

# Phenomenological Non-Equilibrium Quantum Thermodynamics based on Modified von Neumann Equations \*

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**Abstract:** The wide-spread opinion is that original quantum mechanics is a reversible theory, but this statement is only true for undecomposed systems that are those systems which sub-systems are out of consideration. Taking sub-systems into account, as it is by definition necessary for decomposed systems, the interaction Hamiltonians which are absent in undecomposed systems generate irreversibility. Thus, the following two-stage task arises: How to modify von Neumann's equation for undecomposed systems so that irreversibility appears, and how this modification affects decomposed systems? The first step was already done in [1] and is repeated below, whereas the second step to formulate a quantum thermodynamics of decomposed systems is performed here by modifying the von Neumann equations of the sub-systems by a procedure which is similar to that of Lindblad's equation [2], but different because the sub-systems interact with one another through partitions.

**Keywords:** Quantum Thermodynamics, Composed and undecomposed systems, Modified von Neumann equations, Propagator, Contact temperature, Entropy production

## Preface

Thermodynamics can be formulated as a field theory or differently as going on in discrete systems [3, 4, 5]. Especially there is the non-equilibrium system itself and its non-equilibrium environment which are separated by a partition, thus representing a bipartite system with an interior partition. Consequently, three Hamiltonians appear, each one for the system, the environment and for the partition which needs beyond its Hamiltonian a thermodynamic specification (called non-inertness) characterizing, if the partition is heating or cooling. The equation of motion of this bipartite system is the unchanged Schrödinger equation without allowing thermodynamic alterations. Introducing the corresponding statistical operator, the possibility to

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establish thermodynamic items emerge: in original quantum mechanics, the statistical weights of statistical operator are set to be time independent. This presupposition is cancelled here by introducing a so-called propagator which consists of the time derivatives of the statistical weights and which changes the composition of the statistical operator in time. How this propagator allows to introduce thermodynamics is discussed in the paper.

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## 1 Introduction

Referring to the tutorial papers [6, 7], a "theoretical frame work, in which thermodynamic principles are explained and supplemented by quantum-mechanical and statistical considerations, is called quantum thermodynamics". Beyond that, such a coupling of quantum mechanics and thermodynamics has

to define quantum mechanically the thermodynamical basic quantities such as power-, heat- and entropy-exchange, entropy and entropy production .

In this paper, quantum mechanics is introduced by two items: a Hamiltonian which belongs to a Schottky system<sup>1</sup> [8, 9, 10] and by a von Neumann equation which is modified by a so-called *propagator* [1] which allows to introduce the distinction between isolated and non-isolated systems<sup>2</sup>. The here considered systems belong to two classes: the system may be *undecomposed* [1], that means none of its sub-systems is taken into account, and it may be *decomposed*, that means sub-systems are coming into play. Being decomposed or undecomposed are kinds of description of a Schottky system, thus characterizing different degrees of knowledge of the system. The interaction between an undecomposed system and its environment is described *semi-classical* [1], that means no interaction Hamiltonian is introduced for the present, a step which is rejected for decomposed systems later on.

Beyond classifying the systems into decomposed and undecomposed ones, there are some other items which are discussed differently in this paper as usual [6]:

- (i) the system's environment is not necessarily an equilibrium heat reservoir, but may be as the system itself a non-equilibrium system,
- (ii) not only the Hamiltonian of the system depends on the protocol (power variables), but also do the Hamiltonians of the environment and of the interaction,
- (iii) the Hamiltonian does not belong to a so-called "universum" outside the system, but is always the Hamiltonian of the system itself,
- (iv) consequently, there is no "effective non-equilibrium temperature of the universe" which is defined by the internal energy of the universe (?), but the non-equilibrium temperature of the system, the *contact temperature* [11, 12, 13, 14], is used which does not depend on the internal energy,
- (v) use of the system's contact temperature makes possible to define the *entropy exchange* (entropy flux) independently of an external heat reservoir,
- (vi) in original quantum mechanics, the heat exchange between two sub-systems vanishes with the interaction Hamiltonian, thus ignoring active caloric properties of the partition between the sub-systems. In quantum thermodynamics, a so-called *non-inertness* can be introduced by using the propagator describing whether the partition is cooling or heating,
- (vii) statistical operators of the sub-systems of a decomposed system are generated by tracing, thus introducing the partial Shannon entropy of a sub-system as a state function. In original quantum mechanics, this Shannon entropy is time independent for isolated systems, a fact which is not true in quantum thermodynamics because of a *modified von Neumann equation*. In contrast to the observational entropy [6], the definition of the Shannon entropy does not depend on an observer's coarse graining which is not a system property.
- (viii) The modification of von Neumann's equation which does not change Schrödinger's equation represents the core of the paper. This is achieved by introducing time dependent weights of the statistical operator, thus generating irreversibility by changing its composition in time.

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<sup>1</sup>A Schottky system is a discrete system, that means a "box", which is in interaction with its environment. Many of the devices of process engineering are Schottky systems.

<sup>2</sup>An isolated (Schottky) system has no interaction with its environment, a non-isolated one may interact with its environment by power- heat- and material-exchange.

A Schottky system can be represented as being composed or decomposed. Because we consider *bipartite systems* in the sequel (decomposed into two sub-systems #1 and #2), the density operators and the Hamiltonians are of the following shape:

$$\begin{aligned} \text{undecomposed:} & \quad \varrho, \mathcal{H}, \\ \text{decomposed:} & \quad \varrho, \varrho^1, \varrho^2, \mathcal{H} = \mathcal{H}^1 + \mathcal{H}^2 + \mathcal{H}^{12}. \end{aligned}$$

Here,  $\mathcal{H}^{12}$  is the interaction Hamiltonian belonging to the sub-systems which are in contact to each other by a partition #(12) which may have individual properties.

## 2 Retrospect: Undecomposed Systems

For introducing thermodynamics into quantum mechanics, we start with a *modified von Neumann equation* [1, 15]<sup>3</sup>

$$\partial_t \varrho \equiv \dot{\varrho} = -\frac{i}{\hbar} [\mathcal{H}, \varrho] + \dot{\varrho}, \quad \dot{\varrho} := \sum_j \dot{p}_j |\Phi^j\rangle\langle\Phi^j|, \quad (1)$$

$$\varrho := \sum_j p_j |\Phi^j\rangle\langle\Phi^j|, \quad 0 \leq p_j \leq 1, \quad \sum_j p_j = 1, \quad \text{Tr} \varrho = 1, \quad (2)$$

by use of pure quantum states  $\{|\Phi^j\rangle\}$  which are normalized, complete and orthogonal. The self-adjoint Hamiltonian  $\mathcal{H}(\mathbf{a})$  depends on the work variables  $\mathbf{a}$ . The modification in contrast to the original quantum theory consists in the demand

$$\forall j: \quad \dot{p}_j \neq 0 \longrightarrow \dot{\varrho} \neq \underline{0}. \quad (3)$$

The *First Law* writes ( $E$ =energy,  $\dot{W}$ =power,  $\dot{Q}$ =heat exchange,  $\text{Tr}$ =trace)

$$E := \text{Tr}(\mathcal{H}\varrho) \longrightarrow \dot{E} = \text{Tr}(\dot{\mathcal{H}}\varrho) + \text{Tr}(\mathcal{H}\dot{\varrho}), \quad (4)$$

$$\dot{W} := \text{Tr}(\dot{\mathcal{H}}\varrho), \quad \dot{Q} := \text{Tr}(\mathcal{H}\dot{\varrho}), \quad (5)$$

$$\dot{W} = \text{Tr}\left(\frac{\partial \mathcal{H}}{\partial \mathbf{a}} \varrho\right) \cdot \dot{\mathbf{a}} =: \mathbf{K} \cdot \dot{\mathbf{a}}, \quad (6)$$

and by taking (1)<sub>2</sub> into account

$$\dot{Q} = \text{Tr}\left(\mathcal{H} \dot{\varrho}\right) = \text{Tr}\left(\mathcal{H} \sum_j \dot{p}_j |\Phi^j\rangle\langle\Phi^j|\right). \quad (7)$$

Starting with the *Shannon entropy* [16, 17], a state function of the undecomposed system

$$S(\varrho) := -k_B \text{Tr}(\varrho \ln \varrho), \quad (8)$$

the *entropy time rate* becomes according to (1)

$$\dot{S}(\varrho) = -k_B \text{Tr}\left(\dot{\varrho} \ln(Z\varrho)\right), \quad \forall Z \in R_+^1. \quad (9)$$

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<sup>3</sup>⊞ := ⊗ means: ⊞ is defined by ⊗

The *entropy exchange*<sup>4</sup> is according to (7)<sub>2</sub>

$$\Xi := \frac{\dot{Q}}{\Theta} = \text{Tr}\left(\frac{\mathcal{H}}{\Theta} \overset{\circ}{\varrho}\right). \quad (10)$$

Here  $\Theta$  is the non-equilibrium *contact temperature* defined by the *defining inequality* [13, 14, 18]

$$\left(\frac{1}{\Theta} - \frac{1}{T^\square}\right) \dot{Q} \geq 0, \quad (11)$$

or in words

**Definition:** The system's contact temperature  $\Theta$  is that thermostatic temperature  $T^\square$  of the system's equilibrium environment for which the net heat exchange  $\dot{Q}$  between the system and this environment through an inert partition<sup>5</sup> vanishes by change of sign.

The *entropy production*<sup>6</sup> becomes according to (9), (10) and the 2nd law

$$\Sigma = \dot{S} - \Xi = -\text{Tr}\left\{\left(\frac{\mathcal{H}}{\Theta} + k_B \ln(Z\rho)\right) \overset{\circ}{\varrho}\right\} \geq 0. \quad (12)$$

If a discrete non-equilibrium system  $\mathcal{G}$  is isolated, that means the partition  $\partial\mathcal{G}$  between  $\mathcal{G}$  and its environment  $\mathcal{G}^\square$  becomes impervious to heat and power (and matter), the corresponding exchanges are suppressed

$$\dot{W}_{iso} \equiv 0, \quad \dot{Q}_{iso} \equiv 0, \quad (13)$$

and the non-exchange quantities of the system as the energy are unaffected by the system's isolation. That means according to (4)<sub>1</sub>, the density operator  $\rho$  and the Hamiltonian  $\mathcal{H}$  are unaffected by the isolation of the system. Consequently, also the  $\{p_j\}$  and the  $\{|\Phi^j\rangle\}$  are according to (2)<sub>1</sub> unaffected by the system's isolation.

From (13)<sub>2</sub> and (10)<sub>1</sub> follows that in *isolated systems* the entropy exchange vanishes

$$\Xi_{iso} = 0 = \text{Tr}\left(\frac{\mathcal{H}}{\Theta} \overset{\circ}{\varrho}_{iso}\right), \quad (14)$$

that means according to (10), that the act of isolating the system transforms the *propagator*  $\overset{\circ}{\varrho}$  by changing the time rates of the weights of the density operator [19]

$$\overset{\circ}{\varrho} \longrightarrow \overset{\circ}{\varrho}_{iso}. \quad (15)$$

Establishing the definition

$$\overset{\circ}{\varrho}_{ex} := \overset{\circ}{\varrho} - \overset{\circ}{\varrho}_{iso}, \quad (16)$$

we obtain the propagator in

$$\text{non-isolated closed systems:} \quad \overset{\circ}{\varrho} = \overset{\circ}{\varrho}_{ex} + \overset{\circ}{\varrho}_{iso} \quad (17)$$

$$\text{isolated systems:} \quad \overset{\circ}{\varrho}_{iso}. \quad (18)$$

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<sup>4</sup>This entropy exchange refers to the contact temperature of the system and not to the thermostatic temperature of an external heat reservoir.

<sup>5</sup>"Inert" means: the partition does not emit or absorb power or/and heat.

<sup>6</sup>The entropy of discrete systems satisfies the balance equation (12)<sub>1</sub>.

Isolation of the system causes the split of the propagator  $\overset{\circ}{\varrho}$  (17) into an *exchange part*  $\overset{\circ}{\varrho}_{ex}$  and into a *dissipative thermal part*  $\overset{\circ}{\varrho}_{iso}$ .

Because the entropy production is defined as the time rate of entropy in isolated systems according to (12)<sub>1</sub>, (14)<sub>1</sub> and (9)

$$\Sigma := \dot{S}_{iso} = -k_B \text{Tr} \left( \overset{\circ}{\varrho}_{iso} \ln(Z\varrho) \right). \quad (19)$$

Inserting the quantum-theoretical relation (12), (19) results in two expressions for the entropy production

$$\Sigma = -\text{Tr} \left\{ \left( \frac{\mathcal{H}}{\Theta} + k_B \ln(Z\varrho) \right) \overset{\circ}{\varrho} \right\} = -k_B \text{Tr} \left( \overset{\circ}{\varrho}_{iso} \ln(Z\varrho) \right) \geq 0. \quad (20)$$

The first term represents the entropy production in undecomposed non-isolated closed systems according to (17), whereas according to (18), the second term is the entropy production of the same undecomposed, but isolated system: isolation does not influence the entropy production. As the entropy (8) and the entropy time rate (9), also the entropy production (20)<sub>2</sub> does not depend on the Hamiltonian.

Inserting (17) into (20) and taking (14) into account results in

$$0 = -\text{Tr} \left\{ \left( \frac{\mathcal{H}}{\Theta} + k_B \ln(Z\varrho) \right) \overset{\circ}{\varrho}_{ex} \right\} = \dot{S}_{ex} - \Xi_{ex}, \quad (21)$$

by taking (9) and (10) into account, an expression which allows to represent the contact temperature of undecomposed systems quantum theoretically [19]

$$\frac{1}{\Theta} = \frac{-\text{Tr} \left\{ k_B \ln(Z\varrho) \overset{\circ}{\varrho}_{ex} \right\}}{\text{Tr} \left\{ \mathcal{H} \overset{\circ}{\varrho}_{ex} \right\}}, \quad \overset{\circ}{\varrho}_{ex} \neq \underline{0}. \quad (22)$$

depicting that contact temperature can only be measured, if the system is not isolated.

Now equilibrium is discussed which is defined by *necessary equilibrium conditions*. These are<sup>7</sup>

$$\begin{aligned} \blacksquare \quad \text{according to (1):} \quad & \dot{\varrho}^{eq} = \underline{0}, \quad \overset{\circ}{\varrho}^{eq} = \underline{0}, \quad \overset{\circ}{\varrho}_{iso}^{eq} = \underline{0}, \quad (23) \\ \text{according to (6):} \quad & \dot{\mathbf{a}} = \mathbf{0}. \quad \blacksquare \quad (24) \end{aligned}$$

From these necessary equilibrium conditions follow *complementary* ones. These are

$$\text{according to (1)}_1: \quad [\mathcal{H}, \varrho^{eq}] = \underline{0}, \quad (25)$$

$$\text{according to (16):} \quad \overset{\circ}{\varrho}_{ex}^{eq} = \underline{0}, \quad (26)$$

$$\text{according to (6), (7) and (9):} \quad \dot{W}^{eq} = 0, \quad \dot{Q}^{eq} = 0, \quad \dot{S}^{eq} = 0, \quad (27)$$

$$\text{according to (10) and (12)}_1: \quad \Xi^{eq} = 0, \quad \Sigma^{eq} = 0. \quad (28)$$

Now *reversible "processes"*,  $\Sigma^{rev} \equiv \Sigma^{eq} = 0$ , are considered according to (1)<sub>1</sub>

$$\dot{\varrho}^{rev}(\tau) - \overset{\circ}{\varrho}^{rev}(\tau) = -\frac{i}{\hbar} [\mathcal{H}, \varrho^{rev}(\tau)], \quad \tau \geq 0, \quad (29)$$

<sup>7</sup>Thermodynamical demands are put between  $\blacksquare$  and  $\blacksquare$ .

with the time replacing path parameter  $\tau$  along the reversible trajectory and with the initial conditions<sup>8</sup>

$$\varrho^{rev}(0) \doteq \varrho^{eq} \quad \wedge \quad \dot{\varrho}^{rev}(0) \neq \dot{\varrho}^{eq} = 0. \quad (30)$$

The initial condition of the time derivative  $\dot{\varrho}^{rev}(0)$  follows from the equation of "motion" of the reversible "process" (29)

$$\dot{\varrho}^{rev}(0) - \dot{\varrho}^{rev}(0) = -\frac{i}{\hbar}[\mathcal{H}, \varrho^{eq}] = \underline{0}, \quad (31)$$

according to (30)<sub>1</sub> and (25). From (20) follows for

$$\text{non-isolated closed systems:} \quad \text{Tr} \left\{ \left( \frac{\mathcal{H}}{\Theta^{rev}} + k_B \ln(Z \varrho^{rev}) \right) \dot{\varrho}^{rev} \right\} = 0, \quad (32)$$

$$\text{isolated systems:} \quad \text{Tr} \left( \dot{\varrho}_{iso}^{rev} \ln(Z \varrho^{rev}) \right) = 0. \quad (33)$$

Considering (32) and (33) at  $\tau = 0$  and taking the initial condition (30)<sub>1</sub> into account results in

$$\text{non-isolated closed systems:} \quad \text{Tr} \left\{ \left( \frac{\mathcal{H}}{\Theta_{eq}} + k_B \ln(Z \varrho^{eq}) \right) \dot{\varrho}^{rev}(0) \right\} = 0, \quad (34)$$

$$\text{isolated systems:} \quad \text{Tr} \left( \dot{\varrho}_{iso}^{rev}(0) \ln(Z \varrho^{eq}) \right) = 0. \quad (35)$$

Because the initial condition (31) of  $\dot{\varrho}^{rev}(0)$  can be chosen arbitrarily, from (34) and (35) follow necessary, sufficient and excluding each other complementary equilibrium conditions

$$\frac{\mathcal{H}}{\Theta_{eq}} + k_B \ln(Z \varrho^{eq}) = \underline{0} \quad \text{or} \quad \ln(Z \varrho^{eq}) = \underline{0}, \quad (36)$$

resulting in *equilibrium distributions* [1] for

$$\text{isolated systems:} \quad \varrho^{eq} = \frac{1}{N} \sum_{j=1}^N |\Phi_{eq}^j\rangle \langle \Phi_{eq}^j| =: \varrho_{mic}, \quad N < \infty, \quad (37)$$

non-isolated closed systems:

$$\varrho^{eq} = \frac{1}{Z} \exp \left[ -\frac{\mathcal{H}}{k_B \Theta_{eq}} \right] =: \varrho_{can}, \quad Z = \text{Tr} \exp \left[ -\frac{\mathcal{H}}{k_B \Theta_{eq}} \right] \quad (38)$$

which satisfy (25). Thus, the canonical and micro-canonical distributions are derived without statistical arguments modifying the von Neumann equation by a thermodynamical induced propagator  $\dot{\varrho}$  and initial conditions of a special reversible process.

Here finishes the brief repetition of the main results in undecomposed systems characterized by a single density operator and the corresponding Hamiltonian. Decomposed systems are discussed in the sequel.

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<sup>8</sup>(30)<sub>1</sub> is only valid at  $\tau = 0$ , but is not satisfied for the time derivatives (30)<sub>2</sub> for which (31) is valid.

### 3 Decomposed Bipartite Systems

#### 3.1 The density operators

We consider a Schottky system which is decomposed into two sub-systems, #1 and #2 [19]. Each sub-system is described by a partial density operator,  $\varrho^1$  and  $\varrho^2$ , and by a partial Hamiltonian,  $\mathcal{H}^1$  and  $\mathcal{H}^2$ . The interaction between the sub-systems is represented by the interaction Hamiltonian  $\mathcal{H}^{12}$  and by a *partition* #(12) between them. The Hamiltonian  $\mathcal{H}$  of the undecomposed system  $(2)_1$  is the sum of the partial Hamiltonians of the two sub-systems,  $\mathcal{H}^1$  and  $\mathcal{H}^2$ , and of the interaction Hamiltonian  $\mathcal{H}^{12}$

$$(\#1 \cup \#2 \cup \#(12)) : \quad \mathcal{H} = \mathcal{H}^1 + \mathcal{H}^2 + \mathcal{H}^{12}. \quad (39)$$

By choosing an orthogonal basis  $\{|\Psi_1^k \rangle\}$  belonging to sub-system #1 and an other one  $\{|\Psi_2^l \rangle\}$  belonging to the other sub-system #2, the tensor product of these bases form an orthogonal basis of the decomposed system

$$\{|\Psi_1^k \rangle \otimes |\Psi_2^l \rangle\} \equiv \{|\Psi_1^k \rangle |\Psi_2^l \rangle\}. \quad (40)$$

With respect to the tensorial base (40), we used in (39) the abbreviations

$$\mathcal{H}^1 \otimes I^2 \equiv \mathcal{H}^1, \quad I^1 \otimes \mathcal{H}^2 \equiv \mathcal{H}^2, \quad \longrightarrow \quad [\mathcal{H}^1, \mathcal{H}^2] = 0, \quad (41)$$

with the unity operators  $I^i$ ,  $i = 1, 2$ , belonging to the corresponding factors of the tensor product (40).

The interaction of the sub-systems with the environment is for the present described *semi-classically* [1], that means, by power- and heat-exchanges which result from the partial Hamiltonians of the sub-systems,  $\mathcal{H}^1$  and  $\mathcal{H}^2$ , similar as (5). There is for the present no Hamiltonian of the environment and also no interaction Hamiltonian describing the interaction between the environment and the bipartite system. The interaction Hamiltonian  $\mathcal{H}^{12}$  refers exclusively to the interaction between the two sub-systems and is independent of the system's environment<sup>9</sup>.

According to the basis of the bipartite system (40), the corresponding density operator is analogous to  $(2)_1$

$$\varrho = \sum_{kl} p_{kl} |\Psi_1^k \rangle |\Psi_2^l \rangle \langle \Psi_2^l| \langle \Psi_1^k|, \quad \text{Tr} \varrho = 1, \quad (42)$$

and the propabilities  $p_{kl}$  satisfy  $(2)_{2,3}$  analogously. The propagator is analogous to  $(1)_2$

$$\overset{\circ}{\varrho} = \sum_{kl} \overset{\circ}{p}_{kl} |\Psi_1^k \rangle |\Psi_2^l \rangle \langle \Psi_2^l| \langle \Psi_1^k|, \quad \text{Tr} \overset{\circ}{\varrho} = 0. \quad (43)$$

The partial density operators of the sub-systems follow from the density operator  $\varrho$  by tracing

$$\varrho^1 := \text{Tr}^2 \varrho = \sum_k \sum_j p_{kj} |\Psi_1^k \rangle \langle \Psi_1^k|, \quad (44)$$

$$\varrho^2 := \text{Tr}^1 \varrho = \sum_l \sum_j p_{jl} |\Psi_2^l \rangle \langle \Psi_2^l|, \quad (45)$$

Analogous definitions as (43) are valid for the propagators  $\overset{\circ}{\varrho}^1$  and  $\overset{\circ}{\varrho}^2$  of the sub-systems.

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<sup>9</sup>We will get rid of the semi-classical description in sect.3.10

### 3.2 Modified von Neumann equations

Using the decomposition of the Hamiltonian (39)<sub>2</sub>, the modified von Neumann equation (1)<sub>1</sub> of the undecomposed system

$$\dot{\varrho} = -\frac{i}{\hbar} [(\mathcal{H}^1 + \mathcal{H}^2 + \mathcal{H}^{12}), \varrho] + \overset{\circ}{\varrho}. \quad (46)$$

results in two equations of motion for the traced density operators of the sub-systems by taking (263)<sub>1</sub> into account

$$\begin{aligned} \dot{\varrho}^1 &:= \text{Tr}^2 \dot{\varrho} = -\frac{i}{\hbar} \text{Tr}^2 [\mathcal{H}^1, \varrho] - \frac{i}{\hbar} \text{Tr}^2 [\mathcal{H}^{12}, \varrho] + \text{Tr}^2 \overset{\circ}{\varrho} = \\ &= -\frac{i}{\hbar} [\mathcal{H}^1, \varrho^1] - \frac{i}{\hbar} \text{Tr}^2 [\mathcal{H}^{12}, \varrho] + \overset{\circ}{\varrho}^1, \end{aligned} \quad (47)$$

$$\begin{aligned} \dot{\varrho}^2 &:= \text{Tr}^1 \dot{\varrho} = -\frac{i}{\hbar} \text{Tr}^1 [\mathcal{H}^2, \varrho] - \frac{i}{\hbar} \text{Tr}^1 [\mathcal{H}^{12}, \varrho] + \text{Tr}^1 \overset{\circ}{\varrho} = \\ &= -\frac{i}{\hbar} [\mathcal{H}^2, \varrho^2] - \frac{i}{\hbar} \text{Tr}^1 [\mathcal{H}^{12}, \varrho] + \overset{\circ}{\varrho}^2. \end{aligned} \quad (48)$$

As (47) and (48) depict, the traced operators  $\dot{\varrho}^1$  and  $\dot{\varrho}^2$  include as expected the interaction Hamiltonian  $\mathcal{H}^{12}$ , but not the Hamiltonian of the neighboring sub-system. Beyond that, also the density operator  $\varrho$  (2)<sub>1</sub> of the undecomposed system appears in the rate equations belonging to the sub-systems. That means: first of all, the equation of motion (46) of the undecomposed system has to be solved.

Introducing a modified propagator

$$\overset{\vee}{\varrho} := -\frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] + \overset{\circ}{\varrho}, \quad (49)$$

$$\overset{\vee}{\varrho}^1 = -\frac{i}{\hbar} \text{Tr}^2 [\mathcal{H}^{12}, \varrho] + \overset{\circ}{\varrho}^1, \quad \overset{\vee}{\varrho}^2 = -\frac{i}{\hbar} \text{Tr}^1 [\mathcal{H}^{12}, \varrho] + \overset{\circ}{\varrho}^2, \quad (50)$$

the equations of motion (47) and (48) result in

$$\dot{\varrho}^1 = -\frac{i}{\hbar} [\mathcal{H}^1, \varrho^1] + \overset{\vee}{\varrho}^1, \quad \dot{\varrho}^2 = -\frac{i}{\hbar} [\mathcal{H}^2, \varrho^2] + \overset{\vee}{\varrho}^2. \quad (51)$$

The shape of the equations of motion (51) of the sub-systems is identical with that of the undecomposed system (1) except for  $\overset{\circ}{\varrho}$  is replaced by  $\overset{\vee}{\varrho}^1$  and  $\overset{\vee}{\varrho}^2$ . The vanishing of the propagator  $\overset{\circ}{\varrho}$  in original quantum mechanics does not cause vanishing of the modified propagators  $\overset{\vee}{\varrho}^1$  and  $\overset{\vee}{\varrho}^2$ . This fact may be a motivation to consider the modified von Neumann equations (51) also for decomposed systems of original quantum mechanics.

In original quantum mechanics ( $\overset{\circ}{\varrho} \equiv 0$ ) the two sub-systems of the bipartite system are isolated from each other by  $[\mathcal{H}^{12}, \varrho] \equiv 0$  according to (47) and (48). Using the modified von Neumann equation (46), isolation of the sub-systems is described by  $\overset{\vee}{\varrho} \equiv 0$  according to (51), resulting in  $\overset{\circ}{\varrho} = \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho]$ : in the case of mutual isolation of the sub-systems, the propagator  $\overset{\circ}{\varrho}$  removes the quantum mechanical interaction ( $\mathcal{H}^{12} \neq 0$ ).

In equilibrium, (47) and (48) yield by taking (23) into account

$$0 = -\frac{i}{\hbar} [\mathcal{H}_{eq}^A, \varrho_{eq}^A] - \frac{i}{\hbar} \text{Tr}^B [\mathcal{H}_{eq}^{12}, \varrho^{eq}], \quad A = 1, 2; B \neq A. \quad (52)$$

Taking (263)<sub>3</sub> into account, tracing results in

$$0 = \text{Tr}^A[\mathcal{H}_{eq}^A, \varrho_{eq}^A] + \text{Tr}^A \text{Tr}^B[\mathcal{H}_{eq}^{12}, \varrho^{eq}] = \text{Tr}[\mathcal{H}_{eq}^{12}, \varrho^{eq}], \quad (53)$$

an expression which replace (25) in case of decomposed systems. Taking (53)<sub>2</sub> into account, (49) and (51) result in

$$\overset{\nabla}{\varrho}^{eq} = \underline{0}, \quad [\mathcal{H}_{eq}^A, \varrho_{eq}^A] = \underline{0}. \quad (54)$$

Obviously, the propagators which modify the von Neumann equations cannot be established by pure quantum theoretical arguments, because their introduction should connect thermodynamics and quantum mechanics. Consequently, we need thermodynamical argumentation to lay down the properties of the propagators. This will be done in the next sections in several steps.

### 3.3 The exchanges

#### 3.3.1 Power exchanges

The work variables  $\mathbf{a}$  in (6) belong to the undecomposed system. Switching over to a decomposed system, these work variables have to be replaced by those which belong to the sub-systems and their environment,  $\mathbf{a}^1$  and  $\mathbf{a}^2$ , and those  $\mathbf{a}^{12}$  which are related to the interaction between the sub-systems

$$\mathbf{a} \longrightarrow (\mathbf{a}^1, \mathbf{a}^2, \mathbf{a}^{12}) \longrightarrow \mathcal{H}(\mathbf{a}^1, \mathbf{a}^2, \mathbf{a}^{12}). \quad (55)$$

According to their definition, the work variables of the decomposed system (55)<sub>2</sub> are attached to the partial Hamiltonians as follows<sup>10</sup>

$$\mathcal{H}^1(\mathbf{a}^1, \mathbf{a}^{12}), \quad \mathcal{H}^2(\mathbf{a}^2, \mathbf{a}^{12}), \quad \mathcal{H}^{12}(\mathbf{a}^{12}), \quad (56)$$

resulting in

$$\dot{\mathcal{H}}^1 = \frac{\partial \mathcal{H}^1}{\partial \mathbf{a}^1} \cdot \dot{\mathbf{a}}^1 + \frac{\partial \mathcal{H}^1}{\partial \mathbf{a}^{12}} \cdot \dot{\mathbf{a}}^{12}, \quad \dot{\mathcal{H}}^2 = \frac{\partial \mathcal{H}^2}{\partial \mathbf{a}^2} \cdot \dot{\mathbf{a}}^2 + \frac{\partial \mathcal{H}^2}{\partial \mathbf{a}^{12}} \cdot \dot{\mathbf{a}}^{12}, \quad (57)$$

$$\dot{\mathcal{H}}^{12} = \frac{\partial \mathcal{H}^{12}}{\partial \mathbf{a}^{12}} \cdot \dot{\mathbf{a}}^{12}. \quad (58)$$

Starting with (6)<sub>1</sub>, we obtain with (57) and (58) and the suitable tracing

$$\dot{W} = \text{Tr}^2 \text{Tr}^1 \left\{ (\dot{\mathcal{H}}^1 + \dot{\mathcal{H}}^2 + \dot{\mathcal{H}}^{12}) \varrho \right\} = \quad (59)$$

$$= \text{Tr}^1(\dot{\mathcal{H}}^1 \varrho^1) + \text{Tr}^2(\dot{\mathcal{H}}^2 \varrho^2) + \text{Tr}(\dot{\mathcal{H}}^{12} \varrho). \quad (60)$$

This decomposition of the time derivative of the Hamiltonian allows to define external and internal power exchanges: external between each sub-system and the environment and internal exchanges between the sub-systems themselves

$$\dot{W}_{ex}^A := \text{Tr}^A \left( \frac{\partial \mathcal{H}^A}{\partial \mathbf{a}^A} \varrho^A \right) \cdot \dot{\mathbf{a}}^A, \quad A = 1, 2, \quad \frac{\partial \mathcal{H}^{12}}{\partial \mathbf{a}^A} \equiv \mathbf{0}, \quad (61)$$

$$\dot{W}_{int}^A := \text{Tr}^A \left( \frac{\partial \mathcal{H}^A}{\partial \mathbf{a}^{12}} \varrho^A \right) \cdot \dot{\mathbf{a}}^{12}, \quad \dot{W}_{int}^{12} := \text{Tr} \left( \frac{\partial \mathcal{H}^{12}}{\partial \mathbf{a}^{12}} \varrho \right) \cdot \dot{\mathbf{a}}^{12}. \quad (62)$$

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<sup>10</sup>  $\mathbf{a}^{12}$  describes the position of a partition between the sub-systems which is displaceable thus influencing the three Hamiltonians.

Consequently, we obtain according to (60)

$$\dot{W}_{ex} := \dot{W}_{ex}^1 + \dot{W}_{ex}^2, \quad \dot{W}_{int} := \dot{W}_{int}^1 + \dot{W}_{int}^2 + \dot{W}_{int}^{12}. \quad (63)$$

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

$$\blacksquare \quad \dot{W}_{int} = \text{Tr} \left( \frac{\partial \mathcal{H}}{\partial \mathbf{a}^{12}} \varrho \right) \cdot \dot{\mathbf{a}}^{12} \equiv 0, \quad \blacksquare \quad (64)$$

and we obtain from (63)<sub>2</sub>

$$- \dot{W}_{int}^1 = \dot{W}_{int}^2 + \dot{W}_{int}^{12}. \quad (65)$$

If  $\dot{W}_{int}^{12} > 0$ , the partition between the sub-systems is power absorbing, and if  $\dot{W}_{int}^{12} < 0$ , it is power supplying.

### 3.3.2 Heat exchanges

There are three different kinds of heat exchanges: that of the undecomposed system (7)<sub>1</sub>, the external heat exchanges taking place between each sub-system and the equilibrium environment, the internal heat exchanges taking place between the sub-systems themselves. For the present, the quantum theoretical expressions of these heat exchanges are specified and their connection to the corresponding contact temperatures is given below.

According to (5)<sub>2</sub> and (51), the heat exchange of the sub-system #A is defined by taking (260), (41)<sub>3</sub> and (49) into account

$$\begin{aligned} \dot{Q}^A &:= \text{Tr}^A(\mathcal{H}^A \dot{\varrho}^A) = \text{Tr}(\mathcal{H}^A \dot{\varrho}) = \text{Tr} \left\{ \mathcal{H}^A \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}, \varrho] \right) \right\} = \\ &= \text{Tr} \left\{ \mathcal{H}^A \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\} = \text{Tr} \left\{ \mathcal{H}^A \overset{\vee}{\varrho} \right\} = \\ &= \text{Tr}^A(\mathcal{H}^A \overset{\circ}{\varrho}^A) + \frac{i}{\hbar} \text{Tr} \left\{ \mathcal{H}^{12} [\mathcal{H}^A, \varrho] \right\}, \quad A = 1, 2. \end{aligned} \quad (66)$$

Always when the modified propagator  $\overset{\vee}{\varrho}$  appears, original quantum mechanics (characterized by  $\overset{\circ}{\varrho} \equiv 0$ ) of decomposed systems shows "thermodynamical properties", here a "heat exchange" and an "entropy exchange", a non-vanishing "entropy time rate" and not expected an "entropy production" (215) below. These facts are sufficient to consider the modified von Neumann equations (51).

For the partition #(12) between the sub-systems follows analogously to (66)<sub>2</sub>

$$\begin{aligned} \dot{Q}^{12} &:= \text{Tr}(\mathcal{H}^{12} \dot{\varrho}) = \text{Tr} \left\{ \mathcal{H}^{12} \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}, \varrho] \right) \right\} = \\ &= \text{Tr} \left\{ \mathcal{H}^{12} \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [(\mathcal{H}^1 + \mathcal{H}^2), \varrho] \right) \right\}. \end{aligned} \quad (67)$$

Inserting (17), (66) and (67) results in external and internal heat exchanges and in the influences of the partition between the sub-systems

$$\begin{aligned} \dot{Q}_{ex}^A &:= \text{Tr}(\mathcal{H}^A \overset{\circ}{\varrho}_{ex}) = \text{Tr}^A(\mathcal{H}^A \overset{\circ}{\varrho}_{ex}^A), \\ \dot{Q}_{int}^A &:= \text{Tr}(\mathcal{H}^A \overset{\circ}{\varrho}_{iso}) + \frac{i}{\hbar} \text{Tr} \left\{ \mathcal{H}^{12} [\mathcal{H}^A, \varrho] \right\} = \end{aligned} \quad (68)$$

$$= \text{Tr}\left\{\mathcal{H}^A\left(\dot{\varrho}_{iso} - \frac{i}{\hbar}\left[\mathcal{H}^{12}, \varrho\right]\right)\right\}, \quad A = 1, 2, \quad (69)$$

$$\dot{Q}_{ex}^{12} := \text{Tr}(\mathcal{H}^{12} \dot{\varrho}_{ex}), \quad (70)$$

$$\dot{Q}_{int}^{12} := \text{Tr}\left\{\mathcal{H}^{12}\left(\dot{\varrho}_{iso} - \frac{i}{\hbar}\left[(\mathcal{H}^1 + \mathcal{H}^2), \varrho\right]\right)\right\}. \quad (71)$$

From (66)<sub>2</sub>, (67)<sub>1</sub>, (5)<sub>2</sub> and (7)<sub>1</sub> follows the total heat exchange, external and internal, of the system

$$\dot{Q}^1 + \dot{Q}^2 + \dot{Q}^{12} = \dot{Q} = \text{Tr}(\mathcal{H} \dot{\varrho}). \quad (72)$$

According to (39)<sub>2</sub>, the heat exchanges of the decomposed described system ( $\dot{Q}^1, \dot{Q}^2, \dot{Q}^{12}$ ) are additive and equal to the heat exchange (7)<sub>1</sub>  $\dot{Q}$  of the undecomposed described system.

Splitting the propagator  $\dot{\varrho}$  of the undecomposed system according to (17) into its exchange and irreversibility parts, the partial heat exchanges (66) and (67) decompose into an external and an internal part

$$\dot{Q}^A = \dot{Q}_{ex}^A + \dot{Q}_{int}^A, \quad \dot{Q}^{12} = \dot{Q}_{ex}^{12} + \dot{Q}_{int}^{12}. \quad (73)$$

$$\dot{Q}_{ex}^1 + \dot{Q}_{ex}^2 + \dot{Q}_{ex}^{12} =: \dot{Q}_{ex} = \text{Tr}(\mathcal{H} \dot{\varrho}_{ex}), \quad (74)$$

$$\dot{Q}_{int}^1 + \dot{Q}_{int}^2 + \dot{Q}_{int}^{12} =: \dot{Q}_{int} = \text{Tr}(\mathcal{H} \dot{\varrho}_{iso}). \quad (75)$$

If the sum of the internal heat exchanges is set to zero and taking into account that the partition has no contact to the system's environment, from (75)<sub>2</sub> and (70) follows the thermodynamical setting<sup>11</sup>

$$\blacksquare \quad \dot{Q}_{int} = \text{Tr}(\mathcal{H} \dot{\varrho}_{iso}) \equiv 0, \quad \dot{Q}_{ex}^{12} = \text{Tr}(\mathcal{H}^{12} \dot{\varrho}_{ex}) \equiv 0, \quad \blacksquare \quad (76)$$

as conditions which  $\dot{\varrho}_{iso}$  and  $\dot{\varrho}_{ex}$  have to satisfy. According to (68)<sub>2</sub>, (76), (74) and (75) result in

$$\dot{Q}_{ex}^1 + \dot{Q}_{ex}^2 = \dot{Q}_{ex} = \text{Tr}^1(\mathcal{H}^1 \dot{\varrho}_{ex}^1) + \text{Tr}^2(\mathcal{H}^2 \dot{\varrho}_{ex}^2) = \text{Tr}(\mathcal{H} \dot{\varrho}_{ex}), \quad (77)$$

$$\dot{Q}_{int}^1 + \dot{Q}_{int}^2 + \dot{Q}_{int}^{12} = 0 = \text{Tr}(\mathcal{H} \dot{\varrho}_{iso}), \quad (78)$$

depicting that the external heat exchanges are additive and their sum is equal to the heat exchange of the undecomposed system.  $\dot{Q}_{int}^A$  is the heat exchange corresponding to the sub-system #A, and  $\dot{Q}_{int}^{12}$  is the "non-inertness" (with respect to the heat exchange) of the partition #(12).

From (78)<sub>1</sub> follows

$$-\dot{Q}_{int}^1 = \dot{Q}_{int}^2 + \dot{Q}_{int}^{12}, \quad (79)$$

a relation which is analogous to (65), if the partition between the sub-systems is not inert. If  $\dot{Q}_{int}^{12} > 0$ , this partition is heat absorbing, if  $\dot{Q}_{int}^{12} < 0$ , the partition is heat emitting. Consequently,  $\dot{Q}_{int}^{12}$  is not a "heat exchange", but a heating (or cooling) of the partition which prevents continuous heat exchange

<sup>11</sup>(76)<sub>1</sub> already known from (14)

through it.  $\dot{Q}_{int}^{12}$  vanishes with  $\mathcal{H}^{12}$  according to (71). Consequently, the non-inertness is based on the quantum theoretical interaction.

Taking (76)<sub>1</sub> into account, the non-inertness (71) becomes

$$\dot{Q}_{int}^{12} := -\text{Tr}\left\{(\mathcal{H}^1 + \mathcal{H}^2)\left(\overset{\circ}{\varrho}_{iso} - \frac{i}{\hbar}[\mathcal{H}^{12}, \varrho]\right)\right\} = \quad (80)$$

$$= -\text{Tr}^1(\mathcal{H}^1 \overset{\circ}{\varrho}_{iso}^1) - \text{Tr}^2(\mathcal{H}^2 \overset{\circ}{\varrho}_{iso}^2) + \text{Tr}\left\{(\mathcal{H}^1 + \mathcal{H}^2)\frac{i}{\hbar}[\mathcal{H}^{12}, \varrho]\right\}. \quad (81)$$

A comparison with (66)<sub>4</sub> shows that (78)<sub>1</sub> is satisfied.

In general, the internal heat exchanges are not continuous at the partition between the sub-systems #1 and #2, if the non-inertness  $\dot{Q}_{int}^{12}$  does not vanish according to (79). Consequently, an inert partition is according to (71) characterized by

$$\text{inert:} \quad \dot{Q}_{int}^{12} \equiv 0 = \text{Tr}\left\{\mathcal{H}^{12}\left(\overset{\circ}{\varrho}_{iso} - \frac{i}{\hbar}[\mathcal{H}, \varrho]\right)\right\}, \quad (82)$$

and taking (76)<sub>2</sub> and (1)<sub>1</sub> into account,

$$\text{inert:} \quad 0 = \text{Tr}\left\{\mathcal{H}^{12}\left(\overset{\circ}{\varrho} - \frac{i}{\hbar}[\mathcal{H}, \varrho]\right)\right\} = \text{Tr}\left\{\mathcal{H}^{12} \overset{\circ}{\varrho}\right\} \quad (83)$$

is a constraint for the time derivative of the density operator of processes in bipartite systems equipped with an inert partition.

Concerning the heat exchanges, the following facts are valid:

- According to the decomposition of the Hamiltonian of the bipartite system, there are two heat exchanges,  $\dot{Q}^A$ ,  $A=1,2$ , and the non-inertness,  $\dot{Q}^{12}$ , (66) and (67).
- Inserting the decomposed propagator (17), external and internal heat exchanges are generated, (68) to (71).
- As a thermodynamical input is chosen: the sum of all internal heat exchanges vanishes (76)<sub>1</sub>, and the partition has no external contact and therefore the corresponding external heat exchange vanishes (76)<sub>2</sub>.
- The heat exchange of the undecomposed system is the sum of the external heat exchanges (77)<sub>1</sub>.
- The internal heat exchange is not continuous at the partition, if  $\dot{Q}_{int}^{12}$ , the non-inertness, does not vanish. A dynamical constraint is found for processes in bipartite systems equipped with an inert partition (83).

In original quantum mechanics,  $\overset{\circ}{\varrho} \equiv 0$ , the external heat exchanges vanish according to (68) and (70), that means, the considered bipartite system is adiabatically isolated from its environment, but power exchanges may exist according to (61)<sub>1</sub> so long as the time derivatives of the work variables  $\dot{a}^A$  do not vanish. The internal heat exchanges, (69) and (71), vanish with  $\mathcal{H}^{12}$  in original quantum mechanics.

### 3.3.3 External heat exchanges and contact temperature

The contact temperature  $\Theta$  is defined by an inequality such as (11) for **undecomposed systems** in an equilibrium environment of the thermostatic temperature  $T^\square$ <sup>12</sup>

$$\Theta \text{ fix, } T^\square \text{ variable : } \left( \frac{1}{\Theta} - \frac{1}{T^\square} \right) \dot{Q}(T^\square) \geq 0, \quad \dot{Q} \equiv \dot{Q}_{ex}. \quad (84)$$

According to the definition of the contact temperature, the heat exchange vanishes with change of sign at  $T^\square = \Theta$

$$\dot{Q}_{ex}(\Theta) = 0. \quad (85)$$

The external heat exchange  $\dot{Q}_{ex}$  in (84) depends on the temperature difference located in the brackets left of it, described by a constitutive equation of the shape

$$\dot{Q}_{ex}(T^\square) = \text{Tr}(\mathcal{H} \overset{\circ}{\rho}(\Theta, T^\square)) = \Omega^{ex} \left( \frac{1}{\Theta} - \frac{1}{T^\square} \right) \equiv \Omega^{ex}(x) \quad (86)$$

according to (7)<sub>1</sub>.

■ Presupposed that small temperature differences  $x$  generate small heat exchanges<sup>13</sup>,  $\Omega^{ex}(x)$  is a continuous function of  $x$ . Also a fact of experience is that the heat exchange is as greater as the temperature difference  $x$  is

$$x > y \longleftrightarrow \Omega^{ex}(x) > \Omega^{ex}(y), \quad x = y \longleftrightarrow \Omega^{ex}(x) = \Omega^{ex}(y), \quad (87)$$

that means,  $\Omega^{ex}(x)$  is a strictly monotonous function. ■

Because of continuity and monotony of  $\Omega^{ex}(x)$ , the external heat exchange has a single zero which is the environment equilibrium temperature

$$\Omega^{ex}(0) = 0, \quad \Omega^{ex}(x) = 0 \longrightarrow x = 0, \quad (88)$$

$$\dot{Q}_{ex}(T^\square) = 0 \longleftrightarrow T^\square = \Theta \quad (89)$$

according to (86), resulting according to (87)<sub>1</sub> in

$$\Omega^{ex}(x) \gtrless 0 \longleftrightarrow x \gtrless 0. \quad (90)$$

For **decomposed systems** (84) writes

$$\Theta^A \text{ fix, } T^\square \text{ variable : } \left( \frac{1}{\Theta^A} - \frac{1}{T^\square} \right) \dot{Q}_{ex}^A(T^\square) \geq 0, \quad A = 1, 2, \quad (91)$$

with the thermostatic temperature  $T^\square$  of the equilibrium environment. Analogous to (85)

$$T^\square \doteq \Theta^A \longrightarrow \dot{Q}_{ex}^A(\Theta^A) = 0 \quad (92)$$

is valid, also with a change of sign. The constitutive equation of the heat exchanges are according to (86)

$$\dot{Q}_{ex}^A(T^\square) = \Omega_A^{ex} \left( \frac{1}{\Theta^A} - \frac{1}{T^\square} \right). \quad (93)$$

<sup>12</sup>The temperature of the environment is written in brackets  $\dot{Q}_{ex}(T^\square)$ .

<sup>13</sup>this is a fact of experiments

A comparison with (68)<sub>2</sub> shows that the propagators depend on temperature<sup>14</sup>, resulting in

$$\dot{Q}_{ex}^A(T^\square) = \text{Tr}^A \left\{ \mathcal{H}^A \overset{\circ}{\varrho}_{ex}^A(\Theta^A; T^\square) \right\} = \Omega_A^{ex} \left( \frac{1}{\Theta^A} - \frac{1}{T^\square} \right), \quad (94)$$

$$\text{Tr}^A \left\{ \mathcal{H}^A \overset{\circ}{\varrho}_{ex}^A(\Theta^A; \Theta^A) \right\} = 0. \quad (95)$$

Addition of the inequalities (91) and use of (77)<sub>1</sub> results in

$$\frac{\dot{Q}_{ex}^1(T^\square)}{\Theta^1} + \frac{\dot{Q}_{ex}^2(T^\square)}{\Theta^2} - \frac{\dot{Q}_{ex}(T^\square)}{T^\square} \geq 0. \quad (96)$$

Two special cases of (96) ( $T^\square \doteq \Theta^1$  and  $T^\square \doteq \Theta^2$ ) are by taking (92) and (77)<sub>1</sub> into account

$$\left( \frac{1}{\Theta^2} - \frac{1}{\Theta^1} \right) \dot{Q}_{ex}(\Theta^1) \geq 0, \quad \left( \frac{1}{\Theta^1} - \frac{1}{\Theta^2} \right) \dot{Q}_{ex}(\Theta^2) \geq 0, \quad (97)$$

from which follows

$$\text{sign} \left( \dot{Q}_{ex}(\Theta^2) \right) = -\text{sign} \left( \dot{Q}_{ex}(\Theta^1) \right). \quad (98)$$

Consequently according to (85), the following inequalities of the external undecomposed heat exchange are valid

$$\dot{Q}_{ex}(\Theta^2) \underset{\geq}{\underset{\leq}} \left( \dot{Q}_{ex}(\Theta) = 0 \right) \underset{\geq}{\underset{\leq}} \dot{Q}_{ex}(\Theta^1). \quad (99)$$

Consequently according (87)<sub>1</sub>, the contact temperatures satisfy

$$\Theta^2 \underset{\geq}{\underset{\leq}} \Theta \underset{\geq}{\underset{\leq}} \Theta^1. \quad (100)$$

Because there is no contact between the partition #(12) and the system's equilibrium environment,  $T^\square$  cannot be used in connection with the internal heat exchanges  $\overset{\circ}{Q}_{int}^A$ . That means, the defining inequalities (91) have to be replaced by other ones in the next section.

### 3.3.4 Internal heat exchanges and contact temperature

Because the definition of the contact temperature  $\Theta^A$  of the sub-system #A does not depend on the special heat conduction, external or internal, the defining inequality of the contact temperature in case of internal heat conduction is analogous to (91)

$$\blacksquare \quad \Theta^A \text{ fix, } T^A \text{ variable : } \left( \frac{1}{\Theta^A} - \frac{1}{T^A} \right) \dot{Q}_{int}^A(T^A) \geq 0, \quad A = 1, 2. \quad \blacksquare \quad (101)$$

Here, the thermostatic temperature  $T^\square$  of the environment is replaced by the variable  $T^A$ , the replacement temperature [20], so that analogously to (92)

$$T^A \doteq \Theta^A \longrightarrow \dot{Q}_{int}^A(\Theta^A) = 0 \quad (102)$$

is valid.

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<sup>14</sup>See more details in sect.3.4

■ Additionally, it is presupposed that the internal heat exchange is as the external one (87) a continuous and monotonous function, a constitutive equation of the variable  $T^A$

$$\dot{Q}_{int}^A(T^A) = \Omega^{int} \left( \frac{1}{\Theta^A} - \frac{1}{T^A} \right), \quad A = 1, 2. \quad \blacksquare \quad (103)$$

In contrast to (93), here exists only one internal contact between the sub-systems #1 and #2, whereas there are two external contacts between #1 and the environment and #2 and the environment. In (91),  $T^\square$  (and  $\Theta^A$ ) determines the heat exchange  $\dot{Q}_{ex}^A(T^\square)$ , whereas in (101), the heat exchange  $\dot{Q}_{int}^A(T^A)$  determines  $T^A$  (besides the given  $\Theta^A$ ).

A comparison of (103) with (69) shows that also the propagator belonging to the internal heat exchange depends on temperature

$$\dot{Q}_{int}^A(T^A) = \text{Tr}^A \left\{ \mathcal{H}^A \overset{\circ}{\varrho}_{iso}^A(\Theta^A; T^A) \right\} - \frac{i}{\hbar} \text{Tr} \left\{ \mathcal{H}^A \left[ \mathcal{H}^{12}, \varrho \right] \right\}, \quad (104)$$

resulting according to (102) in

$$\dot{Q}_{int}^A(\Theta^A) = \text{Tr}^A \left\{ \mathcal{H}^A \overset{\circ}{\varrho}_{iso}^A(\Theta^A; \Theta^A) \right\} - \frac{i}{\hbar} \text{Tr} \left\{ \mathcal{H}^A \left[ \mathcal{H}^{12}, \varrho \right] \right\} = 0. \quad (105)$$

$$\mathcal{H}^{12} \doteq 0 \longrightarrow \text{Tr}^A \left\{ \mathcal{H}^A \overset{\circ}{\varrho}_{iso}^A(\Theta^A; \Theta^A) \right\} = 0. \quad (106)$$

Inserting (105) into (104) results in

$$\dot{Q}_{int}^A(T^A) = \text{Tr}^A \left\{ \mathcal{H}^A \left( \overset{\circ}{\varrho}_{iso}^A(\Theta^A; T^A) - \overset{\circ}{\varrho}_{iso}^A(\Theta^A; \Theta^A) \right) \right\}. \quad (107)$$

From (79) follows the non-inertness by taking (103) into account

$$\dot{Q}_{int}^1(T^1) + \dot{Q}_{int}^2(T^2) = -\dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2), \quad (108)$$

$$\Omega^{int} \left( \frac{1}{\Theta^1} - \frac{1}{T^1} \right) + \Omega^{int} \left( \frac{1}{\Theta^2} - \frac{1}{T^2} \right) = -\dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2). \quad (109)$$

By taking (103) and (107) into account, (109) results in

$$\begin{aligned} \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2) &= -\text{Tr}^1 \left\{ \mathcal{H}^1 \left( \overset{\circ}{\varrho}_{iso}^1(\Theta^1; T^1) - \overset{\circ}{\varrho}_{iso}^1(\Theta^1; \Theta^1) \right) \right\} - \\ &\quad -\text{Tr}^2 \left\{ \mathcal{H}^2 \left( \overset{\circ}{\varrho}_{iso}^2(\Theta^2; T^2) - \overset{\circ}{\varrho}_{iso}^2(\Theta^2; \Theta^2) \right) \right\}. \end{aligned} \quad (110)$$

The internal heat exchange between the two sub-systems is described by two replacement temperatures,  $T^1$  and  $T^2$ , according to (101), (103) and (109)

$$\left( \frac{1}{\Theta^1} - \frac{1}{T^1} \right) \dot{Q}_{int}^1(T^1) \geq 0, \quad \left( \frac{1}{\Theta^2} - \frac{1}{T^2} \right) \dot{Q}_{int}^2(T^2) \geq 0, \quad (111)$$

$$\dot{Q}_{int}^1(T^1) = \Omega^{int} \left( \frac{1}{\Theta^1} - \frac{1}{T^1} \right), \quad \dot{Q}_{int}^2(T^2) = \Omega^{int} \left( \frac{1}{\Theta^2} - \frac{1}{T^2} \right). \quad (112)$$

Addition of (111)<sub>1</sub> and (111)<sub>2</sub> results in

$$\frac{\dot{Q}_{int}^1(T^1)}{\Theta^1} + \frac{\dot{Q}_{int}^2(T^2)}{\Theta^2} \geq \frac{\dot{Q}_{int}^1(T^1)}{T^1} + \frac{\dot{Q}_{int}^2(T^2)}{T^2}. \quad (113)$$

By taking (108) into account, this inequality yields

$$\begin{aligned}
\frac{\dot{Q}_{int}^1(T^1)}{\Theta^1} + \frac{\dot{Q}_{int}^2(T^2)}{\Theta^2} &\geq \\
&\geq \frac{1}{T^1} \left( -\dot{Q}_{int}^2(T^2) - \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2) \right) + \\
&\quad + \frac{1}{T^2} \left( -\dot{Q}_{int}^1(T^1) - \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2) \right) = \\
&= -\frac{\dot{Q}_{int}^1(T^1)}{T^2} - \frac{\dot{Q}_{int}^2(T^2)}{T^1} - \left( \frac{1}{T^1} + \frac{1}{T^2} \right) \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2). \quad (114)
\end{aligned}$$

Summing up (113) and (114) results in

$$\begin{aligned}
2 \left( \frac{\dot{Q}_{int}^1(T^1)}{\Theta^1} + \frac{\dot{Q}_{int}^2(T^2)}{\Theta^2} \right) &\geq \left( \frac{1}{T^1} - \frac{1}{T^2} \right) \left( \dot{Q}_{int}^1(T^1) - \dot{Q}_{int}^2(T^2) \right) - \\
&\quad - \left( \frac{1}{T^1} + \frac{1}{T^2} \right) \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2). \quad (115)
\end{aligned}$$

The quantum-thermal version of this inequality results from inserting of (107) and (110) into (115)<sup>15</sup>. The heat exchanges, the non-inertness and the expressions in the sequel look like classical relations, but according to (107) and (110), these are of quantum-thermal origin.

According to (115), four cases are possible by combination: (inert or non-inert) combined with ( $T^1 \neq T^2$  or  $T^1 = T^2 =: T^{12}$ ). For the present, **non-inert partitions**

•

$$\boxed{\dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2) \neq 0} \quad (116)$$

are considered starting with

□

$$\boxed{T^1 \doteq T^2 =: T^{12}}. \quad (117)$$

By taking (108) into account, (115) results in

$$\frac{\dot{Q}_{int}^1(T^{12})}{\Theta^1} + \frac{\dot{Q}_{int}^2(T^{12})}{\Theta^2} \geq -\frac{1}{T^{12}} \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^{12}, T^{12}). \quad (118)$$

The interpretation of this inequality is as follows: the non-inert partition #12 between the sub-systems #1 and #2 has its own temperature  $T^{12}$  different from the contact temperatures of the sub-systems,  $\Theta^1$  and  $\Theta^2$ . Consequently, the internal heat exchange takes place through a third non-inert sub-system #12, e.g. a heat reservoir.

A comparison of (118) with (96) shows the similarity between external and internal heat exchanges: the temperature of the environment  $T^\square$  corresponds to the temperature  $T^{12}$  of the non-inert partition, and the non-inertness corresponds to the external heat exchange of the undecomposed system.

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<sup>15</sup>a complex expression which is suppressed here

□ If the contact temperatures of the sub-systems are equal,

$$\boxed{\Theta^1 \doteq \Theta^2 =: \Theta^{12}}, \quad (119)$$

(115) yields by use of (108)

$$0 \geq \left(\frac{1}{T^1} - \frac{1}{T^2}\right) \left(\dot{Q}_{int}^1(T^1) - \dot{Q}_{int}^2(T^2)\right) + \left(\frac{2}{\Theta^{12}} - \frac{1}{T^1} - \frac{1}{T^2}\right) \dot{Q}_{int}^{12}(\Theta^{12}, \Theta^{12}; T^1, T^2). \quad (120)$$

The interpretation of this inequality is as follows: Although the sub-systems #1 and #2 have the same contact temperature  $\Theta^{12}$ , the heat exchanges through the non-inert partition #(12) do not vanish according to (112), if  $T^1 \neq T^2$

$$\dot{Q}_{int}^1(T^1) = \Omega^{int} \left(\frac{1}{\Theta^{12}} - \frac{1}{T^1}\right) \neq \dot{Q}_{int}^2(T^2) = \Omega^{int} \left(\frac{1}{\Theta^{12}} - \frac{1}{T^2}\right). \quad (121)$$

Because  $T^1 \neq T^2$  is presupposed, a thermostatic temperature  $T^{12}$  of the partition #(12) cannot be defined according to (117). The non-inert partition presents itself as a "thermodynamical double-sheet" which has two sides of different temperatures  $T^1$  and  $T^2$ . If this statement seems to be too speculative, the case  $T^1 = T^2$  (the "thermodynamical mono-sheet") is discussed below. According to (115), four kinds of partitions are possible by combination: (inert or non-inert) combined with (mono- or double-sheet).

□ If (117) and (119) are jointly valid

$$\boxed{T^1 \doteq T^2 =: T^{12}} \wedge \boxed{\Theta^1 \doteq \Theta^2 =: \Theta^{12}}, \quad (122)$$

(118) results in

$$\left(\frac{1}{T^{12}} - \frac{1}{\Theta^{12}}\right) \dot{Q}_{int}^{12}(\Theta^{12}, \Theta^{12}; T^{12}, T^{12}) \geq 0, \quad (123)$$

and according to (112), the internal heat exchanges are equal

$$\dot{Q}_{int}^1(T^{12}) = \Omega^{int} \left(\frac{1}{\Theta^{12}} - \frac{1}{T^{12}}\right) = \dot{Q}_{int}^2(T^{12}), \quad (124)$$

a fact which has the following interpretation: the partition #(12) is a heat reservoir of the temperature  $T^{12}$  surrounded by two sub-systems of equal contact temperature  $\Theta^{12}$ , and the heat exchanges between the heat reservoir and each sub-system are equal, thus cooling or heating the sub-systems with identical heat exchanges at both sides of #(12). According to (124) and (102), these heat exchanges vanish, if  $T^{12} = \Theta^{12}$ .

After having discussed the more general case of a non-inert partition, inert partitions are now considered, e.g. diathermal interfaces<sup>16</sup>.

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<sup>16</sup>the most usual contacts

- Presupposing an **inert partition**,

$$\boxed{\dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2) \equiv 0} \longrightarrow \dot{Q}_{int}^1(T^1) = -\dot{Q}_{int}^2(T^2) \quad (125)$$

follows from (108). Consequently by taking (102) and (88) into account, (125)<sub>2</sub> results in

$$T^1 \doteq \Theta^1 \longleftrightarrow T^2 \doteq \Theta^2, \quad (126)$$

$$\Omega^{int}\left(\frac{1}{\Theta^1} - \frac{1}{T^1}\right) = -\Omega^{int}\left(\frac{1}{\Theta^2} - \frac{1}{T^2}\right), \quad (127)$$

$$\longrightarrow \frac{1}{\Theta^1} - \frac{1}{T^1} \begin{matrix} \geq \\ \leq \end{matrix} 0 \begin{matrix} \geq \\ \leq \end{matrix} \frac{1}{\Theta^2} - \frac{1}{T^2} \quad (128)$$

according to (90).

The necessity of using two variables,  $T^1$  and  $T^2$ , can be seen from (126): a single variable  $T^0 := T^1 \equiv T^2$  satisfies (126) only in the case  $\Theta^1 = \Theta^2$  which is not valid in general. Dependent on the contact temperatures of the sub-systems,  $\Theta^1$  and  $\Theta^2$ , the variables  $T^1$  and  $T^2$  determining the internal heat exchanges are connected to each other for inert partitions according to (128)

$$T^1 \begin{matrix} \geq \\ \leq \end{matrix} \Theta^1 \longleftrightarrow T^2 \begin{matrix} \leq \\ \geq \end{matrix} \Theta^2 \quad (129)$$

as a necessary condition of an inert partition.

A sufficient condition for vanishing non-inertness follows from the defining inequalities (111) which yield by taking (125)<sub>2</sub> into account

$$0 \leq \left(-\frac{1}{\Theta^2} + \frac{1}{T^2}\right) \left(-\dot{Q}_{int}^2(T^2)\right) = \left(-\frac{1}{\Theta^2} + \frac{1}{T^2}\right) \dot{Q}_{int}^1(T^1), \quad (130)$$

an inequality which is set identically to (112)<sub>1</sub>, resulting in

$$\blacksquare \quad 0 \leq \left(-\frac{1}{\Theta^2} + \frac{1}{T^2}\right) \dot{Q}_{int}^1(T^1) \doteq \left(\frac{1}{\Theta^1} - \frac{1}{T^1}\right) \dot{Q}_{int}^1(T^1) \quad (131)$$

$$\longrightarrow -\frac{1}{\Theta^2} + \frac{1}{T^2} = \frac{1}{\Theta^1} - \frac{1}{T^1}, \quad \blacksquare (132)$$

in accordance with (128) and (129).

Equation (132) shows, how the variables  $T^1$  and  $T^2$  depend on each other for inert partitions. Inserting (132) into (127) results in

$$\Omega^{int}\left(\frac{1}{\Theta^1} - \frac{1}{T^1}\right) = -\Omega^{int}\left(\frac{1}{\Theta^2} - \frac{1}{T^2}\right) = -\Omega^{int}\left(-\frac{1}{\Theta^1} + \frac{1}{T^1}\right), \quad (133)$$

$$\longrightarrow \Omega^{int}(x) = -\Omega^{int}(-x). \quad (134)$$

This odd-symmetry, derived for inert partitions, supplements the properties (87) to (90) of the constitutive equation of the internal heat exchanges in general.

- If the contact temperatures of the sub-systems separated by an inert double-sheet partition are equal

$$\boxed{\text{inert:}} \quad \boxed{\Theta^1 \doteq \Theta^2 =: \Theta^{12}}, \quad (135)$$

(129) yields

$$T^1 \underset{\leq}{\geq} \Theta^{12} \underset{\leq}{\geq} T^2, \quad (136)$$

and the heat exchanges are according to (127) and (132)

$$\Omega^{int} \left( \frac{1}{\Theta^{12}} - \frac{1}{T^1} \right) = -\Omega^{int} \left( \frac{1}{\Theta^{12}} - \frac{1}{T^2} \right) \neq 0 \quad (137)$$

in contrast to (121) at a non-inert partition, and (120) results by use of (125)<sub>2</sub> and (135) at a double-sheet inert partition in

$$\left( \frac{1}{T^2} - \frac{1}{T^1} \right) \dot{Q}_{int}^1(T^1) \geq 0, \quad \left( \frac{1}{T^1} - \frac{1}{T^2} \right) \dot{Q}_{int}^2(T^1) \geq 0, \quad (138)$$

in accordance with (115). Consequently, the heat exchange between two sub-systems of equal contact temperature does not vanish in general, even if the partition between them is inert, a fact which is different from thermostatics. The reason for the non-vanishing of the internal heat exchange between sub-systems of equal contact temperature is  $T^1 \neq T^2$ , the double-sheet partition. The inequality (138) has the shape of a defining inequality (111)<sub>1</sub> in which the contact temperature  $\Theta^1$  is replaced by the heat exchange variable  $T^2$ .<sup>17</sup>

□ If the partition is inert and has its own temperature  $T^{12}$

$$\boxed{\text{inert:}} \quad \boxed{T^1 \doteq T^2 =: T^{12}}, \quad (139)$$

(129) yields

$$\Theta^1 \underset{\leq}{\geq} T^{12} \underset{\leq}{\geq} \Theta^2, \quad (140)$$

and the heat exchanges are according to (127) and (132)

$$\Omega^{int} \left( \frac{1}{\Theta^1} - \frac{1}{T^{12}} \right) = -\Omega^{int} \left( \frac{1}{\Theta^2} - \frac{1}{T^{12}} \right) \neq 0. \quad (141)$$

The inequality (118) results for an inert mono-sheet partition by use of (125)<sub>2</sub> in

$$\left( \frac{1}{\Theta^1} - \frac{1}{\Theta^2} \right) \dot{Q}_{int}^1(T^{12}) \geq 0, \quad \left( \frac{1}{\Theta^2} - \frac{1}{\Theta^1} \right) \dot{Q}_{int}^2(T^{12}) \geq 0, \quad (142)$$

$$\longrightarrow \left( \frac{1}{\Theta^1} - \frac{1}{T^{12}} \right) \dot{Q}_{int}^1(T^{12}) + \left( \frac{1}{\Theta^2} - \frac{1}{T^{12}} \right) \dot{Q}_{int}^2(T^{12}) \geq 0, \quad (143)$$

a sum of two defining inequalities belonging to the sub-systems #1 and #2 with the common heat exchange variable  $T^{12}$  of the partition.

□ If (135) and (139) are jointly valid

$$\boxed{\text{inert:}} \quad \boxed{T^1 \doteq T^2 =: T^{12}} \wedge \boxed{\Theta^1 \doteq \Theta^2 =: \Theta^{12}}, \quad (144)$$

(136) and (140) result in

$$\Theta^{12} = T^{12}, \quad (145)$$

and (137) and (141) yield

$$\Omega^{int} \left( \frac{1}{\Theta^{12}} - \frac{1}{T^{12}} \right) = -\Omega^{int} \left( \frac{1}{\Theta^{12}} - \frac{1}{T^{12}} \right) = 0. \quad (146)$$

Consequently, the following<sup>18</sup> proposition is valid

<sup>17</sup>therefore the name "replacement temperature" for  $T^A$

<sup>18</sup>almost evident

**Proposition:** The internal heat exchange through an inert mono-sheet partition of temperature  $T^{12}$  which separates two non-equilibrium sub-systems of equal contact temperature  $\Theta^{12}$  vanishes with  $\Theta^{12} = T^{12}$ .

The contact temperature effects with respect to the heat exchange are different from those of the thermostatic temperature: the heat exchange between two non-equilibrium sub-systems of equal contact temperature does not vanish in general according to (137), even if the partition between the sub-systems is inert<sup>19</sup>, except the mono-sheet partition's temperature is equal to the joint contact temperature of the sub-systems according to (146).

- In **equilibrium** follows for arbitrary partitions according to (102) and the fact that the contact temperature changes into the thermostatic one which is equal in the two sub-systems according to equilibrium

$$\dot{Q}_{eq}^\alpha(T^\alpha) = 0 \longrightarrow T^\alpha = \Theta_{eq}^\alpha \equiv T_{eq}^\alpha = T_{eq}, \quad \alpha = 1, 2. \quad (147)$$

- Some **general remarks**

If the von Neumann equation is modified by the propagator  $\overset{\circ}{\varrho}$ , power and heat exchanges, (5)<sub>1</sub> and (7), are introduced. Because the propagator decomposes into an exchange part and an irreversible part,  $\overset{\circ}{\varrho}_{ex}$  and  $\overset{\circ}{\varrho}_{iso}$  according to (17), also the power and the heat exchanges decompose into ex- and int-parts. The decomposition of the power exchanges is achieved by the work variables, (61) and (62), whereas that of the heat exchanges is done by the parts of the decomposed propagator, (68) to (71). For undecomposed and bipartite systems, non-equilibrium contact temperatures are introduced, (84), (94) and (101), which appear in the quantum-thermal representation of the heat exchanges, (94) and (104). The heat exchanges are restricted by strictly monotonous constitutive equations, (86), (94) and (103). Thus, the propagators in the quantum-thermal representation of the heat exchanges are connected with their corresponding classical constitutive equations. This connection has to be taken into account by choosing the propagator of the modified von Neumann equation (1)<sub>1</sub>.

After the discussion of the heat exchanges, that of the entropy exchanges follows in the next section.

### 3.3.5 Entropy exchanges

For **undecomposed systems**, the entropy exchange is defined by heat exchange over contact temperature of the corresponding non-equilibrium sub-system according to (10)<sub>1</sub>. Presupposing that the heat exchange between system and environment takes place through an inert partition resulting in  $\dot{Q} = -\dot{Q}^\square$ , the defining inequality (11) becomes

$$\Xi = \frac{\dot{Q}}{\Theta} \geq \frac{\dot{Q}}{T^\square} = -\frac{\dot{Q}^\square}{T^\square} =: -\Xi^\square. \quad (148)$$

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<sup>19</sup>If the partition is not inert, the non-inertness prevents from vanishing of the heat exchanges according to (123) and (120).

The entropy exchange  $\Xi^\square$  is bound up with the equilibrium environment of temperature  $T^\square$ , whereas  $\Xi$  belongs to the undecomposed described non-equilibrium system of contact temperature  $\Theta$ . Consequently by introducing the non-equilibrium contact temperature, two different definitions of entropy exchange appear: the original one  $\Xi^\square$  bound up with the equilibrium environment, and  $\Xi$  bound up with the non-equilibrium system. The inequality (148) shows that the amounts of these entropy exchanges are different. The quantum-thermal version of (148) is generated by inserting (7)<sub>1</sub>.

For **bipartite systems**, the entropy exchange is as the heat exchange decomposed into an external and an internal part according to (94)<sub>1</sub> and (107). The external part is

$$\Xi_{ex}^A(T^\square) := \frac{\dot{Q}_{ex}^A(T^\square)}{\Theta^A} = \text{Tr}^A\left(\frac{\mathcal{H}^A}{\Theta^A} \dot{\varrho}_{ex}^A(\Theta^A; T^\square)\right), \quad A = 1, 2. \quad (149)$$

and the inequalities (84) and (96) transform into

$$\Xi_{ex}(T^\square) := \frac{\dot{Q}_{ex}(T^\square)}{\Theta} \geq \frac{\dot{Q}_{ex}(T^\square)}{T^\square} = -\frac{\dot{Q}_{ex}^\square(T^\square)}{T^\square} =: -\Xi_{ex}^\square(T^\square), \quad (150)$$

$$\Xi_{ex}^1(T^\square) + \Xi_{ex}^2(T^\square) \geq -\Xi_{ex}^\square(T^\square). \quad (151)$$

The sum of the entropy exchanges of the decomposed system (LHS of (151)) is greater than the original entropy exchange bound up with the equilibrium environment (RHS of (151)).

The inequality of the internal entropy exchanges is charged with the non-inertness which remains out of play for the external part. The inequality (115) results in

$$\begin{aligned} \Xi_{int}^1(T^1) + \Xi_{int}^2(T^2) &\geq \frac{1}{2}\left(\frac{1}{T^1} - \frac{1}{T^2}\right)\left(\dot{Q}_{int}^1(T^1) - \dot{Q}_{int}^2(T^2)\right) - \\ &\quad - \frac{1}{2}\left(\frac{1}{T^1} + \frac{1}{T^2}\right)\dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2), \end{aligned} \quad (152)$$

and the internal entropy exchanges are according to (107) and (104) defined by

$$\begin{aligned} \Xi_{int}^A(T^A) &:= \text{Tr}^A\left\{\frac{\mathcal{H}^A}{\Theta^A}\left(\dot{\varrho}_{iso}^A(\Theta^A; T^A) - \dot{\varrho}_{iso}^A(\Theta^A; \Theta^A)\right)\right\} = \\ &= \text{Tr}^A\left\{\frac{\mathcal{H}^A}{\Theta^A}\dot{\varrho}_{iso}^A(\Theta^A; T^A)\right\} - \frac{i}{\hbar}\text{Tr}\left\{\frac{\mathcal{H}^A}{\Theta^A}[\mathcal{H}^{12}, \varrho]\right\}, \\ &= \text{Tr}\left\{\frac{\mathcal{H}^A}{\Theta^A}\left(\dot{\varrho}_{iso} - \frac{i}{\hbar}[\mathcal{H}^{12}, \varrho]\right)\right\}. \end{aligned} \quad (153)$$

The inequality (152) takes different shapes depending on the special partition between the sub-systems #1 and #2:

$$\text{non-inert, double-sheet: } \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2) \not\equiv 0, \quad T^1 \neq T^2, \quad (154)$$

$$\text{non-inert, mono-sheet: } \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^{12}, T^{12}) \not\equiv 0, \quad T^1 = T^2 =: T^{12}, \quad (155)$$

$$\text{inert, double-sheet: } \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2) \equiv 0, \quad T^1 \neq T^2, \quad (156)$$

$$\text{inert, mono-sheet: } \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^{12}, T^{12}) \equiv 0, \quad T^1 = T^2 =: T^{12}. \quad (157)$$

Taking (125)<sub>2</sub> into account, (152) becomes by use of (156) and (155)

$$\Xi_{int}^1(T^1) + \Xi_{int}^2(T^2) \geq \left( \frac{1}{T^1} - \frac{1}{T^2} \right) \dot{Q}_{int}^1(T^1), \quad (158)$$

$$\Xi_{int}^1(T^{12}) + \Xi_{int}^2(T^{12}) \geq -\frac{1}{T^{12}} \dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^{12}, T^{12}), \quad (159)$$

or for the inert mono-sheet partition (157)

$$\Xi_{int}^1(T^{12}) + \Xi_{int}^2(T^{12}) \geq 0. \quad (160)$$

The inequalities (151) and (152) are quantum-thermal ones: the entropy exchanges (149)<sub>1</sub>, (150)<sub>1</sub> and (153) are defined by using  $\dot{Q}_{ex}^A(T^\square)$ ,  $\dot{Q}_{ex}(T^\square)$ ,  $\dot{Q}_{int}^A(T^A)$  and  $\dot{Q}_{int}^{12}(\Theta^1, \Theta^2; T^1, T^2)$  which on their part are quantum-thermally defined by (94)<sub>1</sub>, (77), (107) and (110).

In contrast to the additivity of the heat exchanges according to (77)<sub>1</sub> and (108), the entropy exchanges are not additive in general according to (151) and (152). Especially, the external entropy exchange of the undecomposed system is not equal to the sum of the external entropy exchanges of the decomposed system according to (151). This fact is called the *compound deficiency* of the entropy exchanges [20, 21]. Compound deficiencies will be treated in more detail in sect.3.9.

A comparison of (61) and (62) with (68) and (69) depicts that the decomposition into the external and internal parts is different for power-, heat- and entropy-exchanges. Whereas this decomposition is achieved for the power exchanges by the work variables, the heat- and entropy-exchanges are decomposed by the decomposition of the propagator. Essential is that the sum of the external entropy exchanges of the sub-systems is not equal to the entropy exchange of the corresponding undecomposed system according to (151).

### 3.4 Propagator's temperature dependence

Because the heat exchanges (94) and (104) depend on the contact temperature of the sub-system and on an additional variable, and because the heat exchanges are represented by a quantum-thermal expression which contains the corresponding propagator, also this propagator depends on the used temperatures. Now, the propagators of the different description of the systems, undecomposed or decomposed, are connected by tracing which influences the domain of the propagators spanned by the temperatures as demonstrated in this section:

According to (11), the heat exchange of an undecomposed system depends on the contact temperature  $\Theta$  and on the temperature of the environment  $T^\square$ . Consequently according to (7)<sub>1</sub>, the temperature dependence of the propagator is for an

$$\text{undecomposed system:} \quad \overset{\circ}{\varrho}(\Theta, T^\square). \quad (161)$$

More specific is the situation of a

$$\text{bipartite system:} \quad \overset{\circ}{\varrho}(\Theta, \Theta^1, \Theta^2, T^\square, T^1, T^2) \quad (162)$$

whose heat exchanges depend on the temperature of the environment  $T^\square$ , on the contact temperatures of the undecomposed system  $\Theta$  and those of the two sub-systems  $\Theta^A$  and on the heat exchange variables  $T^A$  according to (93) and (103). The decomposition of the propagator (17) results in

$$\begin{aligned} \overset{\circ}{\varrho}(\Theta, \Theta^1, \Theta^2, T^\square, T^1, T^2) &= \\ &= \overset{\circ}{\varrho}_{ex}(\Theta, \Theta^1, \Theta^2, T^\square) + \overset{\circ}{\varrho}_{iso}(\Theta^1, \Theta^2, T^1, T^2), \end{aligned} \quad (163)$$

whereas the tracing yields

$$\begin{aligned} \overset{\circ}{\varrho}(\Theta, \Theta^1, \Theta^2, T^\square, T^1, T^2) &\longrightarrow \text{Tr}^2 \overset{\circ}{\varrho} = \overset{\circ}{\varrho}^1, \quad \text{Tr}^1 \overset{\circ}{\varrho} = \overset{\circ}{\varrho}^2, \\ &\longrightarrow \overset{\circ}{\varrho}^1(\Theta^1, T^\square, T^1), \quad \overset{\circ}{\varrho}^2(\Theta^2, T^\square, T^2), \end{aligned} \quad (164)$$

demonstrating that this tracing changes also the domain of the propagators. Thus, (163) results by tracing in

$$\overset{\circ}{\varrho}_{ex}^1(\Theta^1, T^\square), \quad \overset{\circ}{\varrho}_{ex}^2(\Theta^2, T^\square), \quad \overset{\circ}{\varrho}_{iso}^1(\Theta^1, T^1), \quad \overset{\circ}{\varrho}_{iso}^2(\Theta^2, T^2). \quad (165)$$

The same result appears, if the propagators of (164) are decomposed into their ex- and iso-parts

$$\overset{\circ}{\varrho}^1(\Theta^1, T^\square, T^1) = \overset{\circ}{\varrho}_{ex}^1(\Theta^1, T^\square) + \overset{\circ}{\varrho}_{iso}^1(\Theta^1, T^1), \quad (166)$$

$$\overset{\circ}{\varrho}^2(\Theta^2, T^\square, T^2) = \overset{\circ}{\varrho}_{ex}^2(\Theta^2, T^\square) + \overset{\circ}{\varrho}_{iso}^2(\Theta^2, T^2). \quad (167)$$

Decomposition (dec) and tracing (tra) of propagators represent a closed symmetric diagram:

$$(165) \xleftarrow{dec} (164) \xleftarrow{tra} (162) \xrightarrow{dec} (163) \xrightarrow{tra} (165). \quad (168)$$

### 3.5 First Law

The time rate of the energy is determined by those of the power- and heat exchanges. According to (4)<sub>2</sub>, we define the energy time rate of sub-system #A

$$\dot{E}^A := \dot{W}_{ex}^A + \dot{W}_{int}^A + \dot{Q}_{ex}^A + \dot{Q}_{int}^A. \quad (169)$$

The terms including  $\mathcal{H}^{12}$  result in the rate of the interaction energy according to (65) and (79)

$$\dot{E}^{12} := \dot{W}_{int}^{12} + \dot{Q}_{int}^{12} = -\dot{W}_{int}^1 - \dot{W}_{int}^2 - \dot{Q}_{int}^1 - \dot{Q}_{int}^2, \quad (170)$$

resulting in

$$\dot{E}^1 + \dot{E}^2 + \dot{E}^{12} = \dot{W}_{ex} + \dot{Q}_{ex} = \dot{E} \quad (171)$$

according to (63)<sub>1</sub> and (77)<sub>1</sub>. As expected, the sum of the energy changes of the sub-systems ( $\dot{E}^1 + \dot{E}^2$ ) is different from the energy change  $\dot{E}$  of the undecomposed system, a fact which is called *compound deficiency* (see sect.3.9) and which is caused by the quantum-theoretical interaction.

This clear formulation of the First Law indicates that the exchange quantities power- and heat exchange are suitably defined in sects.3.3.1 and 3.3.2.

## 3.6 Entropy

### 3.6.1 Partial entropies

Because in decomposed systems, the density operator  $\varrho$  of the undecomposed system is replaced by those of the sub-systems of the bipartite system, (44) and (45), we are able to define partial entropies of the sub-systems. Starting with the Shannon entropy [22, 23] of the undecomposed system (8)

$$S(\varrho) = -k_B \text{Tr}(\varrho \ln \varrho) \quad (172)$$

the partial entropies of the sub-systems are defined by

$$S_1(\varrho^1) := -k_B \text{Tr}^1(\varrho^1 \ln \varrho^1), \quad S_2(\varrho^2) := -k_B \text{Tr}^2(\varrho^2 \ln \varrho^2) \quad (173)$$

using the partial density operators (44) and (45).

Entropy is by definition a state function. Consequently, it contains only parameters of the system to which the entropy belongs. The Shannon entropies (172) and (173) are such state functions of the undecomposed system and of its sub-systems #1 and #2 <sup>20</sup>. There are a lot of different definitions of entropy [24, 25, 6] which all result in quantum thermodynamics of different shape, because the entropy production depends on the defined entropy. In contrast to the measurable quantities, such as power, heat exchange, contact temperature, there is no measuring instrument for entropy which comes as a definition into play generating an unequivocal thermodynamical structure.

According to (260) in sect.5.1, the partial entropies (173) result in

$$S_1(\varrho^1) = -k_B \text{Tr}(\varrho \ln \varrho^1), \quad S_2(\varrho^2) = -k_B \text{Tr}(\varrho \ln \varrho^2). \quad (174)$$

A comparison of (174) with (172) depicts that the partial entropies are not additive with respect to the entropy of the undecomposed system

$$S_1(\varrho^1) + S_2(\varrho^2) - S(\varrho) = -k_B \text{Tr} \left\{ \varrho \left( \ln(\varrho^1 \varrho^2) - \ln \varrho \right) \right\}, \quad (175)$$

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

Using Klein's inequality [26]

$$\text{Tr}(A \ln B) - \text{Tr}(A \ln A) \leq \text{Tr}B - \text{Tr}A, \quad (176)$$

we obtain according to (176) and (259)

$$\text{Tr} \left\{ \varrho \left( \ln(\varrho^1 \varrho^2) - \ln \varrho \right) \right\} \leq \text{Tr}(\varrho^1 \varrho^2) - \text{Tr} \varrho = 0, \quad (177)$$

$$\text{Tr}(\varrho^1 \varrho^2) = \text{Tr}^1 \text{Tr}^2(\varrho^1 \varrho^2) = 1, \quad (178)$$

and (175) results in

$$S_1(\varrho^1) + S_2(\varrho^2) \geq S(\varrho). \quad (179)$$

If the entropy  $S$  of the undecomposed system does not decompose into the partial entropies of the decomposed system, it is according to (179) smaller than the sum of the partial entropies. From (175) follows

$$\varrho \doteq \varrho^1 \varrho^2 \longrightarrow S_1(\varrho^1) + S_2(\varrho^2) = S(\varrho^1 \varrho^2), \quad (180)$$

and the entropies of the sub-systems are additive in case of a decomposed statistical operator of the undecomposed system.

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<sup>20</sup>The non-inertness (71) of the partition is not taken into the definition of entropy.

### 3.6.2 Entropy rates

Starting with (172) and (173)

$$S_A = -k_B \text{Tr}(\varrho \ln \varrho^A) = -k_B \text{Tr}^A(\varrho^A \ln \varrho^A) \quad (181)$$

results in by taking (47) into account

$$\begin{aligned} \dot{S}_A &= -k_B \text{Tr}^A(\dot{\varrho}^A \ln(Z\varrho^A)) = \\ &= -k_B \text{Tr}^A \left\{ \left( -\frac{i}{\hbar} [\mathcal{H}^A, \varrho^A] - \frac{i}{\hbar} \text{Tr}^B[\mathcal{H}^{12}, \varrho] + \dot{\varrho}^A \right) \ln(Z\varrho^A) \right\} = \\ &= -k_B \text{Tr}^A \left\{ \left( -\frac{i}{\hbar} \text{Tr}^B[\mathcal{H}^{12}, \varrho] + \dot{\varrho}^A \right) \ln(Z\varrho^A) \right\} = \\ &= -k_B \text{Tr} \left\{ \left( \dot{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \ln(Z\varrho^A) \right\}, \quad A, B = 1, 2; A \neq B. \end{aligned} \quad (182)$$

Summing up the entropy time rates of the sub-systems, we obtain from (182)<sub>4</sub> and (9)

$$\begin{aligned} \dot{S}_1 + \dot{S}_2 - \dot{S} &= \\ &= -k_B \text{Tr} \left\{ \left( \dot{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \ln(Z^1 \varrho^1 Z^2 \varrho^2) - \dot{\varrho} \ln(Z\varrho) \right\}, \end{aligned} \quad (183)$$

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 (179) is called *compound deficiency* (sect.3.9).

If the density operator  $\varrho$  of the undecomposed system decomposes, from (175) and (183) the additivity of entropy and entropy time rate is obtained

$$\varrho \doteq \varrho^1 \varrho^2, \quad Z \doteq Z^1 Z^2 \longrightarrow S = S_1 + S_2, \quad (184)$$

$$\text{and additional } \mathcal{H}^{12} \doteq \underline{0} \longrightarrow \dot{S} = \dot{S}_1 + \dot{S}_2. \quad (185)$$

Introducing the decomposition (17), the entropy time rate (182)<sub>4</sub> splits into an external and an internal part

$$\dot{S}_A^{ex} := -k_B \text{Tr} \left\{ \dot{\varrho}_{ex} \ln(Z\varrho^A) \right\}, \quad (186)$$

$$\dot{S}_A^{int} := -k_B \text{Tr} \left\{ \left( \dot{\varrho}_{iso} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \ln(Z\varrho^A) \right\}. \quad (187)$$

### 3.6.3 Separation Axiom

According to (180) and (184), entropy and entropy time rate are additive, if the statistical operator decomposes and if in the case of entropy time rates the interaction operator vanishes  $\mathcal{H}^{12} \doteq \underline{0}$  according to (183). Then, according to (50) and (51), the two sub-systems are separated from each other. Consequently, the heat exchanges  $\dot{Q}^A$  vanish, whereas the entropies  $S_A$  and their time rates  $\dot{S}_A$  are untouched by the separation of the sub-systems. Thus, according to (66)<sub>6</sub> and (182)<sub>5</sub>

$$\blacksquare \quad \dot{Q}_{sep}^A \doteq \text{Tr}^A(\mathcal{H}^A \dot{\varrho}_{sep}^A) = 0, \quad (188)$$

$$\dot{S}_A^{sep} \doteq -k_B \text{Tr}^A \left\{ \dot{\varrho}_{sep}^A \ln(Z\varrho^A) \right\} \neq 0 \quad \blacksquare \quad (189)$$

is valid.

As in sect.5.2 is demonstrated, the following propagator is sufficient for (188) and (189)

$$\blacksquare \quad \overset{\circ}{\varrho}_{sep}^A = \left[ \mathcal{H}^A, \left[ \ln(Z\varrho^A), \mathcal{H}^A \right] \right]. \quad \blacksquare \quad (190)$$

The entropy time rate results in

$$\dot{S}_A^{sep} = -k_B \text{Tr}^A \left\{ \left[ \ln(Z\varrho^A), \mathcal{H}^A \right] \left[ \ln(Z\varrho^A), \mathcal{H}^A \right] \right\} \neq 0. \quad (191)$$

Because of (188)<sub>2</sub>, the entropy production of #A is equal to the corresponding entropy time rate (see next sect. (193))

$$\Sigma_A^{sep} \equiv \dot{S}_A^{sep}. \quad (192)$$

These internal entropy production is unknown in original quantum mechanics because of  $\overset{\circ}{\varrho} \equiv 0$ .

### 3.7 Entropy productions

According to (12)<sub>1</sub>, the entropy production of the sub-system #A of a bipartite system is defined by

$$\Sigma_A := \dot{S}_A - \Xi^A = \dot{S}_A^{ex} + \dot{S}_A^{int} - \Xi_{ex}^A - \Xi_{int}^A. \quad (193)$$

The second equality follows from (17), the decomposition of the propagator into its exchange and its irreversibility part. Because in undecomposed systems the entropy production is defined as the time rate of entropy in isolated systems (19)<sub>1</sub>, the same is demanded for external isolated sub-systems, resulting according to (186) and (187), (149) and (153) in

$$\begin{aligned} \blacksquare \quad \Sigma_A &\doteq \dot{S}_A^{int} - \Xi_{int}^A = -k_B \text{Tr} \left\{ \left( \overset{\circ}{\varrho}_{iso} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \ln(Z\varrho^A) \right\} - \\ &\quad - \text{Tr} \left\{ \frac{\mathcal{H}^A}{\Theta^A} \left( \overset{\circ}{\varrho}_{iso} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\} = \\ &= -\text{Tr} \left\{ \left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z\varrho^A) \right) \left( \overset{\circ}{\varrho}_{iso} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\}, \quad (194) \\ 0 &\doteq \dot{S}_A^{ex} - \Xi_{ex}^A = -k_B \text{Tr} \left\{ \overset{\circ}{\varrho}_{ex} \ln(Z\varrho^A) \right\} - \text{Tr} \left( \frac{\mathcal{H}^A}{\Theta^A} \overset{\circ}{\varrho}_{ex} \right) = \\ &= -\text{Tr} \left\{ \left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z\varrho^A) \right) \overset{\circ}{\varrho}_{ex} \right\}. \quad \blacksquare \quad (195) \end{aligned}$$

This expression corresponds to (21) and yields the contact temperature of sub-system #A in quantum-theoretical formulation

$$\frac{1}{\Theta^A} = \frac{-\text{Tr} \left\{ k_B \ln(Z\varrho^A) \overset{\circ}{\varrho}_{ex} \right\}}{\text{Tr} \left\{ \mathcal{H}^A \overset{\circ}{\varrho}_{ex} \right\}}. \quad (196)$$

Adding (195) and (194) results in the partial entropy production of sub-system #A

$$\Sigma_A = -\text{Tr} \left\{ \left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z\varrho^A) \right) \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\}. \quad (197)$$

If the two sub-systems are separated from each other,  $\mathcal{H}^{12} \doteq \underline{0}$ ,

$$\Sigma_A^0 = -\text{Tr}^A \left\{ \left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z \varrho^A) \right) \overset{\circ}{\varrho}^A \right\} \geq 0, \quad (198)$$

their entropy production is not negative and (197) results in

$$\Sigma_A \geq \text{Tr} \left\{ \left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z \varrho^A) \right) \frac{i}{\hbar} \left[ \mathcal{H}^{12}, \varrho \right] \right\} =: \Sigma_A^{oqu}. \quad (199)$$

Consequently, the entropy production  $\Sigma_A$  of #A in quantum thermodynamics is not smaller than  $\Sigma_A^{oqu}$  that in original quantum mechanics characterized by  $\overset{\circ}{\varrho} \equiv 0$ .

According to (53)<sub>2</sub> and (23)<sub>2</sub>, the partial entropy production (197) vanishes  $\Sigma_A^{eq} = 0$  in equilibrium, as well as  $\Sigma_A^{0eq}$  does for the separated sub-system #A in (198). Because of this separation, the statistical operator  $\varrho_{eq}^A$  is canonical according to (38)

$$\left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z \varrho^A) \right)^{eq} = \underline{0}. \quad (200)$$

Consequently, both brackets of (197) vanish in equilibrium, and (199) becomes

$$\Sigma_A^{eq} = 0 \geq \text{Tr} \left\{ \left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z \varrho^A) \right)^{eq} \frac{i}{\hbar} \left[ \mathcal{H}^{12}, \varrho \right]^{eq} \right\} = 0 = \Sigma_A^{oqu}. \quad (201)$$

As expected, the entropy production vanishes in equilibrium in quantum thermodynamics as well as in original quantum mechanics.

### 3.8 Original quantum mechanics and bipartite systems

Original quantum mechanics is characterized by  $\overset{\circ}{\varrho} \equiv 0$ . Consequently, the discrimination into isolated and non-isolated systems disappears according to (15),  $\overset{\circ}{\varrho}_{iso} = \overset{\circ}{\varrho}_{ex} \equiv 0$  which does not influence the power exchanges (sect.3.3.1).

If the system is undecomposed, the heat exchange, the entropy time rate and the entropy production vanish in original quantum mechanics according to sect.2. This is the reason why original quantum mechanics is characterized as a theory for adiabatically isolated reversible systems.

This characterization changes for bipartite systems. According to (68) to (71), the external heat exchanges vanish likewise as in original quantum mechanics of undecomposed systems (adiabatical isolation), but the internal heat exchanges do not according to (104). Consequently, also entropy exchange and entropy production are not identical to zero according to (153) and (194).

A shortcoming is that the quantum-theoretical definition of the partial contact temperature (196) cannot be given in original quantum mechanics. If the classical definition of contact temperature through the defining inequality (101) is not accepted, entropy exchange and consequently entropy production cannot be defined in original quantum mechanics although heat exchanges are existing. Consequently, the introduction of the propagator is necessary for establishing a consistent quantum thermodynamics.

In original quantum mechanics of decomposed systems, the thermodynamical quantities heat exchange, entropy exchange, entropy time rate and

entropy production vanish with the interaction  $\mathcal{H}^{12}$  between the sub-systems #1 and #2. This result was expected because with  $\mathcal{H}^{12} \doteq \underline{0}$ , the bipartite system decomposes into two undecomposed systems.

The entropy production in original quantum mechanics (199) vanishes with  $\mathcal{H}^{12}$ , that means,  $\Sigma_A^{oqu}$  is generated by the contact between #1 and #2. If the contact is cancelled,  $\mathcal{H}^{12} \doteq \underline{0}$ , both sub-systems are reversible  $\Sigma_A^{oqu0} = 0$ , that means, entropy production is generated by interaction of reversible systems. Thus, the statement is valid: Original quantum mechanics of bipartite closed Schottky systems is an endoreversible theory.

The corresponding statement in quantum thermodynamics is different: Presupposing  $\mathcal{H}^{12} \doteq \underline{0}$ , (197) results in

$$\Sigma_A^0 = -\text{Tr}^A \left\{ \left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z \varrho^A) \right) \overset{\circ}{\varrho}^A \right\}, \quad (202)$$

that means, different from original quantum mechanics, the sub-systems themselves are not reversible, if the contact between them is cancelled. But in equilibrium, the entropy production vanishes in quantum thermodynamics as well as in original quantum mechanics according to (201).

### 3.9 Compound deficiency

If an undecomposed system is divided into a bipartite system, the generated partial quantities of the sub-systems may be or may be not additive. Not additive means, that sum up quantities of the sub-systems do not result in the corresponding quantity of the undecomposed system.

Concerning the power exchanges, additive or not depends on the different work variables (55) which generate external and internal power exchanges, (61) and (62). Concerning the heat exchanges, the split into external and internal ones is achieved by that of the propagator (17). External power and heat exchanges are additive according to (63)<sub>1</sub> and (77)<sub>1</sub>, whereas internal power and heat exchanges, (65) and (78), are not additive, caused by the partition between the sub-systems.

Different contact temperatures of the sub-systems and the partition between them prevent the additivity of the entropy exchanges generating the inequalities (151) and (152). In general, the entropy (179) and the entropy time rates (183) are not additive unless the density operator of the undecomposed system decomposes into those of the sub-systems (184).

More general: If  $\boxtimes$  is a quantity of the undecomposed system and  $\boxtimes^1$  and  $\boxtimes^2$  are the corresponding quantities of the sub-systems after the decomposition of the undecomposed system into a bipartite one, then the *compound deficiency*  $\boxtimes_{cd}$  is defined as follows [20]

$$\boxtimes_{cd} := \boxtimes - \boxtimes^1 - \boxtimes^2 =: \boxtimes - \boxtimes^{da}. \quad (203)$$

Here,  $\boxtimes^{da}$  is the quantity which is generated by decomposed additivity.

Consequently, there are two possibilities to describe a bipartite system: as a decomposed one by  $\boxtimes^{da}$  or as an undecomposed one by  $\boxtimes$ . These descriptions are of different information about the system, if the compound deficiency  $\boxtimes_{cd}$  is not zero. The answer to the question "What is the correct entropy time rate of the system?" depends according to (183) on its description chosen as decomposed or undecomposed.

According to (203), we obtain from (39) the compound deficiency of the Hamiltonian

$$\mathcal{H}_{cd} := \mathcal{H} - \mathcal{H}^1 - \mathcal{H}^2 = \mathcal{H}^{12}, \quad (204)$$

which is caused by the interaction part, a fact which is obvious: the sum of the Hamiltonians of the sub-systems differs from the Hamiltonian of the corresponding undecomposed system.

### 3.10 Removing semi-classical description

Up to now, a decomposed bipartite system is described semi-classically, that means, the external exchange quantities with its environment are not connected to an interaction Hamiltonian, but are represented by the exchange propagator (16). Now, this environment is separated from the decomposed system by isolation

$$\overset{\circ}{\varrho}_{ex} \equiv 0 \longrightarrow \overset{\circ}{\varrho} \equiv \overset{\circ}{\varrho}_{iso}, \quad (205)$$

thus considering an isolated bipartite system consisting of two irreversibly running sub-systems which are connected by an interaction Hamiltonian (204)<sub>2</sub> which describes exchange properties due to the partition between the two sub-systems. Consequently, the two sub-systems are interacting, and the environment is isolated from them. The propagator  $\overset{\circ}{\varrho}$  belongs to the bipartite system and is as well as  $\varrho$  decomposable into those of the interacting sub-systems, (44) and (45),

$$\overset{\circ}{\varrho}^1 := \text{Tr}^2 \overset{\circ}{\varrho}, \quad \overset{\circ}{\varrho}^2 := \text{Tr}^1 \overset{\circ}{\varrho}. \quad (206)$$

Taking into account that the work variables are affected by the isolation according to (57)

$$\dot{\mathbf{a}}_{iso}^1 \equiv \mathbf{0}, \quad \dot{\mathbf{a}}_{iso}^2 \equiv \mathbf{0}, \quad (207)$$

and that the density operator  $\varrho$  of the bipartite system is not affected by the isolation, the in sect.3 derived relations remain valid in the special case of isolation which is characterized by (205) and (207).

The exchanges between the sub-systems are by taking the partition # (12) into account as follows:

- According to (65) and (62) the **power exchange**

$$\left\{ \text{Tr}^1 \left( \frac{\partial \mathcal{H}^1}{\partial \mathbf{a}^{12}} \varrho^1 \right) + \text{Tr}^2 \left( \frac{\partial \mathcal{H}^2}{\partial \mathbf{a}^{12}} \varrho^2 \right) + \text{Tr} \left( \frac{\partial \mathcal{H}^{12}}{\partial \mathbf{a}^{12}} \varrho \right) \right\} \cdot \dot{\mathbf{a}}^{12} = 0. \quad (208)$$

- According to (69), (71) and (78), the **heat exchange**

$$\begin{aligned} & \text{Tr} \left\{ \mathcal{H}^1 \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\} + \text{Tr} \left\{ \mathcal{H}^2 \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\} + \\ & + \text{Tr} \left\{ \mathcal{H}^{12} \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [(\mathcal{H}^1 + \mathcal{H}^2), \varrho] \right) \right\} = 0. \end{aligned} \quad (209)$$

- According to (153), (113) and (112) the **entropy exchange**

$$\begin{aligned} & \text{Tr} \left\{ \frac{\mathcal{H}^1}{\Theta^1} \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\} + \text{Tr} \left\{ \frac{\mathcal{H}^2}{\Theta^2} \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\} \geq \\ & \geq \frac{1}{T^1} \Omega^{int} \left( \frac{1}{\Theta^1} - \frac{1}{T^1} \right) + \frac{1}{T^2} \Omega^{int} \left( \frac{1}{\Theta^2} - \frac{1}{T^2} \right) \end{aligned} \quad (210)$$

which has different appearance due to the partition according to (152).

- According to (169), (62)<sub>1</sub>, (69), (170)<sub>1</sub>, (62)<sub>2</sub>, (71) and (171) the **energy exchange**

$$\dot{E}^A = \text{Tr}^A \left( \frac{\partial \mathcal{H}^A}{\partial \mathbf{a}^{12}} \varrho^A \right) \cdot \dot{\mathbf{a}}^{12} + \text{Tr} \left\{ \mathcal{H}^A \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\}, \quad A = 1, 2, \quad (211)$$

$$\dot{E}^{12} = \text{Tr} \left( \frac{\partial \mathcal{H}^{12}}{\partial \mathbf{a}^{12}} \varrho \right) \cdot \dot{\mathbf{a}}^{12} + \text{Tr} \left\{ \mathcal{H}^{12} \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [(\mathcal{H}^1 + \mathcal{H}^2), \varrho] \right) \right\}, \quad (212)$$

$$\dot{E}^1 + \dot{E}^2 + \dot{E}^{12} = \text{Tr} \left\{ \frac{\partial}{\partial \mathbf{a}^{12}} (\mathcal{H}^1 + \mathcal{H}^2 + \mathcal{H}^{12}) \varrho \right\} \cdot \dot{\mathbf{a}}^{12} = 0. \quad (213)$$

- According to (187) and (194) the **entropy rate and -production**

$$\dot{S}_A = -k_B \text{Tr} \left\{ \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \ln(Z \varrho^A) \right\}, \quad A = 1, 2, \quad C \neq A, \quad (214)$$

$$\Sigma_A = -\text{Tr} \left\{ \left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z \varrho^A) \right) \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\} = \quad (215)$$

$$= -\text{Tr}^A \left\{ \left( \frac{\mathcal{H}^A}{\Theta^A} + k_B \ln(Z \varrho^A) \right) \text{Tr}^C \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}^{12}, \varrho] \right) \right\}. \quad (216)$$

Although the contact temperature cannot be defined in original quantum mechanics ( $\overset{\circ}{\varrho} \equiv 0$ ), the thermodynamical quantities entropy rate and -production, heat- and entropy exchange are established for bipartite systems by  $\mathcal{H}^{12}$  also in this case. The contact temperature which appears according to (210) and (215) in entropy exchange and entropy production is for original quantum mechanics added by hand from phenomenological non-equilibrium thermodynamics. No such problems arise, if quantum thermodynamics takes the propagator  $\overset{\circ}{\varrho}$  into consideration modifying the von Neuman equation.

According to (205) and (207), the relations (208) to (216) belong to an isolated bipartite system whose sub-systems, #1 and #2, are interacting with each other through a material impervious partition described by the interaction Hamiltonian  $\mathcal{H}^{12}$ . We now interpret these sub-systems for getting rid of the semi-classical description of the bipartite system:

$$\#1 \quad \longrightarrow \quad \text{the system } \mathcal{G}, \quad (217)$$

$$\#2 \quad \longrightarrow \quad \text{the environment } \mathcal{G}^\square, \quad (218)$$

$$\#(12) \quad \longrightarrow \quad \text{the partition } \partial \mathcal{G}, \quad (219)$$

$$\varrho, \overset{\circ}{\varrho} \quad \longrightarrow \quad \text{belonging to the undecomposed system } \mathcal{G} \cup \mathcal{G}^\square, \quad (220)$$

$$\varrho^A, \overset{\circ}{\varrho}^A \quad \longrightarrow \quad \text{belonging to the sub-system } \#A. \quad (221)$$

With that, the semi-classical description of sub-systems in contact is replaced by a quantum-thermal one represented by (208) to (216). Special contacts, such as usually considered in quantum thermodynamics [27], are considered in the next section.

### 3.10.1 Inert contacts

Inert partitions between sub-systems establish inert contacts which are defined by equal incoming and outgoing power- and heat exchanges through  $\partial \mathcal{G}$ , according to (208) and (209) [and (82)] resulting in

$$\text{Tr} \left( \frac{\partial \mathcal{H}^{12}}{\partial \mathbf{a}^{12}} \varrho \right) \cdot \dot{\mathbf{a}}^{12} = 0, \quad \text{Tr} \left\{ \mathcal{H}^{12} \left( \overset{\circ}{\varrho} - \frac{i}{\hbar} [(\mathcal{H}^1 + \mathcal{H}^2), \varrho] \right) \right\} = 0. \quad (222)$$

Consequently, the two first terms in (208) and (209) remain, and  $\dot{E}^{12} = 0$  is zero.

Usually, in quantum thermodynamics not only inert but also mono-sheet partitions are considered. Consequently, (139) and (141) are valid, and (210) yields

$$\text{Tr}\left\{\frac{\mathcal{H}^1}{\Theta^1}\left(\overset{\circ}{\varrho} - \frac{i}{\hbar}[\mathcal{H}^{12}, \varrho]\right)\right\} + \text{Tr}\left\{\frac{\mathcal{H}^2}{\Theta^2}\left(\overset{\circ}{\varrho} - \frac{i}{\hbar}[\mathcal{H}^{12}, \varrho]\right)\right\} \geq 0, \quad (223)$$

that means, because of different contact temperatures of the sub-systems, the entropy exchange is discontinuous at  $\partial\mathcal{G}$ . Taking (209) and (222)<sub>2</sub> into account, (223) results in

$$\text{Tr}\left\{\left(\frac{1}{\Theta^2} - \frac{1}{\Theta^1}\right)\mathcal{H}^2\left(\overset{\circ}{\varrho} - \frac{i}{\hbar}[\mathcal{H}^{12}, \varrho]\right)\right\} \geq 0, \quad (224)$$

or using (66)<sub>4</sub>

$$\left(\frac{1}{\Theta^2} - \frac{1}{\Theta^1}\right)\dot{Q}^2 \geq 0, \quad (225)$$

an inequality which is analogous to the defining inequalities (91) and (101).

### 3.10.2 Heat reservoirs

We now choose the environment #2 as a heat reservoir (HR) which is characterized by the following properties: It is a quasi-static system of the thermostatic temperature  $T_{HR}$  whose density operator is form-invariantly canonical during the contact time between #1 and HR according to (38)

$$\varrho_{HR}^2 = \frac{1}{Z} \exp\left[-\frac{\mathcal{H}_{HR}^2}{k_B T_{HR}}\right], \quad (226)$$

$$Z = \text{Tr}^2 \exp\left[-\frac{\mathcal{H}_{HR}^2}{k_B T_{HR}}\right], \quad [\mathcal{H}_{HR}^2, \varrho_{HR}^2] = \underline{0}. \quad (227)$$

Quasi-static means that non-equilibrium variables are not taken into account, and  $T_{HR}$  is the only slowly time dependent equilibrium variable according to (226). The heat reservoir undergoes a slow reversible (quasi-static) process [28], whereas the state of the system #1 may change irreversibly.

Contacting the heat reservoir #2 with the the system #1 through an inert and mono-sheet partition according to (157), exchanges (relative to the HR) happen according to (208), (222)<sub>1</sub> and (209), (222)<sub>2</sub> and (209)

$$\text{power exchange:} \quad \dot{W}_{HR}^2 = \text{Tr}^2\left(\frac{\partial\mathcal{H}_{HR}^2}{\partial\mathbf{a}^{12}}\varrho_{HR}^2\right) \cdot \dot{\mathbf{a}}^{12}, \quad (228)$$

$$\text{heat exchange:} \quad \dot{Q}_{HR}^2 = \text{Tr}^2\left\{\mathcal{H}_{HR}^2\left(\overset{\circ}{\varrho}_{HR}^2 - \frac{i}{\hbar}\text{Tr}^1\left[\mathcal{H}^{12}, \varrho\right]\right)\right\}, \quad (229)$$

$$\text{entropy exchange:} \quad \dot{\Xi}_{HR}^2 = \dot{Q}_{HR}^2/T_{HR}. \quad (230)$$

The heat exchange between HR and #1 is according to (229) determined by the propagator  $\overset{\circ}{\varrho}_{HR}^2$  which appears in the corresponding modified von Neumann equation (48). By taking (227)<sub>2</sub> into account, (48) results in

$$\overset{\circ}{\varrho}_{HR}^2 = -\frac{i}{\hbar}\text{Tr}^1\left[\mathcal{H}^{12}, \varrho\right] + \overset{\circ}{\varrho}_{HR}^2, \quad (231)$$

whereas  $\dot{\varrho}^1$  is determined by (47).

Because of the presupposed form-invariance of the canonical density operator (226) during the thermal contact between HR and #1, an other expression for  $\dot{\varrho}_{HR}^2$  can be generated by differentiation of (226) which is done in sect.5.3. The result is

$$\dot{\varrho}_{HR}^2 = \varrho_{HR}^2 \left\{ \text{Tr}^2 \left( \varrho_{HR}^2 \ln(Z \varrho_{HR}^2) \right) - \ln(Z \varrho_{HR}^2) \right\} \frac{\dot{T}_{HR}}{T_{HR}} =: C_{HR}^2 \dot{T}_{HR}. \quad (232)$$

Comparing (232) with (231) results in the propagator of the HR

$$\dot{\varrho}_{HR}^2 = \frac{i}{\hbar} \text{Tr}^1 \left[ \mathcal{H}^{12}, \varrho \right] + C_{HR}^2 \dot{T}_{HR}, \quad (233)$$

and the heat exchange (229) between HR and #1 becomes

$$\dot{Q}_{HR}^2 = \text{Tr}^2 \left( \mathcal{H}_{HR}^2 C_{HR}^2 \right) \dot{T}_{HR} =: C_{HR} \dot{T}_{HR}. \quad (234)$$

The reversible process of the HR is caused by its huge heat capacity  $C_{HR} \rightarrow \infty$  with respect to that of the contacted system #1 resulting in  $\dot{T}_{HR} \rightarrow 0$ , a property which characterize the HR as an idealized system<sup>21</sup>.

Because the considered partition between HR and #1 is presupposed as being inert,  $-\dot{Q}^1 = \dot{Q}_{HR}^2$ , (222)<sub>2</sub> and (209) result with (229) and (234)<sub>2</sub> in

$$\begin{aligned} -\text{Tr}^1 \left\{ \mathcal{H}^1 \left( \dot{\varrho}^1 - \frac{i}{\hbar} \text{Tr}^2 \left[ \mathcal{H}^{12}, \varrho \right] \right) \right\} &= C_{HR} \dot{T}_{HR} = \\ &= \text{Tr}^2 \left\{ \mathcal{H}_{HR}^2 \left( \dot{\varrho}_{HR}^2 - \frac{i}{\hbar} \text{Tr}^1 \left[ \mathcal{H}^{12}, \varrho \right] \right) \right\}. \end{aligned} \quad (235)$$

As expected, contacting HR with #1 and  $\dot{T}_{HR}$  is small positive, then  $T_{HR}$  is smaller than the contact temperature  $\Theta^1$  of #1, thus (225) is satisfied

$$\left( \frac{1}{T_{HR}} - \frac{1}{\Theta^1} \right) \dot{Q}_{HR}^2 \geq 0, \quad \left( \frac{1}{\Theta^1} - \frac{1}{T_{HR}} \right) \dot{Q}_{HR}^1 \geq 0. \quad (236)$$

### 3.10.3 Equilibrium

Equilibrium is defined by equilibrium conditions which are divided into necessary and complementary ones. The necessary equilibrium conditions for **undecomposed systems** are time independent work variables and vanishing entropy production

$$\dot{\mathbf{a}}_{eq} \equiv \mathbf{0} \longrightarrow \dot{W}_{eq} = 0, \quad \Sigma_{eq} \equiv 0 \longrightarrow 0 = \Xi_{eq} - \dot{S}_{eq}. \quad (237)$$

We obtain from (10) and (9) the necessary equilibrium condition (237)<sub>4</sub>

$$0 = \text{Tr} \left\{ \left( \frac{\mathcal{H}_{eq}}{\Theta_{eq}} + k_B \ln(Z \varrho_{eq}) \right) \dot{\varrho}_{eq} \right\}. \quad (238)$$

The left hand bracket in (238) set to zero, results by use of (1)<sub>1</sub> in a first complementary equilibrium condition ((237)<sub>1</sub> is silent valid)

$$\varrho_{eq} = \frac{1}{Z} \exp \left( - \frac{\mathcal{H}_{eq}}{k_B \Theta_{eq}} \right) \longrightarrow [\mathcal{H}_{eq}, \varrho_{eq}] = \underline{0} \longrightarrow \dot{\varrho}_{eq} = \dot{\varrho}_{eq} \quad (239)$$

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<sup>21</sup> $C_{HR} > 0$  is not proven

which is not sufficient because of (239)<sub>3</sub>. Adding a second complementary equilibrium condition,  $\dot{\varrho}_{eq} \doteq \underline{0}$ , (which alone is also not sufficient) makes both of them

$$\frac{\mathcal{H}_{eq}}{\Theta_{eq}} + k_B \ln(Z \varrho_{eq}) = 0 \quad \wedge \quad \dot{\varrho}_{eq} = 0 \quad (240)$$

sufficient for equilibrium because they induce according to (1) to (10)

$$\dot{\varrho}_{eq} = 0, \quad \dot{E}_{eq} = 0, \quad \dot{Q}_{eq} = 0, \quad \dot{S}_{eq} = 0, \quad \Xi_{eq} = 0, \quad \Theta_{eq} = T^\square. \quad (241)$$

Consequently, the necessary equilibrium conditions (237), especially the vanishing entropy production are not sufficient for equilibrium. Sufficient for equilibrium are the joint supplementary equilibrium conditions (240).

Equilibrium of **bipartite systems** means endoreversible equilibrium: sub-systems are in equilibrium and exchanges between them are zero. The necessary equilibrium conditions are according to (208), (216) and (12)

$$\dot{\mathbf{a}}_{eq}^{12} \equiv \mathbf{0} \longrightarrow \dot{W}_{eq}^A = 0, \quad (242)$$

$$\Sigma_A^{eq} = -\text{Tr}^A \left\{ \left( \frac{\mathcal{H}_{eq}^A}{\Theta_{eq}^A} + k_B \ln(Z \varrho_{eq}^A) \right) \text{Tr}^C \left( \dot{\varrho}_{eq} - \frac{i}{\hbar} [\mathcal{H}_{eq}^{12}, \varrho_{eq}^A] \right) \right\} \equiv 0, \quad (243)$$

$$\longrightarrow 0 = \Xi_{eq}^A - \dot{S}_{eq}^A, \quad A = 1, 2, \quad C \neq A, \quad (244)$$

resulting from (243) in two supplementary equilibrium conditions for vanishing entropy production according to (47), (48) and (1)<sub>1</sub>

$$\dot{\varrho}_{eq}^A - \frac{i}{\hbar} \text{Tr}^C [\mathcal{H}_{eq}^{12}, \varrho_{eq}^A] = \underline{0}, \longrightarrow \dot{\varrho}_{eq}^A = -\frac{i}{\hbar} [\mathcal{H}_{eq}^A, \varrho_{eq}^A], \quad (245)$$

$$\begin{aligned} \varrho_{eq}^A &= \frac{1}{Z} \exp \left( -\frac{\mathcal{H}_{eq}^A}{k_B \Theta_{eq}^A} \right) \longrightarrow [\mathcal{H}_{eq}^A, \varrho_{eq}^A] = \underline{0} \longrightarrow \\ &\longrightarrow \dot{\varrho}_{eq}^A = -\frac{i}{\hbar} \text{Tr}^C [\mathcal{H}_{eq}^{12}, \varrho_{eq}^A] + \dot{\varrho}_{eq}^A. \end{aligned} \quad (246)$$

The interaction of the two supplementary equilibrium conditions (245) and (246) is remarkable: Although each of them gives rise to vanishing entropy production, equilibrium only exists, if both are valid

$$\dot{\varrho}_{eq}^A = \underline{0} = -\text{Tr}^C [\mathcal{H}_{eq}^{12}, \varrho_{eq}^A] + \dot{\varrho}_{eq}^A, \quad A = 1, 2, \quad C \neq A, \quad (247)$$

and if additionally the partial propagator vanishes

$$\dot{\varrho}_{eq}^A = \underline{0} \longrightarrow \text{Tr}^C [\mathcal{H}_{eq}^{12}, \varrho_{eq}^A] = \underline{0}, \quad (248)$$

resulting in a constraint for the interaction Hamiltonian in equilibrium. Clear is that vanishing entropy production is not sufficient for equilibrium. As (243) and (244), also (247) and (248) are a necessary equilibrium conditions. A further one is according to (244)

$$\dot{S}_{eq}^A \doteq 0 \longrightarrow \Xi_{eq}^A = 0 \longleftrightarrow \dot{Q}_{eq}^A = 0. \quad (249)$$

The set of all necessary equilibrium conditions is sufficient for equilibrium.

Because the heat exchange is a continuous and monotonous function according to (103), from (225) and (249)<sub>3</sub> follows the thermostatic temperature  $T$  in equilibrium

$$\Theta_{eq}^1 = \Theta_{eq}^2 =: T. \quad (250)$$

The in 3.10.1 presupposed conditions for inert contacts (222) are satisfied also in equilibrium what can be confirmed by inserting (245)<sub>1</sub> into the first two terms of (209) resulting in (222)<sub>2</sub>.

## 4 Summary and Survey

Deriving the von Neumann equation from the Schrödinger equation in original quantum mechanics, the time rates of the weights of the statistical operator are set to zero without any argumentation. If these time rates are taken into account, a modified von Neumann equation is generated which allows to introduce thermodynamical properties into quantum mechanics, as demonstrated in the first part of this paper [1, 19] for undecomposed Schottky systems. The second part deals with closed decomposed Schottky systems, especially with bipartite systems interacting with an environment semi-classically and with isolated bipartite systems with interacting sub-systems. After a brief repetition of thermodynamics of undecomposed systems, that of closed decomposed systems is discussed in the following steps

- The *von Neumann equation* is modified by a so-called propagator  $\overset{\circ}{\varrho}$  including the time rates of the density operator's weights which are set to zero in original quantum mechanics. Density operator and propagator are adapted to the considered bipartite system by tracing, thus generating the equations of motion of the traced density operators belonging to the two sub-systems of the bipartite system (sect.3.2).
- The *exchanges* between the bipartite system and its environment and between the two sub-systems are taken into consideration (sect.3.3). There are three kinds of exchanges for closed Schottky systems: power-, heat- and entropy-exchange which are defined by the two partial Hamiltonians of the bipartite system and the interaction Hamiltonian belonging to the sub-systems:  $\mathcal{H} = \mathcal{H}^1 + \mathcal{H}^2 + \mathcal{H}^{12}$ .

- For describing the *power exchange*, two kinds of work variables are introduced (sect.3.3.1): those which belong to the external power exchange between the decomposed system and its environment ( $\dot{\mathbf{a}}^1$  and  $\dot{\mathbf{a}}^2$ ) and those which describe the internal power exchange between the sub-systems of the bipartite system ( $\dot{\mathbf{a}}^{12}$ ). Presupposing the dependence of the partial Hamiltonians on the work variables

$$\mathcal{H}^1(\mathbf{a}^1, \mathbf{a}^{12}), \quad \mathcal{H}^2(\mathbf{a}^2, \mathbf{a}^{12}), \quad \mathcal{H}^{12}(\mathbf{a}^{12}),$$

the external power exchange is (61)

$$\dot{W}_{ex} = \sum_A \text{Tr}^A \left( \frac{\partial \mathcal{H}^A}{\partial \mathbf{a}^A} \varrho^A \right) \cdot \dot{\mathbf{a}}^A, \quad A = 1, 2,$$

and the internal power exchange (62), (63)<sub>2</sub> and (64) vanishes

$$\dot{W}_{int} = \sum_B \text{Tr} \left( \frac{\partial \mathcal{H}^B}{\partial \mathbf{a}^{12}} \varrho \right) \cdot \dot{\mathbf{a}}^{12} \equiv 0, \quad B = 1, 2, (12).$$

□ Starting with the definition of *heat exchange* (66) and with the modified von Neumann equation (46)

$$\dot{Q}^B := \text{Tr}(\mathcal{H}^B \dot{\varrho}) = \text{Tr} \left\{ \mathcal{H}^B \left( \dot{\varrho} - \frac{i}{\hbar} [\mathcal{H}, \varrho] \right) \right\}, \quad B = 1, 2, (12),$$

the sum of the heat exchanges results in

$$\sum_B \dot{Q}^B = \text{Tr}(\mathcal{H} \dot{\varrho}).$$

The heat exchange has to be split into its external and its internal part. Whereas the splitting into external and internal exchange is achieved for the power exchange by the work variables, for the heat exchange this splitting is done by that of the propagator (17)

$$\dot{\varrho} = \dot{\varrho}_{ex} + \dot{\varrho}_{iso},$$

at which  $\dot{\varrho}_{iso}$  is generated by isolating the system. Because  $\mathcal{H}^{12}$  belong to the partition separating the two sub-systems which has no contact to the system's environment (76)<sub>2</sub>

$$\text{Tr}(\mathcal{H}^{12} \dot{\varrho}_{ex}) \equiv 0 \longrightarrow \dot{Q}_{ex}^1 + \dot{Q}_{ex}^2 = \dot{Q}_{ex},$$

and because the sum of all internal heat exchanges is zero (76)<sub>1</sub>

$$\text{Tr}(\mathcal{H} \dot{\varrho}_{iso}) \equiv 0 \longrightarrow -\dot{Q}_{int}^1 = \dot{Q}_{int}^2 + \dot{Q}_{int}^{12},$$

the external heat exchanges are additive, and the partition between the two sub-systems is in general not inert ( $-\dot{Q}_{int}^1 \neq \dot{Q}_{int}^2$ ).

□ In the realm of discrete systems, the *entropy exchange* is defined as heat exchange over temperature  $\{(149)_1$  and  $(153)_3$  (sect.3.3.5)<sup>22</sup>\}. The contact temperature is defined by the defining inequalities (84),(101) [13, 18]. Four temperatures appear in bipartite systems:  $\Theta^1, \Theta^2$  and  $\Theta^{12}$ , the contact temperatures of the sub-systems and that of the partition between them and  $T^\square$  or  $T_{HR}$  the temperature of the system's environment. Because of these different temperatures, the entropy exchanges are not additive (151) and not continuous even at inert partitions (223)<sup>23</sup>.

- *Partial density operators* are defined by tracing the density operator of the undecomposed system, (44) and (45). Consequently, the definition of the Shannon entropy of the undecomposed system can be transferred to the sub-systems, with the result that the sum of the partial entropies is not smaller than that of the undecomposed system. Also the sum of the partial entropy time rates is different from the entropy time rate of the undecomposed system<sup>24</sup>.

<sup>22</sup>This may be different in field formulation of thermodynamics because more exchanges appear as those for Schottky systems.

<sup>23</sup>for which power- and heat-exchange are continuous

<sup>24</sup>an effect called: compound deficiency

- *Partial entropy productions* are defined by the partial entropy time rates minus the partial entropy exchanges (193). The quantum-thermal expression of the *partial contact temperature* of a sub-system (196) is achieved by three procedures according to (198): separation of the sub-systems  $\mathcal{H}^{12} \doteq \mathcal{Q}$ , replacing  $\overset{\circ}{\varrho}^A \rightarrow \overset{\circ}{\varrho}^A - \varrho_{iso}^A = \varrho_{ex}^A$  and setting its partial entropy production  $\Sigma_A^0$  to zero which results in (195). The entropy production of separated sub-systems vanishes in original quantum mechanics according to (198), whereas in quantum thermodynamics it does not.
- Sufficient *equilibrium conditions* for undecomposed systems are according to (240) the vanishing propagator and the canonical statistical operator. For the sub-system  $\#A$  of a bipartite system follows from the vanishing entropy production two necessary equilibrium conditions, the equation of "motion" of the statistical operator of reversible "processes" (245)<sub>2</sub> and the canonical shape of this statistical operator (246)<sub>1</sub>. Because the entropy time rate vanishes in equilibrium, heat exchange and entropy exchange vanish, too, representing additional necessary equilibrium conditions which all together are sufficient for equilibrium.
- A *heat reservoir* is defined as a quasi-static system of the thermostatic temperature  $T_{HR}$  whose density operator is form-invariantly canonical during the contact time between the system and the heat reservoir (226). This definition results in a special time rate of the statistical operator of the heat reservoir (232) which is compared with that of a sub-system (233). Additionally is presupposed that the heat capacity of the heat reservoir is huge compared with that of the contacted system, resulting in a tiny time rate of the reservoir's thermostatic temperature. Presupposing an inert partition between heat reservoir and system, the heat exchange between them satisfies a defining inequality (236).

## 5 Appendices

### 5.1 Tracing

Starting with a tensor of the decomposed system

$$A = \sum_{kl} \sum_{pq} |\Psi_1^k\rangle \langle \Psi_2^l| A_{kl}^{pq} \langle \Psi_2^q| \langle \Psi_1^p|, \quad (251)$$

and its traces

$$\text{Tr}^1 A = \sum_{lq} |\Psi_2^l\rangle \langle \Psi_2^q| \left( \sum_m A_{ml}^{mq} \right) =: A^2, \quad (252)$$

$$\text{Tr}^2 A = \sum_{kp} |\Psi_1^k\rangle \langle \Psi_1^p| \left( \sum_m A_{km}^{pm} \right) =: A^1. \quad (253)$$

Considering the density operator (42) and the propagator (43), we obtain two special cases

$$A \doteq \varrho, \quad q \doteq l, \quad p \doteq k, \quad A_{kl}^{pq} = A_{kl}^{kl} = p_{kl}, \quad \sum_{jm} p_{jm} = 1, \quad (254)$$

$$A \doteq \overset{\circ}{\varrho}, \quad q \doteq l, \quad p \doteq k, \quad A_{kl}^{pq} = A_{kl}^{kl} = \overset{\bullet}{p}_{kl}, \quad \sum_{jm} \overset{\bullet}{p}_{jm} = 0, \quad (255)$$

$$\varrho^1 = \sum_k |\Psi_1^k\rangle \left( \sum_j p_{kj} \right) \langle \Psi_1^k|, \quad \varrho^2 = \sum_l |\Psi_2^l\rangle \left( \sum_j p_{jl} \right) \langle \Psi_2^l|, \quad (256)$$

$$\overset{\circ}{\varrho}^1 = \sum_k |\Psi_1^k\rangle \left( \sum_j \overset{\bullet}{p}_{kj} \right) \langle \Psi_1^k|, \quad \overset{\circ}{\varrho}^2 = \sum_l |\Psi_2^l\rangle \left( \sum_j \overset{\bullet}{p}_{jl} \right) \langle \Psi_2^l|, \quad (257)$$

Because partial traces commute, we obtain

$$\text{Tr}^2 A^2 = \text{Tr}^2 \text{Tr}^1 A = \text{Tr} A = \text{Tr}^1 \text{Tr}^2 A = \text{Tr}^1 A^1 = \sum_{mr} A_{rm}^m, \quad (258)$$

$$A \doteq \varrho \longrightarrow \text{Tr}^2 \overset{\circ}{\varrho}^2 = \text{Tr} \varrho = 1 = \text{Tr}^1 \overset{\circ}{\varrho}^1, \quad (259)$$

$$\text{Tr}(A^1 B) = \text{Tr}^1 \text{Tr}^2(A^1 B) = \text{Tr}^1(A^1 B^1). \quad (260)$$

A detailed calculation

$$\begin{aligned} \text{Tr}^1(A^1 B) &= \sum_j \sum_{sr} \sum_{kl} \sum_{pq} \\ &\langle \Psi_1^j | \Psi_1^s \rangle A_s^r \langle \Psi_1^r | \Psi_1^k \rangle |\Psi_2^l\rangle B_{kl}^{pq} \langle \Psi_2^q | \langle \Psi_1^p | \Psi_1^j \rangle = \\ &= \sum_j \sum_k \sum_{ql} A_j^k B_{kl}^{jq} |\Psi_2^l\rangle \langle \Psi_2^q|, \end{aligned} \quad (261)$$

$$\begin{aligned} \text{Tr}^1(BA^1) &= \sum_j \sum_{kl} \sum_{pq} \sum_{sr} \\ &\langle \Psi_1^j | \Psi_1^k \rangle |\Psi_2^l\rangle B_{kl}^{pq} \langle \Psi_2^q | \langle \Psi_1^p | \Psi_1^s \rangle A_s^r \langle \Psi_1^r | \Psi_1^j \rangle = \\ &= \sum_j \sum_p \sum_{ql} B_{jl}^{pq} A_p^j |\Psi_2^l\rangle \langle \Psi_2^q| = \sum_j \sum_k \sum_{ql} B_{kl}^{jq} A_j^k |\Psi_2^l\rangle \langle \Psi_2^q| \end{aligned} \quad (262)$$

results in

$$\text{Tr}^1[A^1, B] = 0 \longrightarrow \text{Tr}^2 \text{Tr}^1[A^1, B] = \text{Tr}^1[A^1, B^1] = 0. \quad (263)$$

## 5.2 Separation Axiom

Starting with (188) and (189)

$$\overset{\bullet}{Q}_{sep}^A \doteq \text{Tr}^A(\mathcal{H}^A \overset{\circ}{\varrho}_{sep}^A), \quad (264)$$

$$\overset{\bullet}{S}_A^{sep} \doteq -k_B \text{Tr}^A \{ \overset{\circ}{\varrho}_{sep}^A \ln(Z \varrho^A) \}, \quad (265)$$

and inserting (190)

$$\overset{\circ}{\varrho}_{sep}^A = \left[ \mathcal{H}^A, \left[ \ln(Z \varrho^A), \mathcal{H}^A \right] \right] =: \left[ \mathcal{H}^A, X^A \right] \quad (266)$$

into (264) and (265) results in

$$\overset{\bullet}{Q}_{sep}^A \doteq \text{Tr}^A \left( \mathcal{H}^A \left[ \mathcal{H}^A, X^A \right] \right) = \text{Tr}^A \left( \mathcal{H}^A \mathcal{H}^A X^A - \mathcal{H}^A \mathcal{H}^A X^A \right) = 0, \quad (267)$$

$$\begin{aligned} \overset{\bullet}{S}_A^{sep} &\doteq -k_B \text{Tr}^A \left\{ \left[ \mathcal{H}^A, X^A \right] \ln(Z \varrho^A) \right\} = \\ &= -k_B \text{Tr}^A \left\{ X^A \left[ \ln(Z \varrho^A), \mathcal{H}^A \right] \right\}. \end{aligned} \quad (268)$$

Inserting the definition of  $X^A$  (266), the entropy time rate results in

$$\overset{\bullet}{S}_A^{sep} = -k_B \text{Tr}^A \left\{ \left[ \ln(Z \varrho^A), \mathcal{H}^A \right] \left[ \ln(Z \varrho^A), \mathcal{H}^A \right] \right\} \neq 0. \quad (269)$$

### 5.3 Heat Reservoirs

Because there is no power exchange  $\dot{\mathbf{a}}^{12} = \mathbf{0}$  between the HR and the system #1,  $\dot{\mathcal{H}}_{HR}^2 = \underline{0}$  is valid, and the differentiation of the canonical statistical operator (226)

$$\varrho_{HR}^2 = \frac{1}{Z} \exp \left[ -\frac{\mathcal{H}_{HR}^2}{k_B T_{HR}} \right] \quad (270)$$

results in

$$\begin{aligned} \dot{\varrho}_{HR}^2 &= -\frac{1}{Z^2} \dot{Z} \exp \left[ -\frac{\mathcal{H}_{HR}^2}{k_B T_{HR}} \right] + \frac{1}{Z} \exp \left[ -\frac{\mathcal{H}_{HR}^2}{k_B T_{HR}} \right] \left( -\frac{\mathcal{H}_{HR}^2}{k_B} \left( -\frac{\dot{T}_{HR}}{T_{HR}^2} \right) \right. \\ &= -\frac{\dot{Z}}{Z} \varrho_{HR}^2 + \varrho_{HR}^2 \left( \frac{\mathcal{H}_{HR}^2}{k_B T_{HR}} \frac{\dot{T}_{HR}}{T_{HR}} \right). \end{aligned} \quad (271)$$

Following the differentiation of the normalization factor (227)

$$Z = \text{Tr}^2 \exp \left[ -\frac{\mathcal{H}_{HR}^2}{k_B T_{HR}} \right] \quad (272)$$

and taking the second term of (272) into account, results in

$$\dot{Z} = \text{Tr}^2 \left\{ Z \varrho_{HR}^2 \left( \frac{\mathcal{H}_{HR}^2}{k_B T_{HR}} \frac{\dot{T}_{HR}}{T_{HR}} \right) \right\}. \quad (273)$$

Inserting (273) into (271) and taking (270) into account results in

$$\begin{aligned} \dot{\varrho}_{HR}^2 &= \varrho_{HR}^2 \left\{ -\text{Tr}^2 \left( \varrho_{HR}^2 \frac{\mathcal{H}_{HR}^2}{k_B T_{HR}} \right) + \frac{\mathcal{H}_{HR}^2}{k_B T_{HR}} \right\} \frac{\dot{T}_{HR}}{T_{HR}} = \\ &= \varrho_{HR}^2 \left\{ \text{Tr}^2 \left( \varrho_{HR}^2 \ln(Z \varrho_{HR}^2) \right) - \ln(Z \varrho_{HR}^2) \right\} \frac{\dot{T}_{HR}}{T_{HR}}. \end{aligned} \quad (274)$$

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