

# Missing Parameters of Non-Equilibrium Macrosystems

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## Abstract

On the basis of the axiom of distinguishability of real processes by their consequences, the principle of determinism of the state of nonequilibrium systems is proved, according to which the number of energy arguments as a function of the state is equal to the number of independent processes occurring in the system. This principle indicates the need to introduce, in contrast to the hypothesis of local equilibrium, additional parameters of nonequilibrium of heterogeneous systems. The introduction of such parameters prevents the occurrence of thermodynamic inequalities and excludes the "underdetermination" or "overdetermination" of systems, which is the reason for most of the methodological errors of modern theories. A general method for finding such parameters is proposed, which makes it possible to extend the deductive thermodynamic research method to heterogeneous and isolated systems without splitting them into conditionally equilibrium elements, which avoids the loss of their system-forming properties. Other advantages of the whole-to-part approach to the study of systems are discussed.

**Key words:** nonequilibrium thermodynamics, real processes, their driving forces and speeds, nonequilibrium parameters, energy and energy.

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## I. Introduction

It is known that changes in the state parameters of nonequilibrium systems can be caused by both external energy exchange and relaxation processes accompanied by the appearance of their internal sources or sinks. In particular, the volume of the system  $V$  can be caused not only by performing compression work on it, but also by its spontaneous expansion into emptiness without performing work. In a similar way, the composition of the system (the number of moles of  $k$ -th substances  $N_k$ ) can be changed both by the diffusion of these substances through the boundaries of the system, and by chemical reactions in it. In the same way, the entropy of the system  $S$  can be changed both by the supply of heat  $d_e Q$  from the outside, and by the appearance of internal heat sources  $d_i Q$  in it due to any dissipative processes.

For spatially inhomogeneous systems and real (non-static) processes, these parameters cease to be the coordinates of the corresponding energy exchange processes (i.e., parameters that necessarily change during their course and remain unchanged in their absence). This circumstance leads to the transition of the equations of classical thermodynamics into inequalities, which makes it impossible to calculate the external energy exchange of the system by changing the above parameters and thereby limits the scope of its applicability to homogeneous (internally equilibrium) systems and quasi-static (infinitely slow) processes. Meanwhile, there is a possibility to avoid the occurrence of such inequalities by introducing the missing parameters of spatial inhomogeneity. This article is devoted to its presentation.

## II. The principle of state determinism

The proposed method of thermodynamic analysis of real (running at a finite speed) processes is based on their classification regardless of what caused the changes in the above-mentioned state parameters - external energy exchange or internal processes in isolated systems [1]. This classification, hereinafter called energodynamics, distinguishes processes by their consequences, that is, by those special, phenomenologically distinguishable and not reducible to other changes in the properties of the system that they cause. This approach differs significantly from the classification of processes for reasons that cause them (like physical kinetics, which distinguishes, for example, concentration diffusion, thermal diffusion and barodiffusion), or according to the mechanism of the process (like the theory of heat transfer, which distinguishes conductive, convective and radiant heat transfer). This is how the isochoric, isobaric, isothermal and adiabatic processes are distinguished in classical thermodynamics. In the same way, in classical mechanics, translational, rotary or oscillatory motion, as well as accelerated or uniform motion, are distinguished. Similarly, in electrical engineering, electrification and magnetization of bodies, electrical conductivity and flux linkage are distinguished; in chemistry - homogeneous

and heterogeneous reactions, etc. The ability to distinguish such independent processes using the entire arsenal of experimental means is confirmed by the experience of many generations of researchers and is so obvious that it can be taken as an axiom, calling it, for convenience of reference, the principle of distinguishability of processes [2]. This principle allows one to prove a rather obvious, but fundamentally important theorem, according to which "the number of independent coordinates determining the state of any (equilibrium or nonequilibrium) system (that is, the number of its degrees of freedom) is equal to the number of independent processes taking place in it". This theorem is easily proved "by contradiction." Since a process is understood as a change in the properties of a system, expressed by state parameters, then at least one of them necessarily changes during their course. Let us assume that in the course of some phenomenologically distinguishable process, several coordinates of the state necessarily change. Then, obviously, these coordinates will not be independent, which contradicts the initial premise. Let us now assume that any of the state coordinates changes as necessary in the course of several processes. Then, obviously, these processes will not be phenomenologically distinguishable, since they cause the same changes in the properties of the system. It remains to conclude that any (equilibrium or nonequilibrium, quasi-static or non-static) phenomenologically distinguishable process corresponds to a single independent state coordinate, i.e., a parameter that necessarily changes during the course of this process and does not change in its absence. These coordinates are extensive quantities, since each of them separately determines the energy of the  $U$  system - a quantity that is also extensive.

The proved statement determines the necessary and sufficient conditions for an adequate (sufficiently complete) description of the state of a particular system. Therefore, for convenience of reference, it is advisable to call it "the principle of state determinism". This principle allows avoiding both "underdetermination" and "overdetermination" of the system, that is, attempts to describe the state of the system with an insufficient or excessive number of parameters, which is the main source of methodological errors and paradoxes of modern theories. It is far from obvious, for example, the "underdetermination" of the state of the continuum, which leads to the adoption of the hypothesis of local equilibrium, which asserts the applicability to the elements of the nonequilibrium continuum of the mathematical apparatus of equilibrium thermodynamics [3] while relaxation processes take place in them, absent in equilibrium systems. On the other hand, the "overdetermination" of the continuous medium is not obvious either, caused by the assignment of an infinite number of degrees of freedom to it (according to the number of elements into which it is split to achieve their homogeneity), while the number of macroprocesses taking place in it is finite. Therefore, our next goal is to show how the "principle of determinism" suggests a specific way to generalize classical thermodynamics to irreversible processes of energy transfer [4] and to systems that carry out useful energy conversion [5].

### III. Specificity of nonequilibrium processes and their parameters

Any extensive parameter of an inhomogeneous system  $\Theta_i$  (its mass  $M$ , the number of moles of  $k$ -th substances  $N_k$ , entropy  $S$ , electric charge  $\Theta_e$ , impulse  $P$ , its moment  $L$ , etc.) can be represented by an integral of its local  $\rho_i = d\Theta_i/dV$  and average  $\bar{\rho}_i = \Theta_i/V$  density by the expression  $\Theta_i = \int \rho_i dV = \int \bar{\rho}_i dV$ . Hence it follows that

$$\int [(d(\rho_i - \bar{\rho}_i)/dt)]dV = 0. \tag{1}$$

When some  $i$ -th processes occur in the system, when  $(d(\rho_i - \bar{\rho}_i)/dt \neq 0)$ , integral (1) vanishes only if the rates of the process  $d(\rho_i - \bar{\rho}_i)/dt$  have different volume elements  $dV$  are of opposite sign and are mutually compensated.

This proposition, which we have called the "principle of the opposite direction of processes", can be regarded as a mathematical expression of the dialectical law of «the unity and struggle of opposites»[6]. The heuristic value of this principle as one of the most general laws of natural science consists in the detection of a specific class of processes of "polarization" of a system in the most general understanding of this term as the appearance in it of parts (areas, phases, components) with opposite properties.

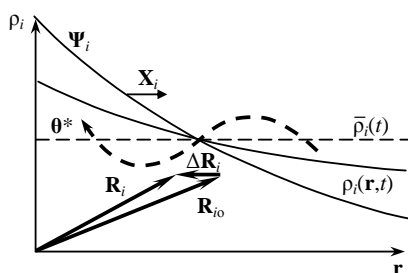


Figure 1. To the formation of the distribution

To distinguish this category of processes, let us first consider the group of equilibrium processes studied by classical thermodynamics [7]. In it, the existence of an independent coordinate  $\Theta_i$  for each  $i$ -th independent quasi-static process of energy exchange was taken for granted. For the process of heat exchange, such a coordinate was the entropy  $S$ , for the process of all-round deformation - the volume of the system  $V$ , for the process of electrification - the charge  $\Theta_e$ , etc. All such quantities have been called since the time of Lagrange "generalized coordinates", and their totality  $\Theta_1, \Theta_2, \dots, \Theta_n$  determined the energy of the system  $U = \sum_i U_i(\Theta_i)$ . Without finding such parameters for each of the processes

occurring in the system, the thermodynamic description of its state was incomplete. Due to their quasi-static nature, such processes practically did not violate the spatial homogeneity of the system and therefore were called equilibrium (uniform).

Processes of a different kind, which consist in the redistribution of the energy carrier  $\Theta_i$  between parts (areas) of a heterogeneous system. They resemble the pumping of liquid from one part of the vessel to another and are accompanied by a decrease in entropy  $S$ , mass  $M$ , charge  $\Theta_e$ , the number of moles of  $k$ -th substances  $N_k$ , impulse  $\mathbf{P}$ , etc. in some parts of the system, and their increase in others (figure 1). These are the processes of transfer of heat, matter, charge and momentum, studied in the thermodynamics of irreversible processes [8,9]. To find their coordinates, consider an inhomogeneous system with an arbitrary distribution over its volume  $V$  of density  $\rho_i(\mathbf{r},t) = \partial\Theta_i/\partial V$  of an arbitrary thermostatic quantity  $\Theta_i$  at time  $t$ . This distribution corresponds to the curves  $\rho_i(\mathbf{r},t)$ , which for clarity are presented as a function of the radius vector of the field point  $\mathbf{r}$ .

As follows from the figure, when the distribution  $\bar{\rho}_i$  deviates from the uniform one with density, a certain amount of this quantity  $\Theta_i^*$  is transferred from one part of the system to another in the direction indicated by the arrow. Such a "redistribution" of the extensive quantity  $\Theta_i$  causes the center of this quantity to shift from the initial position  $\mathbf{R}_{i0}$  to the current  $\mathbf{R}_i$ . It is known that the position of the center of any extensive quantity  $\Theta_i$ , given by the radius vector  $\mathbf{R}_i$ , is determined by the expression:

$$\mathbf{R}_i = \Theta_i^{-1} \int \rho_i(\mathbf{r},t) \mathbf{r} dV, \quad (i = 1, 2, \dots, n) \quad (2)$$

Comparing it with the position  $\mathbf{R}_{i0}$  of the center of the same value  $\Theta_i$  in a homogeneous state with density, we find that the state of a spatially inhomogeneous system is characterized by the appearance of specific "distribution moments"  $\mathbf{Z}_i$  of energy carriers  $\Theta_i$ :

$$\mathbf{Z}_i = \Theta_i (\mathbf{R}_i - \mathbf{R}_{i0}) = \int_V [\rho_i(\mathbf{r},t) - \bar{\rho}_i(t)] \mathbf{r} dV. \quad (3)$$

According to (3), when the system "contracts" to a material point, when  $\rho_i(\mathbf{r},t) \rightarrow \bar{\rho}_i$ , the parameters  $\mathbf{Z}_i$  vanish. This is natural, since there are no processes of redistribution of densities  $\rho_i(\mathbf{r},t)$  at material points. The latter gave the basis for dividing the system into elementary volumes in order to neglect the inhomogeneity. However, when considering the continuum as a single nonequilibrium whole, their introduction is necessary, since such a system has additional degrees of freedom[10].

As follows from the figure 1, the transfer processes cause a change in the position of the center  $\mathbf{R}_i$  of the value  $\Theta_i$  inside the system. Therefore, we called them redistribution processes. These processes are always non-equilibrium, even if they are carried out infinitely slowly (quasi-statically). This kind of state change is caused, for example, by useful external (ordered) work performed by external forces against equilibrium in the system, and vector relaxation processes, accompanied by the equalization of temperatures, pressures, chemical and other potentials of the system. All processes of this kind are directed (ordered) in nature, which distinguishes useful work from the work of uniform expansion or the introduction of a substance or charge. The displacement vectors  $\mathbf{R}_i$  characterize the position of the center of the energy carrier  $\Theta_i$  as a whole relative to external bodies (environment) and therefore in classical thermodynamics of open (non-isolated) systems refer to their external parameters.

The third group consists of processes associated with a change in the direction of the displacement vector  $\Delta\mathbf{R}_i$ . This direction can change both when changing the configuration of the system itself (for example, when rotating bodies with shape anisotropy), and when changing the configuration of external fields. We will call such processes reorientation processes. In the microworld, such processes are manifested, for example, in the establishment of a single orientation of spins, in macrosystems - in the spontaneous magnetization of ferromagnets, in the megaworld - in the alignment in one (close to the equatorial) plane of spirals of galaxies, asteroid belts, orbits of planets of the solar system, their satellites, etc. etc.

To find the coordinates of these processes, it should be taken into account that the formation of the moment of distribution  $\mathbf{Z}_i$  is caused not only by the displacement  $d\mathbf{r}_i = \mathbf{e}_i dR_i$  of the center of the quantity  $\Theta_i$  with a constant direction specified by the unit vector  $\mathbf{e}_i$ , but also with a change in this direction itself  $d\mathbf{Z}_i = \Theta_i R_i d\mathbf{e}_i = \Theta_i R_i d\boldsymbol{\varphi}$ , where  $\boldsymbol{\varphi}$  is the vector of the angle of rotation in the plane of rotation, normal to formed by vectors  $\mathbf{e}_i$  and  $d\mathbf{e}_i$ . As a result, the moment of distribution  $\mathbf{Z}_i$  appears as a function of three groups of independent variables  $\Theta_i$ ,  $\mathbf{R}_i$  and  $\boldsymbol{\varphi}_i$ , which indicates a threefold increase in the number of its degrees of freedom in comparison with the internal equilibrium system.

#### IV. Prevention of thermodynamic inequalities. Energodynamic identity

In accordance with the principle of the adequacy of the description of the state, the energy as a function of the state of the system  $U$ , in which the three groups of the above processes occur, has a pitch  $U = \sum_i U_i(\Theta_i, \mathbf{R}_i, \boldsymbol{\varphi}_i)$ . This means that its total differential can be represented as an identity [5]:

$$dU \equiv \sum_i \Psi_i d\Theta_i + \sum_i \mathbf{F}_i \cdot d\mathbf{R}_i + \sum_i \mathbf{M}_i \cdot d\boldsymbol{\varphi}_i, \quad (4)$$

where  $\Psi_i \equiv (\partial U / \partial \Theta_i)$  are the average value of the generalized local potential of the system  $\psi$ ;  $\mathbf{F}_i \equiv (\partial U / \partial \mathbf{R}_i)$  are the forces in their usual (Newtonian) understanding;  $\mathbf{M}_i \equiv (\partial U / \partial \boldsymbol{\varphi}_i)$  are the torsional moments of these forces.

It is convenient to express the terms of the second sum of this expression through the so-called thermodynamic forces  $\mathbf{X}_i$  in their "energy" representation [4,5], defining them by the relation:

$$\mathbf{X}_i \equiv (\partial U / \partial \mathbf{Z}_i)_{\varphi}. \quad (5)$$

Since at  $\Theta_i, \boldsymbol{\varphi}_i = \text{const}$ , and  $(\partial U / \partial \mathbf{Z}_i) = \Theta_i^{-1} (\partial U / \partial \mathbf{R}_i) = \mathbf{F}_i / \Theta_i$ , the thermodynamic forces  $\mathbf{X}_i$  introduced in this way have the meaning of specific forces (referred to the unit of the quantity they carry  $\Theta_i$ ). These are, in particular, the specific mass, volumetric and surface forces, for which the value  $\Theta_i$  makes sense, respectively, of the mass  $M$ , volume  $V$  and surface of the body  $f$ . As shown in [5], in the elements of the continuum, these forces are expressed by negative gradients of the corresponding potential  $\psi_i$ , that is, they have the same meaning as the strengths of the electric or gravitational fields at these points of the system. For the system as a whole, the thermodynamic forces  $\mathbf{X}_i$  are determined by the mean integral value of these gradients, found from the condition of invariance of the dissipative function (the power of scattering processes) [7, 8]. Therefore, expressions (4) and (5) return the concept of force to thermodynamics and generalize it to the effects of a non-mechanical nature and to short-range forces generated by the fields of temperatures, pressures, chemical, etc. potentials. The use of such "global" forces allows us to express the elementary useful (ordered) work performed on an inhomogeneous system in two equivalent expressions:

$$dW^e = \sum_i \mathbf{F}_i \cdot d\mathbf{r}_i = \sum_i \mathbf{X}_i \cdot d\mathbf{Z}_i. \quad (6)$$

The work described by this expression can be mechanical, thermal, electrical, chemical, etc. (depending on the nature of the forces to be overcome); external or internal (depending on where these forces arise - in the system itself or outside it); useful or dissipative (depending on what accompanies the work - purposeful transformation of energy or its dissipation). This is how the generalization of the concept of force, originally introduced by I. Newton in relation to the acceleration process, to processes of a different kind is achieved. Thanks to this, thermokinetics and energy dynamics acquire the ability, which is not characteristic of classical thermodynamics, to explain the causes of the occurrence of certain processes. This is how the methodological unity of the presentation of the thermodynamics of reversible and irreversible processes is achieved [4]. At the same time, an answer is given to the above question and the nature of the conjugation of intensive and extensive parameters of spatial inhomogeneity.

Expression (4) has the character of identity and therefore is true regardless of what caused the change in the parameters  $\Theta_i$ ,  $\mathbf{R}_i$  and  $\boldsymbol{\varphi}_i$  are external energy exchange or internal (including relaxation) processes. Therefore, it is applicable to any process (both reversible and irreversible). This achieves a solution to the problem of thermodynamic inequalities [10]. At the same time, it is the most detailed of the relations connecting the parameters of spatially inhomogeneous systems, since it takes into account all possible categories of processes occurring in such systems.

The introduction of the moments of distribution  $\mathbf{Z}_i$ , coupled with thermodynamic forces, in the same way as the parameters  $\Theta_i$  are coupled by the potentials  $\psi_i$  in equilibrium thermodynamics, plays a decisive role in the construction of nonequilibrium thermodynamics. It is known that classical thermodynamics took shape as an independent discipline just after R. Clausius managed to find a coordinate (entropy) associated with temperature in the same way as pressure with volume, and thus give a deterministic description of the simplest thermomechanical systems. A similar role in the formation of energy dynamics is played by the moments of the distribution  $\mathbf{Z}_i$ , which play the role of generalized polarization vectors. The result of this approach was the possibility of further generalization of the thermodynamic theory of irreversible transport phenomena [7,8,4] to the processes of useful energy conversion [5]. This made it possible to reveal the unity of the laws of transformation of any forms of energy and to lay the foundations of the theory of similarity [11] and the productivity of energy-converting systems [12].

#### V. A unified method for finding the parameters of nonequilibrium processes

Another equally valuable property of the parameters of spatial inhomogeneity  $\mathbf{Z}_i$  is the ability to directly find the fluxes of entropy, matter, charge, momentum, etc.  $\mathbf{J}_i$  without compiling cumbersome entropy

balance equations using a significant arsenal of information from other fundamental disciplines [13]. In thermokinetics and energy dynamics, these fluxes are called displacement fluxes  $J_i$  and are defined as time derivatives of the distribution moments  $Z_i$ :

$$J_i = dZ_i/dt = \Theta_i v_i, \tag{7}$$

where  $v_i = dr_i/dt$  is the rate of transfer of the value  $\Theta_i$  in the process of its redistribution.

Flows of this kind are caused by the displacement of the center of the quantity  $\Theta_i$  within the system and therefore do not go beyond the boundaries of the system. However, expression (6) is also applicable for finding fluxes across the boundaries of a subsystem, if by the latter we mean a part of a non-uniform system separated from it by a boundary. Due to this generality, the fluxes  $J_i$  acquire a unified meaning of the generalized speed of the transfer process, determined by the product of the transferred quantity  $\Theta_i$  by the speed of its transfer  $v_i$ . For conductors, the vector  $Z_e$  has the meaning of the moment of distribution of free charges, and for a system of unit volume it has the meaning of the vector of electrical induction  $D$ . Thus, expression (6) generalizes the concept of displacement current introduced by Maxwell in 1864. Its original meaning, distorted by the replacement by Heaviside and Hertz in Maxwell's equations of total time derivatives of vectors  $D$  by partial derivatives  $\partial D/\partial t$ , in no way connected with the flow of anything, becomes clear [14].

The introduction of the concept of the displacement flux density of the  $i$ -th energy carrier and  $j_i = \rho_i v_i$  makes it easy to distinguish it from the flux density of a given form of energy  $j_{ui} = \psi j_i$ , and the scalar flux of the  $i$ -th energy  $dU_i/dt$  from the vector carrier flux of this form of motion  $J_i = dZ_i/dt$ . At the same time, it becomes obvious that the "transfer substrate" in the Fourier thermal conductivity equation  $j_q = -\lambda \text{grad} T$  is not heat  $q$ , which he understood as a certain weightless and indestructible fluid, but entropy  $S$  as an impulse of thermal motion that has lost its vector nature due to its randomness and called by us "thermal impulse" [15]<sup>1</sup>. It is also easy to see that the flows  $J_i$  differ from the concept of discharge in dimensionality and in their meaning are close to the concept of momentum  $P = Mv$  in mechanics. For this property, they can also be called "generalized impulses" of the energy carrier. These quantities play an important role in many phenomena. We encounter them in the phenomena of transfer and transformation of any form of energy. It is to such fluxes that  $J_i = \int j_i dV$  is proportional to the Joule and Thomson heats in thermoelements, as well as the force acting on a conductor with a current in Ampere's law [16].

However, a more significant result of introducing the distribution moments  $Z_i$  is the discovery that displacement currents similar to Maxwellian ones can arise in electrically neutral media. To do this, let us first show that the moments of the distribution of  $Z_i$  are similar in meaning to the dipole moment of a dielectric or a magnet. The similarity of expression (2) with the dipole moment will increase if we set  $\bar{\rho}_i = 0$  and take into account the difference of charges or poles  $\Theta_i' = -\Theta_i'' = \Theta_i^*$ . In this case, instead of (7), we can write:

$$Z_i = \int (\rho_i' r_i' + \rho_i'' r_i'') dV = \Theta_i^* \Delta r_i, \tag{8}$$

where  $r_i', r_i''$  are the radius vectors of elementary charges with density  $\rho_i'$  and  $\rho_i''$ ;  $\Delta r_i$  is the average integral value of the dipole arm formed during the polarization of the system in the most general sense of this term.

According to (8), the moments of the distribution  $Z_i$  retain their meaning for systems with a discrete distribution of opposite charges or poles, if they are separated in space, and vanish at  $r_i' = r_i''$ . At the same time, in accordance with this expression displacement flux  $J_i = dZ_i/dt$  appears as the sum of displacement fluxes of dissimilar charges or poles  $J_i' = \Theta_i' dr_i'/dt$  and  $J_i'' = \Theta_i'' dr_i''/dt$ . Since in these expressions not only  $\Theta_i'$  and  $\Theta_i''$  are opposite in sign, but also the directions of displacement displacements  $dr_i' = -dr_i''$ , the flows  $J_i'$  and  $J_i''$  acquire the same sign, that is, they are summed up and not com. Hence it follows that the Maxwell displacement current arises not only in conductors, but also in electrically neutral dielectrics (where  $\Theta_i' + \Theta_i'' = 0$ ). This sheds new light on a number of phenomena that are difficult to explain, such as the Rohland - Eichenwald and Roentgen - Eichenwald effects in the motion of a polarized dielectric, as well as the Wilson - Barnett effect in the polarization of a dielectric plate moving in a magnetic field<sup>2</sup> [17].

Thus, the moments of distribution  $Z_i$  allow not only to give a visual representation of the vectors of electric and magnetic displacement in electrodynamics, but also to generalize them to phenomena of a different physical nature.

## VI. Prevention of loss of system-forming properties in energodynamics

Until now, the absence of extensive parameters of inhomogeneity in continuum mechanics, the theory of heat and mass transfer, hydroaerodynamics, electrodynamics and thermodynamics of the continuum, allowing

<sup>1</sup>Accordingly, the concept of entropy as a measure of the thermodynamic probability of a state is subject to correction, since in relation to the latter, the concept of flux is devoid of any meaning.

<sup>2</sup>At present, these effects are explained by inhomogeneous polarization ( $\Theta_i' + \Theta_i'' \neq 0$ ).

one to consider nonequilibrium systems as a whole, forced researchers to break the objects of their study into an infinite number of elementary domains  $dV$ , assumed to be homogeneous, in the hope of subsequently restoring the properties of the system as a whole with the help of suitable integrals. In nonequilibrium thermodynamics, such an approach is "justified" by the already mentioned "hypothesis of local equilibrium" [3], which assumes the presence in the volume elements of the continuum of local equilibrium (despite the occurrence of irreversible processes in them), the possibility of describing their state the same set of variables as in equilibrium (despite the appearance of gradients) and the validity of all equations of thermodynamics for them (despite their inevitable transition into inequalities).

However, this approach leads to the loss of the so-called "system-forming connections" that appear in a set of microsystems at a certain stage of their evolution. Thanks to such connections, the system acquires properties that were absent in its individual parts. As a result, the properties of the object as a whole are not the sum of the properties of its individual parts, that is, they are not additive. A vivid example of such non-additivity is a heat engine, in the structure of which a heat source, a working fluid, and a heat sink are distinguished. If we exclude the heat source from this scheme, we get a "perpetual motion machine of the 1st kind"; if you remove the working fluid, there will be only heat exchange between the source and the receiver of heat. Finally, if we exclude the heat receiver, the device will turn into a "perpetual motion machine of the second kind." This means that a heat engine can be broken down into elements only by retaining their inherent structure and the nature of the processes taking place in it. In modeling practice, this technique is usually called fragmentation. One of the situations requiring fragmentation of inhomogeneous systems arises in the study of vector relaxation processes caused by the equalization of temperatures, pressures, concentrations, etc. in different parts of macrosystems. The resulting flows of matter, charge, momentum, etc. are excluded if we restrict ourselves to considering systems of infinitely small sizes.

Another non-additive property that requires a systematic approach is the ability to "self-organize" living organisms, in which each organ performs its specific function. This applies in general to any structured systems, because such an ability for self-organization is absent in any of its homogeneous parts. This impossibility to describe the properties of a system by simply summing the properties of their elements was, in the words of A. Poincaré, "the greatest and deepest shock that physics has experienced since Newton's time" [18].

It is here that lies the reason that the solution of differential equations does not always correspond to experiments. Awareness of this circumstance was one of the reasons for the new research methodology, which requires the so-called "systematic approach". Its main requirement is to study the object "from whole to part" in order to preserve all the "system-forming" connections inherent in the object of research. An invaluable role in this is played by the non-additive parameters of inhomogeneity  $Z_i$ , proposed by us more than 20 years ago, which make it possible to extend the thermodynamic method of studying systems as a whole to continuous inhomogeneous media [4]. Now, when the system-forming properties lead to the appearance in it of a new property and the process corresponding to it, the methods of energy dynamics can predict all the parameters characterizing it and indicate the method of their experimental determination, then confirming their reality.

## VII. Elimination of the ambiguity of the concept of energy

Explicit consideration of the spatial inhomogeneity of the systems under study using the moments of distribution  $Z_i$  allows the concept of energy to return to the concept of energy close to the original meaning of the measure of the system's performance. In mechanics, this goal was satisfied by the concept of external energy, which was understood as that part of the energy of the system that does not depend on its internal state and is determined exclusively by the motion or position of the system as a whole relative to other bodies. However, in isolated systems, to which all known conservation laws belong, the concept of external energy is devoid of any meaning. This led to the emergence of thermodynamics, operating with the concept of internal energy  $U$ . However, in equilibrium thermodynamics, internal energy  $U$  was considered as a consequence of the transformation of external energy during its dissipation (dissipation), which made it impossible to interpret the concept of energy as a measure of efficiency. As a result, a situation arose when "modern physics does not know what energy is" [19].

In particular, the problem of distinguishing the quantitative and qualitative aspects of the concept of energy has not yet received a satisfactory solution. A way out of the situation was seen for a long time in the division of energy into "free"  $F = U - TS$  and "associated" (with thermal motion)  $TS$ , proposed by G. Helmholtz. As is known, the decrease in the Helmholtz free energy  $F$  under certain conditions determines the ability of systems to perform the reversible work of volumetric deformation. In relation to works of a different kind, a similar role in a number of cases could be played by the Gibbs "free enthalpy"  $G = H - TS$  (where  $H = U + pV$  is the enthalpy of the system). However, in open systems, as is known, these state functions can no longer play the role of a measure of the work performed by the system [7].

The subsequent introduction of the concepts of exergy and anergy (Z. Rant, 1955) as a correspondingly technically suitable and unsuitable part of it in the conditions of a given environment did not save the situation. At the same time, exergy was defined as the maximum work that the system could perform until its complete thermodynamic equilibrium with the environment was established. However, in this case, exergy, being dependent on the parameters of the environment, was deprived of the properties of the function of the state of the system itself. Moreover, arbitrariness arose in the choice of the origin of its reference in conditions when the parameters of this medium differed significantly and varied in time [20].

Hence the exceptional role that the moments of distribution  $Z_i$  acquire as a measure of the deviation of the system as a whole from the internal equilibrium of the  $i$ -th kind. According to equation (4), in equilibrium systems (where  $Z_i = 0$ ), its second and third sums disappear, and it turns into a generalized expression of the 1st and 2nd principles of equilibrium thermodynamics in the form of the Gibbs relation [6]:

$$dU = \sum_i \Psi_i d\Theta_i \quad (9)$$

The terms on the right-hand side of this expression characterize the work done on the system during the diffusion of the  $k$ -th substance through its boundaries, all-round compression, mass transfer, introduction of an electric charge into it, convective transfer of momentum across the boundaries of the system and heat exchange, which is, in fact, its kind of the latter and therefore attributed by us to the category of "micro-work". Due to the absence of the forces  $F_i$ , all these types of work are classified as disordered, i.e., they do not change the external energy of the system. This makes it possible to single out the non-equilibrium part of the internal energy of the system  $U$ , the decrease of which determines, in contrast to (9), the ordered (useful) work  $dW_i^e$ , performed by the system [21]:

$$dU^o = dW_i^e = - \sum_i X_i \cdot dZ_i \quad (10)$$

We later called this part of the energy "ordered energy" in connection with the fact that the equivalent concept of external energy is not applicable to isolated systems, also considered in ergodynamics [22]. The division of energy into ordered and disordered made it possible to define energy as the most general function of the state, characterizing its ability to perform any (ordered and disordered) work. At the same time, the meaning of the second law of thermodynamics as a statement about the spontaneity of the process of transformation of ordered energy into disordered one became clearer. This allows us to introduce a non-entropy criterion for the evolution of nonequilibrium systems, much more "physical", convenient and informative than entropy, since the change in the parameters of the spatial inhomogeneity  $Z_i$ ,  $X_i$  can reflect the behavior of each degree of its freedom separately, and not only its approach to equilibrium ( $dZ_i, dX_i < 0$ ), but also moving away from it ( $dZ_i, dX_i > 0$ ). Thus, the introduction of the inhomogeneity parameters  $Z_i$  reveals the possibility of anti-dissipative ordering processes in the system of some of its degrees of freedom due to the disordering of others. This behavior is typical not only for technical systems that convert ordered energy from one form to another, but also for objects of living nature [23].

Thus, thanks to the introduction of the missing parameters of spatial inhomogeneity and their derivatives, it is possible to construct a unified thermodynamic theory that allows one to study real processes regardless of their belonging to a particular field of knowledge, in whatever systems they occur: simple and complex, closed and open, homogeneous and heterogeneous, isolated and non-isolated, striving for balance and developing bypassing balance. This is a serious step towards integrating knowledge.

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