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On Onsager's Principle of Microscopic Reversibility

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I. 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 endeavor 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 and a number of variables x^i $(i=1,\cdots,n)$ which in the equilibrium state assume values $x_0{}^i$. We put

$$x^i=x_0{}^i+\alpha^i.$$

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

$$\Delta S=-\tfrac{1}{2}\sum_{i,k} S_{ik}\alpha^i\alpha^k, \tag{1}$$

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

$$W(\alpha^1,\cdots,\alpha^n)d\alpha^1\cdots d\alpha^n =\frac{e^{k\Delta S}d\alpha^1\cdots d\alpha^n}{\int\cdots\int e^{k\Delta S}d\alpha^1\cdots d\alpha^n}, \tag{2}$$

where k is Boltzmann's constant. Define

$$\gamma_i=\textstyle\sum_k S_{ik}\alpha^k; \tag{3}$$

then it is easily shown that

$$\langle\gamma_i\alpha^l\rangle_{\text{Av}}=k\delta_i{}^l \tag{4}$$

$$(\delta_i{}^l=0 \text{ whenever } i\neq l;\ \delta_i{}^i=1).$$

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 α^i, we have

$$\alpha^i=\textstyle\sum_l S^{il}\gamma_l, \tag{5}$$

where S^{ij} is the reciprocal matrix to S_{ij}, we find

$$\langle\alpha^i\alpha^j\rangle_{\text{Av}}=kS^{ij}. \tag{6}$$

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[1] N. Bohr, *Studier over Metallernes Elektronteori* (Copenhagen, 1913).

[2] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

* 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 Professor H. A. Kramers and Mr. B. D. H. Tellegen for valuable discussions.

The variable γ_l defined by (3) will in the following be designed as *conjugate* variables.

(b) Microscopic Reversibility

Suppose that the α^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 behavior of a system having specified values of α^i at a time t is, on the average, identical with its past behavior, can be expressed by the equation

$$\langle\alpha^k(t+\tau)_{\alpha^1(t),\cdots,\alpha^n(t)}\rangle_{\mathrm{Av}}=\langle\alpha^k(t-\tau)_{\alpha^1(t),\cdots,\alpha^n(t)}\rangle_{\mathrm{Av}}, \quad (7)$$

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 $\alpha^l(t)$ and taking the average over all possible values of $\alpha^1(t), \cdots, \alpha^n(t)$ we find

$$\langle\alpha^l(t)\alpha^k(t+\tau\rangle_{\mathrm{Av}}=\langle\alpha^l(t)\alpha^k(t-\tau)\rangle_{\mathrm{Av}}, \quad (8)$$

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 β^κ are odd functions of the velocities, we have

$$\langle\beta^\lambda(t+\tau)_{\beta^1(t),\cdots,\beta^\nu(t)}\rangle_{\mathrm{Av}}$$
$$=\langle-\beta^\lambda(t-\tau)_{-\beta^1(t),\cdots,-\beta^\nu(t)}\rangle_{\mathrm{Av}}, \quad (9)$$

and again we find

$$\langle\beta^\lambda(t)\beta^\mu(t+\tau)\rangle_{\mathrm{Av}}=\langle\beta^\lambda(t)\beta^\mu(t-\tau)\rangle_{\mathrm{Av}}. \quad (10)$$

Let us now combine a number of even quantities α^i $(i=1, \cdots, \nu)$ and a number of odd quantities β^λ $(\lambda=1, \cdots, \nu)$. Then

$$\begin{aligned}&\langle\alpha^k(t+\tau)_{\alpha^1(t),\cdots,\alpha^n(t);\,\beta^1(t),\cdots,\beta^\nu(t)}\rangle_{\mathrm{Av}}\\&\quad=\langle\alpha^k(t-\tau)_{\alpha^1(t),\cdots,\alpha^n(t);\,-\beta^1(t),\cdots,-\beta^\nu(t)}\rangle_{\mathrm{Av}},\\&\langle\beta^\mu(t+\tau)_{\alpha^1(t),\cdots,\alpha^n(t);\,\beta^1(t),\cdots,\beta^\nu(t)}\rangle_{\mathrm{Av}}\\&\quad=\langle-\beta^\mu(t-\tau)_{\alpha^1(t),\cdots,\alpha^n(t);\,-\beta^1(t),\cdots,-\beta^\nu(t)}\rangle_{\mathrm{Av}}\end{aligned} \quad (11)$$

from which it follows

$$\langle\alpha^l(t)\beta^\nu(t+\tau)\rangle_{\mathrm{Av}}=\langle-\alpha^l(t)\beta^\nu(t-\tau)\rangle_{\mathrm{Av}}. \quad (12)$$

As an illustration we may quote the Brownian motion of a galvanometer: if we call the deflection α and the angular velocity β these quantities will satisfy Eq. (12).

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

$$\langle\alpha^l(t)\alpha^k(t+\tau, H)\rangle_{\mathrm{Av}}=\langle\alpha^l(t)\alpha^k(t-\tau, -H)\rangle_{\mathrm{Av}}, \quad (8')$$

and so on.

(c) Regression of Fluctuations

Let us transform the macroscopic equations, which are of the form

$$\dot{\alpha}^i=\textstyle\sum_k L_k{}^i\alpha_k \quad (13)$$

into the form

$$\dot{\alpha}^i=\textstyle\sum_k p^{ik}\gamma_k. \quad (14)$$

We assume that the same equations also describe the average behavior of fluctuations in the following sense: there exists a time interval τ_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; then

$$\langle\alpha^i(t+\tau)_{\alpha^i(t),\cdots,\alpha^n(t)}-\alpha^i(t)\rangle_{\mathrm{Av}}$$
$$=+\tau\textstyle\sum_k p^{ik}\gamma_k(t). \quad (15)$$

This assumption calls for some comment. In the first place it is not legitimate to write $\dot{\alpha}^i$ instead of $\{\alpha^i(t+\tau)-\alpha^i(t)\}/\tau$, for it is a consequence of microscopic reversibility that the mean value of this derivative is zero. The time interval τ_1 is required to establish a state of steady flow and the condition that τ_1 is small 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 behavior 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 amplitudes. 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 $\alpha^l(t)$ and taking the average we find

$$\langle\alpha^l(t)\{\alpha^i(t+\tau)-\alpha^i(t)\}\rangle_{\text{Av}}=\tau p^{il}\cdot k.$$

In the same way

$$\langle\alpha^i(t)\{\alpha^l(t+\tau)-\alpha^l(t)\}\rangle_{\text{Av}}=\tau p^{li}\cdot k.$$

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

$$p^{li}=p^{il}. \tag{16}$$

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

$$p^{\lambda\mu}=p^{\mu\lambda}. \tag{17}$$

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

$$\Delta S=-\tfrac{1}{2}\{\sum S_{ik}\alpha^i\alpha^k+\sum S_{\lambda\nu}\beta^\lambda\beta^\nu\},$$

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

$$\gamma_i=\sum S_{ik}\alpha^k,\quad \gamma_\lambda=\sum S_{\lambda\mu}\beta^\mu.$$

The macroscopic equations are

$$\dot{\alpha}^i=\sum\nolimits_m p^{im}\gamma_m+\sum\nolimits_\lambda p^{i\lambda}\gamma_\lambda,$$
$$\dot{\beta}^\lambda=\sum\nolimits_m p^{\lambda m}\gamma_m+\sum\nolimits_\mu p^{\lambda\mu}\gamma_\mu,$$

and a similar procedure as before leads to:

$$p^{il}=p^{li}, \tag{18a}$$
$$p^{\lambda\mu}=p^{\mu\lambda}, \tag{18b}$$
$$p^{i\lambda}=\gamma p^{\lambda i}. \tag{18c}$$

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

$$p^{il}(H)=p^{li}(-H), \tag{18'}$$

and so on.

3. THERMOMOLECULAR PRESSURE DIFFERENCE; RELATION TO PSEUDO-THERMOSTATIC 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 gram molecules 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

$$\delta n_1+\delta n_2=0;\quad \delta(n_1T_1+n_2T_2)=0.$$

The second condition, which expresses the fact that the total energy is constant, leads to

$$n(\delta T_1+\delta T_2)+\delta n_2(\delta T_2-\delta T_1)=0.$$

Starting from the well-known expression

$$S=nC_v\log T+R\log V-nR\log n,$$

we find a simple calculation yields

$$\Delta S=-\frac{nC_v}{T^2}(\delta T_2)^2-\frac{R}{n}(\delta n_2)^2.$$

We shall now introduce a new set of variables:

$$\alpha_1=\delta n_2,\quad \alpha_2=\delta U_2=(\delta n_2\cdot T+\delta T_2\cdot n)C_v.$$

Then,

$$\Delta S=-\frac{C_v+R}{n}\alpha_1{}^2-\frac{1}{nT^2C_v}\alpha_2{}^2+\frac{2C_v}{nT}\alpha_1\alpha_2.$$

The conjugate quantities are

$$\gamma_1=2\frac{C_v+R}{n}\alpha_1-2\frac{C_v}{nT}\alpha_2=2\left(\frac{R}{n}\delta n_2-\frac{C_v}{T}\delta T_2\right);$$

$$\gamma_2=-\frac{2C_v}{nT}\alpha_1+\frac{2}{nT^2C_v}\alpha_2=2\frac{\delta T_2}{T^2}.$$

Let us now write down the equations for the transport through the hole in the wall:

$$\delta\dot{n}_2=A\,\delta n_2+B\frac{\delta T_2}{T^2},$$

$$\delta U_2=Q\delta\dot{n}_2+w\frac{\delta T_2}{T^2}.$$

The first equation expresses the fact 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, we have:

$$\dot{\alpha}_1 = \frac{1}{2}\frac{An}{R}\gamma_1 + \frac{1}{2}\left(\frac{AnTC_v}{R} + B\right)\gamma_2,$$

$$\dot{\alpha}_2 = \frac{1}{2}\frac{AnQ}{R}\gamma_1 + \frac{1}{2}\left(\frac{AnTC_vQ}{R} + BQ + w\right)\gamma_2.$$

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 $\delta\dot{n} = 0$. Then we have

$$\delta n = -\frac{B}{A}\frac{\delta T}{T^2}$$

or

$$\frac{\delta n}{n} = -\frac{Q/T - C_v}{R}\cdot\frac{\delta T}{T}.$$

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:

$$Q = (C_v + \tfrac{1}{2}R)T,$$

leading to

$$n = \frac{\text{const.}}{\sqrt{T}},$$

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-thermostatic procedure used by several authors. Let us write our equations in the form

$$\dot{\alpha}_1 = \alpha_{11}\gamma_1 + \alpha_{12}\gamma_2,$$
$$\dot{\alpha}_2 = \alpha_{21}\gamma_1 + \alpha_{22}\gamma_2.$$

Consider first a stationary state with $\dot{\alpha}_1 = 0$, then

$$\gamma_1 = -\frac{\alpha_{12}}{\alpha_{11}}\gamma_2.$$

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 γ_2 were zero, so that

$$\delta\alpha_2 = \frac{\alpha_{21}}{\alpha_{11}}\delta\alpha_1,$$

which means here that $\delta U = Q\delta n$. It is now assumed that the change of entropy due to the virtual displacement vanishes:

$$\delta S = -(\gamma_1\delta\alpha_1 + \gamma_2\delta\alpha_2) = \left(-\frac{\alpha_{12}}{\alpha_{11}} + \frac{\alpha_{21}}{\alpha_{11}}\right)\gamma_2\delta\alpha_1 = 0,$$

and hence,

$$\alpha_{12} = \alpha_{21}.$$

Evidently this way of arriving at the relation of symmetry cannot be justified at all by thermodynamic theory. Since, however, all applications of quasi-thermostatic reasoning are based on essentially the same equations, it can now be understood why this procedure has usually led to correct results.

4. CONDUCTION OF HEAT IN CRYSTALS

The equations for the conduction of heat in crystals can be written in the form

$$w_i = \textstyle\sum_k L_{ik}\partial_k T;$$

here ∂_k denotes the derivative with respect to x_k, and we write x_1, x_2, x_3 for the Cartesian coordinates x, y, z. Now this system is certainly not of the form (14), for in a three-dimensional case w_i is not the time derivative of a thermodynamic variable. As a matter of fact, w_i is not even uniquely defined, for only its divergence has a direct macroscopical physical meaning. This means that we may add to L_{ik} a quantity p_{ik}, as long as

$$\sum_{ik} \partial_i(p_{ik}\partial_k T) = \sum_{ik} \{\partial_i(p_{ik})\partial_k T + p_{ik}\partial_i\partial_k T\} = 0.$$

This equation is satisfied for an arbitrary distribution of temperature, if

$$p_{ik} = -p_{ki}$$

and

$$\textstyle\sum_i \partial_i p_{ik} = 0. \qquad (18)$$

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 $L_{[ik]} = \frac{1}{2}(L_{ik} - L_{ki}) = 0$. 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 T_s be 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

$$\Delta S = \textstyle\sum_s V_s \displaystyle\int_{T_0}^{T_s} \frac{C}{T} dT = \textstyle\sum_s V_s \displaystyle\frac{1}{T_0}\int_{T_0}^{T_s} C dT$$

$$-\frac{1}{T_0^2}\sum V_s \int_{T_0}^{T_s} (T - T_0) C dT + \cdots$$

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

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

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

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

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

$$\sum_{Si} \langle V_{Si}\Delta T_{Si}\Delta T_r\rangle_{\text{Av}} = kT_0^2/C, \text{ when } S_i = r \text{ for one } S_i.$$

Passing to the limit of very small cells, we find

$$\left\langle \int\int\int \Delta T(x, y, z)\Delta T(x', y', z') dxdydz \right\rangle_{\text{Av}} = \begin{cases} 0 \\ kT_0^2/C, \end{cases}$$

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

$$\langle \Delta T(x, y, z)\Delta T(x', y', z')\rangle_{\text{Av}} = (kT_0^2/C)\delta(x - x')\delta(y - y')\delta(z - z').$$

We introduce the Fourier components of ΔT:

$$\Delta T(x) = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \int\int\int e^{i(\mathrm{kx})} a(\mathrm{k}) dk_1 dk_2 dk_3,$$

with

$$a(\mathrm{k}) = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \int\int\int e^{-i(\mathrm{kx})} \Delta T(\mathrm{x}) dxdydz$$

and, ΔT being real,

$$a(\mathrm{k}) = a(-\mathrm{k})^*.$$

It is easily seen that $a(\mathrm{k})$ and $a(\mathrm{k})^* C/T_0^2$ are conjugate variables satisfying the equation

$$\langle a(\mathrm{k})a(\mathrm{k}')^*\rangle_{\text{Av}} = (kT_0^2/C)\delta(k_1 - k_1') \times \delta(k_2 - k_2')\delta(k_3 - k_3').$$

Next we determine the rate of change of $a(\mathrm{k})$:

$$\dot{a}(\mathrm{k}) = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \int\int\int e^{-i(\mathrm{kx})} \Delta\dot{T}(\mathrm{x}) dxdydz$$

$$= \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \int\int\int e^{-i(\mathrm{kx})} \frac{1}{C} \sum_{nm} \partial_n \times (L_{nm}\partial_m \Delta T) dxdydz.$$

We assume that L_{ik} is a function of x, y, z which vanishes at infinity. By partial integration we find:

$$\dot{a}(\mathrm{k}) = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \frac{1}{C} \int\int\int \left[-\sum_{nm} \{k_n k_m L_{nm} + ik_n(\partial_m L_{nm})\} \right] e^{-i(\mathrm{kx})} \Delta T dxdydz.$$

Introducing the Fourier integral for ΔT

$$\dot{a}(k) = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \frac{1}{C} \int\int\int \cdot \int\int\int \sum_{nm} (-k_n k_m L_{nm} - ik_n(\partial_m L_{nm})) e^{i((\mathrm{k}' - \mathrm{k})\cdot \mathrm{x})} dxdydz \times \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} a(\mathrm{k}') dk_1' dk_2' dk_3'$$

$$= \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \frac{1}{C} \int\int\int \sum_{nm} \{ -k_n k_m L_{nm}(\mathrm{k} - \mathrm{k}') - (k_m' - k_m) k_n L_{nm}(\mathrm{k} - \mathrm{k}') \} a(\mathrm{k}') dk_1' dk_2' dk_3',$$

where $L_{nm}(k)$ is the Fourier component of L_{nm}, or, finally

$$\dot{a}(\mathrm{k})=\left(\frac{1}{2\pi}\right)^{\frac{3}{2}}\frac{1}{C}\int\int\int-\sum_{nm}k_nk_m'L_{nm}(\mathrm{k}-\mathrm{k}')\times a(\mathrm{k}')dk_1dk_2dk_3.$$

We can now use Onsager's relation of symmetry bearing in mind that the conjugate variable to $a(\mathrm{k})$ is proportional to $a(\mathrm{k})^*$ or $a(-\mathrm{k})$:

$$\sum_{nm}k_n'k_mL_{nm}(\mathrm{k}+\mathrm{k}')=\sum_{nm}k_m'k_nL_{nm}(\mathrm{k}+\mathrm{k}'),$$

or

$$\sum_{nm}k_mk_n'L_{[nm]}(\mathrm{k}+\mathrm{k}')=0.$$

Putting $\mathrm{k}+\mathrm{k}'=\mathrm{K}$ so that $\mathrm{k}'=\mathrm{K}-\mathrm{k}$, we find:

$$\sum_{mn}k_m(K_n-k_n)L_{[nm]}(\mathrm{K})=\sum_{mn}k_mK_nL_{[nm]}(K)=0.$$

This must hold for arbitrary k_m, whence

$$\sum\nolimits_n K_nL_{[nm]}(\mathrm{K})=0.$$

Now we have

$$L_{[nm]}(K)=\left(\frac{1}{2\pi}\right)^{\frac{3}{2}}\int\int\int e^{-i(\mathrm{Kx})}L_{[nm]}(\mathrm{x})dxdydz,$$

and

$$\sum\nolimits_m K_mL_{[nm]}(\mathrm{K})=\left(\frac{1}{2\pi}\right)^{\frac{3}{2}}\int\int\int\sum\nolimits_m -i(\partial_mL_{[nm]})e^{-i(\mathrm{Kx})}dxdydz.$$

Therefore we find ultimately

$$\sum\nolimits_m \partial_mL_{[nm]}=0.$$

This equation can be obtained somewhat more directly though less rigorously by using the ΔT instead of their Fourier components and making a liberal use of δ-functions. We have:

$$\begin{aligned}C\Delta\dot{T}&=\sum_{nm}\partial_n\{L_{nm}\partial_m\Delta T\}\\&=\int\int\int-\sum_{nm}\partial_n'\{\delta(x-x')\delta(y-y')\\&\qquad\times\delta(z-z')\}L_{nm}(\mathrm{x}')\partial_m'\Delta T(\mathrm{x}')dx'dy'dz'\\&=\int\int\int\sum_{nm}\partial_m'\{L_{nm}(\mathrm{x}')\partial_n'[\delta(x-x')\\&\qquad\times\delta(y-y')\delta(z-z')]\}\Delta T(\mathrm{x}')dx'dy'dz',\end{aligned}$$

where ∂_m' denotes differentiation with respect to x_m'. This is of the form

$$\Delta\dot{T}(\mathrm{x})=\int\int\int K(\mathrm{x},\mathrm{x}')\Delta T(x')dx'dy'dz',$$

and Onsager's principle gives:

$$\begin{aligned}&\sum_{nm}\partial_m'[L_{nm}(\mathrm{x}')\partial_n'\{\delta(x_1-x_1')\delta(x_2-x_2')\delta(x_3-x_3')\}]\\&\quad=\sum_{nm}\partial_m[L_{nm}(\mathrm{x})\partial_n\{\delta(x_1-x_1')\\&\qquad\times\delta(x_2-x_2')\delta(x_3-x_3')\}].\end{aligned}$$

In order to draw a conclusion from this equation we multiply by an arbitrary function $f(\mathrm{x}')$ and integrate. We obtain:

$$\sum_{nm}\partial_n(L_{nm}\partial_mf)=\sum_{nm}\partial_m(L_{nm}\partial_nf),$$

or

$$\sum_{nm}\partial_n(L_{nm})\partial_mf=\sum_{nm}\partial_m(L_{nm})\partial_nf,$$

and, f being arbitrary,

$$\sum\nolimits_n \partial_nL_{[nm]}=0.$$

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 proceding 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 difference between A and B and between C and D, then there will hold a set of equations:

$$\begin{aligned} V_1&=A_{11}I_1+A_{12}I_2, \quad \text{or} \quad & I_1&=\alpha_{11}V_1+\alpha_{12}V_2,\\ V_2&=A_{21}I_1+A_{22}I_2, & I_2&=\alpha_{21}V_1+\alpha_{22}V_2. \end{aligned}$$

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:

$$\alpha_{12}=\alpha_{21} \quad \text{or} \quad A_{12}=A_{21}.$$

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

$$\alpha_{12}(\mathrm{H})=\alpha_{21}(-\mathrm{H}).$$

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

$$\begin{aligned} I_1&=b_{11}V_1+b_{12}I_2,\\ V_2&=b_{21}V_1+b_{22}I_2. \end{aligned}$$

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, according to (18c)

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

in agreement 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:

$$E_i=\sum R_{ik}i_k,$$

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 $\alpha_{ik}=\alpha_{ki}$ 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:

$$\begin{aligned} V_1&=A_{11}I_1+A_{12}I_2\\ V_2&=A_{21}I_1+A_{22}I_2 \end{aligned}$$

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

$$I_2=\int_0^b i_2dx,$$

and hence:

$$V_1=R_{12}I_2+R_{11}\left\{\int_0^b i_1dx\right\}_{y=y_A}.$$

Specializing to the case $I_1=0$, we have

$$A_{12}=R_{12}+(R_{11}/I_2)\left\{\int_0^b i_1dx\right\}_{\substack{I_1=0\\ y=y_A}}.$$

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

$$R_{12}+R_{11}\frac{\left\{\int_0^b i_1dx\right\}_{\substack{I_1=0\\ y=y_A}}}{I_2}=R_{21}+R_{22}\frac{\left\{\int_0^l i_2dy\right\}_{\substack{I_1=0\\ x=x_C}}}{I_1}.$$

This equation holds for arbitrary values of x_C and y_A. Let us then suppose that we write it down for n, m arrangements corresponding to

$$\begin{aligned} x_C&=0,\ b/n,\ 2b/n,\ \cdots(n-1)b/n,\\ y_A&=0,\ l/m,\ 2l/m,\ \cdots(m-1)l/m, \end{aligned}$$

and let us sum the result:

$$\begin{aligned} R_{12}+R_{11}\sum_{m,n}&\left\{\int_0^b i_1dx\right\}_{\substack{I_1=0\\ y=y_A}}\Big/ I_2mn\\ &=R_{21}+R_{22}\sum_{m,n}\left\{\int_0^l i_2dx\right\}_{\substack{I_2=0\\ x=x_C}}\Big/ I_1mn. \end{aligned}$$

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 $(I/m)\sum^{(m)} i_1$ 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

$$\sum_i \partial_i R_{[ik]}=0.$$

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

$$R_{ik}(\mathrm{H})=R_{ki}(-\mathrm{H}),$$

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 N, the antisymmetric tensor $R_{[ik]}$ an odd function of N. Introducing the axial vector R (where $R_1=R_{[23]}$ and so on) we can write

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

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.

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[3] J. Meixner, Ann. d. Physik **40**, 165 (1941).

[4] H. B. G. Casimir and A. N. Gerritsen, Physica **8**, 1107 (1941).