The Mathematical Foundations of the Theory of Irreversible Thermodynamical Processes

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It is shown that the Onsager relations

$$\dot{x}_i = \sum_{k=1}^{n} L_{ik}X_k \quad (i = 1, 2, \ldots, n), L_{ik} = L_{ki},$$

when limited to terms of second order in x, are first integrals of a more general set of differential equations

$$d^2x_i / dt^2 = X_i \quad (i = 1, 2, \ldots, n).$$

In the most general case, in which all terms in the expansion of ΔS are kept, we obtain $L_{ik} = L_{ki}$ with accuracy to terms of second order. The theory so developed is applied to the phenomenon of thermal conduction and to the theory of phases in adiabatically isolated systems.

INTRODUCTION

We consider an adiabatically isolated system, whose state is completely determined by the variables $\xi_1, \xi_2, \xi_3, \ldots, \xi_n$. Let $\xi_1^0, \xi_2^0, \ldots, \xi_n^0$ be the values of these variables when the system is in thermal equilibrium. Denoting by $S(\xi_1, \xi_2, \ldots, \xi_n)$ the entropy of the system, we have

$$\Delta S = S(\xi_1, \xi_2, \ldots, \xi_n) - S(\xi_1^0, \xi_2^0, \ldots, \xi_n^0) = \frac{1}{2}\left(\frac{\partial^2 S}{\partial x_1^2} x_1^2 + 2\frac{\partial^2 S}{\partial x_1 \partial x_2} x_1 x_2 + \cdots + \frac{\partial^2 S}{\partial x_n^2} x_n^2\right) + \cdots = -\frac{1}{2}\sum_{k=1}^{n} g_{ik}x_i x_k + \cdots \quad (i = 1, 2, \ldots, n), \tag{1}$$

where $g_{ik} = g_{ki}$, $\chi_i = \xi_i - \xi_i^0$, and where the derivatives are taken at $\chi_1 = \chi_2 = \ldots = \chi_n = 0$. Here $\Sigma g_{ik}\chi_i\chi_k$ is a positive definite quadratic form.

We now set ourselves the problem of determining the differential equations for irreversible thermodynamic adiabatic processes.

Lord Kelvin, studying thermoelectric phenomena, came to the conclusion that it was possible to write down differential equations which give the interaction between electric currents and thermal currents $\dot{\chi}_1, \dot{\chi}_2$ in the form

$$\dot{x}_1 = L_{11}X_1 + L_{12}X_2, \quad \dot{x}_2 = L_{21}X_1 + L_{22}X_2,$$

where X_1 and X_2 are "forces" which depend on the electrical and thermal phenomena in the system. Later, Rayleigh, formulating a "principle of minimum energy dissipation" pointed out the possibility of considering ΔS as a potential function.

Onsager, studying hypothetical unimolecular chemical processes in a substance which can exist in a given homogeneous phase in three forms A, B, C, which undergo spontaneous transition from one to another ("triangular processes"), and also phenomena of thermal conduction in anisotropic crystals, concluded that the tensor L_{ik} was symmetric. Following Boltzman's example and starting from the assumptions of statistical mechanics on the "microscopic reversibility" of elementary processes and from the theory of fluctuation, Onsager[1] established the phenomenological relations

$$\dot{x}_i = \sum_{k=1}^{n} L_{ik}X_k \quad (i = 1, 2, \ldots, n), \tag{2}$$

where $L_{ik} = L_{ki}$, $\dot{\chi}_i$ is the flow of χ_i, X_k are the "forces", which are partial derivatives of the potential function $(-\Delta S)$ with respect to the χ_k, i.e.,

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

$$X_k = \partial(-\Delta S)/\partial x_k. \quad (3)$$

Later Casimir[2] pointed out gaps in Onsager's argument, showing that Onsager assumed that the fluctuations on the average follow the usual phenomenological macroscopic laws. Landau and Lifshitz[3] proved that L_{ik} must be coefficients of essentially positive quadratic form. However, as we have shown[4], this is still not sufficient to establish the Onsager relation. De Groot[5] suggested that the Onsager relations (in those cases where only their applications are concerned) be taken as a new thermodynamic principle.

We consider below the problem of irreversible thermodynamic processes from the mathematical point of view and obtain several consequences from the second law of thermodynamics in conjunction with irreversible processes in adiabatically isolated systems. Following established custom, we keep only quadratic terms in the expansion of ΔS in powers of $\chi_1, \chi_2, \ldots, \chi_n$. Then, following the method of integration developed by Poincaré, we show that consideration of all terms in the expansion of ΔS does not lead to any essential changes in the results.

1. ANALYSIS OF THE PHENOMENOLOGICAL RELATIONS OF ONSAGER

First of all, we note that for each set of initial values $\chi_1^0, \chi_2^0, \ldots, \chi_n^0$ it is necessary, in adiabatically isolated systems, that $\lim \chi_i(t) = 0$ for $t \to +\infty$. Thus the point $\chi_1 = \chi_2 = \ldots = \chi_n = 0$ is a critical point of the integral of the system of differential equations

$$dx_i/dt = L_{i1}X_1 + L_{i2}X_2 + \cdots + L_{in}X_n \quad (i = 1, 2, 3, \ldots, n), \quad (4)$$

where $L_{ik} = L_{ki}$ Since

$$X_i = g_{i1}x_1 + g_{i2}x_2 + \cdots + g_{in}x_n,$$

the integral of the system of linear differential equations of nth order[4] possesses n constants of integration. This characteristic permits us to make an arbitrary choice of the initial values $\chi_1^0, \chi_2^0, \ldots, \chi_n^0$ of the independent variables $\chi_1, \chi_2, \ldots, \chi_n$. However, this is not sufficient to guarantee that the integrals of the given system have physical significance. It is also necessary that $\lim \chi_i(t) = 0$ for $t \to +\infty$ or, in other words, that the point $\chi_1 = \chi_2 = \ldots = \chi_n = 0$ be a common point of the family of integral curves, i.e., that all the integral curves which satisfy the arbitrary set of initial conditions $\chi_1^0, \chi_2^0, \ldots, \chi_n^0$ of the independent variables meet at this point. In order that the integrals

$$x_i(t) = C_1\gamma_{i1}e^{r_1t} + C_2\gamma_{i2}e^{r_2t} + \cdots + C_n\gamma_{in}e^{r_nt} \quad (i = 1, 2, \ldots, n) \quad (5)$$

of this system satisfy the condition $\lim \chi_i(t) = 0$ for $t \to +\infty$, it is necessary that all r_i be negative. But, since the r_i are functions of the L_{ik}, which thus determine the state of the system, this requirement contradicts the basic hypothesis that $\xi_1, \xi_2, \ldots, \xi_n$ are the only variables that define the state of the system.

As an example, for $n = 2$, we have

$$dx_1/dt = L_{11}(g_{11}x_1 + g_{12}x_2) + L_{12}(g_{21}x_1 + g_{22}x_2), \quad (6)$$

$$dx_2/dt = L_{21}(g_{11}x_1 + g_{12}x_2) + L_{22}(g_{21}x_1 + g_{22}x_2).$$

Setting $\chi_1 = \alpha e^{rt}$, $\chi_2 = \beta e^{rt}$, we get the quadratic equation

$$\begin{vmatrix} L_{11}g_{11} + L_{12}g_{21} - r & L_{11}g_{12} + L_{12}g_{22} \\ L_{21}g_{11} + L_{22}g_{21} & L_{21}g_{12} + L_{22}g_{22} - r \end{vmatrix} = 0, \quad (7)$$

for determining r. The roots of this equation are

$$r_{1,2} = \frac{1}{2}(L_{11}g_{11} + 2L_{12}g_{12} + L_{22}g_{22}) \pm \frac{1}{2}\left((L_{11}g_{11} + 2L_{12}g_{12} + L_{22}g_{22})^2 - 4(L_{11}L_{22} - L_{12}^2)(g_{11}g_{22} - g_{12}^2)\right)^{1/2}. \quad (8)$$

[2] H. B. C. Casimir, Rev. Mod. Phys. **17**, 343 (1945); Philips Res. Rep. **1**, 185 (1946)

[3] L. Landau and E. Lifshitz, *Statistical Physics*, 1951

[4] Kyrille Popoff, Compt. rend. **238**, 648 (1952); J. de Math. Phys. Appl. **3**, 42, 440 (1952); **5**, 67 (1954); Compt. rend. **236**, 785, 1640 (1953); Ann. Phys. **9**, 261 (1954)

[5] S. R. de Groot, *Thermodynamics of Irreversible Processes* (North Holland Publ. Co., Amsterdam, 1951)

In order that the differential equations have physical meaning, r_1, r_2 must be negative, i.e.,

$$0<(L_{11}g_{11}+2L_{12}g_{12}+L_{22}g_{22})^2 \quad (9)$$
$$-4(L_{11}L_{22}-L_{12}^2)(g_{11}g_{22}-g_{12}^2)$$
$$<(L_{11}g_{11}+2L_{12}g_{12}+L_{22}g_{22})^2,$$
$$(L_{11}g_{11}+2L_{12}g_{12}+L_{22}g_{22})<0.$$

We now show that the set of differential equations

$$d^2x_i/dt^2=X_i \qquad (i=1,2,\ldots,n), \quad (10)$$
$$X_i=g_{i1}x_1+g_{i2}x_2+\cdots+g_{in}x_n,$$

satisfies the physical requirements and has the phenomenological relations (2) as first integrals.

We rewrite the set (10) in the form

$$d^2x_1/dt^2=g_{11}x_1+g_{12}x_2+\cdots+g_{1n}x_n, \quad (10')$$
$$\cdots\cdots\cdots,$$
$$d^2x_n/dt^2=g_{n1}x_1+g_{n2}x_2+\cdots+g_{nn}x_n.$$

Setting

$$x_1=\alpha e^{rt},\ x_2=\beta e^{rt},\ \ldots,\ x_n=\nu e^{rt},$$

we obtain

$$(g_{11}-r^2)\alpha+g_{12}\beta+g_{13}\gamma+\cdots+g_{1n}\nu=0, \quad (11)$$
$$\cdots\cdots\cdots,$$
$$g_{n1}\alpha+g_{n2}\beta+g_{n3}\gamma+\cdots+(g_{nn}-r^2)\nu=0.$$

In order that this homogeneous system of algebraic equations in α, β, ... , ν possess near zero solutions we must have

$$\begin{vmatrix} g_{11}-r^2 & g_{12} & \cdots & g_{1n} \\ g_{21} & g_{22}-r^2 & \cdots & g_{2n} \\ \vdots & \vdots & & \vdots \\ g_{n1} & g_{n2} & \cdots & g_{nn}-r^2 \end{vmatrix}=0.$$

Since $\Sigma g_{ik}\chi_i\chi_k$ is a positive definite quadratic form, all the roots of the equation of nth degree in

$$\Delta(r^2)=0$$

are real and positive. Thus n roots ($r_1, r_2, \ldots, r_n$) of this system are negative and n roots ($r_{n+1}=-r_1, r_{n+2}=-r_2, \ldots, r_{n+p}=-r_p, \ldots, r_{2n}=-r_n$) are positive.

In the set of equations (11) it is always possible to set $a=1$. Since r appears only as a squared term, the roots r_i and $r_{n+i}=-r_i$ correspond to one and the same set of values $a_i=1, \beta_i, \gamma_i, \ldots, \nu_i$. Then the general integral of the set of differential equations has the form

$$x_1(t)=C_1e^{r_1t}+C_2e^{r_2t}+\cdots+C_ne^{r_nt}$$
$$+C_{n+1}e^{r_{n+1}t}+\cdots+C_{2n}e^{r_{2n}t},$$
$$x_2(t)=C_1\beta_1e^{r_1t}+C_2\beta_2e^{r_2t}+\cdots+C_n\beta_ne^{r_nt}$$
$$+C_{n+1}\beta_{n+1}e^{r_{n+1}t}+\cdots+C_{2n}\beta_{2n}e^{r_{2n}t},$$
$$x_n(t)=C_1\nu_1e^{r_1t}+C_2\nu_2e^{r_2t}+\cdots+C_n\nu_ne^{r_nt}$$
$$+C_{n+1}\nu_{n+1}e^{r_{n+1}t}+\cdots+C_{2n}\nu_{2n}e^{r_{2n}t},$$

where r, α, β, . . . , ν depend only on the g_{ik}. For $\lim_{t\to+\infty}\chi_i(t)=0$, we must have

$$C_{n+1}=C_{n+2}=\cdots=C_{2n}=0.$$

Then we obtain

$$x_1(t)=C_1e^{r_1t}+C_2e^{r_2t}+\cdots+C_ne^{r_nt}, \quad (12)$$
$$x_2(t)=C_1\beta_1e^{r_1t}+C_2\beta_2e^{r_2t}+\cdots+C_n\beta_ne^{r_nt},$$
$$\cdots\cdots\cdots,$$
$$x_n(t)=C_1\nu_1e^{r_1t}+C_2\nu_2e^{r_2t}+\cdots+C_n\nu_ne^{r_nt}$$

In determining $C_1, C_2, \ldots, C_n$, we obtain the relations for $t=0$:

$$x_1^0=C_1+C_2+\cdots+C_n,$$
$$x_2^0=C_1\beta_1+C_2\beta_2+\cdots+C_n\beta_n,$$
$$\cdots\cdots\cdots,$$
$$x_n^0=C_1\nu_1+C_2\nu_2+\cdots+C_n\nu_n,$$

where $\chi_1^0, \chi_2^0, \ldots, \chi_n^0$ are the arbitrarily chosen initial values of $\chi_1, \chi_2, \ldots, \chi_n$.

Substituting $\chi_1(t), \chi_2(t), \ldots, \chi_n(t)$ from Eq. (12) in the expressions (10) for $X_1, X_2, \ldots, X_n$, we get

$$X_1=C_1e^{r_1t}A_1+\cdots+C_ne^{r_nt}A_n, \quad (13)$$
$$X_2=C_1e^{r_1t}B_1+\cdots+C_ne^{r_nt}B_n,$$
$$\cdots\cdots\cdots,$$
$$X_n=C_1e^{r_1t}N_1+\cdots+C_ne^{r_nt}N_n.$$

Here $A, B, \ldots, N$ are functions of g_{ik} only and do not depend on $C_1, C_2, \ldots, C_n$. Further, we have

$$x_i'(t)=C_1\gamma_{i1}r_1e^{r_1t}+C_2\gamma_{i2}r_2e^{r_2t} \quad (14)$$
$$+\cdots+C_n\gamma_{in}r_ne^{r_nt} \quad (i=1,2,\ldots,n).$$

Eliminating $C_1e^{r_1t}, C_2e^{r_2t}, \ldots, C_ne^{r_nt}$ from Eqs.(13) and (14), we get

$$\begin{vmatrix} x_i & \gamma_{i1}r_1 & \gamma_{i2}r_2 & \ldots & \gamma_{in}r_n \\ X_1 & A_1 & A_2 & \ldots & A_n \\ X_2 & B_1 & B_2 & \ldots & B_n \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ X_n & N_1 & N_2 & \ldots & N_n \end{vmatrix} = 0,$$

i.e.,

$$x_i' = L_{i1}X_1 + L_{i2}X_2 + \cdots + L_{in}X_n \qquad (15)$$
$$(i = 1, 2, \ldots, n).$$

Thus the phenomenological relations are first integrals of the system (10). Here the L_{ik} are constant quantities, determined by the coefficients g_{ik} alone.

For $n = 2$, when

$$X_1 = g_{11}x_1 + g_{12}x_2, \quad X_2 = g_{21}x_1 + g_{22}x_2,$$

we have

$$d^2x_1/dt^2 = g_{11}x_1 + g_{12}x_2, \qquad d^2x_2/dt^2 = g_{21}x_1 + g_{22}x_2. \qquad (16)$$

Setting $x_1 = e^{rt}$, $x_2 = \beta e^{rt}$,
we obtain

$$g_{11} - r^2 + g_{12}\beta = 0, \qquad g_{21} + (g_{22} - r^2)\beta = 0. \qquad (17)$$

The determinant of the coefficients now has the form

$$\Delta(r^2) = \begin{vmatrix} g_{11} - r^2 & g_{12} \\ g_{21} & g_{22} - r^2 \end{vmatrix} = 0$$

and, consequently,

$$r_{1,2}^2 = \frac{g_{11} + g_{22}}{2} \pm \sqrt{\left(\frac{g_{11} + g_{22}}{2}\right)^2 - (g_{11}g_{22} - g_{12}^2)}. \qquad (18)$$

Since $\Sigma g_{ik}x_ix_k (i = 1, 2)$ is a positive definite quadratic form, we have

$$g_{11} > 0, \; g_{22} > 0, \; g_{11}g_{22} - g_{12}^2 > 0$$

and consequently

$$\left(\frac{g_{11} + g_{22}}{2}\right)^2 - (g_{11}g_{22} - g_{12}^2) < \left(\frac{g_{11} + g_{22}}{2}\right)^2.$$

On the other hand,

$$\left(\frac{g_{11} + g_{22}}{2}\right)^2 - (g_{11}g_{22} - g_{12}^2) = \left(\frac{g_{11} - g_{22}}{2}\right)^2 + g_{12}^2 > 0,$$

so that

$$r_1^2 > 0, \; r_2^2 > 0.$$

Consequently, all the roots of the equation $\Delta(r^2) = 0$ are real and

$$r_1 = -\sqrt{\left(\frac{g_{11} + g_{22}}{2}\right)^2 + \sqrt{\left(\frac{g_{11} + g_{22}}{2}\right)^2 - (g_{11}g_{22} - g_{12}^2)}} < 0, \; r_3 = -r_1 > 0,$$

$$r_2 = -\sqrt{\left(\frac{g_{11} + g_{22}}{2}\right)^2 - \sqrt{\left(\frac{g_{11} + g_{22}}{2}\right)^2 - (g_{11}g_{22} - g_{12}^2)}} < 0, \; r_4 = -r_2 > 0.$$

Setting $C_3 = C_4 = 0$, we have

$$x_1 = C_1e^{r_1t} + C_2e^{r_2t}, \quad x_2 = C_1\beta_1e^{r_1t} + C_2\beta_2e^{r_2t},$$

where β_1 and β_2 correspond to the roots r_1 and r_2 and are determined by Eq. (17)

Making use of the above values of x_1, x_2, and keeping in mind Eq. (17) we obtain

$$X_1 = C_1e^{r_1t}r_1^2 + C_2e^{r_2t}r_2^2,$$
$$X_2 = C_1e^{r_1t}\beta_1r_1^2 + C_2e^{r_2t}\beta_2r_2^2.$$

On the other hand,

$$x_1' = C_1e^{r_1t}r_1 + C_2e^{r_2t}r_2,$$
$$x_2' = C_1e^{r_1t}\beta_1r_1 + C_2e^{r_2t}\beta_2r_2.$$

Eliminating $C_1e^{r_1t}$ and $C_2e^{r_2t}$ from these four equations we get

$$x_1' = L_{11}X_1 + L_{12}X_2, \quad x_2' = L_{21}X_1 + L_{22}X_2,$$

where

$$L_{12} = -\frac{r_2 - r_1}{r_1r_2(\beta_2 - \beta_1)}, \quad L_{21} = \frac{\beta_1\beta_2(r_2 - r_1)}{r_1r_2(\beta_2 - \beta_1)}.$$

From Eq. (17) we have

$$\beta_1 = -\frac{g_{11} - r_1^2}{g_{12}}, \quad \beta_2 = -\frac{g_{21}}{g_{22} - r_2^2};$$

Consequently,

$$\beta_1\beta_2 = \frac{g_{11} - r_1^2}{g_{22} - r_2^2}.$$

However, keeping (18) in mind, we get

$$g_{11}-r_1^2=\frac{g_{11}-g_{22}}{2}-\sqrt{\left(\frac{g_{11}+g_{22}}{2}\right)^2-(g_{11}g_{22}-g_{12}^2)},$$

$$g_{22}-r_2^2=-\frac{g_{11}-g_{22}}{2}+\sqrt{\left(\frac{g_{11}+g_{22}}{2}\right)^2-(g_{11}g_{22}-g_{12}^2)}.$$

As a consequence,

$$\beta_1\beta_2=-1,$$

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

We now consider a numerical example for $n = 3$, setting

$$g_{11}=5,\quad g_{12}=1,\quad g_{13}=3,$$
$$g_{21}=1,\quad g_{22}=4,\quad g_{23}=2,$$
$$g_{31}=3,\quad g_{32}=2,\quad g_{33}=6.$$

The corresponding quadratic form is positive definite, since

$$g_{11}>0,\ g_{22}>0,\ g_{33}>0,\ \begin{vmatrix} g_{11} & g_{12}\\ g_{21} & g_{22}\end{vmatrix}>0,$$

$$\begin{vmatrix} g_{11} & g_{13}\\ g_{31} & g_{33}\end{vmatrix}>0,\quad \begin{vmatrix} g_{22} & g_{23}\\ g_{32} & g_{33}\end{vmatrix}>0,\quad \begin{vmatrix} g_{11} & g_{12} & g_{13}\\ g_{21} & g_{22} & g_{23}\\ g_{31} & g_{32} & g_{33}\end{vmatrix}>0.$$

The roots of the algebraic equation

$$\begin{vmatrix} g_{11}-r^2 & g_{12} & g_{13}\\ g_{21} & g_{22}-r^2 & g_{23}\\ g_{31} & g_{32} & g_{33}-r^2\end{vmatrix}=0,$$

are

$$r_1^2=9.4189,\ r_2^2=2.1944,\ r_3^2=3.3868,$$

as can be easily verified, so that

$$r_1=-\sqrt{9.4189},\quad r_2=-\sqrt{2.1944},\quad r_3=-\sqrt{3.3868}.$$

Setting $a_1 = a_2 = a_3 = 1$, we get

$$\lg\beta_1=\bar{1}.81185;\qquad \lg\gamma_1=0.09931;$$
$$\lg\beta_2=\bar{1}.98156;\qquad \lg\gamma_2=0.07554\,n;$$
$$\lg\beta_3=0.14968\,n;\qquad \lg\gamma_3=\bar{2}.82822\,n;$$

and

$$L_{12}=-\frac{r_1^2r_2^2r_3^2}{\Delta}0{,}070;\qquad L_{21}=-\frac{r_1^2r_2^2r_3^2}{\Delta}0{.}071;$$
$$L_{13}=-\frac{r_1^2r_2^2r_3^2}{\Delta}0.744;\qquad L_{31}=-\frac{r_1^2r_2^2r_3^2}{\Delta}0{.}741;$$
$$L_{23}=-\frac{r_1^2r_2^2r_3^2}{\Delta}0.515;\qquad L_{32}=-\frac{r_1^2r_2^2r_3^2}{\Delta}0{,}520;$$

where

$$\Delta=\begin{vmatrix} r_1^2 & r_2^2 & r_3^2\\ r_1^2\beta_1 & r_2^2\beta_2 & r_3^2\beta_3\\ r_1^2\gamma_1 & r_2^2\gamma_2 & r_3^2\gamma_3\end{vmatrix}.$$

THE SYMMETRY OF THE TERMS L_{ik} ITERATION METHOD.

The terms L_{ik} in the integrals of the system of differential equations that we have just considered are symmetric under less restrictive conditions than those given above. This fact makes it possible to explain the results obtained by several investigators who started out from the phenomenological relations of Onsager, in which it was not required that $\lim_{t\to+\infty} \chi_i(t) = 0$.

Pierre Curie[6], taking as his point of observation the symmetry in the structure of crystals, had already come to the conclusion that "when certain causes produce a given effect, then elements of symmetry in the cause also appear in the effect produced by these causes", and that "when certain effects display a known asymmetry, then one must find a similar asymmetry in the causes which produce these effects".

In the case in point the symmetry of the matrix g_{ik} requires the symmetry of the matrix L_{ik}.

Considering the system (18), we have established the existence of a set of integrals which satisfies the conditions $\lim \chi_i(t) = 0$, $\lim \chi_i'(t) = 0$ for $t = +\infty$. This is sufficient to establish the phenomenological relations and the symmetry of the matrix L_{ik}, independent of algebraic considerations.

For simplicity we consider the system

$$d^2x/dt^2=ax+by=X,\quad d^2y/dt^2=bx+cy=Y, \tag{19}$$

where a, b, c are arbitrary constants. We find the integrals of this system, which satisfy the condi-

6 P. Curie, J. Phys. , 393 (1894)

tions $t = 0$, $\chi' = 0$, $y' = 0$.

The method of iteration which we have followed is general: we apply it for each n.

Integrating both sides of the first of these equations from 0 to t, and setting $\chi'(0) = 0$, $y'(0) = 0$, we get

$$x'(t) = \int_0^t X dt = Xt - \int_0^t t\dot{X} dt$$

$$= Xt - \tfrac{1}{2}\dot{X}t^2 + \tfrac{1}{2}\int_0^t t^2 \ddot{X} dt.$$

But

$$\ddot{X} = a\ddot{x} + b\ddot{y} = aX + bY, \qquad (20)$$

$$\ddot{Y} = b\ddot{x} + c\ddot{y} = bX + cY,$$

so that

$$x'(t) = Xt - \frac{t^2}{2!}\dot{X} + \frac{1}{3!}\int_0^t (aX + bY)\, dt^3$$

$$= Xt - \frac{t^2}{2!}\dot{X} + \frac{t^3}{3!}(aX + bY)$$

$$- \frac{1}{3!}\int_0^t (a\dot{X} + b\dot{Y})\, t^3 dt$$

$$= Xt - \frac{t^2}{2!}\dot{X} + \frac{t^3}{3!}(aX + bY)$$

$$- \frac{t^4}{4!}(a\dot{X} + b\dot{Y}) + \frac{1}{4!}\int_0^t t^4 (a\ddot{X} + b\ddot{Y})\, dt.$$

Substituting the values of $\ddot{X}$ and $\ddot{Y}$ from Eq. (20) in the last integral and integrating by parts we get, after some simplification (recalling that $\dot{X} = a\dot{x} + b\dot{y}$, $\dot{Y} = b\dot{x} + c\dot{y}$),

$$\left(1 + \frac{a}{2!}t^2 + \frac{a^2 + b^2}{4!}t^4\right)\frac{dx}{dt}$$

$$+ \left(\frac{b}{2!}t^2 + \frac{b(a+c)}{4!}t^4\right)\frac{dy}{dt}$$

$$= \left(t + \frac{a}{3!}t^3 + \frac{a^2+b^2}{5!}t^5\right)X \qquad (21a)$$

$$+ \left(\frac{b}{3!}t^3 + \frac{b(a+c)}{5!}t^5\right)Y$$

$$- \frac{a^2+b^2}{5!}\int_0^t t^5 \dot{X} dt - \frac{b(a+c)}{5!}\int_0^t t^5 \dot{Y} dt.$$

It is necessary to extend the iteration process to infinity.

In the same fashion we get from the second equation,

$$\left(\frac{b}{2!}t^2 + \frac{b(a+c)}{4!}t^4\right)\frac{dx}{dt} + \left(1 + \frac{c}{2!}t^2 + \frac{b^2+c^2}{4!}t^4\right)\frac{dy}{dt} \qquad (21b)$$

$$= \left(\frac{b}{3!}t^3 + \frac{b(a+c)}{5!}t^5\right)X + \left(t + \frac{c}{3!}t^3 + \frac{b^2+c^2}{5!}t^5\right)Y$$

$$- \frac{b(a+c)}{5!}\int_0^t t^5 \dot{X} dt - \frac{b^2+c^2}{5!}\int_0^t t^5 \dot{Y} dt.$$

INVESTIGATION OF THE CONVERGENCE OF THE SERIES

To establish the convergence of the series we consider the dominating system of differential equations

$$d^2x/dt^2 = p(x+y) = X, \qquad (A)$$

$$d^2y/dt^2 = p(x+y) = Y,$$

where p is the largest of the numbers $|a|$, $|b|$, $|c|$.

Proceeding with the system (A) as we did for the system (19) we get

$$\left(1 + \frac{p}{2!}t^2 + \frac{2p^2}{4!}t^4 + \frac{2^2p^3}{6!}t^6 + \cdots + \frac{2^{n-1}p^n}{(2n)!}t^{2n}\right)\frac{dx}{dt}$$

$$+ \left(\frac{p}{2!}t^2 + \frac{2p^2}{4!}t^4 + \frac{2^2p^3}{6!}t^6 + \cdots + \frac{2^{n-1}p^n}{(2n)!}t^{2n}\right)\frac{dy}{dt}$$

$$= \left(t + \frac{p}{3!}t^3 + \frac{2p^2}{5!}t^5 + \cdots + \frac{2^{n-2}}{(2n-1)!}p^{n-1}t^{2n-1}\right)X \qquad (22)$$

$$+ \left(\frac{p}{3!}t^3 + \frac{2p^2}{5!}t^5 + \cdots + \frac{2^{n-2}}{(2n-1)!}p^{n-1}t^{2n-1}\right)Y$$

$$+ \frac{2^{n-1}}{(2n)!}p^n \int_0^t t^{2n}(X+Y)\, dt.$$

Here for each finite value of t

$$\lim_{n\to\infty} \frac{2^{n+1}p^n}{(2n)!}\int_0^t t^{2n}(X+Y)\, dt = 0.$$

Since the relation of the $(n+1)$st to the

nth term in each series tends to zero as $1/n$, then the series which occur in the coefficients of our equations quickly converge for each value of t; consequently, the coefficients in Eqs. (21) also converge. We write these formulas in the form

$$A\frac{dx}{dt}+B\frac{dy}{dt} = \alpha X+\beta Y,\quad B\frac{dx}{dt}+C\frac{dy}{dt}=\beta X+\gamma Y, \tag{23}$$

where

$$A=1+\frac{a}{2!}t^2+\frac{a^2+b^2}{4!}t^4+\cdots,\quad \alpha=t+\frac{a}{3!}t^3+\frac{a^2+b^2}{5!}t^5+\cdots,$$

$$B=\frac{b}{2!}t^2+\frac{b(a+c)}{4!}t^4+\cdots,\quad \beta=\frac{b}{3!}t^3+\frac{b(a+c)}{5!}t^5+\cdots, \tag{24}$$

$$C=1+\frac{c}{2!}t^2+\frac{b^2+c^2}{4!}t^4+\cdots,\quad \gamma=t+\frac{c}{3!}t^3+\frac{b^2+c^2}{5!}t^5+\cdots$$

Here

$$AC-B^2=1+\frac{a+c}{2!}t^2+\cdots\neq 0$$

and, consequently,

$$dx/dt=L_{11}X+L_{12}Y,\quad dy/dt=L_{21}X+L_{22}Y, \tag{25}$$

where

$$L_{11}=\frac{C\alpha+B\beta}{AC-B^2},\quad L_{12}=\frac{C\beta-B\gamma}{AC-B^2},\quad L_{21}=\frac{A\beta-B\alpha}{AC-B^2},\quad L_{22}=\frac{A\gamma-B\beta}{AC-B^2}. \tag{26}$$

Simple calculations show that

$$C\beta-B\gamma=A\beta-B\alpha \tag{27}$$

and thus

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

We have seen that $\chi=0$, $y=0$ is a critical point of the system of differential equations and that all integral curves which correspond to a certain physical problem pass through this point.

If we take the moment of thermodynamic equilibrium at $t_0=0$, then $t<0$ will correspond to thermodynamic processes. For $t_1<t_2<0$, we have

$$x'(t_2)=L_{11}(t_2)X(t_2)+L_{12}(t_2)Y(t_2),\quad y'(t_2)=L_{21}(t_2)X(t_2)+L_{22}(t_2)Y(t_2),\quad L_{12}=L_{21}, \tag{28}$$

where $t_2=t_1+\tau$. If we assume that t_1 is known, and set $t_2=t_1+\tau$, where the positive quantity τ runs from 0 to $-t_1$, all the quantities appearing in Eq. (28) will be functions of τ, so that we can write

$$x'(\tau)=L_{11}(\tau)X(\tau)+L_{12}(\tau)Y(\tau),$$

$$y'(\tau)=L_{21}(\tau)X(\tau)+L_{22}(\tau)Y(\tau),$$

$$L_{12}(\tau)=L_{21}(\tau).$$

If f is any of these quantities, we can write

$$f(t_2)=f(t_1)+\tau f'(t_1)+\frac{\tau^2}{2}f''(t_1)+\cdots$$

For convenience we write $f(\tau)$ in place of $f(t_1+\tau)$. Thus we have again obtained the phenomenological relations of Onsager and $L_{12}=L_{21}$. The application of the general method of iteration which we have used does not present any difficulties for $n>2$, so that in the general case, $L_{ik}=L_{ki}$. Here, however, it is not evident that the coefficients L_{ik} are independent of τ, as was shown in Eq. (15).

2. ANALYSIS OF THE GENERAL CASE IN WHICH ΔS CONTAINS ALL THE TERMS OF THE EXPANSION IN POWERS OF THE VARIABLES

We now examine the most general case. Keeping all the terms in the expansion of ΔS in powers of $\chi_1, \chi_2, \ldots, \chi_n$, we have

$$\Delta S=-\frac{1}{2}\sum_{i,k}g_{ik}x_ix_k+\cdots \tag{2.1}$$

The dots here indicate terms of third and higher order in the variables χ. The corresponding system of differential equations has the form

$$d^2x_1/dt^2 = g_{11}x_1 + g_{12}x_2 + \ldots + g_{1n}x_n + \ldots, \tag{2.2}$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots,$$
$$d^2x_n/dt^2 = g_{n1}x_1 + g_{n2}x_2 + \ldots + g_{nn}x_n + \ldots,$$

with the dots indicating terms of second and higher order. Setting $\xi = dx/dt$, we rewrite this system of $2n$th order in the form

$$\frac{dx_1}{\xi_1} = \frac{dx_2}{\xi_2} = \ldots = \frac{dx_n}{\xi_n} = \frac{d\xi_1}{g_{11}x_1 + \ldots + g_{1n}x_n + \ldots} = \ldots \tag{2.3}$$
$$\ldots = \frac{d\xi_n}{g_{n1}x_1 + \ldots + g_{nn}x_n + \ldots} = dt.$$

With the help of a linear transformation we can rewrite this system in the form

$$\frac{du_1}{r_1u_1 + \ldots} = \frac{du_2}{r_2u_2 + \ldots} = \ldots = \frac{du_n}{r_nu_n + \ldots} = \ldots = \frac{du_{2n}}{r_{2n}u_{2n} + \ldots} = dt, \tag{2.4}$$

with the dots again indicating the terms of second and higher order in u_i. The values $r_1, r_2, \ldots, r_n, r_{n+1}, \ldots, r_{2n}$ are the roots of the algebraic equation of $2n$th degree previously considered:

$$\begin{vmatrix} g_{11} - r_1^2 & g_{12} \cdots & g_{1n} \\ \cdots & \cdots & \cdots \\ g_{n1} & g_{n2} \cdots & g_{nn} - r^2 \end{vmatrix} = 0. \tag{2.5}$$

As we have already seen, n roots $(r_1, r_2, \ldots, r_n)$ of this equation are negative, and n roots $(r_{n+1}, r_{n+2}, \ldots, r_{2n})$ are positive.

Poincare'[7] showed that such a system of differential equations possesses a system of holomorphic integrals of $e^{r_1t}, e^{r_2t}, \ldots, e^{r_nt}$

$$u_i(t) = \psi_i(e^{r_1t}, e^{r_2t}, \ldots, e^{r_nt}) \tag{2.6}$$
$$(i = 1, 2, \ldots, 2n),$$

which approach zero as $t \to +\infty$ and which possess n constants of integration. Consequently these correspond to this set of integrals of the form

7 H. Poincare', *Sur les propriétés des functions définies par les equations aux différences particlles*, Thèse de doctorat, Paris, 1879

$$x_1(t) = \psi_i(e^{r_1t}, e^{r_2t}, \ldots, e^{r_nt}), \tag{2.7}$$
$$\xi_i(t) = \omega_i(e^{r_1t}, e^{r_2t}, \ldots, e^{r_nt})$$
$$(i = 1, 2, \ldots, n),$$

where $\omega_i = d\psi_i/dt$ and ψ_i and ω_i are holomorphic functions of $e^{r_1t}, e^{r_2t}, \ldots, e^{r_nt}$ which approach zero as $t \to +\infty$ and which possess no constants of integration, thus allowing the choice of arbitrary initial values $\chi_1^0, \chi_2^0, \ldots, \chi_n^0$.

All the necessary conditions for this rule are satisfied in this case.

For simplicity we consider the case for $n = 2$. Setting $\chi_1 = \chi$, $\chi_2 = y$, $g_{11} = a$, $g_{21} = g_{12} = b$, $g_{22} = c$, and recalling that $F^2_{xy} = F^2_{yx}$ we get

$$d^2x/dt^2 = ax + by + ex^2 + 2fxy + gy^2 + \ldots = X, \tag{2.8}$$
$$d^2y/dt^2 = bx + cy + fx^2 + 2gxy + hy^2 + \ldots = Y.$$

Since $a\chi^2 + 2b\chi y + cy^2$ is a positive definite quadratic form,

$$a > 0, \quad c > 0, \quad ac - b^2 > 0.$$

Corresponding to this system we have the system

$$\frac{dx}{dt} = \xi = \Xi; \quad \frac{dy}{dt} = \eta = \mathrm{H}; \quad \frac{d\xi}{dt} = X; \quad \frac{d\eta}{dt} = Y, \tag{2.8'}$$

and the equivalent differential equation in partial derivatives

$$\frac{\partial F}{\partial x}\Xi + \frac{\partial F}{\partial \xi}X + \frac{\partial F}{\partial y}\mathrm{H} + \frac{\partial F}{\partial \eta}Y = 0. \tag{2.9}$$

The linear substitution

$$u = \alpha_{11}\xi + \alpha_{12}x + \alpha_{13}\eta + \alpha_{14}y; \tag{2.10}$$
$$w = \alpha_{31}\xi + \alpha_{32}x + \alpha_{33}\eta + \alpha_{34}y,$$
$$v = \alpha_{21}\xi + \alpha_{22}x + \alpha_{23}\eta + \alpha_{24}y;$$
$$z = \alpha_{41}\xi + \alpha_{42}x + \alpha_{43}\eta + \alpha_{44}y$$

yields the system

$$\frac{\partial F}{\partial \xi} = \frac{\partial F}{\partial u}\alpha_{11} + \frac{\partial F}{\partial v}\alpha_{21} + \frac{\partial F}{\partial w}\alpha_{31} + \frac{\partial F}{\partial z}\alpha_{41},$$
$$\frac{\partial F}{\partial x} = \frac{\partial F}{\partial u}\alpha_{12} + \frac{\partial F}{\partial v}\alpha_{22} + \frac{\partial F}{\partial w}\alpha_{32} + \frac{\partial F}{\partial z}\alpha_{42},$$

$$\frac{\partial F}{\partial \eta} = \frac{\partial F}{\partial u}\alpha_{13} + \frac{\partial F}{\partial v}\alpha_{23} + \frac{\partial F}{\partial w}\alpha_{33} + \frac{\partial F}{\partial z}\alpha_{43},$$
$$\frac{\partial F}{\partial y} = \frac{\partial F}{\partial u}\alpha_{14} + \frac{\partial F}{\partial v}\alpha_{24} + \frac{\partial F}{\partial w}\alpha_{34} + \frac{\partial F}{\partial z}\alpha_{44},$$

and the equation

$$\begin{aligned} &\frac{\partial F}{\partial u}(\alpha_{11}X + \alpha_{12}\Xi + \alpha_{13}Y + \alpha_{14}\mathrm{H}) + \\ &+\frac{\partial F}{\partial v}(\alpha_{21}X + \alpha_{22}\Xi + \alpha_{23}Y + \alpha_{24}\mathrm{H}) + \\ &+\frac{\partial F}{\partial w}(\alpha_{31}X + \alpha_{32}\Xi + \alpha_{33}Y + \alpha_{34}\mathrm{H}) + \\ &+\frac{\partial F}{\partial z}(\alpha_{41}X + \alpha_{42}\Xi + \alpha_{43}Y + \alpha_{44}\mathrm{H}) = 0. \end{aligned} \tag{2.11}$$

We choose α_{ik} so that, after some reduction, we get

$$\frac{F}{\partial u}(r_1u_1 + \cdots) + \frac{\partial F}{\partial v}(r_2 v + \ldots) \tag{2.12}$$
$$+\frac{\partial F}{\partial w}(r_3 w + \ldots) + \frac{\partial F}{\partial z}(r_4 z + \ldots) = 0,$$

where the dots indicate terms of higher order of smallness; in this case we must have

$$\begin{aligned} \alpha_{11}X_1 + \alpha_{12}\Xi + \alpha_{13}Y_1 + \alpha_{14}\mathrm{H} &= r_1 u \\ &= r_1(\alpha_{11}\xi + \alpha_{12}x + \alpha_{13}\eta + \alpha_{14}y), \\ \alpha_{21}X_1 + \alpha_{22}\Xi + \alpha_{23}Y_1 + \alpha_{24}\mathrm{H} &= r_2 v \\ &= r_2(\alpha_{21}\xi + \alpha_{22}x + \alpha_{23}\eta + \alpha_{24}y), \\ \alpha_{31}X_1 + \alpha_{32}\Xi + \alpha_{33}Y_1 + \alpha_{34}\mathrm{H} &= r_3 w \\ &= r_3(\alpha_{31}\xi + \alpha_{32}x + \alpha_{33}\eta + \alpha_{34}y), \\ \alpha_{41}X_1 + \alpha_{42}\Xi + \alpha_{43}Y_1 + \alpha_{44}\mathrm{H} &= r_4 z \\ &= r_4(\alpha_{41}\xi + \alpha_{42}x + \alpha_{43}\eta + \alpha_{44}y), \end{aligned} \tag{2.13}$$

where X_1 and Y_1 are the quantities X and Y in which only terms of first order are kept. We then obtain

$$\begin{aligned} \alpha_{i1}a - \alpha_{i2}r_i + \alpha_{i3}b + \alpha_{i4}0 &= 0, \\ -\alpha_{i1}r_i + \alpha_{i2}1 + \alpha_{i3}0 + \alpha_{i4}0 &= 0, \\ \alpha_{i1}b + \alpha_{i2}0 + \alpha_{i3}c - \alpha_{i4}r_i &= 0, \\ \alpha_{i1}0 + \alpha_{i2}0 - \alpha_{i3}r_i + \alpha_{i4}1 &= 0. \end{aligned} \tag{2.14}$$

For the homogeneous system in a_{ik} to have nonzero solutions, we require

$$\begin{vmatrix} a & -r_i & b & 0 \\ -r_i & 1 & 0 & 0 \\ b & 0 & c & -r_i \\ 0 & 0 & -r_i & 1 \end{vmatrix} = \begin{vmatrix} a - r_i^2 & b \\ b & c - r_i^2 \end{vmatrix} = 0. \tag{2.15}$$

We saw in Eq. (18) that the roots of this equation of fourth degree are real, whereupon

$$r_1 < r_2 < 0, \quad r_3 = -r_1, \quad r_4 = -r_2. \tag{2.16}$$

To these roots there correspond the coefficients a_{ik} which, after we set $a_{i1} = 1$, have the values

$$\alpha_{i2} = r_i = \beta_i, \tag{2.17}$$
$$\alpha_{i3} = (r_i^2 - a)/b = \alpha_i, \quad \alpha_{i4} = r_i\alpha_i = \gamma_i.$$

As we have already pointed out, the integrals of Eq. (2.11), which approach zero at $t \to +\infty$, are holomorphic functions of $k_1e^{r_1t}$ and $k_2e^{r_2t}$, where the constants k_1 and k_2 are sufficiently small. These integrals can be expanded in a series in powers of $k_1e^{r_1t}$ and $k_2e^{r_2t}$. The convergence of these series as $t \to \infty$ was investigated by Poincaré[7] and later by Picard[8].

We return to a consideration of Eq. (2.9) and the substitutions (2.10). Since the determinant of the coefficients χ, y, ξ, η in (2.10) differs from zero:

$$\begin{vmatrix} 1 & r_1 & \alpha_1 & \gamma_1 \\ 1 & r_2 & \alpha_2 & \gamma_2 \\ 1 & r_3 & \alpha_3 & \gamma_3 \\ 1 & r_4 & \alpha_4 & \gamma_4 \end{vmatrix} = -4r_1r_2(\alpha_1 - \alpha_2)^2 \neq 0, \tag{2.18}$$

the substitutions (2.10) determine χ, y, ξ, η as linear functions of u, v, w, z. All these quantities approach zero together. Consequently the integrals of $\chi, y, \xi = \chi', \eta = y'$ which go to zero for $t = +\infty$ can be represented by a series of powers of e^{r_1t}, e^{r_2t} which converge for $t = +\infty$. We then have

$$x(t) = C_1k_1e^{r_1t} + C_2k_2e^{r_2t} + C_3k_1^2e^{2r_1t} \tag{2.19}$$
$$+ C_4k_1k_2e^{(r_1+r_0)t} + C_5k_2^2e^{2r_2t} + \cdots,$$
$$y(t) = G_1k_1e^{r_1t} + G_2k_2e^{r_2t} + G_3k_1^2e^{2r_1t}$$
$$+ G_4k_1k_2e^{(r_1+r_2)t} + G_5k_2^2e^{2r_2t} + \cdots,$$
$$\frac{d^2x}{dt^2} = C_1k_1r_1^2e^{r_1t} + C_2k_2r_2^2e^{r_2t} + C_3k_1^2 4r_1^2e^{2r_1t}$$

[8] E. Picard, Traité d'Analyse, Paris, 1908

$$+ C_4k_1k_2(r_1+r_2)^2e^{(r_1+r_2)t} + C_5k_2^2 4r_2^2 e^{2r_2t} + \cdots,$$

and a similar expression for $y''(t)$, where the coefficients G replace the coefficients C.

The values of these coefficients can be found by the method of undetermined coefficients, substituting in X and Y the expressions for χ and y given above.

In this way we obtain

$$\begin{aligned} X &= ax + by + ex^2 + 2fxy + gy^2 + \cdots \\ &= k_1(aC_1 + bG_1)e^{r_1t} + k_2(aC_2 + bG_2)e^{r_2t} \\ &+ k_1^2(aC_3 + bG_3 + eC_1^2 + 2fC_1G_1 + gG_1^2)e^{2r_1t} \\ &+ k_1k_2[aC_4 + bG_4 + 2eC_1C_3 \\ &+ 2f(C_1G_2 + C_2G_1) + 2gG_1G_2]e^{(r_1+r_2)t} \\ &+ k_2^2(aC_5 + bG_5 + eC_2^2 \\ &+ 2fC_2G_2 + gG_2^2)e^{2r_2t} + \cdots; \\ Y &= k_1(bC_1 + cG_1)e^{r_1t} + k_2(bC_2 + cG_2)e^{r_2t} \\ &+ k_1^2(bC_3 + cG_3 + fC_1^2 + 2gC_1G_1 + hG_1^2)e^{2r_1t} \\ &+ k_1k_2[bC_4 + cG_4 + 2fC_1C_2 \\ &+ 2g(C_1G_2 + C_2G_1) + 2hG_1G_2]e^{(r_1+r_2)t} \\ &+ k_2^2(bC_5 + cG_5 \\ &+ fC_2^2 + 2gC_2G_2 + hG_2^2)e^{2r_2t} + \cdots \end{aligned} \tag{2.20}$$

Equating coefficients for corresponding powers of e^{r_1t} and e^{r_2t} in the expressions for X and d^2X/dt^2 and also in the expressions for Y and d^2Y/dy^2, we first obtain

$$\begin{aligned} &C_1(r_1^2 - a) - bG_1 = 0, \\ &\quad -bC_1 + (r_1^2 - c)G_1 = 0, \\ &C_2(r_2^2 - a) - bG_2 = 0, \\ &\quad -bC_2 + (r_2^2 - c)G_2 = 0. \end{aligned} \tag{2.21}$$

The first two of these equations give two values for G_1:

$$G_1 = C_1\frac{r_1^2 - a}{b} \qquad G_1 = C_1\frac{b}{r_1^2 - c}, \tag{2.22}$$

which are equal to each other, since $(r_1^2 - a)(r_1^2 - c) = b^2$. In other words,

$$(r_1^2 - a)/b = \alpha_1,$$

and, consequently, $G_1 = C_1\alpha_1$. In the same way, we obtain

$$G_2 = C_2\alpha_2.$$

from the last pair of the equations (2.21).

Comparison of the coefficients of e^{2r_1t}, $e^{(r_1+r_2)t}$, e^{2r_2t} leads to the following equations for the determination of C_i, G_i:

$$\begin{aligned} &C_3(4r_1^2 - a) - G_3b = eC_1^2 + 2fC_1G_1 + gG_1^2, \\ &-C_3b + G_3(4r_1^2 - c) = fC_1^2 + 2gC_1G_1 + hG_1^2, \\ &C_4|(r_1+r_2)^2 - a| - G_4b \\ &\quad = 2eC_1C_2 + 2f(C_1G_2 + C_2G_1) + 2gG_1G_2, \\ &-C_4b + |(r_1+r_2)^2 - c|G_4 \\ &\quad = 2fC_1C_2 + 2g(C_1G_2 + C_2G_1) + 2hG_1G_2, \\ &C_5(4r_2^2 - a) - G_5b = eC_2^2 + 2fC_2G_2 + gG_2^2, \\ &-C_5b + G_5(4r_2^2 - c) = fC_2^2 + 2gC_2G_2 + hG_2^2. \end{aligned} \tag{2.23}$$

The convergence of the series thus obtained is given by the method of Poincare'[7]. The treatment is also set forth in Picard's work[8].

THE PHENOMENOLOGICAL RELATIONS IN THE GENERAL CASE

In order to show that the phenomenological relations follow from the equations

$$\frac{d^2x}{dt^2} = X = \frac{\partial(-\Delta S)}{\partial x}, \quad \frac{d^2y}{dt^2} = Y = \frac{\partial(-\Delta S)}{\partial y}, \tag{2.8''}$$

even in the general case, we rewrite Eqs. (2.19), keeping terms up to second order in k_1 and k_2:

$$\begin{aligned} x &= e^{r_1t}k_1C_1\left(1 + C_3'k_1e^{r_1t} + \frac{1}{2}C_4'k_2e^{r_2t}\right) \\ &+ e^{r_2t}k_2C_2\left(1 + \frac{1}{2}C_4''k_1e^{r_1t} + C_5''k_2e^{r_2t}\right), \\ y &= e^{r_1t}k_1G_1\left(1 + G_3'k_1e^{r_1t} + \frac{1}{2}G_4'k_2e^{r_2t}\right) \cdot \\ &+ e^{r_2t}k_2G_2\left(1 + \frac{1}{2}G_4''k_1e^{r_1t} + G_5''k_2e^{r_2t}\right), \end{aligned} \tag{2.24}$$

where

$$C_i' = \frac{C_i}{C_1}, \quad C_i'' = \frac{C_i}{C_2}, \quad G_i' = \frac{G_i}{G_1}, \quad G_i'' = \frac{G_i}{G_2}. \tag{2.25}$$

Since $G_1 = C_1\alpha_1$, $G_2 = C_2\alpha_2$,

we can write

$$x = e^{r_1 t}k_1 C_1 (1+\lambda) + e^{r_2 t}k_2 C_2 (1+\mu), \tag{2.26}$$

$$y = e^{r_1 t}k_1 C_1 \alpha_1 (1+\rho) + e^{r_2 t}k_2 C_2 \alpha_2 (1+\pi);$$

$$x' = e^{r_1 t}k_1 C_1 r_1 (1+\lambda_1) + e^{r_2 t}k_2 C_2 r_2 (1+\mu_1), \tag{2.27}$$

$$y' = e^{r_1 t}k_1 C_1 r_1 \alpha_1 (1+\rho_1) + e^{r_2 t}k_2 C_2 r_2 \alpha_2 (1+\pi_1),$$

where $\lambda, \mu, \rho, \pi, \lambda_1, \mu_1, \rho_1, \pi_1$ contain k_1 and k_2 as factors of first power.

Substituting the values of $e^{r_1 t}$, $e^{r_2 t}$ from (2.26) in (2.27) we obtain

$$x'\delta = x[r_1\alpha_2(1+\pi)(1+\lambda_1) - r_2\alpha_1(1+\rho)(1+\mu_1)] + y[r_2(1+\lambda)(1+\mu_1) - r_1(1+\mu)(1+\lambda_1)], \tag{2.28}$$

$$y'\delta = x[r_1\alpha_1\alpha_2(1+\pi)(1+\rho_1) - r_2\alpha_1\alpha_2(1+\rho)(1+\pi_1)] + y[r_2\alpha_2(1+\lambda)(1+\pi_1) - r_1\alpha_1(1+\mu)(1+\rho_1)],$$

where

$$\delta = (1+\lambda)(1+\pi)\alpha_2 - (1+\mu)(1+\rho)\alpha_1. \tag{2.29}$$

We obtain the phenomenological relation directly from (2.28), substituting X and Y for χ and y.

Since

$$X = xL + yM, \quad Y = xM + yN, \tag{2.30}$$

where

$$L = a + ex + fy, \quad M = b + fx + gy, \quad N = c + gx + hy,$$

we get

$$x\Delta = XN - YM, \quad y\Delta = -XM + YL; \tag{2.31}$$

here $\Delta = LN - M^2$

For these values of χ and y we can rewrite the relations (2.28) in the form

$$x'\delta\Delta = X\{N[r_1\alpha_2(1+\pi)(1+\lambda_1) - r_2\alpha_1(1+\rho)(1+\mu_1)] - M[r_2(1+\lambda)(1+\mu_1) - r_1(1+\mu)(1+\lambda_1)]\} + Y\{L[r_2(1+\lambda)(1+\mu_1) - r_1(1+\mu)(1+\lambda_1)] - M[r_1\alpha_2(1+\pi)(1+\lambda_1) - r_2\alpha_1(1+\rho)(1+\mu_1)]\} = AX + BY; \tag{2.32}$$

$$y'\delta\Delta = X\{N[r_1\alpha_1\alpha_2(1+\pi)(1+\rho_1) - r_2\alpha_1\alpha_2(1+\rho)(1+\pi_1)] - M[r_2\alpha_2(1+\lambda)(1+\pi_1) - r_1\alpha_1(1+\mu)(1+\rho_1)]\} + Y\{L[r_2\alpha_2(1+\lambda)(1+\pi_1) - r_1\alpha_1(1+\mu)(1+\rho_1)] - M[r_1\alpha_1\alpha_2(1+\pi)(1+\rho_1) - r_2\alpha_1\alpha_2(1+\rho)(1+\pi_1)]\} = DX + CY.$$

We now show that for the general case which we have considered, we have an almost symmetric tensor L_{ik}, i.e., that D and B differ only by terms which contain $k_1 e^{r_1 t}$, $k_2 e^{r_2 t}$(i.e., by terms which go to zero as $t \to +\infty$) Actually, by keeping in the expressions for B and D only those terms which do not contain k_1 and k_2 explicitly, we would have

$$L = a, \quad M = b, \quad N = c$$

and consequently, recalling the values of a_1, a_2,

$$B = a(r_2 - r_1) - b(r_1\alpha_2 - r_2\alpha_1) = a(r_2 - r_1) - [r_1(r_2^2 - a) - r_2(r_1^2 - a)] = r_1 r_2 (r_1 - r_2) \tag{2.33}$$

and

$$D = c(r_1\alpha_1\alpha_2 - r_2\alpha_1\alpha_2) - b(r_2\alpha_2 - r_1\alpha_1). \tag{2.34}$$

But $ca_1 = a_1 r_1^2 - b$, $ca_2 = a_2 r_2^2 - b$, so that

$$D = \alpha_1\alpha_2(r_2 - r_1) r_1 r_2.$$

On the other hand

$$\alpha_1\alpha_2 = \frac{(r_1^2 - a)(r_2^2 - a)}{b^2} = \frac{r_1^2 r_2^2 - a(r_1^2 + r_2^2) + a^2}{b^2} = -1$$

and consequently

$$D = r_1 r_2 (r_1 - r_2) = B, \tag{2.35}$$

i.e., $L_{12} = L_{21}$ with accuracy to terms which contain k_1 and k_2 as first powers which tend to zero with increasing t.

GENERAL PROPERTIES OF THE INTEGRALS OF THE SYSTEM OF EQUATIONS (2.2)

We consider the system

$$\frac{d^2 x_i}{dt^2} = \frac{\partial(-\Delta S)}{\partial x_i} = X_i \quad (i = 1, 2, \ldots, n), \tag{2.2'}$$

where ΔS is taken in its most general form. Since

$$\delta(-\Delta S) = \sum_i \frac{\partial(-\Delta S)}{\partial x_i}\delta x_i = \sum_i X_i \delta x_i,$$

we have

$$\frac{d}{dt}(-\Delta S) = \sum_i X_i x_i'. \quad (2.36)$$

On the other hand, we get from (2.2′) and (2.36)

$$\sum_i x_i' \frac{d^2 x_i}{dt^2} = \frac{1}{2}\frac{d}{dt}\sum_i (x_i')^2 = \sum_i X_i x_i' = \frac{d}{dt}(-\Delta S);$$

consequently,

$$\frac{x_1'^2 + x_2'^2 \ldots + + x_n'^2}{2} + \Delta S = \text{const.} \quad (2.37)$$

In irreversible thermodynamic processes $\lim \chi_i'(t) = 0$ and $\lim \chi_i(t) = 0$ for $t \to +\infty$ and, consequently, in these processes

$$1/2\,(x_1'^2 + x_2'^2 + \ldots + x_n'^2) + \Delta S = 0. \quad (2.38)$$

ADDITIONAL REMARKS

We pose the following problem: beginning with ΔS, can we obtain a much simpler set of differential equations whose integrals approach zero at $t = +\infty$ and which have n constants of integration, making it possible to choose arbitrarily the initial values $\chi_1^0, \chi_2^0, \ldots, \chi_n^0$ of the independent variables?

We consider the linear system of nth order

$$dx_i/dt = -X_i = -(g_{i1}x_1 + g_{i2}x_2 + \ldots + g_{in}x_n) \quad (i = 1, 2, \ldots, n), \quad (2.39)$$

(which is a partial case of the phenomenological relations of Onsager), in which $L_{ik} = 0$ for $i \neq k$ and $L_{ii} = -1$. Setting $\chi_1 = \alpha e^{-\lambda t}$, $\chi_2 = \beta e^{-\lambda t}, \ldots, \chi_n = \nu e^{-\lambda t}$, we get a system of homogeneous algebraic equations for X: (2.40)

$$(g_{11} - \lambda)\alpha + g_{12}\beta + g_{13}\gamma + \ldots + g_{1n}\nu = 0;$$

$$g_{21}\alpha + (g_{22} - \lambda)\beta + g_{23}\gamma + \ldots + g_{2n}\nu = 0,$$

$$\ldots\ldots\ldots\ldots\ldots\ldots,$$

$$g_{n1}\alpha + g_{n2}\beta + g_{n3}\gamma + \ldots + (g_{nn} - \lambda)\nu = 0.$$

For non-vanishing solutions of this system we must choose for X the roots of the algebraic equation

$$\begin{vmatrix} g_{11}-\lambda & g_{12} & g_{13}\ldots g_{1n} \\ g_{21} & g_{22}-\lambda & g_{23}\ldots g_{2n} \\ \ldots & \ldots & \ldots \\ g_{n1} & g_{n2} & g_{n3} \quad g_{nn}-\lambda \end{vmatrix} = 0. \quad (2.41)$$

which we already know.

As we have seen, all n roots of this equation are real and positive. It is evident from (2.40) that there corresponds to each root λ_i a set of solutions $\alpha_i = 1, \beta_i, \gamma_i, \ldots, \nu_i$ such that the general integral of the system (2.39) has the form: (2.42)

$$x_1 = C_1\alpha_1 e^{-\lambda_1 t} + C_2\alpha_2 e^{-\lambda_2 t} + \ldots + C_n\alpha_n e^{-\lambda_n t},$$

$$x_2 = C_1\beta_1 e^{-\lambda_1 t} + C_2\beta_2 e^{-\lambda_2 t} + \ldots + C_n\beta_n e^{-\lambda_n t},$$

$$\ldots\ldots\ldots\ldots\ldots\ldots$$

$$x_n = C_1\nu_1 e^{-\lambda_1 t} + C_2\nu_2 e^{-\lambda_2 t} + \ldots + C_n\nu_n e^{-\lambda_n t},$$

These tend to zero as $t \to +\infty$. The values of C_1, $C_2, C_3, \ldots, C_n$ are determined by the system

$$x_1^0 = C_1\alpha_1 + C_2\alpha_2 + \ldots + C_n\alpha_n,$$

$$x_2^0 = C_1\beta_1 + C_2\beta_2 + \ldots + C_n\beta_n,$$

$$\ldots\ldots\ldots\ldots$$

$$x_n^0 = C_1\nu_1 + C_2\nu_2 + \ldots + C_n\nu_n.$$

If we compare the set of integrals (2.42) with the set (12) we see that $r_i = -\sqrt{\lambda_i}$ and that both $\alpha_i, \beta_i, \gamma_i, \ldots, \nu_i$ and $C_1, C_2, C_3, \ldots C_n$ have identical values in the two systems.

We now assume that

$$0 < \lambda_1 < \lambda_2 < \lambda_3 < \ldots < \lambda_n.$$

Since $|r_i| = +\sqrt{\lambda_i}$ we get

$$0 < |r_1| < |r_2| < \ldots < |r_n|.$$

Consequently we can write the integrals of the system (12) in the form:

$$x_i = C_1\eta_1 e^{r_1 t}\left[1 + \frac{C_2\eta_2}{C_1\eta_1}e^{(r_2 - r_1)t} + \ldots + \frac{C_n\eta_n}{C_1\eta_1}e^{(r_n - r_1)t}\right] \quad (i = 1, 2, \ldots, n),$$

and the integrals of the system (2.42) in the form

$$x_i = C_1\eta_1 e^{-\lambda_1 t}\left[1 + \frac{C_2\eta_2}{C_1\eta_1}e^{-(\lambda_2 - \lambda_1)t} + \ldots + \frac{C_n\eta_n}{C_1\eta_1}e^{-(\lambda_n - \lambda_1)}\right].$$

But since $r_j - r_1 < 0$ and $-(\lambda_j - \lambda_1) < 0$ for $j = 2, 3, \ldots, n$, then $\exp[(r_j - r_i)t]$ and $\exp[-(\lambda_j - \lambda_i)t]$ are very small for $t > 0$ and approach zero with increasing t. Therefore, the principle values of the integrals of the first set are $\chi_i(t) = C_1\eta_1 e^{r_1 t}$ and of the second set are $\chi_i(t) = C_1\eta_1 e^{-\lambda_1 t}$, i.e., the integral curves of both systems almost coincide, but motion of the particle $(\chi_1, \chi_2, \ldots, \chi_n)$ along these curves proceeds with different velocity. In the first case we have approximately $\chi_i' = C_1\eta_1 r_1 e^{r_1 t}$, and in the second case $\chi_i' = -C_1\eta_1\lambda_1 e^{-\lambda_1 t}$.

3. APPLICATION OF THE GENERAL THEORY TO SPECIFIC PROBLEMS

The Transfer of Heat from One System to Another

We now show that the Fourier hypothesis, which applies to the transfer of heat from one system to another, follows from our general theory of irreversible thermodynamic processes.

We consider a system consisting of two plates, i.e., two thin plane round disks, in thermal contact through their bases, and adiabatically isolated from their surroundings. In this case we shall neglect any work of thermal expansion. We denote by m_1 the mass per unit area of contact, T_1 the absolute temperature, c_1, the specific heat, all of the first plate; m_2, T_2, c_2 are the corresponding quantities for the second plate, T_0 is the overall temperature of the system after thermal equilibrium has been established. We have assumed that these plates were not thick, in order that it would be possible to consider the temperature at any moment to be uniform at all points on either of the two plates.

Let Q_1 be the amount of heat per unit area of contact that the first plate must receive from the second in order that the system come to thermal equilibrium $(T_1 = T_0)$, and let Q_2 be the corresponding amount of heat which the second plate must receive from the first.

Here

$$Q_1 = m_1c_1(T_1 - T_0) = m_1c_1\Delta T_1, \tag{3.1}$$

$$Q_2 = m_2c_2(T_2 - T_0) = m_2c_2\Delta T_2,$$

$$Q_1 + Q_2 = 0. \tag{3.2}$$

Consequently,

$$m_1c_1T_1 + m_2c_2T_2 = T_0(m_1c_1 + m_2c_2), \tag{3.3}$$

$$Q_1 = \frac{m_1c_1\, m_2c_2}{m_1c_1 + m_2c_2}(T_1 - T_2). \tag{3.4}$$

Thus at a given moment t, we get for the entropy ΔS per unit area of thermal contact (keeping only terms of second order),

$$\Delta S = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = -\frac{T_1 - T_2}{T_0^2}Q_1 \tag{3.5}$$

$$= -\frac{m_1c_1 + m_2c_2}{m_1c_1\, m_2c_2}\frac{Q_1^2}{T_0^2}.$$

Here

$$\frac{\partial(-\Delta S)}{\partial Q_1} = \frac{2}{T_0^2}\frac{m_1c_1 + m_2c_2}{m_1c_1\, m_2c_2}Q_1 = aQ_1, \tag{3.6}$$

where $a \geq 0$.

We then have only the one equation

$$d^2Q_1/dt^2 = aQ_1, \tag{3.7}$$

the integral of which is $Q_1 = Ce^{rt}$.

Substituting this value of Q_1 in Eq. (3.7), and recalling that $a \geq 0$, we get

$$r^2 = a, \quad r_{1,2} = \pm\sqrt{a}.$$

Here only $-\sqrt{a}$ is of importance in physical problems, since $\lim Q_1 = 0$ for $t = \mp\infty$. Consequently,

$$\begin{aligned} Q_1 &= ce^{-\sqrt{a}t}, \\ \dot{Q}_1 &= -\sqrt{a}Ce^{-\sqrt{a}t} = -\sqrt{a}Q_1, \end{aligned} \tag{3.8}$$

where $C = Q_1^0$ is the value of Q_1 at the initial time $t = 0$. Recalling the value of Q_1 from Eq. (3.4) and the value of a, we get the Fourier formula for the "heat flow" $\dot{Q}_1$, :

$$\dot{Q}_1 = -\frac{1}{T_0}\sqrt{\frac{2m_1c_1m_2c_2}{m_1c_1 + m_2c_2}}(T_1 - T_2) \tag{3.9}$$

Up to this point we have assumed that at each moment the temperature of each of the two plates is uniform. But even for very small thickness the temperature of each plate, which is a continuous function of position along the axis, must have different values on the opposite faces of each plate, hence different values are obtained for the entropy when one or the other temperature value is inserted in Eq. (3.5). However, this difference is very small, since the temperature difference between the faces of the disks is slight. The entropy of each plate will correspond to a mean temperature which depends on the thermal conductivity of the plate. Denoting by T_1 and T_2 the extreme temperature for each plate at a given moment and by T_0 the temperature at thermal equilibrium, we get

$$\Delta T_1 = T_1 - T_0, \qquad \Delta T_2 = T_2 - T_0;$$

Here we must assume for the average temperature at time t in each of the two plates

$$T_0 + \lambda_1 \Delta T_1, \qquad T_0 + \lambda_2 \Delta T_2,$$

where λ_1 and λ_2 depend on the thermal conductivity of the plates and differ very slightly from unity. We then have

$$Q_1 = m_1 c_1 \lambda_1 \Delta T_1, Q_2 = m_2 c_2 \lambda_2 \Delta T_2, Q_1 + Q_2 = 0, \tag{3.10}$$

which gives

$$Q_1 = \frac{m_1 c_1 \lambda_1 m_2 c_2 \lambda_2}{m_1 c_1 \lambda_1 + m_2 c_2 \lambda_2}(T_1 - T_2), \tag{3.11}$$

$$\frac{Q_1}{m_1 c_1} = \lambda_1 \Delta T_1, \qquad \frac{Q_2}{m_2 c_2} = \frac{-Q_1}{m_2 c_2} = \lambda_2 \Delta T_2,$$

$$\lambda_2 \Delta T_2 - \lambda_1 \Delta T_1 = -Q_1 \frac{m_1 c_1 + m_2 c_2}{m_1 c_1 m_2 c_2}, \tag{3.12}$$

$$\Delta S = \frac{Q_1}{T_0 + \lambda_1 \Delta T_1} + \frac{Q_2}{T_0 + \lambda_2 \Delta T_2}.$$

Limiting ourselves to terms of second order, we get

$$\Delta S = \frac{\lambda_2 \Delta T_2 - \lambda_1 \Delta T_1}{T_0^2} Q_1 = -\frac{m_1 c_1 + m_2 c_2}{m_1 c_1 m_2 c_2} \frac{Q_1^2}{T_0^2},$$

$$\frac{d(-\Delta S)}{dQ_1} = 2\frac{(m_1 c_1 + m_2 c_2)}{m_1 c_1 m_2 c_2} \frac{Q_1}{T_0^2} = aQ_1.$$

Following the method of calculation given above, we get, finally,

$$\dot{Q}_1 = -\sqrt{\frac{2(m_1 c_1 + m_2 c_2)}{m_1 c_1 m_2 c_2}} \frac{m_1 c_1 \lambda_1 m_2 c_2 \lambda_2}{m_1 c_1 \lambda_1 + m_2 c_2 \lambda_2} \frac{T_1 - T_2}{T_0}.$$

HEAT PROPAGATION IN A HOMOGENEOUS ROD

We now consider heat propagation in a cylindrical rod with density ρ and specific heat c. The lateral surfaces of the rod are covered with a thermally insulating jacket. We assume that the temperature of the rod is a continuous function which has derivatives along the axis of the rod, taken as the abscissa. We take three cross-sections of the rod, corresponding to $\chi - d\chi$, χ, and $\chi + d\chi$, and designate the area of each of these cross sections by f. In this way we obtain two adjacent cells of volume $f\,d\chi$ and mass $\rho f d\chi$.

We now turn our attention to the system which consists of these two cells. We denote by $Q(\chi - d\chi)$ the heat flow per unit area into the system from the side at $\chi - d\chi$ and by $\dot{Q}(\chi + d\chi)$ the flow of heat entering from the side at $\chi + d\chi$.

Let dS be the increase in entropy per unit mass of the system of the two cells in the time interval dt. The entropy increase of the system per unit time will then be $2\rho f d\chi \frac{dS}{dt}$. We denote by du the increase of internal energy of the system per unit mass in the time interval dt. The internal energy increase per unit time will then be

$$2\rho f dx \frac{du}{dt} = f[\dot{Q}(x - dx) - \dot{Q}(x + dx)] = -2f dx \frac{d\dot{Q}}{dx}.$$

Thus, neglecting the work of thermal expansion, we have

$$T\rho \frac{dS}{dt} = -\frac{d\dot{Q}}{dx}$$

or

$$\rho \frac{dS}{dt} = -\frac{1}{T}\frac{d\dot{Q}}{dx} = -\frac{d(\dot{Q}/T)}{dx} - \frac{\dot{Q}}{T^2}\frac{dT(x)}{dx}. \tag{3.13}$$

On the other hand,

$$T(x + dx) - T(x - dx) = 2\frac{dT(x)}{dx}dx. \tag{3.14}$$

But this quantity is, from Eq. (3.4), proportional to the quantity of heat Q in an adiabatic process. Setting

$$dT/dx = \mu Q, \tag{3.15}$$

where μ is a proportionality constant, we get from Eq. (3.13)

$$\rho \frac{dS}{dt} = -\frac{d(\dot{Q}/T)}{dx} - \frac{\mu}{T^2} Q\dot{Q}. \tag{3.16}$$

The increase of entropy can be divided into two parts (superposition principle): the first, the divergence of the entropy

$$\left[-\frac{d(\dot{Q}/T)}{dx}\right]$$

and second, the quantity

$$\Delta\dot{\sigma} = -\frac{\mu}{T^2} Q\dot{Q}$$

or entropy flow which, by Eq. (3.5), corresponds to the entropy

$$\Delta\sigma = -\frac{1}{2}\frac{\mu}{T^2} Q^2, \qquad (3.17)$$

which appears in the irreversible adiabatic process considered in the previous section. As a consequence we can write

$$d^2Q/dt^2 = bQ, \qquad b > 0, \qquad (3.18)$$

which leads to the relation

$$\dot{Q} = -\sqrt{b}Q = -\sqrt{1/b}\, dT/dx, \quad (3.19)$$

which appears in the formula for heat flow in Fourier's theory.

Similar results obtained by Prigogine with the help of direct application of the phenomenological relations of Onsager are reproduced in de Groot's work[5]. In this case the coefficients L_{ik}, as we have shown, must satisfy certain conditions in order that lim $Q = 0$ for $t = +\infty$.

APPLICATION TO THE THEORY OF PHASES

Let a liquid (I) and its vapor (II) at temperatures T_1 and T_2 be contained in a given closed reservoir with heat proof walls. Let M, V, U be, respectively, the total mass, volume and energy of this system, M_i ($i = 1, 2$) the masses of the components, p_i the pressure and v_i, u_i, s_i the volume, energy and entropy per unit mass, so that

$$\begin{aligned} M_1 + M_2 = M, \qquad M_1v_1 + M_2v_2 = V,\\ M_1u_1 + M_2u_2 = U, \qquad (3.20)\\ S = M_1s_1 + M_2s_2. \end{aligned}$$

Taking the mass M_1, the energy u_1 and the volume v_1 as the independent variables that define the state of the components, we find that Eqs. (3.20) define M_2, v_2, u_2 as functions of M_1, v_1, u_1. Inasmuch as s_i, T_i appear as functions of u_i, v_i, they are also functions of M_1, v_1, u_1. Therefore the total entropy S of the system is also a function of these three variables.

Denoting by M_1^0, v_1^0, u_1^0 the values of the variables M_1, v_1, u_1 for the equilibrium state, we have, limiting ourselves to terms of the first and second order,

$$\begin{aligned} \Delta S = S(v_1, u_1, M_1) - S(v_1^0, u_1^0, M_1^0)\\ = \left(\frac{\partial S}{\partial v_1}\right)_0 v + \left(\frac{\partial S}{\partial u_1}\right)_0 u + \left(\frac{\partial S}{\partial M_1}\right)_0 m\\ + \frac{1}{2}\left[\left(\frac{\partial^2 S}{\partial v_1^2}\right)_0 v^2 + 2\left(\frac{\partial^2 S}{\partial v_1 \partial u_1}\right)_0 vu\right.\\ + 2\left(\frac{\partial^2 S}{\partial v_1 \partial M_1}\right)_0 vm + \left(\frac{\partial^2 S}{\partial u_1^2}\right)_0 u^2\\ \left. + 2\left(\frac{\partial^2 S}{\partial u_1 \partial M_1}\right) um + \left(\frac{\partial^2 S}{\partial M_1^2}\right) m^2\right], \end{aligned}$$

where

$$v_1 - v_1^0 = v, \qquad u_1 - u_1^0 = u, \qquad M_1 - M_1^2 = m$$

Since the derivatives are taken at v_1^0, u_1^0, M_1^0, which correspond to the maximum of the entropy S,

$$\left(\frac{\partial S}{\partial u_1}\right)_0 = \left(\frac{\partial S}{\partial v_1}\right)_0 = \left(\frac{\partial S}{\partial M_1}\right)_0 = 0 \qquad (3.21)$$

and, consequently,

$$\begin{aligned} \Delta S = \frac{1}{2}\left[\left(\frac{\partial^2 S}{\partial v_1^2}\right)_0 v^2\right.\\ + 2\left(\frac{\partial^2 S}{\partial v_1 \partial u_1}\right)_0 vu + 2\left(\frac{\partial^2 S}{\partial v_1 \partial M_1}\right)_0 vm\\ \left. + \left(\frac{\partial^2 S}{\partial u_1^2}\right)_0 u^2 + 2\left(\frac{\partial^2 S}{\partial u_1 \partial M_1}\right)_0 um + \left(\frac{\partial^2 S}{\partial M_1^2}\right)_0 m^2\right]. \end{aligned}$$

To calculate the second derivatives of S, we make use of the formula for the second total differential:

$$\begin{aligned} d^2S = \frac{\partial^2 S}{\partial v^2} dv^2 + 2\frac{\partial^2 S}{\partial v \partial u} dvdu + 2\frac{\partial^2 S}{\partial v \partial m} dvdm\\ + \frac{\partial^2 S}{\partial u^2} du^2 + 2\frac{\partial^2 S}{\partial u \partial m} dudm + \frac{\partial^2 S}{\partial m^2} dm^2. \end{aligned}$$

The differential equations ot the process under consideration have the form

$$\frac{d^2v}{dt^2} = -\left(\frac{\partial^2 S}{\partial v_1^2}\right)_0 v - \left(\frac{\partial^2 S}{\partial v_1 \partial u_1}\right)_0 u - \left(\frac{\partial^2 S}{\partial v_1 \partial M_1}\right)_0 m,$$
$$\frac{d^2u}{dt^2} = -\left(\frac{\partial^2 S}{\partial u_1 \partial v_1}\right)_0 v - \left(\frac{\partial^2 S}{\partial u_1^2}\right)_0 u - \left(\frac{\partial^2 S}{\partial u_1 \partial M_1}\right)_0 m,$$
$$\frac{d^2m}{dt^2} = -\left(\frac{\partial^2 S}{\partial M_1 \partial v_1}\right)_0 v - \left(\frac{\partial^2 S}{\partial M_1 \partial u_1}\right)_0 u - \left(\frac{\partial^2 S}{\partial M_1^2}\right)_0 m. \qquad (3.22)$$

The interesting integrals of this system depend on the negative root of the algebraic equation

$$\begin{vmatrix} -\left(\frac{\partial^2 S}{\partial v_1^2}\right)_0 - r^2 & -\left(\frac{\partial^2 S}{\partial v_1 \partial u_1}\right)_0 & -\left(\frac{\partial^2 S}{\partial v_1 \partial M_1}\right)_0 \\ -\left(\frac{\partial^2 S}{\partial u_1 \partial v_1}\right)_0 & -\left(\frac{\partial^2 S}{\partial u_1^2}\right)_0 - r^2 & -\left(\frac{\partial^2 S}{\partial u_1 \partial M_1}\right)_0 \\ -\left(\frac{\partial^2 S}{\partial M_1 \partial v_1}\right)_0 & -\left(\frac{\partial^2 S}{\partial M_1 \partial u_1}\right)_0 & -\left(\frac{\partial^2 S}{\partial M_1^2}\right)_0 - r^2 \end{vmatrix} = 0.$$

Since $(-\Delta S)$ is a positive definite quadratic form, three of the roots of this equation are negative and the other three are positive. The results which are obtained are of physical interest only if both masses are positive for the case of thermal equilibrium.

To determine the values of the independent variables which apply to the case of stable equilibrium, we follow the Gibbs method as it is stated in the thermodynamics text of Planck[9].

From Eq. (3.20) we get

$$dM_2 = -dM_1, \qquad (3.24)$$
$$M_2 dv_2 = -M_1 dv_1 - (v_1 - v_2)\, dM_1,$$
$$M_2 du_2 = -M_1 du_1 - (u_1 - u_2)\, dM_1$$

$$dS = M_1 ds_1 + M_2 ds_2 + s_1 dM_1 + s_2 dM_2 \qquad (3.25)$$
$$= M_1 \frac{du_1 + p_1 dv_1}{T_1} + M_2 \frac{du_2 + p_2 dv_2}{T_2} + (s_1 - s_2)\, dM_1$$
$$= M_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) du_1 + M_1\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dv_1 + \left[s_1 - s_2 - \frac{(u_1 - u_2) + p_2(v_1 - v_2)}{T_2}\right] dM_1.$$

Thus Eqs. (3.4), which determine the state of thermodynamic equilibrium, and which in our case, have the form

$$\frac{\partial S}{\partial u_1} = M_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = 0,$$
$$\frac{\partial S}{\partial v_1} = M_1\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) = 0, \qquad (3.26)$$
$$\frac{\partial S}{\partial M_1} = \left[s_1 - s_2 - \frac{(u_1 - u_2) + p_2(v_1 - v_2)}{T_2}\right] = 0$$

lead to Gibb's conditions

$$T_1 = T_2 = T_0, \qquad p_1 = p_2 = p_0. \qquad (3.27)$$

Choosing M_1, ν_1, u_1 as independent variables, we have

$$T_1 = f_1(u_1, v_1).\ T_2 = f_2(u_2, v_2) = f(u_1, v_1, M_1),$$
$$s_1 = \psi_1(u_1, v_1),\ s_2 = \psi_2(u_2, v_2) = \psi(u_1, v_1, M_1),$$
$$p_1 = \varphi_1(u_1, v_1),\ p_2 = \varphi_2(u_2, v_2) = \varphi(u_1, v_1, M_1).$$

Substituting these values of T_1, T_2, s_1, s_2, p_1, p_2 in Eqs. (3.26), we get from them v_1^0, u_1^0, M_1^0, which define the state of thermodynamic equilibrium. We note here that Eqs. (3.26) contain s and u in the form $s_1 - s_2$ and $u_1 - u_2$.

Following Planck, we can give another form to the last of Eqs. (3.26). Since the difference $(s_1 - s_2)$ depends, in thermodynamic equilibrium, only on state I and state II and not on the path from I to II, we can find this difference in the transition from I to II along the isotherm T_0. But, since s_1 and s_2 pertain to a unit mass of one and the same material at the temperature T_0, we have

$$s_1 - s_2 = \int_{(2)}^{(1)} ds$$
$$= \frac{1}{T_0}\int_{(2)}^{(1)} (du + p\,dv) = \frac{u_1 - u_2}{T_0} + \frac{1}{T_0}\int_{(2)}^{(1)} p\,dv.$$

Now, assuming $T_2 = T_0$, we find, from Eq. (3.26)

$$\frac{1}{T_0}\int_{(2)}^{(1)} p\,dv - \frac{p_2(v_1 - v_2)}{T_0} = 0,$$
$$\int_{(2)}^{(1)} p\,dv = p_2(v_1 - v_2).$$

It now remains to find, with the help of d^2S, the second derivatives which enter into Eq. (3.22) and which pertain to the equilibrium state, introducing

[9] M. Planck, *Thermodynamics*, 1930

only such quantities which can be obtained by laboratory measurement.

Recalling Eqs. (3.26) we get, from (3.25),

$$d^2S = \frac{M_1}{T_0^2}(-dT_1 + dT_2)\,du_1 \tag{3.28}$$

$$+ \frac{M_1 p_0}{T_0^2}(-dT_1 + dT_2)\,dv_1$$

$$+ \frac{M_1}{T_0}(dp_1 - dp_2)\,dv_1$$

$$+ \Big[ds_1 - ds_2 - \frac{du_1 - du_2 + p_0(dv_1 - dv_2)}{T_0}$$

$$- \frac{(v_1 - v_2)\,dp_2}{T_0} + \frac{(u_1 - u_2) + p_0(v_1 - v_2)}{T_0^2}\,dT_2\Big]\,dM_1$$

$$= \frac{M_1}{T_0^2}(-dT_1 + dT_2)\,du_1$$

$$+ \frac{M_1 p_0}{T_0^2}(-dT_1 + dT_2)\,dv_1 + \frac{M_1}{T_0}(dp_1 - dp_2)\,dv_1$$

$$+ \Big[\frac{u_1 - u_2 + p_0(v_1 - v_2)}{T_0^2}\,dT_2 - \frac{v_1 - v_2}{T_0}\,dp_2\Big]\,dM_1.$$

The quantities u_1, v_1, u_2, v_2 and M_1, which appear here, relate to the equilibrium state. The differentials dT_1, dT_2, du_2, dv_2, dp_1, dp_2 must be taken as functions of du_1, dv_1 and $dM_1 = dm$. For this purpose we first use

$$M_2 dv_2 = -M_1 dv_1 - (v_1 - v_2)\,dm,$$

$$M_2 = M - M_1.$$

But, inasmuch as we chose M_1, u_1, v_1 as the independent variables, then $T = T(u, v)$; conversely, $u = u(v, T)$ as a function of v and T satisfy the identity relation

$$T \equiv T[u(v, T), v].$$

From this identity we get, by differentiating with respect to T,

$$\frac{\partial T(u, v)}{\partial u}\frac{\partial u(v, T)}{\partial T} = 1,$$

$$\frac{\partial T(u, v)}{\partial u} = \frac{1}{\partial u(v, T)/\partial T} = \frac{1}{c_v},$$

and by differentiating with respect to v,

$$\frac{\partial T(u, v)}{\partial v} =$$

$$-\frac{\partial T(u, v)}{\partial u}\frac{\partial u(v, T)}{\partial v} = -\frac{1}{c_v}\frac{\partial u(v, T)}{\partial v}.$$

From the first law of thermodynamics

$$dq = du(v, T) + p(v, T)\,dv = \frac{du(v, T)}{\partial T}\,dT$$

$$+ \Big[\frac{\partial u(v, T)}{\partial v} + p(v, T)\Big]\,dv = c_v dT + a dv,$$

so that

$$\partial u(v, T)/\partial v = a - p,$$

and therefore

$$\frac{\partial T(u, v)}{\partial v} = -\frac{1}{c_v}(a - p).$$

We finally obtain

$$dT = \frac{\partial T(u, v)}{\partial u}\,du$$

$$+ \frac{\partial T(u, v)}{dv}\,dv = -\frac{a - p}{c_v}\,dv + \frac{1}{c_v}\,du.$$

Consequently,

$$dT_1 = -\frac{a_1 - p_0}{c_{v1}}\,dv_1 + \frac{1}{c_{v1}}\,du_1,$$

$$dT_2 = -\frac{a_2 - p_0}{c''_{v2}}\,dv_2 + \frac{1}{c''_{v2}}\,du_2$$

$$= \frac{a_2 - p_0}{c''_{v2}}\frac{M_1}{M_2}\,du_1 - \frac{1}{c''_{v2}}\frac{M_1}{M_2}\,du_1$$

$$+ [(a_2 - p_0)(v_1 - v_2) - (u_1 - u_2)]\,\frac{dm}{c_{v2}M_2}$$

We now express dp as a function of du, dv. We have

$$dp(u, v) = \frac{\partial p(u, v)}{\partial u}\,du + \frac{\partial p(u, v)}{\partial v}\,dv.$$

From the First Law we get

$$dq = du(p, T) + p dv(p, T)$$

$$= \Big[\frac{\partial u(p, T)}{\partial p} + p\,\frac{\partial v(p, T)}{\partial p}\Big]\,dp$$

$$+ \Big[\frac{\partial u(p, T)}{\partial T} + p\,\frac{\partial v(p, T)}{\partial T}\Big]\,dT = k dp + c_p dT.$$

On the other hand, assuming u, v in the expression for p as functions of p and t, we get the identity

$$p = p(u, v) = p[u(p, T), v(p, T)],$$

and differentiating with respect to p and T, we find

$$\frac{\partial p(u, v)}{\partial u}\frac{\partial u(p, T)}{\partial p} + \frac{\partial p(u, v)}{\partial v}\frac{\partial v(p, T)}{\partial p} = 1,$$

$$\frac{\partial p(u, v)}{\partial u}\frac{\partial u(p, T)}{\partial T} + \frac{\partial p(u, v)}{\partial v}\frac{\partial v(p, T)}{\partial T} = 0.$$

Recalling the expressions for k and c_p introduced above and assuming

$$\Delta = k\frac{\partial v(p, T)}{\partial T} - c_p\frac{\partial v(p, T)}{\partial p},$$

we obtain

$$\Delta\frac{\partial p(u, v)}{\partial v} = -\frac{\partial u(p, T)}{\partial T} = -c_p + p\frac{\partial v(p, T)}{\partial T},$$

$$\Delta\frac{\partial p(u, v)}{\partial u} = \frac{\partial v(p, T)}{\partial T}$$

and, consequently,

$$dp = \frac{\partial p(u, v)}{\partial u}du + \frac{\partial p(u, v)}{\partial v}dv$$

$$= \frac{\partial v(p, T)/\partial T}{\Delta}du - \frac{c_p - p[\partial v(p, T)/\partial T]}{\Delta}dv.$$

We then have

$$dp_1 = \left[\frac{\partial v(p, T)/\partial T}{\Delta}\right]_1 du_1$$

$$- \left[\frac{c_p - p[\partial v(p, T)/\partial T]}{\Delta}\right]_1 dv_1,$$

$$dp_2 = -\frac{M_1}{M_2}\left[\frac{\partial v(p, T)/\partial T}{\Delta}\right]_2 du_1$$

$$+ \frac{M_1}{M_2}\left[\frac{c_p - p[\partial v(p, T)/\partial T]}{\Delta}\right]_2 dv_1$$

$$- \frac{1}{\Delta_2 M_2}\left[[u_1 - u_2 + p_0(v_1 - v_2)]\left(\frac{\partial v(p, T)}{\partial T}\right)_2 - c_{p_2}(v_1 - v_2)\right]dm,$$

where the expressions in square brackets pertain to phase I and II in thermodynamic equilibrium.

From $dq = du + pdv$ we get the following expression for the quantity of heat necessary to vaporize a unit mass at the temperature T_0 and pressure p_0.

$$q_1 - q_2 = (u_1 - u_2) + p_0(v_1 - v_2).$$

Making use of this expression and those for dT and dp obtained earlier, we get from (3.28), after some simplification

$$d^2S = Adu_1^2 + 2Bdu_1dv_1$$

$$+ 2Cdu_1dm + Ddv_1^2 + 2Edv_1dm + Fdm^2,$$

where the coefficients $A, B, \ldots, F$ are identical with the second derivatives which enter into the set of equations (3.20).

In this fashion we get the system of differential equations

$$d^2m/dt^2 = -Cu - Ev - Fm, \quad (3.22'$$

$$d^2u/dt^2 = -Au - Bv - Cm,$$

$$d^2v/dt^2 = -Bu - Dv - Em,$$

which describe the time development of the process.

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