COMPATIBILITY PROPERTY OF STEADY SYSTEMS

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The concept of compatibility of steady nonequilibrium systems, analogous to the equilibrium property in thermostatics, is examined. Compatibility parameters, which play the part of generalized intensive parameters for nonequilibrium steady systems, are introduced.

In thermostatics, a central role is played by the concept of the equilibrium of systems or the individual parts of a certain system.

For any form of equilibrium, the corresponding intensive quantities characterizing the systems (temperatures, pressures, chemical potentials, etc.) must be equal.

A necessary condition of any form of equilibrium is thermal equilibrium determined by equality of temperatures. A basic property of equilibrium is its transitivity.

In the theory of steady nonequilibrium systems, we encounter the concept of compatibility, which serves as a natural extension of the concept of equilibrium to the nonequilibrium region [1]. The concept of compatibility expresses the following property of steady systems: is there exists a means of bringing steady systems into contact and thereby creating the possibility of an exchange of certain extensive quantities without disturbing the macroscopic state, then such systems are called compatible. Like equilibrium, the compatibility property possesses transitivity: if there exists a means of creating interaction between systems A and B without disturbing their macroscopic state, and if such a property is also possessed by systems B and C, then systems A and C are also compatible. With reference to the following example, we show that the compatibility property of steady systems necessarily requires equality of the corresponding thermodynamic forces or, in other words [2], equality of the Lagrangian multipliers X_i introduced to take into account the additional conditions that the systems must satisfy. From the existence of intensive compatibility parameters, there directly follows the transitivity property of these parameters, which are physically measurable, macroscopic characteristics of the steady systems. Since, in the steady systems investigated, standard parameters are employed, one can judge the equality of the corresponding compatibility parameters on the basis of the principle of macroscopic invariance (with respect to compatibility).

Transition probabilities of a steady system. In [2, 3], the author and Karpov proposed a postulate for the statistical description of a steady nonequilibrium system according to which the behavior of the steady system essentially depends not only on the distribution function $\{p_i\}$ but also on the probabilities $\{p_{ij}\}$ of transition from state to state in unit time. An algorithm for determining the transition probabilities on the basis of known information about the system was also proposed. According to this algorithm, the transition probability matrix satisfying this information is found from an equation of the type

$$dH + \sum_{\alpha} X_\alpha dF_\alpha = 0, \tag{1}$$

where the entropy of evolution

$$H = -\sum_i \sum_j p_i p_{ij} \log p_{ij}$$

is related to the probability of the Markov chain trajectory in the discrete space of states $\{i\}$ by the relation

$$P = \exp(-sH), \tag{2}$$

where s is the length of the trajectory (number of transitions from state to state), and the number of trajectories with probability P is equal to exp(sH). In Eq. (1), F_1 are the generalized thermodynamic fluxes, and X_i are the generalized thermodynamic forces (Lagrangian multipliers).

When the information known about the system is exhausted by a knowledge of the two generalized fluxes:

average energy flux $F_1 = E$ $(X_1 = \lambda)$ (3)

and average heat flux $F_2 = Q$ $(X_2 = \mu)$, (4)

in the quasi-equilibrium approximation for a steady system interacting with two external factors (source and sink) that maintain the system in the nonequilibrium state, the probabilities of states p_i with energy ε_i and the probabilities of transition between states p_{ij} take the following form:

$$p_i = c\exp(-\lambda\varepsilon_i), \tag{5}$$

$$p_{ij} = c\exp(-\lambda\varepsilon_j), \tag{6}$$

$$a_{ij} = \frac{c}{2}[\exp(-\lambda\varepsilon_j)]\left[1 + \frac{\mu}{2}(\varepsilon_i - \varepsilon_j)\right], \tag{7}$$

$$b_{ij} = \frac{c}{2}[\exp(-\lambda\varepsilon_j)]\left[1 - \frac{\mu}{2}(\varepsilon_i - \varepsilon_j)\right], \tag{8}$$

where a_{ij} and b_{ij} are the partial transition probabilities of the system with respect to each of the external factors taken separately, and c is the normalization constant. In the quasi-equilibrium approximation, the entropy of evolution H differs from the ordinary entropy S by a small quantity of the second order, i.e.,

$$H = S + \mu Q. \quad (9)$$

Having obtained these necessary relations, we can make a closer examination of the mechanism of energy transport in the steady system. Let the system be in contact with two regions of constant temperature T_1 and T_2. If $T_1 = T_2$,

$$a_{ij} = b_{ij} = \frac{1}{2} p_{ij}.$$

If the temperatures are different, some probabilities decrease, while others increase, and the system will interact with each region differently. To be specific, let $\mu > 0$. (The relation between μ and the temperatures T_1 and T_2 is discussed below.) Then, from (7) and (8), the probabilities a_{ij} increase for $\varepsilon_j < \varepsilon_i$ and decrease for $\varepsilon_j > \varepsilon_i$, i.e., on the average, upon interaction with the first region, transitions to lower levels are more frequent, or on the average, the first region receives more energy than it gives up. Similarly, the probabilities b_{ij} increase for $\varepsilon_j > \varepsilon_i$ and decrease for $\varepsilon_j < \varepsilon_i$, so that, on the average, the second region gives up energy. The probabilities a_{ij} and b_{ij} are somehow balanced, and, in fact, from (5), (7), and (8), it is clear that

$$p_i a_{ij} = p_j b_{ji}, \quad (10)$$

which shows that the probability of a transition of the system in some direction under the influence of one factor is equal to the probability of a transition in the opposite direction under the influence of the other.

The detailed balance for the total conditional probabilities

$$p_i p_{ij} = p_j p_{ji} \quad (11)$$

also holds, but this is a direct consequence of the quasi-equilibrium nature of the approximation (5), (6). However, even a small deviation from equilibrium disturbs the transition balance for interaction with either of the external factors individually, i.e.,

$$p_i a_{ij} \neq p_j a_{ji}; \quad p_i b_{ij} \neq p_i b_{ji}, \quad (12)$$

which, in the last analysis, is also the cause of heat transport.

The detailed balance principle [4] asserts that to each forward process there corresponds a reverse process that follows the same path, and, in a state of thermodynamic equilibrium, the rates of the forward and reverse processes are equal. Hence, it follows that the steady state coincides with the state of thermodynamic equilibrium only if the forward and reverse processes follow the same path. Inequalities (12) explicitly assert that the forward and reverse processes follow different paths. Moreover, the detailed steady state expressed by the balance equations (10) establishes the method of maintaining the energy steady state of the system that is simplest for the simultaneous satisfaction of the energy balance between the source and the sink.

We now turn to an examination of the concept of compatibility.

If a vector flux is present in the systems, it is necessary to consider two types of interactions, parallel and series. In the first case, there is, on the average, no exchange between the systems, and the parameters of the flux type are additive. Then, despite the presence of interaction, by virtue of compatibility, the systems behave like independent systems, and the number of trajectories of the combined system may be assumed equal to the product of the numbers of trajectories of the individual systems,

$$\exp(sH) = \exp(sH_1)\exp(sH_2),$$

which implies the additivity of the entropies of evolution

$$H = H_1 + H_2. \quad (12')$$

Confining our attention, for simplicity, to the quasi-equilibrium approximation (9) for systems with a heat flux, we write the additivity conditions for the flux and ordinary entropy:

$$Q = Q_1 + Q_2,$$
$$S = S_1 + S_2. \quad (13)$$

Since in the approximation adopted, in accordance with (9),

$$H = -\mu Q + S; \; H_1 = -\mu_1 Q_1 + S_1; \; H_2 = -\mu_2 Q_2 + S_2, \quad (14)$$

from (12'), (13), and (14) there immediately follows the necessity that the compatibility parameters be equal:

$$\mu_1 = \mu_2 = \mu. \quad (15)$$

The fact that the interaction is sequential presupposes that the flux from one system passes through the other. This situation arises if we imagine a certain linear steady system divided into two subsystems at right angles to the flux. As an example, we consider a quasi-equilibrium system linked with two regions at slightly different temperatures T_1 and T_2.

Since, according to Klein [5],

$$p_{ij}\exp(-\varepsilon_i/kT) = p_{ji}\exp(-\varepsilon_j/kT), \quad (16)$$

in the case of a system interacting with two regions at the constant temperatures T_1 and T_2, for the corresponding transition probabilities a and b, we can write

$$a_{ij}\exp(-\varepsilon_i/kT_1) = a_{ji}\exp(-\varepsilon_j/kT_1), \quad (17)$$
$$b_{ij}\exp(-\varepsilon_i/kT_2) = b_{ji}\exp(-\varepsilon_j/kT_2). \quad (18)$$

Moreover, from (10)

$$p_i a_{ij} = p_j b_{ji}, \quad (19)$$
$$p_i b_{ij} = p_j a_{ji}, \quad (20)$$

whence,

$$\frac{a_{ij}}{b_{ij}} = \frac{b_{ji}}{a_{ji}}. \quad (21)$$

Dividing both sides of (17) by (18), term by term, we obtain

$$\frac{a_{ij}}{b_{ij}} \exp\left[-\varepsilon_i \Big/ \left(\frac{1}{kT_1} - \frac{1}{kT_2}\right)\right] = \frac{a_{ji}}{b_{ji}} \exp\left[-\varepsilon_j \Big/ \left(\frac{1}{kT_1} - \frac{1}{kT_2}\right)\right], \quad (22)$$

which, after using (21), gives

$$\frac{a_{ij}}{b_{ij}} = \exp\left[(\varepsilon_i - \varepsilon_j)\,\frac{T_2 - T_1}{2kT_1T_2}\right]. \qquad (23)$$

However, it follows from (7) and (8) that, in the quasi-equilibrium case in question, the conditions

$$\frac{a_{ij}}{b_{ij}} = \frac{1 + \frac{\mu}{2}(\varepsilon_i - \varepsilon_j)}{1 - \frac{\mu}{2}(\varepsilon_i - \varepsilon_j)} \cong \exp\left[\mu(\varepsilon_i - \varepsilon_j)\right] \qquad (24)$$

are satisfied correct to terms proportional to μ^2.

By equating (23) with (24), we immediately obtain an expression for the quasi-equilibrium compatibility parameter:

$$\mu = \frac{T_2 - T_1}{2kT_1T_2} \qquad (25)$$

or, adopting the local approach,

$$\mu = \frac{\Delta T}{kT^2}, \qquad (26)$$

where, by virtue of the quasi-equilibrium condition, we have introduced the average temperature $T = (T_1 + T_2)/2$ and $\Delta T = T_2 - T = T - T_1$. The physical significance of this parameter is that the local compatibility of steady quasi-equilibrium systems with a heat flux requires not only equality of the local temperatures (requirement of classical thermodynamics) but also equality of the temperature gradients at the interaction points.

Let us divide the system into two equal parts at right angles to the flux. Hence, the energy levels in the parts will be the same. Each subsystem is linked, on the one hand, with a region of constant temperature and, on the other, with a compatible steady system, which can in each case be replaced with a certain region of constant temperature T, while in both cases, by virtue of the transitivity of the compatibility property, this region must possess the same temperature T.

In fact, each subsystem plays the part of an external factor for the other, replacing the above-mentioned mutually compatible region at constant temperature T. According to (8) and (26), the probability of transition, under the influence of the region at T, for the subsystem also linked with a region at T_1 ($T_1 < T$), is equal to

$$b_{ij}^{(1)} = c\,\frac{\exp(-\varepsilon_j/kT)}{2}\left[1 - \frac{T - T_1}{2kT^2}(\varepsilon_i - \varepsilon_j)\right]. \qquad (27)$$

On the other hand, according to (7) and (26), the probability of transition, under the influence of the same region (T), for the subsystem also linked with the region at T_2 ($T_2 > T$), is

$$a_{ij}^{(2)} = c\,\frac{\exp(-\varepsilon_j/kT)}{2}\left[1 + \frac{T - T_2}{2kT^2}(\varepsilon_i - \varepsilon_j)\right]. \qquad (28)$$

Since the transition probabilities defined by (27) and (28) represent the interaction of identical systems with the same region of constant temperature, they must be equal:

$$a_{ij}^{(2)} = b_{ij}^{(1)}. \qquad (29)$$

Hence, there immediately follows that

$$-T + T_1 = T - T_2$$

or

$$T = \frac{T_1 + T_2}{2}, \qquad (30)$$

and

$$\mu_1 = \frac{\Delta T}{kT^2} = \mu_2, \qquad (31)$$

i. e., the compatibility parameters for serially compatible systems are also equal.

In conclusion, it should be noted that, in accordance with the above reasoning, when heat-conducting systems with different values of the compatibility parameter $\mu = \text{grad}\,T/kT^2$ interact, even if the local temperatures T are equal, there should be a macroscopically observable change in the state of the systems, i. e., changes associated with the flow of energy due to the difference in temperature gradients should take place in the local temperature distribution of the systems. This effect can not be described by the classical heat conduction equation based on Fourier's law, since, in the given case, the temperature difference is by definition equal to zero. On the other hand, from kinetic considerations, it is clear that if energy exchange is possible between two systems having nonidentical distribution functions differing slightly from the Maxwellian and the common parameter T, there should be a flow of energy affecting the value of the principal distribution parameter in both systems. In the case of nonlinear heat conduction, this nonclassical effect of a gradient-difference flow evidently occurs and is effectively described by the temperature dependent thermal conductivity, but is difficult to discriminate from the background of the heat flux associated with the difference of temperatures.

NOTATION

H is the entropy of evolution; X_i is the thermodynamic force; F_i is the thermodynamic flux; s is the length of the trajectory (number of steps); p_i is the probability of state i; p_{ij} is the conditional transition probability; ε_i is the energy of state i; a_{ij}, b_{ij} are the partial transition probabilities; S is the entropy; μ is the the compatibility parameter; c is the normalization constant.

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