

ON THE PHENOMENOLOGICAL BASIS OF IRREVERSIBLE THERMODYNAMICS I

(ONSAGER'S THEORY)

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Introduction

Irreversible thermodynamics developed by ONSAGER is based on a double basis [1], [2]. It is for the most part of phenomenological character, but in essential features it is also founded on statistical laws. The statistical considerations rest on the macroscopic fluctuation theory of thermodynamics. In this theory a systematical statement is valid, which can be formulated in a particular way — with the aid of the correlation functions in time, characterizing the fluctuations of macroscopic parameters — by the hypothesis of microscopic reversibility. However, this hypothesis holds strictly only for the equation of motion of individual particles, and the essential of it can be formulated in the following way: the equations of motion — either in classical or in quantum physics — are invariant against the transformation of sign of time $t \rightarrow -t$. Assuming also that in an “aged” system the average decay of fluctuations follows the ordinary macroscopic laws — which is a new hypothesis, and as has been shown by BECKER [3] not even realized in every case — then the validity of ONSAGER's resp. CASIMIR's reciprocal relations is ensured by the form of microscopic reversibility expressed by the adequate correlation functions. Thus, at present, the ONSAGER's theory of irreversible thermodynamics, because of the above-mentioned hypothesis, should be considered as a particular and not quite natural complexity of phenomenological and statistical elements. Hence, the requirement to develop this theory on the basis of purely phenomenological and rigorously statistical principles is justified. Since already many attempts, which seem to be successful, have been made in the latter direction [4], [5], [6], therefore, we consider the phenomenological building up of the theory as our task. Our investigations were carried out by using such a general mathematical apparatus, which affords a possibility for the extension of ONSAGER's linear theory to a non-linear one.

§ 1. Mathematical fundamentals

A. Non-equilibrium state parameters

Our first task is such an interpretation of the non-equilibrium state parameters, which follows as a consequent result of the laws of classical thermodynamics (thermostatistics). Therefore, let us consider the energy law of thermostatistics in the following general form:

$$(1.1) \quad dE = \sum_i \Gamma_i dA_i^\circ$$

where dE is the elementary change of the internal energy, which is generally obtained as the sum of products of the equilibrium intensity parameters Γ_i and of the reversible dA_i° change of the conjugated extensive properties A_i° . In formula (1.1) the quantities Γ_i can be considered as thermostatical forces, whereas the A_i° parameters as coordinates. We refer here to the fact that B. LEAF [7], I. FÉNYES [8] and more explicitly the author [9] have generalized the traditional Carnot cycle (heat cycle) for an analogous cycle related to any intensity parameter Γ_i , as well as for reversible and irreversible cases, respectively. In an irreversible case, if we denote by ΔA_i the non-equilibrium change of the extensive property in question during the elementary step of the irreversible cycle, compared to the adequate reversible one, the following inequality is obtained:

$$(1.2) \quad \Delta A_i > dA_i^\circ \quad (i = 1, 2, \dots, f)$$

This means, that in the case of irreversible change of state between two neighbouring states of a system, the changes of the extensive properties will always be greater for an irreversible change of state as if between the same states the transformations should have taken place reversibly. This statement is known for the change of entropy since CLAUSIUS, and is the consequence of the definite positive character of the "non-compensated heat" produced by irreversibility. Completing the inequality (1.2) with the aid of the virtual change $\delta A_i'$ of a fictive A_i' parameter, *i. e.*

$$(1.3) \quad \Delta A_i = dA_i^\circ + \delta A_i' \quad (i = 1, 2, \dots, f)$$

then by means of the equality quantitative statements may also be made. The parameters A_i' will be called effective parameters. For their actual values are represented by those points of equilibrium state space, into which the system carrying out whichever kind of process effectively arrived at. Since, in a reversible case $dA_i^\circ \equiv \Delta A_i$, whereas in an irreversible one $\Delta A_i \equiv \delta A_i'$, while allowing for the possibility of both types of transformations (1.3) is valid. The detailed expounding of the interpretation of the effective parameters can

be found in an axiomatic work of the author [9]. If to a first approximation the equilibrium operations d and non-equilibrium ones Δ occurring in (1.3) are considered as identical, *i. e.* $\Delta \rightarrow d$ — by reason of which the virtual operation disappears in a limiting case — instead of (1.3) we can put

$$(1.4) \quad \Delta a_i \equiv \Delta(A_i - A_i^0) = [(\delta = \Delta - d) \rightarrow 0] A_i'$$

by which the non-equilibrium

$$(1.5) \quad a_i = A_i - A_i^0 \quad (i = 1, 2, \dots, f)$$

parameters were interpreted as effective state parameters of first order.

It should be noted, that the ONSAGER "a" parameters analogous to (1.5), are in substance identical with the non-equilibrium extensive quantities a_i , introduced by us. However, ONSAGER's "a" coordinates — according to the theory of fluctuations — ought to be considered as stochastical variables.

B. The effective state space

It is known that each of the states of a system following one another continuously, carrying out a reversible process is to a good approximation an equilibrium state. Such processes can always be illustrated by an adequate number of the equilibrium parameters on the statical state diagram. This is, however, not the case for a system carrying out an irreversible transformation. *I. e.* for a system getting out from the equilibrium state — for instance, owing to external perturbation — and carrying out an irreversible process, the final position of the first elementary step will be a non-equilibrium state, which cannot be illustrated on a statical diagram. At the following elementary steps the situation becomes worse, because in these cases the transition takes place between non-equilibrium states. Introducing now the effective a_i parameters of (1.5), we can proceed so that an adequate number of $\{a_1, a_2, \dots, a_f\}$ parameters can be conjugated as effective ones to the instantaneous states of systems carrying out irreversible processes and not being remote from the equilibrium state. By the independent a_i parameter number f an infinitesimal state space is spanned, which has an f dimension. This space may be called: first order effective state space. The physical essential of this method consists in the fact that the elementary steps of irreversible processes can be described statically in the space of effective parameters, *i. e.* with the mathematical apparatus of thermostatics. Those equilibrium parameters are conjugated as effective state parameters to a non-equilibrium state after the first elementary step of an irreversible process, to which the system would arrive in a reversible manner, but as if the a_i change of the equilibrium parameters A_i^0 would also

have taken place in a reversible way. Thus, proceeding by elementary steps an effective state space — in which irreversible processes can be observed as in a statical projection, — can be given for each instantaneous state of a system.

Let us now develop the fundamental mathematical relations of the first order effective state space in the case of discontinuous systems. Let us consider for that purpose a non-equilibrium system of a degree of freedom f , which consists of two thermodynamically identic and homogeneous subsystems. Let us give the entropy of the subsystems in an instantaneous state as the function of parameters a_i^l number f determining the first order effective state spaces of the subsystems. The index l refers to the subsystems I and II. The scale of the parameters a_i^l is chosen according to (1.5), so that in the equilibrium state $a_1^l = a_2^l = \dots = a_f^l = 0$ is valid. Hence

$$(1.6) \quad S^l(a^l) = S^l(a_1^l, a_2^l, \dots, a_f^l) \quad \text{where } l = I, II.$$

Let us now assume that the entropies of the subsystems are such functions of the adequate a_i^l parameters, which can at any time be continuously differentiated. Thus, by developing these functions in a Taylor series and stopping at the fourth order terms we obtain:

$$(1.7) \quad \begin{aligned} S^l(a^l) = & S_0^l + \sum_{i=1}^f \left(\frac{\partial S^l}{\partial a_i^l} \right)_0 a_i^l + \frac{1}{2} \sum_{i,k=1}^f \left(\frac{\partial^2 S^l}{\partial a_i^l \partial a_k^l} \right)_0 a_i^l a_k^l + \\ & + \frac{1}{6} \sum_{i,k,j}^f \left(\frac{\partial^3 S^l}{\partial a_i^l \partial a_k^l \partial a_j^l} \right)_0 a_i^l a_k^l a_j^l + \frac{1}{24} \sum_{i,k,j,s}^f \left(\frac{\partial^4 S^l}{\partial a_i^l \partial a_k^l \partial a_j^l \partial a_s^l} \right)_0 a_i^l a_k^l a_j^l a_s^l \end{aligned}$$

where S_0^l is the maximum entropy of the stable equilibrium state. Assuming that the total system is isolated with respect to its surroundings, then we may write:

$$(1.8) \quad a_i^I = -a_i^{II} = a_i \quad \text{and} \quad (1.9) \quad \Delta S^I = S^I(a^I) - S_0^I$$

because of which the entropy variation of the total system, which is due to the irreversible processes is

$$(1.10) \quad \Delta S = \frac{\Delta S^I + \Delta S^{II}}{2} = + \frac{1}{2} \sum_{i,k=1}^f \left(\frac{\partial^2 S}{\partial a_i \partial a_k} \right)_0 a_i a_k + \frac{1}{24} \sum_{i,k,j,s=1}^f \left(\frac{\partial^4 S}{\partial a_i \partial a_k \partial a_j \partial a_s} \right)_0 a_i a_k a_j a_s$$

In this expression the linear and third order terms of (1.7) do not occur.

The cancelling of the linear terms means that at the interaction of the two subsystems this term describes the reversible state variation, according to

which one of the subsystems gives just as much entropy to the other as it has received from it. According to (1.7) the entropy change of the system can always be written down as the sum of terms of odd and even order. It is shown by (1.10) that only terms of even order can be responsible for irreversibility. This is in accordance with the second law of thermostatics, *i. e.* ΔS must always be positive definite. Hence, the analytical form (1.10) is not in contradiction with the second law and, thus, is suitable for the quantitative characterization in a stational projection of the irreversible processes. For the sake of the following let us define the following quantities by using (1.10),

$$X_i^* \equiv \frac{\partial \Delta S}{\partial a_i} = \sum_{k=1}^f \left(\frac{\partial^2 S}{\partial a_i \partial a_k} \right)_0 a_k + \frac{1}{6} \sum_{k,j,s=1}^f \left(\frac{\partial^4 S}{\partial a_i \partial a_k \partial a_j \partial a_s} \right)_0 a_k a_j a_s \equiv X_i + Z_i \quad (i = 1, 2, \dots, f) \quad (1.11)$$

which quantities in the first order effective state space are likewise state variables.

C. The velocity space (Space of fluxes)

It has already been mentioned that though the effective state space determined by $\{a_1, a_2, \dots, a_f\}$ parameters characterizes the irreversible processes in a stational picture, their course in time cannot be followed in this space. The fact that different effective state parameters must be conjugated to the successive instantaneous states of a system carrying out an irreversible process shows that a_i quantities depend parametrically on time: *i. e.*, $a_i = a_i(t)$, ($i = 1, 2, \dots, f$). Therefore, the expressions following from (1.10) and (1.11) make sense:

$$\frac{d\Delta S}{dt} = \left[\sum_{i,k=1}^f \left(\frac{\partial^2 S}{\partial a_i \partial a_k} \right)_0 \dot{a}_i a_k + \frac{1}{6} \sum_{i,k,j,s=1}^f \left(\frac{\partial^4 S}{\partial a_i \partial a_k \partial a_j \partial a_s} \right)_0 \dot{a}_i a_k a_j a_s \right] \quad (1.12)$$

$$\frac{dX_i^*}{dt} = \left[\sum_{k=1}^f \left(\frac{\partial^2 S}{\partial a_i \partial a_k} \right)_0 \dot{a}_k + \frac{1}{2} \sum_{k,j,s=1}^f \left(\frac{\partial^4 S}{\partial a_i \partial a_k \partial a_j \partial a_s} \right)_0 \dot{a}_k a_j a_s \right] \quad (i = 1, 2, \dots, f) \quad (1.13)$$

and also the expressions arising from the combination of (1.11) and (1.12)

$$\frac{d\Delta S}{dt} = \sum_{i=1}^f (X_i \dot{a}_i + Z_i \dot{a}_i) = \sum_{i=1}^f X_i^* \dot{a}_i \equiv \sum_{i=1}^f X_i^* I_i \quad (1.14)$$

In the last expression the time derivative of the a_i parameter is denoted identically by $I_i \equiv \dot{a}_i$. This quantity will be called further on, general thermodynamic velocity or flux. The (1.12) gives the entropy change per unit time, *i. e.* the so-called entropy production.

Quantities of a velocity character defined by (1.12) and (1.13) are directly derived from the first order effective state space. It is, however, required both by experimental and theoretical investigations that such relations should also be taken up, by which a connection is indirectly established between the state space and the velocity space $\{\dot{a}_1, \dot{a}_2, \dots, \dot{a}_f\}$ of the parameters a_i . Thus, we can write such general expressions by which the course in time of a_i parameters is determined. This follows from the fact, that the velocity space of the a_i parameters is already determined by the ensemble $\{a_1, a_2, \dots, a_f\}$ (or by the ensemble $\{X_1^*, X_2^*, \dots, X_f^*\}$) expressing the instantaneous state of the spanning of the system. This statement is true, at least for such cases, in which the parameters a_i themselves make sense as non-equilibrium state parameters. In order to attain the differential equations giving the description in time of change of the parameters a_i , unambiguously a velocity space ought to be conjugated to the first order effective state space. The conjugation may be correct only, if from the velocity space we require the satisfaction of those fundamental properties, which are required by the properties of the statical state space for the velocity space determined by it. Briefly, it is necessary that the properties of the state space be compatible with the behaviour of the velocity space conjugated to it. Due to the unambiguous conjugation the following hypothesis is assumed. Provided that, the first order effective state space stretched out by the parameters $\{a_i\}$ determines the velocity space $\{\dot{a}_i\}$. The analytical form of our hypothesis is

$$\text{H.} \quad \dot{a}_i = f_i \{a_1(t), a_2(t), \dots, a_f(t)\} \quad (i = 1, 2, \dots, f)$$

where the functions f_i are at present unknown. Therefore, the following expansion in a series is carried out:

$$(1.15) \quad \dot{a}_i = - \sum_{l=1}^f \left(\frac{\partial f_i}{\partial a_l} \right) a_l - \frac{1}{2} \sum_{l,s=1}^f \left(\frac{\partial^2 f_i}{\partial a_l \partial a_s} \right)_0 a_l a_s \quad (i = 1, 2, \dots, f)$$

which signifies a second order approximation of our hypothesis H. After the problems of mathematical character described above, we shall show in the following paragraphs, keeping in mind more explicitly the physical requirements, that they are suitable for the development of ONSAGER's linear theory, moreover to give two non-linear representations. One of the non-linear theories is dealt with in the following paper referred to as II.

§ 2. Onsager's linear theory

We may now arrive to **ONsager's** linear theory — characterized by the existence of linear laws between the fluxes I_i and the forces X_i — if concerning the first order effective state space the following axiom is considered to be valid.

Axiom I: The S entropy of a system not too remote from its stable equilibrium state shall be the at least twice continuously differentiable positive definite function of the independent parameters $\{a_i\}$.

I. e. for the present analytical form of $S = S(a)$ it now follows:

$$\text{I.} \quad \Delta S = -\frac{1}{2} \sum_{i,k=1}^f g_{ik} a_i a_k > 0$$

which is the reduced form of (1.10). Our axiom also comprises implicitly that in a stable equilibrium state

$$(2.1) \quad S_0 = S(0, 0, \dots, 0) = \text{constant}, \quad \text{i. e. } \Delta S = S - S_0 = 0$$

further that the validity of the following symmetrical relations also holds good,

$$(2.2) \quad g_{ik} \equiv -\left(\frac{\partial^2 S}{\partial a_i \partial a_k}\right)_0 = -\left(\frac{\partial^2 S}{\partial a_k \partial a_i}\right) \equiv g_{ki} \quad (i, k = 1, 2, \dots, f)$$

which are called **MAXWELL's** reciprocal relations. In **ONsager's** theory the thermodynamic forces X_i used to be defined as follows:

$$\text{D.} \quad X_i \equiv \frac{\partial \Delta S}{\partial a_i} = -\sum_{k=1}^f g_{ik} a_k \quad (i = 1, 2, \dots, f)$$

with the aid of which I. can be written

$$(2.3) \quad \Delta S = \frac{1}{2} \sum_{i=1}^f X_i a_i$$

It can immediately be seen that **MAXWELL's** reciprocal relations of (2.2) can also be written with the parameters of the first order effective state space. *I. e.* due to I. and D., the (2.2) — exactly the reciprocal of (2.2) — will be

$$(2.4) \quad \frac{\partial a_i}{\partial X_k} = \frac{\partial a_k}{\partial X_i} \quad (i, k = 1, 2, \dots, f)$$

These equalities are the forms of thermostatical MAXWELL relations expressed by the parameters a_i and X_i of the first order effective state space. Herewith, the denomination referring to (2.2) has also been justified. It is evident, that the reciprocal relations (2.4) ensure the potential character of the ΔS function in the effective state space, which thus become fundamental.

Let us write the matrix form of the expressions mentioned hitherto. If in D. \mathbf{X} and α are column matrices, then their transposed forms $\tilde{\mathbf{X}}$ and $\tilde{\alpha}$ are row matrices. The positive definite matrix \mathbf{G} , consisting of the elements g_{ik} can be called — due to the definition D., the matrix of the “force constants” g_{ik} . Hence the matrix forms are

$$\text{I'}. \quad \Delta S = -\frac{1}{2} \tilde{\alpha} \mathbf{G} \alpha = -\frac{1}{2} \tilde{\alpha} \tilde{\mathbf{G}} \alpha$$

$$(2.2') \quad \mathbf{G} = \tilde{\mathbf{G}}$$

$$\text{D'}. \quad \mathbf{X} = -\mathbf{G} \alpha$$

$$(2.3') \quad \Delta S = \frac{1}{2} \tilde{\mathbf{X}} \alpha \frac{1}{2} = \tilde{\alpha} \mathbf{X}$$

by which the further calculations are rendered particularly perspicuous.

We shall now turn to the investigation of the velocity space belonging to the effective state space determined by axiom I. Let us differentiate the expressions I. and (2.3) over the time, thus, we obtain for the entropy production

$$(2.5) \quad \dot{\Delta S} = -\sum_{i,k=1}^f g_{ik} \dot{a}_i a_k = \sum_{i=1}^f X_i \dot{a}_i \quad (2.5') \quad \dot{\Delta S} = \tilde{\mathbf{X}} \dot{\alpha} = \tilde{\alpha} \dot{\mathbf{X}}$$

where the matrix notation has also been used. Let us consider the form (1.15) of the hypothesis H. to a first approximation in order to produce ONSAGER's linear phenomenological laws,

$$(2.6) \quad \dot{a}_i = -\sum_{l=1}^f c_{il} a_l \quad (i = 1, 2, \dots, f) \quad (2.6') \quad \dot{\alpha} = -\mathbf{C} \alpha$$

where per definicionem we have introduced due to the stable equilibrium condition positive constants

$$(2.7) \quad c_{il} \equiv \left(\frac{\partial f_i}{\partial a_l} \right)_0 \quad (i, l = 1, 2, \dots, f) \quad (2.7') \quad \mathbf{C} = [c_{il}]$$

which will be called the “coupling coefficients of the velocity space”. The “coupling matrix” \mathbf{C} can be defined by the elements c_{il} , which due to (2.7)

is, in general, not symmetrical. The expressions I. and (2.6) together with the definition D. are sufficient for the development of ONSAGER's theory. By D. inverted into a_l we obtain

$$(2.8) \quad a_l = - \sum_{k=1}^f g_{lk}^{-1} X_k \quad (l = 1, 2, \dots, f) \quad (2.8') \quad \alpha = - \mathbf{G}^{-1} \mathbf{X}$$

or taking them into consideration in (2.6)

$$(2.9) \quad I_i \equiv \dot{a}_i = \sum_{k=1}^f c_{ik} g_{lk}^{-1} X_k = \sum_{k=1}^f L_{ik} X_k \quad (i = 1, 2, \dots, f)$$

$$(2.9') \quad \mathbf{I} \equiv \dot{\mathbf{a}} = \mathbf{C} \mathbf{G}^{-1} \mathbf{X} = \mathbf{L} \mathbf{X}$$

These are the linear phenomenological laws between the fluxes I_i and forces X_i expressed by the conductivity coefficients

$$(2.10) \quad L_{ik} \equiv \sum_{l=1}^f c_{il} g_{lk}^{-1} \quad (i, k = 1, 2, \dots, f) \quad (2.10') \quad \mathbf{L} \equiv \mathbf{C} \mathbf{G}^{-1}$$

Hitherto, the essential physical assumption about the irreversible processes was that they are linear; *i. e.* that the fluxes depend linearly on the forces that "cause" them. Here we derived these laws on the basis of our hypothesis H. It is evident, that for the moment nothing can be said of the symmetry of the conductivity matrix \mathbf{L} , formed from the conductivities L_{ik} . On the other hand, it is to be noted that the linear laws of (2.9) proved very productive for the description of the irreversible processes. For most transport processes the linear approximation is satisfactory too. Deviations from it might be expected in non-ohmic electrical networks, in semiconductors of strong space charge, in non-linear deformations, in case of transport processes taking place at very low temperatures and particularly for chemical reactions. The linear laws of (2.9), which are also suitable for the description of the so-called "cross effects" used to be called in irreversible thermodynamics "ONSAGER's equations of motion". We shall, however, suggest this denomination for those differential equations which are derived in the following paragraph.

§ 3. "Equations of motion"

The "equations of motion" of thermodynamics can be attained so, that the effective state space is directly connected with the linear law of velocity space. First of all we shall write an alternative form of the linear laws (2.9).

Let us introduce the reciprocal matrix \mathbf{R} of the conductivity matrix \mathbf{L} , *i. e.*

$$(3.1) \quad \sum_m L_{im} R_{mk} = \sum_m R_{im} L_{mk} = \delta_{ik} \quad (3.1') \quad \mathbf{LR} = \mathbf{RL} = \delta$$

In these expressions the matrix \mathbf{R} determined by the elements R_{ik} is the so-called resistance matrix, δ_{ik} is the KRONECKER symbol and δ is the unit matrix. The \mathbf{L} and \mathbf{R} are not singular matrices, hence they are mutually reciprocal. On the other hand with the aid of (2.10) and (3.1) it can be written:

$$(3.2) \quad R_{ik} = \sum_{l=1}^f g_{il} c_{lk}^{-1} \quad (i, k = 1, 2, \dots, f) \quad (3.2') \quad \mathbf{R} = \mathbf{GC}^{-1}$$

By these expressions the matrix \mathbf{R} is determined with the "coupling matrix of the velocity space" \mathbf{C} and the matrix of the "force constants" \mathbf{G} , which is interpreted in the first order effective state space. Therefore, (3.2) or (3.2') can also be considered as the direct definitions of the resistance matrix \mathbf{R} . With (2.9) and (3.1) the alternative form of the linear laws is obtained:

$$(3.3) \quad X_i = \sum_{k=1}^f R_{ik} \dot{a}_k \quad (i = 1, 2, \dots, f) \quad (3.3') \quad \mathbf{X} = \mathbf{RI}$$

which can be regarded as "equations of motion" in the same sense as (2.9). As we have, however, already pointed out we think it more appropriate to keep this denomination for the following ordinary differential set of equations, which is obtained by combining D. and (3.3),

$$(3.4) \quad \sum_{k=1}^f (R_{ik} \dot{a}_k + g_{ik} a_k) = 0 \quad (i = 1, 2, \dots, f) \quad (3.4') \quad \mathbf{RI} + \mathbf{Ga} = 0$$

By these equations the linear laws are directly connected with the parameters of the effective state space. As the complement of these "equations of motion" we obtain with (2.9) and (2.6)

$$(3.5) \quad \sum_{k=1}^f (L_{ik} X_k + c_{ik} a_k) = 0 \quad (i = 1, 2, \dots, f) \quad (3.5') \quad \mathbf{LX} + \mathbf{Ca} = 0$$

which relations may be called the "strain relations of thermodynamics". These are important in the representation theory of thermodynamics, for the examination of stability problems and particularly for the generalization of LE CHATELIER's principle. (See [9]). The following differential equations are also equivalent with the "equations of motion" in (3.4.) Thus, for instance, the

relation (2.6) — now expressing our hypothesis H. — is equivalent to (3.4), if \mathbf{C} is expressed in it by the matrices \mathbf{G} and \mathbf{L} — which are empirically determined or statistically computed — according to (2.10). By combining (2.6) with (2.10) we obtain

$$(3.6) \quad \dot{a}_i = - \sum_{l,k=1}^f L_{il} g_{lk} a_k \quad (i = 1, 2, \dots, f) \quad (3.6') \quad \mathbf{J} = - \mathbf{L} \mathbf{G} \mathbf{a}$$

and now from these equations just as from (3.4) the quantities $a(t)$ can be determined if the initial values $a_0 = a(t=0)$ are known and the matrix $\mathbf{C} = \mathbf{L} \mathbf{G}$ is not singular. Finally, let us consider the hypothesis H. according to which the a_i coordinates depend on the time. If this is true, as it must be, then the same holds for the forces X_i in D., *i. e.* $X_i = X_i(t)$. Therefore, also D. can be differentiated over the time beside a constant \mathbf{G} . Thus we obtain

$$(3.7) \quad \dot{X}_i = - \sum_{k=1}^f g_{ik} \dot{a}_k \quad (i = 1, 2, \dots, f) \quad (3.7') \quad \dot{\mathbf{X}} = - \mathbf{G} \dot{\mathbf{a}}$$

which combined with (2.9)

$$(3.8) \quad \dot{X}_i = - \sum_{k,l,s=1}^f g_{ik} c_{kl} g_{ls}^{-1} X_s \quad (3.8') \quad \dot{\mathbf{X}} = - \mathbf{G} \mathbf{C} \mathbf{G}^{-1} \mathbf{X}$$

or introducing the matrix

$$(3.9) \quad \mathbf{B} \equiv \mathbf{G} \mathbf{C} \mathbf{G}^{-1} = \mathbf{G} \mathbf{L}$$

equation (3.8) — or rather the matrix form of it — will be

$$(3.10) \quad \dot{\mathbf{X}} = - \mathbf{B} \mathbf{X}.$$

This matrix equation is also an “equation of motion” for the variation in time of the thermodynamic forces X_i . It should be noted, that (3.10) for \mathbf{X} and $\dot{\mathbf{X}}$ is in an analogous relation with (2.6') which refers to a and \dot{a} . Thus matrix \mathbf{B} , similarly to matrix \mathbf{C} , is also conceivable as the “coupling matrix” of the parameters $\{\dot{X}_1, \dot{X}_2, \dots, \dot{X}_f\}$ directly belonging to the velocity space of the forces.

Anyone of the equations (3.4), (3.6) and (3.10), as the matrices \mathbf{G} , \mathbf{R} , and \mathbf{L} , which can be statistically or empirically determined occur in them, will be called the “equations of motion” of irreversible thermodynamics. These differential equations are very suitable for the description in time of equalization processes approaching equilibrium. The differential equations in question

can immediately be integrated formally, *i. e.* the values belonging to the moment $t = 0$ denoted by α_0 and \mathbf{X}_0 the matrix form of the corresponding integrals is:

$$(3.11) \quad \alpha = e^{-Ct} \cdot \alpha_0 \quad (3.12) \quad \mathbf{X} = e^{-Bt} \cdot \mathbf{X}_0 .$$

Since, in general the matrices \mathbf{G} and \mathbf{L} are not commutable, their dyadic product should be carried out for the determination of the general solutions.

It should be noted here that the forms of different thermodynamic potential functions in the first order effective state space can likewise be given. The transformations between potentials require that between the forces X_i and coordinates a_i such linear transformations should be given, which with the aid of the matrices \mathbf{G} , \mathbf{C} , \mathbf{L} , \mathbf{R} , \mathbf{B} , lead to the representation theory of thermodynamics [9]. This theory relying particularly upon the matrices \mathbf{C} and \mathbf{B} renders the transcription of the transformations possible carried out in the α space to the flux space, and gives general relations between the state space and flux space characteristics of thermodynamic potentials. Hereby, those physical fundamentals of the linear transformations used in irreversible thermodynamics become evident, which have already been used hitherto by some authors in the case of several applications [2], [10]. It is shown by these facts that the matrices \mathbf{C} and \mathbf{B} though less usual to now in literature are very productive, both from theoretical and practical point of view. The foregoing statements are confirmed by the consequent introduction of ONSAGER's linear laws with the aid of matrix \mathbf{C} , as well as by the new form (3.6) and (3.10) of the "equations of motion".

§ 4. Reciprocal relations in the flux space

A. Indirect method

In § 1. sec. C. it has already been pointed out, that a velocity space can be conjugated to the first order effective state space only in such a way that this conjugation should be unambiguous, moreover it ought to be compatible with the fundamental properties of the effective state space. The unambiguity is ensured by the hypothesis H. [resp. (2.6)]. There remains, however, the fulfilment of the requirement of compatibility. We should like to emphasize, that the requirement for the satisfaction of compatibility does not mean a new hypothesis, since the quadratic form of I. characterizing the effective state space expresses the non-equilibrium state of the spanning of the system, which owing to H. already determines the flux space. Thus, only such a flux space of a real physical system can be permitted, which is satisfying in every respect (of course in the approximation in question) the state space determined

by I. and characterized by (2.2). In order to demonstrate more clearly the foregoing, let us form the entropy source in every possible way according to I. without making use of the symmetry of \mathbf{G} . Thus we can write

$$(4.1) \quad \Delta S = -\frac{1}{4} \tilde{\alpha} (\mathbf{G} + \tilde{\mathbf{G}}) \alpha$$

Differentiating this over the time we get the entropy production:

$$(4.2) \quad \sigma = -\frac{1}{2} \dot{\tilde{\alpha}} \mathbf{G} \alpha - \frac{1}{2} \tilde{\alpha} \tilde{\mathbf{G}} \dot{\alpha} = -\frac{\tilde{\alpha} \mathbf{G} \dot{\alpha} + \tilde{\tilde{\alpha}} \tilde{\mathbf{G}} \dot{\alpha}}{2}$$

Let us eliminate from this expression the fluxes $\tilde{\alpha}$ and $\dot{\alpha}$ with the aid of the linear law (2.9') (and with the transposed form of it) we obtain

$$(4.3) \quad \sigma = \frac{\tilde{\mathbf{X}} \tilde{\mathbf{L}} \mathbf{G} \alpha + \tilde{\alpha} \tilde{\mathbf{G}} \mathbf{L} \mathbf{X}}{2}$$

This form can be written with the aid of D.' and with the transposed form of it, respectively:

$$(4.4) \quad \sigma = \frac{\tilde{\mathbf{X}} \tilde{\mathbf{L}} \mathbf{X} + \tilde{\mathbf{X}} \mathbf{L} \mathbf{X}}{2}$$

which is reduced to

$$(4.5) \quad \sigma = \tilde{\mathbf{X}} \mathbf{L} \mathbf{X}$$

which is confirmed in ONSAGER's theory if

$$(4.6) \quad \mathbf{L} = \tilde{\mathbf{L}}$$

i. e. if the ONSAGER reciprocal relations are valid. It is to be seen that being symmetric or non-symmetric of \mathbf{G} has no influence on symmetry properties of \mathbf{L} . In other words, hitherto the MAXWELLIAN and ONSAGER's reciprocal relations were properties independent of each other, *i. e.* for example the latter does not follow from the precedings forthwith.

Keeping in mind the logical severity and the gnosiological requirements, the true character of (2.2) and (4.6) for a phenomenological theory can be accepted on the basis of the following test methods:

1. On the basis of experimental criteria MAXWELL's and ONSAGER's reciprocal relations can be considered as axioms in a phenomenological theory.

2. The origin of the symmetry properties of both types are led back to different, but in any case, *logically equivalent axioms*.

3. Accepting some type of the reciprocal relations for true on the basis of an axiom of a correct model theory in a given approximation (for instance the Maxwellian on the basis of axiom I.), let us derive the other type from it, while using some reasonable requirement.

4. Both types of reciprocal relations are confirmed statistically, while relying on the rigorous principles of statistical mechanics.

There is nothing to add to argument 1 with the exception that MAXWELL's relations used not to be considered directly as axioms, but rather as the consequence of axiom I. For the acceptance as axioms of ONSAGER's reciprocal relations in a phenomenological theory DE GROOT has presented a suggestion [2]. The following of the 2nd test method for the MAXWELL relations is generally accepted; it is related to axiom I, which is true according to the model theory of thermostatics. For ONSAGER's relations such a confirmation is hitherto unknown, the giving of it will be dealt with in the following section B. The 3rd method is connected with the problem of compatibility so often already emphasized by us and which will be given in detail in the following. Finally, referring to the test methods of statistical character it should be noted, that for ONSAGER's relations only such a method is known up to now, whereas the general statistical proof of MAXWELL's relations is not given, moreover perhaps the necessity of such a proof is not even raised explicitly yet. It can be seen, that on the basis of points 1—4 concerning the acceptance of the validity of both types of reciprocal relation a strong asymmetry exists between the applicability of the phenomenological and statistical principles. This asymmetry of argumentation is misleading for a rigorous phenomenological theory as well as for a consequent statistical one. One of the aims of the present paper is to eliminate this asymmetry from the phenomenological side. Thus we demonstrate that both reciprocal relations have similar phenomenological fundamentals, assuming that the corresponding fundamentals are measured with an *equivalent logical gauge*.

Let us now demonstrate that inasmuch as axiom I is considered to be sufficient for the confirmation of MAXWELL's relations and if we demand the satisfaction of the requirement of compatibility with the properties of the effective state space for the flux space, then ONSAGER's relations follow from (2.4). The requirement of such a compatibility is a reasonable one, because owing to hypothesis H. the flux space is determined by the first order effective state space. Thus, our proof corresponds to that mentioned in point 3. Differentiating now (2.4) over the time, we get

$$(4.7) \quad \frac{d}{dt} \cdot \left(\frac{\partial a_i}{\partial X_k} \right) = \frac{d}{dt} \cdot \left(\frac{\partial a_k}{\partial X_i} \right) \quad (i, k = 1, 2, \dots, f)$$

Limiting ourselves to the case of constant forces X_i , then interchanging the order of differentiation we can write:

$$(4.8) \quad \frac{\partial}{\partial X_k} \left(\frac{da_i}{dt} \right) = \frac{\partial}{\partial X_i} \left(\frac{da_k}{dt} \right) \quad (i, k = 1, 2, \dots, f)$$

or

$$(4.9) \quad \frac{\partial I_i}{\partial X_k} = \frac{\partial I_k}{\partial X_i} \quad (i, k = 1, 2, \dots, f)$$

which relations should be considered as constraint equations for the fluxes. Due to the linear laws (2.9) it is required by (4.9), that in the flux space the ONSAGER reciprocal relations

$$(4.10) \quad L_{ik} = L_{ki} \quad (i, k = 1, 2, \dots, f)$$

be valid. It should be emphasized that the equations (4.9) follow from (4.7) only in case of forces X_i constant in time. However, in linear approximation the coefficients L_{ik} are constant, thus (4.10) is generally verified. It is evident, that (4.7) and (4.8) (resp. (4.9)) in case of constant X_i forces are equivalent and with those a restriction is expressed for the possible variation in time of the a parameters. The equivalence of (4.9) with (4.10), however, is true only in case of linear laws, i.e. (4.9) cannot be considered as the alternative form of ONSAGER relations. This is particularly evident from my following paper (see II), where a possible non-linear formalism will be discussed. Hereby the program outlined by points 1 and 3 is closed. The discussion of methods 2 and 4 is given in the following section.

B. Direct method

A confirmation independent of the previous one, but formally of a structure analogous with it, can also be given for the phenomenological proof of the ONSAGER relations. The following method, which has been called the direct method, is in accordance with the program of 2, and has been developed in a work under publication of I. FÉNYÉS and the author [11]. The fundamental idea of this method can be realized with the following axiom:

Axiom II: Let the entropy production σ of a system — not too remote from its stable equilibrium state — be, the at least twice continuously differentiable positive definite function of the independent parameters X_i . I. e.

$$(4.11) \quad \sigma = \sigma(X_1, X_2, \dots, X_f) > 0$$

furthermore in the stable equilibrium state let us write:

$$(4.12) \quad \sigma_0 = \sigma_0(0, 0, \dots, 0) = 0$$

It can easily be seen, that this axiom does not require any more from σ than axiom I from S . Moreover, it is also true that since axiom II is a summary of general validity of those experiences according to which the thermodynamic processes are the consequences of the equalization tendency of the forces X_i , thus it is more fundamental than the axiom I relying purely upon the second law of thermostatics. The specification of the theory on such general axiomatic fundamentals is not dealt with here (see [9]). We only demonstrate that in second approximation MAXWELL's and ONSAGER's relations follow from axioms I and II, respectively, as from logically equivalent ones.

Let us write the expressions of S and σ in second approximation, we obtain:

$$(4.13) \quad S = S_{(0)} - \sum_{i=1}^f \left(\frac{\partial S}{\partial \alpha_i} \right)_0 \alpha_i - \frac{1}{2} \sum_{i,k=1}^f \left(\frac{\partial^2 S}{\partial \alpha_i \partial \alpha_k} \right)_0 \alpha_i \alpha_k$$

$$(4.14) \quad \sigma = \sigma_{(0)} + \sum_{i=1}^f \left(\frac{\partial \sigma}{\partial x_i} \right)_0 X_i + \frac{1}{2} \sum_{i,k=1}^f \left(\frac{\partial^2 \sigma}{\partial X_i \partial X_k} \right)_0 X_i X_k$$

On choosing the signs it should be taken into consideration here, that the equilibrium entropy $S_{(0)}$ is a maximum, whereas the entropy production $\sigma_{(0)}$ has a minimum value at equilibrium or more exactly it vanishes according to (4.12). The sum of the linear terms gives zero in a closed system. Introduced provisionally by the denotations

$$(4.15) \quad \mathbf{Q}_1 \equiv [q_{ik}^1] = \left[\left(\frac{\partial^2 S}{\partial \alpha_i \partial \alpha_k} \right)_0 \right] \quad (4.16) \quad \mathbf{Q}_2 \equiv [q_{ik}^2] = \left[\frac{1}{2} \left(\frac{\partial^2 \sigma}{\partial X_i \partial X_k} \right)_0 \right]$$

the matrices \mathbf{Q}_1 and \mathbf{Q}_2 are necessarily symmetric due to axioms I and II, respectively. *I. e.* $\mathbf{Q}_1 = \tilde{\mathbf{Q}}_1$ and $\mathbf{Q}_2 = \tilde{\mathbf{Q}}_2$. Thus we may write

$$(4.17) \quad \Delta S = -\frac{1}{2} \tilde{\alpha} \mathbf{Q}_1 \alpha = -\frac{1}{2} \tilde{\alpha} \tilde{\mathbf{Q}}_1 \alpha$$

and

$$(4.18) \quad \sigma = \tilde{\mathbf{X}} \mathbf{Q}_2 \mathbf{X} = \tilde{\mathbf{X}} \tilde{\mathbf{Q}}_2 \mathbf{X}$$

Since (4.17) must be identical with I, thus $\mathbf{Q}_1 = \mathbf{G}$ owing to it, is $\mathbf{G} = \tilde{\mathbf{G}}$. Differentiating now I (or 4.17) over the time and eliminating the fluxes from the expressions obtained with the linear laws (2.9'), we get

$$(4.19) \quad \dot{A}S = \tilde{X}LX = \tilde{X}\tilde{L}X$$

which expression can be identical with σ of (4.18) only (otherwise the relations between the thermodynamic parameters would not be unambiguous), if $Q_2 \equiv L$ and $\tilde{Q}_2 \equiv \tilde{L}$ respectively. Thus it has been demonstrated, that MAXWELL's and ONSAGER's reciprocal relations are also the consequence of the requirement common in physics, according to which S and σ are at least twice continuously differentiable over the parameters a_i and X_i . Because the axiom I and II are gnosiologically equivalent, thus it would be completely unjustified to accept one type of the reciprocal relations as correct, on the basis of the particulars outlined above, and those of the other type as not. At this point we shall discuss our results or rather raise some problems in connection with the investigations of statistical character.

As regards the confirmation of the MAXWELL's resp. ONSAGER's relation based on the principles of statistical mechanics it should be told, that in the first case it is not given in general. Thus — on the basis of axiom I the MAXWELL relations are considered as proved in a purely phenomenological way. As against this the proof of ONSAGER's relations is built hitherto upon a statistical basis with the aid of the hypothesis of microscopic reversibility. Though, it is also true, that in most part of the cases the examinations carried out do not correspond to the Gibbsian conception of statistical mechanics, but rather to a more or less phenomenological theory of stochastic processes. The theory in question is such for which the name "theory of macroscopic fluctuations" is the most appropriate. A strictly statistical proof of ONSAGER's relations must be built up on the fundamentals of statistical mechanics of the non-equilibrium states, which was up to now represented the best by the works of R. COX [4], N. G. van KAMPEN [5] and H. B. CALLEN [6]. It is namely evident, that in the same way as the statistical interpretation of S became the pillar of ordinary statistical thermodynamics or mechanics respectively, similarly a general and direct interpretation can be given to σ , which will become a touchstone of the statistical theory of non-equilibrium states. This, however, should be the one, which would prove the equalization tendency of intensity parameters purely on the basis of interactions of the microparticles in case of a general model of non-equilibrium systems. The final solution of the problem is a very complicated one, because it is in close connection with the hitherto unsolved problem raised by GIBBS, *i. e.* which are the conditions whereby it can be proved that in course of time a non-canonical distribution goes over into a canonical one.

The problems only just referred to here may become intelligible as to why we insist on the purely phenomenological and equivalent interpretation of MAXWELL's and ONSAGER's relations. Further problems will be mentioned in the following paragraph.

§ 5. Casimir's "β" parameters

In ONSAGER's theory it was usually assumed, that the parameters a were such that they were even functions of the velocity of microparticles [2], [12]. This condition is necessary for the choice of the actual form of microscopic reversibility from which the ONSAGER reciprocity theorem already follows. Later on it had been examined by CASIMIR [13], what happens when we also admit parameters into the expression of the entropy source, which are odd functions of the velocity of particles. These parameters are called "β" variables. It has been demonstrated by CASIMIR that — in this case from the actual form of the correlations in time — for those coefficients L_{iv} by which "cross effects" between fluxes and forces derived from variables of a - and β -type are described, the following antisymmetric relations are valid:

$$(5.1) \quad L_{iv} = -L_{vi} \quad \begin{array}{l} (i = 1, 2, \dots, m) \\ (v = m + 1, \dots, f) \end{array}$$

In 1957, on the basis of statistical investigations CALLEN expressed the view that these relations are not real [6]. DE GROOT in his excellent monograph has derived CASIMIR's reciprocal relations in the case of an electrical "four-pole" as a consequence of a direct transformation only [2]. These facts have prompted us to endeavour to interpret the relations (5.1) in a phenomenological way also. It will be seen that CALLEN's views are supported by our results.

Considering both types of the variables the entropy source will be

$$(5.2) \quad \Delta S = -\frac{1}{2} \sum_{i,k=1}^m g_{ik} a_i a_k - \frac{1}{2} \sum_{\lambda,\nu=m+1}^f g_{\lambda\nu} \beta_\lambda \beta_\nu$$

or

$$(5.2') \quad \Delta S = -\frac{1}{2} \tilde{\alpha} \mathbf{G}(m) \alpha - \frac{1}{2} \tilde{\beta} \mathbf{G}(f-m) \beta$$

since the entropy is an even function of the particle velocities, no cross-terms between a - and β -type variables appear in this expression. The Maxwellians now are

$$(5.3) \quad g_{ik} = g_{ki}; \quad \mathbf{G}(m) = \tilde{\mathbf{G}}(m) \\ (i, k = 1, 2, \dots, m)$$

$$(5.3') \quad g_{\lambda\nu} = g_{\nu\lambda}; \quad \mathbf{G}(f-m) = \tilde{\mathbf{G}}(f-m) \\ (\lambda, \nu = m + 1, \dots, f)$$

where in the matrix notations the number of the elements of the quadratical matrices in question was also shown as argument. The fact, that according

to (5.2) ΔS is separated into two parts depending only on α - and β -variables, should be interpreted as "the splitting of ΔS in the effective state space". The denomination is justified by the following. Let us consider S itself as a state function unambiguously determined by the α - and β -variables, *i. e.*

$$(5.4) \quad S = S(\alpha_1, \alpha_2, \dots, \alpha_m, \beta_{m+1}, \beta_{m+2}, \dots, \beta_f)$$

Developing this quantity in a Taylor series we get

$$(5.5) \quad \Delta S = -\frac{1}{2} \sum_{i,k=1}^m g_{ik} \alpha_i \alpha_k - \frac{1}{2} \sum_{i=1}^m g_{iv} \alpha_i \beta_v - \frac{1}{2} \sum_{i=1}^m g_{vi} \beta_v \alpha_i - \frac{1}{2} \sum_{\lambda, \nu=m+1}^f g_{\lambda\nu} \beta_\lambda \beta_\nu$$

where for the matrices to be formulated from the elements g_{ik} and $g_{\lambda\nu}$ the reciprocal relations (5.3) and (5.3') are valid. This expression is analogous with I and will be identical with (5.2) (which is correct in the present case), if it were required that the following antisymmetric relations be valid for the "hybrid" matrices to be formulated from the elements g_{iv} and g_{vi} :

$$(5.6) \quad g_{iv} \equiv \left(\frac{\partial^2 S}{\partial \alpha_i \partial \beta_v} \right)_0 = - \left(\frac{\partial^2 S}{\partial \beta_v \partial \alpha_i} \right)_0 \equiv -g_{vi} \quad \begin{array}{l} (i = 1, 2, \dots, m) \\ (\nu = m+1, \dots, f) \end{array}$$

Hence, if it were required, that the hypermatrix $G(f)$, which consisting of four blocks

$$(5.7) \quad G(f) = \left[\begin{array}{c|c} \overbrace{\begin{matrix} g_{ik} & g_{\lambda k} \end{matrix}}^{m \quad f-m} \\ \hline \underbrace{\begin{matrix} g_{iv} & g_{\lambda\nu} \end{matrix}}_{f-m} \end{array} \right] \left\{ \begin{array}{l} m \\ f-m \end{array} \right. \quad \begin{array}{l} (i, k = 1, 2, \dots, m) \\ (\lambda, \nu = m+1, \dots, f) \end{array}$$

would be with respect to the blocks $g_{\lambda k}$ and g_{iv} antisymmetric. According to (5.6) hereby the equivalence of (5.2) with (5.5) is evident. Thus, physically only the problem remains, whether the antisymmetric relations — which can be called Maxwellian antisymmetries — are real or not. In these ONSAGER—CASIMIR theory the forces are defined by means of (5.2) in the following way:

$$(5.8) \quad X_i = \frac{\partial \Delta S}{\partial \alpha_i} = - \sum_{k=1}^m g_{ik} \alpha_k \quad (i = 1, 2, \dots, m) \quad (5.8') \quad \mathbf{X} = -G(m) \boldsymbol{\alpha}$$

$$(5.9) \quad Y_\lambda = \frac{\partial \Delta S}{\partial \beta_\lambda} = - \sum_{\nu=m+1}^f g_{\lambda\nu} \beta_\nu \quad (\lambda = m+1, \dots, f) \quad (5.9') \quad \mathbf{Y} = -G(f-m) \boldsymbol{\beta}$$

In the latter case the forces Y_λ belong to the “ β ” parameters. Herewith the part of the ONSAGER—CASIMIR theory which refers to the effective state space is complete.

Let us now introduce the fluxes on the basis of the following conditions expressing the hypothesis H:

$$(5.10) \quad \dot{a}_i = f_i(a_1, a_2, \dots, a_m, \beta_{m+1}, \beta_{m+2}, \dots, \beta_f) \quad (i = 1, 2, \dots, m)$$

$$(5.11) \quad \dot{\beta}_\lambda = f_\lambda(a_1, a_2, \dots, a_m, \beta_{m+1}, \beta_{m+2}, \dots, \beta_f) \quad (\lambda = m+1, \dots, f)$$

from which in an approximation analogous to (2.6) it can be written

$$(5.12) \quad \dot{a}_i = - \sum_{l=1}^m \left(\frac{\partial f_i}{\partial a_l} \right)_0 a_l - \sum_{\gamma=m+1}^f \left(\frac{\partial f_i}{\partial \beta_\gamma} \right)_0 \beta_\gamma \equiv - \sum_{l=1}^m c_{il} a_l - \sum_{\gamma=m+1}^f c_{i\gamma} \beta_\gamma$$

$$(i = 1, 2, \dots, m)$$

$$(5.13) \quad \dot{\beta}_\lambda = - \sum_{l=1}^m \left(\frac{\partial f_\lambda}{\partial a_l} \right)_0 a_l - \sum_{\gamma=m+1}^f \left(\frac{\partial f_\lambda}{\partial \beta_\gamma} \right)_0 \beta_\gamma \equiv - \sum_{l=1}^m c_{\lambda l} a_l - \sum_{\gamma=m+1}^f c_{\lambda\gamma} \beta_\gamma$$

$$(\lambda = m+1, \dots, f)$$

where c_{il} , $c_{i\gamma}$, $c_{\lambda l}$, $c_{\lambda\gamma}$ are the corresponding “coupling matrices”. Inverting (5.8) to a_l and (5.9) to β_γ we get

$$(5.14) \quad a_l = - \sum_{k=1}^m g_{lk}^{-1} X_k \quad (l = 1, 2, \dots, m)$$

$$(5.15) \quad \beta_\gamma = - \sum_{\nu=m+1}^f g_{\gamma\nu}^{-1} Y_\nu \quad (\gamma = m+1, \dots, f)$$

which expressions substituted into (5.12) and (5.13) become:

$$(5.16) \quad \dot{a}_i = \sum_{l,k=1}^m c_{il} g_{lk}^{-1} X_k + \sum_{\gamma,\nu=m+1}^f c_{i\gamma} g_{\gamma\nu}^{-1} Y_\nu \quad (i = 1, 2, \dots, m)$$

$$(5.17) \quad \dot{\beta}_\lambda = \sum_{l,k=1}^m c_{\lambda l} g_{lk}^{-1} X_k + \sum_{\gamma,\lambda=m+1}^f c_{\lambda\gamma} g_{\gamma\nu}^{-1} Y_\nu \quad (\lambda = m+1, \dots, f)$$

Introducing now into these equations the following new quantities

$$(5.18) \quad L_{lk} \equiv \sum_{l=1}^m c_{il} g_{lk}^{-1}; \quad L_{i\nu} \equiv \sum_{\gamma=m+1}^f c_{i\gamma} g_{\gamma\nu}^{-1}; \quad L_{\lambda k} \equiv \sum_{l=1}^m c_{\lambda l} g_{lk}^{-1}; \quad L_{\lambda\nu} \equiv \sum_{\gamma=m+1}^f c_{\lambda\gamma} g_{\gamma\nu}^{-1}$$

the linear laws are attained

$$(5.19) \quad \dot{a}_i = \sum_{k=1}^m L_{ik} X_k + \sum_{v=m+1}^f L_{iv} Y_v \quad (i = 1, 2, \dots, m)$$

or

$$(5.19') \quad \mathbf{I}_\alpha = \mathbf{L}_{\alpha\alpha} \mathbf{X} + \mathbf{L}_{\alpha\beta} \mathbf{Y}$$

and

$$(5.20) \quad \dot{\beta}_\lambda = \sum_{k=1}^m L_{\lambda k} Y_k + \sum_{v=m+1}^f L_{\lambda v} Y_v \quad (\lambda = m+1, \dots, f)$$

or

$$(5.20') \quad \mathbf{I}_\beta = \mathbf{L}_{\beta\alpha} \mathbf{X} + \mathbf{L}_{\beta\beta} \mathbf{Y}$$

It should be kept in mind that according to the expressions (5.19) and (5.20) it is required that also those quantities L_{iv} and $L_{\lambda k}$ must have a meaning now, which had been introduced by the "coupling coefficients" $c_{i\gamma}$ and $c_{\lambda l}$ of mixed indices, *i. e.* "hybrid" ones.

Let us turn for a moment now to the reciprocal relations (5.3) and (5.3') as well as (5.6) and assume the latter ones as being real also. In any case either one of the above-mentioned relations can be formulated with the parameters of the actual effective state space in the following way

$$(5.21) \quad \frac{\partial a_i}{\partial X_k} = \frac{\partial a_k}{\partial X_i} \quad (5.22) \quad \frac{\partial \beta_\lambda}{\partial Y_\nu} = \frac{\partial \beta_\nu}{\partial Y_\lambda}$$

$$(i, k = 1, 2, \dots, m) \quad (\lambda, \nu = m+1, \dots, f)$$

and

$$(5.23) \quad \frac{\partial a_i}{\partial Y_\nu} = - \frac{\partial \beta_\nu}{\partial X_i}$$

$$(i = 1, 2, \dots, m; \nu = m+1, \dots, f)$$

which are fulfilled in the effective state space determined by the parameters a , X , β and Y .

Evidently now again only such a velocity space can be accepted as correct, whose fluxes satisfy the reciprocal relations following from the preceding relations in an analogous manner to (4.8) and (4.9):

$$(5.24) \quad L_{ik} = L_{ki} \quad (i, k = 1, 2, \dots, m)$$

$$(5.25) \quad L_{\lambda\nu} = L_{\nu\lambda} \quad (\lambda, \nu = m+1, \dots, f)$$

and

$$(5.26) \quad L_{iv} = -L_{vi} \quad (i = 1, 2, \dots, m; \nu = m+1, \dots, f)$$

where the relations of (5.26) are the CASIMIR antisymmetrical reciprocal relations. Thus from the phenomenological point of view the relations in (5.26)

can be interpreted in an identical way with the ONSAGER relations, *i. e.* as the consequence of the compatibility of the flux space with the characteristics of the state space. At present three problems arise following strictly from one another.

Primarily, what is the condition, that, inasmuch as the potential ΔS in the state space splits up into two terms which merely contains a - and β -variables (see (5.2)), that then $\dot{\Delta S} \equiv \sigma$ determined as the quadratic form of the independent forces \mathbf{X} and \mathbf{Y} be also splitted into two terms in the following way:

$$(5.27) \quad \sigma = \tilde{\mathbf{X}} \mathbf{L}_{\alpha\alpha} \mathbf{X} + \tilde{\mathbf{Y}} \mathbf{L}_{\beta\beta} \mathbf{Y}$$

Since the forces \mathbf{X} and \mathbf{Y} defined by (5.8) and (5.9) are exclusively determined by variables a and β , it is plausible that neither can $\sigma \equiv \dot{\Delta S}$ (arising from the derivation over the time of (5.2)) contain cross-terms in \mathbf{X} and \mathbf{Y} . The above-mentioned condition is immediately obtained by using the matrix notation, if (5.2') is derived over the time and by eliminating the fluxes $\dot{\alpha} \equiv \mathbf{I}_\alpha$ and $\dot{\beta} \equiv \mathbf{I}_\beta$, thus obtained with the use of (5.19') and (5.20'), finally by making use of the symmetry of the matrices $\mathbf{G}(m)$ and $\mathbf{G}(f-m)$. Thus on the condition that $\sigma \equiv \dot{\Delta S}$ should be of the form given in (5.27), we get

$$(5.28) \quad \mathbf{L}_{\alpha\beta} = -\tilde{\mathbf{L}}_{\beta\alpha}$$

which are the CASIMIR reciprocal relations in a matrix notation. It is to be seen, that just as the split up of ΔS in the state space can be described with the antisymmetric Maxwellian (whether they are real or not), so the split up of σ according to (5.27) can be described with the CASIMIR antisymmetrical relations. Since, the latter fact is also independent from the reality of CASIMIR's relations, thus at this point according to the two medial expressions of (5.5) it can be stated, that the reality of CASIMIR's relations are connected with the reality of the antisymmetric Maxwellian ones. On the other hand it depends on the reality of the "hybrid coupling matrices" $c_{i\gamma}$ and $c_{\lambda l}$. Herewith we reached the second problem, *i. e.* to the problem of what might be said of the physical reality of the antisymmetrical MAXWELL relations?

The strict and general answer to the problem is undoubtedly to be expected from statistical physics. This, however, as has already been mentioned, overemphasizing the statistical nature and origin of the ONSAGER relations has not even been dealt with as yet, in the general direct confirmation of the symmetric MAXWELL relations. It is, however, shown by investigations within the phenomenological framework [9], that the antisymmetric Maxwellian cannot be real. This problem is related to the interpretation of the thermodynamic potential functions in the effective state space and the transformation

properties between them and between the parameters determining them. But since MAXWELL's reciprocal relations show a complete analogy with GREEN's reciprocal relations of electrostatics (see [14]), moreover considering a general energetics the latter are a particular case of the former ones, thus the antisymmetrical relations of GREEN's may give information on the reality of the antisymmetric Maxwellian. However, the non-reality of the GREEN antisymmetrical relations can be understood trivially in every case. *I. e.* their assumption leads either to the formulation of a physically senseless problem or they can be obtained only as the consequence of a formal mathematical manipulation, *l'art pour l'art* transformation. The rigorous statistical confirmation of the problem raised is desirable in any case and at the same time shows the deficiencies encountered, if either the statistical or the phenomenological description is emphasized as the only correct method of research.

The answer to the third problem, *i. e.* the problem of the reality of CASIMIR's relations partly arises from the precedings. Namely if (5.23) are non-real, than (5.26) are identically zero. It is worthwhile to note that in spite of CALLEN's statistical examinations this problem was neglected in literature. It is also important, that DE GROOT in his book ([2], § 80) arrives to the CASIMIR relations through the example of the electrical "four-pole" by carrying out a simple transformation only. The situation here is quite similar to the one that we have stated for the formal transformations directed towards the production of the GREEN antisymmetrical relations. All these facts go to show that the problem of the reality of CASIMIR's reciprocal relations is very actual.

Now without making use of what has already been said on the non-reality of the antisymmetric Maxwellian, the non-reality of CASIMIR's relations can also be understood in a quite different way by considering the definitions of α - and β -variables. It is known from CASIMIR and others [12], [13], that the β variables or their divergencies are the time derivatives of the variables of α type, *i. e.*

$$(5.29) \quad \beta \equiv \dot{\alpha} \qquad (5.30) \quad - \operatorname{div} \beta \equiv \frac{\partial \alpha}{\partial t}$$

where (5.29) refers to a property of a discontinuous system, whereas (5.30) to one of a continuous system. It is evident from these expressions — which can be considered as the phenomenological definitions of the β variables too — that a velocity space of the α parameters is stretched out by β variables. Indeed, β parameters used also to be called "velocity variables" [12]. Hence considering the β parameters in (5.2) in the same way as the α variables of an effective state space, which is otherwise possible, it should be kept in mind that the state space of the β variables is dynamically of a higher order (velocity space)

than the a space (coordinate space). On the basis of the aforesaid relations (5.10) and (5.11) make sense only in the following form:

$$(5.10') \quad \dot{a}_i = f_i(a_1, a_2, \dots, a_m) \quad (i = 1, 2, \dots, m)$$

$$(5.11') \quad \dot{\beta}_\lambda \equiv \ddot{a}_\lambda = f_\lambda(\beta_{m+1}, \dots, \beta_f) \equiv f_\lambda(\dot{a}_{m+1}, \dots, \dot{a}_f) \quad (\lambda = m+1, \dots, f)$$

The latter expression shows that a space of acceleration of the parameters a is actually determined in it. Several examples are known in literature for these general considerations, thus we should like to draw the attention only to the fact, that due to the foregoing the "coupling coefficients" $c_{i\gamma}$ and $c_{\lambda i}$, which are the elements of the "hybrid" matrices are eventually zero. The quantities $c_{\lambda\gamma}$ can perhaps be called "the coupling coefficients of the acceleration space". Thus also the quantities $L_{i\gamma}$ and $L_{\lambda k}$ defined in (5.18) disappear eventually and it shows that CASIMIR's antisymmetry is not real. This means that the matrix of conductivity coefficients is necessarily symmetric in the absence of a magnetic field and Coriolis force respectively. Otherwise, the original ONSAGER theory, at least in the flux space, is complete and correct, without any complements.

The physical situation is evident. Since perhaps it has no sense in taking such "cross effects" into account, which can be described by the quantities $L_{i\gamma}$, which for instance would refer to the interference between the velocity and acceleration of a parameter a . In other words the following theorem can be stated:

Theorem: "Cross effects" cannot be interpreted between flux spaces belonging to effective state space of a different dynamic order.

The theorem is a manifest consequence of the fact that the velocity space of a higher order is unambiguously determined by the state space of a dynamically lower order. Of course it may be that our given theorem is not valid in general and thus the reality of CASIMIR's relations ought to be taken into account. If finally the detailed non-phenomenological examinations lead to such results in contradiction with CALLEN's results, then the derivation given here for CASIMIR's antisymmetry is admissible only in that case, if (5.23) are real relations too.

It is emphasized by the author that he leaves the raised problems opened for drawing the final conclusions. Thus he intended only to demonstrate here that more fundamental problems of ONSAGER's theory can be examined also phenomenological way. In a following paper it will be demonstrated, how the model of a non-linear thermodynamic theory can be built up in a purely phenomenological way on the basis of hypothesis H.

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Summary

On the basis of the second law of classical thermodynamics the ONSAGER "a" coordinates are introduced and an effective state space determined by them is interpreted. ONSAGER's flux space is considered as the one determined by effective state space. With the aid of the "coupling matrix" of the flux space, some representations of the "equations of motion" of irreversible thermodynamics are given. ONSAGER's and CASIMIR's reciprocal relations are discussed in a purely phenomenological way. In connection with MAXWELL's, ONSAGER's and CASIMIR's reciprocal relations many statistical connections and deficiencies are mentioned. The non-reality of CASIMIR's antisymmetrical relations is eventually suggested. The formalism given here can be used for discontinuous systems only.

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