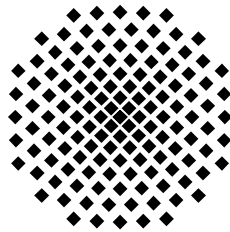


Model Studies Concerning Quantum Fluctuation Theorems

Diplomarbeit von
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Stuttgart, 26.10.2006

Jens Teifel

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Contents

1. Introduction

Theoretical distributions of work
delivered to small objects have
some surprising properties
recently confirmed by
experiment

(S. K. Blau in [1])

Two different fields of physics play an important role for this thesis. On the one hand, thermodynamics and - on the microscopic level - statistical physics and on the other hand quantum mechanics.

In the last decades of the 17th century, thermodynamics was introduced in order to describe several experimental observations, such as pressure, heat flux, temperatures and the behaviour of gases. It is a very successful, phenomenological theory and by using it, one was capable to describe a big variety of different physical situations.

Quite an effort was made in order to deduce the theory of thermodynamics from classical mechanics. The break through was finally achieved by L. BOLTZMANN [2] by introducing the H-theorem. It was now possible to describe the irreversible behaviour of thermodynamical systems with classical mechanics, which equations are symmetric in time and thus reversible. Nevertheless, there still remained some problems with the interpretation and several postulates are still necessary in order to justify the used description.

A new approach, based on quantum mechanics solely, was made at the *Universität Stuttgart* recently [3], [4]. It was shown, that the SCHRÖDINGER equation for composed quantum systems delivers an irreversible time evolution of the subsystems if at least one of them is big enough.

Most equations and statements of thermodynamics relate to systems in thermal equilibrium. So, e.g., only for processes which are quasistatic and reversible, an exact relation between the work performed on a system and the free energy difference between the initial and final state, respectively, is known.

A problem arises if one wants to measure the free energy difference between two states of a system, when there exists no quasistatic process which could transform the initial state into the final one. (A real process is never exactly quasistatic, since it would require an infinite amount of time to be carried out). This is the case in bio-physics, for instance. Here, e.g., one wants to know the free energy difference between the folded and unfolded state of an RNA molecule. The process cannot be performed quasistatically because the folding or unfolding, respectively, happens abruptly. Facing that problem, C. JARZYNSKI introduced a work-dissipation-fluctuation theorem, which connects the exponential of the free energy change to the average amount of the exponential of work

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required for this process to be carried out [5]. By using this relation, it is possible to extract the free energy change during a process by repeated measurements of work performed on the system during an arbitrary process.

The theorem of JARZYNSKI was shown to hold for classical hamiltonian dynamics. Since experimentalists investigate smaller and smaller systems with rising accuracy, the question is, whether these fluctuation theorems still hold in the quantum regime and if not, when they break down. For closed systems without environment, S. MUKAMEL proved that the relation still holds for quantum systems [6].

After starting the thesis with a short review on the basics of thermodynamics, statistical physics, quantum mechanics and classical fluctuation theorems in chapter 2, two model systems will be introduced in chapter 3 which will be used to test the JARZYNSKI relation for systems without environment (chapter 4). All calculations make use of the time-dependent SCHRÖDINGER equation with no further assumptions or approximations if not noted explicitly otherwise. These results yield a good reference test for later studies on systems with environments.

In chapter 5, an analytical proof will be given, that the relation also holds for systems, to which an environment is coupled microcanonically, meaning that no energy transfer between system and environment is allowed. This result is verified by numerical calculations for a modified model system from above.

Chapter 6 describes an attempt to generalize the results from chapter 5 to a canonical coupling scenario. A proof is given, that the relation still holds for very weak coupling between system and environment. It would be interesting to investigate, whether there exist further boundary conditions for which it is possible to show that the JARZYNSKI relation still holds in the quantum regime.

2. Theoretical Background

2.1. Overview

In the following, a short introduction to the theoretical basics which are most often used in this thesis is given. The basics concerning thermodynamics and quantum dynamics can be found in any standard textbook [7], [8], [9], [10], [11]. The sections about fluctuation theorems and the *quantum Jarzynski relation* [6] are rather specific. Throughout the whole thesis we will use adapted units, such that the following relations hold:

$$\hbar \equiv 1, k_B \equiv 1 \quad (2.1)$$

with \hbar being PLANCK's constant divided by 2π and k_B being the BOLTZMANN constant.

2.2. Thermodynamics and Statistical Physics

2.2.1. General Remarks

Almost all equations and state variables used in thermodynamics are only valid for large systems: $N \rightarrow \infty$. This is referred to as the thermodynamic limit [8] with N being the number of particles contained in the system, for instance. Furthermore most statements of thermodynamics relate to systems in equilibrium which means, they can be described by a GIBBSIAN distribution function [9]:

$$\varrho(p, q) = \frac{e^{-\beta E(p, q)}}{Z} \quad (2.2)$$

with $\varrho(p, q)$ being the probability of finding the system at the point (p, q) in phase space, $E(p, q)$ the energy of the system as a function of its coordinates and momenta, β the reciprocal temperature $\frac{1}{T}$ and the partition function Z :

$$Z \equiv \int e^{-\beta E(p, q)} dpdq \quad (2.3)$$

which ensures the normalization of the probability.

2.2.2. State Variables

We will only discuss such variables which will be used later on in this thesis.

2. Theoretical Background

1. *Internal Energy*: The average energy of a system without any center of mass motion. Important are only changes of the internal energy, since we can set the reference point of zero energy arbitrarily. For a canonical ensemble we have:

$$U \equiv \sum_i \frac{E_i e^{-\beta E_i}}{Z} \quad (2.4)$$

where we have used the GIBBSIAN ensemble (see equation 2.2) and the definition of the partition function (see equation 2.3) for discrete energy levels.

2. *Entropy*: $S \equiv -\overline{\ln w(E_n)}$. The entropy S is the negative average of the natural logarithm of the distribution function of the considered subsystem. One should keep in mind, that this definition allows only an interpretation of the entropy if the subsystem is in thermal equilibrium and can be described by a distribution function. This means, that it has a statistical meaning only in a macroscopic system.
3. *Free Energy*: The maximum amount of work a system could perform in a quasi-static adiabatic process. It can be defined in terms of the partition function:

$$F \equiv -T \log Z \quad (2.5)$$

4. *Temperature*: Temperature can be viewed as a parameter of the distribution function. As such it is only defined in an equilibrium ensemble. Two systems, which are in thermal equilibrium, have the same temperature: $T_1 = T_2$. Alternatively, it is possible to define temperature via the reciprocal change of entropy due to a change of the energy of a system: $\frac{\partial S}{\partial E} = \frac{1}{T}$. In this sense temperature has only a meaning as a statistical variable.

2.2.3. Important Equations

The first two fundamental theorems of thermodynamics and the Liouville theorem [12] will be reviewed shortly. The concept of work on a thermodynamic system will be introduced.

2.2.4. The 1st Fundamental Theorem

The first law of thermodynamics can be formulated as follows:

$$dU = \delta A + \delta Q \quad (2.6)$$

This means, that the change of internal energy equals the sum of δA and δQ which denote the work and the heat exchanged with an environment respectively. For a reversible state change, this law can be written as (c. f. 2.2.5)

$$dU = TdS - pdV \quad (2.7)$$

2.2.5. The 2nd Fundamental Theorem

The second law of thermodynamics states, that all irreversible processes in a closed system enlarge the entropy until it reaches its maximum in the equilibrium state. In mathematical notation:

$$dS = 0, S = S_{\max} \quad (2.8)$$

For systems in equilibrium and for irreversible processes we have $dS > 0$. It follows that

$$\delta Q_{\text{irr}} < \delta Q_{\text{rev}} = TdS \quad (2.9)$$

This means, that the heat exchange during an irreversible process is always greater than during a reversible one.

2.2.6. The Liouville Theorem

The LIOUVILLE Theorem states, that the phase space density along a trajectory in phase space is conserved:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \quad (2.10)$$

where the angular brackets are the so-called *Poisson brackets* [13], which can be interpreted as the classical analogue to the commutator in quantum mechanics. If the phase space density is not explicitly time-dependent, equation (2.10) reduces to

$$\{\rho, H\} = 0 \quad (2.11)$$

This means that ρ is a constant of motion.

2.2.7. Work on a Thermodynamic System

If one switches some external parameters of the system, work will be performed on this system in general. If one does this infinitely slowly, the system will always be in thermal equilibrium with the environment and the work W will equal the change of the free energy F :

$$W = \Delta F \quad (2.12)$$

If the process is carried out in finite time, the work will on average exceed the free energy difference (as a consequence of equation (2.9)):

$$\overline{W} \geq \Delta F \quad (2.13)$$

The difference ΔF still refers to the equilibrium free energy difference. We associate the difference between the work necessary to perform this process in finite time and the work for infinitely slow switching of the parameters, as the dissipated work:

$$W_{\text{diss}} = \overline{W} - \Delta F \quad (2.14)$$

2.3. Fluctuations

2.3.1. Overview

In a perfect thermodynamic system, which contains an infinite number of particles, there are no fluctuations and thus all thermodynamic variables have exact values. Since in reality such a perfect system cannot exist, we have to deal with the fact, that all thermodynamic variables represent average values. If one measures such a variable, the outcome can differ from that expected value. A repeated series of measurements on the very same system with the same boundary conditions can yield different results. This is commonly meant if one speaks of fluctuations.

2.3.2. General Remarks

The probability density to find a system at a specific energy E is given via:

$$\rho_{\text{canonical}}(E) = \frac{g(E)}{Z} e^{-\beta E} \quad (2.15)$$

where we have multiplied the GIBBSIAN distribution function (see (2.2)) with the density of states $g(E)$. The most probable energy to be measured is given by:

$$\frac{\partial \rho_{\text{canonical}}(E)}{\partial E} \stackrel{!}{=} 0 \Rightarrow \frac{1}{g(E)} \frac{\partial g}{\partial E} \Big|_{E=E^*} = \frac{1}{\beta} \quad (2.16)$$

This energy equals the average energy of the system. The probability function of a deviation of that energy for small fluctuations is given by (this result can be obtained by an expansion of equation (2.15)) [7]

$$\rho_c(E) \approx \frac{1}{Z} e^{-\beta E^* - TS} e^{-\sigma(E-E^*)^2} \quad (2.17)$$

with $\sigma \equiv -\frac{\partial^2 S}{\partial E^2} \Big|_{E=E^*}$ being a positive constant (S is maximal in an equilibrium ensemble). This is a GAUSSIAN function. For large deviations it is nearly zero due to the last factor in equation (2.17).

2.3.3. Example

As an example (see [14]) we consider a simple model system (see figure 2.1). It consists of a closed box containing N atoms or molecules and it is in contact with a large heat bath at temperature T . We want to look at different thermodynamical variables and probable measurement outcomes:

1. Number of particles N : This is constant since we exclude any particle annihilations, creations or conversions and the container is supposed to be closed.

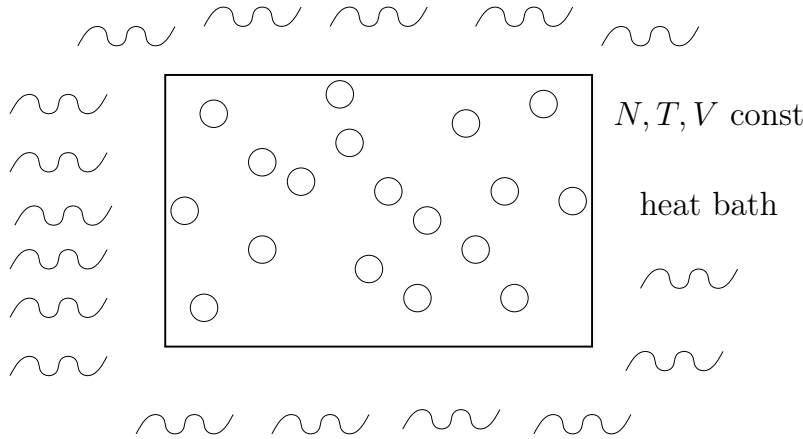


Figure 2.1.: Model system for better illustration of the concept of variation. A closed box of volume V containing N particles in contact with a heat bath at temperature T is shown.

2. *Temperature*: Since the container is supposed to be in thermal equilibrium with the heat bath, it should be constant. It is merely a parameter in the GIBBSIAN distribution function. A different point of view would be to consider the system at different times, where one would measure different energies due to energy fluctuations and therefore one would get another distribution function with another parameter as temperature.
3. *Pressure*: If there are few particles in the container and one would try to measure the pressure via the average momentum exchange of the atoms with the container wall on a short time scale, one would get different results for different measurements for the pressure, depending on the actual number and momenta of particles that hit the wall in the measurement time Δt . This is meant by fluctuation of pressure. If there were an infinite number of particles inside the container or if we would measure infinitely long, the average pressure would be exact.
4. *Work Fluctuations*: In the following, the concept of fluctuations of work will be illustrated using this simple model system. Suppose we want to dilate or compress the container. The amount of work required for such a process is given by

$$W = \int p dV \quad (2.18)$$

If we repeat this process over and over again for fixed initial conditions we would nevertheless have to apply different amounts of work for each process. This can be seen directly from equation (2.18) since the pressure (see point 3) is a fluctuating variable. This means, that depending on the actual movement of the particles inside the container, it is possible that we require more or less work than the average amount. One could, e.g. face the situation that while compressing the container in the sense, that no particle hits the wall during the compression and therefore one does not have to perform any work for this process.

2. Theoretical Background

2.3.4. Distribution of Work

As we have seen in section 2.3.3 point 4, applying the same process on a system with the same initial conditions can lead to different amounts of work consumed by that process. We will often study the so-called *distribution of work*. By this we mean the probability $p(W)$ that one measures a certain amount W of work as a function of this very amount. So, if we measure the same amount of work W^* for each repetition of a fixed process, the distribution of work becomes a delta peak. This would be the case for arbitrary slow processes e. g., where we would get (see (2.12))

$$p(W) = \delta(W - \Delta F) \quad (2.19)$$

One should keep in mind, that while on average $\overline{W} \geq \Delta F$ (see (2.13)) has to hold, there is always the possibility that the outcome of individual measurements violate the inequality $W \geq \Delta F$. This seems to be straightforward, but one is often tempted to think of such results as a violation of the 2nd law of thermodynamics, which is of course not the case. Figures 2.2 to 2.4 show an experimental setup for pulling experiments on RNA and the measurement outcome for the distribution of work [14] respectively.

Variance of Work

Closely connected to the distribution of work is the variance of work:

$$(\delta W)^2 = \overline{W^2} - \overline{W}^2 \quad (2.20)$$

With the help of the conditional transition matrix (see section 2.7), this can be rewritten (for details see appendix A.1):

$$(\delta W)^2 = (\delta H(t_f))^2 + (\delta H(t_i))^2 - 2C \quad (2.21)$$

$$(\delta H(t))^2 \equiv \overline{(H(t))^2} - \overline{H(t)}^2 \quad (2.22)$$

$$C \equiv \sum_{m,n} E_m(t_f) E_n(t_i) K_{mn}(t_f) P_n(t_i) - \overline{H(t_f)} \cdot \overline{H(t_i)} \quad (2.23)$$

with $P_n(t)$ being the probability to find the system in state n at time t . We also often use the relative variance of work, which is the variance divided by the average work $\frac{\delta W}{\overline{W}}$.

2.4. Quantum Dynamics

2.4.1. Overview

In the following we will discuss basic equations and concepts of quantum mechanics such as the SCHRÖDINGER equation [15], the density operator [16] and bi- or multipartite quantum systems [17].

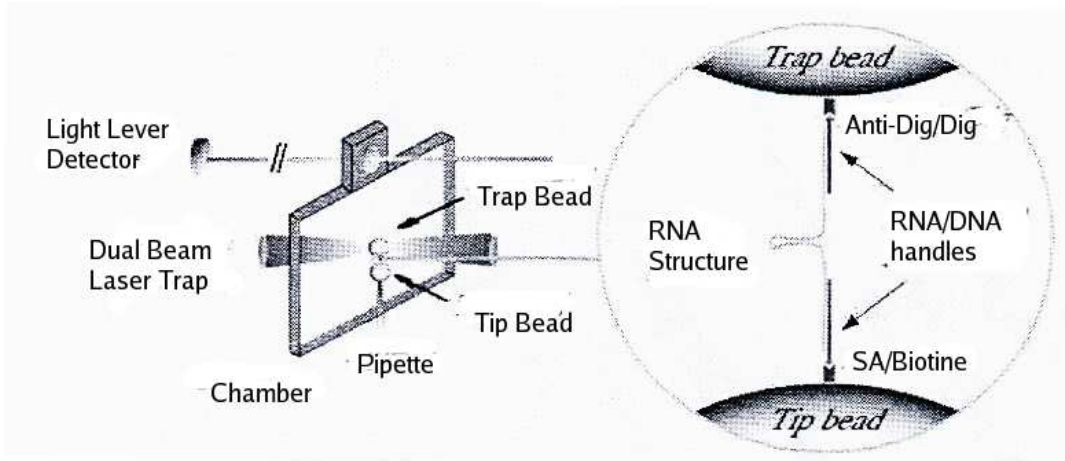


Figure 2.2.: Here, a possible experimental setup for pulling experiments on RNA molecules is shown. It is possible to measure the distance between the two beads, indicating the length of the RNA molecule as a function of the pulling force [14]

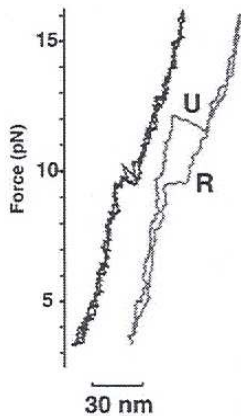


Figure 2.3.: The measurement outcome for different pulling speeds is shown. First, the molecule is stretched and then relaxed again. The Force in pN is measured as a function of the distance of the two beads. In the left figure a very slow pulling speed was chosen ($3 - 4 \frac{pN}{s}$), the molecule unfolding and folding suddenly for the same force at approximately $9.5 pN$. The right figure shows the outcome for a high speed ($52 \frac{pN}{s}$), where a hysteresis was obtained: The R denotes the refolding, the U the unfolding of the molecule [14].

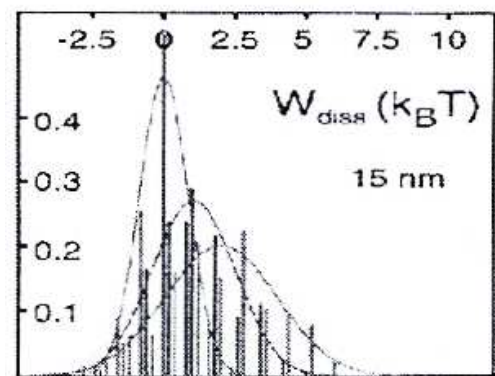


Figure 2.4.: The measurement outcome for the distribution of work for the pulling experiment is shown. The three curves correspond to three different pulling speeds. The faster the pulling speed, the broader the distribution of work. The curves were measured for $3 - 5 \frac{pN}{s}$, $34 \frac{pN}{s}$ and $52 \frac{pN}{s}$ (broadest curve). The x-axis shows the measured amount of work, the y-axis the probability of measuring that amount of work [14].

2.4.2. The Schrödinger equation

The fundamental equation of quantum dynamics is the time-dependent SCHRÖDINGER equation:

$$i\frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle \quad (2.24)$$

$|\Psi(t)\rangle$ denotes the time-dependent state vector and $\hat{H}(t)$ the time-dependent hermitian hamilton operator. The time-independent SCHRÖDINGER equation, which is an eigenvalue equation, reads:

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (2.25)$$

with E being the energy of the corresponding state vector.

2.4.3. Discrete Basis Vectors

For practical calculations, a special set of basis vectors is chosen. The physics are to be independent of that choice, and one can simplify many calculations with a suitable set of basis vectors. One can expand the state vector $|\Psi(t)\rangle$ in a complete orthonormal basis set $|n\rangle$:

$$|\Psi(t)\rangle = \sum_{n=1}^N c_n(t) |n\rangle \quad \text{with } c_n(t) = \langle n|\Psi(t)\rangle \quad (2.26)$$

The basis state vectors $|n\rangle$ span an N-dimensional hilbert space \mathcal{H} , through which the state $|\Psi(t)\rangle$ moves with time. Therefore, it can be viewed as a vector in \mathcal{H} . It is possible to depict the hamilton operator as a matrix in the chosen basis set:

$$H_{mn} = \langle m|\hat{H}|n\rangle \quad (2.27)$$

If one wants to know the probability to find a system described by the state vector $|\Psi(t)\rangle$ in a specific state $|n\rangle$ at a given time t , one has to calculate the square of the absolute of the state vector [18]:

$$p(|n\rangle, t) = |\Psi_n(t)|^2 \equiv |\langle n|\Psi(t)\rangle|^2 \stackrel{(2.26)}{=} |c_n(t)|^2 \quad (2.28)$$

2.4.4. The Unitary Time Evolution Operator

The time evolution operator [19] is used to describe the evolution of an isolated quantum system, which can be predicted exactly. We define the evolution operator through:

$$|\Psi(t)\rangle = \hat{U}(t, t_0) |\Psi(t_0)\rangle \quad (2.29)$$

With the help of equation (2.24), one arrives after formal integration for a time independent hamiltonian at

$$\hat{U}(t, t_0) = e^{-i\hat{H}(t-t_0)} \quad (2.30)$$

with the initial condition

$$\hat{U}(t_0, t_0) = \hat{1} \quad (2.31)$$

If the hamiltonian is explicitly time-dependent and the commutator between the hamilton operator of different times does not vanish, one has for the time evolution operator:

$$\hat{U}(t, t_0) = e^{-i\hat{T} \int_{t_0}^t d\tau \hat{H}(\tau)} \quad (2.32)$$

which is a formal solution since the operator \hat{T} , which is called the Dyson time-ordering operator, has to ensure the correct chronological ordering of the hamilton operators at different times. The time evolution operator has the following useful properties:

1. It is unitary: $\hat{U}^\dagger(t, t_0) = \hat{U}^{-1}(t, t_0)$
2. It can be split into different operators for different time intervals:

$$\hat{U}(t, t_0) = \hat{U}(t, t_1) \hat{U}(t_1, t_0) \quad (2.33)$$

3. From equation (2.33), it follows directly that $\hat{U}^\dagger(t, t_0) = \hat{U}(t_0, t)$.

2.4.5. The Density Operator and the Liouville Equation

If the state of a closed system is not exactly known but only the probabilities p_n of finding the system in a state $|\Psi_n\rangle$, the system is described via the density operator [16]:

$$\hat{\rho} = \sum_{n=1}^N p_n |\Psi_n\rangle \langle \Psi_n| \quad (2.34)$$

This operator has the following properties [16]:

1. It is hermitian (as can be seen easily from equation (2.34)): $\hat{\rho} = \hat{\rho}^\dagger$
2. The diagonal elements of $\hat{\rho}$ are the probabilities of finding the system in the basis states $|i\rangle$:

$$\rho_{ii} = \sum_n p_n |c_n^{(i)}|^2 \quad (2.35)$$

with $c_n^{(i)} = \langle i | \Psi_n \rangle$. Since the diagonal elements are probabilities, it follows immediately from the normalization condition, that $\rho_{ii} \leq 1$ and:

$$\text{Tr}(\hat{\rho}) = \sum_i \rho_{ii} = 1 \quad (2.36)$$

3. The expectation value of any operator \hat{A} is calculated by

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\rho} \hat{A}) \quad (2.37)$$

2. Theoretical Background

It is also possible to describe a pure state $|\Psi\rangle$ in terms of a density operator, which then reads

$$\hat{\rho} = |\Psi\rangle\langle\Psi| \quad \text{with the matrix elements } \rho_{ij} = \Psi_i\Psi_j^* \quad (2.38)$$

To distinguish between pure and mixed states, one can take the trace of the density operator squared:

$$\text{Tr}(\hat{\rho}^2) \begin{cases} = 1 & \text{for pure states} \\ < 1 & \text{for mixed states} \end{cases} \quad (2.39)$$

The dynamics of the density operator is described by the LIOUVILLE or VON-NEUMANN equation (analogue to equation (2.10)) [16]:

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -i\left[\hat{H}, \hat{\rho}(t)\right] \quad (2.40)$$

For the density operator at time t we have, using equation (2.29):

$$\hat{\rho}(t) = \hat{U}(t, t_0)\hat{\rho}(t_0)\hat{U}^\dagger(t, t_0) \quad (2.41)$$

2.4.6. Composed Quantum Systems

In this thesis we consider mostly two interacting systems, thus we will focus on that special case, which can of course be generalized to more subsystems with ease [17]. We consider two interacting subsystems, calling one of them the *system* and the other one will henceforth be called *environment* or *bath* respectively. One can consider the system to be embedded in the environment. The compound system is supposed to be a closed one and thus follows a unitary time evolution, while the small system, which is often called an open system, does not. Only if the two subsystems do not interact with each other, the complete system can be described by a state vector in product form [3]:

$$|\Psi(t)\rangle = |\psi^1\rangle \otimes |\psi^2\rangle = \sum_{i,j} \langle i|\psi^1\rangle \langle j|\psi^2\rangle |ij\rangle \quad (2.42)$$

This vector is defined in the (n_1n_2) -dimensional Hilbert space with n_1 and n_2 being the dimensions of system 1 and 2 respectively. This state can be represented by a density operator according to equation (2.34). If the subsystems interact with each other, it is in general impossible to represent them by pure state vectors:

$$\Psi \stackrel{\text{(in general)}}{\neq} |\psi^1\rangle \otimes |\psi^2\rangle \quad (2.43)$$

If one wants to describe a subsystem or get any information from it, it is generally necessary to take the partial trace over the other subsystem of the complete one. So, if one is interested in the density operator of system 1 e. g., one has to trace out the other subsystem [3]:

$$\hat{\rho}^{(1)} = \text{Tr}^{(2)}(\hat{\rho}) \quad (2.44)$$

or in the matrix representation:

$$\varrho_{ij}^{(1)} = \sum_{n=1}^{n_2} \langle in | \hat{\varrho} | jn \rangle \quad (2.45)$$

The dynamics of the two subsystems are in general no longer unitary. Due to this fact the subsystems dynamics can become irreversible. Systems that interact with each other lose local information in favour of global information about the complete system - the systems are said to be entangled.

For operators which act only on one subspace, we often use a short-hand notation [10]:

$$\hat{A}^{(1),(2)} = \hat{A}^{(1)} \otimes \hat{1}^{(2)} \equiv \hat{A}^{(1)} \quad (2.46)$$

It is important to keep in mind, that the operator is defined in the product space nevertheless.

2.4.7. Thermodynamical Concepts

Here, a short review on standard variables and definitions of thermodynamics in quantum mechanics is given [20].

1. Canonical state: If a system is in equilibrium with a heat bath at temperature T , its density operator reads:

$$\hat{\varrho}_{\text{canonical}} = \frac{e^{-\beta \hat{H}}}{Z} \quad (2.47)$$

with β being the reciprocal temperature $\frac{1}{T}$ and Z being the partition sum given by

$$Z \equiv \sum_n \langle n | e^{-\beta \hat{H}} | n \rangle = \text{Tr} \left(e^{-\beta \hat{H}} \right) \quad (2.48)$$

The partition sum ensures the normalization of the trace of the density operator and is defined for arbitrary states, which means, the system does not need to be thermalized.

2. The von-Neumann entropy S is defined through

$$S \equiv - \text{Tr}(\hat{\varrho} \ln \hat{\varrho}) \quad (2.49)$$

It should be noted that the von-Neumann entropy is invariant under unitary transformations due to the cyclic invariance of the trace. Note that the von-Neumann entropy is defined even in a non-canonical state! Interpretations thus require some care since one normally thinks of systems in a canonical state when speaking of entropy.

3. The free energy is defined as in the classical case (2.5), i. e.:

$$F \equiv -T \log Z \quad (2.50)$$

For this definition, it is not necessary that the system is in a canonical state, since the partition sum is independent of the actual state.

2.5. Fluctuation Theorems

2.5.1. Overview

In this section we concentrate on classical fluctuation theorems [21], [22], [23], [24]. A short review on the various existing theorems is given. We are mainly interested in work-fluctuation-dissipation theorems and will concentrate on a relation found by JARZYNSKI [5]. For better illustration we will briefly discuss an experiment on work-fluctuations [14].

2.5.2. Different Kinds of Fluctuation Theorems

Fluctuation theorems have one feature in common: They are all founded on a fundamental relation between the entropy production along a single system trajectory and the natural logarithm of the probability ratio of the forward and backward trajectory [25].

There are different theorems for different kinds of systems, variables or boundary conditions. We will only give a very short review on selected theorems:

1. Deterministic thermostated systems, non-hamiltonian [21]: A corresponding theorem was derived for the shear stress of a fluid in a steady state far from equilibrium. The fluctuations of the shear stress were studied. Later on, this result was generalized and studied under different viewpoints.
2. Hamiltonian systems: See e. g. [26]. A system coupled to several heat baths which follows microscopically hamiltonian dynamics is investigated. The ratio of probabilities of a set of events in a forward and backward process respectively is connected with the entropy production.
3. Stochastic dynamics: See e. g. [27], [23]. Systems coupled to a heat bath are investigated. We have dynamics of an open system due to the interaction between system and bath, and therefore a stochastic system trajectory. Most often, the system's dynamics is supposed to follow a master equation. Under these restraints, a close connection between the fluctuation theorems and the JARZYNSKI relation can be found.

Keep in mind, that all these theorems apply to classical systems only. In quantum mechanics, fluctuation theorems have been developed so far for a few restricted situations [28], [29], [30]. However, more work has been investigated a quantum version of the JARZYNSKI relation [6] as will be done in this thesis.

2.6. The Jarzynski Relation

2.6.1. Overview

A brief introduction to the classical JARZYNSKI relation will be given. For more detailed reading and a more rigorous proof see [5]. For further motivation and better illustration,

a short description of an experiment will be given [14].

2.6.2. Statement

The JARZYNSKI relation connects an equilibrium property of a thermodynamical system, namely the free energy difference, with a non-equilibrium property, the work performed on the system. We start with a canonical system, so it has a well defined temperature T (see section 2.2.1). Then, an arbitrary process is inferred on the system. As in our simple model system in section 2.3.3, the work for a fixed process, which is repeated over and over again, will in general not be the same for every realization. So, the work fluctuates and will on average exceed the free energy difference (2.13). The JARZYNSKI relation now states:

$$\overline{e^{-\beta W}} = e^{-\beta \Delta F} = \frac{Z(t)}{Z(0)} \quad (2.51)$$

Note that the 2nd law of thermodynamics is automatically fulfilled due to the mathematical relation [31]:

$$\ln \overline{e^f} \geq \overline{f} \quad (2.52)$$

With the help of this equation, one has after taking the logarithm of both sides of equation (2.51): $\overline{W} \geq \Delta F$ (see (2.13)). In the following, we want to give an idea of the proof of this equality. Suppose that the system can be described by a hamiltonian and, that the time-dependency due to the process enters the hamiltonian as a parameter λ . The system is supposed to be closed, but has at some other point in time interacted with a heat bath and is thus thermalized (see 2.2):

$$\varrho(z, 0) = \frac{e^{-\beta H_0(z)}}{Z_0} \quad (2.53)$$

with z being a point in phase space and the index 0 denoting the beginning of the process ($\lambda = 0$). The deterministic time evolution is described by the LIOUVILLE equation (2.10). To get the average of work, we have to integrate the work along each possible trajectory weighted with the probability of that trajectory to be realized:

$$\overline{e^{-\beta W}} = \int dz \varrho(z, t_s) e^{-\beta w(z, t_s)} \quad (2.54)$$

The work performed on a closed system is the energy difference between the initial and final state respectively, which equals the difference of the hamiltonian:

$$w(z, t) = H_\lambda(z) - H_0(z_0) \quad (2.55)$$

The initial condition for the trajectory to cross point z at time t is $z_0 = z_0(z, t)$ and we have with the LIOUVILLE theorem:

$$\varrho(z, t) \stackrel{(2.10)}{=} \varrho(z_0, 0) \stackrel{(2.53)}{=} \frac{e^{-\beta H_0(z_0)}}{Z_0} \quad (2.56)$$

2. Theoretical Background

Multiplying with $e^{-\beta w(z,t)}$ and using equation (2.55) yields

$$\varrho(z, t)e^{-\beta w(z,t)} = \frac{e^{-\beta H_\lambda(z)}}{Z_0} \quad (2.57)$$

Substituting this in equation (2.54), one finally gets at the end of the process ($\lambda = 1$)

$$\overline{e^{-\beta W}} = \frac{1}{Z_0} \int dz e^{-\beta H_1(z)} = \frac{Z_1}{Z_0} \quad (2.58)$$

With

$$\Delta F = -\frac{1}{\beta} \ln \frac{Z_1}{Z_0} \quad (2.59)$$

one has the desired result. The JARZYNSKI relation is a classical work-fluctuation-dissipation theorem, as can be seen if one expands the left side of equation (2.51) [32]:

$$\Delta F = \overline{W} - \frac{\beta}{2} (\overline{W^2} - \overline{W}^2) \quad (2.60)$$

Since for an infinitely slow reversible process one would get $\Delta F = \overline{W}$ (see (2.12)), the rest is associated with dissipated work (see (2.14)). For practical reasons, the systems studied experimentally with this relation should not be very big [5].

Experiment on Work Fluctuations

We refer to the experiment described already in section 2.3.4 [14]. The free energy difference of a DNA or an RNA molecule in its folded and unfolded state respectively is to be determined. Since the folding and unfolding of the molecules happens suddenly, it is not possible to measure this difference via an adiabatic process. The idea is now to measure the work distribution of an unfolding process and by using (2.51), one gets the free energy difference. The work performed on the molecule can be obtained by measuring the force one has to apply in dependence of the length of the molecule. The experimental setup is shown in figure 2.2. The same measurement protocol, e. g. pulling with a specific constant velocity, is now repeated many times, and the work for each repetition, which will in general differ from each other, is calculated. One thus gets the distribution of work. A typical result is shown in figure 2.4.

2.7. The Quantum Jarzynski Relation

Here, we focus on a paper by S. MUKAMEL [6], who has presented a proof, that for closed systems, the JARZYNSKI relation is also valid for quantum systems. The requirements are the same as for the classical relation: The system is supposed to be in a canonical state before starting the process (2.47)

$$\hat{\varrho}(0) = \frac{e^{-\beta \hat{H}(0)}}{Z(0)} \quad (2.61)$$

The system is closed, its time evolution thus deterministic according to the LIOUVILLE equation (2.40)

$$\dot{\hat{\rho}} = -i[\hat{H}, \hat{\rho}] \quad (2.62)$$

Now a special basis vector set is used, such that:

$$\hat{H}(t) |\varphi_n(t)\rangle = \varepsilon_n(t) |\varphi_n(t)\rangle \quad (2.63)$$

This basis set will further on be called adiabatic basis set. Note that the basis vectors are explicitly time-dependent. The LIOUVILLE equation (2.40) in this basis reads

$$\dot{\varrho}_{kl}(t) = -i\omega_{kl}\varrho_{kl}(t) - \sum_{m,n} S_{kl,mn}(t)\varrho_{mn}(t) \quad (2.64)$$

with

$$\omega_{kl} \equiv \varepsilon_k(t) - \varepsilon_l(t) \text{ and } S_{kl,mn}(t) \equiv \langle \varphi_k(t) | \dot{\varphi}_m(t) \rangle \delta_{ln} + \langle \dot{\varphi}_n(t) | \varphi_l(t) \rangle \delta_{km} \quad (2.65)$$

with δ_{ij} being the KRONECKER delta which is defined by

$$\delta_{ij} \equiv \begin{cases} 1 & \text{for } i = j \\ 0 & \text{for } i \neq j \end{cases} \quad (2.66)$$

The sum term in equation (2.64) results from the time-dependency of the used basis vectors. We will now introduce the so-called *conditioned transition matrix* $K_{mn}(t)$. It contains the conditional probability for finding the system in state $|\varphi_m(t)\rangle$ at time t , provided that it was in state $|\varphi_n(0)\rangle$ at time 0. With the help of this matrix, we can write the diagonal elements of the density operator matrix at time $t = 0$ as

$$\varrho_{mm}(t) = \sum_n K_{mn}(t)\varrho_{nn}(0) \quad (2.67)$$

Now one shows, that two sum rules concerning this matrix hold (see appendix A.2):

$$\sum_n K_{mn}(t) = 1 \text{ and } \sum_m K_{mn}(t) = 1 \quad (2.68)$$

With the help of the second identity, it is easy to proof the JARZYNSKI relation: The work performed on a closed system is defined as the difference of the eigenenergies of the eigenstates at the beginning and at the end of the process respectively:

$$W_{fi} \equiv \varepsilon_f(t) - \varepsilon_i(0) \quad (2.69)$$

where the indices denote the final and initial state. The average can thus be calculated:

$$\begin{aligned} \overline{e^{-\beta W}} &\stackrel{(2.69)}{=} \sum_{i,f} e^{-\beta(\varepsilon_f(t) - \varepsilon_i(0))} K_{fi}(t)\varrho_{ii}(0) \\ &\stackrel{(2.47)}{=} \sum_{i,f} e^{-\beta(\varepsilon_f(t) - \varepsilon_i(0))} K_{fi}(t) \frac{e^{-\beta\varepsilon_i(0)}}{Z(0)} \\ &= \frac{1}{Z(0)} \sum_{i,f} e^{-\beta\varepsilon_f(t)} K_{fi}(t) \stackrel{(2.68),(2.48)}{=} \frac{Z(t)}{Z(0)} \end{aligned} \quad (2.70)$$

which yields the desired result using equation (2.50).

2. *Theoretical Background*

3. Model Systems

3.1. Overview

In the following a short review on two widely used one-particle models in quantum mechanics is given, namely the one-dimensional potential well with infinitely high potential steps and the coulomb potential [10]. These two model systems will be used in this thesis to study various aspects of quantum fluctuation theorems. The choice of these two models was made due to their different energy scaling: The energy-eigenvalues scale with n^2 and $\frac{1}{n^2}$ for the potential well and the coulomb potential, respectively. So the density of the energy levels decreases in case one and increases in case two for increasing n . The index n denotes the number of the energy level.

3.2. Potential Well

We consider the standard quantum well with infinitely high potential steps at its edges. The potential thus reads:

$$V(x) = \begin{cases} \infty & \text{for } x \leq 0 \\ 0 & \text{for } 0 < x < L \\ \infty & \text{for } x \geq L \end{cases} \quad (3.1)$$

with L denoting the width of the well. Now the position of one wall can be moved to the left or right, thus compressing or dilating the well (see figure 3.1). The width of the well is therefore no longer constant in time, we get a time-dependent potential due to the time-dependency of the parameter $L = L(t)$. We get for the energy-eigenfunctions and the energy-eigenvalues respectively [10]:

$$|\varphi_n(t)\rangle = \sqrt{\frac{2}{L(t)}} \sin\left(\frac{n\pi}{L(t)} x\right) \quad (3.2)$$

$$E_n(t) = \frac{\pi^2}{2L^2(t)M} n^2 \quad (3.3)$$

with M being the mass of the particle in the well and n the index of the energy-level it occupies. For practical numerical calculations, we neglect higher energy levels (cutoff). This is possible since for moderate temperatures, the probability for higher energy levels to be occupied is nearly zero, as the eigenenergies rise with the second power of the energy level index as can be seen from equation (3.3).

3. Model Systems

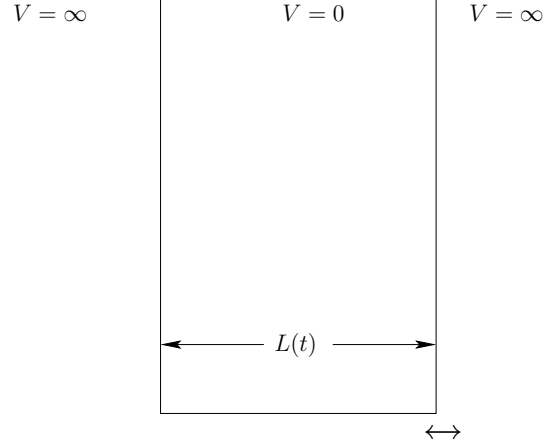


Figure 3.1.: Model system for numerical studies on a quantum well. The left wall is held fixed, the right wall is moveable w.l.o.g.

3.3. Coulomb Potential

We study a charged particle in a coulomb potential. The central charge creating the potential is supposed to be variable. Thus it can be viewed as an external control parameter. In the following we neglect the spin-orbit coupling and any movement of the central charge (its mass is supposed to be much larger than that of the other particle and there is no gravitational pull). For the energy-eigenvalues we have [33]:

$$E_n = -\frac{mZ^2(t)e^4}{2(4\pi\epsilon_0)^2} \frac{1}{n^2} \quad (3.4)$$

with $Z(t)$ being the variable charge with control parameter t , which will be associated with time throughout this thesis. We split the energy-eigenfunctions into a radial and an angular constituent respectively [33]:

$$R_{n,l}(r) = N_{n,l} e^{-\kappa_n r} r^l L_{2\kappa_n r}^{2l+1} \quad (3.5)$$

$$Y_l^m = e^{im\varphi} P_l^m(\cos\theta) \quad (3.6)$$

The indices denote the energy level (n) and the quantum number for the angular momentum (l), which runs from zero to $n - 1$. The radial constituent $R_{n,l}(r)$ contains a normalizing factor $N_{n,l}$, the generalized Laguerre's polynomials $L_{2\kappa_n r}^{2l+1}$ and the κ 's being an abbreviation for bound states (energy less than zero):

$$\kappa_n \equiv \sqrt{-2mE_n} \quad (3.7)$$

The generalized Laguerre polynomials are defined through [31]:

$$L_{n+l}^{2l+1} \equiv \frac{d^{2l+1}}{d\varrho^{2l+1}} L_{n+1}(\varrho) \quad (3.8)$$

$$L_{n+1}(\varrho) \equiv e^\varrho \frac{d^{n+l}}{d\varrho^{n+l}} (e^{-\varrho} \varrho^{n+l}) \quad (3.9)$$

with (3.9) being the known Laguerre polynomials. The angular constituent of equation (3.6) is the spherical harmonic, which contains the Legendre polynomial $P_l^m(\cos \vartheta)$. The time-dependency of the energy-eigenfunctions results from the κ_n which contain the energy term (3.4).

The symmetry of the perturbation (change of the central charge) conserves the angular symmetry, so we get no transitions between states with different angular momentum. In the following we chose the temperature of the initial state, which will be a canonical one, to be very low so that in the beginning mainly the ground state has a non-vanishing occupation probability. Since the ground state ($n = 1$) allows only $l = 0$ and our perturbation conserves the angular momentum, we do not have to consider any degeneracy. The distance of neighbouring energy-eigenvalues decreases with the second power of the number of the energy level.

For practical numerical calculations we use a similar cutoff as in the case of the potential well. This is justified because we are mostly interested in the energy of the system and it is therefore not necessary to know the exact energy level the particle occupies, since the energy difference between different levels is negligible for big n . Moreover we only study bound states which lead to a discrete spectrum.

3. Model Systems

4. Closed Systems - No Environment

4.1. Overview

We start our examination of quantum fluctuation theorems with the easiest possible case: a closed system without any environment to interact with. For this sort of systems, there already exists an analytical proof that the JARZYNSKI relation also holds in the quantum regime as seen above (2.7) [6]. For a start, we want to examine this relation using the two model systems introduced above (see chapter 3) in order to get more familiar with this fluctuation-dissipation theorem and to verify it for these systems numerically. It also yields a good reference test for later calculations with an additional environment. Afterwards, we study the robustness of the system under external perturbations, meaning the probability of the particle to remain in a specific energy level throughout the process. The idea is to check how fast we get non-adiabatic behaviour due to the driving process.

4.2. Requirements

In the following, requirements for our calculations are listed:

1. Initial Conditions: From now on, we require that in the beginning at time $t = 0$ our system is in a canonical state (2.47). This can be achieved by letting the system interact with a huge heat bath, and after the thermalization of the system decoupling the bath so that it is isolated again. This means that our system has a well defined temperature in the beginning. Note that at the end of the process, the system is in general no longer in a canonical state and will in fact most likely be not.
2. Approximations: As mentioned above (see 3.2 and 3.3), we require the temperature of the initial state to be low enough so that we can cut off high energy levels. The perturbation should not be that fast that one has to fear that relativistic effects could be important. In the case of the coulomb potential, the process should not allow the particle to leave the domain of bound states since we only want to consider the discrete spectrum.
3. Process and Calculation: We proceed as follows: By changing the control parameter we invoke an arbitrary but well defined process on the system. Since the

4. Closed Systems - No Environment

system is closed, its state vector $|\Psi\rangle$ evolves deterministically according to the time-dependent SCHRÖDINGER equation (2.24). It is - at least in principle - possible to calculate the whole unitary dynamics exactly. We compute the conditioned transition matrix (see section 2.7) and from that, we get the new density matrix according to equation (2.67). With the help of these two variables and the density matrix of the initial state, we are able to calculate all the necessary variables.

4.3. Expectations

We expect the JARZYNSKI relation to hold for arbitrary fast processes, independent of the specific path. In order to clarify this, we study the potential well for different realizations of “wall movements” always ending up in the same position of the wall and compare the results of the different processes with each other. The result for the free energy change should always be the same. The work distribution is expected to be broader the faster the process is performed.

4.4. Calculations

We solve the time-dependent SCHRÖDINGER equation numerically for specific processes. This is done using the software program MATHEMATICA. We use the time evolution operator $\hat{U}(t, t_0)$ (for details see section 2.4.4) and an adiabatic basis set as described in section 2.7 equation (2.63). We obtain a differential equation for the matrix of the time evolution operator (see appendix A.3):

$$-i\dot{U}_{ki}(t, t_0) - i \sum_n M_{kn}(t)U_{ni}(t, t_0) = \varepsilon_k(t)U_{ki}(t, t_0) \quad (4.1)$$

with

$$M_{kn}(t) \equiv \langle \dot{\varphi}_k(t) | \varphi_n(t) \rangle \quad (4.2)$$

We are interested in the conditioned transition matrix. The probability for ending up in state $|\varphi_n(t)\rangle$, if started in state $|\varphi_i(0)\rangle$, is given by

$$K_{fi}(t) = |\langle \varphi_f(t) | \varphi_i(0) \rangle|^2 \quad (4.3)$$

which can be rewritten with help of equation (2.29):

$$K_{fi}(t) = |\langle \varphi_f(t) | \hat{U}^\dagger(t, 0) | \varphi_i(0) \rangle|^2 = |U_{if}(t, 0)|^2 \quad (4.4)$$

With this we can calculate the work distribution, the free energy change, the density matrix at the end of the process and the von-Neumann entropy.

It was tried to solve this problem analytically by solving equation (4.1) with the help of equation (A.44). Unfortunately, MATHEMATICA was not able to solve the resulting differential equation system with time-dependent coefficients.

4.5. Consistency Checks

In order to check our program and possible numerical errors, several consistency checks are run:

1. Trace of the density matrix: The trace of the density matrix of the closed system has to be constant and equal 1 throughout the process.
2. Density Matrix: It has to be hermitian which can be tested easily, since the following identity has to hold: $(\rho_{ff'})^T = \rho_{ff'}$ with A^T meaning the transpose of the matrix A . It immediately follows that its eigenvalues have to be real.
3. Time evolution operator: It has to be a unitary operator (see section 2.4.4), which can be checked readily by testing the identity $\hat{U}(t, t_0)\hat{U}^\dagger(t, t_0) = \hat{1}$
4. von-Neumann entropy: Since we are studying closed systems, the entropy has to be constant (2.49).
5. Slow Changes: For very slow perturbations one should get no transitions and the work performed on the system should equal the free energy difference (2.12).

If any of these requirements was not met, one would have to check the program for errors. Any small deviations from these conditions could mean numerical errors which have to be kept in mind.

4.5.1. Testing the Jarzynski Relation

Note that the following statement is concerned only with the JARZYNSKI relation. If any of the following checks would fail, it would not mean that there are errors in the calculations, but that the relation would not be valid in the used model system!

We perform several tests in order to check if the relation is valid or not. First of all, for closed systems the sum rules for the conditioned transition matrix (2.68) should be fulfilled. Since it is easy to calculate the partition function at time t with the help of (2.48) for our simple model systems, we can compare this result to the one obtained by calculating the average work and applying the JARZYNSKI relation. To this end, we introduce a test factor, γ_J , in the equation for the average of the exponential of work:

$$\overline{e^{-\beta W}} = \gamma_J \frac{Z(t)}{Z(0)} \quad (4.5)$$

Only if the test factor equals one, the JARZYNSKI relation is valid. We test this by calculating the initial and final partition sum and the average of the exponential of work, respectively. We use these results and equation (4.5) in order to determine γ_J and test the validity of the JARZYNSKI relation.

4.6. Potential Well

First, we study the quantum well as described in section 3.2 on page 19. The time evolution is calculated for different functions $L(t)$ of the width of the quantum well. We study expansions and compressions as well as cyclic perturbations, which mean that the width at the end of the process equals that at the beginning, namely $L(t) = L(0)$. Then, we study the adiabatic behaviour of the quantum well.

Throughout this section, we use adapted units, noted by a prime, such that the relations (2.1) hold. With these conditions we have:

$$1J' \equiv 1.055 \cdot 10^{-34}J, \quad 1\frac{J'}{K'} \equiv 1.381 \cdot 10^{-23}\frac{J}{K} \quad (4.6)$$

We do not want to rescale the time, thus setting $1s \equiv 1s'$. We define our new measure of length to be of same order of magnitude as the initial width of the potential well, $1m' \equiv 1 \cdot 10^{-12}m$. With our choice of the unit of energy, J' , and time, $s \equiv s'$, we implicitly have fixed the new units of mass and temperature respectively: $1kg' \equiv 1.055 \cdot 10^{-10}kg$, since $1J = kg\frac{m^2}{s^2}$ and $1K' \equiv 7.645 \cdot 10^{-12}K$.

4.6.1. Linear Wall Displacements

We want to study wall displacements which have the following time-dependency:

$$L(t) = L(0) + vt \quad (4.7)$$

with v denoting a constant velocity. We solely change the absolute of the velocity keeping $L(t)$ and the initial conditions constant. The free energy difference should thus always be the same for the same $L(t)$.

Compression

As expected, we get independent of the velocity v :

- $\Delta F = 1.81 \cdot 10^{12}$
- $\overline{e^{-\beta W}} = 0.834$
- $S_0 = S_1 = 0.556$

with initial conditions:

$$L(0) \approx 1\text{pm}, \quad T \approx 75\text{K} \quad \text{and} \quad M \approx 1.05 \cdot 10^{-22}\text{kg} \quad (4.8)$$

The compression of the quantum well is $\Delta L = -0.1 L(0)$. Detailed results can be found in tabular 4.1. We can see that the average work performed on the system is positive and increases with increasing velocity and so does the relative variance of work as expected. The faster the process, the wider the distribution function of work. For moving the wall

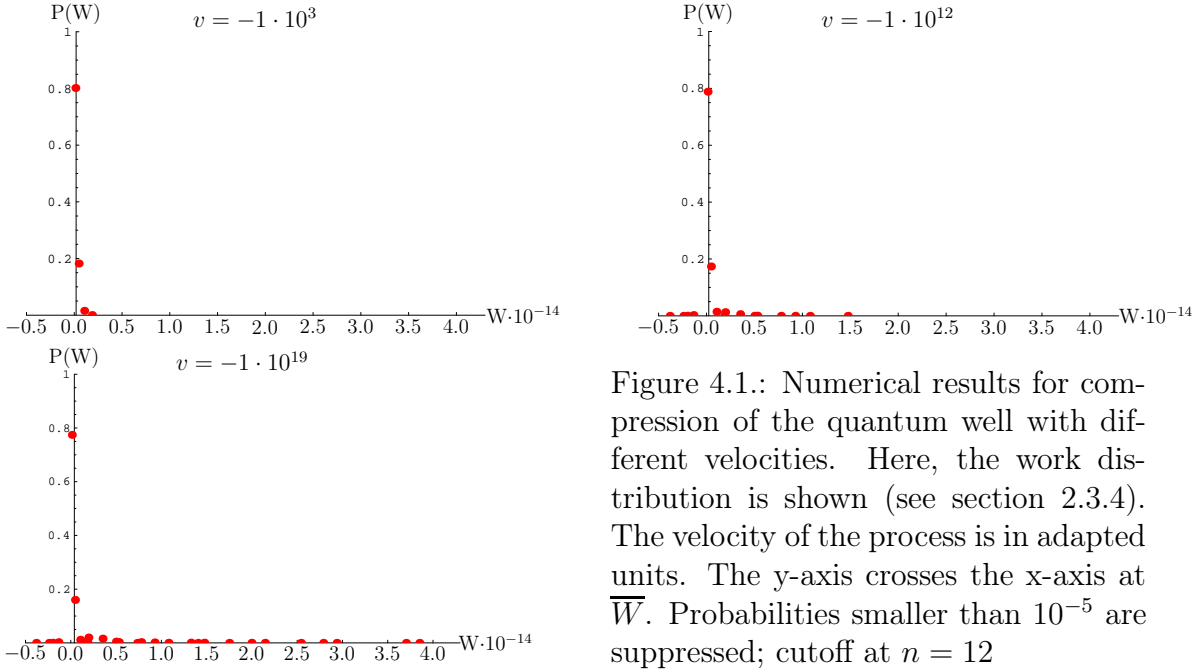


Figure 4.1.: Numerical results for compression of the quantum well with different velocities. Here, the work distribution is shown (see section 2.3.4). The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 12$

very slow, one gets $\overline{W} \approx \Delta F$. In the classical case one would expect $\frac{\delta W}{\overline{W}} \rightarrow 0$ (see 2.3.4). But since we start in a mixed state and end up in a non-canonical state, this is not the case here (see A.1). In order to test this, the same slow process was calculated for a pure initial state, and there, the difference between the free energy change and the work vanished as did the relative variance.

In figure 4.1 the work distribution for different process velocities is shown. For very slow processes one can see, that the work equals the change of the eigen-energies of the energy levels: $W_n = \varepsilon_n(t) - \varepsilon_n(0)$. This is a consequence of the absence of transitions ($K_{mn}(t) = \delta_{mn}$). The probability of measuring a certain amount of work equals the initial probability of that state to be occupied: $P(W_n) = \rho_{nn}(0)$.

Furthermore we see, that there exist processes, for which we can actually gain work by compressing the quantum well. This is very counter-intuitive, but as one can also see, the probability of gaining energy is very small. In average the 2nd law of thermodynamics holds of course.

Expansion

The following results are independent of the velocity v as predicted:

- $\Delta F = -1.53 \cdot 10^{12}$
- $\overline{e^{-\beta W}} = 1.17$
- $S_0 = S_1 = 0.556$

4. Closed Systems - No Environment

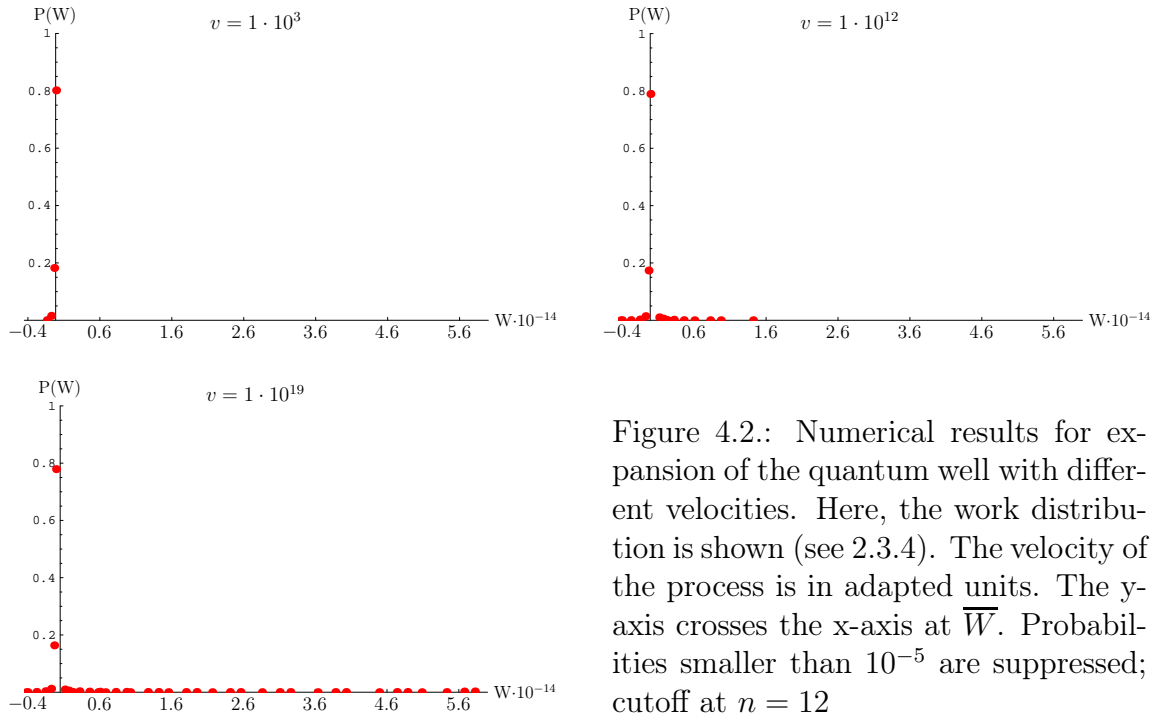


Figure 4.2.: Numerical results for expansion of the quantum well with different velocities. Here, the work distribution is shown (see 2.3.4). The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 12$

The initial conditions can be found in (4.8). The expansion of the quantum well is $\Delta L = 0.1 L(0)$. For more detailed results have a look at tabular 4.1. The average work for moderate process velocities is negative. This means that it is possible to gain work from the expansion of the well. The faster the process, the less work can be extracted. In the case of a very fast expansion one even has to pay work.

See figure 4.2. For very slow processes goes the same as said above for the compression of the quantum well.

Furthermore we see, that there exist processes for which we gain more energy than the free energy difference or where we even have to pay work for the dilatation. In comparison with the compression, the distribution of work seems to be reflected at the average work.

Cyclic Perturbations

We can vary the velocity of both, the dilatation and that of the compression, independent of each other. No matter how we chose these velocities, we always end up with

- $\Delta F = 0$
- $\overline{e^{-\beta W}} = 1.00$
- $S_0 = S_1 = 0.556$

with the same initial conditions as in equation (4.8). For details see tabular 4.1. We see that for very slow and very fast processes, the average work and relative variance both approximately vanish. For moderate velocities it is necessary to invest energy in

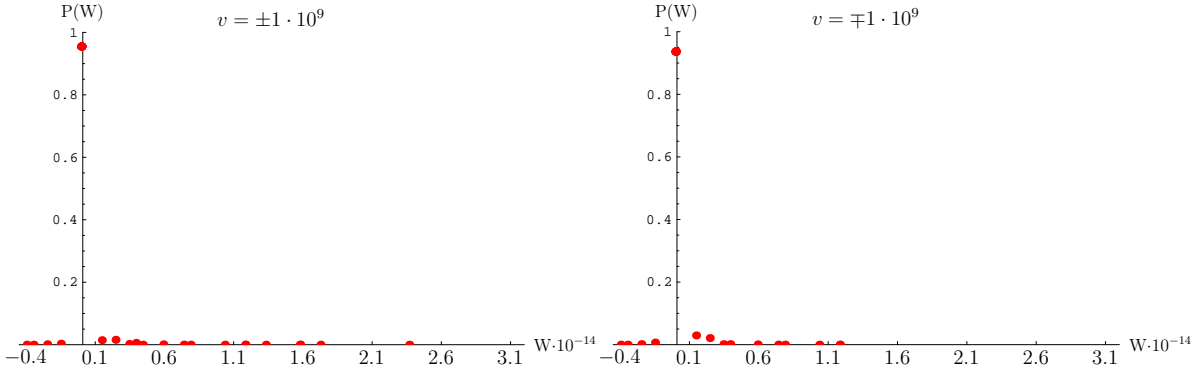


Figure 4.3.: Numerical results for cyclic perturbations of the quantum well with the same velocities for dilatation and compression. Here, the work distribution is shown (see 2.3.4). The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 12$

order to perform the process. The relative variance is bigger than for the expansion and compression. For very slow processes the relative variance approximately vanishes. This is due to the fact that we start and end up in the same canonical state (c. f. A.1).

The work distribution is shown in figure 4.3.

4.6.2. Sinusoidal Wall Displacements

Now, we study sinusoidal wall displacements which have the following form:

$$L(t) = L(0) (1 + A \sin \omega t) \quad (4.9)$$

With an adequate choice of amplitude A , phase, frequency ω and perturbation time t_f , it is possible to end up with the same width of the quantum well as in the case of linear displacements. Since we chose the same initial conditions as above (4.8), the results of this section match those of section 4.6.1 as required in order to verify the JARZYNSKI relation since the free energy change has to be independent of the particular realization of the process. So, we have for the compression $\Delta F = 1.81 \cdot 10^{12}$, $\overline{e^{-\beta W}} = 0.834$ and $\Delta F = -1.53 \cdot 10^{12}$, $\overline{e^{-\beta W}} = 1.17$ for the expansion, respectively. Detailed results of the sinusoidal displacements can be found in tabular 4.2.

The work distributions can be found in figure 4.4 for compressions and figure 4.5 for dilatations. In both cases the result is very similar to that one for linear wall displacements.

4.6.3. Changes in Boundary Conditions

In the following, only one parameter was changed while all others were held fixed. We only consider linear displacements as in section 4.6.1 with initial conditions (4.8) and expansion velocity $v = 1 \cdot 10^{16}$. The results can be found in tabular 4.3. For the old parameters we had $\overline{W} = 4.92 \cdot 10^{12}$ and $\Delta F = -1.53 \cdot 10^{12}$ (c. f. section 4.6.1).

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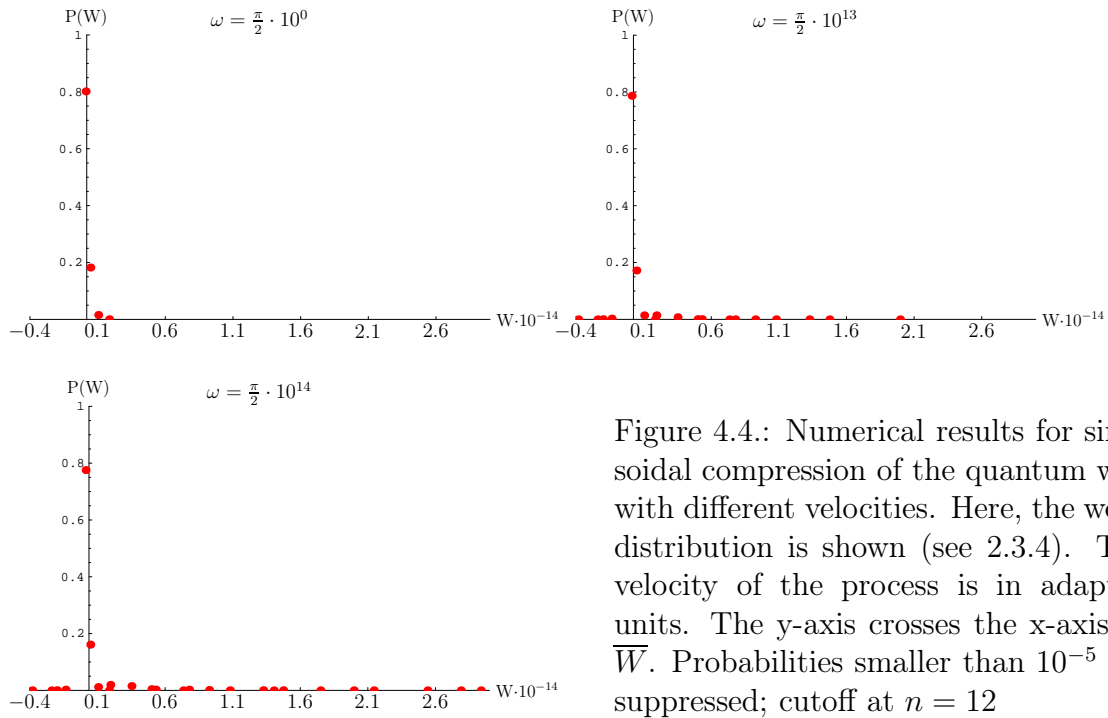


Figure 4.4.: Numerical results for sinusoidal compression of the quantum well with different velocities. Here, the work distribution is shown (see 2.3.4). The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 12$

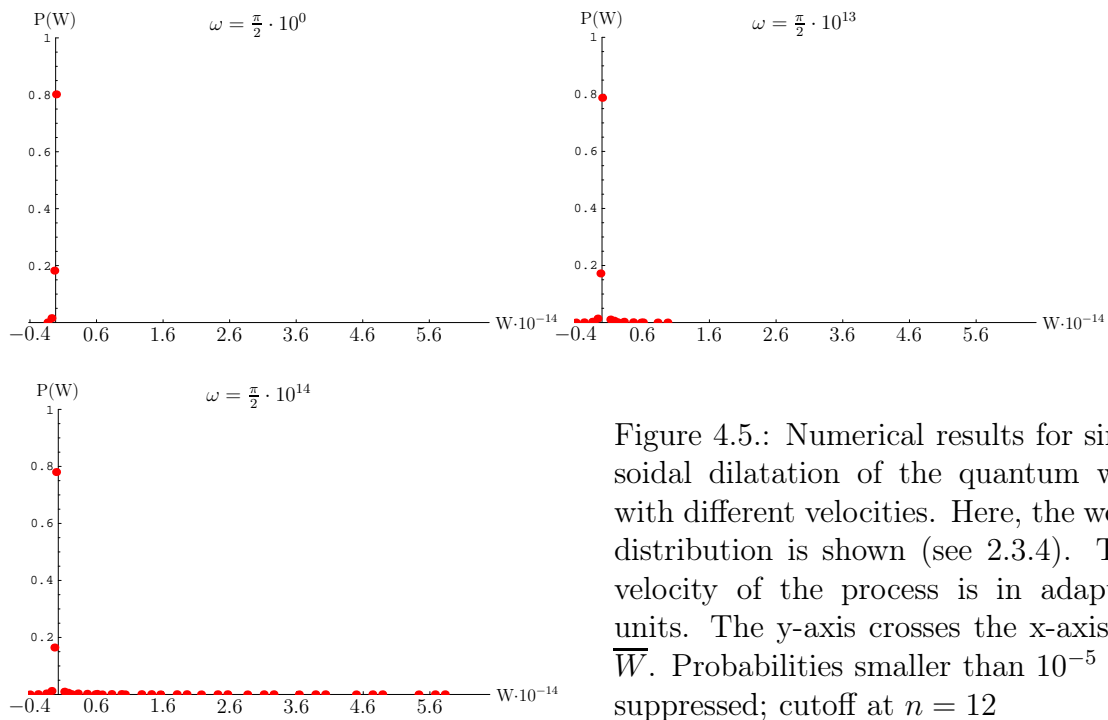


Figure 4.5.: Numerical results for sinusoidal dilatation of the quantum well with different velocities. Here, the work distribution is shown (see 2.3.4). The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 12$

Table 4.1.: Results of numerical calculations for linear wall displacements as described in section 4.6.1; the sign of the velocity indicates whether the well is expanded(+) or compressed(-); cutoff at $n = 12$; Average work in adapted units

velocity v	$\overline{W} \cdot 10^{12}$	$ \frac{\delta W}{W} $
-1.00	1.94	0.90
$-1.00 \cdot 10^9$	2.35	1.91
$-1.00 \cdot 10^{16}$	3.92	3.30
1.00	-1.44	0.90
$1.00 \cdot 10^9$	-1.12	3.03
$1.00 \cdot 10^{16}$	4.92	10.5
± 1.00	≈ 0	≈ 0
$\pm 1.00 \cdot 10^9$	1.00	6.66
$\pm 1.00 \cdot 10^{16}$	≈ 0	≈ 0
∓ 1.00	≈ 0	≈ 0
$\mp 1.00 \cdot 10^9$	1.01	5.74
$\mp 1.00 \cdot 10^{16}$	≈ 0	≈ 0

Table 4.2.: Results of numerical calculations for sinusoidal wall displacements 4.6.2; cutoff at $n = 12$; Average work in adapted units

frequency ω	$\overline{W} \cdot 10^{12}$	$ \frac{\delta W}{W} $	$\overline{W} \cdot 10^{12}$	$ \frac{\delta W}{W} $
	Expansion		Compression	
$\frac{\pi}{2} \cdot 10^0$	-1.44	0.90	1.94	0.90
$\frac{\pi}{2} \cdot 10^{13}$	-1.03	3.78	2.46	2.06
$\frac{\pi}{2} \cdot 10^{14}$	2.44	13.9	3.66	3.14

1. Temperature: $T \approx 7.5\text{K}$: The temperature of the initial canonical state was changed. Since one still wants to use a cutoff, the temperature was chosen to be lower compared to the other cases. The JARZYNSKI relation still holds ($\gamma_J = 1$), the average amount of work consumed by this process is relative low compared to the linear changes with $T \approx 75\text{K}$ in 4.6.1.
2. Width: $L(0) = 0.5\text{pm}$: The well in the beginning is much narrower than in the other cases. Nevertheless, the absolute amount of the wall displacement equals that of the other calculations. The JARZYNSKI relation is still valid of course ($\gamma_J = 1$), and one has to pay a considerable high amount of work.
3. Mass: $M \approx 1.05 \cdot 10^{-25}\text{kg}$: The mass of the particle was reduced by three orders of magnitude. Since the mass enters the eigenenergies in the nominator (see equation (3.3)) one has to make sure that the cutoff is still justified. As in the other cases the JARZYNSKI relation holds ($\gamma_J = 1$). Despite the process being that fast, it is in this case again possible to gain work from the expansion of the quantum well.

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Table 4.3.: Results for numerical calculations for linear wall displacements; Average work in adapted units

Reference	Changed Parameter	ΔF	\overline{W}
$T \approx 75\text{K}$	$T \approx 7.5\text{K}$	$-8.56 \cdot 10^{11}$	$7.02 \cdot 10^{11}$
$L = 1.0\text{pm}$	$L(0) = 0.5\text{pm}$	$-1.75 \cdot 10^{15}$	$3.32 \cdot 10^{15}$
$M \approx 1.05 \cdot 10^{-22}\text{kg}$	$M \approx 1.05 \cdot 10^{-25}\text{kg}$	$-8.56 \cdot 10^{14}$	$-2.15 \cdot 10^{14}$

4.6.4. Adiabatic Behaviour

Here we want to investigate the adiabatic behaviour of the quantum well. Adiabatic means, that no transitions between different states take place throughout the whole process. Since the energy difference of neighbouring energy levels rises for higher n , one could suppose that the transition probability for higher energy levels would decline. This is not the case as we will see in the following. For the adiabatic condition we used (see [34])

$$\max_{0 \leq t \leq T^*} \left| \frac{\langle k | \dot{\hat{H}} | n \rangle}{g_{nk}} \right| \ll \min_{0 \leq t \leq T^*} |g_{nk}|, \quad n \neq k \text{ with } g_{nk} \equiv \varepsilon_n - \varepsilon_k \quad (4.10)$$

with T^* being the total evolution time which is not to be confused with temperature T .

Analytical Results

For now, we want to concentrate on linear wall displacements (see 4.6.1). After a lengthy but straightforward calculation (see appendix A.4) one arrives at the following adiabatic condition for $k > n$:

$$\max \left(\frac{nk}{k^2 - n^2} v \right) \ll \min \left(\frac{k^2 - n^2}{(L + vt)^2} \right) \quad (4.11)$$

where we have suppressed constant parameters since we are interested in qualitative results only. As one can easily see, the most constraining condition on the velocity of the wall displacement for adiabatic processes is set by the upper energy levels, since the maximum is reached for $n \rightarrow k$ and $n, k \rightarrow \infty$. This means that the upper energy levels react more 'sensitive' to the perturbation and are responsible for non-adiabatic behaviour (see figure 4.6 for a numerical example). The higher the energy level, the more constraining the condition for the time of the perturbation. The product of perturbation velocity and time should be very small.

More general, one easily sees from appendix A.4 that independent of the specific realization of the process, the higher energy levels are more unstable:

$$\max_{0 \leq t \leq T} \left| \frac{nk \dot{L}(t)}{L(t)(n^2 - k^2)} \right| \ll \min_{0 \leq t \leq T} \left| \frac{\pi^2}{2ML^2(t)} (n^2 - k^2) \right| \quad (4.12)$$

The maximum and minimum, respectively, may be reached at other times than that mentioned above, but since we are not interested in details, one can say that for the

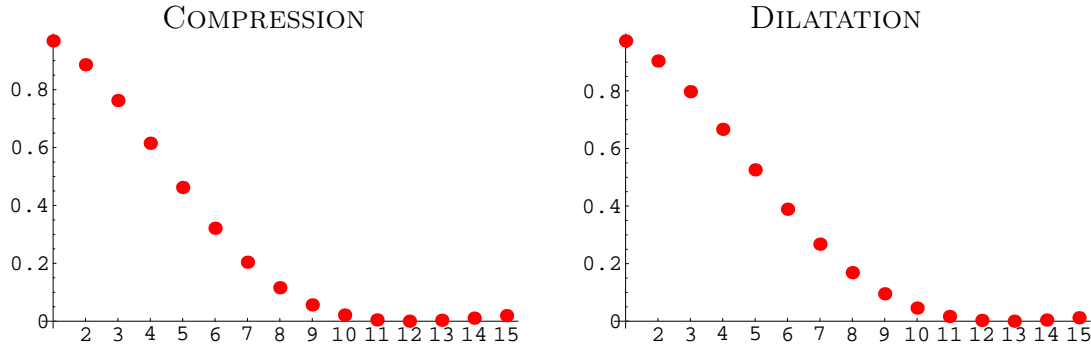


Figure 4.6.: Numerical results for adiabatic behaviour of the quantum well. The x-axis denotes the energy level n and the y-axis the probability for ending up in this same state as started in. Linear displacements with $v = 1 \cdot 10^{10}$, $L(t) = 1.1L(0)$ and $L(t) = 0.9L(0)$ were chosen. Cutoff at $n = 20$

quantum well, the most stable energy levels are the lowest ones. So, if we chose a very low temperature and thus only states with small n are occupied, we have the best chance to enforce a process which is adiabatic. This can be seen by comparing the results for the average amount of work required to expand the quantum well with the very high velocity $v = 1 \cdot 10^{16}$ (c.f. tabulars 4.3 and 4.1). The work required at low temperatures is about an order of magnitude lower than that compared to the higher temperature.

Numerical Results

We may choose any process we like and calculate the time evolution numerically. Then, with the help of the conditional transition matrix, we can evaluate the probability of the particle in the well to end up in the same energy level it started in. In figure 4.6, the results for an expansion of the well with the initial conditions (4.8) can be found. They are in perfect accordance with our analytical results. There is almost no difference between the compression and expansion.

We want to stress, that we are only interested in the initial and final states. No measurement is performed during the whole process. So, for our purpose, we would call a process adiabatic even if the particle had left its initial state somewhere during the process but jumped back again, so that its final state coincides with its initial one. So, adiabatic in our sense does not mean that the particle remained in the same energy level throughout the process. Note, that this point of view is restricted to the numerical study only and does not apply to the analytic one.

4.7. Coulomb Potential

Now the Coulomb potential as described in chapter 3 section 3.3 is studied. We study increments and decrements as well as cyclic perturbations of the central charge. Here a cyclic perturbation is meant to have the same charge before and after the process, thus

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satisfying $Z(t) = Z(0)$. At the end of this section, the adiabatic behaviour of this model is investigated.

Throughout this section, we use adapted units, such that the relations (2.1) hold. We define the adapted unit of time as $1s' \equiv 1s$, so we automatically have for the adapted unit of energy $1J' \equiv 1.055 \cdot 10^{-34}J$. The adapted unit of temperature is the same as above. For simpler calculations, we furthermore chose the adapted unit of mass to be $1kg' \equiv 9.109 \cdot 10^{-31}kg$, the mass of the unmoving electron. This immediately gives for the new measure of length $1m' \equiv 0.0108m$. Finally, we define our new measure of charge to be $1C' \equiv 1.602 \cdot 10^{-19}C$, the elementary charge. This gives for $\varepsilon_0 = 6.34 \cdot 10^{-29} \frac{F'}{m'}$.

4.7.1. Linear Changes

For a start we want to consider changes of the central charge which have the form:

$$Z(t) = Z(0) (1 \pm vt) \quad (4.13)$$

where \pm indicates an increase or decrease of the central charge respectively. Note that we change the charge continuously, thus disregarding that only elementary charges exist. For our calculations we keep the boundary conditions fixed, solely changing the central charge.

Increase

We get independent of the rate of change

- 110% of initial charge at the end of the process:

$$\begin{aligned} \Delta F &= -2.33 \cdot 10^9 \\ \overline{e^{-\beta W}} &= 2.63 \cdot 10^{50} \\ S_0 &= S_1 \approx 0 \end{aligned}$$

- 200% of initial charge at the end of the process:

$$\begin{aligned} \Delta F &= -3.32 \cdot 10^{10} \\ \overline{e^{-\beta W}} &= 1.89 \cdot 10^{720} \\ S_0 &= S_1 \approx 0 \end{aligned}$$

with the initial conditions:

$$Z(0) = 1e, T \approx 300K, \text{ and } m \approx 9.11 \cdot 10^{-31}kg \quad (4.14)$$

with e denoting the elementary charge. We recognize that this equals a hydrogen atom at room temperature. Details can be found in tabular 4.4. The trend is that the faster the process the higher the relative variance of work and the less energy can be gained.

We can see, that for slow changes we approximately have $\overline{W} = \Delta F$. For the very slow increase of 100%, the energy gain was calculated to $\Delta E \approx 40eV$. This value is now

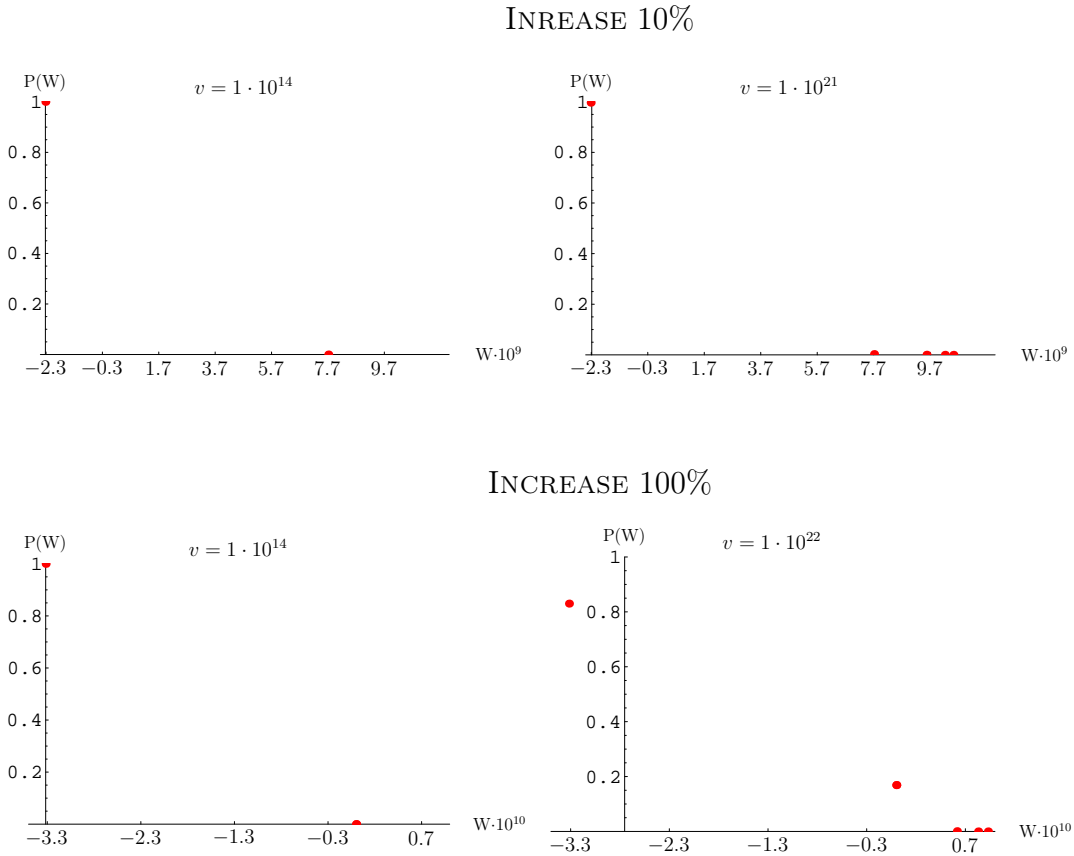


Figure 4.7.: Numerical results for linear increase of central charge with different velocities. Here, the work distribution is shown (see 2.3.4). The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 5$

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Table 4.4.: Numerical results for the coulomb potential; cutoff at $n = 5$; Average work in adapted units

Δt	Increase 10%		Increase 100%		Decrease 10%	
	\overline{W}	$ \frac{\delta W}{\overline{W}} $	\overline{W}	$ \frac{\delta W}{\overline{W}} $	\overline{W}	$ \frac{\delta W}{\overline{W}} $
$1 \cdot 10^{-13}$	$-2.32 \cdot 10^9$	≈ 0	$-3.32 \cdot 10^{10}$	≈ 0	$2.10 \cdot 10^9$	≈ 0
$1 \cdot 10^{-15}$	$-2.32 \cdot 10^9$	0.02			$2.10 \cdot 10^9$	0.02
$1 \cdot 10^{-16}$			$-3.11 \cdot 10^{10}$	0.26		
$1 \cdot 10^{-22}$	$-2.28 \cdot 10^9$	0.28	$-2.75 \cdot 10^{10}$	0.45	$2.13 \cdot 10^9$	0.22

compared to the positively charged helium ion He^+ , since at the end of this process we arrive at such an ion. Due to the low temperature in the beginning almost only the ground state was occupied and a very slow process should not allow any transitions. So, we should be able to gain the ground energy difference of the hydrogen atom and the positively charged helium ion. This energy difference is in fact $\Delta E_{\text{ground states H and He}^+} \approx 40.8\text{eV}$ [33] and thus very near to the result above.

Note, that as mentioned above, almost only the ground state is occupied in the beginning. This means, our initial state, which is a canonical one, very much resembles a pure state. So, for very slow processes, we expect the variance of work to vanish (see A.1).

Figure 4.7 shows the work distributions for different process velocities with initial conditions as in (4.14). The work distribution for slow processes is a delta peak at the average work as predicted. In the case of a 10% increase, even for a relatively fast change the work distribution resembles closely a delta peak. In the case of 100% increase, we have a relatively high probability of paying no work. This is due to a transition from $n = 1 \rightarrow n = 2$ while doubling the central charge, leaving the energy of the particle constant. The process time is the same for $v = 1 \cdot 10^{21}$ and $v = 1 \cdot 10^{22}$ for the increase of 10% and 100% respectively. The left diagrams feature the same process velocity which means, that the process time is an order of magnitude larger for the 100% increase.

If one chooses a higher temperature in the beginning, the work distribution is no longer a delta peak even for slow processes as it should be for a canonical state. Numerical results can be found in figure 4.8.

Decrease

We choose the same initial conditions as in (4.14) and get independent of the velocity v for $Z(t) = 0.9Z(0)$

- $\Delta F = 2.10 \cdot 10^9$
- $\overline{e^{-\beta W}} = 2.41 \cdot 10^{-46}$
- $S_0 = S_1 \approx 0$

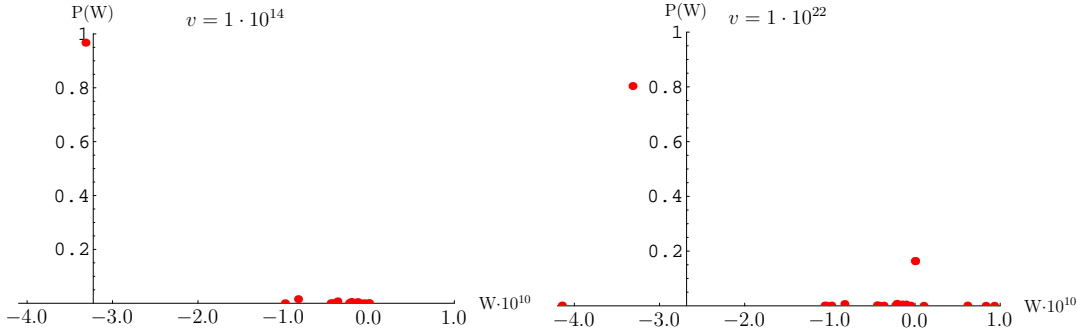


Figure 4.8.: Numerical results for linear increase of central charge with different velocities. The temperature is chosen two orders of magnitude higher than the usual initial conditions. Here, the work distribution is shown (see 2.3.4). The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 5$

For details see tabular 4.4. We can see that the faster the process, the higher the relative variance of work and the more work is required to perform the process. For slow processes the needed amount of energy can be calculated to approximately 2.5eV. This is the loss of the binding energy of the electron. It is still much lower than the energy of the ground state of the hydrogen atom $E_{\text{ground state } H} = 13.6\text{eV}$ [33].

The numerical result for the work distribution (initial conditions as in 4.14) can be found in figure 4.9 for different velocities of changes and different temperatures. In the low temperature case, almost only the ground state is occupied. So, the distribution of work is almost sharp. For higher temperatures (two order of magnitudes higher than low temperature) the distribution of work is smeared out a little bit.

4.7.2. Exponential Changes

In this section we consider exponential changes of the central charge:

$$Z(t) = Z(0)e^{\pm\lambda t} \quad (4.15)$$

with λ being a positive constant and the sign of the exponential determining whether the charge is increased or decreased respectively. The same initial conditions as in (4.14) are used. So, we expect these changes to produce the same results for the free energy difference and the average $\overline{e^{-\beta W}}$ as the linear ones in section 4.7.1. This is actually the case, and independent of the parameter λ the JARZYNSKI relation is verified ($\gamma_J = 1$). For detailed results see table 4.5. The faster the process, the more inefficient it gets.

The distribution of work is shown in figure 4.10. The initial conditions for this calculation were chosen as in (4.14). The distribution of work looks very similar to the one of the linear increases.

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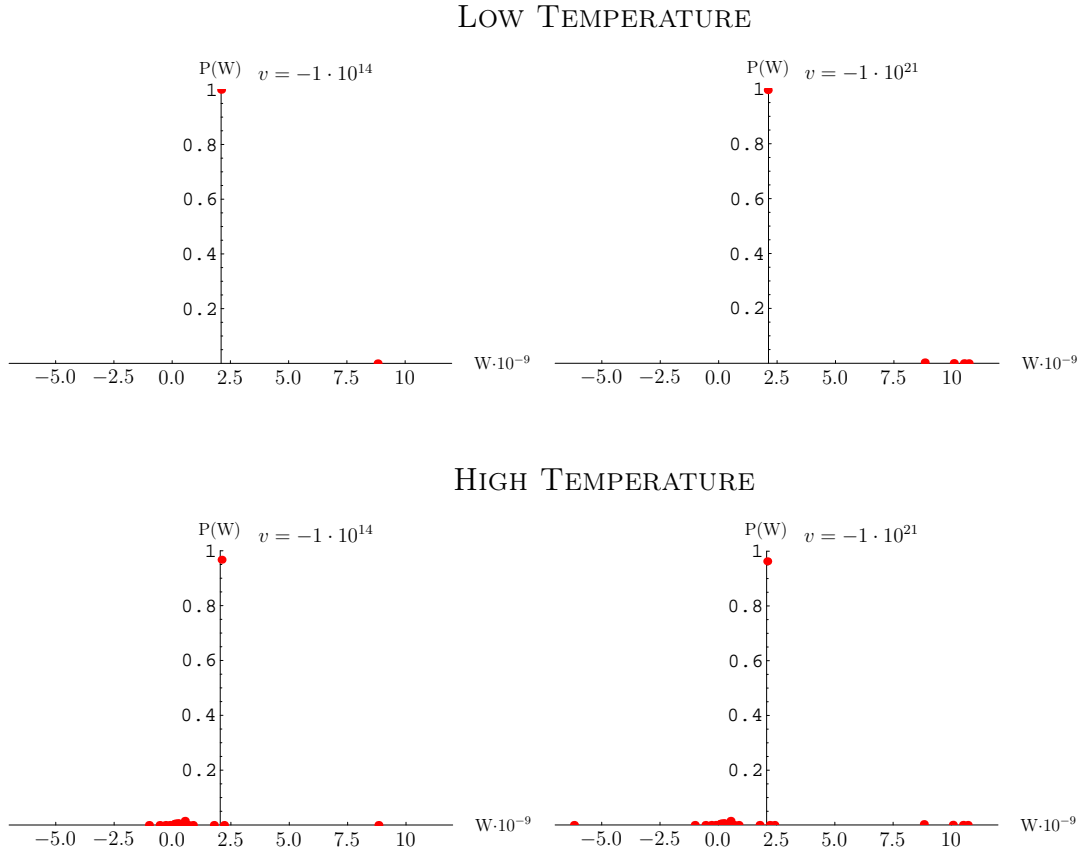


Figure 4.9.: Numerical Results for linear decrease of central charge with different velocities and temperatures ($Z(t) = 0.9Z(0)$). Here, the work distribution is shown (see 2.3.4). The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 5$

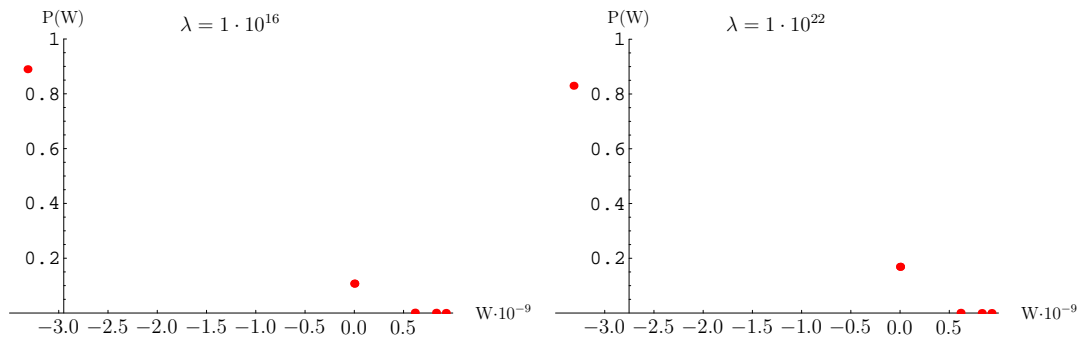


Figure 4.10.: Numerical Results for exponential increase of central charge with different velocities and with $Z(t) = 2Z(0)$ The distribution of work is shown (see 2.3.4). The constant λ is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 5$

Table 4.5.: Numerical results for the Coulomb potential for exponential changes of the central charge; cutoff at $n = 5$; Average work in adapted units

λ	Increase 100%		Decrease 10%	
	$\overline{W} \cdot 10^{10}$	$ \frac{\delta W}{\overline{W}} $	$\overline{W} \cdot 10^9$	$ \frac{\delta W}{\overline{W}} $
$1 \cdot 10^{13}$	-3.32	≈ 0	2.10	≈ 0
$1 \cdot 10^{16}$	-2.95	0.35	2.13	0.22
$1 \cdot 10^{22}$	-2.75	0.45	2.13	0.22

Table 4.6.: Numerical results for the Coulomb potential for cyclic sinusoidal changes of the central charge; $\pm 10\%$; cutoff at $n = 5$; Average work in adapted units

ω	\overline{W}	$ \frac{\delta W}{\overline{W}} $
1	$2.53 \cdot 10^4$	$5.94 \cdot 10^2$
$1 \cdot 10^{17}$	$4.20 \cdot 10^6$	$4.58 \cdot 10^1$
$1 \cdot 10^{20}$	$1.02 \cdot 10^2$	$9.72 \cdot 10^3$

4.7.3. Sinusoidal Changes

Here we study changes of the following form:

$$Z(t) = Z(0) (1 \pm A \sin \omega t) \quad (4.16)$$

Only cyclic perturbations are studied, thus $Z(t) = Z(0)$ and the free energy difference should vanish. The initial conditions were chosen to be the same as in (4.14). Independent of the frequency ω of the perturbation we get $\Delta F \approx 0$ and $e^{-\beta W} \approx 1$. Details can be found in tabular 4.6. The most striking fact is, that for extremely fast perturbations the results are very similar to those for slow changes. This can be explained by the inertia of the system to react to perturbations. The relative variance of work is very high since the average work is very low in these cases.

In figure 4.11 numerical results for the distribution of work can be found. The respective initial conditions used can be found in (4.14). We have chosen processes in which the central charge was first increased by 100% and then decreased to its initial value ($A = 1$).

4.7.4. Adiabatic Behaviour

In this section, the adiabatic behaviour of the coulomb potential will be investigated. Since the distance between neighbouring states declines with bigger n , one expects the higher energy levels to be more unstable. We use the same adiabatic condition as in section 4.6.4 equation (4.10).

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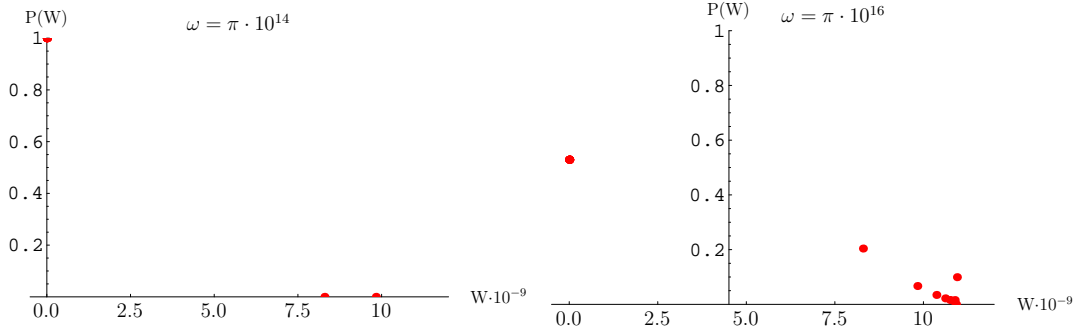


Figure 4.11.: Numerical results for cyclic processes with different velocities and with $Z(\frac{t}{2}) = 2Z(0)$. The distribution of work is shown (see 2.3.4). The frequency ω is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 10$

Analytical Results

Using the adiabatic condition, one arrives at (for details see appendix A.5)

$$\max | \frac{f_{nk}(a)n^2}{1-a^2} | \ll \min | \left(\frac{1}{n^2} - \frac{1}{k^2} \right) | \quad (4.17)$$

with $n > k$ w. l. o. g.. Here, $f_{nk}(a)$ is a monotone decreasing function of a ($a \equiv \frac{n}{k}$), and it is proportional to n^{-2} . The extrema are reached for $k \rightarrow n$ and n maximal (ionization level). For a more detailed discussion see appendix A.5. This is similar to the above case of the quantum well (section 4.6.4 page 32).

Numerical Results

For our understanding of *adiabatic* goes the same as said in section 4.6.4 page 33. We studied a linear increase (see section 4.7.1) of the central charge with a cutoff at $n = 10$. As predicted, the higher the state number, the less stable it is (see figure 4.12).

4.8. Conclusions

The numerical results are in perfect accordance with the JARZYNSKI relation. The free energy difference is independent of the particular realization of the process. It depends solely on the initial and final conditions. Most expectations are met, meaning on average we have to pay work in order to compress the quantum well or decrease the central charge of the coulomb potential, respectively, but there is always the slight chance for a single realization to gain work counter-intuively. The faster the process, the more work has to be paid, the distribution function of work getting wider.

These results present a good reference for further investigations for these model systems coupled to an environment. For an extremely weak coupling parameter the new results will have to reduce to those without an environment.

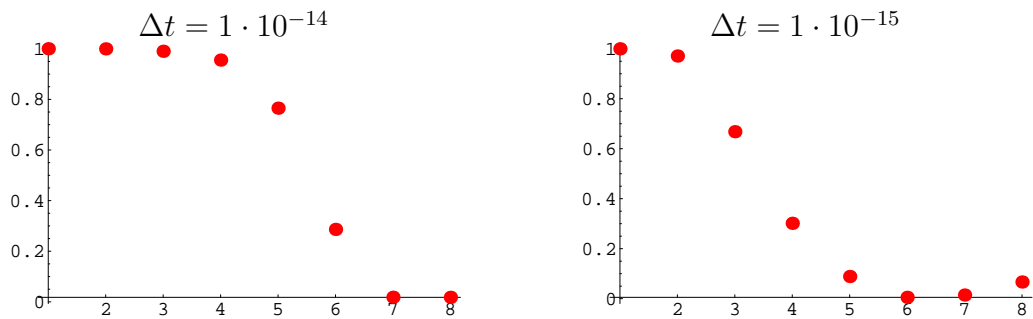


Figure 4.12.: Numerical results for adiabatic behaviour of the coulomb potential. The x-axis denotes the energy level n and the y-axis the probability for ending up in this same state as started in. Linear displacements with $Z(t) = 1.5Z(0)$ were chosen. Cutoff at $n = 10$. The probability for $n = 8$ is a numerical error due to the cutoff.

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5. Closed Systems - Microcanonical Coupling

5.1. Overview

In this chapter, closed systems which are coupled microcanonically [3] to an environment are studied. It will be investigated, if the JARZYNSKI relation still holds in this scenario. First, a short introduction to *microcanonical coupling* will be given since this type of coupling is not commonly known. Then, an analytical proof will be given that the relation has to hold even for arbitrary strong coupling. In the last section, a numerical verification will be given using our model system from above (section 3.2) but now coupled to an environment.

5.2. What is Microcanonical Coupling?

Microcanonical coupling is a special type of coupling inherent to quantum dynamics [3]. It means that the closed system can interact with the environment without exchanging particles or energy. The expectation values of both subsystems have to be constant:

$$\langle \hat{H}^{\text{sys}} \rangle = \text{const.}, \quad \langle \hat{H}^{\text{env}} \rangle = \text{const.} \quad (5.1)$$

Thus, they have to be a constant of motion:

$$\left[\hat{H}^{\text{sys}}, \hat{H} \right] = 0, \quad \left[\hat{H}^{\text{env}}, \hat{H} \right] = 0 \quad (5.2)$$

The complete hamiltonian can be written as follows:

$$\underbrace{\hat{H}^{\text{sys,env}}}_{\text{compound}} \equiv \underbrace{\hat{H}^S \otimes \hat{1}^C}_{\text{system}} + \underbrace{\hat{1}^S \otimes \hat{H}^C}_{\text{environment}} + \underbrace{\hat{H}^I}_{\text{interaction}} \quad (5.3)$$

or using the short-hand notation of operators introduced in section 2.4.6 page 13:

$$\hat{H} = \hat{H}^S + \hat{H}^C + \hat{H}^I \quad (5.4)$$

Since the hamiltonians of the two subsystems, acting only in their subspace respectively, obviously commute with each other, it immediately follows from (5.4) and (5.2) that

$$\left[\hat{H}^S, \hat{H}^I \right] = 0, \quad \left[\hat{H}^C, \hat{H}^I \right] = 0 \quad (5.5)$$

5. Closed Systems - Microcanonical Coupling

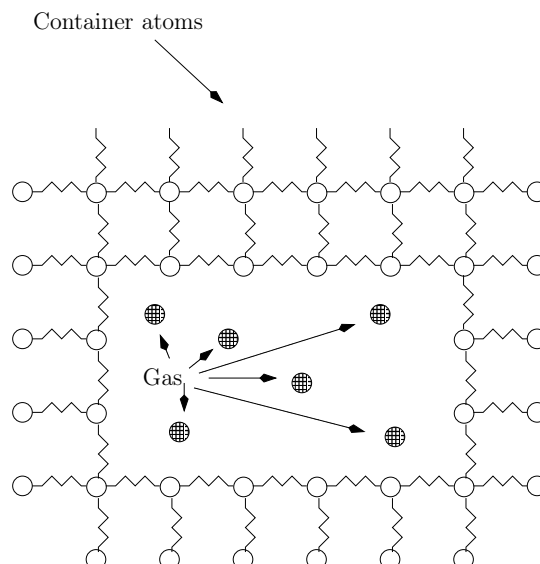


Figure 5.1.: Model system for illustration of microcanonical coupling. The gas atoms interact with the atoms of the container, thus creating entanglement. If they did not interact with the wall atoms, they would leave the container, and the system would not be closed.

This is another form of the microcanonical condition. The overall energy has to be conserved, and since both subsystems conserve their energies, the interaction has to do the same. What is still possible and will in general happen is, that the system and the environment get entangled. This situation is not known in classical physics but it is important for closed systems (see section 5.2.1). This makes this sort of coupling particularly interesting if one wants to investigate whether a known classical relation still holds in the quantum regime.

5.2.1. Realistic or Artificial Coupling?

One could be tempted to think of microcanonical coupling as an artificial coupling without any practical justification. Here, we try to show that this is not the case. Consider, e. g., a model system as in figure 5.1 [3]. A gas (system) trapped in a closed container (environment). The gas is not allowed to exchange energy with the container, and since it is closed, no particle should leave it. If there was no interaction between the gas and the container at all, the gas atoms would leave the container unhindered. So, there has to be an interaction and this causes entanglement inevitably. This is stringently a microcanonical coupling scenario. Furthermore, it could be shown that this type of coupling damps away off-diagonal elements of the density operator $\hat{\rho}$ increasing the VON-NEUMANN entropy [35].

5.3. Analytical Study

Here, a proof will be given for the JARZYNSKI relation in the quantum regime for arbitrarily strong microcanonical coupling. The coupling should however be not that strong, that a clear partition between system and environment is no longer possible. We require the whole system, consisting of two subsystems which couple microcanonically, to be closed. Our working process acts only on subsystem 1, thus the hamiltonian for the subsystem 2 is not explicitly time-dependent. We will now call subsystem 1 the system, which is not to be confused with the whole, compound system, and subsystem 2 the environment or container. Our complete hamiltonian thus reads in short-hand notation:

$$\hat{H}(t) = \hat{H}^S(t) + \hat{H}^C + \hat{H}^I \quad (5.6)$$

Since the hamiltonian of the system acts in a different subspace than that of the environment one trivially has

$$\left[\hat{H}^S(t), \hat{H}^C \right] = 0 \quad (5.7)$$

Here, the expectation value of the environmental hamiltonian has to be constant, thus it is a constant of motion (c. f. (5.2)):

$$0 \stackrel{!}{=} \left[\hat{H}(t), \hat{H}^C \right] \stackrel{(5.7)}{=} \left[\hat{H}^I, \hat{H}^C \right] \quad (5.8)$$

From that we easily obtain (c. f. (5.5)):

$$0 \stackrel{!}{=} \left[\hat{H}(t), \hat{H}^I \right] \stackrel{(5.6)}{=} \left[\hat{H}^S(t) + \hat{H}^C, \hat{H}^I \right] \stackrel{(5.8)}{=} \left[\hat{H}^S(t), \hat{H}^I \right] \quad (5.9)$$

The following proof is based on a closed system. The idea is, that for closed quantum systems, there already exists a proof which can possibly be generalized to our system. Here, the system and environment together represent a closed system whose time evolution is deterministic and can thus be described by a time evolution operator (see section 2.4.4). Now, the result of MUKAMEL (see section 2.7) is used, thus we require the compound system to start in a canonical state with a well defined temperature T . Considering the system as a whole, it is already proven that the following relation holds:

$$\overline{e^{-\beta W}} = \frac{Z^{(1,2)}(t)}{Z^{(1,2)}(0)} \quad (5.10)$$

The indices for the partition sum indicate that the partition sum of the compound system is meant. In the following, they will be omitted if the complete system is concerned. Now, the fraction of these two partition sums is investigated and we try to separate the sums into their system and environment share because we are, of course, only interested in the free energy change of the system and not in that of the environment or of the compound system. From section 2.4.7 equation (2.48) we know:

$$Z(t) = \text{Tr} \left(e^{-\beta \hat{H}(t)} \right) \stackrel{(5.6)}{=} \text{Tr} \left(e^{-\beta (\hat{H}^S(t) + \hat{H}^C + \hat{H}^I)} \right) \quad (5.11)$$

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We exploit the commutator relations (5.7), (5.8) and (5.9) in order to expand the exponential function. We furthermore use the cyclic property of the trace, meaning that cyclic permutations of operators are allowed:

$$\begin{aligned}\mathrm{Tr}\left(e^{-\beta(\hat{H}^S(t)+\hat{H}^C+\hat{H}^I)}\right) &= \mathrm{Tr}\left(e^{-\beta\hat{H}^S(t)\otimes 1^C} e^{-\beta\hat{1}^S\otimes\hat{H}^C} e^{-\beta\hat{H}^I}\right) \\ &= \mathrm{Tr}\left(e^{-\beta\hat{H}^S(t)} \otimes e^{-\beta\hat{H}^C} e^{-\beta\hat{H}^I}\right)\end{aligned}\quad (5.12)$$

With the help of equation (2.47) we can rewrite this:

$$\mathrm{Tr}\left(e^{-\beta\hat{H}^S(t)} \otimes e^{-\beta\hat{H}^C} e^{-\beta\hat{H}^I}\right) = \mathrm{Tr}\left(\varrho_{\mathrm{can}}^S(t) \otimes \varrho_{\mathrm{can}}^C e^{-\beta\hat{H}^I}\right) Z^S(t)Z^C \quad (5.13)$$

with the two canonical density operators for the system and the environment respectively. We used the identity $\mathrm{Tr}(Z) = Z$ which follows immediately from the definition of the partition sum equation (2.48).

If there was no interaction at all or if it was that weak that one could neglect even first order terms, one would readily arrive at the desired result:

$$\begin{aligned}\mathrm{Tr}\left(\varrho_{\mathrm{can}}^S(t) \otimes \varrho_{\mathrm{can}}^C e^{-\beta\hat{H}^I}\right) Z^S(t)Z^C &\approx \mathrm{Tr}\left(\varrho_{\mathrm{can}}^S(t) \otimes \varrho_{\mathrm{can}}^C\right) Z^S(t)Z^C \\ &= \mathrm{Tr}\left(\varrho_{\mathrm{can}}^S(t)\right) \cdot \mathrm{Tr}\left(\varrho_{\mathrm{can}}^C\right) Z^S(t)Z^C \\ &\stackrel{(2.36)}{=} Z^S(t)Z^C\end{aligned}\quad (5.14)$$

since the trace of the density operators equals 1. So one would arrive at

$$\frac{\quad}{e^{-\beta W}} \stackrel{(5.10)}{=} \frac{Z^{(1,2)}(t)}{Z^{(1,2)}(0)} \stackrel{(5.14)}{=} \frac{Z^{(1)}(t)Z^{(2)}}{Z^{(1)}(0)Z^{(2)}} = \frac{Z^{(1)}(t)}{Z^{(1)}(0)} \stackrel{(2.50)}{=} e^{-\beta\Delta F^{(1)}} \quad (5.15)$$

which is the quantum JARZYNSKI relation for the system only. This result was necessary for vanishing coupling and can be thought of to be a consistency check, because without interaction the two subsystems are not able to see each other and so we have a situation equal to a single existing closed system as considered by MUKAMEL.

We now go back to the situation with arbitrarily strong coupling. We want to calculate the fraction of the partition sum before and after the process:

$$\frac{Z(t)}{Z(0)} \stackrel{(5.13)}{=} \frac{\mathrm{Tr}\left(\varrho_{\mathrm{can}}^S(t) \otimes \varrho_{\mathrm{can}}^C e^{-\beta\hat{H}^I}\right) Z^S(t)Z^C}{\mathrm{Tr}\left(\varrho_{\mathrm{can}}^S(0) \otimes \varrho_{\mathrm{can}}^C e^{-\beta\hat{H}^I}\right) Z^S(0)Z^C} \quad (5.16)$$

If the trace in the denominator would equal that of the numerator, we would immediately arrive at the desired result since the Z^C cancel. This is obviously the case for cyclic processes, because there we have:

$$\hat{H}(t) \stackrel{\mathrm{closed}}{=} \hat{H}(0) \implies \varrho_{\mathrm{can}}^S(t) \otimes \varrho_{\mathrm{can}}^C = \varrho_{\mathrm{can}}^S(0) \otimes \varrho_{\mathrm{can}}^C \quad (5.17)$$

So, for cyclic perturbations, the JARZYNSKI relation is also valid for microcanonically coupled systems.

In order to prove this for arbitrary processes, we now study the time-dependence of the trace of the numerator:

$$\frac{d}{dt} \text{Tr} \left(\varrho_{\text{can}}^S(t) \otimes \varrho_{\text{can}}^C e^{-\beta \hat{H}^I} \right) \stackrel{(\dot{H}^I=0)}{=} \text{Tr} \left(\frac{d}{dt} \left(\varrho_{\text{can}}^S(t) \otimes \varrho_{\text{can}}^C \right) e^{-\beta \hat{H}^I} \right) \quad (5.18)$$

We introduce the following abbreviation:

$$\varrho_{\text{can}}^S(t) \otimes \varrho_{\text{can}}^C \equiv \varrho_{\text{cp}}^{S,C}(t) \quad (5.19)$$

which is motivated by the interpretation as a product state of these two subsystems, being in a canonical state each. Using the LIOUVILLE equation (2.40) we can rewrite (5.18):

$$\text{Tr} \left(\frac{d}{dt} \left(\varrho_{\text{can}}^S(t) \otimes \varrho_{\text{can}}^C \right) e^{-\beta \hat{H}^I} \right) = -i \text{Tr} \left(\left[\hat{H}(t'), \varrho_{\text{cp}}^{S,C}(t) \right] e^{-\beta \hat{H}^I} \right) \quad (5.20)$$

Keep in mind, that the hamilton operator at time t does not commute with the hamilton operator at other times:

$$[\hat{H}(t'), \hat{H}(t)] \neq 0 \quad (5.21)$$

Using the cyclic property of the trace we get:

$$\begin{aligned} \text{Tr} \left(\left[\hat{H}(t'), \varrho_{\text{cp}}^{S,C}(t) \right] e^{-\beta \hat{H}^I} \right) &= \left\{ \text{Tr} \left(\hat{H}(t') \varrho_{\text{cp}}^{S,C}(t) e^{-\beta \hat{H}^I} - \varrho_{\text{cp}}^{S,C}(t) \hat{H}(t') e^{-\beta \hat{H}^I} \right) \right\} \\ &= \left\{ \text{Tr} \left(\varrho_{\text{cp}}^{S,C}(t) e^{-\beta \hat{H}^I} \hat{H}(t') - \varrho_{\text{cp}}^{S,C}(t) \hat{H}(t') e^{-\beta \hat{H}^I} \right) \right\} \\ &= \text{Tr} \left(\varrho_{\text{cp}}^{S,C}(t) [e^{-\beta \hat{H}^I}, \hat{H}(t')] \right) \end{aligned} \quad (5.22)$$

Exploiting the commutator relation (5.9) we finally arrive at:

$$\text{Tr} \left(\varrho_{\text{cp}}^{S,C}(t) [e^{-\beta \hat{H}^I}, \hat{H}(t')] \right) = 0 \quad (5.23)$$

because the hamilton operator for the compound system commutes at any time t with the interaction operator. This means that the trace is constant in time:

$$\frac{d}{dt} \text{Tr} \left(\varrho_{\text{cp}}^{S,C}(t) e^{-\beta \hat{H}^I} \right) = 0 \quad \forall t \implies \text{Tr} \left(\varrho_{\text{cp}}^{S,C}(t) e^{-\beta \hat{H}^I} \right) = \text{const.} \quad (5.24)$$

So, we can rewrite equation (5.16) by cancelling the two constant terms of the trace, leaving only:

$$\frac{Z(t)}{Z(0)} = \frac{Z^S(t)}{Z^S(0)} \quad (5.25)$$

Since the quantum version of the JARZYNSKI relation was already proven by MUKAMEL for closed systems without environment, as mentioned above, we end up with:

$$\overline{e^{-\beta W}} \stackrel{(2.51)}{=} \frac{Z(t)}{Z(0)} \stackrel{(5.25)}{=} \frac{Z^S(t)}{Z^S(0)} = e^{-\beta \Delta F^S} \quad (5.26)$$

This proves that the quantum version of the relation also holds for systems which are coupled microcanonically to an environment.

5.4. Numerical Study

5.4.1. Overview

In this section, we want to verify the analytic result using a slightly modified model of the quantum well with variable width (see section 3.2, figure 3.1). First, a comment on possible consistency checks is made, then, the new model system realizing microcanonical coupling is introduced and the numerical results are presented. They will indeed verify the result above.

5.4.2. Consistency Checks

In order to check our numerical results of the quantum well we use the methods described in section 4.5 for the compound system. For the subsystems exists a slightly different set of consistency checks which will now be compared to those mentioned above:

1. Trace of the reduced density operator: It has to equal one. This can easily be seen by using equations (2.36) and (2.44):

$$\text{Tr}^{(1)}(\varrho^{(1)}) = \text{Tr}^{(1)}\left(\text{Tr}^{(2)}\varrho^{(1,2)}\right) = \text{Tr}(\varrho^{(1,2)}) = 1 \quad (5.27)$$

2. Density Matrix: Of course, the reduced density operators still have to be hermitian.
3. Time evolution operator: For the reduced system, the reduced time evolution operator will in general no longer be a unitary operator. Only that of the compound, closed system has to be unitary.
4. The VON-NEUMANN entropy: It is not constant for the subsystems in general, but it will grow with time if it was zero before. It is a good variable to check whether the environment has any effect upon the system at all. If the system's entropy would be constant, the interaction is most likely too weak to influence the system.
5. Slow changes: Since we start our processes with canonical systems, which have no off-diagonal terms in their density operators in the eigenenergy representation, we would expect the environment to have no effect at all since there are no coherence terms the microcanonical coupling could damp.

We have a further possibility to check our calculations: If we choose a vanishing coupling constant, our new results have to equal the old ones from chapter 4. This can be seen if one computes the time evolution operator for the evolution of our compound system (see section 2.4.4):

$$\hat{U}_0(t, t_0) = e^{-i\hat{T} \int_{t_0}^t d\tau \hat{H}^S(\tau)} \otimes e^{-i\hat{H}^C(t-t_0)} \quad (5.28)$$

The time evolutions of the two subsystems are totally separated, thus, the environment has absolutely no effect on the time evolution of our system. Its behaviour has to equal that of a closed system without environment.

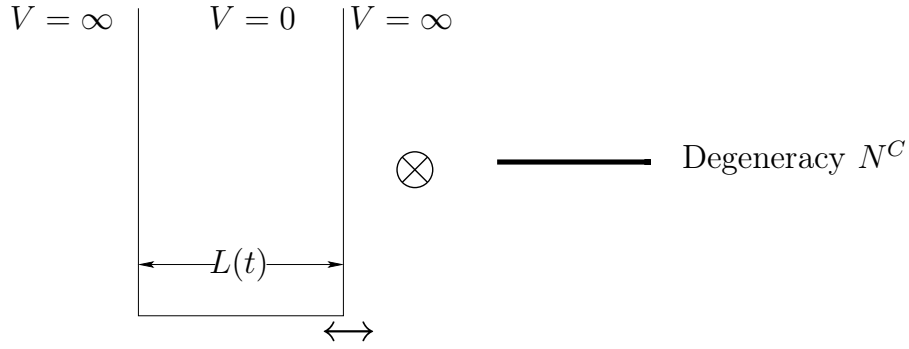


Figure 5.2.: Model system for numerical studies on a quantum well with an environment. The left wall is held fixed, the right wall is moveable w. l. o. g.. We use different numbers of energy levels in the environment. The coupling is microcanonical, the interaction is described by a random hermitian matrix.

5.4.3. Model system for Microcanonical Coupling

As said above, we will use a modified model system for the numerical studies. We couple the quantum well with variable width to an environment, which consists of only one energy level (see figure 5.2). This energy level is highly degenerated thus making the product HILBERT space very large. This sort of environment readily ensures that there will be no energy transfer between the quantum well, our system, and the environment [3]. This is obvious since the environment cannot absorb or emit any energy because it can only make transitions between degenerate states with the same energy. The effect of such environments upon systems coupled microcanonically was shown in [36]. The environment causes decoherence in the reduced density operator of the system.

5.4.4. The Interaction Hamilton Operator

The complete hamiltonian shall be described by equation (5.3). We are going to study the interaction term in the product basis of the eigenenergy basis of the system and environment. Since we do not want to make any special statements but are interested in general ones, we choose the interaction matrix randomly. Nevertheless, it has to be hermitian and the random distribution has to be invariant under unitary transformations [37]. The two requirements are met by distributions of the following form:

$$P(\hat{H}^I) = C e^{-A \text{Tr}\{(\hat{H}^I)^2\}} \quad (5.29)$$

with the constants A and C . The diagonal elements of the interaction matrix have a Gaussian distribution with a standard deviation of $\sigma = \sqrt{2}$:

$$P(\hat{H}_{ii}^I) = \frac{1}{2\sqrt{\pi}} e^{-\frac{1}{4}\hat{H}_{ii}^I} \quad (5.30)$$

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The off-diagonal elements follow also a Gaussian distribution under consideration of the hermiticity:

$$P\left(\Re(\hat{H}_{ij}^I)\right) = \frac{1}{2\sqrt{\pi}} e^{-\frac{1}{4}\Re(\hat{H}_{ij}^I)^2} \quad (5.31)$$

$$P\left(\Im(\hat{H}_{ij}^I)\right) = \frac{1}{2\sqrt{\pi}} e^{-\frac{1}{4}\Im(\hat{H}_{ij}^I)^2} \quad (5.32)$$

We now introduce a sort of normalization in order to have the means to compare different interaction matrices with respect to their strength. We calculate the mean of the elements of the interaction matrix:

$$I \equiv \frac{1}{n} \sqrt{\text{Tr}\left\{(\hat{H}^I)^2\right\}} \quad (5.33)$$

with n being the dimension of the interaction matrix. We then have:

$$\tilde{\hat{H}}^I \equiv \frac{\hat{H}^I}{I} \text{ or } \tilde{\hat{H}}^I \equiv \kappa \hat{H}^I \quad (5.34)$$

with κ denoting the coupling constant. By choosing κ , we can vary the strength of the coupling.

For the microcanonical coupling there exists of course a further condition since no energy transfer between system and environment is allowed. The interaction matrix has block form in this case, each block is distributed as described above. Here, an example for a two level system is given:

$$\hat{H}^I = \begin{pmatrix} \text{Random} & & & & \\ \text{hermitian} & & 0 & & \\ \text{matrix 1} & & & & \\ & & & \text{Random} & \\ & & & \text{hermitian} & \\ & 0 & & \text{matrix 2} & \end{pmatrix} \quad (5.35)$$

The random matrix is of dimension $2 \times n$ with n being the dimension of the environment. In general, the block random matrices have dimension $n_{\text{sys}} \times n_{\text{env}}$ with the dimension of the system and environment respectively. This special form ensures that no energy is exchanged between the two subsystems.

5.4.5. Numerical Results

Overview

For the numerical calculations we restricted ourselves to linear wall displacements as introduced in section 4.6.1 on page 26. Here, we are facing a new problem: We can still choose any velocity v we like and the JARZYNSKI relation has to hold, but if we want to

see any difference between our new model system and the old one without environment, the process has to be slow enough so that the environment has a good chance to interact with the quantum well. On the other hand, if the process is very slow, we will get no transitions, thus no coherence terms, and as said above, there would be nothing for the environment to damp. So, in this case, there would also be no difference between our new system and the old one (This was of course verified by numerical tests). This means, we have to choose our process velocity v appropriately. Keep in mind that this does not mean that for other velocities v we would get deviations from the JARZYNSKI relation, which is not the case, but that we would have no influence from our environment.

In order to give our environment more time to interact with the system, we divide the process in three steps: First, we dilate the quantum well in time Δt_1 , then, we wait a certain time interval Δt_2 doing nothing, and then we go on dilating or compressing with the same velocity for the same time span as in step one. Our initial conditions are the same as in section 4.6.1 page 26 (4.8).

All other parameters were changed and the behaviour of the system investigated. We have two more parameters than in our old model since we can change the coupling strength and the number of the degenerated energy levels of the environment. This number should be relatively high for the environment to have an observable effect.

Environment Tests

Before starting the numerical tests, a short study on the behaviour of the environment is made. The idea is to get a feeling for useful parameters for the degeneracy of the environmental energy level and the order of magnitude of waiting time. For this study, a two level system is chosen. We investigate the entropy in order to decide whether the environment acts as we wish or not. For a given density operator matrix, the environment should be able to maximize the entropy by damping away all off-diagonal elements. So, if we start with a canonical state, the environment will do nothing since there are no off-diagonal elements in the eigen-energy basis which could be damped away. The non-diagonal elements have to remain constant! This is a consequence of the microcanonical coupling. To be more concrete, we chose the initial density operator matrix in the eigen-energy basis to be:

$$\varrho_0 = \begin{pmatrix} 0.150 & 0.357 \\ 0.357 & 0.850 \end{pmatrix} \quad (5.36)$$

It has to be hermitian and the trace has to equal one which is fulfilled here. The energy difference between the two levels is $\Delta E = 1.48 \cdot 10^{13}$. The maximal entropy is supposed to be obtained after waiting time [35]

$$\Delta t \approx \frac{10}{\Delta E} \stackrel{\text{here}}{\approx} 1 \cdot 10^{-12} \quad (5.37)$$

This entropy should equal $S_{\max} = 0.423$ for vanishing off-diagonal elements.

This two level system is now coupled to a one-level environment with the coupling constant $\sigma = 0.01$. Detailed results can be found in tabular 5.1. As one can see,

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Table 5.1.: Numerical results for testing the environment. N^C denotes the number of degenerated energy levels of the environment, Δt the total evolution time and S_{final} the final entropy

N^C	Δt	S_{final}
50	10^{-12}	0.189
	10^{-11}	0.406
	10^{-10}	0.419
25	10^{-12}	0.145
	10^{-11}	0.417
	10^{-10}	0.419
10	10^{-12}	0.060
	10^{-11}	0.379
	10^{-10}	0.390

Table 5.2.: Numerical results for a quantum well coupled microcanonically to an environment; cutoff at $n = 5$; number of energy levels in the environment $N^C = 50$; coupling strength σ (0 for old model without environment); $S_{\text{end}}^{\text{sys}}$ denotes the entropy of the quantum well at the end of the process

velocity v	\overline{W}	$ \frac{\delta W}{\overline{W}} $	$S_{\text{end}}^{\text{sys}}$	σ
$5 \cdot 10^{11}$	$7.12 \cdot 10^{11}$	8.00	0.652	0.01
$5 \cdot 10^{11}$	$7.12 \cdot 10^{11}$	8.07	0.655	0.02
$5 \cdot 10^{11}$	$7.12 \cdot 10^{11}$	8.12	0.556	0
$5 \cdot 10^{08}$	$4.12 \cdot 10^{11}$	9.69	0.590	0.01
$5 \cdot 10^{08}$	$4.12 \cdot 10^{11}$	8.94	0.599	0.02
$5 \cdot 10^{08}$	$4.12 \cdot 10^{11}$	9.82	0.556	0

the maximal entropy is almost obtained after a waiting time of $\Delta t = 1 \cdot 10^{-11}$ if the environment is not very small (meaning only few degenerate levels). A general trend can be extracted: The longer the waiting time and the larger the environment, the bigger the final entropy. This is what one would have expected.

Cyclic Perturbations

We start with perturbations for which $\hat{H}(t) = \hat{H}(0)$ as described above. We chose Δt_1 such that the maximal width $L_{\text{max}} = 1.1 L(0)$ and $\Delta t_2 = 1 \cdot 10^{-11}$. The VON-NEUMANN entropy of the initial state of our system is $S_{\text{start}}^{\text{sys}} = 0.556$. The JARZYNSKI relation is valid for arbitrary process velocities. Detailed results can be found in tabular 5.2 including a comparison with our old model without environment. Independent of the realization of the process, we have $\Delta F^{\text{sys}} \approx 0$.

For this kind of process, the average work is, within our numerical accuracy, unaffected

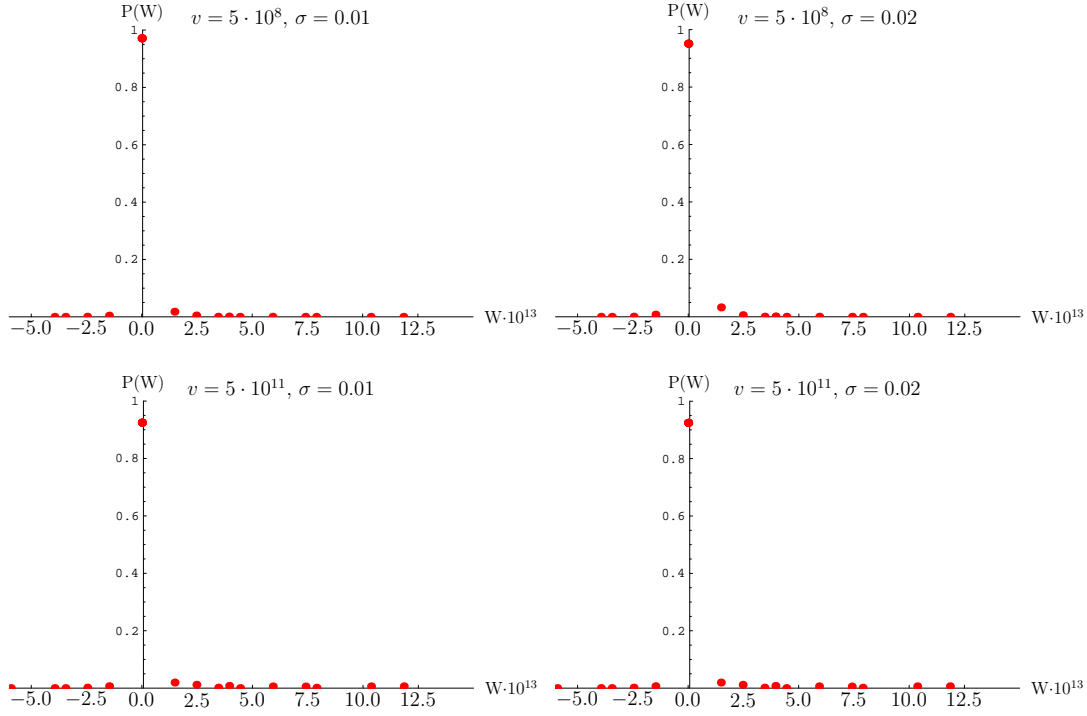


Figure 5.3.: Numerical results for the distribution of work (see 2.3.4) with $\Delta t_2 = 10^{-11}$ and $N^C = 50$. The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 5$

by the environment. That it influences the quantum well nevertheless, can be seen by the VON-NEUMANN entropy which is no longer constant but grows with the process. The faster process requires more work in average. No relation between the relative variance and strength of coupling could be deduced from this data.

Results for the distribution of work, using initial conditions as in (4.8), can be found in figure 5.3. We used such cyclic perturbations for which the well is first dilated and then compressed again to its initial width with $L(\frac{t}{2}) = 2L(0)$.

Expansions

We now turn to expansions in two steps as described above. We vary the coupling strength, the degeneracy of the environment and the velocity of the expansion. We always end up with a quantum well of double width we started with: $L(t) = 2 L(0)$. The waiting time is $\Delta t_1 = 1 \cdot 10^{-11}$ (see page 52). Detailed results can be found in table 5.3. The distribution of work is shown in figure 5.4. Independent of the special realization of the process, we have $\Delta F^{\text{sys}} = -9.70 \cdot 10^{12}$ and since we chose the initial conditions as in (4.8) we have $S_{\text{initial}}^{\text{sys}} = 0.556$. This means that the JARZYNSKI relation was verified numerically. We obtained, independent of the specific realization of a process, for the test factor $\gamma_J = 1$ which means, the JARZYNSKI relation is valid. As one can see by comparison with the closed system, the entropy is no longer constant. The average work

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Table 5.3.: Numerical results for a quantum well coupled to an environment of dimension N^C ; cutoff at $n = 5$; coupling strength σ

velocity v	$\overline{W} \cdot 10^{12}$	$ \frac{\delta W}{W} $	$S_{\text{final}}^{\text{sys}}$	N^C	σ
$1 \cdot 10^{10}$	1.21	10.3	1.19	50	0.01
	-0.46	21.9	1.11	50	0.02
	1.21	8.73	0.556	0	0
$1 \cdot 10^9$	-5.76	1.03	0.610	50	0.01
	-5.80	1.02	0.611	75	
	-5.75	1.03	0.617	100	
	-5.77	1.02	0.627	150	
$1 \cdot 10^9$	-5.74	1.04		50	0.02
	-5.72	1.02	0.652	75	
	-5.63	1.05	0.685	100	
$1 \cdot 10^9$	-5.76	1.06	0.556	0	0

performed on the system is only slightly different with an environment coupled to the quantum well. For the relatively fast perturbation it is necessary to pump work into the system in order to perform the process. Only with a relatively strongly coupled environment, it is possible to gain work. The variance of work is in the relatively slow case ($v = 1 \cdot 10^9$) always smaller if the quantum well is coupled to an environment.

For numerical results of the distribution of work see figure 5.4. We compare the distribution in dependence of the degeneracy of the environment and the coupling strength. For no environment at all, the distribution of work looks different from the other cases. But the difference between $N^C = 50$ and $N^C = 150$ cannot be seen easily as it is almost negligible. The increase of the coupling constant σ does not change much, also. This verifies our environment tests. A degeneracy of $N^C = 50$ with a coupling constant of $\sigma = 0.01$ seems to be enough.

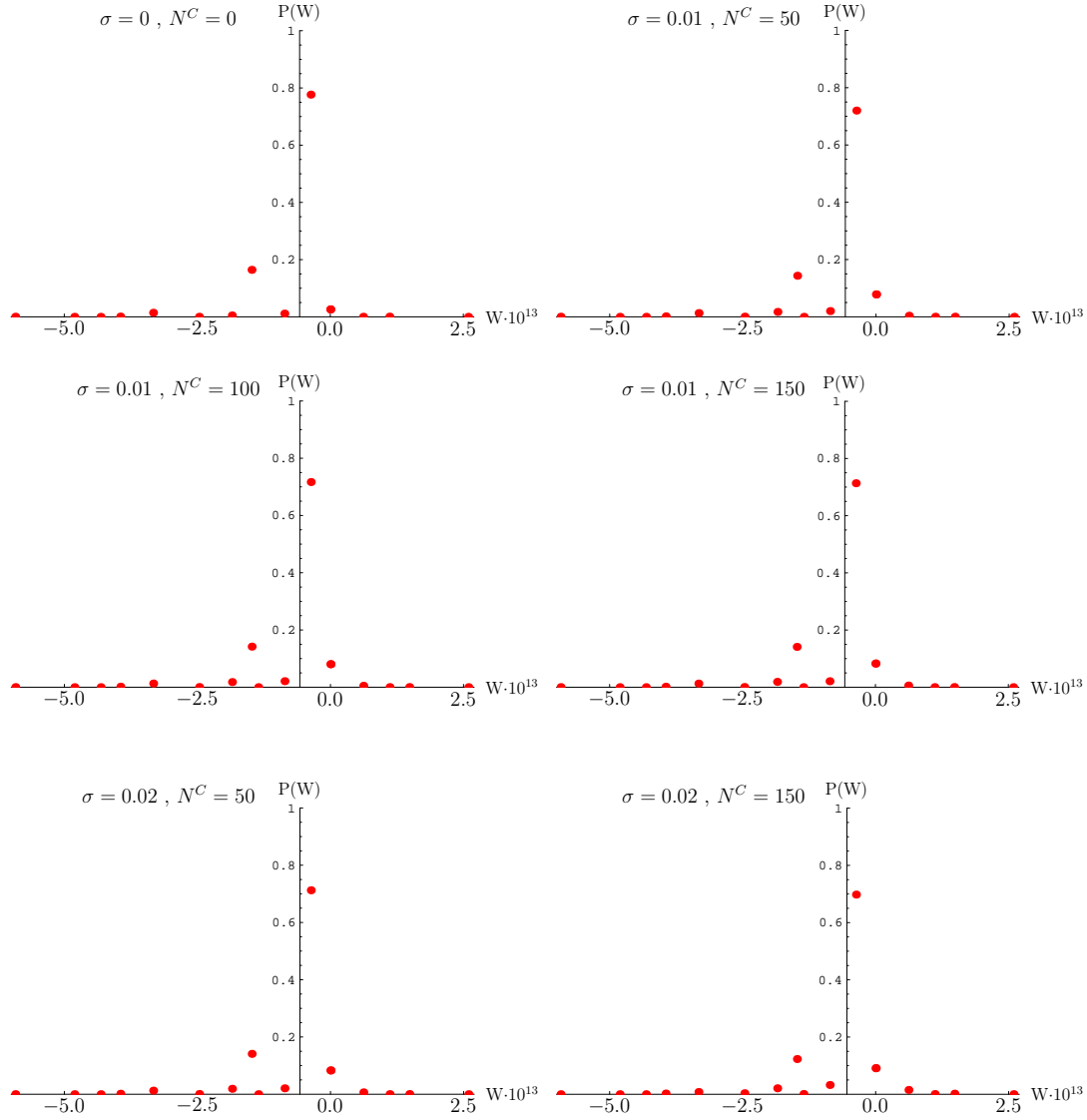


Figure 5.4.: Numerical results for the distribution of work (see 2.3.4) with $\Delta t_2 = 10^{-11}$ and $v = 1 \cdot 10^9$. The velocity of the process is in adapted units. The y-axis crosses the x-axis at \overline{W} . Probabilities smaller than 10^{-5} are suppressed; cutoff at $n = 5$.

5. *Closed Systems - Microcanonical Coupling*

6. Canonical Coupling

6.1. Overview

Now, we turn to a system which is coupled canonically to an environment. The system is allowed to exchange energy with the environment but no particles. The system is called *open* [17]. Its time evolution is no longer unitary, while the time evolution of the compound system consisting of the system and the environment is. We assume a full random hermitian matrix for the interaction (see section 5.4.4 page 49). Inspired by the microcanonical coupling from chapter 5, we try to expand the exponential function under the trace remembering that here:

$$[\hat{H}(t), \hat{H}^S(t)] \neq 0 \text{ and } [\hat{H}(t), \hat{H}^C] \neq 0 \quad (6.1)$$

since energy exchange between the two subsystems is allowed. In order to get some useful results, we apply different boundary conditions on our coupling or system, respectively.

6.2. First Order Perturbation in Coupling Strength

First of all, we require our interaction to be very weak. The coupling parameter σ , introduced in section 5.4.4, is thus taken to be small. Here, we want to study only first order terms in the coupling parameter neglecting all terms of higher order in σ . We try to give a proof of the JARZYNSKI relation in analogy to that of section 5.3.

The compound system, consisting of our system and an environment, is supposed to be closed. Its time evolution is thus deterministic and can be described by the LIOUVILLE equation. Its initial state has to be a canonical one with a well defined temperature T . Then, we know from section 2.7 that the JARZYNSKI relation holds:

$$\overline{e^{-\beta W}} = \frac{Z(t)}{Z(0)} = e^{-\beta \Delta F} \quad (6.2)$$

The work source only acts on our system directly, not on the environment. Our hamilton operator can thus be written as:

$$\hat{H}(t) = \hat{H}^S(t) + \hat{H}^C + \hat{H}^I \quad (6.3)$$

with $\hat{H}^I \equiv \sigma \tilde{\hat{H}}^I$ containing the coupling parameter. The partition sum of the compound system is:

$$Z(t) = \text{Tr}\left(e^{-\beta \hat{H}(t)}\right) = \text{Tr}\left(e^{-\beta(\hat{H}^S(t) + \hat{H}^C + \hat{H}^I)}\right) \quad (6.4)$$

6. Canonical Coupling

This is a situation analogue to that of the microcanonical coupling, but now we face the problem, that the expansion of the exponential function is not that easy, because the hamilton operators do not all commute with each other. Nevertheless, we start by writing down the expansion, keeping in mind, that we are not allowed to interchange the positions of the operators:

$$\mathrm{Tr}\left(e^{-\beta\hat{H}(t)}\right) = \mathrm{Tr}\left(\sum_{n=0}^{\infty} \frac{(\hat{H}(t))^n}{n!}\right) = \mathrm{Tr}\left(\sum_{n=0}^{\infty} \frac{(\hat{H}^S(t) + \hat{H}^C + \hat{H}^I)^n}{n!}\right) \quad (6.5)$$

Disregarding for a moment the denomiator and remembering that the system hamiltonian and that of the environment commute, we have only a problem with the interaction hamiltonian. Since only first order terms in σ are investigated, we make use of the cyclic property of the trace, by permutating the product of the operators until the interaction hamiltonian stands on the right. For better illustration take e. g., the addend with $n = 2$ and the abbreviations $\hat{A} \equiv \hat{H}^S(t) + \hat{H}^C$ and $\hat{B} \equiv \hat{H}^I$:

$$\left(\hat{A} + \hat{B}\right)^2 = \left(\hat{A} + \hat{B}\right) \left(\hat{A} + \hat{B}\right) = \hat{A}^2 + \hat{A}\hat{B} + \hat{B}\hat{A} + \hat{B}^2 \quad (6.6)$$

Now a cyclic permutation of the 3rd addend allows us to write:

$$\left(\hat{A} + \hat{B}\right)^2 = \hat{A}^2 + 2\hat{A}\hat{B} + \hat{B}^2 \quad (6.7)$$

The last term is of the order σ^2 and will be neglected. Since there will be none or only one operator \hat{B} in every addend (those with more than one are of order $\mathcal{O}(\sigma^2)$ and will be neglected), it is always possible to shift that operator to the right end.

Making use of this fact, we can rewrite the partition sum:

$$\mathrm{Tr}\left(e^{-\beta\hat{H}(t)}\right) = \mathrm{Tr}\left\{e^{-\beta(\hat{H}^S(t)+\hat{H}^C)} \left(\hat{1} + \beta\hat{H}^I\right)\right\} + \mathcal{O}(\sigma^2) \quad (6.8)$$

The first addend of the trace is obviously:

$$\begin{aligned} \mathrm{Tr}\left(e^{-\beta(\hat{H}^S(t)+\hat{H}^C)}\right) &= \mathrm{Tr}\left(e^{-\beta\hat{H}^S(t)} \otimes e^{-\beta\hat{H}^C}\right) \\ &= \mathrm{Tr}\left(e^{-\beta\hat{H}^S(t)}\right) \cdot \mathrm{Tr}\left(e^{-\beta\hat{H}^C}\right) = Z^S(t)Z^C \end{aligned} \quad (6.9)$$

This is already the desired result. In order for the JARZYNSKI relation to hold, the 2nd addend of equation (6.8) has to vanish! The 2nd addend can be written as:

$$\mathrm{Tr}\left(e^{-\beta\hat{H}^S(t)} \otimes e^{-\beta\hat{H}^C} \beta\hat{H}^I\right) \stackrel{(5.19)}{=} \beta \mathrm{Tr}\left(\varrho_{cp}^{S,C} \hat{H}^I\right) Z^S(t)Z^C \quad (6.10)$$

We now assume the interaction hamiltonian to be traceless in the product basis in which the system and the environment hamiltonians are diagonal. This is a weak assumption that can always be fulfilled, because if this was not the case, the diagonal elements of

6.3. First Order Perturbation in Energy Exchange

the interaction hamiltonian could easily be transferred to the system and environment hamiltonian respectively. It immediately follows (see appendix A.6.3):

$$\beta \text{Tr} \left(\varrho_{cp}^{S,C} \hat{H}^I \right) Z^S(t) Z^C = 0 \quad (6.11)$$

and so we have:

$$Z(t) = \text{Tr} \left(e^{-\beta \hat{H}(t)} \right) = \text{Tr} \left(e^{-\beta(\hat{H}^S(t) + \hat{H}^C)} \right) = Z^S(t) Z^C \quad (6.12)$$

Substituting this in equation (6.50) we obtain:

$$\frac{\overline{\quad}}{e^{-\beta W}} = \frac{Z(t)}{Z(0)} \stackrel{(6.12)}{=} \frac{Z^S(t) Z^C}{Z^S(0) Z^C} = \frac{Z^S(t)}{Z^S(0)} = e^{-\beta \Delta F^{\text{sys}}} \quad (6.13)$$

The expression shows that in first order perturbation theory for the coupling strength, the JARZYNSKI relation is indeed valid for the open system which is coupled canonically to an environment.

6.3. First Order Perturbation in Energy Exchange

6.3.1. Overview

This section will be governed by the microcanonical coupling scenario, where the system hamiltonian and the environmental one, respectively, commute with the hamiltonian of the interaction. This means, that no energy is exchanged between the system and the environment. We suppose that exchange of energy is allowed, but that it is very weak. Note, that the environment may be coupled relatively strong to the system as long as the energy exchange remains small. The coupling should be weak enough, so that a partition in system and environment is still unambiguously possible.

6.3.2. Analytical Study

We start, as above, with a closed system, initially in a canonical state, for which the JARZYNSKI relation is known to hold.

Here, we are inspired by the microcanonical coupling scenario. There, it was shown that for arbitrarily strong coupling the JARZYNSKI relation holds. First, we face the problem of decomposing the exponential function. If we were able to split this function similarly to section 5.3, a great deal of the proof would be easy and analogue to the case above. Inspired by this, we start from the microcanonical coupling scenario, but now, considered as a perturbation, a small energy exchange is allowed:

$$[A, B] = \varepsilon C \quad (6.14)$$

with $A \equiv \hat{H}^S(t) \otimes \hat{1}^C + \hat{1}^S \otimes \hat{H}^C$, $B \equiv \hat{H}^I$, C being an antihermitian operator and ε being very small. This is a situation similar to the microcanonical coupling where $\varepsilon = 0$.

6. Canonical Coupling

Now, we investigate the partition sum and try to proceed as in section 6.2. We want to shift the B to one end of each addend of the series obtained by the expansion of the EULER function, using the cyclic property. The first problem arises in the 5th addend where we get terms like:

$$(A + B)^2 = \dots + ABAB + \dots \quad (6.15)$$

By using only cyclic permutations, this sort of addends cannot be brought to the desired form with every B standing on the right end. We have to commute one of the operators B with A in order to achieve this. If there are more operators B and A in the sum, even more than one such commutation is necessary. But this is no problem since any further commutation of A 's and B 's would lead to correction terms of order $\mathcal{O}([A, B]^2) \propto \mathcal{O}(\varepsilon^2)$ and would therefore be neglected. The only remaining correction terms are thus of form

$$\text{Tr}(A^n[B, A]B^m) \quad (6.16)$$

Keep in mind, that terms of form of, e. g. , $ABAABA$ can be brought to the form above in the following way:

$$\begin{aligned} \widehat{ABAABA} &= A\widehat{AABA} + A[B, A]\widehat{ABA} \\ &= AAABBA + AA[B, A]BA + A[B, A]BAA - A[B, A][B, A]AA \end{aligned} \quad (6.17)$$

The last addend vanishes since it is of order ε^2 and the remaining addends can be written in the form (6.16) by using the cyclic property of the trace. So, in the end we have

$$A^4B^2 + 2A^3[B, A]B \quad (6.18)$$

We can proceed like this with every term in the expansion of the exponential function. We show now, that the trace of terms of the form (6.16) vanishes:

$$\begin{aligned} \text{Tr}(A^n[B, A]B^m) &= \text{Tr}\left(A^n B \widehat{A} B B^{m-1} - A^{n+1} B^{m+1}\right) \\ &= \text{Tr}\left(A^n B^2 A B^{m-1} + A^n \widehat{B} [A, B] B^{m-1} - A^{n+1} B^{m+1}\right) \\ &= \text{Tr}\left(A^n B^2 A B^{m-1} + A^n [A, B] B^m - A^{n+1} B^{m+1}\right) \end{aligned} \quad (6.19)$$

In the last step, we have successively commuted the operator B with the n operators A , each commutation creating a correction term which can be neglected since the addends are then of order $\mathcal{O}(\varepsilon^2)$. Then, by cyclic permutation, we arrive at the result presented above. Now, we proceed equivalently with the first addend:

$$\text{Tr}\left(A^n B^2 \widehat{A} B B^{n-2}\right) = \text{Tr}\left(A^n B^3 A B^{m-2} + A^n B^2 [A, B] B^{m-2}\right) \quad (6.20)$$

The term with the commutator can be rewritten in the same form as above since any further commutation of A and B leads to a correction of negligible order. With the

other addend we proceed as above. So, in the end we have:

$$\begin{aligned}\mathrm{Tr}(A^n[B, A]B^m) &= \mathrm{Tr}(A^{n+1}B^{m+1} + m \cdot A^n[A, B]B^m - A^{n+1}B^{m+1}) \\ &= m \mathrm{Tr}(A^n[A, B]B^m)\end{aligned}\quad (6.21)$$

From this we conclude that

$$\mathrm{Tr}(A^n[B, A]B^m) = 0 \quad (6.22)$$

meaning that every correction term vanishes and we end up with:

$$\mathrm{Tr}(e^{-\beta(A+B)}) = \mathrm{Tr}(e^{-\beta A}e^{-\beta B}) \quad (6.23)$$

Re-substituting the abbreviations, we have:

$$\mathrm{Tr}(e^{-\beta\hat{H}(t)}) = \mathrm{Tr}(e^{-\beta(\hat{H}^S(t)\otimes\hat{1}^C + \hat{1}^S\otimes\hat{H}^C)}e^{-\beta\hat{H}^I}) \quad (6.24)$$

This expression can be rewritten to

$$\mathrm{Tr}(e^{-\beta\hat{H}(t)}) = \mathrm{Tr}(e^{-\beta\hat{H}^S(t)} \otimes e^{-\beta\hat{H}^C} e^{-\beta\hat{H}^I}) \quad (6.25)$$

With the density operator for canonical product states we get

$$\mathrm{Tr}(e^{-\beta\hat{H}(t)}) = \mathrm{Tr}(\hat{\varrho}_{\mathrm{cp}}(t)e^{-\beta\hat{H}^I}) Z^S(t)Z^C \quad (6.26)$$

For cyclic processes, where $\hat{\varrho}_{\mathrm{cp}}(t) = \hat{\varrho}_{\mathrm{cp}}(0)$, we immediately arrive at

$$\frac{Z(t)}{Z(0)} = \frac{\mathrm{Tr}(e^{-\beta\hat{H}(t)})}{\mathrm{Tr}(e^{-\beta\hat{H}(0)})} = \frac{Z^S(t)}{Z^S(0)} = 1 \quad (6.27)$$

as required by the JARZYNSKI relation. So, we can see that for cyclic processes the relation also holds for a system coupled to an environment since we are able to separate the partition sums of the system and environment respectively. We notice furthermore, that the expectation value of the interaction hamiltonian is in general not constant. So,

$$\mathrm{Tr}(\varrho(0)e^{-\beta\hat{H}^I}) \stackrel{\text{in general}}{\neq} \mathrm{Tr}(\hat{\varrho}(t)e^{-\beta\hat{H}^I}) \quad (6.28)$$

But the actual density operators do not enter equation (6.26), so this is not a hint for the JARZYNSKI relation to fail here.

Furthermore it can be seen that the result we obtain for the relation of the partition sums is independent of the velocity of the process. It solely depends on the initial and final state. So, if we were able to proof the identity for any specific process velocity, the whole class of processes with same initial and final hamilton operators would fulfill the same relation. Thus, the proof would be general.

6. Canonical Coupling

Here, we give only a proof for the class of systems, whose hamilton operator fulfills the following relation:

$$\hat{H}(t) = \hat{H}^S(t) + \hat{H}^C + \hat{H}^I \quad \text{with} \quad \hat{H}^S(t) = f(t)\hat{H}^S(0) \quad (6.29)$$

This means, that only the eigenenergies of the system are time-dependent but not its eigenfunctions. A possible example would be a spin with time-dependent Zeeman splitting. As a consequence, we have

$$[\hat{H}^S(t), \hat{H}^S(t')] = 0 \quad (6.30)$$

We use this relation in order to investigate the change of the trace in equation (6.26):

$$\frac{d}{dt} \left(\text{Tr} \left\{ \hat{\rho}_{\text{cp}}(t) e^{-\beta \hat{H}^I} \right\} \right) = -i \text{Tr} \left\{ [\hat{H}(t), \hat{\rho}_{\text{cp}}] e^{-\beta \hat{H}^I} \right\} \quad (6.31)$$

We substitute equation (6.29) for the hamilton operator and get

$$\frac{d}{dt} \left(\text{Tr} \left\{ \hat{\rho}_{\text{cp}}(t) e^{-\beta \hat{H}^I} \right\} \right) = -i \text{Tr} \left\{ [\hat{H}^S(t) + \hat{H}^C, \hat{\rho}_{\text{cp}}(t)] e^{-\beta \hat{H}^I} \right\} \quad (6.32)$$

Due to the cyclic property of the trace, the addend with the interaction energy in the hamilton operator vanishes as it commutes with $e^{-\beta \hat{H}^I}$. Using the definition of $\hat{\rho}_{\text{cp}}(t)$ (essentially $\hat{\rho}_{\text{cp}}(t) \propto \hat{H}^S(t) + \hat{H}^C$), exploiting the commutator relation (6.30) and regarding $[\hat{H}^S(t), \hat{H}^C] = 0$, since the operators act on different subspaces, we finally have:

$$\frac{d}{dt} \left(\text{Tr} \left\{ \hat{\rho}_{\text{cp}}(t) e^{-\beta \hat{H}^I} \right\} \right) = 0 \implies \text{Tr} \left\{ \hat{\rho}_{\text{cp}}(t) e^{-\beta \hat{H}^I} \right\} = \text{Tr} \left\{ \hat{\rho}_{\text{cp}}(0) e^{-\beta \hat{H}^I} \right\} \quad (6.33)$$

Using this identity we get

$$\frac{Z(t)}{Z(0)} = \frac{\text{Tr} \left(e^{-\beta \hat{H}(t)} \right)}{\text{Tr} \left(e^{-\beta \hat{H}(0)} \right)} = \frac{Z^S(t)}{Z^S(0)} = e^{-\beta \Delta F^S} \quad (6.34)$$

So, for this class of processes, the JARZYNSKI relation is valid in first order energy exchange.

6.4. Assumption of Constant Interaction Energy

Also inspired by the microcanonical coupling scenario and driven by the idea to generalize the proof of the section above, we now allow the system and environment to exchange energy but assume that the interaction energy remains constant all the time. It is thus taken a constant of motion:

$$[\hat{H}(t), \hat{H}^I] = 0 \quad \text{and thus also} \quad [\hat{H}(t), e^{\hat{H}^I}] = 0 \quad (6.35)$$

It then follows with $\hat{H}(t) \equiv \hat{H}^S(t) + \hat{H}^C + \hat{H}^I$ that:

$$[\hat{H}^S(t) + \hat{H}^C, \hat{H}^I] = 0 \Leftrightarrow [\hat{H}^S(t), \hat{H}^I] = -[\hat{H}^C, \hat{H}^I] \quad (6.36)$$

The compound system, which is supposed to start in a canonical state, is closed. So, the work performed on the system will be consumed by the system and the bath, leaving no share for the interaction. This means that the energy that flows out of the system has to be consumed by the bath and vice versa. The proof is very similar to the microcanonical coupling one: Since the compound system is closed and starts in a canonical state, we know that we have:

$$\overline{e^{-\beta W}} = \frac{Z^{S,C}(t)}{Z^{S,C}(0)} \quad (6.37)$$

For the partition sum at time t we have

$$Z^{S,C}(t) = \text{Tr}\left(e^{-\beta(\hat{H}(t))}\right) = \text{Tr}\left(e^{-\beta(\hat{H}^S(t) + \hat{H}^C + \hat{H}^I)}\right) \quad (6.38)$$

Since acting on different subspaces of Hilbert space, $\hat{H}^S(t)$ and \hat{H}^C commute. We introduce the following abbreviations:

$$A \equiv \hat{H}^S(t) + \hat{H}^C, \quad B \equiv \hat{H}^I \quad (6.39)$$

We know from equation (6.36) that $[A, B] = 0$, so we have no problem in splitting up the exponential function:

$$e^{-\beta(A+B)} = e^{-\beta A} e^{-\beta B} \quad (6.40)$$

Then, we split up $e^{-\beta A}$ since both operators commute also and we finally have:

$$\text{Tr}\left(e^{-\beta\hat{H}(t)}\right) = \text{Tr}\left(e^{-\beta\hat{H}^S(t)} \otimes e^{-\beta\hat{H}^C} e^{-\beta\hat{H}^I}\right) = \text{Tr}\left(\varrho_{cp}(t) e^{-\beta\hat{H}^I}\right) Z^S(t) Z^C(0) \quad (6.41)$$

Substituting this in equation (6.37) yields

$$\overline{e^{-\beta W}} = \frac{\text{Tr}\left(\varrho_{cp}(t) e^{-\beta\hat{H}^I}\right) Z^S(t)}{\text{Tr}\left(\varrho_{cp}(0) e^{-\beta\hat{H}^I}\right) Z^S(0)} \quad (6.42)$$

We show now, using the LIOUVILLE equation, analogue to the microcanonical coupling scenario, that the trace is constant in time and thus cancels:

$$\begin{aligned} \frac{d}{dt} \left(\text{Tr}\left(\varrho_{cp}(t) e^{-\beta\hat{H}^I}\right) \right) &= -i \text{Tr}\left([\hat{H}(t'), \varrho_{cp}(t)] e^{-\beta\hat{H}^I}\right) \\ &= -i \text{Tr}\left(\varrho_{cp}(t) [e^{-\beta\hat{H}^I}, \hat{H}(t')]\right) \stackrel{(6.35)}{=} 0 \quad \forall t' \end{aligned} \quad (6.43)$$

From this we conclude that

$$\overline{e^{-\beta W}} = \frac{Z^S(t)}{Z^S(0)} = e^{-\beta\Delta F^S} \quad (6.44)$$

This means that if the interaction energy was, indeed, constant, the JARZYNSKI relation would be valid for canonical coupled systems.

6.5. Compound System in Canonical State

Inspired by the result above, we turn back to a compound system, which is closed and in a canonical state. The system and the environment are coupled canonically. We proceed as above, knowing that for the whole system we have:

$$\overline{e^{-\beta W}} = \frac{Z^{S,C}(t)}{Z^{S,C}(0)} \equiv x \quad (6.45)$$

for any process. So, if we were able to proof that for one special realization

$$x = \frac{Z^S(t)}{Z^S(0)} = e^{-\beta \Delta F^S} \quad (6.46)$$

holds, the JARZYNSKI relation would be valid for systems coupled to an environment under the condition, that the compound system starts in a canonical state. No further assumptions would be necessary.

As above, we choose the realization, that is infinitely fast. Again, the environment has no chance at all to influence our system at such a short time-scale. The energy of the bath and the interaction energy remain constant. This means that we assume that this arbitrarily fast process is always of the type presented in section 6.4, meaning that this sort of process is supposed to keep the interaction energy constant. This seems plausible, but has not be proven to hold for arbitrary systems (see appendix A.7 for a short mathematical discussion). As shown, we have for the case of a constant interaction energy:

$$\overline{e^{-\beta W}} = \frac{Z^S(t)}{Z^S(0)} = x \quad (6.47)$$

This implies that for our arbitrary fast process, the JARZYNSKI relation holds. As stated above, we conclude that it does also hold for arbitrary processes:

$$\overline{e^{-\beta W}} = \frac{Z^S(t)}{Z^S(0)} = e^{-\beta \Delta F^S} \quad (6.48)$$

If the assumption that arbitrary fast processes always conserve the interaction energy was correct, this would prove that the JARZYNSKI relation is valid for any system coupled to an environment, if the compound system is closed and starts in a canonical state. This would be a rather general result.

6.6. Subsystem and Compound System in Canonical State - Behaviour for fast processes

In this section, we impose a further condition on our system. We additionally require the small subsystem, on which the process is enforced, to be in a canonical state at the beginning of the process. The compound system, consisting of our small subsystem and

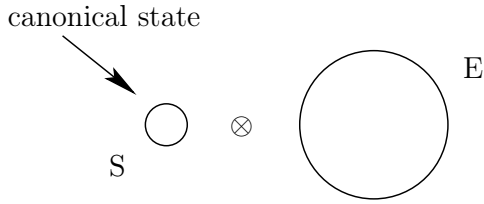


Figure 6.1.: A system S , which is in a canonical state, is coupled to an environment E . The compound system, consisting of the system and the environment is closed and in a canonical state.

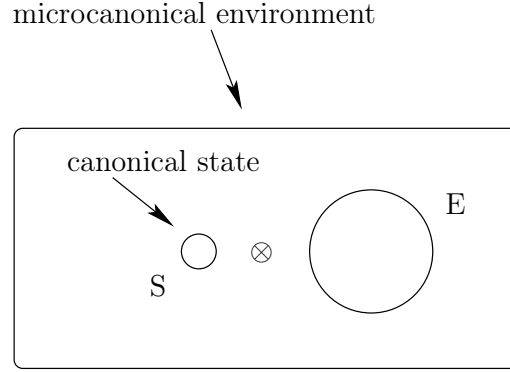


Figure 6.2.: The compound system, consisting of a system S and an environment E , is embedded microcanonically in another environment. The system is in a canonical state as is the compound one.

an environment is also required to start in a canonical state with same β and it has to be closed (see figure 6.1).

If these initial conditions are met, a proof is presented here, that the JARZYNSKI relation holds for arbitrary processes and arbitrary coupling strengths. However, the coupling should not be too strong to allow an unambiguous separation between system and environment respectively [3].

We now consider a class of processes \mathcal{P} , each element p of which satisfying:

$$p \in \mathcal{P}, p_a = \{\hat{H}(0), \hat{H}(t), r_a\} \quad (6.49)$$

This means, each process starts with the same hamilton operator $\hat{H}(0)$ and ends up with a different, but for every $p \in \mathcal{P}$ same hamilton operator $\hat{H}(t)$. Thus, in general we have $\hat{H}(0) \neq \hat{H}(t)$. The r_a represents an arbitrary realization of the process.

We know, that the JARZYNSKI relation holds for arbitrary processes for the compound system, thus:

$$\overline{e^{-\beta W}} = \frac{Z(t)}{Z(0)} \equiv x \quad (6.50)$$

We now choose a special process: We perform the process arbitrarily fast so that the environment has no chance at all to influence our system on which the process is performed (this assumption seems to be very plausible; however, if the bath would have an instant influence on our system, no matter how fast the process, this would not be true and the proof idea presented here would not hold for such systems). Since our system is, in this case, not influenced at all by the environment, it can be considered closed. For closed systems that start in a canonical state, we know the JARZYNSKI relation to hold. This means, that for this special process, the relation is not only valid for the compound

6. Canonical Coupling

system, but for our subsystem, too:

$$\overline{e^{-\beta W}} = \frac{Z(t)}{Z(0)} \stackrel{!}{=} \frac{Z^S(t)}{Z^S(0)} = x \quad (6.51)$$

Since we know, that for *every* element p we have

$$\overline{e^{-\beta W}} = x \quad (6.52)$$

we conclude that

$$\overline{e^{-\beta W}} = x = \frac{Z^S(t)}{Z^S(0)} = e^{-\beta \Delta F^S} \quad (6.53)$$

for arbitrary processes. This shows, that the JARZYNSKI relation would hold for systems coupled to an environment, under the initial conditions given above. Keep in mind that this is only true if, while performing the arbitrary fast process, the environment has no influence at all on our system and thus it can be thought of to be closed. Since we need not to specify the initial and final hamiltonians, respectively, the proof is general.

This proof is easily generalized to compound systems which are not closed, but coupled *microcanonically* to an environment (see figure 6.2). This is due to the fact that the JARZYNSKI relation was shown to hold for the microcanonical coupling scenario earlier in this thesis. So, equation (6.50) is also valid if our compound system is coupled microcanonically to an environment. The rest of the proof presented above remains unaltered.

7. Summary

In this work, a numerical verification of the JARZYNSKI relation for closed quantum systems was given. We only used the time-dependent Schrödinger equation. Thus, no further assumptions or approximations have been involved. The results are therefore numerically “exact”. As model systems, we used a single particle in the quantum well and in the coulomb potential. For arbitrary realizations of different processes with different initial conditions, but always a canonical state, the relation was verified. The adiabatic behaviour of the model systems was investigated. The analytical result, that the higher the energy level n , the more unstable it is, was verified by numerical calculations. This was expected in the case of the coulomb potential since the distance between high energy levels is small, but is rather astonishing for the quantum well, where the distance between neighbouring energy levels grows with increasing n .

Then, focus was set on a system, to which an environment is coupled microcanonically. An analytical proof of the JARZYNSKI relation was given by separating the partition sum of a compound, closed system into its system and environment share respectively. The special form of the commutator between the interaction hamiltonian and the system and environment hamiltonian respectively was used for this proof. For numerical verification, the quantum well with variable width was coupled to an environment, ensuring that no energy could be transferred between the system and the environment. The numerical results were in perfect accordance with the JARZYNSKI relation. The comparison between the quantum well with environment and without showed, that the average amount of work and the distribution of it were only slightly different. The von-Neumann entropy increased for fast processes for systems with environment.

For the canonical coupling scenario, only analytical studies were obtained. The investigation was inspired by that of the microcanonical coupling scenario. For very weak coupling, the JARZYNSKI relation was shown to hold in 1st order perturbation theory. For more restraining initial conditions, namely requiring not only the compound system to start in a canonical state but also our subsystem to do so, a proof for the validity of the JARZYNSKI relation was given under the assumption, that arbitrary fast processes leave the system unaffected by the environment. If the interaction energy is required to be constant, an alternative proof was given that the JARZYNSKI relation holds. As a consequence, it was proven that for compound systems, starting in a canonical state and being closed, the JARZYNSKI relation generally holds under the assumption, that arbitrary fast processes conserve the interaction energy.

No numerical studies were made here. This is due to the fact, that one would need an environment, which would allow for transitions between arbitrary states in the system. The environment has to be in resonance with the system. For a quantum well, the environment could look like as described in [35]. Here, we are facing the problem, that

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we have an explicit time-dependent hamilton operator, i. e., our energy spectrum varies with time. In order to ensure that the environment would still be in resonance with the system, it would be necessary to change the energy spectrum of the environment appropriately or to ensure, that the energy levels of the system are broad enough to allow any transitions at any time. This would result in a very large numerical complexity. An other option would be to use quantum master equations.

A. Appendix

A.1. Variance of Work

We are calculating the variance of work:

$$(\delta W)^2 = \overline{W^2} - \overline{W}^2 \quad (\text{A.1})$$

Since for closed systems the work performed on the system is simply given by the energy difference between initial and final states weighted with the probability for an according transistion, we have:

$$\overline{W^2} = \sum_{m,n} W_{mn}^2 P(W_{mn}) = \sum_{m,n} (E_m(t) - E_n(0))^2 K_{mn}(t) P_n(0) \quad (\text{A.2})$$

with $P(W_{mn})$ denoting the transition probability which is given by the probability for starting in state n and ending up in state m . The $K_{mn}(t)$ is introduced in section 2.7 page 17. Evaluating the quadratic term gives:

$$\begin{aligned} \overline{W^2} &= \sum_{m,n} (E_m^2(t) + E_n^2(0) - 2E_m(t)E_n(0)) K_{mn}(t) P_n(0) \\ &\stackrel{(2.67),(2.68)}{=} \sum_m E_m^2(t) P_m(t) + \sum_n E_n^2(0) P_n(0) - 2 \sum_{m,n} E_m(t) E_n(0) K_{mn}(t) P_n(0) \end{aligned} \quad (\text{A.3})$$

We abbreviate the 3rd addend with \tilde{C} and arrive at:

$$\overline{W^2} = \overline{E^2(0)} + \overline{E^2(t)} - 2\tilde{C} \quad (\text{A.4})$$

We now turn to \overline{W}^2 :

$$\begin{aligned} \overline{W}^2 &= \left(\sum_{m,n} W_{mn} P(W_{mn}) \right)^2 = \left(\sum_{m,n} (E_m(t) - E_n(0)) K_{mn}(t) P_n(0) \right)^2 \\ &= \overline{E(t)}^2 + \overline{E(0)}^2 - 2\overline{E(t) \cdot E(0)} \end{aligned} \quad (\text{A.5})$$

In the last step, we evaluated the quadratic term and used equations (2.67) and (2.68).

Using these expressions, $H(t) = E(t)$ and $C \equiv \tilde{C} - \overline{E(t) \cdot E(0)}$ (2.22) we get for the variance of work:

$$(\delta W)^2 = (\delta H(t))^2 + (\delta H(0))^2 - 2C \quad (\text{A.6})$$

with C defined as in (2.23).

We now want to discuss two special cases:

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1. Adiabatic processes: For an adiabatic process we have $K_{mn}(t) = \delta_{mn}$ since no transitions take place. Therefore, we have for \tilde{C} :

$$\sum_{m,n} E_m(t)E_n(0)\delta_{mn}P_n(0) = \sum_n E_n(t)E_n(0)P_n(0) = \sum_n E_n(t)E_n(0)P_n(t) \quad (\text{A.7})$$

with $P_n(t) = P_n(0)$ from (2.67). We suppose that the change of the eigenenergy of every state scales equally, which is most often the case (as it is in our two model systems):

$$E_n(t) = a(t)E_n(0) \quad (\text{A.8})$$

Using this identity we get:

$$\tilde{C} = a(t)\overline{H^2(0)} \implies C = 0 \quad (\text{A.9})$$

$$\overline{H(t)} = a(t)\overline{H(0)} \quad (\text{A.10})$$

$$\overline{H^2(t)} = a^2(t)\overline{H^2(0)} \quad (\text{A.11})$$

Substituting all this in equation (A.4) we finally arrive at:

$$(\delta W)^2 = (a^2(t) + 1) (\delta H(0))^2 \quad (\text{A.12})$$

Since the variance of the initial hamiltonian does not vanish for canonical states, the variance of work does not vanish even for adiabatic processes! Only if we would start in a pure state, $P_n(0) = \delta_{nm_0}$ we would have $P_n^2(0) = P_n(0)$ and $(\delta H(0))^2 = 0$ and then

$$(\delta W)^2 = 0 \quad (\text{A.13})$$

2. Closed Processes: Here, we have by definition $H(t) = H(0)$ and thus $(\delta H(0))^2 = (\delta H(t))^2$. For C we have:

$$\sum_{m,n} E_m(0)E_n(0)K_{mn}(t)P_n(0) - \overline{H(0)}^2 \quad (\text{A.14})$$

In general, we do of course have a non-vanishing variance of W . If we now assume the process to be adiabatic as above, we get the additional identity $K_{mn} = \delta_{mn}$ and thus $C = (\delta H(0))^2$. Therefore we readily obtain:

$$(\delta W)^2 = 2(\delta H(0))^2 - 2C = 0 \quad (\text{A.15})$$

So, if we have a closed adiabatic process, the variance of work vanishes.

A.2. Sum Rules

Here, we want to show that the sum rules for the conditional transition matrix presented in equation (2.68) hold. First, we turn to the summation over final states:

$$\sum_f K_{fi} = 1 \quad (\text{A.16})$$

This identity follows directly from the invariance of the trace of the density operator under unitary transformations:

$$1 \stackrel{!}{=} \text{Tr } \varrho(t) = \sum_i \varrho_{ii}(t) \stackrel{(2.67)}{=} \sum_{i,j} K_{ij}(t) \varrho_{jj}(0) \quad (\text{A.17})$$

Suppose the $\varrho(0)$ to represent a pure state:

$$\varrho_{jj}(0) = \begin{cases} 1 & \text{for } j = j' \\ 0 & \text{otherwise} \end{cases} \quad (\text{A.18})$$

Entering this in equation (A.17) immediately yields the wanted sum rule for final states. The K_{fi} being the conditional probability for transitions to a state f if started in state i , do not depend on the initial state! So, choosing the special case of $\varrho(0)$ representing a pure state does not restrict our result to such situations. Since we did not oppose any conditions on the final state, our result is valid generally. The sum rule holds for arbitrary initial states.

Making use of this fact, we prove the sum rule for a special initial state which will nevertheless hold for arbitrary states. We choose our initial state to be a totally mixed one:

$$\varrho_{ij} = \frac{1}{N} \delta_{ij} \quad (\text{A.19})$$

Now, we want to show that this density matrix solves the LIOUVILLE equation at any time t . We start with the LIOUVILLE equation in an adiabatic basis set (see equation (2.64)), investigating the sum term first:

$$\begin{aligned} \sum_{m,n} S_{kl,mn}(t) \varrho_{mn}(t) &\stackrel{(2.65)}{=} \sum_{m,n} (\langle \varphi_k(t) | \dot{\varphi}_m(t) \rangle \delta_{ln} + \langle \dot{\varphi}_n(t) | \varphi_l(t) \rangle \delta_{km}) \frac{1}{N} \delta_{mn} \\ &= \frac{1}{N} \sum_n \langle \varphi_k(t) | \dot{\varphi}_n(t) \rangle \delta_{ln} + \langle \dot{\varphi}_n(t) | \varphi_l(t) \rangle \delta_{kn} \\ &= \frac{1}{N} \langle \varphi_k(t) | \dot{\varphi}_l(t) \rangle + \langle \dot{\varphi}_k(t) | \varphi_l(t) \rangle \\ &= \frac{1}{N} \frac{d}{dt} (\langle \varphi_k(t) | \varphi_l(t) \rangle) = 0 \end{aligned} \quad (\text{A.20})$$

Since the first term in equation (2.64) trivially vanishes because of the definition of the ω in equation (2.65), the totally mixed state solves the Liouville equation at any time.

In order to prove the sum rule for initial states, we choose w. l. o. g. (see argumentation above) the totally mixed state as the initial state, and since this state solves the Liouville equation at any time as shown above, we have:

$$\frac{1}{N} \delta_{ij} = \varrho_{ij}(0) \stackrel{!}{=} \varrho_{ij}(t) \quad (\text{A.21})$$

So we have:

$$\frac{1}{N} \stackrel{(A.21)}{=} \varrho_{ff}(t) \stackrel{(2.67)}{=} \sum_i K_{fi}(t) \varrho_{ii}(0) \stackrel{(A.19)}{=} \frac{1}{N} \sum_i K_{fi}(t) \implies \sum_i K_{fi}(t) = 1 \quad (\text{A.22})$$

This shows that both sum rules hold.

A.3. Differential Equation For Time Evolution Operator

We start with the time-dependent SCHRÖDINGER equation (2.24)

$$i\frac{d}{dt}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle \quad (\text{A.23})$$

and use the time evolution operator (2.29):

$$i\frac{d}{dt}\left(\hat{U}(t, t_0)|\Psi(t_0)\rangle\right) = \hat{H}(t)\hat{U}(t, t_0)|\Psi(t_0)\rangle \quad (\text{A.24})$$

We suppose our initial state to be an eigenenergy state and choose $t_0 = 0$:

$$|\Psi(t_0)\rangle = |\varphi_i(0)\rangle \quad (\text{A.25})$$

With this we have:

$$i\dot{\hat{U}}(t, 0)|\varphi_i(0)\rangle = \hat{H}(t)\hat{U}(t, 0)|\varphi_i(0)\rangle \quad (\text{A.26})$$

The eigenenergy basis set is a complete basis vector set and thus:

$$\sum_k |\varphi_k(t)\rangle \langle \varphi_k(t)| = \hat{1} \quad (\text{A.27})$$

Using this identity, we get

$$i\sum_k |\varphi_k(t)\rangle \langle \varphi_k(t)| \dot{\hat{U}}(t, 0)|\varphi_i(0)\rangle = \sum_l |\varphi_l(t)\rangle \langle \varphi_l(t)| \hat{H}(t)\hat{U}(t, 0)|\varphi_i(0)\rangle \quad (\text{A.28})$$

The hamilton operator is, of course, hermitian and can be evaluated easily on the right side since it operates on an eigenvector of itself. On the left side, we change the position of the time derivation, arriving at:

$$\begin{aligned} i\sum_k |\varphi_k(t)\rangle \left\{ \frac{d}{dt} \left(\langle \varphi_k(t)| \hat{U}(t, 0)|\varphi_i(0)\rangle \right) - \langle \dot{\varphi}_k(t)| \hat{U}(t, 0)|\varphi_i(0)\rangle \right\} \\ = \sum_l |\varphi_l(t)\rangle \varepsilon_l(t) \langle \varphi_l(t)| \hat{U}(t, 0)|\varphi_i(0)\rangle \end{aligned} \quad (\text{A.29})$$

We introduce the abbreviation $U_{kl}(t, 0) \equiv \langle \varphi_k(t)| \hat{U}(t, 0)|\varphi_l(0)\rangle$ and insert another unity operator:

$$\begin{aligned} i\sum_k |\varphi_k(t)\rangle \left\{ \frac{d}{dt} U_{ki}(t, 0) - \sum_n \langle \dot{\varphi}_k(t)| \varphi_n(t)\rangle \langle \varphi_n(t)| \hat{U}(t, 0)|\varphi_i(0)\rangle \right\} \\ = \sum_l \varepsilon_l(t) |\varphi_l(t)\rangle U_{li}(t, 0) \end{aligned} \quad (\text{A.30})$$

Using the abbreviation $M_{kl}(t) \equiv \langle \dot{\varphi}_k(t) | \varphi_l(t) \rangle$ we arrive at

$$i \sum_k |\varphi_k(t)\rangle \left\{ \dot{U}_{ki}(t, 0) - \sum_n M_{kn}(t) U_{ni}(t, 0) \right\} = \sum_l \varepsilon_l(t) |\varphi_l(t)\rangle U_{li}(t, 0) \quad (\text{A.31})$$

Since the used basis set of eigenvalue vectors is supposed to be a complete orthonormal basis set, we can compare the coefficients of the states k and l in the equation above and finally arrive at the desired differential equation for the matrix of the time evolution operator:

$$i \frac{d}{dt} U_{ki}(t, 0) - i \sum_n M_{kn}(t) U_{ni}(t, 0) = \varepsilon_k(t) U_{ki}(t, 0) \quad (\text{A.32})$$

Searching for an interpretation of the matrix elements of the time evolution operator, we remember that the probability for a transition from state $|\varphi_i(0)\rangle$ at time $t = 0$ to state $|\varphi_f(t)\rangle$ at time t is given by:

$$|\langle \varphi_f(t) | \varphi_i(0) \rangle|^2 = |U_{fi}(t, 0)|^2 \quad (\text{A.33})$$

using the abbreviation from above. We see that our matrix elements $U_{mn}(t, 0)$ give the probabilities for ending up in state $|\varphi_m(t)\rangle$ at time t if we started in state $|\varphi_n(0)\rangle$. This is the same as the conditioned transition matrix $K_{mn}(t)$ introduced in section 2.7 page 17. So, we finally arrive at:

$$K_{fi}(t) = |U_{fi}(t, 0)|^2 \quad (\text{A.34})$$

A.4. Adiabatic Behaviour of the Quantum Well

First, we study the left-hand side of equation (4.10). The energy difference is given by

$$g_{nk}(t) = \varepsilon_n(t) - \varepsilon_k(t) \stackrel{(3.3)}{=} \frac{\pi^2}{2ML^2(t)} (n^2 - k^2) \quad (\text{A.35})$$

We are now looking for the minimum during the whole time evolution:

$$\frac{d}{dt} g_{nk}(t) = \frac{d}{dt} \frac{\xi}{L^2(t)} = -\frac{2\xi}{L^3(t)} \frac{\partial L(t)}{\partial t} \quad (\text{A.36})$$

with $\xi \equiv \frac{\pi^2}{2M} (n^2 - k^2)$. If we consider linear wall displacements we have $L(t) = L(0) + vt$ and thus:

$$\frac{d}{dt} g_{nk}(t) = -\frac{2\xi}{L^3(t)} v \quad (\text{A.37})$$

This is a monotone function. Depending on the sign of the velocity, we have a monotone increasing (sign $v = -1$, compression) or decreasing (sign $v = +1$, dilatation) function (keep in mind, that $n > k$ w. l. o. g.). So, the minimum can be found either at time $t = 0$ or at the maximal time $t = t_{\max}$.

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Now, we turn to the right-hand side of equation (4.10), considering for a start only the numerator:

$$\begin{aligned}\langle n | \dot{\hat{H}}(t) | k \rangle &= \frac{d}{dt} \langle n | \hat{H}(t) | k \rangle - \langle \dot{n} | \hat{H}(t) | k \rangle - \langle n | \dot{\hat{H}}(t) | k \rangle \\ &= \frac{d}{dt} (\varepsilon_k(t) \langle n | k \rangle) - \varepsilon_k(t) \langle \dot{n} | k \rangle - \varepsilon_n(t) \langle n | \dot{k} \rangle\end{aligned}\quad (\text{A.38})$$

Since we are only considering terms with $n \neq k$, the first term vanishes.

Using the eigenenergy functions of the quantum well (3.3) we get:

$$\begin{aligned}| \dot{k} \rangle &= \frac{d}{dt} \left(\sqrt{\frac{2}{L(t)}} \sin \left(\frac{k\pi}{L(t)} x \right) \right) = -\sqrt{\frac{1}{2L^3(t)}} \sin \left(\frac{k\pi}{L(t)} x \right) \dot{L}(t) \\ &\quad + \sqrt{\frac{2}{L(t)}} \frac{-k\pi x}{L^2(t)} \cos \left(\frac{k\pi}{L(t)} x \right) \dot{L}(t)\end{aligned}\quad (\text{A.39})$$

Now, we calculate $\langle n | \dot{k} \rangle$:

$$\begin{aligned}\langle n | \dot{k} \rangle &= -\int_0^{L(t)} \sqrt{\frac{2}{L(t)}} \sin \left(\frac{n\pi}{L(t)} x \right) \cdot \left\{ \sqrt{\frac{1}{2L^3(t)}} \sin \left(\frac{k\pi}{L(t)} x \right) \dot{L}(t) \right. \\ &\quad \left. + \sqrt{\frac{2}{L(t)}} \frac{k\pi x}{L^2(t)} \cos \left(\frac{k\pi}{L(t)} x \right) \dot{L}(t) \right\} dx\end{aligned}\quad (\text{A.40})$$

For the 1st addend we have:

$$\begin{aligned}-\int_0^{L(t)} \sqrt{\frac{2}{L(t)}} \sin \left(\frac{n\pi}{L(t)} x \right) \cdot \sqrt{\frac{1}{2L^3(t)}} \sin \left(\frac{k\pi}{L(t)} x \right) \dot{L}(t) dx \\ = -\dot{L}(t) \sqrt{\frac{1}{L^4(t)}} \int_0^{L(t)} \sin \left(\frac{n\pi}{L(t)} x \right) \cdot \sin \left(\frac{k\pi}{L(t)} x \right) dx\end{aligned}\quad (\text{A.41})$$

Since $n, k \in \mathbb{N}$ and the integral running over a period, it vanishes for $n \neq k$. So we turn to the second addend of equation (A.40):

$$\begin{aligned}-\int_0^{L(t)} \sqrt{\frac{2}{L(t)}} \sin \left(\frac{n\pi}{L(t)} x \right) \cdot \sqrt{\frac{2}{L(t)}} \frac{k\pi x}{L^2(t)} \cos \left(\frac{k\pi}{L(t)} x \right) \dot{L}(t) dx \\ = -\frac{\dot{L}(t) k\pi}{L^2(t)} \int_0^{L(t)} \sin \left(\frac{n\pi}{L(t)} x \right) \cdot x \cos \left(\frac{k\pi}{L(t)} x \right) dx\end{aligned}\quad (\text{A.42})$$

With the help of MATHEMATICA we get:

$$\int_0^{L(t)} \sin \left(\frac{n\pi}{L(t)} x \right) \cdot x \cos \left(\frac{k\pi}{L(t)} x \right) dx = \frac{nL^2(t)}{\pi(k^2 - n^2)} \frac{1}{\cos((k+n)\pi)}\quad (\text{A.43})$$

Substituting this solution for the integral in (A.42) we finally arrive at:

$$\langle n|\dot{k}\rangle = -\frac{nk\dot{L}(t)}{L(t)(k^2 - n^2)} \frac{1}{\cos((k+n)\pi)} \quad (\text{A.44})$$

Note, that for the cosine we have:

$$\cos((k+n)\pi) = \begin{cases} -1 & \text{for } k \text{ even and } n \text{ odd or vice versa} \\ 1 & \text{for } k, n \text{ both even or odd} \end{cases} \quad (\text{A.45})$$

With this and equation (3.3) we get for (A.38):

$$-\varepsilon_n(t) \frac{nk\dot{L}(t)}{L(t)(n^2 - k^2)} (\pm 1) - \varepsilon_k(t) \frac{nk\dot{L}(t)}{L(t)(k^2 - n^2)} (\pm 1) = (\pm 1) \frac{nk\dot{L}(t)}{L(t)(n^2 - k^2)} g_{nk}(t) \quad (\text{A.46})$$

So, in the end we have:

$$\max_{0 \leq t \leq T^*} \left| \frac{\langle n|\hat{H}(t)|n\rangle}{g_{nk}(t)} \right| = \max_{0 \leq t \leq T^*} \left| \frac{nk\dot{L}(t)}{L(t)(n^2 - k^2)} \right| \quad (\text{A.47})$$

If we now turn to linear wall displacements we have $L(t) = L(0) + vt$ and thus $\dot{L}(t) = v$ which gives the result presented in section 4.6.4.

A.5. Adiabatic Behaviour of the Coulomb Potential

As above, we use the adiabatic condition, equation (4.10). We are interested in the stability of the different energy levels and in order to make a most general statement, we do not want to consider special time dependencies which are always dependent of the realization of a certain process. First, we examine the right-hand side:

$$g_{nk}(t) \stackrel{(3.4)}{=} -\frac{me^4 Z^2(t)}{2(4\pi\varepsilon_0)^2} \left(\frac{1}{n^2} - \frac{1}{k^2} \right) \quad (\text{A.48})$$

Now, we focus on the numerator of the right-hand side:

$$\langle n|\dot{\hat{H}}(t)|k\rangle = \langle n| \left(\lim_{dt \rightarrow 0} \frac{\hat{H}(t+dt) - \hat{H}(t)}{dt} \right) |k\rangle \quad (\text{A.49})$$

with the hamilton operator of the coulomb potential

$$\hat{H}(t) = -\frac{\Delta}{2m} - \frac{Z(t)e^2}{4\pi\varepsilon_0 r} \quad (\text{A.50})$$

we arrive at:

$$\begin{aligned} \langle n|\dot{\hat{H}}(t)|k\rangle &= \langle n| -\frac{e^2}{4\pi\varepsilon_0 r} \dot{Z}(t) |k\rangle \\ &= -\frac{e^2}{4\pi\varepsilon_0} \dot{Z}(t) \langle n| \frac{1}{r} |k\rangle \\ &= -\frac{e^2}{4\pi\varepsilon_0} \dot{Z}(t) \int_0^\infty \varphi_n(t) \frac{1}{r} \varphi_k^*(t) dr \end{aligned} \quad (\text{A.51})$$

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Taking the eigenfunctions of the coulomb potential from section 3.3 and suppressing the constants in front of the integral, we finally arrive at

$$\langle n | \hat{H}(t) | k \rangle = \frac{e^2 m Z(t)}{4\pi \epsilon_0} f_{nk}(a) \quad (\text{A.52})$$

The integral was computed with MATHEMATICA. We have $f_{nk}(a) \propto \frac{1}{n^2}$ and $f_{nk}(a)$ being a monotone decreasing function of a with $a \equiv \frac{n}{k}$ for $n > k$. Taking the denominator into account and suppressing all parameters which are independent of the state number, we have:

$$\frac{\langle n | \hat{H}(t) | k \rangle}{g_{nk}} = \frac{f_{nk}(a)}{\left(\frac{1}{n^2} - \frac{1}{k^2}\right)} = \frac{f_{nk}(a)}{\frac{1}{n^2} - \frac{a^2}{n^2}} = \frac{f_{nk}(a)}{\frac{1-a^2}{n^2}} = \frac{f_{nk}(a)n^2}{1-a^2} \quad (\text{A.53})$$

We see that the maximum is reached for small a since $f_{nk}(a)$ is a monotone decreasing function of a and for $a \rightarrow 1$. Since $n > k$ it follows that $a > 1$, thus the condition for the maximum is fulfilled if $n \rightarrow k$ and $n \rightarrow n_{\max}$. The n_{\max} denotes the ionization level.

A.6. Properties of the Trace for Operators of Special Form

Here, we want to proof special properties of the trace for operators with certain restraints. First, we show that the commutator of any two hermitian operators has always a vanishing trace. Then, we proof that product of two operators, diagonal in the same basis vector set, is still diagonal in the same basis set. We finish with a proof for the trace over the product of a diagonal and a traceless operator to vanish.

A.6.1. Trace over an Arbitrary Commutator

We know from the cyclic property of the trace, that trivially holds:

$$\text{Tr}([\hat{A}, \hat{B}]) = 0 \quad (\text{A.54})$$

We now want to show, that not only the whole trace vanishes, but every single diagonal element of the matrix of the commutator, represented in the eigenbasis set of one of the operators in the commutator, equals zero for hermitian operators. For this, we consider the matrix elements of the commutator, with $|\alpha\rangle$ and $|\beta\rangle$ denoting eigenfunctions of the hermitian operators \hat{A} and \hat{B} respectively. So, we have:

$$\begin{aligned} [\hat{A}, \hat{B}]_{mn} &= \langle \alpha_m | \hat{A}\hat{B} - \hat{B}\hat{A} | \alpha_n \rangle \\ &= \sum_{ij} A_{mm} \langle \alpha_m | \beta_i \rangle \langle \beta_i | \hat{B} | \beta_j \rangle \langle \beta_j | \alpha_n \rangle - \sum_{ij} \langle \alpha_m | \beta_i \rangle \langle \beta_i | \hat{B} | \beta_j \rangle \langle \beta_j | \alpha_n \rangle A_{nn} \end{aligned} \quad (\text{A.55})$$

where we have used that the basis sets are complete ($\sum_i |\beta_i\rangle \langle \beta_i| = \hat{1}$) and that the $|\alpha\rangle$ are eigenfunctions of \hat{A} . With the abbreviation $\gamma_{ij} \equiv \langle \alpha_i | \beta_j \rangle$ we have:

$$\begin{aligned} [\hat{A}, \hat{B}]_{mn} &= \sum_{ij} A_{mm} \gamma_{mi} B_{ij} \gamma_{jn}^* - \sum_{ij} \gamma_{mi} B_{ij} \gamma_{jn}^* A_{nn} \\ &= (A_m - A_n) \sum_{ij} \gamma_{mi} B_{ij} \gamma_{jn}^* \end{aligned} \quad (\text{A.56})$$

We can easily see, that all diagonal elements that fulfill $m = n$ equal zero. So, the diagonal elements of the commutator of arbitrary operators all equal zero. The resulting operator is traceless.

Moreover, using the cyclic property of the trace, the antihermicity of the commutator of hermitian operators and the identity $\text{Tr}(F^\dagger) = \text{Tr}(F)^*$, it can be seen easily that for any hermitian operators A, B, C we have:

$$\text{Tr}(C[A, B])^* = -\text{Tr}([A, B]C) = -\text{Tr}(C[A, B]) \Rightarrow \Re\{\text{Tr}(C[A, B])\} = 0 \quad (\text{A.57})$$

A.6.2. Product of Two Diagonal Operators

The product of two operators that are diagonal in the same eigenbasis, is still diagonal in this basis set:

$$\left(\hat{A}\hat{B}\right)_{mn} = \langle \gamma_m | \hat{A}\hat{B} | \gamma_n \rangle = A_{mm} B_{nn} \delta_{mn} \quad (\text{A.58})$$

A.6.3. Trace of Product of a Traceless Operator and a Diagonal one

We have two operators with one of them being traceless in the eigenbasis set of the other one:

$$\hat{A} = \sum_{ij} a_{ij} |i\rangle \langle j| \quad \text{with } a_{ij} = 0 \quad \forall i \neq j \quad (\text{A.59})$$

$$\hat{B} = \sum_{ij} b_{ij} |i\rangle \langle j| \quad \text{with } b_{ii} = 0 \quad (\text{A.60})$$

With this, we have:

$$\begin{aligned} \left(\hat{A}\hat{B}\right)_{ik} &= \sum_j a_{ij} |i\rangle \langle j| b_{jk} |j\rangle \langle k| \\ &= \sum_j a_{ij} b_{jk} |i\rangle \langle k| \end{aligned} \quad (\text{A.61})$$

For the diagonal elements we have $i = k$ and therefore:

$$\left(\hat{A}\hat{B}\right)_{kk} = \sum_j a_{kj} b_{jk} |k\rangle \langle k| \quad (\text{A.62})$$

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Here, either $a_{kj} = 0$, if $k \neq j$, or $b_{jk} = 0$, if $k = j$. So, in every case we have:

$$\left(\hat{A}\hat{B}\right)_{kk} = 0 \implies \text{Tr}\left(\hat{A}\hat{B}\right) = 0 \quad (\text{A.63})$$

A.7. On the Concept of Fast Processes

We investigate the behaviour of systems under very fast processes. To this end, we have a look at the DYSON series:

$$\hat{U}(t, 0) = \hat{1} + \sum_{n=1}^{\infty} U^n(t, 0) \quad (\text{A.64})$$

with

$$\hat{U}^n(t, 0) = i^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \hat{H}(t_1) \hat{H}(t_2) \cdots \hat{H}(t_n) \quad (\text{A.65})$$

We suppose the hamilton operator to be differentiable and expand it in its power series:

$$\hat{H}(t) = \hat{H}(0) + \underbrace{\frac{\partial \hat{H}}{\partial t}}_{\equiv \hat{C}} \Big|_0 \cdot t + \dots \quad (\text{A.66})$$

Considering changes which happen very fast, we neglect higher order terms in time. Since in the Dyson series higher order terms contain higher order in time t , we now consider only the first addend:

$$\hat{U}(t, 0) = \hat{1} - i \int_0^t d\tau \hat{H}(\tau) \pm \dots \quad (\text{A.67})$$

Substituting our expansion for $\hat{H}(t)$ we get:

$$\begin{aligned} \hat{U}(t, 0) &= \hat{1} - i \int_0^t d\tau \left(\hat{H}(0) + \hat{C}\tau \right) \\ &= \hat{1} - i\hat{H}(0)t - i\frac{1}{2}\hat{C}t^2 \end{aligned} \quad (\text{A.68})$$

Now, we check wether the interaction energy remains constant:

$$\begin{aligned} \text{Tr}\left(\hat{\varrho}(t)\hat{H}^I\right) &= \text{Tr}\left(\hat{U}(t)\hat{\varrho}(0)\hat{U}^\dagger(t)\hat{H}^I\right) \\ &\stackrel{(\text{A.68})}{=} \text{Tr}\left(\left\{\hat{1} - i\hat{H}(0)t - i\hat{C}t^2\right\}\hat{\varrho}(0)\left\{\hat{1} + i\hat{H}(0)t + i\hat{C}t^2\right\}\hat{H}^I\right) \end{aligned} \quad (\text{A.69})$$

Evaluating this term yields:

$$\begin{aligned} \text{Tr}\left(\hat{\varrho}(t)\hat{H}^I\right) &= \text{Tr}\left(\hat{\varrho}(0)\hat{H}^I\right) - \dots \\ &\quad \dots - i\text{Tr}\left(\hat{H}(0)\hat{\varrho}(0)\hat{H}^I\right)t + i\text{Tr}\left(\hat{\varrho}(0)\hat{H}(0)\hat{H}^I\right)t + \mathcal{O}(t^2) \end{aligned} \quad (\text{A.70})$$

Since the compound system is supposed to start in a canonical state, namely

$$\hat{\rho}(0) = \frac{e^{-\beta\hat{H}(0)}}{Z(0)} \quad (\text{A.71})$$

we have $[\hat{\rho}(0), \hat{H}(0)] = 0$ and the last two addends thus cancel. We obtain:

$$\text{Tr}\left(\hat{\rho}(0)\hat{H}^I\right) = \text{Tr}\left(\hat{\rho}(t)\hat{H}^I\right) \Leftrightarrow \langle\hat{H}^I\rangle = \text{const.} \quad (\text{A.72})$$

The interaction energy is thus constant. This supports the guess that infinitely fast processes conserve the interaction energy. However, the truncation of the DYSON series may look questionable since the faster the process, the bigger \hat{C} , in general. This would need further investigation.

A. Appendix

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