COMMENTS ON LIMITED USE OF SMOLUCHOWSKI EQUATION IN KINETIC ANALYSIS OF ELECTRON–TRANSFER PROCESSES*

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The rate of barrier crossing in a cusped potential serves as a model for electron transfer processes in the presence of dissipation. The spatial diffusion limit for the rate constant is known for this case in the strong damping limit when the Smoluchowski equation is valid. The paper discusses comparison of different approximation schemes in derivation of a one dimensional Smoluchowski equation for a linear kinetic model derived by a non-Markovian dynamics. Differences in calculated short- and longtime limit properties of the systems resulting from various method of elimination of fast variables question validity of use of a Smoluchowski equation in the kinetic rate approach. To calculate the rate, the standard definition in the integrated form of the correlation function is used and the results are shown to be consistent with the predictions of numerical analysis presented in literature.

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Dynamics of a Brownian particle subject to a non-Markovian time-dependent friction serves frequently as a basic model to study viscoelastic effects in condensed matter, [1, 2]. Such effects are known to play a role in understanding kinetic rates in condensed phases [3, 4]. One of the most explored example [5–8] is the solvent effect on the prefactor of activated chemical processes usually described in terms of a generalized Langevin equation

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(GLE). A considerable effort has been made to understand kinetic rate for the processes in non-Debye solvents whose relaxation behavior can be mimicked by a multiple-time exponential decay [9, 10] which, in turn, leads to a complex memory kernel at the level of GLE approach. A complementary method, especially practical for mathematical analysis is based on derivation of a Fokker-Planck equation (FPE) associated with a non-Markovian Langevin equation. The method is applicable mostly to the situations where the system dynamics can be characterized by harmonic potentials and Gaussian random forces (the only case where the closed-form FPE can be derived from the starting GLE [5, 11, 12]). In the latter case, it is also possible to relate dynamics of the system with only one coordinate in projected phase space [13, 14] whose time evolution can be recast in terms of "generalized Smoluchowski equation" (SE).

In this paper we address some comments concerning a limited use of SE, even as applied to perfectly linear dynamics. As a particular example, we are dealing with the system whose relaxation properties can be characterized by time-correlation function

$$\Delta(t) = \frac{\langle x(0)x(t)\rangle}{\langle x^2(0)\rangle} \tag{1}$$

associated with the reaction coordinate dynamics governed by GLE

$$\ddot{x}(t) = -\omega^2 x(t) - \int_0^t d\tau \eta(t-\tau)\dot{x}(\tau)d\tau + F(t)\,, \tag{2}$$

where the Gaussian random force $F(t)$ satisfies the fluctuation–dissipation theorem

$$\langle F(t)F(t+\tau)\rangle = 2k_{\mathrm{B}}T\eta(\tau) \tag{3}$$

together with the relations

$$\begin{aligned} \langle F(t)\dot{x}\rangle &= 0\,, \\ \langle F(t)\rangle &= 0\,. \end{aligned} \tag{4}$$

In the case of a strongly overdamped motion, relaxation of the spatial correlation function $\Delta(t)$ is assumed to be represented by two different time relaxation scales:

$$\Delta(t) = f_1\exp(-\Lambda_1 t) + f_2\exp(-\Lambda_2 t)\,. \tag{5}$$

This particular form of $\Delta(t)$ can be associated with a memory kernel $\eta(t)$ modeling time-dependent friction coefficient which is then given by

$$\eta(t) = \gamma\delta(t) + \alpha\exp(-\lambda t)\,. \tag{6}$$

In this version, Eq. (2) has been used [6, 9] to study solvent-controlled electron-transfer reactions in alcohols. In the presence of a nonequilibrium polarization, the free energy of the reaction-polar solvent system changes after instantaneous change in the reactant/product charge distribution. A usual assumption is that these fluctuations in the solvent polarization are governed by a harmonic free energy function (*cf.* Eq. (2)). Non-interacting reactant and product wells are represented as diabatic surfaces of the free energy. When a sufficient interaction occurs between the diabatic surfaces (in the adiabatic or weakly adiabatic regimes of the electron transfer process), the solvent dynamics can have a significant effect on motion across the barrier at the point of intersection of the energy curves [2, 4, 6, 9]. The overall electron-transfer rate is then determined by the interplay of two factors: the strength of electronic coupling between the states and relaxation dynamics of the solvent (which represents "nuclear degrees of freedom"). The time-dependent reaction coordinate $x(t)$ for such a system is commonly identified with a portion of nonequilibrium, orientational polarization for the time-dependent effective charge distribution in the solvent [6, 8, 9] which satisfies Eq. (2) with a time-nonlocal friction term. Solvent adjustments to external perturbations in the system can be interpreted in terms of the response time. A natural choices for this characteristic time scale are then (*cf.* Appendix A)

$$\tau_\infty = \left[- \dot{\Delta}(t)_{t=0} \right]^{-1} \tag{7}$$

which is the time scale on which the system initially reacts to any perturbations or

$$\tau_0 = \int_0^\infty \Delta(t)dt \tag{8}$$

which is the time it takes the system to completely relax after a perturbation. A non-Markovian character of GLE can be understood as an outcome of the projection scheme performed at the level of a fully deterministic (and hence a Markovian) Liouville equation [3, 7, 15, 16]. The method suggested by Ferrario and Grigolini [1, 17] allows to invert the problem: non-Markovian dynamics can be embedded into a multidimensional space of auxiliary variables which can mimic memory kernel properties of $\eta(t)$[1].

[1] Such a frequency-dependent friction can be directly related to the spatial correlation function, $\Delta(t)$. From Laplace transform of Eq. (2), one gets $\hat{\Delta}(s) = (s + \hat{\eta}(s))(s^2 + \omega^2 + s\hat{\eta}(s))^{-1}$ which in the limit of a strongly overdamped motion leads to $\hat{\Delta}(s) \approx (s + \omega^2/\hat{\eta})^{-1}$, where further the ratio $\hat{\eta}(s)/\omega^2$ is identified with an effective longitudinal relaxation time in the medium [4–7] (*cf.* Eq. (8)).

A non-Markovian process (2) is then substituted by a Markovian multivariable process:

$$\begin{aligned}\dot{x}(t) &= \nu(t)\\ \dot{\nu}(t) &= -\omega^2 x(t) - \gamma\nu(t) + w(t) + f_\nu(t)\\ \dot{w}(t) &= -\alpha\nu(t) - \lambda w(t) + f_w(t)\end{aligned} \tag{9}$$

with independent Gaussian white noises $f_w(t)$, $f_\nu(t)$:

$$\langle f_\nu(t)\rangle = 0\,, \qquad \langle f_w(t)\rangle = 0 \tag{10}$$

and

$$\begin{aligned}\langle f_\nu(t) f_\nu(t+\tau)\rangle &= 2\gamma k_{\mathrm{B}} T\delta(\tau)\\ \langle f_w(t) f_w(t+\tau)\rangle &= 2\alpha\lambda k_{\mathrm{B}} T\delta(\tau)\,.\end{aligned} \tag{11}$$

The system of equations (9) can be directly related to a three-variable FPE governing time-evolution of the probability density function $p(x, \nu, w; t)$. One can adiabatically eliminate velocity from the set (9), so that the dynamics of the system becomes expressed in terms of $x(t)$ and $w(t)$ variables only. Further elimination of the auxiliary variable $w(t)$ leads to the expression for the trajectory $x(t)$

$$\begin{aligned}x(t) =& G_{xx}x_0 + \frac{1}{\gamma^{1/2}}\int_0^t G_{xx}(t-\tau) f_\nu(\tau)d\tau\\ &+ \int_0^t G_{xw}(t-\tau)\left(f_w(\tau) - \frac{\alpha}{\gamma^{1/2}} f_\nu(\tau)\right)d\tau\,,\end{aligned} \tag{12}$$

where $G_{xx}(t)$, $G_{xw}(t)$ are the elements of the fundamental matrix for the system (9) after elimination of $\nu(t)$ (*cf.* Appendix B). For the simplicity, it has been assumed that $w(t=0) = 0$. The integral terms on the right-hand side of (12) are linear operand over Gaussian noises and as such can be viewed as random forces. By extending the transformation introduced by Adelman [13], time derivative of $x(t)$ can be now expressed as

$$\begin{aligned}\dot{x}(t) =& \frac{\dot{G}_{xx}(t)}{G_{xx}(t)}x_t + \frac{1}{\gamma^{1/2}}G_{xx}(t)\frac{d}{dt}\int_0^t \frac{G_{xx}(t-\tau)}{G_{xx}(t)} f_\nu(\tau)d\tau\\ &+ G_{xx}(t)\frac{d}{dt}\int_0^t \frac{G_{xw}(t-\tau)}{G_{xx}(t)}\left(f_w(\tau) - \frac{\alpha}{\gamma^{1/2}} f_\nu(\tau)\right)d\tau\\ =& \frac{\dot{G}_{xx}(t)}{G_{xx}(t)}x_t + F_1(t) + F_2(t)\,.\end{aligned} \tag{13}$$

From this point on one can follow a standard derivation of a nonstationary SE based on use of a stochastic Liouville equation [18, 19] together with van Kampen lemma and Novikov formula [20] for the mean

$$\langle \delta(x(t)-x)F_i(t)\rangle = -\frac{\partial}{\partial x}\int_0^t d\tau C_{F_i}(t,\tau)\left\langle\left\{\delta(x(t)-x)\frac{\delta x(t)}{\delta F_i(\tau)}\right\}\right\rangle. \quad (14)$$

In the last expression, $C_{F_i}(t,\tau)$ represents characteristic correlation function of the noise $F_i(t)$. A resulting one-dimensional Smoluchowski equation has the form

$$\frac{\partial\rho(x,t)}{\partial t} = -\frac{\partial}{\partial x}J(x,t)\rho(x,t) + \frac{\partial^2}{\partial x^2}[D_1(x,t)+D_2(x,t)]\rho(x,t), \quad (15)$$

where $\rho(x,t)$ is the probability distribution of x at time t and $J(x,t)$, $D(x,t)$ stand for the drift and diffusion coefficients, respectively:

$$J(x,t) = -\frac{\dot{G}_{xx}(t)}{G_{xx}(t)}x,$$

$$D_1(x,t) = G_{xx}^2(t)k_BT\frac{d}{dt}\int_0^t \frac{G_{xx}^2(t-\tau)d\tau}{G_{xx}^2(t)},$$

$$D_2(x,t) = (\alpha\lambda+a^2)k_BTG_{xx}^2(t)\frac{d}{dt}\int_0^t \frac{G_{xw}^2(t-\tau)d\tau}{G_{xx}^2(t)}. \quad (16)$$

A non-stationary Eq. (15) has a particular simple form in the longtime limit[2] which is characterized by:

$$\lim_{t\to\infty} J(x,t) = \Lambda_1 x,$$

$$\lim_{t\to\infty} D_1(x,t) = k_BT\frac{(\lambda\gamma+\alpha)^2+\lambda\gamma\omega^2}{\gamma^2\Lambda_1(\Lambda_1+\Lambda_2)},$$

$$\lim_{t\to\infty} D_2(x,t) = k_BT\frac{\lambda\alpha+\alpha^2}{\gamma^2\Lambda_1(\Lambda_1+\Lambda_2)} \quad (17)$$

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[2] Stochastic diffusion process, as defined by Eq. (15) is time-inhomogeneous. By "longtime limit" we mean here the limit in which $\lim_{t\to\infty} P(x,t)$ exists and is the solution of the corresponding homogeneous process characterized by the limiting values (17) of the drift $J(x,t)$ and the diffusion $D = D_1(x,t)+D_2(x,t)$ coefficients (*cf.* [21]).

with Λ_1, Λ_2 being eigenvalues of a linear deterministic matrix (*cf.* Appendix A):

$$\Lambda_{1,2}^2 - \Lambda_{1,2}\left(\lambda + \frac{\alpha}{\gamma} + \frac{\omega^2}{\gamma}\right) + \frac{\lambda\omega^2}{\gamma} = 0\,, \qquad \Lambda_1 < \Lambda_2\,. \tag{18}$$

Starting from Eq. (2) Okuyama and Oxtoby [14] derived generalized SE based on the assumption of the initial Maxwellian distribution of velocities and gaussianity of a stochastic force $F(t)$. Their equation, presented as an extension of a non-stationary SE for a free Brownian motion treated by Adelman and Fox [11, 13], differs from Eqs (15, 16) in the expression for the time- dependent diffusion coefficient[3]:

$$D_0(t) = -k_B T \frac{\dot{G}_{xx}(t)}{G_{xx}(t)}\,, \tag{19}$$

which may be obtained from the above discussed scheme provided the effects of $w(t)$ variable were neglected (*cf.* Eq. (12)).

Still different approach to derivation of a SE associated with a non-Markovian LE was proposed by Grigolini *et al.* [17, 18] who started from a mathematical model of a reacting system described by a nonlinear stochastic oscillator with a given coordinate and velocity, coupled *via* interaction to the bath represented by another stochastic oscillator. With the ansatz of "local linearization" the author obtained a SE with renormalized drift coefficient (which is typical for the situation where the noise is coupled to a state variable in a stochastic dynamic system, [21]). In a particular case, when the coupling between the system and an auxiliary oscillator representing noise effects is linear and by assuming the auxiliary oscillator to be strongly overdamped, Grigolini's model coincides with the system (9), the only variation being the form of a deriving force which in his case requires renormalization of a characteristic frequency ω to $\sqrt{\omega^2 - \alpha}$. In the longtime limit[4], Grigolini's approach yields a SE of the form:

$$\begin{aligned}
\frac{\partial}{\partial t}\rho(x,t) &= \frac{\partial}{\partial x} D_G \left[\frac{\partial}{\partial x} + \frac{\Omega^2 x}{k_B T}\right]\rho(x,t)\,,\\
D_G &= \lim_{s\to 0} k_B T \Phi(s) = \lim_{t\to\infty} k_B T L\left[\frac{\langle \nu(t)\nu(0)\rangle}{\langle \nu^2(0)\rangle}\right],\\
\Omega^2 &= (\omega^2 - \alpha)\,,
\end{aligned} \tag{20}$$

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[3] It can be easily proven that in the case of $\eta(t)$ represented solely by a short memory kernel $\eta(t) = \gamma\delta(t)$, $D_0(t)$, (19) and $D_1(t)$, (15) coincide (see derivation of $D_0(t)$ presented in [14] whereas $D_2(t)$ becomes trivially zero.

[4] "Longtime limit" is defined now as a low frequency limit of the velocity correlation function, *cf.* Eq. (20).

where diffusion coefficient D_G is determined by the low-frequency limit of the Laplace transform of a normalized velocity correlation function. If in the set of Eqs (9), $x(t)$ and $w(t)$ are assumed to be slow variables compared to $\nu(t)$, *i.e.* by considering that $x(t)$ and $w(t)$ do not vary in the time scale of variation of $\nu(t)$ (determined by $1/\gamma$), direct integration of $\nu(t)$ leads to the velocity correlation function

$$\begin{aligned}\langle \nu(t)\nu(0)\rangle &= \mathrm{e}^{-\gamma t}\langle \nu^2(0)\rangle - \omega^2\langle x(0)\nu(0)\rangle\frac{1-\mathrm{e}^{-\gamma t}}{\gamma} \\ &+ \langle w(0)\nu(0)\rangle\frac{1-\mathrm{e}^{-\gamma t}}{\gamma} \\ &+ \int_0^t dt'\mathrm{e}^{-\gamma(t-t')}\langle f_\nu(t')\nu(0)\rangle\,. \end{aligned} \tag{21}$$

If all but $\langle \nu^2(0)\rangle$ correlations are assumed to vanish, the system (9) has its SE analog[5] with a characteristic diffusion constant scaled with the velocity relaxation time $1/\gamma$ (*cf.* Eq. (21)) which coincides with τ_∞^{-1} defined in Eq. (7):

$$D = k_\mathrm{B}T(\omega^2\tau_\mathrm{eff})^{-1} = \langle x^2\rangle_\mathrm{eq}\tau_\mathrm{eff}^{-1} = (\beta\gamma)^{-1}\,. \tag{22}$$

From this point on our attention will be focused on derivation of expression for the kinetic rate based on various approaches to the SE described above.

A general chemical-reaction system can be described as a two-level system coupled to a reaction coordinate. It is convenient to introduce a function of the dynamical variable x which describes the progress of the transition from one state (reactants, R) to the other (products, P):

$$N_{R,P}(t) = \int_{-\infty}^{+\infty}\rho(x,t)\theta(\mp x - \delta)dx\,. \tag{23}$$

$N_{R,P}$ stands here for the population number of a given state, $\theta(x)$ is the Heaviside step function,

$$\theta(x) = \begin{cases} 1, & \text{for } x > 0 \\ 0, & \text{for } x < 0 \end{cases} \tag{24}$$

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[5] Note that Grigolini's procedure produces, in the limit specified above, a homogeneous (time independent) SE, similar (apart from the drift coefficient) to the original Smoluchowski equation derived in the strongly overdamped limit of the Kramers [22] problem.

$\rho(x,t)$ is a coarse-grained distribution function for the reaction coordinate value at time t and δ is a half-width of the transition (barrier) region[6]. By use of a definition of a steady-state population number:

$$\overline{N} = \int_{-\infty}^{-\delta} \rho(x, t \to \infty) dx \tag{25}$$

it is possible to introduce (*cf.* Mori, Kapral [15]) a projection operator $\boldsymbol{P}$ which projects the desired population number out of the probability density:

$$P\rho(x,t) = \rho(x, t \to \infty)\theta(-x-\delta)\overline{N}^{-1} \int_{-\infty}^{-\delta} \rho(x,t)dx + \rho(x, t \to \infty)\theta(x-\delta)\overline{N}^{-1} \int_{\delta}^{+\infty} \rho(x,t)dx\,. \tag{26}$$

Evolution equation for $N_{R,P}$ can be derived by use of standard projection-operator techniques, provided a form of time evolution equation for $\rho(x,t)$ is known[7]. A general form of the rate law for $N_{R,P}$ can be then written as:

$$\dot{N}_R(t) = -\int_0^t k_{RR}(t-t')N_R(t')dt' + \int_0^t k_{RP}(t-t')N_P(t')dt'\,, \tag{27}$$

where forms of the rate kernels $k_{RR}(t)$, $k_{RP}(t)$ depend on the action of the projection operator on the evolution equation satisfied by $\rho(x,t)$.

The time-dependence of the rate kernel can be omitted if the decay time of the population number is long compared with some characteristic times in the system such as interval (vibrational, rotational) or translational relaxation times. A memory less rate equation obtained in this way has the

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[6] This schematic analysis of the rate definition assumes symmetric form of a potential in x-variable. The same calculations can be easily generalized to the case of asymmetric potential barrier.

[7] Common approach to the problem as applied to electron-transfer reactions is to start with *e.g.* a quantum version of Liouville equation for $\rho(x,t)$ which incorporates electronic coupling between diabatic surfaces and classical dynamics for motion in the reactants and products wells, respectively (see *e.g.* Zusman [2]).

same form as the phenomenological rate law of an equilibrium chemical reaction:

$$\frac{d\delta N_{R,P}(t)}{dt} = -k_{rxn}\delta N_{R,P}(t)\,, \qquad k_{rxn} = k_{\text{forward}} + k_{\text{backward}}\,, \tag{28}$$

where

$$\delta N_{R,P}(t) = N_{R,P}(t) - \langle N_{R,P}(t)\rangle_{\text{eq}} \tag{29}$$

describes fluctuations in the population number for a given state.

In particular, if $\rho(x,t)$ satisfies a standard SE,

$$\frac{\partial\rho(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial}{\partial x} + \frac{\partial}{\partial x}\beta U(x)\right]\rho(x,t) \tag{30}$$

derivation of the rate as defined in (28) follows analysis of the decay of the survival probability within the reactants well [22–26]:

$$k^{-1}_{\text{forward}} = \int_0^\infty dt \int_{-\infty}^{-\delta} dx\rho(x,t)\,. \tag{31}$$

The definition of the rate constant coincides then with the formal derivation of the mean first passage time (MFPT) for the system described by a Markovian form of SE, [6, 24, 26][8].

In a strongly overdamped limit, for high barriers and with a frequency-independent friction, the rate constant evaluated by this method yields the Kramers rate [22]

$$k_{\text{Kramers}} = \frac{\omega\omega_b}{2\pi\gamma}e^{-\beta\Delta U^*}\,, \tag{32}$$

where ΔU^* stands for the height of the barrier and ω_b is a characteristic frequency at the top of the barrier. For a cusp shaped barrier, Smoluchowski dynamics leads in this case to the rate[9] [22, 26, 6]:

$$k = \frac{\omega^2}{2\gamma}\left(\frac{\beta\Delta U^*}{\pi}\right)e^{\beta\Delta U^*}\,. \tag{33}$$

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[8] Calculation of the mean first passage time requires imposing some boundary conditions on Eq. (20). A typical choice (stemming from the definition of reactants population) is to use a reflecting boundary condition at $x = -\infty$ and an absorbing boundary at the top of the barrier.

[9] As it stands, formula (33) is an approximation to the rate defined in (31). The result is exact within the 10% for the barrier height $\beta\Delta U^* \geq 5$, [24, 26]. For lower barriers the expression has to be corrected with a multiplying factor.

The same result may be inferred from the "longtime limit" SE derived by the Grigolini's method (*cf.* (20), (21)).

To sum up, we conclude that the system of Langevin Eqs (9) can be associated with a generalized SE, after projection of a dynamic flow to one dimensional space of the coordinate x which is chosen as the only relevant coordinate (all other components of the vectorial flow (9) are regarded as irrelevant variables). However, depending on the method of projection, one gets various forms of a SE. Each approximation scheme leads to a Gaussian stochastic process $\{x(t)\}$ (that is an obvious result for the problem of linear dynamics flow perturbed by Gaussian noises, [11–13, 19–21]). A resulting SE is a non-stationary diffusion equation with explicitly time-dependent drift and diffusion coefficients (the mean and variance of the process $\{x(t)\}$ are time-dependent properties).

In this context, we would like to discuss applicability of various schemes in evaluating the kinetic rate of the process (9).

The escape kinetics in cusp-like potentials has been broadly applied in the non-adiabatic rate theory of electron-transfer reactions where diabatic free-energy curves cross each other forming a cusp-shape barrier [23]. System (9) is one of particular exemplifications of the theory used, when the overall kinetic process is limited by the solvent polarization relaxation within the well. Just by inspection of the kinetic equations (9) it is hard to decide *a priori* which one of the characteristic times (7), (8) is an appropriate time-scale governing the reaction kinetics.

Numerical studies of Fonseca [9] together with analysis of Hynes [6] concluded that the decay of reactants' population in non-Debye solvents (because of the multi-exponential or non-exponential decay of the reaction coordinate time correlation function (6), the underlying dynamics governing evolution of $x(t)$ in this cases becomes non-Markovian) can be described by using a Debye representation of the solvent with an effective relaxation time τ_{eff} which, with the increasing height of the barrier tends to τ_∞, the shorter time scale in the system. Effective diffusion coefficient[10] can be then approximated by $D_{\text{eff}} = \langle x^2 \rangle \tau_{\text{eff}}^{-1}$ giving rise to an effective kinetic rate described by an analog of the Kramers formula [6, 9]:

$$k_{\text{eff}} \cong \tau_{\text{eff}}^{-1} \left(\frac{\beta \Delta U^*}{\pi} \right)^{1/2} \mathrm{e}^{-\beta \Delta U^*} . \tag{34}$$

In general, projection of a vectorial Markov process to a lower dimensional space would require special concern about boundary condition which has to accompany a backward (adjoin) SE equation in deriving formula for the mean first passage time. The latter are by no means obvious neither in

[10] Note that this analysis of a dynamic system (9) yields $\omega^2 \tau_{\text{eff}} = \omega^2 \tau_\infty = \gamma$.

the projected non-Markovian system nor in its higher-dimensional Markovian analog with the extra set of auxiliary variables mimicking the effects of the memory (for the discussion see [24]). In fact, application of the mean first passage-time approach [21, 25, 26] when starting from the SE (15) would require evaluation of the integral

$$T_{\mathrm{MFP}} = \int_{-\infty}^{0} dz \rho_0(z) \int_{0}^{z} dy \rho_0^{-1}(y) \int_{-\infty}^{y} dx \int_{0}^{+\infty} dt D^{-1}(t) \frac{\partial \rho(x,t)}{\partial t}, \qquad (35)$$

where, as in a Markovian case, a reflecting and an absorbing boundaries have been specified at $x = -\infty$ and $x = 0$, respectively. By assuming that monotonically-decreasing $D(t)$ relaxes to $D(\infty)$ with some decay time, one can estimate from (23) the effects of short-time dynamics of $D(t)$ on the rate $k(t) = T_{\mathrm{MFP}}^{-1}$, [26]. In contrast to the above mentioned results [6, 9] this analysis rules out the short dynamics effects on the calculated mean first-passage time (35), the discrepancy questioning validity of the mean first passage time approach in the kinetic description of systems with a complex memory dynamics[11].

The problem of surmounting the parabolic barrier in the system described by a set of Langevin equations has been solved positively by Dygas, Matkowsky and Schuss [25] who used the singular perturbation method to compute expressions for the mean exit time of the Brownian particle from the potential well in which it is confined.

The friction memory effects which are known to play a role in the vicinity of a barrier, cease to be observable in a particular case of cusp barriers [27] (but only, if the system does not reach the strong overdamped limit, for a discussion see [10]). Every particle that approaches the barrier from, say, left-hand side with the positive velocity will almost surely leave the potential well, so that the rate is determined by the mean passage time to cross the line of a cusp with the velocity $v > 0$. That results, to a leading order in the barrier height measured in kT, in the transition state theory

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[11] The short-time dynamics effects are also wiped out in the analysis of the rate constant defined by a "flux over population method" [24]. The constant nonequilibrium current builds up a total integrated probability p_0 proportional to the escape time T, $j_0 T = \int_{-\infty}^{x_b} p_0(x) dx$, whose inverse defines the rate. Solving equation (15) for the nonequilibrium probability p_0, by setting $j(x, \infty) = j_0$ one can evaluate the rate which gives then the Kramers result (34) with a characteristic $\tau_{\mathrm{eff}} \sim \Lambda_1^{-1}$.

limit for the kinetic rate[12]:

$$k_{\mathrm{TST}} = \frac{\omega}{2\pi} \exp\left(-\frac{\Delta U^*}{k_{\mathrm{B}}T}\right). \tag{36}$$

The procedure leading to evaluation of (36) is based on the common assumption of equilibrium distribution in velocities whereas strong damping limit requires an "adiabatic elimination" of velocities which effectively yields Smoluchowski-type dynamics in the system with a cusp-rate for escape given by Eq. (34).

Keeping this argument in mind, we have rederived the rate constant for the process (9) following directly definition of Yamamoto [28] in the integrated form proposed by Chandler [29]:

$$\begin{aligned} k(t) &= -\frac{1}{N}\langle \delta N_R(t)\delta N_R(0)\rangle\,, \\ N &= N_R(t) + N_P(t)\,. \end{aligned} \tag{37}$$

An averaging is performed over probability density $\rho(x, w, t; x_0, w_0, t = 0)$ whose conditional form is [22]

$$\rho(x,\nu,w,t/x_0,\nu_0,w_0,0) = (2\pi)^{-1}(\det\sigma^{-1})^{1/2}\exp\left(-\tfrac{1}{2}y^T\sigma^{-1}y\right) \tag{38}$$

with

$$\begin{aligned} y_1 &= x - \langle x(t)\rangle\,, \\ y_2 &= \nu - \langle \nu(t)\rangle\,, \\ y_3 &= w - \langle w(t)\rangle\,, \\ \sigma_{ij} &= \langle y_i(t)y_j(t)\rangle\,, \end{aligned} \tag{39a}$$

and $\langle x(t)\rangle$, $\langle \nu(t)\rangle$, $\langle w(t)\rangle$ given by (*cf.* Appendix B):

$$\langle y(t)\rangle = G(t)y(0)\,. \tag{39b}$$

The validity of this approach holds independently of the nature of the underlying dynamics determining the strength of the friction coefficient and requires only well defined velocity of the reaction coordinate at time $t = 0$. The approach, known in literature as the reactive flux method, works for

[12] This result requires that the characteristic barrier frequency ω_b tends to infinity with a fixed value of friction. The proper limit for the overdamped motion is the Kramers rate (22) derived from the Smoluchowski equation in the limit of $\gamma \gg \omega$, where ω stands for a characteristic well frequency [10].

times much longer than the molecular time which relates to the relaxation dynamics within the well and much shorter than the escape time related to the reactive transfer of the trajectories surmounting the barrier. Obviously, this requirement of the perfect time-scale separation is met if the barrier is high. The method reduces the knowledge of the longtime relaxation behaviour of the correlation function to the knowledge of short time dynamics in the transition region and in the limit of $t \to 0^+$ equals the result of the transition-state theory [24, 29–31].

We assume that the potential $U(x)$ of the system is given by

$$U(x) = \tfrac{1}{2}\omega^2(|x| - x_s)^2 . \tag{40}$$

The molecular flux correlation function (37) can be represented as

$$k(t) = -\tfrac{1}{N}\langle \delta N_R(t)\dot{N}_R(0)\rangle \tag{41}$$

which together with (38), (39) leads to

$$k(t) = \mathrm{e}^{-\beta\Delta U^*} I^{-1} \int_{-\infty}^{+\infty} dx \int\int_{-\infty} \int dx_0 d\nu_0 dw_0 \rho(x, t/x_0, \nu_0, w_0, 0)\theta_R(x) \times \nu_0 \theta_R'(x_0)\rho_{\mathrm{eq}}(x_0, w_0, 0), \tag{42}$$

where I stands for a partition function

$$I = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} d\nu dw \mathrm{e}^{-\beta U(x) - \beta\frac{\nu^2}{2} - \beta\frac{w^2}{2\alpha}} = I_1 2\pi k_{\mathrm{B}} T\alpha^{1/2} \tag{42a}$$

and $\rho(x, t/x_0, \nu_0, w_0, 0)$ is (integrated over ν, w) conditional probability density that the reaction coordinate takes value x at time t provided the process has started with the values x_0, ν_0 and w_0 at time zero:

$$\rho(x, t/x_0, \nu_0, w_0, 0) = (2\pi\sigma_{xx})^{-1/2} \exp\left\{-\frac{(x - \langle x\rangle)}{2\sigma_{xx}}\right\}. \tag{43}$$

The equilibrium probability distribution $\rho(x_0, \nu_0, w_0, 0)$ is a relaxed form of the probability density (43) in each of the products and reactants wells and can be evaluated as a stationary (longtime limit) solution to a diffusion equation associated with the system (9):

$$\rho_{\mathrm{eq}}(x_0, \nu_0, w_0, 0) \sim \exp\left(-\frac{\nu_0^2}{2k_{\mathrm{B}}T} - \frac{w_0^2}{2k_{\mathrm{B}}T\alpha} - \frac{U(x)}{2k_{\mathrm{B}}T}\right). \tag{44}$$

With the definition (44), $k(t)$ reads in this case

$$k(t) = (2\pi k_B T)^{-1} e^{-\beta \Delta U^*} I_1^{-1} \alpha^{-1/2} \int_0^{+\infty} dx \int_{-\infty}^{+\infty} dw_0 \int_{-\infty}^{+\infty} d\nu_0 \times \rho(x, t/0, \nu_0, w_0) \nu_0 \exp\left(-\frac{w_0^2}{2k_B T \alpha} - \frac{\nu_0^2}{2k_B T} \right), \tag{45}$$

Substitution of (43) leads to

$$k(t) = (2\pi k_B T)^{-1} e^{-\beta \Delta U^*} I_1^{-1} \alpha^{-1/2} \int_{-\infty}^{+\infty} d\nu_0 \int_{-\infty}^{+\infty} dw_0 \left[\int_{-G_{x\nu}\nu_0 - G_{xw} w_0}^{+\infty} dy \times \frac{\exp \frac{-y^2}{2\sigma_{xx}}}{\sqrt{2\pi\sigma_{xx}}} \right] \nu_0 \exp\left(-\frac{\nu_0^2}{2k_B T} - \frac{w_0^2}{2k_B T \alpha} \right). \tag{46}$$

The validity of Eqs (41)–(46) holds independently of the nature of the underlying dynamics (no specification of a strong or a weak friction limit has been assumed so far). In the limit of $t \to 0^+$ the rate (41) can be expressed as an equilibrium average of a one-way flux at the transition state $x = 0$, [29]:

$$\lim_{t \to 0^+} k(t) = \langle \theta_R(\dot{x}(0)) \dot{x}(0) \theta_R'(x(0)) \rangle = k_{\mathrm{TST}} . \tag{47}$$

An alternative general formula for the rate (41) involves autocorrelation function of the reactive flux:

$$k(t) = \int_0^t \langle \nu(t') \theta_R'(x(t')) \nu_0 \theta_R'(x_0) \rangle dt' = \int_0^t j(t') dt' . \tag{48}$$

Note that Eq. (48) is equivalent to the definition of rate used by Grote and Hynes [6]. In the limit of $t \to \infty$ and by assuming a parabolic shape of the barrier, Eqs (41)–(48) reproduces the "Grote–Hynes" result [6, 7, 10, 25, 31, 33]:

$$k(\infty) = k_{\mathrm{TST}} \frac{s_r}{\omega_b} , \tag{49}$$

where s_r is a positive root of the equation

$$s(s + \bar{\eta}(s)) = \omega_b^2 , \tag{50}$$

and ω_b stands for the barrier frequency. The cusp-barrier limit can be now easily achieved by assuming $\omega_b/\omega \to \infty$. With Eq. (6), Eq. (50) yields $s_r =$

ω_b, so that the rate (48), (49) yields a trivial TST result. But the limit, we are interested in, is the overdamped dynamics in the cusp-shaped potential, which results in ignoring the inertia at the level of the GLE formulation. Elimination of inertia is possible, if $\gamma = \omega^2\tau_\infty$ (*cf.* Appendix A) whose inverse constitutes the decay times of variables $x(t)$ and $w(t)$. Effectively, that means:

$$\tau_\infty > \left(\omega^2\tau'\right)^{-1} \quad \text{or} \quad \frac{\varepsilon_\infty}{\varepsilon_0}\tau_1\tau_2\omega^2 > 1\,. \tag{51}$$

The high friction limit is thus realized when $\tau_\infty \to \infty$, which is consistent with the assumption that $\nu(t)$ will decay very rapidly to some equilibrium value ν_{eq}. Evaluation of the rate (41), (47) along the lines presented in Appendix B yields then Eq. (34) with $\tau_{\text{eff}} = \gamma/\omega^2 = \tau_\infty$. In other words, formula (34) is an asymptotic result whose validity becomes apparent in the limit of $\gamma \gg 1$. It states that the kinetic rate for the overdamped non-Markovian dynamics (9) in the cusp potential is dominated by the high frequency value of the memory kernel $\eta(t)$. In the context of the electron-transfer reaction in a model non-DEbye solvent (*cf.* Appendix B and Ref. [6, 8, 9]) it shows, that the effective longitudinal relaxation time entering formula (34) is dominated by the fastest solvent relaxation time.

A similar conclusion can be drawn from the analysis of Calef and Wolynes [14] who presented an interpolation formula for the transmission coefficient for the cusped double well potential which derived on an analogy to the parabolic barrier case. Apparent differences between the forms of $k(t)$ for a cusped barrier, as defined through formulae (33), (34) and (36) have been also discussed by Pollak [10] who by use of variational TST has shown the convergence of the formulae in the strong damping limit.

Importance of solvent dynamics effects on mediating the kinetics of electron transfer processes depends on the ratio of the relative time scales governing process of medium relaxation (expressed by nuclear modes which couple to the relevant electronic states) and the electronic electron-transfer rate (usually assumed to be a slow, rate determining process). The ratio determines adiabaticity factor [4, 6, 23] which controls the overall kinetic rate in the system. This simple rate description breaks down if the perfect time scale separation for the nuclear and electronic processes becomes questionable.

Conclusions

Markov embedding of a non-Markovian process (formally described as a procedure of "dressing" a non-Markovian process into auxiliary degrees of freedom, so that eventually, the higher-dimensional process becomes memory less) yields substantial problems of posing appropriate boundary conditions in the presence of auxiliary variables (for the discussion, see *e.g.*

[27] and references therein). Obviously, the problem cannot be avoided in a reduced description of the process, after applying a projection technique leading to a contracted evolution (our Eq. (15)). In fact, as it is discussed in the paper, the concept of the MFTP may lead then to totally misleading results. In the discussion of this issue, we have shown that also, depending on the method of elimination of auxiliary variables leading to a 1-dim Smoluchowski equation, various forms of diffusion and drift coefficients for the diffusion equation can be derived, which, in turn, lead to different long-time predictions of the system dynamics. Utility of the MFPT approach is thus highly reduced in such situations. The kinetic rate for such systems can be estimated by transforming the original non-Markov problem to its multidimensional Markov analog and by further use of a singular perturbation technique [24, 25] which allows evaluation of the mean exit time by assuming a harmonic approximation of the potential at the top of the barrier. More recently, the variational TST [10] for dissipative system governed by GLE has been derived, based on the two degree of freedom Hamiltonian whose parameters depend on the system potential and the time-dependent friction kernel. The method essentially weakens the condition of potential harmonicity used in previous derivations of the rate. To get informative bounds to the rate one has to scale the barrier frequency in terms of the barrier height by defining a variational parameter

$$\Theta \equiv (\beta \Delta U^*)^{-1} \frac{\omega_b^2}{\omega^2} \tag{52}$$

which is then used in variational minimization of the reactive flux [10]. In particular, variational evaluation of the transmission coefficient in the high damping limit leads to the result identical to the Kramers expression Eq. (33).

In this article we have rederived the kinetic rate for non-Markovian process by use of the one-dimensional time-derivative of the correlation function. The method has been shown elsewhere [30] to account both for the high and low-friction limits in the studies of the kinetic rate. The procedure requires information of equilibrium (stationary properties) of the system and, similarly to a traditional TST presents an upper bound for the rate. This approach, used for a cusped barrier potential leads to the result consistent with the Kramers limit [22] which has been postulated in a formal analysis of Hynes [6] and derived in numerical studies of Fonseca [9].

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Appendix A

The GLE for the reaction coordinate fluctuations in reactant and product wells has been discussed in the context of non-Debye solvent dynamics by Hynes (1986) [6]. It has been shown that the dielectric response function

$$E(t) = \frac{\varepsilon(t) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} \tag{A1}$$

can be related to the reaction coordinate time correlation function $\Delta(t)$ whose Laplace transform has the form

$$\overline{\Delta(s)} = \varepsilon_\infty(1 - \overline{E}(s))\{s(\varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\overline{E}(s)\}^{-1}. \tag{A2}$$

By defining a function

$$\tau_L(t) = \omega^{-2}\eta(t) \tag{A3}$$

and by assuming the overdamped limit of GLE, the following relation between the frequency-dependent memory kernel $\eta(t)$ and the dielectric response function $E(t)$ has been established:

$$\bar{\eta}(s) = \omega^2\left(\frac{\varepsilon_\infty}{\varepsilon_0 s}\right)\frac{1 - \overline{E}(s)}{\overline{E}(s)}. \tag{A4}$$

The solvent model which leads to $\eta(t)$ given by Eq. (6) assumes a two relaxation time description of the dielectric response:

$$\overline{E}(s) = \sum_{i=1,2} p_i(1 + s\tau_i)^{-1}, \tag{A5}$$

where p_i is the fractional contribution associated with the relaxation time τ_i. The coefficients α, λ, γ are then expressed as

$$\begin{aligned}
\gamma &= \omega^2\frac{\varepsilon_\infty}{\varepsilon_0}\left[\frac{p_1}{\tau_1} + \frac{p_2}{\tau_2}\right]^{-1} = \omega^2\tau_\infty \\
\lambda &= \frac{1}{\tau'} = \frac{1}{p_1\tau_2 + p_2\tau_1} \\
\alpha &= \omega^2\frac{\tau_0 - \tau_\infty}{\tau'},
\end{aligned} \tag{A6}$$

where

$$\tau_0 = \frac{\varepsilon_\infty}{\varepsilon_0}(p_1\tau_1 + p_2\tau_2). \tag{A7}$$

Appendix B

A fundamental matrix (Green function) for the system (9) can be easily calculated by use of a complete biorthogonal set for the characteristic matrix of linear coefficients (Risken, [23]):

$$A = \begin{pmatrix} 0 & 1 & 0 \\ -\omega^2 & \gamma & 1 \\ 0 & -\alpha & -\lambda \end{pmatrix}. \tag{B1}$$

Let Λ_1, Λ_2 and Λ_3 are all different eigenvalues of A. The fundamental matrix for the system (9) is

$$G_{ij} = \sum_{\alpha} \mathrm{e}^{-\Lambda_\alpha t} u_i^{(\alpha)} \nu_j^{(\alpha)}, \tag{B2}$$

with the eigenvectors u_i, ν_j which fulfill the conditions

$$\sum_{\alpha} \nu_i^\alpha u_j^\alpha = \delta_{ij}$$

$$u_i^\alpha \nu_i^\beta = \delta_{\alpha\beta}. \tag{B3}$$

Diffusion matrix for the process is

$$D = \begin{pmatrix} D_{xx} & D_{x\nu} & D_{xw} \\ D_{\nu x} & D_{\nu\nu} & D_{\nu w} \\ D_{wx} & D_{w\nu} & D_{ww} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2\gamma k_{\mathrm{B}} T & 0 \\ 0 & 0 & 2\alpha\lambda k_{\mathrm{B}} T \end{pmatrix}. \tag{B4}$$

The elements of correlation function σ_{ij} can be evaluated from the formula

$$\sigma_{ij} = 2 \sum_{\alpha,\beta} \frac{1 - \exp\left(-(\Lambda_\alpha + \Lambda_\beta)t\right)}{\Lambda_\alpha + \Lambda_\beta} D^{(\alpha\beta)} u_i^\alpha u_j^\beta,$$

$$D^{(\alpha\beta)} = \nu_k^\alpha D_{kl} \nu_l^\beta. \tag{B5}$$

Appendix C

In the limit of large friction, $\gamma \gg 1$, system (9) can be shown to be asymptotically equivalent to a Langevin equation characteristic for a Smoluchowski (nonmemory) dynamics. To analyze this limit, let us change the

time scale to $s = t/\gamma$ (*cf.* [23, 25]) which gives a result valid for short periods of time. Eq. (9) can be rewritten in the form:

$$\begin{aligned}
\dot{x}(s) &= \gamma\nu(s)\,,\\
\dot{\nu}(s) &= -\omega^2\gamma x(s) - \gamma^2\nu(s) + \gamma w(s) + \gamma^{1/2} f_\nu(s)\,,\\
\dot{w}(s) &= -\alpha\gamma\nu(s) - \lambda\gamma w(s) + \gamma^{1/2} f_w(s)\,.
\end{aligned} \tag{C1}$$

By using the method of Appendix B we can also solve the system (C1) by solving first equations for $\nu(s)$, $w(s)$ as functions of x and s and substituting the result to equation for $x(s)$:

$$\begin{aligned}
\nu = G_{\nu\nu}\nu_0 + G_{\nu w} w_0 - \gamma\omega^2 \int_0^s d\tau G_{\nu\nu}(s-\tau)x(\tau)\\
+\gamma^{1/2}\int_0^s d\tau G_{\nu\nu}(s-\tau) f_\nu(\tau) + \gamma^{1/2}\int_0^s d\tau G_{\nu\nu}(s-\tau) f_w(\tau)
\end{aligned} \tag{C2}$$

where

$$\begin{aligned}
G_{\nu\nu} &= \mathrm{e}^{-\Lambda_1 t}\frac{\Lambda_2 - \gamma^2}{\Lambda_2 - \Lambda_1} - \mathrm{e}^{-\Lambda_2 t}\frac{\Lambda_1 - \gamma^2}{\Lambda_2 - \Lambda_1}\,,\\
G_{\nu w} &= \frac{\gamma\left(\mathrm{e}^{-\Lambda_1 t} - \mathrm{e}^{-\Lambda_2 t}\right)}{\Lambda_2 - \Lambda_1}\,,\\
\Lambda_i^2 &+ \Lambda_i(\gamma^2 + \lambda\gamma) + \alpha\gamma^2 + \lambda\gamma^3 = 0\,.
\end{aligned} \tag{C3}$$

The random forces $f_\nu(t)$, $f_w(t)$ enter Eq. (9) with relative "noise intensities" $\sqrt{2}\gamma k_{\mathrm{B}}T$, $\sqrt{2}\alpha\lambda k_{\mathrm{B}}T$, respectively (*cf.* Eq. (11)). In the limit of $\gamma \to \infty$, one gets:

$$\begin{aligned}
&\lim_{\gamma\to\infty} G_{\nu\nu}(s) = \lim_{\gamma\to\infty} G_{\nu\nu}(s) = 0\\
&\lim_{\gamma\to\infty} \gamma^2 G_{\nu\nu}(s-s') = \delta(s-s')\,,\\
&\lim_{\gamma\to\infty} \gamma^{3/2} G_{\nu w}(s-s') = 0\,.
\end{aligned} \tag{C4}$$

So that the limiting equation for the process $x(s)$ becomes

$$\begin{aligned}
\dot{x}(s) &= -\omega^2 x(s) + \sqrt{2k_{\mathrm{B}}T}\,\tilde{f}_\nu(s)\,,\\
\sqrt{2k\mathrm{B}T}\,\tilde{f}_\nu(s) &= f_\nu(s)\,,
\end{aligned} \tag{C5}$$

which is the Langevin equation for the nonmemory Smoluchowski problem. With the assumption of a cusp-barrier, (B5) leads to the Kramers rate Eq. (33).

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