

NONLINEAR TRANSFER EQUATIONS

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* The transfer between two thermodynamic systems consists of two unilateral flows, each originating in one of the systems and depending on the thermodynamic state of that system alone. Reciprocity is expressed by the fact that these unilateral flows are derivatives of some function *K* of the conjugate forces.

Consider a system Σ composed of subsystems Σ^I . Each Σ^I is in equilibrium and has therefore an entropy S . Although Σ need not be in equilibrium, it has an entropy $S = \sum_I S^I$.

As variables A_ν we choose *conserved extensive* quantities, like the energy ($\nu = 0$) and particle numbers. Their values in each Σ^I are a_ν^I . These values uniquely determine the equilibrium or thermodynamic state; in particular $S^I = S^I(a_0^I, a_1^I, \dots)$.

Any pair of subsystems may be in such contact as to permit transfer of one or more A_ν . A net transfer ΔA_ν from Σ^S to Σ^I increases the total entropy by

$$\Delta S = \sum_\nu \left(\frac{\partial S^I}{\partial a_\nu^I} - \frac{\partial S^S}{\partial a_\nu^S} \right) \Delta A_\nu = \sum_\nu \{X_\nu^I - X_\nu^S\} \Delta A_\nu.$$

When $X_\nu^I - X_\nu^S = 0$ (for all ν) the two subsystems are in equilibrium with each other.

We assume that transfer results from a sequence of "elementary transfer events". Each event originates in one subsystem Σ^S and carries definite amounts of several A_ν into the receiving subsystem Σ^I . For example, take two volumes filled with a dilute gas and connected by a small aperture: each passage of a gas molecule through the aperture is an elementary event transferring the mass and the energy of that molecule.

The probability per unit time for an event to take place is assumed to be determined by the thermodynamic state of the source system Σ^S alone (and by the nature of the contact with Σ^I , but not by the state of Σ^I). Hence the rate equation for the transport process has the form

$$\begin{aligned} \dot{a}_\nu^S &= -f_\nu^{IS}(a_0^S, a_1^S, \dots) + f_\nu^{SI}(a_0^I, a_1^I, \dots) \\ &= -\dot{a}_\nu^I. \end{aligned}$$

The intensive quantities X_ν defined in the third paragraph are functions of the a_ν and form therefore an alternative specification of the thermodynamic state. Hence

$$\dot{a}_\nu^S = -\dot{a}_\nu^I = -F_\nu^{IS}(X_0^S, X_1^S, \dots) + F_\nu^{SI}(X_0^I, X_1^I, \dots).$$

Detailed balance states that this expression must vanish in equilibrium regardless of the other subsystems,

$$F_\nu^{IS}(X^{eq}) = F_\nu^{SI}(X^{eq}).$$

In cases in which an equilibrium exists for all values X it follows that F_ν^{IS} and F_ν^{SI} are the same function.

Of all possible events originating in Σ^S take one specified by the amounts ΔA_ν it carries. In order for it to happen these amounts have to be concentrated on certain particles in a certain configuration. In the example of paragraph 4 the energy ΔA_0 has to be given to one molecule, which has to be located in a certain small volume in front of the aperture. That is, Σ^S is decomposed into two systems: one consists of the few molecules involved in the elementary transfer event; the other consists of all remaining molecules of Σ^S . The thermodynamic quantities of the latter system have the values $a_\nu^S - \Delta A_\nu$.

The probability for this to happen in unit time is proportional to that fraction of phase space of Σ^S in which this decomposition is realized. Let $\Omega(\Delta A) dt$ be the phase space in which the small system has to be located in order to create an event in the ensuing dt . Then that fraction is

$$\frac{\Omega(\Delta A) \exp\{S^S(a_0^S - \Delta A_0, a_1^S - \Delta A_1, \dots)\}}{\exp\{S^S(a_0^S, a_1^S, \dots)\}}$$

$$\Omega(\Delta A) \exp \left\{ - \sum_{\nu} X_{\nu}^s \Delta A_{\nu} \right\}.$$

It follows that the rate of change due to all possible events from Σ^s to Σ^T is

$$F_{\nu}(X^s) = \int \Delta A_{\nu} \Omega(\Delta A) \exp \left\{ - \sum_{\nu} X_{\nu}^s \Delta A_{\nu} \right\} d(\Delta A).$$

It is clear that this has the form of a gradient

$$F_{\nu}(X^s) = - \partial K(X^s) / \partial X_{\nu}^s,$$

$$K(X^s) = \int \Omega(\Delta A) \exp \left\{ - \sum_{\nu} X_{\nu}^s \Delta A_{\nu} \right\} d(\Delta A).$$

The integral extends over positive values of the transferred energy ΔA_0 and sums over the number of particles transferred in the various possible events.

The conclusion is that the evolution of the total system Σ is given in terms of a set of "unilateral flows" F_{ν}^{TS} (of A_{ν} from Σ^s into Σ^T) by the equations

$$\dot{a}_{\nu}^s = \sum_T \{ F_{\nu}^{ST}(X^T) - F_{\nu}^{TS}(X^s) \},$$

$$F_{\nu}^{TS}(X) = - \partial K^{TS}(X) / \partial X_{\nu}.$$

And if detailed balance holds for all X

$$K^{TS}(X) = K^{ST}(X).$$