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

\[
H = - \sum_i \sum_j p_{ij} \log p_{ij}.
\] (1)

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

\[
\delta \left( H + \sum_i X_i F_i \right) = 0,
\]

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 \( \varepsilon_i \), \( p_{ij} \) is the probability of changing the energy \( \varepsilon_i \) to \( \varepsilon_j \) during the interval time \( \tau \). 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 \( i_0, i_1, i_2, \ldots, i_N \), where the transition \( i_0 \rightarrow i_1 \) is due to the first factor, the transition \( i_1 \rightarrow i_2 \) is due to the second factor, the transition \( i_{N-1} \rightarrow i_N \) is equal to the first, etc., is equal to

\[
p_{i_0} a_{i_0 i_1} b_{i_1 i_2} \cdots a_{i_{N-1} i_N}.
\]

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,

\[
H_1 = - \sum_i p_i a_{ii} \log a_{ii} - \sum_i p_i b_{ii} \log b_{ii} - \sum_i p_i \log p_i, \quad p_{ii} = 1 - \sum_j p_{ij}. \tag{2}
\]

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

\[
\langle Q \rangle = \sum_i \sum_j p_{ij} (\varepsilon_i - \varepsilon_j). \tag{4}
\]
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)

\[ \langle Q \rangle = -\sum_{i} \sum_{j} \rho_{ij} \delta(e_{i} - e_{j}). \]

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

\[ H_{1} = -\sum_{j} \sum_{i} \rho_{j} \rho_{ij} \log \rho_{ij} + (\log 2) \left( 1 - \sum_{i} \rho_{i} \rho_{ii} \right), \]

so that \( H_{1} = H \). This is explained by the fact that instead of all of the trajectories of length \( s \) whose number is equal to \( N^{s} = \exp(s \log N) \), we need consider only the class of the "most probable" trajectories whose number for a sufficiently large \( s \) is equal to \( \exp \left( sH_{1} \right) \), while the probability of each of the trajectories from this class is equal to \( \exp \left( -sH_{1} \right) \). For a non-zero 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 \( \exp \left( sH_{1} - s(\log 2) \left( 1 - \sum_{i} \rho_{i} \rho_{ii} \right) \right) \) trajectories, so that within their limits there will remain only \( \exp \left( sH_{1} - s(\log 2) \left( 1 - \sum_{i} \rho_{i} \rho_{ii} \right) \right) \) and this number is, of course, equal to \( \exp \left( sH_{1} \right) \).

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

\[ H = -\sum_{i} \sum_{j} \rho_{i} a_{ij} \log a_{ij} - \sum_{i} \sum_{j} \rho_{i} b_{ij} \log b_{ij} - \sum_{i} \rho_{i} \rho_{ii} \log \rho_{ii} - (\log 2) \left( 1 - \sum_{i} \rho_{i} \rho_{ii} \right). \]

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 \( a_{ij} + b_{ij} = \rho_{ij} \) \( i \neq j \).
2. The standardization of the probabilities

\[ \sum_{i} \rho_{i} = 1, \]

\[ \sum_{j} \rho_{ij} = 1. \]

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

\[ \rho_{i} = \sum_{j} \rho_{ij} \rho_{jj}. \]

4. The results of experiments (3) and (4). Let us rewrite the expression for the entropy in the form

\[ H = -\sum_{i} \sum_{j} \rho_{ij} \left[ a_{ij} \log a_{ij} + (b_{ij} - a_{ij}) \times \log (b_{ij} - a_{ij}) - \sum_{i} \rho_{i} \rho_{ii} \log \left( \frac{1}{2} \rho_{ii} \right) - \log 2 \right]. \]

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

\[ \frac{\partial}{\partial a_{ij}} (H + \mu Q) = 0, \]

which leads to the equation

\[ -\rho_{k} \log a_{kl} - \rho_{h} + \rho_{h} \log (\rho_{hl} - a_{kl}) + \rho_{h} + \mu \rho_{h} (e_{k} - e_{l}) = 0, \]

whence

\[ a_{kl} = \frac{\rho_{hl}}{1 + \exp \left( -\mu (e_{k} - e_{l}) \right)}. \]

Using the derived expression, we make the transformation

\[ H = -\mu Q - \sum_{i} \sum_{j} \rho_{ij} \times \log \left( \frac{\rho_{ij}}{1 + \exp \left( -\mu (e_{i} - e_{j}) \right)} \right) - \log 2, \]

\[ Q = \sum_{i} \sum_{j} \rho_{ij} \frac{e_{i} - e_{j}}{1 + \exp \left( -\mu (e_{i} - e_{j}) \right)}. \]

Maximizing expression (8) for the entropy of evolution relative to the transition probabilities \( \rho_{ij} \) 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 \( \mu \) vanishes, for small \( Q \) the factor \( \mu \) is also small. Let us use the expansion in this parameter of smallness \( \exp \left( -\mu (e_{i} - e_{j}) \right) \approx 1 - \mu (e_{i} - e_{j}) \). In this approximation

\[ H = -\mu Q - \sum_{i} \sum_{j} \rho_{ij} \log \rho_{ij}, \]

\[ Q = \frac{1}{4} \mu \sum_{i} \sum_{j} \rho_{ij} (e_{i} - e_{j})^{2}, \]

i.e., the entropy of evolution differs from the equilibrium entropy only by the magnitude \( \mu Q \) of the second order of smallness, while the flow of heat is associated with its Lagrange factor \( \mu \) by a linear relation-