X. On the law of distribution of energy

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of field, the magnetic-twist curve for nickel is exactly similar to the same for iron. The reason is simply that with nickel there is a field of maximum twist for each value of current passing along the wire, although there is no field of maximum elongation. The explanation of this is given in my paper of 1888 (Trans. R. S. E. vol. xxxv.). It is sufficient to note that the twist, under a given combination of circular and longitudinal magnetizing forces, depends not only upon the elongations but also upon some function of these forces which changes sign with each, and to which the existence of the maximum twist is largely or altogether due. For even in the case of iron, which has a maximum elongation, the maximum twist occurs in quite a different field. Indeed the field of maximum twist varies with the value of the current along the wire.

Meanwhile the broad character of the hysteresis in the magnetic-elongation cycle, as established by Mr. Nagaoka's delicate experiments, agrees perfectly with what might be inferred from the character of the hysteresis in the magnetic-twist cycle—a phenomenon whose experimental study is one of the simplest in the whole subject of magnetic strains.

Edinburgh University,
October 28, 1893.

X. *On the Law of Distribution of Energy.*

By S. H. BURBURY, F.R.S.*

IF there be in any space a great number of mutually acting molecules, Boltzmann's law of distribution of energy requires that the number per unit of volume of molecules whose coordinates and momenta lie between assigned limits varies as $e^{-h(\chi + \Pi)}$ in the known notation. The proofs of that law given by Boltzmann and Watson are based on the hypothesis that, from the instant when mutual action commences between two molecules to the instant when it ceases, no action takes place between either of them and any third molecule, or, as it is called, the encounters are binary. I propose to consider the more general case when, for instance, no group of molecules is ever free from the action of other parts of the system.

PART I.

(1) The following is a known proposition in the theory of Least Squares.

Let the chance of a certain magnitude lying between x and $x + dx$ be $f(x)dx$, $f(x)$ being a function which vanishes

* Communicated by the Author.

for infinite values of x , and is not altered by changing the sign of x , so that

$$\int_{-\infty}^{\infty} f(x) dx = 1.$$

$$\int_{-\infty}^{\infty} f(x) x dx = 0.$$

Let
$$\int_{-\infty}^{\infty} f(x) x^2 dx = \overline{x^2}.$$

Let there be N , a very great number, of such magnitudes, each independent of all the others, denoted by $x_1, x_2 \dots x_N$.

Let it be required to find the chance that

$$\frac{1}{\sqrt{N}} (x_1 + x_2 + \dots + x_N)$$

shall lie between c and $c + dc$, and let this chance be $F(c)dc$.

Then by the known method we find

$$F(c) = C \int_{-\infty}^{\infty} d\theta X^N e^{-c\theta \sqrt{N-1}},$$

in which C is constant and

$$\begin{aligned} X &= \int_{-\infty}^{\infty} dx f(x) e^{\frac{x\theta \sqrt{N-1}}{\sqrt{N}}} dx \\ &= \int_{-\infty}^{\infty} f(x) dx \\ &\quad + \frac{\theta \sqrt{N-1}}{\sqrt{N}} \int_{-\infty}^{\infty} x f(x) dx \text{ (which is zero as stated)} \\ &\quad - \frac{1}{N} \frac{\theta^2}{2} \int_{-\infty}^{\infty} x^2 f(x) dx \\ &\quad + \text{terms involving } \theta^3 \text{ \&c.} \end{aligned}$$

$$= 1 - \frac{1}{N} \overline{x^2} \frac{\theta^2}{2} + \text{terms involving } \theta^3 \text{ \&c.}$$

$$= e^{-\frac{1}{N} \overline{x^2} \frac{\theta^2}{2}} + \text{terms involving } \theta^3 \text{ \&c.,}$$

and therefore

$$X^N = e^{-\frac{\overline{x^2} \theta^2}{2}} + \text{\&c.}$$

It is then shown that

$$\begin{aligned} X &= 1 \text{ if } \theta = 0, \\ X &< 1 \text{ if } \theta \neq 0; \end{aligned}$$

and therefore in forming X^N , N being very great, we may neglect powers of θ above θ^2 , and so

$$X^N = e^{-x^2 \frac{\theta^2}{2}},$$

and

$$F(c) = C \int_{-\infty}^{\infty} d\theta e^{-\left(\frac{\theta^2}{2} + c\theta \sqrt{-1}\right)},$$

which is proportional to

$$e^{-\frac{c^2}{2x^2}};$$

and the constant C is found from the condition that

$$\int_{-\infty}^{\infty} F(c) dc = 1.$$

(2) That proposition has been extended as follows. Let $x_1, x_2 \dots x_n$ be n mutually dependent magnitudes, and let the chance that they shall simultaneously have the values denoted by $x_1 \dots x_1 + dx_1$, &c., be

$$f(x_1 \dots x_n) dx_1 \dots dx_n,$$

where $f(x_1 \dots x_n)$ is a function which vanishes for infinite values of the variables $x_1 \dots x_n$, and which is not altered when they all change sign together. Let us call the simultaneous occurrence of $x_1 \dots x_n$ an *association*. The limits for each x shall be $\pm \infty$. Then we have

$$\begin{aligned} \iint \dots f(x_1 \dots x_n) dx_1 \dots dx_n &= 1, \\ \iint \dots f(x_1 \dots x_n) x_1 dx_1 \dots dx_n &= 0 \text{ \&c.} \\ \text{Let } \iint \dots f(x_1 \dots x_n) x_1^2 dx_1 \dots dx_n &= \overline{x_1^2}, \\ \iint \dots f(x_1 \dots x_n) x_1 x_2 dx_1 \dots dx_n &= \overline{x_1 x_2} \text{ \&c.} \end{aligned}$$

Let there now be N such associations, N being very large, and let each be independent of all the others. The variables in the first association shall for distinction be called $x_{11}, x_{12} \dots x_{1n}$, those in the second association $x_{21}, x_{22} \dots x_{2n}$, and so on to $x_{N1}, x_{N2} \dots x_{Nn}$.

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Let it now be required to find the chance that

$$x_1' = \frac{x_{11} + x_{21} + \dots + x_{N1}}{\sqrt{N}} \text{ shall } = c_1 \dots c_1 + dc_1,$$

$$x_2' = \frac{x_{12} + x_{22} + \dots + x_{N2}}{\sqrt{N}} \text{ shall } = c_2 \dots c_2 + dc_2,$$

&c. &c. &c.

$$x_n' = \frac{x_{1n} + x_{2n} + \dots + x_{Nn}}{\sqrt{N}} \text{ shall } = c_n \dots c_n + dc_n,$$

and let this chance be $F(c_1 \dots c_n)dc_1 \dots dc_n$.

In the same way as for one variable x we find that

$$F(c_1 \dots c_n) = K \int_{-\infty}^{\infty} d\theta_1 \dots \int_{-\infty}^{\infty} d\theta_n X^N \epsilon^{-(c_1\theta_1 + \dots + c_n\theta_n) \sqrt{-1}},$$

in which K is constant and

$$X = \int_{-\infty}^{+\infty} \dots f(x_1 \dots x_n) \epsilon^{\frac{1}{\sqrt{N}}(x_1\theta_1 + \dots + x_n\theta_n) \sqrt{-1}} dx_1 \dots dx_n.$$

That is,

$$\begin{aligned} X = & \iint \dots f(x_1 \dots x_n) dx_1 \dots dx_n \\ & + \frac{\theta_1 \sqrt{-1}}{\sqrt{N}} \iint \dots x_1 f(x_1 \dots x_n) dx_1 \dots dx_n + \&c. \\ & - \frac{1}{N} \frac{\theta_1^2}{2} \iint \dots x_1^2 f(x_1 \dots x_n) dx_1 \dots dx_n \\ & - \frac{1}{N} \theta_1 \theta_2 \iint \dots x_1 x_2 f(x_1 \dots x_n) dx_1 \dots dx_n \\ & - \&c. \end{aligned}$$

+ terms involving powers and products of $\theta_1 \dots \theta_n$ above the second degree.

All terms of the form $\iint \dots x f(x_1 \dots x_n) dx_1 \dots dx_n$ vanish by the conditions of $f(x_1 \dots x_n)$.

The higher powers and products will be neglected for the same reason as in the case of one variable; and therefore

$$\begin{aligned} X &= 1 - \frac{1}{N} \frac{\theta_1^2}{2} \overline{x_1^2} - \frac{1}{N} \theta_1 \theta_2 \overline{x_1 x_2} + \&c. \\ &= \epsilon^{-\frac{1}{N}(\frac{\theta_1^2}{2} \overline{x_1^2} + \overline{x_1 x_2} \theta_1 \theta_2 + \dots)} \\ X^N &= \epsilon^{-\frac{\theta_1^2}{2} \overline{x_1^2} + \overline{x_1 x_2} \theta_1 \theta_2 + \dots}, \end{aligned}$$

the index containing all squares and products of $\theta_1 \dots \theta_n$; and therefore $F(c_1 \dots c_n)$

$$= K \iint \dots \epsilon^{-\{\overline{x_1^2 \theta_1^2} + \overline{x_1 x_2 \theta_1 \theta_2} + \dots + (c_1 \theta_1 + \dots + c_n \theta_n) \sqrt{-1}\}} d\theta_1 \dots d\theta_n,$$

the limits being $\pm \infty$, and K being a constant to be found by making $\iint \dots F(c_1 \dots c_n) dc_1 \dots dc_n = 1$.

(3) Now for two variables x_1, x_2 we find that

$$\begin{aligned} \int_{-\infty}^{\infty} d\theta_1 \int_{-\infty}^{\infty} d\theta_2 \epsilon^{-\{\overline{x_1^2 \theta_1^2} + \overline{x_1 x_2 \theta_1 \theta_2} + \overline{x_2^2 \theta_2^2} + (c_1 \theta_1 + c_2 \theta_2) \sqrt{-1}\}} \\ = \frac{2\pi}{\sqrt{\overline{x_1^2 x_2^2} - \overline{x_1 x_2}^2}} \epsilon^{-\frac{\overline{x_2^2 c_1^2} - \overline{x_1 x_2 c_1 c_2} + \overline{x_1^2 c_2^2}}{\overline{x_1^2 x_2^2} - \overline{x_1 x_2}^2}} \\ = \frac{2\pi}{\sqrt{d}} \epsilon^{-\left(\frac{d_{11} c_1^2}{d} + \frac{d_{12}}{d} c_1 c_2 + \frac{d_{22} c_2^2}{d}\right)}, \end{aligned}$$

where d is the determinant,

$$d = \begin{vmatrix} \overline{x_1^2} & \overline{x_1 x_2} \\ \overline{x_1 x_2} & \overline{x_2^2} \end{vmatrix}$$

and d_{11}, d_{12}, d_{22} are its minors.

We infer, and it can be proved, that the same law holds for n variables. That is that if

$$d = \begin{vmatrix} \overline{x_1^2} & \overline{x_1 x_2} & \dots & \overline{x_1 x_n} \\ \overline{x_1 x_2} & \overline{x_2^2} & \dots & \overline{x_2 x_n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

then

$$F(c_1 \dots c_n) = K \frac{(2\pi)^{\frac{n}{2}}}{\sqrt{d}} \epsilon^{-\{\frac{d_{11} c_1^2}{d} + \frac{d_{12}}{d} c_1 c_2 + \dots\}},$$

in which d_{1r} is the minor formed by omitting the first row and r th column of d , and its sign is such that

$$d = \overline{x_1^2} d_{11} + \sum_{r=2}^n \overline{x_1 x_r} d_{1r}.$$

(4) Now there exists a determinant

$$D = \begin{vmatrix} 2a_1 & b_{12} & \dots & b_{1n} \\ b_{12} & 2a_2 & \dots & b_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

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such that

$$\overline{x_1^2} = \frac{D_{11}}{D}, \quad \overline{x_1 x_2} = \frac{D_{12}}{D}, \quad \&c.,$$

and therefore

$$d = \Sigma \pm \frac{D_{11}}{D} \frac{D_{22}}{D} \dots;$$

and thence by a known proposition * we find

$$\frac{d_{11}}{d} = 2a_1, \quad \frac{d_{12}}{d} = b_{12}, \quad \&c., \quad \text{and } D = \frac{1}{d};$$

and therefore

$$\begin{aligned} F(c_1 \dots c_n) &= K (2\pi)^{\frac{n}{2}} \sqrt{D} \cdot \epsilon^{-(2a_1 \frac{c_1^2}{2} + b_{12} c_1 c_2 + \dots)} \\ &= K (2\pi)^{\frac{n}{2}} \sqrt{D} \cdot \epsilon^{-(a_1 c_1^2 + b_{12} c_1 c_2 + \dots)}. \end{aligned}$$

To determine K we have

$$\iint \dots F(c_1 \dots c_n) dc_1 \dots dc_n = 1.$$

That is, since

$$\iint \dots \epsilon^{-(a_1 c_1^2 + b_{12} c_1 c_2 + \dots)} dc_1 \dots dc_n = \frac{(2\pi)^{\frac{n}{2}}}{\sqrt{D}},$$

$$K = \frac{1}{(2\pi)^n},$$

and

$$F(c_1 \dots c_n) = \frac{1}{(2\pi)^{\frac{n}{2}}} \sqrt{D} \cdot \epsilon^{-(a_1 c_1^2 + b_{12} c_1 c_2 + \dots)}.$$

(5) Again,

$$\begin{aligned} \overline{c_1^2} &= \frac{1}{(2\pi)^{\frac{n}{2}}} \sqrt{D} \iint \dots \epsilon^{-(a_1 c_1^2 + b_{12} c_1 c_2 + \dots)} c_1^2 dc_1 \dots dc_n \\ &= \frac{D_{11}}{D} = \overline{x_1^2} \text{ by hypothesis.} \end{aligned}$$

Similarly,

$$\overline{c_1 c_2} = \overline{x_1 x_2}, \quad \&c.;$$

and therefore

$$\overline{S_c} = \overline{S_x};$$

and these results are true whatever be the form of the function $f(x_1 \dots x_n)$.

* Todhunter, Theory of Equations, 2nd edition, p. 393.

If, further,

$$f(x_1 \dots x_n) = \frac{\sqrt{D}}{(2\pi)^{\frac{n}{2}}} e^{-(a_1 x_1^2 + b_{12} x_1 x_2 + \dots)},$$

we see that

$$F(c_1 \dots c_n) = f(c_1 \dots c_n).$$

Now let us write

$$x_1' = \frac{x_{11} + x_{21} + \dots + x_{N1}}{\sqrt{N}},$$

$$x_2' = \frac{x_{12} + x_{22} + \dots + x_{N2}}{\sqrt{N}}, \text{ \&c.}$$

Also

$$S_1 = a_1 x_{11}^2 + b_{12} x_{11} x_{12} + \dots$$

$$S_2 = a_1 x_{21}^2 + b_{12} x_{21} x_{22} + \dots$$

$$\text{\&c.} = \text{\&c.}$$

$$S' = a_1 x_1'^2 + b_{12} x_1' x_2'.$$

Therefore expanding $x_1'^2$ &c.,

$S' = \frac{S_1 + S_2 + \dots + S_N}{N} + \text{terms containing products of the form } x_{1p} x_{2q}, \text{ that is products of two } x\text{'s taken from different associations, which terms are not generally zero.}$

(6) The truth of the foregoing propositions will not be affected if for a_1 , b_{12} , &c. we write κa_1 , κb_{12} , &c., where κ is any positive constant. In this case D becomes $\kappa^n D$ and S becomes κS . It will be convenient if at this point we introduce a factor corresponding to Boltzmann's h , namely, $\frac{n}{2T}$, so that henceforth we will write

$$S = a_1 x_1^2 + b_{12} x_1 x_2 + \text{\&c.},$$

$$F(x_1 \dots x_n) = C e^{-\frac{nS}{2T}},$$

where

$$C = \frac{\sqrt{D}}{(2\pi)^{\frac{n}{2}}} \left(\frac{n}{2T} \right)^{\frac{n}{2}}$$

and

$$D = \Sigma \pm 2a_1 2a_2 \text{ \&c.}$$

In this case also

$$\overline{x_1^2} = \frac{2T}{n} \frac{D_{11}}{D}, \quad \overline{x_1 x_2} = \frac{2T}{n} \frac{D_{12}}{D}, \text{ \&c.,}$$

and

$$\begin{aligned}\bar{S} &= C \iint \dots \epsilon^{-\frac{nS}{2T}} S dx_1 \dots dx_n \\ &= \frac{2T}{n} \left\{ a_1 \frac{D_{11}}{D} + b_{12} \frac{D_{12}}{D} + \dots \right\} = \frac{2T}{n} \frac{n}{2} = T,\end{aligned}$$

because

$$a_1 D_{11} + b_{12} D_{12} + \dots = \frac{n}{2} D.$$

(7) We have assumed that the quadratic function

$$S = a_1 x_1^2 + b_{12} x_1 x_2 + \&c.$$

must have its coefficients so chosen as that it shall be positive for all values of the variables $x_1 \dots x_n$. The condition that this may be the case is that the determinant

$$D = \begin{vmatrix} 2a_1 & b_{12} & \dots & b_{1n} \\ b_{12} & 2a_2 & \dots & \\ \dots & \dots & \dots & 2a_n \end{vmatrix}$$

and all its coaxial minors shall be positive. Hence each of the coefficients a is positive, and $4a_p a_q - b_{pq}^2$ is positive for all values of p and q .

If S be the energy of an association, the above condition is necessary for its *stability*. So for two associations near to one another, let the energy be $a_1 x_1^2 + b_{12} x_1 x_2 + \dots + a'_1 x_1'^2 + \&c.$, and let Δ be the double determinant $\Sigma \pm 2a_1, 2a_2 \dots 2a'_1 \dots$. Then in order that the two associations, considered as a single system, may be stable, Δ and all its coaxial minors must be positive. If the expression for the energy contains no terms of the form bxx' , where x belongs to one and x' to the other association, Δ is the product of the two single determinants $\Sigma \pm 2a_1, 2a_2 \dots$ and $\Sigma \pm 2a'_1, 2a'_2 \dots$, and if the condition be satisfied for them, it is satisfied for Δ . But if any terms of the form bxx' make their appearance, they may make Δ or some of its coaxial minors negative, and the two associations, though separately stable, may be unstable together, and dissociation may ensue.

PART II.

(8) Now let us suppose that S is proportional to the kinetic energy, or to a part of the energy, of an association. Let the number of associations, or, as we will now call them, systems, be very great. Each has its own S . And we will effect a

redistribution of S among them in the following way. Consider any group of N systems for which the variables are $x_{11}, x_{21}, \&c.$, and for which S has the values $S_1, S_2 \dots S_N$. Let these contribute respectively $\frac{S_1}{N}, \frac{S_2}{N}, \&c.$; and let the contribution $\frac{S_1}{N}$ be represented by the energy of a similar system whose variables are $\frac{x_{11}}{\sqrt{N}}, \frac{x_{12}}{\sqrt{N}}, \&c.$; and let $\frac{S_2}{N} \&c.$ be represented in the same way.

From that group of N systems we will form the variables $x_1' \dots x_n'$ for one system in the new distribution by making

$$\begin{aligned} x_1' &= \frac{x_{11} + x_{21} + \dots + x_{N1}}{\sqrt{N}}, \\ x_2' &= \frac{x_{12} + x_{22} + \dots + x_{N2}}{\sqrt{N}}, \\ &\&c. \qquad \qquad \&c. \end{aligned}$$

see *post.* (11).

Now let us take at random other groups, each of N systems, and deal with them in the same way. And so on until every original system has appeared N times as a member of a group of N . Since in case of each group it loses $\frac{S}{N}$, it will finally have parted with all its energy S . When this process has been carried out, the whole of S for all the systems will have been redistributed among them. And owing to the mode of formation of $x_1' \&c.$, the chance of the variables $x_1' \dots x_n'$ of any system in the new distribution having the values $c_1 \dots c_n + dc_1 \&c.$ is $Ce^{-\frac{nS}{2T}} dc_1 \dots dc_n$, and the aggregate energy will not have been altered.

(9) If, then, for the original systems

$$f(x_1 \dots x_n) = Ce^{-\frac{nS}{2T}},$$

the law of distribution is the same for the new as for the original system. In other words, it is unaffected by our process of redistribution.

If for the original systems $f(x_1 \dots x_n)$ have any other form, we shall choose $a_1, b_{12}, \&c.$, to satisfy the equations

$$\overline{x_1^2} = \frac{D_{11}}{D}, \quad \overline{x_1 x_2} = \frac{D_{12}}{D}, \&c.,$$

where D is the determinant of $\frac{n}{2T}2a_1, \frac{n}{2T}b_{12}, \&c.$, and then in the redistributed system the law will be

$$F(c_1 \dots c_n) = C e^{-\frac{nS}{2T}},$$

as before, and will remain unaffected by any further redistribution. In stationary motion, therefore, $F(c_1 \dots c_n)$ has the form $C e^{-\frac{nS}{2T}}$, with a quadratic function for S , whether the initial distribution $f(x_1 \dots x_n)$ has that form or not.

This assumes that the process of redistribution of the original systems has been carried out completely. If it be carried out only partially, as for instance if only a portion of the original systems be subjected to the process, the distribution in the new system will approximate more and more to the permanent form $C e^{-\frac{nS}{2T}}$, according as the redistribution is more complete. And by successive partial redistributions it will ultimately be reduced to the permanent or stationary form.

(10) The processes which we have supposed to take place successively may, of course, take place simultaneously. Further, we may suppose the whole process of redistribution to take place at a given rate per unit of time. Finally, our results will not be affected if the variables in any association undergo any other series of changes during the same time, provided these changes do not on average alter S .

(11) By the method of art. 8 energy is conserved in the final result, but is not conserved in each separate process, because generally S' , the energy which we suppose to be received by a system in the new distribution, is not equal to $\frac{S_1 + S_2 + \dots + S_N}{N}$, the energy which the contributing systems part with. That may create a difficulty in the application of the method to a physical system, even although, when the contributing systems are rapidly oscillating and in different phases, it may be that $S' = \frac{S_1 + S_2 + \dots + S_N}{N}$ on the average of a very short time.

(12) If our associations be material systems fixed in space, we may suppose the energy, S , of oscillation to be transmitted through space—*i. e.* æther—in waves with conservation of energy, so that the energy of a wave which passes per unit area and time through a spherical surface of radius R

described about the centre of disturbance varies as $\frac{1}{4\pi R^2}$, or varies as $\frac{1}{N}$, if $N=4\pi R^2$ and the coordinates x , of which that energy is a quadratic function, vary as $\frac{1}{\sqrt{N}}$. If, now, we

may further assume that any number of such waves may coexist, so that the disturbance x at any point at any instant is the algebraic sum of the disturbances due to all the waves which are passing the point at that instant, the redistribution of S will go on in the physical system in exactly the same way as in our analytical system—and with the same result,

that the distribution denoted by $Ce^{\frac{ns}{2t}}$ will be permanent. The disturbances $x_1 \dots x_n$ in any system will be respectively

$\frac{1}{2R\sqrt{\pi}}$ times the sums of the values of the corresponding disturbances in systems distant R from the one in question, as they were t seconds ago, $\frac{R}{t}$ being the velocity of wave-

motion. The potential energy, χ , of the internal forces of a system we suppose not to be capable of transmission in that form. But if the law of distribution be $e^{-h(\chi+S)}$, we know that this distribution will not be affected by the internal forces; neither will it be affected, on the above hypothesis, by the transmission of S . It will therefore be permanent.

But if we are not allowed to assume the coexistence of waves in the sense above stated, the law cannot be permanent, except in the known case of binary encounters.

PART III.

(13) Our investigation hitherto has been based on the assumption that the N associations are *independent* of one another; that is, that the chance of the variables $x_1 \dots x_n$ in one association having assigned values is independent of the values of $x'_1 \dots x'_n$ the variables in another association, or, if $f(x)$ be the chance of any one of the first set having assigned value, $\frac{df(x)}{dx} = 0$ for each x' . The condition of complete

independence is that the expression for the energy contains no term of the form bxx' , where x and x' belong to different associations. This condition may not be satisfied if our associations are material systems very near to one another.

It is necessary to replace the stringent condition by one which can be satisfied more easily, as follows:—In the first place it will be shown that our method is applicable even

when the associations are not all independent of each other, provided we can choose in many ways a group of them containing a great number which are independent of each other.

Let there be Nq systems, where N is very large and q a positive integer to which we may assign any value. Let them be called $A_1, A_2 \dots A_{Nq}$. If it be not true that every one of the Nq systems is independent of every other, nevertheless it may be true, and we will assume that it is true, that the N systems A_1, A_{1+q}, A_{1+2q} , &c. are independent of each other. And, similarly, the N systems A_2, A_{2+q} , &c. may be independent of each other, and so on for other groups. On this assumption that A_1, A_{1+q} , &c. are mutually independent, we may apply our method to them. And let $F_1(c_1 \dots c_n)$ $dc_1 \dots dc_n$ be the chance that the sum of the x_1 's in these N systems, each divided by $\sqrt{N}$, shall be $c_1 \dots c_1 + dc_1$, &c.

Then $F(c_1 \dots c_n) = C\epsilon^{-\frac{nS}{2T}}$. Also let $F_2(c_1 \dots c_n)$ be the corresponding chance for the group A_2, A_{2+q} , &c. All the systems being supposed similar in character, evidently

$$F_1(c_1 \dots c_n) = F_2(c_1 \dots c_n) = \&c.$$

But the result for any one of the groups of N systems cannot differ from that for the whole Nq systems. Whence it follows that $F(c_1 \dots c_n)$ for the Nq systems

$$\begin{aligned} &= F_1(c_1 \dots c_n) = F_2(c_1 \dots c_n) = \&c. \\ &= C\epsilon^{-\frac{nS}{2T}}. \end{aligned}$$

We are therefore at liberty to apply our method to the Nq systems, provided that, although they are not all independent of each other, yet we can divide them into groups, each of N systems, the members of which are independent of one another.

(14) Again, in order that the N systems A_1, A_{1+q} , &c. may be independent of each other, it will be sufficient if we make every variable, as x , in A_1 independent of every variable x' in A_{1+q} , &c., that is $\frac{df(x)}{dx'}$ must be zero or negligible.

Let us therefore consider a series of single magnitudes x_1, x_2 , &c. which may be the variables in many systems of n , and let the chance of their simultaneously having assigned values be

$$C\epsilon^{-\frac{n}{2T}(a_1x_1^2 + b_{12}x_1x_2 + \&c.)},$$

and let it be required to find the condition that $\frac{df(x_1)}{dx_r}$ shall

vanish. In order to find $\frac{df(x_1)}{dx_r}$ we integrate according to each of the other variables between the limits $\pm \infty$. The result will be proportional to $e^{-(Ax_1^2+Bx_1x_r)}$, where A does not concern us, and $\frac{df(x_1)}{dx_r} \propto B$, or the condition that $\frac{df(x_1)}{dx_r}$ shall vanish is that $B=0$. Also $B = \frac{\Delta_{1r}}{\Delta_{1rr1}}$, where Δ is the determinant of r rows $\Sigma \pm 2a_1 2a_2 \dots$ and Δ_{1rr1} a coaxial minor.

(15) We have, then, to find a relation between the coefficients $a_1, b_{12}, \&c.$, which will make Δ_{1r} vanish compared with Δ_{1rr1} , without making all the coefficients b vanish which connect the variables in any one of the original associations with those in any other. That can be done in many ways. It will be sufficient to give one example. Let us suppose all the a 's equal to each other, and all the b 's of the form b_{pp+1} equal to one another, and all other b 's zero.

Further, let $b_{12}=b_{23}=\&c.=2a\theta$.

Then the determinant assumes the form

$$\Delta = \begin{vmatrix} 2a & b & . & . \\ b & 2a & b & . \\ . & b & 2a & b \\ . & . & b & 2a \end{vmatrix}$$

and if f_r be its value for r rows, the law of formation is

$$f_r = f_{r-1} - \theta^2 f_{r-2} \dots \dots \dots (A)$$

Since every f is to be positive, $f_{r-1} > f_r$. Ultimately as r increases the ratio $\frac{f_r}{f_{r-1}}$ becomes constant. Let its constant value be λ . Then equation A gives

$$\lambda = 1 - \frac{\theta^2}{\lambda},$$

or

$$\lambda = \frac{1}{2} \pm \frac{\sqrt{1-4\theta^2}}{2},$$

of which the positive sign will be taken. This result shows that if f , or Δ , be always positive, θ^2 cannot be greater than $\frac{1}{4}$, or θ greater than $\frac{1}{2}$. Also if $\theta = \frac{1}{2}$, we easily find $\Delta = \frac{r+1}{2^r} (2a)^r$, and therefore

$$\Delta_{1rr1} = \frac{r-1}{2^{r-2}} (2a)^{r-2}.$$

Again, in this case

$$\Delta_{1r} = \begin{vmatrix} b & 2a & b & . \\ . & b & 2a & b \\ . & . & b & 2a \\ . & . & . & b \end{vmatrix} \\ = (2a)^{r-1} \theta^{r-1} = \frac{1}{2^{r-1}} (2a)^{r-1}.$$

Therefore

$$\frac{\Delta_{1r}}{\Delta_{1r-1}} = \frac{a}{r-1},$$

and vanishes as r increases indefinitely.

PART IV.

Boltzmann's *Minimum Function*.

(16) We have seen that, the law of distribution being $Ce^{\frac{nS}{2T}}$, $\frac{2T}{x_1^2} = \frac{D_{11}}{nD}$, $\frac{2T}{x_1 x_2} = \frac{D_{12}}{nD}$, &c., and $\bar{S} = T$.

Let us consider a varied system in which with these same values of $\overline{x_1^2}$, $\overline{x_1 x_2}$, &c. the law of distribution is $Ce^{\frac{nS}{2T} \overline{1+q}}$, where $1+q$ is any positive function of x_1 , x_2 , &c., and q must satisfy the following conditions, namely:—

(1) In order that the number of systems may be the same in the varied as in the normal state,

$$\iint \dots e^{\frac{nS}{2T}} dx_1 \dots dx_n = \iint \dots e^{\frac{nS}{2T} \overline{1+q}} dx_1 \dots dx_n \\ \text{or} \quad \iint \dots q e^{\frac{nS}{2T}} dx_1 \dots dx_n = 0.$$

(2) In order that the values of $\overline{x_1^2}$, $\overline{x_1 x_2}$, &c., may not be altered,

$$\iint \dots e^{\frac{nS}{2T}} x_1^2 dx_1 \dots dx_n = \iint \dots e^{\frac{nS}{2T} \overline{1+q}} x_1^2 dx_1 \dots dx_n \\ \text{\&c.} \quad \quad \quad \text{\&c.},$$

and therefore also

$$\iint \dots e^{\frac{nS}{2T}} S dx_1 \dots dx_n = \iint \dots e^{\frac{nS}{2T} \overline{1+q}} S dx_1 \dots dx_n.$$

These conditions being satisfied the system will, on free interchange of energy, pass out of the varied state into the normal state. And it can be now shown that the function B

$$= \iint \dots f(x_1 \dots x_n) \{\log f(x_1 \dots x_n) - 1\} dx_1 \dots dx_n$$

diminishes in the process.

For let B_0 be the value of B in the normal state, when $f(x_1 \dots x_n) = C \epsilon^{-\frac{nS}{2T}}$, B its value when

$$f(x_1 \dots x_n) = C \epsilon^{-\frac{nS}{2T} \overline{1+q}}.$$

Then $B - B_0 =$

$$\begin{aligned} & C \iint \dots \epsilon^{-\frac{nS}{2T} \overline{1+q}} (\log C - \frac{nS}{2T} - 1 + \log \overline{1+q}) dx_1 \dots dx_n \\ & - C \iint \dots \epsilon^{-\frac{nS}{2T}} (\log C - \frac{nS}{2T} - 1) dx_1 \dots dx_n \\ & = C \iint \dots \epsilon^{-\frac{nS}{2T} \overline{1+q}} \log \overline{1+q} dx_1 \dots dx_n \\ & = C \iint \dots \epsilon^{-\frac{nS}{2T}} \{\overline{1+q} \log \overline{1+q} - q\} dx_1 \dots dx_n, \end{aligned}$$

because

$$C \iint \dots \epsilon^{-\frac{nS}{2T}} q dx_1 \dots dx_n = 0.$$

Now since $1+q$ is positive, $\overline{1+q} \log \overline{1+q} - q$ is necessarily positive, unless $q=0$, and is then zero; $B - B_0$ is therefore positive. And given T and the coefficients $a_1, b_{12}, \&c.$, B has its least possible value when $q=0$, or $f(x_1 \dots x_n) = C \epsilon^{-\frac{nS}{2T}}$.

And this least possible or minimum value differs by a constant from $\log C$ or $\log \left\{ \left(\frac{n}{2T} \right)^{\frac{n}{2}} \frac{\sqrt{D}}{(2\pi)^{\frac{n}{2}}} \right\}$.

Further, $\frac{d}{dq} (B - B_0) = \log(1+q)$, and therefore $B - B_0$ diminishes as q approaches zero.

The Second Law of Thermodynamics.

(17) In stationary motion the minimum function has the value

$$B = \left(\frac{n}{2T} \right)^{\frac{n}{2}} \frac{\sqrt{D}}{(2\pi)^{\frac{n}{2}}} \text{ plus a constant.}$$

It is a function of T and the parameters $a_1, b_{12}, \&c.$, or any

parameters $v_1, v_2, \&c.$, on which $a_1, b_{12}, \&c.$, depend. The second law may from one point of view be regarded as the law of the variation of B when T and the parameters vary very slowly, so that stationary motion is always attained. On this assumption the proofs of the second law depend.

We have seen that $\bar{S}=T$ and is independent of the parameters, or $\frac{d}{dv} \bar{S}=0$ for each v . But $\frac{d\bar{S}}{dv}$ is not generally zero. It may, therefore, be the case that work has to be done on variation of any parameter v . This work will be denoted by $-\frac{d\bar{S}}{dv} \partial v$. It will include the work done against all external forces. The energy imparted during any small variation of T and the parameters will be denoted by ∂Q . Then the second law requires that $\frac{\partial Q}{T}$ shall be a complete differential.

(18) It will be sufficient to prove the law for any parameter v on which $a_1, b_{12}, \&c.$ depend. So far as this proof is concerned, there may be many such.

We have in this case

$$\begin{aligned} \partial Q &= \partial T - \frac{d\bar{S}}{dv} \partial v \\ &= \partial T - C \partial v \iint \dots \epsilon^{-\frac{nS}{2T}} \frac{dS}{dv} dx_1 \dots dx_n \\ &= \partial T - C \partial v \iint \dots \epsilon^{-\frac{nS}{2T}} \left\{ \frac{da_1}{dv} x_1^2 + \frac{db_{12}}{dv} x_1 x_2 + \dots \right\} dx_1 \dots dx_n \\ &= \partial T - \partial v \frac{2T}{n} \left\{ \frac{da_1}{dv} \frac{D_{11}}{D} + \frac{db_{12}}{dv} \frac{D_{12}}{D} + \dots \right\} \\ &= \partial T - \partial v \frac{2T}{n} \frac{1}{2} \left\{ \frac{da_1}{dv} \frac{1}{D} \frac{dD}{da_1} + \frac{db_{12}}{dv} \frac{1}{D} \frac{dD}{db_{12}} + \dots \right\} \\ &= \partial T - \partial v \frac{T}{n} \frac{1}{D} \frac{dD}{dv}. \\ \frac{\partial Q}{T} &= \partial \log T - \frac{1}{n} \partial \log D. \end{aligned}$$

Now in this case,

$$\begin{aligned} \partial B &= \partial \log \left\{ \sqrt{D} \left(\frac{n}{2T} \right)^{\frac{n}{2}} \right\}; \\ \therefore \frac{1}{n} \partial \log D &= \frac{2}{n} \partial B + \partial \log T; \\ \therefore \frac{\partial Q}{T} &= -\frac{2}{n} \partial B. \end{aligned}$$