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Markovian Description of Irreversible Processes and the Time Randomization (*).

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Summary. — A certain class of kinetic equations, which describe the Markov-type irreversible evolution of the system, consistent with the second law of thermo¬dynamics and with the relaxation postulate, has been distinguished. The physical meaning of these kinetic equations is that they describe thermally activated processes. The time asymmetry, observed on the macrolevel as the thermodyna¬mical irreversibility of the process, is represented on the microlevel by the Markov-type randomization of the moments of the jump-like change of the microstates of the system. As an example, the thermodynamical interpretation of the one-particle stochastic model of the many-body system is discussed.

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1. - Introduction.

In the theory of thermally activated processes one usually describes the rate of the process by means of the Arrhenius law [1, 2]. However, the kinetic theory based on the Arrhenius law has not been discussed in the literature. One of the purposes of this paper is to discuss such a theory, which is obtained by inserting the Arrhenius formula into the collision rates of the kinetic equation. We show that the kinetic equations obtained in that manner are consistent with the second law of thermodynamics, but exhibit an important difference compared with classical theory: in the classical kinetic theory the entropy increases along the solutions of the kinetic equation, whereas in our case the irreversibility is described by the fact that the free energy decreases in time.

The second and more fundamental purpose of this paper is to show how does the Arrhenius law occur naturally, as a result of a discussion of relations between the

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principles of thermodynamics and the structure of evolution described by a Markov process. From everyday experience and from phenomenological physics we know that macroscopics systems relax to the state of thermodynamical equilibrium according to the principles of thermodynamics. This general observation does not specify which mathematical model describes the time evolution of a physical system. In this paper we shall consider such systems, the time evolution of which is described by such Markov processes whose behaviour is consistent with the principles of thermodynamics. This leads to the notion of thermodynamically permitted Markov processes. A certain class of such processes, which describe the thermally activated phenomena, is introduced in sect. 4.

Before formulating a notion of a thermodynamically permitted Markov process, we shall shortly review some useful definitions. As is well known, the thermodynamical irreversibility is described by the second law of thermodynamics:

$$\mathrm{d}S = \delta_i S + \delta_e S, \qquad \delta_i S \geq 0, \tag{1.1}$$

where $\mathrm{d}S$ is the total increment of the entropy S, whereas $\delta_e S$ and $\delta_i S$ are its increments due to interaction of the system with the environment and due to the existence of irreversible processes in this system, respectively.

Usually, randomness of a state of a system is described by a probabilistic measure defined on the space of microstates, whereas the time evolution is described by the action of the one-parameter semi-group (which describes translations in time) in the space of measures. This evolution can be either «deterministic» or «random»; in this paper we shall discuss the case in which the randomness of microstate dynamics takes the form of a Markov process with values in the space of microstates X. The probabilistic representation of microscopic description is then the so-called Markov semi-group; this semi-group is defined by the conditional probabilities of passing from one microstate to another (see sect. 2).

In order to compare the microscopic description with the thermodynamical description, one has to define the probabilistic representation of the state of the thermodynamical equilibrium relation

$$F = E - \theta S, \tag{1.2}$$

between the free energy F, the internal energy E, the temperature θ and the entropy S.

Let us denote by $D_\mu(X)$ the set of probabilistic measures on X which are specified by densities computed with respect to certain distinguished measure μ on X

$$D_\mu(X) = \left\{ f: X \to R, f \geq 0, \int_X f(x)\,\mathrm{d}\mu(X) = 1 \right\}. \tag{1.3}$$

If every microstate $x \in X$ has its own energy E_x, then we can define the mean-energy functional

$$E: D_\mu(X) \to R, \quad E(p) = \int_X e(x)\,p(x)\,\mathrm{d}\mu(x), \qquad e(x) = E_x \tag{1.4}$$

and we can distinguish the class of probabilistic measures giving the same value of

the mean energy equal to the equilibrium internal energy value:

$$D_{\mu,E}(X) = \{p \in D_\mu(X): E(p) = E\}. \tag{1.5}$$

It is well known that the Boltzmann entropy functional defined by

$$S: D_\mu(X) \to R, \quad S(p) = \int_X s(p(x))\, d\mu(x), \quad s(z) = \begin{cases} -k_B z \ln z, & \text{for } z > 0, \\ 0, & \text{for } z = 0, \end{cases} \tag{1.6}$$

takes the maximum value, consistent with the fixed value of the mean energy:

$$\exists \pi \in D_{\mu,E}(X), \quad \forall p \in D_{\mu,E}(X), \quad S(p) \leq S(\pi), \tag{1.7}$$

on the so-called canonical Gibbs distribution π of the following form:

$$\pi(x) = Z^{-1} \exp[-\beta E_x / k_B], \quad Z = \int_X \exp[-\beta E_x / k_B]\, d\mu(x), \tag{1.8}$$

where k_B is the Boltzmann constant; for sufficiently smooth distributions, equality in (1.7) implies that $p = \pi$ a.e. on X [3, 4].

The thermodynamical relation (1.2) is obtained with the help of the following assumptions:

$$\begin{aligned} F &= -k_B \beta^{-1} \ln Z, & \beta &= \theta^{-1}, \\ S &= S(\pi), & E &= E(\pi). \end{aligned} \tag{1.9}$$

Now we can define the thermodynamically permitted Markov process. First of all, such process should be consistent with the second law of thermodynamics. This condition can be formulated in the following way. Let $P^T = \{P^t, t \in T\}$, denote the Markov semi-group,

$$P^t: D_\mu(X) \to D_\mu(X), \quad \forall r, s \in T, \quad P^r \circ P^s = P^{r+s}, \quad P^0 = \mathrm{id}_{D_\mu(X)}. \tag{1.10}$$

Let us calculate the Boltzmann entropy and the mean energy along a trajectory of the Markov semi-group $P^T = \{P^t, t \in R_+\}$ (eqs.(1.3) and (1.10))

$$S(t) = S(P^t p_0), \quad E(t) = E(P^t p_0), \tag{1.11}$$

where $p_0 \in D_\mu(X)$ is an initial distribution; $E(p)$ and $S(p)$ are defined by (1.4) and (1.6). If the environment of the system is a thermostat, then we can generalize the equilibrium definition of the free energy to the nonequilibrium situation. Namely, if θ is the temperature of the thermostat, then we put

$$F(p) = E(p) - \theta S(p), \quad F(t) = F(P^t p_0). \tag{1.12}$$

We can also calculate the Boltzmann entropy increment $\partial_e S$ due to interaction of the system with environment:

$$\partial_e S = \theta^{-1} \partial Q, \tag{1.13}$$

where ∂Q is the heat increment. The Boltzmann entropy increment $\partial_i S$ due to the

existence of irreversible processes in the system can be calculated from eqs. (1.1) and (1.11)-(1.13):

$$\delta_i S = -\theta^{-1}\,\mathrm{d}F + \theta^{-1}(\mathrm{d}E - \delta Q) \geqslant 0\,. \tag{1.14}$$

So, if the interaction of the system with the environment has only thermal character, that is if the first law of thermodynamics takes the following form:

$$\mathrm{d}E = \delta Q\,, \tag{1.15}$$

then the Markov processes is consistent with the second law of thermodynamics if and only if the free energy functional is nonincreasing along the trajectories of the Markovian semi-group:

$$\forall t \in R_+\,, \qquad \dot{F}(t) \leqslant 0\,. \tag{1.16}$$

Such functionals are called *H*-functions. In sect. 4 we shall see that such description of a nonequilibrium system is consistent, *e.g.*, with the theory of thermally activated processes.

The Markov process should be also consistent with the postulate of the existence of the equilibrium state. It means that the Gibbs distribution should be a stationary distribution of the Markovian semi-group, *i.e.*

$$\forall t \in T\,, \quad P^t \pi = \pi\,, \tag{1.17}$$

where $T = R_+$, and that this semi-group has exactly one stationary distribution. Further on, we assume additionally that the process will relax, independently of the choice of the initial condition, towards the state of thermodynamical equilibrium:

$$\forall p_0 \in D_\mu(X)\,, \quad \lim_{t\to\infty} P^t p_0 = \pi\,. \tag{1.18}$$

The above relaxation postulate should be treated as the additional thermodynamic postulate that defines the notion of thermodynamical equilibrium more precisely [5].

Finally, by the *thermodynamically permitted Markov process* we will call the Markov process consistent with the second law of thermodynamics, with the postulate of the existence of the equilibrium state, with the relaxation postulate and with the assumption of the thermal interaction between the system and the environment. The Markov semi-group of such Markov process will be called *thermodynamically permitted Markov semi-group.*

The semi-group character of the evolution of the thermodynamically permitted Markov process represents the thermodynamical irreversibility on the macrolevel. In sect. 3 it is shown that this irreversibility can be represented on the microlevel by the Markov-type randomization of the moments of the jumplike change of the microstates of the system. This randomization is strictly related with the so-called embedded chains of the thermodynamically permitted Markov processes. All considerations of this paper are restricted to the systems with the countable set of states.

2. - The Markov semi-group and the kinetic equation.

We shall call the *state space* of the system the space of the form $X_\mu = (X, \Gamma, \mu)$ where X is a certain set (countable or of the cardinality of the continuum), Γ is a σ-algebra of subsets of X and $\mu: \Gamma \to R_+$ is a σ-finite nonnegative measure. By $L_\mu(X)$ we shall denote the linear space of such measurable functions $f: X \to R$ that

$$\|f\| = \int_X |f(x)|\, \mathrm{d}\mu(x) < \infty , \tag{2.1}$$

considered as the normed space with the norm (2.1). In particular, if X is a countable set (card $X \leqslant \aleph_0$), then Γ is a set of all subsets of X. The so-called counting measure is then defined by

$$\mu(A) = \begin{cases} \operatorname{card} A , & \text{if } \operatorname{card} A < \aleph_0 , \\ \infty , & \text{if } \operatorname{card} A = \aleph_0 , \end{cases} \tag{2.2}$$

and is a nonnegative σ finite measure [6]. For this measure (2.1) takes the form

$$\|f\| = \sum_{x \in X} |f(x)| < \infty . \tag{2.3}$$

The *Markov operator* is a linear mapping $P: L_\mu(X) \to L_\mu(X)$ such that if $f \in L_\mu(X)$ $f \geqslant 0$, then $Pf \geqslant 0$ and $\|Pf\| = \|f\|$ [7]. Let T be a nontrivial semi-group of non-negative real numbers, that is $T \neq \{0\}$ and $t_1 \pm t_2 \in T$ for $t_1 \geqslant t_2 \in T$. By the *stochastic semi-group* we mean the semi-group $\{P^t\}_{t \in T}$ of Markov operators (cf. eq. (1.10)). By the *stationary density* we mean a function $\pi \in D_\mu(X)$ (eq. (1.3)) fulfilling condition (1.17). A stochastic semi-group is called *asymptotically stable* if there exists exactly one stationary density π and [7]

$$\forall f \in D_\mu(X), \quad \lim_{t \to \infty} \|P^t f - \pi\| = 0 . \tag{2.4}$$

A stochastic semi-group can be generated by the Markov process with the values in the state space X. We shall call this kind of stochastic semi-group the *Markov semi-group*. In the case, when the state space is countable and μ is the counting measure, this semi-group can be defined by the family of the so-called stochastic kernels $K_t: X \times X \to R$, satisfying for every $t \in T$ and $x, y \in X$ the following Chapman-Kolmogorov equation [7]:

$$K_{t+s}(x, y) = \sum_{z \in X} K_t(x, z)\, K_s(z, y), \quad \sum_{y \in X} K_t(x, y) = 1, \quad K_t(x, y) \geqslant 0 , \tag{2.5}$$

where

$$\forall t, s \geqslant 0, \quad \forall x, y \in X, \quad K_t(x, y) = P(x_{t+s} = y \mid x_s = x) . \tag{2.6}$$

The Markov operators P^t, $t \in T$, are then defined by

$$\forall f \in L_\mu(X), \quad P^t f(y) = \sum_{x \in X} f(x)\, K_t(x, y) . \tag{2.7}$$

From eq. (2.6) it follows that the considered Markov process (called also a Markov chain if X is a countable set) is homogeneous in time.

For this chain

$$p_x(t) = P(x_t = x) = P^t p(x), \quad \sum_x p_x = 1, \quad p_x = p(x) = P(x_0 = x), \tag{2.8}$$

where $p \in D_\mu(X)$ is the initial distribution.

We shall assume that the stochastic kernels satisfy the following condition ensuring the stochastic continuity of the Markov process and its transition, with nonzero probability, through any arbitrary pair of states $x, y \in X$:

$$\forall x, y \in X, \quad K_t(x, y) \not\equiv 0, \quad \lim_{t \searrow 0} K_t(x, y) = \delta_{xy}, \qquad t \in T, \tag{2.9}$$

where δ_{xy} is the Kronecker symbol. Then [8]

$$\forall t > 0, \quad \forall x, y \in X, \quad K_t(x, y) > 0 \tag{2.10}$$

and

$$\forall f \in L_\mu(X), \quad \lim_{t \searrow 0} P^t f = f. \tag{2.11}$$

From the condition (2.10) additionally there follows the existence of the limit distibution $p_* = (p_{*x}, x \in X)$ defined by

$$\forall x, y \in X, \quad \lim_{t \searrow 0} K_t(x, y) = p_{*y} \tag{2.12}$$

and such, that [8] either for any $x \in X$, $p_{*x} = 0$, **or** $p_{*x} > 0$ for any $x \in X$ and the Markov semi-group is asymptotically stable with the stationary distribution p_*; in this second case p_* is called *ergodic distribution* (for the Markov process), and the Markov process, possessing such distribution, is called the *ergodic Markov process*. In the following we shall assume the ergodicity of the Markov process. Note that an ergodic distribution can be uniform only in such a case, when the state space is finite. Then the condition

$$\forall x \in X, \quad p_{*x} = \frac{1}{\mu(X)}, \tag{2.13}$$

is equivalent to the condition of the so-called double stochasticity of the transition matrix (cf. eq.$(2.5)_z$):

$$\sum_{x \in X} K_t(x, y) = 1. \tag{2.14}$$

We shall also assume the existence and finitness of the so-called *exit intensities* $w(x)$, $x \in X$ (from the states $x \in X$ of the system):

$$\forall x \in X, \quad w(x) = -\frac{\mathrm{d}}{\mathrm{d}t} K_t(x, x)\Big|_{t=0_+} < \infty. \tag{2.15}$$

Then the function $t \to K_t(x, y)$ has on R_+ continuous derivative [9] and the so-called *transition intensities* $W(x, y)$, $x \neq y$, from the state x to the state y are defined; they are given by

$$W(x, y) = \frac{\mathrm{d}}{\mathrm{d}t} K_t(x, y)\Big|_{t=0_+} \tag{2.16}$$

and the properties

$$w(x) = -W(x, x) = \sum_{x \neq y \in X} W(x, y) > 0, \quad W(x, y) \geq 0, \qquad \text{for } x \neq y, \tag{2.17}$$

are satisfied. Under the above assumptions the probabilities $p_x(t)$ given by (2.8) satisfy the so-called *Kolmogorov equation* [9]:

$$\begin{aligned} (dp_x/dt)(t) &= -w(x)\, p_x(t) + \sum_{x \neq y \in X} p_y(t)\, W(y, x), \\ p_x(0) &= p_x, \qquad t \in R_+, \qquad p_x = dp_x/dt. \end{aligned} \tag{2.18}$$

This equation has the physical meaning of the *kinetic equation*, describing the statistical evolution of the system on the basis of the balance of the intensities of reaching and leaving the states of the system.

From (2.17) it follows that eq. (2.18) can be written in the following form:

$$(dp_x/dt)(t) = \sum_{x \neq y \in X} (p_y(t)\, W(y, x) - p_x(t)\, W(x, y)). \tag{2.19}$$

From the uniqueness of the stationary distribution for the asymptotically stable Markov semi-group and from (2.19) it follows that the distribution $p_* \in D_\mu(X)$ will be ergodic if the following condition is satisfied:

$$\forall x, y \in X, \quad x \neq y\colon W(x, y) > 0, \quad p_{*x} W(x, y) = p_{*y} W(y, x). \tag{2.20}$$

Condition (2.20) is called the condition of *microscopic reversibility* (or the condition of detailed balance) since the process of statistical evolution of the system, with the initial condition described by the distribution p_* defined by (2.20), is reversible in time that is (cf. (2.4) and (2.11)) the change of the time direction does not affect the sequence of instantaneous statistical ensembles [10]. The Markov semi-group, satisfying the conditions (2.9), (2.15) and (2.20), will be called *microscopically reversible*. For such semi-group, the so-called equilibrium constants k_{xy} of the system are defined by [4]

$$k_{xy} = \frac{W(x, y)}{W(y, x)} = \frac{p_{*y}}{p_{*x}}. \tag{2.21}$$

Note, that the case $k_{xy} = 1$ for arbitrary $x, y \in X$ can take place only for the finite state space.

Let us denote by L the linear operator in the Banach space $L_\mu(X)$ defined as

$$Lf(x) = -w(x) f(x) + \sum_{x \neq y \in X} f(y)\, W(y, x). \tag{2.22}$$

The operator L (in general unbounded) is the generator of the Markov semi-group defined by the conditions (2.9) and (2.15), that is

$$Lf = \lim_{t \searrow 0} t^{-1} (P^t - I) f, \tag{2.23}$$

where I denotes the identity mapping in $L_\mu(X)$. It is easy to observe that if the exit intensities are commonly bounded:

$$\exists w_0 > 0, \quad \forall x \in X, \quad w(x) \leq w_0, \tag{2.24}$$

then the operator L is bounded and $\|L\| \leqslant 2w_0$. The Markov operators P^t have then the exponential form [8]:

$$P^t = \exp[tL], \quad \exp[tL] = \sum_{n=0}^{n=\infty} \frac{t^n}{n!} L^n, \qquad L^0 = I. \tag{2.25}$$

The existence of the kinetic equations of the form (2.18) is an important fact from the point of view of the physical applications of the semi-group description of irreversible processes. It follows from the following form of the transition pobabilities [9]:

$$\begin{aligned} P(x_{t+h} = y \,|\, x_t = x) &= P(x_h = y \,|\, x_0 = x) = W(x, y)\, h + o(h), \\ P(x_{t+h} \neq y \,|\, x_t = y) &= P(x_h \neq y \,|\, x_0 = y) = w(y)\, h + o(h), \end{aligned} \tag{2.26}$$

where $o(h)/h \to 0$ for $h \to 0$, uniformly with respect to $x \in X$ for given $y \in X$, and $x \neq y$. Hence in this case the description of the irreversible evolution of the system can be reduced to the investigation of its behaviour for the short time periods, that is to the formulation of the physical hypothesis about the form of the transition probabilities $W(x, y)$.

3. - The embedded Markov chain.

Let X_μ be a countable state space with the counting measure (sect. 2) and $\{P^t\}_{t \in T}$ $T = R_+$ asymptotically stable Markov semi-group satisfying the conditions (2.9), (2.15) and additionally the condition (cf. (2.17) and (2.20))

$$\forall x \neq y \in X_\mu, \quad W(x, y) > 0. \tag{3.1}$$

Let $\{x_t\}_{t \in T}$ be the ergodic Markov process corresponding to this Markov semi-group (sect. 2). Since the condition (2.9) is equivalent to the assumptions of the separability and stochastic continuity of the considered Markov process, then its realizations $\Omega \in \omega\colon t \to x_t(\omega) \in X$ (where Ω denotes the probabilistic space of elementary events) are step-functions and for every $x \in X_\mu$, $s \in R_+$

$$\forall \tau > 0, \quad P(x_t = x,\ s < t < s + \tau \,|\, x_s = x) = \exp[-w(x)\tau], \tag{3.2}$$

where $w(x)$ is defined by formulae (2.15)-(2.17). Hence, denoting by $\tau_{x|t}(\omega)$ the residence time of the process in the state x under the condition of reaching this state in the moment t,

$$\tau_{x|t}(\omega) = \inf\{\tau > 0\colon x_t(\omega) = x \wedge x_{t+\tau}(\omega) \neq x\}, \tag{3.3}$$

we obtain (independently on the choice of the moment t):

$$p_x(t) = P(x_t = x) > 0 \Rightarrow P(\tau_{x|t} < \tau) = F_x(\tau), \tag{3.4}$$

where

$$F_x(\tau) = \int_0^\tau f_x(s)\, ds, \quad f_x(s) = w(x) \exp[-w(x)\, s]. \tag{3.5}$$

We may assume, without losing generality, that the realisations $\omega\colon t \to x_t(\omega)$ are (with probability 1) right-hand continuous step functions. Then there exists such sequence of the random moments $t_n(\omega)$, $n = 0, 1, \ldots$ that, if we denote (cf. eq. (3.3))

$$x_n(\omega) = x_{t_n(\omega)}(\omega), \quad \tau_n(\omega) = \tau_{x_n(\omega)|t_n(\omega)}(\omega) \qquad n = 1, 2, \ldots, \tag{3.6}$$

then

$$\begin{aligned} &x_t(\omega) = x_n(\omega) && \text{for } t_n(\omega) \leqslant t \leqslant t_{n+1}(\omega), \ n = 0, 1, \ldots, \\ &t_n(\omega) = \sum_{i=0}^{n-1} \tau_i(\omega), && n = 1, 2, \ldots, \ t_0(\omega) = 0. \end{aligned} \tag{3.7}$$

The Markovian chain (with the discrete time $T = N = \{0, 1, 2, \ldots\}$) $\{x_n\}_{n \in N}$ is called the *embedded Markov chain* of a Markov process $\{x_t\}_{t \in R_+}$. The transition probabilities $Q(x, y)$ for this chain are given by [9]

$$Q(x, y) = P(x_{n+1} = y \mid x_n = x) = \begin{cases} \dfrac{W(x, y)}{w(x)}, & \text{for } x \neq y, \\ 0, & \text{for } x = y \end{cases} \tag{3.8}$$

and initial probabilities are the same as for the chain with the continuous time:

$$P(x_0 = x) = p_x(0) = p_x. \tag{3.9}$$

The matrix $Q = \|Q(x, y);\ x, y \in X\|$ is called the *jump matrix*. Let us denote

$$t_\infty(\omega) = \lim_{n \to \infty} t_n(\omega). \tag{3.10}$$

In order to ensure that the considered Markov process could be defined for each time instant $t > 0$ should be $t_\infty(\omega) = \infty$. If exit intensities are uniformly bounded (condition (2.24)), then [9]

$$P(t_\infty = \infty) = 1. \tag{3.11}$$

Condition (3.11) is satisfied, if the space is finite. If $t_\infty(\omega) < \infty$, then the Markov process $\{x_t\}_{t \in T}$ is defined on the random interval $T = \langle 0, t_\infty(\omega)\rangle$ and is called the interrupted Markov process [9].

Let us now consider the relation between the ergodicity of the embedded Markov chain and the ergodicity of the Markov process corresponding to it. The ergodicity of the embedded Markov chain is equivalent to the existence of such a distribution $\pi \in D_\mu(X)$, called the ergodic distribution, that [8] (cf. sect. 2)

$$\begin{aligned} &\sum_{x \in X} \pi_x Q(x, y) = \pi_y, \quad \sum_{x \in X} \pi_x = 1, && \pi_x > 0, \\ &\lim_{n \to \infty} Q^{(n)}(x, y) = \pi_y, \quad \sum_{y \in X} Q(x, y) = 1, \end{aligned} \tag{3.12}$$

where $Q^{(n)} = \|Q^{(n)}(x, y); x, y \in X\|$ is the n-th matrix power of the jump matrix, describing the n-step conditional transition probability for the embedded chain. Let us denote by $\tau(x)$ the mean residence time of the Markov process in the state x, that is (see (3.3)-(3.5))

$$\tau(x) = \int_0^\infty s \, dF_x(s) = \frac{1}{w(x)}. \tag{3.13}$$

From (3.12) it follows that

$$\pi_x = \lim_{n \to \infty} P(x_n = x). \tag{3.14}$$

If additionally

$$\tau = \sum_{x \in X} \pi_x \tau(x) < \infty, \tag{3.15}$$

then from (3.14) there follows the existence of the limit distribution $p_* \in D_\mu(X)$ for the Markov process with the continuous time [9]

$$p_{*x} = \lim_{t \to \infty} p_x(t), \qquad p_x(t) = P(x_t = x), \qquad \sum_{x \in X} p_{*x} = 1, \tag{3.16}$$

where this limit distribution is of the form

$$p_{*x} = \frac{\tau(x)}{\tau} \pi_x > 0 \tag{3.17}$$

and is identical with the ergodic distribution of the Markov process, defined by (2.12). The physical meaning of the condition (3.15) is the following. Let us denote by $\nu(t)$ the frequency of jumps of the Markov process $\{x_t\}_{t \in R_+}$ (see (3.7)) in the time interval $(0,t)$, that is

$$\nu(t) = \frac{N(t)}{t}, \tag{3.18}$$

where $N(t)$ is the number of jumps in the interval $(0,t)$. There exists a limit (with probability 1)[9]:

$$\nu_\infty = \lim_{t \to \infty} \nu(t) = \frac{1}{\tau} \neq 0. \tag{3.19}$$

Hence, (3.18) and (3.19) imply that in the limit of long times t the mean time τ has the meaning of the mean time between the consecutive jumps. We shall see in the following that this time determines the relaxation time of the system, whose statistical evolution is governed by the kinetic equation (2.18).

Therefore, if conditions (2.9), (2.15), (2.24), (3.1) and (3.15) are satisfied, then the Markov semi-group is determined by the Markov operators of the form (2.25) and it corresponds to the Markov process $x_t: \Omega \to X$, $t \in R_+$ with the jumplike change of states. Moreover, the jumplike character of the process is characterized by the embedded Markov chain and this is the case when the thermodynamical irreversibility exhibits itself on the microlevel in the randomization of the instants of time of the jumplike changes of the states of the system (see the Introduction).

4. - Thermodynamically permitted Markov semi-group.

The analysis, carried out in sect. 3, was based on the assumption that the Markov semi-group, corresponding to the kinetic equation (2.18), is asymptotically stable. It means that the stationary solution p_* of the kinetic equation is the ergodic distribution for the Markov process corresponding to this kinetic equation. In this section we shall confine our attention to the microscopically reversible Markov semi-group (sect. 2). In this case, the existence of the distribution $p_* > 0$ with the above properties is guaranted by the existence of the transition intensities $W(x, y)$ (condition (2.21)). We shall additionally assume that the exit intensities $w(x)$ are uniformly bounded on X (condition (2.24)), because it ensures the compatibility between the definition of the embedded Markov chain and the semigroup property of the solutions $p: R_+ \to D_\mu(X)$ of the kinetic equation. We shall also assume the existence of the finite mean time between the consecutive jumps of the considered Markov process (condition (3.15)). In this case the ergodic distribution p_* of the Markov process (with the continuous time) and the ergodic distribution π of the embedded Markov chain are related by (3.17).

In order to interpret the ergodic distribution as a statistical description of the asymptotic thermal equilibrium of the system, first one has to define the probabilistic representation of the state of thermodynamical equilibrium (see Introduction) in terms of the countable state space X_μ (sect. 2) and of the energy distributions $\varepsilon \in L_\mu(X)$, $\varepsilon \geqslant 0$, assigned to the microstates of the system.

Namely, according to eqs. (1.4) and (1.6), the mean energy E and the Boltzman entropy S functionals have the form

$$E(p) = \sum_{x \in X} p_x \varepsilon_x, \qquad S(p) = \sum_{x \in X} s(p_x), \qquad \sum_{x \in X} p_x = 1, \qquad p_x \geqslant 0, \tag{4.1}$$

where the notations $\varepsilon_x = \varepsilon(x)$, $p_x = p(x)$ have been applied. The canonical Gibbs distributions $\pi = \{\pi_x, x \in X\}$ have then the form (see eq. (1.8))

$$\pi_x = Z^{-1} \exp[-\beta \varepsilon_x / k_B], \quad Z = \sum_{x \in X} \exp[-\beta \varepsilon_x / k_B] \tag{4.2}$$

and, with the designations (1.9), we obtain the thermodynamical relation (1.2). The probabilistic representation (X_μ, π) defined in this way is called *canonical ensemble* (for the countable space) [12].

Let us assume that the ensemble (X_μ, π) determined by the ergodic embedded Markov chain (eq. (3.14)) is the canonical ensemble, that is that the distribution π **is of** the form (4.2) with $\beta = \theta^{-1}$. Equation (3.12) implies that the condition

$$\sum_{x \in X} (\pi_x Q(x, y) - \pi_y Q(y, x)) = 0, \tag{4.3}$$

must be satisfied, which justifies the assumption of the following analogue of the microscopic reversibility condition (2.20):

$$\forall x \neq y, \quad \pi_x Q(x, y) = \pi_y Q(y, x). \tag{4.4}$$

Condition (4.4) is satisfied if the transition probabilities $Q(x,y)$ are of the form

$$Q(x, y) = q(x, y) \exp[\varepsilon_x / k_B \theta], \quad q(x, y) = q(y, x), \qquad \varepsilon_x \geqslant 0, \ x \neq y. \tag{4.5}$$

Formula (4.5) can be written, without losing generality, in the form

$$Q(x, y) = \exp[-(E_{xy} - \varepsilon_x)/k_B\theta], \qquad E_{xy} = E_{yx} \geq 0, \tag{4.6}$$

where E_{xy} are quantities with the dimension of energy, such that

$$Z = \sum_{x \in X} Z_x < \infty, \quad Z_x = \sum_{x \neq y \in X} \exp[-E_{xy}/k_B\theta]. \tag{4.7}$$

We can assume, again without restricting the general character of our reasoning, that in the formula (3.13)

$$\tau(x) = w(x)^{-1} = \nu_*^{-1} \exp[-\sigma_x/k_B\theta], \qquad \sigma_x \geq 0, \tag{4.8}$$

where σ_x is a variable with the dimension of energy and ν_* is a certain constant with the dimension of frequency. From (3.8), (4.6) and (4.8) we obtain that the transition intensities $W(x, y)$ should be of the following form:

$$\begin{aligned} &\forall x \neq y, \quad W(x, y) = \nu_* \exp[-U_{xy}/k_B\theta], \\ &U_{xy} = E_{xy} - E_x, \\ &E_x = \varepsilon_x + \sigma_x \geq 0, \quad E_{xy} = E_{yx} > 0. \end{aligned} \tag{4.9}$$

Formula (4.9) has the form of the well-known law describing the frequency of the transition $x \to y$ in the theory of reaction dynamics and is applied, for example, to the description of the thermally activated processes [1, 2]. Basing on this observation, we shall interpret E_{xy} as the energy barrier between the microstates x and y, with own energies E_x and E_y respectively, whereas U_{xy} will be interpreted as the activation energy of the jumplike change of the microstates of the system from x to y. Then the constant ν_* has the meaning of the effective frequency of efforts to overcome the energy barrier [1, 2].

From (2.20) and (4.9) it follows that

$$p_{*x} = Z_*^{-1} \exp[-E_x/k_B\theta], \quad Z_* = \sum_{x \in X} \exp[-E_x/k_B\theta], \qquad E_x \geq 0. \tag{4.10}$$

Comparing eqs. (3.17), (4.2) (with $\beta = \theta^{-1}$), (4.8) and (4.10), we see that the constant ν_* should be of the form

$$\nu_* = \frac{Z_*}{Z}\tau^{-1}. \tag{4.11}$$

If F_* and F are free energies, associated with the canonical ensembles (X_μ, p_*) and (X_μ, π) respectively, and determined from the formula (1.9), then

$$F_* = F + k_B\theta \ln(\tau\nu_*). \tag{4.12}$$

From (4.11) and (4.12) we obtain the following representation of the effective frequency of efforts to overcome the energy barrier:

$$\nu_* = \nu_\infty \exp[-\Delta F/k_B\theta], \qquad \Delta F = F - F_*. \tag{4.13}$$

From the form of formula (4.13) it follows that the difference ΔF between the free energies of the canonical ensembles (X_μ, p_*) and (X_μ, π) has the meaning of the

so-called free energy of activation, considered in the theory of reaction dynamics [1]. Hence, we see that the effective frequency ν_* is a quantity which depends on ergodic distributions of both considered Markovian pictures of the microstate dynamics: Markov process $(x_t; t \geq 0)$ with continuous time and its embedded Markov chain $(x_n; n = 0, 1, 2, \ldots)$ which is a random sequence of values of that Markov process, taken in random moments t_n, $n = 0, 1, 2, \ldots$ (eq.(3.6)) Note that by introducing the constant τ_*, having the dimension of time, given by (cf. (3.19) and (4.13))

$$\tau_* = \nu_*^{-1} = \tau \exp[\Delta F / k_B \theta], \tag{4.14}$$

denoting $t_* = t/\tau_*$, $p_x(t) = \bar{p}_X(t_*)$ and introducing the notation

$$A_{xy} = \exp[-E_{xy}/k_B\theta] - A_y \text{ for } x \neq y, \quad A_{yx} = A_y = Z\pi_y + Z_y, \quad E_{xx} = \varepsilon_x = E_x - \sigma_x, \tag{4.15}$$

where Z_y is defined in (4.17), we can transform the eq. (2.18) to the following dimensionless form

$$\dot{\bar{p}}_x(t_*) = \sum_{y \in X} A_{xy} \exp[E_y/k_B\theta] \bar{p}_y(t_*), \tag{4.16}$$

where $\bar{p}_x(t_*) \to p_{*x}$ for $t_* \to \infty$, that is, for $t \gg \tau_*$. It means that τ_* has the meaning of the characteristic time of the relaxation process of the system towards the state of thermodynamical equilibrium; we shall call τ_* simply the *relaxation time.*

The Markov semi-group corresponding to the considered Markov process $(x_t; t \geq 0)$ is determined by eqs. (2.8), (2.18) with intensities of the form (4.8) and (4.9). It is an asymptotically stable stochastics semi-group (sect. 2) with the stationary distribution $p_* \in D_\mu(X)$ of the form (4.10). It is also the thermodynamically permitted Markov semi-group (cf. the Introduction). In order to see that let us consider the mean energy $E(t)$ and the mean entropy $S(t)$ along a solution $p: R_+ \to D_\mu(X)$ of the kinetic eq.(2.18):

$$\begin{aligned} E(t) &= \sum_{x \in X} p_x(t) E_x, \qquad p_x(t) > 0, \ t \in R_+, \\ S(t) &= \sum_{x \in X} s(p_x(t)) = -k_B \sum_{x \in X} p_x(t) \ln p_x(t). \end{aligned} \tag{4.17}$$

Then the following limits exist:

$$\begin{aligned} E_* &= \lim_{t \to \infty} E(t) = \sum_{x \in X} p_{*x} E_x = E(p_*), \\ S_* &= \lim_{t \to \infty} S(t) = -k_B \sum_{x \in X} p_{*x} \ln p_{*x} = S(p_*). \end{aligned} \tag{4.18}$$

Moreover, if F_* is the free energy associated with the canonical ensemble (X_μ, p_*) (eqs.(1.9) and (4.10)), then

$$F_* = E_* - \theta S_*. \tag{4.19}$$

If the generalized free energy associated with instantaneous nonequilibrium states is of the form (cf. eqs. (1.11) and (1.12))

$$F(t) = E(t) - \theta S(t), \tag{4.20}$$

where now θ is the temperature of the thermostat (see Introduction), then

$$F(t) - F_* = \theta H(t), \quad F_* = \lim_{t\to\infty} F(t), \tag{4.21}$$

where the notation

$$H(t) = H(p(t)), \quad H(t) = k_B \sum_{x\in X} p_x \ln(p_x/p_{*x}), \tag{4.22}$$

has been applied. It can be easily shown that the functional $p \to H(p)$ is nonincreasing along the solutions of the kinetic eq. (2.18) (with intensities (4.8) and (4.9)) and the second law of thermodynamics (eq. (1.1)) is fulfilled if we put

$$dS = \dot{S}(t)\,dt, \quad \delta_i S = -\dot{H}(t)\,dt, \quad \delta_e S = \theta^{-1}\dot{E}(t)\,dt. \tag{4.23}$$

From (1.15) and (4.23) it follows that in the considered processes

$$dS \geqslant \theta^{-1}\delta Q \tag{4.24}$$

and the equality sign in (4.24) corresponds to the reversible processes, that is to the case $\delta_i S = 0$ which is here equivalent to the condition

$$\forall t \in R_+, \quad \dot{H}(t) = 0, \tag{4.25}$$

determining the canonical equilibrium ensemble (X_μ, p_*)

In the considered process only the energy is exchanged between the system and its environment (the mass transfer does not take place — see Introduction), so the condition that the system is thermodynamically closed, takes the form

$$\forall t \in R_+, \quad \dot{E}(t) = 0. \tag{4.26}$$

In that case

$$\forall t \in R_+, \quad \dot{S}(t) \geqslant 0. \tag{4.27}$$

If the stochastic kernels $K_t(x, y)$ satisfy the condition of double stochasticity (2.14), then condition (4.27) is satisfied for the arbitrary solution of the considered kinetic equation; in such a case this equation is called *Pauli equation* [2]. For example, if the equilibrium constants (eq. (2.21)) fulfill the condition $k_{xy} = 1$ for every $x, y \in X$, then the state space is finite and the kinetic equation is the Pauli equation, describing the closed system, whose state of thermodynamical equilibrium is described by the uniform distribution (2.13).

Let us compute the rate of change of the internal energy of the system (see eq. $(4.17)_1$). It is easy to show that introducing the notations

$$\begin{aligned} &(L_E f)(x) = \sum_{y\in X} W_E(x, y) f_y \mu_E(y), \\ &W_E(x, y) = \nu_* A_{xy} \exp[(E_x + E_y)/k_B\theta], \qquad \mu_E(y) = \exp[-E_y/k_B\theta], \end{aligned} \tag{4.28}$$

where A_{xy} is defined by (4.15), we obtain

$$\dot{E}(t) = \sum_{x\in X} (L_E e)(x)\, p_x(t), \tag{4.29}$$

where $e: x \to e(x) = E_x$ denotes the energy distribution describing the canonical ensemble (X_μ, p_*). If the state space is finite, then eq.(4.29) implies the following relation:

$$\exists C = C(e, \theta) > 0, \quad \forall t \in R_+, \quad |\dot{E}(t)| \leqslant \nu_* C. \tag{4.30}$$

So, in this case, the rate of change of the internal energy, which is equivalent to the rate of exchange of the heat with the environment (eqs. (4.23) and (1.13)), is bounded.

Hence, the considered thermodynamically permitted Markov semi-group describes the thermodynamically irreversible process, which

1) takes place in the isothermal conditions (θ = const) and with the energy exchange (without exchange of mass) with surroundings ($\partial_e S = \theta^{-1} \mathrm{d}E$)

2) relaxes, independently of the choice of the initial conditions (cf. eqs. (2.4) and (3.16)), towards the state of thermal equilibrium described by the canonical ensemble (X_μ, p_*), where $p_* = \{p_{*x}, x \in X\}$ is defined by (4.10);

3) in the case of the finite state space it has the finite rate of the heat exchange with the surroundings (eqs. (1.13), (4.23) and (4.30));

4) on the microlevel exhibits the jumplike character of the change of states, described by the embedded Markov chain (sect. 3 and eqs. (4.6M4.8)).

5. - The system of mutually interacting particles.

In this section we shall consider a finite system of mutually interacting identical particles, whose dynamical behaviour is random. We shall assume that only such configurations of the system are allowable, which are subsets of a certain finite set X. We shall describe the neighbourhoods of the points of the configuration space (and, in consequence, also the neighbourhoods of the particles of the system) by distinguishing a family $\partial = \{\partial x; x \in X\}$ of the (finite) subsets of X such that [13]

a) $x \notin \partial x$,

b) $\forall x, y \in X, \quad y \in \partial x \Leftrightarrow x \in \partial y$.

The element $y \in \partial x$ is called the *neighbour* of x and the family ∂ the *system of neighbours* in X. By a *symplex* we mean such a set $S \subset X$ that [10, 13]

$$\forall x, y \in S, \quad x \neq y: y \in \partial x.$$

The set X will be called a *cube lattice*, if there does not exist in it any symplex containing more than two elements. For example, $X \subset Z^n$, Z—the set of integers, with $\partial x = \{y \in X: \|x - y\| = 1\}$, is the cube lattice in this sense. We shall denote the one-point set $\{x\}$ (so far as it would not become ambiguous), by x.

Let us denote by κ the injective mapping $\kappa: [1, m] \to X$, where $[1, m] = \{1, 2, \ldots, m\}$ is the set of m successive natural numbers. We shall call the mapping κ as well as the image $\kappa_m = \kappa([1, m])$ of the set $[1, m]$ under this mapping—the *m-particle configuration*. The injectivity of κ describes the exclusion of the possibility of finding two particles of the considered system in the same point $x \in X$. The identity of the particles will be taken into account in the following way. Let us denote by Γ the

set of all subsets of X together with their complements relative to X and with the empty set $\emptyset$, and by $K_m(X)$, $1 \leqslant m < \mu(X)$ the set of all m-particle configurations, that is

$$K_m(X) = \{(x_1, \ldots, x_m) \in X^m : x_i \neq x_j \text{ for } i \neq j\}.$$

The identity of the particles corresponds to the physical indistinguishability of the m-partiele configurations, differing by a permutation of the set $[1, m]$:

$$\kappa' \sim \kappa \Leftrightarrow \exists \sigma \in \Sigma_m, \qquad \kappa' = \kappa \circ \sigma,$$

where Σ_m denotes the set of all considered permutations. This is the equivalence relation in the set $K_m(X)$, whose set of equivalence classes can be identified with the family Γ_m of all subsets of X, containing exactly m elements:

$$\Gamma_m = \{A \in \Gamma : \operatorname{card} A = m\}.$$

The sets $A \in \Gamma_m$ will be called the *m-particle states* (of the system of identical particles). If we do not fix the number of (identical) particles, allowing the possibility of their creation and annihilation, then the set Γ should be taken as the state space of the system.

By the *potential* of mutual interactions of the (identical) particles we shall call the function $V: \Gamma \to R$, $V(\emptyset) = 0$. The function V will be called the *closest-neighbour potential* if for every $x, y \in X$, $y \notin \partial x$, and for every $A \subset X \setminus x \setminus y$, the following condition is fulfilled [10]:

$$V(A \cup x \cup y) = V(A \cup x) + V(A \cup y) - V(A). \tag{5.1}$$

If X is the cubic lattice, then the closest-neighbour potential can be written in the form

$$V(A) = \sum_{x \in A} \sum_{y \in A} \Phi(x, y), \tag{5.2}$$

where $\Phi: X \times X \to R$ is the symmetric potential describing the interactions of the particles [10].

Let $\{P^t\}_{t \in R_+}$ be the Markov semi-group defined by the stochastic kernels K_t: $\Gamma \times \Gamma \to R_+$, that is (cf. (2.7) and (2.8))

$$f_B(t) = P^t f(B) = \sum_{A \in \Gamma} f(A) K_t(A, B), \quad P^t: L_\mu(\Gamma) \to L_\mu(\Gamma). \tag{5.3}$$

We shall assume that the stochastic kernels satisfy the conditions (2.5) and (2.9) with Γ, A, B instead X, x, y, respectively. Condition (2.9) ensures the existence of the limit distribution p_*:

$$\forall A, B \in \Gamma, \quad \lim_{t \to \infty} K_t(A, B) = p_*(B) \geqslant 0, \tag{5.4}$$

but does not guarantee its normalization; that is, the asymptotic stability of the considered Markov semi-group is not ensured (see sect. 2). The stochastic kernels

univocally define the function $W: \Gamma \times \Gamma \to R$ such, that [10] (cf. (2.15)-(2.17))

$$\begin{aligned} &\forall A, B \in \Gamma, \quad A \neq B: W(A, B) \geqslant 0, \\ &\forall A \in \Gamma \sum_{B \in \Gamma} W(A, B) = 0; \qquad K_t = \exp[tW], \end{aligned} \tag{5.5}$$

where in $(5.5)_2$ the function W was identified with a square matrix $W = \|W(A, B); A, B \in \Gamma\|$ of the order $\mu(X) \times \mu(X)$ and the notation (2.25) with W instead L and with $I = \|\delta_{A,B}; A, B \in \Gamma\|$ has been applied. Condition $(5.5)_2$ means that the function W is a generator of the family of stochastic kernels $\{K_t\}_{t \in R_+}$. This generator is called *irreducible* if for arbitrary $A, B \in \Gamma$, $A \neq B$ there exists a sequence of sets $A_1, \ldots, A_n \in \Gamma$ such, that $A_1 = A$, $A_n = B$ and

$$\prod_{i=1}^{n-1} W(A_i, A_{i+1}) > 0. \tag{5.6}$$

If the generator W is irreducible, then the limit distribution p_* defined by (5.4) is the stationary density for the considered Markov semi-group (sect. 2). We shall relax the condition (2.20), defining the Markov semi-group is *microscopically reversible,* if[10]

$$\forall A, B \in \Gamma, \quad p_*(A) W(A, B) = p_*(B) W(B, A). \tag{5.7}$$

Condition (5.7) univocally defines the stationary density p_* of the Markov semi-group.

The random movement of m $(m < \mu(X))$ identical and mutually interacting particles through the points of the set X can be described, for example, in the following way [11]. Let us consider the stochastic kernels $\{K_t\}_{t \in R_+}$ describing the transformation of the m-particle states onto the m-particle states, that is the mappings $K_t: \Gamma_m \times \Gamma_m \to R_+$ and let us denote by d and P the following functions:

$$\begin{aligned} &d: X \times \Gamma \to R, \quad d(x, A) > 0, \qquad \text{for } x \notin A \in \Gamma \\ &P: X \times X \to \langle 0, 1\rangle, \quad P(x, y) = P(y, x), \quad P(x, x) = 0. \end{aligned} \tag{5.8}$$

We shall assume that P is irreducible in the sense analogical to the irreducibility of the generator W. Let us define the generator $W: \Gamma_m \times \Gamma_m \to R$ of the considered stochastic kernels by the following rule: if $A \in \Gamma_{m-1}$, $x, y \in X \setminus A$, $x \neq y$, then

$$W(A \cup x, A \cup y) = d(x, A) P(x, y) \tag{5.9}$$

and

$$W(A, B) = 0 \qquad \text{for all other } (A, B) \in \Gamma_m \times \Gamma_m, \ A \neq B. \tag{5.10}$$

We define $W(A, A)$ so that

$$\sum_{B \in \Gamma_m} W(A, B) = 0. \tag{5.11}$$

Since in the probabilistic interpretation (see (2.6) and (2.26))

$$\begin{aligned} &P(A_{t+s} = B \,|\, A_t = A) = K_s(A, B), \\ &P(A_{t+\mathrm{d}t} = B \,|\, A_t = A) = W(A, B)\,\mathrm{d}t + o(\mathrm{d}t), \qquad A \neq B, \end{aligned} \tag{5.12}$$

then $\mathrm{d}(x, A)\,\mathrm{d}t + o(\mathrm{d}t)$, $x \notin A \in \Gamma_{m-1}$ can be interpreted as the probability, that the particle, starting from the point x, will undergo, in the time interval $\langle t, t + \mathrm{d}t\rangle$, a transition to any other point, on the condition that in the time instant t the particles were contained in the set $A \cup x$, $A \in \Gamma_{m-1}$. If this particle undergoes any transition, then the probability that it would reach the point y, is $P(x, y)$. The probability that in the time interval $\langle t, t + \mathrm{d}t\rangle$ more than one transition will take place is equal to $o(\mathrm{d}t)$ The Markov semi-group, corresponding to the so defined generator W, is called the *m-particle semi-group;* $P = \|P(x, y);\, x, y \in X\|$ is called the *transition matrix* for this semi-group, and d—the *rate function* (of the transition) [10]. Since the generator W of the m-particle semi-group is irreducible (on Γ_m), then this stochastic semi-group is asymptotically stable (sect. 2). Then the m-particle semi-group is called the *m-particle closest neighbour semi-group* if

$$\forall x \notin A \in \Gamma, \quad d(x, A) = d(x, A \cap \partial x). \tag{5.13}$$

Theorem on the m-particle semi-group [10].

Let $\{P^t\}_{t \in R_+}$ be the m-particle semi-group with rate function d. Let us assume, that if $A \in \Gamma$, $x, y \in X \setminus A$, then

$$d(x, A \cup y)\, d(y, A) = d(y, A \cup x)\, d(x, A). \tag{5.14}$$

Then

a) There exists exactly one potential V, such that

$$\forall x \notin A \in \Gamma, \quad d(x, A) = \nu_* \exp[V(A \cup x) - V(A)], \tag{5.15}$$

where ν_* is a constant with the dimension of frequency (in [10] $\nu_* = 1$ was assumed).

b) If p_* is the stationary density for the considered semi-group, then

$$\forall A \in \Gamma_m, \quad p_*(A) = Z_*^{-1} \exp[-V(A)], \quad Z_* = \sum_{B \in \Gamma_m} \exp[-V(B)]. \tag{5.16}$$

c) The semi-group $\{P^t\}_{t \in R_+}$ is microscopically reversible (in the sense (5.7)).

d) If $\{P^t\}_{t \in R_+}$ is the m-particle closest-neighbour semi-group, then V is the closest-neighbour potential.

Let $A \in \Gamma_{m-1}$ be an arbitrary but fixed set. We can consider the Chapman-Kolmogorov equation of m-particle semi-group restricted to the sets of the form $A \cup x$, $x \in X_A = X \setminus A$. Let us introduce, for $A \in \Gamma_{m-1}$ and $x, y \in X_A$, the following notation:

$$\begin{aligned} &E_x(A) = k_B \theta V(A \cup x) \geqslant 0, \quad E(A) = k_B \theta V(A) \geqslant 0, \\ &E_{xy} = -k_B \theta \ln P(x, y) = E_{yx} > 0, \qquad \text{for } x \neq y, \\ &W_A(x, y) = W(A \cup x, A \cup y), \quad w_A(x) = -W_A(x, x), \\ &\nu_*(A) = \nu_* \exp[-E(A)/k_B \theta]. \end{aligned} \tag{5.17}$$

From formulae (5.9), (5.10), (5.15) and (5.17) it follows that for $A \in \Gamma_{m-1}$ and for every $x, y \in X_A$, $x \neq y$:

$$W_A(x, y) = \nu_*(A) \exp[(-E_{xy} - E_x(A))/k_B\theta] \tag{5.18}$$

and eq. (5.11) takes the following form:

$$\forall x \in X, \quad w_A(x) = \sum_{x \neq y \in X_A} W_A(x, y), \tag{5.19}$$

analogically to the representations of transition and exit intensities given by (4.19) and (2.17). After taking into account (5.9), (5.10), (5.11) and (5.17), we conclude, that this restriction leads to the following equations:

$$\begin{aligned} &\dot{p}_{A\cup x}(t) = -w_A(x)\, p_{A\cup x}(t) + \sum_{x \neq y \in X_A} p_{A\cup y}(t)\, W_A(y, x), \\ &\sum_{x \in X_A} p_{A\cup x}(t) = p_A = \text{const}, \qquad \sum_{A \in \Gamma_{m-1}} p_A = 1, \\ &A \in \Gamma_{m-1}, \qquad x \in X_A = X \setminus A, \qquad t > 0. \end{aligned} \tag{5.20}$$

By applying the notation

$$p_x(t) = p_{A\cup x}(t)/p_A, \qquad \sum_{x \in X_A} p_x(t) = 1, \qquad p_A > 0, \tag{5.21}$$

we can transform (5.20) to the form of the following kinetic equation on the state space X_A:

$$\dot{p}_x(t) = -w_A(x)\, p_x(t) + \sum_{x \neq y \in X_A} p_y(t)\, W_A(y, x). \tag{5.22}$$

The stationary solution $p_*(A) = \{p_{*x}(A);\, x \in X_A\}$ of the equation (5.22) satisfies the condition of microscopic reversibility in the sense (2.20) and is of the form

$$\begin{aligned} &p_{*x}(A) = Z_*(A)^{-1} \exp[-E_x(A)/k_B\theta], \\ &Z_*(A) = \sum_{x \in X_A} \exp[-E_x(A)/k_B\theta], \qquad A \in \Gamma_{m-1}. \end{aligned} \tag{5.23}$$

Thus we see that the description of the random movement of the system of the identical particles, based on the model of the *m*-particle semi-group, can be restricted to the case of the thermodynamically permitted Markov semi-group, discussed in sect. 4. This thermodynamically permitted Markov semi-group describes the random movement (through the points of the set X_A) of a single particle, subjected to the interaction of the remaining (identical) particles, occupying the points of a certain «hypersurface» $A \in \Gamma_{m-1}$. In this model the thermodynamical description (sect. 4) is therefore constructed on the basis of a single-particle description, but taking into account the influence of the neglected degrees of freedom of the system. As a consequence, for example, the rate of change of the internal energy (and therefore the rate of the heat exchange with the surroundings—see sect. 4) can be estimated,

independently of the choice of the solution of eq. (5.22), by (see (4.30))

$$\exists C = C(e(A), \theta) > 0, \quad \forall t \in R_+, \quad |\dot{E}(t)| \leqslant \nu_*(A)\, C, \tag{5.24}$$

where $\nu_*(A)$ is defined by formula $(5.17)_4$ and the notation $e(A) = \{E_x(A);\, x \in X_A\}$ has been applied. The relaxation time (see (4.14)) depends also on the parameter $A \in \Gamma_{m-1}$

$$\tau_*(A) = \tau_* \exp[V(A)], \quad V(A) = E(A)/k_B\theta. \tag{5.25}$$

If $V(A) \ll 1$, then the effect of the parameter A on the relaxation time and on the rate of change of internal energy can be neglected. If $V(A) \gg 1$, then the relaxation time becomes long and the system can be considered as thermodynamically closed ($E(t) = \text{const}$).

Note that the parameter A is not introduced to the set of variables, describing the thermodynamical state of the system. This parameter is then a hidden variable of the thermodynamical description, affecting the thermodynamical openness of the system (independently of its contact with the surroundings in the topological sense).

The approach described in this section, based on the construction of the single-particle approximation of the many-body problem, is similar to Vineard's model of the diffusion jumps of atoms [2, 14]. However, this similarity exhibits itself only in the basic idea, and not in the mathematical formulation.

6. - Final remarks.

In our paper a certain class of kinetic equations, which describe the Markov-type irreversible evolution of the system, consistent with the second law of thermodynamics and with the relaxation postulate, has been distinguished (Introduction and sect. 4). In this description the time asymmetry of the evolution of the system is observed on the macrolevel through the thermodynamical irreversibility of the process and exhibits itself on the microlevel in the Markov-type randomization of the moments of the (jumplike) change of the microstates of the system (sect. 3 and 4). As a consequence, in the description of the evolution of the system, parameters, having the dimension of time, occur: the mean residence time $\tau(x)$ of the system in the state x and the mean time τ between the consecutive jumps (formulae (3.13), (3.15) and (3.19)). These mean quantities have the character of the internal time characteristics of the state of thermodynamical equilibrium, towards which the system relaxes (sect. 4; formulae (3.17), (4.13) and (5.25)) and of the rate of the heat exchange with the environment (formulae (4.30) and (5.24)).

* * *

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REFERENCES

[1] J. W. CHRISTIAN: *The Theory of Transformations in Metals,* Vol. 1 (Pergamon Press, 1975).
[2] W. L. INDEBOM and A. N. ORLOV: introduction in: *Thermally Activated Processes in Crystals,* edited A. N. ORLOV (Mir, 1973), in Russian.
[3] Z. CIESIELSKI: *Wiadomości Matematyczne,* 12, 233 (1971), in Polish.
[4] A. ISIHARA: *Statistical Physics* (Academic Press, 1971).
[5] J. P. TERLETZKY: *Statistical Physics* (High School Press, 1966), in Russian.
[6] P. BILLINGSLEY: *Probability and Measure* (J. Wiley, 1979).
[7] A. LASOTA: *Equadiff 82,* edited by H. W. KNOBLOCH and K. SCHMITT (Springer-Verlag, 1983).
[8] W. FELLER: *Introduction to Probability,* Vol. 2 (J. Wiley, 1971).
[9] I. N. KOVALENKO, N. J. KUZNETZOW and W. M. SCHURENKOV: *Stochastic Processes* (Naukova Dumka, 1983), in Russian.
[10] K. J. PRESTON: *Gibbs States on Countable Sets* (Cambridge University Press, Cambridge, 1874).
[11] K. L. CHUNG: *Markov Chains with Stationary Transition Probabilities* (Springer-Verlag, 1960).
[12] R. BALESCU: *Equilibrium and Nonequilibrium Statistical Mechanics* (J. Wiley, 1975).
[13] J. G. KEMENY, A. N. KNAPP and J. L. SNELL: *Denunerable Markov Chains* (Springer-Verlag, 1976).
[14] G. H. VINEYARD: *J. Phys. Chem. Sol,* 3, 121 (1957).