Statistical thermodynamics of quantum Brownian motion: Birth of perpetuum mobile of the second kind

Th.M. Nieuwenhuizen$^{1}$ and A.E. Allahverdyan$^{2,1,3}$

$^1$ Institute for Theoretical Physics, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands;
$^2$ S.Ph.T., CEA Saclay, 91191 Gif-sur-Yvette cedex, France;
$^3$ Yerevan Physics Institute, Alikhanian Brothers St. 2, Yerevan 375036, Armenia.

(October 31, 2018)

The Brownian motion of a quantum particle in a harmonic confining potential and coupled to a harmonic quantum thermal bath is exactly solvable. Though this system presents at large temperature a pedagogic example to explain the laws of thermodynamics, it is shown that at low enough temperatures the stationary state is non-Gibbsian due to an entanglement with the bath. In physical terms, this happens when the cloud of bath modes around the particle starts to play a non-trivial role, namely when the bath temperature $T$ is smaller than the coupling energy. Indeed, equilibrium thermodynamics of the total system, particle plus bath, does not imply standard equilibrium thermodynamics for the particle itself at low $T$.

Various formulations of the second law are found to be invalid at low $T$. First, the Clausius inequality can be violated, because heat can be extracted from the zero point energy of the cloud of bath modes. Second, when the width of the confining potential is suddenly changed, there occurs a relaxation to equilibrium during which the entropy production is partly negative. In this process the energy put on the particle does not relax monotonously, but oscillates between particle and bath, even in the limit of strong damping. Third, for non-adiabatic changes of system parameters the rate of energy dissipation can be negative, and, out of equilibrium, cyclic processes are possible which extract work from the bath. Conditions are put forward under which perpetuum mobile of the second kind, having one or several work extraction cycles, enter the realm of condensed matter physics. Fourth, it follows that the equivalence between different formulations of the second law (e.g. those by Clausius and Thomson) can be violated at low temperatures.

These effects are the consequence of quantum entanglement in the presence of the slightly off-equilibrium nature of the thermal bath, and become important when the characteristic quantum time scale $\hbar/k_B T$ is larger than or comparable to other timescale of the system. They show that there is no general consensus between standard thermodynamics and quantum mechanics. The known agreements occur only due to the weak coupling limit, which does not pertain to low temperatures.

Experimental setups for testing the effects are discussed.

PACS: 05.70Ln, 05.10Gg, 05.40-a

1. INTRODUCTION

The faith in the laws of thermodynamics has been strengthened time and again because numerous counterarguments and perpetuum mobile setups failed. It was summarized in the classical statement of Arthur Eddington in 1948 $[1]$: “The law that entropy always increases - the second law of thermodynamics - holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell’s equations - then so much the worse for Maxwell’s equations. If it is found to be contradicted by observation, well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but collapse in deepest humiliation. Nevertheless, what we intend to do in this paper is to show that several formulations of the second law need not apply to systems coupled to a bath in the quantum regime. This paves the way for a new, modest definition of the most despised objects of modern physics, perpetuum mobile of the second kind. We shall propose realizations wherein they can make a few or even many cycles, though not infinitely many. A short version of the material appeared already $[2]$, which was discussed in the scientific press $[3] [4]$.

The laws of equilibrium thermodynamics apply both to (quasi) closed quantum and classical systems, and to open classical subsystems $[5]$. This can all be traced back to the general character of the Gibbs distribution that describes the equilibrium state. The same laws are believed to apply as well to open quantum subsystems. Our aim will be to show that, though this belief is proper for weak coupling, it is not justified for non-weak coupling between system
and bath. Non-weak coupling means physically that a cloud of bath modes has been formed around the particle, which we shall still consider as part of the bath. Although one could defend the opinion that—as an example—for Kondo-type problems there is no need or no sense to describe the impurity spin (“the subsystem”) separately from the Kondo-cloud of conduction electrons (“the bath”), such a viewpoint is not obvious for an array of mesoscopic Josephson junctions, where the “bath” is the electro-magnetic field, to which they may be strongly coupled. Since that regime shows up in many systems at low enough temperature even for a small but fixed coupling, there is an important case to make.

When deriving the Gibbs distribution for a (quasi)closed system, the underlying statistical assumptions do not depend much on the quantum or classical nature. An open subsystem is usually considered as being in contact with an initially equilibrium bath. Under some general statistical conditions concerning the bath, which are again the same for the quantum and classical cases, one derives a Langevin equation. The general behavior of the classical Langevin equation is well known: The stationary distribution is Gibbsian, and, at least for the white noise case, the equivalent Fokker-Planck equation is the main tool to describe the non-equilibrium statistical theory.

Much less is known about the quantum Langevin equation, first proposed by Senitzky in the weakly-damped (weakly coupled) case, and in a more general form by Ford, Kac and Mazur. Its stationary distribution has been obtained for the harmonic potential, in which case it depends explicitly on the coupling constant, becoming Gibbsian only in the limit of weak coupling. However, there are nowadays well-known experimental situations, which are essentially far from the weak-coupling regime. The main example is the case of weak links between superconductive regions, so-called Josephson junctions, in their overdamped regime, where the relevant ranges of parameters were achieved already twenty years ago. Even in quantum optics, which has often been satisfactorily described by weak-coupling theories, there are recent experiments showing the necessity of moderate and strong coupling approaches (see, e.g.,). In NMR experiments, on the other hand, very weak coupling occurs, but it leads to a $T_2$ relaxation time of transverse (non-classical) correlations, that can reach up to minutes. During that time related non-thermodynamic effects can occur.

The cause of the crucial differences between quantum and classical Brownian motion lies in quantum entanglement: A complete description in terms of a wave function is possible only for a closed system; subsystems are necessarily in a mixed state. Since the quantum Gibbs distribution tends to the pure vacuum state for $T \to 0$, it is in that limit not an adequate candidate for the description of the quantum subsystem non-weakly interacting with its thermal bath. Where typically researchers have just guessed that thermodynamics would apply anyhow, we shall provide the opposite answer by analyzing exactly solvable models.

Another important property is embodied in the structure of the quantum Langevin equation: As predicted by the quantum fluctuation-dissipation theorem, but in contrast to the classical case, the time-scales of fluctuations and dissipation are different, and even in the limit of instantaneous friction, the noise does not become white, but has the characteristic quantum timescale $\hbar/k_BT$. During this period the noise has a memory and thus has the possibility to cause non-statistical but “mechanical” or “quenched”, in any case non-thermodynamic, behavior of the system on which it acts. The physical meaning of the classical fluctuation-dissipation theorem thus is stronger, since it insists on equal timescales of friction and noise, which induces the standard thermodynamic behavior.

The new properties become non-effective if the interaction with the thermal bath is weak or if temperature is high, in which case the subsystem relaxes to its own quantum or classical Gibbs distribution. Both these cases will be referred to as the Gibbsian limit. We recall that its existence is typically not connected with very low temperatures, since even for a small but generic coupling between the system and the thermal bath, one always goes out of the weak coupling limit by taking the temperature low enough.

It is a crucial fact that a non-Gibbsian stationary state implies the inadequacy of equilibrium thermodynamics. In the present paper we propose a generalized thermodynamical description of a quantum Brownian particle in a harmonic confining potential. This description is self-consistent, and does not use a priori the concepts of the equilibrium (Gibbsian) statistical thermodynamics. Instead we employ the methods of nonequilibrium statistical thermodynamics developed recently for glasses and applied to black holes, where a separation of timescales allows for a two-temperature approach.

The universal character of equilibrium thermodynamics led to the general expectation that in one way or another,
thermodynamics will be applicable to the full quantum domain. A somewhat stronger point was expressed by Landau and Lifshitz \cite{5}, namely that the proper formulation of equilibrium thermodynamics must be based on quantum mechanics. For the strongly coupling quantum situation one might, however, not be convinced. Let us give three principle arguments that question standard wisdom:

1) The bath modes are correlated during the quantum timescale $\hbar/T$, even when damping is instantaneous. When this timescale is larger than the (largest) relaxation time of the system, the bath acts more like a quenched disorder than as a white noise. Thus the standard condition for going from a Langevin equation to a Gibbs distribution is not fulfilled and new behavior should be expected.

2) Assume that the overall system (the Brownian particle plus the bath) is in equilibrium at a low temperature. One of the many formulations of the second law states that no heat can be extracted from the bath. This just follows from the Clausius inequality: $dQ \leq TdS$ (here $dQ$ is the heat flowing from the bath to the subsystem, the Brownian particle, while $S$ is the entropy of the subsystem) for $T \to 0$. A naive argument in support of this statement will be that the bath is close to its ground state, and therefore its energy cannot be lowered. However, this argument is invalidated by quantum entanglement: Since the bath is not an isolated system itself, it cannot be in a definite energy eigenstate. In particular, it cannot be in the ground state, and its energy fluctuates even for $T \to 0$.

3) If a closed quantum system is its ground state, the only change can be to do work on it. Now suppose that this system consists of a subsystem coupled to a bath, and that the external coupling connects to the subsystem, and not to the bath. Then typically the action of doing work will reshuffle also the separate energies of the subsystem and the bath. As the direction of the exchange depends on the question whether externally work was added or subtracted, in one of the cases the subsystem receives energy from the bath. Since this comes from the unobserved bath modes, it cannot be identified as work, and must be identified as heat extracted from the bath, even at $T = 0$.

Because these arguments question standard wisdom, the only way to investigate the practical situation is to start from first principles, namely from standard quantum mechanics. This is the general strategy of the present paper.

Statements on violations of certain formulations of the second law in the quantum micro world already appeared in literature. Capek and his coworkers \cite{28} noticed such effects in certain biophysically inspired models, and Nikulov \cite{29} reported on violations of the second law in mesoscopic superconductivity. The latter author bases his view on results for permanent currents in inhomogeneous superconducting rings \cite{30}.

Since the subject of violating the second law and introducing perpetuum mobile has such a notorious history, new works in this field should be as convincing as possible. Therefore we present now a somewhat extensive, but self-contained exact analysis that leads to our conclusions, partly already presented in \cite{3}. Our methods are exact since the case of a quantum particle in a harmonic confining potential and coupled to a bath of harmonic oscillators with bilinear couplings is exactly solvable. Notice that in a previous work \cite{4} we also entered the discussion of the approximate solution for a weakly anharmonic force; this will not be touched here.

Our paper is organized as follows. In section 2 we recall the derivation of the quantum Langevin equation. In section 3 we solve the statics of the total system (subsystem plus bath) by elementary techniques. In section 4 we show that the thermodynamics of adiabatic changes can be described through two effective temperatures, and that analogies with the usual two temperature thermodynamics can be stated much further: The generalized relations will have the effective form of the first and second law. Next we first present details on the violation of the Clausius inequality. In section 5 we consider the dynamics of the system for the case where the initial state is Gibbsian, and for which the spring constant is slightly modified at time zero. In section 6 we use those results to derive the energy relaxation and the entropy production. In section 7 we consider work done on the system for that situation of an instantaneously changed spring constant, and we also consider work for smooth, cyclic changes. In section 8 we mention a number of experiments where our results have applications. In section 9 we view those results from the foundations of thermodynamics and the definition of perpetuum mobile. Finally in section 10 we close with a discussion.

2. THE QUANTUM LANGEVIN EQUATION

It is standard wisdom that the analysis of Brownian motion of non-interacting particles may be restricted to a single Brownian particle. This insight goes back to Szilard in his somewhat related work on Maxwell’s demon \cite{31}, for a translation see \cite{32}. In our analysis we shall also make this simplification, but insist that the bath has many degrees of freedom. Therefore it is equally equipped to couple to a gas of $N$ non-interacting Brownian particles, and our results for energy, work, heat, entropy, etc. must just be multiplied by $N$. Because of this, our results yield, without say, the intrinsic variables of a large Brownian system in its thermodynamic limit.
1. The Hamiltonian

The quantum Langevin equation is derived from the exact Hamiltonian description of a subsystem (Brownian particle) and a thermal bath, by tracing out the degrees of freedom of the bath. The influence of the particle on the bath is assumed to be sufficiently small. Thus, only the linear modes of the bath are excited, and the interaction of the particle with the bath is assumed to be linear. To be as pedagogic as possible, we first take a definite model for the bath, namely a collection of harmonic oscillators; later we will relax this assumption. For the total Hamiltonian we thus assume [11]

$$\mathcal{H}_{\text{tot}} = \mathcal{H} + \mathcal{H}_B + \mathcal{H}_I$$

$$\mathcal{H} = \mathcal{K}(p) + \mathcal{V}(x), \quad \mathcal{K}(p) = \frac{p^2}{2m}, \quad \mathcal{V}(x) = \frac{1}{2}ax^2$$

(2.1)

$$\mathcal{H}_B = \sum_i \left[ \frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} x_i^2 \right]$$

$$\mathcal{H}_I = \sum_i \left[ -c_i x_i x + \frac{c_i^2}{2m_i \omega_i^2} x_i^2 \right],$$

where $\mathcal{H}$ is the Hamiltonian of the particle, consisting of the kinetic and potential energies $\mathcal{K}$ and $\mathcal{V}$, $\mathcal{H}_B$ is the Hamiltonian of the bath, and $\mathcal{H}_I$ is the interaction Hamiltonian. $p$, $p_i$, $x$, $x_i$ are the momenta and coordinate operators of the particle and the linear modes of the bath. $\mathcal{V}(x)$ is the confining potential of the particle, and $m$ and $m_i$ are the corresponding masses.

Notice that our total system is closed and its energy is conserved, except for the periods where work is done on it by externally changing a system parameter such as $m$ or $a$. When we later on take as initial density matrix the Gibbs distribution $\exp(-\beta \mathcal{H}_{\text{tot}})/Z$, this still refers to our closed system; in particular it is not part of a larger thermodynamic system, with which heat exchange would be possible [10].

The $x_i$-terms of $\mathcal{H}_B + \mathcal{H}_I$ form a complete square, since $\mathcal{H}_I$ includes a self-interaction term proportional to $x^2$. This guarantees that the total Hamiltonian $\mathcal{H}_{\text{tot}}$ will be positive definite. In certain physical situations (e.g. electromagnetic interaction), such a term is generated automatically by the coupling [10]. Indeed, under a canonical transformation:

$$x_i \rightarrow \frac{p_i}{m_i \omega_i}, \quad p_i \rightarrow -x_i m_i \omega_i$$

(2.2)

$\mathcal{H}_{\text{tot}}$ becomes

$$\mathcal{H}_{\text{tot}}' = \frac{p^2}{2m} + \frac{1}{2}ax^2 + \sum_i \left[ \frac{1}{2m_i} (p_i - c_i \omega_i x_i)^2 + \frac{m_i \omega_i^2}{2} x_i^2 \right],$$

(2.3)

which corresponds to the minimal coupling (or subtraction) scheme.

In other situations (such as certain cases in nuclear and atomic physics, see [10] for more details) the self-interaction term is absent, and one has [9]

$$\mathcal{H} = \frac{p^2}{2m} + \mathcal{V}(x), \quad \mathcal{H}_I = -x \sum_i c_i x_i$$

(2.4)

while $\mathcal{H}_B$ is unchanged. For a harmonic system one will have $\mathcal{V}(x) = \frac{1}{2}bx^2$. In general, the potential energy will have a minimum only if $b = \mathcal{V}'(0)$ is large enough. This happens when the combination

$$a = b - \sum_i \frac{c_i^2}{m_i \omega_i^2}$$

(2.5)

is positive. In the case we shall consider below, with the $c_i$ given by (2.19), this sum can be evaluated, leading to $a = b - \gamma \Gamma$, where $\gamma$ is the coupling strength (damping constant) and $\Gamma$ is a large cut-off frequency. So this system can be mapped on previous one provided we define $\mathcal{V}(x) = \mathcal{V}(x) + \frac{1}{2} \gamma \Gamma x^2$. In doing so we identify with Hamiltonian of the subsystem the expression $\mathcal{H} = \mathcal{K} + \mathcal{V}$ of (2.1), rather than $\mathcal{K} + \mathcal{V}$, and with $\mathcal{H}_I$ the combination $\mathcal{H}_I + \frac{1}{2} \gamma \Gamma x^2$. To give some motivation for this, let us notice that we shall take $\Gamma$ large and $\gamma$ finite. In that case the expectation value $\langle \mathcal{V} \rangle$ is large, proportional to $\gamma \Gamma$, but this is almost fully compensated by an opposite term arising from $\langle \mathcal{H}_I \rangle$. These
cancellations have been accounted for by the mapping to $\mathcal{H}$ and $\mathcal{H}_f$, leaving at most a $\ln \Gamma$ divergence for large $\Gamma$, which actually arises at small temperatures from $\langle \hat{K} \rangle$. We shall come back to pro’s and contra’s of this identification in section 4.2e, where we notice that it is already needed to obtain the standard thermodynamics at very large $T$.

Some word of nomenclature is called for. The case of a harmonic potential $V(x) = \frac{1}{2}ax^2$ is often called “the linear case” in literature, of course referring to its linear force. The expressions “linear potential” and “non-linear potential”, that are sometimes found in literature, are misnomina, and will be avoided by us.

2. Derivation of general quantum Langevin equation

The operator equations of motion for the bath modes read

$$\dot{x}_i = \frac{1}{m_i} p_i, \quad (2.6)$$
$$\dot{p}_i = -x_i m_i \omega_i^2 + c_i x \quad (2.7)$$

After introducing the creation and annihilation operators by

$$x_i = \sqrt{\frac{\hbar}{2m_i \omega_i}} (a_i + a_i^\dagger), \quad p_i = i \sqrt{\frac{\hbar m_i \omega_i}{2}} (a_i^\dagger - a_i) \quad (2.8)$$

we can write Eqs. (2.6, 2.7) in the form

$$\dot{a}_i(t) = -i \omega_i a_i(t) + i \sqrt{\frac{c_i^2}{2\hbar m_i \omega_i}} x(t). \quad (2.9)$$

This equation is solved readily:

$$a_i(t) = e^{-i \omega_i t} a_i(0) + i \sqrt{\frac{c_i^2}{2\hbar m_i \omega_i}} \int_0^t ds e^{-i \omega_i (t-s)} x(s), \quad (2.10)$$

yielding

$$x_i(t) = x_i(0) \cos \omega_i t + \frac{p_i(0)}{m_i \omega_i} \sin \omega_i t + \frac{c_i}{m_i \omega_i} \int_0^t ds \sin \omega_i (t-s) x(s) \quad (2.11)$$
$$p_i(t) = -m_i \omega_i x_i(0) \sin \omega_i t + p_i(0) \cos \omega_i t + c_i \int_0^t ds \cos \omega_i (t-s) x(s) \quad (2.12)$$

The Heisenberg equations of motion for the Brownian particle read

$$\dot{x} = \frac{1}{m} p, \quad (2.13)$$
$$\dot{p} = -ax + \sum_i c_i x_i - x \sum_i \frac{c_i^2}{m_i \omega_i^2} \quad (2.14)$$

Combined with Eq. (2.11) the last equation becomes

$$m \ddot{x}(t) = -ax(t) + \eta(t) - \int_0^t dt' \dot{x}(t-t') x(t') - \gamma \dot{x}(t) \quad (2.15)$$

where

$$\eta(t) = \sum_i c_i [x_i(0) \cos \omega_i t + \frac{p_i(0)}{m_i \omega_i} \sin \omega_i t] = \sum_i \sqrt{\hbar c_i^2 \frac{1}{2m_i \omega_i}} [a_i^\dagger(0) e^{i \omega_i t} + a_i(0) e^{-i \omega_i t}], \quad (2.16)$$
$$\gamma(t) = \sum_i \frac{c_i^2}{m_i \omega_i^2} \cos (\omega_i t), \quad (2.17)$$
are the noise related to the *unperturbed* bath, and the friction kernel, respectively. A partial integration brings

\[
m \ddot{x}(t) = -ax(t) - x(0)\gamma(t) - \int_{0}^{t} ds \gamma(t-s) \dot{x}(s) + \eta(t),
\]

(2.18)

Notice that in this derivation the back-reaction of the bath on the particle has been taken into account in an exact manner. It is described by the integrals in eqs. (2.11), (2.12), and brings the damping terms \(x(t)\gamma(0) - x(0)\gamma(t) - \int_{0}^{t} ds \gamma(t-s) \dot{x}(s)\) in going from eq. (2.14) to (2.18).

3. Drude-Ullersma spectrum

For some, but not all, of our applications it is beneficia to consider a fully explicit case for the bath. The bath is assumed to have uniformly spaced modes

\[
\omega_i = i \Delta \quad i = 1, 2, 3, \ldots
\]

(2.19)

and for the couplings we choose the Drude-Ullersma spectrum [11,9]

\[
c_i = \sqrt{\frac{2 \gamma m_i \omega_i^2 \Delta}{\pi}} \frac{\Gamma^2}{\omega_i^2 + \Gamma^2}
\]

(2.20)

Here \(\Gamma\) is the characteristic Debye cutoff frequency of the bath, and \(\gamma\) stands for the coupling constant; it has dimension \(kg/s\). Our parameter \(\gamma\), related to another one \((\gamma' = \gamma/m)\) sometimes employed, see, e.g., [11], allows to consider changes in the effective mass \(m\) at fixed coupling to the bath.

The thermodynamic limit for the bath is taken by sending \(\Delta \to 0\), which induces relaxational behavior. As usual, the “Heisenberg” timescale \(1/\Delta\) will be extremely large, implying that in the remaining approach the limit of “large times” always means the quasi-stationary non-equilibrium state where time is still much less than \(1/\Delta\). In the limit \(\Delta \to 0\) each coupling \(c_i \sim \sqrt{\Delta}\) is very weak. The fact that the bath has many modes nevertheless induces its non-trivial influence. At finite but small \(\Delta\) the system would have an initial relaxational behavior, which at times of order \(1/\Delta\) is changed in a recurrent behavior.

It is customary to define the spectral density

\[
J(\omega) = \frac{\pi}{2} \sum_i \frac{c_i^2}{m_i \omega_i^3} \delta(\omega - \omega_i) = \frac{\gamma \omega \Gamma^2}{\omega^2 + \Gamma^2}
\]

(2.21)

It has the Ohmic behavior \(J \approx \gamma \omega\) for \(\omega \ll \Gamma\), and \(\gamma\) is called the interaction strength or damping constant. As \(J(\omega)\) is cut off at the “Debye” frequency \(\Gamma\), it is called a quasi-Ohmic spectrum.

For many applications only the spectral density needs to be defined. However, for our further calculations it is advantageous to stick to the fully specified linear bath, with its frequencies (2.19) and couplings (2.20). It can then be shown that the friction kernel (2.17) becomes

\[
\gamma(t) = \frac{2 \gamma}{\pi} \int_{0}^{\infty} d\omega \frac{\Gamma^2}{\omega^2 + \Gamma^2} \cos \omega t = \frac{\gamma \Gamma}{e^{\Gamma |t|}}
\]

(2.22)

It is non-local in time, but on timescales much larger than \(1/\Gamma\) it may be replaced by \(\gamma \delta_+(t)\).

Finally we wish to mention that there are alternative ways to derive the quantum Langevin equation [11], since many of its properties are rigidly determined by general statements like the quantum fluctuation-dissipation theorem [5]. Nevertheless, we choose to focus on concrete models, because they show in detail how the quantum Langevin equation arises from first principles, and thus are better suited for pedagogical purposes.

3. GIBBSIAN STATE FOR A HARMONIC CONFINING POTENTIAL

The case of an oscillator subject to a parabolic confining potential is a celebrated exactly solvable problem in quantum mechanics,
\[ \mathcal{H}(p, x) = \mathcal{K}(p) + \mathcal{V}(x) = \frac{p^2}{2m} + \frac{1}{2}ax^2 \]  

(3.1)

The eigenfrequency is already known from the classical treatment,

\[ \omega_0 = \sqrt{\frac{a}{m}} \]  

(3.2)

When this oscillator is coupled to an oscillator bath with bilinear coupling, as was done in Eq. (2.1), the problem remains exactly solvable. It is in the true sense “the harmonic oscillator model” for quantum Brownian motion.

It is well known that, besides its direct physical meaning, the harmonic oscillator can be interpreted as an LC circuit. Then \( x \) may correspond to the charge \( Q \) on a capacitor, \( 1/a \) to its capacitance \( C \), \( m \) to an inductance \( L \), \( p \) to a flux \( LQ \), \( \gamma \) to a resistance \( R \), and \( \eta(t) \) to a random electro-motoric force. Although we will not use this language explicitly, it is useful to keep it in mind, especially when considering variations of parameters. Indeed, in this setup there should be nothing very difficult in varying \( L \) or \( C \), in our notation \( m \) and \( a \).

The theory of the dissipative harmonic oscillator is considered in many works (see [11] and Refs. there, as well as a recent work for the driven case [39]). We will now be primarily interested in thermodynamical aspects of this problem.

1. Shift of the bath frequencies due to coupling with the central particle

In Fourier space the equation of motion of the particle may be written as

\[ (a - m\omega^2 + \sum_i \frac{c_i^2}{m_i\omega_i^2})x = \sum_i c_ix_i, \]  

(3.3)

and for the bath

\[ (-m_i\omega^2 + m_i\omega_i^2)x_i = c_i\dot{x} \]  

(3.4)

From these relations one derives a condition for the eigenfrequencies \( \nu_k \)

\[ \frac{a}{m} - \nu^2 = \nu^2 \sum_{i \geq 1} \frac{c_i^2}{m_i\omega_i^2(\omega_i^2 - \nu^2)} = \frac{2\gamma\Gamma^2\nu^2}{\pi} \sum_{i \geq 1} \frac{\Delta}{(\omega_i^2 + \Gamma^2)(\omega_i^2 - \nu^2)} \]

\[ = -\frac{2\gamma\Gamma^2\nu^2}{\pi(\nu^2 + \Gamma^2)} \sum_{i \geq 1} \frac{\Delta}{\omega_i^2 + \Gamma^2} + \frac{\gamma\Gamma^2\nu}{\pi(\nu^2 + \Gamma^2)} \sum_{i \geq 1} \left[ \frac{\Delta}{\omega_i - \nu} - \frac{\Delta}{\omega_i + \nu} \right] \]  

(3.5)

(3.6)

where we inserted the definition (2.20) of the \( c_i \). The first sum may be replaced by an integral, while the second can be carried out exactly,

\[ \sum_{i=1}^{\infty} \left[ \frac{\Delta}{\omega_i - \nu} - \frac{\Delta}{\omega_i + \nu} \right] = \lim_{N \to \infty} \left[ \psi(N - \nu) - \psi(1 - \nu) - \psi(N + \nu) + \psi(1 + \nu) \right] = \frac{\Delta}{\nu} - \pi \cot \frac{\pi\nu}{\Delta} \]  

(3.7)

where \( \psi(z) = d \ln \Gamma(z)/dz \) is the di-Gamma function and we used

\[ \psi(z + 1) = \psi(z) + \frac{1}{z}, \quad \psi(1 - z) = \psi(z) + \pi \cot \pi z \]  

(3.8)

The eigenfrequencies \( \nu_k \) of the coupled system thus follow as the roots of

\[ \cot \frac{\pi\nu}{\Delta} - \frac{\Delta}{\pi\nu} = -\frac{(a/m - \nu^2)(\nu^2 + \Gamma^2) + \gamma\Gamma\nu^2}{\gamma\Gamma^2\nu} \]  

(3.9)

The transcendental equation has no solution for \( 0 \leq \nu \leq \Delta \). For \( \nu > \Delta \) there is one solution in each period of the cotangens, except for the period that contains the point \( \nu = \omega_0 \equiv \sqrt{a/m} \), where there occur either three solutions or one. One can then check that in the limit of vanishing coupling \( \gamma \to 0 \), there occur the modes \( \omega_i = i\Delta \) (i = 1, 2, ⋯),
and $\omega_0$. Notice, however, that this behavior only pertains in the regime of infinitesimal coupling $\gamma < \gamma_c$ with $\gamma_c \sim m\Delta$. For $\gamma \geq \gamma_c$, however, the interval containing $\omega_0$ has only one solution, so $\omega_0$ is lost as a separate mode, its influence being taken by a shift of neighboring modes.

For finite $\gamma$ the solution of (3.9) shows that the bath modes $\omega_k \gg \Delta$ now get shifted to

$$\nu_k = k\Delta - \frac{1}{\pi} \phi(k\Delta)\Delta = \omega_k - \frac{1}{\pi} \phi(\omega_k)\Delta \quad \text{(3.10)}$$

where

$$\phi(\nu) = \arctan \left( \frac{\gamma \Gamma^2 \nu}{(a - m\nu^2)(\nu^2 + \Gamma^2) + \gamma \Gamma \nu^2} \right) \quad \text{(3.11)}$$

Here the definition of the arctan is such that $\phi$ goes monotonously from $\phi(0) = 0$ to $\phi(\infty) = \pi$. We shall need

$$\sin \phi(\nu) = \left( \frac{\gamma \Gamma^2 \nu}{(a - m\nu^2)(\nu^2 + \Gamma^2) + \gamma \Gamma \nu^2} \right) \approx \frac{1}{\gamma^2 \nu^2} \left( \frac{2}{a - m\nu^2} \right)^{1/2} \quad \text{(3.12)}$$

where the approximation holds for large $\Gamma$.

2. The Gibbsian state of the particle and its bath

The steps of last section allow to calculate the Gibbs free energy of the total system,

$$\beta F_{\text{tot}}(T, \gamma) = \sum_k \ln 2 \sinh \frac{1}{2} \beta \hbar \nu_k \quad \text{(3.13)}$$

For small $\Delta$ one may use the identity

$$\sum_{k=1}^{\infty} A(\nu_k) = \frac{1}{\Delta} \int_0^\infty d\omega_k A(\nu_k) = \frac{1}{\Delta} \int_0^\infty d\nu_k \frac{d\omega_k}{d\nu_k} A(\nu_k) = \int_0^\infty d\nu \left[ \frac{1}{\Delta} + \frac{1}{\pi} \frac{d\phi(\nu)}{d\nu} \right] A(\nu) + O(\Delta) \quad \text{(3.14)}$$

and one gets

$$\beta F_{\text{tot}}(T, \gamma) = \beta F_B(T, \gamma = 0) + \beta F_p(a, \gamma, \Gamma, m, T) \quad \text{(3.15)}$$

where the first term is the free energy of the bath in absence of the particle. Neglecting its divergent zero point energy one gets

$$\beta F_B(T, \gamma = 0) = \frac{1}{\Delta} \int_0^\infty d\omega \ln(1 - e^{-\beta \hbar \omega}) = -\frac{\pi^2 T}{6\hbar \Delta} \quad \text{(3.16)}$$

It is of order $1/\Delta$, showing the extensivity of the bath, and implies the energy

$$U_B(T, \gamma = 0) = \frac{\pi^2 T}{6\hbar \Delta} T^2 \quad \text{(3.17)}$$

and the linear specific heat and entropy

$$C_B(T, \gamma = 0) = S_B(T, \gamma = 0) = \frac{\pi^2 T}{3\hbar \Delta} \quad \text{(3.18)}$$

The free energy shift due to the central particle, its coupling to the bath and the resulting disturbance of the bath, follows from Eq. (3.14) as

$$\beta F_p = \frac{1}{\pi} \int_0^\infty d\nu \ln[2 \sinh \frac{1}{2} \beta \hbar \nu] \frac{d\phi}{d\nu} \quad \text{(3.19)}$$

$$= \frac{\gamma \Gamma^2}{\pi} \int_0^\infty d\nu \ln[2 \sinh \frac{1}{2} \beta \hbar \nu] \frac{a\Gamma^2 + (m\Gamma^2 + \gamma \Gamma - a)\nu^2 + 3m\nu^4}{[(a - m\nu^2)(\nu^2 + \Gamma^2) + \gamma \Gamma \nu^2]^2 + \gamma^2 \Gamma^4 \nu^2} \quad \text{(3.20)}$$

A useful identity is

$$\beta F_p = \ln 2 \sinh (\frac{1}{2} \beta \hbar \nu_1) + \frac{1}{2} \beta \hbar \int_0^\infty d\nu \left[ \theta(\nu - \nu_1) - \frac{1}{\pi} \phi(\nu) \right] \coth (\frac{1}{2} \beta \hbar \nu) \quad \text{(3.21)}$$

where $\nu_1$ is arbitrary and $\theta$ is the Heaviside step function.
The present model for a damped harmonic oscillator has three characteristic frequencies, that do not depend on temperature. They just follow from the linear equations of motion, and thus have the same value at high and low temperatures.

The denominator in (3.20) is a fourth order polynomial in $\nu^2$. It decomposes as

$$m^2(\nu^2 + \Gamma^2)P_3(i\nu)P_3(-i\nu)$$

where

$$P_3(s) = s^3 - \Gamma s^2 + (\omega_0^2 + \frac{\gamma \Gamma}{m})s - \omega_0^2 \Gamma = (s - \Gamma)(s^2 + \omega_0^2) + \frac{\gamma \Gamma}{m}s$$

The roots $s = \omega_{1,2,3}$ of $P_3(s)$ satisfy the relations

$$\omega_1 + \omega_2 + \omega_3 = \Gamma$$

$$\omega_1 \omega_2 + \omega_2 \omega_3 + \omega_3 \omega_1 = \omega_0^2 + \frac{\gamma \Gamma}{m}$$

$$\omega_1 \omega_2 \omega_3 = \Gamma \omega_0^2$$

Two different situations can arise: Either all three roots are real (this is the case in the overdamped regime), or, in the underdamped regime, two of them are complex conjugate: $\omega_1 = \omega_2$, whereas $\omega_3$ is real. In both cases one has $\Re \omega_{1,2,3} > 0$, which indicates that with time the particle relaxes toward a stationary state.

For small $\gamma$ these roots read:

$$\omega_{1,2} = \pm i \omega_0 + \frac{\gamma \omega_0^2}{m \Gamma (\Gamma + i \omega_0)} + \left( \frac{\gamma \omega_0^2}{m} \right)^2 \frac{\Gamma^2 (\Gamma + i \omega_0)}{8 \omega_0 (\Gamma + i \omega_0)^3}$$

$$\omega_3 = \Gamma - \frac{\gamma \omega_0^2}{m (\Gamma^2 + \omega_0^2)} - \left( \frac{\gamma \omega_0^2}{m} \right)^2 \frac{\Gamma^3 (\Gamma^2 - \omega_0^2)}{(\Gamma^2 + \omega_0^2)^3}$$

On the other hand, for a large $\Gamma$ one gets

$$\omega_{1,2} = \frac{\gamma}{2m} \left( 1 \pm \sqrt{1 - \frac{4am}{\gamma^2}} \right) + \frac{1}{2\Gamma} \left( \frac{\gamma}{m} \right)^2 \left[ 1 \pm \frac{1 - 2am/\gamma^2}{\sqrt{1 - 4am/\gamma^2}} \right]$$

$$\omega_3 = \Gamma - \frac{\gamma}{m} - \frac{1}{\Gamma} \left( \frac{\gamma}{m} \right)^2$$

We shall only need them to leading order in $1/\Gamma$

$$\omega_1 = \frac{\gamma(1 - w)}{2m} = \frac{2a}{\gamma(1 + w)}$$, \quad \omega_2 = \frac{\gamma(1 + w)}{2m}$$, \quad \omega_3 = \Gamma - \frac{\gamma}{m}$$

where we denoted

$$\epsilon = \frac{am}{\gamma^2}$$, \quad w = \sqrt{1 - 4\epsilon}$$

Later on we shall need

$$a \frac{dw}{da} = m \frac{dw}{dm} = -\frac{1 - w^2}{2w}$$, \quad a \frac{d\omega_{1,2}}{da} = \pm \frac{\gamma(1 - w^2)}{4m w}$$, \quad m \frac{d\omega_{1,2}}{dm} = \pm \frac{\gamma}{4mw} (1 + w)^2$$

For overdamping ($\epsilon < \frac{1}{4}$) $w$ is real positive. Our interest is in particular the strong damping regime $\gamma^2 \gg am$, where

$$\omega_1 = \frac{a}{\gamma}$$, \quad \omega_2 = \frac{\gamma}{m} \left( 1 - \frac{am}{\gamma^2} \right)$$, \quad \omega_3 = \Gamma - \frac{\gamma}{m}$$
and the approximations hold to leading order in $\varepsilon$.

Already in the classical regime our system has three characteristic relaxation times: for the coordinate, for the momentum and for the noise. For large $\Gamma$ and $\gamma$ they are well separated

$$
\tau_x = \frac{1}{\omega_1} \approx \frac{\gamma}{a} \gg \tau_p = \frac{1}{\omega_2} \approx \frac{m}{\gamma} \gg \tau_\eta = \frac{1}{\Gamma} \tag{3.35}
$$

In the quantum regime the quantum time-scale

$$
\tau_\hbar = \frac{\hbar}{T} \tag{3.36}
$$
is comparable to or larger than $\tau_x$, inducing quantum coherence effects of the noise and thus new physics.

In case of underdamping, ($\varepsilon > \frac{1}{4}$) one has $w = i\bar{w}$, with

$$
\bar{w} = \sqrt{4\varepsilon - 1}, \quad \omega_{1,2} = \frac{\gamma(1 \mp i\bar{w})}{2m} \tag{3.37}
$$

This leads to the renormalized oscillation time $\tau_0$ and the damping time $\tau_d$

$$
\tau_0 = \frac{1}{\sqrt{\omega_0^2 - \gamma^2/4m^2}}, \quad \tau_d = \frac{2m}{\gamma} \tag{3.38}
$$

Since $\tau_d$ differs from $\tau_p$ by a factor of order unity, we may skip the latter and use $\tau_p$ and $\tau_0$ as the relevant timescales in the underdamped regime.

It is worth to mention that the weak-coupling limit commutes with the quasi-Ohmic limit, in the sense that taking large $\Gamma$ in Eqs. (3.27, 3.28) we get the same main term and at least the first correction as having taken small $\gamma$ limit in Eqs. (3.31, 3.30).

### b. Continuing the main argument for the Gibbsian state

In order to calculate the free energy (3.20), we shall first determine the following integral

$$I(a, A, B) = \int_0^\infty \frac{d\nu \, \coth(\frac{1}{2}a\nu)}{(A^2 + \nu^2)(B^2 + \nu^2)}. \tag{3.39}$$

We can write

$$
I(a, A, B) = \int_0^\infty \frac{d\nu}{(A^2 + \nu^2)(B^2 + \nu^2)} + 2 \int_0^\infty \frac{d\nu}{(e^{\nu} - 1)(A^2 + \nu^2)(B^2 + \nu^2)}
$$

$$= \frac{1}{B^2 - A^2} \ln \frac{B + A}{B - A} + \frac{2}{B^2 - A^2} \left[ \int_0^\infty \frac{d\nu}{(e^{\nu} - 1)(A^2 + \nu^2)} - \int_0^\infty \frac{d\nu}{(e^{\nu} - 1)(B^2 + \nu^2)} \right]
$$

$$= \frac{1}{B^2 - A^2} \left[ \psi \left( \frac{aB}{2\pi} \right) - \psi \left( \frac{aA}{2\pi} \right) \right] - \frac{\pi}{a} \ln \frac{A}{B}(A + B), \tag{3.40}
$$

where we used the known formula

$$
2 \int_0^\infty \frac{tdt}{(\exp(2\pi t) - 1)(t^2 + z^2)} = \ln z - \psi(z) - \frac{1}{2z} \tag{3.41}
$$

By integration we obtain

$$
J(a, A, B) = \int_0^\infty \frac{d\nu}{\pi} \ln(2\sinh \frac{1}{2}a\nu) \left( \frac{1}{A^2 + \nu^2} - \frac{1}{B^2 + \nu^2} \right)
$$

$$= -\frac{1}{A} \ln \Gamma \left( \frac{aA}{2\pi} \right) - \frac{1}{2A} \ln \frac{aA}{4\pi^2} + \frac{1}{B} \ln \Gamma \left( \frac{aB}{2\pi} \right) + \frac{1}{2B} \ln \frac{aB}{4\pi^2} \tag{3.42}
$$

In terms of the roots $\omega_i$, we may write Eq. (3.10) as
\[ \phi(\nu) = \arctan \frac{\nu}{\omega_1} + \arctan \frac{\nu}{\omega_2} + \arctan \frac{\nu}{\omega_3} - \arctan \frac{\nu}{\Gamma} \]  

(3.43)

The derivation follows immediately after using (3.24) with \( P_3(s) = (s-\omega_1)(s-\omega_2)(s-\omega_3) \) and expressing the arctan in logarithm’s. The integral in Eq. (3.20) can now be done by adding to \( \phi(\nu) \) a term \([\Gamma - \omega_1 - \omega_2 - \omega_3]/\omega_4] \arctan(\nu/\omega_4) \), which vanishes for any \( \omega_4 \) on account of Eq. (3.24), and then using Eq. (3.42) with \( a = h\beta \).

This finally brings the shift of the free energy due the presence of the particle

\[ \beta F_p = \ln \Gamma \left( \frac{\beta h \Gamma}{2\pi} \right) - \ln \left( \frac{\beta h \omega_1}{2\pi} \right) - \ln \left( \frac{\beta h \omega_2}{2\pi} \right) - \ln \left( \frac{\beta h \omega_3}{2\pi} \right) - \ln \frac{\beta h \omega_0}{(2\pi)^2} \]  

(3.44)

This is just equal to \( -\ln Z' \) with \( Z' \) calculated in Eq. (4.20) of Grabert et al. [35]. These authors did not point at the physical role of their \( Z' \). Here we see it is the part of the partition sum of the total system related to the central particle and its coupling to the bath with its linear unperturbed spectrum \( \omega_k = k\Delta \). We nevertheless expect that the statics and the dynamics hold for more general bath spectra, as long as the interaction is bilinear, and the spectra ensure relaxation.

The internal energy reads

\[ U_p = \frac{\hbar \Gamma}{2\pi} \left( \frac{\beta h \Gamma}{2\pi} \right) - \frac{\hbar \omega_1}{2\pi} \left( \frac{\beta h \omega_1}{2\pi} \right) - \frac{\hbar \omega_2}{2\pi} \left( \frac{\beta h \omega_2}{2\pi} \right) - \frac{\hbar \omega_3}{2\pi} \left( \frac{\beta h \omega_3}{2\pi} \right) - T \]  

(3.45)

3. The effective temperatures

We shall now study two objects, \( T_x = a\langle x^2 \rangle \) and \( T_p = \langle p^2 \rangle/2m \), that would in classical equilibrium be equal to \( T \) and which we shall interpret below as effective temperatures. As in the classical situation, it holds that

\[ T_x = a\langle x^2 \rangle = 2a \frac{\partial F_p}{\partial a} \]  

(3.46)

We find

\[ T_x = -T + \frac{\hbar a}{\pi m} \left\{ \frac{\omega_1}{\omega_2 - \omega_1}(\omega_3 - \omega_1) \psi \left( \frac{\beta h \omega_1}{2\pi} \right) + \frac{\omega_2}{\omega_1 - \omega_2}(\omega_3 - \omega_2) \psi \left( \frac{\beta h \omega_2}{2\pi} \right) + \frac{\omega_3}{\omega_1 - \omega_3}(\omega_2 - \omega_1) \psi \left( \frac{\beta h \omega_3}{2\pi} \right) \right\} \]  

(3.47)

Likewise,

\[ T_p = \frac{\langle p^2 \rangle}{m} = -2m \frac{\partial F_p}{\partial m} = T_x + \frac{\hbar \gamma \Gamma}{\pi m} \left\{ \frac{\omega_1}{\omega_2 - \omega_1}(\omega_3 - \omega_1) \psi \left( \frac{\beta h \omega_1}{2\pi} \right) + \frac{\omega_2}{\omega_1 - \omega_2}(\omega_3 - \omega_2) \psi \left( \frac{\beta h \omega_2}{2\pi} \right) + \frac{\omega_3}{\omega_1 - \omega_3}(\omega_2 - \omega_1) \psi \left( \frac{\beta h \omega_3}{2\pi} \right) \right\} \]  

(3.48)

To find the Gibbsonian values for \( \gamma \to 0 \) one has to notice that

\[ \psi \left( \frac{i\omega_0}{2\pi T} \right) - \psi \left( -\frac{i\omega_0}{2\pi T} \right) = 2\pi i \frac{\hbar \omega_0}{\hbar \omega_0 + 2i\pi T} \]  

(3.49)

and this yields the standard weak-coupling result known from all the books,

\[ U = \frac{1}{2} T_x + \frac{1}{2} T_p = T_x = T_p = \frac{\hbar \omega_0}{2} \coth \frac{\beta h \omega_0}{2} = \frac{1}{2} \hbar \omega_0 + \frac{\hbar \omega_0}{e^{\beta h \omega_0} - 1}, \quad (\gamma \to 0). \]  

(3.50)

a. Thermodynamics and effective temperatures at high \( T \)

Using that for small \( z \)

\[ \ln \Gamma(z) = -\ln z - \gamma z + \frac{\pi^2}{12} z^2 \]  

(3.51)
where $\gamma_E = 0.5772156$ is Euler’s constant, one gets the free energy

$$F_p = T \ln \beta \hbar \omega_0 + \frac{\beta \hbar^2}{48} \left[ \Gamma^2 - \omega_1^2 - \omega_2^2 - \omega_3^2 \right] \approx T \ln \beta \hbar \omega_0 + \frac{\beta \hbar^2 (a + \gamma \Gamma)}{24m}$$  \hspace{1cm} (3.52)

where $\omega_0 = \sqrt{a/m}$ and $\Gamma$ has been taken large in the second identity. The internal energy and entropy become

$$U_p = T + \frac{\beta \hbar^2 (a + \gamma \Gamma)}{12m}, \quad S_p = \ln \frac{T}{\hbar \omega_0} + 1 + \frac{\beta \hbar^2 (a + \gamma \Gamma)}{6m}$$  \hspace{1cm} (3.53)

From eqs. (3.47), (3.48) we obtain at large $T$

$$T_x = T + \frac{\beta \hbar^2 a}{12m} - \frac{\beta^3 \hbar^4 a (a + \gamma \Gamma)}{720 m^2};$$  \hspace{1cm} (3.54)

and

$$T_p = T + \frac{\beta \hbar^2 (a + \gamma \Gamma)}{12m} - \frac{\beta^2 \hbar^2 \Gamma^2}{4 \pi^2 m} \zeta(3) + \frac{\beta^3 \hbar^4 [\gamma \Gamma^3 m - (a + \gamma \Gamma)^2]}{720 m^2}$$  \hspace{1cm} (3.55)

b. Thermodynamics and effective temperatures at low $T$

Further results can be obtained with the improved Stirling formula

$$\ln \Gamma(z) = (z - \frac{1}{2}) \ln z - z + \frac{1}{2} \ln(2\pi) + \frac{1}{12z} - \frac{1}{360z^3}$$  \hspace{1cm} (3.56)

One gets for arbitrary and for large $\Gamma$

$$F_p = \frac{\hbar}{2\pi} [\Gamma \ln \Gamma - \sum_{k=1}^{3} \omega_k \ln \omega_k] - \frac{\pi \gamma}{6 \hbar a} T^2$$

$$= \frac{\hbar \gamma}{2\pi m} \ln \frac{2m \Gamma}{\gamma} + 1 - \frac{\hbar \gamma}{4 \pi m} [(1 + w) \ln(1 + w) + (1 - w) \ln(1 - w)] - \frac{\pi \gamma}{6 \hbar a} T^2,$$  \hspace{1cm} (3.57)

$$U_p = \frac{\hbar}{2\pi} [\Gamma \ln \Gamma - \sum_{k=1}^{3} \omega_k \ln \omega_k] + \frac{\pi \gamma}{6 \hbar a} T^2$$

$$= \frac{\hbar \gamma}{2\pi m} \ln \frac{2m \Gamma}{\gamma} + 1 - \frac{\hbar \gamma}{4 \pi m} [(1 + w) \ln(1 + w) + (1 - w) \ln(1 - w)] + \frac{\pi \gamma}{6 \hbar a} T^2,$$  \hspace{1cm} (3.58)

$$S_p = \beta (U_p - F_p) = \frac{\pi \gamma}{3 \hbar a} T,$$  \hspace{1cm} (3.59)

Notice that $S_p$, the shift in total von Neumann entropy due to the presence of the Brownian particle, differs strongly from the von Neumann entropy of the particle itself, which remains finite at $T = 0$, as we shall show in Eqs. (4.34) and (4.35). The non-additivity of entropies encountered here is a deep aspect of quantum physics, where a subsystem can have a larger von Neumann entropy than the full system.

Using (3.53) one finds at low temperatures and arbitrary $am/\gamma^2$, $w = \sqrt{1 - 4am/\gamma^2}$:

$$T_p = \frac{\hbar \gamma}{2\pi m} \ln \frac{2m \Gamma}{\gamma} + \frac{\hbar \gamma}{4 \pi m w} [(1 - w)^2 \ln(1 - w) - (1 + w)^2 \ln(1 + w)] + O(T^4),$$  \hspace{1cm} (3.60)

$$T_x = \frac{\hbar a}{\pi \gamma w} \ln \frac{1 + w}{1 - w} + \frac{\pi \gamma}{3 \hbar a} T^2 + O(T^4),$$  \hspace{1cm} (3.61)

The above expressions simplify in the limit of strong damping, see Eq. (4.33):

$$F_p(T) = \frac{\hbar \gamma}{2\pi m} [\Gamma \ln \Gamma + 1] + \frac{\hbar a}{2\pi \gamma} \ln \frac{\gamma^2}{am} - \frac{\pi \gamma}{6 \hbar a} T^2,$$

$$U_p(T) = \frac{\hbar \gamma}{2\pi m} [\Gamma \ln \Gamma + 1] + \frac{\hbar a}{2\pi \gamma} \ln \frac{\gamma^2}{am} + \frac{\pi \gamma}{6 \hbar a} T^2.$$  \hspace{1cm} (3.62)
and

\begin{align*}
T_p &= \frac{\hbar \gamma}{\pi m} \ln \frac{\Gamma m}{\gamma} + \frac{\hbar a}{2m} + O(T^4), \\
T_x &= \frac{\hbar a}{\gamma} \ln \frac{\gamma^2}{a m} + \frac{\pi \gamma T^2}{3 \hbar a} + O(T^4),
\end{align*}

(3.63) (3.64)

4. THERMODYNAMIC ASPECTS OF ADIABATIC CHANGES

1. Generalized thermodynamic formulation

We now make clear that the relation with standard thermodynamics can be continued much further by introducing the two effective temperatures

\begin{align*}
T_p &= \frac{\langle p^2 \rangle}{m}, \quad T_x = a \langle x^2 \rangle,
\end{align*}

(4.1)

One reason to do this is that the stationary state for the harmonic potential has a quasi-Gibbsian expression for the Wigner function

\begin{align*}
W(p, x) &= W_p(p)W_x(x) = e^{-K(p)/T_p} e^{-V(x)/T_x} \\
&= \frac{1}{\sqrt{2\pi m T_p}} e^{-\frac{1}{2m} T_p p^2} \frac{1}{\sqrt{2\pi T_x}} e^{-\frac{1}{2} T_x x^2} e^{-V(x)/T_x},
\end{align*}

(4.2)

with \( K(p) = p^2/2m \) the kinetic energy and \( V(x) = \frac{1}{2} ax^2 \) the potential energy. This expression is quasi-Gibbsian, since there occur two different temperature-like variables. (Notice that the normalization is \( \int dp dx W = 1 \)). There occur the Boltzmann entropies of momenta and coordinate,

\begin{align*}
S_p &= - \int dp W(p) \ln[W(p) \sqrt{\hbar}] = \frac{1}{2} \ln \frac{m T_p}{\hbar} + \frac{1}{2}, \\
S_x &= - \int dx W(x) \ln[W(x) \sqrt{\hbar}] = \frac{1}{2} \ln \frac{T_x}{\hbar a} + \frac{1}{2},
\end{align*}

(4.3) (4.4)

(in \( S_p \) and \( S_x \) we skipped terms \( \ln 2\pi \)). The complete “Boltzmann” entropy is

\begin{align*}
S_B &= S_p + S_x = - \int dp dx W(p, x) \ln[W(p, x) \hbar] = \frac{1}{2} \ln \frac{m T_p T_x}{\hbar^2 a} + 1
\end{align*}

(4.5)

a. Internal energy and interaction energy

The energy of the central particle reads

\begin{equation}
U = \frac{\langle p^2 \rangle}{2m} + \frac{1}{2} a \langle x^2 \rangle = \frac{1}{2} T_p + \frac{1}{2} T_x
\end{equation}

(4.6)

For a discussion of this identification in systems without a self-interaction term, see section 2.1.

The interaction energy, i.e. the energy of the cloud of bath modes that surround the particle, is defined as

\begin{equation}
U_{\text{int}} = U_{\text{tot}}(\gamma = 0) - U = U_p - U = U_p - \frac{1}{2} T_p - \frac{1}{2} T_x
\end{equation}

(4.7)

At high temperatures one gets from Eqs. (3.53) and (3.54)

\begin{align*}
U &= T + \frac{\beta \hbar^2}{24m} (2a + \gamma \Gamma), \\
U_{\text{int}} &= \frac{\beta \hbar^2}{24m} (6a + 7\gamma \Gamma)
\end{align*}

(4.8)

Since the energy of the cloud is involves \( \hbar \), the non-triviality of the cloud is a quantum effect.
At low temperatures one gets the internal energy
\[ U = \frac{\hbar \gamma}{2\pi m} \ln \frac{2m\Gamma}{\gamma} - \frac{\hbar \gamma}{2\pi m} (1 + w) \ln (1 + w) + (1 - w) \ln (1 - w)) + \frac{\pi \gamma}{6\hbar} T^2 \] (4.9)

For large damping this reduces to
\[ U = \frac{\hbar \gamma}{\pi m} \ln \frac{m \Gamma}{\gamma} + \frac{\hbar a}{2\pi \gamma} \left[ \ln \left( \frac{\gamma^2}{am} + 1 \right) \right] + \frac{\pi \gamma}{6\hbar} aT^2. \] (4.10)

The interaction energy of the cloud is now independent of \( w \),
\[ U_{\text{int}} = \frac{\hbar \gamma}{2\pi m} + \mathcal{O}(T^4), \] (4.11)
provided that \( \Gamma \) is large.

b. Generalized free energy and the first and second law

The definition of the effective temperatures admits a clear thermodynamical interpretation. For studying the role of an adiabatically slow variation of an arbitrary parameter, such as \( a \) or \( m \), that we shortly denote by \( \alpha \), the free energy \( F \) is defined as
\[ F = -T_p \ln Z_p - T_x \ln Z_x, \] (4.12)
The definitions \( Z_p = \int dp \exp[-K(p)/T_p], \ Z_x = \int dx \exp[-V(x)/T_x] \) bring
\[ F = -\frac{1}{2} T_p \ln m T_p - \frac{1}{2} T_x \ln T_x a \] (4.13)

For considering changes in system parameters one needs
\[ \frac{d}{d\alpha} \left( -T_p \ln Z_p \right) = -\ln Z_p \frac{d}{d\alpha} T_p - \frac{T_p}{Z_p} \frac{dZ_p}{d\alpha} = \frac{1}{Z_p} \int dp e^{-\beta_p K(p)} d\alpha, \]
\[ \frac{d}{d\alpha} \left( -T_x \ln Z_x \right) = -\ln Z_x \frac{d}{d\alpha} T_x - \frac{T_x}{Z_x} \frac{dZ_x}{d\alpha} = \frac{1}{Z_x} \int dx e^{-\beta_x V(x)} d\alpha \] (4.14)

Eq. (4.12) then yields
\[ dF = -S_x dT_x - S_p dT_p + dW_{\text{rev}}. \] (4.15)

with, in agreement with the derivations (4.21) and (4.24) below, the work added to the system
\[ dW_{\text{rev}} = -T_p \frac{dm}{2m} + T_x \frac{da}{2a} \] (4.16)

These relations are valid in spite of the fact that both \( T_x \) and \( T_p \) are functions of \( a \) and \( m \). Because of Eqs. (4.14), (4.13) and (4.14), the definition (4.12) is compatible with the standard identification [23,24]
\[ F = U - T_p S_p - T_x S_x \] (4.17)
that one would write down immediately for a two-temperature system. From this relation one will indeed reproduce the standard formulation for the first law for situations with two temperatures,
\[ dU = dQ_{\text{rev}} + dW_{\text{rev}}, \] (4.18)
\[ dQ_{\text{rev}} = T_p dS_p + T_x dS_x, \] (4.19)
where \( dQ_{\text{rev}} \) is the heat reversibly added to the particle. A detailed discussion concerning the general definitions of the work and heat is given below, in section 7.1.

14
The generalized thermodynamical relations \[4.14-4.18\] are in close analogy with those proposed recently for nonequilibrium glassy systems \[23-25\]. Analogous to that situation, \( F \) pertains to the particle alone, and, except at high \( T \), it differs from the \( F \) of Eq. \[3.44\] in previous section, which relates to the whole system, to be more precise, to the particle and the cloud of bath modes around it.

Let us recall that \( F \) satisfies Gibbsian thermodynamics, while \( F \) does not. There are many physical systems, such as a Josephson junction strongly coupled to the electromagnetic field, where the natural object to study is nevertheless \( F \), since it relates for that case to properties of the junction only.

It is standard wisdom that energy is dispersed if the variations are non-adiabatic changes. This is confirmed by Eq. \[7.43\], which holds provided the whole time-domain where \( m \) and \( a \) vary is accounted for. This leads to the general result

\[
dQ \leq T_p dS_p + T_x dS_x
\]

that is also known from the study of glasses and, more generally, from two-temperature systems.

2. Violation of the Clausius inequality

a. The Clausius inequality at small \( T \).

Let us now consider two concrete examples, and study the Clausius inequality \( dQ \leq T dS_{vN} \), which is one of possible formulations of the second law.

For a very slow variation of the spring constant \( a \) one gets

\[
dW_{rev} = \int dx dp(w(x, p, a) \frac{\partial H}{\partial a} da = \int dx w(x) \frac{1}{2} x^2 da = T_x \frac{da}{2a}
\]

in agreement with Eq. \[4.16\]. The first law implies for the heat added adiabatically to the particle at low \( T \)

\[
dQ_{rev} = dU - dW_{rev} = \left( \frac{\partial T_x}{\partial a} + \frac{\partial T_{p}}{\partial a} \right) \frac{T_x}{a} \frac{da}{2} = -\frac{\pi \gamma}{3 ha^2} T^2 da + \mathcal{O}(T^4 da)
\]

It is seen that \( dQ_{rev} = 0 \) at \( T = 0 \) for all \( \gamma \). Using Eqs. \[4.1, 4.4\] we derive for large \( \gamma \) and very large \( \Gamma \),

\[
dS_B = -\frac{da}{2a} \left[ \frac{1}{\ln(\gamma^2/\gamma m)} - \frac{ma}{\gamma^2 \ln(\gamma m/\gamma)} + \frac{\pi^2 \gamma^2 T^4}{3a^2 h^4 (\gamma^2/\gamma m)} \right.
\]

At \( T = 0 \) the Clausius inequality says that no heat can be taken from the bath, at best heat can go from the central system (here: the Brownian particle) to the bath. In our situation \( dQ \) is of order \( T^2 \), while \( T dS_{vN} \) is of order \( T \). Since we only do powercounting in \( T \) and both expressions are non-trivial, we may replace here \( S_{vN} \) by \( S_B \). Thus for the case \( da > 0 \), where an amount of work \( dW_{rev} > 0 \) is done on the system, the Clausius relation is violated at low but non-zero \( T \).

In the same way one can consider the variation of the (effective) mass \( m \). Here one has

\[
dW_{rev} = \int dx dp w(p, x) \frac{\partial H}{\partial m} dm = -\int dp w(p) \frac{p^2}{2m^2} dm = -T_p \frac{dm}{2m},
\]

again in concordance with Eq. \[4.11\]. This implies

\[
dQ_{rev} = (T_p \frac{\partial S_p}{\partial m} + T_x \frac{\partial S_x}{\partial m}) dm = \left( \frac{\partial T_p}{\partial m} + \frac{\partial T_x}{\partial m} \right) \frac{dm}{2} = \frac{h \gamma}{2 \pi m^2} \frac{dm}{m} + \mathcal{O}(T^2)
\]

In contrast to the previous case there is a transfer of heat even if the bath temperature is zero. Thus, violation of the Clausius inequality is even stronger in this case, since for \( dm > 0 \) one has \( dQ > 0 \), even though \( T dS_{vN} = 0 \) (for \( T \to 0 \)). This situation with \( dW_{rev} < 0 \) corresponds to work performed by the system on the environment. To underline that the heat comes from the cloud of bath modes, we notice that the general relations

\[
dW_{rev} = dF_p, \quad dU = dU_p - dU_{int} = dQ_{rev} + dW_{rev}
\]

imply
\[ dQ_{\text{rev}} = TdS_p - dU_{\text{int}} \] (4.27)

For changing \( m \) in the \( T = 0 \) situation it indeed holds that
\[ dQ_{\text{rev}} = -dU_{\text{int}} \] (4.28)

for all values of \( w \), even when \( \Gamma \) is not very large. For a change in \( a \) it holds that \( dU_{\text{int}} = \mathcal{O}(T^4) \), but Eq. (4.27) nevertheless reproduces Eq. (4.22), because of relation (3.59).

Let us briefly discuss consequences drawn from the violation of the Clausius inequality in the quantum regime. First of all it seen that it occurs in the overall Gibbsian state, so that globally (i.e., when applied to the overall closed system) thermodynamics is valid by definition. In particular, since the overall system does not absorb heat during any variation of a parameter, and \( dQ = 0 \) is consistent with the \( T \to 0 \) case of the Clausius inequality (later we will see that this is also the case at finite temperatures, where \( dQ \) is still zero). Nevertheless, the local state of the particle is not Gibbsian and does allow violations as we have seen. We stress that this violation arises due to quantum entanglement, which leads to non-gibbsian effective temperatures for the stationary state of the brownian particle. If the effective temperatures for \( T \to 0 \) would equal to their gibbsian values \( \hbar \omega_0/2 \), the state of the particle would be pure, which is impossible since it does interact with the bath.

When later discussing the Thomson’s formulation of the second law, we will see that it is perfectly valid for the overall Gibbsian state, so that the above violation of the Clausius inequality provides us with an explicit example showing that at low temperatures the very equivalence between different formulations of the second law is lost.

A further aspect of this matter is the squeezing of phase space and entropy, relevant for computing in the quantum regime. In a separate paper we have shown that the so-called Landauer bound for the erasure of one bit of information, that arises from the Clausius inequality, is violated in a similar manner [40].

Notice again that the effective temperatures remain finite in the limit \( T \to 0 \) (see Eqs. (3.63, 3.64) and Fig. 3), and both are larger than the bath temperature \( T \). The fact that they are non-equal is due to a mixed state of the particle. Indeed, a quantum system non-weakly interacting with its environment, will be in a mixed state even if the whole closed system (the particle and environment together) is in a pure state (e.g., the vacuum state).

![FIG. 4.1. The effective temperatures \( T_p, T_x \) versus the bath temperature \( T \) for two values of the dimensionless damping. For the involved parameters we take the following values: \( \hbar \gamma/(4\pi m) = 1, \hbar \Gamma/(2\pi) = 100 \). Left figure: \( am/\gamma^2 = 80 \) (underdamping); from the top to the bottom: \( T_p, T_x, T \). Right figure: the same, but with \( am/\gamma^2 = 0.2 \) (moderate overdamping).](image)

The existence of different temperatures \( T_x, T_p \) and \( T \) for the subsystem and bath seems to contradict the zeroth law, which states that systems interacting for a long time are in equilibrium, and share common temperature. Notice especially that the above difference between temperatures is not a consequence of any metastability and/or incomplete equilibration, so that our effective temperatures do not depend on the dynamics of the particle and have somewhat more definite status compared with those defined, e.g., for glassy systems [23,24,26]. Typical derivations of the zeroth law (see e.g. Ref. [3] for one of the most clear examples) essentially use the assumptions that the interaction with the bath is very weak, and that the total entropy can be considered as the sum of entropies of the subsystem and the bath. Evidently, this last condition is not satisfied in our case, except for the limit \( \gamma \to 0 \), where \( T_x \) and \( T_p \) tend to their Gibbsian value, see Eq. (3.50), of the harmonic oscillator coupled very weakly to its bath, the situation treated in all textbooks.

Let us notice that in literature some other ways were proposed to establish effective characteristics for non-underdamped Brownian oscillator. In [11] it is shown that there is a mapping to the Gibbsian (underdamped)
oscillator through the definition of an effective mass and frequency. For the description of He\textsubscript{3} Prokof'ev studies a related model with a gap in $J(\omega)$ at small $\omega$\cite{Prokofev}. In this approach he makes a different identification for the effective temperature. Surely, the choice which quantity to take as “effective temperature” is to some extent a matter of taste, that can only be justified by the induced simplification of the physical results. For our thermodynamic approach other definitions of effective temperatures will not be very helpful. Our $T_p$ and $T_x$, however, allow to formulate the generalized Clausius inequality and they also occur in the Maxwell-Boltzmann-like form \cite{Prokofev} of the Wigner function. Last but not least, these effective temperatures enter in the same way as in glasses and other two-temperature systems, such a black holes.

\paragraph{b. Von Neumann entropy}

In next part we shall discuss the von Neumann entropy of the central particle. To investigate it one needs the density matrix corresponding to the Wigner function \cite{Prokofev}. For the harmonic oscillator this can be worked out explicitly. One approach is to introduce an effective mass and an effective frequency \cite{Prokofev}, and insert these results in the expression for the entropy of the effective harmonic oscillator. We found it more insightful to redo the derivation. The standard relation

$$\langle x + \frac{u}{2}|\rho| x - \frac{u}{2} \rangle = \int dp \ e^{-ipu/\hbar} W(p,x)$$

(4.29)

connects the density matrix in coordinate representation with the Wigner function. From this relation one gets the following formula \cite{Prokofev}

$$\langle x|\rho|x' \rangle = \frac{1}{\sqrt{2\pi \langle x^2 \rangle}} \exp \left[ -\frac{(x + x')^2}{8\langle x^2 \rangle} - \frac{(x - x')^2}{2\hbar^2 / \langle p^2 \rangle} \right]$$

(4.30)

The physical meaning of Eq. (4.30) is clear: The diagonal elements ($x = x'$) are distributed at the scale $\sqrt{\langle x^2 \rangle}$, while the maximally off-diagonal elements ($x = -x'$), which characterize coherence, are distributed with the characteristic scale $\hbar / \sqrt{\langle p^2 \rangle}$.

We have to find eigenfunctions and eigenvectors of this density matrix

$$\int dx' \langle x|\rho|x' \rangle f_n(x') = p_n f_n(x)$$

(4.31)

The solution of this problem uses some tabulated formulas for Hermite polynomials, and results in

$$p_n = \frac{1}{v + \frac{1}{2}} \left[ \frac{v - \frac{1}{2}}{v + \frac{1}{2}} \right]^n,$$

(4.32)

$$f_n(x) = c H_n(cx) e^{-c^2 x^2 / 2},$$

(4.33)

$$c = \left( \frac{\langle p^2 \rangle}{\hbar^2 \langle x^2 \rangle} \right)^{1/4}, \quad v = \Delta p \Delta x / \hbar = \sqrt{\langle p^2 \rangle \langle x^2 \rangle / \hbar^2} = \sqrt{\frac{m T_p T_x}{\hbar^2 a}}$$

(4.34)

where $H_n$ are Hermite polynomials, and it holds that $v \geq \frac{1}{2}$ due to the Heisenberg uncertainty relation. The result for the von Neumann entropy now reads \cite{Prokofev}

$$S_{vN} = -\sum_n p_n \ln p_n = \left( v + \frac{1}{2} \right) \ln(v + \frac{1}{2}) - (v - \frac{1}{2}) \ln(v - \frac{1}{2})$$

(4.35)

The first terms in its large $v$-expansion are

$$S_{vN} = \ln v + 1 - \frac{1}{24 v^2} - \frac{1}{320 v^4} - \frac{1}{2688 v^6}$$

(4.36)

From (4.3), (4.4) and (4.5) we notice that the same quantity $v$ governs behavior of the Boltzmann entropy

$$S_B = \frac{1}{2} \ln \frac{\langle x^2 \rangle \langle p^2 \rangle}{\hbar^2} + 1 = \ln v + 1$$

(4.37)
This appears to coincide with the leading terms of (4.36). It is known to be larger than the Von Neumann entropy, and this is obvious from the sign of the correction terms.

If some parameter \(a\) or \(m\) is varied, then the derivative of \(S_{vN}\) with respect to it reads:

\[
dS_{vN} = \ln \left( \frac{v + \frac{1}{2}}{v - \frac{1}{2}} \right) \, dv
\]

In other words, the sign of the change in \(S_{vN}\) is determined by the sign of the change in \(v\). This holds as well for the change in \(S_B\), so qualitatively they carry the same information, and this already was used above to simplify one point of the discussion.

Let us stress that von Neumann entropy \(S_{vN}\) is the unique quantum measure of localization, whereas the entropies \(S_p\) and \(S_x\) characterize localizations of momentum and coordinate separately. The differences between \(S_B\) and \(S_{vN}\) are due to the fact that in quantum theory momentum and coordinate cannot be measured simultaneously; in this sense \(S_p\) and \(S_x\) characterize two different measurement setups. Nevertheless, for the harmonic particle if \(S_{vN}\) increases (decreases), then \(S_p + S_x\) increases (decreases) as well. Notice that the real importance of \(S_p\) and \(S_x\) becomes clear when they have to be used to generalize the Clausius inequality. The von Neumann entropy cannot be used for this purpose whenever \(T_x \neq T_p\).

c. Clausius inequality at large \(T\).

At low \(T\) only power counting in \(T\) was needed for showing the violation of the Clausius inequality. The precise definition of entropy, and the quantitative difference between the Boltzmann entropy and the von Neumann entropy were not essential, since then \(TdS \to 0\) anyhow. Here we wish to show that the same violation already happens at arbitrarily large temperature. To do this we have to use the von Neumann entropy of the subsystem.

In this section we consider very large temperatures, \(T \gg \hbar \nu\). Using (3.53) we find from (4.25) for a change in \(m\) that

\[
dQ = [1 - \frac{\beta^2 \hbar^2 a}{12m}] \frac{T}{2m} \, dm, \quad dS_{vN} = [1 - \frac{\beta^2 \hbar^2 (a + \gamma \nu)}{12m}] \frac{1}{2m} \, dm,
\]

(4.39)

So, for a change \(dm > 0\) it is seen that at arbitrarily large temperature the Clausius inequality is violated. The relative violation \(dQ - TdS_{vN})/dQ\) is of order \(\hbar^2 \gamma \nu/(mT^2)\).

For a change in \(a\) we find

\[
dQ = \left\{ -\frac{1}{2a} + \frac{\hbar^2 \beta^2}{24m} - \frac{\beta^4 \hbar^4 (a + (2/3) \gamma \nu)}{480m^2} \right\} \, T \, da
\]

\[
TdS_{vN} = \left\{ -\frac{1}{2a} + \frac{\hbar^2 \beta^2}{24m} - \frac{\beta^4 \hbar^4 (a + \gamma \nu)}{480m^2} \right\} \, T \, da
\]

(4.41)

These expressions differ at relative order \(\beta^4 \hbar^4 \gamma \nu/m^2\), and the Clausius inequality is violated for \(da > 0\).

The important conclusion of this section is that the violation of the Clausius inequality already occurs at arbitrarily high temperatures. Later we point out that a similar conclusion can be drawn about the violation of the zeroth law at large temperatures.

We stress that the Clausius inequality is violated for any finite coupling, and the violating terms only disappear in the weak coupling limit \(\gamma \to 0\), or in the classical limit \(\hbar \to 0\), equivalent to the high-temperature limit.

d. Clausius inequality for comparing two systems.

For non-equilibrium systems the question has not been settled whether the von Neumann entropy is the true physical entropy. As we are inclined to believe that it is, we have discussed that entropy above.

Let us, however, now consider cases where there is no doubt: For systems in true Gibbsian equilibrium the proper entropy of the subsystem is surely its von Neumann entropy. We can now compare two such equilibrium systems, having slightly different system parameters. In standard thermodynamics such a comparison does not yield a new insight,
as the equilibrium state of the system is independent of its history. We should point out that in the thermodynamics of glasses it is customary to compare cooling experiments at different but fixed pressures. A related comparison was also made for black holes: it could be shown that comparing the situation of a single black hole before and after a small amount of matter was added, is analogous to comparing two different black holes with slightly different masses [2]. This universality pointed at a thermodynamic behavior of black holes, and the physical framework could indeed be provided by one of us, by drawing an analogy with the thermodynamics of glasses [26].

For our present case we can compare two equilibrium systems at slightly different temperatures. This has the benefit that the work term is absent, thus needing no interpretation, and it implies \( d\bar{Q} = dU \). Using the fully exact expressions for the energy and the von Neumann entropy, it is then straightforward to show that at large \( T \)

\[
d\bar{Q} - TdS_{vN} = \frac{\beta^2 \hbar^2 \gamma \Gamma}{24m} dT
\]  

(4.42)

The standard expectation that this should vanish is again seen to be invalid, and the Clausius inequality is violated for \( dT > 0 \). As before, the terms in the right hand side vanish only in the weak coupling limit \( \gamma \to 0 \), the classical limit \( \hbar \to 0 \), or the infinite temperature limit \( \beta \to 0 \).

e. On our identification of the energy of the subsystem

In section 2.1 we have considered two physical situations. In the first case the Hamiltonian contains a self-interaction term \( \sim x^2 \). For that case the above results on the Clausius inequality apply unambiguously. In the second case there is no such self-interaction, but the potential energy \( \frac{1}{2} bx^2 \) is split as \( \frac{1}{2} ax^2 + \frac{1}{2} \gamma \Gamma x^2 \), and the first part is counted in the energy of the subsystem, while the last part is counted with the interaction energy. Let us now shortly look at what happens when this is not done, and \( \bar{U} = \langle \bar{H} \rangle \) is considered as energy of the subsystem. At large \( T \) one will have \( \bar{U} = U + \frac{1}{2} (\gamma \Gamma / a) T = T + \frac{1}{2} (\gamma \Gamma / a) T \). Since the work is not modified by this identification, one will have a shift in the change of heat, \( d\bar{Q} = dQ + \frac{1}{2} \gamma \Gamma [dT/a - T da/a^2] \). From (4.41) and (4.42) it is seen that then even at very large temperatures \( d\bar{Q} - TdS_{vN} \) will not vanish whenever \( \gamma \) is non-zero. Thus, when there is no self-interaction our identification of \( \mathcal{H} \) as the Hamiltonian of the subsystem is already mandatory for having a proper classical limit. The underlying reason is that the Wigner function has the Maxwell-Boltzmann form \( \exp(-[\frac{\Gamma}{2m} v^2 + \frac{1}{2} a x^2] / T) \), involving \( a \) and not \( b = a + \gamma \Gamma \). This fixes the entropy, and leaves one consistent choice for the energy.

5. EXACT DYNAMICAL SOLUTION

We now consider the situation where our closed system starts at time \( t = 0^- \) from a Gibbsian initial distribution. It could arise if long before the total system was coupled to a ‘superbath’, that allowed relaxation to equilibrium, after which the connection was cut [3]. A more realistic situation occurs when the bath has small non-linearities, that drive the whole system to its global Gibbsian state.

1. The case when the initial state is a modified Gibbsian

We assume that for \( t < 0 \) the system is in a Gibbsian state at temperature \( T \) with certain parameters \( a = a_0 \), \( m = m_0 \), \( \gamma = \gamma_0 \). At \( t = 0 \) these parameters are instantaneously changed to \( a \), \( m \) and \( \gamma \), and the system will relax to a steady state. This new setup generalizes previous studies with for times \( t \leq 0 \) particle and bath are uncoupled, described by \( \gamma_0 = 0 \). An important benefit is that in the strong damping limit the present initial state can be close to the final state, which is, of course, impossible if \( \gamma_0 = 0 \) but \( \gamma \) is large. When making the change \( \gamma_0 \to \gamma \) at \( t = 0 \), a amount of work \( \frac{1}{2} \gamma_0 \Gamma \langle x^2 \rangle_0 \) has to be supplied to the system. This was truly large in our Letter [2], where we took \( \gamma_0 = 0 \), but \( \Gamma \) and \( \gamma \) large. In the present setup we can choose \( \gamma_0 = \gamma \), but \( a_0 \neq a \), implying that the work need not be not large, even when the Debye frequency \( \Gamma \) is large.

a. The eigenmodes of the initial state

In the most general case the Hamiltonian has for \( t < 0 \) the parameters \( a_0 \), \( \gamma_0 \) and \( m_0 \). It reads
\[ H = \sum_{i \geq 0} \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{i,j \geq 0} \sqrt{m_im_j} x_i A_{ij} x_j \]  

(5.1)

with

\[ A_{00} = \frac{a_0 + \gamma_0 \Gamma}{m_0}; \quad A_{0i} = A_{i0} = -\frac{c_i(0)}{\sqrt{m_0 m_i}}; \quad A_{ij} = \omega_i^2 \delta_{ij} \]  

(5.2)

where \( c_i(0) \) is given by Eq. (2.20) with \( \gamma_0 \) replacing \( \gamma \),

\[ c_i(0) = \sqrt{\frac{2\gamma_0 m_i \omega_i^2 \Delta}{\pi}} \frac{\Gamma^2}{\omega_i^2 + \Gamma^2} \]  

(5.3)

Let us denote the eigenvalues of \( A \) by \( \nu_k^2 \). From a previous section, Eqs. (3.10, 3.12), we infer that the eigenfrequencies are shifted,

\[ \nu_k = \omega_k - \frac{1}{\pi} \phi_0(\omega_k) \Delta \]  

(5.4)

where \( \phi_0 \), satisfying \( 0 \leq \phi_0 \leq \pi \), is given by

\[ \phi_0(\nu) = \arctan \frac{\gamma_0 \Gamma^2 \nu}{(a_0 - m_0 \nu^2)(\nu^2 + \Gamma^2) + \gamma_0 \Gamma \nu^2} \]  

(5.5)

In later sections we only need that for large \( \Gamma \)

\[ \sin \phi_0(\nu) = \frac{\gamma_0 \nu}{\{(a_0 - m_0 \nu^2)^2 + \gamma_0^2 \nu^2\}^{1/2}} \]  

(5.6)

The eigenvectors are

\[ e_0^k = \alpha_k, \quad e_i^k = \frac{c_i(0) \alpha_k}{\sqrt{m_0 m_i (\omega_i^2 - \nu_k^2)}} \]  

(5.7)

with normalization factor

\[ \frac{1}{\alpha_k^2} = 1 + \sum_{i \geq 1} \frac{[c_i(0)]^2}{m_0 m_i (\omega_i^2 - \nu_k^2)} \]  

(5.8)

The following normalization conditions hold:

\[ \sum_k e_i^k e_j^k = \delta_{ij}, \quad \sum_{i \geq 0} e_i^k e_i^l = \delta_{kl} \]  

(5.9)

For small \( \Delta \) one may use

\[ \sum_{i=-\infty}^{\infty} \frac{1}{[\omega_k + \phi_0(\omega_k)]^2} = \frac{1}{\sin^2 \phi_0(\omega_k)} \]  

(5.10)

to find

\[ \alpha_k = \sqrt{\frac{2m_0 (\Gamma^2 + \omega_k^2)}{\pi \gamma_0 \Gamma^2}} \sin \phi_0^k, \quad e_i^k = \frac{\sqrt{\Gamma^2 + \omega_k^2} 2\Delta \omega_i \sin \phi_0^k}{\Gamma^2 + \omega_i^2 \pi (\omega_i^2 - \nu_k^2)} \]  

(5.11)

where \( \phi_0^k = \phi_0(\omega_k) \). In the zero coupling limit \( \gamma_0 \to 0 \) one has \( \phi_0^k \to 0 \), so that \( \nu_k \to \omega_k \) and indeed \( e_i^k \to \delta_{ik} \). The latter setup occurs in the standard treatments where bath and subsystem are initially uncoupled.
We consider Gibbsian equilibrium for \( t \leq 0 \). Let us now introduce the creation and annihilation operators \( b_k^\dagger, b_k \), satisfying \([b_k, b_l^\dagger] = \delta_{kl}\) by

\[
  x_i = \sum_k \sqrt{\frac{\hbar}{2m_i \nu_k}} c_i^k (b_k^\dagger e^{i\nu_k x} + b_k e^{-i\nu_k x}), \quad p_j = i \sum_k \sqrt{\frac{\hbar m_i \nu_k}{2}} c_j^k (b_k^\dagger e^{i\nu_k x} - b_k e^{-i\nu_k x}) \tag{5.12}
\]

\[
x = \sum_k \sqrt{\frac{\hbar \Delta (\Gamma^2 + \nu_k^2)}{\pi \gamma_0 \Gamma^2 \nu_k}} \sin \phi_0^k (b_k^\dagger e^{i\nu_k x} + b_k e^{-i\nu_k x}), \quad p = \sum_k \sqrt{\frac{\hbar \Delta (\Gamma^2 + \nu_k^2)}{\pi \gamma_0 \Gamma^2 \nu_k}} \sin \phi_0^k m_0 \nu_k (i b_k^\dagger e^{i\nu_k x} - i b_k e^{-i\nu_k x}) \tag{5.13}
\]

They indeed satisfy \([x_i, p_j] = i \hbar \delta_{ij}\) due to the normalization condition, as well as \([x, p] = i \hbar, [x, p_i] = [x_i, p] = 0\). For \( t < 0 \) the Hamiltonian then reads

\[
  \mathcal{H} = \frac{1}{2} \sum_k \hbar \nu_k (b_k^\dagger b_k + b_k^\dagger b_k^\dagger) = \sum_k \hbar \nu_k (b_k^\dagger b_k + \frac{1}{2}) \tag{5.14}
\]

In the Gibbsian state that describes our closed system for \( t < 0 \), the density matrix is

\[
  \rho = \frac{1}{Z} e^{-\beta \mathcal{H}} \tag{5.15}
\]

It has the Bose occupation numbers

\[
  (b_k^\dagger b_k + b_k^\dagger b_k^\dagger) = 1 + \frac{2}{e^{\beta \hbar \nu_k} - 1} = \coth(\frac{1}{2} \beta \hbar \nu_k) \tag{5.16}
\]

Combining (2.11) and (5.13) we now have for the noise

\[
  \eta(t) = \sum_{i \geq 1} \sum_k \sqrt{\frac{\hbar}{2m_i \nu_k}} c_i^k \cos \omega_i t \left( (b_k^\dagger + b_k) \cos \omega_i t + i \nu_k (b_k^\dagger - b_k) \sin \omega_i t \right) \tag{5.17}
\]

To carry out the \( i \)-sum, we have to evaluate

\[
  \sum_{i \geq 1} \frac{c_i e^{i k x} \cos \omega_i t}{\sqrt{m_i}} = \sqrt{\frac{2 \gamma \Gamma^2 \Delta}{\pi (\Gamma^2 + \nu_k^2)}} \frac{2 \Delta \sin \phi_0^k}{\pi} \sum_{i \geq 1} \left( \frac{\nu_k^2}{\omega_i^2 - \nu_k^2} + \frac{\Gamma^2}{\omega_i^2 + \Gamma^2} \right) \cos \omega_i t \tag{5.18}
\]

Gradstein & Ryzhik \[43\] present on page 40, Eq. 1.445.2 the equality

\[
  \sum_{k=1}^{\infty} \frac{\cos k x}{k^2 + \alpha^2} = -\frac{1}{2 \alpha^2} + \frac{\pi \cosh(\pi \alpha - \alpha x)}{2 \alpha \sinh \pi \alpha} \tag{5.19}
\]

According to them it holds for \( 0 \leq x \leq 2 \pi \), but it actually only holds for \( 0 \leq x \leq \pi \), while further it is symmetric and periodic. We have to apply this with \( x = t \Delta \), which is surely between 0 and \( \pi \), for the cases \( \alpha = i \nu / \Delta \) and \( \alpha = \Gamma / \Delta \)

\[
  \sum_{i \geq 1} \frac{c_i e^{i k x} \cos \omega_i t}{\sqrt{m_i}} = \sqrt{\frac{2 \gamma \Gamma^2 \Delta}{\pi (\Gamma^2 + \nu_k^2)}} \sin \phi_0^k \left[ \frac{\cosh(\pi \nu_k / \Delta - \nu_k t)}{\sinh(\pi \Gamma / \Delta)} - \nu_k \cos(\pi \nu_k / \Delta - \nu_k t) \right] \tag{5.20}
\]

\[
  = \sqrt{\frac{2 \gamma \Gamma^2 \Delta}{\pi (\Gamma^2 + \nu_k^2)}} \left[ \Gamma \sin \phi_0^k e^{-\Gamma t} + \nu_k \cos(\phi_0^k + \nu_k t) \right] \tag{5.21}
\]

In the last step we have neglected terms of order \( \exp(-2\Gamma / \Delta) \), which are extremely small. The primitive of this relation yields
### The noise correlator

The noise correlator now decomposes in two parts

\[
K(s, t) = \frac{1}{2} \left( \langle \eta(s) \eta(t) + \eta(t) \eta(s) \rangle \right) = K_0(s - t) + K_1(s, t)
\]

The first term is the stationary noise known from the situation where system and bath were initially uncoupled,

\[
K_0(s - t) = \frac{1}{\pi} \int_0^\infty d\omega \tilde{K}_0(\omega) \cos(\omega(t - s))
\]

with spectrum

\[
\tilde{K}_0(\omega) = \frac{\gamma \hbar \omega}{\tanh \frac{1}{2} \beta \hbar \omega} \frac{\Gamma^2}{\Gamma^2 + \omega^2}
\]

It indeed does not involve parameters of the initial state. The connection between properties of the noise and the friction kernel is a consequence of quantum fluctuation-dissipation theorem \[\text[10,11]\].

As shown in Ref. \[38\], the quantum noise has correlation \( K_0(t) = -\ln(\Gamma t) > 0 \) at small times, \( t \ll 1/\Gamma \). At \( T = 0 \) there occurs for large times the celebrated power-law, anti-correlated decay

\[
K_0(t) = -\frac{\hbar \gamma}{\pi t^2}
\]

This is cut off at times larger than the universal quantum coherence time \( \tau_h = \hbar/T \), where

\[
K_0(t) = -\frac{\pi \gamma T^2}{\hbar} \left[ \sinh \left( \frac{\pi t}{\beta \hbar} \right) \right]^{-2}
\]

The divergence of this expression at \( t = 0 \) shows that a regulator like \( \Gamma \) is needed.

Let us briefly explain qualitative reasons for the above structure of the quantum noise. As seen from Eq. \[2.16\], the quantum noise is just a weighted sum of the unperturbed coordinates of the baths oscillators. For \( T \to 0 \) the unperturbed bath appears in its lowest energy level, and since energy and coordinate do not commute (just because coordinate and momentum do not commute), the quantum noise fluctuates even for \( T \to 0 \), and brings a non-trivial structure to \( K(t) \) in contrast to the classical case, where the noise is just absent for zero temperatures. On the other hand, the total intensity of the quantum noise is zero for \( T \to 0 \): as seen from \[2.20\], \( \int dtK(t) = 2\gamma T \). For the total integral to be zero, the correlator \( K(t) \) should change its sign at some intermediate time \( t \). For longer times the quantum noise is anticorrelated. The correlator displays a power-law behavior, since the correlation time-scale \( \hbar/T \) is now infinite. A colored noise generated by the low-temperature quantum thermal bath will be the main cause of our effects. The classical white noise situation \( K_0(t) = 2\gamma T \delta(t) \) is recovered by taking the high-temperature limit \( (T \gg \hbar \Gamma) \).

The second term is due to the initial correlation of particle and bath,
\[ K_1(s, t) = K_{11}e^{-\Gamma(s+t)} + K_{12}(s)e^{-\Gamma t} + K_{12}(t)e^{-\Gamma s} \]  
(5.29)

\[
K_{11} = \frac{1}{\pi} \int_0^\infty d\omega \bar{K}_0(\omega) \frac{\Gamma^2 + \omega^2}{\omega^2} \sin^2 \phi(\omega)
\]  
(5.30)

\[
K_{12}(t) = \frac{1}{\pi} \int_0^\infty d\omega \bar{K}_0(\omega) \left[ \frac{\Gamma}{\omega} \cos(\phi(\omega) + \omega t) - \sin(\phi(\omega) + \omega t) \right] \sin \phi(\omega)
\]  
(5.31)

where \( \phi_0 \) is defined by (5.5).

The standard case of initially uncoupled Brownian particle and bath is recovered for \( \gamma_0 \to 0 \), where \( \phi_0 \to 0 \). Then \( K_{12} \) and \( K_{11} \) vanish, making the noise correlator time-translation invariant. In the general case, the initial correlation only affects the very short time regime \( t \leq \tau_\eta = 1/\Gamma \) (remember that we assume that \( \Gamma \) is larger than other characteristic frequencies of the damped Brownian particle).

**d. Variances and covariance arising from the initial state**

The Gibbsian initial state leads to three coupled Gaussian random variables: the random initial conditions, \( z_1 = p_0 \) and \( z_2 = x_0 \), and the noise \( z_3(t) = \eta(t) \). More precisely, when we discretize the time-axis in points \( t_i \), the function \( z_3(t) \) becomes a set of variables \( z_{3,i} \). Their correlations and cross correlations are

\[
\langle p_{0}^2 \rangle = m_0 T_p(a_0, m_0, \gamma_0), \quad \langle x_{0}^2 \rangle = \frac{T_x(a_0, m_0, \gamma_0)}{a_0}, \quad K(s, t) = \frac{1}{2} \langle \eta(s)\eta(t) + \eta(t)\eta(s) \rangle,
\]  
(5.32)

\[
\langle p_0x_0 \rangle = 0, \quad S_1(t) = \frac{1}{2} \langle \eta(t)p_0 + p_0\eta(t) \rangle, \quad S_2(t) = \frac{1}{2} \langle \eta(t)x_0 + x_0\eta(t) \rangle
\]  
(5.33)

The new terms read

\[
S_1(t) = \frac{h m_0 \sqrt{\gamma}}{\pi \sqrt{\gamma_0}} \int_0^\infty d\nu \sin \phi_0(\nu) \sin(\phi_0(\nu) + \nu t) \coth \frac{1}{2} \beta \hbar \nu
\]  
(5.34)

\[
S_2(t) = \frac{h \sqrt{\gamma}}{\pi \sqrt{\gamma_0}} \int_0^\infty d\nu \sin \phi_0(\nu) \cos(\phi_0(\nu) + \nu t) \coth \frac{1}{2} \beta \hbar \nu
\]  
(5.35)

**2. Exact solution of the Langevin equation**

Next we consider the exact solution of the quantum Langevin equation:

\[
\dot{x} = \frac{p}{m}, \quad \dot{p} = -ax - \gamma(t)x(0) - \int_0^t dt' \gamma(t-t')\dot{x}(t') + \eta(t)
\]  
(5.36)

The general solution of Eq. (5.36) is obtained with help of Laplace transformation. The reader may recall the following standard relations between functions \( A(t) \), \( B(t) \) and their Laplace-transforms \( \mathcal{L}\{A\} = \hat{A}(s) = \int_0^\infty dt e^{-st} A(t) \),

\[
\mathcal{L} \left\{ \int_0^t dt' A(t-t')B(t') \right\} = \hat{A}(s)\hat{B}(s), \quad \mathcal{L} \{ A \} = -A(0) + s\hat{A}(s),
\]  
(5.37)

One gets

\[
ms\dot{x}(s) - mx(0) = \hat{p}(s), \quad s\hat{p}(s) - p(0) = -a\dot{x}(s) - \gamma(s)x(s) + \hat{\eta}(s)
\]  
(5.38)

Together this yields

\[
\dot{x}(s) = \frac{1}{m} [mx(0)s + p(0) + \hat{\eta}(s)] f(s)
\]  
(5.39)
where
\[ \hat{f}(s) = \frac{m}{ms^2 + a + s\gamma(s)} \] (5.40)

Thus, the solution of Eq. (5.36) reads
\[ x(t) = x(0)f(t) + \frac{1}{m}p(0)f(t) + \frac{1}{m}\int_0^tdt'f(t-t')\eta(t'), \] (5.41)
\[ p(t) = p(0)f(t) + mx(0)f(t) + \int_0^tdt'f(t-t')\eta(t') \] (5.42)

where \( \omega_0 = \sqrt{a/m} \); \( \hat{f}(s) \) and \( \hat{\gamma}(s) \) are the Laplace transforms of \( f(t) \), \( \gamma(t) \). Expanding \( \hat{f}(s) \) for large \( s \), one finds that \( f(0) = \hat{f}(0) = 0, \hat{f}(0) = 1 \). Now we turn to our standard case of the Drude-Ullersma spectrum:
\[ \gamma(t) = \gamma \Gamma e^{-\Gamma|t|}, \quad \hat{\gamma}(s) = \frac{\gamma \Gamma}{\Gamma + s} \] (5.43)

For \( \hat{f}(s) \) one has
\[ \hat{f}(s) = \frac{m(\Gamma + s)}{(s + \Gamma)(ms^2 + a + s\gamma) + s\gamma} = \frac{\Gamma + s}{(s + \omega_1)(s + \omega_2)(s + \omega_3)} = \frac{\Gamma + s}{P_3(-s)} \] (5.44)

where \( P_3(s) \) was defined in (3.23), where also its roots \( \omega_{1,2,3} \) are discussed.
Likewise one has for the initial Gibbsian states
\[ \hat{f}_0(s) = \frac{m_0(\Gamma + s)}{(s + \Gamma)(m_0 s^2 + a_0) + s\gamma_0} \] (5.45)

One may write
\[ \hat{f}(s) = \sum_{i=1}^{3} \frac{f_i}{s + \omega_i}, \quad f(t) = \sum_{i=1}^{3} f_i e^{-\omega_i t}, \quad f_i = \frac{\Gamma - \omega_i}{(\omega_{i+1} - \omega_i)(\omega_{i-1} - \omega_i)} \] (5.46)

where, in this connection, \( \omega_0 = \omega_3 \), not to be confused with the definition \( \omega_0 = \sqrt{a/m} \) elsewhere in the work.

For large \( \Gamma \) one has
\[ f_1 = -f_2 = \frac{m}{\gamma w}, \quad f_3 = \frac{1}{\Gamma} \] (5.47)

with \( w \) defined in (3.32).

Let us now set, in analogy with (5.13),
\[ x(t) = \sum_k \sqrt{\frac{\hbar \Delta(\Gamma^2 + \nu_k^2)}{2\pi \gamma \sqrt{\Gamma^2 + \nu_k^2}}} [\beta_k(t)b^\dagger_k + \beta_k^*(t)b_k], \] (5.48)

This implies
\[ p(t) = m \sum_{k} \sqrt{\frac{\hbar \Delta(\Gamma^2 + \nu_k^2)}{2\pi \gamma \sqrt{\Gamma^2 + \nu_k^2}}} [\hat{\beta}_k(t)b^\dagger_k + \hat{\beta}_k^*(t)b_k] \] (5.49)

One has from (5.41), (5.44) and (5.46): \( \hat{\beta}_k = \beta(\nu_k) \) with

\[ \beta(\nu) = \sqrt{\frac{\gamma}{\gamma_0}} \sin \phi_0(\nu) \sum_{i=1}^{3} f_i(-\omega_i + i\nu)e^{-\omega_i t} + \frac{\gamma \Gamma^2 \nu}{m(\Gamma^2 + \nu^2)} \sum_{i=1}^{3} f_i \left[ \sin \phi_0(\nu) \frac{\Gamma - i\nu e^{-\omega_i t} - e^{-\Gamma t}}{\Gamma - \omega_i} + e^{i\phi_0(\nu)} \frac{e^{i\nu t} - e^{-\omega_i t}}{\omega_i + i\nu} \right] \] (5.50)

The \( e^{-\Gamma t} \) terms cancel since, due to (5.44),
Next one can check that

\[ e^{i\phi(\nu)} = \frac{m(\Gamma^2 + \nu^2) \sin \phi(\nu)}{\gamma \Gamma^2 \nu \tilde{f}(i\nu)}, \quad e^{i\phi_0(\nu)} = \frac{m_0(\Gamma^2 + \nu^2) \sin \phi_0(\nu)}{\gamma_0 \Gamma^2 \nu f_0(i\nu)} \]  

(5.52)

which brings

\[ \frac{\gamma \Gamma^2 \nu}{m(\Gamma^2 + \nu^2)} \times e^{i\phi_0(\nu)} \times \sum_{i=1}^{3} \frac{f_i}{\omega_i + i\nu} = \frac{\gamma m_0}{\gamma_0 m f_0(i\nu)} \sin \phi_0(\nu) \]  

(5.53)

This leads to the exact result

\[ \beta(\nu, t) = \beta_0 e^{\nu t} + \sum_{i=1}^{3} \beta_i(\nu) e^{-\omega_i t} \]

\[ \beta_0(\nu) = \sin \phi(\nu) e^{i\phi(\nu) - i\phi(\nu)} \]

\[ \beta_i(\nu) = \sin \phi_0(\nu) f_i \left[ \sqrt{\frac{\gamma}{\gamma_0}} (-\omega_i + i\nu) + \frac{\gamma \Gamma^2}{m(\Gamma + i\nu)(\Gamma - \omega_i)} - \frac{\gamma m_0}{\gamma_0 m f_0(i\nu)(\omega_i + i\nu)} \right] \]  

(5.54)

For large times only the first term remains, and the initial condition only enters through its phase factor \( e^{i\phi_0 - i\phi} \), which has no physical effect, thus showing that the central particle relaxes to its equilibrium state independent of its initial condition. The expression for \( \beta_i \) can be simplified by writing it as the ratio of two polynomials, and using the fact that \( \omega_i \) is a zero of \( 1/e^{i\phi} \), allowing to eliminate the \( \omega^i \) term of the numerator. This brings

\[ \beta_i(\nu) = \sin \phi_0(\nu) \frac{a - a_0 + (m_0 - m)\nu^2}{m} \frac{f_i}{\omega_i + i\nu} \]  

(5.55)

which is still exact. Using (5.52) we can also express the result as

\[ \beta(\nu, t) = \frac{\gamma \Gamma^2 \nu}{m(\Gamma^2 + \nu^2)} \left\{ \tilde{f}(i\nu)e^{\nu t} + \left[ a - a_0 - (m - m_0)\nu^2 \right] f_0(i\nu) \sum_{i=1}^{3} \frac{f_i}{\omega_i + i\nu} e^{-\omega_i t} \right\} \]  

(5.56)

It is trivial to check that, when no change is made at \( t = 0 \) \( (\gamma_0 = \gamma, m_0 = m \text{ and } a_0 = a) \), the result \( \beta(\nu) = \sin \phi \exp(i\nu t) \) extends the negative time behavior (5.13) to all positive times, even though the noise and the damping payed a special (but in that case unphysical) role to \( t = 0 \).

In the rest of this work we shall be mainly interested in the situation \( \gamma_0 = \gamma, m_0 = m \text{ while } a_0 \) is different from but close to \( a \). One gets in the regime of large \( \Gamma \) and \( t \gg 1/\Gamma \) to linear order in \( a - a_0 \)

\[ \beta(\nu) = \sin \phi(\nu) e^{i\phi_0(\nu) - i\phi(\nu) + i\nu t} \left[ 1 + \frac{a - a_0}{\gamma w} \left( \frac{e^{-\omega_1 t - i\nu}}{\omega_1 + i\nu} - \frac{e^{-\omega_2 t - i\nu}}{\omega_2 + i\nu} \right) \right] \]  

(5.57)

where \( w \) is defined in (3.33) and \( \omega_{1,2} \) in (3.31).

### 6. ENERGY OSCILLATION AND NEGATIVE ENTROPY PRODUCTION

We consider the dynamical evolution of a system initially in equilibrium characterized by a spring constant \( a_0 \), which at \( t = 0 \) is instantaneously changed to \( a_1 = a \). These parameters are connected as

\[ a_0 = (1 - a_0)a \]  

(6.1)

We shall assume that \( |a_0| \ll 1 \). We also assume a large Debye frequency \( \Gamma \), but this does not lead to principal changes.
1. Non-monotonous relaxation of the energy at low $T$

Let us now consider how the system relaxes to its steady state. From (5.48) and (5.16) one has

$$\langle x^2 \rangle = \int_0^\infty d\nu \frac{\hbar (\nu^2 + \nu^4)}{\pi \nu^2} \beta \coth \frac{1}{2} \beta \hbar \nu, \quad \langle p^2 \rangle = m^2 \int_0^\infty d\nu \frac{\hbar (\nu^2 + \nu^4)}{\pi \nu^2} \beta \coth \frac{1}{2} \beta \hbar \nu \quad (6.2)$$

The infinite time values, discussed already in Eqs. (3.47,3.48), can be checked from these expressions. For the evolution from the initial state to these values, we shall consider times $t \gg 1/\Gamma$, and we can just take the limit $\Gamma \to \infty$ since no divergencies occur, except for the $\ln \Gamma$ term of the static part $\langle p^2 \rangle$ at $T = 0$. Inserting (5.57) we get to linear order in $\alpha_0$

$$V(t) = \frac{1}{2} a \langle x^2 \rangle = \frac{1}{2} T_x + \alpha_0 \frac{\hbar a}{2 \pi \gamma} C_x \left( \frac{\gamma t}{2m} \right), \quad (6.3)$$

$$K(t) = \frac{\langle p^2 \rangle}{2m} = \frac{1}{2} T_p + \alpha_0 \frac{\hbar a}{2 \pi \gamma} C_p \left( \frac{\gamma t}{2m} \right), \quad (6.4)$$

$$U(t) = \frac{1}{2} T_\nu + \frac{1}{2} T_x + \alpha_0 \frac{\hbar a}{2 \pi \gamma} C_E \left( \frac{\gamma t}{2m} \right) \quad (6.5)$$

with the relaxation functions of coordinate and momentum and energy

$$C_x(\tau) = \frac{2(1 - w^2)}{w} \int_{-\infty}^{\infty} \frac{dy \coth(\beta \hbar \gamma y/4m)}{[1/(1 + w)^2 + y^2][1/(1 - w)^2 + y^2]} \left[ \frac{e^{-(1-w+iy)\tau}}{1-w+iy} - \frac{e^{-(1+w+iy)\tau}}{1+w+iy} \right] \quad (6.6)$$

$$C_p(\tau) = \frac{2}{w} \int_{-\infty}^{\infty} \frac{dy \coth(\beta \hbar \gamma y/4m)}{[1/(1 + w)^2 + y^2][1/(1 - w)^2 + y^2]} \left[ \frac{iy(1-w)e^{-(1-w+iy)\tau}}{1-w+iy} - \frac{iy(1+w)e^{-(1+w+iy)\tau}}{1+w+iy} \right] \quad (6.7)$$

$$C_E(\tau) = \frac{2}{w} \int_{-\infty}^{\infty} \frac{dy \coth(\beta \hbar \gamma y/4m)}{1/(1 - iy)^2 - w^2} \left[ \frac{(1-w)e^{-(1-w+iy)\tau}}{1-w+iy^2} - \frac{(1+w)e^{-(1+w+iy)\tau}}{1+w+iy^2} \right] \quad (6.8)$$

Of course, one just has $C_E = C_p + C_x$. The integration variable is $y = 2m\nu/\gamma$. The appearance of the dimensionless timescale $\tau = \gamma t/2m$ is natural, since in the underdamped regime, where $w$ is imaginary, the damping time is just $\tau_d = 2m/\gamma$, see Eq. (3.38). In the overdamped regime the timescales $\tau_x$ and $\tau_p$ from Eq. (3.33) are coded in the terms $(1 \mp w)\tau$ in the exponentials, respectively. In particular, for strong overdamping one has $t/\tau_x = (1-w)\gamma t/2m \to at/\gamma$.

### a. Classical regime

At large $T$ the tanh linearizes. One can do contour integration to find for overdamping, i.e. for $\varepsilon = am/\gamma^2 < 1/4$ and $w = \sqrt{1-4\varepsilon} > 0$, the exact results

$$C_x(\tau) = \frac{\pi \gamma T}{\hbar a} e^{-2\tau} \left[ \cosh(w\tau) + \frac{\sinh(w\tau)}{w} \right]^2 \quad (6.9)$$

$$C_p(\tau) = \frac{\pi \gamma T}{\hbar a} e^{-2\tau} (1-w^2) \left[ \frac{\sinh(w\tau)}{w} \right]^2 \quad (6.10)$$

$$C_E(\tau) = \frac{\pi \gamma T}{\hbar a} e^{-2\tau} \left\{ \left[ \cosh(w\tau) + \frac{\sinh(w\tau)}{w} \right]^2 + (1-w^2) \left[ \frac{\sinh(w\tau)}{w} \right]^2 \right\} \quad (6.11)$$

For overdamping ($0 < w < 1$) these functions are strictly positive. For underdamping one has to replace $w \to i\tilde{w}$, implying $\cosh(w\tau) \to \cos \tilde{w}\tau$ and $\sinh(w\tau)/w \to \sin(\tilde{w}\tau)/\tilde{w}$. Then $C_x$ and $C_p$ get zeroes, but remain non-negative, while $C_E$ remains strictly positive.

For the relaxation of the energy this implies

$$U = T + \frac{1}{2} \alpha_0 T \left\{ \left[ \cosh(w\tau) + \frac{\sinh(w\tau)}{w} \right]^2 + (1-w^2) \left[ \frac{\sinh(w\tau)}{w} \right]^2 \right\} e^{-2\tau} \quad (6.12)$$

For strong overdamping ($\varepsilon \to 0, w \approx 1-2\varepsilon$) this becomes a simple exponential decay,
In case of underdamping, \( \varepsilon > \frac{1}{4} \), one has \( w = i\bar{w} \) with \( \bar{w} = \sqrt{4\varepsilon - 1} \). This yields by analytic continuation

\[
U = T + \frac{1}{2} \alpha_0 T e^{-4\varepsilon \tau} \quad (6.13)
\]

The term multiplying \( \alpha_0 \) is an oscillating function, and it is strictly positive. Its derivative,

\[
\dot{U} = -\gamma \alpha_0 T \left( 1 + \frac{\bar{w}^2}{\bar{w}^2} \sin^2(\bar{w}\tau) \right) e^{-2\tau} \quad (6.14)
\]

has zeros but does not change sign. Physically this means: depending on the sign of \( \alpha_0 \), both the kinetic and the potential energy oscillate either above or below their final value, and the total energy flow is unidirected; it goes towards the bath when \( a > a_0 \), i.e. \( \alpha_0 > 0 \) and from the bath to the particle in the opposite case.

In the limit of weak damping (\( \bar{w} \gg 1 \)) one gets

\[
U = T + \frac{1}{2} \alpha_0 T \left( 1 + \frac{\sin(2\omega_0 t)}{\bar{w}} \right) e^{-\gamma t/m}, \quad \dot{U} = -\gamma \alpha_0 T m \sin^2(\omega_0 t) e^{-\gamma t/m} \quad (6.15)
\]

Notice that the small but oscillating term in \( U \) has become of leading order for \( \dot{U} \).

FIG. 6.2. The underdamped situation. \( C_x \) as a function of the rescaled dimensionless time \( z = \tau\delta = \tau/|w| \), normalized to unity at \( z = 0 \), for large \( T \) and \( \delta = 0.5 \).

FIG. 6.3. The underdamped situation. \( C_x \) as a function of the rescaled dimensionless time \( z = \tau\delta = \tau/|w| \), normalized to unity at \( z = 0 \), for large \( T \) and \( \delta = 0.1 \).
b. Weak damping regime

In the weak damping limit it holds that

\[ \bar{w} = -iw \approx \frac{2\sqrt{am}}{\gamma} \gg 1 \]  

(6.17)

For performing the integrals, we write \( C_x(\tau) \) first as an integral from 0 to infinity, and make the shift \( y \to \bar{w} + u \), yielding up to order \( 1/\bar{w}^2 \)

\[ C_x(\tau) = e^{-\tau} \int_{-\infty}^{\infty} du \frac{\coth(b + bu/\bar{w})}{u^2 + 1} \left( \frac{-u \cos u \tau + \sin u \tau}{1 + u^2} + \frac{\cos(2\omega_0 t + u\tau)}{2\bar{w}} \right) \]  

(6.18)

where a correction factor \( 1 + u/\bar{w} \) in numerator and denominator have canceled, and we denoted

\[ b = 1/2 \beta \hbar \omega_0 \]  

(6.19)

Evaluating this to leading order in \( 1/\bar{w} \) we get

\[ C_x(\tau) = \frac{\pi \gamma}{4\sqrt{am}} \left( \frac{1/2 \beta \hbar \omega_0}{\sinh^2 1/2 \beta \hbar \omega_0} + \coth 1/2 \beta \hbar \omega_0 \cos 2\omega_0 t \right) e^{-2\tau} \]  

(6.20)

For large \( T \) this agrees with Eq. (6.9), of which the last factor now becomes \( \cos^2 \omega_0 t \). For \( T = 0 \) and \( \tau = 0 \) it agrees with Eq. (6.27) below. Likewise

\[ C_p(\tau) = \frac{\pi \gamma}{4\sqrt{am}} \left( \frac{1/2 \beta \hbar \omega_0}{\sinh^2 1/2 \beta \hbar \omega_0} - \coth 1/2 \beta \hbar \omega_0 \cos 2\omega_0 t \right) e^{-2\tau} \]  

(6.21)

As in the classical limit, \( C'_E = C'_x + C'_p \) picks up a contribution of \( C_E \) that is subleading but oscillating; it is most easily obtained by evaluating \( C'_E \) in a manner similar to (6.18),

\[ C'_E(\tau) = -\frac{\pi \gamma}{\sqrt{am}} \left( \frac{1/2 \beta \hbar \omega_0}{\sinh^2 1/2 \beta \hbar \omega_0} - \coth 1/2 \beta \hbar \omega_0 \cos 2\omega_0 t \right) e^{-2\tau} \]  

(6.22)

When inserting \( C_p + C_x \) in Eq. (6.5) we have for the leading decay of the energy

\[ U = \frac{1}{2} \hbar \omega_0 \coth 1/2 \beta \hbar \omega_0 + \frac{1}{2} \alpha_0 T \left( \frac{(1/2 \beta \hbar \omega_0)^2}{\sinh^2 1/2 \beta \hbar \omega_0} e^{-\gamma t/m} \right) \]  

(6.23)

showing that to leading order in \( \gamma \) in the weak damping limit the energy does not oscillate, but monotonously leaks into the bath (when \( \alpha_0 > 0 \)) or is taken from the bath (when \( \alpha_0 < 0 \)). At low temperature this happens with an exponentially small rate. But the rate of energy transfer, determined by (6.22),

\[ \dot{U} = -\frac{\gamma \alpha_0 T}{2m} \left( \frac{(1/2 \beta \hbar \omega_0)^2}{\sinh^2 1/2 \beta \hbar \omega_0} - \frac{1/2 \beta \hbar \omega_0}{\tanh 1/2 \beta \hbar \omega_0} \cos 2\omega_0 t \right) e^{-\gamma t/m} \]  

(6.24)

is an oscillating function that changes sign in each period whenever \( T \) is not infinite. Thus the rate of energy transfer is not uni-directed except for the classical limit. When averaged over one period, the cosine is subleading and a unidirected flow emerges.

c. Quantum regime for non-weak damping

At \( T = 0 \) one has \( y/\coth(\beta \gamma y/4m) = |y| \). For time \( \tau = 0 \) one finds by direct integration

\[ C_x(0) = \frac{1}{w^2} - \frac{1 - w^2}{2w^3} \ln \frac{1 + w}{1 - w}, \]  

(6.25)

28
and we define the short hand
\[ \lambda(w) = \frac{1}{2w} \ln \frac{1 + w}{1 - w} \]  
(6.26)

It further holds that
\[ C_p(0) = -C_x(0), \quad C_E(0) = 0 \]  
(6.27)

These results can be verified using the relations
\[ a \langle x^2(t = 0^+) \rangle - T_x(a) = \frac{a}{a_0} T_x(a_0) - T_x(a) = -\alpha_0 a^2 \frac{d(T_x/a)}{da} = \alpha_0 \frac{\hbar a}{\pi \gamma} C_x(0) \]
\[ \frac{1}{m} \langle p^2(t = 0^+) \rangle - T_p(a) = -\alpha_0 a \frac{dT_p}{da} = \alpha_0 \frac{\hbar a}{\pi \gamma} C_p(0) \]  
(6.28)

So after the instantaneous change of the spring constant \((t \gg 1/\Gamma)\), the deviation of the potential energy from its final value is, to leading order in \(\alpha_0\), just opposite to the one of the kinetic energy. Consequently, the particle has already the proper energy, but this will not remain so; for \(\alpha_0 > 0\) first a flow from the bath will occur and then a reversed flow, after which the equilibrium will be reached by a second energy flow from the bath to the particle.

At large times \((\tau \gg 1)\) and still \(T = 0\) one gets in case of overdamping \((w > 0)\)
\[ C_x(\tau) = -\frac{1}{2\varepsilon^2 \tau^2} e^{-\tau} \left[ \cosh \omega \tau + \frac{\sinh \omega \tau}{\omega} \right] \]
\[ C_p(\tau) = -\frac{1}{\varepsilon^2 \tau^3} e^{-\tau} \frac{\sin \omega \tau}{\omega} \]
\[ C_E(\tau) = -\frac{1}{2\varepsilon^2 \tau^2} e^{-\tau} \left[ \cosh \omega \tau + \frac{\sin \omega \tau}{\omega} \right] \]  
(6.29)

and for underdamping \((\bar{w} > 0)\)
\[ C_x(\tau) = \frac{1}{2\varepsilon^2 \tau^2} e^{-\tau} \left[ \cos \bar{w} \tau + \frac{\sin \bar{w} \tau}{\bar{w}} \right] \]
\[ C_p(\tau) = -\frac{1}{\varepsilon^2 \tau^3} e^{-\tau} \frac{\sin \bar{w} \tau}{\bar{w}} \]
\[ C_E(\tau) = \frac{1}{2\varepsilon^2 \tau^2} e^{-\tau} \left[ \cos \bar{w} \tau + \frac{\sin \bar{w} \tau}{\bar{w}} \right] \]  
(6.30)

The latter expressions all exhibit an infinity of oscillations around \(C = 0\). For overdamping one has \(C_x(0) > 0\), while it has a negative tail; consequently there remains one oscillation even in the limit of strong damping. In that limit \((\gamma \tau \) large), one may set \(\sigma = (1 - w)\tau = at/\gamma\). For large, but fixed \(\alpha\) one gets \(C_x = C_E = -2 \exp(-\sigma)/\sigma^2\), \(C_p = -8\varepsilon \exp(-\sigma)/\sigma^3\).

d. Strong damping at low \(T\)

Let us now write \(C_x(t)\) as
\[ C_x(t) = f_x(\tau, w) + f_x(\tau, -w), \]  
(6.31)

\[ f_x(\tau, w) = \frac{2(1 - w^2)}{w} e^{-(1 - w)^\tau} \int_{-\infty}^{\infty} dy \frac{y \coth(b y/\sqrt{1 - w^2}) [(1 - w) \cos y \tau - y \sin y \tau]}{[(1 + w)^2 + y^2][(1 - w)^2 + y^2]^2}, \]  
(6.32)

where \(b\) was defined in Eq. (6.19).

We investigate in some greater detail two particular cases: \(w \to 1\) (strong overdamping) and \(w = 0\) (the border between overdamping and underdamping). For the first case one changes the integrating variable \(y \to y/(1 - w)\) and arrives at:
\[ f_x(\tau, w) = f_1(2\varepsilon \tau), \quad f_1(\sigma) = e^{-\sigma} \int_{-\infty}^{\infty} dy \frac{y \coth(b y \sqrt{\varepsilon}) [\cos y \sigma - y \sin y \sigma]}{[1 + y^2]^2}, \]  
(6.33)

\[ f_x(\tau, -w) = -\varepsilon e^{-2\tau} \int_{-\infty}^{\infty} dy \frac{y \coth(b y \sqrt{\varepsilon}) \cos 2\varepsilon y \tau}{[1 + y^2]^2}. \]  
(6.34)
Recall that \( w = \sqrt{1 - 4\varepsilon} \), and in the limit \( \varepsilon \to 0 \) one has \( w = 1 - 2\varepsilon \to 1 \). It is seen that in this limit \( f_x(\tau, -w) \) is small compared to \( f_x(\tau, w) \) due to an extra factors \( \varepsilon \) and, above all, a quickly decaying exponential \( e^{-2\tau} = e^{-\sigma/\varepsilon} \).

Thus, we will omit \( f_x(\tau, -w) \). Then one has a scaling form:

\[
C_E(\tau, \varepsilon) = C_x(\tau, \varepsilon) = f_1(2\varepsilon\tau) = f_1(\frac{at}{\gamma}) = f_1(\frac{t}{\tau_x}).
\] (6.35)

Notice also that for this function small and large temperatures are determined by the dimensionless ratio: \( b \sqrt{\varepsilon} = \frac{\beta}{2} \frac{h \sqrt{a}}{\varepsilon \gamma} = \frac{h}{\gamma \tau_x T} \). If this parameter is small (which is always achieved for large temperature and also for fixed temperature and large damping), then we go back to the situation of eq. (6.13),

\[
f_1(2\varepsilon\tau) = \frac{\pi T}{\hbar \omega_0 \sqrt{\varepsilon}} e^{-4\varepsilon\tau}.
\] (6.36)

In the zero-temperature limit one takes \( y \coth(b \sqrt{\varepsilon}) = |y| \) and gets:

\[
f_1(\sigma) = 2e^{-\sigma} \int_0^\infty dy \frac{y \cos y\sigma - y \sin y\sigma}{1 + y^2}.
\] (6.37)

This function can be exactly expressed through Meijer functions, but we will not write down this representation explicitly, since it is useful only for numerical computations. Notice that (6.47) can be once more checked with help of (6.37). The behavior of \( f_1(\sigma) \) for different temperatures is presented in Fig. 6.4.

---

**FIG. 6.4.** The case of strong damping. \( f_1(t) \) as function of dimensionless time \( t \), normalized to unity at \( t = 0 \), for different values of the dimensionless temperature \( \vartheta = 1/(b \sqrt{\varepsilon}) = 2T\sigma/(\hbar a) \). Upper curve: \( \vartheta \to \infty \) (the expression given by (6.36), taking into the normalization). Middle curve: \( \vartheta = 1 \) (see Eq. (6.33) ). Lower curve: \( T = \vartheta = 0 \) (the expression given by (6.37) ). In the latter case there is still an oscillation, despite the strong damping.

It starts with \( f(0) = 1 \), becomes negative at \( \tau_n = 0.407211889989 \), goes trough a minimum, and finally bends up to \( 0^- \) for \( \tau \to \infty \). The minimum is characterized by

\[
\sigma_{\text{min}} = 0.87908730804, \quad f_1(\sigma_{\text{min}}) = -0.0918980496, \quad c_2 \equiv f_1''(\sigma_{\text{min}}) = 0.404842
\] (6.38)

In this limit \( C_p \) has an interesting behavior. We discussed already that \( C_p(0) = -C_x(0) \). For small \( \sigma \), \( C_p \) quickly grows, goes trough zero, and then becomes of order \( \varepsilon \), starting as \( \varepsilon \ln 1/\sigma \) for small, but not too small \( \sigma \). For finite \( \sigma \) one thus has \( C_E \approx C_x \), implying that now the total energy makes one oscillation, despite the strong damping.

For \( \alpha_0 > 0 \) it says that, after initially energy has been put on the particle by the change of \( a_0 \to a \), this energy leaks away into the bath. However, at intermediate times more leaks away than in the final state, so a part has to come back at moderately late times. This non-monotonous behavior (“bouncing”) is familiar of the noise correlator, which is anti-correlated at large times in the quantum regime.

Let us now turn to the behavior of \( C_x \) for \( w = 0 \):

\[
C_x(\tau) = 8\tau e^{-\tau} \int_0^\infty dy \frac{y \coth(b y) [ \cos y\tau - y \sin y\tau ]}{[1 + y^2]^3} + 8 e^{-\tau} \int_0^\infty dy \frac{y \coth(b y) [ (1 - y^2) \cos y\tau - 2y \sin y\tau ]}{[1 + y^2]^4}.
\] (6.39)
The behavior of this function is depicted in Fig. 6.5. It is seen that the cases \( w = 0 \) and \( w = 1 \) are qualitatively similar. As expected, the negative tail of \( C_x(t) \) is more pronounced for \( w = 0 \).

For \( C_p(t) \) one has:

\[
C_p(t) = f_p(\tau, w) + f_p(\tau, -w),
\]

\[
f_p(\tau, w) = \frac{2(1-w)}{w} e^{-(1-w)\tau} \int_{-\infty}^{\infty} dy \frac{y \coth(y/\sqrt{1-w^2})[y^2 \cos y\tau + y(1-w) \sin y\tau]}{[(1+w)^2 + y^2][(1-w)^2 + y^2]^2}. \tag{6.40}
\]

The behavior of \( C_p(t) \) in the overdamped situation can be studied along exactly the same lines as for \( C_x(t) \),

\[
C_p(t) = 2\epsilon e^{-2\epsilon\tau} \int_{0}^{\infty} dy \frac{y \coth(y/\sqrt{\epsilon})[y^2 \cos(2\epsilon\tau y) + y \sin(2\epsilon\tau y)]}{[1+y^2]^2 (1+\epsilon^2 y^2)}
- 2e^{-2\tau} \int_{0}^{\infty} dy \frac{\coth(y/\sqrt{\epsilon})[y \cos(2\tau y) + \sin(2\tau y)]}{[1+y^2]^2}. \tag{6.42}
\]

Due to the additional factor \( \epsilon \), this is smaller than \( C_x(t) \) for \( \tau > 1 \), and this justifies Eq. (6.35). Nevertheless, in the qualitative level \( C_p(t) \) displays nearly the same behavior as \( C_x(t) \). This is demonstrated by Fig. 6.6.

FIG. 6.5. The case with \( w = 0 \) (the border between overdamping and underdamping). \( C_x(t) \) as a function of dimensionless time \( t \), normalized to unity at \( t = 0 \), for different values of the dimensionless temperature \( \theta = 1/b = T\sqrt{2m}/(\hbar a) \). Upper curve: \( \theta = 1; \) middle curve: \( \theta = 0.2; \) lower curve: \( T = \theta = 0. \) In the two latter cases there is an oscillation.

FIG. 6.6. The overdamped situation: \( \epsilon = 0.1 \ (w = 0.7745) \). \( C_p(t) \) as a function of time, for different values of the dimensionless temperature \( \theta = 1/(b\sqrt{\epsilon}) = 2T\gamma/(\hbar a) \). Upper curve: \( \theta = 33; \) lower curve: \( \theta = 0. \)
Let us now investigate properties of $C_x(t)$ in the underdamped limit, where $w = i\bar{w} = i\sqrt{4\varepsilon - 1}$, and $\bar{w}$ is real. In the additional weak damping limit one has $\bar{w} \sim 1/\gamma \to \infty$. Using (6.32, 6.33) one gets:

$$C_x(t) = \frac{8(\bar{w}^2 + 1)}{\bar{w}^4} e^{-\tau} \text{Im} \left[ e^{i\tau\bar{w}} \int_0^\infty \frac{dy}{y \coth \left( \frac{y\bar{w}}{\sqrt{\bar{w}^2 + 1}} \right)} \left( (1/\bar{w} - i) \cos (y\tau\bar{w}) - y \sin (y\tau\bar{w}) \right) \right],$$  \hspace{1cm} (6.43)

$$C_p(t) = \frac{8}{\bar{w}^2} e^{-\tau} \text{Im} \left[ (1/\bar{w} - i) e^{i\tau\bar{w}} \int_0^\infty \frac{dy}{y \coth \left( \frac{y\bar{w}}{\sqrt{\bar{w}^2 + 1}} \right)} \left( y^2 \cos (y\tau\bar{w}) + (1/\bar{w} - i) y \sin (y\tau\bar{w}) \right) \right].$$  \hspace{1cm} (6.44)

The behavior of these functions, as well as $C_E(t) = C_x(t) + C_p(t)$, is depicted in Figs. 6.8, 6.9 for $T = 0$. It is seen that for the initial time of order $1/\bar{w}$, $C_x$ and $C_p$ oscillate with the amplitude higher for larger $\bar{w}$.

FIG. 6.8. The underdamped situation. 1: $C_x$ as a function of the rescaled dimensionless time $t = \tau/|\bar{w}|$, for $T = 0$ and $\bar{w} = 2$; 2: $C_p$ as a function of $t$; 3: $C_E$ as a function of $t$ both for the same values of the parameters.
are quite close to each other. $T = 0$ and $\bar{w}$ gets a larger weight than its positive center. These results follow from the Laplace-transform

$$B(w, z) = \frac{1}{\Gamma(w) \Gamma(z) / \Gamma(w + z)}$$

The Laplace transform of $C$ is defined in Eq. (6.26), and $\beta$ reads in that case

$$\hat{C}(\tau, u, T) = 0 = \frac{1}{24\pi^2} \Gamma(\frac{24\pi^2}{\hbar a})$$

This surprising zero-temperature outcome will have important consequences when it comes to work extraction. It is similar to $\int_{-\infty}^{\infty} dt K(t) = 2\gamma T \to 0$ for $T \to 0$, where $K(t)$ is the autocorrelation function of the quantum noise. For small $T$ one gets

$$C_x^{(0)}(T) = \int_0^\infty d\tau C_x(\tau) = \frac{64\pi^2}{3(1 - w^2)} \left( \frac{mT}{\hbar\gamma(1 - w^2)} \right)^2 = \frac{1}{12\pi} \left( \frac{2\pi\gamma T}{\hbar a} \right)^2$$

It can also be verified that at zero $T$

$$C_x^{(1)} = -\int_0^\infty d\tau C_x(\tau, T = 0) = \frac{1}{24\pi^2} \hat{C}_x^{(1)}$$

$$\hat{C}_x^{(1)} = \frac{(3 + w^2)(3w^2 - 1) + 3(1 - w^2)\lambda(w)}{8w^4}$$

where $\lambda$ is defined in Eq. (6.26), and

$$C_x^{(2)} = -\int_0^\infty d\tau \tau C_x(\tau, T = 0) = \frac{8}{3(1 - w^2)^3} = \frac{1}{24\pi^2}$$

These coefficients are positive for all $w$. The minus signs in the integrals arise because the negative tail of $C_x(\tau, T = 0)$ gets a larger weight than its positive center. These results follow from the Laplace-transform

$$\hat{C}_x(2u, T = 0) = \int_0^\infty d\tau C_x(\tau, T = 0) e^{-2u\gamma}$$

$$\hat{C}_E(2u, T = 0) = \int_0^\infty d\tau C_E(\tau, T = 0) e^{-2u\gamma}$$

At $T = 0$ all even moments of $C_x$ vanish. This implies in particular that the integral of $C_E = C_p - C_x$ vanishes. The Laplace transform of $C_E$ reads in that case

$$\hat{C}_E(2u, T = 0) = \frac{(1 + w)(1 + 2u + w)}{4au^2w(1 + u)(1 + u + w)} \ln \frac{1 + 2u + w}{1 + w} - \frac{(1 - w)(1 + 2u - w)}{4au^2w(1 + u)(1 + u - w)} \ln \frac{1 + 2u - w}{1 - w}$$
The Laplace transform \( \hat{C}_E(2u, T = 0) \) follows as \( \hat{C}_E(2u, T = 0) - \hat{C}_z(2u, T = 0) \).

For later use we introduce the coefficients

\[
C^{(0)}_E = \int_0^\infty d\tau C_E(\tau) = \frac{1}{12\varepsilon} \left( \frac{2\pi\gamma T}{\hbar a} \right)^2 + \mathcal{O}(T^4)
\]

\[
C^{(1)}_E = -\int_0^\infty d\tau C_E(\tau) = \frac{1}{24\varepsilon^2} + \mathcal{O}(T^2)
\]

\[
C^{(2)}_E = -\int_0^\infty d\tau^2 C_E(\tau) = \frac{1}{24\varepsilon^3} + \mathcal{O}(T^2)
\]

They differ from the \( C^{(0,1,2)}_x \) only by the factor \( \tilde{C}^{(1)}_x \), which goes to unity for large damping.

2. Entropy production versus energy dispersion

To derive the rate of entropy production we first need the Wigner function and its temporal evolution.

a. Fokker-Planck equation for the Wigner function

To derive the evolution equation for the Wigner function, we shall write the Langevin eq. (2.18) in the form

\[
\dot{p} = -ax - \frac{\gamma}{m}p + \eta + \delta \dot{p}
\]

(6.54)

where \( \delta \dot{p} \) is small as \( 1/\Gamma \). Indeed, from this definition and the exact dynamical solution (5.41,5.42) one may derive

\[
\delta \dot{p}(t) = mx_0 \dot{g}(t) + p_0 g(t) + \int_0^t dt' g(t - t') \eta(t')
\]

(6.55)

where

\[
g(t) = \frac{\gamma}{m} \sum_{i=1}^3 \frac{\omega_i^2}{\Gamma - \omega_i} f_i e^{-\omega_i t}
\]

(6.56)

is of order \( 1/\Gamma \) for large \( \Gamma \). Now recall that for the harmonic situation the Wigner function is given us

\[
W(p,x,t) = \int dp_0 dx_0 W(p_0,x_0,0) \langle \delta(p(t) - p)\delta(x(t) - x) \rangle,
\]

(6.57)

where the average is taken with respect to the noise, \( W(p,x,t) \) and \( W(p_0,x_0,0) \) are final and initial Wigner functions, while \( p(t), x(t) \) are the solutions of (2.18) for the corresponding initial conditions, and for a particular realization of the Gaussian noise. Eq. (6.57) is not the most general definition of the Wigner function, but it is exact for harmonic systems.

We now seek a closed equation for the Wigner function (6.57). Differentiating \( W(y_1,y_2,t) \) we get

\[
\frac{\partial W(y_1,y_2,t)}{\partial t} = -\sum_{k=1}^2 \frac{\partial (v_k W)}{\partial y_k} - \frac{\partial}{\partial y_1} \langle \delta(p(t) - y_1)\delta(x(t) - y_2)[\eta(t) + \delta \dot{p}(t)] \rangle,
\]

(6.58)

where

\[
v_1 = -ax - \frac{\gamma}{m} p, \quad v_2 = \frac{p}{m}.
\]

(6.59)

are the damped Newtonian acceleration and the velocity, respectively. The term \( \delta \dot{p} \) is a linear combination of \( p_0, x_0 \) and \( \eta(t) \). Due to the Gibbsian initial state, these are Gaussian random variables and their cross-correlations were given in Eqs. (5.32)-(5.35). Let us denote these variables by the vector \( z = \{p_0, x_0, \eta(t)\} \), and their correlations by the matrix \( M_{ij} = \langle z_i z_j \rangle \). One then has for its joint distribution
\[ P_0(z) = \frac{1}{\sqrt{\det(2\pi M)}} \exp\left(-\frac{1}{2}z_iM^{-1}z_j\right) \]  
(6.60)

Using the relation
\[ z_iP_0(z) = -\sum_j M_{ij} \delta_{z_j} P_0(z) \]  
(6.61)

one can perform a partial integrations, which brings a closed equation for \( W \). The final result is that we obtain a diffusion-type equation (Fokker-Planck-Kramers-Klein equation) for \( W \) itself:
\[ \partial_t W(p, x, t) = \mathcal{L} W = -\frac{p}{m} \partial_p W + \frac{\partial}{\partial p} \left( \left( \frac{\gamma}{m} p + ax \right) W \right) + \left( D_x(t) - D_p(t) \right) \frac{\partial^2}{\partial p \partial x} W + \gamma D_p(t) \frac{\partial^2 W}{\partial p^2}, \]  
(6.62)

where the diffusion coefficients \( D_x \) and \( D_p \) are instantaneous functions \( t \). (Notice that in ref. \[2\] we used the notation \( D_{pp} = D_p \), \( D_p = D_x \), \( D_{xp} = D_x - D_p \).) The derivation along this road is somewhat lengthy. A quicker way to derive the result is to use the solution of the Fokker-Planck equation, determined by the moments
\[ \langle p^2 \rangle = 2mK(t), \quad \langle px \rangle = m \frac{\dot{V}(t)}{a}, \quad \langle x^2 \rangle = \frac{2m}{a} V(t) \]  
(6.63)

where \( K(t) = \langle K(p) \rangle \) and \( V(t) = \langle V(x) \rangle \) are the expectation values of kinetic and potential energy, respectively. The time-dependent Wigner function thus reads
\[ W(p, x, t) = \frac{a}{\sqrt{2\pi mDV - m^2V^2}} \exp \left( -\frac{aKx^2 - \dot{V}px + Vp^2/m}{2KV - mV^2/a} \right) \]  
(6.64)

Inserting this in equation (6.62), one finally gets
\[ D_p(t) = 2K(t) + \frac{m}{\gamma} \left[ \dot{K}(t) + \dot{V}(t) \right] \]  
(6.65)

\[ D_x(t) = 2V(t) + \frac{m}{\gamma} \left[ \dot{K}(t) + \dot{V}(t) \right] + \frac{\gamma}{a} \dot{V}(t) + \frac{m}{a} \ddot{V}(t) \]  
(6.66)

Let us also define the time-dependent but current-less state
\[ W_{st}(p, x, t) = \frac{\sqrt{a}}{2\pi \sqrt{mD_p(t)D_x(t)}} \exp \left( -\frac{p^2}{2mD_p(t)} - \frac{ax^2}{2D_x(t)} \right) \]  
(6.67)

for which indeed the right hand side of the Fokker-Planck equation (6.62) vanishes, though the left hand side does not. This is the locally-stationary distribution. For sufficiently long times, that is when \( D_x(t) \) and \( D_p(t) \) are changing with time slowly enough, \( W_{st} \) becomes a solution of the Fokker-Planck equation.

\[ b. \ H-function \ and \ entropy \ production \]

The \( \mathcal{H} \)-function is defined as the information theoretical distance between the actual Wigner function \( W(x, p, t) \) and the locally-stationary Wigner function \( W_{st}(x, p, t) \):
\[ \mathcal{H} = \int dx dp W(x, p, t) \ln \frac{W(x, p, t)}{W_{st}(x, p, t)} \geq 0. \]  
(6.68)

The \( \mathcal{H} \)-function is non-negative due to the inequality
\[ \frac{W}{W_{st}} \ln \frac{W}{W_{st}} \geq \frac{W}{W_{st}} - 1, \]  
(6.69)

\[ \mathcal{H} \geq \int dx dp [W(x, p, t) - W_{st}(x, p, t)] = 0. \]  
(6.70)

35
Thus, $\mathcal{H}$ is equal to zero only for $W(x,p,t) = W_{st}(x,p,t)$, i.e., in the stationary state. Since values of $\mathcal{H}$ at intermediate times are higher than its final value, it is reasonable to look at its rate of change. In particular, $\mathcal{H}$ changes with time due to the time-dependence of the reference Wigner distribution $W_{st}$, whereas the remaining part of $d\mathcal{H}/dt$ appears to be induced solely by the bath (see below). We define the \textit{entropy production} $d_tS/dt$ by

$$- \frac{d\mathcal{H}}{dt} = \int dx dp \dot{W}_{st}(x,p,t) \frac{W(x,p,t)}{W_{st}(x,p,t)} + \frac{d_tS}{dt}. \quad (6.71)$$

This leads to

$$\frac{d_tS}{dt} = - \int dx dp \dot{W}(x,p,t) \ln \frac{W(x,p,t)}{W_{st}(x,p,t)} \quad (6.72)$$

This definition has the following properties: 1) It is equal to zero in the stationary state; 2) It is equal to zero if the brownian particle does not couple with the bath; 3) It is non-negative in the classical case, where $D_x = D_p = T$. The last two properties are proved below.

Using (6.67) and denoting

$$R(x,p,t) = \frac{W(x,p,t)}{W_{st}(x,p,t)}, \quad (6.73)$$

one gets:

$$\frac{d\mathcal{H}}{dt} = \int dx dp [\mathcal{L} W(x,p,t)] \ln R(x,p,t) - \int dx dp \dot{R}(x,p,t) \dot{W}_{st}(x,p,t) = \int dx dp W(x,p,t) \mathcal{L}^\dagger \ln R(x,p,t) - \int dx dp \dot{R}(x,p,t) \dot{W}_{st}(x,p,t). \quad (6.74)$$

where $\mathcal{L}$ is the Fokker-Planck operator of the right hand side of Eq. (6.62). Noting that

$$\mathcal{L}^\dagger \ln R = \frac{1}{R} \mathcal{L}^\dagger R - \frac{1}{R^2} \left( \gamma D_p(t) \left[ \frac{\partial R}{\partial p} \right]^2 + [D_x(t) - D_p(t)] \frac{\partial R}{\partial x} \frac{\partial R}{\partial p} \right), \quad (6.75)$$

and making once more integration by parts one ends up with

$$\frac{d_tS}{dt} = \int dx dp \frac{W(x,p,t)}{R^2(x,p,t)} \left( \gamma D_p(t) \left[ \frac{\partial R(x,p,t)}{\partial p} \right]^2 + [D_x(t) - D_p(t)] \frac{\partial R(x,p,t)}{\partial x} \frac{\partial R(x,p,t)}{\partial p} \right). \quad (6.76)$$

Now it is clear that in the classical white-noise limit, where $D_x = D_p$, the entropy production is non-negative. The positivity of $d_tS/dt$ just means that from the global viewpoint the approach to the stationary state is monotonous. In contrast, in the quantum case the positivity of the entropy production is endangered. It is also clear that for a free brownian particle ($\gamma = 0$) the entropy production is zero.

Finally we mention that the difference between $dS_B/dt$ and the entropy production is just the entropy flux:

$$\frac{d_tS}{dt} = \frac{dS_B}{dt} - \frac{d_tS}{dt} = - \int dx dp \dot{W}(x,p,t) \ln W_{st}(x,p,t). \quad (6.77)$$

It takes the value

$$\frac{d_tS}{dt} = \dot{K}(t) \frac{D_p(t)}{D_x(t)} + \dot{V}(t) \frac{D_p(t)}{D_x(t)}. \quad (6.78)$$

Let us recall that in the relaxation process no work is performed, so a change in energy can only be due to a change of heat exchanged with the bath. Therefore the last relation can be written as

$$\frac{d_tS}{dt} = \dot{Q}_p \frac{D_p}{D_x} + \dot{Q}_x \frac{D_p}{D_x}. \quad (6.79)$$

where $Q_p = \dot{K}$ and $Q_x = \dot{V}$ are the changes of heat in the momentum and coordinate sector, respectively, while $D_{p,x}$ are the corresponding diffusion coefficients in the Fokker-Planck operator $\mathcal{L}$ of Eq. (6.62). Notice that this entropy
flow deviates from the standard expression \( \frac{d}{dt} S = \dot{Q}/T = \dot{Q}_p/T + \dot{Q}_x/T \), that could not make sense since \( \dot{Q} \) does not scale with \( T \) at low \( T \).

The Boltzmann entropy reads

\[
S_B = -\int dp dx W(p, x, t) \ln \frac{1}{h} W(p, x, t) = 1 + \frac{1}{2} \ln \left[ \frac{m}{h^2 a} (4KV - \frac{m}{a} V^2) \right]
\]

(6.80)

Its rate of change is

\[
\frac{dS_B}{dt} = \frac{2aKV + 2aKV - mV \dot{V}}{4aKV - mV^2}
\]

(6.81)

The entropy production is the difference between them and appears to be quadratic in the deviation from the equilibrium state. To second order in the small parameter \( \alpha_0 \) it becomes

\[
\frac{d}{dt} S = \frac{\hbar \gamma a \alpha_0^2}{16\pi^2 m^2} \left\{ \frac{C_p'^2}{T_p^2} + \varepsilon(C_p' + C_p'')(\frac{C_p'}{T_p^2} + \frac{C_x'}{T_x^2}) + \frac{T_p - T_x}{2T_pT_x} C_x' C_x'' \right\}
\]

where \( C_{p,x}' \) denote the dimensionless derivatives \( \frac{dC_{p,x}}{d\tau} \).

c. Classical limit

In the classical limit, where \( T_x = T_p = T \), the rate of entropy production this becomes the sum of two squares, much alike the energy relaxation function \( C_E \) of eq. (6.11).

\[
\frac{d}{dt} S = 4a \alpha_0^2 \frac{\gamma e^{-4at/\gamma} \sin^2 w\tau}{w^2} \left\{ \left( \frac{\cosh w\tau + \sinh w\tau}{w} \right)^2 + (1 - w^2) \frac{\sinh^2 w\tau}{w^2} \right\}
\]

(6.83)

The total entropy production is thus

\[
\Delta_i S = \int_0^\infty dt \frac{d}{dt} S = \frac{\alpha_0^2}{4}
\]

(6.84)

This result holds for all \( w \).

In Eq. (7.42) we derive the general result for the energy dispersion. In the present setup we have \( \alpha(t) = \alpha_0 \delta(t) \), yielding

\[
\Delta \Pi = \frac{\hbar a \alpha_0^2}{4\pi \gamma} C_x(0)
\]

(6.85)

With help of Eq. (6.9) we find

\[
\frac{\Delta \Pi}{T} = \frac{\alpha_0^2}{4}
\]

(6.86)

This just coincides with \( \Delta_i S \), explaining that both describe the same physics.

In the strong damping limit \( w \to 1 \) one a simple exponential decay,

\[
\frac{d}{dt} S = \frac{\alpha_0^2}{\gamma} e^{-4at/\gamma}
\]

(6.87)

In the weak damping limit, but still at high temperatures, the result oscillates, but is non-negative,

\[
\frac{d}{dt} S = \frac{\gamma a \alpha_0^2}{m} \sin^2 \omega_0 t e^{-2\gamma t/m}
\]

(6.88)

Notice the similarity with the rate of energy decay (6.11).
d. Weak damping limit at moderate temperature

In the weak-damping limit $\gamma \to 0$, where $T_p = T_x = \frac{1}{\bar{\hbar}\omega_0} \coth(\frac{1}{2}\beta\bar{\hbar}\omega_0)$, the entropy production follows from (3.82), (3.20) and (3.22) to leading order as

$$\frac{dS}{dt} = \frac{\gamma \alpha_0^2}{4m} \left( \sin^2 2\omega_0 t + \cos 2\omega_0 t - \frac{\beta\bar{\hbar}\omega_0}{\sinh \beta\bar{\hbar}\omega_0} \right)^2 + \frac{2}{\pi} \Delta \psi \tanh \frac{1}{2} \beta\bar{\hbar}\omega_0 \sin 4\omega_0 t \left( e^{-2\gamma t/m} \right)$$  \hspace{1cm} (6.89)

The term $\Delta \psi$ comes from the difference $T_p - T_x$, given in (3.48). It reads

$$\Delta \psi = \psi \left( \frac{\beta\Gamma}{2\pi} \right) - \Re \psi \left( \frac{\beta\bar{\hbar}\omega_0}{2\pi} \right)$$  \hspace{1cm} (6.90)

At high $T$ the last contribution of (6.89) vanishes (at least, it is of order $1/\Gamma$, which we discard everywhere in this work), so Eq. (6.88) is recovered.

The term with $\Delta \psi$ is responsible for the occurrence of both positive and negative values of the rate of entropy production. At low $T$ one has $\Delta \psi \to \ln \Gamma/\omega_0$, which is moderately large. Therefore, below some specific temperature $T^* \sim \hbar\omega_0/\ln(\Gamma/\omega_0)$ the rate of entropy production can be negative, a surprising result. This finding goes against the formulation of the second law in the form of positivity of the entropy production. In our system the negative rates are not totally unexpected since oscillatory behavior is also exhibited already in the rate of energy decay (6.24).

The integrated entropy production is, to leading order in $\gamma$, insensitive to the oscillations. When averaged over one period, the cosine and sine are subleading and a positive rate emerges. The full integral reads

$$\Delta_t S = \frac{\alpha_0^2}{8} \left( 1 + \frac{(\beta\bar{\hbar}\omega_0)^2}{\sinh^2 \beta\bar{\hbar}\omega_0} \right)$$  \hspace{1cm} (6.91)

while the energy dispersion is

$$\frac{\Delta^-}{T_x} = \frac{\alpha_0^2}{8} \left( 1 + \frac{\beta\bar{\hbar}\omega_0}{\sinh \beta\bar{\hbar}\omega_0} \right)$$  \hspace{1cm} (6.92)

Both expressions have the same order of magnitude, and coincide at large and small $T$.

Consequently, in the Gibbsian limit the rate of entropy production oscillates in case of underdamping, as does the rate of internal energy. After averaging over one period the oscillations are washed out. This justifies our identifications of entropy flux and production.

e. Entropy production at zero temperature

Also at zero temperature the entropy production can be negative. Let us consider the case of strong damping, where $\varepsilon \ll 1$ and $T_x \sim \varepsilon T_p$, implying

$$\frac{dS_x}{dt} \approx \frac{\hbar^2 \gamma \alpha_0^2}{16\pi^2 m^2 T_x^2} \left\{ (1 + \varepsilon) C_x'' + \frac{1}{2} C_x'' \right\} = \frac{a(1 + \varepsilon)}{4\gamma \lambda^2} f' f_1' + \varepsilon f_1'' + O(\varepsilon^2)$$  \hspace{1cm} (6.93)

Now we know that $f_1$ has a negative minimum at $\sigma_{\text{min}}$. Let us expand, using the numerical constants from Eq. (5.38),

$$f_1(\sigma) = f_1(\sigma_{\text{min}}) + \frac{1}{2} c_2 (\sigma - \sigma_{\text{min}})^2$$  \hspace{1cm} (6.94)

Then we get

$$\frac{dS_x}{dt} = \frac{a(1 + \varepsilon)\alpha_0^2}{4\gamma \lambda^2} c_2^2 (\sigma - \sigma_{\text{min}})(\sigma - \sigma_{\text{min}} + \varepsilon)$$  \hspace{1cm} (6.95)

This is negative for $\sigma_{\text{min}} - \varepsilon < \sigma < \sigma_{\text{min}}$. The minimum is of order $-\varepsilon^2$, and the area of the negative part is of order $\varepsilon^3$. Notice that negative value holds over a time window $\delta t = \varepsilon$, corresponding to $\Delta t = \tau_p = m/\gamma$. This is much less than the free oscillation period $\tau_0 = \sqrt{m/a}$, so after averaging over one period it disappears. However, in the (strongly) overdamped regime there are no oscillations, so there is no compelling reason to average over one period.
For a numerical investigation of the entropy production at \( T = 0 \) we will first of all introduce a new parametrization for the effective temperatures:

\[
T_p = \frac{h \gamma}{\pi m} \theta_p, \quad \theta_p = \frac{1}{4w} \left( (1+w)^2 \ln \left( \frac{\Lambda}{1+w} \right) - (1-w)^2 \ln \left( \frac{\Lambda}{1-w} \right) \right),
\]

\[
T_x = \frac{h \gamma}{\pi m} \varepsilon \theta_x, \quad \theta_x = \frac{1}{w} \ln \frac{1+w}{1-w},
\]

\[
\theta = \frac{\theta_x}{\theta_p},
\]

where \( \Lambda = 2m \Gamma/\gamma \) is a large dimensionless parameter. Then Eq. (6.82) can be presented in a more convenient form:

\[
\frac{d_0 S}{dt} = \frac{a_0^2}{16 \gamma \varepsilon^2 \theta_x^2} \left( C''_x + \varepsilon (C'_x + C''_x)(C'_x + \varepsilon^2 C''_x) + \frac{1-\theta}{2} C''_x C''_x \right).
\]

As for the functions involved in this expression, one notice:

\[
\frac{d f_x(\tau, w)}{d\tau} = -4(1-w^2) \frac{w e^{-(1-w)\tau}}{w} \int_0^\infty dy \coth \left( b y \sqrt{\frac{1-w}{1+w}} \right) \frac{\cos(y(1-w)\tau)}{[(1+w)^2 + (1-w)^2 y^2] [1+y^2]},
\]

\[
\frac{d^2 f_x(\tau, w)}{d\tau^2} = 4(1-w^2)(1-w) \frac{w e^{-(1-w)\tau}}{w} \int_0^\infty dy \coth \left( b y \sqrt{\frac{1-w}{1+w}} \right) \frac{\cos(y(1-w)\tau) + y \sin(y(1-w)\tau)}{[(1+w)^2 + (1-w)^2 y^2] [1+y^2]},
\]

\[
\frac{d f_p(\tau, w)}{d\tau} = -4(1-w^2) \frac{w e^{-(1-w)\tau}}{w} \int_0^\infty dy \coth \left( b y \sqrt{\frac{1-w}{1+w}} \right) \frac{y^2 \sin(y(1-w)\tau)}{[(1+w)^2 + (1-w)^2 y^2] [1+y^2]},
\]

Recall that \( C_{p,x}(\tau) = f_{p,x}(\tau, w) + f_{p,x}(\tau, -w) \).

The behavior of the entropy production is depicted in Fig. 6.10. It is seen that there is a small region, where the curves are negative. For \( w = 0.1 \) (weak overdamping) the negative region is yet noticeable, but already for \( w = 0.7 \) (moderate overdamping) this region is almost indistinguishable. This is in agreement with the above analytical analysis in the limit \( \varepsilon \to 0 \).

![Fig. 6.10. Rate of entropy production (up to a factor \( a_0^2/(16\gamma \varepsilon^2 \theta_x^2) \)) versus dimensionless time \( \tau \). Left figure: \( T = 0 \), \( w = 0.1 \). Right figure: magnification of the region around \( \tau = 1.75 \).](image)

### 7. WORK AND HEAT

So far we have discussed the system’s relaxation from a non-equilibrium initial state. Since the total system is isolated, in this process energy is transferred from the subsystem to the bath, or vice versa. This energy is related to the unobservable bath modes, so it is identified as heat. In particular, in no way work was added to or extracted from the system, except for the initial moment, where the strength of the central spring was modified.

We shall now consider the possibility of additional changes in the spring constant and its implications for work extracted from the system.

39
1. General definition of work and heat

The behavior of a statistical system under interaction with external macroscopic sources is the standard area of applications for any thermodynamical theory. As known well, in this setup one neglects the influence of the statistical system to the dynamics of the source. Therefore, one can keep the parameters of the system as given functions of time, and solve the corresponding equations for the system’s dynamics. We start with general remarks about the energy budget of any variation.

Let us consider the change of a system parameter \( \alpha \). It is assumed to be intrinsic, that is to say, to characterize the Brownian particle but not the bath or the interaction between the particle and bath. In the situation discussed in the body of this work, \( \alpha \) can stand for the spring constant \( \alpha \) of the harmonic potential, the effective width of the anharmonic potential, or the mass \( m \) (for electrical circuits and junctions mass is connected with inductivity and can be subjected to variations; this also makes sense in systems where \( m \) is an effective mass, that can be modified by changing other system parameters, such as pressure).

First one has to identify the Hamiltonian of the subsystem. In Eq. (2.3) we have chosen \( \mathcal{H} = \frac{1}{2}p^2/m + \frac{1}{2}ax^2 \), as in absence of the bath. It should be stressed that we did not include the self-coupling \( \frac{1}{2} \gamma \Gamma x^2 \) or (part of) the interaction energy in \( \mathcal{H} \). Our choice is the natural one in the sense that the limits of large Debye frequency \( \Gamma \) and subsequent large damping \( \gamma \) lead to moderately large values of the energy of system and bath, and not to large terms of opposite sign that cancel in the total energy, as would occur, e.g. if \( \frac{1}{2} \gamma \Gamma x^2 \) were counted for the subsystem. See also the discussion in section 1.2 e.

A change with time of the mean energy is considered due to a variation of a parameter \( \alpha(t) \):

\[
\frac{d U}{dt} = d \int dx dp \ W(p, x, t) \mathcal{H}(p, x) = \int dx dp \mathcal{H}(p, x) \frac{dW(p, x, t)}{dt} + \int dx dp \ W(p, x, t) d\mathcal{H}(p, x), \tag{7.1}
\]

where \( W(p, x) \) is the Wigner function of the Brownian particle. The last term results from the change in the Hamiltonian, so it is a mechanical, non-statistical object. Following other authors \( \{6, 8, 9, 27\} \), we shall associate it with the work \( d\mathcal{W} \) produced by external sources, in close relation with the definition of work in classical mechanics and standard thermodynamics. The first term in the right hand side represents the variation due to the statistical redistribution of the phase space. We shall identify it with the change in heat \( dQ \). Eq. (7.1) can then be written as the usual first law:

\[
\frac{d U}{dt} = dQ + d\mathcal{W} \tag{7.2}
\]

The work, as defined in Eq. (7.1) can be shown to be the change of the total closed system’s (the particle plus bath) energy due to the variation of the parameter \( \alpha \). First one notices that for closed systems with a unitary evolution any change of energy is determined solely by work. This fact is due to the conservation of energy, and can be easily illustrated using the von Neumann equation of motion for the density matrix \( \rho_{tot} \) of the total system. Indeed, since

\[
\frac{d \rho_{tot}}{dt} = -i \hbar [\rho_{tot}, \mathcal{H}_{tot}],
\]

one has

\[
\frac{dU_{tot}}{dt} = d \text{tr}(\rho_{tot} \mathcal{H}_{tot}) = \text{tr}(\rho_{tot} d\mathcal{H}_{tot}) + \text{tr}(\mathcal{H}_{tot} d\rho_{tot}) = \text{tr}(\rho_{tot} d\mathcal{H}_{tot}) - \frac{i}{\hbar} \int dt \text{tr}(\mathcal{H}_{tot} [\rho_{tot}, \mathcal{H}_{tot}]) = \text{tr}(\rho_{tot} d\mathcal{H}_{tot}) \tag{7.3}
\]

due to the cyclic character of the trace. If now \( W_{tot}(p, x, p_1, x_1, ...) \) is the Wigner function of the whole system, then this implies the identity

\[
\frac{dU_{tot}}{dt} = \int dp \int dx \prod_k dp_k dx_k W_{tot}(p, x, p_1, x_1, ...) d\mathcal{H}_{tot}(p, x, p_1, x_1, ...) = \int dx \int dp W(p, x, t) d\mathcal{H}(p, x), \tag{7.4}
\]

since we only consider cases where forces are attached to the central particle, so \( d\mathcal{H}_{tot}(p, x, p_1, x_1, ...) = d\mathcal{H}(p, x) \), implying that the \( p_k, x_k \) integrals over the full Wigner function just bring the Wigner function of the subsystem. Taking into account that no heat was added to the total system, \( dQ_{tot} = 0 \), we may conclude that the work \( d\mathcal{W} \) extracted from the subsystem equals the work subtracted from the total system, \( dW_{tot} = dU_{tot} = d\mathcal{W} \).
We again consider the situation where at \( t = 0 \) the system was Gibbsian, with spring constant \( a_0 \), and it is instantaneously changed to a new value \( a \). For achieving this an amount of work \( W_0 \), given in (7.13) has to be added to the system. For \( a > a_0 \) this is just the work needed to make the spring attached to the particle stiffer. When \( a_0 < a \) this work is negative; energy is extracted, since the spring is weakened. For work extraction from the thus created non-equilibrium state we shall make additional changes in the spring constant.

### 2. Maximally extractable work

Now the total system consisting of central particle and bath is out of equilibrium, some work can be extracted from it. Before the interaction between the bath and the particle has been switched on, the total energy was

\[
U_{\text{tot}}(0^-) = U_B(T) + U_p(T, a_0)
\]  (7.5)

where \( U_B(T) = \pi^2 T^2/(6h\Delta) \) and \( U_p(T) \) are the initial energies of the unperturbed bath and the perturbation due to the Brownian particle, defined in (3.17) and by \( U_p = \partial[\beta F_p]/\partial \beta \) with \( F_p \) taken from (3.44), respectively. After the switching of the interaction has been completed, the energy has become

\[
U_{\text{tot}}(0^+) = W_0 + U_B(T) + U_p(T, a_0)
\]  (7.6)

Let us now consider what is the maximal amount of work that can be extracted from the overall isolated system in the considered non-equilibrium state. First of all, we notice that we are interested in the work done due to the non-equilibrium state. (Let us recall that thermal isolation means that no external supply of heat is given; the allowed transformations are variation of parameters by external sources). (i) No work can be extracted from a system in its equilibrium state. (Let us recall that thermal isolation means that no external supply of heat is given; the allowed transformations are variation of parameters by external sources). (ii) The converse is true as well under certain general conditions: If no work can be extracted by any means from a system in a given state, then this state is equilibrium.

As follows from (i) some work can be extracted from non-equilibrium states. In the same way (ii) implies that if work has been extracted in all possible ways, the system is left in an equilibrium state at some temperature \( T_{\text{fin}} \). Since the overall system is thermally isolated, the extracted work is in magnitude equal to the complete change of energy (this is the statement of the first law): \(|W_{\text{max}}| = U_{\text{tot}}(T_{\text{fin}}) - U_{\text{tot}}(T_{\text{fin}})\), where \( U_{\text{fin}}(T_{\text{fin}}) = U_{\text{tot}}(T_{\text{fin}}, a) \) is the energy of the final equilibrium state. Because the entropy is conserved during variations of parameters, the optimal final equilibrium state will have a density matrix

\[
\rho_{\text{fin}} = \frac{\exp[-\beta_{\text{fin}} H_{\text{tot}}]}{Z},
\]  (7.7)

involving the temperature \( T_{\text{fin}} = 1/\beta_{\text{fin}} \), which is determined by constancy of the von Neuman entropy of the total system:

\[
S_{\text{tot}}(T) = S_B(T, \gamma = 0) + S_p(T, a_0) = S_{\text{tot}}(T_{\text{fin}}) = S_B(T_{\text{fin}}, \gamma = 0) + S_p(T_{\text{fin}}, a)
\]  (7.8)

with \( S_B(T, \gamma = 0) = \pi^2 T/3h\Delta \) from (3.18). Remembering that the level splitting \( \Delta \) of the bath modes is very small, one can solve

\[
T_{\text{fin}} = T + \frac{3h\Delta}{\pi^2} [S_p(T, a_0) - S_p(T, a)]
\]  (7.9)

This yields

\[
|W_{\text{max}}| = W_0 + U_{\text{tot}}(T, a_0) - U_{\text{tot}}(T, a) - TS_p(T, a_0) + T_p(T, a)
\]

\[
= W_0 + F_{\text{tot}}(T, a_0) - F_{\text{tot}}(T, a) = W_0 + F_p(T, a_0) - F_p(T, a)
\]  (7.10)

In the last step we canceled the contributions of the unperturbed bath. Not unexpectedly, the result depends on the free energies of the total system.

Notice that for a cycle consisting of the changes \( a_0 \rightarrow a \) and (much) later \( a \rightarrow a_0 \), the maximally extractable work becomes the sum of the amounts of work \( W_0(a_0 \rightarrow a) + W_0(a \rightarrow a_0) \), so for cycles in principle all work can be recovered.
a. Values at high and low $T$

In the classical limit the free energy is given in (3.52), just the value for a harmonic oscillator, whether or not coupled to other harmonic oscillators. The maximally extractable work is

$$\left|W_{\text{max}}\right| = \frac{1}{2} \left[ \frac{\alpha_0}{1 - \alpha_0} + \ln(1 - \alpha_0) \right] T = \frac{1}{4} \alpha_0^2 T + O(\alpha_0^3) \quad (7.11)$$

At low $T$ the difference in free energy of the total system between the equilibrium states at the initial and final value of the spring constant is

$$F_{\text{tot}}(a) - F_{\text{tot}}(a_0) = F_p(a) - F_p(a_0) = \frac{\hbar a}{2\pi} \left[ \frac{\alpha_0}{w} \ln \frac{1 + w}{1 - w} + \frac{\alpha_0^2}{2w^2} (1 - \frac{1 - w^2}{2w} \ln \frac{1 + w}{1 - w}) \right] + (\alpha_0 + \alpha_0^2) \frac{\pi \gamma T^2}{6\hbar a} \quad (7.12)$$

The energy added at $t = 0$ is

$$W_0 = \frac{1}{2} \left( \frac{a}{a_0} - 1 \right) T_x(a_0) = \frac{\hbar a}{2\pi} \left[ \frac{\alpha_0}{w} \ln \frac{1 + w}{1 - w} + \frac{\alpha_0^2}{2w^2} (1 - \frac{1 - w^2}{2w} \ln \frac{1 + w}{1 - w}) \right] + (\alpha_0 + 2\alpha_0^2) \frac{\pi \gamma T^2}{6\hbar a} \quad (7.13)$$

So by making the instantaneous change in $a$ the maximally extractable work (7.10) reads

$$\left|W_{\text{max}}\right| = \alpha_0^2 \left[ \frac{\hbar a}{4\pi} \frac{1}{w^2} (1 - \frac{1 - w^2}{2w} \ln \frac{1 + w}{1 - w}) + \frac{\pi \gamma T^2}{6\hbar a} \right] \quad (7.14)$$

If we let the system relax, this will run away in the bath on a timescale $\tau_x$. By making clever subtraction schemes, we may recover some of it, and in principle all of it.

For the case $T = T_{\text{inh}} = 0$ Eq. (7.10) merely says that that all energy exceeding the groundstate energy of the new system can, in principle, be extracted.

3. Work extraction by further sudden changes

Here we present the formalism of work-extraction via sudden changes of a parameter. Besides presenting the general setup, we will display the validity of the Thomson’s equilibrium formulation of the second law within the present situation.

Let there be a closed system with a Hamiltonian $\mathcal{H}$ in a state $\rho(t_1)$ at the moment $t_1$. Certain parameters of the Hamiltonian are varied in a very fast way such that for $t_1+\epsilon$ its Hamiltonian becomes $\mathcal{H}_1$, but the state remains $\rho(t_1)$ due to the sudden character of the variation. The work done by an external source reads:

$$\mathcal{W}_1 = \text{tr}[\rho(t_1)(\mathcal{H}_1 - \mathcal{H})] \quad (7.15)$$

In the second step the system is allowed to involve according to the new Hamiltonian $\mathcal{H}_1$. At the moment $t_2$ when the system reaches the state:

$$\rho(t_2) = e^{-i(t_2-t_1)\mathcal{H}_1/\hbar} \rho(t_1) e^{i(t_2-t_1)\mathcal{H}_1/\hbar} \quad (7.16)$$

its parameters are suddenly returned to their original value. The work done in this step reads:

$$\mathcal{W}_2 = \text{tr}[\rho(t_2)(\mathcal{H} - \mathcal{H}_1)]. \quad (7.17)$$

The total work done by the source for this cyclic variation of the parameter reads:

$$\mathcal{W} = \mathcal{W}_1 + \mathcal{W}_2 = \text{tr} \left[ \rho(t_1) \left( e^{i(t_2-t_1)\mathcal{H}_1/\hbar} \mathcal{H} e^{-i(t_2-t_1)\mathcal{H}_1/\hbar} - \mathcal{H} \right) \right], \quad (7.18)$$

where we have used Eq. (7.16). Notice that we consider the closed overall system, and only due to this fact the evolution of the system for times between $t_1$ and $t_2$ is given by the Hamiltonian $\mathcal{H}_1$.

It is not difficult to see from Eq. (7.18) that the second law is satisfied for the present setup. Let us first assume that at the moment $t$ the system was in the ground state of $\mathcal{H}$: $\rho(t_1) = |0\rangle\langle 0|$. Then one has:
\[ \mathcal{W} = \langle 0 | e^{i(t_2-t_1)H_t/\hbar} \mathcal{H} e^{-i(t_2-t_1)H_t/\hbar} | 0 \rangle - \langle 0 | \mathcal{H} | 0 \rangle \geq 0, \]  

(7.19)

just by the definition of the ground state. The same statement, namely \( W \geq 0 \), holds when \( \rho(t) \) is the Gibbs distribution of the initial state at positive temperature \( T = 1/\beta \); \( \rho(t_1) = \exp(-\beta \mathcal{H})/Z \), \( Z = \text{tr} \exp(-\beta \mathcal{H}) \).

Our work extraction mechanism involves a second change of the spring constant, which is cyclic: at time \( t_2 \) we impose a jump \( a \rightarrow a_2 = a(1 - \alpha_2) \) and it keeps that value, until at \( t_3 \) it is put back to \( a \). The work involved in this cyclic two-step process is

\[ \Delta \mathcal{W} = U_{tot}(t_2^+) - U_{tot}(t_2^-) + U_{tot}(t_3^+) - U_{tot}(t_3^-) = \frac{1}{2}(a_2 - a)[\langle x^2 \rangle_{t_2} - \langle x^2 \rangle_{t_3}] \]  

(7.20)

The change in particle energy between \( t_2^- \) and \( t_3^+ \) is

\[ \Delta U = \frac{1}{2m}[\langle p^2 \rangle_{t_3} - \langle p^2 \rangle_{t_2}] + \frac{1}{2}a_2[\langle x^2 \rangle_{t_3} - \langle x^2 \rangle_{t_2}] \]  

(7.21)

Thus the change in heat during the work extraction process is

\[ \Delta \mathcal{Q} = \frac{1}{2m}[\langle p^2 \rangle_{t_3} - \langle p^2 \rangle_{t_2}] + \frac{1}{2}a_2[\langle x^2 \rangle_{t_3} - \langle x^2 \rangle_{t_2}] \]  

(7.22)

The values of \( \langle x^2 \rangle \) and \( \langle p^2 \rangle \) at time \( t_2 \) are set by the spring constants \( a_0 \) and \( a \) solely, and can be taken from previous section. When we take \( t_3 \) large, we can take for that situation the limiting values for a system with spring constant \( a_2 \). We then find

\[ \Delta \mathcal{W} = (a_2 - a)[\frac{T_x(a)}{2a} + \frac{\alpha_0 \hbar}{2\pi \gamma} C_x(\frac{\gamma t_2}{2m}) - \frac{T_x(a_2)}{2a_2}] \]  

(7.23)

\[ \Delta U = \frac{1}{2}T_p(a_2) - \frac{1}{2}T_p(a) + \frac{a}{2a_2} T_x(a_2) - \frac{1}{2}T_x(a) - \frac{\alpha_0 \hbar a}{2\pi \gamma} C_E(\frac{\gamma t_2}{2m}) \]  

(7.24)

\[ \Delta \mathcal{Q} = \frac{1}{2}T_p(a_2) - \frac{1}{2}T_p(a) + \frac{1}{2}T_x(a_2) - \frac{a_2}{2a} T_x(a) - \frac{\alpha_0 \hbar a}{2\pi \gamma} C_p(\frac{\gamma t_2}{2m}) - \frac{\alpha_0 \hbar a_2}{2\pi \gamma} C_x(\frac{\gamma t_2}{2m}) \]  

(7.25)

\( a \). Classical regime

In the classical case with strong damping we use \( 6.13 \) and obtain

\[ \Delta \mathcal{W} = \frac{1}{2}a_0^2 T - \frac{1}{4}\alpha_0 a_2 T e^{-2at_2/\gamma} \]  

(7.26)

This has a minimum

\[ a_2^* = \frac{1}{2}a_0 e^{-2at_2/\gamma}, \quad \Delta \mathcal{W}_{\text{min}} = -\frac{1}{8}\alpha_0^2 T e^{-4at_2/\gamma} \]  

(7.27)

Work can only be extracted under proper conditions, that is to say, when \( a_2 \) is between 0 and \( \alpha_0 \exp(-2\omega_t t_2) \). Else the cycle \( a \rightarrow a_2 \rightarrow a \) disperses energy.

The heat absorbed by the subsystem is at linear order in \( \alpha_0 \) insensitive to the work extraction,

\[ \Delta \mathcal{Q} = \Delta U = -\frac{1}{4}\alpha_0 T e^{-4at_2/\gamma} \]  

(7.28)

There are two cases:

- \( \alpha_0 > 0 \): The central spring is stiffened, \( a > a_0 \), and energy is supplied at \( t = 0 \). This energy leaks away, mostly as heat into the bath, \( (\Delta \mathcal{Q} < 0) \) and partly as work extracted from the total system \( (\Delta \mathcal{W} < 0) \), more precisely, from the particle.

The ratio of extracted work to maximally extractable energy is, in the regime where \( \alpha_0 \) is small but finite and \( T \gg \hbar \omega_0 \),

\[ \eta = \frac{|\Delta \mathcal{W}|}{|\mathcal{W}_{\text{max}}|} = \frac{1}{2} e^{-4\omega_t t_2} \]  

(7.29)
So our mechanism extracts maximally 50% of maximum; for doing this it must start immediately \((t_2 = 0)\) and last as long as possible \((t_3 = \infty)\).

- \(\alpha_0 < 0\): the central spring is weakened at \(t = 0\). Energy is taken out from the system. The amount, \(\frac{1}{2} T (|\alpha_0| - \alpha_0^2)\), is less than the amount that could have been extracted by an adiabatic change, \(\frac{1}{2} T (|\alpha_0| + \frac{1}{4} \alpha_0^2)\). After that has been done, heat flows from the bath to the particle \((\Delta Q > 0)\), as if the particle were at a lower temperature. In the course of this process work can be extracted, maximally the absolute value of Eq. (7.27), as is usual for two-temperature systems. The basic issue to extract work is to have a mechanism that, given the initial change in \(a\), is the closer to adiabaticity.

These conclusions also hold for moderate and weak damping.

\[ b. \text{ Low temperature regime} \]

At \(T = 0\) we get from Eq. (7.23)

\[
\Delta W = \frac{\hbar a}{2\pi\gamma} \left[ \alpha_0^2 C_x(0) - \alpha_0 \alpha_2 C_x \left( \frac{\gamma t_2}{2m} \right) \right] \tag{7.30}
\]

where \(C_x(0)\) is defined in (1.25) and \(C_x(\tau)\) in (1.6). The minimum occurs for

\[
\alpha_2^* = \frac{\alpha_0}{2C_x(0)} C_x \left( \frac{\gamma t_2}{2m} \right), \quad \Delta W_{\text{min}} = -\frac{\hbar \omega_2 \alpha_0^2}{8\pi C_x(0)} C_x^2 \left( \frac{\gamma t_2}{2m} \right) \tag{7.31}
\]

The change in heat and internal energy is

\[
\Delta Q = \Delta U = -\alpha_0 \frac{\hbar a}{2\pi\gamma} C_E \left( \frac{\gamma t_2}{2m} \right) \tag{7.32}
\]

We consider again the separate cases:

- \(\alpha_0 > 0\): The spring is stiffened at \(t = 0\) and energy \(W_0\) is supplied. At \(t = 0^+\) the energy is, to linear order in \(\alpha_0\), equal to its final value, since \(C_E(0) = 0\). This change since energy comes from the bath, on a timescale \(\tau_p\) which is short for strong damping, where \(\tau_p = m/\gamma\). In the initial time regime \(\gamma t_2/2m < \tau_0\) this mainly leaks away to the bath, and a small part can be extracted as work. In the regime \(\tau_0 < \gamma t_2/2m < \sigma_{\text{min}}\) this also happens, but the energy of the subsystem goes below its final value, so the particle becomes “too cold”. In the final regime \(\gamma t_2/2m > \sigma_{\text{min}}\) energy flows back to the particle and again a small part can be extracted as work. This is then work extracted from the non-equilibrium bath, and the surprise is that this can be done although initial energy was put on the particle. This recovery of energy stored in the bath is a quantum effect. \(\Delta W < 0\) means that work is extracted from the total system. Eq. (7.31) is the maximally extractable amount of work with the present mechanism. As efficiency factor way may normalize with respect to the maximally extractable energy from eq. (7.11), the energy that would otherwise leak away into the bath.

\[
\eta = \frac{-\Delta W_{\text{min}}}{|W_{\text{max}}|} = \frac{1}{2} C_E(\omega_2 t_2) \tag{7.33}
\]

When one starts the extraction quickly after the initial change \((\tau_1 \approx 0)\) one can still get half of the work back in this way, the same rate as in the classical regime. Even more is obtained when one still starts at \(t_2 = 0\) but stops at the moment that the energy current goes no longer towards the particle, but away from it, i.e. at \(\omega_2 t_3 = \sigma_{\text{min}}\). One then has

\[
\Delta W = -\frac{1}{2} \alpha_2 a [\langle x^2 \rangle_{t=0; a_0} - \langle x^2 \rangle_{t=1; a_2}] = \frac{\hbar a}{2\pi\gamma} \{ \alpha_0^2 - \alpha_0 \alpha_2 [1 - C_x(\omega_2 t_3)] \} \geq -\frac{\hbar a}{8\pi\gamma} \alpha_0^2 [1 - C_x(\omega_2 t_3)]^2 \tag{7.34}
\]

The efficiency is

\[
\eta = \frac{-\Delta W}{|W_{\text{max}}|} = \frac{1}{2} [1 - C_x(\omega_2 t_3)]^2 \tag{7.35}
\]

which indeed has the proper behavior for \(t_3 \to 0\) and \(t_3 \to \infty\). The maximum is, due to (6.33) and (5.38),
\[ \eta_{\text{max}} = \frac{1}{2} [1 - C_x(\sigma_{\text{min}})]^2 = 0.5961 \]  

(7.36)

the maximum exceeds the classical efficiency \( \eta = 1/2 \). So the quantum statistical excess energy flow from the particle into the bath indeed allows a more optimal recovery of energy initially put on the particle.

The most interesting feature is that with the present mechanism it is also possible to extract work solely from the bath, a mechanism forbidden by the original Thomson formulation of the second law. Indeed, after \( \omega_2 t = \sigma_{\text{min}} \), energy will flow back from the bath to the particle. By starting the extraction mechanism at \( \omega_2 t_2 = \sigma_{\text{min}} \) and exploiting all times after this for the work extraction, the maximal efficiency \( \eta_{\text{max}} \) is

\[ \eta_{\text{max}} = \frac{1}{2} C_x^2(\sigma_{\text{min}}) = 0.00422262576 \]  

(7.37)

In contrast to the classical case, it goes to a finite limit when \( \alpha_0 \to 0 \). This occurs because in the quantum case the energy \( \sim \alpha_0^2 \), with respect to which the extracted work has been normalized, is one order of magnitude smaller than the initially supplied energy \( W_0 \sim \alpha_0^2 \).

\( \bullet \) \( \alpha_0 < 0 \): The spring is weakened and energy \( W_0 \) is extracted. Some energy can be extracted. For \( \omega_2 t_2 < \sigma_{\text{min}} \) it comes from the bath, but in the regime \( \omega_2 t_2 > \sigma_{\text{min}} \) the particle has an excess energy, which then supplies the work.

4. Work extraction by smooth changes of the spring constant

Let us now consider the case where the spring constant \( a(t) = [1 - \alpha(t)]a \), is slightly changed (\( |\alpha(t)| \ll 1 \)) in a smooth manner, starting from the equilibrium state \( a(-\infty) = a \). In appendix A we derive for the rate of work added to the system

\[ \frac{dW}{dt} = \frac{dW_{\text{rev}}}{dt} + \frac{d\Pi}{dt} \]  

(7.38)

where

\[ \frac{dW_{\text{rev}}}{dt} = -\frac{\gamma}{2m} \frac{d\alpha(\tau)}{d\tau} \left[ \frac{1}{2} T_x + \frac{\hbar a}{2\pi\gamma} \alpha(\tau) C_x(0) \right] \]  

(7.39)

is the adiabatic (‘reversible’ or ‘recoverable’) rate of work and

\[ \frac{d\Pi}{dt} = \frac{\hbar a}{4\pi m} \frac{d\alpha(\tau)}{d\tau} \int_{0}^{\infty} d\tau' \alpha'(\frac{\gamma t}{2m} - \tau) C_x(\tau) \]  

(7.40)

is the rate of energy dispersion.

\[ a. \text{ Completed changes} \]

Integrating over the full change one has

\[ W_{\text{rev}} = -\frac{1}{2} (\alpha_f - \alpha_i) T_x - \frac{\hbar a}{4\pi\gamma} C_x(0)[\alpha_f^2 - \alpha_i^2] \]  

(7.41)

where \( \alpha_i = \alpha(-\infty) \) and \( \alpha_f = \alpha(\infty) \), and

\[ \Pi = \frac{\hbar a}{4\pi\gamma} \int_{-\infty}^{\infty} d\tau_1 \alpha'(\tau_1) \int_{-\infty}^{\infty} d\tau_2 \alpha'(\tau_2) C_x(|\tau_1 - \tau_2|) \]  

(7.42)

For a full process (covering the whole region where \( \alpha' \neq 0 \)) \( \Pi \) is non-negative, since it is an integral over a non-negative function,

\[ \Pi = \frac{\hbar a}{2\gamma} \int_{-\infty}^{\infty} d\zeta |A(\zeta)|^2 \Re C_x(i\zeta) \]  

(7.43)

45
where the Laplace transform $\hat{C}_x$ was defined in Eq. (6.51); it can be verified that $\Re \hat{C}_x(i\zeta)$ is positive for all real $\zeta$. Furthermore

$$A(\zeta) = \int \frac{d\tau}{2\pi} \alpha'(\tau) e^{i\zeta \tau} \tag{7.44}$$

The positive energy dispersion for a completed, non-adiabatic cyclic change of system parameters is the Thomson formulation of the second law. We see that a positive dispersion also holds for non-cyclic but completed changes, as is known to occur on general grounds.

We can check previous case $\alpha(t) = \alpha_0 \delta(-t)$, $\alpha'(t) = -\alpha_0 \delta(\tau)$, for which Eq. (7.13) is at $T = 0$ equivalent to

$$W_0 = W_{\text{rev}} + \Pi = \frac{1}{2} \alpha_0 T_x + \frac{h a}{2\pi \gamma} \alpha_0^2 C_x^{(0)} \tag{7.45}$$

b. Incomplete changes

Let us now consider the temporal build up of this result in the regime of strong damping. Let $\alpha$ have the form

$$\alpha(\tau) = \alpha_m h(\Omega t) \tag{7.46}$$

where $\alpha_m$ is a small amplitude and $h$ is a bounded function ($|h| \leq 1$), with $h(-\infty) = 0$, $h'(\infty) = 0$. If $h(\infty) \neq 0$ it could be an error function; if $h(\infty) = 0$ a Gaussian. $1/\Omega$ is the typical duration time of the change. Using Eqs. (7.46, 6.48, 6.50) we get from (A.10)

$$\frac{d\Pi}{dt} = \frac{ha}{4\pi m} \alpha' \left[ C_x^{(0)} + \alpha'' C_x^{(1)} - \frac{1}{2} \alpha'' C_x^{(2)} \right] = \frac{h\Omega^2 a\alpha_m^2}{12\pi} h'(\Omega t) \left[ \left( \frac{2\pi \gamma T}{ha} \right)^2 h'(\Omega t) + \frac{\gamma \Omega C_x^{(1)}}{a} h''(\Omega t) \right] \tag{7.47}$$

where $C_x^{(1)}$ was defined in (3.49); for weak damping it equals $3\pi \sqrt{am}/8\gamma$, while for large damping it becomes unity. The integrated effect is

$$\Pi(t) = \frac{h\Omega a_m^2}{12\pi} \left\{ \left( \frac{2\pi \gamma T}{ha} \right)^2 \int_{-\infty}^0 d\xi [h'(\xi)]^2 + \frac{\gamma \Omega C_x^{(1)}}{2a} [h'(\Omega t)]^2 + \frac{\gamma^2 \Omega^2}{a^2} \left[ -h'(\Omega t) h''(\Omega t) \right] \right\} \tag{7.48}$$

For a completed change the second and third term vanish, leading to a positive energy dispersion, in concordance with (7.43). It is seen that then the standard behavior $\Pi \sim \Omega$ applies when $T$ is large enough or when $\Omega$ is small enough. However, in the quantum regime where the duration $1/\Omega$ is smaller than the quantum timescale $\tau_h = h/T$, the last term in Eq. (7.48) dominates, with a new behavior $\Pi \sim \Omega^3$.

Another new quantum effect is that at low $T$ and for typical times the second term in (7.47) is larger in magnitude than the other ones. This too occurs since the integral of $C_x(\tau)$ vanishes at $T = 0$, and leads to new possibilities, that we discuss now.

c. Work extraction from a smooth cyclic change

One definition for a perpetuum mobile of the second kind is that there is a machine that performs a cycle in which it receives heat from a bath and converts this fully into work done on the surrounding. Additional requirements can occur; we shall discuss them in section 9.7. Here we analyze whether such a full energy conversion can be realized in our setup. The aim is thus to have a cyclic change of a system parameter with the properties

$$\Delta U = 0, \quad \Delta Q = -\Delta W > 0 \tag{7.49}$$

Including in (A.9) also the contribution of the momentum, we have to linear order in $\alpha$

$$U(t) = \frac{1}{2} T_p(a) + \frac{1}{2} T_x(a) + \frac{ha}{2\pi \gamma} \alpha \left( \frac{\gamma t}{2m} \right) C_E(0) - \int_0^\infty d\tau \alpha' \left( \frac{\gamma t}{2m} - \tau \right) C_E(\tau) \tag{7.50}$$
Let us choose for $\alpha(\tau)$ a curve in the shape of a double bell, and consider the system at some time $t_1$ after the first peak, and compare it to the situation at a later time $t_2$, after the second peak. We require that the spring constant has the same values at these instants, $\alpha(t_1) = \alpha(t_2)$, where $\tau_{1,2} = \gamma t_{1,2}/2m$. This implies for the internal energy

$$\Delta U = U(t_2) - U(t_1) = \frac{\hbar a}{2\pi \gamma} \int_0^\infty d\tau [\alpha'(t_1 - \tau) - \alpha'(t_2 - \tau)] C_E(\tau)$$

(7.51)

For slow changes this can be expanded

$$\Delta U = \frac{\hbar a}{2\pi \gamma} \left\{ [\alpha'(t_1) - \alpha'(t_2)] C_E(0) + [\alpha''(t_1) - \alpha''(t_2)] C_E(1) - \frac{1}{2} [\alpha'''(t_1) - \alpha'''(t_2)] C_E(2) \right\}$$

(7.52)

where the coefficients are given in (6.53).

Let us assume that we have two consecutive changes, characterized by a common bell-shaped function $k(x)$ with $|k(x)| \leq 1$, but involving different rates of change $\Omega_{1,2}$,

$$h(\tau) = k(\Omega_1 t) + k(\Omega_2 (t - t_2^2))$$

(7.53)

where the parameters $\Omega_1 > \Omega_2 > 0$ and $t_2 > 0$ are such that the profiles have negligible overlap. Choosing the times $t_{1,2}$ as

$$t_1 = \frac{\bar{x}}{\Omega_1}, \quad t_2 = t_2^2 + \frac{\bar{x}}{\Omega_2}$$

(7.54)

we indeed satisfy the cyclic condition $\alpha(t_1) = \alpha(t_2) = \alpha_m k(x)$. The difference in energy is

$$\Delta U = \frac{\alpha_m h(\Omega_1 - \Omega_2)}{12\pi} \left\{ \left( \frac{2\pi \gamma T}{\hbar a} \right)^2 k'(\bar{x}) + \frac{\gamma (\Omega_1 + \Omega_2)}{a} k''(\bar{x}) - \frac{\gamma^2 (\Omega_1^2 + \Omega_1 \Omega_2 + \Omega_2^2)}{a^2} k'''(\bar{x}) \right\}$$

(7.55)

Let us assume that $\bar{x}$ is fixed but such that $k' < 0$ while $k'' > 0$; this is possible because $k$ has both convex and concave parts, implying that there is an interval with such behavior. In the example $k(x) = \exp(-x^2/2)$, there is an inflection point $x_{id} = 1$ and one needs $\bar{x} > 1$. Let us also assume that $T \ll \hbar a/\gamma$. Then for

$$\Omega_1 + \Omega_2 = \frac{4\pi^2 \gamma T^2 |k'(\bar{x})|}{\hbar^2 a}$$

(7.56)

the first two terms can cancel, while the exposed correction term and the higher ones are small. Thus under these conditions it is possible to have a cyclic process with $\Delta U = 0$ to order $\alpha_m$; if $\alpha_m$ corrections are taken into account, the condition for cancellation is shifted an amount of order $\alpha_m$ and can again be met. Thus it is possible to start from the equilibrium state, make a first cyclic change of $a$ and then a second, which process contains itself a cyclic change of $a$ with $\Delta U = 0$. The work during this cycle comes solely from the energy dispersion. Using Eq. (7.48) we obtain the leading terms

$$\Delta W = \frac{\alpha_m^2 h}{12\pi} \left\{ \left( \frac{2\pi \gamma T}{\hbar a} \right)^2 \left( \Omega_1 \int_{-\infty}^\infty \! d\xi [k'(\xi)]^2 + \Omega_2 \int_{-\infty}^\bar{x} \! d\xi [k'(\xi)]^2 \right) + \frac{\gamma (\Omega_1^2 - \Omega_2^2)}{2a} [k''(\bar{x})]^2 \right\}$$

(7.57)

The higher order terms are small for the same reason as above. If $\Delta W < 0$ this amounts to work exerted by the system on the environment. One can always have $k''(\bar{x})$ small enough (by choosing $\bar{x}$ close to the inflection point) to make the combination of the $\Omega_1$ terms negative, and choose $\Omega_2$ so small that the whole expression remains negative. So it is indeed possible to have a cycle where the extracted work $|\Delta W|$ comes solely from the bath.

We should stress that these work cycles are realizable only because in the first part of the process, for $t < t_1$, energy was lost ($W(t_1) - W(-\infty) > 0$); a part of this is recovered. If, on the other hand, all the work is counted, then no work extraction is possible ($W(\infty) - W(-\infty) > 0$), c.f. Eq. (7.42).

Alternatively one may conclude that there are non-equilibrium initial conditions (for instance, the state of the total system at time $t_1$) which allow cycles which fully consume heat obtained from the bath into work done on the environment.

From the analysis it is clear that under less strict conditions it is even possible to make a cycle that extracts work that comes partly from the bath and partly from the system (“efficiency larger than 100%”).
One can make several of these cycles. Even though the previous finding that complete cycles disperse energy should temper the hope to gain more work by doing more cycles, we consider the issue here, since work extraction from many cycles is one of the ways to express our unexpected results.

Let there be \( N \) cycles with \( \alpha(t) = \alpha_n h(t) \) having \( N \) non-overlapping bell-shaped parts, like in Eq. (7.53), where \( k(x) \) could be the Gaussian \( \exp(-\frac{1}{2}x^2) \). Each cycle is characterized its typical inverse duration time \( \Omega_n \ll a/\gamma \) and location \( t_n \), and each new cycles is slower than the previous one, \( \Omega_{n+1} < \Omega_n \). For having cyclic behavior in the energy one finds from (7.55) that for low \( T \) and small but almost equal \( \Omega_n \)'s, one should choose \( \bar{x} \) close to the inflection point \( x_{\text{if}} \) of \( k \):

\[
\bar{x}_n - x_{\text{if}} = \frac{a}{2\gamma \Omega_n} \left[ k'(x_{\text{if}}) \right] \left( \frac{2\pi \gamma T}{ha} \right)^2 + \frac{3\gamma \Omega_n}{2a} + O\left( \frac{\gamma^2 \Omega_n^2}{a^2} \right) \tag{7.58}
\]

In order that this be small for all \( n \) one needs that \( \Omega_N \gg \gamma T^2/h^2a \). Strictly speaking the \( \alpha_n = \alpha_m h(\bar{x}_n) \) are now not exactly equal; this can be healed by slightly adjusting the profile in the \( n \)'th cycle: \( k(\Omega_n(t - t_n)) \rightarrow k(\Omega_n(t - t_n))k(x_{\text{if}})/k(\bar{x}_n) \), yielding \( \alpha(t_n) = \alpha_m h(x_{\text{if}}) \) for all \( n \). For small \( \bar{x}_n - x_{\text{if}} \) this correction factor is close to unity and can be omitted from the rest of the argument.

Let us define

\[
\tilde{T} = \frac{2\pi \gamma T}{ha} \tag{7.59}
\]

Taking Eq. (7.48) at \( t = t_n \), where \( n \) cycles have been performed, and using that \( \bar{x} - x_{\text{if}} \ll 1 \) and that \( |\Omega_n - \Omega_{n+1}| \ll \Omega_n \), brings for the yield of the \( n \)'th cycle

\[
\Pi(t_n) - \Pi(t_{n-1}) = \frac{\alpha_m^2}{12\pi \gamma} ha \left\{ I_1 \Omega_n \tilde{T}^2 + I_2 \frac{\gamma (\Omega_n^2 - \Omega_{n-1}^2)}{2a} + I_3 \frac{\gamma^2 \Omega_n^2}{a^2} \right\} \tag{7.60}
\]

where

\[
I_1 = \int_{-\infty}^{\infty} d\xi [k'(\xi)]^2, \quad I_2 = \tilde{C}'^{(1)}[k'(x_{\text{if}})]^2, \quad I_3 = \int_{-\infty}^{\infty} d\xi [k''(\xi)]^2 \tag{7.61}
\]

For having an equal yield per cycle, one demands

\[
\Pi(t_n) - \Pi(t_{n-1}) = W_{\text{cycle}} = -\frac{\alpha_m^2 ha}{12\pi \gamma} w = -\frac{\alpha_m^2 ha}{12\pi \gamma} \tilde{T}^3 v \tag{7.62}
\]

where \( v > 0 \) and \( w = \tilde{T}^3 v \) are dimensionless. It will turn out that there exists a consistent solution for \( v \) in some definite range. Assuming that \( \Omega(n) = \Omega_n \) is a smooth function of \( n \) one obtains

\[
I_1 \Omega \tilde{T}^2 + I_2 \frac{\gamma}{a} \Omega' + I_3 \Omega^2 a^3 = -w \tag{7.63}
\]

Solving for \( dn/d\Omega \) and going to a new variable \( y = \beta \Omega/(2\pi) \) one gets the total number of cycles

\[
N = \frac{I_2}{\tilde{T}} \int_{\beta \Omega N / 2\pi}^{\beta \Omega / 2\pi} \frac{dy}{v + I_1 y + I_3 y^3} \tag{7.64}
\]

The total yield is then

\[
W_{\text{tot}} = NW_{\text{cycle}} = -\frac{\alpha_m^2 I_2 \gamma h a}{12\pi \tilde{T}^2} \int_{\beta \Omega N / 2\pi}^{\beta \Omega / 2\pi} \frac{dy}{v + I_1 y + I_3 y^3} \tag{7.65}
\]

Here the minus sign indicates that work is performed by the system on the environment. This is possible because Eq. (7.48) expresses that, in order to make the work extraction cycles, one had to start from the equilibrium state and change \( \alpha \) from \( \alpha(-\infty) = 0 \) up to \( \alpha(\tau_1) \). In this first part of the process energy was dispersed at an amount
\[ \Pi(t_1) = +\frac{\alpha_n^2 I_2 \hbar \gamma}{24\pi} \Omega_1^2 \]  

(7.66)

Notice that for \( v \gg (\beta \hbar \Omega_1)^3 \) the extracted work becomes according to (7.65)

\[ W_{\text{tot}} = -\frac{\alpha_n^2 I_2 \hbar \gamma}{24\pi} \frac{1}{\alpha \omega} (\Omega_1^2 - \Omega_2^2) \]  

(7.67)

so for \( \Omega_N \ll \Omega_1 \) there an almost perfect recovery, which is possible since the number of cycles is still large.

For moderate \( v \) more cycles are possible, but less work is recovered. For the lower integration variable Eq. (7.58) gives

\[ y_N \equiv \frac{\beta \hbar \Omega_N}{2\pi} \gg \frac{\gamma T}{2\pi \hbar a} \]  

(7.68)

For strong damping the physical timescale is \( \tau_x = \gamma/a \). One assumes that \( \Omega_1 \) is a large but finite number times \( 1/\tau_x \). Choosing \( T \ll \hbar a/\gamma \) means that the upper integration limit \( y_1 = \beta \hbar \Omega_1/2\pi \) is much larger than unity. But it is still possible to choose \( y_N \ll 1 \), which is a useful condition for achieving many cycles. One then has for small \( v \)

\[ N = \frac{I_2}{4\sqrt{I_1 I_3}} \frac{\hbar a}{\gamma T} \]  

(7.69)

which is indeed large. In the overdamped regime the yield can thus be expressed as

\[ W_{\text{tot}} = -\frac{\alpha_n^2 I_2 \hbar a}{24\sqrt{I_1 I_3}} \frac{\gamma T}{v} \]  

(7.70)

In the limit of weak damping we should notice that

\[ I_2 \equiv \bar{I}_2 \sqrt{\varepsilon} \]  

(7.71)

where \( \varepsilon = a m/\gamma^2 \gg 1 \) and where \( \bar{I}_2 \) is a numerical constant of order unity. Thus the work dispersed for achieving the non-equilibrium condition at \( t_1 \) is

\[ \Pi(t_1) = +\frac{\alpha_n^2 I_2 \hbar \gamma}{24\pi} \]  

(7.72)

where \( \omega_0 = \sqrt{a/m} \) is the free oscillation frequency. Let us recall that \( \tau_d = 2m/\gamma \) is the damping time. For \( T \ll \hbar \Omega_1 \) it holds that

\[ N = \frac{\bar{I}_2}{4\sqrt{I_1 I_3}} \frac{\hbar \omega_0}{v T} \]  

(7.73)

At the typical temperature \( T \lesssim \hbar \omega_0 \) this carries an additional large factor \( \varepsilon \). The yield per cycle carries a factor \( 1/\varepsilon \), so this total yield is independent of \( \varepsilon \). For small \( v \) it reads

\[ W_{\text{tot}} = -\frac{\alpha_n^2 \bar{I}_2^2 \hbar \omega_0}{6\sqrt{I_1 I_3}} \frac{v T^2}{\omega_0} = -\frac{\alpha_n^2 \bar{I}_2^3 \hbar \omega_0}{96(I_1 I_3)^{3/2}} \frac{v \varepsilon^2}{N^2} \]  

(7.74)

which can be comparable to the dispersed work, but it is always less.

Summarizing this section, we have investigated the presence of many work extraction cycles both in the strongly and weakly damped regime. At low \( T \) their maximal number can be large but it is finite. The divergence \( N \sim 1/T \) is probably cut of at low enough \( T \) when the amplitude \( \alpha_0 \) of our changes is small but finite. When more than \( N \) cycles are made, the possibility of work extraction is lost, because of the dispersion inherent to cycles. At moderate \( T \) the possibility of work extraction by cyclic changes is quickly lost; it is a strictly quantum effect.

8. ON EXPERIMENTS TO TEST THE BREAKDOWN OF THE SECOND LAW

In this section we will briefly comment on practical realizations of the low-temperature, non-weakly damped quantum Brownian motion. We do not intend to make detailed proposals for experimental setups, but we will mention certain fields, which according to commonly shared experimental views, display the above-mentioned strong-coupling and/or low-temperature regime.
1. Once more: the characteristic timescales

Let us first recall once more that there are several important time-scales in the problem. \( \tau_0 \) is the characteristic time brought about by the external potential, which the particle will have if there is no interaction with thermal bath. For reasonably simple confining potentials there is only one such a time. In particular, for the harmonic external potential \( V(x) = \frac{1}{2}ax^2 \) it is read \( \tau_0 = 1/\omega_0 = \sqrt{m/a} \). Since no indications of damping are seen in this time, it can have a physical meaning only for very weak damping: \( \gamma \to 0 \).

If damping is large, then the characteristic dynamical times are \( \tau_p = m/\gamma, \tau_x = \gamma/a \). The overdamped regime appears with \( \tau_p \ll \tau_x \), and in this case \( \tau_p \) and \( \tau_x \) can be interpreted as the relaxation times of the momentum and coordinate, respectively.

In contrast, very weak damping means \( \gamma \to 0 \), and the damping time \( \tau_d \sim \tau_p = m/\gamma \) is the longest characteristic time. For intermediate values of \( \gamma \) the characteristic dynamical times in the overdamped regime are \( 1/\omega_{1,2} \) defined in Eq. (3.33), and for the underdamped regime they are given in (3.35).

The issue of this work is to consider the regime where another timescale, the characteristic quantum timescale \( \tau_h = h/T \), plays a dominant role. In particular, this timescale governs quantum correlations of the bath \( \tau_d \). The high-temperature classical case naturally corresponds to \( \tau_h \ll \tau_0, \tau_p, \tau_x \) and there quantum correlation effects can be neglected.

Equilibrium quantum thermodynamics is recovered in the limit \( \tau_h, \tau_0 \ll \tau_p \), which means that the momentary motion of the Brownian particle practically does not notice damping, though it does so at long times. Obviously, this condition cannot be satisfied at low temperatures. In the present paper we are interested in the regime where both damping and quantum correlation effects are important: \( \tau_p \sim \tau_x \sim \tau_h \), including possibilities of \( \tau_p \ll \tau_x \) or \( \tau_p, \tau_x \ll \tau_h \), where our results are only strengthened. As noticed at the end of Section 7, new possibilities for work extraction has been found to occur in this last domain, where the inequality \( \tau_p \ll \tau_x \ll \tau_h \) says that the noise is (anti-)correlated throughout the systems relaxation. It thus looks more like a quenched random variable than an annealed one, thus not at all behaving like a white noise, the standard ingredient needed to derive from a Langevin equation a Gibbsian equilibrium state.

Before proceeding with concrete examples, let us just notice that there is nothing exotic in the quantum time-scale itself: \( \tau_0 = 7.6 \text{ ps at } T = 1 \text{ K}, \) which is fully in range of the modern technologies.

2. Possible experimental realizations

a. Josephson junctions

The first example to be discussed are Josephson junctions \([17,18,53,54]\). This well-known phenomenon represents a standard example of quantum Brownian motion. The Josephson junction consists of two superconductors separated by a thin insulating barrier. Cooper pairs of electrons (or holes) are able to tunnel through this barrier, thereby maintaining phase coherence in the process, and leading to a possibility to have superconducting current. There is a direct map between properties of this junction, and the standard model of the quantum Brownian motion \([17,18,53,54]\). In particular, the coordinate \( x \) can be corresponded to the phase difference of the Cooper pair wave functions, the friction founds its place as resistance, mass is related to capacitance, and the current noise has the standard spectrum \([2,25,5,24]\), and can be related to \( \eta(t) \). Under certain well-defined conditions one can neglect tunneling of the phase from one metastable state to another \([17]\), and consider it in a confining, nearly-harmonic potential. This system couples to the environment, which acts as the bath of our theory. In practice one can notice the occurrence of strong coupling at low \( T \) since then a careful shielding of the sample is needed in order to prevent an influence of the environment to the measuring apparatus. It appears that the non-weakly damped and low-temperature limits are well-known for Josephson junctions, and were a subject of rather long experimental activity \([17,18,54]\). For example, the following regime was explicitly realized as a condition of “really-quantum effects” \([18]\): \( \tau_p \sim 0.1 \text{ ps} \) which is smaller than \( \tau_0 \) at 1 K. The ratio \( \tau_p/\tau_p \) need not be of order one, but can vary significantly (from 0.1 to 10) depending on the construction of the junction; for details see \([18]\). In experiments reported in \([17]\) the authors achieved \( \tau_h/\tau_x \sim 10 \) at \( T = 1 \text{ K} \), and \( \tau_p/\tau_x \sim 0.1 \), which is a typical overdamped, low-temperature case. Notice that these experiments were among the first ones, where the spectrum of the low-temperature quantum noise was measured and found in the perfect agreement with the assumed standard form of the quantum Langevin equations.
3. Low temperature electrical circuits

Experiments on mesoscopic, low-temperature electrical circuits\cite{55,56} provide yet another example, where non-gibbsian values of $T_x$ were clearly observed, and found in a good agreement with the theoretical predictions. We recall that the linear RLC can be mapped to the harmonic brownian particle: the coordinate $x$ and the momentum $p$ of the particle correspond to the charge and the current of the circuit, and $m$ and $a$ are directly connected with the inductance $L$ and the inverse capacitance $1/C$ of the circuit (see also our discussion after Eq. (3.1)). Finally, the damping constant $\gamma$ corresponds to the ohmic resistance $R$. One notices that the (quasi) Ohmic limit, where $\Gamma$ is the largest characteristic frequency of the problem, is conveniently realized in the present context.

First of all we notice that for experiments described in Refs.\cite{55,56} all the relevant characteristic time-scales have basically similar values: $\tau_\hbar \sim \tau_p \sim \tau_x = 10^{-8}$ s, which makes the situation especially relevant for our purposes.

Here we will briefly discuss the possibilities of experimental detection the Clausius inequality violation at low temperatures, since this seems to be the simplest possible issue. Moreover, the most evident situation is realized upon a slow variation of the inductivity (mass) $L$, where for $T \rightarrow 0$ — according to Eq. (4.25) and in the clear contrast with the Clausius inequality $dQ \leq 0$ — one gets a finite positive heat provided that $dL = dL > 0$. One needs to observe $\langle x^2 \rangle$ and $\langle p^2 \rangle$ for several different values of the inductivity (mass) $L$. This is sufficient to recover the corresponding changes of the average energy, as well as to recover the work according to Eq. (4.24). The heat is then obtained by subtracting the work from the energy. In the second step one can check the consistency of the results by observing directly the work done by the external source. Altogether, the challenge of the main experimental observation is in observation of the variances.

In Ref.\cite{57} the authors considered mesoscopic electrical circuits in the context of single charge tunneling. The used circuits had thickness of the order 10 nm and wideness of the order 1 \textmu m. The observations allowed indirect determination of $\langle x^2 \rangle$. With the subsequent improvement made in\cite{58} the correspondence with the theoretical expression (3.41) is perfect. The observations were done with $C = 1/a = 4.5 \text{ F}$, $L = 4.5 \text{ nH}$ and for $R = \gamma$ in the range $10^{-1} - 10^{3}$ k\Omega. For damped circuits the relative importance of damping is quantified by the quality factor $\tau_\gamma/\tau_0$, which in the above range of parameters varies from $10^{-1}$ to $10^{-3}$. To avoid thermal noises the circuits were cooled up to 20 mK. At such a low temperature quantum effects are dominating, since the quantum time-scale $\tau_\hbar = \hbar/T \sim 10^{-8}$ s is larger than the other ones: $\tau_0 \sim 10^{-9} - 10^{-10}$, $\tau_p \sim 10^{-8}$ and $\tau_x \sim 10^{-9}$ s. To get an idea for the magnitude of the expected effect, let us estimate the outcome for $\Delta Q \sim L \frac{dQ}{dL}$. With the above parameters and $R = \gamma = 10^3$ k\Omega one gets from (4.25) $\Delta Q \sim 10^{-15}$ J = 1 eV.

Since for mesoscopic circuits the formula for $T_x$ was already verified, it is now a matter to perform three measurements (the equivalents of $T_p$, $T_x$ and the work production) on a single sample, to verify unambiguously the breakdown of the Clausius inequality.

a. Trapped ions

As another, more elementary example one can mention a trapped ion immersed in a photon bath. Taking as an estimate the mass of proton ($m = 10^{-26}$ kg), and $\gamma = 10^{-15}$ kg s$^{-1}$\cite{12}, one gets $\tau_\gamma \sim \tau_\hbar$ at 1 K, so the quantum coherence effects are still active. The ideal example of a harmonic Brownian particle will be an ion trapped in a so-called Paul trap\cite{44}, or an electron or ion in a Penning trap\cite{45}. These electromagnetic traps are nowadays well realizable and suited for variation of parameters. In particular, high quantum number Rydberg states may have a long lifetime and a strong coupling to the radiation field.

9. ON THE FOUNDATIONS OF THERMODYNAMICS AND PERPETUUM MOBILE

This section intends to summarize to what extent the standard relations and laws of thermodynamics can be applied to a quantum Brownian particle. There are many formulations of the second law, and some of them have been found invalid in previous discussion. One may go to the extreme limit as saying that there is no motivation to discuss a thermodynamics in the way we did. To show that there is justice in doing it, we summarize our results in the light of standard thermodynamic wisdom, and point at the agreements and contradictions.

For a general, pedagogic text on the history and today’s status of thermodynamics and the second law, we refer to the recent work by Uffink\cite{16}. For a collection and discussion of the original papers, see the book by Kestin\cite{17}. A very recent discussion on the base of the axiomatic thermodynamics was presented by Lieb and Yngvason\cite{58}. For a discussion of what can be meant by “the” entropy of a system, see\cite{59}. 

51
1. Has thermodynamics been violated or did it never apply?

The conclusion of our analysis is that thermodynamics does not work when, in the quantum regime, one considers the Brownian particle in its reduced Hilbert space, thus summing out the bath variables of the total system. This implies that the characteristics of the particle are directly observable which is indeed the case with the standard examples of the brownian motion. There are, however, situations, where only some composite (system-plus-bath) quantities are measured, and the need for a separation between particle and bath is questionable (there still can be a possibility that such a separation can be done on a different, more coarse-grained description of the overall system, but we will not enter into that discussion here). This is the case with a Kondo system, where the measured quantity is for instance the magnetization, which is set by the magnetic impurity and the bath together (i.e. it lives in the common space of the particle and the bath). Also for the dressing of a ‘bare’ electron by photons, it is the standard practice of the quantum field theory to consider the dressed mass and charge as directly observables quantities. However, when the system is a Josephson junction or a mesoscopic circuit, its own characteristics are perfectly measurable, so there is an important case to make. When looking at the budget of the junction alone, one has to keep in mind that it can exchange energy with its environment. At low enough temperature this mechanism displays unexpected behavior and is responsible for non-thermodynamic characteristics.

If one accepts to consider the subsystem as a Brownian particle immersed in a heat bath, then first it should be noticed that the particle acquires a cloud of bath modes around it. This dressing is a manifestation of the (strong) damping of the particle by the bath. One can then ask the question: “if thermodynamics does not apply, where was it lost?” If no technical errors have been made in our derivations, then the answer must be: “It never applied”. An argument in favor of this point of view is the fact that the interaction energy is non-vanishing, thus violating a well known condition for the derivation of the standard equilibrium thermodynamics. The interaction energy reads

\[ U_{\text{int}} = U_p - \frac{1}{2} T_p - \frac{1}{2} T_x \quad (9.1) \]

The result is given explicitly by Eqs. (3.45) and (3.48). In a strict formulation of thermodynamics one requires that the equilibrium value of the interaction energy \( U_{\text{int}} \) is negligible, in order to separate what is meant by the system from what is meant by the bath. In our case this would imply \( \gamma \to 0 \) or \( T \to \infty \), and indeed in both limits standard thermodynamics is recovered. However, in general the same system has a non-zero interaction energy and, in the strict formulation, should not be considered to be thermodynamic at finite \( \gamma \) or \( T \). Whereas the limit of large \( T \) can be naturally achieved in practice, the weak-coupling limit \( \gamma \to 0 \) is much more difficult to realize, since coupling constants are generally fixed numbers whose magnitude cannot be manipulated at will. Likewise, all physical systems having a non-vanishing interaction energy with their baths should then not be considered as thermodynamic systems. This would apply to very many systems at low enough temperature, leaving an uncomfortable situation with respect to the well behaved high temperature properties of the same systems. Already at high \( T \) the analysis of the Clausius inequality in section 4.2 gave a compelling argument in favor of our choice for the Hamiltonian of the subsystem, leaving the rest of the total Hamiltonian for the bath.

Let us inspect in some detail the weak damping limit \( \gamma \ll \sqrt{\alpha m} \). Here it can be shown that, even at \( T = 0 \), one has \( U_{\text{int}} \ll U \), since, due to (3.48), \( U_{\text{int}} \sim \gamma \) but \( U \to \frac{1}{2} \hbar \omega_0 \), implying that the condition for \( \gamma \to 0 \) is almost fulfilled. Nevertheless, the Clausius inequality is typically violated, by an amount of, again, order \( \gamma \). This argument somewhat weakens the point of view that thermodynamics should never apply. One can also argue that it is compatible with it, since the violation of thermodynamics is of order of the small interaction energy.

Putting all arguments together, we reach the unavoidable conclusion: there are principle problems to define thermodynamics at not very large temperatures and, in particular, in the regime of quantum entanglement. There is no resolution to this, and thermodynamically unexpected energy flows appear to be possible.

2. Zeroth law

The zeroth law is often said to state that in an equilibrium situation there will be a unique temperature. A standard formulation is that if two bodies are each in equilibrium with a third body, then they are also in equilibrium with each other, and the three bodies have a common temperature. Let us look, however, at a careful formulation out of equilibrium: If two parts of the system have an infinitesimally small temperature difference, then they will spontaneously equilibrate and reach a common temperature.

For the (nearly) harmonic situation two different effective temperatures \( T_p \) and \( T_x \) can be related to the momentum and the coordinate. Recall that these temperatures arise from the generalized form (4.13-4.15) of the Clausius
inequality. The legitimation of such a definition of effective temperatures is confirmed by their successful use in glassy thermodynamics [23,25].

In our case, Eq. (3.54) shows that \( T_p \) deviates at large \( T \) from \( T_x \) by a term \( \beta A \Gamma \), with \( A = \bar{h}^2/12m \). So for any infinitesimal \( \epsilon \), the regime \( T > A \Gamma/\epsilon \) indeed has temperatures \( T_p \) and \( T_x \) that differ less than \( \epsilon \). However, since they are parameters of the steady state, they will not equalize spontaneously, in conflict with the above formulation of the zeroth law. Instead, they become more and more different from each other at lower temperatures, and at zero bath temperature \( T_p \) and \( T_x \) are both finite but different from each other. The fact that they remain finite just indicates that the corresponding quantum state does not have sharp values for \( p \) and \( x \); so this is a consequence of quantum complementarity. The fact that these effective temperatures take non-gibbsian values is a consequence of the quantum entanglement. In the Gibbsian limit of weak coupling (i.e. \( \gamma \to 0 \)) for the harmonic oscillator, both temperatures \( T_p \), \( T_x \) tend to their common value \( \frac{1}{2} \hbar \omega_0 \cotanh(\frac{1}{2} \hbar \beta \omega_0) \) of the harmonic oscillator weakly coupled to its bath.

We should mention that the existence of the zero law is frequently viewed just as an axiom, but under certain conditions it can be derived from the second law (the entropy of a closed system never decreases) [5]. As we mentioned already, this derivation is based on the use of a weak interaction between the particle and its thermal bath. It confirms that if this weak-coupling condition is valid, then the two effective temperatures are indeed approximately equal.

The fact that these unequal effective temperatures do not cause heat currents that equalize them, as would be required by standard thermodynamics, is reminiscent of the classical paradox that atoms should radiate, but, being in the quantum regime, they do not.

3. First law

The first law relates the change of system’s energy into the heat added to it and the work done on it. It can not be broken, since it is a direct consequence of energy conservation, a central concept in quantum mechanics. Nevertheless the formulation of this law is not merely a tautology, because it allows to separate clearly those ingredients of the energy change, which arise from non-observable degrees of freedom (heat obtained by the Brownian particle from the thermal bath) and external sources (work done by them on the whole system). Our identification of the energy of the subsystem as the expectation value of the Hamiltonian \( \mathcal{H} \) was supported in section 4.2 by requiring application of standard thermodynamics at high \( T \), and is imposed by the form of the Wigner function. We stress that, given this identification of energy, our identification of the heat \( \bar{Q} \) added to the subsystem and the work \( \bar{W} \) done on it, are well accepted and widely discussed in literature, see e.g. the books by Keizer [37], Balian [27] and Klimontovich [6].

4. Second law

Let us stress that there are many formulations of the second law. There are several formulations of the second law that are, at least apparently, violated by the solution of our problem.

a. Thomson’s formulation, Kelvin’s principle

The formulation by William Thomson, the later Lord Kelvin of Largs, is: \textit{It is impossible to perform a cyclic process with no other result than that heat is absorbed from a reservoir, and work is performed.} An earlier and more particular version of this statement appeared due to Carnot.

For general quantum systems starting from the equilibrium state, this can be proven mathematically [33]: a simplified proof will be presented elsewhere [57]. In our setups it can always be verified, see for example the fact that the energy dispersion (7.43) is non-negative. After finishing the cycle the bath is not exactly in its Gibbsian state, but it is still very close to it, because the bath is extensive. Basically the dispersed energy has run away to infinity, leaving the system locally again in a Gibbsian state. This implies that also successive cycles will always disperse energy.

However, out of equilibrium Thomson’s formulation appears to be endangered. The first point to notice is that this can already occur at the classical level. The reason is simple. Consider, as we did in section 7.3, a sudden weakening of the central spring. In doing so, energy is extracted from the system, but, due to the sudden nature, it is not the optimal amount. One can improve on this by making the following cycle: quickly put the spring back at its original value, and then make the change slower. This cycle, that started in a non-equilibrium state, will yield work, and this work comes from the bath. We conclude that the Thomson formulation can only refer to system changes on long enough timescales, such that the initial state is practically in equilibrium.

53
A more exciting violation of the non-equilibrium Thomson formulation was observed for smooth changes of the spring constant at low enough temperature. In section 7.4 we discussed the case of \( N \gg 1 \) bell-shaped cycles in the spring constant; each cycle has two inflection points, pre-peak and post-peak. Starting in the Gibbsian state, the first cycle up to the post-peak inflection point is considered as a mechanism that produces for us a proper ‘initial’ non-equilibrium state. If the typical duration of the successive cycles increases, parameters can be chosen such that after each return of the spring constant to its post-peak inflection point value, the system has the same energy, while a prescribed, fixed amount of work is extracted. There can be \( N \sim 1/T \) of these cycles, which can be large at low enough \( T \). They extract heat from the bath and convert it fully into work, forbidden by the general (i.e. non-equilibrium) Thomson formulation. It could be checked that the total amount of extracted work is less than the energy dispersed in the first part of the first cycle, so energy conservation is not endangered. The interesting fact is nevertheless that there can be \( N \sim 1/T \) of these cycles, which can be large at low enough \( T \). Actually, making more cycles implies a smaller total extracted work \( \sim 1/N^2 \), since these cycles themselves lead to additional dispersion.

In contrast to the violation of the Clausius inequality, to be discussed below, the violation of Thomson’s formulation is a consequence of both quantum regime (low temperatures) and the non-equilibrium character of the whole system (particle and bath). Indeed, any amount of work extracted by means of the particle is in fact extracted from the whole system. If this global system is in equilibrium (namely it is exactly described by the Gibbs distribution), there will be no possibility to extract work by making a cyclic change of a system parameter, since this formulation of the second law applies as well to any closed equilibrium system \[33,60\]. On the other hand, the full account of quantum effects is necessary to show our work extraction, since it disappears in the Gibbsian limit, namely both at moderate temperatures and/or for weak coupling to the thermal bath.

\[ b. \text{ Clausius’ Principle} \]

Clausius states: *It is impossible to perform a cyclic process which has no other result than that heat is absorbed from a reservoir with a low temperature and emitted into a reservoir with a higher temperature.*

The gained work could be used to drive some frictional process at a higher temperature, which would turn it into heat, in conflict with this principle. Nevertheless, this principle is obeyed at high temperatures, and only violated in the quantum regime at low \( T \).

\[ c. \text{ Clausius inequality} \]

This formulation claims that in any thermodynamical process (in particular, for variation of a system parameter) the amount of heat received from the thermal bath by the particle is limited from above by the bath temperature times the change of the von Neumann entropy of the particle:

\[ dQ \leq T dS_{vN}. \]

A particular formulation of this law is that no heat can be extracted from a zero-temperature thermal bath, it can only be dumped in it (i.e., then it is impossible to have \( dQ \geq 0 \)). This situation is particularly interesting, since it does not employ in any way the concept of entropy, and therefore can be applied to situations, where entropy is not known, or not well-defined. Physically it is also easy to understand. The energy of the cloud of bath modes around the subsystem will change if a system parameter is changed, even at \( T = 0 \). This change in energy of non-observable modes is heat, and it can be positive or negative, depending on the sign of the change. In one of the cases energy from the cloud will increase the subsystem’s energy, violating the Clausius inequality. For a closed system \( dQ \) goes to zero, and one recovers from the above inequality the more standard formulation \( dS_{vN} \geq 0 \), which appears to be a particular case of the Clausius inequality.

We have shown that both those general (all \( T \)) and particular (\( T = 0 \)) formulations are violated in quantum case. Although at high temperatures these violations are small, they nevertheless do exist. For researchers who are reluctant to follow our identification of the effective temperatures, it will perhaps be hard to agree on the violation of the zeroth law, discussed above. However, the violation of the second law, which also sets in at arbitrarily large temperatures, should be easier to accept, since the Clausius inequality does not employ the notion of effective temperatures. Moreover, in section 4.2 we have discussed a formulation which compares only equilibrium systems.

For our harmonic system we succeeded in generalizing the Clausius inequality, involving two temperatures and two entropies, in the very same way it was done for glassy systems and which applies to black holes.
In hindsight, the derivation of the Clausius inequality is nontrivial in the case under consideration. In standard thermodynamics one formulation of the second law is that the total entropy of a closed system cannot decrease. When applied to a subsystem coupled to its equilibrium bath, this immediately leads to the Clausius inequality. Herein one makes two assumptions: equilibration of the bath and additivity of the entropy. Let us follow the subsequent steps. Because of its equilibrium nature, the heat received by the bath is associated with an entropy change, $dQ_{\text{bath}} = TdS_{\text{bath}}$. Energy conservation says that $dQ_{\text{bath}} + dQ = 0$, where the latter is the heat received by the subsystem. This implies

$$dS - \frac{dQ}{T} = dS + dS_{\text{bath}} = dS_{\text{tot}} \geq 0 \quad (9.2)$$

In the world of quantum entanglement, however, both assumptions are less obvious. First, it does not hold that $S_{\text{tot}} = S + S_B$. We have shown this explicitly, since at $T = 0$ one has $S_{\text{tot}} = S_B = 0$, but $S = S_{vN} > 0$. Both the fact that energy is not quickly redistributed in the bath and the non-additivity of the entropy imply that there is no a priori reason to expect that the Clausius inequality is satisfied. In concordance with that, we have shown that it is indeed not valid.

d. The rate of energy dispersion is non-negative

In section 7.4b we have pointed out that at low enough temperatures the rate of energy dispersion can easily be negative. This holds even when one starts in equilibrium. Thus non-negativity of energy dispersion cannot serve as a universal formulation of the second law.

e. The total entropy of a closed system cannot decrease

The most standard formulation of the second law is that the (coarse grained) entropy of a closed system cannot decrease. In classical physics for a subsystem in contact with a heat bath the equivalent is that the rate of entropy production of the subsystem is nonnegative. For situations close to equilibrium it can often be expressed as a bilinear expression in generalized currents, and the matrix elements are called Onsager coefficients; this matrix is positive definite in all known examples.

The rate of production of Boltzmann entropy was also considered by us. In the case of weak damping there occur oscillations in the production rate around zero in each period; this sets in at moderate temperatures, and is akin to the oscillations in the temperature, that occur already at any non-infinite temperature. In sections 6.2d and 6.2e we have pointed out that even at low temperatures and in the limit of strong damping the rate of Boltzmann entropy production can be negative. So also this criterion does not qualify as a solid definition of the second law.

We should stress that we did not find sensible production rates for other entropies. Perhaps not accidentally, the Boltzmann entropies of the coordinate and momentum sectors are the ones that enter our generalized, two temperature version of the Clausius inequality.

In our setup the von Neumann entropy for the full closed system (fine grained entropy) should not be confused with the von Neumann or Boltzmann entropies of the subsystem, which pertain to the Brownian particle only. The von Neumann entropy of the full system is not altered by changing the strength of the spring constant. This entropy remains constant during the overall unitary evolution of the whole system, and also remains constant during variations of a parameter, since also there the overall evolution is still unitary. The formulation of the second law in terms of non-decrease of entropy definitely refers to the coarse grained entropy. In the classical situation the fine-grained entropy is conserved as well, by the Liouville dynamics. For more definitions of entropy, see [59].

In passing we notice that if one starts from a Gibbsian state of the total system (central particle coupled to the bath), and changes a system parameter, then the conservation of entropy prevents the system to relax to a new Gibbsian state of the total system, since our total system is isolated. Nevertheless, the subsystem (the central particle) does relax to a state characterized by the parameters, which can be coded in the effective temperatures, of that would-be global Gibbsian state. It is the finite amount of energy dumped in the extensive bath that does not relax, since our bath lacks anharmonic interactions, or coupling to an external superbath. In contrast to a superbath, anharmonic interactions do not change the essence of the argument on the overall unitary evolution, conservation of both the von Neumann entropy and the energy. However, they can widen the set of observables having would-be Gibbsian values.
5. Third law

This law claims that if the ground state of the Brownian particle is non-degenerate, then its von Neumann entropy is equal to zero. This is a direct consequence of the quantum Gibbs distribution, which predicts the pure vacuum state at low temperatures. In our case neither the von Neumann entropy nor the Boltzmann entropy vanishes when the bath temperature is zero. This occurs because of the quantum Brownian particle is in an entangled mixed state, and therefore cannot have vanishing von Neumann entropy.

The third law is recovered when taking the weak-coupling limit. In that case $T_p = T_x = \frac{1}{2} \bar{\hbar} \omega_0 \cotanh(\frac{1}{2} \beta \bar{\hbar} \omega_0)$, implying that the parameter $v$ of Eq. (4.34) takes the value $v = \frac{1}{2} \cotanh \frac{1}{2} \beta \bar{\hbar} \omega_0$, which causes the von Neumann entropy of the particle (4.35) to vanish at $T = 0$. In a certain sense the violation of the third law reported here for non-weak coupling is the most straightforward consequence of quantum entanglement.

6. Perpetuum mobile of the first kind

Taken literally, a perpetuum mobile performs perpetual, i.e., everlasting, motion. Nevertheless, rotational currents in ordinary superconductors, which may exist several days, are rarely connected to perpetual motion. We shall therefore employ the word “perpetuum mobile” for any principle that yields work.

One speaks of a perpetuum mobile of the first kind when the first law is violated, leading to an everlasting performance of work without any cost. Such a setup is impossible in quantum mechanics, since it satisfies the first law by principle. So here is no issue in the question what “perpetuum” means precisely.

7. Perpetuum mobile of the second kind

Another formulation of the second law is: It is impossible to construct an engine which will work in a complete cycle, and convert all heat it absorbs from a reservoir, into mechanical work [61]. A machine which would do so is called a perpetuum mobile of the second kind, and the second law states that such a machine is impossible.

a. “Perpetuum” mobile or perpetuum mobile?

When the first law is respected but the second is violated, one speaks of a “perpetuum mobile of the second kind”. However, we wish to make some remarks on the word ‘perpetuum’. Surely, in the eighteenth century such a perpetuum mobile was imagined, for instance, to cross the Atlantic by boat using only the energy stored in the ocean water. As such, there would be a basically infinite bath, and the mobile, if realized, could function perpetual, i.e. “for ever”. In general, when the bath is finite, it obviously has a finite energy at its disposal. In many setups, such as those with a finite rate of energy extraction, this implies also finite duration of the process. Thus even in the classical situation, the term “perpetuum” need not be a precise adjective for this type of mobile, and the point of view could be taken that a perpetuum mobile of the second kind need not function arbitrarily long, but must only work many cycles. In view of the failure to find so far any practical realization, this stretch of the definition seems allowable to us.

In quantum physics the situation is even more clear. In a closed system the energy can never go below the ground state energy, so the amount of extracted work is always finite. As a result, there can never be an infinite amount of cycles for which a definite amount of work is extracted per cycle. One of the formulations of the second law is: “Perpetuum mobile of the second kind do not exist”. Such a strong physical statement must, of course, be richer than the general statement on the existence of a ground state. The crux is that already one of such cycles, that extracts work from a thermal bath, is forbidden. So, already in general, perpetual motion of the second kind does not have its literal meaning of everlasting motion; rather, it is a notion for a work extraction principle, and one cycle is therefore good enough for the birth of a ‘baby perpetuum mobile’.

b. The present situation

For our aim the allowance of non-eternal duration of perpetuum mobile is relevant, since our effects only hold as long as both the particle does not relax, which happens on the timescale $\tau_x$, and are quantum coherent, which involves the quantum timescale $\hbar/T$. 

56
We have discussed a work extraction mechanism that cyclicly changes the spring constant in a certain time interval. Each of these cycles is slower than the relaxation time of the system. When the quantum timescale $\tau_Q = \hbar / T$ is also slower than the relaxation time, there occurs unexpected behavior: the contribution to the rate of dispersion inversely proportional to the duration of the cycle, normally the leading term, has a small prefactor quadratic in temperature. Therefore quadratic and cubic terms in the inverse duration also play a role. Out of equilibrium cycles have been designed where a constant amount of heat is extracted from the bath is fully converted into work, while the energy of the subsystem is at the end of each cycle back at the value of the beginning. In this sense, systems described by our models, with parameters in the appropriate regime, present at low temperatures true realizations of perpetuum mobile of the second kind. Probably, it is also possible to extract work both from the bath and from the subsystem (“efficiency larger than 100%”).

In a more stringent definition of perpetuum mobile one requires that in the cycles work is extracted “without any further change”. For our system this can be expressed as the requirement that the Wigner function of the subsystem be back at its original value. This would imply the requirements that $\Delta K = 0$, $\Delta V = 0$ and $\Delta \dot{V} = 0$ over each cycle, rather than only having $\Delta K + \Delta V = 0$, where $K$ is the expectation of the kinetic energy and $V$ of the potential energy. The question whether this extended constraint can satisfied by changing the spring constant and possibly also the mass, is left for the future.

We should stress the conceptual difference between the present situation and the well-known case, where work can be extracted due to a temperature difference between two thermal baths [5]. The latter is the standard setup for the thermodynamic heat engine: two baths are explicitly separated from each other, and therefore the whole system is in a nonequilibrium state, and can be used to perform work. If those baths are kept in a direct contact for a sufficiently long time, then they will go to equilibrium and after that no work can be extracted any more [48]. In contrast, here we are have presented a case with one single thermal bath. After a sudden increase of the strength of the central spring, the central particle will go to equilibrium after one relaxation time $\tau_x$ or $\tau_d$. But in doing so, more than the initial surplus energy is transfered to the bath, and in particular to the cloud of bath modes in its immediate surrounding. After a certain moment, this heat flow towards the bath stops, and then a smaller backflow occurs from the bath to the particle, before the whole comes into equilibrium. This backflow of heat is the mechanism that makes it possible to extract work from the bath by manipulating the particle, in a situation where this would be impossible classically. In particular, for smooth changes at zero temperatures the integral of this relaxation function is needed, but it appears to vanish, leading to a variety of new effects at low temperatures.

On a thermodynamic level, the analogy with the classical case was strengthened because we could identify effective temperatures, though we also stressed that by themselves they do not tend to become equal to each other. All these intriguing aspects arise due to quantum effects, since we showed in detail that the same system coupled to the same bath displays at high temperatures the fully expected thermodynamical behavior.

8. Perpetuum mobile of the third kind

One can define a perpetuum mobile of the third kind when work is performed at the cost of a diminishing, but still non-vanishing zero-temperature entropy. This can, in principle occur in systems, such as glasses, which are able to relax to equilibrium, but are temporarily stuck in certain metastable states. Then the zero-temperature entropy can be used as a measure of this metastability [49].

One could wonder whether our extraction of work is due to the present non-vanishing zero-point entropy. However, this is not the case, since for the purely Gibbsian case of particle and bath, the particle would have the same zero point entropy, but no work could be extracted. Moreover, in our case the zero point entropy is an indication of quantum entanglement and not of metastability.

10. CONCLUSION

This paper is devoted to the statistical thermodynamics of the quantum Brownian motion. The high-temperature case of this model can serve as a convenient pedagogic example, where almost all main statements of statistical thermodynamics are derived exclusively from the first principles. Among other advantages, such an approach makes possible to reveal the conceptual restrictions and limitations of the standard thermodynamical wisdom. With this aim in mind we focussed in the paper on the low-temperature (quantum) situation of the Brownian motion model.

The stationary state of a quantum Brownian particle non-weakly interacting with its thermal bath is non-Gibbsian. It is this property which makes the quantum Brownian motion a challenging problem, and classical thermodynamical
Wisdom appears to be inadequate even if the total state of the system and the bath is Gibbsian. Both the classical and the quantum Gibbsian thermodynamic theories emerge as particular limits in this more general setup. The classical Gibbs distribution with all its thermodynamic consequences is recovered for high temperatures, and the quantum Gibbs distribution is obtained for very weak damping.

In section 2 we start from the quantum Langevin equation. At low temperatures this equation contains a colored Gaussian noise; because of quantum coherence, the bath cannot generate white noise even in the limit where the friction has no memory. To achieve this interesting situation, no more is needed than the observation that quantum mechanics applies (see detailed explanations after Eq. (5.26)). Moreover, the quantum fluctuation-dissipation theorem predicts different time-scales of noise and dissipation at low enough temperatures. This is how quantum coherence enters into the considerations. Its characteristic timescale is $\hbar/\tilde{t}$, where we had set the Boltzmann constant $k_B$ equal to unity so far. Restoring it, we have $t_B = \hbar/(k_B T) = (6.23/T) K ps$. At $T = 1 K$ one has $t_B = 6.23 ps$, in the range of typical microscopic processes in condensed matter.

Since the stationary distribution is non-Gibbsian there are conceptual differences compared with the equilibrium case. For the harmonic potential one can define effective temperatures [4.1] for momentum and coordinate. Both temperatures are different from the bath temperature $T$. Generalized thermodynamic relations can be introduced, which take a quasi-Gibbsian form, Eq. (4.21-4.22), and are closely related to the ones in the thermodynamics of glasses [24-25].

The inapplicability of standard thermodynamics is most clearly illustrated by the violation of the Clausius relation: $dQ \leq T dS$: heat received by the particle from the bath is restricted by temperature of the bath times the change of the particle’s entropy. In section 1.3 we construct an explicit example which at low temperatures realizes $dQ > 0$. This violation is significant at low temperatures, where quantum effects are relevant, and is small for high temperatures. It is important to notice that this violation exists already for the totally equilibrium (Gibbsian) state of the overall (particle plus bath) system (see our discussion after Eq. (4.27)). Since Thomson's formulation of the second law is valid for such a state [33], we have the explicit counterexample showing that the very equivalence between different formulations of the second law is broken at low temperatures.

For the dynamical consideration we start from a non-equilibrium initial state obtained from the total Gibbsian by changing the width of the confining potential. This change involves a small, controllable energy input, and can be more realistic than the hitherto studied case where particle and bath are initially uncorrelated. After the non-equilibrium state has been prepared, the ensuing relaxation of the particle presents a number of thermodynamical anomalies at low temperatures of the bath. First, energy put into the bath does not completely dissipates there (in contrast to the classical situation), and thus work-extraction from a single thermal bath is possible. This violates the second law in Thomson’s formulation as applied to non-equilibrium. As a consequence of this, adiabatic changes of parameters are not the most optimal ones anymore. It is interesting to notice that at low temperatures a large (but finite) number of work-extracting cycles is possible. According to our opinion, this explicitly realizes the basic non-trivial content of the perpetuum mobile of the second kind, because any possibility for infinite number of such cycles is ruled out merely by the existence of the ground state for the overall system.

The second aspect of the low-temperature relaxation is that no H-theorem exists at low temperatures, i.e. the properly defined entropy production appears to be negative for some times. This holds even in the moderately overdamped regime, when the brownian particle relaxes monotonously. (Recall that without any bath those frequencies are purely imaginary which leads to the known oscillatory behavior.) Within the underdamped (weakly-coupled) situation negative entropy production persists up to high temperatures, and disappears only in the explicitly classical limit.

Let us recall that Thomson’s formulation of the second law in its most general and universally applicable form [3]: In cyclic processes no work can be extracted from a closed equilibrium system, remains satisfied. This statement was derived in Ref. [33], and we will present a very simply proof elsewhere [41]. It obviously applies to the analysis of this paper, since we start from a Gibbsian with modified spring constant, and the work extraction disappear when the change in the spring constant vanishes. Also for cyclic smooth changes that start from equilibrium we could verify the non-negativity of the energy dispersion.

We now make some remarks concerning the definition of the thermal bath in our problem. The harmonic oscillator bath model, which was used by us, is technically convenient, but at the same time it possesses all relevant properties of a thermal bath, which are typically postulated in the statistical thermodynamics. The main of them is that the bath should have infinite amount of degrees of freedom, a necessary condition to ensure relaxation of the Brownian particle. On the other hand, the quantum Langevin equation, which is the starting point of our analysis, can be derived from rather different schemes (see e.g. [41]), since in a sense they are more universal than the detailed properties of the considered thermal bath.

Finally, let us relax the conditions under which our results have been derived. We have already mentioned that they
hold as well for $N \gg 1$ Brownian particles in an external potential. Though mutual interactions would complicate the analysis, it would not modify our basic statements. This can already be seen from the case of non-interacting harmonically bound Brownian particles: under a change of variables they become interacting ones, while the characteristics of the bath remains basically unaffected because it has very many degrees of freedom.

Our findings on the non-thermodynamical character of the low-temperature brownian motion may have a wide scope of applications such as cooling, energy storage, and thermodynamical limits of low-temperature computing. Indeed, in the domain of information theory there is a large literature based on the fact that only the erasure of information must necessarily involve a dissipation of heat (see extensive reviews in [32]), and the claim that the erasure of one bit of information costs at least an amount of energy $k_B T \ln 2$, the so-called Landauer bound. It is well known that this bound is based on a straightforward application of the Clausius inequality. From our observations it is clear that the Landauer bound can also be broken, and strong effects may occur at low temperatures. This may have implications for computing in the quantum regime [41].

For spins coupled to a bath the quantum nature expresses itself in off-diagonal elements of the density matrix. These decay after the time $T_2$, which can range up to seconds. In this regime related work extraction setups are possible.

Our results can be phrased in the statement that Maxwell’s demon exists: it is the property of quantum entanglement in quantum mechanics [51]. They may further have implications for thermodynamics in high-energy physics and the early Universe.

The aim of the paper has been to show that violations of the second law have a natural place in the physics of quantum particles that are non-weakly coupled to quantum baths. In this domain we have given conditions for the realization of the most notorious objects in the history of physics: perpetuum mobile of the second kind.

**ACKNOWLEDGMENTS**

We thank R. Balian, H. van Beijeren, H. Knops, R. Lipowsky, C. Pombo, H. Spohn, L. Suttorp and M. Wagner for discussion and R. Lipowsky also for hospitality at the Max Planck Institute for Colloids and Interfaces in Golm, where a part of this work was done. We stress that the responsibility for the presented results and interpretations lies with the authors alone. The research of A.E. A. was supported by FOM (The Netherlands) and by NATO.

**APPENDIX A: SMOOTH CHANGES OF THE SPRING CONSTANT**

In this appendix we derive the work for continuous changes of the spring constant. Hereto we first notice that perturbative expression (5.55), (5.57) of the exact result (5.54) can be derived directly by perturbation theory. Let us first denote $a$ by $a_1$ and expand also $\phi$ to first order in $a_1 - a_0$. We may use

$$
\sin \phi e^{i\phi_0 - i\phi} = \sin \phi_0 + (a_1 - a_0) e^{-i\phi_0} \frac{d\phi}{d\phi} = \sin \phi_0 - (a_1 - a_0) \sin^2 \phi_0 e^{-i\phi_0} \frac{\Gamma^2 + \nu^2}{\gamma^2 \nu^2}
$$

(A.1)

Now inserting (5.52) and taking the large $\Gamma$ limit of $\hat{f}(i\nu)$ from (5.44), we get from Eq. (5.57)

$$
\beta(\nu) = \sin \phi_0(\nu) e^{i\nu t} \left[ 1 + \frac{a_0 - a_1}{\gamma \nu} \left( 1 - e^{-\omega_1 t - i\nu t} \frac{1 - e^{-\omega_2 t - i\nu t}}{\omega_1 + i\nu} \right) \right]
$$

(A.2)

Now let us remember that for $t < 0$ the spring constant was $a_0$, while for $t > 0$ it is $a_1$. Thus one could write in (5.36): $a \to a(t) = a_0 + (a_1 - a_0) \theta(t)$. By treating the term $(a_0 - a_1) \theta(t) x(t)$ together with $\eta(t)$, one can read off the formal solution from the analog of Eq. (5.44), and solve it perturbatively to first order in $(a_1 - a_0)$. It can be verified that the result coincides with (A.3).

This first order perturbation theory can immediately be generalized for many steps,

$$
a(t) = a_k = (1 - a_k)a, \quad (t_k < t < t_{k+1})
$$

(A.3)

where $t_0 = -\infty$ and $t_1$ was taken equal to zero so far, but can be arbitrary. One writes $a(t) = a_0 + \sum_{k \geq 1} (a_k - a_{k-1}) \theta(t - t_k)$ and gets
At a given instant of time the sum has a finite number of terms because of the $\theta$ functions.

In Eq. (A.4) we considered that effect of many small changes in the spring constant. When we make many changes with small $\alpha(t) = \alpha_k$ in the domain $t_k < t < t_{k+1}$, we get

$$\langle x^2 \rangle = \frac{T_x(a)}{a} + \frac{h}{\pi \gamma} \left[ \alpha_k C_x(0) - \sum_{j=1}^{k} (\alpha_j - \alpha_{j-1}) C_x \left( \frac{\gamma(t - t_j)}{2m} \right) \right]$$

where $t_1 = t_k$ is the moment of the first change, taken equal to zero so far. Let us write $\alpha_k = \alpha(\tau_k)$ assume and that the changes are small. Then the sum can be replaced by an integral,

$$2V(t) = a \langle x^2(t) \rangle = T_x(a) + \frac{h}{\pi \gamma} \left[ \alpha(t) C_x(0) - \int_0^\infty d\tau \, \alpha'(\frac{\gamma t}{2m} - \tau) C_x(\tau) \right]$$

where the upper integration border could be put equal to $\infty$, since $\alpha'$ vanishes for times less than $t_i$.

The work needed to make the change $a_{k-1} \rightarrow a_k$ at time $t_k$ is equal to $(a_k - a_{k-1})\langle x^2(t_k) \rangle$, so it equals

$$dW_k = (\alpha_{k-1} - \alpha_k) \left\{ \frac{1}{2} T_x(a) + \frac{h}{2\pi \gamma} \left[ \alpha_k C_x(0) - \sum_{j=1}^{k} (\alpha_j - \alpha_{j-1}) C_x \left( \frac{\gamma(t_k - t_j)}{2m} \right) \right] \right\}$$

If there are many steps with small increments, we can go to a continuum limit. Replacing the sum by an integral, we obtain the rate of work added to the system

$$\frac{dW}{dt} = \frac{dW_{\text{rev}}}{dt} + \frac{d\Pi}{dt}$$

where

$$\frac{dW_{\text{rev}}}{dt} = -\frac{\gamma}{2m} \frac{d\alpha(\tau)}{d\tau} \left[ \frac{1}{2} T_x + \frac{h}{2\pi \gamma} \alpha(\tau) C_x(0) \right]$$

is the adiabatic (recoverable) rate of work and

$$\frac{d\Pi}{dt} = \frac{h}{4\pi m} \frac{d\alpha(\tau)}{d\tau} \int_0^\infty d\tau \, \alpha'(\frac{\gamma t}{2m} - \tau) C_x(\tau)$$

is the rate of energy dispersion.

**APPENDIX B: MODERATE CUTOFF FREQUENCY AND FINITE CHANGE OF SPRING CONSTANT**

In this section we address the vanishing of work dispersion at $T = 0$, without making the approximation of large Debye frequency $\Gamma$. Then the full equation (5.56) has to be employed, rather than the approximation (5.57). With help of an algebraic manipulation program we have checked that at $T = 0$ the important findings $C_x^{(0)} = 0$, see Eq. (B.47), and $C_p^{(0)} = C_E^{(0)} = 0$ (c.f. Eq. (5.53)) remain valid then. So a negative rate of energy dispersion occurs also for a finite cutoff.

Let us mention, however, that the effect is weakened when $\alpha_0$, the amplitude of the change of the spring constant, is not very small. This probably affects the maximal number of work extraction cycles.

If one changes the mass and not the spring constant, the system does not exhibit this interesting behavior, since the analog is $C_x^{(0)}$ does not vanish then, implying that the leading term in the energy dispersion does not vanish at low $T$. 

60
Notice that in the present paper we completely neglected situations, where the bath is an open system itself. Then it can happen that the times $\tau_n$, with $n=1,2,\ldots$, differ significantly even for $T\to 0$. The simplest realization is to couple each bath oscillator to a 'superbath', consisting again of harmonic oscillators. This approach was worked out for a model used for the quantum measurement process, see [52].
A celebrated example to verify the non-additivity of the entropy is the case of two spin $\frac{1}{2}$ particles, in the pure $s = 0$ state, $|\psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle)$. The density matrix reads

$$
\rho = \frac{1}{2} |\uparrow\uparrow\rangle\langle\uparrow\uparrow| - \frac{1}{2} |\uparrow\downarrow\rangle\langle\downarrow\uparrow| - \frac{1}{2} |\downarrow\uparrow\rangle\langle\uparrow\downarrow| + \frac{1}{2} |\downarrow\downarrow\rangle\langle\downarrow\downarrow|
$$

When summing out spin 2 one has

$$
\rho^{(1)} = \text{tr}_2 \rho = \frac{1}{2} |\uparrow\cdot\rangle\langle\uparrow\cdot| + \frac{1}{2} |\downarrow\cdot\rangle\langle\downarrow\cdot|
$$

The entropy of that state is $S_1 = -\text{tr}(\rho^{(1)} \ln \rho^{(1)}) = \ln 2$. Likewise, it is seen that $S_2 = \ln 2$, so $S_1 + S_2 = 2\ln 2$. But $S = -\text{tr} \rho \ln \rho = 0$, since $\rho = \text{diag}(1, 0, 0, 0)$ in the basis of the total spin $(s = m = 0)$, $(s = 1; m = 0, \pm 1)$. This non-additivity remains when both systems become large.