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BARRIER CROSSING AT LOW TEMPERATURES

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1. INTRODUCTION

Processes in which a particle must overcome an intervening potential barrier are ubiquitous in science, occurring in such fields as chemical kinetics, diffusion in condensed matter systems, biological transport, nuclear reactions, and possibly even describe the birth of the Universe. At high temperatures, the rate of such processes obeys the law by Van't Hoff [1] and Arrhenius [2], according to which the rate of escape k (rate coefficient) is proportional to the Boltzmann factor for thermal activation up the barrier top (see Fig. 1), i.e. with k_B the Boltzmann constant and T the temperature

$$k \propto \exp-(\Delta U / k_B T) \tag{1}$$

As one continuously lowers the temperature, this law predicts an exponential decrease of the rate, with no action taking place at absolute zero. However, at low temperatures the role of quantum mechanics provides a new mechanism by which a classically stable state can become unstable via quantum mechanical tunneling.

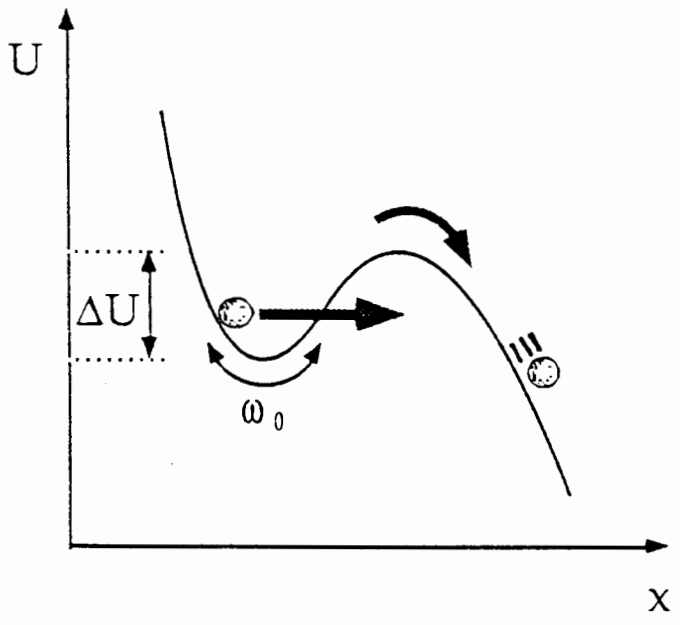

Fig.1. Barrier crossing in a metastable potential. The particle can leave the metastable well either via thermal activation (high temperature regime) or via quantum mechanical tunneling through the classically forbidden regime.

Reactive processes usually take place while in contact with random interactions between the system and its environment. The situation that a reaction proceeds essentially as a "free flight" over the barrier, which leads to simple Transition State Theory (TST), with no dynamical influence arising from the environment (solvent, solid, etc.) is rather exceptional. The article written by H.A. Kramers in 1940 [3] represents a milestone in the quantitative analysis of *dissipative* reaction processes. Up to this date, it continues to serve as a source of inspiration in an ever growing community of chemists, physicists, biologists and engineers [4]. Kramers investigated a model of nonlinear Brownian motion coupled to a thermal bath in such a way that the particle experiences a frictional force being proportional to its velocity. As just mentioned above, the original article contains a series of real gems: Most of all, it gives the description for the reaction rate for the "low friction" and the "high friction" regime. With $\beta = (k_B T)^{-1}$ denoting the inverse temperature the barrier crossing rate k can be cast into the form

$$k = \kappa \frac{\omega_0}{2\pi} \exp(-\beta \Delta U) \quad , \tag{2}$$

where ΔU is the barrier height (see Fig. 1), ω_0 is the angular frequency inside the metastable well, and κ denotes the "transmission coefficient" which corrects the simple transition state theory result for the effects of dissipation. The key results in Kramers work [3,4] have been the analytic estimate for the transmission factor in the weak friction regime, or *energy-diffusion* (ED) controlled regime, i.e. [3,4]

$$\kappa_{ED} = \gamma \beta I_b \qquad ; \qquad \text{if} \qquad \gamma \beta I_b << 1 \tag{3}$$

wherein γ denotes the (Ohmic-like) friction coefficient, and I_b is the (abbreviated) classical action of the escaping particle at the barrier energy. In the opposite regime, i.e. the *spatial-diffusion* (SD) controlled regime, Kramers found

$$\kappa_{SD} = \left(1 + \gamma^2 / 4\omega_b^2\right)^{1/2} - \gamma / 2\omega_b \quad \xrightarrow{\gamma >> \omega_b} \quad \frac{\omega_b}{\gamma} \quad , \tag{4}$$

where ω_b is the (unstable) angular frequency at the barrier top. In recent years there has been a tremendous activity aimed at extending and superseding the original Kramers theory [4, 10b, 20e]. In here we shall focus on two major extensions: The first one is the theory for the "turnover", i.e. the theory which bridges between the above two limiting regimes, while the second extension refers to the effects induced by quantum mechanics at low temperatures, where quantum tunneling events contribute to the reaction rate.

2. THE TURNOVER THEORY

It should be pointed out that no nonlinear potential possessing a well and a barrier is known for which the Kramers equation governing the (Markovian) nonlinear Brownian

motion can be solved analytically. In his original work [3] Kramers does confess that he has not found the solution for the transmission coefficient that bridges the regime of weak-to-moderate-to-strong friction on a unified level ("Kramers turnover problem"). A large number of authors have addressed this problem with varying level of success [4, 5-11]. Generally, all the previous attempts contain an element of arbitrariness, such as "ad hoc" assumptions used in the process of "button up" improved results obtained within the two limiting regimes. Inspired by Pollak´s normal mode approach to the barrier crossing problem [12, 13], Pollak, Grabert and Hänggi [14] put forward a solution of the turnover problem *without* the need to resort to "ad hoc" assumptions. The result[1] of the turnover theory then reads [14] in virtue of κ_{SD} in Eq. 4

$$\kappa = \kappa_{SD} \exp\left\{\frac{1}{\pi}\int_{-\infty}^{\infty} dy \frac{1}{1+y^2} \ln\left[1-\exp\left\{-\delta\left(1+y^2\right)/4\right\}\right]\right\} \quad . \tag{5}$$

Here, $\delta \equiv \Delta E\beta$ is the (dimensionless) average reduction of the energy in the unstable normal mode [14] when the particle starts at the barrier top, traverses the potential well and returns to the vicinity of the barrier top. Note that for $\delta >> 1$, Eq. 5 approaches κ_{SD}, whereas for $\delta << 1$ it reduces to the weak friction limit in Eq. 3. Quite recently, this turnover theory has been tested against numerical simulations by several groups [15a, 15b]: Given the situation in Fig. 1, Linkwitz et al. [15a] consider a cubic metastable potential for the reaction coordinate x, i.e.

$$U(x) = \frac{1}{2} M\omega_0^2 x^2 \left(1 - \frac{x}{x_0}\right) \tag{6}$$

with a minimum at x = 0 and the maximum at $x = (2/3)x_0$, and where M denotes the mass of the reactive particle. This yields a barrier height E_b of

$$E_b \equiv \Delta U = \frac{2}{27} M\omega_0^2 x_0^2 \tag{7}$$

and the (positive valued) angular barrier frequency ω_b equals the angular well frequency ω_0. For the energy loss δ one finds explicitly [14, 15a]

$$\delta \equiv \beta\Delta E = \beta\frac{36}{5}\Delta U\left\{\frac{\gamma}{\omega_0}\kappa_{SD}\left(1+\frac{\gamma^2}{4\omega_0^2}\right)^2\left[1+60\frac{\gamma}{\omega_0}\left(1+\frac{\gamma^2}{4\omega_0^2}\right)^{1/2}\kappa_{SD}^{-8}\right.\right. \times$$

[1] For a potential with two metastable wells the transmission factor κ in Eq. 5 must be modified to include the energy loss inside both wells, i.e. $\kappa \to \kappa_{SD} E(\delta_1)E(\delta_2)/E(\delta_1+\delta_2)$, where E(...) denotes the exponential function in Eq. 5, see Eq. 6.11 in Ref. [4].

$$\times \left[\psi'\left(\kappa_{SD}^{-2}\right) - \kappa_{SD}^{2} - \kappa_{SD}^{4}/2 - \kappa_{SD}^{6}/6\right]\Bigg]\Bigg\} \quad , \tag{8}$$

where $\psi'(z)$ denotes the trigamma function. For $\gamma / \omega_0 << 1$ one finds

$$\delta \xrightarrow{\gamma/\omega_0 \to 0} \beta\frac{36}{5}\Delta U\left\{\frac{\gamma}{\omega_0} - 1.804\left(\frac{\gamma}{\omega_0}\right)^2 + O\left(\frac{\gamma}{\omega_0}\right)^3\right\} \quad . \tag{9}$$

The comparison between the turnover theory [14] and the numerical simulations [15a] is depicted in Fig. 2.

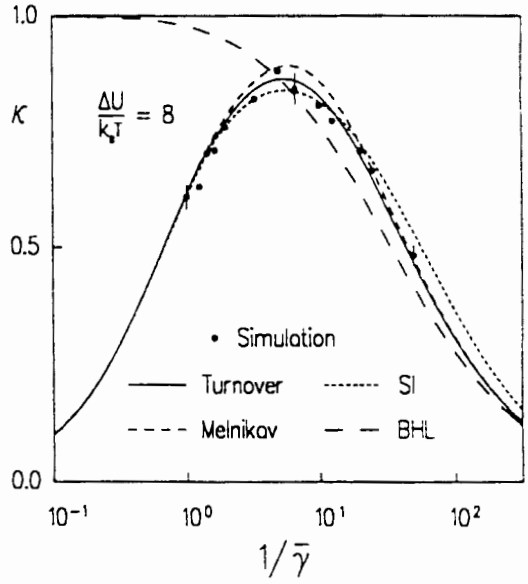

Fig. 2. The transmission factor κ is depicted versus the inverse dimensionless friction $\bar{\gamma} = \gamma / \omega_0$ (after Ref. 15a). The dots give the results of the simulation for the Kramers equation with Ohmic friction in the metastable cubic potential in Eq. 6 at $\beta\Delta U = 8$. The simulation is compared with the turnover theory [14] in Eq. 5 (solid line), the approach due to Melnikov [10] (short-dashed), the (weak-friction) bridging expression (BHL) in Ref. [7] (long-dashed) and the simple interpolation (SI) result, i.e. $\kappa^{-1} \equiv \kappa_{ED}^{-1} + \kappa_{SD}^{-1}$, (dotted). The error bars indicate the statistical uncertainties of the numerical simulation.

As can read off from Fig. 2, the turnover theory [14] very well coincides with the simulation. The result due to Melnikov [10] overestimates the transmission factor within the turnover region. The simple interpolation (SI), i.e., $\kappa^{-1} = \kappa_{ED}^{-1} + \kappa_{SD}^{-1}$ is qualitatively correct in the whole regime. Thus, seen from a practical point of view – when high precision predictions are of no necessity – the simple interpolation (SI) estimate suffices in many cases. (Note that the SI-estimate can fail considerably, however, for different potentials and – most importantly – for the case of strong memory friction [4, 20d, e]).

Before we proceed with the discussion of the rate coefficient at low temperatures we emphasize for the (high temperature) *classical rate* the following features:

(i) The dissipative mechanism enters not the exponential part of the rate, but influences the *prefactor* (the transmission factor) only.

(ii) The turnover result for the transmission coefficient in Eq. 5 depends not only on the actual dissipative friction mechanism but involves as well – via the energy loss δ – a dependence on the potential shape.

(iii) The strong-friction regime is characterized by the fact that the transmission κ does not involve the actual potential shape, but only depends on the corresponding values of local quadratic curvatures at the well bottom, ω_0, and at the barrier top, ω_b, respectively.

(iv) The transmission factor depends generally on the *dimension* of the metastable potential landscape [4] (note in particular the contributions in this book by Nitzan and Schuss, and by Han, Lapointe and Lukens).

(v) The transmission coefficient in Eq. 5 is evaluated to leading order within the steepest descent approximation. The fact of a finite barrier height $\beta\Delta U$ necessarily implies higher order corrections. Such higher order corrections to the transmission coefficient are both of *static* [16-19] (i.e. due to the potential nonlinearity) and *dynamic* (i.e. due to friction-induced) origin. By use of the reactive flux expression for the rate [4, 20a-e, 21] and expanding about the parabolic barrier limit one finds an improved result for κ_{SD} [22]. It explicitly reads for a cubic oscillator in Eq. 6, cf. Fig. 1, (see Eq. 4.12 in Ref. [22a])

$$\kappa_{SD} = \kappa_{SD}\,(Eq.4)\left(\frac{1}{\hbar\omega_0\beta Z_0}\right)\left\{1+(\beta\Delta U)^{-1}\frac{1}{36\chi^3}\right. \times$$

$$\left.\times\left[2-3\chi-\frac{1}{2}(\chi+1)^3+\frac{3}{2}\frac{(\chi-1)^2(\chi+1)(3\chi^2+12\chi+1)}{9\chi^2-1}\right]\right\}. \qquad (10a)$$

Here,

$$\chi = 2\omega_b\left(1+\frac{\gamma^2}{4\omega_b^2}\right)^{1/2}/\gamma \qquad (10b)$$

denotes the nonlinearity parameter [22]. The term within the large angular brackets accounts for the nonlinearity corrections within the metastable well, with Z_0 being the (nonlinear) partition function of the metastable well.

(vi) The turnover theory in Eq. 5 can now be considerably improved for dynamic and static finite barrier corrections: If we substitute κ_{SD} from Eq. 4 by the new, corrected expression in Eq. 10a, and in addition correct for nonlinearity corrections inside the small friction regime, we set (by following the reasoning in Ref. [8])

$$\kappa_{SD}\ (\text{Eq. 4}) \rightarrow \kappa_{SD}\ (\text{Eq. 10a}) \left\{ 1 + \theta\left[1 - \gamma\beta \mathrm{I}_b\right] \left(\frac{k(\text{Eq. 18 in Ref. [8]})}{\gamma\beta \mathrm{I}_b \frac{\omega_0}{2\pi} \exp(-\beta E_b)} - 1 \right) \right\}, \tag{11}$$

wherein θ denotes the unit-step function. Alternatively, we could set instead of the rate k (Eq. 18 in Ref. [8]) the inverse of the exact mean first passage time to reach the threshold energy $E = E_b$, cf. Eq. (5.41) in Ref. [4]. With Eq. 11 we include – via the quadrature expressions for the improved energy-diffusion rate in Ref. [8] – the effect of the nonlinear energy-diffusion D(E) induced by the potential nonlinearity inside the well region below barrier top.

We conclude this section by further pointing out that the effect of *both* a nonlinear metastable potential and a nonlinear bath-coupling (i.e. a nonlinear friction) has recently been studied via reactive-flux simulations by Voth et al. [23].

3. QUANTUM RATE THEORY

3.1 Traditional Approach: Simple Quantum TST

As can be noted from the classical rate formula of Van't Hoff (1884) and Arrhenius (1889), cf. Eq. 1, one finds a vanishing rate as the temperature is lowered to absolute zero. A crude, but frequently employed rate formula for the total rate k is obtained by adding to the classical rate, k_{cl}, a Gamow-type tunneling rate, k_{qm}, at zero temperature, i.e. the total rate is then written as

$$k = k_{cl} + k_{qm} \quad , \tag{12}$$

see e.g. Ref. [24]. The basic philosophy 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 the reasoning of Wigner [25], temperature effects have been incorporated into the quantum rate in the absence of dissipation by averaging the (non-dissipative) quantum transmission t(E) with the canonical equilibrium probability [24, 26, 27]. This procedure is analogous to simple transition state theory and will therefore be termed *"simple quantum TST"*; i.e. with Z_0 denoting the quantum partition function of the metastable state one obtains

$$k_{qm}^{TST} = Z_0^{-1}(2\pi\hbar)^{-1}\int_0^{\infty} t(E)\exp(-\beta E)dE \quad , \tag{13}$$

wherein we measure energy from the well bottom. The inclusion of dissipation is certainly more subtle: With the reactive particle being coupled to the environment during the whole reactive scattering process it can gain or lose energy at arbitrary instances. Thus, the concept of a transmission factor for the reactant becomes ill-defined in presence of dissipation. A convenient approach which overcomes this difficulty has recently been put forward on the basis of the functional integral formalism. Following the reasoning of Langer [28] (which he originally invented to study the classical nucleation problem) the approach to the dissipative tunneling rate can be based on the imaginary-time functional integral approach (imaginary free-energy method). This method itself is not exact within the full time-dependent quantum approach, but is restricted to the semiclassical limit. The essence of the approach consists in a semiclassical steepest descent evaluation of the free energy. This latter approximation leads to the so called "dissipative bounce solution" as the primary object of the theory. At zero temperature this approach has been pioneered by Caldeira and Leggett [29, 30]. The method has been extended by the Augsburg-Essen-Polytechnic-Stuttgart - group and the Moscow School to finite temperatures, covering all temperatures in the range from T = 0 up to the classical regime [31, 32, 33, 34, 35, 36]. We shall not further belabour this approach herein, because there exists a convenient multi-dimensional WKB-approach based on periodic orbits [37] which – if applied to the dissipative case [38] – yields identical results (see Chapt. 4).

3.2. The Exact Quantum-Rate: Flux-Flux-Autocorrelation Integral

The beginning point for the discussion of the quantum rate is a formally exact rate expression, which is rooted in previously derived formally exact correlation function results [39, 40]. Let Z_0 denote the quantum partition function of system plus bath for the metastable state located inside the well minimum, see Fig. 1. Further, let $s(q_1,...,q_f)$ denote the surface separating reactants from products in full configuration space $\{q_1,...,q_f\}$. $x(q_1,...,q_f)$ is the reaction coordinate, and let $\mathbf{p}$ be the momentum operator of the reactive particle in configuration space. The derivative ∇s, is the derivative normal to the surface. Then, with M being the reduced mass of the reactive system, the flux-through-a-surface operator has the form

$$F = \delta(s)\nabla s \cdot \mathbf{p} / \mathrm{M} \tag{14}$$

The thermally averaged tunneling rate k is formally given by [39, 40, 41, 42]

$$k = \mathrm{Re}\left\{Tr\left[\exp(-\beta\mathcal{H})F\mathcal{P}\right]\right\} / Z_0 \quad , \tag{15}$$

where Re denotes the "real part", Tr indicates the trace, $\mathcal{H}$ is the time-independent Hamiltonian operator of the total system, and $\beta = (k_B T)^{-1}$ again is the inverse temperature. The operator $\mathcal{P}$ reads

$$\mathcal{P} = \lim_{t \to \infty} \exp(i\mathcal{H}t / \hbar) h(\mathbf{p}) \exp(-i\mathcal{H}t / \hbar) \quad , \tag{16}$$

with $h(\mathbf{p}) = 1$, if $p > 0$ and $h(\mathbf{p}) = 0$, if $p < 0$. The operator $\mathcal{P}$ projects onto all states that have positive momentum in the infinite future ($t \to \infty$). By use of a few formal manipulations the exact rate in Eq. 15 can be recast in terms of a time integral over a flux-flux autocorrelation function, i.e. with the symmetrized flux operator

$$\hat{F} = \frac{1}{2M} [\delta(s) \nabla s \cdot \mathbf{p} + \mathbf{p} \cdot \nabla s \, \delta(s)] \tag{17}$$

and

$t_c \equiv t - i\hbar\beta / 2$, Eq. 15 can be written in the form [42],

$$k = \frac{1}{2} Z_0^{-1} \int_{-\infty}^{\infty} C(t) dt \quad , \tag{18}$$

where

$$C(t) = Tr\left[\hat{F}(t_c)\hat{F}(0)\right] \quad , \tag{19}$$

with

$$\hat{F}(t_c) = \exp(-i\mathcal{H}t_c / \hbar)\hat{F}(0)\exp(i\mathcal{H}t_c^* / \hbar) \quad . \tag{20}$$

Miller et al. [42] have further demonstrated that the rate in Eq. 18 is fully equivalent with the quantum-correlation function formalism due to Yamamoto [39]. Nevertheless, the correlation function in Eq. 19 distinctly differs from Yamamoto´s one, and in fact only their integrals agree. Moreover, note that the correlation function formalism in Eq. 18 presents a dynamical approach. Therefore, the formally exact expression covers both, the quantum energy-diffusion limited as well as the quantum spatial-diffusion limited rate regime.

The correlation function result in Eq. 18 is analogous to the Green-Kubo formulas for transport coefficients. For a simple situation, such as for a one-dimensional barrier, i.e.

$$U(x) = E_b - \frac{M}{2} \omega_b^2 (x - x_b)^2 \tag{21}$$

the exact result for Eq. 18 becomes

$$Z_0 k = \frac{\left(\frac{1}{2}\hbar\beta\omega_b\right)}{\sin\left(\frac{1}{2}\hbar\beta\omega_b\right)}\left[\frac{k_B T}{h}\exp(-\beta E_b)\right] \tag{22}$$

In other situations, however, with generally non-separable potential fields it becomes essentially impossible to evaluate analytically the result in Eq. 18.

Recently the feasibility of an evaluation of the rate expression in Eq. 18 has been demonstrated for a series of different non-dissipative reactions via a *numerical* evaluation of the corresponding quantum flux-flux autocorrelation function. By use of a variety of methods, the research group of Light et al. has impressively calculated quantum rates for the collinear $H + H_2$ reaction [43], the three-dimensional $H + H_2$ reaction scheme [44], as well as for the exchange reaction of hydrogen isotopes [45,46]. The authors have found good agreement with the experiments for temperatures between 300-1000 K.

We like to point out again that the appealing flux-flux-correlation expression in Eq. 18 is not unique, but there exist a whole number of different but equivalent correlation function expressions [42]. In particular, a *quantum* version of the reactive-flux [5, 20, 21] has been put forward by Voth et al. in Ref. [47].

3.3 Multidimensional Quantum Transition State Theory (QTST)

There is presently no universal agreement on the correct form of a *quantum* generalization of classical transition state theory [37, 40, 41, 48, 49, 50, 51]. An intuitive appealing form of quantum-TST is obtained if we replace the projector $\mathcal{P}$ in Eq. 15 by the step function $h(\mathbf{p})$ alone [40]. This approximation however, invokes an ordering problem for the flux operator [37, 40]. In effect, the difference between such a QTST and the exact time-dependent approach is that in the exact approach the projection of the flux onto positive momentum states is performed for all times t on [0,∞] while in QTST the projection is carried out at t = 0 only. Therefore, the QTST cannot – in distinct contrast to Eqs. 15 and 18 – account for the flux recrossing! A different form of QTST is based on the path centroid-density. With x(t) denoting the reaction coordinate, and the constrained partition function reading [50]

$$Q(x^*) \equiv \int \mathcal{D}x(\tau)\mathcal{D}\mathbf{q}(\tau)\delta(\hat{x} - x^*)\exp(-S[x(\tau),\, q(\tau)]/\hbar) \quad , \tag{23}$$

wherein $S[x(\tau), \mathbf{q}(\tau)$: non-reactive bath coordinates] is the Euclidean time (τ = it) action, and $\hat{x}$ is the zero-frequency component, or "centroid", i.e.

$$\hat{x} = \frac{1}{\beta\hbar}\int_0^{\beta\hbar} x(\tau)\, d\tau \quad , \tag{24}$$

this QTST rate is defined by [50, 51]

$$k^{QTST} = \frac{k_B T}{h} Z_0^{-1} Q(x^* = x_{TST}) \quad , \tag{25}$$

where x_{TST} is the transition state location at the barrier top. At present, it is not totally clear how these different approaches to the QTST-rate compare among each other. This author suspects, however, that within a *semiclassical description* of QTST all these different QTST-theories [40,41,48,49,50] become equivalent. For reactions in condensed phases it is evident from Eqs. 15 and 18, that all these quantum rate expressions become rather complex to evaluate, due to the huge number of degrees of freedom modelling the system-environment interaction. Thus, we definitely have to make further concessions, such as e.g. the *description within a semiclassical limit.* In this context, we should point out, however, that the effect of dissipation generally forces the system to behave "more classical" [4,35]. Put differently, a semiclassical description likely is an appropriate starting point to model quantum-dissipative effects.

Armed with the results derived in this section we are now ready to tackle the quantum generalization of the dissipative (Kramers) reaction-theory presented in section 2.

4. PERIODIC-ORBIT APPROACH TO THE DISSIPATIVE QUANTUM RATE

4.1 Unified Quantum-Kramers Rate

In order to obtain explicit results for a coupled many degrees of freedom metastable system we use QTST together with semiclassical methods. By use of the semiclassical approximation for the propagator, $\exp(-\beta\mathcal{H})$, cf. Eq. 15, 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, being unstable with respect to small perturbations, just is the bounce solution (often also denoted as the "instanton-solution") in full configuration space of (N + 1)-degrees of freedom of the metastable *system, x, which is (bi-linearly) coupled to a thermal bath with coordinates,* $q_1,\ldots,q_N$. This bounce solution describes 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 is the reaction coordinate which 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 q_0- coordinate cannot be performed in such a way. The latter, however, is trivially accomplished in virtue of the

δ-function in Eq. 14, see in Ref. [38c]. Making use of similar calculations (periodic orbit theory) originally put forward by Gutzwiller [52], one ends up with the result [37]

$$k = Z_0^{-1} \frac{1}{2\pi\hbar} \int_0^{\infty} dE\, k(E) \exp(-\beta E) \quad . \tag{26}$$

Here, we have measured the energy from the well bottom, with $U(x_b) \equiv E_b$. The quantity k(E) is the microcanonical, cumulative semiclassical reaction probability at the total energy E, i.e. [37]

$$k(E) = \sum_{n=1}^{\infty} (-1)^{n-1} \exp[-n\phi(E)/\hbar] \times$$

$$\times \prod_{i=1}^{N} \left\{ 2\sinh\left[\frac{1}{2} nT(E)\omega_i(E) \right] \right\}^{-1} \quad , \tag{27}$$

with

$$\phi(E) = \int_0^{T(E)} \mathbf{p}(\tau)\dot{\mathbf{q}}(\tau) \mathrm{d}\tau \tag{28}$$

being the abbreviated action integral along the periodic orbit in complex time t = – iτ (Wick rotation) of period T(E) that rocks forth and back through the saddle point region on the upside-down potential energy surface in (N + 1) dimensions. The parameters $\{\omega_i(E)\}$ are the stability frequencies (Hill-Floquet coefficients) characterizing the unstable periodic orbit with period T(E) = $-\phi'(E)$. Upon expanding the sinh-functions in Eq. 27 into geometric series, one obtains a well-behaved result for $k(E)$, i.e.

$$k(E) = \sum_{(n_1,\ldots,n_N)=0}^{\infty} \left(1 + \exp\left\{ \left[\phi(E) - \phi'(E) \sum_{i=1}^{N} \left(n_i + \frac{1}{2} \right) \hbar\omega_i(E) \right] / \hbar \right\} \right)^{-1} \quad . \tag{29}$$

With the solution of

$$E_T = E - \sum_{i=1}^{N} \left(n_i + \frac{1}{2} \right) \hbar\omega_i(E_T) \quad , \tag{30}$$

being the energy E_T left in the tunneling mode while crossing the saddle point, we approximate the answer in Eq. 29 by the more appealing expression [38b,38c]

$$k(E) = \sum_{(n_1,\ldots,n_N)=0}^{\infty} \left\{ 1 + \exp[\phi(E_T)/\hbar] \right\}^{-1} \quad , \tag{31}$$

wherein we have *"unexpanded"* the first two terms in the Taylor series in Eq. 29. The form in Eq. 31 becomes exact for tunneling in a multidimensional, separable inverted parabolic-like potential landscape.

It should be noted that the quantity in Eq. 31 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. 31 is quite distinct from the familiar uniform-WKB expression $t^{pw}(E)$ for the transmission probability of a parabolic-like barrier, i.e. [53, 54]

$$t^{pw}(E) = \{1 + \exp[\phi(E)/\hbar]\}^{-1} \quad . \tag{32}$$

In *absence of dissipation* the generalization in Eq. 31 reduces, of course, with $E_T = E$ to the single-term equation in Eq. 32.

With Eq. 31, the evaluation of the thermally averaged, dissipative tunneling rate follows after the integration in Eq. 26. The remaining problem in obtaining an analytical result consists in the determination of 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 the result in Eq. 26 combined with Eq. 31 presents an expression for the dissipative quantum-Kramers rate, or the equivalent semiclassical multidimensional quantum TST, *that holds true for all temperatures*!

4.2 Results for the Quantum-Kramers Rate

In this subsection we follow the reasoning of Hänggi and Hontscha [38b, 38c] to derive explicit results for the dissipative tunneling reaction rate in various temperature regimes, in a metastable potential field of the form sketched in Fig. 1 containing a single metastable well.

4.2.1. Dissipative Tunneling Above Crossover

Let us first address the high temperature regime $T > T_0$, where

$$T_0 \equiv \hbar\lambda^*(2\pi k_B)^{-1} \tag{33}$$

is the "crossover temperature" to thermally-activated dominated escape [31,55]. The quantity λ^* denotes the friction renormalized barrier frequency of Grote-Hynes [56] and Hänggi-Mojtabai [57], i.e.

$$\lambda^* = \left(\frac{\hat{\gamma}^2(\lambda^*)}{4} + \omega_b^2\right)^{1/2} - \frac{1}{2}\hat{\gamma}(\lambda^*) \quad , \tag{34}$$

with $\hat{\gamma}$ being the Laplace transform of the corresponding memory friction. For Ohmic damping we have $\gamma(t-s) = 2\gamma\delta(t-s)$; *i.e.* $\hat{\gamma}(\lambda^*) = \gamma$. In this high temperature regime $T > T_0$ we can use a harmonic, local adiabatic approximation, in which the period $T(E_T)$ equals a constant $T(E_T) = 2\pi / \lambda^*$, 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 abbreviated action in Eq. 28 becomes $\phi(E_T) = (E_b - E_T)2\pi / \lambda^* < 0$. Then, interchanging the integration in Eq. 26 with the summations in Eq. 31 yields, by virtue of an identity due to Pollak [58] – 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

$$k = \left[\frac{\lambda^*}{\omega_b}\left(\frac{\omega_0}{2\pi}\right)\exp(-\beta E_b)\right]\left\{\prod_{n=1}^{\infty}\frac{\omega_0^2 + n^2\zeta^2 + n\zeta\hat{\gamma}(n\zeta)}{-\omega_b^2 + n^2\zeta^2 + n\zeta\hat{\gamma}(n\zeta)}\right\}, \quad T > T_0 \quad , \tag{35}$$

where $\zeta \equiv 2\pi / (\hbar\beta)$. This high temperature dissipative quantum limit was obtained first by Wolynes [59], and has been subsequently re-derived along quite different lines of reasoning by various authors [55,58,60,61].

The first term inside the *square brackets* denotes the classical generalized Kramers rate for memory friction [56,57]. We recall the definition of $\omega_0^2 = U''(x=0)/M$, being the (angular) frequency in the well bottom. For temperatures T >> T_0 the quantum correction Q, given by the curly brackets in Eq. 35, 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 $\hat{\gamma}(\lambda^*)$, there exists an accurate and quite simple approximation to the quantum correction Q in Eq. 35, which in leading order is *independent of the dissipation* $\hat{\gamma}$, i.e. [55],

$$Q \sim \exp\left[\frac{\hbar^2}{24}\beta^2(\omega_0^2 + \omega_b^2)\right] \quad . \tag{36}$$

Thus, for temperatures $T > T_0$, the Arrhenius factor undergoes a temperature-dependent renormalization towards *smaller values*, i.e.

$$E_b \rightarrow E_b - \frac{\hbar^2}{24}\beta(\omega_0^2 + \omega_b^2) \quad . \tag{37}$$

The effect of quantum tunneling has repeatedly been observed in a number of physical systems such as in biophysical transport [62,63], chemical conversion processes involving proton exchange [64,65,66], or tunneling of magnetization in ferromagnetic systems [67a-e], to name but a few. In particular, a very recent study of the diffusion of H2 and HD molecules in molecular solids (zeolites) [68] beautifully confirmed the quantum correction in Eqs. 36 and 37, see Fig. 3.

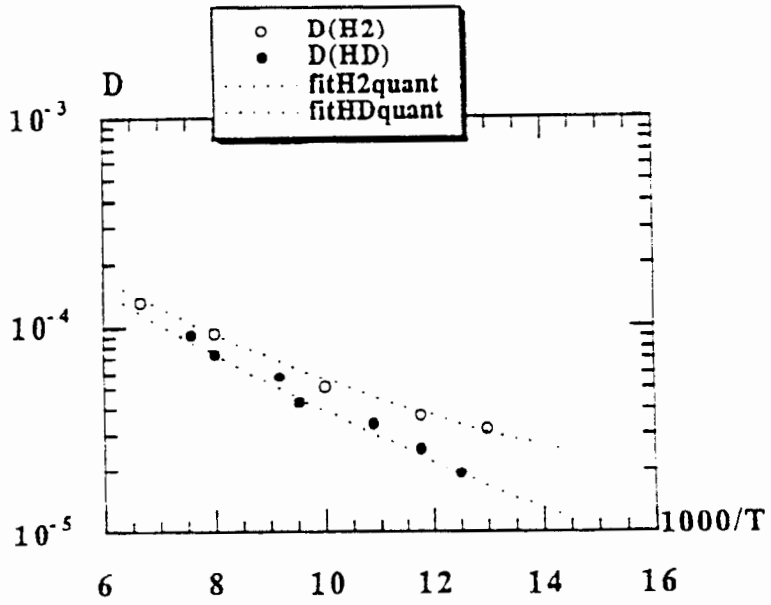

Fig. 3 The measured quantum corrections to the temperature dependence of the diffusion coefficient D of H2(∘)and HD (•) sorbed in zeolites. Dashed lines denote the result in Eq. 36, i.e. $\ln D_x = \ln D_0 - \beta E_b + (\hbar^2/24)\beta^2 \left[|U''_{top}| + |U''_{bottom}|\right] / M_x$ fits convincingly the measured data (after Ref. [68]). Note, that the quantum correction Q, being proportional to β^2, yields a characteristic upward curvature in the Arrhenius plot which accounts for the temperature-dependent lowering of the barrier height, cf. Eq. 37.

4.2.2 *Dissipative Tunneling Near Crossover*

At temperatures $T \sim T_0$, the integral in Eq. 26 becomes dominated by energies $E_T \leq E_b$, where $\phi(E_T) > 0$. Setting for the abbreviated action more accurately with $|T'| \equiv |\phi''(E = E_b)|$, cf. Ref. [38b]

$$\phi(E_T) = (E_b - E_T)\frac{2\pi}{\lambda^*} + \frac{1}{2}(E_b - E_T)^2|T'| \quad , \tag{38}$$

we recover the result

$$k = \left(\frac{2\pi}{\hbar|T'|}\right)^{1/2}\left(\frac{\omega_0}{\omega_b}\frac{\omega_0^2 + \zeta^2 + \zeta\hat{\gamma}(\zeta)}{a}\prod_{n=2}^{\infty}\frac{\omega_0^2 + n^2\zeta^2 + n\zeta\hat{\gamma}(n\zeta)}{-\omega_b^2 + n^2\zeta^2 + n\zeta\hat{\gamma}(n\zeta)}\right)\times$$

$$\times\left(\exp\left[-\beta E_b + \frac{\hbar}{2|T'|}(\beta_0 - \beta)^2\right]\right)\frac{1}{2}erfc\left\{\left(\frac{\hbar}{2|T'|}\right)^{1/2}(\beta_0 - \beta)\right\} \quad , \tag{39}$$

where

$$a = \omega_b^2 + (\lambda^{\neq})^2\left[1 + (\partial\hat{\gamma}(z)/\partial z)|_{z=\lambda^{\neq}}\right], \quad \beta_0 = \left(kT_0\right)^{-1}, \text{ and erfc(x)} = 2\pi^{-1/2}\int_x^{\infty} dy\, \exp\left(-y^2\right).$$

For strict Ohmic friction $\gamma(t) = 2\gamma\delta(t)$, we obtain $a = \zeta_0(2\zeta_0 + \gamma)$, with $\zeta_0 = 2\pi/(\hbar\beta_0)$. Note also that the result in Eq. 39 approaches for $T > T_0$ the previous answer in Eq. 35. Moreover, Grabert and Weiss [69] have shown that near $T \sim T_0$, there exists 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.

4.2.3 Dissipative Tunneling Below Crossover

At lower temperatures the small action $\phi(E_T)$ in Eq. 38 must be evaluated by taking the *full nonlinearity of the potential U(x) into account*! In that regime, however, the contribution from multiple traversals of the classically forbidden regime with period nT(E), n > 1, do not significantly contribute to the sum in Eq. 27. Hence, we can evaluate Eq. 26 by keeping only the n = 1 term for Eq. 27, and the remaining integral can be performed by the method of steepest descent. The steepest descent condition yields for the period: $T(E) = \hbar\beta \equiv \theta$. With E_θ determined so that T(E = E_θ) = $\hbar\beta$, and the full extremal Euclidean action S_b, defined as the extremal action for the periodic orbit at $E = E_\theta$, i.e.

$$S_b \equiv \theta E_\theta + \phi(E_\theta) \tag{40}$$

$$= \int_0^{\theta}\left[V(\mathbf{q}(\tau)) + \frac{1}{2}\dot{\mathbf{q}}(\tau)\mathbf{p}(\tau)\right]d\tau \quad , \tag{41}$$

wherein $V[\mathbf{q} = (x, q_1, \ldots, q_N)]$ denotes the potential function of *all* degrees of freedom (system plus bath), the low temperature dissipative quantum rate reads [38a, b, c]

$$k = Z_0^{-1}|2\pi\hbar T'(E = E_\theta)|^{-1/2}\exp(-S_b/\hbar)\ \mathrm{x}$$

$$\mathrm{x}\prod_{i=1}^{N}\left\{2\sinh\left[\frac{1}{2}\hbar\beta\omega_i(E_\theta)\right]\right\}^{-1} \quad . \tag{42}$$

By use of the identity derived in Ref. [38c], the prefactor in Eq. 42 can be related to the eigenvalue spectrum around the *dissipative bounce trajectory* $x_e(\tau)$ of period $\hbar\beta = \theta$, to yield the result [31, 32, 33, 34, 35, 36]

$$k = \left\{\frac{M}{2\pi\hbar}\int_{-\theta/2}^{\theta/2} d\tau\left[\dot{x}_e(\tau)\right]^2\right\}^{1/2}\left(\frac{Det(\delta^2 S_E/\delta x^2)_{x=0}}{|Det'(\delta^2 S_E/\delta x^2)_{x=x_e(\tau)}|}\right)^{1/2}\exp(-S_b/\hbar) \quad . \tag{43}$$

Here, S_E denotes the Eucledian, dissipative action which at the stable minimum $x = 0$ equals $S_E[x_e(\tau) = 0] = 0$ and $S_E[x = x_e(\tau)] = S_b$, is the dissipative bounce action in Eq.

41. Det′ means that the eigenvalue zero has to be omitted. It should be noted that in presence of dissipation the part of the prefactor inside the curly brackets in Eq. 43, – stemming from the zero-mode normalization –, *differs* from the dissipative bounce action S_b: Only for an undamped system (i.e. $\hat{\gamma} = 0$) at zero temperature, T = 0, does this part equal the bounce action S_b.

Dissipation was introduced first into the bounce formalism for the zero temperature quantum decay rate by Caldeira and Leggett [29,30]. The result in the form of Eq. 43, being valid for finite temperatures and dissipation, has originally been obtained within the dissipative functional bounce-methodology in the papers by Grabert and Weiss [32], Larkin and Ovchinnikov [33], and Riseborough, Hänggi and Freidkin [34]. For an undamped system, the answer in Eq. 43 reduces to the low temperature, steepest descent evaluation of simple quantum TST [27]. Because of quantum tunneling, the rate k does now not decrease continuously as the temperature T is lowered, but flattens off at low temperatures. In the high temperature (or classical) regime, the rate is reduced compared to the gas phase rate ($\hat{\gamma} = 0$, *i.e.* $\lambda^* = \omega_b$) by the dissipative transmission factor $\lambda^* / \omega_b < 1$, cf. Eq. 35. In contrast, the zero temperature rate is *exponentially* reduced by the dissipative action factor $S_b(T = 0)$ [29, 30]. For *extreme* weak damping $\hat{\gamma}(\lambda^*) \equiv 0$, the thermal fluctuations have little effect on the low temperature behavior of the rate, i.e. the temperature dependence for the quantum rate is essentially negligible below T_0. For a *damped system*, however, there exists a large regime where quantal and thermal fluctuations interplay. In this low temperature regime one finds a *universal exponential temperature enhancement* in the form of a power law [31]

$$\ln\{k(T) / k(T = 0)\} = cT^n \quad , \quad T_0 > T \geq 0 \quad , \tag{44}$$

where n = 2 for all systems with finite low frequency damping, i.e. $\hat{\gamma}(\omega = 0) \equiv \gamma_0 > 0$. This universal low temperature reaction rate enhancement arises from the thermally excited low frequency states of the *environment* and not from the thermal excitations among the states in the metastable well. An appealing re-derivation of Eq. 44 in terms of quantum noise theory has recently been given in Ref. [70]. For Ohmic-like damping, this characteristic low temperature T^2-law, as well as the quantum corrections in Eqs. 35, 36 and 39, have been observed in several experiments, cf. sect. XI in Ref. 4, and the reviews in Refs. [71] and [72]. With n = 4 it has recently been observed by Careri et al. [73, 74] in polycrystalline ice, and by Kleemann et al. [75] for phonon-assisted tunneling in perovskites, see Figs. 4 & 5. The power n is directly related to the behavior of the spectral density $J(\omega)$ (for its definition see in Ref. 30) of the environment at low frequencies, i.e. $J(\omega) \propto \omega^{n-1}$, as $\omega \to 0$. The slope c in Eq. 44 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) [31].

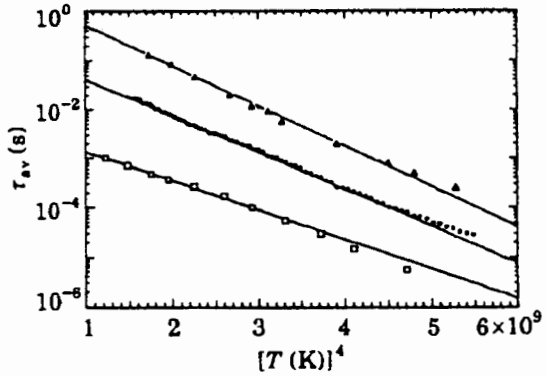

Fig. 4. The average relaxation times τ_{av} of H_2O polycrystalline ice (solid circles) as a function of T^4. The data marked by open triangles (Δ) are taken from O. Wörz and R.H. Cole [J. Chem. Phys. **51** (1969) 1546] and the open squares ($\square$) are data from S.R. Gough and D.W. Davidson [J. Chem. Phys. **52** (1970) 5442]. The data for the triangles are shifted vertically by a factor 10 and the open squares by a factor 0.1, respectively. After Careri et al., [74].

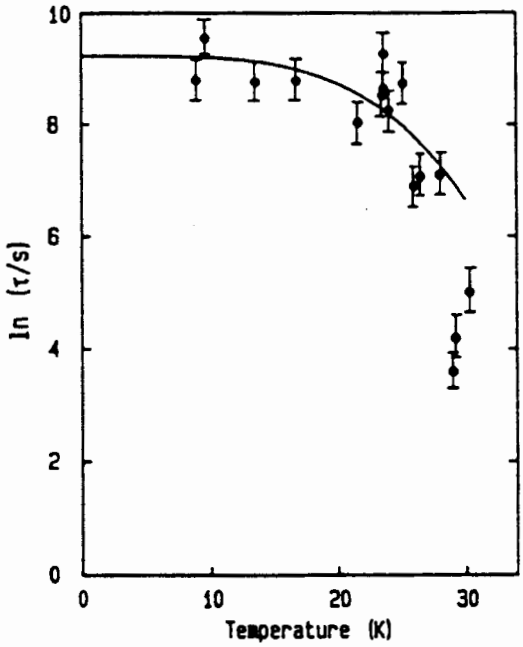

Fig. 5. The quadrapolar relaxation, measured via linear birefringence, in the perovskite $K_{1-x}Li_xTaO_3$, with x = 0.011. The relaxation of the birefringence follows a strechted exponential $\propto [1 - \exp-(t/\tau)^{\beta}]$ where both β and τ are temperature dependent. The relaxation rate τ (solid circles with estimated error bars) follows a T^4-dependence (indicated by the solid line) in agreement with the theory in Ref. [31]; after Kleemann et al. [75].

In contrast to the classical Kramers rate in Eqs. 2 and 4, the exponential part of the low temperature quantum rate, Eq. 42, and particularly, its prefactor are much more difficult to evaluate. An analytical treatment of the prefactor is possible, but rather difficult [34, 76a,b]. In practice, one must therefore resort to numerical methods [36,77,78], or varia-

tional approximations [79,80]. 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 $\nu\equiv k\exp(S_b/\hbar)$, the following low-temperature results: With weak friction and a dimensionless damping $\alpha\equiv\gamma(2\omega_0)^{-1}$ one finds for the dissipative action S_b in terms of the zeta-function $\zeta(3)=1.202$ ... [76a, b]

$$S_b(T\geq 0)=\frac{36E_b}{5\omega_0}\left\{1+\alpha\left[\frac{45\zeta(3)}{\pi^3}-\frac{5}{2\pi}\left(\frac{2\pi k_BT}{\hbar\omega_0}\right)^2-\frac{\pi}{12}\left(\frac{2\pi k_BT}{\hbar\omega_0}\right)^4+\ldots\right]\right\}\ ,\ \alpha\to 0 \quad (45)$$

which agrees at T = 0 with the action calculated by Caldeira and Leggett [30]. For the quantum prefactor we have [76a, b]

$$\nu(T=0)\ =\ 12\omega_0\left[3E_b(2\pi\hbar\omega_0)^{-1}\right]^{1/2}\exp(2.860\alpha)\quad ,\quad \alpha\to 0\ , \quad (46)$$

which at zero friction $\alpha=0$ again agrees with Caldeira and Leggett [30]. On the other hand, for very strong damping one obtains [33, 36] for $T\leq T_0=\hbar\omega_0(4\pi k_B\alpha)^{-1}$:

$$S_b(T\geq 0)=\alpha\left(6\pi\frac{E_b}{\omega_0}\right)\left[1+\frac{1}{4}\alpha^{-2}-\frac{4}{3}\alpha^2\left(\frac{2\pi}{\omega_0\hbar\beta}\right)^2\right]\quad ,\quad \alpha=(\gamma/2\omega_0)\to\infty \quad (47)$$

The quantum prefactor in this limit reads [33, 36]

$$\nu(T=0)\ =\ 8\omega_0\alpha^{7/2}\left(\frac{6E_b}{\hbar\omega_0}\right)^{1/2}\left[1+2\alpha^{-2}\ln\alpha+1.107\alpha^{-2}\right]\ ,\ \alpha\to\infty\ . \quad (48)$$

The same characteristic dependence on friction γ, i.e. $\nu\propto\alpha^{7/2}$ is obtained for strong friction in a titled sinusoidal potential [81]. In contrast to the exponential part of the rate, cf. Eq. 44, the prefactor at low temperatures exhibits only a *very weak* dependence on temperature [31, 36].

The result for the dissipative low temperature quantum Kramers rate in Eqs. 42 and 43 has been tested repeatedly via several experiments, see above, as well as in section XI in Ref. [4]. In the context of the quantum rate expression in Eq. 43, there has been performed a particularly beautiful experiment by the Saclay group [82]. They have measured the quantum rate out of the zero voltage state of a Josephson junction shunted by a delay line terminated by a resistor. This experiment implies an Ohmic-like memory-friction [83] which is monitored by varying the delay time t_D, obtained by changing the length of the transmission line. In Fig. 6 we depict the experimental results for the decay time (inverse rate) which are compared with theory. Indeed, the agreement between Eqs. 42 or 43, and the experimental results is striking.

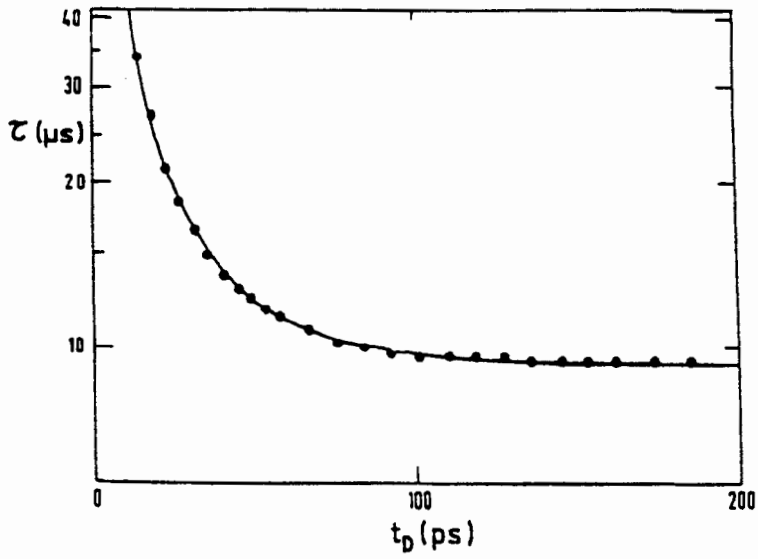

Fig. 6. The inverse quantum rate $k^{-1}(T) = \tau$ versus the delay time t_D at T = 18 mK measured for the decay of the zero voltage state in a Josephson junction shunted by a delay line whose length is varied in situ. The change of t_D implies a corresponding change for the frequency-dependent friction, cf. Eq. (3.2) in Ref. [83]. The solid circles denote the experiments in Ref. [82], and the solid line is the theoretical prediction based on Eq. 43 for T = 18 mK. The crossover temperature in this system is around 50 mK.

5. CONCLUSIONS AND OUTLOOK

Here, we summarized the state of the art for the dissipative barrier crossing problem with special emphasis set on the Kramers turnover problem and the low temperature, tunneling–modified reaction rate behavior. Compared with the original paper by Kramers [3], the field has witnessed a series of significant developments in recent years. Most of all we mention here the solution of the Kramers turnover problem [14], see section 2, and the corrections to the transmission factor induced by finite barrier heights (i.e. the reaction rate beyond steepest descent) [22]. It should be pointed out, however, that thus far all of these finite barrier height corrections could be obtained only within the spatial-diffusion limited regime, but not for the weak-to-moderate friction regime where nonequilibrium effects for the energy population control the rate. In the weak friction regime the potential nonlinearity can be accounted for by the inverse mean first passage time expression, cf. Eq. 11, being explicitly known up to quadratures, cf. see sections IV.D and V.B in Ref. [4].

Clearly, the study of quantum tunneling for the barrier crossing problem can hardly be considered to completed, despite the many recent important developments [4]: For example, the quantum corrections to the turnover theory have been determined in Ref. [4], see section 9.E.2 therein. With quantum mechanics acting during the reactive scattering process the classical rate becomes modified both via quantum transmission and

quantum reflection. In particular, the effect of quantum reflection can at *extreme weak* friction – under certain conditions – dominate the transmission, thereby yielding a quantum corrected rate which does not enhance, but rather *suppress the rate below its classical value* [84].

It should further be emphasized that all of the explicit *dissipative* tunneling work considered herein has been restricted to a bi-linear coupling between the system and a thermal bath, which essentially consists of mutually coupled linear oscillators. In other words, while the *nonlinearity of the metastable potential is fully taken into account* within the periodic orbit approach, see Eq. 38 and Eq. 41, the effect of

(i) nonlinear system-bath interactions

and

(ii) nonlinear bath degrees of freedom

are not taken care of with the dissipative quantum rate approach in section 4.2. A first attempt into this endeavour has recently been put forward by Riseborough in Ref. [85], who considered a bi-linear coupling together with a bi-quadratic coupling. Presumably, the effects of nonlinear bath modes most likely become suppressed as the temperature is severely lowered. Nevertheless, there is certainly a need to address in more detail other realistic nonlinear coupling schemes and non-harmonic bath degrees of freedom. In this context, a tractable generalization of the variational (classical) transition state theory for condensed phases, as put forward by Pollak et al. [86, 87], (note also his contribution in this book) *into the quantum regime* is much needed. Taking the analytical complexity of nonlinear system-bath and/or bath interactions into account, the progress will greatly have to rely on numerical studies. This author hopes that the combination of the quantum TST, as put forward with the path centroid-density approach by Voth et al. [50, 51], together with (stationary phase) quantum Monte Carlo simulations in imaginary time (for the treatment within QTST) and in real time (to go beyond QTST) – which do make use of filtering techniques [88-92] – will prove to be of use in future years.

There is also need to consider dissipative quantum rates in finite-dimensional metastable landscapes without and/or with disorder, as well as extended metastable systems (i.e. metastable fields). The latter is of course crucial for the study of friction-modified quantum nucleation. A couple of studies in this difficult problem area have already appeared [93, 94]; but due to the inherent difficulties characteristic for nonlinear dissipative quantum fields, the progress on this front promises no smooth sailing, but lots of cumbersome work instead.

Finally, we would like to mention another area carrying great potential for various applications. In short, it can be characterized by the interplay among: Metastability – Dissipation – Periodic Forcing. Both, within classical and quantum statistical mechanics

the application of external periodic driving can manifestly alter the escape dynamics. Classically, the novel phenomenon has been labelled "stochastic resonance" [95, 96], whereas on the quantum level it is known as "resonantly enhanced quantum decay" [97].

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REFERENCES

1. J.H. Van't Hoff, *Etudes de dynamiques chimique* (F. Muller and Co. Amsterdam, 1884) p. 114.
2. S. Arrhenius, *Zeitschrift f. Phys. Chemie* **4** (1889) 226.
3. H.A. Kramers, *Physica* **7** (1940) 284.
4. P. Hänggi, P. Talkner, and M. Borkovec, *Rev. Mod. Phys.* **62** (1990) 251.
5. P.B. Visscher, *Phys. Rev.* **B14** (1976) 347.
6. J.L. Skinner, and P.G. Wolynes, *J. Chem. Phys.* **72** (1980) 4993.
7. M. Büttiker, E.P. Harris, and R. Landauer, *Phys. Rev.* **B28** (1984) 1268.
8. P. Hänggi, and U. Weiss, *Phys. Rev.* **A29** (1984) 2265.
9. (a) B. Carmeli, and A.N. Nitzan, *Phys. Rev.* **A29** (1984) 1481.
   (b) A. Nitzan, *J. Chem. Phys.* **86** (1987) 2734.
10. (a) V.I. Melnikov, *Sov. Phys. JETP* **60** (1984) 380.
    (b) V.I. Melnikov, *Phys. Rep.* **209** (1991) 1.
11. M.M. Klosek, B.J. Matkowsky, and Z. Schuss, *Ber. Bunsenges. Phys. Chem.* **95** (1991) 331.
12. E. Pollak, *J. Chem. Phys.* **85** (1986) 865.
13. A.M. Levine, M. Shaprio, and E. Pollak, *J. Chem. Phys.* **88** (1988) 1959.
14. E. Pollak, H. Grabert, and P. Hänggi, *J. Chem. Phys.* **91** (1989) 4073.
15. (a) S. Linkwitz, H. Grabert, E. Turlot, D. Esteve, and M.H. Devoret, *Phys. Rev.* **A45** (1992) R 3369.
    (b) for the case of a periodic potential see also in: R. Ferrando, R. Spadacini, and G.E. Tommei, *Phys. Rev.* **A46** (1992) R 699.
16. R.S. Larson, and M.D. Kostin, *J. Chem. Phys.* **69** (1978) 4821.
17. W. Bez, and P. Talkner, *Phys. Lett.* **A82** (1981) 313.
18. D. Edholm, and O. Leimar, *Physica* **98A** (1979) 313.
19. F. Marchesoni, *Adv. Chem. Phys.* **63** (1985) 603.
20. (a) D.J. Chandler, *J. Chem. Phys.* **68** (1978) 2959.
    (b) J.A. Montgomery, D. Chandler, and B.J. Berne, *J. Chem. Phys.* **70** (1979) 4056.
    (c) B.J. Berne, in *Multiple Time Scales*, "Molecular Dynamcis and Monte Carlo Simulations of Rare Events", p. 419-436 (Academic Press, New York, 1985).
    (d) J.E. Straub, M. Borkovec, and B.J. Berne, *J. Chem. Phys.* **84** (1986) 1788.
    (e) B.J. Berne, M. Borkovec, and J.E. Straub, *J. Phys. Chem.* **92** (1988) 3711.
21. M. Borkovec, and P. Talkner, *J. Chem. Phys.* **92** (1990).
22. (a) E. Pollak, and P. Talkner, *Phys. Rev.* **E 47**(1993) 922.
    (b) A.M. Berezhkovskii, E. Pollak, and V.Yu. Zitserman, *J. Chem. Phys.* **97** (1992) 2422.
23. J.B. Straus, and G.A. Voth, *J. Chem. Phys.* **96** (1992) 5460.

24. R.P. Bell, *The Tunnel Effect in Chemistry* (Chapman and Hall, London, 1980).
25. E.P. Wigner, *Z. Phys. Chem. Abt.* **B19** (1932) 203.
26. R.T. Skodje, and D.G. Truhlar, *J. Phys. Chem.* **85** (1981) 624.
27. I. Affleck, *Phys. Rev. Lett.* **46** (1981) 388.
28. J.S. Langer, *Ann. Phys. (N.Y.)* **41** (1967) 108.
29. A.O. Cladeira, and A.J. Leggett, *Phys. Rev. Lett.* **46** (1981) 211.
30. A.O. Caldeira, and A.J. Leggett, *Ann. Phys. (N.Y.)* **149** (1983) 374; **153** (1984) 445 (Erratum).
31. H. Grabert, U. Weiss, and P. Hänggi, *Phys. Rev. Lett.* **52** (1984) 2193.
32. H. Grabert, and U. Weiss, *Z. Phys.* **B56** (1984) 171.
33. A.I. Larkin, and Yu. N. Ovchinnikov, *Sov. Phys. JETP* **59** (1984) 420.
34. P.S. Riseborough, P. Hänggi, and E. Freidkin, *Phys. Rev.* **A32** (1985) 489.
35. P. Hänggi, *J. Stat. Phys.* **42** (1986) 105; **44** (1986) 1003.
36. H. Grabert, P. Olschowski, and U. Weiss, *Phys. Rev.* **B36** (1987) 1931.
37. W.H. Miller, *J. Chem. Phys.* **62** (1975) 1899.
38. (a) P. Hänggi, *Z. Phys.* **B68** (1987) 181.
    (b) P. Hänggi, and W. Hontscha, *J. Chem. Phys.* **88** (1988) 4094.
    (c) P. Hänggi, and W. Hontscha, *Ber. Bunsenges. Phys. Chemie* **95** (1991) 379.
39. T. Yamamoto, *J. Chem. Phys.* **33** (1960) 281.
40. W.H. Miller, *J. Chem. Phys.* **61** (1974) 1823.
41. F.J. Mc Lafferty, and P. Pechukas, *Chem. Phys. Lett.* **27** (1974) 511.
42. W.H. Miller, S.D. Schwartz, and J.W. Tromp, *J. Chem. Phys.* **79** (1983) 4889.
43. T.J. Park, and J.C. Light, *J. Chem. Phys.* **88** (1988) 4897.
44. T.J. Park, and J.C. Light, *J. Chem. Phys.* **91** (1989) 974.
45. T.J. Park, and J.C. Light, *J. Chem. Phys.* **94** (1991) 2946.
46. T.J. Park, and J.C. Light, *J. Chem. Phys.* **96** (1992) 8853.
47. G.A. Voth, D. Chandler, and W.H. Miller, *J. Phys. Chem.* **93** (1989) 7009.
48. (a) P. Pechukas, in *Dynamics of Molecular Collisions*, part B, ed. by W.H. Miller (Plenum, New York, 1976) p. 269-322.
    (b) P. Pechukas, *Ber. Bunsenges. Phys. Chem.* **86** (1982) 372.
49. W.H. Miller, *Ber. Bunsenges. Phys. Chem.* **95** (1991).
50. G.A. Voth, D. Chandler, and W.H. Miller, *J. Chem. Phys.* **91** (1989) 7749.
51. G.A. Voth, *Ber. Bunsenges. Phys. Chem.* **95** (1991) 393.
52. M.C. Gutzwiller, *J. Math. Phys.* **12** (1971) 343.
53. E.C. Kemble, *Phys. Rev.* **48** (1935) 549.
54. K.W. Ford, D.L. Hill, M. Wakano, and J.A. Wheeler, *Ann. Phys. (N.Y.)* **7** (1959) 239.
55. P. Hänggi,H. Grabert, G.L. Ingold, and U. Weiss, *Phys. Rev. Lett.* **55** (1985) 761.
56. R.F. Grote, and J.T. Hynes, *J. Chem. Phys.* **73** (1980) 2715.
57. P. Hänggi, and F. Mojtabai, *Phys. Rev.* **A26** (1982) 1168.
58. E. Pollak, *Chem. Phys. Lett.* **127** (1986) 178.

59. P.G. Wolynes, *Phys. Rev. Lett.* **47** (1981) 968.
60. V.I. Melnikov, and S.V. Meshkov, *JETP Lett.* **38** (1983) 130.
61. Yu.I. Dakhnovski, and A.A. Ovchinnikov, *Phys. Lett.* **A113** (1985) 147.
62. N. Alberding, R.H. Austin, K.W. Beeson, S.S. Chan, L. Eisenstein, H. Frauenfelder, and T.M. Nordlund, *Science* **192** (1976) 1002.
63. H. Frauenfelder, in *Tunneling in Biological Systems*, ed. by B. Chance et al. (Academic, New York, 1979) p. 627 ff.
64. V.I. Goldanski, *Annu. Rev. Phys. Chem.* **27** (1976) 85.
65. D.C. Robie, S. Arepalli, N. Presser, T. Kitsopoulos, and R.J. Gordon, *Chem. Phys. Lett.* **134** (1987) 579.
66. K.W. Zilm, D.M. Heinekey, J.M. Millar, N.G. Payne, S.P. Neshyba, J.C. Duchamp, and J. Szczyrba, *J. Am. Chem. Soc.* **112** (1990) 920.
67. (a) W. Riehemann, and E. Nembach, *J. Appl. Phys.* **55** (1984) 1081.
    (b) E.M. Chudnovsky, and L. Gunther, *Phys. Rev. Lett.* **60** (1988) 661.
    (c) A. Garg, and G.H. Kim, *Phys. Rev. Lett.* **63** (1989) 2512.
    (d) H. Simanjuntak, *J. Low Temp. Phys.* (1993) in press.
    (e) L. Balcells, J. Tholence, S. Linderoth, B. Barbara, and J. Tejada, *Z. Phys.* **B89** (1992) 209.
68. J.P. Bouchand, E. Cohen de Lara, and R. Kahn, *Europhys. Lett.* **17** (1992) 583.
69. H. Grabert, and U. Weiss, *Phys. Rev. Lett.* **53** (1984) 1787.
70. J.M. Martinis, and H. Grabert, *Phys. Rev.* **B38** (1988) 2371.
71. (a) J. Clarke, A.N. Cleland, M.H. Devoret, D. Esteve, and J.M. Martinis, *Science* **239** (1988) 992.
    (b) A.N. Cleland, J.M. Martinis, and J. Clarke, *Phys. Rev.* **B37** (1988) 5950.
72. M.H. Devoret, J.M. Martinis, D. Esteve, and J. Clarke, *Helv. Phys. Acta* **61** (1988) 622.
73. G. Careri, and G. Consolini, *Ber. Bunsenges. Phys. Chem.* **95** (1991) 376.
74. G. Consolini, F. Burni, and G. Careri, *Europhys. Lett.* **19** (1992) 547.
75. W. Kleemann, V. Schönknecht, D. Sommer, and D. Rytz, *Phys. Rev. Lett.* **66** (1991) 762.
76. (a) E. Freidkin, P.S. Riseborough, and P. Hänggi, *Z. Phys.* **B64** (1986) 237; **B67** (1987) 271 (Erratum).
    (b) E. Freidkin, P.S. Riseborough, and P. Hänggi, *J. Phys.* **C21** (1988) 1543.
77. L.D. Chang, and S. Chakravarty, *Phys. Rev.* **B29** (1984) 130; **B30** (1984) 1566 (Erratum).
78. H. Grabert, P. Olschowski, and U. Weiss, *Phys. Rev.* **B32** (1985) 3348.
79. (a) E. Freidkin, P.S. Riseborough, and P. Hänggi, *Phys. Rev.* **B34** (1986) 1952; **B35** (1986) 5298 (Erratum).
    (b) E. Freidkin, P.S. Riseborough, and P. Hänggi, *Physica* **A142** (1987) 178.
80. H. Chang, and P.S. Riseborough, *Phys. Rev.* **B40** (1989) 2120.
81. S.E. Korshunov, *Sov. Phys. JETP* **65** (1987) 1025.
82. D. Esteve, J.M. Martinis, C. Urbina, E. Turlot, M.H. Devoret, H. Grabert, and S. Linkwitz, *Physica Scripta* **29** (1989) 121.
83. H. Grabert, and S. Linkwitz, *Phys. Rev.* **A37** (1988) 963.

84. U. Griff, H. Grabert, P. Hänggi, and P.S. Riseborough, *Phys. Rev.* **B40** (1989) 7295.
85. P.S. Riseborough, *Phys. Rev.* **B43** (1991) 13269.
86. E. Pollak, S.C. Tucker, and B. Berne, *Phys. Rev. Lett.* **65** (1990) 1399.
87. (a) E. Pollak, *J. Chem. Phys.* **95** (1991) 533.
(b) E. Pollak, *J. Phys. Chem.* **95** (1991) 10235.
88. J.D. Doll, D.L. Freeman, M.J. Gillan, *Chem. Phys. Lett.* **143** (1988) 277.
89. T.L. Beck, J.D. Doll, D.L. Freeman, *J. Chem. Phys.* **90** (1989) 3181.
90. C.H. Mak, and D. Chandler, *Phys. Rev.* **A44** (1991) 2352.
91. C.H. Mak, *Phys. Rev. Lett.* **68** (1992) 899.
92. R. Egger, and U. Weiss, *Z. Phys.* **B89** (1992) 97.
93. K. Hida, and U. Eckern, *Phys. Rev.* **B30** (1984) 4096.
94. P. Hänggi, F. Marchesoni, and P. Riseborough, *Europhys. Lett.* **13** (1990) 217.
95. For an authoritative review see: F. Moss, *Ber. Bunsenges. Phys. Chem.* **95** (1991) 303.
96. P. Jung, Periodically Driven Stochastic Systems, *Physics Reports* (1993) in press.
97. (a) F. Großmann, and P. Hänggi, *Europhys. Lett.* **18** (1992) 1.
(b) F. Großmann, P. Jung, T. Dittrich, and P. Hänggi, *Z. Phys.* **B84** (1991) 315.
(c) F. Großmann, and P. Hänggi, *Chem. Phys.* **170** (1993) 295.