PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 42, NO. 2, PP. 85–96 (1998)

A PHENOMENOLOGICAL FOUNDATION OF NON-LINEAR OC-RECIPROCAL RELATIONS

(IRREVERSIBLE THERMODYNAMICS APPROACH)

Wolfgang MUSCHIK

Institute for Theoretical Physics
Technical University Berlin
Hardenbergstraße 36
10623 Berlin, Germany

Received: March 30, 1997

Abstract

Onsager-Casimir reciprocal relations are phenomenologically derived by considering the reversal of so-called rm-parameters. These parameters are defined as being odd under time reversal, if the force densities remain invariant. The reversal of the rm-parameters transforms to an existing process, whereas the time reversal itself is different from the reversal of the rm-parameters and transforms to a macroscopically non-existing process. The derivation of the reciprocal relations needs the second law and the axiom, that the reversal of the rm-parameters induces not only a transformation of the coordinates of thermodynamic forces and fluxes.

Keywords: Onsager-Casimir reciprocal relations, non-linear reciprocal relations.

1. Introduction

The classical proof of Onsager-Casimir reciprocal relations is of statistical nature [1, 2, 3]. The usual interpretation of this item is as follows: The reciprocal relations are caused by the fact that macroscopic systems consist of microscopic objects which move reversibly under reversal of motion. This is denoted by 'microscopic reversibility'. Because microscopic reversibility is a concept which cannot be explained by macroscopic terms – macroscopic systems move irreversibly, and systems generated by reversal of motion do not exist – the reciprocal relations are the manifestation for the microscopic background behind all macroscopic systems. Although the reciprocal relations do not contain microscopic quantities, they cannot be derived by macroscopic tools.

In this paper the reversal of motion is replaced by the reversal of so-called rm-parameters (a better name may be: Casimir parameters). These rm-parameters are defined indirectly by the reversal of motion, but their reversal generates in contrast to the reversal of motion a process of non-negative entropy production density. Therefore the reversal of rm-parameters is different from the reversal of motion and fits in the macroscopic concept. Just this is meant by 'phenomenological foundation': The microscopic reversibility is replaced by symmetry properties of the phenomenological equations under macroscopic rm-parameter reversal.

Concerning the non-linearity the situation is as follows: In the case of Onsager's reciprocal relations (vanishing rm-parameters) the following statement holds [4, 5]

If linear O-reciprocal relations are valid, forces and fluxes can be introduced, so that non-linear O-reciprocal relations hold.

Till now this statement could not be extended to OC-reciprocal relations. Consequently the interesting case is to include the rm-parameter, as it is done in this paper.

In the next section the fluxes are split into dissipation-free and entropy producing parts. In the third part entropy production conserving tranformations of the forces and fluxes are considered. After having introduced the rm-parameters their reversal is investigated in the fourth and fifth section. In the sixth section an axiom concerning the connection between the reversal of rm-parameters and tranformation of forces and fluxes is formulated stating that the rm-parameter reversal transforms the dissipation-free fluxes differently from the entropy producing ones. This axiom, replacing the reversal of motion, allows for deriving OC-reciprocal relations. The appendix contains all necessary proofs.

2. Entropy Production and Phenomenological Equations

We consider the fields of the thermodynamic forces X and fluxes $Y(X)$ as described e.g. in [6]

$$X(x,t) \in \mathbf{R}^n, \qquad Y(X(x,t);x,t) \in \mathbf{R}^n. \tag{1}$$

The field of the entropy production density

$$\sigma(X) = X \cdot Y(X) \geq 0 \tag{2}$$

is according to the second law here used not negative for all positions at all times. Forces and fluxes are connected by the *phenomenological equations* which are non-linear in general

$$Y(x,t) = f(X(x,t)). \tag{3}$$

By use of the following

Proposition I [7]: If

$$X \cdot Y(X) \geq 0, \ \bigwedge X \ \text{ and } \lim_{X \to \mathbf{0}} Y(X) = Y(\mathbf{0}), \tag{4}$$

then

$$\boldsymbol{Y}(\mathbf{0}) = \mathbf{0} \tag{5}$$

is valid, i.e., $\boldsymbol{Y}$ is homogeneous in $\boldsymbol{X}$,

according to (2), (4), and (5) the non-linear phenomenological equations (3) satisfy

$$\mathbf{0} = \boldsymbol{f}(\mathbf{0}). \tag{6}$$

Taylor expansion of (3) around $\boldsymbol{X} = \mathbf{0}$ results in

$$\boldsymbol{Y}(\boldsymbol{X}(\boldsymbol{x}, t); \boldsymbol{x}, t) = \mathbf{L}(\boldsymbol{X}(\boldsymbol{x}, t); \boldsymbol{x}, t) \cdot \boldsymbol{X}(\boldsymbol{x}, t). \tag{7}$$

The fluxes can be split into a *dissipation-free* part

$$\boldsymbol{Y}^{\boldsymbol{a}} := \mathbf{L}^{\boldsymbol{a}} \cdot \boldsymbol{X}, \qquad \boldsymbol{Y}^{\boldsymbol{a}} \cdot \boldsymbol{X} = 0, \tag{8}$$

and an *entropy producing* part

$$\boldsymbol{Y}^{\boldsymbol{s}} := \mathbf{L}^{\boldsymbol{s}} \cdot \boldsymbol{X}, \qquad \boldsymbol{Y} = \boldsymbol{Y}^{\boldsymbol{s}} + \boldsymbol{Y}^{\boldsymbol{a}}. \tag{9}$$

Here $\mathbf{L}^{\boldsymbol{s}}$ is the symmetric, $\mathbf{L}^{\boldsymbol{a}}$ the antisymmetric part of the constitutive mapping $\mathbf{L}$.

In general the entropy production density (2) can be split in different ways into a product of forces and fluxes. Therefore we consider in the next section transformations of forces and fluxes which leave the entropy production invariant.

3. Transformation of Forces and Fluxes

First of all forces and fluxes can be transformed independently of each other. Here we are interested in linear transformations, because the superposition principle should also be valid for the transformed quantities. Also the transformed entropy production density is identically defined by the transformed forces and fluxes. We prove in the appendix A the following

Proposition II [8]: If A and B are linear, regular, and entropy production conserving transformations of forces and fluxes, respectively, called transformation of coordinates of the forces and fluxes (*c-transformation*)

$$\boldsymbol{X}^{\diamond} = \mathrm{A} \cdot \boldsymbol{X}, \quad \boldsymbol{Y}^{\diamond} = \mathrm{B} \cdot \boldsymbol{Y} \to \sigma = \boldsymbol{X} \cdot \boldsymbol{Y} = \boldsymbol{X}^{\diamond} \cdot \boldsymbol{Y}^{\diamond} = \sigma^{\diamond}, \tag{10}$$

we obtain for the transformed phenomenological coefficients

$$\mathbf{L}^{\diamond \boldsymbol{s}} = \mathrm{A}^{\top -1} \cdot [\mathbf{L}^{\boldsymbol{s}}(\boldsymbol{X}) + \mathrm{Z}^{\boldsymbol{s}}(\boldsymbol{X})] \cdot \mathrm{A}^{-1}, \tag{11}$$

$$\mathbf{L}^{\diamond a} = \mathbf{A}^{\top -1} \cdot [\mathbf{L}^{a}(\boldsymbol{X}) + \mathbf{Z}^{a}(\boldsymbol{X})] \cdot \mathbf{A}^{-1}, \tag{12}$$

$$\boldsymbol{X} \cdot \mathbf{Z}^{s}(\boldsymbol{X}) \cdot \boldsymbol{X} = 0, \quad \mathbf{Z}(\boldsymbol{X}) := [\mathbf{A}^{\top} \cdot \mathbf{B} - \mathbf{1}] \cdot \mathbf{L}. \tag{13}$$

This formal c-transformation has first of all no physical background. It mixes different components of the forces and fluxes, and consequently also the phenomenological equations are transformed. The transformed forces and fluxes are as suitable for describing the phenomena as are the original ones.

In the next section we consider another different transformation of the forces and fluxes.

4. Reverse Motion Parameters

By definition a *reversal of motion* transforms an original process to the one which can be observed in the backward moving movie of the original process. Force densities, such as Lorentz, Coriolis, and Euler forces are invariant under reversal of motion because otherwise the considered process does not run along the reversed path. This causes that special quantities, such as the magnetic induction and the angular velocity, are odd under reversal of motion. Thus we give the

DEFINITION [8]: *Reverse motion parameters* (rm-parameters) $\boldsymbol{p}$ change their signs under reversal of motion, because force densities (Lorentz, Coriolis, Euler) are even under reversal of motion:

$$\boldsymbol{k} \sim \boldsymbol{v} \times \boldsymbol{B}, \quad \boldsymbol{k} \sim \boldsymbol{v} \times \boldsymbol{\omega} \quad \Longrightarrow \quad \boldsymbol{p} \doteq (\boldsymbol{B}, \boldsymbol{\omega}, ...). \tag{14}$$

Because the Euler force density

$$\boldsymbol{k} \sim \dot{\boldsymbol{\omega}} \times \boldsymbol{x} \tag{15}$$

is even under reversal of motion $\dot{\boldsymbol{\omega}}$ is even, too. Consequently it does not belong to the rm-parameters, although $\dot{\boldsymbol{\omega}}$ is odd under reversal of the rm-parameters.

In general thermodynamic forces and fluxes depend on the set of rm-parameters $\boldsymbol{p}$:

$$\boldsymbol{X}_{\pm} := \boldsymbol{X}(\boldsymbol{x}, t; \pm\boldsymbol{p}), \qquad \boldsymbol{Y}_{\pm} := \boldsymbol{Y}(\boldsymbol{x}, t; \pm\boldsymbol{p}). \tag{16}$$

The transformation of the forces and fluxes by changing the signs of the rm-parameters

$$\boldsymbol{X}_{+} \longrightarrow \boldsymbol{X}_{-}, \qquad \boldsymbol{Y}^{s}_{+} \longrightarrow \boldsymbol{Y}^{s}_{-}, \qquad \boldsymbol{Y}^{a}_{+} \longrightarrow \boldsymbol{Y}^{a}_{-} \tag{17}$$

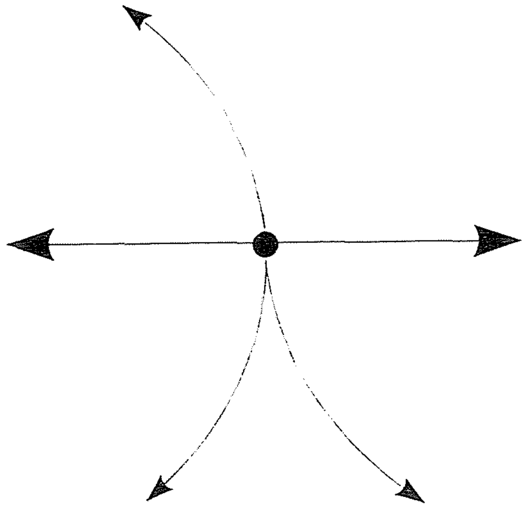

Fig. 1. Original motion, reversal of motion, and motion for reversed rm-parameters. The force density $\boldsymbol{k}$ is odd under reversal of rm-parameters. The reversal of motion does not exist macroscopically, whereas the rm-parameter reversed motion is an existing process.

does not transform the forces and fluxes to their values in the backward moving movie, because only the rm-parameters change their signs, whereas the velocity remains invariant. Consequently, also the force densities are odd under reversal of rm-parameters which is different from their behaviour under reversal of motion (see *Fig. 1*). Beyond that the entropy producing fluxes may transform differently from the dissipation-free fluxes.

Thus the transformation (17) of the forces, the entropy producing and the dissipation-free fluxes induce three involutoric mappings K, M, and N

$$\mathrm{K} \cdot X_{\pm} = X_{\mp}, \quad \mathrm{M} \cdot Y^{s}_{\pm} = Y^{s}_{\mp}, \quad \mathrm{N} \cdot Y^{a}_{\pm} = Y^{a}_{\mp}, \tag{18}$$

$$\mathrm{K} \cdot \mathrm{K} = 1, \quad \mathrm{M} \cdot \mathrm{M} = 1, \quad \mathrm{N} \cdot \mathrm{N} = 1. \tag{19}$$

We now prove in the appendix B the following

Proposition III: K, M, and N are linear mappings.

The forces can be split into their even (g) and odd (u) parts under reversal of the rm-parameters. By $(18)_1$ we obtain

$$X_g := \frac{1}{2}[X_+ + X_-] \;=\; \frac{1}{2}[1 + \mathrm{K}] \cdot X_+ =: \mathbf{P} \cdot X_+, \tag{20}$$

$$\boldsymbol{X}_u := \frac{1}{2}[\boldsymbol{X}_+ - \boldsymbol{X}_-] \;=\; \frac{1}{2}[1 - \mathrm{K}] \cdot \boldsymbol{X}_+ =: \mathbf{Q} \cdot \boldsymbol{X}_+, \tag{21}$$

$$\boldsymbol{X}_g + \boldsymbol{X}_u = \boldsymbol{X}_+, \qquad \boldsymbol{X}_g - \boldsymbol{X}_u = \boldsymbol{X}_- = \mathrm{K} \cdot \boldsymbol{X}_+, \tag{22}$$

$$\mathrm{K} \cdot \boldsymbol{X}_g = \boldsymbol{X}_g, \qquad \mathrm{K} \cdot \boldsymbol{X}_u = -\boldsymbol{X}_u, \tag{23}$$

$$\mathbf{P}^2 = \mathbf{P}, \qquad \mathbf{Q}^2 = \mathbf{Q}, \tag{24}$$

$$\mathbf{P} + \mathbf{Q} = \mathbf{1}, \qquad \mathbf{P} \cdot \mathbf{Q} = \mathbf{Q} \cdot \mathbf{P} = \mathbf{0}. \tag{25}$$

From (22) and $(18)_1$ follows immediately

$$\boldsymbol{X}_\pm = \mathbf{0} \qquad \longleftrightarrow \qquad \boldsymbol{X}_g = \mathbf{0} \quad \wedge \quad \boldsymbol{X}_u = \mathbf{0}, \tag{26}$$

$$\boldsymbol{X}_g = \boldsymbol{X}_u \qquad \longrightarrow \qquad \boldsymbol{X}_\pm = \mathbf{0}. \tag{27}$$

The division into even and odd parts under the reversal of the rm-parameters is not only valid for forces as derived in the equations (20) to (27), but holds true for the entropy producing and dissipation-free fluxes, if $\mathbf{K}$ in (20), (21), and (23) is replaced by $\mathbf{M}$ and N, respectively. Beyond that the relations remain also valid for the entropy production density and other scalar products, what we will exploit in the next section.

5. Reversal of rm-Parameters

Because the scalar product between the forces and the dissipation-free fluxes vanishes for an arbitrary set of rm-parameters, it also vanishes for the reversed set according to (26). In more detail we have:

$$w_+ := \boldsymbol{Y}_+^a \cdot \boldsymbol{X}_+ = w_g + w_u = 0, \tag{28}$$

$$w_g = -w_u \quad \rightarrow \text{parameter reversal} \quad w_g = w_u = 0, \tag{29}$$

$$w_- := \boldsymbol{Y}_-^a \cdot \boldsymbol{X}_- = w_g - w_u = 0. \tag{30}$$

Thus we proved the

Proposition IV [8]: Dissipation-free fluxes remain dissipation-free under reversal of the rm-parameters

$$\boldsymbol{Y}_+^{\boldsymbol{a}} \cdot \boldsymbol{X}_+ = 0 = \boldsymbol{Y}_-^{\boldsymbol{a}} \cdot \boldsymbol{X}_-. \tag{31}$$

The entropy producing fluxes do not satisfy such an easy relation as (31). In the appendix C we prove the following

Proposition V [8]: By use of the Second Law

$$\sigma_+ \geq 0, \qquad \sigma_- \geq 0, \tag{32}$$

we obtain

$$\sigma_+ = \sigma_- \geq 0, \tag{33}$$

$$\mathbf{Y}^s_- = \mathbf{K}^\top \cdot \mathbf{Y}^s_+, \quad \mathbf{Y}^a_- = \pm \mathbf{K}^\top \cdot \mathbf{Y}^a_+, \tag{34}$$

$$\mathbf{L}^s_+ = \mathbf{K}^\top \cdot \mathbf{L}^s_- \cdot \mathbf{K}, \quad \mathbf{L}^a_+ = \pm \mathbf{K}^\top \cdot \mathbf{L}^a_- \cdot \mathbf{K}. \tag{35}$$

Presupposition (32) is easy to understand: The original process belonging to an arbitrary set of rm-parameters, denoted by the index $_+$, has non-negative entropy production density. After reversal of the rm-parameters the resulting process is also of non-negative entropy production density, because this process is a real one, and not the process generated by reversal of motion (see *Fig. 1*). According to (33) the rm-parameter reversed process has the same entropy production density as the original one. The fluxes transform according to (34). Here the sign is not yet decided for the dissipation-free fluxes, because for them the inequalities (32) and (33) do not hold. If the +-sign holds in (34), the tranformation of the fluxes by rm-parameter reversal is a c-transformation according to $(10)_2$. The reversal of the rm-parameters is not a simple tranformation of the coordinates of the forces and fluxes with no physical background, but just the dissipation-free parts of the fluxes are affected by the rm-parameter reversal as we can see from *Fig. 1.* Consequently disspation-free fluxes transform differently from the entropy producing ones.

6. OC-Reciprocal Relations

First of all we have to formulate the last remark of the previous section as an

AXIOM *Reversal of the rm-parameters is not included in the c-transformations of the coordinates of the forces and fluxes*

Comparing now $(10)_2$ with (34) we see that the −sign holds, because otherwise the entropy producing and the dissipation-free fluxes would transform in the same way, which according to $(10)_2$ results in a c-transformation. Consequently the axiom induces by adding both the equations (35)

Proposition VI [8]:

$$\mathbf{L}_+ = \mathbf{K}^\top \cdot \mathbf{L}^\top_- \cdot \mathbf{K}. \tag{36}$$

These reciprocity relations can be tranformed because of the following

Proposition VII [8]: The mapping $\mathbf{K}$ is symmetric

$$\mathbf{K}^{\top} = \mathbf{K} \tag{37}$$

which is proved in appendix D. By proposition VII we can transform (36) to the statement

Proposition VIII [8]: There are forces and fluxes for which the Onsager-Casimir reciprocal relations are valid

$$\mathbf{L}^{\star}(\boldsymbol{B},\omega,....) = \Lambda \cdot \mathbf{L}^{\star\top}(-\boldsymbol{B},-\omega,....)\cdot \Lambda, \tag{38}$$

$$\Lambda \quad \text{diagonal}, \qquad \Lambda \cdot \Lambda = 1. \tag{39}$$

Appendix

A Proof of Proposition II

From (10) follows immediately

$$\boldsymbol{X} \cdot (\mathbf{A}^{\top} \cdot \boldsymbol{Y}^{\diamond} - \boldsymbol{Y}) = 0. \tag{A.1}$$

Inserting the transformation equations and the phenomenological equations we obtain

$$\boldsymbol{X} \cdot (\mathbf{A}^{\top} \cdot \mathbf{B} - 1) \cdot \mathbf{L} \cdot \boldsymbol{X} = 0. \tag{A.2}$$

Using the abbreviation

$$\mathbf{Z}(\boldsymbol{X}) := [\mathbf{A}^{\top} \cdot \mathbf{B} - 1] \cdot \mathbf{L} \tag{A.3}$$

(A.2) and (A.1) result in

$$\boldsymbol{X} \cdot \mathbf{Z} \cdot \boldsymbol{X} = 0, \qquad \mathbf{A}^{\top} \cdot \boldsymbol{Y}^{\diamond} - \boldsymbol{Y} = \mathbf{Z} \cdot \boldsymbol{X}. \tag{A.4}$$

From $(A.4)_1$ follows $(13)_1$, and from $(A.4)_2$

$$\boldsymbol{Y}^{\diamond} = \mathbf{A}^{\top -1} \cdot (\boldsymbol{Y} + \mathbf{Z} \cdot \boldsymbol{X}). \tag{A.5}$$

Inserting the transformation equations and the phenomenological equations we obtain

$$\boldsymbol{Y}^{\diamond} = \mathbf{A}^{\top -1} \cdot (\mathbf{L} + \mathbf{Z}) \cdot \mathbf{A}^{-1} \cdot \boldsymbol{X}^{\diamond} =: \mathbf{L}^{\diamond} \cdot \boldsymbol{X}^{\diamond}. \tag{A.6}$$

The symmetric and antisymmetric parts of $\mathbf{L}^{\diamond}$ are (11) and (12).

B Proof of Proposition III

According to (16) for two fields $\boldsymbol{a}$ and $\boldsymbol{b}$

$$\boldsymbol{a}_+ + \boldsymbol{b}_+ = (\boldsymbol{a}+\boldsymbol{b})_+ \tag{B.1}$$

holds. According to $(18)_1$ we obtain

$$\begin{aligned} \mathrm{K}\cdot(\boldsymbol{a}_+ + \boldsymbol{b}_+) &= \mathrm{K}\cdot((\boldsymbol{a}+\boldsymbol{b})_+) = (\boldsymbol{a}+\boldsymbol{b})_- = \\ &= \boldsymbol{a}_- + \boldsymbol{b}_- = \mathrm{K}\cdot\boldsymbol{a}_+ + \mathrm{K}\cdot\boldsymbol{b}_+ . \end{aligned} \tag{B.2}$$

Thus K and also M and N are linear mappings on their domain.

C Proof of Proposition V

We consider the space of forces $\mathcal{O}$ being orthogonal to an arbitrary, but fixed $\boldsymbol{Y}^{\boldsymbol{s}}_+$

$$\mathcal{O} := \{\boldsymbol{S}^O_+ | \boldsymbol{Y}^{\boldsymbol{s}}_+ \cdot \boldsymbol{S}^O_+ = 0\}. \tag{C.1}$$

Therefore we obtain according to proposition IV

$$0 = \boldsymbol{Y}^{\boldsymbol{s}}_+ \cdot \boldsymbol{S}^O_+ = \boldsymbol{Y}^{\boldsymbol{s}}_- \cdot \boldsymbol{S}^O_- = \boldsymbol{Y}^{\boldsymbol{s}}_- \cdot \mathrm{K} \cdot \boldsymbol{S}^O_+ . \tag{C.2}$$

Because (C.2) is valid for all elements of $\mathcal{O}$ we obtain that $\boldsymbol{Y}^{\boldsymbol{s}}_+$ and $\boldsymbol{Y}^{\boldsymbol{s}}_- \cdot \mathrm{K}$ are parallel to each other

$$\mathrm{K}^\top \cdot \boldsymbol{Y}^{\boldsymbol{s}}_- = \lambda(\boldsymbol{Y}^{\boldsymbol{s}}_+)\boldsymbol{Y}^{\boldsymbol{s}}_+ , \tag{C.3}$$

$$\boldsymbol{Y}^{\boldsymbol{s}}_- = \lambda(\boldsymbol{Y}^{\boldsymbol{s}}_+)\mathrm{K}^\top \cdot \boldsymbol{Y}^{\boldsymbol{s}}_+ , \qquad \bigwedge \boldsymbol{Y}^{\boldsymbol{s}}_+ . \tag{C.4}$$

Especially we obtain by the following replacement

$$\boldsymbol{Y}^{\boldsymbol{s}}_+ \longrightarrow \boldsymbol{Y}^{\boldsymbol{s}}_g , \quad \boldsymbol{Y}^{\boldsymbol{s}}_u \tag{C.5}$$

from (C.3) and (C.4)

$$\boldsymbol{Y}^{\boldsymbol{s}}_g = \lambda(\boldsymbol{Y}^{\boldsymbol{s}}_g)\mathrm{K}^\top \cdot \boldsymbol{Y}^{\boldsymbol{s}}_g , \tag{C.6}$$

$$-\boldsymbol{Y}^{\boldsymbol{s}}_u = \lambda(\boldsymbol{Y}^{\boldsymbol{s}}_u)\mathrm{K}^\top \cdot \boldsymbol{Y}^{\boldsymbol{s}}_u . \tag{C.7}$$

Thus eigenvalues for $\mathrm{K}^\top$ are

$$\lambda(\boldsymbol{Y}^{\boldsymbol{s}}_g) = \pm 1, \qquad \lambda(\boldsymbol{Y}^{\boldsymbol{s}}_u) = \pm 1. \tag{C.8}$$

Consequently (C.6) and (C.7) result in

$$\boldsymbol{Y}^{\boldsymbol{s}}_g = a\mathrm{K}^\top \cdot \boldsymbol{Y}^{\boldsymbol{s}}_g , \tag{C.9}$$

$$-\boldsymbol{Y}^{\boldsymbol{s}}_u = b\mathrm{K}^\top \cdot \boldsymbol{Y}^{\boldsymbol{s}}_u , \quad a = \pm 1, \quad b = \pm 1. \tag{C.10}$$

Addition of (C.9) and (C.10) yield

$$\boldsymbol{Y}^{\boldsymbol{s}}_{-} = \mathrm{K}^{\top} \cdot (a\boldsymbol{Y}^{\boldsymbol{s}}_{g} + b\boldsymbol{Y}^{\boldsymbol{s}}_{u}). \tag{C.11}$$

A comparison with (C.4) results in

$$a = b = \lambda(\boldsymbol{Y}^{\boldsymbol{s}}_{+}) = \pm 1. \tag{C.12}$$

Therefore we obtain from (C.4)

$$\boldsymbol{Y}^{\boldsymbol{s}}_{-} = \pm \mathrm{K}^{\top} \cdot \boldsymbol{Y}^{\boldsymbol{s}}_{+}, \tag{C.13}$$

and analogously:

$$\boldsymbol{Y}^{\boldsymbol{a}}_{-} = \pm \mathrm{K}^{\top} \cdot \boldsymbol{Y}^{\boldsymbol{a}}_{+}. \tag{C.14}$$

Consequently the entropy production becomes

$$\sigma_{-} = \boldsymbol{X}_{-} \cdot \boldsymbol{Y}^{\boldsymbol{s}}_{-} = \pm \boldsymbol{X}_{+} \cdot \boldsymbol{Y}^{\boldsymbol{s}}_{+} = \pm \sigma_{+} \geq 0. \tag{C.15}$$

This results in (34)

$$\boldsymbol{Y}^{\boldsymbol{s}}_{-} = \mathrm{K}^{\top} \cdot \boldsymbol{Y}^{\boldsymbol{s}}_{+}, \tag{C.16}$$

$$\boldsymbol{Y}^{\boldsymbol{a}}_{-} = \pm \mathrm{K}^{\top} \cdot \boldsymbol{Y}^{\boldsymbol{a}}_{+}. \tag{C.17}$$

D Proof of Proposition VII

We consider the space $\mathcal{P}$ of forces being orthogonal to an arbitrary, but fixed $\boldsymbol{X}_{+}$

$$\mathcal{P} := \{\boldsymbol{R}^{0}_{+} | \boldsymbol{X}_{+} \cdot \boldsymbol{R}^{0}_{+} = 0\}. \tag{D.1}$$

Therefore we obtain according to proposition IV

$$0 = \boldsymbol{X}_{+} \cdot \boldsymbol{R}^{0}_{+} = \boldsymbol{X}_{-} \cdot \boldsymbol{R}^{0}_{-} = \boldsymbol{X}_{+} \cdot \mathrm{K}^{\top} \cdot \mathrm{K} \cdot \boldsymbol{R}^{0}_{+}. \tag{D.2}$$

Because (D.2) is valid for all elements of $\mathcal{P}$, we obtain that $\boldsymbol{X}_{+}$ and $\boldsymbol{X}_{+} \cdot \mathrm{K}^{\top} \cdot \mathrm{K}$ are parallel to each other

$$\mathrm{K}^{\top} \cdot \mathrm{K} \cdot \boldsymbol{X}_{+} = \boldsymbol{X}_{+}. \tag{D.3}$$

Multiplication from the left by $\mathrm{K}^{\top}$ yields

$$\mathrm{K} \cdot \boldsymbol{X}_{+} = \mathrm{K}^{\top} \cdot \boldsymbol{X}_{+}, \qquad \bigwedge \boldsymbol{X}_{+}. \tag{D.4}$$

Thus K is symmetric.

E Proof of Proposition VIII

Because $\mathbf{K}$ is symmetric, there exists an orthogonal transformation to diagonal form Λ

$$\mathbf{K} =: \mathbf{Q} \cdot \Lambda \cdot \mathbf{Q}^{\top}, \qquad \mathbf{Q}^{\top} = \mathbf{Q}^{-1}, \tag{E.1}$$

$$\mathbf{L}_{\pm} =: \mathbf{Q} \cdot \mathbf{L}^{*}_{\pm} \cdot \mathbf{Q}^{\top}. \tag{E.2}$$

Inserting (E.2) into (36) we obtain

$$\mathbf{Q} \cdot \mathbf{L}^{*}_{+} \cdot \mathbf{Q}^{\top} = \mathbf{K}^{\top} \cdot \mathbf{Q} \cdot \mathbf{L}^{*\top}_{-} \cdot \mathbf{Q}^{\top} \cdot \mathbf{K}. \tag{E.3}$$

Using (E.1) this results in

$$\mathbf{L}^{*}_{+} = \Lambda \cdot \mathbf{L}^{*\top}_{-} \cdot \Lambda. \tag{E.4}$$

Inserting the rm-parameter we obtain proposition (38).

From $(18)_1$ we obtain with (E.1)

$$\mathbf{Q} \cdot \Lambda \cdot \mathbf{Q}^{\top} \cdot X_{+} = X_{-}. \tag{E.5}$$

Introducing the transformed forces

$$X^{*}_{+} := \mathbf{Q}^{\top} \cdot X_{+} \tag{E.6}$$

(E.5) results in

$$\Lambda \cdot X^{*}_{+} = X^{*}_{-}. \tag{E.7}$$

Therefore the Λ_i transform the components of the forces under reversal of the rm-parameters. According to $(\text{E.1})_1$ $\mathbf{K}$ and Λ have the same eigenvalues, namely ± 1. Consequently the transformation $\mathbf{Q}$ transforms the forces to those which are even or odd under reversal of the rm-parameters, and we have

$$\Lambda \cdot \Lambda = 1. \tag{E.8}$$

References

[1] ONSAGER, L.: Reciprocal Relation in Irreversible Processes, *Phys. Rev.* Vol. 37, (1931) p. 405 ; Vol. 38, (1931) p. 2265.

[2] CASIMIR, H. B. G.: On Onsager's Principle of Microscopic Reversibility, *Rev. Mod. Phys.* Vol. 17, (1945) p. 343.

[3] MAZUR, P.: Onsager's Reciprocal Relations and Thermodynamics of Irreversible Processes, in P.C. Hemmer, H. Holden, S. Kjelstrup Ratkje (Eds), The Collected Works of Lars Onsager (With Commentary), World Scientific Singapore 1996.

[4] SAUER, F.: Nonequilibrium Thermodynamics of Kidney Tubule Transport, in Handbook of Physiology, Renal Physiology, pp. 399–414.

[5] MUSCHIK, W.: in F. Reif, Statistische Physik und Theorie der Wärme, 2nd Edition, de Gruyter Berlin 1985, sect. 15.19.

[6] DE GROOT, S. R. – MAZUR, P.: Non-Equilibrium Thermodynamics, North-Holland Amsterdam 1961, Chap. IV, §3.

[7] MUSCHIK, W.: Fundamental Remarks on Evaluating Dissipation Inequalities, in J. Casas-Vázquez, D. Jou, G. Lebon (Eds), Recent Developments in Nonequilibrium Thermodynamics, Lecture Notes in Physics 199, Springer Berlin 1984, p. 387.

[8] MUSCHIK, W.: A Phenomenological Foundation of Non-Linear Onsager-Casimir Reciprocity Relations, *J. Non-Equilib. Thermodyn.* Vol. 2, (1977) p. 109.