

## DERIVATION OF THE PHENOMENOLOGICAL EQUATIONS FROM THE MASTER EQUATION

### II. EVEN AND ODD VARIABLES \*)

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#### Synopsis

The analysis of Part I is extended to the case in which both even and odd variables are needed to describe the macroscopic state of a system. In linear approximation this leads to the usual phenomenological equations, obeying reciprocal relations in the form given by Casimir. The fluctuations about this average behaviour are also fully described by the master equation; as an example the Nyquist formula is derived.

1. *Introduction.* From the microscopic equations of motion for a system with many degrees of freedom it is possible to derive by means of suitable randomness assumptions the equation

$$\dot{P}_J = \sum_{J'} (W_{JJ'} P_{J'} - W_{J'J} P_J). \quad (1)$$

Here  $J$  labels the phase cells,  $P_J$  is the probability of finding the system in phase cell  $J$ , and  $W_{JJ'}$  is the transition probability per unit time from cell  $J'$  into  $J$ .<sup>1) 2)</sup> The construction of the phase cells may be considered as the 'kinematics' of the system, while the dynamics is contained in the matrix  $W_{JJ'}$ . Our problem is to derive the actually observed phenomenological equations from the 'master equation' (1).

An essential feature of the transition probabilities  $W_{JJ'}$  is that they satisfy some symmetry relation. This symmetry does not only give rise to the law of detailed balancing and to Onsager's reciprocal relations, but it is also often employed in proving that (1) leads to a stable equilibrium state<sup>\*\*</sup>). The precise form of the symmetry relation depends on the dynamics of the system and on the choice of phase cells, that is, on the choice of the macroscopically observed quantities. The simplest possible form is

$$W_{JJ'} G_{J'} = W_{J'J} G_J,$$

where  $G_J$  is the phase volume of cell  $J$ . This simple form obtains when

\*) Part I, dealing with even variables only, appeared in Physica **23** (1957), p. 707.

\*\*\*) See for example <sup>3)</sup>. Actually a weaker condition suffices, as mentioned by Stueckelberg and by Thomsen <sup>4)</sup>.

the Hamiltonian and all observed quantities are even variables, *i.e.*, when their values do not change if the microscopic motion of the system is reversed. This case was treated in Part I.

The present Part II deals with the next simple case. The Hamiltonian is still supposed to be an even variable, so that an external magnetic field and an over-all rotation are excluded. Among the observed quantities, however, there may now be odd variables, *i.e.*, variables whose values change sign on reversal of the motion of the system. In this case the phase cells occur in pairs: to each phase cell  $J$  corresponds another one, to be denoted by  $-J$ , in the following way. All even variables have the same values in  $J$  and  $-J$ , while the odd variables have opposite values in  $J$  and  $-J$ . One then has  $G_{-J} = G_J$ , and the symmetry relation is in this case<sup>1)</sup>

$$W_{JJ'}G_{J'} = W_{-J', -J}G_J. \quad (2)$$

Our task is to derive phenomenological equations from (1) and (2).

In this article only the linear form of the phenomenological equations, which is valid in the neighbourhood of equilibrium, is studied. The symmetry relation (2) then leads to the reciprocal relations that were first given by Casimir<sup>5) 6)</sup> as an extension of Onsager's relations to the case of odd variables. It is of some interest to note that these additional relations — which state that the coefficients connecting even variables with odd variables are anti-symmetrical in their subscripts — are of mechanical rather than of statistical nature. For they do not change sign when time is reversed. Accordingly it will appear in section 4 that they arise in a different way than the symmetrical reciprocal relations.

*2. Differential form of the master equation.* The observed quantities will again be denoted by  $A^{(r)}$ . It is convenient to introduce quantities  $\varepsilon_r$ , such that  $\varepsilon_r = +1$  for even  $A^{(r)}$  and  $\varepsilon_r = -1$  for odd  $A^{(r)}$ . The transition to  $a$ -space can be performed in the same way as in Part I. A phase cell then is no longer labelled by  $J$ , but by a set of parameters  $a_1, a_2, \dots$ , which are the values assumed by the observed quantities  $A^{(1)}, A^{(2)}, \dots$  in this cell. The parameters corresponding to  $-J$  are  $\varepsilon_1 a_1, \varepsilon_2 a_2, \dots$ . The master equation takes the form

$$\dot{P}(a) = \int \{W(a, a')P(a') - W(a', a)P(a)\} da', \quad (3)$$

and the symmetry relation (2) becomes

$$W(a, a') G(a') = W(\varepsilon a', \varepsilon a) G(a). \quad (4)$$

The latter relation is equivalent to the following statement: If  $P(a, t)$  and  $P^*(a, t)$  are two arbitrary functions satisfying (3), then one has (see appendix)

$$\int \frac{P^*(\varepsilon a) \dot{P}(a)}{G(a)} da = \int -\frac{P(a) \dot{P}^*(\varepsilon a)}{G(a)} da. \quad (5)$$

Under suitable conditions the integral equation (3) can be replaced by a Fokker-Planck differential equation, which may be written in the form

$$\dot{P} = \partial_r \{ \xi_{rs} G \partial_s (P/G) \} + \partial_r (\eta_r P) \quad (6)$$

(henceforth the tilde on  $\eta_r$  used in Part I will be omitted). Here  $\eta_r$  and  $\xi_{rs} = \xi_{sr}$  are certain functions of  $a_1, a_2, \dots$ , depending on the specific  $W(a, a')$ . If  $f(A)$  is any function of the observed quantities  $A^{(1)}, A^{(2)}, \dots$ , the average of  $f(A)$  is given by

$$\langle f(A) \rangle = \int f(a) P(a) da.$$

The time variation of this average value is

$$\begin{aligned} (d/dt) \langle f(A) \rangle &= \int f(a) \dot{P}(a) da \\ &= \langle G^{-1} \partial_s \xi_{rs} G \partial_r f \rangle - \langle \eta_r \partial_r f \rangle. \end{aligned} \quad (7)$$

In particular one has

$$(d/dt) \langle a_m \rangle = \langle G^{-1} \partial_s \xi_{ms} G \rangle - \langle \eta_m \rangle. \quad (8)$$

3. *The symmetry relation.* The functions  $\xi_{rs}(a)$  and  $\eta_r(a)$  have certain properties corresponding to the symmetry relation (4), which will now be derived. Substituting (6) into the left-hand side of (5) one obtains

$$\int \frac{P^*(\varepsilon a)}{G} \partial_r \xi_{rs}(a) G \partial_s \frac{P(a)}{G} da + \int \frac{P^*(\varepsilon a)}{G} \partial_r \eta_r(a) P(a) da. \quad (9)$$

The right-hand side of (5) is, since  $G(\varepsilon a) = G(a)$ , \*

$$\int \frac{P(a)}{G} \varepsilon_r \partial_r \xi_{rs}(\varepsilon a) G \varepsilon_s \partial_s \frac{P^*(\varepsilon a)}{G} da + \int \frac{P(a)}{G} \varepsilon_r \partial_r \eta_r(\varepsilon a) P^*(\varepsilon a) da.$$

As (9) must be identical to (10) for every function  $P^*$ , one must have

$$\begin{aligned} \partial_r \xi_{rs}(a) G \partial_s \{ P(a)/G \} - \varepsilon_r \varepsilon_s \partial_s \xi_{rs}(\varepsilon a) G \partial_r \{ P(a)/G \} + \\ + \partial_r \eta_r(a) P(a) + \varepsilon_r \eta_r(\varepsilon a) G \partial_r \{ P(a)/G \} = 0. \end{aligned} \quad (11)$$

As this must be true for every function  $P$ , the coefficients of the second-order derivatives  $\partial_r \partial_s P$  must certainly be zero:

$$\xi_{rs}(a) - \varepsilon_r \varepsilon_s \xi_{rs}(\varepsilon a) = 0. \quad (**)$$

Consequently the first line in (11) vanishes. In the second line one may collect the first-order derivatives  $\partial_r P$  and put their coefficients equal to zero:

$$\eta_r(a) + \varepsilon_r \eta_r(\varepsilon a) = 0. \quad (13)$$

\*) When applying the convention that double subscripts imply summation, the subscript of  $\varepsilon_r$  should not be counted.

\*\*) For this conclusion it is necessary to remember that  $\xi_{rs} = \xi_{sr}$  according to the definition of  $\xi_{rs}$ .

Finally, the coefficient of  $P$  itself must be zero:

$$\partial_r \eta_r(a) - \varepsilon_r \eta_r(\varepsilon a) \partial_r \log G = 0;$$

or, using (13) \*),

$$\partial_r \{ \eta_r(a) G \} = 0. \tag{14}$$

Thus we have found that the symmetry relation (4) entails the three relations (12), (13), and (14), and *vice versa*: if (12), (13), (14) are satisfied, then (5) holds and hence (4). Clearly, when all observed quantities are even, (12) reduces to nothing, whereas (13) yields  $\eta_r(a) \equiv 0$ , which was the result of Part I. Our present result can be made more concrete by the following remark. If (6) is transformed by changing  $t$  into  $-t$  and  $a_r$  into  $\varepsilon_r a_r$ , the equation becomes

$$-\dot{P} = \varepsilon_r \partial_r \xi_{rs}(\varepsilon a) G \varepsilon_s \partial_s (P/G) + \varepsilon_r \partial_r \eta_r(\varepsilon a) P,$$

or, using (12) and (13),

$$\dot{P} = -\partial_r \xi_{rs}(a) \partial_s (P/G) + \partial_r \eta_r(a) P.$$

Thus the first term on the right changes sign, but the second one remains the same. Consequently, the symmetry relation has the effect of identifying the two terms on the right of (6) as respectively the irreversible and the reversible part of the time variation of  $P$  \*\*). Similarly in (7) and (8) the two terms on the right represent irreversible and reversible changes.

4. *The linear approximation.* The equations (8) become linear if one has

$$\begin{aligned} G(a) &= G(0) e^{-\frac{1}{2} a_r a_r a_s}, \\ \xi_{rs}(a) &= \xi_{rs}(0) \equiv \xi_{rs}, \\ \eta_r(a) &= \eta_r(0) + \eta_{rs} a_s, \end{aligned} \tag{15}$$

with constant coefficients  $g_{rs}$ ,  $\xi_{rs}$  and  $\eta_{rs}$ . In that case (8) reduces to

$$(d/dt) \langle a_m \rangle = -\xi_{ms} g_{sp} \langle a_p \rangle - \eta_m(0) - \eta_{ms} \langle a_s \rangle.$$

This leads to the usual phenomenological equations <sup>6)</sup>

$$\dot{\alpha}_m = L_{ms} X_s = -L_{ms} g_{sp} \alpha_p,$$

provided that one has  $\eta_m(0) = 0$  and that one puts

$$L_{ms} = \xi_{ms} + \eta_{mp} (g^{-1})_{ps}. \tag{16}$$

We shall show that indeed  $\eta_m(0)$  vanishes, and that the  $L_{ms}$  defined in this way do satisfy Onsager's reciprocal relations as extended by Casimir to odd variables. More specifically, the following will turn out to be true.

\*) Equation (14) can also be obtained more directly by noting that the equilibrium distribution  $P(a) = G(a)$  must satisfy (6).

\*\*) This is of course only correct because we have chosen the special form (6) for the Fokker-Planck equation.

If  $A^{(m)}$  and  $A^{(s)}$  are both even or both odd, then the last term in (16) is zero, so that  $L_{ms} = \xi_{ms}$  and hence  $L_{ms} = L_{sm}$ . If, on the other hand,  $A^{(m)}$  and  $A^{(s)}$  are of different type, then  $\xi_{ms} = 0$ , and

$$\eta_{mp} (g^{-1})_{ps} = -\eta_{sp} (g^{-1})_{pm}. \quad (17)$$

All this follows from (12), (13) and (14), when applied to the linearised expressions (15).

Firstly, (12) gives  $\xi_{rs} = \varepsilon_r \varepsilon_s \xi_{rs}$ , so that  $\xi_{rs}$  can only differ from zero if  $\varepsilon_r$  and  $\varepsilon_s$  are both  $+1$  or both  $-1$ . Secondly, (13) gives

$$(1 + \varepsilon_r) \eta_r(0) + (1 + \varepsilon_r \varepsilon_s) \eta_{rs} a_s \equiv 0.$$

Hence  $\eta_{rs}$  can only differ from zero if  $\varepsilon_r = +1$ ,  $\varepsilon_s = -1$  or *vice versa*. Thirdly, (14) gives

$$\eta_{rr} - \{\eta_r(0) + \eta_{rs} a_s\} g_{rp} a_p \equiv 0. \quad (18)$$

Hence  $\eta_r(0) g_{rp} a_p \equiv 0$ , which can only be true if all  $\eta_r(0)$  are zero, because  $g_{rp}$  is a non-singular matrix. Moreover, (18) gives  $\eta_{rs} g_{rp} a_s a_p \equiv 0$ , or

$$\eta_{rs} g_{rp} + \eta_{rp} g_{rs} = 0;$$

this is equivalent with the equation (17), which was to be proved. Thus we have completed the proof of the properties mentioned above, including Casimir's extension of Onsager's relations\*).

In order to summarise the results, we write temporarily  $\alpha_k$  for the even variables, and  $\beta_\kappa$  for the odd variables; the corresponding 'forces' or 'affinities' are  $X_k = -g_{kl} \alpha_l$  and  $Y_\kappa = -g_{\kappa\lambda} \beta_\lambda$ . The matrix of the phenomenological coefficients  $L_{mn}$  then looks as follows.

	$X_l$	$Y_\lambda$
$\dot{\alpha}_k$	$L_{kl} = \xi_{kl}$	$L_{k\lambda} = \eta_{k\nu} (g^{-1})_{\nu\lambda}$
$\dot{\beta}_\kappa$	$L_{\kappa l} = \eta_{\kappa h} (g^{-1})_{hl}$	$L_{\kappa\lambda} = \xi_{\kappa\lambda}$

As already mentioned in the introduction, the antisymmetry  $L_{k\lambda} = -L_{\lambda k}$  arises in a different way than the symmetries  $L_{kl} = L_{lk}$  and  $L_{\kappa\lambda} = L_{\lambda\kappa}$ . These latter symmetries are based on the symmetry of  $\xi_{rs}$ , which is not restricted to the linear approximation; whereas the antisymmetry of  $L_{k\lambda}$  has no counterpart in the non-linear case.

It is sometimes convenient to write the phenomenological equations in the form

$$\begin{aligned} \dot{\alpha}_k &= \xi_{kl} X_l + \eta_{k\lambda} \beta_\lambda, \\ \dot{\beta}_\kappa &= \eta_{\kappa l} \alpha_l + \xi_{\kappa\lambda} Y_\lambda. \end{aligned} \quad (19)$$

For the benefit of practical applications we add the explicit form of (6)

\*) One may also conclude from (18) that  $\eta_{rr} = 0$ , but this embodies no new information, since we have already found that all diagonal elements of  $\eta_{rs}$  vanish.

in linear approximation:

$$\begin{aligned} \dot{P}(a, b, t) = & \xi_{kl} \partial_k \partial_l P + \xi_{\kappa\lambda} \partial_\kappa \partial_\lambda P \\ & - \xi_{kl} g_{li} \partial_k (a_i P) - \xi_{\kappa\lambda} g_{\lambda i} \partial_\kappa (b_i P) \\ & + \eta_{k\lambda} b_\lambda \partial_k P + \eta_{\kappa l} a_l \partial_\kappa P. \end{aligned} \tag{20}$$

5. *The Brownian motion approach.* In the linear approximation (8) may be written

$$(d/dt) \langle a_m \rangle = - \zeta_{ms} \langle a_s \rangle, \tag{21}$$

where

$$\zeta_{ms} = \xi_{mp} g_{ps} + \eta_{ms}.$$

Similarly one finds as a special application of (7), in linear approximation

$$(d/dt) \langle a_m a_n \rangle = 2\xi_{mn} - \zeta_{ms} \langle a_s a_n \rangle - \zeta_{ns} \langle a_m a_s \rangle. \tag{22}$$

In the same way as in section 4 of Part I, we now consider a fictitious stochastic process described by the set of equations

$$\dot{a}_m = - \zeta_{ms} a_s + \kappa_m(t), \tag{23}$$

where  $\kappa_m(t)$  are fictitious random 'forces'. The stochastic properties of these 'forces' are to be adjusted in such a way that the averages  $\bar{a}_m$  and  $\overline{a_m a_n}$  satisfy the same equations (21) and (22).

Obviously, to obtain (21) it suffices to put

$$\overline{\kappa_m(t)} = 0. \tag{24}$$

In order to obtain (22) one must have

$$\overline{\kappa_m(t) \kappa_n(t')} = C_{mn} \delta(t - t') \tag{25}$$

with appropriately chosen  $C_{mn}$ . To find the  $C_{mn}$  we shall solve both (23) and (22) explicitly and compare both results\*). This can be done by applying a linear transformation to the  $a_m$ ,

$$\begin{aligned} a_m &= S_{mp} a'_p, \\ \kappa_m(t) &= S_{mp} \kappa'_p(t), \\ C_{mn} &= S_{mp} S_{nq} C'_{pq}, \end{aligned} \tag{26}$$

in such a way that  $\zeta_{mn}$  is cast into diagonal form \*\*):

$$\zeta'_{mn} = (S^{-1})_{mp} \zeta_{pq} S_{qn} = \zeta'_{(m)} \delta_{mn}.$$

\*) An apparently easier method would consist in constructing the Fokker-Planck equation belonging to the stochastic process (23), and adjust the  $C_{mn}$  in it so as to make this equation coincide with the differential equation for  $P(a, t)$ . However, since the construction of the Fokker-Planck equation requires the solution of (23) anyway, this method amounts to practically the same as the one used above.

\*\*) As  $\zeta_{mn}$  is not symmetrical, its diagonalisation may be impossible if two or more roots of the characteristic equation coincide. One then obtains solutions of the type  $te^{-t}$ , as for instance in the case of a critically damped harmonic oscillator. However, this only happens when a certain relation, involving both the  $\xi_{mn}$  and the  $\eta_{mn}$ , is obeyed. Since the  $\xi$ 's and the  $\eta$ 's refer to different physical mechanisms, this case must be considered exceptional.

In the new variables  $a'_m$  the set of equations (23) becomes

$$\dot{a}'_m = -\zeta'_{(m)} a'_m + \kappa'_m(t)$$

(no summing over  $m$ !). This is simply Langevin's equation for Brownian motion, whose solution is

$$a'_m(t) = a'_m(0) e^{-\zeta'_{(m)} t} + e^{-\zeta'_{(m)} t} \int_0^t \kappa'_m(t') e^{\zeta'_{(m)} t'} dt'$$

One subsequently finds, using (24) and (25),

$$\overline{a'_m(t) a'_n(t)} = \overline{a'_m(0) a'_n(0)} e^{-(\zeta'_{(m)} + \zeta'_{(n)}) t} + C'_{mn} (\zeta'_{(m)} + \zeta'_{(n)})^{-1} \{1 - e^{-(\zeta'_{(m)} + \zeta'_{(n)}) t}\}. \quad (27)$$

The same transformation (26) makes it possible to solve (22). In the new variables (22) becomes

$$(d/dt) \langle a'_m a'_n \rangle = 2\xi'_{mn} - (\zeta'_{(m)} + \zeta'_{(n)}) \langle a'_m a'_n \rangle.$$

The solution of this differential equation is clearly

$$\langle a'_m a'_n \rangle_t = \langle a'_m a'_n \rangle_0 e^{-(\zeta'_{(m)} + \zeta'_{(n)}) t} + 2\xi'_{mn} (\zeta'_{(m)} + \zeta'_{(n)})^{-1} \{1 - e^{-(\zeta'_{(m)} + \zeta'_{(n)}) t}\}.$$

This is identical with (27) if  $C'_{mn} = 2\xi'_{mn}$ ; or, transforming back to the original quantities,  $C_{mn} = 2\xi_{mn}$ . Substitution into (25) yields

$$\overline{\kappa_m(t) \kappa_n(t')} = 2\xi_{mn} \delta(t - t'). \quad (28)$$

Thus we have derived from the master equation the stochastic properties of the random 'forces'. A special example of (28) is the Nyquist formula, as will be shown in the next section.

The result (28) is analogous to the one found in Part I for the case without odd variables\*). It should be noted, however, that (28) involves the  $\xi_{mn}$ , which are now only identical with the phenomenological coefficients  $L_{mn}$  when  $m$  and  $n$  refer both to even or both to odd variables. The random forces acting on even variables and those acting on odd variables are mutually uncorrelated.

6. *Example; derivation of the Nyquist formula.* Consider an electric circuit with condenser  $C$ , self-induction  $L$  and resistance  $R$ ; the latter is in contact with a heat bath with (constant) heat capacity  $c$ . In equilibrium the charge  $Q$  on the condenser and the current  $I$  are zero, and let the temperature be  $T_0$ . A non-equilibrium state is macroscopically determined by the values of  $Q$  and  $I$ , whereas the temperature  $T$  of the heat bath is connected with  $Q$  and  $I$  by the energy law:

$$cT_0 = cT + Q^2/2C + \frac{1}{2}LI^2.$$

\*) In equation (29) of Part I a factor 2 on the right has erroneously been omitted. Similarly in equation (30) a factor 4 should be added.

The entropy difference with the equilibrium state is

$$S - S_{\text{eq}} = c \log T - c \log T_0 = \\ = - (1/2T_0C) Q^2 - (L/2T_0) I^2 = k \log G.$$

Hence there is one even variable  $\alpha \equiv Q$  and one odd variable  $\beta \equiv I$ ; their associated affinities are

$$X = - Q/kT_0C = - V/kT_0, \quad Y = - (L/kT_0) I.$$

The phenomenological equations are

$$\dot{\alpha} = \beta = - (kT_0/L) Y, \\ \dot{\beta} = - (1/LC) \alpha - (R/L) \beta = (kT_0/L) X + (kT_0R/L^2) Y.$$

Clearly the reciprocal relations are satisfied.

Comparison with (19) yields

$\xi_{11} = 0$	$\eta_{12} = 1$
$\eta_{21} = - 1/LC$	$\xi_{22} = kT_0R/L^2$

Thus the differential equation for  $P(a, b, t) = P(Q, I, t)$  becomes

$$\frac{\partial P}{\partial t} = \frac{kT_0R}{L^2} \frac{\partial^2 P}{\partial I^2} + \frac{1}{L} \left( RI - \frac{Q}{C} \right) \frac{\partial P}{\partial I} + I \frac{\partial P}{\partial Q} + \frac{R}{L} P.$$

This equation describes the evolution of the joint distribution of charge and current in an ensemble of identical electric circuits.

From this equation one may compute, like in the previous section, the evolution of  $\langle Q \rangle$ ,  $\langle I \rangle$ , and of  $\langle Q^2 \rangle$ ,  $\langle QI \rangle$  and  $\langle I^2 \rangle$ . One may then define a fictitious stochastic process

$$\dot{Q} = I + \kappa_1(t) \\ \dot{I} = - (1/LC)Q - (R/L) I + \kappa_2(t) \tag{29}$$

and adjust the stochastic properties of  $\kappa_1(t)$  and  $\kappa_2(t)$  in such a way that the same values are obtained for  $\bar{Q}$ ,  $\bar{I}$  and  $\bar{Q}^2$ ,  $\bar{QI}$ ,  $\bar{I}^2$ . According to (24) and (25) one must put  $\overline{\kappa_1(t)} = 0$ , and

$$\overline{\kappa_1(t) \kappa_1(t')} = 0, \quad \overline{\kappa_1(t) \kappa_2(t')} = 0.$$

This amounts to  $\kappa_1(t) = 0$ . This result was to be expected, because the relation between  $Q$  and  $I$  is not of stochastic nature. Next one has  $\overline{\kappa_2(t)} = 0$  and

$$\overline{\kappa_2(t) \kappa_2(t')} = (2kT_0R/L^2) \delta(t - t').$$

According to the definition (29) of  $\kappa_2(t)$ , one may regard  $L\kappa_2(t)$  as a fictitious random electromotive force  $E(t)$ , which satisfies

$$\overline{E(t) E(t')} = 2kT_0R \delta(t - t').$$

From this auto-correlation function of  $E(t)$  follows the spectral density  $E_{\omega}^2$

according to standard methods (Wiener-Khintchine theorem, see *e.g.* references <sup>7)</sup> and <sup>8)</sup>). One finds

$$E_{\omega}^2 = (1/\pi) \int_{-\infty}^{+\infty} \overline{E(t) E(t + \tau)} \cos \omega \tau \, d\tau = (2/\pi) kT_0 R,$$

which is the Nyquist formula <sup>9)</sup> <sup>8)</sup> \*).

#### APPENDIX

*Proof of equation (5).* Equation (1) may be written more simply as

$$\dot{P}_J = \sum_{J'} W_{JJ'} P_{J'}, \quad (30)$$

where the summation now includes the term with  $J' = J$ ,  $W_{JJ}$  being defined by

$$W_{JJ} = - \sum_{J' \neq J} W_{J'J}.$$

(The reason why this term was written separately in (2) was that it is the only negative term.) It is essential to note that, according to its derivation, (2) remains valid for  $J = J'$ . One now finds easily with the aid of (30),

$$\sum_J \frac{P_{-J}^* \dot{P}_J}{G_J} = \sum_{J'} P_{-J}^* \frac{W_{JJ'}}{G_J} P_{J'} = \sum_{J'} P_{J'} \frac{W_{-J', -J}}{G_{J'}} P_{-J}^* = \sum_{J'} \frac{P_{J'} \dot{P}_{-J}^*}{G_{J'}}.$$

On replacing the summation on  $J$  with an integration in  $a$ -space, this relation takes the form (5).

*Note.* Professor S. R. de Groot and Dr. P. Mazur kindly informed me that they have recently developed a very similar analysis, which will be published in a forthcoming monograph on thermodynamics of non-equilibrium states.

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\* ) For the derivation of the Nyquist formula even a simpler circuit, with resistance and condenser but no self-induction would have sufficed.