Strong Friction Limit in Quantum Mechanics: The Quantum Smoluchowski Equation

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For a quantum system coupled to a heat bath environment the strong friction limit is studied starting from the exact path integral formulation. Generalizing the classical Smoluchowski limit to low temperatures, a time evolution equation for the position distribution is derived and the strong role of quantum fluctuations in this limit is revealed.

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Quantum systems coupled to a heat bath environment can be found almost everywhere in physics and chemistry [1]. Transport processes in Josephson junctions [2] or electron transfer reactions in large molecules [3] are typical examples. What one aims to describe here is the effective dynamics of the relevant system degrees of freedom, i.e., the reduced dynamics. While the corresponding classical theory is well established and based on Fokker-Planck equations, the formulation of dissipation in quantum mechanics is more complicated. In general a simple time evolution equation for the reduced density matrix does not exist [1]; a formally exact expression for the reduced dynamics in terms of path integrals is available, but the path integral expression in many cases cannot be evaluated even numerically. In the past years efforts have focused on the weak coupling regime where a description in terms of Master equations is possible [4]. The opposite limit of strong coupling has been left basically untouched [5].

In this Letter, we study this limit. For the first time we show that for large friction the exact dynamics of a dissipative quantum system can be cast into a time evolution equation for the position distribution, the so-called quantum Smoluchowski equation (QSE) derived below in Eq. (13).

In classical physics the Smoluchowski limit is well known in all areas [6]. For large friction the Fokker-Planck equation in phase space reduces to a time evolution equation in position space, the Smoluchowski equation (SE). There, the basic condition is a time scale separation between relaxation of momentum and position which allows for an adiabatic elimination of the former degree of freedom. Corrections to the Smoluchowski equation turn out to be algebraically small in the friction constant. Applications are countless; recent examples include transport in systems with fluctuating barriers [7] or ratchets [8] as found in complex macromolecules [9] and tunnel diodes [10], and decay in periodically driven metastable potentials [11]. The QSE should be important for the description of similar processes at low temperatures.

Quantum dissipation.—The standard way to describe dissipation in quantum mechanics is based on system + reservoir models with a total Hamiltonian $H = H_S + H_R + H_I$ [1]. The reservoir H_R (heat bath) consists of a quasicontinuum of harmonic oscillators which are coupled bilinearly with the system H_S via the interaction H_I. Classically, this model leads back to a generalized Langevin equation for the reduced system. The quantum dynamics for the reduced density matrix follows from $\rho(t) = \mathrm{Tr}_R\{\exp(-iHt/\hbar)W(0)\exp(iHt/\hbar)\}$ with the correlated initial state $W(0)$. In the position representation the path integral approach allows for an exact elimination of the bath degrees of freedom. Now, as in the classical Smoluchowski limit we focus on the position probability distribution $P(q,t) = \rho(q,q,t)$ and obtain the exact result [1,12]

$$P(q_f,t) = \int dq_i\, dq_i'\, J_t(q_f,q_i,q_i')\Lambda(q_i,q_i')\,. \qquad (1)$$

Here, the propagating function J_t is a threefold path integral (two in real, one in imaginary time) over the system degrees of freedom only. The real time paths $q(s)$ and $q'(s)$ run in time t from q_i and q_i' to the fixed end point q_f, while the imaginary time paths $\bar{q}(\sigma)$ connect q_i with q_i' in the interval $\hbar\beta$ ($\beta = 1/k_BT$). The contribution of each path is weighted by $\exp(i\Sigma[\bar{q},q,q']/\hbar)$ with an effective action Σ [1,12] not written down here explicitly. The real time paths describe the dynamics of the system and the imaginary time paths specify the initial probability distribution

$$P(q_i,0) = [\rho_\beta(q_i,q_i')\Lambda(q_i,q_i')]_{q_i=q_i'}\,, \qquad (2)$$

where $\rho_\beta(q,q') = \langle q|\mathrm{Tr}_R\exp(-\beta H)|q'\rangle$ is the reduced equilibrium density matrix while the preparation function Λ describes the deviations from equilibrium. This way we avoid a factorizing initial state used in ordinary Feynman-Vernon theory [1], which does not apply for strong friction. In Eq. (1) the influence of the bath is completely determined by the spectral density $I(\omega)$ of the bath oscillators. Effectively, the reduced system gains an additional interaction contribution (influence functional) which is nonlocal in time and strongly depends on friction and temperature. Since the influence functional couples real and imaginary time paths, an exact solution to Eq. (1) is accessible only in certain cases. Here, we explore to what extent the dynamics in (1) can be well approximated by a time evolution equation when the friction is large. For a particle of

mass M we assume Ohmic damping $I(\omega) = 2M\gamma$ (damping constant γ) supplemented by a high frequency cutoff $\omega_c > \gamma$ according to spectral densities in real systems and to avoid the well-known ultraviolet divergencies of a pure Ohmic model. Further, as in the classical SE we take sufficiently smooth potentials for granted in this study.

Harmonic oscillator.—For the quantum Brownian motion in the harmonic potential $V(q) = \frac{1}{2}M\omega_0^2 q^2$ the propagating function is known exactly [1,12]. To get insight in the Smoluchowski simplification we particularly study the relaxation of $\langle q(t)\rangle$ and $\langle p(t)\rangle$ in the overdamped limit $\gamma/\omega_0 \gg 1$ and for times $t \gg 1/\gamma$. One finds $\langle q(t)\rangle \approx \langle q(t)\rangle_{\rm cl} + \delta q(t)$ and $\langle p(t)\rangle \approx \langle q(t)\rangle_{\rm cl}/\gamma + M\delta\dot{q}(t)$. The classical part shows the well-known sluggish decay $\langle q(t)\rangle_{\rm cl} \propto \exp(-\omega_0^2 t/\gamma)$ and to leading order $\langle p(t)\rangle \approx M\delta\dot{q}(t)$. Quantum effects show up in $\delta q(t)$ which depends on the initial correlations between system and bath and for temperatures $T > 0$ decays as $\exp(-\nu t)$ where $\nu = 2\pi/\hbar\beta$ is the Matsubara frequency. Hence, on the time scale where the position relaxes, i.e., γ/ω_0^2, the momentum can be considered as already equilibrated, i.e., $\langle p(t)\rangle \approx 0$, only if a separation of time scales is guaranteed, i.e., $\gamma/\omega_0^2 \gg \hbar\beta, 1/\gamma$ (cf. Fig. 1). This latter condition defines the Smoluchowski range also for temperatures where quantum fluctuations are important. Now, neglecting terms of order $\exp(-\gamma t)$ and $\exp(-\nu t)$ or smaller the time evolution for $P(q,t)$ follows from

$$\partial_t P(q,t) = (\omega_0^2/\gamma)\partial_q[q + \langle q^2\rangle\partial_q]P(q,t), \qquad (3)$$

where the variance reads

$$\langle q^2\rangle \approx \frac{1}{M\omega_0^2\beta} + \frac{2}{M\beta}\sum_{n\geq 1}\frac{1}{\nu_n^2 + \nu_n\gamma}, \qquad \nu_n = n\nu. \qquad (4)$$

Inspection of the sum in Eq. (4) reveals that the Smoluchowski range $\gamma/\omega_0^2 \gg \hbar\beta, 1/\gamma$ comprises two particular subsets: one is the known classical range, $\gamma \ll \nu$, the other is a quantum mechanical region with $\gamma \gg \nu$, unstudied so far (Fig. 1). While in both ranges to leading order

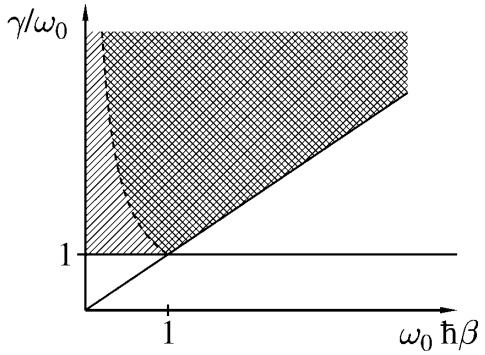

FIG. 1. Smoluchowski range $\gamma/\omega_0^2 \gg \hbar\beta, 1/\gamma$ (shaded). The classical range ($\gamma \ll \nu$) is simple shaded, the quantum range ($\gamma \gg \nu$) double shaded.

$\langle q^2\rangle \approx \langle q^2\rangle_{\rm cl}$, differences appear in the respective corrections. Classically, these are of order $\hbar^2\beta/M$ and negligible against dynamical corrections of order $1/M\beta\gamma^2$. In contrast, in the quantum range to first order

$$\langle q^2\rangle - \langle q^2\rangle_{\rm cl} \approx (\hbar/\pi M\gamma)\log(\hbar\beta\gamma/2\pi) \equiv \lambda \qquad (5)$$

with $\lambda \gg 1/M\beta\gamma^2$. We conclude that for $\hbar\gamma \gg k_{\rm B}T$ the dynamics of the quantum oscillator follows in leading order from the classical SE with quantum fluctuations as the dominating corrections. Since these are no longer algebraically small, they are of substantial relevance (see below). We note in passing that in the quantum range one finds $\langle p^2\rangle \approx (M\hbar\gamma/\pi)[1 + \log(\omega_c/\gamma)]$.

Quantum Smoluchowski equation.—Qualitatively, to leading order we expect the position diagonal element $P(q_f,t)$ to obey the classical SE even in anharmonic potentials and throughout the quantum Smoluchowski range (QSR)

$$\gamma/\omega_0^2 \gg \hbar\beta, 1/\gamma \quad \text{and} \quad \hbar\gamma \gg k_{\rm B}T, \qquad (6)$$

where ω_0 is interpreted as the ground state frequency. To quantify this statement we analyze the path integrals involved in Eq. (1) in more detail. For that purpose, it is convenient to introduce difference and sum real time paths $x = q - q'$ and $r = (q + q')/2$, respectively. Then, it turns out that the action $\Sigma[\bar{q}, x, r]$ has friction dependent parts in imaginary and in real time [12] which suppress nondiagonal matrix elements. Accordingly, to leading order we assume $|\bar{q}(\sigma) - \bar{q}(0)|$ and $|x(s)|$ to be sufficiently small and later verify this ansatz self-consistently.

First, by expanding $\Sigma[\bar{q}, x, r]$ up to second order in the x paths, we arrive at a solvable Gaussian x-path integral where x and r paths are coupled bilinearly. We put $x(s) = x_i + \delta x(s)$ with fluctuations $\delta x(s)$ obeying $\delta x(0) = \delta x(t) = 0$ and to leading order obtain

$$\int \mathcal{D}x\, e^{i(\Sigma[\bar{q},x,r]-\Sigma[\bar{q},0,0])/\hbar} \approx \delta(x_i)e^{-S[r]/4M\gamma k_{\rm B}T} \qquad (7)$$

with the action

$$S[r] = \int_0^t ds\,[M\gamma\dot{r} + V'(r)]^2. \qquad (8)$$

The path integral over the imaginary time path $\bar{q}$ with $\bar{q}(0) = \bar{q}(\hbar\beta) = r_i$ is easily evaluated. It yields a contribution proportional to $\exp[-\beta V(r_i)]$. Eventually, Eq. (1) for $P(q_f,t) = \rho(q_f,q_f,t)$ reduces to

$$P(q_f,t) = \int dq_i\, G(q_f,t,q_i)P(q_i,0). \qquad (9)$$

Here, the propagator stems from the remaining r-path integral and thus, is a sum over all paths $r(s)$ with $r(0) = q_i, r(t) = q_f$ where each contribution is weighted with $\exp(-S[r]/4M\gamma k_{\rm B}T)$. However, this is exactly the path integral representation of the classical Smoluchowski dynamics [6]. Hence, to leading order the quantum SE looks like the classical one also for anharmonic potentials: $\partial_t P = (1/M\gamma)\partial_q\hat{L}_{\rm cl}P$ with

$$\hat{L}_{\rm cl} = V' + k_{\rm B}T\partial_q, \qquad (10)$$

where $V'(q) = dV(q)/dq$. To justify our initial assumption we estimate that $[\bar{q}(\sigma) - \bar{q}(0)]^2$ is at most of order λ [see Eq. (5)] and $x(s)^2$ at most of order $\hbar^2\beta/M\gamma t$.

Of course, the most interesting issue is to specify contributions from quantum fluctuations to Eq. (10). However, before we do so let us first look at the simpler static problem and determine the equilibrium distribution. In the relevant parameter range the path integral for $P_\beta(q) = \rho_\beta(q,q)$ is calculated by putting $\bar{q}(\sigma) = \bar{q}_{\rm ma}(\sigma) + y(\sigma)$. The minimal action path $\bar{q}_{\rm ma}$ with $\bar{q}_{\rm ma}(0) = \bar{q}_{\rm ma}(\hbar\beta) = q$ and its Euclidean action $S[\bar{q}_{\rm ma}]$ are evaluated up to terms linear in λ. The result is $S(q)/\hbar = \beta[V(q) - \lambda\beta V'(q)^2/2]$. The path integral over y is approximated by a Gaussian integral since $(\bar{q}_{\rm ma} - y)^2 \lesssim O(\lambda)$ and is solved by expanding $y(\sigma) = \frac{1}{\hbar\beta}\sum y_n \exp(i\nu_n\sigma)$ with the boundary condition $\Sigma y_n = 0$. As an important result we obtain the unnormalized equilibrium position distribution in the QSR

$$P_\beta(q) = P_\beta^{\rm cl}(q)\exp\{\lambda\beta[\beta V'(q)^2/2 - 3V''(q)/2]\} \tag{11}$$

with $P_\beta^{\rm cl}(q) = \exp[-\beta V(q)]$. Next order corrections are much smaller, namely, of order $(\hbar\beta V''/M\gamma)^2$. Amazingly, for low temperatures P_β will be squeezed by friction without limit.

Let us now turn to the dynamical aspect of the QSR and evaluate quantum fluctuations to Eq. (10). For this purpose we write $\partial_t P = (1/M\gamma)\partial_q \hat{L}_{\rm qm} P$ with $\hat{L}_{\rm qm} = \hat{L}_{\rm cl} + \lambda\delta\hat{L}$ where $\hat{L}_{\rm cl}$ is given in (10) and $\delta\hat{L} = \delta V' + \delta D\partial_q$ with appropriate corrections to the potential and diffusion terms. To determine δV and δD requires one to solve the full dynamical problem Eq. (1) perturbatively in λ. Further, we need only to study the broad time range $\hbar\beta, 1/\gamma \ll t < \gamma/\omega_0^2$. Once we have $\delta\hat{L}$ in this time interval, we have it for all times as the time scale separation renders the operator $\hat{L}_{\rm qm}$ time independent on the coarse grained time scale (6). The general strategy is as above: evaluate the minimal action paths to $\Sigma[\bar{q}, x, r]$ and the corresponding fluctuations including corrections of order λ. Again, a small x expansion of Σ allows us to neglect higher than bilinear couplings between x and r paths. Within the relevant time range it is also consistent to assume the difference $|r(s) - r_i|$ to be sufficiently small so that we may write $V[r(s)] \approx V(r_i) + V'(r_i)[r(s) - r_i] + V''(r_i)/2[r(s) - r_i]^2$.

The solution to the classical x path is then simply $x_{\rm cl}(s) = x_i \exp[-sV''(r_i)/M\gamma]$. Since the r path is coupled to both the x and the $\bar{q}$ path, the expression for $r_{\rm cl}$ is rather lengthy and not given here. The same holds true for the imaginary time path, which can be put in the form $\bar{q}(\sigma) = r_i + \lambda\bar{q}_1[\sigma; x]$ where $\bar{q}_1$ contains also the coupling to the x path. As for the equilibrium case, the fluctuation path integrals can be evaluated in a Gaussian approximation: The contribution from the imaginary time path reads as in Eq. (11), while the real time path integrals provide a factor of order γ. As a result we gain the propagating function in the QSR which determines $P(q,t)$ via ordinary integrations over the initial coordinates x_i and r_i; see Eq. (1). Now, further progress can be made by introducing the scaled coordinate $k_i = x_i\gamma$. Then, as a function of k_i the propagating function is basically a Gaussian with a width of order $M\gamma\beta/t$, so that for sufficiently smooth preparations in x_i space, i.e., sufficiently localized preparations in momentum space, it is consistent to set $\Lambda(k_i/\gamma, r_i) \approx \Lambda(0, r_i)$. This allows us to carry out the k_i integration. The time evolution of $P(q,t)$ in the QSR and within the relevant time range is therefore of the form (9) with the propagator

$$G(q,y,t) = \frac{1}{\sqrt{4\pi\sigma(y,t)}}\, e^{-[q-r(y,t)]^2/4\sigma(y,t)}. \tag{12}$$

Here, the width is $\sigma = \sigma_0 + \lambda\sigma_1$ with $\sigma_0 = (t/M\gamma\beta)[1 - V''t/M\gamma]$ and $\sigma_1 = -[1 - V''t/M\gamma]$, and the local motion reads $r = r_0 + \lambda r_1$ with $r_0 = y - [V't/M\gamma](1 - V''t/2M\gamma)$ and $r_1 = y\beta V''\sigma_1$.

The propagator (12) is now used to determine $\delta V'$ and δD in $\hat{L}_{\rm qm}$. Starting from Eq. (9) one applies $\partial_t - (1/M\gamma)\partial_q\hat{L}_{\rm qm}$ to $G(q,y,t)$ and then expands y dependent terms in the integral up to second order around $y = q$. After tedious algebra we find $\delta V' = 3V'''/2$ and $\delta D = V''$. This leads us to the central result of this paper, namely, the dynamical equation of an overdamped quantum system, the so-called quantum Smoluchowski equation, $\partial_t P = (1/M\gamma)\partial_q\hat{L}_{\rm qm}P$ with

$$\hat{L}_{\rm qm} = V' + \lambda V'''/2 + k_{\rm B}T\partial_q[1 + \lambda\beta V'']. \tag{13}$$

Two observations can be made here: First, quantum effects give rise to a temperature and friction dependent effective potential $V_{\rm eff} = V + (\lambda/2)V''$ and a friction and position dependent effective diffusion term $D_{\rm eff} = k_{\rm B}T[1 + \lambda\beta V'']$. Second, seen as a continuity equation it turns out that the equilibrium distribution Eq. (11) indeed fulfills $\hat{L}_{\rm qm}P_\beta = 0$. Corrections to the QSE are of order $\beta(V''\hbar)^2/M^3\gamma^3$ and can thus safely be disregarded in the QSR.

Having the evolution equation for $P(q,t)$ at hand the quantum analog to the classical Langevin equation can also be given. It is (in the Stratonovich sense [13])

$$M\gamma\dot{q}(t) + V'(q) + \lambda V''' = \sqrt{1 + \lambda\beta V''}\,\xi(t) \tag{14}$$

with Gaussian noise $\langle\xi(t)\rangle = 0$ and $\langle\xi(t)\xi(t')\rangle = 2M\gamma k_{\rm B}T\delta(t - t')$. Hence, the quantum stochastic process in the QSR is equivalent to a classical process in an effective potential and with multiplicative noise.

Applications.—We illustrate the significance of quantum fluctuations in the QSR in the following two paradigmatic applications:

Imagine a metastable barrier potential $V(q)$ where the barrier height V_b is the largest energy scale in the system, i.e., $V_b \gg k_{\rm B}T$. Then, preparing the system initially in an equilibrium state restricted to the well region

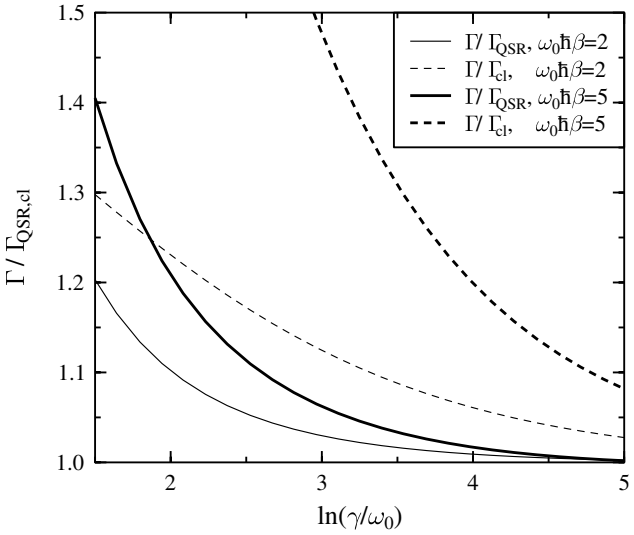

FIG. 2. Ratio of the exact rate with the classical (dashed) and the Smoluchowski (solid) rate vs friction for $|V''(q_b)| = V''(0) = M\omega_0^2$.

(around $q = 0$), for intermediate times (plateau range) the distribution becomes quasistationary $P(q,t) \rightarrow P_{\rm st}(q)$. This state corresponds to a constant flux across the barrier (around $q = q_b$) $J_{\rm st} = (1/M\gamma)\hat{L}_{\rm qm}P_{\rm st}$ determining the escape rate through $\Gamma = J_{\rm st}/N$ with the normalization N given by the well population. Now, adopting the classical procedure we obtain from Eq. (13)

$$\Gamma_{\rm QSR} = \frac{\sqrt{V''(0)|V''(q_b)|}}{M\gamma}\, e^{-\beta V_b} e^{\lambda\beta[V''(0)+|V''(q_b)|]}. \quad (15)$$

Here, the second factor accounts for the quantum fluctuations and is not small at all (see Fig. 2). The point is that λ dependent terms in the QSE enter exponentially and thus lead to a substantial rate increase compared to the classical rate. Already for moderate friction $\Gamma_{\rm QSR}$ agrees well with the exact rate (for $V_b/k_{\rm B}T \gg 1$) [14].

In order to analyze $V_{\rm eff}$ and $D_{\rm eff}$ in more detail we consider the dynamics of a Gaussian wave packet in a bistable potential $V(q) = -M\omega_0^2 q^2/2[1 - q^2/2q_a^2]$. The barrier top is located at $q = 0$ and the wells at $q = \pm q_a$. Then, scaling times with γ/ω_0^2 and coordinates with $\sqrt{\hbar/M\omega_0}$ we solve the time evolution of a wave packet initially localized near the barrier top numerically also for longer times. High precision results are presented in Fig. 3 for $\langle q(t)\rangle$ at two different temperatures. For moderate temperature the influence of $V_{\rm eff}$ prevails: the barrier height is diminished, i.e., $V_{{\rm eff},b} = V_b - 3\lambda M\omega_0^2/2$, thus increasing the population around $q = 0$ so that $\langle q(t)\rangle < \langle q(t)\rangle_{\rm cl}$. In contrast, at low temperatures diffusion effects dominate as the spreading of the wave packet near $q = 0$ is retarded since the local effective temperature is lowered $T_{\rm eff}(0) < T$, i.e., $\langle q(t)\rangle > \langle q(t)\rangle_{\rm cl}$.

To summarize we have derived the time evolution equation for dissipative quantum systems in the strong friction regime and have shown the substantial impact of quantum fluctuations. As the classical Smoluchowski limit is of importance for all overdamped systems at high temperatures, our results have potentially an equally wide range of applications for overdamped quantum systems in low temperature physics and chemistry.

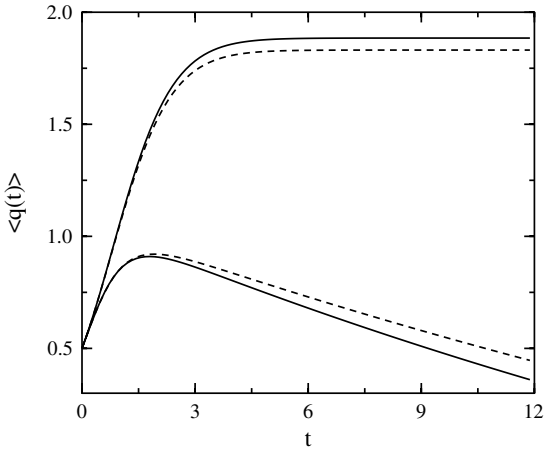

FIG. 3. Mean position vs time of a Gaussian wave packet with $\langle q(0)\rangle = 0.5$ moving in a bistable potential. Dashed (solid) lines are classical (quantum) results with $\lambda = 0.035$. Lower (upper) curves are for $\omega_0\hbar\beta = 1$ ($\omega_0\hbar\beta = 6$).

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