



The Significance of Non-ergodic Property of Statistical Mechanics Systems for Understanding Resting State of a Living Cell

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Abstract

A better grasp of the physical foundations of life is necessary before we can understand the processes occurring inside a living cell. In his physical theory of the cell, American physiologist Gilbert Ling introduced an important notion of the resting state of the cell. He describes this state as an independent stable thermodynamic state of a living substance in which it has stored all the energy it needs to perform all kinds of biological work. This state is characterized by lower entropy of the system than in an active state. The main contribution to this reduction in entropy is made by the cellular water (the dominant component with a concentration of 14 M) which remains in a bound quasi-crystallized state in a resting cell. When the cell becomes active the water gets desorbed and the system's entropy goes up sharply while the free energy of the system decreases as it is used up for biological work. However, Ling's approach is primarily qualitative in terms of thermodynamics and it needs to be characterized more specifically. To this end, we propose a new thermodynamic approach to studying Ling's model of the living cell (Ling's cell), the centrepiece of which is the non-ergodicity property which has recently been proved for a wide range of systems in statistical mechanics (Prokhorenko, 2009). In many ways this new thermodynamics overlaps with the standard quasi-stationary thermodynamics and is therefore compatible with the principles of the Ling cell, however a number of new specific results take into account the existence of several non-trivial motion integrals communicating with each other, whose existence follows from the non-ergodicity of the system (Ling's cell). These results allowed us to develop general thermodynamic approaches to explaining some of the well-known physiological phenomena, which can be used for further physical analysis of these phenomena using specific physical models.

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1 Introduction

The living state of a substance has always attracted the attention of physicists. And indeed, only a clear understanding of the thermodynamic characteristics of the living matter can give us insight into the processes that occur in living organisms. However, despite the fact that there is a lot of interest in this problem, this field can't be said to be developing by leaps and bounds.

Before proceeding with our analysis we have to establish its boundaries and conditions. There are two very different approaches to the thermodynamics of living systems: one based on the thermodynamics of equilibrium process (Ling 1962, 2001, 1997, Bauer 1935) and the other on thermodynamics of non-equilibrium processes (Prigogin, 1968). Schroedinger's research in this area (Schroedinger, 1994) differs from both of these.

An obscure Russian scientist of Hungarian descent Ervin Bauer (Bauer, 1935) was probably the first to suggest that the living state should be regarded as an unstable equilibrium. Treating the physical state of living substance in this way allowed him to draw a number of interesting conclusions and generalizations, but on the whole the most part of research was purely theoretical.

According to Ling (Ling, 1962, 2001, 1997), whose position is of special interest to us, the minimal cell in the physical sense is a complex comprising protein in an unfolded configuration and water with ions. The most significant characteristic of this complex is the state of water in it; it is absorbed by the protein in the form of a multi-layered structure that surrounds it along the entire length of the polypeptide. This 'coat' consisting of water molecules is stabilized by hydrogen links that are stronger than the hydrogen links in volumetric water. This increase in strength is a result of an increase in the dipole moment of the water molecules under the influence of other dipoles that are stronger than water such as the functional groups in the peptide link bound (NH and CO). The polarization of water molecules explains both their strong binding by the polypeptide frame of the protein and the multi-layered absorption of water on the surface of the unfolded protein. According to Ling, almost all the water in a the cell is in a bound state. Because, in terms of the number of molecules, water is the most abundant compound inside the cell, its transition into a quasi-crystal state results in a significant fall in the entropy of the cell. This lower entropy is what brings about the rise in the amount of free energy of the resting living cell.

The introduction of the concept of a resting state is one of Ling's achievements. It's this state that is used as the reference point for all the physical and chemical processes that take place inside the cell. When a cell is activated by an external stimulant or some other signal, it changes its state from resting to active. The active state is characterized by the disintegration of the water-protein-ions complex. The bound water breaks free and the system's entropy increases. The free energy of the resting state is released and is used up for all kinds of biological work. This is the Ling model of the living cell (Ling's cell) that will be the focus of our analysis.

According to Ling, a cell can remain resting without exchanging energy or substances with the external environment. The cell just maintains diffusion equilibrium with the environment. This view directly contradicts Prigozhin's approach according to which a living cell can only maintain its organization as long as it keeps exchanging substance and energy with the environment on a continuous basis. In other words, a cell can be likened to a burning candle flame; the flame will remain 'alive' only as long as there is sufficient supply of fuel and oxidizer.

Ling believes that such understanding of the thermodynamics of life is completely inadequate in the case of a living cell. His calculations demonstrate that if a continuous inflow of energy was really necessary for the experimentally observed exchange of Na⁺ ions between a resting cell and the environment (as is postulated in the traditional mechanism), the cell would simply be incapable to produce the necessary amounts of energy (Ling, 1997) and therefore the universally adopted model

of ion transport contradicts the energy preservation law. Ling's other argument proceeds as follows; if a living cell and a burning candle were to be frozen to the temperature of liquid nitrogen, both the flame and the life in the cell will 'go out', but if they're heated back to room temperature, the flame won't start burning again, but the life processes in the cell will resume.

The contradictions between the thermodynamic approaches to the phenomenon of life are so pronounced that the need for further research in this field is self-evident. The purpose of this paper is to demonstrate that the property of non-ergodicity that has recently been proved for a large number of systems in statistical mechanics can help better understand the nature of the resting state of a Ling's cell and supports his understanding of the living cell's thermodynamics.

One feature of this approach is that it suggests that the resting state of a Ling's cell should be considered to be a non-equilibrium stationary state, whose existence is a direct consequence of the non-ergodicity property that we postulate for Ling's cells. In this approach thermodynamics of non-equilibrium stationary states must be constructed (analogous to the standard quasi-stationary thermodynamics) to explain why biological work becomes possible in the context of the proposed approach (biological work here means any changes in the cell that have a biological significance and that use up energy, for instance muscle contraction). There is no real contradiction between Ling's stationary resting state and the obviously continuous metabolism necessary to maintain life, because a real cell constantly changes its state from active to resting and back. Metabolism and energy are needed to go back to a resting state rather than maintain it.

Non-ergodicity means that there exist non-trivial first integrals of the system (i.e. that are invariant under the Heisenberg and Hamilton motion equations). Because by definition we consider these first integrals to be real, then, in the case of quantum mechanics, they must be represented by self-adjoint operators and be experimentally observable values. It's then only natural to ask how come they can only be observed in biological systems (as is shown below) as well as in liquid helium and superconductors, systems that are as far from biological as can be? When answering this question we come across a certain mathematical similarity between the super-fluid state of helium and the resting state of the Ling cell, and this similarity helps us better understand the physics of the living state.

The main result of this paper is that by looking at the Ling cell as a non-ergodic system we were able to propose a common physical mechanism for various physiological phenomena, which were previously explained with the help of separate mechanisms barely related to each other. The main goal of physics in physiology must be to find out the thermodynamic nature of an active living cell, i.e. the source of all the manifestations of life. With this goal in mind we only discuss some of the characteristics of the Ling cell and provide only a most general physical description for them. We demonstrate, for example, that when a Ling's cell is activated it emits heat rather than absorbs it. When we consider the properties of the physical model we use, it becomes perfectly clear why it is that unfolded proteins that make up the structural foundation of a resting Ling's cell, begin to fold when it goes active, why potassium ions exit the cell into the environment and why an active cell changes its size (usually it shrinks) and what makes a cell dead. It is not our goal in this paper to compare the results we obtain for the Ling's cell with the properties of a real living cell.

2 Non-Ergodicity of Statistical Mechanics System

In this section we first give the definition of ergodicity in statistical mechanics. We then formulate the main result of (Prokhorenko, 2009) and its classical analogue. After that we demonstrate how non-ergodicity follows from this result on the classical level.

Definition. Suppose that a quantum system is described by Hamiltonian H and some set of self-adjoint integrals of motion K_1, \dots, K_l commuting to each other. We say that the system is ergodic with respect to the integrals K_1, \dots, K_l , if each dynamical variable commuting with H, K_1, \dots, K_l , is their function, or in other words the joint spectrum of operators H, K_1, \dots, K_l is simple.

The classical version of this definition can be easily obtained by replacing the word commutator with a Poisson bracket.

In our case of Bose gas, apart from the Hamiltonian, there are the following trivial commuting first integrals: impulse \vec{P} and the number of particles N . We will be looking at ergodicity relative to this set of first integrals.

Let us now formulate the main result of our work (Prokhorenko, 2009). Let $\Psi(x)$ and $\Psi^+(x)$ be secondary quantized wave functions of Bose gas that satisfy the canonical commutative relations

$$\begin{aligned} [\Psi(x), \Psi(x')] &= [\Psi^+(x), \Psi^+(x')] = 0, \\ [\Psi(x), \Psi^+(x')] &= \delta(x - x'), \end{aligned} \quad (2.1)$$

where the brackets designate a commutator and $\delta(x - x')$ - means Dirac δ — function of a vector argument. An algebra generated by secondary-quantized wave functions is called the algebra of canonical commutative relations. The main result of (Prokhorenko, 2009) can be formulated as the following theorem.

Theorem 1. There exist a linear functional $\langle \cdot \rangle$ on the algebra of canonical commutative relations (within a formal perturbation theory applied to an interaction constant) such that:

a) It is stationary, i.e. $\langle [H, v] \rangle = 0$, where H is a Hamiltonian of the system and v is an arbitrary element of the canonical commutative relations algebra.

b) $\langle \cdot \rangle$ is translation-invariant.

c) $\langle \cdot \rangle$ Commutates with the operator of the number of particles N , i.e. $\langle [N, v] \rangle = 0$, where N is the operator of the number of particles in the system and v is an arbitrary element of the algebra of canonical commutative relations.

d) Satisfy to the weak cluster property, i.e.

$$\begin{aligned} \lim_{|a| \rightarrow \infty} \int \langle \Psi^\pm(t, x_1 + \delta_1 e_1 a) \dots \Psi^\pm(t, x_n + \delta_n e_1 a) \rangle f(x_1, \dots, x_n) d^3 x_1 \dots d^3 x_n \\ = \int \langle \Psi^\pm(t, x_{i_1}) \dots \Psi^\pm(t, x_{i_k}) \rangle \langle \Psi^\pm(t, x_{i_k}) \dots \Psi^\pm(t, x_{i_n}) \rangle \\ \times f(x_1, \dots, x_n) d^3 x_1 \dots d^3 x_n, \end{aligned} \quad (2.2)$$

where $\delta_i \in \{1, 0\}$, $i = 1, 2 \dots n$ and

$$\begin{aligned} i_1 < i_2 < \dots < i_k, \\ i_{k+1} < i_{k+2} < \dots < i_n, \\ \{i_1, i_2, \dots, i_k\} &= \{i = 1, 2 \dots n | \delta_i = 0\} \neq \emptyset, \\ \{i_{k+1}, i_{k+2}, \dots, i_n\} &= \{i = 1, 2 \dots n | \delta_i = 1\} \neq \emptyset. \end{aligned} \quad (2.3)$$

$f(x_1, \dots, x_n)$ - is a test function (i.e. it is sufficiently smooth and it decreases sufficiently fast at infinity with all its derivatives), e_1 is a unit vector parallel to the x axis.

e) $\langle \cdot \rangle$ is not described by the Gibbs distribution.

Before proving the non-ergodicity of the system from this result, we will formulate its classical analogue. In classical statistical mechanics a system containing N particles $N \rightarrow +\infty$, is described by a distribution function of the form $\rho((x_1, p_1), \dots, (x_N, p_N))$, where (x_i, p_i) are the coordinates and momenta of the i -th particle $i = 1, \dots, N$. The distribution function ρ is assumed to be symmetrical relative to the permutation of its arguments $(x_1, p_1), \dots, (x_N, p_N)$.

Also partial distribution functions are introduced:

$$\begin{aligned} \rho_0 &= 1, \\ \rho_1(x_1) &= V \int dx_2 dp_2 \dots dx_N dp_N \rho((x_1, p_1) \dots (x_N, p_N)), \\ \rho_2((x_1, p_1), (x_2, p_2)) &= V^2 \int dx_3 dp_3 \dots dx_N dp_N \rho((x_1, p_1) \dots (x_N, p_N)), \\ &\dots \dots \dots \end{aligned} \tag{2.4}$$

V is a volume of the system. Partial distribution functions $\rho_0 = 1, \rho_1, \dots, \rho_n \dots$ satisfy the following consistency condition:

$$\begin{aligned} &\rho_n((x_1, p_1), \dots, (x_n, p_n)) = \\ &= V^{-m} \int dx_{m+1} dp_{m+1} \dots dx_{n+m} dp_{n+m} \rho_n((x_1, p_1), \dots, (x_{n+m}, p_{n+m})). \end{aligned} \tag{2.5}$$

If the number of particles in the system is variable, then in a similar way to (2.4), we can also define partial distribution functions. They will also satisfy the consistency conditions if N approaches infinity. If we take the main result of (Prokhorenko, 2009) and pass it through the limit we get the following theorem.

Theorem 1’. There exists such a state ρ (not necessarily positively defined and possibly with a varied number of particles) of a gas consisting of particles with weak interaction, that

- a) This state is stationary, i.e. it doesn't change with time due to its motion equations.
- b) This state is translation-invariant.
- c) This state satisfies the weak cluster property, i.e. $\forall n = 1, \dots, \infty$ and $\forall k = 1, \dots, n$

$$\begin{aligned} \lim_{|l| \rightarrow \infty} \rho_n((x_1, p_1), \dots, (x_k, p_k), (x_{k+1} + le_1, p_{k+1}), \dots, (x_n + le_1, p_n)) &= \\ = \rho_k((x_1, p_1), \dots, (x_k, p_k)) \rho_{n-k}((x_{k+1}, p_{k+1}), \dots, (x_n, p_n)) \end{aligned} \tag{2.6}$$

- d) The state ρ cannot be described by a Gibbs distribution.

Let us finally demonstrate how this result leads to the non-ergodicity of our system. To simply things we'll only be considering the case of classical mechanics. For a detailed discussion of the quantum version of this result see (Prokhorenko, 2009).

Let us suppose that our system is ergodic, i.e. that its energy and momentum form a maximal set of first integrals in involution. Two dynamic variables are said to be in involution if their Poisson bracket equals zero. From here on for the sake of brevity, we'll be simply talking about energy rather than energy, momentum and the number of particles. Let f be a distribution function for our system in a phase space that corresponds to the state we talked about before. Then because of the system is assumed ergodic it must be a function of only energy $f = f(E_\Gamma)$ (Γ - is a point in the phase space) and can be presented as a superposition of micro-canonical distributions:

$$f(E_\Gamma) = \sum_{\alpha} c_{\alpha} \delta(E_\Gamma - E_{\alpha}), \tag{2.7}$$

The summation in this context is understood in the broadest possible sense and can be continuous (in other words it can be replaced with integration).

Let 1 be a sufficiently large but finite subsystem of our system and let 2 - be a subsystem obtained from 1 by shifting it along the x axis by a distance of l . Let 12 - be a union of systems 1 and 2. Let Γ_1, Γ_2 and Γ_{12} designate points in the phase space for our systems 1, 2 and 12 respectively. Let $f_1(\Gamma_1), f_2(\Gamma_2)$ and $f_{12}(\Gamma_{12})$ be distribution functions for systems 1, 2 and 12 respectively. Then using

the same method that is used for obtaining a canonical distribution from a microcanonical one, for $|l| = \infty$ we can find that:

$$f_{12} = \sum c_\alpha d_\alpha \frac{e^{-\frac{E_{\Gamma_1}}{T_\alpha}}}{Z_\alpha} \frac{e^{-\frac{E_{\Gamma_2}}{T_\alpha}}}{Z_\alpha}. \quad (2.8)$$

Here $d_\alpha > 0$ - is a weight multiplier, E_{Γ_1} and E_{Γ_2} - are the energies of subsystems 1 and 2, T_α - is the temperature corresponding to energy E_α , and Z_α - is the statistical sum:

$$Z_\alpha = \int d\Gamma_1 e^{-\frac{E_{\Gamma_1}}{T_\alpha}}. \quad (2.9)$$

But from the weak cluster property it follows that:

$$f_{12} = f_1 f_2. \quad (2.10)$$

Therefore it follows from (2.8) that all $c_\alpha = 0$ except one and:

$$f(E) = c\delta(E - E_0), \quad (2.11)$$

(for some c and E_0), i.e. the whole system is described by a microcanonical distribution while any of its sufficiently large but finite subsystems is described by a canonical Gibbs distribution, which contradicts the fact that our state is not a Gibbs state. This contradiction proves that our system is non-ergodic.

3 Discussion of Non-Ergodicity

Because not enough research has been conducted into the specific features of the dynamics of statistical mechanics systems connected with non-ergodic property, the discussion in this section will be informal and hypothetical in places.

Boltzmann's hypothesis. Boltzmann hypothesis (1871) postulates that in statistical mechanical systems the dynamic variables that are averaged in time are equal to the dynamic variables that are averaged across the (micro) canonical ensemble. We will only consider the quantum mechanics case. The discussion presented here was taken from (Prokhorenko, 2009). Before we can formulate the Boltzmann hypothesis for a Bose gas with weak pair interaction, some designations need to be introduced. Let $\langle a \rangle_{\beta, \vec{v}, \mu}$ be the Gibbs state corresponding to the inverse temperature β , the system velocity \vec{v} and its chemical potential μ , i.e.

$$\langle a \rangle_{\beta, \vec{v}, \mu} = \frac{1}{Z_{\beta, \vec{v}, \mu}} \text{tr}(a e^{-\beta(H - \mu N + \vec{v}\vec{P})}), \quad (3.1)$$

where a is an arbitrary element from the algebra of canonical commutative relations algebra, H is the Hamiltonian of the system, N is the operator of the number of particles in the system, \vec{P} is the operator of the system impulse and Z is the so called grand statistical sum, i.e.

$$Z_{\beta, \vec{v}, \mu} = \text{tr}(e^{-\beta(H - \mu N + \vec{v}\vec{P})}). \quad (3.2)$$

Let V'_G be a space of all linear functionals on the algebra of canonical commutative relations, each of which is a superposition of Gibbs states.

Let $\langle \cdot \rangle$ be a translation-invariant functional on the algebra of canonical commutative relations such that $\forall t \in \mathbb{R} \langle e^{itH}(\cdot)e^{-itH} \rangle$ is a well defined linear functional. The Boltzmann hypothesis states

that in this case there will be a linear functional $\langle \cdot \rangle' \in V'_G$ such that for any element a from the algebra of commutative relations:

$$\lim_{T \rightarrow +\infty} \frac{1}{T} \int_0^T \langle e^{itH} a e^{-itH} \rangle dt = \langle a \rangle'. \quad (3.3)$$

Let us demonstrate that formulated in this way the Boltzmann hypothesis is wrong. Theorem 1 states that there exists a translation invariant stationary linear functional on the algebra of canonical commutative relations and that said functional is not a superposition of Gibbs functions. However, this functional is built only in the form of a formal power series on the interaction constant and nothing is known about whether this series has a finite sum or not. (Prokhorenko, 2009), however, demonstrates that there is a way around the issue of whether this series converges or not and that there exists a stationary translation invariant functional on the algebra of canonical commutative relations $\langle \cdot \rangle_s$ that does not belong to V'_G . If this composite function is substituted for $\langle \cdot \rangle'$ in the left side of equation (3.3), then the left side itself will equal $\langle \cdot \rangle_s$ and from equation (3.3) it will then follow that $\langle \cdot \rangle_s$ is superposition of Gibbs states. This contradiction shows that the Boltzmann hypothesis does not hold.

Discussion of the relation between a system's behaviour on its boundaries and its tendency towards thermodynamic equilibrium. Non-ergodicity means that Bose gas (with weak pair interaction) will not tend towards thermodynamic equilibrium in an infinite volume. Consequently to prove the tendency towards thermodynamic equilibrium we have to take into account its behaviour on the boundary of the system. In fact if the role played by the boundary is disregarded we may end up with an infinite system.

In (Prokhorenko, 2009) the role of boundaries is illustrated with Bogolubov's derivation of Boltzmann's kinetic equation. Bogolubov's programme for deriving equations considers an infinite strengthening chain of equations for partial distribution functions (BBGKI chain) equivalent to Luiville's equations, and then closed kinetic equations are obtained by selecting the suitable conditions for breaking the chain (correlation breaking conditions). The first member of this chain has the form:

$$\begin{aligned} \frac{\partial}{\partial t} \rho_1((x_1 p_1)|t) + \frac{p}{m} \nabla \rho_1((x_1, p_1)|t) + \int dx_2 dp_2 \frac{p_2}{m} \frac{\partial}{\partial x_2} \rho_2((x_1, p_1), (x_2, p_2)|t) = \\ = \int dx_2 dp_2 \frac{\partial V(x_1 - x_2)}{\partial x_1} \frac{\partial \rho_2((x_1, p_1), (x_2, p_2)|t)}{\partial p_1}. \end{aligned} \quad (3.4)$$

Here t is time, m is the mass of the particles, and V is the potential of pair interaction. An integral over the coordinates in the last term in the equation on the left (3.4) may be transformed into an integral along the boundary of a three-dimensional space using the Gauss theorem, and usually this fact is used as the basis for assuming that this integral equals to zero. However in (Prokhorenko, 2009) it is demonstrated if the last term on the left side of (3.4) is not discarded and Bogolubov's strategy for deriving a Boltzmann equation is followed (if translation-invariant distributions are considered from the start), then this term will eventually cancel out with the collision integral and the system will have no kinetic evolution. Even though, it is possible that this effect is purely mathematical, it does make one wonder about the role that the system's behaviour on its boundary plays in proving its tendency towards thermodynamic equilibrium.

Although it is now clear that the system's behaviour on the boundary must be taken into account when proving its tendency towards thermodynamic equilibrium, the following question now arises: if the linear sizes of the system equal $\sim L$ and tend to infinity, then the volume of the system will behave like L^3 while the surface area of its boundary will equal L^2 which makes one think that the influence of the boundaries must be very insignificant.

A similar situation can be observed in the theory of second order phase transitions, for instance in the theory of ferromagnetism. If, for instance, you take a two dimensional Ising model at a temperature below the critical level, and assume that all the spins are directed upwards along the boundaries of the crystal, then Peierls estimates (see (Glimm, Jaffe, 1981)) show that in the thermodynamic limit

there will be a non-zero magnetization. Second order phase transitions are often related to breaking of some symmetry. In the case of the Ising model, the symmetry that is broken is the symmetry relative to the change in the direction of all the spins in the grid. In the case of kinetic evolution there is also as symmetry that gets broken, it's the symmetry relative to the time sign (Boltzmann's H-theorem). We will have a more detailed discussion of this similarity later on.

The necessity to take into account a system's behaviour on its boundaries when proving the system's tendency towards thermodynamic equilibrium raises an interesting philosophical question. If a system's behaviour on its boundaries must be taken into account when proving the system's tendency towards thermodynamic equilibrium, then it means we have to know about the behaviour of the particles outside the system's boundaries because those influence the behaviour of the particles immediately inside the system's boundaries, in other words we have to know how the environment that the system is a part of behaves. This in turn means that we have to know the behaviour of the larger environment around the immediate environment of the system and so on and so forth. So how do we escape from this infinite regress?

To answer this question we will consider the following example. It is a known fact that there are black holes in our universe. Black holes are known to emit energy but for this phenomenon to be explained certain boundary conditions have to be assumed, which essentially are based on the fact that a black hole is formed as a result of the collapse of a mass body. According to one theorem of Penrose, this means that at one time in the past there existed a certain feature of the space time. The surface of a black hole, the so called event horizon, is the boundary at which the dependence of the particles inside the system on particles outside the system is broken. In fact due to the structure of light cones, information on the event horizon can only fall into the black hole, while the Hawking radiation is in equilibrium and therefore carries only the bare minimum of information.

On the other hand one of Penrose-Hawking's theorems (Penrose, 1968) (whose conditions are confirmed by reliable astronomical observations) postulates that at some time in the past there was a singularity of space-time which can be equated to the Big Bang. At the same time Boltzmann also posited (on the basis of his *H*-theorem) that there had to have been a moment in time which can be equated to the beginning of the universe. In the theorems of Penrose and Hawking there appears entropy (equal to the surface area of the event horizon), which increase and is related to the temperature of the Hawking radiation through a known thermodynamic relation. It follows from all of this that there is a much deeper link between the 'proof' of Boltzmann's Big Bang and Penrose — Hawking's singularity than a simple mathematical similarity.

It is also worth noting that due to the arguments presented above, the non-ergodicity of Bose gas with weak pair interaction can be interpreted as the impossibility of deriving macroscopic dynamics from microscopic dynamics.

The non-ergodicity theorem, as follows from its proof (see (Prokhorenko, 2009)), is applicable to a broad range of systems in statistical mechanics and we make the assumption that it can also be applied to the Ling's cell. Therefore, the general results obtained for all non-ergodic systems can also be applied in this case.

A more detailed study of how the properties of a system's surface influence the process whereby it achieves thermodynamic equilibrium can be helpful in improving our understanding of living cells and the role of the cell's surface in the physiological processes inside it.

Analogy with second order phase transitions. Let's discuss in more detailed the aforementioned analogy between the broking of the symmetry relative to the time sign and second order phase transitions. We'll do this by discussing the Green-Kubo formula that describes the linear response of a system to small perturbations. Let there be n fluctuating (commuting) variables in the system x_1, \dots, x_n and let $\hat{x}_1, \dots, \hat{x}_n$ be corresponding quantum mechanics operators. Let us assume that the fluctuations are sufficiently small and that the system's entropy can be expressed with the formula

$$S = S_0 - \beta_{ij} x_i x_j, \quad (3.5)$$

where β_{ij} is some positively defined matrix (here and through the end of this section indexes repeated

twice mean summation). Let X_1, \dots, X_n be thermodynamically conjugate values to x_1, \dots, x_n i.e.

$$X_k = -\frac{\partial S}{\partial x_k}. \quad (3.6)$$

The equations describing the relaxation of this system look like this:

$$\dot{x}_i = -\gamma_{ik} X_k, \quad (3.7)$$

where γ_{ik} - are the so called kinetic coefficients. This coefficients satisfy Onsanger's symmetry principle:

$$\gamma_{ik} = \gamma_{ki}. \quad (3.8)$$

If the system is affected by external forces f_k $k = 1, \dots, n$, in other words if the system's Hamiltonian looks like this

$$H = H_0 + f_k \hat{x}_k, \quad (3.9)$$

(H_0 is the Hamiltonian of an unperturbed system), then we can determine the generalized sensitivity of the system $\alpha_{ik}(\tau)$ in such a way that

$$x_k(t) = \int_{-\infty}^{+\infty} \alpha_{ki}(t - \tau) f_i(\tau) d\tau. \quad (3.10)$$

Let's use $\tilde{\alpha}_{ik}(\omega)$ to designate the Fourier transform of the generalized sensitivity

$$\tilde{\alpha}_{ik}(\omega) = \int e^{i\omega t} \alpha_{ik}(t) dt. \quad (3.11)$$

The generalized sensitivity can be found from the Green — Kubo formula:

$$\alpha_{ik}(t) = -i\theta(t) \langle [\hat{x}_i(t), \hat{x}_k(0)] \rangle, \quad (3.12)$$

where $\theta(t)$ is a Heaviside step function that equals 1 when its argument is positive and zero if its negative and $\langle \cdot \rangle$ is the averaging over the equilibrium state of an unperturbed system. It has to be noted, however, that when the Green — Kubo formula is applied the system is assumed to be in equilibrium with $t = -\infty$. If we assume, on the contrary, that the system is in equilibrium with $t = +\infty$, then by transforming the time in the Green — Kubo — formula, we will get the following formula for the generalized sensitivity

$$\alpha'_{ik}(t) = i\theta(-t) \langle [\hat{x}_i(t), \hat{x}_k(0)] \rangle. \quad (3.13)$$

It can be easily seen that

$$\tilde{\alpha}'_{ik}(\omega) = (\tilde{\alpha}_{ik}(\omega))^*, \quad (3.14)$$

where the asterisk means complex conjugation. If, however, we start with an approximation in which relaxation equations (3.7) hold, then it can be shown that there exists the following relations between the matrices α, β and γ :

$$\tilde{\alpha}_{ik}(\omega) = \frac{1}{T} (\beta_{ik} - i\omega \gamma_{ik}^{-1})^{-1}. \quad (3.15)$$

It can be seen from this formula that if t is replaced with $-t$ and vice versa in the Green – Kubo formula, then γ_{ik} will become $-\gamma_{ik}$ and will no longer describe kinetic evolution.

So, how can we choose between the requirement for equilibrium with $t = -\infty$ and with $t = +\infty$, in other words how can we determine whether the equation with a retarded commutator (3.12) or

the equation with a advanced commutator (3.15) should be used for the generalized sensitivity of the system?

It should be noted that a similar problem arises in classical electrodynamics when working out the formula for retarded potentials. A vector potential A^μ , $\mu = 0, 1, \dots, 3$ in classical electrodynamics satisfies the heterogeneous wave equation:

$$\square A^\mu = J^\mu, \tag{3.16}$$

where

$$\square = \frac{\partial^2}{(\partial x^0)^2} - \frac{\partial^2}{(\partial x^1)^2} - \frac{\partial^2}{(\partial x^2)^2} - \frac{\partial^2}{(\partial x^3)^2}, \tag{3.17}$$

and J^μ is a four-vector of current, satisfying the continuity equation:

$$\partial_\mu J^\mu = \frac{\partial}{\partial x^0} J^0 + \frac{\partial}{\partial x^1} J^1 + \frac{\partial}{\partial x^2} J^2 + \frac{\partial}{\partial x^3} J^3 = 0. \tag{3.18}$$

Where x_0 is time, and x_1, x_2, x_3 are the spacial Euclidean coordinates.

The solution to equation (3.17) usually has the form:

$$A^\mu(x) = \int D(x-y) J^\mu(x) d^4x, \tag{3.19}$$

where $D(x)$ is the fundamental solution to the wave equation:

$$\square D(x) = \delta(x), \tag{3.20}$$

with a support in the upper light cone:

$$\text{supp}D(x) \subset \bar{V}^+ = \{x|x_0 \geq 0, x^2 \geq 0\}. \tag{3.21}$$

There exists a single fundamental solution that satisfies this property. Formula (3.19) is called the formula of retarded potentials. The similarity to the Green—Kubo formula becomes even closer if we remember that the vacuum mean of the commutators of the secondary quantum vector potential in electrodynamics is presented in the following form

$$\langle 0|[A^\mu(x), A^\nu(y)]|0\rangle\theta(x^0 - y^0) = ig^{\mu\nu} D(x-y), \tag{3.22}$$

where $g^{\mu\nu}$ is a metric tensor:

$$g^{\mu\nu} = 0, \text{ if } \mu \neq \nu, \\ g^{00} = 1, g^{ii} = -1, i = 1, 2, 3. \tag{3.23}$$

If in (3.17) we switch to the Fourier transform in time, then we will get:

$$\{\omega^2 + \frac{\partial^2}{(\partial x^1)^2} + \frac{\partial^2}{(\partial x^2)^2} + \frac{\partial^2}{(\partial x^3)^2}\} A^\mu(\omega, \vec{x}) = -J^\mu(\omega, \vec{x}). \tag{3.24}$$

The solution to this equation, corresponding to the formula of retarded potentials, will have the form:

$$A^\mu(\omega, \vec{x}) = -\frac{1}{4\pi} \int \frac{e^{i\omega|x-y|}}{|x-y|} J^\mu(\omega, \vec{y}) d^3\vec{y}. \tag{3.25}$$

If S_R is a sphere with a radius R and its center at zero and $R \rightarrow \infty$, then $A^\mu(\omega, \vec{x})$ on this sphere will satisfy the Sommerfeld radiation condition:

$$\frac{\partial}{\partial \vec{n}} A^\mu(\omega, \vec{x}) - i\omega A^\mu(\omega, \vec{x}) = O(\frac{1}{R^2}), \tag{3.26}$$

where $\frac{\partial}{\partial \vec{n}}$ means differentiation along the external normal to sphere S_R . By applying an inverse Fourier transform to this formula, we will find the condition that must be met by S_R , to ensure that a retarded commutator is selected in the formula for retarded potentials:

$$\frac{\partial}{\partial \vec{n}} A^\mu(x) + \frac{\partial}{\partial x^0} A^\mu(x) = O\left(\frac{1}{R^2}\right). \quad (3.27)$$

The selection of an advanced commutator would result in the following formula

$$\frac{\partial}{\partial \vec{n}} A^\mu(x) - \frac{\partial}{\partial x^0} A^\mu(x) = O\left(\frac{1}{R^2}\right). \quad (3.28)$$

Thus we can see that an advanced or a retarded commutator in Green—Kubo formulas can be selected (which is necessary to specify the direction of time), at least in electrodynamics, by applying appropriate boundary conditions on the infinitely removed boundary of a three-dimensional space. This approach is in full accord with our ideas about the role that the boundaries of a system play in proving its tendency towards thermodynamic equilibrium. It should also be noted that boundary condition (3.27) imposes a limit on the flow of information (this interpretation is also possible): information can only go out of the system (flow outside). This restriction on the direction of the flow of information is realized, for instance, on the event horizon of a black hole due to the structure of the light cones on it, as has already been noted above.

Let us go back to our analogy with ferromagnetism (Ising model). We said earlier that non-zero magnetization can be obtained by changing the direction of the spins on the boundary of the grid. However, non-zero magnetization can also be achieved in another way. We can introduce a fictitious infinitesimally small external field, which is expressed by adding the following expression to the system's Hamiltonian

$$h \sum_p \sigma_p, \quad (3.29)$$

where the summation is done for all the nodes p of the grid, and σ_p is the spin in the node of the grid with $\sigma_p \in \{-1, 1\}$. Then the system passes to an unlimited volume and after that h starts approaching zero, however it always remains positive or negative. The means calculated in this way are called quasi-means (Bogolubov's quasi-means). It turns out that non-zero magnetization occurs in this case as well (and it's equal to the magnetization that results when the spins on the boundaries are given a certain direction).

It begs the question whether it is possible to make the right choice between an advanced and retarded commutator method when working out a Green—Kubo formula, by analogy with Bogolubov's quasi-means? The answer to this question is positive and here is why. Let $H(t)$ be a Hamiltonian of the system dependent on time:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}f(t), \quad (3.30)$$

Let $f(t)$ be an external and infinitesimally small classical force changing with time. The von Neumann equation for the density matrix will look like this:

$$\frac{d}{dt} \rho(t) = -i[\hat{H}(t), \rho(t)] = -i[\hat{H}_0, \rho(t)] - if(t)[\hat{V}, \rho(t)]. \quad (3.31)$$

If $f(t) \equiv 0$, $\rho = \rho_0$ is the density matrix of the equilibrium of an unperturbed system. Consequently if we're looking for ρ in the first order over $f(t)$, then the following equation can be used for ρ :

$$\frac{d}{dt} \rho(t) = -i[\hat{H}_0, \rho(t)] - if(t)[\hat{V}, \rho_0]. \quad (3.32)$$

The standard method for solving this equation when working out a Green—Kubo formula involves choosing a boundary condition $\rho(t) \rightarrow \rho_0$ with $t \rightarrow -\infty$ and solving (3.32) by using the constant

variation method. What we get then is:

$$\rho = \rho_0 - i \int_{-\infty}^t e^{-i\hat{H}_0(t-\tau)} [\hat{V}, \rho_0] e^{+i\hat{H}_0(t-\tau)} f(\tau) d\tau. \quad (3.33)$$

This expression for the density matrix immediately leads to a Green—Kubo formula with a retarded commutator. Instead of imposing initial conditions on the density matrix, we will introduce an infinitesimally small term $\varepsilon\rho(t)$, $\varepsilon > 0$, $\varepsilon \rightarrow 0$ into the left side of (3.32). In other words instead of (3.32) we will be solving the following equation for the density matrix:

$$\frac{d}{dt}\rho(t) + \varepsilon\rho + i[\hat{H}_0, \rho(t)] = -if(t)[\hat{V}, \rho_0]. \quad (3.34)$$

Applying a Fourier transform to this equation we get:

$$(-i\omega + \varepsilon + i[\hat{H}_0])\tilde{\rho}(\omega) = -i\tilde{f}(\omega)[\hat{V}, \rho_0], \quad (3.35)$$

where $[\hat{H}_0]$ designates the following super-operator:

$$[\hat{H}_0]\rho := [\hat{H}_0, \rho]. \quad (3.36)$$

Therefore it follows from (3.35) that:

$$\rho(\omega) = \frac{-i}{-i\omega + \varepsilon + i[\hat{H}_0]} [\hat{V}, \rho_0] f(\omega). \quad (3.37)$$

Since a Fourier transform transforms convolution into product we can find:

$$\rho(t) = \int_{-\infty}^{+\infty} \alpha(t - \tau) f(\tau) d\tau, \quad (3.38)$$

where

$$\alpha(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \frac{-i}{-i\omega + \varepsilon + i[\hat{H}_0]} [\hat{V}, \rho_0] d\omega. \quad (3.39)$$

The super-operator $[\hat{H}_0]$ is the Liouvillian of an unperturbed system and is therefore self-adjoint (if we define the scalar product of the operators applicable in the space of states as $\langle \hat{A}, \hat{B} \rangle = \text{tr}(\hat{A}^* \hat{B})$). Then, calculating the integral in (3.39) through residue we will get: (3.39)

$$\alpha(t) = -i\theta(t)e^{(-i[\hat{H}_0] - \varepsilon)t} [\hat{V}, \rho_0] = \theta(t)e^{-\varepsilon t} e^{-i\hat{H}_0 t} [\hat{V}, \rho_0] e^{i\hat{H}_0 t} \quad (3.40)$$

Substituting the expression we just found in (3.38) for $\alpha(t)$ and assuming that $\varepsilon \rightarrow 0$ we will find:

$$\rho = \rho_0 - i \int_{-\infty}^t e^{-i\hat{H}_0(t-\tau)} [\hat{V}, \rho_0] e^{i\hat{H}_0(t-\tau)} f(\tau) d\tau, \quad (3.41)$$

Thus we've once again got expression (3.33) for the density matrix. Thus we see that boundary conditions for a density matrix can be chosen using a method similar to Bogolubov's method of quasi means, i.e. by introducing an appropriate infinitesimally small term in the equations describing the evolution of the density matrix through time. This should explain the similarity between spontaneous breaking of the symmetry in second order phase transitions and the breaking of the time symmetry in kinetic equations.

4 Thermodynamics of Stationary Non-Equilibrium States

In section 1 we said that according to the results obtained in (Prokhorenko, 2009), even the most realistic systems in statistical mechanics are non-ergodic. It should also be reminded at this stage, that a system is ergodic if its trivial first integrals (Hamiltonian, momentum, number of particles) form the maximum set of first integrals in involution. Hereinafter for the sake of brevity we will use the term energy to mean the energy and the impulse of a system. From the non-ergodicity of a system it follows that it must have stationary states that are not super-positions of Gibbs states. We will call the states of a system that are super-positions of Gibbs states equilibrium states.

It therefore makes sense to build thermodynamics of non-equilibrium stationary states. This thermodynamics will really come in handy in the next section when we formulate the principle that the substance inside a living cell is in a non-equilibrium stationary state, which is the goal of this paper. This section describes how we build this thermodynamics. The equations we derive in this section will be applicable to any system in statistical mechanics, including the Ling's cell. For the sake of simplicity we will only consider the case of classical mechanics.

Some basic concepts of classical (Hamiltonian) mechanics should be remembered here. The phase space Γ of a Hamiltonian system is a $2n$ -dimensional $n = 1, 2, \dots$ smooth manifold in which for any two (good) functions f, g there is a function (f, g) defined on their Poisson brackets, which satisfies the following conditions:

- 1) $(fg, h) = f(g, h) + g(f, h)$ (Leibniz rule)
- 2) $(f, g) = -(g, f)$ (Anti-symmetry)
- 3) $(f, (g, h)) + (g, (h, f)) + (h, (f, g)) = 0$ (Jacobi identity)
- 4) For any point $x \in \Gamma$, and for any function $f: \text{grad}f(x) \neq 0$, there is a function g on Γ such that $(f, g)(x) \neq 0$ (non-degeneracy).

n is called the number of degrees of freedom of the system.

An example of a phase space would be $\Gamma = \{(p_1, \dots, p_n, q_1, \dots, q_n) \mid p_i, q_i \in \mathbb{R}\}$ in which the Poisson bracket is defined as:

$$(f, g) = \sum_{i=1}^n \left(\frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} - \frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} \right). \quad (4.1)$$

According to the Darboux theorem (see [10]) local coordinates $p_1, \dots, p_n, q_1, \dots, q_n$ can always be introduced in which the Poisson bracket will look like (4.1). Such coordinates are called canonical or symplectic.

The evolution of a Hamiltonian system is described by a one-parameter group of diffeomorphisms (i.e. homeomorphisms which are smooth with their inverse), $x \mapsto G_\tau(x)$, $\tau \in \mathbb{R}$ preserving the Poisson bracket (τ is time). This one-parameter group of diffeomorphisms is called a phase flow.

It can be shown that for any phase flow G_τ (locally) there is a function H on Γ , called a Hamiltonian, such that

$$\frac{d}{d\tau} f_\tau = (H, f_\tau), \quad (4.2)$$

Where $f_\tau(x) := f(G_\tau(x))$. For more about Hamiltonian dynamics see (Arnold, 1978).

Thus, let's assume we have a Hamiltonian system in which in addition to Hamiltonian H there is also, $k = 1, 2, 3, \dots$ first integrals K_1, \dots, K_k in involution, i.e. all the matching Poisson brackets equal zero: $\forall i, j = 1, \dots, k (K_i, K_j) = 0$. We want to describe a state of our system in which it is in equilibrium with its environment and in which its Hamiltonian H and the first integrals K_1, \dots, K_k take on some specific values E, K'_1, \dots, K'_k respectively.

The requirement that the first integrals K_1, \dots, K_k must be in involution can be explained as follows: we want to describe states in which the integrals of motion K_1, \dots, K_k take on specific values: E, K'_1, \dots, K'_k . But in quantum mechanics (see (von Neumann, 1932)) simultaneous measurability of the observables means that they are commutative. Now it becomes clear why K_1, \dots, K_k must be in

involution, if we take into account the fact that the commutator is the quantum mechanics counterpart of the Poisson bracket (see (Dirac, 1958)).

Let us first consider the way the above task is solved with $k = 0$. The state of a system in statistical mechanics is described by a distribution function $\rho(x)$ on the phase space Γ , i.e. by a function that satisfies the following conditions

- a) $\forall x \in \Gamma \rho(x) \geq 0$ (Positive definiteness),
- b) $\int \rho(x) d\Gamma_x = 1$ (Normalization).

Here the phase volume is determined in the following way: in canonical coordinates it looks like $d\Gamma = dp_1 \dots dp_n dq_1 \dots dq_n$. It can be demonstrated that this definition is correct. The observed macroscopic value \bar{F} of dynamic variable $F(x)$ has the form:

$$\bar{F} = \int F(x) \rho(x) d\Gamma_x. \quad (4.3)$$

The role of the distribution function $\rho(x)$ is assigned to the so called micro-canonical Gibbs distribution:

$$\rho(x) = c \delta(H(x) - E), \quad (4.4)$$

In which the constant c is chosen on the basis of the normalization condition.

It's important to note here that we assumed that the system under consideration is in thermodynamic equilibrium with its environment. For this reason $H(x)$ takes into account interaction with the particles in the environment and $H(x)$ is a function of time and time is included in $H(x)$ through the coordinates and impulses of the particles in the environment. This will be important further down the road. It has also be remembered, however, that in the thermodynamic limit these extra terms in $H(x)$ that account for the interaction with the environment, can be disregarded.

If the system's Hamiltonian is a function of time, $H(t)$, then the system's evolution will be described by a co-cycle, i.e. $\forall t_1, t_2$ there are canonical transformations (i.e. transformation that preserves the Poisson bracket) $x \mapsto G_{t_1, t_2}(x)$ meets the co-cycle property:

$$G_{t_1, t_2} G_{t_2, t_3} = G_{t_1, t_3}. \quad (4.5)$$

Any dynamic variable f is a function of time by definition $f_t(x) := f(G_{t,0}(x))$. Now it has to be said that in actuality, the motion of the system is described by some trajectory through the phase space and for this reason the left side of (4.3) has to be interpreted as a mean over time, or

$$\lim_{T \rightarrow 0} \frac{1}{T} \int_0^T F(G_{\tau,0}(x)) d\tau = c \int F(x) \delta(H(x) - E) d\Gamma_x. \quad (4.6)$$

Equation (4.6) does not in any way mean that the system is ergodic, because from the very beginning we said that our system is a subsystem of a large system.

A phase flow preserves its phase volume(see (Arnold, 1978)). Therefore the system's distribution function ρ with time will evolve into:

$$\rho_t(x) = \rho(G_{0,t}(x)). \quad (4.7)$$

Function ρ_t will satisfy the following differential equation:

$$\frac{d}{dt} \rho_t = (\rho_t, H(t)). \quad (4.8)$$

Now let us assume that the system's Hamiltonian H_λ is a function of some parameter λ . We will demonstrate that if λ undergoes adiabatic changes the micro-canonical distribution remains the same. Let $\lambda(t)$ be some function of time and let ε be some small positive number. Let $\lambda_\varepsilon(t) := \lambda(\varepsilon t)$. Let x be a point in the phase space such that $H_{\lambda(\varepsilon t)}(x) = E$. Let $[0, \Delta]$ be a sufficiently long period of

time such that a mean over this period is the same as the mean over the micro-canonical ensemble. Let us now select such a small ε that will not change very much in this time period. Let's calculate

$$H_{\lambda_\varepsilon(t)}(G_{t,0}(x))|_{t=\Delta}. \tag{4.9}$$

What we get is:

$$\begin{aligned} & H_{\lambda_\varepsilon(t)}(G_{t,0}(x))|_{t=\Delta} = \\ & = H_0((x)) + \int_0^\Delta dt \left\{ \frac{d\lambda}{dt} \frac{\partial H_{\lambda_\varepsilon(t)}}{\partial \lambda} + (H_{\lambda_\varepsilon(t)}, H_{\lambda_\varepsilon(t)}) \right\} (G_{t,0}(x)) = \\ & = H_0((x)) + \int_0^\Delta dt \frac{d\lambda}{dt} \frac{\partial H_{\lambda_\varepsilon(t)}}{\partial \lambda} (G_{t,0}(x)) = \\ & = H_0((x)) + \Delta \frac{d\lambda}{dt} \frac{\partial \overline{H_{\lambda_\varepsilon(t)}}}{\partial \lambda} + O(\varepsilon^2) \end{aligned} \tag{4.10}$$

Thus with a precision of up to ε^2 canonical transformation $G_{t,0}$ transforms function $H_{\lambda_\varepsilon(t)}(x) - E - \Delta \frac{d\lambda}{dt} \frac{\partial \overline{H_{\lambda_\varepsilon(t)}}}{\partial \lambda}$ into $H_{\lambda_\varepsilon(0)}(x) - E$, i.e. transformation $G_{t,0}$ transforms the micro-canonical distribution $c\delta(H_{\lambda_\varepsilon(0)}(x) - E)$ into $c\delta(H_{\lambda_\varepsilon(t)}(x) - E - \Delta \frac{d\lambda}{dt} \frac{\partial \overline{H_{\lambda_\varepsilon(t)}}}{\partial \lambda})$ with a precision of up to $\frac{1}{\varepsilon}$. The function $\lambda_\varepsilon(t)$ changes by a finite amount within an interval of order $\frac{1}{\varepsilon}$. Therefore, if we break down this time period into sub-intervals of duration Δ we will find that after time period $\frac{1}{\varepsilon}$ elapses the form of the micro-canonical distribution will change by a value of order ε . If we have an ε approaching zero, we can prove the above contention.

Now we will consider the case when the system has k - first integrals in involution. By analogy with the micro-canonical distribution we will assume that in this case if the values of the parameters E, K'_1, \dots, K'_k are fixed the system's distribution function will have the form:

$$\rho(x) = c\delta(H(x) - E) \prod_{i=1}^k \delta(K_i(x) - K'_i), \tag{4.11}$$

where c is a normalizing multiplier. First of all let us note that this definition is correct, i.e. the form of the distribution will not change if the integrals K_1, \dots, K_k are replaced with the functions $\hat{K}_1, \dots, \hat{K}_k$ of these integrals and the Hamiltonian. In fact:

$$\begin{aligned} & c\delta(H - E) \prod_{i=1}^k \delta(\hat{K}_i - \hat{K}'_i) = \\ & = c\delta(H - E) \prod_{i=1}^k \delta(K_i - K'_i) \frac{D(H, K_1, \dots, K_k)}{D(H, \hat{K}_1, \dots, \hat{K}_k)}, \end{aligned} \tag{4.12}$$

where

$$\frac{D(H, K_1, \dots, K_k)}{D(H, \hat{K}_1, \dots, \hat{K}_k)} \tag{4.13}$$

- is the Jacobian of the transformation of the variables $H, \hat{K}_1, \dots, \hat{K}_k$ into the variables H, K_1, \dots, K_k . This Jacobian is constant on the shared level surface of the functions H, K_1, \dots, K_k , which proves the correctness of the definition.

We will call distribution (4.11) the generalized micro-canonical distribution. It has to be said that the generalized micro-canonical distribution can be derived from the requirement that the Von Neumann entropy must achieve its maximum if the energy value and the values of the first integrals

K_1, \dots, K_k , are fixed. In other words, the generalized micro-canonical distribution corresponds to a state of the system in which the information that is available about it (with the fixed values of the Hamiltonian and the first integrals K_1, \dots, K_k) is minimal.

Using a method similar to that we used above, we can demonstrate that the micro-canonical distribution does not change its form as a result of quasi-static processes. The following formula has to be noted here: if the Hamiltonian H and the first integrals K_1, \dots, K_k are functions of parameter λ , then in quasi stationary processes:

$$\left(\frac{\partial K'_i}{\partial \lambda}\right)_{qs} = \frac{\partial K_i}{\partial \lambda}, \tag{4.14}$$

where qs means that the derivative is calculated along the quasi-static process. We will now define the entropy corresponding to the micro-canonical distribution as:

$$S(E, K'_1, \dots, K'_k) = \ln W(E, K'_1, \dots, K'_k), \tag{4.15}$$

Where $W(E, K'_1, \dots, K'_n)$ is the so called statistical weight:

$$W(E, K'_1, \dots, K'_k) = \int d\Gamma_x \delta(H(x) - E) \prod_{i=1}^k \delta(K_i(x) - K'_i). \tag{4.16}$$

Let's found out how correct this definition is, i.e. how will the entropy change if we move from the integrals H, K_1, \dots, K_k to the integrals $H, \hat{K}_1, \dots, \hat{K}_k$. What we get is:

$$W(E, K'_1, \dots, K'_n) = c \int d\Gamma_x \delta(H(x) - E) \prod_{i=1}^n \delta(\hat{K}_i(x) - \hat{K}'_i), \tag{4.17}$$

where c is the transformation Jacobian. The appearance of this multiplier next to the statistical weight will create an additional term in the entropy $\ln c$. It has to be noted here, that a similar problem also arises in standard thermodynamics ($k = 0$), where this parameter is simply discarded because it is assumed that it's influence in the thermodynamic limit is infinitesimally small. We will do the same here. It also has to be noted that instead of (4.11) the following formula can be used for the micro-canonical distribution:

$$\rho(x) = c \Delta(H(x) - E) \prod_{i=1}^k \Delta(K_i(x) - K'_i), \tag{4.18}$$

Where function Δ equals one in the small neighborhood of zero and equals zero outside this neighborhood. In the thermodynamic limit, this neighborhood will be so narrow that Δ -function can be replace with δ -function, and we will get back to (4.11). In light of the above notes, the statistical weight can be defined as:

$$W(E, K'_1, \dots, K'_n) = \int d\Gamma_x \Delta(H(x) - E) \prod_{i=1}^k \Delta(K_i(x) - K'_i). \tag{4.19}$$

It can be seen from this formula that the statistical weight can be interpreted as the number of microscopic states compatible with a given macroscopic state, or as the thermodynamic probability.

Now let's assume our system is in equilibrium with the environment. Let's demonstrate that we can choose the first integrals $\hat{K}_1, \dots, \hat{K}_n$ in such a way that their values will remain the same as the system heats up. And indeed, the energy level E corresponds to the integral values $K'_1(E), \dots, K'_n(E)$. Let's replace the integrals K_1, \dots, K_n with the integrals $\hat{K}_1, \dots, \hat{K}_n$ using the formula $\hat{K}_i = K_i - K'_i(H)$. It can be seen that these integrals remain constant as the system heats up. We then assume that these integrals also remain constant when the system temperature increases. What we then have is

$$\left(\frac{\partial K'_i}{\partial \lambda}\right)_{qs} = \frac{\partial K_i}{\partial \lambda}. \tag{4.20}$$

From which we can derive: But because:

$$\left(\frac{\partial K'_i}{\partial \lambda}\right)_{qs} = \left(\frac{\partial K'_i}{\partial \lambda}\right)_E + \left(\frac{\partial K'_i}{\partial E}\right)_\lambda \left(\frac{\partial E}{\partial \lambda}\right)_{qs}, \quad (4.21)$$

and $\left(\frac{\partial K'_i}{\partial E}\right)_\lambda = 0$ we have

$$\left(\frac{\partial K'_i}{\partial \lambda}\right)_E = \left(\frac{\partial K'_i}{\partial \lambda}\right)_{qs} = \overline{\frac{\partial K_i}{\partial \lambda}}. \quad (4.22)$$

It has to be noted that the entropy remains constant in a quasi-static process. Indeed, in a quasi-static process, the (generalized) micro-canonical distributions corresponding to the various parameters turn out to be bound, as was demonstrated above, by a canonical transformation and their entropy is the same because canonical transformations preserve the phase volume. One important result of this section is the conclusion that in the thermodynamics of stationary non-equilibrium states, the standard thermodynamic equations hold true. Let's derive the standard thermodynamic equation:

$$dE = TdS - PdV, \quad (4.23)$$

where T is the temperature, P is the pressure, and V is the volume of the system. Put by definition that

$$\frac{1}{T'} = \frac{dS}{dE} \quad (4.24)$$

and demonstrate that $T' = T$, i.e. that it is the same as the ordinary temperature. Let E' be the energy of the environment around the system and $S(E')$ its entropy. We will assume that our system is in equilibrium with its environment (but it's not in equilibrium with itself, being in a stationary non-equilibrium state.) The probability $P(E, E')$ that the system's energy equals E , and the energy of the environment equals $\sim e^{S(E)+S'(E')}$ because we earlier defined the system's entropy $S(E)$ as the logarithm of thermodynamic probability. If the system is in equilibrium with its environment, then $P(E, E')$ reaches its maximum (with an additional condition that $E+E' = \text{const}$), because equilibrium is the most probable state in this case. Consequently:

$$\left(\frac{dS(E)}{dE} - \frac{dS'(E')}{dE'}\right)dE = 0, \quad (4.25)$$

i.e.

$$T' = T, \quad (4.26)$$

and that is exactly what we've been trying to prove.

Let us remind you that $S = \ln W$, where

$$W = \int d\Gamma_x \delta(E - H(x)) \prod_{i=1}^n \delta(K'_i(V) - K_i(x)). \quad (4.27)$$

Here we directly specify the dependence of K_i on V . We just demonstrated that $\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$. Now all we've got left to do is to demonstrate that $\left(\frac{\partial S}{\partial V}\right)_E = \frac{1}{T}P$. Hereinafter derivatives are taken with

$V = V_0$ for some V_0 . What we get is:

$$\begin{aligned}
 \left(\frac{\partial S}{\partial V}\right)_E &= \\
 &= \frac{1}{W} \int d\Gamma_x \left\{ -\frac{\partial H(x)}{\partial V} \delta'(E - H(x)) \prod_{i=1}^n \delta(K'_i(V) - K(x)) + \right. \\
 &+ \delta(E - H(x)) \sum_{j=1}^n \left[\prod_{i=1, i \neq j} \delta(K'_i - K_i(x)) \delta'(K'_j - K_j(x)) \left(\frac{\partial K'_j(V)}{\partial V} - \frac{\partial K_j(x)}{\partial V} \right) \right] \Big] = \\
 &= \frac{1}{W} \int d\Gamma_x \left\{ -\frac{\partial H(x)}{\partial V} \delta'(E - H(x)) \prod_{i=1}^n \delta(K'_i - K(x)) + \right. \\
 &+ \sum_{j=1}^n \frac{1}{W} \frac{\partial}{\partial K'_j} \left[W \left(\left(\frac{\partial K'_j}{\partial V} \right)_E - \overline{\frac{\partial K_j(x)}{\partial V}} \right) \right] \Big\} - \frac{\partial}{\partial V} \left(\frac{\partial K'_j(V)}{\partial K'_j(V_0)} \right). \quad (4.28)
 \end{aligned}$$

Because of equation (4.22) the second to last term on the right of the last equation (4.28) equals zero. As far as the last term is concerned, the most reasonable assumption would be that $\frac{\partial K'_j(V)}{\partial K'_j(V_0)} \approx 1$ or $\frac{\partial K'_j(V)}{\partial K'_j(V_0)} = 1 - \text{const} \frac{V - V_0}{V_0}$, with $V \approx V_0$. Therefore the last term in (81) disappears in the thermodynamic limit. Thus the final result is:

$$\begin{aligned}
 \left(\frac{\partial S}{\partial V}\right)_E &= -\frac{1}{W} \int d\Gamma_x \frac{\partial H(x)}{\partial V} \delta'(E - H(x)) \prod_{i=1}^n \delta(K'_i - K(x)) = \\
 &= -\frac{1}{W} \frac{\partial}{\partial E} \int d\Gamma_x \frac{\partial H(x)}{\partial V} \delta(E - H(x)) \prod_{i=1}^n \delta(K'_i - K(x)) = \\
 &= -\frac{1}{W} \frac{\partial}{\partial E} \left(\overline{\left(\frac{\partial H(x)}{\partial V} \right)} W \right). \quad (4.29)
 \end{aligned}$$

But $-\overline{\left(\frac{\partial H(x)}{\partial V} \right)}$, as was already demonstrated earlier, is the speed at which the energy changes in an adiabatic process, in which the changing parameter is the volume, i.e. pressure. Thus

$$\begin{aligned}
 \left(\frac{\partial S}{\partial V}\right)_E &= \frac{1}{W} \frac{\partial}{\partial E} (PW) = \\
 &= P \frac{\partial S}{\partial E} + \frac{\partial P}{\partial E}. \quad (4.30)
 \end{aligned}$$

But energy is an extensive value while pressure is an intensive one. For this reason in the thermodynamic limit $\frac{\partial P}{\partial E} = 0$. Finally, remember that $\frac{\partial S}{\partial E} = \frac{1}{T}$ we get:

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{1}{T} P, \quad (4.31)$$

This is what we've been trying to prove. U

Using the standard method and applying the Legendre transformation we can introduce thermodynamic functions. The free energy F is defined as:

$$F := E - TS. \quad (4.32)$$

Using (4.23) we can find:

$$dF = -SdT - PdV. \quad (4.33)$$

Similarly we can define the thermodynamic potential Φ :

$$\Phi := F + PV. \quad (4.34)$$

What we get is:

$$d\Phi = -SdT + VdP. \quad (4.35)$$

If the number of particles in the system N is variable then (4.23) should be changed to:

$$dE = TdS - PdV + \mu dN. \quad (4.36)$$

Using the theorem of small additions we can find that:

$$\begin{aligned} dF &= -SdT - PdV + \mu dN, \\ d\Phi &= -SdT + VdP + \mu dN. \end{aligned} \quad (4.37)$$

Integrating the last equation with constant V and T between zero and N , we can find that:

$$\Phi = \mu N. \quad (4.38)$$

If the system has particles of various sorts numbered with $i = 1, \dots, M$ and N_i is the number of particles of sort i , then in all the previous formulas the term μdN needs to be replaced with $\sum_{i=1}^M \mu_i dN_i$.

We also have:

$$\Phi = \sum_{i=1}^M \mu_i N_i. \quad (4.39)$$

In all of the above all the thermodynamic values, including the entropy, proved to be dependent on the values K'_1, \dots, K'_k of the motion integrals K_1, \dots, K_k . Now we're going to formulate the following **Equivalence principle**. The entropy $S(E, K'_1, \dots, K'_k)$ does not depend on K'_1, \dots, K'_k (if all the other parameters of the system are constant).

Here is how it can be substantiated. We assigned some specific value to the energy E , and for the sake of simplicity assume that $n = 1$. We normalize $K' := K'_1$ in such a way as to ensure that K' changes from -1 to 1 and that at 0 the entropy reaches its maximum.

If $S(K')$ depends on K' and our system is in thermodynamic equilibrium with its environment then it will be established such a value of K' that corresponds to maximum entropy, i.e. $K' = 0$.

In a sufficiently small neighborhood of $K' = 0$, $S(K')$ will look like this:

$$S(K') = S_0 - cK'^2, \quad (4.40)$$

$c > 0$. Because our system is macroscopic and c must be comparable to S_0 , we have to assume that c is very great. In this case the thermodynamic probability will look like this:

$$W(K') = \text{conste}^{-cK'^2}, \quad (4.41)$$

i.e. $W(K')$ will have a pronounced peak at $K' = 0$, while all the other values of K' will be extremely improbable. This means that, in other words, that it doesn't really matter whether we're averaging using the micro-canonical distribution

$$\rho(x) = c\delta(E - H(x)) \quad (4.42)$$

or using the generalized micro-canonical distribution:

$$\rho(x) = c\delta(E - H(x))\delta(K' - K(x)). \quad (4.43)$$

Thus if $S(E, K')$ depends on K' then we don't have to use the micro-canonical distribution with a fixed value of the integral K .

Thus the most general case which we can come across is where the entropy $S(H, K'_1, \dots, K'_k)$ depends only on the values of the integrals K_1, \dots, K_l , $l = 1, \dots, k$ and does not at all depend on the

values of the integrals K_{l+1}, \dots, K_k . The integrals K_1, \dots, K_l are assigned values corresponding to maximum entropy and the mean for the generalized micro-canonical distribution, corresponding to the values of the integrals $K_1 = K'_1, \dots, K_l = K'_l, K_{l+1} = K'_{l+1}, \dots, K_k = K'_k$ will equal the mean for the distribution:

$$c\delta(H - E) \prod_{i=l+1}^k \delta(K_i - K'_i). \quad (4.44)$$

The observed values of the integrals K_{l+1}, \dots, K_k can be arbitrary.

Now let us consider an example from the condensed matter physics where the general case above is realized. The case in hand is the superfluid helium.

Let us consider a system of N particles enclosed in a certain macroscopic volume V and obeying the Bose statistics. The Hamiltonian of such system takes the form:

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=1}^N \sum_{j=i+1}^N \Phi(|x_i - x_j|), \quad (4.45)$$

where $\Phi(|x_i - x_j|)$ is the potential energy of the i -th and j -th particles.

Let us assume that

$$\nu(p) = \int \Phi(|x|) e^{ipx} d^3x. \quad (4.46)$$

Then, in secondary quantization representation the Hamiltonian will take the form:

$$\begin{aligned} \Gamma := H - \mu N = & \sum_p \left(\frac{p^2}{2m} - \mu \right) b_p^+ b_p + \\ & + \frac{1}{2V} \sum_{p_1, p_2, p'_1, p'_2} \Delta(p_1 + p_2 - p'_1 - p'_2) \nu(p_1 - p'_1) b_{p_1}^+ b_{p_2}^+ b_{p'_1} b_{p'_2}. \end{aligned} \quad (4.47)$$

Here $\Delta(x)$ is the function equal to 1 when $x = 0$ and equal to zero in all the other cases. b_p^+, b_p are particle creation-annihilation operators in a state with the momentum of p .

With low interaction between the particles almost all of them are in condensed state. And as $b_0, b_0^+ \sim \sqrt{N}$, in commuting relation we can neglect 1 and consider b_0, b_0^+ commutation variables. Let us denote the number of particles in the condensate by N_0 .

Keeping only the terms that are quadratic by the creation-annihilation operators of the supercondensate particles in the Hamiltonian, we derive:

$$\begin{aligned} \Gamma = & -\frac{1}{2} \frac{N_0^2}{V} \nu(0) + \sum_{p \neq 0} \left\{ \frac{p^2}{2m} + \frac{N_0}{V} \nu(p) \right\} b_p^+ b_p + \\ & + \frac{N_0}{2V} \sum_{p \neq 0} \nu(p) (b_p^+ b_{-p}^+ + b_{-p} b_p). \end{aligned} \quad (4.48)$$

This Hamiltonian can be diagonalized by the canonical Bogoliubov transformation (Bogoliubov N.N., Bogoliubov N.N. (jr.), 1984):

$$\begin{aligned} \xi_p & := \frac{b_p - A_p b_{-p}^+}{\sqrt{1 - A_p^2}}, \\ \xi_p^+ & := \frac{b_p^+ - A_p b_{-p}}{\sqrt{1 - A_p^2}}, \end{aligned} \quad (4.49)$$

where

$$A_p = \frac{V}{N_0 \nu(p)} \left\{ E(p) - \frac{p^2}{2m} - \frac{N_0}{V} \nu(p) \right\},$$

$$E(p) = \sqrt{\frac{N_0}{V} \frac{p^2 \nu(p)}{m} + \frac{p^4}{4m}}. \quad (4.50)$$

In new variables the Hamiltonian of the system will take the form:

$$H = H_0 + \sum_{p \neq 0} E_p \xi_p^+ \xi_p. \quad (4.51)$$

If the condensate moves at non-zero rate u , then the Hamiltonian of the systems takes the form:

$$H = H_0 + \sum_{p \neq 0} (E_p - up) \xi_p^+ \xi_p. \quad (4.52)$$

This Hamiltonian has the evident motion integrals — the occupation numbers. Or rather let us divide the set of all non-zero momentums $\{p\}$ into disjoint subsets S_i , containing G_i elements, corresponding to the close values of the momentums. We assume that $G_i \rightarrow \infty$ when $V \rightarrow \infty$, but, together with that, $\frac{G_i}{V} \rightarrow 0$ when $V \rightarrow \infty$. Then the motion integrals will be the occupation numbers N_i of the cells S_i . Let us assume $n_i = \frac{N_i}{G_i}$. The entropy of the system will take form:

$$S = \sum_i G_i [(1 + n_i) \ln(1 + n_i) - n_i \ln n_i]. \quad (4.53)$$

This value reaches the maximum under the fixed energy and number of particles on Bose distribution.

On the other side, except the occupation numbers, Bose gas has one more first integral — the condensate motion velocity. Let us analyze the dependence of the thermodynamic values of our system on the value of this integral. The state of the liquid helium is convenient to be described via the condensate wave function Ξ (Lifshitz, Pitaevskii, 1978). It satisfies the following differential equation:

$$i \frac{\partial}{\partial t} \Xi(x, t) = -\frac{1}{2m} \nabla^2 \Xi(x, t) + U_0 \Xi(x, t) |\Xi(x, t)|^2 - c \Xi(x, t), \quad (4.54)$$

where $U_0, c > 0$.

If the system is kept at a constant temperature and its state is described by the number of $\lambda_1, \dots, \lambda_l$, then in equilibrium the free energy $F(T, \lambda_1, \dots, \lambda_l)$ must reach the minimum. In our case the condensate wave function $\Xi(x, t)$ performs the role of these parameters. But the condensate wave function can vary with time and in meaning, $\Xi(x, t), \Xi^+(x, t)$ represent canonically conjugate variables. That is why the requirement of free energy minimality should be replaced by the requirement of stationary action:

$$A[\Xi, \Xi^+] = \int_{t_1}^{t_2} [i \int d^3x \Xi^+ \frac{\partial}{\partial t} \Xi - F[\Xi, \Xi^+]] dt. \quad (4.55)$$

As F is defined accurate to constant, we will find:

$$F[\Xi, \Xi^+] = \int d^3x \left\{ -\frac{1}{2m} \Xi^+(x) \nabla^2 \Xi(x) + \frac{U_0}{2} |\Xi(x)|^4 - c |\Xi(x)|^2 \right\}. \quad (4.56)$$

To show that the thermodynamic characteristics do not depend on the velocity of the condensate motion it is sufficient to show that the action $A[\Xi, \Xi^+]$ is invariant under Galilean transformation:

$$\Xi(x, t) \mapsto e^{i \left(\frac{mv^2}{2} t + mvx \right)} \Xi(x - vt, t), \quad (4.57)$$

v is relative motion velocity. But the invariance of the action $A[\Xi, \Xi^+]$ in relation to the Galilean transformation is easy to find out by direct calculation.

So, the action $A[\Xi, \Xi^+]$ does not depend on the condensate flow velocity and this fact provides the stability of the condensate flow.

We needed this example to illustrate the stability of the generalized microcanonical distributions. Besides we obtained the answer to the question of why not all the first integrals residing in the system are observed. Only those integrals are observed that have the entropy unchanged while the values of these integrals are changing (at constant values of other integrals).

In the next section when we analyze the Ling cell, it will be essential that some of the first integrals of the Ling cell satisfy the equivalence principle. In addition to that, these first integrals have never been observed directly the way that the velocity of the Bose condensate through the capillary can be observed. These first integrals could only be observed indirectly by analyzing physiological phenomena testifying their presence. For this reason there would be a lot of doubts about or theory if no inorganic systems could be found for which there exist non-trivial first integrals satisfying the equivalence principle and which can therefore be observed. The example cited above allows us to dispense with such doubts.

Let us discuss the equivalence principle more detailed. For the sake of simplicity we will assume that the entropy of the system $S(E, K')$ depends on the value of K' of one integral K , however, the reasoning given below is directly generalized for the case when the entropy depends on the values of the two and more first integrals in involution.

According to the equivalence principle the entropy $S(E, K')$ does not depend on K' . But it would be more precise to say that the entropy reaches its maximum on the certain interval of the values of the integral $K' [\alpha(\lambda), \beta(\lambda)]$ and steeply decreases out of this interval. Here λ — the parameter on which the Hamiltonian of the system depends. Here the energy of the system depending on the parameter λ is chosen the way that at any value of λ the entropies of the system were always the same.

At the adiabatic infinitesimal change of the parameter λ , $\lambda_0 \mapsto \lambda' = \lambda_0 + \delta\lambda$ the value of the integral K' is transformed by the formula $K' \mapsto K' + \frac{\partial K'}{\partial \lambda} \delta\lambda$. Let us show that at this process the plateau $[\alpha(\lambda_0), \beta(\lambda_0)]$ transforms into the plateau $[\alpha(\lambda'), \beta(\lambda')]$.

Our system is in equilibrium with the thermostat and let us assume that $K'_e \in [\alpha(\lambda_0), \beta(\lambda_0)]$ any equilibrium value of the integral K' ($\lambda = \lambda_0$). Let us show that when the system's energy is fixed at E and $K' \in [\alpha(\lambda_0), \beta(\lambda_0)]$ the temperature of the system does not depend on K' .

Let us assume that T — the temperature corresponding to the equilibrium value of K'_e of the integral K , and equal to the temperature of the thermostat. Let us assume that K'_1 — any value of the integral K from the interval $[\alpha(\lambda_0), \beta(\lambda_0)]$. Let us assume that T' — The temperature corresponding to it, and $T' \neq T$. Let us surround our system by an adiabatic membrane and change $K'_e \mapsto K'_1$. When this happens neither the system energy + thermostat nor the system entropy + thermostat are not changing. Now let us make our system contact the thermostat again which will lead to the equalization of the temperatures of the system and the thermostat. At this stage we assume that system + thermostat is an isolated system, particularly, its full energy is constant. As at the process of temperature equalization a self-induced heat flow takes place, the entropy of the system and the thermostat increases. That means, at the value of the integral K $K' = K'_e$ for fixed full value of the common energy of the system and the thermostat, the entropy of the system and the thermostat is not maximal which contradicts the fact that K'_e — the equilibrium value of the integral K .

The same way we will demonstrate that at the fixed energy of the system the pressure P_1 , corresponding to the value of the integral K'_1 is equal to the ambient pressure P . The pressure is defined by formula $P = (\frac{\partial E}{\partial \lambda})_S$. Let us assume, for definiteness, that $P_1 > P$. As it was demonstrated above the temperature corresponding to the value of the integral K'_1 is equal to the ambient temperature T . Let us make the system expand isothermally, doing work against the external forces. Meanwhile the system pressure P_1 will be decreasing by virtue of the known thermodynamic inequation, fair in our case as well, that states that the module of the isothermal compressibility is

positive. We will allow the system to expand quasistatically until its pressure is equal to the pressure of the thermostat. At that the system + thermostat will do a certain positive work, i.e. the full energy of the system + thermostat will decrease by this value. But as the process of the system expansion is quasistatic and therefore reversible, the full entropy of the system + thermostat will not change. Therefore we can conclude that at the value of the integral K'_e , and for fixed full entropy of the system and the thermostat, the energy minimum is not reached which means the value of the integral K'_e is not equilibrium.

So, we demonstrated that for fixed energy of the system E , The values of the pressure and temperature are constant on the whole interval $[\alpha(\lambda_0), \beta(\lambda_0)]$ of the values of the integral K' .

Let us now adiabatically change the λ , $\lambda_0 \mapsto \lambda' = \lambda_0 + \delta\lambda$. At this change the entropy of the system will not change and the energy of the system will increase by the value $P\delta\lambda$, i.e. the value that does not depend on K' . In other words, at the transformation $K' \mapsto K' + \frac{\partial K}{\partial \lambda} \delta\lambda$ the points of the plateau will pass again into points of the plateau but corresponding to the changed parameter λ . When making the inverse adiabatic change of the parameter λ $\lambda' \mapsto \lambda_0 = \lambda' - \delta\lambda$, we see that the formula $K' \mapsto K' + \frac{\partial K}{\partial \lambda} \delta\lambda$ sets a one-to-one correspondence between the points of the plateau $[\alpha(\lambda_0), \beta(\lambda_0)]$ and $[\alpha(\lambda'), \beta(\lambda')]$.

We recall that we proceed from the assumption that the system is in equilibrium with the environment but is not in equilibrium with itself, being in a stationary non-equilibrium state. Let us describe a possible way for the system to change from stationary non-equilibrium to equilibrium. Let us use the (4.18) for the distribution function. This expression uses k independent first integrals in involution K_1, \dots, K_k . However that does not mean that there no other integrals in the system except K_1, \dots, K_k , being in involution with them. For example in the formula for the ordinary microcanonical distribution only the energy function takes part but, as it was discussed in the section 1, even the most realistic systems of the statistical mechanics are nonergodic at the thermodynamyc limit, i.e. there are other first integrals except the energy. We will call first integrals that are included in formula (4.18) active. A possible way of changing to equilibrium is that the more and more first integrals from the list K_1, \dots, K_k cease being active.

Let us assume that in this system the active integrals were K_1, \dots, K_k and the integral K_k ceased being active. Let us use the symbol $(\delta S)_E$ to denote the change of the entropy at this process (at constant energy). Let us prove the following important proposition:

Proposition. $(\delta S)_E$ does not change at quasistatic processes, that is to say

$$(d(\delta S)_E)_{qs} = 0. \tag{4.58}$$

Proof. Let us assume that the active integrals are K_1, \dots, K_k . Then the generalized microcanonical distribution corresponding to these integrals will take the form:

$$w_k(E, K'_1, \dots, K'_k, x) = c\Delta(H(x) - E) \prod_{i=1}^k \Delta(K_i(x) - K'_i). \tag{4.59}$$

Let us note that $w_k(E, K'_1, \dots, K'_k, x)$ is proportional to the characteristic function of a certain set. If the integral K_k becomes inactive then the generalized microcanonical distribution $w_{k-1}(E, K'_1, \dots, K'_{k-1}, x)$ turns out to be composed of a certain number M of microcanonical distributions $w_k(E, K'_1, \dots, K'_k, x)$, the entropies of which are the same. It is evident that $(\delta S)_E = \ln M$.

Let us consider the adiabatic change of the parameter $\lambda \mapsto \lambda' = \lambda_0 + \delta\lambda$. We can assume that $\forall i = 1, \dots, k$

$$\overline{\left(\frac{\partial K_i}{\partial \lambda}\right)}_{K'_1, \dots, K'_k} |_{\lambda=\lambda_0} = 0. \tag{4.60}$$

In this formula the low indices K'_1, \dots, K'_k mean that the averaging corresponding to the vinculum is taken over the microcanonical distribution $w_k(E, K'_1, \dots, K'_k, x)$. This can be reached by replacing

$\forall i = 1, \dots, k \ K_i \mapsto K_i - (\lambda - \lambda_0)f_i(K_1, \dots, K_k, H)$, where $f_i(K_1, \dots, K_k, H)$ is the suitable functions of the first integrals and Hamiltonian.

We will suppose that at this adiabatic process the point in the phase space that represents the state of our system, constantly moves in such a way that the values K_1, \dots, K_k are the motion integrals. Meanwhile the microcanonical distribution $w_k(E, K'_1, \dots, K'_k, x)$ transforms into the microcanonical distribution $w_k(E', K'_1, \dots, K'_k, x)$. But, because of the above, the value $\delta E := E' - E$ will not depend on the value K'_k and will be the same if we calculate it for the distribution $w_{k-1}(E, K'_1, \dots, K'_{k-1}, x)$. In the same adiabatic process the microcanonical distribution $w_{k-1}(E, K'_1, \dots, K'_{k-1}, x)$, corresponding to the value of the parameter $\lambda = \lambda_0$, will transform into the distribution $w_{k-1}(E', K'_1, \dots, K'_{k-1}, x)$, and by virtue of the fact that δE can be calculated over the distribution $w_{k-1}(E, K'_1, \dots, K'_{k-1}, x)$, the entropies corresponding to the distribution $w_{k-1}(E, K'_1, \dots, K'_{k-1}, x)$ with $\lambda = \lambda_0$ and the distribution $w_{k-1}(E', K'_1, \dots, K'_{k-1}, x)$ with $\lambda = \lambda'$ will be the same. But at the adiabatic process (such as the one described in the beginning of the proof) the evolution of the distributions simply resolves into the canonical substitution of the arguments of these distributions. That is why with $\lambda = \lambda'$, the distribution $w_{k-1}(E', K'_1, \dots, K'_{k-1}, x)$ will turn out to be composed from the same number of M generalized microcanonical distributions $w_k(Ey, K'_1, \dots, K'_k, x)$. That is to say $M = \text{const}$. That is to say $((\delta S)_E)_{qs} = \ln M = \text{const}$, which was to be proved.

In case if there are too many of first integrals and if the process of decrease of the number of active integrals can be considered continuous, it is reasonable to introduce the continuous parameter s , characterizing the number of active integrals the way that $s \in [0, 1]$, the value $s = 0$ corresponds to the case when no integrals are active and the decrease of the number of active integrals corresponds to the decrease of the parameter s . Therefore we have:

$$\frac{dS}{ds} \leq 0. \tag{4.61}$$

The formula $\frac{dS}{ds} \leq 0$ is correct when it is assumed that the system energy and volume are kept constant. Let us assume, however, that the system temperature and volume are kept constant. Then:

$$\begin{aligned} 0 \geq \left(\frac{dS}{ds}\right)_{E,V} &= \left(\frac{dS}{ds}\right)_{T,V} - \left(\frac{\partial S}{\partial E}\right)_{V,s} \left(\frac{dE}{ds}\right)_{V,T} = \\ &= \left(\frac{dS}{ds}\right)_{T,V} - \frac{1}{T} \left(\frac{dE}{ds}\right)_{V,T} = \\ &= \frac{1}{T} \left(\frac{d(ST - E)}{ds}\right)_{T,V}. \end{aligned} \tag{4.62}$$

That is to say:

$$\left(\frac{dF}{ds}\right)_{T,V} \leq 0. \tag{4.63}$$

The same way let us assume that the system temperature and pressure are kept constant. Then:

$$\begin{aligned} 0 \geq \left(\frac{dF}{ds}\right)_{T,V} &= \left(\frac{dF}{ds}\right)_{T,P} - \left(\frac{\partial F}{\partial V}\right)_{s,T} \left(\frac{dV}{ds}\right)_{P,T} = \\ &= \left(\frac{dF}{ds}\right)_{T,P} - P \left(\frac{dV}{ds}\right)_{P,T} = \\ &= \left(\frac{d\Phi}{ds}\right)_{P,T}. \end{aligned} \tag{4.64}$$

So, in case when the temperature and pressure are kept constant:

$$\left(\frac{d\Phi}{ds}\right)_{P,T} \leq 0. \tag{4.65}$$

The statement, that the number of independent first integrals in involution for the system must be very large can be established, for example, by the following way. Let us decompose the system \mathfrak{C}

into disjoint union of enough large number N of small but macroscopic subsystems $\mathfrak{S}_i, i = 1, \dots, N$. Let $H_i, i = 1, \dots, N$ be a Hamiltonian of subsystems \mathfrak{S}_i and $H_{ij}, i, j = 1, \dots, N, i \neq j$ be the total interaction Hamiltonian of subsystems \mathfrak{S}_i and \mathfrak{S}_j . Then $\sum_{i=1}^N H_i$ is proportional to the volume of system \mathfrak{S} and $\sum_{1 \leq i < j \leq N}^N H_{i,j}$ is proportional to the total area of boundaries between different subsystems \mathfrak{S}_i . But each subsystem \mathfrak{S}_i is macroscopic. So we can neglect by the interaction Hamiltonian of different subsystems in total hamiltonian H of system \mathfrak{S} . Therefore we can write that

$$H = \sum_{i=1}^N H_i \quad (4.66)$$

But each subsystem \mathfrak{S}_i is macroscopic. So, according to the nonergodic theorem for each subsystem \mathfrak{S}_i there exists at least one its first integral K_i . It is easy to see that for different $i = 1, \dots, N$ integrals K_i are independent and in involution. It follows from (4.66) that integrals K_i are the first integrals of whole system \mathfrak{S} at the same time.

5 E.S. Bauer's Stable Non-Equilibrium Principle and the Resting State of G. Ling

For the sake of further analysis we will consider the contribution that E.S. Bauer and G. Ling made to the issue at hand. According to Bauer (Bauer, 1935) the substance of the living cell can be in one of two states: the stable-non-equilibrium (resting) and thermodynamic equilibrium (active). The work produced by living system a living system is done when the system passes from stable non-equilibrium to equilibrium. Bauer used this principle (the two basic states and the change between them) as the basis for his "theoretical biology" and deductively derived the basic properties of such biological processes as assimilation, growth, excitability, adaptability and reproduction. That is what Bauer himself says [Bauer, 4, p. 143] about this principle:

"Nonliving systems are ever in equilibrium and due to their free energy they do work against equilibrium required by the laws of physics and chemistry in the existing ambient conditions."Further Bauer expands on it: "We will call this principle as stable none-equilibrium principle of the living systems. This name clearly expresses the meaning of the principle and the unique feature of living systems from the point of view of thermodynamics. The same way as a system in stable equilibrium when disturbed returns back to it, a living system in stable non-equilibrium also keeps coming back to it. Our principle also characterizes the unique feature of living systems as we do not know any nonliving systems that would be in stable non-equilibrium."

The ground rule of Ling's Association-Induction Hypothesis (Ling, 1962, 2001, 1997) is that the cell as a quasi-solid body is a system with a non-maximal entropy in a resting state. We proceed from the approach based on the fact that the resting state of the living cell, according to both Ling and Bauer, is a stationary non-equilibrium state, the possibility of existence of which was proven by one of us for a large class of realistic systems in statistical mechanics (Prokhorenko, 2009). Here we simply apply it to the living cell. The appropriateness of the proposed approach to the living will be verified by comparing the results of the theoretical analysis and the available experimental data.

Based on the assumption that the state of the living cell is stationary non-equilibrium we will give a thermodynamic description of the following phenomena:

- 1) When the cell is excited and when it dies heat is generated.
- 2) When the cell is excited and when it dies the cells' size changes (mostly decreases).
- 3) When the cell is excited and when it dies , the cell's key protein molecules fold.
- 4) When the cell is excited and when it dies, efflux of potassium ions from the cell takes place.

Let us begin with the explanation of the first phenomenon. Let us assume that the substance inside the cell is in stationary non-equilibrium corresponding to a number of active first integrals in involution and the process of excitation and death manifests through some of these first integrals becoming inactive. Let's assume that just like in the section 3 that the number of the active first integrals is characterized by a continuous $s \in [0, 1]$, Where $s = 0$ corresponds to the case, when neither of first integrals are active and the value of $s = 1$ to the case when the maximum number of the first integrals are active. The question why there must be so many nontrivial integrals that their number can be described by a continuous parameter, can be answered, for example, by the fact that the muscle fibres can be contracted to different degrees and is able to algebraically summate the nerve impulses that enter it. It will be clear when we consider the changes in the size of the Ling cell when it's activated and when it dies. We can choose s in such a way that s is proportionate to the number of active first integrals. The system's volume is supposed to be constant.

Let us make an infinitesimal change in the parameter s :

$$s \mapsto s' = s - \delta s, \quad (5.1)$$

where $\delta > 0$, δs is are infinitely small.

It has been established that the knowledge of k of the first integrals in involution allows decreasing the number of degrees of freedom by k units (the Whittaker reduction). For each s we have $\text{const } s$ of active first integrals and the entropy that corresponds to the parameter s is the entropy of the reduced system, corresponding to these constant s first integrals. If $s \mapsto s' = s - \delta s$, then the number of degrees of freedom of reduced system increases by $\text{const } \delta s$ units, and we may consider that these new 'turned-on' degrees of freedom corresponding to the new system $\delta\mathfrak{S}$, that is in thermodynamic equilibrium with the initial system \mathfrak{S} . We will change the parameter s at a fixed temperature T . If $s \mapsto s' = s - \delta s$ the system's energy changes:

$$E \mapsto E' = E + (\delta E)_T, \quad (5.2)$$

and entropy:

$$S \mapsto S' = S + (\delta S)_T. \quad (5.3)$$

We can equate $(\delta E)_T$ to the energy of the system $\delta\mathfrak{S}$, and $(\delta S)_T$ to the entropy of the same system. As the system $\delta\mathfrak{S}$ is in thermodynamic equilibrium with the system \mathfrak{S} , it is essential that the temperature of the system $\delta\mathfrak{S}$ should also be equal to T , in other words, it is necessary that:

$$\frac{1}{T} = \frac{d(\delta S)_T}{d(\delta E)_T}. \quad (5.4)$$

But this equality can also be derived directly. We have:

$$\begin{aligned} \frac{dS}{dE} &= \frac{1}{T}, \\ \frac{dS + d(\delta S)_T}{dE + d(\delta E)_T} &= \frac{1}{T}. \end{aligned} \quad (5.5)$$

From these two equalities we derive (5.4) by using the elementary transformation.

But in order for $\delta\mathfrak{S}$ to be in equilibrium with \mathfrak{S} the equation (5.4) is not enough. It is necessary that

$$\frac{d^2(\delta S)_T}{(d(\delta E)_T)^2} < 0. \quad (5.6)$$

This inequality results from the requirement for maximum entropy in the system $\mathfrak{S} + \delta\mathfrak{S}$ under condition that the energy remains constant, if we take into account the fact that the number of degrees

of freedom of the system $\delta\mathfrak{G}$ is far less than the number of degrees of freedom of the system \mathfrak{G} . The detailed discussion of this inequality is found in Appendix 1. This inequality leads to

$$\begin{aligned} \frac{d}{d(\delta E)_T} \left(\frac{1}{T} \right) &< 0, \\ -\frac{1}{T^2} \frac{dT}{d(\delta E)_T} &< 0, \end{aligned} \quad (5.7)$$

or

$$\delta c_v := \frac{d(\delta E)_T}{dT} > 0. \quad (5.8)$$

We will make the following assumption about the value of $(\delta E)_T$. There is a temperature T_0 , that makes the temperature $T > T_0$ incompatible with the existence of life in the cell. This means that if the temperature $T \rightarrow T_0$ the interval Δ from the formula (4.18) becomes more and more comparable to the range spaces of the integrals K_1, \dots, K_k values, and the generalized micro-canonical distribution degenerates into a usual micro-canonical distribution. Then, if $T > T_0$

$$(\delta S)_E = \text{const}, \quad (5.9)$$

) i.e. if $T > T_0$ the dependence of T on E for \mathfrak{G} will be the same as the one for $\mathfrak{G} + \delta\mathfrak{G}$, i.e. $(\delta E)_T = 0$. This boundary condition is discussed in more detail in the Appendix 2. We have:

$$\begin{aligned} (\delta E)_T &= (\delta E)_{T_0} - \int_T^{T_0} \frac{d(\delta E)_{T'}}{dT'} dT' = \\ &= (\delta E)_{T_0} - \int_T^{T_0} \delta c_v(T') dT' = \\ &= - \int_T^{T_0} \delta c_v(T') dT' < 0. \end{aligned} \quad (5.10)$$

i.e. $(\delta E)_T < 0$, and that's what we set out to prove initially.

Let us proceed now to the explanation of why the Ling cell changes size when it is excited and when it dies. Let us examine a resting cell in equilibrium with the environment at a constant temperature T and pressure P , and show that when the cell is excited and when it dies its size decreases. So, we assume that as above $s \mapsto s' = s - \delta s$, $\delta s > 0$, and that $(\delta S)_E$ means the change in the entropy of the cell if its energy is constant.

In section 3 we demonstrated that $(\delta S)_E = \text{const}$ in an adiabatic process and that is why $(\delta S)_E$ is a function of the entropy only, that is to say:

$$(\delta S)_E = \delta f(S), \quad (5.11)$$

for some function δf of one variable. Let us show now that δf is a decreasing function. We have:

$$\begin{aligned} (\delta S)_E &= (\delta S)_T - (\delta E)_T \frac{\partial S}{\partial E}, \\ (\delta S)_E &= (\delta S)_T - \frac{1}{T} (\delta E)_T. \end{aligned} \quad (5.12)$$

Because of the thermodynamic inequality $c_V > 0$ (c_V -the thermal capacity of the cell at constant volume) the energy, and as a consequence, the entropy are strictly increasing functions of the

temperature. That is why it is enough to show that $\frac{\partial}{\partial T}((\delta S)_E) < 0$. But

$$\begin{aligned} \frac{\partial}{\partial T}((\delta S)_E) &= \frac{\partial}{\partial T}((\delta S)_T) - \frac{1}{T} \frac{\partial}{\partial T}((\delta E)_T) + \frac{1}{T^2}(\delta E)_T = \\ &= \frac{1}{T^2}(\delta E)_T. \end{aligned} \quad (5.13)$$

And by virtue of this, as it was already proved, $(\delta E)_T < 0$ we find: $\frac{\partial}{\partial T}((\delta S)_E) < 0$, i.e. δf is a decreasing function of its argument.

Now let us define the minor additions that appear in the thermodynamic potentials under $s \mapsto s' = s - \delta s$. We have:

$$\begin{aligned} (\delta S)_E &= (\delta S)_T - (\delta E)_T \frac{\partial S}{\partial E}, \\ (\delta S)_E &= (\delta S)_T - \frac{1}{T}(\delta E)_T. \end{aligned} \quad (5.14)$$

i.e. under $s \mapsto s' = s - \delta s$,

$$E(V, S) \mapsto E(V, S) - T\delta f(S). \quad (5.15)$$

According to the minor additions theorem for free energy F and the thermodynamic potential Φ we have:

$$\begin{aligned} F(V, T) &\mapsto F(V, T) - T\delta f(S), \\ \Phi(P, T) &\mapsto \Phi(P, T) - T\delta f(S). \end{aligned} \quad (5.16)$$

As

$$V = \left(\frac{\partial \Phi(P, T)}{\partial P}\right)_T, \quad (5.17)$$

Then change in the cell size with $s \mapsto s' = s - \delta s$ takes the form:

$$\delta V = -T(\delta f)'(S) \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial S}{\partial V}\right)_T. \quad (5.18)$$

As $(\delta f)' < 0$ by virtue of what was proven above and $\left(\frac{\partial V}{\partial P}\right)_T < 0$ (thermodynamic inequality, which is always true), the sign δV is opposite to the sign $\left(\frac{\partial S}{\partial V}\right)_T$.

Let us set the sign $\left(\frac{\partial S}{\partial V}\right)_T$. But because of a known thermodynamic relation

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T. \quad (5.19)$$

That is why the statement that $\left(\frac{\partial S}{\partial V}\right)_T > 0$ is therefore equivalent to the statement that the cell expands when heated (at constant pressure). This behavior is demonstrated by most solid bodies when heated. If we accept that this is true (the cell expands when heated at constant pressure) then we find $\delta V < 0$, which was to be proved. We thus conclude that the cell's size decrease. We consider our description to be a general thermodynamic prerequisite that explains the phenomenon of the Ling cell contraction, a prototype of muscle contraction.

Before we consider the aggregation of key proteins in the Ling's model, let us go back to the question of the transformation of the internal energy of the cell when it dies. We have demonstrated above that death occurs then

$$(\delta E)_{T,V} < 0. \quad (5.20)$$

If we use the symbol δQ to denote the amount of heat that entered the cell, we will find:

$$\delta Q = (\delta E)_{T,V} + T\left(\frac{\partial S}{\partial V}\right)_T \delta V. \quad (5.21)$$

But we already know that δV and have opposite signs, i.e.

$$\delta Q < 0. \quad (5.22)$$

In other words, the death and excitation of the cell are exothermic reactions.

Let us consider now the thermodynamic prerequisites of the aggregation of proteins that are present in a resting Ling's cell in an expanded state.

Our analysis draws on the fact that the energy of an unfolded protein molecule is greater than the energy of a folded protein molecule and is based on the protein model in which the configuration of the protein molecule can be characterized by a real parameter $x \in [0, 1]$, describing the degree to which the molecule has unfolded. We assume that the energy of the protein molecule is a function only of x and it is an increasing function. We assume also that $x = 0$ corresponds to a completely folded molecule whose energy is at a minimum; and $x = 1$ corresponds to a completely unfolded molecule whose energy is at its maximum.

Let us use the following supporting procedure. We will identify a single protein molecule in the cell's protoplasm and call it \mathfrak{X} , and we'll use x as a parameter characterizing the degree to which our single molecule is unfolded. If we call the system's temperature T , then all the thermodynamic equations derived in the previous section can be applied to \mathfrak{X} , more particularly we have the equation:

$$dE = TdS - hdx, \quad (5.23)$$

for a certain function $h(E, S)$ of the energy and entropy \mathfrak{X} . The value $h(E, S)$ is a generalised force that is thermodynamically conjugated to x . When the external forces that affect our protein molecule, are absent, $h(E, S) = 0$. The relation (5.23) is equivalent to the equation

$$dE = TdS - PdV, \quad (5.24)$$

And that is why we can more or less directly apply to case the conclusions for the cell interacting with the environment, changing $x \mapsto V$, $P \mapsto h$. So, Let's assume again that $s \mapsto s' = s - \delta s$, then

$$(\delta x)_{T,h} = -T(\delta f)'(S)\left(\frac{\partial S}{\partial h}\right)_{T,x}. \quad (5.25)$$

We see that the sign of δx is the same as the sign of $\left(\frac{\partial S}{\partial h}\right)_T$. But by virtue of the known thermodynamic relation:

$$\left(\frac{\partial S}{\partial h}\right)_T = -\left(\frac{\partial x}{\partial T}\right)_h. \quad (5.26)$$

So, the sign $\left(\frac{\partial S}{\partial h}\right)_T = -\left(\frac{\partial x}{\partial T}\right)_h$ will only be negative if the protein molecules unfold and the cell temperature increases. So we have proved that the protein molecules fold when the protoplasm is activated and when the cell dies only if they unfold when the cell is heated. It is clear that this statement is true only for the protein model used here.

But the property of the protein molecule to unfold when heated appears to be physically evident. This assumption seems to be reasonable as the protein molecules are supposed to change to states with more energy when heated, and the energy is an increasing function of the parameter x . That is why the protein molecule folds under $s \mapsto s' = s - \delta s$, which was to be proved.

The question of how we apply this general method we used for the analysis of more realistic protein models needs further research.

Let us consider now the question of why the Ling cell's nonergodicity includes ion flows between the cell and the environment when the physiological state of the Ling cell is changed. When analyzing

this phenomenon we will restrict ourselves to potassium ions that play an important role in the physiological processes of the cell. We will try to answer the question of why this positive ions are released by excited or dead cells. The answer to this question will explain another phenomenon well-known from the classical cytology: why the damaged area in a cell always has the negative charge to the adjoining intact areas that are not affected by excitation or injury.

It is clear that our approach must be improved in order for us to be able to consider a broader spectrum of ion characteristics, such as: ion chemical nature, their physical properties, their concentration in solution, etc.

Let us assume that N means the number of potassium ions in the cell \mathcal{C} . We can regard N as a parameter, and it will be now clear why. Our analysis is carried out in the thermodynamic limit and from this point of view the cell can be considered very big. Let us attach a very small vessel \mathcal{S} , to the cell which will be separated from it a semipermeable membrane that is permeable only for potassium ions. We will assume that in \mathcal{S} we have only potassium ions and that \mathcal{S} is so small that the entropy of the ions inside it is equal to zero. As a model for \mathcal{S} we can take a very narrow potential well, the quantum energy levels of which are not degenerate and the distance between adjoining energy levels is much greater than the temperature T . Then potassium ions in \mathcal{S} will be mostly in a basic energy state and the thermodynamic probability $W = 1$, and $S_{\mathcal{S}} = \ln W = 0$. Let us also introduce an external electric field the potential of which φ everywhere except \mathcal{S} is equal to zero, and inside \mathcal{S} is constant and equal to φ_0 . Adiabatically changing φ_0 , we can pump the potassium ions from \mathcal{S} to the cell and back. Meanwhile the entropy of the whole system will be constant and equal to the entropy of the cell S . By virtue of the fact that φ_0 is a parameter in the Hamiltonian of the whole system, $((\delta S)_E)_{qs} = \text{const}$ during adiabatic change φ_0 . Here E means the energy of the entire system. Let us assume that $E_{\mathcal{C}}$ means the energy of the cell. All the motion integrals that are related to the entire system $\mathcal{S} + \mathcal{C}$ are equally related to the cell \mathcal{C} because the potassium ions in \mathcal{S} are immovable, and their coordinates and momentums can be removed from the list of the dynamic variables. But

$$(\delta S)_E = (\delta S)_{E_{\mathcal{C}}, N} + \frac{\partial S}{\partial E_{\mathcal{C}}} \delta E_{\mathcal{C}} + \frac{\partial S}{\partial N} \delta N. \quad (5.27)$$

But $\delta E_{\mathcal{C}} = -\varphi_0 \delta N$, as the full energy of the cell and of the vessel is constant. Considering that in equilibrium:

$$-\frac{\partial S}{\partial E_{\mathcal{C}}} \varphi_0 \delta N + \frac{\partial S}{\partial N} \delta N = 0, \quad (5.28)$$

we find:

$$(\delta S)_E = (\delta S)_{E_{\mathcal{C}}, N}. \quad (5.29)$$

That is why during an adiabatic change in the parameter φ_0 or, of the number of particles in the cell N

$$((\delta S)_{E_{\mathcal{C}}, N})_{qs} = \text{const}, \quad (5.30)$$

Which means that N can be considered as a parameter.

Let us proceed now to the question of the amount of potassium ions released by the cell during its activation and death. We assume that the cell is immersed in a potassium ion solution and the chemical potential of the potassium ions is constant and equal to μ . The following thermodynamic relation will hold true:

$$dE = TdS + \mu dN \quad (5.31)$$

and all its corollaries. This equation similar to the thermodynamic equation

$$dE = TdS - PdV, \quad (5.32)$$

if we equate $N \leftrightarrow V$, $\mu \leftrightarrow -P$. Therefore, to prove that the potassium ion yield from the cell takes place when $s \mapsto s' = s - \delta s$ all we have to show is that

$$\left(\frac{\partial S}{\partial N}\right)_T > 0. \quad (5.33)$$

To find $\left(\frac{\partial S}{\partial N}\right)_T$ we will note that the concentration of potassium ions in the cell is low and that is why we can use the strong electrolyte theory (see (Lifshitz, Pitaevskii, 1995)). This theory suggests that in a low concentration of potassium ions the cell's entropy (at fixed temperature) $S = S_0 + S^{K^+} + N\varphi(P, T)$, where S_0 - the cell entropy at zero ion concentration, S^{K^+} - the entropy of only the potassium ions, calculated for a ideal gas, and $\varphi(P, T)$ is a function of the cell temperature and pressure. That is why for the entropy of the potassium ions we can use the standard formula (see (Lifshitz, Pitaevskii, 1995)):

$$S^{K^+} = N \ln \frac{eV}{N} - Nf'(T), \quad (5.34)$$

where

$$f(T) = -T \ln\left(\left(\frac{mT}{2\pi}\right)^{3/2}\right). \quad (5.35)$$

Here m is the mass of a potassium ion. It is clear that if the potassium ion solution in the cell is thin enough $\left(\frac{\partial S}{\partial N}\right)_T > 0$.

So, $\delta N < 0$, which was to be proved.

For simplicity of the analysis we assumed above that there are only potassium ions in the cell. But in reality there are different kinds of ions and all the derived formulas should be true for each kind of ions. Particularly, during the activation and death of the cell all kinds of ions should come out of the cell if their concentration is low enough. But it is known that some ions, for example sodium ions, are on the contrary, absorbed by the cell during activation or death (according to Ling's model). However, the cell becomes negatively charged during activation, i.e. our explanation leads to the correct answer "in average". This gives us hope that our explanation is genuinely true and can be improved in a proper way.

To conclude of this section let us note that we considered the resting state of the cell to be stationary non-equilibrium and the state corresponding to the excitation and death to be equilibrium. We considered these states as given and never asked the question why there are transitions between these two states. One of the possible hypotheses is that such transitions appear due to changes in the conditions on the cell's boundaries. That is why in section 3 we discussed in detail the role that the conditions on the system's boundaries play in the establishment of thermodynamic equilibrium inside the cell. The question of how true this hypothesis is will be the subject of further research.

6 Conclusions

Findings/conclusions of this research are summarized below:

- 1) We used the results of (Prokhorenko, 2009) to analyze the Ling cell in this paper, assuming that this kind of cell is a nonergodic system.
- 2) Using the property of nonergodicity as a starting point for our research, we first discussed the nonergodicity of statistical mechanics systems, we then developed the thermodynamics of stationary non-equilibrium states assuming the existence of several nontrivial first integrals that commute between them. These thermodynamics are applicable to any system in statistical mechanics, including the Ling cell.
- 3) The analysis of the Ling cell properly demonstrated that using the approach based on our unique thermodynamics of stationary non-equilibrium we managed to derive such realistic properties

of the excited Ling's cell as heat generation, decrease of the cell size, the folding of the proteins that are unfolded when the cell is resting and the releasing of potassium ions. The applicability of the proposed approach to the living cell model, such as the Ling cell, testifies to the applicability and adequacy of our analysis for studying the living state of matter.

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Appendix 1. Discussion of the Inequality (5.6).

In this section we will try to justify the inequality (5.6). Let us see the Hamiltonian dynamical system with $n + k$ degrees of freedom ($k \ll n$) and k independent first integrals in involution K_1, \dots, K_k . Locally we can always choose the canonical coordinates $(p_1, q_1), \dots, (p_{n+k}, q_{n+k})$ in such a way that K_1, \dots, K_k will only be the functions of $(p_{n+1}, q_{n+1}), \dots, (p_{n+k}, q_{n+k})$. First, let us assume that the coordinates that measure up this property can be chosen globally. So, the phase space M of our system represents as a direct product of the phase spaces $M = M_1 \times M_2$, where M_1 corresponds to the coordinates $(p_1, q_1), \dots, (p_n, q_n)$, and M_2 — to the coordinates $(p_{n+1}, q_{n+1}), \dots, (p_{n+k}, q_{n+k})$. Let us denote through $d\Gamma$ the element of the phase volume on M , and through $d\Gamma^1$ and $d\Gamma^2$ the elements of the phase volumes on M_1 and M_2 , correspondingly. Let us assume that $H(x, y)$ — the Hamiltonian of our system, $x \in M_1, y \in M_2$.

Let us assume that $S(E)$ is the entropy calculated for the microcanonical distribution and $S_1(E, K'_1, \dots, K'_k)$ is the entropy calculated for the generalized microcanonical distribution corresponding to the K'_1, \dots, K'_k of the first integrals K_1, \dots, K_k . Let us recall that

$$S_1(E, K'_1, \dots, K'_k) = \ln \int d\Gamma \delta(H - E) \prod_{i=1}^k \delta(K_i - K'_i). \quad (6.1)$$

We assume that $S_1(E, K'_1, \dots, K'_k)$ measures up the equivalence principle (see section 4).

Locally on M_2 we can build the function $\varphi_1, \dots, \varphi_k$, and do it in such a way that the set of functions $(K_1, \varphi_1), \dots, (K_k, \varphi_k)$ will represent the set of canonical coordinates, i.e. the Poisson bracket in these coordinates will have the standard form. In other words, we can build a partition M_2 in the area V_i , $i = 1, 2, \dots$ with a piecewise-smooth boundary and in each of them we can choose the functions $\varphi_1^i, \dots, \varphi_k^i$, that satisfy the requirement mentioned above. Let us assume that Σ — a certain joint surface of the level of the integrals K_1, \dots, K_k , and $x \in \Sigma$. If (without losing generality) we assume that Σ is connected, then the Hamiltonian phase flows generated by K_1, \dots, K_k transitively acts on Σ . And as these phase flows keep the phase volume on M and the Hamiltonian, then

$$S_1(E, K'_1, \dots, K'_k) = \ln \int d\Gamma_x^1 \delta(H(x, y) - E) + c, \quad (6.2)$$

where $x \in M_1$, and c is the constant equal to:

$$c = \ln \sum_{i=1}^{\infty} \int_{\Sigma \cap V_i} d\varphi_1^i \dots d\varphi_k^i. \quad (6.3)$$

The constant c does not depend on E and can be discarded.

Let us now turn to the calculation of $(\delta S)_T$. If the system $M = M_1 \times M_2$ is described by the Gibbs distribution then the probability to find the system M at the point (x, y) , $x \in M_1$, $y \in M_2$ takes the form:

$$w_{12}(x, y) = \frac{1}{Z(T)} e^{-\frac{H(x, y)}{T}}, \quad (6.4)$$

where

$$Z(T) := \int d\Gamma_x^1 d\Gamma_y^2 e^{-\frac{H(x, y)}{T}}. \quad (6.5)$$

The probability to find the system M_2 at the point y is given then by the expression:

$$w_2(y) = \int d\Gamma_x^1 w_{12}(x, y). \quad (6.6)$$

Let us introduce the conditional probability $w_{1|2}(x|y)$ to find a system M_1 at the point x at condition that the system M_2 is at the point y by the formula:

$$w_{12}(x, y) = w_{1|2}(x|y)w_2(y). \quad (6.7)$$

Von Neumann entropy of the system M takes the form:

$$S(E(T)) = - \int d\Gamma_x^1 d\Gamma_y^2 w_{12}(x, y) \ln w_{12}(x, y). \quad (6.8)$$

Using (6.7) $S(E(T))$ we can transform to the form:

$$S(E(T)) = \langle S_1(E(T), y) \rangle_{M_2} + S_2(T), \quad (6.9)$$

where

$$S_1(E(T), y) = - \int d\Gamma_x^1 w_{1|2}(x|y) \ln w_{1|2}(x|y), \quad (6.10)$$

$\langle \cdot \rangle_{M_2}$ means the averaging over M_2 by the measure $w_2(y)d\Gamma_y$, and

$$S_2(T) = - \int d\Gamma_y^2 w_2(y) \ln w_2(y). \quad (6.11)$$

Note that only averaged values can be measured at experiment. We find:

$$(\delta S)_T = S_2(T). \quad (6.12)$$

At that we meant the formula (6.2) and the fact that within the thermodynamic limit the descriptions by the microcanonical and canonical assemblies coincide. At the same time we also consider, of course, that the constant c from the formula (6.3) does not depend on K'_1, \dots, K'_k . When we will proceed to the discussion of the general case that will not require the presentability of M in the form of the direct product M_1 and M_2 we will see that this assumption is justified.

Let us try to describe the dynamics of the system M_2 , using the fact that the number of degrees of freedom M_2 n is much greater than the number of degrees of freedom M_1 k . The Hamiltonian canonical equations for M_2 take the form:

$$\begin{aligned} \dot{p}_i &= - \frac{\partial H(p_1, q_1, \dots, p_{n+k}, q_{n+k})}{\partial q_i}, \\ \dot{q}_i &= \frac{\partial H(p_1, q_1, \dots, p_{n+k}, q_{n+k})}{\partial p_i}, \\ & i = n + 1, \dots, n + k. \end{aligned} \quad (6.13)$$

As the number of degrees of freedom M_2 is much less than the number of degrees of freedom M_1 we can average the right parts of the last equation by $w_{1|2}(x, y)$. As a result, skipping some quite trivial calculations we will find:

$$\begin{aligned} \dot{p}_i &= -\frac{\partial F(p_{n+1}, q_{n+1}, \dots, p_{n+k}, q_{n+k}|T)}{\partial q_i}, \\ \dot{q}_i &= \frac{\partial F(p_{n+1}, q_{n+1}, \dots, p_{n+k}, q_{n+k}|T)}{\partial p_i}, \\ & i = n + 1, \dots, n + k, \end{aligned} \tag{6.14}$$

where

$$\begin{aligned} F(p_{n+1}, q_{n+1}, \dots, p_{n+k}, q_{n+k}|T) &= -T \ln Z_1(y|T), \\ Z_1(y|T) &= \int d\Gamma_x^1 e^{-\frac{H(x,y)}{T}}, \\ y &= (p_{n+1}, q_{n+1}, \dots, p_{n+k}, q_{n+k}). \end{aligned} \tag{6.15}$$

So, this way the dynamics of the system M_2 will be described by the canonical Hamiltonian equations with the Hamiltonian $F(y|T)$.

Let us note that this way the defined Hamiltonian is not defined uniquely but accurate to the temperature arbitrary function $f(T)$. Let us define the new Hamiltonian of the system M_2

$$H_2(y|T) = F(y|T) + f(T), \tag{6.16}$$

in such a way that makes true the following:

$$(\delta E)_T = \langle H_2(y|T) \rangle_{M_2}. \tag{6.17}$$

Let us show that in this case

$$\left\langle \frac{d}{dT} H_2(y|T) \right\rangle_{M_2} = 0. \tag{6.18}$$

For this we will proceed from the identical equation:

$$\frac{\frac{d}{dT}(\delta S)_T}{\frac{d}{dT}(\delta E)_T} = \frac{1}{T}. \tag{6.19}$$

But

$$\begin{aligned} (\delta S)_T &= S_2(E(T)) = - \int d\Gamma_y^2 w_2(y) \ln w_2(y). \\ \frac{d}{dT} S_2(E(T)) &= \int d\Gamma_y^2 \frac{H_2(y|T)}{T} \frac{d}{dT} \frac{e^{-\frac{H_2(y|T)}{T}}}{Z_2(T)}, \end{aligned} \tag{6.20}$$

where

$$Z_2(T) := \int d\Gamma_y^2 e^{-\frac{H_2(y|T)}{T}}. \tag{6.21}$$

We have:

$$\frac{d}{dT} S_2(E(T)) = - \langle \Delta \left(\frac{H_2(y|T)}{T} \right) \Delta \left(\frac{d}{dT} \frac{H_2(y|T)}{T} \right) \rangle_{M_2}, \tag{6.22}$$

where we assumed by definition:

$$\Delta g(y) := g(y) - \langle f(y) \rangle_{M_2}. \quad (6.23)$$

Making the similar calculations, we find:

$$\frac{d}{dT} \langle H_2(y|T) \rangle = \left\langle \frac{d}{dT} H_2(y|T) \right\rangle - \langle \Delta(H_2(y|T)) \Delta \left(\frac{d}{dT} \frac{H_2(y|T)}{T} \right) \rangle_{M_2}. \quad (6.24)$$

Comparing (6.22) and (6.24) we will find:

$$\left\langle \frac{d}{dT} H_2(y|T) \right\rangle_{M_2} = 0, \quad (6.25)$$

which was to be proved.

Let us describe now the effective Hamiltonian of the whole system $M_1 \times M_2$. The dynamics of the system M_1 can be described by the Hamiltonian $H(x, y)$ where $y \in M_2$ and depends on time, and $x \in M_1$. But because of K_1, \dots, K_k are the motion integrals, the value $H(x, y)$ at fixed x is the same for all y corresponding to the same value of the motion integrals. That is why the system M_1 is described by the Hamiltonian $H(x, y)$, where y is constant with time and is chosen the same way as in the formula (6.2).

Further the effective Hamiltonian of the system M_2 $H_2(y|T)$ depends on the temperature T of the system M_1 , but temperature is an intensive parameter and instead of T we can use the energy of the system M_1 , falling within one degree of freedom. Let us assume by definition:

$$H_2'(y) \frac{E_1}{n} = H_2(y|T), \quad (6.26)$$

where E_1 — the energy of the system M_1 .

As an effective Hamiltonian of the system $M = M_1 \times M_2$ the following expression will be used:

$$H_{eff}(y, z) = H(y, x) + H_2'(z) \frac{H(y, x)}{n}. \quad (6.27)$$

Let us recall that according to this formula x is chosen the same way as in (6.2).

Let us show that within the limit $n \rightarrow \infty$ the Hamiltonian equation for H_{eff} will coincide with the Hamiltonian equations for the initial Hamiltonian if the point x is on the same joint surface of the level of the integrals K_1, \dots, K_k , that z .

Let us assume that $(y, z) \in M = M_1 \times M_2$. Let us analyze the derivative with time of the point z by virtue of the Hamiltonian equations for the Hamiltonian H_{eff} . This will be exactly the derivative by virtue of the Hamiltonian motion equations corresponding to the Hamiltonian $H_2(z|T)$ and the fact that this derivative coincide with the derivative with time by virtue of the Hamiltonian motion equations built by $H(y, z)$ was shown by us above. Let us assume now that $R(y)$ is the dynamic variable on M_1 . Let us calculate its derivative with time by virtue of H_{eff} . We have:

$$\dot{R}(y) = (H(y, x), R(y)) \left(1 + \frac{1}{n} H_2''(z, \frac{H(y, x)}{n}) \right). \quad (6.28)$$

Here the symbol $H_2''(\varepsilon, z)$ denotes the derivative $H_2'(\varepsilon, z)$ by the first argument. Within the limit $n \rightarrow \infty$ the right part of (6.28) evidently transforms into $(H(y, x), R(y))$, i.e. within this limit

$$\dot{R}(y) = (H(y, x), R(y)), \quad (6.29)$$

which was to be proved.

Let us note as well that H_{eff} depends on the choice of the point $x \in M_2$. However, because of the equivalence principle, the entropic properties of the system $M = M_1 \times M_2$ will not depend on this choice and these last ones are the only ones that are important for us. That is why from the point of

view of the calculations of the entropic properties the Hamiltonian $H_{eff}(y, z)$ is as good as the initial $H(y, z)$ and we will further use only the first one.

Let us note finally that the effective Hamiltonian with the form of (6.27) is defined accurate to the arbitrary function $f(\frac{H(y,x)}{n})$. I.e. the effective Hamiltonians corresponding to the different choices of such normalization induce the same motion equations. That is why all the thermodynamic characteristics calculated by H_{eff} corresponding different choices of the normalization must coincide. And this is really so. Actually at the old temperature the adding of $f(\frac{H(y,x)}{n})$ to H_{eff} the arbitrary function can be considered by the corresponding change $H_1(y, x)$. But at the same time with $n \rightarrow \infty$ the average value of the energy E_1 of the system M_1 will change by the value ~ 1 , and that is why the entropy of the system M_2 will change by the value $\sim \frac{1}{n}$, i.e. it will not change at all within the thermodynamic limit.

Let us use $S(T)$ to denote the entropy of the system M , as the function of the temperature T , calculated using Gibbs distribution for the Hamiltonian H_{eff} . Let us use E_1 to denote the average $H_1(y, x)$, and E_2 to denote the average $H_2(y|T)$ by the measures on M_1 and M_2 respectively, induced by the same Gibbs distribution. Let us assume also $E = E_1 + E_2$. The direct calculation shows that $\frac{dS}{dE} = \frac{1}{T}$. From the other point of view we normalized $H_2(y|T)$ in such a way that $\frac{dS_2(T(E_2))}{dE_2} = \frac{1}{T}$ would be true. From these two equalities we obtain $\frac{dS_1(E_1)}{dE_1} = \frac{1}{T}$. I.e. in the thermodynamic equilibrium state the temperatures of the systems M_1 and M_2 coincide, and this equality is true precisely and not only in the thermodynamic limit $k = \text{const}, n \rightarrow \infty$.

If k is very large (being at the same time much less than n), then according to the main principles of the statistical mechanics, instead of the description of M_2 by means of Gibbs canonical distribution we can use the description by means of the microcanonical distribution and the function of the distribution for the whole system M , at which the energies of the systems M_1 and M_2 will be equal to E_1 and E_2 respectively, will take the form:

$$\delta(H(y, x) - E_1)\delta(H_2'(z|\frac{E_1}{n}) - E_2), \quad (6.30)$$

$y \in M_1, z \in M_2$. The entropies of the systems M_1 and M_2 will be equal to

$$\begin{aligned} S_1(E_1) &= \ln \int \delta(H(y, x) - E_1) d\Gamma_y^1, \\ S_2(E_2, E_1) &= \ln \int \delta(H_2'(z|\frac{E_1}{n}) - E_2) d\Gamma_z^2. \end{aligned} \quad (6.31)$$

To obtain the inequality that we need let us make the following conceptual experiment. Let us make the system M_2 contact the thermostat T , which is at the temperature T . As for the system M_1 , we will take a very large system M_3 that will be connected to the system M_1 via a heat pump N , working by Carnot cycle. We will consider the working body of this pump to be so small that its thermal capacity can be neglected. Let us also assume that during the thermal contact with M_1 or M_3 the temperature of the working body of the pump is equal to the temperature of M_1 or M_3 (depending on which one has thermal contact with the working body of the pump), i.e. the heat pumping is done without the entropy increase. The working body of the pump is connected to a shaft by something like a connecting rod gear, this shaft can rotate and on the axis of which there is a spring P , possessing the energy E_P .

Let us note that because of our assumptions about the effective Hamiltonian $H_{eff}(y, z)$ the dynamics given by it on M_1 are exactly the dynamics given by $H(y, x)$ and that is why the system M_1 can be considered closed. Or more precisely as the system M_1 is related to M_3 by means of the heat pump N the system that consists from M_1, M_3, N, P can be considered closed. We will now assume that the elastic characteristics of the spring P are picked the way that the work that must be done to the working body N is exactly equal to the change of the spring energy. So this way we have a whole continuum of equilibrium states of the system consisting of M_1, M_3, N, P , which is parameterized by, for example, the angle of rotation of the pump shaft and at $S_1 + S_3 = \text{const}, E_1 + E_3 + E_P = \text{const}$.

When our whole system obtains the equilibrium then the temperature of the thermostat is equal to the temperature of M_1 and the temperature of M_3 . From the condition of maximal entropy of the whole system that consists of M_1, M_2, M_3, T, N, P at fixed full energy considering the equalities: $S_1 + S_3 = \text{const}, E_1 + E_3 + E_P = \text{const}$ we will find that in the equilibrium the following value

$$S_2(E_2, E_1) + S_T(E_T) \tag{6.32}$$

should reach the maximum at the additional condition

$$E_2 + E_T = \text{const}. \tag{6.33}$$

Here E_T — the energy of the thermostat and $S_T(E_T)$ — the entropy of the thermostat.

Instead of the dependence $S_2(E_2, E_1)$ on E_1 it appears more convenient to consider the dependence S_2 from the system temperature $M_1 \lambda(E_1)$. Let us introduce a new function

$$S'(E, \lambda(E_1)) := S_2(E, E_1). \tag{6.34}$$

The condition of the maximality of the entropy of the system M_2 and the thermostat lead to the equalities:

$$\begin{aligned} \frac{\partial S'(E, \lambda)}{\partial \lambda} \Big|_{\lambda=T, E=E(T)} &= 0, \\ \frac{\partial S'(E, \lambda)}{\partial E} \Big|_{\lambda=T, E=E(T)} &= \frac{1}{T}. \end{aligned} \tag{6.35}$$

But these equalities can be obtained directly. The second equality is obtain from the ordinary formulas of the statistical mechanics if we assume that the system M_2 is described by the Gibbs canonical distribution with Hamiltonian $H_2(y, \lambda)$. Let us set up the first equality. Let us adiabatically change the parameter $\lambda, \lambda \mapsto T + \delta\lambda$. At such change of the parameter λ the entropy of the system M_2 will not change. But by virtue of (6.18) the energy M_2 will not change. I.e. the derivative of the entropy of the system M_2 by λ at fixed energy is equal to zero, which is exactly the equality that we needed.

But for the maximality of the entropy of the system M_2 and the thermostat it is also necessary that the matrix of the second derivatives $S'(E, \lambda)$ at the point $E = E(T), \lambda = T$ would be negatively defined.

To prove now the inequality (5.6), we should prove that

$$\frac{d^2}{dE^2} S'(E, T(E)) \leq 0. \tag{6.36}$$

But,

$$\begin{aligned} \frac{d^2}{dE^2} S'(E, T(E)) &= \frac{\partial^2 S'(E, T)}{\partial E^2} + 2 \frac{dT(E)}{dE} \frac{\partial^2 S'(E, T)}{\partial E \partial T} + \\ &+ \left(\frac{dT(E)}{dE}\right)^2 \frac{\partial^2 S'(E, T)}{\partial^2 T} \leq 0, \end{aligned} \tag{6.37}$$

And the last inequality is true by virtue of the negative determination of the matrix of the second derivatives $S'(E, \lambda)$ at the point $E = E(T), \lambda = T$. Which was to be proved.

In a general case when M is impossible to be conceived as a direct product $M = M_1 \times M_2$ it can be shown that for some covering (\tilde{M}, \tilde{H}) of our Hamiltonian system (M, H) such factorization is possible. Deriving from the beginning all the thermodynamic relations for (\tilde{M}, \tilde{H}) , as it was done in section 3, we come again to the inequality (5.6).

Or more exactly we want to say the following. In all our thermodynamic analysis the Hamiltonian H and the integrals K_1, \dots, K_k depended on a certain parameter λ (volume), $H(\lambda), K_1(\lambda), \dots, K_k(\lambda)$. Further the dynamic variable $X(\lambda)$, depending on the parameter λ at $\lambda = 0$ will be denoted simply as X .

We can build a covering Hamiltonian system (\tilde{M}, \tilde{H}) of the system (M, H) , so that \tilde{M} would be conceived as a direct product $\tilde{M} = \tilde{M}_1 \times \tilde{M}_2$ and so that will measure up one more additional condition. Let us assume that π is a canonical projection of \tilde{M} on M and let us assume that $\tilde{H}(\lambda)$, $\tilde{K}_1(\lambda), \dots, \tilde{K}_k(\lambda)$ are the lift $H(\lambda)$, $K_1(\lambda), \dots, K_k(\lambda)$ on \tilde{M} . The additional condition mentioned above is that the canonical coordinates on \tilde{M}_2 are $\tilde{K}_1, \dots, \tilde{K}_k$ and the conjugated variables $\varphi_1, \dots, \varphi_k$, and $\forall i = 1, \dots, k$ φ_i runs all the real axis.

We will now derive all the thermodynamic relations for (\tilde{M}, \tilde{H}) . But here we get the difficulty related to the fact that \tilde{M}_2 is not compact. There is how we propose to overcome this difficulty. We propose to deal with unnormalized distributions w for which the following is true $\int_{\tilde{M}} w(x) d\tilde{\Gamma}_x = \infty$,

where $d\tilde{\Gamma}_x$ is the element of the phase volume on \tilde{M} .

Let us assume that $R_L = \{x \in \tilde{M} | \forall i = 1, \dots, k |\varphi_i(x)| < L\}$. To calculate the average of the dynamic variable \tilde{f} on \tilde{M} by w we propose to use the following formula:

$$\langle \tilde{f} \rangle = \lim_{L \rightarrow \infty} \frac{\int_{R_L} \tilde{f}(x) w(x) d\tilde{\Gamma}_x}{\int_{R_L} w(x) d\tilde{\Gamma}_x}. \quad (6.38)$$

The existence of the limit (6.38) — a nontrivial question but we are going to show that in all the cases we are interested the limit (6.38) exists.

We will say that the function \tilde{f} on \tilde{M} is periodical if $\forall x, y \in \tilde{M}$ such that $\pi(x) = \pi(y)$ $\tilde{f}(x) = \tilde{f}(y)$. All the lifts of the functions given on M on \tilde{M} are periodical and all the periodical functions can be obtained this way. All the interesting for us dynamic variables on \tilde{M} appear exactly as lifts of the functions given on M and that is why are periodical. Further the generalized microcanonical distributions on \tilde{M} , built by $\tilde{H}(\lambda)$, $\tilde{K}_1(\lambda), \dots, \tilde{K}_k(\lambda)$ are also periodical. We are going to demonstrate that if $\tilde{f}(x)$ and $w(x)$ are periodical functions then the limit (6.38) exists.

Let us assume that $d\tilde{\Gamma}^{-1}$ is the element of the phase volume on \tilde{M}_1 . Let us assume that $\tilde{M}_{K'_1, \dots, K'_k}$ is the surface of the level on \tilde{M} , corresponding to the values K'_1, \dots, K'_k of the integrals $\tilde{K}_1, \dots, \tilde{K}_k$. Let us assume that $d\tilde{\nu} = d\tilde{\Gamma}^{-1} d\varphi_1, \dots, d\varphi_k$ is the measure on $\tilde{M}_{K'_1, \dots, K'_k}$. The projection π reflects $\tilde{M}_{K'_1, \dots, K'_k}$ on $M_{K'_1, \dots, K'_k}$ is the surface of the level on M corresponding to the values K'_1, \dots, K'_k of the integrals K_1, \dots, K_k . On $M_{K'_1, \dots, K'_k}$ we have a measure $d\nu$, That can be characterized as a quotient of the phase volume $d\Gamma$ by $dK_1 \dots dK_k$: $d\Gamma = d\nu dK_1 \dots dK_k$. It is evident that the measure $d\tilde{\nu}$ is a lift of the measure $d\nu$ from $M_{K'_1, \dots, K'_k}$ to $\tilde{M}_{K'_1, \dots, K'_k}$ by virtue of the canonical projection π . To prove the conclusion about the existence of the limit (6.38), it is evidently enough to prove that for any K'_1, \dots, K'_k the following limit

$$\lim_{L \rightarrow \infty} \frac{1}{L^k} \int_{R_L \cap \tilde{M}_{K'_1, \dots, K'_k}} \tilde{f}(x) d\tilde{\nu}(x) \quad (6.39)$$

exists for any (good enough) periodical function $\tilde{f}(x) = f \circ \pi(x)$. And for this it is enough, evidently, to prove that for any differentiable function ψ on \tilde{M}_1 with a compact support there is a limit:

$$\lim_{L \rightarrow \infty} \frac{1}{L^k} \int_{\tilde{M}_1} \psi(x) d\tilde{\Gamma}_x^{-1} \int_{|\varphi_i| < L} \tilde{f}(x, \varphi_1, \dots, \varphi_k). \quad (6.40)$$

But on second thought, the existence of the last limit succeeds directly from k - dimensional analogue of the von Neumann ergodic theorem (Riesz, Sz-Nagy, 1972), applied to the commutated flows on $M_{K'_1, \dots, K'_k}$, that are induced by the Hamiltonians K_1, \dots, K_k keeping the measure $d\nu$ and to restriction of the function f on $M_{K'_1, \dots, K'_k}$.

Now in order to establish all the necessary to us thermodynamic relations, for example the relation $dE = TdS - PdV$, we derive them for \tilde{M} cut of R_L , and then tend L to infinity. The only

difficulty that can occur is the divergence of the entropy at $L \rightarrow \infty$, but this divergence is removed by the diminution of the logarithmically divergent constant $k \ln L$ from the entropy and this constant is the same at any value of the parameter λ .

The inequality (5.6) that we need is now derived as before but at $\lambda = 0$. It is enough to obtain again all our conclusions concerning the Ling cell.

Appendix 2. Discussion of the Boundary Condition (5.9).

The aim of this appendix is to make more or less obvious the existence of such temperature T_0 , above which $(\delta S)_E = \text{const}$.

Let us assume that at $s \mapsto s + \delta s$ the integral K becomes inactive. The entropy of the system $S(E, K')$ at fixed energy E depends on the value K' of this integral and the values of the other integrals that we will not name here. When discussing the equivalency principle we said that $S(E, K')$ should not depend on K' , but it would be more precise to say that $S(E, K')$ reaches the maximum on some interval $[\alpha, \beta]$ of the values K , and decreases drastically outside it. It is clear that $(\delta S)_E = \ln(\beta - \alpha)$. But this kind of dependence $S(E, K')$ from K' is not analytical and is proper to the systems with an infinite number of degrees of freedom, i.e. in the thermodynamic limit.

As an example of non-analyticity within the thermodynamic limit we can see the phase transition liquid \leftrightarrow vapor. Let us see the dependence of the system pressure from its volume at temperature lower than critical. When the volume is decreasing from infinity the system pressure first begins to increase and then on some interval of volume change will remain constant. This interval corresponds to the co-existence of the liquid and vapor phases. At further volume decrease the pressure will increase again. So this way this isotherm is not describe by the analytical function. When temperature is increasing the analyticity is restored. The temperature at which the analyticity is restored is called critical. Above this temperature the difference between vapor and liquid disappears.

Another example of the non-analytical behavior of the thermodynamic values which is more close to the Ling cell is borrowed from the van der Waals theory of the second-order phase transitions (Landau, Lifshitz, 1995). The second-order phase transition is usually related to some symmetry breaking and the breaking of this symmetry is described by a certain parameter of the order η . We will analyze here the simplest case of the real-valued η and \mathbb{Z}_2 -symmetry that only changes the sign $\eta; \eta \mapsto -\eta$.

In the neighborhood of the point of phase transition the Taylor approximation of the thermodynamic potential $\Phi(\eta, T)$ accurate to the inappreciable terms with higher orders, takes the form:

$$\Phi(\eta, T) = c_0 \eta^4 + c_1 (T - T_c) \eta^2, \quad (6.41)$$

where T_c — critical temperature and c_0, c_1 — certain positive constants.

At $T \geq T_c$ $\Phi(\eta, T)$ has by T one minimum in zero. At $T < T_c$ $\Phi(\eta, T)$ has one local maximum by η in zero and two minimums in the points

$$\eta_{1,2} = \pm \sqrt{\frac{c_1}{2c_0} (T_c - T)}. \quad (6.42)$$

We assume that the parameter of the order η is additive and that is why is lower than critical temperature, the analyzed system is separated into domains and in each of them η takes one of the two opposite values, corresponding to the minimum of the thermodynamic potential of the domain. The resulting value η will be bounded between two values η_1 and η_2 . From the other side, as the domains are big enough we can neglect the interaction between the different domains when calculating the thermodynamic potential and the thermodynamic potential will be equal to the minimal value of $\Phi(\eta, T)$ by η .

So this way we come to conclusion that instead of $\Phi(\eta, T)$ we should use its upper envelope $\tilde{\Phi}(\eta, T)$ (by η) and at $T > T_c$ $\tilde{\Phi}(\eta, T)$ will have the plateau, i.e. $\tilde{\Phi}(\eta, T)$ will not be the analytic function anymore.

The recovery of the analyticity at the temperature increase is explained in the following way. At the temperatures high enough the kinetic energy of every particle becomes much more than the potential energy of the particle interaction and the particles can be considered non-interacting. I.e. at high temperatures all the particles that compose the system can be considered free and for such system all the characteristics must be analytical.

The same way we will assume that at the temperature high enough $S(E, K')$ will be the analytical function of the parameter K' . Then it is either constant or reaches the maximum at an isolated point. But $(\delta S)_E = \ln(\beta - \alpha)$, as it was shown above, decreases with the temperature increase, i.e. at temperature high enough $S(E, K')$ can not be constant on the whole interval of the change of K' . I.e. $S(E, K')$ reaches the maximum at an isolated point and there is no more difference between using the generalized microcanonical distribution or just the microcanonical distribution.

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