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THE STEADY STATE IN CONDUCTING SYSTEMS

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The author examines a system through which passes a flux of a certain extensive quantity created by two constant sources. The properties and the characteristic steady state of this system are studied, as well as the process of transition to the steady state.

In the study of steady irreversible processes it is of interest to establish which properties of the steady state essentially distinguish it from the unsteady state. From a thermodynamic point of view it is important to ascertain the properties on which a phenomenological theory may be based. In this regard the principle of minimum rate of entropy production, based on Prigogine's theorem [1], is of definite value. The minimum principle is applicable to the case of superposition of several processes, and when certain boundary conditions are fulfilled, it is a necessary criterion of the steady state.

In fact, a necessary and sufficient criterion of the steady state is that heterogeneous fluxes J_1 and J_2 flowing along the axis 0X should be constant with respect to the coordinates, i. e., $J_1(x) = \text{const}_1$ and $J_2(x) = \text{const}_2$. If the boundary conditions maintain flux J_1, but do not maintain flux J_2, a steady state is established corresponding to $J_2 = 0$ and $J_1 = \text{const} \neq 0$. The minimum principle relates precisely to this case. Here it can be shown [2] that condition $J_2 = 0$ is equivalent to the condition of minimum rate of entropy production. However, this condition is formulated for circumstances from which it does not at all follow that the condition $J_1(x) = \text{const.}$ is fulfilled. Thus, the minimum principle does not exhaust all the characteristic properties of the steady state, and the search for new principles is important from both the theoretical and the practical viewpoint.

In the present paper a system in the steady state is examined, in the simplest case when the flux, directed along the axis 0X, may be represented by the equation*

$$J(x,t) = -k(x, y(x, t))\frac{\partial y}{\partial x}. \tag{1}$$

The direct dependence of k on x takes account of the possibility of heterogeneity of the system.

If constant boundary conditions are maintained, a steady state is established, in which the flux at all sections of the system has the same value and direction. We shall take this direction as positive, and the opposite direction as negative. Hence, examining an unsteady state with the same boundary conditions at any instant of time, we shall assign a different algebraic value to the flux at different sections. At some section or other, the algebraic value of the flux proves to be a minimum J_{min}. The flux J at any section x may be represented by the sum

$$J(x, t) = J_{\min}(t) + J_{ex}(x, t), \quad J_{ex} \geqslant 0. \tag{2}$$

If $J_{min} > 0$, the system in this state becomes conducting, and the value J_{min} acquires a simple physical meaning. It is the portion of the total flux J passing through all sections of the system. In time dt the flux J creates in the conducting system the changes that would be caused by a flux $J_{ex(cess)} = J - J_{min}$. In this sense J_{min} characterizes the rapid transmission of a certain extensive quantity through the whole system without change of the properties of the conducting system itself. We shall call J_{min} the through flux J_{thr}. Clearly, in the steady state, $J_{thr \cdot st} = J_{st}$.

For convenience, we shall now consider the specific case of one-dimensional heat conduction along the axis 0X. We shall assume that constant temperatures T_1 and T_2 are maintained at the ends of the conducting system by means of thermal reservoirs. Let the system be inhomogeneous, and the thermal conductivity be $k = f(x, T)$. Then, for the heat flux J at a fixed instant of time, according to (1) and to our condition regarding choice of sign, we obtain

$$J(x) = \pm \left| f(x, T)\frac{dT}{dx} \right|,$$

where the plus sign obtains if $\frac{dT}{dx}$ coincides with the direction of the gradient in the steady state, and the minus sign if the directions in question are opposite.

*The more general case when there are several heterogeneous fluxes in the system, and interaction between them, will be examined in another article.

We shall now show that the system examined attains its greatest rate of heat transmission from the hot source to the cold region in the steady state, i. e., the through flux in the steady state is a maximum.

Let the temperature distribution in the steady state be given by the function $T_{st} = Y(x)$. The difference in the temperature distribution for some unsteady state is given by the function $z(x) = T(x) - Y(x)$. $Y(x)$ and $Z(x)$ are defined in the interval $a \leq x \leq b$. $Y(x)$ has a finite derivative in $[a, b]$, such that $|Y'(x)| < C$. $z(x)$ has a continuous first derivative $z'(x)$ in $[a, b]$, and, with the possible exception of a finite number of points, a finite second derivative $z''(x)$. Here $z''(x)$ changes sign in $[a, b]$, and, with the possible exception of a finite number of points, a finite second derivative $z''(x)$. Here $z''(x)$ changes sign in $[a, b]$ a finite number of times.

The boundary conditions are expressed in the form $z(a) = z(b) = 0$, (but $z(x) \not\equiv 0$), and let $Y(a) < Y(b)$.

The thermal conductivity is given by the function $f(x, T) > 0$. $f(x, Y)$ is bounded below, such that $E > f(x, Y)$. Moreover, the derivative $f'_T(x, T)$ exists, and is also finite, i. e., $|f'_T(x, T)| > B$; B, C, E are certain finite positive numbers.

We shall show that in the interval $[a, b]$ there exists a ζ for which

$$f[\zeta,\ Y(\zeta)]\,Y'(\zeta) > f[\zeta,\ Y(\zeta) + z(\zeta)]\,[Y'(\zeta) + z'(\zeta)] \tag{3}$$

is satisfied. With the assumptions we have made, the following may be proved. In the interval $[a, b]$ there exists a point ξ for which $z(\xi) = 0$. In some region near the point ξ to the left or the right ($\gamma_1 \leqslant x < \xi$ or $\xi < x \leqslant \gamma_2$) $z'(x) < 0$. For any two values x_1 and x_2 belonging to this region and satisfying the condition $|\xi - x_1| \leqslant |\xi - x_2|$, we have

$$\left|\frac{z'(x_1)}{z'(x_2)}\right| < A,$$

where A is a finite positive number. Later on we shall examine this region near the point ξ.

We set

$$\Delta = f(x,\ Y + z)\,\frac{d(Y+z)}{dx} - f(x,\ Y)\,\frac{dY}{dx},$$

$$\Delta f = f(x,\ Y + z) - f(x,\ Y).$$

Let us write Δ in the form

$$\Delta = [f(x,\ Y) + \Delta f]\left[\frac{dY}{dx} + \frac{dz}{dx}\right] - f(x,\ Y)\,\frac{dY}{dx} = f(x,\ Y)\,\frac{dz}{dx} +$$

$$+ \Delta f\,\frac{dY}{dx} + \Delta f\,\frac{dz}{dx} = f(x,\ Y)\,\frac{dz}{dx}\left[1 + \frac{\Delta f Y'}{fz'} + \frac{\Delta f z'}{fz'}\right]. \tag{4}$$

According to the mean value theorem $\Delta f = f'_T(x, Q(x))\,z$, where Q is some number satisfying the condition $|Q - Y| + |Q - Y - z| = |z|$,

$$\lim_{x\to\xi}\left|\frac{\Delta f}{z'}\right| = \lim_{x\to\xi}\left|\frac{f'_T(x,\ Q(x))\,z}{z'}\right| \leqslant \lim_{x\to\xi} B\left|\frac{z}{z'}\right|.$$

We once again make use of the mean value theorem

$$z(x) = z(\xi) + z'(\theta)(x - \xi) = z'(\theta)(x - \xi),$$

where θ satisfies $|\theta - \xi| + |\theta - x| = |\xi - x|$, and, therefore,

$$|\xi - \theta| < |\xi - x|,$$

$$B\lim_{x\to\xi}\left|\frac{z}{z'}\right| = B\lim_{x\to\xi}\left|\frac{z'(\theta)(x-\xi)}{z'(x)}\right| \leqslant B\lim_{x\to\xi}|A(x - \xi)| = 0.$$

Hence

$$\lim_{x\to\xi}\left|\frac{\Delta f}{z'}\right| = 0.$$

Also,

$$\lim_{x\to\xi}\left|\frac{\Delta f z'}{z' f(x,\ Y)}\right| = \lim_{x\to\xi}\left|\frac{\Delta f}{z'}\right| \lim_{x\to\xi}\left|\frac{z'}{f(x,\ Y)}\right| = 0\cdot\text{const} = 0,$$

$$\lim_{x\to\xi}\left|\frac{\Delta f Y'(x)}{z' f(x,\ Y)}\right| \leqslant \lim_{x\to\xi}\left|\frac{\Delta f C}{z' E}\right| = \frac{C}{E}\lim_{x\to\xi}\left|\frac{\Delta f}{z'}\right| = 0.$$

Thus, the last two terms in the square brackets of (4) are infinitely small values when $x \to \xi$. Therefore, for some ζ, sufficiently close to ξ, the whole square bracket is positive. But, since $f(\zeta, Y(\zeta)) > 0$ and $z'(\zeta) < 0$, when $x = \zeta\Delta < 0$. and (3) is satisfied. Because of the boundary conditions that we assumed, $Y'(\zeta) > 0$, and therefore, the left part of (3) is $J_{st}(\zeta)$, and the right side is $J(\zeta)$. According to (2),

$$J(\zeta) = J_{\min} + J_{ex}(\zeta), \quad J_{ex}(\zeta) > 0.$$

According to what has been proved, $J_{st}(\zeta) > J(\zeta)$. Therefore,

$$J_{thr\ st} > J_{thr}.$$

We shall now evaluate the validity of the assumptions made in formulating the theorem. The assumption of the existence of the derivatives and their finiteness is quite reasonable from the physical point of view. The matter of $f(x, Y(x))$ having a lower bound may be regarded as a consequence of the continuity of $f(x, Y(x))$ in the interval $[a, b]$, which is always permissible physically.

The exclusion from consideration of curves for which the second derivative $z''(x)$ in the interval $[a, b]$ changes sign an infinite number of times goes beyond the usual framework of constraints. However, such a case can scarecely be represented physically. This would imply that in a region as small as we please in the vicinity of some point $z''(x)$ changes sign an infinite number of time. We need thus concern ourselves here too only with the limitation of mathematical generality.

An actual physical limitation on our arguments can be set only by applicability of the basic equation (1). According to the above, this equation is applicable to the simplest cases: heat conduction in a solid rod, one-component isothermal diffusion, isothermal electric conduction, etc. This does not imply, however, that our relation (5) breaks down in cases when (1) is inapplicable. In these cases similar results may be obtained from quite different consideration.

For example, consider successive chemical reactions. This is the very case examined by Prigogine to illustrate the principle of minimum entropy production [3]. We have here a chain of successive transformations occurring under isobaric and isothermal conditions:

$$M_l \to M \to N \to O \to P \to F \to F_l, \tag{6}$$

where letters without subscripts correspond to the various components in the reactor, and the subscript l refers to components in the external medium. The over-all result of this interesting process is expressed briefly as $M_l \to F_l$, and its rate is determined by the rate in the slowest link in the chain (6), i. e., by the through flux J_{thr}. If a steady state is attained, the rate of the processes in all the elements will be equal to $J_{st} = J_{thr \cdot st}$. We shall show that relation (5) is valid here also.

Let us assign boundary conditions in the form of constant concentrations

$$n_{M_l} = \text{const and } n_{F_l} = \text{const}.$$

It should be noted that if the concentration of any component of (6) is increased, other things being equal, the rate of the process designated by the arrow to the right of this component increases, while the rate on the left decreases. To avoid decrease of the rate on the left, it is necessary to increase the concentration of all components to the left of the one chosen in (6). This is impossible, however, since $n_{M_l} = \text{const}$.

If the concentration of any component is decreased, a decrease follows in the rate of the process to the right. It is not possible to restore the rates in all elements because of the condition $n_{F_l} = \text{const}$. Therefore, if we go from the steady state to an unsteady state, the rate in some element decreases. For this element we have

$$J_{thr \cdot st} = J_{st} > J = J_{\min} + J_{ex} \geqslant J_{\min}, \text{ i. e. } J_{thr\ st} > J_{thr}.$$

Finally, we shall explain how the through flux varies with time in the case of heat conduction that we have just examined. The total flux must now be represented as a function of the coordinates and time, i. e.,

$$J = J(x, t).$$

Let $c = c(x, T)$ be the heat capacity per unit length of the system. Considering the element dx of the conducting system, and assuming the existence of the appropriate derivatives, we obtain the relation

$$\frac{\partial T}{\partial t} = -\frac{1}{c}\frac{\partial J}{\partial x}, \tag{7}$$

which is valid for all values of x and t. Moreover,

$$\frac{\partial^2 T}{\partial t \partial x} = -\frac{1}{c}\frac{\partial^2 J}{\partial x^2} - \frac{\partial J}{\partial x}\frac{\partial}{\partial x}\left(\frac{1}{c}\right). \tag{8}$$

According to Eq. (1),

$$\frac{\partial J}{\partial t} = -k\frac{\partial^2 T}{\partial x \partial t} - \frac{\partial T}{\partial x}\frac{\partial k}{\partial T}\frac{\partial T}{\partial t}. \tag{9}$$

From (9), (8), and (7) we obtain

$$\frac{\partial J}{\partial t} = \frac{k}{c}\frac{\partial^2 J}{\partial x^2} + k\frac{\partial J}{\partial x}\frac{\partial}{\partial x}\left(\frac{1}{c}\right) + \frac{1}{c}\frac{\partial J}{\partial x}\frac{\partial k}{\partial T}\frac{\partial T}{\partial t}. \tag{10}$$

We shall examine (10) at any time for the section at which the flux at that time is least. If this section lies within the interval c = c (x, T), the usual conditions for a minimum must be satisfied: $\frac{\partial J}{\partial x} = 0$ and $\frac{\partial^2 J}{\partial x^2} \geqslant 0$. If the section in question coincides with a boundary of the interval [a, b], we must turn our attention to the boundary conditions. Together with (7), they give $\left(\frac{\partial J}{\partial x}\right)_{x=a} = 0$, $\left(\frac{\partial J}{\partial x}\right)_{x=b} = 0$. Therefore the condition for attainment of the least value is expressed uniquely in all cases by

$$\frac{\partial J}{\partial x} = 0,\ \frac{\partial^2 J}{\partial x^2} \geqslant 0. \tag{11}$$

From (10), taking account of (11), we obtain $\frac{\partial J}{\partial t} \geqslant 0$.

The last relation indicates that if at a given instant of time the least value of flux exists at section x, then at section x at that instant of time the flux does not decrease. This result, together with (5), leads to the conclusion that in transition to the steady state, the through flux varies, and varies only in an increasing direction. This expresses the tendency of the system to maximize its conductivity. The steady state corresponds to maximum conductivity.

Notation

t—time; x—coordinate; J—flux of some extensive quantity; ∂y/∂x—gradient of the corresponding intensive quantity; k—conductivity.

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