

RECIPROCAL RELATIONS IN IRREVERSIBLE PROCESSES. II.

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ABSTRACT

A general reciprocal relation, applicable to transport processes such as the conduction of heat and electricity, and diffusion, is derived from the assumption of microscopic reversibility. In the derivation, certain average products of fluctuations are considered. As a consequence of the general relation $S = k \log W$ between entropy and probability, different (coupled) irreversible processes must be compared in terms of entropy changes. If the displacement from thermodynamic equilibrium is described by a set of variables $\alpha_1, \dots, \alpha_n$, and the relations between the rates $\dot{\alpha}_1, \dots, \dot{\alpha}_n$ and the "forces" $\partial S/\partial \alpha_1, \dots, \partial S/\partial \alpha_n$ are linear, there exists a quadratic dissipation-function,

$$2\Phi(\dot{\alpha}, \dot{\alpha}) \equiv \Sigma \rho_{ij} \dot{\alpha}_i \dot{\alpha}_j = dS/dt = \dot{S}(\alpha, \dot{\alpha}) \equiv \Sigma (\partial S/\partial \alpha_j) \dot{\alpha}_j$$

(denoting definition by \equiv). The symmetry conditions demanded by microscopic reversibility are equivalent to the variation-principle

$$\dot{S}(\alpha, \dot{\alpha}) - \Phi(\dot{\alpha}, \dot{\alpha}) = \text{maximum},$$

which determines $\dot{\alpha}_1, \dots, \dot{\alpha}_n$ for prescribed $\alpha_1, \dots, \alpha_n$. The dissipation-function has a statistical significance similar to that of the entropy. External magnetic fields, and also Coriolis forces, destroy the symmetry in past and future; reciprocal relations involving reversal of the field are formulated.

I. INTRODUCTION

IN A previous communication¹ a reciprocal theorem for heat conduction in an anisotropic medium was derived from the principle of microscopic reversibility, applied to fluctuations. In the following we shall derive reciprocal relations for irreversible processes in general, particularly transport processes: conduction of electricity and heat, and diffusion.

As before we shall assume that the average regression of fluctuations will obey the same laws as the corresponding macroscopic irreversible processes. In (I) we considered fluctuations in "aged" systems, i.e., systems which have been left isolated for a length of time that is normally sufficient to secure thermodynamic equilibrium. For dealing with the conduction of heat we naturally considered the fluctuations of the distribution of heat, and we studied the behavior of the quantities $\alpha_1, \alpha_2, \alpha_3$ = the total displacements of heat in the directions x_1, x_2 and x_3 , respectively.

We brought the laws of irreversible processes into the theory of fluctuations by studying averages

$$\overline{\alpha_1(t)\alpha_2(t+\tau)} = \lim_{t'' \rightarrow \infty} \frac{1}{t'' - t'} \int_{t=t'}^{t=t''} \alpha_1(t)\alpha_2(t+\tau) dt \quad (1.1)$$

¹ L. Onsager, Phys. Rev. **37**, 405 (1931). Cited in the following as (I).

of the values of two fluctuating quantities α_1 and α_2 (in this particular case displacements of heat in two perpendicular directions) observed with a prescribed time interval τ . The condition of microscopic reversibility we applied in the form:

$$\overline{\alpha_1(t)\alpha_2(t+\tau)} = \overline{\alpha_2(t)\alpha_1(t+\tau)}. \quad (1.2)$$

The calculation of averages of the type (1.1) involves several steps. First of all, something must be known about the distribution of values of the fluctuating quantities $\alpha_1, \alpha_2 \dots$; we shall employ standard methods for calculating the average products:

$$\overline{\alpha_1^2}, \overline{\alpha_1\alpha_2}, \dots \quad (1.3)$$

with but a slight variation. In addition, we must know the average changes (of quantities $\alpha_2, \alpha_3 \dots$) which accompany a given deviation α_1' of a quantity α_1 from its normal value $\bar{\alpha}_1 (=0)$. On this basis a certain *initial state* of an irreversible process is associated with the displacement $\alpha_1 = \alpha_1'$; the average regression towards the normal state will obey the ordinary macroscopic laws governing such processes.

The average regression is described by the functions:

$$\overline{\alpha_i(\tau, \alpha_j')}$$

defined as the average of the quantity α_i , taken over all cases, (picked at random for an aged system), in which, τ seconds earlier, the quantity α_j had the value α_j' . Whenever these functions are linear in α_j' , which will be the common case when reasonable variables α are chosen, the knowledge of the averages (1.3) suffices for evaluating (1.1).

In (I), §4, we derived reciprocal relations for heat conduction in an anisotropic body, showing that the conducting properties of the most general (triclinic) crystal can be represented by a *symmetrical tensor* (ellipsoid). In that particular case it was not necessary to calculate the averages (1.3), nor to determine completely the state associated with a displacement $\alpha_1 = \alpha_1'$, because the necessary information could be derived from considerations of symmetry. Even so, these considerations were based on the proposition that, in regard to the probability for a given distribution of energy, the different volume elements of a *homogeneous* crystal would be equivalent, so that the anisotropy of the crystal could be neglected in this particular connection. This proposition involves the fundamental principles of statistical mechanics although it obviates a part of the general mathematical apparatus.

We shall review the derivation briefly. If J_1, J_2, J_3 denote the components of the heat flow along the coordinate axes x_1, x_2, x_3 , respectively, and T the absolute temperature, the phenomenological laws of heat conduction in a triclinic crystal take the general form

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + L_{13}X_3 \\ J_2 &= L_{21}X_1 + L_{22}X_2 + L_{23}X_3 \\ J_3 &= L_{31}X_1 + L_{32}X_2 + L_{33}X_3 \end{aligned} \quad (1.4)$$

where X_1, X_2, X_3 are the components of the "force" on the heat flow

$$X_1 = - (1/T)\partial T/\partial x_1; \quad X_2 = - (1/T)\partial T/\partial x_2; \quad X_3 = - (1/T)\partial T/\partial x_3 \quad (1.5)$$

(Carnot). In order to derive the reciprocal relations

$$L_{12} = L_{21}; \quad L_{23} = L_{32}; \quad L_{31} = L_{13}$$

we considered the fluctuations of the moments

$$\begin{aligned} \alpha_1 &= \int \epsilon x_1 dV \\ \alpha_2 &= \int \epsilon x_2 dV \end{aligned} \quad (1.6)$$

of the distribution of energy, $\epsilon = \epsilon(x_1, x_2, x_3)$. When we chose the external boundary of the crystal spherical, center at the origin, all questions pertaining to the *instantaneous* distribution of energy have spherical symmetry (cf. above). Thus

$$\overline{\alpha_1} = \overline{\alpha_2} = 0; \quad \overline{\alpha_1^2} = \overline{\alpha_2^2}; \quad \overline{\alpha_1 \alpha_2} = 0, \quad (1.7)$$

and with a displacement of energy there is associated a temperature gradient in the same direction:

$$\begin{aligned} \overline{\partial T/\partial x_1}^{\alpha_1', \alpha_2'} &= - T\overline{X_1}(\alpha_1', \alpha_2') = CT\alpha_1' \\ &- T\overline{X_2}(\alpha_1', \alpha_2') = CT\alpha_2' \end{aligned} \quad (1.8)$$

where C is for our immediate purposes a mere constant. (Certain rather trivial considerations are needed to justify our assumption of a *linear* relation between displacement (α_1', α_2') and gradient $(T\overline{X_1}, T\overline{X_2})$. When we take that much for granted, the more special form (1.8) follows from the spherical symmetry.)

The gradient (1.8) determines the heat flow J according to (1.4), and the rate of change $\dot{\alpha}$ of the displacement α is the same as the total flow

$$\begin{aligned} \dot{\alpha}_1(\alpha_1', \alpha_2', \alpha_3') &= d\alpha_1/dt = \int J_1 dV = - CV(L_{11}\alpha_1' + L_{12}\alpha_2' + L_{13}\alpha_3') \\ \dot{\alpha}_2(\alpha_1', \alpha_2', \alpha_3') &= - CV(L_{21}\alpha_1' + L_{22}\alpha_2' + L_{23}\alpha_3'). \end{aligned} \quad (1.9)$$

Then in a short interval of time Δt

$$\overline{\alpha_2(\Delta t, \alpha_1')} = \overline{\alpha_2(0, \alpha_1')} + \dot{\alpha}_2(\alpha_1')\Delta t = 0 - L_{21}CV\alpha_1'\Delta t,$$

where $\overline{\alpha_2(0, \alpha_1')}$ vanishes by symmetry. From this, obviously

$$\overline{\alpha_1(t)\alpha_2(t + \Delta t)} = \overline{\alpha_1'\overline{\alpha_2(\Delta t, \alpha_1')}} = - L_{21}CV\overline{\alpha_1'^2}\Delta t$$

and, by analogy

$$\overline{\alpha_2(t)\alpha_1(t + \Delta t)} = - L_{12}CV\overline{\alpha_2'^2}\Delta t.$$

Since, by (1.7): $\overline{\alpha_1^2} = \overline{\alpha_2^2}$, the requirement:

$$\overline{\alpha_1(t)\alpha_2(t + \Delta t)} = \overline{\alpha_2(t)\alpha_1(t + \Delta t)}$$

for microscopic reversibility imposes the condition:

$$L_{12} = L_{21}.$$

The more general case of simultaneous transport of heat, electricity and matter (diffusion) in isotropic or anisotropic media leads us to consider the fluctuations of a set of variables $\alpha_1, \alpha_2, \dots$, measuring displacements of heat, electricity and matter, eventually in different directions. We shall have to actually evaluate the averages (1.3); symmetry considerations can yield the necessary information only in a few cases, as above. The calculation of (1.3) involves directly Boltzmann's fundamental relation between entropy S and probability W :

$$S = k \log W + \text{constant}$$

The exceedingly general character of this relation is the reason that the *rates* of irreversible processes, not solely the ultimate equilibrium, are subject to reciprocal laws, in which *different processes have to be compared in terms of the entropy changes involved*.

Sometimes, of course, it may be more convenient to employ other thermodynamic potentials, particularly the free energy, the main reason being that conditions of *mechanical* equilibrium (pressure, elastic) frequently enter into the laws of irreversible processes, and that the description in terms of energy involves more familiar derived functions (thermodynamic potential, electromotive force, electrical resistance). Above, we purposely considered the "force" on heat, although the concept was not necessary for dealing with the problem in hand, just to demonstrate how the concept of "force" could be extended beyond the familiar.

Fundamentally, however, the *entropy* is the simplest among the thermodynamic potentials, and it is the only one that will serve our purposes in all cases. In our example, where displacements $\alpha_1, \alpha_2, \alpha_3$ of heat are considered, the state of the system being determined by these displacements, so that

$$S = \sigma(\alpha_1, \alpha_2, \alpha_3),$$

the temperature gradients are essentially the same as $\partial S/\partial\alpha_1$ etc., or rather

$$\partial\sigma/\partial\alpha_r = \partial(1/T)/\partial x_r.$$

In order to see this, we recall the fundamental thermodynamic relation

$$\delta S = (1/T)(\delta E - \delta A) - (\mu/T)\delta m,$$

where E = energy; A = work; m = amount of substance; μ = Gibbs' thermodynamic potential. The amount of heat added to a volume element is $\delta Q = \delta E - \delta A$. Now if there is a uniform gradient of temperature (or $1/T$ in the r -direction, then an amount of heat δQ transported a distance Δx_r changes the entropy by the amount

$$\delta S = \delta Q \cdot \Delta(1/T) = \delta Q \cdot \Delta x_r \cdot \partial(1/T)/\partial x_r = \delta\alpha_r \cdot \partial(1/T)/\partial x_r,$$

whereby $\delta\alpha_r$ measures a displacement of heat (in units $\text{cm} \times \text{cal}$).

Similarly, where a displacement α of matter (in the x direction) is considered,

$$\partial\sigma/d\alpha = -\partial(\mu/T)/dx,$$

and if α is a displacement of electricity, then

$$\partial\sigma/d\alpha = X/T,$$

where X is the intensity of the electric field.

According to the empirical laws of transport processes the flow J of matter, heat or electricity is proportional to the gradient of the corresponding specific potential, that is

$$J \sim -\text{grad } T$$

for heat conduction and

$$J \sim X; J \sim -\text{grad } \mu,$$

respectively, for electrical conduction (Ohm's law) and isothermal diffusion (alternative form of Fick's law). In the following we shall write these empirical relations in the general form

$$d\alpha_r/dt = \dot{\alpha}_r \sim \partial S/d\alpha_r,$$

where the rate of displacement $\dot{\alpha}$ is essentially the same as the flow J , (by definition), except for a volume factor. Whenever different transport processes interfere with each other the simple proportionality is replaced by a system of linear relations

$$\dot{\alpha}_r = G_{r1}\partial\sigma/d\alpha_1 + \dots + G_{rn}\partial\sigma/d\alpha_n, \quad (r = 1, \dots, n), \quad (1.11)$$

where again $S = \sigma(\alpha_1, \dots, \alpha_n)$. In taking for granted the linear form (1.11) we are still making use of empirical laws, mostly familiar, which are understood and expected from simple and equally familiar kinetic considerations of very wide scope. Examples have been enumerated in (I), §§ 1-2, and need not be repeated here.

Our object is to show that the condition (1.2) for microscopic reversibility leads to the general reciprocal relation

$$G_{rs} = G_{sr}. \quad (1.12)$$

2. GENERAL THEORY OF FLUCTUATIONS

It was shown by L. Boltzmann that a mechanical theory of molecules requires a statistical interpretation of the second law of thermodynamics. Thermodynamic equilibrium is explained as a statistical equilibrium of elementary processes, and Boltzmann gave a direct relation between the entropy S and the "thermodynamic probability" W of a thermodynamic state:

$$S = k \log W + \text{const.}, \quad (2.1)$$

where k is the gas constant per molecule (1.371×10^{-16} erg/degree). The apparent rest associated with thermodynamic equilibrium is explained by the

smallness of the factor k . According to (2.1), under circumstances which normally lead to such equilibrium, the probability

$$e^{\Delta S/k}$$

for a deviation involving an entropy change ΔS (necessarily negative), is appreciable only when ΔS is (at the outmost) of the order of magnitude of k . The *fluctuations* permitted by this restriction can be observed only in very favorable cases, for example the opalescence of liquids near the critical point² and Brownian motion of small particles in liquids,³ or of a mirror in delicate elastic suspension.⁴

The premises and the consequences of Boltzmann's principle (2.1) have been discussed by A. Einstein⁵ to an extent which will be practically sufficient for our purposes. It is essential that a thermodynamic equilibrium state, specified in terms of energy and external parameters (volume etc.), is incompletely specified from a molecular point of view; the quantity W measures the number (or extent) of different possibilities for realizing a given thermodynamic state. In order to calculate W one needs a complete (molecular) theory of the system in hand: If one assumes that molecules obey the laws of classical mechanics, then W equals an extension in phase-space, while on the basis of quantum theory W equals the number of stationary states corresponding to the prescribed energy. However, as Einstein has pointed out, the calculation of fluctuations according to (2.1) is *independent of all special assumptions regarding the laws which may govern elementary processes* (we must of course assume that these laws do permit statistical equilibrium of some kind).

We shall have to make certain *general assumptions* about *aged systems*, i.e., systems which have been left isolated for a length of time that is normally sufficient to secure thermodynamic equilibrium. We expect that such a system will in the course of time pass through *all* the (thermodynamic) states $\Gamma^1, \Gamma^2, \dots, \Gamma^l$ that are compatible with the conditions of isolation, whereby the energy, the values of external parameters (volume, etc.) and the numbers of indestructible elementary particles (atoms, molecules) are prescribed.⁶ In the course of a long time t the system will spend a total t_r of time intervals in the state Γ^r ; we expect that t_1, t_2, \dots, t_l will be proportional to the regions W_1, W_2, \dots, W_l . This statement contains an assumption even if W_1, W_2, \dots are considered as unknown, namely that $t_1/t, t_2/t, \dots$ will be fully determined by the nature of the system, (and the conditions of isolation), independently of the initial state. Granted this assumption, we may define W_1, W_2, \dots as pro-

² M. v. Smoluchowski, Ann. d. Physik [4], **25**, 205 (1909). Theory accompanied by a general discussion of fluctuations is given by A. Einstein, Ann. d. Physik [4], **33**, 1275 (1910).

³ A. Einstein, Ann. d. Physik [4], **17**, 549 (1905). M. v. Smoluchowski, Ann. d. Physik [4], **21**, 756 (1906).

⁴ P. Zeeman and O. Houdyk, Proc. Acad. Amsterdam **28**, 52 (1925). W. Gerlach, Naturwiss. **15**, 15 (1927). G. E. Uhlenbeck and S. Goudsmit, Phys. Rev. **34**, 145 (1929).

⁵ Einstein, reference 2.

⁶ In a discussion of the fundamental questions involved, W. Schottky introduces the term "resistent groups." Ann. d. Physik [4], **68**, 481 (1922).

portional $t_1/t, t_2/t \dots$, without reference to any detailed theory of the system. (On the basis of the underlying picture, every W is still a large integer, equal to the number of "microscopic" states contained in a given thermodynamic state. Here, however, we are only interested in the ratios of W_1, W_2, \dots). The various assumptions involved in this application of Boltzmann's principle may be summarized in the formula:

$$S_r = k \log (t_r/t) + \text{const.} \tag{2.2}$$

where S_r is the entropy of the state Γ^r ; we shall refer to t_r/t as the *probability* for this state.

A thermodynamic state $\Gamma^r = \Gamma(\alpha_1^r, \dots, \alpha_n^r)$ may be defined in terms of given values $\alpha_1^r, \dots, \alpha_n^r$ for such variables $\alpha_1, \dots, \alpha_n$ as can be measured by ordinary means. From a statistical point of view we must allow latitudes $\Delta\alpha_1, \dots, \Delta\alpha_n$ in this specification (the probability for a region of no extension equals zero). We have to introduce a distribution-function

$$f(\alpha_1, \dots, \alpha_n)$$

and the probability for the state Γ^r becomes equal to the integral of $f(\alpha_1, \dots, \alpha_n)$ over the region

$$\begin{aligned} \alpha_1^{(r)} < \alpha_1 < \alpha_1^{(r)} + \Delta\alpha_1 \\ & \dots \dots \dots \dots \dots \dots \\ \alpha_n^{(r)} < \alpha_n < \alpha_n^{(r)} + \Delta\alpha_n. \end{aligned}$$

Then (2.2) takes the form

$$S_r = k \log f(\alpha_1^{(r)}, \dots, \alpha_n^{(r)}) + k \log (\Delta\alpha_1 \dots \Delta\alpha_n) + \text{const.} \tag{2.3}$$

Our only direction for the appropriate choice of latitudes $\Delta\alpha$ is that they ought to be taken of the same order of magnitude as the common fluctuations of the quantities α in the state Γ^r . This convention takes care of all important cases; because thermodynamic measurements of entropy are possible only for equilibrium states.⁷ A more accurate specification of $\Delta\alpha_1, \dots, \Delta\alpha_n$ is unnecessary because, say, doubling each $\Delta\alpha$ will change the right side of (2.3) only by the amount $nk \log 2$, where $k = 1.371 \times 10^{-16}$ erg/degree, and an entropy difference of this magnitude is far too small to affect any measurement. Actually, where reasonable variables $\alpha_1, \dots, \alpha_n$ are chosen, the order of magnitude of the product $\Delta\alpha_1, \Delta\alpha_2 \dots \Delta\alpha_n$ varies so little that the contribution $k \log (\Delta\alpha_1' \dots \Delta\alpha_n' / \Delta\alpha_1'' \dots \Delta\alpha_n'')$ to the entropy difference between two thermodynamic states is entirely negligible in comparison with $k \log (f(\alpha_1', \dots, \alpha_n') / f(\alpha_1'', \dots, \alpha_n''))$; it is the factor $f(\alpha_1, \dots, \alpha_n)$ that causes the tremendous difference in the probabilities of different thermodynamic states, and is responsible for measurable entropy differences. Thus, as long as we restrict ourselves to cases where S_r is a measured entropy, we may neglect the variability of the term $k \log (\Delta\alpha_1 \dots \Delta\alpha_n)$ on the right side of (2.3) and write

⁷ We allow ourselves, following the custom of thermodynamics, to consider states that may be approximated in some way by equilibrium states. Cf. Schottky, reference 6.

$$S_r = k \log f(\alpha_1^{(r)}, \dots, \alpha_n^{(r)}) + \text{const.} \quad (2.4)$$

So far we have assumed that the variables $\alpha_1, \dots, \alpha_n$ define the state of the system in hand *completely* from the thermodynamic (phenomenological) point of view. As pointed out by Einstein⁸ the relation (2.4) remains valid in cases where this definition is incomplete. We merely have to adopt the convention that among all the states which fulfill the given specifications, we select the one with the greatest entropy. This theorem again depends on the probabilities for different states being of different order of magnitude, so that the given set of values of $\alpha_1, \dots, \alpha_n$ will be realized by the chosen state much more frequently than by all other states taken together. We shall summarize these results for subsequent applications. The greatest entropy allowed by a given set $\alpha_1', \dots, \alpha_n'$ of values of the variables $\alpha_1, \dots, \alpha_n$ we denote by

$$\sigma_{1\dots n}(\alpha_1', \dots, \alpha_n').$$

The corresponding (thermodynamic) state we denote by

$$\Gamma_{1\dots n}' = \Gamma_{1\dots n}(\alpha_1', \dots, \alpha_n').$$

Then

$$\sigma_{1\dots n}(\alpha_1', \dots, \alpha_n') = k \log f(\alpha_1', \dots, \alpha_n') + \text{const.} \quad (2.5)$$

gives the probability for finding the variables $\alpha_1, \dots, \alpha_n$ with a given set of values $\alpha_1', \dots, \alpha_n'$. Practically every time when $\alpha_1, \dots, \alpha_n$ assume this set of values, the system will be in the state $\Gamma_{1\dots n}(\alpha_1', \dots, \alpha_n')$.

We shall calculate at once certain averages which will be needed for the subsequent derivations. We denote by $f_p(\alpha_p)$ the distribution-function for the variable α_p . We have according to (2.5):

$$k \log f_p(\alpha_p) = \sigma_p(\alpha_p) + \text{const.}, \quad (2.6)$$

where $\sigma_p(\alpha_p')$ is the greatest entropy possible when $\alpha_p = \alpha_p'$, realized by the state $\Gamma_p(\alpha_p')$. The function f_p is determined by (2.6) together with the condition

$$\int_{-\infty}^{\infty} f_p(\alpha_p) d\alpha_p = 1.$$

We obtain from (2.6) by differentiation

$$k df_p/d\alpha_p = f_p(\alpha_p) d\sigma_p/d\alpha_p,$$

assuming that the differential quotient exists. We shall also assume that the entropy $\sigma_p(\alpha_p)$ attains its maximum for a finite value α_p^0 of α_p , corresponding to the equilibrium state Γ^0 , and that $(\alpha_p - \alpha_p^0)f_p(\alpha_p)$ approaches zero for large values of $|\alpha_p - \alpha_p^0|$.⁹ Then it is easy to calculate the average

$$\begin{aligned} \overline{(\alpha_p - \alpha_p^0) d\sigma_p/d\alpha_p} &= \int_{-\infty}^{\infty} (\alpha_p - \alpha_p^0) (d\sigma_p/d\alpha_p) f_p(\alpha_p) d\alpha_p \\ &= k \int_{-\infty}^{\infty} (\alpha_p - \alpha_p^0) (df_p/d\alpha_p) d\alpha_p. \end{aligned}$$

⁸ Einstein, reference 2.

⁹ Otherwise this function must have an infinite number of maxima. All the conditions stated are fulfilled whenever α_p is a reasonable thermodynamic variable.

Integration by parts yields

$$k[(\alpha_p - \alpha_p^0)f_p(\alpha_p)]_{-\infty}^{\infty} - k \int_{-\infty}^{\infty} f_p(\alpha_p) d\alpha_p.$$

The first term vanishes, and the second equals $-k$; thus

$$\overline{(\alpha_p - \alpha_p^0) \partial \sigma_p / d\alpha_p} = -k. \tag{2.7}$$

In the same manner, and under the same assumptions we find

$$\begin{aligned} &\overline{(\alpha_p - \alpha_p^0) \partial \sigma_{1\dots n} / d\alpha_p} \\ &= \int_{-\infty}^{\infty} \dots \int (\alpha_p - \alpha_p^0) (\partial \sigma / d\alpha_p) f_{1\dots n} d\alpha_1 \dots d\alpha_n = -k, \end{aligned} \tag{2.8a}$$

and

$$\overline{(\alpha_q - \alpha_q^0) \partial \sigma_{1\dots n} / d\alpha_p} = 0, \quad (p \neq q). \tag{2.8b}$$

In the following we shall find it convenient to apply the simple formula (2.7) directly. However, it seems desirable to show the connection with the ordinary formulas for the averages of the products $(\alpha_p - \alpha_p^0)(\alpha_q - \alpha_q^0)$. We must assume that the entropy $\sigma_{1\dots n}$ can be expressed by a multiple power series, and that the abridged Taylor development

$$\sigma_{1\dots n}(\alpha_1, \dots, \alpha_n) = S_0 + \frac{1}{2} \sum_{p,q=1}^n \eta_{pq} (\alpha_p - \alpha_p^0)(\alpha_q - \alpha_q^0), \tag{2.9}$$

where

$$\eta_{pq} = \eta_{qp} = [\partial^2 \sigma_{1\dots n} / d\alpha_p d\alpha_q]_{\alpha_1=\alpha_1^0; \dots; \alpha_n=\alpha_n^0}, \tag{2.10}$$

will suffice in the entire region of values of $\alpha_1, \dots, \alpha_n$, for which the contribution to any of the averages (2.8 a, b) is at all appreciable. (Since $f \sim \exp(\sigma/k)$, the maximum of $f_{1\dots n}$ is very sharp). Then we may substitute in (2.8 a, b):

$$\partial \sigma_{1\dots n} / d\alpha_p = \sum_{q=1}^n \eta_{pq} (\alpha_q - \alpha_q^0), \tag{2.11}$$

and we obtain a system of linear equations

$$\sum_{r=1}^n \eta_{pr} \overline{(\alpha_r - \alpha_r^0)(\alpha_q - \alpha_q^0)} = -k \delta_{pq} = \begin{cases} -k, & (p = q) \\ 0, & (p \neq q), \end{cases} \tag{2.12}$$

from which the mean squares and products of fluctuations may be computed.

3. THE REGRESSION OF FLUCTUATIONS

We are accustomed to observe that the course of an irreversible process taking place in an isolated system is entirely determined by the initial thermodynamic state according to definite laws, such as the laws for conduction of heat. On the basis of a statistical interpretation of the second law of thermodynamics, no process can be completely predetermined by an initial thermodynamic state; because such a state is itself incompletely defined (from a

molecular point of view; cf. §2). However, we can understand a predetermination with practical certainty, within limits of the order of magnitude of ordinary fluctuations, whereby much greater deviations will be very rare. From this statistical point of view we may still interpret the predictions of irreversible processes from empirical laws as valid for averages taken over a large number of similar cases, which in this connection means cases of irreversible processes starting from the same initial *thermodynamic* state.

Strictly speaking, this rule does not specify uniquely the more refined "microscopic" (molecular) interpretation of laws derived from relatively crude "macroscopic" observations. It makes a considerable difference whether we take an average of the type $\bar{\alpha} = (\alpha' + \alpha'')/2$ or one of the type $\bar{\alpha} = [(\alpha'^5 + \alpha''^5)/2]^{1/5}$. However, in all important concrete cases the natural answer to this question will be obvious. For example, if α is a total displacement of heat, itself the sum of many local displacements whose changes depend on local conditions, there may be no doubt that the straight average $\bar{\alpha} = (\alpha' + \alpha'')/2$ is correct.

Now we are able to solve the problem of predicting the *average regression* of fluctuations: Suppose that we start out with a certain isolated system, and watch the fluctuations of the variables $\alpha_1, \dots, \alpha_n$ for a great length of time. Whenever the values of $\alpha_1, \dots, \alpha_n$ happen to be (simultaneously) $\alpha_1', \dots, \alpha_n'$, we make a record of the values which these variables (and perhaps other quantities $\alpha_{n+1}, \dots, \alpha_{n+p}$) assume τ seconds later. The averages of such records we denote by

$$\overline{\alpha_1}(\tau, \alpha_1', \dots, \alpha_n'), \dots, \overline{\alpha_{n+p}}(\tau, \alpha_1', \dots, \alpha_n').$$

We know that almost every time when $\alpha_1 = \alpha_1'; \dots; \alpha_n = \alpha_n'$, the system will be in the (phenomenological) state $\Gamma'_{1\dots n} = \Gamma(\alpha_1', \dots, \alpha_n')$, and the average course of an irreversible process following that state, described by the functions

$$\overline{\alpha_1}(\tau, \Gamma'_{1\dots n}), \dots, \overline{\alpha_{n+p}}(\tau, \Gamma'_{1\dots n}),$$

we know from macroscopic experiments. These functions may be considered as properties (in an extended sense) of the state $\Gamma'_{1\dots n}$. The "normal" (common) properties of states corresponding to prescribed values $\alpha_1', \dots, \alpha_n'$ of the fluctuating quantities $\alpha_1, \dots, \alpha_n$ are certainly those of the state $\Gamma'_{1\dots n}$. The question whether we are allowed to interchange "normal" and average properties must be decided from the consideration of individual cases, as outlined above.

Assuming that the variables $\alpha_1, \dots, \alpha_n$ are suitable in this regard, we have:

$$\overline{\alpha_i}(\tau, \alpha_1', \dots, \alpha_n') = \overline{\alpha_i}(\tau, \Gamma'_{1\dots n}), \quad (i = 1, \dots, n + p), \quad (3.1)$$

as a general rule for predicting the average regression of fluctuations from the laws of irreversible processes.

4. RECIPROCAL RELATIONS

For a discussion of the requirements of microscopic reversibility the averages

$$A_{ji}(\tau) = \overline{\alpha_j(t)\alpha_i(t + \tau)} = \overline{\alpha_j'\bar{\alpha}_i(\tau, \alpha_j')} \quad (4.1)$$

afford a convenient point of attack. The quantities $A_{ij}(\tau)$ may also be defined as time averages (1.1)

$$A_{ji}(\tau) = \lim_{t'' \rightarrow \infty} \frac{1}{t'' - t'} \int_{t=t'}^{t=t''} \alpha_j(t)\alpha_i(t + \tau) dt.$$

In the following it will be convenient to assume that the variables $\alpha_1, \dots, \alpha_n$ measure deviations from the thermodynamic equilibrium, whereby their averages $\bar{\alpha}_1, \dots, \bar{\alpha}_n$ for this state (and also the "normal" values α_j^0) vanish:

$$\bar{\alpha}_i = \alpha_i^0 = 0, \quad (i = 1, \dots, n). \quad (4.2)$$

The assumption of microscopic reversibility requires that, if α and β be two quantities which depend only on the configuration of molecules and atoms, *the event $\alpha = \alpha'$, followed τ seconds later by $\beta = \beta'$, will occur just as often as the event $\beta = \beta'$, followed τ seconds later by $\alpha = \alpha'$* . The same will be true if α and β depend on the velocities of elementary particles in such a manner that they are not changed when the velocities are reversed, for example, when α depends on the distribution of energy in a system.¹⁰ If α_j and α_i are two such "reversible" variables of a reversible system, then obviously

$$A_{ji}(\tau) = \overline{\alpha_j(t)\alpha_i(t + \tau)} = \overline{\alpha_i(t)\alpha_j(t + \tau)} = A_{ij}(\tau). \quad (4.3)$$

We shall consider cases where the course of an irreversible process starting from any state of the type $\Gamma_1 \dots \Gamma_n$ can be described by a set of linear differential equations of the form (1.11):

$$\frac{d\bar{\alpha}_i}{dt} = \dot{\alpha}_i = \sum_{r=1}^n G_{ir} \frac{\partial \sigma_{1\dots n}(\alpha_1, \dots, \alpha_n)}{d\alpha_r}, \quad (i = 1, \dots, n). \quad (4.4)$$

According to (3.1) we have

$$\bar{\alpha}_i(\tau, \alpha_j') = \bar{\alpha}_i(\tau, \Gamma_j'),$$

where Γ'_j is the state of maximum entropy for a given value α_j' of the variable α_j . Mathematically this state is characterized by the relations

$$\begin{aligned} \alpha_j &= \alpha_j' \\ \partial \sigma_{1\dots n} / d\alpha_r &= 0, \quad (r \neq j), \end{aligned} \quad (4.5)$$

and we have for the set of values of $\alpha_1, \dots, \alpha_n$ determined by these conditions:

$$\partial \sigma_{1\dots n} / d\alpha_j = [d\sigma_j / d\alpha_j]_{\alpha_j = \alpha_j'}. \quad (4.6)$$

¹⁰ Cf. (I) p. 418.

From (4.4) we have in a short interval of time Δt

$$\overline{\alpha_i}(\Delta t, \alpha_j') = \overline{\alpha_i}(0, \alpha_j') + \dot{\alpha}_i \Delta t = \overline{\alpha_i}(0, \alpha_j') + \sum_{r=1}^n G_{ir} (\partial \sigma_{1 \dots n} / \partial \alpha_r) \Delta t,$$

or substituting (4.5) and (4.6):

$$\overline{\alpha_i}(\Delta t, \alpha_j') = \overline{\alpha_i}(0, \alpha_j') + G_{ij} (d\sigma_j(\alpha_j') / d\alpha_j) \Delta t.$$

Calculating according to (4.1) the average $A_{ji}(\Delta t)$ we obtain

$$A_{ji}(\Delta t) = \overline{\alpha_j(t) \alpha_i(t + \Delta t)} = \overline{\alpha_j' \overline{\alpha_i}(0, \alpha_j')} + G_{ij} \Delta t \overline{\alpha_j d\sigma_j / d\alpha_j},$$

or, observing (2.7) and the convention (4.2):

$$A_{ji}(\Delta t) = A_{ji}(0) - k \Delta t G_{ij}. \quad (4.7)$$

Similarly, of course

$$A_{ij}(\Delta t) = A_{ij}(0) - k \Delta t G_{ji}.$$

Applying the condition (4.3) for microscopic reversibility we find

$$G_{ij} = G_{ji}, \quad (4.8)$$

as announced at the end of §1. The importance of considering fluctuations for the derivation of this result is apparent from the occurrence of Boltzmann's constant k in (4.7).

5. THE PRINCIPLE OF THE LEAST DISSIPATION OF ENERGY

The symmetry relation (4.8) contains the important reciprocal relations in transport processes. An alternative form of (4.8) is convenient for many applications, and commands considerable intrinsic interest. The description (4.4) of a set of simultaneous irreversible processes may be rewritten in the form

$$\frac{\partial \sigma_{1 \dots n}(\alpha_1, \dots, \alpha_n)}{d\alpha_i} = \sum_{r=1}^n \rho_{ir} \dot{\alpha}_r, \quad (i = 1, \dots, n), \quad (5.1)$$

where, according to the equations

$$\sum_{r=1}^n \rho_{ir} G_{rj} = \sum_{r=1}^n G_{ir} \rho_{rj} = \delta_{ij} = \begin{cases} 1, & (i = j) \\ 0, & (i \neq j), \end{cases} \quad (5.2)$$

the coefficients (ρ_{ij}) form the inverse matrix of (G_{ij}) , which enter into (4.4). The symmetry relations (4.8) may be replaced by the equivalent

$$\rho_{ij} = \rho_{ji}, \quad (i = 1, \dots, n). \quad (5.3)$$

We introduce the *dissipation-function*

$$\Phi(\dot{\alpha}, \dot{\alpha}) \equiv \frac{1}{2} \sum_{i,j} \rho_{ij} \dot{\alpha}_i \dot{\alpha}_j, \quad (5.4)$$

and incorporate the symmetry relations (5.3) into the description of irreversible processes by writing

$$\partial \sigma_{1 \dots n}(\alpha_1, \dots, \alpha_n) / d\alpha_i = \partial \Phi(\dot{\alpha}, \dot{\alpha}) / d\dot{\alpha}_i, \quad (5.5)$$

in place of (5.1). Further, if we define a function

$$\dot{S}(\alpha, \dot{\alpha}) \equiv \sum_{r=1}^n (\partial\sigma_{1\dots n}/\partial\alpha_r)\dot{\alpha}_r, \quad (5.6)$$

representing the rate of increase of the entropy, we can formulate a *variation-principle*, namely

$$\delta[\dot{S}(\alpha, \dot{\alpha}) - \Phi(\dot{\alpha}, \dot{\alpha})] = 0. \quad (5.7)$$

Our convention is that only the velocities $\dot{\alpha}_1, \dots, \dot{\alpha}_n$ should be varied, thus

$$\delta[\dot{S}(\alpha, \dot{\alpha}) - \Phi(\dot{\alpha}, \dot{\alpha})] = \sum_{i=1}^n \left(\frac{\partial\sigma_{1\dots n}}{\partial\alpha_i} - \frac{\partial\Phi}{\partial\dot{\alpha}_i} \right) \delta\dot{\alpha}_i = 0,$$

according to (5.5). The variation principle (5.7), which we shall call the *principle of the least dissipation of energy*, for reasons mentioned in (I), §6, provides convenient means for transforming the reciprocal relations (5.3), or (4.8), to cases where the conventional description of irreversible processes involves an infinite number of variables, for example the temperatures in all parts of a space. The dissipation-function equals half the rate of production of entropy

$$2\Phi(\dot{\alpha}, \dot{\alpha}) = \dot{S}(\alpha, \dot{\alpha}), \quad (5.8)$$

because of (5.5), (5.6) and (5.4), which may be written

$$\Phi(\dot{\alpha}, \dot{\alpha}) = \frac{1}{2} \sum_{i,j} \rho_{ij} \dot{\alpha}_i \dot{\alpha}_j = \frac{1}{2} \sum_i \dot{\alpha}_i \partial\Phi/\partial\dot{\alpha}_i.$$

It is evident from (5.8) that $\Phi(\dot{\alpha}, \dot{\alpha})$ must be essentially positive (definite or semidefinite), because the second law of thermodynamics demands $\dot{S} \geq 0$. Therefore the extremum given by (5.7) is always a maximum

$$\dot{S}(\alpha, \dot{\alpha}) - \Phi(\dot{\alpha}, \dot{\alpha}) = \text{maximum}. \quad (5.9)$$

Applications of this principle will be given in a later publication; in (I), §§4–5, a special result was derived by a direct method.

It is worth pointing out that in the dissipation-function has a direct statistical significance. A detailed discussion would be out of place in this article, where a compact presentation of important theorems is intended, but we may state without derivation the result, which is an extension of Boltzmann's principle (2.1). The equilibrium condition of thermodynamics

$$S = \text{maximum}$$

characterizes the most probable state, and the probability W for a state $\Gamma(\alpha_1, \dots, \alpha_n)$ is given by Boltzmann's principle

$$k \log W(\alpha_1, \dots, \alpha_n) = S(\alpha_1, \dots, \alpha_n) + \text{const.};$$

for the precise interpretation of this theorem we must refer to the discussion in §2. In a similar manner, Eq. (5.9) describes the most probable course of an

irreversible process. It is also possible to show, under assumptions approximately equivalent to those that are necessary for deriving, (simultaneously), (5.5) and (2.12), that the probability

$$W(\Gamma', \Delta t, \Gamma'') = W(\alpha_1', \dots, \alpha_n', \Delta t, \alpha_1'', \dots, \alpha_n'')$$

for the states $\Gamma' = \Gamma(\alpha_1', \dots, \alpha_n')$ and $\Gamma'' = \Gamma(\alpha_1'', \dots, \alpha_n'')$ occurring at the times t' and $t'' = t' + \Delta t$, respectively, is given by the formula

$$k \log W(\Gamma', \Delta t, \Gamma'') = S' + S'' - \frac{\Phi(\Delta\alpha, \Delta\alpha)}{\Delta t} + \text{const.}, \quad (5.10)$$

where $S' = S(\alpha_1', \dots, \alpha_n')$, $S'' = S(\alpha_1'', \dots, \alpha_n'')$, and

$$\Phi(\Delta\alpha, \Delta\alpha) = \frac{1}{2} \sum_{i,j} \rho_{ij} (\alpha_i'' - \alpha_i') (\alpha_j'' - \alpha_j').$$

(Needless to say, we assume that we are dealing with an aged system.)

6. NONREVERSIBLE SYSTEMS

As mentioned in (I), §7, we know from our macroscopic experience certain conservative dynamical systems which do not exhibit dynamical reversibility, namely systems where external magnetic fields are acting, and systems whose motion is described relatively to a rotating frame of coordinates, the rotation being equivalent to a field of Coriolis forces. In such cases, where the macroscopic laws of motion are non-reversible, the microscopic motion cannot be reversible.

In dealing with cases of this kind it is advantageous to consider the intensities of magnetic and Coriolis fields as variable external parameters of the system in hand. Then macroscopic dynamical systems subject to external magnetic and Coriolis forces have the following symmetry with regard to reversal of the time: If $[q] = [Q(t-t_0)]$ is a possible motion (succession of configurations $[q]$) of a system left to itself in a magnetic (or Coriolis) field of intensity Θ , then the reverse succession of configurations $[q] = [Q(t_0-t)]$ is a possible motion of the same system when placed in a field of intensity $-\Theta$. Further, let α and β be two functions of the state (and of the parameters) of the system in hand, such that their values are not changed when all the velocities in the system are reversed, (simultaneously with Θ). Then, when we consider the fluctuations in an aged system, as in §4, the succession of events $\alpha = \alpha'$, $\beta = \beta'$, with an intervening lapse of time τ , will occur in a system placed in a field of intensity $+\Theta$, just as often as the succession of events $\beta = \beta'$, $\alpha = \alpha'$, (with a time-interval τ), will occur in a system placed in a field of intensity $-\Theta$.

If we may apply this symmetry condition to the motion of elementary particles, and α_i , α_j are two "reversible" dynamical variables, the averages (4.1) will be functions of the time τ and the field intensity Θ :

$$A_{ij}(\Theta, \tau),$$

and we have the symmetry condition

$$A_{ji}(\Theta, \tau) = A_{ji}(-\Theta, -\tau) = A_{ij}(-\Theta, \tau). \quad (6.1)$$

Supposing that a certain irreversible process can be described in the form (4.4), the coefficients G_{ji} being functions of Θ ,

$$\frac{d\alpha_i}{dt} = \dot{\alpha}_i = \sum_{j=1}^n G_{ij}(\Theta) \frac{\partial \sigma_{1 \dots n}(\alpha_1, \dots, \alpha_n)}{d\alpha_j}, \quad (i = 1, \dots, n), \quad (6.2)$$

we can derive (4.7) as before

$$\begin{aligned} A_{ji}(\Theta, \Delta t) &= A_{ji}(\Theta, 0) - k\Delta t G_{ij}(\Theta) \\ A_{ij}(-\Theta, \Delta t) &= A_{ij}(-\Theta, 0) - k\Delta t G_{ji}(-\Theta), \end{aligned}$$

and upon applying the symmetry condition (6.1) we find

$$G_{ij}(\Theta) = G_{ji}(-\Theta). \quad (6.3)$$

This theorem contains a reciprocal relation between the Nernst effect and the Etingshausen effect, which has been derived previously by P. W. Bridgman¹¹ and by H. A. Lorentz¹² on a quasi-thermodynamic basis.

¹¹ P. W. Bridgman, *Phys. Rev.* **24**, 644 (1924); Fourth Solvay Congress ("Conductibilité Electrique des Metaux"), 352 (1924).

¹² H. A. Lorentz, Fourth Solvay Congress, 354 (1924).