THE PHENOMENOLOGICAL PROPERTIES OF CONDUCTING SYSTEMS

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A study is made of the properties of conducting systems with fixed boundary conditions on the bases of the phenomenological equations of the thermodynamics of irreversible processes.

An examination has been made in [1] of the behavior of through flows in the simple case when the processes occurring in the system are not interrelated, or when they are all due to the action of a single force. We shall now generalize the results obtained there by assuming that there are several interrelated flows and that several forces are acting simultaneously.

In addition, we shall also examine the question of the nature of the direct interconnection between different flows when the system goes over into the nonequilibrium stationary state.

Let a system be described by n independent intensive parameters $y_1, y_2, \ldots, y_n$. We assume that for the flows the linear relations

$$I_j = \sum_{k=1}^{n} L_{jk} X_k, \quad j = 1, 2, \ldots, n \tag{1}$$

are satisfied, and that the forces and the coefficients may be represented in the form

$$X_k = f_k(y_1, y_2, \ldots, y_n) \operatorname{grad} \varphi_k(y_1, y_2, \ldots, y_n), \tag{2}$$

$$L_{jk} = L_{jk}(y_1, y_2, \ldots, y_n). \tag{2a}$$

For a one-dimensional system, $\operatorname{grad} \varphi_k = \frac{d\varphi_k}{dx}$. Therefore

$$I_j = \sum_{k=1}^{n} L_{jk} f_k \sum_{r=1}^{n} \frac{\partial \varphi_k}{\partial y_r} \frac{dy_r}{dx} = \sum_{r=1}^{n} \sum_{k=1}^{n} L_{jk} f_k \frac{\partial \varphi_k}{\partial y_r} \frac{dy_r}{dx},$$

or

$$I_j = \sum_{r=1}^{n} \psi_{jr} \frac{dy_r}{dx}, \tag{3}$$

where

$$\psi_{jr} = \sum_{k=1}^{n} L_{jk} f_k \frac{\partial \varphi_k}{\partial y_r}.$$

Later on it will be assumed that the coefficents ψ_{jr} do not go to zero.† If, for example, $\psi_{\alpha\beta} = 0$, this means that the nature of the distribution of the parameter y_β has no influence on the value of flux I_α.

We now assume that the system attains the stationary state described by the following distribution of the parameters:

$$y_r(x) = Y_r(x), \quad r = 1, 2, \ldots, n. \tag{4}$$

Starting from this state, we vary some curve $y_l(x)$, keeping the boundary values y_l unchanged and a fixed distribution of the remaining independent parameters throughout the system. According to Eqs. (3) and (4), we obtain

$$I_j = \sum_{r=1}^{n} \psi_{jr}(Y_1 \ldots y_l \ldots Y_n) \frac{dy_r}{dx} = \sum_{r=1}^{l-1} \psi_{jr} \frac{dY_r}{dx} + \sum_{r=l+1}^{n} \psi_{jr} \frac{dY_r}{dx} + \psi_{jl} \frac{dy_l}{dx} = F_{jl}(x, y_l(x)) + \psi_{jl}(x, y_l(x)) \frac{dy_l}{dx},$$

where

$$F_{jl} = \sum_{r=1}^{l-1} \psi_{jr} \frac{dY_r}{dx} + \sum_{r=l+1}^{n} \psi_{jr} \frac{dY_r}{dx}.$$

We designate

$$z_l(x) = y_l(x) - Y_l(x),$$

$$\Delta\psi_{jl} = \psi_{jl}(x, y_l) - \psi_{jl}(x, Y_l),$$

$$\Delta F_{jl} = F_{jl}(x, y_l) - F_{jl}(x, Y_l),$$

$$\Delta_{jl} = \psi_{jl}(x, y_l) \frac{dy_l}{dx} - \psi_{jl}(x, Y_l) \frac{dY_l}{dx},$$

$$h_{jl} = 1 + \frac{\Delta\psi_{jl} Y_l'}{\psi_{jl}(x, Y_l) z_l'} + \frac{\Delta\psi_{jl}}{\psi_{jl}(x, Y_l)},$$

$$\Delta I_j = I_j - I_{j\,\mathrm{st}} = \Delta_{jl} + \Delta F_{jl}.$$

By choosing the direction of the OX axis, we make $I_{j\mathrm{st}} > 0$.

Under the above-mentioned variation of the curve $y_l(x)$, the through flow in the stationary state $I_{j\mathrm{str}\cdot\mathrm{st}}$ $(j = 1, 2, \ldots, n)$ is larger than the flux $I_{j\mathrm{str}}$ in any other state compatible with the conditions of variation.

To prove this statement, as in [1], with $\psi_{jl}(x, y_l) > 0$ we shall examine the neighborhood of some point ξ $(z_l(\xi) = 0)$, where $z_l(x) < 0$ and when $|\xi - x_1| \le |\xi - x_2|$, $\left|\frac{z_l'(x_1)}{z_l'(x_2)}\right| < A = \mathrm{const}$ is satisfied while with $\psi_{jl}(x, y_1) < 0$ we shall examine the neighborhood of the point ξ_1†, where the same conditions are satisfied,

†The coefficients ψ_{jr} must retain the sign of $[a, b]$.

†For the point ξ_1 to exist, we require the same conditions as for ξ in [1]. It is sufficient, for example, that $z(x)$ in $[a, b]$ be piecewise-analytic.

but $z_l'(x) > 0$. In the above-mentioned neighborhood we may put

$$\Delta_{jl} = \psi_{jl}(x, Y_l) z_l' h_{jl},$$
$$\Delta F_{jl} = F_y'(x, Q) z_l'(\Theta)(x - \xi), \qquad (5)$$

where $F_y' = \frac{\partial F_{jl}}{\partial y_l}$, it being true that $\left|\frac{\partial F_{jl}}{\partial y_l}\right| < D = \text{const}$, and Q and Θ are some numbers satisfying the relations

$$|Q - Y_l| + |Q - Y_l - z_l| = |z_l|$$

and

$$|\Theta - \xi| + |\Theta - x| = |\xi - x|.$$

As was shown in [1], $\lim_{x\to\xi} h_{jl} = 1$. Therefore

$$\lim_{x\to\xi}\left|\frac{\Delta F_{jl}}{\Delta_{jl}}\right| = \lim_{x\to\xi}\left|\frac{F_y'(x, Q) z_l'(\Theta)(x-\xi)}{\psi_{jl}(x, Y_l) z_l'(x) h_{jl}}\right| \leqslant$$
$$\leqslant DA \lim_{x\to\xi}\left|\frac{x-\xi}{\psi_{jl} h_{jl}}\right| = \frac{DA}{\psi_{jl}(\xi, Y(\xi))}\cdot 0 = 0.$$

Since $\Delta I_j = \Delta_{jl}\left(1 + \frac{\Delta F_{jl}}{\Delta_{jl}}\right)$ then for x values sufficiently close to ξ, the sign of ΔI_j is determined by that of Δ_{jl}. But, as may be seen from (5), for some $x = \zeta$, $\Delta_{jl}(\zeta) < 0$. Therefore, $I_j(\zeta) < I_{jst}(\zeta) = I_{jst}$. Hence we obtain $I_{jstr} < I_{jstr \cdot st}$.

Particular attention should be paid to the case when ψ_{jr} (j, r = 1, 2, ..., n) is a function only of y_r or may be considered in general to be a constant coefficient. It is then easy to show that even simultaneous change of all the parameters leads to a reduction of the through flows in comparison with their stationary-state values.

In fact, on the basis of Eq. (3), the flux may be represented in the form

$$I_j = \sum_{r=1}^{n} \psi_{jr}(y_r)\frac{dy_r}{dx}, \; j = 1, 2, \ldots, n.$$

Further,

$$\int_a^b I_j\,dx = \sum_{r=1}^{n}\int_{y_r(a)}^{y_r(b)} \psi_{jr}(y_r)\,dy_r = \text{const},$$

since the values of all the parameters $y_r(a) = Y_r(a)$ and $y_r(b) = Y_r(b)$ are kept constant at the boundaries of the system. If we assume that at all points x of the intercept $[a, b]$, $I_j(x) \geq I_{jst}$, $I_j > I_{jst}$ strictly for some points, then

$$\int_a^b I_j(x)\,dx > \int_a^b I_{jst}\,dx,$$

which is impossible. There must therefore exist some ζ, for which $I_j(\zeta) < I_{jst}$. Hence

$$I_{jstr} < I_{jstr \cdot st}.$$

Turning now to a study of the direct interrelation between different flows, we shall examine (1) with n = 2:

$$I_1 = L_{11}X_1 + L_{12}X_2,$$
$$I_2 = L_{21}X_1 + L_{22}X_2.$$

We assume that the selected flows and forces correspond to the equation

$$\sigma = I_1X_1 + I_2X_2.$$

Now let it be that the conducting system is removed from the equilibrium state by the action of some other factor. Let, for example $\varphi_1(a) \neq \varphi_1(b)$, while $\varphi_2(a) = \varphi_2(b)$ (see Eq. (2)). In accordance with this, we shall call I_1 the main flux, and I_2 the secondary flux. We represent the main flux in the form

$$I_1 = (L_{11} - L_{12}L_{21}/L_{22})X_1 + (L_{12}/L_{22})I_2. \qquad (6)$$

Here, L_{12}/L_{22} is the value of flux I_1 transported by unit flux of I_2 in excess of the value created directly by force X_1. If we have a discrete system, $X_2 = f_2[\varphi_2(b) - \varphi_2(a)] = 0$. In the case of a continuous system, according to the Rolle theorem, there also exists a section at which $X_2 = 0$.

When $X_2 = 0$, the directions of I_1 and I_2 coincide if $L_{11}L_{21} > 0$, and they are opposite, if $L_{11}L_{21} < 0$. According to the Onsager reciprocal relation, $L_{21} = L_{12}$. Therefore $L_{11}L_{21} = L_{11}L_{22}\frac{L_{12}}{L_{22}}$. But $L_{11}L_{21} > 0$, and the sign of $L_{11}L_{21}$ is determined by that of L_{12}/L_{22}. Hence the secondary flux I_2 always has a direction such that the contribution it makes to Eq. (6) increases the main flux I_1.

This phenomenological rule is applicable in different cases, independently of their molecular-kinetic nature. It expresses generally what is characteristic for the interrelation of any inhomogeneous processes. If the flows are dependent, i.e., $I_2 = f(I_1)$, then the result obtained is trivial. The cases are more interesting when the flows are not connected by the above functional relation. As an example of this kind we shall examine thermal osmosis—the percolation of a gas through rubber membrane due to a temperature difference [2].

Since the thermostats which maintain the temperature difference may be changed by energy only in the form of heat, it is convenient to choose, as Prigogine [3] has done, a system of forces and flows such that

$$I_1 = I_e - HI_m, \quad I_2 = I_m,$$
$$X_1 = -\Delta T/T^2, \quad X_2 = -V\Delta P/T.$$

By maintaining the same pressure at different temperatures on the two sides of the membrane, we achieve the condition

$$X_2 = -V\Delta P/T = 0, \; X_1 = -\Delta T/T^2 = \text{const} \neq 0.$$

Then I_1 will represent (to an accuracy up to $I_2\Delta H$) the heat flow from the hot thermostat to the cold one, while $L_{12}/L_{22} = Q^*$ is the so-called heat of transport [2, 3].

The conditions for which the phenomenological rule was formulated are satisfied, and we may draw the following conclusion. Whatever may be the direction of the flow of matter—from the cold side of the membrane to the hot side, or vice versa—this flow, by its appearance, always increases the transfer of heat from the hot reservoir to the cold one.

Thermal osmosis may also be observed under other conditions by permitting change of the boundary values of pressure for the system. This is obtained if two closed vessels filled with gas are joined by means of a membrane and different temperatures are maintained in them. The flow of matter will gradually decrease, but at any instant of time its direction corresponds to the above rule.

The same result is obtained for cyclic thermal osmosis. In order to observe this phenomenon, the above-mentioned vessels must be joined in two places by membranes to which correspond different heats of transport, Q_1^* and Q_2^*. Then a cyclic mass flow is created, which will exist as long as the temperature difference is maintained. Independently of the signs of Q_1^* and Q_2^*, the mass flow arises in a direction such as to increase the heat flow from the hot thermostat to the cold one.

From this point of view, it is interesting to compare cyclic thermal osmosis and the thermoelectric effect. The two phenomena are outwardly and fundamentally similar.

It is known that if the junction of two different metals is maintained at different temperatures, a flow of electricity is created in addition to the flow of heat. Due to the Peltier effect, heat is liberated at one junction and absorbed at the other. The current flows in such a direction that heat is absorbed in the hot junction and liberated at the cold one. In other words, the phenomenon of the electric current is associated with an increase of heat flow from the hot source to the cold.

Thus, if, under the action of some factor or other (in our examples a temperature difference), a conducting system is brought from an equilibrium state into a nonequilibrium stationary state, then a secondary process occurs and is directed in such a way as to increase the main process.

NOTATION

a, b are the coordinates of origin and end of one-dimensional conducting system; I_{jst} is the flux I_j in the stationary state; I_{jstr} is the through flux corresponding to I_j in the nonstationary state; I_e is the total energy flux; I_m is the mass flux expressed in moles; σ is a quantity describing the rate of entropy production; T is the temperature on one side of membrane; ΔT is the temperature difference between two sides of membrane, small in comparison with T; P, ΔP are the pressure and small pressure difference on two sides of membrane, respectively; V is the mole volume of gas at inlet side of membrane; H and ΔH are the molar enthalpy of gas at inlet side of membrane, and difference in molar enthalpies on two sides of membrane, respectively.

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