

Extraction of Work from a Single Thermal Bath in the Quantum Regime

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The stationary state of a quantum particle strongly coupled to a quantum thermal bath is known to be non-Gibbsian, due to entanglement with the bath. For harmonic potentials, where the system can be described by effective temperatures, thermodynamic relations are shown to take a generalized Gibbsian form that may violate the Clausius inequality. For the weakly anharmonic case, a Fokker-Planck-type description is constructed. It is shown that then work can be extracted from the bath by cyclic variation of a parameter. These apparent violations of the second law are the consequence of quantum coherence in the presence of the slightly off-equilibrium nature of the bath.

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The laws of thermodynamics are at the basis of our understanding of nature, so we all expect them to govern also systems coupled to a bath in the quantum regime. However, recently thought-provoking claims were made about a violation of Thomson's formulation of the second law (the impossibility to do work periodically without losing heat) [1] and even about a perpetuum mobile acting in an inhomogeneous superconducting ring [2].

Most of our thermodynamic understanding is based on the Gibbs distribution. The laws of equilibrium thermodynamics apply equally well to closed classical and quantum systems, as to open classical subsystems [3]. The setting for the classical case is well known: Under general statistical conditions [3–6] one derives a Langevin equation. The corresponding probability distribution is described by the Fokker-Planck equation, and it converges in time to the Gibbs distribution.

Much less is known about the quantum Langevin equation [3,4,6–8]. The stationary distribution has been obtained only for the harmonic potential. It depends explicitly on the damping constant and becomes Gibbsian only in the limit of weak damping [3,4], thus preventing the applicability of equilibrium thermodynamics. Entanglement is the very reason of this crucial difference, as subsystems are necessarily in a mixed state.

In the present paper, we examine the standard model for quantum Brownian motion, the so-called Caldeira-Leggett model [9]; see Eq. (1). Here, we employ methods developed recently for glasses [10]. For a particle in harmonic potential we define effective temperatures, and put the thermodynamic relations in a generalized Gibbsian form. For weakly anharmonic confining potentials Fokker-Planck equations will be constructed, which allow one to obtain the stationary distribution and elucidate important aspects of nonstationary properties.

We shall provide a nontrivial thermodynamic interpretation for the relaxation towards the steady non-Gibbsian state and for the slow change of a system parameter. Our

main results are rather dramatic, apparently contradicting the second law: We show that the Clausius inequality $\dot{d}Q \leq TdS$ can be violated, and that it is even possible to extract work from the bath by cyclic variations of a parameter ("perpetuum mobile"). The physical cause for this appalling behavior will be traced back to quantum coherence in the presence of the near-equilibrium bath.

The quantum Langevin equation is derived from the exact Hamiltonian description of a particle and a thermal bath, when tracing out the degrees of freedom of the bath. For $t < 0$, the particle and bath do not interact, and the whole system is described by a density matrix $\rho_0 = \rho_b \otimes \rho_s$, where $\rho_b \sim \exp(-\beta \mathcal{H}_b)$ is the Gibbs distribution for the bath, and ρ_s describes the state of the particle. At $t = 0$ a linear coupling is switched on instantaneously, and the total Hamiltonian reads as follows for $t > 0$ [6]:

$$\mathcal{H} = \frac{p^2}{2m} + V(x) + \sum_i \left[\frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} \left(x_i - \frac{c_i x}{m_i \omega_i^2} \right)^2 \right], \quad (1)$$

where p , p_i , x , x_i , and m , m_i are, respectively, the momentum and coordinate operators and the masses of the particle and the modes of the bath. The latter have a constant frequency gap Δ , so $\omega_i = i\Delta$. For the couplings we choose the Drude-Ullersma spectrum [6,8,11],

$$c_i = \sqrt{\frac{2\gamma m_i \omega_i^2 \Delta}{\pi} \frac{\Gamma^2}{\omega_i^2 + \Gamma^2}}, \quad (2)$$

where γ is the damping constant, quantifying the strength of interaction, and Γ is the cutoff frequency of the interaction with the bath. The thermodynamic limit is taken for the bath by sending $\Delta \rightarrow 0$, which creates an infinite "Heisenberg" time scale $1/\Delta$.

For fast switching on the interaction, an amount of work

$$\mathcal{W}_0 = \text{tr}\{\rho_0[\mathcal{H}(0^+) - \mathcal{H}(0^-)]\} = \frac{\gamma\Gamma}{2} \text{tr}(\rho_s x^2) \quad (3)$$

has to be supplied to the system. The large internal energy of the whole system $U = \langle p^2 \rangle_0 / 2m + \langle V \rangle_0 + \pi^2 T^2 / (6\hbar\Delta) \sim 1/\Delta$ is increased by the finite amount \mathcal{W}_0 . This brings the system slightly out of equilibrium, since the von Neumann entropy $\text{tr}(-\rho_0 \ln \rho_0)$ is exactly conserved under the switching. Notice that the switching energy $\mathcal{W}_0 = \frac{1}{2}\gamma\Gamma\langle x^2 \rangle_0$ is purely a classical effect.

The resulting quantum Langevin equation reads [4,7]

$$\dot{p} + \frac{\gamma\Gamma}{m} \int_0^t dt' e^{-\Gamma(t-t')} p(t') + V'(x) = \eta(t), \quad (4)$$

with Gaussian noise having $\langle \eta \rangle = 0$ and anticommutator

$$K(t) = \frac{\langle \{\eta(t), \eta(0)\} \rangle}{2} = \int \frac{d\omega}{2\pi} \frac{\gamma\hbar\omega \coth(\frac{1}{2}\beta\hbar\omega) e^{i\omega t}}{1 + (\omega/\Gamma)^2}, \quad (5)$$

which is the consequence of quantum fluctuation-dissipation theorem [3,6]. $K(t)$ has correlation time $\max(1/\Gamma, \hbar/T)$, so the quantum noise has a long memory at low T ("quantum coherence"). Equation (4) with physically suitable forms of the potential and friction describes a rich variety of physical phenomena, such as Josephson junctions [12,13], processes in plasma and condensed matter [3,4,8], interaction of atoms with blackbody radiation [3], and the Lamb shift of an electron [3].

We shall restrict ourselves to the *quasi-Ohmic* case, where Γ is much larger than other characteristic times. For $t \gg 1/\Gamma$ we may expand the memory kernel in Eq. (4):

$$\Gamma \int_0^t dt' e^{-\Gamma(t-t')} p(t') = p(t) - \frac{\dot{p}(t)}{\Gamma}. \quad (6)$$

Compared to the classical white noise case, one can thus adjust only the noise [see Eq. (5)], while keeping the friction instantaneous. The same conclusion was reached in Refs. [14,15] for the exactly solvable harmonic potential.

Work and heat.—Let us explain the ingredients for the thermodynamic description of the Brownian particle having Hamiltonian $H = p^2/2m + V(x)$ and Wigner function $W(p, x, t) = \langle \delta(p(t) - p)\delta(x(t) - x) \rangle$. A change with time of the mean energy $U = \langle H \rangle \equiv \int dp dx WH$ is considered when slowly varying a system parameter α , such as m or $V''(0)$, according to a prescribed trajectory $\alpha(t)$:

$$dU \equiv d\langle H \rangle = \langle Hd \ln W \rangle + \langle dH \rangle. \quad (7)$$

The last term is the averaged mechanical work $\bar{d}\mathcal{W}$ produced by external sources [3,16]. For a variation of an intrinsic parameter (for which $dH = d\mathcal{H}$), $\bar{d}\mathcal{W}$ is the change of the total (particle + bath) mean energy. The first term on the right-hand side is due to the statistical redistribution in phase space. We shall identify it with the change of heat $\bar{d}\mathcal{Q} = \langle Hd \ln W \rangle$, so Eq. (7) is just the first law.

In the harmonic case $V(x) = \frac{1}{2}ax^2$, Eqs. (4) and (6) can be integrated directly; see, e.g., [6,11,14,15]. In particular, the stationary Wigner distribution reads

$$W_s(p, x) = \frac{1}{2\pi} \sqrt{\frac{a}{mT_p T_x}} \exp\left[-\frac{p^2}{2mT_p} - \frac{ax^2}{2T_x}\right]. \quad (8)$$

The effective temperatures T_p and T_x approach T in the classical limit, and have for large damping, $\gamma^2 \gg am$, the following values at $T \rightarrow 0$:

$$T_p = \frac{\hbar\gamma}{\pi m} \ln \frac{\Gamma m}{\gamma} + \frac{\hbar a}{\pi\gamma}, \quad T_x = \frac{\hbar a}{\pi\gamma} \ln \frac{\gamma^2}{am}. \quad (9)$$

The Brownian particle has semiclassical behavior due to its interaction with the bath, and entropy $S = S_p + S_x$ with $S_p = \frac{1}{2} \ln emT_p/\hbar$, $S_x = \frac{1}{2} \ln eT_x/a\hbar$.

For an adiabatic variation of a parameter α , the situation is still described by Eq. (8) with $\alpha = \alpha(t)$. One can check for U and the free energy $F = U - T_p S_p - T_x S_x$:

$$dU = \bar{d}\mathcal{Q}_{\text{ad}} + \bar{d}\mathcal{W}_{\text{ad}} = T_p dS_p + T_x dS_x + \bar{d}\mathcal{W}_{\text{ad}}, \quad (10)$$

$$dF = -S_x dT_x - S_p dT_p + \bar{d}\mathcal{W}_{\text{ad}}. \quad (11)$$

These generalized thermodynamical relations are in close analogy with those proposed for glassy systems [10].

To demonstrate a violation of the fundamental Clausius inequality $d\mathcal{Q} \leq TdS$, we consider a slow variation of the mass m at $T \rightarrow 0$. Using Eqs. (8)–(10), one gets

$$\bar{d}\mathcal{W}_{\text{ad}} = -T_p \frac{dm}{2m}, \quad \bar{d}\mathcal{Q}_{\text{ad}} = \frac{\hbar\gamma}{m^2\pi} \frac{dm}{2}. \quad (12)$$

Thus, there is transfer of heat even for $T = 0$, and the Clausius inequality is violated when $\bar{d}\mathcal{Q} > 0$, i.e., for $dm > 0$. The latter also happens when varying a .

The Fokker-Planck equation.—Except for the solvable harmonic potential, Eq. (4) is hardly tractable. Another approach, having started from (4), goes further to the weak-coupling (small γ) limit described by a Markovian master equation [4]. In the opposite, strong-coupling limit one can consider the terms in (4) as c numbers, but with the quantum noise correlator [12,13]. The correspondence with the underlying quantum problem is established through the Wigner function. Since this approach is still exact for the harmonic case, one of the conditions of its validity involves a characteristic scale L where the nonlinearity remains small: $L \gg \sqrt{\hbar/\gamma}$ [12]. Based on this condition, we have derived a closed equation for the Wigner function. Here, we give only the final result, while details will be presented elsewhere [17]:

$$\begin{aligned} \frac{\partial W(x, p, t)}{\partial t} = & -\frac{p}{m} \frac{\partial W}{\partial x} + \frac{\partial}{\partial p} \left\{ \left[\frac{\gamma}{m} p + V'(x) \right] W \right\} \\ & + \frac{\partial^2}{\partial p \partial x} [D_{xp}(x, t)W] \\ & + \gamma D_{pp}(x, t) \frac{\partial^2 W}{\partial p^2}. \end{aligned} \quad (13)$$

For our purposes it is enough to indicate the stationary values of the diffusion coefficients D_{xp} and D_{pp} :

$$D_{pp}(x) = \int_0^\infty \frac{d\omega}{\pi m} \frac{\bar{K}(\omega)\omega^2}{(\omega^2 + \omega_1^2)(\omega^2 + \omega_2^2)}, \quad (14)$$

$$D_{xp}(x) = \int_0^\infty \frac{d\omega}{\pi m^2} \frac{\bar{K}(\omega)[V''(x) - m\omega^2]}{(\omega^2 + \omega_1^2)(\omega^2 + \omega_2^2)},$$

where $\bar{K}(\omega)$ is the spectrum of $K(t)$ in Eq. (5) and $\omega_{1,2} = [\gamma \pm \sqrt{\gamma^2 - 4mV''(x)}]/(2m)$. Equation (13) was derived under the same assumptions as the semiclassical Langevin equation itself. For ensuring the convergence of the diffusion coefficients [$\text{Re}(\omega_{1,2}) \geq 0$], we will demand $V'' \geq 0$ (local stability). In the classical limit, $D_{xp} \rightarrow 0$, $D_{pp} \rightarrow T$, and Eq. (13) tends to the usual Fokker-Planck equation [4,11]. For the harmonic case, D_{xp} and D_{pp} become space independent, and Eq. (13) is in agreement with previous results [11,14,15], obtained for a more general type of the environment.

In the physically interesting case of overdamped motion, where the characteristic times of the momenta m/γ and coordinate $\gamma/V''(0)$ are widely separated, $\gamma/V''(0) \gg m/\gamma$, a solution of the Fokker-Planck equation for $t \gg m/\gamma$ can be presented as

$$W(p, x, t) = \frac{\exp\{-p^2/[2mD_{pp}(x, t)]\}}{\sqrt{2\pi mD_{pp}(x, t)}} W(x, t). \quad (15)$$

Here, $W(x, t)$ is the solution of a reduced equation

$$\partial_t W(x, t) + \frac{\partial J(x, t)}{\partial x} = 0, \quad (16)$$

$$J = -\frac{1}{\gamma} V'(x)W(x, t) - \frac{1}{\gamma} \frac{\partial}{\partial x} [D(x, t)W(x, t)], \quad (17)$$

$$D(x, t) = D_{xp}(x, t) + D_{pp}(x, t). \quad (18)$$

It still contains the inhomogeneous, time-dependent diffusion coefficient. As we discussed, a large, but finite, $\Gamma \gg \omega_{1,2}$ is necessary only for the statistics of the momenta; see Eq. (9). Taking $\Gamma \rightarrow \infty$ in Eq. (18), we obtain

$$D(x) = \frac{\hbar\gamma V''(x)}{\pi m^2} \int_0^\infty d\omega \frac{\omega \coth(\frac{1}{2}\beta\hbar\omega)}{(\omega^2 + \omega_1^2)(\omega^2 + \omega_2^2)}. \quad (19)$$

In the stationary state, one has $J(x) = 0$, which implies for the corresponding distribution

$$W_s(x) = \frac{e^{-\beta V_e(x)}}{Z}, \quad (20)$$

$$V_e(x) = T \int_0^x dy \frac{V'(y) + D'(y)}{D(y)},$$

where V_e is an effective potential. Notice that $W_s(x)$ is non-Gibbsian. For the harmonic potential, Eq. (8) is recovered from this expression while the classical Gibbs distribution appears in the limit $\hbar\beta \rightarrow 0$. Equations (15) and (20) show that the statistics of momenta is influenced by the coordinate, yielding its non-Maxwellian form.

In the classical case, universal (thermodynamical) properties of the relaxation are described by an \mathcal{H} theorem, which is intimately connected with a formulation of the second law [3,5]. This theorem can be generalized in our case, at least for times $t \gg m/\gamma$, where the momenta already came to the local equilibrium, and the relevant variable is x . The \mathcal{H} function is defined as [3,5]

$$\mathcal{H} = \int dx W_1(x, t) \ln \frac{W_1(x, t)}{W_2(x, t)} \geq 0, \quad (21)$$

where $W_{1,2}(x, t)$ are solutions of Eq. (16) corresponding to different initial conditions. Calculating $\dot{\mathcal{H}}$ from Eq. (16), one performs partial integrations to obtain

$$\dot{\mathcal{H}} = -\frac{1}{\gamma} \int dx W_1(x, t) D(x, t) \left[\frac{\partial}{\partial x} \ln \frac{W_1(x, t)}{W_2(x, t)} \right]^2. \quad (22)$$

Since $D(x, t) > 0$, \mathcal{H} is a monotonically decreasing function, and attains its minimum in the stationary state [5]. On the other hand, \mathcal{H} is limited from below by zero, so we conclude that all solutions of the Fokker-Planck equation (16) converge with time to the stationary solution. Let us define the currentless state $W_s(x, t)$, obtained from $W_s(x)$ by the substitution $D(x) \rightarrow D(x, t)$. Starting from Eq. (22), one can show that the entropy of the coordinate sector obeys

$$\frac{dS_x}{dt} = - \int dx \dot{W}(x, t) \ln W(x, t) = \frac{d_e S_x}{dt} + \frac{d_i S_x}{dt}. \quad (23)$$

Here the quantity

$$\frac{d_e S_x}{dt} = \int dx \dot{W}(x, t) \ln \frac{1}{W_s(x, t)} = \int dx J(x) \beta V'_e(x, t)$$

can be interpreted as the flux of entropy. Indeed, $J(x)$ is the probability current and $-\beta V'_e$ represents a force divided by temperature. The second term in (23),

$$\frac{d_i S_x}{dt} = \frac{1}{\gamma} \int dx W(x, t) D(x, t) \left[\frac{\partial}{\partial x} \ln \frac{W(x, t)}{W_s(x, t)} \right]^2,$$

is the *entropy production* during the relaxation. This quantity is strictly positive out of the steady state, and becomes zero in the long-time limit. In the classical case, Eq. (23) leads to the well-known relation $TdS_x = \bar{d}Q + Td_iS_x$, since $W_s(x, t)$ becomes time independent and coincides with the Gibbs distribution. Although, in the general quantum case this relation is broken, it can still be recovered in the harmonic case. Applying Eq. (23), we find $T_p dS_p + T_x dS_x = dU + \bar{d}\Pi$, where $T_p(t) = D_{pp}(t)$ and $T_x(t) = D(t)$ are the time-dependent effective temperatures, and $\bar{d}\Pi = T_x d_iS_x \geq 0$ is the energy dissipated during the relaxation.

Returning to the case of varying a system parameter, we are now interested in the first nonadiabatic correction to the stationary distribution, arising when the time of the variation is large, but finite. Since the dynamics is in

the overdamped regime, the main correction comes from the deviation of $W(x, t)$ [and not the full $W(p, x, t)$] from its stationary form. The variation starts at $t = t_i$ (the particle already reached its stationary state), and ends at $t = t_f$. We shall assume a “smooth” start of the variation, i.e., $\dot{\alpha}(t_i) = 0$. It can be checked directly from Eq. (16) that W now reads as follows for small $\dot{\alpha}$:

$$W(x, t) = W_s(x, \alpha) \left[1 + \frac{\gamma}{T} \dot{\alpha} [B(x, t) - \langle B \rangle] \right], \quad (24)$$

$$B(x, t) = \int_{-\infty}^x \frac{dy}{D(y, \alpha) W_s(y, \alpha)} \mathcal{A} \left(y, \frac{\partial V_e}{\partial \alpha} \right), \quad (25)$$

$$\mathcal{A}(y, f) = \int_y^{\infty} dz W_s(z, \alpha) [f(z) - \langle f \rangle], \quad (26)$$

where $\alpha = \alpha(t)$ and the average is taken with respect to $W_s(x, \alpha)$. The work finally becomes $\bar{d}\mathcal{W} = \bar{d}\mathcal{W}_{\text{ad}} + \bar{d}\Pi$, with

$$\bar{d}\mathcal{W}_{\text{ad}} = \dot{\alpha} dt \int dx dp W_s(p, x, \alpha) \frac{\partial H(p, x, \alpha)}{\partial \alpha}, \quad (27)$$

$$\bar{d}\Pi = \frac{\gamma}{T} \dot{\alpha}^2 dt \int \frac{dx \mathcal{A}(x, \partial_\alpha V) \mathcal{A}(x, \partial_\alpha V_e)}{D(x, \alpha) W_s(x, \alpha)}. \quad (28)$$

In the Gibbsian case at large T , where $V_e \rightarrow V$, one recovers $\mathcal{W}_{\text{ad}} = U - TS$ and the known result for $\bar{d}\Pi \geq 0$ [3,16]. We stress that $\bar{d}\Pi$ is always relevant for cyclic processes $\alpha(t_i) = \alpha(t_f)$, where $\Delta \mathcal{W}_{\text{ad}} = 0$.

For the oscillator with $V(x) = ax^2/2 + gx^4/12$ with small g , the anharmonicity is displayed at the scale $L = \sqrt{a/g} \gg \langle |x| \rangle$. We shall now investigate the nonadiabatic correction to the work caused by temporal variation of L . For $T \rightarrow 0$ we additionally take the limit of large γ in Eqs. (19) and (20), which yields

$$\beta V_e(x) \rightarrow \frac{\gamma \pi}{2\hbar \ln \gamma} \left[\frac{x^2}{6} + \frac{L^2}{3} \ln \left(1 + \frac{x^2}{L^2} \right) \right]. \quad (29)$$

Although $\partial_L V(x) = -[a/(6L^3)]x^4$ is negative, $\partial_L V_e(x) \approx +[\gamma \pi T / (6\hbar L^3 \ln \gamma)]x^4$ is positive. Therefore $\bar{d}\Pi$ is negative. For small g , we obtain from Eqs. (28) and (29),

$$\Delta \Pi = -\frac{7}{3} \gamma \left[\frac{2\hbar \ln \gamma}{\pi \gamma} \right]^3 \int_{t_i}^{t_f} dt \frac{\dot{L}^2(t)}{L^6(t)}. \quad (30)$$

The possibility to extract this energy from the bath is due to its nonequilibrium state, which is ensured by the energy (3) supplied in the switching.

In conclusion, we have considered a Brownian quantum particle strongly interacting with a quantum thermal bath. The non-Gibbsian statistics of the particle is completely described by Fokker-Planck equations [(13) and (16)]. An \mathcal{H} theorem is formulated in Eqs. (22) and (23). For the harmonic potential, generalized Gibbsian relations can be constructed in terms of effective temperatures (8) and (9), as happens also in glassy systems [10]. Two formulations of the second law, namely, the Clausius inequality and the impossibility to extract work during cyclical variations, can be apparently violated at low temperatures. One could thus speak of a “perpetuum mobile of the second kind.” We

should mention, however, that the number of cycles can be large, but not arbitrarily large. As a result, the total amount of extractable work is modest [17]. In any case, the system energy can never be less than its ground state energy.

These violations of the second law are due to quantum coherence in the presence of the slightly off-equilibrium nature of the bath. This coherence is reflected in the quantum noise correlation time $\max(1/\Gamma, \hbar/T)$, which exceeds the damping time $1/\Gamma$ for $T < \hbar\Gamma/k_B$. We call them apparent violations, since, the standard requirements for a thermal bath not being fulfilled, thermodynamics just does not apply. Let us stress that also in the classical regime the harmonic oscillator bath is not in full equilibrium, but there noise and damping have the same time scale $1/\Gamma$, allowing the Gibbs distribution to save the day and thermodynamics to apply. Our results thus make clear that the characterization of the heat bath should be given with care. If it thermalizes on the observation time, standard thermodynamics always applies. Otherwise, thermodynamics need not have a say.

Let us close by noting that in the harmonic case the unequal effective temperatures do not cause heat currents that equalize them. This situation is reminiscent of the classical paradox that atoms should radiate, but, being in the quantum regime, they do not. The finding that work can be extracted from quantum baths may have a wide scope of applications such as cooling.

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