
NEW METHODOLOGICAL PRINCIPLES OF NONEQUILIBRIUM THERMODYNAMICS

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It is shown that the thermodynamic theory of speed of irreversible processes should be built on own methodological basis, but not by extrapolation of classical thermodynamics for strict frames of its initial concepts of equilibrium and reversibility. The principles of creation of such theory are offered. They are based on the systems concept, exclude application of hypotheses, postulates and model representations in the theory bases, don't resort to idealization of processes and systems in them and explicitly consider spatial non-uniformity of the researched systems.

1. Introduction. There are periods occurring now and then in the development of any natural-science theory when new ideas and experimental facts can not be crammed into “Procrustean bed” of its obsolete notional and conceptual system. Then the theory itself – its presuppositions, logical structure and body of mathematics – becomes the object of investigation. Thermodynamics went through such periods more than once [1]. So was yet in the mid-XIX century when under the pressure of new experimental facts the concept of heat as an indestructible fluid collapsed and “entrained” (as seemed then) the S. Carnot’s theory of heat engines [2] based on it. A few decades later the threatening clouds piled up over the R. Clausius’ mechanical theory of heat [3] because of the “heat death of the Universe” – a conclusion deemed then as inevitable.

In the late XIX century great difficulties arose from attempts to conduct a thermodynamic analysis of composition variation in heterogeneous systems (at diffusion, chemical reactions, phase transitions, etc). J. Gibbs [4] overcame the majority of those difficulties by representing closed system as a set of open subsystems (phases and components), which allowed him to reduce the internal processes of system composition variation to the external mass transfer processes. However, some of those difficulties have remained as yet and are showing, in particular, in the unsuccessful attempts to thermodynamically resolve the “Gibbs’ paradox” – a conclusion of stepwise entropy rise when mixing non-interacting gases and independence of these steps on the nature the gases feature and the degree they differ in [5-7].

During the XIX century thermodynamics also more than once encountered paradoxical situations that arose around it with the human experience outstepped. One of such situations arose with thermodynamics applied to the relativistic heat engines (contain fast moving heat wells) and showed in the statement that those could reach efficiency higher than in the Carnot’s reversible engine within the same temperature range [8-10] as well as in the recognized ambiguity of relativistic transformations for a number of thermodynamic values [7]. A little bit later a situation, not any less paradoxical, arose as connected with attempts to thermodynamically describe the systems of nuclear magnets (spin systems) with inverted population of energy levels. The negative absolute temperature concept introduced for such states led investigators to a conclusion of possibility for heat to completely convert into work in such systems and, on the contrary, impossibility for work to completely convert into heat, i.e. to the “inversion” of the principle fundamental for thermodynamics – excluded perpetuum mobile of the second kind [11-12],[10],[7].

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That fate became common for also the theory of irreversible processes (TIP) created by extrapolating classic thermodynamics to non-equilibrium systems with irreversible (non-static) processes running therein. Problems arose primarily from the necessity to introduce into thermodynamics the transfer concepts inherently extraneous for it, from the incorrectness to apply the equations of equilibrium thermodynamics to irreversible processes in view of their inevitable change to inequalities, from the inapplicability of the classic notions of entropy and absolute temperature to thermally heterogeneous media, etc, which demanded to introduce a number of complimentary hypotheses and to attract from outside balance equations for mass, charge, momentum, energy and entropy with time involved as a physical parameter. Even heavier obstructions arise with attempts to generalize TIP to non-linear systems and states far away from equilibrium where the Onsager's reciprocal relations [13] appear to be violated [14],[15] and the law of entropy minimal production becomes invalid [16],[17].

Attempts to overcome these difficulties without whatever correction on the conceptual fundamentals and body of mathematics of classic thermodynamics failed. A remedy can be found in building of irreversible thermodynamic (thermokinetics) [18] on its own more general notional and conceptual foundation with maximal care for the classic thermodynamic heritage.

2. Exclusion of Hypotheses and Postulates from Theory Grounds

One of the most attractive features of the thermodynamic method has always been the possibility to obtain a great number of consequences of various phenomena as based on few primary principles ("the beginnings"), which are empirical laws in their character for the thermomechanical systems. Being consistently phenomenological (i.e. empirical), that method enabled to reveal general behavior of various processes without intrusion into their molecular mechanism and resort to simulation of structure and composition of a system under investigation. Therefore, it is not by pure accident that all the greatest physicists and many mathematicians of the last century in their investigations placed high emphasis on thermodynamics and, based on it, have obtained many significant results.

However, thermodynamics have presently lost its peculiar position among other scientific disciplines. It sounds now in increasing frequency that thermodynamics relates to real processes to the same degree as Euclidean geometry to the Egyptian land surveyors' work. Such a standpoint is not groundless. Classic thermodynamics is known to have always done with two primary postulates taken for its "beginnings" – the laws of excluded "perpetuum mobile" of the first and second kinds. Those principles have had the exclusion character and empirical status. However, classic thermodynamics restricted to those two laws appeared to have been unable to solve the problems that arose with its extension to phenomena of another nature. So in consideration of open systems exchanging substance with the environment, the entropy absolute value and the substance internal energy had to be known. To know the values, the third "beginning" would be needed as stating their becoming zero at the absolute zero of temperature.

In-depth analysis of the thermodynamic logic structure in works [19-21] and their followers later led to the comprehension that the second law of thermodynamics would need to be split in two independent laws (existence and rise of entropy), as well as to realizing the important role of the equilibrium transitivity principle named the *zeroth law of thermodynamics* [1]. Starting to study non-equilibrium systems with irreversible processes running therein additionally required the L. Onsager's reciprocity principle sometimes named the *fourth law of thermodynamics* from the phenomenological positions. Further investigations have revealed the fundamental difference between statistical thermodynamics and phenomenological thermodynamics and the fundamental role that plays for the latter the equilibrium self-nondisturbance principle, which has been assigned a part of its "general beginning" [7]. Thus present day thermodynamics appears to be arisen from not two, but even seven beginnings! Meantime, the disputable consequences of thermodynamics are growing in number thus causing doubts in its impeccability as a theory. As

R. Feynman wittily noted about this, “we have so many beautiful beginnings...but can’t make ends meet nonetheless” [22].

The law of excluded perpetuum mobile of the second kind being denied in open system thermodynamics [23], relativistic thermodynamics [8], spin system thermodynamics [24] excludes the possibility for thermokinetics to be based on the postulates of such a kind adopted for “the beginnings”. The grave dissatisfaction investigators feel with such state of affairs has resulted in multiple attempts to build thermodynamics as based on other fundamental disciplines. This tendency has been most highlighted by A. Veinik [25] in his *thermodynamics of real processes* based on a number of postulates of quantum-mechanical character, by M. Tribus [26] in his *informational thermodynamics* based on the information theory formalism, and by C. Truesdall [27] in his *rational thermodynamics* topology-based. All these theories feature a denial of the consistently phenomenological (i.e. based on only empirical facts) approach to the theory of irreversible processes, which deprives them of the basic advantage intrinsic for the classic thermodynamic method – the indisputable validity of its consequences.

In our opinion, one of the reasons of such a situation is that thermodynamics has lost its phenomenological nature with considerations of statistical-mechanical character gaining influence in its conceptual basis. Whereas the founders of statistical mechanics strived to lay the thermodynamic laws into the foundation of statistical theories, a statement has become now common that phenomenological thermodynamics itself needs a statistical-mechanical substantiation (despite “there are much ambiguity” in the grounds of the statistical theories [28]. In particular, L. Onsager, the founder of the theory of irreversible processes (TIP), in order to substantiate the most fundamental concept of his theory – reciprocal relations, appealed to the principle of microscopic reversibility, the theory of fluctuations with a complementary postulate for linear character of their attenuation. All these statements evidently outspread beyond the thermodynamic applicability, therefore L. Onsager, not without reason, termed his theory *quasi-thermodynamics* [13]. Adoption of the *local equilibrium* hypothesis I. Prigogine [16] for a basis of TIP construction became even “further-reaching” assumption. This hypothesis assumes (a) equilibrium in the elements of heterogeneous systems (despite the absence of the necessary equilibrium criterion therein – termination of whatever macro-processes); (b) possibility to describe their status with the same set of parameters as for equilibrium (despite the actual use of additional variables – thermodynamic forces) and (c) applicability of the basic equation of thermodynamics to these elements (despite its inevitable transformation into inequality in case of irreversible processes).

As a result, the existing theory of irreversible processes does not reach the rigor and completeness intrinsic for the classic thermodynamic method. Striving for excluding postulates from the grounds of nonequilibrium thermodynamics dictates the necessity to base its on only those statements that are beyond any doubt and construed as axioms [29]. These statements include, in particular, the *equilibrium self-non-disturbance axiom* reading that a thermodynamic system once having reached equilibrium cannot spontaneously leave it. Unlike the equilibrium self-non-disturbance principle (general law of thermodynamics), this axiom does not claim that a thermodynamic system, being isolated, reaches equilibrium for a finite time. The axiom just reflects the evident fact that processes in a system that has reached equilibrium may be generated by only impact applied to it from outside and are, therefore, never observed in isolated systems. Being a result of the experience accrued, this axiom excludes the possibility the macrophysical state of a system will vary as a result of short-term spontaneous deviations from equilibrium (fluctuations) caused by the micro-motion of the constituent particles. Indeed, if fluctuations do not cause any variation in the microscopic (statistical in their nature) parameters of the system, they can not be considered as an energy-involving process since the energy of the system remains invariable. Here lies the fundamental difference between thermodynamics and statistical physics – the latter does consider fluctuations as the object of investigation. At the same time the equilibrium self-nondisturbance axiom allows for existence of systems that omit the equilibrium

state in their development since this axiom does not claim for relaxation time finiteness, which is hardly provable.

The *processes discernibility axiom* is another primary statement thermokinetics appeals to [30]. It states there are processes existing and definable (by all experimental means) which cause system state variations as specific, qualitatively distinguishable and irreducible to any other ones. In classic thermodynamics these are isothermal, isobaric, adiabatic, etc processes. It will be shown hereinafter that these two axioms, in conjunction with experimental data underlying the energy conservation, are enough to construct a theory both internally and externally consistent and generalizing thermodynamics to transfer processes and conversion of energy in any forms.

2. System Approach to Objects of Investigation

The deductive interpretation of classic thermodynamics (thermostatistics) and the theory of non-static (irreversible) transfer processes as consequences from thermokinetics demands considering systems of a more general class as the object of its investigation [18]. Classic thermodynamics is known to have been restricted to the investigation of intrinsically equilibrium (spatially homogeneous) systems wherein the intensive parameters such as temperature T , pressure p , chemical, electrical etc potentials were similar for all points of the system. It was dictated by not so much the simplicity of system description as by the necessity to keep the equations of thermodynamics from passing into inequalities with the spontaneous variations of system parameters. Thermodynamics of irreversible processes resting upon the local equilibrium hypothesis divided, with the same purpose, a system in whole heterogeneous into a number of homogeneous subsystems (down to elementary, supposedly equilibrium, volumes). The same is typical for the field theories such as continuum mechanics, hydrodynamics and electrodynamics, which also assume the continuum properties to be at that identical in whole to the properties of these elements and may be described in terms of relevant integrals. However, the extensive properties of heterogeneous systems are far from being always additive ones, i.e. the sum of properties of constituent elements. First of all, non-additive is the property of a heterogeneous system to do useful work as none of its local parts possesses it. It was S. Carnot who awoke to that statement in application to heat engines [2] and put it into historically the first wording of the second law of thermodynamics. According to it, only thermally heterogeneous media possess a “vis viva (living force)”, i.e. are able to do useful work. In itself the notion of *perpetual motion of the second kind* as a system with no heat well and heat sink in its structure evidences the importance of considering such media as a single whole (but not as a set of thermally homogeneous elements). This is just the reason, why, at study of heat engines, the so-called “extended” systems have to be considered, which include, along with heat wells (sources), also heat sinks (receivers) (the environment).

Another non-additive property of heterogeneous media is the internal relaxation processes progressing and resulting, in absence of external constraint, in the equalization of densities, concentrations, electric charges, etc. among various parts of such a system. These processes are, however, absent in any element of the continuum considered as a locally equilibrium part of the system. More non-additive properties are the *self-organization* ability of a number of systems, which is absent in any of their homogeneous part [31-33] as well as the *synergism* (collective action) phenomena appearing at only a definite hierarchic level of the system organization. The said refers in general to any structured systems, which specific features are determined by the inter-location and inter-orientation of the functionally detached elements and disappear with decomposition of the object of investigation into these elements [34]. Many of such elements (e.g., macromolecules and cells) being detached remain, however, spatially heterogeneous (locally non-equilibrium) despite their microscopic size (constituting *microcosmos* of a kind). This demands them being approached in the same way as the “extended” macro-systems.

For the further reasoning it is very important to show in the most general form that the main differential calculus technique – discretization of an object of investigation into infinity of homogeneous elementary volumes – results in the loss of *backbone* (system-forming) links. With this in mind let us consider the most general case of a system comprising the entire set of interacting material objects. Such a system is isolated by definition, while its internal energy U remains invariable with time t , i.e. $dU/dt = 0$. Let us represent this energy as the space integral $U = \int \rho u dV$ of the energy density ρu . This gives for the system as a whole $dU/dt = \int (\partial \rho u / \partial t) dV = 0$. This integral may be equal to zero with some processes available in a system if only the sign of the derivative $(\partial \rho u / \partial t)$ is opposite in different areas of this system. This conclusion regards not only energy, but any other parameter obeying the law of conservation (mass, charge, momentum and angular momentum of the system), as well as the internal forces acting in such a system (as a closed one). From this it follows the *principle of processes counterdirectivity* [35] as the major assertion for natural science in whole: processes running in isolated (closed) systems cause opposite variations of the properties in the different parts (areas) of such systems. That is why the set of interacting systems acquires new properties. From this it follows the main feature of the system approach, viz. the requirement to keep all backbone links undisturbed when investigating some part of a system, i.e. investigating the part through the whole (but not vice versa).

The system approach involves the binding consideration of *spatial heterogeneity* of the object under investigation. This becomes a necessary requirement for any theory pretending to be the one adequately explaining the reasons of processes running within whatever system. It is hardly necessary to prove the invalidity of the fundamental sciences to meet this requirement when they fraction systems into infinity of “elementary” areas, material points or particles supposed to be intrinsically equilibrium (homogeneous). The such approach to objects of investigation dictates in itself the necessity of changing to consideration of spatially heterogeneous systems, which dichotomy (existing subsystems with opposite properties) is the reason of whatever processes arising therein. In line with this requirement the object of investigation by thermokinetics comprises spatially heterogeneous media considered as a *single nonequilibrium whole*. The size of such a system depends on the rate of its heterogeneity; therefore thermokinetics covers the broadest range of material objects – from nanoworld to megaworld – providing their properties can be successfully described with a finite number of state parameters. At the same time thermokinetics does not either exclude from consideration such a set of interacting bodies which may be considered, with acceptable accuracy, as a closed or isolated system. Thus, what was considered in thermodynamics as an “extended” system (including the environment besides the system itself), in thermokinetics becomes just a part of the system (subsystem) existing along with the similar other subsystems or with the object of work. In this case thermokinetics, from the very outset, has been consistent with the general scientific paradigm stating that any material object may not be deprived of its key property – extent, while any extended object – structure determined by its spatial heterogeneity [36].

3. Negation of Process and System Idealization outside the Framework of Uniqueness Conditions

Thermokinetics as a successive science needs to be extremely delicate to the classic thermodynamic inheritance. First of all this applies to the scope of the correctives introduced at that into the primary notions of thermodynamics. Let us dwell on those absolutely necessary in view of changing to consideration of systems of a broader class. Such a correction relates, in the first turn, to the notion of *process* as itself because of existing in heterogeneous systems a specific class of *stationary irreversible processes* wherein local parameters of a system as the object under investigation remain invariable despite the flows of heat, substance, charge, etc available in this system. Striving to keep the primary notion of “process” as a *succession of state variations* makes it necessary to define this notion as *any space-time variation of macro-physical*

properties pertaining to an object of investigation. Thereby the state variations associated with the spatial transfer of various energy forms are included in the notion of process. Changing to consideration of real processes also demands to negate the process idealization as implied in such notions as the *quasi-static, reversible, equilibrium*, etc process. The notion of *process* as a sequence of state variations of an object under investigation and the notion of *equilibrium* as a state featuring the termination of whatever processes are mutually exclusive. To eliminate this contradiction is to recognize that any non-static (running with a finite rate) process means equilibrium disturbance and is, therefore, irreversible. The acknowledgment of the fact that any nonstatic (running with finite rate) process involves the equilibrium disturbance and thus is irreversible was a turning point in the logical structure of thermodynamics. That demanded, as will be shown hereinafter, to negate the first law of thermodynamics as based on the energy balance equation and to seek for other ways to substantiate the law of energy conservation.

Being though somewhat previous, we can note that the solution to that problem was found by construing energy as the function of state for a spatially heterogeneous system and through its representation in terms of the parameters of that state without respect to the character of the processes in the system. As a result, all the remainder information about an object under investigation including the equation of its state and the kinetic equations of the processes running therein may be successfully attributed to the uniqueness conditions that thermodynamics imports “from outside” when applied to solving particular problems. In thermodynamics so constructed all the assumptions an investigator imposes on the uniqueness conditions (including the hypotheses on matter structure and process molecular mechanism, which simplify the preconditions for the equations of state and laws of transfer) do not affect the core of the theory itself, viz. those relations which follow from the mathematical properties of energy and other characteristic functions of system state [36].

4. The adequacy principle at System State Description

Changing over to non-equilibrium systems with spontaneous processes running therein needs to generalize the thermodynamic principle of *process classification* itself. The point is that the same state variations (e.g., heating of a body) in spatially heterogeneous systems may be caused by both the external heat exchange and appearing internal friction heat sources, chemical reactions, diathermic heating, magnetization reversal, etc. In the same way the cubic strain of a system can be induced by not only the compression work, but a spontaneous expansion into void as well. Hence processes in thermokinetics should be classified regardless of what causes whatever state variations – the external heat exchange or internal (including relaxation) processes. In this respect thermokinetics differs from both physical kinetics that classifies processes by reasons causing them (distinguishing, in particular, concentration diffusion, thermal diffusion and pressure diffusion) and the heat exchange theory that distinguishes processes by the mechanism of energy transfer (conductive, convective and radiant). Processes in thermokinetics will be classified by their *consequences, i.e. by special state variations they cause as phenomenologically distinguishable and irreducible to others.* We will call such processes, for short, *independent.* These include, in particular, isochoric, isobaric, isothermal and adiabatic processes thermal physics considers. Here comes the *heat process* as well (K. Putilov, 1971) [37], which we will construe as a variation of the body internal thermal energy U regardless of what causes it – either heat exchange or internal heat sources. Other processes are also included, e.g., the system composition variation process that may be caused both by substance diffusion across the system borders and chemical reactions inside the system.

With the principle of process classification adopted as based on distinguishability of processes specific demands are made on choosing their “coordinate”, i.e. a *physical value which variation is the necessary and sufficient criterion of running a particular process.* These demands consist in choosing only such a parameter as the process coordinate that *does not vary,*

when other, also independent, processes are simultaneously running in the same space points. It is that approach wherefrom the requirement in classic thermodynamics follows for the invariability of entropy as the heat exchange coordinate in adiabatic processes as well as the requirement itself for the process reversibility, i.e. the absence of spontaneous entropy variations not connected with the external heat exchange.

The principle of classification of real processes by their consequences and the axiom of their distinguishability enable substantiating a quite evident though fundamental statement stipulating that *the number of independent coordinates conditioning the state of any (either equilibrium or non-equilibrium) thermokinetic system equals the number of degrees of its freedom, i.e. the number of independent processes running in the system* [18]. This statement (or theorem) is easily provable “by contradiction”. Since a thermodynamic process is construed as variation of the properties of a system expressed in terms of state parameters, at least one of such parameters necessarily varies when processes are running. Let’s assume that several state parameters necessarily vary when some independent process is running. Then these parameters will not evidently be independent, which violates the primary premise. Now let’s assume that some coordinate of the system necessarily varies when several processes are running. Then these processes will not evidently be independent since they cause the same variations of the system properties – the fact that also violates the primary premise. We have nothing to do, but to conclude that *only one independent state coordinate corresponds to any (equilibrium or non-equilibrium, quasistatic or non-static) independent process*. Such coordinates are generally extensive variables since each of them defines, in the absence of other degrees of freedom, the energy of a system, which is an extensive value as well .

The proven statement makes the content of the *principle of adequacy* of the description of a status of any system. It defines the *necessary and sufficient* conditions for unique (deterministic) definition of state for whatever system. Therefore, it may be, for ease of reference, reasonably called the state *determinacy principle*. This principle makes it possible to avoid both the “underdetermination” and “over-determination” of a system. The continuum state “under-determination” as resulting from the local equilibrium hypothesis adopted is, e.g., far from evidence. This hypothesis excludes the necessity of the gradients of temperature, pressure and other generalized potentials (i.e. thermodynamic forces) in the fundamental equation of non-equilibrium thermodynamics on the ground that the bulk elements are assumed to be equilibrium. On the other hand, the continuum “over-determination” due to the infinite number of degrees of freedom ascribed to it despite the finite number of macroprocesses running therein is either not evident [18].

The theorem proven allows, in its turn, to concretize the notion of system *thermokinetic state*, which is construed as a set of only such properties that are characterized by the set of state coordinates strictly defined in their number. This means that such system properties as color, taste, smell, etc, which are not characterized by state parameters quantitatively and qualitatively may not be considered as thermodynamic. This relates, in particular, to also the “rhinal”, “haptic”, etc number of freedom A . Veinik arbitrarily introduced for a system [25]. One of the consequences of the determinacy principle consists in the necessity to introduce additional parameters of spatial non-uniformity as coordinates for systems where, along with external heat exchange processes, internal (relaxation) processes are observed as tending to approximate the system to the equilibrium state [38]. Without such variables introduced it is impossible to construct a theory covering the entire spectrum of real processes – from quasi-reversible up to critically irreversible [39].

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