Concepts of Phenomenological Irreversible Quantum Thermodynamics I: Closed Undecomposed Schottky Systems in Semi-classical Description

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

Abstract
If the von Neumann equation is modified by time dependent statistical weights, the time rate of entropy, the entropy exchange and production of a Schottky system are derived whose Hamiltonian does not contain the interaction with the system’s environment. This interaction is semi-classically described by the quantum theoretical expressions of power- and entropy exchange.

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 into 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. The second way is to alter von Neumann’s equation by introducing time dependent weights of the statistical operator, thus obtaining irreversibility. Other possibilities, introducing a restricted set of observables thus creating irreversibility by loss of information [1], or using statistical concepts as ad-hoc microcanonical or canonical ensembles, are out of scope of this paper.

An undecomposed closed system interacting with its environment by heat

∗Corresponding author: muschik@physik.tu-berlin.de
and power exchange is considered. Undecomposed means, that the Hamiltonian of the system does not contain an interaction part, neither for internal interaction nor for that with its environment. As usual for Schottky systems, the interaction with the environment is phenomenologically described by heat-, power- and material exchange which is here suppressed considering closed systems. From a quantum theoretical point of view, this description is semi-classical. The task of quantum thermodynamics is to determine entropy production and exchange quantum-theoretically. This is done by using a modified von Neumann equation which allows a non-vanishing entropy rate by introducing time dependent weights of the statistical operator.

The paper is organized as follows: After recalling and modifying the von Neumann equation, the preliminary expressions of entropy exchange and production are introduced. The entropy exchange contains the contact temperature, a non-equilibrium analogue of the thermostatic temperature, which is shortly discussed. The consideration of special processes, such as adiabatic and reversible ones, and of equilibria in isolated and in closed systems allows to derive a quantum theoretical expression of the contact temperature.

2 Schottky Systems

As usual in thermodynamics, we consider a Schottky system \([2, 3, 4]\), that is a discrete system in interaction with its environment exchanging heat, power and material. Here, we restrict ourselves first of all to closed discrete systems for which the material exchange is suppressed by a suitable partition between the system and its environment. The interaction between them is described by the heat exchange \(\dot{Q}\) and by the power exchange \(\dot{W}\), not introducing a Hamiltonian of interaction. Consequently, we use for the present a semi-classical description of the undecomposed system. The entropy exchange for this easy case is given by the heat exchange over the contact temperature \(\Theta\), a non-equilibrium temperature which is defined phenomenologically \([5, 6]\) and quantum theoretically later on. The sum of the entropy exchange and the entropy production is the entropy time rate of the closed system \([7]\) whose quantum theoretical expression is derived by using the Shannon entropy.

3 The Modified von Neumann Equation

Starting with a basis of pure quantum states \(\{|\Phi^j>\}\) which are normalized, complete and orthogonal \([8]\)

\[<\Phi^j|\Phi^j> = 1, \quad \land k \neq l : <\Phi^k|\Phi^l> = 0, \quad \sum_j |\Phi^j><\Phi^j| = 1, \quad (1)\]
and satisfying the Schrödinger equation

\[ i\hbar \partial_t |\Phi^j > = \mathcal{H}|\Phi^j >, \quad j = 1, 2, 3, \ldots \]

(2)

the self-adjoint non-equilibrium density operator \( \varrho \) is defined by introducing the weights \( \{p_j\} \)

\[ \varrho := \sum_j p_j |\Phi^j > < \Phi^j|, \quad 0 \leq p_j \leq 1, \quad \sum_j p_j = 1, \quad \text{Tr} \varrho = 1 \]

(3)

From (3) and (2) follows

\[ \partial_t \varrho = \sum_j \dot{p}_j |\Phi^j > < \Phi^j| + \sum_j p_j |\frac{1}{i\hbar} \mathcal{H}\Phi^j > < \Phi^j| + \sum_j p_j |\Phi^j > < \frac{1}{i\hbar} \mathcal{H}\Phi^j| \]

(5)

Taking into account that the trace is defined as

\[ \text{Tr}(A) = \text{Tr} \sum_k a_k |\varphi_k > < \psi_k| = \sum_k a_k < \psi_k| \varphi_k > \]

(6)

and that the Hamilton operator is self-adjoint, \( \mathcal{H}^+ = \mathcal{H} \), we obtain with (1) and (3)

\[ \text{Tr}(\partial_t \varrho) = \sum_j \dot{p}_j = 0 \]

(7)

Consequently, the von Neumann equation (5)

\[ \partial_t \varrho \equiv \dot{\varrho} = -\frac{i}{\hbar} [\mathcal{H}, \varrho] + \ddot{\varrho}, \quad \ddot{\varrho} := \sum_j \dot{p}_j |\Phi^j > < \Phi^j| \]

(8)

results in

\[ \text{Tr}(\partial_t \varrho) = \text{Tr}(\ddot{\varrho}) = 0 \]

(9)

In contrast to the conventional quantum theory, we introduce the

**Axiom I:**

\[ \forall j : \quad \dot{p}_j \neq 0 \rightarrow \ddot{\varrho} \neq 0 \]

(10)

which generates the propagator (8)2 modifying the von Neumann equation (8)1.

The modified von Neumann equation shows that the time dependence of the
density operator has two reasons: the quantum mechanical dynamics represented by the commutator in \((8)_1\) and the time dependence of the propagator in \((8)_2\). 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 axiom I means, that irreversibility is generated by an in time changing composition of the density operator \(\varrho\).

### 3.1 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 system and its environment. The energy of the considered system is

\[
E := \text{Tr}(\mathcal{H}\varrho),
\]

(11)

and the time rate

\[
\dot{E} = \text{Tr}(\dot{\mathcal{H}}\varrho) + \text{Tr}(\mathcal{H}\dot{\varrho})
\]

(12)

can be split into power- and heat-exchange according to the 1st law of thermodynamics for closed systems

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

(13)

According to \((8)_1\), the heat exchange becomes

\[
\dot{Q} = \text{Tr}\left(\mathcal{H}\left(-\frac{i}{\hbar}[\mathcal{H}, \varrho] + \hat{\varrho}\right)\right).
\]

(14)

Taking

\[
\text{Tr}
\left(\mathcal{H}\left[\mathcal{H}, \varrho\right]\right) = \text{Tr}\left[\mathcal{H}, \mathcal{H}\varrho\right] = 0
\]

(15)

into account, we obtain by \((8)_2\)

\[
\dot{Q} = \text{Tr}\left(\mathcal{H}\hat{\varrho}\right) = \text{Tr}\left(\mathcal{H} \sum_j \hat{p}_j |\Phi^j><\Phi^j|\right),
\]

(16)

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

\[
\dot{W} = \text{Tr}\left(\frac{\partial\mathcal{H}}{\partial\mathbf{a}}\right) \cdot \dot{\mathbf{a}} =: \mathbf{A} \cdot \dot{\mathbf{a}}.
\]

(17)

Power- and energy-rates are exchange quantities between the undecomposed system and its environment. An interaction Hamiltonian describing the dependence of the system on its environment is not introduced. System and environment are not treated as a composed (bipartite, compound) system,
but their interaction with each other is described *semi-classically* by the time dependent composition \( \{ \dot{p}_j \} \) of the density operator and by the time rates of the work variables \( \dot{a} \). Consequently, the considered system is for the present an undecomposed one with an undecomposed Hamiltonian \( H \). Bipartite systems will be treated quantum theoretically in a following paper.

### 3.2 Entropy exchange and production

The non-equilibrium entropy \( S \) of the considered system, the Shannon entropy, is introduced [9] as an

\[
\text{Axiom II:} \quad S(\rho) := -k_B \text{Tr}(\rho \ln \rho) \tag{18}
\]

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

Inserting the modified von Neumann equation (8) into the Shannon non-equilibrium entropy (18), we obtain

\[
\dot{S} = -k_B \text{Tr}\left(\left(-\frac{i}{\hbar} [H, \rho] + \dot{\rho} \right) \ln \rho \right) - k_B \text{Tr}(\rho \partial_t (\ln \rho)). \tag{19}
\]

Inserting

\[
[H, \rho] \ln \rho = H\rho \ln \rho - \rho H \ln \rho = (H \ln \rho)\rho - \rho H \ln \rho = \left[ H, \rho \right] \ln \rho \tag{20}
\]

we obtain

\[
\dot{S} = -k_B \text{Tr}(\dot{\rho} \ln \rho) - k_B \text{Tr}(\partial_t \rho) = -k_B \text{Tr}(\dot{\rho} \ln \rho). \tag{21}
\]

The last term vanishes according to (9).

Starting with

\[
\text{Tr}\left(\dot{\rho} \ln(Z\rho)\right) = \text{Tr}\left(\dot{\rho} \left( \ln Z1 + \ln \rho \right) \right) = \text{Tr}(\dot{\rho} \ln \rho), \tag{22}
\]

we obtain by taking (9) and (21) into account

\[
\dot{S} = -k_B \text{Tr}\left(\dot{\rho} \ln(Z\rho)\right), \quad \forall Z \in R^1_+. \tag{23}
\]

Introducing (8)\(2\), the entropy rate becomes

\[
\dot{S}(\rho, \dot{\rho}) = -k_B \text{Tr}\left[ \sum_j \dot{p}_j |\Phi^j \rangle \langle \Phi^j | \ln(Z\rho) \right] =
\]

\[
= -\sum_j \dot{p}_j |\Phi^j \rangle \langle k_B \ln(Z\rho) |\Phi^j \rangle =: -\mathbf{p} \cdot \mathbf{f}^I, \quad \forall Z \in R^1_+, \tag{24}
\]

\[
f^I_k := <\Phi^k | k_B \ln(Z\rho) |\Phi^k \rangle. \tag{25}
\]
The entropy rate $\dS$ does not depend on $Z$ according to (22). Consequently, $Z$ can be chosen arbitrarily later on. A suitable choice of $Z$ will be discussed below in connection with equilibrium. In more detail, we obtain by use of (3)
\[
\ln(Z\varrho) = \sum_j \ln(Zp_j)\Phi^j\Phi^j, \quad (26)
\]
resulting in
\[
f_k^I = \sum_j k_B \ln(Zp_j)\delta_k^j = k_B \ln(Zp_k). \quad (27)
\]
The entropy rate is thermodynamically decomposed into the entropy exchange $\Xi$ and the entropy production $\Sigma$ [7]
\[
\dS = \Xi + \Sigma. \quad (28)
\]
In this easy case of a closed system, the entropy exchange is defined by multiplying the heat exchange with the reciprocal of the contact temperature $\Theta$ which is discussed in sect.4
\[
\Xi := \frac{\dot{Q}}{\Theta} = \frac{1}{\Theta}(E - \mathbf{A} \cdot \mathbf{a}) \quad \rightarrow \quad \dS = \Sigma + \frac{1}{\Theta}(E - \mathbf{A} \cdot \mathbf{a}) \quad (29)
\]
according to the first law (12) and (28). Using (16), we obtain for the entropy exchange in the case of a non-isolated closed system
\[
\Xi = \text{Tr}\left(\frac{\mathcal{H}}{\Theta} \sum_j \mathbf{p}_j |\Phi^j\Phi^j|\right) = \sum_j \mathbf{p}_j <\Phi^j|\frac{\mathcal{H}}{\Theta} \Phi^j > =: \mathbf{f}^{II}, \quad f_k^{II} := <\Phi^k|\frac{\mathcal{H}}{\Theta} \Phi^k >. \quad (30)
\]
Because the entropy rate (23) and the entropy exchange (30) do not depend on the parameter $Z$, also the entropy production is independent of it. As we demonstrate below, $Z$ is chosen differently for isolated and for closed non-isolated systems.

The exchange quantities $\dot{Q}$ and $\Xi$ depend on the state of the system and on that of its environment [10]. Consequently, $\dot{\mathbf{p}}$ contains a part which is determined by the environment, as we will see below in more detail. The thermodynamic quantities, entropy rate (24), entropy exchange (30) and entropy production require a modified von Neumann equation according to (10), demonstrating as expected: conventional quantum theory with $\dot{\mathbf{P}} \equiv 0$ is a non-thermal theory.

According to (2), (3)$_1$ and (17), the Hamilton operator $\mathcal{H}$ and the density
operator $\rho$ do not depend on $\dot{p}$ and $\dot{a}$. Consequently, also the quantum theoretical expressions $f^I$ and $f^{II}$ in (24) and (30) are independent of $\dot{p}$ and $\dot{a}$, and the interaction between system and environment is semi-classically described by $\rho$, that means by $\dot{p}$ and $\dot{a}$.

According to (28), (24) and (30), the entropy production results in

$$\Sigma = \dot{S} - \Xi = - \dot{p} \cdot (f^I + f^{II}) =: - \dot{p} \cdot f \geq 0, \quad (31)$$

The entropy production is an internal quantity of the system, that means, it does not depend on the exchange quantities between system and environment, here in semi-classical description:

■ Axiom III:
Power- and heat exchange, $W(t)$ and $Q(t)$, are independent of each other and do not influence the entropy production $\Sigma(t)$ locally in time. ■

4 Contact Temperature

The non-equilibrium contact temperature $\Theta$ in (29) is defined by the inequality $[5, 6, 11, 12, 13]$

$$\dot{Q} \left( \frac{1}{\Theta} - \frac{1}{T_\bigotimes} \right) \geq 0 \quad (32)$$

as follows: the system is contacted with an equilibrium environment of the thermostatic temperature $T_\bigotimes$ generating the net heat exchange $\dot{Q}$. For defining the contact temperature, we choose a special equilibrium environment so that the net heat exchange between system and environment vanishes. That occurs, if the environment has the thermostatic temperature $T_\bigotimes$. Now using the

■ Proposition [14]

$$X \cdot f(X) \geq 0 \quad \text{(for all } X \wedge f \text{ continuous at } X = 0) \implies f(0) = 0 \iff f(X) = M(X) \cdot X,$$

$M(X)$ positive semi-definite, ■

(33)

a comparison with (32) shows that

$$\dot{Q} = 0 \iff \Theta = T_\bigotimes. \quad (34)$$

In more detail:
Definition: The system’s contact temperature is that thermostatic temperature of the system’s equilibrium environment for which the net heat exchange between the system and this environment through an inert partition vanishes by change of sign.

We need the non-equilibrium contact temperature $\Theta$ because it is a quantity belonging to the system, a state function. A quantum theoretical definition of the contact temperature is given below.

As easily to demonstrate, contact temperature $\Theta$ and the internal energy $U$ are independent of each other. For this purpose, a rigid inert partition ($\dot{a} \equiv 0$) is chosen which is impervious to matter ($\dot{n}^e \equiv 0$) and a time-dependent environment temperature $T^\odot(t)$ which is always set equal to the value of the momentary contact temperature $\Theta(t)$ of the closed system:

$$T^\odot(t) \doteq \Theta(t) \rightarrow \dot{Q}^\odot = - \dot{Q} = 0 \rightarrow \dot{U} = 0$$

according to (34) and an inert partition between system and environment. Because $\Theta$ is time-dependent and $U$ is constant, totally different from thermostatics, both quantities are independent of each other.

5 Special Processes

In this section, 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.

5.1 Isolated systems

Isolated systems are phenomenological defined by a partition between system and its environment which is impervious to heat, power and material. That means, heat-, power- and material-exchange vanish identically for arbitrary states of system and environment. Because the particle number operator was not taken into account in the energy rate (12), the systems considered here are of constant particle number. Consequently, the particle number is not a variable of the system, and therefore the material exchange between system and environment vanishes identically and chemical reactions are absent. Such systems are denoted as closed systems without chemical reactions.

*Isolated* systems are closed systems with identically vanishing heat-, power-
and entropy-exchange. According to (17) and (30), we have the following conditions of isolation

\[ \dot{a}_{iso} \equiv 0 \rightarrow \dot{W}_{iso} \equiv 0, \quad \dot{Q}_{iso} \equiv 0 \rightarrow \Xi_{iso} \equiv 0. \]  

(36)

These conditions are achieved by introducing an isolating partition between system and environment which does not influence the state of the system. Thus we accept the following

**Axiom IV:**

The introduction of an isolating partition between system and environment does not change the Hamiltonian and the density operator of an undecomposed system in semi-classical description. This isolation influences the time rate of the density operator by changing the time rates of its weights

\[ \dot{p} \rightarrow \dot{p}^{iso}. \]  

(37)

Evident is that the exchange quantities \( \dot{W} \) and \( \dot{Q} \) depend also on the state of the system’s environment. According to (17), the power exchange is controlled by the rates of the work variables \( \dot{a} \), whereas the heat exchange (16) is represented by the rates of the weights \( \dot{p} \) because the Hamiltonian does not depend on \( \dot{a} \) and does not contain any interaction with the environment in semi-classical description. Consequently, when isolating the system from its environment, these rates change according to axiom IV (37).

Introducing

\[ \dot{p}^{ex} := \dot{p} - \dot{p}^{iso}, \quad \rightarrow \dot{p}^{ex,iso} = 0, \]  

(38)

we obtain for the time rates of the weights in

\[ \text{non-isolated closed systems} \quad \dot{p} = \dot{p}^{iso} + \dot{p}^{ex}, \]  

(39)

\[ \text{isolated systems} \quad \dot{p}^{iso}. \]  

(40)

The quantities \( f^I \) and \( f^{II} \), (25) and (30), are independent of an isolation of the system.

According to (30) and (36), we obtain for an isolated system

\[ \Xi_{iso} \equiv 0 = \dot{p}^{iso}. f^{II}, \quad \sum_j \dot{p}_j^{iso} = 0. \]  

(41)

From (8) we obtain the split into an exchange propagator \( \dot{\varrho}_{ex} \) which can be quantum theoretically identified later on, and a dissipative thermal part \( \dot{\varrho}_{iso} \).
called the *irreversibility propagator*,

$$\dot{\varrho} = \dot{\varrho}_{ex} + \dot{\varrho}_{iso}.$$  \hspace{1cm} (42)

$$\dot{\varrho}_{ex} = \sum_j \left\{ \dot{p}_j^{ex} | \Phi_j \rangle \langle \Phi_j | \right\}, \quad \dot{\varrho}_{iso} = \sum_j \left\{ \dot{p}_j^{iso} | \Phi_j \rangle \langle \Phi_j | \right\}. \hspace{1cm} (43)$$

Because of (7)\(_2\) and (41)\(_2\), we obtain

$$\sum_j \dot{p}_j^{ex} = 0, \quad \rightarrow \quad e \cdot \dot{p}^{ex} = 0, \quad e \cdot \dot{p}^{iso} = 0, \quad e_j = 1,$$

and the traces of both parts of the propagator vanish

$$\text{Tr} \dot{\varrho}_{ex} = 0, \quad \text{Tr} \dot{\varrho}_{iso} = 0.$$  \hspace{1cm} (45)

According to (30)\(_3\) and (41)\(_1\), the entropy exchange becomes

$$\Xi = \dot{p}^{ex} \cdot \mathbf{f}^{II},$$  \hspace{1cm} (46)

and the entropy production (31) yields

$$\Sigma = -\dot{p} \cdot \mathbf{f} - \dot{p}^{ex} \cdot \mathbf{f}^{II} = -\dot{p}^{iso} \cdot \mathbf{f} - \dot{p}^{ex} \cdot \mathbf{f} - \dot{p}^{ex} \cdot \mathbf{f}^{II}. \hspace{1cm} (47)$$

According to (24)\(_3\), the entropy rate in an isolated system is

$$\dot{S}_{iso} = -\dot{p}^{iso} \cdot \mathbf{f},$$  \hspace{1cm} (48)

resulting (47) in

$$\Sigma = \dot{S}_{iso} - \dot{p}^{ex} \cdot \mathbf{f}.$$  \hspace{1cm} (49)

Taking axiom III into consideration, entropy production and entropy rate are connected by the following

**Axiom V.**

The entropy production of a non-isolated closed system is defined as the entropy rate of the same system in isolation

$$\Sigma := \dot{S}_{iso} \rightarrow \dot{p}^{ex} \cdot \mathbf{f} = 0 \rightarrow \dot{p}^{ex} \cdot \mathbf{f}^{II} = -\dot{p}^{ex} \cdot \mathbf{f}^{I} \hspace{1cm} (50)$$

according to (49).

According to (31)\(_3\), (48) and (50)\(_1\), we obtain

$$\Sigma = -\dot{p} \cdot \mathbf{f} = -\dot{p}^{iso} \cdot \mathbf{f}^{I} \geq 0.$$  \hspace{1cm} (51)

Taking (24)\(_3\), (51)\(_2\), (50)\(_3\) and (46) into account, the entropy rate becomes

$$\dot{S} = \dot{p}^{ex} \cdot \mathbf{f}^{II} - \dot{p}^{iso} \cdot \mathbf{f}^{I},$$  \hspace{1cm} (52)

and we realize the different meanings of \(\dot{\varrho}_{ex}\) and \(\dot{\varrho}_{iso}\): the irreversibility propagator \(\dot{\varrho}_{iso}\) belongs to the entropy production \(\Sigma\) according to (48) and (50)\(_1\), whereas the exchange propagator \(\dot{\varrho}_{ex}\) belongs to the entropy exchange \(\Xi\) according to (46).
5.2 Adiabatic processes

If an isolated system is opened for power exchange, it performs an adiabatic process which is characterized by

\[ Q_{ad} = 0 \rightarrow \Xi_{ad} = 0 \land E_{ad} = A \cdot \dot{a} \neq 0 \]  

(53)

according to (29). As in isolated systems (36), the heat exchange vanishes in adiabatic isolated systems, whereas the rates of the work variables are different from zero. Because the entropy production does not depend on the rates of the work variables \( \dot{a} \) according to axiom III, the entropy rate is the same in isolated and adiabatic systems according to (29), a fact which is also true for the vanishing entropy exchanges. Consequently, the thermal statements are identical for isolated and adiabatic systems.

5.3 Reversible processes and quantum theory

According to (51), reversible processes in are defined by

\[ \Sigma_{rev} = -\dot{p}_{rev} \cdot f = -\dot{p}_{iso} \cdot f^I = 0. \]  

(54)

The "time" in the rates of (54) is the path parameter along the reversible process on the equilibrium sub-space. According to (54), we have to distinguish between reversible processes in

non-isolated systems: \( \dot{p}_{rev} \cdot f = 0, \ f \neq 0, \ \dot{p}_{rev} \neq 0 \),

isolated systems: \( \dot{p}_{iso} \cdot f^I = 0, \ f^I \neq 0, \ \dot{p}_{iso} \neq 0 \).  

(55)

(56)

In conventional quantum mechanics of undecomposed closed systems, the \( \dot{p} \) and therefore \( \dot{\rho} \) are zero, and according to (38)

\[ \dot{p}_{ex}^{qu} = -\dot{p}_{iso}^{qu} \]  

(57)

is valid. According to (46), (50), (57) and (51), we obtain for an (adiabatic) process in conventional quantum mechanics

\[ 0 = \Xi_{ad} = -\dot{p}_{ad}^{ex} \cdot f^I = \dot{p}_{iso}^{qu} \cdot f^I = -\Sigma_{qu} \rightarrow S_{qu} = 0. \]  

(58)

Consequently, entropy exchange, -production and -rate vanish in conventional quantum theory. That is the reason, why it is regarded as a reversible theory of adiabatic processes.
6 Equilibria

Reversible processes are defined as trajectories on the equilibrium sub-space, that means, a reversible process consists of equilibrium states which are defined according to (55) and (56) by the following equilibrium conditions

\[
\begin{align*}
\dot{a}^{eq} & = 0 \quad \land \quad \dot{\varrho}_{eq} = 0, \\
\dot{p}_{eq} & = 0 \quad \land \quad \dot{p}_{iso}^{eq} = 0 \quad \land \quad f^{eq} = 0 \quad \land \quad f^{Ieq} = 0.
\end{align*}
\]

(59) \hspace{1cm} (60)

According to (17), (8) and (16), (23), (30) and (31), we obtain from (59) and (60)

\[
\begin{align*}
\dot{W}_{eq} & = 0, \quad \dot{\varrho}_{eq} = 0, \quad [\mathcal{H}, \varrho_{eq}] = 0, \\
\dot{Q}_{eq} & = 0, \quad \dot{S}_{eq} = 0, \quad \Xi_{eq} = 0, \quad \Sigma_{eq} = 0.
\end{align*}
\]

(61) \hspace{1cm} (62)

According to (60), we have to distinguish between different kinds of equilibria: equilibrium in non-isolated systems according to (60)

\[
\begin{align*}
f^{eq}_{j} = f^{Ieq}_{j} + f^{IIeq}_{j} = <\Phi_{j}|(k_B \ln(Z\varrho_{eq}) + \frac{\mathcal{H}}{\Theta_{eq}})\Phi_{j}> = 0, \quad \land \ j.
\end{align*}
\]

(63)

and equilibrium in isolated systems according (25) and (27)

\[
\begin{align*}
f^{Ieq}_{k} = <\Phi_{eq}^{k}|k_B \ln(Z\varrho_{eq})\Phi_{eq}^{k}> = 0 = k_B \ln(Zp_{eq}^{k}). \quad \land \ k.
\end{align*}
\]

(64)

6.1 Isolated systems

From (64) follows

\[
Zp_{eq}^{k} = 1 \longrightarrow p_{eq}^{k} = \frac{1}{Z} \longrightarrow \varrho_{eq} = \frac{1}{Z} \sum_{k} |\Phi^{k}><\Phi^{k}| = \frac{1}{Z}.1. (65)
\]

Tracing the density operator according to (3) results in

\[
1 = \sum_{j} <\Phi_{j}|\varrho_{eq}\Phi_{j}> = \frac{1}{Z} \sum_{j} <\Phi_{j}|\Phi_{j}> = \frac{1}{Z} \sum_{j} 1_{j}. (66)
\]

The last sum must be restricted because of convergence: \(1 \leq j \leq N\). Consequently according to (66), \(Z = N\) is valid, and the density operator (65) of an isolated system has, as expected, the micro-canonical form

\[
\varrho_{mic} = \frac{1}{N} \sum_{j=1}^{N} |\Phi^{j}><\Phi^{j}|, \quad N < \infty. (67)
\]
6.2 Non-isolated closed systems

According to (61)\textsubscript{3}, 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 (4). Consequently, from (63)\textsubscript{3} follows

\[ k_B \ln(Z p^e q_k) + \frac{E_k}{\Theta_{eq}} = 0 \rightarrow \]

\[ \rightarrow k_B \sum_k \ln(Z p^e q_k) |\Phi_k|^2 \Phi_k > < \Phi_k | + \sum_k |\Phi_k > E_k < \Phi_k | = 0, \quad (68) \]

resulting according to (26) in

\[ k_B \ln(Z \rho_{eq}) + \frac{\mathcal{H}}{\Theta_{eq}} = 0. \quad (69) \]

From (69) follows the canonical density operator for a closed non-isolated system in equilibrium

\[ \rho_{can} = \frac{1}{Z} \exp \left[ - \frac{\mathcal{H}}{k_B \Theta_{eq}} \right], \quad Z = \operatorname{Tr} \exp \left[ - \frac{\mathcal{H}}{k_B \Theta_{eq}} \right]. \quad (70) \]

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

\[ \Theta_{eq} = T_\odot, \quad (71) \]

representing an additional equilibrium condition.

The micro-canonical and the canonical equilibrium density operators, (67) and (70), are derived by a pure phenomenological argumentation: starting with the entropy production in isolated and non-isolated systems (51), reversible processes (54) are defined by vanishing entropy production, a condition which is also satisfied for equilibria. But for equilibria, the vanishing entropy production follows from the equilibrium conditions (59) and (60), thus distinguishing reversible processes from equilibria. The equilibrium density operators \( \rho_{mic} \) (67) and \( \rho_{can} \) (70) follow from the phenomenological equilibrium conditions without using the 2nd law and a quantum theoretical background. A comparison of (55) and (56) with (60) shows that the entropy production in equilibrium vanishes with a ”higher grade” than that for reversible processes.
7 Constitutive Equations of the Propagators

In conventional quantum theory, the constitutive properties of the considered system are described by the Hamiltonian which is not equipped with the usual properties in semi-classical description. Here, the constitutive properties are introduced by the propagators (43).

As in classical non-equilibrium thermodynamics, the entropy production in quantum thermodynamics has also the typical form of a product of “fluxes” \( \dot{\mathbf{p}} \) and “forces” \( \mathbf{f} \) according to (51). 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. According to the equilibrium conditions (60), we obtain the non-linear constitutive equations

\[
\begin{align*}
\dot{\mathbf{p}}^{iso} & = \mathbf{B}(\mathbf{f}^I) \cdot \mathbf{f}^I, \quad \mathbf{B}^\top = \mathbf{B}, \text{ negative definite, singular}, \\
\dot{\mathbf{p}}^{ex} & = \mathbf{A}(\mathbf{f}, \Xi) \cdot \mathbf{f}, \quad \mathbf{A}^\top = -\mathbf{A}, \quad \mathbf{A}(\mathbf{f}, 0) = 0.
\end{align*}
\]

These constitutive equations satisfy the relevant relations of chap.6 and 5, as we will demonstrate below.

According to (46) and (73), the entropy exchange becomes

\[
\Xi = \mathbf{f}^{II} \cdot \mathbf{A}(\mathbf{f}, \Xi) \cdot \mathbf{f},
\]

and the following relations are valid according to (51)2, (41)1, and (50)2,

\[
\mathbf{f}^I \cdot \mathbf{B}(\mathbf{f}^I) \cdot \mathbf{f}^I \leq 0, \quad \mathbf{f}^{II} \cdot \mathbf{B}(\mathbf{f}^I) \cdot \mathbf{f}^I = 0, \quad \mathbf{f} \cdot \mathbf{A}(\mathbf{f}, \Xi) \cdot \mathbf{f} = 0.
\]

According to (31)3,4, the negative entropy production is by use of (72), (73), (38)1, (75) and (31)3

\[
-\Sigma = \dot{\mathbf{p}} \cdot \mathbf{f} = \mathbf{f} \cdot \left( \mathbf{A} \cdot \mathbf{f} + \mathbf{B} \cdot \mathbf{f}^I \right) = \mathbf{f} \cdot \mathbf{B} \cdot \mathbf{f}^I = \\
= \left( \mathbf{f}^I + \mathbf{f}^{II} \right) \cdot \mathbf{B} \cdot \mathbf{f}^I = \mathbf{f}^I \cdot \mathbf{B} \cdot \mathbf{f}^I \leq 0.
\]

We now consider the equilibria in isolated systems

\[
f^I = 0 \quad \rightarrow \quad \dot{\mathbf{p}}^{iso}_{eq} = 0 \quad \land \quad \mathbf{f} = \mathbf{f}^{II} \quad \rightarrow \quad \Xi = 0 \quad \rightarrow \quad \dot{\mathbf{p}}^{ex}_{eq} = 0,
\]

and in non-isolated closed systems

\[
f = 0 \quad \rightarrow \quad \dot{\mathbf{p}}^{ex}_{eq} = 0 \quad \land \quad \Xi = 0 \quad \land \quad f^I = -f^{II} \quad \rightarrow \quad -\mathbf{B} \cdot f^{II} = \dot{\mathbf{p}}^{iso}_{eq} \neq 0.
\]

The setting

\[
\mathbf{B} \cdot f^{II} = 0
\]
is compatible with (75)\textsubscript{2}. Thus, the constitutive equations (72) and (73) are in accordance with the constraints (75), with the entropy production (76) and with the equilibria (77) and (78) in isolated and non-isolated closed systems.

Taking (72) and (73) into account, the modified von Neumann equation (8)\textsubscript{1} writes with (42) and (43)

\[ \dot{\rho} = -\frac{i}{\hbar} [\mathcal{H}, \rho] + \sum_{jk} \left( B_{jk} f_k^I + A_{jk} f_k^I \right) |\Phi_j^j\rangle <\Phi_j^j|, \]  

\[
(80)
\]

The last term becomes by taking (31)\textsubscript{3} into account

\[ \sum_{jk} \left\{ (B_{jk} + A_{jk}) f_k^I + A_{jk} f_k^{II} \right\} |\Phi_j^j\rangle <\Phi_j^j| = \]

\[ = \sum_{jk} \left\{ (B_{jk} + A_{jk}) <\Phi_k^k| k_B \ln(Z_{\varrho}) \Phi_k^k > + 

+ A_{jk} <\Phi_k^k| \mathcal{H}_{N} \Phi_k^k > \right\} |\Phi_j^j\rangle <\Phi_j^j|. \]

\[
(81)
\]

The modified von Neumann equation (8)\textsubscript{1} contains the time derivatives of the weights of the density operator which are connected with the entropy exchange (30)\textsubscript{1} and with the entropy production (31). In conventional quantum mechanics, the constitutive properties of the system are given by the Hamiltonian which determines the power exchange (17) with the system’s environment. In the semi-classical description of quantum thermodynamics, the power exchange is supplemented by the entropy exchange and by the entropy production as an internal quantity of the system, whereas the Hamiltonian remains undecomposed\textsuperscript{1}. As the power exchange, also the entropy exchange and the entropy production are constitutive quantities which are transferred to the time derivatives of the weights of the density operator according to (72) and (73). Thus, the Hamiltonian and the constitutive mappings \textbf{A} and \textbf{B} determine the constitutive quantities of semi-classical quantum thermodynamics: power and heat exchange, entropy production and contact temperature\textsuperscript{2} and consequently the entropy exchange.

### 8 Temperature as a Quantum Quantity

Starting with (50)\textsubscript{3}, we obtain by taking (30), (24) and (43)\textsubscript{1} into consideration

\[ \text{Tr} \left( \mathcal{H}_{N} \hat{\varrho}_{ex} \right) = -k_B \text{Tr} \left( \hat{\varrho}_{ex} \ln(Z_{\varrho}) \right). \]

\[
(82)
\]

\textsuperscript{1}that means: no interaction term is in the Hamiltonian

\textsuperscript{2}as we will see in the next section (83)
This results in a quantum mechanical expression for the reciprocal contact temperature of an undecomposed non-isolated closed system

\[
\frac{1}{\Theta} = - \frac{\text{Tr} \left( k_B \hat{\varrho}_{\text{ex}} \ln(Z \varrho) \right)}{\text{Tr}(\mathcal{H} \hat{\varrho}_{\text{ex}})},
\]

(83)

\[
\hat{\varrho}_{\text{ex}} = \sum_{jk} \left\{ A_{jk} < \Phi^k \left| \left( k_B \ln(Z \varrho) + \frac{\mathcal{H}}{\Theta} \right) \Phi^k \right. > \right\} | \Phi^j > < \Phi^j |.
\]

(84)

Consequently, axiom IV does not only determine the entropy production (51) and the entropy exchange (46), but allows to replace the classical contact temperature by the quantum mechanical expression (83).

According to (60)\textsubscript{1,2}, (77) and (78), we obtain in equilibrium

\[
\hat{\varrho}_{\text{ex}}^\text{eq} = 0.
\]

(85)

Consequently, the contact temperature cannot be represented by (83) in equilibrium of non-isolated closed systems for which the equilibrium condition (71) is valid according to (34) and (32). The contact temperature is according to (32) not defined for isolated systems, because \( \mathcal{Q} \) is identically zero independent of the environment’s temperature \( T \).\textdagger

\section{Summary}

The von Neumann equation (8) is modified by introducing time dependent weights (10) of the statistical operator generating an additional term, the propagator (8)\textsubscript{2} which is traceless and decomposes into two parts (42), an exchange part (43)\textsubscript{1} and an irreversibility part (43)\textsubscript{2}. This decomposition is caused by the presupposition that the propagator is sensitive to an isolation of the considered system (37). The exchange part determines the entropy exchange (46) between the undecomposed system and its environment, whereas the irreversibility part determines the non-negative entropy production (51) which is insensitive to any isolation of the system.

Starting with the Shannon entropy (18), the time rate of the entropy (24) and also the entropy exchange (30) are in contrast to the conventional quantum mechanics different from zero. Having derived the time rate of the entropy and the entropy exchange, the entropy production (31) is determined.

Because in undecomposed systems the Hamiltonian does not contain an interaction term, the exchanges between the closed system and its environment are treated semi-classically by using the power exchange and the entropy exchange which contains the system’s contact temperature (34). Because the
entropy production is insensitive to an isolation of the system, the contact temperature can be represented quantum mechanically (83) by the exchange propagator, the Hamiltonian and by the density operator of the non-isolated system.

The equilibrium density operators, (70) and (67), for closed non-isolated and isolated systems are derived by a thermodynamical induced procedure using a quantum mechanical background, but without any concept and use of statistical thermodynamics (therefore the headline expression: phenomenological). Especially, the basic postulate of statistical physics, the microcanonical density operator in isolated systems (67), is not postulated here, but is derived by using the modified von Neumann equation (8) and the four axioms I to IV.

Evident is that the semi-classical treatment of quantum thermodynamics represents only an approximation which needs an extension. Decomposed Schottky systems, that means system which are described by a Hamiltonian containing an interaction term, are treated in a second paper: Concepts of Phenomenological Irreversible Quantum Thermodynamics II: Closed Bipartite Schottky Systems.

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