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

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Upper bounds for the classical escape rate of a particle trapped in a metastable well and interacting with a dissipative medium are derived based on the periodic orbits of a reduced two-degree-of-freedom Hamiltonian involving the unstable normal mode and a collective bath mode. It is shown that even in what is usually thought of as the spatial diffusion limit the reactive flux can involve an energy diffusion term due to energy transfer from the dissipative media, in addition to the standard spatial diffusion term.

KEY WORDS: Escape rate; transition-state theory; Langevin equation; Kramers theory.

1. INTRODUCTION

There has been a recent push to understand reaction processes in solutions and in solids at the microscopic level.(1–3) Such processes are generally classified by the strength of interaction between the system reactive mode and the dissipative medium. As first detailed by Kramers,(4) in the weak coupling limit the reaction rate is energy-diffusion-controlled, whereas in the strong coupling limit the reaction rate is controlled by spatial diffusion. Kramers' pioneering approach, however, is not general. His solution, as well as subsequent beautiful formal developments such as that of Mel'nikov and Meshkov(5) (for a recent review see ref. 1), rely heavily on the Langevin equation of motion, recast in terms of a Fokker–Planck equation.(6) Such theories have two major limitations. First, it is clear

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today that memory effects are important,(7–13) and one should replace the Langevin equation by a generalized Langevin equation (GLE) which includes memory effects. However, a two-dimensional Fokker–Planck equation cannot be derived in general from the GLE, necessitating a new and different approach to the problem. Second, it is well understood that even a GLE is not sufficiently general. A GLE implies that the dissipative bath is harmonic and that the system bath interaction is bilinear.(14–16) A realistic liquid is not harmonic and so the true validity of the Kramers-based approach when dealing with reactions in liquids is unclear.

An alternative theoretical approach is based on (classical) transition state theory(17, 18) whose formal development has reached maturity during the past three decades.(1, 2, 19–28) Originally, application of the theory was limited to isolated reactive processes such as bimolecular collisions or unimolecular dissociations. The rigorous applicability of transition-state theory to reactions in condensed phases was first demonstrated by Chandler,(29) who showed that the conventional (canonical) multidimensional transition-state-theory expression for a reaction in a dissipative medium can be written in the form of a one-dimensional transition-state-theory expression. In this one-dimensional expression the barrier height of the potential along the system coordinate is replaced by the barrier height of the potential of mean force (free energy of activation) along the same coordinate.(29) The potential of mean force is a well-defined object even when the system–bath and/or the bath–bath interactions are highly nonlinear. The only restriction imposed by using Chandler's one-dimensional expression is to limit the choice of dividing surface to one-dimensional functions of the system coordinate. Since the accuracy of transition-state-theory rate constants depends critically on the choice of dividing surface, such a severe constraint can lead in some cases to gross overestimates of the rate.(28)

Chandler's original result has recently been extended by replacing the potential of mean force with a free energy of activation surface in more than one, say n, dimensions.(30) The resulting expression is then an n-degree-of-freedom transition-state-theory rate expression in which the dividing surface may be written as a function of these n dimensions, rather than as a function of just the one-dimensional system coordinate. Such free energy surfaces have been utilized in different contexts, including studies of reactive dynamics in solution.(31–34) For a GLE, because of the harmonic nature of the bath and the system–bath interaction, it is possible to obtain an analytic expression for such a free energy surface.(30–32) The canonical variational transition-state-theory (CVTST) rate expression for dissipative systems described by GLEs which is given in refs. 31 and 32 is a specific case of such a two-degree-of-freedom variational transition-state-theory rate expression, and it involves a two-dimensional free energy of activation surface. This two-degree-of-freedom CVTST expression is equivalent to canonical variational transition-state theory of the full dissipative problem under the restriction that the dividing surface is a function of only two coordinates. In the CVTST method these two coordinates are specifically a collective reaction coordinate and a collective bath mode, as defined in Section 2. Additional restriction of the dividing surface to be linear allows one to demonstrate how this method leads to the well-known spatial diffusion-limited rate expression as obtained by Kramers, Grote–Hynes, and others.(4,35–37) The CVTST rate expression is more powerful than previous methods, since it allows an easy extension of theory beyond the steepest descent approximation which is inherent to the Kramers approach. (It should be stressed that several authors have estimated corrections to the steepest descent result(38–42) using other methods.)

The effective two-degree-of-freedom Hamiltonian of the CVTST method, which is made up simply of the two-dimensional free energy of activation surface plus a two-dimensional kinetic energy term, can be thought of as providing a first-order approximation to the dynamics of the full problem (see the associated equations of motion(31)). It is therefore tantalizing to understand how far one can go by considering only the dynamics of such an effective Hamiltonian, ignoring the rest of the bath. For an isolated Hamiltonian, a better estimate of the canonical rate constant than the CVTST result can be found by optimizing the dividing surface at each total energy instead of at each temperature.(24,43) In this case, the reactive flux is calculated as a function of total energy and Boltzmann-averaged to yield a canonical (temperature-dependent) result. This procedure is called microcanonical variational transition-state theory (μVTST). The μVTST rate constant at a fixed temperature must be less than or equal to the CVTST result, and hence, by the bounding properties of transition-state theory,(22,24,43) it will be a better result. In fact, for an isolated two-degree-of-freedom Hamiltonian it can be shown that, in some cases, μVTST gives the exact result.(44) Implementation of μVTST for this "size" Hamiltonian is particularly straightforward, as it is known analytically that the optimized fixed energy dividing surfaces are given by classical periodic orbits, i.e., pods (periodic orbit dividing surfaces),(24,26,43,44) which are relatively simple to find numerically. Thus, for the dissipative system, in the first approximation where only the effective two-degree-of-freedom Hamiltonian is considered, the μVTST result (using the pods) gives a better estimate of the rate constant than does the CVTST result.

However, the effective two-degree-of-freedom Hamiltonian is not the full problem. While the CVTST result for the reduced dimensionality problem is equivalent to that for the full problem, this is not true for the microcanonical result. The purpose of this paper is to explore the validity of an approximation to the rate based on the pods of the effective two-degree-of-freedom Hamiltonian. Although the analysis in this paper is restricted specifically to dynamical systems described by GLEs, the structure of the theory will be the same for anharmonic systems, allowing the methodology used here to be generalized. For this purpose, we derive a μVTST expression which is based on the effective two-degree-of-freedom Hamiltonian (or, equivalently, on the two-degree-of-freedom free energy of activation surface), but which is exactly derivable from the multidimensional μVTST expression for the full problem. By using an exactly derivable expression, one preserves the bounding properties of transition-state theory, so that, as in CVTST, an upper bound to the rate constant for the full problem can be found by solving the reduced dimensionality problem.

One of the new physical aspects of the derived μVTST expression is the emergence of an energy diffusion term which is important in what is usually thought of as the spatial diffusion limit. Even though in this limit the reactants are in thermal equilibrium, the energy diffusion mechanism is important because energy transfer from the dissipative medium to the effective two-degree-of-freedom Hamiltonian can cause crossing of the transition-state dividing surface. This energy diffusion mechanism is most prevalent at very strong system–bath coupling strengths, that is, in the Kramers "spatial diffusion regime." This energy diffusion-induced crossing of the transition-state dividing surface should not be confused with the Kramers "energy diffusion regime," which occurs at very weak system–bath coupling strengths, when energy transfer is limited. In the Kramers "energy diffusion regime," population of reactant states with energies greater than the barrier height is the rate-limiting step, and hence the reaction in this regime is energy-diffusion-controlled. In this regime transition-state theories will overestimate the true rate. In contrast, the energy transfer from the dissipative medium to the reduced dimensionality Hamiltonian in the μVTST formalism is a mechanism for crossing an (energy-dependent) transition-state dividing surface. It is particularly important in the limit of strong coupling, where energy transfer is large.

In Section 2 the canonical theory is reviewed, setting the stage for Section 3, in which the microcanonical theory (μVTST) is derived. The underlying physics and other consequences of this derivation are discussed in Section 4.

2. REVIEW OF CVTST

In order to derive the dissipative CVTST, we started with a model Hamiltonian from which a generalized Langevin equation—

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

where q is the reactive system coordinate with mass m and potential $V(q)$, $\gamma(t)$ is the friction kernel, and $\xi(t)$ is the Gaussian random force—can be derived without invoking linear response theory (and all associated assumptions).$^{(14,15,45,46)}$ This Hamiltonian is$^{(14,15)}$

$$H = \frac{p_q^2}{2m} + V(q) + \sum_j \frac{1}{2}\left[\frac{p_{x_j}^2}{m_j} + m_j\left(\omega_j x_j - \frac{c_j q}{m_j \omega_j}\right)^2\right] \tag{2}$$

where q is coupled linearly to a bath of harmonic oscillators with coordinates x_j, masses m_j, and frequencies ω_j. Performing a normal coordinate transformation on H at the saddle point[4] allows one to write

$$H = \frac{1}{2}\left[p_\rho^2 - \lambda^{\ddagger 2}\rho^2 + \sum_j (p_{y_j}^2 + \lambda_j^2 y_j^2)\right] + V_1\left(m^{-1/2}\left[u_{00}\rho + \sum_j u_{j0}\, y_j\right]\right) \tag{3}$$

where the reaction coordinate ρ is associated with the unstable mode of frequency $\lambda^\ddagger$, $\{y_j\}$ are the remaining normal coordinates with associated stable frequencies $\{\lambda_j\}$, and the u_{j0} are elements of the orthogonal normal mode transformation such that $\sqrt{m}q = u_{00}\rho + \sum_j u_{j0}\, y_j$. Note that the unstable mode frequency and the transformation coefficients depend upon the system–bath coupling coefficients and, in the limit that the number of bath modes goes to infinity, can be written as functions of the friction kernel $\gamma(t)$.$^{(31)}$ The anharmonic part of the system potential, V_1, is defined by

$$V_1(q) = V(q) + \tfrac{1}{2} m\omega^{\ddagger 2} q^2 \tag{4}$$

where $\omega^\ddagger$ is the frequency associated with q at the saddle point. We also define the barrier height along q to be $V^\ddagger$ and the frequency along q in the reactants well to be ω_0.

In transition-state theory the rate constant is directly related (by a normalization constant) to the flux through a dividing surface.$^{(19-28,44)}$

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[4] As shown by Graham,$^{(50)}$ elucidation of the normal coordinate ρ does not require introduction of the Hamiltonian equation (2); ρ can be found directly from the GLE, as can a corollary of the collective mode σ [Eq. (8)].

Because this normalization is simply the reactants partition function, a well-known equilibrium quantity, we initially confine our attention to the calculation of the flux. For a general dividing surface in configuration space $[f(\rho, \mathbf{y}) = 0]$ the canonical flux for the Hamiltonian, Eq. (4) is

$$F^{\mathrm{CVTST}} = \int_{-\infty}^{\infty} dp_\rho \, d\rho \prod_j dp_{y_j} \, dy_j \, \delta[f(\rho, \mathbf{y})][\nabla f \cdot \mathbf{p}] \, \theta[\nabla f \cdot \mathbf{p}] \exp(-\beta H) \quad (5)$$

where δ is the Dirac delta function and θ is the Heaviside step function. With little loss of generality, one can choose the dividing surface to have the form $f = \rho - g(\mathbf{y})$, so that the component of the momentum perpendicular to the dividing surface is

$$\nabla f \cdot \mathbf{p} = \left[1 + \sum_j \left(\frac{\partial g}{\partial y_j}\right)^2\right]^{1/2} (\mathbf{p} \cdot \hat{n}_s) \quad (6)$$

$$= \left(p_\rho - \sum_j \frac{\partial g}{\partial y_j} p_{y_j}\right) \quad (7)$$

Here, $\hat{n}_s$ is the unit normal to the surface. As shown previously,(31) the expression for the CVTST flux can be considerably simplified by (1) introducing

$$\sigma \equiv (1/u_1) \sum_j u_{j0} \, y_j \qquad \text{and} \qquad p_\sigma \equiv (1/u_1) \sum_j u_{j0} \, p_{y_j} \quad (8)$$

where $u_1 \equiv (1 - u_{00}^2)^{1/2}$, and (2) restricting the dividing surface to the (ρ, σ) space. The result is the two-dimensional expression

$$F^{\mathrm{CVTST}} = F_0 \left(\frac{\beta^2 \Omega}{2\pi}\right) \int dp_\rho \, dp_\sigma \, d\rho \, d\sigma \, (\mathbf{p} \cdot \hat{n}_s) \, \theta(\mathbf{p} \cdot \hat{n}_s)$$
$$\times \delta[\rho - g(\sigma)] \left[1 + \left(\frac{dg}{d\sigma}\right)^2\right]^{1/2} \exp(-\beta H^\ddagger) \quad (9)$$

Here $H^\ddagger$ is the effective two-degree-of-freedom Hamiltonian

$$H^\ddagger = \frac{1}{2} p_\rho^2 + \frac{1}{2} p_\sigma^2 - \frac{1}{2} \lambda^{\ddagger 2} \rho^2 + \frac{1}{2} \Omega^2 \sigma^2 + V_1(\rho, \sigma) \quad (10)$$

$$\Omega^2 = \frac{u_1^2}{\sum_j (u_{j0}^2 / \lambda_j^2)} = \frac{u_1^2}{u_{00}^2 / \lambda^{\ddagger 2} - 1/\omega^{\ddagger 2}} \quad (11)$$

which depends, through $\lambda^\ddagger$, Ω, and V_1, on the friction kernel.(31,48) As shown in ref. 30, this effective Hamiltonian may be termed a "free energy

Hamiltonian," since it is obtained by a constrained canonical average over all coordinates and momenta of the system keeping the two collective modes and momenta (ρ, σ, p_ρ, p_σ) fixed. For the GLE, because of the harmonic nature of the bath, this constrained averaging reduces to Gaussian integrals which can be solved analytically. For a more general and realistic description of a liquid, such a free energy Hamiltonian may be obtained numerically using standard Monte Carlo methods.$^{(30)}$

The prefactor F_0 in Eq. (9) is the canonical flux as calculated from conventional ($f = \rho = 0$) harmonic ($V_1 = 0$) transition-state theory, i.e.,

$$F_0 = \left(\frac{1}{\beta}\prod_j \frac{2\pi}{\beta\lambda_j}\right) \tag{12}$$

The harmonic flux F_0 can be equated to the canonical flux as calculated from the Grote–Hynes theory,$^{(2,36)}$ as shown in ref. 47. Also, the frequency $\lambda^\ddagger$ is equal to the reactive frequency of the Grote–Hynes theory,$^{(36,47)}$ so that

$$\lambda^{\ddagger 2} = \omega^{\ddagger 2}/[1 + \hat{\gamma}(\lambda^\ddagger)/\lambda^\ddagger] \tag{13}$$

where $\hat{\gamma}(s)$ designates the Laplace transform of the friction kernel $\gamma(t)$ [Eq. (1)].

3. μVTST

At each energy $E^\ddagger$ of the effective two-degree-of-freedom Hamiltonian $H^\ddagger$ [Eq. (10)] the optimum dividing surface is given by a pods, which we denote as $f_{E^\ddagger}(\rho, \sigma) = 0$. Because $H^\ddagger$ is a first approximation to the full dissipative problem, it is likely that these pods also provide a set of optimal (or at least good) dividing surfaces for the full problem. In this section we show that the set of pods for $H^\ddagger$ can indeed be used to provide a rigorous upper bound to the canonical rate constant for the full problem.

In μVTST, then, microcanonical refers explicitly to the optimization of the dividing surface at fixed "reduced" energy $E^\ddagger$, rather than at fixed total energy. For an infinite bath, the total energy of the bath remains effectively unchanged by energy changes in $H^\ddagger$ (or any other effective Hamiltonian with a finite number of modes), and thus the total energy of the system plus infinite bath is irrelevant for understanding the reactive process. Hence, the only sensible end result is a canonical rate constant which, in μVTST, is based on the "reduced"-energy-dependent pods of $H^\ddagger$. The set of pods of $H^\ddagger$ at all energies $E^\ddagger$ can be considered to comprise a single dividing surface which is now a function of (ρ, σ, $E^\ddagger$), that is, $f(\rho, \sigma, E^\ddagger) = 0$. In phase space this becomes $f(\rho, \sigma, H^\ddagger) = 0$. The expression for the canonical flux of the full problem using this microcanonical dividing surface is

$$F^{\mu\mathrm{VTST}}=\int_{-\infty}^{\infty} dp_\rho\, d\rho \prod_j dp_{y_j}\, dy_j\, \delta[f(\rho,\sigma,H^\ddagger)][\nabla f\cdot\mathbf{p}]\,\theta[\nabla f\cdot\mathbf{p}]\exp(-\beta H) \tag{14}$$

where it must be remembered that the generalized velocity $\mathbf{p}$ has $2N+2$ components (N being the number of bath oscillators), all of whose time dependence is determined by the full Hamiltonian (not by $H^\ddagger$). For the μVTST dividing surface the momentum component perpendicular to the dividing surface, $\nabla f\cdot\mathbf{p}$, becomes

$$\begin{aligned}\nabla f\cdot\mathbf{p}=&\left(\frac{\partial f}{\partial\rho}+\frac{\partial f}{\partial H^\ddagger}\frac{\partial H^\ddagger}{\partial\rho}\right)p_\rho+\left(\frac{\partial f}{\partial\sigma}+\frac{\partial f}{\partial H^\ddagger}\frac{\partial H^\ddagger}{\partial\sigma}\right)\sum_j\frac{\partial\sigma}{\partial y_j}p_{y_j}\\&+\frac{\partial f}{\partial H^\ddagger}\frac{\partial H^\ddagger}{\partial p_\rho}\dot{p}_\rho+\frac{\partial f}{\partial H^\ddagger}\frac{\partial H^\ddagger}{\partial p_\sigma}\sum_j\frac{\partial p_\sigma}{\partial p_{y_j}}\dot{p}_{y_j}\end{aligned} \tag{15}$$

Making use of Hamilton's equations of motion for the full Hamiltonian H and the definitions of σ and p_σ [Eq. (8)] yields, for the momentum orthogonal to the dividing surface,

$$\begin{aligned}\nabla f\cdot\mathbf{p}&=\frac{\partial f}{\partial\rho}p_\rho+\frac{\partial f}{\partial\sigma}p_\sigma+\frac{\partial f}{\partial H^\ddagger}\left(\frac{\partial H^\ddagger}{\partial\sigma}-\frac{\partial H}{\partial\sigma}\right)p_\sigma\\&=\frac{\partial f}{\partial\rho}p_\rho+\frac{\partial f}{\partial\sigma}p_\sigma+\frac{\partial f}{\partial H^\ddagger}\left[\frac{1}{u_1}\sum_j u_{j0}(\Omega^2-\lambda_j^2)\,y_j\right]p_\sigma\end{aligned} \tag{16}$$

The third term on the RHS arises because the σ mode can have its energy increased by the bath when propagated by the full H, but not when propagated by the isolated $H^\ddagger$. Thus, the third term accounts for motion through the dividing surface caused by energy diffusion from the bath to $H^\ddagger$ via σ. It is useful to define a new energy diffusion coordinate $\mathscr{X}$ such that

$$\mathscr{X}\equiv\left[\frac{1}{u_1}\sum_j u_{j0}(\Omega^2-\lambda_j^2)\,y_j\right] \tag{17}$$

The flux normal to the surface f, $\nabla f\cdot\mathbf{p}$, now depends only upon the coordinates and momentum of $H^\ddagger$ and the energy diffusion coordinate $\mathscr{X}$.

Following the CVTST derivation,(31) we introduce the Fourier expansions of three delta functions (one more than in the CVTST derivation) into the flux expression [Eq. (14)] and switch the order of integration to get

$$F^{\mu\mathrm{VTST}} = \int d\rho\, dp_\rho\, d\sigma\, dp_\sigma\, d\mathscr{X}\, \delta[f(\rho, \sigma, H^\ddagger)][\nabla f\cdot \mathbf{p}]\, \theta[\nabla f\cdot \mathbf{p}] \times \left(\exp\left\{-\beta\left[\frac{p_\rho^2}{2} - \frac{1}{2}\lambda^{\ddagger 2}\rho^2 + V_1(\rho, \sigma)\right]\right\}\right) G(\sigma, p_\sigma, \mathscr{X}) \quad (18)$$

where G stands for

$$\left(\frac{1}{2\pi}\right)^3 \int d\kappa\, dl\, dz \prod_j dy_j\, dp_{y_j} \times \exp\left\{-\frac{\beta}{2}\sum (p_{y_j}^2 + \lambda_j^2 y_j^2) + i\kappa\left(\sigma - \frac{1}{u_1}\sum u_{j0}\, y_j\right) + il\left(p_\sigma - \frac{1}{u_1}\sum u_{j0}\, p_{y_j}\right) + iz\left[\mathscr{X} - \frac{1}{u_1}\sum u_{j0}(\Omega^2 - \lambda_j^2)\, y_j\right]\right\} \quad (19)$$

Carrying out the Gaussian integration in Eq. (19) yields

$$G = \frac{\beta\Omega}{2\pi}\prod_j \frac{2\pi}{\beta\lambda_j}\exp\left[-\frac{\beta}{2}(p_\sigma^2 + \Omega^2\sigma^2)\right]\left(\frac{\beta}{2\pi\, \Delta\Omega^2}\right)^{1/2}\exp\left(-\frac{\beta}{2}\frac{\mathscr{X}^2}{\Delta\Omega^2}\right) \quad (20)$$

where $\Delta\Omega^2$ is defined by

$$\Delta\Omega^2 \equiv \sum_j \frac{u_{j0}^2}{u_1^2}\lambda_j^2 - \Omega^2 \quad (21)$$

The first term in Eq. (21) can be related to the parameters of the generalized Langevin equation via the spectral density function $I(s)$ of the bath stable normal modes [$\{y_j\}$ of Eq. (3)],$^{(49)}$ that is,

$$\sum_j \frac{u_{j0}^2}{u_1^2}\lambda_j^2 = \frac{u_{00}^2}{u_1^2}\frac{2}{\pi}\int_0^\infty ds\, s^3 I(s) \quad (22)$$

where

$$I(s) = \frac{1}{s}\operatorname{Re}[\hat{K}(is)] \quad (23)$$

and

$$\hat{K}(p) = \frac{1}{u_{00}^2}\frac{p}{p^2 + p\hat{\gamma}(p) - \omega^{\ddagger 2}} - \frac{p}{(p^2 - \lambda^{\ddagger 2})} \quad (24)$$

Thus, Eqs. (22)–(24), along with Eq. (11), allow $\Delta\Omega^2$ to be defined in terms of parameters of the generalized Langevin equation.

Next Eq. (20) is substituted into Eq. (18) and the delta function

$$1 = \int dE^{\ddagger}\, \delta(E^{\ddagger} - H^{\ddagger}) \tag{25}$$

is introduced, so that $e^{-\beta H^{\ddagger}}$ becomes $e^{-\beta E^{\ddagger}}$ and $\partial f/\partial H^{\ddagger}$ becomes $\partial f/\partial E^{\ddagger}$. The flux then becomes

$$F^{\mu\mathrm{VTST}} = \frac{\beta^2 \Omega}{2\pi} F_0 \int d\mathscr{X} \left(\frac{\beta}{2\pi\, \Delta\Omega^2} \right)^{1/2} \times \exp\left(-\frac{\beta}{2} \frac{\mathscr{X}^2}{\Delta\Omega^2} \right) \int dE^{\ddagger}\, [\exp(-\beta E^{\ddagger})]\, F(E^{\ddagger}, \mathscr{X}) \tag{26}$$

where [using Eqs. (16) and (17)]

$$F(E^{\ddagger}, \mathscr{X}) = \int d\rho\, dp_\rho\, d\sigma\, dp_\sigma\, \delta(f)\, \delta(E^{\ddagger} - H^{\ddagger}) \left[p_\rho \frac{\partial f}{\partial \rho} + p_\sigma \left(\frac{\partial f}{\partial \sigma} + \frac{\partial f}{\partial E^{\ddagger}} \mathscr{X} \right) \right] \times \theta \left[p_\rho \frac{\partial f}{\partial \rho} + p_\sigma \left(\frac{\partial f}{\partial \sigma} + \frac{\partial f}{\partial E^{\ddagger}} \mathscr{X} \right) \right] \tag{27}$$

In order to highlight the physical interpretation of the flux expression, we rearrange the order of integration in Eq. (26) and define a total microcanonical flux as a function of the reduced energy $E^{\ddagger}$, that is,

$$F_{\mathrm{tot}}(E^{\ddagger}) = \left(\frac{\beta}{2\pi\, \Delta\Omega^2} \right)^{1/2} \int d\mathscr{X} \left[\exp\left(-\frac{\beta}{2} \frac{\mathscr{X}^2}{\Delta\Omega^2} \right) \right] F(E^{\ddagger}, \mathscr{X}) \tag{28}$$

Equation (26) now has the standard form,

$$F^{\mu\mathrm{VTST}} = \frac{\beta^2 \Omega}{2\pi} F_0 \int dE^{\ddagger}\, e^{-\beta E^{\ddagger}} F_{\mathrm{tot}}(E^{\ddagger}) \tag{29}$$

For the *isolated* two-degree-of-freedom Hamiltonian, the microcanonical flux would be, instead of Eq. (29),

$$F^{\mu\mathrm{VTST}} = \int dE^{\ddagger}\, e^{-\beta E^{\ddagger}} F_{\mathrm{2D}}(E^{\ddagger}) \tag{30}$$

where $F_{\mathrm{2D}}(E^{\ddagger}) = F(E^{\ddagger}, \mathscr{X} = 0)$. Equations (29) and (30) differ first simply by a constant prefactor, which is the same prefactor as appears in the

CVTST expression, Eq. (9). More importantly, the total flux $F_{\text{tot}}(E^{\ddagger})$, Eq. (28), which appears in the full expression (29), differs from the flux $F_{\text{2D}}(E^{\ddagger})$ in the isolated expression (30) by a Gaussian average over the energy diffusion coordinate $\mathscr{X}$. The flux through the "reduced"-energy ($E^{\ddagger}$)-dependent dividing surface in the full problem is increased over that in the isolated two-degree-of-freedom Hamiltonian because in the full problem energy transfer from the bath to $H^{\ddagger}$—represented by $\mathscr{X}$—can cause barrier crossing (see Fig. 1). Finally, inspection of Eq. (27) shows that if $\partial f/\partial E^{\ddagger}=0$, that is, if the dividing surface is independent of energy, $F(E^{\ddagger}, \mathscr{X})$, and hence $F_{\text{tot}}(E^{\ddagger})$, reduces to $F(E^{\ddagger}, \mathscr{X}=0)$, and Eq. (29) will give back the CVTST result for the flux, Eq. (9).

To make the numerical evaluation of $F^{\mu\text{VTST}}$ practical, the flux expression (27) is further simplified. First, the integral over p_{ρ} is rewritten in terms of p_z, where

$$p_z \equiv p_{\rho}\frac{\partial f}{\partial \rho} + p_{\sigma}\left(\frac{\partial f}{\partial \sigma} + \mathscr{X}\frac{\partial f}{\partial E^{\ddagger}}\right)$$

The Heaviside step function $\theta(p_z)$ is then used to change the lower limit of integration to zero. Next, the integration over p_{σ} is performed by making use of the delta function $\delta(E^{\ddagger}-H^{\ddagger})$. Integration over p_z then yields

$$\begin{aligned} F(E^{\ddagger}, \mathscr{X}) = 2^{3/2} \int d\rho\, d\sigma\, \delta[f(\rho, \sigma, E^{\ddagger})] \\ \times \left[\left(\frac{\partial f}{\partial \rho}\right)^2 + \left(\frac{\partial f}{\partial \sigma} + \mathscr{X}\frac{\partial f}{\partial E^{\ddagger}}\right)^2\right]^{1/2} [E^{\ddagger} - V(\rho, \sigma)]^{1/2} \qquad (31) \end{aligned}$$

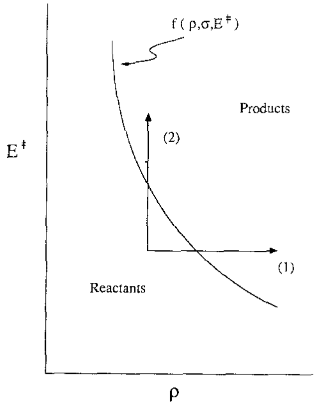

Fig. 1. A fixed σ slice through a typical dividing surface f; (1) illustrates spatially induced crossing of the dividing surface at fixed energy $E^{\ddagger}$; (2) illustrates energy diffusion-induced crossing of the dividing surface. Only crossings of type (1) occur in isolated systems. Both types must be accounted for in dissipative systems.

If the dividing surface is restricted to the form[4]

$$f = \rho - g(\sigma, E^{\ddagger}) \tag{32}$$

(valid for the pods of $H^{\ddagger}$), then the integration over ρ is simple. The resulting expression for the flux has the form of an action integral, that is,

$$F(E^{\ddagger}, \mathscr{X}) = 2^{3/2} \int_{\sigma_<}^{\sigma_>} d\sigma \left[1 + \left(\frac{\partial g}{\partial \sigma} + \mathscr{X} \frac{\partial g}{\partial E^{\ddagger}} \right)^2 \right]^{1/2} [E^{\ddagger} - V(g, \sigma)]^{1/2} \tag{33}$$

The integration is along the fixed-$E^{\ddagger}$ dividing surface defined by $g(\sigma)$, and $(\sigma_<, \sigma_>)$ limits the integration to the region where $E^{\ddagger} \geqslant V(g, \sigma)$. Combining Eq. (33) with Eq. (28) gives the total expression for the energy-dependent flux,

$$\begin{aligned} F_{\text{tot}}(E^{\ddagger}) = {} & 2^{3/2} \left(\frac{\beta}{2\pi\, \Delta\Omega^2} \right)^{1/2} \int d\mathscr{X} \exp\left(-\frac{\beta}{2} \frac{\mathscr{X}^2}{\Delta\Omega^2} \right) \\ & \times \int_{\sigma_<}^{\sigma_>} d\sigma \left[1 + \left(\frac{\partial g}{\partial \sigma} + \mathscr{X} \frac{\partial g}{\partial E^{\ddagger}} \right)^2 \right]^{1/2} [E^{\ddagger} - V(g, \sigma)]^{1/2} \end{aligned} \tag{34}$$

The $\mathscr{X}$-dependent flux expression in (33) gives back the action integral expression for the isolated two-degree-of-freedom Hamiltonian, that is,

$$F_{2\text{D}}(E^{\ddagger}) = 2^{3/2} \int_{\sigma_<}^{\sigma_>} d\sigma \left[1 + \left(\frac{\partial g}{\partial \sigma} \right)^2 \right]^{1/2} [E^{\ddagger} - V(g, \sigma)]^{1/2} \tag{35}$$

when either $\mathscr{X}$ or $\partial g / \partial E^{\ddagger}$ is zero. The pods of $H^{\ddagger}$ are the paths which minimize the (isolated) flux in Eq. (35). Hence, using the pods of $H^{\ddagger}$ to make up the energy-dependent dividing surface f for the full dissipative problem is equivalent to optimizing Eq. (35) for the isolated flux instead of optimizing the full expression, Eq. (34).

4. DISCUSSION

Derivation of the μVTST flux expression for dissipative systems [Eq. (34) combined with Eq. (29)] involves no approximation beyond those of the initial transition-state-theory flux expression [Eq. (14)]. It

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[5] The use of Eq. (32) to define the dividing surface precludes the case of a fixed-energy dividing surface that is independent of ρ and σ. If such a surface is to be used, one must work directly from Eq. (31), rather than from Eq. (33). However, in the spatial diffusion limit where the μVTST theory should be most useful, a constant-energy surface is not likely to provide a good bottleneck to reaction and would therefore not normally be used.

follows that the μVTST flux expression provides a rigorous upper bound to the reactive flux, and can thus be used to provide a rigorous upper bound to the rate constant. As in the CVTST result derived previously, all effects of system anharmonicity are accounted for and optimization of the dividing surface, this time as a function of the energy of the two-degree-of-freedom effective Hamiltonian, is also allowed.

As in all applications of variational transition-state theory, the degree to which the upper bound result will approximate the true result will depend upon the optimization of the dividing surface. Optimization of the dividing surface does not guarantee an exact result, since the optimization is invariably performed under some set of restrictions. For example, optimization is almost always confined to coordinate space, instead of full phase space. Although there are other reasons why transition-state theory may not give an exact result, these have been discussed extensively elsewhere,(1,3,24,26,27,43) and do not concern us here. The usefulness of the μVTST result over the CVTST result will depend upon the degree to which the pods, which are highly optimized for the isolated system, provide a good dividing surface for the full problem. Comparing Eq. (34) for the total flux with Eq. (35) for the isolated flux—which is minimized by the pods path—we see that they differ by the energy diffusion term, $\mathscr{X}\ \partial g/\partial E^{\ddagger}$. The pods path will therefore provide a good estimate of the optimum dividing surface for the total flux [Eq. (34)] when either $\partial g/\partial E^{\ddagger}$ or $\mathscr{X}$ or both are small.

The gradient of the energy surface, $\partial g/\partial E^{\ddagger}$ (at fixed σ), will be small if the pods change only very gradually with the energy of the isolated two-degree-of-freedom Hamiltonian. The value of the energy diffusion coordinate $\mathscr{X}$ is governed by a Gaussian distribution around an average value of zero. Hence, the narrower this distribution, that is, the smaller the fluctuations in the energy transfer from the bath to $H^{\ddagger}$ through the collective bath mode σ, the less important will be the energy diffusion contribution to the total flux. The width of this Gaussian distribution is determined by the parameter $\Delta\Omega^2$ [Eq. (21)], which is given by the difference between a weighted sum of the squares of all (stable normal mode) bath frequencies and the square of the frequency of the collective bath mode Ω.

In general, $\Delta\Omega^2$ will vary only slightly with increasing static friction $\hat{\gamma}(0)$. It is determined more strongly by the general characteristics of the spectral density [Eqs. (23), (24)]. An extreme example is Ohmic friction, $\gamma(t)=\eta\delta(t)$, for which $\Delta\Omega^2$ is infinite [by virtue of the first term in Eq. (21)] for any value of the static friction η. For the Ohmic friction case, energy diffusion is unchecked because there is no system–bath frequency mismatch, and, therefore, energy diffusion dominates if $\partial g/\partial E^{\ddagger}$ is nonzero. For Ohmic friction a nontrivial upper bound to the rate is obtained

Table I. The Energy Transfer Width Parameter $\Delta\Omega^2$ As a Function of the Static Friction α for Gaussian Friction ($\omega_0\tau_D=10$)[a]

α	$\Delta\Omega^2$	$\lambda^{\ddagger 2}$	Ω^2
0.1	0.0193	0.992	0.0097
1.0	0.0192	0.921	0.0104
2.5	0.0192	0.803	0.0119
5.0	0.0191	0.607	0.0155
7.0	0.0190	0.453	0.0204
9.0	0.0192	0.304	0.0294
10.0	0.0196	0.233	0.0372

[a] The square of the reactive frequency $\lambda^{\ddagger 2}$ and the collective bath mode frequency Ω^2 are given for comparison. All squared frequencies are given in units of the bare barrier frequency (squared) ω_0^2, and the static friction α is in units of ω_0.

only if the dividing surface is energy independent, and one must resort to CVTST. In contrast, for Gaussian friction, $\gamma(t)=(2/\pi)^{1/2}(\alpha/\tau_D)\exp(-t^2/2\tau_D^2)$, one finds $\Delta\Omega^2\approx 2\tau_D^{-2}$, where τ_D is inversely related to the characteristic frequency of the bath motion. For example, to model the breaking of a chemical bond of a solute molecule in a highly structured liquid, it would be reasonable to assume a reactive barrier frequency of $1000\,\text{cm}^{-1}$ and an average librational frequency of the bath of $100\,\text{cm}^{-1}$. For this scenario, $\tau_D=10$ in units of one over the barrier frequency (cf. Table I), and $\Delta\Omega^2$ ranges from a low of 0.0190 to a high of 0.0196 over a variation of two orders of magnitude in the coupling strength, α. For problems with memory friction, the μVTST prescription using pods to define the dividing surface should provide a good upper bound whenever there is a large time-scale discrepancy between the reactive system and bath motions.

5. CONCLUSION

A μVTST flux expression for reactions occurring in a dissipative medium has been derived. This expression is expected to provide accurate rate constants for systems in the Kramers spatial diffusion regime. It defines an optimum energy-dependent dividing surface by the pods of an effective two-degree-of-freedom Hamiltonian which is composed of one reactive mode and one well-defined collective bath mode. The μVTST flux expression, when normalized by the reactant partition function, provides a rigorous upper bound to the rate constant for any system which can be modeled with a generalized Langevin equation. We have shown that, to provide an upper bound, the flux expression for dissipative systems must include contributions from energy diffusion across the dividing surface, not just contributions from spatial diffusion. The energy diffusion contribution arises because the dissipation in the full problem allows for energy transfer from the bath to the single collective bath mode. This energy diffusion contribution is not to be confused with the Kramers energy diffusion-controlled regime at weak coupling. The energy diffusion mechanism which contributes to the μVTST rate is most prevalent at strong coupling, where energy transfer is large. The conditions under which the μVTST prescription using pods is expected to provide a useful upper bound have been discussed. In particular, if the pods change slowly with energy or if there is a large time-scale discrepancy between the reactive and bath frequencies, μVTST should provide a better estimate for the rate constant than the CVTST method.

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