Reaction-rate theory: fifty years after Kramers

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The calculation of rate coefficients is a discipline of nonlinear science of importance to much of physics, chemistry, engineering, and biology. Fifty years after Kramers' seminal paper on thermally activated barrier crossing, the authors report, extend, and interpret much of our current understanding relating to theories of noise-activated escape, for which many of the notable contributions are originating from the communities both of physics and of physical chemistry. Theoretical as well as numerical approaches are discussed for single- and many-dimensional metastable systems (including fields) in gases and condensed phases. The role of many-dimensional transition-state theory is contrasted with Kramers' reaction-rate theory for moderate-to-strong friction; the authors emphasize the physical situation and the close connection between unimolecular rate theory and Kramers' work for weakly damped systems. The rate theory accounting for memory friction is presented, together with a unifying theoretical approach which covers the whole regime of weak-to-moderate-to-strong friction on the same basis (turnover theory). The peculiarities of noise-activated escape in a variety of physically different metastable potential configurations is elucidated in terms of the mean-first-passage-time technique. Moreover, the role and the complexity of escape in driven systems exhibiting possibly multiple, metastable stationary nonequilibrium states is identified. At lower temperatures, quantum tunneling effects start to dominate the rate mechanism. The early quantum approaches as well as the latest quantum versions of Kramers' theory are discussed, thereby providing a description of dissipative escape events at all temperatures. In addition, an attempt is made to discuss prominent experimental work as it relates to Kramers' reaction-rate theory and to indicate the most important areas for future research in theory and experiment.

CONTENTS

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LIST OF SYMBOLS

$A(T)$	temperature-dependent quantum rate prefactor
$C(t)$	correlation function
D	diffusion coefficient
E	energy function
E_b	activation energy (=barrier energy with the energy at the metastable state set equal to zero)
$E^{(A)}$	Hessian matrix of the energy function at the stable state
$E^{(S)}$	Hessian matrix of the energy function around the saddle-point configuration
I	action variable of the reaction coordinate
J	Jacobian
$K(x,x')$	transition probability kernel
M	mass of reactive particle
$P(E)$	period of oscillation in the classically allowed region
$P(E,E')$	classical conditional probability of finding the energy E, given initially the energy E'
Q	quantum correction to the classical prefactor
S_b	dissipative bounce action
T	temperature
T_0	crossover temperature
$T(E)$	period in the classically forbidden regime
$U(x)$	metastable potential function for the reaction coordinate
V	volume of a reacting system
Z	partition function, inverse normalization
Z_0, Z_A	partition function of the locally stable state (A)
$Z^{\neq}$	partition function of the transition rate
$\mathcal{H}$	Hamiltonian function of the metastable system
$\mathcal{F}$	complex-valued free energy of a metastable state
$\mathcal{L}$	Fokker-Planck operator
$\mathcal{L}^{\dagger}$	backward operator of a Fokker-Planck process
j	total probability flux of the reaction coordinate
h	Planck's constant
$\hbar$	$h(2\pi)^{-1}$
k_B	Boltzmann constant
k	reaction rate
k^+	forward rate
k^-	backward rate
k_{TST}	transition-state rate
$k(E)$	microcanonical transition-state rate, semiclassical cumulative reaction probability
k_S	spatial-diffusion-limited Smoluchowski rate
m_i	mass of ith degree of freedom
$p(x,t)$	probability density
$p_0(x)$	stationary nonequilibrium probability density for the reaction coordinate
p_i	momentum degree of freedom
q_i	configurational degree of freedom
$r(E)$	quantum reflection coefficient
$s(x)$	density of sources and sinks
$t(E)$	quantum transmission coefficient
$t_\Omega(x)$	mean first-passage time to leave the domain Ω, with the starting point at x
t_{MFPT}	constant part of the mean first-passage time to leave a metastable domain of attraction
$v=\dot{x}$	velocity of the reaction coordinate
x	reaction coordinate
x_0, x_a	location of well minimum or potential minimum of state A, respectively
x_b	barrier location
x_T	location of the transition state
β	inversion temperature $(k_B T)^{-1}$

γ	damping relaxation rate
$\gamma(t)$	memory friction
$\hat{\gamma}(z)$	Laplace transform of the memory friction
δ	dimensionless energy loss
ε	parameter measuring the small noise intensity
$\varepsilon(t)$	exponentially correlated Gaussian noise (Ornstein-Uhlenbeck noise)
$\theta(x)$	characteristic function for the reaction coordinate
$\xi(t)$	classical noise
τ_c	noise correlation time
τ_e	escape time (inverse rate)
τ_s	local system relaxation time
λ_1	first nonzero eigenvalue of a master operator
λ_+	eigenvalue describing the growth rate of a deviation from the saddle-point configuration
ν	classical rate prefactor
$\rho(x,v)$	phase-space nonequilibrium probability density
κ	rate transmission factor
$\zeta(x)$	nonequilibrium form factor
ω_0	angular frequency of the metastable state
ω_b	positive-valued angular frequency of the unstable state at the barrier
Ω	domain of attraction
$\Omega(E)$	density of states
Σ	phase space
$\partial\Omega$	boundary of domain of attraction
Γ	master operator

I. INTRODUCTION

The problem of escape from metastable states is ubiquitous in almost all scientific areas. Reaction-rate theory has received major contributions from fields as diverse as chemical kinetics, the theory of diffusion in solids, homogeneous nucleation, and electrical transport theory, to name but a few. It was recognized early on that rate processes are characterized by rare events, i.e., rate processes are phenomena that take place on a long time scale when compared to dynamic time scales characterizing the states of local stability (see Fig. 1).

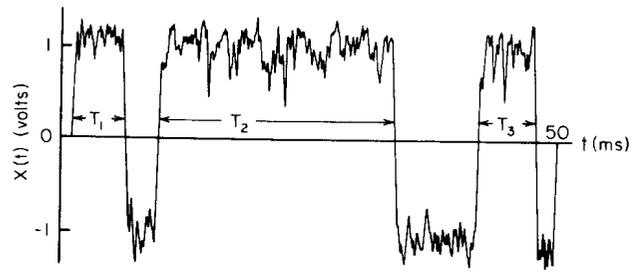

FIG. 1. A typical stochastic realization sampling the random sojourn times $\{T_1, T_2$, etc.$\}$ in a symmetric bistable potential $U(x) = -\frac{1}{2}x^2 + \frac{1}{4}x^4$, with the metastable states located at $x = \pm 1$. Data are from Hänggi, Mroczkowski, Moss, and McClintock, (1985).

The discipline of rate theory was created when Svante Arrhenius gave an extensive discussion of various reaction-rate data which, as a function of the inverse temperature $\beta = (k_B T)^{-1}$, vary on a logarithmic scale. In other words, the rate coefficient k, or simply the *rate* of escape, follows the Van't Hoff-Arrhenius law (Van't Hoff, 1884, Arrhenius, 1889)[1]

$$k = \nu \exp(-\beta E_b) , \tag{1.1}$$

where E_b denotes the threshold energy for activation and ν is a prefactor. Figure 2 depicts the Van't Hoff-Arrhenius plot for various reactions over a large temperature range. Further quantitative progress in the field was slow during the late 19th century. It was realized that escape from a state of local stability can happen only via noise-assisted hopping events. Therefore, the calculation of escape rate posed, at first glance, a daunting problem. The field had thus to await a theory of fluctuations. This concern with fluctuations started with pioneering contributions by Lord Rayleigh (1891), Einstein (1905), Smoluchowski (1906, 1913, 1915), Fokker (1913, 1914), Planck (1917), Ornstein (1917), Pontryagin *et al.* (1933), and many others. The work in early Brownian motion theory has been reviewed in an excellent paper by Chandrasekhar (1943). A more detailed account on early studies of Brownian motion can be found in recent review articles by Pais (1982) and Coffey (1985). Certainly, a major first piece of work in rate theory must be attributed to Smoluchowski (1917). He evaluated the diffusion-controlled rate coefficient k_c of coagulation, $k_c = 4\pi(D_A + D_B)(R_A + R_B)$, where $D_{A,B}$ and $R_{A,B}$ denote the diffusion constant and the radius of the scavenger species A and B, respectively. The present status of this important field of diffusion-controlled encounter reactions has recently been beautifully surveyed by Calef and Deutch (1983).

The first quantitative ideas related to general activated rate theory have their origins in the study of homogeneous nucleation in supersaturated vapors (Frenkel, 1955; Zinsmeister, 1970; Abraham, 1974). Naturally, homogeneous nucleation is a rather complex subject for which at present no complete solution is available, i.e., various interesting fundamental questions still remain (Abraham, 1974; Binder and Stauffer, 1976; Langer, 1980; Gunton San Miguel, and Sahni, 1983). In a pioneering paper,

[1]Beautiful historical accounts of the development of the Arrhenius equation have been given by Logan (1982), Laidler (1984, 1987), and Stiller (1989). On inspecting the original paper of Arrhenius, the authors of this review were abashed when they realized that Arrhenius does not present a single Arrhenius plot and, furthermore, credits the equation $k = \nu \exp -(B/T)$, commonly known as "the Arrhenius equation," to Van't Hoff. In his discussion of rate data, however, he introduces a "hypothetical body," i.e., an active state commonly known as the "activated complex," and proposes an equilibrium between normal and active reactant molecules. This concept in itself is certainly a most important contribution to reaction-rate theory.

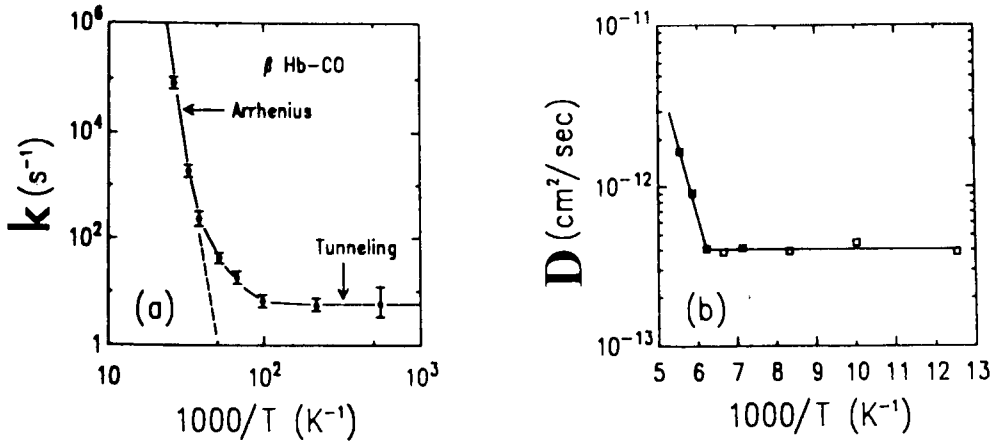

FIG. 2. Van't Hoff-Arrhenius plots of reaction-rate data for two different physical systems in which both thermal activation and tunneling events occur: (a) Rate of CO migration to a separated β chain of hemoglobin (Alberding *et al.*, 1976; Frauenfelder, 1979); (b) diffusion coefficient D of atomic hydrogen moving on the (110) plane of tungsten at a relative H-coverage of 0.1 (data taken from DiFoggio and Gomer, 1982). The diffusion D is directly proportional to the hopping rate k.

Farkas (1927) considered the rate of homogeneous nucleation by treating the detailed kinetics of atoms arriving at the droplet or evaporating from it. He introduced an approach that is known today as the "Markovian birth and death process."[2] Moreover, in his paper, Farkas described the cornerstone idea underlying any rate calculation—clearly, the rate of escape from a metastable state is characterized by the flux of particles that pass through the bottleneck separating products from reactants. The key input in any modern rate calculation is thus the evaluation of this very flux (normalized to one particle) across the bottleneck. The flux follows from a nonequilibrium probability, subject to the boundary conditions that stationary equilibrium prevails inside the metastable state and that the probability approaches zero beyond the bottleneck region, where the particles are removed (or absorbed) immediately and then reinjected into the initial well, yielding a stationary flux. On p. 237 of his article Farkas (1927) explicitly introduced this crucial concept, nowadays widely known as the flux-over-population method (see Sec. II.C), when he stated (freely translated from German)

> ...In order to calculate for a diffusion problem the number of particles that go through a bottleneck one must know the concentration at two locations. In our case the diffusion process is not allowed to perturb the stationary distribution towards smaller particle numbers, (i.e., for numbers $n < n_0$, with n_0 denoting the size of the critical nucleus); therefore one has an equilibrium concentration below ($n < n_0$); above ($n > n_0$), however, one must have for very large n a vanishing concentration of droplets...

[2]Note also that Farkas (1927) himself attributes the basic idea for his treatment to L. Szilard.

Here, the text in parentheses has been included for clarification of the terms "below" and "above." Farkas then proceeded to derive an explicit result for the rate of nucleation, which is identical with the result popularized later on by Becker and Döring (1935). In the meantime, the chemists had not been inactive. In the early twenties, Lindemann (1922) developed a multiple-step mechanism for unimolecular gas phase reactions (or more generally first-order reactions, $A \rightarrow B$, in which $\dot{c}_A = -kc_A$, with c denoting the concentration). Soon after, Hinshelwood (1926a, 1926b), among others, developed a quantitative approach. This chemical reaction-rate theory, as well as the early theory of bimolecular reactions (or more generally second-order reactions, $A + B \rightarrow C$, $\dot{c}_A = -k_{\rm bim} c_A c_B$) was reviewed by Fowler (1929) in Chap. XVIII of his book, and also by Moelwyn-Hughes (1933).

The next major development again came from the chemical physics community. This is represented by the works of Polanyi and Wigner (1928), Pelzer and Wigner (1932), Evans and Polanyi (1935), Eyring (1935), and Wynne-Jones and Eyring (1935). Polanyi and Wigner (1928) and Eyring (1935) treated the case of a nonlinear decomposing molecule consisting of n atoms. Eyring (1935) expressed the rate in terms of quantities that are available from the underlying potential surface and in addition made explicit use of (quantum) statistical mechanics for the partition function Z_A of the metastable state (A) and the activated complex ($\neq$), respectively. In this way he arrived at an epoch-making rate formula (Eyring, 1935; Laidler and King, 1983),

$$k = \kappa \left[\frac{k_B T}{h} \right] \frac{Z^{\neq}}{Z_A} \exp(-\beta E_b) \equiv \kappa k_{\rm TST} \,. \tag{1.2}$$

The parameter κ was originally introduced by Eyring (1935) as an *ad hoc* fudge factor (transmission coefficient), which corrects for those reactive trajectories $x(t)$ that recross the transition state and return without decomposing. Clearly, this fact always reduces the reaction rate k so that $\kappa \leq 1$. Within the chemical physics community this "Grande Concept" (Hirschfelder, 1982) in Eq. (1.2) has been the reigning method ever since. Its impact may be construed from the fact that, in their textbook, Glasstone, Laidler, and Eyring (1941) refer to this approximate theory as the *Absolute Rate Theory*. Setting $\kappa \equiv 1$ the result in Eq. (1.2) is commonly known as the transition-state theory (TST) rate, $k_{\rm TST}$. As with all great discoveries, there exist of course some precursors. For example, we mention here that in calculating the thermionic emission current, Richardson (1902, 1912), Laue (1918), and Dushman (1923) all implicitly made use of a simplified, one-dimensional version of TST (see also Herzfeld, 1919) wherein an electron e, with the work function ϕ (i.e., $E_b \equiv e\phi$) crossed the threshold barrier in free flight without dynamic influence from the surrounding lattice.

Hendrik Antonie Kramers (1894–1952) was engaged in reaction-rate theory from early on. During his Copenhagen years from 1916 to 1926 he pursued research with Christiansen (Christiansen and Kramers, 1923) on the theory of unimolecular reactions. They combined Boltzmann collision theory with Einstein's theory of radiation in an attempt to characterize within an energy-chain mechanism the prefactor of the rate. Within classical rate theory, all later theoretical efforts up to the present day focus precisely on the behavior of this complex prefactor quantity ν in Eq. (1.1). Kramers returned to the subject in 1940 with his celebrated paper on "Brownian Motion in a Field of Force and the Diffusion Model of Chemical Reactions" (Kramers, 1940). He understood well the mechanism of the escape process as a noise-assisted reaction. Starting from a derivation of the Fokker-Planck equation for the Brownian motion in phase space in the presence of a nonlinear potential field [which historically had been derived earlier by Klein (1922)], he pictured the escape process as governed by Brownian motion dynamics driven by thermal forces, which in turn are connected—via the fluctuation-dissipation theorem—with the temperature T and the friction γ. He analyzed separately the cases of strong and weak friction. In particular, his work on the weak-friction case was pioneering: For the first time he derived a diffusion equation for the dynamics of the action (or energy) of the reactive particle. For this part of his paper he must surely have been guided by his early work on unimolecular gas phase reactions (Christiansen and Kramers, 1923), working along the lines developed previously by Lindemann (1922), Christiansen (1926), and Hinshelwood (1926a). In particular, the rate of unimolecular gas phase reactions had been given by Polanyi (1920), Lewis and Smith (1925), Wigner (1925), Christiansen (1926), Hinshelwood (1926a, 1926b), and Polanyi and Wigner (1928) as

$$k = \frac{\alpha}{(n-1)!}(\beta E_b)^{n-1}\exp(-\beta E_b) \ . \tag{1.3}$$

Here n denotes the number of strongly coupled vibrational modes and α denotes the collision frequency, which is proportional to the pressure (concentration). Thus the rate in Eq. (1.3) approaches zero for low pressure or weak friction.

Kramers *does not cite* these papers, but he must have been aware of these developments through Eyring's and Evans and Polanyi's works (Evans and Polanyi, 1935; Eyring, 1935) which he does cite. His mathematical insight was remarkable. He did manage to evaluate, by use of some subtle, almost acrobatic mathematics, the rate of escape for very weak friction, thereby demonstrating that the transition-state $k_{\rm TST}$ seriously overestimates the true rate,

$$k(\gamma \to 0) = \gamma \beta I_b k_{\rm TST}, \quad \gamma \beta I_b < 1 \ , \tag{1.4}$$

where I_b denotes the action of the escaping particle at the barrier. Moreover, for the case of moderate-to-strong damping he succeeded in evaluating the stationary, nonequilibrium probability current in two-dimensional phase space $(x, \dot{x} = v$; see Sec. IV below). In doing so, he invented an ingenious approximation scheme, which transforms a partial differential equation in two variables into an ordinary differential equation [see Eqs. (4.24)–(4.26) below], yielding for the prefactor ν in Eq. (1.1) the seminal result[3]

$$\nu = \left[\left[\frac{\gamma^2}{4} + \omega_b^2 \right]^{1/2} - \frac{\gamma}{2} \right] \frac{\omega_0}{2\pi\omega_b} \ . \tag{1.5}$$

Here, $\omega_0^2 \equiv M^{-1}U''(x_a)$ is the squared angular frequency inside the metastable minimum, and $\omega_b^2 \equiv M^{-1}|U''(x_b)|$ denotes the squared angular frequency at the transition state (see Fig. 3). For a long period, his result for the Smoluchowski limit, $\gamma \gg \omega_b$, became the one most widely appreciated:

$$\nu \underset{\gamma \gg \omega_b}{\longrightarrow} \frac{\omega_b}{\gamma}\frac{\omega_0}{2\pi} \ . \tag{1.6}$$

There is certainly an irony here; this very case of overdamped one-dimensional diffusion escape dynamics had actually been solved prior to Kramers with greater generality, accounting also for state-dependent diffusion, in papers by Farkas (1927), Kaischew and Stranski (1934), and Becker and Döring (1935), which all deal with the rate of homogeneous nucleation. The overdamped result had also been anticipated via the calculation of the mean first-passage time of one-dimensional Fokker-Planck processes in a paper by Pontryagin, Andronov, and Vitt (1933). Curiously enough, Kramers did not cite any of this prior work.

[3]See Eq. (25) in Kramers' (1940) original paper. Note that Kramers (1940) uses the symbol ω to denote not the angular frequency $\omega = 2\pi\nu$ but the frequency ν itself.

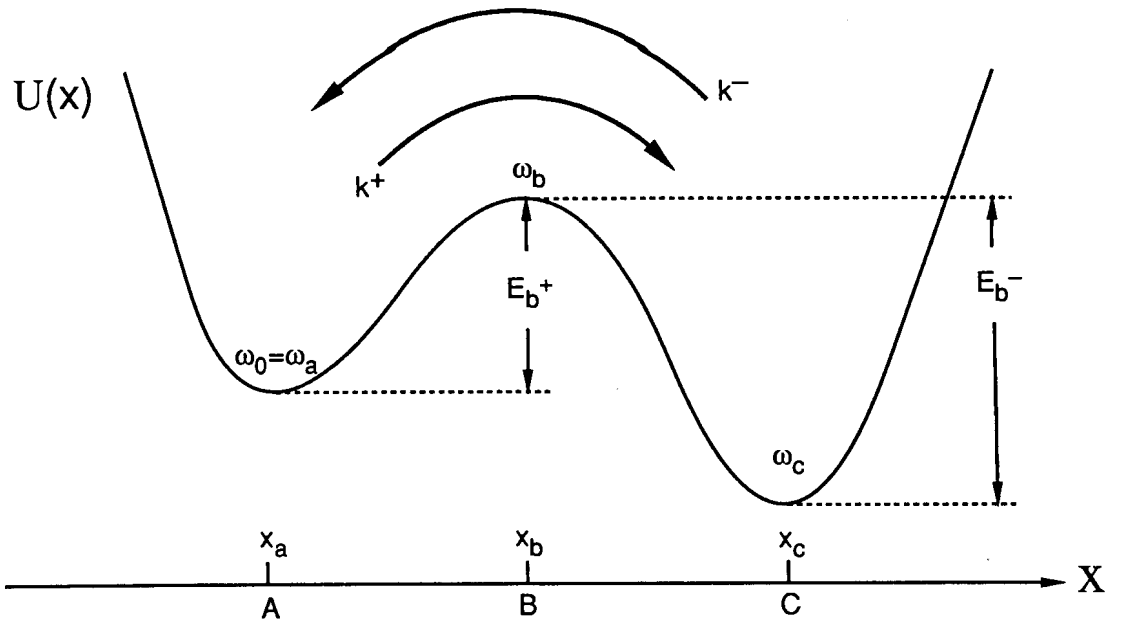

FIG. 3. Potential $U(x)$ with two metastable states A and C. Escape occurs via the forward rate k^+ and the backward rate k^-, respectively, and $E_b^{\pm}$ are the corresponding activation energies.

Although Kramers' paper contained the term "chemical reaction" in its title, the chemical world at that time had no direct use for his predictions. For unimolecular gas phase reactions, a description of the rate in terms of *discrete* energy exchanges was more suitable than the continuous energy-exchange mechanism underlying energy diffusion in Kramers' model (see Sec. V). Work on chemical reactions in condensed phases, for which the Kramers theory is most appropriate, had to await the experimental progress achieved in the late seventies and eighties. Likewise, experiments in nonlinear optics and condensed-matter physics, which can be interpreted rather accurately in terms of Kramers' rate theory, have been undertaken only recently (see Sec. XI). This is probably one of the reasons why recognition and appreciation of the most elegant scheme Kramers had provided came very slowly. In the years since 1940, only little cross-fertilization between physics and chemistry has taken place. It is somewhat striking to note that otherwise very authoritative recent books on physical chemistry and kinetics (Berry, Rice, and Ross, 1980; Laidler, 1987) do not discuss Kramers' results. Likewise, rarely does one find a book on kinetics or nonequilibrium statistical mechanics written by a physicist in which is discussed the important transition-state theory pioneered by Polanyi and Wigner, Eyring, and others. Indeed, it took almost fifty years after the work by Eyring (1935) before it was realized that Kramers' theory with (memory) friction (Grote and Hynes, 1980; Hänggi and Mojtabai, 1982; Carmeli and Nitzan 1984; Straub, Borkovec, and Berne, 1985, 1986; Talkner and Braun, 1988) also resulted as a special form of multidimensional TST in full phase space of all degrees of freedom (Hänggi, 1986a; Pollak 1986a, 1986b; note also Sec. III.C). Fortunately, the once fruitful cross-fertilization of the twenties between physics and chemistry has undergone a renaissance, beginning with the late seventies, involving research on quantum chaos (Chirikov, 1979; Pechukas, 1983; Casati, 1985) and on the quantum theory of reaction rates (Miller, 1975; Wolynes, 1981; Caldeira and Leggett, 1981, 1983a; Weiss, Grabert, Hänggi, and Riseborough, 1987; Hänggi and Hontscha, 1988).

In the following sections we have attempted to review the present status of the field fifty years after Kramers' historic cornerstone paper in 1940. The present time is particularly suitable for such a comprehensive review. The last two decades have produced (apart from a large number of papers that could be classified as reformulations, or rediscoveries of older findings) essential new insights and profound developments, both in theory and experiment. Worth mentioning are not only the above-mentioned generalization of Kramers' theory and the many realistic applications of rate theory with memory friction, but also the intriguing developments in rate theory at weak friction (see Sec. V), the turnover between weak and strong friction (see Sec. VI), and the recent developments in stationary nonequilibrium rate theory (see Sec. VIII). Much of the exciting recent progress also has had a quantum-mechanical flavor (see Sec. IX). Moreover, the recent experimental rate studies in liquids and in Josephson-junction systems provided an additional impetus for the study of rate processes in complex situations. Some other, more confined review papers, which in several aspects complement our account and provide additional insight into topics covered herein, are those by Slater (1959), Troe (1975, 1986), Hase (1976), Pechukas (1976), Kapral (1981), Truhlar, Hase, and Hynes (1983), Hynes (1985, 1986a), Fonseca *et al.* (1985), Frauenfelder

and Wolynes (1985), Chandler (1986), Fleming, Courtney, and Balk (1986), Hänggi (1986a, 1986b), Landauer (1987), Berne, Borkovec, and Straub (1988), Nitzan (1988), Sceats (1988), and Büttiker (1989).

II. ROADWAY TO RATE CALCULATIONS

Before we elaborate on the various theoretical methods used in rate calculations we begin with a few general considerations relating to escape from a domain of attraction.

A. Separation of time scales

Let us consider two states A and C of local stability, as pictured in Fig. 3. We shall assume that the coordinate x describes the dynamics of the escape process, i.e., x plays the role of a reaction coordinate which generally is coupled to an environment (or a collection of physically different surroundings), which can either donate or remove energy from the reaction coordinate. Due to such a coupling the reaction coordinate is not a deterministic dynamic variable, but becomes a stochastic process, i.e., $x(t)$ is a random trajectory (Fig. 1). In order to make an escape from well A, the "random walker" $x(t)$ must necessarily acquire energy to become activated toward the barrier, and upon reaching the barrier top it must again lose energy to become trapped inside the neighboring well C. In a more general situation, the two states A and C correspond to two different attractors in a multidimensional phase space, which are separated by a barrier B, containing one or possibly more saddle points, possibly unstable limit cycles, or even more complex unstable attractors, including combinations thereof. For most of the following we shall restrict our discussion of the theory to the situation in which two attracting basins are separated by a single saddle point. The time scale of escape clearly depends on the size of the fluctuations $f(t)$,

$$f(t)=x(t)-\langle x(t)\rangle \ . \tag{2.1}$$

If we relate the fluctuations $f(t)$ to an appropriate energy scale $E_{\rm noise}$, transitions between the two attracting regions A and C will be *infrequent* whenever the condition

$$\frac{E_{\rm noise}}{E_b^{\pm}} \ll 1 \tag{2.2a}$$

holds, Here, $E_b^{\pm}$ denotes the barrier height for forward- and backward-activated events, respectively (see Fig. 3). For systems in contact with a thermal environment at temperatures T the energy scale $E_{\rm noise}$ is given by $\beta^{-1}\equiv k_B T$ (k_B is Boltzmann's constant), i.e., the condition in Eq. (2.2a) reduces to

$$\beta E_b^{\pm} \gg 1 \ . \tag{2.2b}$$

The time scale τ_s describing decay within the attractor A is given by

$$\tau_s \sim M^{1/2}\left[\frac{d^2U(x\simeq A)}{dx^2}\right]^{-1/2} , \tag{2.3}$$

where M is the effective mass of the reacting particle. Thus, with the condition in Eqs. (2.2a) and (2.2b), the time τ_s is well separated from the time scale of escape τ_e,

$$\tau_e \sim \tau_s \exp(E_b^{\pm}/E_{\rm noise}) \gg \tau_s \ . \tag{2.4}$$

In the above discussion of time-scale separation between the activation process and the relaxation of the local system we have adopted a simplified picture in which all of the fast scales could be characterized by a single local-system relaxation time τ_s. In reality, however, there exist many such fast time scales, such as, for example, the time of relaxation in either of the two (or many) locally stable wells, the correlation time τ_c of the noise, the time τ_b for a trajectory to cross the barrier region, or the time τ_R to lose (gain) the energy $E_{\rm noise}$, etc. All these various time scales will, of course, be of importance in the detailed description of the rate of escape k,

$$k \sim \tau_e^{-1} \ . \tag{2.5}$$

The crucial requirement for a separation of time scales is that τ_e be much larger than all these other relevant time scales $\{\tau_s,\tau_b,\tau_c,\tau_R,\text{ etc.}\}$ of the system dynamics. In this sense, τ_s stands for the collection of all these *fast* time scales relevant to the process of activation.

B. Equation of motion for the reaction coordinate

As mentioned above, the stochastic motion of the reaction coordinate $x(t)$ is a combined effect induced by the coupling among a multitude of environmental degrees of freedom. In principle all these may couple directly to the reaction coordinate $x(t)$. Let Σ denote the full phase space of the system plus environment(s), which are prepared according to some initial statistical weighting of all initial (generalized) coordinates and (generalized) momenta. Then the dynamics of the pair $\mathbf{X}(t)\equiv[x(t),\dot{x}(t)]$ (where the overdot refers to a differentiation with respect to time t) is the result of a *reduced* description from the full phase space $\Sigma\rightarrow[x(t),\dot{x}(t)]$. This approach entails new concepts, which can be characterized loosely as *friction* and *entropy*. The entropy factor concerns the reduction of all coupled degrees of freedom from a high-dimensional potential energy surface in full phase space to an effective potential (i.e., a potential of mean force) for the reduced dynamics of the reaction coordinate. Friction concerns the reduced action of the degrees of freedom that are lost upon contraction of the complete phase-space dynamics. Clearly, the two concepts are not independent of each other. The mathematics of such a reduction has been worked out in full generality within the framework of statistical mechanics, using the technique of projection operators (Berne and Harp, 1970; Berne, 1971; Forster, 1975; Hynes and Deutch, 1975; Grabert, 1982).

The "coarse-grained" dynamics $\mathbf{X}(t)=[x(t),\dot{x}(t)]$ can be cast either in the form of a generalized Langevin equation or in the form of a generalized master equation. For a detailed account of this reduction scheme and the interesting interrelationships between the two formulations, we refer the reader to the discussion by Grabert, Hänggi, and Talkner (1980), in which the previous literature on this topic is also cited. One basic result of such a reduction scheme is—depending on the detailed form of the coupling among the degrees of freedom—the occurrence of a renormalization of mass as well as a renormalization of bare potential fields. Both are classical effects, but they also affect the quantum treatment of the escape process (see Sec. IX). Clearly, a reduction from typically $\sim 10^{23}$ degrees of freedom in Σ phase space to a single reaction coordinate $\mathbf{X}(t)=[x(t),\dot{x}(t)]$ makes the problem formally more tractable; the price to be paid, however, is that the resulting dynamics generally contain memory. In other words, the projection of the full dynamics in Σ onto $\mathbf{X}$ yield in general a non-Markovian process with an equation of motion (Kawasaki, 1973; Grabert, Hänggi, and Talkner, 1980)

$$\dot{\mathbf{X}}(t)=\mathbf{V}[\mathbf{X}(t)]+\int_0^t \bar{p}^{-1}[\mathbf{X}(t-s)]\frac{\partial}{\partial \mathbf{X}(t-s)}\{\Pi[\mathbf{X}(t-s);s]\bar{p}[\mathbf{X}(t-s)]\}ds+\xi(t)\ . \tag{2.6a}$$

The effect of mass renormalization is contained in a generalized, time-dependent (memory)-friction tensor $\Pi(\mathbf{X};s)$, which obeys the fluctuation-dissipation relation (Grabert, Hänggi, and Talkner, 1980)

$$\langle \xi(t)\xi(0)|\mathbf{X}(0)=\mathbf{X}\rangle=\Pi(\mathbf{X};t)\ , \tag{2.6b}$$

while the renormalization of the bare potential occurs via the drift field

$$\mathbf{V}(\mathbf{X})=\int \delta[\mathbf{X}(\Sigma)-\mathbf{X}]\dot{\mathbf{X}}(\Sigma)\frac{\bar{p}(\Sigma)}{\bar{p}(\mathbf{X})}d\Sigma\ , \tag{2.6c}$$

where $\bar{p}(\Sigma)$ and $\bar{p}(\mathbf{X})$ denote the corresponding (thermal or nonthermal) stationary probabilities carrying zero flux.

This generalized Brownian motion dynamics for $\mathbf{X}(t)=[x(t),\dot{x}(t)]$ forms the starting point for all further approximations. In particular, *for thermal systems with extremely short noise correlation times τ_c, one can use a Markovian approximation* for Eq. (2.6). Such a Markovian description of $\mathbf{X}(t)$ can be obtained from an underlying Hamiltonian dynamics in full phase space Σ with initial coordinates and momenta distributed according to a canonical thermal equilibrium, and with the reacting particle (mass M) moving in a potential $U(x)$ that is coupled bilinearly to a bath of harmonic oscillators. With a suitable limiting procedure (Zwanzig, 1973; see Sec. III.C), Eq. (2.6a) then reduces with an infinite number of bath oscillators to the familiar (Markovian) Langevin equation for nonlinear Brownian motion,

$$\dot{x}=v,\quad \dot{v}=-M^{-1}\frac{\partial U}{\partial x}-\gamma v+M^{-1}\xi(t)\ . \tag{2.7}$$

In Eq. (2.7), $\xi(t)$ denotes Gaussian white noise of vanishing mean with the δ correlation function

$$\langle \xi(t)\xi(s)\rangle=2k_BT\gamma M\delta(t-s)\ . \tag{2.8}$$

Here γ denotes a uniform, temperature-independent velocity relaxation rate.

Equations (2.7) and (2.8) are the starting point for Kramers' treatment of the reaction rate, reviewed in Sec. IV [see Eq. (4.1)]. Without a clear-cut separation between the system relaxation time scale τ_s in Eq. (2.3) and the noise correlation time τ_c one is generally dealing with nonlinear non-Markovian Brownian motion dynamics with memory friction [Eq. (2.6)]. In many applications, however, the dependence on x and $\dot{x}$ of the friction tensor might become negligible, yielding a non-Markovian generalization of Eq. (2.7) with a linear memory friction, i.e., the friction force γv may then be replaced by $\int_0^t \gamma(t-s)\dot{x}(s)ds$. The rate theory for this idealized non-Markovian Brownian motion dynamics will be studied in greater detail in Sec. III.C.

C. Theoretical concepts for rate calculations

Here we present a discussion of the most familiar approaches used in rate theory.

1. The flux-over-population method

A common procedure, pioneered by Farkas (1927; see Introduction), is to evaluate the steady-state current j that results if particles are continuously fed into the domain of attraction and subsequently are continuously removed by an observer in the neighboring domain of attraction. This scheme results in a steady-state current which builds up a stationary nonequilibrium probability density p_0 inside the initial domain of attraction. This nonequilibrium probability is subject to the boundary conditions

$$p_0(x=x_1)=\bar{p}(x_1),\quad p_0(x=x_2)=0\ . \tag{2.9}$$

Here x_1 denotes the value of the reaction coordinate inside the initial domain of attraction, and $x=x_2$ is the value of the reaction coordinate beyond the transition state $x_b\equiv x_T$ inside the neighboring domain of attraction. The stationary probability $\bar{p}(x)$ corresponds to a vanishing current, $j=0$, along the reaction coordinate. The second condition in Eq. (2.9) implies an absorbing boundary, where the particles are removed immediately at an infinite rate. If

$$n_0=\int_{x<x_T} p_0(x)dx \tag{2.10}$$

denotes the (nonequilibrium) population inside the initial domain of attraction (which usually is normalized to one

particle), the rate of escape k is given by the ratio

$$k=\frac{j}{n_0} . \tag{2.11}$$

Clearly, this general procedure relies in practice on the explicit knowledge of a (Markovian or non-Markovian) master equation governing the time dependence for the single-event probability $p(x,t)$ of the reaction coordinate. In view of the reduction procedure $\Sigma\rightarrow x(t)$, this corresponding equation of motion for the single-event probability is generally strongly non-Markovian in structure. Therefore, in practice, it is often preferable to work with a less coarse-grained description of the escape dynamics such as, for example, the full phase-space dynamics of the reaction coordinate $\mathbf{X}(t)=[x(t),\dot{x}(t)]$ [see Eq. (2.7)]. The condition in Eq. (2.9) is then replaced by the requirement that near the attractor there exists stationary equilibrium $p_0(x,\dot{x})=\bar{p}(x,\dot{x})$, whereas the flux-carrying nonequilibrium probability $p_0(x,\dot{x})$ vanishes outside the domain of attraction. The attracting domain Ω is thus separated from the neighboring domain of attraction by a separatrix. We shall explicitly utilize this procedure in Sec. IV, where we elaborate on Kramers' rate approach for the Langevin dynamics in Eq. (2.7).

2. Method of reactive flux

In this subsection we confine ourselves to thermal systems only, with $\bar{p}$ denoting stationary thermal equilibrium. The dynamics of spontaneous fluctuations and relaxation toward stationary equilibrium of a *large* nonequilibrium concentration are connected, if we note that the (long-time) decay occurs in both cases on the same time scale τ_e. This concept, which is valid whenever there is a clear-cut separation between time scales, is known as the "regression hypothesis" (Onsager, 1931; Chandler 1978, 1987, 1988). For example, consider the dynamics (Fig. 3) of the two relative populations $n_a(t)$ and $n_c(t)$, corresponding to the two regions of local stability. In terms of the rate coefficients k^+,k^- the population dynamics reads

$$\dot{n}_a=-k^+n_a+k^-n_c,\quad \dot{n}_c=k^+n_a-k^-n_c . \tag{2.12}$$

At equilibrium, i.e., $0=-k^+\bar{n}_a+k^-\bar{n}_c$, we have in terms of the equilibrium constant K the detailed balance relation

$$\frac{\bar{n}_a}{\bar{n}_c}=\frac{k^-}{k^+}\equiv K . \tag{2.13}$$

The relaxation of $n_a(t)$ from an initial nonequilibrium deviation, $\Delta n_a(0)=n_a(0)-\bar{n}_a$, thus reads

$$\frac{n_a(t)-\bar{n}_a}{\Delta n_a(0)}\equiv\frac{\Delta n_a(t)}{\Delta n_a(0)}=\exp(-\lambda t) , \tag{2.14a}$$

with the relaxation rate given by

$$\lambda=k^++k^- . \tag{2.14b}$$

The population $n_a(t)$ can be described as a nonequilibrium average of a characteristic function $\theta(x)$ where

$$\theta(x)=\begin{cases}1, & \text{for } x>0\\ 0, & \text{for } x<0 .\end{cases} \tag{2.15}$$

Here we have introduced a reaction coordinate $x(\mathbf{q})$ that is *positive* in the domain of attraction of the metastable state A and is *negative* elsewhere. Moreover, throughout this section and Sec. III we use a coordinate system such that $x_T=0$ defines the dividing surface between the metastable states A and C. The expectation value

$$\langle\theta\rangle=\bar{n}_a \tag{2.16}$$

denotes the equilibrium population. The fluctuations of θ obey

$$\langle\delta\theta^2\rangle=\langle\theta^2\rangle-\langle\theta\rangle^2=\bar{n}_a\bar{n}_c , \tag{2.17}$$

where $\langle\theta^2\rangle=\bar{n}_a$ and $\bar{n}_a+\bar{n}_c=1$.

According to Onsager's regression hypothesis, the nonequilibrium average $\Delta n_a(t)$ decays according to the same dynamic law as the equilibrium correlation function of the fluctuation

$$\delta\theta[x(t)]=\theta[x(t)]-\langle\theta\rangle ,$$

namely [see Eq. (2.14a)],

$$\frac{\langle\delta\theta[x(0)]\delta\theta[x(t)]\rangle}{\langle\delta\theta^2\rangle}=\exp(-\lambda t) . \tag{2.18}$$

This relation, however, cannot be valid at all times t; for short times $t\leq\tau_s$ the transient behavior does not correspond to an exponential decay. Next we introduce a time scale τ, obeying

$$\frac{1}{\lambda}=\tau_e\gg\tau\gg\tau_s . \tag{2.19}$$

Let us now consider the time derivation of Eq. (2.18) on this intermediate time scale τ. The *reactive flux* is given by

$$\frac{\langle\delta\theta[x(0)]\dot{\theta}[x(t)]\rangle}{\langle\delta\theta^2\rangle}=-\frac{\langle\delta[x(0)]\dot{x}(0)\theta[x(t)]\rangle}{\langle\delta\theta^2\rangle}$$
$$=-\lambda\exp(-\lambda t)\xrightarrow{t\sim\tau}-\lambda . \tag{2.20}$$

Thus, with $\exp(-\lambda\tau)\sim 1$, we obtain an explicit expression for the relaxation rate (Keck, 1960, 1967; Yamamoto, 1960; Fischer, 1970; Kapral, 1972; Anderson, 1973; Rosenstein, 1973; Bennett, 1977; Chandler 1978, 1987, 1988; Stillinger, 1978, Montgomery, Chandler, and Berne, 1979; Berne, 1985)

$$\lambda=\frac{\langle\delta[x(0)]\dot{x}(0)\theta[x(\tau)]\rangle}{\bar{n}_a\bar{n}_c} . \tag{2.21}$$

Equivalently, by use of Eqs. (2.13) and (2.14b), we find for the forward rate

$$k^+=\frac{\langle\delta[x(0)]\dot{x}(0)\theta[x(\tau)]\rangle}{\langle\theta(x)\rangle} . \tag{2.22}$$

The results in Eqs. (2.21) and (2.22) have been derived by Chandler (1978) in more rigorous terms utilizing projection operators. In particular, his derivation makes explicit that the correlation formula in Eq. (2.22) contains *relative errors* of the order $\exp(-E_b/k_BT)$, where E_b denotes the corresponding barrier heights for k^+ or k^-, respectively. For activated events obeying Eqs. (2.2) and (2.3) such errors are of course negligible.

It is important to note that the validity of Eqs. (2.21) and (2.22) holds independently of the nature of the underlying dynamics. In particular, the expressions in Eqs. (2.21) and (2.22) hold equally well for situations in which the reaction coordinate $x(t)$ moves primarily via spatial diffusion (i.e., strong friction) and those in which $x(t)$ moves via inertia-dominated Brownian motion (i.e., weak friction).

Formally, let us consider the limit of Eq. (2.22) as $\tau \to 0^+$. In this case the rate can be expressed as an equilibrium average of a one-way flux at the transition state $x_T=0$,

$$k^+_{\rm TST}=\frac{\langle \delta[x(0)]\dot{x}(0)\theta[\dot{x}(0)]\rangle}{\langle\theta(x)\rangle} . \tag{2.23}$$

Equation (2.23) equals the result of transition-state theory (Hill, 1960; Keck, 1967; Rosenstein, 1973; Pechukas, 1976, Hynes, 1985; Chandler, 1987; see Sec. III). Upon comparison of Eqs. (2.23) and (2.22) one finds that transition-state theory always overestimates the true rate (see, for example, Chandler, 1987),

$$k^+_{\rm TST} \geq k . \tag{2.24}$$

This important inequality is due to the observation that within transition-state theory recrossings of reactive trajectories are neglected. In other words, with $\theta_{\rm TST}[x(\tau)]\equiv 1$, if $\dot{x}(0^+)>0$, and $\theta_{\rm TST}[x(\tau)]\equiv 0$, if $\dot{x}(0^+)<0$, transition-state theory assumes that all trajectories heading toward the product region from the transition state will indeed end up in the product region C.

The reactive flux in Eq. (2.22),

$$k^+(t)=\frac{\langle \dot{x}(0)\delta[x(0)]\theta[x(t)]\rangle}{\langle\theta(x)\rangle} , \tag{2.25}$$

is sketched in Fig. 4. From Eq. (2.22) we note that the asymptotic forward rate k^+ appears within a molecular dynamic simulation (Montgomery, Chandler, and Berne, 1979; Berne 1985) after a time increment $\Delta t > \tau_s$ as the *plateau value*. If no such plateau value behavior can be observed, we have no well-defined rate k^+ that is independent of time. The results in Eqs. (2.21) and (2.22), are rather suitable for a rate evaluation via computer simulations (see Sec. X). Clearly, however, the plateau value, or its inverse, the plateau time, are not appropriate quantities to be calculated on analytical grounds. Thus almost all of the analytical work discussed below rests upon the flux-over-population method, the TST approximation in Eq. (2.23), or alternative concepts such as the eigenvalue method or the mean-first-passage-time concept, which will be discussed in detail in Sec. VII.

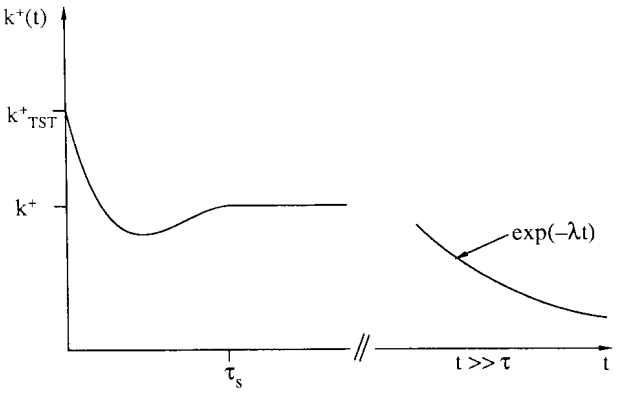

FIG. 4. Characteristic behavior of the reactive flux $k^+(t)$ in Eq. (2.25) with $\lambda \equiv k^+ + k^-$. At times $t < \tau_s$ one observes transient recrossings. The rate k^+ appears as the plateau value at long times $t \gg \tau_s$. At extremely long times $t \sim (k^+)^{-1}$, the reactive flux exhibits an exponential decay, which is not yet noticeable on the intermediate time scale τ defined through Eq. (2.19).

Equations (2.21)–(2.25) are analogous to the Green-Kubo formulas for transport coefficients (Kirkwood, 1946, 1947; Green, 1952, 1954; Kubo, 1957, 1959; Zwanzig, 1965; Forster, 1975). Nevertheless, the form of Eqs. (2.21)–(2.25) requires that the velocity of the reaction coordinate $\dot{x}(t=0)$ be well defined. Hence Eq. (2.21) cannot be directly applied to stochastic trajectories that are driven by *white-noise forces,* implying for $x(t)$ nondifferentiable trajectories of unbounded variation (Hänggi and Thomas, 1982). In this latter case, a preferable procedure consists in introducing for the correlation in Eq. (2.18) the generalized version (Borkovec and Talkner, 1990)

$$C(t)=\frac{\langle f[x(0)]\theta[x(t)]\rangle}{\langle f[x(0)]\rangle} \sim \frac{k^+}{k^++k^-}\exp(-[k^++k^-]t) , \tag{2.26}$$

where $f(x)$ is a conveniently chosen function that essentially equals unity inside the domain of attraction of the metastable state and vanishes outside. The rate k^+ is then obtained as

$$k^+=-\frac{\partial}{\partial\tau}C(\tau)\equiv -\dot{C}(\tau) = -\dot{C}(0^+)\kappa \leq -\dot{C}(0^+) , \tag{2.27}$$

where $\kappa=\dot{C}(\tau)/\dot{C}(0^+)$ is the transmission factor, and

$$-\dot{C}(0^+)=-\frac{\partial}{\partial\tau}C(\tau=0^+) \equiv \frac{\langle \dot{f}[x(0)]\theta[x(0^+)]\rangle}{\langle f[x(0)]\rangle} \tag{2.28}$$

presents an analog of the (TST) rate in Eq. (2.23). Note that, for a well-defined velocity $\dot{x}(0)$, the choice $f(x)=\theta(x)$ in Eq. (2.27) equals the previous result in Eq. (2.22).

3. Method of lowest eigenvalue, mean first-passage time, and the like

The flux-over-population method and the reactive flux approach present general methods for the evaluation of the escape rate. There exist, however, a number of other techniques that, under certain circumstances, might be invoked preferably. Most importantly, there is the connection between the rate of escape and the smallest nonvanishing eigenvalue governing the time evolution of an initial nonequilibrium probability. An important example is the case in which the escape dynamics is governed by a (Markovian) master equation for the single-event probability $p(x,t)$

$$\dot{p}(x,t)=\int \Gamma(x,y)p(y,t)dy \ . \tag{2.29}$$

Here the master operator Γ is a time-independent, in general nonsymmetric dissipative operator with generally complex-valued eigenvalues (Hänggi and Thomas, 1982). From Eqs. (2.12)–(2.14) one obtains the connection

$$\lambda=k^{+}+k^{-}\simeq|\mathrm{Re}\lambda_1| \ , \tag{2.30}$$

where $\mathrm{Re}\lambda_1<0$ denotes the real part of the (possibly complex-valued) eigenvalue of Γ possessing the smallest, nonvanishing absolute value for the real part of the set of eigenvalues $\{\lambda\}$ of Γ. From Eq. (2.13) one finds in terms of the equilibrium constant K the relations

$$k^{+}=|\mathrm{Re}\lambda_1|\frac{1}{K+1} \tag{2.31}$$

and

$$k^{-}=|\mathrm{Re}\lambda_1|\frac{K}{K+1} \ . \tag{2.32}$$

From a technical point of view, the quantity $|\mathrm{Re}\lambda_1|$ in Eq. (2.30) can be calculated by a number of procedures, e.g., the matrix-continued fraction method (Risken and Vollmer, 1979, 1980; Risken, 1984), eigenfunction analysis (Tomita *et al.*, 1976; Visscher, 1976; Van Kampen, 1977; Caroli *et al.*, 1979; Edholm and Leimar, 1979), variational methods (Larson and Kostin, 1980; Bez and Talkner, 1981; Brand, Schenzle, and Schröder, 1982; Gaveau and Schulman, 1988), supersymmetry techniques (Bernstein and Brown, 1984; Marchesoni, Sodano, and Zannetti, 1988), correlation function and Laplace transform techniques (Skinner and Wolynes, 1978; Grote and Hynes, 1980), or path-integral methods (Weiss and Häffner, 1980; Caroli *et al.*, 1981; Weiss, 1982; Weiss, Grabert, Hänggi, and Riseborough, 1987), to name but a few.

Another alternative to the approaches already mentioned is the concept of the mean first-passage time (MFPT). This is the average time that a random walker, starting from a point x_0 *inside* the initial domain of attraction, takes to leave the domain of attraction for the first time, i.e., the MFPT is the average time needed to reach the separatrix manifold for the first time (Talkner, 1987). At weak noise [see Eq. (2.2)] this MFPT, $t(x_0)$, becomes essentially independent of the starting point, i.e., $t(x_0)\simeq t_{\mathrm{MFPT}}$ for all starting configurations away from the immediate neighborhood of the separatrix. If we note that the probability of crossing the separatrix in either direction equals one half, the total escape time τ_e equals $2t_{\mathrm{MFPT}}$. Thus the rate of escape k itself is given by

$$k=\frac{1}{2t_{\mathrm{MFPT}}} \ . \tag{2.33}$$

Unfortunately, the MFPT is a rather complex notion for a general (non-Markovian) stochastic process $x(t)$ (Hänggi and Talkner, 1981, 1983). In particular, extreme care must be taken in the choice of the correct boundary (Hänggi, Jung, and Talkner, 1988). Moreover, the corresponding boundary conditions on $t(x_0)$ itself are generally not readily constructed (Weiss and Szabo, 1983; Hänggi and Talkner, 1985; Balakrishnan, Van den Broeck, and Hänggi, 1988). The use of the MFPT is well known for one-dimensional Markov processes $x(t)$ which are of the Fokker-Planck form (Pontryagin, Andronov, and Vitt, 1933; Weiss, 1967; Schulten, Schulten, and Szabo, 1981), or for one-dimensional master equations of the birth and death type involving nearest-neighbor transitions (Weiss, 1967; Gillespie, 1979, 1981), as well as for one-dimensional master equations with one- and two-step transitions only (Hänggi and Talkner, 1981). In all these cases $t(x_0)$ can be solved for *exactly in terms of quadratures, or corresponding summations;* see Sec. VII.

III. CLASSICAL TRANSITION-STATE THEORY

Transition-state theory (TST) is fundamentally a classical mechanical theory. The basic assumption of the theory—namely, that passage through a transition state without subsequent return is a "'moment of decision" for the reacting system—is an assumption that can be stated with precision only within classical mechanics (Wigner, 1937, 1938). In Sec. IX a generalization of this concept is presented which accounts for the leading quantum corrections within semiclassical quantum mechanics. Here we restrict ourselves to the classical approach. The transition state is identified as a dividing surface separating reactants from products, or more generally, any two physical states that are separated by a bottleneck in phase space. There are two key assumptions to TST.

(i) Strong-coupling assumption: Thermodynamic equilibrium must prevail throughout the entire system for all degrees of freedom. All effects that result from a deviation from the thermal equilibrium distribution, such as the Boltzmann distribution, are neglected.

(ii) Point of no return: Any orbit crossing the dividing surface will not recross it.

The TST rate is proportional to the total flux of classical trajectories from reactant to product side of the dividing surface. This flux is calculated either with the Boltzmann weighting function at a given temperature T (canonical TST) or with a delta-function weighting accounting only for the trajectories of a given total energy

E (microcanonical TST). Canonical TST was originally put forward by Polanyi and Wigner (1928) and developed further by Pelzer and Wigner (1932), Eyring (1935), Wynne-Jones and Eyring (1935), and Evans and Polanyi (1935). Microcanonical TST was developed mainly by Rice and Ramsperger (1927), Kassel (1928a, 1928b), and Marcus (1952, 1965). When applied to unimolecular reactions it is known in the chemical physics community as the RRKM theory (Hase, 1976; Callear, 1983).

The conventional choice for the dividing surface of a reaction on an (electronically) adiabatic potential surface with a saddle point located between reactants and products is the subspace perpendicular to the unstable mode, determined by normal-mode analysis of small vibrations around the saddle point. Therefore any other dividing surface is by definition a "generalized transition state" (Pechukas, 1982). From the assumptions in (i) and (ii) it follows that microcanonical TST is exact only if no trajectory of a given energy crosses the transition-state dividing surface more than once; canonical TST is exact if no trajectory, of any energy whatever, recrosses the dividing surface. We stress that for any dividing surface the TST rate is *always an upper bound to the true rate* [see Eq. (2.24)].

As will be demonstrated below, the number of recrossings of the reaction coordinate depends strongly on the level of coarse graining in the phase space of the total system. If the reaction is described by all degrees of freedom in the full phase space of the reacting system plus bath, a classical trajectory has generally very little chance of returning to the narrow bottleneck region around the saddle point with activation energy $E=E_b$. The probability of correlated recrossings increases with an increase in the level of coarse-graining for the reaction coordinate. In other words, simple TST is expected to fail badly in complex systems, such as reactions in condensed phases when these are being approximated in terms of only a few coarse-grained degrees of freedom, so that the dividing surface is restricted to lie on a low-dimensional subspace.

In view of the fact that TST always overestimates the true rate, the dividing surface should be chosen so as to *minimize the flux through it.* Within microcanonical TST, the conventional choice for the dividing surface becomes increasingly suspect with increasing energy $E>E_b$. This conventional choice is usually good for energies just above the threshold energy E_b. In this case the bottleneck is still narrow, i.e., there is generally little chance that any reactive trajectory will find its way back. For canonical TST (and not too high temperatures) it is this energy region that contributes most significantly to the rate, due to the Boltzmann weighting. In microcanonical TST, however, one has no such helping hand from the Boltzmann factor. Then both energetic factors (i.e., minimization of the mean velocity of trajectories passing the surface) and entropic factors (i.e., the size of the dividing surface) must be accounted for in choosing the best dividing surface. This variational problem has recently been solved by Pollak and Pechukas (1978). They find that the only dividing surfaces worth considering for *microcanonical* TST are those whose space is made up of unstable invariant manifolds on the multidimensional, potential-energy surface (such as the unstable periodic orbits in systems with 2 degrees of freedom). At higher energies $E>E_b$, it is then possible that the bottleneck to reaction may move out from the saddle-point region toward the asymptotic reaction (or product) regime (Pechukas, 1976; Pollak and Pechukas, 1978; Sverdlik and Koeppl, 1978; Pechukas and Pollak, 1979; for reviews see Truhlar and Garrett, 1984; Pollak, 1985; Wardlaw and Marcus, 1987).

As mentioned earlier, within a full phase-space description of the system plus environment, assumption (ii) is reasonable if within canonical TST the considered temperatures are not too high (i.e., if the Arrhenius factor is not becoming too small). A difficulty of more fundamental nature results from assumption (i), namely, that of thermodynamic equilibrium throughout the whole escape process. In reaction-rate theory we are interested in the process of evolution from one metastable state to another neighboring state of metastable equilibrium. This process sets the time scale for the problem (see Sec. II.A). *A priori,* it would be farfetched to assume that true equilibrium prevails at all times throughout this escape process. Equilibrium is assumed if the vertical thermalization (inside the initial well) is more rapid than the outflow into the product region (Hänggi, 1986a). The consequences of a violation of assumption (i) have already been appreciated by Lindemann (1922), Christiansen (1926), Hinselwood (1926b), and Kramers (1940). For the rest of this review we shall primarily confine ourselves to *energy-independent* escape rates, i.e., to canonical TST.

A. Simple transition-state theory

We start with the simplest form of TST, namely, that of a one-dimensional system that is not coupled to a bath. If a particle with mass M and momentum $p=M\dot{q}$ moves in a metastable potential $U(q)$ of the form shown in Fig. 3, the reaction coordinate x equals the configuration coordinate q. For this discussion we assume that thermal equilibrium prevails in the presence of a vanishingly small coupling or friction $\gamma\simeq 0$, i.e., we prepare a canonical equilibrium of particles inside the initial well—even if this means that we must have recourse to Maxwell's demon. The transition-state forward rate $k_{\rm TST}^{+}$ equals, from Eq. (2.23),

$$k_{\rm TST}^{+}=Z_0^{-1}\frac{1}{2\pi\hbar}\int dq\,dp\,\delta(q)\dot{q}\,\theta(\dot{q})\times\exp[-\beta\mathcal{H}(q,p)]\,, \tag{3.1}$$

where we have identified the transition state with the location of the maximum of $U(q)$ at $q=0$, while $\beta=(k_BT)^{-1}$ is the inverse temperature, and Z_0 denotes the partition function in the initial well,

$$Z_0=\frac{1}{2\pi\hbar}\int_{q<0}dp\,dq\exp[-\beta\mathcal{H}(q,p)]\ . \tag{3.2}$$

$\mathcal{H}(q,p)=p^2/2M+U(q)$ is the Hamiltonian of the system. Equation (3.1) can be evaluated by a transformation from phase-space variables (q,p) to the energy-phase representation (E,φ); that is, $dp\,dq=dE\,d\varphi/\omega(E)$, with $\omega(E)=2\pi\,dE/dI(E)$, where $I(E)$ denotes the action. In terms of the barrier height E_b^+ for the forward transition $A\rightarrow C$ (see Fig. 3), one finds

$$k_{\rm TST}^+=\frac{1}{2\pi\hbar}\frac{\beta^{-1}\exp(-\beta E_b^+)}{\hbar^{-1}\int_0^\infty\frac{1}{\omega(E)}\exp(-\beta E)dE} \tag{3.3}$$

$$=\left[\frac{k_BT}{h}\right]\frac{1}{Z_0}\exp(-\beta E_b^+) \tag{3.4}$$

$$\approx\frac{\omega_0}{2\pi}\exp(-\beta E_b^+)\ . \tag{3.5}$$

Here $\omega_0=\omega(E=0)=[(1/M)U''(q_0)]^{1/2}$ is the (angular) frequency at the well bottom. Equation (3.5) is of course a well-known textbook result.

B. Canonical multidimensional transition-state theory

As before, let x denote the reaction coordinate of a complex system (e.g., a molecule with N degrees of freedom). The reaction coordinate $x\ (q_1,\ldots,q_N;\ p_1,\ldots,p_N)$ is then a function of all these degrees of freedom. It is again chosen so that it is *negative for products* and *positive for reactants,* i.e., we place the transition state at $x_T=x_b=0$. The forward multidimensional TST rate $k_{\rm TST}^+$ is, in analogy to Eq. (3.1), given by [see Eq. (2.23)]

$$k_{\rm TST}^+=\frac{\langle\delta[x(0)]\dot{x}(0)\theta[\dot{x}(0)]\rangle}{\langle\theta(x)\rangle}\ ,$$

$$\text{with }\theta(x)=\begin{cases}1; & x>0\\ 0; & x<0\ .\end{cases} \tag{3.6}$$

Here the average $\langle\cdots\rangle$ denotes an equilibrium average over the canonical probability density $p(q_1,\ldots,q_N;\ p_1,\ldots,p_N)=Z^{-1}\exp(-\beta\mathcal{H})$, where $\mathcal{H}$ denotes the Hamiltonian of the total system. Equation (3.6) can be simplified by integrating over the momenta explicitly. By use of the mass-weighted coordinates

$$Q_i=q_im_i^{1/2},\quad P_i=p_im_i^{-1/2},\quad \dot{x}=\sum_{i=1}^N\frac{\partial x}{\partial Q_i}\dot{Q}_i\ , \tag{3.7}$$

where $\{m_i\}$ are the masses of the corresponding configurational degrees of freedom, one finds after an integration over all the momenta

$$k_{\rm TST}^+=(2\pi\beta)^{-1/2}\frac{\{\delta(x)|\nabla_Q(x)|\}}{\{\theta(x)\}}\ , \tag{3.8}$$

where $\{\cdots\}$ indicates an average over coordinates $\{q_1,\ldots,q_N\}$ only:

$$\{f(x)\}=\int dq^Nf[x(q_1,\ldots,q_N)]\exp[-\beta U(q_1,\ldots,q_N)]\ . \tag{3.9}$$

The result in Eq. (3.8) can be further simplified by integrating over the coordinates of the center-of-mass position R and all orientations Ω relative to a reference configuration of the system. We introduce new coordinates $\{Q_1,\ldots,Q_N\}\rightarrow\{R,\Omega;f_1,\ldots,f_m\}$, where the set $\{f_i\}$ are internal coordinates whose total number shall be denoted by m, for example, $m=N-6$ for a polyatomic molecule. The Jacobian of this transformation, integrated over the center-of-mass coordinates and the orientations, is denoted by $J(\mathrm{f})$. It contains the volume V of the system and a factor stemming from the angular orientations. For the partition function $\{\theta(x)\}$, therefore, we have

$$\{\theta(x)\}=\int df_1\cdots df_mJ(\mathrm{f})\theta[x(\mathrm{f})]\exp[-\beta U(\mathrm{f})]\ , \tag{3.10}$$

where $U(f_1,\ldots,f_m)$ denotes the potential function as a function of the internal degrees of freedom. With $\beta U(\mathrm{f})\gg1$, we can evaluate Eq. (3.8) with a Gaussian steepest-descent approximation. The total effective potential $U_{\rm eff}(\mathrm{f})$, given by

$$U_{\rm eff}(\mathrm{f})=U(\mathrm{f})-k_BT\ln J(\mathrm{f})\ , \tag{3.11}$$

must be expanded up to a second order at the saddle point (b) and at the local minimum (0), respectively. The eigenvalues of the matrix (with respect to mass-weighted internal coordinates)

$$K_{ij}=\frac{\partial^2U_{\rm eff}}{\partial f_i\partial f_j},\quad i,j=1,\ldots,m \tag{3.12}$$

are denoted at the saddle point by $\{\lambda_i^{2(b)}$, with $-\lambda_{i=m}^{2(b)}<0\}$, and at the minimum by $\{\lambda_k^{2(0)}\}$. This yields for the TST rate (Borkovec, 1986)

$$k_{\rm TST}^+=\frac{1}{2\pi}\frac{|\mathbf{M}^{-1/2}(\nabla_qx)|_b}{|\nabla_fx|_b}\left[\frac{J_b}{J_0}\right]\frac{\prod_{i=1}^m\lambda_i^{(0)}}{\prod_{i=1}^{m-1}\lambda_i^{(b)}}\exp(-\beta E_b^+)\ , \tag{3.13a}$$

where $\mathbf{M}$ is the mass matrix

$$\mathbf{M}=\begin{bmatrix}m_1 & & \\ & \ddots & \\ & & m_N\end{bmatrix}\ . \tag{3.13b}$$

The indices (b) and (0) in Eq. (3.13a) indicate that the corresponding quantities are evaluated at the saddle point and the local minimum, respectively.

In the following we shall apply the transition-state for-

mula in Eqs. (3.6) and (3.13) to four archetypal situations relevant to chemical reaction-rate theory.

1. Multidimensional transition-state rate for a collection of N vibrational bath modes

A straightforward application of Eq. (3.13) follows for a metastable system consisting of a nonlinear coordinate ($i=0$) coupled to N vibrational degrees of freedom only. In the absence of rotational degrees of freedom the Jacobian is a constant, $J=\text{const}$, thus yielding from Eq. (3.13) with $E_b^+ \equiv E_b$ the well-known result (Polanyi and Wigner, 1928; Eyring, 1935; Slater, 1956, 1959; Vineyard, 1957)

$$k_{\rm TST}^+ = \frac{1}{2\pi} \frac{\prod_{i=0}^{N} \lambda_i^{(0)}}{\prod_{i=1}^{N} \lambda_i^{(b)}} \exp(-\beta E_b) , \tag{3.14}$$

where the normal-mode eigenvalues $\{\lambda_i^{2(0)} > 0,\ i=0, 1, \ldots N\}$, $\{-\lambda_0^{2(b)} < 0,\ \lambda_i^{2(b)} > 0,\ i=1, \ldots N\}$ have been defined previously in Sec. III.B, Eq. (3.12).

Using for the partition function Z_0 the harmonic approximation

$$Z_0 \equiv \prod_{i=0}^{N} \left[\frac{k_B T}{\hbar \lambda_i^{(0)}} \right] , \tag{3.15}$$

and setting for the partition function of the transition state

$$Z^{\neq} = \prod_{i=1}^{N} \left[\frac{k_B T}{\hbar \lambda_i^{(b)}} \right] , \tag{3.16}$$

we can recast the result in Eq. (3.14) as (Evans and Polanyi, 1935; Eyring, 1935; Wynne-Jones and Eyring, 1935; Glasstone, Laidler, and Eyring, 1941; Laidler, 1987)[4]

$$k_{\rm TST}^+ = \left[\frac{k_B T}{h} \right] \frac{Z^{\neq}}{Z_0} \exp(-\beta E_b) . \tag{3.17}$$

This result for the TST rate is in the familiar form commonly used by the chemistry community. By use of thermodynamic functions such as the Helmholtz free energy F, the result in Eq. (3.17) can be recast in various other forms which are of course all equivalent with Eq. (3.14). In particular, with the substitution $Z = \exp[-\beta(E-TS)] = \exp(-\beta F)$ the prefactor in Eq. (3.14) can be formally recast as an entropy term,

$$\frac{1}{2\pi} \frac{\prod_{i=0}^{N} \lambda_i^{(0)}}{\prod_{i=1}^{N} \lambda_i^{(b)}} = \frac{k_B T}{h} \exp(\Delta S^{\neq}/k_B) , \tag{3.18}$$

where $\Delta S^{\neq} = S^{\neq} - S_0$ denotes the change in entropy. Likewise, for chemical reactions being monitored under fixed pressure, the appropriate thermodynamic function is

$$Q(T,p,N) = \int Z(T,V,N) \exp(-pV/k_B T) dV = \exp(-\beta G) ,$$

with G denoting the Gibbs free enthalpy. With the appropriate substitution $Z \to Q(T,p,N)$ we obtain from Eq. (3.17) the familiar result (Wynne-Jones and Eyring, 1935)[5]

$$k_{\rm TST}^+ = \left[\frac{k_B T}{h} \right] \exp(-\beta \Delta G) , \tag{3.19}$$

where we defined $\Delta G = G^{\neq} - G_0$. For the case in Eq. (3.17), in which we account only for vibrational degrees of freedom, we have $\Delta G = \Delta F$, because the corresponding reactive volume $\Delta V = (V^{\neq} - V_0)$ is vanishing.

2. Atom-transfer reaction

For a one-dimensional bimolecular atom-transfer reaction, $A + BC \to AB + C$, we have a potential of the form depicted in Fig. 5. Let $\dot{x} = v$ denote the velocity, μ the (reduced) mass, and L the typical length on the side of the reactant region. With

$$\langle \theta(x) \rangle \equiv \int_0^L dx \int_{-\infty}^{\infty} dv \exp(-\tfrac{1}{2}\beta\mu v^2) = L \left[\frac{2\pi}{\beta\mu} \right]^{1/2} , \tag{3.20}$$

the TST atom-transfer rate k is given by

$$k = \frac{\exp(-\beta E_T) \int_0^{\infty} dv\, v \exp(-\beta\mu v^2/2)}{L(2\pi/\beta\mu)^{1/2}} = L^{-1}(2\pi\beta\mu)^{-1/2} \exp(-\beta E_T) \equiv L^{-1} k_{\rm bim} . \tag{3.21}$$

Here, E_T is the barrier height in Fig. 5(a), and $k_{\rm bim}$ denotes the well-known bimolecular rate of product formation with dimension (sec^{-1}m) (Pechukas, 1976).

3. Dissociation reaction

As an illustration of the effect of a nonconstant Jacobian $J(\mathbf{f})$ [see Eq. (3.11)], we consider the dissociation $AB \to A + B$ of a diatomic molecule in an adiabatic potential of the form sketched in Fig. 6.

When Eq. (3.6) is used, the TST rate for dissociation k_D follows as

[4]For the origin of the notation ($\neq$) for the activated state, note the amusing anecdote given by Eyring (1982).

[5]The reader might have noticed that we refer to the rate coefficient k simply as the "rate," whereas with c denoting the concentration a rate almost universally means $-dc/dt$ in kinetics. In our notation the rate k carries the dimension sec^{-1}.

$$k_{\mathcal{D}}=\frac{\int d\mathbf{q}_1^3 d\mathbf{v}_1^3 \int d\mathbf{q}_2^3 d\mathbf{v}_2^3 \dot{r}\theta(\dot{r})\delta(r-a)\exp\{-\beta[U(r)+\frac{1}{2}m_1\mathbf{v}_1^2+\frac{1}{2}m_2\mathbf{v}_2^2]\}}{\int d\mathbf{q}_1^3 d\mathbf{v}_1^3 \int d\mathbf{q}_2^3 d\mathbf{v}_2^3 \exp\{-\beta[U(r)+\frac{1}{2}m_1\mathbf{v}_1^2+\frac{1}{2}m_2\mathbf{v}_2^2]\}} , \tag{3.22}$$

where $r\equiv|\mathbf{q}_1-\mathbf{q}_2|$ denotes the internal coordinate and $\dot{\mathbf{q}}_1=\mathbf{v}_1,\ldots,$ etc. With the reaction coordinate $x=r-a$, that is, $r_T=a$ (see Fig. 6), one finds in terms of the integrated Jacobian $J(r)=4\pi Vr^2$, and with the reduced mass $\mu^{-1}=m_1^{-1}+m_2^{-1}$,

$$k_D=\frac{4\pi V(\beta\mu)^{-1}\int_0^\infty dr\, r^2\delta(r-a)\exp[-\beta U(r)]}{4\pi V(2\pi/\beta\mu)^{+1/2}\int_0^a dr\, r^2\exp[-\beta U(r)]} . \tag{3.23}$$

Using a harmonic approximation for the well region, $U(r-r_0)=U(r_0)+\frac{1}{2}\mu\omega_0^2(r-r_0)^2$, one thus obtains

$$k_D=\left[\frac{a}{r_0}\right]^2\frac{\omega_0}{2\pi}\exp(-\beta E_d) , \tag{3.24}$$

where the factor $(a/r_0)^2=J_b/J_0$ denotes the ratio of the corresponding two Jacobians in Eq. (3.13).

4. Recombination reaction

Likewise, one finds for the inverse reaction $A+B\rightarrow C=AB$ the TST recombination rate k_R (see Fig. 6),

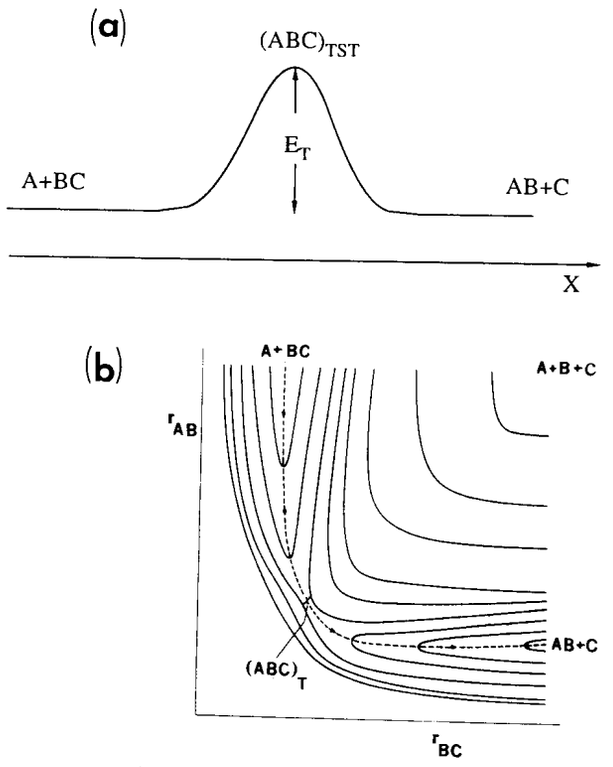

FIG. 5. Atom-transfer reaction: (a) the typical potential form vs the reaction coordinate x; (b) the potential-energy surface for a hypothetical one-dimensional reaction $A+BC\rightarrow(ABC)_T\rightarrow AB+C$. The dashed line indicates the reaction coordinate x.

$$k_R=(2\pi\beta\mu)^{-1/2}\frac{a^2\exp[-\beta U(a)]}{\int_a^L dr\, r^2\exp[-\beta U(r)]} . \tag{3.25}$$

Upon noticing that the volume V is $V=(4\pi/3)L^3$, we see that Eq. (3.25) can be reduced approximately to

$$k_R=\frac{1}{V}\left[\frac{8\pi}{\beta\mu}\right]^{1/2}a^2\exp(-\beta E_r) . \tag{3.26}$$

This result for the TST recombination rate should be contrasted with the corresponding result in the position-diffusion-controlled regime described in terms of a Smoluchowski-Fokker-Planck equation [see Eq. (4.54) below]; for detailed reviews see Calef and Deutch, 1983; Sceats, 1988.

For the case in which $U(r)=$const for $r>a$, and is strongly attractive for $r<a$, one has $E_r=0$, i.e., the free molecular limit is given by (Wagner and Kerker, 1977)

$$k_R=V^{-1}\left[\frac{8\pi}{\beta\mu}\right]^{1/2}a^2\equiv V^{-1}k_{\text{bim}}^R , \tag{3.27}$$

where k_{bim}^R is the bimolecular recombination rate. For a realistic dissociative potential, such as the Morse potential with no local maximum, one must optimize the value of the transition point $r_T\equiv a$ by looking for the minimum of the product $r^2\exp[-\beta U(r)]$, that is, $a^2\exp[-U(a)]\rightarrow r_T^2\exp[-U(r_T)]$. It should be pointed out that the existence of the three-dimensional metric factor r^2 is important for the existence of such a transition point r_T. Thus in dimension $d=1$ there exists generally no well-defined transition state for potential forms such as the Morse potential sketched in Fig. 7; see also Eq. (7.34). In addition note that the prefactor of the rate exhibits a different dependence on temperature, i.e., $T^{1/2}$ in Eq. (3.26) versus T dependence of D in Eq. (7.38).

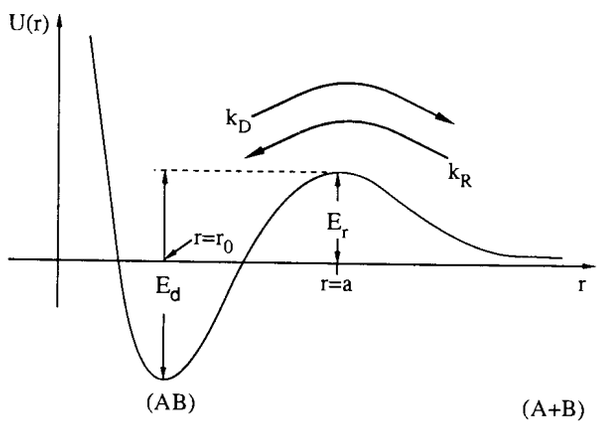

FIG. 6. Schematic representation of a dissociation reaction $(AB)\rightarrow(A+B)$ with rate k_D, and a recombination reaction $(A+B)\rightarrow(AB)$ with rate k_R.

The above considerations can of course be generalized to more complicated situations (Borkovec, 1986; Sceats, 1988). For example, with a triatomic molecule one has three internal coordinates ($m=3$), and the center-of-mass integrated Jacobian then reads

$$J(\mathbf{f})=V8\pi^2r^2s^2\sin\theta\ , \tag{3.28}$$

where r and s denote the corresponding two bond lengths, and θ is the angle between the two bonds.

C. Model case: particle coupled bilinearly to a bath of harmonic oscillators

1. The model

As a model for a particle of mass M that interacts via a *linear dissipative mechanism* with a thermal environment, we consider a bath composed of an infinite set of harmonic oscillators coupled bilinearly to the particle coordinate x of a metastable system. The total Hamiltonian $\mathcal{H}$ of the system and bath is then of the form (Zwanzig, 1973; Gross, 1980; Caldeira and Leggett, 1983, Pollak, 1986a; Levine, Shapiro, and Pollak, 1988)[6]

$$\mathcal{H}=\frac{p^2}{2M}+U(x)+\mathcal{H}_{\rm bath}(q_1,\ldots,q_N,p_1,\ldots,p_N;x)\ , \tag{3.29}$$

where

$$\mathcal{H}_{\rm bath}=\frac{1}{2}\sum_{i=1}^{N}m_i\left[\dot q_i^{\,2}+\omega_i^2\left[q_i+\frac{C_i}{m_i\omega_i^2}x\right]^2\right]\ . \tag{3.30}$$

Here the coupling to the bath of harmonic oscillators with masses $\{m_i\}$ and frequencies $\{\omega_i\}$ is of a form such that no coupling-induced renormalization of the metastable potential $U(x)$ occurs. A detailed discussion of related, similar harmonic bath models can be found in Ford *et al.* (1988). In this context, it should be pointed out, while each bath mode may perturb the particle only weakly, the combined effect of all the bath modes on the particle motion is not necessarily weak, i.e., the coupling

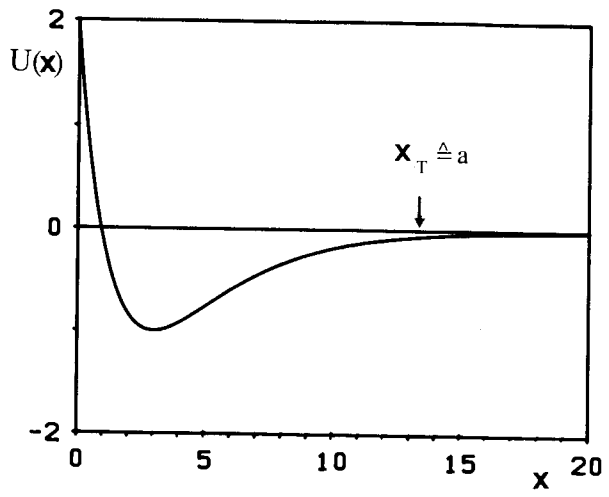

FIG. 7. The one-dimensional Morse potential $U(x)=-E_D+E_D\{1-\exp[-(x-x_e)/b]\}^2$, with $E_D=1$, $x_e=b=3$. The state $x_T=a$ denotes the arbitrarily chosen transition point.

can also cause strong dissipation for the reaction coordinate. Upon integrating over all the bath variables $\{q_1,\ldots,q_N\}$, one finds from Eq. (3.29) the generalized Langevin equation (Zwanzig, 1973)

$$M\ddot x+\frac{\partial U}{\partial x}+M\int_0^t\gamma(t-\tau)\dot x(\tau)d\tau=\xi(t)\ . \tag{3.31}$$

When the total system is prepared initially in thermal equilibrium, the random force $\xi(t)$ becomes a stationary Gaussian noise of vanishing mean,

$$\xi(t)=-\sum_{i=1}^{N}C_i\left[\left[q_i(0)+\frac{C_i}{m_i\omega_i^2}x(0)\right]\cos(\omega_i t)+\frac{\dot q_i(0)}{\omega_i}\sin(\omega_i t)\right]\ , \tag{3.32}$$

obeying the fluctuation-dissipation theorem

$$\langle\xi(t)\xi(s)\rangle=k_BTM\gamma(t-s)\ . \tag{3.33}$$

The friction kernel $\gamma(t)$ itself reads

$$\gamma(t)=\frac{1}{M}\sum_{i=1}^{N}\frac{C_i^2}{m_i\omega_i^2}\cos(\omega_i t)\ , \tag{3.34}$$

which with N finite is a (quasi)-periodic function in time.

Thus a phenomenologically decaying memory friction $\gamma(t)$ [$\gamma(t)\to0$ as $t\to\infty$] can be modeled by a suitable choice of parameters in Eq. (3.30) by performing a continuum limit for the distribution of frequencies which densely extends down to zero frequencies *(elimination of Poincaré recurrences).*

2. Normal-mode analysis

The partition functions entering the transition-state rate may be evaluated via normal-mode analysis at the saddle point of the full Hamiltonian and at the well bot-

[6]Coupled harmonic-oscillator models such as Eqs. (3.29) and (3.30) have a long history. With nearest-neighbor couplings only, the model is known as the "Bernoulli Chain," and its statistical mechanical treatment has been studied by various authors (Hemmer, 1959; Rubin, 1960, 1963, 1968; Ford, Kac, and Mazur, 1965; Nakazawa, 1966, Ullersma, 1966). Its classical mechanics was first considered by D. Bernoulli (1732, 1734), who studied the small-amplitude coplanar vibrations of a compound pendulum consisting of particles suspended in series in a gravity field by means of weightless connecting strings. These two papers contain a treatment of the oscillations of a double and a triple pendulum, and a figure depicting a five-particle pendulum, as well as the classic treatment of the continuum limit in which the Bessel function $J_0(x)$ occurs.

tom. We assume that the potential $U(x)$ can be approximated at the well bottom as

$$U(x)\approx\tfrac{1}{2}M\omega_0^2(x+x_0)^2,\quad x_0>0\ , \tag{3.35}$$

and at the barrier by

$$U(x)\approx E_b-\tfrac{1}{2}M\omega_b^2x^2\ . \tag{3.36}$$

The harmonic approximation given in Eqs. (3.35) and (3.36) implies that the total Hamiltonian may be written in the vicinity of the well and the barrier in a separable form as a sum of $(N+1)$ harmonic oscillators. Using standard techniques we first transform to mass-weighted coordinates,

$$x'=M^{1/2}x,\quad q_i'=m_i^{1/2}q_i\ , \tag{3.37}$$

and then diagonalize the $(N+1)\times(N+1)$ force-constant matrix $\mathbf{K}$ (with respect to the mass-weighted coordinates). From Eqs. (3.29) and (3.35)–(3.37) it follows that the saddle point is located at $x'=0$, $q_j'=0$; $j=1,\ldots N$. Likewise, the well is located at $x'=-x_0'$, $q_j'=[C_j/(m_jM)^{1/2}\omega_j^2]x_0'$, $j=1,\ldots N$. The second derivative matrix at the saddle point, denoted by $\mathbf{K}^{(b)}$, has the structure (Pollak, 1986b)

$$\mathbf{K}^{(b)}=\begin{bmatrix} \left[-\omega_b^2+\sum_{j=1}^{N}\dfrac{C_j^2}{m_jM\omega_j^2}\right] & C_1(m_1M)^{-1/2} & C_2(m_2M)^{-1/2} & \cdots & C_N(m_NM)^{-1/2} \\ C_1(m_1M)^{-1/2} & \omega_1^2 & 0 & \cdots & 0 \\ C_2(m_2M)^{-1/2} & 0 & \omega_2^2 & \cdots & 0 \\ \vdots & \vdots & & & \vdots \\ C_N(m_NM)^{-1/2} & 0 & 0 & \cdots & \omega_N^2 \end{bmatrix}\ . \tag{3.38}$$

The second-order derivative matrix $\mathbf{K}^{(0)}$ at the well bottom is of the same structure as $\mathbf{K}^{(b)}$, the only difference being that $-\omega_b^2<0$ is replaced by $\omega_0^2>0$. We denote the eigenvalues of $\mathbf{K}$ by $\{\lambda^2\}$. From Eq. (3.38) one can now prove the following useful identities for the determinants of $\mathbf{K}^{(0)},\mathbf{K}^{(b)}$ (Pollak, 1986a):

$$\det(\mathbf{K}^{(b)})=-(\lambda_0^{(b)})^2\prod_{i=1}^{N}(\lambda_i^{(b)})^2=-\omega_b^2\prod_{i=1}^{N}\omega_i^2 \tag{3.39}$$

and

$$\det(\mathbf{K}^{(0)})=(\lambda_0^{(0)})^2\prod_{i=1}^{N}(\lambda_i^{(0)})^2=\omega_0^2\prod_{i=1}^{N}\omega_i^2\ . \tag{3.40}$$

3. The rate of escape

The TST rate [see Eq. (3.14)] is given in terms of the product of all stable mode frequencies at the minimum and the inverse product of stable mode frequencies at the saddle point, respectively. By use of Eqs. (3.39) and (3.40) we can thus recast Eq. (3.14) as (Pollak, 1986a)

$$k_{\mathrm{TST}}=\frac{\lambda_0^{(b)}}{\omega_b}\frac{\omega_0}{2\pi}\exp(-\beta E_b)\ . \tag{3.41}$$

Next we express the positive-valued, unstable normal mode frequency $\lambda_0^{(b)}$ in terms of the friction kernel $\gamma(t)$ or its Laplace transform $\hat{\gamma}(z)$,

$$\hat{\gamma}(z)=\frac{1}{M}\sum_{i=1}^{N}\frac{C_i^2}{m_i\omega_i^2}\left[\frac{z}{z^2+\omega_i^2}\right]\ . \tag{3.42}$$

By virtue of Pollak's relation (Pollak, 1986b), in which $\mathbf{I}$ denotes the identity matrix,

$$\begin{aligned}\det(\mathbf{K}^{(b)}+z^2\mathbf{I})&=[-(\lambda_0^{(b)})^2+z^2]\prod_{i=1}^{N}[(\lambda_i^{(b)})^2+z^2]\\&=[-\omega_b^2+z^2+z\hat{\gamma}(z)]\prod_{i=1}^{N}(\omega_i^2+z^2)\ ,\end{aligned} \tag{3.43}$$

one finds, with $z=\lambda_0^{(b)}>0$ (assuming that all $\lambda_i^{(b)}>0$, $\omega_i>0$, $i>0$) from $\det[\mathbf{K}^{(b)}+(\lambda_0^{(b)})^2\mathbf{I}]=0$, that is, $-\omega_b^2+(\lambda_0^{(b)})^2+\lambda_0^{(b)}\hat{\gamma}(\lambda_0^{(b)})=0$, the central result

$$\lambda_0^{(b)}=\frac{\omega_b^2}{\lambda_0^{(b)}+\hat{\gamma}(\lambda_0^{(b)})}\ . \tag{3.44}$$

In this context, note also the application to a finite, two-dimensional oscillator reaction system by Van der Zwan and Hynes (1983). With all $\lambda_i^{(b)}>0$ for $i>0$ and all $\omega_i>0$ for $i\geq 0$, the solution of Eq. (3.44) has a *unique positive* solution. Alternatively, the quantity $\lambda_0^{(b)}$ can from Eq. (3.44) be given the appealing form

$$\lambda_0^{(b)}\equiv\mu=\left[\frac{\hat{\gamma}^2(\mu)}{4}+\omega_b^2\right]^{1/2}-\frac{\hat{\gamma}(\mu)}{2}\ . \tag{3.45}$$

In conclusion, the many-body (TST) rate in Eq. (3.41) reads explicitly

$$k_{\mathrm{TST}}=\left[\frac{\left[\dfrac{\hat{\gamma}^2(\mu)}{4}+\omega_b^2\right]^{1/2}-\dfrac{\hat{\gamma}(\mu)}{2}}{\omega_b}\right]\frac{\omega_0}{2\pi}\exp(-\beta E_b)\ . \tag{3.46}$$

This is a cornerstone result in rate theory: Equation (3.46) coincides precisely with the Kramers rate result for general memory friction $\gamma(t)$ (Grote and Hynes, 1980; Hänggi and Mojtabai, 1982; Carmeli and Nitzan, 1984; Dakhnovskii and Ovchinikov, 1985; Pollak, 1986a). Ohmiclike damping is realized whenever $\hat{\gamma}(z=0)>0$. In particular, with a memory-free friction, $\gamma(t)=2\gamma\delta(t)$, that is $\hat{\gamma}(\mu)=\hat{\gamma}(z=0)\equiv\gamma$, and we recover precisely Kramers' rate expression. In contrast to Kramers' result in Eq. (1.5), however, it is not the static friction value $\hat{\gamma}(\mu=0)\equiv\gamma$ that determines the transmission factor in the presence of memory friction, but rather the friction value on the short time scale τ_s, that is $\tau_s\sim\mu^{-1}\sim O(\omega_b^{-1})$. This latter friction value $\hat{\gamma}(\mu\sim\omega_b)$ might drastically differ from the static value γ.

Moreover, the result that Eq. (3.46) is obtained from multidimensional TST in full phase space of a metastable system coupled bilinearly to a bath of harmonic oscillators implies, in view of Eq. (2.24), that this (*generalized*) Kramers rate itself presents (within the validity of the harmonic approximation)[7] an upper bound for the true rate k as given by the reactive flux result in Eq. (2.22) or, likewise, by the exact lowest eigenvalue expression in Eq. (2.31).

The central result for memory friction in Eq. (3.46) requires further discussion. For a memory friction $\gamma(t)$, consisting of a sum of exponentially decaying terms, the above generalization of Kramers rate theory was derived originally within the Markovian stable-state picture (see Northrup and Hynes, 1980) by Grote and Hynes (1980). Applying the flux-over-population method to a general metastable non-Markovian Brownian dynamics with a nonrestricted memory friction $\gamma(t)$, Hänggi and Mojtabai (1982) subsequently obtained the result in Eq. (3.46). Additional insight along the same line of reasoning was provided by Carmeli and Nitzan (1984). In all these cited derivations of Eq. (3.46) no explicit reference was made to a bilinear coupling between reaction system and harmonic bath. The crucial assumptions made in obtaining the generalized Kramers result in Eq. (3.46) are, however, as follows.

(i) Strong-coupling assumption: Deviations from the thermal equilibrium distribution away from the immediate neighborhood of the barrier region, or more generally, the influences of the well dynamics, are negligible. Put differently, the rate is truly controlled by the diffusive barrier dynamics.

(ii) The effective potential near the barrier is assumed to be parabolic, and the barrier dynamics itself can be approximated by a *linear* generalized Langevin equation (GLE), i.e., with $y=x-x_b$ one has

$$\ddot{y}=\omega_b^2 y-\int_0^t\gamma(t-s)\dot{y}(s)ds+M^{-1}\xi(t)\ , \tag{3.47}$$

with $\xi(t)$ a Gaussian random force obeying the fluctuation-dissipation theorem in Eq. (3.33).

Such a linear GLE was originally postulated by Kubo (1966) on a purely phenomenological basis, but has since found wide applications in a variety of physical situations (e.g., Forster, 1975; Hynes and Deutch, 1975; Grabert, 1982). Clearly, a GLE of the form in Eq. (3.47) can with an appropriately chosen (although not unique) set of coupling parameters $\{C_i,\omega_i,m_i\}$ also be embedded into a model Hamiltonian of the form in Eq. (3.29), thus showing again the formal equivalence with a harmonic, multidimensional TST. Nevertheless, while the TST result in Eq. (3.46) holds rigorously in the harmonic limit for the model in Eq. (3.29), the result itself might hold approximately in a great variety of realistic physical systems (see, for example, Bergsma *et al.*, 1987; Grabert and Linkwitz, 1988; Zhu, Lee, and Robinson, 1988a; Gertner *et al.*, 1989) with possible nonlinear bath couplings—if the combined effect of the bath on the barrier dynamics could be satisfactorily modeled by a linear GLE over a corresponding range of parameters involving the temperature, barrier height, friction strength $\hat{\gamma}(\mu)$, friction-relaxation or noise correlation time τ_c, etc. In general, however, the above central result is subject to a series of limitations, even for the case in which the linear GLE turns out to be a valid approximation of the barrier dynamics (Hänggi, 1986a; see, as well, the peculiarities and the limitations discussed in Sec. VI.C for an exponentially decaying memory friction). In particular, realistic situations such as chemical reactions in condensed phases might require a strongly nonlinear friction mechanism of the form in Eq. (2.6a), where the memory friction depends both on the actual state x and possibly on its velocity $\dot{x}$. For example, while the effective barrier friction is sufficiently strong, the effective well friction might be of quite different form, approaching a critical regime so that nonequilibrium effects in the energy population may no longer be negligible, hence violating assumption (i). See also Secs. IV.D and VI.C.

In conclusion, the role and, particularly, the regime of validity of the memory-friction Kramers rate result in Eq. (3.46) is at present not settled when it is applied to realistic situations involving strong nonlinear interaction potentials for the bath degrees of freedom and/or system-bath interaction, notwithstanding claims made to the contrary (Bergsma *et al.*, 1987; Hynes, 1988; Gertner *et al.*, 1989).

IV. KRAMERS RATE THEORY

A. The model

Kramers' (1940) model for a chemical reaction consists of a classical particle of mass M moving in a one-

[7]Equation (3.46) follows from Eq. (2.23) as a rigorous upper bound only under the assumption that the influence of anharmonicity effects for Z_0 and $Z^{\neq}$ [Eq. (3.17)] can safely be neglected. Variational upper bounds for the transition-state rate in dissipative systems that do take into account the nonlinearity of the metastable potential have recently been put forward by Pollak, Tucker, and Berne (1989) and Pollak (1990).

dimensional asymmetric double-well potential $U(x)$ (see Fig. 3). The particle coordinate x corresponds to the reaction coordinate, and its values at the minima of the potential $U(x)$, x_a and x_c, denote the reactant and product states, respectively. The maximum of $U(x)$ at x_b separating these states corresponds to the transition state (or activated complex). In this simple model all of the remaining degrees of freedom of both reacting and solvent molecules constitute a heat bath at a temperature T, whose total effect on the reacting particle is described by a fluctuating force $\xi(t)$ and by a linear damping force $-M\gamma\dot{x}$, where γ is a constant damping rate. These forces enter Newton's equation of motion of the particle in the form of a Langevin equation, Eq. (2.7),

$$M\ddot{x} = -U'(x) - \gamma M\dot{x} + \xi(t) , \tag{4.1}$$

where the prime indicates the differentiation with respect to the coordinate x. The fluctuating force $\xi(t)$ denotes Gaussian white noise with zero mean, which obeys the fluctuation-dissipation theorem,

$$\langle \xi(t) \rangle = 0 , \tag{4.2}$$

$$\langle \xi(t)\xi(s) \rangle = 2M\gamma k_B T \delta(t-s) . \tag{4.3}$$

The resulting two-dimensional stochastic dynamics for the reaction coordinate x and the velocity $v = \dot{x}$ are Markovian. The time evolution of the probability density $p(x,\dot{x}=v,t)$ is governed by the Klein-Kramers equation (Klein, 1922; Kramers, 1940; Risken, 1984),

$$\frac{\partial p(x,v,t)}{\partial t} = \left[-\frac{\partial}{\partial x} v + \frac{\partial}{\partial v} \frac{U'(x) + M\gamma v}{M} + \frac{\gamma k_B T}{M} \frac{\partial^2}{\partial v^2} \right] p(x,v,t) . \tag{4.4}$$

Equation (4.4) provides a complete description of the process defined by Eqs. (4.1)–(4.3). Although known for a long time, a detailed numerical treatment of the dynamics in Eq. (4.4) with $U(x)$ a metastable nonlinear potential, such as for example, $U(x) = -\frac{1}{2}x^2 + \frac{1}{4}x^4$, has been given only recently (Visscher, 1976a, 1976b; Blomberg, 1977; Marchesoni and Grigolini, 1983; Baibuz *et al.*, 1984; Marchesoni, 1985a; Risken and Voigtlaender, 1985; Voigtlaender and Risken, 1985; Hu, 1986; Cartling, 1987; Ebeling, 1988).

The qualitative behavior of the nonlinear dynamics in Eq. (4.4) can readily be elucidated. If the thermal energy $k_B T$ is much smaller than the respective barrier heights, the random force is acting only as a small perturbation, whose influence may typically be neglected on the time scale of the unperturbed damped deterministic motion (see Fig. 8),

$$\ddot{x} = -\frac{U'(x)}{M} - \gamma\dot{x} . \tag{4.5}$$

Hence the reaction coordinate will relax toward one of the minima of the potential, say x_a, and the system will stay there for an extremely long time until eventually the accumulated action of the random force will drive it over the barrier into a neighboring metastable state (see Sec. II). Although rare, such events will surely occur within finite time. The average of this (escape) time equals the inverse of the rate $k_{A\to C}$ [see Eq. (2.5)].

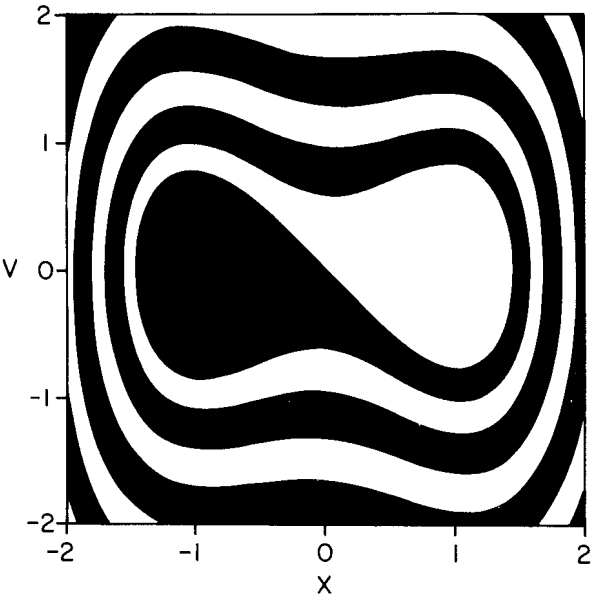

FIG. 8. Dissipative separatrix line of the deterministic motion in Eq. (4.5) in a symmetric double-well potential in the presence of weak friction. The blackened region denotes the domain of attraction of the metastable state located at $x=-1$, $\dot{x}=v=0$, which is separated by the boundary (separatrix) from the neighboring domain of attraction (white), with the metastable state located at $x=1$, $v=0$.

On the other hand, if the thermal energy $k_B T$ is comparable with, or even larger than, the barrier height(s) $E_b^{\pm}$, the particle can move almost freely from x_a to x_c. In this case, there is no separation of time scales, and a rate description makes no sense. Below we shall not consider the latter case and shall always assume the condition in Eq. (2.2),

$$E_b^{\pm} \equiv E_b \gg k_B T . \tag{4.6}$$

Within this simple phenomenological model the strength of the interaction between the reaction coordinate and the remaining degrees of freedom is fixed by a single constant, the damping rate γ. Two limiting regimes may be distinguished, one with strong friction (spatial-diffusion regime) and the other with a low damping rate (energy-diffusion regime); see Fig. 9.

For strong friction γ the reaction coordinate undergoes a creeping motion, and the velocity may be eliminated adiabatically from Eq. (4.1):

$$\dot{x} = -(M\gamma)^{-1}U'(x) + (M\gamma)^{-1}\xi(t) . \tag{4.7}$$

The time evolution of the corresponding reduced probability

$$p(x,t) = \int_{-\infty}^{+\infty} dv\, p(x,v,t) \tag{4.8}$$

is governed by the Smoluchowski equation (Smolu-

chowski, 1915; Fürth, 1917),

$$\frac{\partial p(x,t)}{\partial t}=\left[(M\gamma)^{-1}\frac{\partial}{\partial x}U'(x)+(M\gamma)^{-1}k_BT\frac{\partial^2}{\partial x^2}\right]p(x,t)\ . \tag{4.9}$$

In order for the Smoluchowski equation to hold, Kramers (1940) requires that both $-U'(x)$ and $p(x,t)$ be almost constant on the thermal length scale $(k_BT/M)^{1/2}\gamma^{-1}$. More explicit conditions in terms of $U(x)$ can be read off from the corrections to the Smoluchowski equation (Tikhonov, 1960; Lee, 1971; Wilemski, 1976; Titulaer, 1978, 1980; Chaturvedi and Shibata, 1979; Skinner and Wolynes, 1979). For the lowest-order correction one still obtains a Smoluchowski equation but with an effective, γ-dependent potential and an x- and γ-dependent diffusion term,

$$\frac{\partial p(x,t)}{\partial t}=(M\gamma)^{-1}\frac{\partial}{\partial x}[1+\gamma^{-2}M^{-1}U''(x)]\left[k_BT\frac{\partial}{\partial x}+U'(x)\right]p(x,t)\ . \tag{4.10}$$

Higher-order corrections in powers of γ^{-1} can no longer be cast in such a Fokker-Planck form. The next correction is of order γ^{-5} and contains derivatives whose degree is higher than second order, thereby breaking the Fokker-Planck structure (Skinner and Wolynes, 1979; Risken *et al.*, 1980; San Miguel and Sancho, 1980; Titulaer, 1980; Kaneko, 1981; Haake, 1982; Gouyet and Bunde, 1984; for reviews see Grigolini and Marchesoni, 1985; Marchesoni, 1985b; Van Kampen, 1985).

In the case of extremely weak friction, the energy, or equivalently the action

$$I(E)=\oint p\,dq\ , \tag{4.11}$$

is almost constant compared with the rapidly changing angle variable φ (see Fig. 9). The averaging procedure over the angle φ then yields a diffusion equation for the probability density of the action (Kramers, 1940; Zwanzig, 1959),

$$\frac{\partial p(I,t)}{\partial t}=\gamma\frac{\partial}{\partial I}I\left[1+\frac{2\pi k_BT}{\omega(I)}\frac{\partial}{\partial I}\right]p(I,t)\ , \tag{4.12}$$

where $\omega(I)$ is the angular frequency at the action I,

$$\frac{\partial E}{\partial I}=\frac{\omega(I)}{2\pi}\ . \tag{4.13}$$

Although, in principle, the same methods apply as for the Smoluchowski equation (Titulaer, 1978), finite γ corrections to Eq. (4.12) are rather difficult to obtain. This is due to the fact that the transformation $(x,v)\rightarrow(I,\varphi)$ now contains both *fast and slow* contributions, to the *slow* action I and the *fast* angle variable φ, respectively. Thus far, such corrections have been obtained only for the case of a potential with a single well (Renz, 1985).

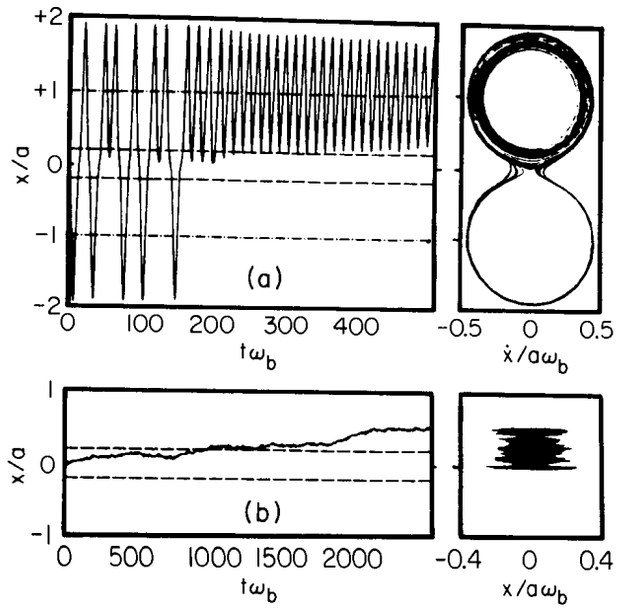

FIG. 9. Typical sample trajectories of a particle that starts at the barrier top of a symmetric double well, with the minima separated by a distance $2a$, showing the noisy trajectory and the phase-space motion x vs $\dot{x}$. The dashed lines indicate the position where the curvature changes sign: (a) the weak-damping regime where the escape is governed by energy diffusion; (b) the spatial-diffusion-controlled high-damping regime. Data are from Straub, Borkovec, and Berne (1986).

B. Stationary flux and rate of escape

Following the original reasoning of Farkas (1927) and of Kramers (1940), we determine the steady-state escape rate, say from A to C, by considering a stationary situation in which a steady probability current from A to C is maintained by sources and sinks. The sources supply the A-well with particles at energies that are a few k_BT below the barrier top. These particles first thermalize before they eventually leave the well over the barrier. Beyond the barrier the particles are removed again by sinks. The total probability flux j over the barrier is then given by the product of the escape rate from A to C, $k_{A\rightarrow C}$, and the population of the A-well, n_a. Equivalently, the rate equals the flux over the population, i.e., from Eq. (2.11),

$$k^+\equiv k_{A\rightarrow C}=\frac{j}{n_a}\ . \tag{4.14}$$

For the construction of a stationary current whose probability density is denoted by $\rho(x,v)$, several requirements must be fulfilled. Clearly, neither sources nor

sinks should exist at the barrier. The probability $\rho(x,v)$ around the barrier obeys the stationary Fokker-Planck equation, i.e., with $\omega_b^2=-M^{-1}U''(x_b)>0$,

$$\left[-\frac{\partial}{\partial x}v-\frac{\partial}{\partial v}[\omega_b^2(x-x_b)-\gamma v]+\frac{\gamma k_BT}{M}\frac{\partial^2}{\partial v^2}\right]\rho(x,v)=0,\quad x\simeq x_b\ . \tag{4.15}$$

Here we have assumed the linearized potential

$$U(x)=U(x_b)-\tfrac{1}{2}M\omega_b^2(x-x_b)^2\ , \tag{4.16}$$

because x is confined to a small neighborhood around the (parabolic) barrier top. Near the bottom of the A-well all particles are thermalized. Therefore, with Z^{-1} denoting a normalization constant, we find the condition

$$\rho(x,v)=Z^{-1}\exp\{-[\tfrac{1}{2}Mv^2+U(x)]/k_BT\}\ ,\quad x\approx x_a,\ \text{and all } v\ . \tag{4.17}$$

On the other hand, near the bottom of the C-well, all particles are removed by the sinks,

$$\rho(x,v)\approx 0,\quad x>x_b\ . \tag{4.18}$$

Once the probability density ρ fulfilling Eqs. (4.15)–(4.18) is known, the population of the A-well and the flux over the barrier can be readily calculated to give

$$n_a=\int_{A\text{-well}}dx\,dv\,\rho(x,v) \tag{4.19}$$

and

$$j=\int_{-\infty}^{+\infty}dv\,v\rho(x_b,v)\ . \tag{4.20}$$

Moreover, the density of sources and sinks $s(x,v)$ follows from the stationarity of the nonequilibrium probability $\rho(x,v)$ wherein $s(x,v)$ enters the right-hand side in Eq. (4.4). Thus we obtain

$$s(x,v)=-\left[-\frac{\partial}{\partial x}v+\frac{\partial}{\partial v}\left[\frac{U'(x)}{M}+\gamma v\right]+\frac{\gamma k_BT}{M}\frac{\partial^2}{\partial v^2}\right]\rho(x,v)\ . \tag{4.21}$$

Obviously, $s>0$ corresponds to sources and $s<0$ to sinks, respectively. We recall that the validity of the approach requires that there be no sources injecting particles with energies comparable to, or even higher than, the barrier energy E_b.

The next objective is to construct $\rho(x,v)$. Still following Kramers (1940) we make the ansatz

$$\rho(x,v)=\zeta(x,v)\exp\{-[\tfrac{1}{2}Mv^2+U(x)]/k_BT\}\ . \tag{4.22}$$

When x is in the neighborhood of the barrier top, Eq. (4.15) yields a partial differential equation for $\zeta(x,v)$, reading

$$\left[-v\frac{\partial}{\partial x}-[\omega_b^2(x-x_b)+\gamma v]\frac{\partial}{\partial v}+\frac{\gamma k_BT}{M}\frac{\partial^2}{\partial v^2}\right]\zeta(x,v)=0\ . \tag{4.23}$$

We observe that this is simply the adjoint equation for the time-reversed process in Eq. (4.1). According to the boundary conditions in Eqs. (4.17) and (4.18), the function $\zeta(x,v)$ must approach unity inside the well and vanish beyond the barrier region. This behavior may be achieved if $\zeta(x,v)$ is allowed to depend on a linear combination of x and v only (Kramers, 1940),

$$u=(x-x_b)+av\ . \tag{4.24}$$

Equation (4.23) therefore transforms into

$$-[(1+\gamma a)v+\omega_b^2a(x-x_b)]\zeta'+\frac{\gamma k_BTa^2}{M}\zeta''=0\ , \tag{4.25}$$

where the prime now denotes the derivative with respect to u. In order that Eq. (4.25) become *a proper ordinary differential equation,* the factor in front of the first derivative must be proportional to u,

$$(1+\gamma a)v+\omega_b^2a(x-x_b)=-\lambda u\ ,\quad \text{for all } x\approx x_b \text{ and all } v\ . \tag{4.26}$$

From Eqs. (4.24) and (4.26) the coefficients λ and a are readily obtained as

$$\lambda_\pm=-\frac{\gamma}{2}\pm\sqrt{\omega_b^2+(\gamma/2)^2}\ , \tag{4.27}$$

$$a_\pm=\frac{-\lambda_\pm}{\omega_b^2}\ . \tag{4.28}$$

The solution of Eq. (4.25) thus reads

$$\zeta(x,v)=Z^{-1}\omega_b^2\sqrt{M/2\pi\gamma k_BT\lambda_+}\int_{(x-x_b)-(\lambda_+v/\omega_b^2)}^{\infty}\exp\left[-\frac{M\omega_b^4u^2}{2\gamma k_BT\lambda_+}\right]du\ , \tag{4.29}$$

where λ_+ has been chosen in order to obtain the physically correct asymptotic behavior for large positive x given by Eq. (4.18). The asymptotic behavior for $x\approx x_a$ [see Eq. (4.17)] determines the normalization factor in front of the integral. With Eq. (4.19) we obtain in leading order (k_BT) for the well population from Eqs. (4.22) and (4.29) assuming the linearized potential $U(x)=U(x_a)+\frac{1}{2}M\omega_0^2(x-x_a)^2$,

$$n_a=\frac{2\pi k_BT}{M\omega_0}Z^{-1}\exp[-\beta U(x_a)]\ . \tag{4.30}$$

The probability current, Eq. (4.20), becomes

$$j=\lambda_+\frac{k_BT}{M\omega_b}Z^{-1}\exp[-\beta U(x_b)]\ . \tag{4.31}$$

Thus, combining Eq. (4.14) with Eqs. (4.27), (4.30), and (4.31), we find with the activation energy $E_b=U(x_b)-U(x_a)$ the celebrated Kramers result (Kramers, 1940)

$$k_{A\to C}=\frac{\lambda_+}{\omega_b}\left[\frac{\omega_0}{2\pi}\exp(-\beta E_b)\right] \tag{4.32}$$

$$=\frac{\left[\frac{\gamma^2}{4}+\omega_b^2\right]^{1/2}-\frac{\gamma}{2}}{\omega_b}\frac{\omega_0}{2\pi}\exp(-\beta E_b)\ . \tag{4.33}$$

This result describes the *spatial-diffusion-controlled rate* of escape at moderate-to-strong friction γ, see Secs. C and G below. In Eq.(4.32) the expression in large parentheses is the result of *simple* transition-state theory $k_{\rm TST}$, given in Eq. (3.5). One observes that with $\hat{\gamma}(\mu)=\gamma$, the result in Eq. (4.33) coincides with the multidimensional TST rate in Eq. (3.46) for a heat bath describing strict Ohmic friction, i.e., $\gamma(t)=2\gamma\delta(t)$. The ratio $k_{A\to C}/k_{\rm TST}$ versus friction γ is sketched in Fig. 10. As can be deduced from Fig. 10, in the presence of a finite-damping rate γ the diffusive transmission factor $\kappa\equiv(\lambda_+/\omega_b)$ is always less than one, due to the ever-present diffusive recrossings (see Fig. 9). A correction of order $(\beta E_b\gamma/\omega_b)^{-1}$ to the transmission factor in Eq. (4.33) has recently been evaluated by Ryter (1987).

For strong friction, the transmission factor simplifies further to give the rate in the overdamped regime, i.e., for $\gamma\gg\omega_b$ (Kramers, 1940)

$$k_{A\to C}^{\rm overdamped}=\frac{\omega_0\omega_b}{2\pi\gamma}\exp(-\beta E_b)\ , \tag{4.34}$$

which approaches zero as $\gamma\to\infty$. This same result may also be obtained directly by working with the Smoluchowski equation, Eq. (4.9); see Sec. IV.E.

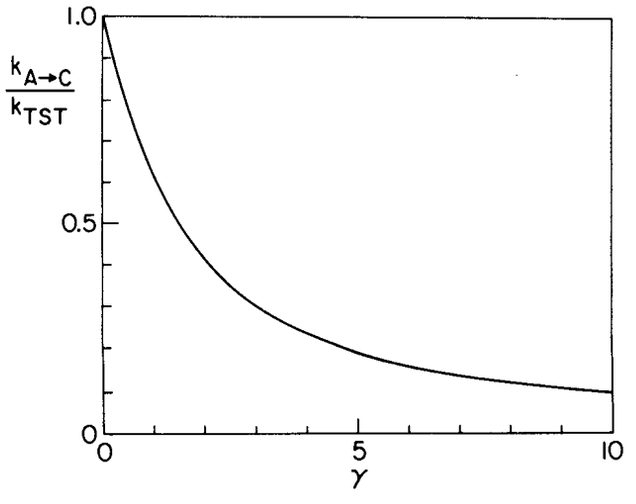

FIG. 10. The Ohmic transmission factor of the Kramers result in Eq. (4.33) vs the (dimensionless) friction γ, with $\omega_b=1$.

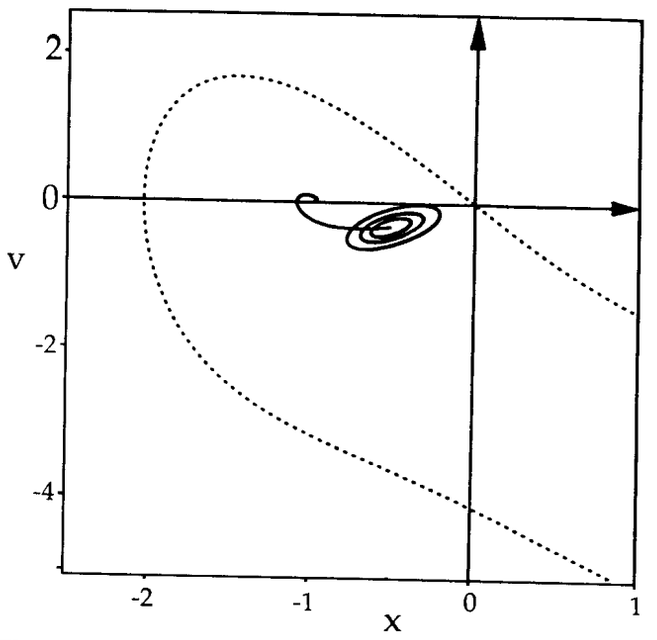

FIG. 11. Contour plot of the density of sources and sinks $s(x,v)$ [see Eq. (4.35)] in a symmetric double-well potential $U(x)=-\frac{1}{2}x^2+\frac{1}{4}x^4$: dotted line, the separatrix in the presence of friction [see Eq. (4.5)]; solid line, a deterministic trajectory that starts out at the maximum of the source density. Here we address the spatial-diffusion-controlled situation with $\beta E_b=10$ and moderate friction at $\gamma/\omega_b=1$.

C. Energy of injected particles

In order to elucidate the limits of applicability of the Kramers rate in Eq. (4.33) we focus here on the energy of the injected particles.

For the density of sources and sinks rendering $\rho(x,v)$ stationary, we find from Eqs. (4.21) and (4.22) combined with Eq. (4.29) (Talkner, 1989; see Figs. 11 and 12 below)

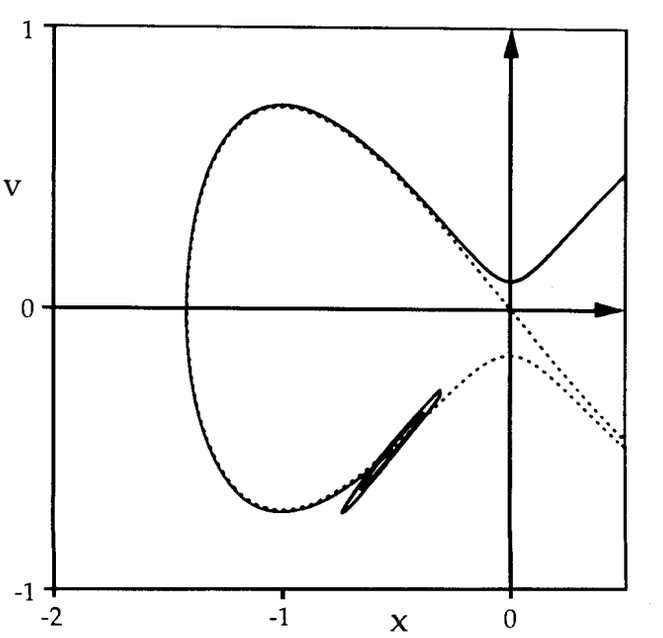

FIG. 12. Same as in Fig. 11, but now for an energy-diffusion-controlled situation with $\beta E_b=10$ and $\gamma/\omega_b=0.01$. Note that in this case the density of sources is located mainly beyond the separatrix, i.e., the injected particles assume an energy $E>E_b$.

$$s(x,v)=-\left[\frac{\lambda_+}{2\pi\gamma M k_B T}\right]^{1/2} V'(x)\exp\left[-\frac{M\omega_b^4\beta}{2\gamma\lambda_+}\left[(x-x_b)-\frac{\lambda_+ v}{\omega_b^2}\right]^2\right] p_{\rm eq}(x,v)\ . \tag{4.35}$$

Here $p_{\rm eq}(x,v)=Z^{-1}\exp\{-\beta[\frac{1}{2}Mv^2+U(x)]\}$ is the thermal equilibrium probability. The potential $V(x)$ is given by

$$V(x)=U(x)+\frac{M}{2}\omega_b^2(x-x_b)^2\ . \tag{4.36}$$

The maximal values of $s(x,v)$ lie on the line

$$v=\lambda_+(x-x_b) \tag{4.37}$$

and are located at those x values which solve

$$[V'(x)]^2=k_B T V''(x)\ . \tag{4.38}$$

For the archetypal symmetric Ginzburg-Landau potential,

$$U(x)=E_b-\tfrac{1}{2}M\omega_b^2x^2+\tfrac{1}{4}bx^4,\quad b>0\ , \tag{4.39}$$

where with $U(x_a)=0$ the barrier energy becomes $E_b=M^2\omega_b^4/(4b)$, one finds, besides the trivial solution $x=x_b$ where s vanishes, two solutions of Eq. (4.38), namely,

$$x_\pm=x_b\pm\left[\frac{3k_BT}{b}\right]^{1/4}\ . \tag{4.40}$$

The strength of the sink and the source, respectively, is thus maximal at x_+ and x_-. The particles injected at x_- have from Eq. (4.37) an energy

$$E=\tfrac{1}{2}M[\lambda_+(x_--x_b)]^2+U(x_-)$$
$$=\left[-\frac{\gamma\lambda_+}{\omega_b^2}\left[\frac{3E_b}{k_BT}\right]^{1/2}+\frac{3}{4}\right]k_BT+E_b\ . \tag{4.41}$$

At *moderate and large values of the friction* γ the first term renders this energy *smaller* than the barrier energy. Thus almost all injected particles are caught by the stable attractor at $x_a<0$ and $v=0$, where they undergo thermalization before they eventually escape; see Fig. 11. However, if at constant temperature the damping rate γ decreases, the energy of injected particles becomes greater than the barrier energy E_b. At the same time the energy loss along the deterministic trajectories (see Fig. 8) decreases with decreasing damping rate. As can be deduced from Fig. 12, the injected particles assume an energy $E>E_b$ performing one round trip at a high energy level and become trapped immediately after reaching the region behind the barrier. In Eq. (4.33) these events with $E\geq E_b$ are counted as if a particle from the bottom of the well had escaped at once. Consequently, Eq. (4.33) overestimates the true rate for weak friction, thus indicating a breakdown of the Kramers method in the low-friction regime. At low damping rates the energy loss ΔE during a round trip at initial energy $E<E_b$ follows from the deterministic limit of Eq. (4.1),

$$\Delta E=\gamma I(E)\ , \tag{4.42}$$

where Eq. (4.11) has also been used. In conclusion, Eq.(4.33) can be safely applied only if during one round trip the energy dissipated is greater than the thermal energy,

$$\gamma I(E)>k_BT\ . \tag{4.43}$$

D. Energy-diffusion-limited rate

If the condition in Eq. (4.43) is violated, the Kramers method described in Sec. IV.B fails, and the rate must be evaluated along a different line of reasoning. With Eq. (4.43) strongly violated, both the energy and the action are necessarily slowly varying quantities undergoing diffusive motion. The diffusion of the action given in Eq. (4.12) can immediately be transformed into a diffusion equation for the energy E,

$$\dot p(E,t)=\gamma\frac{\partial}{\partial E}I(E)\left[1+k_BT\frac{\partial}{\partial E}\right]\frac{\omega(E)}{2\pi}p(E,t)\ . \tag{4.44}$$

For the moment we consider the simplest case of a potential $U(x)$ with only one metastable well, as sketched in Fig. 13.

As soon as the particle has acquired an energy slightly larger than the threshold energy E_b, the particle escapes from the well. The rate is then given by the probability flux of particles in *energy space* through E_b over the population of the well. Equivalently, the probability flux in action space through $I_b=I(E_b)$ may be used. In this

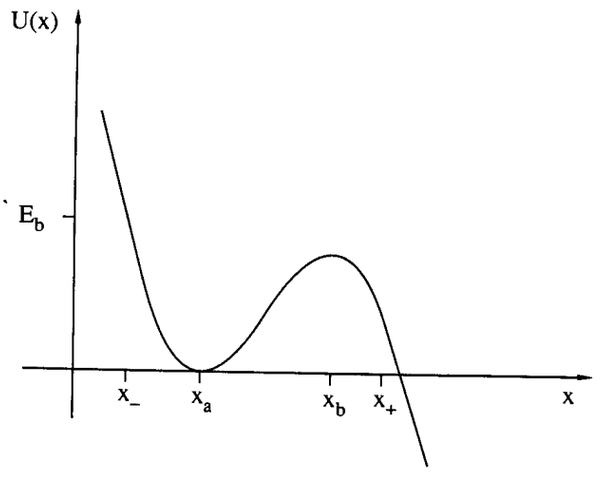

FIG. 13. Metastable potential field used in text. Particles are injected at x_- and immediately removed when they arrive at x_+.

case one solves for the stationary probability distribution $\rho(I)$ with an arbitrarily prescribed probability current j,

$$j=-\gamma I\left[1+\frac{2\pi k_B T}{\omega(I)}\frac{\partial}{\partial I}\right]\rho(I),\quad 0<I\le I_b\ . \tag{4.45}$$

Imposing an immediate absorption at $I=I_b$, that is, $\rho(I=I_b)=0$, one finds with $\beta=(k_BT)^{-1}$ from Eq. (4.45)

$$\rho(I)=j(\gamma k_BT)^{-1}\exp[-\beta E(I)] \times\int_I^{I_b}\frac{\exp[\beta E(I')]}{I'}\frac{\omega(I')}{2\pi}dI'\ . \tag{4.46}$$

At $I=0$, $\rho(I)$ has a logarithmic singularity which originates from the fact that the probability source is concentrated at $I=0$,

$$s(I)=j[\delta(I)-\delta(I-I_b)]\ . \tag{4.47}$$

However, for $\beta E_b\gg 1$ this singularity does not contribute to the population n_0 in the well,

$$n_0=\int_0^{I_b}\rho(I)dI\ .$$

By virtue of Eq. (2.11) one obtains the inverse rate as

$$k^{-1}=n_0/j=(\gamma k_BT)^{-1}\int_0^{I_b}dI\exp[-\beta E(I)]\int_I^{I_b}dI'\frac{\omega(I')}{2\pi}\frac{\exp[\beta E(I')]}{I'}\ . \tag{4.48a}$$

In the limit of a high barrier ($\beta E_b\gg 1$), a change of variables, that is, $dE=[\omega(I)/2\pi]dI$, yields to leading order

$$k^{-1}=\frac{2\pi k_BT}{\gamma\omega_0 I(E_b)}\exp(\beta E_b)\ . \tag{4.48b}$$

Hence, for very weak damping, $\gamma\ll\omega_b$, we recover precisely the result derived by Kramers (1940) for the energy-diffusion-controlled rate of escape,

$$k=\gamma\beta I(E_b)\frac{\omega_0}{2\pi}\exp(-\beta E_b)\ , \tag{4.49}$$

which is a valid expression for the rate if

$$k_BT/E_b\ll 1,\quad\text{and}\quad\gamma I(E_b)\ll k_BT\ . \tag{4.50}$$

Note that, in contrast to Eq. (4.33), the result in Eq. (4.48) or Eq. (4.49) involves the value of the action at the barrier energy, i.e., the *anharmonic* part of the well dynamics affects the final result for the energy-diffusion-controlled rate.

In the more general case of a potential with two metastable wells, as depicted in Fig. 14, a particle that acquires sufficient energy to escape, say, from inside the left well may bounce back and forth until it thermalizes with a probability p inside the right well, or with probability $(1-p)$ falls back into the initial well. Hence the forward rate k^+ reads

$$k^+\equiv k_{A\to C}=p\gamma\frac{I(E_b^+)}{k_BT}\frac{\omega_a}{2\pi}\exp(-\beta E_b^+) \tag{4.51}$$

and vice versa

$$k^-\equiv k_{C\to A}=(1-p)\gamma\frac{I(E_b^-)}{k_BT}\frac{\omega_c}{2\pi}\exp(-\beta E_b^-)\ , \tag{4.52}$$

where ω_a and ω_c are the angular frequencies in the left and right wells, respectively.

The two rates are connected by the principle of detailed balancing, Eq. (2.13). Since the equilibrium populations $\{\bar n_a,\bar n_c\}$ are known, that is, $\bar n_a\propto\omega_a^{-1}\exp(\beta E_b^+)$, $\bar n_c\propto\omega_c^{-1}\exp(\beta E_b^-)$ [see Eq. (2.13)], one finds for the yet undetermined probability p the result

$$p=\frac{I(E_b^-)}{I(E_b^+)+I(E_b^-)}\ . \tag{4.53}$$

For a symmetric bistable potential $U(-x)=U(x)$, p assumes the obvious value of $p=\frac{1}{2}$.

E. Spatial-diffusion-limited rate: the Smoluchowski limit

In this subsection we address in greater detail the escape dynamics in the Smoluchowski limit [see Eq. (4.9)].

In the limit of large damping γ, the rate in Eq. (4.33) decreases inversely proportional to the friction,

$$k=\frac{\omega_0\omega_b}{2\pi\gamma}\exp(-\beta E_b)\ . \tag{4.54}$$

This result may also be obtained directly from Eq. (4.9), which in the form of a one-dimensional diffusion equation may be treated analogously to the energy-diffusion equation. A source may be placed at $x_-<x_a$ and a sink at $x_+>x_b$ (see Fig. 13). The stationary solution $\rho(x)$, which carries the current j and obeys the absorbing boundary condition in Eq. (2.9), $\rho(x=x_+)=0$, becomes

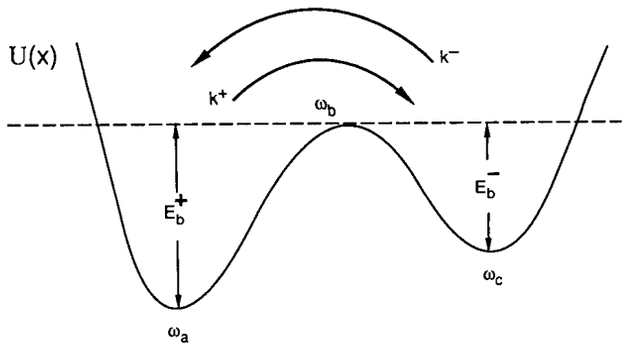

FIG. 14. Asymmetric potential field $U(x)$ with two metastable wells.

$$\rho(x)=\frac{M\gamma j}{k_B T}\exp[-U(x)/k_B T] \times\int_x^{x_+}\exp[U(y)/k_B T]dy\ , \tag{4.55}$$

while the population n_0 is readily found to read

$$n_0=\int_{-\infty}^{x_b} dx\,\rho(x)\ .$$

By virtue of Eqs. (2.11) and (4.14) we therefore obtain

$$k^{-1}=n_0/j=\int_{-\infty}^{x_+}dy\exp[-U(y)/k_B T] \times\int_y^{x_+}dz\frac{\exp[U(z)/k_B T]}{(k_B T/M\gamma)}\ . \tag{4.56a}$$

By use of a partial integration this becomes

$$k^{-1}=\int_{-\infty}^{x_+}dy\frac{\exp[U(y)/k_B T]}{(k_B T/M\gamma)} \times\int_{-\infty}^{y}dz\exp[-U(z)/k_B T]\ , \tag{4.56b}$$

which precisely equals the MFPT result, $t(x=-\infty)$, with $x=-\infty$ a natural boundary and $x=x_+$ absorbing[8] [see Eq. (7.8) below]. With $\beta E_b\gg 1$, Eq. (4.56b) can be evaluated within a Gaussian steepest-descent approximation as

$$k^{-1}=2\pi\gamma(\omega_0\omega_b)^{-1}\exp(\beta E_b)\ , \tag{4.56c}$$

whose inverse again coincides with the rate in Eq. (4.54).

Skinner and Wolynes (1979) have calculated corrections up to order γ^{-5} to this overdamped Kramers result, induced by the γ corrections to the Smoluchowski equation [see Eq. (4.10)]. These corrections coincide, of course, with the corresponding terms in the series expansion of the rate in Eq. (4.33), in powers of γ^{-1}. Moreover, the correction to the steepest-descent approximation for the rate in Eq. (4.56c) can from Eq. (4.56b) explicitly be evaluated to give (Larson and Kostin, 1978; Edholm and Leimar, 1979; Bez and Talkner, 1981; Marchesoni, 1985b)

$$k=\frac{\omega_b\omega_0}{2\pi\gamma}\exp(-\beta E_b)\left[1-k_B T\left[\frac{1}{8}\frac{U^{(4)}(x_b)}{[U^{(2)}(x_b)]^2}-\frac{1}{8}\frac{U^{(4)}(x_a)}{[U^{(2)}(x_a)]^2}+\frac{5}{24}\frac{[U^{(3)}(x_b)]^2}{|U^{(2)}(x_b)|^3}+\frac{5}{24}\frac{[U^{(3)}(x_a)]^2}{[U^{(2)}(x_a)]^3}\right]+O[(k_B T)^2]\right], \tag{4.57}$$

where $U^{(n)}$ indicates the nth-order derivative $d^n U(x)/dx^n$, and the vertical bars indicate the absolute value.

F. Spatial-diffusion-limited rate in many dimensions and fields

It has already been remarked by Kramers (1940) that a Markovian description [see Eq. (4.1)], with a one-dimensional model for the potential field may fail to yield correct rate expressions in cases where other slow variables are present that may interact with the reaction coordinate x. In this section we shall—by definition—call the rate *spatial-diffusion-controlled* whenever non-equilibrium effects for the energy population dynamics of the type discussed in Sec. IV.D can safely be neglected. As has been demonstrated in Secs. IV.B and IV.C, this regime is not exclusively restricted to the overdamped Smoluchowski region, but might also involve inertial dynamic effects, like those expressed with the Klein-Kramers equation, if the rate-determining parameters, such as the dimensionless barrier height βE_b and the friction value, are of sufficient strength. The generalization of Kramers' moderate-to-strong friction treatment in Sec. IV.B to multidimensional metastable potential fields did not come immediately. In the late fifties, Brinkman (1956), Landauer and Swanson (1961), the dislocation physicists Stenzel (1965), Seeger and Schiller (1966), and Langer (1968) were among the first to generalize Kramers' treatment to an N-dimensional Smoluchowski equation, i.e., to the case of overdamped motion in an N-dimensional potential landscape. In terms of an N-dimensional generalization of the Klein-Kramers equation, Langer (1969) subsequently gave a most thorough treatment of the nucleation rate governing the early stage of a first-order phase transition. In the following we shall discuss this work in some detail. The earlier results for the overdamped, N-dimensional Smoluchowski equation may be obtained from this result as a special limiting case.

1. The model

Langer (1969) considered the following $(2N)$-dimensional Fokker-Planck equation:

$$\frac{\partial p(\{\eta\},t)}{\partial t}=\sum_{i,j}\frac{\partial}{\partial\eta_i}M_{ij}\left[\frac{\partial E}{\partial\eta_j}+k_B T\frac{\partial}{\partial\eta_j}\right]p(\{\eta\},t)\ , \tag{4.58}$$

[8] In order that the results in Eqs. (4.56a) and (4.56b) exist we assume a confining potential that grows faster than x^2 as $x\to-\infty$.

where the phase-space point $\{\eta\}=(\eta_1,\ldots,\eta_{2N})$ consists of an order-parameter field $\eta(x)$ such as the magnetization in a magnet or the density in a fluid taken at N fixed space points x_i,

$$\eta_i=\eta(x_i),\quad i=1,\ldots,N\ , \tag{4.59a}$$

The conjugate momentum field $\pi(x)$ is taken at the same points,

$$\eta_{i+N}\equiv\pi(x_i),\quad i=1,\ldots,N\ . \tag{4.59b}$$

$E(\{\eta\})$ is a (Hamiltonian) energy function having a locally stable state at $\{\eta^A\}$, which is separated by an energy barrier from another stable state with lower energy. The point $\{\eta^S\}$ with minimal energy on the barrier ridge is a saddle point of $E(\{\eta\})$, which must be overcome in leaving the original metastable state $\{\eta^A\}$.

In the deterministic limit the system moves according to the solutions of

$$\dot{\eta}_i=-\sum M_{ij}\frac{\partial E}{\partial\eta_j}\ , \tag{4.60}$$

where, for the sake of simplicity, the transport matrix (M_{ij}) is assumed to be constant. Langer (1969) assumes that the matrix (M_{ij}) is the sum of a non-negative definite symmetric matrix (D_{ij}) and a symplectic matrix (A_{ij}) (see Goldstein, 1980), which accounts for the inertial motion,

$$M_{ij}=D_{ij}+A_{ij}\ . \tag{4.61}$$

With $\mathbf{D}=\mathbf{0}$, the motion according to Eq. (4.60) would be purely conservative, while in the presence of a nonzero diffusion matrix $\mathbf{D}$ energy would be dissipated,

$$\dot{E}=-\sum_{ij}\frac{\partial E}{\partial\eta_i}D_{ij}\frac{\partial E}{\partial\eta_j}\le 0\ , \tag{4.62}$$

where η_i is found from Eq. (4.60).

At finite temperatures the stationary equilibrium probability density reads

$$p_{\rm eq}(\{\eta\})=Z^{-1}\exp[-\beta E(\{\eta\})]\ . \tag{4.63}$$

The rate at which the metastable state decays may again be calculated in terms of the ratio of the total probability flux crossing the energy barrier, and the population of the metastable state corresponding to a stationary, current-carrying situation. Because of the presence of the saddle point, the total probability flux over the barrier will essentially be concentrated in a narrow region around $\{\eta^S\}$.

In the following calculation of the rate we shall consider the more general case in which A_{ij} is only antisymmetric but not necessarily symplectic. As a consequence the number of components of $\{\eta\}$ need no longer be restricted to an even number.

2. Stationary current-carrying probability density

As in the one-dimensional case dealt with in Sec. IV.B, the stationary current-carrying probability density $\rho(\{\eta\})$ obeys the following conditions.

(i) There are no sources and sinks in the neighborhood of the saddle point, i.e., $\rho(\{\eta\})$ obeys near $\{\eta\}\simeq\{\eta^S\}$ the relation

$$\sum_{ij}\frac{\partial}{\partial\eta_i}M_{ij}\left[\sum_k e_{jk}(\eta_k-\eta_k^s)+k_BT\frac{\partial}{\partial\eta_j}\right]\rho(\{\eta\})=0\ , \tag{4.64}$$

where it is sufficient to consider the energy in the harmonic approximation

$$E(\{\eta\})=E_b-\tfrac{1}{2}\sum_{ij}e_{ij}(\eta_i-\eta_i^s)(\eta_j-\eta_j^s)\ ,\qquad \{\eta\}\simeq\{\eta^S\}\ . \tag{4.65}$$

(ii) Near the metastable state $\{\eta^A\}$, $\rho(\{\eta\})$ agrees with the equilibrium distribution in Eq.(4.63),

$$\rho(\{\eta\})\simeq p_{\rm eq}(\{\eta\}),\quad \text{for}\quad \{\eta\}\simeq\{\eta^A\}\ . \tag{4.66}$$

(iii) Beyond the saddle $\{\eta^S\}$, $\rho(\{\eta\})$ vanishes,

$$\rho(\{\eta\})\simeq 0,\quad \{\eta\}\ \text{beyond}\{\eta^S\}\ . \tag{4.67}$$

The conditions (i)–(iii) present a straightforward generalization of the reasoning pioneered by Farkas (1927). By use of the same ansatz for $\rho(\{\eta\})$ as in the one-dimensional case, Eq. (4.22),

$$\rho(\{\eta\})=\zeta(\{\eta\})p_{\rm eq}(\{\eta\})\ , \tag{4.68}$$

one obtains from Eqs. (4.63) and (4.64)

$$\sum_{ij}M_{ji}\left[-\sum_k e_{jk}(\eta_k-\eta_k^S)-k_BT\frac{\partial}{\partial\eta_j}\right]\frac{\partial}{\partial\eta_i}\zeta(\{\eta\})=0\ ,\qquad \text{for}\ \{\eta\}\simeq\{\eta^s\}\ . \tag{4.69}$$

In view of Eq. (4.29) we make for $\zeta(\{\eta\})$ an ansatz that already satisfies the boundary conditions (ii) and (iii),

$$\zeta(\{\eta\})=\frac{1}{\sqrt{2\pi k_BT}}\int_u^\infty\exp\left[-\frac{z^2}{2k_BT}\right]dz\ . \tag{4.70}$$

Here u is assumed to be linear in the deviations from the saddle point:

$$u=\sum_i U_i(\eta_i-\eta_i^s)\ . \tag{4.71}$$

By insertion, we find that the U_i are the components of the left eigenvector of the time-reversed ($\sim$) dynamical matrix $\sum_j\tilde{M}_{ij}e_{jk}$ belonging to the unique positive eigenvalue λ_+ describing the growth rate of a small deviation from the saddle point,

$$-\sum_{ji}U_i\tilde{M}_{ij}e_{jk}=\lambda_+U_k\ . \tag{4.72}$$

The normalization of U_i is fixed so that

$$\lambda_+=\sum_{ij}U_iM_{ij}U_j\ . \tag{4.73}$$

This requires that the component of the diffusion matrix

in the dynamically unstable direction is not vanishing. For later use we note that the normalization of U, Eq. (4.73), is equivalent to

$$\sum_{ij} U_i e_{ij}^{-1} U_j = -1 \ , \tag{4.74}$$

where (e_{ij}^{-1}) denotes the inverse matrix of (e_{ij}). We shall comment on the case in which this matrix may not be inverted [see Eq. (4.83) below].

3. The rate of nucleation

From the general form of the probability current

$$J_i(\{\eta\},t) = -\sum_j M_{ij} \left[\frac{\partial E}{\partial \eta_j} + k_B T \frac{\partial}{\partial \eta_j} \right] \rho(\{\eta\},t) \tag{4.75}$$

we obtain with Eqs. (4.63), (4.70), and (4.71) for the stationary current density

$$J_i\{\eta\} = \sqrt{k_B T/2\pi} \sum_j M_{ij} U_j p_{\rm eq}(\{\eta\}) \exp(-\tfrac{1}{2}\beta u^2) \ . \tag{4.76}$$

In order to obtain the total probability flux over the barrier, we would in principle have to integrate the current over a hypersurface containing the saddle point and surrounding the metastable state $\{\eta^A\}$. As already mentioned above, because the probability current is strongly concentrated in a small neighborhood within the bottleneck region it is sufficient to integrate the current over a plane containing the saddle point. The orientation of the plane may be chosen almost arbitrarily. We require only that the probability current not flow completely parallel to the chosen plane. We now integrate the current over the plane $u=0$,

$$j = \sum_i \int_{u=0} dS_i J_i(\{\eta\}) \ . \tag{4.77}$$

Within the harmonic approximation for the energy near the saddle point, Eq. (4.65), the integration yields for the total flux (see Appendix A)

$$j = \frac{\sum_{ij} U_i M_{ij} U_j}{\left| \sum_{ij} U_i e_{ij}^{-1} U_j \right|^{1/2}} \frac{1}{2\pi} |\det(\mathbf{E}^{(S)}/2\pi k_B T)|^{-1/2} Z^{-1} \exp(-\beta E_b) \ , \tag{4.78}$$

where $\det \mathbf{E}^{(S)}$ denotes the determinant of the matrix $\mathbf{E}^{(S)} = (e_{ij})$ [see Eq. (4.65)]. With Eqs. (4.73) and (4.74) the flux simplifies further to give

$$j = \frac{\lambda_+}{2\pi} |\det[(2\pi k_B T)^{-1} \mathbf{E}^{(S)}]|^{-1/2} Z^{-1} \exp(-\beta E_b) \ . \tag{4.79}$$

In order to obtain the rate, we must divide the flux by the population n_A inside the initial well, which in the Gaussian approximation emerges as

$$n_A = \{\det[(2\pi k_B T)^{-1} \mathbf{E}^{(A)}]\}^{-1/2} Z^{-1} \ , \tag{4.80}$$

with $\mathbf{E}^{(A)}$ denoting the Hessian matrix of the energy at the metastable point $\{\eta^A\}$ where the energy is assumed to vanish. If we combine Eqs. (4.79) and (4.80) we find for the rate the important result (Langer, 1969)

$$k = \frac{\lambda_+}{2\pi} \left[\frac{\det[(2\pi k_B T)^{-1} \mathbf{E}^{(A)}]}{|\det[(2\pi k_B T)^{-1} \mathbf{E}^{(S)}]|} \right]^{1/2} \exp(-\beta E_b) \ . \tag{4.81}$$

Hence the rate is given by the deterministic growth rate λ_+ [see Eq. (4.72)] of a small deviation from the saddle point times the relative frequency

$$\{\det[(2\pi k_B T)^{-1} \mathbf{E}^{(A)}]/|\det[(2\pi k_B T)^{-1} \mathbf{E}^{(S)}]|\}^{1/2} \times \exp(-E_b/k_B T)$$

of finding the system at the saddle rather than at the stable state $\{\eta^A\}$. Earlier, Langer (1967) obtained this frequency factor as the imaginary part of the equilibrium free energy of a metastable state, evaluated in a steepest-descent approximation about the stable point and the saddle point,

$$\frac{\mathrm{Im}\mathcal{F}}{k_B T} = \frac{1}{2} \left[\frac{\det[(2\pi k_B T)^{-1} \mathbf{E}^{(A)}]}{|\det[(2\pi k_B T)^{-1} \mathbf{E}^{(S)}]|} \right]^{1/2} \exp(-E_b/k_B T) \ . \tag{4.82}$$

Therefore the rate in Eq. (4.81) may also be expressed as (Langer, 1969, 1980)

$$k = \frac{\lambda_+}{\pi k_B T} \mathrm{Im}\mathcal{F} \ . \tag{4.83}$$

The form of the result in Eqs. (4.81) and (4.83) makes explicit that this generalization of the Kramers rate is equivalent with a harmonic, multidimensional TST rate in which the dissipative motion is modeled in the full phase space of the total system, i.e., one treats explicitly the coupling to the degrees of freedom of the heat bath. Put differently, just as the multidimensional TST rate in Eq. (3.46) exhibits equivalence with the spatial-diffusion-controlled Kramers escape rate in Eq. (4.33), the result in Eq. (4.81) can be obtained as the TST rate in full phase space of all degrees of freedom. In particular, the growth rate λ_+ plays the role of a generalized, friction-

renormalized barrier frequency [see Eq. (3.44)], which is known in the chemical physics community as the "Grote-Hynes frequency" (Grote and Hynes, 1980).

So far, we have completely neglected the influence of symmetries that may lead either to a discrete number of equivalent saddle points or to a whole continuum of saddle points, as would be the case for a continuous symmetry. In the first case, Eq. (4.81) gives the escape rate over one saddle and the total escape rate is this rate multiplied by the number of equivalent saddle points. In the case of a continuous symmetry, the matrix of second derivatives of the energy at the saddle point has vanishing eigenvalues corresponding to Goldstone modes. These must be excluded from the calculation of the Hessian. Integration over the Goldstone modes yields a factor proportional to the volume of the symmetry group, which for the case of translational symmetry of an extended system is determined by the physical volume of the system (Langer, 1967, 1980; Günther, Nicole, and Wallace, 1980).

In the special case of Smoluchowski dynamics where the transport matrix is proportional to the unit matrix

$$M_{ij}=\frac{1}{\gamma M}\delta_{ij} , \tag{4.84}$$

and the energy function E consists of a potential energy $U(q)$, Eq. (4.81) simplifies to (Brinkman, 1956; Landauer and Swanson, 1961; Langer, 1968)

$$k=\frac{\omega_b}{2\pi\gamma}\frac{\Pi_i\omega_i^A}{\Pi_i'\omega_i^S}\exp(-E_b/k_BT) . \tag{4.85}$$

Here $\{\omega_i^S\}$ are the angular frequencies of the stable modes at the saddle point, $\omega_b>0$ denotes the unstable angular frequency, and the set $\{\omega_i^A\}$ denotes those at the metastable state $\{\eta^A\}$. The notation (Π') indicates that the unstable angular frequency mode has been excluded from the product.

As we point out below Eq. (4.83), the appealing treatment by Langer for the escape rate does not hold in all physical situations, but applies only in the strong-coupling limit, when effects of nonequilibrium due to energy-diffusion-controlled processes can safely be neglected. The regime of its validity will be discussed in greater detail next.

G. Regime of validity for Kramers' rate theory

In conclusion, various results for the Kramers' escape rate are derived in Eqs. (4.33), (4.49), (4.54), and (4.81) under the condition of weak thermal noise, $\beta E_b\gg1$. This condition assures a clear-cut separation of time scales, as noted previously [see Eq. (2.2)]. The regime of validity of the various results depends further in a characteristic way on the dimensionless coupling parameter (γ/ω_b). With $(\gamma/\omega_b)>1$ we generally find that thermal equilibrium prevails throughout the escape process, and the rate k becomes spatial-diffusion limited (Fig. 9). This in turn implies the validity of Eqs. (4.33), (4.34), and (4.56), as well as of Eqs. (4.81), (4.83), and (4.85) in the multidimensional generalization. The escape dynamics becomes controlled by energy diffusion whenever the condition in Eq. (4.43), $\gamma I(E_{(b)})>k_BT$, starts to fail. Since the action $I(E_b)$ is of the order (E_b/ω_b), we find a turnover region (see Sec. VI) around $k_BT/E_b=(\gamma/\omega_b)$, with $k_BT/E_b\leq1$. When $\gamma I_b\simeq(\gamma/\omega_b)E_b<k_BT$, the thermalization process inside the metastable well takes place on a time scale τ_e comparable to, or even larger than, the time scale set by the simple transition-state theory in Eq. (3.5), i.e., $\tau_e\geq(2\pi/\omega_0)\exp(\beta E_b)$. This in turn implies a deviation from the thermal equilibrium probability inside the metastable well, as specified by the current-carrying stationary nonequilibrium energy density in Eq. (4.46). With $\rho(E)=\rho(I)[2\pi/\omega(E)]$, one finds deviations from the Boltzmann distribution within a narrow region of order k_BT below the barrier energy E_b. In particular, we note that from Eq. (4.46), $\rho(E=E_b)=0$. The two dimensionless parameters, k_BT/E_b and (γ/ω_b), therefore characterize the regimes of validity of the different results for the rate in the spatial-diffusion limited regime and in the energy-diffusion limited regime. This behavior can be characterized by the classical rate-phase diagram depicted in Fig. 15.

In view of the rate treatment for the energy-diffusion-controlled regime, it should also be stressed here that so far we have treated the dynamics of energy exchange within Kramers' model in terms of a Fokker-Planck equation only [see Eq. (4.44)]. In other words, the energy dynamics has been approximated by a continuous Markov process for which the change of energy upon a single collision is continuous. More realistic, however, is a model in which the energy upon a collision may change by a finite amount. The latter situation is typical for chemical reactions in the gas phase. Rate theory at weak friction has therefore been a topic of considerable interest within the chemical physics community, where it is known as "unimolecular rate theory." A survey of the

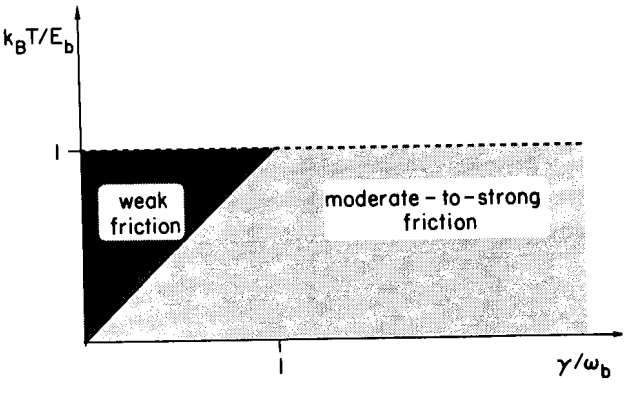

FIG. 15. Regime of validity of Kramers rate expressions for weak friction [see Eq. (4.49)], and for moderate-to-large friction [see Eq. (4.33)], as a function of the two relevant dimensionless parameters, the inverse Van't Hoff-Arrhenius factor k_BT/E_b and the friction strength γ/ω_b.

recent major developments in this field in one and many dimensions is the subject of the following section.

V. UNIMOLECULAR RATE THEORY

The theory of unimolecular reactions (or first-order reactions $\dot{c}=-kc$) in the gas phase is a classical topic of physical chemistry. Pioneering work of Lindemann (1922) and Hinshelwood (1926a, 1926b) initiated the formulation of the theory by Rice and Ramsperger (1927), Kassel (1928a, 1928b), and Marcus (1952, 1965), commonly known as RRKM theory. Recently it has been further developed, by among others, Keck and Carrier (1965) and Troe (1975). The topic is well documented in the chemical physics literature, in review articles, and monographs (Forst, 1973; Hase, 1976; Callear, 1983). Probably because this theory has been applied mostly to unimolecular chemical reactions, it has remained virtually unknown within the physics community. Only recently has it been recognized that several results in the reaction-rate theory of weakly damped systems can be obtained as special cases of unimolecular rate theory. One example, which we shall discuss in detail below, is the energy-diffusion-limited rate in Eq. (4.49) of the Kramers problem. In this section we review the most important aspects of unimolecular rate theory in thermal systems and investigate within this framework the predictions for weakly damped systems.

The basic physics of the problem was set forth by Lindemann (1922). He considered the dissociation of a molecule A in an inert bath gas. As the molecule A undergoes collisions with the gas molecules M, a very energetic collision may impart more than the barrier energy to the molecule. As the energy of the resulting activated molecule A^* is now above the dissociation threshold, the molecule may cross the barrier and dissociate into the product B. Collisions, in turn, may also remove energy and deactivate the molecule. Therefore we have the reaction scheme

$$A+M \xrightarrow{k_1} A^*+M \quad \text{(activation)},$$

$$A^*+M \xrightarrow{k_2} A+M \quad \text{(deactivation)},$$

$$A^* \xrightarrow{k_3} B \quad \text{(dissociation)}.$$

The kinetic equations for these reactions read

$$\dot{c}_A=-k_1c_Ac_M+k_2c_{A^*}c_M\ , \tag{5.1}$$

$$\dot{c}_{A^*}=k_1c_Ac_M-k_2c_{A^*}c_M-k_3c_{A^*}\ , \tag{5.2}$$

where c_i denotes the number concentration of species i. Assuming that the inert bath gas M is in excess of species A, A^* and that the number of activated molecules A^* reaches a steady state, that is $\dot{c}_{A^*}=0$, the rate for the unimolecular decomposition of A becomes

$$k_{\rm uni}=\frac{k_3k_1c_M}{k_3+k_2c_M}\ . \tag{5.3}$$

In a dilute gas the number concentration c_M is proportional to the pressure of the gas, i.e., to the collision rate α or the damping rate γ. The dependence of the overall rate on pressure (or collision rate) is shown in Fig. 16. If the pressure is large, the rate constant becomes independent of pressure, namely, $k_{\rm uni}=k_3k_1/k_2\equiv k_{\rm TST}$. As we shall discuss later, the high-pressure limit is equivalent to transition-state theory. For low pressures, on the other hand, $k_{\rm uni}=k_1c_M\equiv k_C$, that is, the rate equals the rate of collisional activation and increases in proportion to the pressure (or collision rate α). Note that Eq. (5.3) can be rewritten as

$$k_{\rm uni}^{-1}=k_C^{-1}+k_{\rm TST}^{-1}\ . \tag{5.4}$$

This relation can be interpreted as the sum of two average lifetimes, and therefore the dissociation can be viewed as a succession of two steps. A collisional activation step, characterized by a rate k_C, and the barrier-crossing step, with a rate $k_{\rm TST}$. At low pressures the collisional activation is slow, and thus k_C determines the overall rate. At higher pressures, on the other hand, the collisional activation is rapid and the overall rate is determined by the rate $k_{\rm TST}$ for the barrier crossing.

Let us pose the problem more precisely. Consider an isolated molecule described by the classical Hamiltonian

$$\mathcal{H}=\sum_{i=1}^{n}\frac{p_i^2}{2m_i}+U(q_1,\ldots,q_n)\ , \tag{5.5}$$

where the $\{q_i\}$ are the coordinates of particles $i=1,\ldots,n$ with masses m_i, and the $\{p_i\}$ are the conjugate momenta. We assume that the n degrees of freedom are strongly coupled so that a rapid equipartitioning of the total energy E is possible. The potential energy U has a single metastable well with its minimum given by $U=0$, and the saddle point is located at a barrier energy $U=E_b$. We introduce a reaction coordinate $x(\mathbf{q})$, which

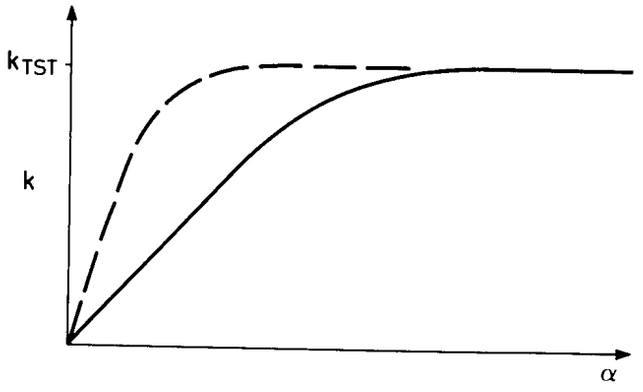

FIG. 16. Schematic plot of the transition of the rate between weak and strong collision rates α: solid line, behavior for a single degree of freedom; dashed line, behavior for several degrees of freedom [see Eq. (5.32)].

is *positive* for the undissociated species A and vanishes at the dividing surface, which passes through the saddle point. Let us investigate the situation in which the species (A) is assumed to undergo a dissociation reaction in a dilute gas. At zero pressure ($c_M=0$) the molecule undergoes no collisions and the total energy of the isolated molecule $E=\mathcal{H}$ is a conserved quantity. At low pressures, the molecule will experience infrequent collisions with the gas molecules. During these collisions the energy of the molecule will change in a jumplike manner. As long as the pressure is low enough, the collisional events will be uncorrelated, because the average time between the collisions is much longer than the typical duration of a collision. As soon as the energy of the molecule is higher than the dissociation energy E_b, the molecule will dissociate with an energy-dependent rate. Therefore the probability density $p(E,t)$ of finding the undissociated molecule with an energy E can be modeled by a Markovian master equation (Montroll and Shuler, 1958; Widom, 1959; Ree *et al.*, 1962; Keck and Carrier, 1965; Nikitin, 1966; Forst, 1973; Troe, 1975) of the form

$$\frac{\partial p(E,t)}{dt}=\int_0^\infty dE'[K(E,E')p(E',t)-K(E',E)p(E,t)] -k(E)p(E,t) . \tag{5.6}$$

The change in energy of the molecule due to collisions is described by the integral term in Eq. (5.6), while the loss of molecules due to dissociation is taken into account by the last term in Eq. (5.6). The transition probability $K(E\to E')\equiv K(E',E)$ per unit time obeys the detailed balance condition

$$K(E,E')p_{\rm eq}(E')=K(E',E)p_{\rm eq}(E) . \tag{5.7}$$

Here we have introduced the thermal distribution

$$p_{\rm eq}(E)=\frac{1}{Z}\Omega(E)\exp(-\beta E) , \tag{5.8}$$

and denoted the density of states of the undissociated molecule by

$$\Omega(E)=\int d\mathbf{q}^{3N}d\mathbf{p}^{3N}\delta[E-\mathcal{H}(\mathbf{p},\mathbf{q})] . \tag{5.9}$$

The normalization is given by the partition function

$$Z=\int_0^\infty dE\ \Omega(E)\exp(-\beta E) . \tag{5.10}$$

We abbreviate the *canonical average* as

$$\langle f\rangle=\frac{\int d\mathbf{q}^{3N}d\mathbf{p}^{3N}\exp[-\beta\mathcal{H}(\mathbf{p},\mathbf{q})]f(\mathbf{p},\mathbf{q})}{\int d\mathbf{q}^{3N}d\mathbf{p}^{3N}\exp[-\beta\mathcal{H}(\mathbf{p},\mathbf{q})]} , \tag{5.11}$$

and the *microcanonical average* constrained to the energy E of the undissociated molecule as

$$\langle f\rangle_E=\frac{\int d\mathbf{q}^{3N}d\mathbf{p}^{3N}\delta[E-\mathcal{H}(\mathbf{p},\mathbf{q})]f(\mathbf{p},\mathbf{q})}{\int d\mathbf{q}^{3N}d\mathbf{p}^{3N}\delta[E-\mathcal{H}(\mathbf{p},\mathbf{q})]} . \tag{5.12}$$

For a single degree of freedom the density of states equals the period

$$\Omega(E)=\frac{2\pi}{\omega(E)} . \tag{5.13}$$

For a collection of n harmonic oscillators with (angular) frequencies $\{\omega_i\}$, one has the well-known power-law expression (Polanyi, 1920; Troe, 1975)

$$\Omega(E)=\frac{E^{n-1}}{(n-1)!}\prod_{i=1}^{n}\left[\frac{2\pi}{\omega_i}\right]\propto E^{n-1} . \tag{5.14}$$

The transition probability density can also be written as

$$K(E',E)=\alpha P(E',E) , \tag{5.15}$$

where α is the collision frequency and $P(E',E)$ denotes the conditional probability density of a molecule with initial energy E which after collision assumes the energy E'. In general, the collision frequency α will also depend on the energy of the molecule prior to the collision, but we shall simplify the present discussion by neglecting this energy dependence.

The dissociation rate constant $k(E)$ can be estimated using microcanonical transition-state theory. In analogy to Eq. (2.23) we write

$$k(E)=\frac{\langle\delta(x)\dot{x}\theta(\dot{x})\rangle_E}{\langle\theta(x)\rangle_E} . \tag{5.16}$$

Obviously, molecules with an energy below the threshold barrier cannot dissociate, and hence

$$k(E)=0, \quad \text{for } E<E_b . \tag{5.17}$$

For a single degree of freedom Eq. (5.16) reduces to the frequency of motion

$$k(E)=\theta(E-E_b)/\tau(E) , \tag{5.18}$$

where $\tau(E)$ is the round trip time for a particle starting out at $x=x_b$ to go to the domain of attraction of state x_a and to return to $x=x_b$ (see Fig. 3).

For a collection of n harmonic oscillators Eq. (5.16) yields the RRKM expression (Forst, 1973; Troe, 1975)

$$k(E)=\frac{1}{2\pi}\frac{\prod_{i=1}^{n}\omega_i^{(0)}}{\prod_{i=1}^{n-1}\omega_i^{(b)}}\left[\frac{E-E_b}{E}\right]^{n-1}, \quad \text{for } E\geq E_b , \tag{5.19}$$

where the set $\{\omega_i^{(0)}\}$ are the angular frequencies at the bottom of the well and $\{\omega_i^{(b)}\}$ are the stable angular frequencies at the saddle point.

Even for sufficiently low collision frequencies, a simple equation such as Eq. (5.6) cannot describe the dynamics of an arbitrary molecule exactly. We shall discuss in Sec. V.D the approximations inherent in Eq. (5.6) and demonstrate how to relax some of these assumptions. Now, let us consider the wide variety of results that follow from Eq. (5.6).

The most popular method of evaluating the rate $k_{\rm uni}$ from Eq. (5.6) is the flux-over-population method, which

was discussed in Sec. II.C.1. To build up a steady-state current, we feed in particles at $E=0$ which give rise to a steady-state distribution $p_0(E)$ satisfying Eq. (5.6). The loss term proportional to $k(E)$ in Eq. (5.6) is responsible for the removal of the injected particles. The rate $k_{\rm uni}$ (i.e., the dissociation rate of the molecule) is related to the constant probability flux j by [see Eq. (2.11)]

$$k_{\rm uni}=\frac{j}{n_0}=\frac{\int_{E_b}^{\infty}dE\,k(E)p_0(E)}{\int_0^{E_b}dE\,p_0(E)}\ . \tag{5.20}$$

The steady-state distribution satisfies [see Eq. (5.6)][9]

$$\int_0^{\infty}dE'[K(E,E')p_0(E')-K(E',E)p_0(E)]=k(E)p_0(E)\ . \tag{5.21}$$

In the present context it is useful to introduce a normalized steady-state distribution such that $\int_0^{E_b}dE\,p_0(E)\simeq\int_0^{\infty}dE\,p_0(E)=1$. The extension of the upper integration limit to infinity is permissible as it introduces only exponentially small errors. The rate constant then equals the probability flux j, and Eq. (5.20) simplifies, with $k(E)=0$, $E<E_b$, to

$$k_{\rm uni}=\int_{E_b}^{\infty}dE\,k(E)p_0(E)\ . \tag{5.22}$$

In principle, given $K(E',E)$ and $k(E)$, Eq. (5.21) can be solved for the normalized steady-state distribution $p_0(E)$ with the rate $k_{\rm uni}$ then evaluated from Eq. (5.22). Unfortunately, this involves the solution of the integral equation in Eq. (5.21), for which an explicit expression is generally not available. In some special cases, however, this solution can be obtained in closed form.

First we consider the special cases of high and low collision rates α, respectively, as discussed in the beginning of this section in connection with Lindemann's (1922) work. In the case of a high collision rate (implying a high pressure, i.e., $\alpha\to\infty$) the dissociation rate $k(E)$ (which is of the order of a typical vibrational frequency) becomes much smaller than the collision rate α. The collisions will then maintain the equilibrium distribution, so that $p_0(E)=p_{\rm eq}(E)$. In this case Eq. (5.20) becomes

$$\begin{aligned}k_{\rm uni}&=k_{\rm TST}\\&\equiv\frac{\int_{E_b}^{\infty}dE\,k(E)p_{\rm eq}(E)}{\int_0^{E_b}dE\,p_{\rm eq}(E)}\\&=\frac{\langle\delta(x)\dot{x}\theta(\dot{x})\rangle}{\langle\theta(x)\rangle},\quad\text{for }\alpha\to\infty\ .\end{aligned} \tag{5.23}$$

Here we have used Eq. (5.16). This obviously is the result of canonical transition-state theory discussed in Sec. III [see Eq. (3.6)]. For a collection of harmonic oscillators Eq. (5.23) simplifies to [see Eq. (3.14)]

$$k_{\rm TST}=\frac{1}{2\pi}\frac{\prod_{i=1}^{n}\omega_i^{(0)}}{\prod_{i=1}^{n-1}\omega_i^{(b)}}\exp(-\beta E_b)\ . \tag{5.24}$$

On the other hand, in the low-collision-rate limit (implying low pressure, i.e., $\alpha\to0$), the collision rate is less than the dissociation rate $k(E)$ of an activated molecule. Therefore the barrier threshold acts as a perfect sink, implying $p_0(E)\to0$ for $E\geq E_b$, as $\alpha\to0$. In this case, Eq. (5.22) shows that the rate vanishes in the low-collision-rate limit. With $\alpha\to0$, the rate of energy activation becomes proportional to the collision rate, $k_{\rm uni}=k_C\propto\alpha$. To obtain the explicit expression for k_C we integrate Eq. (5.21) from $E=E_b$ to $E=\infty$. Using Eq. (5.22) and the fact that $p_0(E)\simeq0$ for $E>E_b$, we obtain for the rate in the low collision limit

$$k_{\rm uni}=k_C\equiv\int_{E_b}^{\infty}dE\int_0^{E_b}dE'K(E,E')p_0(E')\ ,\quad\text{as }\alpha\to0\ . \tag{5.25}$$

A useful quantity of a given collision kernel $K(E',E)$ is its first moment, which is related to the average loss of energy per unit time [see Eq. (5.15)],

$$A(E)=\int_0^{\infty}dE'K(E',E)(E'-E)\equiv\alpha\langle\Delta E\rangle\ , \tag{5.26}$$

where we have introduced the average energy transferred per collision,

$$\langle\Delta E\rangle=\int_0^{\infty}dE'P(E',E)(E'-E)<0\ . \tag{5.27}$$

The case in which the energy transfer is very effective, such that $|\langle\Delta E\rangle|\gg k_BT$, is commonly termed the *strong collision limit.* In the opposite case of ineffective collisions with $|\langle\Delta E\rangle|\ll k_BT$ we encounter the *weak collision limit.* Before we investigate the general case in Sec. V.C, we discuss these two limits in more detail.

A. Strong collision limit

The collision kernel which allows for large energy transfers is independent of the initial energy of the molecule. From Eq. (5.7) it then follows that

$$K_{\rm SC}(E',E)=\alpha p_{\rm eq}(E')\ . \tag{5.28}$$

In this *strong collision approximation,* a collision simply resamples the energy from a thermal ensemble. Inserting this collision kernel, Eq. (5.28), into Eq. (5.21) and using the fact that the probabilities are normalized, one finds

$$p_0(E)=\frac{\alpha}{\alpha+k(E)}p_{\rm eq}(E)\ . \tag{5.29}$$

Inserting Eq. (5.29) into Eq. (5.22) we obtain the explicit expression for the rate in the strong collision approximation,

$$k_{\rm SC}=\int_{E_b}^{\infty}dE\,p_{\rm eq}(E)\frac{\alpha k(E)}{\alpha+k(E)}\ . \tag{5.30}$$

[9]To obtain from Eq. (5.6) a nonvanishing steady state, one reinjects the lost particles back at $E=0$ with a rate $k_{\rm uni}$.

A typical plot of the rate constant as a function of collision frequency is shown in Fig. 16. As $\alpha\to\infty$, Eq. (5.30) reduces to the transition-state theory [see Eq. (5.23)], while

$$k_{\rm SC}=\alpha\int_{E_b}^{\infty}dE\,p_{\rm eq}(E),\quad \text{as } \alpha\to 0\ . \tag{5.31}$$

This result can also be obtained by inserting Eq. (5.28) into Eq. (5.25) and observing that in this case $p_0(E)=p_{\rm eq}(E)$ for $E<E_b$. Equation (5.31) can be interpreted as the collision rate α times the probability of finding a molecule above the threshold barrier in a thermal ensemble. For a harmonic density of states, Eq. (5.14), we obtain from Eq. (5.31) for high barriers ($\beta E_b\gg n$, with n the number of strongly coupled degrees of freedom) the well-known result (Polanyi, 1920; Lewis and Smith, 1925; Wigner, 1925; Christiansen, 1926; Hinshelwood, 1926a, 1926b; Polanyi and Wigner, 1928)

$$k_{\rm SC}\simeq\alpha\frac{(\beta E_b)^{n-1}}{(n-1)!}\exp(-\beta E_b),\quad \text{as } \alpha\to 0\ . \tag{5.32}$$

Note the rapid increase of the rate constant with increasing number of degrees of freedom n (see the dashed line in Fig. 16). Other strong collision models have been suggested in the literature (Montgomery *et al.*, 1979; Skinner and Wolynes, 1980; Borkovec and Berne, 1985b). Nevertheless, the corresponding results are always well approximated by the strong collision approximation in Eq. (5.28).

B. Weak collision limit

In the case where the energy exchange upon a collision is small, $|\langle\Delta E\rangle|\ll k_BT$, we perform a Kramers-Moyal expansion of the master equation in Eq. (5.6) up to second order (for the details of this procedure the reader is referred to Hänggi and Thomas, 1982). We thus obtain an energy-diffusion approximation of the form

$$\frac{\partial p(E,t)}{\partial t}=-\frac{\partial}{\partial E}[A(E)p(E,t)]+\frac{\partial^2}{\partial E^2}[D(E)p(E,t)]-k(E)p(E,t)\ , \tag{5.33}$$

where we have introduced the energy-diffusion coefficient

$$D(E)=\tfrac{1}{2}\int dE'K(E',E)(E'-E)^2=\tfrac{1}{2}\alpha\langle\Delta E^2\rangle \tag{5.34}$$

with

$$\langle\Delta E^2\rangle=\int dE'P(E',E)(E'-E)^2\ . \tag{5.35}$$

$D(E)$ is related to the rate of energy exchange by

$$A(E)=\frac{1}{p_{\rm eq}(E)}\frac{d}{dE}[D(E)p_{\rm eq}(E)]=-\beta D(E)+D'(E)+D(E)\frac{d\ln\Omega(E)}{dE}\ . \tag{5.36}$$

This relation follows from the detailed balance condition in Eq. (5.7). Note that for energies $E\gg k_BT$ and smooth $D(E)$, Eq. (5.36) can be approximated by

$$A(E)=-\beta D(E)\ , \tag{5.37}$$

i.e.,

$$\langle\Delta E^2\rangle\simeq 2\beta^{-1}|\langle\Delta E\rangle|\ . \tag{5.38}$$

The energy-diffusion equation, Eq. (5.33), is a good approximation of the full master equation (5.6) when the truncation of the Kramers-Moyal expansion is permissible. This applies if $\beta|\langle\Delta E^{m+1}\rangle|\ll|\langle\Delta E^m\rangle|$ for all $m\geq 2$ (Hänggi and Thomas, 1982). In most cases the condition $\beta|\langle\Delta E\rangle|\ll 1$ is sufficient, since common collision kernels are of the form $P(E',E)=f(E,x)$ where $x=(E'-E)/a$, with a approaching zero. Unfortunately, the general steady-state solution of Eq. (5.33) has not been found. We can consider several special cases, however. For energies $E<E_b$, where $k(E)=0$ [see Eq. (5.17)], the steady-state solution of Eq. (5.33) can be written as

$$\zeta(E)=C_1+C_2\int_E^{E_b}\frac{dE}{D(E)p_{\rm eq}(E)}\ , \tag{5.39}$$

where we have abbreviated the deviation of the steady-state distribution from the equilibrium distribution as

$$\zeta(E)=p_0(E)/p_{\rm eq}(E)\ , \tag{5.40}$$

with C_1 and C_2 being two integration constants to be determined. In the low-collision-rate limit $\alpha\to 0$, the steady-state distribution vanishes above threshold, i.e., $p_0(E)\simeq 0$ for $E>E_b$. From the related continuity requirement, $\zeta(E_b)=0$, one thus finds $C_1=0$. The second integration constant C_2 can be obtained from the normalization condition, and C_2 is found to equal the steady-state probability flux j, that is, C_2 equals the inverse rate $k_{\rm WC}$. After a partial integration [see Eq. (4.48a)], the result reads explicitly

$$k\equiv k_{\rm WC}=\left[\int_0^{E_b}\frac{dE}{D(E)p_{\rm eq}(E)}\int_0^{E}dE'p_{\rm eq}(E')\right]^{-1},\quad \text{as } \alpha\to 0\ . \tag{5.41}$$

The energy-diffusion coefficient is given in terms of the collision kernel by Eq. (5.34). For a collection of n damped degrees of freedom this quantity can be directly related to the damping rate. In the case of a non-Markovian (NM), time-dependent memory friction one assumes the equation of motion [see Eqs. (2.6) and (3.31)]

$$m_i\ddot{q}_i=-\frac{\partial U}{\partial q_i}-\sum_{i=1}^{n}\int_0^t dt'\eta_{ij}(t-t')\dot{q}_j(t')+\xi_i(t)\ , \tag{5.42}$$

where $\eta_{ij}(t)$ are the elements of the time-dependent friction matrix and $\{\xi_i(t)\}$ are the random forces. The corresponding energy-diffusion coefficient has been evalu-

ated by Zawadzki and Hynes (1985) to give

$$D_{\mathrm{NM}}(E)=\sum_{i,j}\frac{k_BT}{m_im_j}\int_0^\infty dt\,\eta_{ij}(t)\langle p_i(0)p_j(t)\rangle_E\ , \tag{5.43a}$$

where $\langle\cdots\rangle_E$ denotes the microcanonical average.

In *one dimension,* this result simplifies with $\eta(t)/M=\gamma(t)$ [see Eq. (3.31)] to (Zwanzig, 1959; Carmeli and Nitzan, 1982, 1984; Grote and Hynes, 1982)

$$D_{\mathrm{NM}}(E)=\frac{k_BT}{M}\int_0^\infty\gamma(\tau)\langle p(\tau)p(0)\rangle_E d\tau \tag{5.43b}$$

$$=k_BTI(E)[\omega(E)/2\pi]\int_0^\infty\gamma(\tau)\langle p(\tau)p(0)\rangle_E/\langle p^2\rangle_E d\tau\ , \tag{5.43c}$$

where $I(E)$ denotes the action variable in Eq. (4.11).

In the case of *Markovian (M) friction* $\eta_{ij}(t)=2\eta_{ij}\delta(t)$, Eq. (5.43a) simplifies further to give (Borkovec and Berne, 1985a)

$$D_M(E)=\left[\sum_{i=1}^n\frac{\eta_{ii}}{m_i}\right]\frac{k_BT}{\Omega(E)}\int_0^E dE'\Omega(E')\ . \tag{5.44}$$

Kramers (1940) solved the problem for a one-dimensional system ($n=1$) using the action I as a slow variable; see Sec. IV.D. This approach is entirely equivalent to the present discussion, which uses instead the energy E as a slow variable. Kramers' model [Eq. (4.12)] leads to an energy-diffusion coefficient

$$D(E)=\gamma k_BTI(E)\omega(E)/2\pi\ , \tag{5.45}$$

where $\omega(E)$ is the angular frequency and $\gamma=\eta/M$ plays the role of the collision rate α. Using Eq. (5.13) and the fact that $\Omega^{-1}(E)=dE/dI=\omega(E)/(2\pi)$ (Goldstein, 1980), we can readily verify that for $n=1$ Eq. (5.44) reduces to Eq. (5.45). The resulting rate in Eq. (5.41) simplifies in the limit of high barriers, $\beta E_b\gg1$, to the Kramers result given in Eq. (4.49),

$$k\equiv k_{\mathrm{WC}}=\gamma\beta I(E_b)\frac{\omega_0}{2\pi}\exp(-\beta E_b)$$

$$=\gamma\beta I(E_b)k_{\mathrm{TST}},\quad\text{as }\gamma\to0\ , \tag{5.46}$$

where k_{TST} is the simple TST rate in Eq. (3.5).

A further simplification can be obtained if we approximate the action with the result for a harmonic oscillator where $I(E)=2\pi E/\omega_0$, yielding

$$k\equiv k_{\mathrm{WC}}=\gamma\beta E_b\exp(-\beta E_b),\quad n=1\ . \tag{5.47}$$

To obtain the rate for the case of n strongly coupled degrees of freedom, we again approximate the density of states by that for a collection of harmonic oscillators [Eq. (5.14)]. With $\beta E_b\gg n$ and $\gamma\equiv(1/n)\sum_i\eta_{ii}/m_i$, we find with Eq. (5.44) the n-dimensional generalization of Eq. (5.47) (Matkowsky *et al.*, 1982; Borkovec and Berne, 1985a),

$$k\equiv k_{\mathrm{WC}}=\gamma\frac{(\beta E_b)^n}{(n-1)!}\exp(-\beta E_b)\ ,$$

$$\text{as }\gamma\to0,\quad n\geq1\ . \tag{5.48}$$

Again, the approach to the TST limit with increasing friction is considerably accelerated with increasing number of degrees of freedom n. Moreover, note that upon a comparison with the corresponding answer for the strong collision limit, Eq. (5.32), the dependence on the threshold energy (βE_b) is raised in Eq. (5.48) from the power $(n-1)$ to the power n. The additional factor (βE_b) is due to the weak collisions in energy space, $|\langle\Delta E\rangle|\ll k_BT$, which imply a nonequilibrium density for $p_0(E)$ of width (k_BT) below the threshold barrier with $p_0(E=E_b)=0$. This is in contrast to the strong collision limit, where $p_0(E_b)\neq0$. The limitation of the result in Eqs. (5.46) and (5.47) will be further discussed in Sec. V.D.

The asymptotic weak-noise solution of Eq. (5.33) has been extended for weak-to-moderate friction γ for a one-dimensional system ($n=1$) by Büttiker, Harris, and Landauer (1983), and its non-Markovian generalization [memory friction $\gamma(t)$] has been put forward by Hänggi and Weiss (1984). For $E<E_b$ the density of the steady-state distribution is still given by Eq. (5.39). For $E\simeq E_b\gg k_BT$, the deviation of the steady-state probability from the equilibrium distribution $\zeta(E)$ [see Eq. (5.40)] obeys from Eq. (5.33)

$$\frac{d^2\zeta}{dE^2}-\beta\frac{d\zeta}{dE}-\frac{\beta^2}{z}\zeta=0,\quad E\simeq E_b\ , \tag{5.49}$$

where

$$z=\gamma\beta I(E_b)=k_{\mathrm{WC}}/k_{\mathrm{TST}}\ . \tag{5.50}$$

The solution of Eq. (5.49) is an exponential function $\zeta(E)=C_3\exp(-\nu E),E>E_b$, where ν is the positive root of the characteristic equation $\nu^2+\beta\nu-\beta^2=0$. The three unknown constants C_1, C_2, and C_3 are found from the normalization condition of $p_0(E)$ and the continuity requirements of $\zeta(E)$ and $d\zeta/dE$ at $E=E_b$. The rate k_{uni} then equals the steady-state flux $j=C_2$, yielding

$$\frac{k_{\mathrm{uni}}}{k_{\mathrm{TST}}}=z\frac{\sqrt{1+4/z}-1}{\sqrt{1+4/z}+1},\quad n=1\ . \tag{5.51}$$

This result agrees with that of the RRKM theory in Eq. (5.33), where the loss term $k(E)$ is defined in Eq. (5.18) (Borkovec and Berne, 1987).

The analysis can be generalized to the case of an arbitrary number of strongly coupled degrees of freedom n, where the corresponding density of states $\Omega(E)$ [Eq. (5.9)] and the energy-dependent rate constant $k(E)$ enter [Eq. (5.19)]. Performing for $n=2$ the same analysis as led to Eq. (5.51), we obtain with $z=k_{\rm WC}^{n=2}/k_{\rm TST}^{n=2}=k_{\rm WC}/k_{\rm TST}$

$$\frac{k_{\rm uni}}{k_{\rm TST}}=z\frac{K_{2/3}(z/12)-K_{1/3}(z/12)}{K_{2/3}(z/12)+K_{1/3}(z/12)},\quad n=2\ . \tag{5.52}$$

Here $K_y(x)$ denotes the modified Bessel function. For $n\geq 1$, one again defines z as $z=k_{\rm WC}/k_{\rm TST}$. The leading corrections to Eq. (5.48) can be evaluated for general n with the result (Borkovec and Berne, 1987)

$$k_{\rm uni}=k_{\rm WC}(1-a_n z^{1/(n+1)}+\cdots)\ , \tag{5.53}$$

where in terms of the gamma function $\Gamma(x)$

$$a_n=[(n+1)^2\Gamma(n)]^{1/(n+1)}\Gamma\left[\frac{n+2}{n+1}\right]\Big/\Gamma\left[\frac{n}{n+1}\right]\ . \tag{5.54}$$

The first coefficients $a_n, n=1,\ldots,5$ are listed in Table I. Note that a_n increases slowly with increasing n.

Equation (5.53) can be verified for $n=1$ and 2 by expanding for small z Eqs. (5.51) and (5.52), respectively. *Note that the correction to the weak collision limit in Eq. (5.41) is nonanalytic in* γ. The presence of these nonanalytic corrections has been pointed out by Troe (1967, 1975, 1977), Leuthäuser (1981), Büttiker, Harris, and Landauer (1983), and Melnikov (1984). They have also been verified in numerical studies by Risken and Voigtlaender (1985) and Risken, Vogel, and Vollmer (1988) for $n=1$, and by Straub, Borkovec, and Berne (1987) for $n=2$.

TABLE I. Numerical coefficients $\{a_n\}$ for the leading, nonanalytic correction to the low-friction result of Kramers as a function of the number n of coupled degrees of freedom undergoing an energy diffusion. The RRKM theory in Eqs. (5.19), (5.33), and (5.54) predicts equal coefficients for a metastable well and a symmetric double well. The last two columns show the accurate results for a single degree of freedom, i.e., a one-dimensional metastable potential $U(x)$ obeying the Kramers equation (4.4), with a small friction coefficient γ (Melnikov, 1984; Risken and Voigtlaender, 1985; Melnikov and Meshkov, 1986).

n	RRKM theory	Metastable well	Double well, periodic potential
1	1	0.8239	0.483
2	1.372		
3	1.759		
4	2.148		
5	2.536		

C. Between strong and weak collisions

The transition between strong and weak collision models has been studied in detail by Troe (1977). Even in the limit of a low collision frequency ($\alpha\to 0$), the calculation of the steady-state distribution involves the solution of an integral equation that is obtained from Eq. (5.21) by observing that $p_0(E)\to 0$ for $E>E_b$, namely,

$$\int_0^{E_b} dE' K(E',E)\zeta(E')=\alpha\zeta(E),\quad \text{for } E<E_b\ , \tag{5.55}$$

and $\zeta(E)=0$ for $E>E_b$. The function $\zeta(E)$ defined in Eq. (5.40) represents the deviation of the steady-state distribution from the equilibrium distribution. It should be noted that the function $\zeta(E)$ is *discontinuous* at the boundary $E=E_b$, except in the weak collision limit, Eq. (5.39). This behavior is illustrated schematically in Fig. 17. Upon solving the integral equation (5.55) for $\zeta(E)$ we can insert the steady-state distribution $p_0(E)=\zeta(E)p_{\rm eq}(E)$ into Eq. (5.25), which yields the rate constant in the low collision limit. Numerical solutions of Eq. (5.55) have been investigated for different collision kernels. In cases when $K(E',E)=f(E'-E)$, Eq. (5.55) becomes a Wiener-Hopf-type integral equation, and analytical solutions may be extracted. In a different context this technique has been applied by Melnikov and Meshkov (1986) in the case of a Gaussian kernel (Sec. V.D).

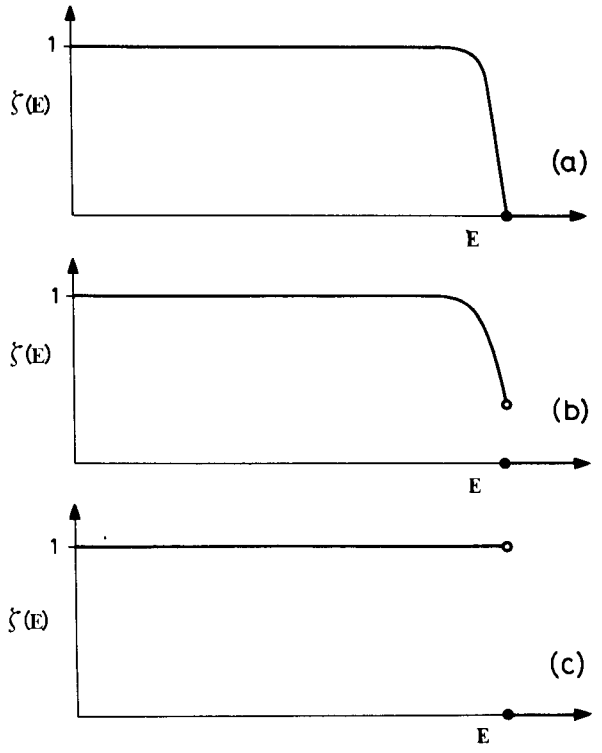

FIG. 17. Behavior of the form function in Eq. (5.55) near the exit energy E_b denoted by the solid circle on the E axis: (a) the weak collision limit equivalent to the energy-diffusion limit in Eq. (4.46), where $\rho(I_b)=0$, that is, $\zeta(E=E_b)=0$; (b) intermediate case between weak and strong collision limits [see Eq. (5.56)]; (c) strong collision limit.

Troe (1975, 1977) has presented a simple analytical solution in the case of the exponential collision kernel, with $a>0$, $b>0$,

$$K(E',E)=\begin{cases}\dfrac{\alpha}{a+b}\exp(-|E'-E|/a), & \text{for } E'>E\ ,\\ \dfrac{\alpha}{a+b}\exp(-|E'-E|/b), & \text{for } E'<E\ ,\end{cases} \tag{5.56}$$

and found the rate k_C, Eq. (5.25), to be determined by the implicit relation

$$\frac{\eta_C}{1-\sqrt{\eta_C}}=-\frac{|\langle\Delta E\rangle|}{k_BT},\quad \text{for } \alpha\to 0\ , \tag{5.57}$$

where $\eta_C=k_C/k_{SC}$ is the collision efficiency, with k_{SC} defined by Eq. (5.31) and $\langle\Delta E\rangle$ given by Eq. (5.27). Note that this equation correctly reduces to $\eta_C=1$ in the strong collision limit, where $|\langle\Delta E\rangle|\gg k_BT$ and to Eq. (5.48) in the weak collision limit, where $|\langle\Delta E\rangle|\ll k_BT$. Numerical studies (Troe, 1977) have shown that Eq. (5.57) is approximately valid for many different collision kernels.

These ideas can be generalized to the case of more than one metastable well. In this case one must consider several coupled master equations which describe the evolution of the energy probability density for the particle's being in either well. The coupling arises from rate processes that result from the loss or gain of particles from the other well. In the low collision limit, the rate constant can be determined from the rate of energy activation. The energy activation rate is given by Eq. (5.25), but reduced by a finite probability p for the trapping in the other well. The trapping probability p can be determined using the detailed balance condition. This has already been discussed in connection with the Kramers problem in Sec. IV.D [see Eq. (4.53)] and carries over to the more general situations discussed in this section.

D. Beyond simple unimolecular rate theory

Serious problems arise if one attempts to investigate more general models. These approaches can be most easily reviewed in discussing the assumptions involved in unimolecular rate theory. In the beginning of this section we shall focus on one-dimensional systems without memory. Then we elaborate on systems with more dimensions (without memory), and finally we shall point out some subtleties for memory friction.

The only approximation in applying unimolecular rate theory to a one-dimensional system without memory is the treatment of the isolated system by RRKM theory. A more accurate description was put forward by Iche and Nozières (1976) (see also Leuthäuser, 1981) in a different context. Following this same line of reasoning Melnikov and Meshkov (1986) evaluated the Kramers rate at weak-to-moderate friction by considering the probability per unit time $f(E)$ of finding a system with energy E in the barrier region near a classical turning point of the trajectory. In analogy to Eq. (5.22) they wrote for the rate constant

$$k=\int_{E_b}^{\infty}dE\,f(E)\ . \tag{5.58}$$

This function $f(E)$ obeys the integral equation [see also Eq. (5.55)]

$$\int_0^{E_b}dE'P(E|E')f(E')=f(E)\ . \tag{5.59}$$

$P(E|E')$ is the conditional probability that a system leaving the barrier region with energy E' will return with energy E. Assuming a high barrier, $\beta E_b\gg 1$, one can approximate the kernel $P(E|E')$ by a Gaussian with its mean value $\langle(E'-E)\rangle$ centered around the energy loss $\langle\Delta E\rangle$. In the Kramers case $\langle\Delta E\rangle$ equals $-\gamma I(E_b)$, and its variance is given by Eq. (5.38); that is, $\langle\Delta E^2\rangle=2k_BT|\langle\Delta E\rangle|$. Using the Wiener-Hopf technique Melnikov and Meshkov (1986) found for a single metastable well the explicit solution

$$k/k_{TST}=\exp\left\{\frac{1}{\pi}\int_{-\infty}^{\infty}dy\,\ln\left[1-\exp\left[-\frac{z}{4}(1+y^2)\right]\right]\Big/(1+y^2)\right\}, \tag{5.60}$$

with z defined in Eq. (5.50). This solution exhibits the proper $\sqrt{\gamma}$ correction [Eq. (5.53)]. The coefficients $a_1=0.824$ for the metastable well and $a_1=0.683$ for the symmetric double-well potential (see Melnikov and Meshkov, 1986) are in close agreement with the numerical studies by Risken, Vogel, and Vollmer (1988). Before we proceed it should be pointed out here that—in contrast to the turnover theory treatment in Sec. VI—the result in Eq. (5.60) is restricted to the weak-friction regime only, where the quantity z just agrees with the dimensionless energy loss in Kramers' energy-diffusion-limited regime. Formally, the result in Eq. (5.60) approaches unity with $z\geq 1$, i.e., the rate k rapidly approaches the simple TST value in Eq. (3.5), but fails to cross over into the spatial-diffusion-controlled regime where the rate $k\to 0$, as $\gamma\to\infty$.

Let us next consider more complex situations with several coupled, dissipative degrees of freedom, but without memory friction. While the unimolecular rate theory applies for a single degree of freedom without memory friction to good accuracy, it can fail seriously in the case of many degrees of freedom, or in the presence of memory.

The simplification inherent in unimolecular rate theory

for a many-dimensional system was introduced with the assumption that the total energy of the isolated molecule is the only slowly varying variable. Obviously this is not true, as for a molecule the total angular momentum **L** is also approximatively conserved (and possibly some other hidden variables as well) and will therefore also relax slowly if coupled to a dilute bath gas. Multidimensional master equations describing such processes have been studied in some detail for the strong collision model (Forst, 1973) and for exponential models (Troe, 1977). Such problems become more tractable in the weak collision limit, where the resulting multidimensional diffusion equations can be solved by use of asymptotic techniques (Matkowsky *et al.*, 1982; Borkovec and Berne, 1986).

The most severe limitations in using unimolecular rate theory for a multidimensional system are the assumptions of ergodicity near barrier energies and rapid relaxation on the energy shell. The importance of this effect in rate theory was recognized by Rice (1930). More detailed discussions had to await the developments of nonlinear mechanics (Lichtenberg and Lieberman, 1983). While for a single degree of freedom a trajectory explores the energy shell in a periodic fashion, this need not be so for 2 or more degrees of freedom. The validity of unimolecular rate theory rests upon full ergodicity of the motion in phase space. In general, a trajectory will cover only a fraction of the whole energy shell. In the present context it is useful to distinguish between crossing tori and trapping tori (de Leon and Berne, 1981, 1982; Berne, 1984). In the isolated system, trajectories of crossing tori will cross to the other side of the barrier. On the other hand, trajectories of trapping tori are trapped on one side of the barrier and thus will never cross. Because such trapping tori exist also *above the threshold energy* their presence will reduce the overall rate constant. The failure of the ergodicity assumption inherent in unimolecular theory can be seen if we consider a damped two-dimensional system without memory, a bistable well coupled to a stable oscillator (Borkovec, Straub, and Berne, 1986; Straub and Berne, 1986). Suppose that for a certain coupling strength the motion is ergodic and the rate constant is well described by Eq. (5.48) with $n=2$. As the coupling strength is decreased, the stochastic two-variable system must approach a one-dimensional system with a rate given by Eq. (5.48), but now with $n=1$. This transition cannot be described by unimolecular rate theory. It is caused by the progressive shrinking of the crossing region of the phase space. This crossover between $n=2$ and $n=1$ has been demonstrated numerically for the BGK model (Borkovec, Straub, and Berne, 1986) and the Kramers model (Straub, Borkovec, and Berne, 1987).

Similar, but more subtle, effects may arise in a one-dimensional system with non-Markovian memory (Straub and Berne, 1986). Consider a bistable system that is bilinearly coupled to damped harmonic oscillators (see Sec. III.C). This system can be described by a Langevin equation with a memory friction $\gamma(t)$ [see Eq. (3.31)]. One is thus tempted to apply Eq. (5.43) for $n=1$ in order to evaluate the (non-Markovian) rate at low friction [see Eq. (5.41)]. Nevertheless, such a procedure is applicable only when the coupling between the system and the harmonic bath is sufficiently weak. With increasing coupling strength to the damped oscillators, the prediction might severely underestimate the correct result (Straub and Berne, 1986).

VI. TURNOVER BETWEEN WEAK AND STRONG FRICTION

In Secs. III and V we have considered two familiar approximations to classical activated rate theory, namely, multidimensional transition-state theory and unimolecular rate theory or, more generally, rate theory at weak dissipation. Both theoretical approaches are based on some simplifying assumptions and, as we have discussed in Sec. IV.G, thus accurately describe the rate in specific regimes only. For example, the Kramers rate in Eq. (4.33), which coincides with the multidimensional TST approach in Eq. (3.46), will be correct for moderate-to-large friction γ, whereas at very weak friction, $\gamma \to 0$, the rate becomes energy-diffusion limited. In particular, one observes from the corresponding limiting rate expressions in Eqs. (4.33), (4.34), (4.57), and Eq. (4.49) that the rate approaches zero both for $\gamma \to \infty$ and $\gamma \to 0$. As already noted by Kramers, these two limiting behaviors imply a maximal rate at some damping value intermediate between the two limits. The transmission factor $\kappa = k(\gamma)[(\omega_0/2\pi)\exp(-\beta E_b)]^{-1}$, therefore, undergoes a *turnover* in the form of a bell-shaped curve (see Fig. 18).

A. Interpolation formulas

Many attempts have been made to provide a single expression for the rate k which would bridge the two limits

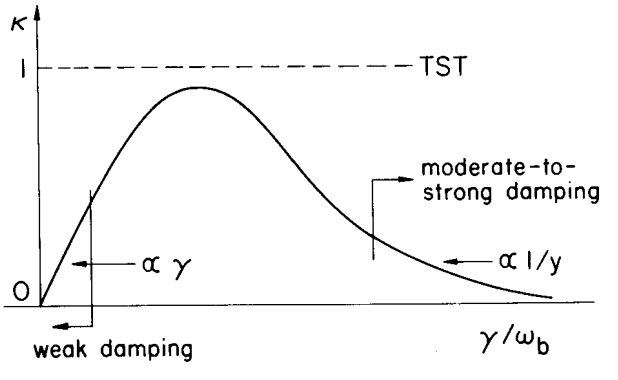

FIG. 18. A sketch of the transmission factor κ for classical activated escape vs the friction γ. With increasing friction the transmission factor undergoes a turnover from linear behavior at very weak friction to an inverse behavior in the Smoluchowski limit $\gamma/\omega_b \gg 1$. The dashed line indicates the upper limit for κ, given by simple TST theory [see Eq. (3.5)].

(Troe, 1975; Grote and Hynes, 1980; Carmeli and Nitzan, 1984; Hänggi and Weiss, 1984; Matkowsky, Schuss, and Tier, 1984; Zawadzki and Hynes, 1985; Straub and Berne, 1986; Straub, Borkovec, and Berne, 1986; Janssen, 1988). Perhaps the most frequent suggestion made is the *ad hoc* formula [see also Eq. (5.4)]

$$k^{-1}=k^{-1}(\text{low damping}) + k^{-1}(\text{moderate-to-large damping}) . \tag{6.1}$$

For the Kramers model in Sec. IV this gives for the forward rate k^+

$$(k^+)^{-1}=\left\{[p\gamma\beta I(E_b^+)]^{-1} + \frac{\omega_b}{\left[\left(\frac{\gamma^2}{4}+\omega_b^2\right)^{1/2}-\frac{\gamma}{2}\right]}\right\}\frac{2\pi}{\omega_0}\exp(\beta E_b^+) , \tag{6.2}$$

with p given in Eq. (4.53). An alternative bridging formula can be obtained if one applies a multiplicative form (Troe, 1975), i.e., if we recall that the unimolecular rate in Eqs. (5.4), (5.23), (5.51), and (5.53) approaches for high friction (i.e., high pressure) the result of the simple transition-state theory in Eq. (3.5), where we set for the overall rate

$$k=\frac{k(\text{unimolecular})k(\text{moderate-to-large damping})}{(\omega_0/2\pi)\exp(-\beta E_b)} . \tag{6.3}$$

For the Kramers model in Sec. IV one finds with Eqs. (4.33) and (5.51) the explicit *ad hoc* expression

$$k=\gamma\beta I(E_b)\left[\frac{\{1+4[\gamma\beta I(E_b)]^{-1}\}^{1/2}-1}{\{1+4[\gamma\beta I(E_b)]^{-1}\}^{1/2}+1}\right] \times\frac{\omega_0}{2\pi\omega_b}[(\tfrac{1}{4}\gamma^2+\omega_b^2)^{1/2}-\tfrac{1}{2}\gamma]\exp(-\beta E_b) , \tag{6.4}$$

where we used $p=1$. Still other, more sophisticated bridging formulas have been proposed (Skinner and Wolynes, 1980; Melnikov and Meshkov, 1986; Cartling, 1987). In all these bridging formulas, however, there is always an element of arbitrariness. Even the recent beautiful approach for the low-friction regime by Melnikov and Meshkov (1986) uses an *ad hoc* multiplicative transmission factor, given by the last part in Eq. (6.4), to assure that the bridging expression reduces to the correct spatial-diffusion limit [see Eq. (4.34)] when $\gamma/\omega_b \gg 1$. For the Kramers problem, the above bridging expressions yield results that agree roughly to within $\leq 20\%$ with the numerically precise answers inside the turnover region. In higher dimensions, and for the case of memory friction [see Eq. (3.31)], these interpolation formulas may eventually fail seriously, however, and it becomes difficult to assess the regions of their validity (Straub, Borkovec, and Berne, 1987). Generally speaking, the multiplicative form in Eqs. (6.3) and (6.4) yields better results than the additive form in Eqs. (6.1) and (6.2).

B. Turnover theory: a normal-mode approach

As mentioned previously, the application of the above interpolation formulas in Eqs. (6.1) and (6.3) sometimes requires caution. What is needed, therefore, is an analytical theory for the rate of escape that covers the whole damping regime on a common basis. Such a theory, which is applicable also for memory friction, does indeed exist (Pollak, Grabert, and Hänggi, 1989). Following the reasoning put forward by Grabert (1988), the basic idea underlying the approach is the observation that the escape dynamics is governed by the unstable normal-mode coordinate—and *not* the particle configuration coordinate. *The final result for the rate can be expressed solely in terms of the quantities that enter the generalized Langevin dynamics in Eq. (3.31).* Here we present only the main result and refer the reader for details to the original papers (Grabert, 1988; Pollak, Grabert, and Hänggi, 1989). In Fig. 19 we compare the results for this turnover theory with recent numerical computations (Straub, Borkovec, and Berne, 1985, 1986) of the Kramers theory with exponential memory friction,

$$\gamma(t)=\alpha^{-1}\exp(-t/\alpha\gamma) , \tag{6.5}$$

in a piecewise continuous parabolic single-well metastable potential $U(x)$,

$$U(x)=\begin{cases}\frac{1}{2}M\omega_0^2(x+x_0)^2, & x\leq -x^* ,\\ E_b-\frac{1}{2}M\omega_b^2x^2, & x\geq -x^* .\end{cases} \tag{6.6}$$

Here x^* is the smooth matching point, $E_b=\frac{1}{2}M\omega_b^2x_0x^*$, with $x^*=x_0(1+\omega_b^2/\omega_0^2)^{-1}$.

This theory is based on the following two observations.

(i) The multidimensional normal-mode TST theory in Eq. (3.46) equals the spatial-diffusion-controlled Kramers rate in Eq. (4.33); and

(ii) the unstable normal-mode dynamics decouples from the other modes in the close vicinity of the barrier, where the normal-mode dynamics are virtually exact.

These facts make possible a formulation in terms of a one-dimensional stochastic process for the energy in the unstable mode. The loss of energy ΔE in this unstable mode then determines the conditional probability $P(E|E')dE$ that a system leaving the barrier region with energy E' in the unstable mode returns to the barrier with an energy between E and $E+dE$. The quantity $P(E|E')$ satisfies detailed balance and determines the probability $f(E)$ per unit time of finding the system within the energy E and $E+dE$ in the normal unstable mode near a turning point as the solution of the integral equation

$$f(E)=\int_0^{E_b}dE'P(E|E')f(E') . \tag{6.7}$$

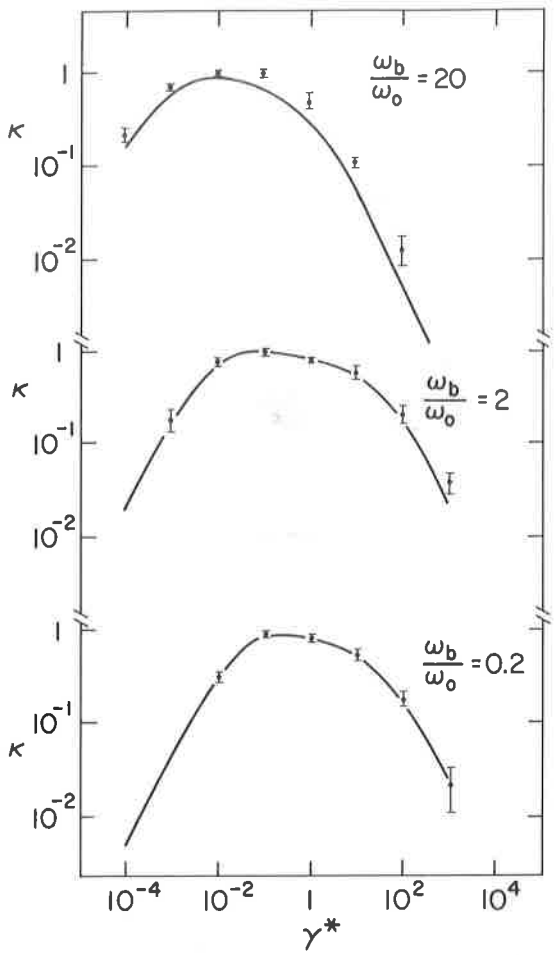

FIG. 19. Turnover in the presence of exponential memory friction [see Eq. (6.5)] as a function of the dimensionless damping $\hat{\gamma}(\omega=0)/\omega_b \equiv \gamma^*$ in the metastable potential of Eq. (6.6) for various frequency ratios, with ω_b denoting the barrier frequency and ω_0 the well frequency, respectively: solid circles with error bars, the SBB transmission coefficient data (Straub, Borkovec, and Berne, 1986) for a single-well potential; solid lines, the theory of Pollak, Grabert, and Hänggi (1989). The data are for an Arrhenius factor of $\beta E_b = 20$, and $\alpha^* = \alpha\omega_b^2 = \frac{4}{3}$.

For $E \to \infty$, $f(E)$ approaches zero, while deep inside the well, $E/E_b \ll 1$, $f(E)$ assumes its equilibrium value, $f(E)_{\rm eq} = \beta\omega_0\mu(2\pi\omega_b)^{-1}\exp(-\beta E)$, with μ defined in Eq. (3.45).

In terms of this steady-state probability $f(E)$, the rate of escape equals

$$k = \int_{E_b}^{\infty} dE\, f(E)\ , \tag{6.8}$$

since all particles reaching the barrier with energy $E > E_b$ will escape with probability one. In the limit $\beta E_b \gg 1$, the probability $P(E|E')$ becomes a Gaussian, in the variable $(E-E')$, and the integral equation in Eq. (6.7) can be transformed into a Wiener-Hopf equation that can be solved by standard methods (Melnikov and Meshkov, 1986; Pollak *et al.*, 1989). The final answer for the transmission coefficient $\kappa_{\rm sw}$ for the single-well potential then reads (Pollak, Grabert, and Hänggi, 1989)

$$\kappa_{\rm sw} \equiv \frac{k}{(\omega_0/2\pi)\exp(-\beta E_b)} = \frac{\mu}{\omega_b}\exp\left[\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{dy}{1+y^2} \times \ln\{1-\exp[-\delta(1+y^2)/4]\}\right], \tag{6.9a}$$

where μ is the unstable normal-mode (angular) frequency [see Eq. (3.45)], and where[10]

$$\delta = \beta\Delta E \tag{6.9b}$$

denotes the dimensionless (positive-valued) energy loss of the *unstable normal-mode* motion, i.e., ΔE is generally not the energy loss along the physical particle coordinate. For $\delta \gg 1$, the transmission factor in Eq. (6.9a) approaches the multidimensional TST value, μ/ω_b, exponentially fast. For δ of order one, or smaller, the probability per unit time $f(E)$ of finding the system in the barrier region assumes nonequilibrium effects which yield a transmission factor *below* the multidimensional TST value. For very weak damping, the transmission factor in Eq. (6.9a) approaches

$$\kappa_{\rm sw} = \left[\frac{\mu}{\omega_b}\right]\beta\Delta E, \quad \delta \ll 1\ , \tag{6.10}$$

which reduces for Kramers' model [Sec. IV, where $\Delta E = \gamma I(E_b)$, as $\delta \ll 1$] to the well-known energy-diffusion-limited rate in Eq. (4.49).

The above turnover theory for a single metastable well can readily be generalized to an asymmetric double-well system. Let $\delta_{L,R}$ denote the dimensionless energy loss for the left-hand and right-hand wells, respectively. If we denote the exponential on the right-hand side in Eq. (6.9a) simply by $E(\delta)$, we obtain for the transmission factor $\kappa_{\rm dw}$ for the double-well system the generalization

$$\kappa_{\rm dw} = \frac{\mu}{\omega_b}\frac{E(\delta_L)E(\delta_R)}{E(\delta_L+\delta_R)}\ . \tag{6.11}$$

This result is consistent with Eqs. (4.51)–(4.53) as δ_L and δ_R approach zero. With a strong asymmetry one finds, for example, for a deep right well $\delta_R \gg 1$, that is, $E(\delta_R \gg 1) \sim 1$, so that $\kappa_{\rm dw}$ again approaches $\kappa_{\rm sw}$ in Eq. (6.9a).

In the intermediate regime the result of the turnover theory in Eqs. (6.9a) and (6.11) intrinsically exhibits the proper nonanalytic damping contributions discussed in Secs. V.B and V.D. In conclusion, Eqs. (6.9) yield a smooth description of the turnover for the escape rate, covering both weak and strong damping simultaneously (see Fig. 18). For a detailed discussion of the regime of

[10]For an explicit presentation of ΔE in terms of the quantities entering the generalized Langevin equation, Eq. (3.31), we refer the reader to Pollak, Grabert, and Hänggi (1989).

validity of Eq. (6.9) in the presence of arbitrary memory friction we refer the reader to the original literature (Pollak, Grabert, and Hänggi, 1989). Moreover, Eq. (6.9a) does not account for anharmonic corrections within the *potential barrier* [see Eq. (4.57) for the Smoluchowski case].

C. Peculiarities of Kramers' theory with memory friction

Although Kramers' (1940) landmark paper on the rate of escape has found numerous applications, it still lacks general applicability owing to the Markovian assumption made for the stochastic forces in Eqs. (4.1)–(4.3), i.e., that the particle moves very slowly compared to the time scale τ_c set by the correlations of the random forces. However, in certain situations (Beece *et al.*, 1980; Hasha *et al.*, 1982; Velsko *et al.*, 1982, 1983; Doster, 1983; Rothenberger *et al.*, 1983; Courtney and Fleming, 1984; Otto *et al.*, 1984; Maneke *et al.*, 1985; Fleming, Courtney and Balk, 1986; Bergsma *et al.*, 1987; Seifert and Dietrich, 1987; Grabert and Linkwitz, 1988; Gertner *et al.*, 1989; Turlot *et al.*, 1989) the relevant motion of the escape dynamics takes place on the same time scale τ_c, or may even be more rapid than τ_c. Therefore memory effects of the type exhibited by the generalized Langevin equation in Eq. (2.6) or Eq. (3.31) must be accounted for. In many applications typical barrier frequencies are of the order 10^{11}–10^{14} $\sec^{-1}$, and the environmental forces are likely to be correlated on this same time scale, i.e., $\hat{\gamma}(\omega=10^{13}\ \sec^{-1})\neq\hat{\gamma}(\omega=0)$, with $\hat{\gamma}(\omega)=\int_0^\infty\gamma(t)\exp(-\omega t)dt$. Grote and Hynes (1980) and Hänggi and Mojtabai (1982), as well as Carmeli and Nitzan (1984), extended the original work of Kramers described in Sec. IV.B to an arbitrary memory friction $\gamma(t)$ and found that the rate can often be much greater than one would obtain from the Kramers theory evaluated at the static friction value. Memory effects were also found to modify the rate in the limit of weak damping (see Sec. V.B), where the energy-diffusion mechanism is the rate-limiting process (Carmeli and Nitzan, 1982; Grote and Hynes, 1982; Hänggi and Weiss, 1984).

Indeed, these versions of Kramers theory with memory friction have proved to be quite useful in correctly describing recent experiments, whereas the Markovian theory of Kramers may fail considerably in a number of realistic physical situations (Beece *et al.*, 1980; Doster, 1983; Bergsma *et al.*, 1987; Seifert and Dietrich, 1987; Grabert and Linkwitz, 1988; Zhu, Lee, and Robinson, 1988; Gertner *et al.*, 1989; Turlot *et al.*, 1989).

The various rate theories for frequency-dependent damping were tested numerically over a very wide range of parameters in two illuminating papers by Straub, Borkovec, and Berne (SBB; 1985, 1986). This work was based on the *exponential memory friction* (Berne *et al.*, 1966) in Eq. (6.5), and in certain parameter regimes it revealed striking deficiencies in the existing predictions of current non-Markovian rate theories. In particular, the results of SBB presented a twofold challenge.

(a) Previous theories were not able to predict correctly the SBB rate k when $\gamma^*\equiv\hat{\gamma}(\omega=0)/\omega_b\to\infty$.

(b) A novel turnover was observed, for which the rate becomes limited by energy diffusion in both low and high damping limits $\hat{\gamma}(\omega=0)\equiv\gamma$.

Thus SBB stimulated quite a few theoretical papers. Hänggi (1986a) realized that for their strong damping limit the bath correlation time is long, leading to a memory-induced energy-diffusion-controlled limit. He derived a corresponding set of conditions [see Eq. (2.60) in Hänggi (1986a)], which allowed for the *safe application* of Eq. (3.46). Similar ideas were developed subsequently by Straub and Berne (1986) and by Zwanzig (1987). An insightful solution for both the *weak and the strong damping limits* which contains no adjustable parameters was obtained only recently by Talkner and Braun (1988), thus answering the first challenge. Without a restriction to exponential memory friction, both challenges can be met within the turnover theory presented in the previous subsection (Pollak, Grabert, and Hänggi, 1989), see Fig. 19.

For the SBB problem, a sufficient and necessary set of conditions for the breakdown of the Grote-Hynes-Hänggi-Mojtabai rate expression in Eq. (3.46) can be obtained if we follow the reasoning put forward in Sec. IV.C (see also Talkner, 1989). By use of the work of Talkner and Braun (1988) one finds for the energy E of the injected particles [Eq. (4.41)], in the SBB case

$$E-E_b=\tfrac{1}{2}k_BT-E_b\left[1-\left[\frac{\mu}{\omega_b}\right]^2\right]\left\{1-\alpha^*\left[1-\left[\frac{\mu}{\omega_b}\right]^2\right]\right\}\left\{1+\frac{\omega_b}{\omega_0}\frac{k_BT}{2E_b}\right\}^2\left[1+\left[\frac{\omega_b}{\omega_0}\right]^2\right]^{-1}, \tag{6.12}$$

where μ is given in Eq. (3.45) and $\alpha^*\equiv\alpha\omega_b^2$. If the right-hand side in Eq. (6.12) is larger than zero, the injected particle energy exceeds the barrier energy E_b, implying a breakdown of the many-body TST result in Eq. (3.46). In particular, this occurs whenever $\mu^2\to\omega_b^2$, or $\alpha^*[1-(\mu/\omega_b)^2]\to1$. The set of sufficient and necessary conditions for the *breakdown* of validity of the Kramers (exponential) memory-friction result in Eq. (3.46) thus reads

$$\text{(i)}\quad\left[\frac{\mu}{\omega_b}\right]^2\to1,\ \text{i.e.,}\ \gamma^*\to0$$

or

$$\text{(ii)}\quad\alpha^*\left[1-\left[\frac{\mu}{\omega_b}\right]^2\right]\to1,\ \text{i.e.,}\ \gamma^*\to\infty\ ,\quad\text{with}\ \alpha^*\geq1\ . \tag{6.13}$$

These criteria are in accordance with the numerical findings of SBB (1985, 1986).

VII. MEAN-FIRST-PASSAGE-TIME APPROACH

A. The mean first-passage time and the rate

For every stochastic process $x(t)$ with values in a state space Σ, the mean first-passage time (MFPT) $t_\Omega(x)$ is defined as the *average time* elapsed until the process starting out at point x leaves a prescribed domain Ω of Σ for the first time (Schrödinger, 1915; Pontryagin, Andronov, and Vitt, 1933; Darling and Siegert, 1953; Montroll and Shuler, 1958; Widom, 1959; Kac, 1962; Stratonovich, 1963; Weiss, 1967; Goel and Richter-Dyn, 1974). The connection of this mathematical notion with a reaction rate is simply established by taking the phase space Σ of the reacting system as the state space. Further, the point x_a that characterizes the reactant state is identified with the starting point x, and a domain Ω is chosen which *does contain* x_a, *but not the product state* x_c. For example, one may take a small ball with the center located at x_c as the part of Σ not belonging to Ω. Starting from any point inside this excluded part of Ω the product state x_c is readily reached. Provided that the transition from the reactant to the product may be characterized by a rate, i.e., that there is a reasonable separation of time scales (Sec. II.A), this rate is simply determined by the inverse mean first-passage time,

$$k_{A\to C}=t_\Omega^{-1}(x_a)\ . \tag{7.1}$$

Under such conditions the mean first-passage time is rather insensitive to various simplifications of the model. For example, it remains unchanged if rapidly varying variables are adiabatically eliminated and only the slow ones are taken into account. Further simplifications may result from the fact that the domain Ω can be modified up to a certain extent; for some cautions, however, see Hänggi, Jung, and Talkner (1988). Nevertheless, the class of processes for which the mean first-passage time may be calculated explicitly is rather limited (Pontryagin, Andronov, and Vitt, 1933; Kac, 1962; Stratonovich, 1963; Weiss, 1967; Hänggi and Talkner, 1981, 1985). Other important cases can be treated by asymptotic methods (Ventsel and Freidlin, 1970; Matkowsky and Schuss, 1977; Talkner, 1987). In all these cases one uses a Markovian process as the appropriate starting point. For a formal connection between the MFPT and the flux-over-population method we refer the reader to Appendix B.

B. The general Markovian case

We shall summarize here what may be termed the traditional approach to first-passage-time problems in continuous time (Kac, 1962; Stratonovich, 1963; Feller, 1966; Weiss, 1967; Goel and Richter-Dyn, 1974; van Kampen, 1981). Consider a Markovian process $x(t)$ starting at x in a domain Ω. For the mean first-passage time $t_\Omega(x)$ the random trajectory $x(t)$ is only important up to the moment it leaves Ω. Therefore we may assume that the whole exterior of Ω is absorbing. This guarantees that the trajectories cannot recross the boundary $\partial\Omega$ of the considered domain Ω. A process so modified is still Markovian and hence may be completely characterized by its conditional probability density $P_\Omega(y,t|x)$ of visiting the point $y\in\Omega$ at time t, if it started out at time $t=0$ from $x\in\Omega$ and did not leave Ω. In terms of this probability the MFPT reads

$$t_\Omega(x)=\int_0^\infty dt\int_\Omega dy\, P_\Omega(yt|x)\ , \tag{7.2a}$$

where in the derivation of this result it is assumed that $\lim_{t\to\infty} t\int_\Omega P_\Omega(yt|x)dy$ vanishes, otherwise $t_\Omega(x)$ diverges. Being a conditional probability of a Markov process, $P_\Omega(yt|x)$ obeys the backward equation

$$\frac{\partial}{\partial t}P_\Omega(yt|x)=\Gamma^\dagger P_\Omega(yt|x),\quad x\in\Omega\ , \tag{7.2b}$$

with

$$P_\Omega(yt|x)=0,\quad x\notin\Omega\ , \tag{7.2c}$$

where $\Gamma^\dagger$ is the adjoint master operator, known as the backward operator (Feller, 1966; Hänggi and Thomas, 1982), acting on the x dependence of $P_\Omega(yt|x)$. Combining Eqs. (7.2a)–(7.2c) yields an equation for the mean first-passage time

$$\Gamma^\dagger t_\Omega(x)=-1,\quad x\in\Omega\ , \tag{7.3a}$$

$$t_\Omega(x)=0,\quad x\notin\Omega\ . \tag{7.3b}$$

In the particular case of a Fokker-Planck process, the trajectories are continuous, and thus it is sufficient that *only the boundary* $\partial\Omega$ of Ω be absorbing. Provided that the diffusion across $\partial\Omega$ does not vanish, the MFPT $t_\Omega(x)$ approaches its boundary value zero continuously when $x(t)$ reaches the boundary. This is quite clear, because though the trajectories are continuous they nevertheless are extremely shaky. Hence, for a Fokker-Planck process, Eq. (7.3b) may be replaced by a proper boundary condition,

$$t_\Omega(x)=0,\quad x\in\partial\Omega\ . \tag{7.4}$$

For all other Markov processes random jumps occur with a finite probability. If the process may jump from $\partial\Omega$ into Ω with nonvanishing probability, the MFPT exhibits a discontinuity at $\partial\Omega$ (Troe, 1977; Weiss and Szabo, 1983; Hänggi and Talkner, 1985; Knessl, Matkowsky, Schuss, and Tier, 1986). The same phenomenon happens for Fokker-Planck processes at those parts of $\partial\Omega$ over which neither the drift nor the diffusion can drive the system (Kac, 1962). Finally we note that nth-order moments of the first-passage time $t_\Omega^n(x)$ may be iteratively calculated by use of the formula (Weiss, 1967)

$$\Gamma^{\dagger} t_{\Omega}^{n}(x) = -n t_{\Omega}^{n-1}(x), \quad x \in \Omega \ , \tag{7.5a}$$

$$t_{\Omega}^{n}(x) = 0, \quad x \notin \Omega \ . \tag{7.5b}$$

C. Mean first-passage time for a one-dimensional Smoluchowski equation

For a process described by a one-dimensional Smoluchowski equation [see Eq. (4.9)], the MFPT out of the interval $[a,b]$ is a solution of the differential equation [see Eq. (7.3a)]

$$-(M\gamma)^{-1} U'(x) t'(x) + (M\gamma)^{-1} k_B T t''(x) = -1 \ , \quad a \le x \le b \ , \tag{7.6}$$

where we have dropped the index $[a,b]$ at $t(x)$ indicating the domain out of which the process escapes. Note that Eq. (7.6) is of first order in $t'(x)$, where the prime denotes differentiation with respect to x. In order to fix the boundary conditions one must know whether the process may directly escape from both boundary points a and b, or whether one point, say a, is reflecting and b is the only exit point.[11] At a reflecting point the slope of $t(x)$ vanishes and at an absorbing point $t(x)$ itself vanishes (Feller, 1966; Goel and Richter-Dyn, 1974). In these two cases we obtain the explicit quadrature formulas

$$t(x) = \frac{M\gamma}{k_B T} \frac{\int_a^b dy \exp[U(y)/k_B T] \int_a^y dz \exp[U(z)/k_B T]}{\int_a^b dy \exp[U(y)/k_B T]} \times \int_a^x dy \exp[U(y)/k_B T] - \frac{M\gamma}{k_B T} \int_a^x dy \exp[U(y)/k_B T] \int_a^y dz \exp[-U(z)/k_B T] \ , \tag{7.7}$$

when both a and b are absorbing; and (Pontryagin, Andronov, and Vitt, 1933)

$$t(x) = \frac{M\gamma}{k_B T} \int_x^b dy \exp[U(y)/k_B T] \int_a^y dz \exp[-U(z)/k_B T] \ , \tag{7.8}$$

when a is reflecting, and b is absorbing. We shall next discuss these results for a number of archetypal potential forms.

1. The transition rate in a double-well potential

We consider a double-well potential $U(x)$ (see Fig. 20), with well and barrier frequencies ω_0 and ω_b, respectively. Further we choose the interval $[a,b]$ such that it contains one stable point x_a to the left of the barrier x_b, $a < x_a < x_b = 0 < b$ (see Fig. 20). We shall consider the case in which the boundary point a is reflecting, and b is absorbing. Then the relation $k = t^{-1}(x = x_a)$ yields, with the quadrature formula in Eq. (7.8), an explicit result for the rate that includes all the steepest-descent corrections [Eq. (4.57)] in closed form. For a high barrier, i.e., for $U(x_b) - U(x_a) \equiv E_b >> k_B T$, the integrals in Eq. (7.8) can be evaluated by a steepest-descent approximation, yielding in terms of the error function $\mathrm{erf}(x) = 2\pi^{-1/2} \int_0^x \exp(-t^2) dt$

$$t(x) = k^{-1} \begin{cases} 1 \quad \text{for } a \le x \le -l_{\mathrm{th}} \ , \\ \frac{1}{2}[1 - \mathrm{erf}(x/l_{\mathrm{th}})] \quad \text{for } |x| \le l_{\mathrm{th}} \ , \\ \dfrac{\omega_b}{|U'(x)|} \sqrt{k_B T M / 2\pi} \, (1 - \exp[-(b-x)|U'(x)|/k_B T]) P_0(x) \\ \qquad\qquad \text{for } l_{\mathrm{th}} < x < b \text{ and } U(x_a) < U(x) \ , \\ k\gamma M \int_x^b |U'(x)|^{-1} dx \quad \text{for } l_{\mathrm{th}} < x < b \text{ and } U(x_a) \ge U(x) \ , \end{cases} \tag{7.9}$$

where $l_{\mathrm{th}} = (2k_B T / M\omega_b^2)^{1/2}$ is the thermal length scale and $P_0(x) = \exp\{-[U(x_b) - U(x)]/k_B T\}$. Here k coincides with the spatial-diffusion rate in the potential $U(x)$ [Eq. (4.54)],

$$k = \frac{\omega_0 \omega_b}{2\pi\gamma} \exp\{-[U(x_b) - U(x_a)]/k_B T\} \ . \tag{7.10}$$

In order to obtain the result in Eq. (7.9) one has to assume that the potential $U(x)$ is growing faster than $|x|$ for large negative a and x; otherwise $t(x)$ increases indefinitely for large negative x. The different qualitative behavior in the three regions (see Fig. 21) is easily understood. If the particle starts out at a point x to the right

[11] One may still impose other boundary conditions describing, for example, a partial absorption; for a review see Calef and Deutch (1983).

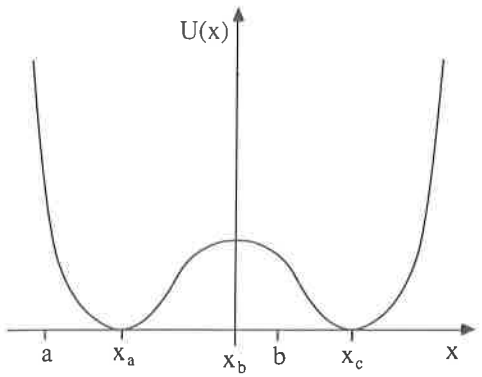

FIG. 20. Double-well potential used in text.

of the barrier, $l_{\rm th} \le x \le b$, it will typically move along a deterministic trajectory and will leave the interval in the deterministic time $\tau_D = \gamma M \int_x^b |U'(x)|^{-1} dx$. However, in very rare cases, which occur with a frequency proportional to $\exp\{-[U(x_b)-U(x)]/k_BT\}$, the random force pushes the particle over the barrier into the well bottom x_a, from whence it escapes in a time of the order of magnitude of the inverse rate k^{-1}. The product of k^{-1} and the frequency factor contributes to the mean time and dominates it as long as $U(x_a) < U(x)$. In the immediate neighborhood of the barrier top, $|x| < l_{\rm th}$, the fluctuating force will govern the dynamics. Hence, if the particle starts exactly at the top, it has equal probability of going to either side. Again, it is the long escape time $\tau \sim k^{-1}$ which dominates $t(x)$. Finally, if the particle starts at x somewhere inside well A, $a \le x \le -l_{\rm th}$, it will typically move almost deterministically along a trajectory to the bottom of the well, where it sits for most of the time before it eventually is pushed out of the well by the random force. Clearly, the time needed to relax toward x_a is negligible compared with the time spent in the immediate neighborhood of x_a. Therefore in this region the mean first-passage time is almost constant and equals the inverse escape rate. Moreover, the mean first-passage time for these points is almost independent of the precise location of the exit point b, as long as b is located at a sufficiently remote distance from the barrier, i.e., $x_c > b > l_{\rm th}$. If b coincides with the location of the barrier top, one finds

$$t(x) = (2k)^{-1} \begin{cases} 1, & a \le x \le -l_{\rm th} , \\ \mathrm{erf}[|x|/l_{\rm th}], & -l_{\rm th} \le x \le 0 . \end{cases} \tag{7.11}$$

Hence, compared with Eq. (7.9), $t(x)$ is reduced by the amount $-\frac{1}{2}k^{-1}$. The factor $\frac{1}{2}$ [see Eq. (2.33)] is due to the fact that all trajectories arriving at $x_b = 0$ contribute with their arrival time with a probability $\frac{1}{2}$ to the MFPT, and not with a weight of one as is the case for b located beyond the barrier $b > x_b$. Finally we note that, for $b = 0$ and for x inside the well, the higher moments of the first-passage time follow from Eqs. (7.5) and (7.11) (Shenoy and Agarwal, 1984; Talkner, 1987), as

$$t^{(n)}(x) = \frac{n!}{(2k)^n} , \quad \text{if } a \le x \le -(2k_BT/M)^{1/2}/\omega_b . \tag{7.12}$$

Therefore the first-passage time $\tau(x)$ (a random quantity) is exponentially distributed on time scales beyond the local relaxation time,

$$P(\tau \in [t, t+dt]) = 2k \exp(-2kt) dt , \quad \text{with } t > \omega_0^{-1} . \tag{7.13}$$

Hence, in this simple model, the negative part of the real axis can be identified with a single metastable state with a waiting time distribution without memory (Weiss and Rubin, 1983).

2. Transition rates and effective diffusion in periodic potentials

For a Brownian particle obeying a Smoluchowski dynamics in a periodic potential, each period constitutes a metastable state[12] (see Fig. 22). There exist rates to neighboring states that can be determined by means of a MFPT out of one period, say $[0, L]$. If one end point, say $x = 0$, is chosen to be reflective, Eq. (7.8) yields (Lifson and Jackson, 1962; Jackson and Coriell, 1963)

$$t(x) \simeq t(x_0) \simeq \frac{\gamma L^2 M}{2k_BT} \langle \exp[U(x)/k_BT] \rangle \langle \exp[-U(x)/k_BT] \tag{7.14}$$

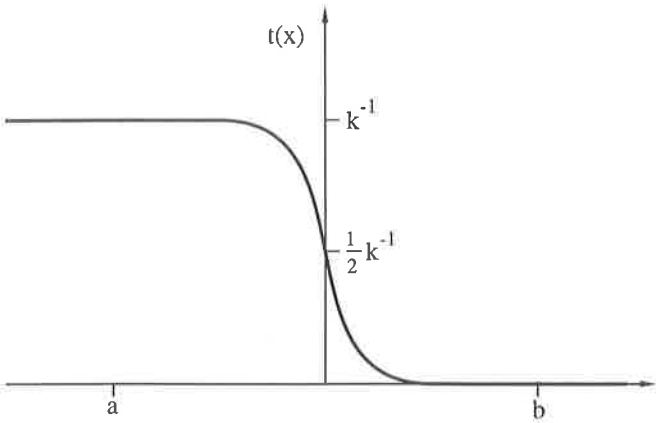

FIG. 21. Sketch of the behavior of the mean first-passage time $t(x)$ to leave the domain of attraction to the left of the barrier. The value of $\frac{1}{2}k^{-1}$ corresponds to the barrier location.

[12]For the sake of simplicity we disregard potentials with several local minima within one period. These can of course be treated by the same method.

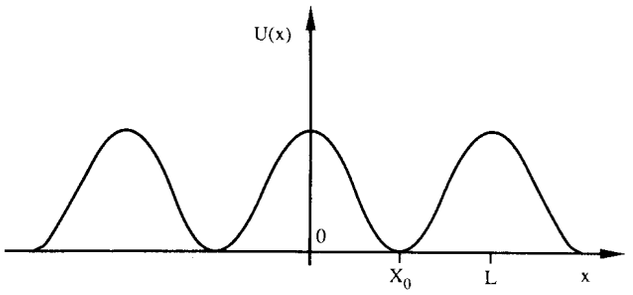

FIG. 22. Periodic potential exhibiting an infinite number of metastable states separated by a distance L.

for all x with $0 \le x \le L - (2k_BT/M)^{1/2}/\omega_b$. The brackets denote an average over one period,

$$\langle h \rangle = \frac{1}{L}\int_0^L h(x)dx \ . \tag{7.15}$$

Hence, the rate k between neighboring states is given by (Lifson and Jackson, 1962)

$$\begin{aligned} k &= [2t(x_0)]^{-1} \\ &= \frac{k_BT/M}{\gamma L^2}\langle \exp[U(x)/k_BT]\rangle^{-1} \\ &\quad \times \langle \exp[-U(x)/k_BT]\rangle^{-1} \ . \end{aligned} \tag{7.16}$$

In terms of the rate k the effective diffusion constant is $D_{\text{eff}} = kL^2$. The Cauchy-Schwartz inequality can be used to show that

$$\begin{aligned} D_{\text{eff}} &= D\langle \exp[U(x)/k_BT]\rangle^{-1}\langle \exp[-U(x)/k_BT]\rangle^{-1} \\ &\le D \ , \end{aligned} \tag{7.17}$$

where

$$D \equiv \frac{k_BT}{\gamma M} = (\gamma M\beta)^{-1} \tag{7.18}$$

is the free diffusion constant in the absence of a periodic potential.

Within a steepest-descent approximation the free diffusion is reduced by the factor

$$\begin{aligned} &\langle \exp[U(x)/k_BT]\rangle^{-1}\langle \exp[-U(x)/k_BT]\rangle^{-1} \\ &\qquad \simeq \frac{M\omega_0\omega_bL^2}{2\pi k_BT}\exp(-\beta E_b) \ . \end{aligned} \tag{7.19}$$

If both ends of a period are absorbing, the mean first-passage time is given by Eq. (7.7). The presence of a second exit point identical to the first leads to a reduction of the mean first-passage time by a factor of one-half for almost all starting points, except for those near the additional exit point where $t(x)$ vanishes.

3. Transition rates in random potentials

Diffusion in random potentials has recently been studied in the context of relaxation, transport, and chemical kinetics in various disordered media such as glasses (Binder and Young, 1986; Jäckle, 1986), polymers (De Gennes, 1975), and proteins (Ansari *et al.*, 1985), or in electrical transport in disordered solid-state systems (Alexander *et al.*, 1981; Weiss and Rubin, 1983; Ebeling *et al.*, 1984; Bernasconi and Schneider, 1985; Haus and Kehr, 1987; Engel and Moss, 1988; Tao, 1988). As a particularly simple model we consider a Brownian particle of mass M in the Smoluchowski limit, moving in a quenched random potential $V(x)$. The average $\overline{V(x)}$ over the realization of $V(x)$,

$$\overline{V(x)} = U(x) \ , \tag{7.20}$$

is assumed to have a single metastable well (see Fig. 23). The fluctuations $\delta V(x)$ are superimposed about this mean potential and are assumed to be Gaussian, spatially homogeneous, and short ranged compared with the distance between the local extrema of the mean potential $U(x)$,

$$\overline{\delta V(y)\delta V(x)} = g(y-x) \ , \tag{7.21}$$

with

$$g(x_b - x_a) \simeq 0 \ . \tag{7.22}$$

The mean sojourn time t_V in the metastable well of a fixed realization of the potential $V(x)$ can be calculated as a MFPT by Eq. (7.8),

$$\begin{aligned} t_V(x) &= \beta\gamma M\int_x^b dy \exp[\beta V(y)] \\ &\quad \times \int_a^y dz \exp[-\beta V(z)] \ , \end{aligned} \tag{7.23}$$

where x is a point in the well and where a and b are reflecting and absorbing boundaries, respectively (see Fig. 23). The mean waiting time is still a random variable, which may be averaged over the realizations of the random potential $V(x)$:

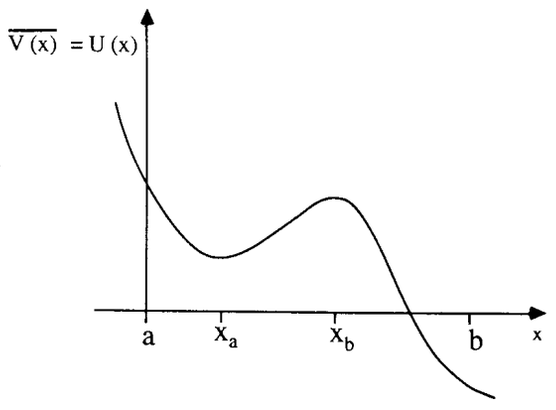

FIG. 23. Averaged metastable, random potential used in text.

$$\overline{t_V(x)}=\beta\gamma M\exp[\beta^2 g(0)]\int_x^b dy\int_a^y dz\exp[\beta(U(y)-U(z))]\exp[\beta^2 g(y-z)]\ , \tag{7.24}$$

where we have used the familiar formula

$$\overline{\exp(\xi)}=\exp(\tfrac{1}{2}\overline{\xi^2})\ , \tag{7.25}$$

which is valid for any Gaussian random variable ξ of vanishing mean.

Because $g(x)$ is short ranged [see Eq. (7.22)], it does not contribute to the integrals in Eq. (7.24). As a result one finds that the averaged MFPT becomes *enhanced* exponentially over the MFPT for the averaged potential (De Gennes, 1975; Zwanzig, 1988); i.e., substituting $U(x)$ for $V(x)$ in Eq. (7.23), we find

$$\overline{t_V(x)}=t_U(x)\exp[\beta^2 g(0)]>t_U(x)\ . \tag{7.26}$$

Note that the sojourn time is no longer exponentially distributed. This can already be seen from its second moment $t^{(2)}$. Because for a fixed random potential the MFPT is exponentially distributed, one has [Eq. (7.12)]

$$\overline{t_V^{(2)}}=2\overline{(t_V)^2}\ . \tag{7.27}$$

With Eqs. (7.22), (7.23), and (7.25) we obtain in leading order in k_BT

$$\overline{t_V^{(2)}}=2(\overline{t_V})^2[1-2\beta g''(0)/(M\omega_0^2)]^{-1/2}\times[1-2\beta g''(0)/(M\omega_b^2)]^{-1/2}\exp[2\beta^2 g(0)]\ , \tag{7.28}$$

where ω_0 and ω_b denote the well and the barrier frequencies, respectively, of the averaged potential $U(x)$. The second derivative of the correlation function, $g''(x)$, is non-negative at $x=0$,

$$-g''(0)\geq 0\ , \tag{7.29}$$

so that Eq. (7.28) stays always positive.

The exponential enhancement factor $\exp[2\beta^2 g(0)]$ may also be obtained from an ensemble of Arrhenius-type waiting times with Gaussian distributed activation energies. In this simplified model a much slower than exponential decay is observed (Vilgis, 1988). The prefactor $[1-2\beta g''(0)/M\omega_0^2]^{-1/2}[1-2\beta g''(0)/M\omega_b^2]^{-1/2}$ is always smaller than unity. For small but very irregular potential fluctuations the prefactor may compensate for even the exponential enhancement factor.

4. Diffusion in spherically symmetric potentials

A special case that allows the explicit solution of the MFPT in higher dimensions is that of diffusive problems in a spherically symmetric potential $U(r)$, in a spherically symmetric domain (Lifson and Jackson, 1962; Tachiya, 1978; Deutch, 1980; Szabo, Schulten, and Schulten, 1980; Shoup and Szabo, 1982); this case is governed by the Smoluchowski equation

$$\frac{\partial}{\partial t}p(r,\Omega,t)=Dr^{1-n}\frac{\partial}{\partial r}r^{n-1}\left[\beta\frac{\partial U}{\partial r}+\frac{\partial}{\partial r}\right]p(r,\Omega,t)+Dr^{1-n}L_n^2 p(r,\Omega,t)\ . \tag{7.30}$$

Here, (r,Ω) denotes the spherical coordinates in n dimensions, D is the diffusion constant, and L_n^2 denotes the Laplacian restricted to the surface of an n-dimensional sphere. The MFPT $t(r)$ out of a spherically symmetric domain depends only on the radius r and consequently obeys

$$\left[-\beta\frac{d}{dr}U(r)\right]\frac{d}{dr}t(r)+r^{1-n}\frac{d}{dr}r^{n-1}\frac{d}{dr}t(r)=-D^{-1},\quad r_0\leq r\leq R\ . \tag{7.31}$$

Again, different boundary conditions may be imposed at the inner and outer spheres with radii r_0 and R, respectively. For an absorbing boundary condition at r_0, and a reflecting one at R, one obtains from Eq. (7.31)

$$t(r)=\frac{1}{D}\int_{r_0}^{r}d\rho\int_{\rho}^{R}d\sigma\left[\frac{\sigma}{\rho}\right]^{n-1}\exp\{\beta[U(\rho)-U(\sigma)]\}\ . \tag{7.32}$$

For r_0 reflecting and R absorbing,

$$t(r)=\frac{1}{D}\int_{r}^{R}d\rho\int_{r_0}^{\rho}d\sigma\left[\frac{\sigma}{\rho}\right]^{n-1}\exp\{\beta[U(\rho)-U(\sigma)]\}\ . \tag{7.33}$$

Equation (7.32) has been used to determine the recombination rate of a diffusing molecule in the short-range potential $U(r)$ (see Fig. 24) of a fixed molecule (for a review, see Calef and Deutch, 1983). If the absorbing boundary r_0 is put inside the attractive part of the poten-

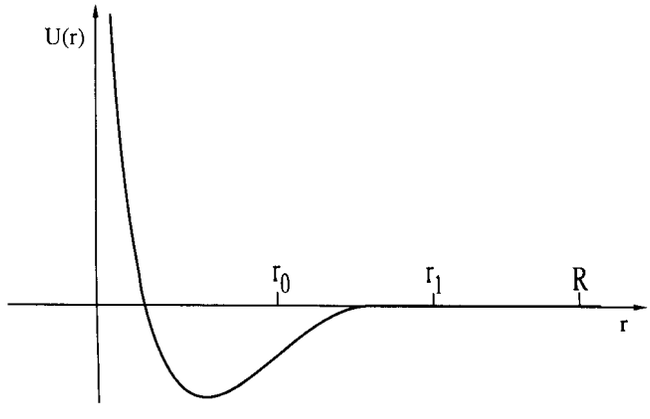

FIG. 24. Potential form used for a recombination reaction, exhibiting a short-range attracting part. Absorption takes place at r_0 and reflection at $r=R$, while r_1 denotes the initial separation.

tial, and the initial separation is assumed to be large compared to the range of the potential, one obtains from Eq. (7.32) for the mean time of recombination

$$t(r_1)=\frac{V_n(R)}{D}\begin{cases}\dfrac{1}{S_n(n-2)a_{\rm eff}^{n-2}}, & n\geq 3\ ,\\ \dfrac{1}{2\pi}\ln\dfrac{r_1}{r_0}, & n=2\ ,\\ r_1, & n=1\ ,\end{cases} \tag{7.34}$$

where $V_n(R)$ denotes the volume of an n-dimensional sphere with radius R, S_n is the surface of the unit sphere in n dimensions, and $a_{\rm eff}$ denotes an effective range of the potential defined by

$$a_{\rm eff}^{n-2}=\left[(n-2)\int_{r_0}^{r_1}\frac{\exp[\beta U(r)]}{r^{n-1}}dr\right]^{-1}. \tag{7.35}$$

We note that in dimensions larger than $n=2$ the mean recombination time is independent of the initial separation $r_1\gg r_0$. Therefore one may define a recombination rate for $n\geq 3$ by setting

$$k=\frac{1}{t(r_1)}=\frac{1}{V(R)}k_{\rm sm}\ , \tag{7.36}$$

where $k_{\rm sm}$ denotes the Smoluchowski rate (Smoluchowski, 1917; Debye, 1942)

$$k_{\rm sm}=DS_n(n-2)a_{\rm eff}^{n-2}\ . \tag{7.37}$$

In three dimensions it takes the familiar form

$$k_{\rm sm}=4\pi Da_{\rm eff}\ . \tag{7.38}$$

For a constant potential, $a_{\rm eff}$ is given by the radius r_0 of the absorbing inner sphere. The above theory has also been generalized to partially absorbing boundaries (Collins and Kimball, 1949; Wilemski and Fixman, 1972; Shoup and Szabo, 1982).

D. Mean first-passage times for Fokker-Planck processes in many dimensions

Except for highly symmetrical problems such as effectively one-dimensional escape problems from n-dimensional spherical potential wells (studied in Sec. VII.C.4), the MFPT generally cannot be calculated exactly in more than one dimension. Because ordinary perturbation theory fails to give the nonanalytical temperature dependence of the MFPT, asymptotic methods have been invoked to obtain the leading behavior for large Arrhenius factors, or more generally, for low noise levels (Matkowsky and Schuss, 1977; Schuss and Matkowsky, 1979; Talkner and Ryter, 1982, 1983; Talkner and Hänggi, 1984; Talkner, 1987). In order to apply these asymptotic methods it is convenient to consider the first passage out of the *domain Ω of attraction* of the reactant state.[13] Just as for the one-dimensional case [see Eq. (7.13)], in the limit of weak noise the first-passage time is exponentially distributed (Shenoy and Agarwal, 1984). Further, its mean assumes an almost constant value $t_{\rm MFPT}$ practically everywhere on the domain of attraction Ω. Therefore one may write with $\mathbf{x}$ denoting a point in Ω

$$t(\mathbf{x})=t_{\rm MFPT}f(\mathbf{x})\ , \tag{7.39a}$$

where the form function $f(\mathbf{x})$ equals

$$f(\mathbf{x})=1 \quad \text{almost everywhere on } \Omega\ . \tag{7.39b}$$

When approaching the boundary $\partial\Omega$ from the interior, $f(\mathbf{x})$ steeply decreases to zero,

$$f(\mathbf{x})=0,\quad x\in\partial\Omega\ . \tag{7.40}$$

As in the one-dimensional case, the almost constant value $t_{\rm MFPT}$ for the escape time out of the domain of attraction of the metastable state determines the decay rate (Schuss and Matkowsky, 1979),

$$k=(2t_{\rm MFPT})^{-1}\ . \tag{7.41}$$

Using the backward equation (7.3) for $t(\mathbf{x})$ together with Eq. (7.39) one obtains an equation for the form function, reading

$$\mathcal{L}^{\dagger}f(\mathbf{x})=-t_{\rm MFPT}^{-1},\quad \mathbf{x}\in\Omega\ , \tag{7.42a}$$

and

$$f(\mathbf{x})=0,\quad \mathbf{x}\in\partial\Omega\ , \tag{7.42b}$$

where $\mathcal{L}^{\dagger}$ is the backward operator of the considered Fokker-Planck process possessing a drift vector $\mathbf{K}$ and a diffusion matrix $\varepsilon\mathbf{D},\varepsilon\ll 1$. The drift field $\mathbf{K}$ may generally contain a fluctuation-induced part which is proportional to ε; this merely modifies the prefactor of the solution w in Eq. (7.45), i.e., the quantities $\{Z_A,Z_S\}$ in Eqs. (7.47a) and (7.55) below. Assuming that $\mathbf{D}$ is bounded, $\mathcal{L}^{\dagger}$ reads

$$\mathcal{L}^{\dagger}=\sum_i K_i(\mathbf{x})\frac{\partial}{\partial x_i}+\varepsilon\sum_{i,j}D_{ij}(\mathbf{x})\frac{\partial^2}{\partial x_i\partial x_j}\ . \tag{7.43}$$

Because the form function $f(\mathbf{x})$ is expected to vary at $\partial\Omega$ only on a thin boundary layer, one may neglect the small inhomogeneity $t_{\rm MFPT}^{-1}$ in Eq. (7.42a) and replace it by a matching condition (Matkowsky and Schuss, 1977)

$$\mathcal{L}^{\dagger}f(\mathbf{x})=0\ , \tag{7.44a}$$

[13] To be more precise: In the deterministic limit the metastable reactant state becomes a stable state with a proper domain of attraction. If the domain of attraction happens to be unbounded, it often suffices to consider a suitably chosen bounded part of it, which defines the exit domain Ω (Talkner and Hänggi, 1984).

with

$$f(\mathbf{x})\simeq 1 \text{ inside the interior of } \Omega\ , \tag{7.44b}$$

$$f(\mathbf{x})=0,\quad \mathbf{x}\in\partial\Omega\ . \tag{7.44c}$$

We recall that Ω is a complete domain of attraction of the drift field $\mathbf{K}$ and that, consequently, its boundary $\partial\Omega$ is a *separatrix* of the drift field $\mathbf{K}$, i.e., there exists no transverse drift on $\partial\Omega$. Before we proceed to solve Eq. (7.44) we express the constant part $t_{\rm MFPT}$ of the MFPT in terms of the form function $f(\mathbf{x})$ and a stationary solution $w(\mathbf{x})$ of the Fokker-Planck equation,[14] obeying

$$\mathcal{L}w=0\ . \tag{7.45}$$

For this purpose Eq. (7.3a) is multiplied by the stationary probability density $w(\mathbf{x})$ and subsequently integrated over the domain Ω. Using the Gauss theorem and Eq. (7.39a), one finds (Matkowsky and Schuss, 1977)

$$t_{\rm MFPT}=-\frac{\int_\Omega d^n x\, w(\mathbf{x})}{\varepsilon\sum_i\int_{\partial\Omega} dS_i \sum_j D_{ij}(\mathbf{x})w(\mathbf{x})\dfrac{\partial f(\mathbf{x})}{dx_j}}\ , \tag{7.46}$$

where dS denotes the oriented surface element on $\partial\Omega$. The fact that for weak noise the stationary probability density is sharply peaked at stable stationary points of the drift field $\mathbf{K}$ allows one to evaluate both integrals in Eq. (7.46) in Gaussian approximation. The integral in the numerator in Eq. (7.46) is dominated by the immediate neighborhood of the considered attractor, and yields in leading order in the noise strength ε

$$P_A\equiv\int_\Omega d^n x\, w(\mathbf{x}) \simeq\left[\det\frac{\varphi_A}{2\pi\varepsilon}\right]^{-1/2} Z_A^{-1}\exp(-\phi_A/\varepsilon)\ , \tag{7.47a}$$

where the quantities Z_A, ϕ_A, and the matrix $\varphi_A=(\varphi_{ij}^A)$ are determined by the local Gaussian approximation of the stationary solution about the attractor A,

$$w(\mathbf{x}_A+\delta\mathbf{x}) =Z_A^{-1}\exp(-\phi_A/\varepsilon)\exp\left[-\frac{1}{2\varepsilon}\sum_{ij}\varphi_{ij}^A\delta x_i\delta x_j\right]\ . \tag{7.47b}$$

Clearly, if the well dynamics is not parabolic, the population P_A differs from the Gaussian approximation in Eq. (7.47a). For example, for a Brownian motion in a quartic *well*, $\frac{1}{4}ax^4$, the only change occurs in the prefactor, which now assumes a temperature dependence. If we denote in this quartic case the integral in the numerator of Eq. (7.46) by $P_A^{\rm QW}$, we find the correction

$$P_A^{\rm QW}=\left[\frac{2}{\Gamma(\frac{1}{4})}\left[\frac{\pi}{M\omega_0^2}\right]^{1/2}(ak_BT)^{1/4}\right]^{-1}P_A\ . \tag{7.48}$$

The impact of a quartic *barrier* on the rate is referred to in Sec. VII.E.1.

The integral in the denominator in Eq. (7.46) is dominated by the saddle point on the separatrix $\partial\Omega$, exhibiting maximal probability density on $\partial\Omega$. Again, one may expand the probability density about the saddle point, yielding[15]

$$w(\mathbf{x}_S+\delta\mathbf{x}) =Z_S^{-1}\exp\left[-\frac{\phi_S}{\varepsilon}\right]\exp\left[\frac{-1}{2\varepsilon}\sum_{ij}\varphi_{ij}^S\delta x_i\delta x_j\right]\ . \tag{7.49}$$

Note that the eigenvalues of the matrix $\varphi_S=(\varphi_{ij}^S)$ are all positive, except for one that belongs to the unstable direction at the considered saddle point.[16] For the form function $f(\mathbf{x})$ obeying Eq. (7.44) it is then convenient to make the following ansatz (Talkner and Ryter, 1982):

$$f(\mathbf{x})=\sqrt{2/\pi\varepsilon}\int_0^{\rho(\mathbf{x})}dz\,\exp[-z^2/(2\varepsilon)]\ , \tag{7.50}$$

where $\rho(\mathbf{x})$ vanishes at the separatrix and increases when $\mathbf{x}$ leaves the separatrix. From Eq. (7.44a) one obtains in leading order in ε the following first-order partial differential equation for $\rho(\mathbf{x})$:

$$\sum_i K_i\frac{\partial\rho}{\partial x_i}-\sum_{i,j}D_{ij}\frac{\partial\rho}{\partial x_i}\frac{\partial\rho}{\partial x_j}\rho=0\ . \tag{7.51}$$

In the neighborhood of the saddle point that dominates the integral in the denominator of the MFPT in Eq. (7.46), one finds as the solution of Eq. (7.51)

$$\rho=(D_{rr}/\lambda_+)^{-1/2}r\ , \tag{7.52}$$

where r is the unstable direction of the vector field $\mathbf{K}$ at the saddle point. In Eq. (7.52), λ_+ denotes the corresponding (positive) eigenvalue,

$$K_r=\lambda_+ r+O(r^2)\ , \tag{7.53}$$

and D_{rr} is the matrix element of the diffusion in this direction. Combining Eqs. (7.49), (7.50), and (7.52), we obtain for the denominator of $t_{\rm MFPT}$ in Eq. (7.46) (Talkner, 1987)

[14]For an equilibrium system the stationary probability density is always known; it may present a major problem, however, to obtain it for a nonequilibrium system. It is worth noting that Eq. (7.45) need only hold on Ω, the only restriction being that its integral over Ω exist.

[15]For the sake of simplicity we have assumed that both the attractor and the saddle consist of isolated points. More general limit sets, for example, limit cycles, may be handled in an analogous way (Talkner, 1987).

[16]For the case of a quartic barrier where the matrix φ_S has a neutral direction, see Sec. VII.E.1.

$$\sum_{ij}\int_{\partial\Omega} dS_i D_{ij}(\mathbf{x})w(\mathbf{x})\frac{\partial f(\mathbf{x})}{\partial x_j}\simeq -\lambda_+(\pi\varepsilon)^{-1}P_S\ , \tag{7.54}$$

where P_S denotes the probability of finding the system at the saddle if the unstable saddle direction is inverted into a stable one,

$$P_S=\left|\det\frac{\varphi_S}{2\pi\varepsilon}\right|^{-1/2} Z_S^{-1}\exp(-\phi_S/\varepsilon)\ . \tag{7.55}$$

The final result for the MFPT follows from Eqs. (7.46), (7.47), and (7.54) as (Talkner, 1987)

$$t_{\mathrm{MFPT}}=\frac{\pi}{\lambda_+}(P_A/P_S)\ . \tag{7.56}$$

This yields, with Eqs. (7.41), (7.47), (7.53), the rate

$$k=\frac{\lambda_+}{2\pi}(P_S/P_A)\ ,$$

or explicitly

$$k=\frac{\lambda_+}{2\pi}\left[\frac{Z_A}{Z_S}\right]\left[\frac{\det\varphi_A}{|\det\varphi_S|}\right]^{1/2}\exp[-(\phi_S-\phi_A)/\varepsilon]\ . \tag{7.57}$$

Hence the rate is given by the positive eigenvalue of the deterministic dynamics at the relevant saddle point, stretched by the relative frequency of finding the system at the saddle, rather than at the attractor. Equation (7.57) represents the correct, asymptotic result for the rate in the limit of large barrier heights $(\phi_S-\phi_A)/\varepsilon\gg 1$. From Eqs. (7.47), (7.55), and (7.57) one immediately recovers Langer's rate expression in Eq. (4.81) by identifying $(\phi_S-\phi_A)/\varepsilon$ with E_b/k_BT and φ_S/ε and φ_A/ε with $\mathbf{E}^S/k_BT$ and $\mathbf{E}^A/k_BT$, respectively. We recall that Kramers' rate expression is simply a special case of Langer's result in Eq. (4.81), and therefore is implicitly a part of Eq. (7.57).

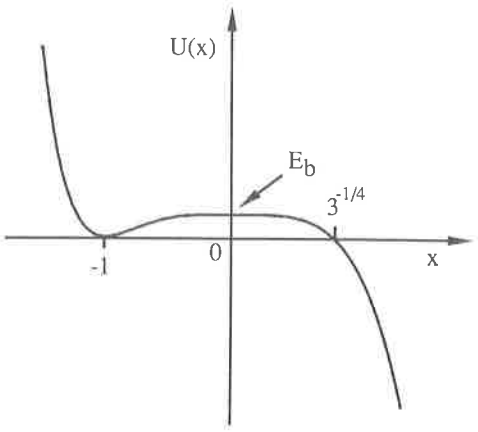

FIG. 25. Escape over a quartic barrier with $U(x)=-\frac{1}{4}x^4+\frac{1}{6}x^6\theta(-x)+\frac{1}{12}$, with $\theta(x)$ denoting the step function. The barrier height equals $E_b=\frac{1}{12}$.

E. Sundry topics from contemporary mean-first-passage-time theory

In most of the previous sections we considered escape processes in multistable potentials that are characterized by parabolic, unstable barrier regions. Moreover, in view of the central limit theorem for many degrees of freedom, we considered mainly random forces with Gaussian statistics. Here we shall relax some of these assumptions.

1. Escape over a quartic ($-\mathbf{x}^4$) barrier

Let us focus on a Brownian motion dynamics [see Eq. (4.1)] in a metastable potential $U(x)$ of the form sketched in Fig. 25, exhibiting a parabolic well and a *quartic* barrier. First we consider the case of strong friction, i.e., we deal with the Smoluchowski equation (4.9). From Eq. (7.8) we thus obtain in leading order for the escape time t_{MFPT} at weak noise, $\beta E_b\ll 1$,

$$t_{\mathrm{MFPT}}=M\gamma\beta\exp(\beta E_b)\int_{-\infty}^{0}dy\,\exp(-\tfrac{1}{4}a\beta y^4)\int_{-\infty}^{\infty}dz\,\exp(-\tfrac{1}{2}M\beta\omega_0^2z^2)\ , \tag{7.58}$$

where we have approximated $U(x)$ by

$$U(x)\sim\begin{cases}-\frac{1}{4}ax^4, & \text{near the saddle point } x=0\ ,\\ \frac{1}{2}M\omega_0^2(x-x_0)^2-E_b, & \text{at the bottom of the well}\ ,\end{cases} \tag{7.59}$$

and where we have extended the reflecting boundary toward $-\infty$, where no contributions are expected. The absorbing boundary is located at the transition state $x=0$. The quadratures can be readily evaluated [see Eq. (3.326) in Gradshteyn and Ryzhik (1980)], to give for the rate of escape

$$k=(2t_{\mathrm{MFPT}})^{-1}=\frac{\omega_0(ak_BT)^{1/4}}{(\pi M)^{1/2}\gamma\Gamma(\frac{1}{4})}\exp(-\beta E_b)\ , \tag{7.60}$$

with $\Gamma(x)$ the gamma function.

Next we turn to the regime of moderate damping values. In this case we must consider the Brownian motion dynamics of the Klein-Kramers equation [Eq. (4.4)] in its full phase space $(x,\dot{x})$ rather than in configuration space only. By use of the general equation (7.46) for the MFPT, we must take account of the fact that the form function $f(x,v)$ changes its behavior in the presence of a quartic barrier. In this case, the MFPT, as well as the

form function, will fall off *more steeply* than in the parabolic barrier case (Talkner and Ryter, 1982), i.e., one finds

$$f(x,v)=\frac{4}{(4k_BT)^{1/4}\Gamma(\frac{1}{4})}\int_0^{\rho(x,v)}\exp(-\tfrac{1}{4}\beta z^4)dz\ . \quad (7.61)$$

With Eq. (7.44) one finds in the neighborhood of the saddle point

$$v\frac{\partial}{\partial x}f(x,v)+\left[\frac{a}{M}x^3-\gamma v\right]\frac{\partial}{\partial v}f(x,v) +(M\beta)^{-1}\gamma\frac{\partial^2}{\partial v^2}f=0\ , \quad (7.62)$$

or, for $\rho(x,v)$, in leading order β^{-1},

$$v\frac{\partial\rho}{\partial x}+\left[\frac{a}{M}x^3-\gamma v\right]\frac{\partial\rho}{\partial v}-M^{-1}\gamma\left[\frac{\partial\rho}{\partial v}\right]^2\rho^3=0\ . \quad (7.63)$$

The solution of Eq. (7.63), with $f(x,v)$ obeying the boundary conditions in Eqs. (7.44b) and (7.44c), reads

$$\rho=(\gamma^{-1}a^{1/4})r+O(r^2)\ , \quad (7.64)$$

where r denotes a coordinate measuring the distance from the separatrix, chosen so that the deterministic motion in the neighborhood of the saddle has the form

$$\dot r=(\gamma^3M)^{-1}ar^3 +\text{fourth- and higher-order corrections in } v \text{ and } r \quad (7.65a)$$

and

$$\dot v=-\gamma v+\text{third- and higher-order terms in } v \text{ and } r\ . \quad (7.65b)$$

In leading order in the configuration coordinate x and the velocity v the distance r is given by

$$r=\gamma x+v\ . \quad (7.66)$$

Thus, in order to obtain the leading weak-noise contribution for the denominator in Eq. (7.46), one must integrate along the line $r=0$. With w the canonical equilibrium probability the integration in Eq. (7.46) can be performed exactly, see Eqs. (3.323,3) in Gradshteyn and Ryzhik (1980), to give for the rate in Eq. (7.41) the main result

$$k=2^{3/4}[\Gamma(\tfrac{1}{4})]^{-1}\zeta\exp(\zeta^4)K_{1/4}[\zeta^4]k_{\rm TST}\ , \quad (7.67)$$

where ζ is a dimensionless damping parameter

$$\zeta=\left[\frac{M^2\beta}{8a}\right]^{1/4}\gamma\ , \quad (7.68)$$

$K_{1/4}[x]$ denotes a modified Bessel function of the second kind, and $k_{\rm TST}=(\omega_0/2\pi)\exp(-\beta E_b)$ is the simple TST rate in Eq. (3.5). Note that $k/k_{\rm TST}$ approaches unity as $\gamma\to 0$, while Eq. (7.67) crosses over into the previous result in Eq. (7.60) for $(\gamma/\omega_0)\gg 1$. Note also that this limiting large damping regime described by Eq. (7.67) is assumed both for $\gamma\to\infty$ and by virtue of Eq. (7.68), for $\beta\to\infty$, i.e., for low temperatures.[17]

Finally, we address the *regime of extremely weak damping* (see Sec. IV.D), where the rate is limited by energy diffusion. Using for $U(x)$ the *symmetric* prototype potential

$$U(x)=-\tfrac{1}{4}ax^4+\tfrac{1}{6}bx^6,\quad a>0,\quad b>0\ , \quad (7.69)$$

we find that Eqs. (4.11), (4.49), and (4.51) yield for the energy-diffusion-limited rate k_E, with $p=\frac{1}{2}$,

$$k_E=[\tfrac{9}{8}\sqrt{6}\,\pi(\beta E_b\gamma/\omega_0)]\frac{\omega_0}{2\pi}\exp(-\beta E_b)\ , \quad (7.70)$$

where $E_b=a^3(12b^2)^{-1}$ and $\omega_0^2=2a^2(Mb)^{-1}$.

2. Escape over a cusp-shaped barrier

In a potential with a cusp at the barrier (see Fig. 26) every particle that approaches the barrier from the left-hand side with positive velocity will almost surely leave the potential well. Hence the rate is simply determined by the reciprocal MFPT to cross the line $x=0$ with $v>0$, which is given by (Matkowsky and Schuss, 1977)

$$\tau^{\rm cusp}=\frac{\int_{-\infty}^{0}dx\int_{-\infty}^{+\infty}dv\exp\left[-\left[\frac{M}{2}v^2+U(x)\right]\Big/k_BT\right]}{\int_0^{\infty}dv\,v\exp\left[-\left[\frac{Mv^2}{2}+U(0)\right]\Big/k_BT\right]}\ . \quad (7.71)$$

In leading order in E_b/k_BT one obtains precisely the TST answer in Eq. (3.5) (Marcus, 1963; Dogonadze and Kuznetzov, 1970; Ulstrup, 1979; Hynes, 1986b),

$$k^{\rm cusp}=[\tau^{\rm cusp}]^{-1}=\frac{\omega_0}{2\pi}\exp(-\beta E_b)\ . \quad (7.72)$$

The same result still holds for non-Markovian processes with memory friction obeying a fluctuation-dissipation theorem (Talkner and Braun, 1988). Note that this TST result follows readily from the Kramers rate in Eq. (4.33), if we formally let the barrier frequency $\omega_b\to\infty$, with γ held fixed. Moreover, it should be remarked that with a cusp, $\omega_b\to\infty$, the fluctuation length scale $l_{\rm th}=(2k_BT/M\omega_b^2)^{1/2}$ vanishes; hence the statistical factor of 2, due to diffusion over the length scale $l_{\rm th}$, no longer enters the relation between the MFPT and the rate [Eqs. (7.11) and Eq. (7.72)].

By contrast, if one considers the Smoluchowski dynamics, i.e., $(\gamma/\omega_0\gg 1)$, for a cusp-shaped barrier (see Fig. 26), one finds from Eq. (4.56b) a rate $k^s_{\rm cusp}$ *different*

[17]Of course, the temperature must not fall below a crossover value beyond which tunneling effects prevail over classical activation; see Sec. IX.

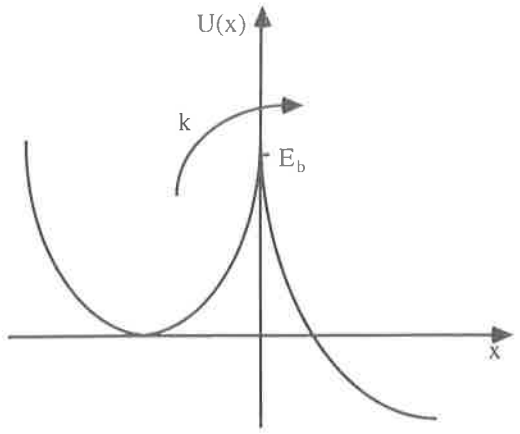

FIG. 26. Escape in a cusp-shaped metastable potential.

from the TST rate (Kramers, 1940),[18]

$$k^s_{\text{cusp}} = \frac{\omega_0^2}{2\pi\gamma}(\pi\beta E_b)^{1/2}\exp(-\beta E_b) \ . \tag{7.73}$$

A treatment of the crossover between Eqs. (7.72) and (7.73) has recently been given by Pollak (1990).

The problem of escape in a cusp-shaped metastable potential is of great practical importance in nonadiabatic rate theory for applications such as electron transfer reactions (Nikitin, 1974; Tully, 1976; Zusman, 1980; Calef and Wolynes, 1983; Frauenfelder and Wolynes, 1985; Hynes, 1985; Chandler, 1986; Nadler and Marcus, 1987; Rips and Jortner, 1987; Straub and Berne, 1987), where two corresponding diabatic energy curves cross each other, yielding a cusplike potential form.

3. Mean first-passage time for shot noise

If the escape takes place on a discrete ladder, rather than a continuum of states, a master-equation description (see Sec. V) is more appropriate. As mentioned earlier, this case is generally trickier, and exact results can be obtained only in a few special cases (Weiss, 1967; Troe, 1977; Weiss and Szabo, 1983; Hänggi and Talkner, 1985). Of particular importance is the case of a birth-and-death process with transitions only between nearest neighbors. If one considers a discrete state space with states $N=0,1,2\ldots$ possessing jump transition probabilities $W^+(N\to N+1)=W^+(N)$ and $W^-(N\to N-1)=W^-(N)$, respectively, the probability $P(N,t)$ obeys the Markovian master equation

$$\dot{P}(N=0,t)=W^-(1)P(1,t)-W^+(0)P(0,t), \quad N=0 \ , \tag{7.74a}$$

$$\dot{P}(N,t)=W^+(N-1)P(N-1,t)+W^-(N+1)P(N+1,t)-[W^+(N)+W^-(N)]P(N,t), \quad N=1,\ldots \ . \tag{7.74b}$$

These birth-and-death processes occur in a multitude of physical and chemical systems (see, for example, Haken, 1975; Van Kampen, 1976; Nicolis, 1979; Hänggi and Thomas, 1982). For the problem of the rate of escape, the exact analysis of such processes was pioneered by scientists treating homogeneous nucleation (Farkas, 1927; Kaischew and Stranski, 1934; Becker and Döring, 1935; Zeldovich, 1943), including many rediscoveries, which in most cases, however, added additional insight. For example, Farkas (1927), Kaischew and Stranski (1934), Christiansen (1936), Zeldovich (1943), Frenkel (1957), Landauer (1962), and Zinsmeister (1970) all noted the close analogy between a birth-and-death description and the differential equation for a one-dimensional Fokker-Planck process (see Sec. VII. C). For the problem of the MFPT the exact analog of Eq. (7.8), with $N=N_0$ absorbing, reads (Weiss, 1967; Gillespie, 1979, 1981; Seshardi, West, and Lindenberg, 1980)

$$t(N)=\sum_{M=N}^{N_0-1}[W^+(M)P_S(M)]^{-1}\sum_{K=0}^{M}P_S(K) \ , \quad 0\le N<N_0 \ . \tag{7.75}$$

In Eq. (7.75)

$$P_S(N)=P_S(0)\prod_{M=0}^{N-1}W^+(M)/W^-(M+1) \tag{7.76}$$

is the stationary probability of the master equation in Eq. (7.74). The result in Eq. (7.75) can also be generalized to birth-and-death processes including both one- and two-step jumps (Hänggi and Talkner, 1981). Moreover, recent studies have revealed that the long-time dynamics of a master equation can be modeled by a novel, effective Fokker-Planck approximation yielding on an intensive scale $x=N/V$, with V measuring the system size, identical stationary probabilities, and identical weak-noise escape rates (Hänggi, Grabert, Talkner, and Thomas, 1984). It has further been demonstrated that when the Kramers-Moyal expansion is truncated (at second order), yielding the usual Fokker-Planck approximation to a shot-noise master equation, it always *exponentially* overestimates the rate (Hänggi, Grabert, Talkner, and Thomas, 1984; Hänggi and Jung, 1988). This feature is due to the systematic overestimation of the correspond-

[18]This Smoluchowski case for a cusp-shaped barrier was studied by Kramers (1940) in his original paper, note the text and the formula below his Eq. (17).

ing Kramers-Moyal diffusion. Finally, we mention that the same methodology underlying the MFPT–Fokker-Planck approach can be extended not only to discrete state spaces, but also to *systems with a discrete dynamics,* i.e., systems with a discrete time, as they occur in the description of noisy chaos (Talkner *et al.,* 1987). In contrast to Eq. (7.8) for the Fokker-Planck process and Eq. (7.75) for the birth-and-death process, however, closed-form expressions for the MFPT in a system with discrete dynamics are not possible; this problem requires the solution of a corresponding integral equation for the form function (Talkner *et al.,* 1987). Numerical studies of escape dynamics in chaotic maps have been undertaken recently by Grassberger (1989) and Beale (1989).

4. First-passage-time problems for non-Markovian processes

Due to the explicit quadrature and summation formulas given in Eqs. (7,7), (7.8), and (7.75) for one-dimensional processes, the MFPT concept enjoys great popularity among physicists, chemists, and engineers. In higher dimensions, however (see Sec. VII.D), the problems caused by boundary conditions in the presence of auxiliary degrees of freedom, e.g., velocity degrees of freedom, can be quite substantial (Kac, 1962; Doering *et al.,* 1987, 1988; Hänggi, Jung, and Talkner, 1988). For processes with memory, implying a non-Markovian behavior, the MFPT problem is rather delicate, and its general theory has been developed only recently (Hänggi and Talkner, 1981, 1983). The difficulty arises with the contracted description inherent in any non-Markovian behavior; the boundary problem cannot be treated in a straightforward way, but must be handled with extreme care so as to prevent any backflow of probability into the domain of attraction via hidden channels, which result when a non-Markovian process is formally embedded into a state space of larger dimension exhibiting dynamics without memory (Markov embedding of a non-Markovian process). A particular illustrative case is that of nonlinear flows $x(t)$ driven by dichotomic, or two-state, noise $\zeta_D(t)$,

$$\dot{x}(t)=f(x)+g(x)\zeta_D(t) , \tag{7.77}$$

where $\langle \zeta_D(t) \rangle = 0$, and where $\zeta_D(t)$ jumps between two states ± 1 with exponentially distributed (with rate μ) jump times, yielding for the noise correlation an exponential decay,

$$\langle \zeta_D(t)\zeta_D(s) \rangle = \exp(-2\mu|t-s|) . \tag{7.78}$$

With the simplicity of only two possible noise states, the MFPT for Eq. (7.77) can be evaluated explicitly, both for two absorbing boundaries (Hänggi and Talkner, 1985; Masoliver *et al.,* 1986; Rodriguez and Pesquera, 1986; Doering, 1987; Hernandez-Garcia *et al.,* 1987), and for one absorbing and one reflecting boundary (Balakrishnan *et al.,* 1988; Behn and Schiele, 1989). Nevertheless, for the problem of escape between neighboring domains of attraction at a weak noise level, the flux-over-population method in Sec. II.C.1 can be used to advantage (Hänggi and Riseborough, 1983; Van den Broeck and Hänggi, 1984). This is due to the simplicity of imposing an absorbing boundary condition for the nonequilibrium probability in the neighboring domain of attraction [see Eq. (2.9)].

VIII. TRANSITION RATES IN NONEQUILIBRIUM SYSTEMS

Whereas equilibrium states of thermodynamic systems with homogeneous boundary conditions are always time independent and spatially homogeneous, driven systems may settle down in more complicated states which may exhibit both temporal and spatial structures (see, for example, Haken, 1975). Within a phenomenological, deterministic description of driven systems it frequently happens that two or more of these states ("attractors") coexist. The presence of thermal or external noise will in general induce transitions between the attractors and thus render them metastable. In principle the same methods as for equilibrium systems are available for the determination of rates at which transitions between nonequilibrium metastable states occur. Both the flux-over-population method and the mean first-passage time, however, rely on a knowledge of the stationary probability density, which is readily found only for equilibrium systems. Because most nonequilibrium systems lack detailed balance symmetry (Green, 1952; van Kampen, 1957; Uhlhorn, 1960; Graham and Haken, 1971; Risken, 1972; Hänggi and Thomas, 1982), it is a formidable task to determine the probability density of a multidimensional stationary nonequilibrium system.[19]

In the most relevant case of low noise, a WKB-type method has been employed to construct stationary probability densities (Cohen and Lewis, 1967; Ventsel' and Freidlin, 1970; Kubo *et al.,* 1973; Ludwig, 1975; Matsuo, 1977; Graham, 1981; Talkner and Ryter, 1983). This method represents a singular perturbation theory in the noise strength. In leading exponential order it yields a generalized potential which, though always continuous, often happens to be nondifferentiable (Graham and Tel, 1984a, 1984b; Jauslin, 1987). Of course, these potentials are smooth for systems with detailed balance. Perturbative expansions about cases with smooth generalized potentials have been performed by Graham and Tel (1987; Tel, 1988) and have been used to determine the lifetime of an attractor in the vicinity of a bifurcation characterized by a simultaneous vanishing of two eigenvalues, i.e.,

[19]The two-dimensional model of dispersive optical bistability, with equal atomic and cavity detuning, put forward by Graham and Schenzle (1981) represents a rare exception to this rule. The transition rates between the absorbing and transparent states have been determined by Talkner and Hänggi (1984).

a "codimension-two bifurcation" (Graham, 1986). Schimansky-Geier, Tolstopjatenko, and Ebeling (1985) proposed a polynomial approximation of the generalized potential about a fixed point for systems in the vicinity of a bifurcation at which this fixed point loses its stability. However, there are examples (Hu, 1989; Tel, Graham, and Hu, 1989) of codimension-two bifurcations at which the generalized potential is still a smooth although nonanalytical function. Within this WKB-type approximation a systematic improvement to the leading exponential term can only be achieved if the generalized potential is piecewise twice differentiable (Ludwig, 1975).[20] Therefore, transition rates including their prefactors can be obtained in most cases only for (a) Markovian one-dimensional nonequilibrium systems and (b) higher-dimensional systems in which the essential nonlinear dynamics reduces approximately to an effective one-dimensional Markovian treatment, or which—by chance—obey a detailed balance condition. Some such cases are discussed next.

A. Two examples of one-dimensional nonequilibrium rate problems

1. Bistable tunnel diode

Following Landauer (1962) (see also Sec. 6.3 in Hänggi and Thomas, 1982; Hänggi and Jung, 1988), one may describe the state of a tunnel diode fed through a series resistor R by the number N of electrons charging or discharging the diode capacitance C (see Fig. 27). The time evolution of the diode is then fairly well described by a Markovian master equation of the birth-and-death type [Eq. (7.74)],

$$\frac{\partial}{\partial t}P(N,t)=W^{+}(N-1)P(N-1,t)+W^{-}(N+1)P(N+1,t)-[W^{+}(N)+W^{-}(N)]P(N,t)\ ,\qquad N=0,\pm1,\pm2,\ldots\ , \tag{8.1}$$

where the birth rates $W^{+}(N)$ and the death rates $W^{-}(N)$ are given by the probabilities per unit time of charging and discharging the capacitance by the elementary charge e.

In the deterministic limit in which the charge may be considered as a continuous quantity at a given voltage across the diode, $V=V_b-V'$, where V' is the voltage across the resistor with the fixed voltage V_b supplied by a battery, two locally stable states may occur (see Fig. 28). These states are rendered metastable by fluctuations in a

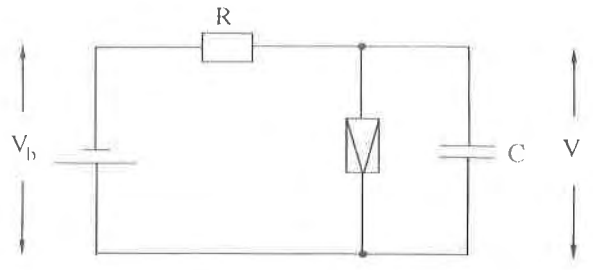

FIG. 27. Nonlinear tunnel diode fed through a series resistance R and a diode capacitance C. The diode is driven by an external constant-voltage source V_b. V denotes the voltage across the nonlinear diode. After Landauer (1962).

diode of finite size. The transition rates follow directly from the master equation in Eq. (8.1), by use of Eq. (7.75). In the limit of a large system it is convenient to introduce the intensive quantity

$$x=\frac{N}{\Omega} \tag{8.2}$$

as a quasicontinuous variable. For the tunnel diode the size of the system Ω is given by the area of the junction. Using as a scaling property for the transition rates

$$W^{\pm}(N)=\Omega\gamma^{\pm}(x)\ , \tag{8.3}$$

one obtains from Eq. (7.75) for the forward rate from the state A to C in leading order in Ω^{-1} (Hänggi and Thomas, 1982; Hänggi, Grabert, Talkner, and Thomas, 1984)

$$k_{A,C}=\left[\frac{\gamma^{+}(x_a)}{2\pi}[\phi''(x_a)|\phi''(x_b)|]^{1/2}+O(\Omega^{-1})\right]\times\exp\{-\Omega[\phi(x_b)-\phi(x_a)]\}\ , \tag{8.4}$$

where x_a and x_b refer to the surface charge densities at the capacitance in the locally stable state A and the unstable state B, respectively, and where the generalized po-

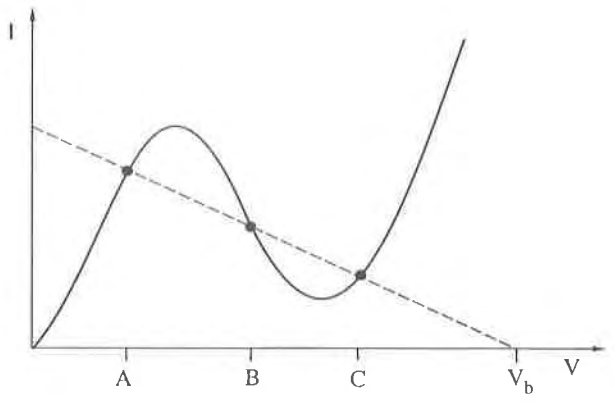

FIG. 28. Static current-voltage characteristic $I(V)$ (solid line) and the load line (dashed line) of a tunnel diode corresponding to the circuit in Fig. 27. The states A and C are locally stable voltage states, while state B located within the negative resistance region is locally unstable.

[20]A corresponding problem has only recently been solved in the simpler case of one-dimensional maps (i.e., discrete time dynamics) perturbed by Gaussian white noise (Reimann and Talkner, 1989).

tential $\phi(x)$ is given by (Landauer, 1962; Hänggi and Thomas, 1982)

$$\phi(x)=-\int_{x_0}^{x} dy \ln\left[\frac{\gamma^{+}(y)}{\gamma^{-}(y)}\right] . \tag{8.5}$$

The corresponding result for the backward rate $k_{C\to A}$ is obtained from Eq. (8.5) if we replace the state x_a in Eq. (8.5) by the corresponding state x_c. We remark that the rate expression which follows from the standard truncated Kramers-Moyal expansion deviates from the asymptotically correct result [see Eq. (8.4)] by an exponentially large factor (Hänggi, Grabert, Talkner, and Thomas, 1984). An improved Fokker-Planck description, which in turn yields a rate identical to that in Eq. (8.4) has been put forward by Hänggi, Grabert, Talkner, and Thomas (1984). Recently, this scheme has been applied to a realistic model for Landauer's tunnel diode (Hänggi and Jung, 1988).

2. Nonequilibrium chemical reaction

An example of a nonequilibrium chemical reaction with two locally stable steady states is provided by the second Schlögl model (Schlögl, 1972):

$$A+2X \leftrightarrows 3X , \tag{8.6a}$$

$$B+X \leftrightarrows C , \tag{8.6b}$$

where the concentrations of the species A, B, and C are held fixed, while the concentration of X is allowed to vary. This autocatalytic reaction can be described by a birth-and-death process [Eq. (8.1)] for the number $N \geq 0$ of molecules of species X with birth and death rates determined by the reaction scheme of Eq. (8.6) (McQuarrie, 1967). In this case the system size Ω is given by the reaction volume, and within the asymptotic regime $\Omega \to \infty$ the transition (forward) rate between the different locally stable states is again of the form in Eqs. (8.4) and (8.5) (see also Janssen, 1974; Matheson, Walls, and Gardiner, 1975; Kottalam and Hunt, 1984).

B. Brownian motion in biased periodic potentials

A well-known case of stationary nonequilibrium is that of Brownian motion subject to an external force in a nonconfining potential $U(x)$. In particular, the driven Brownian motion in a periodic potential has a broad variety of applications in physics and engineering sciences (see, for example, Risken, 1984). For the sake of definiteness we shall consider a Brownian particle moving in a tilted periodic potential (see Fig. 29).

In dimensionless variables (see p. 286 in Risken, 1984) the Langevin equations for a particle of unit mass read

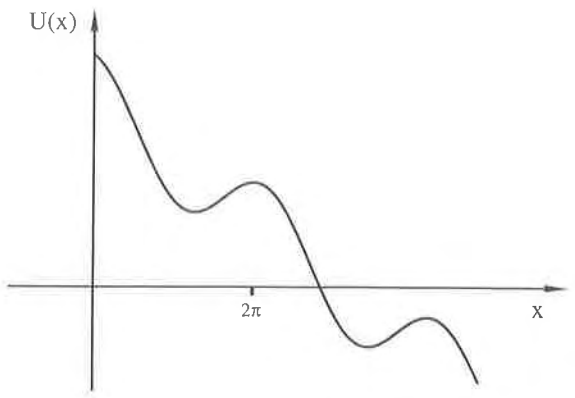

FIG. 29. Form of the biased periodic potential used in text. Note that the states x and $x+2\pi$ are considered distinguishable.

$$\dot{x}=v , \tag{8.7a}$$

$$\dot{v}=-\frac{\partial f(x)}{\partial x}+F-\gamma v+(2\gamma\theta)^{1/2}\xi(t) , \tag{8.7b}$$

$$\langle \xi(t)\xi(s)\rangle=\delta(t-s) , \tag{8.7c}$$

where the dimensionless constants F, γ, and θ measure the constant bias yielding the tilt, the damping constant, and the temperature, respectively. The periodic part of the potential $f(x)$ has a period of 2π and exactly one minimum in each period. Let us first look qualitatively at the possible types of deterministic attractors as a function of the bias F and the damping constant γ. For a more detailed account see Andronov, Vitt, and Khaikin (1966) and Falco (1976). After that we shall consider the influence and the consequences of low-intensity noise $\xi(t)$.

Obviously for a bias larger than some critical value, $F>F_c$, the only stable motion is that in which the particle runs down the monotonically declining potential with periodically varying velocity (see Fig. 30). Clearly this attractor has the whole phase space as a basin of attraction.

If F is lowered beyond the critical value F_c, the potential shows a minimum within each period corresponding to a locally stable attractor, referred to hereafter as a locked state. Each of these attractors has a domain of attraction. If the bias F is sufficiently small, or the damping γ sufficiently large, there are no other attractors, and the basins of attraction of the locked solutions form parallel strips covering the whole phase space (see Fig. 31).

Note that there are no triple points at which more than two basins meet. For larger forces but with $F<F_c$, and sufficiently small damping rates γ, the upper parts of these strips merge to form the basins of attraction of a running state, whereas the remaining lower parts disintegrate into tadpolelike basins of attraction of locked states, separated by parts of the phase space that are attracted by the running state (see Fig. 32). Note that again there are no triple points. Figure 33 is a phase dia-

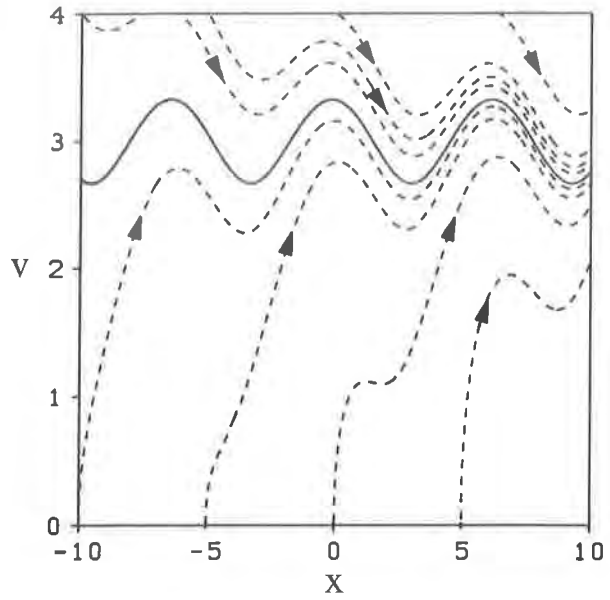

FIG. 30. Sketch of an attracting running state (solid line) above the critical bias $F > F_c$. The whole phase space forms the basin of attraction for the running state. Some typical deterministic trajectories approaching the running state are depicted by the dashed lines.

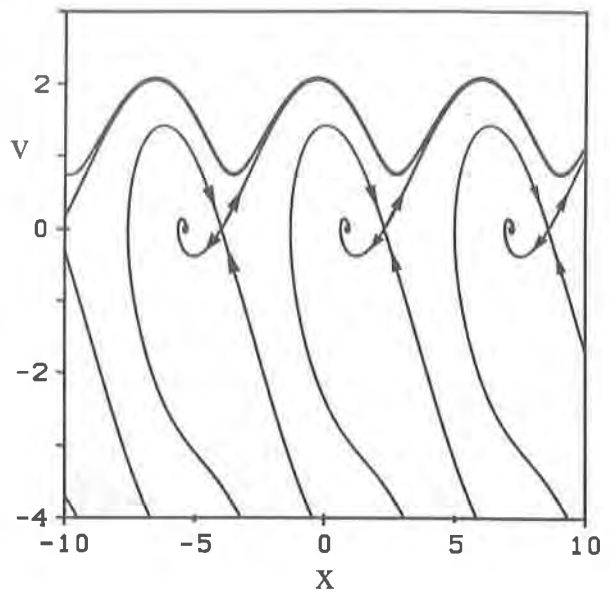

FIG. 32. Regions of deterministically attracting domains among coexisting locked states (tadpolelike regions) separated from the domain of attraction of the coexisting running state, which is present at sufficiently weak damping.

gram showing qualitatively the regions of the monostable running solution (1), the coexisting running and locked solutions (2), and the coexisting locked solutions (3).

In both regions exhibiting multistability, fluctuating forces lead to finite-transition rates between the coexisting states—generally, two different rates in each region. In region (3) both rates characterize transitions between neighboring locked states, one to a state with lower energy, the other to a state with higher energy. In region (2) one rate belongs to the transition from a locked to a running state and the other to the transition in the opposite direction. In a layer at the boundary of regions (2) and (3) more complicated correlated transitions to farther than nearest-neighbor states may occur (Ryter and Meyer, 1978). We shall not consider these events any further.

Let us now consider the corresponding rates in more detail as far as they are known in the literature. As we have already emphasized at the beginning of this section, for both the flux-over-population method and the mean first-passage time a stationary solution of the Fokker-Planck equation must be known. This solution need not

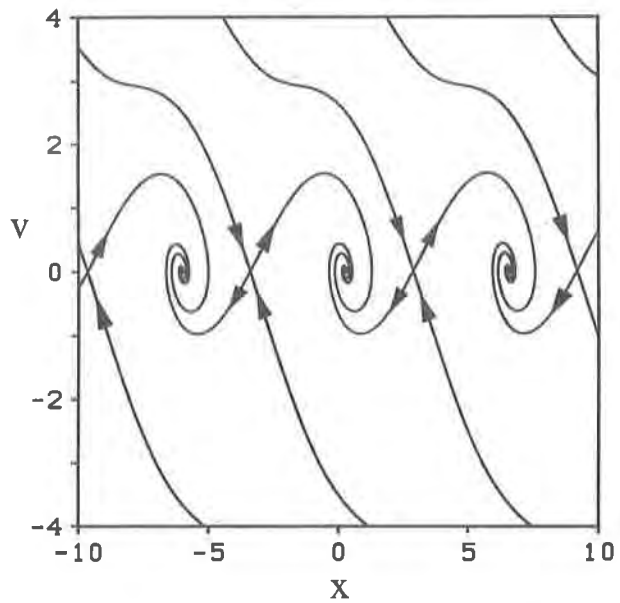

FIG. 31. Regions of deterministically attracting domains of coexisting locked states at $F < F_c$.

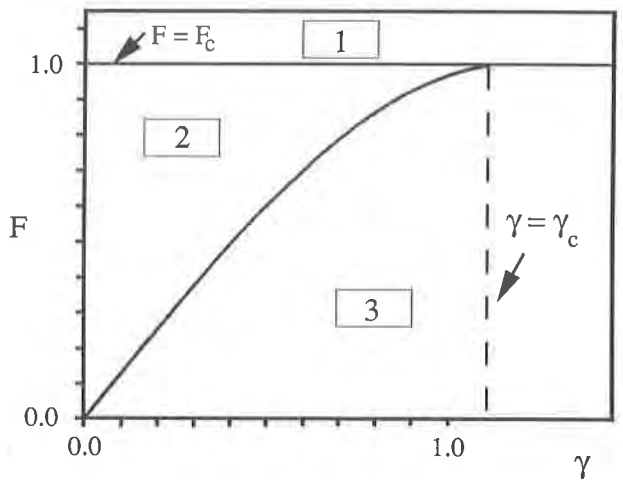

FIG. 33. Phase diagram showing the various regions with stable solutions as a function of the external bias F vs damping γ: region 1, monostable running state; region 2, coexisting running and locked states; region 3, coexisting locked states.

define a proper probability density on the whole state space, but need only be normalizable on the domain of attraction of the initial state. For transitions out of a locked state such a stationary solution is obviously given by

$$w(x,v)=Z^{-1}\exp\{-[\tfrac{1}{2}v^2+U(x)]/\theta\} , \tag{8.8}$$

where $U(x)$ is the nonperiodic potential that includes the external bias,

$$U(x)=f(x)-Fx . \tag{8.9}$$

The transition rate out of a locked state is then given by Eq. (4.33), where the frequencies ω_0 and ω_b are determined by the square roots of the potential $U(x)$ at one of its local minima and maxima, respectively, and the barrier height is given by the potential difference between a minimum and the lower neighboring maximum. For the particular choice of a sinusoidal potential

$$U(x)=-\cos x-Fx , \tag{8.10}$$

Büttiker, Harris, and Landauer (1983) obtained

$$\omega_0^2=\omega_b^2=(1-F^2)^{1/2} , \tag{8.11}$$

$$E_b=2(1-F^2)^{1/2}-2F\arccos F . \tag{8.12}$$

This rate expression from an initially locked state holds true independently of whether the final state is locked or running, i.e., in both regions (2) and (3). In region (3) there is, in addition, a rate to the neighboring state with higher potential $U(x)$, which is exponentially smaller by a factor $\exp(-2F\arccos F/\theta)$. Just as for the original Kramers model with *a large* damping constant γ, the rate out of a locked state in the overdamped limit may also be obtained from a Smoluchowski equation for the coordinate x [Eq. (4.54)] (Stratonovich, 1967; Ambegaokar and Halperin, 1969). Clearly, this limiting case can only be observed in region (3). The other limit of extremely weak damping with finite temperature is mainly relevant in region (2). The rate out of the locked state is then limited by the diffusion of the action of the undamped deterministic motion. As in the original Kramers case this rate is given by Eq. (4.49). In the limit of weak confining wells of the sinusoidal potential $U(x)$ [Eq. (8.9)], i.e., for forces approaching the critical value $F\to F_c=1$, with $F<1$, the relevant action at the barrier energy I_b reads (Büttiker, Harris, and Landauer, 1983)

$$I_b=\tfrac{24}{5}[2(1-F)]^{5/4} . \tag{8.13}$$

For transitions from a running to a locked state, i.e., in region (2), two different regimes must be distinguished, one an action-diffusion-limited regime at extremely weak damping and finite temperatures, and the other a phase-space-diffusion-limited regime at finite damping rates and sufficiently low temperatures (see Sec. IV.C). For the action-diffusion-limited rate from a running to a locked state, Ben-Jacob, Bergman, Matkowsky, and Schuss (1982) obtained the result

$$k=\frac{\gamma}{\sqrt{\pi}}(E_b^R/\theta)^{1/2}\exp(-E_b^R/\theta) , \tag{8.14}$$

where the barrier height relative to the running state is given by

$$E_b^R=\frac{1}{2}\left[\frac{F}{\gamma}-\frac{4}{\pi}\right]^2 . \tag{8.15}$$

From the lowest nonvanishing eigenvalue of an approximate Fokker-Planck equation describing the energy diffusion, Jung and Risken (1984) obtained a different result [Eq. (5.25b) in Jung and Risken (1984)], for the same rate; their result agrees with that of Ben-Jacob *et al.* (1982) *only in the limit of a small bias F*. In accordance with this observation Graham and Tel (1986) pointed out that the approximate WKB-type expansion of the stationary probability density on which the rate expression, Eq. (8.14), is based can only hold true if both the damping constant γ and the bias F are sufficiently small with a finite ratio for F/γ. In the other limiting cases $F\to 1$, $\gamma\to 0$, Cristiano and Silvestrini (1986) obtained a rather involved expression for the rate. Some quantum corrections in these limiting regimes have been discussed recently by Melnikov and Sütö (1986), Zwerger (1987), and Chen, Fisher, and Leggett (1988).

Finally, we note that closed-form rate expressions from a running to a locked state in the regime of intermediate bias, and outside the action-diffusion-limited regime, are still unknown. For some numerical studies within these various regimes, see Vollmer and Risken (1983), Jung and Risken (1984), and Kautz (1988).

C. Escape driven by colored noise

As we have noted in Secs. III.C and VI.C, correlated thermal noise, which via the fluctuation-dissipation theorem induces memory friction $\gamma(t)$ [see Eq. (3.33)], can substantially modify the transmission coefficient [see Eqs. (3.31) and (3.46)]. In contrast to Secs. III.C and VI.C *our focus here is on correlated noise in nonthermal systems.* In this latter case, there no longer exists a relationship between friction and noise correlation, and moreover, the stationary probability is no longer of canonical form. The study of realistic noise sources with a finite noise correlation time τ_c, i.e., "colored noise," in nonlinear stationary nonequilibrium systems has recently attracted rapidly growing interest (see, for example, the contributions in Moss and McClintock, 1989). Compared to the thermal case, the role of colored noise in stationary nonequilibrium systems is more complex; it not only crucially affects the dynamic properties, but even strongly affects the form of the *stationary probability.* Due to the lack of a detailed balance symmetry this stationary nonequilibrium probability cannot in most cases be expressed in analytical form. The archetypal situation is a nonequilibrium Ginzburg-Landau-type bistable stochastic dynamics first worked out by Hänggi, Marchesoni, and Grigolini (1984). In terms of dimensionless

variables (Jung and Hänggi, 1988), we consider a symmetric, bistable potential $U(x)=-\frac{1}{2}x^2+\frac{1}{4}x^4$, driven by Gaussian, exponentially correlated noise of zero mean,

$$\dot{x}=x-x^3+\varepsilon(t)\ , \tag{8.16a}$$

with correlation

$$\langle\varepsilon(t)\varepsilon(s)\rangle=\frac{D}{\tau}\exp(-|t-s|/\tau)\ . \tag{8.16b}$$

Throughout this section we denote the noise correlation time τ_c simply by $\tau_c\equiv\tau$. Alternatively, this one-dimensional non-Markovian flow can be embedded into a two-dimensional Markovian flow of the form (Hänggi, Marchesoni, and Grigolini, 1984)

$$\dot{x}=x-x^3+\varepsilon,\quad \dot{\varepsilon}=-\varepsilon/\tau+D^{1/2}\tau^{-1}\xi(t)\ , \tag{8.17}$$

where $\xi(t)$ is Gaussian white noise of zero mean and correlation $\langle\xi(t)\xi(s)\rangle=2D\delta(t-s)$, and where $\varepsilon(t)$ is prepared with a stationary Gaussian probability of vanishing mean. For $\tau\to 0$, $\varepsilon(t)$ itself becomes white noise and the escape is governed by the (Markovian) Smoluchowski equation (4.9), with the corresponding rate given by Eqs. (4.56c) and (4.57). The early work of Hänggi, Marchesoni, and Grigolini (1984) stimulated further research into the effects of finite noise color of various correlation times τ upon the stationary and dynamic properties of nonthermal nonlinear systems. These recent efforts not only make use of approximate theory (see the many references cited in Jung and Hänggi, 1988), but also include precise numerical methods (Jung and Hänggi, 1988), precise simulation techniques (Fox, 1989), and analog simulation techniques (Hänggi, Mroczkowski, Moss, and McClintock, 1985; Moss *et al.*, 1986).

We confine ourselves here to a discussion of the colored noise modified escape rate. In this case, the approximate theories work best for the regime of low ($\tau\to 0$) and extremely high ($\tau\to\infty$) noise color. The theory at low noise color is nontrivial due to the *presence of two small parameters,* the weak noise strength D and the noise color τ, and the asymptotic result for the rate depends on how the limits $\tau\to 0$ and $D\to 0$ are taken. If we denote the Smoluchowski rate [Eq. (4.54)] at $\tau=0$ by

$$k_s=(\pi\sqrt{2})^{-1}\exp\left[-\frac{1}{4D}\right][1+O(D)]\ ,$$

we find at low noise color $\tau\to 0$ (Hänggi, Marchesoni, and Grigolini, 1984; Luciani and Verga, 1987, 1988; Dygas, Matkowsky, and Schuss, 1988; Bray and McKane, 1989; see Fig. 34)

$$k(\tau)=k_s\{1-\tau[\tfrac{3}{2}+O(D)]\}\exp\left[-\frac{\tau^2}{8D}+\frac{3\tau^4}{10D}+O(\tau^6/D)\right],\quad \tau\ll 1\ , \tag{8.18}$$

which for $(\tau/D)\ll 1$ reduces to (Hänggi, Marchesoni, and Grigolini, 1984),

$$k(\tau)=k_s(1-\tfrac{3}{2}\tau),\quad \tau/D\ll 1\ . \tag{8.19}$$

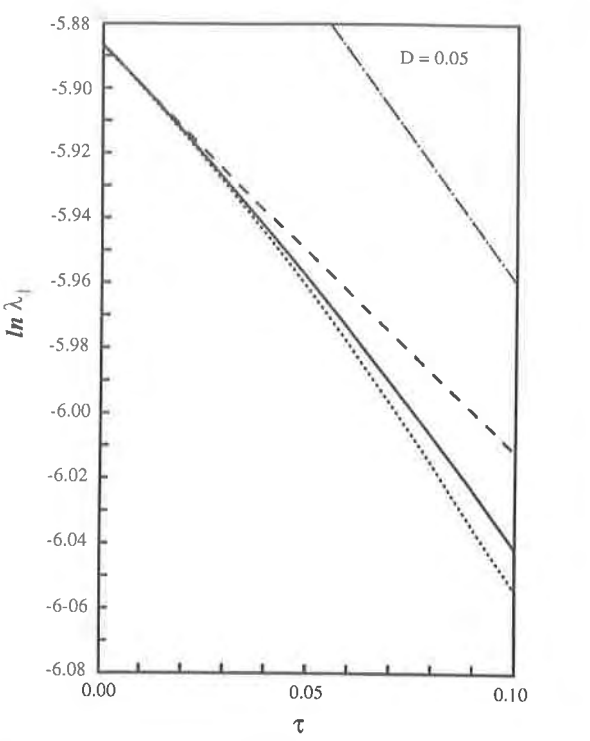

FIG. 34. Behavior of the smallest positive-valued eigenvalue $\lambda_1(\tau)=2k(\tau)$ of the equivalent exact, two-dimensional Fokker-Planck system, Eq. (8.17), at low noise correlation times τ: solid line, numerical result obtained via an improved matrix-continued fraction method (Jung and Hänggi, 1988); dashed line, numerical evaluation of $\lambda^{\mathrm{EFP}}(\tau)$ of the one-dimensional effective Fokker-Planck (EFP) approximation of Fox (1988); dotted line, numerical evaluation of $\lambda^{\mathrm{EFP}}(\tau)$ of the one-dimensional, standard small-τ EFP approximation (Hänggi, Marchesoni, and Grigolini, 1984); dot-dashed line, steepest-descent result in Eq. (8.19).

This latter result has been recovered in a multitude of later studies; see, for example, the various references given in Jung and Hänggi (1988).

With increasing noise color a crossover occurs with a characteristic exponential (τ/D) dependence [see Fig. 35] (Hänggi, Mroczkowski, Moss, and McClintock, 1985; Leiber, Marchesoni, and Risken, 1988; Jung and Hänggi, 1988),

$$k(\tau)\propto\exp(-\alpha\tau/D),\quad 0.2<\tau<1.5\ , \tag{8.20}$$

with $\alpha\simeq 0.10$. Upon further increasing the noise color $\tau\to\infty$, we find that this exponential characteristic behavior undergoes yet another, slowly varying crossover to an asymptotic ($\tau\to\infty$) regime given by (Luciani and Verga, 1987, 1988; Jung and Hänggi, 1988; Tsironis and Grigolini, 1988; Hänggi, Jung, and Marchesoni, 1989)

$$k(\tau)\propto\exp\left[-\frac{2\tau}{27D}\right],\quad \text{as } \tau\to\infty,\ D\to 0\ . \tag{8.21}$$

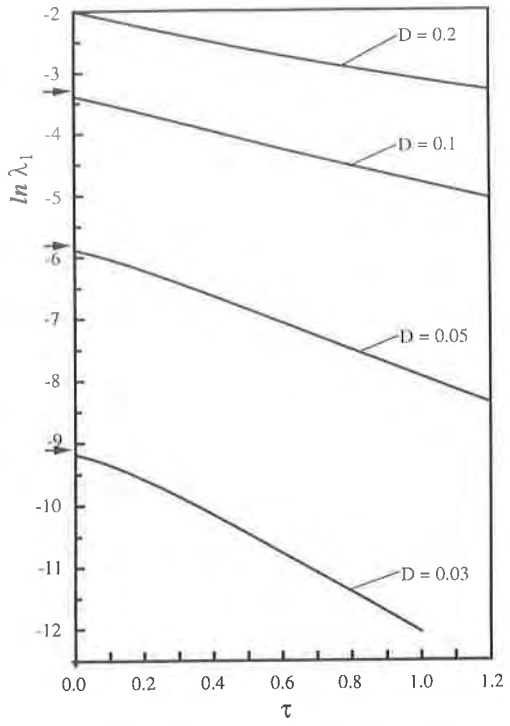

FIG. 35. Plot of the lowest eigenvalue $\lambda_1(\tau)=2k(\tau)$ at small-to-moderate noise color $\tau \leq 1.2$ for various noise strengths D. The arrow indicates the steepest-descent approximation of the Smoluchowski rate k_S at zero noise color. After Jung and Hänggi (1988).

A more detailed study of high noise color exhibits quite a few interesting and unexpected features. For example, the separatrix of Eq. (8.17) shows a cusplike behavior as $\tau \to \infty$, and the most probable point of escape is shifted away from the deterministic saddle point located at $x=0$ (Hänggi, Jung, and Marchesoni, 1989). Moreover, with increasing noise correlation times the two-dimensional stationary probability $p_{st}(x,\varepsilon)$ undergoes a topological change near the origin (Marchesoni and Moss, 1988; Debnath *et al.*, 1989; Hänggi, Jung, and Marchesoni, 1989) where the deterministic saddle point, located at $x=0$, $\varepsilon=0$, is replaced by a pair of off-axis saddles, implying a "hole" for the two-dimensional stationary probability around the origin $x=\varepsilon=0$. For the rate itself one finds in the asymptotic regime more accurately (Jung and Hänggi, 1988; Hänggi, Jung, and Marchesoni, 1989)

$$k(\tau)=[54\pi D(\tau+\tfrac{1}{2})]^{-1/2}\exp\left[-\frac{1}{4D}(\tfrac{4}{9}+\tfrac{8}{27}\tau)\right], \quad \text{as } \tau\to\infty \ . \tag{8.22}$$

The escape time to the separatrix, i.e., $T(\tau)=\frac{1}{2}k^{-1}(\tau)$ in the physically relevant regime of small-to-moderate noise color τ, is depicted for the noise strength $D=0.1$ in Fig. 36.

In order to overcome some of the difficulties that plague the analytical evaluation of statistical properties of realistic nonequilibrium flows driven by colored noise,

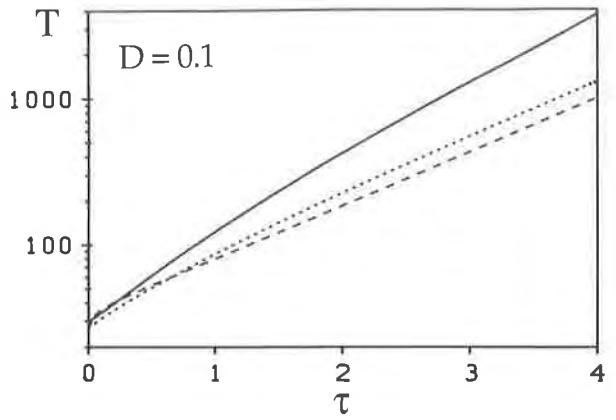

FIG. 36. The escape time $T(\tau)$ to the separatrix vs the noise correlation time τ at weak-to-moderately-strong noise color: solid line, numerical result (Jung and Hänggi, 1988; Jung, Hänggi, and Marchesoni, 1989); dotted line, bridging expression based on the theory of Luciani and Verga (1987, 1988); dashed line, bridging formula due to Tsironis and Grigolini (1988).

an idealized correlated-noise source, namely, two-state noise (Klyatskin, 1977; Lefever *et al.*, 1980) has been introduced. For flows driven by such strongly simplified noise, which, nevertheless, may model electronic, optical, or chemical bistable nonequilibrium reactions, the corresponding rates of escape can be calculated up to simple quadratures (Hänggi and Riseborough, 1983; Van den Broeck and Hänggi, 1984; Balakrishnan *et al.*, 1988; L'Heureux and Kapral, 1988).

D. Nucleation of driven sine-Gordon solitons

In Sec. IV.F we presented the field-theoretical approach (Langer, 1969) to thermal escape problems in the presence of many particles or dimensions. This field-theoretic approach is particularly suitable for describing nucleation phenomena in metastable systems, such as condensation in supersaturated vapors (Langer and Turski, 1973; Langer, 1980) or the decay of the persistent current in a filamentary superconductor (McCumber and Halperin, 1970). In contrast to the classical approach to nucleation, i.e., the kinetics of cluster formation (Farkas, 1927; Becker and Döring, 1935; Zeldovich, 1943; Frenkel, 1955; Feder *et al.*, 1969; Zinsmeister, 1970), a field-theoretic approach does not make any *ad hoc* assumptions regarding the overall fluctuation rate that drives the nucleation process. In this context we also point out that a direct experimental check of the nucleation rate predictions of the two theoretical approaches is difficult because of the simultaneous presence of droplet growth and droplet formation (Binder and Stauffer, 1976; Langer, 1980). In particular, the growth process is diffusion controlled and thus becomes very slow near critical points. Here we consider a simpler situation, namely, nucleation phenomena in one space dimension only, thereby avoiding the problem of critical phenomena. In contrast to our discussion of thermal nucleation in Sec. IV.F, howev-

er, we consider here an infinite number of particles in a biased periodic potential, *implying stationary nonequilibrium,* typified by a driven, damped sine-Gordon field $\theta(x,t)$. Such systems are of physical interest in dislocation theory (Seeger and Schiller, 1966), charge-density waves in dielectrics, pulses in optical fibers, or Josephson transmission lines, to name but a few (Scott *et al.,* 1973; Dodd *et al.,* 1982). Because the classical sine-Gordon equation does not exhibit an intrinsic scale, we use the damped sine-Gordon dynamics in a form with a unit speed for the sound velocity of the free string,

$$\frac{\partial^2\theta}{\partial t^2}-\frac{\partial^2\theta}{\partial x^2}+\omega_0^2\sin\theta=-\alpha\frac{\partial\theta}{\partial t}-F+\xi(x,t)\ , \tag{8.23}$$

where $\xi(x,t)$ is a Gaussian fluctuating field of vanishing mean and correlation,

$$\langle\xi(x,t)\xi(x',t')\rangle=2\alpha k_BT\delta(t-t')\delta(x-x')\ , \tag{8.24}$$

and F, α, and ω_0 denote the external bias, the friction coefficient, and an amplitude scale.

1. Nucleation of a single string

We first consider the case of the nucleation of a single kink-antikink pair, which proceeds without perturbation due to other nucleating pairs. Throughout the following we shall restrict the discussion to the *overdamped limit,*

$$\alpha\gg\omega_0\ . \tag{8.25}$$

Under this restriction a kink-antikink collision within the region of multistability, $F/\omega_0^2<1$, always becomes destructive (Pederson *et al.,* 1984). Let n_0 denote the steady-state kink density and τ_F be the mean lifetime of a kink, which Hänggi, Marchesoni, and Sodano (1988) evalauated as

$$\tau_F=\frac{D}{u_F^2}\left\{-1+\left[1+\left[\frac{u_F}{Dn_0}\right]^2\right]^{1/2}\right\}\ . \tag{8.26}$$

Here $D=k_BT(8\alpha\omega_0)^{-1}$ and u_F is the propagation velocity of a driven kink. For bias forces exceeding the thermal threshold value F_T, i.e., with

$$F_c>F\gg F_T=k_BTn_0/(2\pi)\ , \tag{8.27}$$

the nucleating kink and antikink gain an energy larger than k_BT moving away from each other prior to annihilation, and thus they *do not strongly interact* with other nucleating pairs. $F_c=\omega_0^2$ denotes the critical bias below which one observes multistability. With the nondiffusive, ballistic limit for the mean lifetime given by

$$\tau_F\to\tau_0=(u_Fn_0)^{-1},\quad F\gg F_T\ , \tag{8.28}$$

the nucleation per unit length becomes

$$k_0=2n_0/\tau_0=2u_Fn_0^2\ . \tag{8.29a}$$

Under these assumptions Eq. (8.29a) becomes equivalent with Langer's expression [Eq. (4.83), (Hänggi, Marchesoni, and Sodano, 1988),

$$k_0=\frac{\lambda_+}{\pi k_BT}\mathrm{Im}\mathcal{F}\ , \tag{8.29b}$$

where Im $\mathcal{F}$ is the imaginary part (per unit length) of the energy of the metastable critical nucleus configuration and λ_+ denotes the (positive-valued) growth rate which corresponds to the saddle-point configuration of the nucleus. This noninteracting, single-string nucleation rate was originally studied by Petukhov and Pokrovskii (1972) and independently by Büttiker and Landauer (1981). Equation (8.29b) can be evaluated analytically in various limits. At strong fields one obtains (Petukhov and Pokrovskii, 1972; Büttiker and Landauer, 1981)

$$k_0=(2\pi)^{-3/2}\tfrac{5}{2}(15)^{1/2}\frac{\omega_0^3}{\alpha}\left[1-\left[\frac{F}{\omega_0^2}\right]^2\right]^{3/2}\left[\frac{2E_F}{k_BT}\right]^{1/2}\exp(-2\beta E_F),\quad\frac{1}{2}<\frac{F}{\omega_0^2}<1\ , \tag{8.30}$$

where $2E_F$ denotes the activation energy for nucleation E_N, approximately given by (Hänggi, Marchesoni, and Sodano, 1988)

$$E_N\equiv2E_F=2E_0\left\{1+\frac{\pi}{8}\frac{F}{\omega_0}\left[\ln\left[\frac{\pi F}{16\omega_0^2}\right]-1\right]\right\},\qquad\frac{F}{\omega_0^2}<0.9\ . \tag{8.31}$$

Here $E_0=8\omega_0$ denotes the rest energy of an undriven kink. At weaker fields, Hänggi, Marchesoni, and Sodano evaluated the nucleation rate analytically as

$$k_0=\frac{\omega_0^2}{\pi\alpha}(2F)^{1/2}\left[\frac{E_F}{k_BT}\right]^{1/2}\exp(-2\beta E_F)\ ,\qquad\frac{1}{2}>\frac{F}{\omega_0^2}>\frac{k_BT}{E_0}\ . \tag{8.32}$$

At even weaker fields obeying

$$\frac{F_T}{\omega_0^2}\ll\frac{F}{\omega_0^2}<\frac{k_BT}{E_0}\ , \tag{8.33}$$

the nucleus attains a rather broad extension, thereby

yielding an additional "breathing mode" contribution (Weiss, Grabert, Hänggi, and Riseborough, 1987). This breathing mode is characterized (apart from the ever-present exact Goldstone mode with eigenvalue zero) by a second, near-zero eigenvalue corresponding to a quasi-zero mode. Accounting explicitly for the Goldstone mode and this breathing mode contribution in Eq. (8.29b), one finds (Hänggi, Marchesoni, and Sodano, 1988)

$$k_0=\omega_0\frac{F}{\alpha}\frac{E_F}{k_BT}\exp(-2\beta E_F)\ , \qquad \frac{F_T}{\omega_0^2}\ll\frac{F}{\omega_0^2}<\frac{k_BT}{E_0}\ , \tag{8.34}$$

i.e., the nucleation rate per unit length is now *proportional to the external bias F,* and in addition becomes proportional to the inverse temperature T.

2. Nucleation of interacting pairs

The nucleation rate in Eq. (8.29b) can be pictured as the escape of a "single" particle, characterizing the profile of the forming nucleus, over a potential barrier $E_N=2E_F$ into the vacuum, i.e., the effect of a finite lifetime plays a subordinate role when $F\gg F_T$. At exponentially weak fields, however, the propagation velocity $u_F\simeq\frac{1}{4}\pi F/(\omega_0\alpha)$ falls below the diffusive limit

$$u_F\ll Dn_0\ , \tag{8.35}$$

so that the production rate of kink-antikink pairs becomes controlled by the *diffusive lifetime* τ_D, i.e., using Eq. (8.26) one finds with Eq. (8.35)

$$\tau_F\to\tau_D=(2Dn_0^2)^{-1},\quad F\ll F_T\ . \tag{8.36}$$

The production rate of thermal kink-antikink pairs per unit length is then given by the ratio of twice the steady-state kink density n_0 over the kink mean lifetime τ_D (Hänggi, Marchesoni, and Sodano, 1988),

$$k_D=4Dn_0^3=\left[\frac{2}{\pi}\right]^{3/2}\omega_0^2\left[\frac{E_F}{2\alpha}\right](\beta E_F)^{1/2}\exp(-3\beta E_F)\ , \qquad F\ll F_T\ , \tag{8.37}$$

where we have used the steady-state density given by

$$n_0=\left[\frac{2}{\pi}\right]^{1/2}\omega_0\left[\frac{E_F}{k_BT}\right]^{1/2}\exp(-\beta E_F),\quad \frac{F}{\omega_0^2}<\frac{k_BT}{E_0}\ . \tag{8.38}$$

With $F\ll F_T$, n_0 essentially equals the thermal equilibrium density, $n_{eq}=n_0(F=0)$. Upon a comparison of Eq. (8.37) with Eqs. (8.30), (8.32), and (8.34), we note that the diffusive limit now involves *three times the rest energy of a driven kink.*

The various results given in this subsection should be of relevance both for experiments in extended Josephson-junction systems, and for the interpretation of finite-temperature simulations of general kink-antikink pair-production processes (Bochkarev and Forcrand 1989; Marchesoni, 1990).

IX. QUANTUM RATE THEORY

In this section we report on the present status of quantum rate theory, which has seen important and intriguing developments in recent years.

A. Historic background and perspectives; traditional quantum approaches

In the previous sections our focus was on noise-activated escape from a metastable state in the classical regime, and no efforts were made to account for the effect of quantum-mechanical tunneling (see Fig. 37). As one lowers the temperature, however, the metastable state is rendered progressively less stable by such quantum-mechanical tunneling processes (see Fig. 2).

The tunnel effect was recognized long ago, during the heyday of quantum mechanics. The first to introduce tunneling was Friedrich Hund (1927), who demonstrated that quantum tunneling describes the intramolecular rearrangements in pyramidal molecules such as ammonia, as manifested by tunnel splittings of vibrational spectra. It is interesting to note that the problem of pyramidal molecules, i.e., the question of *delocalized* ground states (e.g., for ammonia NH_3) versus *localized* ground states (e.g., in AsH_3) continues to be an area of active research (Primas, 1978; Wooley, 1978; Pfeifer, 1982, 1983; Claverie and Jona-Lasinio, 1986). The tunneling mechanism became a well-known effect shortly afterward when Oppenheimer (1928a, 1928b) employed it for the description of the ionization of atoms in intense electric fields, Fowler and Nordheim (1928) used it for the electric field emission of electrons from cold metals, and Gamow (1928) as well as Gurney and Condon (1928,

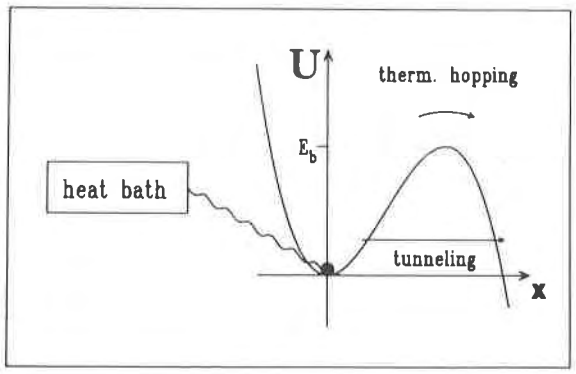

FIG. 37. Escape of a particle from a metastable state. The particle can leave the well minimum either via thermal activation over the barrier or via tunneling through the classically forbidden regime. The interaction between the particle and the thermal environment is modeled by frictional forces.

1929) invoked it to explain the radioactive decay of nuclei. Quantum-mechanical tunneling entered the field of reaction rates with the pioneering study by Bourgin (1929), which was continued by Wigner (1932), who evaluated up to order $(\hbar^2)$ the quantum corrections to the Boltzmann-averaged flux through a parabolic potential barrier. Since then, the tunneling mechanism has been invoked and developed further in a multitude of fields, encompassing biology, electronic devices, crystalline and amorphous solids, and tunneling microscopy, to name but a few (for a survey see Jortner and Pullman, 1986).

Our focus here is on *tunneling in the presence of dissipation* (Feynman and Vernon, 1963; Brink, Neto, and Weidenmüller, 1979; Möhring and Smilansky, 1980; Caldeira and Leggett, 1981, 1983). This area of research has been stimulated considerably by Leggett's (1980, 1984a, 1986) initial discussion of quantum mechanics and realism at the macroscopic level, and also by developments in describing the fusion and deep-inelastic collisions of heavy ions (e.g., Brink *et al.*, 1979; Möhring and Smilansky, 1980; Balantekin and Takigawa, 1985).

The publication of the Einstein-Podolsky-Rosen paradox (1935) triggered Schrödinger's (1935) "Generalbeichte" (general confession) on the status of quantum mechanics. Best known from this article is the paradox of Schrödinger's cat, in which he illustrates the indecisiveness of observations that is possible in quantum mechanics. To this end he links the life of a cat, to which so many of us are compassionate, with the state of a radioactive nucleus. In this way he "infects" the cat with the quite common uncertainty of the subatomic world. Specifically, the linear structure of quantum mechanics seems to contradict our common sense, which is not ready to accept that a cat can be in a combination of "dead and alive" for an appreciable time (the half-life of a nucleus whose decay triggers a device which then kills the cat), while at the same time we are ready to accept the analogous situation for the atomic nucleus.

In recent years it has become feasible to construct laboratory cousins of Schrödinger's cat by observing the quantum mechanics of macroscopic quantum variables such as the decay of a zero-voltage state in a biased Josephson junction, or fluxoid quantum transitions in a superconducting quantum interference device. This area of research is now known as macroscopic quantum mechanics (Leggett, 1980, 1984a, 1986; Caldeira and Leggett, 1981, 1983a; Grabert, Olschowski, and Weiss, 1987; Hänggi 1986a, 1986b, 1987; Leggett *et al.*, 1987; Weiss, Grabert, Hänggi, and Riseborough, 1987).

As with many developments, the problem of tunneling in the presence of a coupling to many degrees of freedom such as phonons, magnons, and the like, thereby giving rise to quantum friction for the metastable configuration coordinate, has several precursors. Tunneling in the presence of phonon modes is naturally a well-studied problem in solid-state physics. Early studies of phonon effects on tunneling include, among others, those by Pirc and Gosar (1969), Sander and Shore (1969), and Sussmann (1971). Actually some of these authors may have overlooked the full relevance of Holstein's (1959a, 1959b; Emin and Holstein, 1969) early multiphonon treatment (of the polaron problem) for this topic. Further work on the tunneling mechanism in the presence of phonon couplings includes, among others, that of Flynn and Stoneham (1970), Hopfield (1974), Phillips (1976), Sethna (1981, 1982), Riseborough (1983, 1984), Kassner and Reineker (1986a, 1986a), and Skinner and Hsu (1986). In many of these approaches it was necessary to make the so-called "Condon approximation," i.e., that the tunneling matrix element is independent of the phonon positions. The merits and shortcomings of the early approaches have been beautifully discussed in Sethna's articles (1981, 1982).

As can be noted from the classical rate formula of Van't Hoff (1884) and Arrhenius (1889) [Eq. (1.1)], one finds a vanishing rate as the temperature is lowered to absolute zero. A crude but frequently employed rate formula for the full rate k is obtained by adding to the classical rate $k_{\rm cl}$ a Gamow-type tunneling rate at zero temperature; the total rate is written as

$$k = k_{\rm cl} + k_{\rm qm} \tag{9.1}$$

(see, for example, Bell, 1980). The basic reasoning behind this formula is that quantum effects open a new channel for barrier crossings, thus enhancing the rate above the corresponding classical value. Moreover, following Wigner (1932), we incorporate temperature effects into the quantum rate in the absence of dissipation by averaging the undamped quantum transmission $t(E)$ with the canonical equilibrium probability (Bell, 1959, 1980; Affleck, 1981; Skodje and Truhlar, 1981). This procedure is analogous to the simple transition-state theory discussed in Sec. III.A and will therefore be termed "simple quantum TST." With Z_0 denoting the quantum partition function of the metastable state one obtains

$$k_{\rm qm}^{\rm TST} = Z_0^{-1}(2\pi\hbar)^{-1}\int_0^\infty dE\, t(E)\exp(-\beta E)\ . \tag{9.2}$$

Here we have measured energy from the well bottom.

The inclusion of dissipation in the quantum escape rate is certainly more subtle. Common approaches for obtaining the zero-temperature, undamped quantum rate are not readily extended to finite temperatures and cases with dissipation. These approaches include (a) the axiomatic S-matrix theory (Bohr and Mottelson, 1969; Fonda *et al.*, 1978), in which one associates quantum decay rates in a one-to-one correspondence with the poles of the S matrix close to the real axis on the unphysical sheet of the Riemann energy surface (provided that the S matrix can there be analytically continued) and (b) a time-dependent wave-function approach, whereby one considers the outgoing wave near a resonance energy (see, for example, Fuda, 1984), which in turn implies a typical time delay (as compared to the resonance-free situation) $t_D = 2/k_{\rm qm}$ in the arrival of the scattered wave. This delay is of the order of the inverse quantum rate.

A promising approach to quantum dissipation and finite temperatures is based on a dynamical semigroup approach for the evolution of the density operator (see, for example, Sinha, 1972; Gorini *et al.*, 1976; Alicki, 1977; and particularly Haake, 1973; Alicki and Lendi, 1987). This type of approach proved to be quite useful in describing damping phenomena in nonlinear optics (Haake, 1973; Agarwal, 1974; Sargent, Scully, and Lamb, 1974; Haken, 1975), as well as in spin-relaxation theory (Hynes and Deutch, 1975; Grabert, 1982). However, these semigroup methods treat the coupling to the environment perturbatively (weak-coupling regime). This severely restricts the method to the weak-damping regime, with the strongest damping γ typically obeying the inequalities

$$\gamma \ll \omega_0, \quad \hbar\gamma \ll k_B T \ . \tag{9.3}$$

Here ω_0 is the lowest frequency typical of reversible motions. Note that in a double-well system ω_0 may differ from zero just by the tunnel splitting; i.e., the first inequality of Eq. (9.3) is already violated for weak friction. Moreover, macroscopic quantum phenomena in superconducting Josephson tunnel junctions occur at extremely low temperatures (Eckern, Schön, and Ambegaokar, 1984; Leggett, 1986), so the second inequality is often violated for moderate amounts of dissipation. Further shortcomings of the semigroup approach have been discussed by Talkner (1986). This state of affairs calls for a more flexible and more accurate description of dissipation in quantum mechanics.

B. The functional-integral approach

As is widely appreciated, general tunneling problems can be investigated to advantage in terms of complex-time path integrals (Pechukas, 1969a, 1969b; McLaughlin, 1972; Miller, 1975; Coleman, 1977; Caldeira and Leggett, 1983a, 1983b; Weiss *et al.*, 1984, 1987; Hänggi, 1986b, 1987; Hänggi, Weiss, and Riseborough, 1986; Grabert, Olschowski, and Weiss, 1987; Grabert, Schramm, and Ingold, 1988). To achieve this objective it is convenient to employ the functional-integral representation of quantum mechanics (Feynman and Hibbs, 1965; Feynman, 1972; Schulman, 1981). We shall present here only a brief outline of the technique, from which we shall use some results later on, but refer the interested reader to the literature cited above.

Let us consider the partition function

$$Z = \mathrm{Tr}\{\exp(-\beta\mathcal{H})\} \ , \tag{9.4}$$

where $\mathcal{H}$ denotes the full Hamiltonian operator corresponding to the system plus environment, and Tr indicates the trace. Following Feynman (1972), this quantity can be expressed (without recourse to any obscure analytic continuation procedures) in the form of a (Euclidean) functional path integral over the tunneling coordinate $x(\tau)$,

$$Z = \int \mathcal{D}x(\tau) \exp\{-S_E[x(\tau)]/\hbar\} \ , \tag{9.5}$$

where $\tau =$ it is a real variable (Wick rotation). The integral in Eq. (9.5) runs over all paths that are periodic with period $\theta = \hbar\beta$. Each trajectory $x(\tau)$ is thus weighted by the Euclidean action S_E.

For our rate theory we also account for dissipation induced by the coupling of the tunneling coordinate $x(\tau)$ to other degrees of freedom. In doing so we start out from the functional-integral equation (9.5) in the full space of the system plus environment(s). Here we shall use a bilinear coupling mechanism between system and environment. Such a scheme results in a linear damping mechanism with an equation of motion of the form in Eq. (3.31). The effective Euclidean action corresponding to the Hamiltonian in Eqs. (3.29) and (3.30) *after integration over the bath modes* $\{q_i\}$ thus takes the form

$$\begin{aligned} S_E[x] &= S_E^{\mathrm{rev}} + S_E^{\mathrm{diss}} \\ &= \int_{-\theta/2}^{\theta/2} d\tau \{\tfrac{1}{2}M\dot{x}^2(\tau) + U[x(\tau)]\} \\ &\quad + \tfrac{1}{2}\int_{-\theta/2}^{\theta/2} d\tau \int_{-\theta/2}^{\theta/2} d\tau' k(\tau-\tau')x(\tau)x(\tau') \ . \end{aligned} \tag{9.6}$$

The first term describes the reversible motion in the metastable nonlinear potential $U(x)$, while the second, nonlocal part describes the influence of dissipation. The influence kernel $k(\tau)$ is periodic with period θ. It can therefore be represented in terms of a Fourier series as (Grabert and Weiss, 1984a; Grabert, Weiss, and Hänggi, 1984; Grabert, Olschowski, and Weiss, 1987; Grabert, Schramm, and Ingold, 1988)

$$k(\tau) = \frac{M}{\theta} \sum_{n=-\infty}^{\infty} |\nu_n| \hat{\gamma}(|\nu_n|) \exp(i\nu_n\tau) \ , \tag{9.7}$$

obeying

$$\int_{-\theta/2}^{\theta/2} k(\tau) d\tau = 0 \ . \tag{9.8}$$

Here $\nu_n = n2\pi/\theta$, and $\hat{\gamma}(z)$ is the Laplace transform of the memory friction in Eq. (3.34), that is $\hat{\gamma}(z) = \int_0^\infty \gamma(t)\exp(-zt)dt$. Note that the dissipative part of S_E is nonlocal even for strict, memory-free friction $\hat{\gamma}(z) = \gamma$. Moreover, the nonlocal action in Eq. (9.6) can by virtue of Eq. (9.8) also be recast as

$$S_E^{\mathrm{diss}} = -\tfrac{1}{4}\int_{-\theta/2}^{\theta/2} d\tau \int_{-\theta/2}^{\theta/2} d\tau' k(\tau-\tau')[x(\tau)-x(\tau')]^2 \ , \tag{9.9}$$

which reveals explicitly the translational invariance of the dissipative action. Other, formally equivalent, forms for the dissipative part S_E^{diss} have been used by Caldeira and Leggett (1981, 1983a), Weiss *et al.* (1984), and Riseborough, Hänggi, and Freidkin (1985). The form of the nonlocal kernel in Eq. (9.7) can also be directly related to the real-time memory friction $\gamma(t)$, i.e., from Eq. (9.7) one has with $\nu = \nu_1$ (Grabert, Olschowski, and Weiss, 1987)

$$k(\tau)=\frac{M}{\theta}\int_0^\infty ds\,\gamma(s)\frac{\partial}{\partial s}\left[\frac{\sinh(\nu s)}{\cos(\nu\tau)-\cosh(\nu s)}\right]$$
$$+M\gamma(0)\sum_{n=-\infty}^{\infty}\delta(\tau-n\theta)\,. \tag{9.10}$$

Instead of the Euclidean (imaginary-time) formulation, a real-time functional-integral formulation (Feynman and Vernon, 1963; Möhring and Smilansky, 1980; Schmid, 1982; Caldeira and Leggett, 1983b; Balantekin and Takigawa, 1985; Grabert, Schramm, and Ingold, 1988) can be invoked which is of relevance for *dissipative quantum coherence effects* as they typically occur in weakly damped double-well systems (Bray and Moore, 1982; Chakravarty, 1982; Chakravarty and Leggett, 1984, Leggett *et al.*, 1987; Weiss, Grabert, and Linkwitz, 1987; Weiss and Wollensak, 1989). Because our focus will be mostly on nonoscillatory, *incoherent quantum tunneling processes,* we shall not discuss the real-time functional-integral formalism further, but refer the interested reader to reviews given in the recent literature (Leggett *et al.*, 1987; Grabert, Schramm, and Ingold, 1988).

C. The crossover temperature

Upon a closer inspection of Fig. 2 one notices that the rate becomes controlled solely by quantum effects below a characteristic temperature. This crossover from the classical regime, where thermal activation events dominate over tunneling-induced transitions, is characterized within the semiclassical limit,

$$E_b/(\hbar\omega_0)\gg 1\,, \tag{9.11}$$

by a temperature T_0. This temperature will be found in terms of the complex-time path-integral methodology introduced in the previous section. The dominant contributions to the functional integral come from the vicinity of tunneling paths for which the action in Eq. (9.6) is stationary. The extremal action paths $x_e(\tau)$ obey the equation of motion

$$M\ddot{x}_e(\tau)-\frac{\partial U[x_e(\tau)]}{\partial x_e(\tau)}-\int_{-\theta/2}^{\theta/2}d\tau' k(\tau-\tau')x_e(\tau')=0\,, \tag{9.12}$$

with the periodic boundary condition

$$x_e(\tau=-\theta/2)=x_e(\tau=\theta/2)\,. \tag{9.13}$$

Thus we note that in the absence of dissipation, $\hat{\gamma}=0$, that is, $k(\tau)=0$, the evolution of $x_e(\tau)$ in imaginary time $t=-i\tau$ corresponds to a real-time (τ) motion in the metastable, inverted potential $-U(x)$. Because of the property in Eq. (9.8), Eq. (9.12) has two *trivial* solutions; a first one $x_e^{(1)}(\tau)=x_a$, where the particle simply sits on top of the inverted potential, at the minimum of $U(x)$, and a second, saddle-point solution $x_e^{(2)}(\tau)=x_b$, where the particle is located at the minimum of $-U(x)$, i.e., at the barrier top of $U(x)$ (see Fig. 38). A nontrivial periodic solution $x_e(\tau)$, the so-called *bounce solution* (Miller, 1975; Callan and Coleman, 1977; Coleman, 1977, 1979) exists only below a critical *dissipative crossover temperature* (Hänggi, Grabert, Ingold, and Weiss, 1985),

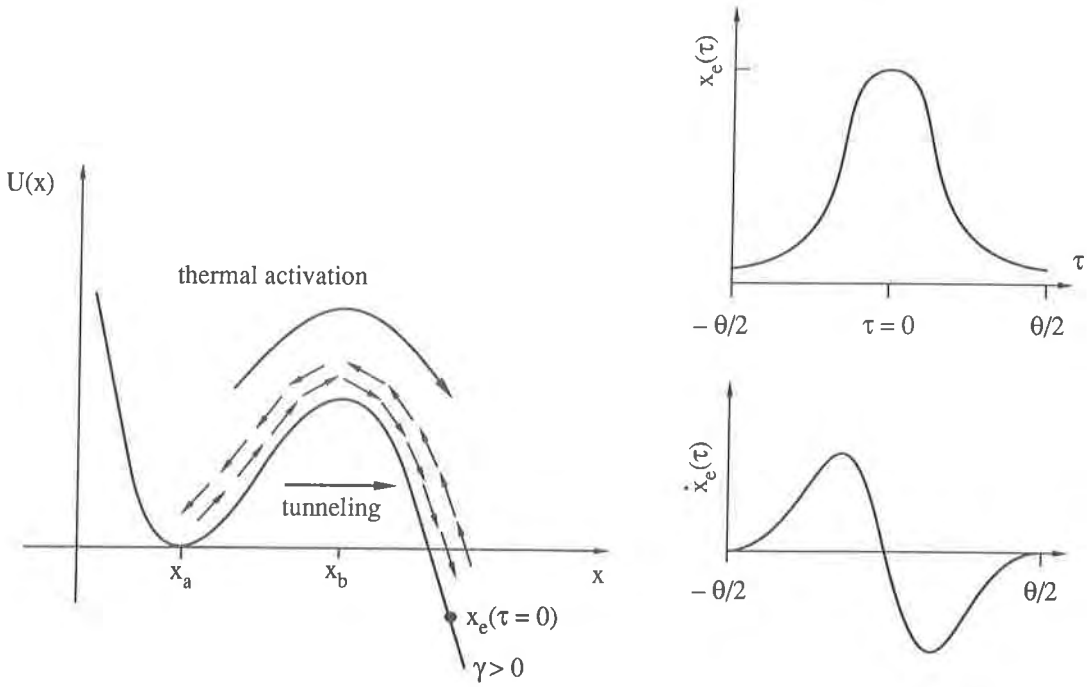

FIG. 38. Potential $U(x)$ used in the description of the quantum-Kramers rate. The periodic bounce trajectory $x_e(\tau)$, with period $\hbar\beta=\theta$, describes low-temperature tunneling under the barrier and is a stationary point of the Euclidean action in Eq. (9.6), obeying the classical equation of motion in the inverted potential $-U(x)$ [see Eq. (9.12)]. The Goldstone mode $\propto\dot{x}_e(\tau)$ processes one node; i.e., there is a fluctuation mode with a negative eigenvalue. The point marked $x_e(\tau=0)$ gives the zero-temperature bounce point in the presence of finite damping γ, which characterizes the loss of energy during tunneling under frictional influence (Weiss *et al.*, 1984).

$$T_0=\hbar\mu(2\pi k_B)^{-1}=(1.216\times10^{-12}\ \text{sec}\ K)\mu\ , \quad (9.14)$$

where μ denotes the positive root of Eq. (3.44). For temperatures $T>T_0$, the period of the θ-periodic orbit is *not* of sufficient length to admit an oscillation of the particle in the classically forbidden regime (see Fig. 38).

The characteristic tunneling temperature in the absence of any dissipation ($\hat{\gamma}=0$),

$$T_0=\hbar\omega_b(2\pi k_B)^{-1},\ \text{as}\ \hat{\gamma}\to0\ , \quad (9.15)$$

was originally derived in the late fifties by Goldanskii (1959a, 1959b, 1976) essentially by equating the Arrhenius factor βE_b for a parabolic barrier with the zero-temperature Gamow factor $2\pi E_b(\hbar\omega_b)^{-1}$. It should be noted that this crossover temperature T_0 can be quite large. For example, one finds with a characteristic chemical activation energy of $E_b\sim0.4$ eV and a tunneling distance of 2×10^{-10} m, which yields for hydrogen a barrier frequency $\omega_b\sim10^{14}$ Hz, a crossover temperature $T_0\sim150K$ [see also Fig. 2(b)].

The nontrivial bounce solution $x_e(\tau)$ [Eq. (9.12)], which is influenced both by temperature and by dissipation (see Fig. 38), is not a minimum of the action S_E, but corresponds to a saddle-point solution with an *unstable* direction. For temperatures $T>T_0$, the role of $x_e(\tau)$ is taken over by the constant solution $x_e^{(2)}(\tau)=x_b$. Thus at all temperatures a fluctuation mode exists in function space with respect to which the bounce is a maximum of the action. Associated with this fluctuation mode, $x_e(\tau)=x_b$ for $T>T_0$, and $x_e(\tau)$ for $T<T_0$ is therefore a *negative* eigenvalue. Below T_0 the extremal action $S_E[x_e(\tau)=x_b]$ exceeds the value obtained by the nontrivial solution $x_e(\tau)$, hence $S_E[x_e(\tau)]\equiv S_b<S_E[x(\tau)=x_b]=\hbar\beta E_b$. Here we have set for the action $S_E[x_e(\tau)=x_a]$ a value of zero. In other words, the trivial solution x_b can be disregarded for $T<T_0$, except within the crossover region $T\sim T_0$, where both $x_e^{(2)}(\tau)=x_b$ and the nontrivial solution $x_e(\tau)$ with period $\hbar\beta$ are of equal importance (see Fig. 39). Analytical results for the bounce solution are generally not available. For a cubic potential $U(x)=M(\frac{1}{2}\omega_0^2x^2-\frac{1}{3}ux^3)$, exact results have been obtained for zero friction and $T=0$, by Caldeira and Leggett (1983a), and at finite temperatures by Freidkin *et al.* (see Appendix 2 in Freidkin, Riseborough, and Hänggi, 1986a). For strictly Ohmic friction γ, explicit solutions have been found for very strong damping by Caldeira and Leggett (1983a) and by Larkin and Ovchinnikov (1983, 1984). For one particular, intermediate damping value, Riseborough *et al.* (1985) were able to find analytic solutions (see Fig. 39). In the over-

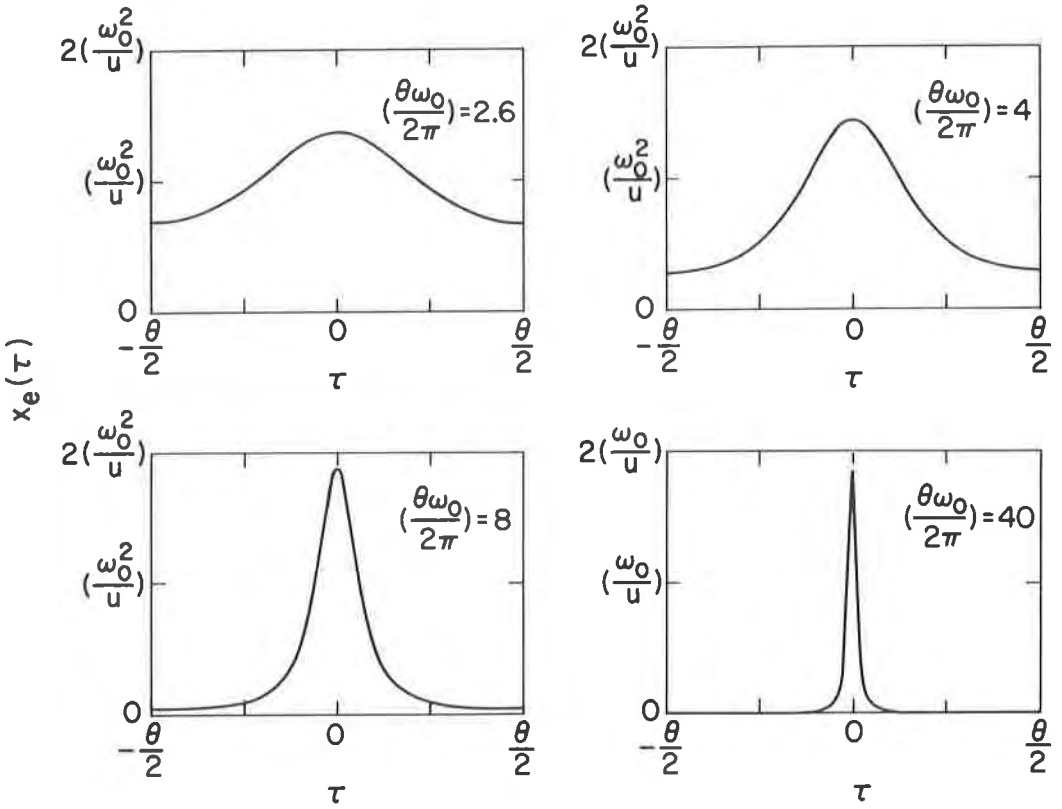

FIG. 39. Bounce trajectories $x_e(\tau)$ in a cubic metastable potential at moderate Ohmic damping γ. Note the approach of the bounce trajectory toward the constant saddle-point solution $x_e(\tau)=x_b\equiv\omega_0^2/u$ with increasing temperature θ^{-1}. At crossover, $\theta_0\omega_0/(2\pi)=\sqrt{6}$, the periodic bounce solution coalesces with the constant solution $x_e(\tau)=x_b$. After Riseborough *et al.* (1985).

damped limit again, a further analytic solution in a tilted sinusoidal potential was found recently by Korshunov (1987).

This feature of a negative eigenvalue obviously plagues the evaluation of the free energy and equivalently, the partition function of a metastable state. What one needs is an analytical continuation, in which the integral of the unstable (negative-valued eigenvalue) mode is distorted in the complex plane yielding a finite, but complex, part for the partition function of the metastable state (Langer, 1967; Coleman, 1977, 1979). This omnipresent negative-eigenvalue mode is therefore the origin of the exponentially small imaginary part of the free energy of a metastable state [see Eq. (4.83)].

With the collapse of $x_e(\tau)$ toward $x_e(\tau)=x_b$ as $T\uparrow T_0$, it becomes clear that T_0 is the temperature at which the crossover from thermal-dominated escape to tunneling-dominated escape occurs. This temperature T_0 [see Eq. (9.14)] is *reduced* with increasing dissipation strength. On the other hand, T_0 *increases* monotonically toward the dissipation-free value given by $\mu\to\omega_b$ *with increasing memory-friction relaxation time,* while $\hat{\gamma}(\omega=0)$ is held fixed (Hänggi, Grabert, Ingold, and Weiss, 1985). In Fig. 40 we depict schematically the various temperature regimes of the escape rate as a function of temperature.

Within the crossover regime $T\sim T_0$, any linear combination of the two extremal solutions $x_e(\tau)$ and $x_e=x_b$ is an almost stationary solution of the Euclidean action S_E. Each of these two solutions separately induces an exact zero mode and a quasizero mode (Grabert and Weiss, 1984b; Riseborough *et al.*, 1985), which dominate the result of the prefactor for the rate of escape around $T\sim T_0$ (Grabert and Weiss, 1984b; Larkin and Ovchinnikov, 1984; Riseborough *et al.*, 1985). At temperatures $T>T_0$, the Gaussian fluctuation modes $x_n(\tau)$ around the solution $x^{(2)}(\tau)=x_b$ possess the eigenvalues

$$\lambda_n^b=n^2\nu^2-\omega_b^2+|n|\nu\hat{\gamma}(|n|\nu),\quad n=0,\pm1,\quad T>T_0\ , \tag{9.16}$$

where $\nu=2\pi(\hbar\beta)^{-1}$ denotes the fundamental Matsubara frequency. We note that $\lambda_0^b=-\omega_b^2$ is the negative eigenvalue associated with $x_e(\tau)=x_b$, and that the eigenvalues $\lambda_1^b=\lambda_{-1}^b$ become mutually zero (zero modes) at precisely the crossover temperature T_0,

$$\nu_0^2+\nu_0\hat{\gamma}(\nu_0)=\omega_b^2\ , \tag{9.17}$$

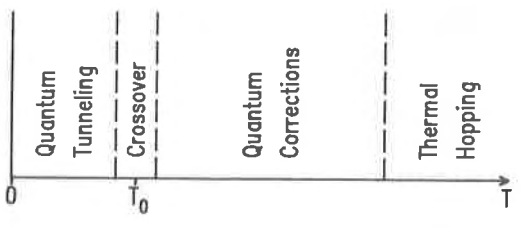

FIG. 40. Dominant escape mechanism depicted schematically as a function of temperature.

where $\nu_0=2\pi k_bT_0/\hbar$. Interestingly enough, this critical frequency ν_0 defining T_0 [see Eq. (9.14)] just coincides (Hänggi, Grabert, Ingold, and Weiss, 1985) with the memory-friction renormalized barrier frequency in Eq. (3.45), $\nu_0\equiv\mu$. While at $T=T_0$ the modes x_n and x_{-n} are exactly degenerate, this degeneracy is lifted by the mutual coupling around $T\sim T_0$. Near $T\sim T_0$ one finds (Riseborough *et al.*, 1985; Grabert, 1986; Grabert, Olschowski, and Weiss, 1987) that $\lambda_{-1}^b=0$ is an exact zero mode, while in leading order $(T-T_0)$

$$\lambda_1^b=a(T-T_0)/T_0,\quad T\geq T_0\ , \tag{9.18}$$

and

$$\lambda_1^b=2a|T-T_0|/T_0,\quad T\leq T_0\ , \tag{9.19}$$

with $a=\omega_b^2+\mu^2(1+\partial\hat{\gamma}/\partial z|_{z=\mu})$. Thus $\lambda_1^b(T\sim T_0)$ always stays slightly positive.

D. The dissipative tunneling rate

The theory of dissipative tunneling was developed only recently. The field has undergone rapid development since Caldeira and Leggett (1981, 1983a) discussed the problem of macroscopic dissipative quantum tunneling at zero temperature. Following the reasoning of Langer (1967), which he invented for the classical nucleation problem, the original approaches to dissipative tunneling were based on an imaginary-time functional-integral approach [known as the imaginary free-energy ($\mathrm{Im}\,\mathcal{F}$) method; see Eq. (4.83)]. The essence of the method consists in a semiclassical steepest-descent evaluation of the free energy, which leads to the dissipative bounce solution [see Eq. (9.12)], as the primary object in the theory (Miller, 1975; Callan and Coleman, 1977; Coleman, 1979; Affleck, 1981). The important qualitative result of the zero-temperature studies (Caldeira and Leggett, 1981, 1983a) was the observation that dissipation will *exponentially decrease* the tunneling rate relative to the gas phase rate, defined as the tunneling rate without dissipation.

The functional-integral approach was extended by the Augsburg-Essen-Polytechnic-Stuttgart school and the Moscow school to finite temperatures, covering all temperatures in the range from $T\simeq0$ up to the classical regime (Grabert and Weiss, 1984a, 1984b; Grabert, Weiss, and Hänggi, 1984; Larkin and Ovchinnikov, 1984, 1985; Grabert, 1985; Riseborough *et al.*, 1985; Hänggi, 1986a, 1986b, 1987; Grabert, Olschowski, and Weiss, 1987; Weiss, Grabert, Hänggi, and Riseborough, 1987; Hänggi and Hontscha, 1988). Below we shall present the main results of the finite-temperature theory of dissipative tunneling by use of a unified *multidimensional* WKB approach for the reactive system plus bath, which covers both low temperatures and high temperatures on the same basis (Miller, 1975; Hänggi and Hontscha, 1988).

1. Flux-flux autocorrelation function expression for the quantum rate

We begin our more detailed discussion of tunneling rates by a formally exact rate expression. Let Z_0 denote the quantum partition function of the system plus bath of a metastable state inside the well minimum (see Fig. 37). Further, let x denote the reaction coordinate in full configuration space, with the activation barrier located at $x=0$, and let p be its conjugate momentum, i.e., x is the coordinate perpendicular to the surface which divides "reactants" from "products." The flux-through-a-surface operator F has the form

$$F=\delta(x)(p/M) . \tag{9.20}$$

The thermally averaged tunneling rate k is formally given by (McLafferty and Pechukas, 1974; Miller, 1974; Pechukas, 1976; Miller, Schwartz, and Tromp, 1983)

$$k=\mathrm{Re}\{\mathrm{Tr}[\exp(-\beta\mathcal{H})F\mathcal{P}]\}/Z_0 , \tag{9.21}$$

where Re denotes the "real part," Tr indicates the trace, and $\beta=(k_BT)^{-1}$ again is the inverse temperature. The operator $\mathcal{P}$ reads

$$\mathcal{P}=\lim_{t\to\infty}\exp(i\mathcal{H}t/\hbar)h(p)\exp(-i\mathcal{H}t/\hbar) , \tag{9.22}$$

with $h(p)=1$ if $p>0$ and $h(p)=0$ if $p<0$. The operator $\mathcal{P}$ projects onto all states that have positive momentum in the infinite future ($t\to\infty$), with the reaction coordinate ranging from $x=-\infty$ to $x=+\infty$. By use of a few formal manipulations we can recast the exact rate in Eq. (9.21) in terms of a time integral over a flux-flux autocorrelation function. With $\hat{F}=\frac{1}{2}[\delta(x)(p/M)+(p/M)\delta(x)]$, and $t_c=t-i\hbar\beta/2$, Eq. (9.21) can be written in the form (Yamamoto, 1960; Miller *et al.*, 1983)

$$k=\tfrac{1}{2}Z_0^{-1}\int_{-\infty}^{\infty}C(t)dt , \tag{9.23}$$

where (Miller, Schwartz, and Tromp, 1983)

$$C(t)=\mathrm{Tr}[\hat{F}\exp(i\mathcal{H}t_c^*/\hbar)\hat{F}\exp(-i\mathcal{H}t_c/\hbar)] . \tag{9.24}$$

Miller *et al.* (1983) have further demonstrated that the rate in Eq. (9.23) is fully equivalent with the quantum correlation-function formalism due to Yamamoto (1960). Nevertheless, the correlation function in Eq. (9.24) distinctly differs from Yamamoto's, and in fact it is only the integrals over the correlation function that do agree. Moreover, note that the correlation-function formalism in Eq. (9.23) presents a dynamical approach in the same spirit as the reactive flux reasoning in Sec. II.B; the formally exact expression thus covers both the quantum energy-diffusion-limited and the quantum spatial-diffusion-limited rate regime.

The correlation-function result is analogous to the Green-Kubo formulas for transport coefficients. Except in simple situations, however, e.g., for a one-dimensional parabolic barrier with curvature

$$\omega_b^2=|M^{-1}U''(q=q_b)|>0 ,$$

yielding

$$Z_0k=\frac{k_BT}{h}(\tfrac{1}{2}\hbar\beta\omega_b)[\sin(\tfrac{1}{2}\hbar\beta\omega_b)]^{-1} ,$$

it is generally impossible to calculate Eq. (9.23) analytically for nonseparable systems. Therefore it is more practical to evaluate for Eq. (9.21) the semiclassical approximation (Miller, 1975; Schmid, 1986).

2. Unified approach to the quantum-Kramers rate

In order to make progress on analytical grounds we first approximate the projector $\mathcal{P}$ in Eq. (9.22) by the simple step function $h(p)$, thereby neglecting dynamical nonequilibrium kinetics. This procedure is known in the chemical physics literature as the quantum transition-state theory approximation (QTST). By use of the semiclassical approximation for the propagator $\exp(-\beta\mathcal{H})$, one finds after a first stationary phase approximation a periodic trajectory in configuration space which represents a continuum of stationary phase points. This periodic trajectory which is unstable with respect to small perturbations, is simply the bounce solution (often denoted as the "instanton solution") in full configuration space of $(N+1)$ degrees of freedom of the *system plus bath* [see Eq. (3.29)]; it describes the tunneling at fixed total energy E. The dividing surface will next be chosen so that the periodic trajectory crosses it perpendicularly, i.e., $q_0\equiv x$ is the coordinate that measures distance along the unstable periodic trajectory, with the other N coordinates being orthogonal displacements away from it. In contrast to the remaining N orthogonal coordinates, which can be evaluated by the stationary phase approximation, the integral over the x coordinate cannot be performed in such a way. It is, however, trivially accomplished by use of the δ function in Eq. (9.20). Making use of similar calculations (periodic orbit theory) originally put forward by Gutzwiller (1971, 1982), one ends up with the result (Miller, 1975)

$$k=Z_0^{-1}\frac{1}{2\pi\hbar}\int_0^{\infty}dE\,k(E)\exp(-\beta E) , \tag{9.25}$$

where we have measured the energy from the well bottom, $U(x_b)=E_b$. The quantity $k(E)$ is the microcanonical, cumulative semiclassical reaction probability at the total energy E (Miller, 1975),

$$k(E)=\sum_{n=1}^{\infty}(-1)^{n-1}\exp[-n\phi(E)/\hbar]\times\prod_{i=1}^{N}\{2\sinh[\tfrac{1}{2}nT(E)\omega_i(E)]\}^{-1} , \tag{9.26}$$

with

$$\phi(E)=\int_0^{T(E)} d\tau\, \mathbf{p}(\tau)\dot{\mathbf{q}}(\tau) \tag{9.27}$$

being the "small action" integral along the periodic orbit in complex time $t=-i\tau$ (Wick rotation) of period $T(E)$ that passes through the saddle-point region on the upside-down potential energy surface in $(N+1)$ dimensions. Note that Eq. (9.26) includes a sum over multiple traversals of the periodic orbit. The parameters $\{\omega_i(E)\}$ are the stability frequencies (Hill-Floquet coefficients) characterizing an unstable periodic orbit with period $T(E)=-\phi'(E)$. Upon expanding the sinh functions in Eq. (9.26) into geometric series, one obtains a well-behaved result for $k(E)$,[21] reading

$$k(E)=\sum_{(n_1,\ldots,n_N)=0}^{\infty}\left\{1+\exp\left[\left\{\phi(E)-\phi'(E)\sum_{i=1}^{N}(n_i+\tfrac{1}{2})\hbar\omega_i(E)\right\}\Big/\hbar\right]\right\}^{-1}. \tag{9.28}$$

With the solution of

$$E_T=E-\sum_{i=1}^{N}(n_i+\tfrac{1}{2})\hbar\omega_i(E_T)\,, \tag{9.29}$$

which is the energy E_T left in the tunneling mode while the system is crossing the saddle point, we approximate the answer in Eq. (9.28) by the more appealing expression (Hänggi and Hontscha, 1988)

$$k(E)=\sum_{(n_1,\ldots,n_N)=0}^{\infty}\{1+\exp[\phi(E_T)/\hbar]\}^{-1}\,, \tag{9.30}$$

where we have "unexpanded" the first two terms in the Taylor series in Eq. (9.28). The form in Eq. (9.30) becomes exact for tunneling in a multidimensional, separable inverted parabolic potential landscape.

It should be noted that the quantity in Eq. (9.30) involves *a summation* over all the orthogonal states $\{n_i\}$ within the barrier region; i.e., the cumulative reaction probability $k(E)$ can exceed unity. Thus, despite its appealing form, the result in Eq. (9.30) is quite distinct from the familiar uniform WKB expression $t^{\mathrm{pw}}(E)$ for the transmission probability of a parabolic barrier (Kemble, 1935; Miller and Good, 1953; Ford, Hill, Wakano, and Wheeler, 1959):

$$t^{\mathrm{pw}}(E)=\{1+\exp[\phi(E)/\hbar]\}^{-1}\,. \tag{9.31}$$

In the *absence of dissipation* Eq. (9.30) reduces, of course, with $E_T=E$ to the single-term equation (9.31).

With Eq. (9.30), the evaluation of the thermally averaged, dissipative tunneling rate follows after the integration in Eq. (9.25). The remaining problem in obtaining an analytical result consists in determining the small action $\phi(E_T)$, the Hill-Floquet coefficients $\{\omega_i(E_T)\}$, and the period $T(E_T)$. In particular, it should be stressed that Eq. (9.25) combined with Eq. (9.30) presents an expression for the dissipative quantum-Kramers rate, or the equivalent multidimensional quantum TST, that *holds true for all temperatures.*

3. Results for the quantum-Kramers rate

In this subsection we follow the reasoning of Hänggi and Hontscha (1988) who use for the *system-plus-bath* a multidimensional, finite-temperature WKB approach to derive explicit results for the dissipative tunneling rate in various temperature regimes, [see Fig. 40], in a metastable potential field of the form sketched in Figs. 37 and 38 with a single metastable well.

a. Dissipative tunneling above crossover

In this high-temperature regime we can use a harmonic, local adiabatic approximation, in which the period $T(E_T)$ equals a constant $T(E_T)=2\pi/\mu$, and the Hill-Floquet coefficients can be approximated by the normal-mode (angular) frequencies of the orthogonal coordinates at the saddle point. Moreover, with imaginary-valued coordinates $\mathbf{q}(\tau)$ and momenta $\mathbf{p}(\tau)$, when $E_T>E_b$ the small action in Eq. (9.27) becomes $\phi(E_T)=(E_b-E_T)2\pi/\mu<0$. Then, interchanging the integration in Eq. (9.25) with the summations in Eq. (9.30) yields, by virtue of an identity due to Pollak (1986) which relates the product of the (unknown) normal-mode frequencies at the saddle point and at the well bottom, respectively, to the (known) Laplace transform of the memory friction $\hat{\gamma}$, the central result

$$k=\left|\frac{\mu}{\omega_b}\left|\frac{\omega_0}{2\pi}\right|\exp(-\beta E_b)\right| \times\left|\prod_{n=1}^{\infty}\frac{\omega_0^2+n^2\nu^2+n\nu\hat{\gamma}(n\nu)}{-\omega_b^2+n^2\nu^2+n\nu\hat{\gamma}(n\nu)}\right|,\quad T>T_0\,. \tag{9.32}$$

This high-temperature dissipative quantum limit was first obtained by Wolynes (1981) and has been subsequently rederived along quite different lines by various authors (Melnikov and Meshkov, 1983; Dakhnovskii and Ovchinnikov, 1985; Hänggi, Grabert, Ingold, and Weiss, 1985; Pollak, 1986b).

[21] In other words, we use in Eq. (9.26) an analytic continuation of the series over n which formally might be divergent when $E>E_b$, where E_b denotes the threshold energy for activation.

The first term inside the square brackets denotes the classical generalized Kramers rate for memory friction [Eq. (3.46)]. We recall the definition of ν, $\nu=2\pi/(\hbar\beta)$, while $\omega_0^2=U''(q=q_a)/M$ is the (angular) frequency in the well bottom (see Fig. 37). For temperatures $T\gg T_0$ the quantum correction Q, given by the large curly brackets in Eq. (9.32), approaches unity. Moreover, this quantum correction always exceeds unity, i.e., *the quantum-Kramers rate theory always enhances the classical rate.* In particular, for weak-to-moderate damping strengths $\hat{\gamma}(\mu)$, there exists an accurate and quite simple approximation to the quantum correction Q in Eq. (9.32), which in leading order is *independent of the dissipation* $\hat{\gamma}$ (Hänggi, Grabert, Ingold, and Weiss, 1985),

$$Q\sim\exp\left[\frac{\hbar^2}{24}\beta^2(\omega_0^2+\omega_b^2)\right] . \tag{9.33}$$

Thus, for temperatures $T>T_0$, the Arrhenius factor formally undergoes a temperature-dependent renormalization toward *smaller values,*

$$E_b\to E_b-\frac{\hbar^2}{24}\beta(\omega_0^2+\omega_b^2) . \tag{9.34}$$

Moreover, upon a comparison with Eq. (7.26), we note in passing that the temperature correction for the rate due to tunneling, which is also proportional to T^{-2} [Eq. (9.33)], is *opposite* in sign to the classical correction due to a *random* metastable potential function.

b. Dissipative tunneling near crossover

At temperatures $T\sim T_0$, the integral in Eq. (9.25) becomes dominated by energies $E_T\le E_b$, where $\phi(E_T)>0$. When we set, more accurately (Hänggi and Hontscha, 1988),

$$\phi(E_T)=(E_b-E_T)\frac{2\pi}{\mu}+\frac{1}{2}(E_b-E_T)^2|T'| \tag{9.35}$$

for the small action, with $|T'|\equiv|\phi''(E=E_b)|$, we recover the result (Grabert and Weiss, 1984b; Larkin and Ovchinnikov, 1984; Riseborough *et al.*, 1985)

$$k=\left[\frac{2\pi}{\hbar|T'|}\right]^{1/2}\frac{\omega_0}{\omega_b}\frac{\omega_0^2+\nu^2+\nu\hat{\gamma}(\nu)}{a}\prod_{n=2}^{\infty}\frac{\omega_0^2+n^2\nu^2+n\nu\hat{\gamma}(n\nu)}{-\omega_b^2+n^2\nu^2+n\nu\hat{\gamma}(n\nu)}$$
$$\times\exp\left[-\beta E_b+\frac{\hbar}{2|T'|}(\beta_0-\beta)^2\right]\frac{1}{2}\mathrm{erfc}\left[\left[\frac{\hbar}{2|T'|}\right]^{1/2}(\beta_0-\beta)\right] , \tag{9.36}$$

where

$$a=\omega_b^2+\mu^2\{1+[\partial\hat{\gamma}(z)/\partial z]|_{z=\mu}\} ,$$

$$\beta_0=(kT_0)^{-1} ,$$

and

$$\mathrm{erfc}(x)=2\pi^{-1/2}\int_x^{\infty}dy\,\exp(-y^2) .$$

For strict Ohmic friction $\gamma(t)=2\gamma\delta(t)$ we obtain $a=\nu_0(2\nu_0+\gamma)$, with $\nu_0\equiv 2\pi/(\hbar\beta_0)$. Note also that the result in Eq. (9.36) approaches for $T>T_0$ the previous answer in Eq. (9.32). Moreover, Grabert and Weiss (1984b) have shown that near $T\sim T_0$ there exist both a frequency scale Λ and a temperature scale X that depend on the particular system under consideration, so that within the crossover region the rate exhibits a universal scaling behavior.

c. Dissipative tunneling below crossover

At lower temperatures the small action $\phi(E_T)$ in Eq. (9.35) must be evaluated by taking the full nonlinearity of the potential $U(x)$ into account. In that regime, however, the contribution from multiple crossings of the classically forbidden regime with period $nT(E)$, $n>1$, do not significantly contribute to the sum in Eq. (9.26). Hence we can evaluate Eq. (9.25) by keeping only the $n=1$ term for Eq. (9.26), and the remaining integral can be evaluated by the method of steepest descent. The steepest-descent condition yields the period $T(E)=\hbar\beta\equiv\theta$. With E_θ determined so that $T(E=E_\theta)=\hbar\beta$, and the full extremal action S_b defined as

$$S_b\equiv\theta E_\theta+\phi(E_\theta) \tag{9.37a}$$

$$=\oint_0^\theta d\tau[V(\mathbf{q}(\tau))+\tfrac{1}{2}\dot{\mathbf{q}}(\tau)\mathbf{p}(\tau)] , \tag{9.37b}$$

where $V(\mathbf{q})$ denotes the potential function of all degrees of freedom (system plus bath), the low-temperature dissipative quantum rate reads (Hänggi, 1987; Hänggi and Hontscha, 1988)

$$k=Z_0^{-1}|2\pi\hbar T'(E=E_\theta)|^{-1/2}\exp(-S_b/\hbar)$$
$$\times\prod_{i=1}^{N}\{2\sinh[\tfrac{1}{2}\hbar\beta\omega_i(E_\theta)]\}^{-1} . \tag{9.38}$$

Note that S_b equals the dissipative, Euclidean action in Eq. (9.6) when it is evaluated at the bounce solution $x_e(\tau)$. By use of the identities discussed in Secs. III.B and III.C of the paper by Dashen, Hasslacher, and Neveu (1974), we can relate the prefactor in Eq. (9.38) to the eigenvalue spectrum around the dissipative bounce trajectory $x_e(\tau)$ of period $\hbar\beta=\theta$, to give the known result (Grabert and Weiss, 1984a; Larkin and Ovchinnikov, 1984; Riseborough *et al.*, 1985; Hänggi, 1986a, 1986b, 1987; Grabert, Olschowski, and Weiss, 1987)

$$k=\frac{2}{\hbar}\,\mathrm{Im}\mathcal{F}=\left|\frac{M}{2\pi\hbar}\int_{-\beta\hbar/2}^{\beta\hbar/2}d\tau[\dot{x}_c(\tau)]^2\right|^{1/2}\left|\frac{\mathrm{Det}(\delta^2 S_E/\delta x^2)_{x=x_a}}{|\mathrm{Det}'(\delta^2 S_E/\delta x^2)_{x=x_c(\tau)}|}\right|^{1/2}\exp(-S_b/\hbar)\,. \tag{9.39}$$

Here S_E denotes the Euclidean, dissipative action with $S_E[x_c(\tau)=q_a]=0$ and $S_E[x=x_c(\tau)]=S_b$ [see Eq. (9.37)], and Det′ means that the eigenvalue zero has to be omitted. It should be noted that in the presence of dissipation the part of the prefactor inside the large curly brackets in Eq. (9.39), stemming from the zero-mode normalization, *differs* from the dissipative bounce action S_b; only for an undamped system does this part equal the bounce action S_b.

Dissipation was first introduced into the bounce formalism for the zero-temperature quantum decay rate by Caldeira and Leggett (1981, 1983a). The result in the form of Eq. (9.39), which is valid for finite temperatures and dissipation, was originally obtained within the dissipative functional bounce methodology by Grabert and Weiss (1984a), Larkin and Ovchinnikov (1984), and Riseborough *et al.* (1985). For an undamped system, the answer in Eq. (9.39) reduces to the low-temperature, steepest-descent evaluation of simple quantum TST (Affleck, 1981). An alternative multidimensional WKB derivation of the central result in Eq. (9.39), which uses the concept of the multidimensional quasistationary wave function rather than the unstable, multiple periodic orbits that characterize the approach of Hänggi and Hontscha (1988), has been given for zero temperature by Schmid (1986), and recently has been extended to finite temperatures by Ludviksson (1989).

Arrhenius plots of some numerical results for the dissipative tunneling rate with strict Ohmic friction $\hat{\gamma}(z)=\gamma$ are depicted in Fig. 41. Because of quantum tunneling, the rate k does not decrease continuously as the temperature T is lowered, but flattens off at low temperatures (see also Fig. 2). In the high-temperature (or classical) regime, the rate is reduced compared to the gas phase rate ($\hat{\gamma}=0$, that is, $\mu=\omega_b$) by the dissipative transmission factor $\mu/\omega_b<1$ [Eq. (9.32)]. In contrast, the zero-temperature rate is *exponentially* reduced by the dissipative action factor $S_b(T=0)$ (Caldeira and Leggett, 1983a). For very weak damping, $\hat{\gamma}(\mu)\to 0$, thermal fluctuations have little effect on the low-temperature behavior of the rate, i.e., the temperature dependence is essentially negligible below T_0. For a damped system, however, there is a large regime in which quantal and thermal fluctuations interact. In this low-temperature regime one finds a universal exponential temperature enhancement in the form of a power law (Grabert, Weiss, and Hänggi, 1984)

$$\ln[k(T)/k(T=0)]=cT^n,\quad T_0>T\geq 0\,, \tag{9.40}$$

where $n=2$ for all systems with finite low-frequency damping, $\hat{\gamma}(\omega=0)=\gamma_0>0$. The universal low-temperature rate enhancement arises from thermally excited low-frequency states of the *environment* and not from thermal excitations among the states in the metastable well. An appealing rederivation of Eq. (9.40) in terms of quantum noise theory has recently been given by Martinis and Grabert (1988). For Ohmic damping, this characteristic low-temperature T^2 law (see Fig. 42), as

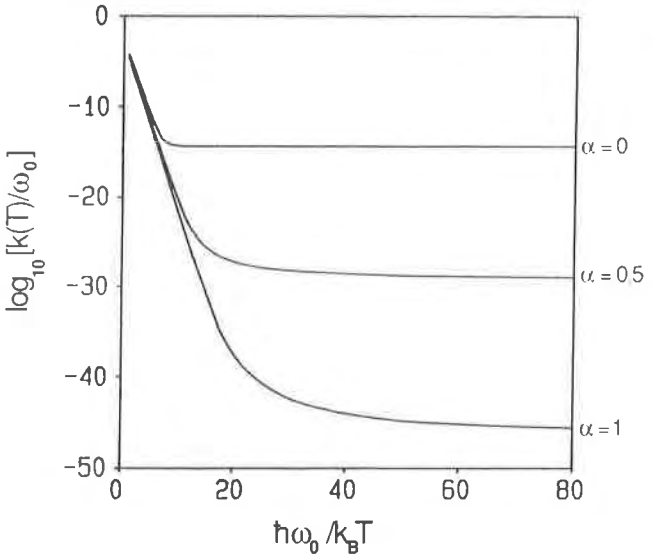

FIG. 41. Van't Hoff-Arrhenius plot of the quantum-Kramers rate in a cubic potential $U(x)=\frac{1}{2}M\omega_0^2x^2(1-x/x_0)$, with activation energy $E_b=2M\omega_0^2x_0^2/27=5\hbar\omega_0$ at various damping strengths $\gamma=2\alpha\omega_0$. After Grabert, Olschowski, and Weiss (1987).

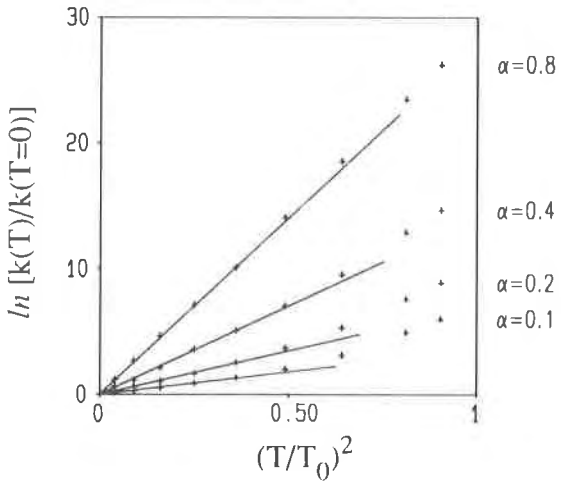

FIG. 42. The natural logarithm of the ratio between the low-temperature quantum-Kramers rate and the zero-temperature rate in a cubic potential (see Fig. 41), at various values of Ohmic damping $\gamma=2\alpha\omega_0$. The plot vs squared temperature clearly exhibits the universal T^2 law in Eq. (9.40). After Grabert, Olschowski, and Weiss (1987).

well as the quantum corrections in Eqs. (9.32), (9.33), and (9.36), have been observed in several experiments (Schwartz *et al.*, 1985; Washburn *et al.*, 1985; Washburn and Webb, 1986; Clarke *et al.*, 1988; Cleland *et al.*, 1988; Sharifi *et al.*, 1988; Iansiti *et al.*, 1989). With $n=6$ it has recently been observed by Careri and Consolini (1989). The power n is directly related to the behavior of the spectral density

$$J(\omega)=\frac{\pi}{2}\sum C_i^2(m_i\omega_i)^{-1}\delta(\omega-\omega_i)$$

of the environment at low frequencies, $J(\omega)\propto\omega^{n-1}$, as $\omega\to 0$. The slope c in Eq. (9.40) increases with the strength of dissipation, but depends further on the details of the model for the dissipative mechanism and the metastable potential function $U(x)$ (Grabert, Weiss, and Hänggi, 1984).

In contrast to the classical Kramers rate in Eq. (4.33), the exponential part of the low-temperature quantum rate, Eq. (9.39), and particularly its prefactor are much more difficult to evaluate. An analytical treatment of the prefactor is possible, but rather difficult (Riseborough *et al.*, 1985; Freidkin *et al.*, 1986a, 1988). In practice one must therefore resort to numerical methods (Chang and Chakravarty, 1984; Grabert, Olschowski, and Weiss, 1985, 1987), variational approximations (Freidkin *et al.*, 1986b, 1987; Chang and Riseborough, 1989), or approximate WKB approaches (Pollak, 1986c; Hontscha and Hänggi, 1987). For the cubic metastable potential $U(x)=\frac{1}{2}M\omega_0^2x^2(1-x/x_0)$ and strict Ohmic friction $\hat{\gamma}=\gamma$, one finds with $E_b=2M\omega_0^2x_0^2/27$ for the action S_b and with the quantum prefactor $A\equiv k\exp(S_b/\hbar)$, the following low-temperature results. With weak friction and dimensionless damping $\alpha\equiv\gamma(2\omega_0)^{-1}$, the dissipative action S_b in terms of the zeta function $\zeta(3)=1.202$ is (Freidkin *et al.*, 1986a)

$$S_b(T\geq 0)=\frac{36E_b}{5\omega_0}\left\{1+\alpha\left[\frac{45\zeta(3)}{\pi^3}-\frac{5}{2\pi}\left[\frac{2\pi k_BT}{\hbar\omega_0}\right]^2-\frac{\pi}{12}\left[\frac{2\pi k_BT}{\hbar\omega_0}\right]^4+\cdots\right]\right\},\quad \alpha\to 0 \qquad (9.41)$$

which agrees at $T=0$ with the action calculated by Caldeira and Leggett (1983a). For the quantum prefactor we have (Freidkin *et al.*, 1986a, 1988)

$$A(T=0)=12\omega_0[3E_b(2\pi\hbar\omega_0)^{-1}]^{1/2}\exp(2.860\alpha)\,,\quad \alpha\to 0\,, \qquad (9.42)$$

which at zero friction $\alpha=0$ agrees with Caldeira and Leggett (1983a). On the other hand, for very strong damping one obtains (Larkin and Ovchinnikov, 1984; Grabert, Olschowski, and Weiss, 1987)

$$S_b(T\geq 0)=\alpha\left[6\pi\frac{E_b}{\omega_0}\right]\left[1+\tfrac{1}{4}\alpha^{-2}-\tfrac{4}{3}\alpha^2\left[\frac{2\pi}{\omega_0\hbar\beta}\right]^2\right],\quad T\leq T_0=\hbar\omega_0(4\pi k_B\alpha)^{-1},\ \alpha\to\infty\,, \qquad (9.43)$$

and for the prefactor (Larkin and Ovchinnikov, 1984; Grabert, Olschowski, and Weiss, 1987)

$$A(T=0)=8\omega_0\alpha^{7/2}\left[\frac{6E_b}{\hbar\omega_0}\right]^{1/2}(1+2\alpha^{-2}\ln\alpha+1.107\alpha^{-2})\,,\quad \alpha\to\infty\,. \qquad (9.44)$$

The same characteristic dependence on friction γ, that is, $A\propto\alpha^{7/2}$, is found for strong friction in a tilted sinusoidal potential (Korshunov, 1987). In contrast to the exponential part of the rate [Eq. (9.40)], the quantum prefactor at low temperatures exhibits only a *very weak* dependence on temperature (Grabert, Weiss, and Hänggi, 1984; Grabert, Olschowski, and Weiss, 1987).

4. Regime of validity of the quantum-Kramers rate

In Sec. IV.G we discussed the conditions under which the Kramers rate in Eq. (4.33) yields the correct rate. In the high-temperature regime essentially the same classical conditions, namely,

$$[\hat{\gamma}(\mu)/\omega_b]E_b>k_BT,\quad T\geq T_0\,, \qquad (9.45)$$

hold true for the validity of the quantum-Kramers rate, or multidimensional (QTST) rate, in Eqs. (9.32) and (9.36). Again, with a high barrier, $\beta E_b\gg 1$, there remains sufficient time for thermalization inside the metastable well, even for weak damping obeying Eq. (9.45). Upon a further lowering of the temperature, $T<T_0$, quantum tunneling dominates over termally activated escape. In the quantum regime the three dimensionless parameters $[x_1=k_BT/E_b,\ x_2=\hat{\gamma}(\mu)/\omega_b,\ x_3=\hbar\omega_b/(2\pi k_BT)]$ determine the behavior of the rate. Then, the plane intersecting the positive (x_2,x_3) plane at

$$\frac{\hbar\omega_b}{2\pi k_BT}=\frac{\hbar\omega_b}{2\pi k_BT_0}=\frac{\omega_b}{\mu}\xrightarrow{\hat{\gamma}(\mu)\gg\omega_b}\frac{\hat{\gamma}(\mu)}{\omega_b} \qquad (9.46)$$

(see Fig. 43) describes the crossover between thermal-activation-controlled and quantum-tunneling-controlled escape. At temperatures $T<T_0$, the quantum rate is already so small (or, equivalently, the time for escape is so large) that for most practical purposes weak friction has no impact on deviations from a thermalized Boltzmann weighting. A simple Fermi's "golden rule" argument for a well containing two quantum levels shows that the rate of thermalization is proportional to the damping, i.e., the rate of decay of excited levels into lower ones, thereby emitting energy into phonon modes, is directly proportional to $\hat{\gamma}(\mu)$. Using as an upper limit the simple quantum TST rate [see Eq. (9.2)], which essentially equals the zero-temperature undamped quantum rate $k(T=0,\gamma=0)\equiv k_0$, we can expect that the validity of the low-

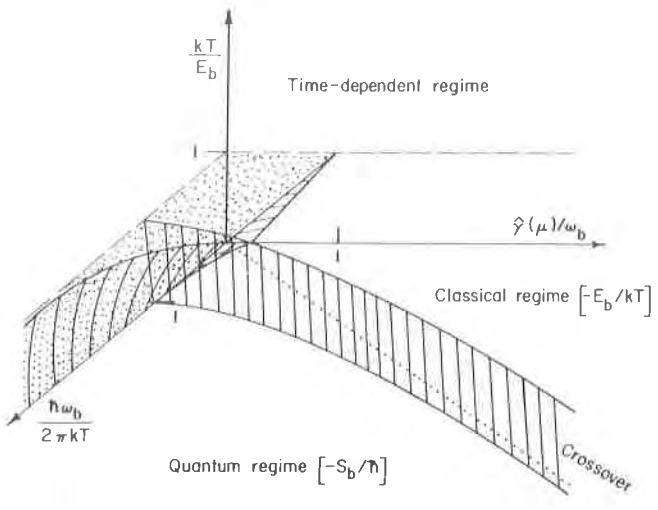

FIG. 43. The "Thomas diagram" (Hänggi, 1987). The cylinder with $k_B T/E_b \leq 1$ (hatched vertically) separates the classical thermal activation regime from the tunneling-dominated regime in which the Van't Hoff-Arrhenius factor is taken over by the dissipative bounce action $S_b = S_E[x_c(\tau)]$ [see Eq. (9.37)]. The three-dimensional volume (dotted region) at the left indicates the regime in which nonequilibrium effects (due to weak-friction-induced deviations from a Boltzmann weighting) must be accounted for (see Sec. IX.E) as a function of friction, barrier height, and temperature. Moreover, note that the "classical regime" is affected by quantum corrections to the classical prefactor. In the figure the Boltzmann constant is denoted by $k_B \equiv k$.

temperature quantum-Kramers rate in Eq. (9.39) *will start to break down only at exponentially small friction,* obeying (Hänggi, 1987)

$$\frac{\hat{\gamma}(\mu)}{\omega_0} \leq \frac{k_0}{\omega_0} = 12 \left[\frac{3E_b}{2\pi\hbar\omega_0} \right]^{1/2} \exp\left[-\frac{36E_b}{5\hbar\omega_0} \right] . \tag{9.47}$$

Typically one has $E_b > 2\hbar\omega_0$ in order for the semiclassical approximation to be valid [see Eq. (9.11)]. Therefore we find from Eq. (9.47)

$$\frac{\hat{\gamma}(\mu)}{\omega_0} \leq 10^{-6} , \tag{9.48}$$

which with $\omega_0 \sim 10^{11}-10^{14}$ Hz indeed implies extremely weak dissipation.

E. Dissipative tunneling at weak dissipation

The quantum-Kramers theory presented in Sec. IX.D.2 did not account for effects of possible deviations from a thermal Boltzmann weighting. Such deviations can occur at extremely weak friction, when the internal mechanism for replenishing the upper energy states may start to fail (this can happen if those states are not continuously prepared in thermal equilibrium by an outside mechanism). In other words, for extremely weak friction one finds a tiny population below the Boltzmann weighting at the upper energy levels. This possible nonequilibrium effect generally plays a very subordinate role in the low-temperature regime $T < T_0$ (Sec. IX.D.4), where the time available for equilibration grows exponentially. It may become observable, however, at temperatures above the crossover T_0, where quantum corrections to the classical Kramers weak-damping result (see Hänggi, 1986a; Büttiker, 1989) are of considerable interest (Melnikov, 1984, 1985; Larkin and Ovchinnikov, 1985; Rips and Jortner, 1986; Chow and Ambegaokar, 1988; Dekker, 1988; Griff *et al.*, 1989). This problem of *nonequilibrium quantum tunneling above* $T > T_0$ out of a metastable state at weak dissipation is most conveniently discussed in terms of the probability per unit time $f(E)$ of finding the system in the barrier region near a classical turning point with energy E. Moreover, let $P(E|E')$ again denote the classical conditional probability that the particle leaves the barrier region with energy E' and returns after a round trip with energy E. The steady-state function $f(E)$ therefore obeys the integral equation

$$f(E) = \int_0^\infty dE' P(E|E') r(E') f(E') , \tag{9.49}$$

where $r(E) = 1 - t(E)$ denotes the *quantum reflection,* while $t(E)$ is the quantum transmission. Here we again measure energy from the well bottom, $U(x = x_b) = E_b$. The boundary conditions on $f(E)$ are given as follows. For $E \to \infty$, $f(E)$ approaches zero, whereas deep inside the well $f(E)$ approaches the quantum-mechanical equilibrium value. The quantum rate of escape k is given by the outgoing flux,

$$k = \int_0^\infty dE\, t(E) f(E) . \tag{9.50}$$

Together, Eqs. (9.49) and (9.50) yield a solution of the quantum rate problem for any given quantum transmission $t(E)$; but in contrast to the multidimensional quantum transition-state theory in Sec. IX.D.2, the solution of the integral equation (9.49) also allows for deviations from the corresponding equilibrium solution.

1. Quantum escape at very weak friction

At extremely weak damping the conditional probability $P(E|E')$ is peaked sharply around $E \sim E'$, due to the small loss of energy along the undamped, deterministic trajectory. Upon expanding Eq. (9.49) up to second order in $(E - E')$, one finds the differential approximation to the integral equation (Griff *et al.*, 1989)

$$t(E) f(E) = \frac{\partial}{\partial E} \Lambda(E) \left[1 + \beta^{-1} \frac{\partial}{\partial E} \right] r(E) f(E) , \tag{9.51}$$

where $\Lambda(E)$ denotes the energy-loss coefficient

$$\Lambda(E) = \int_0^\infty \gamma(s) J(E,s) ds ,$$

with $J(E,s)$ the delayed action along the undamped trajectory,

$$J(E,s)=M\int_0^{P(E)}dt\,\dot{q}(E,t)\dot{q}(E,t-s)\ ,$$

and with $P(E)$ the period of oscillation in the metastable well region at energy E. In contrast to previous approaches (Melnikov, 1984, 1985; Rips and Jortner, 1986; Chow and Ambegaokar, 1988; Dekker, 1988), the right-hand side of Eq. (9.51) explicitly contains the quantum reflection $r(E)$. Here we want to determine the quantum corrections to the classical Kramers rate. In this case $f(E)$ will deviate from the equilibrium value $f_{\rm eq}(E)=(\pi\hbar)^{-1}\sinh(\frac{1}{2}\hbar\beta\omega_0)\exp(-\beta E)$, only for energies near the barrier energy E_b. Hence we may approximate the transmission coefficient $t(E)$ by the parabolic barrier result, $t(E)=\{1+\exp[-2\pi(E-E_b)/(\hbar\omega_b)]\}^{-1}$. The solutions of Eqs. (9.50) and (9.51) then yield the central result (Griff *et al.*, 1989)

$$k=\frac{\omega_0}{2\pi}\frac{\sinh(\frac{1}{2}\hbar\beta\omega_0)}{\frac{1}{2}\hbar\beta\omega_0}\frac{\pi\rho}{\sin(\pi\rho)}\left[\frac{(\rho)^\rho}{\Gamma(1+\rho)}\right]^2\delta^{1-\rho}\exp(-\beta E_b)\ , \tag{9.52}$$

where $\rho=\hbar\beta\omega_b(2\pi)^{-1}$ and where $\delta=\beta\Lambda(E_b)$ is the dimensionless energy loss at the barrier energy. For Ohmic friction $\gamma(t)=2\gamma\delta(t)$, one finds $\delta=\beta\gamma I(E_b)$. The result in Eq. (9.52) holds at extremely weak friction, $\delta\ll 1$, and at temperatures T above crossover T_0, that is, $\rho<1$. Moreover, Eq. (9.52) *holds uniformly* both for $\rho^2\ll 1$, and $\delta\ll 1$. At high temperatures $[\rho,\hbar\beta\omega_0(2\pi)^{-1}\ll 1]$, Eq. (9.52) approaches the weak-damping result of Kramers (1940), $k\to k_{\rm cl}=\omega_0(2\pi)^{-1}\delta\exp(-\beta E_b)$ [see Eq. (4.49)]. The leading weak-damping ($\delta\ll 1$) quantum corrections Q follow from Eq. (9.52) with $k=Qk_{\rm cl}$ as

$$Q=\exp\left\{\frac{\hbar\beta\omega_b}{2\pi}\left[2C+\ln\left[\frac{\hbar^2\omega_b^2\beta^2}{4\pi^2\delta}\right]\right]+\frac{1}{24}(\hbar\beta\omega_0)^2\right\}\ , \tag{9.53}$$

where $C=0.5772\ldots$ is Euler's constant.

Clearly, for $\rho^2<\delta\ll 1$ the logarithmic term in the exponent of Eq. (9.53) gives a negative contribution that may compensate for the other positive terms. Hence, within the range of validity of our formula, there exists a region in parameter space where the correction factor Q is actually less than one. In this region quantum reflection above the barrier dominates over quantum transmission, thus leading to a net *reduction of the full rate below its corresponding classical value* (Griff *et al.*, 1989). This feature runs counter to common knowledge and intuition—the full rate is often approximated by simply adding the classical rate and the zero-temperature rate [see Eq. (9.1)]. Such an approach not only entirely disregards the complex interplay between thermal and quantal fluctuations (see Sec. IX.D), but also neglects the role of quantum reflection and nonequilibrium. We also remark that the leading correction in (9.53) is proportional to $\hbar$, pointing to nontrivial quantum corrections, since the underlying Hamiltonian or the Schrödinger equation contains only $\hbar^2$. This possible novel quantum reduction below the classical rate is most pronounced for systems with very flat barriers (e.g., potentials of the Morse type) as they occur in absorption-desorption problems on surfaces.

2. Quantum turnover

In view of the different behavior above crossover $T>T_0$ inherent in the quantum-Kramers rate in Eq. (9.32) and the weak-damping quantum rate in Eq. (9.52), a turnover occurs as a function of the damping strength, analogous to the classical turnover discussed in Sec. VI. Following the same reasoning put forward by Pollak, Grabert, and Hänggi (1989), the turnover theory in Sec. VI.B can readily be generalized to the quantum case. We again use a multidimensional normal-mode description of the escape dynamics. Making use of Pollak's equations (1986b), which relate the products of quantum partition functions to the memory friction, we find that the quantum equilibrium probability $f_{\rm eq}(E)$ now reads

$$f_{\rm eq}(E)=\beta\frac{\omega_0}{2\pi}\frac{\mu}{\omega_b}\frac{\sin(\frac{1}{2}\hbar\beta\mu)}{(\frac{1}{2}\hbar\beta\mu)}\prod_{n=1}^{\infty}\frac{\omega_0^2+n^2\nu^2+n\nu\hat{\gamma}(n\nu)}{-\omega_b^2+n^2\nu^2+n\nu\hat{\gamma}(n\nu)}\exp(-\beta E)\ , \tag{9.54}$$

where μ is given in Eq. (3.45) and $\nu=2\pi(\hbar\beta)^{-1}$. For an undamped system this result reduces to the one given below Eq. (9.51).

The quantum rate itself can be obtained from Eqs. (9.49) and (9.50). With the solution of the integral equation in Eq. (9.49), using for $P(E|E')$ the Gaussian form of Pollak *et al.* (1989) and for $r(E)$ the corresponding parabolic approximation, $r(E)=\{1+\exp[2\pi(E-E_b)/(\hbar\mu)]\}^{-1}$, one obtains for the quantum transmission factor $\kappa_{\rm qm}$ [Eq. (6.9)] the result (Hänggi, Pollak, and Grabert, 1989)

$$\kappa_{\rm qm} \equiv k \left[\frac{\omega_0}{2\pi} \exp(-\beta E_b) \right]^{-1}$$

$$= \frac{\mu}{\omega_b} \prod_{n=1}^{\infty} \frac{\omega_0^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)}{-\omega_b^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)} \exp\left[\lambda \sin(\pi\lambda) \int_{-\infty}^{\infty} dx \frac{\ln\{1-\exp[-\delta(x^2+\frac{1}{4})]\}}{\cosh(2\pi\lambda x) - \cos(\pi\lambda)} \right], \tag{9.55}$$

where $\lambda = \hbar\beta\mu(2\pi)^{-1}$ and δ is defined in Eq. (6.9b). By use of the Euler-Maclaurin formula, the result in Eq. (9.55) can be recast as

$$\kappa_{\rm qm} = \frac{\mu}{\omega_b} \prod_{n=1}^{\infty} \frac{\omega_0^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)}{-\omega_b^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)} \prod_{n=0}^{\infty} \{1-\exp[-\delta(n^2+\tfrac{1}{4})]\}^{z_n}, \tag{9.56}$$

with

$$z_0 = \lambda \cot(\pi\lambda/2),$$
$$z_n = 2\lambda \sin(\pi\lambda)/[\cosh(2\pi n\lambda) - \cos(\pi\lambda)]. \tag{9.57}$$

With a dimensionless energy loss $\delta > \frac{1}{4}$, the quantum rate converges rapidly to the dissipative quantum-Kramers result in Eq. (9.32). In the classical limit, $\lambda \to 0$, $\nu \to \infty$, the result in Eq. (9.55) approaches the previous classical turnover expression in Eq. (6.9). Quantum effects on the conditional probability $P(E|E')$ have been further studied by Rips and Pollak (1990), who find an improved turnover theory in which the argument of the logarithm in Eq. (9.55) attains a correction of order $\hbar^2$, reflecting a quantum-induced skewedness for the probability $P(E|E')$.

F. Sundry topics on dissipative tunneling

The material in the preceding subsections make it clear that the problem of the quantum escape rate exhibits a much richer variety than that of the classical case. In particular, even in the regime of moderate-to-strong friction the detailed form of the metastable potential is of primary importance for the result of the action S_b and the prefactor of the quantum rate [see Eq. (9.39]. All the material on the quantum rate presented in the foregoing sections assumed a nonlinear potential $U(x)$ containing only a single metastable well (see Fig. 38). Below we shall discuss prominent results concerning the quantum rate behavior in double-well-like metastable situations. A detailed survey of the present state of the art of quantum effects for the important area of *nonadiabatic rate theory* is beyond the scope of the present review. For a brief discussion of this latter topic and the appropriate references we refer the reader to Sec. XII.

1. Incoherent tunneling in weakly biased metastable wells

An important case of anomalous tunneling behavior is that of potentials exhibiting a weak bias (see Fig. 44). In this case the standard WKB analysis or the instanton analysis must be modified due to the impact of back-scattering effects at weak dissipation (Hänggi, Weiss, and Riseborough, 1986). If we consider sufficiently strong Ohmic dissipation, however, the tunneling is *incoherent*, and the quantum rate at low temperature is the same both for a weakly biased single well and for a weakly biased double well (Weiss *et al.*, 1984). The forward rate k^+ has been calculated at zero temperature and Ohmic friction γ by Weiss *et al.* (1984) as

$$k^+(T=0) = \frac{\Delta^2}{2\omega_0} \frac{\pi}{\Gamma(2\alpha_c)} \left[\frac{\sigma}{\omega_0} \right]^{2\alpha_c - 1}. \tag{9.58}$$

It exhibits a *nonanalytic dependence on the bias* σ, while $k^-(T=0)=0$. At finite but low temperatures $T \ll T_0$, one finds (Fisher and Dorsey, 1985; Grabert and Weiss, 1985; Weiss, Grabert, Hänggi, and Riseborough, 1987)

$$k^+(T) = \frac{\Delta^2}{2\omega_0} \left[\frac{\beta\hbar\omega_0}{2\pi} \right]^{1-2\alpha_c} \frac{|\Gamma(\alpha_c + i\hbar\beta\sigma/2\pi)|^2}{\Gamma(2\alpha_c)} \times \cosh(\hbar\beta\sigma/2) \tag{9.59}$$

which with $\hbar|\sigma| \gg k_B T$, too, exhibits the universal T^2 dependence at low temperatures. For $\sigma \to 0$, $k^+(T)$ becomes proportional to $T^{2\alpha_c - 1}$ (Bray and Moore, 1982; Chakravarty and Leggett, 1984). The backward rate

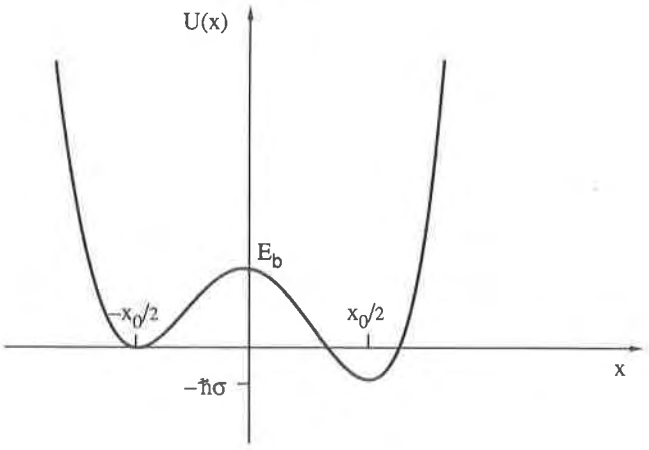

FIG. 44. An asymmetric double-well potential $U(x)$. The potential minima located at $\pm\frac{1}{2}x_0$ are separated by a weak bias energy $-\hbar\sigma$.

$k^-(T)$ is related to $k^+(T)$ by the detailed balance relation

$$k^-(T)=k^+(T)\exp(-\beta\hbar\sigma)\ . \tag{9.60}$$

In Eqs. (9.58) and (9.59) σ denotes the asymmetry parameter (see Fig. 44), and $\alpha_c=M\gamma x_0^2(2\pi\hbar)^{-1}$, where x_0 is the tunneling length, is a dimensionless dissipation constant. The quantity Δ is the dissipation-modified tunnel splitting element, whose exponential part, and in particular whose prefactor part, have been evaluated explicitly by Weiss, Grabert, Hänggi, and Riseborough (1987).

2. Coherent dissipative tunneling

In a double-well structure, a particle placed in either well will at zero temperature and zero dissipation clearly undergo undamped oscillations. For example, let $P_L(t)$, $[P_R(t)]$ denote the probability that a particle initially placed in the left-hand well, at time $t=0$, will be found in the left-hand (right-hand) well at a later time t (see Fig. 44). The dynamics of such a system is conveniently described by the relative occupation probability $P(t)=P_L(t)-P_R(t)$. In the presence of zero dissipation we find for $P(t)$ the oscillatory behavior

$$P(t)=\left[\frac{\sigma}{\Delta_b}\right]^2+\left[\frac{\Delta_0}{\Delta_b}\right]^2\cos(\Delta_b t)\ , \tag{9.61}$$

where $\Delta_b=(\sigma^2+\Delta_0^2)^{1/2}$ and $\hbar\Delta_0$ is the bare tunnel splitting at zero bias σ. Now it is quite plausible that sufficiently strong dissipation will not only modify, but eventually even destroy, the phase coherence exhibited by Eq. (9.61) (Simonius, 1978; Harris and Stodolsky, 1978, 1981). It is precisely this effect of dissipation on the phase coherence in Eq. (9.61) that commonly is studied as *dissipative quantum coherence* (Bray and Moore, 1982; Chakravarty, 1982; Schmid, 1983; Chakravarty and Leggett, 1984; De Raedt and De Raedt, 1984; Silbey and Harris, 1984; Aslangul, Pottier, and Saint-James, 1985, 1986; Carmeli and Chandler, 1985; Garg, 1985; Grabert and Weiss, 1985; Guinea, Hakim, and Muramatsu, 1985a; Stratt, 1985; Gillan, 1987; Weiss, Grabert, and Linkwitz, 1987; Weiss and Wollensak, 1989; for an authoritative review see Leggett *et al.*, 1987). In particular one finds at $T=0$ and $\sigma=0$ that in the presence of sufficiently strong Ohmic dissipation ($\alpha_c\geq 1$) a localization transition takes place (Bray and Moore, 1982; Chakravarty, 1982), $P(t)=1$ for all times t. Depending on the interaction mechanism, the question of just when the coupling is of sufficient strength is rather subtle, and in this context we refer the reader to the above-mentioned authoritative review (Leggett *et al.*, 1987). Generally speaking one finds for Ohmic dissipation $\hat{\gamma}(\omega=0)=\gamma>0$ that the phase-coherence oscillations survive only at short times and weak dissipation, i.e., for $\alpha_c=M\gamma x_0^2(2\pi\hbar)^{-1}<\frac{1}{2}$, low temperatures $\alpha_c k_B T\ll\hbar\Delta_0$, and a weak bias $\sigma<\Delta_0$.

3. Tunneling with fermionic dissipation

In the preceding sections we essentially restricted ourselves to a quantum treatment of the escape rate for particles coupled to an environment made up of harmonic oscillators. In other words, we mainly treated the case of a heat bath consisting of bosons. However, from a statistical physics point of view, there are profound differences between Fermi statistics and Bose statistics. It has been conjectured that in the weak coupling limit, i.e., with the coupling so weak that second-order perturbation theory is adequate, any environment can be approximated by a harmonic oscillator bath of bosonic nature (Feynman and Vernon, 1963; Caldeira and Leggett, 1983a). In recent years, the effect of a fermionic environment has been studied by Hamann (1970), Eckern *et al.* (1984), Guinea (1984), Kondo (1984), Yu and Anderson (1984), Chang and Chakravarty (1985), Guinea, Hakim, and Muramatsu (1985b), Vladar, Zimanyi, and Zawadowski (1986, 1988a, 1988b), Chen (1987), Hedegard and Caldeira (1987), and Sols and Guinea (1987). For a specific type of coupling to fermions a fermionic bath is equivalent to the coupling to a boson bath if one makes a suitable correspondence for the coupling constants (Chang and Chakravarty, 1985; Chen, 1987; Hedegard and Caldeira, 1987). This procedure has been utilized to study the effect of conduction electrons on the quantum mechanics of defects in metals (Kondo, 1984, 1988; Grabert, Linkwitz, Dattagupta, and Weiss, 1986; Richter, 1987; Dattagupta *et al.*, 1989; Weiss and Wollensak, 1989). For more general situations, however, like the description of two-level systems strongly interacting with a degenerate Fermi gas (Vladar, Zimanyi, and Zawadowski, 1986, 1988a, 1988b; Kondo, 1988), such a formal mapping no longer holds exact.

X. NUMERICAL METHODS IN RATE THEORY

Basically, two different approaches have been employed for the numerical evaluation of escape rates. The first method attempts to solve numerically the time evolution of the probability [Eq. (2.29)]

$$\frac{\partial p(t)}{\partial t}=\Gamma p(t)\ , \tag{10.1}$$

where $p_t\equiv p(\mathbf{x},t)$ is the probability density and Γ denotes the master operator characterizing the temporal evolution of the system. The second method investigates stochastic trajectories generated by a convenient numerical procedure from corresponding stochastic equations of motion

$$\dot{\mathbf{x}}=\mathbf{A}(\mathbf{x})+\xi\ , \tag{10.2}$$

where $\mathbf{A}(\mathbf{x})$ denotes the drift vector and the vector ξ denotes the appropriate random noise sources. In the case of the Kramers problem, the time evolution equation for the probability density is the Klein-Kramers equation [Eq. (4.4)],

$$\frac{\partial p(x,v,t)}{\partial t} = -v\frac{\partial p(x,v,t)}{\partial x} + \frac{\partial}{\partial v}\left[\left(\frac{1}{M}\frac{dU}{dx}+\gamma v\right)p(x,v,t)\right] + \frac{k_B T\gamma}{M}\frac{\partial^2}{dv^2}p(x,v,t) \ . \tag{10.3}$$

The corresponding stochastic equations of motion thus read

$$\dot{x} = v \ , \tag{10.4}$$

$$\dot{v} = -\frac{1}{M}\frac{dU}{dx} - \gamma v + M^{-1}\xi \ , \tag{10.5}$$

with the Gaussian random force obeying

$$\langle \xi(0)\xi(t)\rangle = 2M\gamma k_B T\delta(t) \ . \tag{10.6}$$

The first type of approach is based on a general numerical procedure for investigating the time-dependent solutions of Eq. (10.1). This methodology is well known (see, for example, Stratonovich, 1963) and has been described in detail by Risken and co-workers (Risken, 1984). In using it, one considers the eigenvalue expansion, which for a one-dimensional state vector is of the form

$$p(x,t) = \sum_i \phi_i(x)\exp(-\lambda_i t) \ , \tag{10.7}$$

where $\{\phi_i(x)\}$ and $\{\lambda_i\}$ are the eigenfunctions and the eigenvalues of the master operator Γ. The eigenfunctions are represented as linear combinations in a convenient infinite basis set $\chi_j(x)$,

$$\phi_i(x) = \sum_j \alpha_{ij}\chi_j(x) \ . \tag{10.8}$$

For numerical purposes this basis set is truncated, and after calculating the matrix elements $\langle \chi_i \Gamma \chi_j \rangle$ one finds that the problem reduces to the evaluation of the eigenvalue spectrum of a generally non-Hermitian matrix. When one makes a convenient choice of the basis set functions and explores the symmetries of the master operator, the matrix often turns out to be a band matrix, i.e., most of the matrix elements vanish. Effective matrix-continued fraction methods (Risken and Vollmer, 1979, 1980) can then be employed to evaluate the eigenvalue spectrum of such a matrix. The rate is obtained from the smallest nonzero eigenvalue λ_1 by means of Eqs. (2.31) and (2.32). Risken and co-workers (Risken, 1984) have successfully used this powerful method to evaluate rates for the Kramers problem out of a single metastable state, and in a double well, periodic potentials, or with the BGK collision operator for a double-well potential (Voigtlaender and Risken, 1984).

Stationary nonequilibrium situations may also be tackled using this same method (Jung and Risken, 1985; Jung and Hänggi, 1988; Jung, 1989). Such eigenfunction expansion methods allow for the accurate calculation of the rate with a relatively minor computational effort in systems consisting of a small number of variables n, typically $n \leq 2$, and for not too high Van't Hoff-Arrhenius factors, say $\beta E_b < 10$. Another advantage of the method is that, besides the rate, several other dynamical quantities, such as correlation functions, can be evaluated as well in a straightforward way.

In the second type of approach one generates realizations of stochastic trajectories using the equations of motion (10.2). Effective procedures exist for solving stochastic differential equations (Fox, 1988; Greiner, Strittmatter, and Honerkamp, 1988) or problems in many-dimensional systems by molecular dynamics methods (Rahman, 1964; Hoover *et al.*, 1982; Evans, 1983; Nose, 1984). A conceptually simple approach consists of starting the trajectories at the bottom of the metastable well and integrating the equations of motion. This approach has, for example, been used by Zhu *et al.* (1988a) to evaluate (*cis-trans*) isomerization rates. The particle will spend most of its time near the well but, very rarely, large excursions will allow the particle to surmount the barrier and relax to the other side of the well. A typical such trajectory is shown in Fig. 1. The average lifetime τ_e of the trajectory in either well is directly related to the rate $k \sim \tau_e^{-1}$.

This latter procedure is equivalent to the calculation of the correlation time of the correlation function (Sec. II),

$$C(t) = \frac{\langle \theta[x(0)]\theta[x(t)]\rangle}{\langle \theta[x(0)]\rangle} \ , \tag{10.9}$$

where $x(t)$ is the reaction coordinate, which is positive for a particle in the domain of attraction of the metastable state, and negative otherwise, and $\theta(x)$ denotes the characteristic function [see Eq. (2.15)]. Here we need to define a dividing surface ($x = 0$), which divides the phase space between reactants and products. Note, however, that since the probability density has its major contributions near the wells, the rate will be essentially insensitive (actually up to correction terms of order $O[\exp(-\beta E_b)]$) to the precise position of the dividing surface. The correlation function $C(t)$ will for long times decay according to

$$C(t) \sim \frac{k^+}{k^+ + k^-}\exp[-(k^+ + k^-)t] \tag{10.10}$$

[(Eq. (2.26)], which can be used to evaluate the rate.

The obvious drawback of this method is the inherent vast separation of time scales. Let us consider a simple estimate based on a characteristic microscopic time scale of our system τ_s (e.g., the period in the well). To intergrate the equations of motion over one period τ_s to some given accuracy, we need N (maybe $N \simeq 10^2$) time steps. The largest possible rate is given by the transition-state theory estimate $\tau_e^{-1} \sim \exp(-\beta E_b)$, i.e., the average time for one escape is $\tau_s \exp(\beta E_b)$. Therefore, to determine an average for just a *single* reactive event we must integrate the equations of motion over $N\exp(\beta E_b)$ time steps. In spite of present state-of-the-art computers, such an undertaking is feasible only for very low barriers, say ap-

proximately $\beta E_b \sim 5$. In other words, the problem of calculating a rate is enormously unwieldy. A practical method for calculating the escape rate ought to be able to overcome this problem.[22] This is possible with the reactive flux method (Sec. II.2) (Keck, 1960, 1967; Yamamoto, 1960; Fischer, 1970; Kapral, 1972; Bennett, 1975; Chandler, 1978, 1988; Montgomery *et al.*, 1979; Berne, 1985). One has only to consider the negative of the time derivative of Eq. (10.9),

$$\frac{\langle \delta[x(0)]\dot{x}(0)\theta[x(t)]\rangle}{\langle \theta(x)\rangle} \sim k^+ \exp[-(k^+ + k^-)t] . \tag{10.11}$$

Therefore the value of this function will approach the rate after an initial transient period. This now happens on a characteristic time scale of the system which is, most importantly, no longer exponentially large.

As shown in Sec. II we write with $k^+ \equiv k$

$$k = k_{\mathrm{TST}} \kappa , \tag{10.12}$$

where the transition-state value

$$k_{\mathrm{TST}} = \frac{\langle \delta[x(0)]\dot{x}(0)\theta[\dot{x}(0)]\rangle}{\langle \theta\rangle} \tag{10.13}$$

can be evaluated from an equilibrium average. The transmission coefficient κ is then related to the plateau value of

$$\kappa(t) = \frac{\langle \delta[x(0)]\dot{x}(0)\theta[x(t)]\rangle}{\langle \delta[x(0)]\dot{x}(0)\theta[\dot{x}(0)]\rangle} = \langle \theta[x(t)]\rangle_+ - \langle \theta[x(t)]\rangle_- \sim \kappa e^{-kt} . \tag{10.14}$$

The initial conditions for the trajectory calculations correspond to the nonequilibrium averages (Berne, 1985)

$$\langle \cdots \rangle_{\pm} = \frac{\langle \delta(x)\dot{x}\theta(\pm\dot{x})\cdots\rangle}{\langle \delta(x)\dot{x}\theta(\pm\dot{x})\rangle} , \tag{10.15}$$

and can be sampled by a convenient Monte Carlo procedure (Montgomergy *et al.*, 1979; Voter, 1985; Binder, 1986; Heermann, 1986; Doll and Voter, 1987).

The normalized reactive flux decays from unity to a constant (plateau value) after an initial transient period. Therefore, in a calculation of an escape rate, one would proceed in two steps. First, an appropriate dividing surface is chosen. This can be done by a variational procedure; the best choice for the dividing surface would minimize k_{TST}. However, almost any surface through the saddle point will do; the precise choice only slightly affects the efficiency of the calculation. Then one evaluates the transition-state value [Eq. (10.13)], which is an equilibrium average, and carries out a dynamical simulation for the reactive flux [Eq. (10.14)]. Usually the reactive flux rapidly approaches a constant plateau value from which the transmission coefficient κ can be determined. Having obtained k_{TST} and κ, one can then find the overall rate directly from Eq. (10.12).

At present, the reactive flux method is the only numerical approach that allows the calculation of equilibrium rates for arbitrarily high barrier energies. It can, moreover, handle systems with many degrees of freedom with a tractable computational effort. The reactive flux method can also become computationally very expensive if one attempts to obtain very accurate rates, say better than 5%, or if one applies it for the case of small transmission coefficients, say $\kappa < 0.1$. In particular, at low damping the convergence to the plateau value might sometimes require a substantial computational effort. The Columbia group has devised an approximate, but surprisingly accurate, modification of the reactive flux method, the *absorbing barrier method* (Straub and Berne, 1985; Straub, Hsu, and Berne, 1985), which allows one to evaluate very small transmission coefficients. This method and related approaches have been used to follow chemical reactions in liquids studying the full-time evolution of a many-particle system using molecular dynamics methods (Rosenberg, Berne, and Chandler, 1980; Karim and McCammon, 1986; Bergsma *et al.*, 1987; Gertner *et al.*, 1989). In the present formulation the reactive flux method is applicable only to cases in which the time derivative $\dot{x}$ is well behaved. Borkovec and Talkner (1990), however, have presented a generalization of the reactive flux method which accounts for nondifferentiable reactive trajectories as well [see Eq. (2.27)].

Computational methods for the quantum case have recently seen some enlightening developments. For example, a formulation of the quantum reactive flux, in which the thermal averaging process is separate from the quantum dynamics, has been presented by Voth, Chandler, and Miller (1989a). Moreover, following the reasoning of Gillan (1987), an intriguing procedure for computing the quantum rate, and particularly its semiclassical limit, has been developed by the same three authors (Voth, Chandler, and Miller, 1989b).

XI. EXPERIMENTS

In this section our focus will be on experiments investigating the rate between metastable states. Given the fact that the authors of this work must be classified loosely as "theoretical practitioners," our selection of examples is necessarily incomplete and has been determined by our knowledge and prejudices only.

Rate processes are of course ubiquitous in the fields of chemistry and transport theory. The earliest experimental efforts date back to the pioneering chemical reaction experiments in the laboratories of Jacobus Henricus Van't Hoff (1884) and Wilhelm Ostwald (1884). These early experiments, beautifully discussed by Arrhenius

[22] A related problem also arises in the expansion method using a basis set $\{\chi_i(x)\}$. In the case of high barriers, the large gap in the eigenvalues will give rise to ill-conditioning of matrices and lead to severe roundoff errors.

(1889), initiated an enormous research effort which persists until the present day and surely will continue into the future. While in earlier days most of the effort within the chemical physics community focused on gas phase reactions, the diversity of the field has grown considerably, including, among other reactions, state-selective chemical reactions in molecular beams, photochemical, radical, and catalytic processes, reactions in condensed phases, and surface chemical reactions. For example, within the context of chemisorption experiments (Stewart and Ehrlich, 1972; Balooch *et al.*, 1974; Auerbach *et al.*, 1984), the measurement of the activation energy alone can provide information about the internal mechanism (Brass and Ehrlich, 1986).

Other important areas that have provided many prominent contributions to rate theory are electrical transport (Shockley, 1950) and, more generally, diffusion processes[23] in solids (Vineyard, 1957; Dietrich, Fulde, and Peschl, 1980; Rezayi and Suhl, 1982; Toller, Jacucci, DeLorenzi, and Flynn, 1985; Doll and Voter, 1987; Jacucci *et al.*, 1987; Voter, 1989), on surfaces [Ehrlich and Stolt, 1960; Di Foggio and Gomer, 1982; see also Fig. 2(b)], and in amorphous or disordered materials (Alexander, Bernasconi, Schneider, and Orbach, 1981; Haus and Kehr, 1987). In this context, the anomalous temperature dependence of the Van't Hoff-Arrhenius factor [see Eq. (7.26)] has been observed recently in amorphous metallic alloys (Kronmüller and Frank, 1989).

In rate measurements, just as with theory, the detailed prefactor behavior of the rate is naturally more difficult to extract from measured data sets. In the remainder of this section we shall restrict our discussion to experiments relating to Kramers theory.

A. Classical activation regime

We start our discussion with physical systems used to check the classical Kramers theory (see Sec. IV). An ideal system for the experimental study of the Kramers model is that of a Josephson junction measuring the decay of the supercurrent. Early experiments dealt mainly with Kramers' intermediate-to-strong damping regime (Fulton and Dunkleberger, 1974; Jackel *et al.*, 1974; Klein and Mukherjee, 1982) and have been extended to the Kramers weak-damping regime only recently (Silvestrini *et al.*, 1988; Turlot *et al.*, 1989). In particular, in the work by Turlot *et al.* (1989), escape measurements have been carried out in which the (memory) damping alone is modified, while all other parameters are kept constant, thereby yielding *direct evidence* for Kramers' energy-diffusion-controlled rate formula [see Eqs. (4.48a), (5.41), and (5.43c)]. The results of this important experiment are depicted in Fig. 45.

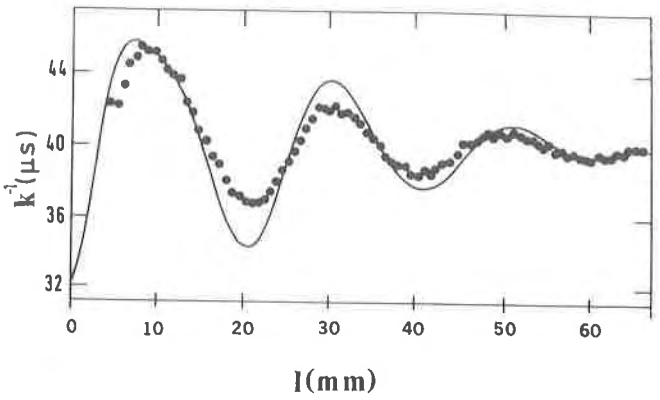

FIG. 45. Inverse thermal rate of escape (lifetime) k^{-1} of the zero-voltage state in a current-biased Josephson junction shunted by a transmission delay line, whose length l is increased *in situ*. In this memory-friction case, the energy-controlled Kramers rate, Eq. (5.41), exhibits a characteristic oscillatory pattern. The theoretical prediction (Grabert and Linkwitz, 1988) is shown by the solid line. From Turlot *et al.* (1989).

Experimental tests of the Kramers theory in higher dimensions, modeling the metastable potential field [see Eqs. (4.81) and (4.85)], and in the multidimensional low-friction case (see Sec. V.B) have been limited thus far (Naor *et al.*, 1982; Han *et al.*, 1989; Lefevre-Seguin *et al.*, 1990). Under normal circumstances the effect of higher dimensions on the prefactor is weak, due to a partial cancellation of the ratio of the potential well frequencies with the potential saddle-point frequencies [see Eqs. (4.81) and (4.85)]. A more direct test of the reaction dynamics in many dimensions would be given within an intermediate temperature regime in which one dimension behaved classically while the other dimension was quantum controlled.

For rate theory in nonthermal systems (see Sec. VIII) there is an immense theoretical literature, mostly relating to nonlinear optics (e.g., Hänggi *et al.*, 1980; Farina *et al.*, 1981, Lugiato, 1984; Shenoy and Agarwal, 1984; Talkner and Hänggi, 1984; Drummond, 1986), but thus far, only a few data are available on the switching rate between two modes in a dye-ring laser (Mandel, Roy, and Singh, 1981; Lett and Mandel, 1986). In contrast, some very beautiful experiments have been carried out for the mean first-passage time in the decay of an initially unstable state (Roy, Yu, and Zhu, 1985, Zhu, Yu, and Roy, 1986; James *et al.*, 1988).

Most of the chemical research has been restricted to a limited range of pressures or densities. More recent studies, pioneered mainly by the Göttingen group (Troe, 1986; Schroeder and Troe, 1987), attempt to cover a pressure range of several orders of magnitude. These recent data are shown in Figs. 46 and 47, in which a Kramers-like turnover (see Sec. VI), is clearly visible. Nevertheless, a detailed comparison of these experimental data sets with the theoretical models presented in earlier sec-

[23]Note that the diffusion coefficient D in a one-dimensional array of period L between neighboring metastable states is related to the rates by $D=\frac{1}{2}(k^{+}+k^{-})L^{2}$.

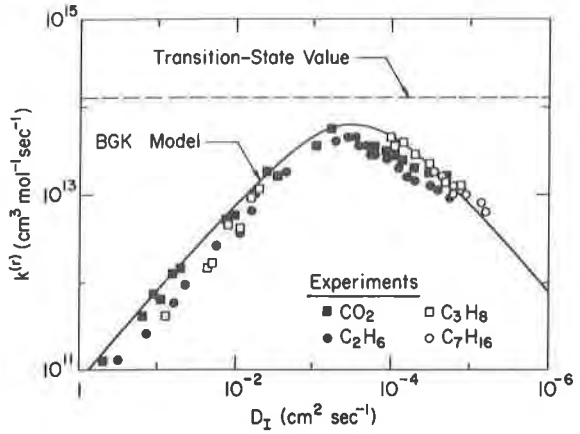

FIG. 46. Iodine atom recombination rates measured in different inert solvents (see inset) around 300 K, vs the diffusion coefficient D_I of a single iodine atom. Experimental data are from Troe and co-workers (Hippler *et al.*, 1973; Luther *et al.*, 1980; Otto *et al.*, 1984): solid line, prediction from a collisional BGK model without adjustable parameters (Borkovec and Berne, 1985b); dashed line, value of the transition-state rate. From Borkovec and Berne (1985). Reprinted with permission. © American Chemical Society.

tions of this review is rather difficult. The theoretical analysis is plagued by a number of complications, such as solvent-density-dependent modifications of the barrier height as a function of pressure (Schroeder and Troe, 1987), possible competition between different electronic states, curve crossing effects, and different reaction channels.

The first experiments exhibiting a rate turnover involved halogen recombination reactions, measured at two temperatures of 298 K and 314 K as a function of pressure in different inert supercritical gases (Hippler and Troe, 1976; Hippler *et al.*, 1984; Otto, Schroeder and Troe, 1984). The typical picture for iodine (see Fig. 46) clearly displays a turnover as a function of density (Luther *et al.*, 1980; Otto *et al.*, 1984). A theoretical analysis based on the BGK collisional model gives very good agreement (Borkovec and Berne, 1985b). The agreement is somewhat fortuitous in the low damping regime, since the BGK model, like the Kramers model (Sceats, Dawes, and Millar, 1985), does not predict the correct temperature dependence of the rate, which is dominated by a complex reaction mechanism not present in the model (Borkovec and Berne, 1985b; Berne, Borkovec, and Straub, 1988). A recent bridging expression due to Zawadzki and Hynes (1989) overcomes this shortcoming to some extent.

Other experiments that are of relevance to Kramers' ideas have been carried out on isomerization reactions in cyclohexane (Hasha, Eguichi, and Jonas, 1982a, 1982b) and particularly on stilbene isomerization (Brey *et al.*, 1979; Rothenberger *et al.*, 1983; Lee, Holtom, and Hochstrasser, 1985; Maneke, Schroeder, Troe, and Voss, 1985; Fleming, Courtney, and Balk, 1986). These are represented in Fig. 47. Note that the turnover in Fig. 47

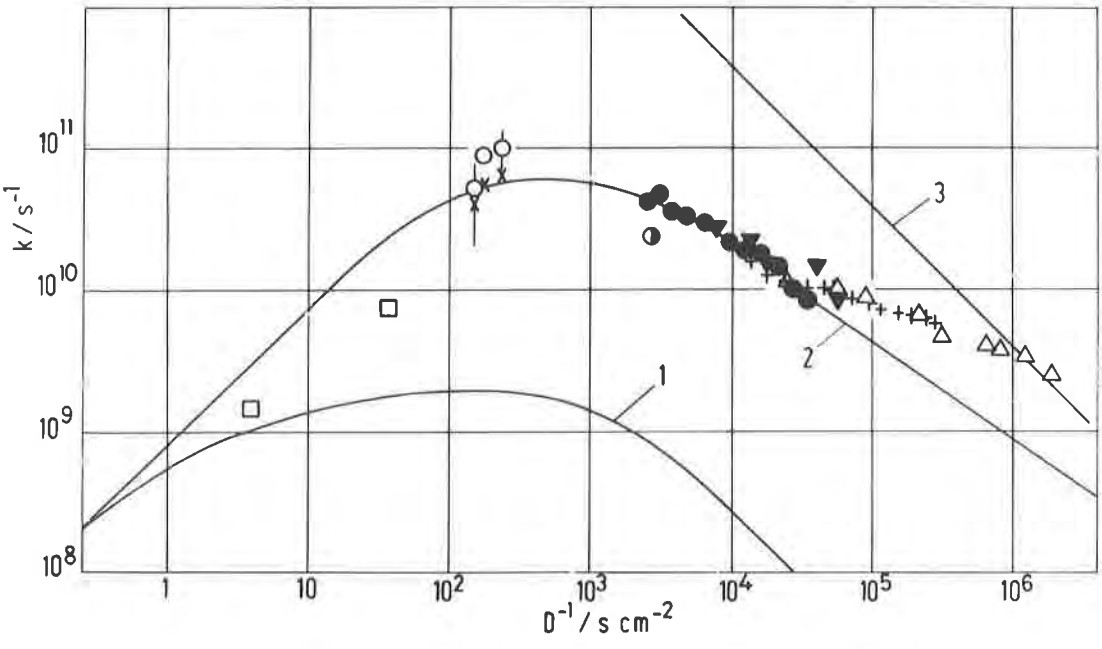

FIG. 47. Measured rates for the photoisomerization of *trans*-stilbene in the S_1 state extending from the low-pressure gas into the compressed-liquid range vs the inverse of the self-diffusion coefficient of the corresponding solvent (Maneke *et al.*, 1985): ○, ethane in the gas phase below 370 K; ×, same values converted to 295 K; □, methane (Fleming, Courtney, and Balk, 1988); ●, liquid ethane at 295 K; ▼, liquid propane at 298 K; ◑, liquid SF_6 at 298 K: +, linear *n*-alkanes at ambient pressure and temperature (Rothenberger, Negus, and Hochstrasser, 1983); △, liquid hexane at room temperature (Brey, Schuster, and Drickamer, 1979); curve 1, modeled unimolecular rate with turnover into spatial-diffusion control ($E_b = 1100$ cm^{-1}); curve 2, same as curve 1, but with a solvent density-dependent lowering of the activation barrier ($E_b = 700$ cm^{-1}); curve 3, free overdamped rotational rate proportional to inverse friction, $k \sim \omega_0^2/\gamma$. Figure provided by Professor Troe.

is broader than in Fig. 46. This broadening is caused by an increased number of degrees of freedom (see Sec. V). Due to strong interactions of the excited stilbene with the solvent, the activation energy shifts substantially with solvent density (Maneke *et al.*, 1985; Schroeder and Troe, 1987). Therefore a theory that does not account for such a barrier modification effect is obsolete—an essential fact repeatedly emphasized by Troe.

Further notable experimental work on chemical reactions, which can be interpreted along the lines inherent in Kramers' ideas, includes that of Zhu *et al.* (1988b) and Sivakumar *et al.* (1989) on isomerization reactions, the experiments of McManis and Weaver (1989) on electron transfer, and the electron-spin-resonance experiments of Fischer and Paul (1987) on radical reactions in the Smoluchowski regime.

B. Low-temperature quantum effects

The classical rate expression predicts that at zero temperature the rate will vanish completely, a disappearance that is formally expressed by the singularity of the Van't Hoff-Arrhenius factor. However, at lower temperatures the quantum effects discussed in Sec. IX take over and start to dominate. The phenomenon of quantum tunneling has been observed experimentally in a large number of metastable systems, e.g., in biophysical transport [Alberding *et al.*, 1976; Frauenfelder, 1979; Doster *et al.*, 1987; see Fig. 2(b)], quantum diffusion in solids (Alefeld and Völkl, 1978; Richter, 1987) or on surfaces [see Fig. 2(b)], chemical conversion processes (Goldanskii, 1976; Goldanskii *et al.*, 1987; Robie *et al.*, 1987), tunneling of domain walls in ferromagnetic materials (Riehemann and Nembach, 1984), or electron tunneling in amorphous alloys (Mansingh *et al.*, 1984; Kronmüller *et al.*, 1988), to name but a few. The effect of tunneling in these rate experiments is exhibited by a characteristic convex curvature in the corresponding Van't Hoff-Arrhenius plots (e.g., in Fig. 2), reflecting a temperature-dependent lowering of the activation energy [Eq. (9.34)].

Again, in the context of the quantum-Kramers theory presented in Sec. IX, our focus here will be on dissipative quantum rate processes as they occur in the nucleation of vortices in He II (Hendry *et al.*, 1988), in the escape of electrons from the surface of liquid helium (Goodkind *et al.*, 1988; Saville *et al.*, 1988), and most notably in low-temperature Josephson-junction systems (Jackel *et al.*, 1981; Prance *et al.*, 1981, Voss and Webb, 1981; Bol *et al.*, 1985; Devoret *et al.*, 1985; Dmitrenko *et al.*, 1985; Martinis *et al.*, 1985, 1987; Schwartz *et al.*, 1985; Washburn *et al.*, 1985; Washburn and Webb, 1986; Bol and de Bruyn Ouboter, 1988; Clarke *et al.*, 1988; Cleland *et al.*, 1988; Sharifi *et al.*, 1988; Esteve *et al.*, 1989; Han *et al.*, 1989; Iansiti *et al.*, 1989).

Figure 48 shows the recent results of the Berkeley group (Cleland, Martinis, and Clarke, 1988) on the decay of the zero-voltage state in a current-biased Josephson junction shunted with a normal-metal resistor in a temperature regime above crossover $T_0 \equiv T_{cr}$ [Eq. (9.14)], where thermal activation still dominates over quantum tunneling. There is good agreement with theory [Eqs. (9.32), (9.36), and (9.55)].

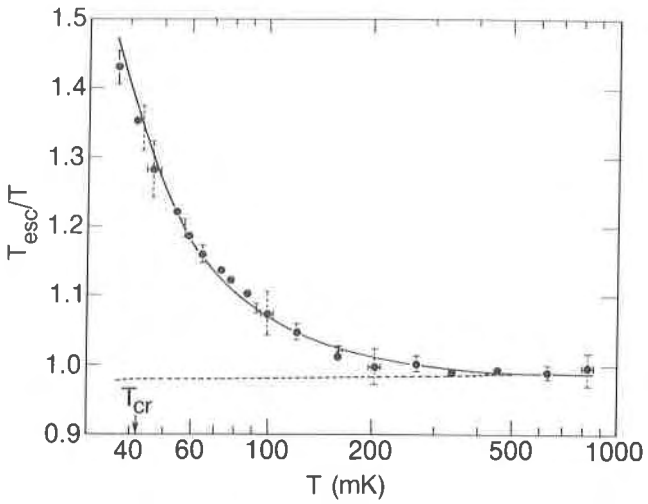

FIG. 48. Quantum-Kramers rate with Ohmic friction for the decay of the zero-voltage state in a current-biased Josephson junction near crossover $T \geq T_{cr}$. The quantity T_{esc} is defined as $k(\tau) \equiv (\omega_0/2\pi)\exp(-E_b/k_B T_{esc})$. Solid line, theoretical prediction based on Eq. (9.36); ●, the experimental values. $T_{cr} = 42 \pm 2$ mK denotes the crossover temperature [see Eq. (9.14)]. The dashed line gives the prediction of the classical Kramers theory. The Van't Hoff-Arrhenius factor βE_b ranges from 12.4 to 14.0. The solid bars represent the uncertainty in the junction parameters, while the dashed error bars represent uncertainty in the temperature calibration. After Cleland *et al.* (1988).

The quantum dissipative escape time, i.e., the inverse quantum-Kramers rate at $T = 18$ mK $< T_0 = 47$ mK has been measured very accurately in a Josephson system with Ohmic-memory friction, by the Saclay group (Estéve *et al.*, 1989); see Fig. 49. The agreement between the low-temperature quantum-Kramers theory in Eq. (9.39) and the experimental data is indeed striking. At low temperatures the quantum-Kramers rate exhibits a universal exponential temperature enhancement proportional to $\exp(\text{const}T^2)$ [Eq. (9.40)]. This characteristic signature of any Ohmic-low-temperature quantum behavior of the escape mechanism is shown in Figs. 50–52 for three different experiments on Josephson-junction systems. The tunneling of protons on hydrated protein powders in a recent experiment by Careri and Consolini (1989) has given evidence for a non-Ohmic dissipative mechanism. Their observation is similar, from a physics point of view, to the tunneling of impurities in solids which is described by Eq. (9.40) with $n = 4$.

XII. CONCLUSIONS AND OUTLOOK

Fifty years after Kramers, most of the theoretical and numerical groundwork has been laid for an understanding of the principles and the content of thermal reaction-

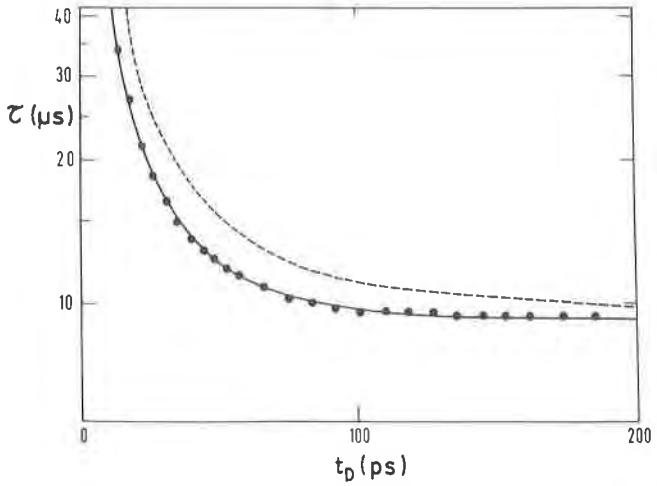

FIG. 49. Escape time $\tau = k^{-1}(T)$ of the quantum-Kramers rate vs delay time t_D at a temperature of $T = 18$ mK measured for the decay of the zero-voltage state in a Josephson junction shunted by a delay line whose length is increased *in situ*. An increase in the length yields an increase in the delay with which the resistor damps the junction. The solid circles are the experiments (Esteve *et al.*, 1989) and the solid line is the theoretical prediction based on Eq. (9.39) at $T = 18$ mK. The dashed line corresponds to the theoretical prediction at zero temperature using as prefactor the undamped value, while the exponential dissipative action [see Eqs. (9.6) and (9.37)] is evaluated up to first order in the dissipation strength (see Leggett, 1984b). Figure provided by Esteve *et al.* (1989).

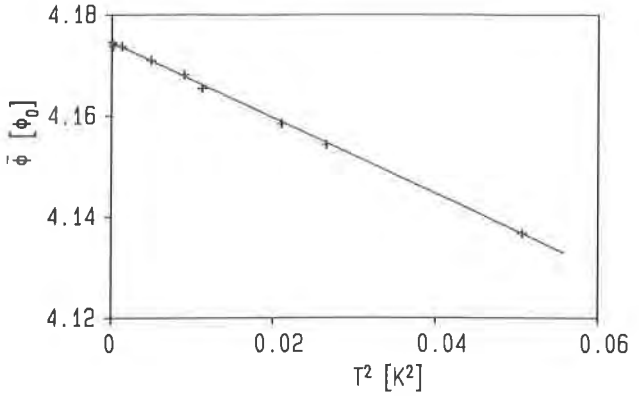

FIG. 51. The observed mean flux measured in a superconducting ring that is interrupted by a Josephson junction. The data are from Schwartz, Sen, Archie, and Lukens (1985). The mean flux is proportional to the temperature squared, indicating a corresponding temperature dependence of the rate itself, as predicted theoretically by Eq. (9.40) with $n = 2$.

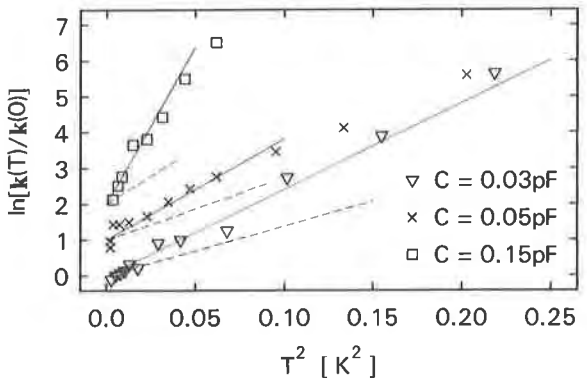

FIG. 50. The natural logarithm of the low-temperature quantum-Kramers rate for the decay of the zero-voltage state in a current-biased Josephson junction as a function of the squared temperature. The data are from Washburn, Webb, Voss, and Faris (1985), measured in three different samples with differing junction capacitances. The data fall on strength lines in accordance with the T^2 law of Grabert, Weiss, and Hänggi (1984). The dashed lines are theoretical predictions in which the value of the slope c [see Eq. (9.40)] has been taken for an idealized resistively shunted junction; these are about one-half of the experimental values for the nonideal junction used in the experiment.

rate calculations over the whole friction and temperature regime. To a somewhat lesser extent, the same holds true for metastable, stationary nonequilibrium systems. Most significantly, Kramers' original reasoning on how to calculate the escape rate for a damped, metastable Brownian motion dynamics has since been extended in several directions: If the rate is spatial-diffusion controlled, that is, if nonequilibrium effects for the population dynamics can safely be neglected, both the role of Brownian motion in phase space in the presence of a number of spatial di-

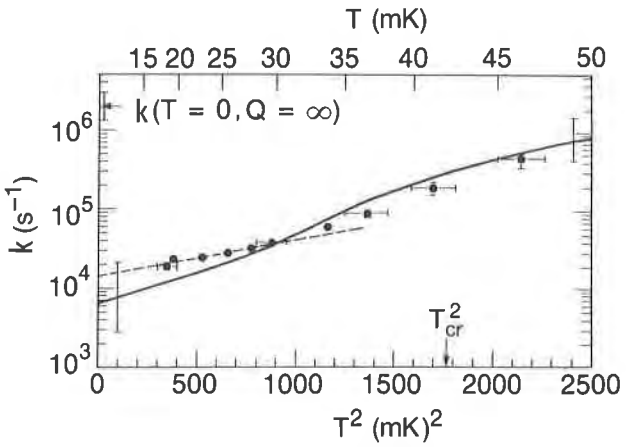

FIG. 52. Low-temperature quantum-Kramers rate data from the Berkeley experiment (Cleland, Martinis, and Clarke, 1988). The solid line is the theoretical crossover prediction of Grabert and Weiss (1984b). The vertical error bars arise from systematic errors for the parameters of the junction; the horizontal error bars indicate the uncertainty in the temperature calibration. The horizontal arrow denotes the zero-temperature, undamped quantum rate, and T_{cr}^2 denotes the squared crossover temperature, Eq. (9.14). The dashed line indicates a least-squares linear fit of the data below 30 mK to $\ln k(T) = A + BT^2$. The asymptote of the data is $A = 9.4 \pm 0.5$, while the theory in Eq. (9.39) predicts $A = 8.8 \pm 1.0$. The slope of the T^2 law [see Eq. (9.40)] for the data is $B = (1.3 \pm 0.1)\ (\mathrm{mK})^{-2}$, while theory yields $B = (1.9 \pm 0.2)\ (\mathrm{mK})^{-2}$. Figure obtained from Professor Clarke.

mensions or fields (see Sec. IV.F) and the impact of correlated thermal noise, i.e., memory friction, have been accounted for by the approaches presented in Secs. IV.F and III.C, respectively. These results have also been shown (Sec. III.C) to emerge as well from a multidimensional, harmonic transition-state theory in full phase space that incorporates both the degree(s) of freedom for the nonlinear reactive system and the degrees of freedom of the thermal bath. This connection makes explicit the fact that the theory developed by Kramers for moderate-to-strong friction, together with its generalizations to many spatial dimensions and to memory friction [such as, for example, the imaginary free-energy method due to Langer (1967, 1969)] does not contain kinetics that could account for possible nonequilibrium effects of the population dynamics. Such nonequilibrium effects, which play a crucial role in the weak-friction regime, are taken into account in the theory developed by Kramers for this regime, but appreciation and understanding of this work (Sec. IV.D) has been slow. Until recently, it had escaped the attention of many physicists engaged in rate calculations, starting with Chandrasekhar's (1943) otherwise authoritative survey. This area of weak-friction-controlled rate processes has since been developed considerably by chemical physicists, extending Kramers' continuous energy-diffusion model to models with discrete energy transfers. Chemical physicists have also generalized weak-friction rate theory to many dimensions with Markovian and/or non-Markovian reaction kinetics (see Sec. V). The above connection between multidimensional TST for the total system and Kramers' theory for the spatial-diffusion-controlled regime has proven extremely useful in constructing a classical turnover theory (Sec. VI.B) or its quantum generalization (Sec. IX.E.2), which unifies the weak-friction regime and the corresponding spatial-diffusion-controlled regime. Moreover, various criteria could be found (see Secs. IV.G and VI.C) for identifying the regime of validity for the mass of specialized rate formulas.

The striking advantages, i.e., the closed-quadrature expressions, as well as the disadvantages of the MFPT concept in higher dimensions and/or with a non-Markovian dynamics, have been elucidated in Sec. VII. Although the MFPT is closely connected with the flux-over-population technique (see Appendix B), the mean first-passage time has found widespread application in rate calculations for stationary nonequilibrium (see Sec. VIII). It has, however, almost exclusively been invoked in one-dimensional metastable situations only. Clearly, the absence of a detailed balance symmetry renders the rate problem in stationary nonequilibrium with more than one dimension a formidable task, which has been solved thus far only in special cases. As shown in Sec. IX, most of the original Kramers theory has, in recent years, been successfully generalized to lower temperatures down to absolute zero, thereby also accounting for the crossover between quantum-controlled and thermal-activation-controlled escape. Many of the theoretical rate formulas could be checked against powerful numerical rate procedures, such as the reactive-flux technique (see Secs. II.B and X).

Despite the many specific results in one and many spatial dimensions, there remain several open problems. In particular, there is a need for more detailed work with realistic models describing the actual experiments.

Within classical rate theory, one such area is the study of the rate mechanism at weak dissipation in multidimensional metastable systems and in metastable field-theoretic approaches (see Secs. V.D and VIII.D). For example, there is at present no detailed study of the soliton nucleation rate in the underdamped regime which consistently accounts for the field character of the metastable potential. Likewise, the rate at weak damping in a system of strongly coupled degrees of freedom can give rise to a complex memory friction with sharp resonancelike structures for its Fourier transform, which in turn may imply a breakdown of the assumptions used for the weak-friction theory in Sec. V.

Another open problem is the Kramers turnover in the presence of a multidimensional metastable potential function. This case is particularly delicate, because different metastable multidimensional systems might exhibit the *same* behavior for the rate at *moderate-to-strong friction,* as described by Eq. (4.81), while the weak-friction behavior might be *different* for each individual system (see Sec. V.D). Very little is known at present about the rate in coupled metastable systems in which the transitions between adjacent metastable states are correlated; the rate in one subunit may depend on the history of neighboring transitions.

Recently, some exciting observations in weakly damped metastable systems driven by external, time-periodic forces have been reported (Devoret *et al.*, 1984, 1987; Carmeli and Nitzan, 1985; Munakata *et al.*, 1985; Esteve, Devoret, and Martinis, 1986; Larkin and Ovchinnikov, 1986; Munakata, 1986; Chow and Ambegaokar, 1988; Turlot *et al.*, 1989). These observations have been labeled "resonance activation"; surprisingly enough, similar observations have been made in overdamped metastable systems, with the effect being termed "stochastic resonance" (Benzi *et al.*, 1981, 1982; Gammaitoni *et al.*, 1989, McNamara *et al.*, 1988; Debnath, Zhou, and Moss, 1989; Jung, 1989; Jung and Hänggi, 1989; Vemuri and Roy, 1989). Such systems exhibit *after* an averaging over a random phase, or over a period, undamped oscillations still present for the time-homogeneous correlation function, i.e., these systems are *not strongly mixing* (Jung and Hänggi, 1989). The decay in these overdamped metastable, periodically forced systems undergoes a typical modulation-induced rate enhancement characterized by the Hill-Floquet coefficient with the smallest, nonvanishing real part (Jung, 1989). Obviously there is still a rich variety of phenomena between these two limiting cases which deserves more detailed theoretical and experimental investigation.

We mention here, as well, the problem of *nonexponential decay laws* in reactions as they occur in spin glasses

(Binder and Young, 1986; Jäckle, 1986) and disordered media (Alexander *et al.*, 1981; Kelly and Kostin, 1986; Haus and Kehr, 1987; Rajagopal, Ngai, Rendell, and Teitler, 1988). In these cases the usual rate equations of the form in Eq. (2.12) do not exist.

With regard to quantum rate theory, all of the above open problems have their quantum counterparts. Moreover, the effect of nonlinear bath couplings yielding a state-dependent friction or a state-dependent diffusion coefficient [see Eqs. (2.6), (4.12), and (7.43)], and the influence of many dimensions for a nonlinear metastable potential function $U(\mathbf{x})$ [see Sec. IV.G], i.e., multidimensional quantum-Kramers theory, quantum nucleation, and the role of stationary nonequilibrium (Hida and Eckern, 1984; Hida, 1985; Nakaya and Hida, 1986; Ivlev and Melnikov, 1987), are only beginning to be investigated on a quantitative level.

Finally we remark that most of the material reviewed here concerns escape governed by a reaction coordinate moving on an adiabatic potential surface $U(\mathbf{x})$. An important category of quantum effects in the presence of electronic degrees of freedom is that of nonadiabatic transitions (Dogonadze *et al.*, 1968; Zusman, 1980; Trakhtenberg *et al.*, 1982; Calef and Wolynes, 1983; Frauenfelder and Wolynes, 1985; Garg, Onuchic, and Ambegaokar, 1985; Chandler, 1986; Goldanskii *et al.*, 1987; Kayanuma, 1987; Rips and Jortner, 1987; Straub and Berne 1987; Wolynes, 1987; Wilkinson, 1988; Ao and Rammer, 1989a, 1989b; Borgis *et al.*, 1989). For example, in chemical reactions both electrons and nuclei move. Because of the mass difference between electrons and nuclei, one frequently assumes that the electrons follow the nuclear motion adiabatically (Born-Oppenheimer approximation). In Fig. 53 we show two such neighboring Born-Oppenheimer surfaces corresponding to two different electronic states. The interaction between the two electronic states then results in a splitting Δ. A reaction from $A \rightarrow B$, or vice versa, is moderated by two characteristic time scales. Let $\tau_1 = \hbar/\Delta$ denotes the time within which the electronic charge will fluctuate between the two neighboring electronic states, and τ_2 be the typical time within which the nuclear reaction coordinate crosses the barrier region. For $\tau_1 \ll \tau_2$, the electronic degrees of freedom will successfully adjust to the nuclear coordinates (adiabatic transition), with the dynamics evolving on the lower adiabatic ground-state surface, which for small Δ often is characterized by a cusp-shaped potential form (see Sec. VII.E.2). On the other hand, for $\tau_1 \geq \tau_2$ nonadiabatic dynamic effects become important; the rate will be modified by an additional multiplicative factor P, which gives the probability for staying on the adiabatic ground-state surface. Traditional Landau-Zener-Stückelberg theory (Landau, 1983; Stückelberg, 1932; Zener, 1932) yields for this probability

$$P = 1 - \exp(-z\Delta^2) , \tag{12.1}$$

where z depends on the nuclear dynamics. For $z\Delta^2 \gg 1$, that is, $P \sim 1$, one recovers the adiabatic theory discussed throughout this review. By contrast, when $z\Delta^2 \ll 1$, yielding $P \propto \Delta^2$ (golden rule-like behavior), we have the hallmark of a truly nonadiabatic reaction. In a simple-minded approximation we can thus obtain for the rate transmission factor $\kappa = k/k_{\mathrm{TST}}$ the result

$$\kappa_{\mathrm{ad}} \rightarrow \kappa \simeq P\kappa_{\mathrm{ad}} = [1 - \exp(-z\Delta^2)]\kappa_{\mathrm{ad}} , \tag{12.2}$$

where κ_{ad} is the adiabatic transmission factor obtained from standard Kramers theory [see, for example, Eqs. (3.46), (4.33), (5.51), (6.9), and (9.55)]. Undoubtedly we shall see more research work in future years aimed at describing the influence of temperature and dissipation on the probability P itself, and on the parameters z and Δ.

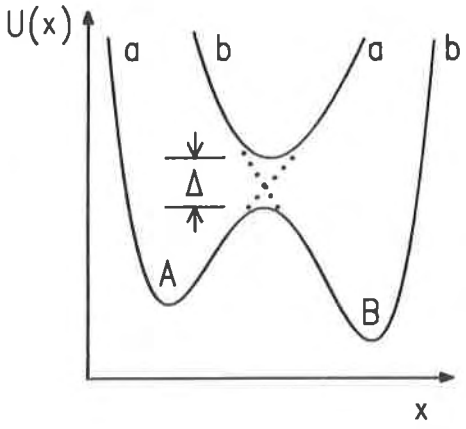

FIG. 53. Two neighboring Born-Oppenheimer (i.e., adiabatic) surfaces. For two electronic states *a* and *b* that do not interact, the resulting (diabatic) surfaces cross each other. In the presence of an interaction the two curves repel each other, yielding an adiabatic ground-state surface with two minima (lower solid line) and an excited surface. The two surfaces are separated in the transition region by the energy Δ.

ACKNOWLEDGMENTS

The authors would like to thank Bruce Berne, Hans-Benjamin Braun, Hermann Grabert, Waldemar Hontscha, Gert Ingold, Peter Jung, Fabio Marchesoni, Eli Pollak, Peter Reimann, Dieter Ryter, John Straub, Jürgen Troe, and Uli Weiss for enjoyable discussions and collaborations on classical rate theory, dissipative tunneling, and quantum rate theory. Many stimulating critical comments by these collaborators have added significantly to the form and content of this review. Moreover, we gratefully acknowledge insightful discussions with, among others, Markus Büttiker, Benny Carmeli, Sudip Chakravarty, David Chandler, John Clarke, Michel Devoret, Wolfgang Doster, Werner Ebeling, Uli Eckern, Daniel Esteve, Mathew Fisher, Hans Frauenfelder, James Hynes, Raymond Kapral, Yuri Klimontovich, Rolf Landauer, Anthony Leggett, Sebastian Linkwitz, John Martinis, Bernard Matkowsky, Frank Moss, Peter Olschowski, Philip Pechukas, Ilya Rips, Hannes Risken,

James Skinner, Attila Szabo, Harry Thomas, Nico Van Kampen, Peter Wolynes, and Robert Zwanzig. Further, the authors deeply thank Peter Jung for providing numerical results, and along with him, Lutz H'walisz and Sebastian Linkwitz for preparing many of the figures. Last but not least we wish to thank Mrs. Sigrid Schmidt for skillfully and patiently typing and correcting the manuscript. Support for this research has been provided by the Deutsche Forschungsgemeinschaft and the Schweizerischer Nationalfonds.

APPENDIX A: EVALUATION OF THE GAUSSIAN SURFACE INTEGRAL IN EQ. (4.77)

In this appendix we shall give some intermediate steps leading from the integral expression [Eq. (4.77)] for the probability current over the saddle to its explicit form [Eq. (4.78)].

First we get rid of the surface integral over the hyperplane $u=U_i(\eta_i-\eta_i^S)=0$ by introducing an appropriate δ function,

$$j=\int d\eta\,\delta(u)\sum_i U_i J_i(\{\eta\})\ . \tag{A1}$$

With the explicit expression for the probability current density $J_i(\{\eta\})$ [Eq. (4.76)] and the normalization of the vector U_i [Eq. (4.73)], we obtain

$$j=\left[\frac{k_BT}{2\pi}\right]^{1/2}\lambda_+Z^{-1}\int d\eta\,\delta(u)\exp[-\beta E(\{\eta\})]\ , \tag{A2}$$

where Eq. (4.63) for the equilibrium density has been used.

Next we use the Fourier representation of the delta function and introduce the quadratic approximation of $E(\{\eta\})$ about the saddle at $\{\eta\}=\{\eta^S\}$ [Eq. (4.65)]. This is a sufficient approximation in the desired order in k_BT,

$$j=\left[\frac{k_BT}{2\pi}\right]^{1/2}\lambda_+Z^{-1}\exp(-\beta E_b)\frac{1}{2\pi}\int d\eta\int dk\exp\left[ik\sum_j U_j(\eta_j-\eta_j^S)\right]\exp\left[-\tfrac{1}{2}\beta\sum_{ij}e_{ij}(\eta_i-\eta_i^S)(\eta_j-\eta_j^S)\right]\ . \tag{A3}$$

By an appropriate rotation $\mathbf{S}=(S_{ij})$ of coordinates about the saddle point, we can diagonalize the matrix $\mathbf{E}^{(S)}=(e_{ij})$ [cf. Eq. (4.65)],

$$\eta_i-\eta_i^S=\sum_j S_{ij}x_j\ , \tag{A4}$$

$$\tfrac{1}{2}\sum_{ij}e_{ij}(\eta_i-\eta_i^S)(\eta_j-\eta_j^S)=-\tfrac{1}{2}\mu_1x_1^2+\tfrac{1}{2}\sum_{l\geq 2}\mu_l^2x_l^2\ , \tag{A5}$$

where $-\mu_1$ is the negative eigenvalue of the matrix of second derivatives of the energy at the saddle and where μ_l, $l\geq 2$ are the positive eigenvalues of that matrix. Recall that in the derivation of Eq. (4.77) we assumed that η^S is a saddle point without any neutral direction. Consequently no vanishing eigenvalues of the matrix $\mathbf{E}^{(S)}$ can exist.

The integration over all coordinates x_l with $l\geq 2$ may be interchanged with the integration over k and can easily be performed to yield

$$\prod_{l\geq 2}\int_{-\infty}^{+\infty}dx_l\exp(ik\tilde{U}_lx_l)\exp(-\tfrac{1}{2}\beta\mu_lx_l^2)=\exp\left[-\frac{k^2}{2\beta}\sum_{l\geq 2}\frac{\tilde{U}_l^2}{\mu_l}\right]\left[\prod_{l\geq 2}\frac{\beta\mu_l}{2\pi}\right]^{-1/2}\ , \tag{A6}$$

where $\tilde{U}_l$ is the l component of the rotated vector U,

$$\tilde{U}_l=\sum_i S_{il}U_i\ . \tag{A7}$$

The remaining Gaussian integrals over k and x_1 are readily evaluated to yield for the probability flux

$$j=(2\pi\beta)^{-1/2}\lambda_+Z^{-1}\exp(-\beta E_b)\frac{1}{2\pi}\left[\prod_{l\geq 2}\frac{\beta\mu_l}{2\pi}\right]^{-1/2}\left[2\pi\beta\Big/\left[\sum_{l\geq 2}\frac{\tilde{U}_l^2}{\mu_l}\right]\right]^{-1/2}\left[\frac{2\pi}{\beta\mu_1}\sum_{l\geq 2}\frac{\tilde{U}_l^2}{\mu_l}\right]^{1/2}\left[\frac{\tilde{U}_1^2}{\mu_1}-\sum_{l\geq 2}\frac{\tilde{U}_l^2}{\mu_l}\right]^{1/2}\ , \tag{A8}$$

which with Eq. (A4) and Eqs. (4.73) and (4.74) simplifies to give Eq. (4.79).

APPENDIX B: A FORMAL RELATION BETWEEN THE MFPT AND THE FLUX-OVER-POPULATION METHOD

In this appendix we shall elaborate on a formal connection between the flux-over-population expression for the rate and the mean first-passage time. For this purpose we consider a Fokker-Planck process in an n-dimensional state space Σ. According to Eq. (7.3) the mean first-passage time $t_\Omega(x)$ out of a domain Ω of Σ is the solution of the boundary-value problem

$$\mathcal{L}^\dagger t(x)=-1,\quad x\in\Omega\ , \tag{B1a}$$

$$t(x)=0,\quad x\in\partial\Omega\ , \tag{B1b}$$

where $\mathcal{L}^\dagger$ denotes the backward operator (Feller, 1966; Hänggi and Thomas, 1982), i.e., the adjoint Fokker-Planck operator. Further let us consider the Green's function of the Fokker-Planck operator on Ω,

$$\mathcal{L}_x g(x,y) = -k\delta(x-y), \quad x \text{ on } \Omega \tag{B2a}$$

$$g(x,y) = 0, \quad x \text{ on } \partial\Omega , \tag{B2b}$$

where the subscript x at $\mathcal{L}$ merely denotes the set of variables on which $\mathcal{L}$ acts, and where $\delta(x-y)$ denotes the n-dimensional δ function. Clearly, the Green's function $g(x,y)$ may be interpreted as a stationary probability density of the given Fokker-Planck process with an additional point source of strength $k>0$ at $y \in \Omega$, and perfect sinks at the boundary $\partial\Omega$. Due to the conservation of probability the source strength k may be expressed in terms of the probability's being absorbed per unit time

$$k = -\int_\Omega \mathcal{L}_x g(x,y) d^n x = \int_{\partial\Omega} dS_i J_i(x,y) , \tag{B3}$$

where $\mathbf{J}(x,y)$ is the probability current density defined by

$$\frac{\partial}{\partial x_i} J_i(x,y) = -\mathcal{L}_x g(x,y) . \tag{B4}$$

If Eq. (B2a) is multiplied by the mean first-passage time $t(x)$ and then integrated over Ω, one obtains with Eqs. (B1b), (B2b), and (B3)

$$t(y) = \frac{\int_\Omega d^n x\, g(x,y)}{\int_{\partial\Omega} dS_i J_i(x,y)} . \tag{B5}$$

Hence, the mean first-passage time is represented in a population-over-flux expression analogous to the Kramers rate. We note that Eq. (B5) is a valid expression for the mean first-passage time irrespective of whether Ω is a domain of attraction and whether the noise is weak. However, only in these latter cases will the mean first-passage time be essentially independent of the starting point y, i.e., will the precise location of the source not matter. The presence of perfect sinks at the boundary in Eq. (B5) rather than a smooth distribution of sinks outside of Ω as in the Kramers expression [see text before Eq. (4.14)] must be compensated by a factor of 2 [Eq. (7.41)].

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