

## WHY SO MANY “SCHOOLS” OF THERMODYNAMICS?

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**ABSTRACT.** A classification representing some main branches of phenomenological non-equilibrium thermodynamics is discussed. Differences and similarities of these selected branches are explained. Starting out with basic concepts of phenomenological thermodynamics, more developed theories with different back-grounds contributing to contemporary thermodynamics are considered. Because of its vast extent, this field cannot be presented completely in a single reasonably sized paper without any omissions.

### 1. Introduction

The question, why there are so many schools of thermodynamics, can be answered concisely: There is no natural extension from thermostatics to thermodynamics. This extension from thermostatics to thermodynamics seems to be easy: one has to replace the reversible processes of thermostatics by real ones and has to extend the balances of continuum mechanics by the appropriate thermal quantities such as heat flux density, internal energy and entropy.

But it is not so easy as supposed [1], because usually thermostatics is formulated for discrete systems [2], whereas thermodynamics can be presented in two forms, as a non-equilibrium theory of discrete systems [3, 4] or in a field formulation extending the balances of continuum mechanics [5]. Both descriptions are used in practice which is widespread for thermodynamics. Its methods can be successfully applied in various different disciplines such as Physics and Physical Chemistry, Mechanical and Chemical Engineering, Heat and Steam Engine Engineering, Material Science, Bio-Sciences, Energy Conversion Techniques, Air Conditioning and Refrigeration. Consequently, it is impossible to mention the different terminologies [6], methods and schools completely in this brief survey.

Presupposing that classical thermostatic is well-known, we will proceed along a way which is sketched in Table 1. Beginning with the original irreversible thermodynamics [7], a field which was methodically finished in the middle of the sixties, we will discuss contemporary non-equilibrium thermodynamics which we have divided into seven sections (that is only one possible incomplete classification): Rational [8], extended [9, 10], endoreversible [11] and quantum thermodynamics [12], mesoscopic theory [13], GENERIC [14] and evolution and variational criteria [15, 16, 17]. This classification is not at all complete and unique: Bio-thermodynamics [18, 19, 20], second law analysis [21], finite time thermodynamics [22], mathematical foundation and relativistic formulations of thermodynamics [23] are

missing, as well as all non-phenomenological theories: Statistical Thermodynamics, transport theory and molecular simulations.

## Classical Irreversible Thermodynamics

<b>Thermodynamics of Irreversible Processes</b>
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## Non-Equilibrium Thermodynamics

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**Table 1**

There are basic concepts which can be found in all schools of thermodynamics, thus allowing for a classification of these schools [24]. Such a classification can be done by answering the following questions [1]:

- Is the considered system described as a discrete one or in field formulation?
- Are temperature and entropy primitive concepts or derived quantities?
- Is the chosen state space small or large?
- Are all constitutive equations properly defined on the chosen state space?
- Is the dissipation inequality global or local in time, postulated or based on experimental facts?

- What is the procedure for exploiting the dissipation inequality [25]?
- Is the relation between heat flux density and entropy flux density universal or material-dependent?
- Are complex materials described by a mesoscopic theory or by introducing additional fields and their balances [26, 27]?
- Are the non-equilibrium processes restricted to endoreversible thermodynamics or are they described without reversible parts?
- Has the phenomenological description of a non-equilibrium system a correct quantum mechanical background?

## 2. Basic Variables

**2.1. Discrete systems.** A system which is separated by a partition from its surroundings is called a *discrete thermodynamic system* or a Schottky system [28], if the interaction between the system and its environment can be described by the heat exchange  $\dot{Q}$ , the power exchange  $\dot{W}$  and the material exchange  $\dot{\mathbf{n}}^e$ , represented by the external rates of the mole numbers [29].

The *basic variables* of a discrete system are the work variables  $\mathbf{a}$ , the mole numbers  $\mathbf{n}$ , the internal energy  $U$ , the contact temperature  $\Theta$  [30, 31] and additional internal variables  $\boldsymbol{\xi}$

$$(1) \quad (\mathbf{a}, \mathbf{n}, U, \Theta, \boldsymbol{\xi})(t).$$

The “equation of motion” of these variables is the first law of thermodynamics valid in non-equilibrium [32]

$$(2) \quad \dot{U} = \dot{Q} + \mathbf{A} \cdot \dot{\mathbf{a}} + \mathbf{h} \cdot \dot{\mathbf{n}}^e.$$

Here the  $\mathbf{A}$  are the generalized forces and  $\mathbf{h}$  the molar enthalpies describing the change of the internal energy of the open system. Both quantities,  $\mathbf{A}$  and  $\mathbf{h}$ , are constitutive ones given by non-equilibrium constitutive equations. The rates  $\dot{Q}$ ,  $\dot{\mathbf{a}}$  and  $\dot{\mathbf{n}}^e$  which are determined by the environment are also given by constitutive equations.

The rate of a non-equilibrium entropy is defined by

$$(3) \quad \dot{S} := \frac{1}{\Theta} \dot{U} - \frac{\mathbf{A}}{\Theta} \cdot \dot{\mathbf{a}} - \frac{\boldsymbol{\mu}}{\Theta} \cdot \dot{\mathbf{n}} + \alpha \dot{\Theta} + \boldsymbol{\beta} \cdot \dot{\boldsymbol{\xi}}.$$

The entropy production follows from isolating the system

$$(4) \quad \Sigma = -\frac{\boldsymbol{\mu}}{\Theta} \cdot \dot{\mathbf{n}}^i + \alpha \dot{\Theta} + \boldsymbol{\beta} \cdot \dot{\boldsymbol{\xi}}.$$

Here the  $\dot{\mathbf{n}}^i$  are the internal mole number rates by chemical reactions. For determining the entropy production, the rate equations of  $\dot{\mathbf{n}}^i$ ,  $\dot{\Theta}$  and  $\dot{\boldsymbol{\xi}}$  are necessary. The second law of thermodynamics, the *dissipation inequality*, is given by

$$(5) \quad \Sigma(t) \geq 0.$$

If this dissipation inequality is accepted as a formulation of the second law of thermodynamics, Clausius inequality can be derived by integrating along a process (1), but not vice-versa [33].

**2.2. Field formulation.** The basic variables in field formulation depend on the system under consideration. Describing a solid, the deformation gradient  $\mathbf{F}$  and the temperature are the suitable variables, if no internal degrees of freedom are relevant

$$(6) \quad (\mathbf{F}, \Theta)(\mathbf{x}, t).$$

A fluid with internal orientational degrees of freedom has eight basic variables at the classical level of description: mass density, velocity, spin density, internal energy density

$$(7) \quad (\varrho, \mathbf{v}, \mathbf{s}, \varepsilon)(\mathbf{x}, t).$$

The basic variables of a fluid described in extended thermodynamics contain variables belonging to dissipation: the dissipative part of the stress tensor  $\mathbf{T} + p\mathbf{1}$  and the heat flux density  $\mathbf{q}$

$$(8) \quad (\varrho, \mathbf{v}, \varepsilon, \mathbf{T} + p\mathbf{1}, \mathbf{q})(\mathbf{x}, t).$$

Here  $p$  is the hydrodynamic pressure of the fluid.

The “equations of motion” of the basic variables are the balance equations which are the starting-point of every field formulation

$$(9) \quad \partial_t(\varrho \mathbf{a}) + \nabla \cdot (\mathbf{v} \varrho \mathbf{a} + \mathbf{\Psi}) = \varphi + \sigma.$$

Here the symbols have the following meaning: basic fields  $\mathbf{a}(\mathbf{x}, t)$ , velocity  $\mathbf{v}(\mathbf{x}, t)$ , mass density  $\varrho(\mathbf{x}, t)$ , conductive fluxes  $\mathbf{\Psi}(\mathbf{x}, t)$ , supplies  $\varphi(\mathbf{x}, t)$  and productions  $\sigma(\mathbf{x}, t)$ .

There are three classes of fields included in the balances (9): the *basic fields*, the *given fields*, such as  $\varphi$  and fields determined by *constitutive equations*, such as  $\mathbf{\Psi}$  and some of the  $\sigma$ .

In more detail, the balances of the basic variables are [34]

- Mass

$$(10) \quad \partial_t \varrho + \nabla \cdot (\mathbf{v} \varrho) = 0$$

- Momentum

$$(11) \quad \partial_t (\varrho \mathbf{v}) + \nabla \cdot (\mathbf{v} \varrho \mathbf{v} - \mathbf{T}^\top) - \varrho \mathbf{k} = \mathbf{0}$$

- Angular momentum

$$(12) \quad \mathbf{M}(\mathbf{x}, t) := \mathbf{x} \times \mathbf{v}(\mathbf{x}, t) + \mathbf{s}(\mathbf{x}, t)$$

$$(13) \quad \frac{\partial}{\partial t} (\varrho \mathbf{M}) + \nabla \cdot (\mathbf{v} \varrho \mathbf{M} - [\mathbf{x} \times \mathbf{T}]^\top - \mathbf{W}^\top) - \varrho [\mathbf{x} \times \mathbf{k} + \mathbf{g}] = 0$$

- Spin

$$(14) \quad \partial_t (\varrho \mathbf{s}) + \nabla \cdot (\mathbf{v} \varrho \mathbf{s} - \mathbf{W}^\top) - \epsilon : \mathbf{T} - \varrho \mathbf{g} = 0$$

- Total energy

$$(15) \quad e(\mathbf{x}, t) := \frac{1}{2} \mathbf{v}^2(\mathbf{x}, t) + \frac{1}{2} \mathbf{s}(\mathbf{x}, t) \cdot \Theta^{-1}(\mathbf{x}, t) \cdot \mathbf{s}(\mathbf{x}, t) + \varepsilon(\mathbf{x}, t)$$

$$(16) \quad \frac{\partial}{\partial t}(\rho e) + \nabla \cdot [\mathbf{v} \rho e - \mathbf{T}^\top \cdot \mathbf{v} - \mathbf{W}^\top \cdot \Theta^{-1} \cdot \mathbf{s} + \mathbf{q}] - \rho \mathbf{k} \cdot \mathbf{v} - \rho \mathbf{g} \cdot \Theta^{-1} \cdot \mathbf{s} - \rho r = 0$$

- Internal energy

$$(17) \quad \partial_t(\rho \varepsilon) + \nabla \cdot (\mathbf{v} \rho \varepsilon + \mathbf{q}) - \nabla \mathbf{v} : \mathbf{T} - \rho r - \nabla(\Theta^{-1} \cdot \mathbf{s}) : \mathbf{W} - (\Theta^{-1} \cdot \mathbf{s}) \cdot \boldsymbol{\epsilon} : \mathbf{T} = 0$$

- Entropy, dissipation inequality

$$(18) \quad \partial_t(\rho s) + \nabla \cdot (\mathbf{v} \rho s + \Phi) - \varphi = \sigma \geq 0, \quad \forall(\mathbf{x}, t).$$

The meaning of the particular quantities in the balances is as follows:

**The basic fields:**

$$(19) \quad \text{mass density:} \quad \rho(\mathbf{x}, t)$$

$$(20) \quad \text{material velocity:} \quad \mathbf{v}(\mathbf{x}, t)$$

$$(21) \quad \text{specific internal energy:} \quad \varepsilon(\mathbf{x}, t)$$

$$(22) \quad \text{specific spin:} \quad \mathbf{s}(\mathbf{x}, t)$$

**External given quantities:**

$$(23) \quad \text{specific external force density:} \quad \mathbf{k}(\mathbf{x}, t)$$

$$(24) \quad \text{specific external angular momentum:} \quad \mathbf{g}(\mathbf{x}, t)$$

**Constitutive equations:**

$$(25) \quad \text{Cauchy stress tensor:} \quad \mathbf{T}(\mathbf{x}, t)$$

$$(26) \quad \text{couple stress tensor:} \quad \mathbf{W}(\mathbf{x}, t)$$

$$(27) \quad \text{moment of inertia tensor:} \quad \Theta(\mathbf{x}, t)$$

$$(28) \quad \text{heat flux density:} \quad \mathbf{q}(\mathbf{x}, t)$$

$$(29) \quad \text{specific energy supply:} \quad r(\mathbf{x}, t)$$

$$(30) \quad \text{specific entropy density:} \quad s(\mathbf{x}, t)$$

$$(31) \quad \text{entropy flux density:} \quad \Phi(\mathbf{x}, t)$$

$$(32) \quad \text{entropy production density:} \quad \sigma(\mathbf{x}, t)$$

$$(33) \quad \text{entropy supply density:} \quad \varphi(\mathbf{x}, t)$$

$$(34) \quad \text{temperature:} \quad \Theta(\mathbf{x}, t)$$

### 3. Constitutive Equations

**3.1. State space.** The constitutive equations (25) to (34) have to be inserted into the balance equations for solving them by taking initial and boundary conditions into consideration. There are different types of constitutive equations with respect to their domain:

**Def.:** The domain of the constitutive equations is called the *state space* or the *constitutive space*. We distinguish between large and small state spaces:

Def.: A state space is called a *large* one, if the material properties  $\mathcal{M}$  are defined by maps which are local in time on the basic fields  $z(t)$

$$(35) \quad \mathcal{M} : z(t) \mapsto M(t), \quad \forall t.$$

For defining the other class of constitutive equations, we need the concept of the process history:

Def.: For a fixed time  $t$  and real  $s \geq 0$ , the expression

$$(36) \quad z^t(s) := z(t - s), \quad s \in [0, \tau]$$

is called the *history of the process*  $z(\cdot)$  between  $t - \tau$  and  $t$ .

Def.: A state space is called a *small* one, if the material properties  $\mathcal{M}$  are defined by maps on the process histories  $z^t(\cdot)$  of the basic fields

$$(37) \quad \mathcal{M} : z^t(\cdot) \mapsto M(t), \quad \forall t.$$

The difference between the two types of state spaces is as follows: Small state spaces do not include so many basic variables so that a description of the material being local in time is possible. Therefore these materials may show after-effects, such as hysteresis or creeping. Large state spaces are large enough for allowing an in time local description of the material properties.

The choice of the state space is not restricted. If the state space is small, it includes locally independent variables. In general, these variables are different from the wanted fields. An example for that is Fourier heat conduction: The heat flux density depends on the temperature gradient  $\mathbf{q} = \mathbf{Q}(\nabla T, \dots)$ , but the temperature itself is the basic field and not its gradient. The choice of the state space determines a *class of materials* which is defined by all constitutive equations which are compatible with the state space and the material axioms [35, 29] which will be briefly discussed in the next section.

Without taking material axioms into consideration first of all, some examples of small state spaces  $Z(\mathbf{x}, t)$  are:

$$(38) \quad Z(\mathbf{x}, t) = (\varrho, \mathbf{v}, \varepsilon)(\mathbf{x}, t), \quad \text{no heat conduction, no internal friction,}$$

$$(39) \quad Z(\mathbf{x}, t) = (\varrho, \varepsilon, \mathbf{v}, \nabla \varrho, \nabla \varepsilon, \nabla \mathbf{v})(\mathbf{x}, t),$$

$$(40) \quad Z(\mathbf{x}, t) = (\varrho, \mathbf{v}, \varepsilon, \boldsymbol{\xi}, \nabla \varrho, \nabla \mathbf{v}, \nabla \varepsilon, \nabla \boldsymbol{\xi}, \dot{\varrho}, \dot{\mathbf{v}}, \dot{\varepsilon}, \dot{\boldsymbol{\xi}})(\mathbf{x}, t),$$

$$(41) \quad Z^{ext}(\mathbf{x}, t) = (\varrho, \mathbf{v}, \varepsilon, \mathbf{T} + p\mathbf{1}, \mathbf{q})(\mathbf{x}, t), \quad \text{Extended Thermodynamics.}$$

The constitutive space of extended thermodynamics is identical to the space spanned by its basic variables  $Z^{ext}(\mathbf{x}, t) \equiv z^{ext}(\mathbf{x}, t)$ .

$$(42) \quad Z(\mathbf{x}, t) = (\mathbf{F}, \Theta, \nabla \Theta)(\mathbf{x}, t), \quad \text{Thermoelasticity,}$$

$$(43) \quad Z(\mathbf{x}, t) = (\mathbf{F}, \Theta, \nabla \Theta, \boldsymbol{\xi})(\mathbf{x}, t), \quad \text{Thermoviscoelasticity,}$$

$$(44) \quad Z(\mathbf{x}, t) = (\mathbf{F}_e, \mathbf{F}_p, \Theta, \nabla \Theta)(\mathbf{x}, t), \quad \text{Thermoviscoplasticity,}$$

$$(45) \quad Z(\mathbf{x}, t) = \mathbf{F}^t(\cdot), \Theta^t(\cdot)(\mathbf{x}), \quad \text{Thermal After Effects.}$$

**3.2. Entropy- and heat flux density.** Two classes of theories can be distinguished with respect to the general relation between the heat flux density  $\mathbf{q}(Z(\mathbf{x}, t))$  and the entropy flux density  $\Phi(Z(\mathbf{x}, t))$ :

$$(46) \quad \Phi(Z(\mathbf{x}, t)) = \frac{1}{\Theta} \mathbf{q}(Z(\mathbf{x}, t)) + \mathbf{K}(Z(\mathbf{x}, t))$$

In general,  $\mathbf{K} \neq \mathbf{0}$  is valid, and the entropy excess flux density  $\mathbf{K}$  is a constitutive equation.

There are schools presupposing that  $\mathbf{K} \equiv \mathbf{0}$  is universally valid. Theories using this presupposition are called *Clausius-Duhem theories*. Consequently, the entropy balance in Clausius-Duhem theories is according to (18)

$$(47) \quad \partial_t(\rho s) + \nabla \cdot (\rho \mathbf{q} s + \frac{\mathbf{q}}{\Theta}) - \varphi = \sigma \geq 0, \quad \forall \mathbf{x}, t.$$

Interesting is that the temperature does not appear in the balances (10) to (18). Temperature is introduced into the balances by constitutive properties, here, in Clausius-Duhem theories, by  $\Phi = (1/\Theta)\mathbf{q}$ .

**3.3. Material axioms.** Material axioms are rules restricting the arbitrariness of the constitutive mappings  $\mathcal{M}$  in (35) and (37). These material axioms are called equipresence, objectivity, material frame indifference [36], standard frame dependence [37] and the second law. The particular schools differ in applying these axioms.

A brief characterization of the material axioms is as follows: *Equipresence* means that the domain – the constitutive space – for all parts of  $\mathcal{M}$  – for all material properties – is the same. *Objectivity* means that domain and range of the constitutive mapping are spanned by objective quantities which transform by definition as tensor components under changing the observer. *Material frame indifference* means that the constitutive mapping is observer-independent and that a uniform motion of the material with respect to a standard frame of reference does not influence material properties. *Standard frame dependence* means that material properties depend on the motion of the material with respect to an arbitrary, but fixed chosen frame of reference, called standard frame of reference. These axioms are not independent of each other: If a material mapping is objective, then it is also observer-independent. All in all, the denotation and the use of the material axioms is not unique and differs from school to school [38]. This is even true for the least axiom, the second law which is discussed in more detail in the next section.

#### 4. Dissipation Inequality

The second law can be formulated in various different shapes [39, 25]. There are several dissipation inequalities which are global in time: First of all, *Clausius inequality* which is valid for discrete systems is [40]

$$(48) \quad \oint \left[ \frac{\dot{Q}}{\Theta} + \sum_j s^j \dot{n}_j^e \right] dt \leq 0.$$

Here,  $\Theta$  is the contact temperature [30, 31],  $s_j$  the molar entropy of the  $j$ -th component and  $\dot{n}_j^e$  the external change of the mole number of the  $j$ -th component of the system.

Meixner [41] introduced two different temperatures, a non-equilibrium one  $\Theta$  and an equilibrium temperature  $T_{eq}$ . His dissipation inequality runs as follows

$$(49) \quad \int_A^B \left[ \dot{s}_{eq} + \frac{1}{\varrho} \nabla \cdot \frac{\mathbf{q}}{\Theta} \right] dt \geq 0, \quad \frac{\partial s_{eq}}{\partial u} =: \frac{1}{T_{eq}}.$$

Instead of introducing two temperatures, two different internal energies can be considered, if a so-called *accompanying process* is created by projecting the non-equilibrium process onto the equilibrium sub-space [42, 43]. Because of the gradient in (49)<sub>1</sub>, this inequality belongs to a field formulation. This is also the case for the in time global dissipation inequality used by Day [44] and Coleman/Owen [45]

$$(50) \quad \oint \left[ \frac{1}{\varrho} \nabla \cdot \frac{\mathbf{q}}{\Theta} - \frac{r}{\Theta} \right] dt \geq 0.$$

Dissipation inequalities being local in time are first of all those of discrete systems (5) and in field formulation (18). An other dissipation inequality was created by Gurtin/Williams [46]. Introducing two temperatures, a surface temperature  $\Theta$  and a bulk temperature  $\vartheta$ , this dissipation inequality estimates the entropy rate for a discrete system by surface and volume integrals using field formulation:

$$(51) \quad \dot{S}_G(t) \geq - \oint_{\partial G} \frac{\mathbf{q}}{\Theta} \cdot d\mathbf{f} + \int_G \frac{\varrho r}{\vartheta} dV.$$

The most imaginative dissipation inequalities are useless, if one is not able to exploit them. In the next section we will do that for in time local dissipation inequalities in field formulation. Examples for exploiting in time global dissipation inequalities can be found in [44].

## 5. Exploitations of the 2nd Law

**5.1. Original irreversible thermodynamics.** State space of original irreversible thermodynamics is the equilibrium sub-space, in case of one-component fluids (38) without the velocity according to the material axiom of objectivity

$$(52) \quad Z(\mathbf{x}, t) = Z^{eq}(\mathbf{x}, t) = (\varrho, \varepsilon)(\mathbf{x}, t).$$

This choice of the state space is usually called the *hypothesis of local equilibrium*. The entropy production  $\sigma$  can be represented as a product of forces  $\mathbf{X}$  and fluxes  $\mathbf{Y}$

$$(53) \quad \sigma(\mathbf{x}, t) = \mathbf{X}(\mathbf{x}, t) \cdot \mathbf{Y}(\mathbf{x}, t) \geq 0.$$

Forces and fluxes are not defined on the state space (52); they depend on constitutive equations [7]

$$(54) \quad \mathbf{X} = \mathcal{X}(\nabla T, \nabla \mu, \mathbf{k}, \mathbf{T} + p\mathbf{1}),$$

$$(55) \quad \mathbf{Y} = \mathcal{Y}(\mathbf{q}, \nabla v).$$



Forces and fluxes are related by phenomenological equations

$$(56) \quad \mathbf{Y} = \mathbf{Y}(\mathbf{X}), \quad \mathbf{0} = \mathbf{Y}(\mathbf{0})$$

which are presupposed to be linear

$$(57) \quad \mathbf{Y}(\mathbf{X}) = \mathbf{L} \cdot \mathbf{X}, \quad \sigma = \mathbf{X} \cdot \mathbf{L} \cdot \mathbf{X} \geq 0.$$

The positive definite phenomenological matrix  $\mathbf{L}$  satisfies the *Onsager-Casimir relations* [7] which can be proved by statistical back-ground considerations or also by phenomenological arguments [47]

$$(58) \quad \mathbf{L}(-\mathbf{B}, -\boldsymbol{\omega}, \dots) = \boldsymbol{\Lambda} \cdot \mathbf{L}^\top(\mathbf{B}, \boldsymbol{\omega}, \dots) \cdot \boldsymbol{\Lambda}^\top, \quad \mathbf{X}(-t) = \boldsymbol{\Lambda} \cdot \mathbf{X}(t).$$

Here  $\boldsymbol{\Lambda}$  is a diagonal matrix which describes the parity of  $\mathbf{X}$  under time reversal. The phenomenological matrix depends on parameters which are odd under time reversal ( $\mathbf{B}$ =magnetic induction,  $\boldsymbol{\omega}$ = angular velocity). The use of the reciprocal relations was vehemently attacked by the school of Rational Thermodynamics [48].

The exploitation of the dissipation inequality (57)<sub>2</sub> in irreversible thermodynamics is clear: The phenomenological matrix  $\mathbf{L}$  has to be positive definite or at least positive semi-definite.

**5.2. Extended irreversible thermodynamics.** This extension of original irreversible thermodynamics consists in an other choice of the state space (52), that means, the hypothesis of local equilibrium is cancelled. The state space (52) is replaced by that of extended thermodynamics (41) [49]. Result is that the entropy density depends on the heat flux density and on the dissipative part of the stress tensor. Consequently, balance equations for these additional basic fields are needed. Apart from the different choice of the state space, the procedure of extended irreversible thermodynamics is as in the original one.

**5.3. Non-Equilibrium Thermodynamics.** The methods of exploiting the dissipation inequality are the same in extended rational and non-equilibrium thermodynamics, only the choice of the constitutive space is different: The large state space in non-equilibrium thermodynamics can be chosen arbitrarily, whereas in extended rational thermodynamics (41) is taken.

The balances (10) to (17) and the dissipation inequality (18) can be written in the shape

$$(59) \quad \rho \dot{\mathbf{a}} + \nabla \cdot \boldsymbol{\Psi} = \boldsymbol{\Sigma}, \quad \mathbf{a} \in \mathbb{R}^n,$$

$$(60) \quad \rho \dot{s} + \nabla \cdot \boldsymbol{\Phi} \geq \varphi.$$

The fields  $\mathbf{a}(\mathbf{z})$  and  $s(\mathbf{z})$  depend on the state space variables  $\mathbf{z}(\mathbf{x}, t)$ . Consequently, the derivatives in the balances have to be performed by the chain rule

$$(61) \quad \partial_t \mathbf{a} = \frac{\partial \mathbf{a}}{\partial \mathbf{z}} \cdot \partial_t \mathbf{z}, \quad \nabla \cdot \mathbf{a} = \frac{\partial \mathbf{a}}{\partial \mathbf{z}} \cdot \nabla \mathbf{z}.$$

Introducing them into the balances (59) and (60), we obtain the *balance equations on state space* which are linear in the *higher derivatives*  $\mathbf{y}$ . We obtain in matrix formulation

$$(62) \quad \mathbf{y}^\top := (\partial_t \mathbf{z}, \nabla \mathbf{z}) \longrightarrow \mathbf{A}(\mathbf{z}) \mathbf{y} = \mathbf{C}(\mathbf{z}), \quad \mathbf{B}(\mathbf{z}) \mathbf{y} \geq \mathbf{D}(\mathbf{z}).$$

The abbreviations  $\mathbf{A}$ ,  $\mathbf{C}$ ,  $\mathbf{B}$  and  $\mathbf{D}$  depend on the constitutive quantities  $\partial \mathbf{a} / \partial \mathbf{z}$ , and thus on the state space variables  $\mathbf{z}$ .

Now the question arises, how to exploit the dissipation inequality (62)<sub>3</sub>? There are two possibilities to proceed:

#1: For fixed  $\mathbf{A}$ ,  $\mathbf{C}$ ,  $\mathbf{B}$  and  $\mathbf{D}$  the dissipation inequality excludes certain higher derivatives  $\mathbf{y}$  (process selective),

#2: The  $\mathbf{A}$ ,  $\mathbf{C}$ ,  $\mathbf{B}$  and  $\mathbf{D}$  have to be determined so that all process directions  $\mathbf{y}$  are possible (material selective).

The second statement can be expressed by the Coleman-Mizel formulation of the 2nd law [50]:

□ All solutions of the balance equations on state space  $\mathbf{y}$  have to satisfy the dissipation inequality

$$(63) \quad \wedge \mathbf{y} : [ \mathbf{A}(\mathbf{z})\mathbf{y} = \mathbf{C}(\mathbf{z}) \longrightarrow \mathbf{B}(\mathbf{z})\mathbf{y} \geq \mathbf{D}(\mathbf{z}) ]. \quad \square$$

The possibilities #1 and #2 are excluding each other, and the question arises what statement is valid? This question cannot be answered by the usual formulation of the second law, because both the statements #1 and #2 refer to the same dissipation inequality. Consequently, an amendment to the second law is needed. This amendment is the *no-reversible direction axiom* [51]:

Except in equilibrium sub-space, reversible process directions in state space do not exist.

Using this axiom, a proof of the Coleman-Mizel formulation (63) is possible [5], and the second law is detected to be material selective.

The first exploitation method of the dissipation inequality, called *Coleman-Noll technique* [52], is used in Clausius-Duhem theories and starts out with (47). Introducing the free energy density

$$(64) \quad f := u - \Theta s,$$

one obtains the dissipation inequality in the form

$$(65) \quad \rho f^\bullet + \nabla \cdot \Psi \geq \psi.$$

After having chosen a constitutive space and having inserted the energy balance, the dissipation inequality on the state space (62)<sub>3</sub> becomes

$$(66) \quad \mathbf{G}\mathbf{y} \geq \mathbf{H}.$$

Now the constitutive constraints in Coleman-Noll technique are obtained by setting

$$(67) \quad \mathbf{G}(\mathbf{z}) \doteq 0 \quad \wedge \quad \mathbf{H}(\mathbf{z}) \leq 0.$$

This setting is of course an only sufficient condition, but whenever (67) is satisfied, the second law is taken into account, but without considering other balances beyond the energy balance. Those can be introduced additionally into the procedure, or one chooses the second technique which is based on

□ Liu's Proposition [53, 51]: Presupposing the Coleman-Mizel formulation of the 2nd

law, the following statement is valid: In large state spaces constitutive equations satisfy the Liu relations

$$(68) \quad \mathbf{B}(\mathbf{z}) = \boldsymbol{\lambda}(\mathbf{z})\mathbf{A}(\mathbf{z}), \quad \boldsymbol{\lambda}(\mathbf{z})\mathbf{C}(\mathbf{z}) \geq \mathbf{D}(\mathbf{z}).$$

Here  $\boldsymbol{\lambda}(\mathbf{z})$  and the entropy production density are state functions

$$(69) \quad \sigma(\mathbf{z}) := \boldsymbol{\lambda}\mathbf{C} - \mathbf{D} \geq 0.$$

The entropy production density is independent of the higher derivatives  $\mathbf{y}$  (62)<sub>1</sub>, and therefore independent of the process direction.  $\square$

The *Liu technique* takes all balances properly into account. This can be done also by the Coleman-Noll technique, if the balances are additionally introduced into (65) as constraints.

## 6. Endoreversible Thermodynamics

If reversible discrete systems interact irreversibly with each other by exchanges as discussed in sect. 2.1, we call such systems endoreversible ones [11]. This *endoreversible description* corresponds to the hypothesis of local equilibrium in field formulation. Because a cycle time is attached to the reversible discrete systems, this theory is also called *finite time thermodynamics* [22].

Prototypes of endoreversible systems are the Novikov [54] and the Curson-Ahlborn [55] machines. Here we discuss briefly the Novikov machine with heat leak (see fig.1). The power  $P$  of this machine is defined by introducing a cycle time  $\tau$  by which the work  $-W$  is divided

$$(70) \quad P := \frac{-W}{\tau} = \frac{Q_H}{\tau} \left( 1 + \frac{Q_L}{Q_H} \right) \geq 0.$$

The entropy production of this two-reservoir machine (temperatures  $T_H$  and  $T_L$ ) is

$$(71) \quad \Sigma = Q_H \left( \frac{1}{T_i} - \frac{1}{T_H} \right) + \Delta Q \left( \frac{1}{T_L} - \frac{1}{T_i} \right) - \frac{Q_H - \Delta Q}{T_i} - \frac{Q_L + \Delta Q}{T_L}.$$

Note that the term proportional to  $\Delta Q$  is zero, and that consequently the entropy production does not depend on  $\Delta Q$  and  $T_i$ , if  $Q_H, Q_L, T_H$  and  $T_L$  are given.

First of all, the temperature  $T_i$ ,  $T_L < T_i < T_H$ , is arbitrary. We now demand that according to the philosophy of endoreversible thermodynamics the Novikov machine is a reversible one. Consequently Clausius equality, the reversibility condition of the Novikov machine, becomes

$$(72) \quad -\frac{Q_H - \Delta Q}{T_i} - \frac{Q_L + \Delta Q}{T_L} = 0$$

by which  $T_i$  is determined, if the heat leak  $\Delta Q$  is known. It is determined by the temperature difference, the cycle time and by heat conductivity  $\kappa$  of the heat leak

$$(73) \quad \Delta Q = \kappa\tau \left( \frac{1}{T_L} - \frac{1}{T_i} \right).$$

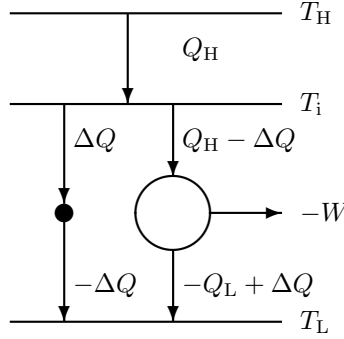


Fig.1 Thermodynamic diagram of a 2-reservoir Novikov engine with heat leak

As from the diagram can be seen, an analogous relation is valid for the heat exchange  $Q_H$

$$(74) \quad Q_H = \lambda\tau \left( \frac{1}{T_i} - \frac{1}{T_H} \right).$$

Inserting (74), (72) and (73) into (70), we obtain for the power

$$(75) \quad P = T_L \left( \frac{1}{T_L} - \frac{1}{T_i} \right) \left[ \lambda \left( \frac{1}{T_i} - \frac{1}{T_H} \right) - \kappa \left( \frac{1}{T_L} - \frac{1}{T_i} \right) \right].$$

The arbitrary temperature  $T_i$  is now determined by the demand “ $P \rightarrow \text{extremal}$ ” under constant heat conductivities [56]. This results in

$$(76) \quad (\lambda + 2\kappa) \left( \frac{1}{T_L} - \frac{1}{T_i} \right) - \lambda \left( \frac{1}{T_i} - \frac{1}{T_H} \right) = 0,$$

$$(77) \quad P_{extr} = T_L \frac{\lambda^2}{4(\lambda + \kappa)} \left( \frac{1}{T_L} - \frac{1}{T_H} \right).$$

How these endoreversible machines represent realistic models is discussed in [57].

## 7. Mesoscopic Theory

**7.1. Mesoscopic space.** For describing *complex materials* one needs additional fields  $\mathbf{m}$  beyond the usual ones of a five-field or a eight-field theory whose basic fields are mentioned in (7). In principle, there are two possibilities for introducing these additional fields: One can add them together with their balance equations to the basic fields, or one can add them as variables completing the space-time [58]. In the first case which is the conventional concept, we have to generate the balances of the additional fields  $\mathbf{m}(\mathbf{x}, t)$ , an enterprise which is often difficult. In the second case which is called the *mesoscopic theory*, we know already, as we will see, all balance equations defined on the *mesoscopic space* [59]

$$(78) \quad (\cdot) \equiv (\mathbf{m}, \mathbf{x}, t) \in \mathcal{M} \times \mathbf{R}^3 \times \mathbf{R}^1$$

which is spanned by space-time extended by the set  $\mathbf{m}$  of the mesoscopic variables.

**7.2. Mesoscopic balances.** The mesoscopic balances are defined on the mesoscopic space. Consequently, they are of the shape [34]

$$(79) \quad \begin{aligned} \partial_t[\varrho(\cdot)\mathbf{a}(\cdot)] + \nabla_x \cdot [\mathbf{v}(\cdot)\varrho(\cdot)\mathbf{a}(\cdot) + \Psi(\cdot)] + \\ + \nabla_m \cdot [\mathbf{u}(\cdot)\varrho(\cdot)\mathbf{a}(\cdot) + \Xi(\cdot)] = \boldsymbol{\varphi}(\cdot) + \boldsymbol{\sigma}(\cdot). \end{aligned}$$

Here  $\varrho(\cdot)$  is the mesoscopic mass density, that is the mass density of all particles in a volume element at  $(\mathbf{x}, t)$  whose mesoscopic variable has the value  $\mathbf{m}$ . The mesoscopic mass balance is according to (79)

$$(80) \quad \frac{\partial}{\partial t}\varrho(\cdot) + \nabla_x \cdot \{\varrho(\cdot)\mathbf{v}(\cdot)\} + \nabla_m \cdot \{\varrho(\cdot)\mathbf{u}(\cdot)\} = 0.$$

The mesoscopic velocity  $\mathbf{v}(\cdot)$  and the mesoscopic change velocity  $\mathbf{u}(\cdot)$  are defined by

$$(81) \quad (\mathbf{m}, \mathbf{x}, t) \longrightarrow (\mathbf{m} + \mathbf{u}(\cdot)\Delta t, \mathbf{x} + \mathbf{v}(\cdot)\Delta t, t + \Delta t).$$

The mesoscopic balance of momentum becomes

$$(82) \quad \begin{aligned} \frac{\partial}{\partial t}[\varrho(\cdot)\mathbf{v}(\cdot)] + \nabla_x \cdot [\mathbf{v}(\cdot)\varrho(\cdot)\mathbf{v}(\cdot) - \mathbf{T}^\top(\cdot)] + \\ + \nabla_m \cdot [\mathbf{u}(\cdot)\varrho(\cdot)\mathbf{v}(\cdot) - \mathcal{T}^\top(\cdot)] = \varrho(\cdot)\mathbf{k}(\cdot). \end{aligned}$$

Because the molecules in a volume element at  $(\mathbf{x}, t)$  have different values of  $\mathbf{m}$ , we can define a *mesoscopic distribution function*  $f(\mathbf{m}, \mathbf{x}, t)$  which is normalized as usual

$$(83) \quad \int f(\mathbf{m}, \mathbf{x}, t) d\mathcal{M} = 1.$$

The mesoscopic distribution function is related to the mesoscopic mass density by [60]

$$(84) \quad \varrho(\cdot) = f(\cdot)\varrho(\mathbf{x}, t)$$

which is in accordance with (83). From (80) and (84) follows the balance of the mesoscopic distribution function [59]

$$(85) \quad \begin{aligned} \frac{\partial}{\partial t}f(\cdot) + \nabla_x \cdot [\mathbf{v}(\cdot)f(\cdot)] + \nabla_m \cdot [\mathbf{u}(\cdot)f(\cdot)] + \\ + f(\cdot) \left[ \frac{\partial}{\partial t} + \mathbf{v}(\cdot) \cdot \nabla_x \right] \ln \varrho(\mathbf{x}, t) = 0 \end{aligned}$$

which is a Fokker-Planck type equation [62].

Using the mesoscopic distribution function, we obtain macroscopic *fields of the order parameters* of different order which extend the eight-field theory

$$(86) \quad \mathbf{A}(\mathbf{x}, t) := \int f(\cdot)\mathbf{m}d\mathcal{M}, \quad \mathbf{a}(\mathbf{x}, t) := \int f(\cdot) \overline{\mathbf{m}\mathbf{m}} d\mathcal{M},$$

$$(87) \quad \underline{\mathbf{a}}_N(\mathbf{x}, t) := \int f(\cdot) \overline{\mathbf{m}\dots N \text{ times}\dots\mathbf{m}} d\mathcal{M}.$$

Here  $\overline{\mathbf{ab}}$  is the symmetric traceless part of  $\mathbf{ab}$ .

The mesoscopic constitutive theory is not well developed up to now [61], but there is some progress in applying the mesoscopic theory to microcracks [63] and other fields.

## 8. GENERIC <sup>1</sup>

An other approach to non-equilibrium thermodynamics is that of GENERIC [64, 65]. The idea is to modify the canonical equations of reversible mechanics in such a way that one obtains the equations of motion of irreversible thermodynamics.

Starting out with a balance of an open system

$$(88) \quad \partial_t(\varrho a) + \nabla \cdot (\mathbf{v} \varrho a + \mathbf{A}) = \alpha, \quad A := \int \varrho a dV,$$

$$(89) \quad \dot{A} = \frac{d}{dt} \int \varrho a dV = \int [\partial_t(\varrho a) + \nabla \cdot (\mathbf{w} \varrho a)] dV$$

in which the fields  $a(\mathbf{Z})$  depend on the basic variables  $\mathbf{Z}$ , the functional derivative of  $A$  is

$$(90) \quad \frac{\delta A}{\delta \mathbf{Z}} = \frac{\partial(\varrho a)}{\partial \mathbf{Z}}.$$

This results in

$$(91) \quad \partial_t(\varrho a) = \frac{\partial(\varrho a)}{\partial \mathbf{Z}} \cdot \partial_t \mathbf{Z}.$$

Now the question arises: What are the rates of the basic variables  $\mathbf{Z}$ ? The answer is special to GENERIC.

**8.1. Modified canonical equations.** For transforming “reversible” mechanics into “irreversible” non-equilibrium thermodynamics, one has to start out with the canonical equations

$$(92) \quad \frac{d}{dt} \begin{pmatrix} \mathbf{p} \\ \mathbf{q} \end{pmatrix} = \begin{pmatrix} \mathbf{0} & -\mathbf{1} \\ \mathbf{1} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \frac{\partial H}{\partial \mathbf{p}} \\ \frac{\partial H}{\partial \mathbf{q}} \end{pmatrix}, \quad H = H(\mathbf{p}, \mathbf{q}).$$

The transformation from canonical mechanics to thermodynamics is performed by the following setting [66]

$$(93) \quad (\mathbf{p}, \mathbf{q}) \longrightarrow \mathbf{Z},$$

$$(94) \quad H(\mathbf{p}, \mathbf{q}) \longrightarrow E(\mathcal{Z}) = \int e(\mathcal{Z}(\mathbf{x}, t)) dV.$$

Here  $e$  is the energy density, and  $\mathcal{Z}(\mathbf{x}, t)$  presents the variables of the constitutive space. The symplectic is replaced by an other matrix

$$(95) \quad \text{symplectic} \longrightarrow \mathcal{L},$$

and one obtains first of all the modified canonical equations of the reversible part of GENERIC

$$(96) \quad \dot{\mathbf{Z}}^{rev} := \mathcal{L} \odot \frac{\delta E}{\delta \mathbf{Z}},$$

$$(97) \quad \mathcal{L}(\mathcal{Z}) \odot \frac{\delta E}{\delta \mathbf{Z}} := \int \mathcal{L}[\mathcal{Z}(\mathbf{x}, t), \mathcal{Z}(\mathbf{x}', t)] \cdot \frac{\delta E}{\delta \mathbf{Z}(\mathbf{x}', t)} dV'.$$

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<sup>1</sup>General Equation for the Non-Equilibrium Reversible-Irreversible Coupling

**8.2. The irreversible part.** Analogous to (96), the irreversibility of GENERIC is introduced by an additional matrix  $\mathcal{M}$  and the entropy density  $S$

$$(98) \quad \text{irreversibility} \longrightarrow \mathcal{M}, \quad S(\mathcal{Z}) = \int s(\mathcal{Z}(\mathbf{x}, t)) dV,$$

$$(99) \quad \dot{\mathbf{Z}}^{irr} := \mathcal{M} \odot \frac{\delta S}{\delta \mathbf{Z}}.$$

The rate of the basic variables is generated by the sum of the reversible and the irreversible rates

$$(100) \quad \text{Axiom:} \quad \partial_t \mathbf{Z} = \mathcal{L}(\mathcal{Z}) \odot \frac{\delta E}{\delta \mathbf{Z}} + \mathcal{M}(\mathcal{Z}) \odot \frac{\delta S}{\delta \mathbf{Z}}.$$

**8.3. The building blocks.** Summarized, the fundamentals of GENERIC are [67]:

- i) The basic (wanted) fields of the system:  $\mathbf{Z}$
- ii) The state space  $\mathcal{Z}$  which is not identical to the basic fields  $\mathbf{Z}$
- iii) The two global potentials: total energy  $E(\mathcal{Z})$  and total entropy  $S(\mathcal{Z})$  which are functionals defined on the constitutive space
- iv) Two, in general operator-valued matrices:  $\mathcal{L}(\mathcal{Z})$  and  $\mathcal{M}(\mathcal{Z})$  defined on the state space
- v) The rate equation (100) of the basic variables.

The difficulty of GENERIC consists in finding the matrices  $\mathcal{L}$  and  $\mathcal{M}$  which determine the constitutive properties of the system. In easy cases, GENERIC and non-equilibrium thermodynamics yield the same result [68].

## 9. Evolution Criteria

Presupposing the hypothesis of local equilibrium and a Gibbs fundamental equation for the differential of the entropy, evolution criteria of thermodynamical systems can be formulated [69]. The dissipation inequality which is used in Clausius-Duhem theories as a constraint for the constitutive mappings represents here a stability or an evolution criterion. Beyond the positive definiteness (53) of the entropy production density, its Ljapunov property

$$(101) \quad \dot{\sigma} \leq 0$$

is postulated [70]. If the phenomenological equations (57) are linear, the Châtelier-Braun principle

$$(102) \quad \mathbf{Y} \cdot \delta \mathbf{X} \geq 0$$

follows [71]. Here  $\delta$  means a variation out of a stationary state (impossible process). If the phenomenological equations are non-linear, the Châtelier-Braun principle is replaced by the evolution criterion of Glansdorff-Prigogine [72]

$$(103) \quad \sigma_X := \mathbf{Y} \cdot \dot{\mathbf{X}} \leq 0.$$

The connection between Ljapunov stability and excess entropy

$$(104) \quad \partial_t \delta^2 s \geq 0$$

was postulated by Glansdorff et al. [73]. The mentioned evolution criteria need some presuppositions and are postulated beyond the second law (57).

An other possibility for formulating evolution criteria is to start out with the integrated dissipation inequality (18) [74]

$$(105) \quad \frac{d}{dt} \int_{\mathcal{G}} (\varrho s) dV + \oint_{\partial \mathcal{G}} \mathbf{\Phi} \cdot d\mathbf{f} - \int_{\mathcal{G}} \varphi \geq 0.$$

This inequality is valid beyond local equilibrium and needs no statements about stability or excess entropy. If special conditions are satisfied

- i) the environment of the discrete system has reservoir properties and is a perfect fluid
- ii) the entropy flux density through the surface of the system is purely thermal
- iii) the force density is conservative
- iv) there are no volume torques, no energy and entropy supplies,

the dissipation inequality (105) can be written as an evolution criterion

$$(106) \quad \frac{d}{dt} \int_{\mathcal{G}(t)} \otimes dV \geq 0.$$

Here  $\otimes$  is a modified negative free energy density. The integral (106) takes a maximum at all times compared with earlier events. Consequently, in equilibrium it is in its absolute maximum. The evolution criterion (106) represents a variational principle without any constraints, because the balances of momentum, spin and energy are taken into account during the exploitation of (105). Applied to liquid crystals, the evolution criterion results in the Landau equations which here are derived and not set ad-hoc [74] and in a variational principle for free-standing liquid crystal films [75]. Also in electrodynamics, the evolution criterion (106) can be applied to electromagnetic bodies [76].

## 10. Quantum Thermodynamics

In contrast to quantum mechanics, non-equilibrium thermodynamics is an irreversible theory. Consequently for introducing quantum effects into thermodynamics, irreversibility has to be implant into quantum mechanics, a task which is performed by *quantum thermodynamics*. This expression is not well defined, because different procedures hide behind this name.

In equilibrium, quantum mechanics and thermodynamics fits together, because the different types of the quantal density operator belonging to different thermal equilibrium situations are well known: micro-canonical, canonical and grand-canonical ensembles belonging to isolated, closed and open discrete systems [77]. The temperature is the equilibrium temperature of thermostatics.

In non-equilibrium, the situation is much more complicated: One has to create an irreversible quantum mechanics. This can be done on different stages. Firstly, one can change



the Schrödinger equation by introducing damping or other generalizations [78], a way which cannot be recommended.

**10.1. Irreversible density operator.** Secondly, one can change the von Neumann equation leaving the Schrödinger equation unaltered. That is possible by defining the *irreversible part*  $\overset{\circ}{\varrho}$  of the density operator [79]

$$(107) \quad \overset{\circ}{\varrho} := \dot{\varrho} + (i/\hbar)[\mathcal{H}, \varrho]$$

which is

$$(108) \quad \overset{\circ}{\varrho} \neq 0$$

for irreversible processes and which is

$$(109) \quad \overset{\circ}{\varrho} \equiv 0,$$

if the reversible von Neumann equation is valid. In both the cases (108) and (109), the Schrödinger equation is untouched, and we have

$$(110) \quad \dot{\varrho} = \sum_k \dot{p}_k P_k + \sum_k p_k \dot{P}_k, \quad P_k := |\psi_k\rangle\langle\psi_k|, \quad \sum_k p_k = 1.$$

In the reversible case (109), all rates of the statistical weights vanish by taking the Schrödinger equation into account for the time rates  $\dot{P}_k$  of the projectors (110)<sub>2</sub>

$$(111) \quad \dot{p}_k = 0, \quad \text{for all } k, \text{ if } \overset{\circ}{\varrho} \equiv 0.$$

Also the rate of the entropy

$$(112) \quad \dot{S} := -k_B \text{Tr}(\dot{\varrho} \ln \varrho), \quad \dot{S} = -k_B \text{Tr}(\overset{\circ}{\varrho} \ln \varrho) = 0$$

vanishes in equilibrium. In the irreversible case (108), entropy change appears according to (112)<sub>2</sub>, although the reversible Schrödinger equation is valid. Consequently, the Schrödinger equation is compatible with non-vanishing entropy rate, if the statistical weights of the density operator are chosen to be time dependent.

**10.2. Beobachtungsebene.** The third case to introduce irreversibility into quantum mechanics is by paying attention to the limited information which one has from the system under consideration [80]. This limited information stems from the fact that only a limited number of measuring devices are available and that therefore the number of measurable observables is restricted. These available selfadjoint observables  $G_j$  form a set, called the *beobachtungsebene* [81],

$$(113) \quad \mathcal{B} := \{G_1, G_2, \dots, G_n\} \equiv \{\mathbf{G}\}$$

which is analogous to the wanted basic fields (19) to (22). The expectation values of the  $\mathbf{G}$  are

$$(114) \quad \mathbf{g} := \text{Tr}(\varrho \mathbf{G}).$$

Because of the restricted set of observables in  $\mathcal{B}$ , the statistical operator  $\varrho$  is not determined by the available expectation values, that means, there are other different density operators  $\hat{\varrho}$  also satisfying (114)

$$(115) \quad \mathbf{g} = \text{Tr}(\hat{\varrho} \mathbf{G}) = \text{Tr}(\varrho \mathbf{G}).$$

According to Jaynes [80], we choose for describing the system instead of the quantal  $\varrho$  that coarse-grained density operator  $R$  which maximizes the entropy of the system

$$(116) \quad S_{max} := -k_B \min_{\hat{\varrho}} \text{Tr}(\hat{\varrho} \ln \hat{\varrho}) = -k_B \text{Tr}(R \ln R),$$

$$(117) \quad \mathbf{g} = \text{Tr}(R\mathbf{G}) = \text{Tr}(\varrho\mathbf{G}), \quad \text{Tr}R = 1.$$

This maximized entropy satisfies the well known relations [79]

$$(118) \quad S_{max} = -k_B \text{Tr}(R \ln R) = -k_B \text{Tr}(\varrho \ln R) \geq -k_B \text{Tr}(\varrho \ln \varrho)$$

which shows that  $\ln R$  is the *entropy operator* for every arbitrarily chosen beobachtungsebene. Often, the so-called *extropy* is introduced [82]

$$(119) \quad \text{Ex} := k_B \text{Tr}[\varrho(\ln \varrho - \ln R)] \geq 0.$$

The time rate of the maximized entropy is

$$(120) \quad \dot{S}_{max} = -k_B \text{Tr}(\dot{R} \ln R) = -k_B \text{Tr}(\dot{\varrho} \ln R) - k_B \text{Tr}[\varrho(\ln R)^\bullet].$$

Of course,  $R$  does not satisfy the von Neumann equation although the Schrödinger equation is valid. There are different methods for constructing the dynamics of  $\dot{R}$  [83]. The most famous one is the Robertson dynamics [84].

The maximization (116) determines the form of the *generalized canonical density operator*  $R$  in non-equilibrium [80]

$$(121) \quad R = \frac{1}{Z} e^{-\boldsymbol{\lambda} \cdot \mathbf{G}}, \quad Z = \text{Tr}(e^{-\boldsymbol{\lambda} \cdot \mathbf{G}}).$$

The number of the to  $\mathbf{G}$  *conjugated variables*  $\boldsymbol{\lambda}$  is equal to that of the observables in the beobachtungsebene  $\mathcal{B}$ , and consequently equal to the number of the expectation values  $\mathbf{g}$  (114).

Inserting (121) into (120) yields

$$(122) \quad \dot{S}_{max} = k_B \boldsymbol{\lambda} \cdot \text{Tr}(\dot{R}\mathbf{G}) = k_B \boldsymbol{\lambda} \cdot [\dot{\mathbf{g}} - \text{Tr}(R\dot{\mathbf{G}})].$$

If we take into consideration that the Hamiltonian  $\mathcal{H}$  is always included in  $\mathcal{B}$ , (113) becomes by splitting

$$(123) \quad \mathcal{B} = \{\mathbf{G}\} = \{\mathcal{H}, \mathbf{H}\},$$

and (122)<sub>1</sub> results in an expression which is analogous to (3) for closed systems

$$(124) \quad \dot{S}_{max} = k_B \beta \text{Tr}(\dot{R}\mathcal{H}) + k_B \boldsymbol{\kappa} \cdot \text{Tr}(\dot{R}\mathbf{H}).$$

This can be transformed into

$$(125) \quad \begin{aligned} \dot{S}_{max} = k_B \beta \left\{ \dot{E} - \left[ \text{Tr}\left(R \frac{\partial \mathcal{H}}{\partial \mathbf{a}}\right) - \frac{\boldsymbol{\kappa}}{\beta} \cdot \text{Tr}\left(\mathbf{H} \frac{\partial R}{\partial \mathbf{a}}\right) \right] \cdot \dot{\mathbf{a}} \right\} + \\ + k_B \boldsymbol{\kappa} \cdot \text{Tr}\left(\mathbf{H} \frac{\partial R}{\partial \boldsymbol{\lambda}}\right) \cdot \dot{\boldsymbol{\lambda}}. \end{aligned}$$

Consequently, the power and the heat exchanges are according to (2) and (3) for closed systems

$$(126) \quad \dot{W} = \left[ \text{Tr}\left(R \frac{\partial \mathcal{H}}{\partial \mathbf{a}}\right) - \frac{\boldsymbol{\kappa}}{\beta} \cdot \text{Tr}\left(\mathbf{H} \frac{\partial R}{\partial \mathbf{a}}\right) \right] \cdot \dot{\mathbf{a}},$$

$$(127) \quad \dot{Q} = \text{Tr}(\dot{R}\mathcal{H}) + \left[ \frac{\boldsymbol{\kappa}}{\beta} \cdot \text{Tr}\left(\mathbf{H} \frac{\partial R}{\partial \mathbf{a}}\right) \right] \cdot \dot{\mathbf{a}}.$$

Here  $k_B\beta = 1/\Theta$  is the reciprocal contact temperature, and the expression

$$(128) \quad k_B\boldsymbol{\kappa} \cdot \text{Tr}\left(\mathbf{H} \frac{\partial R}{\partial \boldsymbol{\lambda}}\right) \cdot \dot{\boldsymbol{\lambda}} = \Sigma$$

represents the entropy production in closed systems according to (3) and (4).

**10.3. Equilibrium.** The quantal density operator  $\varrho$  depends on the macroscopic variables  $\mathbf{a}$  and  $\boldsymbol{\lambda}$  in general. This can be seen by considering the special case of equilibrium. Equilibria in closed discrete systems are quantum-mechanically described by the canonical density operator

$$(129) \quad \varrho^{eq} = \frac{1}{Z^{eq}} \exp\left(-\frac{\mathcal{H}}{k_B T}\right), \quad Z^{eq} = \text{Tr}\left[\exp\left(-\frac{\mathcal{H}}{k_B T}\right)\right].$$

Here  $\mathcal{H}$  is the Hamilton operator of the considered system and  $T$  its thermostatic temperature which is equal to that of the controlling reservoir. Comparing (121) with (129), we obtain for the beobachtungsebene in this equilibrium situation

$$(130) \quad \mathcal{B} = \{\mathcal{H}\},$$

and (121) results in

$$(131) \quad R^{eq} = \frac{1}{Z^{eq}} e^{-\beta\mathcal{H}} = \varrho^{eq}, \quad Z^{eq} := \text{Tr}(e^{-\beta\mathcal{H}}), \quad \beta \equiv (1/k_B T).$$

We now consider a reversible process which is defined by a trajectory in the equilibrium sub-space spanned by  $(\mathbf{a}, \mathbf{n}, U)$  according to (1). Consequently, a reversible process consists of equilibrium states and does therefore not exist in nature. Along the equilibrium trajectory, the beobachtungsebene (130) and the density operator (131) hold true. Consequently, the derivative along the reversible process (that is not the time derivative!) is according to (131) and (107)

$$(132) \quad R^{\dot{rev}} = \dot{\varrho}^{rev} = \left[ \frac{1}{Z^{eq}} e^{-\beta\mathcal{H}} \right]^{\bullet} = \overset{\circ}{\varrho}^{rev} - (i/\hbar)[\mathcal{H}, \varrho^{rev}].$$

Because according to (121) the variables  $\mathbf{a}$  and  $\boldsymbol{\lambda}$  are changing also along a reversible process,  $\dot{R}^{rev}$  is non-zero in general. The commutator in (132) vanishes according to (131)<sub>2</sub>. Consequently,  $\overset{\circ}{\varrho}^{rev}$  does also not vanish, a result which proves that in quantum mechanics even reversible *thermodynamical* processes do not appear according to (109).

If such processes should be included into a quantum mechanical description, the reversible von Neumann equation (109) cannot hold for these processes. There remain only two possibilities: Even reversible thermodynamical processes are excluded from a quantum mechanical description or the von Neumann equation has to be extended by the irreversible

part  $\overset{\circ}{\varrho}$  of the density operator. This extension causes that the statistical weights (110)<sub>3</sub> of the density operator cannot be constant, because the projectors (110)<sub>2</sub> depend only on the work variables  $\mathbf{a}$ . Consequently, (111) does not hold, and (108) and the irreversible von Neumann equation (107) are valid. That means, the quantum mechanical ensemble generating the density operator changes in time, if thermodynamical processes are described quantum mechanically.

From (124) follows the reversible rate of the maximized entropy (122)

$$(133) \quad \dot{S}_{max}^{rev} = k_B \beta \text{Tr}[\dot{R}^{rev} \mathcal{H}] = k_B \beta [\dot{E}^{rev} - \text{Tr}(R \dot{\mathcal{H}}^{rev})]$$

which is consistent with the reversible heat exchange  $\text{Tr}[\dot{R}^{rev} \mathcal{H}]$  in (127).

**10.4. Sufficient dynamics.** The expectation value of the observables  $\mathbf{G} \in \mathcal{B}$  are

$$(134) \quad \mathbf{g} = \text{Tr}(\varrho \mathbf{G}) = \text{Tr}(R \mathbf{G}).$$

Consequently, we obtain for the rates of the expectation values  $\mathbf{g}$

$$(135) \quad \text{Tr}(\dot{\varrho} \mathbf{G}) + \text{Tr}(\varrho \dot{\mathbf{G}}) = \text{Tr}(\dot{R} \mathbf{G}) + \text{Tr}(R \dot{\mathbf{G}}).$$

which results in

$$(136) \quad \text{Tr}[(\dot{\varrho} - \dot{R}) \mathbf{G}] = \text{Tr}[(R - \varrho) \dot{\mathbf{G}}].$$

Because in general  $\dot{\mathbf{G}} \notin \mathcal{B}$  and  $\dot{\mathbf{G}} \neq \mathbf{0}$ , we obtain that the expectation values of  $\dot{\mathbf{G}}$  calculated by  $R$  or  $\varrho$  are different, because the left-hand side of (136) does not vanish in general

$$(137) \quad \text{Tr}(R \dot{\mathbf{G}}) \neq \text{Tr}(\varrho \dot{\mathbf{G}}).$$

This is an awkward situation because the power cannot be calculated by the density operator  $R$  to which belongs the beobachtungsebene. But there is a possibility to enforce the equality in (137): We choose the free irreversible part of the density operator (107) so that

$$(138) \quad \text{Tr}[(\dot{\varrho} - \dot{R}) \mathbf{G}] = \mathbf{0}$$

is valid. Of all the possibilities, one taking  $\mathcal{B}$  into account is very easy [79]

$$(139) \quad \dot{\varrho} = \overset{\circ}{\varrho} - \frac{i}{\hbar} [\mathcal{H}, \varrho] \doteq \dot{R} - \mu(\varrho - R).$$

This equation determines  $\overset{\circ}{\varrho}$ , if  $R$ ,  $\dot{R}$  and  $\varrho$  are given, that means, the dynamics of  $R$  is not restricted by (139) which represents the extended von Neumann equation for calculating the microscopic dynamics. According to (139), it results in [79]

$$(140) \quad \varrho(t) = e^{-\mu t} \left[ \int_{t_0}^t (\dot{R}(\tau) + \mu R(\tau)) e^{\mu \tau} d\tau + e^{\mu t_0} \varrho(t_0) \right].$$

Here, the dynamics of  $R$  is given by other considerations [83]. The Schrödinger equation is still valid. According to (138) and (136), the expectation values of all time derivatives of  $\mathbf{G}$  are now correctly represented by  $R$ , although these time derivatives are not included into  $\mathcal{B}$ . In this case, the beobachtungsebene and the dynamics (140) is called *sufficient for  $\dot{\mathbf{G}}$* .

## Final Remark

Although presentations, presuppositions, theoretical concepts and even philosophical back-grounds may be different in various forms of thermodynamics, there is a common core for all: The basic variables, the constitutive properties and the Laws of thermodynamics which also includes the principles of mechanics and electrodynamics. Today’s thermodynamics is understood as a general description of classical systems in non-equilibrium including the reversible limit. Consequently, thermodynamical methods are in vivid development and have a wide range of application.

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