Non-Equilibrium Thermodynamics: Steady State Thermodynamic Relations in the Non-Linear Current-Affinity Region

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A simple heat conduction example is used to show that the choice of boundary conditions for describing a steady process, although of no consequence in the linear current-affinity region, governs the applicability (or the lack thereof) of various thermodynamic assertions to the non-linear current-affinity region. The need for a whole family of classificatory principles to aid us in organizing our knowledge about steady processes is pointed out.

Steady state non-equilibrium situations can be described in thermodynamic terms;[1] the rate of entropy production $\theta \equiv \dot{S}(\text{system}) + \dot{S}(\text{surroundings})$ normally plays a central role in such descriptions. By combined use of the First and Second Laws of thermodynamics it is always possible to resolve the rate of entropy production in a steady state into a set of *currents* Y_i and *affinities* Ω_i, with the currents being time derivatives of extensive thermodynamic variables:

$$\theta = \textstyle\sum_i Y_i \Omega_i \gtrsim 0. \tag{1}$$

In a neighborhood of a thermodynamic equilibrium state σ, we can express each current Y_i as a Taylor's series in the affinities Ω_j:

$$\begin{aligned} Y_i &= Y_i(\Omega_j, \sigma) \\ &= \textstyle\sum_j L_{ij}(\sigma)\Omega_j + 1/2\sum_{j,k} L_{ijk}(\sigma)\Omega_j\Omega_k + \cdots ; \end{aligned} \tag{2}$$

the coefficients are functions of the parameters describing the thermodynamic equilibrium state σ. If we stop with the linear terms in the expansion in Eq. (2), we define a *linear* current-affinity *neighborhood* of the thermodynamic reference state σ. In such a linear neighborhood of a reference state σ, many interesting theorems hold for situations not involving magnetic or centrifugal fields:[1-3]

a) The matrix of the coefficients L_{ij} is symmetric: $L_{ij}=L_{ji}$.

b) The determinant of the coefficients L_{ij} and all principal minors of that determinant are positive: $L_{ii}>0$, $L_{ii}L_{jj}-L_{ij}L_{ji}>0$ $(i \neq j), \cdots$.

c) For a given reference state σ and a set of affinities Ω_j and currents Y_j $(j \neq i)$, the following relations hold:

$$(\partial Y_i/\partial \Omega_i)_{\Omega_j,\sigma} \gtrsim (\partial Y_i/\partial \Omega_i)_{Y_j,\sigma} > 0.$$

d) For a given reference state σ and a constant set of affinities Ω_j $(j \neq i)$, the rate of entropy production has a minimum at the point $Y_i=0$;

$$0 = (\partial\theta/\partial Y_i)_{\Omega_j,\sigma}|_{Y_i=0}, \quad 0 < (\partial^2\theta/\partial Y_i^2)_{\Omega_j,\sigma}|_{Y_i=0}.$$

e) For any given expression involving only the rate of entropy production, the currents Y_i, and the affinities Ω_i (in any combination), consider whether the expression equals zero or does not equal zero—*i.e.*, consider the *mystic properties* (the vanishing or non-vanishing) of the expression. Generate from the given expression a *dual* expression by everywhere exchanging the roles of currents and affinities, and examine the mystic properties of the dual expression. In the linear neighborhood of a reference state σ, a given expression of the appropriate type and its dual expression have the same mystic properties.

Let

$$B_{ij}(\sigma) \equiv (\partial Y_i/\partial \Omega_j)_{\Omega',\sigma}, \quad D_{ij} \equiv (\partial Y_i/\partial \Omega_j)_{Y',\sigma},$$

$$(\delta/\tilde{\delta} Y_j)_{\Omega',\sigma} \equiv (\partial/\partial Y_j)_{\Omega',\sigma}|_{Y_j=0},$$

$$(\delta/\tilde{\delta}\Omega_j)_{Y',\sigma} \equiv (\partial/\partial\Omega_j)_{Y',\sigma}|_{\Omega_j=0},$$

where the subscript $\Omega'(Y')$ means constant $\Omega_k(Y_k)$ for each $k \neq j$. Then in the linear current-affinity neighborhood of σ, the relations a)—e) take the forms

$$B_{ij}(\sigma) = B_{ji}(\sigma), \tag{3}$$

$$B_{ii}(\sigma) > 0, \quad B_{ii}(\sigma)B_{jj}(\sigma) - B_{ij}(\sigma)B_{ji}(\sigma) > 0 \quad (i \neq j), \cdots, \tag{4}$$

$$B_{ii}(\sigma) \gtrsim D_{ii}(\sigma) > 0, \tag{5}$$

$$(\delta\theta/\tilde{\delta} Y_i)_{\Omega',\sigma}, \quad (\delta^2\theta/\tilde{\delta} Y_i^2)_{\Omega',\sigma} > 0, \tag{6a, b}$$

$$0 = (\delta\theta/\tilde{\delta} Y_i)_{\Omega',\sigma=0} \leftrightarrow (\delta\theta/\tilde{\delta}\Omega_i)_{Y',\sigma=0}, \text{ etc.} \tag{7}$$

The question of interest is; Are there any general relations of the form (3)—(7) that hold *outside* the linear current-affinity neighborhood of reference state σ?

I shall now describe a simple heat conduction example that yields non-linear current-affinity relations and which is particularly rich in counter-examples for relations of the type (3)—(7).

Heat Conduction Example

Stretch a homogeneous metallic wire between two heat reservoirs (thermostats) α, β; cut the wire at its mid point and let the two thereby exposed faces of the wire communicate with a thermostat (heat reservoir) x; insulate the wire so that there are no lateral heat losses. Consider the case of a wire of constant thermal conductivity κ, and choose the dimensions of the wire so that $2\text{ß}\kappa/\Lambda=1$, where Λ is the length and ß is the cross sectional area of the wire. Let $\dot{Q}_\alpha^{(r)}$, $\dot{Q}_\beta^{(r)}$, $\dot{Q}_x^{(r)}$ represent the rate of influx of heat into the appropriate reservoir (of temperature T_α, T_β, or T_x). In the steady state we have the following relations:

$$\dot{Q}_\alpha^{(r)} + \dot{Q}_\beta^{(r)} + \dot{Q}_x^{(r)} = 0, \tag{8}$$

1) R. J. Tykodi, "Thermodynamics of Steady States," The Macmillan Company, New York (1967).
2) S. de Groot, "Thermodynamics of Irreversible Processes," North-Holland Publishing Company, Amsterdam (1951).
3) I. Prigogine, "Introduction to the Thermodynamics of Irreversible Processes," John Wiley & Sons, New York (1968).

$$\dot{Q}_\alpha^{(r)} = T_x - T_\alpha, \quad \dot{Q}_\beta^{(r)} = T_x - T_\beta,$$

$$\dot{Q}_x^{(r)} = T_\alpha + T_\beta - 2T_x, \tag{9}$$

$$\theta = \dot{Q}_\alpha^{(r)}\left(\frac{1}{T_\alpha} - \frac{1}{T_x}\right) + \dot{Q}_\beta^{(r)}\left(\frac{1}{T_\beta} - \frac{1}{T_x}\right)$$

$$\equiv Y_1\Omega_1 + Y_2\Omega_2, \tag{10}$$

$$= \dot{Q}_\alpha^{(r)}\left(\frac{1}{T_\alpha} - \frac{1}{T_\beta}\right) + \dot{Q}_X^{(r)}\left(\frac{1}{T_X} - \frac{1}{T_\beta}\right)$$

$$\equiv y_1\omega_1 + y_2\omega_2. \tag{11}$$

For a given thermodynamic state σ the linear current-affinity neighborhood is infinitesimal; it is thus easy to investigate relations such as (3)—(7) in the non-linear current-affinity region. By way of example, note that at constant T_β (let the state at β play the role of a reference state σ, *i.e.*, $\sigma=\beta$)

$$\dot{Q}_\alpha^{(r)} = Y_1 = Y_1(\Omega_1, \Omega_2, \sigma) = T_x - T_\alpha$$
$$= T_\beta(1 - T_\beta\Omega_2)^{-1} - T_\beta(1 + T_\beta\Omega_1 - T_\beta\Omega_2)^{-1}$$
$$= T_\beta\{T_\beta\Omega_1 - (T_\beta\Omega_1)^2 + 2T_\beta{}^2\Omega_1\Omega_2 + (T_\beta\Omega_1)^3 + \cdots\}. \tag{12}$$

Let us now check the validity of relations (3)—(7) in the non-linear current-affinity region for various choices of reference state σ: $\sigma=\alpha$, β, x; a subscript σ in an equation means that the thermodynamic state at σ is being held constant, *i.e.*, subscript σ means constant T_σ.

Relations (3). The validity of relations (3) varies with the choice of reference state σ; thus (*e.g.*)

$$B_{12}(x) = B_{21}(x) = 0, \quad b_{12}(x) = b_{21}(x) = -T_\alpha{}^2, \tag{13}$$

but

$$B_{12}(\beta) \neq B_{21}(\beta), \quad b_{12}(\beta) \neq b_{21}(\beta), \tag{14}$$

except in the limit $T_\alpha \to T_\beta$, $T_x \to T_\beta$. (The upper and lower case convention introduced in Eqs. (10) and (11) applies throughout the paper.)

Relations (4). Relations (4) remain valid for either choice of currents and affinities—Eq. (10) or (11)—and for all choices of reference state.

Relations (5). The validity of relations (5) varies with the choice of reference state; thus (*e.g.*)

$$B_{ii}(\sigma) = D_{ii}(\sigma) > 0, \quad \sigma = \alpha, \beta, x, \quad i = 1, 2 \tag{15}$$

and

$$b_{11}(\beta) > d_{11}(\beta) > 0, \tag{16}$$

but

$$b_{11}(\alpha) = T_x{}^2, \quad d_{11}(\alpha) = T_\beta{}^2/2. \tag{17}$$

There is, consequently, no necessary ordering relation between $b_{11}(\alpha)$ and $d_{11}(\alpha)$, except in the limit $T_x \to T_\alpha$, $T_\beta \to T_\alpha$.

Relations (6). The relations

$$(\partial^2\theta/\partial Y_i{}^2)_{\Omega',\sigma} > 0, \quad (\partial^2\theta/\partial y_i{}^2)_{\omega',\sigma} > 0,$$
$$\sigma = \alpha, \beta, x, \quad i = 1, 2, \tag{18}$$

hold for all choices of reference state, but the validity of the relations

$$(\delta\theta/\tilde{\delta}Y_i)_{\Omega',\sigma} = 0, \quad (\delta\theta/\tilde{\delta}y_i)_{\omega',\sigma} = 0$$

varies with the choice of reference state; thus (*e.g.*)

$$(\delta\theta/\tilde{\delta}Y_1)_{\Omega_2,\beta} = 0, \quad (\delta\theta/\tilde{\delta}y_1)_{\omega_2,\beta} = 0, \tag{19}$$

but

$$(\delta\theta/\tilde{\delta}Y_1)_{\Omega_2,\alpha} \neq 0, \quad (\delta\theta/\tilde{\delta}y_1)_{\omega_2,\alpha} \neq 0, \tag{20}$$

and

$$(\delta\theta/\tilde{\delta}y_2)_{\omega_1,\sigma} \neq 0 \quad \sigma = \alpha, \beta, x, \tag{21}$$

except in the appropriate limit.

Relations (7). A given expression and its dual expression need not have the same mystic properties outside the linear current-affinity region; thus (*e.g.*)

$$(\delta\theta/\tilde{\delta}y_1)_{\omega_2,x} = 0 \text{ and } (\delta\theta/\tilde{\delta}\omega_1)_{y_2,x} = 0, \tag{22}$$

$$(\delta\theta/\tilde{\delta}y_2)_{\omega_1,\beta} \neq 0 \text{ and } (\delta\theta/\tilde{\delta}\omega_2)_{y_1,\beta} \neq 0, \tag{23}$$

but

$$(\delta\theta/\tilde{\delta}y_1)_{\omega_2,\beta} = 0 \text{ whereas } (\delta\theta/\tilde{\delta}\omega_1)_{y_2,\beta} \neq 0, \tag{24}$$

$$(\delta\theta/\tilde{\delta}y_2)_{\omega_1,\alpha} \neq 0 \text{ whereas } (\delta\theta/\tilde{\delta}\omega_2)_{y_1,\alpha} = 0, \tag{25}$$

except, of course, in the appropriate limit.

Observations

The relations (3)—(7) form an interrelated, compact set in the linear neighborhood of any arbitrary thermodynamic reference state σ. As we move outside the linear current-affinity region, we find that relations (4) and (6b) remain generally valid, but that the other relations become sensitive to the choice of reference state and cannot be counted on to remain valid for any arbitrary choice of reference state. Outside the linear current-affinity region, then, we can expect to find [with the exception of relations (4) and (6b)] only a series of special thermodynamic relations, relations that hold only for special choices of current-affinity representation and for special sets of reference states. We are thus faced with the task of categorizing steady states in such a way that we can immediately tell which of relations (3)—(7) is applicable to a given situation.

Consider, for example, the following situation: for an arbitrary reference state σ and fixed affinities Ω_j $(j \neq k)$ make a plot of θ *versus* Y_k; such a plot will always be concave upward—relation (6b)— and will always show a minimum. Now, start from an equilibrium configuration, the entire system being in state σ, and make θ *vs.* Y_k plots for various choices of the affinities Ω_j, moving (with each successive plot) farther and farther away from reference state σ. Let us examine the locus of the minima in the θ *vs.* Y_k plots as we move away from the equilibrium state; we observe one of two patterns: i) either the locus of the minima lies on the line $Y_k=0$ (Fig. 1), or ii) the locus of the minima lies off the line $Y_k=0$ (Fig. 2). We can accordingly categorize steady state situations by noting whether they follow the pattern of Fig. 1 or whether they follow that of Fig. 2—the thermoelectric effect[1] (*e.g.*), with Y_k being the electric current, follows the Fig. 1 pattern, whereas our heat conduction example, with $Y_k=\dot{Q}_x^{(r)}$ [Eq. (21)], follows the Fig. 2 pattern. What we would very much like to have is a criterion for recognizing a Fig. 1 situation *without* actually having to compute θ as a function of Y_k.

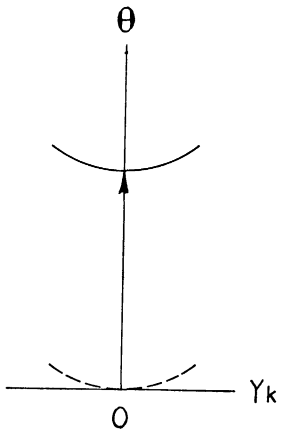

Fig. 1

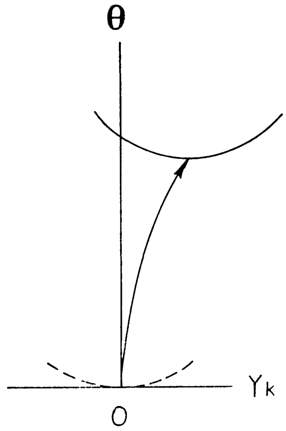

Fig. 2

A fruitful field for further effort, then, is the search for classificatory principles, *a la* Mendeleeff, for steady state situations so that we can treat such situations in groups according to their thermodynamic deserts.

Appendix

In this appendix I offer a tentative criterion for a situation of the Fig. 1 type. From the various steady-state currents Y_k, I single out a class of *conservative currents* Y_k^*: a conservative current (i) flows in a closed loop or (ii) flows from a source (χ) to a sink (ψ) without loss or branching, *i.e.* $Y_k^*(\chi)+Y_k^*(\psi)=0$, or (iii) is the rate of change of the degree of reaction variable ($\dot{\xi}$) for a chemical reaction. In considering the flow of a given current, I single out a class of *associated fundamental reference states* σ^*: an associated fundamental reference state for a current Y_k is a reference state such that the condition of constant Ω', σ implies that all the intensive variables in each Ω' are kept constant. To illustrate these ideas in terms of the heat conduction example of this paper, note that none of the currents $\dot{Q}_\alpha^{(r)}$, $\dot{Q}_\beta^{(r)}$, $\dot{Q}_x^{(r)}$ are conservative currents since they satisfy the three-term relation (8) instead of the two-term relation [(ii) above] required of a conservative current. Note also that in Eq. (10) with respect to current Y_1 reference state x is an associated fundamental reference state since constant Ω_2, x implies constant T_β, T_x; on the other hand reference state α is not an associated fundamental reference state for Y_1 since constant Ω_2, α implies only that the combination $T_\beta^{-1}-T_x^{-1}$ is to remain constant whereas the separate temperatures T_β, T_x may change.

The criterion that I tentatively propose is the following: A situation involving both a conservative current Y_k^* and an associated fundamental reference state σ^* follows the pattern of Fig. 1, *i.e.*

$$(\delta\theta/\tilde{\delta} Y_k^*)_{\Omega',\sigma^*} = 0. \tag{26}$$

Of the four possible combinations of current type (Y_k^* or Y_k) and reference state type (σ^* or σ)—$(\delta\theta/\tilde{\delta} Y_k^*)_{\Omega',\sigma^*}$, $(\delta\theta/\tilde{\delta} Y_k^*)_{\Omega',\sigma}$, $(\delta\theta/\tilde{\delta} Y_k)_{\Omega',\sigma^*}$, $(\delta\theta/\tilde{\delta} Y_k)_{\Omega',\sigma}$—we know that each of the four expressions vanishes in a linear neighborhood of the appropriate thermodynamic reference state; I am now suggesting that it is only the Y_k^*,σ^* combination that unfailingly continues to vanish outside the appropriate linear neighborhood.

In considering the behavior of θ as a current Y_k vanishes, let the residual currents (the non-vanishing currents) be indicated by Y_ι. If any of the Y_ι are mass currents involving sensible amounts of kinetic energy, it is generally impossible to find an associated fundamental reference state σ^* for the vanishing current Y_k. This observation means that relation (26) can only be tested in the case of a vanishing current (Y_ι) of mass or electricity or chemical reaction ($\dot{\xi}$) in the presence of a residual current (or currents) Y_ι of heat or electricity. The various steady-state non-equilibrium effects that could conceivably meet the requirements of Eq. (26) are some of the electrokinetic effects, the thermomolecular pressure effect, thermoösmosis, thermal diffusion, thermoelectricity, and effects involving a stationary chemical reaction ($\dot{\xi}=0$) in the presence of residual flows of heat or electricity; see Ref. 1 for a full discussion of these non-equilibrium effects.