

## Variational Transition-State Theory for Reaction Rates in Dissipative Systems

Eli Pollak,<sup>(a)</sup> Susan C. Tucker, and Bruce J. Berne

*Department of Chemistry, Columbia University, New York, New York 10027*

(Received 23 October 1989)

Variational upper bounds are derived for the escape rate of a particle trapped in a metastable well and interacting with a dissipative medium. The theory leads to a reduced two-degrees-of-freedom Hamiltonian involving the unstable normal mode and a newly defined collective bath mode. Explicit treatment of strong nonlinearities or low-barrier systems presents no special problem.

PACS numbers: 05.40.+j, 34.10.+x, 51.10.+y, 82.20.-w

The theory of activated rate processes in condensed media arises in connection with a large variety of phenomena<sup>1</sup> extending from tunneling in Josephson junctions<sup>2</sup> to liquid-state chemical reactions<sup>3,4</sup> to electron-transfer processes.<sup>5</sup> Kramers<sup>6</sup> considered the case of a particle, moving on a bistable or metastable potential-energy surface, subjected to both frictional (dissipative) and random forces exerted on it by a heat bath. He solved the problem in both the high-friction regime, where the escape rate is limited by spatial diffusion, and in the weak-damping limit, where the rate is dominated by energy diffusion. In both cases, he considered only the parabolic approximation to the potential at the stationary points. Much effort has been devoted to extending Kramers's solution.<sup>7</sup> In the limit of large friction, where one can neglect inertial forces, the problem simplifies to a one-dimensional Fokker-Planck equation which may be solved for its lowest (nonzero) eigenvalue.<sup>8</sup> In this limit, variational approaches have been developed which provide upper bounds for the escape rate.<sup>9</sup> However, in other friction regimes such (nontrivial) bounding properties have not been derived.

Implicit in the Kramers model is the assumption of a large separation of time scales between particle and bath dynamics. It is now widely appreciated that this separation is often invalid, so that the original Kramers problem must be generalized to include memory friction.<sup>3,7</sup> Attempts to solve this more difficult problem are based on an estimate of the mean first passage time<sup>1,7,10</sup> or, perhaps more frequently, a methodology in which the true potential governing the motion of the particle is replaced by a parabolic barrier.<sup>3</sup> In the latter case, the generalized Langevin equation<sup>3,4,7</sup> (GLE) which includes memory friction can be solved exactly. Both approaches have serious deficiencies (see Ref. 7), although they do give the exact solution under restrictive conditions such as high-barrier potentials and strong damping. There is no universal statement as to whether Kramers's original result and existing generalizations to include memory friction are upper bounds or just estimates, valid only in the high-barrier, large-friction limit.

The purpose of this Letter is to report a new approach which provides rigorous variational upper bounds to the classical escape rate for arbitrary potential functions and arbitrary memory friction. The theory includes the full nonlinearity of the potential and is not limited to high-barrier problems. This approach allows us to show that

there is a large class of potential functions for which the parabolic-barrier-based approximation<sup>3</sup> yields a larger estimate for the rate than does the new theory. For this class of systems we have thus proved that the parabolic estimate is indeed an upper bound, yet a specific example demonstrates that it may be significantly higher than the upper bound given by the new theory.

The methodology used in this new approach is based on classical transition-state theory.<sup>7,11</sup> A key element of the theory is the identification of a dividing surface in configuration space—the transition state—which has the property that any reactive trajectory must cross it at least once. The classical flux across this surface in a given direction gives a rigorous upper bound to the reaction probability.<sup>12</sup> Since trajectories may recross the dividing surface, one is at most overcounting the reactive flux. Classical variational transition-state theory (VTST) results from this upper bound property.<sup>13</sup> By varying the dividing surface one finds the transition state which leads to the lowest upper bound. Except for some recent developments,<sup>14,15</sup> the theory has been restricted to systems with a finite number of degrees of freedom. In this Letter we show that VTST can be extended to the continuum limit, where it leads to an interesting new result: Many of the effects of dissipation may be understood from the dynamics of an effective two-degrees-of-freedom nonlinear Hamiltonian where one coordinate is a generalized reaction coordinate and the other is a collective bath mode. This Hamiltonian is well defined in the continuum limit and is a function of both the original potential and the memory friction.

The theory is developed for the GLE extension of Kramers's problem<sup>6,7</sup> for a particle with mass  $m$  and coordinate  $q$ :

$$m\ddot{q} + \frac{dV(q)}{dq} + m \int_0^t d\tau \gamma(t-\tau)\dot{q}(\tau) = \xi(t). \quad (1)$$

The Gaussian random force  $\xi(t)$  is related to the friction kernel  $\gamma(t)$  (with  $\beta = 1/k_B T$ ) through the second fluctuation-dissipation theorem:  $\langle \xi(t)\xi(0) \rangle = (m/\beta)\gamma(t)$ . The system potential  $V(q)$  has a barrier height  $V^\ddagger$  and is assumed to have a well at  $-q_0$  such that  $V(q) \approx \frac{1}{2}m\omega_0^2 \times (q+q_0)^2 - V^\ddagger$ . To elucidate the role of the anharmonicity in the potential we write it without loss of generality in the form

$$V(q) = -\frac{1}{2}m\omega^{\ddagger 2}q^2 + V_1(q), \quad (2)$$

such that  $V_1(0)=0$ . When the coupling to the bath is turned off [ $\gamma(t)=0$ ] the canonical escape rate from the well is<sup>7,16</sup>  $\Gamma_0=(\omega_0/2\pi)\exp(-\beta V^\ddagger)$ . The equilibrium rate in the presence of friction, within the parabolic-barrier approximation, is<sup>17</sup>

$$\Gamma=(\lambda^\ddagger/\omega^\ddagger)\Gamma_0. \quad (3)$$

The reactive frequency of Grote and Hynes,<sup>17</sup>  $\lambda^\ddagger$ , is the solution of the equation

$$\lambda^\ddagger=\omega^\ddagger/[1+\hat{\gamma}(\lambda^\ddagger)/\lambda^\ddagger], \quad (4)$$

where  $\hat{\gamma}(s)$  denotes the Laplace transform of the friction kernel  $\gamma(t)$ . Equation (3) is a well-known generalization of the Kramers spatial diffusion limit<sup>6</sup> to include memory effects. It is a steepest-descent estimate, expected to be valid and relevant for moderate to strong damping and for large barriers ( $\beta V^\ddagger \gg 1$ ), but it has not previously been shown to have any rigorous bounding property.

Instead of trying to deal directly with the GLE, we study the dynamics of the equivalent Hamiltonian<sup>18</sup>

$$H=p_q^2/2m+V(q)+\sum_j \frac{1}{2} [p_{x_j}^2/m_j+m_j(\omega_j x_j-C_j q/m_j \omega_j)^2], \quad (5)$$

where the system coordinate  $q$  is coupled linearly to a bath of harmonic oscillators with coordinates  $x_j$ , masses  $m_j$ , and frequencies  $\omega_j$ . By solving explicitly for the time dependence of each of the bath coordinates, it is found<sup>7,18</sup> that Hamilton's equation of motion for the system coordinate  $q$  reduces to the GLE [Eq. (1)], with the identification that  $\gamma(t)=\sum_j (C_j^2/mm_j \omega_j^2)\cos(\omega_j t)$ . If

one now ignores the anharmonicity in the potential, then the Hamiltonian in Eq. (5) is quadratic and may be diagonalized using a normal-mode transformation.<sup>15</sup> The normal modes are characterized by one unstable mode  $\rho$  associated with the negative eigenvalue  $-\lambda^\ddagger$  and by stable modes  $y_j$  with associated frequencies  $\lambda_j$ . The unstable mode frequency  $\lambda^\ddagger$  is identical to the reactive frequency given by Eq. (4). Identifying  $\rho=0$  as the dividing surface, and evaluating the equilibrium flux through the surface, leads to Eq. (3), demonstrating that the Grote-Hynes results is the continuum limit of *harmonic* transition-state theory.<sup>14,15</sup>

To derive a VTST which has a (nontrivial) bounding property for the reactive flux and includes the full anharmonicity of  $V(q)$  we rewrite the Hamiltonian in terms of the normal modes (of the saddle point),

$$H=\frac{1}{2} \left[ p_\rho^2 - \lambda^\ddagger \rho^2 + \sum_j (p_{y_j}^2 + \lambda_j^2 y_j^2) \right] + V_1 \left[ m^{1/2} \left[ u_{00} \rho + \sum_j u_{j0} y_j \right] \right], \quad (6)$$

where the  $u_{j0}$ 's are elements of the orthogonal normal-mode transformation such that  $\sqrt{m}q=u_{00}\rho+\sum_j u_{j0}y_j$ . In the continuum limit the matrix element  $u_{00}$  can also be determined through the Laplace transform of the friction kernel,<sup>19</sup>

$$u_{00}^2=\{1+\frac{1}{2}[\hat{\gamma}(\lambda^\ddagger)/\lambda^\ddagger+\partial\hat{\gamma}(s)/\partial s|_{s=\lambda^\ddagger}]\}^{-1}. \quad (7)$$

The canonical equilibrium flux through a dividing surface,<sup>7,11</sup> characterized without loss of generality as  $\rho=f(\mathbf{y})$ , is proportional to the integral  $F$  defined as

$$F=\int_{-\infty}^{\infty} \prod_j dp_{y_j} dy_j dp_\rho d\rho (\mathbf{p}\cdot\mathbf{n}_s)\theta(\mathbf{p}\cdot\mathbf{n}_s)\delta(\rho-f(\mathbf{y})) \left[ 1+\sum_j \left( \frac{\partial f}{\partial y_j} \right)^2 \right]^{1/2} \exp(-\beta H), \quad (8)$$

where  $\mathbf{n}_s$  is the unit normal to the surface and  $\mathbf{p}\cdot\mathbf{n}_s$  is the component of the multidimensional momentum normal to the surface. The unit-step function  $\theta(\mathbf{p}\cdot\mathbf{n}_s)$  assures that one is evaluating the flux in the direction from the metastable state to the products. The Dirac  $\delta$  function limits the integration to the dividing surface. When  $V_1(q)=0$  and the dividing surface is chosen as  $\rho=0$ , the flux integral reduces to  $F_H=(1/\beta)\prod_j (2\pi/\beta\lambda_j)$ . For a general dividing surface, retaining the anharmonicity, the VTST estimate for the rate constant is<sup>20</sup>  $\Gamma_{\text{VTST}}=(\lambda^\ddagger/\omega^\ddagger)(F/F_H)\Gamma_0$ . Thus, it suffices to study the ratio  $P=F/F_H$ .

The anharmonicity  $V_1$  couples *all* normal modes in a nontrivial fashion. Interestingly, we note that the anharmonicity may be thought of as a function of only two variables. These are the unstable mode  $\rho$  and a collective bath mode  $\sigma$  which we define as

$$\sigma=(1-u_{00}^2)^{-1/2}\sum_j u_{j0}y_j \equiv (1/u_1)\sum_j u_{j0}y_j. \quad (9)$$

With this in mind, we insert the identity

$$1=\int_{-\infty}^{\infty} d\sigma \int_{-\infty}^{\infty} dp_\sigma \delta\left(\sigma-(1/u_1)\sum_j u_{j0}y_j\right)\delta\left(p_\sigma-(1/u_1)\sum_j u_{j0}p_{y_j}\right) \quad (10)$$

into the flux integral  $F$  [Eq. (8)].

We now introduce the *only* restrictive assumption of the proposed theory. The dividing surface is taken to be a function of the unstable mode  $\rho$  and the collective bath mode  $\sigma$  only, so that  $\rho=f(\sigma)$ . As a result the unit vector normal to the surface,  $\mathbf{n}_s$ , is

$$\mathbf{n}_s=\left[-\hat{\rho}+(df/d\sigma)\sum_j (u_{j0}/u_1)\hat{y}_j\right]/\left[1+(df/d\sigma)^2\right]^{1/2}, \quad (11)$$

where  $\hat{\rho}, \hat{y}_j$  are unit vectors in the direction of the normal modes and use was made of the identity  $\sum_j u_{j0}^2 = 1 - u_{00}^2$ . It follows that

$$\mathbf{p} \cdot \mathbf{n}_s = [-p_\rho + (df/d\sigma)p_\sigma]/[1 + (df/d\sigma)^2]^{1/2}$$

and is a function *only* of  $p_\rho, p_\sigma$ , and  $\sigma$ . It is therefore possible after changing the order of integration in the expanded flux integral to integrate without loss of generality over the variables  $y_1, p_{y_1}$  of one of the stable modes. One finds that

$$F = \int d\rho dp_\rho d\sigma dp_\sigma (\mathbf{p} \cdot \mathbf{n}_s) \theta(\mathbf{p} \cdot \mathbf{n}_s) \delta(\rho - f(\sigma)) \left[ 1 + \left( \frac{df}{d\sigma} \right)^2 \right]^{1/2} \exp \left[ -\beta \left( \frac{p_\rho^2 - \lambda^{\ddagger 2} p_\sigma^2}{2} + V_1 \right) \right] \frac{u_1^2}{u_{f0}^2} Z_{\rho\sigma}, \quad (12)$$

$$Z_{\rho\sigma} = \int \prod' dy_j dp_{y_j} \exp \left[ -\frac{\beta}{2} \left[ \sum' (p_{y_j}^2 + \lambda_j^2 y_j^2) + \frac{(u_1 p_\sigma - \sum' u_{j0} p_{y_j})^2 + \lambda_1^2 (u_1 \sigma - \sum' u_{j0} y_j)^2}{u_{f0}^2} \right] \right], \quad (13)$$

where the prime denotes a product or sum over all stable modes  $j$ , except for  $j=1$ . Diagonalizing the exponent in Eq. (13) at fixed  $\sigma, \rho$  and integrating leads to the central result of this Letter:

$$P = [\beta^2 \Omega / 2\pi] \int dp_\rho dp_\sigma d\rho d\sigma (\mathbf{p} \cdot \mathbf{n}_s) \theta(\mathbf{p} \cdot \mathbf{n}_s) \delta(\rho - f(\sigma)) \left[ 1 + \left( \frac{df}{d\sigma} \right)^2 \right]^{1/2} \exp(-\beta H^\ddagger), \quad (14)$$

$$H^\ddagger = p_\rho^2/2 + p_\sigma^2/2 - \lambda^{\ddagger 2} p_\sigma^2/2 + \Omega^2 \sigma^2/2 + V_1(\rho, \sigma). \quad (15)$$

The averaged bath frequency  $\Omega$  is found to be

$$\Omega^2 = u_1^2 / \sum_j (u_{j0}^2 / \lambda_j^2) = u_1^2 / (u_{00}^2 / \lambda^{\ddagger 2} - 1 / \omega^{\ddagger 2}). \quad (16)$$

The last equality on the right-hand side follows from properties of the normal-mode transformation; cf. Ref. 19.

This result shows that VTST for dissipative systems is identical to minimizing the transition-state flux for the effective two-degrees-of-freedom Hamiltonian  $H^\ddagger$ , which is well defined in the continuum limit for arbitrary friction kernels  $\gamma(t)$  [see Eqs. (4), (7), and (16)]. The effective Hamiltonian includes the full anharmonicity of the system potential and, within the  $(\rho, \sigma)$  configuration space, there is no restriction on the dividing surface. As shown by Pechukas,<sup>11</sup> the formal solution for the minimum flux dividing surface for two-degrees-of-freedom Hamiltonians is a periodic-orbit dividing surface (known as a pods). The classical action of the periodic orbit is the variational upper bound to the microcanonical flux and the canonical variational flux is obtained from the optimized microcanonical flux by canonical averaging. This formal solution can be readily applied (numerically) to Eqs. (14) and (15).

To demonstrate the practical utility of Eqs. (14) and (15) we will consider the simple dividing surface  $\rho=0$  which, although not fully optimized, allows for analytic results. In this case  $P$  is

$$P(\rho=0) = (\beta \Omega^2 / 2\pi)^{1/2} \times \int_{-\infty}^{\infty} d\sigma \exp \{ -\beta [\Omega^2 \sigma^2 / 2 + V_1(m^{1/2} u_1 \sigma)] \}. \quad (17)$$

If  $V_1(q)$  is positive definite, then  $P \leq 1$ . This means that for the general class of system potentials whose anharmonicity as defined in Eq. (2) is positive definite the har-

monic estimate [Eq. (3)] is in fact an upper bound to the classical equilibrium rate. In the weak-damping limit the collective bath frequency  $\Omega$  will be of the order of the bare barrier frequency while  $u_1$  will be very small (proportional to the square root of the damping constant), justifying a steepest-descent estimate of the integral. However, in the strong-damping limit, the frequency  $\Omega$  may become small, leading to noticeable deviations from the harmonic estimate. In addition, the integral in Eq. (17) is easily evaluated for *any* barrier height. The present VTST will thus give a meaningful upper bound even when  $\beta V^\ddagger$  is of the order of 1.

As a concrete example for the present theory we consider a symmetric quartic potential (mass  $m=1$ )  $V(q) = -\omega^{\ddagger 2} q^2/2 + (\alpha/4)q^4$ . The integration in Eq. (17) then yields

$$P(\rho=0) = (V_x/\pi)^{1/2} \exp(V_x/2) K_{1/4}(V_x/2), \quad (18)$$

$$V_x = \beta V^\ddagger / (x-1)^2,$$

where  $x = u_{00}^2 \omega^{\ddagger 2} / \lambda^{\ddagger 2}$  and  $K_{1/4}$  is a modified Bessel function of the second kind. The result for  $P$  is a monotonic function of  $V_x$ , which goes as  $1 - 3/16V_x$  for  $V_x \gg 1$  and as  $(2\pi)^{-1/2} \Gamma(\frac{1}{4}) V_x^{1/4}$  for  $V_x \ll 1$ . For Ohmic dissipation,<sup>2,7</sup>  $\gamma(t) = 2\gamma\delta(t)$ , one finds that  $x-1 = \gamma / (4\omega^{\ddagger 2} + \gamma^2)^{1/2}$ . In this case, corrections to the harmonic estimate will be small for any value of the damping constant unless the barrier height is very small. However, for memory friction, one may find that  $x-1 \gg 1$ . Specifically, if we choose an exponential friction<sup>4</sup>  $\gamma(t) = \omega^\ddagger \exp(-\omega^\ddagger t / \gamma^*)$ , we find that for strong damping  $x \sim \frac{2}{3} \gamma^{*2/3}$ . This leads to  $P \sim \gamma^{*-1/3}$ , so that even if  $\beta V^\ddagger \gg 1$ , the actual upper bound to the reactive flux will be substantially smaller than that predicted by the harmonic estimate.

The result that the reactive flux may be evaluated

from an effective two-degrees-of-freedom Hamiltonian suggests that the dynamics of this Hamiltonian might have a significance extending beyond the derivation of variational bounds for the rate. One may write the *exact* equation of motion (with  $m=1$ ) from the full Hamiltonian [Eq. (6)] for the  $j$ th bath oscillator as  $\ddot{y}_j + \lambda_j^2 y_j = -u_{j0} dV_1(q)/dq$ , where as noted above  $q = u_{00}\rho + u_1\sigma$ . This is the equation of motion of a forced harmonic oscillator whose formal solution is well known.<sup>19</sup> Using the definition of the collective bath mode [Eq. (9)] one finds after integration by parts and rearrangement of the following *exact* equation of motion:

$$\ddot{\sigma} + \Omega^2 \sigma + u_1 \frac{dV_1}{dq} + u_1 \int_0^t d\tau H(t-\tau) \frac{d^2 V_1(q(\tau))}{dq^2} \dot{q}(\tau) = \zeta(t). \quad (19)$$

Here, the effective memory function

$$H(t) = \sum_j \frac{u_{j0}^2}{u_1^2} \left[ 1 - \frac{\Omega^2}{\lambda_j^2} \cos(\lambda_j t) \right]$$

may be expressed in the continuum limit solely in terms of the Laplace transform of the time-dependent friction (cf. Ref. 19). The “noise function”  $\zeta(t)$  is dependent on initial conditions of the stable modes and is thus a Gaussian random force. From the full Hamiltonian [Eq. (6)] one also finds the exact equation of motion for the reaction coordinate,<sup>19,21</sup>  $\ddot{\rho} - \lambda^{\ddagger 2} \rho = -u_{00} dV_1/dq$ . Together with Eq. (19), these equations of motion are identical to the original GLE, Eq. (1). If one ignores the memory term and random force in Eq. (19), then these two equations are just Newton’s equations for the dynamics of a system governed by  $H^\ddagger$ . Since in many cases  $u_1$  and the effective memory function  $H(t)$  will be small, this opens the possibility of a new perturbation theory for dissipative systems. In contrast to previous results,<sup>19,21</sup> this approach has as a zero-order solution the dynamics of a nonlinearly coupled two-degrees-of-freedom system.

The derivation of  $H^\ddagger$  is based on coordinate transformations; hence its applicability is not limited to classical mechanics. Because it is not difficult to obtain numerical solutions for the decay rates of this generic type of Hamiltonian, understanding the effect of dissipative media on quantum systems can be transformed to the problem of understanding the relation between the quantum resonance states of  $H^\ddagger$  and the full dissipative dynamics. This problem should present an interesting challenge.

In summary, we have shown that VTST can be extended to dissipative systems described by a GLE. The variational upper bound to the barrier crossing rate constant can be formulated in terms of an effective two-degrees-of-freedom dynamical system. This approach allows full inclusion of strong anharmonicities and under physically realizable circumstances can lead to large

corrections to current theories. It is not difficult to apply this approach to systems with cusped or quartic barriers, and the method is generalizable to two or more degrees of freedom coupled to a dissipative bath. The major outstanding problem not addressed here is the case where the dissipative bath is not harmonic.

We thank Professor H. Grabert and Professor P. Hänggi for stimulating discussions. This work has been supported by grants from the NSF and the U.S.-Israel Binational Science Foundation.

<sup>(a)</sup>Permanent address: Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel.

<sup>1</sup>N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981); H. Risken, *The Fokker Planck Equation*, Springer Series in Synergetics Vol. 18 (Springer-Verlag, Berlin, 1984).

<sup>2</sup>A. O. Caldeira and A. J. Leggett, *Phys. Rev. Lett.* **46**, 211 (1981); *Ann. Phys. (N.Y.)* **149**, 374 (1983); H. Grabert, in *SQUID 85*, edited by H. D. Hahlbohm and H. Lübbig (de Gruyter, Berlin, 1985).

<sup>3</sup>J. T. Hynes, in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC, Boca Raton, FL, 1985), Vol. 4, p. 171ff.

<sup>4</sup>B. J. Berne, M. Borkovec, and J. E. Straub, *J. Phys. Chem.* **92**, 3711 (1988).

<sup>5</sup>R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **811**, 265 (1985).

<sup>6</sup>H. A. Kramers, *Physica (Utrecht)* **7**, 284 (1940).

<sup>7</sup>For a recent excellent review, see P. Hänggi, P. Talkner, and M. Borkovec, *Rev. Mod. Phys.* **62**, 251 (1990).

<sup>8</sup>N. G. Van Kampen, *J. Stat. Phys.* **17**, 71 (1977).

<sup>9</sup>M. Bernstein and L. S. Brown, *Phys. Rev. Lett.* **52**, 1933 (1984).

<sup>10</sup>B. J. Matkowsky, Z. Schuss, and C. Tier, *J. Stat. Phys.* **35**, 443 (1984).

<sup>11</sup>P. Pechukas, in *Dynamics of Molecular Collisions, Part B*, edited by W. H. Miller (Plenum, New York, 1976), Chap. 6.

<sup>12</sup>E. P. Wigner, *Trans. Faraday Soc.* **34**, 29 (1938); J. C. Keck, *Adv. Chem. Phys.* **13**, 85 (1967).

<sup>13</sup>D. G. Truhlar and B. C. Garrett, *Annu. Rev. Phys. Chem.* **35**, 159 (1984); E. Pollak, in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC, Boca Raton, FL, 1985), Vol. 3, p. 123ff.

<sup>14</sup>Yu. Dakhnovskii and A. A. Ovchinnikov, *Phys. Lett.* **113A**, 147 (1985).

<sup>15</sup>E. Pollak, *J. Chem. Phys.* **85**, 865 (1986).

<sup>16</sup>We are assuming that the partition function of reactants is given accurately by its harmonic estimate.

<sup>17</sup>R. F. Grote and J. T. Hynes, *J. Chem. Phys.* **73**, 2715 (1980); P. Hänggi and F. Mojtabai, *Phys. Rev. A* **26**, 1168 (1982).

<sup>18</sup>R. Zwanzig, *J. Stat. Phys.* **9**, 215 (1973).

<sup>19</sup>E. Pollak, H. Grabert, and P. Hänggi, *J. Chem. Phys.* **91**, 4073 (1989).

<sup>20</sup>In principle, one should also include anharmonic corrections for the reactants partition function, which may be obtained using similar methods. These are ignored in this Letter which deals only with the reactive flux.

<sup>21</sup>H. Grabert, *Phys. Rev. Lett.* **61**, 1683 (1988).