# ON THE PHENOMENOLOGICAL BASIS OF IRREVERSIBLE THERMODYNAMICS II.

(ON A POSSIBLE NON-LINEAR THEORY)

By

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(Received October 19, 1960)

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## Introduction

The properties of non-linear dissipative systems in the case of very particular models have been recently investigated by several authors ; MACDONALD [2], VAN KAMPEN [3], [4], DAVIES [5], ALKEMADE [6], BRINKMAN [7]. These investigations were first of all concerned with a simple electrical circuit, with a vacuum diode containing a non-linear element and with the motion of a Brownian particle. They were rather of statistical nature and did not lead to an unambiguous and satisfactory result, in the particular questions raised, either. A detailed critical analysis is to be found in a recent work of VAN KAMPEN [3]. Another general defectiveness of the majority of the works enumerated is, that their relation with the linear Onsager theory cannot be directly given, moreover in some cases the well proved results of the linear theory are destroyed by the higher approximations. The non-linear theory — more appropriate quasi-linear — to be developed in the followings, will be completely general for the flux space to be conjugated to the Onsager $a$ space and for the discontinuous systems. On the other hand, since our theory follows from the direct generalization of the linear one, it does not destroy it. Though the foregoings are without doubt pillars of the theory, we do not as yet consider it as complete, and in several respects, first of all experimentally, it calls for confirmation.

So from the experimental as well as the theoretical points of view the non-linearity might occur because of two different reasons. Statistically non-linear effects can be described by considering the higher approximations of the Boltzmann factor. In other cases non-linearity might be produced from the actual interaction of particles, which are responsible for the transition between the states. The development of a non-linear theory for the latter case seems to be considerably more difficult, at least as regards the statistical description. From a phenomenological point of view the fundamentals of a non-linear theory can also be outlined in two different manners. The first way is obtained as the extension of the validity of our axiom I — see part I of this paper [1] — in the direction of a higher approximation, for instance by the acceptance of (1.10) as axiom. This way the formulae obtainable from (1.10) [for example in part I, (1.11), (1.12), (1.13) and (1.14) lead to the direct non-linear forms of the forces $X_i$ in the effective state space by which formally a non-linear theory can be built up. It seems that such a development corresponds to the statistical method, when the Boltzmann factor is considered in a non-linear approximation. We consider this method to be very formal, from the statistical as well as from the phenomenological points of view, therefore its further specification is not dealt with here.

The most important is such a non-linear theory, which can also take into consideration the non-linearity of the actual molecular transition mechanisms. At present the building out of such a statistical theory cannot be expected. In a phenomenological theory, however, since the non-linearity in question should be evidently expressed by the non-linear relations to be given between the fluxes and forces, an easy and consequent method can be given for this case. Now the non-linearity refers to the flux space and to a first approximation leads to the dependence of the phenomenological coefficients on the thermodynamic forces. Our theory, which can be built up on the basis of the (1.15) of the hypothesis H. (see in I [1]) will thus be a quasi-linear theory. In this theory the most properties of the linear Onsager theory can be recognized, its theorems can be generalized if in the meantime the dependence on the thermodynamic forces of conductivities or resistances is taken into consideration.

## § 1. The effective state pace

All the expressions characterizing the "first order effective state space" in Onsager's theory are considered as valid unaltered. The most fundamental is the entropy source :

$$\Delta S = -\frac{1}{2} \sum_{i,k=1}^{f} g_{ik}\, a_i\, a_k \tag{1.1}$$

the definition of thermodynamic forces

$$X_i = \frac{\partial \Delta S}{\partial a_i} = -\sum_{k=1}^{f} g_{ik}\, a_k \qquad (i = 1, 2, \ldots, f) \tag{1.2}$$

Finally the Maxwell's reciprocal relations are

$$\frac{\partial a_i}{\partial X_k} = \frac{\partial a_k}{\partial X_i} \qquad (i, k = 1, 2, \ldots f) \tag{1.3}$$

expressing the symmetry of $g_{ik}$ by the parameters of the effective state space. (Further problems are investigated in paper I in full detail.)

## § 2. Quasi-linear phenomenological laws

The touchstone of the theory is the total form of (1.15) in part I of this paper, which is considered in this approximation as an axiom. The expressions in question are

$$\dot{a}_i = -\sum_{l=1}^{f} c_{il}\, a_l - \frac{1}{2}\sum_{l,s=1}^{f} \gamma_{ils}\, a_l\, a_s \qquad (i = 1, 2, \ldots, f) \tag{2.1}$$

where the quantities $c_{il}$ are the well known "coupling coefficients" of the linear flux space, whereas the quantities $\gamma_{ils}$ can be called the "non-linear coupling coefficients". The latter ones are symmetrical in the indices $l$ and $s$, since per definicionem

$$\left(\frac{\partial^2 f_i}{\partial_{a_e}\,\partial_{a_s}}\right)_0 \equiv \gamma_{i\,[l,s]} = \gamma_{i\,[s,l]} \equiv \left(\frac{\partial^2 f_i}{\partial_{a_s}\,\partial_{a_e}}\right)_0 \qquad (i, l, s = 1, 2, \ldots, f) \tag{2.2}$$

where the symmetry in the last two indices have also been shown by the bracket. By means of the quantities $c_{il}$ and $\gamma_{ils}$ a new matrix, expressing the total coupling of the velocity space, can now be interpreted in the following way :

$$c^*_{ir} \equiv c_{ir} + \gamma'_{ir} \qquad (i, r = 1, 2, \ldots, f) \tag{2.3}$$

where

$$\gamma'_{ir} \equiv \frac{1}{2}\sum_{s=1}^{f} \gamma_{irs}\, a_s \tag{2.4}$$

It should be noted here, that owing to (2.4) the quantities $c^*_{ir}$ are not constant and on the other hand are neither symmetric. The physical situation is that the inconstancy of the quantities $c^*_{ir}$ might involve the consequence, that though in general $c_{ir} > \gamma_{irs}$, this statement cannot be referred to the quantities $\gamma'_{ir}$ which depend on the parameters $a$ of the effective state space. Thus the latter ones in actual cases — in cases somewhat distant from equilibrium or giving rise to the singularity of the matrix $c_{ir}$ — can be compared with the coefficients $c_{ir}$ or may be even greater than those. Just in these actual cases, when $\gamma'_{ir}$ cannot be neglected in $c^*_{ir}$ either, we speak of non-linearity. With the quantities $c^*_{ir}$ the formula (2.1) will be

$$\dot{a}_i = -\sum_{l=1}^{f} c^*_{il}\, a_l \qquad (i = 1, 2, \ldots, f) \tag{2.5}$$

Herewith we have given all the new quantities which are suitable for the derivation of the quasi-linear laws. Now, using the form of (1.2) referring to two different indices $l$ and $s$ can be eliminated $a_l$ and $a_s$ from (2.1). Thus we obtain

$$(2.6)\qquad \dot{a}_i = \sum_{l,k=1}^{f} c_{il}\, g_{lk}^{-1} X_k + \frac{1}{2} \sum_{l,k,s,j=1}^{f} \gamma_{ils}\, g_{lk}^{-1}\, g_{sj}^{-1} X_k X_j \qquad (i = 1, 2, \ldots, f)$$

Taking into consideration (2.3), (2.4) and (2.5) the quasi-linear relations between the new fluxes $\dot{a}_i \equiv I_i^*$ and forces will be

$$(2.7)\quad I_i^* = \sum_{l,k=1}^{f} c_{il}\, g_{lk}^{-1} X_k + \sum_{l,k=1}^{f} \gamma'_{il}\, g_{lk}^{-1} X_k = \sum_{k=1}^{f} L_{ik}^* X_k \qquad (i = 1, 2, \ldots, f)$$

where we introduced the new

$$(2.8)\qquad L_{ik}^* \equiv \sum_{l=1}^{f} c_{il}^*\, g_{lk}^{-1} \qquad (i,k = 1, 2, \ldots, f)$$

conductivity coefficients, which are not constant. Namely owing to (2.3), (2.4) and (2.6) for (2.8), it can be written, that

$$(2.9)\qquad L_{ik}^* = L_{ik} + \sum_{j=1}^{f} l_{ikj} X_j \qquad (i, k = 1, 2, \ldots, f)$$

where

$$(2.10)\qquad L_{ik} \equiv \sum_{l=1}^{f} c_{il}\, g_{lk}^{-1}$$

$$(2.11)\qquad l_{ikj} \equiv \frac{1}{2} \sum_{l,s=1}^{f} \gamma_{ils}\, g_{lk}^{-1}\, g_{sj}^{-1}$$

are the linear and non-linear, but constant conductivity coefficients. The determination of the values of the constants $L_{ik}$ belonging to the linear effects as well as of the constants $l_{ikj}$ belonging to the non-linear effects is possible on an empirical way or rather on the basis of the kinetic theories. In the latter case it is advisable to consider the third approximation of Enskog's solution of the Boltzmann equation. Due to (2.9) the quasi-linearity of (2.7) is evident.

## § 3. "Equations of motion"

As in the ordinary Onsager theory the quasi-linear laws of (2.7) can be called the "equations of motion". We, however, maintain this denomination for the forms analogous with equations (3.4), (3.6) and (3.10) of the linear theory.

(See these equations in paper I.) Here the one corresponding to (3.10) is being derived only. This we obtain by combining the time derivative of (1.2) with (2.6) also considering still (2.10) and (2.11). Hence we get

$$\dot{X}_l = = \sum_{k=1}^{t} B_{lk} X_k - \frac{1}{2} \sum_{k,j=1}^{f} D_{lkj} X_k X_j \qquad (l = 1, 2, \ldots, f) \tag{3.1}$$

where the following denotations have been introduced :

$$B_{lk} \equiv \sum_{l=1}^{f} g_{il} L_{ik} \qquad (l, k = 1, 2, \ldots, f) \tag{3.2}$$

$$D_{lkj} \equiv \sum_{i=1}^{f} g_{il} l_{ikj} \qquad (l, k, j = 1, 2, \ldots, f) \tag{3.3}$$

It is worth while to note, that the "restoring character" of the thermodynamic forces $X_i$ directed from (3.10) in paper I as well as from (3.1) towards the equilibrium state is evident.

## § 4. New forms of the reciprocal relations

In the same manner as that followed in paper I in sect. A of § 4 for the phenomenological interpretation of Onsager's ordinary reciprocal relations, we can arrive at some supplementary relations referring to the second order conductivity coefficients. It is even now our conception, that according to (2.1) expressing our hypothesis the properties of the flux space $\{\dot{a}_1, \dot{a}_2, \ldots, \dot{a}_f\}$ determined by the parameters of the effective state space, must satisfy the characteristical properties of the "$a$" space. Hence, the quasi-linear fluxes $I_i^*$ in (2.7) can be such as will satisfy the reciprocal relations (1.3) valid in the effective state space. Differentiated over the time (1.3) — also now in case of forces constant in time — it can be written, that

$$\frac{\partial}{\partial X_k}\left(\frac{d_{a_i}}{dt}\right) = \frac{\partial}{\partial X_i}\left(\frac{d_{a_k}}{dt}\right) \qquad (i, k = 1, 2, \ldots, f) \tag{4.1}$$

or

$$\frac{\partial I_i^*}{\partial X_k} = \frac{\partial I_k^*}{\partial X_i} \qquad (i, k = 1, 2, \ldots, f) \tag{4.2}$$

by which constraint equalities the validity of the following relations are postulated for the coefficients of quasi-linear fluxes given by (2.7)

$$L_{ik}^* + \sum_{j=1}^{f} l_{ijk} X_j = L_{ki}^* + \sum_{j=1}^{f} l_{kji} X_j \qquad (i, k = 1, 2, \ldots, f) \tag{4.3}$$

It can be seen, that by equation (4.3) following from (4.1) the symmetry of the new $L^*_{ik}$ coefficients is not required. This means an essential departure from the linear theory (see I), where the symmetry of the constant $L_{ik}$ coefficients, *i. e.* the validity of Onsager's reciprocal relations could have been derived from (4.1). Turning back now with (2.9) to the ordinary Onsager coefficients, then (4.3) can be written as well

$$(4.4) \quad L_{ik} + \sum_{j=1}^{f} (l_{ikj} + l_{ijk}) X_j = L_{ki} + \sum_{j=1}^{f} (l_{kij} + l_{kji}) X_j \quad (i, k = 1, 2, \ldots, f)$$

It is evident that the symmetry of the $L_{ik}$ coefficients neither follows from (4.4) only as well as from (4.3) that one of the $L^*_{ik}$ quantities. However, by the condition (4.4) it is enabled to keep the reciprocal relations of the linear theory *i.e.*,

$$(4.5) \qquad L_{ik} = L_{ki} \qquad (i, k = 1, 2, \ldots, f)$$

completing than by the relations

$$(4.6) \qquad l_{ikj} + l_{ijk} = l_{kij} + l_{kji} \qquad (i, k, j = 1, 2, \ldots f)$$

following from the differentiation over $X_j$ of both sides of (4.4). In other words, the relations (1.3) expressing the characteristical property of the "$a$" space require for the quasi-linear fluxes of (2.7) the validity of the conditions (4.4) and these conditions can be satisfied by the ordinary (4.5) reciprocal relations, further on by the supplementary relations referring to the second order conductivity coefficients. Hence, the structure of the linear theory is not destroyed by our theory, but is completed accordingly. In this paper the fundamental character of the hypothesis H. became also evident, whose approximative expressions of different order were equally adequate for the theoretical deduction of both the linear and the quasi-linear laws.

## § 5. Applications

We give two simple applications of the outlined non-linear theory for such cases where the experimental verification of the obtainable new formulae might be, perhaps, the most quickly expected.

### *A) Thermomechanical and mechanocaloric effects*

These effects are particularly fundamental in liquid He II. (The detailed treatment of the effects on the basis of ONSAGER's linear theory is to be found in DE GROOT's book [8]. The method of notation used here follows the § 9 of the cited book.) The thermomechanical and mechanocaloric effects can be described with the aid of a flux of matter $I^*_m$ and a flow of energy $I^*_u$ by the following quasi-linear laws :

$$I^*_m = L^*_{mm} X_m + L^*_{mu} X_u \tag{5.1}$$

$$I^*_u = L^*_{um} X_m + L^*_{uu} X_u \tag{5.2}$$

where the explicit forms of forces are

$$X_m = -\frac{v}{T} \Delta P + \frac{h}{T^2} \Delta T \tag{5.3}$$

$$X_u = -\frac{\Delta T}{T^2} \tag{5.4}$$

The new coefficients are connected with ONSAGER's constant quantities as the particular case of (2.9) in the following way :

$$L^*_{mm} = L_{mm} + l_{mmm} X_m + l_{mmu} X_u \tag{5.5}$$

$$L^*_{mu} = L_{mu} + l_{mum} X_m + l_{muu} X_u \tag{5.6}$$

$$L^*_{um} = L_{um} + l_{umm} X_m + l_{umu} X_u \tag{5.7}$$

$$L^*_{uu} = L_{uu} + l_{uum} X_m + l_{uuu} X_u \tag{5.8}$$

The quasi-linear laws (5.1) and (5.2) expressed by the forces (5.3) and (5.4) are the following :

$$I^*_m = -\frac{L^*_{mm} v}{T} \Delta P + \frac{L^*_{mm} h - L^*_{mu}}{T^2} \Delta T \tag{5.9}$$

$$I^*_u = -\frac{L^*_{um} v}{T} \Delta P + \frac{L^*_{um} h - L^*_{uu}}{T^2} \Delta T \tag{5.10}$$

These equations are analogous with corresponding equations of the linear theory, but expressed now by the non-symmetric $L^*_{ik}$ coefficients. If we want to observe the non-linearity of the equations in an explicit manner, then the fluxes $I^*_m$ and $I^*_u$ must be expressed by the constant $L_{ik}$ and $l_{ikj}$, which coefficients are independent of the forces $X_m$ and $X_u$. Hence, introducing the relations (5.5)—(5.8) into (5.1) and (4.2) we get :

$$\begin{aligned} I^*_m = L_{mm} X_m + L_{mu} X_u + l_{mmm} X^2_m + l_{mmu} X_m X_u + \\ + l_{mum} X_u X_m + l_{muu} X^2_u \end{aligned} \tag{5.11}$$

$$\begin{aligned} I^*_u = L_{um} X_m + L_{uu} X_u + l_{umm} X^2_m + l_{umu} X_m X_u + \\ + l_{uum} X_u X_m + l_{uuu} X^2_u \end{aligned} \tag{5.12}$$

In these expressions for the linear coefficients Onsager's reciprocal relations are valid, i. e.

$$L_{mu} = L_{um} \tag{5.13}$$

whereas for the second order coefficients following from (4.5)

$$2l_{umm} = l_{mmu} + l_{mum} \tag{5.14}$$

$$2l_{muu} = l_{uum} + l_{umu} \tag{5.15}$$

equalities are valid. The quasi-linear laws (5.11) and (5.12) can be written also in an explicit manner with the aid of the forms (5.3) and (5.4) of the forces. Introducing namely the following constants :

$$A_1 = -\frac{L_{mm} v}{T} \; ; \; A_2 = \frac{L_{mm} h - L_{uu}}{T^2} \tag{5.16}$$

$$B_1 = -\frac{L_{um} v}{T} \; ; \; B_2 = \frac{L_{um} h - L_{uu}}{T^2} \tag{5.17}$$

and

$$\begin{cases} a_1 = \dfrac{l_{mmm} v^2}{T^2} \\ a_2 = \dfrac{2v}{T^3}(l_{umm} - l_{mmm} h) \\ a_3 = \dfrac{1}{T^4}(l_{mmm} h^2 + l_{uuu} - 2h\, l_{umm}) \end{cases} \tag{5.18}$$

further

$$\begin{cases} b_1 = \dfrac{l_{umm} v^2}{T^2} \\ b_2 = \dfrac{2v}{T^3}(l_{muu} - l_{umm} h) \\ b_3 = \dfrac{1}{T^4}(l_{umm} h^2 + l_{uuu} - 2h\, l_{muu}) \end{cases} \tag{5.19}$$

where the coefficients $a_2, a_3$ and $b_2, b_3$ have been reduced by the relations (5.14) and (5.15). Thus the fluxes of (5.9) and (5.10) will be non-linear expressions in terms of $\Delta P$ and $\Delta T$, *i. e.*,

$$I_m^* = A_1 \Delta P + A_2 \Delta T + a_1(\Delta P)^2 + a_2 \Delta P \Delta T + a_3(\Delta T)^2 \tag{5.20}$$

$$I_u^* = B_1 \Delta P + B_2 \Delta T + b_1(\Delta P)^2 + b_2 \Delta P \Delta T + b_3(\Delta T)^2 \tag{5.21}$$

The linear parts of the complete fluxes

$$I_m^1 = A_1 \Delta P + A_2 \Delta T \tag{5.22}$$

$$I_u^2 = B_1 \Delta P + B_2 \Delta T \tag{5.23}$$

give the flux of energy and flux of matter of the original Onsager's theory. The non-linear terms are

$$I_m^2 = a_1(\Delta P)^2 + a_2 \Delta P \Delta T + a_3(\Delta T)^2 \tag{5.24}$$

$$I_u^2 = b_1(\Delta P)^2 + b_2 \Delta P \Delta T + b_3(\Delta T)^2 \tag{5.25}$$

where the constants $a_1$, $a_2$, $a_3$ and $b_1$, $b_2$, $b_3$ of the part-fluxes are, in general, in the order of magnitude smaller than the linear constants $A_1$, $A_2$ and $B_1$, $B_2$. Disregarding the experimentally well known non-linear effects (non-newtonian viscosity, non-ohmic conduction, chemical reactions etc.) it can be easily seen from the actual expressions (5.18) and (5.19) of the constants of non-linear part-fluxes that their general occurrence might be particularly expected in the region of low temperatures. This is a direct and general consequence of the fact, that the actual values of the constants $a_1$, $a_2$, $a_3$ and $b_1$, $b_2$, $b_3$ are governed by the ever increasing powers of $T$. Now for the sake of the description of the thermomechanical and mechanocaloric effects the following particular cases are considered.

**1.** In the first special case let the temperature be uniform, $\Delta T = 0$, when a pressure difference $\Delta P$ is fixed. Then three important subcases can be investigated.

**a.** Let us consider linear effects only. Then non-linear fluxes vanish identically, *i. e.*, $I_m^2 = I_u^2 \equiv 0$. Now by dividing (5.23) with (5.22) we get

$$\frac{I_u^1}{I_m^1} = \frac{B_1}{A_1} = \frac{L_{um}}{L_{mm}} \equiv U^* \tag{5.26}$$

or

$$I_u^1 = U^* I_m^1 \tag{5.26'}$$

Here $U^*$ is per definicionem the "energy of transfer" by the linear flow of matter per unit of mass. This quantity is constant and does not depend on the non-equilibrium quantity $\Delta P$ causing the effect.

**b.** As another subcase, let us consider the idealized case when only non-linear effects are present in the system. Then taking the linear part of fluxes identically as zero, *i. e.* $I_m^1 = I_u^1 \equiv 0$, then the $U^{**}$ "energy of transfer" due to the non-linear part-flux of matter per unit of mass, can be defined. Now dividing (5.25) by (5.24) under condition $\Delta T = 0$ we get

(5.27) $$I_u^2 = U^{**} I_M^2$$
where

(5.27′) $$U^{**} \equiv \frac{b_1}{a_1} = \frac{l_{umm}}{l_{mmm}}$$

**c.** The general case satisfying the condition of **1.** is, when the linear and non-linear effects should be observed simultaneously. First of all let us notice that the quantities $U^*$ and $U^{**}$ introduced by the expressions (5.26) and (5.27) are also well utilisable in our present case. Let us consider (5.20) with the condition $\Delta T = 0$, then the energy flux existing under this condition is evidently delivered by the fluxes of matter $I_m^1$ and $I_m^2$ taken also at constant temperature in the following sense :

(5.28)
$$I_u^* = U^* I_m^1 + U^{**} I_m^2 = U^* A_1 \Delta P + U^{**} a_1 (\Delta P)^2 = = -\frac{U^* L_{mm} v}{T} \Delta P + U^{**} \frac{l_{mmm} v^2}{T^2} (\Delta P)^2$$

Indeed, if we now take into account (5.26), (5.27) and (5.20) it can be seen that (5.28) really identical with (5.21) is valid in our particular case, *i. e.*, with the expression

(5.29) $$I_u^* = B_1 \Delta P + b_1 (\Delta P)^2 = -\frac{L_{um} v}{T} \Delta P + \frac{l_{umm} v^2}{T^2} (\Delta P)^2$$

The determination of the constants $U^*$ and $U^{**}$ is possible on the basis of the kinetic theory. Considering the Enskog's solutions of the Boltzmann transport equation, then some approximation $f = f^{(0)} + f^{(1)} + f^{(2)} + \ldots$ of the distribution function must be used. The linear "energy of transfer" $U^*$ depending on actual cases is already given by the approximations $f^{(0)}$ and $f^{(0)} + f^{(1)}$ respectively. Thus, it may be expected that the determination of the non-linear quantity $U^{**}$ is possible by taking into consideration further approximation terms.

In the precedings the case of the simultaneous presence of the linear and non-linear effects was given in a description operating with quantities introduced for the separate realization of the above mentioned cases. Now a description relying upon universal quantities, in the general case, is being dealt with. Dividing (5.10) by (5.9) — or directly (5.28) by (5.9) — under condition $\Delta T = 0$ the total "energy of transfer" $^*U$ can be interpreted. This will be

(5.30) $$\frac{I_u^*}{I_m^*} = \frac{U^* I_m^1 + U^{**} I_m^2}{I_m^1 + I_m^2} = \frac{L_{um}^*}{L_{mm}^*} \equiv {}^*U$$

(5.30′) $$I_u^* = {}^*U (I_m^1 + I_m^2) = {}^*U \, I_m^*$$

which quantity is the direct generalization of $U^*$ in (5.26), however, ${}^*U$ depends now on the actual thermodynamic parameter. This may immediately be seen by taking the coefficients $\overset{*}{L}_{mm}$ and $\overset{*}{L}_{um}$ from (5.5) and (5.7) with the reduced forces $X'_m = -\frac{v}{T}\Delta P$ and $X'_u = 0$ corresponding to our case. Hence we can write,

$$(5.31) \qquad {}^*U \equiv \frac{\overset{*}{L}_{um}}{\overset{*}{L}_{mm}} = \frac{TL_{um} + l_{umm}\, v\Delta P}{TL_{mm} + l_{mmm}\, v\Delta P}$$

by which expression the dependence in question is explicitely shown. Since by kinetic calculations in general the constant quantities $U^*$ and $U^{**}$ can be determined, whereas on the other hand the quantity ${}^*U$ is in direct relation with the quasi-linear laws (5.9) and (5.10) — and in an analogous relation with the correspondent quantities of the linear theory — thus the expressions (5.30) and (5.31) are of great importance. Now we are going over to the treatment of an other particular case, the stationary one.

**2.** Under the stationary state of our system such a particular case is to be understood, where no mass transfer, *i.e.*, $I_m = 0$, but a non-vanishing energy transfer exists. In such a case a constant pressure difference arises for the equalization of the temperature difference. Now also three subcases should be distinguished.

**a.** Confining ourselves to a linear approximation only, *i. e.*, $\overset{2}{I}_m \equiv 0$ and $\overset{*}{I}_m = \overset{1}{I}_m = 0$, then with use of the ordinary Onsager relation in (5.13) we get from (5.22)

$$(5.32) \qquad \frac{\Delta P}{\Delta T} = \frac{h - \dfrac{L_{mu}}{L_{mm}}}{vT} = \frac{h - U^*}{vT}$$

which is well known from the linear theory.

**b.** Let the other case be the one — as a fictitious case — when the stationarity is observed purely in non-linear respect. Then $\overset{1}{I}_m \equiv 0$ and the condition of stationarity is $\overset{*}{I}_m \equiv \overset{2}{I}_m = 0$, which requiring for (5.24) and dividing it by $(\Delta T)^2$ we get for the ratio $\frac{\Delta P}{\Delta T}$ an equation of second order, *i. e.*,

$$(5.33) \qquad a_1 \left(\frac{\Delta P}{\Delta T}\right)^2 + a_2 \left(\frac{\Delta P}{\Delta T}\right) + a_3 = 0$$

The solutions of this equation are

$$(5.34) \qquad \left(\frac{\Delta P}{\Delta T}\right)_{1,2} = \frac{a_2 \pm \sqrt{a_2^2 - 4a_1 a_3}}{2a_1} = \frac{1}{vT}\left(h - U^{**} \pm \sqrt{(U^{**})^2 - \frac{l_{uuu}}{l_{mmm}}}\right)$$

while the relations in (5.27′) have been used. According to (5.34) the equation (5.32) has real solutions only if one of the conditions

$$l_{umm}^2 \geqq l_{mmm}\, l_{uuu} \tag{5.35}$$

is fulfilled. From these conditions on a purely theoretical way important conclusions can be drawn. In any case the case of equality is of particularly interest which corresponds to a single real solution. In this particular case

$$\frac{\Delta P}{\Delta T} = \frac{h - U^{**}}{vT} \tag{5.36}$$

which is in complete analogy with the corresponding linear expression 5.32. Of course, this case has not much significance in reality, however, owing to this fact and on the basis of condition (5.35) we may draw important conclusions concerning non-linear effects. According to the conditions the properties of pure second order effects — described by $l_{mmm}$ and $l_{uuu}$ — are such, that they are at the best of an equal order of magnitude with the second order cross-effects. In other words, the linearity is more sensitively destroyed throughout the cross-coefficients of the second order effects as by the pure second order terms. This means that the complete system of the linear phenomenological laws has a lower range of validity as compared to the case when only single flux is involved. Hence, the departure from linearity, in general, arises from the fact that $L_{mu}$ and $L_{mu}$ coefficients remain constants only up to a certain values of $\Delta P$ and $\Delta T$. As regards the question the dependence of which parameters of the $\overset{*}{L}_{ik}$ coefficients is the stronger and thus eventually which ones may be omitted, is of course an experimental problem.

**c.** Let us now consider the general case when the stationarity is required for the total flux of matter $\overset{*}{I}_m$. In this case we get from the quasi-linear law (5.9)

$$\frac{\Delta P}{\Delta T} = \frac{h - \dfrac{\overset{*}{L}_{mu}}{\overset{*}{L}_{mm}}}{vT} \tag{5.37}$$

which relation is though similar to the linear case (5.32), but owing to $\overset{*}{L}_{mu} \neq = \overset{*}{L}_{um}$ cannot be further analized. However, in this general respect some information can be obtained from (5.20) writing it under stationarity condition as follows :

$$\left(\frac{\Delta P}{\Delta T}\right)_{I_m^* = 0} = -\frac{A_2}{A_1} - \frac{a_1}{A_1}\frac{(\Delta P)^2}{\Delta T} - \frac{a_2}{A_1}\Delta P - \frac{a_3}{A_1}\Delta T \tag{5.38}$$

Namely considering the conditions (5.35) as well as the differences consisting in the order of magnitude of the first and second order conductivity coefficients the following can be postulated :

(5.39) $$L_{mm} \gg \begin{Bmatrix} l_{mmm} \\ l_{uuu} \end{Bmatrix} < l_{umm}$$

Using these conditions rationally and applying the expressions (5.16) and (5.18) we can write approximately

(5.40) $$\left(\frac{\Delta P}{\Delta T}\right)_{I_m^* = 0} \approx \frac{h - U^*}{vT} - \frac{2h}{vT^3} \frac{l_{umm}}{L_{mm}} \Delta T$$

the experimental verification of which may be suggested.

## B. *Thermoelectric phenomena*

Now similarly to the foregoing the theory of thermoelectric phenomena is developed. (The detailed treatment on the basis of the linear theory of these effects is to be found in DE GROOT's monograph [8] § 57.) The quasi-linear laws for the electric current $I_e^*$ and energy flow $I_u^*$ are the following :

(5.41) $$I_e^* = L_{ee}^* X_e + L_{eu}^* X_u$$

(5.42) $$I_u^* = L_{ue}^* X_e + L_{uu}^* X_u$$

where the forces are

(5.43) $$X_e = -\frac{\Delta \varphi}{T}$$

(5.44) $$X_u = -\frac{\Delta T}{T^2}$$

The new coefficients with the Onsager's constant coefficients — as the particular case of (2.9) — are in following relations :

(5.45) $$L_{ee}^* = L_{ee} + l_{eee} X_e + l_{eeu} X_u$$

(5.46) $$L_{eu}^* = L_{eu} + l_{eue} X_e + l_{euu} X_u$$

(5.47) $$L_{ue}^* = L_{ue} + l_{uee} X_e + l_{ueu} X_u$$

(5.48) $$L_{uu} = L_{uu} + l_{uue} X_e + l_{uuu} X_u$$

The quasi-linear laws (5.41) and (5.42) with the aid of these relations can be written

(5.49) $$I_e^* = \overbrace{A_1 \Delta\varphi + A_2 \Delta T}^{I_e^1} + \overbrace{a_1 (\Delta\varphi)^2 + a_2 \Delta\varphi \Delta T + a_3 (\Delta T)^2}^{I_e^2}$$

(5.50) $$I_u^* = \overbrace{B_1 \Delta\varphi + B_2 \Delta T}^{I_u^1} + \overbrace{b_1 (\Delta\varphi)^2 + b_2 \Delta\varphi \Delta T + b_3 (\Delta T)^2}^{I_u^2}$$

where the constants are

(5.51) $$A_1 = -\frac{L_{ee}}{T}; \quad A_2 = -\frac{L_{eu}}{T^2}$$

(5.52) $$B_1 = -\frac{L_{ue}}{T}; \quad B_2 = -\frac{L_{uu}}{T^2}$$

and

(5.53) $$a_1 = \frac{l_{eee}}{T^2}; \quad a_2 = \frac{l_{eeu} + l_{eue}}{T^3}; \quad a_3 = \frac{l_{euu}}{T^4}$$

(5.54) $$b_1 = \frac{l_{uee}}{T^2}; \quad b_2 = \frac{l_{ueu} + l_{uue}}{T^2}; \quad b_3 = \frac{l_{uuu}}{T^4}$$

ONSAGER's reciprocal relations are valid for the linear coefficients occurring in these constants

(5.55) $$L_{eu} = L_{ue}$$

whereas for the second order coefficients the relations following from 4.5

(5.56) $$2 l_{uee} = l_{eeu} + l_{eue}$$

(5.57) $$2 l_{euu} = l_{uue} + l_{ueu}$$

hold. Now we can utilize the equation (5.49) and (5.50) for the description of the thermoelectric phenomena in linear and non-linear approximations too. We consider two special cases.

**1.** *The Peltier effect.* The fundamental equations of this effect are attained with the condition $\Delta\varphi$ fix and $\Delta T = 0$. Then (5.49) and (5.50) will be :

(5.58) $$I_e^* = A_1 \Delta\varphi + a_1 (\Delta\varphi)^2$$

(5.59) $$I_u^* = B_1 \Delta\varphi + b_1 (\Delta\varphi)^2,$$

By dividing (5.59) with (5.58) the Peltier heat is obtained in the general case, when both linear and non-linear effects are considered. Hence

(5.60) $$\frac{I_u^*}{I_e^*} = \frac{L_{ue}^*}{L_{ee}^*} \equiv \pi^{**} = \frac{B_1 + b_1 \Delta\varphi}{A_1 + a_1 \Delta\varphi} = \frac{T L_{ue} - l_{uee} \Delta\varphi}{T L_{ee} - l_{eee} \Delta\varphi}$$

where $\pi^{**}$ is the Peltier heat of the total effect, which depends also now on the potential difference $\Delta\varphi$. The Peltier heat of linear and non-linear effects can also be interpreted, however, separately. By dividing the correspondent part-fluxes of (5.50) by the correspondent part-fluxes of (5.49) we get

$$\frac{I_u^1}{I_e^1} = \frac{L_{ue}}{L_e e} \equiv \pi \tag{5.61}$$

and

$$\frac{I_u^2}{I_e^2} = \frac{b_1}{a_1} = \frac{l_{uee}}{l_{eee}} \equiv \pi^* \tag{5.62}$$

where $\pi$ is the linear and $\pi^*$ is the Peltier heat of non-linear effect. Herewith the total energy flow under condition $\Delta T = 0$ will be :

$$I_u^* = \pi I_e^1 + \pi^* I_e^2 \tag{5.63}$$

and evidently it is true also now, that

$$\pi^{**} = \frac{I_u^*}{I_e^*} = \frac{\pi I_e^1 + \pi^* I_e^2}{I_e^1 + I_e^2} \tag{5.64}$$

*i. e.*

$$I_u^* = \pi^{**} (I_e^1 + I_e^2) = \pi^{**} I_e^* \tag{5.64'}$$

which are analogous with the expressions 5.30 and 5.30'.

**2.** *The Seebeck effect.* We can arrive to another particular case, if $\Delta T$ is fixed and $I_u^* \neq 0$, but stationary case characterized by condition $I_e^* = 0$ are considered. According to the possible approximation now also three subcases are possibl .

**a.** Confining ourselves to linear effects only, *i. e.*, $I_e^2 \equiv 0$, $I_e^* \equiv I_e^1 = 0$. Then with the use of the ordinary (5.55) ONSAGER's relation we get from the reduced (5.49) for the thermoelectric force

$$\frac{\Delta\varphi}{\Delta T} = -\frac{A_2}{A_1} = -\frac{1}{T}\frac{L_{eu}}{L_{ee}} = -\frac{\pi}{T} \tag{5.65}$$

which is the well known THOMSON's second relation.

**b.** The study of the pure non-linear idealized effects is of particular interest. Then $I_e^1 \equiv 0$ and the stationarity is required now for the non-linear part-fluxes $I_2^e$ only. I. e. with $I_e^2 = 0$ we arrive from the reduced (5.49) to the following second order equation :

$$a_1 \left(\frac{\Delta\varphi}{\Delta T}\right)^2 + a_2 \left(\frac{\Delta\varphi}{\Delta T}\right) + a_3 = 0 \tag{5.66}$$

from which two solutions are given for the thermoelectric force. Taking into consideration the second order coefficients of (5.53) with relation (5.56) the solutions in question are

$$(5.67)\qquad \left(\frac{\Delta\varphi}{\Delta T}\right)_{1,2} = \frac{-a_2 \pm \sqrt{a_2^2 - 4a_1 a_3}}{2a_1} = \frac{1}{T}\left(-\pi^* \pm \sqrt{\pi^{*2} \frac{l_{euu}}{l_{eee}}}\right)$$

where even the expression of (5.62) of the non-linear Peltier heat $\pi^*$ has been used. The physical meaning of (5.67) comparing it with the linear (5.65) is evident, thus (5.67) can be called Thomson's second relation for non-linear effects. According to (5.67) the equation (5.66) has real solutions only if one of the conditions

$$(5.68)\qquad l_{uee}^2 \geq l_{euu}\, l_{eee}$$

is fulfilled. From these conditions on a purely theoretical way important conclusions can be drawn. In any case the case of equality is of particularly interest which corresponds to a single real solution. In this case

$$(5.69)\qquad \frac{\Delta\varphi}{\Delta T} = -\frac{\pi^*}{T}$$

which is in complete analogy with the corresponding linear expression (5.65). Now what has been said for thermomechanical and mechanocaloric effects can be repeated. Namely according to our theory the conditions (5.58) signify, that the pure second order effects are such, that they are at best of an equal order of magnitude with the second order cross-effects. This means that the departure from linearity in a real situation arises from the fact, that mainly would cease to be constant.

**c.** Let us now consider the general case when the stationarity is required for the total flux of matter. In this general respect some information can be obtained from (5.49) writing it under stationarity condition as follows

$$(5.70)\qquad \frac{\Delta\varphi}{\Delta T} = -\frac{A_2}{A_1} - \frac{a_1}{A_1}\frac{(\Delta\varphi)^2}{\Delta T} - \frac{a_2 \Delta\varphi}{A_1} - \frac{a_3}{A_1}\Delta T$$

If the coefficients are substituted in this expression owing to (5.51) and (5.53) then in the non-linear order only the last from among the terms representing the cross effect is maintained we receive

$$(5.71)\qquad \frac{\Delta\varphi}{\Delta T} \approx -\frac{1}{T}\frac{L_{eu}}{L_{ee}} + \frac{l_{euu}}{T^3 L_{ee}}\Delta T$$

This relation can be immediately compared with the following experimental expression :

$$\Delta\varphi = a_1 (t - t_0) + a_2 (t - t_0)^2 \tag{5.72}$$

which gives in the case of several thermo-couples and in a very large range of temperature a good approximation. In this formula $a_1$ and $a_2$ are material constants whereas $t_0$ and $t$ are the temperatures of the cold and hot junctions in degrees centigrade. If a thermo-couple made of two metals whose junctions are kept at temperatures $T_1 = 273{,}16 + t_0$ (for cold junction) and $T_2 = 273{,}16 + t$ (for hot junction), then

$$\Delta T = T_2 - T_1 = t - t_0$$

Thus can be seen, that (5.71) goes over into the experimental formula (5.72) in that case if

$$a_1 = -\frac{1}{T}\frac{L_{eu}}{L_{ee}}; \quad a_2 = \frac{l_{euu}}{T^3 L_{ee}} \tag{5.73}$$

It is evident that after the determination of $a_1$ and $a_2$ in the knowledge of $L_{ee}$ (what is in Ohm's law with the $\sigma$ ordinary electrical conductivity in the relation $L_{ee} = T\sigma$) quantities $L_{eu}$ and $l_{euu}$ can be determined too.

### C. *States of minimum entropy production in non-linear case*

It is known that in the linear ONSAGER's theory the theorem of minimum entropy production is of great importance because of unambigous definition of the stationary state of different order is enabled. PRIGOGINE and DE GROOT formulated the theorem as follows [8] : "When a system, characterized by $f$ independent forces $X_1, X_2, \ldots X_f$, is kept in a state with fixed $X_1, X_2, \ldots X_r$ ($r$ is one of the numbers $0, 1, 2, \ldots, f$) and minimum entropy production $\sigma$ the fluxes $I_i$ with the index numbers $i = r + 1, r + 2, \ldots, f$ vanish." An isolated system the stationary state of zeroth order corresponds to the thermostatic equilibrium state. For the justification of this theorem the ONSAGER's reciprocal relations are used in the linear theory. In the following we should like to examine the theorem in the non-linear case developed in the precedings.

In the non-linear theory developed here the entropy production can be written with the aid of the time derivative of (1.1) and the use of (1.2) and (2.7) as follows :

$$\sigma \equiv \Delta \cdot S = \sum_{i} I_i^* X_i = \sum_{i,k} L_{ik} X_i X_k + \sum_{i,k,j} l_{ikj} X_i X_k X_j \tag{5.74}$$

where the last term is the entropy production arising from the non-linearity. When the values of $X_1, X_2, \ldots, X_r$ are fixed, the state of minimum entropy production is found from conditions :

$$\frac{\partial \sigma}{\partial X_i} = 0 \qquad (i = r+1, r+2, \ldots, f). \tag{5.75}$$

Now the case of two independent forces dealt with in detail in the foregoing for a better understanding of the conditions in our non-linear case. By this simplification the theoretical generality is not affected.

Considering (5.74) in the case of two independent forces $X_1$ and $X_2$, then taking $X_1$ as fixed and diferentiating $\sigma$ over $X_2$ (first order stationary state) the particular form of (5.75) will be :

$$\begin{aligned} \frac{\partial \sigma}{\partial X_2} = 0 = 2L_{22}X_2 + L_{12}X_2 + L_{21}X_1 + (l_{112} + l_{121} + l_{211})X_1^2 + \\ + 2(l_{122} + l_{212} + l_{211})X_1X_2 + 3l_{222}X_2^2 \end{aligned} \tag{5.76}$$

Making now use of ONSAGER's relation (4.5) and the conditions (4.6) completing those in our non-linear theory, *i. e.*,

$$L_{12} = L_{21} \tag{5.77}$$

$$\begin{cases} 2l_{211} = l_{112} + l_{121} \\ 2l_{122} = l_{221} + l_{212} \end{cases} \tag{5.78}$$

relations, then for the state of minimum entropy production we obtain

$$2(L_{21}X_1 + L_{22}X_2) + 3(l_{211}X_1^2 + 2l_{122}X_1X_2 + l_{222}X_2^2) = 0 \tag{5.79}$$

This condition of the state of minimum entropy production is just equal to the following expression :

$$2I_2^1 + 3I_2^2 = 0 \tag{5.80}$$

where $I_2^1$ is the linear and $I_2^2$ is the non-linear part-flux of the flux $I_2^*$. From this relation the following conclusions can be drawn. In the non-linear theory the state of minimum entropy production is attained, if for the linear and non-linear part-fluxes of the non fixed forces the conditions

$$2I_i^1 + 3I_i^2 = 0 \qquad (i = r+1,\ r+2, \ldots f) \tag{5.81}$$

are fulfilled. Characteristical for such a state is that the linear and non-linear part of the fluxes belonging to the non-fixed forces are compensating themselves according to (5.81). The state arising owing to the compensation in question does not correspond to the conception of stationary state of the linear theory for which

$$I_i^1 = 0 \qquad (i = r + 1,\ r + 2, \ldots, f) \tag{5.82}$$

conditions are valid. The analysis of the more detailed conditions can be performed only by taking into consideration the expression of the rate of entropy production and the "equations of motion" (3.1).

Herewith we have demonstrated several examples that in the precedings developed non-linear theory presents all the results which are also given by ONSAGER's original theory, supplementing those by such new relations, which are the straight generalization of ONSAGER's apparatus towards the non-linear orders.

The author is deeply indebted to Prof. Dr. G. SCHAY for his interest and encouragement.

## Summary

In connection with our preceding paper — referred to here as I — a possible non-linear theory is built up now also in a purely phenomenological way. We give here quasi-linear phenomenological laws between the thermodynamic fluxes and forces. Then the conductivities and resistances already depending on the non-equilibrium thermodynamic parameters. A representation of the "equations of motion" is given which is suitable for the description of the course in time of non-linear effects near the equilibrium state. The validity of the Onsager reciprocal relations is extended to the conductivity coefficients of quasi-linear laws. Additional relations are given. Finally, the theory is applied for the phenomena of thermal migration and thermoelectricity.

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