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Finite Temperature Tunnelling in Reaction Theory

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Kinetic processes hindered by one or a series of intervening potential barriers are of fundamental importance in a variety of systems, including chemical reactions, biological transport, diffusion in solids, nuclear reactions, and possibly even the birth of the Universe. At high enough temperatures, such processes obey the ubiquitous law of S. Arrhenius, 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 sufficiently low temperature, quantum effects provide a helping hand.

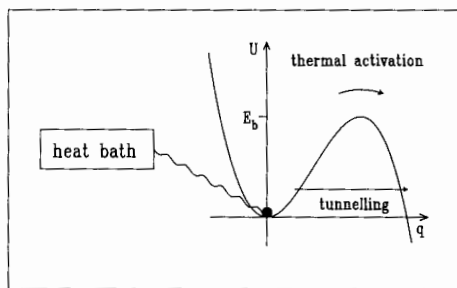


Fig. 1 — Escape of a particle from a metastable state. The particle can leave the potential well either via thermal activation over the barrier or via tunnelling through the classically forbidden region. The interaction between the particle and the surrounding heat bath is modelled by frictional forces.

As is well known, quantum mechanics allows for a tunnel effect whereby the particle penetrates the classically forbidden regime under the barrier (Fig. 1). The role of quantum effects in reactive processes was recognized long ago, during the heydays of quantum mechanics. In 1927, F. Hund demonstrated that quantum tunnelling can be important for intramolecular rearrangements in pyramidal molecules such as ammonia as manifested by tunnel-splittings of vibrational spectra. As early as 1929, D. Bourgin hinted at the possible role of the tunnel effect in chemical kinetics and since then, tunnelling has been invoked and developed further in a multitude of fields, encompassing biology, crystalline and amorphous solids, electronic devices and, more recently, tunnelling-microscopy¹).

The classical kinetics of reactions is not only slowed down by the intervening activation barrier of height E_b , but also by dissipative forces which damp the particle's motion. Generally, reactive particles interact with both a potential field $U(q)$ and a large number of environmental degrees of freedom. For several decades, the reigning description of reactive processes has been simple transition state theory. In such a theory one pictures the escape of a thermally activated particle over a potential barrier as a free flight with no dynamical influence arising from the solvent or surrounding lattice. The effect of the surroundings on the dynamics of the passage of a barrier was first elucidated in a seminal paper by H.A. Kramers in 1940. He pioneered the idea of investigating the escape problem in terms of Brownian motion. In such a picture, one describes an interaction in terms of a particle motion along an effective (generally temperature dependent) potential $U(q)$, known in the chemical physics community as the "potential of mean force". The residual interaction with the huge number of microscopic degrees of freedom of the environment leads to friction of the particle's motion. Moreover the interaction with the surroundings causes thermal fluctuations described by noise forces. Kramers succeeded in showing that the effect of friction results in transmission being reduced by a factor $\kappa < 1$. For large values of the friction γ , κ is proportional to $1/\gamma$. In this regime, the rate of escape is limited by spatial diffusion across the barrier (see Fig. 2), lowering the net rate as the result of frequent recrossings at the barrier top. In contrast, for very weak friction γ , there is almost no coupling of the reaction coordinate to the bath surroundings. Then energy activation (or deactivation) up to the top of the barrier becomes very difficult, as there is no fast mechanism which would replenish the upper energy states $E > E_b$, once the first particles have escaped. The escape rate which is proportional to γ approaches zero for vanishing bath coupling (Lindemann regime, see Fig. 2). This implies that the qualitative behaviour of the classical transmission factor κ , as a function of the damping γ , is a bell-shaped curve

with a maximum at some intermediate coupling strength. All of this was clear to Kramers who was relying on a simplified model with a one-dimensional metastable potential $U(q)$, and an idealized Gaussian, white (i.e. δ -correlated) noise. Over a long period, Kramers' viewpoint was appreciated by a few theoreticians

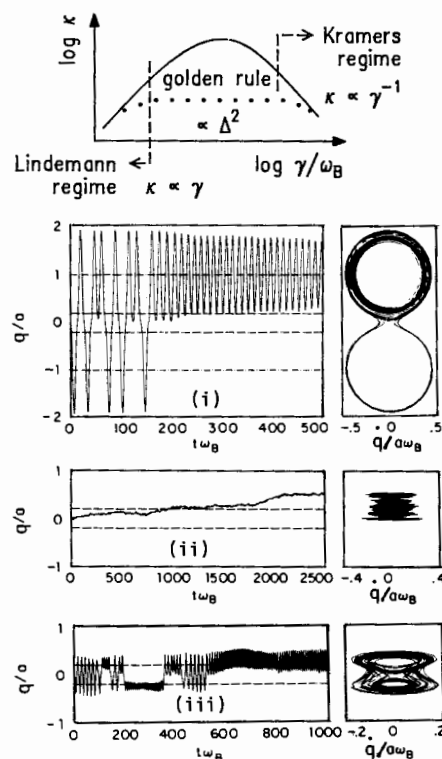


Fig. 2 — Sketch of the transmission coefficient κ for an activated process, as a function of the dimensionless friction strength γ/ω_B , where ω_B is the angular frequency at the barrier top. The dotted line, the 'golden rule' corresponds to the case of a non-adiabatic reactive transmission discussed in the text. The transmission approaches zero for high friction, as well as for vanishing friction. Typical sample trajectories of a particle that starts at the top of a symmetric double well, with the minima separated by a distance $2a$, are depicted below. (i): the trajectory and phase-space motion corresponds to the low coupling (Lindemann) regime where the escape is governed by energy-diffusion. This behaviour is in clear contrast to the spatial-diffusion controlled high friction (Kramers) regime shown in Fig. (ii). Figure (iii) exhibits the complex interplay between spatial and energy diffusive mechanisms which occurs for a frequency-dependent damping. (data for Fig. (i) - (iii) are from Straub J.E., Borkovec M. and Berne B., J. Chem. Phys. **84** (1986) 1788.)

only, but more recently, his ideas have re-surfaced in many theoretical and experimental studies, and significant advances have been made by extending and superseding the original Kramers theory²).

One example is the effect of frequency-dependent damping on reaction rates. Typically, the relevant time scale for motion near the barrier top is of the order $10^{-11} - 10^{-14}$ s, and the random forces are likely to be correlated on a similar scale. This results in a frequency-dependent friction $\hat{\gamma}(\omega)$, which is the Laplace transform of the time-delayed or 'memory' friction. Now $\hat{\gamma}(\omega \cong 10^{13}$ Hz) may drastically differ from its static value $\hat{\gamma}(\omega = 0) \equiv \gamma_0$. The importance of this effect has been recognized in recent experimental studies of chemical reactions in condensed media, proteins (see Fig. 3a), where protein fluctuations influence the migration of small molecules, and in activation processes at surfaces — such as desorption or oxidation — near phase transitions of the underlying substrate. In this latter case³), the noise is critically slowed down; *i.e.* its correlation time tends to diverge as the transition temperature is approached. The theory shows that the incorporation of frequency damping is remarkably simple: It proceeds by using in the original Kramers formulae, memory-renormalized transport coefficients such as the energy diffusion coefficient or the spatial diffusion coefficient. For instance, in the regime of moderate-to-strong damping, where the escape is ruled by spatial diffusion across the barrier, we only need to substitute for the Kramers transmission factor κ (see Fig. 2), the dissipation and memory renormalized value κ_R , which is given by the largest positive solution²) of:

$$\kappa_R = 1/[\kappa_R + \hat{\gamma}(\kappa_R \omega_B)/\omega_B]$$

where $\omega_B > 0$ and is the angular frequency of small particle oscillations in the inverted potential characterizing the curvature of the barrier top.

It is rather surprising that this very relation not only describes the influence of dissipation and memory on the classical rate but also characterizes the effect of the environmental modes on the temperature T^* below which the tunnel effect becomes predominant over activated Arrhenius-type transitions. In 1959, Goldanskii formulated a simple criterion for this cross-over temperature for an uncoupled particle (*i.e.* zero damping): Quantum tunnelling will dominate whenever the Gamow factor for barrier penetration exceeds the Arrhenius factor, the cross-over temperature being:

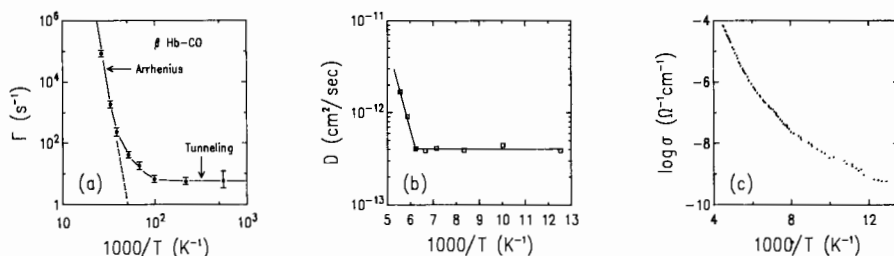


Fig. 3 — Arrhenius plots of reaction data for three different physical systems in which tunnelling events enter: (a) rate of CO-migration to a separated β -chain of haemoglobin (Hb), (data from Frauenfelder *et al.*, Science **192** (1976) 1002); (b) the diffusion coefficient of hydrogen moving on the (110)-plane of tungsten at a relative H-coverage of 0.1 (data from Di Foggia R. and Gomer R., Phys. Rev. **B25** (1982) 3490); (c) electronic conductivity of a 0.8% Ti-doped sample of VO_2 (Mansingh *et al.*, Phys. Chem. Solids **45** (1984) 79).

$$T_0^* = (\hbar/2\pi\kappa) \omega_B \\ = (1.216 \times 10^{-12} \text{ s K}) \omega_B, (\hat{\gamma}(\omega) = 0).$$

Only recently has the above relation been generalized to account for dissipation, frequency-dependent damping where $\hat{\gamma}(\omega) \neq 0$ ^{2,4}). Again, the result is remarkably simple. As the prefactor of the classical rate, the cross-over temperature is just modified by the same multiplicative transmission factor κ_R ; *i.e.*

$$T^* = \kappa_R T_0^*$$

Since $\kappa_R < 1$, any friction mechanism tends to lower the temperature where the cross-over between activated hopping and tunnelling-dominated transitions occurs. It should be noted that this cross-over temperature can be quite large. For example, given a typical chemical activation energy of $E_b \cong 0.4$ eV, and a tunnelling distance of 2 \AA , one obtains for hydrogen: $\omega_B \cong 10^{14}$ Hz, and $T^* \leq 150$ K. The signature of tunnelling is that the Arrhenius plot (see Fig. 3) becomes curved around T^* , and levels off at lower temperatures.

While T^* sets the temperature scale for the transition between activated hopping and quantum mechanical transmission, tunnelling events do not occur suddenly, but influence the rate already at temperatures above T^* . For weak-to-moderate damping $\hat{\gamma}(\omega)$, these quantum

corrections to the classical rate have a rather simple form, resulting in a temperature-dependent lowering of the activation energy²):

$E_b - E_b - [\hbar^2/24] [\omega_0^2 + \omega_B^2]/kT$, $T > T^*$ with ω_0 and ω_B being the angular frequencies of small oscillations at the well bottom and barrier top, respectively. Thus, quantum tunnelling enhances the classical rate. The first part of the correction proportional to ω_0^2 arises from quantum statistics inside the metastable well, while the second part, being proportional to ω_B^2 , originates from the quantum mechanical transmission factor for a parabolic barrier. Even at temperatures two to five times T^* , there are significant quantum effects (typically of the order of 30% – 200%) which enhance the rate. Such deviations from the Arrhenius law in the thermally activated regime have been observed, for example, in adiabatic electron transfer in polar solvents⁵) and in the dissipative decay of the zero-voltage state of Josephson junction elements.

At temperatures below T^* , tunnelling prevails over activated events. In this regime the role of the Arrhenius factor, E_b/kT , is taken over by a new quantity, the so-called "bounce-action" S_B/\hbar . Tunnelling mainly takes place along a

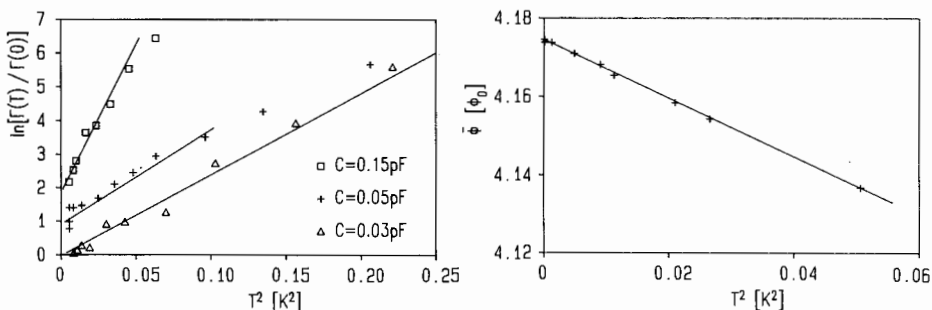


Fig. 4 — Left: The natural logarithm of the decay rate Γ of the zero-voltage state in a current biased Josephson junction as a function of the temperature squared for three samples with differing junction capacitances. (The experimental data are from Washburn S., Webb R.A., Voss R.F. and Faris S.M., Phys. Rev. Lett. **54** (1985) 2712.) The data fall on straight lines in accordance with the theoretical prediction⁶).

Right: The observed mean flux for the decay of the flux state in a SQUID ring. (data from Schwartz D.B., Sen B., Archie C.N., Jain A.K. and Lukens J.E., Phys. Rev. Lett. **55** (1985) 1547). The mean flux is proportional to the temperature squared, indicating a corresponding temperature dependence of the decay rate itself.

most probable escape path which can be related to the orbit of period \hbar/kT on the *inverted* potential surface — $U(q)$. S_B is then the action of this oscillating solution, if complex valued momenta are used in the classically forbidden region. This concept of periodic tunnelling paths was developed in a series of papers by the physical chemist W.H. Miller and has since been rediscovered several times. The periodic solution applies at low temperatures only, $T < T^*$, a property which serves as the definition for the cross-over temperature T^* . The approach towards T^* is characterized by the softening of a fluctuation mode around the saddle point of the potential surface⁴⁾. At T^* , the Arrhenius factor smoothly joins the bounce action S_B/\hbar .

The influence of dissipation on the reaction is quite different at temperatures below T^* . In contrast to the Arrhenius factor, E_b/kT , the exponent of the quantum rate, S_B/\hbar , involves the detailed shape of the non-linear metastable potential $U(q)$, and also becomes a function of the damping. For the usual frictional force laws, the value of S_B increases; *i.e.* the barrier transmission undergoes a characteristic suppression with increasing dissipation. More distinctive is the dependence on temperature: whenever friction remains at low frequencies so that $\hat{\gamma}(\omega = 0) > 0$, the rate Γ at low temperatures is thermally enhanced according to $\Gamma \sim \exp(c T^2)$ ⁶⁾, independently of the potential shape and damping strength. An example of this is incoherent tunnelling in an asymmetric double well. In decisive experiments done recently on macroscopic quantum tunnelling in Josephson systems⁷⁾, the same behaviour has been observed in current biased Josephson junctions and SQUID rings (see Fig. 4).

By now, a great deal of the theoretical groundwork has been laid to understand the principles of rate calculations over the whole temperature regime, extending from zero temperature up to room temperature. However, many details and more realistic models need to be addressed in future work. For example, the effect of non-linear bath couplings or the influence of non-equilibrium at lower temperatures and weak friction are only beginning to be investigated. Much work is also needed to describe specific reaction schemes in a variety of scientific disciplines.

In this context, a particularly interesting topic is the role played by electronic degrees of freedom in adiabatic versus non-adiabatic transitions⁸⁾. In the preceding discussions, we implicitly assumed that the reaction coordinate q

moves on a unique (adiabatic) potential surface $U(q)$. In chemical reactions, however, both electrons and nuclei move. Because of the mass difference between electrons and nuclei one frequently assumes that the electrons follow adiabatically the nuclear motion so that the electronic state is a function of the distance between the nuclei (Born-Oppenheimer approximation). Fig. 5 shows two neighbouring Born-Oppenheimer surfaces corresponding to two different electronic states. The interaction between the two electronic states then results in a splitting Δ . A reaction from A to B, or *vice versa*, is moderated by two characteristic time scales: Let $\tau_1 = \hbar/\Delta$ denote the time within which the electronic charge will fluctuate between two neighbouring electronic states, and $\tau_2 \equiv \tau_b$ the typical time within which the nuclear reaction coordinate traverses the barrier region. For $\tau_1 \ll \tau_2$, the electronic degrees of freedom will successfully adjust to the nuclear coordinates (adiabatic transition) with the dynamics evolving on the lower adiabatic ground-state surface. On the other hand, for $\tau_1 \geq \tau_2$ non-adiabatic dynamic effects become important; and the classical rate will be modified by an additional multiplicative factor P which gives the probability for staying on the adiabatic ground-state surface. Traditional Landau-Zener-Stückelberg theory yields for P the form:

$$P = 1 - \exp(-z\Delta^2)$$

where z depends on the nuclear dynamics. For $z\Delta^2 \gg 1$ ($P \equiv 1$) one recovers the adiabatic theory discussed previously. By contrast, for $z\Delta^2 \ll 1$, *i.e.* $P \sim \Delta^2$,

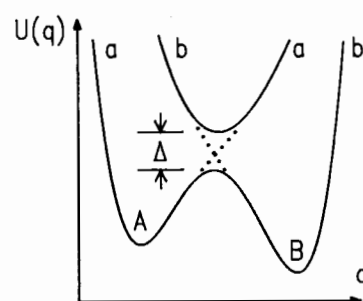


Fig. 5 — Two neighbouring Born-Oppenheimer (*i.e.* adiabatic) surfaces. For two electronic states (a) and (b) that do not interact, the resulting (diabatic) surfaces cross each other. In the presence of an interaction the two curves repel each other yielding an adiabatic ground state surface with two minima, and an excited surface. In the transition region these two curves are separated by Δ .

we have a truly non-adiabatic reaction (see the golden-rule plateau in Fig. 2). Non-adiabatic processes are particularly important in gas phase reactions between molecular radicals or open shell atoms as found, for example in combustion chemistry. Undoubtedly, we shall see much research work aimed at describing the influence of temperature and dissipation on the parameters z and Δ in the future.

Similarly, electronic degrees of freedom have also been found to have a profound influence on the quantum diffusion of defects in metals⁹⁾. The non-adiabatic response of the electronic screening cloud to tunnelling transitions causes an effective damping of the process which leads to a characteristic power law dependence of the quantum diffusion coefficient proportional to

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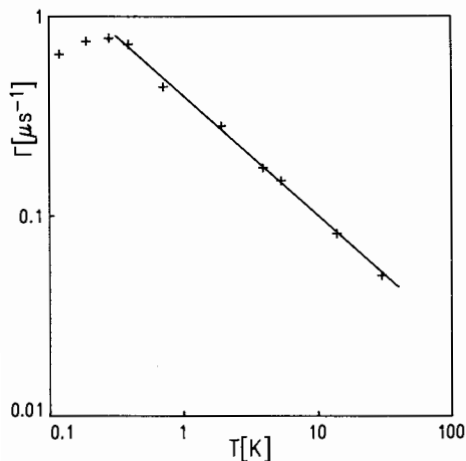


Fig. 6 — The muon jump rate in Cu undergoes a typical enhancement on lowering the temperature. The data are from various groups as collected by Richter D. in Ref. (9). The solid is a theoretical fit with $K = 0.2$.

$T^{(2K-1)}$. The parameter K depends on the electron-defect interaction, and is less than $\frac{1}{2}$ implying that the low temperature diffusion coefficient increases as the temperature is lowered. Such behaviour has, in fact, been observed for the mobility of muons in Al and Cu for temperatures below 10 K (Fig. 6). The influence of a fermionic environment on tunnelling is presently being investigated very actively and new interesting results can be expected to emerge in the next few years.

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