Phenomenological Quantum Thermodynamics of Closed Bipartite Schottky Systems *

W. Muschik†
Institut für Theoretische Physik
Technische Universität Berlin
Hardenbergstr. 36
D-10623 BERLIN, Germany

Abstract
How to introduce thermodynamics to quantum mechanics? Among from numerous possibilities of solving this task, the simple choice is here: The conventional von Neumann equation deals with a density operator whose probability weights are time independent. Because there is no reason apart from the reversible quantum mechanics that these weights have to be time independent, this constraint is waived, thus making possible to introduce thermodynamical concepts to quantum mechanics. This procedure is similar to that of Lindblad’s equation, but different on principle. But beyond this simple starting-point, the applied thermodynamical concepts of discrete systems may perform a ”source theory” for other versions of phenomenological quantum thermodynamics.

Keywords: Quantum Thermodynamics, Compound Systems, Modified von Neumann Equation, Discrete Systems, Propagator

1 Introduction

Conventional quantum mechanics is a reversible theory because the entropy production vanishes for all its processes. There are two possibilities to introduce irreversibility to quantum mechanics without restricting the full set of observables: One can change Schrödinger’s equation by introducing e.g. friction terms, an adventurous procedure which we will not follow. Here

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*In memory of Bob Axelrad
†Corresponding author: muschik@physik.tu-berlin.de
we follow an other way which modifies von Neumann’s equation by introducing time dependent weights of the statistical operator, thus generating irreversibility. That means, the in time changing composition of the ensemble which belongs to the statistical operator allows to introduce thermodynamical concepts of irreversibility to quantum mechanics. This procedure is similar to that of Lindblad’s equation, but different on principle, because the entropy producing operators of the modified von Neumann equation are generated by constitutive equations. Consequently, the dynamics of the considered system is decomposed into a quantum mechanical part and a material dependent part which is described beyond the Hamiltonians by constitutive equations. Other possibilities of implementing irreversibility, introducing a restricted set of observables thus creating irreversibility by loss of information [1], or using statistical concepts such as microcanonical or canonical ensembles as ad-hoc concepts are out of scope of this paper.

We consider Schottky systems, that are discrete systems whose interaction with their environment is macroscopically described by heat-, power- and material exchange which here is especially suppressed by considering closed systems. Such a discrete system can be described as an undecomposed or as a decomposed one. Undecomposed means that the special structure of the interior of the Schottky system is out of scope whereas the internal structure of the system is taken into account by a decomposed description [4, 5]. Here in quantum thermodynamics, undecomposed means that the Hamiltonian of the system is not decomposed into the partial Hamiltonians of the sub-systems and their interaction Hamiltonian. This case was sketched in a previous paper [6], whereas here the decomposed Schottky system is treated, that means, the Hamiltonian of the system is decomposed into its parts.

The task of quantum thermodynamics is to determine quantum-theoretically the entropy, its time rate and production and the entropy exchange between system and its environment and between its sub-systems. For this purpose, we start with a modified von Neumann equation which allows to introduce a non-vanishing entropy rate by time dependent weights of the statistical operator which are set to zero in conventional quantum mechanics resulting in a non-thermal theory.

The paper is organized as follows: First of all, we remember the quantum thermodynamics of undecomposed Schottky systems [6] in sect[2] by using a modified von Neumann equation. Because non-equilibrium thermodynamics works with a non-equilibrium temperature [7, 8], a short repetition concerning contact temperature is given in sect[3]. Sect[4] deals in detail with compound systems which are characterized by a decomposed Hamiltonian, but by an undecomposed density operator. Equilibria, constitutive equations, adiabatic and reversible processes are considered. The results achieved for

1Discrete systems are ”boxes” which interact with their environment through ”partitions” [2, 3].
compound systems are transferred to decomposed systems in sect. Decomposed means, the Hamiltonian as well as the density operator are decomposed into parts belonging to sub-systems. A summary and two appendices finish the paper.

2 Undecomposed Systems

2.1 Schottky systems

A discrete system $G \subset \mathbb{R}^3$, described as undecomposed and homogeneous which is separated by a partition $\partial G$ from its environment $G^\Diamond$ is called a Schottky system [9], if the interaction between $G$ and $G^\Diamond$ through $\partial G$ can be macroscopically described by

- heat exchange $\dot{Q}$,
- power exchange $\dot{W}$, and
- material exchange $\dot{n}^e$. (1)

The power exchange is related to the work variables $a$ of the system

$$\dot{W} = K \cdot \dot{a}.$$ (2)

Here, $K$ are the generalized forces which are as well known as the work variables. Kinetic and potential energy are constant and therefore out of scope. The heat exchange $\dot{Q}$ is measurable by calorimetry and the time rate of the mole numbers $\dot{n}^e$ due to material exchange between $G$ and $G^\Diamond$ by weigh.

Here, we restrict ourselves to closed discrete systems for which the material exchange is suppressed by a material impervious partition between the system and its environment and chemical reactions are absent. The Hamiltonian of an undecomposed closed system contains no interaction parts, and the interaction between system and environment is macroscopically (semi-classically [3]) described by $\dot{Q}$ and $\dot{W}$.

2.2 The modified von Neumann equation

The undecomposed closed system is described by a density operator

$$\varrho := \sum_j p_j |\Phi^j\rangle \langle \Phi^j|, \quad 0 \leq p_j \leq 1, \quad \sum_j p_j = 1$$ (3)

which is composed of pure quantum states $\{|\Phi^j\rangle\}$ which are normalized, complete and orthogonal [10]

$$\langle \Phi^j | \Phi^j \rangle = 1, \quad \forall k \neq l : \langle \Phi^k | \Phi^l \rangle = 0, \quad \sum_j |\Phi^j\rangle \langle \Phi^j| = 1.$$ (4)

Semi-classical means: heat- and power-exchange are not influenced by the system’s Hamiltonian.
Beyond that, the dynamics of these quantum states is given by the Schrödinger equation
\[ i\hbar \partial_t |\Phi_j\rangle = \mathcal{H} |\Phi_j\rangle, \quad j = 1, 2, 3, \ldots \] (5)
in which the Hamiltonian is self-adjoint \( \mathcal{H}^+ = \mathcal{H} \). Inserting (5) in (3) results in the modified von Neumann equation \[ \partial_t \rho \equiv \dot{\rho} = -i\frac{\hbar}{\mathcal{H}} [\mathcal{H}, \rho] + \dot{\rho}, \quad \dot{\rho} := \sum_{j} \dot{p}_j |\Phi_j\rangle\langle \Phi_j| \] (6)
The modification is, that in contrast to the conventional quantum theory, the time rates of the weights \( \dot{p}_j \) of the density operator (3) do not all vanish.

\[ \forall j : \quad \dot{p}_j \neq 0 \quad \longrightarrow \quad \dot{\rho} \neq 0. \] (7)

The modified von Neumann equation shows that the time dependence of the density operator (3) has two reasons: the quantum mechanical dynamics represented by the commutator in (6) and the time dependence of the propagator \( \dot{\rho} \) in (3). In conventional quantum theory of isolated systems, the propagator does not appear, because the \( \{p_j\} \) are presupposed to be time independent, a fact which causes reversibility, as we will see below.

Accepting setting I means, that irreversibility is generated by an in time changing composition of the density operator \( \rho \).

From (3), (1) and (6) follows
\[ \rho |\Phi_k\rangle = p_k |\Phi_k\rangle, \quad \text{Tr} \rho = \sum_j p_j = 1, \quad \text{Tr} \dot{\rho} = \sum_j \dot{p}_j = 0. \] (8)

\subsection*{2.3 The first law}

The Hamiltonian \( \mathcal{H} \) belongs to a non-isolated closed undecomposed system: no material exchange and missing chemical reactions, but power- and heat-exchange between the system and its environment. The energy of the considered system is
\[ E := \text{Tr}(\mathcal{H} \rho), \] (9)
and the time rate of the energy
\[ \dot{E} = \text{Tr}(\dot{\mathcal{H}} \rho) + \text{Tr}(\mathcal{H} \dot{\rho}) \] (10)

\footnote{A "definition" is a formal short form for an expression without any physical background. A "setting" is a hypothesis induced by physics determining the axiomatic structure of a theory, whereas "axiom" and "postulate" characterize established principles of formal theories without any physical background.}
can be split into power- and heat-exchange according to the 1st law of thermodynamics of closed systems

\[ W := \text{Tr}(\dot{\mathcal{H}} \varrho), \quad Q := \text{Tr}(\mathcal{H} \dot{\varrho}). \quad (11) \]

Inserting the modified von Neumann equation (8) into (11), we obtain after a short, but simple calculation

\[ \dot{Q} = \text{Tr}\left(\mathcal{H} \sum_j p_j |\Phi_j\rangle \langle \Phi_j| \right), \quad (12) \]

and by introducing suitable work variables \( a \), we obtain the power exchange

\[ \dot{W} = \text{Tr}\left(\frac{\partial H}{\partial a} \varrho \right) \cdot \dot{a} =: K \cdot \dot{a}. \quad (13) \]

Here, \( K \) are the so-called generalized forces.

### 2.4 Entropy time rate

The non-equilibrium entropy \( S \) of the considered system, the Shannon entropy, is introduced as

\[ S(\varrho) := -k_B \text{Tr}(\varrho \ln \varrho) \quad (14) \]

\((k_B = \text{Boltzmann constant}).\)

Inserting the modified von Neumann equation (8) into the Shannon non-equilibrium entropy (14), we obtain after a short calculation by taking (8) and (8) into account

\[ \dot{S}(\varrho, \dot{\varrho}) = -k_B \text{Tr}(\dot{\varrho} \ln \varrho) = -k_B \text{Tr}\left(\dot{\varrho} \ln(Z \varrho)\right) = -k_B \text{Tr}\left(\dot{\varrho} \ln(Z \varrho)\right) = -k_B \text{Tr}\left(\dot{\varrho} \ln(Z \varrho)\right) = k_B \ln(Z) \varrho, \quad (15) \]

\[ f_k^I := \langle \Phi^k | k_B \ln(Z) \varrho \rangle \Phi^k \rangle = k_B \ln(Zp_k), \quad \forall Z \in R^4. \quad (16) \]

Using (8), the second equal sign in (15) follows from

\[ \text{Tr}\left(\dot{\varrho} \ln(Z \varrho)\right) = \text{Tr}\left(\dot{\varrho} \left(\ln(Z) \varrho + \ln \varrho\right)\right) = \text{Tr}(\dot{\varrho} \ln \varrho). \quad (17) \]

Consequently, the entropy rate \( \dot{S} \) does not depend on \( Z \) according to (17).

Therefore, \( Z \) can be chosen arbitrarily below in connection with equilibrium. Beyond that, \( \dot{S} \) does not depend on the Hamiltonian.
2.5 Entropy exchange and production

In this easy case of a closed non-isolated undecomposed system, the entropy exchange is defined by multiplying the heat exchange with the reciprocal of the contact temperature Θ which is discussed at some length in sect. 3.

Starting with (12)\textsuperscript{2}, we obtain an expression which looks formally like the entropy rate (15)\textsuperscript{4}

\[ \Xi := \frac{\dot{Q}}{\Theta} = \text{Tr} \left( \frac{\mathcal{H}}{\Theta} \sum_j \dot{p}_j |\Phi^j\rangle \langle \Phi^j| \right) = \sum_j \dot{p}_j \langle \Phi^j | \mathcal{H} | \Phi^j \rangle =: \dot{p} \cdot f^{II}, \quad f_k^{II} := \langle \Phi^k | \mathcal{H} | \Phi^k \rangle. \]  

The entropy rate (15)\textsuperscript{4} is thermodynamically decomposed into the entropy exchange Ξ and the entropy production Σ [12]

\[ \dot{S} = \Xi + \Sigma. \]  

Consequently, the entropy production is according to (15)\textsuperscript{4} and (19)

\[ \Sigma = \dot{S} - \Xi = -\dot{p} \cdot (f^I + f^{II}) =: -\dot{p} \cdot f. \]  

The conclusions which result from (15), (18) and (20) for undecomposed systems are discussed in detail in [6]. Here we are interested in decomposed systems which differ from undecomposed ones by a different shape of the Hamiltonian containing an interaction term according to the decomposition of the system into sub-systems. But before discussing compound and decomposed systems in sect 4 and sect 5, some properties of the non-equilibrium contact temperature are presented in the next section.

3 Contact Temperature and Internal Energy

The thermal description of compound systems in non-equilibrium requires a concept of temperature beyond the thermostatic equilibrium temperature as the following example demonstrates: two systems of different thermostatic temperatures are in thermal contact which each other. The resulting compound system is in non-equilibrium, and a joint thermostatic temperature for it does not exist. Looking for a coarse description of this compound system—we do not ask for the origin of the non-equilibrium (here the heat conduction)— we need a non-equilibrium analogue of the thermostatic temperature, that is the contact temperature which is discussed in the sequel.
The non-equilibrium contact temperature $\Theta$ in \cite{13} is defined for closed systems without chemical reactions by the inequality \cite{7, 8, 9, 13, 14, 15}

$$\dot{Q} \left( \frac{1}{\Theta} - \frac{1}{T^\square} \right) \geq 0 \quad (21)$$

as follows: the closed system is contacted with an equilibrium environment $G^\circ$ of the thermostatic temperature $T^\square$ generating the net heat exchange $\dot{Q}$ between the system and its environment. For defining the contact temperature, we choose a special equilibrium environment of the thermostatic temperature $T^\square_\circ$ so that the net heat exchange vanishes $\dot{Q} = 0$. If according to \cite{21}, the heat exchange has a change of sign

$$\dot{Q} = \pm \eta(\varepsilon), \quad (22)$$

then $T^\square_\circ$ is by definition the contact temperature of the non-equilibrium system

$$\Theta := T^\square_\circ \longrightarrow \dot{Q} = 0 \quad (23)$$

and according to \cite{22}, the bracket in \cite{21} is continuous at $\dot{Q} = 0$. Now using the

\textbf{Proposition} \cite{16}

$$X \cdot f(X) \geq 0 \text{ (for all } X \land f \text{ continuous at } X = 0) \implies f(0) = 0 \iff f(X) = M(X) \cdot X, \quad M(X) \text{ positive semi-definite.} \quad (24)$$

By use of the setting \cite{4}

$$X \doteq \left( \frac{1}{\Theta} - \frac{1}{T^\square} \right), \quad f(X) \doteq \dot{Q}, \quad (25)$$

we obtain from \cite{24} the constitutive equation of the heat exchange including a material dependent "heat conduction" $\kappa$

$$\dot{Q} = \kappa \left( \frac{1}{\Theta} - \frac{1}{T^\square} \right), \quad \kappa \left[ \frac{1}{\Theta} - \frac{1}{T^\square} \right] > 0. \quad (26)$$

In words, we created the following statement:

\textbf{Definition:} The system’s contact temperature $\Theta$ is that thermostatic temperature of the system’s equilibrium environment $T^\circ$ for which the net heat exchange $\dot{Q}$ between the system and this environment through an inert partition \cite{3} vanishes by change of sign.
The non-equilibrium contact temperature is a state variable of the system and the question arises: what is the connection between contact temperature and (internal) energy?

As easily demonstrated, contact temperature $\Theta$ and the energy $E$ of a closed discrete system are independent of each other. For this purpose, a rigid inert partition $\partial G (\dot{\mathbf{a}} \equiv \mathbf{0})$ and a time-dependent environment temperature $T^\ominus(t)$ is chosen which is always set equal to the value of the momentary contact temperature $\Theta(t)$ of the closed system. We obtain according to the first law (10) and (11) and an inert partition between system and environment

$$T^\ominus(t) \equiv \Theta(t) \quad \rightarrow \dot{Q} = 0 \quad \rightarrow \dot{E} = 0.$$  \hspace{1cm} \text{(27)}

Because $\Theta$ is time-dependent and $E$ is constant, totally different from thermostatics, both quantities are independent of each other.

A quantum theoretical definition of the contact temperature is given in sect.4.4.3.

### 4 Compound Systems

First of all, we have to define the following expressions:

- **undecomposed**, compound and decomposed description

of a Schottky system. **Undecomposed systems** which were discussed in sect.2 are not decomposed into sub-systems, whereas **compound** and **decomposed systems** are composed of sub-systems. Compound systems are described by only one joint density operator $\varrho_{\text{com}}$ which belongs to both sub-systems, whereas in decomposed systems each sub-system has its particular density operator, $\varrho^1$ and $\varrho^2$. Consequently, the description of undecomposed and compound systems is similar because of their single density operator, whereas the description of decomposed systems is more complex than that of undecomposed and compound systems. Considering **bipartite systems** in the following sections, the density operators and the Hamiltonians are as follows:

- **undecomposed**: $\varrho$, $\mathcal{H}$, \hspace{1cm} sect.2
- **compound**: $\varrho_{\text{com}}$, $\mathcal{H} = \mathcal{H}^1 + \mathcal{H}^2 + \mathcal{H}^{12}$, \hspace{1cm} sect.4
- **decomposed**: $\varrho^1$, $\varrho^2$, $\mathcal{H} = \mathcal{H}^1 + \mathcal{H}^2 + \mathcal{H}^{12}$, \hspace{1cm} sect.5

### 4.1 Partial Hamiltonians

In bipartite compound systems, the Hamiltonian $\mathcal{H}$ of the undecomposed system is decomposed into the sum of the partial Hamiltonians of the two
sub-systems, $\mathcal{H}^1$ and $\mathcal{H}^2$, and of the interaction Hamiltonian $\mathcal{H}^{12}$ describing the interaction between these two sub-systems:

$$\mathcal{H} = \mathcal{H}^1 + \mathcal{H}^2 + \mathcal{H}^{12}. \quad (28)$$

With respect to the tensorial base (30), we used in (28) the abbreviations

$$\mathcal{H}^i \otimes I^2 \equiv \mathcal{H}^i, \quad I^1 \otimes \mathcal{H}^2 \equiv \mathcal{H}^2, \quad \rightarrow [\mathcal{H}^1, \mathcal{H}^2] = 0, \quad (29)$$

with the unity operators $I^i, \ i = 1, 2$, belonging to the corresponding factors of the tensor product (30). The interaction of one sub-system with the environment is for the present described semi-classically, that means, by power- and heat-exchanges which result from the partial Hamiltonians $\mathcal{H}^1$ and $\mathcal{H}^2$. The interaction Hamiltonian $\mathcal{H}^{12}$ refers only to the interaction between the two sub-systems and is independent of the system’s environment.

### 4.2 Tensorial density operator

The undecomposed system together with its density operator $\rho$ (3) and its propagator $\hat{\rho}$ (6) is divided into two sub-systems by choosing a basis $\{|\Psi^k_1\rangle\}$ belonging to sub-system #1 and an other one $\{|\Psi^l_2\rangle\}$ belonging to the other sub-system #2. The tensor product of these bases form an orthogonal basis of the compound system

$$\{|\Psi^k_1\rangle \otimes |\Psi^l_2\rangle\} \equiv \{|\Psi^{kl}_{12}\rangle\}. \quad (30)$$

The pure quantum states $|\Phi^j\rangle$ in (4) of the undecomposed system are replaced by pure tensorial quantum states of the compound system

$$|\Phi^j\rangle \rightarrow |\Phi^{kl}_{12}\rangle \equiv (|\Psi^k_1\rangle|\Psi^l_2\rangle), \quad \forall k, l \quad (31)$$

Consequently, we define the density operator and the propagator of the compound system according to (3) and (6)

$$\rho_{\text{com}} := \sum_{kl} p_{kl} |\Phi^{kl}_{12}\rangle\langle \Phi^{kl}_{12}|, \quad \hat{\rho}_{\text{com}} := \sum_{kl} \rho_{\Psi^k_1\Psi^l_2} |\Phi^{kl}_{12}\rangle\langle \Phi^{kl}_{12}|, \quad (32)$$

and like (8) and (16)

$$\rho_{\text{com}} |\Phi^{rs}_{12}\rangle = p_{rs} |\Phi^{rs}_{12}\rangle. \quad (33)$$

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6Using the semi-classical description, $\mathcal{H}^{12}$ does not contain any interaction between the bipartite system and its environment

7We will get rid of the semi-classical description in sect 5.7
The time derivative of the density operator \( \dot{\varrho}_{\text{com}} \) is
\[
\dot{\varrho}_{\text{com}} = \varrho_{\text{com}} + \sum_{kl} p_{kl} \left\{ (|\Psi_{1}^{k}\rangle |\Psi_{2}^{l}\rangle)| \langle \Psi_{2}^{l}| \langle \Psi_{1}^{k}| \rangle + (|\Psi_{1}^{k}\rangle |\Psi_{2}^{l}\rangle)^* | \langle \Psi_{2}^{l}| \langle \Psi_{1}^{k}| \rangle + (|\Psi_{1}^{k}\rangle |\Psi_{2}^{l}\rangle) | \langle \Psi_{2}^{l}| \langle \Psi_{1}^{k}| \rangle + (|\Psi_{1}^{k}\rangle |\Psi_{2}^{l}\rangle)^* | \langle \Psi_{2}^{l}| \langle \Psi_{1}^{k}| \rangle \right\}
\] (34)

We now presuppose the validity of the Schrödinger equation for \( |\Psi_{m}^{X}\rangle \) taking into account the partial interaction operators \(-\mathcal{H}_{12}^{1}\) and \(-\mathcal{H}_{22}^{2}\) between the two sub-systems
\[
|\Psi_{1}^{k}\rangle^* = -\frac{i}{\hbar} (\mathcal{H}^{1} + \mathcal{H}_{12}^{1}) |\Psi_{1}^{k}\rangle, \quad |\Psi_{2}^{l}\rangle^* = -\frac{i}{\hbar} (\mathcal{H}^{2} + \mathcal{H}_{22}^{1}) |\Psi_{2}^{l}\rangle.
\] (35)

Consequently, (34) results in
\[
\dot{\varrho}_{\text{com}} = \varrho_{\text{com}} - \frac{i}{\hbar} \left[ (\mathcal{H}^{1} + \mathcal{H}_{12}^{1}), \varrho_{\text{com}} \right] - \frac{i}{\hbar} \left[ (\mathcal{H}^{2} + \mathcal{H}_{22}^{1}), \varrho_{\text{com}} \right].
\] (36)

Introducing the total Hamiltonian
\[
\mathcal{H} := \mathcal{H}^{1} + \mathcal{H}_{12}^{1} + \mathcal{H}^{2} + \mathcal{H}_{22}^{1},
\] (37)

(36) results in
\[
\dot{\varrho}_{\text{com}} = -\frac{i}{\hbar} \left[ \mathcal{H}, \varrho_{\text{com}} \right] + \varrho_{\text{com}}.
\] (38)

The interaction Hamiltonian is composed of the partial interaction operators
\[
\mathcal{H}_{12} = \mathcal{H}_{12}^{1} + \mathcal{H}_{22}^{1}
\] (39)

which operate on the quantum states (31) of the corresponding sub-systems.

4.3 The exchanges

From (11) and (12) follows the power and heat exchange\(^8\)
\[
\dot{W} = \text{Tr} \left( \mathcal{H} \sum_{kl} p_{kl} |\Phi_{12}^{kl}\rangle \langle \Phi_{12}^{kl}| \right), \quad \dot{Q} = \text{Tr} \left( \mathcal{H} \sum_{kl} \dot{p}_{kl} |\Phi_{12}^{kl}\rangle \langle \Phi_{12}^{kl}| \right),
\] (40)

and from (15) and (16) the entropy time rate:
\[
\dot{S} = -\sum_{kl} \dot{p}_{kl} \langle \Phi_{12}^{kl}| k_B \ln(Z_{\varrho_{\text{com}}}) \Phi_{12}^{kl}\rangle =: - \dot{\mathbf{p}} \cdot \mathbf{f}',
\] (41)

\(^8\)for simplicity, we use the same symbols for undecomposed and compound systems: \( W_{\text{com}} \rightarrow W \)
with the abbreviation
\[ f_{kl}^I = \langle \Phi_{12}^k | k_B \ln(Z \varrho_{\text{com}}) \Phi_{12}^k \rangle = k_B \ln(Zp_{kl}). \] (42)

According to (18), the entropy exchange is
\[ \Xi = \text{Tr} \left( \frac{H}{\Theta} \sum_{kl} p_{kl} | \Phi_{12}^k \rangle \langle \Phi_{12}^k | \right) = \hat{p} \cdot f^{II}, \] (43)

\[ f_{kl}^{II} := \langle \Phi_{12}^k | \frac{H}{\Theta} \Phi_{12}^k \rangle. \] (44)

The density operator (32), the propagator (32) and the entropy time rate (41) do not depend on the Hamiltonian or on the contact temperature, whereas the power exchange (40) and the heat exchange (40) depend on the Hamiltonian and the entropy exchange (43) additionally on the contact temperature. According to (20), the entropy production is
\[ \Sigma = \dot{S} - \Xi = - \hat{p} \cdot (f^I + f^{II}) = - \hat{p} \cdot f, \] (45)

\[ f_{kl} := \langle \Phi_{12}^k | (k_B \ln(Z \varrho_{\text{com}}) + \frac{H}{\Theta}) \Phi_{12}^k \rangle. \] (46)

4.4 Externally isolated and non-isolated systems

Evidently, the temporal progress is different in isolated and non-isolated systems. The act of isolating the system is achieved by introducing an insulating partition between the system and its environment which does not influence the state of the system, but all its time rates. These time rates in consideration are \( \dot{S}, \Xi, \Sigma \) and \( \hat{p} \), and they change by isolating the system (\( \rightarrow \)) into
\[ \dot{S} \rightarrow \dot{S}_{\text{iso}}, \quad \dot{S}_{\text{ex}} := \dot{S} - \dot{S}_{\text{iso}}, \] (47)

\[ \Xi \rightarrow \Xi_{\text{iso}}, \quad \Xi_{\text{ex}} := \Xi - \Xi_{\text{iso}}, \] (48)

\[ \Sigma \rightarrow \Sigma_{\text{iso}}, \quad \Sigma_{\text{ex}} := \Sigma - \Sigma_{\text{iso}}, \] (49)

\[ \hat{p} \rightarrow \hat{p}_{\text{iso}}, \quad \hat{p}_{\text{ex}} := \hat{p} - \hat{p}_{\text{iso}}. \] (50)

The so called external time rates \( \Xi_{\text{ex}} \) which represent the jumps induced by isolating the system are defined by \( \Xi_{\text{ex}} \) to \( \Xi_{\text{ex}} \).

Consequently, the time rates decompose considering (41), (43) and (45)
\[ \dot{S} = \dot{S}_{\text{ex}} + \dot{S}_{\text{iso}} = - \hat{p} \cdot f^I, \] (51)

\[ \Xi = \Xi_{\text{ex}} + \Xi_{\text{iso}} = \hat{p} \cdot f^{II}, \] (52)

\[ \Sigma = \Sigma_{\text{ex}} + \Sigma_{\text{iso}} = - \hat{p} \cdot f, \] (53)

\[ \hat{p} = \hat{p}_{\text{ex}} + \hat{p}_{\text{iso}}. \] (54)
In more detail, we accept the following

Setting III [6]:
The installation of an isolating partition between the bipartite system $G$ and its environment $G^\square$ does not change the partial Hamiltonian $H$ and the density operator of the system in semi-classical description. This isolation influences the propagator, that means, the time rate of the density operator transforms by changing the time rates of its weights

$$\dot{\rho} \rightarrow \dot{\rho}_{iso}. \quad \text{(55)}$$

Evident is that the exchange quantities $\dot{W}$ and $\dot{Q}$ depend also on the state of the system’s environment. According to (53), the power exchange is controlled by the rates of the work variables $\dot{a}$, whereas the heat exchange (26) is controlled by the difference of the contact temperature and the thermodynamic temperature of the controlling equilibrium environment according to (26). Consequently, the rates of the weights $\dot{\rho}$ of the density operator depend on the $\dot{W}$ and $\dot{Q}$, controlling quantities in semi-classical description.

When isolating the bipartite system from its environment, these rates change according to setting III (55). According to (54)

$$\dot{\rho}_{ex} := \dot{\rho} - \dot{\rho}_{iso}, \quad \rightarrow \dot{\rho}_{ex,iso} = 0, \quad \text{(56)}$$

we obtain for the time rates of the weights of the density operator in

- non-isolated closed systems: $\dot{\rho} = \dot{\rho}_{iso} + \dot{\rho}_{ex}$, \quad \text{(57)}
- isolated systems: $\dot{\rho}_{iso}$. \quad \text{(58)}

The quantities $f^I$ and $f^{II}$, (42) and (44), are independent of an external isolation of the system.

We obtain from (40) and (57) the split into an exchange propagator $\dot{\rho}_{ex}$ and a dissipative thermal part $\dot{\rho}_{iso}$, called the irreversibility propagator,

$$\dot{\rho}_{com} = \dot{\rho}_{ex} + \dot{\rho}_{iso}, \quad \text{(59)}$$

$$\dot{\rho}_{ex} := \sum_{kl} \left\{ \dot{\rho}_{kl}^{ex} |\Phi_{12}^{kl}\rangle \langle \Phi_{12}^{kl} | \right\}, \quad \dot{\rho}_{iso} := \sum_{kl} \left\{ \dot{\rho}_{kl}^{iso} |\Phi_{12}^{kl}\rangle \langle \Phi_{12}^{kl} | \right\}. \quad \text{(60)}$$

The splitting into external and internal quantities in (51) to (54) allows to formulate the following

$^9$ $H_{12}$ describes the interaction between the sub-systems. That between system and environment is for the present described semi-classically by heat- and power-exchange without any Hamiltonian.

$^{10}$ This ”jumping” of the propagator by an external isolation of the system is similar to the ”reduction of the wave function” in quantum mechanics.
Setting IV:
The entropy production is not influenced by isolating the system:
\[ \Sigma \equiv \Sigma_{iso} \rightarrow \Sigma_{ex} \equiv 0. \] (61)
An isolation of the system induces that the entropy exchange vanishes:
\[ \Xi_{iso} \equiv 0 \rightarrow \Xi \equiv \Xi_{ex}. \] (62)
Taking (43) and (57) into account, (61) results in
\[ -\mathbf{p} \cdot \mathbf{f} = -\mathbf{p}_{iso} \cdot \mathbf{f} = -\mathbf{p}_{ex} \cdot \mathbf{f} \rightarrow \mathbf{p}_{ex} \cdot \mathbf{f} \equiv 0. \] (63)
Taking (43) and (57) into account, (62) results in
\[ \mathbf{p} \cdot \mathbf{f}_{II} = \mathbf{p}_{ex} \cdot \mathbf{f}_{II} = \mathbf{p}_{ex} \cdot \mathbf{f}_{II} + \mathbf{p}_{iso} \cdot \mathbf{f}_{II} \rightarrow \mathbf{p}_{iso} \cdot \mathbf{f}_{II} \equiv 0. \] (64)
Using (63) and (64), we obtain from (45) and (43)
\[ \Sigma = -\mathbf{p} \cdot \mathbf{f} = -\mathbf{p}_{iso} \cdot \mathbf{f}, \quad \Xi = \mathbf{p}_{ex} \cdot \mathbf{f}_{II} = -\mathbf{p}_{ex} \cdot \mathbf{f}. \] (65)

4.4.1 Power exchange
The work variables in (13) belong to the undecomposed system. Switching over to a compound system, these work variables have to be replaced by those which belong to the sub-systems \( a^1, a^2 \) and those which are related to the interaction between them \( a^{12} \)
\[ a \rightarrow (a^1, a^2, a^{12}) \rightarrow \mathcal{H}(a^1, a^2, a^{12}). \] (66)
According to their definition, the work variables of the compound system (66) are attached to the partial Hamiltonians as follows:
\[ \mathcal{H}^1(a^1, a^{12}), \quad \mathcal{H}^2(a^2, a^{12}), \quad \mathcal{H}^{12}(a^{12}), \] (67)
resulting in
\[ \dot{\mathcal{H}}^1 = \frac{\partial \mathcal{H}^1}{\partial a^1} \cdot \dot{a}^1 + \frac{\partial \mathcal{H}^1}{\partial a^{12}} \cdot \dot{a}^{12}, \quad \dot{\mathcal{H}}^2 = \frac{\partial \mathcal{H}^2}{\partial a^2} \cdot \dot{a}^2 + \frac{\partial \mathcal{H}^2}{\partial a^{12}} \cdot \dot{a}^{12}, \] (68)
\[ \dot{\mathcal{H}}^{12} = \frac{\partial \mathcal{H}^{12}}{\partial a^{12}} \cdot \dot{a}^{12}. \] (69)
According to (40),
\[ \text{Tr}(\mathcal{H}^A_{\text{com}}) =: \mathcal{W}^A, \quad A = 1, 2, 12, \] (70)
\[ a^{12} \] describes the position of a partition between the sub-systems which is displacable thus influencing the tree Hamiltonians.
this decomposition of the time derivative of the Hamiltonian allows to define external and internal power exchanges: external between the sub-systems and the environment of the compound system and internal exchanges between the sub-systems themselves

\[ W_{ex}^A := \text{Tr} \left( \frac{\partial H^A}{\partial a^A} \rho_{com} \right) \cdot \dot{a}^A, \quad A = 1, 2, \quad \frac{\partial H^{12}}{\partial a^{12}} = 0, \]  
(71)

\[ W_{int}^A := \text{Tr} \left( \frac{\partial H^A}{\partial a^{12}} \rho_{com} \right) \cdot \dot{a}^{12}, \quad A = 1, 2, 12. \]  
(72)

Consequently, we obtain

\[ \dot{W}_{ex} = \dot{W}_{ex}^1 + \dot{W}_{ex}^2, \quad \dot{W}_{int} = \dot{W}_{int}^1 + \dot{W}_{int}^2 + \dot{W}_{int}^{12}. \]  
(73)

Accepting that the sum of the internal power exchanges is zero, we have the following

\[ \text{Setting } V: \quad W_{int} = \text{Tr} \left( \frac{\partial H}{\partial a^{12}} \rho_{com} \right) \cdot \dot{a}^{12} \equiv 0, \]  
(74)

and we obtain from (73)

\[ -\dot{W}_{int}^1 = \dot{W}_{int}^2 + \dot{W}_{int}^{12}. \]  
(75)

If \( \dot{W}_{int}^{12} \neq 0 \), the partition between the sub-systems is power absorbing and if \( \dot{W}_{int}^{12} = 0 \) power supplying.

Formally, five cases appear, if \( \dot{W}_{int}^{12} \) is zero

\[ \dot{W}_{int}^{12} = 0 = \text{Tr} \left( \frac{\partial H^{12}}{\partial a^{12}} \rho_{com} \right) \cdot \dot{a}^{12} \rightarrow \]  
(76)

\[ \rightarrow 1) \quad \dot{a}^{12} = 0 \quad \land \quad W_{int}^A = 0, \]  
(77)

\[ \rightarrow 2) \quad H^{12} = 0 \quad \land \quad W_{int}^A \neq 0, \]  
(78)

\[ \rightarrow 3) \quad \frac{\partial H^{12}}{\partial a^{12}} = 0 \rightarrow \dot{H}^{12} = 0, \]  
(79)

\[ \rightarrow 4) \quad \text{Tr} \left( \frac{\partial H^{12}}{\partial a^{12}} \rho_{com} \right) = 0, \]  
(80)

\[ \rightarrow 5) \quad \text{Tr} \left( \frac{\partial H^{12}}{\partial a^{12}} \rho_{com} \right) \perp \dot{a}^{12}. \]  
(81)

Here, we only consider the cases \#1 and \#2 which demonstrate that an internal power exchange can appear, even if the interaction Hamiltonian \( H^{12} \) vanishes because the \( H^A \) depend on \( \dot{a}^{12} \) according to (68).
4.4.2 Heat exchange

Similar to the Hamiltonians, there are also three contact temperatures: $\Theta^1$ and $\Theta^2$ belonging to the sub-systems, and $\Theta^{12}$—for the present an unknown contact temperature— which belongs to the quantum mechanical interaction. Besides these three contact temperatures of the bipartite system, according to (21), an additional contact temperature $\Theta$ of the undecomposed description of the compound system exists.

According to (21), we define the partial heat- and entropy-exchanges by taking the equation of motion (6) and the decomposition of the Hamiltonian (28) into account

\begin{align*}
\dot{Q}^A &:= \text{Tr}\left(\mathcal{H}^A \dot{\varrho}_{\text{com}}\right) = \\
&= -\frac{i}{\hbar} \text{Tr}\left(\mathcal{H}^A \left[\mathcal{H}^{12}, \varrho_{\text{com}}\right]\right) + \text{Tr}\left(\mathcal{H}^A \varrho_{\text{com}}^\ominus\right), \quad A=1,2, & (82) \\
\dot{Q}^{12} &:= \text{Tr}\left(\mathcal{H}^{12} \dot{\varrho}_{\text{com}}\right) = \\
&= -\frac{i}{\hbar} \text{Tr}\left(\mathcal{H}^{12} \left[\left(\mathcal{H}^1 + \mathcal{H}^2\right), \varrho_{\text{com}}\right]\right) + \text{Tr}\left(\mathcal{H}^{12} \varrho_{\text{com}}^\ominus\right), & (83) \\
\Xi^A &:= \frac{\dot{Q}^A}{\Theta^A} \quad A=1,2,12. & (84)
\end{align*}

The partial heat- and work-exchanges are additive according to (28), whereas the entropy exchanges are not additive because of the different contact temperatures of the sub-systems and the partition between them:

\begin{align*}
\dot{Q}^1 + \dot{Q}^2 + \dot{Q}^{12} &= \dot{Q}, \quad \frac{\dot{Q}^1}{\Theta^1} + \frac{\dot{Q}^2}{\Theta^2} + \frac{\dot{Q}^{12}}{\Theta^{12}} \geq \frac{\dot{Q}}{\Theta}, & (85)
\end{align*}

A proof of the inequality (85) can be found in [4] and more detailed in app.7.2 [211]. The fact, that the entropy exchange of the undecomposed system is not equal to the sum of the entropy exchanges of the compound system according to (85), is called the compound deficiency of the entropy exchanges [4, 5]. Compound deficiencies will be treated in more detail in sect.5.6.

The power exchange was decomposed into its external and its internal part according to (73) and (74). A similar decomposition is true for the heat- and entropy-exchange which is based on the following statement: the sum of the internal heat exchanges vanishes and each partial internal heat exchange vanishes with vanishing quantum mechanical interaction. We now consider the sum of the first terms of (82) and (83)

\begin{align*}
-\frac{i}{\hbar} \sum_{A=1,2} \text{Tr}\left(\mathcal{H}^A \left[\mathcal{H}^{12}, \varrho_{\text{com}}\right]\right) - \frac{i}{\hbar} \text{Tr}\left(\mathcal{H}^{12} \left[\left(\mathcal{H}^1 + \mathcal{H}^2\right), \varrho_{\text{com}}\right]\right) &= 0 =
\end{align*}
\[ \frac{i}{\hbar} \sum_{A=1,2}^{12} \text{Tr} \left( \mathcal{H}^A \left[ \mathcal{H}, \varrho_{\text{com}} \right] \right) \] (86)

which vanishes according to (28). Beyond that, each term of (86) vanishes with vanishing \( H^{12} \). Consequently, we accept according to (82) and (83) the following

\[ \text{Setting VI:} \]

\[ Q^A_{\text{int}} := -\frac{i}{\hbar} \text{Tr} \left( \mathcal{H}^A \left[ \mathcal{H}, \varrho_{\text{com}} \right] \right) + \text{Tr} \left( \mathcal{H}^A \varrho^\circ_{\text{iso}} \right), \quad A=1,2,12. \] (87)

Because

\[ \dot{Q}^A = \dot{Q}_{\text{ex}}^A + \dot{Q}_{\text{int}}^A, \quad A=1,2,12, \] (88)

the external heat exchanges are according to (82) and (83)

\[ \dot{Q}_{\text{ex}}^A = \text{Tr} \left( \mathcal{H}^A \varrho_{\text{ex}}^\circ \right), \quad A=1,2,12. \] (89)

the corresponding entropy exchanges are according to (83) and (87)

\[ \Xi_{\text{ex}}^A = -\frac{i}{\hbar} \text{Tr} \left( \mathcal{H}^A \varrho_{\text{ex}}^\circ \right) = \mathbf{p} \cdot \mathbf{f}^{IIA}, \] (90)

\[ f^{IIA} := \langle \Phi_k^+ \mathcal{H}^A \Phi_k^- \rangle \quad A=1,2,12. \] (91)

\[ \Xi_{\text{int}}^A = -\frac{i}{\hbar} \text{Tr} \left( \mathcal{H}^A \left[ \mathcal{H}, \varrho_{\text{com}} \right] \right) + \text{Tr} \left( \mathcal{H}^A \varrho_{\text{com}}^\circ \right), \quad A=1,2,12. \] (92)

According to (86), we obtain from (87)

\[ \sum_{A=1,2}^{12} Q_{\text{int}}^A = 0 \quad \rightarrow \quad \text{Tr} (\mathcal{H} \varrho_{\text{iso}}^\circ) \equiv 0, \quad \wedge \text{Tr} \left( \mathcal{H} \varrho_{\text{iso}}^\circ \right) \equiv 0. \] (93)

According to (85), (86) and (87), the heat- and entropy-exchanges satisfy

\[ \dot{Q}_{\text{ex}} = \dot{Q}_{\text{ex}}^1 + \dot{Q}_{\text{ex}}^2 + \dot{Q}_{\text{ex}}^{12}, \] (94)

\[ 0 = \dot{Q}_{\text{int}}^1 + \dot{Q}_{\text{int}}^2 + \dot{Q}_{\text{int}}^{12}, \quad \dot{Q}_{\text{int}} \equiv 0, \] (95)

\[ \Xi_{\text{ex}} \leq \Xi_{\text{ex}}^1 + \Xi_{\text{ex}}^2 + \Xi_{\text{ex}}^{12}, \] (96)

\[ 0 \leq \Xi_{\text{int}} + \Xi_{\text{int}}^2 + \Xi_{\text{int}}^{12}, \quad \Xi_{\text{int}} \equiv 0. \] (97)

The decomposition into the external and internal parts is achieved for the power exchanges by the work variables according to (71) and (72). With respect to the heat- and entropy-exchanges, this decomposition is not determined by the work variables but by the thermodynamical properties of the internal heat exchanges (87).
4.4.3 Entropy rate and 2nd law

As already mentioned, the entropy rate (15) of the compound system depends neither on the Hamiltonian nor on the contact temperatures and is therefore not influenced by the decomposition of the Hamiltonian

\[ \dot{S} = -k_B \text{Tr} \left( \dot{\rho}_{\text{com}} \ln(Z_{\rho_{\text{com}}}) \right) = -k_B \text{Tr} \left( \dot{\rho}_{\text{com}} \ln(Z_{\rho_{\text{com}}}) \right). \]  

(98)

According to (19), (61), (62) and (51), the entropy rate results in

\[ \dot{S} = \Sigma + \Xi = \Sigma_{\text{iso}} + \Xi _{\text{ex}} = \Sigma_{\text{iso}} + \frac{\dot{Q}_{\text{ex}}}{\Theta} = \dot{S}_{\text{iso}} + \dot{S}_{\text{ex}}. \]  

(99)

Consequently, we obtain a quantum mechanical expression of the contact temperature of the compound system taking (98) and (89) into account

\[ \frac{1}{\Theta} = \frac{\dot{S}_{\text{ex}}}{\dot{Q}_{\text{ex}}} = -\frac{k_B \text{Tr} \left( \dot{\rho}_{\text{ex}} \ln(Z_{\rho_{\text{com}}}) \right)}{\text{Tr}(\mathcal{H} \dot{\rho}_{\text{ex}})}. \]  

(100)

The sum of the entropy exchanges is according to (89), (85) and (96)

\[ \sum_{A=1,2}^{12} \Xi_{\text{ex}}^A = -\frac{i}{\hbar} \text{Tr} \left( \sum_{A=1,2}^{12} \frac{\mathcal{H}^A}{\Theta^A} \dot{\rho}_{\text{ex}} \right) \leq -\frac{i}{\hbar} \text{Tr} \left( \frac{\mathcal{H}}{\Theta} \dot{\rho}_{\text{ex}} \right). \]  

(101)

Introducing the

**Second Law:**

\[ \Sigma \geq 0, \]  

(102)

and taking (21) into account, (99) results in

\[ \dot{S} \geq \dot{S}_{\text{ex}} = \frac{\dot{Q}_{\text{ex}}}{\Theta} \geq \frac{\dot{Q}_{\text{ex}}}{T^2}. \]  

(103)

A similar representation as (103) of the contact temperatures of the sub-systems, \( \Theta^1 \) and \( \Theta^2 \), is not possible because partial entropies of the sub-systems are not defined for compound systems with respect to the joint propagator and density operator (32). The entropy rate (11) does not depend on the Hamiltonian or its decomposition. Partial entropies can be defined for decomposed systems which are discussed in sect.5

The entropy production (65) is not negative according to the Second Law (102)

\[ \Sigma = -\dot{p} \cdot f = -\dot{p}^{\text{iso}} \cdot f^I \geq 0. \]  

(104)
But pay attention to the fact that different expressions of the entropy production belong to different controlled systems: (104) belongs according to (57) to a non-isolated system, whereas (104)2 represents the entropy production of an isolated system according to (58). The value of the entropy production is equal in both systems because isolation of a system does not influence the entropy production according to (61). This difference of the meaning of (104)1 and (104)2 comes into sight, if equilibria are discussed sect.4.6.

The propagator $\hat{\varrho}_{\text{com}}$ vanishes in conventional quantum mechanics and with it also the entropy rate and entropy exchange and production according to (98) and (101). The entropy itself is constant in time according to (15), and the heat exchange (82) vanishes in conventional quantum mechanics. That is the reason why conventional quantum mechanics is characterized as an adiabatical and reversible theory.

As in [6], we consider special thermodynamical processes and their quantum theoretical interpretations. The well-known phenomenological concepts of adiabatic, irreversible and reversible processes in isolated and in closed systems and the concept of equilibrium are interpreted quantum-theoretically without using methods of statistical thermodynamics: we are looking for a phenomenological irreversible quantum thermodynamics.

4.5 Vanishing quantum mechanical interaction

4.5.1 Internal exchanges

If the quantum mechanical interaction vanishes, we obtain from (87) by taking (95) and (97) into account:

$$\text{if } H^{12}_t = 0 \quad \rightarrow \quad \dot{Q}^{12}_t = 0 \quad \rightarrow \quad \dot{Q}^1_{\text{int}} = - \dot{Q}^2_{\text{int}}, \quad (105)$$

$$\rightarrow \quad \Xi^{12}_t = 0 \quad \rightarrow \quad \Xi^1_{\text{int}} \geq -\Xi^2_{\text{int}}, \quad (106)$$

According to (105), the partition between the two sub-systems is inert and heat- and power-exchange through this partition are continuous, if the quantum mechanical interaction vanishes. Or in other words, the quantum mechanical interaction causes according to (75) and (95) that the partition between the sub-systems is not inert, that means, it absorbs or emits $\dot{Q}^{12}_{\text{int}}$ or/and $W^{12}_{\text{int}}$, representing a "moving heat absorbing partition with friction".

Presupposing that the entropy exchange through the partition between the sub-systems is continuous, we obtain by use of (95)

$$0 \equiv \frac{\dot{Q}^1_{\text{int}}}{\Theta^1} + \frac{\dot{Q}^2_{\text{int}}}{\Theta^2} = \frac{\dot{Q}^1_{\text{int}}}{\Theta^1} - \frac{\dot{Q}^1_{\text{int}} + \dot{Q}^{12}_{\text{int}}}{\Theta^2} = \dot{Q}^1_{\text{int}} \left( \frac{1}{\Theta^1} - \frac{1}{\Theta^2} \right) - \frac{\dot{Q}^{12}_{\text{int}}}{\Theta^2}, \quad (107)$$

\[\text{concerning power exchange, see (76)}\]

\[\text{inert means: the partition does not emit or absorb neither heat nor power}\]
resulting in the *condition of continuous entropy exchange*

\[
\frac{\dot{Q}_{\text{int}}^{12}}{\Theta^2} = \dot{Q}_{\text{int}}^{1} \left( \frac{1}{\Theta^1} - \frac{1}{\Theta^2} \right).
\]  
(108)

If the quantum mechanical interaction vanishes, and consequently the heat exchange is continuous according to (105)\textsubscript{3},

\[
\mathcal{H}^{12} = 0 : \quad 0 = \dot{Q}_{\text{int}}^{1} \left( \frac{1}{\Theta^1} - \frac{1}{\Theta^2} \right) \quad (109)
\]

follows by taking (105)\textsubscript{2} into account. Because the contact temperatures of the two sub-systems are presupposed to be different, we obtain from (109), (105) and (106)

\[
\mathcal{H}^{12} = 0 \land \Theta^1 \neq \Theta^2 \longrightarrow \dot{Q}_{\text{int}}^{1} = 0 = \dot{Q}_{\text{int}}^{2} = \Xi_{\text{int}}^{2} = \Xi_{\text{int}}^{1}. \quad (110)
\]

that means, we have proved the following  

■ Proposition:  

1. If the quantum mechanical interaction does not vanish \( \mathcal{H}^{12} \neq 0 \):  
   - the heat exchange through the partition between the sub-systems is not continuous,  
   - the corresponding entropy exchange is continuous, if the continuity condition (108) is satisfied.  

2. If the quantum mechanical interaction vanishes \( \mathcal{H}^{12} = 0 \):  
   - the heat exchange through the partition between the sub-systems is continuous: the partition is inert (105)\textsubscript{2},  
   - the corresponding entropy exchange is not continuous (106)\textsubscript{2},  
   - heat exchange and entropy exchange are jointly continuous only in the trite case that the partition between the two sub-systems is insulating and consequently the internal exchanges vanish (110).  

■  

4.5.2 External exchanges  

In this section, we consider the following problem: A bipartite compound system is in contact with a macroscopic equilibrium environment of the thermostatic temperature \( T^\text{\textbullet} \). The interaction of the bipartite system with the environment is semi-classically described by heat- and entropy-exchanges \( \dot{Q}_{\text{ext}}^{B}, \Xi_{\text{ext}}^{B}, B = 1, 2 \), according to (94) and (96). According to (21), the
contact temperatures $\Theta^B$ of the sub-systems satisfy the following inequalities
\[
Q_{ex}^B \left( \frac{1}{\Theta^B} - \frac{1}{T^\circ} \right) \geq 0, \quad B = 1, 2. \tag{111}
\]

Presupposing
\[
\mathcal{H}^{12} = 0 \quad \rightarrow \quad \dot{Q}_{ex}^{12} = 0, \quad \Xi_{ex}^{12} = 0, \tag{112}
\]
and using the contact temperature $\Theta$ of the undecomposed system, we obtain according to (96) and (94)
\[
\Xi_{ex}^1 + \Xi_{ex}^2 = \frac{\dot{Q}_{ex}^1}{\Theta^1} + \frac{\dot{Q}_{ex}^2}{\Theta^2} \geq \frac{\dot{Q}_{ex}}{\Theta} = \frac{\dot{Q}_{ex}^1}{\Theta^1} + \frac{\dot{Q}_{ex}^2}{\Theta^2} = \dot{Q}_{ex}, \tag{113}
\]
resulting in
\[
\dot{Q}_{ex}^1 \left( \frac{1}{\Theta^1} - \frac{1}{T^\circ} \right) + \dot{Q}_{ex}^2 \left( \frac{1}{\Theta^2} - \frac{1}{T^\circ} \right) \geq \dot{Q}_{ex} \left( \frac{1}{\Theta} - \frac{1}{T^\circ} \right) \geq 0, \tag{114}
\]
\[
\rightarrow \quad \frac{\dot{Q}_{ex}^1}{\Theta^1} + \frac{\dot{Q}_{ex}^2}{\Theta^2} \geq \frac{\dot{Q}_{ex}}{T^\circ}, \tag{115}
\]
an inequality which demonstrates the compatibility of the contact temperatures $\Theta^1$ and $\Theta^2$ of the sub-systems with $\Theta$, the contact temperature of the undecomposed system. The relations presented in app.7.2 are satisfied by taking the entropy exchange inequality (85) into account.

### 4.6 Equilibria

#### 4.6.1 Equilibrium conditions

Equilibria are defined by the following equilibrium conditions
\[
\begin{align*}
\dot{\varrho}^{eq}_{com} & \doteq 0, \quad \land \quad \dot{\varrho}^{eq}_{ex} \doteq 0 \quad \land \quad \dot{\varrho}^{eq}_{iso} \doteq 0, \\
\dot{a}^A_{eq} & \doteq 0, \quad A = 1, 2, 12, \quad \Theta^A_{eq} \doteq \Theta_{eq}.
\end{align*} \tag{116}
\]
From (38) and (116) follows
\[
[\mathcal{H}, \varrho^{eq}_{com}] = 0, \tag{118}
\]
and from (71), (72) and (117)
\[
\begin{align*}
W^{Aeq}_{ex} & = 0, \quad A = 1, 2, \quad W^{Aeq}_{int} = 0, \quad A = 1, 2, 12. \tag{119}
\end{align*}
\]
According to (116)$_{2,3}$ and (118), the heat- and entropy-exchanges (89), (90) and (87), (92) vanish in equilibrium
\[
\begin{align*}
\dot{Q}^{Aeq}_{ex} & = 0, \quad \Xi^{Aeq}_{ex} = 0, \quad A = 1, 2, 12, \tag{120}
\end{align*}
\]
\[
\begin{align*}
\dot{Q}^{Aeq}_{int} & = 0, \quad \Xi^{Aeq}_{int} = 0, \quad A = 1, 2, 12. \tag{121}
\end{align*}
\]
An other shape of \((116)_{2,3}\) is
\[
\dot{p}_{eq}^{ex} = 0 \quad \land \quad \dot{p}_{eq}^{iso} = 0. \tag{122}
\]
Consequently, the entropy rate \((98)_{1}\) and the entropy production \((104)\) vanish in equilibrium
\[
\dot{S}_{eq} = 0, \quad \Sigma_{eq} = 0. \tag{123}
\]

### 4.6.2 Equilibrium distributions

We now consider the following situation: a system (isolated or non-isolated) is in equilibrium. According to \((104)\), we obtain for the two different kinds of systems
\[
\Sigma_{eq} = 0 \implies 0 = \dot{p}_{eq}^{iso} \cdot f_{eq}^{l} \quad \lor \quad 0 = \dot{p}_{eq} \cdot f_{eq}^{\#}. \tag{124}
\]
An external manipulation brings the system out of equilibrium by changing the equilibrium condition \((122)\) of the propagator arbitrarily\(^{15}\)
\[
\dot{p}_{eq}^{ex} \rightarrow \dot{p}_{eq}^{ex}^{\#} \quad \lor \quad \dot{p}_{eq}^{iso} \rightarrow \dot{p}_{eq}^{iso}^{\#} \tag{125}
\]
which does not influence \(f_{eq}^{l}\) and \(f_{eq}^{\#}\) according to \((42)\) and \((46)\). Because of \((104)\), the replacement \((125)\) generates
\[
\left(0 \leq -\dot{p}_{eq}^{iso}^{\#} \cdot f_{eq}^{l} \quad \lor \quad 0 \leq -\dot{p}_{eq}^{iso}^{\#} \cdot f_{eq}^{\#}\right), \quad \text{for all} \quad (\dot{p}_{eq}^{iso}, \dot{p}_{eq}^{ex}). \tag{126}
\]
Because \(\dot{p}_{eq}^{iso}^{\#}\) and \(\dot{p}_{eq}^{\#}\) can be chosen arbitrarily\(^{16}\), the only possibility to satisfy \((126)\) is
\[
f_{eq}^{l} = 0, \quad \text{in isolated systems} \tag{127}
\]
\[
f_{eq}^{\#} = 0, \quad \text{in non-isolated closed systems}. \tag{128}
\]
Consequently, \((127)\) and \((128)\) result in\(^{17}\)
\[
f_{eq}^{l} = \langle \Phi_{eq}^{kl} | k_{B} \ln(Z_{eq}^{com}) \Phi_{eq}^{kl} \rangle = 0 = k_{B} \ln(Z p_{eq}^{kl}), \quad \land kl, \tag{129}
\]
\[
f_{eq}^{\#} = \langle \Phi_{eq}^{kl} | \left(k_{B} \ln(Z_{eq}^{com}) + \frac{\mathcal{H}}{\Theta_{eq}}\right) \Phi_{eq}^{kl} \rangle = 0, \quad \land kl. \tag{130}
\]
The equilibrium density operator \(\rho_{eq}^{com}\) follows from \((129)\) for isolated systems and from \((130)\) for non-isolated closed systems, as derived in the next two sections. Catchword like, one can say: The Second Law applied to equilibrium generates the equilibrium distributions.

\(^{15}\) A more detailed argumentation can be found in sect.\(4.7.2\)

\(^{16}\) More details in sect.\(4.7.2\)

\(^{17}\) See \(4.7.2\)
4.6.3 Isolated systems: micro-canonical ensemble

From (129) follows

$$Z_{p_{eq}}^{kl} = 1 \rightarrow p_{kl}^{eq} = \frac{1}{Z} \rightarrow \rho_{com}^{eq} = \frac{1}{Z} \sum_{kl} |\Phi_{eq}^{kl}\rangle \langle \Phi_{eq}^{kl}| = \frac{1}{Z}. \quad (131)$$

Tracing the density operator according to (8) results in

$$1 = \sum_{kl} \langle \Phi_{eq}^{kl}| \rho_{com}^{eq} |\Phi_{eq}^{kl}\rangle = \frac{1}{Z} \sum_{kl} \langle \Phi_{eq}^{kl}| \Phi_{eq}^{kl}\rangle = \frac{1}{Z} \sum_{kl} 1_{kl}. \quad (132)$$

The last sum must be restricted because of convergency: $1 \leq kl \equiv J \leq N$. Consequently, according to (132) $Z = N$ is valid, and the density operator (131) of an isolated system has, as expected, the micro-canonical form

$$\rho_{mic} = \frac{1}{N} \sum_{J=1}^{N} |\Phi_{eq}^{J}\rangle \langle \Phi_{eq}^{J}|, \quad N < \infty. \quad (133)$$

4.6.4 Non-isolated closed systems: canonical ensemble

According to (118), the Hamilton operator commutes with the density operator in equilibrium. Consequently, a common system of eigenfunctions exists for both operators, and we presuppose that this system is given by (33). Consequently, from (130) follows by taking (129) into account

$$k_B \ln(Z_{p_{eq}}^{kl}) + \frac{E_{kl}}{\Theta_{eq}} = 0 \rightarrow$$

$$\rightarrow k_B \sum_{kl} \ln(Z_{p_{eq}}^{kl}) |\Phi_{eq}^{kl}\rangle \langle \Phi_{eq}^{kl}| + \sum_{kl} |\Phi_{eq}^{kl}\rangle \frac{E_{kl}}{\Theta_{eq}} \langle \Phi_{eq}^{kl}| = 0. \quad (134)$$

resulting according to (42) in

$$k_B \ln(Z_{\rho_{com}}^{eq}) + \frac{H}{\Theta_{eq}} = 0. \quad (135)$$

From (135) follows the canonical density operator of a closed non-isolated system in equilibrium

$$\rho_{can} = \frac{1}{Z} \exp \left[ - \frac{H}{k_B \Theta_{eq}} \right], \quad Z = \text{Tr} \exp \left[ - \frac{H}{k_B \Theta_{eq}} \right]. \quad (136)$$

If we presuppose that the equilibrium environment which contacts the system is a heat reservoir of the thermostatic temperature $T_{\odot}$, the equilibrium contact temperature $\Theta_{eq}$ of the system is replaced by $T_{\odot}$

$$\Theta_{eq} = T_{\odot}. \quad (137)$$
representing an additional equilibrium condition.

The micro-canonical and the canonical equilibrium density operators, \( (133) \) and \( (136) \), are derived by a pure phenomenological argumentation: starting with the entropy production in isolated and non-isolated systems \( (104) \), vanishing entropy production \( (123) \) follows from the equilibrium conditions \( (122) \). Considering a process which brings the system off equilibrium, \( (125) \), results in equilibrium distributions \( (127) \) and \( (128) \), in isolated and non-isolated closed systems.

4.7 Constitutive equations

4.7.1 Heat- and entropy-exchange

According to the constitutive equation \( (26) \), the heat exchanges \( (94) \) and \( (95) \) result in

\[
-\dot{Q}_{12}^{\text{ex}} = \dot{Q}_{1}^{\text{ex}} + \dot{Q}_{2}^{\text{ex}} - \dot{Q}_{\text{ex}} = \\
\kappa_{1}^{\text{ex}} \left( \frac{1}{\Theta} - \left( \frac{1}{T} \right) \right) + \kappa_{2}^{\text{ex}} \left( \frac{1}{\Theta} - \left( \frac{1}{T} \right) \right) - \kappa_{\text{ex}} \left( \frac{1}{\Theta} - \left( \frac{1}{T} \right) \right),
\]

(138)

\[
-\dot{Q}_{12}^{\text{int}} = \dot{Q}_{1}^{\text{int}} + \dot{Q}_{2}^{\text{int}} = \\
\kappa_{1}^{\text{int}} \left( \frac{1}{\Theta} - \left( \frac{1}{\Theta} \right) \right) + \kappa_{2}^{\text{int}} \left( \frac{1}{\Theta} - \left( \frac{1}{\Theta} \right) \right).
\]

(139)

From \( (138) \) follows

\[
-\dot{Q}_{12}^{\text{ex}} = \frac{1}{T} \left( \kappa_{\text{ex}} - \kappa_{1}^{\text{ex}} - \kappa_{2}^{\text{ex}} \right) + \frac{\kappa_{1}^{\text{ex}}}{\Theta} + \frac{\kappa_{2}^{\text{ex}}}{\Theta} - \frac{\kappa_{\text{ex}}}{\Theta}.
\]

(140)

Because \( Q_{12}^{\text{ex}} \) and the \( \kappa_{\text{ex}} \) do not depend on \( T \), we obtain finally by taking \( (89) \) into account

\[
-\dot{Q}_{12}^{\text{ex}} = \kappa_{1}^{\text{ex}} \left( \frac{1}{\Theta} - \frac{1}{\Theta} \right) + \kappa_{2}^{\text{ex}} \left( \frac{1}{\Theta} - \frac{1}{\Theta} \right) = -\text{Tr} \left( H_{12}^{\text{ex}} \Theta_{\text{ex}} \right).
\]

(141)

Consequently, the heat exchanges are additive, if \( \dot{Q}_{12}^{\text{ex}} \) and \( \dot{Q}_{12}^{\text{int}} \) which depend on the quantum mechanical interaction vanish. Beyond that, the contact temperatures and the heat conductivities are related to the quantum mechanical interaction by \( (139) \), \( (87) \) and \( (141) \), thus demonstrating the dependence of the constitutive equations on the quantum mechanical background.

4.7.2 Propagators

Thus far, the time rates of the weights \( \{ \dot{p}_{kl} \} \) of the density operator are unknown, and they need equations for their determination. Three aspects
are of interest: what quantities determine these time rates, on what way
come different materials into play and what is the difference between the
\{p_{kl}^{ex}\} and \{p_{kl}^{iso}\} in non-isolated and isolated systems?

As in classical non-equilibrium thermodynamics, the entropy produc-
tion in quantum thermodynamics has also the typical form of a product of “fluxes”
\(\dot{\mathbf{p}}\) and “forces” \(\mathbf{f}\) according to (104). The term \(\dot{\mathbf{p}}^{iso} \cdot \mathbf{f}^{I}\) belongs to an isolated
system, whereas the term \(\dot{\mathbf{p}} \cdot \mathbf{f}\) to a non-isolated closed system. Constitutive
equations according to the usual scheme (24) cannot be used because the
equilibrium distributions \(\mathbf{f}^{I} = 0\) and \(\mathbf{f} = 0\) do not induce the vanishing of
the propagators due to their missing sufficiency for equilibrium. Therefore
we start out with (64) and (65)
\[
\dot{\mathbf{p}}^{iso} \cdot \mathbf{f}^{II} = 0, \quad \dot{\mathbf{p}}^{ex} \cdot \mathbf{f}^{II} = \Xi_{ex},
\] (142)
and we accept the

\[\text{Setting VII:}\]
\[
\dot{\mathbf{p}}^{iso} \text{ and } \dot{\mathbf{p}}^{ex} \text{ depend on } \mathbf{f}^{II},
\] (143)
that means according to (141), \(\dot{\mathbf{p}}^{iso}\) and \(\dot{\mathbf{p}}^{ex}\) depend on the total Hamiltonian
and on the contact temperature of the corresponding undecomposed system.
Beyond that, the choice of the constitutive equations have to satisfy (122)
in equilibrium. Consequently, we introduce matrices \(\mathbf{A}\) and \(\mathbf{B}\) creating the
constitutive equations of the propagators
\[
\dot{\mathbf{p}}^{iso} = \mathbf{A}(\mathbf{z}^{iso}, \mathbf{f}^{II}) \cdot \mathbf{f}^{II}, \quad \mathbf{A}^\top = -\mathbf{A}, \quad \dot{\mathbf{p}}^{ex} = \mathbf{B}(\mathbf{z}^{ex}, \mathbf{f}^{II}) \cdot \mathbf{f}^{II} (144)
\]
according to (142). The \(\mathbf{z}^{iso}\) and \(\mathbf{z}^{ex}\) take the equilibrium in isolated and
non-isolated closed systems into account
\[
\mathbf{z}^{iso} := \mathbf{a}_{12}, \Theta_{1}, \Theta_{2}, \Theta_{12}, \mathbf{f}^{I}, \quad \mathbf{z}^{ex} := \mathbf{a}_{1}, \mathbf{a}_{2}, \Theta_{1}, \Theta_{2}, T^{Q}, \mathbf{f},
\] (145)
\[
\mathbf{z}^{iso}_{eq} = 0, \Theta_{eq}, \Theta_{eq}, \Theta_{eq}, 0, \quad \mathbf{z}^{ex}_{eq} = 0, 0, T^{Q}, T^{Q}, T^{Q}, 0,
\] (146)
\[
\mathbf{A}_{eq} = \mathbf{A}(\mathbf{z}^{iso}_{eq}, \mathbf{f}^{II}) = 0, \quad \mathbf{B}_{eq} = \mathbf{B}(\mathbf{z}^{ex}_{eq}, \mathbf{f}^{II}) = 0.
\] (147)

As the equilibrium conditions (116) and (117) demonstrate, the equilib-
rium distributions (127) and (128) are only necessary, but not sufficient for
equilibrium. This fact can be represented by
\[
\mathbf{z}^{iso}_{#} = \mathbf{a}_{12}, \Theta_{1}, \Theta_{2}, \Theta_{12}, 0, \quad \mathbf{z}^{ex}_{#} = \mathbf{a}_{1}, \mathbf{a}_{2}, \Theta_{1}, \Theta_{2}, T^{Q}, 0.
\] (148)
Consequently, the non-vanishing propagators in (125) become by use of (144)
\[
\dot{\mathbf{p}}^{iso}_{#} = \mathbf{A}(\mathbf{z}^{iso}_{#}) \cdot \mathbf{f}^{II}, \quad \dot{\mathbf{p}}^{ex}_{#} = \mathbf{B}(\mathbf{z}^{ex}_{#}) \cdot \mathbf{f}^{II}.
\] (149)
in presence of the equilibrium distributions $f^I = 0$ and $f = 0$.

The $A$ and $B$ have to satisfy the following relations according to (104)

$4 \rightarrow \Sigma = -f^I \cdot A \cdot f^{II} \geq 0$,  

(150)

$142 \rightarrow \Xi = f^{II} \cdot B \cdot f^{II} = \Xi_{ex}$,  

(151)

$\rightarrow \dot{S} = -f^I \cdot (A + B) \cdot f^{II}$,  

(152)

$3 \rightarrow 0 = f \cdot B \cdot f^{II}$.  

(153)

The relations (150) and (153) are constraints which have to be satisfied by the constitutive matrices $A$ and $B$.

4.8 Special processes

4.8.1 Adiabatic processes

We distinguish two kinds of adiabatic processes: according to (94), we define

weak adiabatic: \[ \dot{Q}_{ex} = 0, \quad \dot{Q}^1_{ex} = -\dot{Q}^2_{ex} \neq 0, \]  

(154)

strong adiabatic: \[ \dot{Q}_{ex} = 0, \quad \dot{Q}^1_{ex} = \dot{Q}^2_{ex} = 0. \]  

(155)

In both cases, $\dot{Q}_{ex}^{12}$ vanishes according to (94) and (141) results in

\[ \kappa_{ex}^1 \left( \frac{1}{\Theta^1} - \frac{1}{\Theta} \right) = -\kappa_{ex}^2 \left( \frac{1}{\Theta^2} - \frac{1}{\Theta} \right), \]  

(156)

that means, the contact temperatures depend in the weak adiabatic case on $\kappa_{ex}^1$ and $\kappa_{ex}^2$, whereas in the strong adiabatic case $\Theta = T^\Theta = \Theta^1 = \Theta^2$ is valid.

4.8.2 Reversible processes

Reversible processes are defined by vanishing entropy production without equilibrium, according to (103)

\[ \left( \Sigma_{rev} = -\dot{p}_{rev}^{iso} \cdot f^I_{rev} = 0 \right) \land \left( \dot{p}_{rev}^{iso} \neq 0 \lor f^I_{rev} \neq 0 \right). \]  

(157)

According to (144)\textsubscript{1},

\[ f^I_{rev} \cdot A(z_{rev}^{iso}, f^{II}) \cdot f^{II} = 0 \]  

(158)

represents the condition of reversibility. There are two cases for satisfying this condition

\[ \left( f^I_{rev} \cdot A(z_{rev}^{iso}, f^{II}) = 0 \lor f^I_{rev} = f^{II} \cdot C \right), \quad C \cdot A = -A^\top \cdot C^\top. \]  

(159)
The special case
\[ C = -1 \rightarrow f_{rev}^I = -f^{II} \rightarrow f_{rev} = 0 \quad (160) \]

belongs to the equilibrium of non-isolated closed systems (128). Be aware that the \( f \) are quantum mechanically defined items according to (42), (44) and (46).

5 Decomposed Systems

According to the definition given in the beginning of sect. 4, the density operator \( \varrho_{com} \) of the compound description is replaced by the two partial density operators \( \varrho^1 \) and \( \varrho^2 \) of the two sub-systems #1 and #2 of the bipartite system according to (32) and (31):
\[
\begin{align*}
\text{Tr}_2 \varrho_{com} &=: \varrho^1 = \sum_{kj} p_{kj} |\Psi^k_1\rangle\langle \Psi^k_1|, \\
\text{Tr}_1 \varrho_{com} &=: \varrho^2 = \sum_{jl} p_{jl} |\Psi^l_2\rangle\langle \Psi^l_2|,
\end{align*}
\]
\[
\begin{align*}
\text{Tr}_2 \varrho_{com} &=: \varrho^{\circ 1} = \sum_{kj} \tilde{p}_{kj} |\Psi^k_1\rangle\langle \Psi^k_1|, \\
\text{Tr}_1 \varrho_{com} &=: \varrho^{\circ 2} = \sum_{jl} \tilde{p}_{jl} |\Psi^l_2\rangle\langle \Psi^l_2|.
\end{align*}
\]

The decomposition of the Hamiltonian is the same as for the compound description (28).

The traces of the density operators and of the propagators are by taking (161) to (164) into account
\[
\begin{align*}
1 &= \text{Tr} \varrho_{com} = \text{Tr}^1 \varrho^1 = \text{Tr}^2 \varrho^2 = \sum_{ij} p_{ij}, \\
0 &= \text{Tr} \varrho_{com} = \text{Tr}^1 \varrho^{\circ 1} = \text{Tr}^2 \varrho^{\circ 2} = \sum_{ij} \tilde{p}_{ij}.
\end{align*}
\]

5.1 Partial entropies

Because in decomposed systems, the density operator \( \varrho_{com} \) of the compound system is replaced by those of the bipartite system –(161) and (162)– we are able to define partial entropies of the sub-systems\(^{18}\) starting with the entropy of the compound system (11)
\[
S(\varrho_{com}) = -k_B \text{Tr}(\varrho_{com} \ln \varrho_{com}) \quad (167)
\]
\(^{18}\)Thermodynamical quantities of the bipartite system are written in bold face.
we define

\[ S_1(\rho^1) := -k_B \text{Tr}(\rho^1 \ln \rho^1), \quad S_2(\rho^2) := -k_B \text{Tr}(\rho^2 \ln \rho^2) \]  

(168)

by using the partial density operators (161) and (162). According to (227) in sect.7.1, these partial entropies result in

\[ S_1(\rho^1) = -k_B \text{Tr}(\rho_{\text{com}} \ln \rho^1), \quad S_2(\rho^2) = -k_B \text{Tr}(\rho_{\text{com}} \ln \rho^2). \]  

(169)

A comparison of (169) with (167) depicts that the partial entropies are not additive with respect to the entropy of the compound system

\[ S_1 + S_2 - S = -k_B \text{Tr}\left\{ \rho_{\text{com}} \left( \ln(\rho^1 \rho^2) - \ln \rho_{\text{com}} \right) \right\}, \]  

(170)

because the density operator of the compound system does not decompose in general.

Using Klein’s inequality [17]

\[ \text{Tr}(A \ln B) - \text{Tr}(A \ln A) \leq \text{Tr}(B) - \text{Tr}A, \]  

(171)

we obtain according to (171) and (165)

\[ \text{Tr}\left\{ \rho_{\text{com}} \left( \ln(\rho^1 \rho^2) - \ln \rho_{\text{com}} \right) \right\} \leq \text{Tr}(\rho^1 \rho^2) - \text{Tr}\rho_{\text{com}} = 0, \]  

(172)

\[ \text{Tr}(\rho^1 \rho^2) = \text{Tr}^1 \text{Tr}^2(\rho^1 \rho^2) = 1, \]  

(173)

and (170) results in

\[ S_1 + S_2 \geq S. \]  

(174)

If the entropy of the compound system does not decompose into the partial entropies of the decomposed system, it is according to (174) smaller than the sum of the partial entropies. The descriptions of a system as a compound one or as a decomposed one are different, a fact which is denoted as compound deficiency [4].

### 5.2 Equations of motion

Using the calculation rules of app.7.1 and the decomposition of the Hamiltonian (28), the modified von Neumann equation (38)

\[ \dot{\rho}_{\text{com}} = -\frac{i}{\hbar} \left[ (\mathcal{H}^1 + \mathcal{H}^2 + \mathcal{H}^{12}), \rho_{\text{com}} \right] + \rho_{\text{com}} \]  

(175)

results in two equations of motion for the traced density operators of the sub-systems by taking (230) into account

\[ \dot{\rho}^1 := \text{Tr}^2 \dot{\rho}_{\text{com}} = -\frac{i}{\hbar} \text{Tr}^2 \left[ \mathcal{H}^1, \rho_{\text{com}} \right] - \frac{i}{\hbar} \text{Tr}^2 \left[ \mathcal{H}^{12}, \rho_{\text{com}} \right] + \text{Tr}^2 \rho_{\text{com}} = \]
\[
\dot{\varrho}^1 := \text{Tr}^1 \varrho_{\text{com}} = -\frac{i}{\hbar} \text{Tr}^1 \left[ \mathcal{H}^1, \varrho_{\text{com}} \right] + \dot{\varrho}^1, \quad (176)
\]

\[
\dot{\varrho}^2 := \text{Tr}^2 \varrho_{\text{com}} = -\frac{i}{\hbar} \text{Tr}^2 \left[ \mathcal{H}^2, \varrho_{\text{com}} \right] + \text{Tr}^1 \varrho_{\text{com}} = -\frac{i}{\hbar} \left[ \mathcal{H}^2, \varrho^2 \right] - \frac{i}{\hbar} \text{Tr}^1 \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] + \dot{\varrho}^2. \quad (177)
\]

As (176) and (177) depict, the traced operators \( \dot{\varrho}^1 \) and \( \dot{\varrho}^2 \) include as expected the interaction Hamiltonian \( \mathcal{H}^{12} \) and beyond that, also the density operator \( \varrho_{\text{com}} \) of the compound system. That means, traced operators, although acting on the sub-space of a sub-system include quantities belonging to the bipartite compound system on the whole. The density operators \( \varrho^1 \) and \( \varrho^2 \) and the propagators \( \dot{\varrho}^1 \) and \( \dot{\varrho}^2 \) of the sub-systems \#1 and \#2 result from uninvertible tracing according to (161) to (164):

\[
\varrho_{\text{com}} \rightarrow (\varrho^1, \varrho^2) \rightarrow \varrho_{\text{com}}, \quad \dot{\varrho}_{\text{com}} \rightarrow (\dot{\varrho}^1, \dot{\varrho}^2) \rightarrow \dot{\varrho}_{\text{com}}. \quad (178)
\]

That means, the knowledge of \( \varrho^1 \) and \( \varrho^2 \) does not replace \( \varrho_{\text{com}} \).

If we introduce

\[
\dot{\varrho}^1 := -\frac{i}{\hbar} \text{Tr}^2 \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] + \dot{\varrho}^1, \quad \dot{\varrho}^2 := -\frac{i}{\hbar} \text{Tr}^1 \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] + \dot{\varrho}^2, \quad (179)
\]

the equations of motion (176) and (177) result in

\[
\dot{\varrho}^1 = -\frac{i}{\hbar} \left[ \mathcal{H}^1, \varrho^1 \right] + \dot{\varrho}^1, \quad \dot{\varrho}^2 = -\frac{i}{\hbar} \left[ \mathcal{H}^2, \varrho^2 \right] + \dot{\varrho}^2. \quad (180)
\]

The shape of the partial equations of motion (180) of the sub-sytems is identical with that of the compound system (38) except for \( \dot{\varrho} \) is replaced by \( \dot{\varrho}^1 \) and \( \dot{\varrho}^2 \).

5.3 The exchanges

5.3.1 Power exchange

The Hamiltonian and its decomposition (28) is identical to those of compound systems (68) and (69). Consequently, also the power exchanges (71) and (72) remain unchanged by the transfer to compound systems

\[
\dot{W}^{\text{ex}}_1 \equiv \dot{W}^{\text{ex}}_{1\text{c}} = \text{Tr}^1 \text{Tr}^2 \left( \frac{\partial \mathcal{H}^1}{\partial a^1} \varrho_{\text{com}} \right) \cdot \dot{a}^1 = \text{Tr}^1 \left( \frac{\partial \mathcal{H}^1}{\partial a^1} \varrho^1 \right) \cdot \dot{a}^1, \quad (181)
\]

\[
\dot{W}^{\text{int}}_1 \equiv \dot{W}^{\text{int}}_{1\text{c}} = \text{Tr}^1 \text{Tr}^2 \left( \frac{\partial \mathcal{H}^1}{\partial a_{12}} \varrho_{\text{com}} \right) \cdot \dot{a}^{12} = \text{Tr}^1 \left( \frac{\partial \mathcal{H}^1}{\partial a_{12}} \varrho^1 \right) \cdot \dot{a}^{12}, \quad (182)
\]

\[
\dot{W}^{\text{int}}_{12} \equiv \dot{W}^{\text{int}}_{12\text{c}} = \text{Tr} \left( \frac{\partial \mathcal{H}^{12}}{\partial a_{12}} \varrho_{\text{com}} \right) \cdot \dot{a}^{12}. \quad (183)
\]
Also the relations of external and internal power exchange (73) and (75) remain their validity for decomposed described systems. The concept of an inert partition is independent of a compound or decomposed description: $\dot{W}_{12}^{\text{int}} \equiv 0$.

### 5.3.2 Heat- and entropy-exchange

First of all, the relations (85) and (94) to (97) remain valid in decomposed systems because they are of thermodynamical origin and thus independent of the quantum mechanical description of the system. As the power exchanges, also the heat exchanges are independently defined of the system’s description. Consequently, we have according to (82) and (83)

$$Q_A = \text{Tr}^A( H_A \hat{\varrho}_A ) = \text{Tr}(H_A \hat{\varrho}_{\text{com}}) = \dot{Q}_A, \text{ A}=1,2. \quad (184)$$

$$\Xi_A := \text{Tr}^A \left( \frac{H_A}{\Theta_A} \hat{\varrho}_A \right) = \text{Tr} \left( \frac{H_A}{\Theta_A} \hat{\varrho}_{\text{com}} \right) = \Xi_A, \text{ A}=1,2. \quad (185)$$

According to (88), this heat exchange has to be split into its internal and external part. Taking (87) and (89) into account, we obtain

$$\dot{Q}_{\text{int}}^A := -\frac{i}{\hbar} \text{Tr}^A \left( H_A \text{Tr}^B \left[ H, \hat{\varrho}_{\text{com}} \right] \right) + \text{Tr}^A \left( \frac{H_A}{\Theta_A} \hat{\varrho}_{\text{iso}} \right), \quad (186)$$

$$\dot{Q}_{\text{ex}}^A := \text{Tr}^A \left( \frac{H_A}{\Theta_A} \hat{\varrho}_{\text{ex}}^A \right), \quad A,B=1,2, A \neq B, \quad (187)$$

$$\dot{Q}_{12}^{\text{int}} = \dot{Q}_{12}^{\text{int}}, \quad \dot{Q}_{12}^{\text{ex}} = \dot{Q}_{12}^{\text{ex}} \quad (188)$$

As the heat exchanges, also the entropy exchanges are identical in compound and decomposed description

$$\Xi_{\text{int}}^A := -\frac{i}{\hbar} \text{Tr}^A \left( \frac{H_A}{\Theta_A} \text{Tr}^B \left[ H, \hat{\varrho}_{\text{com}} \right] \right) + \text{Tr}^A \left( \frac{H_A}{\Theta_A} \hat{\varrho}_{\text{iso}} \right), \quad (189)$$

$$\Xi_{\text{ex}}^A := \text{Tr}^A \left( \frac{H_A}{\Theta_A} \hat{\varrho}_{\text{ex}}^A \right), \quad A,B=1,2, A \neq B, \quad (190)$$

$$\Xi_{12}^{\text{int}} = \Xi_{12}^{\text{int}}, \quad \Xi_{12}^{\text{ex}} = \Xi_{12}^{\text{ex}}. \quad (191)$$

### 5.4 Entropy rate and contact temperature

Starting with (169)

$$S_A = -k_B \text{Tr}(\hat{\varrho}_{\text{com}} \ln \hat{\varrho}^A) = -k_B \text{Tr}^A(\hat{\varrho}^A \ln \hat{\varrho}^A) \quad (192)$$

results by taking (176) into account

$$\dot{S}_A = -k_B \text{Tr}^A(\hat{\varrho}^A \ln \hat{\varrho}^A) =$$
\[
\begin{align*}
= -k_B \text{Tr}^A \left\{ \left( -\frac{i}{\hbar} [\mathcal{H}^A, \varrho^A] - \frac{i}{\hbar} \text{Tr} B \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] + \varrho^A \right) \ln \varrho^A \right\} & = \\
= -k_B \text{Tr}^A \left\{ \left( -\frac{i}{\hbar} \text{Tr} B \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \right. \right. & = \\
= k_B \text{Tr} \left( \frac{i}{\hbar} \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \right) \ln \varrho^A & = \\
= -k_B \text{Tr} \left\{ \left( \varrho_{\text{com}} - \frac{i}{\hbar} \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \right) \ln \varrho^A \right\}.
\end{align*}
\] (193)

Summing up the entropy time rates of the sub-systems, we obtain from (193) and (98)

\[
\dot{S}_1 + \dot{S}_2 - \dot{S} = \\
= -k_B \text{Tr} \left\{ \left( \varrho_{\text{com}} - \frac{i}{\hbar} \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \right) \ln (\varrho^1 \varrho^2) - \varrho_{\text{com}} \ln \varrho_{\text{com}} \right\} = \\
= -k_B \text{Tr} \left\{ -\frac{i}{\hbar} \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \ln (\varrho^1 \varrho^2) + \varrho_{\text{com}} \left( \ln (\varrho^1 \varrho^2) - \ln \varrho_{\text{com}} \right) \right\}, \tag{194}
\]

that means, the sum of the entropy rates of the sub-systems is different from the entropy rate of the undecomposed system. The same non-additivity which appears for the entropy itself according to (174) is called compound deficiency. Some more details are discussed in sect. 5.6.

According to (20) and taking (184) and (185) into account, the entropy production of the sub-system #A is defined by

\[
\Sigma_A := \dot{S}_A - \Xi_A = \dot{S}_A - \frac{\dot{Q}_A}{\Theta_A} = \dot{S}_A - \frac{\dot{Q}^A}{\Theta^A}. \tag{195}
\]

Consequently, the quantum mechanical expression of the contact temperature \(\Theta_A\) of sub-system #A results in

\[
\frac{1}{\Theta^A} = \frac{\dot{S}_A}{\dot{Q}_A} = -k_B \text{Tr} \left\{ \left( \varrho_{\text{com}} - \frac{i}{\hbar} \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \right) \ln \varrho^A \right\} - \frac{i}{\hbar} \text{Tr} \left( \mathcal{H}^A \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \right) + \text{Tr} \left( \mathcal{H}^A \varrho_{\text{com}} \right), \tag{196}
\]

by taking (193), (184), and (82) into account.

### 5.5 Entropy production

Inserting (193), (84) and (82) into (195), we obtain

\[
\Sigma_A = -k_B \text{Tr} \left\{ \left( \varrho_{\text{com}} - \frac{i}{\hbar} \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \right) \ln \varrho^A \right\} + \\
+ \frac{i}{\hbar} \text{Tr} \left( \mathcal{H}^A \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \right) - \text{Tr} \left( \mathcal{H}^A \varrho_{\text{com}} \right) = \\
= -k_B \text{Tr} \left\{ \left( \ln \varrho^A + \frac{\mathcal{H}^A}{\Theta^A} \right) \varrho_{\text{com}} \right\} + \\
+ k_B \text{Tr} \left\{ \frac{i}{\hbar} \left[ \mathcal{H}^{12}, \varrho_{\text{com}} \right] \left( \ln \varrho^A + \frac{\mathcal{H}^A}{\Theta^A} \right) \right\}. \tag{197}
\]

30
From (197) follows that vanishing entropy production is not sufficient for equilibrium. If the density operator \( \rho^A \) of the sub-system \( \#A \) is canonical, the entropy production vanishes in the sub-system, but \( \dot{\rho}^A \) may be different from zero and no equilibrium is present. If vice-versa \( \dot{\rho}^A \) vanishes, the entropy production in the sub-system is according to (195), (193), and (184), zero, but \( \rho^A \) can be arbitrary and equilibrium is absent. The equilibrium conditions (116) and (117) are more farreaching than the vanishing of the entropy production.

5.6 Compound deficiency

As already discussed, heat- and entropy exchanges (94) to (97), the entropies of sub-systems (174) and the entropy rates (194) are not additive, that means, summing up quantities of the sub-systems does not result in the corresponding quantity of the undecomposed system. As already mentioned, there are two reasons for this non-additivity which is called compound deficiency: the classical decomposition of the system and the quantum interaction between the sub-systems. This item will be discussed in more detail.

For elucidating the compound deficiency, we compare quantities of the compound system with the corresponding ones of the undecomposed system. The general definition of the compound deficiency \( \mathfrak{cd} \) of the quantity \( \mathfrak{x} \) is

\[
\mathfrak{cd} := \mathfrak{x} - \mathfrak{x}^1 - \mathfrak{x}^2 =: \mathfrak{x} - \mathfrak{x}^{da}.
\]

(198)

Here, \( \mathfrak{x} \) belongs to the undecomposed system, whereas \( \mathfrak{x}^1 \) and \( \mathfrak{x}^2 \) belong to the sub-systems of the corresponding bipartite system, and \( \mathfrak{x}^{da} \) is the quantity generated by decomposed additivity. In general, the compound deficiency does not vanish. Consequently, there are two possibilities to describe a system: as a decomposed one by \( \mathfrak{x}^{da} \) or as an undecomposed one by \( \mathfrak{x} \). These descriptions are of different information about the system, if the compound deficiency is not zero. The answer to the question “What is the correct entropy production of the system?” depends on its description chosen as decomposed or undecomposed.

According to (198), we obtain from (28) the compound deficiency of the Hamiltonian

\[
\mathcal{H}_{cd} := \mathcal{H} - \mathcal{H}^1 - \mathcal{H}^2 = \mathcal{H}^{12},
\]

(199)

which is caused by the interaction part, a fact which is obvious: the sum of the Hamiltonians of the sub-sytems differ from the Hamiltonian of the corresponding undecomposed system.
5.7 Removing semi-classical description

Up to now, the systems, described in sect 2 and sect 4, are treated semi-classically, that means, the external exchange quantities are not connected to an interaction Hamiltonian. Thus, the external heat exchange \( \Theta \), and the external entropy exchange \( \Theta_1 \), vanish in isolated systems not by the vanishing of an interaction Hamiltonian, but by that of the exchange propagator \( \Pi \). This procedure is called semi-classical, because the contact temperature \( T \) is used as a classical quantity whose quantum-mechanical definition \( \Theta \) was not taken into account (because it is unknown on this level). We now remove this semi-classical description by introducing an interaction Hamiltonian describing the partition between an undecomposed sub-system and its environment which is later on chosen as an equilibrium heat reservoir.

We now consider an externally isolated bipartite system which is according to \( (200) \) described by

\[
\begin{align*}
\gamma_{ex} &\equiv 0, \quad \gamma_{com} \equiv \gamma_{iso}.
\end{align*}
\]

The sub-system #2 is now the environment of sub-system #1. The quantum mechanical interaction between them is represented by the Hamiltonian \( \mathcal{H}^{ia} \). For more convenience, we change the denotation of the partial Hamiltonians

\[
\begin{align*}
\mathcal{H}^1 &\Rightarrow \mathcal{H}, \\
\mathcal{H}^2 &\Rightarrow \mathcal{H}^{\square}, \\
\mathcal{H}^{12} &\Rightarrow \mathcal{H}^{ia}, \\
\mathcal{H} &\Rightarrow \mathcal{H}_{tot}, \\
\mathcal{H}_{tot} &= \mathcal{H} + \mathcal{H}^{\square} + \mathcal{H}^{ia},
\end{align*}
\]

the density operators

\[
\begin{align*}
\text{Tr}^2 \gamma_{com} &= \gamma^1 \Rightarrow \gamma, \\
\text{Tr}^1 \gamma_{com} &= \gamma^2 \Rightarrow \gamma^{\square},
\end{align*}
\]

the work variables

\[
\begin{align*}
\hat{a}^1 &\Rightarrow 0, \\
\hat{a}^2 &\Rightarrow 0, \\
\hat{a}^{ia} &\Rightarrow \hat{a}^{ia},
\end{align*}
\]

and the contact temperatures

\[
\begin{align*}
\Theta^1 &\Rightarrow \Theta, \\
\Theta^2 &\Rightarrow \Theta^{\square}, \\
\Theta^{12} &\Rightarrow \Theta^{ia}.
\end{align*}
\]

System and its environment are each undecomposed sub-systems of the bipartite system whose environment is not defined and excluded by \( \gamma_{ex} \equiv 0 \). In more detail, we obtain after having inserted the changed denotations:
5.7.1 Equations of motion

from (175):

\[ \dot{\rho}_{\text{com}} = -\frac{i}{\hbar} \left[ \mathcal{H} + \mathcal{H}^\square + \mathcal{H}^{ia}, \rho_{\text{com}} \right] + \dot{\rho}_{\text{com}}, \quad \text{Tr}^{\text{com}} = \text{Tr}^\square, \quad (205) \]

from (176) and (177):

\[ \dot{\varrho} = -\frac{i}{\hbar} \left[ \mathcal{H}, \varrho \right] - \frac{i}{\hbar} \text{Tr}^\square \left[ \mathcal{H}^{ia}, \rho_{\text{com}} \right] + \varrho, \quad (206) \]

\[ \dot{\varrho}^\square = -\frac{i}{\hbar} \left[ \mathcal{H}^\square, \varrho \right] - \frac{i}{\hbar} \text{Tr} \left[ \mathcal{H}^{ia}, \rho_{\text{com}} \right] + \varrho^\square. \quad (207) \]

5.7.2 Power exchange

from (182), (183) and (74)

\[ \left\{ \text{Tr} \left( \frac{\partial \mathcal{H}}{\partial a^{ia}} \dot{\rho} \right) + \text{Tr}^\square \left( \frac{\partial \mathcal{H}^\square}{\partial a^{ia}} \dot{\rho}^\square \right) + \text{Tr}^{\text{com}} \left( \frac{\partial \mathcal{H}^{ia}}{\partial a^{ia}} \rho_{\text{com}} \right) \right\} \cdot \dot{a}^{ia} = \dot{\mathbf{W}} + \dot{\mathbf{W}}^\square + \dot{\mathbf{W}}_{ia} = 0. \quad (208) \]

5.7.3 Heat exchange

from (186)

\[ \dot{Q} = -\frac{i}{\hbar} \text{Tr} \left( \mathcal{H} \text{Tr}^\square \left[ \mathcal{H}_{\text{tot}}, \rho_{\text{com}} \right] \right) + \text{Tr} \left( \mathcal{H} \varrho^A \right), \quad (209) \]

\[ \dot{Q}^\square := -\frac{i}{\hbar} \text{Tr}^\square \left( \mathcal{H} \text{Tr} \left[ \mathcal{H}_{\text{tot}}, \rho_{\text{com}} \right] \right) + \text{Tr}^\square \left( \mathcal{H}^\square \varrho^\square \right), \quad (210) \]

\[ \dot{Q}_{ia} := -\frac{i}{\hbar} \text{Tr}^{\text{com}} \left( \mathcal{H}^{ia} \left[ \mathcal{H}_{\text{tot}}, \rho_{\text{com}} \right] \right) + \text{Tr}^{\text{com}} \left( \mathcal{H}^{ia} \varrho_{\text{com}} \right), \quad (211) \]

from (95)

\[ \dot{Q} + \dot{Q}^\square + \dot{Q}_{ia} = 0. \quad (212) \]

5.7.4 Entropy rate and production

from (194)

\[ \dot{S} + \dot{S}^\square - \dot{S} = -k_B \text{Tr}^{\text{com}} \left\{ \left( \rho_{\text{com}} - \frac{i}{\hbar} \left[ \mathcal{H}^{ia}, \rho_{\text{com}} \right] \right) \ln(\rho^\square) - \rho_{\text{com}} \ln \rho_{\text{com}} \right\}, \quad (213) \]

\[ = -k_B \text{Tr}^{\text{com}} \left\{ -\frac{i}{\hbar} \left[ \mathcal{H}^{ia}, \rho_{\text{com}} \right] \ln(\rho^\square) + \rho_{\text{com}} \left( \ln(\rho^\square) - \ln \rho_{\text{com}} \right) \right\}. \quad (214) \]

The entropy rates are additive, if the quantum mechanical interaction vanishes and the density operator of the decomposed system decomposes into the product of the density operators of the sub-systems.

from (197)

\[ \Sigma_A = -k_B \text{Tr} \left\{ \left( \ln q^A + \frac{\mathcal{H}^A}{\Theta^A} \right) \rho_{\text{com}} \right\} \quad (215) \]
5.7.5 Equilibrium and heat reservoir

A part of the necessary equilibrium conditions (116) and (117) is

\[ \dot{\rho}_{eq} = 0, \quad \dot{\rho}^{\bullet}_{eq} = 0, \quad \rho^{\circ}_{eq} = 0, \quad \rho^{\circ\bullet}_{eq} = 0. \]  
(216)

According to (176) and (177), the equilibrium conditions (216) result in

\[ \left[ H, \rho_{eq} \right] = -\text{Tr}^\bullet \left[ H^a, \rho^a_{com} \right], \] 
(217)

\[ \left[ H^\bullet, \rho^\bullet_{eq} \right] = -\text{Tr}^\circ \left[ H^a, \rho^a_{com} \right]. \] 
(218)

Obvious is, that \( \rho_{eq} \) and \( \rho^\bullet_{eq} \) are not of canonical or micro-canonical form, (136) or (133), because the RHSs of (217) and (218) are not zero in general, except if the quantum mechanical interaction vanishes. If there is a mutual equilibrium of two interacting sub-systems, the density operators of these sub-systems do not commute with the corresponding Hamiltonians, if the right-hand traces do not vanish.

We now presuppose that the environment \( \overset{\bullet}{\#} \) of the system is a heat reservoir. In this case, the density operator \( \rho^\bullet_{eq} = \rho_{can} \) is canonical (136) and commutes with \( H^\bullet \). Consequently,

\[ 0 = \text{Tr} \left[ H^a, \rho^a_{com} \right] \] 
(219)

is valid. Reservoir property means that the heat reservoir, during the contact with the undecomposed system in consideration, is always in equilibrium having the thermostatic temperature \( T^\bullet \). Because it is a closed non-isolated system in equilibrium, the density operator of the heat reservoir is canonical for all times

\[ \rho^\bullet_{eq}(t) = \rho_{can} = \frac{1}{Z} \exp \left\{ - \frac{H^\bullet}{k_B T^\bullet_{eq}} \right\} = \text{Tr} \rho^a_{com}. \] 
(220)

The equilibrium density operator \( \rho^a_{com} \) of the undecomposed system which belongs to the considered bipartite system has to satisfy (219) and according to (217)

\[ \left[ H, \text{Tr}^\bullet \rho^a_{com} \right] = -\text{Tr}^\circ \left[ H^a, \rho^a_{com} \right]. \] 
(221)

Beyond that

\[ 0 = \text{Tr}^\circ \left[ H^a, \rho^a_{com} \right] \] 
(222)

is valid according to (217) and (219).
6 Summary

The density operator satisfying the von Neumann equation is in conventional quantum mechanics time independently composed of pure quantum states. If this time independence is waived, the von Neumann equation is modified by a so-called propagator without changing the quantum mechanical dynamics. The composition of the density operator becomes time dependent in contrast to the original von Neumann equation. This introduction of the propagator makes possible to define thermodynamical quantities beyond quantum mechanics.

The following non-equilibrium quantities of an undecomposed system in contact with an equilibrium environment can be defined by combined thermodynamical and quantum mechanical settings: power- and heat-exchange, the entropy time rate based on the Shannon entropy, entropy exchange and production. The interaction between system and environment is preliminary semi-classically described. Heat- and entropy-exchange depend on the propagator and on the Hamiltonian, whereas the power exchange is independent of the propagator. The entropy production is an internal quantity of the system, independent of the environment, of the Hamiltonian and of the contact temperature, it depends only on the propagator.

Taking the decomposition of the Hamiltonian into its parts according to the sub-systems and their interaction into account, a compound system can be defined. The above mentioned exchanges are decomposed into internal and external ones by decomposing the propagator. As a preliminary auxiliary procedure, the interaction between system and environment is described semi-classically. Some special cases are investigated: vanishing quantum mechanical interaction between the sub-systems, external heat- and entropy-exchanges, equilibria and the equilibrium distributions of the isolated and non-isolated system are derived by thermodynamical considerations. The Second Law is taken into consideration, and a quantum theoretical expression of the contact temperature is derived. Preliminary constitutive equations of the propagator are sketched.

The decomposition of the density operator by tracing out one or the other sub-system makes the semi-classical description dispensable. Partial entropies and entropy rates of the sub-systems, and equations of motion of the sub-system density operators are introduced. Equilibria of bipartite systems are considered, especially those for which one sub-system is a heat reservoir. Restrictions for the density operator of the corresponding compound system in equilibrium are derived.

\[19\] undecomposed means: neither the Hamiltonian nor the density operator of the bipartite system are decomposed according to the sub-systems

\[20\] semi-classical means: heat- and entropy-exchange between system and environment are classically described without a special interaction Hamiltonian
7 Appendices

7.1 Appendix 1: Tracing

Starting with a tensor of the decomposed system

\[ A = \sum_{kl} \sum_{pq} |\Psi_{1}^{k}\rangle |\Psi_{2}^{l}\rangle A_{kl}^{pq} \langle \Psi_{2}^{q}| \langle \Psi_{1}^{p}|, \]  

(223)

and its traces

\[ \text{Tr}^{1} A = \sum_{lq} |\Psi_{2}^{l}\rangle \sum_{m} A_{ml}^{m} \langle \Psi_{2}^{q}| =: A^2, \]  

(224)

\[ \text{Tr}^{2} A = \sum_{kp} |\Psi_{1}^{k}\rangle \sum_{m} A_{km}^{m} \langle \Psi_{1}^{p}| =: A^1. \]  

(225)

Because partial traces commute, we obtain

\[ \text{Tr}^{2} A^2 = \text{Tr}^{2} \text{Tr}^{1} A = \text{Tr} A = \text{Tr}^{1} \text{Tr}^{2} A = \text{Tr}^{1} A^1 = \sum_{mr} A_{rm}^{m}. \]  

(226)

\[ \text{Tr}(A^{1} B) = \text{Tr}^{1} \text{Tr}^{2}(A^{1} B) = \text{Tr}^{1}(A^{1} B^{1}). \]  

(227)

A detailed calculation

\[ \text{Tr}^{1}(A^{1} B) = \sum_{j} \sum_{sr} \sum_{kl} \sum_{pq} \langle \Psi_{2}^{j}| \Psi_{1}^{s}\rangle A_{j}^{s} \langle \Psi_{1}^{k}| \Psi_{2}^{l}\rangle B_{kl}^{pq} \langle \Psi_{2}^{q}| \langle \Psi_{1}^{p}| \]  

(228)

\[ = \sum_{j} \sum_{k} \sum_{ql} A_{j}^{k} B_{kl}^{pq} \langle \Psi_{2}^{q}| \langle \Psi_{1}^{p}|. \]

\[ \text{Tr}^{1}(B A^{1}) = \sum_{j} \sum_{kl} \sum_{pq} \sum_{sr} \langle \Psi_{1}^{j}| \Psi_{2}^{k}\rangle B_{kl}^{pq} \langle \Psi_{1}^{s}| \Psi_{2}^{l}\rangle A_{j}^{s} \langle \Psi_{2}^{q}| \]  

(229)

\[ = \sum_{j} \sum_{p} \sum_{ql} B_{jl}^{pq} A_{j}^{p} \langle \Psi_{2}^{q}| = \sum_{j} \sum_{k} \sum_{ql} B_{kl}^{pq} A_{j}^{k} \langle \Psi_{2}^{q}| \]  

results in

\[ \text{Tr}^{1}[A^{1}, B] = 0 \implies \text{Tr}^{2} \text{Tr}^{1}[A^{1}, B] = \text{Tr}^{1}[A^{1}, B^{1}] = 0. \]  

(230)
7.2 Appendix 2: Entropy exchange inequality

Consider an undecomposed system of the contact temperature \( \Theta \) which exchanges heat \( \dot{Q}(T^\circ) \) with its equilibrium environment of the thermostatic temperature \( T^\circ \). According to (21), we have after the decomposition of the heat exchange into its positive and negative parts

\[
\dot{Q}^+(T^\circ) \geq 0, \quad \dot{Q}^-(T^\circ) \leq 0, \quad \dot{Q}^+(T^\circ) + \dot{Q}^-(T^\circ) = Q(T^\circ),
\]

(231)

\[
\left( \dot{Q}^+(T^\circ) + \dot{Q}^-(T^\circ) \right) \left( \frac{1}{\Theta} - \frac{1}{T^\circ} \right) \geq 0.
\]

(232)

\[
\dot{Q}^+(T^\circ) \left( \frac{1}{\Theta^+} - \frac{1}{T^\circ} \right) \geq 0, \quad \dot{Q}^-(T^\circ) \left( \frac{1}{\Theta^-} - \frac{1}{T^\circ} \right) \geq 0.
\]

(233)

The contact temperatures are independent of the thermostatic temperatures of the environment. Consequently, we obtain from (233) and (232) for the special choice

\[
T^\circ = \Theta^- \rightarrow \dot{Q}^-(\Theta^-) = 0;
\]

(234)

\[
\dot{Q}^+(\Theta^-) \left( \frac{1}{\Theta^+} - \frac{1}{\Theta^-} \right) \geq 0, \quad \dot{Q}^+(\Theta^-) \left( \frac{1}{\Theta^-} - \frac{1}{\Theta^+} \right) \geq 0,
\]

(235)

and

\[
T^\circ = \Theta^+ \rightarrow \dot{Q}^+(\Theta^+) = 0;
\]

(236)

\[
\dot{Q}^-(\Theta^+) \left( \frac{1}{\Theta^-} - \frac{1}{\Theta^+} \right) \geq 0, \quad \dot{Q}^-(\Theta^+) \left( \frac{1}{\Theta^+} - \frac{1}{\Theta^-} \right) \geq 0,
\]

(237)

resulting in

\[
\Theta^+ \leq \Theta \leq \Theta^-.
\]

(238)

Taking (238) into account, we obtain

\[
\frac{\dot{Q}^+(T^\circ)}{\Theta^+} \geq \frac{\dot{Q}^+(T^\circ)}{\Theta^-}, \quad \frac{\dot{Q}^-(T^\circ)}{\Theta^-} \geq \frac{\dot{Q}^-(T^\circ)}{\Theta^+},
\]

(239)

\[
\Rightarrow \frac{\dot{Q}^+(T^\circ)}{\Theta^+} + \frac{\dot{Q}^-(T^\circ)}{\Theta^-} \geq \frac{\dot{Q}(T^\circ)}{T^\circ} \geq \frac{\dot{Q}^+(T^\circ)}{\Theta^+} + \frac{\dot{Q}^-(T^\circ)}{\Theta^-}.
\]

(240)

Consider a set of heat exchanges \( \dot{Q}^j(T^\circ) \) between a set of sub-systems of the contact temperatures \( \Theta^j \) and an equilibrium environment of the thermostatic temperature \( T^\circ \). The proof of the inequality (239) runs as follows:

\[
\sum_j \frac{\dot{Q}^j(T^\circ)}{\Theta^j} = \sum_k \frac{\dot{Q}^{k+}(T^\circ)}{\Theta^k} + \sum_m \frac{\dot{Q}^{m-}(T^\circ)}{\Theta^m} = \frac{\dot{Q}^+(T^\circ)}{\Theta^+} + \frac{\dot{Q}^-(T^\circ)}{\Theta^-}.
\]

(241)
The sum (241) is decomposed into its positive and negative parts which are transformed by the mean value theorem

\[
\begin{align*}
\dot{Q}^+ (T^\square) := & \sum_k \dot{Q}^{k+} (T^\square), \\
\dot{Q}^-(T^\square) := & \sum_k \dot{Q}^{k-} (T^\square), \\
\rightarrow & \Theta^+ \text{ and } \Theta^-.
\end{align*}
\] (242)

Taking (240) into account, we obtain

\[
\sum_j \frac{\dot{Q}^j (T^\square)}{\Theta^j} \geq \frac{\dot{Q} (T^\square)}{\Theta} \geq \frac{\dot{Q} (T^\square)}{T^\square}.
\] (243)

The inequality (85) is a special case of (243).

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