrovsky and Z. Schuss, SIAM J. Appl. Math. **42**, 174 (1982).
[28]C. M. Bender and S. M. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* (McGraw-Hill, New York, 1978).