INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

INTERNATIONAL ATOMIC ENERGY AGENCY

UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

Proceedings of the Adriatico Research Conference on

QUANTUM FLUCTUATIONS IN MESOSCOPIC AND MACROSCOPIC SYSTEMS

Miramare, Trieste, Italy 3 – 6 July 1990

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World Scientific
Singapore • New Jersey • London • Hong Kong

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 9128

USA office: 687 Hartwell Street, Teaneck, NJ 07666

UK office: 73 Lynton Mead, Totteridge, London N20 8DH

Library of Congress Cataloging-in-Publication Data

Adriatico Research Conference on Quantum Fluctuations in Mesoscopic and Macroscopic Systems (1990 : Miramare, Italy)

Proceedings of the Adriatico Research Conference on Quantum Fluctuations in Mesoscopic and Macroscopic Systems, 3–6 July 1990, Miramare, Trieste, Italy / editors: H.A. Cerdeira, F. Guinea López, U. Weiss.

p. cm.

ISBN 9810206291

1. Mesoscopic phenomena (Physics) -- Congresses. 2. Fluctuations (Physics) -- Congresses. 3. Energy dissipation -- Congresses. I. Cerdeira, H. A. II. Guinea López, F. III. Weiss, U. (Ulrich) IV. Title.

QC176.8.M46A37 1991

530.4'1--dc20 91-13208

CIP

Foreword

With the rapid advances in microfabrication technology in recent years, physical behaviours that are in between the macroscopic classical picture and the pure quantum nature on the molecular level became increasingly apparent. This regime has been popularized in the field of condensed matter physics as the "mesoscopic" regime. Among the mesoscopic effects that have been observed at low temperatures are a variety of transport phenomena in small metallic samples and semiconductor hetero-structures assigned to quantum coherence, dissipative influences in macroscopic systems ranging from Josephson devices to interstitials in metals, and tunneling phenomena of single electrons and Cooper pairs in small capacitance junctions and junction arrays. The importance of quantum fluctuations in the understanding of such systems is now well established.

The objective of this Adriatico Research Conference was to bring together physicists working in the various sub-fields of mesoscopic physics and to review the status of research in this rapidly developing field with emphasis on current advances and future possibilities. The Conference covered a wide spectrum including quantum transport in small samples, macroscopic quantum tunnelling and quantum coherence, charging effects in tunnel junctions, and correlated charge transfer and quantum vortices in junction arrays. Experimental review talks were given in each of these fields. The emphasis, however, was put on the theoretical understanding of the new phenomena observed. The authors were asked to ensure that their contributions were at a level which would be accessible to graduate students and to non-specialists in their field. This volume should therefore be of use to all those whose work impinges on any part of mesoscopic physics.

It is a pleasure to thank Mrs. Milena Poropat who helped us in the organisation of the Conference and in the completion of this book. We are particularly grateful to ICTP, SISSA and IBM for their financial help.

The Editors.

PERIODIC ORBIT APPROACH TO DISSIPATIVE QUANTUM TUNNELING AT FINITE TEMPERATURES

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Abstract: *We consider nonlinear metastable quantum systems which interact with a thermal bath of bosons. This interaction thereby induces a friction (dissipation) on the original metastable system. An important quantity characterizing many transport quantities is the quantum decay rate which sensitively depends on temperature T and friction strength. The calculation of this tunneling rate is achieved by use of a many-dimensional WKB-approach which is based on multiple traversals of unstable periodic orbits. Explicit results are given in closed form in various temperature regimes extending from T= 0 up to room temperature. Finally we address the quantum decay at very weak friction where nonequilibrium effects in the energy population must be accounted for.*

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 is proportional to the Boltzmann factor for thermal activation up to the barrier top (see Fig. 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 (see Fig. 2).

The tunnel effect was recognized long ago, during the heydays of quantum mechanics. In 1927, Friedrich Hund[6] demonstrated that quantum tunneling is of importance for intramolecular rearrangements in pyramidal molecules such as ammonia, as manifested by tunnel-splittings of vibrational spectra. The tunneling phenomena became a well known effect shortly afterwards when Oppenheimer[7,8] employed it for the description of the ionization of atoms in intense electric fields, or when Fowler and Nordheim[9] used tunneling for the electric field emission of electrons from cold metals, and by Gamow[10] as well as by Gurney and Condon[11,12] which explained the radioactive decay of nuclei. Quantum mechanical tunneling entered the field of reaction rates with the pioneering study by Bourgin[13], which then was continued by Wigner[14] who evaluated up to order ($\hbar^2$) the quantum corrections to the tunneling-modified Boltzmann averaged flux through a parabolic-shaped 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[15].

Our focus here is on *tunneling in presence of dissipation*. This area of research has been nurtured considerably by Leggett's[16,17,18] initial discussion of quantum mechanics and realism at the macroscopic level. The publication of the Einstein-Podolsky-Rosen Paradox[19] triggered Schrödinger's[20] "Generalbeichte" (general confession) on the status of quantum mechanics. Best known from this article is the

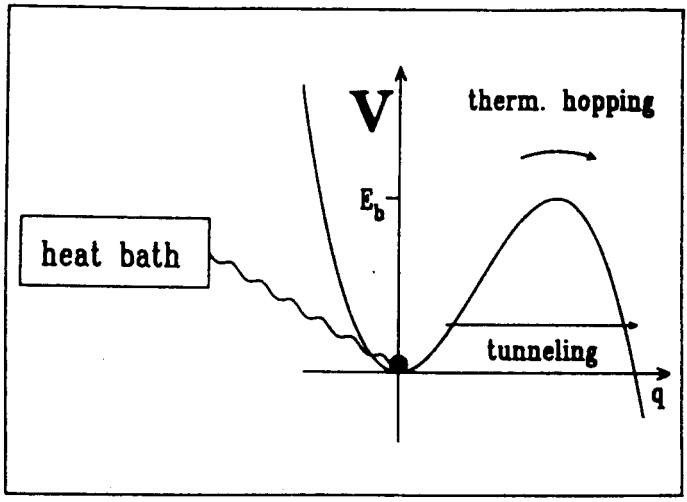

Figure 1: Escape of a particle from a metastable state. The particle can leave the potential well either via thermal activation over the barrier or via tunneling through the classically forbidden regime. The interaction between the particle and the surrounding heat bath is modelled by frictional forces giving rise to dissipation.

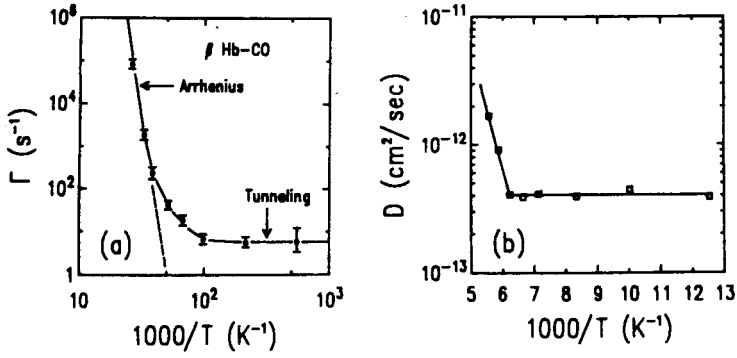

Figure 2: Arrhenius plots of reaction data for two different physical systems in which tunneling events occur: (a) rate of CO-migration to a separated β-chain of haemoglobin (Hb) (data from Alberding et al.[3]; Frauenfelder[4]); (b) the diffusion coefficient of hydrogen moving on the (110)-plane of tungsten at a relative H-coverage of 0.1 (data from Di Foggio and Gomer[5]).

paradox of Schrödinger's cat (see Fig. 3) in which he illustrates the indecisiveness of observations which 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 for a cat to be in a combination of "dead and alive" for an appreciable time (~ half-time of a nucleus whose decay triggers a device which then kills the cat),

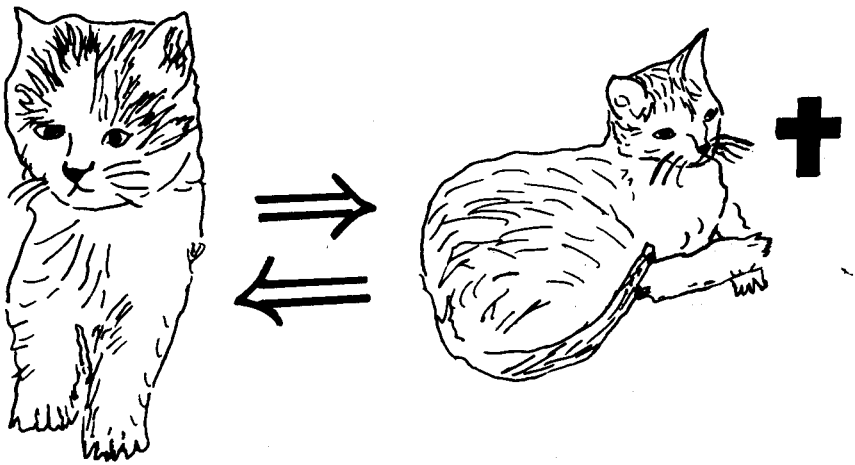

Figure 3: Schrödinger's cat. Is the cat alive, or dead (or if you prefer in a state of permanent sleep, †) only when one looks?

while at the same time we are ready to accept the analogous situation for the atomic nucleus. In the recent past 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 the zero-voltage state in a biased Josephson junction, or fluxoid quantum transitions in a superconducting quantum interference device. This area of research is nowadays known as *Macroscopic Quantum*

Mechanics[18,21,22,23,24]. In the following we shall restrict our discussion of dissipative tunneling to the case of *incoherent quantum tunneling processes*, i.e. we do not consider dissipative quantum coherence effects as they occur typically in weakly damped double-well systems[25,26]. Such incoherent tunneling processes of damped observables occur in biased Josephson junctions[27-33], nucleation of vortices in He II[34] or quantum diffusion in solids[35], in biological transport[4,36] and in low temperature vibrational spectroscopy of small molecules in inert solvents.

2. Formulation of the Problem

For the description of the dissipation for the quantum particle dynamics in a metastable potential V(q) (see Fig. 1) we rely on the standard methods known from statistical mechanics. As a rather general model we consider a particle of mass M that interacts via a linear dissipative mechanism with a thermal environment at temperature T, i.e. we consider a bath composed of an infinite set of harmonic oscillators being coupled bilinearly to the particle coordinate q. The total Hamiltonian, $\mathcal{H}$, of the system plus the bath is then of the form[37,38,39]

$$\mathcal{H} = \frac{M}{2}\,\dot{q}^2 + V(q) + \frac{1}{2}\sum_{i=1}^{N} m_i\left[\dot{q}_i^2 + \omega_i^2\left(q_i + \frac{C_i}{m_i\omega_i^2}\,q\right)^2\right] \quad . \tag{1}$$

In Eq. (1) the coupling to the bath of harmonic oscillators with masses $\{m_i\}$ and (angular) frequencies $\{\omega_i\}$ is of a form such that no coupling-induced renormalization of the metastable potential V(q) occurs. Upon integrating over all bath variables $\{q_1, \ldots, q_N\}$, one obtains in a canonical ensemble the generalized Langevin equation

$$M\,\ddot{q} + \frac{\partial V(q)}{\partial q} + M\int_0^t \gamma(t-\tau)\,\dot{q}(\tau)\,d\tau = \xi(t) \tag{2}$$

with the memory-friction $\gamma(t)$ obeying the fluctuation-dissipation theorem

$$< \xi(t)\, \xi(s) > = kTM\, \gamma(|\, t - s\, |) \quad . \tag{3}$$

Here k denotes the Boltzmann constant. The Gaussian stochastic force $\xi(t)$ and the memory-friction $\gamma(t)$ are determined by the parameters of the Hamiltonian[37,39]. Thus, a phenomelogical decaying memory-friction $\gamma(t)$, i.e. $\gamma(t) \rightarrow 0$, as $t \rightarrow \infty$, can be modelled by a suitable choice of the parameters in Eq. (1) by performing a continuum limit (i.e. $N \rightarrow \infty$) for the distribution of frequencies which densely extends down to zero frequencies (elimination of Poincare recurrences). In Kramers' [22,40] seminal study on classical reaction rates it was assumed that the frictional influence of the environment can be modelled by a frequency-independent damping $\gamma(t) \rightarrow 2\gamma\, \delta(t)$. In recent years, however, several experiments on the behavior of thermally activated (classical) reaction rates have shown a failure of the memory-free friction mechanism[22,41,42]. This is due to the fact that barrier frequencies are often of the order of $10^{11} - 10^{14}$ Hz, and environmental influences are likely to be correlated on this time scale, thereby giving rise to frequency-dependent damping effects for the classical rate[22,43,44]

3. The Dissipative Tunneling Rate

The theory for dissipative tunneling was developed only recently. The field has seen a rapid development after Caldeira and Leggett[38,45] discussed the problem of macroscopic quantum tunneling at zero temperature. Following the reasoning of Langer[46] used for the classical nucleation problem, the original approaches for dissipative tunneling are based on an imaginary-time functional integral approach (imaginary free energy method, $\mathrm{Im}\mathcal{F}$). The essence of the method consists in a semiclassical steepest descent evaluation of the free energy which leads to the so-called "bounce"[47,48,49] as the primary object in the theory. The important qualitative result of the zero temperature studies[38] was the observation that at zero temperature

the presence of dissipation will exponentially decrease the tunneling rate relative to the gas phase rate, defined as the tunneling rate without dissipation ($\gamma = 0$).

The functional integral approach was extended by the Augsburg- Essen - Polytechnic - Stuttgart and the Moscow school to finite temperatures, covering all temperatures in the range from $T \cong 0$ up to the classical regime[21-24,50-56]. In the sequel we shall present the main results of the finite temperature theory to dissipative tunneling by use of a unified approach which covers both, low temperatures and high temperatures on the same basis[56].

3.1 Flux-Flux Autocorrelation Function Expression for the Quantum Mechanical Rate

We start our more detailed tunneling rate discussion by a formally exact rate expression, originally put forward by Miller[57]. Let Z_0 denote the quantum partition function of system plus bath for the metastable state located inside the well minimum (see Fig. 4).

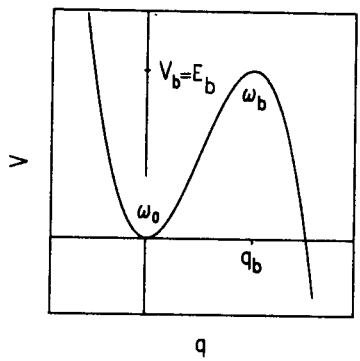

Figure 4: Metastable cubic potential used in the text.

Further let s denote the reaction coordinate in full configuration space with the activation barrier being located at s = 0, and let p be its conjugate momentum, i.e. s is

the coordinate perpendicular to the surface which divides "reactants" from "products". The flux-through-a-surface operator F has the form

$$F = \delta(s)\ (p/M)\ , \tag{4}$$

and the thermally averaged tunneling rate Γ is formally given by[57)]

$$\Gamma = \mathrm{Re}\{\mathrm{Tr}\ [\exp(-\beta\mathcal{H})\ F\ \mathcal{P}]\}\ /\ Z_0\ , \tag{5}$$

where Re denotes the "real part", Tr indicates the trace, $\beta = (kT)^{-1}$ is the inverse temperature and

$$\mathcal{P} = \lim_{t\to\infty}\ \exp(i\ \mathcal{H}t/\hbar)\ h(p)\ \exp(-i\ \mathcal{H}t/\hbar) \tag{6}$$

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 $s = -\infty$ to $s = +\infty$. By use of a few formally exact manipulations the rate in Eq. (5) can be recast in terms of a time integral over a flux-flux autocorrelation function, i.e. with $\hat{F} = \frac{1}{2}\ [\delta(s)\ (p/M) + (p/M)\ \delta(s)]$, and $t_c = t - i\ \hbar\ \beta/2$, Eq. (6) can be written in the form[58,59)].

$$\Gamma = \frac{1}{2} Z_0^{-1} \int_{-\infty}^{\infty} C(t)\ dt\ , \tag{7a}$$

where[59)]

$$C(t) = \mathrm{Tr}\ [\hat{F}\ \exp(\ i\ \mathcal{H}t_c^*/\hbar\ )\ \hat{F}\exp(-i\ \mathcal{H}t_c/\hbar)]\ . \tag{7b}$$

Note that this result is analogous to the Green-Kubo formulas for transport coefficients. Except in simple situations (e.g. for the one-dimensional parabolic barrier with

curvature $\omega_b^2 = | M^{-1} V''(q = q_b) | > 0$, yielding $Z_0 \Gamma = \frac{kT}{h} (\frac{1}{2}\hbar\beta\omega_b) [\sin(\frac{1}{2}\hbar \beta\omega_b)]^{-1}$), it is with non-separable systems generally impossible to simplify analytically the expression in Eq. (7). Therefore, it is more practical to evaluate for Eq. (5) the semiclassical approximation.

3.2 Unified Approach to the Quantum - Kramers Rate

In order to make progress on an analytical basis we first approximate the projector $\mathcal{P}$ in Eq. (6) by the simple step function h(p). This procedure is known in the chemical physics literature as the quantum-transition-state 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, being unstable with respect to small perturbations, just constitutes the "bounce-solution" (often also denoted as "instanton-solution") in full configuration space of system and bath, see Eq. (1), which 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. $q_0 \equiv s$ is the 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 s-coordinate cannot be performed in such a way. The latter, however, is trivially accomplished by virtue of the δ-function in Eq. (4). Making use of similar calculations (periodic orbit theory) originally put forward by Gutzwiller[60,61] one ends up with the result[47]

$$\Gamma = Z_0^{-1} \frac{1}{2\pi\hbar} \int_0^\infty dE\, k(E) \exp(-\beta E) \quad , \tag{8}$$

where k(E) is the microcanonical cumulative reaction probability given by

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

$$\cdot \prod_{i=1}^{N} [2 \sinh(\frac{1}{2} nT(E)\omega_i(E))]^{-1} \qquad (9)$$

with

$$\phi(E) = \int_0^{T(E)} d\tau \, \underset{\sim}{p}(\tau) \, \dot{\underset{\sim}{q}}(\tau) \qquad (10)$$

being the "small action" integral along the periodic orbit with period T(E) (in complex time τ = it) that rocks back and forth 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. (9) in geometric series one obtains a well-behaved result for k(E) (i.e. we use an analytic continuation of the series over n in Eq. (9) which might formally be divergent when $E > E_b$, where E_b is the threshold energy for activation) reading

$$k(E) = \sum_{(n_1, \ldots, n_N)=0}^{\infty} \{1 + \exp[(\phi(E) - \phi'(E) \sum_{i=1}^{N} (n_i + \frac{1}{2}) \hbar \omega_i(E))/\hbar]\}^{-1}. \qquad (11a)$$

With $[T(E)]^{-1} = \nu(E)$ being the frequency at energy E, the quantity

$$\Gamma(E) = \nu(E) \, k(E) \qquad (11b)$$

denotes the *semiclassical, microcanonical tunneling decay rate at energy E.*

With the solution of

$$E_T = E - \sum_{i=1}^{N} (n_i + \frac{1}{2}) \hbar\omega_i (E_T) \tag{12}$$

being the energy left in the tunneling mode while crossing the saddle point we approximate the answer in (11) by the more appealing expression[56)]

$$k(E) = \sum_{(n_1, \ldots, n_N)=0}^{\infty} \{1 + \exp[\phi(E_T)/\hbar]\}^{-1} \tag{13}$$

wherein we have "unexpanded" the first two terms in the Taylor series in Eq. (11). Note that the form in Eq. (13) becomes exact for tunneling in the case of a multi-dimensional separable parabolic-like potential function.

With Eq. (13), the evaluation of the thermally averaged, dissipative tunneling rate follows after the integration in Eq. (8). 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. (8) combined with Eq. (13) presents an expression for the dissipative tunneling rate that *is valid for all temperatures.*

3.3 Results for the Quantum-Kramers Rate

In this subsection we follow the reasoning of Hänggi and Hontscha[56)] to derive explicit results for the dissipative tunneling rate in various temperature regimes. Let μ denote the (positive-valued) relaxation (angular) frequency along the reaction coordinate, s, at the saddle point. Then the temperature

$$T_o = \hbar\mu/(2\pi k), \text{ with } \mu = [\frac{1}{4}\hat{\gamma}^2(\mu) + \omega_b^2]^{1/2} - \frac{1}{2}\hat{\gamma}(\mu) \tag{14}$$

denotes the dissipative crossover temperature above which thermally activated events dominate over tunneling transitions. In Eq. (14) $\hat{\gamma}$ denotes the Laplace transform of the memory friction $\gamma(t)$, while $\omega_b^2 = |V''(q = q_b) / M|$ is the barrier (angular) frequency.

3.3.1 Dissipative Tunneling Above T_o

In this regime we can use a harmonic, local adiabatic approximation, i.e. 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, and $\phi(E_T) = (E_b - E_T)\, 2\,\pi/\mu$. Then, interchanging the integration in Eq. (8) with the summations in Eq. (13) yields, by virtue of an identity due to Pollak[63] which relates the product of the (unknown) normal mode frequencies at the saddle point and at the well bottom to the (known) memory-friction $\hat{\gamma}$, the result[62,63,64,65,66]

$$\Gamma = \left[\frac{\mu}{\omega_b} \left(\frac{\omega_0}{2\pi} \right) \exp(-\beta E_b) \right] \left\{ \prod_{n=1}^{\infty} \frac{\omega_0^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)}{-\omega_b^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)} \right\} . \qquad (15)$$

The first term inside the square brackets denotes the classical generalized Kramers rate[22]. The definition of ν is $\nu = 2\pi/(\hbar\beta)$ and $\omega_0^2 = V''(q = q_0)/M$ is the (angular) frequency in the well bottom, see Fig. 4. For temperatures $T >> T_0$ the quantum correction Q, given by the curly brackets in Eq. (15), approaches unity. Moreover, this quantum correction always exceeds unity, i.e. this quantum-Kramers rate theory always *enhances* the classical rate. In particular, for weak-to-moderate damping strength $\hat{\gamma}(\mu)$ there exists an accurate and quite simple approximation to the quantum correction Q in Eq. (15) which in leading order is *independent of the dissipation* $\hat{\gamma}$, i.e.[62]

$$Q \sim \exp\left\{ \frac{\hbar^2}{24} \beta^2 (\omega_0^2 + \omega_b^2) \right\} . \qquad (16)$$

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

$$E_b \rightarrow E_b - \frac{\hbar^2}{24}\beta\,(\omega_0^2 + \omega_b^2) \quad . \tag{17}$$

3.3.2 Dissipative Tunneling Near T_0

At temperatures $T \sim T_o$, the integral in Eq. (8) becomes dominated by energies $E_T \leq E_b$, where $\phi(E_T) > 0$. Setting for the small action more accurately[56] with $|T'| \equiv |\phi''(E = E_b)|$,

$$\phi(E_T) = (E_b - E_T)\frac{2\pi}{\mu} + \frac{1}{2}(E_b - E_T)^2\,|T'| \tag{18}$$

we find the result[52,54,67]

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

$$\cdot\left(\exp[-\beta E_b + \frac{\hbar}{2|T'|}(\beta_0 - \beta)^2]\right)\frac{1}{2}\,\mathrm{erfc}\left\{\left(\frac{\hbar}{2|T'|}\right)^{1/2}(\beta_0 - \beta)\right\} \quad , \tag{19}$$

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 constant friction $\gamma(t) = 2\gamma\delta(t)$ we obtain for $a = \nu_0\,(2\nu_0 + \gamma)$, with $\nu_0 = 2\pi/(\hbar\beta_0)$. Note also that the result in Eq. (19) approaches for $T > T_0$ the previous answer in Eq. (15).

3.3.3 Dissipative Tunneling Below T_o

At lower temperatures the action $\phi(E_T)$ in Eq. (18) must be evaluated by taking the *full nonlinearity* of the potential V(q) 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. (9). Hence, we can evaluate Eq. (8) by keeping only the n = 1 term in Eq. (9), 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 $T(E = E_\theta) = \hbar\beta$, we find in terms of the full extremal action S_b

$$S_b = \theta E_\theta + \phi(E_\theta) \tag{20a}$$

$$= \oint_0^\theta d\tau [U(\underset{\sim}{q}(\tau)) + \frac{1}{2}\dot{\underset{\sim}{q}}(\tau)\underset{\sim}{p}(\tau)] \tag{20b}$$

wherein $U(\underset{\sim}{q})$ denotes the potential function of all degrees of freedom (system plus bath) for the low temperature dissipative quantum rate the result[55)]

$$\Gamma = Z_0^{-1} \mid 2\pi\hbar T'(E = E_\theta) \mid^{-1/2} \exp(-S_b/\hbar)$$

$$\cdot \prod_{i=1}^{N} [\, 2 \sinh(\tfrac{1}{2}\hbar\beta\omega_i(E_\theta))]^{-1} \,. \tag{21}$$

By use of the identities discussed in the paper by Dashen, Hasslacher and Neveu[68)], the prefactor in Eq. (21) can be related to the eigenvalue spectrum around the dissipative bounce trajectory $q_b(\tau)$ of period $\hbar\beta = \theta$ to give the known result[21-24,50-52)], i.e.

$$\Gamma = \frac{2}{\hbar}\,\mathrm{Im}\,\mathcal{F}$$

$$= \left\{\frac{M}{2\pi\hbar}\int_{-\frac{\theta}{2}}^{\theta/2} d\tau[\dot{q}_b(\tau)]^2\right\}^{1/2}\left(\frac{\mathrm{Det}\,(\delta S/\delta q^2)_{q=q_0}}{|\,\mathrm{Det}'\,(\delta^2 S/\delta q^2)_{q=q_b(\tau)}|}\right)^{1/2} \exp(-S_b/\hbar)\ . \tag{22}$$

Here S denotes the Euclidean, dissipative action with $S(q(\tau) = q_0) = 0$, and $S(q = q_b(\tau)) = S_b$, see in Eq. (20), and Det′ means that the eigenvalue zero has to be omitted. Arrhenius plots of some numerical results for the dissipative tunneling rate with Ohmic friction $\hat{\gamma}(z) = \gamma$ are depicted in Fig. 5. Because of quantum tunneling the rate Γ 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, i.e. $\mu=\omega_b$) by the dissipative transmission factor $\mu/\omega_b < 1$, see Eq. (15). In contrast, the zero temperature rate is *exponentially* reduced by the dissipative action factor S_b (T = 0)[38]. For very weak damping $\hat{\gamma}(\mu) \cong 0$, the thermal fluctuations have little effect on the low temperature behavior of the rate, i.e. the temperature dependence is almost neglible below T_0 for $\hat{\gamma}$=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[50]

$$\ln\{\Gamma(T)/\Gamma(T=0)\} = c\,T^n \tag{23}$$

where n = 2 for all systems with finite low frequency damping, i.e. $\hat{\gamma}(\omega=0) = \gamma_0 > 0$. For Ohmic-like damping, this characteristic low temperature T^2 - law, as well as the quantum corrections in Eqs. (15,16,19), have been observed in several experiments[27,28,29,32,33]. Moreover, 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, i.e. $J(\omega) \propto \omega^{n-1}$, as $\omega \to 0$. The slope c in Eq. (23) increases with the

strength of dissipation, but depends further on the details of the model for the dissipative mechanism and the metastable potential function V(q).

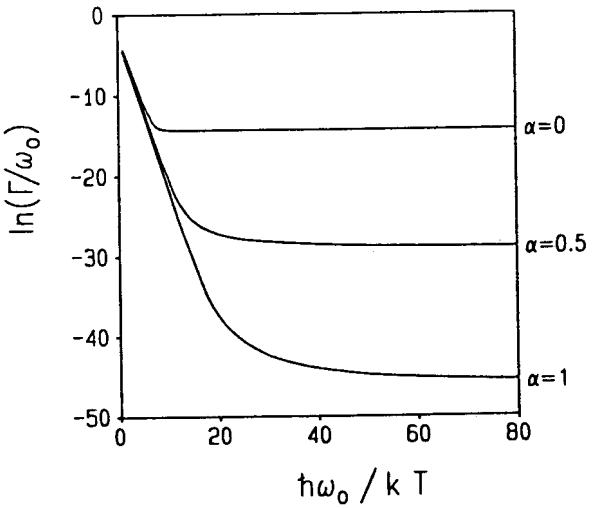

Figure 5: Arrhenius plots of the dissipative tunneling rate Γ for the system in Fig. 4 with $\omega_0 = \omega_b$, $E_b = V_b = 5\,\hbar\omega_0$, and frequency - independent Ohmic dissipation $\hat{\gamma}(z) = \gamma = 2\omega_0\alpha$ for various values of α (data are from Grabert et al., Ref. 24).

4. Quantum Tunneling at weak Dissipation

The quantum Kramers theory presented in the previous section did not account for effects caused by possible deviations from a thermal Boltzmann weighting. Such latter deviations can occur at extreme weak friction where the internal mechanism to replenish the upper energy states may start to fail (i.e. such nonequilibrium effects can occur if those states are not continuously prepared in thermal equilibrium by an outside mechanism). In other words, for extreme weak friction one faces a diminutive population below the Boltzmann weighting at the upper energy levels. This possible nonequilibrium effect plays generally a very subordinate role in the low temperature regime $T < T_0$ where the time available for equilibrization grows exponentially[55]. It may become observable, however, at temperatures above crossover T_0, where

quantum corrections to the classical Kramers´ weak damping result (see Ref. 22) are of considerable interest[69,70,71,72,73].

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), to find the system in the barrier region near a classical turning point with energy E. Moreover, let P(E/E´) denote the classical conditional probability that the particle leaves the barrier energy E´and returns after a round trip with energy E. The steady state function f(E) therefore obeys the integral equation

$$f(E) = \int_0^\infty dE'\, P(E/E')\, r(E')\, f(E') \tag{24}$$

wherein $r(E) = 1 - t(E)$ denotes the *quantum reflection*, while t(E) is the quantum transmission. Hereby we have measured energy from the well bottom, i.e. $V(q = q_b) = E_b$. 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 Γ is given by the outgoing flux, i.e.

$$\Gamma = \int_0^\infty dE\, t(E)\, f(E) \quad . \tag{25}$$

Together, Eqs. (24 - 25) yield a solution of the quantum rate problem for any given transmission t(E). In contrast to the (multidimensional) quantum transition state theory in section 3, the solution of the integral equation in (24) allows for deviations from the corresponding equilibrium solution. At extreme 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 an expansion of (24) up to second order in $(E - E')$ one finds the differential approximation to the integral equation[73]

$$t(E)\, f(E) = \frac{\partial}{\partial E} \Lambda(E) \left[1 + \beta^{-1} \frac{\partial}{\partial E} \right] r(E)\, f(E) \quad , \tag{26}$$

where $\Lambda(E)$ denotes the energy loss coefficient $\Lambda(E) = \int_0^\infty \gamma(s)\, J(E, s) ds$, with J(E,s)

being the delayed action along the undamped trajectory, i.e. $J(E, s) = M \int_0^{P(E)} dt\, \dot{q}\,(E, t)\, \dot{q}\,(E, t-s)$, with P(E) being the period of oscillation in the metastable region with energy E. In the following we want to determine the quantum corrections to the classical Kramers rate. In this case f(E) will deviate from the equilibrium value, $f(E) = \sinh(\frac{1}{2}\hbar\beta\omega_0)\,(\pi\hbar)^{-1}\exp(-\beta E)$, only for energies near the barrier energy E_b. Hence we may approximate the transmission coefficient t(E) by the parabolic barrier result, i.e. $t(E) = \left\{1 + \exp[-2\pi(E - E_b)/(\hbar\omega_b)]\right\}^{-1}$. The solution of Eqs. (25) and (26) then yields the central result[73]

$$\Gamma = \frac{\omega_0}{2\pi}\,\frac{\sinh(\frac{1}{2}\hbar\beta\omega_0)}{\frac{1}{2}\hbar\beta\omega_0}\,\frac{\pi\rho}{\sin(\pi\rho)}\left[\frac{(\rho)^\rho}{\Gamma(1+\rho)}\right]^2 (\beta\delta)^{1-\rho}\exp(-\beta E_b)\quad , \tag{27}$$

where $\rho = \hbar\beta\omega_b\,(2\pi)^{-1}$ and $\delta = \Lambda(E_b)$ is the energy loss at the barrier energy. For Ohmic friction $\gamma(t) = 2\gamma\delta(t)$, we obtain $\delta = \gamma\, J(E_b)$. The result in Eq. (27) holds at extreme weak friction $\beta\delta << 1$, and temperatures T above crossover T_0, i.e. $\rho < 1$. Moreover, the expression in Eq. (27) *holds uniformly* both for $\rho^2 << 1$, and $\beta\delta << 1$. At high temperatures ($\rho, \hbar\beta\omega_0(2\pi)^{-1} << 1$), Eq. (27) approaches the weak damping result of Kramers[40], i.e. $\Gamma \to \Gamma_{cl} = \omega_0(2\pi)^{-1}\,\beta\delta\exp(-\beta E_b)$. The leading weak damping ($\beta\delta << 1$) quantum corrections Q follow from Eq. (27) with $\Gamma = Q\,\Gamma_{cl}$ as

$$Q = \exp\left[\frac{\hbar\beta\omega_b}{2\pi}\left(2\,C + \ln\left(\frac{\hbar^2\omega_b^2\beta}{4\pi^2\delta}\right)\right) + \frac{1}{24}(\hbar\beta\omega_0)^2\right] \tag{28}$$

where C = 0.5772 ... is Euler's constant.

Clearly, for $\rho^2 < \beta\delta << 1$ the logarithmic term in the exponent of Eq. (28) gives a negative contribution that may compensate 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 smaller 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[73]. This feature is contrary to common knowledge and intuition, i.e. the full rate is often approximated by simply adding the

classical rate and the zero temperature rate, i.e. $\Gamma \rightarrow \Gamma = \Gamma_{cl} + \Gamma(T = 0)$ (see e.g. Bell, Ref. 74). Such an approach not only entirely disregards the complex interplay between thermal and quantal fluctuations, see section 3, but also neglects the role of quantum reflection and nonequilibrium. We also remark that the leading correction in (28) 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.

Acknowledgement

The author would like to thank H. Grabert, W. Hontscha, G.L. Ingold, P. Olschowski, U. Weiss, (Augsburg-Essen-Stuttgart collaboration) as well as P.S. Riseborough and E. Freidkin (Polytechnic University) for the many helpful discussions and the enjoyable collaboration in tunneling problems.

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