Reciprocity and Boundary Conditions for Transport-Relaxation Equations

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(Z. Naturforsch. **31 a**, 1439–1450 [1976]; received November 3, 1976)

Recently a reciprocity theorem has been derived from the transport-relaxation equations for a simple system, consisting of one medium (Ref. [1]). With a composite system, consisting of two immiscible media in contact, a plausible generalized reciprocity scheme, here called universal reciprocity postulate, is suggested now. It leads to an equivalent reciprocity requirement at the interface between both media and thus decisively restricts — in form of provable Onsager relations — the possible constitutive laws connecting the thermodynamical forces and fluxes at the interface. For the formulation of these ideas, some mathematical tools are developed in advance. Finally, heat conduction is treated, as the most simple example, first in the direct way, then according to the more sophisticated mathematical tools.

In the preceding papers on the boundary conditions for transport-relaxation equations [2, 3] – a sort of generalized linear thermohydrodynamics – the method of non-equilibrium thermodynamics was used. In a straight unambiguous way one can find out the rate of entropy production in the interface between two immiscible media. It is expressed by a two-dimensional integral over a quadratic form of the system-variables. After transposing this form to principal axes, it was clear how to introduce thermodynamical "forces and fluxes" which allow a simple bilinear representation (scalar product form) of the interfacial entropy production. The usual procedure of non-equilibrium thermodynamics then leads to constitutive laws, i. e. boundary or matching conditions, for the interface. The same procedure was followed in the papers [4, 5] dealing with hydrodynamics in the proper sense. So, the method used in the previous papers was based on the "physical language".

In the present paper the problem is tackled in a more mathematical manner – nonchalant anyhow. At the centre of the considerations will be the reciprocity theorem derived recently [1]. This implies that now the Onsager relations for the matching conditions are treated predominantly (the foregoing papers [2, 3] were not elaborate in that respect). In the new context, the symmetry restrictions of the matching conditions arise from what will be called the "postulate of universal reciprocity". This postulate requires that with a composite system, consisting of two immiscible media side by side, the same type of reciprocity statement shall be valid at the overall-envelope as with a simple system consisting only of one medium. The postulate guarantees that for a composite system similar global Onsager relations – in the sense of de Groot-Mazur's discontinuous systems [6] – arise as for a simple system. There is no doubt that this postulate is physically sound.

After a short reminder of some basic concepts in § 1, a new coordinate – free treatment of surface quantities, especially of the appropriate thermodynamical forces and fluxes, Eqs. (3.1) and (3.2), is developed in § 2 and 3. This concise mathematical device is first applied to a simple system, § 4. Then follows in § 5 the formulation of universal reciprocity, Eq. (5.4), and of its requirements for the interfacial matching, Equation (5.6). In § 6 the matching conditions or interfacial constitutive laws are formulated, Eqs. (6.1), and the symmetries (6.5) of their coefficient matrices are derived. The last section, § 7, offers a simple example, heat conduction. This is directly treated first and then used as an illustration of the general mathematical tools developed before.

§ 1. Recapitulation of Transport-Relaxation Equations, Surface Entropy Production and Reciprocity Theorem

The set of transport-relaxation equations, more or less equivalent with the linearized Boltzmann equation, basis of our generalized thermohydrodynamics, has been described earlier [1–3] and is

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written down without much comment:

$$\frac{\partial a_i}{\partial t} + \sum_{i'=1}^{z} c_{\nu i i'} \frac{\partial a_{i'}}{\partial x_\nu} + \sum_{i'=1}^{z} \omega_{ii'} a_{i'} = 0 \qquad (1.1)$$

or in shorthand matrix form [1]

$$\frac{\partial a}{\partial t} + c_\nu \cdot \frac{\partial a}{\partial x_\nu} + \omega \cdot a = 0 . \qquad (1.2)$$

Thus, the "state vector" $\boldsymbol{a}$ with its z components $a_i(t, \boldsymbol{x})$ (the dot always signifies the scalar product with respect to these z components) obeys a linear partial differential equation of first order in time and space, with three constant $z \times z$-"transport matrices" c_ν ($\nu = 1, 2, 3$ are Cartesian indices subject to the summation rule) and one constant $z \times z$-"relaxation matrix" ω. The three matrices c_ν originate from the streaming term of the kinetic equation. They are symmetrical (at least for dilute gases)

$$c_\nu = \tilde{c}_\nu . \qquad (1.3)$$

With the "time reversal" operation Θ, also a $z \times z$-matrix characterized by [1]

$$\Theta = \tilde{\Theta} ; \quad \Theta \cdot \Theta = 1 , \qquad (1.4)$$

the (symmetrical) c_ν's anti-commute [1]:

$$\Theta \cdot c_\nu = -\tilde{c}_\nu \cdot \Theta = -c_\nu \cdot \Theta . \qquad (1.5)$$

The matrix ω originates from the collision term of the kinetic equation and has the Onsager symmetry [1]

$$\Theta \cdot \omega = \tilde{\omega} \cdot \Theta . \qquad (1.6)$$

So much about the transport-relaxation equation.

By scalar multiplication of (1.2) with the "line vector" $\tilde{a}$, the transposed of the "column vector" a, one obtains the identity [2, 3]

$$\frac{\partial}{\partial t}(-\tfrac{1}{2}\tilde{a} \cdot a) = \frac{\partial}{\partial x_\nu}(\tfrac{1}{2}\tilde{a} \cdot c_\nu \cdot a) + \tilde{a} \cdot \omega \cdot a . \qquad (1.7)$$

This consequence of the transport-relaxation equation is interpreted as the local entropy balance (apart from the factor "number density times Boltzmann's constant" which is omitted everywhere [3]), the scalar $-\frac{1}{2}\tilde{a} \cdot a$ being the entropy density, varying in time according to the negative divergence of the entropy flux $-\frac{1}{2}\tilde{a} \cdot c_\nu \cdot a$ and the entropy production density $\tilde{a} \cdot \omega \cdot a$. Integrating Eq. (1.7) over the volume of the system gives the rate of total entropy change (in the volume) as the sum of the entropy production in bulk – from the second term on the right – and the entropy entering the volume per unit time through the closed surface or envelope σ

$$\dot{S}_{\text{surface}} = \int_\sigma \tfrac{1}{2}\tilde{a} \cdot c \cdot a \, d\sigma , \qquad (1.8)$$

coming from the first term on the right by use of Gauß's theorem. The surface coefficient matrix c is given by

$$c = c_\nu n_\nu [= c(\boldsymbol{n})] , \qquad (1.9)$$

where $\boldsymbol{n}(\boldsymbol{x})$ is the local outward unit normal of the surface σ. The rate of bulk entropy change has to be positive in order to guarantee that a closed system (without surface influences) goes to thermal equilibrium: second law of thermodynamics. Likewise, for an open system the sum of the surface contribution (1.8) and the analogous contribution to the medium on the other side of σ, has to be positive. So, one should rather speak of the positive *interface* entropy production. The part (1.8) itself, with a closed σ, is negative in stationary case.

Besides the entropy balance, a second identity can be derived for two different solutions $a^{(1)}(\boldsymbol{x})$, $a^{(2)}(\boldsymbol{x})$ of the stationary (time-free) transport-relaxation Eq. (1.2). Prerequisite for the derivation are the symmetry relations (1.5 and 6). This second identity was called the reciprocity theorem [1]. In Eq. (21 b) of Ref. [1] it has been laid down in the integral form

$$\int_\sigma \tilde{a}^{(2)} \cdot \Theta \cdot c \cdot a^{(1)} \, d\sigma = 0 . \qquad (1.10)$$

Here, σ again denotes any closed surface within or at the border of the medium and c is the surface coefficient matrix from Equation (1.9). The reciprocity theorem or requirement will play the decisive role in the following.

Incidentally it is remarked that the theorem (1.10) does not presuppose symmetrical c_ν's. The proof in Ref. [1] depends only on the part $\Theta \cdot c_\nu = -\tilde{c}_\nu \cdot \Theta$ of Equation (1.5). It will be true in all cases, whereas the symmetry $c_\nu = \tilde{c}_\nu$ is, for the time being, not generally established.

§ 2. Eigen-Projectors of the c-Matrix and their Properties

In the previous treatments [2, 3] an orthogonal transformation of the a-vector with its z components was performed so that the c-matrix became diagonal and the integrand in the expression (1.8) simply was a sum of squares. This sum has $2Z < z$ terms corresponding to the non-zero eigenvalues C^K, $K = \pm 1, \ldots, \pm Z$, of the c-matrix. Besides them the eigenvalue $C = 0$ occurs $(z - 2Z)$-times; it does not contribute in (1.8). The non-vanishing $2Z$ square terms after some rearrangement led to the natural definition of Z "forces" and Z "fluxes" at the surface. These forces and fluxes had to be linearly coupled with each other to give boundary or, more properly, matching conditions: the constitutive laws for the interface [2, 3].

In the present paper, an equivalent but more general formulation is introduced and used afterwards. This formulation will avoid the explicit reference to the principal axes of c; it is free from a special choice of the coordinate system. There is another difference with the previous treatments. Formerly the properties of the c-eigenvalues were deduced from arguments of invariance under three-dimensional rotations. Presently the anticommutation relation

$$\Theta \cdot c = -c \cdot \Theta \tag{2.1}$$

of the c-matrix with the time reversal matrix Θ will be the starting point. It is known from other special cases, simple enough, that both arguments can lead to the same conclusion. But the time reversal argument certainly is the most general one and therefore to be preferred.

To begin with, let us consider an eigen-projector P^K of the c-matrix with the eigenvalue C^K

$$c \cdot P^K = P^K \cdot c = C^K P^K . \tag{2.2}$$

The eigen-projectors are $z \times z$-dyadics constructed from the z-dimensional eigenvectors of the symmetrical $z \times z$-matrix c. That the P's depend on the local surface normal, as c does, is not explicitly indicated in the notation. The P's are symmetrical and orthonormalized:

$$P^K = \tilde{P}^K ; \quad P^K \cdot P^{K'} = P^K \delta^{KK'} . \tag{2.3}$$

To Eq. (2.2), we multiply the time reversal matrix from both sides and use the anti-commutation (2.1)

$$\Theta \cdot c \cdot P^K \cdot \Theta = -c \cdot \Theta \cdot P^K \cdot \Theta = C^K \, \Theta \cdot P^K \cdot \Theta ,$$

or more distinctly

$$c \cdot (\Theta \cdot P^K \cdot \Theta) = -C^K (\Theta \cdot P^K \cdot \Theta) . \tag{2.4}$$

The transformed matrix $\Theta \cdot P^K \cdot \Theta$ again is a projector. Indeed one has

$$(\Theta \cdot P^K \cdot \Theta) \cdot (\Theta \cdot P^K \cdot \Theta) = \Theta \cdot P^K \cdot \Theta$$

after (1.4) and (2.3). It is the eigen-projector of c with the eigenvalue $-C^K$, as P^K is the one with the eigenvalue $+C^K$. So, the non-vanishing eigenvalues are pairwise with opposite signs. For convenience we number them symmetrically [2, 3]

$$\text{with} \quad \left. \begin{array}{c} K = \pm 1, .., \pm Z \\ C^{-K} = -C^K, \; C^K > 0 \text{ for } K > 0 . \end{array} \right\} \tag{2.5}$$

The connection between the eigen-projectors of a pair then is

$$P^{-K} = \Theta \cdot P^K \cdot \Theta . \tag{2.6}$$

In addition to these Z pairs there are $z - 2Z$ eigen-projectors $P^{0,\lambda}$ with eigenvalue $C = 0$:

$$c \cdot P^{0,\lambda} = P^{0,\lambda} \cdot c = 0 , \tag{2.7}$$

where $\lambda = 1, \ldots, z - 2Z$ is the index of degeneracy.

The sum of the complete set of z eigen-projectors gives unity:

$$\sum_{K=1}^{Z} P^K + \sum_{K=-1}^{-Z} P^K + \sum_{\lambda=1}^{z-2Z} P^{0,\lambda} = 1 .$$

We introduce the projectors to the "states with positive C's"

$$P_+ = \sum_{K=1}^{Z} P^K , \quad P_+ \cdot P_+ = P_+ \tag{2.8}$$

and analogously

$$P_- = \sum_{K=-1}^{-Z} P^K , \quad P_- \cdot P_- = P_- , \quad P_+ \cdot P_- = P_- \cdot P_+ = 0 , \tag{2.9}$$

as well as

$$P_0 = \sum_{\lambda=1}^{z-2Z} P^{0,\lambda} , \quad P_0 \cdot P_0 = P_0 , \quad P_0 \cdot P_\pm = P_\pm \cdot P_0 = 0 . \tag{2.10}$$

With these abbreviations the completeness relation simply is

$$P_+ + P_- + P_0 = 1 . \tag{2.11}$$

For later use we note, from (2.6), the connection

$$\Theta \cdot P_+ \cdot \Theta = P_- , \quad \Theta \cdot P_- \cdot \Theta = P_+ , \tag{2.12}$$

and from (2.7) the eigen-equation

$$c \cdot P_0 = 0 . \tag{2.13}$$

Now we return to the physical questions.

§ 3. Surface Entropy Production and Reciprocity Theorem in Terms of Surface "Forces and Fluxes"

The first aim of this section is to rewrite the "surface entropy production rate" (1.8) *. Instead

* Precautions against the inexactitude of this wording have already been taken in § 1, after Equation (1.9).

of the original "state vector" a, we desire a pair of "vectors" f and j to appear, each of which has only Z non-vanishing components with respect to the principal axes of the c-matrix. The remaining $z-Z$ components shall be zero. The ansatz for these surface "forces and fluxes" is

$$f = P_+ \cdot (1+\Theta) \quad \cdot a \tag{3.1}$$

$$j = P_+ \cdot (1+\Theta) \cdot c \cdot a \,. \tag{3.2}$$

The corresponding transposed "line vectors" then are

$$\tilde{f} = \tilde{a} \quad \cdot (1+\Theta) \cdot P_+ \tag{3.3}$$

$$\tilde{j} = \tilde{a} \cdot c \cdot (1+\Theta) \cdot P_+ \,. \tag{3.4}$$

The definitions (3.1 and 2) are nothing but the coordinate-free formulation of the previous ansatz, Eq. (7.3) of Ref. [3], which referred to the principal axes system of the c-matrix. Some further comments thereon are near the end of this section. The force f and the flux j indeed have non-vanishing components only in the Z-dimensional subspace characterized by the projection P_+. That P_+ is distinguished does not matter. One might choose P_- as well. The important thing is that the redundant part of a, belonging to the subspace characterized by the projector P_0, is cut off. It should be remarked that, via c and P_+, the local unit normal $\boldsymbol{n}(\boldsymbol{x})$ of the surface σ enters the definitions of f and j.

Now we shall prove the identity

$$\tilde{a} \cdot c \cdot a \equiv \tilde{f} \cdot j \,. \tag{3.5}$$

With it, the "surface entropy production" (1.8) can be rewritten in form of a scalar product of surface forces and fluxes

$$\dot{S}_{\text{surface}} = \int_\sigma \tfrac{1}{2} \tilde{f} \cdot j \, d\sigma \,. \tag{3.6}$$

Indeed, inserting (3.1) – (3.4) gives

$$\begin{aligned}\tilde{f} \cdot j &\equiv \tfrac{1}{2}(\tilde{f} \cdot j + \tilde{j} \cdot f) \\ &= \tilde{a} \cdot \tfrac{1}{2}\{(1+\Theta) \cdot P_+ \cdot (1+\Theta) \cdot c + c \cdot (1+\Theta) \cdot P_+ \\ &\qquad \cdot (1+\Theta)\} \cdot a \,.\end{aligned}$$

According to the anti-commutation (2.1), the commutation (2.2), the connection (2.12), the completeness (2.11) and the eigen-equation (2.13), one gets for the parenthesis

$$\begin{aligned}\tfrac{1}{2}\{\ldots\} &= \tfrac{1}{2}[(1+\Theta) \cdot P_+ \cdot (1+\Theta) \\ &\quad + (1-\Theta) \cdot P_+ \cdot (1-\Theta)] \cdot c \\ &= (P_+ + \Theta \cdot P_+ \cdot \Theta) \cdot c = (P_+ + P_-) \cdot c \\ &= (1-P_0) \cdot c = c \,.\end{aligned}$$

This ends the proof of (3.5).

Next, the reciprocity theorem (1.10) shall be rewritten in terms of f's and j's. For this purpose, let us consider the most simple bilinear form which is antisymmetrical in two stationary solutions and then insert (3.1 – 4):

$$\begin{aligned}\tfrac{1}{2}(\tilde{f}^{(2)} \cdot j^{(1)} - \tilde{f}^{(1)} \cdot j^{(2)}) &\equiv \tfrac{1}{2}(\tilde{f}^{(2)} \cdot j^{(1)} - \tilde{j}^{(2)} \cdot f^{(1)}) \\ = \tilde{a}^{(2)} \cdot \tfrac{1}{2}\{(1+\Theta) \cdot P_+ \cdot (1+\Theta) \cdot c &- c \cdot (1+\Theta) \cdot P_+ \\ &\cdot (1+\Theta)\} \cdot a^{(1)} \,.\end{aligned}$$

Again, according to (2.1, 2, 12, 11 and 13) one obtains for the parenthesis

$$\begin{aligned}\tfrac{1}{2}\{\ldots\} &= \tfrac{1}{2}[(1+\Theta) \cdot P_+ \cdot (1+\Theta) \\ &\quad - (1-\Theta) \cdot P_+ \cdot (1-\Theta)] \cdot c \\ &= (\Theta \cdot P_+ + P_+ \cdot \Theta) \cdot c = \Theta \cdot (P_+ + P_-) \cdot c \\ &= \Theta \cdot (1-P_0) \cdot c = \Theta \cdot c \,.\end{aligned}$$

So, the result is

$$\tilde{a}^{(2)} \cdot \Theta \cdot c \cdot a^{(1)} = \tfrac{1}{2}(\tilde{f}^{(2)} \cdot j^{(1)} - \tilde{j}^{(2)} \cdot f^{(1)}) \tag{3.7}$$

and the reciprocity theorem (1.10) can be rewritten in form of scalar products of the surface forces and fluxes of two stationary solutions:

$$\begin{aligned}&\int_\sigma (\tilde{f}^{(2)} \cdot j^{(1)} - \tilde{j}^{(2)} \cdot f^{(1)}) \, d\sigma \\ &\equiv \int_\sigma (\tilde{f}^{(2)} \cdot j^{(1)} - \tilde{f}^{(1)} \cdot j^{(2)}) \, d\sigma = 0 \,.\end{aligned} \tag{3.8}$$

It is remarkable that the time reversal matrix Θ is no more visible in this form; it is, so to say, sufficiently incorporated in the definitions (3.1 and 2).

In order to convince oneself that the ansatz (3.1 and 2) is equivalent with the previous ansatz (7.3) of Ref. [3] [or, immaterially different, Eq. (7.1) in Ref. [2]], it is best to look at the detailed representation of matrices in the coordinate system where the c-matrix is diagonal. The c-matrix itself is here represented by the following quadratic $z \times z$-array:

$$\begin{matrix} Z\left\{\begin{matrix}\\ \\ \end{matrix}\right. \\ Z\left\{\begin{matrix}\\ \\ \end{matrix}\right. \\ z-2Z\left\{\begin{matrix}\\ \\ \end{matrix}\right. \end{matrix} \begin{pmatrix} C^1 & & & & & & & \\ & \ddots & & & & & & \\ & & C^Z & & & & & \\ & & & C^{-1} & & & & \\ & & & & \ddots & & & \\ & & & & & C^{-Z} & & \\ & & & & & & 0 & \\ & & & & & & & \ddots \\ & & & & & & & & 0 \end{pmatrix} \quad \text{with } C^K = -C^{-K} > 0 \text{ for } K = 1 \ldots Z \,.$$

In all the empty places of this and the following four matrices, zeros have to be imagined. The projector

P_+, commuting with c, also is a diagonal $z \times z$-array:

$$\begin{array}{r} Z\{ \\ \\ Z\{ \\ \\ z-2Z\{ \end{array} \left|\begin{array}{ccc} \begin{smallmatrix}1 & & \\ & \ddots & \\ & & 1\end{smallmatrix} & & \\ & \begin{smallmatrix}0 & & \\ & \ddots & \\ & & 0\end{smallmatrix} & \\ & & \begin{smallmatrix}0 & & \\ & \ddots & \\ & & 0\end{smallmatrix} \end{array}\right| .$$

It makes evident that only the first Z components F^K, J^K of the vectors f, j from (3.1, 2) are non-zero, whatever the z components A^K are. The projectors P_- and P_0 are given by

$$\left|\begin{array}{ccc} \begin{smallmatrix}0 & & \\ & \ddots & \\ & & 0\end{smallmatrix} & & \\ & \begin{smallmatrix}1 & & \\ & \ddots & \\ & & 1\end{smallmatrix} & \\ & & \begin{smallmatrix}0 & & \\ & \ddots & \\ & & 0\end{smallmatrix} \end{array}\right| \quad \text{and} \quad \left|\begin{array}{ccc} \begin{smallmatrix}0 & & \\ & \ddots & \\ & & 0\end{smallmatrix} & & \\ & \begin{smallmatrix}0 & & \\ & \ddots & \\ & & 0\end{smallmatrix} & \\ & & \begin{smallmatrix}1 & & \\ & \ddots & \\ & & 1\end{smallmatrix} \end{array}\right| .$$

The time reversal matrix Θ however, anti-commutative with c, is non-diagonal:

$$\begin{array}{r} Z\{ \\ \\ Z\{ \\ \\ z-2Z\{ \end{array} \left|\begin{array}{ccc} & \begin{smallmatrix}1 & & \\ & \ddots & \\ & & 1\end{smallmatrix} & \\ \begin{smallmatrix}1 & & \\ & \ddots & \\ & & 1\end{smallmatrix} & & \\ & & \begin{smallmatrix}1 & & \\ & \ddots & \\ & & 1\end{smallmatrix} \end{array}\right| .$$

Writing down the prescriptions (3.1 and 2) in this special representation immediately gives

$$\left.\begin{aligned} F^K &= A^K + A^{-K} \\ J^K &= C^K\,(A^K - A^{-K}) \end{aligned}\right\} \text{ for } K = 1\,..\,Z \text{ and zero otherwise.}$$

This is indeed Eq. (7.3) of Ref. [3]. Of course, all the matrix equations of § 2 can be checked by means of the above arrays.

Finally a remark is made on the "time reversed" (better: motion reversed) state a_{T} associated with the original state a:

$$a_{\mathrm{T}} = \Theta \cdot a \,. \tag{3.9}$$

The surface forces and fluxes belonging to the time reversed state are, after (3.1 and 2) with a_{T} instead of a,

$$f_{\mathrm{T}} = P_+ \cdot (1 + \Theta) \cdot \Theta \cdot a \quad = f \,, \tag{3.10}$$

$$j_{\mathrm{T}} = P_+ \cdot (1 + \Theta) \cdot c \cdot \Theta \cdot a = -j \,. \tag{3.11}$$

This shows that f and j are defined in such a way that under time reversal all the components of f are invariant, whereas all those of j are reversed. This fact has to do with the later result in § 6 that the interfacial L-matrices have pure Onsager symmetries.

§ 4. Boundary Conditions for a Simple System

"Simple system" signifies that only one medium is present within the volume τ in which – with inclusion of the closed surface σ – a continuously differentiable solution $a(t, \boldsymbol{x})$ of the transport-relaxation equation (1.2) exists. For a stationary solution $a(\boldsymbol{x})$ the entropy balance (1.7) is

$$0 = \int_\sigma \tfrac{1}{2}\, \tilde{a} \cdot c \cdot a \, \mathrm{d}\sigma + \int_\tau \tilde{a} \cdot \omega \cdot a \, \mathrm{d}\tau \,,$$

or, rewritten in terms of the surface force and flux from (3.1 and 2),

$$-\int_\sigma \tfrac{1}{2}\, \tilde{f} \cdot j \, \mathrm{d}\sigma = \int_\tau \tilde{a} \cdot \omega \cdot a \, \mathrm{d}\tau > 0 \,. \tag{4.1}$$

Two different stationary solutions $a^{(1)}(\boldsymbol{x})$, $a^{(2)}(\boldsymbol{x})$ have the reciprocity property which we repeat:

$$\int_\sigma (\tilde{f}^{(2)} \cdot j^{(1)} - \tilde{f}^{(1)} \cdot j^{(2)}) \, \mathrm{d}\sigma = 0 \,. \tag{4.2}$$

The closed surface σ, situated within the domain of validity of the differential equation, may otherwise be arbitrary.

Equation (4.2) shows that the f and j of a solution are (linearly) dependent on each other. As an obvious conjecture one will surmise a relation of the form

$$j(\boldsymbol{x} \in \sigma) = -\int_\sigma G(\boldsymbol{x}, \boldsymbol{x}') \cdot f(\boldsymbol{x}') \, \mathrm{d}\sigma' \,. \tag{4.3}$$

The matrix Green-function G, meaningful only for $\boldsymbol{x}, \boldsymbol{x}' \in \sigma$, will be uniquely determined by the stationary differential Eq. (1.2) and by the geometry of the chosen surface σ. Of course, the analogous formula with the roles of f and j interchanged would serve as well. Inserting in (4.2) yields

$$\begin{aligned} &\iint_\sigma [\tilde{f}^{(2)}(\boldsymbol{x}) \cdot G(\boldsymbol{x}, \boldsymbol{x}') \cdot f^{(1)}(\boldsymbol{x}') - \tilde{f}^{(1)}(\boldsymbol{x}) \cdot G(\boldsymbol{x}, \boldsymbol{x}') \\ &\qquad\qquad \cdot f^{(2)}(\boldsymbol{x}')] \, \mathrm{d}\sigma \, \mathrm{d}\sigma' \\ \equiv &\iint_\sigma \tilde{f}^{(2)}(\boldsymbol{x}) \cdot [G(\boldsymbol{x}, \boldsymbol{x}') - \tilde{G}(\boldsymbol{x}', \boldsymbol{x})] \\ &\qquad\qquad \cdot f^{(1)}(\boldsymbol{x}') \, \mathrm{d}\sigma \, \mathrm{d}\sigma' = 0 \,. \end{aligned}$$

This has to be fulfilled by any $f^{(1)}$, $f^{(2)}$ on σ. Therefore, the matrix Green-function must have the symmetry

$$G(\boldsymbol{x},\boldsymbol{x}') = \tilde{G}(\boldsymbol{x}',\boldsymbol{x}) \,. \tag{4.4}$$

Another property of G can be concluded from Equation (4.1). Inserting (4.3) gives

$$\iint_\sigma \tfrac{1}{2}\tilde{f}(\boldsymbol{x})\cdot G(\boldsymbol{x},\boldsymbol{x}')\cdot f(\boldsymbol{x}')\,\mathrm{d}\sigma\,\mathrm{d}\sigma' = \int_\tau \tilde{a}\cdot\omega\cdot a\,\mathrm{d}\tau > 0\,. \tag{4.5}$$

The volume integral on the right side is positive because the ω-matrix is positive-definite (we don't bother about semi-definitenesses here). Hence, the matrix function G – the variables $\boldsymbol{x}$, $\boldsymbol{x}'$ should be considered on the same footing with the discrete indices – is positive – definite too.

Now the boundary problem can be discussed. The question is: what is to be prescribed at the given boundary σ, so that a unique existing solution of the stationary differential Eq. (1.2) is determined? After (4.3), f and j are already linked to each other. So, in any case only one of them can be prescribed freely. A first possibility is to assign given values $g(\boldsymbol{x})$ on σ to the "force":

$$f(\boldsymbol{x}\in\sigma) = g(\boldsymbol{x})\,. \tag{4.6 a}$$

Another possibility obviously is

$$j(\boldsymbol{x}\in\sigma) = h(\boldsymbol{x})\,, \tag{4.6 b}$$

where $h(\boldsymbol{x})$ is another arbitrarily given set of functions on σ. Of course, g and h must belong to the P_+-subspace everywhere on σ:

$$P_+\cdot g = g\,, \quad P_+\cdot h = h\,.$$

A general possibility, encompassing the other two, is

$$j(\boldsymbol{x}\in\sigma) = B(\boldsymbol{x})\cdot f(\boldsymbol{x}) + k(\boldsymbol{x})\,. \tag{4.6 c}$$

Here, B is a coefficient matrix characterizing the boundary condition [it has nothing at all to do with the G from (4.3)], $k(\boldsymbol{x})$ again can be arbitrarily given at σ.

The uniquity of a solution in cases (4.6 a, b) is readily established. If in case (4.6 a) two different solutions, $a^{(1)}$ and $a^{(2)}$, existed with the same inhomogeneity $g(\boldsymbol{x})$, then the f for the difference solution $a^* = a^{(1)} - a^{(2)}$, namely

$$f^* = f^{(1)} - f^{(2)}\,,$$

would vanish:

$$f^*(\boldsymbol{x}\in\sigma) = 0\,.$$

So, the left side of Eq. (4.1) would be zero for the difference solution. But the right side of this equation, valid for a^* as well, is zero only if $a^*(\boldsymbol{x})$ is zero everywhere in τ. Hence, the solution is unique. In case (4.6 b) the argument is the same. Finally, the mixed boundary condition (4.6 c) for a would-be difference solution a^* again is homogeneous

$$j^*(\boldsymbol{x}\in\sigma) = B(\boldsymbol{x})\cdot f^*(\boldsymbol{x})$$

and gives in (4.1)

$$-\int_\sigma \tfrac{1}{2}\tilde{f}^*(\boldsymbol{x})\cdot B(\boldsymbol{x})\cdot f^*(\boldsymbol{x})\,\mathrm{d}\sigma = \int_\tau \tilde{a}^*\cdot\omega\cdot a^*\,\mathrm{d}\tau\,.$$

Hence, if one requires for all $\boldsymbol{x}\in\sigma$

$$B(\boldsymbol{x}) \text{ to be positive-definite}\,, \tag{4.7}$$

then the left side of the preceding equation is always negative for a non-vanishing difference solution. But the right side is always positive. Equality is fulfilled only by $a^* = 0$ everywhere. So much about uniquity. Of course it is much harder to answer the question of existence.

From the present point of view – simple system –, (4.7) is the only restriction to be imposed on B. There are no symmetry obligations for it. The symmetry statements are exhaustively incorporated in Equation (4.4). This is not surprising. Symmetry properties of surface coefficients would be something new and can appear only on the basis of some appropriate postulate. But such a postulate can and will be formulated only for composite systems, in the next section. To try this for a simple system, is certainly inadequate.

From the physicist's point of view, the boundary value problem of this section is academic anyway: how come that one should exactly know the values $g(\boldsymbol{x})$ or $h(\boldsymbol{x})$ or $k(\boldsymbol{x})$ of some function at the surface σ? There will be matter and there will be transport-relaxation processes going on also beyond σ. Hence, in general one does not exactly know or cannot arbitrarily prescribe the $f(\boldsymbol{x})$ or the $j(\boldsymbol{x})$ at the surface; they are variables themselves to be determined in a broader context. This naturally leads to the consideration of an interface between two media I and II and to the question of the matching conditions on it. These conditions now describe a real physical process and therefore will be restricted by physical requirements, second law of thermodynamics and reciprocity.

§ 5. The Postulate of Universal Reciprocity for a Composite System

By "composite system" it is understood that at least two different substances, I and II, are present. Their volumes are called τ_{I} and τ_{II} and the whole system shall be bounded by the envelope σ_∞ (the subscript not necessarily indicates a boundary at infinity). The two immiscible substances are characterized by different sets of variables $a_{\text{I}}(t, \boldsymbol{x})$, $a_{\text{II}}(t, \boldsymbol{x})$ and are in contact with each other along the interface $\sigma_{\text{I II}}$. At it, certain discontinuities occur, which will be our main concern. The a's in general have different numbers of components, $z_{\text{I}} + z_{\text{II}}$, and obey transport-relaxation Eqs. (1.2) with different coefficient matrices $c_{\nu\,\text{I}}$, $c_{\nu\,\text{II}}$ and ω_{I}, ω_{II}. The interface $\sigma_{\text{I II}}$ shall extend as far as the closed envelope σ_∞ which is thus divided into two parts, $\sigma_{\infty\,\text{I}}$ and $\sigma_{\infty\,\text{II}}$, as sketched in Figure 1.

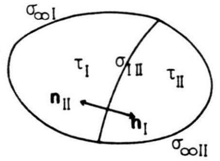

Fig. 1. The composite system with intersecting surfaces.

Within the volumes $\tau_{\text{I, II}}$, the solutions $a_{\text{I, II}}$ are determined as continuously differentiable functions by the respective transport-relaxation equation. However, this does not determine a unified solution on the whole. The discontinuous connection between the different a-values on both sides of the interface $\sigma_{\text{I, II}}$ has still to be disposed of. This is effectuated by the matching conditions or constitutive laws for the interface. They will contain phenomenological coefficient matrices, restricted by the requirements of the second law of thermodynamics and of the Onsager symmetries. The second law has been sufficiently done with earlier [2, 3]. The symmetry requirements will now be worked out explicitly, by adapting the reciprocity concept for a simple system [1] to the new situation of a composite system.

In the interior of the partial volumes τ_{I} and τ_{II}, the respective transport-relaxation equations, for two stationary states distinguished by the superscripts (1), (2), automatically lead to the identities

$$\frac{\partial}{\partial x_\nu}\,(a^{(2)} \cdot \Theta \cdot c_\nu \cdot a^{(1)})_{\text{I and II}} = 0\,. \qquad (5.1)$$

This is the reciprocity theorem in differential form, Eq. (21 a) of Ref. [1], a consequence of the Onsager symmetries inherent in the bulk coefficient matrices of (1.2). By Gauß's theorem, applied in the situation of Fig. 1, one concludes from Eqs. (5.1) for domain I

$$\int_{\sigma_{\infty\text{I}}} \tilde{a}_{\text{I}}^{(2)} \cdot \Theta_{\text{I}} \cdot c_{\text{I}} \cdot a_{\text{I}}^{(1)}\,\mathrm{d}\sigma + \int_{\sigma_{\text{I II}}} \tilde{a}_{\text{I}}^{(2)} \cdot \Theta_{\text{I}} \cdot c_{\text{I}} \cdot a_{\text{I}}^{(1)}\,\mathrm{d}\sigma = 0 \quad (5.2)$$

and for domain II

$$\int_{\sigma_{\infty\text{II}}} \tilde{a}_{\text{II}}^{(2)} \cdot \Theta_{\text{II}} \cdot c_{\text{II}} \cdot a_{\text{II}}^{(1)}\,\mathrm{d}\sigma + \int_{\sigma_{\text{I II}}} \tilde{a}_{\text{II}}^{(2)} \cdot \Theta_{\text{II}} \cdot c_{\text{II}} \cdot a_{\text{II}}^{(1)}\,\mathrm{d}\sigma = 0\,. \quad (5.3)$$

Equations (5.2 and 3) are the integral reciprocity theorems for the partial simple systems I and II contained in their respective enclosures $\sigma_{\infty\text{I}} + \sigma_{\text{I II}}$ and $\sigma_{\infty\,\text{II}} + \sigma_{\text{I II}}$. However, the analogous reciprocity integral on the overall-envelope σ_∞ of the composite system does not vanish automatically. We will force it to do so, by decree.

Indeed, the global symmetry statements to be derived from reciprocity for the whole of a system [examples for this "proliferation of Onsager relations" were given in [1]] should be the same whether one has to do with a simple or with a composite system. This is a reasonable physical conviction. To comply with it, it is obviously sufficient (and necessary) to *require* the analogous sort of reciprocity property, as it is eo ipso valid for a simple system, to be valid also at the overall-envelope of a composite system:

$$\int_{\sigma_{\infty\text{I}}} \tilde{a}_{\text{I}}^{(2)} \cdot \Theta_{\text{I}} \cdot c_{\text{I}} \cdot a_{\text{I}}^{(1)}\,\mathrm{d}\sigma + \int_{\sigma_{\infty\text{II}}} \tilde{a}_{\text{II}}^{(2)} \cdot \Theta_{\text{II}} \cdot c_{\text{II}} \cdot a_{\text{II}}^{(1)}\,\mathrm{d}\sigma = 0\,. \quad (5.4)$$

This is the crucial equation of the paper and shall be called the *postulate of universal reciprocity*. It is a natural appealing generalization of the reciprocity theorem for the simple system: the parts $\sigma_{\infty\text{I}}$ and $\sigma_{\infty\,\text{II}}$ of the overall-envelope contribute according to the respective values of a_{I} and a_{II}.

The postulate (5.4) essentially reduces the possibilities for the matching conditions at the interface $\sigma_{\text{I II}}$. By summing (5.2 and 3) which are mere consequences of the transport-relaxation equations, and by taking (5.4) into account, we conlude that our postulate is equivalent with the vanishing of the following interfacial integral:

$$\int_{\sigma_{\text{I II}}} (\tilde{a}_{\text{I}}^{(2)} \cdot \Theta_{\text{I}} \cdot c_{\text{I}} \cdot a_{\text{I}}^{(1)} + \tilde{a}_{\text{II}}^{(2)} \cdot \Theta_{\text{II}} \cdot c_{\text{II}} \cdot a_{\text{II}}^{(1)})\,\mathrm{d}\sigma = 0\,. \quad (5.5)$$

The postulate (5.4), with fixed solutions $a_{\text{I, II}}^{(1,2)}$, shall hold for any closed $\sigma_\infty = \sigma_{\infty\,\text{I}} + \sigma_{\infty\,\text{II}}$ chosen within the maximal $\sigma_{\infty,\max}$ (i. e. the physical envelope or real surface of the system). This means that the $\sigma_{\rm I\,II}$ in (5.5) may be an arbitrary part of the entire physical interface $\sigma_{\rm I\,II,\max}$. Therefore, even the integrand of (5.5) must be zero:

$$\tilde{a}_{\rm I}^{(2)}\cdot\Theta_{\rm I}\cdot c_{\rm I}\cdot a_{\rm I}^{(1)}+\tilde{a}_{\rm II}^{(2)}\cdot\Theta_{\rm II}\cdot c_{\rm II}\cdot a_{\rm II}^{(1)}=0 \quad \text{at } \sigma_{\rm I\,II}, \tag{5.6}$$

with a little bit of "proviso": instead of being zero, it might be equal to an interfacial divergence. By the integration (5.5) and the two-dimensional Gauß-theorem, such a divergence term namely leads to an integral along the closed intersection line $\sigma_{\rm I\,II}/\sigma_\infty$. This line integral however, if it occurs at all, is to be considered a (singular) contribution to the envelope-integral (5.4) and does not invalidate the equation (5.5). (In § 7 this ramification is exemplified.) – Hence, one may say that Eq. (5.6) is the *local interfacial reciprocity requirement* which must be fulfilled everywhere at the interface in order that the overall integral reciprocity postulate (5.4) is valid for any closed surface σ_∞ within the domain of existence of the solutions $a_{\rm I,II}$.

The matching conditions connecting the values $a_{\rm I}$ and $a_{\rm II}$ on both sides of the interface have now to be established in such a way that Eq. (5.6) is eo ipso fulfilled, with any choice of those elements of the $a_{\rm I,II}$ at the interface which can be freely prescribed at all. The details are worked out in the next section.

§ 6. The Matching Conditions at an Interface

In order to investigate the restrictions imposed on the matching conditions by the postulate of universal reciprocity, we make use again of the variables f and j, introduced in (3.1 – 4), for medium I and II respectively. In the previous Eq. (7.5) of Ref. [3] the matching conditions have been formulated in the principal axes systems of the c-matrices. In the present coordinate-free formulation the same constitutive law obviously is

$$\left.\begin{aligned} j_{\rm I}(\boldsymbol{x}) &= L_{\rm I\,I}(\boldsymbol{x})\cdot f_{\rm I}(\boldsymbol{x}) + L_{\rm I\,II}(\boldsymbol{x})\cdot f_{\rm II}(\boldsymbol{x}),\\ j_{\rm II}(\boldsymbol{x}) &= L_{\rm II\,I}(\boldsymbol{x})\cdot f_{\rm I}(\boldsymbol{x}) + L_{\rm II\,II}(\boldsymbol{x})\cdot f_{\rm II}(\boldsymbol{x}),\end{aligned}\right\} \tag{6.1}$$
$$\boldsymbol{x}\in\sigma_{\rm I\,II},$$

or in transposed form

$$\left.\begin{aligned} \tilde{j}_{\rm I} &= \tilde{f}_{\rm I}\cdot\tilde{L}_{\rm I\,I} + \tilde{f}_{\rm II}\cdot\tilde{L}_{\rm I\,II},\\ \tilde{j}_{\rm II} &= \tilde{f}_{\rm I}\cdot\tilde{L}_{\rm II\,I} + \tilde{f}_{\rm II}\cdot\tilde{L}_{\rm II\,II}.\end{aligned}\right\} \tag{6.1 a}$$

In the vein of condition (5.6) a local connection is assumed, as already in Reference [3]. The matrices $L_{\rm I\,I}$ and $L_{\rm II\,II}$ are quadratic with $z_{\rm I}$ resp. $z_{\rm II}$ lines and columns, $z_{\rm I}$ being the number of components of vectors $a_{\rm I}$, $f_{\rm I}$, $j_{\rm I}$. The matrices $L_{\rm I\,II}$, $\tilde{L}_{\rm II\,I}$ resp. $L_{\rm II\,I}$, $\tilde{L}_{\rm I\,II}$ are rectangular if $z_{\rm I}\neq z_{\rm II}$, with $z_{\rm I}$ resp. $z_{\rm II}$ lines and $z_{\rm II}$ resp. $z_{\rm I}$ columns. Of course, the L's have to have the projection properties

$$P_{+\rm I}(\boldsymbol{x})\cdot L_{\rm I\,I}(\boldsymbol{x})\cdot P_{+\rm I}(\boldsymbol{x}) = L_{\rm I\,I}(\boldsymbol{x}), \tag{6.2}$$
$$P_{+\rm I}(\boldsymbol{x})\cdot L_{\rm I\,II}(\boldsymbol{x})\cdot P_{+\rm II}(\boldsymbol{x}) = L_{\rm I\,II}(\boldsymbol{x}), \text{ etc.}$$

The spatial dependences of the L's and of the projectors $P_{+\rm I}$ etc. are indicated. They go back to the spatial dependences of the unit normals $\boldsymbol{n}_{\rm I}(\boldsymbol{x}) = -\boldsymbol{n}_{\rm II}(\boldsymbol{x})$ of $\sigma_{\rm I\,II}$.

According to (3.8) we express the interfacial reciprocity requirement (5.6) in terms of f's and j's:

$$\tilde{f}_{\rm I}^{(2)}\cdot j_{\rm I}^{(1)} - \tilde{f}_{\rm I}^{(1)}\cdot j_{\rm I}^{(2)} + \tilde{f}_{\rm II}^{(2)}\cdot j_{\rm II}^{(1)} - \tilde{f}_{\rm II}^{(1)}\cdot j_{\rm II}^{(2)} = 0 \quad \text{at } \sigma_{\rm I\,II}. \tag{6.3}$$

By reordering the second and fourth scalar product one has the equivalent

$$\tilde{f}_{\rm I}^{(2)}\cdot j_{\rm I}^{(1)} - \tilde{j}_{\rm I}^{(2)}\cdot f_{\rm I}^{(1)} + \tilde{f}_{\rm II}^{(2)}\cdot j_{\rm II}^{(1)} - \tilde{j}_{\rm II}^{(2)}\cdot f_{\rm II}^{(1)} = 0. \tag{6.3 a}$$

Now we insert the interfacial constitutive law (6.1 with 1 a) into (6.3 a) and obtain

$$\begin{aligned} &\tilde{f}_{\rm I}^{(2)}\cdot(L_{\rm I\,I}\cdot f_{\rm I}^{(1)} + L_{\rm I\,II}\cdot f_{\rm II}^{(1)}) - (\tilde{f}_{\rm I}^{(2)}\cdot\tilde{L}_{\rm I\,I} + \tilde{f}_{\rm II}^{(2)}\cdot\tilde{L}_{\rm I\,II})\cdot f_{\rm I}^{(1)}\\ &+ \tilde{f}_{\rm II}^{(2)}\cdot(L_{\rm II\,I}\cdot f_{\rm I}^{(1)} + L_{\rm II\,II}\cdot f_{\rm II}^{(1)})\\ &\qquad - (\tilde{f}_{\rm I}^{(2)}\cdot\tilde{L}_{\rm II\,I} + \tilde{f}_{\rm II}^{(2)}\cdot\tilde{L}_{\rm II\,II})\cdot f_{\rm II}^{(1)} = 0.\end{aligned}$$

Written more concisely, this is:

$$\begin{aligned} &\tilde{f}_{\rm I}^{(2)}\cdot(L_{\rm I\,I} - \tilde{L}_{\rm I\,I})\cdot f_{\rm I}^{(1)} + \tilde{f}_{\rm II}^{(2)}\cdot(L_{\rm II\,II} - \tilde{L}_{\rm II\,II})\cdot f_{\rm II}^{(1)} \\ &+ \tilde{f}_{\rm I}^{(2)}\cdot(L_{\rm I\,II} - \tilde{L}_{\rm II\,I})\cdot f_{\rm II}^{(1)} + \tilde{f}_{\rm II}^{(2)}\cdot(L_{\rm II\,I} - \tilde{L}_{\rm I\,II})\cdot f_{\rm I}^{(1)} = 0.\end{aligned} \tag{6.4}$$

The forces $f_{\rm I}$, $f_{\rm II}$ for solutions (1) and (2) can be freely chosen. Indeed, Eqs. (6.1) then give the associated fluxes $j_{\rm I}$, $j_{\rm II}$ and starting from the known values $f_{\rm I}$, $j_{\rm I}$ resp. $f_{\rm II}$, $j_{\rm II}$ on each side of the interface $\sigma_{\rm I\,II}$, each solution "spreads" into its volume $\tau_{\rm I}$ resp. $\tau_{\rm II}$ according to the respective transport-relaxation equation. So, with any choice of $f_{\rm I}{}^{(1)}$, $f_{\rm II}{}^{(1)}$ and $f_{\rm I}{}^{(2)}$, $f_{\rm II}{}^{(2)}$, $\boldsymbol{x}$-dependent along $\sigma_{\rm I\,II}$, the reciprocity (6.4) has to be fulfilled identically. This is possible only if the symmetries hold

$$L_{\rm I\,I}(\boldsymbol{x}) = \tilde{L}_{\rm I\,I}(\boldsymbol{x}), \quad L_{\rm II\,II}(\boldsymbol{x}) = \tilde{L}_{\rm II\,II}(\boldsymbol{x}), \tag{6.5}$$
$$L_{\rm I\,II}(\boldsymbol{x}) = \tilde{L}_{\rm II\,I}(\boldsymbol{x}).$$

This is our main result about the coefficient matrices of the matching conditions (6.1).

It is remarkable that the time reversal matrix Θ, decisive in the Onsager relations (1.6) for the bulk, does not show up in the symmetries (6.5) for the interface. These are pure Onsager relations, not Onsager-Casimir relations. (This was not realized in References [2, 3].) The reason is that the L's refer to the variables f and j with the uniform time reversal behaviour (3.10 and 11). The Θ-matrix is already incorporated in the connection (3.1 and 2) of these variables with the original variable a.

We summarize, in reversing the argument: The symmetries (6.5), when postulated for the phenomenological matrices L of the interfacial matching conditions (6.1), together with the transport-relaxation equations I, II, guarantee that the reciprocity (5.4), now as a theorem, universally holds for a closed surface σ_∞ within a composite system like that one sketched in Figure 1.

The conceptual situation is analogous as with a simple system where the reciprocity theorem followed alone from the symmetries of the phenomenological matrices occuring in the transport-relaxation equation.

What can one say about the other type of composite system which is sketched in Figure 2? The interface $\sigma_{\mathrm{I\,II}}$ is now closed and does not reach the envelope σ_∞ which is formed by, say, medium II exclusively. In contrast with this, the case of Fig. 1 did not distinguish between both media and therefore is more general. That is the reason why it had to be treated first. What is now said about the case of Fig. 2, are mere consequences.

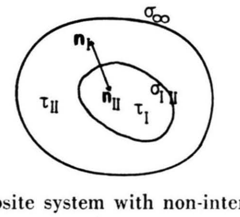

Fig. 2. The composite system with non-intersecting surfaces.

After the foregoing discussions, the symmetries (6.5) are by now well established and taken for granted. Then, Eqs. (6.4), (6.3) and (5.6) are fulfilled, and a fortiori the integral reciprocity (5.5), for any interface $\sigma_{\mathrm{I\,II}}$, especially for the closed one of Figure 2. But in this case the reciprocity theorem for the simple domain I tells that

$$\int_{\sigma_{\mathrm{I\,II}}} \tilde{a}_{\mathrm{I}}^{(2)} \cdot \Theta_{\mathrm{I}} \cdot c_{\mathrm{I}} \cdot a_{\mathrm{I}}^{(1)} \, \mathrm{d}\sigma = 0 \,. \qquad (6.6)$$

This is also Eq. (5.2), but without the first integral which does not appear because there is no $\sigma_{\infty\mathrm{I}}$ in the arrangement of Figure 2. The special Eq. (6.6), plotted into Eq. (5.5) which is true in all cases, gives another special statement:

$$\int_{\sigma_{\mathrm{I\,II}}} \tilde{a}_{\mathrm{II}}^{(2)} \cdot \Theta_{\mathrm{II}} \cdot c_{\mathrm{II}} \cdot a_{\mathrm{II}}^{(1)} \, \mathrm{d}\sigma = 0 \,. \qquad (6.7)$$

This we insert into the identity (5.3) which again is a mere consequence of the transport-relaxation equation. So, we obtain the desired reciprocity statement for the envelope σ_∞ which in the case of Fig. 2 is identical with $\sigma_{\infty\mathrm{II}}$:

$$\int_{\sigma_\infty} \tilde{a}_{\mathrm{II}}^{(2)} \cdot \Theta_{\mathrm{II}} \cdot c_{\mathrm{II}} \cdot a_{\mathrm{II}}^{(1)} \, \mathrm{d}\sigma = 0 \,. \qquad (6.8)$$

Comparing this with the reciprocity postulate (5.4) from which everything started, we see that (6.8) is consistent with (5.4) as the special case thereof in which medium I does not reach the overall-envelope σ_∞. Thus, the universality of Eq. (5.4) is corroborated: one of its terms may be absent because of the geometrical lay-out.

The form of postulate (5.4) in the case of the most general geometry is now clear. This case – particulate matter I dispersed in the background medium II – is sketched in Figure 3. The overall-envelope σ_∞ has several parts $\sigma_{\infty\mathrm{I},\dots}$ and $\sigma_{\infty\mathrm{II}}$ each of which contributes on the left side of Eq. (5.4) according to the respective local values of $a_{\mathrm{I}}^{(1)}$, $a_{\mathrm{I}}^{(2)}$ and $a_{\mathrm{II}}^{(1)}$, $a_{\mathrm{II}}^{(2)}$. This case is already covered by formula (5.4) as it stands. One has only to look at the integrations over $\sigma_{\infty\mathrm{I}}$ and $\sigma_{\infty\mathrm{II}}$ in the correct sense, namely as summations also over the respective disjoined parts of the envelope. The "proviso" mentioned after Eq. (5.6) must not be forgotten: if the envelope σ_∞ intersects with some of the interfaces $\sigma_{\mathrm{I\,II}}$ and if two-dimensional interfacial fluxes at the $\sigma_{\mathrm{I\,II}}$'s are assumed to exist (i. e. that their interfacial divergences occur in the matching conditions), then one has to embody the contributions

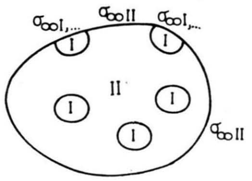

Fig. 3. Composite system with several non-intersecting and intersecting surfaces.

of the ensuing one-dimensional integrals along the closed intersection lines into the reciprocity integral (5.4).

In conclusion let us ask what the analogon is, for a composite system, of the matrix Green-function G appearing in the Eq. (4.3) for a simple system. There will be such an analogon: Eq. (4.3) originated from the reciprocity relation (1.10) at the (overall-) envelope σ of the simple system which is analogous to the relation (5.4) at the overall-envelope σ_∞ of the composite system. The said analogon is

$$\left.\begin{aligned} j_{\rm I}(\boldsymbol{x}\in\sigma_{\infty\rm I}) &= -\int_{\sigma_{\infty\rm I}} G_{\rm I\,I}(\boldsymbol{x},\boldsymbol{x}') \cdot f_{\rm I}(\boldsymbol{x}')\,{\rm d}\sigma' - \int_{\sigma_{\infty\rm II}} G_{\rm I\,II}(\boldsymbol{x},\boldsymbol{x}')\cdot f_{\rm II}(\boldsymbol{x}')\,{\rm d}\sigma' \\ j_{\rm II}(\boldsymbol{x}\in\sigma_{\infty\rm II}) &= -\int_{\sigma_{\infty\rm I}} G_{\rm II\,I}(\boldsymbol{x},\boldsymbol{x}') \cdot f_{\rm I}(\boldsymbol{x}')\,{\rm d}\sigma' - \int_{\sigma_{\infty\rm II}} G_{\rm II\,II}(\boldsymbol{x},\boldsymbol{x}')\cdot {\rm f}_{\rm II}(\boldsymbol{x}')\,{\rm d}\sigma' . \end{aligned}\right\} \quad (6.9)$$

The matrix Green-functions $G\ldots$ depend on the transport-relaxation equations I, II and on the geometry of the surfaces $\sigma_{\infty\rm I}$, $\sigma_{\infty\rm II}$, $\sigma_{\rm I\,II}$. The j's, calculated from (6.9) with arbitrary f's, together with their f's identically fulfill the reciprocity (5.4). So, the G's will show the symmetries

$$G_{\rm I\,I}(\boldsymbol{x},\boldsymbol{x}') = \tilde{G}_{\rm I\,I}(\boldsymbol{x}',\boldsymbol{x}) , \qquad (6.10)$$
$$G_{\rm I\,II}(\boldsymbol{x},\boldsymbol{x}') = \tilde{G}_{\rm II\,I}(\boldsymbol{x}',\boldsymbol{x}) , \text{ etc.}$$

Again, the G's (as a matrix) are positive-definite, in analogy with Equation (4.5). This guarantees a unique existing solution $a_{\rm I}$, $a_{\rm II}$ everywhere in $\tau_{\rm I}$, $\tau_{\rm II}$, if the forces $f_{\rm I}$ resp. $f_{\rm II}$ are, decently enough, prescribed at the parts $\sigma_{\infty\rm I}$ resp. $\sigma_{\infty\rm II}$ of the overall-envelope. This is the generalization of the boundary condition (4.6 a) for the simple system; with cases (4.6 b and c) the situation is analogous.

§ 7. A Simple Example: Heat Conduction

First we treat this example, simple as it is, in the straightforward way; afterwards we use it to illustrate the more sophisticated notions of § 2 and 3.

To describe heat conduction in three dimensions, a transport-relaxation equation for four functions $\{a\}$ is appropriate which, apart from normalization factors, are the temperature and the heat flux $\{T, q_\mu\}$, $\mu = 1, 2, 3$. The reciprocity theorem for a simple heat conducting system has been given in Eq. (27) of Ref. [1]:

$$\int_\sigma (T^{(2)}\, q^{(1)} - q^{(2)}\, T^{(1)})\,{\rm d}\sigma = 0 . \qquad (7.1)$$

This may be compared with the present Eq. (3.8). The temperature T plays the role of the "surface force" and

$$q = n_\mu\, q_\mu ,$$

the normal component of the heat flux, is the "surface flux".

For a sphere, the boundary value problem of heat conduction can readily be solved in terms of spherical harmonics. This implies that also the Green-function defined in (4.3), with T and q for f and j, is known:

$$G(\boldsymbol{x},\boldsymbol{x}') = \frac{\lambda}{R^3} \sum_l \sum_m l\, Y_{lm}(\vartheta,\varphi)\, Y^*_{lm}(\vartheta',\varphi') .$$

Here, λ means the heat conductivity, R the radius of the sphere and the Y's are normalized spherical harmonics.

One can immediately write down the interfacial reciprocity requirement (5.6) or (6.3 a) for the interface between two media I and II with different thermal properties

$$T_{\rm I}^{(2)} q_{\rm I}^{(1)} - q_{\rm I}^{(2)} T_{\rm I}^{(1)} + T_{\rm II}^{(2)} q_{\rm II}^{(1)} - q_{\rm II}^{(2)} T_{\rm II}^{(1)} = 0 . \quad (7.2)$$

The matching conditions are inferred from Eq. (6.1)

$$\left.\begin{aligned} q_{\rm I} &= L_{\rm I\,I}\, T_{\rm I} + L_{\rm I\,II}\, T_{\rm II} , \\ q_{\rm II} &= L_{\rm II\,I}\, T_{\rm I} + L_{\rm II\,II}\, T_{\rm II} . \end{aligned}\right\} \quad (7.3)$$

They have scalar L's and must fulfill (7.2) identically when $T_{\rm I}(\boldsymbol{x})$ and $T_{\rm II}(\boldsymbol{x})$, (1) and (2), are arbitrarily chosen at the interface. On insertion in (7.2), the $L_{\rm I\,I}$- and $L_{\rm II\,II}$-terms drop out and one is left with

$$(L_{\rm I\,II} - L_{\rm II\,I})\,(T_{\rm I}^{(2)} T_{\rm II}^{(1)} - T_{\rm II}^{(2)} T_{\rm I}^{(1)}) = 0 .$$

This leads to the symmetry

$$L_{\rm I\,II} = L_{\rm II\,I} . \qquad (7.4)$$

The matching conditions have also to obey the conservation laws, here of energy. These were hitherto not mentioned in this paper, but have been discussed earlier [4]. The simplest way to cope with energy conservation in our case is to put

$$q \equiv q_{\rm I} + q_{\rm II} = 0 , \qquad (7.5)$$

in words: nowhere heat enters the interface. As $T_{\rm I}$ and $T_{\rm II}$ are "free", conservation (7.5) requires

$$L_{\rm I\,I} + L_{\rm II\,I} = 0 , \quad L_{\rm I\,II} + L_{\rm II\,II} = 0 . \qquad (7.6)$$

Combined with (7.4) this gives

$$L_{\rm I\,I} = -L_{\rm II\,I} = -L_{\rm I\,II} = L_{\rm II\,II} \equiv L ,$$

so that one has

$$q_{\rm I}=L(T_{\rm I}-T_{\rm II})\,, \quad q_{\rm II}=L(-T_{\rm I}+T_{\rm II})\,.$$

With the abbreviations

$$T_{\rm I\,II}=T_{\rm I}-T_{\rm II}\,, \quad q_{\rm I\,II}=\tfrac{1}{2}(q_{\rm I}-q_{\rm II}) \qquad (7.7)$$

we get the boundary condition of temperature jump [cf. Eq. (8.10) of Ref. [4]] in the form

$$q_{\rm I\,II}=L\,T_{\rm I\,II}\,. \qquad (7.8)$$

The phenomenological coefficient L has to be positive in order to yield a positive interfacial entropy production.

The theory becomes richer if a two-dimensional interfacial heat flux $\mathbf{Q}$, a new variable, is admitted. Instead of (7.5) one has then

$$q\equiv q_{\rm I}+q_{\rm II}=\boldsymbol{\nabla}^\sigma\cdot\mathbf{Q}\,, \qquad (7.9)$$

in words: the heat entering the unit area of the interface from the adjacent media I, II acts as the source (two-dimensional divergence) of the interfacial heat flux $\mathbf{Q}$ (more details are in Reference [4]). For further exploitation we rewrite the expression in (7.2) by using the abbreviations q, $q_{\rm I\,II}$, $T_{\rm I\,II}$ from (7.5 and 7) and in addition

$$T=\tfrac{1}{2}(T_{\rm I}+T_{\rm II})\,. \qquad (7.10)$$

That gives instead of (7.2)

$$T^{(2)}\,q^{(1)}-q^{(2)}\,T^{(1)}+T^{(2)}_{\rm I\,II}\,q^{(1)}_{\rm I\,II}-q^{(2)}_{\rm I\,II}\,T^{(1)}_{\rm I\,II}=0\,.$$

Now we plot (7.9) into this and obtain as the integral reciprocity requirement (5.5) for the interface, specialized to our heat conduction case

$$\int_{\sigma_{\rm I\,II}}(T^{(2)}\,\boldsymbol{\nabla}^\sigma\cdot\mathbf{Q}^{(1)}-\boldsymbol{\nabla}^\sigma\cdot\mathbf{Q}^{(2)}\,T^{(1)}+T^{(2)}_{\rm I\,II}\,q^{(1)}_{\rm I\,II}-q^{(2)}_{\rm I\,II}\,T^{(1)}_{\rm I\,II})\,{\rm d}\sigma=0\,. \qquad (7.11)$$

The $T^{(2)}$, $T^{(1)}$ in the first two terms are not genuine "thermodynamical forces" because they don't vanish in thermal equilibrium. As the usual remedy for this, we shift the differentiation from the $\mathbf{Q}$'s to the T's:

$$\int_{\sigma_{\rm I\,II}}(-\boldsymbol{\nabla}^\sigma T^{(2)}\cdot\mathbf{Q}^{(1)}+\mathbf{Q}^{(2)}\cdot\boldsymbol{\nabla}^\sigma T^{(1)}+T^{(2)}_{\rm I\,II}\,q^{(1)}_{\rm I\,II}-q^{(2)}_{\rm I\,II}\,T^{(1)}_{\rm I\,II})\,{\rm d}\sigma+\int_{\sigma_{\rm I\,II}}\boldsymbol{\nabla}^\sigma\cdot(T^{(2)}\,\mathbf{Q}^{(1)}-\mathbf{Q}^{(2)}\,T^{(1)})\,{\rm d}\sigma=0\,.$$

In the first integral appears the temperature gradient $\boldsymbol{\nabla}^\sigma T$ along the interface. The second integrand is an interfacial divergence. By the two-dimensional Gauß-theorem it can be transformed into a curve integral along the one-dimensional closed intersection of $\sigma_{\rm I\,II}$ with σ_∞ (we assume the geometry of Figure 1). This line integral has of course to be incorporated (as a singular part) into the σ_∞-reciprocity integral (5.4)*. So, the second of the above integrals can and should be removed from the interfacial reciprocity requirement. Now, as $\sigma_{\rm I\,II}$ is an otherwise arbitrary part of the entire $\sigma_{\rm I\,II,\,max}$ [cf. the remarks after Eq. (5.5)], even the integrand of the first integral has to vanish:

$$-\boldsymbol{\nabla}^\sigma T^{(2)}\cdot\mathbf{Q}^{(1)}+\mathbf{Q}^{(2)}\cdot\boldsymbol{\nabla}^\sigma T^{(1)}+T^{(2)}_{\rm I\,II}\,q^{(1)}_{\rm I\,II}-q^{(2)}_{\rm I\,II}\,T^{(1)}_{\rm I\,II}=0 \quad \text{at } \sigma_{\rm I\,II}\,. \qquad (7.12)$$

This is the local interfacial reciprocity requirement. The last two terms immediately cancel if the boundary condition (7.8) is adopted. The first two terms of (7.12) cancel if the interfacial heat flux obeys the two-dimensional Fourier law

$$\mathbf{Q}=-\Lambda\,\boldsymbol{\nabla}^\sigma T\,, \qquad (7.13)$$

where Λ is the positive interfacial heat conductivity and T the average temperature defined in (7.10). All these results coincide with those obtained by standard non-equilibrium thermodynamics [4].

For a handy example of the developments in § 2 and 3, we now apply them to the case of heat conduction. The a is a "4-vector" $\{a_0,\boldsymbol{a}\}\triangleq\{T,\boldsymbol{q}\}$. The matrices c_ν from Eqs. (1.1 or 2) are isotropic (no preferential direction)

$$c_{\nu 00}=0\,, \quad c_{\nu\mu 0}=c_{\nu 0\mu}=\delta_{\nu\mu}\,, \quad c_{\nu\mu\mu'}=0\,,$$

where $\nu,\mu,\mu'=1,2,3$ are Cartesian indices and convenient units have been used (so that the c's are dimensionless). From that, one gets as the surface coefficient 4×4-matrix c, defined in Eq. (1.9),

$$c=\begin{pmatrix}0 & \tilde{\boldsymbol{n}}\\ \boldsymbol{n} & \boldsymbol{0}\end{pmatrix} \text{ with } \tilde{\boldsymbol{n}}\cdot\boldsymbol{n}=1\,.\,^{**}$$

The last three lines and columns have been contracted in a self-explanatory way. The form of c is not surprising, $\boldsymbol{n}$ being the only three-dimensional vector which is available. The time reversal matrix Θ from Eq. (1.4) is

$$\Theta=\begin{pmatrix}1 & \tilde{\boldsymbol{0}}\\ \boldsymbol{0} & -\mathbf{1}\end{pmatrix},$$

where again the last three lines and columns, forming a minus unity matrix, have been contracted. The form of Θ is clear: T is even, $\boldsymbol{q}$ is odd under time reversal. With the above matrices c and Θ, Eq. (2.1)

* This exemplifies the "proviso" after Equation (5.6).

** $\boldsymbol{n}$ is to be read as a column, $\tilde{\boldsymbol{n}}$ as a line.

is readily checked. Further, the matrix c, which fulfills the equation $c^2(c^2-1)=0$, has the eigenvalues ± 1 and twofold the eigenvalue 0. The eigenvectors associated with the eigenvalues ± 1 are $1/\sqrt{2}\{1,\pm \boldsymbol{n}\}$. The projectors $P_{\pm}$ from (2.8 and 9) in this case coincide with $P^{\pm 1}$ which can immediately be formed as the dyadics composed of the said eigenvectors. One gets

$$P_+ = \tfrac{1}{2}\begin{pmatrix}1 & \tilde{\boldsymbol{n}}\\ \boldsymbol{n} & \boldsymbol{n}\tilde{\boldsymbol{n}}\end{pmatrix},\quad P_- = \tfrac{1}{2}\begin{pmatrix}1 & -\tilde{\boldsymbol{n}}\\ -\boldsymbol{n} & \boldsymbol{n}\tilde{\boldsymbol{n}}\end{pmatrix}.$$

Equation (2.6) is readily checked. In (3.1 and 2) the matrices occur

$$P_+\cdot(1+\Theta) = \begin{pmatrix}1 & \tilde{\boldsymbol{0}}\\ \boldsymbol{n} & 0\end{pmatrix},\quad P_+\cdot(1+\Theta)\cdot c = \begin{pmatrix}0 & \tilde{\boldsymbol{n}}\\ \boldsymbol{0} & \boldsymbol{n}\tilde{\boldsymbol{n}}\end{pmatrix}.$$

With them, one obtains the surface force and flux "4-vectors"

$$f = \begin{pmatrix}1 & \tilde{\boldsymbol{0}}\\ \boldsymbol{n} & 0\end{pmatrix}\cdot\begin{pmatrix}a_0\\ \boldsymbol{a}\end{pmatrix} = \begin{pmatrix}1\\ \boldsymbol{n}\end{pmatrix} a_0 \;\triangleq\; \begin{pmatrix}1\\ \boldsymbol{n}\end{pmatrix} T,$$

$$j = \begin{pmatrix}0 & \tilde{\boldsymbol{n}}\\ \boldsymbol{0} & \boldsymbol{n}\tilde{\boldsymbol{n}}\end{pmatrix}\cdot\begin{pmatrix}a_0\\ \boldsymbol{a}\end{pmatrix} = \begin{pmatrix}1\\ \boldsymbol{n}\end{pmatrix}\tilde{\boldsymbol{n}}\cdot\boldsymbol{a} \triangleq \begin{pmatrix}1\\ \boldsymbol{n}\end{pmatrix} q.$$

Hence, the force and flux are essentially T and q, "plotted on the coordinate 4-vector $\{1,\boldsymbol{n}\}$". This had to be anticipated from (7.1). – In conclusion we note the L-matrices occurring in the interfacial constitutive law (6.1):

$$L_{\text{I I}} = L^{(s)}_{\text{I I}} P_{+\text{I}},\quad L_{\text{II II}} = L^{(s)}_{\text{II II}} P_{+\text{II}}$$

and

$$L_{\text{I II}} = L^{(s)}_{\text{I II}}\tfrac{1}{2}\begin{pmatrix}1 & \tilde{\boldsymbol{n}}_{\text{II}}\\ \boldsymbol{n}_{\text{I}} & \boldsymbol{n}_{\text{I}}\tilde{\boldsymbol{n}}_{\text{II}}\end{pmatrix},$$

$$L_{\text{II I}} = L^{(s)}_{\text{I II}}\tfrac{1}{2}\begin{pmatrix}1 & \tilde{\boldsymbol{n}}_{\text{I}}\\ \boldsymbol{n}_{\text{II}} & \boldsymbol{n}_{\text{II}}\tilde{\boldsymbol{n}}_{\text{I}}\end{pmatrix} = \tilde{L}_{\text{I II}}.$$

The $L^{(s)}$ are scalar factors. They are the important coefficients; the rest is geometry and determined by the projection properties (6.2) which are readily checked. After plotting the above f, j and L's into Eq. (6.1), the coordinate 4-vector $\{1,\boldsymbol{n}_{\text{I}}\}$ appears as a factor in each term of the first line, $\{1,\boldsymbol{n}_{\text{II}}\}$ in the second line. These factors can be dropped and one recovers the scalar matching conditions (7.3). The scalar L's of (7.3) are identical with the scalars $L^{(s)}$ which were introduced just now. – So much about heat conduction.

Of course, the methods of this paper can also be applied to the mildly generalized hydrodynamics and its boundary conditions which have been developed in part A of Reference [3]. Especially interesting are, in such context, applications to particulate matter and porous media. The extent of that subject forbids to treat it here.

Finally, on this occasion a shortcoming at the end of Ref. [1] shall be remedied. There, the reciprocity theorem of the linearized Boltzmann equation had unintendedly been written down for a Lorentz gas. For the pure gas, instead of Eq. (40) of Ref. [1], the reciprocity theorem takes the form

$$\frac{\partial}{\partial x_\nu}\,[\mathrm{Tr}\int d^3p\, f_0(p^2, j^2, ..)\cdot \Phi^{(2)}(\boldsymbol{x}, -\boldsymbol{p}, -\overleftarrow{j}, \ldots)\, c_\nu\, \Phi^{(1)}(\boldsymbol{x}, \boldsymbol{p}, \overrightarrow{j}, \ldots)] = 0. \tag{7.14}$$

The stationary one-particle distribution

$$f(\boldsymbol{x}, \boldsymbol{p}, \overrightarrow{j}, ..) = f_0(p^2, j^2, ..)\;\; [1 + \Phi(\boldsymbol{x}, \boldsymbol{p}, \overrightarrow{j}, \ldots)]$$

is assumed to deviate only slightly from absolute equilibrium f_0, so that "Φ is small". By the way, it seems impossible to formulate a reciprocity theorem for the *quadratic* Boltzmann equation.

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