QUANTUM DYNAMICS WITH STRONG FRICTION: THE QUANTUM SMOLUCHOWSKI EQUATION AND BEYOND*

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Recently, the strong friction limit for a quantum system coupled to a heat bath environment has been explored starting from the exact path integral formulation. Generalizing the classical Smoluchowski limit to low temperatures a time evolution equation for the position distribution, the quantum Smoluchowski equation, has been derived. This important result can even be extended to a quantum Fokker–Planck equation in full phase space. Here, we review these fundamental findings from a physical perspective and apply them to the Kramers barrier escape problem at low temperatures and strong friction.

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1. Introduction

In the last decade or so the study of systems in strongly condensed phase has evolved into a fascinating, interdisciplinary field attracting physicists and chemists from both theory and experiment. One reason for that is their omnipresence in nature, *e.g.* in tunnel diodes in mesoscopic physics, in macromolecules in biological and soft matter systems, and in chemical reactions. Another reason is the rich phenomenology associated with strong friction dynamics comprising prominent effects such as stochastic resonance [1], resonant activation [2], transport in ratchets [3], and adiabatic electron transfer [4]. Most of these studies, however, have focused on the classical high temperature domain and much less is known about corresponding quantum properties. While classically the description of Brownian motion is well-established and founded on Langevin or Fokker–Planck equations [5], the

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situation for quantum dissipative systems is more difficult [6]. In fact, in general a simple time evolution equation for the reduced density matrix is not available, even though a formally exact expression in terms of path integrals exists. Typically, quantum fluctuations appear on a time scale $\hbar\beta$ ($\beta = 1/k_{\rm B}T$) so that at lower temperatures the quantum stochastic process becomes strongly non-Markovian and intimately depends on the initial correlations between system and environment.

In the weak friction range progress has been made by invoking the Born–Markov approximation. This way, *e.g.* for quantum optical systems [7], so-called master equations have been derived. Does the opposite limit of strong friction also allow for such simplifications? This question has been explored recently [8–11] and by generalizing the classical Smoluchowski range to lower temperatures it has been shown that the diagonal part of the density matrix, the probability distribution, obeys a quantum analogue of the classical Smoluchowski equation. This result can even be extended to a quantum Fokker–Planck equation in full phase space. In this paper we review these studies focusing on the physics behind the mathematics. As an application classical Kramers rate theory [12] is extended to the overdamped quantum range.

In Sec. 2 the path integral approach for dissipative quantum systems is introduced and specified to the strong friction range. Then, in Sec. 3 the quantum Smoluchowski equation and in Sec. 4 its phase space generalization are discussed. The quantum Kramers theory is developed in Sec. 5.

2. Quantum dissipation

The description of classical Brownian motion in terms of generalized Langevin equations or, equivalently, in terms of Fokker–Planck equations for phase space distributions has a long tradition [5]. In contrast, the inclusion of dissipation within quantum mechanics has evoked controversial discussions and has been established only since the mid $80^{\rm ties}$. In the standard formulation one starts with a system+heat bath formulation so that the dynamics of the density matrix starting at $t = 0$ from a general initial state $W(0)$ reads [6]

$$W(t) = \exp\left(\frac{-iHt}{\hbar}\right) W(0) \exp\left(\frac{iHt}{\hbar}\right) , \tag{2.1}$$

where the Hamiltonian $H = H_{\rm S} + H_{\rm R} + H_{\rm I}$ contains a system, a reservoir (heat bath), and a system-bath interaction part, respectively. The crucial point is now, that dissipation is not *a priori* inherent in the system, but arises only if one looks on the effective impact of the bath degrees of freedom within a reduced picture $\rho(t) = {\rm Tr}_{\rm R}\{W(t)\}$. The Gaussian statistics

of the heat bath is modeled by a quasi-continuum of harmonic oscillators bilinearly coupled with the relevant system degree of freedom. Although the interaction between each bath degree of freedom and the system is supposed to be weak, the overall impact of the reservoir may cause also strong friction.

The only non-perturbative way to deal with the elimination of the bath degrees of freedom is to apply the path integral approach. In the ordinary Feynman Vernon theory [6] the initial state is assumed to be a factorizing state $W(0) = \rho_{\rm S}(0)\,\exp(-\beta H_{\rm R})$ so that each one, system and equilibrated bath, lives in splendid isolation at $t = 0$. While this assumption may be justified in the weak friction/high temperature range, it definitely fails for moderate to strong dissipation or lower temperature. Even the Langevin equation is not regained in the classical limit, but differs by initial boundary terms that may persist up to long times. A realistic initial state reflecting the experimental situation is thus a correlated one described by [13]

$$W(0) = \sum_i \; O^i_{\rm S}\, {\rm e}^{-\beta H}\, \tilde{O}^i_{\rm S}\,, \tag{2.2}$$

where the operators $O^i_{\rm S}, \tilde{O}^i_{\rm S}$ act onto the system degree of freedom only and prepare a nonequilibrium state. In the sequel we focus on the case where the preparation operators depend exclusively on position and refer to [13] for the generalization. As an example think about a position measurement with a Gaussian slit, in which case the preparation operators are Gaussian weighted projection operators onto position. Then, representing the forward and backward time evolution operators in (2.1) and the statistical operator in (2.2) as path integrals in real and imaginary time, respectively, the harmonic bath degrees of freedom can be integrated out exactly. For the position representation of the reduced density matrix one ends up with

$$\rho(q_{\rm f}, q'_{\rm f}, t) = \int dq_i\, dq'_i\; J(q_{\rm f}, q'_{\rm f}, t, q_i, q'_i)\; \lambda(q_i, q'_i)\,. \tag{2.3}$$

Here, the propagating function $J(\cdot)$ is a threefold path integral over the system degree of freedom only. The two real time paths $q(s)$ and $q'(s)$ connect in time t the initial points q_i and q'_i with the fixed end points $q_{\rm f}$ and $q'_{\rm f}$, 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 by $\exp(i\Sigma[q, q', \bar{q}]/\hbar)$ with an effective action $\Sigma[q, q', \bar{q}]$ not specified here explicitly. Basically, it comprises the actions of the bare system in imaginary and real time, respectively, and additional interaction contributions (influence functional), non-local in time, which in the reduced picture rule the influence of the reservoir onto the system. While the imaginary time paths describe the initial state, the two real time paths govern the dynamics of the reduced system. Accordingly,

the distribution of end-points of the former and starting points of the latter q_i, q_i' are weighted in (2.3) also by the preparation function $\lambda(\cdot)$ being the position representation of the preparation operators in (2.2). In the limit $t \to 0$ one has $J(q_\mathrm{f}, q_\mathrm{f}', t, q_i, q_i') \to \rho_\beta(q_i, q_i')\,\delta(q_\mathrm{f} - q_i)\,\delta(q_\mathrm{f}' - q_i')$ so that

$$\rho(q_\mathrm{f}, q_\mathrm{f}', 0) = \rho_\beta(q_i, q_i')\ \lambda(q_i, q_i') \tag{2.4}$$

with the reduced equilibrium density matrix $\rho_\beta(q, q') = \langle q|\,\mathrm{Tr}_\mathrm{R}\exp(-\beta H)|q'\rangle$. In fact, this formulation reproduces in the classical limit the generalized Langevin equation.

The nonequilibrium time evolution of a dissipative quantum system is governed by (2.3) together with (2.4). The good news is that this path integral expression is exact, also in the system-bath coupling. The bad news is that its evaluation for specific situations is extremely complicated and even numerically (*e.g.* via Monte Carlo simulations) feasible only in certain cases. The reason for that is twofold: First the propagating function is complex and, therefore, highly oscillatory which renders numerical algorithms unstable for sufficiently long times. Second and more severe, however, is the non-locality, in time, of the influence functional; the reduced time evolution in the time interval $s \in [t', t]$ is affected by the history of the dynamics for $s < t'$ and particularly by the initial correlations between system and bath. As a direct consequence, this means that in general a simple time evolution equation $\dot\rho = \mathcal{L}\,\rho$ of the reduced density with a time independent generator $\mathcal{L}$ does not exist. It is well-known that progress can be made in the weak friction limit where a variety of so-called master equations have been derived. For example in quantum optical system this is often an accurate and powerful approach. For strong friction and low temperatures, however, these known master equations are not applicable.

3. Strong friction limit and the quantum Smoluchowski equation

The effective impact of the bath described by the influence functional is controlled by the damping kernel

$$K(\theta) = \int_0^\infty \frac{d\omega}{\pi}\, I(\omega)\, \frac{\cosh\left[\omega\left(\frac{\hbar\beta}{2} - i\theta\right)\right]}{\sinh\left(\frac{\omega\hbar\beta}{2}\right)}\,, \tag{3.1}$$

where $\theta = s - i\tau$, $0 \le s \le t$, $0 \le \tau \le \hbar\beta$ and $I(\omega)$ is the spectral density of the heat bath. For real times the imaginary part of $K(s) = K'(s) + iK''(s)$ is related to the macroscopic damping kernel

$$\gamma(s) = \frac{2}{M}\int_0^\infty \frac{d\omega}{\pi}\,\frac{I(\omega)}{\omega}\,\cos(\omega s)\,, \tag{3.2}$$

via $K''(s) = (M/2)d\gamma(s)/ds$, while $K'(s) \to M\gamma(s)/\hbar\beta$ in the classical limit $\omega_c\hbar\beta \to 0$ where M is the mass of the Brownian particle and ω_c the bath cut-off frequency.

Let us now consider the strong friction range. For this purpose we define a typical damping strength

$$\gamma \equiv \hat{\gamma}(0) = \lim_{\omega\to 0} \frac{I(\omega)}{M\omega} \tag{3.3}$$

with $\hat{\gamma}(\omega)$ the Laplace transform of $\gamma(t)$. For instance, in the ohmic case $I(\omega) = M\bar{\gamma}\omega$ and for the more realistic Drude model $I(\omega) = M\bar{\gamma}\omega\omega_c^2/(\omega^2+\omega_c^2)$ one finds $\gamma = \bar{\gamma}$. Given a typical frequency ω_0 of the bare system, *e.g.* the ground state frequency, by strong damping we then mean

$$\frac{\gamma}{\omega_0^2} \gg \hbar\beta, \frac{1}{\omega_c}, \frac{1}{\gamma}\,. \tag{3.4}$$

In other words, we assume the time scale separation well-known from the classical overdamped regime [5] and extend it to the quantum range by incorporating the time scale for quantum fluctuations $\hbar\beta$. Correspondingly, we examine the dynamics Eq. (2.3) on the coarse grained time scale $s \gg \hbar\beta, \frac{1}{\omega_c}, \frac{1}{\gamma}$ and $\sigma \gg \frac{1}{\omega_c}, \frac{1}{\gamma}$. The consequences are substantial: *(i)* the strong friction suppresses non-diagonal elements of the reduced density matrix during the time evolution. This simply reflects the fact that a quantum system behaves more classically, the stronger coherences are destroyed by the presence of a heat bath. *(ii)* The real-time part $K(s)$ of the damping kernel becomes local on the coarse grained time scale so that a time evolution equation of the form $\dot{\rho}(t) = \mathcal{L}\,\rho(t)$ with a time independent operator $\mathcal{L}$ may exist. While these simplifications apply to a wide range of spectral bath densities, we consider in the sequel the quasi-ohmic case with a very large cut-off frequency $\omega_c \gg \gamma$. The corresponding range in parameter space covered by (3.4) is shown in Fig. 1. It is well separated from the weak fric-

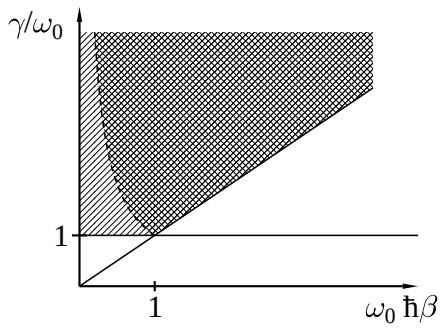

Fig. 1. Smoluchowski range $\gamma/\omega_0^2 \gg \hbar\beta, 1/\gamma$ (shaded). The classical range ($\gamma\hbar\beta \ll 1$) is simple shaded, the quantum range ($\gamma\hbar\beta \gg 1$) double shaded.

tion region and comprises temperatures from the classical ($\gamma\hbar\beta \ll 1$) to the deep quantum domain ($\gamma\hbar\beta \gg 1$).

Following the above simplifications the path integral formulation now allows for a perturbative treatment in the *strong damping limit*. The idea is to evaluate the path integrals in the sense of a semiclassical approximation by assuming self-consistently that non-diagonal elements remain small during the time evolution (for details see [8]). Hence the effective action $\Sigma[q, q', \bar{q}]$ is expanded up to second order in the difference $\bar{q} - \bar{q}'$ coordinate of the imaginary time path and in the excursions $q(s) - q'(s)$ of the real-time path integrals. Doing so we take sufficiently smooth potentials for granted.

This way it has been shown in [8] that the diagonal part of the density matrix $P(q,t) = \rho(q,q,t)$ obeys the equation of motion

$$\frac{\partial P(q,t)}{\partial t} = \frac{1}{\gamma M}\frac{\partial}{\partial q}\left\{V'_{\rm eff}(q) + \frac{\partial}{\partial q}\left[\frac{1}{\beta} + \Lambda V''(q)\right]\right\} P(q,t)\,, \tag{3.5}$$

where V denotes the potential field, $'$ abbreviates d/dq, and $V_{\rm eff} = V + \Lambda V''/2$. Here

$$\Lambda = \frac{2}{M\beta}\sum_{n=1}^{\infty}\frac{1}{\nu_n^2 + \nu_n\hat{\gamma}(\nu_n)}\,, \tag{3.6}$$

with the Matsubara frequencies $\nu_n = 2\pi n/\hbar\beta$ measures typical quantum fluctuations in position space. In the particular case of a harmonic potential this means $\langle q^2\rangle \approx \langle q^2\rangle_{\rm cl} + \Lambda$ with the classical variance $\langle q^2\rangle_{\rm cl}$. Within a Drude model for the damping, Λ can be expressed in terms of Ψ functions. Then, for high temperatures $\gamma\hbar\beta \ll 1$ one finds $\Lambda \approx \hbar^2\beta/12M$. The friction dependence appears as a genuine quantum effect for lower temperatures and for $\gamma\hbar\beta \gg 1$ one has $\Lambda \approx (\hbar/M\gamma\pi)\log(\gamma\hbar\beta/2\pi)$. Thus, the strong squeezing due to friction leads to small quantum fluctuations in position. Effectively, the quantum dynamics described by (3.5) follows a classical Smoluchowski equation within an effective force field and with position dependent diffusion, and has thus been coined Quantum Smoluchowski Equation (QSE). In leading order it is identical to the classical Smoluchowski equation, but particularly in the deep quantum range $\gamma\hbar\beta \gg 1$ the influence of quantum fluctuations, *i.e.* the influence of Λ terms, on typical observables like *e.g.* rate constants is significant [9].

4. Overdamped quantum dynamics in phase space

In the previous section we have focused on the diagonal part of the reduced density. One may wonder: What about non-diagonal elements? To answer this question we have recently extended the procedure of evaluating path integrals for strong friction from $\rho(q_{\rm f}, q_{\rm f}, t)$ to the full density $\rho(q_{\rm f}, q'_{\rm f}, t)$

[10]. In essence, since deviations from diagonality $x(s) = q(s) - q'(s)$ remain small during the time evolution, they run effectively at each instantaneous mean position $r(s) = [q(s) + q'(s)]/2$ in a harmonic force field $V''(r)x$. Exploiting also the sluggish motion of $r(s)$, this allows for an analytical solution which eventually leads to a time evolution equation for $\rho(q_{\rm f}, q'_{\rm f}, t)$. After switching to classical phase space $\{x_{\rm f}, r_{\rm f}\} \to \{p, q\}$, *i.e.* $\rho(x_{\rm f}, r_{\rm f}, t) \to W(p, q, t)$, one arrives at

$$\frac{\partial}{\partial t} W(p,q,t) = \left\{ \frac{\partial}{\partial p} \left[V'_{\rm eff}(q) + \gamma\, p \right] - \frac{p}{M} \frac{\partial}{\partial q} + \gamma \langle p^2 \rangle \frac{\partial^2}{\partial p^2} + \frac{\partial^2}{\partial q \partial p} \left[\frac{1}{\beta} + \Lambda\, V''(q) - \frac{\langle p^2 \rangle}{M} \right] \right\} W(p,q,t)\,. \tag{4.1}$$

Here, $V_{\rm eff}$ is given in (3.5) and in the strong friction range the equilibrium variance in momentum reads

$$\langle p^2 \rangle = \frac{M}{\beta} + \frac{2M}{\beta} \sum_{n=1}^{\infty} \frac{\hat{\gamma}(\nu_n)}{\nu_n + \hat{\gamma}(\nu_n)}\,. \tag{4.2}$$

The first line on the r.h.s of (4.1) coincides with a classical Fokker–Planck operator in an effective force field [5], the second line describes quantum mechanical coupled p–q diffusion. In the high temperature regime $\gamma\hbar\beta \ll 1$ with $\langle p^2 \rangle \approx M/\beta$ the classical Kramers equation is recovered. For low temperatures $\gamma\hbar\beta \gg 1$ it is (for Drude damping) $\langle p^2 \rangle \approx (M\hbar\gamma/\pi)\, \log(\omega_{\rm c}/\gamma)$ so that the strong friction induces, in contrast to position space, large quantum fluctuations in momentum and the coupled p–q diffusion becomes important.

What about the time scale separation between relaxation of momentum and relaxation of position which is characteristic for the strong friction range? From the evaluation of the path integrals and also upon closer inspection of the above Quantum Fokker–Planck equation (QFP) we observe that $W(p, q, t) \to \exp[-p^2/(2\langle p^2 \rangle)]\, P(q, t)$ on the time scale $1/\gamma$ with corrections depending on $\hbar\beta$, ω_0^2/γ, and $\gamma/\omega_{\rm c}$.

Now, based on the QFP (4.1) or its reduction to position space in form of the QSE (3.5) [14], quantum Brownian motion can be studied in detail in the overdamped limit (3.4) and for high and low temperatures as well.

5. Quantum Kramers rate theory at strong friction

The role of quantum fluctuations in the overdamped range has already been elucidated for several phenomena elsewhere. In the remaining part of this paper we consider thermally activated decay over a high potential barrier, and with the QFP at hand, will give the extension of Kramers classical phase space theory [12] to the overdamped quantum domain.

The situation is the following: A high potential barrier (barrier height $V_{\rm b}$ much larger than $k_{\rm B}T$) separates two well regions. Initially particles stay in local thermal equilibrium, say, in the well left to barrier. In the future, particles surmounting the barrier and reaching the right well are immediately removed and re-injected into the left well. Accordingly, after a transient period of time a stationary flux $j_{\rm st}$ across the barrier appears corresponding to a time independent decay rate $\Gamma = j_{\rm st}$. If friction is sufficiently strong the changeover from quasi-thermal equilibrium in the left well to nonequilibrium in the right well is restricted to the vicinity of the barrier top located at $q_{\rm b}$. Hence, the stationary nonequilibrium state $W_{\rm st}(p,q)$ takes the form $W_{\rm st}(p,q) = W_\beta(p,q)\, g(p,q)$ with a "form factor" $g(p,q)$ obeying $g(p,q) \to 1$ in the vicinity to the left of $q_{\rm b}$ and $g(p,q) \to 0$ in the vicinity to the right of $q_{\rm b}$. This way, (assuming smooth potentials, of course) $g(p,q)$ is calculated in the parabolic range around $q_{\rm b}$ and $W_{\rm st}(p,q)$ is then matched onto the thermal equilibrium in the left well. The unnormalized thermal equilibrium $W_\beta(p,q)$ for strong friction and anharmonic potentials has already been derived in [10]. Near the minimum of the left well at q_w and near the barrier top at $q_{\rm b}$, respectively, it takes the form

$$W_\beta(p,q) = \frac{1}{n_{\rm well}}\, {\rm e}^{-p^2/2\langle p^2\rangle}\, {\rm e}^{-\beta M \Omega^2 (q-Q)^2/(1+\Lambda M\beta\Omega^2)}\, {\rm e}^{-\beta\Lambda 3\Omega^2/2}\,, \qquad (5.1)$$

where $Q = q_w$ and $\Omega^2 = \omega_w^2$ near the harmonic well minimum with frequency ω_w, and $Q = q_{\rm b}$ and $\Omega^2 = -\omega_{\rm b}^2$ near the parabolic barrier top with frequency $\omega_{\rm b}$. The distribution is normalized with respect to the well population $n_{\rm well}$. Now, with (5.1) the QFP (4.1) reads for $g(p,q)$

$$\left\{ \left[\left(-M\omega_{\rm b}^2 - \frac{D_{qp}}{D_{qq}} \right)(q-q_{\rm b}) - \gamma p \right] \partial_p - \frac{p}{M} \left(1 + \frac{M D_{qp}}{\langle p^2\rangle} \right) \partial_q \right.$$
$$\left. + \gamma\langle p^2\rangle \partial_p^2 + D_{qp}\partial_q\partial_p \right\} g(p,q) \;=\; 0\,. \qquad (5.2)$$

In the above, we have defined $D_{qq} = -(1 - \Lambda M\beta\omega_{\rm b}^2)/(M\beta\omega_{\rm b}^2)$ and $D_{qp} = 1/\beta - \Lambda M\omega_{\rm b}^2 - \langle p^2\rangle/M$. Further, ∂_x denotes partial derivation with respect to x. The crucial point is that $g(p,q)$ does actually not depend on p and q separately, but is a function of the linear combination $u = q + a\,p/M$ with a proper constant a. This is fixed by the condition that after transforming to the new coordinate u, (5.2) must become an ordinary differential equation for u (functions in front of derivatives must depend only on u). The result is

$$a = -\frac{M\omega_{\rm b}^2}{\gamma\left(M\omega_{\rm b}^2 + \frac{D_{qp}}{D_{qq}} \right)} = \frac{M^2\omega_{\rm b}^2 D_{qq}}{\gamma\langle p^2\rangle}\,. \qquad (5.3)$$

What remains to do is straightforward. The ordinary differential equation for $g(u)$ can easily be solved. One obtains after re-expressing u as a function of q and p

$$g(p,q) = \frac{1}{\sqrt{\pi}} \int\limits_{\xi(p,q)}^{\infty} dx\, \mathrm{e}^{-x^2}\,, \tag{5.4}$$

with

$$\xi(p,q) = \frac{1}{\sqrt{-2D_{qq}}} \left[(q - q_\mathrm{b}) + D_{qq} \frac{M\omega_\mathrm{b}^2}{\gamma \langle p^2 \rangle}\, p \right]. \tag{5.5}$$

Let us briefly discuss this interesting result in detail. Obviously, for large $|q - q_\mathrm{b}|$, $q < q_\mathrm{b}$ the form factor approaches 1, while for large $|q - q_\mathrm{b}|$, $q > q_\mathrm{b}$ it tends to 0, as expected. Near the barrier top there is a boundary layer in phase space around the line $\xi(p,q) = 0$ (*cf.* Fig. 2).

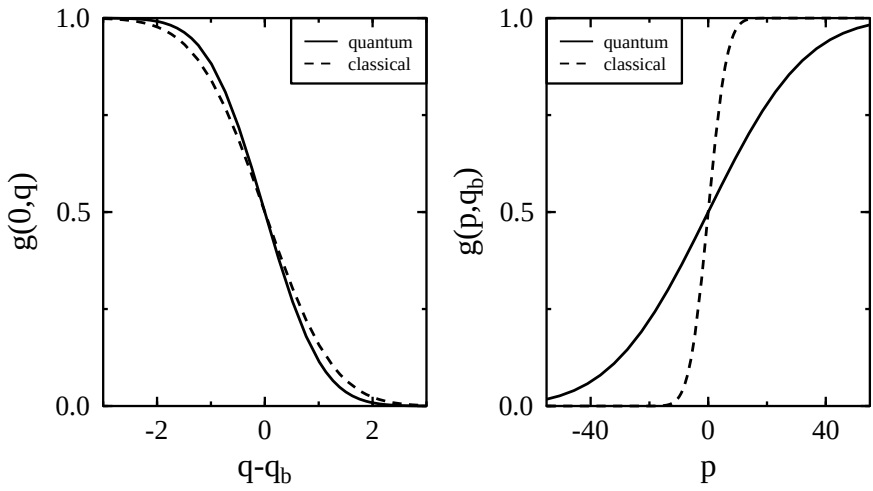

Fig. 2. Form factor $g(p,q)$ of the stationary flux state for fixed position $q = q_\mathrm{b}$ (left) and fixed momentum $p = 0$ (right) at temperature $\omega_\mathrm{b}\hbar\beta = 1$ and for a Drude model with $\gamma/\omega_\mathrm{b} = 5, \omega_\mathrm{c}/\omega_\mathrm{b} = 50$. q is scaled by $\sqrt{\hbar/M\omega_\mathrm{b}}$ and p by $\sqrt{\hbar M\omega_\mathrm{b}}$.

For $\gamma\hbar\beta \ll 1$ this line is given by $p = (q - q_\mathrm{b}) M\gamma$ and becomes much steeper for low temperatures $\gamma\hbar\beta \gg 1$, where $p = (q - q_\mathrm{b})\, \beta\gamma^2\hbar M\, \log(\omega_\mathrm{c}/\gamma)/\pi$. The reason for that is the reduction of fluctuations in position near the barrier top ($|D_{qq}|$ decreases) compared to the classical case, but the enhancement of fluctuations in momentum. The width of the boundary layer $\sqrt{2|D_{qq}|}$ shrinks accordingly.

To obtain the decay rate the well population is calculated in the harmonic approximation using (5.1)

$$n_{\rm well} = 2\pi \left[\frac{\langle p^2\rangle\,(1+\Lambda M\,\beta\omega_w^2)}{M\,\omega_w^2\,\beta}\right]^{1/2} . \tag{5.6}$$

Eventually, the stationary flux $j_{\rm st} = \int dp\, p\, W_{\rm st}(p,q_{\rm b})/M$ gives us the rate constant

$$\Gamma \equiv j_{\rm st} = \frac{\omega_{\rm b}\,\omega_w}{2\pi\,\gamma}\; {\rm e}^{-\beta\, V_{\rm b}}\; {\rm e}^{\beta\Lambda M\,(\omega_{\rm b}^2+\omega_w^2)} . \tag{5.7}$$

Apparently, (5.7) is identical to the classical overdamped Kramers result up to an exponential containing the contributions of quantum fluctuations. The latter one leads to an enhancement of the quantum rate compared to the classical one. The accuracy of the strong damping result (5.7) is shown in Fig. 3 where the ratios of the exact asymptotic quantum rate in the limit $\beta V_{\rm b} \gg 1$, [15] with the quantum and the classical Smoluchowski rates, respectively, are depicted. The overdamped quantum rate is accurate already for moderate damping strengths and the influence of quantum fluctuations becomes quite important for lower temperatures.

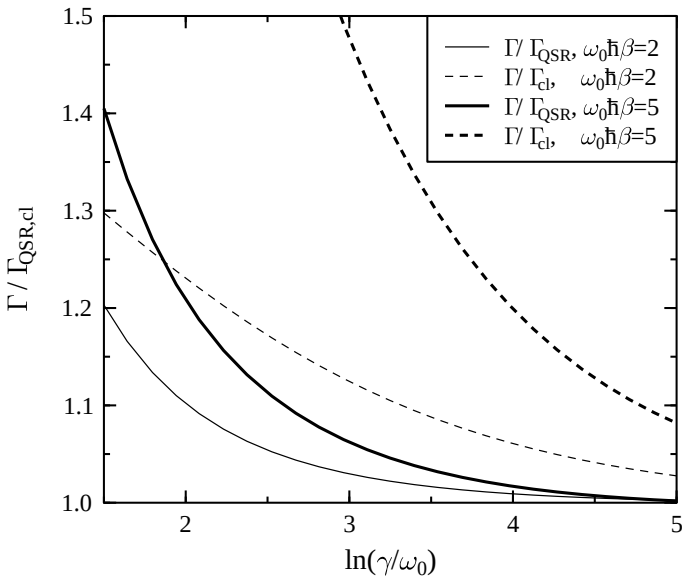

Fig. 3. Ratio of the exact rate (Γ) with the classical (dashed, $\Gamma_{\rm cl}$) and the Smoluchowski (solid, $\Gamma_{\rm QSR}$) rate *vs* friction for $|V''(q_{\rm b})| = V''(0) = M\omega_0^2$.

6. Conclusions

We have analyzed the time evolution of strongly damped quantum systems based on the exact path integral expression for the reduced density matrix in position space. In addition to the characteristic time scale separation known already from the classical Smoluchowski limit, a separation of quantum fluctuations occurs at lower temperatures: Fluctuations in position are suppressed so that an overdamped system behaves more classically in position space, while for fluctuations in momentum strong quantum effects prevail. This allows to derive a quantum Smoluchowski equation and its phase space extension, a quantum Fokker–Planck equation, for high and low temperatures as well. The door is now open to study the dynamics of overdamped systems also in the quantum domain. While we here presented the quantum Kramers theory, there is a wide range of further applications including soft matter systems, transport in macromolecules, and adiabatic electron transfer.

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