Self-Organized Electron Transfer

L. Pohlmann and H. Tributsch

Hahn-Meitner-Institut, Dept. Solare Energetik, D-14109 Berlin, Germany

Abstract

As other energy fluxes can be largely enhanced under non-linear conditions which permit local entropy export, such as heat flow under the ordered Benard convection, this should also be possible on a microscopic scale for electron transfer. As a precondition an autocatalytic molecular loop must exist, which transfers a small fraction of the energy, which drives the reaction, through the surrounding medium to assist the electron transfer in a non-linear way. Such an autocatalytic side loop, which may be facilitated by transfer of phonon energy, leads to microscopic self-organization, i.e. to a temporary dissipative structure. It may significantly improve electron transfer through a non-equilibrium electron distribution and a decrease of the activation barrier. The problem is theoretically treated as a Kramers approach, a Brownian motion in a non-uniform force field, in which the friction term may become active (e.g. through phonon assisted autocatalytic energy input leading to a dissipative activated complex). A formula for "self-organized" electron transfer is obtained which yields - for finite activation barriers - significantly higher rates than the Marcus formula. The derived new type of electron transfer mechanism is analyzed. It may help to explain how biological catalysts have evolved the ability of generating favourable energy barriers for multi-electron transfer near the thermodynamic overall potential.

I. Introduction

Since the beginning of the 1960s Marcus has developed and tested a fundamental electron transfer theory[1], which has been enlarged, supported and extended by many theoretical and experimental studies[2]. The Marcus formula for electron transfer

$$k = \nu \exp(-(\Delta G^o + \lambda)^2/4\lambda kT)$$

(where ν is a characteristic frequency for the nuclear motion, ΔG^o is the redox free energy change and λ the reorganization energy) has demonstrated a remarkable predictive and correlative applicability and has guided basic understanding of electron transfer in both small molecules and proteins.

Ever since first thoughts by Scent-Gyorgi in 1941[3], the role of the intervening protein medium in modifying and controlling the rate of electron transfer has been in the center of interest for biological electron transfer[4]. In the meanwhile a lot of problems have been theoretically and experimentally addressed, such as the influence of the nature of the medium, the calculation of the reorganization energy, the role of well defined electronic bridges and of conformational changes. The latter have, for example, been invoked to explain electron transfer rates independent of the driving force ΔG^o.[5]

Biological structures are governed by self-organization, non-linear autocatalytic processes, which control the structurization of matter, the repair of membranes and of macromolecules as well as biological function. Biological structures, in which energy conversion via charge transfer processes occur (electron and proton transfer), are also known to oscillate under certain conditions (mitochondria, photosynthetic membranes), which means that they are involved in feedback mechanisms. The question arises, whether biological electrocatalytic processes, that require optimized transition states, which means highly ordered transient molecular structures, also take advantage of self-organization. Such far- from- equilibrium non-linear mechanisms allow in an elegant way a local reduction of entropy and thus increase of order at the expense of the overall entropy turnover. In several publications the authors have shown that useful mechanisms can theoretically be derived on the basis of such concepts, as, for example, highly unidirectional electron transfer (applied to the primary process of charge separation in photosynthesis), multi-electron transfer and photosynthetic water splitting.[8] Characteristic properties of the manganese complex of photosynthesis, such as its labile structure, the ability of manganese to form many co-ordination compounds, its participation in thylacoid membrane oscillations, fit into a synergetic scheme of water oxidation (see Ref. 8(c)).

Such a mechanism is the more plausible, since it has been theoretically shown that none of the stable manganese cluster structures described in the literature are able to oxidize water due to excessive activation barriers[6]. Water oxidation must therefore occur in a structurally dynamic process as expected for self-organizing mechanisms.

The present work aims at a more fundamental description of self-organized or synergetic electron transfer.

II. Dissipative Structures Supporting Energy Transfer

Beginning from the pioneering work of Prigogine[7] it is well known that thermodynamically open systems (i.e. which are exposed to a flux of energy and matter) which are far enough from the equilibrium can develop spontaneously complicated dynamical pattern (the so called "dissipative structures"). From a functional point of view these dissipative structures are characterized by an interplay of positive and negative feedback loops leading to non-linear relationships between the system elements. Consequently, these dynamical structures can be found in all regions of nature (living and non-living) and society, playing frequently a crucial role in the functioning of the systems concerned.

Besides the effect of spontaneous creation of dynamical pattern (accompanied by symmetry breaking), these structures often represent different types of process regimes with new properties. This can be shown with one of the frequently used examples of dissipative structures, the so called Benard convection. Here a viscous fluid in a flat pan is heated from below in a homogeneous way (see Fig. 1).

For small temperature differences, the heat conduction is the only way for the system to transport heat energy through the fluid layer. But if the temperature difference increases up to a critical value, a dissipative structure consisting of regularly ordered roll cells appears. This new regime accelerates the heat transport through the fluid layer dramatically due to the now included heat convection. So one can say that after the appearance of the roll-cell structure the system drastically increases the effectivity of energy transport (see Fig. 2a).

It is obvious that nature must have widely applied the possibilities of optimization by dissipative structuring. Following this line it seems to be allowed to suppose that also the astonishing high (from the technological point of view) effectivity and selectivity of the photosynthetic electron transfer becomes possible due to a temporary dissipative structuring of the photosystem (including the protein environment). This way a little part of the photon excitation energy should be used by the system to form a dissipative structure which itself accelerates the rate of electron transfer (see Fig. 2b). On the basis of phenomenological models it was possible to show that processes with positive feedback loops are, in principle, able to describe some experimental known properties of biological electron transfer systems (as, e.g. the high directedness, the four-electron transfer, the negative activation energy).[8] A limitation of the models was, however, that they were formulated on a macroscopic level, i.e. in on the basis of chemical species (or electronical and conformational states of a large biomolecule, which can be characterized as "quasispecies") interacting according to the laws of macroscopical chemical kinetics.

III. Co-operativity and Application to Microscopic Structures

The properties of a (permanent or temporary) dissipative structure are characterized first of all by a higher degree of ordering which becomes possible, if the elements of the system (e.g. molecules, vibrational modes, chemical reaction events) behave, despite of their stochastic motion, in a co-operative way leading to macroscopical dynamical structures. It was Haken, who firstly has recognized this fact finding a mathematical description in form of the so called "enslaving principle"[9]. This means that near a bifurcation point (the point at which a new dissipative structure becomes possible) in the system one or few "order parameters" appear which during further evolution in time "enslave" all the other microscopical degrees of freedom of the system. This system behavior finds its explanation in the frame of the theory of dynamical systems. In this sense the "slaving principle" is a special case of a theorem stating that under well defined conditions the trajectory of a system with many degrees of freedom can be "attracted" by a hyperplane in the phase space (the "Center Manifold") with only one or very few degrees of freedom.

In this way, a co-operative behavior of the system elements appears to be applicable also in complex biomolecular systems to increase the effectivity and selectivity of electron transfer reactions. To model such systems it would be desirable to look for a more microscopic level of description. Accordingly it is necessary to suppose that the mentioned possibilities of a non-linear theory with feedback processes are applicable to a more elementary level, at least for large biomolecules, which itself are embedded in a suitable matrix (i.e. the molecular environment within a biomembrane or inside of the living cell).[10] Then a description of the biomolecule as a dissipative system could allow dynamic pattern formation processes (leading to molecular arrangements and(or) temporary limit-cycle oscillations), which may promote the electron transfer process. In this case part of the supplied energy would be consumed for the formation of the "microscopic dissipative structure". The present paper supposes, that this temporary ordering should be able to facilitate the reaction probability, possibly through an increase of the steric factor, a decrease of the activation barrier, or through an additional activation process. The latter both processes would lead to a lowering of the effective activation barrier.

Such kind of a mixed-level description is often used in electron transfer theory: On the one hand the electron transfer will be described on an elementary level, on the other the complex biomolecular environment will be handled like a macroscopic dissipative system. The latter should be possible due to the large number of atoms in complex biomolecular systems. It appears that this kind of description can be done in a very transparent way using the Kramers approach to reaction rate theory. Here, the reaction rate (e.g. of the electron transfer) is treated as the escape of a particle from a potential well, whereas all the actions from the environment are condensed in a single friction term and a randomly fluctuating force. This approach is very useful for reactions occurring under normal conditions (environmental temperature) in an sufficiently dense medium (fluid, but also dense gases and macromolecular complexes), where the pure quantum mechanical description becomes a hopeless task. Moreover, the classical quantum mechanics is not able to describe truly irreversible processes on a microscopic level due to the reversibility of the the Schrödinger equation. However, this more philosophical question does not affect the here discussed model of electron transfer if the electron follows, as supposed, adiabatically the slow environmental modes. (A completely quantum mechanical description of dissipative structuring processes on the microscopic level however should be only possible on the basis of a quantum mechanics including intrinsic irreversibility. Although in recent time some progress has been made in this direction[11], the theories are still far away from usability for explicit calculation.) Another, more practicable, way consists in the splitting of the whole system into a subsystem coupled to a heat bath and the subsequent reduction of the density matrix of the whole system to the reduced density matrix of the subsystem under consideration.[12] However, the coupling to the heat bath is always considered to be purely dissipative. It is clear, that such an assumption can only lead to a quantum mechanical response theory not able to describe the non-linear processes of dissipative structuring. Therefore in the following an extended Kramers approach will be used to describe self-organized electron transfer.

IV. The Kramers Approach to Reaction Rate Theory

In his famous paper he published in 1940 H.A. Kramers treated the escape from a potential well, which is formally equivalent to an unimolecular chemical reaction, as a problem of Brownian motion in a non-uniform force field[13]. This problem can be described by a linear Langevin equation

$$m\frac{d^2x}{dt^2}+\gamma\frac{dx}{dt}+\frac{d}{dx}U(x)=\xi(t) \quad ,$$

Equ. (1)

with x and m - its location and mass of the Brownian particle in the potential well $U(x)$, γ - the friction coefficient and $\xi(t)$ - a stochastic acting force. By this way Kramers was able to give the transition-state theory (TST) of chemical reactions a firm base showing that the TST rate constant,

$$k_{TST}=\frac{\omega_A}{2\pi}\exp(-\frac{E_b}{k_BT}),$$

Equ. (2)

(with the oscillation frequency of the molecule ω_A , and under the assumption that quantum effects are negligible, i.e. $k_BT >> (h/2\pi)\omega_A$), is only an upper bound to the real rate constant. Kramers found exact expressions for the rate constant for the low damping limit (with $\eta \to 0$, where $\eta = \gamma/m$ is the reduced friction coefficient)

$$k_{low}=\eta\frac{I_C}{k_B\ T}k_{TST} \quad ,$$

Equ. (3)

(here I_C denotes the action of the escaping particle at the barrier), as well as for the large (down to medium) damping limit:

$$k_{high}=\frac{1}{\omega_C}\left[\sqrt{\frac{\eta^2}{4}+\omega_C^2}-\frac{\eta}{2}\right]k_{TST} \quad ,$$

Equ. (4)

For very large damping, ($\gamma >> \omega_b$), Equ. (4) has the limit:

$$k_{vh}=\frac{\omega_C}{\eta}k_{TST} \, .$$

Equ. (5)

Here, $\omega_A^2 = m^{-1}U''(x_A)$ is the squared angular frequency inside the metastable minimum, and $\omega_C^2 = m^{-1}\ |U''(x_C)|$ is the squared angular frequency at the barrier. In the following years up to now these results were many times rediscovered[14] and extended in several directions[15]. An elaborated theory was also developed which accounts for a generalized non-Markovian (i.e. with memory friction $\gamma(t)$) description of the dynamics of chemical reactions.[16]

An important recent paper analyzes the limits of applicability and the connection with other competing theories.[17] It turns out that, generally speaking, in all cases where the chemical reaction takes place in an randomly acting environment, i.e. in dense gases, solutions or solid states, the friction and the thermal forces (which are connected via the fluctuation-dissipation theorem) must be taken into account. In these cases the knowledge of the potential surface of the reaction alone is not sufficient to obtain the rate constant expression. Indeed, there are regions in the parameter space (e.g. for medium friction values) where the frictional effects become unimportant and the classical expressions (Landau-Zener Theory, Fermi's Golden Rule) can be used with success. But nevertheless the limits of applicability of these classical theories must be determined by the use of the more general Kramers-like theory (or by the equivalent multidimensional TST in full phase space of all degrees of freedom[18]).

For this reason a Kramers-like approach is adequate to describe the proposed non-linear and feedbacking properties of the bioorganic environment influencing the rate of complex biomolecular reactions. Some attempts to explain the high reaction rate constants of enzymatic reactions (by a factor 10^6 or more higher than usual chemical catalysis) have been done by Ebeling, Schimansky-Geier and co-workers.[19] But all these approaches are affecting only the preexponential factor in the rate constant[20]. In turn this means, e.g., that the acceleration of reaction rates by several orders of magnitude as well as the effect of negative activation energies can hardly be understood in terms of such models.

V. Active Non-linear Friction

All above mentioned cases of modified Kramers-like theories and models have in common that they use the concept of passive friction (i.e. $\gamma > 0$, the energy of the Brownian particle always will be lost through dissipation). For processes occurring in far-from (thermodynamic) equilibrium situations, where the laws of irreversible non-linear thermodynamics apply, this may not be the case. Indeed, in so called "dissipative structures" the system is fed by an energy flux, which often can be interpreted as an active friction.

Active friction is a well known physical phenomenon. A simple example is the function of the violin string as visualized in Fig. 3.

The bow, described as a rotating belt, exerts a force on a string, which is able to oscillate, as visualized by a horizontal spring. Due to the oscillating property of the string, the effective friction between bow and string becomes alternatively positive and negative. Through this non-linear energy input a limit cycle oscillation is generated, which is the explanation for the astonishing stability of the violin sound. The frequency is stabilized by a feedback process.

However, there are several examples of positive feedback mechanisms acting on a more molecular level (see Ref. 8a and references cited therein): Cytochrome c_3 from Desulfovibrio vulgaris changes its redox potential with every change of oxidation state in such a way, that the first electron transfer facilitates the subsequent electron transfer step. Another example is the behaviour of some molybdenum containing metal clusters involved in multi-electron transfer catalysis. Here, the first electron transferred to a chemisorbed species will produce an electronic change in the cluster having a positive feedback effect on the transfer rate of the second electron.

Therefore, the aim of this Section is to derive a simple model treating the complex macromolecular system of reacting biomolecules as a dissipative structure with active friction. For the purpose of developing a molecular model one can imagine a large biomolecule, perhaps imbedded in a complex protein or membrane environment, which is supplied with energy from the outside, e.g. with light energy or chemical energy from ATP molecules. If in such an excited state the biomolecule is far enough from equilibrium, the subsequent relaxation process can proceed through a transient dissipative structuring. This can be some kind of temporal non-monotonicity (e.g. quasi-stationary limit cycle oscillations or chaotic behaviour) in the relaxation process as well as a spatial ordering. This temporary dissipative structures are well known in many macroscopic physical, chemical and biological systems (e.g. *Lac* Operon, Glycolytic Cycle). Further, the Belousov-Zhabotinsky reaction in a closed batch reactor proceeds trough sustained oscillations in intermediate product concentrations lasting several hours until the equilibrium is reached. Therefore it is reasonable to suppose that in complex biomolecules embedded in a large protein matrix, i.e. in mesoscopic systems consisting of several thousands of atoms, this process of dissipative structuring can also take place. This temporary structuring could - this is our hypothesis - be utilized by the reacting part of the biosystem itself to accelerate the reaction rate.

This way the presented model supposes that after the energetic activation the biomolecular system is far enough from equilibrium. Part of the energy can be used to build up a temporal dissipative structuring, which acts on the reacting part of the biomolecule as an active friction. This is schematically explained in Fig. 4.

An excited molecular system relaxes into the lowest excited state while releasing phonons (vibrational energy) or structural energy (molecular distortions, polarisation energy) into the environment. Since these processes withdraw energy from the electron, they can classically be considered as positive friction forces. Our model now assumes that this friction energy is not entirely lost as thermal energy but can partially be used - as negative friction energy - to facilitate the electron transfer process. This is visualized in Fig. 4 where this energy from the side loop is seen to decrease the energy barrier for an electron transfer reaction.

From the system logic it follows immediately, that the friction term in the Kramers approach must be non-linear and able to change its sign. Otherwise an acceleration without any termination, i.e. the explosive destruction of the system, would be the consequence. Therefore, the simplest form of a Kramers-like model with active friction would be the Kramers equation with a Van-der-Pol-like friction term. Here, for the sake of mathematical simplicity and from symmetry considerations it is reasonable to assume the following form of the Van-der-Pol-like friction: $\gamma\, f(E,\alpha,E_D)\, v$, with the term

$$f(E,\alpha,E_D) = 1 + \alpha\left(E - E_D\right),$$

Equ. (6)

depending on the energy

$$E(x,v) = \frac{m v^2}{2} + U(x)$$

with E - the whole energy of the Brownian particle, v and m - its velocity and mass, $U(x)$ - the function of the potential well, γ - the friction coefficient, E_D- some energy characterizing the amplitude of the corresponding limit cycle oscillation in the phase space and α- some parameter with the dimension of reciprocal energy expressing the strength of the active friction (i.e. E_D and α describe the non-linear dissipative properties of the system). In the limit $\alpha \to 0$ the non-linear effect vanishes and the ordinary passive friction $\gamma > 0$ of the ordinary Kramers approach remains. Otherwise, if α is sufficiently large, the friction coefficient is negative (i.e. active) as long as the system energy E is smaller than the limit cycle amplitude E_D. Thus with the help of the parameter α one can trace the transition of the system from purely passive (and linear) friction (the classical Kramers case) to purely active friction (the here proposed Van-der-Pol case).

The Langevin equation of the Kramers problem with active friction has the form:

$$m\frac{d^2x}{dt^2} + \gamma\, f(E,\alpha,E_D)\frac{dx}{dt} + \frac{d}{dx}U(x) = \xi(t) \quad ,$$

Equ. (7)

with the non-linear friction term $f(E)$ defined above. The corresponding deterministic equation has, for a purely parabolic potential, a stable limit cycle solution with the constant energy

$$E_{LC} = E_D - 1/\alpha \; .$$

Equ. (8)

From this equation follows immediately the existence condition of a limit cycle with finite energy:

$$\alpha > 1/\,E_D \; .$$

Equ. (9)

(The opposite case $\alpha < 1/\,E_D$ is not discussed here. In this case the stable limit cycle converts into an unstable one. Whether it still can promote the escape probability remains to be investigated.) The potential $U(x)$ is assumed to contain only one well (at $x = 0$, see Fig. 5) to sort out the effects of back-bouncing, i.e. for the sake of simplicity here only strictly irreversible unimolecular reactions are described.

The random force is assumed to be white noise,

$$\langle \xi(t) \rangle = 0 \; , \quad \langle \xi(t)\xi(t') \rangle = 2\mu\delta(t - t') \; ,$$

Equ. (10)

with the fluctuation-dissipation relation:

$$\mu = \gamma k_B T \; .$$

Equ. (11)

It should be noted here, that the Langevin equation Equ. (7) was postulated (but not derived) to trace the consequences of an occuring "dissipative structure" (the stable limit cycle) for the changes in the activated escape process. It is obvious, that an equation like (7) can not be derived from first principles in the usual way (see, e.g. Ref. 15). In these derivations usually a low-dimensional mechanical system coupled to a large passive heat bath of independent oscillators (modelling the surrounding medium) is analyzed. By using projection operator techniques a reduced description of the low-dimensional system is derived in the form of a generalized Langevin equation (see, e.g. Equ. (2.6) in Ref. 15). This integro-differential equation contains a dissipative memory kernel accounting for memory friction, which also can be non-linear in dependence on the bath coupling. As a consequence of the supposed system properties (the bath is passive and the whole system is thermodynamically closed) the friction term must be nonnegative according to the second law of thermodynamics. Correspondingly, the fluctuation correlations of the reduced system are connected with the dissipative memory kernel through an fluctuation-dissipation relation. If the noise correlation time is very short comparing to the system relaxation time, the fluctuations can be assumed to be δ-correlated and a ordinary Langevin equation like Equ. (1) is retained.

On the other hand, the model system used in the present paper represents a system, which is not only thermodynamically open but also exposed to a directed energy input (pumped system). A simple model system, which may represent this physical situation is, for example, a semiconductor diode through which current is passed and in which electrical energy is dissipated into heat. By illuminating this diode (input of external energy) the potential loss (ohmic drop) can be converted into potential gain (photovoltage). With a properly adjusted electrical circuit including feedback elements, such a system can also be made to behave synergetically (i.e. exhibiting "active friction"). A straightforward derivation of a Langevin equation corresponding to such a synergetic pumped system from first principles is not yet, to our knowledge, done. But in principle a mathematically strong derivation would lead to a "synergetic" generalized Langevin equation, which effective friction term now no longer must be nonnegative (the second law of thermodynamics is not valid in open systems). All derivations of such reduced equations introduce some phenomenological levels of description (see, e.g. Haken[21]). But it seems to be clear, that the exact generalized Langevin equations for pumped synergetic systems will be at least so complicated, as the corresponding equations of passive systems (containing memory friction, colored and multiplicative noise). Furthermore, there do not exist general fluctuation-dissipation relationsin systems far from equilibrium.

Being aware of all these complications, in this paper an opposite approach was utilized: A simple Langevin equation was postulated with the only new property of an active friction force. All other complications, as e.g. memory friction and multiplicative noise, were rigorously avoided to facilitate an exact mathematical solution of the problem. Correspondingly, a simple fluctuation-dissipation relation was used, which indeed can not be true in this form for an synergetic system. Nevertheless this relation was used here to model the tendency, that a higher temperature of the system will increase the fluctuation amplitude. This drastic simplification of the problem is also motivated by the circumstance that the effect of the here neglected properties of the system (e.g. the effect of frequency dependent friction[22] leading, in general, to a lowering of the escape rate) was already analyzed by other authors in a more or less isolated way. The goal of this paper is, in contrast, to show that the introduction of an active friction can increase the escape rate.

Furthermore the general condition for the validity of the Kramers problem, i.e.

$$k_B T << E_b \ , \qquad \text{Equ. (12)}$$

(the thermal activation energy must be small compared with the energy barrier E_b - otherwise it would not be an activated rate process) must be taken into account, accompanied by the new condition

$$E_D < E_b \ ,$$

Equ. (13)

(the non-linear activation level has to be smaller than the energy barrier E_b). The corresponding Fokker-Planck equation for the electron distribution function $\rho(v,x,t)$ reads then as follows (for the derivation see, e.g. Ref. 21):

$$\frac{\partial\rho}{\partial t} = \left[-v\frac{\partial\rho}{\partial x} + \frac{1}{m}\frac{dU(x)}{dx}\frac{\partial\rho}{\partial v} \right] + \frac{1}{m}\frac{\partial}{\partial v}\left(v \cdot f(E,\alpha,E_D) \cdot \rho \right) + \frac{1}{m^2}\mu\frac{\partial^2}{\partial v^2}\rho \ .$$

Equ. (14)

The stationary solution of this equation has been obtained for the case of very weak friction magnitudes using the method which Kramers himself had applied to this case (concerning only the diffusion along the energy coordinate).[23] In the next Section another approach will be adopted which is able to solve approximately the problem for all magnitudes of friction.

VI. Solution for Arbitrary Friction Magnitudes

One of the drawbacks of the Kramers approach to reaction rate theory is that it is in general difficult to decide how large the phenomenological friction coefficient is. Therefore it is very desirable to solve the Kramers problem for all magnitudes of the friction coefficient. Unfortunately, an exact analytical solution of this important "Kramers turnover problem" has not been found until now - even if some authors had claimed the opposite in their papers. Since Kramers work many efforts have been made to find approximative analytical solutions of the turnover problem leading, however, only to several kinds of interpolation formulas containing, more or less explicitly, adjustable parameters.[24] Only in 1990 Naeh, Klosek, Matkowsky and Schuss (NKMS) succeeded in deriving an asymptotic approximation of the turnover problem without any adjustable parameters.[25] This solution became possible because the authors used the method of matched asymptotic expansions with

$$\varepsilon = \frac{k_B T}{E_b}$$

Equ. (15)

as a smallness parameter, instead of using the smallness or largeness of the friction coefficient γ, as done in all previous papers. An important point is that the smallness parameter here coincides with the physical validity condition (Equ. (12)) of the Kramers problem itself.

Moreover, the authors of the cited paper were able to prove that the Kramers rate constant k depends on the friction coefficient γ analytically, so that fractional powers of γ cannot appear in the expansion of k, such as presented in previous papers. This way a uniform solution of the Kramers turnover problem was found, which is correct in the leading term of the asymptotic ε-expansion:

$$k_{unif} = \frac{\omega_A}{2\pi}\left[\frac{\sqrt{\eta^2 + 4\omega_C^2} - \eta}{2\omega_C} - \exp(-\frac{\eta I_C}{k_B T})\right]\exp(-\frac{E_b}{k_B T})$$

Equ. (16)

This formula contains the limiting cases obtained already by Kramers (see Equ. (3) - Equ. (5)), but has the correct TST-result (Equ. (2)) as an upper bound. Formally the TST-result can be obtained, according to the method of matched asymptotic expansions[25], by computing the limit $\eta \to 0$ in the first term inside the square brackets of Equ. (16), and omitting the second one. The full "turnover" for the classical Kramers problem is shown in Fig. 6. for some typical parameters.

Despite of the above mentioned advantages of the NKMS-approach there is another point being principally important with respect to the modified Kramers problem concerning active friction: All earlier attempts to solve the turnover problem required the linearity of the friction term in the classical Kramers problem. On the contrary, the NKMS-approach does not need this linearity assumption and is therefore the only one of the known approaches, which can be extended to problems with non-linear friction terms. In the Appendix it is shown how the NKMS-approach was adopted to obtain the turnover solution for the modified Kramers problem with active friction. The result, finally obtained using the condition of Equ. (9), is formally very similar to the classical one (see Fig. 7.):

$$k_{SO} = \frac{\omega_A}{2\pi f_C}\sqrt{\frac{\alpha k_B T}{2\pi}}\left[\frac{\sqrt{(\eta f_C)^2 + 4\omega_C^2} - \eta f_C}{2\omega_C} - \exp(-\frac{\eta I_C f_C^2}{k_B T})\right]\exp(-\frac{\alpha(E_b - E_{LC})^2}{2 k_B T})$$

Equ. (17)

with

$$f_C = f(E_b, \alpha, E_D) = \alpha(E_b - E_{LC}).$$

Consequently, this solution must have the same structure of the limiting cases as the NKMS-Kramers solution (Equ. (16)), e.g. the TST limit:

$$k_{SO}^{TST} = \frac{\omega_A}{2\pi}\sqrt{\frac{\alpha k_B T}{2\pi f^2}}\ \exp(-\frac{\alpha(E_b - E_{LC})^2}{2 k_B T}) \ .$$

Equ. (18)

Equ. (2At the first glance this is a paradoxial result: The TST-limit of the classical Kramers problem does, by definition, not depend on the friction coefficient explicitly (see Equ. (2). For this reason it is usually concluded, that the TST-result represents the strict upper bound for the reaction rate constant. On the other hand, the result of the modified Kramers problem, which in the TST-limit also does not depend explicitly on the friction (see Equ. (18), can exceed the classical TST-result significantly! The solution of the paradox is, that also the classical TST result obtained from the Kramers approach in the vincinity of the maximum of the function $k(\gamma)$ is implicitly dependent on the underlying friction mechanism through the established non-equilibrium probability distribution, which here is Boltzmann-like. Equally the TST-like result of the active friction problem depends indirectly on the corresponding non-equilibrium and non-Boltzmannian probability distribution (the maximum $\rho(x,v)$ is not located at the origin $x = 0, v = 0$).

Analogously the other limiting cases of the self-organized transfer rate are obtained, for very low friction

$$k_{SO}^{low} = \frac{\eta l_C f_C^2}{k_B T} k_{SO}^{TST} \ ,$$

Equ. (19)

and for high friction

$$k_{SO}^{high} = \frac{\sqrt{(\eta f_C)^2 + 4\omega_C^2} - \eta f_C}{2\omega_C} k_{SO}^{TST} \ .$$

Equ. (20)

Accordingly, to compare the new result (Equ. (17)) with the classical one (Equ. (16)) is sufficient to compare the classical TST result (Equ. (3)) with the new TST limit (Equ. (18)). For this purpose an "acceleration coefficient"κ_{SO} is defined:

$$\kappa_{SO} \equiv \frac{k_{SO}^{TST}}{k_{TST}} = \frac{1}{f_C}\sqrt{\frac{\alpha k_B T}{2\pi}} \ \exp(-\frac{\alpha(E_b - E_{LC})^2}{2k_B T} + \frac{E_b}{k_B T})$$

Equ. (21)

The necessary condition for this acceleration effect is that the activation level E_D exceeds a well defined value of$E_b/2$, which together with the condition Equ. (13) gives:

$$\frac{E_b}{2} < E_D < E_b \ .$$

Equ. (22)

The value of α, at which (for a given value of E_D according to Equ. (22)) the correction factor reaches its maximum, is easy to obtain approximately: For this it is sufficient to determine the value of α at which the exponent itself reaches its maximum:

$$\alpha_{max} = \frac{1}{E_b - E_D} .$$

Equ. (23)

The typical dependence of the acceleration coefficient κ_{SO} on the strength of the self-organisation parameter α is shown in Fig. 8. (here it should be remembered that Equ. (21) as well as Equ. (17) are only valid for values of α exceeding the limit of $1/E_D$, see Appendix).

It is easy to see that there exists an optimum value of the self-organisation parameter α, at which the acceleration reaches its maximum. Another important point is, that in activated rate processes often the barrier height E_b exceeds the thermal activation level k_BT more than one order of magnitude. Thus it is interesting to trace the dependence of the acceleration coefficient κ_{SO} on the relative barrier height $1/\varepsilon$, as shown in Fig. 9. It is seen that for barrier heights E_b sufficiently exceeding the thermal activation level k_BT (i.e. for very small ε) the acceleration coefficient may reach the factor 10^4.

VII. Discussion

Our attempt to consider microscopic self-organization in biological and macromolecular electron transfer by calculating the Kramers problem of reaction rates with active non-linear friction, yielded an electron transfer formula with remarkable properties: In dependence on the magnitude of active friction, which describes a non-linear, "autocatalytic" energy input from the environment, a significant increase of transfer rates is observed. When optimal parameter combinations are given (Fig. 8), an increase of rate constants by a few orders of magnitude appear to be feasible: A small fraction of the energy, which is provided for the electron transfer reaction (photon energy, chemical energy) is deviated through the medium and reintroduced into the reaction complex to induce a temporary microscopic self-organization of parameters which determine the electron transfer rate (see Fig. 4.). The described phenomenon is explained, in a simplified way, in Fig. 10, which describes the potential profile for an electron escape reaction near equilibrium and far from equilibrium.

Near equilibrium the distribution of electron density is Boltzmann-like and localized around the potential minimum. The escape probability over the activation barrier (E_b) is correspondingly low. Far from equilibrium (during self-organization) the electron density is redistributed according to Fig. 10, which yields a significantly higher electron escape rate. It is simultaneously expected that during self-organization also the height of the activation barrier is affected and may be reduced (to E_b^*). such a mechanism, which for reasons of simplicity has not explicitly been included into our mathematical formalism, has to be expected, since entropy reduction during self-organization is equivalent to increased molecular order.

The Marcus approach to electron transfer kinetics is, in contrast to our non-linear formalism, a linear extrapolation from equilibrium and does not include the possibility of self-organization. However, it elegantly replaces an unknown activation energyΔG^* by an expression

$$\Delta G^* = (\Delta G^0 + \lambda)^2/4\lambda$$

Equ. (24)

which contains the free energy variation ΔG^0 and the reorganization energy λ, which is experimentally and theoretically accessible. In order to take advantage of this valuable approximation, Equ. (24) may be inserted into Equ. (17) to replace the activation energy E_b from our modified Kramers treatment of the problem (this is, obviously, only possible for the case of finite activation barriers ΔG^*, otherwise the validity conditions for the Kramers approach would be violated):

$$k_{SO}^{ET} = \frac{\omega_A}{2\pi}\sqrt{\frac{\alpha k_B T}{2\pi {f_M}^2}}\left[\frac{\sqrt{(\eta f_M)^2 + 4\omega_C^2} - \eta f_M}{2\omega_C} - \exp\left(-\frac{\eta l_C {f_M}^2}{k_B T}\right)\right]\exp\left\{-\frac{{f_M}^2}{2\alpha k_B T}\right\}$$

Equ. (25)

with

$$f_M = \alpha\left[\frac{\left(\Delta G^0 + \lambda\right)^2}{4\lambda} - E_{LC}\right] .$$

It should, however, be kept in mind that the reorganization energy, which is related to the degree of molecular motion of the electron transfer complex accompanying the charge transfer, is calculated on the basis of near-equilibrium assumptions. From Equ. (25) which considers the Marcus approach for self-organized electron transfer it can be deduced that there is a significant potential for improvement of electron transfer (for finite activation barriers as demonstrated in Fig. 8 and Fig. 9).

Fig. 8. shows that already with a restrictive choice of reaction parameters ($E_b = 10\ k_BT$) an acceleration of the rate constant by one order of magnitude can be obtained. Further increases by some orders of magnitude becomes possible (under an optimum parameter choice) when $E_b >> 10\ k_BT$ (as shown in Fig. 9)). It should be noted that the special form of the friction term $f(E)$ in Equ. (6) presents, as a linear function, the simplest choice. Other, non-linear, forms of the friction term $f(x,v)$ could also be used to model accelerated reaction rates. For all functions depending only through $E(x,v)$ on (x,v) the above used procedure can be applied straightforwardly. As explained in a preceding publication (see Ref. 8(c)) self-organized, "stimulated" or "co-operative" multi-electron transfer reactions may proceed, when electrons of different co-ordination groups "communicate" with each other through the bonding system of the complex involved. In these systems the "energy side loops" for non-linear response link different electron pathways. As possible example we mentioned the complexes studied by Anson and co-workers[26] where $Ru(NH_3)_3^{2+}$ groups co-ordinated to unsaturated ligand sites on the periphery of cobalt porphyrin rings convert two-electron to four-electron catalysis of oxygen reduction.

The presented approach of self-organized electron transfer offers an explanation of how biological catalytic reactions can proceed more efficiently than classical chemical systems. Significant additional experimental and theoretical work will, however, be needed to support this hypothesis. It is realized, that the molecular environment of the electron transfer system plays an important active role for electron transfer. This, typically, requires that it is not purely dominated by thermal motion, but allows the existence of molecular structures (complexes, membranes) for the energy side loop required for self-organization. Many biological electron transfer environments fulfil this condition and allow even some speculation on possible mechanisms of evolution of self-organized electron transfer.

During evolution a chance mutation in a molecular structure may have led to a situation where a small part of the energy input for an electron transfer reaction, a phonon, originally generating heat, was redirected to interfere, as positive friction, with an ongoing electron transfer process. From now on, after a small advantage was created, evolution could have continued to optimize the self-organized electron transfer process. The rate of electron transfer may have gradually evolved from the non-autocatalytic situation (Marcus theory) towards the maximum indicated in Fig. 8. Long range electron transfer may have, for example, been stimulated by gradually evolving a temporal conformational change of the barrier between donor and acceptor during electron transfer (gradual increase of α, which is responsible for the feedback coupling, during the biological evolution). (If this was the case and if the skeched mathematical correlations between electron transfer and micro-environmental feedback must be fulfilled, it may not be so easy to experimentally simulate such processes with simple organic model systems.) A new degree of freedom of evolution of catalysis may have become this way accessible with astonishing possibilities: the ability to actively organize the reaction path of electrons with part of the energy input. This may include the ability for molecular recognition and binding through self-organization for controlled biological electron transport. Macromolecular recognition during electron transfer is a subject which has received some attention[27]. Local temporary self-organization may also have been an efficient tool towards development of new catalytic centers and molecular catalytic diversity: the highly non-linear systems may have occasionally approached bifurcation regions, where instabilities are able to generate entirely new structural patterns for evolutionary experiments

The consideration of biological electron transfer and electrocatalytic centers as self-organizing systems will require careful experimental and further theoretical studies, which ask questions different from those, which were asked before. This may be an opportunity to learn more about the extraordinary efficiency of biological energy conversion systems which are basically of electrochemical nature.

VIII. Appendix

In the following a short description of how the method developed by Naeh, Klosek, Matkowsky and Schuss can be applied to solve the Kramers problem with active friction is given. For all further details we refer to the original source[25]. The method is based on the construction of an asymptotic solution for the corresponding stationary Fokker-Planck equation (FPE) with an absorbing boundary and with a source at the equilibrium point. Then the mean first passage time (MFPT) for electron escape can be expressed as the quotient of the total population and of the total probability flux on the boundary. The underlying ansatz is that the stationary probability density function $p(x,y)$ can be factorized asymptotically in, on the one hand, a WKB solution $p_W(x,y)$ of the stationary FPE inside the domain of attraction D in the phase space, with the separatrix Γ as boundary, but not satisfying the absorbing boundary condition, and, on the other hand, a boundary layer type function $q(x,y)$ satisfying the boundary condition and matching to unity away from the boundary.

Using the following units

$$\text{length: } L = \frac{1}{\omega_A}\sqrt{\frac{E_b}{m}}\,, \quad \text{time: } T = \frac{1}{\omega_A}\,, \quad \text{energy: } E = E_b$$

Equ. (26)

one obtains the stationary FPE with a particle injection at the bottom of the well ($x = 0$, $y = 0$) in a dimensionless form (according toEqu. (14)):

$$\mathrm{grad}(\vec{J}) = -F \cdot \delta(x, y)$$

with the probability current density

$$\vec{J} = (-y \cdot p(x, y)\ ,\ \ (\beta y f(E, \alpha, E_D) + \frac{dV}{dx}) \cdot p(x, y) + \beta\varepsilon \frac{\partial p}{\partial y})$$

Equ. (27)

where F is the total flux on the boundary, x and y the dimensionless coordinate and velocity, and $\beta = \frac{\gamma}{m\omega_A}$, $\varepsilon = \frac{k_B T}{E_b}$, $V(x) = U(x) / E_b$. Due to the absorbing boundary condition,

$$[p(x, y)]_\Gamma = 0\ ,$$

Equ. (28)

the current density at Γ is given by:

$$\vec{J}|_\Gamma = (0\ , -\beta\varepsilon \frac{\partial p}{\partial y}|_\Gamma\ )\ .$$

To find the asymptotic structure of the solution $p(x,y)$ of the FPE the ansatz

$$p(x,y) = p_W(x,y)\ q(x,y)$$

Equ. (29)

is used, where the WKB-like solution is obtained by setting

$$p_W(x, y) = \exp(-\frac{w(x, y)}{\varepsilon}) \text{ with } \varepsilon \to 0$$

leading to the general result for all kinds of "friction functions"$f(E)$:

$$w(E) = \int_{E_{LC}}^{E} f(z)\ dz\ .$$

This function is normalized in a way that $p_W(x,y)$ is unity along the limit cycle $E(x,y) = E_{LC}$. For the choice of function $f(E)$ (see Equ. (6)) used in this paper $p_W(x,y)$ becomes:

$$p_W(E) = \exp\left(-\frac{\alpha}{2\varepsilon}(E - E_{LC})^2 \right)\ .$$

Equ. (30)

This way the WKB solution $p_W(x,y)$ satisfies the FPE inside the domain D asymptotically. The main goal is now to find the asymptotic solution of the boundary layer function $q(x,y)$. After inserting of Equ. (29) into the FPE the corresponding stationary backward Kolmogorov equation for $q(x,y)$ is obtained. This function has to be unity inside the domain

$$q(x,y) \to 1, \quad \varepsilon \to 0$$

and must satisfy the absorbing boundary condition Equ. (28). To obtain the boundary layer expansion of $q(x,y)$, as a new variable the distance ρ to the boundary Γ is introduced, which then is stretched by setting

$$\zeta = \frac{\rho}{\sqrt{\varepsilon}} \ .$$

The method developed in Ref. 25 now can be applied straightforwardly to get the first term in the boundary layer expansion of $q(x,y)$. The corresponding MFPT then can be determined as the quotient of the total population inside the domain D and the total flux on the boundary Γ:

$$\langle \tau \rangle = \frac{\int_D p(x,y)\, dx\, dy}{\int_\Gamma \vec{J}(x,y)\, \vec{v}(x,y)\, ds} \ .$$

Equ. (31)

The integrals in numerator and denominator can be calculated using the Laplace method. Then the escape constant k is related to the MFPT by:

$$k = \frac{1}{2\langle \tau \rangle} \ ,$$

since trajectories that hit Γ return to D or cross over with equal probabilities. Following this procedure one obtains a formula being similar to the classical Kramers formula for the medium and high friction limit which reads in dimensional units:

$$k_{SO}^{kr} = \frac{\omega_A}{2\pi f_C \omega_C} \sqrt{\frac{\alpha k_B T}{2\pi}}\, \frac{\sqrt{(\eta f_C)^2 + 4\omega_C^2} - \eta f_C}{1 + \operatorname{erf}\left(\frac{\alpha E_D - 1}{\sqrt{2\alpha k_B T}} \right)} \cdot \exp\!\Big(-\frac{\alpha (E_b - E_{LC})^2}{2k_B T}\Big) \text{ with } f_C = \alpha (E_b - E_{LC})$$

.

Equ. (32)

The denominator containing the error function is important to facilitate the limit $\alpha \to 0$ (complete absence of active friction) leading to the common Kramers result. However for values of α satisfying the condition given in Equ. (9) the denominator rapidly converges to a constant value of 2. Therefore for all cases of significant active friction the denominator can be replaced by 2.

The result in Equ. (32) cannot be correct in the extremely underdamped regime, since the escape rate must vanish as $\beta \to 0$ (i.e. if the reduced friction coefficient $\eta \to 0$). To solve this problem the NKMS-approach uses the fact that the critical energy contour $y_C(x)$ (i.e. where $E(x,v) = E_b$) nearly coincides with the domain boundary $y_\Gamma(x)$ for small β. Another stretching transformation of variables must be done to obtain the boundary layer expansion in this case:

$$\eta(x,y) = \frac{y_\Gamma^2(x) - y^2}{2\varepsilon} \quad , \quad \zeta(x,y) = \frac{y_\Gamma^2(x) - y_C^2(x)}{2\varepsilon} \quad .$$

After expanding the new boundary layer function $Q(x,y)$ in a double asymptotic series in powers of β and ε (for small β and ε) for the leading term the following equation is obtained:

$$\frac{\partial^2 Q^0(\eta,\zeta)}{\partial \eta^2} + 2f_C \frac{\partial Q^0(\eta,\zeta)}{\partial \eta} + f_C \frac{\partial Q^0(\eta,\zeta)}{\partial \zeta} = 0$$

with the new term f_C responsible for the active friction effect. Solving this equation and using the boundary and matching conditions one obtains, in the original dimensionless variables, the asymptotic expression for the probability distribution function for small friction:

$$p(x,y) = p_W(E) \cdot \left(1 - \exp\left(-f_C \frac{y_\Gamma^2(x) - y^2}{\varepsilon}\right)\right),$$

which differs from the corresponding Kramers result (in the NKMS-approach) by the factor f_C and through the new form of the WKB result (compare Equ. (30)). Applying Equ. (31) one obtains after integration for the rate constant (now in dimensional variables):

$$k_{SO}^{NKMS} = \frac{\omega_A}{2\pi} \frac{\operatorname{erf}\left(\frac{f_C}{\sqrt{2\alpha k_B T}}\right) - \operatorname{erf}\left(\frac{f_C \cdot (1 + \alpha\eta I_C)}{\sqrt{2\alpha k_B T}}\right)}{1 + \operatorname{erf}\left(\frac{\alpha E_D - 1}{\sqrt{2\alpha k_B T}}\right)} \quad .$$

Equ. (33)

This equation can be, for small β and ε, and for a value of the self-organization parameter α, which is sufficiently high, further simplified leading to:

$$k_{SO}^{NKMS} = \frac{\omega_A}{2\pi f_C}\sqrt{\frac{\alpha k_B T}{2\pi}}\left(1-\exp\left(-\frac{\eta l_C f_C^2}{k_B T}\right)\right)\cdot\exp(-\frac{\alpha(E_b - E_{LC})^2}{2k_B T}) \ .$$

Following the method of matched asymptotic expansions one can construct a uniform solution for all magnitudes of friction fromEqu. (32) and Equ. (33) by

$$k_{SO}^{unif} = k_{SO}^{NKMS} + k_{SO}^{Kr} - k_{SO}^{TST} \ ,$$

where the TST-result is obtained as the inner limit of Equ. (32) or Equ. (33), respectively (i.e. the limit $\eta \to 0$ for Equ. (32) or the limit $\eta \to \infty$ for Equ. (33)). This uniform result gives, after considering that the denominator containing the error function can be replaced by 2, the final result for the rate of self-organized electron transferEqu. (17).

Figures

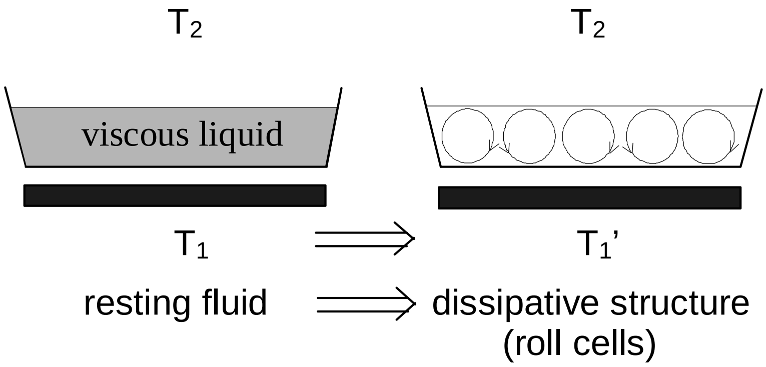

Fig. 1. Benard instability in a uniformly heated layer of a viscous fluid ($T_1' > T_1 > T_2$)

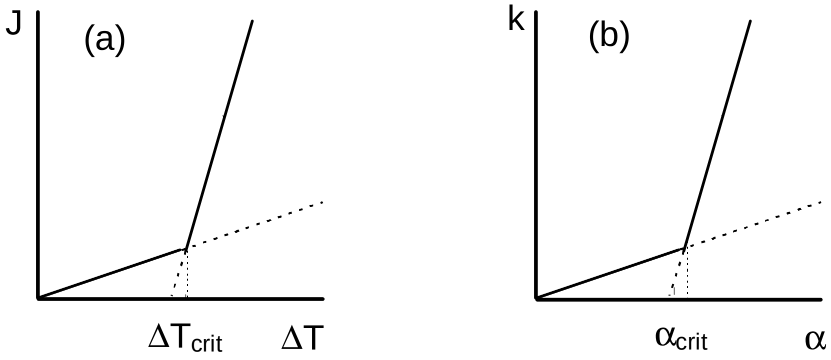

Fig. 2. (a) Schematic picture of the acceleration of the heat transfer J through the liquid layer after the bifurcation point ΔT_{crit}; (b) Hypothetical picture for the acceleration of the electron transfer rate k in dependence of a feedback parameter α.

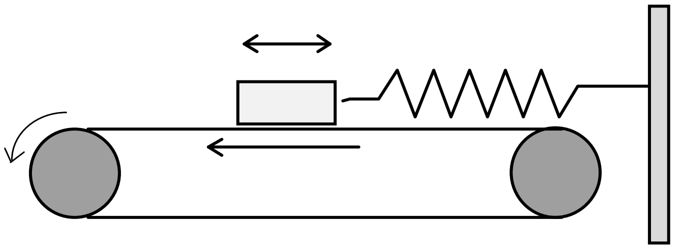

Fig. 3. Mechanically equivalent representation of the oscillating violin string

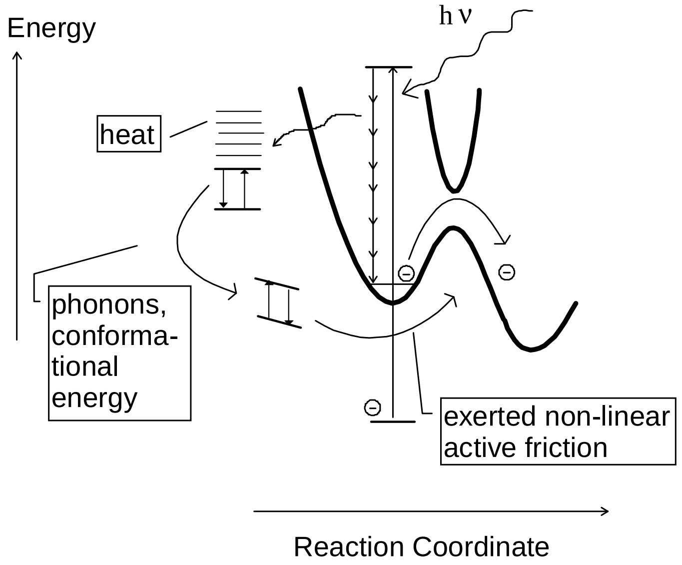

Fig. 4. Schematic visualization of the mechanism leading to active non-linear friction after the photoexcitation of a biomolecular complex

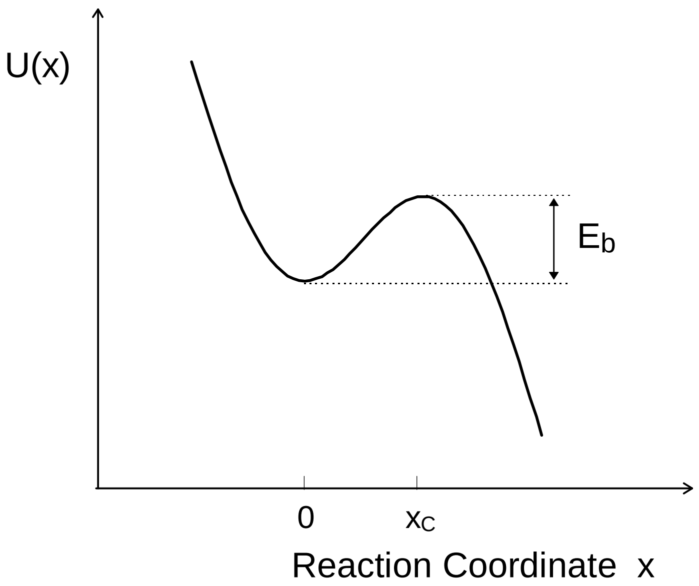

Fig. 5. Schematic form of the one-well potential U(x)

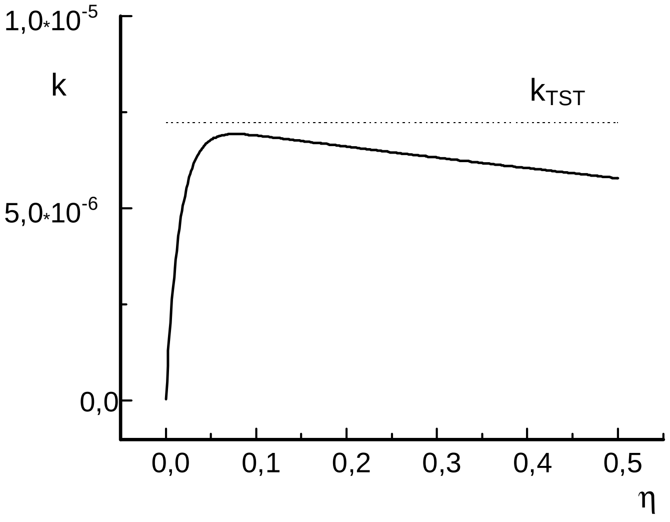

Fig. 6. Solution of the classical Kramers turnover problem (with $\varepsilon = 0.1$, $E_b = 10$, $I_C = 6.5$, $\omega_C = 1.12$, and with k_BT as the energy unit and $1/\omega_A$ as the time unit). The plot shows the classical rate constant as a function of the reduced friction.

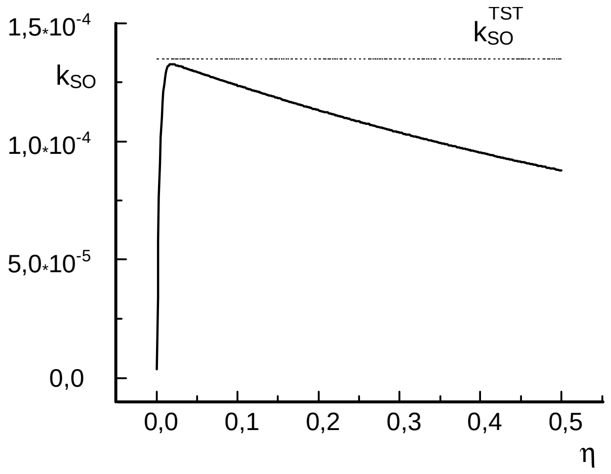

Fig. 7. Solution of the turnover problem for the case of active friction (with $\varepsilon = 0.1$, $I_C = 6.5$, $\omega_C = 1.12$, $E_b = 10$, $E_D = 7.5$, $E_{LC} = 5.0$, $\alpha = 0.4$, and with k_BT as the energy unit and $1/\omega_A$ as the time unit). The plot shows the "self-organized" rate constant as a function of the reduced friction.

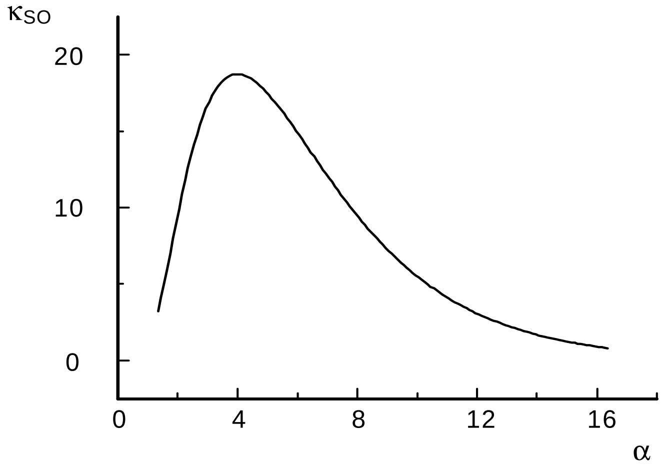

Fig. 8. Dependence of the acceleration coefficient on the self-organization parameter α (with all other parameters as in Fig. 7.)

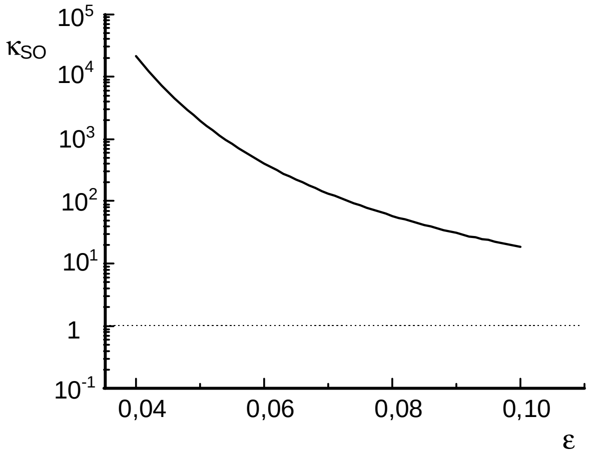

Fig. 9. Dependence of the acceleration coefficient κ_{SO} on the parameter $\varepsilon = k_BT/E_b$ (with all other parameters as in Fig. 7.)

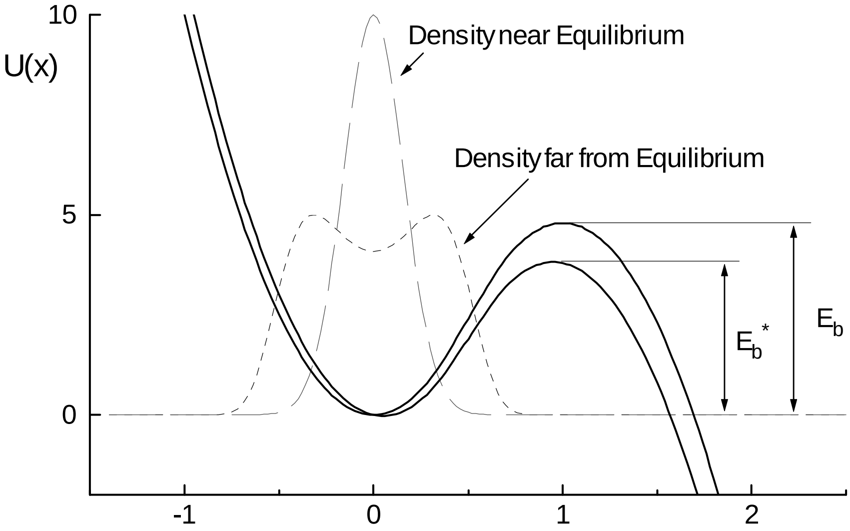

Fig. 10. Energy profile and electron density distribution before and during self-organization. The energy barrier (solid line) is lowered (broken line) while the equilibrium distribution of electrons is changed into a non-equilibrium distribution.

References

1 R.A. Marcus, J. Chem.Phys. 24, 966 (1956). Disc. Farad. Soc. 29,21 (1960), J. Chem. Phys. 43,679(1965); R.A. Marcus, N. Sutin, Biochim, Biophys. Acta 811, 265 (1985).

[2] V.G. Levich, Adv. Electrochem. Electrochem. Eng. 4 (1966)249;

R.R. Dogonadze, A.M. Kuznetsov, M.A. Vorotyntsev, Phys. Stat. Sol B. 54, 125 (1972);

J. Jortner, Biophys. Biochem. Acta 594,193 (1980).
A.M. Kuznetsov, Charge Transfer in Physics, Chemistry and Biology, Gordon and Breach, Amsterdam 1995.

[3] A. Scent-Gyorgi, Science 93, 609 (1941).

[4] Long-Range Electron Transfer in Biology, Structure and Bonding, Vol 75 , Springer Verlag, Berlin, Heidelberg 1991, seven contributions to electron transfer

[5] G. Mc Lendon, K. Pardue, P. Bak, J. Am Chem. Soc. 109 ,7540 (1987)).

[6] D. M Proserpio, R. Hoffmann and G.C. Dismukes, J. Am. Chem. Soc. 114, 4374 (1992).

[7] G. Nicolis, I. Prigogine, Self-Organization in Nonequilibrium Systems, John Wiley, New York et al. 1977.

[8] (a) L. Pohlmann, H. Tributsch, J. theor. Biol. 155, 443 (1992) (Part I)
and 156, 63 (1992) (Part II);
(b) L. Pohlmann, H. Tributsch, J. Phys. Chem. 97, 11318 (1993);
(c) H. Tributsch, L. Pohlmann, J. Electroanal. Chem. 396, 53 (1995).

[9] H. Haken, Synergetics. An Introduction, 3rd. edn., Springer, Berlin et al. 1983.

[10] H. Tributsch, L. Pohlmann, 1995, in: "Frontiers in Theoretical Biology", 1th International Workshop, Monteroduni, Italy, Aug 8-13, Conference Proceedings, Ed. C.A. Dreismann, to appear.

[11] see, e.g. I.E. Antoniou, I. Prigogine, Physica A192, 443 (1993);
A. Bohm, S. Maxson, M. Loewe, 1994, 27th Symposium on Mathematical Physics, Torun, Dec. 6 - 9;
C.A. Chatzidimitrou-Dreismann, Adv. Chem. Phys. 80, 201 (1991).

[12] see, e.g. K. Blum, Density Matrix, Theory and Applications, Plenum Press, New York and London, 1981.

[13] H.A. Kramers, Physica 7, 284 (1940).

[14] R. Landauer, in: Noise in nonlinear dynamical systems, Eds. F. Moss, and P.V.E. McClintock, Cambridge University press, Cambridge 1989, Vol. 1, p. 1; see also Ref.15.

[15] P. Hänggi, P. Talkner, M. Borkovec, Rev. Mod. Phys. 62, 251 (1990).

[16] R.F. Grote, J.T. Hynes, J. Chem. Phys. 73, 2715 (1980).

[17] A.I. Burstein, Yu. Georgievski, J. Chem. Phys. 100, 7319 (1994); see also Refs. 14 and 18.

[18] P. Hänggi, J.Stat. Phys. 42, 105 (1986) and 44, 1003;
Yu.I. Dakhnovskii, A.A. Ovchinnikov, Phys. Lett. 113A, 147 (1985).

[19] W. Ebeling, Yu.M. Romanovsky, Z. phys. Chem. (Leipzig) 266, 836 (1985);
R. Brettschneider, L. Schimansky-Geier, Wiss. Z. HU Berlin, Math.-Nat. R. 35, 450 (1986);
L. Schimansky-Geier, Phys. Lett. A 126, 455 (1988);
W. Ebeling, M. Jenssen, Z. phys. Chemie (Leipzig) 269, 1 (1988);
L. Schimansky-Geier, Ch. Zülicke, Z. Phys. B - Condensed Matter 79, 451 (1990).

[20] W Ebeling, , Z. phys. Chemie (Leipzig) 269, 275 (1988).

[21] H. Haken, Rev. Mod. Phys. 47, 67 (1975).

[22] E. Pollak, H. Grabert, P. Hänggi, J. Chem. Phys. 91, 4073 (1989).

[23] L. Pohlmann, H. Tributsch, 1995, in: "Frontiers in Theoretical Biology", 1th International Workshop, Monteroduni, Italy, Aug 8-13, Conference Proceedings, Ed. C.A. Dreismann, to appear.

[24] See the excellent review by Hänggi et al. (Ref.15) and the references cited therein.

[25] T. Naeh, M.M. Klosek, B.J. Matkowsky, Z. Schuss, SIAM J. Appl. Math. 50, 595 (1990).

[26] B. Steigers, F.C. Anson, Inorg. Chem. 33, 5767 (1994);
C.Shi, F.C. Anson, Inorg. Chim. Acta 225, 215 (1994);
B. Steigers, C.Shi, F.C. Anson, Inorg. Chem. 32, 2107 (1993).

[27] G. McLendon, Long-Range Electron Transfer in Biology, Structure and Bonding, Vol 75 , Springer Verlag, Berlin, Heidelberg 1991, p159.