Quantum Brownian Motion With Large Friction

Joachim Ankerhold\textsuperscript{1,2}, Hermann Grabert\textsuperscript{1} and Philip Pechukas\textsuperscript{3}

\textsuperscript{1} Physikalisches Institut, Albert-Ludwigs-Universität, 79104 Freiburg, Germany
\textsuperscript{2} Service de Physique de l’Etat Condensé, Centre d’Etudes de Saclay, 91191 Gif-sur-Yvette, France
\textsuperscript{3} Department of Chemistry, Columbia University, New York, New York 10027, USA

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Abstract

Quantum Brownian motion in the strong friction limit is studied based on the exact path integral formulation of dissipative systems. In this limit the time-nonlocal reduced dynamics can be cast into an effective equation of motion, the quantum Smoluchowski equation. For strongly condensed phase environments it plays a similar role as master equations in the weak coupling range. Applications for chemical, mesoscopic, and soft matter systems are discussed and reveal the substantial role of quantum fluctuations.

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Quantum Brownian motion is much more involved than its classical analog since in general tractable equations of motion do not exist. Progress has been made in the weak friction regime leading to a variety of master equations. Here, we analyze the opposite domain of very strong friction and reveal that a generalization of the classical Smoluchowski equation, the quantum Smoluchowski equation, can be derived from first principles. This opens the door to study the dynamics of strongly condensed phase systems at lower temperatures. In particular, quantum fluctuations turn out to play a substantial role as shown explicitly for three examples from chemical reactions, mesoscopic physics, and charge transfer in molecules.

I. INTRODUCTION

Brownian motion, that is the fate of a heavy particle immersed in a fluid of lighter particles, is the prototype of a dissipative system coupled to a thermal bath with infinitely many degrees of freedom. The work by Einstein in 1905 [1] has developed a mathematical language to describe the random motion of the particle and has uncovered the fundamental relation between friction, diffusion and the temperature $T$ of the bath. Half a century later, this seed had grown into the theory of irreversible thermodynamics [2], which governs the relaxation and fluctuations of classical systems near equilibrium. At that time, a new challenge had emerged, the quantum mechanical description of dissipative systems.

In contrast to classical Brownian motion, where right from the beginning the work by Einstein and Smoluchowski [1, 3] had allowed to consider both weak and strong friction, for a long time, the quantum mechanical theory could handle the limit of weak dissipation only. In this case the interaction between the “particle” and the “bath” can be treated perturbatively and one can derive a master equation for the reduced density matrix of the “particle” [4]. This approach, based on the so-called Born and Markov approximations, has been very successful in quite a number of fields emerging in the fifties and sixties of the last century, such as nuclear magnetic resonance [5, 6] and quantum optics [7].

Roughly, a dissipative quantum system can be characterized by three typical energy scales, an excitation energy $\hbar \omega_0$, where $\omega_0$ is a characteristic frequency of the system, a coupling energy $\hbar \gamma$ to the bath, where $\gamma$ is a typical damping constant, and the thermal energy $k_B T$. The weak coupling master equation is limited to the region $\hbar \gamma \ll \hbar \omega_0, k_B T$. This is the case whenever the typical linewidth caused by environmental interactions is small
compared to the line separation and the thermal “Matsubara” frequency $2\pi k_B T/h$. On the other hand, the approach will fail for strong damping and/or low temperatures.

The work by Feynman and Vernon \[8\] has shown how to take advantage of the path integral representation of quantum mechanics to derive an expression for the reduced density matrix of the “particle” as a sum over forward and backward paths, which is valid for arbitrary damping strength and temperature. These two sets of paths arise from the two time evolution operators in the formal expression for the time–dependent density matrix $W(t) = \exp[-(i/\hbar)Ht] W(0) \exp[(i/\hbar)Ht]$, where $H$ is the Hamiltonian of the system. In the path integral representation of the reduced density matrix the influence of the bath emerges as time–nonlocal terms in the action governing the path probability. These terms include also a coupling between the forward and backward paths and make it difficult to evaluate the path integral explicitly, although progress can be made in some cases \[9, 10\].

Everything becomes simpler in the limits of weak and strong damping. While the former case leads to the master equation approach mentioned above, the latter case is usually referred to as the Smoluchowski limit. In the classical case this limit is well understood and simplifies matter considerably, since the momentum $P$ of a heavily damped particle with position $Q$ is a slow variable that can be eliminated adiabatically. It is intuitively clear, that a quantum mechanical theory cannot entirely dispose of the variable $P$ conjugate to $Q$. In fact, for a classical system with characteristic frequency $\omega_0$ the roots $\lambda_\pm = \pm i\omega_0$ of the characteristic equation in the undamped case are in the presence of damping turned into

$$\lambda_\pm = -\frac{\gamma}{2} \pm \sqrt{\frac{\gamma^2}{4} - \omega_0^2}.$$  

For large friction, $\gamma \gg \omega_0$, this can be approximated by

$$\lambda_\pm = \begin{cases} -\frac{\omega_0^2}{\gamma} \\ -\gamma + \frac{\omega_0^2}{\gamma} \end{cases}.$$  

While in the strong friction limit the slow classical dynamics is governed by the small root $\omega_0^2/\gamma$, quantum mechanics accompanies reduced fluctuation of $Q$ with enlarged fluctuations of the conjugate variable $P$. Both roots $\lambda_\pm$ are essential to determine the fluctuation spectrum. That is why quantum effects are not restricted to the temperature range $k_B T \leq \hbar \omega_0^2/\gamma$, rather, in quantities sensitive to fluctuations, quantum effect can manifest themselves in the strong friction limit even up to higher temperatures than in the weak damping limit. This makes the quantum Smoluchowski limit addressed in this article non-trivial.
The paper is organized as follows. In the next section II we shortly review the formulation of dissipation within the path integral formalism and sketch the derivation of the Quantum Smoluchowski Equation (QSE) \[11\]. The second part (Sec. III) is devoted to three specific applications.

II. THE QUANTUM SMOLUCHOWSKI EQUATION

A. Reduced dynamics

As already pointed out in the Introduction the inclusion of quantum dissipation in a non-perturbative way has been established only since the early 80s. The standard approach \[12\] starts from a system+reservoir model

\[ H = H_S + H_R + H_I \] (1)

with a system part \( H_S \), an environmental part \( H_R \), and a system-bath interaction \( H_I \). The reservoir (heat bath) is mimicked by a quasi-continuum of harmonic oscillators bilinearly coupled to the system. Dissipation appears when one considers the reduced dynamics by properly eliminating the bath degrees of freedom. In fact, one this way regains in the classical limit a generalized Langevin equation. It is thus important to realize that the only restriction associated with the oscillator bath is the Gaussian stochastic nature of the environment, which in turn means that the relevant impact of the bath onto the system dynamics is completely determined by the average and the autocorrelation function of the bath force.

The quantum dynamics of the reduced system follows from

\[ \rho(t) = \text{Tr}_R \{ \exp(-iHt/\hbar) \, W(0) \, \exp(iHt/\hbar) \} \] (2)

where \( W(0) \) describes the initial state of the total system. In the ordinary Feynman-Vernon theory \[8\] this state is assumed to be a factorizing state, \( W(0) = \rho_S(0) \, \exp(-\beta H_R)/Z_R \) \( (Z_R \) is the bath partition function and \( \beta = 1/k_B T \)), so that each one, system and equilibrated bath, lives in splendid isolation at \( t = 0 \). While this assumption may be justified in the weak damping/high temperature limit, it certainly fails for moderate to strong friction and/or lower temperatures. It can be shown explicitly that in the classical limit even the Langevin equation is not regained, but differs by initial boundary terms that may persist up to long times. In the strong damping realm considered here, the initial state must be correlated
where the propagating function $J$ at $t = 0$ contains harmonic degrees of freedom only, it can be integrated out exactly and one arrives within the position representation by employing the path integral formalism. Since the bath (which may be very complicated), but rather chooses the preparation function properly. For a specific initial state, one does not need to know the specific form of these operators (which may be very complicated), but rather chooses the preparation function properly.

The reduced quantum dynamics (2) starting with an initial state (3) is now obtained within the position representation by employing the path integral formalism. Since the bath contains harmonic degrees of freedom only, it can be integrated out exactly and one arrives at

$$\rho(q_f, q'_f, t) = \int dq_i dq'_i J(q_f, q'_f, t, q_i, q'_i) \lambda(q_i, q'_i)$$

(4)

where the propagating function $J(\cdot)$ is a threefold path integral—two in real time, one in imaginary time—over the system degree of freedom only

$$J(q_f, q'_f, t, q_i, q'_i) = \frac{1}{Z} \int \mathcal{D}[q] \mathcal{D}[q'] \mathcal{D}[\bar{q}] \exp[q \mathcal{L} - S_S[q] - S_S[q'] + i S'[\bar{q}] + i \phi[q, q', \bar{q}]]$$

(5)

with $Z = \text{Tr}\{\exp(-\beta H)\}/Z_R$. The two real time paths $q(s)$ and $q'(s)$ connect in time $t$ the initial points $q_i$ and $q'_i$ with fixed end points $q_f$ and $q'_f$, while the imaginary time path $\bar{q}(\sigma)$ runs from $q_i$ to $q'_i$ in the interval $\hbar \beta$. The contribution of each path is weighted with an effective action $\Sigma[q, q', \bar{q}] = S_S[q] - S_S[q'] + i S'[\bar{q}] + i \phi[q, q', \bar{q}]$ which consists of the actions of the bare system in real and imaginary time, respectively, and an additional interaction contribution (influence functional) non-local in time. The latter one can be written as

$$\phi[\bar{q}] = \int dz \int_{z' \geq z} dz' \bar{q}(z) K(z - z') \bar{q}(z') + i \mu \int dz \bar{q}(z)^2$$

(6)

where the ordered time integration is understood along the contour: $z = s$ from $t \to 0$, $z = -i\tau$ from $0 \to \hbar \beta$, $z = -i\hbar \beta + s$ from $0 \to t$ with

$$\bar{q}(z) = \begin{cases} q'(s) & \text{for } z = s, \ 0 \leq s \leq t \\ \bar{q}(\tau) & \text{for } z = -i\tau, \ 0 \leq \tau \leq \hbar \beta \\ q(s) & \text{for } z = -i\hbar \beta + s, \ 0 \leq s \leq t \end{cases}$$

(7)
The effective impact of the bath is completely controlled by the damping kernel
\[ K(z) = \int_0^\infty \frac{d\omega}{\pi} I(\omega) \frac{\cosh[\omega(\hbar\beta - iz)]}{\sinh(\omega\hbar\beta/2)} \]  
(8)
where \( I(\omega) \) denotes the spectral density of the environment. As expected \( \hbar K(z) \) coincides with the autocorrelation function of the bath force. In particular, for real times the kernel \( K(s) = K'(s) + iK''(s) \) is related to the macroscopic damping kernel entering the classical generalized Langevin equation
\[ \gamma(s) = \frac{2}{M} \int_0^\infty \frac{d\omega}{\pi} \frac{I(\omega)}{\omega} \cos(\omega s) \]  
(9)
via \( K''(s) = (M/2)d\gamma(s)/ds \) and \( K'(s) \to M\gamma(s)/\hbar\beta \) in the classical limit (\( M \) is the mass of the Brownian particle). The term with \( \mu = \lim_{\hbar\beta \to 0}\hbar\beta K(0) \) in (6) gives a potential renormalization due to shifts of the minima of the bath oscillators by the coupling to the system.

B. Quantum Smoluchowski range and thermal equilibrium

The classical Smoluchowski limit is related to a separation of time scales between fast equilibration of momentum and slow equilibration of position. In this way, the Fokker-Planck equation for the phase space distribution can be adiabatically reduced to a Smoluchowski equation for the marginal distribution in position space [13]. For quantum dissipative systems the expectation is that friction makes the system to behave more classically so that for strong friction the complicated path integral expression [4] simplifies considerably. This is indeed the case as we have shown recently [11]. In the sequel we will briefly collect the main findings and, to keep things as transparent as possible, consider a one-dimensional system only moving in a sufficiently smooth potential field \( V(q) \).

A typical damping strength in the long time limit is defined as
\[ \gamma \equiv \hat{\gamma}(0) = \lim_{\omega \to 0} \frac{I(\omega)}{M\omega} \]  
(10)
where \( \hat{\gamma}(\omega) \) is the Laplace transform of the classical damping kernel \( \gamma(s) \). For ohmic friction, \( I(\omega) = M\tilde{\gamma}\omega \), for instance, one finds \( \gamma = \tilde{\gamma} \). The same is true for the more realistic Drude damping \( I(\omega) = M\tilde{\gamma}\omega\omega_c^2/(\omega^2 + \omega_c^2) \) with cut-off frequency \( \omega_c \). Now, given a typical frequency \( \omega_0 \) of the bare system (e.g. its ground state frequency) by strong damping we then mean (cf. fig. 1)
\[ \frac{\gamma}{\omega_0^2} \gg \frac{\hbar\beta}{2\pi}, \frac{1}{\omega_c}, \frac{1}{\gamma} \]  
(11)
FIG. 1: Quantum Smoluchowski range according to (11) (shaded). The classical range $\gamma \hbar \beta < 1$ is simple shaded, the quantum range $\gamma \hbar \beta > 1$ double shaded.

Hence, we extend the time scale separation known from the classical Smoluchowski range to incorporate the time scale for quantum fluctuations $\hbar \beta$. As we will see, this does not mean, however, that quantum effects are negligible at all, since they are related to Matsubara frequencies $\nu_n = 2\pi n / \hbar \beta, n = 1, 2, 3, \ldots$ which can be arbitrarily large.

The idea is now, to evaluate for strong friction $\gamma / \omega_0 \gg 1$ the path integral expression (6) on a coarse-grained time scale $s \gg \hbar \beta, 1/\omega_c, 1/\gamma$ and $\tau \gg 1/\omega_c, 1/\gamma$. The consequences are the following: (i) Non-diagonal elements of the reduced density matrix are strongly suppressed during the time evolution, (ii) the real time part of the kernel $K(s)$ becomes local on the coarse grained time scale, and (iii) initial correlations described by (3) survive for times of order $\gamma / \omega_0^2$ verifying that factorizing initial states cannot be used.

In a first step, this program is applied to calculate the thermal (unnormalized) equilibrium density matrix

$$\rho_\beta(\bar{q}, \bar{q}') = \int \mathcal{D}[\bar{q}] \, e^{\hat{\Sigma}[\bar{q}] / \hbar}$$

with $\hat{\Sigma}[\bar{q}] = \Sigma[0, 0, \bar{q}]$. Due to (i) the strategy is to invoke a semiclassical type of approximation by assuming self-consistently that $|\bar{q}(\tau) - \bar{q}(0)|$ remains small on the time interval $\hbar \beta$. In function space the path integral is then dominated by the contributions of the minimal action paths and Gaussian fluctuations around them. The former ones are determined perturbatively up to corrections of order $1/\gamma$ and its corresponding minimal action—conveniently expressed in terms of the sum $\bar{r} = (\bar{q} + \bar{q}')/2$ and difference coordinate $\bar{x} = \bar{q} - \bar{q}'$—follows as

$$\frac{-i}{\hbar} \hat{\Sigma}(\bar{r}, \bar{r}) = \beta V(\bar{r}) - \Lambda \beta^2 V'(\bar{r})^2 + \frac{\Omega}{2\hbar^2} \bar{x}^2 + O \left( \frac{\Lambda}{\gamma} \right)$$

(13)
with

\[
\Lambda = \frac{2}{M\beta} \sum_{n=1}^{\infty} \frac{1}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n)},
\]

\[
\Omega = \frac{M}{\beta} + \frac{2M}{\beta} \sum_{n=1}^{\infty} \frac{\hat{\gamma}(\nu_n)}{\nu_n + \hat{\gamma}(\nu_n)}.
\]

(14)

Note that in \( \Lambda \) the quadratic dependence on \( \nu_n \) originating from the inertia part in the equation of motion and in \( \Omega \) the cut-off frequency \( \omega_c \) appearing in \( \hat{\gamma}(\omega) \) are essential for the convergence of the corresponding sums. This reveals a fundamental difference to the classical Smoluchowski limit and indicates the importance of quantum fluctuations even for strong friction. From the above, one observes that \( \Lambda \) measures the typical strength of quantum fluctuations in position and \( \Omega \) is related (via the identification \( \hbar / \Delta x \rightarrow \Delta p \)) with the equilibrium variance in momentum \( \Omega = \langle p^2 \rangle \). Before we discuss further details, let us arrive at the complete expression of the thermal equilibrium density matrix. The remaining Gaussian fluctuations around the minimal action paths are treated by switching to Matsubara frequency space. Correspondingly, a straightforward calculation provides together with (13)

\[
\rho_\beta(\bar{x}, \bar{r}) = \frac{1}{Z} e^{-\beta V(\bar{r}) - \Omega \bar{x}^2 / 2\hbar^2} e^{\Lambda \beta [V'(\bar{r})^2 / 2 - 3V''(\bar{r}) / 2]} \]

(15)

where \( Z \) denotes a proper normalization factor, e.g. \( Z = \int dq \rho_\beta(0, q) \). This is the first important result of the strong friction analysis: The equilibrium distribution of a strongly damped quantum system in arbitrary (sufficiently smooth) potentials. In particular, for a harmonic oscillator the known result is recovered [12]. To be specific we consider Drude damping \( \hat{\gamma}(z) = \gamma \omega_c / (\omega_c + z) \) with a high frequency cut-off \( \omega_c \gg \gamma \). Then, the functions \( \Lambda \) and \( \Omega \) can be expressed in terms of \( \Psi \) functions

\[
\Omega \approx \frac{M\hbar\gamma}{\pi} \left[ \Psi \left( \frac{\omega_c}{\nu} \right) - \Psi \left( \frac{\gamma + \nu^2 \omega_c}{2\gamma} \right) - \frac{\nu}{2\gamma} + \frac{2\nu}{\omega_c} \right]
\]

\[
\Lambda \approx \frac{\hbar}{M\gamma\pi} \left[ \Psi \left( \frac{\gamma}{\nu} \right) - C + \frac{\nu}{\gamma} \right]
\]

(16)

where \( C = 0.577\ldots \) is Euler’s constant. In the high temperature limit \( \gamma \hbar \beta \ll 1 \), one finds \( \Lambda \approx \hbar^2 \beta / 12M \) and \( \Omega \approx M / \beta \) so that the Wigner transform of (15) reduces to the classical phase space distribution. The dependence on friction appears for lower temperatures as a genuine quantum effect. Of particular interest is the limit \( \gamma \hbar \beta \gg 1 \) where we have \( \Lambda \approx (\hbar / M\gamma\pi) \log(\gamma \hbar \beta / 2\pi) \) and \( \Omega \approx (M\hbar\gamma / \pi) \log(\omega_c / \gamma) \). Quantum fluctuations in position are suppressed by friction, not algebraically though, but much weaker. They also show a nonlinear dependence on \( \hbar \) meaning that for \( \gamma \hbar \beta \gg 1 \) we work nevertheless in a deep
quantum domain. The same can be seen from the momentum variance which grows with friction to guarantee Heisenberg’s uncertainty relation. Accordingly, as assumed above, off-diagonal elements of the distribution $\rho_\beta(\bar{q}, \bar{q}')$ are strongly suppressed with $|\bar{x}|$ being of order $1/\sqrt{\gamma \log(\omega_c/\gamma)}$ or smaller. Concluding this section, we mention that higher order corrections in $\Lambda$ are associated with higher than second order derivatives of the potential $V(q)$.

**C. Quantum Smoluchowski equation**

The analysis of the previous section already indicated the strong suppression of off-diagonal elements of the density distribution in thermal equilibrium. While in principle we could now proceed to study the reduced dynamics in real time for the total distribution $\rho(q_f, q_f', t)$ [14], we concentrate in the sequel on the quantum analog of the classical Smoluchowski limit and thus restrict ourselves to the time evolution of its diagonal part, the position distribution $P(q_f, t) = \rho(q_f, q_f, t)$ [11]. In fact, one can show that off-diagonal elements relax to thermal equilibrium with respect to the instantaneous position of the Brownian particle on a time scale of order $1/\gamma$ [15]. For this purpose it is convenient to introduce sum and difference paths also in real time

$$r(s) = [q(s) + q'(s)]/2, \quad x(s) = q(s) - q'(s)$$

(17)

with corresponding fixed end-coordinates $r_f = r(t) = q_f, x_f = x(t) = 0$ and initial coordinates $r_i = r(0), x_i = x(0)$ distributed according to the initial state [3]. Already the classical Smoluchowski limit reduces the set of acceptable initial states to those with momenta sufficiently bounded from above. In the quantum domain, the detailed analysis reveals that the $x_i$-dependence of the preparation function $\lambda(x_i, r_i)$ must be sufficiently smooth within the range $|x_i/\sqrt{\hbar/M\gamma}| \lesssim \sqrt{\hbar/(\gamma/\omega_0^2)}$ such that we may put $\lambda(x_i, r_i) \approx \lambda(0, r_i)$.

Now, let us first look at the leading order contribution where quantum fluctuations in position are neglected, i.e. $\Lambda = 0$. This is expected to lead us back to the classical Smoluchowski equation, for $\gamma \hbar \beta \gg 1$ though, i.e. far from the classical limit $\gamma \hbar \beta \ll 1$. As above, we assume excursions from diagonality, encoded in the $x$-paths, to be small, roughly at most of order $1/\sqrt{\gamma}$. By expanding the effective action $\Sigma[\bar{q}, x, r]$ up to second order in $x$ we arrive at a solvable Gaussian path integral for the $x$-paths. We put $x(s) = x_i + \delta x(s)$ with deviations $\delta x(0) = \delta x(t) = 0$ and obtain to leading order

$$\int \mathcal{D}[x] \, e^{i(\Sigma[\bar{q}, x, r] - \Sigma[\bar{q}, 0, 0])/\hbar} \approx \delta(x_i) \, e^{-S[r]/4M\gamma k_B T}$$

(18)
with the action
\[ S[r] = \int_0^t ds \left[ M\gamma \dot{r} + V'(r) \right]^2. \] (19)

Thus, the imaginary time path contribution follows from the leading order expression of \([13]\) for \(\bar{x} = x_i = 0, r_i = \bar{r}\). One is left with the \(r\)-path integral which, written in form of a propagator, appears as
\[ P(q_f, t) = \int dq_i G(q_f, t, q_i) P(q_i, 0) \] (20)

where in \(G(\cdot)\) the paths \(r(s)\) run from \(r(0) = q_i\) to \(r(t) = q_f\), each one weighted with the exponential on the right hand side of \([13]\). One this way ends up with the path integral representation of the classical Smoluchowski dynamics where \(P(q, t)\) obeys
\[ \frac{\partial P(q, t)}{\partial t} = \frac{1}{M\gamma} \frac{\partial}{\partial q} L_{cl} P(q, t) \] (21)
with the classical Smoluchowski operator \(L_{cl} = V' + k_B T \partial_q\). Indeed, from this derivation one finds \(x(s)^2\) to be at most of order \(\bar{\hbar}^2/\beta/M\gamma t\).

To include quantum fluctuations to lowest order in \(\Lambda\), we could proceed to directly calculate corrections to the propagator as in \([11]\), which is rather involved, however. Here, we follow a somewhat simpler route and first exploit that the flux vanishes in thermal equilibrium. Accordingly, one writes \(\partial_t P = (1/\gamma M)\partial_q (1 + \delta f) L_{qm} P\) with a dynamical correction \(\delta f\), and an operator \(\tilde{L}_{qm}\) determined perturbatively up to order \(\Lambda\) by \(\tilde{L}_{qm}\rho_\beta = O(\Lambda^2)\) with the equilibrium density specified in \([13]\). The latter one already contains the dominant part of the quantum fluctuations in the QSE (see below). To verify that \(\delta f\) can be disregarded, it suffices to study the path integral dynamics in the time range \(\hbar \beta, 1/\gamma, 1/\omega_c \ll t \ll \gamma/\omega_c^2\) where it becomes effectively Markovian. Then, along the lines described above a semiclassical approximation applies and leads to a propagator including \(\Lambda\) dependent corrections. From this, one finds \(\delta f \propto O(\Lambda/\gamma^2)\) and thus to be negligible. As the result, the equation for \(P(q, t)\) is of the form of the classical Smoluchowski equation \([21]\) but with \(L_{cl}\) replaced by \(\tilde{L}_{qm}\), i.e.,
\[ \tilde{L}_{qm} = U_{eff}'(q) + k_B T \partial_q \tilde{D}(q) \] (22)

where we introduced an effective force field and a diffusion coefficient, respectively,
\[ U_{eff}(q) = V'(q) + \frac{\Lambda}{2} V''(q), \quad \tilde{D}(q) = 1 + \Lambda \beta V''(q). \] (23)

The expressions \([22]\) and \([23]\) determine the dynamics of overdamped quantum systems at lower temperatures. The corresponding quantum Smoluchowski equation has still one deficiency though, which is directly related to the fact that it has been derived perturbatively.
Namely, it conserves thermodynamic symmetries, as e.g. vanishing stationary currents in thermal equilibrium, only to order \( \Lambda \) meaning that in a direct numerical integration higher order terms may give rise to unphysical results. The most obvious way to see this, is to consider the stationary current 

\[
J_{\text{st}} = \lim_{t \to \infty} \langle \dot{q} \rangle / a
\]

in a periodic, asymmetric potential 

\[
V(q + a) = V(q), \quad V(q) \neq V(-q)
\]

with no external bias (ratchet potential) \[16\]. It is determined from the stationary distribution \( P_{\text{st}} \) via

\[
L_{\text{qm}} q m P_{\text{st}} = -\gamma M J_{\text{st}}
\]

as

\[
J_{\text{st}} = \frac{1 - e^{-\beta \tilde{\psi}(a)}}{\gamma M \beta} \left[ \int_0^a dq \frac{e^{-\beta \tilde{\psi}(q)}}{D(q)} \int_q^{q+a} dy e^{\beta \tilde{\psi}(y)} \right]^{-1}.
\]  

(24)

where \( \tilde{\psi}(q) = \int_0^q dy U'_\text{eff}(y)/\tilde{D}(y) \). Apparently, the diffusion coefficient in (23) leads to \( \tilde{\psi}(a) = O(\Lambda^2) \) and thus to \( J_{\text{st}} \neq 0 \). The strategy to cure this problem is to look for a ”uniformization” of the operator \( \tilde{L}_{\text{qm}} \) by finding a proper diffusion coefficient \( D(q) \) which coincides with \( \tilde{D} \) in order \( \Lambda \), leads to the equilibrium distribution (15), and, of course, respects \( J_{\text{st}} = 0 \) in thermal equilibrium. The only functional form consistent with these constraints brings us to

\[
D(q) = 1/\left[1 - \Lambda \beta V''(q)\right].
\]  

(25)

We note that \( D \) can be seen as a Padé approximant to a series in \( |\Lambda \beta V'| < 1 \) starting with the terms included in \( \tilde{D} \). The corresponding expression (24) for the stationary current is now given by the potential \( \tilde{\psi}(q) = \psi(q) - \psi(0) \) with

\[
\psi(q) = U_{\text{eff}}(q) - \frac{\beta \Lambda}{2} \left[V'(q)^2 + (\Lambda/2)V''(q)^2\right],
\]  

(26)

which obeys full periodicity in agreement with the correct symmetry \( J_{\text{st}} = 0 \). Further, \( P_\beta(q) \propto \exp[-\beta \psi(q)]/D(q) \) coincides with \( \rho_\beta(0,q) \) \[15\] up to corrections of order \( \Lambda^2 \) in the exponential which is consistent with our perturbation theory.

Eventually, we arrive at the quantum generalization of the classical Smoluchowski equation, the so-called quantum Smoluchowski Equation (QSE),

\[
\frac{\partial P(q,t)}{\partial t} = \frac{1}{\gamma M} \frac{\partial}{\partial q} \left[ U_{\text{eff}}(q) + k_B T \frac{\partial}{\partial q} D(q) \right] P(q,t)
\]  

(27)

with \( U_{\text{eff}} \) specified in (23) and \( D \) in (25). The quantum analog to the classical Langevin equation in the strong damping limit follows (in the Ito sense) as

\[
M \gamma \dot{q} + U'_{\text{eff}}(q) = \xi(t) \sqrt{D(q)}
\]  

(28)

with Gaussian white noise \( \langle \xi(t) \rangle = 0, \langle \xi(t) \xi(t') \rangle = 2M \gamma k_B T \delta(t-t') \). Eqs. (27) and (28) are the main results of this study. They describe the reduced dynamics of an overdamped
quantum system from high down to very low temperatures and show that the corresponding quantum stochastic process is equivalent to a classical process in an effective potential and with multiplicative noise.

III. APPLICATIONS OF THE QUANTUM SMOLUCHOWSKI EQUATION

The QSE plays in the strong friction limit a similar role as the quantum master equations in the weak damping limit, since it allows for explicit results in strongly condensed phase systems. Three examples from chemistry, mesoscopic physics, and soft matter will be presented in this second part.

A. Escape from a Metastable Well

The problem of escape from a metastable well can be found in a variety of realizations including chemical reactions, diffusion in solids, or nuclear fission processes, to name but a few (see also the contribution by Hänggi and Ingold [17]). Its particular feature is a separation of time scales between local well motion and long time decay characterized by a decay rate. Classically, a first thorough analysis has been performed in a seminal work by Kramers [18] with substantial extensions since then [19]. For quantum mechanical systems a large amount of research has been done in the 1980s in the context of macroscopic quantum tunneling and the field has gained renewed interest recently due to its importance for solid-state based implementations of qubits. Here, we look at the problem at strong friction and low temperatures.

The archetypical situation is the following: In a metastable potential $V(q)$ a barrier with height $V_b \gg k_B T, \hbar \omega_0$ separates a well region (well frequency $\omega_0$) from a continuum. Initially particles stay in local thermal equilibrium inside the well. As time elapses, particles surmount the barrier and for intermediate times (plateau range) their position distribution becomes quasi-stationary $P(q,t) \to P_{st}(q)$ describing a constant flux across the barrier

$$J_{st} = -\frac{1}{\gamma M} L_{qm} P_{st}.$$  

The decay rate follows from

$$\Gamma = \frac{J_{st}}{Z_{\text{well}}}$$

with the well population $Z_{\text{well}}$. For strong friction the changeover from quasi-equilibrium in the well around $q = 0$ and nonequilibrium on the other side of the barrier is restricted to
the vicinity of the barrier top located at \( q_b > 0 \). Hence, the stationary distribution takes the form \( P_{\text{st}}(q) = P_{\beta}(q) g_{\text{st}}(q) \) with a form factor obeying \( g_{\text{st}}(q) \rightarrow 1 \) in a close range to the left of \( q_b \) and \( g_{\text{st}}(q) \rightarrow 0 \) in a close range to the right of \( q_b \). In fact, from (29) a direct integration yields

\[
P_{\text{st}}(q) = \frac{M\gamma\beta J_{\text{st}}}{D(q)} e^{-\beta \psi(q)} \int_q^\infty dy e^{\beta \psi(y)}
\]

with \( \psi \) specified in (26). We note in passing that this distribution is identical to that obtained from real-time calculations [19]. Now, inserting \( Z_{\text{well}} = \int_{-\infty}^{q_b} dq P_{\text{st}}(q) \) into (30) and by invoking a harmonic approximation around the well minimum and the barrier top according to the above discussion, we obtain the rate in the quantum Smoluchowski range as

\[
\Gamma_{\text{QSR}} = \frac{\sqrt{V''(0)||V''(q_b)||}}{2\pi M\gamma} e^{-\beta V_b} e^{\beta \Lambda(V''(0) + |V''(q_b)|)}.
\]

In this expression the second exponential accounts for quantum fluctuations, while the first factors coincide with the overdamped Kramers rate. Note that \( \Lambda \) dependent terms enter exponentially and thus substantially enhance the quantum rate compared to the classical one (see fig. 2). Particularly in the high temperature domain the rate enhancement is damping independent and takes the form already derived by Wigner [12]. In the low temperature domain, however, a complicated dependence on damping appears associated with a strong increase of the rate compared to its classical value. A quantum rate expression that becomes exact in the semiclassical limit of a high barrier has been derived in [20]. For strong friction this formula reduces to (32) and already for moderate friction agrees well with the QSE-
result, fig. 2. Remarkably, the rate enhancement is observable already at relatively high temperatures $\sqrt{V''(0)/Mh}\beta < 1$ provided damping is sufficiently strong to guarantee $\gamma h\beta \gg 1$.

B. Phase Diffusion and Charging Effects in Josephson Junctions

Since the discovery of the Josephson effect, devices based on Josephson junctions (JJ) have revealed an extraordinary wealth of phenomena studied theoretically and experimentally as well [21, 22, 23]. Recent realizations of the underlying system, two superconducting domains separated by a tunnel barrier, comprise superconducting atomic contacts [24] and solid-state based quantum bits [25]. In essence, two parameters determine the dynamics, namely, the coupling energy of the adjacent domains (Josephson energy) $E_J$ and the charging energy of the contact $E_c = 2e^2/C$ of a junction with capacitance $C$. It turns out that the competition between these two scales is crucially influenced by the electromagnetic environment surrounding the junction, i.e. its impedance which in the simplest case is given by an ohmic resistor with resistance $R$.

In the context considered here, a particular feature of a JJ is the fact that its dynamics can be visualized as a diffusive motion of a fictitious particle (RSJ model) [21]. This mapping is due to the famous Josephson relations

$$I_S = I_c \sin(\phi), \quad \dot{\phi}(t) = \frac{2e}{\hbar} V(t)$$

with $I_c = (2e/\hbar)E_J$, the difference between left and right superconducting phases $\phi$, and where the phase velocity is related to the voltage drop $V(t)$ across the junction. Charge transfer captured by these relations corresponds to a phase coherent Cooper-pair current. With the translation rules to the mechanical analog

$$M = \left(\frac{\hbar}{2e}\right)^2 C, \quad \gamma = \frac{1}{RC}$$

the diffusive dynamics of the phase is determined by a generalized Langevin equation. The case of very small capacitance corresponds to very strong friction so that for a current biased JJ the classical time evolution reads

$$M\gamma\dot{\phi} + dU(\phi)/d\phi = \xi(t)$$

with the Josephson potential $U(\phi) = -E_J \cos(\phi) - E_I \phi$ where the energy $E_I$ is related to the bias current $(\hbar/2e)I$, and current noise $\langle \xi(t) \rangle = 0, \langle \xi(t)\xi(t') \rangle = (2\gamma/\beta)\delta(t-t')$. 
This classical Smoluchowski dynamics has been studied in detail already in the 60s [26, 27]. The QSE developed above, provides a generalization of this description to lower temperatures where charging effects enter the game [28]. In fact, it has been shown in the context of single charge tunneling that for sufficiently low temperatures these lead to Coulomb blockade associated with incoherent transfer of Cooper pairs through the junction [29].

We start by translating the constraints for the QSE dynamics to the case of JJs. Here, in addition to the relation (11) we also have to take into account that typically the junction is subject to an external voltage (or a corresponding current). Accordingly, in order for the momentum $M \dot{\phi}$ to relax within the $RC = 1/\gamma$—time to a Boltzmann-like distribution around $\langle \dot{\phi} \rangle$, the external voltage $V$ is restricted by $eV \ll \bar{\hbar} \gamma$. By combining $\gamma^2/\omega_0^2 \gg 1$, $\gamma\bar{\hbar} \beta$, where $\omega_0 = \sqrt{2E_cE_J}/\hbar$ is the plasma frequency of the unbiased JJ, with this latter condition and expressing them in junction parameters we expect the QSE to capture quantum phase diffusion in JJ if

$$\frac{E_c}{E_J 2\pi^2 \rho^2} \gg 1, \quad \frac{\beta E_c}{2\pi^2 \rho}, \quad \frac{V}{RI_c}.$$  \hspace{1cm} (36)

In the above, $\rho = R/R_Q$ with the resistance quantum $R_Q = \hbar/4e^2$. Since typically $\rho \ll 1$ the above condition allows for a broad range of values for $E_c/E_J$, $\beta E_J$, and also large voltages $V/RI_c$. We note in passing that the above relation also ensures that the actual non-ohmic impedance seen by the junction can effectively be treated as ohmic.

Now, with the Josephson relations [33] the effective potential and the corresponding diffusion constant entering the QSE (27) are found as

$$U_{\text{eff}}(\phi) = -E_J^* \cos(\phi) - E_J \phi, \quad E_J^* = E_J \left(1 - \frac{\Lambda}{2}\right)$$ \hspace{1cm} (37)

and

$$D(\phi) = [1 - \theta \cos(\phi)]^{-1}, \quad \theta = \Lambda \beta E_J.$$ \hspace{1cm} (38)

From the crucial $\Lambda$-function specified in (16) and reading here

$$\Lambda = 2\rho \left[ c + \frac{2\pi^2 \rho}{\beta E_c} + \Psi \left(\frac{\beta E_c}{2\pi^2 \rho}\right)\right]$$ \hspace{1cm} (39)

one sees immediately that $\beta E_c/\pi \rho = \gamma \hbar \beta$ controls the changeover from classical to quantum Smoluchowski dynamics. In particular, it turns out that barrier related quantum fluctuations incorporated in $E_J^*$ dominate in the limit of $\beta E_J \ll 1$, while diffusion related ones, accounted for by the parameter $\theta$, prevail in the opposite range $\beta E_J \gg 1$.

The important observable is now the response of the JJ to an external bias current, namely, the average voltage $\langle V \rangle$. It is related to the steady state current via
FIG. 3: Range of the QSE for a JJ with $\rho \ll 1$, $\gamma e / R I_c < 1$. The classical IZT range (shaded) and the domains of Coulomb blockade (CB) and macroscopic quantum tunneling (MQT) are indicated. The QSE is applicable above the thick line, see (36), and the arrows illustrate various changeovers discussed in the text.

$$\langle V \rangle = (h/2\pi) \lim_{t \to \infty} \langle \dot{\phi} \rangle = 2\pi J_{st}.$$ $J_{st}$ reads as in (24) with periodicity $a = 2\pi$, the diffusion constant from (38), and the potential (22) adapted according to (37) and (38). One then finds the current voltage–characteristics of a current biased junction to read

$$\langle V \rangle = \rho \pi \frac{1 - e^{-2\pi E_I}}{T_{qm}}.$$ (40)

Here, the nominator $T_{qm}$ results from normalizing the steady state phase distribution to 1 and can be written as

$$T_{qm} = \frac{1}{2\pi} \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' e^{-2\pi E_I} e^{-2\beta E_J \cos(\phi') \sin(\phi/2)} \times [1 - \theta \sin(\phi' - \phi/2)] e^{2\beta \xi(\phi, \phi')},$$ (41)

with

$$\xi(\phi, \phi') = \sin(\phi') \sin(\phi/2) [E_I + E_J^* \cos(\phi') \cos(\phi/2)].$$ (42)

The expression (40) together with (41) is the central result from which various known findings can be derived as limiting cases (see fig. 3). (i) For $\beta E_c / \rho \ll 1$ the function $T_{qm}$ reduces to its classical form ($E_J^* \to E_J$, $\theta \to 0$) and the classical Ivanchenko-Zil’berman Theory (IZT) [26] is recovered. (ii) In the low temperature domain $\beta E_c / \rho \gg 1$, but for smaller couplings $\beta E_J < 1$, we have $\theta \ll 1$ so that diffusion related quantum fluctuations are negligible. As a consequence, quantum effects in the transport can be described by a
FIG. 4: Left: Current-voltage characteristics for $\beta E_J = 2$, $\rho = 0.04$. The quantum results [$\beta E_c = 1$ (dashed), $\beta E_c = 20$ (solid)] are shown with the classical one ($\beta E_c = 0$, dotted). Right: Supercurrent vs. voltage for $\beta E_J = 0.25$, $\rho = 0.04$. The classical result (dotted, from [26]) and the CB expression [dashed, from [31]] are depicted together with the QSE result [solid, from [28]] for $\beta E_c = 0.15$ (top), $\beta E_c = 20$ (middle), $\beta E_c = 1000$ (bottom).

renormalized coupling energy $E^*_J$. This important extension of IZT has first been derived in [31] based on a direct evaluation of the real-time path integral expression. The supercurrent across the junction coincides with results from Coulomb blockade (CB) theory (cf. fig. 4), thus describing an incoherent transfer of charges. (iii) For $\beta E_c/\rho \gg 1$ and sufficiently larger couplings $\beta E_J > 1$, coherent Cooper pair tunneling exists. Then, for $\alpha = I/I_c < 1$ occasional phase slips occur and lead to the voltage

$$
\langle V \rangle_{RI_c} = \frac{\sqrt{1 - \alpha^2}}{2\pi} e^{-2\beta E_J (1-\alpha^2)^{3/2}/(3\alpha^2)} e^{2\theta \sqrt{1-\alpha^2}}
$$

(43)

which via $\theta$ is affected by diffusion related quantum fluctuations. As can be observed in fig. 3, the result [43] tends for $\theta \to 0$ to classical thermal activation over the barriers of the washboard potential $U(\phi)$, where quantum corrections are of the known damping independent form [32]. At lower temperatures, i.e. for finite $\theta$, they show a complicated dependence on $\rho$ and capture the precursors of macroscopic quantum tunneling (MQT) found at very low temperatures [33]. Thus, the central result [40] fills the gap between established results in different transport domains: On the one hand, for fixed $\beta E_c/\rho > 1$ it leads with increasing $\beta E_J$ from Coulomb blockade to coherent Cooper pair tunneling [fig. 3, arrow (a)]. On the other hand, for fixed $\beta E_J > 1$ it connects with varying $\beta E_c/\rho$ classical thermal activation with MQT [fig. 3, arrow (b)]. Apart from limiting cases, [40] is easily evaluated numerically; some results are shown in fig. 4. Hence, the QSE approach allows to give, in a seemingly transparent manner, a complete description throughout a broad range in parameter space and must be supplemented only for very low temperatures ($T \to 0$) by more sophisticated techniques [30].
C. Electron transfer in condensed phase

The most prominent example of molecular electron transfer (ET) is the primary step of photosynthesis, but it is of fundamental relevance in a large variety of chemical and biological compounds [34, 35]. In the simplest case, two electronic sites denoted as donor and acceptor, respectively, interact with a bath of harmonic oscillators (spin-boson model [36]). Completely equivalent is a formulation where the electronic system is coupled to a collective vibronic degree of freedom (Reaction Coordinate, RC) embedded in a thermal environment [37], see fig. 5. The theoretical foundations to describe these systems have already been laid in the 1980s with the pioneering work by Marcus et al. [34]. It turned out that qualitatively two dynamical domains must be distinguished: For vibronic dynamics fast compared to the bare ET, characteristic for long-distance ET, one speaks of nonadiabatic reactions; in the opposite case of very slow vibronic motion, realized e.g. in mixed-valence compounds, the reaction is said to be adiabatic. Accordingly, for a donor-acceptor system transfer rates have been successfully calculated in the nonadiabatic regime by invoking golden rule techniques and for adiabatic reactions at sufficiently high temperatures by Kramers’ flux over population method [12]. These quite different approaches reflect the different physical processes that control the transfer, namely, in the former case the electronic coupling between diabatic donor/acceptor states, in the latter one the sluggish activated bath motion on the lower adiabatic surface. For sufficiently high temperatures and slow to moderately slow bath modes, first Zusman [38] and later Garg [37] derived equations of motion for the electronic dynamics interacting with a damped RC treated in the classical Smoluchowski limit. Since these Zusman Equations (ZE) allow to derive a rate expression which to some extent comprises adiabatic as well as nonadiabatic effects, it is important to look for a low temperature extension [39].

The corresponding Hamiltonian is of the form (1) with a system part $H_S = H_{EL} + H_{RC}$ where

$$H_{EL} = -\frac{\hbar \epsilon}{2} \sigma_z - \frac{\hbar \Delta}{2} \sigma_x$$  \hspace{1cm} (44)

represents the bare electronic two-state system (EL) as an artificial spin-$\frac{1}{2}$ system with donor $|{-}\rangle$ and acceptor $|{+}\rangle$, a bias $\hbar \epsilon$, and an electron transfer coupling $\hbar \Delta$; the second part

$$H_{RC} = \frac{p^2}{2M} + \frac{M \omega_0^2}{2} q^2 - c_0 q \sigma_z$$  \hspace{1cm} (45)

describes a harmonic collective vibronic degree of freedom linearly coupled to the electronic system and to a heat bath (see fig. 5). What one is interested in is the dynamics of a state
FIG. 5: Diabatic potential surfaces for the reaction coordinate (RC) in an ET process. A wave packet is excited by a laser pulse from a dark state (thin line) to the donor state (thick line, minimum at $-q_0$). There it evolves on the coupled donor and acceptor (thick line, minimum at $+q_0$) surfaces where the ET occurs in the Landau-Zener region near $q = 0$.

Initially prepared on the donor surface. It is given by the exact path integral expression for the reduced density matrix of the EL+RC system $\rho_{\alpha\beta}(q, q', t)$, $\alpha, \beta \in \{-, +\}$ [40].

Now, for strong damping (slow RC) a simplification according to the scenario discussed above is applicable. The difficulty then lies in the coupling between overdamped RC and electronic motion which basically makes a transition from one electronic state to the other only possible in the Landau-Zener (LZ) region where the harmonic surfaces of the RC intersect (see fig. 5). Thus, three additional time scales enter the game: The typical time for thermal activation into the LZ range, $t_{\text{act}}$, the typical time the RC diffuses, after activation, in the LZ range, $t_{\text{LZ}}$, and the typical time the density matrix resides in a non-diagonal state, $t_{\text{blip}}$. It turns out that (46) must be extended to

$$\frac{1}{\gamma} \frac{\hbar \beta}{2\pi} \ll t_{\text{blip}} \ll t_{\text{LZ}} < \frac{\gamma}{\omega_0} \ll t_{\text{act}} \quad (46)$$

in order to reduce the path integral expression. This way, one derives for the probabilities $P_{\alpha\beta}(q, t) = \rho_{\alpha\beta}(q, q, t)$ the extension of the ZE to lower temperatures, the Generalized Zusman Equations (GZE),

$$\dot{P}_{\mp\mp}(q, t) = \mathcal{L}^\mp P_{\mp\mp}(q, t) \pm i\frac{\Delta}{2} \left[ P_{\mp+}(q, t) - P_{\mp-}(q, t) \right]$$

$$\dot{P}_{\mp\pm}(q, t) = \mathcal{L}^0 P_{\mp\pm}(q, t) \pm i\frac{\Delta}{2} \left[ P_{\pm-}(q, t) - P_{\pm+}(q, t) \right]$$

$$\mp i \left( \epsilon + \frac{2c_0}{\hbar \kappa} q \right) P_{\mp\pm}(q, t). \quad (47)$$
Here, the quantum Smoluchowski operators \([\text{see (27)}]\) read

\[
L^\eta = \frac{1}{M\gamma} \frac{\partial}{\partial q} \left[ M\omega_0^2 (q - \eta q_0) + \frac{\kappa}{\beta} \frac{\partial}{\partial \eta} \right]
\]

and describe the overdamped quantum dynamics of the harmonic RC on the donor \((\eta = -)\), the acceptor \((\eta = +)\), and the averaged potential surface \((\eta = 0)\). Note that the effect of quantum fluctuations also shows up in the \(c_0/\kappa\) dependent coupling terms of the non-diagonal matrix elements. The coefficient \(\kappa\) contains the equilibrium variance of a damped harmonic oscillator

\[
\kappa = \frac{\langle q^2 \rangle}{\langle q^2 \rangle_{cl}} \approx 1 + M\omega_0^2 \beta \Lambda.
\]

By invoking again the time scale separation \([\text{46}]\) the electron transfer rate can be derived from the GZE \([\text{39, 41, 42}]\). In case of a vanishing bias one finds for the total (forward+backward) rate

\[
k = \frac{\Delta^2}{1 + g} \sqrt{\frac{\hbar^2 \pi \beta}{4 E_r / \kappa}} \exp \left( -\beta E_r / 4\kappa \right)
\]

with an adiabaticity parameter

\[
g = \pi \kappa \frac{\Delta}{\omega_0^2 / \gamma} \frac{\hbar \Delta}{E_r}
\]

and with the reorganization energy \(E_r = 2c_0^2 / M\omega_0^2\). For \(g \gg 1\) one recovers the adiabatic, for \(g \ll 1\) the nonadiabatic rate constant. The above rate expression looks like the classical Marcus/Zusman result with a renormalized reorganization energy \(E_r \to E_r / \kappa\). Note that this simple renormalization only appears if quantum fluctuations in the \(c_0\)-coupling terms of the GZE are properly taken into account. Since \(\kappa \geq 1\) quantum fluctuations always reduce the effective energy barrier which is to be surmounted. Of course, in the high temperature limit \((\kappa \to 1)\) we regain the known result, for lower temperature, however, significant deviations are observed. (i) The ratio \(\kappa\) grows with decreasing temperature, at very low temperatures roughly linearly with \(\beta\). As a consequence, keeping all other parameters fixed, \(g\) becomes larger with lower \(T\) meaning that one approaches the range where the transfer is dominated by adiabatic processes at smaller values of \(\Delta\) compared to the classical range. (ii) At lower \(T\), the exponent in the rate expression \(\beta E_r / \kappa\) tends to become temperature independent in contrast to the classical result. Since \(\kappa\) enters the exponent in \([\text{50}]\), even relatively small deviations from the classical behavior \(\kappa / \beta = 1 / \beta\) substantially influence the rate. In fact, if formally the limit of very low temperatures \(\gamma \hbar \beta \gg 1, \omega_0 \hbar \beta \gg \gamma / \omega_0\) is taken [which in a strict sense is out of the range of validity of \([\text{50}]\)], \(\kappa / \beta\) saturates and one obtains

\[
\frac{\beta E_r}{4\kappa} \to \frac{\pi \gamma}{8\omega_0 \ln(\gamma / \omega_0)} \frac{E_r}{\hbar \omega_0}
\]
FIG. 6: Electron transfer rates vs. temperature for a symmetric system ($\epsilon = 0$) according to the expression (50) (solid line), the classical result ($\kappa = 1$, dashed line), and precise Quantum Monte Carlo data (diamonds, from [43]). $E_r/\hbar \Delta = 10$ and $\Delta/(\omega_0^2/\gamma) = 2$.

which is identical to the overlap of two Gaussian wave packets with overdamped harmonic variance localized around $\mp eg_0/M\omega_0^2$. Hence, nuclear tunneling is included in the above rate formula, at least in a nondynamical way. In comparison with precise path integral Monte Carlo results (from [43]) a remarkable agreement is seen over a broad temperature range, fig. 6. At low $T$, the rate enhancement due to nuclear tunneling is substantial.

IV. CONCLUSIONS

The description of quantum Brownian motion is still a challenging problem. In general it does not allow for ”simple” solutions in terms of tractable time evolution equations and even a direct numerical evaluation of the exact path integral expression for the reduced dynamics is not always feasible. While in the limit of weak friction various master equations have successfully been applied in the past, the opposite limit of strong friction has been left basically untouched. However, the naive expectation is that a strongly condensed phase environment quenches quantum fluctuations, thus forcing the system to behave more classically. In fact, this is only one facet of the problem since quantum mechanically small fluctuations in position are immediately accompanied by large fluctuations in the conjugate momentum. A systematic simplification within the path integral formulation leads indeed to an equation of motion which to leading order coincides with the classical Smoluchowski equation, but contains substantial quantum corrections.
Applications for chemical, mesoscopic, and soft matter systems have shown the decisive impact of corresponding quantum mechanical fluctuations on transport properties even up to high temperatures where thermal energies exceed relevant time scales of the damped dynamics. So far, this analysis has focused on one-dimensional systems, but by exploiting the developed techniques extensions to two and three dimensions are certainly feasible.

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