ON ONSAGER'S PRINCIPLE OF MICROSCOPIC REVERSIBILITY *)

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Summary

After a short synopsis of Onsager's theory of reciprocal relations in irreversible processes, the theory is applied to a number of simple examples. In the first place we consider the thermomolecular pressure difference; this example will also offer an opportunity of discussing the "quasi-thermostatic" methods. In the second place the conduction of heat is studied and it is shown that Onsager's relation leads to \( \sum \partial_i L_{ij} = 0 \) rather than to \( L_{ij} = 0 \). Finally we discuss the conduction of electricity by first deriving a relation of symmetry for an arbitrary four-pole from which a symmetry relation for the conductivity tensor is then easily deduced.

1. Introduction

There exist a number of relations pertaining to irreversible processes — the symmetry of the tensor of heat conduction and Kelvin's relations, between thermoelectric quantities are among the best known examples — that appear to be universally valid although they cannot be proved by thermodynamics or by considerations on macroscopic symmetry. Yet when a theory of the irreversible process based on a particular model is worked out, these relations are always confirmed. N. Bohr 1) was the first to demonstrate this clearly in the case of Kelvin's relations and he found that their validity was ultimately owing to the circumstance that the fundamental equations governing the motion of individual particles are symmetric with respect to past and future, or, mathematically speaking, that they are invariant under a transformation \( t \rightarrow (-t) \). More recently Onsager 2) has tried to show that a general class of reciprocal relations can be derived from this principle of microscopic reversibility without having recourse to any particular model and he has applied his theory to numerous examples, including those mentioned above, thus adding a new and very fundamental principle to macroscopic thermodynamics. But although we do not doubt the essential truth of Onsager's ideas, his application of these ideas to particular cases is, in our opinion, not always entirely satisfactory. In this paper we shall endeavour to treat a few simple cases somewhat more explicitly, but for completeness sake we shall first give a short summary of the general theory. In this way we shall also have an opportunity of discussing the essential assumptions involved in Onsager's analysis **).

2. General Theory

a) Theory of fluctuations. Let us consider an adiabatically insulated system

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**) The whole subject was extensively discussed in a colloquium organized during the spring of 1944 by the "Nederlandsche Natuurkundige Vereeniging"; the author would like to express his thanks to many of those present, especially to Prof. H. A. Kramers and Mr. B. D. H. Tellegen for valuable discussions.
and a number of variables \( x^i (i = 1, \ldots, n) \) which in the equilibrium state assume values \( x^i_0 \). We put

\[
x^i = x^i_0 + \alpha^i.
\]

The entropy in a state differing from the equilibrium state will be \( S = S_0 + \Delta S \), where \( \Delta S \) is of the form

\[
\Delta S = -\frac{1}{2} \sum_{i,k} S_{ik} \alpha^i \alpha^k,
\]

where \( S_{ik} \) is a positive definite form. The probability distribution for the \( \alpha^i \) is given by

\[
W (\alpha^1, \ldots, \alpha^n) \, d\alpha^1 \cdots d\alpha^n = \frac{e^{k\Delta S} \, d\alpha^1 \cdots d\alpha^n}{\int \cdots \int e^{k\Delta S} \, d\alpha^1 \cdots d\alpha^n},
\]

where \( k \) is Boltzmann's constant. Define

\[
\gamma_i = \sum_k S_{ik} \alpha^k,
\]

then it is easily shown that

\[
\frac{\gamma_i \alpha^i}{k} = \delta^i_i,
\]

\((\delta^i_i = 0 \text{ whenever } i \neq l; \quad \delta^i_i = 1)\)

According to the fundamental notions of statistical mechanics this average may be interpreted either as an average over a microcanonical ensemble of systems, or as a time average for one single system.

By solving eq. (3) for \( \alpha^i \):

\[
\alpha^i = \sum_i S^{ji} \gamma_j,
\]

where \( S^{ji} \) is the reciprocal matrix to \( S_{ij} \), we find

\[
\alpha^i \alpha^i = k S^{ji}.
\]

The variables \( \gamma_i \) defined by (3) will in the following be designed as conjugate variables.

b) Microscopic reversibility. Suppose that the \( \alpha^i \) are even functions of the velocities of the individual particles, so that they are invariant when \( t \) is replaced by \(-t\). The fact that the future behaviour of a system having specified values of \( \alpha^i \) at a time \( t \), on the average, is identical with its past behaviour, can be expressed by the equation

\[
\overline{\alpha^i (t + \tau) \alpha^i (t), \ldots, \alpha^n (t)} = \overline{\alpha^i (t - \tau) \alpha^i (t), \ldots, \alpha^n (t)},
\]

the suffixes denoting that the values remain fixed, so that the average is taken over a section of the microcanonical ensemble corresponding to these values. Multiplying by \( \alpha^i (t) \) and taking the average over all possible values of \( \alpha^i (t), \ldots, \alpha^n (t) \) we find

\[
\overline{\alpha^i (t) \alpha^k (t + \tau)} = \overline{\alpha^i (t) \alpha^k (t - \tau)},
\]

where the average is now again over the total microcanonical ensemble and may also be interpreted as an average over \( t \).
Similarly, if a number of variables \( \beta^x \) are odd functions of the velocities, we have

\[
\beta^x (t + \tau) \beta^y (0), ..., \beta^y (t) = - \beta^x (t - \tau) \beta^y (0), ..., \beta^y (t)
\]  

and again we find

\[
\beta^x (t) \beta^y (t + \tau) = \beta^x (t) \beta^y (t - \tau).
\]  

Let us now combine a number of even quantities \( \alpha^i (i = 1, ..., \nu) \) and a number of odd quantities \( \beta^i (\lambda = 1, ..., \nu) \). Then

\[
\alpha^i (t + \tau) \alpha^i (0), ..., \alpha^i (t), ..., \beta^i (t) = \alpha^i (t - \tau) \alpha^i (0), ..., \alpha^i (t), ..., -\beta^i (t)
\]  

\[
\beta^i (t + \tau) \alpha^i (0), ..., \alpha^i (t), ..., \beta^i (t) = -\beta^i (t - \tau) \alpha^i (0), ..., \alpha^i (t), ..., -\beta^i (t)
\]  

from which it follows

\[
\alpha^i (t) \beta^i (t + \tau) = -\alpha^i (t) \beta^i (t - \tau).
\]  

As an illustration we may quote the brownian motion of a galvanometer: if we call the deflection \( \alpha \) and the angular velocity \( \beta \) these quantities will satisfy eq. (12).

If a magnetic field is present the equations (8), (10) and (12) are no longer valid, but must be replaced by

\[
\alpha^i (t) \alpha^i (t + \tau, H) = \alpha^i (t) \alpha^i (t - \tau, -H),
\]  

and so on.

c) Regression of fluctuations. Let us transform the macroscopic equations, which are of the form

\[
\dot{\alpha}^i = \sum_k L^i_k \alpha_k
\]  

into the form

\[
\dot{\alpha}^i = \sum_k p^{ik} \gamma_k
\]  

We assume that the same equations also describe the average behaviour of fluctuations in the following sense: there exists a time interval \( \tau_1 \) such that for \( \tau > \tau_1 \), but \( \tau \ll T \) (where \( T \) is the time in which, according to our equations, a disturbance of equilibrium is appreciably reduced)

\[
\alpha^i (t + \tau) \alpha^i (0), ..., \alpha^i (t) - \alpha^i (t) = + \tau \sum_k p^{ik} \gamma_k (t).
\]  

This assumption calls for some comment. In the first place it is not legitimate to write \( \dot{\alpha}^i \) instead of \( \frac{1}{\tau} \alpha^i (t + \tau) - \alpha^i (t) \) for it is a consequence of microscopic reversibility that the mean value of this derivative is zero. The time interval \( \tau_1 \) is required to establish a state of steady flow and the condition that \( \tau_1 \) be small as compared with the time in which the deviation from equilibrium is appreciably reduced imposes evidently some sort of limitation on the mechanics of the system. It should be borne in mind, however, that many applications of the macroscopic equations are based on essentially the same condition. Further it is by no means evident that a set of equations, applying originally to deviations large compared with fluctuations, can also be applied to the average behaviour of these fluctuations themselves. Of course, the fact that the macroscopic equations are linear partly justifies an extrapolation to very small deviations, but in principle one may imagine a pseudo-linearity holding only at reasonably large ampli-
tudes. The acceptance of eq. (15) is really a new hypothesis and although the same hypothesis is made in the theory of brownian motion, we do not think that it can rigorously be proved without referring in some way or another to kinetic theory. The author feels satisfied, however, that it will hold in all cases that can be treated by means of the usual method based on the equation of Maxwell and Boltzmann.

Once eq. (15) is accepted, the analysis is very simple. Multiplying by \( \alpha^i(t) \) and taking the average we find

\[
\overline{\alpha^i(t)} \langle \alpha^i(t + \tau) - \alpha^i(t) \rangle = \tau p_{ii} \mu k.
\]

In the same way

\[
\overline{\alpha^i(t)} \langle \alpha^j(t + \tau) - \alpha^j(t) \rangle = \tau p_{ij} \mu k.
\]

But according to eq. (8) the left-hand sides of these equations are equal; hence

\[ p_{ii} = p_{ii} \] (16)

This is Onsager's fundamental relation. The same relation holds if the macroscopic equations are expressed in terms of variables of the "\( \beta \)-type":

\[ p_{\beta \mu} = p_{\alpha \nu} \] (17)

If both even and odd quantities enter into the equations the situation is slightly more complicated. In this case the entropy, being an even function, is a sum of two terms

\[ \Delta S = -\frac{1}{2} \sum S_{\alpha \alpha} \alpha^i \alpha^k + \sum S_{\beta \beta} \beta^i \beta^k \]

and also the conjugate quantities fall into two groups, that are even and odd in time:

\[ \gamma_i = \sum S_{\alpha \alpha} \alpha^i \quad \gamma_\mu = \sum S_{\beta \beta} \beta^\mu. \]

The macroscopic equations are

\[ \dot{\alpha}^i = \sum p_{\alpha \alpha}^m \gamma_m + \sum p_{\alpha \beta}^\mu \gamma_\mu \]
\[ \dot{\beta}^i = \sum p_{\beta \alpha}^m \gamma_m + \sum p_{\beta \beta}^\mu \gamma_\mu \]

and a similar procedure as before leads to:

\[ p_{ii} = p_{ii}, \quad p_{ij} = p_{ji}, \quad -p_{ij} = p_{ji}. \] (18)

If a magnetic field is present, these equations have to be replaced by

\[ p_{ii}^i(H) = p_{ii}^i(-H) \] (16’)

and so on.

3. Thermomolecular pressure difference; relation to pseudo-thermodynamic methods

As a first example, we shall discuss a case where the application of the general theory is perfectly simple and straightforward. We consider a vessel containing an ideal gas and divided into two equal compartments by a wall with a small hole. Let \( n_1 \) and \( n_2 \) be the number of grammolecules in the two compartments and \( T_1, T_2 \) the respective temperatures.
In equilibrium
\[ n_1 = n_2 = n; \quad T_1 = T_2 = T. \]

The fluctuations of numbers and temperatures are subject to the conditions
\[ \delta n_1 + \delta n_2 = 0; \quad \delta (n_1 T_1 + n_2 T_2) = 0. \]

The second condition, which expresses the fact that the total energy is constant, leads to
\[ n (\delta T_1 + \delta T_2) + \delta n_2 \left( \delta T_2 - \delta T_1 \right) = 0. \]

Starting from the well-known expression
\[ S = n C_v \log T + R \log V - n R \log n \]
a simple calculation yields
\[ \Delta S = -\frac{n C_v}{T^2} (\delta T_2)^2 - \frac{R}{n} (\delta n_2)^2. \]

We shall now introduce a new set of variables:
\[ a_1 = \delta n_2 \]
\[ a_2 = \delta U_2 = (\delta n_2 \cdot T + \delta T_2 \cdot n) C_v. \]

Then
\[ \Delta S = -\frac{C_v + R}{n} a_1^2 - \frac{1}{nT^2} C_v a_2^2 + \frac{2C_v}{nT} a_1 a_2. \]

The conjugate quantities are
\[ \gamma_1 = 2 \frac{C_v + R}{n} a_1 - 2 \frac{C_v}{nT} a_2 = 2 \left( \frac{R}{n} \delta n_2 - \frac{C_v}{T} \delta T_2 \right), \]
\[ \gamma_2 = -\frac{2}{nT} a_1 + \frac{2}{nT^2} C_v a_2 = 2 \frac{\delta T_2}{T^2}. \]

Let us now write down the equations for the transport through the hole in the wall:
\[ \delta n_2 = A \delta n_2 + B \frac{\delta T_2}{T^2}, \]
\[ \delta U_2 = Q \delta n_2 + w \frac{\delta T_2}{T^2}. \]

The first equation expresses that a flow of gas may be caused both by a difference of concentration and by a difference of temperature (since we assume that a linear approximation is valid, we have \( \delta T_1 = -\delta T_2 \) and \( T_2 - T_1 = 2\delta T_2 \)); the second equation states that energy is transported by the moving molecules, but also by conduction of heat.

Transforming to conjugate variables:
\[ \dot{a}_1 = \frac{1}{2} \frac{An}{R} \gamma_1 + \frac{1}{2} \left( \frac{AnTC_v}{R} + B \right) \gamma_2, \]
\[ \dot{a}_2 = \frac{1}{2} \frac{AnQ}{R} \gamma_1 + \frac{1}{2} \left( \frac{AnTC_vQ}{R} + BQ + w \right) \gamma_2. \]
We can now apply Onsager's general equation:
\[
\frac{AnQ}{R} = \frac{AnTC_v}{R} + B,
\]
or
\[
\frac{B}{A} = \frac{Q - TC_v}{R} n.
\]
Suppose that a difference of temperature is artificially maintained, but that we wait until \(\delta n = 0\). Then we have
\[
\delta n = -\frac{B}{A} \frac{\delta T}{T^2}
\]
or
\[
\frac{\delta n}{n} = -\frac{Q/T - C_v}{R} \frac{\delta T}{T}.
\]
Onsager's theory gives a general relation between the difference of concentration caused by a difference of temperature and the energy carried by moving molecules. Of course the value of \(Q\) can only be derived from a kinetic theory. If the diameter of the hole is small compared with the free path, a simple calculation gives:
\[
Q = (C_v + \frac{1}{2} R) T,
\]
leading to
\[
n = \text{Const} \frac{1}{\sqrt{T}},
\]
or
\[
p = \text{Const.} \sqrt{T},
\]
which is Knudsen's well-known formula. For a large orifice on the other hand
\[
Q = (C_v + R) T
\]
and it follows
\[
P_1 = P_2.
\]
Our example affords also an interesting illustration of the quasi-thermodynamic procedure used by several authors. Let us write our equations in the form
\[
\dot{\alpha}_1 = a_{11} \gamma_1 + a_{12} \gamma_2,
\]
\[
\dot{\alpha}_2 = a_{21} \gamma_1 + a_{22} \gamma_2.
\]
Consider first a stationary state with \(\dot{\alpha}_1 = 0\), then
\[
\gamma_1 = -\frac{a_{12}}{a_{11}} \gamma_2.
\]
Next we carry out a virtual displacement \(\delta\alpha_1\) (in our case: we transport a number of molecules) and we assume that the quantity \(\delta\alpha_2\), which is displaced along with \(\delta\alpha_1\), is the same as if \(\gamma_2\) were zero, so that
\[
\delta\alpha_2 = \frac{a_{21}}{a_{11}} \delta\alpha_1,
\]
which means here that \(\delta U = Q \delta n\). It is now assumed that the change of entropy due to the virtual displacement vanishes:
The addition of an antisymmetric tensor to $L_{ik}$ has no physical consequences as long as eq. (18) is fulfilled, and it is therefore not to be expected that Onsager's theory correctly applied will lead to the result $L_{il}(tL_{kl} - tL_{kl}) = 0$. To apply Onsager's theory we must begin with a discussion of temperature fluctuations. Let us consider a solid of total volume $V$ and divide it into a number of cells $V_s$. Let us consider such a cell, $T_s$, the temperature in each respective cell, $T_0$, being the equilibrium temperature and $C$ the specific heat per unit volume, then the change of entropy will be given by:

$$\Delta S = \sum_s \int_{T_0}^{T_s} C \frac{dT}{T} = \sum_s T_s \int_{T_0}^{T_s} C dT - \frac{1}{T_0^2} \sum_s V_s \int (T - T_0) C dT + \ldots =$$

$$= -\frac{1}{2} \frac{C}{T_0^2} \sum_s (\Delta T_s)^2 V_s + \ldots$$

where we have put $T_s - T_0 = \Delta T_s$. The variable conjugate to $\Delta T_s$ is thus found to be $(C/T_0^2) V_s \Delta T_s$ and eq. (4) gives

$$V_s \Delta T_s \Delta T_r = k \frac{T_0^2}{C} \delta_{sr}.$$ 

Let us sum this equation over a number of cells $S_i$, then

$$\sum_{S_i} V_{Si} \Delta T_{Si} \Delta T_r = 0, \text{ when } S_i \neq r \text{ for all } S_i,$$

$$\sum_{S_i} V_{Si} \Delta T_{Si} \Delta T_r = k T_0^2/C, \text{ when } S_i = r \text{ for one } S_i.$$
Passing to the limit of very small cells
\[ \int \int \int \Delta T(x, y, z) \Delta T(x', y', z') \, dx \, dy \, dz = \begin{cases} 0, \\ kT_0^2/C \end{cases} \]
the upper or lower result holding according as \( x', y', z' \) is outside or inside the range of integration. This can also be written in the symbolical form
\[ \Delta T(x, y, z) \Delta T(x', y', z') = (kT_0^2/C) \delta(x-x') \delta(y-y') \delta(z-z'). \]

We introduce the Fourier components of \( \Delta T \):
\[ \Delta T(x) = \left( \frac{1}{2\pi} \right)^{3/2} \int \int \int e^{i(k \cdot x)} \, a(k) \, dk_1 \, dk_2 \, dk_3 \]
with
\[ a(k) = \left( \frac{1}{2\pi} \right)^{3/2} \int \int \int e^{-i(k \cdot x)} \Delta T(x) \, dx \, dy \, dz \]
and, \( \Delta T \) being real
\[ a(k) = a(-k)^*. \]

It is easily seen that \( a(k) \) and \( a(k)^* \) are conjugate variables satisfying the equation
\[ a(k) a(k)^* = (kT_0^2/C) \delta(k_1-k_1') \delta(k_2-k_2') \delta(k_3-k_3'). \]

Next we determine the rate of change of \( a(k) \):
\[ \dot{a}(k) = \left( \frac{1}{2\pi} \right)^{3/2} \int \int \int e^{-i(k \cdot x)} \Delta \dot{T}(x) \, dx \, dy \, dz = \]
\[ = \left( \frac{1}{2\pi} \right)^{3/2} \int \int \int e^{-i(k \cdot x)} \frac{1}{C} \sum_{nm} \partial_n (L_{nm} \partial_m \Delta T) \, dx \, dy \, dz. \]

We assume that \( L_{ik} \) is a function of \( x, y, z \) which vanishes at infinity. By partial integration we find:
\[ \begin{align*}
\dot{a}(k) &= \left( \frac{1}{2\pi} \right)^{3/2} \frac{1}{C} \int \int \left[ -\sum_{nm} k_n k_m L_{nm} + i k_n (\partial_m L_{nm}) \right] e^{-i(k \cdot x)} \Delta T \, dx \, dy \, dz \\
&= \left( \frac{1}{2\pi} \right)^{3/2} \frac{1}{C} \int \int \sum_{nm} (-k_n k_m L_{nm} - i k_n (\partial_m L_{nm})) e^{i((k-k') \cdot x)} \, dx \, dy \, dz.
\end{align*} \]
Introducing the Fourier integral for \( \Delta T \)
\[ \dot{a}(k) = \left( \frac{1}{2\pi} \right)^{3/2} \frac{1}{C} \int \int \sum_{nm} (-k_n k_m L_{nm} - i k_n (\partial_m L_{nm})) e^{i((k-k') \cdot x)} \, dx \, dy \, dz. \]

where \( L_{nm} \) is the Fourier component of \( L_{nm} \), or, finally
\[ \dot{a}(k) = \left( \frac{1}{2\pi} \right)^{3/2} \frac{1}{C} \int \int \sum_{nm} \{ -k_n k_m L_{nm} (k-k') - (k_n\' - k_m\') k_n L_{nm} (k-k') \} a(k') \, dk_1' \, dk_2' \, dk_3' = \]
\[ = \left( \frac{1}{2\pi} \right)^{3/2} \frac{1}{C} \int \int \sum_{nm} \{ -k_n k_m L_{nm} (k-k') \} a(k') \, dk_1' \, dk_2' \, dk_3'. \]

We can now use Onsager's relation of symmetry bearing in mind that the conjugate variable to \( a(k) \) is proportional to \( a(k)^* \) or \( a(-k) \):
\[ \sum_{nm} k_n k_m L_{nm} (k+k') = \sum_{nm} k_n k_m L_{nm} (k+k'), \]
or
\[ \sum_{nm} k_n k_m L_{nm} (k+k') = 0. \]
Putting \( k + k' = K \) so that \( k' = K - k \), we find:
\[
\sum k_m (K_n - k_n) L_{[nm]} (K) = \sum k_m K_n L_{[nm]} (K) = 0.
\]
This must hold for arbitrary \( k_m \), whence
\[
\sum K_n L_{[nm]} (K) = 0.
\]
Now we have
\[
L_{[nm]} (K) = \left( \frac{1}{2\pi} \right)^{3/2} \iiint e^{-i (K \cdot x)} L_{[nm]} (x) \, dx \, dy \, dz
\]
and
\[
\sum K_m L_{[nm]} (K) = \left( \frac{1}{2\pi} \right)^{3/2} \iiint \sum_m -i (\partial_m L_{[nm]}) e^{-i (K \cdot x)} \, dx \, dy \, dz.
\]
Therefore we find ultimately
\[
\sum \partial_m L_{[nm]} = 0.
\]
This equation can be obtained somewhat more directly though less rigorously by using the \( \Delta T \) instead of their Fourier components and making a liberal use of \( \delta \)-functions. We have:
\[
C \Delta T = \sum \partial_m \{ L_{nm} \partial_m \Delta T \} =
\]
\[
= \iiint -\sum \partial_m' \{ \delta (x-x') \delta (y-y') \delta (z-z') \} L_{nm} (x') \partial_m' \Delta T (x') \, dx' \, dy' \, dz' =
\]
\[
= \iiint \sum \partial_m' \{ L_{nm} (x') \partial_m' [\delta (x-x') \delta (y-y') \delta (z-z')] \} \Delta T (x') \, dx' \, dy' \, dz',
\]
where \( \partial_m' \) denotes differentiation with respect to \( x_m' \).

This is of the form
\[
\Delta T (x) = \iiint K (x, x') \Delta T (x') \, dx' \, dy' \, dz',
\]
and Onsager's principle gives:
\[
\sum \partial_m' [L_{nm} (x') \partial_m' \{ \delta (x_1-x_1') \delta (x_2-x_2') \delta (x_3-x_3') \} ] =
\]
\[
= \sum \partial_m [L_{nm} (x) \partial_m \{ \delta (x_1-x_1') \delta (x_2-x_2') \delta (x_3-x_3') \} ].
\]
In order to draw a conclusion from this equation we multiply by an arbitrary function \( f (x') \) and integrate. We obtain:
\[
\sum \partial_m (L_{nm} \partial_m f) = \sum \partial_m (L_{nm} \partial_n f)
\]
or
\[
\sum \partial_n (L_{nm}) \partial_m f = \sum \partial_m (L_{nm}) \partial_n f.
\]
and, \( f \) being arbitrary,
\[
\sum \partial_n L_{[nm]} = 0.
\]
Our result is, that an antisymmetric component of \( L_{ik} \) has no observable physical consequences whatever and it is permissible to put it equal to zero. It must be zero if we agree that \( L_{ik} \) is zero in vacuum and that \( L_{ik} \) for a given substance does not depend on the shape of the sample. Though it would of course be very foolish not to accept this convention it is interesting to note that Onsager's relation by itself does not compel us to do so.
An analysis similar to that given above applies to all cases where a current, the divergence of which has a physical meaning, is given in terms of the gradient of a thermodynamic variable.

5. Conduction of electricity

In agreement with the remark at the end of the preceding section, the conduction of electricity in solids might be treated on similar lines as the conduction of heat. There is, however, an additional complication inasmuch as the divergence of the current gives the rate of change of the charge density, whereas the current is determined by the gradient of the electric potential which is in general a complicated function of the charge. Therefore we prefer to use a different method. We consider a sample of a conducting solid with four leads attached at the points A, B, C, D. If we restrict ourselves to situations where the current $I_1$ entering at A is equal to the current going out at B, and the current $I_2$, entering at C is equal to the current going out at D, and if $V_1$ and $V_2$ be the potential differences between A and B and between C and D, then there will hold a set of equations:

$$V_1 = A_{11} I_1 + A_{12} I_2,$$
$$V_2 = A_{21} I_1 + A_{22} I_2,$$

or

$$I_1 = a_{11} V_1 + a_{12} V_2,$$
$$I_2 = a_{21} V_1 + a_{22} V_2.$$

Let us now suppose that a large capacitor $C_1$ is connected to A and B and similarly a capacitor $C_2$ to C and D. Then $I_1$ and $I_2$ are the derivatives of the charges on these capacitors and moreover the potentials are, apart from a constant factor, the conjugate variables to these charges. Therefore Onsager’s relation gives:

$$a_{12} = a_{21} \text{ or } A_{12} = A_{21}.$$

This equation of symmetry will hold for an arbitrary fourpole as long as no magnetic field is present. In that case:

$$a_{12} (H) = a_{21} (-H).$$

It is interesting to note that our equations may also be written as

$$I_1 = b_{11} V_1 + b_{12} I_2,$$
$$V_2 = b_{21} V_1 + b_{22} I_2.$$

Now if C and D are not connected to a capacitor but to a self-inductor, the magnetic flux in this inductor, which is proportional to $I_2$, may be regarded as a dynamical variable and $V_2$ is its derivative with respect to time. So we can again write down an equation of symmetry. But now $I_2$ is an odd quantity, $V_1$ an even quantity, hence

$$b_{12} = -b_{21},$$

in accordance with what is found by direct transformation. The author is indebted to Mr. Tellegen for drawing his attention to this case, which made him aware of the necessity of making a distinction between even and odd quantities in the formulation of the general theory.

We shall now investigate the symmetry relations for the tensor of electric resistance:

$$E_i = \Sigma R_{ik} i_k,$$
where \( E_i \) are the components of the electric field strength and \( i_k \) the components of the current density. We shall arrive at the following theorem: if for a certain substance a relation \( a_{ik} = a_{ki} \) holds for all possible fourpoles, then we have also \( R_{ik} = R_{ki} \). To establish this theorem we consider a thin rectangular plate in the \( xy \)-plane, with its corners at \((0, 0), (0, l), (b, 0), (b, l)\) and with leads \( C \) and \( D \) attached to the sides parallel to the \( x \)-axis at points with arbitrary but equal \( x \)-coordinate \( x_c \), the leads \( A \) and \( B \) being similarly attached to the sides parallel to the \( y \)-axis at points with \( y \)-coordinate \( y_A \). We have:

\[
V_1 = A_{11} I_1 + A_{12} I_2
\]

\[
V_2 = A_{21} I_1 + A_{22} I_2
\]

with

\[
A_{12} = A_{21},
\]

but on the other hand

\[
V_1 = \int_0^b (R_{11} i_1 + R_{12} i_2)_{y=y_A} \, dx.
\]

Now

\[
I_2 = \int_0^b i_2 \, dx
\]

and hence:

\[
V_1 = R_{12} I_2 + R_{11} \int_0^b i_1 \, dx_{y=y_A}.
\]

Specializing to the case \( I_1 = 0 \)

\[
A_{12} = R_{12} + (R_{11}/I_2) \int_0^b i_1 \, dx_{y=y_A}.
\]

In the same way we can calculate \( V_2 \) and our symmetry relation becomes

\[
R_{12} + R_{11} \int_0^b i_1 \, dx_{y=y_A} \int_0^{y_A} i_1 \, dy_{I_1=0} = R_{21} + R_{22} \int_0^b i_2 \, dx_{x=x_c} \int_0^{y_A} i_1 \, dy_{I_1=0}.
\]

This equation holds for arbitrary values of \( x_c \) and \( y_A \). Let us then suppose that we write it down for \( n \times m \) arrangements corresponding to

\[
x_c = 0, b/n, 2b/n, \ldots, (n-1)b/n
\]

\[
y_A = 0, l/m, 2l/m, \ldots, (m-1)l/m
\]

and let us sum the result:

\[
R_{12} + R_{11} \sum_{m,n} \int_0^b i_1 \, dx_{y=y_A} \int_0^{y_A} i_1 \, dy_{I_1=0} / I_{2 \cdot mn} = R_{21} + R_{22} \sum_{m,n} \int_0^b i_2 \, dx_{x=x_c} \int_0^{y_A} i_1 \, dy_{I_1=0} / I_{1 \cdot mn}.
\]

On the left-hand side we shall first carry out the summation over \( m \) which leaves the distribution of current unchanged, since this depends only on the position of the points \( C \) and \( D \) through which \( I_2 \) enters and goes out. But in the limit of very high \( m \), the expression \((1/m) \sum_{m=0}^n i_1 \) is proportional to \( \int i_1 \, dy \) and therefore it is zero when \( I_1 = 0 \). In the same way we find that the sum over \( n \) at the right-hand side vanishes, which establishes the desired result.

It is of some interest to note that the symmetry of one special fourpole is not sufficient for deriving the symmetry of the conductivity tensor; it is only the symmetry of all fourpoles which enables us to obtain this result.
Further one might be astonished that we arrive here at once at the symmetry relation and not at the relation

$$\sum \partial_i R_{ik} = 0.$$ 

The reason is that our analysis tacitly assumes that $R_{ik}$ is identical for the whole series of $m,n$ fourpoles and that $R_{ik} = 0$ in vacuum. If we had chosen to treat also the conduction of heat by using "thermal fourpoles" we should also at once have found $L_{ik} = 0$.

If a magnetic field is present we have

$$R_{ik} (H) = R_{ik} (-H),$$

a relation which was first given by Meixner 3).

This result may also be expressed by the statement that the symmetric tensor $R_{(ik)}$ is an even function of $H$, the antisymmetric tensor $R_{[ik]}$ an odd function of $H$. Introducing the axial vector $R$ (where $R_1 = R_{[23]}$ and so on) we can write

$$E_i = \sum_k R_{(ik)} i_k + [I \times R]_i.$$

The total electric field strength is given by a symmetric resistance tensor which is an even function of $H$ and a Hall vector which is an odd function of $H$. The situation was discussed by Gerritsen and the author 4) in connection with the conductivity of bismuth in a magnetic field and we refer to their note for further details.

Eindhoven, February 1945

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1) N. Bohr. Studier over Metallernes Elektronteori, Copenhagen 1913.
4) H. B. G. Casimir and A. N. Gerritsen, Physica 8, 1107, 1941.