ACTIVATED RATE PROCESSES IN CONDENSED PHASES: THE KRAMERS THEORY REVISITED

ABRAHAM NITZAN

School of Chemistry, Sackler Faculty of Sciences Tel Aviv University, Tel Aviv 69978, Israel

CONTENTS

I. INTRODUCTION

Kramers' treatment of the escape of a Brownian particle out of a potential well[1-4] as a model for chemical reactions in condensed phases has played a central role in many areas of physics and chemistry. The original application to chemical reaction rates has in fact been disregarded by chemists until the last decade. Other applications were mostly in solid-state physics: desorption

from surfaces,[5a,6] atom or ion diffusion in solids[5b] or on solid surfaces,[5c] dynamics of Josephson junctions,[5d] and more.

During the last decade new interest has emerged and much research effort has been developed in the study of chemical reactions in condensed phases, mostly in liquid solution or in the high-pressure gas phase. The Kramers theory has been used for the interpretation of some of the data, but it has soon become recognized that the theory, as it stood, cannot account for the physical reactions in normal liquids or solid matrices. Many of the needed generalizations have been developed during the past few years, so that we now have a reasonable understanding of the theory as applied to chemical reaction rates.[3,4] The still missing ingredients are not associated with the conceptual structure of the theory, but rather with knowledge of molecular energetics and dynamics on the microscopic level [the molecular potential surfaces dressed by solvent interactions on one hand, and intramolecular vibrational relaxation (IVR) or, more generally, the dynamic behavior of highly excited molecules on the other].

This chapter reviews the generalizations of the Kramers model that were developed during the past few years. The result of this effort, which we may call the generalized Kramers theory, provides a useful framework for the theoretical description of activated rate processes in general and of chemical reaction rates in condensed phases in particular. Some applications of this framework as well as its limitations are also discussed. In the last few years there has also been substantial progress in the study of the quantum mechanical Kramers model,[2b] which may prove useful for condensed phase tunneling reactions. This aspect of the problem is not covered by the present review.

II. THE KRAMERS TREATMENT

In this section we briefly review the original work of Kramers.[1] It will be seen that much of the new developments still rely heavily on the insight obtained from Kramers' work.

The Kramers model consists of a classical particle of mass m moving on a one-dimensional potential surface $V(x)$ (Fig. 1) under the influence of Markovian random force $R(t)$ and damping γ, which are related to each other and to the temperature T by the fluctuation dissipation theorem,

$$\ddot{x} = -\frac{1}{m}\frac{dV(x)}{dx} - \gamma\dot{x} + \frac{1}{m}R(t) \tag{2.1}$$

$$\langle R(t)\rangle = 0; \qquad \langle R(0)R(t)\rangle = 2\gamma mk_BT\delta(t) \tag{2.2}$$

The Langevin equation (2.1) is equivalent to the Fokker–Planck equation for
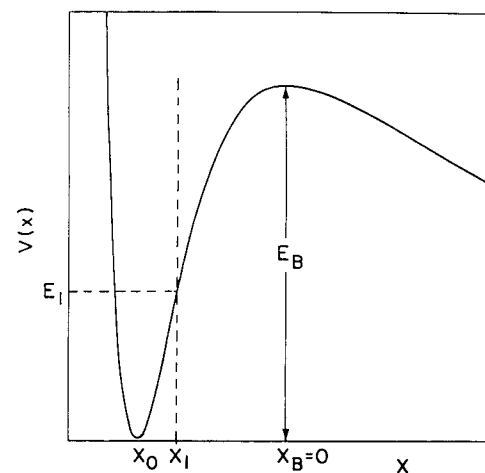
Figure 1. Schematic representation of single well potential. x_1, E_1—position and energy associated with matching point discussed in Section VI.

the probability distribution $P = P(x, v, t)$,

$$\frac{\partial P}{\partial t} = \frac{1}{m}\frac{dV}{dx}\frac{\partial P}{\partial v} - v\frac{\partial P}{\partial x} + \gamma\left[\frac{\partial}{\partial v}(vP) + \frac{k_BT}{m}\frac{\partial^2 P}{\partial v^2}\right] \tag{2.3}$$

The objective is to find the steady-state escape rate k out of the potential well. Before presenting the Kramers solution it is important to note that for such a (quasi) steady state to be established, a clear separation of time scales has to exist, whereupon the escape occurs on a time scale much longer than all time scales associated with the motion inside the well. In particular this implies that the well should be deep enough (see below).

Kramers solved Eq. (2.3) in two different regimes.

A. Moderate to Large Damping

In this case the well is assumed to be in thermal equilibrium (which is established on a time scale proportional to γ^{-1}), and thus the dynamics is determined by the motion near the barrier top ($x = x_B = 0$). The potential is approximated about this point as a parabola,

$$V(x) = E_B - \tfrac{1}{2}m\omega_B^2 x^2 \tag{2.4}$$

where

$$\omega_B = \sqrt{-m^{-1}V''(0)} \tag{2.5}$$

is the frequency associated with the barrier top. The steady-state solution $P_{ss}^{(B)}(x, v)$ is written in terms of the equilibrium solution

$$P_{eq}(x, v) = N \exp[-\beta(\tfrac{1}{2}mv^2 + V(x))], \qquad \beta = (k_B T)^{-1}$$
$$P_{ss}^{(B)}(x, v) = P_{eq}(x, v)f(x, v) \qquad (2.6)$$

Equations (2.6), (2.4), and (2.3) with $\partial P/\partial t = 0$ lead to the following equation for the correction function f:

$$v\frac{\partial f}{\partial x} + \omega_B^2 x\frac{\partial f}{\partial v} = \gamma\frac{k_B T}{m}\frac{\partial^2 f}{\partial v^2} - \gamma v\frac{\partial f}{\partial v} \qquad (2.7)$$

f should also satisfy the boundary conditions

$$f(x \to +\infty) \to 0 \qquad (2.8a)$$
$$f(x \to -\infty) \to 1 \qquad (2.8b)$$

Using the ansatz

$$f(x, v) \equiv f(u) = f(v + \Gamma x) \qquad (2.9)$$

leads to

$$[(\Gamma + \gamma)v + \omega_B^2 x]\frac{df}{du} = \frac{k_B T\gamma}{m}\frac{d^2 f}{du^2} \qquad (2.10)$$

To be consistent with Eq. (2.9) we must have $\omega_B^2 = (\Gamma + \gamma)\Gamma$, namely Γ should satisfy the equation

$$\Gamma^2 + \Gamma\gamma - \omega_B^2 = 0 \qquad (2.11)$$

Equation (2.9) becomes

$$\frac{k_B T}{m}\frac{d^2 f}{du^2} + \alpha u\frac{df}{du} = 0 \qquad (2.12)$$

with

$$\alpha = -\frac{\Gamma + \gamma}{\gamma} \qquad (2.13)$$

A general solution of Eq. (2.12) is

$$F(u) = F_1 + F_2 \int_0^u dz \exp\left[-\frac{\alpha mz^2}{2k_B T}\right] \qquad (2.14)$$

where F_1 and F_2 are constants to be determined from the boundary conditions. First note that the integral in Eq. (2.14) should remain finite for $|u| \to \infty$. This implies that $\alpha > 0$, namely, of the two roots of Eq. (2.11) only

$$\Gamma = -\left\{\frac{\gamma}{2} + \left[\left(\frac{\gamma}{2}\right)^2 + \omega_B^2\right]^{1/2}\right\} \qquad (2.15)$$

is relevant. Then the requirement $f(u) \to 0$ for $u \to \infty$ implies

$$F_1 = -F_2 \int_0^{-\infty} dz \exp\left[-\frac{\alpha mz^2}{2k_B T}\right] = \left[\frac{\pi k_B T}{2\alpha m}\right]^{1/2} F_2 \qquad (2.16)$$

Thus, replacing F_2 by F,

$$P_{ss}^{(B)}(x, v) = F \int_{-\infty}^{v-|\Gamma|x} dz \exp\left[-\frac{\alpha mz^2}{2k_B T}\right] P_{eq}(x, v) \qquad (2.17)$$

The current associated with this distribution is, using Eq. (2.4),

$$j^{(B)} = \int_{-\infty}^{\infty} dv\, vP_B(x, v) = FN\left(\frac{k_B T}{m}\right)^{3/2}\left(\frac{2\pi}{\alpha + 1}\right)^{1/2} e^{-\beta E_B} \qquad (2.18)$$

This result is independent of position x, as expected of a steady-state current. The remaining constant F is determined from Eq. (2.8b),

$$F = \sqrt{\frac{\alpha m}{2\pi k_B T}} \qquad (2.19)$$

and the rate is obtained by dividing Eq. (2.18) by the well population. The latter is given by

$$\int_{well} dx \int_{-\infty}^{\infty} dv\, P_{ss}(x, v) \simeq \frac{2\pi N}{\beta m\omega_0} \qquad (2.20)$$

This result is obtained by using the fact that most of the contribution to this integral comes from the region near the well bottom, and that in this region

the steady-state distribution P_{ss} can be approximated by the equilibrium form

$$P_{ss}(x,v) \simeq P_{eq}(x,v) \simeq N \exp[-\beta(\tfrac{1}{2}mv^2 + \tfrac{1}{2}m\omega_0^2(x-x_0)^2)] \qquad (2.21)$$

where x_0 and ω_0 are the position and the frequency associated with the well bottom. Dividing Eq. (2.18) by Eq. (2.20) and using the identity, obtained from Eqs. (2.13) and (2.15),

$$\sqrt{\frac{\alpha}{\alpha+1}} = \frac{1}{\omega_B}\left[\sqrt{\omega_B^2 + \left(\frac{\gamma}{2}\right)^2} - \frac{\gamma}{2}\right] \qquad (2.22)$$

we finally get

$$k = k^{(B)} = \frac{\omega_r}{\omega_B}\frac{\omega_0}{2\pi}e^{-\beta E_B} \qquad (2.23)$$

where the reactive frequency ω_r is

$$\omega_r = \left(\omega_B^2 + \frac{\gamma^2}{4}\right)^{1/2} - \frac{\gamma}{2} \qquad (2.24)$$

For $\gamma \to 0$, $\omega_r \to \omega_B$ and the rate becomes

$$k \to k_{TST} = \frac{\omega_0}{2\pi}e^{-\beta E_B} \qquad (2.25)$$

This is the rate obtained from transition state theory (TST) by dividing the equilibrium outgoing flux at the barrier position, that is, $\int_0^\infty dv\, v P_{eq}(x_B,v)$, by the well population, Eq. (2.20). This procedure relies on the two assumptions of TST: (1) the establishment of equilibrium throughout the well occurs much faster than the escape rate, and (2) the probability that particles return to the well after going past x_B is zero. It is the second assumption that the Kramers theory in the intermediate-to-large friction regime corrects for, and the inequality $\omega_r/\omega_B < 1$ (that is, $k^{(B)} < k_{TST}$) for $\gamma \neq 0$ reflects the fact that the rate is smaller than the TST rate on account of returning trajectories. The possibility of nonequilibrium well equilibrium is disregarded in this limit of the Kramers theory. Therefore TST is obtained in the vanishing γ limit of Eq. (2.23).

For $\gamma \to \infty$ Eqs. (2.23) and (2.24) lead to

$$k \to \frac{\omega_0 \omega_B}{2\pi\gamma}e^{-\beta E_B} \qquad (2.26)$$

The same result is obtained[1] from the Smoluchowski limit[6] of Eq. (2.3),

$$\frac{\partial P(x,t)}{\partial t} = \left[\frac{\partial}{\partial x}D\left(\beta\frac{\partial V}{\partial x} + \frac{\partial}{\partial x}\right)\right]P(x,t) \qquad (2.27)$$

where the diffusion coefficient D is

$$D = (\beta m\gamma)^{-1} \qquad (2.28)$$

Equation (2.27) may be solved for the more general case where γ depends on the coordinate, or $D = D(x)$ in Eq. (2.27). The steady-state flux associated with Eq. (2.27) is

$$j = -D(x)\left(\beta\frac{\partial V}{\partial x} + \frac{\partial}{\partial x}\right)P_{ss}(x) \qquad (2.29)$$

so that in terms of j and of the equilibrium distribution $P_{eq}(x) = e^{-\beta V(x)}$

$$P_{ss}(x) = P_{eq}(x)\left[1 - j\int_{x_0}^x \frac{dy}{D(y)P_{eq}(y)}\right] \qquad (2.30)$$

The lower bound in the integral in Eq. (2.30) was chosen so as to satisfy the boundary condition $P_{ss}(x_0) = P_{eq}(x_0)$. If we also require $P_{ss}(\infty) = 0$, we get

$$j = \left[\int_{x_0}^\infty \frac{dy}{D(y)P_{eq}(y)}\right]^{-1} = D(x_B)\sqrt{\frac{\beta m\omega_B^2}{2\pi}}e^{-\beta E_B} \qquad (2.31)$$

[To obtain this result we approximate P_{eq} near the barrier top by $\exp(-\beta E_B + \tfrac{1}{2}m\omega_B^2 x^2)$ and replace x_0 by $-\infty$ in the integral.] The rate is obtained by dividing Eq. (2.21) by the well population $\int_{-\infty}^{x_B} dx \exp(-\tfrac{1}{2}\beta m\omega_0^2 x^2) = [2\pi/(\beta m\omega_0^2)]^{1/2}$. This leads again to Eq. (2.26) with $\gamma = \gamma(x_B)$.

B. Low Damping

When γ is very small, the thermal relaxation in the well is not fast relative to the escape rate, and the assumption that the distribution within the well can be represented by the equilibrium Boltzmann distribution no longer holds. On the other hand we can make use of the fact that the total energy E varies on a time scale much longer than either x or v (it is conserved for $\gamma = 0$). Thus changing variables from (x,v) to (E,ϕ) and eliminating the fast phase variable ϕ leads to a Smoluchowski (diffusion) equation for E. [Kramers[1] gave the equivalent equation in terms of the action variable $J(E)$.]

$$\frac{\partial P(E,t)}{\partial t} = \frac{\partial}{\partial E}\left[D(E)\left(k_B T\frac{\partial}{\partial E} + 1\right)\omega(E)P(E,t)\right] \qquad (2.32)$$

with

$$D(E) = \gamma J(E) \qquad (2.33)$$

where $J(E)$ is the action defined so that

$$\frac{dE}{dJ} = \omega \qquad (2.34)$$

The evaluation of the escape rate from Eq. (2.32) proceeds along lines similar to those used to obtain Eq. (2.26) from Eq. (2.27). It is assumed that $E = E_B$ constitutes an absorbing barrier [so $P_{ss}(E_B) = 0$] and that $P_{ss}(E) \to P_{eq}(E)$ as $E \to 0$. The steady-state flux on the energy axis is

$$j_E = -D(E)\left(k_B T\frac{\partial}{\partial E} + 1\right)\omega(E)P_{ss}(E) \qquad (2.35)$$

and the equilibrium distribution ($j_E = 0$) is

$$P_{eq}(E) = \omega^{-1}(E)e^{-\beta E} \qquad (2.36)$$

$P_{ss}(E)$ is obtained from Eq. (2.35) in terms of j_E,

$$P_{ss}(E) = P_{eq}\left[1 - \beta j_E \int_0^E dE'\frac{e^{\beta E'}}{D(E')}\right] \qquad (2.37)$$

This form satisfies the boundary condition at $E = 0$. The requirement $P_{ss}(E_B) = 0$ implies

$$j_E = \left[\beta \int_0^{E_B} dE'\frac{e^{\beta E'}}{D(E')}\right]^{-1} \qquad (2.38)$$

The escape rate is again obtained by dividing the current by the well population

$$k = k^{(W)} = \left[\beta \int_0^{E_B} dE\,\omega^{-1}(E)e^{-\beta E}\int_0^{E_B} dE'\frac{e^{\beta E'}}{D(E')}\right]^{-1} \qquad (2.39)$$

The superscript (W) stresses the fact that in this limit the rate is determined

by the well dynamics. For deep wells we may approximate the integrals in Eq. (2.39) as

$$\int_0^{E_B} dE'\frac{e^{\beta E'}}{D(E')} \simeq (\beta D(E_B))^{-1}e^{\beta E_B} \qquad (2.40a)$$

$$\int_0^{E_B} dE\,\omega^{-1}(E)e^{-\beta E} \simeq (\beta\omega_0)^{-1} \qquad (2.40b)$$

and hence, using also Eq. (2.33)

$$k^{(W)} \simeq \beta\gamma J(E_B)\omega_0 e^{-\beta E_B} \qquad (2.41)$$

The product $J(E_B)\omega_0$ is equal to E_B for a harmonic oscillator potential truncated at $E = E_B$, and to $2E_B$ for a Morse potential with dissociation energy equal to E_B. Equation (2.41) is the low-friction limit result of Kramers.[1]

There are other methods to derive the results obtained in the previous section. One is to look for the eigenvalue λ_1 with smallest positive real part of the operator L defined so that $\partial P/\partial t = -LP$ is the relevant Fokker–Planck or Smoluchowski equation.[7] Under the usual condition of time scale separation this smallest real part is the escape rate for a single well potential. Another way uses the concept of mean passage time.[8] For the one-dimensional Fokker–Planck equation of the form

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[a(x) - b(x)\frac{\partial}{\partial x}\right]P(x,t) \qquad (2.42)$$

with a reflecting boundary condition at x_1 and an absorbing boundary condition at $x_2 > x_1$, the mean time for the stochastic variable X, whose probability density to take the value x is $P(x,t)$, to reach the absorbing barrier starting from $X = x$ is[8]

$$\tau = \int_x^{x_2}\frac{dx'}{b(x')P_{eq}(x')}\int_{x_1}^{x'} dx''P_{eq}(x'') \qquad (2.43)$$

where $P_{eq}(x)$ is the equilibrium solution of Eq. (2.42),

$$P_{eq}(x) = N\exp\left[\int dx'\frac{a(x')}{b(x')}\right] \qquad (2.44)$$

Consider now Eq. (2.27), which is of the form of Eq. (2.42) with $a(x) = -\beta D(dV/dx)$ and $b(x) = D(x)$. Without loss of generality we may assume

reflecting boundary conditions at some point x_1 to the far left of x_0 and absorbing boundary conditions at some point x_2 to the far left of x_B. Using Eq. (2.44), Eq. (2.43) yields

$$\tau(x) = \int_x^{x_2} dy \frac{e^{\beta V(y)}}{D(y)} \int_{x_1}^y dz \, e^{-\beta V(z)} \qquad (2.45)$$

If the barrier is high $[\beta V(x_B) \gg 1]$, then for starting positions x that satisfy $x < x_B$ and $\beta[V(x_B) - V(x)] > 1$ this result is practically independent of x. The main contribution to the y integral in this case is form $y = x_B$, and

$$\tau(x) \simeq \frac{1}{D(x_B)} \int_{x_1}^{x_B} dz \, e^{-\beta V(z)} \int_x^{x_2} dy \, e^{\beta V(y)} \qquad (2.46)$$

Also

$$\int_x^{x_2} dy \, e^{\beta V(y)} \simeq \int_{-\infty}^{\infty} dy \exp\left[\beta\left(E_B - \frac{1}{2}m\omega_B^2 x^2\right)\right] \qquad (2.47)$$

and

$$\int_{x_1}^{x_B} dz \, e^{-\beta V(z)} \simeq \int_{-\infty}^{\infty} dz \exp\left[-\frac{1}{2}\beta m\omega_0^2(x - x_0)^2\right] \qquad (2.48)$$

This, with Eq. (2.28), leads to

$$\tau(x) \simeq \frac{2\pi\gamma}{\omega_0 \omega_B} e^{\beta E_B} \qquad (2.49)$$

The mean exit time from the well should be actually obtained by averaging $\tau(x)$ over the steady-state distribution

$$\langle\tau\rangle = \frac{\int_{x_1}^{x_B} dx \, P_{ss}(x)\tau(x)}{\int_{x_1}^{x_B} dx \, P_{ss}(x)}$$

However, since $\tau(x)$ is independent of x in the region that contributes mostly to this integral, the result, Eq. (2.49), is the final one. This is exactly the inverse of Eq. (2.26).

Similarly Eq. (2.32) is of the form of Eq. (2.42) with

$$a(E) = -\left[D(E)\omega(E) + \frac{1}{\beta}D(E)\frac{d\omega(E)}{dE}\right]$$

and $b(E) = D(E)\omega(E)/\beta$. Imposing a reflecting barrier at $E = 0$ and an absorbing barrier at $E = E_B$ we get

$$\tau(E) = \beta \int_E^{E_B} dE' \frac{1}{D(E)\omega(E)P_{eq}(E')} \int_0^{E'} dE'' P_{eq}(E'') \qquad (2.50)$$

where $P_{eq}(E)$ is given by Eq. (2.36). For high barrier the result for $|E - E_B| > k_B T$ is independent of E and is given by

$$\tau = \frac{e^{\beta E_B}}{\beta\omega_0 D(E_B)} \qquad (2.51)$$

which is the inverse of Eq. (2.41).

III. THE NEED FOR GENERALIZATION OF THE KRAMERS THEORY

Although the Kramers model contains much of the essential physics of the activated escape problem, it cannot be used for quantitative discussion of many realistic activated processes. In particular the model is too oversimplified for the original application intended by Kramers for chemical rate processes. The theory needs to be generalized to correct the following shortcomings of the Kramers model.

1. The Markovian description, inherent in Eqs. (2.1) and (2.2), is unrealistic for most chemical situations as it assumes that the relaxation time of the medium surrounding the molecule is faster than all molecular time scales. This medium surrounding the molecule is faster than all molecular time scales. This assumption obviously breaks down in the low-friction regime where the escape rate is dominated (or at least influenced) by the well dynamics (that is, escape is dominated (or at least influenced) by the well dynamics (that is, intramolecular motion), since typical molecular frequencies are of the same order or larger than intermolecular (solvent) frequencies. Even for higher friction, where the escape is dominated by the dynamics in the barrier regime, the Markovian assumption can fail because the characteristic barrier time ω_B^{-1} is often shorter than the solvent relaxation time.

2. While Kramers has considered escape of a particle from a single well, many processes involve transitions between locally stable states of a double well potential (Fig. 2). Dissociation and desorption are examples of single well problems; unimolecular isomerization is a double well problem. Many-well problems are also of interest, such as diffusion of atoms or ions in solids.

3. There have recently been a number of measurements of unimolecular reaction rates as a function of molecule–solvent interaction over a large range of such interactions—from the low-pressure gas phase (where damping is
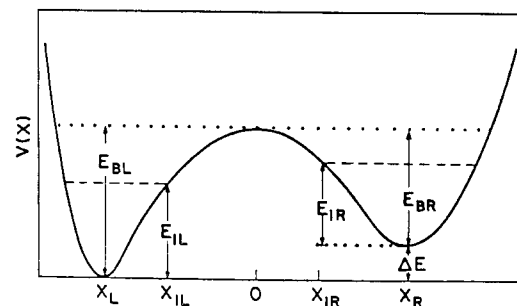
Figure 2. Schematic representation of double well potential.

caused by isolated collisions) to high-viscosity solvents.[9-14] The Kramers theory provides two results, Eqs. (2.23) and (2.24), for the intermediate-to-large friction range and Eq. (2.41) for the low-friction limit. A unified expression to account for the transition between these two dynamic regimes is needed.

4. The friction (more generally, molecule–solvent interaction) is taken in the Kramers model to be a constant, independent of the position along the reaction coordinate. As seen, generalization to position-dependent friction is trivial in the Smoluchowski limit. In many systems position-dependent friction should be considered also in the underdamped case. An obvious example is desorption where the dissociating particle ceases to feel the thermal bath as it draws further away from the surface.

5. The Kramers model is one-dimensional. In the terminology of molecular reaction processes this model considers the reaction coordinate only and disregards the role played by nonreactive modes. Such modes, which couple to the reaction coordinate, affect both the equilibrium properties of the system (with implications to TST) and its dynamic behavior. Formally the nonreactive modes may be thought of as part of the solvent heat bath felt by the reactive modes, but this does not lead to practical results because the time scales associated with intramolecular and intermolecular relaxation can be quite different. The effect of nonreactive molecular modes on the rate of chemical reactions can in principle be very complicated. The exchange of energy between these modes and the reaction coordinate is a process which may be quite complicated for highly vibrationally excited molecules. Fortunately for many cases (in most cases involving large molecules) IVR is fast relative to the other molecular time scales, in particular relative to the total energy relaxation rate and to the chemical reaction rate. Under such conditions statistical considerations similar to those used in the RRKM theory should lead to a generalization of the Kramers theory, which includes as a new parameter the number n of molecular modes which are coupled to the

reaction coordinate. This will thus lead to an explicit molecular size dependence of the chemical reaction rate.

6. Some escape processes of interest are affected by external forces; a typical situation is escape in the presence of a radiation field whose frequency is close to resonance with the well motion. Experimental examples are molecular photodissociation in condensed phases,[15] photodesorption,[16] and microwave-induced transitions in Josephson junctions.[17-19] To describe such processes within the Kramers theory one needs to analyze the effect of an additional periodic force in Eq. (2.1) (or its non-Markovian counterpart).

In the following we review a generalized Kramers theory which overcomes many of the problems mentioned. Some of the ingredients of this generalized theory were developed many years ago, while may others are results obtained in recent years by us and other workers.

IV. THE GENERALIZED KRAMERS MODEL

In what follows we use the terminology of chemical rate processes. However, with a suitable change of language the formulation is relevant to many other situations of non–chemical nature. To account for the many degrees of freedom usually involved in a chemical reaction and for the non-Markovian nature of the molecule–solvent interaction, the starting point for the present treatment is, instead of Eqs. (2.1) and (2.2), a set of generalized Langevin equations (GLE) for the atomic (mass-weighted) coordinates[20,21]

$$\ddot{x}_a = -\frac{\partial U}{\partial x_a} - \sum_b \int_0^t d\tau \, Z_{ab}(t - \tau)\dot{x}_b(\tau) + R_a(t) \tag{4.1}$$

$$\langle R_a(t)R_a(t')\rangle = \frac{Z_{ab}(t - t')}{\beta}; \qquad \beta = (k_B T)^{-1} \tag{4.2}$$

where $U(x)$, $\{x\} = x_1, x_2, \ldots, x_N$, N being the number of atoms, is the molecular potential surface, and $Z_{ab}(t)$ and $R_a(t)$, $a = 1, 2, \ldots, 3N$, are the friction kernels and the random forces associated with the surrounding medium. Nondiagonal friction kernels may arise from hydrodynamic interactions between different atoms via the surrounding medium[20] and also from medium-induced impulsive interactions between modes (see below). The mass-weighted form, Eq. (4.1), is obtained by scaling the regular atomic equations

$$m_a\ddot{\xi}_a = \frac{\partial W(\{\xi\})}{\partial \xi_a} - \int_0^t d\tau \, z_{ab}(t - \tau)\xi_a(\tau) + \rho_a(t)$$

according to $\sqrt{m_a}\xi_a = x_a$, $W(\{x/\sqrt{m}\}) = U(\{x\})$, $z_{ab}/\sqrt{m_a m_b} = Z_{ab}$, and $\rho_a/\sqrt{m_a} = R_a$. Also note that the indices a and b $(= 1, 2, \ldots, 3N)$ stand for both the atom and the three Cartesian components of the atomic coordinate. Finally, the Markovian friction γ is related to the memory kernels Z by $\gamma_{ab} = \int_0^\infty dt\, Z_{ab}(t)$.

The chemical reaction is assumed to proceed when the molecule passes irreversibly from a region of configuration space identified as the reactant to a region identified as the product through a saddle point in the multidimensional potential surface. It is assumed that this saddle point is characterized by a local maximum of the potential along one degree of freedom (the reaction coordinate), while the other intramolecular degrees of freedom maintain stable oscillations about their local minima. This saddle point constitutes the potential barrier to the reaction.

Near the barrier, Eqs. (4.1) and (4.2) can be linearized and transformed to

$$\ddot{x}_R = \omega_B^2 x_R - \int_c^t d\tau \sum_j Z_{Rj}(t-\tau)\dot{x}_j(\tau) - \int_0^t d\tau\, Z_{RR}(t-\tau)\dot{x}_R(\tau) + R_R(\tau) \quad (4.3)$$

$$\ddot{x}_j = -\omega_j^{(B)2} x_j - \int_c^t d\tau \sum_{j'} Z_{jj'}(t-\tau)\dot{x}_{j'}(\tau) - \int_0^t d\tau\, Z_{jR}(t-\tau)\dot{x}_R(\tau) + R_j(t) \quad (4.4)$$

$$\langle R_i(t) R_{i'}(t')\rangle = \frac{Z_{ii'}(t-t')}{\beta}; \qquad i, i' = \{j\}, R \quad (4.5)$$

where the x_R denote the reactive modes, (x_j) is the set of $3N-7$ nonreactive modes (the six overall translational and rotational coordinates are considered here as part of the thermal environment), ω_B is the barrier frequency in the direction of the local maximum, and $\omega_j^{(B)}$ are the frequencies associated with the nonreactive modes near the barrier.

The description of the molecular motion in the barrier region, Eqs. (4.3)–(4.5), has to be supplemented by a description of the dynamics in the stable reactant well. Here the model makes the following important assumption. Energy redistribution between intramolecular modes takes place on a time scale much shorter than the energy exchange between the molecule and its environment. This is generally believed to be the case for large molecules in the low-pressure gas phase, but is not obvious for similar molecules in condensed phases at room temperature. However, there are indications that this assumption is valid also in the latter case. Gottfried et al.[22] observed the intramolecular vibrational energy redistribution (IVR) rate in the S_1 state of anthracene in C_2Cl_4 to be within the temporal resolution of their apparatus (~ 2 ps), while cooling the vibrationally excited molecule, that is, energy

transfer to the solvent, was observed to proceed an order of magnitude slower (~ 25 ps).

The assumption that IVR is much faster than intermolecular energy relaxation considerably simplifies the description of the well dynamics. In the following discussion the molecular motion in the reactant well is taken to be completely characterized (on the relevant time scale) by the time evolution of the total molecular energy E_T; the energies in the different modes are determined from E_T by statistical considerations. In Section VI we also present the solution of a model in which IVR is slow relative to intermolecular relaxation, though this case is probably less relevant to the chemical reaction dynamics of polyatomic molecules in solution.

Finally we assume that the well dynamics region (determined by the time evolution of E_T) and the barrier dynamics region (governed by the one-dimensional flux across the saddle point) overlap somewhere below the barrier. Furthermore we assume that the reactive mode (defined near the barrier) keeps its identity below the barrier, at least down to this overlap region. The latter assumption is trivially always valid in a one-dimensional model.

Most of the ingredients of the model described above have been formerly postulated in treatments of unimolecular reactions. In particular, the model for the barrier dynamics is inherent in the usual TST for unimolecular reactions involving polyatomic molecules, while taking the total molecular energy E_T as the important dynamic variable in the well is the underlying assumption in theories that use a master or a diffusion equation for E_T as their starting point.

Use of the GLE, Eq. (4.1), as the starting point for the present treatment may raise questions concerning the generality of the model. Langevin equations are usually used in the context of Brownian motion, where a heavy particle exchanges energy in small steps with a bath made of light particles. The GLE, Eq. (4.1), is not limited in this way and with proper choice of the random force $R(t)$ may even describe low-pressure collisional relaxation. [In this case $R(t) \propto f(t - t_i)$, where $f(t)$ is a strongly peaked function centered about $t = 0$ which describes a single collisional event and $\{t_i\}$ are random times sampled from an appropriate distribution of collision times.] In the low-pressure (or low-friction) regime where energy relaxation dominates the escape rate, an alternative description of the process is provided by the energy master equation

$$\frac{\partial P(E, t)}{\partial t} = \int dE'\, K(E, E') P(E') - k(E) P(E) \quad (4.6)$$

where $k(E)$ is the dissociation rate of a molecule with energy E. The Langevin description with the reduction process that lead to an energy diffusion equa-

tion corresponds to the weak collision limit of Eq. (4.6), where $K(E, E')$ is strongly peaked about $E = E'$. This limit covers a large range of energy exchange processes in both condensed and gas-phase systems. The choice of kernel $Z(t)$ in Eqs. (4.1), (4.3), and (4.4) depends of course on the details of the interaction dynamics between the molecule and its environment. This issue has recently been discussed by Grote, van der Zwan, and Hynes.[23] In particular, following insight obtained from molecular dynamics simulations[24] on liquid Ar, these authors separate the friction Kernel into its collisional (short-time) and hydrodynamic (long-time) components. Hynes[25] has shown that for parabolic barrier crossing, the rate calculated from the GLE, Eq. (2.3), with a friction kernel approximated by its collisional component is numerically very close to that calculated from the BGK collision model[26] for the same system.

Another objection to the present model may be made on the basis of an interesting observation made by Rosenberg, Berne, and Chandler.[27] These authors performed molecular dynamics simulations for the isomerization of n-butane in liquid CCl_4 and observed that the computed rate does not change when the CCl_4 molecules are frozen in their initial configuration. As noted by the authors, for this system, which is characterized by a large solvent-to-solute mass ratio ($m_{CH}/m_{CCl} = 0.11$), once the molecule has enough energy to react, the dominant solvent effect is to cause energy transfer between intramolecular modes during collisions between the solute molecule and the surrounding solvent cage. In terms of the system's potential energy surface, this process is associated with the occurrence of three-body (two solute, one solvent) and higher order interaction terms. Part of the dynamics associated with such terms will be reflected in the impulsive part of the nondiagonal friction kernel $Z_{ab}(t)$ of Eq. (4.1). In addition such interactions will lead to anharmonic coupling terms between the reactive and nonreactive modes in Eqs. (4.3) and (4.4). These, together with anharmonic interactions associated with the intramolecular potential surface that were neglected in Eqs. (2.3) and (2.4), will give rise to an effective intramolecular friction affecting the motion of the reactive mode. Thus the reduced reactive mode equation, Eq. (4.1), is expected to remain formally the same. However, the effective friction tensor Z_R will contain contributions associated with the energy exchange between reactive and nonreactive modes. With this understanding the following discussion remains unchanged.

To end this section we note again that the assumption of fast intramolecular energy redistribution in the reactant well introduced the number n of molecular modes as an important parameter of the theory. In a broader context n is taken to be the number of strongly coupled molecular modes, and it is assumed that the reaction coordinate is part of this set. In liquid solvents n is expected to be equal to the total number $3N - 7$ of modes. In the low-pressure gas phase n can be smaller, and the possible slow energy transfer between different

regions of the molecular phase space (disregarded in the present model) may have a substantial influence on the reaction rate. Rates larger or smaller than those predicted by RRKM theory may be observed in isolated photoexcited molecules according to whether the reaction coordinate does or does not belong to the set of strongly coupled modes, which is initially excited.[28]

V. NON-MARKOVIAN EFFECTS IN THE ONE-DIMENSIONAL CASE

In this section we present an approximate solution for the rate associated with the multidimensional model, Eqs. (4.1) and (4.2). Here we focus on the equivalent one-dimensional model which disregards all modes but the reaction coordinate

$$\ddot{x} = -\frac{1}{m}\frac{dV(x)}{dx} - \int_0^t d\tau\, Z(t - \tau)\dot{x}(\tau) + \frac{1}{m}R(t) \tag{5.1}$$

$$\langle R(t)R(t')\rangle = Z(t - t')mk_BT, \quad \langle R(t)\rangle = 0 \tag{5.2}$$

The memory function $Z(t)$ is characterized by its Fourier–Laplace components

$$\hat{Z}_n(\omega) = \int_0^\infty dt\, Z(t)e^{-in\omega t} \tag{5.3}$$

with

$$\hat{Z}_0(\omega) = \int_0^\infty dt\, Z(t) = \gamma \tag{5.4}$$

In addition, $Z(t)$ is associated with the correlation time τ_c, which characterizes the time scale for its decay to zero. For specificity we shall often refer to the simple example

$$Z(t) = \frac{\gamma}{\tau_c}e^{-t/\tau_c} \tag{5.5}$$

$$\hat{Z}_n(\omega) = \frac{\gamma}{1 + in\omega\tau_c} \tag{5.6}$$

This model is often not realistic enough for a quantitative analysis of chemical

reactions in solutions (see below), but it contains much of the essential physics associated with the solvent relaxation.

Several workers have recently treated different aspects of the escape problem represented by Eqs. (5.1) and (5.2). Grote and Hynes[29] and later Hanggi and Mojtabai[30] have treated the non-Markovian problem associated with the barrier dynamics. This case corresponds to the Kramers intermediate-to-large friction case (Section II), where the escape rate at the top of the barrier is the rate-determining step. Carmeli and Nitzan[31] and Grote and Hynes[32] have treated the non-Markovian well dynamics (the analog of the Kramers low-friction limit where the escape is dominated by the well dynamics). A singular perturbation approach to these two cases was recently described by Dygas, Matkowski, and Schuss.[33]

Consider first the barrier dynamics problem, which is defined by replacing the potential barrier by an inverted parabola, Eq. (2.4), and by looking for a steady-state probability distribution which satisfies Eqs. (2.6) and (2.8). Here we follow the treatment of Hanggi and Mojtabai.[30] Equations (5.1) and (5.2), with $V(x) = E_B - \frac{1}{2}m\omega_B^2 x^2$, are used to obtain (with a procedure due to Adelman[34]) a generalized Fokker–Planck equation,

$$\frac{\partial P(x,v,t)}{\partial t} = \left[-v\frac{\partial}{\partial x} - \bar{\omega}^2(t)x\frac{\partial}{\partial v} \right]P + \bar{\gamma}(t)\frac{\partial}{\partial v}(vP) + \frac{k_B T}{m}\bar{\gamma}(t)\frac{\partial^2 P}{\partial v^2}$$
$$+ \frac{k_B T}{m\omega_B^2}[\bar{\omega}^2(t) - \omega_B^2]\frac{\partial^2}{\partial v\partial x}P \qquad (5.7)$$

where

$$\bar{\gamma}(t) = -\frac{d}{dt}\ln\phi(t) \qquad (5.8)$$

$$\bar{\omega}_B^2(t) = -\frac{\theta(t)}{\phi(t)} \qquad (5.9)$$

$$\phi(t) = \dot{\rho}(t)\left[1 + \omega_B^2\int_0^t d\tau\, \rho(\tau)\right] - \omega_B^2\rho^2(t) \qquad (5.10)$$

$$\theta(t) = \omega_B^2[\rho(t)\ddot{\rho}(t) - \dot{\rho}^2(t)] \qquad (5.11)$$

and where the function $\rho(t)$ is defined from

$$\rho(t) = \mathscr{L}^{-1}\left[\frac{1}{s^2 - \omega_B^2 + s\hat{Z}(-is)}\right] \qquad (5.12)$$

with $\mathscr{L}^{-1}$ being the inverse Laplace transform. Note that by Eq. (5.3),

$$\hat{Z}_1(-is) = \int_0^\infty dt\, e^{-st}Z(t) \qquad (5.13)$$

is the Laplace transform of $Z(t)$. In the Markovian limit,

$$\rho(t) = \mathscr{L}^{-1}\left[\frac{1}{s^2 - \omega_B^2 + s\gamma}\right] \qquad (5.14)$$

which may be used to show that $\bar{\gamma}(t) = \gamma$ and $\bar{\omega}_B^2(t) = \omega_B^2$ in this limit. To proceed we follow steps similar to those used to obtain Eqs. (2.23) and (2.24). We again look for a solution of the form

$$P(x,v,t) = f(x,v,t)\exp\left[-\frac{\frac{1}{2}mv^2 + V(x)}{k_B T}\right] \qquad (5.15)$$

and seek for F the form

$$f(x,v,t) = f(u,t), \qquad u = v + \Gamma x \qquad (5.16)$$

Inserting Eqs. (5.15) and (5.16) into Eq. (5.7) we get

$$\frac{\partial f}{\partial t} = -\frac{k_B T}{m}[\bar{\lambda}(t) + \Gamma]\frac{\partial^2 f}{\partial u^2} + \bar{\lambda}(t)\left[v - \frac{\omega_B^2}{\bar{\lambda}(t)}x\right]\frac{\partial f}{\partial u} \qquad (5.17)$$

where

$$\bar{\lambda}(t) - \left[\bar{\gamma}(t) + \Gamma\frac{\omega_B^2(t)}{\omega_B^2}\right] \qquad (5.18)$$

We further require, as our choice for Γ in Eq. (5.16), that

$$\lim_{t\to\infty}\bar{\lambda}(t) = -\frac{\omega_B^2}{\Gamma} \qquad (5.19)$$

It may be shown[35] that this limit exists. In fact, defining

$$\lim_{t\to\infty}\bar{\lambda}(t) = \lambda_0 \qquad (5.20)$$

it may be shown [35] that λ_0 is the largest (real and positive) root of the equation

$$\lambda^2 - \omega_B^2 + \lambda \hat{Z}_1(-i\lambda) = 0 \tag{5.21}$$

Note also that Eqs. (5.18) and (5.19) imply

$$\lambda_0 = \lim_{t\to\infty} \left[\bar{\omega}_B^2(t) + \left(\frac{\bar{\gamma}(t)}{2}\right)^2 \right]^{1/2} - \frac{\bar{\gamma}(t)}{2} \tag{5.22}$$

which becomes identical to ω_r of Eq. (2.24) in the Markovian limit.

Equations (5.18) and (5.19) imply that Eq. (5.17) admits a long-time steady-state solution which satisfies the equation

$$\frac{k_B T}{m} \frac{\partial^2 f}{\partial u^2} + \alpha u \frac{\partial f}{\partial u} = 0 \tag{5.23}$$

with

$$\alpha = \frac{\omega_B^2}{\Gamma^2 - \omega_B^2} \tag{5.24}$$

These results are identical in form to the expressions obtained in the Markovian case. [Note that Eqs. (2.11) and (2.13) yield Eq. (5.24).] The values of Γ and α are different here, but become identical to the values given by Eqs. (2.11) and (2.13) in the Markovian limit. Since the forms are the same, we may proceed as in Section II, Eqs. (2.14) to (2.19). In particular the steady-state distribution and current are given by

$$P_{ss}^{(B)}(x,v) = F \int_{-\infty}^{v-|\Gamma|x} dz \exp\left[-\frac{\alpha m z^2}{2k_B T} \right] P_{eq}(x,v) \tag{5.25}$$

$$j_B = FN \left[\frac{k_B T}{m}\right]^{3/2} \left(\frac{2\pi}{\alpha+1}\right)^{1/2} e^{-\beta E_B} \tag{5.26}$$

with

$$F = \left(\frac{\alpha m}{2\pi k_B T}\right)^{1/2} \tag{5.27}$$

and where α and Γ are defined by Eqs. (5.19) and (5.24). Dividing j_B by the normalization constant, Eq. (2.20), leads to

$$k = k^{(B)} = \frac{\lambda_0}{\omega_B} \frac{\omega_0}{2\pi} e^{-\beta E_B} \tag{5.28}$$

In the Markov limit this becomes identical to Eq. (2.23). From now on we shall use ω_r and λ_0 interchangeably.

Turning now to the non-Markovian well dynamics, one first needs to generalize the energy diffusion equation (2.32) to the non-Markovian regime. We recall that in this limit the damping is taken to be small enough so that in the energy-phase representation the phase distribution can be taken uniform and the energy may be focused on as the variable of interest. It is important to realize the existence of a well-defined time scale hierarchy associated with this limit

$$k \ll \gamma \; [\text{or } Z_n(\omega)] \ll \tau_c^{-1} \ll \omega \tag{5.29}$$

where k is the escape rate and ω the well frequency (for the energy considered). $\tau_c^{-1} \ll \omega$ implies that the process is non-Markovian in nature, while $\gamma \ll \tau_c^{-1}$ means that a Markovian description should be valid for the energy relaxation itself. [Note that, as is shown below, $\hat{Z}_n(\omega)$ replace γ as the rates associated with the energy relaxation in the non-Markovian case.] The condition for the escape rate to be a meaningful, measurable quantity is that k be smaller than all other rates. γ [or $Z_n(\omega)$] $\ll \omega$ is the (low damping) condition needed for the reduced (phase-eliminated) energy description to be valid. Other time scale hierarchies are of course possible. However, Eq. (5.29) is the most common one for molecular problems.

It is also important to realize that in most situations inequalities such as $\gamma \ll \omega$ hold for small enough energies, but break down near the barrier ($\omega \to 0$ at the escape threshold). The fact that the barrier solution, Eq. (5.28), is useful in many situations follows not because Eq. (5.29) is not valid inside the well but because the barrier, not the well, dynamics is the rate-limiting process in these situations. The energy diffusion equation to be derived below is almost always valid for describing vibrational energy relaxation inside the well, even when the barrier controls the escape rate.

Starting from Eqs. (5.1) and (5.2) and assuming that Eq. (5.29) holds, we first make the transformation $(x,v) \to (J,\phi)$, J being the action variable related to the energy by $E = \int^J \omega(J)\,dJ$ or $dE/dJ = \omega$. This transformation may be expressed in the form

$$x(J,\phi) = \sum_{n=0}^{\infty} x_n(J) e^{in\phi} \tag{5.30a}$$

$$v(J,\phi) = \sum_{n=0}^{\infty} v_n(J) e^{in\phi} \tag{5.30b}$$

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with

$$x_n = x_{-n}^*, \qquad v_n = v_{-n}^* \tag{5.31}$$

and

$$v_n(J) = in\omega(J)x_n(J) \tag{5.32}$$

Equation (5.1) then leads to

$$\dot{J} = -im \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} nx_n e^{in\phi} \int_0^t d\tau\, Z(t-\tau)v_m e^{im\phi} + iR(t) \sum_{n=-\infty}^{\infty} nx_n e^{in\phi} \tag{5.33}$$

$$\dot{\phi} = \omega(J) + m \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{\partial x_n}{\partial J} e^{in\phi} \int_0^t d\tau\, Z(t-\tau)v_m e^{im\phi}$$

$$- R(t) \sum_{n=-\infty}^{\infty} \frac{\partial x_n}{\partial J} e^{in\phi} \tag{5.34}$$

We now introduce an approximation based on the time scale ordering, Eq. (5.29). The memory kernel $Z(t)$ decays to zero in times of orders τ_c. For such short times we can write $|t - \tau| \lesssim \tau_c$,

$$\phi(\tau) \simeq \phi(t) - \omega(t - \tau) \tag{5.35}$$

$$v_m(\tau) \simeq v_m(t) \tag{5.36}$$

Therefore

$$\int_0^t d\tau\, Z(t-\tau)v_m(\tau)e^{im\phi(\tau)} \simeq v_m(t)e^{im\phi(t)} \int_0^t d\tau\, Z(t-\tau)e^{-im\omega(t-\tau)} \tag{5.37}$$

and for $t \gg \tau_c$,

$$\int_0^t d\tau\, Z(t-\tau)v_m(\tau)e^{im\phi(\tau)} \simeq v_m(t)e^{im\phi(t)}\hat{Z}_m(\omega) \tag{5.38}$$

where $\hat{Z}_m(\omega)$ is defined by Eq. (5.6).

Substituting Eq. (5.38) into Eqs. (5.33) and (5.34) leads to

$$\dot{J} = -im \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} nx_n v_m \hat{Z}_m e^{i(n+m)\phi} + iR(t) \sum_{n=-\infty}^{\infty} nx_n e^{in\phi} \tag{5.39}$$

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$$\dot{\phi} = \omega + m \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} x_n' v_m \hat{Z}_m e^{i(n+m)\phi} - R(t) \sum_{n=-\infty}^{\infty} x_n' e^{in\phi} \tag{5.40}$$

where $x_n' = dx_n/dJ$. Despite their appearance these equations are not Markovian because the random force $R(t)$ is characterized by the finite correlation time τ_c.

The time evolution of the probability distribution $P(J, \phi, t)$ is determined by the equation

$$\frac{\partial P}{\partial t} = \lim_{\tau \to 0+} \left\{ \frac{1}{\tau} \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \sum_{\substack{m,k=0 \\ (m+k=n)}}^{\infty} \left(\frac{\partial}{\partial J}\right)^m \left(\frac{\partial}{\partial \phi}\right)^k [\langle (\Delta J_t)^m (\Delta \phi_t)^k \rangle P] \right\} \tag{5.41}$$

where $\Delta W_t = \Delta W_t(\tau) = W(t + \tau) - W(t)$, W being J or ϕ. The limit in Eq. (5.41) should be understood as taking $\tau \ll \gamma^{-1}$. However, τ is kept larger than τ_c (and ω^{-1}) in order to yield a coarse-grained Markovian equation. Our task is therefore to evaluate moments of the form $\langle (\Delta J_t)^m (\Delta \phi_t)^k \rangle$. The standard procedure[36] is to use

$$\Delta J_t(\tau) = \int_0^\tau ds\, \dot{J}(J(t+s), \phi(t+s), t+s)$$

where $\dot{J}(J, \phi, t)$ is given by Eq. (5.39), as a basis for iteration in the form

$$\Delta J_t^{(l)}(\tau) = \int_0^\tau ds\, \dot{J}(J(t) + \Delta J_t^{(l-1)}(s), \phi(t) + \Delta \phi_t^{(l-1)}(s), t+s)$$

where l denotes the lth iteration stage. A similar iteration procedure is used to evaluate $\Delta \phi$.

In the Markovian case, where τ_c is the shortest time scale, it is usually found[36] that (1) moments of the form $\langle (\Delta J)^m (\Delta \phi)^k \rangle$ with $m + k > 2$ are of order τ^n, $n \geq 2$, and therefore do not contribute to Eq. (5.41), and (2) all the relevant terms (that is, terms of order τ) which contribute to the first and second moments ($m + k = 1$ or 2) are obtained at the second iteration stage. This leads to the standard Fokker–Planck equation.

The present non-Markovian case is different. Terms of order τ are obtained in all orders of the iteration procedure, forcing us in principle to consider an infinite number of contributions to Eq. (5.41). Simplification is achieved by, in calculating the moments $\langle (\Delta J_t)^m (\Delta \phi_t)^k \rangle$, neglecting terms of order τ^n, $n > 1$, as required by Eq. (5.41), or $[\hat{Z}(\omega)/\omega]^n$, $n \geq 1$. (This is the low-friction limit.) Note that $\hat{Z}(\omega)/\omega \ll 1$ may be satisfied even if $\gamma (= \hat{Z}(\omega = 0))$ is not smaller than ω [see Eq. (5.6)].

We skip the technical details,[31] which are straightforward but very cumbersome, and note only that, as in the Markovian case, only first and second moments yield terms that are not negligible by these criteria. Unlike in the Markovian case, three iteration steps are needed to collect all relevant contributions to these moments. The final result is the Fokker–Planck equation for $P(J, \phi, t)$,

$$\frac{\partial P(J, \phi, t)}{\partial t} = \frac{\partial}{\partial J} \left\{ \varepsilon(J) \left[k_B T \frac{\partial}{\partial J} + \omega(J) \right] P \right\} + \Gamma(J) \frac{\partial^2 P}{\partial \phi^2} - \Omega(J) \frac{\partial P}{\partial \phi} \quad (5.42)$$

where*

$$\varepsilon(J) = 2m \sum_{n=1}^{\infty} n^2 |x_n|^2 \hat{Z}_n^c \quad (5.43)$$

$$\Gamma(J) = 2mk_B T \sum_{n=1}^{\infty} \left| \frac{dx_n}{dJ} \right|^2 \hat{Z}_n^c + mk_B T \left(\frac{dx_0}{dJ} \right)^2 \gamma \quad (5.44)$$

$$\Omega(J) = \omega(J) + m \left(\omega(J) - k_B T \frac{\partial}{\partial J} \right) \sum_{n=1}^{\infty} n \left| \frac{dx_n}{dJ} \right|^2 \hat{Z}_n^s, \quad (5.45)$$

and where

$$\hat{Z}_n^c = \int_0^{\infty} dt \, Z(t) \cos(n\omega t)$$

$$\hat{Z}_n^s = \int_0^{\infty} dt \, Z(t) \sin(n\omega t) \quad (5.46)$$

If at $t = 0$, $P(J, \phi) = P(J)$, independent of ϕ, it will remain independent of ϕ at all time and will satisfy the equation

$$\frac{\partial P(J, t)}{\partial t} = \frac{\partial}{\partial J} \left\{ \varepsilon(J) \left[k_B T \frac{\partial}{\partial J} + \omega(J) \right] P \right\} \quad (5.47)$$

Finally, transforming variables from J to E, using $dE = \omega(E) \, dJ$, Eq. (5.47) yields the energy diffusion equation

$$\frac{\partial P(E, t)}{\partial t} = \frac{\partial}{\partial E} \left[D(E) \left(k_B T \frac{\partial}{\partial E} + 1 \right) \omega(E) P(E, t) \right] \quad (5.48)$$

* The second term of Eq. (5.44) is erroneously missing in Eqs. (51) of Carmeli and Nitzan.[31a]

where, with $\varepsilon(E) = \varepsilon(J(E))$, $\omega(E) = \omega(J(E))$,

$$D(E) = \varepsilon(E)\omega(E) \quad (5.49)$$

Equation (5.48) is of the same form as Eq. (2.32), with a different function $D(E)$. In the Markov limit $Z(t) = 2\gamma\delta(t)$, $\hat{Z}_n(\omega) = \gamma$, and Eq. (5.42) becomes

$$\varepsilon(J) = \frac{\gamma J}{\omega(J)} \quad (5.50)$$

To prove Eq. (5.50), the identity $J = 2m\omega(J) \sum_{n=1}^{\infty} n^2 |x_n|^2$ is used. This identity is obtained by inserting the expansions (5.30) into the definition

$$J = \left(\frac{m}{2\pi} \right) \oint v(x) \, dx = \frac{m}{2\pi} \int_0^{2\pi} d\phi \, v(J, \phi) \left(\frac{\partial x(J, \phi)}{\partial \phi} \right)$$

Thus Eq. (5.49) leads to Eq. (2.33).

If the well dynamics dominates the escape rate, we can now follow the development that leads from Eq. (2.32) to Eq. (2.39). In particular the steady-state energy distribution $P_{ss}^{(W)}(E)$, the steady-state energy flux, and the well dynamics dominated rates are [see Eqs. (2.37) to (2.39)]

$$P_{ss}^{(W)}(E) = P_{eq}(E) \left[1 - \beta j_E \int_0^E dE' \frac{e^{\beta E'}}{D(E')} \right] \quad (5.51)$$

$$j_E = \left[\beta \int_0^{E_B} dE' \frac{e^{\beta E'}}{D(E')} \right]^{-1} \quad (5.52)$$

$$k = k^{(W)} = \left[\beta \int_0^{E_B} dE \, \omega^{-1}(E) e^{-\beta E} \int_0^{E_B} dE' \frac{e^{\beta E'}}{D(E')} \right]^{-1} \quad (5.53)$$

with $D(E)$ given by Eq. (5.49). For deep enough wells the same approximation that leads to Eq. (2.41) results in

$$k^{(W)} = \beta D(E_B) \omega_0 e^{-\beta E_B} \quad (5.54)$$

In this limit, however, non-Markovian effects are no longer important because $\omega(E \to E_B) \to 0$ so that $\omega(E) \ll \tau_c^{-1}$, so the evolution becomes Markovian near the barrier. Eqs. (5.49) and (5.50) then imply that Eq. (5.54) is identical to Eq. (2.41) in this limit.

To compute $k^{(W)}$ from Eq. (5.53) one needs to know the functions $\omega(E)$ and $D(E)$ [or $\varepsilon(E)$]. $\omega(E)$ is a property of the potential, while $\varepsilon(E)$ depends on the

potential surface and on the dissipation process. For some cases $\varepsilon(E)$ may be obtained analytically. For a harmonic oscillator $x_n(E) = E/(2m\omega^2)\delta_{|n|,1}$ so that

$$\varepsilon(E) = \frac{E}{\omega^2}\hat{Z}_1^c \qquad (5.55)$$

For a Morse oscillator, $V(x) = D\{e^{-2(x-x_0)/a} - 2e^{-(x-x_0)/a}\}$, it can be shown[31] that

$$|x_n(J)|^2 = \frac{a^2}{n^2}\left(\frac{\omega_0 J}{4D - \omega_0 J}\right)^n, \qquad n \geq 1 \qquad (5.56)$$

[the relation between J and E is $E = -D(1 - \omega_0 J/2D)^2$] which, with Eq. (5.43), may be used for an easy numerical evaluation of $\varepsilon(J)$. For other potential surfaces ε can be evaluated from

$$\varepsilon(E) = \frac{m}{\omega^2(E)}\int_0^\infty dt\, Z(t)\overline{(v(0)v(t))}_E \qquad (5.57)$$

where $\overline{(v(0)v(t))}_E$ is obtained from the motion of the isolated system at a given E (the average is over the initial phase). Equation (5.57) may be obtained from Eq. (5.43) (see Appendix D of Carmeli and Nitzan[35]) but is most easily obtained as follows. From Eq. (5.48) at $T = 0$ we get, by multiplying by E and integrating over it,

$$\frac{d\langle E\rangle}{dt} = -\langle D(E)\omega(E)\rangle \qquad (5.58)$$

where the average is over the instantaneous energy distribution. This means that $-D(E)\omega(E)$ is the rate of energy damping when the system energy is E. On the other hand from the zero temperature limit of Eq. (5.1),

$$\ddot{x} = -\frac{1}{m}\frac{dV(x)}{dx} - \int_0^t d\tau\, Z(t - \tau)\dot{x}(\tau) \qquad (5.59)$$

by multiplying by $\dot{x}$ and using $m\ddot{x}\dot{x} + \dot{x}\,dV(x)/dx = dE/dt$, we get

$$\left(\frac{dE}{dt}\right)_{T=0} = -m\int_0^t d\tau\, Z(t - \tau)\dot{x}(t)\dot{x}(\tau) \qquad (5.60)$$

Averaging over all initial conditions associated with a given total energy E (that is, over the phase) leads to

$$\left(\frac{dE}{dt}\right)_{T=0} = -m\int_0^\infty d\tau\, Z(t)\overline{(\dot{x}(t)\dot{x}(0))}_E \qquad (5.61)$$

The subscript E on the right-hand side denotes fixed E (undamped trajectory). Computing $\dot{x}(t)\dot{x}(0)$ without damping is consistent with the low-friction limit where damping is assumed to be small on the time scale τ_c associated with $Z(t)$ [see Eq. (5.29)]. Comparing the two results for $(dE/dt)_{T=0}$ and using Eq. (5.49) we get the result Eq. (5.57). Equation (5.57) provides a convenient numerical way to compute $\varepsilon(E)$; all one needs is to run a trajectory over the undisturbed molecular motion at the given E for a time of several τ_c.

In the small damping limit it is also possible to obtain an energy diffusion equation for the case where the friction kernel (and the associated random noise) are position dependent.[37] A convenient model with such property is given by*

$$\dot{x} = v \qquad (5.62)$$

$$\dot{v} = -\frac{1}{m}\frac{dV(x)}{dx} - f(x(t))\int_0^t d\tau\, Z(t - \tau)f(x(\tau))v(\tau) + \frac{1}{m}f(x(t))R(t) \quad (5.63)$$

$$\langle R(t)\rangle = 0, \qquad \langle R(t_1)R(t_2)\rangle = mk_B T Z(t_1 - t_2) \qquad (5.64)$$

It should be noted that Eq. (5.63) may be derived from a microscopic model[39,40] only for the special case where the friction kernel does not depend on the particle's velocity. This is not generally the case, and a rigorous derivation of reduced stochastic equations describing the motion of a subsystem coupled nonlinearly to its thermal environment leads to more complicated equations. (See the References for further discussions of this issue[39–42].) Equation (5.63) may still be derived for special cases. An analysis very similar to that presented above leads to the energy diffusion equation (5.48) where now $D(E)$ is given by

$$D(E) = 2m\omega(E)\sum_{n=1}^\infty n^2|G_n(E)|^2\hat{Z}_n^c(\omega(E)) \qquad (5.65)$$

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* For a discussion of the limitation of Langevion equations with position-dependent random noise, see van Kampen.[38] As discussed there, there is no ambiguity for non-Markovian equations of this type.

and where $G_n(E) = G_n(J(E))$ is related to $G(x) = \int^x dx' f(x')$ by

$$G(J, \phi) = \sum_{n=-\infty}^{\infty} G_n(J)e^{in\phi} \qquad (5.66)$$

where the transformation $(xv) \rightarrow (J\phi)$ has been used. Note that $D_1(E)$ of Eq. (5.49) is a special case of Eq. (5.64), in which $f(x) = 1$ and $G(x) = x$. With the new $D(E)$ the results, Eqs. (5.51)–(5.54), remain unchanged.

VI. THE ESCAPE RATE OF A NON-MARKOV MULTIDIMENSIONAL PROCESS

In this section we present the general solution for the steady-state ecape rate associated with the model desirbed in Section IV. First the treatment of Section V is generalized to the multidimensional case. Second the solutions for the barrier region and for the well region are combined such as to satisfy appropriate boundary conditions. Finally the overall rate is obtained from the combined solution.

A. Barrier Dynamics

Starting from the set of equations (4.3) and (4.4), which are linearized about the saddle point, we follow Grote and Hynes[20] and derive a single equation for the reactive mode by formally solving Eq. (4.4), then inserting the solution for $x_j(t)$ into Eq. (4.3). The result is

$$\ddot{x}_R(t) = \omega_B^2 x_R - \int_0^t d\tau \, Z_R(t - \tau)\dot{x}_R(\tau) + \rho_R(t) \qquad (6.1)$$

$$\langle \rho_R(t)\rho_R(t')\rangle = Z_R(t)/\beta \qquad (6.2)$$

where $Z_R(t)$ is given in terms of its inverse Laplace transform $\hat{Z}_R(s) = \int_0^\infty dt \, e^{-st} Z_R(t)$,

$$\hat{Z}_R(s) = \hat{Z}_{RR}(s) - \sum_j \sum_{j'} \hat{Z}_{Rj}(s) M_{jj'}(s)\hat{Z}_{j'R}(s) \qquad (6.3)$$

$$\hat{M}(s) \equiv \left(s\mathbf{I} + \hat{\mathbf{Z}}(s) + \frac{1}{s}\mathbf{\Omega}^2\right)^{-1} \qquad (6.4)$$

$$\mathbf{\Omega}^2 \equiv \begin{pmatrix} \omega_1^2 & & 0 \\ & \omega_2^2 & \\ 0 & & \ddots \end{pmatrix} \qquad (6.5)$$

Here $\mathbf{I}$ is the unit matrix and $\mathbf{\Omega}^2$ is the frequency square matrix in the space of nonreactive modes. Equation (6.1) is a generalized Langevin equation of the form used in treating the one-dimensional case in Section V, and leads to the result of Eq. (5.25) (with $m = 1$) for the steady-state probability distribution of the reactive mode near the barrier. In the present multidimensional treatment it is convenient to redefine the distribution according to

$$P^{(B)}(x, v) = \frac{Q_{n-1}(x, v)}{2\pi\hbar Q_n} F e^{-\beta E(x,v)} \left[\sqrt{\frac{\pi}{2\alpha\beta}} + \int_0^{v-|\Gamma|x} dz \, e^{-1/2\beta\alpha z^2} \right] \qquad (6.6)$$

where

$$E(x, v) = E_B + \tfrac{1}{2}v^2 - \tfrac{1}{2}\omega_B^2 x^2 \qquad (6.7)$$

[α and Γ are defined by Eqs. (5.19–5.21) and (5.24)], and where Q_n and $Q_{n-1}(x, v)$ are, respectively, the molecular partition function and the partition function corresponding to the $n - 1$ nonreactive modes, given that the reactive mode is held in position x and velocity v,

$$Q_n = \int_0^\infty dE_T \, \rho_n(E_T)e^{-\beta E_T} \qquad (6.8)$$

$$Q_{n-1}(x, v) = \int_0^\infty dE_{n-1} \, \rho_{n-1}(E_{n-1}|x, v)e^{-\beta E_{n-1}} \qquad (6.9)$$

$\rho_n(E)$ is the molecular density of states per unit energy, and $\rho_{n-1}(E|x, v)$ is the density of states associated with the $n - 1$ nonreactive modes given that the reactive mode is in state (x, v). The notations E_T and E_{n-1} for the integration variables keep track of the meaning of E_T as the total molecular energy and E_{n-1} as the energy associated with the nonreactive modes. [The energy of interaction between reactive and nonreactive modes is assumed small and is neglected in Eq. (6.9) apart from the x, v dependence of ω_j, $j = 1, \ldots, n - 1$, which is the source of the x, v dependence of ρ_{n-1} and Q_{n-1}. This assumption is valid near the barrier. Also note that in most applications the v dependence of $\rho_{n-1}(E_{n-1}|x, v)$ and of $Q_{n-1}(x, v)$ may be disregarded.]

The steady-state molecular distribution near the saddle point may be written explicitly by invoking two assumptions valid in that region. First, because the reactive and nonreactive modes are nearly uncoupled, the molecular distribution is written as a product of both. Second because near the barrier the reactive flux is directed along the reactive mode coordinate, the distribution function of the $n - 1$ nonreactive mode system is approximated by its

thermal equilibrium form

$$P_M^{(B)}(x, v; E_{n-1}) = P^{(B)}(x, v)P_{n-1, \text{eq}}^{(B)}(E_{n-1}|x, v) \qquad (6.10)$$

$$P_{n-1, \text{eq}}^{(B)}(E_{n-1}|x, v) = \frac{1}{Q_{n-1}(x, v)} \rho_{n-1}(E_{n-1}|x, v)e^{-\beta E_{n-1}} \qquad (6.11)$$

Note that the total energy associated with the state $(x, v; E_{n-1})$ is

$$E_T = E_{n-1} + E(x, v) \qquad (6.12)$$

where $E(x, v)$ is given near the barrier by Eq. (6.7) and the reactive–nonreactive interaction energy was again neglected.

It is important to understand the difference between the forms of Eqs. (5.25) and (6.6) for the reactive mode distribution. Equation (5.25) is the strictly one-dimensional form whose equilibrium limit is the unnormalized form, $\exp[-\beta E(x, v)]$. Equation (6.6) is the proper expression for the multi-dimensional case, obtained by integrating the overall molecular distribution $P_M^{(B)}$ over all the nonreactive coordinates and momenta. Its extension beyond the barrier region, for all (x, v), is normalized to unity because $\int (dx\, dv/2\pi\hbar)Q_{n-1}(x, v)P(x, v) = Q_n$.* The difference between Eqs. (5.25) and (6.6) accounts for the different volumes of phase space associated with the presence of the nonreactive modes.

The steady-state flux along the reaction coordinate is obtained from

$$j^{(B)} = \int_0^\infty dE_{n-1} \int_{-\infty}^\infty dv\, vP_M^{(B)}(x, v; E_{n-1})$$

$$= \int_{-\infty}^\infty dv\, vP^{(B)}(x, v) \qquad (6.13)$$

Using Eq. (6.6) and replacing near the barrier $Q_{n-1}(x, v)$ by $Q_{n-1}(E_B)$, to be denoted by $Q_{n-1}^{(B)}$, lead to

$$j^{(B)} = \frac{Q_{n-1}^{(B)}}{2\pi\hbar Q_n} F\beta^{-3/2} \sqrt{\frac{2\pi}{\alpha + 1}} e^{-\beta E_B} \qquad (6.14)$$

If the thermal relaxation within the reactant well is fast, the constant F in Eq.

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* The partition function corresponding to an equilibrium situation is obtained for deep enough wells, because most of the contribution to the integral comes from the well region where the equilibrium distribution is a good approximation.

(6.6) can be determined by the requirement that $P^{(B)}(x, v) \to P_{\text{eq}}(x, v)$ as $x \to -\infty$. This and Eq. (6.6) imply that under this condition

$$F = \sqrt{\frac{\alpha\beta}{2\pi}} \qquad (6.15)$$

Using Eq. (6.15), Eq. (6.14) leads to the barrier dominated steady-state rate

$$k^{(B)} = j^{(B)} = \frac{1}{2\pi\hbar\beta} \frac{Q_{n-1}^{(B)}}{Q_n} \frac{\omega_r}{\omega_B} e^{-\beta E_B} \qquad (6.16a)$$

An equivalent expression is obtained by using

$$Q_n = \frac{1}{\hbar} \int_0^\infty dE \frac{Q_{n-1}(E)e^{-\beta E}}{\omega_R(E)} \simeq \frac{Q_{n-1}^{(0)}}{\beta\hbar\omega_R(0)} \qquad (6.17)$$

where $Q_{n-1}(0)$ denotes the partition function associated with the subsystem of nonreactive modes when the reactive mode is in its ground state. Equation (6.16a) then becomes identical to the result of Hynes and coworkers,[20,21]

$$k^{(B)} = \frac{\omega_r}{\omega_B} \frac{\omega_R(0)}{2\pi} \frac{Q_{n-1}^{(B)}}{Q_{n-1}^{(0)}} e^{-\beta E_B} = k_{\text{TST}} \frac{\omega_r}{\omega_B} \qquad (6.16b)$$

In the Markovian limit, $Z_R(t) = 2\gamma_R\delta(t)$ and $\hat{Z}_R(\lambda) = \gamma_R$. ω_r is then given by Eq. (2.24), and Eq. (6.16b) becomes the well-known Markovian multidimensional result.[43-45] If moreover $Q_{n-1}^{(B)} = Q_{n-1}^{(0)}$, that is, the nonreactive subsystem is not affected by the state of the reactive mode, this becomes the Kramers one-dimensional result.

B. Well Dynamics

As in the one-dimensional treatment, the atomic motion in the reactant well is assumed to be characterized by a time scale separation between the slow energy variable and the rapidly varying phases. However, in accordance with our model assumption (Section IV) it is the total molecular energy that is assumed to be (relatively) slow. Individual mode energies fluctuate rapidly and are estimated only by statistical considerations.

In order to make contact later with the barrier dynamics, we need $P^{(W)}(E)$, the probability that the energy of the reactive mode is E. We note in passing that $P^{(W)}(E)$ is meaningful only provided that the reactive mode (defined near the barrier) keeps its identity in the well region. We show below that it is enough that this will be so high in the well, below the barrier region.

The probability $P^{(W)}(E)$ can be expressed in terms of $P_M^{(W)}(E_T)$, the probability distribution for the total molecular energy E_T, and the conditional probability distribution $P^{(W)}(E|E_T)$ for the reactive mode to have energy E, given that the total molecular energy is E_T,

$$P^W(E) = \int_0^\infty dE_T\, P_M^{(W)}(E_T) P^{(W)}(E|E_T) \tag{6.18}$$

Note that $P^{(W)}(E|E_T) = 0$ for $E_T < E$, so the lower bound in the integration can be taken to be E.

The assumption of complete statistical distribution of energy within the n strongly coupled modes leads immediately to the following expression for $P^{(W)}(E|E_T)*$:

$$P^{(W)}(E|E_T) = \frac{1}{\hbar\omega_R(E)} \frac{\rho_{n-1}(E_T - E)}{\rho_n(E_T)} \tag{6.19}$$

To find the distribution $P_M^{(W)}(E_T)$ of the molecular energy, we need a diffusion equation for E_T which is analogous to the one-dimensional equation (5.48). In Eq. (5.48) $D(E)$ is related to the rate of energy loss at zero temperature,

$$\left(\frac{dE}{dt}\right)_{T=0} = -D(E)\omega(E) \tag{6.20}$$

and the frequency $\omega(E)$ appears in order to satisfy detailed balance. At equilibrium $(k_B T \partial/\partial E + 1)\omega(E) P_{eq}(E) = 0$ leads to

$$P_{eq}(E) \propto \frac{1}{\omega(E)} e^{-\beta E} \tag{6.21}$$

The obvious generalization of Eq. (5.48) to the multidimensional case is therefore

$$\frac{\partial P_M^{(W)}(E_T, t)}{\partial t} = \frac{\partial}{\partial E_T}\left[D(E_T)\left(k_B T \frac{\partial}{\partial E_T} + 1\right)\rho_n^{-1}(E_T) P_M^{(W)}(E_T, t)\right] \tag{6.22}$$

where $D(E_T)$ is related now to the rate of molecular energy dissipation at

* Note that $\rho_n(E_T - E)$ depends not only on the differences $E_T - E$, but also explicitly on E. This explicit E dependence comes from the dependence of the nonreactive mode frequencies on the reactive mode energy E.

$T = 0$,

$$\left(\frac{dE_T}{dt}\right)_{T=0} = -D(E_T)\rho^{-1}(E_T) \tag{6.23}$$

An explicit expression for $D(E_T)$ can be obtained from Eq. (4.1) which, for $T = 0$,

$$\ddot{x}_a = -\frac{\partial U}{\partial x_a} - \int_0^t d\tau \sum_b Z_{ab}(t - \tau)\dot{x}_b(\tau) \tag{6.24}$$

Multiplying by $\dot{x}_a$ and summing over $a = 1, \ldots, n$, using also $E_T = \frac{1}{2}\sum_a \dot{x}_a^2 + U(\{x\})$ and $\sum_a(\partial U/\partial x_a)\dot{x}_a = dU/dt$, we get

$$\left(\frac{dE_T}{dt}\right)_{T=0} = -\int_0^t d\tau \sum_a \sum_b Z_{ab}(t - \tau)\dot{x}_a(t)\dot{x}_b(\tau) \tag{6.25}$$

Invoking the model assumption that slow variation of E_T relative to the relaxation time associated with $Z_{ab}(t - \tau)$ (the latter being essentially the characteristic solvent relaxation time), and averaging the product $\dot{x}_a(t)\dot{x}_b(\tau)$ over all initial phases, assuming further that the averaged product $\dot{x}_a(t)\dot{x}_b(\tau)$ depends only on $t - \tau$, we get

$$\left(\frac{dE_T}{dt}\right)_{T=0} = -\int_0^\infty dt \sum_a \sum_b Z_{ab}(t)\overline{\dot{x}_a(t)\dot{x}_b(0)} \tag{6.26}$$

and

$$D(E_T) = \rho_n(E_T) \int_0^\infty dt \sum_a \sum_b Z_{ab}(t)\overline{(\dot{x}_a(t)\dot{x}_b(0))}_{E_T} \tag{6.27}$$

Equation (6.27) may be used for evaluating $D(E_T)$ using simulations based on Eq. (4.1). Such simulations will yield the correlation function $(\overline{\dot{x}_a(t)\dot{x}_b(0)})_E$. The average is over the initial phase and the subscript E_T denotes the fact that the total molecular energy does not change during these simulations. For a small molecule $\overline{\dot{x}_a(t)\dot{x}_b(0)}$ can be evaluated in the absence of molecule–thermal bath coupling, so that E_T is obviously constant. This is the lowest order approximation in the molecule bath coupling to Eq. (6.27). For large molecules the coupling to the environment may strongly affect intramolecular energy redistribution and should be included in evaluating $\overline{\dot{x}_a(t)\dot{x}_b(0)}$ using Eq.(4.1). Our model assumptions still imply that E_T does not change appreciably during

the relevant time for this calculation, that is, the relaxation time associated with $Z_{ab}(t)$.

Equation (6.27) has also been derived by Zawadzki and Hynes,[46a] and its Markovian equivalent has been obtained by Borkovec and Berne.[46b] Zawadzki and Hynes[46a] have also shown that for the case where only diagonal elements ($a = b$) appear in Eq. (6.27), it may be simplified to

$$D(E_T) = N(E) \int_0^\infty dt \sum_{a=1}^n Z_a(t)\pi_a(t) \qquad (6.28)$$

where

$$N(E) = \int_0^E dE' \rho_n(E') \qquad (6.29)$$

and

$$\pi_a(t) = \frac{(\overline{\dot{x}_a(t)\dot{x}_a(0)})_{E_T}}{(\dot{x}_a^2)_{E_T}} \qquad (6.30)$$

The Smoluchowski type equation (6.22) is of the same formal form as the equivalent equation (5.48) of the one-dimensional case. Its general steady state ($\partial P_M^{(W)}/\partial t = 0$) solution is

$$P_{M,ss}^{(W)}(E_T) = \frac{1}{Q_n}\rho_n(E_T)e^{-\beta E}\left[A_1 + A_2 \int_{E_T}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}\right] \qquad (6.31)$$

and the steady-state flux $[j = D(k_BT\partial/\partial E + 1)\rho_n^{-1}P_{M,ss}^{(W)}]$ is

$$j^{(W)} = \frac{A_2}{Q_n\beta} \qquad (6.32)$$

In Eq. (6.31) A_1, A_2, and E_{1T} are constants to be destermined by the boundary conditions. Note that only two of these are independent. At equilibrium $A_2 = 0$ and $A_1 = 1$.

Having found explicit expressions for $P^{(W)}(E|E_T)$ [Eq. (6.19)] and for $P^{(W)}(E|E_T)$ [Eq. (6.31)], we can insert them into Eq. (6.18) to get the reactive mode steady-state distribution $P^{(W)}(E)$. This calculation (Appendix A) yields

$$P_{ss}^{(W)}(E) = \frac{Q_{n-1}(E)e^{-\beta E}}{\hbar\omega_R(E)Q_n}\left[A_1 + A_2 \int_E^{E_1} dE' \frac{e^{\beta(E'+\bar{\varepsilon})}}{D(E+\bar{\varepsilon})}\right] \qquad (6.33)$$

where

$$E_1 = E_{1T} - \bar{\varepsilon} \qquad (6.34)$$

and where $\bar{\varepsilon}$ is the value of ε for which the expression $\rho_{n-1}(\varepsilon)e^{-\beta\varepsilon}$ achieves its maximum value. In the high-barrier high-temperature limit it is approximately equal to the thermal energy in the nonreactive modes,

$$\bar{\varepsilon} \simeq (n-1)\beta \qquad (6.35)$$

Note that, in this approximation, if E is the energy in the reactive mode, $E + \bar{\varepsilon}$ is approximately the corresponding total molecular energy.

The steady-state flux $j^{(W)}(E)$ associated with the reactive-mode steady-state distribution, Eq. (6.33), is the same as that [Eq. (6.32)] associated with the total energy distribution, Eq. (6.31),*

$$j^{(W)}(E) = \frac{A_2}{Q_n\beta} \qquad (6.36)$$

C.　The Combined Solution

The assumption that relaxation within the reactant well is fast so that $P^{(W)}(E)$ is well described by a Boltzmann distribution (that is, $A_2 = 0$) leads to the barrier dominated rate, Eq. (6.16). When this assumption does not hold, the unknown constants F in Eq. (6.6) and A_1, A_2, and E_1 in Eq. (6.33) have to be determined by matching these barrier and well solutions together. To this end we follow the procedure of Carmeli and Nitzan[35] and choose to match the solutions at some point (x_1, $v_1 = 0$) corresponding to an energy E_1 in the reactive mode ($E_1 = E_B - \frac{1}{2}\omega_B^2 x^2$). We assume that there is at least one such point where both the barrier and the well solutions are valid. Since E_1 in Eq. (6.33) can be chosen arbitrarily, we choose it to be this matching energy. At this point we require that the well steady-state distribution [Eq. (6.33)] and the corresponding barrier distribution [Eq. (6.6)] be equal,

$$\frac{\omega_R(E_1)}{2\pi}p^{(W)}(E_1) = P^{(B)}(x_1, v_1 = 0) \qquad (6.37a)$$

The $\omega/2\pi$ term arises from the $(x,v) \to (E,\phi)$ transformation together with the observation that in the well the ϕ distribution is $(2\pi)^{-1}$. Similarly the energy

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* This follows from the assumption that the intramolecular vibrational energy redistribution is fast on the relevant time scale.

derivatives are taken to be equal at this point,

$$\left[\frac{\partial}{\partial E}P^{(B)}(x, v = 0)\right]_{x_1} = \frac{1}{2\pi}\left[\frac{\partial}{\partial E}(\omega(E)P^{(W)}(E))\right]_{E_1} \quad (6.37b)$$

Finally the steady-state fluxes, Eqs. (6.14) and (6.35), should be the same

$$j^{(B)} = j^{(W)} \quad (6.38)$$

The three conditions, Eqs. (6.36)–(6.38), together with the requirement that the overall distribution be normalized, are just sufficient to determine the three unknown constants A_1, A_2, and F and the matching point energy E_1. These conditions lead to

$$\frac{A_2}{F} = Q_{n-1}^{(B)}\beta^{-1/2}\sqrt{\frac{2\pi}{\alpha + 1}}e^{-\beta E_B} \quad (6.39)$$

$$\frac{A_1}{F} = \pi\hbar\beta^{-1/2}\sqrt{\frac{2\pi}{\alpha}}\{1 + \mathrm{erf}[\sqrt{(\alpha + 1)\beta(E_B - E_1)}]\} \quad (6.40)$$

and

$$\frac{Q_{n-1}^{(B)}}{(\alpha + 1)D(E_1 + \bar{\varepsilon})}\left[\frac{\alpha(E_B - E_1)}{\pi\beta}\right]^{1/2}e^{\beta[\alpha(E_B - E_1) + \bar{\varepsilon}]} = 1 \quad (6.41)$$

Equation (6.41) may be solved for E_1. To see its significance, consider the limits of large and small molecules. For $n = 1$, $\bar{\varepsilon} = 0$, $Q_{n-1} = 1$, and $D(E) = \omega^{-1}\int_{-\infty}^{\infty}dt\,Z(t)\dot{x}(t)\dot{x}(0) = \omega(E)\varepsilon(E)$, where $\varepsilon(E)$ is defined in Section V. In this limit Eq. (6.41) reduces to Eq. (3.19) of Carmeli and Nitzan.[35] For a particular model of the memory kernel the resulting E_1 is displayed as a function of friction in their Fig. 2.[35] Generally $E_1 \to E_B$ for small friction and $E_1 \to 0$ when the friction becomes very large.

In the opposite limit of large n, both factors $Q_{n-1}^{(B)}e^{\beta\bar{\varepsilon}}$ and $D(E_1 + \bar{\varepsilon})$ increase rapidly with the number of degrees of freedom. Their ratio, however, depends only weakly on n so that E_1 will not be very sensitive to molecular size. A typical dependence of E_1 on molecular size and on molecule–solvent interaction is shown in Fig. 3.

The last step in evaluating the steady-state distribution is the calculation of the normalization constant

$$N = \int_{-\infty}^{\infty}d\{x^{n-1}\}d\{v^{n-1}\}\int_{-\infty}^{x_B}dx\int_{-\infty}^{\infty}dv\,P_M(x, v) = \int_0^{\infty}dE_T\,\rho_n(E_T)P_M(E_T) \quad (6.42)$$
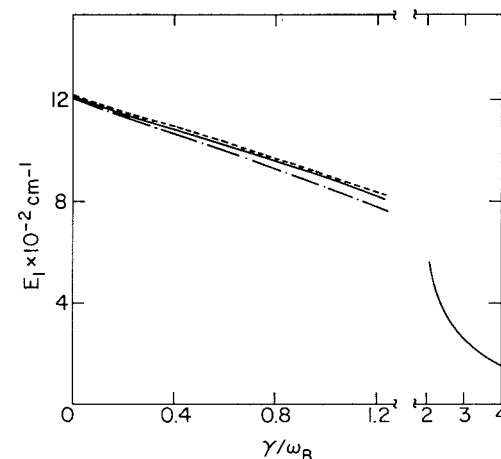
Figure 3. Matching energy E_1 for *trans*-stilbene (full line) obtained using normal modes of stilbene as calculated by Warshel[47] and taking $D(E) = 0.1\gamma\rho(E)E$, $\rho(E)$ being density of states, and $\omega_0 = \omega_B = 88\ \mathrm{cm}^{-1}$. - - - molecule with same reactive mode parameters and with partition function of nonreactive subsystem larger by a factor of 5 than that of *t*-stilbene; -·-similar molecule with partition function of nonreactive subsystem smaller by a factor of 5 than that of *t*-stilbene. (From Nitzan.[42])

where $\{x^{n-1}\}$ and $\{v^{n-1}\}$ denote the sets of coordinates and velocities of the nonreactive modes. The reaction rate is given by the steady-state flux divided by N,

$$k = j/N \quad (6.43)$$

Evaluating N from Eq. (6.42) yields[42]

$$N = \frac{\pi\hbar A_2\eta e^{\beta E_B}}{Q_{n-1}^{(B)}} + \frac{A_2\tau_1}{Q_n\beta}$$

$$+ \frac{\pi(2 - \eta)A_2 e^{\beta E_B}}{Q_n Q_{n-1}^{(B)}}\frac{\omega_B}{\omega_r}\int_{E_1}^{\infty}dE_T\int_{E_1}^{E_T}dE\,\frac{e^{-\beta E_T}\rho_{n-1}(E_T - E|E)}{\omega_R(E)}$$

$$+ \frac{A_2}{Q_n}\int_0^{E_1}dE_T\,\rho_n(E_T)e^{-\beta E_T}\int_{E_1}^{E_{1T}}dE'\frac{e^{\beta E'}}{D(E')}$$

$$+ \frac{A_2}{\hbar Q_n}\int_{E_1}^{\infty}dE_T\int_0^{E_1}dE\,\frac{e^{\beta E_T}\rho_{n-1}(E_T - E|E)}{\omega_R(E)}\int_E^{E'}dE'\frac{e^{\beta(E' + \bar{\varepsilon})}}{D(E' + \bar{\varepsilon})} \quad (6.44)$$

where

$$\tau_1 = \beta \int_{E_{0T}}^{E_1} dE' \frac{e^{\beta E'}}{D(E')} \int_0^{E'} dE_T \rho_n(E_T) e^{-\beta E_T} \qquad (6.45)$$

$$\eta = 1 + \text{erf}[\sqrt{(\alpha + 1)\beta(E_B - E_1)}] \qquad (6.46)$$

$$E_{1T} = E_1 + \bar{\varepsilon} \qquad (6.47)$$

and where E_{0T} is some arbitrary source point on the energy axis near the bottom of the reactant well. τ_1 is the mean first passage time for a molecule that starts with total energy E_{0T} to reach the total energy E_1. For $E_{0T} \ll E_B$ the choice of E_{0T} does not affect the result.

The reaction rate may now be obtained from Eqs. (6.32) and (6.44). To simplify the resulting rate note that the ratios between the flux $j = A_2/Q_n\beta$ and the first and third terms of Eq. (6.44) contain the term $k^{(B)}$, the barrier dominated rate [Eq. (6.16)]. The final result for the rate is thus

$$k = \left\{ \left[\left(\frac{2}{\tilde{\eta}} \right) k^{(B)} \right]^{-1} + \tau \right\}^{-1} \qquad (6.48)$$

$$k^{(B)} = \frac{\omega_r}{\omega_B} \frac{\omega_R(0)}{2\pi} \frac{Q_{n-1}^{(B)}}{Q_{n-1}^{(0)}} e^{-\beta E_B} \qquad (6.49)$$

$$\tilde{\eta} = \eta + (2 - \eta) \frac{1}{Q_n} \int_{E_1}^{\infty} dE_T\, e^{-\beta E_T} \int_{E_1}^{E_T} dE \frac{\rho_{n-1}(E_T - E|E)}{\hbar\omega_R(E)} \qquad (6.50)$$

$$\tau = \tau_1 + \tau_2 + \tau_3 \qquad (6.51a)$$

where τ_1 is given by Eq. (6.45),

$$\tau_2 = \beta \int_0^{E_1} dE_T\, \rho_n(E_T) e^{-\beta E} \int_{E_1}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \qquad (6.51b)$$

$$\tau_3 = \beta \int_{E_1}^{\infty} dE_T \int_0^{E_1} dE \frac{e^{-\beta E}\rho_{n-1}(E_T - E|E)}{\hbar\omega_R(E)} \int_E^{E_1} dE' \frac{e^{\beta(E' + \bar{\varepsilon})}}{D(E' + \bar{\varepsilon})} \qquad (6.51c)$$

In the one-dimensional case $E_{1T} = E_1$, $\tau_2 = \tau_3 = 0$, and $\tau = \tau_1$. In Appendix B we show that for deep wells

$$\tau \lesssim \beta Q_n \int_0^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \qquad (6.52)$$

where the equality is a reasonable approximation. The right-hand side of Eq. (6.52) is a good approximation to

$$\beta \int_0^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \int_0^{E'} dE\, e^{-\beta E} \rho_n(E) \qquad (6.53)$$

This is the mean first passage time to reach from the bottom of the well to the energy $E_{1T} = E_1 + \bar{\varepsilon} = E_1 + (n - 1)/\beta$. Thus τ correspond approximately to this mean first passage time, in analogy to the one-dimensional case.

In the one-dimensional case $\rho_{n-1} = 0$ so $\tilde{\eta} = \eta$. For a very large molecule the double integral in Eq. (6.50) can be approximated by

$$\int_0^{\infty} dE_T\, e^{-\beta E_T} \int_0^{E_T} dE \frac{\rho_{n-1}(E_T - E|E)}{\hbar\omega_R(E)} = Q_n \qquad (6.54)$$

because most of the contribution to Eq. (6.54) comes from energy regions E_T, $E \gg E_1$. In this case $\tilde{\eta} = 2$.

In summary, the escape rate from the polyatomic reactant well has been obtained in the form

$$k = \left\{ \left[\left(\frac{2}{\tilde{\eta}} \right) k^{(B)} \right]^{-1} + \tau \right\}^{-1} \qquad (6.55)$$

τ is given by Eq. (6.51), which for large barriers may be approximated by

$$\tau \sim \beta Q_n \int_0^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}, \qquad \beta = (k_B T)^{-1} \qquad (6.56)$$

which is approximately the mean first passage time for the reactant to reach the energy

$$E_{1T} = E_1 + \bar{\varepsilon} \qquad (6.57)$$

$\bar{\varepsilon}$ is defined as the energy where $\rho_{n-1}(E)e^{-\beta\varepsilon}$ achieves its maximum, and in the high-temperature large barrier limit it is equal to the energy in the nonreactive modes $\bar{\varepsilon} \simeq (n - 1)/\beta$, n being the number of strongly coupled internal degrees of freedom. $\tilde{\eta}$ is given by

$$\tilde{\eta} = \eta + (2 - \eta) \frac{1}{Q_n} \int_{E_1}^{\infty} dE_T\, e^{-\beta E_T} \int_{E_1}^{E_T} dE \frac{\rho_{n-1}(E_T - E|E)}{\hbar\omega_R(E)} \qquad (6.58)$$

$$\eta = 1 + \text{erf}[\sqrt{(\alpha + 1)\beta(E_B - E_1)}] \qquad (6.59)$$

where α is given by Eq. (5.24) and E_1 is the solution of Eq. (6.41) whose typical dependence on the solvent friction is shown in Fig. 3. Q_n is the equilibrium

partition function of the n-mode system. $D(E)$, given by

$$D(E) = \rho_n(E) \int_0^\infty dt \sum_a \sum_b Z_{ab}(t) \overline{(\dot{x}_a(t)\dot{x}_b(0))}_{E_T} \tag{6.60}$$

is related to the rate of energy damping by the reactant molecule,

$$\left(\frac{dE}{dt}\right)_{T=0} = -D(E)\rho_n^{-1}(E) \tag{6.61}$$

Finally $k^{(B)}$ is the barrier dominated rate given by

$$k^{(B)} = \frac{Q_{n-1}^{(B)}}{2\pi\hbar\beta Q_n} \frac{\omega_r}{\omega_B} e^{-\beta E_B} \simeq \frac{\omega_R(0)}{2\pi} \frac{Q_{n-1}^{(B)}}{Q_{n-1}^{(0)}} \frac{\omega_r}{\omega_B} e^{-\beta E_B} \tag{6.62}$$

A few comments should be made concerning these results.

1. The result, Eq. (6.55), exhibits a smooth transition from a well-dominated rate τ^{-1} to a barrier dominated rate k. For very weak solvent interactions the denominator in the right-hand side of Eq. (6.55) is dominated by the energy accumulation times τ, and the rate is given by $k \sim \tau^{-1}$. (Note that in this limit E_1 is equal to E_B, the barrier height along the reaction coordinate.) When solvent interactions become stronger, τ decreases and at the same time $\tilde{\eta}$ approaches 2, so k becomes dominated by $k^{(B)}$. Note that the low-friction limit of $k^{(B)}$ is the transition state expression for the transition rate. Also note that the way in which the rate depends on solvent friction changes with the molecular size. In the large molecule limit (large n) $\tilde{\eta}$ becomes 2 as discussed above. Also in this limit τ can be neglected (see below) unless the friction is so low that E_1 is equal to E_B. Equation (6.55) can then be written as

$$k = \left[k^{(B)-1} + \beta Q_n \int_0^{E_B+\bar{\varepsilon}} dE' \frac{e^{\beta E'}}{D(E')} \right]^{-1} \tag{6.63}$$

In this form the rate is given as the inverse of the sum of two times, the barrier crossing time $k^{(B)-1}$ and a time characteristic to the energy relaxation rate within the reactant well.

2. The calculation which leads to Eq. (6.55) is based on a single well (dissociation) model. Its extension to a double well (isomerization) situation can be carried out in complete analogy to the single well treatment. The result is simply (for the left to right transition rate, for example)

$$k_{R\leftarrow L} = [k_{R\leftarrow L}^{(B)-1} + \tau_L + q_e\tau_R]^{-1} \tag{6.64}$$

where $k_{R\leftarrow L}^{(B)}$ is the barrier dominated rate, Eq. (6.62), for the $L \to R$ transition,

$$\tau_W \simeq \beta Q_W \int_0^{E_{1T}^{(W)}} dE' \frac{e^{\beta E'}}{D_W(E')}, \qquad W = L, R \tag{6.65}$$

$$E_{1T}^{(W)} = E_{1W} + \bar{\varepsilon}_W \tag{6.66}$$

$$q_e = Q_L/Q_R \tag{6.67}$$

The subscripts W ($= R, L$) in Eqs. (6.64)–(6.67) denote quantities related to the right (R) or left (L) wells. Thus Q_R is the partition function, n_R the number of strongly coupled modes, and $D_R(E)$ the relaxation function in the right well. $k_{R\leftarrow L}$ and $k_{R\leftarrow L}^{(B)}$ are, respectively, the overall and the barrier dominated transition rates from left to right.

To obtain the result, Eq. (6.64), for the model displayed in Fig. 2 of Carmeli and Nitzan,[48] we need to start with the solutions for the three different regimes: left and right well solutions, both of the form of Eq. (6.33) with energy fluxes of the form of Eq. (6.36) (with two sets of coefficients: A_{1L}, A_{1R}, A_{2L}, A_{2R}), and the barrier solution, Eq. (6.6), modified to include two free parameters,

$$P_{ss}^{(B)}(x,v) = \frac{Q_{n-1}(x,v)}{2\pi\hbar Q_n} Fe^{-\beta E(x,v)} \left[F' + \int_0^{v-|\Gamma|x} dz \exp\left(-\frac{1}{2}\beta\alpha z^2\right) \right] \tag{6.68}$$

[Before we had $F' = \sqrt{\pi/2\alpha\beta}$ so as to have $P_{ss}^{(B)} \to 0$ for $x \to \infty$.] We then use the matching conditions, Eqs. (6.37) and (6.38), at the two points (x_{1R}, $v = 0$) and (x_{1L}, $v = 0$) in the right and left wells, and the flux continuity conditions, Eq. (6.39), for both wells. We then obtain two equations of the form of Eq. (6.41) for the energies E_{1L} and E_{1R} associated with the two matching points. The six matching conditions together with the (assumed given) populations in the right and left wells are enough to determine the six parameters A and F and the two matching energies E_1.

When the escape rate is dominated by the barrier (so that τ_L and τ_R may be neglected), the result, Eq. (6.64), is the same for a single well and a double well model. The difference between the two processes becomes evident in the low-friction limit where for the escape from a single well $k \sim \tau^{-1}$, while in the double well case $k_{R\leftarrow L} \sim (\tau_L + q_e\tau_R)^{-1}$. The two contributions to the escape time are associated with different, though closely related physical processes. τ_L is the characteristic time for energy pumping in the left well, while the inverse dependence of $k_{R\leftarrow L}$ on $q_e\tau_R$ is related[48] to the effect of trajectories returning to the left well after colliding with the far wall of the right well.

3. The rates of Eqs. (6.55) and (6.64) go through a maximum when the friction grows from zero. For extremely small damping the rate is given by τ^{-1}, which grows linearly with the friction, while for large damping the rate is dominated by $k^{(B)}$, which decreases with increasing damping.* The quantitative behavior is very sensitive to molecular size. The barrier term in Eq. (6.55) [or Eq. (6.64)] is not much different. The additional factor $Q_{n-1}^{(B)}/Q_{n-1}$ is, for isomerization reactions, on the order of 0.1–10. The relaxation time τ may, however, be orders of magnitude different. To see this take as a rough estimate for τ (which holds for $E_{1T} \gg k_B T$) the expression

$$\tau \simeq \frac{Q_n e^{\beta E_{1T}}}{D(E_{1T})} \simeq Q_n e^{n-1} \frac{e^{\beta E_1}}{D(E_{1T})} \tag{6.69}$$

and use†

$$D(E) = \rho(E) E k_{VR}(E) \tag{6.70}$$

where $k_{VR}(E)$ is the vibrational energy relaxation rate of the molecule at total vibrational energy E. Using also the classical approximations for Q_n and ρ, with ω a characteristic molecular frequency,

$$Q_n = \left(\frac{k_B T}{\hbar\omega}\right)^n; \qquad \rho(E) = \frac{(E/\hbar\omega)^{n-1}}{\hbar\omega(n-1)!} \tag{6.71}$$

leads to

$$\tau = k_{VR}(E_{1T})^{-1} e^{\beta E_1} \frac{e^{n-1}(n-1)!}{(\beta E_1 + n - 1)^n} \tag{6.72}$$

$$\left(k_{VR}\,\beta\,E_1\,e^{-\beta E_1}\right)^{-1}$$

For $n = 1$ this yields $\tau = (k_{VR}^\beta E_1 e^{-\beta E})^{-1}$, which is exactly the low-friction generalized Kramers result. (The friction γ is replaced here by the more general k_{VR}, which incorporates non-Markovian effects if present. In this low-friction limit $E_1 = E_B$.) For intermediate large values of n Eq. (6.72) may be approximated by vibrational relaxation rate $k_{VR}(E) = E^{-1} dE/dt$,

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* It should be kept in mind that increasing the solvent viscosity does not necessarily imply stronger damping, because it may be accompanied with slower solvent motion (longer solvent relaxation time) and smaller effective friction due to the larger non-Markovian nature of the solvent molecule interaction. See, for example, Bagchi and Oxtoby.[49]

† Equation (6.70) results from Eq. (6.60) together with the definition of the vibrational relaxation rate $k_{VR}(E) = E^{-1} dE/dt$.

$$\tau = (\beta E_{1T} k_{VR}(E_{1T}) e^{-\beta E_1})^{-1} e^{-(n-1)\ln[\beta E_{1T}/(n-1)]} \tag{6.73}$$

For $n \to \infty$ this leads to the nonactivated form

$$\tau \to (\beta E_{1T} k_{VR}(E_{1T}))^{-1} \tag{6.74}$$

It is unphysical, however, to assume in this limit that energy redistribution between the modes is the fastest process in the system.

Equations (6.72)–(6.74) show that τ decreases dramatically for an increasing number of molecular degrees of freedom. This results both because of the larger k_{VR} expected for larger molecules and because of the n-dependent correction in Eqs. (6.72)–(6.74). Equation (6.55) then implies that the turnover from well dynamics to barrier dynamics dominated rate occurs for large molecules at much smaller solvent viscosities (or pressure in the gas phase) than for small molecules. This point was discussed in the literature[42,46] and was the subject of several recent experimental investigations. Since for this small friction the barrier dominated rate is identical to the TST rate, it may be concluded that for large molecules a plateau in the rate versus solvent friction, where $k = k_{TST}$, should be observed.

4. While the model employed in the present work provides a reasonable picture of a unimolecular reaction involving a large molecule in solution, other ingredients not considered here may play a role in some systems. The possible role played by intramolecular friction (nonlinear coupling between the reaction coordinate and other nonreactive modes near the barrier) has been discussed in Section IV. Also, the dependence of the molecular potential surface, in particular the activation barrier on the molecule–solvent interaction, may dominate in some cases the observed solvent effect on the rate. Such may be the case (see Section VIII) in a polar solvent when the reaction involves a change in the molecular dipole moment (such as a charge transfer reaction).

5. The results listed above are based on several approximations. Some are essential parts of the model: the assumption that intramolecular relaxation is much faster in the well region than intermolecular energy exchange, the decoupling between the reactive coordinate and the nonreactive mode in the barrier region, and the assumption that a unimolecular rate is well defined (which is valid if $E_B \gg k_B T$). Other approximations serve to simplify the results. Thus Eq. (6.56) is the large barrier approximation to Eq. (6.51), while Eq. (6.35) for $\bar{\varepsilon}$ and Eq. (6.72) for τ are based on the assumption that the temperature is high enough to permit the use of classical statistical thermodynamics in evaluating the molecular distribution. While these approximations served to illustrate the essential points in the theory, they are not valid in many practical situations. In the much studied isomerization of *trans-*

stilbene, for example, the barrier to isomerization is ~ 1150 cm^{-1}, while the largest molecular frequencies are in the 3000-cm^{-1} range. The theory may be applied to such situations by avoiding the simplifying classical approximation and resorting instead to numerical integrations. In particular the high-temperature expression $\bar{\varepsilon} = (n-1)/\beta$ canot be used in this case. Instead $\bar{\varepsilon}$ can be computed as the energy for which $\rho_{n-1}(E)e^{-\beta E}$ attains its maximum. For t-stilbene at $T = 300$ K this yields $\bar{\varepsilon} = 1870$ cm^{-1}. The plot of E_1 versus friction in Fig. 3 was obtained using such numerical estimates.

6. The results of Eqs. (4.1)–(4.15) stress the number of strongly coupled modes n as an important parameter of the theory which, together with the activation barrier height and the solvent frequency dependent friction, determine the reaction rate. The barrier height and the friction can in principle be determined by independent measurements (Arrhenius temperature dependence of the rate in the transition state regime and molecular vibrational relaxation rates). The number of strongly coupled degrees of freedom is an undetermined parameter of the theory. In this respect our situation is similar to that of the RRKM theory, and in fact the present results may be viewed as a unification of the RRKM and the generalized Kramers theories of chemical reaction rates. Using n as a fitting parameter has been a traditional way of applying the RRKM theory to the interpretation of experimental data. Because of the large sensitivity of the calculated rate to n (in both the RRKM theory and its present extension) such a fitting can at best lead to very crude estimates. An interesting possibility is to estimate n from transition state (high-pressure gas-phase) data and to use the so obtained number of strongly coupled modes to predict the full-range pressure–viscosity dependence. Such a procedure may work if intramolecular energy distribution is dominated by intramolecular interactions. More likely we may find that the number of strongly coupled modes is pressure dependent at low pressures, as discussed at the end of Section II.

7. The assumption that IVR is much faster in the well region than intermolecular energy exchange is reasonable for large molecules where the density of states is very large, so that IVR can be induced by long-range soft collisions with solvent molecules.* The situation is less clear for small molecules (2–4 degrees of freedom) where the molecular density of states is small and the time scale associated with vibrational energy spacing is short relative to the duration of most collisions. In such cases IVR may be as slow as or slower than the energy accumulation and relaxation process.

* Recent numerical simulations by Borkovec et al.[50] indicate that increasing solvent–molecule interaction may give rise to effective decoupling between molecular modes, that is, the dynamics appear more one-dimensional with increasing solvent interaction. However, in these simulations interactions of the kind discussed here were not included.

A simplified model, which illustrates these effects and may be solved analytically if IVR is slow relative to the total energy relaxation rate, is given by (for simplicity we use the Markov limit for the following demonstration)[51]

$$\ddot{x}_1 = -m_1^{-1}\partial V(x_1, x_2)/\partial x_1 - \gamma_1 \dot{x}_1 + m_1^{-1}R_1(t) \tag{6.75}$$

$$\ddot{x}_2 = -m_2^{-1}\partial V(x_1, x_2)/\partial x_2 - \gamma_2 \dot{x}_2 + m_2^{-1}R_2(t) \tag{6.76}$$

with

$$\langle R_i(t)R_j(t)\rangle = 2\gamma_i m_i k_B T \delta_{ij}\delta(t - t') \tag{6.77}$$

and with the potential $V(x_1, x_2)$ taken to be

$$V(x_1, x_2) = U(x_1) + \tfrac{1}{2}m_2\omega_2^2(x_2 - \mu x_1)^2 \tag{6.78}$$

$U(x_1)$ may be any one-dimensional potential along which the escape occurs. x_1 is thus the reactive coordinate while x_2 is the nonreactive coordinate. The calculations reported below use the potential

$$U(x_1) = \begin{cases} \tfrac{1}{2}m_1\omega_1^2(x_1 - a)^2, & \text{for } x \le b \\ E_B - \tfrac{1}{2}m_1\omega_B^2 x_1^2, & \text{for } x > b \end{cases} \tag{6.79}$$

with a, $b < 0$ and $a < b$. The requirement that $U(x)$ and its derivative be continuous at $x = b$ leads to

$$b = \frac{a\omega_1^2}{\omega_1^2 + \omega_B^2} \tag{6.80}$$

and

$$\omega_B^2 = \frac{2E_B\omega_1^2}{m_1\omega_1^2 a^2 - 2E_B} \tag{6.81}$$

To solve the escape problem associated with this model, Eq. (6.76) may be solved for x_2 and the result inserted in Eq. (6.75). This leads to a non-Markovian equation of motion for the reaction coordinate of the kind solved in Section V.

A simple result is obtained for this model if the nonreactive mode is fast relative to the reactive mode. [From Eq. (6.76) the time scale associated with x_2 is given by the roots of its characteristic equation, $1/2[\gamma_2 \pm (\gamma_2^2 - 4\omega_2^2)^{1/2}]$.] In this case the nonreactive oscillator may be considered as part of the heat
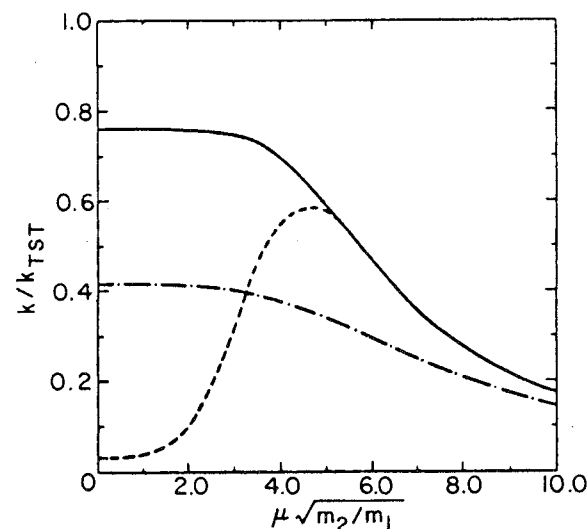
Figure 4. Transmission coefficient k/k_{TST} as a function of $\mu\sqrt{m_1/m_2}$ for model defined by Eqs. (6.75) and (6.76). Parameters are $\omega_B = 1$, $\omega_1 = 5$, $\omega_2 = 4.5$, $E_B/k_B T = 10$, and $\gamma_2 = 0.05$. --, $\gamma_1 = 10^{-3}$. $\gamma_1 = 10^{-1}$. --, $\gamma_1 = 2.0$. (From Carmeli and Nitzan.[51])

bath. Indeed, in this case an equation of motion of the form of Eq. (6.75) for x_1 is recovered with γ_1 replaced by[51]*

$$\gamma = \gamma_1 + \gamma_2 \mu^2 \frac{m_2}{m_1} \tag{6.82}$$

In the general case the escape rate may be obtained as described in Section V. Some characteristic results are given in Fig. 4. Two important observations can be made about these results.

1. Qualitatively mode–mode coupling increases the effect of the thermal bath (solvent). If the one-dimensional system is in the low-friction regime (dashed curve of Fig. 4), increasing μ causes first an increase then a decrease in the escape rate, the same as what increasing friction would have done. Similarly in the higher friction cases, increasing μ has the same qualitative effect as increasing γ.

2. For larger friction the effect of mode–mode coupling appears smaller (dot–dashed curve of Fig. 4). This is reminiscent of the results of Bokovec et

* A different, but related model was considered in Fonseca et al.[52]

al.[50] Note that in our model we have taken μ to be independent of γ, while in reality collisions may affect the coupling between intramolecular modes.

VII. ESCAPE IN THE PRESENCE OF EXTERNAL PERIODIC FORCE: THE LOW-FRICTION LIMIT

A relatively unexplored extension of the Kramers theory is the escape of a Brownian particle out of a potential well in the presence of an external periodic force. Processes such as multiphoton dissociation and isomerization of molecules in high-pressure gas or in condensed phases,[15] laser-assisted desorption,[16] and transitions in current-driven Josephson junctions under the influence of microwaves[17-19] may be described with such a model, where the periodic force results from the radiation field.

It is to be expected that an external oscillating force will have a major effect in the low-friction regime where the motion is characterized by well-defined frequencies that can be pumped by the field. Recently treatments of such models were given by Carmeli and Nitzan,[53] Sazonov and Zatsepin,[54] Faetti et al.,[55] and Frouzoni et al.[56] Here we follow the treatment of Carmeli and Nitzan.[53]

The simplest problem of this kind is the escape from a truncated harmonic well in the low-friction Markovian limit. This problem was treated by Ben Jacob et al.[17] The model is defined by

$$\ddot{x} + \gamma\dot{x} + \omega^2 x = A\cos(\omega_R t) + \frac{1}{m}R(t) \tag{7.1}$$

where A is the amplitude of the external force divided by M, of frequency ω_R. The termal noise R satisfies

$$\langle R \rangle = 0; \qquad \langle R(t_1)R(t_2) \rangle = 2\gamma k_B T \delta(t_1 - t_2) \tag{7.2}$$

The equilibrium distribution for this model was found to be

$$P_{ss}(E) = N_E \exp\left[-\frac{2\omega_R^2}{\omega^2 + \omega_R^2} \frac{(E^{1/2} - \bar{E}^{1/2})^2}{k_B T} \right] \tag{7.3}$$

where

$$\bar{E} = \frac{m(\omega^2 + \omega_R^2)A^2}{4[(\omega^2 - \omega_2^2)^2 + \gamma^2\omega_R^2]} \tag{7.4}$$

and the mean first passage time to reach the threshold energy E_B, which may

be identified with the inverse escape rate, is, for $\omega = \omega_R$,

$$\tau = (\gamma k_B T)^{-1} \int_E^{E_B} \frac{dy}{y} \exp\left(\frac{y^{1/2} - \bar{E}^{1/2}}{k_B T}\right) \int_0^y dz \exp\left[-\frac{(z^{1/2} - \bar{E}^{1/2})^2}{k_B T}\right] \quad (7.5)$$

For high barriers or low temperatures ($E_B - E \gg k_B T$) Eq. (5) reduces to

$$\tau = \frac{1}{\gamma}\left(\frac{4\pi\bar{E}}{k_B T}\right)^{1/2} \frac{E_B - \bar{E}}{E_B} \exp\left[\frac{(E_B^{1/2} - \bar{E}^{1/2})^2}{k_B T}\right] \quad (7.6)$$

For anharmonic potential surfaces the problem becomes much more complicated. The underlying deterministic equation (zero-temperature limit) may have several locally stable state solutions corresponding to resonance of the external force with higher harmonics and subharmonics of the potential well. These give rise to the phenomenon of steps in the current–voltage characteristics of the microwave-driven Josephson junction.[18] For a strong external driving force the deterministic motion becomes chaotic and it seems impossible to identify a slow dynamic variable for a convenient reduction of the problem. [The simplicity of the solution, Eqs. (7.3)–(7.5), stems from the fact that in the low-friction limit the energy near steady state varies much more slowly than the phase.] An analytical treatment is therefore possible only in the weak oscillating force limit.[57]

In many physical systems the situation becomes simpler due to the inherent stochastic nature of the driving field itself. To see the possible significance of this effect, consider a conventional CO_2-laser pulse with 10-ns duration and a bandwidth of 1 cm^{-1} incident on a diatomic molecule characterized by an environment-induced energy relaxation time of ~ 100 ns. The laster pulse is obviously not uncertainty limited, and its width is associated with the random fluctuations in its phase and/or amplitude. For simplicity we consider random phase fluctuations, whence the external field is

$$F(t) = F_0 \cos\left[\omega_R t + \int^t dt' \phi(t')\right] \quad (7.7)$$

with ϕ being a Gaussian random variable,

$$\langle \phi(t) \rangle = 0; \qquad \langle \phi(t_1)\phi(t_2) \rangle = 2\Gamma \delta(t_1 - t_2) \quad (7.8)$$

so that

$$\langle F(t_1)F(t_2) \rangle = F_0^2 \exp(-\Gamma|t_1 - t_2|)\cos[\omega(t_1 - t_2)] \quad (7.9)$$

Γ^{-1} is the inverse correlation time and Γ may be shown to be an additive part of the beam spectral width. For the present example τ_c is thus 10^{-11} sc. This is much shorter than the energy relaxation time, so that in this respect the radiation field is similar to a thermal bath. In particular, phase coherence necessary to generate deterministic chaos does not exist in this situation.

Another source of dephasing originates within the system itself and arises from the presence of the random noise $R(t)$. In this context we find it useful to generalize $R(t)$ to include multiplicative noise terms $g(x)R(t)$.[38] In the presence of such terms [and also for the case of purely additive noise, if the potential $V(x)$ is anharmonic] it is possible, in analogy to quantum statistical mechanics, to distinguish between pure dephasing (T_2) processes and dephasing associated with energy relaxation (T_1) processes. We will show that in the presence of strong internal dephasing processes, reduction to a simple energy Fokker–Planck equation is possible, and an expression for the low-friction escape rate easily follows.

A. Phase-Diffusing Driving Field

The model is defined by

$$\dot{x} = v$$

$$\dot{v} = -\frac{1}{m}\frac{dV(x)}{dx} - \int_0^t d\tau\, Z(t - \tau)v(\tau) + \frac{1}{m}R(t) + \frac{1}{m}F(t) \quad (7.10)$$

where R is a Gaussian random function satisfying $\langle R \rangle = 0$ and

$$\langle R(t_1)R(t_2) \rangle = mk_B T Z(t_1 - t_2) \quad (7.11)$$

and F is the external driving force which satisfies

$$\langle F(t_1)F(t_2) \rangle = mY(t_1 - t_2) \quad (7.12)$$

The correlation functions $Z(t)$ and $Y(t)$ decay to zero on time scales τ_c and τ_c^y, respectively. We assume that the time scales characterizing the process satisfy

$$\omega(E)^{-1} \ll \tau_c, \qquad \tau_c^y \ll \left(\frac{d\ln E}{dt}\right)^{-1} \quad (7.13)$$

where $\omega(E)$ is the frequency associated with the potential $V(x)$ and with the particle's mass m and energy E. Under these conditions we can use a reduction procedure identical to that described for the purely thermal case (Section V) to derive a Smoluchowski equation for the energy. The result is[53]

$$\frac{\partial P(E,t)}{\partial t} = \frac{\partial}{\partial E}\left[D_1(E)\left(k_B T \frac{\partial}{\partial E} + 1\right)\omega(E)P(E,t)\right]$$
$$+ \frac{\partial}{\partial E}\left[D_2(E)\frac{\partial}{\partial E}(\omega(E)P(E,t))\right] \qquad (7.14)$$

with

$$D_1(E) = \omega(E)\varepsilon(E) \qquad (7.15)$$

$$D_2(E) = \omega(E)\mu(E) \qquad (7.16)$$

where

$$\varepsilon(E) = 2m \sum_{n=1}^{\infty} n^2 |x_n|^2 \hat{Z}_n^c \qquad (7.17)$$

$$\mu(E) = 2m \sum_{n=1}^{\infty} n^2 |x_n|^2 \hat{Y}_n^c \qquad (7.18)$$

The results, Eqs. (7.14)–(7.16), are a generalization of the energy-diffusion equation (5.48) obtained in the absence of the external phase-diffusing driving force ($D_2 = 0$). It is interesting to note that Eq. (7.14) may be written in the form

$$\frac{\partial P(E,t)}{\partial t} = \frac{\partial}{\partial E}\left[D_1(E)\left(k_B T_{\text{eff}}(E)\frac{\partial}{\partial E} + 1\right)\omega(E)P(E,t)\right] \qquad (7.19)$$

where the energy-dependent effective temperature is given by

$$T_{\text{eff}}(E) = T + \frac{D_2(E)}{k_B D_1(E)} \qquad (7.20)$$

The general steady-state solution ($\partial P_{\text{ss}}/\partial t = 0$) of Eq. (7.19) is

$$P_{\text{ss}}(E) = \frac{A_1}{\omega(E)}\exp\left[-\int_0^E dE' \beta(E')\right]$$
$$- \frac{A_2}{\omega(E)}\int_0^E \frac{dE' \beta(E')}{D_1(E')}\exp\left[-\int_{E'}^E dE'' \beta(E'')\right] \qquad (7.21)$$

where

$$\beta(E) = [k_B T_{\text{eff}}(E)]^{-1} \qquad (7.22)$$

and where A_1 and A_2 are constants. One of them may be determined from the normalization condition and the other is easily shown to be the steady-state current

$$j_{\text{ss}} = -D_1(E)\left[\beta^{-1}(E)\frac{d}{dE} + 1\right]\omega(E)P_{\text{ss}}(E) = A_2 \qquad (7.23)$$

The equilibrium solution (in the presence of the driving field) corresponds to zero current,

$$P_{\text{eq}}(E) = \frac{A_1}{\omega(E)}\exp\left[-\int_0^E dE' \beta(E')\right] \qquad (7.24)$$

In the very low friction limit the barrier energy E_B may be considered to be an absorbing boundary for the diffusion motion described by Eq. (7.19), that is, $P_{\text{ss}}(E_B) = 0$. This and Eq. (7.21) imply

$$A_1 = A_2 \int_0^{E_B} dE' \frac{\beta(E')}{D_1(E')}\exp\left[\int_0^{E'} dE'' \beta(E'')\right] \qquad (7.25)$$

The rate is given by

$$k = \frac{j_{\text{ss}}}{\int_0^{E_B} dE\, P_{\text{ss}}(E)} \qquad (7.26)$$

which, using Eqs. (7.21)–(7.26), results in

$$k = \left[\int_0^{E_B} dE \frac{\beta(E)}{\omega(E)D_1(E)}[P_{\text{eq}}(E)]^{-1}\int_0^E dE' P_{\text{eq}}(E')\right]^{-1} \qquad (7.27)$$

The following observations can be made concerning these results.

1. When $\beta(E)$ is replaced by $(k_B T)^{-1}$, the result, Eq. (7.27), becomes identical to the low-viscosity rate obtained in the purely thermal case (Section V).
2. The effect of the phase-diffusion driving force enters through the (generally energy-dependent) effective temperature $T_{\text{eff}}(E)$.

To see the significance of the effective temperature more explicitly, we may consider the harmonic-oscillator case together with the simple choices

$$Z(t) = \frac{\gamma}{\tau_c} e^{-t/\tau_c} \qquad (7.28)$$

$$Y(t) = \bar{F}^2 e^{-\Gamma t} \cos(\omega_R t) \tag{7.29}$$

τ_c and $\tau_c^y = \Gamma^{-1}$ are the thermal and the driving-force correlation times, respectively. Equations (7.17) and (7.18) become

$$\varepsilon(J) = \frac{J}{\omega} \frac{\gamma}{1 + (\omega\tau_c)^2} \tag{7.30}$$

$$\mu(J) = \frac{J\bar{F}^2}{2} \frac{\Gamma}{\Gamma^2 + (\omega_R - \omega)^2} \tag{7.31}$$

[In the harmonic-oscillator case only the term $n = 1$ appears and $x_1 = (J/2m\omega)^{1/2} = \omega^{-1}(E/2m)^{1/2}$. In Eq. (7.31) we disregard a small term proportional to $\Gamma[\Gamma^2 + (\omega_R + \omega)^2]^{-1}$.]

From Eq. (7.20) we get

$$k_B T_{\text{eff}} = k_B T + \frac{\bar{F}^2}{2\Gamma\gamma} \frac{1 + (\omega\tau_c)^2}{1 + [(\omega_R - \omega)/\Gamma]^2} \tag{7.32}$$

We see that T_{eff} goes through a maximum near the resonance condition $\omega_R = \omega$, where ω is the oscillator frequency. The phase-diffusing driving force results in thermallike kinetics with a renormalized temperature, which is resonantly enhanced relative to the bare temperature.

B. External Oscillating Force in the Fast Thermal Dephasing Limit

The model is defined by [compare Eqs. (5.62)–(5.64)]

$$\dot{x} = v \tag{7.33}$$

$$\dot{v} = -\frac{1}{m} \frac{dV(x)}{dx} - f(x(t)) \int_0^t d\tau \, Z(t - \tau) f(x(\tau)) v(\tau)$$

$$+ \frac{1}{m} f(x(t)) R(t) - \frac{1}{m} \frac{d\mu(x)}{dx} \cos(\omega_R t) \tag{7.34}$$

$$\langle R(t) \rangle = 0; \qquad \langle R(t_1) R(t_2) \rangle = m k_B T Z(t_1 - t_2) \tag{7.35}$$

and it is assumed that

$$\gamma = \int_0^\infty dt \, Z(t) \ll \tau_c^{-1} \ll \omega(E) \tag{7.36}$$

Here τ_c is the characteristic time of relaxation for $Z(t)$. In addition it is assumed

that the external force is not too strong so that

$$\frac{d\mu_1(E)}{dE} \ll 1 \tag{7.37}$$

and that dephasing is fast. The last assumption is expressed by

$$\frac{d\mu_1(E)}{dE} \ll \frac{\Gamma_0}{\omega} \tag{7.38}$$

In Eqs. (7.37) and (7.38) the $\mu_n(E)$ functions are defined as the coefficients of the expansion (see Section V)

$$\mu(x) = \sum_n \mu_n(E) e^{in\phi} \tag{7.39}$$

and Γ_0 is the pure dephasing rate given by

$$\Gamma_0(E) = m k_B T \gamma \left| \omega(E) \frac{dG_0}{dE} \right|^2 \tag{7.40}$$

where G_0 is the $n = 0$ coefficient in the expansion of $G(x) = \int^x dx' f(x')$ in (E, ϕ) coordinates,

$$G(x) = \sum_{n=-\infty}^\infty G_n(E) e^{in\phi} \tag{7.41}$$

With these assumptions it is again possible to derive an energy diffusion equation. The result is of the form of Eq. (7.19), but with different functions $\beta(E)$ and $D(E)$,

$$D(E) = \varepsilon(E)\omega(E) - \eta(E) \tag{7.42}$$

$$\beta(E) = \beta \frac{\varepsilon(E) - \eta(E)/\omega(E)}{\varepsilon(E) + \lambda(E)} \tag{7.43}$$

$$\varepsilon(E) = 2m \sum_{n=1}^\infty n^2 |G_n|^2 \hat{Z}_n^c \tag{7.44}$$

$$\lambda(E) = \frac{1}{2} \sum_{n=1}^\infty \frac{n^4 |\mu_n|^2 \Gamma_0 / k_B T}{(n\omega - \omega_R)^2 + n^4 \Gamma_0^2} \tag{7.45}$$

$$\eta(E) = \frac{1}{2} \sum_{n=1}^\infty n^4 |\mu_n|^2 \frac{d\Gamma_0}{dJ} \frac{n^4 \Gamma_0^2 - (n\omega - \omega_R)^2}{[n^4 \Gamma_0^2 + (n\omega - \omega_R)^2]^2} \tag{7.46}$$

The energy diffusion equation (7.19) leads again to the form of Eq. (7.27) for the rate, with $D(E)$ of Eq. (7.42) replacing $D_1(E)$. Again an energy-dependent inverse temperature $\beta(E)$ replaces $(k_B T)^{-1}$. For the special case of harmonic oscillator with $Z(t) = (\gamma/\tau_c)e^{-t/\tau_c}$, $\mu(x) = ax$, and $f(x) = 1 + x/\xi$, a and being parameters, Eqs. (7.42)–(7.46) become[53]

$$\Gamma_0 = \frac{k_B T \gamma}{4m\omega^2 \xi^2} \tag{7.47}$$

$$\eta(E) = 0 \tag{7.48}$$

$$\varepsilon(E) = \frac{E\gamma}{\omega^2(E)} \left\{ \frac{1}{1 + [\omega(E)\tau_c]^2} + \frac{E}{2m\omega^2(E)\xi^2} \frac{1}{1 + [2\omega(E)\tau_c]^2} \right\} \tag{7.49}$$

$$\lambda(E) = \frac{\Gamma_0}{2k_B T} \frac{a^2 E/2m\omega^2(E)}{[\omega(E) - \omega_R]^2 + \Gamma_0^2} \tag{7.50}$$

$$D(E) = \varepsilon(E)\omega(E) \tag{7.51}$$

$$\beta(E) = k_B T \left(1 + \frac{\lambda(E)}{\varepsilon(E)} \right)^{-1} \tag{7.52}$$

Again the effective temperature $\beta(E)$ is resonantly enhanced when $\omega(E) \simeq \omega_R$.

The results obtained in the presence of dephasing, both in the external driving field and in the system itself, stand in sharp contrast to those obtained for a coherent radiation field [Eqs. (7.3)—(7.6)]. There, in the harmonic limit, the equilibrium distribution in the presence of the field [Eq. (7.3)] has a maximum for $E = \bar{E}$, and the resonant behavior enters through the resonant nature of $\bar{E}$ [Eq. (7.4)]. In the present case the driving field enters through the effective temperature. Physically the difference between the two situations arises from the fact that in the former one the deterministic $(T \to 0)$ system has a well-defined phase relative to the radiation field, while here, because of the field's phase diffusion, this coherence is lost and the field operates in this respect as a temperature source. Remarkably, this effective-temperature source still maintains its resonance properties. The difference between the three models is shown in the Markovian limit $(\tau_c = 0)$ by the results displayed in Fig. 5. It is seen that the effects of external driving on the energy distribution function lead to qualitatively different results for the different cases. As seen in Fig. 5, in the absence of dephasing an external periodic force leads to a peak at finite energy in $P_{eq}(E)$, while in the presence of strong dephasing this peak is absent and the enhancement is best associated with a (generally E-dependent) effective temperature.

Figure 6 shows, for a Morse potential $[V(x) = E_B(e^{-2x/\alpha} - 2e^{-x/\alpha})]$ in the Markovian limit the resonant nature of the low-friction escape rate for the model of Eqs. (7.33)–(7.35). The strong asymmetry in the resonant behavior
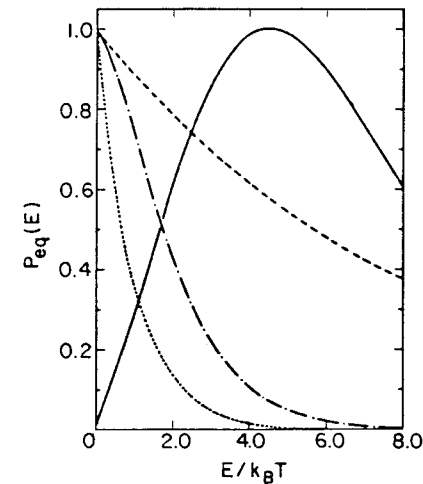

Figure 5. $P_{eq}(E)$ versus $E/k_B T$ for harmonic well potential. ——————coherent external field [Eq. (7.3)]; —·—phase-diffusing external field [Eq. (7.24)]; – – – coherent external field with intrinsic dephasing [Eq. (7.24) with Eq. (7.43)]; ·····distribution obtained in absence of driving field. Parameters used in calculation are $a/\sqrt{k_B T m^2} = 0.03$; $\gamma = 0.01$; $\Gamma = \Gamma_0 = 0.025$; $E_B/k_B T = 8.0$; $\omega = \omega_R$, $\tau_c = 0$. (From Carmeli and Nitzan.[53])
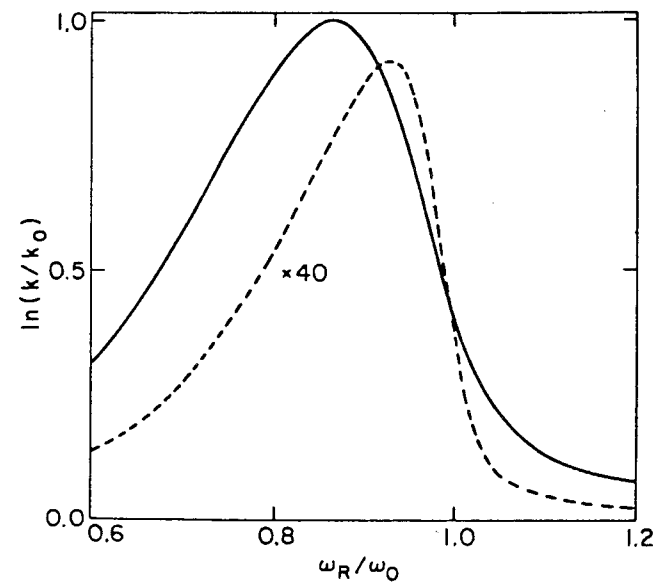

Figure 6. $\ln(k/k_0)$ versus ω_R/ω_0 for Morse potential with multiplicative random noise (intrinsic dephasing). Parameters for solid line are $a\alpha/k_B T = 0.45$; $E_B/k_B T = 8.0$; $\xi/\alpha = 0.42$; $\gamma = 0.0225$. (From Carmeli and Nitzan.[53])

of the field-enhanced rate and the red shift of the peak from the bottom frequency ω_0 result from the unharmonicity of the potential well, namely, the existence of lower frequencies associated with higher energy states in the well. Asymmetry and shift are well known in multiphoton dissociation of large molecules and were recently observed in the microwave-induced transition from the zero-voltage state to the nonzero-voltage state of an underdamped current biased Josephson junction.[19]

VIII.   NUMERICAL RESULTS AND APPLICATIONS

One of the important recent developments in generalizing the Kramers theory of escape processes was the solution of the model equations of motion in the entire friction regime. Such a solution is given by Eq. (6.55) for a single well[35] or by Eq. (6.64) for a double well model.[48] These results were obtained using some approximations as described in Section VI. In order to check the quality of these approximate analytical solutions, Carmeli and Nitzan[35] have carried numerical simulations for a single degree of freedom based on the geralized Langevin equation, Eqs. (5.1) and (5.2). The potential used in these calculations is

$$V(x) = D[e^{-(x/a)} - e^{-(x/b)}]^2 \tag{8.1}$$

with $a/b = 20.0$ (so that $E_B = 0.658D$ and $\omega_0/\omega_B = 5.236$). The memory kernel is give by Eq. (5.5). For these parameters the matching energy E_1, obtained from the numerical solution of the one-dimensional analog of Eq. (6.41),[35] is shown in Fig. 7. The transmission coefficient k/k_{TST} as a function of γ/ω_0 is shown in Fig. 8, together with simulation results for $\omega_0\tau_c = 0$ and $\omega_0\tau_c = 4$. The agreement between the approximate analytical results and the simulations is very good.*

Several other authors[60-64] have recently obtained solutions of the Kramers problem extended to larger friction regimes than in the original Kramers work. Matkowsky et al.[60] calculate the escape rate as the inverse of the sum of two times: the mean first passage time to reach the barrier energy E_B and the mean first passage time to reach from E_B to the separatrix, which separates the well region and the unstable escape region in phase space. Their result, obtained for a symmetric double well in the Markov limit, is, with mass $m = 1$

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* Recent simulations by Straub et al.[58] show that the non-Markovian theory of Section V may break down for very large friction and very large correlation times τ_c of the thermal bath. This failure is due to the fact that in such extreme (and unphysical) limits of the parameters, the well motion may become again the rate-limiting step in the process, in contrast to the theoretical assumption.[58,59]
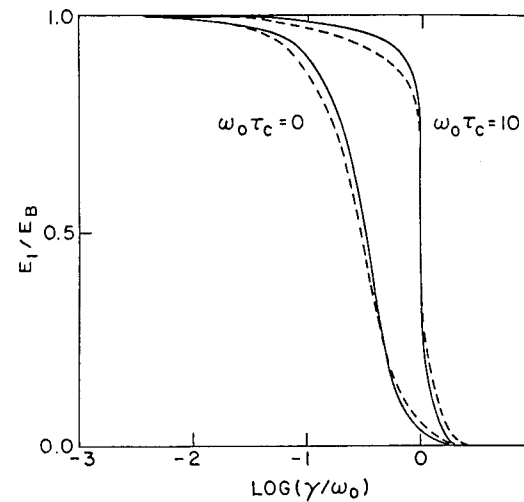

Figure 7. E_1/E_B versus $\log_{10}(\gamma/\omega_0)$ for one-dimensional model [Eq. (8.1)] in Markovian ($\omega_0\tau_c = 0$) and non-Markovian ($\omega_0\tau_c = 10$) limits. ————$E_B = 10k_BT$; ———$E_B = 4k_BT$. (From Carmeli and Nitzan.[35])
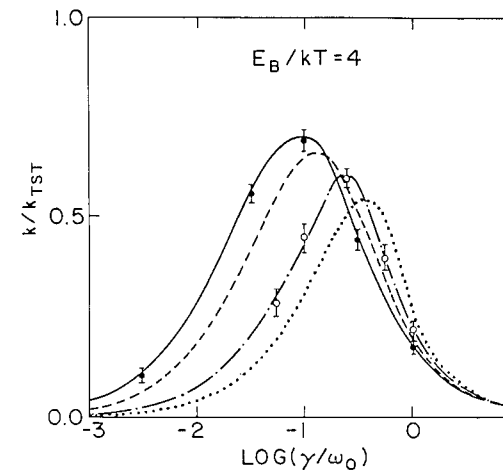

Figure 8. k/k_{TST} as a function of γ for particle moving in potential (8.1) with $E_B = 4k_BT$. ———$\omega_0\tau_c = 0$; ———$\omega_0\tau_c = 2$; —·—$\omega_0\tau_c = 4$; ·····$\omega_0\tau_c = 10$. Circles with error bars are results of numerical simulation based on Langevin equation [Eqs. (5.1) and (5.2) with Eq. (5.6)]. ●, $\omega_0\tau_c = 0$; ○, $\omega_0\tau_c = 4$. (From Carmeli and Nitzan.[35])

$$k = \frac{1}{\tau_1 + 2\tau_2} \qquad (8.2)$$

where τ_1 is the inverse of Eq. (2.41) and where

$$\tau_2 = \frac{2\pi}{\omega_0} \frac{\omega_B}{(4\omega_B^2 + \gamma^2)^{1/2} - \gamma} e^{\beta E_B} \eta \qquad (8.3a)$$

$$\eta = \oint_{E=E_B} \frac{v_B(x)}{2\pi J_B} \mathrm{erf}\left(\frac{d\gamma}{\sqrt{2k_B T}}\right) dx \qquad (8.3b)$$

In Eq. (8.3b) $v_B(x)$ is the closed velocity versus position curve for $E = E_B$, $J_B = (1/2\pi) \oint v_B(x)\, dx$ is the action for $E = E_B$, erf is the error function, and d is the distance between the curve $E(x, v) = E_B$ and the separatrix.

The solution of Buttiker et al.[63] (see also Hanggi and Weiss[64]) connects between the low-friction limit, Eq. (2.41), and the transition state behavior, Eq. (2.25). This solution is obtained by disposing the low-friction assumption that the escape occurs once E_B is reached, and allowing for such trajectories to escape in finite time or to return to $E < E_B$.

These three solutions, together with the Kramers limiting solutions, are shown in Fig. 9 (taken from Matkowsky et al.[60]). The close agreement between the result of Carmeli and Nitzan[35] and that of Matkowski et al.[60] is strong evidence for the validity of both.
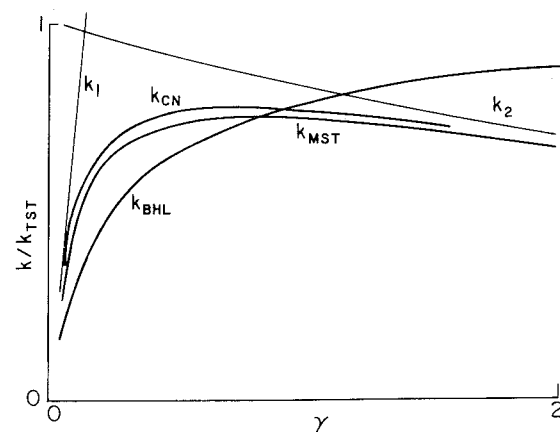

Figure 9. Comparison between Kramers low (k_1) and intermediate-to-large (k_2) friction rates and results of Carmeli and Nitzan (k_{CN}), Matkowsky et al. (k_{MST}), and Buttiker et al. (k_{BHL}) for potential $V(x) = x^2(x^2 - 16x/5 + 6)$. $\beta E_B = 2$. (From Matkowsky et al.[60])

The Kramers theory and its extensions have found many applications since the original work by Kramers. Recent application of the non-Markovian theory in the low-friction limit to thermal desorption was described by Nitzan and Carmeli.[66] Another novel application of the Markovian theory is to transition from a nonequilibrium state of a Josephson junction.[67, 5d] In what follows we shall briefly review the recent application of the generalized Kramers theory to chemical rate processes. More detailed reviews of the experimental and theoretical status of this field may be found in Hynes.[3, 4]

Interest in unimolecular reactions in condensed phases has been increasing over the last decade. Of particular relevance to the present review are meaurements of the rate as a function of the strength of the reactant molecule–solvent interaction (as expressed, for example, by solvent viscosity).[9-14, 68-75] Time-resolved spectroscopy has been utilized to study photochemical isomerization of *trans*-stilbene,[14,68] diphenyl butadiene,[9,69] DODCI,[70] binaphthyl,[71,72] and triphenyl methane[73] in various solvents. High-pressure nuclear magnetic resonance technique has been used to study solvent effects on the rate of ring inversion in cyclohexane[74] and difluorocyclohexane.[75] In another important development the isomerization of *t*-stilbene and of DPB has been studied also in supersonic jet expansions,[76-81] thus making it possible to directly compare chemical dynamics in solution and in isolated condition. Combining these results with high-pressure gas-phase kinetic data, it has now become possible to study the activated chemical rate process throughout all the relevant friction (or other measure of the molecule–environment coupling) range, from the isolated (beam) condition through the low-pressure gas phase to the high-pressure gas phase and to the liquid phase up to pressures of several kilobar. Such studies have now been completed for the *t*-stilbene isomerization,[10, 14] and somewhat less complete results are available also for DPB.[9, 11] Hochstrasser and coworkers[82] have recently carried out such measurements (for *t*-stilbene) in ethane above its critical temperature, thus maintaining the solvent as a uniform fluid throughout the relevant viscosity range. A different but related experiment is the photo dissociation and atom recombination in the reaction $Br_2 \rightleftharpoons 2\,Br$, carried out by Troe and coworkers[13] in different inert gases in the pressure range of 1–7000 bar.

In addition to yielding a large body of data about the systems studied, these experiments have raised several issues of interest from the standpoint of general theory.

1. The viscosity η dependence of the rate k in some of the studied systems (stilbene in alkanes,[68] DPB in alkanes,[69] and DODCI in alcohols[70]) is weaker (that is, $k \sim \eta^\alpha$, $0 < \alpha < 1$) than predicted by the Kramers theory in the Smoluchowski limit. In others (stiff stilbene in alkanes,[68] stilbene in alcohols,[83] and DPB in alcohols[84]) the "usual" η^{-1} dependence was observed. These

observations were interpreted[68,70,48,30b] as arising from the non-Markovian nature of the molecule–solvent coupling in systems involving high curvature barriers using the barrier-controlled dynamics described in Section V. While this interpretation is plausible, it has to be kept in mind that solvent effects on the potential surface associated with the reaction coordinate may also give rise to deviations from the Kramers behavior.[14,85,86]

2. For some unimolecular reactions involving large molecules in supersonic beams, the microcanonical RRKM theory appears to overestimate (by about one order of magnitude) the rate. This has been reported for t-stilbene[79b,87] and for A-$(CH_2)_3$-ϕ where A is anthracene and ϕ is N, N-dimethylaniline.[88] This obviously cannot be a conclusive statement since there are many unknown parameters in the calculation. Obviously the RRKM rate can be made smaller by postulating transition state frequencies larger than the corresponding frequencies near the bottom of the reactant well. (In some studies[79b,87,88] the two sets of frequencies were taken equal.) This has recently been demonstrated by Troe and coworkers for both t-stilbene[89] and PDB.[90] Alternatively simple modifications of the RRKM theory can be invoked to explain the discrepancy. If fast intramolecular vibrational energy redistribution occurs only within subspaces of the full phase space, while those subspaces are only weakly connected, the rate can be either larger or smaller than that predicted by the RRKM theory, depending on whether or not the reaction coordinate and the pumped mode belong to the same subspace. This issue stresses the significance of the set of strongly coupled modes and the sensitivity of the result to the number of these modes and to whether the reaction coordinate is a part of this set, as discussed in Section VI.

More significant for our discussion is the observation, for t-stilbene, that in low-viscosity solvents the isomerization rate is larger by about one order of magnitude than that predicted from infinite pressure extrapolation of the observed beam rates, or that observed in low-pressure host gas environments.[10,11,79a,89] (Although there are data in support of the existence of a similar phenomenon in PDB, a recent analysis by Troe, Amirav, and Jortner[90] has led these authors to conclude that this is not the case.) The interpretation of this observation is still an open question: Syage, Felker, and Zewail[79b] have suggested that the difference arises from nonadiabatic effects which are more pronounced in the gas phase because of the large velocity along the reaction coordinate.[91] Courtney and Fleming[10] suggest that in the gas phase energy transfer still controls, at least partly, the rate, while in the liquid energy relaxation is fast and the rate achieved (for low-viscosity solvents) its maximal TST value. Troe and coworkers[14,85,89] suggest that the difference has no dynamic origin and reflects the solvent influence on the potential energy surface.

3. The crossover from energy controlled dynamics to diffusion controlled dynamics and the range of validity of the statistical approach (TST) have been the focus of several recent studies. In Section VI we have seen that this phenomenon is very sensitive to molecular size, more specifically to the number of strongly coupled modes. A turnover region is always expected to exist. Obviously the thermal unimolecular rate vanishes in the zero-pressure limit and is a decreasing function of solvent viscosity in liquid solutions. Although there have been some reports of experimental observation of energy controlled dynamics and of the turnover in solutions,[72–74] other experiments[10–14,82] indicate that for large molecules the turnover region may be in the intermediate-pressure gas phase. Schroeder and Troe[85] have suggested that some of the apparent observations of turnover in solutions may be due to pressure dependence of the potential surface, in particular the threshold energy (barrier height). A similar suggestion was recently made by Hicks et al.[92] for reactions involving substantial charge redistribution. For such reactions the barrier height strongly depends on solvent polarity, which in turn is affected by the same factors (temperature, pressure, composition) that affect the viscosity.

Zawadzki and Hynes[93] have very recently carried out a series of calculations based on the model of Eqs. (4.1) and (4.2) and in particular the result of Eq. (6.64)* in order to estimate the solvent interaction effect on several unimolecular reactions. In these calculations the possibility of solvent shift of the barrier energy is disregarded. The friction kernel is taken in the form

$$Z(t) = Z(0)e^{-t^2(2\tau_c)^2} + A_0 t^4 e^{-t/\tau_h} \qquad (8.4)$$

This form is adopted from the molecular dynamics computer results of Levesque and Verlet.[23,24] The first term in Eq. (8.4) is the short-time collisional contribution characterized by the collisional time τ_c, while the second term originates from long-range many-body interactions and is characterized by the hydrodynamic time τ_h. From the discussion of Section VI it follows that in highly non-Markovian situations (such as large ω_B in barrier dominated processes) the collisional term in Eq. (8.4) makes the dominant contribution. (This observation is very significant for the analysis of the viscosity dependence of the rate.[23,93]) Within this model and using available informa-

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* The expression used by Zawadski and Hynes (ZH) is in fact not identical to Eq. (6.64). First ZH use the symmetric well result [$q_e = 1$ in Eq. (6.64)]. More important is the fact that in the ZH calculation the times τ in Eq. (6.64) are the mean times to reach E_B from the left or right wells, while the calculation of Section VI shows that τ should be taken as the mean times to reach $E_B + (n - 1)^\beta$. This difference makes no change in the formal form of the theory, but presumably the parameter estimates made by ZH will be somewhat different if our result was used.

tion on molecular potential surfaces and normal modes, these authors estimated the turnover in the rate versus friction dependence to be at liquid densities for butane isomerization in Ar or CCl_4. This is due to the small number (2) of strongly coupled degrees of freedom estimated for this reaction. For stilbene in Ar methane or ethane the calculation predicts the turnover to be in the high-pressure gas phase, in accord with a recent estimate by Nitzan[42] and in agreement with the experimental results mentioned above. For cyclohexane inversion the calculation places the turnover in the gas phase in contrast to the experimental estimates of Hasha et al.[74] The latter result is based on the assumption that k_{TST} is independent of pressure.[24]

Although these calculations represent the best that we can do at present in applying the generalized Kramers theory to chemical rate processes, we should keep in mind that in view of the uncertainty about some key parameters (such as the number of strongly coupled degrees of freedom, the dependence of the activation energy and the activation volume on the molecule–solvent interaction and the possible role played by nonadiabatic (curve crossing) effects in the unimolecular isomerization process) these estimates should be considered as only intelligent guesses about the behavior of the corresponding systems. Obviously we are only at the beginning of a long road in our quest to understand chemical reaction in solutions. More experimental work and more detailed theoretical calculations are needed to sort out and to distinguish between the different effects of solvent interactions on chemical reaction rates. In particular we would like, by controlled experiments or by a combination of theory and experiment, to separate the dynamic (friction) solvent effects from static solvent renormalization of the molecular potential surface. Also a greater and better understanding of the possible role played by nonadiabatic effects in condensed phase reactions is needed. Finally, more experimental and theoretical work is needed to sort out the effect of molecular size. In these efforts, the formalism of the generalized Kramers theory has played so far and is expected to continue to play a central role.

APPENDIX A. EVALUATION OF THE REACTIVE MODE WELL DISTRIBUTION

Inserting Eqs. (6.31) and (6.19) into Eq. (6.18) leads to

$$P^{(W)}(E) = \frac{e^{-\beta E}}{\hbar \omega_R(E) Q_n} I(E) \tag{A.1}$$

$$I(E) = \int_E^\infty dE_T \, \rho_{n-1}(E_T - E) e^{-\beta(E_T - E)} \left[A_1 + A_2 \int_{E_T}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \right] \tag{A.2}$$

Note that at equilibrium where $A_2 = 0$ and $A_1 = 1$, $I(E)$ becomes $\int_0^\infty dE' \rho_{n-1}(E'|E) e^{-\beta E'} Q_{n-1}(E)$. (Here the dependence of ρ_{n-1} on the reactive mode energy E was written explicitly.) Thus,

$$P_{eq}^{(W)}(E) = \frac{Q_{n-1}(E)}{\hbar \omega_R(E) Q_n} e^{-\beta E} \tag{A.3}$$

To simplify $I(E)$, define $E_T - E = \varepsilon$,

$$I(E) = \int_0^\infty d\varepsilon \, \rho_{n-1}(\varepsilon|E) e^{-\beta \varepsilon} \left[A_1 + A_2 \int_{E+\varepsilon}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \right] \tag{A.4}$$

and notice that the term $\rho_{n-1}(\varepsilon|E) e^{-\beta \varepsilon}$ is strongly peaked at some $\varepsilon \, (\equiv \bar{\varepsilon})$ while the remaining term in the integrand is constant at equilibrium and monotonically decreasing with increasing ε. Therefore

$$I(E) \simeq Q_{n-1}(E) \left[A_1 + A_2 \int_{E+\bar{\varepsilon}}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \right] \tag{A.5}$$

Equations (A.1) and (A.5) lead, after changing variables ($E' \to E' + \bar{\varepsilon}$ and $E_{1T} \to E_1 + \bar{\varepsilon}$), to Eq. (3.40). $\bar{\varepsilon}$ is approximated by

$$\bar{\varepsilon} \simeq \frac{\int_0^\infty d\varepsilon \, \varepsilon \rho_{n-1}(\varepsilon) e^{-\beta E}}{\int_0^\infty d\varepsilon \, \rho_{n-1}(\varepsilon) e^{-\beta \varepsilon}} \simeq \frac{n-1}{\beta} \tag{A.6}$$

where the second equality holds for high T.

APPENDIX B. EVALUATION OF τ [EQS. (6.51)]

For deep enough wells τ_1 [Eq. (6.45)] is independent of E_{0T} and the latter may be replaced by zero. An upper limit on τ_1 is

$$\tau_1 \lesssim \beta \int_0^{E_1} dE' \frac{e^{\beta E'}}{D(E')} \int_0^{E_1} dE'' \rho_n(E'') e^{-\beta E''} \tag{B.1}$$

This is actually a good approximation to τ_1 because $e^{\beta E'}/D(E')$ is strongly peaked near the upper limit E_1.*

---

* This is true provided that $D(E)$ increases with E much more slowly than $e^{\beta E}$. $D(E)$ depends on E like $\rho_n(E)$. Using the semiclassical expression $\rho_n(E) = (E/\hbar\omega)^{n-1}/\hbar\omega(n-1)!$ we see that for large enough E this is indeed the case.

Using Eqs. (B.1) and (6.51b) we get

$$\tau_1 + \tau_2 \leq \beta \int_0^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \int_0^{E_1} dE' \rho_n(E') e^{-\beta E'} \tag{B.2}$$

where again the equality is a good approximation for deep wells.

Consider now τ_3 [Eq. (6.51c)],

$$\tau_3 = \beta \int_{E_1}^{\infty} dE\, e^{-\beta E} \int_0^{E_1} dE' \frac{\rho_{n-1}(E - E'|E')}{\hbar\omega_R(E')} \int_{E'}^{E_1} dE'' \frac{e^{\beta(E''+\bar{\varepsilon})}}{D(E''+\bar{\varepsilon})} \tag{B.3}$$

Integration by parts yields

$$\tau_3 = \beta \int_{E_1}^{\infty} dE\, e^{-\beta E} \int_0^{E_1} dE' \frac{e^{\beta(E'+\bar{\varepsilon})}}{D(E'+\bar{\varepsilon})} \int_0^{E'} dE'' \frac{\rho_{n-1}(E - E''|E'')}{\hbar\omega_R(E'')} \tag{B.4}$$

Replacing E' in the upper limit of the E'' integration by E and using $\int_0^E dE'' \rho_{n-1}(E - E''|E'')/\hbar\omega_R(E'') = \rho_n(E)$ leads to an upper bound on τ_3,

$$\begin{aligned}
\tau_3 &\leq \beta \int_{E_1}^{\infty} dE\, e^{-\beta E} \rho_n(E) \int_0^{E_1} dE' \frac{e^{\beta(E'+\bar{\varepsilon})}}{D(E'+\bar{\varepsilon})} \\
&= \beta \int_{E_1}^{\infty} dE\, e^{-\beta E} \rho_n(E) \int_{\bar{\varepsilon}}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \\
&\leq \beta \int_0^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \int_{E_1}^{\infty} dE\, e^{-\beta E} \rho_n(E)
\end{aligned} \tag{B.5}$$

For large βE_1 the equality in Eq. (B.5) is a good approximation to τ_3. Equations (B.2) and (B.5) now yield

$$\tau \leq \beta Q_n \int_0^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}$$

which is Eq. (6.52).

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