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On the kinetics of entropy of a system with discrete microscopic states

I. G. Minkevich

G. K. Skryabin Institute of Biochemistry and Physiology of Microorganisms, FRC Pushchino Centre for Biological Research, Russian Academy of Sciences,
Pushchino, Moscow Region, 142290, Russia

E-mail: minkevich@pbcras.ru

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An isolated system, which possesses a discrete set of microscopic states, is considered. The system performs spontaneous random transitions between the microstates. Kinetic equations for the probabilities of the system staying in various microstates are formulated. A general dimensionless expression for entropy of such a system, which depends on the probability distribution, is considered. Two problems are stated: 1) to study the effect of possible unequal probabilities of different microstates, in particular, when the system is in its internal equilibrium, on the system entropy value, and 2) to study the kinetics of microstate probability distribution and entropy evolution of the system in nonequilibrium states. The kinetics for the rates of transitions between the microstates is assumed to be first-order. Two variants of the effects of possible nonequiprobability of the microstates are considered: i) the microstates form two subgroups the probabilities of which are similar within each subgroup but differ between the subgroups, and ii) the microstate probabilities vary arbitrarily around the point at which they are all equal. It is found that, under a fixed total number of microstates, the deviations of entropy from the value corresponding to the equiprobable microstate distribution are extremely small. The latter is a rigorous substantiation of the known hypothesis about the equiprobability of microstates under the thermodynamic equilibrium. On the other hand, based on several characteristic examples, it is shown that the structure of random transitions between the microstates exerts a considerable effect on the rate and mode of the establishment of the system internal equilibrium, on entropy time dependence and expression of the entropy production rate. Under definite schemes of these transitions, there are possibilities of fast and slow components in the transients and of the existence of transients in the form of damped oscillations. The condition of universality and stability of equilibrium microstate distribution is that for any pair of microstates, a sequence of transitions should exist, which provides the passage from one microstate to next, and, consequently, any microstate traps should be absent.

Keywords: thermodynamics, microscopic states, random transitions, probability distribution, kinetic equations, entropy, equilibrium state, transients

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МОДЕЛИ В ФИЗИКЕ И ТЕХНОЛОГИИ

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К кинетике энтропии системы с дискретными микроскопическими состояниями

И. Г. Минкевич

Институт биохимии и физиологии микроорганизмов им. Г. К. Скрябина РАН,
ФИЦ «Пущинский научный центр биологических исследований РАН»,
Россия, 142290, Московская область, г. Пущино, пр. Науки, д. 5

E-mail: minkevich@pbcras.ru

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Рассматривается изолированная система, обладающая дискретным множеством микроскопических состояний, которая совершает спонтанные случайные переходы между микросостояниями. Сформулированы кинетические уравнения для совокупности вероятностей пребывания системы в различных микросостояниях. Рассмотрено общее безразмерное выражение для энтропии такой системы, зависящее от распределения этих вероятностей. Поставлены две задачи: 1) изучить влияние возможной неравновероятности микроскопических состояний системы, в том числе в состоянии ее общего равновесия, на величину ее энтропии; 2) изучить кинетику изменения энтропии в неравновесном состоянии системы. Для скоростей переходов между микросостояниями принята кинетика первого порядка. Влияние возможной неравновероятности микросостояний системы рассмотрено в двух вариантах: а) микросостояния образуют две подгруппы с вероятностями, одинаковыми внутри каждой подгруппы, но отличающимися по величине между подгруппами; б) вероятности микросостояний произвольно варьируют вблизи точки, где они равны одной и той же величине. Показано, что, когда общее число микросостояний фиксировано, отклонения энтропии от значения, соответствующего равновероятному распределению по микросостояниям, крайне малы, что дает строгое обоснование известной гипотезы о равновероятности микросостояний при термодинамическом равновесии. С другой стороны, на нескольких характерных примерах показано, что структура случайных переходов между микросостояниями оказывает большое влияние на скорость и характер установления внутреннего равновесия системы, на временную зависимость энтропии и на выражение для скорости продукции энтропии. При определенных схемах этих переходов возможно наличие быстрых и медленных компонент в переходных процессах и существование этих процессов в виде затухающих колебаний. Условием универсальности и устойчивости равновесного распределения является то, что для любой пары микросостояний должны существовать последовательность переходов из одного в другое и, соответственно, отсутствие состояний-«ловушек».

Ключевые слова: термодинамика, микроскопические состояния, случайные переходы, распределение вероятностей, кинетические уравнения, энтропия, равновесное состояние, переходные процессы

Introduction

Entropy is an integral index describing the variation of the macroscopic state of a multicomponent system. In particular, it is used in thermodynamics as a separate quantity and as a term in expressions of other thermodynamic quantities widely used in descriptions of physicochemical and biological processes. A well-known property of entropy is its tendency to a maximal value, which is achieved when an isolated system in the course of time achieves internal equilibrium. In a phenomenological statement of thermodynamics, this property is considered as a basic experimental fact without any analysis of its reasons. In statistical thermodynamics, which deals with objects described by classical or quantum mechanics, the entropy is considered based on the dynamics of an object's microscopic states.

A problem inherent in all approaches used is substantiation of mechanisms resulting in an increase of entropy and its tendency to a maximal value in the case of an isolated system. Besides, the equiprobable distribution of microscopic states is always assumed for the state of thermodynamic equilibrium and corresponding entropy value of an isolated system [Balescu, 1975; Kittel, Kroemer, 1980; Landau, Lifshits, 1995; Sethna, 2006; Huang, 2010; Sekerka, 2015; Reichl, 2016; Nolting, 2018; Sadovskii, 2019; Hoch, 2021; Kennett, 2021; Müller-Kirsten, 2022]. In this connection, the following questions are of interest: 1) an effect of a possible nonequiprobability of microstates on the value of isolated system entropy, and 2) an effect of differences in the general structure of transitions between the microstates on the evolution of microstate probability distribution and the entropy value in time.

The present work is devoted to the study of these questions.

Formulation and the general properties of the model

The work considers the objects, which possess discrete sets of microscopic states (e. g., quantum mechanical many-particle systems). Transitions between the microstates are randomly spontaneous. Staying of the system in one microstate or another is a random event described by its probability. The total state of the system at any point of time is described by the distribution of these probabilities. In the stationary state of the whole system this distribution is independent of time. In transient processes, the aggregate of the above-mentioned probabilities depends on time.

An isolated system of magnetic dipoles in a constant external magnetic field may be taken as an example [Kittel, Kroemer, 1980; Hoch, 2021; Kennett, 2021]. A part of magnetic moments of the dipoles is oriented along the direction of the external field, the remaining magnetic moments are opposite. Because of its isolation the system has a fixed total energy value, which depends on the number of dipoles oriented against the field. The exchange between two differently directed dipoles consists in the change of both magnetic moment directions to the opposite. It means the transition of the whole system from one microstate to another, the system energy being invariable. Generally, a random transition from one microstate to another in this example is the exchange between some number of randomly selected dipoles directed against the external field and the same number of randomly selected dipoles "looking" in the opposite direction. Let N be the total number of the dipoles, n of which have moments oriented against the external field. Then, the number of various microstates of the magnetic dipole system, when N and n are fixed, equals C_n^N — the number of n combinations of an N-set.

In a general case we enumerate the system microstates by an index l and denote their total quantity as L. It should be emphasized that it is the *number of microstates* that we consider here. Its relation to the number of material particles that make up the system is not considered in the general analysis described.

Let $P(l, t)$ be the probability of the system staying in the lth microstate at time t. To derive the kinetic equations for $P(l, t)$ we apply the approach used for derivation of Poisson distribution in the case of radioactive decay [Hudson, 1964] and shot noise [Davenport, Root, 1987].

Let us introduce a set of quantities $\alpha_{l,\bar l}$, which are the specific rates of spontaneous random transitions from an lth microstate to an $\bar l$th one, where $\bar l \neq l$. We accept the following rule: the first index relates to a microstate, which the system leaves, and the second, to the microstate at which the system arrives. All $\alpha_{l,\bar l}$ are nonnegative in value. The rates above are constants [Sokolov, Ternov, Zhukovsky, 1979; Fermi, 1995; Svelto, 2010].

The kinetic equations for all the probabilities $P(l, t)$ are as follows:

$$\frac{dP(l, t)}{dt} = -\left(\sum_{\bar l\neq l}\alpha_{l,\bar l}\right)P(l, t) + \sum_{\bar l\neq l}\alpha_{\bar l,l}P(\bar l, t), \quad l = 1 \div L, \quad \bar l = 1 \div L, \tag{1}$$

where the first term of the right-hand side describes the system transition from the microstate l to any other with the summary specific rate $\left(-\sum\limits_{\bar l\neq l}\alpha_{l,\bar l}\right) < 0$, and the second one describes the arrival of the system at the lth microstate from all the remaining microstates.

The system of equations (1) in standard form is written as

$$\frac{dP(l, t)}{dt} = \sum_{\bar l=1}^{L} r_{l,\bar l}P(\bar l, t), \quad l = 1 \div L, \tag{2}$$

where $r_{l,\bar l}$ is a matrix of specific rates of $P(l, t)$ change. Here $r_{l,\bar l} = \alpha_{\bar l,l}$ $(\bar l \neq l)$, $r_{l,l} = -\sum\limits_{\bar l\neq l}\alpha_{l,\bar l}$.

Let us show that the sum of probabilities of the system staying in all the microstates is invariable. Summation of all Eqs. (1) by l gives

$$\frac{d}{dt}\sum_{l=1}^{L}P(l, t) = -\sum_{l=1}^{L}\left(\sum_{\bar l\neq l}\alpha_{l,\bar l}\right)P(l, t) + \sum_{l=1}^{L}\sum_{\bar l\neq l}\alpha_{\bar l,l}P(\bar l, t).$$

Since the summation is done by both indices, we may interchange denotations $\bar l$ and l in the first right-hand side term, due to which it turns to $\sum\limits_{\bar l=1}^{L}\sum\limits_{l\neq\bar l}\alpha_{\bar l,l}P(\bar l, t)$. Thus, both summands of the right-hand side contain identical expressions under the double sums. They differ only by the order of summation and by the fact that the case $l = \bar l$ in both terms is excluded from the sums by different indices. This results in $\frac{d}{dt}\sum\limits_{l=1}^{L}P(l, t) = 0$, and $\sum\limits_{l=1}^{L}P(l, t) = \text{const}$. Since $P(l, t)$ are probabilities, and an aggregate of the microstates is the full set of random events,

$$\sum_{l=1}^{L}P(l, t) = 1. \tag{3}$$

The equality $\sum\limits_{l=1}^{L}P(l, t) = \text{const}$ derived from the system of kinetic equations confirms the correction of the accepted kinetic scheme. Besides, it denotes an important property of the system of differential equations (2), viz., the existence of a rigid constraint between the variables due to which the number of degrees of the system freedom is $L - 1$ but not L. One of the quantities of $P(l, t)$ can be expressed in terms of the remaining P's using Eq. (3). We assign the number L to this microstate and its probability. The system of equations for the remaining $L - 1$ probabilities $P(l, t)$ is as follows:

$$\frac{dP(l, t)}{dt} = \sum_{\bar l=1}^{L} r_{l,\bar l}P(\bar l, t), \quad l = 1 \div (L - 1). \tag{4}$$

To exclude the terms with $P(L, t)$ from Eqs. (4) we use Eq. (3) after replacement of l by $\bar{l}$: $P(L, t) = 1 - \sum_{\bar{l}=1}^{L-1} P(\bar{l}, t)$,

$$\frac{dP(l, t)}{dt} = \sum_{\bar{l}=1}^{L-1}\left(r_{l,\bar{l}} - r_{l,L}\right)P(\bar{l}, t) + r_{l,L}, \quad l = 1 \div (L-1). \tag{5}$$

Let us represent the microstate probabilities as

$$P(l, t) = P^{\mathrm{st}}(l) + P^{\mathrm{tr}}(l, t), \tag{6}$$

where the superscripts “st” and “tr” denote quantities related to a stationary (equilibrium) state and a transient process, respectively. The components $P^{\mathrm{tr}}(l, t)$ are deviations of the probabilities $P(l, t)$ from their stationary values $P^{\mathrm{st}}(l)$. For these quantities, Eqs. (5) give the following equations:

$$\sum_{\bar{l}=1}^{L-1}\left(r_{l,\bar{l}} - r_{l,L}\right)P^{\mathrm{st}}(\bar{l}) = -r_{l,L}, \qquad l = 1 \div (L-1), \tag{7}$$

$$\frac{dP^{\mathrm{tr}}(l, t)}{dt} = \sum_{\bar{l}=1}^{L-1}\left(r_{l,\bar{l}} - r_{l,L}\right)P^{\mathrm{tr}}(\bar{l}, t), \quad l = 1 \div (L-1). \tag{8}$$

Summation of Eq. (6) over all l gives: $\sum_{l=1}^{L} P(l, t) = \sum_{l=1}^{L} P^{\mathrm{st}}(l) + \sum_{l=1}^{L} P^{\mathrm{tr}}(l, t)$. As Eq. (3) is valid for all t’s, $\sum_{l=1}^{L} P^{\mathrm{st}}(l) = 1$, and, hence, the interrelation

$$\sum_{l=1}^{L} P^{\mathrm{tr}}(l, t) = 0 \tag{9}$$

is valid at all times.

Evidently, it is always possible to assign the index L to a microstate for which at least one of the quantities $r_{l,L}$ is nonzero. Then, Eqs. (7) are an inhomogeneous system of equations due to which the vector $P^{\mathrm{st}}(\bar{l})$ is nonzero. The solution of a linear differential system of equations (8) for a transient process, as is well known, is searched for in the following form: $P^{\mathrm{tr}}(l, t) = C(l)e^{\lambda t}$. Substituting these expressions into Eqs. (8) results in a system of linear algebraic equations for $C(l)$:

$$\sum_{\bar{l}=1}^{L-1}\left(r_{l,\bar{l}} - r_{l,L} - \delta_{l,\bar{l}}\lambda\right)C(\bar{l}) = 0, \quad l = 1 \div (L-1), \tag{10}$$

where $\delta_{l,\bar{l}}$ is a unit matrix of the size of $(L-1)\times(L-1)$. A nonzero solution $C(l)$ of Eqs. (10) is known to exist under the condition

$$\det\left(r_{l,\bar{l}} - r_{l,L} - \delta_{l,\bar{l}}\lambda\right) = 0. \tag{11}$$

The number of different solutions λ in a general case is $L-1$, i. e., it is highly large. This means that the behavior of the probability distribution $P(l, t)$ can be extremely complex. It depends on the values of matrix $r_{l,\bar{l}}$ elements, i. e., on the pattern of transitions between the microstates.

Entropy as a macroscopic index of system evolution is expressed by a known formula:

$$S = -\sum_{l=1}^{L} P(l)\ln P(l). \tag{12}$$

Here S is a dimensionless quantity. For description of physicochemical systems the dimensional entropy, $S^{\mathrm{dim}} = k_{\mathrm{B}}S$, is used, where $k_{\mathrm{B}} = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann constant. In information theory, the quantity $S^{\mathrm{inf}} = k_{\mathrm{S}}S$ is used, where $k_{\mathrm{S}} = \frac{1}{\ln 2}$ [Kennett, 2021]. In a transient process the entropy of the system depends on time:

$$S(t) = -\sum_{l=1}^{L} P(l,\, t) \ln P(l,\, t). \tag{13}$$

Similarly to Eq. (6), we represent entropy as a sum of its stationary (equilibrium) value S^{st} and a deviation from it, $S^{\mathrm{tr}}(t)$:

$$S(t) = S^{\mathrm{st}} + S^{\mathrm{tr}}(t).$$

In a stationary state $S(t) = S^{\mathrm{st}}$, and then

$$S^{\mathrm{st}} = -\sum_{l=1}^{L} P^{\mathrm{st}}(l) \ln P^{\mathrm{st}}(l).$$

Substituting Eq. (6) into Eq. (13) gives the following expression for $S^{\mathrm{tr}}(t)$:

$$S^{\mathrm{tr}}(t) = S(t) - S^{\mathrm{st}} = -\sum_{l=1}^{L} P^{\mathrm{st}}(l) \ln\left(1 + \frac{P^{\mathrm{tr}}(l,\, t)}{P^{\mathrm{st}}(l)}\right) - \sum_{l=1}^{L} P^{\mathrm{tr}}(l,\, t) \ln P^{\mathrm{st}}(l) - \sum_{l=1}^{L} P^{\mathrm{tr}}(l,\, t) \ln\left(1 + \frac{P^{\mathrm{tr}}(l,\, t)}{P^{\mathrm{st}}(l)}\right). \tag{14}$$

From here, it can be seen that $S^{\mathrm{tr}}(t)$ depends not only on transient components of the microstate probabilities, but also on the stationary ones. In the neighborhood of the stationary state when all $P^{\mathrm{tr}}(l,\, t) \ll P^{\mathrm{st}}(l)$, an approximate equality, $\ln\left(1 + \frac{P^{\mathrm{tr}}(l,t)}{P^{\mathrm{st}}(l)}\right) \approx \frac{P^{\mathrm{tr}}(l,t)}{P^{\mathrm{st}}(l)}$, takes place. Using also Eq. (9), we find from Eq. (14) that in the neighborhood of the stationary state

$$S^{\mathrm{tr}}(t) = -\sum_{l=1}^{L} P^{\mathrm{tr}}(l,\, t) \left[\ln P^{\mathrm{st}}(l) + \frac{P^{\mathrm{tr}}(l,\, t)}{P^{\mathrm{st}}(l)}\right].$$

The rate of entropy production, $\frac{d_{\mathrm{i}}S}{dt}$, in an isolated system equals the total rate of entropy change. It can be easily obtained by differentiation of Eq. (13) over time and substitution of Eq. (4):

$$\frac{d_{\mathrm{i}}S}{dt} = \frac{dS}{dt} = -\sum_{l=1}^{L} \left[\sum_{\bar{l}=1}^{L} r_{l,\bar{l}} P(\bar{l},\, t)\right] (\ln P(l,\, t) + 1).$$

Then, using the expressions $r_{l,\bar{l}} = \alpha_{\bar{l},l}$ $(\bar{l} \neq l)$, $r_{l,l} = -\sum_{\bar{l}\neq l} \alpha_{l,\bar{l}}$, we find the expression of $\frac{d_{\mathrm{i}}S}{dt}$ over the quantities α:

$$\frac{d_{\mathrm{i}}S}{dt} = -\sum_{l=1}^{L} \sum_{\bar{l}\neq l} \alpha_{\bar{l},l} P(\bar{l},\, t) \ln P(l,\, t) + \sum_{l=1}^{L} \left(\sum_{\bar{l}\neq l} \alpha_{l,\bar{l}}\right) P(l,\, t) \ln P(l,\, t) -$$

$$- \sum_{l=1}^{L} \sum_{\bar{l}\neq l} \alpha_{\bar{l},l} P(\bar{l},\, t) + \sum_{l=1}^{L} \left(\sum_{\bar{l}\neq l} \alpha_{l,\bar{l}}\right) P(l,\, t).$$

Earlier, during the calculation of $\frac{d}{dt} \sum\limits_{l=1}^{L} P(l,\, t)$, it was found that the sum of two last terms of the equation above equals zero. Using this fact and Eq. (1), we obtain

$$\frac{d_{\mathrm{i}}S}{dt} = \sum_{l=1}^{L} \left[\sum_{\bar{l}\neq l} \left(\alpha_{l,\bar{l}} P(l,t) - \alpha_{\bar{l},l} P\left(\bar{l},t\right)\right)\right] \ln P(l,t) = -\sum_{l=1}^{L} \ln P(l,t) \frac{dP(l,t)}{dt}. \tag{15}$$

For different sets of transition rates between the microstates the expressions (14) and (15) take different forms. Some thematic examples of them are considered below.

Entropy values at nonequiprobable distribution of the microscopic states

It is well known that the maximal entropy value takes place at the equiprobable distribution of the system staying in various microstates. This property is found when searching for the form of the distribution $P(l)$ providing a maximum of the expression (12) under the condition of Eq. (3). The criterion for finding the conditional extremum of S is a quantity $V = -\sum_l P(l)\ln P(l) + \chi\left(\sum_l P(l) - 1\right)$, where χ is the Lagrange multiplier. Equating all the derivatives of V by $P(l)$ to zero results in $\frac{\partial V}{\partial P(l)} = -\ln P(l) - 1 + \chi = 0$. Since χ has a similar value for all l, all the $P(l)$ equal one another. Therefore, according to the normalizing condition $\sum_{l=1}^{L} P(l) = 1$, all $P(l) = \frac{1}{L}$.

This probability distribution of the microstates results in a unique S extremum having the known value $S = \ln L$. It is a maximum which is checked by calculation of S for another $P(l)$ different from the found extremal one. For example, if the system stays in one of the microstates with $P(l) = 1$, all the remaining $P(l) = 0$. Then, according to Eq. (12) and the known interrelation $\lim_{x\to 0} x\ln x = 0$, we obtain $S = 0$, which proves that the found S extremum is maximum.

As already mentioned above, the statement that any isolated system being in an internal equilibrium has equiprobable distribution of all its microstates, is present in every description of statistical physics. Nevertheless, the equilibrium distribution $P^{\mathrm{st}}(l)$, as can be seen from Eqs. (7), depends on the set of rates $r_{l,\bar{l}}$. Therefore, it is interesting to study the effect of possible microstate nonequiprobability on the equilibrium value of entropy.

Consider the case when the microstates are subdivided into two subgroups with the probabilities uniform inside every subgroup but different between the subgroups. Let the first and the second subgroups contain $L^{(1)}$ and $L^{(2)}$ microstates, respectively, where $L^{(1)} + L^{(2)} = L$. Denote the microstate probabilities in the subgroups 1 and 2 as $P\left(l^{(1)}\right)$ and $P\left(l^{(2)}\right)$, where $l^{(1)}$ and $l^{(2)}$ are separate numerations in the subgroups. Then Eq. (3) takes the form

$$\sum_{l^{(1)}} P\left(l^{(1)}\right) + \sum_{l^{(2)}} P\left(l^{(2)}\right) = L^{(1)}P\left(l^{(1)}\right) + L^{(2)}P\left(l^{(2)}\right) = 1, \tag{16}$$

from which $P\left(l^{(2)}\right) = \frac{1-L^{(1)}P\left(l^{(1)}\right)}{L^{(2)}}$. The formula (12) for the entropy in this case is as follows:

$$S = -L^{(1)}P\left(l^{(1)}\right)\ln P\left(l^{(1)}\right) - L^{(2)}P\left(l^{(2)}\right)\ln P\left(l^{(2)}\right). \tag{17}$$

This simple variant of $P(l)$ inhomogeneity makes it possible to evaluate the effect of microstate nonequiprobability on the entropy deviation from its maximal value $S = \ln L$. The inhomogeneity of the $P(l)$ distribution is characterized by two parameters: interrelations between the microstate numbers in the subgroups and between $P\left(l^{(1)}\right)$ and $P\left(l^{(2)}\right)$.

Consider first an extremal case where one of the subgroups (let it be subgroup 2) has zero probabilities of its microstates: all $P\left(l^{(2)}\right) = 0$. This means that microstates of subgroup 2 are inaccessible for the whole macroscopic system. Then $1-L^{(1)}P\left(l^{(1)}\right) = 0$, and Eq. (16) results in $P\left(l^{(1)}\right) = \frac{1}{L^{(1)}}$, $S = \ln L^{(1)}$, which is natural for this situation. If $L^{(1)} = 1$, then $S = 0$.

Next, we consider the case where the probabilities of microstates in both subgroups are nonzero. Let us introduce deviations of these probabilities from the uniform distribution when all $P(l) = \frac{1}{L}$. The probabilities of the first-group microstates are $P\left(l^{(1)}\right) = \frac{1}{L} + \Delta P_1$, those of the second group microstates are $P\left(l^{(2)}\right) = \frac{1}{L} + \Delta P_2$. The deviations ΔP_1 and ΔP_2 are interrelated by the normalizing condition of Eq. (16). In this $P\left(l^{(1)}\right)$ and $P\left(l^{(2)}\right)$ representation it gives: $L^{(1)}\Delta P_1 + L^{(2)}\Delta P_2 = 0$, from which $\Delta P_2 = -\frac{L^{(1)}}{L^{(2)}}\Delta P_1$: the deviations from $\frac{1}{L}$ in subgroup 2, naturally, have an opposite sign compared with ΔP_1.

We introduce the following parameters: 1) $\rho_1 = \frac{L^{(1)}}{L}$ and 2) κ_1 according to $\Delta P_1 = \frac{1}{L}\kappa_1$. The parameter ρ_1 is the fraction of the first-subgroup microstates in the total microstate number. Then $L^{(1)} = \rho_1 L$, $L^{(2)} = (1-\rho_1)L$ $(0 \leqslant \rho_1 \leqslant 1)$. The parameter κ_1 is a relative deviation of $P\left(l^{(1)}\right)$ from the equiprobable value $\frac{1}{L}$. Its minimal value is -1 (an extremal case where $P\left(l^{(1)}\right) = 0$ and therefore the first subgroup is inaccessible). The maximal κ_1 value is restricted by the case where $\Delta P_2 = -\frac{1}{L}$, i. e., $P\left(l^{(2)}\right) = 0$ and the second subgroup of microstates is inaccessible. Using the expression $\Delta P_2 = -\frac{L^{(1)}}{L^{(2)}}\Delta P_1 = -\frac{\rho_1}{1-\rho_1}\frac{1}{L}\kappa_1$, we find that in the latter case $\kappa_1 = \frac{1-\rho_1}{\rho_1}$. Hence, $-1 < \kappa_1 < \frac{1-\rho_1}{\rho_1}$.

Substituting $\Delta P_1 = \frac{1}{L}\kappa_1$ and $\Delta P_2 = -\frac{\rho_1}{1-\rho_1}\frac{1}{L}\kappa_1$ into Eq. (17), we obtain:

$$S = \ln L - S_1, \quad \text{where} \quad S_1 = \rho_1(1+\kappa_1)\ln(1+\kappa_1) + (1-\rho_1)\left(1-\kappa_1\frac{\rho_1}{1-\rho_1}\right)\ln\left(1-\kappa_1\frac{\rho_1}{1-\rho_1}\right). \quad (18)$$

In the case of unequal microstate probabilities $P\left(l^{(1)}\right)$ and $P\left(l^{(2)}\right)$ the entropy value is diminished by the value S_1. It can be seen from Eq. (18) that $S_1 = 0$ when $\kappa_1 = 0$ (microstate probabilities in both subgroups are similar and equal to $\frac{1}{L}$) independently of ρ_1, i. e., the total microstate set subdivision by the subgroups.

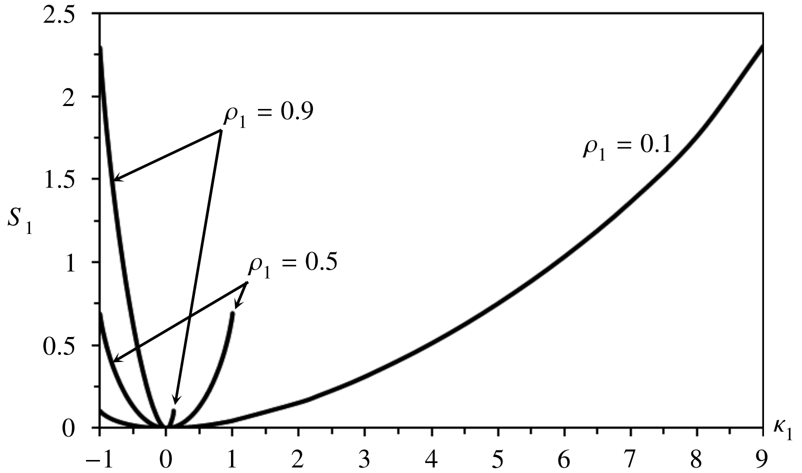

Figure 1. Dependence of S_1 (difference of an isolated system entropy from the case of equiprobable microstate distribution) on the parameter κ_1 at various ρ_1 values. Boundary points of all plots correspond to the limiting κ_1 values

Dependences of S_1 on the parameters κ_1 and ρ_1 are shown in Figs. 1 and 2. It can be seen from Fig. 1 that, when $\kappa_1 \neq 0$ $\left(P\left(l^{(1)}\right) \neq P\left(l^{(2)}\right)\right)$, the values of S_1 are positive, i. e., the inequality of these probabilities, naturally, diminishes the entropy of the whole system. However, an important question arises: how much is this decrease compared with the case $P\left(l^{(1)}\right) = P\left(l^{(2)}\right)$, i. e., $S = \ln L$.

Consider this question using the above-mentioned example of the system of magnetic dipoles in the constant external magnetic field. First, we calculate the entropy of this system in the case of equiprobable microstate distribution when $S = \ln L$. Let the number of the dipoles be N. The n of them have moments oriented against the external field and therefore have a higher energy compared with the

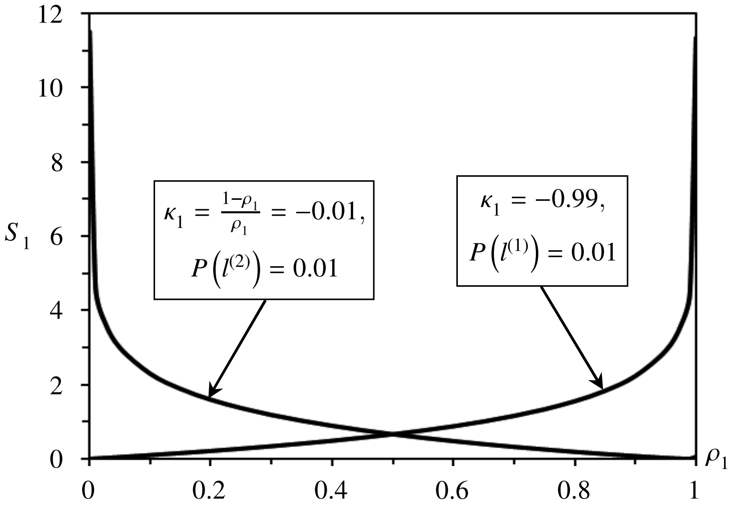

Figure 2. Dependence of S_1 (difference of an isolated system entropy from the case of equiprobable microstate distribution) on the parameter ρ_1 in the cases where one of the microstate probabilities $P\left(l^{(1)}\right)$ or $P\left(l^{(2)}\right)$ is close to zero

remaining dipoles. As mentioned above, the number of different microscopic states, L, corresponding to the same energy (i. e., the same n) equals C_n^N, the number of n combinations of an N-set, where $C_n^N = \frac{N!}{n!(N-n)!}$. According to the Stirling formula, the quantity $\ln K!$ at large K can be represented as $\ln K! = K \ln K - K$ with high precision. Then, if N, $(N-n)$ and n are large numbers, then

$$S = \ln C_N^n = NK_\mathrm{E}, \quad \text{where} \quad K_\mathrm{E} = -\frac{n}{N}\ln\frac{n}{N} - \ln\left(1-\frac{n}{N}\right) + \frac{n}{N}\ln\left(1-\frac{n}{N}\right).$$

This representation is suitable since the coefficient K_E depends only on the fraction of high-energy microstates in any of their total numbers. When n is close to zero or to N the Stirling formula becomes imprecise and the initial form for the combination number should be used: $S = \ln C_n^N = \ln\left(\frac{N!}{n!(N-n)!}\right)$. At $n = 0$ and $n = N$ the value of S becomes zero (taking the equality $0! = 1$ into account). The reason is that in these cases the system stays in a single microstate. At $\frac{n}{N} = \frac{1}{2}$ the coefficient K_E takes the maximal value $\ln 2$. The dependence of K_E on $\frac{n}{N}$ is shown in Fig. 3.

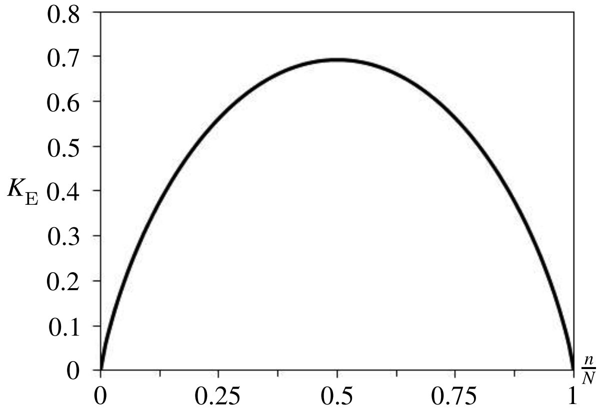

Figure 3. The dependence of K_E, the proportionality coefficient between the number of magnetic dipoles and entropy of the dipole system, on $\frac{n}{N}$, the fraction of the magnetic moments oriented against the external field

Let us compare the values of the expression $S = NK_\mathrm{E}$ with the quantity S_1, the entropy decrease at nonequiprobable microstate distribution (see Eq. (18)). At one-molar number of the microscopic *objects* (magnetic dipoles in this case) $N = N_{\text{A}}$, where $N_{\text{A}} = 6.02 \cdot 10^{23}$ mol^{-1} is the Avogadro number. Then the maximal value of S equal to $S = N_{\text{A}} \ln 2$ has the order of magnitude 10^{23}. On the other hand, S_1, according to Figs. 1 and 2, within a wide range of ρ_1 and κ_1 values has the order of magnitude from very small values compared with unity up to 10. Hence, any deviations from the regularity $S = \ln L$ can be noticeable only in extreme cases where either the number of microscopic objects composing the system is rather small, or the energy of the system is very close to its boundary value (n or $N - n$ close to zero), or, finally, a very small fraction of microstates has a high probability of realization but the overwhelming majority of the microstates are extremely improbable (the last case is most likely unrealistic).

Next, we consider a general form of the distribution $P(l)$. In this case the quantity S_1 in the neighborhood of the point $P(l) = \frac{1}{L}$ can be expressed as a formula only approximately. Let us represent $P(l)$ as $P(l) = \frac{1}{L} + \Delta P(l)$. Then $\sum_{l=1}^{L} \Delta P(l) = 0$, $S = -\sum_{l=1}^{L} \left(\frac{1}{L} + \Delta P(l)\right) \ln \left(\frac{1}{L} + \Delta P(l)\right)$. It is found in Appendix 1 that

$$S \approx \ln L - \frac{1}{2}\frac{1}{L} \sum_{l=1}^{L} \left(\frac{\Delta P_l}{P_l}\right)^2. \tag{19}$$

The quantity $\gamma = \frac{1}{L} \sum_{l=1}^{L} \left(\frac{\Delta P_l}{P_l}\right)^2$ is an average square of a relative deviation of the probabilities $P(l)$ from $\frac{1}{L}$. The order of the γ value is from very small to about 1. Therefore, at an arbitrary ΔP_l distribution the subtrahend in Eq. (19) is extremely small compared with $\ln L$ for a system with a high number of microstates.

Hence, the assumption about the equiprobability of a system staying in various microstates restricts neither the generality of reasoning nor the accuracy of entropy calculation (except extreme cases described above) when the total number of the system microstates remains constant. Therefore, the expression $S = \ln L$ is correct and suitable for entropy calculation.

Kinetics of microstate probabilities and entropy value change

1°. Consider first the simplest case where the rates of all possible transitions between the microstates are identical: $\alpha_{l,\bar{l}} = \alpha_{\bar{l},l} = a$ at $l \neq \bar{l}$. Diagonal elements of the matrix on the right-hand side of Eq. (2) are $r_{l,l} = -(L-1)a$. Then the coefficients at $P^{\text{st}}(\bar{l})$ and $P^{\text{tr}}(\bar{l}, t)$ in Eqs. (7) and (8) become as follows. When $\bar{l} \neq l$, all the terms $r_{l,\bar{l}} - r_{l,L} = a - a = 0$. When $\bar{l} = l$: $r_{l,l} - r_{l,L} = -(L-1)a - a = -La$. Then Eq. (7) takes the form $-LaP^{\text{st}}(l) = -a$, from which we obtain a natural result: all $P^{\text{st}}(l) = \frac{1}{L}$, which is the case of maximal entropy.

For a transient process the set of Eqs. (8) is as follows: $\frac{dP^{\text{tr}}(l,t)}{dt} = -LaP^{\text{tr}}(l, t)$, from which all $P^{\text{tr}}(l, t) = P^{\text{tr}}(l, 0)e^{-Lat}$. It can be seen from here that under this form of matrix α the stationary value of the vector $P(l, t)$ is a stable node. The system of microscopic objects uniformly spreads along the whole set of microscopic states. A value of the rate constant a should be taken from experimental data or based on theoretical considerations, which are beyond the scope of this work. This value is L times, i. e., many orders increased. It takes place due to the fact that in the present particular case the transition to an lth microstate is possible from every remaining microstates with the same specific rate.

The entropy of the system in this case depends on time as

$$S = -\sum_{l=1}^{L} \left(\frac{1}{L} + P^{\text{tr}}(l, 0)e^{-Lat}\right) \ln \left(\frac{1}{L} + P^{\text{tr}}(l, 0)e^{-Lat}\right).$$

If the system initially stays in a microstate number l^{ini} with the probability $P\left(l^{\text{ini}}, 0\right) = 1$ and, correspondingly, all the remaining $P(l, 0) = 0$ $\left(l \neq l^{\text{ini}}\right)$, then:

$$C_{l^{\text{ini}}} = 1 - \frac{1}{L}, \quad C_{l \neq l^{\text{ini}}} = -\frac{1}{L}, \quad P\left(l^{\text{ini}}, t\right) = \frac{1}{L} + \left(1 - \frac{1}{L}\right) e^{-Lat}, \quad P\left(l \neq l^{\text{ini}}, t\right) = \frac{1}{L}\left(1 - e^{-Lat}\right).$$

Since all $P(l, t)$ come into a stationary state with the rate of the term e^{-Lat} decay, the entropy of the system takes its maximal value $S = \ln L$ very quickly even in the extreme case of a single initial state $\left(P\left(l^{\text{ini}}, 0\right) = 1\right)$.

Let us find the rate of entropy production for this scheme of transitions between the microstates. Substituting into Eq. (15) all α's by a and taking $\sum\limits_{l=1}^{L} \ln P(l, t) = \ln \prod\limits_{l=1}^{L} P(l, t)$ into account, we obtain

$$\frac{d_{\text{i}} S}{dt} = a\left(LS + \ln \prod_{l=1}^{L} P(l, t)\right). \tag{15a}$$

Since all $P(l, t) \leqslant 1$, it follows that $\ln \prod\limits_{l=1}^{L} P(l, t) \leqslant 0$.

For the stationary state, when $\frac{d_{\text{i}} S}{dt} = \frac{dS}{dt} = 0$, the equation $LS + \ln \prod\limits_{l=1}^{L} P(l, t) = 0$ yields the above-mentioned value $S = \ln L$. However, to get it, we need to place the above found values $P(l) = \frac{1}{L}$ into this equation. Even in this simplest case of the set of transitions between the microstates, the expression for the rate of entropy production rate cannot serve as a kinetic equation of entropy evolution since, in addition to the quantity S, this expression contains the probabilities of the system staying in various microstates and, therefore, it is insufficient for description of entropy evolution.

2°. Consider another variant of microkinetics: there is one particular microscopic state such that the transitions are possible from all the remaining microstates to that particular one, assigned with the number L. It is an extremal case opposite to that considered in the previous item. Two variants of this situation are possible. One of them assumes that the transitions from microstates with numbers $l \neq L$ to the Lth one are possible but back transitions are impossible. Then the system inevitably comes to the Lth microstate and remains in it forever. If there were some initial probability distribution $P(l, 0)$, the initial entropy value would have been nonzero but would have come to zero. Such a case does not take place in physical objects and its analysis is not of interest.

Another variant is really interesting: transitions from all microstates with $l \neq L$ to the Lth one are possible; back transitions from the Lth to all the remaining ones are also possible, but direct transitions between the microstates with $l \neq L$ are forbidden. This means that one selected microstate is a single "bridge" between all others.

Consider first a general case where nonzero elements of matrix $\alpha_{l,\bar{l}}$, which correspond to the transition scheme above may have different values. Then Eqs. (3) take the form

$$\begin{aligned} \frac{dP(l, t)}{dt} &= -\alpha_{lL} P(l, t) + \alpha_{Ll} P(L, t), \quad l = 1 \div (L - 1), \\ \frac{dP(L, t)}{dt} &= \left(\sum_{l=1}^{L-1} \alpha_{lL} P(l, t)\right) - \left(\sum_{l=1}^{L-1} \alpha_{Ll}\right) P(L, t). \end{aligned} \tag{20}$$

The matrix of the system of equations (20) is as follows:

$$r_{l,\bar{l}} = \begin{pmatrix} -\alpha_{1L} & 0 & 0 & \cdots & 0 & \alpha_{L1} \\ 0 & -\alpha_{2L} & 0 & \cdots & 0 & \alpha_{L2} \\ 0 & 0 & -\alpha_{3L} & \cdots & 0 & \alpha_{L3} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & -\alpha_{(L-1)L} & \alpha_{L(L-1)} \\ \alpha_{1L} & \alpha_{2L} & \alpha_{3L} & \cdots & \alpha_{(L-1)L} & -\sum\limits_{l=1}^{L-1} \alpha_{Ll} \end{pmatrix}. \tag{21}$$

The diagonal elements of this matrix satisfy the conditions $r_{l,l} = -\sum\limits_{\bar{l} \neq l} \alpha_{l,\bar{l}}$.

From Eqs. (20) we obtain interrelations for stationary solutions:

$$P^{\mathrm{st}}(l) = \frac{\alpha_{Ll}}{\alpha_{lL}} P^{\mathrm{st}}(L), \quad l = 1 \div (L-1).$$

They are similar to the condition of “chemical” equilibrium between the stationary microstates of the given system. These interrelations and the normalizing condition for $P^{\mathrm{st}}(l)$ yield the following:

$$P^{\mathrm{st}}(l) = \frac{\frac{\alpha_{lL}}{\alpha_{Ll}}}{\sum\limits_{l=1}^{L-1} \frac{\alpha_{lL}}{\alpha_{Ll}} + 1} \text{ at } l = 1 \div (L-1), \quad P^{\mathrm{st}}(L) = \frac{1}{\sum\limits_{l=1}^{L-1} \frac{\alpha_{lL}}{\alpha_{Ll}} + 1}. \tag{22}$$

From Eqs. (22), a stationary entropy value can be easily found. Consider the case where all nonzero α’s equal the same value a. Then all the $P^{\mathrm{st}}(l)$ including $P^{\mathrm{st}}(L)$ equal $\frac{1}{L}$ as in the case where transitions inside all microstate pairs are possible and equiprobable. Accordingly, the entropy value in this case is equal to $\ln L$ despite a quite different structure of microstate transitions.

For description of transients we apply Eq. (8). The matrix $r_{l,\bar{l}} - r_{l,L}$ in the given case is as follows (see Eq. (21)):

$$r_{l,\bar{l}} - r_{l,L} = \begin{pmatrix} -\alpha_{1L} - \alpha_{L1} & -\alpha_{L1} & -\alpha_{L1} & \cdots & -\alpha_{L1} & -\alpha_{L1} & 0 \\ -\alpha_{L2} & -\alpha_{2L} - \alpha_{L2} & -\alpha_{L2} & \cdots & -\alpha_{L2} & -\alpha_{L2} & 0 \\ -\alpha_{L3} & -\alpha_{L3} & -\alpha_{3L} - \alpha_{L3} & \cdots & -\alpha_{L3} & -\alpha_{L3} & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ -\alpha_{L(L-2)} & -\alpha_{L(L-2)} & -\alpha_{L(L-2)} & \cdots & -\alpha_{(L-2)L} - \alpha_{L(L-2)} & -\alpha_{L(L-2)} & 0 \\ -\alpha_{L(L-1)} & -\alpha_{L(L-1)} & -\alpha_{L(L-1)} & \cdots & -\alpha_{L(L-1)} & -\alpha_{(L-1)L} - \alpha_{L(L-1)} & 0 \\ \alpha_{1L} + \sum\limits_{l=1}^{L-1} \alpha_{Ll} & \alpha_{2L} + \sum\limits_{l=1}^{L-1} \alpha_{Ll} & \alpha_{3L} + \sum\limits_{l=1}^{L-1} \alpha_{Ll} & \cdots & \alpha_{(L-2)L} + \sum\limits_{l=1}^{L-1} \alpha_{Ll} & \alpha_{(L-1)L} + \sum\limits_{l=1}^{L-1} \alpha_{Ll} & 0 \end{pmatrix}. \tag{23}$$

In Eqs. (7) and (8) we use this matrix without the last row and the last column. The solution is searched for in a standard form: $P^{\mathrm{tr}}(l,\, t) = C_l e^{-\lambda t}$. The general equation for eigenvalues λ of the matrix $r_{l,\bar{l}}$, when the latter has the form Eq. (21), is derived in Appendix 2. This equation is as follows:

$$(\alpha_{(L-1)L} + \alpha_{L(L-1)} + \lambda) \prod_{m=1}^{L-2} (\alpha_{Lm} + \lambda) + (\alpha_{L(L-1)} + \lambda) \sum_{j=1}^{L-2} \alpha_{jL} \prod_{\substack{m \neq j, \\ m \neq L-1}} (\alpha_{Lm} + \lambda) = 0. \tag{24}$$

Let us consider the case where nonzero elements of the matrix (21) have the form: $r_{lL} = \alpha_{Ll} = a$, $r_{Ll} = \alpha_{lL} = Ka$ for all $l = 1 \div (L-1)$. (Then, as it can be seen from Eq. (21), the diagonal elements are $r_{ll} = -Ka$ at $l = 1 \div (L-1)$, $r_{LL} = -(L-1)a$.) This means that the specific rates of transitions from all lth microstates to the Lth one are identical, the specific rates of back transitions are also identical but both sets of the rates can differ from each other and the rates are equal to one another only at $K = 1$. Then Eq. (22) turns into:

$$P^{\mathrm{st}}(l) = \frac{1}{L+K-1} \text{ at } l = 1 \div (L-1), \quad P^{\mathrm{st}}(L) = \frac{K}{L+K-1}.$$

In the case where L is large and K is close to unity or differs from it only by several orders to a larger or smaller side, all $P^{\mathrm{st}}(l)$ are close to $\frac{1}{L}$ and entropy S is close to $\ln L$. It is in accord with the result obtained above.

Equation (24) for the eigenvalues in this case has the form (see Appendix 2):

$$(Ka+\lambda)^{L-2}[(L+K-1)a+\lambda] = 0.$$

From this we obtain two λ values: $\lambda_1 = -(K+L-1)a$, $\lambda_2 = -Ka$. Also, λ_2 has the multiplicity $L-2$. It is shown in Appendix 2 that the general solution for the transient component in this case is

$$P^{\mathrm{tr}}(l, t) = C_l^{(f)} e^{-(L+K-1)at} + C_l^{(0)} e^{-Kat} \quad \text{for } l = 1 \div (L-1). \tag{25}$$

Here the multiplicity of the root λ_2 does not result in the appearance of power terms in the expression for $P^{\mathrm{tr}}(l, t)$. The constants present in Eq. (25) satisfy the following interrelations (see Appendix 2): 1) $C_l^{(f)} = -\frac{1}{L-1} C_L^{(f)}$ for $l = 1 \div (L-1)$, i. e., in this set of constants there is only one constant based on the initial conditions, and 2) $\sum\limits_{l=1}^{L-1} C_l^{(0)} = 0$. Further, according to Eq. (9), $P^{\mathrm{tr}}(L, t) = 1 - \sum\limits_{l=1}^{L-1} P^{\mathrm{tr}}(l, t)$. Substituting here Eqs. (25) and applying the above interrelations between the C-coefficients, we obtain for $l = L$: $P^{\mathrm{tr}}(L, t) = C_L^{(f)} e^{-(L+K-1)at}$. Finally, the complete solution of the problem of microstate probability distribution kinetics in the considered case is as follows:

$$P(l, t) = \frac{1}{L+K-1} + \frac{1}{L-1} C_L^{(f)} e^{-(L+K-1)at} + C_l^{(0)} e^{-Kat} \quad \text{for } l = 1 \div (L-1), \tag{26}$$

$$P(L, t) = \frac{K}{L+K-1} + e^{-(L+K-1)at} C_L^{(f)}. \tag{27}$$

A peculiar property of transient processes at the considered structure of transitions between the microstates in a general case is the existence of fast and slow components of the process. The fast component has the form $e^{-(L+K-1)at}$. The transient of an Lth microstate, which is central in the total pattern of transitions, according to Eq. (27), contains only the fast component after completion of which a stationary state $P(L)$ is established. The probabilities of the remaining microstates, according to Eq. (26), contain both fast and relatively slow components.

The general expression for the rate of entropy production in this case is described by Eq. (A.2.12) (see Appendix 2). When $r_{lL} = \alpha_{Ll} = a$, $r_{Ll} = \alpha_{lL} = Ka$,

$$\frac{d_{\mathrm{i}}S}{dt} = a \sum_{l=1}^{L-1} (KP(l, t) - P(L, t)) \ln \frac{P(l, t)}{P(L, t)}. \tag{15b}$$

3°. Finally, let us consider one more example of the structure of microstate transitions. Suppose that all microstates pass around a cycle: at $l = 1 \div (L-1)$ from every lth to $(l+1)$th one and from Lth to that with $l = 1$. This scheme is taken because in this case the appearance of oscillating transients may be expected.

Equations for $P(l,\ t)$ in this case are:

$$\begin{aligned}
\frac{dP(1,\ t)}{dt} &= \alpha_{L1}P(L,\ t) - \alpha_{12}P(1,\ t),\\
\frac{dP(l,\ t)}{dt} &= \alpha_{(l-1)l}P(l-1,\ t) - \alpha_{l(l+1)}P(l,\ t), \quad l = 2 \div (L-1),\\
\frac{dP(L,\ t)}{dt} &= \alpha_{(L-1)L}P(L-1,\ t) - \alpha_{L1}P(L,\ t).
\end{aligned} \tag{28}$$

The equations for a stationary $P(l,\ t)$ component are

$$\begin{aligned}
P^{\mathrm{st}}(1) &= \frac{\alpha_{L1}}{\alpha_{12}}P^{\mathrm{st}}(L),\\
P^{\mathrm{st}}(l) &= \frac{\alpha_{(l-1)l}}{\alpha_{l(l+1)}}P^{\mathrm{st}}(l-1), \quad l = 2 \div (L-1),\\
P^{\mathrm{st}}(L) &= \frac{\alpha_{(L-1)L}}{\alpha_{L1}}P^{\mathrm{st}}(L-1).
\end{aligned}$$

Successively expressing $P^{\mathrm{st}}(l)$ in terms of $P^{\mathrm{st}}(l-1)$, we obtain

$$P^{\mathrm{st}}(l) = \frac{\alpha_{L1}}{\alpha_{l(l+1)}}P^{\mathrm{st}}(L), \quad l = 1 \div (L-1).$$

Applying the normalizing condition, we find

$$P^{\mathrm{st}}(L) = 1 - \sum_{l=1}^{L-1} P^{\mathrm{st}}(l) = 1 - \alpha_{L1}\left(\sum_{l=1}^{L-1}\frac{1}{\alpha_{l(l+1)}}\right)P^{\mathrm{st}}(L).$$

Hence, for $l = L$:

$$P^{\mathrm{st}}(L) = \frac{\frac{1}{\alpha_{L1}}}{\frac{1}{\alpha_{L1}} + \sum\limits_{l=1}^{L-1}\frac{1}{\alpha_{l(l+1)}}};$$

for $l = 1 \div (L-1)$:

$$P^{\mathrm{st}}(l) = \frac{\frac{1}{\alpha_{l(l+1)}}}{\frac{1}{\alpha_{L1}} + \sum\limits_{l=1}^{L-1}\frac{1}{\alpha_{l(l+1)}}}.$$

When all α are equal to a, all $P^{\mathrm{st}}(l) = \frac{1}{L}$ $(l = 1 \div L)$, and the entropy of the stationary (equilibrium) state (as well as in the other cases where all nonzero α are equal to a) equals $\ln L$.

The matrix $r_{l,\bar{l}}$ for the system of equations (28) is as follows:

$$r_{l,\bar{l}} = \begin{pmatrix}
-\alpha_{12} & 0 & 0 & \cdots & 0 & \alpha_{L1}\\
\alpha_{12} & -\alpha_{23} & 0 & \cdots & 0 & 0\\
0 & \alpha_{23} & -\alpha_{34} & \cdots & 0 & 0\\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots\\
0 & 0 & 0 & \cdots & -\alpha_{(L-1)L} & 0\\
0 & 0 & 0 & \cdots & \alpha_{(L-1)L} & -\alpha_{L1}
\end{pmatrix}. \tag{29}$$

The size of $r_{l,\bar{l}}$ is $L \times L$. To search for the solution in the form $P^{\mathrm{tr}}(l,\, t) = C_l e^{-\lambda t}$, as it was done above, we use the matrix $r_{l,\bar{l}} - r_{l,L}$ without its last row and the last column, i. e.,

$$\begin{pmatrix}
-(\alpha_{12} + \alpha_{L1}) & -\alpha_{L1} & -\alpha_{L1} & \cdots & -\alpha_{L1} & -\alpha_{L1} & -\alpha_{L1} \\
\alpha_{12} & -\alpha_{23} & 0 & \cdots & 0 & 0 & 0 \\
0 & \alpha_{23} & -\alpha_{34} & \cdots & 0 & 0 & 0 \\
0 & 0 & \alpha_{34} & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & -\alpha_{(L-3)(L-2)} & 0 & 0 \\
0 & 0 & 0 & \cdots & \alpha_{(L-3)(L-2)} & -\alpha_{(L-2)(L-1)} & 0 \\
0 & 0 & 0 & \cdots & 0 & \alpha_{(L-2)(L-1)} & -\alpha_{(L-1)L}
\end{pmatrix}. \tag{30}$$

The size of the matrix Eq. (30) is $(L - 1) \times (L - 1)$.

The general equation for eigenvalues λ of the matrix $r_{l,\bar{l}}$ determined by Eq. (29) is derived in Appendix 3 (see Eq. (A.3.6)).

Similar to the previous examples, a case is of interest when all α's are identical and equal to a. The eigenvalues of the characteristic equation for the given case are found in Appendix 3 (see Eq. (A.3.10)):

$$\lambda = a\left(-1 + e^{i\frac{2\pi}{L}k}\right) = a\left[\left(-1 + \cos\frac{2\pi}{L}k\right) + i\sin\frac{2\pi}{L}k\right],$$

where $k = 1, 2, 3, \ldots, (L - 2), (L - 1)$. Since $k \neq 0$ and $k \neq L$, we have $\cos\frac{2\pi}{L}k \neq 1$, due to which the values of all $\operatorname{Re}\lambda$ are negative and, therefore, all partial solutions for transients in a system with the considered structure of microstate transitions have damping trends. Recall that these solutions are components of $P^{\mathrm{tr}}(L,\, t)$, which are deviations from stationary solutions $P^{\mathrm{st}}(l)$. When L is even, at $k = \frac{L}{2}$ the transient process completely lacks an oscillatory component. In all the remaining cases such components are present. The frequencies of the particular solution oscillations are $\omega_k = \operatorname{Im}\lambda = a\sin\frac{2\pi}{L}k$ and the corresponding attenuation coefficients are $\delta_k = -\operatorname{Re}\lambda = a\left(1 - \cos\frac{2\pi}{L}k\right)$. Dependencies of $\operatorname{Im}\lambda$ and $\operatorname{Re}\lambda$ on $\frac{k}{L}$ are shown in Fig. 4.

The most low-frequency solution takes place at $k = 1$, $\left(\frac{L}{2} \pm 1\right)$, $(L - 1)$: $\omega_k = \pm 2\pi\frac{a}{L}$. The attenuation coefficient $\delta_k = -\operatorname{Re}\lambda$ is small at $k = 1$ and $k = L - 1$: $\delta_k = a\frac{1}{2}\left(\frac{2\pi}{L}\right)^2$ and relatively large at $k = \frac{L}{2} \pm 1$: $\delta_k = 2a$. The most high-frequency solutions take place at $k = \frac{L}{4}$ and $k = \frac{3L}{4}$. Then $\delta_k = a$.

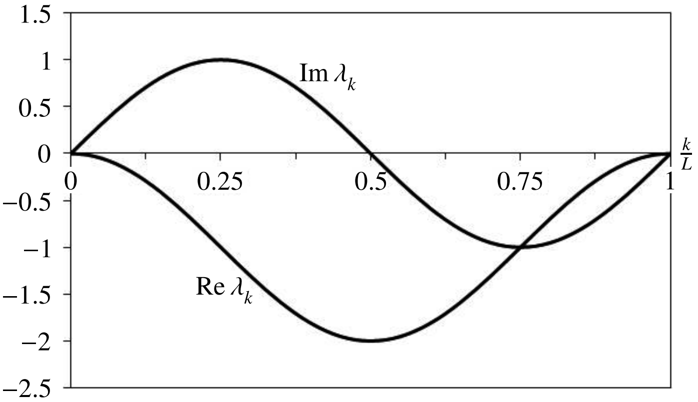

Figure 4. Dependencies of the real and imaginary components of the eigenvalues λ_k on $\frac{k}{L}$ in the case of the cyclic structure of intermicrostate transitions

The general expression for the rate of entropy production in the present case is given by Eq. (A.3.11) (see Appendix 3). If all the nonzero $r_{l,\bar{l}}$ are equal to a by their modules (with signs indicated in Eq. (29)), then

$$\frac{d_{\mathrm{i}}S}{dt} = a\left[(P(1,\, t) - P(L,\, t))\ln P(1,\, t) + \sum_{l=2}^{L}(P(l,\, t) - P(l-1,\, t))\ln P(l,\, t)\right]. \tag{15c}$$

Results and discussion

The subject of the present study is the entropy of an isolated **macro**scopic system, which is expressed by the formula $S(t) = -\sum_{l=1}^{L} P(l,\, t)\ln P(l,\, t)$, where $P(l,\, t)$ is the probability of a system staying in an lth **micro**scopic state at time t, L is the total number of microstates. (Recall that this expression has different coefficients at the sum when it is applied in different fields of science.) Transitions of the system between the microstates are spontaneous and random. When the given system is in a stationary (for an isolated system it means equilibrium) state, these probabilities relate to the average time of the system staying in corresponding microstates. In a nonequilibrium case the best approach to understanding $P(l,\, t)$ is given by the notion of Gibbs statistical assembly when a large set of **macro**scopically identical systems, distributed over **micro**states, is considered. The notion of statistical assembly by itself does not require equiprobable system distribution over the microstates, when the system is in internal equilibrium. Two problems are stated in the present work: to study 1) the effect of possible nonequiprobability of the microscopic states on the value of the system entropy, and 2) the kinetics of the entropy change in nonequilibrium states of the system. These problems inevitably require the investigation of the quantities $P(l,\, t)$ themselves.

The effect of a possible nonequiprobability of an isolated system's microstates on the value of entropy S is considered here for two cases. A general condition in these cases is the constancy of the total number of microstates.

a) An example is analyzed when all microstates form two subgroups with probabilities identical within every subgroup but differing between them. Besides, both the difference between the probabilities and the ratio between the subgroup sizes may be arbitrary. It was found that the nonequiprobability of the microstates can affect the entropy value only in extremal cases where only one microstate or a small group of them have high probabilities but the remaining majority of microstates is hardly probable. In the opposite situation the distinction of the entropy value from that in the case of microstate equiprobability is vanishingly small.

b) The behavior of the entropy value in the neighborhood of the case of equiprobable microstates was studied. Here, the deviations of all probabilities from the same value were accepted to be arbitrary (but, certainly, satisfying the normalizing condition). It was found that in this case the entropy differences from its equiprobable value were extremely small as well.

Thus, it is found that for real isolated systems the possible nonequiprobability of microscopic states exerts a vanishingly small effect on the entropy value under one important condition: the total microstate number is fixed. It is valid not only for an equilibrium state of the object but for its nonequilibrium state as well except for the case where initially the object is in one or several microstates the probability sum of which is very close to unity. With the exception of this case, the main factor determining the entropy value is the total number of microstates.

In the literature on the statistical physics the entropy is usually expressed as $S = k_{\mathrm{B}}\ln L$, where L is the number of microstates and k_{B} is Boltzmann's constant. If all the microstates are strictly equiprobable, all $P(l) = \frac{1}{L}$ and the expression $-\sum_{l=1}^{L} P(l)\ln P(l)$ exactly equals $\ln L$. In the present work it is shown that the expressions $S = k_\mathrm{B} \ln L$ and $S = -k_\mathrm{B} \sum_{l=1}^{L} P(l) \ln P(l)$ with the extremely high accuracy coincide by their values both in an equiprobable and nonequiprobable case.

Time dependences of the probabilities of the system staying in various microstates are considered for the case where random transitions between the microstates occur by the law of the first-order kinetics. It is valid for physicochemical objects conforming to quantum mechanical regularities, e. g., for spontaneous transitions between different variants of a degenerate state. Therefore, for many objects such a model of transitions between microstates is not a simplification.

It should be emphasized that the analysis described above is essentially based on the discreteness of the **microstate** set. Not any spatially discrete model of a considered object inevitably provides the discreteness of the microstate set. As an example, consider a system of many mass points interconnected by elastic linear bonds (a chain of mass points, an idealized crystal, etc.). Since such a model meets the laws of classical mechanics, the spatial discreteness in it is combined with a continuity of the set of dynamic states ("microstates"). The latter is continual since the amplitude of each mode is a continual quantity. The dynamics of such an object meets the same problem as the dynamics of any classical mechanical system, viz., the constancy of the phase volume based on the Liouville theorem, and, as a consequence, the constancy of entropy. Within the framework of the discrete model considered in this work, the latter is similar to the case where any mechanism providing transitions between the microstates is absent. Such a system when it initially gets to one of the microstates stays in it forever with probability equal to one and entropy equal to zero. This case is not of interest. Real thermodynamic systems always contain stochastic (i. e., not classical mechanical) possibilities of transitions between the microstates.

We have considered several essentially different schemes of random transitions of an isolated system between its microscopic states.

One of the schemes assumes that the system is capable of passing from any microstate to any other one without restrictions. Then the transition rate matrix does not contain zero elements. The analytical finding and examination of the solution in the general case of this scheme is mostly complicated. Therefore, we considered the case where all the rate constant values are similar. Then the analytical solution has the simplest form. A stationary (equilibrium) system distribution over all the microstates is stable, the damping rate of deviations from that distribution is the highest, and the damping has an aperiodic form.

Another scheme assumes that there exists some nodal microstate, such that the transitions between the remaining microstates are possible only via the nodal one as an obligatory intermediate stage. For this case a general equation for the eigenvalues of the kinetic equation matrix is derived. Based on it, a simple variant of the kinetics is considered when all the rate constants of transitions to the nodal microstate are similar, all the rate constants of leaving the nodal microstate are also equal to one another, but the rate constants of the former and the latter transitions are different. In this case an exact analytical solution for time dependences of all the microstate probabilities is found. This solution reveals a peculiar property of these dependences, viz., the existence of fast and relatively slow components in the processes of a stationary state establishment. The kinetics of the nodal microstate occupancy has only a fast component, while all the remaining probabilities in the general case of the initial conditions have both fast and slow summands. As in the previous scheme of transitions, the equilibrium microstate distribution is stable and the damping of deviations from the equilibrium is also aperiodic.

The third scheme assumes random transitions between the microstates along a cycle in one direction. For this scheme a general equation for matrix eigenvalues is also found, and the exact analytical solution in the case where all the rate constants have identical values is obtained. In this case the eigenvalues are complex numbers with negative real parts. Accordingly, the equilibrium distribution is stable and the establishment process has the form of damping oscillations, both the frequencies and damping coefficients of which lie within very wide ranges.

In all three schemes, when the rate constants of allowed transitions between the microstates are identical, the equilibrium probabilities of the microstates are equal to one another and independent of the specific scheme of transitions between the microstates. The equilibrium probabilities in this case are $P(l) = \frac{1}{L}$, equilibrium dimensionless entropy $S = \ln L$. The condition of generality and stability of the equilibrium distribution is that for every pair of microstates a sequence of transitions from one to another should exist and no microstate should be a trap from which a system could not get out after falling into it.

A general property of the considered transients is that all of them result in damping of deviations from the equilibrium state. Evidently, this property takes place for any system with random transitions between the microstates described by the first-order kinetics. It should be emphasized that we consider an isolated system with a fixed number of microscopic states. The question about what could be in the case when the transition kinetics between the microstates had a nonlinear mode is of separate interest.

On the other hand, a species of the transition scheme considerably affects the evolution of the system including the time dependence of its entropy and the rate of entropy production $\frac{d_\mathrm{i}S}{dt}$. In the linear regime the latter quantity is usually represented in the following form: $\frac{d_\mathrm{i}S}{dt} = \sum\limits_k F_k J_k$ where J_k are flows and F_k are forces which give rise to these flows; the flows depend on the forces linearly: $J_k = \sum\limits_j L_{kj} F_j$ [Kondepudi, Prigogine, 1998]. The expressions for $\frac{d_\mathrm{i}S}{dt}$ obtained in this work depend on the microstate probability distribution (Eqs. (15a), (15b), (15c)). They have the form essentially different from that mentioned here. It indicates that the notion of the driving force of entropy production meets some challenges. The entropy itself is an integral index of a process of the equilibrium establishment in an isolated system rather than its driving force.

Appendix 1. Entropy in a neighborhood of its maximum at an arbitrary distribution of microstate probabilities

Consider an expression for entropy, when the microstate probabilities have the general form $P(l) = \frac{1}{L} + \Delta P(l)$ where deviations $\Delta P(l)$ are arbitrary:

$$S = -\sum_{l=1}^{L} \left(\frac{1}{L} + \Delta P(l)\right) \ln \left(\frac{1}{L} + \Delta P(l)\right). \tag{A.1.1}$$

According to the normalizing condition of Eq. (3), $\sum\limits_{l=1}^{L} \Delta P(l) = 0$. Earlier it was found: $S|_{\Delta P_l = 0} = \ln L$. Let us decompose S by $\Delta P(l)$ in the neighborhood of entropy maximum $S_{\max} = \ln L$ to square terms by $\Delta P(l)$:

$$S = S|_{\Delta P_l=0} + \sum_l \left.\frac{\partial S}{\partial(\Delta P_l)}\right|_{\Delta P_l=0} \Delta P_l +$$

$$+ \frac{1}{2}\left[\sum_l \left.\frac{\partial^2 S}{\partial(\Delta P_l)^2}\right|_{\Delta P_l=0} (\Delta P_l)^2 + 2 \sum_{l_1 \neq l_2} \sum_{l_2} \left.\underbrace{\frac{\partial^2 S}{\partial\left(\Delta P_{l_1}\right)\partial\left(\Delta P_{l_2}\right)}}_{=0}\right|_{\Delta P_{l_1}=0,\ \Delta P_{l_2}=0} \left(\Delta P_{l_1}\right)\left(\Delta P_{l_2}\right)\right] + \ldots$$

From Eq. (A.1.1) it follows that: $\frac{\partial S}{\partial(\Delta P_l)} = -\ln\left(\frac{1}{L}+\Delta P_l\right)-1$, $\frac{\partial^2 S}{\partial(\Delta P_l)^2} = -\frac{1}{\frac{1}{L}+\Delta P_l}$, $\frac{\partial^2 S}{\partial\left(\Delta P_{l_1}\right)\partial\left(\Delta P_{l_2}\right)} = 0$. Substituting these expressions into the equation for S decomposition, we obtain:

$$S = \ln L+(\ln L-1)\underbrace{\sum_{l=1}^{L}\Delta P_l}_{=0}-\frac{1}{2}L\sum_{l=1}^{L}(\Delta P_l)^2 = \ln L-\frac{1}{2}L\sum_{l}\left(\frac{1}{L}\right)^2\left(\frac{\Delta P_l}{\left(\frac{1}{L}\right)}\right)^2+\ldots = \ln L-\frac{1}{2}\frac{1}{L}\sum_{l=1}^{L}\left(\frac{\Delta P_l}{P_l}\right)^2+\ldots$$

Appendix 2. Eigenvalues of the matrix of a differential equation system for the case where the transitions between the microstates occur via a single (nodal) microstate

1°. Consider Eq. (11) for the eigenvalues, when the matrix of the kinetic equation system for $P^{\mathrm{tr}}(l, t)$ has the form of Eq. (23), the Lth row and Lth column of the matrix being eliminated:

$$\det\begin{pmatrix}
-\alpha_{1L}-\alpha_{L1}-\lambda & -\alpha_{L1} & -\alpha_{L1} & \cdots & -\alpha_{L1} & -\alpha_{L1}\\
-\alpha_{L2} & -\alpha_{2L}-\alpha_{L2}-\lambda & -\alpha_{L2} & \cdots & -\alpha_{L2} & -\alpha_{L2}\\
-\alpha_{L3} & -\alpha_{L3} & -\alpha_{3L}-\alpha_{L3}-\lambda & \cdots & -\alpha_{L3} & -\alpha_{L3}\\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots\\
-\alpha_{L(L-2)} & -\alpha_{L(L-2)} & -\alpha_{L(L-2)} & \cdots & -\alpha_{(L-2)L}-\alpha_{L(L-2)}-\lambda & -\alpha_{L(L-2)}\\
-\alpha_{L(L-1)} & -\alpha_{L(L-1)} & -\alpha_{L(L-1)} & \cdots & -\alpha_{L(L-1)} & -\alpha_{(L-1)L}-\alpha_{L(L-1)}-\lambda
\end{pmatrix}=0.$$

The matrix of this determinant has the size $(L-1)\times(L-1)$. The known property of any determinant is that its value does not change if one of its columns, being multiplied by any number, is added to some or all other columns. According to this rule, let us subtract the last column from all the remaining ones:

$$\det\begin{pmatrix}
-\alpha_{1L}-\lambda & 0 & 0 & \cdots & 0 & -\alpha_{L1}\\
0 & -\alpha_{2L}-\lambda & 0 & \cdots & 0 & -\alpha_{L2}\\
0 & 0 & -\alpha_{3L}-\lambda & \cdots & 0 & -\alpha_{L3}\\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots\\
0 & 0 & 0 & \cdots & -\alpha_{(L-2)L}-\lambda & -\alpha_{L(L-2)}\\
\alpha_{(L-1)L}+\lambda & \alpha_{(L-1)L}+\lambda & \alpha_{(L-1)L}+\lambda & \cdots & \alpha_{(L-1)L}+\lambda & -\alpha_{(L-1)L}-\alpha_{L(L-1)}-\lambda
\end{pmatrix}=0. \quad \text{(A.2.1)}$$

2°. To calculate this determinant, let us consider a matrix of an arbitrary size $N\times N$, which has zero and nonzero elements on the same places as the matrix in Eq. (A.2.1):

$$B=\begin{pmatrix}
b_{11} & 0 & 0 & \cdots & 0 & b_{1N}\\
0 & b_{22} & 0 & \cdots & 0 & b_{2N}\\
0 & 0 & b_{33} & \cdots & 0 & b_{3N}\\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots\\
0 & 0 & 0 & \cdots & b_{(N-1)(N-1)} & b_{(N-1)N}\\
b_{N1} & b_{N2} & b_{N3} & \cdots & b_{N(N-1)} & b_{NN}
\end{pmatrix}.$$

Here $N = L-1$. Let us decompose the determinant of this matrix by the elements of its first row:

$$\det B = b_{11}\det B^{(1)}+(-1)^{N+1}b_{1N}\det\widetilde{B},$$

where

$$B^{(1)} = \begin{pmatrix} b_{22} & 0 & 0 & \cdots & 0 & b_{2N} \\ 0 & b_{33} & 0 & \cdots & 0 & b_{3N} \\ 0 & 0 & b_{44} & \cdots & 0 & b_{4N} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & b_{(N-1)(N-1)} & b_{(N-1)N} \\ b_{N2} & b_{N3} & b_{4N} & \cdots & b_{N(N-1)} & b_{NN} \end{pmatrix},$$

$$\widetilde{B} = \begin{pmatrix} 0 & b_{22} & 0 & \cdots & 0 & 0 \\ 0 & 0 & b_{33} & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & b_{(N-2)(N-2)} & \cdots \\ 0 & 0 & 0 & \cdots & 0 & b_{(N-1)(N-1)} \\ b_{N1} & b_{N2} & b_{N3} & \cdots & b_{N(N-2)} & b_{N(N-1)} \end{pmatrix}.$$

The value of $\det \widetilde{B}$ can be easily calculated using its decomposition by its first column, which has a single nonzero element b_{N1}. The matrix corresponding to this element is diagonal and the factor (-1) is in the power $(N - 1) + 1 = N$:

$$\det \widetilde{B} = (-1)^N b_{N1} \prod_{l=2}^{N-1} b_{ll}.$$

Taking into account that $(-1)^{2N} = 1$, we obtain

$$\det B = b_{11} \det B^{(1)} - b_{1N} b_{N1} \prod_{l=2}^{N-1} b_{ll}. \tag{A.2.2}$$

The matrix $B^{(1)}$ has the same form as B, but its size is smaller by 1. Hence, this procedure can be repeated.

Next, we introduce the following notation:

k is the number of the fulfilled procedures decreasing the size of the matrix B (the algorithm steps);

b_{ij} are elements of the initial matrix B;

$B^{(k)}$ is a matrix obtained from B after k steps (correspondingly, $B^{(0)} = B$);

$b^{(k)}_{gh}$ are elements of the matrix $B^{(k)}$ (correspondingly, $b^{(0)}_{gh} = b_{gh}$);

$D = \det B$ is the determinant of the initial matrix B;

$D^{(k)} = \det B^{(k)}$ is the determinant of the matrix $B^{(k)}$ (correspondingly, $D^{(0)} = D$);

$N^{(k)}$ is the size of the matrix $B^{(k)}$.

The numerations of elements of matrices $B^{(k)}$ and B are related by: $b^{(k)}_{gh} = b_{(g+k)(h+k)}$. Sizes of matrices $B^{(k)}$ and B: $N^{(k)} = N - k$.

From (A.2.2) we obtain the recurrence relation:

$$D^{(k)} = b^{(k)}_{11} D^{(k+1)} - b^{(k)}_{1,N^{(k)}} b^{(k)}_{N^{(k)},1} \prod_{g=2}^{N^{(k)}-1} b^{(k)}_{gg}. \tag{A.2.3}$$

At $k = 0$ the expression (A.2.3) coincides with Eq. (A.2.1). Let us write Eq. (A.2.3) as

$$D^{(k)} = b^{(k)}_{11} D^{(k+1)} + w^{(k)}. \tag{A.2.3a}$$

Here $w^{(k)} = -b^{(k)}_{1,N^{(k)}} b^{(k)}_{N^{(k)},1} \prod_{g=2}^{N^{(k)}-1} b^{(k)}_{gg}$. To express $D^{(0)}$ (i. e., D) in terms of $D^{(k)}$, it is suitable to find first such expressions for several first numbers k.

1) Eq. (A.2.3a) gives an expression $D\left(D^{(1)}\right)$;

2) substituting $D^{(1)}\left(D^{(2)}\right)$ into $D\left(D^{(1)}\right)$, we find $D\left(D^{(2)}\right)$;

3) substituting then $D^{(2)}\left(D^{(3)}\right)$ into $D\left(D^{(2)}\right)$, we find $D\left(D^{(3)}\right)$; etc.

Generalizing the resulting expressions, we find the following interrelation:

$$D = \left(\prod_{q=0}^{k-1} b^{(q)}_{11}\right) D^{(k)} + \left[w^{(0)} + \sum_{q=1}^{k-1}\left(w^{(q)} \prod_{p=0}^{q-1} b^{(p)}_{11}\right)\right]. \tag{A.2.4}$$

To calculate D we need to use Eq. (A.2.4) at $k = N - 1$. Then the matrix $B^{(N-1)} = b_{NN}$ where b_{NN} is the last diagonal element of the initial matrix B, and $\det B^{(N-1)} = D^{(N-1)} = b_{NN}$. Taking the interrelation $b^{(k)}_{gh} = b_{(g+k)(h+k)}$ into account, we have: $b^{(q)}_{11} = b_{(q+1)(q+1)}$. Then the first summand in Eq. (A.2.4):

$$\left.\left(\prod_{q=0}^{k-1} b^{(q)}_{11}\right) D^{(k)}\right|_{k=N-1} = \left(\prod_{q=0}^{N-2} b_{(q+1)(q+1)}\right) D^{(N-1)} = \left(\prod_{q=1}^{N-1} b_{qq}\right) b_{NN} = \prod_{q=1}^{N} b_{qq}.$$

Similarly, using the above interrelations between the quantities b and N related both to every kth step and to the initial matrix B, we obtain

$$w^{(k)} = -b_{(k+1)N} b_{N(k+1)} \prod_{g=2}^{N-k-1} b_{(g+k)(g+k)}, \quad \sum_{q=1}^{k-1}\left(w^{(q)} \prod_{p=0}^{q-1} b^{(p)}_{11}\right) = -\sum_{q=2}^{N-1} b_{qN} b_{Nq} \prod_{\substack{g \neq q \\ g \neq N}} b_{gg},$$

from which

$$D = \prod_{q=1}^{N} b_{qq} - \sum_{q=1}^{N-1} b_{qN} b_{Nq} \prod_{\substack{g \neq q \\ g \neq N}} b_{gg}. \tag{A.2.5}$$

3°. We apply (A.2.5) to (A.2.1) taking into account that 1) $N = L - 1$ and 2) every product of the elements b_{ij} in Eq. (A.2.5) after substitution of b_{ij} by elements of the determinant Eq. (A.2.1) contains a factor $(-1)^{L-1}$ (in the second term of Eq. (A.2.5); the factor $(-1)^{L-1}$ includes a minus at $\sum_{j=1}^{N-1} \ldots$ as well). This factor will be cancelled. Then we obtain the following equation for the eigenvalues of the matrix of a kinetic equation system for $P^{\mathrm{tr}}(l, t)$:

$$(\alpha_{(L-1)L} + \alpha_{L(L-1)} + \lambda) \prod_{l=1}^{L-2} (\alpha_{lL} + \lambda) + \sum_{q=1}^{L-2} \alpha_{Lq} \prod_{l \neq q} (\alpha_{lL} + \lambda) = 0. \tag{A.2.6}$$

When $\alpha_{lL} = Ka$ and $\alpha_{Ll} = a$ ($l = 1 \div (L - 1)$) we have

$$\prod_{l=1}^{L-2} (Ka + \lambda) = \prod_{l \neq q} (Ka + \lambda) = (Ka + \lambda)^{L-2},$$

and (A.2.6) takes the form

$$(Ka+\lambda)^{L-2}[(L+K-1)a+\lambda]=0.$$

From this we obtain two λ values: $\lambda_1 = -(L+K-1)a$, $\lambda_2 = -Ka$. Here λ_1 is a simple root (its multiplicity equals 1), but λ_2 has the multiplicity $(L-2)$. From these λ values it can be seen that fast and relatively low transient processes are possible in the given system.

Let us consider full solutions for the transient processes under the given structure of transitions between the microstates. For $\lambda = \lambda_1$ a transient has the form $P^{\text{tr}}(l,t) = C_l^{(f)} e^{-(L+K-1)at}$ (the superscript (f) means that these $P^{\text{tr}}(l,t)$ are fast transients). The matrix (23) without the last row and last column is as follows:

$$\begin{pmatrix} -a-Ka & -a & -a & \cdots & -a & -a \\ -a & -a-Ka & -a & \cdots & -a & -a \\ -a & -a & -a-Ka & \cdots & -a & -a \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ -a & -a & -a & \cdots & -a-Ka & -a \\ -a & -a & -a & \cdots & -a & -a-Ka \end{pmatrix} = -a \begin{pmatrix} K+1 & 1 & 1 & \cdots & 1 & 1 \\ 1 & K+1 & 1 & \cdots & 1 & 1 \\ 1 & 1 & K+1 & \cdots & 1 & 1 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 1 & 1 & 1 & \cdots & K+1 & 1 \\ 1 & 1 & 1 & \cdots & 1 & K+1 \end{pmatrix}.$$

The quantities $\frac{dP^{\text{tr}}(l,t)}{dt}$ form a column:

$$-(K+L-1)a \begin{pmatrix} C_1^{(f)} \\ C_2^{(f)} \\ C_3^{(f)} \\ \vdots \\ C_{L-2}^{(f)} \\ C_{L-1}^{(f)} \end{pmatrix} e^{-(L+K-1)at}.$$

Substituting these expressions into the following system of equations

$$\sum_{\bar{l}=1}^{L-1} \left(r_{l,\bar{l}} - r_{l,L}\right) P^{\text{tr}}(\bar{l}, t) = \frac{dP^{\text{tr}}(l,t)}{dt} \qquad \text{(A.2.7)}$$

(see Eq. (8)) and cancelling $-ae^{-(L+K-1)at}$ results in a system of $L-1$ equations:

$$\begin{cases} -(L-2)C_1^{(f)} + C_2^{(f)} + C_3^{(f)} + \cdots + C_{L-2}^{(f)} + C_{L-1}^{(f)} = 0, \\ C_1^{(f)} - (L-2)C_2^{(f)} + C_3^{(f)} + \cdots + C_{L-2}^{(f)} + C_{L-1}^{(f)} = 0, \\ C_1^{(f)} + C_2^{(f)} - (L-2)C_3^{(f)} + \cdots + C_{L-2}^{(f)} + C_{L-1}^{(f)} = 0, \\ \vdots \\ C_1^{(f)} + C_2^{(f)} + C_3^{(f)} + \cdots - (L-2)C_{L-2}^{(f)} + C_{L-1}^{(f)} = 0, \\ C_1^{(f)} + C_2^{(f)} + C_3^{(f)} + \cdots + C_{L-2}^{(f)} - (L-2)C_{L-1}^{(f)} = 0. \end{cases}$$

Equation (9) gives the interrelation between the coefficients $C_l^{(f)}$:

$$\sum_{\bar{l}=1}^{L-1} C_l^{(f)} = -C_L^{(f)}. \qquad \text{(A.2.8)}$$

We attach (A.2.8) to the preceding equations. Then we obtain the following system of equations

$$(L-1)C_l^{(f)} + C_L^{(f)} = 0 \quad \text{for } l = 1 \div (L-1),$$

from which all the $C_l^{(f)}$ are identical and equal to $C_l^{(f)} = -\frac{1}{L-1}C_L^{(f)}$. The quantity $C_L^{(f)}$ remains a single constant for the solution vector $P^{\mathrm{tr}}(l,\,t) = C_l^{(f)}e^{-(L+K-1)at}$ to be determined from the initial conditions.

The eigenvalue $\lambda = \lambda_2$ has the multiplicity $(L-2)$. According to the known algorithm for the search for basic solutions of a system of linear differential equations [Tikhonov, Vasil'eva, Sveshnikov, 1980], in this case the solution should be searched for in the following form: $P^{\mathrm{tr}}(l,\,t) = \left[\sum\limits_{p=0}^{L-3} C_l^{(p)}t^p\right]e^{-Kat}$. Differentiating this expression by time gives

$$\frac{dP^{\mathrm{tr}}(l,\,t)}{dt} = -Ka\left[\sum_{p=0}^{L-3} C_l^{(p)}t^p\right]e^{-Kat} + \left[\sum_{p=1}^{L-3} pC_l^{(p)}a^p t^{p-1}\right]e^{-Kat} = \\ = \left\{-KaC_l^{(L-3)}t^{L-3} + \sum_{p=0}^{L-4}\left[-KaC_l^{(p)} + (p+1)C_l^{(p+1)}a^{p+1}\right]t^p\right\}e^{-Kat}.$$

Substituting both this expression and the above given matrix $\left(r_{l,\bar{l}} - r_{l,L}\right)$ into (A.2.5) and cancelling $-ae^{-Kat}$ yields

$$\begin{pmatrix} K+1 & 1 & 1 & \cdots & 1 & 1 \\ 1 & K+1 & 1 & \cdots & 1 & 1 \\ 1 & 1 & K+1 & \cdots & 1 & 1 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 1 & 1 & 1 & \cdots & K+1 & 1 \\ 1 & 1 & 1 & \cdots & 1 & K+1 \end{pmatrix} \begin{pmatrix} \sum\limits_{p=0}^{L-3} C_1^{(p)}t^p \\ \sum\limits_{p=0}^{L-3} C_2^{(p)}t^p \\ \sum\limits_{p=0}^{L-3} C_3^{(p)}t^p \\ \vdots \\ \sum\limits_{p=0}^{L-3} C_{L-2}^{(p)}t^p \\ \sum\limits_{p=0}^{L-3} C_{L-1}^{(p)}t^p \end{pmatrix} = \begin{pmatrix} KC_1^{(L-3)}t^{L-3} + \sum\limits_{p=0}^{L-4}\left[KC_1^{(p)} - (p+1)C_1^{(p+1)}a^p\right]t^p \\ KC_2^{(L-3)}t^{L-3} + \sum\limits_{p=0}^{L-4}\left[KC_2^{(p)} - (p+1)C_2^{(p+1)}a^p\right]t^p \\ KC_3^{(L-3)}t^{L-3} + \sum\limits_{p=0}^{L-4}\left[KC_3^{(p)} - (p+1)C_3^{(p+1)}a^p\right]t^p \\ \vdots \\ KC_{L-2}^{(L-3)}t^{L-3} + \sum\limits_{p=0}^{L-4}\left[KC_{L-2}^{(p)} - (p+1)C_{L-2}^{(p+1)}a^p\right]t^p \\ KC_{L-1}^{(L-3)}t^{L-3} + \sum\limits_{p=0}^{L-4}\left[KC_{L-1}^{(p)} - (p+1)C_{L-1}^{(p+1)}a^p\right]t^p \end{pmatrix}.$$

Then the terms on the left- and right-hand sides of this system at the identical powers of t should be equated. For $p = (L-3)$:

$$\begin{pmatrix} K+1 & 1 & 1 & \cdots & 1 & 1 \\ 1 & K+1 & 1 & \cdots & 1 & 1 \\ 1 & 1 & K+1 & \cdots & 1 & 1 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 1 & 1 & 1 & \cdots & K+1 & 1 \\ 1 & 1 & 1 & \cdots & 1 & K+1 \end{pmatrix} \begin{pmatrix} C_1^{(L-3)} \\ C_2^{(L-3)} \\ C_3^{(L-3)} \\ \vdots \\ C_{L-2}^{(L-3)} \\ C_{L-1}^{(L-3)} \end{pmatrix} = K\begin{pmatrix} C_1^{(L-3)} \\ C_2^{(L-3)} \\ C_3^{(L-3)} \\ \vdots \\ C_{L-2}^{(L-3)} \\ C_{L-1}^{(L-3)} \end{pmatrix},$$

from which

$$\begin{pmatrix} 1 & 1 & 1 & \cdots & 1 & 1 \\ 1 & 1 & 1 & \cdots & 1 & 1 \\ 1 & 1 & 1 & \cdots & 1 & 1 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 1 & 1 & 1 & \cdots & 1 & 1 \\ 1 & 1 & 1 & \cdots & 1 & 1 \end{pmatrix} \begin{pmatrix} C_1^{(L-3)} \\ C_2^{(L-3)} \\ C_3^{(L-3)} \\ \vdots \\ C_{L-2}^{(L-3)} \\ C_{L-1}^{(L-3)} \end{pmatrix} = 0,$$

i. e.,

$$\sum_{l=1}^{L-1} C_l^{(L-3)} = 0. \tag{A.2.9}$$

For $p = 0 \div (L - 4)$ we obtain similarly:

$$\begin{pmatrix} 1 & 1 & 1 & \cdots & 1 & 1 \\ 1 & 1 & 1 & \cdots & 1 & 1 \\ 1 & 1 & 1 & \cdots & 1 & 1 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 1 & 1 & 1 & \cdots & 1 & 1 \\ 1 & 1 & 1 & \cdots & 1 & 1 \end{pmatrix} \begin{pmatrix} C_1^{(p)} \\ C_2^{(p)} \\ C_3^{(p)} \\ \vdots \\ C_{L-2}^{(p)} \\ C_{L-1}^{(p)} \end{pmatrix} = -(p+1)a^p \begin{pmatrix} C_1^{(p+1)} \\ C_2^{(p+1)} \\ C_3^{(p+1)} \\ \vdots \\ C_{L-2}^{(p+1)} \\ C_{L-1}^{(p+1)} \end{pmatrix},$$

from which

$$\sum_{\bar{l}=1}^{L-1} C_{\bar{l}}^{(p)} = -(p+1)a^p C_l^{(p+1)}. \tag{A.2.10}$$

Summation of Eqs. (A.2.10) by l results in:

$$(L-1) \sum_{\bar{l}=1}^{L-1} C_{\bar{l}}^{(p)} = -(p+1)a^p \sum_{l=1}^{L-1} C_l^{(p+1)}. \tag{A.2.11}$$

Equation (A.2.11) is a recurrence relation. At $p = L-4$ the Eq. (A.2.11) gives: $(L-1) \sum\limits_{\bar{l}=1}^{L-1} C_{\bar{l}}^{(L-4)} =$ $= -(L-3)a^{L-4} \sum\limits_{l=1}^{L-1} C_l^{(L-3)}$. From this, using (A.2.7), we obtain: $\sum\limits_{l=1}^{L-1} C_l^{(L-4)} = 0$. Similarly: $\sum\limits_{l=1}^{L-1} C_l^{(p)} = 0$ for all $p = 0 \div (L-3)$. Further, from (A.2.10) it follows that for all $p = 0 \div (L-4)$ we have: $C_l^{(p+1)} = 0$, i. e., $C_l^{(p)} = 0$ for all $p = 1 \div (L-3)$. It is valid for $l = 0 \div (L-1)$, and, hence, according to (A.2.8), for $l = L$ as well.

It should be emphasized that the equality $C_l^{(p)} = 0$ relates to $p = 1 \div (L-3)$, but not to $p = 0$. Hence, the quantities $C_l^{(0)}$ are not equal to zero individually. A single requirement for $C_l^{(0)}$ is $\sum\limits_{l=1}^{L-1} C_l^{(0)} = 0$.

From the above it follows that although the eigenvalue $\lambda = \lambda_2 = -Ka$ has a high multiplicity, the corresponding basic solution has a simple form: $P^{\mathrm{tr}}(l, t) = C_l^{(0)} e^{-Kat}$.

The general expression for the rate of entropy production in this case is obtained by substituting Eqs. (20) into Eq. $\frac{d_{\mathrm{i}}S}{dt} = -\sum\limits_{l=1}^{L} \ln P(l, t) \frac{dP(l,t)}{dt}$ (see Eq. (15)):

$$\frac{d_{\mathrm{i}}S}{dt} = \sum_{l=1}^{L-1} (\alpha_{lL} P(l, t) - \alpha_{Ll} P(L, t)) \ln \frac{P(l, t)}{P(L, t)}. \tag{A.2.12}$$

Appendix 3. Eigenvalues of the matrix of a differential system of equations in the case where transitions between the microstates occur along a cycle in one-way direction

1°. In this case the quantities λ, present in the time dependence $P^{\mathrm{tr}}(l,\,t) = C_l e^{-\lambda t}$, are the eigenvalues of the matrix (30) and are the solutions of the following equation:

$$\det\begin{pmatrix} -(\alpha_{12}+\alpha_{L1})-\lambda & -\alpha_{L1} & -\alpha_{L1} & \cdots & -\alpha_{L1} & -\alpha_{L1} & -\alpha_{L1} \\ \alpha_{12} & -\alpha_{23}-\lambda & 0 & \cdots & 0 & 0 & 0 \\ 0 & \alpha_{23} & -\alpha_{34}-\lambda & \cdots & 0 & 0 & 0 \\ 0 & 0 & \alpha_{34} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & -\alpha_{(L-3)(L-2)}-\lambda & 0 & 0 \\ 0 & 0 & 0 & \cdots & \alpha_{(L-3)(L-2)} & -\alpha_{(L-2)(L-1)}-\lambda & 0 \\ 0 & 0 & 0 & \cdots & 0 & \alpha_{(L-2)(L-1)} & -\alpha_{(L-1)L}-\lambda \end{pmatrix} = 0.$$

Attention should be paid to the fact that the subscripts of the α's are not row and column numbers, they are numbers of microstates between which the transitions occur.

We begin solving this equation from an identical transform similar to that made in Appendix 2, viz., subtracting the last column of this determinant from all the remaining ones:

$$\det\begin{pmatrix} -\alpha_{12}-\lambda & 0 & 0 & \cdots & 0 & 0 & -\alpha_{L1} \\ \alpha_{12} & -\alpha_{23}-\lambda & 0 & \cdots & 0 & 0 & 0 \\ 0 & \alpha_{23} & -\alpha_{34}-\lambda & \cdots & 0 & 0 & 0 \\ 0 & 0 & \alpha_{34} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & -\alpha_{(L-3)(L-2)}-\lambda & 0 & 0 \\ 0 & 0 & 0 & \cdots & \alpha_{(L-3)(L-2)} & -\alpha_{(L-2)(L-1)}-\lambda & 0 \\ \alpha_{(L-1)L}+\lambda & \alpha_{(L-1)L}+\lambda & \alpha_{(L-1)L}+\lambda & \cdots & \alpha_{(L-1)L}+\lambda & \alpha_{(L-2)(L-1)}+\alpha_{(L-1)L}+\lambda & -\alpha_{(L-1)L}-\lambda \end{pmatrix} = 0. \tag{A.3.1}$$

2°. To calculate the latter determinant, we consider again an auxiliary $N \times N$ matrix B, which has zero and nonzero elements in the same places as the matrix in Eq. (A.3.1):

$$B = \begin{pmatrix} b_{11} & 0 & 0 & \cdots & 0 & 0 & b_{1N} \\ b_{21} & b_{22} & 0 & \cdots & 0 & 0 & 0 \\ 0 & b_{32} & b_{33} & \cdots & 0 & 0 & 0 \\ 0 & 0 & b_{43} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & b_{(N-2)(N-2)} & 0 & 0 \\ 0 & 0 & 0 & \cdots & b_{(N-1)(N-2)} & b_{(N-1)(N-1)} & 0 \\ b_{N1} & b_{N2} & b_{N3} & \cdots & b_{N(N-2)} & b_{N(N-1)} & b_{NN} \end{pmatrix}.$$

As earlier, $N = L - 1$. Decompose the determinant of this matrix by elements of the first row:

$$\det B = b_{11} \det B^{(*)} + (-1)^{N+1} b_{1N} \det H,$$

where

$$B^{(*)} = \begin{pmatrix} b_{22} & 0 & \cdots & 0 & 0 & 0 \\ b_{32} & b_{33} & \cdots & 0 & 0 & 0 \\ 0 & b_{43} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & b_{(N-2)(N-2)} & 0 & 0 \\ 0 & 0 & \cdots & b_{(N-1)(N-2)} & b_{(N-1)(N-1)} & 0 \\ b_{N2} & b_{N3} & \cdots & b_{N(N-2)} & b_{N(N-1)} & b_{NN} \end{pmatrix},$$

$$H = \begin{pmatrix} b_{21} & b_{22} & 0 & \cdots & 0 & 0 \\ 0 & b_{32} & b_{33} & \cdots & 0 & 0 \\ 0 & 0 & b_{43} & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & b_{(N-2)(N-2)} & 0 \\ 0 & 0 & 0 & \cdots & b_{(N-1)(N-2)} & b_{(N-1)(N-1)} \\ b_{N1} & b_{N2} & b_{N3} & \cdots & b_{N(N-2)} & b_{N(N-1)} \end{pmatrix}. \tag{A.3.2}$$

Matrices $B^{(*)}$ and H differ from matrices $B^{(1)}$ and $\widetilde{B}$ obtained in Appendix 2. Here

$$b_{11} \det B^{(*)} = b_{11} \prod_{n=2}^{N} b_{nn} = \prod_{n=1}^{N} b_{nn},$$

from which

$$\det B = \prod_{n=1}^{N} b_{nn} + (-1)^{N+1} b_{1N} \det H. \tag{A.3.3}$$

In this case, matrix H is not similar to matrix B as a consequence of which Eq. (A.3.3) is not a recurrence relation. To obtain such a relation, a further transformation of H is required. To avoid difficulties, which can be met during such a transformation, let us introduce a temporal designation h_{ij} for the elements of H and a separate numbering for h_{ij}. Then, $\det H$ takes the following form:

$$\det H = \det \begin{pmatrix} h_{11} & h_{12} & 0 & 0 & \cdots & 0 & 0 & 0 \\ 0 & h_{22} & h_{23} & 0 & \cdots & 0 & 0 & 0 \\ 0 & 0 & h_{33} & h_{34} & \cdots & 0 & 0 & 0 \\ 0 & 0 & 0 & h_{44} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & h_{(M-3)(M-2)} & 0 & 0 \\ 0 & 0 & 0 & 0 & \cdots & h_{(M-2)(M-2)} & h_{(M-2)(M-1)} & 0 \\ 0 & 0 & 0 & 0 & \cdots & 0 & h_{(M-1)(M-1)} & h_{(M-1)M} \\ h_{M1} & h_{M2} & h_{M3} & h_{M4} & \cdots & h_{M(M-2)} & h_{M(M-1)} & h_{MM} \end{pmatrix}, \tag{A.3.4}$$

where $M = N - 1$. Decomposing $\det H$ by elements of the first row, we obtain

$$\det H = h_{11} \det H^{(1)} - h_{12} \det \widetilde{H}^{(1)},$$

where

$$H^{(1)} = \begin{pmatrix} h_{22} & h_{23} & 0 & \cdots & 0 & 0 & 0 \\ 0 & h_{33} & h_{34} & \cdots & 0 & 0 & 0 \\ 0 & 0 & h_{44} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \ldots & h_{(M-3)(M-2)} & 0 & 0 \\ 0 & 0 & 0 & \ldots & h_{(M-2)(M-2)} & h_{(M-2)(M-1)} & 0 \\ 0 & 0 & 0 & \cdots & 0 & h_{(M-1)(M-1)} & h_{(M-1)M} \\ h_{M2} & h_{M3} & h_{M4} & \cdots & h_{M(M-2)} & h_{M(M-1)} & h_{MM} \end{pmatrix},$$

$$\widetilde{H}^{(1)} = \begin{pmatrix} 0 & h_{23} & 0 & \cdots & 0 & 0 & 0 \\ 0 & h_{33} & h_{34} & \cdots & 0 & 0 & 0 \\ 0 & 0 & h_{44} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & h_{(M-3)(M-2)} & 0 & 0 \\ 0 & 0 & 0 & \cdots & h_{(M-2)(M-2)} & h_{(M-2)(M-1)} & 0 \\ 0 & 0 & 0 & \cdots & 0 & h_{(M-1)(M-1)} & h_{(M-1)M} \\ h_{M1} & h_{M3} & h_{M4} & \cdots & h_{M(M-2)} & h_{M(M-1)} & h_{MM} \end{pmatrix}.$$

These matrices have the size $(M-1)\times(M-1)$. Decomposing $\det \widetilde{H}^{(1)}$ by elements of the first column, we obtain

$$\det \widetilde{H}^{(1)} = (-1)^{(M-1)+1} h_{M1} \det \begin{pmatrix} h_{23} & 0 & \cdots & 0 & 0 & 0 \\ h_{33} & h_{34} & \cdots & 0 & 0 & 0 \\ 0 & h_{44} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & h_{(M-3)(M-2)} & 0 & 0 \\ 0 & 0 & \cdots & h_{(M-2)(M-2)} & h_{(M-2)(M-1)} & 0 \\ 0 & 0 & \cdots & 0 & h_{(M-1)(M-1)} & h_{(M-1)M} \end{pmatrix} =$$

$$= (-1)^M h_{M1} \prod_{m=2}^{M-1} h_{m(m+1)}.$$

This yields $\det H = h_{11} \det H^{(1)} - (-1)^M h_{12} h_{M1} \prod_{m=2}^{M-1} h_{m(m+1)}$. Since $h_{12} \prod_{m=2}^{M-1} h_{m(m+1)} = \prod_{m=1}^{M-1} h_{m(m+1)}$, it follows that

$$\det H = h_{11} \det H^{(1)} - (-1)^M h_{M1} \prod_{m=1}^{M-1} h_{m(m+1)}. \tag{A.3.5}$$

The matrix $H^{(1)}$ is similar to H, but its size is smaller by unity. This procedure can be repeated more than once.

Next, we introduce the following notation:

k is the number of the procedures decreasing the size of the matrix H (the algorithm steps);

h_{ij} are the elements of the initial matrix H;

$H^{(k)}$ is the matrix obtained from H after k steps (hence, $H^{(0)} = H$);

$h_{gh}^{(k)}$ are the elements of the matrix $H^{(k)}$ (hence, $h_{gh}^{(0)} = h_{gh}$);

$D = \det H$ is the determinant of the initial matrix H;

$D^{(k)} = \det H^{(k)}$ is the determinant of the matrix $H^{(k)}$ (correspondingly, $D^{(0)} = D$);

$M^{(k)}$ is the size of the matrix $H^{(k)}$.

Numerations of elements of matrices $H^{(k)}$ and H are interrelated as follows: $h_{gh}^{(k)} = h_{(g+k)(h+k)}$. The sizes of matrices $H^{(k)}$ and H: $M^{(k)} = M - k$.

Generalizing Eq. (A.3.5) for any k, we find:

$$D^{(k)} = h_{11}^{(k)} D^{(k+1)} + (-1)^{M^{(k)}-1} h_{M^{(k)},1}^{(k)} \prod_{m=1}^{M^{(k)}-1} h_{m(m+1)}^{(k)}.$$

Using further interrelations $h_{gh}^{(k)} = h_{(g+k)(h+k)}$ and $M^{(k)} = M - k$, we obtain a recurrence relation for determinants $D^{(k)}$:

$$D^{(k)} = h_{(k+1)(k+1)} D^{(k+1)} + (-1)^{M-(k+1)} h_{M(k+1)} \prod_{m=1}^{M-(k+1)} h_{(m+k)(m+k+1)}.$$

To express D in terms of $D^{(k)}$, we apply the technique used in Appendix 2. The interim expression is

$$D = \prod_{g=1}^{k+1} h_{gg} D^{(k+1)} + (-1)^{M-1} \left[h_{M1} \prod_{m=1}^{M-1} h_{m(m+1)} + \sum_{p=1}^{k} (-1)^{-p} \left(\prod_{g=1}^{p} h_{gg} \right) h_{M(p+1)} \prod_{m=1}^{M-p-1} h_{(m+p)(m+p+1)} \right].$$

The size of D is M, and the size of $D^{(k+1)}$ is $M-(k+1)$. To obtain $D^{(k+1)} = h_{MM}$ (when the matrix retains only the last element of its main diagonal), it is necessary that $M - (k + 1) = 1$, from which $k = M - 2$. Then $\prod_{g=1}^{k+1} h_{gg} D^{(k+1)} = \left(\prod_{g=1}^{M-1} h_{gg} \right) h_{MM} = \prod_{g=1}^{M} h_{gg}$,

$$D = \prod_{g=1}^{M} h_{gg} + (-1)^{M-1} \left[h_{M1} \prod_{m=1}^{M-1} h_{m(m+1)} + \sum_{p=1}^{M-2} (-1)^{-p} \left(\prod_{g=1}^{p} h_{gg} \right) h_{M(p+1)} \prod_{m=1}^{M-p-1} h_{(m+p)(m+p+1)} \right].$$

Let us return to Eq. (A.3.2) for the matrix H. Interrelations for the quantities present in Eqs. (A.3.2) and (A.3.4) are $h_{pq} = b_{(p+1)q}$, $M = N - 1$, $N = M + 1$, from which:

$$\det H = D = \prod_{g=1}^{N-1} b_{(g+1)g} +$$
$$+ (-1)^{N-2} \left[b_{N,1} \prod_{m=1}^{N-2} b_{(m+1)(m+1)} + \sum_{p=1}^{N-3} (-1)^{-p} \left(\prod_{g=1}^{p} b_{(g+1)g} \right) b_{N(p+1)} \prod_{m=1}^{N-p-2} b_{(m+p+1)(m+p+1)} \right].$$

Finally, substituting the latter quantity into Eq. (A.3.3), then replacing the elements b by elements of the determinant Eq. (A.3.1) and cancelling $(-1)^{L-1}$, we obtain the equation for the eigenvalues of the matrix $r_{l,\bar{l}} - r_{l,L}$:

$$\prod_{n=1}^{L-1} \left(\alpha_{n(n+1)} + \lambda \right) + \alpha_{L1} \left(\alpha_{(L-2)(L-1)} + \alpha_{(L-1)L} + \lambda \right) \prod_{n=1}^{L-3} \alpha_{n(n+1)} + \alpha_{L1} \left(\alpha_{(L-1)L} + \lambda \right) \prod_{n=2}^{L-2} \left(\alpha_{n(n+1)} + \lambda \right) +$$
$$+ \alpha_{L1} \sum_{p=1}^{L-4} \left(\prod_{n=1}^{p} \alpha_{n(n+1)} \right) \left(\alpha_{(L-1)L} + \lambda \right) \prod_{m=p+2}^{L-2} \left(\alpha_{m(m+1)} + \lambda \right) = 0. \quad \text{(A.3.6)}$$

3°. Now let us consider the case where all α's are identical and equal to a. Then, taking the equality $a^{L-2}(2a+\lambda) = a^{L-1} + a^{L-2}(a+\lambda)$ into account, we obtain from Eq. (A.3.6):

$$(a+\lambda)^{L-1} + a^{L-1} + (a+\lambda)a^{L-2} + a(a+\lambda)^{L-2} + a\sum_{p=1}^{L-4}\left[(a^{p})\,(a+\lambda)^{L-2-p}\right] = 0.$$

Using a new index $k = L-2-p$ in the sum $\sum\limits_{p=1}^{L-4}\ldots$ and then dividing all the expression by a^{L-1}, we find

$$\left(1+\frac{\lambda}{a}\right)^{L-1} + 1 + \left(1+\frac{\lambda}{a}\right) + \left(1+\frac{\lambda}{a}\right)^{L-2} + \sum_{k=2}^{L-3}\left[\left(1+\frac{\lambda}{a}\right)^{k}\right] = 0.$$

Since $1 = \left(1+\frac{\lambda}{a}\right)^{0}$, this equation is equivalent to $\sum\limits_{k=0}^{L-1}\left[\left(1+\frac{\lambda}{a}\right)^{k}\right] = 0$, or, after the replacement of k by $k+1$:

$$\sum_{k=1}^{L}\left[\left(1+\frac{\lambda}{a}\right)^{k-1}\right] = 0. \tag{A.3.7}$$

Next, we apply the formula for the geometric progression sum $\sum\limits_{k=1}^{n}\beta_1 q^{k-1} = \frac{\beta_1(q^n-1)}{q-1}$, where β_1 is the first term of the progression and q is the geometric ratio. Equation (A.3.7) gives

$$\frac{\left(1+\frac{\lambda}{a}\right)^{L} - 1}{\frac{\lambda}{a}} = 0. \tag{A.3.8}$$

It should be taken into account that the value $\lambda = 0$ is inadmissible since it does not satisfy Eq. (A.3.7). Then Eq. (A.3.8) gives the equation for λ values:

$$\left(1+\frac{\lambda}{a}\right)^{L} = 1. \tag{A.3.9}$$

Extracting the root of the Lth degree should be done on the set of complex numbers. Let us represent the left-hand side of Eq. (A.3.9) in the form: $\left(1+\frac{\lambda}{a}\right)^{L} = e^{i2\pi k}$. Then $1+\frac{\lambda}{a} = e^{i\frac{2\pi}{L}k}$,

$$\lambda = a\left(-1+e^{i\frac{2\pi}{L}k}\right) = a\left[\left(-1+\cos\frac{2\pi}{L}k\right) + i\sin\frac{2\pi}{L}k\right]. \tag{A.3.10}$$

Since $\lambda \neq 0$, the values $k = 0$ and $k = L$ should be excluded due to which $\cos\frac{2\pi}{L}k \neq 1$.

The general expression for the rate of entropy production in this case is obtained by substitution of Eqs. (28) into the equation $\frac{d_{\mathrm{i}}S}{dt} = -\sum\limits_{l=1}^{L}\ln P(l,t)\frac{dP(l,t)}{dt}$ (see Eq. (15)):

$$\begin{aligned}\frac{d_{\mathrm{i}}S}{dt} = {}& -\alpha_{L1}P(L,t)\ln P(1,t) + \alpha_{12}P(1,t)\ln P(1,t) - \\ & -\sum_{l=2}^{L-1}\alpha_{(l-1)l}P(l-1,t)\ln P(l,t) + \sum_{l=2}^{L-1}\alpha_{l(l+1)}P(l,t)\ln P(l,t) - \\ & -\alpha_{(L-1)L}P(L-1,t)\ln P(L,t) + \alpha_{L1}P(L,t)\ln P(L,t).\end{aligned} \tag{A.3.11}$$

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