On reduced dynamics of quantum-thermodynamical systems

vorgelegt von
Diplom-Physikerin
Akiko Kato

von der Fakultät II - Mathematik und Naturwissenschaften
der Technischen Universität Berlin
zur Erlangung des akademischen Grades

Doktor der Naturwissenschaften
Dr. rer. nat.

genehmigte Dissertation

Promotionsausschuß:

Vorsitzender:	Prof. Dr. M. Schoen
Gutachter:	Prof. Dr. W. Muschik
Gutachter:	Prof. Dr. A. Knorr

Tag der wissenschaftlichen Aussprache: 9. Dezember 2004

Berlin 2004
D 83

Danksagung

Ich danke herzlich

Herrn Prof. Dr. W. Muschik für die Betreuung dieser Arbeit und dafür, daß ich sowohl durch Gespräche mit ihm, als auch in seinen Vorlesungen und Seminaren viel über Physik im allgemeinen und über Thermodynamik im speziellen lernen konnte.

Herrn Prof. Dr. A. Knorr für konstruktive Diskussionen und dafür, daß er sich als zweiter Gutachter zur Verfügung gestellt hat.

Herrn Prof. Dr. M. Schoen als Vorsitzendem des Promotionsausschusses.

den Mitgliedern der Arbeitsgruppe, Dr. Christina Papenfuß, Dr. Sebastian Gümbel, Dr. Heiko Herrmann und Dr. Gunnar Rückner für eine schöne gemeinsame Zeit am Institut und für interessante Einblicke in ihre Arbeitsgebiete.

Herrn Dr. habil. J.-P. Kaufmann für die fröhlichen Stunden im Musikkreis der Physik.

Herrn Dipl.-Phys. Andreas Staude als meinem persönlichen Lieferanten von Ferrero-Küßchen.

Hiermit versichere ich an Eides statt, daß ich die Dissertation selbständig verfaßt habe.

Berlin, 3. Oktober 2004

Zusammenfassung

Für die Behandlung irreversibler Prozesse diskreter quantenthermodynamischer Systeme eignet sich die reduzierte Beschreibung. Hierfür betrachtet man bezüglich einer gegebenen Beobachtungsebene verschiedene begleitende Prozesse zur quantenmechanischen von Neumann Dynamik. Während die kanonische Dynamik auch unabhängig von einer mikroskopischen Bewegungsgleichung hergeleitet werden kann, wird die von Neumann Dynamik im Rahmen des Projektionsformalismus in einen relevanten und einen irrelevanten Anteil bezüglich der Beobachtungsebene aufgeteilt. Als Beispiel für die Projektionsdynamik geben wir die Robertson Dynamik und die Fick Sauermann Dynamik an und untersuchen deren Eigenschaften sowie geeignete Projektionsoperatoren. Hierbei können wir den Zugang über das Mori Skalarprodukt und dem entsprechenden Kawasaki Gunton Operator über den generalisiert kanonischen Dichteoperator hinaus auf allgemeine begleitende Operatoren erweitern. Unter Verwendung der kanonischen Dynamik wird die Rate der von Neumann Entropie bestimmt und analysiert. In der thermodynamischen Anwendung sind zeitabhängige Observablen, die von Arbeitsvariablen abhängen, von besonderem Interesse. Um den ersten Hauptsatz anwenden zu können, müssen die grundlegenden thermodynamischen Gößen, Arbeits- und Wärmeaustausch, bekannt sein. Deswegen fordern wir, daß begleitende Prozesse hinreichend für die zugehörigen Arbeits- und Flußobservablen sind. Im allgemeinen sind weder die kanonische Dynamik noch die Projektionsdynamiken hinreichend, so daß wir anschließend einen Ansatz für eine hinreichende Dynamik angeben. In Zusammenhang mit der Extended Thermodynamics verallgemeinern wir die Forderung nach der hinreichenden Dynamik auf eine schwächere Formulierung. Anhand des Beispiels der kanonischen Dynamik diskreter Systeme unter thermischem Kontakt analysieren wir die Entropierate und wenden das Konzept der Kontakttemperatur auf die zugehörigen Wärmeübergänge an. In einem anderen Beispiel behandeln wir die Elektron-Phonon-Wechselwirkung im Festkörper. Hier wird die Robertson Projektion durchgeführt, um den Einteilchenanteil vom Korrelationsanteil für Mehrteilchen zu trennen. Beide Anteile sind relevant, um die Elemente der Elektronendichtematrix zu bestimmen. Die Dynamik von Teilsystemen sowie deren begleitende Prozesse werden untersucht, auch im Hinblick auf das Hinreichendsein. Die von Neumann Dynamik eines Teilsystems wird um einen Term ergänzt, der die Entropieproduktion bei innerem Wärmestrom berücksichtigen soll.

Abstract

Irreversible processes in quantum-thermodynamical discrete systems can be treated by means of reduced information dynamics. For this, we consider different accompanying processes of the quantum mechanical von Neumann dynamics with respect to a given beobachtungsebene. While canonical dynamics can be derived independently from any quantum mechanical dynamics, projection formalism induces the isolation of the relevant part of the von Neumann dynamics from its irrelevant part according to the beobachtungsebene. We present the Robertson dynamics and the Fick Sauermann dynamics as projection dynamics, their properties and appropriate projectors. We are able to generalise the conventional approach through the Mori product and the according Kawasaki Gunton operator for the generalised canonical density operator to any accompanying operator. Starting from canonical dynamics, it is possible to calculate and analyse the rate of the von Neumann entropy. In thermodynamical applications, observables depending on work variables are of special interest. In order to apply the First Law, the essential thermodynamical quantities of work and heat exchange have to be known. Thus we demand the sufficiency of accompanying processes for the according work and flux observables. In general, neither canonical dynamics nor projected dynamics are sufficient for them, so we give an ansatz to obtain sufficient dynamics. With regard to the Extended Thermodynamics, we generalise the demand of the sufficiency to a weaker formulation. As an example, we consider the canonical dynamics of discrete systems in thermal contact, where we analyse the rate of entropy and apply the concept of contact temperature to the heat exchange. Another example is the electron-phonon interaction in a solid. Here, the Robertson projection is used to divide the von Neumann dynamics into a single particle part and a many particle correlation part, which are both relevant to determine the according electron density matrix elements. Concerning the dynamics of a subsystem, its accompanying processes are investigated, also with regard to the suffuciency. The von Neumann dynamics for a subystem is supplemented with an additional term takig the entropy production by internal heat fluxes into account.

Contents

Chapter 1

Introduction

In the quantum mechanical approach of thermodynamics, the projection operator formalism has been successful in many applications. This technique was introduced by Nakajima [Nak58] and Zwanzig [Zwa60], and expanded later by Robertson [Rob66] to derive Langevin Mori theory [Fic83], [Bal86] and generalised Fokker Planck equation [Gra82].

The main argument, why people use reduced information dynamics, is that one needs evolution equation for only few “relevant” macroscopic variables, neglecting all “irrelevant” parts regarding the considered experiment [Rau96]. A macroscopic thermodynamical system has practically an infinite number of microscopic degrees of freedom. It is not possible to find out its exact quantum mechanical state, not to mention its density operator ϱ, because we have only restricted information about the system, represented by a limited number of measuring instruments. It is not necessary to know the microstate, if we only have measuring devices to obtain a state which is macroscopically not distinguishable from the exact microstate. Therefore we do not need the time development of the microstate, but only that of the macroscopically indistinguishable state which belongs to the microstate. This can be performed by the reduced description implemented by the projection technique. Choosing a set, called “beobachtungsebene”, including a limited number of relevant independent observables, we look for a density operator $\hat{\varrho}$ different from the microscopic density operator which generates the correct expectation values with respect to the chosen beobachtungsebene. Such dynamics are called accompanying processes according to [Mus94].

This lack of information leads to an other desired characteristic of the projected description, the irreversibility [Zwa60], [Zub74], [Zub96]. On the one hand, we have the explicit dependence of the dynamics on memory effects in terms of a time integral. On the other hand, the method described above do not suffice determining a unique relevant density matrix. There exist in fact a lot of possible trace class operators satisfying the same macroscopic conditions. Jayne’s information theory approach [Jay57a], [Jay57b] tells us, how to choose that density operator R which maximises the von Neumann entropy, implying minimum and most bias free information. Consequently, R has the well-known form of a generalised canonical operator. Assuming the von Neumann dynamics for an isolated quantum mechanical system

$$\dot{\varrho} = -\frac{i}{\hbar}\,[H, \varrho] \ , \tag{1.1}$$

which is a direct conclusion of the Schrödinger equation, it is a fact, that the time derivative of the von Neumann entropy vanishes. The increase of entropy manifested in the Second Law cannot be explained here, because usual quantum mechanics is a reversible theory. There are three ways to introduce irreversibility, that means non vanishing entropy production, into quantum mechanics: First of all the already discussed reduced description by introducing the projection technique. Here irreversibility is generated by missing information. In [Schi94], [Kat00a], [Kat99] projection formalism is used to show the validity of the Second Law under certain conditions. The second possibility for introducing irreversibility is to change the von Neumann equation without altering the Schrödinger equation. In this case an additional term appears in the von Neumann equation which is directly connected to the entropy production [Kau96], [Lin83], chapter 8.3. This kind of entropy production has nothing to do with missing information as in the case of projector formalism, but it is generated by special construction of mixed states from pure ones. The third possibility is to change the Schrödinger equation by introducing friction terms, that means by introducing microscopic irreversibility [Arb96], [Gis81].

Another motivation to use the reduced description concerns the treatment of subsystems of an isolated compound system. Even if we only consider reduced dynamics of a subsystem, the evolution equation derived from (1.1) still contains the full density matrix of the compound system, which is unknown in general (chapter 8). This problem does not arise in projection operator formalism.

When using the projection operator formalism, a problem arises, if the work variables of the considered system (volume, magnetic field etc.) are time dependent: Are the expectation values belonging to the time derivatives of the work variables correctly described by the projections? Or are these time derivatives only represented approximatively? This question is essential for thermodynamics, because the power differential appearing in the First Law is described by these time derivatives of the work variables. This problem is characterised by the concept of "sufficiency" of the beobachtungsebene, which is treated in chapter 4.

In chapter 2 and 3, we briefly recapitulate the projection operator formalism and the corresponding dynamics. Next, in chapter 4 and 5, we analyse to what extend we can describe thermodynamical quantities like work and heat flux in this context. Is it possible to calculate such quantities from the relevant statistical operator even if it belongs to a beobachtungsebene that does not include the work or flux operators? This is the quite fundamental question of sufficiency which must be dealt with, if the thermodynamical behavior of the quantum system is regarded. In order to examine work quantities, we will consider operators with explicit time dependence, while most authors neglect the exchange of work, cf. [Rau96], [Ali88]. In chapter 6 we show an example of two discrete systems in purely thermal contact, that means no work nor particle exchange is considered. Chapter 7 includes an example of many body quantum mechanics, the electron phonon interaction.

At last in chapter 8, we treat dynamics of subsystems derived from (1.1), where we turn our special attention to the increase of entropy due to internal heat fluxes. Thermodynamical factors which lead to increasing entropy are internal heat- and material fluxes and other entropy productions. The material flux will be omitted here. The entropy production we can explain with an additional term in von Neumann dynamics, as shown in [Ber84], [Kau96]. Concerning the heat flux, we will investigate the connection between the corresponding entropy term and a possible additional term in (1.1) as a result of time depending probablities of the quantuum mechanical states.

Chapter 2

Fundamentals

In this chapter we will present basic concepts which are needed for the mesoscopic description of quantum thermodynamics. Some terms like beobachtungsebene and accompanying process are introduced, and the thermodynamical situation is explained that is adequate for the theory of discrete systems.

2.1 The Density Operator and its Dynamics

The vector space of linear operators on Hilbert space is called Liouville space $\mathcal{L}$ [Fic83]. Let us define:

Definition 1

$$\begin{aligned} \mathcal{L}^{ob} &:= \{X \in \mathcal{L} \,|\, X = X^+\} && (2.1)\\ \mathcal{L}^{ob}_{tr} &:= \{X \in \mathcal{L} \,|\, X = X^+, |\,Tr\,X| < \infty\} && (2.2)\\ \mathcal{L}^{ob}_{\varrho} &:= \{X \in \mathcal{L} \,|\, X = X^+, X \geq 0, Tr\,X = 1\} && (2.3) \end{aligned}$$

$\mathcal{L}^{ob}$ is the set of quantum mechanical observables and $\mathcal{L}^{ob}_{\varrho}$ the set of quantum mechanical density operators. $\mathcal{L}^{ob}$ and $\mathcal{L}^{ob}_{tr}$ are vector spaces.

The derivative of the density matrix ϱ associated to a quantum mechanical system yields the **von Neumann dynamics** [Fic84]

$$\dot{\varrho} = -iL\,\varrho + \overset{\circ}{\varrho}\ . \tag{2.4}$$

Here, L is the Liouville operator.

Definition 2 ***Liouville operator*** *belonging to the system whith Hamiltonian* H*:*

$$L : \mathcal{L} \to \mathcal{L}$$

$$L\,X := \frac{1}{\hbar}\,[H, X]\,. \tag{2.5}$$

$\overset{\circ}{\varrho}$ can be justified with time depending probabilities of the eigenstates: the time derivative of

$$\varrho = \sum_m |\varphi_m\rangle \varrho_m \langle\varphi_m| \tag{2.6}$$

using Schrödinger's equation yields

$$\dot{\varrho} = -\frac{i}{\hbar} H \varrho + \frac{i}{\hbar} \varrho H + \underbrace{\sum_m |\varphi_m\rangle \dot{\varrho}_m \langle\varphi_m|}_{:=\overset{\circ}{\varrho}} \ . \tag{2.7}$$

The starting point within the framework of projection dynamics is the classical von Neumann equation without additional term $\overset{\circ}{\varrho}$. In chapter 8 we will dwell on $\overset{\circ}{\varrho}$.

2.2 Beobachtungsebene

The mesoscopic description of a system is based on the choise of a limited set of observables that are relevant to the considered problem. This set of relevant observables is called **beobachtungsebene** [Schw65].

$$\mathcal{B} := \{G_1, \ldots, G_n\} \quad \text{with} \quad n \in \mathbb{N} \tag{2.8}$$

$$G_i \in \mathcal{L}^{ob} \quad \text{for all} \quad i \in \{1, \ldots, n\} \tag{2.9}$$

The observables in the beobachtungsebene do not necessarily commute, but they must be linearily independent to simplify matters.

Let us introduce the following abbreviation:

$$\underline{G} := (G_1 \ldots G_n)^t \ . \tag{2.10}$$

The expectation values of these observables are given by

$$g_i \ := \ \mathrm{Tr}\,(G_i\, \varrho) =: \langle G_i \rangle \quad \text{for all} \quad i \in \{1, \ldots, n\} \tag{2.11}$$

$$\text{or} \quad \underline{g} \ := \ \mathrm{Tr}\,(\underline{G}\, \varrho) \ =: \langle \underline{G} \rangle\,, \tag{2.12}$$

if ϱ is the quantum mechanical density operator of the considered system.

In general, the observables $\underline{G}$ in the beobachtungsebene depend on some work variables $a_1(t)$, ..., $a_m(t)$. This is for instance the case, if we vary the volume of the considered discrete system with a piston during the experiment. Consequently, the Hamiltonian becomes a function of the time dependent work variable $V(t)$. The abbreviation

$$\underline{a} := (a_1 \ldots a_m)^t \tag{2.13}$$

will be used henceforth.

2.3 Accompanying Processes of Statistical Operators

Considering a macroscopic system it is not possible to determine its exact quantum mechanical state ϱ, because the only information being available are measured values of a finite number of observables, carried out by their measurement devices. In the mesoscopic level of discription we are even not interested in the exact quantum mechanical state, but in the expectation values $\underline{g} = \mathrm{Tr}\,(\underline{G}\,\varrho)$ of these few observables. For a chosen set of observables $\underline{G}(\underline{a})$, there exist a lot of quantum mechanical states that are macroscopically indistinguishable, because their expectation values $\underline{g}$ are the same. Therefore, we are free to choose any state $\hat{\varrho} \in \mathcal{L}_{\varrho}^{ob}$ instead of ϱ, if

$$\mathrm{Tr}\,(\underline{G}\,\varrho) = \mathrm{Tr}\,(\underline{G}\,\hat{\varrho}) \tag{2.14}$$

is stastisfied for $\mathcal{B} = \{\underline{G}\}$.

Definition 3 *Let be $\varrho : \mathbb{R} \to \mathcal{L}_{\varrho}^{ob}$ a quantum mechanical process. A dynamics of a density operator $\hat{\varrho} : \mathbb{R} \to \mathcal{L}_{\varrho}^{ob}$ is called* ***accompanying process of ϱ with respect to $\mathcal{B} = \{\underline{G}\}$****, if*

$$\mathrm{Tr}\left(\underline{G}(t)\,\varrho(t)\right) = \mathrm{Tr}\left(\underline{G}(t)\,\hat{\varrho}(t)\right) \qquad \textit{for} \quad t \in \mathbb{R}. \tag{2.15}$$

It is implied that each accompanying process is sufficiently often times continuously differentiable.

2.4 von Neumann Entropy and Generalised Canonical Operator

There exist a method to distinguish one special accompanying process from the practically unfinite numbers of other accompanying processes. In information theory, we use the Shannon measure to express how uncertain the outcome of an random experiment is. Suppose there are n possible results $F_1, \ldots, F_n$ in this experiment, whose probabilities are $p_1, \ldots, p_n$, then the Shannon entropy is given by $-k \sum_{j=1}^{n} p_j \ln p_j$, where k is a constant. The quantum mechanical equivalent can be defined and be used to determine the $\hat{\varrho}$ which maximises this entropy. This $\hat{\varrho}$ represents the greatest uncertainty and is mostly unbiassed.

Definition 4 ***von Neumann Entropy***

$$S : \mathcal{L}_{\varrho}^{ob} \to \mathbb{R}_0^+$$
$$S\,(X) := -k\; Tr(X\,\ln X) \tag{2.16}$$

Here, k is the Boltzmann constant.

Definition 5 *Let be ϱ the quantum mechanical density operator of a system. Let be $\mathcal{B} = \{\underline{G}\}$ a beobachtungsebene. That $\hat{\varrho} \in \mathcal{L}_{\varrho}^{ob}$ satisfying (2.14) which maximises the entropy of the considered system is called* ***generalised canonical operator with respect to $\mathcal{B}$*** *and will be denoted as $R_{\mathcal{B}}$:*

$$S_{\mathcal{B}} := \max_{\hat{\varrho}} S\,(\hat{\varrho}) = -k \min_{\hat{\varrho}} \left(Tr(\hat{\varrho}\,\ln \hat{\varrho}) \right) = -k\; Tr(R_{\mathcal{B}}\,\ln R_{\mathcal{B}})\,. \tag{2.17}$$

If it is clear which beobachtungsebene is meant, we will omit the index $\mathcal{B}$.

Theorem 1 *The generalised canonical operator $R_{\mathcal{B}}$ with respect to a beobachtungsebene $\mathcal{B} = \{\underline{G}\}$ has the following form:*

$$R_{\mathcal{B}} = \frac{1}{Z}\, e^{-\underline{\lambda}\cdot\underline{G}} \tag{2.18}$$

with the partition function

$$Z := Tr\, e^{-\underline{\lambda}\cdot\underline{G}}\,. \tag{2.19}$$

The $\underline{\lambda}$ are called Lagrangian multipliers.

Proof: See [Gra87] [Gra88]. □

Consider a thermodynamical process. Let the maximisation take place at every moment during the time intervall of this process, based on the expectation values at each time point.

Definition 6 *Let be $\varrho : \mathbb{R} \to \mathcal{L}^{ob}_{\varrho}$ a quantum mechanical process. That accompanying process of ϱ with respect to $\mathcal{B} = \{\underline{G}\}$ which maximises the entropy for all times is called* ***canonical****.*

This process preserves the canonical form of the generalised canonical operator for all time, so we denote its dynamics by

$$R_{\mathcal{B}} : \mathbb{R} \to \mathcal{L}^{ob}_{\varrho}\,. \tag{2.20}$$

We will omit the index $\mathcal{B}$, if it is clear which beobachtungsebene to use.

Theorem 2 *Let be ϱ the quantum mechanical density operator of a system. Let be R the according generalised canonical operator with respect to a beobachtungsebene $\mathcal{B} = \{G_1, \ldots, G_n\} = \{\underline{G}\}$. If*

$$\underline{s} \cdot \left(\underline{G} - \underline{g}\,\mathbb{I}\right) \neq 0 \quad \textit{for all} \quad \underline{0} \neq \underline{s} \in \mathbb{R}^n\,, \tag{2.21}$$

then the Lagrangian multipliers $\underline{\lambda}$ are uniquely determined by the $n+1$ constraints

$$Tr\,(\underline{G}\,R) = Tr\,(\underline{G}\,\varrho) \tag{2.22}$$

$$Tr\,R = 1\,. \tag{2.23}$$

Proof: See [Kat67], [Kau96]. □

We can rewrite the generalised canonical operator in the following manner:

$$R = e^{-\lambda_0} e^{-\underline{\lambda}\cdot\underline{G}}\,. \tag{2.24}$$

The $n+1$ constraints (2.22) and (2.23) that determine the Lagrangian multipliers $\lambda_0 \ldots \lambda_n$ can be also be written in terms of the partition function as

$$\underline{g} = -\frac{\partial \ln Z}{\partial \underline{\lambda}} \tag{2.25}$$

$$\text{and} \qquad \lambda_0 = \ln Z\,. \tag{2.26}$$

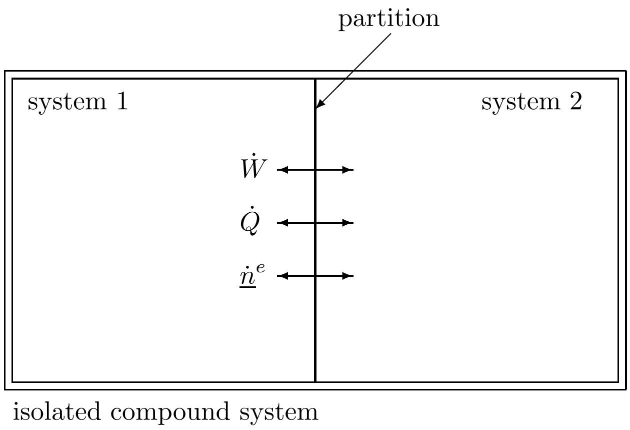
(2.25) is a consequence of Snider's derivation rule [Sni64]

$$\frac{\partial}{\partial z}\, e^{\,f(z)} = \int_0^1 e^{\,(1-\mu)f(z)}\, \frac{\partial f}{\partial z}\, e^{\,\mu f(z)}\, d\mu\,. \tag{2.27}$$

This is necessary, if $f(z)$ and $\frac{\partial f}{\partial z}$ do not necessarily commute, like here $\frac{\partial(\underline{\lambda}\cdot\underline{G})}{\partial\underline{\lambda}} = \underline{G}$ and $e^{\underline{\lambda}\cdot\underline{G}}$ [Fic83].

2.5 The Thermodynamical Situation

Thermodynamics of discrete systems deals with the following standard situation: consider an isolated compound system consisting of two interacting subsystems. According to the First Law of thermodynamics the change of energy in one subsystem is caused by exchange of work, heat and material with its environment represented by the second subsystem. Such systems are called Schottky systems according to [Scho29].



We will neglect material exchange mostly in this work, except for the example in chapter 7.

The Hamiltonian H of the whole system is described by

$$H = H_1 + H_{12} + H_2\,, \tag{2.28}$$

where H_{12} is the Hamiltonian describig the interaction between the two subsystems, denoted in the following as partition. Therefore it is valid

$$[H_1, H_2] = 0 \quad , \quad [H_1, H_{12}] \neq 0 \quad , \quad [H_2, H_{12}] \neq 0\,. \tag{2.29}$$

The compound system is isolated.

$$\dot{H} = 0 \tag{2.30}$$

Because of

$$\mathrm{Tr}\,(H_1\varrho)^{\bullet} = \mathrm{Tr}\left(\dot{H}_1\varrho\right) + \mathrm{Tr}\,(H_1\dot{\varrho}) \tag{2.31}$$

we can identify

$$\dot{W}_1 := \mathrm{Tr}\left(\dot{H}_1\,\varrho\right) \tag{2.32}$$

$$\dot{Q}_1 := \mathrm{Tr}\left(H_1\,\dot{\varrho}\right) = i\mathrm{Tr}\left(\varrho\,L\,H_1\right)\,, \tag{2.33}$$

which are expressions for work and heat exchange between the considered system no. 1 and its environment consisting of the partition and system no. 2. Thus we can define:

Definition 7 *In the situation described above, we call* $\dot{H}_1(\underline{a}(t)) = \frac{\partial H_1}{\partial \underline{a}} \cdot \underline{\dot{a}}(t)$ *the* ***thermodynamical work operator*** *and* iLH_1 *the* ***heat flux operator*** *of the first system.*

Using the same definition for all three systems, we have

$$\dot{W} := \mathrm{Tr}\left(\dot{H}\,\varrho\right) = \dot{W}_1 + \dot{W}_2 + \dot{W}_{12} \tag{2.34}$$

$$\dot{Q} := \mathrm{Tr}\left(H\,\dot{\varrho}\right) = \dot{Q}_1 + \dot{Q}_2 + \dot{Q}_{12}\,. \tag{2.35}$$

We will use later following two definitions [Mus94]:

Definition 8

$$\textit{The compound system is isolated.} \quad :\Leftrightarrow \quad \dot{W} = \dot{Q} = 0 \tag{2.36}$$

Definition 9

$$\textit{The partition is inert.} \quad :\Leftrightarrow \quad \dot{W}_{12} = \dot{Q}_{12} = 0\,. \tag{2.37}$$

Chapter 3

Dynamics of Statistical Operators

In this chapter we will present a few dynamics with reduced information based on a chosen beobachtungsebene, among them the canonical dynamics and the projected dynamics. The dynamics of von Neumann entropy is strongly coupled to the utilised dynamics. Some entropy rates are discussed as regards their definiteness.

3.1 Canonical Dynamics

The time derivative of the canonical accompanying process of ϱ with respect to $\mathcal{B} = \{\underline{G}\}$ (2.20) is called canonical dynamics [Mus94]. So the concept of beobachtungsebene is essential for this dynamics. In contrast to other dynamics presented in this work, we do not derive this dynamics from quantum mechanical dynamics (2.4), but the dynamics is constructed in matching with the measured values of the relevant observables.

Let us first introduce a term that will allow us to write the canonical dynamics in an elegant way.

Definition 10 ***Mori product***

$$\begin{aligned} (\,\cdot\,|\,\cdot\,) : \mathcal{L}^{ob} \times \mathcal{L}^{ob} &\rightarrow \mathbb{R} \\ (A, B) &\mapsto (A\,|\,B) := \int_0^1 Tr\big(A^+ \, e^{-\mu \underline{\lambda} \cdot \underline{G}} \, B \, e^{\mu \underline{\lambda} \cdot \underline{G}} \, R\big) \, d\mu \end{aligned} \tag{3.1}$$

This is a generalised version of the Mori product given in [Mor65].

Theorem 3 *The generalised Mori product is a real scalar product.*

Proof: See [Schi94]. □

With the abbreviation $\Delta G := G - \mathrm{Tr}\,(G\,\varrho)\,\mathbb{I}$ we get:

Theorem 4 ***Canonical dynamics*** *is given by*

$$
\begin{aligned}
\dot{R} &= R\,Tr\left(R\,(\underline{\lambda}\cdot\underline{G})^{\bullet}\right) - R\int_0^1 e^{\mu\underline{\lambda}\cdot\underline{G}}\ (\underline{\lambda}\cdot\underline{G})^{\bullet}\ e^{-\mu\underline{\lambda}\cdot\underline{G}}\,d\mu && (3.2)\\
&= -R\int_0^1 e^{\mu\underline{\lambda}\cdot\underline{G}}\ \left(\Delta\,(\underline{\lambda}\cdot\underline{G})^{\bullet}\right)\,e^{-\mu\underline{\lambda}\cdot\underline{G}}\,d\mu && (3.3)
\end{aligned}
$$

Proof: See [Mus94] or use the derivation rule (2.27). □

This results in

Theorem 5 *Canonical dynamics of the expectation values*

$$
\begin{aligned}
\underline{\dot{g}} = \frac{d}{dt}\,Tr\left(\underline{G}R\right) &= Tr\left(\underline{\dot{G}}\,R\right) + Tr\left(\underline{G}\,R\right)\,Tr\left(R\,(\underline{\lambda}\cdot\underline{G})^{\bullet}\right)\\
&\quad - Tr\left(\underline{G}\,R\int_0^1 e^{\mu\underline{\lambda}\cdot\underline{G}}\ (\underline{\lambda}\cdot\underline{G})^{\bullet}\ e^{-\mu\underline{\lambda}\cdot\underline{G}}\,d\mu\right) && (3.4)\\
&= Tr\left(\underline{\dot{G}}\,R\right) - \left(\underline{G}\,\middle|\,\Delta\,(\underline{\lambda}\cdot\underline{G})^{\bullet}\right)\,. && (3.5)
\end{aligned}
$$

From (2.18) and (2.19) we see that the generalised canonical operator depends on the $\underline{\lambda}$ and the $\underline{G}(\underline{a})$. Thus we can write the canonical dynamics as follows:

$$
\dot{R} = \frac{\partial R}{\partial\underline{\lambda}}\cdot\underline{\dot{\lambda}} + \frac{\partial R}{\partial\underline{a}}\cdot\underline{\dot{a}}\,, \tag{3.6}
$$

where the coefficients can be read off in (3.3):

$$
\begin{aligned}
\frac{\partial R}{\partial\underline{\lambda}} &= -R\int_0^1 e^{\mu\underline{\lambda}\cdot\underline{G}}\,(\Delta\underline{G})\,e^{-\mu\underline{\lambda}\cdot\underline{G}}\,d\mu && (3.7)\\
\frac{\partial R}{\partial\underline{a}} &= -R\,\underline{\lambda}\cdot\int_0^1 e^{\mu\underline{\lambda}\cdot\underline{G}}\left(\Delta\frac{\partial\underline{G}}{\partial\underline{a}}\right)e^{-\mu\underline{\lambda}\cdot\underline{G}}\,d\mu\,. && (3.8)
\end{aligned}
$$

(Note that the differentiation with respect to $\underline{a}$ and $\underline{\lambda}$ are in fact functional derivatives, to be noted correctly as $\frac{\delta}{\delta\underline{a}(t)}$ or $\frac{\delta}{\delta\underline{\lambda}(t)}$.)

The dynamics of the expectation values is then given by

$$
\underline{\dot{g}} = \frac{\partial\underline{g}}{\partial\underline{\lambda}}\cdot\underline{\dot{\lambda}} + \frac{\partial\underline{g}}{\partial\underline{a}}\cdot\underline{\dot{a}} \tag{3.9}
$$

with the coefficients

$$
\begin{aligned}
\frac{\partial g_i}{\partial\lambda_j} &= -\left(G_i\,\middle|\,\Delta G_j\right) && (3.10)\\
\frac{\partial g_i}{\partial a_j} &= \left(\mathbb{I}\,\middle|\,\frac{\partial G_i}{\partial a_j}\right) - \left(G_i\,\middle|\,\Delta\frac{\partial\underline{G}}{\partial a_j}\right)\cdot\underline{\lambda}\,, && (3.11)
\end{aligned}
$$

as can be seen in (3.5) using the identity

$$(\mathbb{I} \mid B) = \mathrm{Tr}\,(B\,R) \quad \text{for} \quad B \in \mathcal{L}^{ob}\,. \tag{3.12}$$

This is not a dynamics with practical use anyhow, because we need the dynamics of the Lagrangian multipliers to solve the differential equation (3.5) or (3.6). From theorem 2 we know that the Lagrangian multipliers are unique, but there is no way to get out $\underline{\lambda}$ explicitly of (2.22) and (2.23). This leads us to the next section where we discuss another way in deriving a mesoscopic dynamics.

3.2 The Relevant Part of the Density Operator

In this section we will treat dynamics of the relevant part of the density operator. Density operators of quantum mechanical systems contain much more information than we need practically for a specific problem. This was why we introduced the concept of reduced information level. The operators in the chosen beobachtungsebene $\mathcal{B} = \{\underline{G}\}$ do not form a complete base normally, so the density matrix has for this paticular beobachtungsebene a relevant part, which contributes to the calculation of expectation values, and an irrelevant part, which does not show any effect on the trace. Here, specific operators are introduced for the purpose of isolating the relevant part from the irrelevant part of the density operator taking into account the chosen beobachtungsebene.

$$\varrho = \varrho_{rel} + \varrho_{irrel} \qquad \text{with} \tag{3.13}$$

$$\varrho_{rel} \in \mathcal{L}^{ob}_{\varrho} \quad , \quad \mathrm{Tr}\,\varrho_{irrel} = 0 \tag{3.14}$$

$$\begin{aligned} \mathrm{Tr}\left(\underline{G}\,\varrho\right) &= \mathrm{Tr}\left(\underline{G}\,\varrho_{rel}\right) & (3.15)\\ \underline{0} &= \mathrm{Tr}\left(\underline{G}\,\varrho_{irrel}\right) & (3.16) \end{aligned}$$

The isolation of these two parts is achieved by mappings on the Liouville space. With this operator, the von Neumann equation (2.4) (whith $\overset{\circ}{\varrho}= 0$)

$$\dot{\varrho}(t) = -iL\,\varrho(t) \tag{3.17}$$

is transformed into a mesoscopic dynamics of the relevant part of the statistical operator. The choice of $\overset{\circ}{\varrho}= 0$ means that we start out here from pure quantum mechanics without a dissipative term. Increasing entropy in an isolated system is not achieved by the additional dissipative term in this context. It is rather the limited available information of the system that produces artificially an increase of entropy for the observer of the system. If it were possible to determine the exact quantum mechanical state at one time point, we know its time evolution given by (3.17), and the entropy should remain constant. In chapter 8 we will consider a few examples for dynamics with $\overset{\circ}{\varrho}\neq 0$.

In the literature, we can find different sorts of such mappings. Let be $\varrho : \mathbb{R} \to \mathcal{L}^{ob}_{\varrho}$ a quantum dynamical process.

$$
\begin{array}{rrcll}
\text{Nakajima Zwanzig type} & P : \mathcal{L}_{\varrho}^{ob} & \to & \mathcal{L}_{\varrho}^{ob} & \\
 & \varrho & \mapsto & P\,\varrho = \varrho_{rel} \quad \text{and} \quad \dot{P} = 0 & (3.18) \\
 & & & \dot{\varrho}_{rel} = P\,\dot{\varrho} & (3.19)
\end{array}
$$

$$
\begin{array}{rrcll}
\text{Robertson type} & P : \mathcal{L}_{\varrho}^{ob} & \to & \mathcal{L}_{\varrho}^{ob} & \\
 & \varrho & \mapsto & P\,\varrho = \varrho_{rel} \quad \text{and} \quad \dot{P}\,\varrho = 0 & (3.20) \\
 & & & \dot{\varrho}_{rel} = P\,\dot{\varrho} & (3.21)
\end{array}
$$

$$
\begin{array}{rrcll}
\text{Fick Sauermann type} & P : \mathcal{L}_{\varrho}^{ob} & \to & \mathcal{L}_{\varrho}^{ob} & \\
 & \varrho & \mapsto & P\varrho = \varrho_{rel} & (3.22) \\
 & & & \dot{\varrho}_{rel} = P\,\dot{\varrho} + \dot{P}\,\varrho & (3.23)
\end{array}
$$

Here, P is supposed to be linear in all three cases, and idempotent $P^2 = P$, because it is desirable that

$$
\begin{array}{rrcll}
 & P\,\varrho_{rel} & = & \varrho_{rel} & (3.24) \\
\text{or} & P\dot{\varrho}_{rel} & = & \dot{\varrho}_{rel} & (3.25)
\end{array}
$$

is valid. Since P is linear and idempotent, it is often called projector. It is necessary to distinguish between such projectors and orthogonal projectors, which are both idempotent and selfadjoint with respect to a given scalar product, as we will see later.

Let us define the operator:

$$Q := \mathbb{I} - P \tag{3.26}$$

with the corresponding operator P in each cases. Q is that mapping which maps ϱ to ϱ_{irrel} by definition. If P is idempotent, Q is idempotent, too.

The idea is now to derive dynamics of accompanying processes ϱ_{rel} (definition 3) using these mappings. In this case the mapping P can be also time-dependent. Linear mappings on the Liouville space $\mathcal{L}$ are called superoperators. An example of a superoperator is the Liouville operator (definition 2). Here, superoperators that enable the derivation of the dynamics of the relevant statistical operator are interesting. Nonlinear mappings delivering the relvant part are treated in [Kat99].

Originally, the projection dynamics was developed by Nakajima and Zwanzig [Nak58], [Zwa60] with time independent projection operators, to isolate for example the diagonal matrix elements of a Hamiltonian from its non diagonal elements. Robertson [Rob66] introduced time dependent projectors, keeping the dynamics (3.19) unchainged, followed by Fick and Sauermann [Fic83], who considered a more general dynamics (3.23) including the time derivative of the projector.

3.2.1 Robertson Dynamics

The dynamics that is based on equation (3.20) and (3.21) has been treated by Robertson [Rob66]. Starting out with the von Neumann equation (3.17) and taking into accout (3.20), it is possible to derive the so called Robertson Dynamics, an integro-differential equation for ϱ_{rel}.

Theorem 6 ***Robertson dynamics***
The dynamics of ϱ_{rel} using the linear mapping (3.20), (3.21) is given by

$$\dot{\varrho}_{rel}(t) = -iP(t)\,L(t)\,\varrho_{rel}(t) - \int_{t_0}^{t} P(t)\,L(t)\,T(t,s)\,Q(s)\,L(s)\,\varrho_{rel}(s)\,ds \qquad (3.27)$$

$$\begin{aligned} \textit{with} \qquad \frac{\partial}{\partial s}T(t,s) &= iT(t,s)\,Q(s)\,L(s) && (3.28)\\ T(t,t) &= 1 && (3.29)\\ \varrho(t_0) &= \varrho_{rel}(t_0)\,. && (3.30) \end{aligned}$$

We will recapitulate the derivation of this dynamics exemplarily, because all the other following relevant-part-dynamics are derived in the similar way.

Proof: Starting from (3.21) and using the von Neumann equation (3.17) we get

$$\begin{aligned} \dot{\varrho}_{rel}(t) &= P(t)\,\dot{\varrho}(t)\\ &= -iP(t)\,L(t)\,\varrho(t)\\ &= -iP(t)\,L(t)\,\varrho_{rel}(t) - iP(t)\,L(t)\big(\varrho(t)-\varrho_{rel}(t)\big)\,. \qquad (3.31) \end{aligned}$$

In order to get a differential equation for $\varrho_{rel}(t)$ we must somehow remove $\varrho(t)$ from this equation. Therefore we calculate the following expression

$$\begin{aligned} \dot{\varrho}(t)-\dot{\varrho}_{rel}(t) &= -iL(t)\,\varrho(t) + iP(t)\,L(t)\,\varrho(t)\\ &= -iQ(t)\,L(t)\,\varrho(t)\\ &= -iQ(t)\,L(t)\,\varrho_{rel}(t) - iQ(t)\,L(t)\big(\varrho(t)-\varrho_{rel}(t)\big)\,. \qquad (3.32) \end{aligned}$$

Because of (3.20) we can identify

$$\dot{\varrho}(t)-\dot{\varrho}_{rel}(t) = \frac{d}{dt}\left(\varrho(t)-\varrho_{rel}(t)\right). \qquad (3.33)$$

Let us define a function $T(t,s)$ with (3.28) and (3.29). We multiply (3.32) by this function and integrate it from t_0 to t.

$$\begin{aligned} &\int_{t_0}^{t} T(t,s)\,\frac{d}{ds}\big(\varrho(s)-\varrho_{rel}(s)\big)\,ds\\ = \; & -i\int_{t_0}^{t} T(t,s)\,Q(s)\,L(s)\,\varrho_{rel}(s)\,ds - \int_{t_0}^{t}\frac{\partial}{\partial s}T(t,s)\big(\varrho(s)-\varrho_{rel}(s)\big)\,ds \qquad (3.34) \end{aligned}$$

Bringing the last integral to the left hand side, we can integrate the left term by using the initial condition (3.30).

$$\varrho(t)-\varrho_{rel}(t) = -i\int_{t_0}^{t} T(t,s)\,Q(s)\,L(s)\,\varrho_{rel}(s)\,ds\,, \qquad (3.35)$$

which we insert in equation (3.31), so we finally obtain (3.27). □

Robertson derived with this technique the dynamics of the generalised canonical operator. That is, he assumed in particular that $\varrho_{rel}(t)$ preserves the form of the generalised canonical operator $R(t)$ for all time:

$$\dot{R}(t) = P(t)\,\dot{\varrho}(t)\,, \qquad (3.36)$$

and so do most authors who use this dynamics. Indeed, this is a completely different way of deriving the dynamics than in the last section 3.1. The dynamics there is not based on the quantum mechanical dynamics. In fact, the phenomenological quantities $\underline{\lambda}(t)$ and $\underline{a}(t)$ are essential for the canonical dynamics, while the dynamics here is derived out of von Neumann dynamics using the projector P, with is now of fundamental importance. The dynamics (3.27) of the generalised canonical operator (3.36) is the basis for a series of stochastical dynamics that can be found in literature: Langevin type equation [Fic83], generalised Fokker Planck equation [Gra82], perturbation theory approach [Luz00] and so on.

3.2.2 Fick Sauermann Dynamics

The more general case in which a linear P maps $\varrho(t)$ to $\varrho_{rel}(t)$ or specially to $R(t)$, (3.22), has been treated by Fick and Sauermann [Fic83].

Theorem 7 ***Fick Sauermann dynamics***
The dynamics of ϱ_{rel} using the linear mapping (3.22) is given by

$$\begin{aligned} \dot{\varrho}_{rel}(t) &= -i\big(P(t)\,L(t) + i\dot{P}(t)\big)\,\varrho_{rel}(t) \\ &\quad - \int_{t_0}^{t} \big(P(t)\,L(t) + i\dot{P}(t)\big)\,T(t,s)\,\big(Q(s)\,L(s) - i\dot{P}(s)\big)\,\varrho_{rel}(s)\,ds \end{aligned} \tag{3.37}$$

$$\textit{with} \qquad \frac{\partial}{\partial s}T(t,s) = iT(t,s)\,\big(Q(s)\,L(s) - i\dot{P}(s)\big) \tag{3.38}$$

$$T(t,t) = 1 \tag{3.39}$$

$$\varrho(t_0) = \varrho_{rel}(t_0)\,. \tag{3.40}$$

Proof: Similar to the proof of theorem 6 □

As we have mentioned above, both Fick Sauermann and Robertson dynamics are based on the dynamics derived by Nakajima [Nak58] and Zwanzig [Zwa60] [Zwa64]. They treated a beobachtungsebene containig only time independent observables with constant work variables and a time independent operator P (3.18), (3.19). The Nakajima Zwanzig dynamics is given by

$$\dot{\varrho}_{rel}(t) = -iP\,L\,\varrho_{rel}(t) - \int_{t_0}^{t} P\,L\,e^{-iQ\,L\cdot(t-s)}Q\,L\,\varrho_{rel}(s)\,ds\,, \tag{3.41}$$

as we can conclude immediately from (3.27) or (3.37). This is an integro-differential equation like all other dynamics in this section. The exponential function appeares under the integral as a time-evolution operator, because L is assumed to be explicitly time independent. There is a formal similarity between this dynamics and the Robertson dynamics, because in both cases $\dot{\varrho}_{rel} = P\,\dot{\varrho}$ is valid. Nakajima and Zwanzig allowed for time independent projection operator, while Robertson considered time dependent projectors in principle, only on the condition $\dot{P}\,\varrho = 0$.

Equation (3.41) is also called "generalised master equation" and was derived in connection with the perturbation theory. P is time independent, because ϱ_{rel} is given there for all times by the diagonal part of ϱ, its eigenvalues, if the unperturbed Hamiltonian $\mathcal{H}_0$ is chosen appropriately. The irrelevant part $Q\,\varrho$ is then the nondiagonal part of ϱ.

3.2.3 Projector P

A prominent example for P in the Fick Sauermann dynamics is the Kawasaki Gunton operator [Kaw73] which projects the density operator onto its relevant part in the generalised canonical form with respect to a chosen beobachtungsebene. To do so, we choose the Mori product introduced in definition 10 and give an orthogonal projector that projects any observable onto the beobachtungsebene $\mathcal{B} \cup \{\mathbb{I}\}$.

Of course it is allowed to use any other inner product in $\mathcal{L}$ than the generalised Mori product, as described in [Kau96]. We recommend the following inner product with is a kind of generalisation of definition 10. This definition includes the definition 10 as one special case.

Definition 11 ***generalised Mori product***
Let be $\hat{\varrho} \in \mathcal{L}_\varrho^{ob}$ an accompanying process of the quantum mechanical density operator ϱ with respect to $\mathcal{B} = \{\underline{G}\}$.

$$\begin{aligned} (\,\cdot\,|\,\cdot\,) : \mathcal{L} \times \mathcal{L} &\rightarrow \mathbb{R} \\ (X, Y) &\mapsto (X\,|\,Y) := \int_0^1 Tr\left(\hat{\varrho}\, X^+\, \hat{\varrho}^\mu\, Y\, \hat{\varrho}^{-\mu}\right) d\mu \end{aligned} \tag{3.42}$$

If we choose $\hat{\varrho} = R$, then we have the "generalised Mori product" in [Kau96]. If $\hat{\varrho} = Z^{-1} e^{-\beta H}$, we have the original Mori product [Mor65].

Theorem 8 *The generalised Mori product is a scalar product.*

Proof:

(i) $(F + G\,|\,H) = (F\,|\,H) + (G\,|\,H)$ for all $F, G, H \in \mathcal{L}$

(ii) $(\lambda F\,|\,G) = \lambda^*\,(F\,|\,G)$ for all $F, G \in \mathcal{L}, \lambda \in \mathbb{C}$

(iii)

$$\begin{aligned} (F\,|\,G)^* &= \int_0^1 \mathrm{Tr}\left(\hat{\varrho}\, F^+\, \hat{\varrho}^\mu\, G\, \hat{\varrho}^{-\mu}\right)^+ d\mu = \int_0^1 \mathrm{Tr}\left(\hat{\varrho}^{-\mu}\, G^+\, \hat{\varrho}^\mu\, F\, \hat{\varrho}\right) d\mu \\ &= \int_0^1 \mathrm{Tr}\left(\hat{\varrho}\, G^+\, \hat{\varrho}^\mu\, F\, \hat{\varrho}^{-\mu}\right) d\mu = (G\,|\,F) \quad \text{for all} \quad F, G \in \mathcal{L} \end{aligned}$$

(iv) Use the spectral representation $\hat{\varrho} = \sum_j p_j\, |\psi_j\rangle\langle\psi_j|$. Since $\hat{\varrho} \in \mathcal{L}_\varrho^{ob}$, $p_j \geq 0$ for all j is valid.

$$\begin{aligned} (F\,|\,F) &= \int_0^1 \mathrm{Tr}\left(\hat{\varrho}\, F^+\, \hat{\varrho}^\mu\, F\, \hat{\varrho}^{-\mu}\right) d\mu \\ &= \int_0^1 \sum_{j,k,l,m} \langle\psi_j\,|\,\psi_k\rangle p_k \langle\psi_k\,|\,F^+\,|\,\psi_l\rangle p_l^\mu \langle\psi_l\,|\,F\,|\,\psi_m\rangle p_m^{-\mu} \langle\psi_m\,|\,\psi_j\rangle d\mu \\ &= \int_0^1 \sum_{j,l} p_j \langle\psi_j\,|\,F^+\,|\,\psi_l\rangle p_l^\mu \langle\psi_l\,|\,F\,|\,\psi_j\rangle p_j^{-\mu} d\mu \\ &= \int_0^1 \sum_{j,l} p_j p_l^\mu p_j^{-\mu}\, |\langle\psi_l\,|\,F\,|\,\psi_j\rangle|^2\, d\mu \geq 0 \end{aligned}$$

And

$$(F\,|\,F) = 0 \quad \Leftrightarrow \quad \langle \psi_l\,|\,F\,|\,\psi_j \rangle = 0 \quad \text{for all} \quad l, j \quad \Leftrightarrow \quad F = 0$$

□

Definition 12 ***Mori projector***
Let be $\hat{\varrho} \in \mathcal{L}^{ob}_{\varrho}$ an accompanying process of the quantum mechanical density operator ϱ with respect to $\mathcal{B} = \{\underline{G}\}$. Let be $(\,\cdot\,|\,\cdot\,)$ the generalised Mori product with respect to $\hat{\varrho}$.

$$\begin{array}{rcl} P^M : \mathcal{L}^{ob} & \rightarrow & span\,(\mathcal{B} \cup \{\mathbb{I}\}) \\ X & \mapsto & P^M X := (X\,|\,\mathbb{I})\,\mathbb{I} + (X\,|\,\Delta\underline{G}) \cdot (\Delta\underline{G}\,|\,\Delta\underline{G})^{-1} \cdot \Delta\underline{G} \end{array} \tag{3.43}$$

where we use the scalar product of definition 11, and

$$\Delta\underline{G} := \underline{G} - (\underline{G}\,|\,\mathbb{I})\,\mathbb{I}\,. \tag{3.44}$$

Theorem 9 *The Mori projector is an orthogonal projector with respect to the generalised Mori product. It projects observables on $\mathcal{B} \cup \{\mathbb{I}\}$.*

Proof:

1. $P^M P^M X = P^M X \quad$ for all $\quad X \in \mathcal{L}^{ob} \quad$ obviously.
2. $\left(P^M\right)^+ = P^M \quad$ because of $\quad \left(P^M X\,|\,Y\right) = \left(X\,|\,P^M Y\right) \quad$ for all $\quad X, Y \in \mathcal{L}^{ob}$ evidently.
3. P^M projects on $\mathcal{B} \cup \{\mathbb{I}\}$, see [Kau96] □

Now we can introduce a uniquely defined mapping P^{KG} acting on $\mathcal{L}^{ob}_{tr}$ which is connected to the Mori projector in the following way:

$$\mathrm{Tr}\left(\left(P^M X\right) Y\right) = \mathrm{Tr}\left(X\left(P^{KG} Y\right)\right) \quad \text{for all} \quad X \in \mathcal{L}^{ob}, Y \in \mathcal{L}^{ob}_{tr}. \tag{3.45}$$

Theorem 10 *Equation (3.45) is equivalent to*

$$\begin{array}{rcl} P^{KG} : \mathcal{L}^{ob}_{tr} & \rightarrow & \mathcal{L}^{ob}_{tr} \\ X & \mapsto & P^{KG} X \end{array}$$

$$P^{KG} X := \hat{\varrho}\; Tr X + \left(\int_0^1 \hat{\varrho}^{\mu}\, \Delta\underline{G}\, \hat{\varrho}^{-\mu}\, \hat{\varrho}\, d\mu \right) \cdot (\Delta\underline{G}\,|\,\Delta\underline{G})^{-1} \cdot Tr(\Delta\underline{G}\, X) \tag{3.46}$$

Proof: Simple calculation □

Theorem 11 *If we choose the accompanying generalised canonical operator R in definition 12 and in theorem 10, $\hat{\varrho} = R$, then it is valid*

$$P^M X \;=\; Tr(R\,X)\,\mathbb{I} + Tr\left(X\,\frac{\partial R}{\partial \underline{g}}\right) \cdot \left(\underline{G} - \underline{g}\,\mathbb{I}\right) \quad \textit{for all} \quad X \in \mathcal{L}^{ob} \tag{3.47}$$

$$P^{KG} X \;=\; R\; Tr\,X + \frac{\partial R}{\partial \underline{g}} \cdot \left(Tr(\underline{G}\,X) - \underline{g}\; Tr\,X\right) \quad \textit{for all} \quad X \in \mathcal{L}^{ob}_{tr}\,. \tag{3.48}$$

The second mapping is called ***Kawasaki Gunton operator****.*

Proof: Use the following equations:

$$
\begin{aligned}
(X \,|\, \Delta \underline{G}) &= -\mathrm{Tr}\left(X \frac{\partial R}{\partial \underline{\lambda}} \right) && (3.49)\\
(\Delta \underline{G} \,|\, \Delta \underline{G}) &= -\frac{\partial \underline{g}}{\partial \underline{\lambda}} && (3.50)\\
\int_0^1 R^{\mu}\, \Delta \underline{G}\, R^{-\mu}\, \hat{\varrho}\, d\mu &= -\frac{\partial R}{\partial \underline{\lambda}}\,. && (3.51)
\end{aligned}
$$

□

Theorem 12 *The Kawasaki Gunton operator is a projector.*

Proof: It can be easily seen that P^{KG} is idempotent. □

So we can use (3.46) for the Fick Sauermann dynamics (3.37), and especially the Kawasaki Gunton operator (3.48), if we choose $\varrho_{rel} = R$ in the dynamics. In this case, the dynamics is an implicit differential equation:

$$
\begin{aligned}
\dot{P}^{KG} X &= (PX)^{\bullet} - P\dot{X}\\
&= \dot{R}\,\mathrm{Tr}X + \left(\frac{\partial R}{\partial \underline{g}}\right)^{\bullet} \cdot \big(\mathrm{Tr}\,(\underline{G}\,X) - \underline{g}\,\mathrm{Tr}X\big) + \frac{\partial R}{\partial \underline{g}} \cdot \big(\mathrm{Tr}\,(\dot{\underline{G}}\,X) - \dot{\underline{g}}\,\mathrm{Tr}X\big)\,,
\end{aligned}
\tag{3.52}
$$

hence $\dot{R}$ appears on the righthand side of the equation (3.37), too.

In case that $\dot{\underline{a}} = \underline{0}$ is valid, $\dot{\underline{G}}$ is equal to zero, hence we have

$$
\dot{P}^{KG}\,\varrho = \dot{R} - \frac{\partial R}{\partial \underline{g}} \cdot \dot{\underline{g}} = \dot{R} - \dot{R} = 0\,, \tag{3.53}
$$

so that equation (3.20) is fulfilled, thus we can use this operator for the Robertson dynamics (3.27), too.

3.2.4 Other Mappings P

Apart from the Kawasaki Gunton operator (3.48), there exist some other linear mappings which induces the Robertson dynamics (3.27) or the Fick Sauermann dynamics (3.37) but which are no orthogonal projectors with respect to a scalar product any more.

Definition 13 ***generalised Kawasaki Gunton projector***
Let be ϱ_{rel} an accompanying process of ϱ with respect to a beobachtungsebene $\mathcal{B} = \{\underline{G}\}$.

$$
\begin{aligned}
P^{gKG} : \mathcal{L}_{tr}^{ob} &\rightarrow \mathcal{L}_{tr}^{ob}\\
X &\mapsto P^{gKG}\,X := \varrho_{rel}\,Tr\,X + \frac{\partial \varrho_{rel}}{\partial \underline{g}} \cdot \big(Tr\,(\underline{G}\,X) - \underline{g}\;Tr\,X\big)\,.
\end{aligned}
\tag{3.54}
$$

This mapping is idempotent as can be easily seen, and satisfies the properties (3.22) and (3.24), thus it induces the Fick Sauermann dynamics (3.37). The generalised Kawasaki Gunton operator is also a proper projector for the Robertson dynamics (3.27), if no time dependent observables are considered. In this case, the equations (3.20) are valid, as we discussed in the last section.

The Robertson dynamics (3.27) in section 3.2.1 is valid independently from the fact whether the considered observables are time dependent or not. But it is difficult to construct an appropriate projector satisfying the nessasary conditions (3.21), (3.20), and taking account of time dependent observables at the same time. This is why it is not possible to describe systems with time dependent work variables by Robertson dynamics so far, although such systems are standard situations in thermodynamics. Basically, time dependent observables are seldom treated in literature in the context of reduced-information-dynamics, as can be seen in [Rau96].

3.2.5 Canonical Dynamics vs. Fick Sauermann Dynamics using Kawasaki Gunton Operator

For both Fick Sauermann dynamics (3.37) using Kawasaki Gunton operator (3.48) and canonical dynamics (3.2), the maximisation takes place at every moment. In canonical dynamics one does this by fitting the langrange multipliers to the measured values. The Fick Sauermann dynamics is derived from a time dependent projector. So both dynamics allow for same physical issue, namely the dynamics of generalised canonical operator, but their derivations are completely different.

As mentioned above, canonical dynamics is not based on von Neumann dynamics. It is a dynamics on its own, derived from the time derivative of the generalised canonical operator. This leads to the problem, that we must know the dynamics of Lagrange parameters to obtain the dynamics. Fick Sauermann dynamics is a projection of the von Neumann dynamics. Such a projected dynamics depends strongly on the chosen dissipative term $\overset{\circ}{\varrho}$ (which is chosen zero in this chapter). The projector is known, because it is composed on the relevant observables and their expectation values, which can be replaced practically by the measured values. The only difficulty is that the dynamics becomes implicit, because the projector itself contains the relevant part.

As a result, R depends on different variables in the two cases, which makes the comparison of the two dynamics very difficult [Hag98]. In case of canonical dynamics the generalised canonical operator R is assumed to be dependent on the work variables $\underline{a}$ and the Lagrangian multipliers $\underline{\lambda}$, while Fick Sauermann dynamics is based upon both, an explicit and a non-explicit time dependence, as Schirrmeister showed [Schi94].

$$R\big(\underline{a}(t), \underline{\lambda}(t)\big) \qquad \textbf{canonical dynamics} \tag{3.55}$$

$$R\big(t, \underline{a}(t)\big) \qquad \textbf{Fick Sauermann dynamics} \tag{3.56}$$

The different dependences can be explained as follows: if we look at the form of the generalised canonical operator (2.18), it is evident that R depends on the $\underline{\lambda}$ and on the relevant observables $\underline{G}$, which are again depending on the work variables $\underline{a}$.

The macroscopic variables, on which R in Fick Sauermann dynamics depends, are $\underline{a}$ and $\underline{g}$.

$$R\big(\underline{a}(t), \underline{g}(t)\big) \tag{3.57}$$

The $\underline{g}$ can also be calculated with the quantum mechanical density operator ϱ. Therefore, we have in Fick Sauermann dynamics an implicit dependence on t by $\underline{a}(t)$ and an explicit dependence on t by $\varrho(t)$, see (3.56). Though (3.55) and (3.56) describe the same physical object, they are different functions from the mathematical point of view, to be noted correctly by different symbols $\widetilde{R}\big(\underline{a}(t), \underline{\lambda}(t)\big)$ and $\widehat{R}\big(t, \underline{a}(t)\big)$.

3.3 About the Rate of Entropy and Entropy Production

The time rate of von Neumann entropy (2.16) is strictly connected to the dynamics of the statistical operator. Since an explicit calculation is only possible, if we use the generalised canonical form of ϱ_{rel}, we investigate here the rate of entropy and entropy production for canonical dynamics and for Fick Sauermann dynamics using Kawasaki Gunton projector.

3.3.1 Canonical Dynamics

The rate of the maximised von Neumann entropy (2.17) belonging to the generalised canonical operator (2.18) results in [Mus94]:

$$\dot{S} = -k\,\mathrm{Tr}\,(\dot{R}\,\ln R) = k\,\mathrm{Tr}\,(\underline{\lambda} \cdot \underline{G}\,\dot{R})\,. \tag{3.58}$$

Note that if we do not consider work, then the $\underline{G}$ become time-independent, and we get the commonly used formulation

$$\dot{S} = k\,\underline{\lambda} \cdot \langle\,\underline{G}\,\rangle^{\bullet}\,. \tag{3.59}$$

Inserting canonical dynamics (3.2) into (3.58), we obtain

$$\dot{S} = k\,\mathrm{Tr}\left(R\,(\underline{\lambda} \cdot \underline{G})^{\bullet}\,\right)\mathrm{Tr}\,(R\,(\underline{\lambda} \cdot \underline{G})) - k\,\mathrm{Tr}\left(R\,(\underline{\lambda} \cdot \underline{G})^{\bullet}\,(\underline{\lambda} \cdot \underline{G})\right)\,. \tag{3.60}$$

Theorem 13 *Let be R the generalised canonical operator with respect to a beobachtungsebene $\mathcal{B}$. The following conditions are sufficient for the definiteness of the appropriate rate of entropy, $\dot{S} \geq 0$.*

(i) $(\underline{\lambda} \cdot \underline{G})^{\bullet} = -\alpha\,\underline{\lambda} \cdot (\underline{G} - \langle\underline{G}\rangle\mathbb{I})$ *with* $\alpha \geq 0$

(ii) $\dot{\underline{\lambda}} \cdot \underline{G} = -\alpha\,\underline{\lambda} \cdot (\underline{G} - \langle\underline{G}\rangle\mathbb{I})$ *with* $\alpha \geq 0\,,$ *if* $\dot{\underline{a}} = \underline{0}$

(iii) $\dot{\underline{\lambda}} = \alpha\left(Tr\,(\underline{G}\,R)^2 - Tr\,(\underline{G}^2\,R)\right) \cdot \underline{\lambda}$ *with* $\alpha \geq 0\,,$ *if* $\dot{\underline{a}} = \underline{0}$

Proof: Equation (3.60) can be written as

$$\dot{S} = k\,\dot{\underline{\lambda}} \cdot \Big(\mathrm{Tr}\,(\underline{G}\,R)^2 - \mathrm{Tr}\,\big(\underline{G}^2\,R\big)\Big) \cdot \underline{\lambda}\,, \tag{3.61}$$

if all work variables are constant. From this we get immediately (iii), using the standard scalar product. Using the generalised Mori scalar product of definition 10, (3.60) results in

$$\dot{S} = -k\left((\underline{\lambda} \cdot \underline{G})^{\bullet}\;\middle|\;\Delta\,(\underline{\lambda} \cdot \underline{G})\right)\,. \tag{3.62}$$

From this we get (i) and (ii). □

The condition of constant work variables $\underline{\dot{a}} = \underline{0}$ becomes plausible, when we bear in mind that the second law deals with isolated systems. The formula (3.61) gives, on condition that no heat and material transfer with its environment takes place, the entropy production of the system. A more detailed description is possible, if we distinguish external work variables from internal ones. In chapter 6 the rate of entropy is analysed for examples with discrete systems. See also appendix 10.3 containing some remarks on maximised entropy.

3.3.2 Fick Sauermann Dynamics

Since Fick Sauermann dynamics (3.37) using Kawasaki Gunton operator (3.48) is described by an implicit differential equation, there is no way to calculate the exact rate of entropy (3.58). Nevertheless, we can insert the righthand side of the dynamics (3.37) into (3.58) and make a few assumption and small time approximation. Then the expression of $\dot{S}$ does not contain $\dot{R}$ any more, and we get the following theorem [Kat00a], [Kat00b], [Schi94]:

Theorem 14 *Let be $Tr\,(R\,(iL\underline{G})) = 0$. Using the Fick Sauermann dynamics in small time approximation we get for the time rate of entropy*

$$\dot{S} = k\left(iL\,(\underline{\lambda} \cdot \underline{G}) + \widetilde{Q}\,\big(\underline{\lambda} \cdot \underline{\dot{G}}\big)\;\middle|\;iL\,(\underline{\lambda} \cdot \underline{G}) + \widetilde{Q}\,\big(\underline{\lambda} \cdot \underline{\dot{G}}\big)\right)\Delta t \geq 0$$

with

$$\widetilde{Q} := \mathbb{I} - |\,\Delta\underline{G}) \cdot (\Delta\underline{G}\,|\,\Delta\underline{G}) \cdot (\Delta\underline{G}\,|\,.$$

Proof: See [Kat00a]. □

The condition $\mathrm{Tr}\,(R\,(iL\underline{G})) = 0$ means that the expectation values of generalised fluxes are nearly vanishing, if we assume $\mathrm{Tr}\,(R\,(iL\underline{G})) \approx \mathrm{Tr}\,(\varrho\,(iL\underline{G}))$.

Chapter 4

Sufficiency

In thermodynamics observables depend on work variables, normally. To apply the First Law in the quantum thermodynamical frame of this work, we must ask the question under what condition the mesoscopic dynamics delivers the correct expectation values for work observables. We will analyse the dynamics of chapter 3 in this regard, and present a dynamics that describe the generalised works always correctly.

4.1 Definitions and Illustration

4.1.1 Sufficiency for Observables

In this section it is explained what is meant by so called sufficiency. An accompanying process with respect to a beobachtungsebene $\mathcal{B}$ is called sufficient for an observable not included in $\mathcal{B}$, if its expectation value is correctly given by this process.

Definition 14 *Let K be an observable $K \notin \mathcal{B}$. Let be $\hat{\varrho} \in \mathcal{L}^{ob}_{\varrho}$ an accompanying process of ϱ with respect to $\mathcal{B}$. $\hat{\varrho}$ is called* ***sufficient for K****, if*

$$\mathrm{Tr}\left(K(t)\,\varrho(t)\right) = \mathrm{Tr}\left(K(t)\,\hat{\varrho}(t)\right) \quad \textit{for} \quad t \in \mathbb{R}. \tag{4.1}$$

In general, this is not satisfied for an arbitrary observable. However, the accompanying process is apparently sufficient for an observable included in the span of $\mathcal{B}$. This motivate us to the next definition.

Definition 15 *Let be $\hat{\varrho} \in \mathcal{L}^{ob}_{\varrho}$ an accompanying process of ϱ with respect to $\mathcal{B}$. The set of all observables $K \in \mathcal{L}^{ob}$ for that $\hat{\varrho}$ is sufficient will be denoted as $\overline{\mathcal{B}}\,[\hat{\varrho}]$.*

$$K \in \overline{\mathcal{B}}\,[\hat{\varrho}] \quad :\Leftrightarrow \quad \mathrm{Tr}\left(K(t)\,\varrho(t)\right) = \mathrm{Tr}\left(K(t)\,\hat{\varrho}(t)\right) \quad \textit{for} \quad t \in \mathbb{R}. \tag{4.2}$$

For example:

Theorem 15 *Let be $\hat{\varrho} \in \mathcal{L}_{\varrho}^{ob}$ an accompanying process of ϱ with respect to $\mathcal{B}$. Then it is valid:*

(i) *span* $\mathcal{B} \subseteq \overline{\mathcal{B}}\,[\hat{\varrho}]$

(ii) $\hat{\varrho}$ *is sufficient for* $\mathbb{I}$. $\mathbb{I} \in \overline{\mathcal{B}}\,[\hat{\varrho}]$

(iii) *let be* $R \in \mathcal{L}_{\varrho}^{ob}$ *the generalised canonical operator with respect to* $\mathcal{B}$*. Then* $\hat{\varrho}$ *is sufficient for the entropy operator* $\ln R$. $\ln R \in \overline{\mathcal{B}}\,[\hat{\varrho}]$

Proof:

(i) trivial

(ii) trivial

(iii) According to (2.18) the entropy operator is given by

$$\ln R = -\underline{\lambda} \cdot \underline{G} - \ln Z\, \mathbb{I}\,. \tag{4.3}$$

As a linear combination of $\underline{G}$ and $\mathbb{I}$, its expectation value is given correctly by any accompanying process, and it follows:

$$\mathrm{Tr}\,(\hat{\varrho}\, \ln R) = \mathrm{Tr}\,(\varrho\, \ln R) = \mathrm{Tr}\,(R\, \ln R) = -\frac{1}{k}\, S_{\mathcal{B}}\,. \tag{4.4}$$

□

4.1.2 Sufficient Dynamics

In this section we apply the concept of sufficiency in connection with a chosen dynamics of a statistical operator. This means that the dynamics is sufficient for the time derivatives of $\underline{G}$ for all time. Its necessity particularly in thermodynamics becomes clear, when we consider the following example.

Let be the Hamiltonian $H(V(t))$ a function of the system's volume which is variable in time. Let be $H(V(t))$ included in $\mathcal{B}$. Demanding the sufficiency of the dynamics of an accompanying process $\hat{\varrho}$ means:

$$\mathrm{Tr}\left(\dot{H}\,\varrho\right) \stackrel{!}{=} \mathrm{Tr}\left(\dot{H}\,\hat{\varrho}\right) \quad \Leftrightarrow \quad \dot{V}\,\mathrm{Tr}\left(\frac{\partial H}{\partial V}\,\varrho\right) \stackrel{!}{=} \dot{V}\,\mathrm{Tr}\left(\frac{\partial H}{\partial V}\,\hat{\varrho}\right)\,. \tag{4.5}$$

Classical thermodynamics tells us:

$$\left.\frac{\partial E}{\partial V}\right|_{S} = -p\,. \tag{4.6}$$

So in this situation we demand, that $\hat{\varrho}$ describes the system's pressure and work correctly.

As we can see, we need such observables which depend on work variables in thermodynamics to calculate work. This is an essential quantity according to the First Law. An accompanying process $\hat{\varrho}$ to a chosen $\underline{G}(\underline{a})$ is only useful in thermodynamics, if the expectation values of the time derivatives $\dot{\underline{G}}$, or of even higher derivatives, are correctly given by $\hat{\varrho}$. If not, this description of the system does not fit the real thermodynamical process, because work is not correctly given, and this kind of description becomes worthless.

As a generalisation of definition 7 we define:

Definition 16 *Let be $G \in \mathcal{L}^{ob}$ an observable. $\dot{G}(\underline{a}(t))$ is called* ***generalised work operator*** *belonging to G.*

Definition 17 *Let be $\hat{\varrho} : \mathbb{R} \to \mathcal{L}^{ob}_{\varrho}$ an accompanying process of $\varrho : \mathbb{R} \to \mathcal{L}^{ob}_{\varrho}$ with respect to $\mathcal{B} = \{\underline{G}\}$. The dynamics of $\hat{\varrho}$ is called* ***sufficient with respect to $\mathcal{B}$****, if $\dot{\underline{G}} \in \overline{\mathcal{B}}\,[\hat{\varrho}]$.*

Definition 18 *Let be $n \in \mathbb{N}$. Let be $\hat{\varrho} : \mathbb{R} \to \mathcal{L}^{ob}_{\varrho}$ an accompanying process of $\varrho : \mathbb{R} \to \mathcal{L}^{ob}_{\varrho}$ with respect to $\mathcal{B} = \{\underline{G}\}$. The dynamics of $\hat{\varrho}$ is called* ***sufficient in n-th order with respect to $\mathcal{B}$****, if $\underline{G}^{(j)} \in \overline{\mathcal{B}}\,[\hat{\varrho}]$ for all $j \in \{1, \ldots, n\}$.*

Definition 19 *Let be $\hat{\varrho} : \mathbb{R} \to \mathcal{L}^{ob}_{\varrho}$ an accompanying process of $\varrho : \mathbb{R} \to \mathcal{L}^{ob}_{\varrho}$ with respect to $\mathcal{B} = \{\underline{G}\}$. The dynamics of $\hat{\varrho}$ is called* ***totally sufficient with respect to $\mathcal{B}$****, if $\underline{G}^{(j)} \in \overline{\mathcal{B}}\,[\hat{\varrho}]$ for all $j \in \mathbb{N}$.*

There is an other possibility to handle this problem. Instead of demanding the sufficiency of $\mathcal{B}$ for all time derivatives of the $\underline{G}$, we can simply include all these derivatives into the beobachtungsebene. Then an accompanying process would satisfy all constraints per definition. But it is desirable that a beobachtungsebene includes only observables that are really relevant, that means measurable during the experiment. Otherwise, we have an infinite number of operators in the beobachtungsebene, and it does not make sense to call it "observation level" any more, because they cannot be all observed or measured.

Theorem 16 *Let $\hat{\varrho}$ be an accompanying process of ϱ with respect to $\mathcal{B}$. Then these propositions are equivalent:*

$$\begin{aligned} & \dot{\underline{G}} \in \overline{\mathcal{B}}\,[\hat{\varrho}] \\ \Leftrightarrow \quad & Tr\,(\dot{\underline{G}}\,\varrho) = Tr\,(\dot{\underline{G}}\,\hat{\varrho}) \\ \Leftrightarrow \quad & Tr\,(\underline{G}\,\dot{\varrho}) = Tr\,(\underline{G}\,\dot{\hat{\varrho}})\,. \end{aligned} \tag{4.7}$$

Theorem 17 *Let $\hat{\varrho}$ be an accompanying process of ϱ with respect to $\mathcal{B}$. Let be $n \in \mathbb{N}$. If $n > 1$, let be $\hat{\varrho}$ sufficient in $(n-1)$-th order with respect to $\mathcal{B}$. Then these propositions are equivalent:*

$$\begin{array}{ccccc} & & \underline{G}^{(n)} \in \overline{\mathcal{B}}\,[\hat{\varrho}] & & \\ \Leftrightarrow & Tr\left(\underline{G}^{(n)}\varrho\right) & = & Tr\left(\underline{G}^{(n)}\hat{\varrho}\right) & \\ \Leftrightarrow & Tr\left(\underline{G}^{(n-1)}\varrho^{(1)}\right) & = & Tr\left(\underline{G}^{(n-1)}\hat{\varrho}^{(1)}\right) & \\ & & \vdots & & \\ \Leftrightarrow & Tr\left(\underline{G}\,\varrho^{(n)}\right) & = & Tr\left(\underline{G}\,\hat{\varrho}^{(n)}\right)\,. & \end{array} \tag{4.8}$$

We have here $n+1$ equivalent equations.

Proof: We can proof this by mathematical induction. If $n = 1$, we can derive (2.15)

$$\mathrm{Tr}\left(\underline{G}\,\varrho\right) = \mathrm{Tr}\left(\underline{G}\,\hat{\varrho}\right).$$

Since $\hat{\varrho}$ is sufficient for $\underline{\dot{G}}$, we immediately get the last equation in (4.7). If (4.8) is valid for one $n \in \mathbb{N}$, we can derive these $n+1$ equation and get:

$$\begin{aligned}
\mathrm{Tr}\left(\underline{G}^{(n+1)}\left(\varrho - \hat{\varrho}\right)\right) &= \mathrm{Tr}\left(\underline{G}^{(n)}\left(\hat{\varrho}^{(1)} - \varrho^{(1)}\right)\right) \\
\mathrm{Tr}\left(\underline{G}^{(n)}\left(\varrho^{(1)} - \hat{\varrho}^{(1)}\right)\right) &= \mathrm{Tr}\left(\underline{G}^{(n-1)}\left(\hat{\varrho}^{(2)} - \varrho^{(2)}\right)\right) \\
&\vdots \\
\mathrm{Tr}\left(\underline{G}^{(1)}\left(\varrho^{(n)} - \hat{\varrho}^{(n)}\right)\right) &= \mathrm{Tr}\left(\underline{G}\left(\hat{\varrho}^{(n+1)} - \varrho^{(n+1)}\right)\right). \qquad (4.9)
\end{aligned}$$

If we set

$$\mathrm{Tr}\left(\underline{G}^{(n+1)}\varrho\right) = \mathrm{Tr}\left(\underline{G}^{(n+1)}\hat{\varrho}\right), \qquad (4.10)$$

all terms in (4.9) are vanishing and we get (4.8) for $n+1$. □

To complete our discussion, let us show that the time-derivative of an observable is also an observable.

Theorem 18

$$A(t) \in \mathcal{L}^{ob} \quad \Rightarrow \quad \frac{d}{dt}A(t) \in \mathcal{L}^{ob} \qquad (4.11)$$

Proof:

$$\begin{aligned}
&\langle A\phi \,|\, \psi \rangle &=& \langle \phi \,|\, A^{+}\psi \rangle \\
\Rightarrow \quad &\langle \dot{A}\phi \,|\, \psi \rangle &=& \langle A\phi \,|\, \psi \rangle^{\bullet} - \langle A\dot{\phi} \,|\, \psi \rangle - \langle A\phi \,|\, \dot{\psi} \rangle \\
& &=& \langle \phi \,|\, A^{+}\psi \rangle^{\bullet} - \langle \dot{\phi} \,|\, A^{+}\psi \rangle - \langle \phi \,|\, A^{+}\dot{\psi} \rangle \\
& &=& \langle \phi \,|\, \left(A^{+}\right)^{\bullet}\psi \rangle \qquad (4.12)
\end{aligned}$$

Thus if A is an observable, i. e. $A = A^{+}$, it follows that $\dot{A} = \left(\dot{A}\right)^{+}$. □

4.2 Investigation of Sufficiency of Dynamics

Here we will test different dynamics of chapter 3 for above defined sufficiency.

4.2.1 Canonical Dynamics

Theorem 19 *The accompanying process of maximal entropy R of ϱ with respect to $\mathcal{B}$ is not necessarily sufficient.*

We will consider a counter-example as a proof, which is at the same time an simple example for the generalised canonical operator of definition 5.

Proof: Consider a spin $\frac{1}{2}$ particle in a homogenous magnetic field $\underline{B}$. The potential part of its Hamiltonian in the spin space is

$$H = -\gamma \frac{\hbar}{2} \sum_{k=1}^{3} \sigma_k B_k = -\gamma \frac{\hbar}{2} \begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix} \tag{4.13}$$

where the σ_k are Pauli-matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{4.14}$$

and γ is the gyromagnetic ratio [Coh77]. Choosing $B = \{H\}$ as beobachtungsebene, we get the generalised canonical operator

$$\begin{aligned} R &= \frac{e^{-\mu H}}{\mathrm{Tr}\, e^{-\mu H}} \\ &= \frac{1}{\mathrm{Tr}\, e^{-\mu H}} \exp\left(\mu\gamma\frac{\hbar}{2} \begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}\right) && (4.15) \\ &= \frac{1}{Z} \frac{1}{|\underline{B}|} \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix} && (4.16) \end{aligned}$$

with

$$\begin{aligned} Z &= 2\cosh\left(\mu\gamma\frac{\hbar}{2}|\underline{B}|\right) \\ R_{11} &= |\underline{B}|\cosh\left(\mu\gamma\frac{\hbar}{2}|\underline{B}|\right) + B_z \sinh\left(\mu\gamma\frac{\hbar}{2}|\underline{B}|\right) \\ R_{12} &= (B_x - iB_y)\sinh\left(\mu\gamma\frac{\hbar}{2}|\underline{B}|\right) \\ R_{21} &= (B_x + iB_y)\sinh\left(\mu\gamma\frac{\hbar}{2}|\underline{B}|\right) \\ R_{22} &= |\underline{B}|\cosh\left(\mu\gamma\frac{\hbar}{2}|\underline{B}|\right) - B_z \sinh\left(\mu\gamma\frac{\hbar}{2}|\underline{B}|\right). \end{aligned}$$

To get (4.16) from (4.15) we used the diagonalised Hamiltonian:

$$\begin{aligned} &\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix} \\ = &\begin{pmatrix} B_z + |\underline{B}| & B_z - |\underline{B}| \\ B_x + iB_y & B_x + iB_y \end{pmatrix} \begin{pmatrix} |\underline{B}| & 0 \\ 0 & -|\underline{B}| \end{pmatrix} \begin{pmatrix} \frac{1}{2|\underline{B}|} & \frac{|\underline{B}| - B_z}{2|\underline{B}|(B_x + iB_y)} \\ -\frac{1}{2|\underline{B}|} & \frac{|\underline{B}| + B_z}{2|\underline{B}|(B_x + iB_y)} \end{pmatrix}. \end{aligned}$$

Using (2.25) we calculate the Lagrangian multiplier μ.

$$\begin{aligned} \frac{\partial}{\partial\mu} \ln Z = \gamma\frac{\hbar}{2}|\underline{B}|\tanh\left(\mu\gamma\frac{\hbar}{2}|\underline{B}|\right) &= -\langle H\rangle \\ \Leftrightarrow \quad \mu = \frac{2}{\gamma\hbar|\underline{B}|} \operatorname{artanh}\left(-\frac{2\langle H\rangle}{\gamma\hbar|\underline{B}|}\right) && (4.17) \end{aligned}$$

with $\langle\bullet\rangle := \mathrm{Tr}\,(\varrho\,\bullet)$. Inserting this in (4.16) we get:

$$R = \frac{1}{2|\underline{B}|} \begin{pmatrix} |\underline{B}| - B_z \frac{2\langle H\rangle}{\gamma\hbar|\underline{B}|} & -(B_x - iB_y)\frac{2\langle H\rangle}{\gamma\hbar|\underline{B}|} \\ -(B_x + iB_y)\frac{2\langle H\rangle}{\gamma\hbar|\underline{B}|} & |\underline{B}| + B_z\frac{2\langle H\rangle}{\gamma\hbar|\underline{B}|} \end{pmatrix}. \tag{4.18}$$

Now we are able to calculate some expectation values explicitly, both with the generalised canonical operator and the exact quantum mechanical density operator, which is known:

$\{\mathbb{I}, \sigma_x, \sigma_y, \sigma_z\}$ is a basis in the space of 2×2-matrices. For an arbitrary 2×2-matrix M it holds [Coh77]:

$$M = a_0\mathbb{I} + \sum_{k=1}^{3} a_k\sigma_k \quad \text{with} \quad a_0 = \frac{1}{2}\,\mathrm{Tr}\, M \quad \text{and} \quad a_k = \frac{1}{2}\,\mathrm{Tr}\,(M\sigma_k)\,. \tag{4.19}$$

Applying this to the density matrix $\varrho = M$ in our example, we obtain:

$$\varrho = \frac{1}{2}\left(\mathbb{I} + \sum_{k=1}^{3}\langle\sigma_k\rangle\,\sigma_k\right) = \frac{1}{2}\begin{pmatrix} 1+\langle\sigma_z\rangle & \langle\sigma_x\rangle - i\langle\sigma_y\rangle \\ \langle\sigma_x\rangle + i\langle\sigma_y\rangle & 1-\langle\sigma_z\rangle \end{pmatrix}. \tag{4.20}$$

Using (4.13), (4.18) and (4.20), the expectation values result in:

$$\begin{aligned} \mathrm{Tr}\,(\varrho\, H) &= -\frac{\gamma\hbar}{2}\langle\underline{\sigma}\rangle\cdot\underline{B} = \langle H\rangle & (4.21)\\ \mathrm{Tr}\,(R\, H) &= \langle H\rangle & (4.22)\end{aligned}$$

If the magnetic field changes in time, from (4.13), (4.18) and (4.20) we get further:

$$\begin{aligned} \mathrm{Tr}\left(\varrho\,\dot{H}\right) &= -\frac{\gamma\hbar}{2}\langle\underline{\sigma}\rangle\cdot\underline{\dot{B}} = \langle H\rangle\,\frac{\langle\underline{\sigma}\rangle\cdot\underline{\dot{B}}}{\langle\underline{\sigma}\rangle\cdot\underline{B}} = \langle\dot{H}\rangle & (4.23)\\ \mathrm{Tr}\left(R\,\dot{H}\right) &= \frac{\langle H\rangle}{|\underline{B}|^2}\,\underline{B}\cdot\underline{\dot{B}} & (4.24)\end{aligned}$$

We show now that (4.23) and (4.24) are not identical. Since we need only one counter-example, let be

$$\dot{B}_x = \dot{B}_y = 0 \quad , \quad \dot{B}_z \neq 0 \quad , \quad B_x = 0 \quad , \quad B_y \neq 0 \quad , \quad B_z \neq 0\,. \tag{4.25}$$

Then we get

$$\mathrm{Tr}\left(\varrho\,\dot{H}\right) = \mathrm{Tr}\left(R\,\dot{H}\right) \quad \Leftrightarrow \quad B_y = B_z\,. \tag{4.26}$$

This is not necessarily true. □

In the proof it is shown that even the conventional thermodynamical work (2.32) is not correctly given with canonical dynamics.

4.2.2 Projected Dynamics of ϱ_{rel}

Here we want to examine the sufficiency of projected dynamics presented in section 3.2. The basic equation of motion is the von Neumann equation with $\overset{\circ}{\varrho} = 0$. We must of course consider those which take time dependent work variables into account. Otherwise, there is no reason of considering sufficient dynamics (see definition 17).

Robertson Dynamics

We noted that there is no known mapping P for the Robertson dynamics (theorem 6) taking non-constant work variables in account. Nevertheless we can formulate an interesting theorem:

Theorem 20 *Let be $P : \mathcal{L}^{ob}_{\varrho} \to \mathcal{L}^{ob}_{\varrho}$ linear and idempotent with (3.21) and (3.20), taking into account non-constant work variables. Let be valid $Tr(\underline{G}\,P\,L\,X) = Tr(\underline{G}\,L\,X)$ for all $X \in \mathcal{L}^{ob}$, then the Robertson dynamics using this mapping is sufficient.*

Proof: With the given conditions it is valid:

$$\begin{aligned} \mathrm{Tr}\,(\underline{G}\,P\,L\,\varrho) &= \mathrm{Tr}\,(\underline{G}\,L\,\varrho) \\ \Leftrightarrow \quad \mathrm{Tr}\,(\underline{G}\,P\,\dot{\varrho}) &= \mathrm{Tr}\,(\underline{G}\,\dot{\varrho}) \\ \Leftrightarrow \quad \mathrm{Tr}\,(\underline{G}\,\dot{\varrho}_{rel}) &= \mathrm{Tr}\,(\underline{G}\,\dot{\varrho}) \end{aligned} \tag{4.27}$$

□

For example the Kawasaki Gunton projector (3.48) and its generalised version (3.54) have the property $\mathrm{Tr}\,(\underline{G}\,P\,X) = \mathrm{Tr}\,(\underline{G}\,X)$ for all $X \in \mathcal{L}^{ob}$. But they do not take time dependent observables into account. This theorem cannot be applied to Fick Sauermann Dynamics, because the last step of the proof is not possible in that case.

Fick Sauermann Dynamics

Theorem 21 *Let ϱ_{rel} be an accompanying process of ϱ with respect to a beobachtungsebene $\mathcal{B}$. The Fick Sauermann dynamics of ϱ_{rel} is sufficient, iff*

$$\begin{aligned} Tr\,(\underline{G}(t)\,\dot{\varrho}_{rel}(t)) &= -i\;Tr\,(\underline{G}(t)\,L(t)\,\varrho_{rel}(t)) \\ &\quad - \int_{t_0}^{t} Tr\left(\underline{G}(t)\,L(t)\,T(t,s)\left(Q(s)\,L(s) - i\dot{P}(s)\right)\varrho_{rel}(s)\right) ds \end{aligned} \tag{4.28}$$

is satisfied.

This equation can be implicit, if P contains ϱ_{rel}.

Proof: Inserting Fick Sauermann dynamics (3.37). into (4.7), we obtain

$$\begin{aligned} -i\,\mathrm{Tr}\,(\underline{G}\,L\,\varrho)\,(t) &= -i\,\mathrm{Tr}\,\big(\underline{G}\,P\,L\,\varrho_{rel}\big)(t) + \mathrm{Tr}\,\big(\underline{G}\,\dot{P}\,\varrho_{rel}\big)(t) \\ &\quad - \int_{t_0}^{t} \mathrm{Tr}\left(\underline{G}\left(P\,L + i\dot{P}\right)(t)\,T(t,s)\left(Q\,L - i\dot{P}\right)\varrho_{rel}(s)\right) ds\,. \end{aligned}$$

We eliminate the quantum mechanical density matrix ϱ using

$$\varrho(t) - \varrho_{rel}(t) = -i\int_{t_0}^{t} T(t,s)\,\big(Q(s)\,L(s) - i\dot{P}(s)\big)\,\varrho_{rel}(s)\,ds\,, \tag{4.29}$$

which is used in the derivation of the dynamics [Schi94], analogous to (3.35) in the derivation of the Robertson dynamics.

$$\begin{aligned} & -i\,\mathrm{Tr}\,(\underline{G}\,L\,\varrho_{rel})\,(t) - \int_{t_0}^{t} \mathrm{Tr}\left(\underline{G}\,L(t)\,T(t,s)\left(Q\,L - i\dot{P}\right)\varrho_{rel}(s)\right) ds \\ = & -i\,\mathrm{Tr}\,(\underline{G}\,P\,L\,\varrho_{rel})\,(t) + \mathrm{Tr}\left(\underline{G}\,\dot{P}\,\varrho_{rel}\right)(t) \\ & -\int_{t_0}^{t} \mathrm{Tr}\left(\underline{G}\left(P\,L + i\dot{P}\right)(t)\,T(t,s)\left(Q\,L - i\dot{P}\right)\varrho_{rel}(s)\right) ds \end{aligned} \tag{4.30}$$

On the other side, we have the dynamics of expectation values using Fick Sauermann dynamics:

$$\begin{aligned} \mathrm{Tr}\,(\underline{G}\,\dot{\varrho}_{rel}) = & -i\,\mathrm{Tr}\,(\underline{G}\,P\,L\,\varrho_{rel})\,(t) + \mathrm{Tr}\left(\underline{G}\,\dot{P}\,\varrho_{rel}\right)(t) \\ & -\int_{t_0}^{t} \mathrm{Tr}\left(\underline{G}\left(P\,L + i\dot{P}\right)(t)\,T(t,s)\left(Q\,L - i\dot{P}\right)\varrho_{rel}(s)\right) ds\,. \end{aligned} \tag{4.31}$$

Comparing (4.30) with (4.31), we obtain (4.28). □

If P is specially chosen as the generalised Kawasaki Gunton operator (3.54), we get the following

Theorem 22 *Let ϱ_{rel} be an accompanying process of ϱ with respect to a beobachtungsebene $\mathcal{B}$. The Fick Sauermann dynamics of ϱ_{rel} generated by the generalised Kawasaki Gunton operator P is sufficient, iff*

$$Tr\left(\underline{G}(t)\,\dot{P}(t)\,T(t,s)\left(Q(s)\,L(s) - i\dot{P}(s)\right)\varrho_{rel}(s)\right) = \underline{0} \qquad \text{for all} \qquad s \in [t_0, t]\,. \tag{4.32}$$

One necessary condition for the sufficiency is

$$Tr\left(\dot{\underline{G}}\,Q\,L\,\varrho_{rel}\right)(t) = i\;Tr\left(\dot{\underline{G}}\,\dot{P}\,\varrho_{rel}\right)(t)\,, \tag{4.33}$$

which is equivalent to

$$Tr\left[\dot{\underline{G}}\,(-iL\varrho_{rel} - \dot{\varrho}_{rel})\right](t) = Tr\left(\dot{\underline{G}}\,\frac{\partial \varrho_{rel}}{\partial \underline{g}}\right) Tr[\underline{G}\,(-iL\varrho_{rel} - \dot{\varrho}_{rel})]\,(t)\,. \tag{4.34}$$

Proof: The generalised Kawasaki Gunton projector has following properties:

$$\mathrm{Tr}\,(\underline{G}\,P\,X) = \mathrm{Tr}\,(\underline{G}\,X) \qquad \text{for all} \qquad X \in \mathcal{L}^{ob} \tag{4.35}$$

$$\mathrm{Tr}\,(\underline{G}\,\dot{P}\,\varrho_{rel}) = \underline{0} \tag{4.36}$$

Using these, we obtain from (4.31)

$$\begin{aligned} & \mathrm{Tr}\,(\underline{G}\,\dot{\varrho}_{rel}) \\ = & -i\,\mathrm{Tr}\,(\underline{G}\,L\,\varrho_{rel})\,(t) - \int_{t_0}^{t} \mathrm{Tr}\left(\underline{G}L(t)\,T(t,s)\left(Q\,L - i\dot{P}\right)\varrho_{rel}(s)\right) ds \\ & -i\int_{t_0}^{t} \mathrm{Tr}\left(\underline{G}\dot{P}(t)\,T(t,s)\left(Q\,L - i\dot{P}\right)\varrho_{rel}(s)\right) ds \end{aligned} \tag{4.37}$$

We get (4.32) by comparison with (4.28). The time-evolution operator vanishes in (4.32) for $s = t$. We can simplify the equation to (4.33) and (4.34) using (3.48) and (3.52). □

4.3 A Sufficient Dynamics

In the previous section we have seen that conventional dynamics with reduced information are not sufficient in general. Here we will present an ansatz to get sufficient accompanying dynamics. The idea of [Mus94] is formulated here again more precisely including a generalisation and a possible interpretation.

Theorem 23 *Let $\hat{\varrho}$ be an accompanying process of ϱ with respect to $\mathcal{B}$. Let be*

$$\begin{aligned} (\hat{\varrho}-\varrho)^\bullet(t) &= -\dot{h}(t)\,(\hat{\varrho}-\varrho)(t) + Y(t) && (4.38)\\ Tr\left(\underline{G}(t)\,Y(t)\right) &= 0 \qquad \textit{for } t\in\mathbb{R} && (4.39)\\ Tr\,Y(t) &= 0 \qquad \textit{for } t\in\mathbb{R} && (4.40)\end{aligned}$$

with a function of time $h(t)$ and a time dependent operator $Y(t)$. Then the dynamics of $\hat{\varrho}$ is sufficient.

Proof: Using (4.38) we get

$$\mathrm{Tr}\left(\underline{G}\,(\hat{\varrho}-\varrho)^\bullet\right) = -\dot{h}\,\mathrm{Tr}\left(\underline{G}\,(\hat{\varrho}-\varrho)\right) + \mathrm{Tr}\,(\underline{G}\,Y) = 0 \tag{4.41}$$

because of (4.39) and the fact, that $\hat{\varrho}$ is an accompanying process. Due to (4.7), (4.41) is equivalent to

$$\mathrm{Tr}\left(\dot{\underline{G}}\,(\hat{\varrho}-\varrho)\right) = 0\,. \tag{4.42}$$

We need (4.40), because the trace of (4.38) should vanish on each side of the equality. □

The condition (4.39) may be interpreted like this: since $\mathrm{Tr}\,(A\,B^*)$ is an inner product in $\mathcal{L}$, Y is an operator being orthogonal to the chosen beobachtungsebene with respect to this inner product. One possible operator is $Y=\varrho-\hat{\varrho}$ (see the discussion below).

Theorem 24 *Let $\hat{\varrho}$ be an accompanying process of ϱ with respect to $\mathcal{B}$. Let be $n\in\mathbb{N}$ and*

$$\begin{aligned} (\hat{\varrho}-\varrho)^\bullet(t) &= -\dot{h}(t)\,(\hat{\varrho}-\varrho)(t) + Y(t) && (4.43)\\ Tr\left(\underline{G}^{(j)}(t)\,Y(t)\right) &= 0 \qquad \textit{for all } j\in\{0,\ldots,n-1\} \textit{ and } t\in\mathbb{R} && (4.44)\\ Tr\,Y(t) &= 0 \qquad \textit{for } t\in\mathbb{R}\,. && (4.45)\end{aligned}$$

Here $h(t)$ is a function of time and $Y(t)$ a time dependent operator. Then the dynamics of $\hat{\varrho}$ is sufficient in n-th order.

Proof: By mathematical induction. The proposition has already been prooved for $n=1$. Let be the proposition valid for one $n\in\mathbb{N}$. Then

$$\mathrm{Tr}\left(\underline{G}^{(n)}\,(\hat{\varrho}-\varrho)\right) = 0 \tag{4.46}$$

is valid. The derivation yields

$$\begin{aligned} \mathrm{Tr}\left(\underline{G}^{(n+1)}\,(\hat{\varrho}-\varrho)\right) &= -\mathrm{Tr}\left(\underline{G}^{(n)}\,(\hat{\varrho}-\varrho)^\bullet\right)\\ &= \dot{h}\,\mathrm{Tr}\left(\underline{G}^{(n)}\,(\hat{\varrho}-\varrho)\right) - \mathrm{Tr}\,(\underline{G}^{(n)}\,Y)\\ &= 0\,, && (4.47)\end{aligned}$$

if we additionally assume $\mathrm{Tr}\,(\underline{G}^{(n)}\,Y) = 0$. Thus $\hat{\varrho}(t)$ is sufficient in $(n+1)$-th order.
$\square$

The solution of (4.38) and (4.43) is

$$\hat{\varrho}(t) - \varrho(t) \;=\; e^{-h(t)+h(t_0)} \left(\hat{\varrho}(t_0) - \varrho(t_0) + \int_{t_0}^{t} e^{h(s)-h(t_0)} Y(s) ds \right) \tag{4.48}$$

$$\;=\; e^{-h(t)} \int_{t_0}^{t} e^{h(s)}\, Y(s)\, ds\,, \tag{4.49}$$

if we set

$$\hat{\varrho}(t_0) = \varrho(t_0)\,. \tag{4.50}$$

An other possibility to get rid of the first addend in (4.48) is to choose an increasing positive definite function h.

In the special case of $Y = 0$ we have $\hat{\varrho} = \varrho$ for all time, or at least the difference between them decreases exponentially in time by choice of a suitable h.

Let us investigate whether this dynamics is given by a projection. In this case the condition (4.39) suggests itself that Y is given by the irrelevant part of ϱ or its multiple. But from this, it would follow that we can sum up both terms on the right hand side of (4.38). Then the irrelevant part $\varrho - \hat{\varrho}$ would again decrease exponentially in time by choice of a suitable h. $\hat{\varrho}$ is then nearly equal to ϱ, so it makes no sence of speaking about projection dynamics.

We can apply the same considerations to the dynamics of (4.43). If Y is the irrelevant part of ϱ, the the conditions (4.44) demand that the dynamics is sufficient in $(n-1)$-th order:

$$\mathrm{Tr}\left(\underline{G}^{(j)}\,Q\,\varrho\right) = 0 \quad \Rightarrow \quad \mathrm{Tr}\left(\underline{G}^{(j)}\,P\,\varrho\right) = \mathrm{Tr}\left(\underline{G}^{(j)}\,\varrho\right)\,. \tag{4.51}$$

So it make no difference if we include the derivatives $\underline{\dot{G}}, \ldots \underline{G}^{(n-1)}$ into the beobachtungsebene, but then we can use again theorem 23.

Chapter 5

Further Considerations on Sufficiency

5.1 Generalised Fluxes

In chapter 4 we discussed about how work can be calculated in thermodynamics. In thermodynamical applications we need dynamics, being sufficient for the $\underline{\dot{G}}$, in order to get correct expectation values for work. We will see here that a similar problem already arises even if we consider systems without work exchange, i.e. systems with time-independent observables. It concerns the generalised flux observables, cf. definition 7.

Definition 20 *Let be $G \in \mathcal{L}^{ob}$ an observable. iLG is called the generalised flux operator with respect to G.*

5.1.1 Canonical Dynamics

Theorem 25 *In general, the generalised canonical operator $R_{\mathcal{B}}$ does not deliver the correct expectation value for a generalised flux operator iLG, if $iLG \notin \mathcal{B}$ and $G \in \mathcal{B}$.*

Proof: Let be $\dot{G} = 0$, $\mathcal{B} = \{G\}$. Then

$$i\mathrm{Tr}\,(R\,L\,G) = 0 \tag{5.1}$$

because $e^{\lambda G}$ and G commute, and

$$0 \neq \mathrm{Tr}\left(\dot{R}\,G\right) = \mathrm{Tr}\,(R\,G)^{\bullet} = \mathrm{Tr}\,(\varrho\,G)^{\bullet} = i\mathrm{Tr}\,(\varrho\,L\,G) \tag{5.2}$$

in general. $\square$

If we choose the Hamiltonian of a subsystem H_1 for G, this means, that in general, neither work (2.32) nor heat flux (2.33) are given correctly by the generalised canonical operator!

5.1.2 Robertson Dynamics

Let be $H_1 \in \mathcal{B}$. Using the Robertson dynamics (3.27) to obtain the heat flux, we get:

$$\begin{aligned} \langle H_1 \rangle^\bullet(t) &= \frac{d}{dt} \mathrm{Tr}\,(\varrho_{rel}(t)\, H_1) \\ &= \mathrm{Tr}\,(\varrho_{rel}(t)\, iLH_1) - \int_{t_0}^{t} \mathrm{Tr}\,(H_1\, L\, T(t,s)\, Q(s)\, L\, \varrho_{rel}(s))\, ds\,. \end{aligned} \quad (5.3)$$

Here, we used the common property (4.35) of the generalised Robertson operator and of the generalised Kawasaki Gunton operator, which are possible for this dynamics. In general,

$$\mathrm{Tr}\,(\varrho(t)\, iLH_1) \neq \mathrm{Tr}\,(\varrho_{rel}(t)\, iLH_1) \quad (5.4)$$

is valid. At this point, we face the same dilemma as in the previous chapter. After all, heat exchange is a quantity that is as important as work in thermodynamics according to the First Law. Should we include iLH_1 into the beobachtungsebene, or should we demand that the dynamics gives the correct flux? As we can see above, the second way would make vanish process history in Robertson dynamics.

In general, we have the following situation: $\mathcal{B} = \{\underline{G}\}$ is our beobachtungsebene. The Robertson dynamics (3.27) with time independent observables delivers the following dynamics of expectation values:

$$\begin{aligned} \langle \underline{G} \rangle^\bullet(t) &= \frac{d}{dt} \mathrm{Tr}\,(\underline{G}\, \varrho_{rel}(t)) \\ &= \mathrm{Tr}\,(\varrho_{rel}(t)\, iL\underline{G}) - \int_{t_0}^{t} \mathrm{Tr}\,(\underline{G}\, L\, T(t,s)\, Q(s)\, L\, \varrho_{rel}(s))\, ds\,. \end{aligned} \quad (5.5)$$

On the other hand,

$$\langle \underline{G} \rangle^\bullet(t) = \frac{d}{dt} \mathrm{Tr}\,(\underline{G}\, \varrho(t)) = \mathrm{Tr}\,(\varrho(t)\, iL\underline{G})\,. \quad (5.6)$$

Demanding the sufficiency of the dynamics for $iL\underline{G}$, or even of all $(iL)^n\underline{G}$, we would get a dynamics whose process history is not macroscopically noticeable, which is consequently von Neumann-like. On the other hand, each Robertson dynamics of ϱ_{rel} with vanishing process history is sufficient for the generalised fluxes.

5.1.3 Fick Sauermann Dynamics

We observe the same problem in Fick Sauermann dynamics (3.37) with time dependent observables.

$$\langle \underline{G} \rangle^\bullet = \frac{d}{dt} \mathrm{Tr}\,(\underline{G}\varrho) = \mathrm{Tr}\left(\varrho\left(\underline{\dot{G}} + iL\underline{G}\right)\right) \quad (5.7)$$

$\underline{\overset{\circ}{G}} := \underline{\dot{G}} + iL\underline{G}$ can be interpreted as the observale of work and exchange quantities. The Fick Sauermann dynamics yields

$$\langle \underline{G} \rangle^\bullet(t) = \frac{d}{dt} \mathrm{Tr}\,(\underline{G}\, \varrho_{rel})\,(t)$$

$$
\begin{aligned}
= \quad & \mathrm{Tr}\left(\varrho_{rel}\left(\underline{\dot{G}}+iL\underline{G}\right)\right)(t) \\
& -\int_{t_0}^{t}\mathrm{Tr}\left(\left(\underline{G}\left(PL+i\dot{P}\right)\right)(t)\,T(t,s)\left(\left(QL-i\dot{P}\right)\varrho_{rel}\right)(s)\right)ds
\end{aligned}
\tag{5.8}
$$

by using (4.36). Demanding the sufficiency of the dynamics for $\underline{\dot{G}}+iL\underline{G}$ (or $\underline{\dot{G}}$, if we suppress exchange quantities, or $iL\underline{G}$, if we suppress work) is equivalent to the process history becoming macroscopically irrelevant.

5.2 Possible Conditions for an Extended Sufficiency

In this section we investigate the question, under what condition accompanying processes are sufficient for flux or work observables. For this purpose it becomes necessary to make assumptions on $\overset{\circ}{\varrho}$ (cf. (2.4)), that has been set zero hitherto except for the cases of canonical dynamis (3.2) and sufficient dynamics (4.38), (4.43). Also the quantity $\overset{\circ}{\hat{\varrho}}:=\dot{\hat{\varrho}}+iL\hat{\varrho}$ of the accompanying process becomes interesting.

Theorem 26 *Let be $\mathcal{B}=\{\underline{G}\}$ a beobachtungsebene. Let be $\hat{\varrho}(t)$ an accompanying process of $\varrho(t)$ with respect to $\mathcal{B}$. Let be*

$$
\overset{\circ}{\hat{\varrho}}=\overset{\circ}{\varrho}\ . \tag{5.9}
$$

Then $\hat{\varrho}$ is sufficient for $\overset{\circ}{\underline{G}}:=\underline{\dot{G}}+iL\underline{G}$:

$$
Tr\left(\varrho\left(\underline{\dot{G}}+iL\underline{G}\right)\right)=Tr\left(\hat{\varrho}\left(\underline{\dot{G}}+iL\underline{G}\right)\right)\ . \tag{5.10}
$$

Proof:

$$
\begin{aligned}
& \mathrm{Tr}\left(\underline{G}\,\varrho\right)^{\bullet}=\mathrm{Tr}\left(\underline{G}\,\hat{\varrho}\right)^{\bullet} \\
\Leftrightarrow\quad & \mathrm{Tr}\left(\underline{\dot{G}}\,\varrho\right)+\mathrm{Tr}\left(\underline{G}\left(\dot{\varrho}-\overset{\circ}{\varrho}\right)\right)=\mathrm{Tr}\left(\underline{\dot{G}}\,\hat{\varrho}\right)+\mathrm{Tr}\left(\underline{G}\left(\dot{\hat{\varrho}}-\overset{\circ}{\hat{\varrho}}\right)\right) \\
\Leftrightarrow\quad & \mathrm{Tr}\left(\underline{\dot{G}}\,\varrho\right)-i\mathrm{Tr}\left(\underline{G}L\varrho\right)=\mathrm{Tr}\left(\underline{\dot{G}}\,\hat{\varrho}\right)-i\mathrm{Tr}\left(\underline{G}L\hat{\varrho}\right) \\
\Leftrightarrow\quad & \mathrm{Tr}\left(\varrho\left(\underline{\dot{G}}+iL\underline{G}\right)\right)=\mathrm{Tr}\left(\hat{\varrho}\left(\underline{\dot{G}}+iL\underline{G}\right)\right)
\end{aligned}
\tag{5.11}
$$

□

This proposition gains in importance, if we apply it on subsystems, see section 8.2.2.

Theorem 27 *Let be $\mathcal{B}=\{\underline{G}\}$ a beobachtungsebene. Let be $\hat{\varrho}(t)$ an accompanying process of $\varrho(t)$ which is sufficient with respect to $\mathcal{B}$. Let be*

$$
\overset{\circ}{\hat{\varrho}}=\overset{\circ}{\varrho}\ . \tag{5.12}
$$

Then $\hat{\varrho}$ is sufficient for $iL\underline{G}$:

$$
i\,Tr(\varrho\,L\,\underline{G})=i\,Tr(\hat{\varrho}\,L\,\underline{G})\ . \tag{5.13}
$$

Proof: Use theorem 26. □

5.3 Weak Sufficiency

If an accompanying process is sufficient for K (definition 14), the expectation value of an observable K, that is not included in the chosen beobachtungsebene, can be nonetheless correctly calculated by this process. Here we will present a weaker formulation of sufficiency.

Let be $\mathcal{B} = \{\underline{G}\}$ a beobachtungsebene, $\hat{\varrho}(t)$ an accompanying process.

$$\mathrm{Tr}\left(\underline{G}(t)\varrho(t)\right) = \mathrm{Tr}\left(\underline{G}(t)\hat{\varrho}(t)\right) \qquad \forall t\,. \tag{5.14}$$

Since this equation is exact for all time, the time derivatives of both sides are equal.

$$\begin{aligned} \frac{d}{dt}\mathrm{Tr}\left(\underline{G}\hat{\varrho}\right) = \langle\underline{G}\rangle^{\bullet} = \frac{d}{dt}\mathrm{Tr}\left(\underline{G}\varrho\right) &= \mathrm{Tr}\left(\underline{\dot{G}}\varrho\right) - i\mathrm{Tr}\left(\underline{G}L\varrho\right) \\ &= \mathrm{Tr}\left(\varrho\left(\underline{\dot{G}} + iL\underline{G}\right)\right) \end{aligned} \tag{5.15}$$

The expectation values of $\underline{\dot{G}}+iL\underline{G}$ can be calculated correctly using the dynamics of the accompanying process, even if they are not included in the beobachtungsebene theirselves. If the observables are time-independent, we have the expectation value of $iL\underline{G}$. Nonetheless, $\mathrm{Tr}\left(\varrho\left(\underline{\dot{G}} + iL\underline{G}\right)\right) \neq \mathrm{Tr}\left(\hat{\varrho}\left(\underline{\dot{G}} + iL\underline{G}\right)\right)$ in general. This is a weaker form of sufficiency than (4.1).

Definition 21 *Let K be an observable $K \notin \mathcal{B}$. Let be $\hat{\varrho} \in \mathcal{L}^{ob}_{\varrho}$ an accompanying process of ϱ with respect to $\mathcal{B}$. $\hat{\varrho}$ is called* ***weakly sufficient for K****, if it is possible to give the dynamics of the expectation value of K, provided that the dynamics of $\hat{\varrho}$ is known.*

Definition 22 *Let be $\hat{\varrho} \in \mathcal{L}^{ob}_{\varrho}$ an accompanying process of ϱ with respect to $\mathcal{B}$. The set of all observables $K \in \mathcal{L}^{ob}$ for that $\hat{\varrho}$ is weakly sufficient will be denoted as $\overline{\mathcal{B}}_w\left[\hat{\varrho}\right]$.*

$$K \in \overline{\mathcal{B}}_w\left[\hat{\varrho}\right] \quad :\Leftrightarrow \quad \hat{\varrho}(t) \quad \textit{is weakly sufficient for} \quad t \in \mathbb{R}. \tag{5.16}$$

Obviously, it is valid that $\hat{\varrho}$ is weakly sufficient for K, $\overline{\mathcal{B}}_w\left[\hat{\varrho}\right] \subseteq \overline{\mathcal{B}}\left[\hat{\varrho}\right]$, if $\hat{\varrho}$ is sufficient for K in terms of definition 14.

Theorem 28 *Let be $\mathcal{B} = \{\underline{G}\}$ a beobachtungsebene, $\hat{\varrho}(t)$ an accompanying process with respect to $\mathcal{B}$. Let the observables $\underline{G}$ and the system Hamiltonian H be time-independent. Then $\quad i^n L^n \underline{G} \in \overline{\mathcal{B}}_w\left[\hat{\varrho}\right] \quad$ for all $\quad n \in \mathbb{N}$.*

Proof:

$$\frac{d^n}{dt^n}\mathrm{Tr}\left(\underline{G}\hat{\varrho}\right) = \langle\underline{G}\rangle^{(n)} = \frac{d^n}{dt^n}\mathrm{Tr}\left(\underline{G}\varrho\right) = i^n\mathrm{Tr}\left(\varrho L^n \underline{G}\right) \tag{5.17}$$

The last step by complete induction. □

Theorem 29 *Let be $\mathcal{B} = \{\underline{G}\}$ a beobachtungsebene, $\hat{\varrho}(t)$ an accompanying process with respect to $\mathcal{B}$. The observables $\underline{G}$ may be time-dependent, but let be the full Hamiltonian of the system time-independent. Then $\quad \sum_{k=0}^{n}\binom{n}{k} i^k L^k \underline{G}^{(n-k)} \in \overline{\mathcal{B}}_w\left[\hat{\varrho}\right] \quad$ for all $\quad n \in \mathbb{N}$.*

Proof: By complete induction: o.k. for $n = 1$ see (5.15). Let be the proposition correct for one $n \in \mathbb{N}$. Then

$$\begin{aligned}
& \frac{d}{dt}\mathrm{Tr}\left(\varrho\sum_{k=0}^{n}\binom{n}{k}i^k L^k \underline{G}^{(n-k)}\right) \\
= & \sum_{k=0}^{n}\binom{n}{k}i^k \mathrm{Tr}\left(\varrho L^k \underline{G}^{(n-k+1)}\right) + \sum_{k=0}^{n}\binom{n}{k}i^{k+1}\mathrm{Tr}\left(\varrho L^{k+1}\underline{G}^{(n-k)}\right) \\
= & \mathrm{Tr}\left(\varrho\sum_{k=0}^{n+1}\binom{n+1}{k}i^k L^k \underline{G}^{(n+1-k)}\right) \qquad (5.18)
\end{aligned}$$

because of

$$\begin{aligned}
& \sum_{k=0}^{n}\binom{n}{k}i^k L^k \underline{G}^{(n-k+1)} + \sum_{k=0}^{n}\binom{n}{k}i^{k+1}L^{k+1}\underline{G}^{(n-k)} \\
= & \binom{n}{0}\underline{G}^{(n+1)} + \sum_{k=1}^{n}\binom{n}{k}i^k L^k \underline{G}^{(n-k+1)} \\
& + \sum_{k=0}^{n-1}\frac{k+1}{n-k}\binom{n}{k+1}i^{k+1}L^{k+1}\underline{G}^{(n-k)} + \binom{n}{n}i^{n+1}L^{n+1}\underline{G} \\
= & \binom{n}{0}\underline{G}^{(n+1)} + \sum_{k=1}^{n}\binom{n}{k}i^k L^k \underline{G}^{(n-k+1)} \\
& + \sum_{k=1}^{n}\frac{k}{n-k+1}\binom{n}{k}i^k L^k \underline{G}^{(n-k+1)} + \binom{n}{n}i^{n+1}L^{n+1}\underline{G} \\
= & \binom{n}{0}\underline{G}^{(n+1)} + \sum_{k=1}^{n}\frac{n+1}{n-k+1}\binom{n}{k}i^k L^k \underline{G}^{(n-k+1)} + \binom{n}{n}i^{n+1}L^{n+1}\underline{G} \\
= & \binom{n+1}{0}\underline{G}^{(n+1)} + \sum_{k=1}^{n}\binom{n+1}{k}i^k L^k \underline{G}^{(n-k+1)} + \binom{n+1}{n+1}i^{n+1}L^{n+1}\underline{G} \\
= & \sum_{k=0}^{n+1}\binom{n+1}{k}i^k L^k \underline{G}^{(n+1-k)} \qquad (5.19)
\end{aligned}$$

□

We conclude:

Theorem 30 *Let be $\mathcal{B} = \{\underline{G}\}$ a beobachtungsebene, $\hat{\varrho}(t)$ an accompanying process which is sufficient with respect to $\mathcal{B}$. Then $\hat{\varrho}(t)$ is weakly sufficient for $iL\underline{G}$.*

5.4 Time Independent Observables

Let us continue the discussion on the special case of time independent observables. Including the terms $iL\underline{G}$ into the beobachtungsebene, we force a vanishing process history of Robertson dynamics, as discussed in section 5.1. A similar effect is known in thermodynamics, where there are different types of state spaces depending on the description of process history [Mus90], [Mus96]. So we name $\{\underline{G}, iL\underline{G}\}$ a large (or extended) beobachtungsebene and $\{\underline{G}\}$ a small beobachtungsebene [Els93].

Even though we use the large beobachtungsebene, the process history would not vanish for the expectation value of $iL\underline{G}$, when we use Robertson dynamics:

$$\begin{aligned}\langle iL\underline{G}\rangle^{\bullet}(t) &= -\mathrm{Tr}\left(\varrho_{rel}(t)LL\underline{G}\right) - i\int_{t_0}^{t}\mathrm{Tr}\left(\left(L\underline{G}\right)LT(t,s)Q(s)L\varrho_{rel}(s)\right)ds \\ &= -\mathrm{Tr}\left(\varrho(t)LL\underline{G}\right) \end{aligned} \tag{5.20}$$

In general, any dynamics of an accompanying process ϱ_{rel} with respect to a large beobachtungsebene $\{\underline{G}, iL\underline{G}\}$ has the following properties:

$$\langle\underline{G}\rangle = \mathrm{Tr}\left(\varrho\underline{G}\right) = \mathrm{Tr}\left(\varrho_{rel}\underline{G}\right) \tag{5.21}$$

$$\langle\underline{G}\rangle^{\bullet} = \mathrm{Tr}\left(\underline{G}\dot{\varrho}\right) = i\mathrm{Tr}\left(\varrho L\underline{G}\right) = i\mathrm{Tr}\left(\varrho_{rel}L\underline{G}\right) = \langle iL\underline{G}\rangle \tag{5.22}$$

$$\langle\underline{G}\rangle^{\bullet\bullet} = \mathrm{Tr}\left(\underline{G}\ddot{\varrho}\right) = -\mathrm{Tr}\left(\varrho LL\underline{G}\right) \neq -\mathrm{Tr}\left(\varrho_{rel}LL\underline{G}\right)\ . \tag{5.23}$$

In this case, in addition to the expectation values, their first derivatives will be correctly given by the accompanying process, but not their higher derivatives. To solve this problem, we can either add $L^n\underline{G}$ into the beobachtungsebene, or demand the sufficiency to the dynamics of ϱ_{rel}. In case of the Robertson dynamics, such a totally sufficient dynamics would indeed make vanish process histories in all derivatives.

Using the Nakajima Zwanzig dynamics (3.41) with the Kawasaki Gunton operator, we get the same results as above with Robertson dynamics. With the large beobachtungsebene the dynamics of the expectation values $\langle\underline{G}\rangle$ does not need the process history, but the second derivative does.

Considering canonical dynamics (3.2), we get the following generalised canonical operator and its evolution equation for the large beobachtungsebene $\{\underline{G}, iL\underline{G}\}$:

$$R = \frac{1}{Z}\,e^{-\underline{\lambda}\cdot\underline{G}-\underline{\mu}\cdot iL\underline{G}} \tag{5.24}$$

$$\begin{aligned}\dot{R} &= R\left(\mathrm{Tr}\left(R\underline{G}\right) - \int_0^1 e^{\nu\underline{\lambda}\cdot\underline{G}}\,\underline{G}\,e^{-\nu\underline{\lambda}\cdot\underline{G}}\,d\nu\right)\cdot\dot{\underline{\lambda}} \\ &\quad + R\left(\mathrm{Tr}\left(RiL\underline{G}\right) - \int_0^1 e^{\nu\underline{\mu}\cdot iL\underline{G}}\,iL\underline{G}\,e^{-\nu\underline{\mu}\cdot iL\underline{G}}\,d\nu\right)\cdot\dot{\underline{\mu}}\end{aligned} \tag{5.25}$$

Since the operators $\underline{G}$ do not commute in general, we cannot simplify this equation further. As a simple example let us consider the beobachtungsebene $\mathcal{B} = \{H_{12}, iLH_{12}\}$. Here, the Liouville operator is deduced from the full Hamiltonian H of the system. As explained in section 2.5, H_{12} is the exchange Hamiltonian, called Hamiltonian of the partition. The operator iLH_{12} delivers the value of the partition's heat exchange with the two subsystems. Thus iLH_{12} can be interpreted as the observable of the heat flux. This is why this large beobachtungsebene is called here extended beobachtungsebene according to the Extended Thermodynamics [Jou96]. From the generalised canonical operator

$$R = \frac{1}{Z}e^{-\lambda_{12}H_{12}-\lambda_Q iLH_{12}} \tag{5.26}$$

follows the canonical dynamics

$$\begin{aligned}\dot{R} &= R\left(\langle H_{12}\rangle - \int_0^1 e^{\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\,H_{12}\,e^{-\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\,d\alpha\right)\dot{\lambda}_{12} \\ &\quad + R\left(\langle iLH_{12}\rangle - \int_0^1 e^{\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\,iLH_{12}\,e^{-\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\,d\alpha\right)\dot{\lambda}_Q\end{aligned} \tag{5.27}$$

and the dynamics of expectation values

$$
\begin{aligned}
\langle H_{12}\rangle^{\bullet} &= \Bigg(\langle H_{12}\rangle^2 - \mathrm{Tr}\Bigg(\int_0^1 e^{\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\, H_{12} \\
&\qquad\qquad e^{-\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\, d\alpha H_{12}R\Bigg)\Bigg)\dot\lambda_{12} \\
&\quad + \Bigg(\langle H_{12}\rangle\langle iLH_{12}\rangle - \mathrm{Tr}\Bigg(\int_0^1 e^{\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\, iLH_{12} \\
&\qquad\qquad e^{-\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\, d\alpha H_{12}R\Bigg)\Bigg)\dot\lambda_{Q} \\
&= -\left(H_{12}\,\middle|\,\Delta\, H_{12}\right)\dot\lambda_{12} - \left(H_{12}\,\middle|\,\Delta\, iLH_{12}\right)\dot\lambda_{Q} \\
&= \langle iLH_{12}\rangle\,,
\end{aligned}
\tag{5.28}
$$

$$
\begin{aligned}
\langle iLH_{12}\rangle^{\bullet} &= \Bigg(\langle iLH_{12}\rangle\langle H_{12}\rangle - \mathrm{Tr}\Bigg(\int_0^1 e^{\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\, H_{12} \\
&\qquad\qquad e^{-\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\, d\alpha\,(iLH_{12})\,R\Bigg)\Bigg)\dot\lambda_{12} \\
&\quad + \Bigg(\langle iLH_{12}\rangle^2 - \mathrm{Tr}\Bigg(\int_0^1 e^{\alpha(\lambda_{12}H_{12}+\nu iLH_{12})}\, (iLH_{12}) \\
&\qquad\qquad e^{-\alpha(\lambda_{12}H_{12}+\lambda_Q iLH_{12})}\, d\alpha\,(iLH_{12})\,R\Bigg)\Bigg)\dot\lambda_{Q} \\
&= -\left(iLH_{12}\,\middle|\,\Delta H_{12}\right)\dot\lambda_{12} - \left(iLH_{12}\,\middle|\,\Delta iLH_{12}\right)\dot\lambda_{Q}\,.
\end{aligned}
\tag{5.29}
$$

If the partition is an inert one, then of course the internal energy $\langle H_{12}\rangle$ is constant in time.

Chapter 6

Examples for Discrete Systems in Thermal Contact

In this chapter we will assume the situation described in section 2.5, that is the isolated compound system (2.36) of two subsystems, the interaction between them represented by a partition. Using canonical dynamics of section 3.1, we discuss some example situations concerning the purely thermal contact without material and work exchange. Therefore all observables are chosen to be time independent, and the rate of entropy is given by (3.59).

Another application of canonical dynamics on one dimensional ideal gas and harmonic lattices is given in [Kat01].

6.1 Considering the Partition

Let us begin with the last example in section 5.4. Let be the beobachtungsebene given by $\mathcal{B} = \{H_{12}, iLH_{12}\}$. Since there is no time dependence of observables, H_{12} contains the same information as the sum H_1+H_2, if the constant total Hamiltonian is known. The partition is not necessarily assumed to be inert. In this case the canonical density operator is given by

$$R(t) = \frac{1}{Z(t)} e^{-\lambda_{12}(t)H_{12} - \lambda_Q(t) iLH_{12}} , \tag{6.1}$$

and (3.59) yields the rate of entropy

$$\dot{S}(t) = k \left(\lambda_{12}(t)\dot{Q}_{12}(t) + \lambda_Q(t)\frac{d\dot{Q}_{12}}{dt}(t) \right) . \tag{6.2}$$

Theorem 31 *Let be*

$$\begin{aligned} \dot{\lambda}_{12} &= -\alpha\lambda_{12} \quad , \quad \alpha > 0 && (6.3) \\ \dot{\lambda}_Q &= -\beta\lambda_Q \quad , \quad \beta > 0 && (6.4) \end{aligned}$$

$$\Delta H_{12} \neq 0 \quad , \quad \Delta\, iLH_{12} \neq 0 \tag{6.5}$$

$$\Delta iLH_{12} \not\parallel \Delta H_{12} \tag{6.6}$$

the last assumption with respect to the Mori product. Then the rate of entropy (6.2) is positive definite.

Proof: Inserting the assumptions (6.3) and (6.4) into (5.28) and (5.29), we get

$$\begin{aligned} \dot{Q}_{12} &= \alpha\left(H_{12} \,\middle|\, \Delta H_{12}\right)\lambda_{12} + \beta\left(H_{12} \,\middle|\, \Delta\, iLH_{12}\right)\lambda_Q & (6.7)\\ \frac{d\dot{Q}_{12}}{dt} &= \alpha\left(iLH_{12} \,\middle|\, \Delta H_{12}\right)\lambda_{12} + \beta\left(iLH_{12} \,\middle|\, \Delta iLH_{12}\right)\lambda_Q\,. & (6.8) \end{aligned}$$

The Mori scalar product has the property

$$\left(A \,\middle|\, \Delta B\right) = \left(\Delta A \,\middle|\, \Delta B\right) \quad \text{for all} \quad A, B \in \mathcal{L}^{ob}. \tag{6.9}$$

This, allowing for the conditions in (6.5), (6.3) and (6.4), results in

$$\alpha\left(H_{12} \,\middle|\, \Delta H_{12}\right) > 0 \quad , \quad \beta\left(iLH_{12} \,\middle|\, \Delta iLH_{12}\right) > 0\,, \tag{6.10}$$

and the Schwarz inequality

$$\left|\left(A \,\middle|\, B\right)\right| \leq \|A\| \cdot \|B\| \tag{6.11}$$

with the conditions (6.5), (6.6) yields

$$\det\begin{pmatrix} \alpha\left(H_{12} \,\middle|\, \Delta H_{12}\right) & \beta\left(H_{12} \,\middle|\, \Delta\, iLH_{12}\right) \\ \alpha\left(iLH_{12} \,\middle|\, \Delta H_{12}\right) & \beta\left(iLH_{12} \,\middle|\, \Delta iLH_{12}\right) \end{pmatrix} > 0\,. \tag{6.12}$$

From (6.2), (6.7), (6.8) we get

$$\dot{S} = k \begin{pmatrix} \lambda_{12} \\ \lambda_Q \end{pmatrix}^T \begin{pmatrix} \alpha\left(H_{12} \,\middle|\, \Delta H_{12}\right) & \beta\left(H_{12} \,\middle|\, \Delta\, iLH_{12}\right) \\ \alpha\left(iLH_{12} \,\middle|\, \Delta H_{12}\right) & \beta\left(iLH_{12} \,\middle|\, \Delta iLH_{12}\right) \end{pmatrix} \begin{pmatrix} \lambda_{12} \\ \lambda_Q \end{pmatrix}. \tag{6.13}$$

Since the determinants (6.10) and (6.12) are all positive, the quadratic form (6.13) is positive definite. □

Actually, it is paradox to make an ansatz for the Lagrange parameters, like the relaxation ansatz (6.3) and (6.4), because theorem 2 states, that the parameters are uniquely determined by the $n+1$ constrains (2.22) and (2.23). However, the theorem is based upon the uniqueness theorem for solutions of initial value problems, and it is utterly unknown, how to determine the parameters expicitly. It is not possible to resolve (2.18) with respect to the parameters. The assumptions (6.3) and (6.4) are so particular, that unfortunately, it is not possible to show that the derivative of (6.7) yields (6.8). In [Mus94], the question is investigated how one can derive a dynamics of the Lagrange parameters out of the canonical dynamics (3.2).

6.2 Subsystems and their Contact Temperature

Let us now consider the beobachtungsebene $\mathcal{B} = \{H_1, H_2\}$. Then the generalised canonical operator according to the maximum entropy procedure is given by

$$R(t) = \frac{1}{Z(t)} e^{-\lambda_1(t)H_1 - \lambda_2(t)H_2}\,. \tag{6.14}$$

From (3.59) we get the rate of entropy

$$\dot{S}(t) = k\left(\lambda_1(t)\dot{Q}_1(t) + \lambda_2(t)\dot{Q}_2(t)\right) . \tag{6.15}$$

If the partition is inert (2.37), we get

$$\dot{S}(t) = k\left(\lambda_1(t) - \lambda_2(t)\right)\dot{Q}_1(t) . \tag{6.16}$$

Theorem 32 *Let be $\mathcal{B} = \{H_1, H_2\}$, the compound system isolated, the partition inert and the system no. 2 in equilibrium. With the identification*

$$\lambda_1(t) + X(t) = \frac{1}{k\theta_1(t)} \quad , \quad \lambda_2(t) + X(t) = \frac{1}{kT_2(t)} \tag{6.17}$$

where θ_1 is the contact temperature of system no. 1,

$$\dot{S} \geq 0 \tag{6.18}$$

is valid.

Proof: (6.16) results in

$$\dot{S} = \left(\frac{1}{\theta_1(t)} - \frac{1}{T_2(t)}\right)\dot{Q}_1(t) \geq 0 . \tag{6.19}$$

The inequality is induced by the definition of contact temperature [Mus94]. □

If both systems are not in equilibrium the entropy production caused by heat exchange is positive, if the heat exchange $\dot{Q}_1$ has the form

$$\dot{Q}_1 = k_{11}\left(\lambda_1(t) - \lambda_2(t)\right) \quad , \quad k_{11} \geq 0 \tag{6.20}$$

as follows from (6.16). For example:

Theorem 33 *If*

$$\left(H_1 \,\middle|\, \Delta H_1\right) = -\left(H_1 \,\middle|\, \Delta H_2\right) \tag{6.21}$$

$$\Delta H_1 \neq 0 \tag{6.22}$$

$$(\lambda_1 - \lambda_2)^{\bullet} = -\alpha\,(\lambda_1 - \lambda_2) \quad , \quad \alpha > 0 \tag{6.23}$$

are valid, then the rate of entropy (6.16) for $\mathcal{B} = \{H_1, H_2\}$ with an inert partition is positive definite.

Proof: According to (3.5), we have

$$\begin{aligned}
\dot{Q}_1 \quad &= \quad -\left(H_1 \,\middle|\, \Delta H_1\right)\dot{\lambda}_1 - \left(H_1 \,\middle|\, \Delta H_2\right)\dot{\lambda}_2 && (6.24)\\
&\overset{(6.21)}{=} \quad -\left(H_1 \,\middle|\, \Delta H_1\right)(\lambda_1 - \lambda_2)^{\bullet} && (6.25)\\
&\overset{(6.23)}{=} \quad \alpha\left(H_1 \,\middle|\, \Delta H_1\right)(\lambda_1 - \lambda_2) . && (6.26)
\end{aligned}$$

Inserting this into (6.16), it is clear that $\dot{S}$ is positive definite because of (6.9). □

The assumption (6.23) is plausible as a sort of Newton's law of cooling. (6.21) may be valid when we bear in mind that the partition is assumed to be inert.

If the partition is not specified, it is reasonable to extend the beobachtungsebene for $\mathcal{B} = \{H_1, H_2, H_{12}\}$ with the generalised canonical operator

$$R(t) = \frac{1}{Z(t)} e^{-\lambda_1(t)H_1 - \lambda_2(t)H_2 - \lambda_{12}(t)H_{12}}\,. \tag{6.27}$$

Since the compound system is isolated $\dot{Q} = 0$ (2.36), we get from (3.59) the rate of entropy

$$\dot{S}(t) = k\Big(\left(\lambda_1(t) - \lambda_{12}(t)\right)\dot{Q}_1(t) + \left(\lambda_2(t) - \lambda_{12}(t)\right)\dot{Q}_2(t)\Big)\,. \tag{6.28}$$

Theorem 34 *If*

$$\begin{aligned}\big(H_1 \,\big|\, \Delta H_1\big) + \big(H_1 \,\big|\, \Delta H_2\big) &= -\big(H_1 \,\big|\, \Delta H_{12}\big) && (6.29)\\ \big(H_2 \,\big|\, \Delta H_1\big) + \big(H_2 \,\big|\, \Delta H_2\big) &= -\big(H_2 \,\big|\, \Delta H_{12}\big) && (6.30)\end{aligned}$$

$$\Delta H_1 \neq 0 \quad , \quad \Delta H_2 \neq 0 \quad , \quad \Delta H_1 \not\parallel \Delta H_2 \tag{6.31}$$

$$\begin{aligned}(\lambda_1 - \lambda_{12})^{\bullet} &= -\alpha\,(\lambda_1 - \lambda_{12}) \quad , \quad \alpha > 0 && (6.32)\\ (\lambda_2 - \lambda_{12})^{\bullet} &= -\beta\,(\lambda_2 - \lambda_{12}) \quad , \quad \beta > 0 && (6.33)\end{aligned}$$

are valid, then the rate of entropy (6.28) for $\mathcal{B} = \{H_1, H_2, H_{12}\}$ is positive definite.

Proof: Analogically to the proof of theorem 31 and 33, we get

$$\begin{pmatrix} \dot{Q}_1(t) \\ \dot{Q}_2(t) \end{pmatrix} = \begin{pmatrix} \alpha\big(H_1 \big| \Delta H_1\big) & \beta\big(H_1 \big| \Delta H_2\big) \\ \alpha\big(H_2 \big| \Delta H_1\big) & \beta\big(H_2 \big| \Delta H_2\big) \end{pmatrix} \begin{pmatrix} \lambda_1(t) - \lambda_{12}(t) \\ \lambda_2(t) - \lambda_{12}(t) \end{pmatrix}. \tag{6.34}$$

Since all diagonal elements of the above matrix are positive, as well as its determinant according to (6.11), (6.31), (6.32) and (6.33), we receive the positive definite quadratic form

$$\dot{S} = k \begin{pmatrix} \lambda_1(t) - \lambda_{12}(t) \\ \lambda_2(t) - \lambda_{12}(t) \end{pmatrix}^T \begin{pmatrix} \alpha\big(H_1 \big| \Delta H_1\big) & \beta\big(H_1 \big| \Delta H_2\big) \\ \alpha\big(H_2 \big| \Delta H_1\big) & \beta\big(H_2 \big| \Delta H_2\big) \end{pmatrix} \begin{pmatrix} \lambda_1(t) - \lambda_{12}(t) \\ \lambda_2(t) - \lambda_{12}(t) \end{pmatrix}. \tag{6.35}$$

□

Theorem 35 *With the identification of the Lagrange parameter in (6.34) by the contact temperature*

$$\lambda_1(t) = \frac{1}{\theta_1(t)} \quad , \quad \lambda_2(t) = \frac{1}{\theta_2(t)} \tag{6.36}$$

we obtain

$$\lambda_{12}(t) = \frac{1}{\theta_1(t)} = \frac{1}{\theta_2(t)}\,. \tag{6.37}$$

Proof: From (6.36) we get by definition of contact temperature

$$\dot{Q}_1 = \dot{Q}_2 = 0\,. \tag{6.38}$$

Inserting this into (6.34) it follows that (6.37) is valid, because the matrix in (6.34) is invertible. □

So the reciprocal temperature λ_{12} of the partition is identical to its reciprocal contact temperature $\frac{1}{\theta_1}$.

Chapter 7

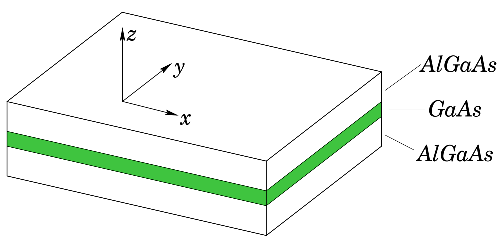
An Example: Electron Phonon Interaction

In this chapter, we will consider an example of many body quantum mechanics in second quantisation. In the first part, we will briefly recapitulate the characteristics of a semiconductor quantum well, and then analyse the treatment of such a semiconductor component by means of projection operator technique [Wal03]. Next, some thermodynamical quantities in this model are calculated and analysed. All pictures in this chapter are copied from [Ull04].

7.1 Quantum Well

A single quantum well is composed of three thin semiconductor layers. A narrow bandgap semiconductor is sandwiched between two layers of large bandgap semiconductor. The active layer thickness is there near wavelength of the charge carrier, thus quantum effects become apparent. An example is the quantum well using GaAs and $Al_xGa_{1-x}As$, $0 < x < 0.45$, as potential barriers, shown in figure 7.1.

Figure 7.1: Scheme of a single quantum well AlGaAs/GaAs/AlGaAs



In the application to quantum laser, one layer is n-type AlGaAs, the other p-type AlGaAs. The forward biased quantum well emits light in order of eV due to interband transitions. In the resonant cavity, this light is reflected back and forth to enforce induced emission. Besides, there are intersubband and intrasubband transitions in order of meV. They are caused by interaction of electrons ond phonons, which is investigated here.

Figure 7.2: Band structure of AlGaAs/GaAs/AlGaAs, $E(z)$

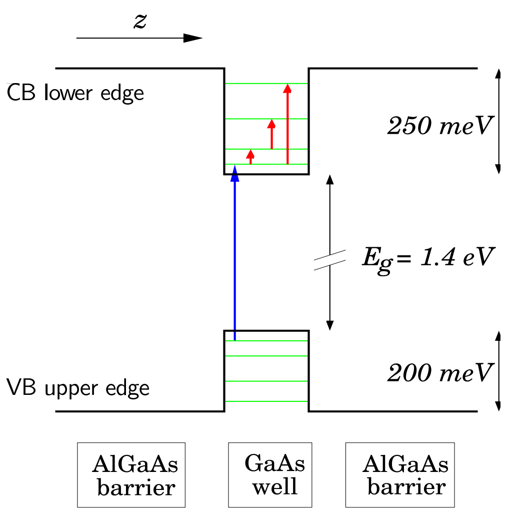


Figure 7.3: Subband structure of a quantum well, $E(z)$, $E(\mathbf{q}_{||})$

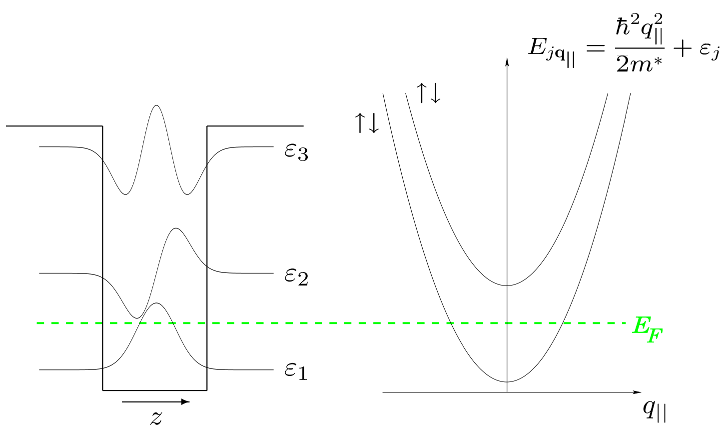


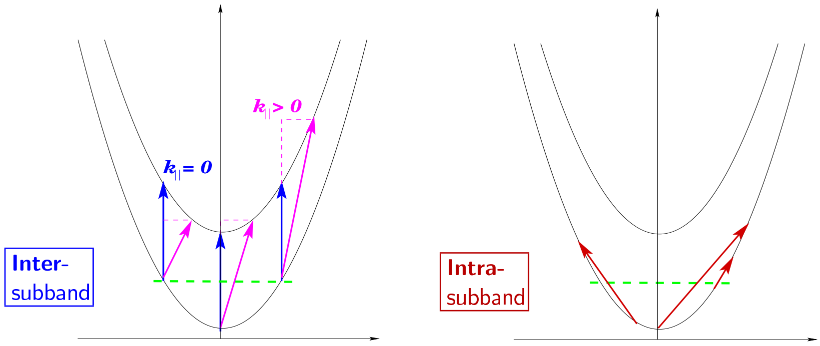
Figure 7.3 shows the subband structure and the corresponding dispersion relation. $\mathbf{q}_{||}$ denotes the wave vector which is in-plane for electrons in a quantum well. They are confined in z direction.

The electron density operator [Nol02]

$$\varrho_{ij} = \mathrm{Tr}\left(a^{+i} a^{j}\, \varrho\right) \tag{7.1}$$

can be interpreted as microscopic dipole density describing the electron intersubband coherence. The macroscopic polarisation of a single quantum well is then a

Figure 7.4: Intersubband and intrasubband transitions, $E(\mathbf{k}_\parallel)$



function of these density matrix elements. Waldmüller et al. derive differential equations for ϱ_{ij} to determine them [Wal03]. Here, a^{+i} is the generator of an electron in subband i, a^j denotes the annihilator of an electron in subband j. Since the operators are time independent, we calculate the following dynamics

$$\frac{d}{dt}\varrho_{ij} = \frac{d}{dt}\mathrm{Tr}\left(a^{+i}a^j\varrho\right) = -i\mathrm{Tr}\left(a^{+i}a^jL\varrho\right) = i\mathrm{Tr}\left(\varrho L\left(a^{+i}a^j\right)\right) . \tag{7.2}$$

The last term in (7.2) can be calculated using the Liouville operator L given by the corresponding Hamiltonian:

$$\begin{aligned} H &= H_{0c} + H_{0p} + H_{cf} + H_{cc} + H_{cp} && (7.3)\\ &= \sum_i \varepsilon_i a^{+i}a^i + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} b^+_{\mathbf{q}} b_{\mathbf{q}} + \sum_{i,j}\int \mathbf{d}_{ij}\cdot\mathbf{E}(z,t)a^{+i}a^j dz \\ &\quad + \sum_{i,j,m,n}\frac{1}{2}V_{ijmn}a^{+i}a^{+j}a^n a^m \\ &\quad + \sum_{i,j,\mathbf{k},\mathbf{q}}\left(g^{ij}_{\mathbf{q}} a^{+i}_{\mathbf{k}} b_{\mathbf{q}} a^j_{\mathbf{k}-\mathbf{q}_\parallel} + g^{*ji}_{\mathbf{q}} a^{+i}_{\mathbf{k}-\mathbf{q}_\parallel} b^+_{\mathbf{q}} a^j_{\mathbf{k}}\right) , && (7.4) \end{aligned}$$

ε_i: energy of an electron in subband i, $\hbar\omega_{\mathbf{q}}$: energy of an longitudinal optical phonon with wave vector $\mathbf{q}$, $b^+_{\mathbf{q}}/b_{\mathbf{q}}$: generator/annihilator of an phonon with wave vector $\mathbf{q}$, $\mathbf{d}_{ij}$: intersubband dipole matrix element, $\mathbf{E}$: external electric field, V_{ijmn}: Coulomb potential, $g^{ij}_{\mathbf{q}}$: Fröhlich coupling matrix. (7.2) can be interpreted as the dynamics of particle number in subband i if $i = j$, or else as the dynamics of transition probability of the electron from subband j to subband i.

In order to make a mean field approximation of this model, one applies the projection operator technique using Robertson dynamics. As relevant operators, single electron observables and phonon number operators are chosen, where phonons form a bath with constant temperature. Therefore the beobachtungsebene is

$$\mathcal{B} = \left\{a^{+i}a^j, b^+_{\mathbf{q}} b_{\mathbf{q}}\right\} . \tag{7.5}$$

$$\begin{aligned} P\varrho &= \varrho_{MF} = \frac{1}{Z(t)} e^{-\sum_{i,j}\lambda_{ij}(t)a^{+i}a^j - \sum_{\mathbf{q}}\beta\hbar\omega_{\mathbf{q}} b^+_{\mathbf{q}} b_{\mathbf{q}}} && (7.6)\\ Q\varrho &= \varrho_{Corr} && (7.7) \end{aligned}$$

While the mean field part is supposed to be generalised canonical, no assumption is made for the correlation part.

The commutation relations of the electron and phonon operators yield:

$$iL_{0c}a^{+a}a^{b} = \frac{i}{\hbar}\left(\varepsilon_a-\varepsilon_b\right)a^{+a}a^{b} \tag{7.8}$$

$$iL_{0p}a^{+a}a^{b} = 0 \tag{7.9}$$

$$iL_{cf}a^{+a}a^{b} = \frac{i}{\hbar}\int \mathbf{d}_{ba}\cdot\mathbf{E}(z,t)\left(a^{+b}a^{b}-a^{+a}a^{a}\right)dz \tag{7.10}$$

$$iL_{cc}a^{+a}a^{b} = \frac{i}{\hbar}\sum_{i,j,m,n}\left(V_{ijam}a^{+i}a^{+j}a^{m}a^{b}-V_{bimn}a^{+a}a^{+i}a^{n}a^{m}\right) \tag{7.11}$$

$$\begin{aligned} iL_{cp}a^{+a}a^{b} = \frac{i}{\hbar}\sum_{i,j,\mathbf{k},\mathbf{q}} &\Big(g_{\mathbf{q}}^{ia}a^{+i}_{\mathbf{k}+\mathbf{q}_\parallel}b_{\mathbf{q}}a^{b}_{\mathbf{k}}-g_{\mathbf{q}}^{bj}a^{+a}_{\mathbf{k}}b_{\mathbf{q}}a^{j}_{\mathbf{k}-\mathbf{q}_\parallel} \\ &+g_{\mathbf{q}}^{*ai}a^{+i}_{\mathbf{k}-\mathbf{q}_\parallel}b^{+}_{\mathbf{q}}a^{b}_{\mathbf{k}}-g_{\mathbf{q}}^{*jb}a^{+a}_{\mathbf{k}}b^{+}_{\mathbf{q}}a^{j}_{\mathbf{k}+\mathbf{q}_\parallel}\Big) \end{aligned} \tag{7.12}$$

The following table contains all contributions to (7.2), that are in the form of $i\mathrm{Tr}\left(\varrho_x L_y a^{+a}a^{b}\right)$.

	ϱ_{MF}	ϱ_{Corr}
L_{0c}	$\frac{i}{\hbar}\left(\varepsilon_a-\varepsilon_b\right)\varrho_{ab}$	0
L_{0p}	0	0
L_{cf}	$\frac{i}{\hbar}\int \mathbf{d}_{ba}\cdot\mathbf{E}(z,t)\left(\varrho_{bb}-\varrho_{aa}\right)dz$	0
L_{cc}	$\frac{i}{\hbar}\sum_{i,j,m}\left(V_{ijam}\left(\varrho_{ib}\varrho_{jm}-\varrho_{im}\varrho_{jb}\right) -V_{bimj}\left(\varrho_{am}\varrho_{ij}-\varrho_{aj}\varrho_{im}\right)\right)$	$\frac{i}{\hbar}\sum_{i,j,m}\left(V_{ijam}\mathrm{Tr}\left(\varrho_{Corr}a^{+i}a^{+j}a^{m}a^{b}\right) -V_{bimj}\mathrm{Tr}\left(\varrho_{Corr}a^{+a}a^{+i}a^{j}a^{m}\right)\right)$
L_{cp}	0	$\frac{i}{\hbar}\sum_{i,\mathbf{k},\mathbf{q}}\Big(g_{\mathbf{q}}^{ia}\mathrm{Tr}\left(\varrho_{Corr}a^{+i}_{\mathbf{k}+\mathbf{q}_\parallel}b_{\mathbf{q}}a^{b}_{\mathbf{k}}\right) -g_{\mathbf{q}}^{bi}\mathrm{Tr}\left(\varrho_{Corr}a^{+a}_{\mathbf{k}}b_{\mathbf{q}}a^{i}_{\mathbf{k}-\mathbf{q}_\parallel}\right) +g_{\mathbf{q}}^{*ai}\mathrm{Tr}\left(\varrho_{Corr}a^{+i}_{\mathbf{k}-\mathbf{q}_\parallel}b^{+}_{\mathbf{q}}a^{b}_{\mathbf{k}}\right) -g_{\mathbf{q}}^{*ib}\mathrm{Tr}\left(\varrho_{Corr}a^{+a}_{\mathbf{k}}b^{+}_{\mathbf{q}}a^{i}_{\mathbf{k}+\mathbf{q}_\parallel}\right)\Big)$

For $i\mathrm{Tr}\left(\varrho_{MF}L_{cc}a^{+a}a^{b}\right)$, the 4-point expectation value has been factorised taking into account the canonical form of ϱ_{MF} [Fic83], and $i\mathrm{Tr}\left(\varrho_{MF}L_{cp}a^{+a}a^{b}\right)$ vanishes assuming the phonon bath.

The mean field part of the wanted differential equations for ϱ_{ij} are now quite clear, even without using any dynamics. This is a consequence of (7.2), because we can shift the Liouville operator onto the time independent $a^{+i}a^j$. Both the many particle correlation terms are treated further by means of Robertson dynamics [Wal03]. Interesting fact is, that this approach modifies the actual philosophy of projection formalism. The quantum mechanical expectation value (7.2) is no longer split into a relevant and an irrelevant term, but both the projected terms $P\varrho$ and $Q\varrho$ are taken into account, whereas usually the "irrelevant" part is neglected. Here, the relevant part represents the mean field part considering only single particle contributions, the irrelevant part is the many particle correlation part, as can be seen in the table. Thus, neglecting the irrelevant part means here to abandon the correlations. As a result, all terms in the above table are exact, approximations are performed only in the Robertson evaluation of ϱ_{Corr}.

7.2 Some Thermodynamical Quantities

Using the model discussed in 7.1, we are able to calculate some thermodynamical quantities. We will neglect here the external electric field and confine ourselves to consider the pure electron phonon interaction. The considered Hamiltonian is now according to (7.3)

$$\begin{aligned} H &= H_{0c} + H_{0p} + H_{cc} + H_{cp} && (7.13) \\ &= \sum_i \varepsilon_i a^{+i} a^i + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} b^+_{\mathbf{q}} b_{\mathbf{q}} + \sum_{i,j,m,n} \frac{1}{2} V_{ijmn} a^{+i} a^{+j} a^n a^m \\ &\quad + \sum_{i,j,\mathbf{k},\mathbf{q}} \left(g^{ij}_{\mathbf{q}} a^{+i}_{\mathbf{k}} b_{\mathbf{q}} a^j_{\mathbf{k}-\mathbf{q}_\parallel} + g^{*ji}_{\mathbf{q}} a^{+i}_{\mathbf{k}-\mathbf{q}_\parallel} b^+_{\mathbf{q}} a^j_{\mathbf{k}} \right) . && (7.14) \end{aligned}$$

Since the complete system is isolated, we split it into two interacting subsystems of electrons and phonons according to (2.28):

$$H_1 = H_{0c} + H_{cc} \quad , \quad H_2 = H_{0p} \quad , \quad H_{12} = H_{cp} \, . \tag{7.15}$$

Calculating the following commutators

$$\begin{aligned} iL_{0c} b^+_{\mathbf{q}} b_{\mathbf{q}} &= 0 && (7.16) \\ iL_{0p} b^+_{\mathbf{q}} b_{\mathbf{q}} &= 0 && (7.17) \\ iL_{cc} b^+_{\mathbf{q}} b_{\mathbf{q}} &= 0 && (7.18) \\ iL_{cp} b^+_{\mathbf{q}} b_{\mathbf{q}} &= \frac{i}{\hbar} \sum_{i,j,\mathbf{k}} \left(g^{ij}_{\mathbf{q}} a^{+i}_{\mathbf{k}} b_{\mathbf{q}} a^j_{\mathbf{k}-\mathbf{q}_\parallel} - g^{*ji}_{\mathbf{q}} a^{+i}_{\mathbf{k}-\mathbf{q}_\parallel} b^+_{\mathbf{q}} a^j_{\mathbf{k}} \right) && (7.19) \end{aligned}$$

$$\begin{aligned} iL_{0c} H_{cc} &= \frac{i}{\hbar} \frac{1}{2} \sum_{i,j,m,n} V_{ijmn} \left(\varepsilon_i + \varepsilon_j - \varepsilon_n - \varepsilon_m \right) a^{+i} a^{+j} a^n a^m && (7.20) \\ iL_{0p} H_{cc} &= 0 && (7.21) \\ iL_{cc} H_{cc} &= 0 && (7.22) \\ iL_{cp} H_{cc} &= \frac{i}{\hbar} \sum_{a,b,\mathbf{k},\mathbf{q}} \sum_{i,j,m,n} \sum_{\mathbf{l},\mathbf{p}} \Big(g^{ab}_{\mathbf{q}} V_{bjmn} a^{+a}_{\mathbf{k}} b_{\mathbf{q}} a^{+j}_{\mathbf{l}+\mathbf{p}+\mathbf{q}-\mathbf{k}_\parallel} a^n_{\mathbf{l}} a^m_{\mathbf{p}} \\ &\quad - g^{ab}_{\mathbf{q}} V_{ijma} a^{+j}_{\mathbf{k}-\mathbf{l}} a^{+i}_{\mathbf{p}+\mathbf{l}} a^m_{\mathbf{p}} b_{\mathbf{q}} a^b_{\mathbf{k}-\mathbf{q}_\parallel} + g^{*ba}_{\mathbf{q}} V_{bjmn} a^{+a}_{\mathbf{k}-\mathbf{q}_\parallel} b^+_{\mathbf{q}} a^{+j}_{\mathbf{l}+\mathbf{p}-\mathbf{k}} a^n_{\mathbf{l}} a^m_{\mathbf{p}} \\ &\quad - g^{*ba}_{\mathbf{q}} V_{ijma} a^{+j}_{\mathbf{k}-\mathbf{q}-\mathbf{l}_\parallel} a^{+i}_{\mathbf{p}+\mathbf{l}} a^m_{\mathbf{p}} b^+_{\mathbf{q}} a^b_{\mathbf{k}} \Big) , && (7.23) \end{aligned}$$

we are able to give expressions for heat exchange between the subsystems:

$$
\begin{aligned}
\dot{Q}_1 &= \dot{Q}_{0c} + \dot{Q}_{cc} = i\mathrm{Tr}\left(\varrho L H_1\right) \\
&= \frac{i}{\hbar}\sum_{a,j,\mathbf{k},\mathbf{q}} \varepsilon_a \left(g_{\mathbf{q}}^{ja}\mathrm{Tr}\left(\varrho a^{+j}_{\mathbf{k}+\mathbf{q}_\parallel} b_{\mathbf{q}} a^{a}_{\mathbf{k}}\right) - g_{\mathbf{q}}^{aj}\mathrm{Tr}\left(\varrho a^{+a}_{\mathbf{k}} b_{\mathbf{q}} a^{j}_{\mathbf{k}-\mathbf{q}_\parallel}\right)\right. \\
&\quad \left. + g_{\mathbf{q}}^{*aj}\mathrm{Tr}\left(\varrho a^{+j}_{\mathbf{k}-\mathbf{q}_\parallel} b^{+}_{\mathbf{q}} a^{a}_{\mathbf{k}}\right) - g_{\mathbf{q}}^{*ja}\mathrm{Tr}\left(\varrho a^{+a}_{\mathbf{k}} b^{+}_{\mathbf{q}} a^{j}_{\mathbf{k}+\mathbf{q}_\parallel}\right)\right) \qquad (7.24) \\
&\quad + \frac{i}{\hbar}\sum_{a,b,\mathbf{k},\mathbf{q}}\sum_{i,j,m}\sum_{\mathbf{l},\mathbf{p}} \left(g_{\mathbf{q}}^{ab} V_{bjmi}\mathrm{Tr}\left(\varrho a^{+a}_{\mathbf{k}} b_{\mathbf{q}} a^{+j}_{\mathbf{l}+\mathbf{p}+\mathbf{q}-\mathbf{k}_\parallel} a^{i}_{\mathbf{l}} a^{m}_{\mathbf{p}}\right)\right. \\
&\quad - g_{\mathbf{q}}^{ab} V_{ijma}\mathrm{Tr}\left(\varrho a^{+j}_{\mathbf{k}-\mathbf{l}} a^{+i}_{\mathbf{p}+\mathbf{l}} a^{m}_{\mathbf{p}} b_{\mathbf{q}} a^{b}_{\mathbf{k}-\mathbf{q}_\parallel}\right) \\
&\quad + g_{\mathbf{q}}^{*ba} V_{bjmi}\mathrm{Tr}\left(\varrho a^{+a}_{\mathbf{k}-\mathbf{q}_\parallel} b^{+}_{\mathbf{q}} a^{+j}_{\mathbf{l}+\mathbf{p}-\mathbf{k}} a^{i}_{\mathbf{l}} a^{m}_{\mathbf{p}}\right) \\
&\quad \left. - g_{\mathbf{q}}^{*ba} V_{ijma}\mathrm{Tr}\left(\varrho a^{+j}_{\mathbf{k}-\mathbf{q}-\mathbf{l}_\parallel} a^{+i}_{\mathbf{p}+\mathbf{l}} a^{m}_{\mathbf{p}} b^{+}_{\mathbf{q}} a^{b}_{\mathbf{k}}\right)\right) \qquad (7.25) \\
\dot{Q}_2 &= \dot{Q}_{0p} = i\mathrm{Tr}\left(\varrho L H_2\right) \\
&= i\sum_{i,j,\mathbf{k},\mathbf{q}} \omega_{\mathbf{q}} \left(g_{\mathbf{q}}^{ij}\mathrm{Tr}\left(\varrho a^{+i}_{\mathbf{k}} b_{\mathbf{q}} a^{j}_{\mathbf{k}-\mathbf{q}_\parallel}\right) - g_{\mathbf{q}}^{*ji}\mathrm{Tr}\left(\varrho a^{+i}_{\mathbf{k}-\mathbf{q}_\parallel} b^{+}_{\mathbf{q}} a^{j}_{\mathbf{k}}\right)\right) \qquad (7.26) \\
\dot{Q}_{12} &= \dot{Q}_{cp} \overset{*}{=} -\dot{Q}_{0c} - \dot{Q}_{0p} - \dot{Q}_{cc} \qquad (7.27) \\
&= \frac{i}{\hbar}\sum_{a,j,\mathbf{k},\mathbf{q}} \varepsilon_a \left(-g_{\mathbf{q}}^{ja}\mathrm{Tr}\left(\varrho a^{+j}_{\mathbf{k}+\mathbf{q}_\parallel} b_{\mathbf{q}} a^{a}_{\mathbf{k}}\right) + g_{\mathbf{q}}^{aj}\mathrm{Tr}\left(\varrho a^{+a}_{\mathbf{k}} b_{\mathbf{q}} a^{j}_{\mathbf{k}-\mathbf{q}_\parallel}\right)\right. \\
&\quad \left. - g_{\mathbf{q}}^{*aj}\mathrm{Tr}\left(\varrho a^{+j}_{\mathbf{k}-\mathbf{q}_\parallel} b^{+}_{\mathbf{q}} a^{a}_{\mathbf{k}}\right) + g_{\mathbf{q}}^{*ja}\mathrm{Tr}\left(\varrho a^{+a}_{\mathbf{k}} b^{+}_{\mathbf{q}} a^{j}_{\mathbf{k}+\mathbf{q}_\parallel}\right)\right) \\
&\quad + i\sum_{i,j,\mathbf{k},\mathbf{q}} \omega_{\mathbf{q}} \left(-g_{\mathbf{q}}^{ij}\mathrm{Tr}\left(\varrho a^{+i}_{\mathbf{k}} b_{\mathbf{q}} a^{j}_{\mathbf{k}-\mathbf{q}_\parallel}\right) + g_{\mathbf{q}}^{*ji}\mathrm{Tr}\left(\varrho a^{+i}_{\mathbf{k}-\mathbf{q}_\parallel} b^{+}_{\mathbf{q}} a^{j}_{\mathbf{k}}\right)\right) \\
&\quad - \frac{i}{\hbar}\sum_{a,b,\mathbf{k},\mathbf{q}}\sum_{i,j,m}\sum_{\mathbf{l},\mathbf{p}} \left(g_{\mathbf{q}}^{ab} V_{bjmi}\mathrm{Tr}\left(\varrho a^{+a}_{\mathbf{k}} b_{\mathbf{q}} a^{+j}_{\mathbf{l}+\mathbf{p}+\mathbf{q}-\mathbf{k}_\parallel} a^{i}_{\mathbf{l}} a^{m}_{\mathbf{p}}\right)\right. \\
&\quad - g_{\mathbf{q}}^{ab} V_{ijma}\mathrm{Tr}\left(\varrho a^{+j}_{\mathbf{k}-\mathbf{l}} a^{+i}_{\mathbf{p}+\mathbf{l}} a^{m}_{\mathbf{p}} b_{\mathbf{q}} a^{b}_{\mathbf{k}-\mathbf{q}_\parallel}\right) \\
&\quad + g_{\mathbf{q}}^{*ba} V_{bjmi}\mathrm{Tr}\left(\varrho a^{+a}_{\mathbf{k}-\mathbf{q}_\parallel} b^{+}_{\mathbf{q}} a^{+j}_{\mathbf{l}+\mathbf{p}-\mathbf{k}} a^{i}_{\mathbf{l}} a^{m}_{\mathbf{p}}\right) \\
&\quad \left. - g_{\mathbf{q}}^{*ba} V_{ijma}\mathrm{Tr}\left(\varrho a^{+j}_{\mathbf{k}-\mathbf{q}-\mathbf{l}_\parallel} a^{+i}_{\mathbf{p}+\mathbf{l}} a^{m}_{\mathbf{p}} b^{+}_{\mathbf{q}} a^{b}_{\mathbf{k}}\right)\right) . \qquad (7.28)
\end{aligned}
$$

On the condition of phonon bath, all mean field parts of the heat exchanges are vanishing, so we can replace all ϱ by ϱ_{Corr} [Wal03]. Equation $*$ in (7.27) is valid, because the system is isolated, and because we took all Hamiltonian parts into account (7.13), (7.15):

$$\dot{Q}_1 + \dot{Q}_2 = i\mathrm{Tr}\left(\varrho L\left(H_1 + H_2\right)\right) = -i\mathrm{Tr}\left(\varrho L H_{12}\right) = -\dot{Q}_{12}\,. \qquad (7.29)$$

It is remarkable, that the partition (section 2.5) is not inert (2.37) in this example, as can be seen in (7.28). Although H_{cc} is not included in H_{12}, $\dot{Q}_{12}$ contains terms with Coulomb potential V_{ijmn}. So both electron electron and electron phonon interactions contribute to the heat exchange $\dot{Q}_{12}$. If there is no electron phonon interaction ($g^{ij} = 0 = g^{*mn}$), all heat exchanges obviously vanish.

The von Neumann entropy (2.16) with respect to the generalised canonical operator

$$R(t) = \frac{1}{Z(t)}\exp\left(-\sum_{i,j}\lambda_{ij}(t)a^{+i}a^{j} - \sum_{\mathbf{q}}\beta\hbar\omega_{\mathbf{q}} b^{+}_{\mathbf{q}} b_{\mathbf{q}}\right) \qquad (7.30)$$

is given by

$$\begin{aligned}
\dot{S}(t) &= k\sum_{i,j}\lambda_{ij}(t)\frac{d}{dt}\mathrm{Tr}\left(\varrho a^{+i}a^{j}\right) + k\sum_{\mathbf{q}}\beta\hbar\omega_{\mathbf{q}}\frac{d}{dt}\mathrm{Tr}\left(\varrho b^{+}_{\mathbf{q}}b_{\mathbf{q}}\right) \\
&= k\frac{i}{\hbar}\sum_{i,j}\lambda_{ij}(t)\left(\varepsilon_i-\varepsilon_j\right)\mathrm{Tr}\left(\varrho a^{+i}a^{j}\right) \\
&\quad +k\frac{i}{\hbar}\sum_{i,j}\lambda_{ij}(t)\sum_{a,b,m,n}\left(V_{abim}\mathrm{Tr}\left(\varrho a^{+a}a^{+b}a^{m}a^{j}\right)\right. \\
&\quad \left.-V_{jamn}\mathrm{Tr}\left(\varrho a^{+i}a^{+a}a^{n}a^{m}\right)\right) \\
&\quad +k\frac{i}{\hbar}\sum_{i,j}\sum_{l,\mathbf{k},\mathbf{q}}\lambda_{ij}(t)\left(g^{li}_{\mathbf{q}}\mathrm{Tr}\left(\varrho a^{+l}_{\mathbf{k}+\mathbf{q}_{\parallel}}b_{\mathbf{q}}a^{j}_{\mathbf{k}}\right) - g^{jl}_{\mathbf{q}}\mathrm{Tr}\left(a^{+i}_{\mathbf{k}}b_{\mathbf{q}}a^{l}_{\mathbf{k}-\mathbf{q}_{\parallel}}\right)\right. \\
&\quad \left.+g^{*il}_{\mathbf{q}}\mathrm{Tr}\left(\varrho a^{+l}_{\mathbf{k}-\mathbf{q}_{\parallel}}b^{+}_{\mathbf{q}}a^{j}_{\mathbf{k}}\right) - g^{*lj}_{\mathbf{q}}\mathrm{Tr}\left(\varrho a^{+i}_{\mathbf{k}}b^{+}_{\mathbf{q}}a^{l}_{\mathbf{k}+\mathbf{q}_{\parallel}}\right)\right) \\
&\quad +\beta k\sum_{\mathbf{q}}\sum_{i,j,\mathbf{k}}i\omega_{\mathbf{q}}\left(g^{ij}_{\mathbf{q}}\mathrm{Tr}\left(\varrho a^{+i}_{\mathbf{k}}b_{\mathbf{q}}a^{j}_{\mathbf{k}-\mathbf{q}_{\parallel}}\right) - g^{*ji}_{\mathbf{q}}\mathrm{Tr}\left(\varrho a^{+i}_{\mathbf{k}-\mathbf{q}_{\parallel}}b^{+}_{\mathbf{q}}a^{j}_{\mathbf{k}}\right)\right)\,,
\end{aligned} \tag{7.31}$$

as can be followed directly from (7.8)–(7.12) and (7.16)-(7.19). The internal energy of the electrons contribute to the rate of entropy as well as the many particle potentials V and g.

Chapter 8

The Dissipative Term

For the mesoscopic dynamics derived from von Neumann dynamics (2.4) we have set so far the dissipative term equal to zero. On the quantum mechanical level we wanted no dissipation, and irreversibility arises when we project the dynamics on a beobachtungsebene, due to the loss of information. In [Kau96], [Ali01], [Lin83] one can find general treatments of the dissipative term in the von Neumann dynamics. Here, we will consider some examples of the dissipative term, how they appear in the quantum mechanical theory, and what consequences they have.

8.1 Pure Quantum Mechanical Dynamics of a Subsystem

So far in this work, we treated beobachtungsebenen with a finite number of observables (2.8). Another ansatz is the following. Consider an isolated system consisting of two (or $n, n \in \mathbb{N}$) subsystems. One subsystem can be considered as the system of interest (noted as S), the other as its environment (E), which is probably very large with bath characteristica. Only the observables of S are relevant, and we are interested in eliminating bath quantities. This can be done by setting the Liouville space $\mathcal{L} = \mathcal{L}_S \otimes \mathcal{L}_E$ as a product of two Liouville spaces. Each observable in $\mathcal{L}^{ob}$ has a part in $\mathcal{L}_S^{ob}$ and in $\mathcal{L}_E^{ob}$. Let us use a more general notation of system no. 1 and system no. 2 in the following:

$$\mathcal{L} = \mathcal{L}_1 \otimes \mathcal{L}_2 \tag{8.1}$$

Theorem 36 *With the assumptions given above, the quantum mechanical von Neumann dynamics (3.17) for one subsystem reads as*

$$\dot{\varrho}_1 = -iL_1\,\varrho_1 - i\,Tr_2\left(L_{12}\,\varrho\right)\,, \tag{8.2}$$

and the corresponding Liouville operators are

$$L_1 : \mathcal{L}_1 \to \mathcal{L}_1 \quad , \quad L_1\,X := \frac{1}{\hbar}\,[H_1, X] \tag{8.3}$$

$$L_{12} : \mathcal{L} \to \mathcal{L} \quad , \quad L_{12}\,X := \frac{1}{\hbar}\,[H_{12}, X]\,. \tag{8.4}$$

Proof:

$$\dot{\varrho}_1 = \mathrm{Tr}_2\,\dot{\varrho} = -\frac{i}{\hbar}\,\mathrm{Tr}_2\,[H_1 \otimes \mathbb{I}_2, \varrho] - \frac{i}{\hbar}\,\mathrm{Tr}_2\,[\mathbb{I}_1 \otimes H_2, \varrho] - i\,\mathrm{Tr}_2\,(L_{12}\,\varrho) \tag{8.5}$$

and

$$\begin{aligned} \mathrm{Tr}_2\,[\mathbb{I}_1 \otimes A_2, B] &= 0 \\ \mathrm{Tr}_2\,((A_1 \otimes \mathbb{I}_2)\,B) &= A_1\,(\mathrm{Tr}_2 B) \\ \mathrm{Tr}_2\,(B\,(A_1 \otimes \mathbb{I}_2)) &= (\mathrm{Tr}_2 B)\,A_1 \quad \text{for} \quad A_1 \in \mathcal{L}_1, A_2 \in \mathcal{L}_2, B \in \mathcal{L} \end{aligned}$$

yield (8.2). □

Note that holds:

$$\dot{\varrho}_1(t) = \mathrm{Tr}_2\,(\dot{\varrho}(t)) \neq (\mathrm{Tr}_2\,\varrho)^{\bullet}\,(t)\,. \tag{8.6}$$

The trace should act on ϱ at every moment. In the last formulation the trace acts uniquely at one time point so the time evolution of ϱ_1 no longer contains the interaction terms with its environment.

A similar dynamics holds for the second subsystem naturally, but we omit it here to simplify matters. The additional term $-i\mathrm{Tr}_2\,(L_{12}\,\varrho)$ for non isolated systems in (8.2) corresponds to $\overset{\circ}{\varrho}$ in (2.4).

Theorem 37 *Total energy, heat exchange and work exchange of system no. 1 with its environment is given by*

$$\begin{aligned} E_1 &= Tr_1\,(\varrho_1\,H_1) && (8.7)\\ \dot{Q}_1 &= Tr_1\,(H_1\,\dot{\varrho}_1) = -i\,Tr((H_1 \otimes \mathbb{I}_2)\,(L_{12}\,\varrho)) && (8.8)\\ \dot{W}_1 &= Tr_1\left(\dot{H}_1\,\varrho_1\right) && (8.9) \end{aligned}$$

Proof:

$$E_1 := \mathrm{Tr}_1\mathrm{Tr}_2\,(\varrho\,(H_1 \otimes \mathbb{I}_2)) = \mathrm{Tr}_1\,(\varrho_1\,H_1) \tag{8.10}$$

Use the definitions (2.32), (2.33):

$$\dot{Q}_1 = i\mathrm{Tr}\,(\varrho\,L_{12}\,(H_1 \otimes \mathbb{I}_2)) = -i\mathrm{Tr}_1\,(H_1\,L_1\,\varrho_1) - i\mathrm{Tr}\,((H_1 \otimes \mathbb{I}_2)\,L_{12}\,\varrho) = \mathrm{Tr}_1\,(H_1\,\dot{\varrho}_1) \tag{8.11}$$

$$\dot{W}_1 = \mathrm{Tr}_1\mathrm{Tr}_2\left(\left(\dot{H}_1 \otimes \mathbb{I}_2\right)\varrho\right) = \mathrm{Tr}_1\left(\dot{H}_1\,\varrho_1\right)\,. \tag{8.12}$$

□

Note that Tr_2 is not a projector. A projector should map from a vector space to the same vector space to satisfy $P^2\,X = P\,X$. Here we use $\mathrm{Tr}_2 : \mathcal{L} \to \mathcal{L}_1$ or $\mathrm{Tr}_2 : \mathcal{L}_2 \to \mathbb{C}$. Strictly speaking ϱ_1 is not an accompanying process according to our definition 3, because it does not belong to the same Liouville space like ϱ. Nevertheless, ϱ_1 is “sufficient” for all observables $G \in \mathcal{L}_1$:

$$\mathrm{Tr}\,((G \otimes \mathbb{I}_2)\,\varrho) = \mathrm{Tr}_1\,(G\,\mathrm{Tr}_2\,\varrho) = \mathrm{Tr}_1\,(G\,\varrho_1)\,. \tag{8.13}$$

The dynamics of ϱ_1 is sufficient for work observables, too:

$$\mathrm{Tr}\,((G \otimes \mathbb{I}_2)\,\dot{\varrho}) = \mathrm{Tr}_1\,(G\,\dot{\varrho}_1)\,. \tag{8.14}$$

The sufficiency makes sense, because the dynamics of ϱ_1 is still a quantum mechanical one where no information about the system 1 is yet lost.

8.2 Dynamics of a Subsystem with Reduced Information

If we only have reduced information about subsystem no. 1 represented by a beobachtungsebene $\mathcal{B} = \{\underline{G}\}$ with $G_1, \ldots, G_n \in \mathcal{L}_1^{ob}$, we use mesoscopic dynamics for ϱ_1 in place of the full quantum mechanical dynamics (8.2).

8.2.1 Some Remarks

We can adopt the original canonical dynamics (3.2) for subsystems, if we only change the domain, now $\mathcal{L}_{1\varrho}^{ob}$ instead of $\mathcal{L}_{\varrho}^{ob}$. This dynamics is so robust, because it is not based on any quantum mechanical dynamics. However, problems arises, when we try to derive the dynamics of the generalised canonical operator out of a projection operator formalism, like in section 3.2. There are two possible ways to perform this:

(i) One can project either the exact evolution equation (8.2) onto the beobachtungsebene as we did it in section 3.2,

$$\dot{\varrho} \xrightarrow{\mathrm{tr}_2} \dot{\varrho}_1 \xrightarrow{P_1} \dot{\varrho}_{1rel} \tag{8.15}$$

(ii) or we execute the trace Tr_2 on the reduced dynamics ϱ_{rel} of the full Liouville space $\mathcal{L}^{ob} = \mathcal{L}_1^{ob} \otimes \mathcal{L}_2^{ob}$, (3.27) or (3.37).

$$\dot{\varrho} \xrightarrow{P} \dot{\varrho}_{rel} \xrightarrow{\mathrm{tr}_2} \dot{\varrho}_{1rel} \tag{8.16}$$

In the following we will explain why it does not make sence to use a projected dynamics for ϱ_1, neither with method (i) nor with (ii).

For (ii), it is clear: if we are only interested in the observables of the first subsystem, we can choose a beobachtungsebene with relevant observables only of $\mathcal{L}_1^{ob}$, right from the beginning, and use one of the projected dynamics. More precisely, we choose the beobachtungsebene $\mathcal{B} = \{G_1 \otimes \mathbb{I}_2, \ldots, G_n \otimes \mathbb{I}_2\}$ and take a projector $P : \mathcal{L}_{\varrho}^{ob} \to \mathcal{L}_{\varrho}^{ob}$ on the full Liouville space to use (3.27) or (3.37). The trace in (8.16) becomes unnecessary in this case.

Examining the first possibility (i), we obtain first the following Robertson dynamics for a subsystem:

The dynamics of ϱ_{1rel} with respect to $\mathcal{B}_1 = \{\underline{G}\}$ with $G_1, \ldots, G_n \in \mathcal{L}_1^{ob}$ using a linear mapping

$$\begin{aligned} P_1 : \mathcal{L}_{1\varrho}^{ob} &\to \mathcal{L}_{1\varrho}^{ob} \\ \dot{\varrho}_1 &\mapsto P_1\, \dot{\varrho}_1 = \dot{\varrho}_{1rel} \quad \text{where} & (8.17) \\ \varrho_1 &\mapsto P_1\, \varrho_1 = \varrho_{1rel} \quad \text{and} \quad \dot{P}_1\, \varrho_1 = 0 & (8.18) \end{aligned}$$

is given by

$$\begin{aligned}\dot{\varrho}_{1rel}(t) &= -iP_1(t)\,L_1(t)\,\varrho_{1rel}(t) - iP_1(t)\,\mathrm{Tr}_2\left(L_{12}(t)\varrho(t)\right)\\ &\quad - \int_{t_0}^{t} P_1(t)\,L_1(t)\,T_1(t,s)\,Q_1(s)\,L_1(s)\,\varrho_{1rel}(s)\,ds\\ &\quad - \int_{t_0}^{t} P_1(t)\,L_1(t)\,T_1(t,s)\,Q_1(s)\,\mathrm{Tr}_2\left(L_{12}(s)\varrho(s)\right)\,ds\,, \end{aligned} \tag{8.19}$$

$$\text{if}\quad \frac{\partial}{\partial s}\,T_1(t,s) = iT_1(t,s)\,Q_1(s)\,L_1(s) \tag{8.20}$$

$$T_1(t,t) = 1 \tag{8.21}$$

$$\varrho_1(t_0) = \varrho_{1rel}(t_0)\,. \tag{8.22}$$

It can be proved analogously to the proof of theorem 6. However, (8.19) contains terms with ϱ and H_{12} that stems from the additional term in (8.2). On that score, this dynamics is not of practical use, unless the interaction Hamiltonian H_{12} is negligible. In this case we obtain the conventional Robertson dynamics. To get rid of ϱ we must introduce one more projector.

The dynamics of ϱ_{1rel} with respect to $\mathcal{B}_1 = \{\underline{G}\}$ and $\mathcal{B} = \{\underline{G}\otimes\mathbb{I}_2\}$ with $G_1,\ldots,G_n \in \mathcal{L}_1^{ob}$ using linear mappings

$$\begin{aligned} P_1 : \mathcal{L}_{1\varrho}^{ob} &\to \mathcal{L}_{1\varrho}^{ob}\\ \dot{\varrho}_1 &\mapsto P_1\,\dot{\varrho}_1 = \dot{\varrho}_{1rel} \quad \text{where} && (8.23)\\ \varrho_1 &\mapsto P_1\,\varrho_1 = \varrho_{1rel} \quad \text{and} \quad \dot{P}_1\,\varrho_1 = 0 && (8.24)\end{aligned}$$

$$\begin{aligned} P : \mathcal{L}_{\varrho}^{ob} &\to \mathcal{L}_{\varrho}^{ob}\\ \dot{\varrho} &\mapsto P\,\dot{\varrho} = \dot{\varrho}_{rel} \quad \text{where} && (8.25)\\ \varrho &\mapsto P\,\varrho = \varrho_{rel} \quad \text{and} \quad \dot{P}\,\varrho = 0 && (8.26)\end{aligned}$$

is given by

$$\begin{aligned}\dot{\varrho}_{1rel}(t) &= -iP_1(t)\,L_1(t)\,\varrho_{1rel}(t) - \int_{t_0}^{t} P_1(t)\,L_1(t)\,T_1(t,s)\,Q_1(s)\,L_1(s)\,\varrho_{1rel}(s)\,ds\\ &\quad - \int_{t_0}^{t} P_1(t)L_1(t)T_1(t,s)Q_1(s)\mathrm{Tr}_2\bigg(L_{12}(s)\varrho_{rel}(s)\\ &\qquad\qquad -i\int_{t_0}^{s} L_{12}(s)T(s,u)Q(u)L(u)\varrho_{rel}(u)du\bigg)\,ds\\ &\quad -iP_1(t)\mathrm{Tr}_2\left(L_{12}(t)\varrho_{rel}(t) - i\int_{t_0}^{t} L_{12}(t)T(t,s)Q(s)L(s)\varrho_{rel}(s)ds\right)\end{aligned} \tag{8.27}$$

$$\text{if}\quad \frac{\partial}{\partial s}\,T_1(t,s) = iT_1(t,s)\,Q_1(s)\,L_1(s) \tag{8.28}$$

$$T_1(t,t) = 1 \tag{8.29}$$

$$\varrho_1(t_0) = \varrho_{1rel}(t_0)\,. \tag{8.30}$$

$$\begin{aligned} \text{and} \qquad \frac{\partial}{\partial s} T(t,s) &= iT(t,s)\, Q(s)\, L(s) && (8.31)\\ T(t,t) &= 1 && (8.32)\\ \varrho(t_0) &= \varrho_{rel}(t_0)\,. && (8.33) \end{aligned}$$

Anyhow, the projector (8.25), (8.26) is the same kind of projector we used for the conventional Robertson dynamics (3.27). So again, we could have used (3.27) instead.

Similar results can be obtained regarding the Fick Sauermann dynamics. The conclusion is, that we do not need an extra projected dynamics for a subsystem, because (3.27) and (3.37) already cover this special case.

8.2.2 Sufficiency

Now we will apply theorem 26 to subsystems.

Theorem 38 *Let be $\mathcal{B} = \{\underline{G}\}$ a beobachtungsebene with $G_1, \ldots, G_n \in \mathcal{L}_1^{ob}$. Let be $\hat{\varrho}_1(t)$ an accompanying process of $\varrho_1(t)$ with respect to $\mathcal{B}$. Let be*

$$\overset{\circ}{\hat{\varrho}}_1 := \dot{\hat{\varrho}}_1 + iL_1\hat{\varrho}_1 = \dot{\varrho}_1 + iL_1\varrho_1 := \overset{\circ}{\varrho}_1 \ . \tag{8.34}$$

Then $\hat{\varrho}_1$ is sufficient for $\overset{\circ}{\underline{G}} := \dot{\underline{G}} + iL_1 G$. In particular, $\hat{\varrho}_1$ is sufficient for $\dot{H}_1$.

Proof:

$$\begin{aligned} & \mathrm{Tr}\,(\underline{G}\,\varrho_1)^\bullet = \mathrm{Tr}\,(\underline{G}\,\hat{\varrho}_1)^\bullet \\ \Leftrightarrow\quad & \mathrm{Tr}\left(\dot{\underline{G}}\,\varrho_1\right) + \mathrm{Tr}\,(\underline{G}\,\dot{\varrho}_1) = \mathrm{Tr}\left(\dot{\underline{G}}\,\hat{\varrho}_1\right) + \mathrm{Tr}\,(\underline{G}\,(\dot{\varrho}_1 + iL_1\varrho_1 - iL_1\hat{\varrho}_1)) \\ \Leftrightarrow\quad & \mathrm{Tr}\left(\dot{\underline{G}}\,\varrho_1\right) - i\mathrm{Tr}\,(\underline{G}L_1\varrho_1) = \mathrm{Tr}\left(\dot{\underline{G}}\,\hat{\varrho}_1\right) - i\mathrm{Tr}\,(\underline{G}L_1\hat{\varrho}_1) \\ \Leftrightarrow\quad & \mathrm{Tr}\left(\varrho_1\left(\dot{\underline{G}} + iL_1\underline{G}\right)\right) = \mathrm{Tr}\left(\hat{\varrho}_1\left(\dot{\underline{G}} + iL_1\underline{G}\right)\right) && (8.35) \end{aligned}$$

And

$$\overset{\circ}{H}_1 = \dot{H}_1 + iL_1H_1 = \dot{H}_1\,. \tag{8.36}$$

□

This is of course a stronger proposition than the weak sufficiency in section 5.3. The sufficiency for the work operator $\dot{H}_1$ is achieved by the special ansatz that the quantum mechanical exchange term in the dynamics is equal to the mesoscopic one.

8.3 Entropy Production by Heat Conduction

In section 8.1, we have considered the dissipative term in the dynamics of a subsystem. This term was a direct consequence from the von Neumann dynamics without

$\overset{\circ}{\varrho}$. In this section, we will make an ansatz for the dissipative term in the dynamics of the full system.

Let us assume the von Neumann dynamics (3.17) and the corresponding dynamics (8.2) for both subsystems. Then the solution of the initial value problem

$$\begin{aligned} \dot{\varrho}(t) &= -\frac{i}{\hbar}\left[H(t), \varrho(t)\right] && (8.37) \\ \varrho\left(t_0\right) &= \varrho_1\left(t_0\right) \otimes \varrho_2\left(t_0\right) && (8.38) \end{aligned}$$

should be unique. For $t = t_0$, we can rewrite the differential equation (8.37) in two eqivalent formulations:

$$\begin{aligned} \left(\varrho_1 \otimes \varrho_2\right)^{\bullet} &= -\frac{i}{\hbar}\left[H_1 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes H_2, \varrho_1 \otimes \varrho_2\right] - \frac{i}{\hbar}\left[H_{12}, \varrho_1 \otimes \varrho_2\right] && (8.39) \\ \left(\varrho_1 \otimes \varrho_2\right)^{\bullet} &= -\frac{i}{\hbar}\left[H_1 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes H_2, \varrho_1 \otimes \varrho_2\right] - \frac{i}{\hbar}\mathrm{Tr}_2\left[H_{12}, \varrho_1 \otimes \varrho_2\right] \otimes \varrho_2 \\ &\quad -\frac{i}{\hbar}\varrho_1 \otimes \mathrm{Tr}_1\left[H_{12}, \varrho_1 \otimes \varrho_2\right] . && (8.40) \end{aligned}$$

Proof: We obtain the first formulation immediately from (3.17) and from the initial condition (8.38). For the second formulation, we use (8.2) with the same initial condition:

$$\begin{aligned} \left(\varrho_1 \otimes \varrho_2\right)^{\bullet} &= \dot{\varrho}_1 \otimes \varrho_2 + \varrho_1 \otimes \dot{\varrho}_2 \\ &= \left(-\frac{i}{\hbar}\left[H_1, \varrho_1\right] - \frac{i}{\hbar}\mathrm{Tr}_2\left[H_{12}, \varrho_1 \otimes \varrho_2\right]\right) \otimes \varrho_2 \\ &\quad + \varrho_1 \otimes \left(-\frac{i}{\hbar}\left[H_2, \varrho_2\right] - \frac{i}{\hbar}\mathrm{Tr}_1\left[H_{12}, \varrho_1 \otimes \varrho_2\right]\right) \\ &= -\frac{i}{\hbar}\left[H_1 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes H_2, \varrho_1 \otimes \varrho_2\right] - \frac{i}{\hbar}\mathrm{Tr}_2\left[H_{12}, \varrho_1 \otimes \varrho_2\right] \otimes \varrho_2 \\ &\quad -\frac{i}{\hbar}\varrho_1 \otimes \mathrm{Tr}_1\left[H_{12}, \varrho_1 \otimes \varrho_2\right] . && (8.41) \end{aligned}$$

$\square$

Comparing (8.39) with (8.40), it must hold:

$$\left[H_{12}, \varrho_1 \otimes \varrho_2\right] = \mathrm{Tr}_2\left[H_{12}, \varrho_1 \otimes \varrho_2\right] \otimes \varrho_2 + \varrho_1 \otimes \mathrm{Tr}_1\left[H_{12}, \varrho_1 \otimes \varrho_2\right] . \qquad (8.42)$$

In the diagonal representation of ϱ_1 and ϱ_2

$$\begin{aligned} \varrho_1 &= \sum_i \left|\varphi_1^i\right\rangle \varrho_1^i \left\langle\varphi_1^i\right| && (8.43) \\ \varrho_2 &= \sum_j \left|\varphi_2^j\right\rangle \varrho_2^j \left\langle\varphi_2^j\right| && (8.44) \\ H_{12} &= \sum_{mnpq} \left|\varphi_1^m\right\rangle \left|\varphi_2^n\right\rangle h_{12}^{mnpq} \left\langle\varphi_2^p\right| \left\langle\varphi_1^q\right| , && (8.45) \end{aligned}$$

(8.42) is equivalent to

$$\begin{aligned} &\sum_{mnpq} \left|\varphi_1^m\right\rangle \left|\varphi_2^n\right\rangle h_{12}^{mnpq} \left(\varrho_1^q \varrho_2^p - \varrho_1^m \varrho_2^n\right) \left\langle\varphi_2^p\right| \left\langle\varphi_1^q\right| \\ = &\sum_{mnpq} \left|\varphi_1^m\right\rangle \left|\varphi_2^n\right\rangle h_{12}^{mppq} \left(\varrho_1^q \varrho_2^p - \varrho_1^m \varrho_2^p\right) \varrho_2^n \left\langle\varphi_2^n\right| \left\langle\varphi_1^q\right| \\ &+ \sum_{mnpq} \left|\varphi_1^m\right\rangle \left|\varphi_2^n\right\rangle h_{12}^{qnpq} \left(\varrho_1^q \varrho_2^p - \varrho_1^q \varrho_2^n\right) \varrho_1^m \left\langle\varphi_2^p\right| \left\langle\varphi_1^m\right| . && (8.46) \end{aligned}$$

This cannot be valid in general. Probable causes are the neglect of $\overset{\circ}{\varrho}$ in (8.37), or an improper initial condition (8.38).

Inserting the von Neumann dynamics (3.17) into the von Neumann entropy (2.16), it is a fact that the entropy is constant for all time. This conflicts with the following postulate:

Postulate 1 *The isolated compound system cannot be in equilibrium ($\dot{S} = 0$), if its subsystems are in nonequilibrium ($\dot{S} > 0$).*

Classical thermodynamics teaches us for example that the entropy of an isolated system increases, if there are internal material flux or heat flux. To handle this problem, we can either take into account the $\overset{\circ}{\varrho}$-term, or use a different entropy definition, as done for example in [Kam92] or [Gav02].

The heat exchange between the subsystems is in our special interest here. We will present a suitable term for $\overset{\circ}{\varrho}$ in (2.4) to describe the entropy production caused by internal heat fluxes, while we omit material and work exchange.

Theorem 39 *Let be*

$$\dot{\varrho} = -iL\varrho + iL_{12}X \tag{8.47}$$

where

$$[H, H_{12}] = 0. \tag{8.48}$$

Then it holds:

(i) $Tr\,\dot{\varrho} = 0$

(ii) The compound system is isolated: $\dot{Q} = 0$.

(iii) The partition is inert: $\dot{Q}_{12} = 0$

(iv)

$$\dot{\varrho}_1 = -\frac{i}{\hbar}[H_1, \varrho_1] - \frac{i}{\hbar} Tr_2 [H_{12}, \varrho - X] \tag{8.49}$$

(v)

$$\dot{Q}_1 = -\frac{i}{\hbar} Tr((H_1 \otimes \mathbb{I}_2)[H_{12}, \varrho - X]) \tag{8.50}$$

Proof:

(i) Trivial.

(ii) With (8.48) it is obvious that $\mathrm{Tr}\,(H\,\dot{\varrho}) = 0$.

(iii) With (8.48) it is also obvious that $\mathrm{Tr}\,(H_{12}\,\dot{\varrho}) = 0$.

(iv) Use the proof of (8.2) and (8.47).

(v) Use (8.49) to calculate $\dot{Q}_1 = \mathrm{Tr}_1\,(H_1\,\dot{\varrho}_1)$.

□

$\overset{\circ}{\varrho} := iL_{12}X$ in (8.47) vanishes, if there is no heat exchange between the subsystems, that is if $H_{12} = 0$. With the dynamics (8.47), the equations (8.39) and (8.40) at $t = t_0$ become:

$$\begin{aligned} (\varrho_1 \otimes \varrho_2)^\bullet &= -\frac{i}{\hbar}\left[H_1 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes H_2, \varrho_1 \otimes \varrho_2\right] - \frac{i}{\hbar}\left[H_{12}, \varrho_1 \otimes \varrho_2 - X\right] && (8.51) \\ (\varrho_1 \otimes \varrho_2)^\bullet &= -\frac{i}{\hbar}\left[H_1 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes H_2, \varrho_1 \otimes \varrho_2\right] - \frac{i}{\hbar}\mathrm{Tr}_2\left[H_{12}, \varrho_1 \otimes \varrho_2 - X\right] \otimes \varrho_2 \\ &\quad -\frac{i}{\hbar}\varrho_1 \otimes \mathrm{Tr}_1\left[H_{12}, \varrho_1 \otimes \varrho_2 - X\right] . && (8.52) \end{aligned}$$

Both terms are equivalent, if for example

$$X(t_0) = \varrho_1(t_0) \otimes \varrho_2(t_0) = \varrho(t_0) \tag{8.53}$$

holds. The conjecture is, that

$$X(t) = \varrho_1(t) \otimes \varrho_2(t) \tag{8.54}$$

is valid for all time.

Theorem 40 *Let be $\overset{\circ}{\varrho} = iL_{12}X$ defined by (2.7). From (8.47) follows:*

$$\dot{S} = -k\frac{i}{\hbar}\,Tr([H_{12}, X] \ln \varrho) \ . \tag{8.55}$$

Let be

$$\overset{\circ}{\varrho}_1 = \sum_j |\varphi_1^j\rangle \dot{\varrho}_1^j \langle\varphi_1^j| = -\frac{i}{\hbar}\,Tr_2\left[H_{12}, \varrho - X\right] \tag{8.56}$$

analogous to (2.7). From (8.49) follows for the time rate of the entropy S_1:

$$\dot{S}_1 = k\frac{i}{\hbar}\,Tr([H_{12}, \varrho - X](\ln \varrho_1 \otimes \mathbb{I}_2)) \ . \tag{8.57}$$

The excess entropy [Mus04] is then given by

$$\dot{S} - \dot{S}_1 - \dot{S}_2 = k\frac{i}{\hbar}\,Tr(H_{12}\left[\varrho - X, \ln \varrho - \ln(\varrho_1 \otimes \varrho_2)\right]) \ . \tag{8.58}$$

Proof: Use (2.7) to show [Mus94]

$$\mathrm{Tr}\left(\varrho\,(\ln \varrho)^\bullet\right) = 0 = \mathrm{Tr}_1\left(\varrho_1\,(\ln \varrho_1)^\bullet\right) \ . \tag{8.59}$$

□

Chapter 9

Conclusions

The mesoscopic theory of quantum thermodynamics based on restricted macroscopic information is one possible way of describing irreversibility in nonequilibrium quantum systems. This is performed using a limited set of relevant observables, called beobachtungsebene. All statistical operators, that yield the same expectation values of the relevant observables for all time, as the quantum mechanical density matrix ϱ does, can be used equivalently in the mesoscopic theory. Such dynamics are called accompanying processes of ϱ.

Canonical dynamics is defined by the time derivative of the generalised canonical operator which maximises the von Neumann entropy with respect to a given beobachtungsebene $\mathcal{B}$. This dynamics preserves the canonical form of the statistical operator for all time, and is not derived from any quantum mechanical dynamics. As long as the time dependence of the Lagrangian multipliers is unknown, this differential equation cannot be solved. The other approach makes use of the projection operator technique. Such a projector isolates the relevant part of the density matrix from its irrelevant part with respect to a given beobachtungsebene. In the ideal case, this projector is generated by an inner product on the Liouville space, the generalised Mori product. Assuming different properties of the projector, one can derive for example the Robertson dynamics or the Fick Sauermann dynamics from the von Neumann dynamics. Here, the relevant part can be chosen to be generalised canonical. The rate of von Neumann entropy can be analysed if we presuppose the canonical form of the statistical operator. One can specify different conditions for the positivity of this time rate.

In thermodynamical applications, the quantity of work is very essential. Since generalised work is given as expectation value of the time derivative of a relevant observable, we demand the sufficiency for accompanying dynamics: This means, that these work expectation values are correctly given by the considered dynamics, even though the time derived observables are not themselves included in the beobachtungsebene. In general, neither canonical dynamics nor projected Fick Sauermann dynamics is sufficient. This means, that the irreversible theory using these dynamics is only an approximative one, because it is not possible to calculate work from other known quantities. In this case, relevant work observables should be included into the beobachtungsebene as they are measured. A sufficient accompanying process is obtained using a relaxation ansatz for the difference between ϱ and its accompanying process. Heat exchange is the other quantity, that changes the internal energy of a system according to the First Law. In general, canonical dynamics is not sufficient for the generalised flux observables. A projected dynamics is only sufficient for generalised fluxes, if its process history vanishes indentically for all time. We can extend the concept of sufficiency for $\overset{\circ}{G}$-observables to that of weak sufficiency.

Applying the canonical dynamics to discrete systems in contact, we are able to use the contact temperature to interpret Lagrangian multipliers. On some relaxation conditions, it is possible to show the definiteness of the rate of entropy in different situations. Another example comes from the field of many particle quantum mechanics, and treats the electron-phonon interaction. Here, projection technique can be used to divide the von Neumann dynamics into two parts with regard to different physical subject matter: the single particle part and the many particle correlation part. We can see, that the electron-phonon coupling terms stongly affects the heat transfer in the system. The rate of entropy contains kinetic parts of Bloch electrons and potential contributions induced by many body interaction.

The pure quantum mechanical dynamics of a subsystem can be considered as a reduced dynamics, too. This dynamics is von Neumann like with an additional dissipative term represented by the interaction Hamiltonian between the subsystem and its environment. The next step of information reduction is given by the accompanying process of the subsystem with respect to a given beobachtungsebene. In this case, one has to use reduced dynamics based on the full von Neumann dynamics, and not on the reduced von Neumann dynamics of the subsystem. We can conclude the weak sufficiency for subsystems, if the dissipative terms of reduced von Neumann dynamics and of its accompanying process are equal. In this case, the accompanying process is sufficient for internal work exchange.

Consider the initial value problem with von Neumann dynamics and two discrete systems set in contact to each other at the initial time. For an arbitrary interaction Hamiltonian, this problem leads to some contradictions. So we have to modify either the initial value by including an interaction term, or we can set an additional term into the von Neumann dynamics taking the interaction into account. In the special case of heat exchange between the subsystems, this additional term shall warrant the entropy production due to internal heat flux. A suggestion for this dissipative term is made. This certainly is a point which requires further inverstigations. It is necessary to find an explicit formula for the abstract positive dissipation term, which is treated so often in literature. With this, the positivity of the entropy production should be verified.

Chapter 10

Appendices

10.1 Appendix 1: An example

Theorem 41 *Consider one particle with spin* $\frac{1}{2}$ *in a magnatic field with the beobachtungsebene* $\mathcal{B} = \left\{x, p, x^2, p^2, S_z, H_s\right\}$. *Then the generalised canonical operator is given by*

$$R = e^{-\lambda_0 - \lambda_1 x - \lambda_2 x^2 - \lambda_3 p - \lambda_4 p^2 - \lambda_5 S_z - \lambda_6 H_s} \tag{10.1}$$

$$\begin{aligned}
\lambda_0 &= \ln(Z_p Z_s) = \ln\left(\frac{\Delta x \Delta p}{\hbar} + \frac{1}{2}\right) \\
&\quad + \left(\frac{\Delta p \langle x\rangle^2}{2\hbar\Delta x} + \frac{\Delta x \langle p\rangle^2}{2\hbar\Delta p} - \frac{1}{2}\right) \ln\left[1 + \left(\frac{\Delta x \Delta p}{\hbar} - \frac{1}{2}\right)^{-1}\right] \\
&\quad + \ln 2\left(\cosh\left(\nu_1 \frac{\hbar}{2}\right) \cosh\left(\nu_2 \gamma \frac{\hbar}{2}\left|\underline{B}\right|\right) - \frac{B_z}{\left|\underline{B}\right|} \sinh\left(\nu_1 \frac{\hbar}{2}\right) \sinh\left(\nu_2 \gamma \frac{\hbar}{2}\left|\underline{B}\right|\right)\right) \\
\lambda_1 &= -\frac{\Delta p \langle x\rangle}{\hbar \Delta x} \ln\left(1 + \left(\frac{\Delta x \Delta p}{\hbar} - \frac{1}{2}\right)^{-1}\right) \\
\lambda_2 &= \frac{\Delta p}{2\hbar\Delta x} \ln\left(1 + \left(\frac{\Delta x \Delta p}{\hbar} - \frac{1}{2}\right)^{-1}\right) \\
\lambda_3 &= -\frac{\Delta x \langle p\rangle}{\hbar \Delta p} \ln\left(1 + \left(\frac{\Delta x \Delta p}{\hbar} - \frac{1}{2}\right)^{-1}\right) \\
\lambda_4 &= \frac{\Delta x}{2\hbar\Delta p} \ln\left(1 + \left(\frac{\Delta x \Delta p}{\hbar} - \frac{1}{2}\right)^{-1}\right) \\
\lambda_5 &= \nu_1 \\
\lambda_6 &= \nu_2
\end{aligned}$$

with ν_1, ν_2 *given by*

$$\langle S_z\rangle = -\frac{\hbar}{2} \frac{\left|\underline{B}\right| \tanh(\nu_1 \frac{\hbar}{2}) - B_z \tanh(\nu_2 \gamma \frac{\hbar}{2}\left|\underline{B}\right|)}{\left|\underline{B}\right| - B_z \tanh(\nu_2 \gamma \frac{\hbar}{2}\left|\underline{B}\right|) \tanh(\nu_1 \frac{\hbar}{2})} \tag{10.2}$$

$$\langle H_s\rangle = -\frac{\gamma\hbar}{2}\left|\underline{B}\right| \frac{\left|\underline{B}\right| \tanh(\nu_2 \gamma \frac{\hbar}{2}\left|\underline{B}\right|) - B_z \tanh(\nu_1 \frac{\hbar}{2})}{\left|\underline{B}\right| - B_z \tanh(\nu_2 \gamma \frac{\hbar}{2}\left|\underline{B}\right|) \tanh(\nu_1 \frac{\hbar}{2})}. \tag{10.3}$$

Proof: First we introduce linear transformations and consider the following operator instead of (10.1).

$$R = e^{-\mu_0 - \mu_1 (b^+(a) - \alpha^*)(b(a) - \alpha)} e^{-\nu_0 - \nu_1 S_z - \nu_2 H_s} = R_p R_s \tag{10.4}$$

with

$$b(a) = \frac{1}{\sqrt{2\hbar a}} (ax + ip) \quad , \quad b^+(a) = \frac{1}{\sqrt{2\hbar a}} (ax - ip) \ . \tag{10.5}$$

Then $(b^+(a) - \alpha^*), (b(a) - \alpha)$ have the same properties like the usual creation and annihilation operators a^+, a. Now $\mu_0, \mu_1, a, \alpha^*, \alpha, \nu_0, \nu_1, \nu_2$ are to be determined.

Spin part $\mathbf{R_s}$

For the spin part R_s we consider a spin $\frac{1}{2}$ particle in a homogenous magnetic field $\underline{B}$. The potential part of its Hamiltonian in the spin space is

$$H_s = -\gamma \frac{\hbar}{2} \sum_{k=1}^{3} \sigma_k B_k = -\gamma \frac{\hbar}{2} \begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix} \tag{10.6}$$

where the σ_k are Pauli-matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \tag{10.7}$$

With $\mathcal{B}^1 = \{S_z, H_s\}$, $S_z = \frac{\hbar}{2}\sigma_z$ we get

$$\begin{aligned} R_s &= \frac{e^{-\nu_1 S_z - \nu_2 H_s}}{\mathrm{Tr}\, e^{-\nu_1 S_z - \nu_2 H_s}} \qquad (10.8) \\ &= \frac{1}{\mathrm{Tr}\, e^{-\nu_1 S_z - \nu_2 H_s}} \cdot \frac{\cosh(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|)}{|\underline{B}|} \cdot \\ & \begin{pmatrix} e^{-\nu_1 \frac{\hbar}{2}} \left(|\underline{B}| + B_z \tanh(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|)\right) & e^{-\nu_1 \frac{\hbar}{2}} (B_x - iB_y) \tanh(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|) \\ e^{\nu_1 \frac{\hbar}{2}} (B_x + iB_y) \tanh(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|) & e^{\nu_1 \frac{\hbar}{2}} \left(|\underline{B}| - B_z \tanh(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|)\right) \end{pmatrix} , \end{aligned}$$

$$\begin{aligned} Z_s &= \mathrm{Tr}\, e^{-\nu_1 S_z - \nu_2 H_s} \\ &= 2 \left(\cosh\left(\nu_1 \frac{\hbar}{2}\right) \cosh\left(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|\right) - \frac{B_z}{|\underline{B}|} \sinh\left(\nu_1 \frac{\hbar}{2}\right) \sinh\left(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|\right) \right) . \end{aligned} \tag{10.9}$$

According to (2.25), we calculate

$$\frac{\partial}{\partial \nu_1} \ln Z_s = \frac{\hbar}{2} \frac{|\underline{B}| \tanh(\nu_1 \frac{\hbar}{2}) - B_z \tanh(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|)}{|\underline{B}| - B_z \tanh(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|) \tanh(\nu_1 \frac{\hbar}{2})} = -\langle S_z \rangle \tag{10.10}$$

$$\frac{\partial}{\partial \nu_2} \ln Z_s = \frac{\gamma \hbar}{2} |\underline{B}| \frac{|\underline{B}| \tanh(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|) - B_z \tanh(\nu_1 \frac{\hbar}{2})}{|\underline{B}| - B_z \tanh(\nu_2 \gamma \frac{\hbar}{2} |\underline{B}|) \tanh(\nu_1 \frac{\hbar}{2})} = -\langle H_s \rangle \, . \tag{10.11}$$

Free particle part $\mathbf{R_p}$

For R_p, we use first the condition $\mathrm{Tr}\, R_p = 1$ with $\mathcal{B}^2 = \{(b^+ - \alpha^*)(b - \alpha)\}$. Using (2.26), we get

$$\mu_0 = \ln \mathrm{Tr}\, e^{-\mu_1 (b^+ - \alpha^*)(b - \alpha)} = \ln \left(1 - e^{-\mu_1}\right)^{-1} . \tag{10.12}$$

$$R_p = e^{-\left(\mu_0 + \mu_1 \left(\alpha^* \alpha - \frac{1}{2}\right)\right)} e^{-\mu_1 \left(\frac{a}{2\hbar} x^2 + \frac{1}{2\hbar a} p^2 - \sqrt{\frac{2a}{\hbar}} (\mathrm{Re}\, \alpha) x - \sqrt{\frac{2}{\hbar a}} (\mathrm{Im}\, \alpha) p \right)} \tag{10.13}$$

and $\mathcal{B}^3 = \left\{x, x^2, p, p^2\right\}$ result in

$$\ln Z_p = \mu_0 + \mu_1 \left(\alpha^* \alpha - \frac{1}{2}\right) = \mu_0 + \mu_1 \left((\mathrm{Re}\,\alpha)^2 + (\mathrm{Im}\,\alpha)^2 - \frac{1}{2}\right) \tag{10.14}$$

$$\frac{\partial \ln Z_p}{\partial \mathrm{Re}\,\alpha} = 2\mu_1 \mathrm{Re}\,\alpha = \mu_1 \sqrt{\frac{2a}{\hbar}} \langle x \rangle \qquad \Rightarrow \qquad \mathrm{Re}\,\alpha = \sqrt{\frac{a}{2\hbar}} \langle x \rangle \tag{10.15}$$

$$\frac{\partial \ln Z_p}{\partial \mathrm{Im}\,\alpha} = 2\mu_1 \mathrm{Im}\,\alpha = \mu_1 \sqrt{\frac{2a}{\hbar}} \langle p \rangle \qquad \Rightarrow \qquad \mathrm{Im}\,\alpha = \sqrt{\frac{1}{2\hbar a}} \langle p \rangle \tag{10.16}$$

$$R_p = e^{-\left(\mu_0 - \frac{1}{2}\mu_1\right)} e^{-\mu_1 \left(\frac{a}{2\hbar}(x - \langle x \rangle)^2 + \frac{1}{2\hbar a}(p - \langle p \rangle)^2\right)} . \tag{10.17}$$

With $\mathcal{B}^4 = \left\{\frac{a}{2\hbar}\left(x - \langle x \rangle\right)^2 + \frac{1}{2\hbar a}\left(p - \langle p \rangle\right)^2\right\}$ we analyse the following condition using (10.17) and (10.12):

$$\frac{\partial}{\partial \mu_1} \ln Z_p = -\frac{1}{2} - \frac{1}{e^{\mu_1} - 1} = -\frac{a}{2\hbar}\Delta x^2 - \frac{1}{2\hbar a}\Delta p^2$$

$$\Leftrightarrow \quad \mu_1 = \ln \left[\left(\frac{1}{2\hbar}\left(a\Delta x^2 + \frac{1}{a}\Delta p^2\right) + \frac{1}{2}\right)\left(\frac{1}{2\hbar}\left(a\Delta x^2 + \frac{1}{a}\Delta p^2\right) - \frac{1}{2}\right)^{-1}\right] . \tag{10.18}$$

To determine a, we calculate:

$$x - \langle x \rangle = \sqrt{\frac{\hbar}{2a}} \left((b - \alpha) + (b^+ - \alpha^*)\right) \tag{10.19}$$

$$p - \langle p \rangle = -i\sqrt{\frac{\hbar a}{2}} \left((b - \alpha) - (b^+ - \alpha^*)\right) \tag{10.20}$$

$$\left\langle n \left| (x - \langle x \rangle)^2 \right| n \right\rangle = \Delta x_n^2 = \frac{\hbar}{a}\left(n + \frac{1}{2}\right) \tag{10.21}$$

$$\left\langle n \left| (p - \langle p \rangle)^2 \right| n \right\rangle = \Delta p_n^2 = \hbar a \left(n + \frac{1}{2}\right) . \tag{10.22}$$

It follows

$$a = \frac{\Delta p}{\Delta x} , \tag{10.23}$$

and inserting this into (10.15), (10.16), (10.18) and (10.12), we get the above theorem.

□

Similar examples with less relevant observables can be found in [Fic83], [Kau96].

10.2 Appendix 2: Gümbel's approach

In the outlook of [Güm04], the following problem is briefly discussed: starting with an accompanying process, how can one construct another accompanying process which is sufficient for some other observables not included in the beobachtungsebene?

$$\mathrm{Tr}\,(\varrho\, K) = \mathrm{Tr}\,(\hat{\varrho}\, K) \quad , \quad K \notin \mathcal{B}$$

The next theorems show which problems arise if one considers accompanying processes interacting with observables outside the beobachtungsebene.

Theorem 42 *Let be $\varrho_1, \varrho_2 \in \mathcal{L}^{ob}_{\varrho}$ accompanying processes of the quantum mechanical density operator ϱ with respect to $\mathcal{B} = \{\underline{G}\}$. Let be $(\,\cdot\,|\,\cdot\,)_1, (\,\cdot\,|\,\cdot\,)_2$ the generalised Mori products belonging to ϱ_1, ϱ_2 respectively. Let be P^M_1, P^M_2 the corresponding Mori projectors. Let be $K \in \mathcal{L}^{ob}$ an arbitrary observable. Then follows*

$$Tr(\varrho_1\, K) = Tr\left(K\, P^{KG}_1\, \varrho_2\right) = Tr\left(\varrho_2\, P^M_1\, K\right)\ . \tag{10.24}$$

Proof:

$$\begin{aligned}
\left(P^M_1\, K\,|\,\mathbb{I}\right)_2 &= (K\,|\,\mathbb{I})_1 \cdot (\mathbb{I}\,|\,\mathbb{I})_2 + (K\,|\,\Delta\underline{G}_1)_1 \cdot (\Delta\underline{G}_1\,|\,\Delta\underline{G}_1)^{-1}_1 \cdot (\Delta\underline{G}_1\,|\,\mathbb{I})_2 \\
&= (K\,|\,\mathbb{I})_1 + (K\,|\,\Delta\underline{G}_1)_1 \cdot (\Delta\underline{G}_1\,|\,\Delta\underline{G}_1)^{-1}_1 \cdot ((\underline{G}\,|\,\mathbb{I})_2 - (\underline{G}\,|\,\mathbb{I})_1 \cdot (\mathbb{I}\,|\,\mathbb{I})_2) \\
&= (K\,|\,\mathbb{I})_1
\end{aligned}$$

□

From (10.24) follows

$$\mathrm{Tr}\,(\hat{\varrho}\, K) = \mathrm{Tr}\left(K\, P^{KG}_{\hat{\varrho}}\, \varrho\right) = \mathrm{Tr}\left(\varrho\, P^M_{\hat{\varrho}}\, K\right) \neq \mathrm{Tr}\,(\varrho\, K) \tag{10.25}$$

$$\mathrm{Tr}\,(\varrho\, K) = \mathrm{Tr}\left(K\, P^{KG}_{\varrho}\, \hat{\varrho}\right) = \mathrm{Tr}\left(\hat{\varrho}\, P^M_{\varrho}\, K\right) \neq \mathrm{Tr}\,(\hat{\varrho}\, K) \tag{10.26}$$

in general. The last inequality in (10.26) is valid, because we restrict ourselves to a bounded beobachtungsebene. Normally, the quantum mechanical density matrix ϱ is related to the "beobachtungsebene" of whole $\mathcal{L}^{ob}$. But the choice of $\mathcal{B} = \mathcal{L}^{ob}$ would make any discussion about the "accompanying process" $\hat{\varrho}$ nonsensical. Therefore, the next theorem deals with two beobachtungsebenen $\mathcal{B}_1 \subset \mathcal{B}_2$ to get rid of this problem.

Theorem 43 *Let be $\varrho_1, \varrho_2 \in \mathcal{L}^{ob}_{\varrho}$ accompanying processes of the quantum mechanical density operator ϱ with respect to $\mathcal{B}_1 = \{\underline{G}\}, \mathcal{B}_2 = \{\underline{K}\}$ respectively. Let be $\mathcal{B}_1 \subset \mathcal{B}_2$. Let be $(\,\cdot\,|\,\cdot\,)_1, (\,\cdot\,|\,\cdot\,)_2$ the generalised Mori products belonging to ϱ_1, ϱ_2 respectively. Let be P^M_1, P^M_2 the corresponding Mori projectors. Let be $F \in \mathcal{L}^{ob}$ an arbitrary observable. Then follows:*

$$Tr(\varrho_1\, F) = Tr\left(F\, P^{KG}_1\, \varrho_2\right) = Tr\left(\varrho_2\, P^M_1\, F\right)\ , \tag{10.27}$$

$$Tr(\varrho_2\, F) \neq Tr\left(F\, P^{KG}_2\, \varrho_1\right) = Tr\left(\varrho_1\, P^M_2\, F\right)\ . \tag{10.28}$$

Proof:

$$\begin{aligned}
\left(P^M_1\, F\,|\,\mathbb{I}\right)_2 &= (F\,|\,\mathbb{I})_1 \cdot (\mathbb{I}\,|\,\mathbb{I})_2 + (F\,|\,\Delta\underline{G}_1)_1 \cdot (\Delta\underline{G}_1\,|\,\Delta\underline{G}_1)^{-1}_1 \cdot (\Delta\underline{G}_1\,|\,\mathbb{I})_2 \\
&= (F\,|\,\mathbb{I})_1 + (F\,|\,\Delta\underline{G}_1)_1 \cdot (\Delta\underline{G}_1\,|\,\Delta\underline{G}_1)^{-1}_1 \cdot ((\underline{G}\,|\,\mathbb{I})_2 - (\underline{G}\,|\,\mathbb{I})_1 \cdot (\mathbb{I}\,|\,\mathbb{I})_2) \\
&= (F\,|\,\mathbb{I})_1
\end{aligned}$$

$$\begin{aligned}
\left(P^M_2\, F\,|\,\mathbb{I}\right)_1 &= (F\,|\,\mathbb{I})_2 \cdot (\mathbb{I}\,|\,\mathbb{I})_1 + (F\,|\,\Delta\underline{K}_2)_2 \cdot (\Delta\underline{K}_2\,|\,\Delta\underline{K}_2)^{-1}_2 \cdot (\Delta\underline{K}_2\,|\,\mathbb{I})_1 \\
&= (F\,|\,\mathbb{I})_2 + (F\,|\,\Delta\underline{K}_2)_2 \cdot (\Delta\underline{K}_2\,|\,\Delta\underline{K}_2)^{-1}_2 \cdot ((\underline{K}\,|\,\mathbb{I})_1 - (\underline{K}\,|\,\mathbb{I})_2 \cdot (\mathbb{I}\,|\,\mathbb{I})_1) \\
&\neq (F\,|\,\mathbb{I})_2
\end{aligned}$$

□

From (10.27) follows:

$$\mathrm{Tr}\,(\hat{\varrho}\,F) = \mathrm{Tr}\,\left(F\,P_{\hat{\varrho}}^{KG}\,\varrho\right) = \mathrm{Tr}\,\left(\varrho\,P_{\hat{\varrho}}^{M}\,F\right) \neq \mathrm{Tr}\,(\varrho\,F) \tag{10.29}$$

in general, and from (10.28) we obtain

$$\mathrm{Tr}\,(F\,\varrho) \neq \left(F\,P_{\varrho}^{KG}\,\hat{\varrho}\right) = \left(\hat{\varrho}\,P_{\varrho}^{M}\,F\right)\ . \tag{10.30}$$

Even if we choose $\mathcal{B} = \mathcal{L}^{ob}$, we get the inequality $\mathrm{Tr}\,(\hat{\varrho}\,F) \neq \mathrm{Tr}\,(\varrho\,F)$. Thus, Gümbel's problem cannot be solved in this manner.

10.3 Appendix 3: Entropy of Canonical Dynamics

We remember: if

$$h(x,p) = f(x,y) - yp \qquad \text{with} \qquad p = \frac{\partial f}{\partial y} \tag{10.31}$$

is valid, then h is the Legendre-transform of f , and $\frac{\partial h}{\partial p} = -y$ is valid.

According to (2.25) and (4.4), $\left(-\frac{1}{k}\,S_{\mathcal{B}}\right)$ is the Legendre transformed of $(-\ln Z)$, if the work variables are constant [Kat67]

$$\left(-\frac{S_{\mathcal{B}}}{k}\right)(\underline{g}) = (-\ln Z)(\underline{\lambda}) - \underline{\lambda}\cdot\underline{g}\,. \tag{10.32}$$

We get

$$\frac{\partial}{\partial \underline{g}}\left(-\frac{1}{k}\,S_{\mathcal{B}}\right) = -\underline{\lambda}\,, \tag{10.33}$$

which is consistent with the entropy formula for constant work variables

$$\dot{S} = k\,\underline{\lambda}\cdot\underline{\dot{g}}\,. \tag{10.34}$$

If we have work variables $\underline{a}$ depending on time, then the partition function depends from them, too. This leads to the following theorem.

Theorem 44 *If $\mathcal{B} = \{\underline{G}\,(\underline{a})\}$ with explicitly time dependent observables, $\left(-\frac{1}{k}\,S_{\mathcal{B}}\right)(\underline{a},\underline{g})$ is not the Legendre transformed of $(-\ln Z)\,(\underline{a},\underline{g})$.*

Proof
Let be the work variables $\underline{a}$ not constant in time, and let be $\left(-\frac{1}{k}\,S_{\mathcal{B}}\right)$ the Legendre transformed of $(-\ln Z)$:

$$\left(-\frac{S_{\mathcal{B}}}{k}\right)(\underline{a},\underline{g}) = (-\ln Z)(\underline{a},\underline{\lambda}) - \underline{\lambda}\cdot\underline{g}\,. \tag{10.35}$$

Then

$$\begin{aligned}
\dot{S} &= \frac{\partial S}{\partial \underline{a}} \cdot \underline{\dot{a}} + \frac{\partial S}{\partial \underline{g}} \cdot \underline{\dot{g}} = \frac{\partial}{\partial \underline{a}} \left(k \ln Z + k\, \underline{\lambda} \cdot \underline{g}\right) \cdot \underline{\dot{a}} + k\, \underline{\lambda} \cdot \underline{\dot{g}} \\
&= k\, \frac{1}{Z} \operatorname{Tr}\left(\frac{\partial}{\partial \underline{a}}\, e^{-\underline{\lambda}\cdot\underline{G}}\right) \cdot \underline{\dot{a}} + k\, \frac{\partial}{\partial \underline{a}} \operatorname{Tr}\left(\underline{\lambda} \cdot \underline{G}\, R\right) \cdot \underline{\dot{a}} + k\, \underline{\lambda} \cdot \underline{\dot{g}} \\
&= -k\, \frac{1}{Z} \operatorname{Tr}\left(\int_0^1 e^{-(1-\mu)\underline{\lambda}\cdot\underline{G}}\, \underline{\lambda} \cdot \underline{\dot{G}}\, e^{-\mu\underline{\lambda}\cdot\underline{G}}\, d\mu\right) + k \operatorname{Tr}\left(\underline{\lambda} \cdot \underline{\dot{G}}\, R\right) \\
&\quad + k \operatorname{Tr}\left(\underline{\lambda} \cdot \underline{G}\, R\right) \operatorname{Tr}\left(R\, \underline{\lambda} \cdot \underline{\dot{G}}\right) - k \operatorname{Tr}\left(\underline{\lambda} \cdot \underline{G}\, R \int_0^1 e^{\mu\underline{\lambda}\cdot\underline{G}}\, \underline{\lambda} \cdot \underline{\dot{G}}\, e^{-\mu\underline{\lambda}\cdot\underline{G}}\, d\mu\right) \\
&\quad + k\, \underline{\lambda} \cdot \underline{\dot{g}} \\
&= k \operatorname{Tr}\left(\underline{\lambda} \cdot \underline{G}\, R\right) \operatorname{Tr}\left(R\, \underline{\lambda} \cdot \underline{\dot{G}}\right) - k \operatorname{Tr}\Big(R \left(\underline{\lambda} \cdot \underline{\dot{G}}\right) \left(\underline{\lambda} \cdot \underline{G}\right)\Big) + k\, \underline{\lambda} \cdot \underline{\dot{g}}\,. \qquad (10.36)
\end{aligned}$$

On the other hand,

$$\dot{S} = -k \operatorname{Tr}\left(\dot{R} \ln R\right) = k \operatorname{Tr}\left(\underline{\lambda} \cdot \underline{G}\, \dot{R}\right) = k\, \underline{\lambda} \cdot \underline{\dot{g}} - k \operatorname{Tr}\left(\underline{\lambda} \cdot \underline{\dot{G}}\, R\right)\,. \qquad (10.37)$$

Since the expressions are not equal, (10.35) cannot be valid.

□

Bibliography

[Ali88] Aliagra J, Otero D, Plastino A and Proto A N Physical Review A **38** (1988) 918–929
Quantum Thermodynamics and Information Theory

[Ali01] Alicki R and Fannes M (2001)
Quantum Dynamical Systems (Oxford: Oxford University Press)

[Arb96] Arbuzov B A Theoretical and Mathematical Physics **106** (1996) 249–253
On a quantum-mechanical description of motion with friction

[Bal86] Balian R, Alhassid Y and Reinhardt H Physics Reports **131** (1986) 1–146
Dissipation in Many-Body Systems: A Geometric Approach Based on Information Theory

[Ber84] Beretta G P, Gyftopoulos E P, Park J L and Hatsopoulos G N Il Nuovo Cimento B **82** (1984) 169–191
Quantum Thermodynamics. A New Equation of Motion for a Single Constituent of Matter

[Coh77] Cohen-Tannoudji C, Diu B and Laloë F (1977)
Quantum Mechanics Vol 1 (Paris: Hermann)

[Els93] Elstner M (1993) Diplomarbeit
Beobachtungsebene und Dynamik für die Extended Themodynamik zur Begründung der Gleichungen vom Maxwell-Cattaneo-Typ (Berlin)

[Fic83] Fick E and Sauermann G (1983)
Quantenstatistik Dynamischer Prozesse Bd 1: Generelle Aspekte (Frankfurt am Main: Harri Deutsch)

[Fic83] Fick E and Sauermann G (1983)
Quantenstatistik Dynamischer Prozesse Bd 2a: Antwort- und Relaxationstheorie (Frankfurt am Main: Harri Deutsch)

[Fic84] Fick E (1984)
Einführung in die Grundlagen der Quantentheorie (Wiesbaden: Aula-Verlag)

[Gav02] Gaveau B, Martinás K, Moreau M and Tóth J Physica A **305** (2002) 445–466
Entropy, extropy and information potential in stochastic systems far from equilibrium

[Gis81] Gisin N Progress of Theoretical Physics **66** (1981) 2274–2275
Brownian motion of a quantum spin with friction

[Gra82] Grabert H (1982)
Projection Operator Techniques in Nonequilibrium Statistical Mechanics (Berlin: Springer-Verlag)

[Gra87] Grandy W T (1987)
Foundations of Statistical Mechanics Vol 1: Equilibrium Theory (Dordrecht: D. Reidel Publishing Company)

[Gra88] Grandy W T (1988)
Foundations of Statistical Mechanics Vol 2: Nonequilibrium Phenomena (Dordrecht: D. Reidel Publishing Company)

[Güm04] Gümbel S (2004)
Nichtgleichgewichtsthermodynamik und statistische Mechanik dissipativer diskreter Systeme (`http://edocs.tu-berlin.de/diss/index.html`)

[Hag98] Hagemeister B (1998) Diplomarbeit
Quantenmechanische Dynamiken und Beobachtungsebenen für geschlossene Systeme mit zeitabhängigen Arbeitsvariablen (Berlin)

[Jay57a] Jaynes E T Physical Review **106** (1957) 620–630
Information Theory and Statistical Mechanics

[Jay57b] Jaynes E T Physical Review **108** (1957) 171–190
Information Theory and Statistical Mechanics II

[Jou96] Jou D, Casas-Vázquez J and Lebon G (1996)
Extended Irreversible Thermodynamics (Heidelberg: Springer-Verlag)

[Kam92] van Kampen N G (1992)
Stochastic processes in physics and chemistry (Amsterdam: North Holland)

[Kat99] Kato A (1999) Diplomarbeit
Dynamics of Statistical Operators and Entropy Production in Non-isolated Discrete Nonequilibrium Systems (Berlin)

[Kat00a] Kato A, Kaufmann M, Muschik W and Schirrmeister D Journal of Non-Equilibrium Thermodynamics **25** (2000) 63–86
Different Dynamics and Entropy Rates in Quantum-Thermodynamics

[Kat00b] Kato A, Muschik W and Schirrmeister D Rend. Sem. Mat. Univ. Pol. Torino **58** (2000) 147–153
Dynamics in Quantum Thermodynamics

[Kat01] Kato A and Jou D Physical Review E **64** (2001) 052201
Breaking of equipartition in one-dimensional heat-conducting system

[Kat67] Katz A (1967)
Principles of statistical mechanics - The information theory approach (San Francisco: W. H. Freeman and Co.)

[Kau96] Kaufmann M (1996)
Quantum Thermodynamics of Discrete Systems Endowed with Time Dependent Work Variables and Based on a Dissipative v. Neumann Equation (Berlin: Wissenschaft und Technik Verlag)

[Kaw73] Kawasaki K and Gunton J D Physical Review A **8** (1973) 2048–2064
Theory of Nonlinear Transport Processes: Nonlinear Shear Viscosity and Normal Stress Effects

[Luz00] Luzzi R, Vasconcellos A R and Ramos J G (2000)
Statistical Foundation of Irreversible Thermodynamics (Stuttgart: B. G. Teubner)

[Lin83] Lindblad G (1983)
Non-equilibrium entropy and irreversibility (Dordrecht: D. Reidel Publishing Company)

[Mor65] Mori H Progress of Theoretical Physics **34** (1965) 399 - 416
A Continued-Fraction Representation of the Time-Correlation Functions

[Mus90] Muschik W (1990)
Aspects of Non-Equilibrium Thermodynamics (Singapore: World Scientific)

[Mus94] Muschik W and Kaufmann M Journal of Non-Equilibrium Thermodynamics **19** (1994) 76–94
Quantum-Thermodynamical Description of Discrete Non-Equilibrium Systems

[Mus96] Muschik W, Papenfuss C and Ehrentraut H (1996)
Concepts of Continuum Thermodynamics (Kielce: Kielce University of Technology)

[Mus04] Muschik W and Berezovski A Journal of Non-Equilibrium Thermodynamics **29** (2004) 237–255
Thermodynamic Interaction between Two Discrete Systems in Non-Equilibrium

[Nak58] Nakajima S Progress of Theoretical Physics **20** (1958) 948–959
On Quantum Theory of Transport Phenomena

[Nol02] Nolting W (2002)
Grundkurs Theoretische Physik 7: Viel-Teilchen-Theorie (Berlin: Springer-Verlag)

[Rau96] Rau J and Müller B Physics Reports **272** (1996) 1–59
From reversible quantum microdynamics to irreversible quantum transport

[Rob66] Robertson B Physical Review **144** (1966) 151–161
Equations of Motion in Nonequilibrium Statistical Mechanics

[Schi94] Schirrmeister D (1994) Diplomarbeit
Unterschiedliche mikroskopische Dynamiken zur Quantenthermodynamik unter Berücksichtigung explizit zeitabhängiger thermodynamischer Zustände (Berlin)

[Scho29] Schottky W (1929)
Thermodynamik (Berlin: Verlag von Julius Springer)

[Schw65] Schwegler H Zeitschrift für Naturforschung **20** (1965) 1543–1553
Verallgemeinerte physikalische Entropien auf informationstheoretischer Grundlage

[Sni64] Snider R F Journal of Mathematical Physics **5** (1964) 1580–1587
Perturbation Variation Methods for a Quantum Boltzman Equation

[Ull04] Ullrich C A (2004)
Intersubband dynamics in semiconductor quantum wells (I) (`http://web.umr.edu/~ullrichc/Lectures/Ullrich1.pdf`)

[Wal03] Waldmüller I, Förster J and Knorr A (2003) unpublished
Self-consistent Projection Operator Theory of Intersubband Absorbance in Semiconductor Quantum Wells

[Zub74] Zubarev D N (1974)
Nonequilibrium Statistical Thermodynamics (New York: Consultants Bureau)

[Zub96] Zubarev D N, Morozov V and Röpke G (1996)
Statistical mechanics of nonequilibrium processes Vol 1: Basic concepts, kinetic theory (Berlin: Akademie Verlag GmbH)

[Zwa60] Zwanzig R Journal of Chemical Physics **33** (1960) 1338–1341
Ensemble Method in the Theory of Irreversibility

[Zwa64] Zwanzig R Physica **30** (1964) 1109–1123
On the Identity of Three Generalized Master Equations

Lebenslauf

Name	Akiko Kato	
Geburtsdatum	25 September 1974	
Geburtsort	Akashi/Japan	
Staatsangehörigkeit	japanisch	
Schulausbildung	1980–1983	Grundschule “Ecole Ile des Sœurs” (Montréal/Canada)
	1983–1985	Grundschule “Schule Vorhornweg” (Hamburg/Deutschland)
	1985–1987	“Gymnasium Othmarschen” (Hamburg)
	1987–1989	Gymnasium “Luisenschule” (Essen)
	1989–1994	Gymnasium “Goethe-Oberschule” (Berlin)
	Juni 1994	Abitur
Studium	1994–1999	Studium der Physik an der TU Berlin
	Okt 1996	Vordiplom
	Sept 1999	Diplom
Stipendium	1995–1999	Stipendiatin der Studienstiftung des deutschen Volkes
Auszeichnungen	Dez 1999	Studienförderpreis der Wilhelm und Else Heraeus-Stiftung
	Juli 2000	Erwin-Stephan-Preis der Helene und Erwin Stephan-Stiftung
Lehrerfahrungen	1997–1999	studentische Mitarbeiterin am Institut für Mathematik der TU Berlin
	1999–2004	wissenschaftliche Mitarbeiterin an der mathematisch-naturwissenschaftlichen Fakultät der TU Berlin
Forschungsaufenthalt	April–Mai 2001	sechswöchiger Aufenthalt bei Prof. Dr. David Jou Departament de Física, Universitat Autònoma de Barcelona