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On Work and Heat in Time-Dependent Strong Coupling

Erik Aurell [1,2]

[1] KTH—Royal Institute of Technology, AlbaNova University Center, SE-106 91 Stockholm, Sweden; eaurell@kth.se

[2] Departments of Computer Science and Applied Physics, Aalto University, FIN-00076 Aalto, Finland

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Abstract: This paper revisits the classical problem of representing a thermal bath interacting with a system as a large collection of harmonic oscillators initially in thermal equilibrium. As is well known, the system then obeys an equation, which in the bulk and in the suitable limit tends to the Kramers–Langevin equation of physical kinetics. I consider time-dependent system-bath coupling and show that this leads to an additional harmonic force acting on the system. When the coupling is switched on and switched off rapidly, the force has delta-function support at the initial and final time. I further show that the work and heat functionals as recently defined in stochastic thermodynamics at strong coupling contain additional terms depending on the time derivative of the system-bath coupling. I discuss these terms and show that while they can be very large if the system-bath coupling changes quickly, they only give a finite contribution to the work that enters in Jarzynski's equality. I also discuss that these corrections to standard work and heat functionals provide an explanation for non-standard terms in the change of the von Neumann entropy of a quantum bath interacting with a quantum system found in an earlier contribution (Aurell and Eichhorn, 2015).

Keywords: stochastic thermodynamics; strong coupling; Zwanzig model; quantum-classical correspondence for heat

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1. Introduction

Stochastic thermodynamics has become an established paradigm to describe fluctuating work and heat on mesoscopic scales. Main results in this field are fluctuation relations. The archetypal relation is Jarzynski's Equality (JE) [1]:

$$\left\langle e^{-\beta\delta W}\right\rangle_{eq} = e^{-\beta\Delta F} \tag{1}$$

where the average is over an initial equilibrium state at inverse temperature $\beta = \frac{1}{k_B T}$ and the realization of the process, δW is the work done on the system over some time interval and ΔF is the difference in free energy between the states given by the initial and final values of the parameters. While the initial state in (1) is taken to be in equilibrium with a bath, later states and in particular the final state do not have to be. Another key result is the Integral Fluctuation Theorem (IFT) [2], which states that:

$$\left\langle e^{\Delta\log P-\beta\delta Q}\right\rangle = 1 \tag{2}$$

where the average is over the initial position of the system with respect to the initial state (initial probability density) and over the stochastic trajectory of the system from the initial to the final time. $\Delta\log P$, known as stochastic entropy, is the log-change in probability density from an initial position at the initial time to a final position at the final time, and δQ is the heat given off to the environment during the process. A consequence of (2) is a version of the second law $\Delta S_{sys} + \beta \langle \delta Q \rangle \geq 0$ where $S_{sys} = -\sum_i p_i \log p_i$ is the system entropy and ΔS_{sys} is its change from the initial to the final state. Stochastic thermodynamics is covered by several excellent reviews to which I direct the reader for further information and pointers to the literature [3–7].

A limitation of stochastic thermodynamics in the standard formulation is that it neglects the energy stored in the coupling between the system and the bath. This issue was first discussed from different points of view by Cohen and Mauzerall [8], Jarzynski [9] and later by Esposito and co-workers [10]. The scientific question is whether the theory extends also to this setting and in particular if and when the relevant mesoscopic quantities (heat, work) can be taken as functionals (typically stochastic functionals) of the system only. Recently, this has given rise to an active discussion where on one side, one can find [11–13], and on the other [14]; and an intermediate position taken by [15].

The first goal of the present paper is to circumvent part of the ongoing discussion by taking the system-bath coupling dependent on time so that it vanishes at the beginning and the end of a process. Since no energy is then stored in the interactions between the system and the bath, the more involved definitions that can be found in the literature collapse. The work done by the control is simply the sum of the energy changes of the system and the bath between the beginning and the end of the process, while the heat is the change of bath energy. The price to pay are effects arising from the rate-of-change of the system-bath coupling. In particular, there appears from this process a work that is entirely dissipated into heat. When the change of the system-bath coupling is fast, this work is large and can path-wise and on average be (much) larger than the standard Jarzynski work. Due to a cancellation effect, most of it however does not contribute to the average in JE (1).

The second goal is to explain the results on the classical limit of the corresponding quantum problem, which were found in an earlier contribution [16]. The background on the Feynman–Vernon method is well presented in several monographs, e.g., [17], and the extensions to treat heat have now been considered by two other groups; see [18–20]. A time-dependent system-coupling is a further extension of these contributions, but also brings important simplifications. As in the classical case, it allows one to disregard the energy stored in system-bath interaction energy, which is possible, but rather complicated to treat by the Feynman–Vernon-derived method. It will further be shown that the extra term found in [16] was an artifact from assuming that the total density matrix of the system and the bath was initially factorized, while the system and the bath were nevertheless interacting from the beginning of the process. If instead the system-bath coupling goes to zero smoothly at the beginning and the end of the process, the classical limit of heat is recovered fully, and quantum-classical correspondence holds on the level of expected heat.

The paper is organized as follows. In Section 2, I introduce the basic model of a bath of harmonic oscillators with a time-dependent system-bath coupling. Standard material connecting the dynamics of a (large) bath of harmonic oscillators to a stochastic description of the system is given in Appendices A and B. In Section 3, I consider work, internal energy and heat as recently defined in stochastic thermodynamics at strong coupling and relate them to ΔH_B (change of bath energy), and in Section 4, I show how these functionals of the system history are modified when the system-bath coupling depends on time. In Section 5, I discuss the extra work referred to above, and in Section 6, I compare the expectation value of ΔH_B to the earlier computed classical limit of the change of the von Neumann entropy of the bath. In Section 7, I sum up the results. In Appendix C, I discuss for completeness an additional term in the classical limit of the change of the von Neumann entropy that was also found in [16], but which has a different origin than the main focus of this paper.

2. Preliminaries and Definitions of Terms

Throughout this work, I will consider a collection of N harmonic oscillators governed by the Hamiltonian:

$$H_B = \sum_b \frac{p_b^2}{2m_b} + \frac{1}{2}m_b\omega_b^2 q_b^2. \tag{3}$$

The mass and spring constant of oscillator b are m_b and $m_b\omega_b^2$; ω_b is the natural frequency in units of rad/s, and q_b and p_b are respectively the oscillator's coordinate and momentum. The number of oscillators N will be very large, eventually taken to infinity. I will call the collection of oscillators the bath. The bath starts in thermal equilibrium at some inverse temperature β, which will be the bath temperature. I also consider another externally-driven system described by a Hamiltonian:

$$H_S = \frac{P^2}{2M} + V(X,t) \tag{4}$$

where X and P are the position and momentum, and the potential V depends explicitly on time. The system and the bath interact linearly during some finite time interval. The interaction Hamiltonian is thus:

$$H_I(t) = -\sum_b C_b(t) q_b X \tag{5}$$

where the $C_b(t)$ are functions of time. For reasons that will be clear in the following. I add also the Caldeira–Leggett counter-term (a correction to the system potential):

$$H_C(t) = \sum_b \frac{C_b^2(t)X^2}{2m_b\omega_b^2}. \tag{6}$$

The total Hamiltonian of the bath and the system is:

$$H_{TOT} = H_S + H_B + H_I + H_C. \tag{7}$$

The counter-term in (6), the interaction term in (5) and the potential in (3) together form a sum of complete squares, $\sum_b \frac{1}{2}m_b\omega_b^2\left(q_b - \frac{C_b(t)X}{m_b\omega_b}\right)^2$.

The basic setting in the current paper is that all the $C_b(t)$ together rise rapidly from zero to some steady values C_b after an initial time t_i and decrease rapidly back to zero before some final time t_f. The system and the bath are then disconnected before and at time t_i, as well as at and after time t_f. It is natural to postulate that δQ, the heat exchanged between the system and the bath during the process, is ΔH_B, the change of the energy of the bath in the time interval $[t_i : t_f]$. It is also natural to postulate that the work done during a process is the total energy change of the system and the bath, $\delta W = \Delta H_B + \Delta H_S$. With these definitions, work and heat satisfy the first law $\Delta U = \delta W - \delta Q$ where $\Delta U = \Delta H_S$ is the change of the energy of the system. In Section 3 below, I will show that these simple prescriptions are in agreement with strong-coupling stochastic thermodynamics, for the cases under study.

It is well known that a system coupled to an Ohmic bath obeys in the suitable limit the Fokker–Planck equation with an extra harmonic force when the system-bath coupling depends on time:

$$\dot{X} = \frac{P}{M} \qquad \dot{P} = -V'(X,t) + F_{fric} + F_{if} + \xi(t) \tag{8}$$

where ξ is white noise, and the two deterministic forces from the bath on the system are:

$$F_{fric} = -\eta \dot{X} \tag{9}$$

$$F_{if} = -\frac{1}{2}\frac{\dot{\eta}(t)}{\eta(t)} X \tag{10}$$

For completeness, the derivation of (8)–(10) is summarized in Appendix A and B. A main assumption is that each of the coupling constants $C_b(t)$ is proportional to the square root of a time-dependent friction coefficient $\eta(t)$, which encodes all the time-dependence of the system-bath coupling. For the following discussion, it is convenient to introduce, in analogy with the "Sekimoto force" [3,21],

$$F_S = \xi + F_{fric} + F_{if} \tag{11}$$

It is also convenient to introduce an auxiliary quantity with dimension velocity:

$$\dot{X}_B = -\frac{1}{2}\frac{\dot{\eta}(t)}{\eta(t)} X \tag{12}$$

such that:

$$F_{fric} + F_{if} = -\eta \left(\dot{X} - \dot{X}_B \right). \tag{13}$$

The interpretation of $\dot{X}_B$ is that it is a time- and coordinate-dependent velocity of the system such that the force F_S from the bath on the system vanishes in expectation. The velocity $\dot{X}_B$ is zero when the system-bath coupling is constant in time.

3. Work and Heat of Stochastic Thermodynamics at Strong Coupling

We start by reviewing the derivation of Jarzynski's equality at strong coupling following [9], with adjustments arising from time-dependent system-bath coupling. The system and the bath together constitute a closed system, and the work done on the combined system is the change of the total energy:

$$\Delta H_{TOT} = \Delta H_S + \Delta H_B + \Delta H_I + \Delta H_C. \tag{14}$$

As was first shown in [9], the combined system satisfies a Jarzynski equality:

$$\left\langle e^{-\beta \Delta H_{TOT}} \right\rangle_{eq} = e^{-\beta \Delta F_{TOT}} \tag{15}$$

where the average is over the equilibrium state of the combined system and bath and ΔF_{TOT} is the change of total equilibrium free energy. If F_B is the (constant) free energy of the bath, then $\tilde{F}_s = F_{TOT} - F_B$ is the thermodynamic potential (free energy) of the system appropriate for strong coupling [11–13,22], and the quantity appearing in the exponent of the right-hand side of (15) is $\Delta \tilde{F}_s$.

Since we assume that the system and the bath are uncoupled at the initial and the finite time, ΔF_{TOT} in (1) is however in fact here equal to ΔF, the free energy change of the system only. This is one major simplification and a reason for considering a time-dependent system-bath coupling. For the same reason, we can write:

$$\delta W = \Delta H_{TOT} = \Delta H_S + \Delta H_B \tag{16}$$

the other two terms vanishing on the boundaries. On the other hand, in a mechanical system, the change of the total Hamiltonian (14) is given by the direct time-dependence only, and therefore, we also have:

$$\delta W = \int \partial_t H_S + \partial_t H_I + \partial_t H_C \tag{17}$$

which has two extra terms compared to Jarzynski work when the system-bath coupling depends on time. The bath Hamiltonian H_B does not contribute to (17) as it is independent of time.

From here, the reader may continue directly below to Equation (21). To however connect to the recent discussion of heat in stochastic thermodynamics at strong coupling, we note that it starts from a Hamiltonian of the system at mean force [11,12,14]:

$$\mathcal{H} = H_S + H_C - \beta^{-1} \log \left\langle e^{-\beta H_I} \right\rangle_B \tag{18}$$

where the average is over the Boltzmann distribution of the bath only. From this is derived an internal energy function at mean force defined as:

$$E = \mathcal{H} + \beta \partial_\beta \mathcal{H} \tag{19}$$

A main simplification of the model under consideration here is that for a bath of Hamiltonian oscillators linearly coupled to the system, the average in $\mathcal{H}$ cancels with the counter-term H_C, so that for the case at hand, we have simply:

$$E = \mathcal{H} = H_S. \tag{20}$$

The change in this internal energy can be written as a time integral:

$$\Delta E = \int \partial_t H_S + \dot{X} \partial_X H_S + \dot{P} \partial_P H_S. \tag{21}$$

A definition of a path-wise heat functional that satisfies the first law with (16) and (20) is then:

$$\delta Q = \delta W - \Delta E = \Delta H_B. \tag{22}$$

In a round-about way, we have thus arrived at the same notion of heat as in Section 2. Using (17) and (21), we can write δQ as a time integral as:

$$\delta Q = \int \partial_t H_I + \partial_t H_C - \dot{X} \partial_X H_S - \dot{P} \partial_P H_S \tag{23}$$

4. Work and Heat with a Time-Dependent Ohmic Bath

We start by writing out (21), (17) and (23) explicitly for the model at hand:

$$\begin{aligned}
\Delta E &= \int \partial_t H_S + \frac{P}{M} \sum_b C_b \left(q_b - \frac{C_b X}{m_b \omega_b^2} \right) dt & (24) \\
\delta W &= \int \partial_t H_S - X \sum_b \dot{C}_b \left(q_b - \frac{C_b X}{m_b \omega_b^2} \right) dt & (25) \\
\delta Q &= \int \sum_b \left(-\dot{C}_b X - \frac{P}{M} C_b \right) \left(q_b - \frac{C_b X}{m_b \omega_b^2} \right) dt & (26)
\end{aligned}$$

For the change of internal energy, it is seen that the sum over the bath oscillators is the same as that which gives rise to the force F_S in (11) (for details, see Appendixes A and B), and we can thus write:

$$\Delta E = \int (\partial_t H_S) dt + F_S \circ dX \tag{27}$$

The stochastic integral above is in the Stratonovich convention (mid-point prescription in a discretization), as it is the limit of ordinary integrals when the cut-off frequency Ω of the bath is taken to infinity.

Equation (27) is the Jarzynski work ($\int \partial_t H_S dt$) plus a term expressing the work done on the system from the total force F_S that arises from system-bath coupling. It can therefore be read as the sum of the flow of energy into the system from the external system and from the bath, that is the same standard form in stochastic thermodynamics [21]. Equation (27) only involves the time-dependence of the system-bath coupling through the additional force F_{if} entering F_S.

The work functional can be read off by comparing (24) and (25). The sum over oscillators is now not multiplied by $\frac{P}{M}dt = dX$, but by $-X\frac{\dot{C}_b}{C_b}dt$, which is the virtual increment dX_B from (12). The work is therefore:

$$\delta W \quad = \quad \int (\partial_t H_S)dt + F_S \circ dX_B \tag{28}$$

which is the Jarzynski work (the first term) plus the work done by the Sekimoto force through the virtual increment of the system position dX_B. To emphasize the parallelism with (27), the second term has been written as a Stratonovich integral, but it is in fact just an ordinary integral, F_S being a random force acting on momentum variable P and the virtual increment dX_B being proportional to dt. The heat can similarly be written:

$$\delta Q \quad = \quad \int (-F_S) \circ (dX - dX_B) \tag{29}$$

and is the work done by the Sekimoto reaction force $(-F_S)$ through the difference between the actual increment dX and the virtual increment dX_B.

An alternative way to divide up the different contributions to the heat, which will be used in Section 6 below, is:

$$\delta Q \quad = \quad \int -\xi \circ (dX - dX_B) + \left(\frac{d}{dt}(\sqrt{\eta}X)\right)^2 dt \tag{30}$$

When η is constant in time, this reduces to Sekimoto's heat functional $\int -\xi \circ dX + \eta \dot{X}^2 dt$.

5. The Work Done by the Time-Dependent System-Bath Coupling

It has been seen above that both the heat and the work contain a term $\int F_S \circ dX_B$, which is not reflected in the internal energy change at all. Changing the system-bath coupling can be considered an external control acting on the system, which implies a kind of work. An original feature is that this work is entirely dissipated into heat (change of energy of the bath); nothing remains as internal energy changes. Since $\dot{X}_B$ has been assumed non-zero only near the initial and final time, this work is also approximately a change of state function.

The first part of this work, corresponding to the first of the three terms in F_S, is:

$$\int F_{fric} \circ dX_B = \int \frac{P}{2M}\dot{\eta} X \, dt. \tag{31}$$

Assuming that η changes from zero to a finite value $\overline{\eta}$ over a short time period Δt, the force F_{if} is going to dominate all the other forces in the Kramers–Langevin equation (8). This means that we have:

$$P(t) = P_i - \frac{1}{2}\eta X + \mathcal{O}(\sqrt{\Delta t}) \qquad t \in [t_i, t_i + \Delta t] \tag{32}$$

while at the same time:

$$X(t) = X_i + \mathcal{O}(\Delta t) \tag{33}$$

From this, the contribution to (31), from the beginning of the process, is $\frac{X_i P_i}{2M}\overline{\eta} - \frac{X_i^2}{8M}\overline{\eta}^2$ and analogously just before the final time. The contribution of this part is therefore the change of an auxiliary friction-dependent energy:

$$\int F_{fric} \circ dX_B = \Delta V_{frict} + \mathcal{O}(\Delta t) \tag{34}$$

$$V_{frict} = -\frac{\overline{\eta} XP}{2M} + \frac{\overline{\eta}^2 X^2}{8M} \tag{35}$$

The second part of $\int F_S \circ dX_B$ is:

$$\int F_{if} \circ dX_B = \int \frac{1}{4} X^2 \frac{\dot{\eta}^2}{\eta} dt \tag{36}$$

Similarly to above, this can be written as a functional of X_i, P_i and the function η in the interval $[t_i, t_i + \Delta t]$ and the same at the final time. We can therefore write:

$$\int F_{if} \circ dX_B = A_i[X_i, P_i, \eta] + A_f[X_f, P_f, \eta] + \mathcal{O}(\Delta t) \tag{37}$$

with two functionals A_i and A_f. The largest (most divergent) contributions to A_i and A_f are $\frac{1}{4} X^2 \int \frac{\dot{\eta}^2}{\eta} dt$, which diverge as $(\Delta t)^{-1}$. The third part of $\int F_S \circ dX_B$ is:

$$\int \xi \circ dX_B. \tag{38}$$

This is a random variable that depends on the realization of ξ just after the initial time and just before the final time. If dX_B is considered an externally-given virtual displacement, then (38) is a weighted integral of white noise and then a random variable of mean zero. The same result holds also when dX_B is a combination involving X because X is here a smooth function of time (no Itô correction). The variance of (38) can be computed from the noise-noise correlation and by comparing the increment dX_B with the (similar) boundary force F_{if}, with the result:

$$\left\langle \left(\int \xi \circ dX_B \right)^2 \right\rangle = 2 k_B T \left(A_i + A_f \right) \tag{39}$$

The second and the third part of $\int F_S \circ dX_B$ are hence potentially both large, and when Δt tends to zero, they can both be larger than standard Jarzynski work by an arbitrary amount.

Let us now consider the contribution of $\int F_S \circ dX_B$ to the Jarzynski equality, which we write:

$$\left\langle e^{-\beta(\int (\partial_t H_S) + F_S \circ dX_B)} \right\rangle_{fact.eq} = e^{-\beta \Delta F} \tag{40}$$

to emphasize that the initial equilibrium distribution is factorized between the system and the bath. For given initial and final coordinates and momenta, the first and second parts contribute simply $e^{-\beta\left(\Delta V_{fric} + A_i + A_f\right)}$. The third part (38) on the other hand contributes:

$$\int \frac{1}{N} e^{-\frac{\beta}{2} \frac{x^2}{2\left(A_i + A_f\right)}} e^{-\beta x} dx = e^{\beta\left(A_i + A_f\right)}. \tag{41}$$

The (potentially divergent) contributions from the second and the third part hence cancel for each given initial and final coordinate and momenta (up to terms as small as Δt), and must therefore cancel in the Jarzynski equality overall.

Combining this result and (34), we have an alternative form of the Jarzynski equality:

$$\left\langle e^{-\beta \int (\partial_t H_S) - \beta \Delta V_{frict}} \right\rangle_{fact.eq} = e^{-\beta \Delta F}. \tag{42}$$

This may be compared to the strong-coupling form of the Jarzynski equality, which holds when η is strictly constant in time:

$$\left\langle e^{-\beta\int(\partial_t H_S)}\right\rangle_{eq} = e^{-\beta\Delta F_{TOT}} \tag{43}$$

In the above, the average is over the system and the bath initially in joint equilibrium with the terms H_I and H_C included, and the free energy change is of the combined system and bath. Path-wise, the contributions to (42) and (43) from the Jarzynski work $\int(\partial_t H_S)$ are the same up to terms $\mathcal{O}(\Delta t)$. The differences between the two averages therefore stem from the additional term ΔV_{frict} and the different distributions over the initial conditions.

6. Comparison to Quantum Heat Exchange

In the present section, I will switch gears and discuss an approach to quantum heat considered in an earlier contribution, there in the guise of a first-order change of the von Neumann entropy of a bath [16]. As in the previous sections, the heat will be related to the change of energy of a bath. In the spirit of Kurchan's approach to quantum fluctuation relations [23,24], it is assumed that the system is measured at the beginning and the end of a process. The outcome of the initial measurement will be state $|i>$ of the system, and the outcome of the final measurement will be state $|f>$; these letters will be used as subscripts to compactify some of the following expressions. The first such notational simplification, introduced by Feynman and Vernon [25], is to write P_{if} for the conditional probability of measuring the system in final state $|f>$ given that it was initially in $|i>$. It is here assumed that between the measurements, the system develops in interaction with the bath, which was initially in equilibrium. Using the shorthand:

$$\int_{if}(\cdots) = \int dX_i dY_i dX_f dY_f \psi_i(X_i)\psi_i^*(Y_i)\psi_f^*(X_f)\psi_f(Y_f)\,(\cdots)$$

where ψ_i and ψ_f are the wave functions of the states $|i>$ and $|f>$, I will write the transition probability as:

$$P_{if} = \int_{if}\mathcal{D}X\mathcal{D}Ye^{\frac{i}{\hbar}S_S[X]-\frac{i}{\hbar}S_S[Y]+\frac{i}{\hbar}S_i[X,Y]-\frac{1}{\hbar}S_r[X,Y]} \tag{44}$$

where the two path integrals are over respectively the forward path $X(t)$ from X_i to X_f and the backward path $Y(t)$ from Y_i to Y_f. These two path integrals emanate from a representation of the total unitary U and its inverse U^{-1} in the time development of the total density operator of the bath and the system $\hat{\rho}_f^{TOT} = U\hat{\rho}_i^{TOT}U^{-1}$ and then integrating out the bath variables. The effects of the bath are thus captured by the two kernels S_i and S_r in (44), which couple the forward and backward paths and which are referred to as the real and the imaginary part of the Feynman–Vernon action. This important theory is lucidly explained in the original 1963 paper [25], by Caldeira and Leggett in [26], as well as in several reviews and monographs; cf. [17,27].

In a slight extension of this well-established theory, we now assume that the Hamiltonians of the system and the bath are described by operators $\hat{H}_s$, $\hat{H}_B$, $\hat{H}_I$ and $\hat{H}_C$, which are translations to the quantum domain of the classical Hamiltonians in Section 2. The expected final energy of the bath, after first measuring the system, is Tr $\left[\hat{\rho}_B^{post}\hat{H}_B\right]$, where the reduced density matrix of the bath is $\hat{\rho}_B^{post} = \frac{1}{P_{if}} < f|\hat{\rho}_{TOT}|f>$. Using the shorthand:

$$\langle A_B\rangle_{if} = \mathrm{Tr}_B < f|\hat{\rho}_{TOT}A_B \oplus \mathbf{1}_S|f> \tag{45}$$

where A_B is an operator acting on the bath and $\mathbf{1}_S$ is the identity operator on the system, Tr_B is the trace of the bath and the system starts out from pure state $|i>$, the conditional expected quantum heat is:

$$\mathrm{E}\left[\delta Q|if\right] = \frac{1}{P_{if}}\left(\left\langle \hat{H}_B(t_f)\right\rangle_{if} - \langle \hat{H}_B(t_i)\rangle_{if}\right) \tag{46}$$

Path integral expressions for (46) or closely connected quantities have by now been developed by several groups [16,18,19], notably recently in [20]. I here follow the notation in [16] where the first main result (Equation (15)) is equivalent to:

$$\mathrm{E}\left[\delta Q|if\right] = \frac{1}{P_{if}}\left\langle \mathcal{I}^{(2)} + \mathcal{I}^{(3)} \right\rangle_{if} = \frac{1}{P_{if}}\int_{if} \mathcal{D}X\mathcal{D}Y e^{\frac{i}{\hbar}S_S[X]-\frac{i}{\hbar}S_S[Y]+\frac{i}{\hbar}S_i[X,Y]-\frac{1}{\hbar}S_r[X,Y]}\left(\mathcal{I}^{(2)} + \mathcal{I}^{(3)}\right) \tag{47}$$

where $\mathcal{I}^{(2)}$ and $\mathcal{I}^{(3)}$ are two quadratic functionals. In this section, their classical limit will be discussed and shown to be identical to the expected value of the classical heat discussed above in Section 4. In [16] (Equation (15)), there was also a first functional $\mathcal{I}^{(1)}$, which is related to the choice of subtraction at the initial time and which is for completeness discussed in Appendix C.

Adapting to the setting of the present paper, we from now on take the system-bath coupling coefficients C_b to depend on time as in Appendix A. This leads to:

$$\mathcal{I}^{(2)} = \int_{t_i}^{t_f}\int_{t_i}^{t_f} XY'h^{(2)}ds'ds \tag{48}$$

$$\mathcal{I}^{(3)} = \int_{t_i}^{t_f}\int_{t_i}^{t_f} XY'h^{(3)}ds'ds. \tag{49}$$

where the corresponding two kernels (up to a factor β) are given in [16] Equation 16:

$$h^{(2)} = i\sum_b \frac{C_b(s)C_b(s')}{2m_b}\coth(\frac{\beta\hbar\omega_b}{2})\sin\omega_b(s-s') \tag{50}$$

$$h^{(3)} = \sum_b \frac{C_b(s)C_b(s')}{2m_b}\cos\omega_b(s-s') \tag{51}$$

Caldeira and Leggett in [26] were the first to explicitly consider the classical open system limit of the quantum mechanical transition amplitude P_{if} in (44). That limit is achieved in three steps. The first is taking the bath as large and with the Ohmic spectrum as in Appendix B. When the spectral cut-off Ω is much larger than thermal relaxation time $\hbar\beta$, the kernel S_i in (44) tends to the derivative of the delta function. The second step is to assume a large bath temperature in the sense that $\hbar\beta$ should be much smaller than any characteristic time of the system, which turns the other kernel S_r in (44) into a delta function. The time development of the kernel in (44) is then Markov, i.e., it satisfies a partial differential equation, first derived in [26], and compared to the Lindblad equation in, e.g., [17]. The Wigner function, which is related to the kernel in (44) by a Fourier transform, then also satisfies a partial differential equation and, as found in [26], in fact, a Fokker–Planck equation. The standard interpretation of this result is that the bath "observes" the system and destroys its quantum coherence such that the open system quantum dynamics is fully described (in this limit) by the open system classical dynamics.

We now want to consider the same Caldeira–Leggett limit for the functionals $\mathcal{I}^{(2)}$ and $\mathcal{I}^{(3)}$ in (48) and (49). Similarly to S_i and S_r, the kernels tend to:

$$h^{(2)} \approx -\beta^{-1}\frac{i}{\hbar}2\sqrt{\eta(s)\eta(s')}\frac{d}{d(s-s')}\delta(s-s') \tag{52}$$

$$h^{(3)} \approx -\sqrt{\eta(s)\eta(s')}\frac{d^2}{d(s-s')^2}\delta(s-s') \tag{53}$$

Assuming that both η and $\dot{\eta}$ vanish at the initial and final time, we can integrate by parts freely to find:

$$\left\langle \mathcal{I}^{(2)} + \mathcal{I}^{(3)} \right\rangle_{if} = \left\langle \int \beta^{-1}\frac{i}{\hbar}\left(\left(\frac{d}{dt}(\sqrt{\eta}X)\right)(\sqrt{\eta}Y) - (\sqrt{\eta}X)\left(\frac{d}{dt}(\sqrt{\eta}Y)\right)\right) + \left(\frac{d}{dt}(\sqrt{\eta}X\right)\left(\frac{d}{dt}(\sqrt{\eta}Y\right)\right\rangle_{if} \tag{54}$$

In the above, the (quantum) expectation is the same as in (47), and X and Y are the forward and backward quantum paths. If we substitute for X and Y a classical path Q and average over its probability distribution, the term $\left\langle \mathcal{I}^{(3)} \right\rangle_{if}$ in (54) is the same as the expectation value of the corresponding term in (30). The other term can be re-expressed as:

$$\left\langle \mathcal{I}^{(2)} \right\rangle_{if} = \beta^{-1} \frac{i}{\hbar} \left\langle \int \eta \left(\frac{d}{dt}(X+Y) \right) (Y-X) + \frac{1}{2}\dot{\eta} \left(Y^2 - X^2 \right) + \frac{1}{2}\frac{d}{dt} \left(\eta X^2 \right) - \frac{1}{2}\frac{d}{dt} \left(\eta Y^2 \right) \right\rangle_{if} \tag{55}$$

In the above, the last two terms vanish since they are complete integrals, and η has been taken as zero at the initial and final time. A similar separation was used in [16], Section 5, and there expressed as $\frac{2i}{\hbar} S_i^{mid}$ and ΔS_b; in that case (where η was constant), the extra term ΔS_b was however not zero.

To discuss the first two terms in (55), we use the procedure of [16], Sections 6 and 7. The first step is to express the quantum averages through the Wigner transform. For the first term in (55) that leads to the result in [16], we use Equation (34). For the second term in (55), we have that $\frac{1}{2}(Y^2 - X^2) = Q\alpha$ where $Q = \frac{1}{2}(X+Y)$ is the average (eventually classical) path and $\alpha = (Y - X)$ is the quantum deviation; a term $\frac{i\alpha}{\hbar}$ translates to a partial derivative with respect to momentum variable P in the Wigner transform. Collecting both terms, we have hence:

$$\left\langle \mathcal{I}^{(2)} \right\rangle_{if} = \beta^{-1} \int dsdQdP\ P(Q,P,Q_i,P_i) \left(-\frac{2\eta}{M} p\partial_p - \frac{\eta}{M} - \dot{\eta} q \partial_p \right) P(Q_f,P_f,Q,P) \tag{56}$$

$P(q',p',q,p)$ in the above is the Wigner function, which in the Caldeira–Leggett limit tends to the transition kernel of the classical stochastic process (8).

The second step is to compare the right-hand side of (55) to the expectation value of the first term in (30) $\langle \int -\xi \circ (dQ - dQ_B) \rangle_{if}$. The expectation is conditioned on the initial and final states, which are assumed to be given by definite classical coordinates and momenta. It is convenient to re-write this as:

$$\int_{Q_i,P_i}^{Q_f,P_f} \mathcal{D}\mathrm{Prob}(\mathrm{path}) \left[\int \left(-\frac{P}{M} - \frac{\dot{\eta}}{2\eta} Q \right) \circ d\Xi \right] \tag{57}$$

where $\mathrm{Prob}(\mathrm{path})$ is a weight over paths and $d\Xi$ is the increment of the aggregated random force, a Gaussian random variable with mean zero and variance $2k_B T \eta dt$. One can therefore discretize the inner integral in (57) and consider the contribution from the short time interval $[s, s+\Delta s]$:

$$\text{Term from Equation (57)} = \int dQdPdQ'dP' \left(-\frac{P'+P}{2M} - \frac{\dot{\eta}}{2\eta} Q\Delta s \right) \Delta\Xi\ P(\cdot,Q',P') P_{\Delta s}(Q',P',Q,P) P(Q,P,\cdot). \tag{58}$$

The short-time propagator of the Kramers–Langevin process is:

$$P_{\Delta s}(Q',P',Q,P) = \frac{1}{\mathcal{N}} e^{-\frac{1}{4k_B T \eta \Delta s} \left(P' - P + \left(\partial_Q V + \eta \frac{p+p'}{2M} + \frac{1}{2}\dot{\eta} Q \right) \Delta s \right)^2} \delta \left(Q' - Q - \frac{P'+P}{2M} \Delta s \right) \tag{59}$$

and has the property that:

$$\Delta\Xi P_{\Delta s}(Q',P',Q,P) = -2k_B T \eta \Delta s \partial_{P'} P_{\Delta s}(Q',P',Q,P) + \mathcal{O}\left(\Delta s^2 \right) \tag{60}$$

Integration by parts moves over the derivative with respect to P' to respectively $P(Q_f,P_f,Q',P')$ and $\frac{P'+P}{2M}$, which gives the expression in (55). The same analysis through the Wigner function as outlined here can of course also be applied to the last (simpler) term in (54), with the same result as given above up to terms of order $\hbar^2$.

7. Discussion

The study of the interaction of a classical or quantum system with a bath of harmonic oscillators has a long history, and it behooves the author to motivate the need for another paper on the subject.

Consider the assumption of the Feynman–Vernon theory that the system and the bath are originally decoupled and the bath is at equilibrium. If the coupling is not weak, this is questionable because if the system and the bath were in contact precisely at the initial time, they should have been so also slightly before, and then, they could not have been initially fully decoupled. Nevertheless, this assumption is needed to integrate out the bath variables and arrive at the Feynman–Vernon open system development operator of the system only; although the bath oscillators can be integrated out also if the system and the bath are originally in equilibrium together, the analysis is then considerably more complicated [27] and that possibility has not been considered here. It could therefore be argued that the Caldeira–Leggett theory of quantum Brownian motion [26], which is based on Feynman–Vernon, is only valid at weak coupling. Indeed, it has been noted several times that the classical limit (Kramers–Langevin equation) of an Ohmic bath has a delta-function force proportional to the friction acting at the initial time and that the random and deterministic forces from the bath therefore do not obey an Einstein relation. It has also been noted that there is a difference whether one assumes that the decoupled initial conditions pertain exactly at the initial time or only slightly after.

To resolve these (and other) issues, Caldeira and co-workers [28] investigated the possibility that the bath is initially in equilibrium conditional on the position of the system, i.e., with respect to Hamiltonian $\sum_b \frac{p_b^2}{2m_b} + \frac{1}{2}m_b\omega_b^2\left(q_b - \frac{C_b(t)Q}{m_b\omega_b^2}\right)^2$. These initial conditions are mathematically possible and physically allowed, but raise the question of how the system and the bath would find themselves in such a state. If some control would have been exercised on the bath prior to the process, this control must have been aware of the position of the system, and only a very exquisite procedure would have resulted in exactly the assumed initial state.

In this paper, I have aimed to address these issues anew by allowing the system-bath coupling to depend on time. It is then not a problem to have the system and the bath initially decoupled, but the price to pay is the new effects that arise from the time-dependent friction. On the level of classical equations, these effects are just the extra force F_{if} of (10), which when the switching on and off of the bath-system coupling is fast, reduces to the previously known delta-function force. On the level of classical heat and work functionals, the situation is more involved and described by (28) and (29). There appears a part of the work denoted $\int F_S \circ dX_B$, which is entirely dissipated into heat, which has support only at the beginning and the end of the process and which is potentially quite large. Nevertheless, it only makes a finite contribution to the work functional that enters Jarzynski's equality; see (42).

Although the work $\delta W_{if} = \int F_S \circ dX_B$ is (to the author's knowledge) new, it is in retrospect not entirely surprising from a physical point of view. If the bath and the system are initially independent and if they then move so that the bath is in conditional equilibrium with the system, then that is a relaxation process. By analogy with finite-time (macroscopic) thermodynamics, one would expect the heat in such a process to be inversely proportional to the duration of the process. To compare, it is well known that when a system changes state in a finite time interval Δt, the expected heat given off to the environment diverges as $(\Delta t)^{-1}$ [29,30]. The current model is not exactly the same, as the divergent heat arrives to an explicitly-modeled set of oscillators and not to a system coupled to an external and more abstract bath. Nevertheless, in both cases, the leading divergence is inversely proportional to the duration of the process, and the operational meaning is that extra work has to be done on the system to effectuate a transformation in a finite time. The extra work may hence be assimilated to finite-time corrections to Landauer's law [29,30].

On the quantum level of the expected change of the bath energy, the analysis can be carried out using the Feynman–Vernon formalism, as done previously for constant system-bath coupling in [16]. The classical limit of these expressions can then be seen to be the same as the classical heat functional with time-dependent friction. This is hence an example of quantum-classical correspondence [31], on the level of the expected heat. The extra term ΔS_b found in [16] arises from using factorized initial conditions with a finite system-bath interaction present from the very beginning of the process and has therefore here been shown to be a kind of artifact.

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Appendix A. Recall of the Zwanzig Theory

All the calculations in this section are straightforward and mostly re-statements of known results [32]. The equations of motion of the bath and the system that follow from (3)–(6) are:

$$\begin{aligned} \dot{p_b} &= -m_b\omega_b^2 q_b + C_b(t)X && \text{(A1)}\\ \dot{q_b} &= \frac{p_b}{m_b} && \text{(A2)}\\ \dot{P} &= -V'(X,t) + \sum_b C_b(t)\left(q_b - \frac{C_b(t)}{m_b\omega_b^2}X\right) && \text{(A3)}\\ \dot{X} &= \frac{P}{M} && \text{(A4)} \end{aligned}$$

The initial position and momentum of the system (X^i, P^i) are assumed known. All randomness in this problem is hence due to lack of knowledge of the initial positions and momenta of the bath. These are $2N$ real numbers, while the time history of the system over the finite time interval, $\{X,P\}_{t_i}^{t_f}$, needs infinitely many variables to be completely specified. One may therefore assume that a complete knowledge of the system history uniquely specifies the initial positions and momenta of the bath; to the equilibrium probability P^{eq} in the bath then corresponds a probability distribution $P\left[\{X,P\}_{t_i}^{t_f}\right]$ on system histories. This will be assumed throughout the following.

The equations of motion for the bath oscillators can be solved as:

$$\begin{aligned} \begin{pmatrix} q_b(t) \\ p_b(t) \end{pmatrix} &= e^{(t-t_i)\begin{pmatrix} 0 & \frac{1}{m_b} \\ -m_b\omega_b^2 & 0 \end{pmatrix}} \begin{pmatrix} q_b(t_i) \\ p_b(t_i) \end{pmatrix} + \\ & \int_{t_i}^{t} e^{-(t-s)\begin{pmatrix} 0 & \frac{1}{m_b} \\ -m_b\omega_b^2 & 0 \end{pmatrix}} \begin{pmatrix} 0 \\ C_b Q \end{pmatrix} \qquad \text{(A5)} \end{aligned}$$

Observing that the exponentiated matrix multiplying the initial conditions is:

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \cos\omega_b(t-t_i) + \begin{pmatrix} 0 & \frac{1}{m_b} \\ -m_b\omega_b^2 & 0 \end{pmatrix} \frac{1}{\omega_b}\sin\omega_b(t-t_i)$$

the solution for the position can then be written:

$$\begin{aligned} q_b(t) &= q_b(t_i)\cos\omega_b(t-t_i) + p_b(t_i)\frac{1}{\omega_b m_b}\sin\omega_b(t-t_i) \\ & \quad - \int_{t_i}^{t}[\frac{1}{\omega_b m_b}\sin(\omega_b(t-s))C_b(s)Q(s)]ds \qquad \text{(A6)} \end{aligned}$$

which by one integration by parts can be rewritten as:

$$\begin{aligned} q_b(t) &= \left(q_b(t_i) - \frac{C_b(t_i)X(t_i)}{m_b\omega_b^2}\right)\cos\omega_b(t-t_i) + \frac{C_b(t)X(t)}{m_b\omega_b^2} - \\ & \frac{1}{\omega_b^2 m_b}\int_{t_i}^{t}[\cos(\omega_b(t-s))\left(\dot{C}_b(s)X(s) + C_b(s)\dot{X}(s)\right)]ds + p_b(t_i)\frac{1}{\omega_b m_b}\sin\omega_b(t-t_i) \end{aligned} \tag{A7}$$

By the assumption that the system and the bath are initially disconnected, $C_b(t_i)X(t_i)$ vanishes. Inserting $q_b(t)$ into the equations of motion for the system gives:

$$\begin{aligned} \dot{X} &= \frac{P}{M} \qquad \dot{P} = -V'(X,t) + \xi(t) \\ & \qquad - \int_{t_i}^{t}\gamma(t,s)\dot{X}(s) + \chi(t,s)X(s)ds \end{aligned} \tag{A8}$$

using the ancillary quantities:

$$\xi(t) = \sum_b C_b(t)\left[q_b(t_i)\cos\omega_b(t-t_i) + p_b(t_i)\frac{1}{\omega_b m_b}\sin\omega_b(t-t_i)\right] \tag{A9}$$

$$\gamma(t,s) = \sum_b \frac{C_b(t)C_b(s)}{m_b\omega_b^2}\cos\omega_b(t-s) \tag{A10}$$

$$\chi(t,s) = \sum_b \frac{C_b(t)\dot{C}_b(s)}{m_b\omega_b^2}\cos\omega_b(t-s) \tag{A11}$$

Equations (8) and (A9)–(A11) are the solutions to the general problem of a system interacting linearly with a bath of harmonic oscillators. The physical meaning of γ is friction, while χ is a reaction force of the bath on the system, a counter-party of the force that the system exerts on each bath oscillator if it is not in equilibrium with the instantaneous position of the system. The term $\xi(t)$ is on the other hand a force of the bath on the system, which is explicitly independent of the system. It is a random force if the initial positions and momenta of the bath are random.

Appendix B. The Time-Dependent Ohmic Bath and Its Forces

In this Appendix, I summarize the additional assumptions needed so that the final Equation (A8) in Appendix A is the classic Kramers–Langevin equation when the system-bath coupling is constant, and I make explicit the additional harmonic force that arises from a variable system-bath interaction and which is given in (8) in the main text.

This extra force is related to the relaxation of the bath to the instantaneous state of the system and has been known for quite some time in the specialized literature [28,33–36]. A convenient starting point is to follow Caldeira and Leggett [26] and assume an Ohmic bath, i.e., that the spectrum of the bath oscillators is continuous up to an upper cut-off Ω and increases quadratically with frequency. The number of oscillators with frequencies in the interval $[\omega, \omega + d\omega]$ is $f(\omega)d\omega$ and:

$$\begin{aligned} f(\omega) &= \tfrac{2}{\pi}\omega_c^{-3}\omega^2 & \omega < \Omega \\ f(\omega) &= 0 & \omega > \Omega \end{aligned} \tag{A12}$$

where ω_c is some characteristic frequency less than Ω. The total number of oscillators is hence $\frac{2}{3\pi}\left(\frac{\Omega}{\omega_c}\right)^3$. We also assume a function $\eta(s)$ with dimension (mass/time) such that:

$$C_b(s) = \sqrt{\omega_c^3 m_b \eta(s)} \tag{A13}$$

which implies, for every bath oscillator,

$$\dot{C}_b(t) = \frac{1}{2}\frac{\dot{\eta}(t)}{\eta(t)}C_b(t). \tag{A14}$$

It is customary to refer to quantities pertaining to a bath oscillator having angular velocity ω by that angular velocity, i.e., m_ω for the mass of the oscillator and C_ω for the coupling coefficient. The two kernels in (A10) and (A11) then follow from:

$$\frac{C_\omega(t)C_\omega(s)f(\omega)}{m_\omega} = \frac{2\sqrt{\eta(t)\eta(s)}}{\pi}\omega^2 \qquad \omega < \Omega \tag{A15}$$

and are:

$$\begin{aligned} \gamma(t,s) &= \frac{2\sqrt{\eta(t)\eta(s)}}{\pi}\int_0^\Omega \cos\omega(t-s)d\omega & \text{(A16)}\\ \chi(t,s) &= \frac{\dot{\eta}(t)}{\pi}\sqrt{\frac{\eta(s)}{\eta(t)}}\int_0^\Omega \cos\omega(t-s)d\omega & \text{(A17)} \end{aligned}$$

We now further assume that $C_b(t)$ changes between zero and the full value on a time scale much longer than Ω^{-1} so that the integrals in (A16) and (A17) can be approximated by delta functions. This leads to:

$$\begin{aligned} \gamma(t,s) &\approx 2\eta(t)\delta(t-s) & \text{(A18)}\\ \chi(t,s) &\approx \dot{\eta}(t)\delta(t-s) & \text{(A19)} \end{aligned}$$

which means that the two terms inside the integral in (8) are evaluated as:

$$\begin{aligned} F_{fric} &= -\eta(t)\dot{X}(t) & \text{(A20)}\\ F_{if} &= -\frac{1}{2}\dot{\eta}(t)X(t)) & \text{(A21)} \end{aligned}$$

as given in Equations (9) and (10) in the main text. The first of the above is a standard friction force, while the second is a time-dependent harmonic force, proportional to the time derivative of the friction coefficient.

Turning now to force term ξ, it varies rapidly in time and depends directly on the initial positions and momenta of the bath oscillators. Its statistical properties follow from averaging over these initial positions and momenta, and it follows from the explicit Formula (A9) that $\mathrm{E}\left[\xi(t)\right] = 0$ where the expectation value is taken with respect to $\mathcal{P}_\beta^{eq}$, the equilibrium initial distribution of the bath at inverse temperature β. The second moment for the force is:

$$\begin{aligned} \mathrm{E}\left[\xi(t)\xi(s)\right] &= \int \mathcal{P}_\beta^{eq}\left(\{q_b(t_i), p_b(t_i)\}\right)\prod_b dq_b(t_i)dq_b(t_i)\left[\xi(t)\xi(s)\right] \\ &= \sum_b C_b(t)C_b(s)\frac{k_B T}{m_b\omega_b^2}\cos\omega_b(t-s) \approx 2k_B T\eta(t)\delta(t-s) & \text{(A22)} \end{aligned}$$

The random force ξ therefore satisfies an Einstein relation with only the friction force F_{fric}.

Appendix C. An Extra Term Found in [16]

The purpose of this Appendix is to detail the connection between the path integral representation for heat developed in Section 6 and the one for the first order change in von Neumann entropy studied in the earlier contribution [16]. To translate, we first note that the central quantity computed in the earlier paper (Equation (3) in [16]) was:

$$\overline{\delta S_q} = \mathrm{E}\left[\beta \hat{H}_B(t_f)|if\right] - \beta U(\beta) \tag{A23}$$

where $U(\beta)$ is the equilibrium energy of the bath at inverse temperature β. This differs from (46) by the factor β that makes the quantity dimensionless and by the subtraction at the initial time. We will show that an extra term found [16] is explained by this subtraction.

We then note that the first main result (Equation (15)) of [16] reads:

$$\overline{\delta S_q} = \frac{1}{P_{if}} \left\langle \mathcal{I}^{(1)} + \mathcal{I}^{(2)} + \mathcal{I}^{(3)} \right\rangle_{if} = \frac{1}{P_{if}} \int_{if} \mathcal{D}X\mathcal{D}Y e^{\frac{i}{\hbar}S_S[X] - \frac{i}{\hbar}S_S[Y] + \frac{i}{\hbar}S_i[X,Y] - \frac{1}{\hbar}S_r[X,Y]} \left(\mathcal{I}^{(1)} + \mathcal{I}^{(2)} + \mathcal{I}^{(3)}\right) \tag{A24}$$

where the notation is as in Section 6 with only the slight change that $\mathcal{I}^{(2)}$ and $\mathcal{I}^{(3)}$ include an additional factor β. The first functional is:

$$\mathcal{I}^{(1)} \quad = \int^{t_f} \int^{s} (X-Y)(X'-Y') h^{(1)} ds' ds \tag{A25}$$

with the kernel:

$$h^{(1)} \quad = -\sum_b \tfrac{C_b^2}{4m_b} \sinh^{-2}(\tfrac{\beta\hbar\omega_b}{2}) \cos\omega_b(s-s') \tag{A26}$$

As noted in [16], Equation (A25) equals $\partial_\beta \frac{1}{\hbar} S_r$ where S_r is the real part of the Feynman–Vernon action. Writing the quantum expectation value of $\mathcal{I}^{(1)}$ in the Feynman–Vernon theory therefore means:

$$\frac{1}{P_{if}} \left\langle \mathcal{I}^{(1)} \right\rangle_{if} \quad = \quad \frac{1}{P_{if}} \int_{if} \mathcal{D}X\mathcal{D}Y e^{\frac{i}{\hbar}S_S[X] - \frac{i}{\hbar}S_S[Y] + \frac{i}{\hbar}S_i[X,Y] - \frac{1}{\hbar}S_r[X,Y]} \left(\partial_\beta \frac{1}{\hbar} S_r\right) = -\partial_\beta \log P_{if} \tag{A27}$$

where the notation is as in Section 6 above. The second equality follows because in the exponent, only S_r depends on β.

We want to relate the term in (A27) to the difference between $\mathrm{E}\left[\hat{H}_B(t_i)|if\right]$ and $U(\beta)$, where $U(\beta)$ is the unconditioned expected energy of the bath at inverse temperature β. To do so, we write more formally:

$$P_{if} \quad = \quad \left\langle f|\mathrm{Tr}_B \left[U\left(\rho_B^{eq}(\beta) \oplus |i\right\rangle \langle i|\right) U^\dagger\right] |f\right\rangle \tag{A28}$$

$$\mathrm{E}\left[\hat{H}_B(t_i)\right] \quad = \quad \left\langle f|\mathrm{Tr}_B \left[U\left((\hat{H}_B \oplus \mathbf{1})\left(\rho_B^{eq}(\beta) \oplus |i\right\rangle \langle i|\right)\right) U^\dagger\right] |f\right\rangle \tag{A29}$$

$$\mathrm{E}\left[\hat{H}_B(t_f)\right] \quad = \quad \left\langle f|\mathrm{Tr}_B \left[(\hat{H}_B \oplus \mathbf{1})\left(U\left(\rho_B^{eq}(\beta) \oplus |i\right\rangle \langle i|\right) U^\dagger\right)\right] |f\right\rangle \tag{A30}$$

$$U(\beta) \quad = \quad \mathrm{Tr}_B\left[\hat{H}_B \rho_B^{eq}(\beta)\right] \tag{A31}$$

where U (not to be confused with $U(\beta)$) is the total unitary operation on the system and the bath and $\rho_B^{eq}(\beta)$ is the initial (equilibrium) density matrix of the bath. Using that $\rho_B^{eq}(\beta) = e^{-\beta\hat{H}_B}/Z(\beta)$ and $-\partial_\beta \log Z = U$, we have $\mathrm{E}_{if}\left[\hat{H}_B(t_i)\right] = -\partial_\beta P_{if} + UP_{if}$. Therefore:

$$-\partial_\beta \log P_{if} \quad = \quad \frac{1}{P_{if}} \langle \hat{H}_B(t_i) \rangle_{if} - U(\beta). \tag{A32}$$

which was to be shown.

As a final remark, the expected energy of the bath energy measured at the initial time, conditioned on the future observation of the final state f of the system, is not the same as the unconditioned equilibrium internal energy of the bath times the transition probability, an (simple) example of quantum retro-diction [37,38].

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