DESCRIPTION OF STEADY TRANSPORT PROCESSES BY THE METHOD OF THE MOST PROBABLE PATH OF EVOLUTION

A. A. Filyukov and V. Ya. Karpov

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The method of the most probable path of evolution is applied to determine the stochastic matrix of transition probabilities under quasi-equilibrium conditions, as well as under conditions far removed from equilibrium.

The method of the most probable path of evolution describes nonequilibrium steady systems by means of stochastic models of discrete-time Markov processes. The essence of the method involves the following.

1. If the system is not in equilibrium and a steady flow has been established, the properties of the system are defined not only by the distribution function $\{p_i\}$, but by the conditional probabilities $\{p_{ij}\}$ of transition per unit time between the states.

2. The principal postulate of the thermokinetics of irreversible processes, generalizing the second law of thermodynamics, must necessarily contain the algorithm defining the transition probabilities on the basis of the information known about the system.

3. Based on considerations whose detailed coverage will be given separately, we derived the following formulation of the principal postulate: the stochastic matrix $\{p_{ij}\}$ of the conditional transition probabilities, satisfying all of the macroscopic conditions imposed on the system, in the steady state causes the entropy of evolution to pass to the maximum through the step

$$H = -\sum_i \sum_j p_i p_{ij} \log p_{ij}. \tag{1}$$

Hence it follows that the elements of the stochastic matrix can be determined by solving a variational equation of the form

$$\delta\left(H + \sum_i^k X_i F_i\right) = 0,$$

where k of the equation $F_i = 0$, $(i = 1 \ldots k)$ represents macroscopic conditions imposed on the system and X_i are the Lagrange multipliers introduced to take this information into consideration in the variation. The proposed postulate actually satisfies the principle of correspondence in the sense of degeneration to the second law of thermodynamics on transition to the equilibrium conditions.

Here we will consider solutions of the above-cited variational equation for a system with a steady flow of heat; separate consideration is given to the case of a small flow of heat, when the nonequilibrium system is close to the equilibrium position. This case has been well developed by the method of the thermodynamics of the quasi-equilibrium state [1], involving the use of linear phenomenological relationships between thermodynamic flows and forces. Within the framework of the present model, this last concept is easily generalized to the case of arbitrary deviations from the equilibrium state.

The entropy of evolution for a system with heat flow. Let the states of the system be the energy levels $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N$. Then p_i is the probability of having energy ε_i, p_{ij} is the probability of changing the energy ε_i to ε_j during the interval time τ. We will assume that the transitions between the levels occur under the influence of two factors (thermostats), with only one of these acting in each step, so that it is possible to trace the average transfer of energy from one thermostat to another and to use the result of this experiment in the form of a condition imposed on the system.

Let a_{ij} and b_{ij} denote the conditional probabilities of transition from level i to level j under the influence of the first and second factors, respectively. Here

$$a_{ij} + b_{ij} = p_{ij} \quad (i \neq j).$$

The probability of the sequence of states $i_0, i_1, i_2, \ldots, i_s$, where the transition $i_0 \to i_1$ is due to the first factor, the transition $i_1 \to i_2$ is due to the second factor, the transition $i_{s-1} \to i_s$ is equal to the first, etc., is equal to

$$p_{i_0} a_{i_0 i_1} b_{i_1 i_2} \ldots a_{i_{s-1} i_s},$$

and since the number of transitions with probability unity in sufficiently long sequences of states is proportional to the probability of these transitions, the probability of a sufficiently long sequence of states, according to the considerations covered in [2], is equal to $\exp(-sH_1)$, where s is the number of steps in the sequence, and H_1 is the entropy of the chain per interval,

$$H_1 = -\sum_{i \neq j}{}' p_i a_{ij} \log a_{ij} - \sum_{i \neq j}{}' p_i b_{ij} \log b_{ij} - \\ - \sum_i p_i p_{ii} \log p_{ii}, \qquad p_{ii} = 1 - \sum_{i \neq j}{}' p_{ij}. \tag{2}$$

The mean energy of this system is equal to

$$\langle E \rangle = \sum_i \varepsilon_i p_i. \tag{3}$$

Let us determine the mean flow of heat for the interval (the mean energy taken by the system from the first thermostat during the time of a single interval) according to the expression

$$\langle Q \rangle = \sum_i \sum_j p_i a_{ij} (\varepsilon_i - \varepsilon_j). \tag{4}$$

Of course, since the mean energy of the system remains constant, on the average as much heat is given off by the system to the second thermostat, i. e., in addition to (4)

$$\langle Q \rangle = -\sum_i \sum_j p_i b_{ij} (\varepsilon_i - \varepsilon_j).$$

At first glance, in the absence of an energy flux (in this case $a_{ij} = b_{ij} = p_{ij}/2$, since the thermostats are identical) expression (2) must change into (1); however, substituting the indicated values of a_{ij} and b_{ij} into (2), we obtain

$$H_1 = -\sum_i \sum_j p_i p_{ij} \log p_{ij} + (\log 2)\left(1 - \sum_i p_i p_{ii}\right),$$

so that $H_1 \neq H$. This is explained by the fact that instead of all of the trajectories of length s whose number is equal to $N^s \equiv \exp(s \log N)$, we need consider only the class of the "most probable" trajectories whose number for a sufficiently large s is equal to $\exp(sH_1)$, while the probability of each of the trajectories from this class is equal to $\exp(-sH_1)$. For a nonzero energy flux the trajectories of the system in the space of the states differ not only in terms of the original and final position of the system in this given step, but also in terms of the factor (first or second) responsible for this transition. In the absence of flow both factors must be regarded as fundamentally indistinguishable in view of the identity of the thermostats. Certain groups of trajectories in this case cease to be different and are thus reduced to a single trajectory.

If the trajectories of a system associated with two external factors are sufficiently long (for a length s the number of trajectories is $\exp(sH_1)$) with a reduction in the flow they will group into $\exp\left[\left(s - s\sum_i p_i p_{ii}\right)\log 2\right]$ trajectories, so that within their limits there will remain only $\exp\left[sH_1 - s(\log 2)\left(1 - \sum_i p_i p_{ii}\right)\right]$ and this number is, of course, equal to exp (sH).

The cited considerations demonstrate that with an energy flux different from zero and brought about by two distinct external factors, the entropy of the evolution for the interval reduces to the form

$$H = -\sum_{i \neq j}{}' \sum_j p_i a_{ij} \log a_{ij} - \sum_{i \neq j}{}' \sum_j p_i b_{ij} \log b_{ij} - \\ - \sum_i p_i p_{ii} \log p_{ii} - (\log 2)\left(1 - \sum_i p_i p_{ii}\right).$$

The probability of transition in linear approximation. We can now employ the principal postulate and determine the probability of transition, with consideration of additional conditions. Let us write the relationships to which the variables are subject:

1. By definition $a_{ij} + b_{ij} = p_{ij} \quad i \neq j$.
2. The standardization of the probabilities

$$\sum_i p_i = 1, \tag{5}$$

$$\sum_j p_{ii} = 1. \tag{6}$$

3. The condition for the steadiness of motion in the system

$$p_i = \sum_j p_j p_{ji}. \tag{7}$$

4. The results of experiments (3) and (4).

Let us rewrite the expression for the entropy in the form

$$H = -\sum_{i \neq j}{}' \sum_j p_i \left[a_{ij} \log a_{ij} + (p_{ij} - a_{ij}) \times \right. \\ \left. \times \log (p_{ij} - a_{ij})\right] - \sum_i p_i p_{ii} \log\left(\frac{1}{2} p_{ii}\right) - \log 2.$$

Since the probabilities a_{ij} pertain only to condition (4), we can maximize H relative to a_{ij} for fixed values of p_{ij}. Denoting the Lagrange multiplier by μ, we will seek the maximum with the parameters a_{ij}:

$$\frac{\partial}{\partial a_{kl}} (H + \mu Q) = 0,$$

which leads to the equation

$$-p_k \log a_{kl} - p_k + p_k \log (p_{kl} - a_{kl}) + \\ + p_k + \mu p_k (\varepsilon_k - \varepsilon_l) = 0,$$

whence

$$a_{kl} = \frac{p_{kl}}{1 + \exp[-\mu(\varepsilon_k - \varepsilon_l)]}.$$

Using the derived expression, we make the transformation

$$H = -\mu Q - \sum_i \sum_j p_i p_{ij} \times \\ \times \log\left[\frac{p_{ij}}{1 + \exp[-\mu(\varepsilon_i - \varepsilon_j)]}\right] - \log 2,$$

$$Q = \sum_i \sum_j p_i p_{ij} \frac{\varepsilon_i - \varepsilon_j}{1 + \exp[-\mu(\varepsilon_i - \varepsilon_j)]}. \tag{8}$$

Maximizing expression (8) for the entropy of evolution relative to the transition probabilities p_{ij} for conditions (3), (5), (6), and (7) leads to rather cumbersome expressions and it is therefore tentatively reasonable to limit ourselves to the case of a small flow of energy. Since when $Q = 0$ the factor μ vanishes, for small Q the factor μ is also small. Let us use the expansion in this parameter of smallness $\exp[-\mu(\varepsilon_i - \varepsilon_j)] \cong 1 - \mu(\varepsilon_i - \varepsilon_j)$. In this approximation

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

$$Q = \frac{1}{4} \mu \sum_i \sum_j p_i p_{ij} (\varepsilon_i - \varepsilon_j)^2,$$

i. e., the entropy of evolution differs from the equilibrium entropy only by the magnitude μQ of the second order of smallness, while the flow of heat is associated with its Lagrange factor μ by a linear relationship. The maximization is now accomplished easily, and specifically leads to the relationship

$$p_{ij} = p_j = \frac{\exp(-\varepsilon_j/kT)}{Z},$$

where T is the temperature of the system and Z is its (equilibrium) statistical sum. Thus, the formulated problem has been completely solved: the transition probabilities have been expressed in terms of the three parameters, Z, T, and μ, ensuring satisfaction of Eqs. (3), (4), and (5). The conditional probabilities of transition in the subject quasi-equilibrium case of a small flow of heat have the form

$$a_{ij} = \frac{\exp(-\varepsilon_j/kT)}{2Z}\left[1+\frac{\mu}{2}(\varepsilon_i-\varepsilon_j)\right],$$

$$b_{ij} = \frac{\exp(-\varepsilon_j/kT)}{2Z}\left[1-\frac{\mu}{2}(\varepsilon_i-\varepsilon_j)\right].$$

For the heat flow we obtain the final expression

$$Q = \frac{\mu}{2}\left[\sum_i p_i\varepsilon_i^2 - \left(\sum_i \varepsilon_i p_i\right)^2\right] = \frac{\mu}{2}kT^2C_V,$$

where C_V denotes the heat capacity of the system at constant volume.

The general case. With an arbitrary deviation from the equilibrium state, the procedure for the determination of the transition probabilities reduces to a variation of the entropy of evolution, taken in the form of (8), or using the denotation

$$d_{ij} = \frac{1+\exp[-\mu(\varepsilon_i-\varepsilon_j)]}{2} \tag{9}$$

in the form

$$H = -\mu Q - \sum_i\sum_j p_i p_{ij}\log\left(\frac{p_{ij}}{d_{ij}}\right) \tag{10}$$

for the additional conditions: α) $\sum_j p_{ij} = 1$, β) $\sum_i p_i\varepsilon_i = E$, γ) $\sum_i p_i = 1$, δ) $\sum_i p_i p_{ij} = p_j$.

The condition by means of which we take into consideration the information known about the heat flow Q had been used in an earlier stage of variation with respect to a_{ij} and has been included in the definition of the entropy of evolution in the form of the term μQ.

The first stage of the variation of H is carried out for fixed p_i for the variables p_{ij} for the conditions α) and δ) which were taken into consideration by the Lagrange multipliers $\alpha_i p_i$ and δ_j:

$$\frac{\partial}{\partial p_{kl}}\left(H + \sum_i \alpha_i p_i \sum_j p_{ij} + \sum_j \delta_j \sum_i p_i p_{ij}\right) = 0,$$

whence

$$-p_k\log\frac{p_{kl}}{d_{kl}} - p_k + \alpha_k p_k + \delta_l p_k = 0$$

or

$$p_{kl} = d_{kl}\exp[-1+\alpha_k+\delta_l], \tag{11}$$

where α_k and δ_l are defined from conditions α) and δ).

In the place of α_k and δ_l let us introduce the parameters ξ_k, and χ_l, i.e., instead of (11) let

$$p_{kl} = d_{kl}\,\xi_k\chi_l,$$

while the unknown parameters ξ_k and χ_l are defined by the relationships replacing α) and δ):

$$\sum_l d_{kl}\xi_k\chi_l = 1, \quad \sum_k p_k d_{kl}\xi_k\chi_l = p_l.$$

These can be symmetrized by introducing $\varphi_k = p_k\xi_k$. Then

$$\varphi_k \sum_l d_{kl}\chi_l = p_k, \tag{12}$$

$$\chi_l \sum_k d_{kl}\varphi_l = p_l. \tag{13}$$

In new denotations

$$p_k p_{kl} = d_{kl}\varphi_k\chi_l, \tag{14}$$

and substitution into (10) yields

$$H = -\mu Q - \sum_i\sum_j p_i p_{ij}\log\frac{\varphi_i\chi_j}{p_i} = -\mu Q -$$

$$-\sum_i p_i\left(\log\frac{\varphi_i}{p_i}\right)\sum_j p_{ij} - \sum_j(\log\chi_j)\sum_i p_i p_{ij} =$$

$$= -\mu Q - \sum_i p_i\log\frac{\varphi_i\chi_i}{p_i}. \tag{15}$$

The factor d_{kl} determines the existence of a detailed balance.

Let us examine the expressions following from definition (14):

$$p_k p_{kl} = d_{kl}\varphi_k\chi_l,$$

$$p_l p_{lk} = d_{lk}\varphi_l\chi_k.$$

If $d_{kl} = d_{lk}$, which is the case, according to (9), only when $\mu = 0$, Eqs. (12) and (13) transform to

$$\varphi_k\sum_l d_{kl}\chi_l = p_k, \quad \chi_k\sum_l d_{lk}\varphi_l = \chi_k\sum_l d_{kl}\varphi_l = p_k$$

from the obvious conclusion that in view of symmetry $\varphi_k = \chi_k$. Thus we immediately have satisfaction of the detailed balance

$$p_k p_{kl} = d_{kl}\varphi_k\chi_l = d_{lk}\chi_k\varphi_l = p_l p_{lk}.$$

The second stage of variation is carried out with respect to p_i with consideration of conditions β) and γ). The condition of the maximum

$$\frac{\partial}{\partial p_k}\left[H + (\gamma+1)\sum_i p_i + \beta\sum_i \varepsilon_i p_i\right] = 0$$

yields the relationship

$$-\log\frac{\varphi_k\chi_k}{p_k} - \sum_i\left(\frac{p_i}{\chi_i}\frac{\partial\chi_i}{\partial p_k} + \frac{p_i}{\varphi_i}\frac{\partial\varphi_i}{\partial p_k}\right) + \\ + \gamma + 2 + \beta\varepsilon_k = 0. \qquad (16)$$

To calculate the sum contained here we will use (12) and (13) which, after differentiation, yield

$$\frac{\partial\varphi_i}{\partial p_k}\sum_j d_{ij}\chi_j + \varphi_i\sum_j d_{ij}\frac{\partial\chi_j}{\partial p_k} = \delta_{ik},$$

$$\frac{\partial\chi_i}{\partial p_k}\sum_j d_{ji}\varphi_j + \chi_i\sum_j d_{ji}\frac{\partial\varphi_i}{\partial p_k} = \delta_{ik}.$$

Using (12) and (13) repeatedly, we obtain the value

$$\sum_i\left(\frac{p_i}{\chi_i}\frac{\partial\chi_i}{\partial p_k} + \frac{p_i}{\varphi_i}\frac{\partial\varphi_i}{\partial p_k}\right) =$$

$$= 2 - \sum_i\sum_j\left(\varphi_i d_{ij}\frac{\partial\chi_j}{\partial p_k} + \chi_i d_{ji}\frac{\partial\varphi_j}{\partial p_k}\right) =$$

$$= 2 - \frac{\partial}{\partial p_k}\sum_i\sum_j d_{ij}\varphi_i\chi_j = 2.$$

Thus from (16) we have the following final form of the state and transition probabilities:

$$p_k = \varphi_k\chi_k \exp(-\gamma - \beta\varepsilon_k)$$

$$p_{kl} = \frac{d_{kl}\chi_l}{\chi_k}\exp(\gamma + \beta\varepsilon_k), \qquad (17)$$

where φ_k and χ_l should be sought from the simultaneous solution of the system of equations (12), (13), α), β), which is possible only for specifically given energy spectra.

Substitution of distribution (17) into expression (15) for the entropy of evolution yields the final expression of the latter in terms of the macroscopic parameters

$$H = -\mu Q - \beta E - \gamma.$$

The contribution to the entropy of evolution by the thermokinetic term μQ here may be arbitrarily large in comparison with the "thermostatic residue," representing the thermokinetic analog of conventional entropy.

REFERENCES

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Institute of Applied Mathematics
AS USSR, Moscow