Part 1

FROM THERMODYNAMICS – TO ENERGODYNAMICS

The interdisciplinary theory developed here is a further generalization of the thermodynamic method to processes of transfer and conversion of energy in any forms irrespective of the field of knowledge they belong to. Being consistently phenomenological (i.e. based on experience) and deductive (i.e. going from the general to the particular) that method, allowed to receive huge set of the consequences concerning the various phenomena and having within applicability of these beginnings the status of indisputable truths on the basis of a small number of the fixed primary principles (beginnings). It favourably distinguished it from other fundamental disciplines which are based on variety of hypotheses, postulates and modelling representations. Naturally therefore aspiration to receive main principles, laws and the equations of these disciplines, not resorting to the mentioned assumptions. More low we will try to find out the minimum volume of corrective amendments, which are necessary for bringing in thermodynamics to make its method suitable for research of the suitable for research enough wide range of scientific disciplines, processes and systems.

Chapter 1

METHODOLOGICAL PRINCIPLES OF ENERGODYNAMICS

There are periods 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 (Gelfer, 1981). 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 (1824) based on it. A few decades later the threatening clouds piled up over the R. Clausius' mechanical theory of heat (1876) 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 (1875) 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 (Chambadal, 1967; Kedrov, 1969; Gelfer, 1981; Bazarov, 1991).

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 (Ott, 1963; Arzelies, 1965; Meller, 1970; Krichevsky, 1970), as well as in the recognized ambiguity of relativistic transformations for a number of thermodynamic values (Bazarov, 1991). 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 perpetual motion of the second kind (Ramsey, 1956; Abragam, 1958; Krichevsky, 1970, Bazarov, 1991).

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-Casimir reciprocal relations appear to be violated (S. Grot, 1956; R. Mason et al, 1972) and the law of entropy minimal production becomes invalid (I. Prigogine, 1960; I. Gyarmati, 1974). 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 energodynamics on its own more general notional and conceptual foundation with maximal care for the classic thermodynamic heritage.

1.1. System Approach to Objects of Investigation.

The intention to keep the advantages of the thermodynamic method when generalizing it to non-thermal forms of energy and non-static processes impelled us to base energodynamics on the same methodological principles of the consistently phenomenological and deductive theory as classic thermodynamics. The deductive method (from the general to the particular) is much closer to *the system* approach accepted nowadays for the standard which assumes the account of all correlations. Its basic difference is part studying through whole (rather the reverse).

Hardly it is necessary to prove, as far from it other fundamental disciplines adhering to a return (inductive) method of research. This method assumes possibility of studying whole through its elementary parts by summation of their extensive properties. With that end in view investigated system is split up on huge (in case of a continuum – infinite) number of elementary volumes, material points, elementary particles, etc., assumed internally equilibrium (homogeneous). It deprives investigated objects of the basic property of material bodies **-** their *spread,* and any lengthy object – *the structure* caused by spatial heterogeneity of object of research.

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 (1824) 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.

One more non-additive property is the impulse of system which can be absent in system as whole, being distinct from zero for any its part. In the same way are non-additive the forces of a gravitational or electrostatic attraction proportional to product of co-operating mass or charges.

More non-additive properties are the *self-organization* ability of a number of systems, which is absent in any of their homogeneous part (S. Keplen, E. Essig, 1968; I. Prigogine, 1973,1986), 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 interlocation and inter-orientation of the functionally detached elements and disappear with decomposition of the object of investigation into these elements (G. Gladyshev, 1988). 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.

Non-additivity of properties may also manifest itself in the so-called "scale factor" consisting in loosing some key characteristics of an object at its modeling and being presently a close-attention-focus in the theory of fractals. Therefore to export test results from a test model to a full-scale installation, e.g. a chemical reactor, is far from being always feasible.

Lastly, the internal energy of a system in itself is non-additive when fragmentizing the last into ever-diminishing parts due to surface or long-range forces presenting and exerting on these parts. Potential energy of these forces belongs to the entire set of interacting (inter-moving) bodies or body parts and may not be referred to the internal energy (self-energy) of any of them taken separately. This is known to have restricted the applicability of thermodynamics both "from below" and "from above" enforcing consideration of the thermodynamic systems just as "simple" systems where these forces may be neglected (Caratheodori, 1907). This restriction refers, strictly speaking, to also the external energy of a system, which may be attributed to one of the field-forming bodies just in particular cases (within the applicability of such a notion as "test" charge or "test" mass). In particular, momentum variation in some part of a heterogeneous system is inevitably followed by the same of equal magnitude but opposite sign in its other parts. Therefore to restrict oneself to considering the properties of a particular part of the system is far not always applicable.

In sum, one may conclude that investigating elements of continuum may far not always enable sound judgment of its properties in whole. It is the system approach that allows for all interrelations between the whole and the parts. Such an approach dictates a necessity of considering spatially heterogeneous media as *a non-equilibrium single whole* in all cases when a doubt arises in validity of fragmentizing the object of investigation into some parts. Thus energodynamics considers such a set of the interacting bodies as a primary object of investigation, which may be construed as an isolated (self-contained) system. Scale of the system depends on its heterogeneity rate and covers a wide range of material objects – from nano- to mega-world. Herein, what is considered in classic thermodynamics as the "extended" system (comprising both heat sources and heat receivers) becomes just its part (subsystem) in the energodynamics.

The system approach allows discovering a special class of processes existing in heterogeneous systems and featuring opposite directivity. To demonstrate this, let us compare the density $\rho_i = d\Theta_i/dV$ of any extensive parameter Θ_i (mass M, entropy S, charge Θ_e, number of moles N_k in the kth substance, etc.) in some system part with its mean integral value $\bar{\rho}_i = V^{-1}\int\rho_i dV = \Theta_i/V$. Then it is easy to mark out areas in the system with volumes of V' and V'' where the densities $\rho_i'(\mathbf{r},t)$ and $\rho_i''(\mathbf{r},t)$ are higher and lower than $\bar{\rho}_i$, respectively. Indeed, dividing such a system into areas with the volumes V' and V'' wherein $\rho_i' > \bar{\rho}_i$ and $\rho_i''/< \bar{\rho}_i$, on account of $\int\rho_i dV - \int\bar{\rho}_i dV \equiv 0$, gives:

$$\int_{V'} [\rho_i'(\mathbf{r},t) - \bar{\rho}_i(t)]dV' + \int_{V''} [\rho_i''(\mathbf{r},t) - \bar{\rho}_i(t)]dV'' = 0. \qquad (1.1.1)$$

Hence it always follows the possibility to mark out *areas with processes of opposite directivity* in a heterogeneous system:

$$\int_{V'} [d(\rho_i' - \bar{\rho}_i)/dt]dV' = -\int_{V''} [d(\rho_i'' - \bar{\rho}_i)/dt]dV''. \qquad (1.1.2)$$

The dissociation processes featuring $\bar{\rho}_i = 0$ are a particular case. This statement will appear to be a cornerstone of the whole energodynamics. In its sence and generality it is in line with a well-known law of unity and struggle of opposites in materialistic dialectics. Its means so much for comprehending the specific character of heterogeneous processes that it should reasonably be endued with a status of special principle which we call the **principle of processes opposite directivity:** *there are always subsystems with processes of opposite directivity existing within heterogeneous systems.* Hereafter it will be shown that these are such processes that cause the energy interconversion and finally the evolution of physical, biological and cosmologicall systems.

1.2. 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 (Lorenz, Poincaré, Planck, Nernst, Caratheodory, Sommerfeld, Einstein, Born, Fermi, Neiman, Landau, Zeldovich, Feynman, etc) 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 perpetual motion 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 of C. Caratheodory (1907), T.A. Afanasjeva-Erenfest (1926), A.A. Guhman (1947, 1986) 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* (Gelfer, 1981). 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-non-disturbance principle, which has been assigned a part of its "general beginning" (I. Bazarov, 1991). 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".

The law of excluded perpetual motion of the second kind being denied in open system thermodynamics (M. Mamontov, 1970), relativistic thermodynamics (H. Ott, 1963), spin system thermodynamics (M. Vukalovich, I. Novikov, 1968) excludes the possibility for energodynamics 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 (1968) in his *thermodynamics of real processes* based on a number of postulates of quantum-mechanical character, by M. Tribus (1970) in his *informational thermodynamics* based on the information theory formalism, and by C. Truesdall (1975) 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 (R. Cubo, 1970)). 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*.

Adoption of the *local equilibrium* hypothesis (I. Prigogine, 1947) 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 energodynamics dictates the necessity to base energodynamics on only those statements that are beyond any doubt and construed as axioms. 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 macro-physical 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 energodynamics and statistical physics – the latter does consider fluctuations as the object of investigation. At the same time the equilibrium self-non-disturbance 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 *process distinguishability axiom* is another primary statement energodynamics appeals to. 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.

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

Present-day thermodynamics has long outgrown the initial frames of the heat-engine theory and transmuted into a rather general macroscopic method for studying kinetics of various transfer processes in their inseparable connection with the thermal form of motion. However, it is still rooted in the conceptual system of equilibrium thermodynamics (thermostatics) distant from the transfer concept and in its body of mathematics going over into inequalities when considering real (non-static, irreversible) processes. Even in the current manuals on thermodynamics its construction quite often starts with describing the theory of ideal cycles and ideal gases as its working media. Such a "squared idealization" in the theory grounds themselves could not help creating problems in the further generalization of thermodynamics to systems differing from those idealized. 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 non-static (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.

Such a construction of thermodynamics is advisably to be started off with a notion of *action* introduced into thermodynamics long before the law of energy conservation was discovered. The action in mechanics is construed as something that causes the momentum variation $Md\mathbf{v}_o$, where M – mass of the system, $\mathbf{v}_o$ – velocity of the mass center. According to the laws of mechanics the action value is expressed by the product of the force $\mathbf{F}$ and the duration of its action dt. This value is also called the *impulse of force*, N·s. A mechanical action is always associated with state variation, i.e. with process. Generalizing this notion to non-mechanical forms of motion the action will be construed as a *quantitative measure of a process associated with overcoming some forces*. The product of the action and the moving velocity $\mathbf{v} = d\mathbf{r}/dt$ of the object the force is applied to characterizes the amount of *work* W, J. The notion of work came to thermodynamics from mechanics (L. Carnot, 1783; J. Poncelet, 1826) where it was measured by the scalar product of the resultant force vector $\mathbf{F}$ and the induced displacement $d\mathbf{r}$ of the object it was applied to (radius vector $\mathbf{r}$ of the force application center)

$$đW = \mathbf{F}\cdot d\mathbf{r} \qquad (1.3.1)$$

Thus work was considered as a quantitative measure of action from one body on another[1]. Later on forces were called mechanical, electrical, magnetic, chemical, nuclear, etc depending on their nature. We will denote the forces of the i^{th} kind by $\mathbf{F}_i$ – according to the nature of this particular interaction form carrier. Forces are additive values, i.e. summable over the mass elements dM, bulk elements dV, surface elements df, etc. This means that in the simplest case they are proportional to some factor of their additivity Θ_i (mass M, volume V, surface f, etc) and accordingly called *mass, bulk, surface,* etc *forces*. Forces are also subdivided into *internal* and *external* depending on whether they act between parts (particles) of the system or between the system and surrounding bodies (the environment).

However, when considering non-equilibrium and, in particular, spatially heterogeneous media, another property of forces takes on special significance, viz. availability or absence of their resultant $\mathbf{F}$. To clarify what conditions this availability or absence, it should be taken into con-

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[1] Note that according to the dominating scientific paradigm only the interaction (mutual action) of material objects exists so that work is the *most universal* measure of their action on each other.

sideration that from the positions of mechanics the work some force does is the only measure of action from one body (particle) on another. The forces of the ith kind generally act on the particles of different (the kth) sort and hierarchical level of matter (nuclei, atoms, molecules, cells, their combinations, bodies, etc) possessing this form of interaction. Denoting the radius vectors of these elementary objects of force application by $\mathbf{r}_{ik}$ and the "elementary" force acting on them by $\mathbf{F}_{ik}$ gives that any ith action on a system as a whole is added of elementary works

$$đW_{ik} = \mathbf{F}_{ik} \cdot d\mathbf{r}_{ik} \qquad (1.3.2)$$

done on each of them ($đW_i = \Sigma_k \mathbf{F}_{ik} \cdot d\mathbf{r}_{ik} \neq 0$).

The result of such action will evidently be different depending on the direction of the elementary forces $\mathbf{F}_{ik}$ and the displacements $d\mathbf{r}_{ik}$ they cause. Let us first consider the case when the elementary forces $\mathbf{F}_{ik}$ cause the like-sign displacement $d\mathbf{r}_{ik}$ of the objects of force application (particles of the k^{th} sort), i.e. change the position of the radius vector $\mathbf{R}_i$ for the entire set of the k^{th} objects the elementary forces $\mathbf{F}_{ik}$ are applied to. In such a case $d\mathbf{R}_i = \Sigma_k d\mathbf{r}_{ik} \neq 0$ and the forces $\mathbf{F}_{ik}$ acquire the resultant $\mathbf{F}_i = \Sigma_k \mathbf{F}_{ik}$. This is the work done by mechanical systems and technical devices (machines) intended for the purposeful energy conversion from one kind into another. Therefore in technical thermodynamics such a work is usually called *useful external* or *technical* (A.I. Andryushchenko, 1975, et al). However, since in the general case such a work is done by not only technical devices, but biological, astrophysical, etc systems as well, we will call it just the *ordered* work and denote by W^e. The work of the ith kind is defined as the product of the resultant $\mathbf{F}_i$ and the displacement $d\mathbf{r}_i$ it causes on the object of its application:

$$đW_i^e = \mathbf{F}_i \cdot d\mathbf{r}_i . \qquad (1.3.3)$$

In Chapter 4 we will make certain that this work definition is universal. The ordered work process features its *vector character.*

The work done at the uniform compression or expansion of a gas with no pressure gradients ∇p therein is another kind of work. Considering the local pressure p as a mechanical force acting on the vector element of the closed surface df in the direction of the normal and applying the gradient theorem to the pressure forces resultant $\mathbf{F}_p$, gives:

$$\mathbf{F}_p = \int p df = \int \nabla p \, dV = 0. \qquad (1.3.4)$$

Thus the uniform compression work on an equilibrium (spatially homogeneous) system is not associated with the pressure forces resultant to be overcome, while the compression or expansion process itself is not associated with changing the position of the body as a whole. From the standpoint of mechanics where work has always been understood as an exclusively quantitative measure of energy conversion from one form into another (e.g., kinetic energy into potential one) this means that at the uniform compression the energy *conversion* process itself is absent. Due to the absence of the ordered motion of the i^{th} object (its displacements $d\mathbf{r}_i = 0$) the work of such a kind will be hereinafter called *unordered* and denoted by $W^{\text{н}}$. This category should also include many other kinds of work not having a resultant, in particular, the work of uniformly introducing the k^{th} substances (particles) or charge into the system, imparting relative motion momentum to the system components, etc. This category should further include heat exchange that is nothing but "micro-work" against chaotic intermolecular forces. As will be made certain hereinafter, the absolute value of the specific unordered forces F_i/Θ_i is construed as the *generalized potential* Ψ_i (absolute temperature T, pressure p, electrical φ, chemical μ_k potential of the k^{th} substances, etc). Thus the unordered work is done against forces not having a resultant. Therefore the unordered work process features the scalar character characterizing the transfer of energy in the same form (without energy conversion). This is the situation we encounter at the equilibrium heat or mass exchange and uniform cubic strain.

The work of dissipative character W^{d} constitutes a special work category. This work is done by the ordered forces $\mathbf{F}_i$ against the so-called *dissipative forces* not having a resultant because of their chaotic directivity. Therefore the dissipative work features a mixed (scalar-vector) character, i.e. is associated with changing from *ordered* forms of energy to *unordered* ones.

Fig. 1.1 illustrated a work classification based on the force difference. energy conversion available in the ordered work processes is here indicated by superseding the subscript i by the subscript $j = 1, 2, \ldots$, n according to the nature of the forces being overcome. External work done (against environmental forces) is denoted by the superscript "*env*".

This work involves transferring a part of energy in a modified form to other bodies (environment). Internal work keeps the energy of the system invariable and involves its conversion from one form into another (as it occurs in oscillation processes or cyclic chemical reactions of Belousov-Zhabotinsky's type). Hereinafter this classification will underlie the classification of energy by its forms.

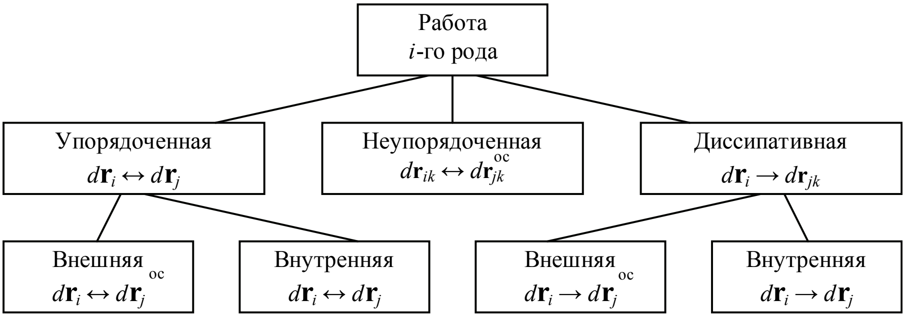

Fig.1.1. Work Classification for Non-Equilibrium Systems

The term *heat* in the present-day technical literature is used in two meanings: as a *state* function (called briefly the *body heat*) and as a *process* function serving as a *quantitative measure of heat exchange* (and called briefly the *process heat*)[1]. This duality in construing heat appeared historically with considering heat as a chaotic form of motion (amongst such phenomena as light, sound, electricity, magnetism) and has remained notwithstanding multiple discussions. The conception of heat as a form of energy has been reflected in the notion of heat capacity of system. It has as well strengthened its position in the heat exchange theory (to the principle: a system can exchange only what it has). In non-equilibrium systems such an understanding of heat is dictated by a number of thermal effects caused by dissipation (friction, diathermic or induction heating, chemical transformations, etc). These heats are not supplied from outside either, though relate to *process*. However, in equilibrium systems of such a kind thermal effects are absent and heat becomes just a quantitative measure of heat exchange process. Therefore in equilibrium thermodynamics heat is often interpreted as the energy being transited from one body to another, i.e. something that is supplied from outside across the system borders, but not contained in the system itself.

Accepting the said duality for objectivity we will take into consideration both the body heat and the process heat denoting the former by U_{B} (to avoid mishmash), while the latter – by Q and applying the exact differential sign d for infinitesimal increments of any state function (including U_{B}), while the inexact differential đ – for the elementary heat amounts $\text{đ}Q$ as process functions (C. Neuman, 1875). The same inexact

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[1] Thermodynamics. Terminology // under the editorship of I.I. Novikov. M.: AN USSR, 1973. Edition 85

differential sign will be applied for also the work $đW$ when it becomes dependent on the process path (i.e. becomes process function).

A specific kind of the energy exchange existing in the general case of open systems and associated with the substance (mass) exchange compels us to completely refuse the classic division of the energy exchange in such systems into *heat exchange* and *work*. The point is that putting substance into material medium always involves the so-called “input work” and the interchange of internal heat energy (body heat) between bodies. Therefore the notions of heat and work lose their sense “on the border where substance diffusion takes place” (M. Tribus, 1970).

The impossibility to reduce the process heat to only “one of the forms of energy exchange” (K. Putilov, 1971), as well as the existence of only one kind of energy exchange (mass exchange) in open systems forces absolutely rejecting the classic division of energy exchange into *heat* and *work* in non-equilibrium systems. The fundamental difference between the *ordered* and *unordered* work in non-equilibrium systems being perceived, heat exchange needs to be ascribed to the category of unordered work (against forces not having a resultant like the work of dissipative character). Interpreting the heat exchange as some *micro-work* against intermolecular forces directed in random way means the above notions are realized as different in their scale, while work is realized as a unitary quantitative measure of action from some material objects on other ones.

The abovementioned order of concepts clarifies the meaning and position of the notion of *energy*. The term *energy* (from Greek *activity*) was introduced into mechanics in the early XIX century by T. Young, an authoritative physicist, as a substitution for the notion of *living force* and meant the work which a system of bodies could do when decelerating or going over from a particular configuration into the “zeroth” one (adopted for the base). The energy was accordingly divided into kinetic $E^{к}$ и потенциальную E^{p}. The term *potential* meant that the energy could be realized in the form of work only with appearing the relative motion of interacting bodies, i.e. with changing their mutual position. The sum of kinetic and potential energies in an isolated (closed) system did not remain constant because of a known phenomenon of energy *dissipation* caused by unordered work done against the dissipation (friction) forces. Because of dissipation the real systems (with friction) spontaneously lost their capacity for external work. That meant the only thing, viz. the transition of energy as a microscopically ordered form of motion into the latent (microscopic) form of motion (interaction). Later, with thermodynamics appeared, that standpoint was supported by proving the internal energy U as inherent to bodies. That allowed stating the law of conservation of total energy that was construed as the sum of kinetic $E^{к}$, potential E^{p} and internal U energies of an isolated system:

$$(E^{\kappa} + E^{p} + U)_{isol} = \text{const.} \qquad (1.3.5)$$

However, in that case the notion of energy lost its primary sense of the capacity for external work as ensued from the word-group etymology of Greek εν (en) for *external* and εργον (ergon) for *action*. Indeed, according to the second law of thermodynamics the internal energy U can not be entirely converted into work. For this reason the energy of real systems ceased to be determined by the amount of useful work done. And the work itself ceased to be the exact differential since became dependant on the process path and rate (dissipation conditioning), but not on exclusively the initial and final states of the system. To simplify the situation, mechanics was supplemented with a provisional notion of *conservative* system, where the sum of kinetic and potential energies could be considered as a value kept and dependant on exclusively the initial and final states of the system. However, in that case all the consequences of mechanics as having ensued from the energy conservation law were naturally restricted to only the conservative systems.

That engendered some ambiguity in the notion of energy, which has not yet been resolved. A reader is usually very surprised with not finding in physical guides and encyclopedia a definition of this notion more substantial than the philosophic category of *general quantitative measure of all kinds of matter*. As H. Poincaré bitterly noted, “we can say of energy nothing more but that something exists remaining invariable”. Regarding the value that brings together all phenomena of the surrounding world such a definition is absolutely insufficient, the more so because not only energy remains invariable in isolated systems, but also mass, momentum, charge and angular momentum!

The definition energodynamics offers for work through action and work interpreted as the only quantitative measure of action from some bodies on other ones allows returning to energy its simple and clear meaning as the capacity of a system to do work. However, now energy becomes a quantitative measure of all (ordered and unordered, external and internal, useful and dissipative) works a system can do. This approximates to the J. Maxwell’s definition of energy as the “sum of all effects a system can have on the surrounding bodies”. Next chapters will be dedicated to the substantiation of formal consistency and advisability of such an approach.

1.4. Compliance with 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 energodynamics should be classified regardless of what causes whatever state variations – the external heat exchange or internal (including relaxation) processes.

In this respect energodynamics 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 energodynamics 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), which we will construe as a variation of the body internal thermal energy U_B 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.

This statement is reasonable to be called for easy reference as the **distinguishability principle**: *There are independent processes existing – each causing system state variations as specific, phenomenologically distinguishable and irreducible to others.*

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) energodynamics system equals the number of degrees of its freedom, i.e. the number of independent processes running in the system*.

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, quasi-static 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 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 **adequacy principle**: *The number of the independent parametes describing the state of some system is equal to the number of the independent processes running therein.*This principle makes it possible to avoid both the "under-determination" and "over-determination" of a system[1] as the main cause of the methodological errors and paradoxes of present-day thermodynamics (V. Etkin, 1979, 1991). 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-

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[1] I.e. the attempts to describe the system state by a deficient or excessive number of coordinates.

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 macro-processes running therein is either not evident.

The theorem proven allows, in its turn, to concretize the notion of system *energodynamic 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 (1968) for a system.

One of the consequences of the determinacy principle consists in the necessity to introduce additional state 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. 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.

1.5. Change to Absolute Reference System

The fact that relaxation vector processes (temperature, pressure, concentration, etc equalization) run in non-equilibrium systems requires introducing specific parameters of spatial heterogeneity characterizing the state of continuums as a whole. To do so, it is necessary, however, to find a way how to change over from the distribution functions of some extensive physical values Θ_i to the parameters of the system as a whole, which thermodynamics operates with. This change may be conducted in the same way as used in mechanics to change over from motion of separate points to system center-of-mass motion. To better understand such a change, let us consider an arbitrary continuum featuring non-uniform density distribution $\rho_i = \rho_i(\mathbf{r},t)$ of energy carriers¹⁾ over the system volume V. Fig.1.2 illustrates the arbitrary density distribution $\rho_i(\mathbf{r},t)$ as a function of spatial coordinates (the radius vector of a field point $\mathbf{r}$) and time t. As

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1) The Energy carrier is construed as a material carrier of the i^{th} Energy component, which quantitative measure is the physical value Θ_i. So the mass M_k of the k^{th} substance is a carrier of the rest Energy; the charge Θ_e – a carrier of the electrostatic Energy of the system; the component momentum $M_k\mathbf{v}_k$ – a carrier of its kinetic Energy, etc.

may be seen from the figure, when the distribution Θ_i deviates from that uniform (horizontal line), some amount of this value (asterisked) migrates from one part of the system to other, which displaces the center of this value from the initial $\mathbf{r}_{i0}$ to a current position $\mathbf{r}_i$.

Position of the center of a particular extensive value Θ_i defined by the radius vector $\mathbf{r}_i$ is given by a known expression:

$$\mathbf{r}_i = \Theta_i^{-1} \int \rho_i(\mathbf{r},t)\, \mathbf{r}\, dV\,, \quad (i = 1,2,\ldots,n) \qquad (1.5.1)$$

For the same system, but in a homogeneous state, the Θ_i center position $\mathbf{r}_{i0}$ may be derived if factoring $\rho_i = \bar{\rho}_i(t)$ in equation (2.1.1) outside the integral sign:

$$\mathbf{r}_{i0} = \int_V \bar{\rho}_i(t)\, \mathbf{r}\, dV = V^{-1} \int_V \mathbf{r}\, dV. \qquad (1.5.2)$$

Thus the state of a heterogeneous system features the emergence of specific “distribution moments” $\mathbf{Z}_i$ of the energy carriers Θ_i:

$$\mathbf{Z}_i = \Theta_i(\mathbf{r}_i - \mathbf{r}_{i0}) = \int_V \left[\rho_i(\mathbf{r},t) - \bar{\rho}_i(t)\right] \mathbf{r}\, dV. \qquad (1.5.3)$$

Expression (1.5.3) most evidently manifests that the parameters $\mathbf{Z}_i$ of spatial heterogeneity are additive values and summed up providing the $\bar{\rho}_i(t)$ value remains the same in various parts of a heterogeneous system. This follows from the conservation of integral (1.5.3) at its partition into parts with a volume $V' < V$[1]. However, these parameters become zero at “contraction” of the system to a material point, when $\rho_i(\mathbf{r},t) \to \bar{\rho}_i(t)$. This stands in absolute conformity with the degrees-of-freedom theorem because the

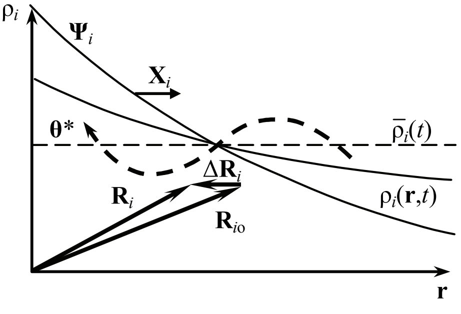

Fig.1.2. To Generation of Distribution Moment

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[1] With symmetrical density $\rho_i(\mathbf{r},t)$ distributions for whatever parameter, e.g., fluid-velocity profiles in tubes, expression (1.5.3) should be integrated with respect to annular, spherical, etc layers with $V' > 0$, wherein the function $\rho_i(\mathbf{r},t)$ is monotone increasing or decreasing.

processes of density redistribution $\rho_i(\mathbf{r},t)$ are absent in material points. And once again this confirms the fact that an entity of continuum elements considered as a system, non-equilibrium in whole, possesses additional degrees of freedom.

For any part of a homogeneous isolated system the $\mathbf{r}_{i0}$ value remains unvaried since running of any processes is herein impossible. Therefore the $\mathbf{r}_{i0}$ may be accepted for such systems as a reference point $\mathbf{r}$ or $\mathbf{r}_i$ and set equal zero ($\mathbf{r}_{i0} = 0$). In this case the vector $\mathbf{r}_i$ will define a displacement of the Θ_i center from its position for the system being in internal equilibrium state, and the moment of distribution of a particular value Θ_i in it will become:

$$\mathbf{Z}_i = \Theta_i \mathbf{r}_i \tag{1.5.4}$$

Herein the moment $\mathbf{Z}_i$ becomes an *absolute extensive measure of the system heterogeneity* with respect to one of the system properties – like such absolute parameters of classic thermodynamics as mass, volume, entropy, etc.

Let's show now, that all moments of distribution $\mathbf{Z}_i$ address in zero in homogeneous systems. With that end in view we will break non-uniform system V on two parts with volume V' and V'', in which limits the difference sign $\rho_i(\mathbf{r}, t) - \bar{\rho}_i(t)$ remains invariable. On fig. 1.2 them are areas, where $\rho_i(\mathbf{r}, t) > \bar{\rho}_i(t)$ and $\rho_i(\mathbf{r}, t) < \bar{\rho}_i(t)$. The moments of distribution $\mathbf{Z}_i'$, $\mathbf{Z}_i''$ and radiuses-vectors $\mathbf{r}_i'$, $\mathbf{r}_i''$ for these areas are defined by expression:

$$\boldsymbol{Z}_i = \int_{V'} [\rho_i(\mathbf{r},t) - \rho_i(t)]\mathbf{r}\,dV' + \int_{V''} [\rho_i(\mathbf{r},t) - \rho_i(t)]\mathbf{r}\,dV'' = \Theta_i'\mathbf{r}_i' + \Theta_i''\mathbf{r}_i'' \tag{1.5.5}$$

As $\Theta_i' = -\Theta_i''$, the moment of distribution $\mathbf{Z}_i$ can give a kind of dipole moment:

$$\mathbf{Z}_i = \Theta_i'(\mathbf{r}_i' - \mathbf{r}_i'') = \Theta_i^* \Delta\mathbf{r}_i\,, \tag{1.5.6}$$

where $\mathbf{Z}_i$, $\Theta_i^* = \Theta_i' = -\Theta_i''$; $\Delta\mathbf{r}_i$ – the sizes similar on sense of doublet moment, dipole charge and a dipole shoulder. From here follows, that the distribution moments, similarly to the dipoles moments, address in zero with disappearance of spatial heterogeneity of system ($\Delta\mathbf{r}_i = 0$) irrespective of a parametre reference mark Θ_i^*.

In case of discrete systems the integration over system volume will be replaced by the summation with respect to elements $d\Theta_i$ of the Θ_i value:

$$\mathbf{Z}_i = \Theta_i \mathbf{r}_i = \Sigma_i\, \mathbf{r}_i\, d\Theta_i\,, \tag{1.5.7}$$

where $\mathbf{r}_i$ – radius vector of the element $d\Theta_i$ center. Therefore expressions (1.5.4) through (1.5.6) remain valid for also the systems with discrete distribution of charges, poles, elementary particles, etc. Only the geometrical meaning of the $\Delta\mathbf{r}_i$ vector changes; for symmetrical distributions the vector is defined by the sum of the displacements $\Delta\mathbf{r}_i$ of all elements $d\Theta_i$. This may be instantiated by the centrifugal "shrinkage" of the particles' momentum flow in moving liquid when forming turbulent or laminar fluid-velocity profiles in channels ("boundary layer" formation and build-up).

Explicitly taking into account the spatial heterogeneity of systems under investigation is decisive in further generalization of the thermodynamic investigation method to non-equilibrium systems. As a matter of fact, this is the spatial heterogeneity (heterogeneity of properties) of natural objects that causes various processes running in them. This implies the exclusive role the distribution moments $\mathbf{Z}_i$ play as a measure for deviation of a system in whole from internal equilibrium of the i^{th} kind. Introducing such parameters allows precluding the major drawback of non-equilibrium thermodynamics, viz. lack of extensive variables relating to the gradients of temperature, pressure, etc. Classic thermodynamics is known to have crystallized into an independent discipline after R. Clausius succeeded in finding a coordinate (entropy) related to temperature in the same way as pressure to volume and thus determinately described the simplest thermo-mechanical systems. The distribution moments $\mathbf{Z}_i$ play the same part in energodynamics coming into being. As will be shown later, these relate to the main parameters introduced by non-equilibrium thermodynamics – thermodynamic forces, in the same way as the generalized potentials to the coordinates in equilibrium thermodynamics. These are the distribution moments which make the description of heterogeneous media a deterministic one thus enabling introducing in natural way the concept of generalized velocity of some process (flow) as their time derivatives. They visualize such parameters as the electrical displacement vectors in electrodynamics and generalize them to phenomena of other physical nature. In mechanics the $\mathbf{Z}_i$ parameters have the dimension of action (Θ_i – momentum of a body, $\mathbf{r}_i$ – its displacement from equilibrium position), imparting physical meaning to this notion. These are the parameters which allow giving the analytic expression to the system working capacity having thus defined the notion of system energy. Using such parameters provides a clear view of the degree of system energy order, enables proposing a universal criterion of the non-equilibrium system evolution, etc. Paraphrasing a M. Planck's statement regarding entropy one may positively say that the distribution moments are exactly the parameters entire non-equilibrium thermodynamics is “standing and falling” with.

1.6. Counterdirectivity of Processes Allowed for When Finding Their Coordinates

As follows from expressions (1.5.2) and (1.5.3), the distribution moment $\mathbf{Z}_i$ contain vectors of displacement $\mathbf{r}_i$, each of which can be expressed product of a basic (individual) vector $\mathbf{e}_i$, characterising its direction, on module $R_i = |\mathbf{R}_i|$ this vector. Therefore the complete variation of the displacement vector $\mathbf{R}_i$ may be expressed as the sum of two summands:

$$d\mathbf{r}_i = \mathbf{e}_i dr_i + r_i\, d\mathbf{e}_i = \mathbf{e}_i dr_i + r_i\, d\boldsymbol{\varphi}_i \times \mathbf{e}_i, \qquad (1.6.1)$$

where the augend $\mathbf{e}_i dr_i$ characterizes elongation of the vector $\mathbf{r}_i$, while the addend $r_i\, d\mathbf{e}_i$ – its turn.

Let us express now the $d\mathbf{e}_i$ value characterizing the variation of the distribution moment direction in terms of an angular displacement vector $\boldsymbol{\varphi}$ normal to the plane of rotation formed by the vectors $\mathbf{e}_i$ and $d\mathbf{e}_i$. Then the $d\mathbf{e}_i$ will be defined by the external product $d\boldsymbol{\varphi}_i \times \mathbf{e}_i$ of vectors $d\boldsymbol{\varphi}_i$ and $\mathbf{e}_i$, so the addend in (1.6.1) will be $\Theta_i r_i d\mathbf{e}_i = d\boldsymbol{\varphi}_i \times \mathbf{Z}_i$. Hence, expression of full differential of the distribution moments looks like:

$$d\mathbf{Z}_i = d(\Theta_i \mathbf{e}_i r_i) = \mathbf{r}_i\, d\Theta_i + \Theta_i \mathbf{e}_i\, dr_i + d\boldsymbol{\varphi}_i \times \mathbf{Z}_i, \qquad (1.6.2)$$

According to the degrees-of-freedom theorem this means that any state function describing a heterogeneous system in whole are generally defined by also the full set of variables Θ_i, r_i and $\boldsymbol{\varphi}_i$. Since further resolution of the vector $\mathbf{Z}_i$ is impossible, expression (1.6.2) indicates there are three categories of processes running in heterogeneous media, each having its own group of independent variables. The first-category processes running at $\mathbf{r}_i$ = const involve the uniform variation of the physical value Θ_i in all parts of the system. Such processes resemble the uniform rainfall onto an irregular (in the general case) surface. Here comes, in particular, the pressure field altered in liquid column with variation of free-surface pressure. These processes also cover phase transitions in emulsions, homogeneous chemical reactions, nuclear transformations and the similar scalar processes providing the composition variations they induce are the same in all parts of the system. We will call them hereinafter the *uniform processes* regardless of what causes the increase or decrease in amount of whatever energy carrier Θ_i (and the momentum associated) – either the external energy exchange or internal relaxation phenomena. These processes comprise, as a particular case, the reversible (equilibrium) processes of heat exchange, mass exchange, cubic strain, etc, which, due to their quasi-static nature, practically do not disturb the system spatial homogeneity. The counterdirectivity of these processes shows up in the opposite variation of the parameters Θ_i in the system and the environment.

Processes described by the addend in (1.5.5) run with the Θ_i parameters being constant and consist in their redistribution among the parts (zones) of a heterogeneous system. They involve decreasing, e.g., the entropy S', mass M', its momentum $\mathbf{P}'$, its volume V', etc, in some parts of the system and by increasing the same in other parts. Such processes are associated with the Θ_i value center position variation $\mathbf{r}_i$ within the system and resemble the migration of fluids from one part of a vessel into another. Therefore we will call them the *redistribution* processes. The electrical displacement vector $\mathbf{D} = \Theta_\mathrm{e}\Delta\mathbf{r}_\mathrm{e}$ is one of such moments with Θ_e as electrical charge and $\Delta\mathbf{r}_\mathrm{e}$ as displacement of its center.

Such processes are always non-equilibrium even if they run infinitely slowly (quasi-statically) since the system remains spatially heterogeneous in this case. State modifications of such a kind are caused by, e.g., the useful external work of external forces, the non-equilibrium energy exchange processes that induce non-uniform variation of the Θ_i coordinates inside the system, and the vector relaxation processes involving equalization of temperature, pressure, chemical and other system potentials. All processes of such a kind feature a directional (ordered) character, which distinguishes the useful work from the work of uniform (quasi-static) introduction of substance, charge, etc, or the expansion work. Their counterdirectivity shows up in the opposite displacement of centers for the values Θ_i' and Θ_i'' in the subsystems V' and V''. According to (1.3.2) the coordinates of the processes pertaining to this category are understood as the displacement vectors $\mathbf{r}_i$. These coordinates should be attributed to the *external parameters* of the system since they characterize the *position* of the energy carrier Θ_i center in whole relative to external bodies (the environment) just as the center of mass $\mathbf{r}_m$ of the system or its center of inertia $\mathbf{r}_w$.

There are also the processes of *reorientation* of magnetic domains, electrical and magnetic dipoles, axes of rotation of bodies, etc., running in a number of systems, e.g., in ferromagnetic materials. The micro-world manifests them in, e.g., the unified spin-orientation arrangement' the macro-systems – in the spontaneous magnetization of ferromagnetic materials, while the mega-world – in the close-to-equatorial plane alignment of the galaxies' spirals, asteroidal belts, orbits of the primary planets and their satellites, etc. The counterdirectivity of these processes shows up in the opposite displacement of the vector $\mathbf{Z}_i$ termini at vector turn. The systems with processes of such a kind will hereafter be called, for short, *oriented*. These include also the bodies with shape anisotropy. The reorientation processes are not reducible to the transfer and redistribution processes either. This means that the coordinate of such kind a process is a variation of the angle $\boldsymbol{\varphi}_i$ characterizing the orientation of distribution moment $\mathbf{Z}_i$ of the system as a whole.

Thus, all processes running in heterogeneous systems may be broken down into three groups: *uniform, redistribution* and *reorientation processes*, which coordinates are, respectively, variables Θ_i, r_i and $\boldsymbol{\varphi}_i$. This fundamentally distinguishes energodynamics from classic thermodynamics and the theory of irreversible processes, where the state of a system is defined by exclusively a set of thermostatic variables Θ_i.

For lack of processes of reorientation $\mathbf{Z}_i = \mathbf{Z}_i(\Theta_i, \mathbf{r}_i)$ and expression (1.6.2) becomes:

$$d\mathbf{Z}_i = \mathbf{r}_i\, d\Theta_i + \Theta_i d\mathbf{r}_i, \tag{1.6.3}$$

resulting in:

$$\Theta_i = \nabla\cdot\mathbf{Z}_i \text{ and } \rho_i = \nabla\cdot\mathbf{Z}_{iV}, \tag{1.6.4}$$

where $\mathbf{Z}_{iV} = \partial\mathbf{Z}_i/\partial V$ – distribution moment in the system unit volume.

The undertaken expansion of the space of variables by introducing the vectors of displacement $\mathbf{r}_i$ makes it possible to cover not only quantitative, but as well *qualitative* variations of energy in various forms. The fact that *vector processes* run in systems along with *scalar processes* means that both the *ordered* W^e and *unordered* W^a works are generally done in such systems. It becomes clear that the irreversibility of real processes associated with the energy dissipation (i.e. with losing the capacity for ordered work) becomes apparent in the process «*scalarization*», i.e. in losing vector character of the process. Furthermore, a possibility appears to further distinguish between the *energy transfer* processes (i.e. the energy transfer between bodies in the same form) and the *energy transformation* processes (i.e. the energy conversion from one form into another)[1].

This is enough in principle to construct a unitary theory of real processes enabling investigation of any systems (simplex and complex, closed and open, homogeneous and heterogeneous, isolated and non-isolated, tending to and omitting equilibrium) not outstepping the strict applicability of its primary concepts.

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[1] As will be shown hereinafter, the Energy transfer is associated with unordered work done, whereas the Energy conversion – with ordered work.

Chapter 2

POSTULATE-FREE DERIVATION OF BASIC RELATIONS IN THE THEORY

As the practice shows, studying a scientific discipline, especially acquiring it inasmuch as necessary for an independent activity is most successful if a reader is from the very first introduced to a critical presentation of the existing situation, to fundamentals of the discipline and general methods of solving particular problems. Therefore in this chapter we will review, along with a historical synopsis, specific features of energodynamics allowing it to apply its body of mathematics to any systems – simplex and complex, closed and open, homogeneous and heterogeneous, tending to and omitting equilibrium in their development.

2.1. Substantiation of Total energy Conservation Law

Classic thermodynamics is known to be based on the principle of heat Q and work W equivalence. R. Clausius, the founder of classic thermodynamics, formulated this principle as follows, ”In all cases, when heat becomes work in a cyclic process, the amount of the heat expended is proportional to the work done and vice versa, work done is converted into an equivalent amount of heat” (Clausius, 1876). If heat and work are measured in the same units of the international system of units, SI, the equivalence principle may be written as a simple relationship:

$$W_c / Q_c = \oint đW / \oint đQ = 1, \qquad (2.1.1)$$

где W_c, Q_c – work done and heat supplied for cycle; $đW$, $đQ$ – their elementary amounts for particular parts of the cyclic process under consideration.

Taking into consideration the rule of signs accepted in thermodynamics (the work done by a system and the heat supplied to it are positive) equation (2.1.1) becomes:

$$\oint (đQ - đW) = 0. \qquad (2.1.2)$$

Clausius was the first who noticed that the above result did not depend on the path of the process under consideration. That allowed him to use a known mathematical theorem of curvilinear integrals. It states that if a curvilinear integral of an arbitrary differential form (in our case $đQ - đW$) becomes zero along any closed path within some space of variables, the integrand represents the exact differential of function of these variables U:

$$dU = đQ - đW \text{ or } đQ = dU + đW. \qquad (2.1.3)$$

R. Clausius did not concretize the space of variables wherein he considered the curvilinear integral (2.1.2) since he had not yet found the heat exchange (entropy) coordinate. Therefore he initially called the function U the *total heat of a body* having construed it as the sum of the heat the body received from outside and the heat released as a result of the *disgregation work* (of dissipative character). That caused some confusion in notions since imparted the status of state function to heat and disgregation work. Therefore a rather heated discussion combusted about the U function. In particular, W. Thomson recommended the term *mechanical energy of a body in particular state* for the U value. From that time on this function has been referred to as the *internal energy*. Being the state function of a system, that function did not depend on the motion or position of the system relative to the environment. In such a case the isolation of the system from the environment (Q, $W = 0$) left that function invariable. Based on that fact, expression (2.1.3) started to be considered in classic thermodynamics as a particular case of the *energy conservation law* called the first law of thermodynamics.

Since classic thermodynamics from its origin has always been restricted to describing the behavior of internally equilibrium (spatially homogeneous) systems with parameters the same for all of the system parts, all kinds of work such a system could do had the *unordered* character (see Chapter 1). Here comes, in particular, the uniform compression work $đW_p$ expressed through the product of the absolute pressure p and the volume variation dV. In such a case the U function could actually be construed as the dissipated part of energy, which corresponded to the law of energy conservation in the form of (1.3.4). However, in the more general case of non-equilibrium and especially spatially heterogeneous systems this is far from being so. In particular, the chemical and nuclear energy of homogeneous systems is also partly convertible into other forms despite they do not either depend on the position of the system relative to surrounding bodies, i.e. relate to internal energy. The situation became even more complicated with changing to the spatially heterogeneous systems to be studied, in particular, to the so-called *extended* systems with the environment included. Such systems can do some useful work before internal equilibrium has set in there. These systems may comprise also polarized and magnetized bodies located in external force fields. In all those cases the internal energy U ceased being that “dissipated” part of energy meant in (1.3.4).

All this impels to search for a more general substantiation of the law of its conservation. To this end let us consider the results of those experiments on definition of the heat and work equivalence principle, which related to non-equivalent systems with relaxation processes running therein. Their specific character was such that heat was obtained there by friction (dissipation). These include classic experiments by Joule, in particular, the experiment with calorimeter and agitator driven by dropping weight; also his experiment with the Proney brake that brakes the drum calorimeter (1843-1878); Girn’s experiments with lead flattening on anvil with drop hammer (1859); Lenz’s experiments with solenoid discharging to active resistance in vessel calorimeter (1972) and many other experiments involving battery charging, gas transfer between vessels, electrolyte decomposition, etc (J. Gelfer, 1969,1973). Those experiments had such a result that a system disturbed from equilibrium by a mechanical (ordered) work $W_i^{\mathrm{e}} = W_i^{\mathrm{e}}(\mathbf{r}_i)$ done on it returned to the initial equilibrium state after a heat amount Q strictly equivalent to the work had been removed from the system. Taking the work of both ordered and unordered character (according to the above classification) into consideration means the necessity to extend the space of variables wherein the above considered cyclic processes take place. It is easy to reveal in this case that integrand (2.1.2) constitutes a state function in the space of variables (Θ_i, $\mathbf{r}_i$), i.e. a more general one than the system internal energy. This function depends on both the internal Θ_i and external $\mathbf{r}_i$ system coordinates, i.e. constitutes the sum of the external and internal system energies. Such energy is usually called the *total* energy of the system. The decrease of the function $U=U(\Theta_i, \mathbf{r}_i)$ defines the sum of all (ordered and unordered) works the system do:

$$-\,dU(\Theta_i, \mathbf{r}_i) = \Sigma_i\, \text{đ}W_i^a + \Sigma_i\, \text{đ}W_i^e. \qquad (2.1.4)$$

According to this expression the energy of a system, in the absence of external impacts on the system ($\Sigma_i \text{đ}W_i^a = 0$, $\Sigma_i \text{đ}W_i^e = 0$), remains invariable at any variations of its state. In other words, the *energy of an iso-*

lated system is constant. Thus the generalization of the heat and work equivalence principle to non-equilibrium systems directly leads to the law of conservation of "total" energy as a state function for the entire set of interacting (mutually moving) bodies. However, for such a system (isolated) all its energy is *internal*. This fact reveals the imperfection of dividing the energy into *external* and *internal*. From the position of energodynamics considering the entire set of interacting bodies as a single non-equilibrium whole it is more important that its energy be measured in an *own* (absolute) reference frame not connected with the state of any of the bodies within the environment[1]. Since the term *system energy* with regard to the function $U(\Theta_i, \mathbf{r}_i)$ unambiguously tells the energy belongs to the system itself, the terms "total", "external", "internal", etc energies become superfluous. This allows focusing on other properties of energy and its other components which characterize its conversion capacity.

2.2. Force and Its Moment as the Notions Introduced into Basic Equation of Energodynamics

Let us consider the consequences ensuing from the fact itself of existing the system energy $U(\Theta_i, \mathbf{r}_i)$ as a function of the quite certain set of arguments (state coordinates) As shown above, the energy of a heterogeneous system as a function of its state is generally expressed as $U = U[\mathbf{Z}_i(\Theta_i,\ r_i, \boldsymbol{\varphi}_i)]$, where $i = 1, 2, \ldots, n$ – number of energy components equal to the maximal number of independent processes for some of their categories (uniform processes, redistribution and reorientation processes). This means that the exact differential of energy may be expressed by the following relationship:

$$dU = \Sigma_i(\partial U/\partial \Theta_i)d\Theta_i + \Sigma_i\,(\partial U/\partial r_i)\,\mathbf{e}_i dr_i + \Sigma_i\,(\partial U/\partial \boldsymbol{\varphi}_i)d\boldsymbol{\varphi}_i. \qquad (2.2.1)$$

Derivatives of some system parameters (U) with respect to other ones (Θ_i, r_i , $\boldsymbol{\varphi}_i$) are also system parameters. Therefore denoting them as:

$$\Psi_i \equiv (\partial U/\partial \Theta_i); \qquad (2.2.2)$$

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[1] Otherwise, should the Energy conservation be violated, the Energy of a system would vary with the state variation of these bodies despite the absence of Energy exchange with the system.

$$\mathbf{F}_i \equiv -\,(\partial U/\partial\, \mathbf{r}_i\,); \tag{2.2.3}$$

$$\mathbf{M}_i \equiv -\,(\partial U/\partial \boldsymbol{\varphi}_i), \tag{2.2.4}$$

gives the fundamental identity of energodynamics in the form:

$$dU \equiv \Sigma_i \Psi_i\, d\Theta_i - \Sigma_i\, F_i dr_i\, - \Sigma_i\, \mathbf{M}_i{\cdot}d\boldsymbol{\varphi}_i, \tag{2.2.5}$$

For isolated systems the right-hand member of identity (2.2.5) becomes zero. For systems not changing its spatial orientation the two last terms in (2.2.1) and (2.2.6) may be combined $(\Theta_i\mathbf{e}_i dr_i + \mathbf{Z}_i d\mathbf{e}_i = \Theta_i d\mathbf{r}_i)$, then the fundamental identity of energodynamics becomes:

$$dU \equiv \Sigma_i \Psi_i\, d\Theta_i - \Sigma_i\, \mathbf{F}_i{\cdot}d\mathbf{r}_i. \tag{2.2.6}$$

Identities (2.2.5) and (2.2.6) are nothing else but a result of the joint definition of the related parameters Ψ_i and Θ_i, $\mathbf{F}_i$ and r_i or $\mathbf{Z}_i$, $\mathbf{M}_i$ and $\boldsymbol{\varphi}_i$. To clarify the physical meaning of the parameters thus introduced, let us first consider the particular case of internally equilibrium (spatially homogeneous) and stationary thermo-mechanical systems. Such simplest systems may be instantiated as the working media of heat engines in the vaporous or gaseous state. They have two degrees of freedom – thermal and mechanical, i.e. the capacity for the heat exchange Q and the uniform expansion work W_{ex}. Due to the absence of redistribution and reorientation processes in homogeneous systems (dr_i, $d\boldsymbol{\varphi}_i = 0$) the parameters Ψ_i are the same for all points of such a system and equal to their local values ψ_i, so that identity (2.2.5) goes over into a joint equation of the first and second laws of thermodynamics for closed systems:

$$dU = \Sigma_i\, \Psi_i\, d\Theta_i = TdS - pdV\,. \tag{2.2.7}$$

Since the variation of the coordinates Θ_i in an equilibrium system is caused by exclusively the external heat exchange (their internal sources are absent), the terms of this relationship characterize, respectively, the elementary heat exchange in the system $\text{đ}Q = TdS$ and the elementary expansion work $\text{đ}W_{\mathrm{ex}} = pdV$. In this case the parameters Ψ_i acquire the meaning of the absolute temperature T and absolute pressure p. In the more general case of spatially heterogeneous systems the parameters Ψ_i are, as will be shown hereinafter, the generalized local potentials ψ_i averaged by mass in all elements of the system.

To clarify the meaning of the terms of the second sum in (2.2.5), we must take into account that they correspond to the redistribution processes running at constant parameters Θ_i and $\boldsymbol{\varphi}_i$, i.e. with invariable direction of the unit vector **e**. Then $(\partial U/\partial r_i) = \mathbf{e}{\cdot}(\partial U/\partial \mathbf{r}_i) = \mathbf{F}_i{\cdot}\mathbf{e}$, i.e. represents a projection of the resultant $\mathbf{F}_i$ on the direction of movement of the object Θ_i the force is applied to. Thus the terms of the second sum in (2.2.5) characterize the elementary useful work $đW_i^{\mathrm{e}} = \mathbf{F}_i \cdot d\mathbf{r}_i$ that has the same form as in mechanics. This work may be expressed in terms of the so-called thermodynamic forces $\mathbf{X}_i$ defined as:

$$\mathbf{X}_i \equiv -(\partial U/\partial \mathbf{Z}_i). \qquad (2.2.8)$$

Since at Θ_i, $\boldsymbol{\varphi}_i$ = const, $(\partial U/\partial \mathbf{Z}_i) = \Theta_i^{-1}(\partial U/\partial \mathbf{r}_i) = \mathbf{F}_i/\Theta_i$, then the $\mathbf{X}_i$ thermodynamic forces thus introduced are actually the specific forces in their usual (Newtonian) meaning, i.e. the forces $\mathbf{F}_i$ per unit of the value Θ_i they transfer. These are, in particular, the specific mass, bulk and surface forces, for which the Θ_i value is construed as, respectively, mass M, volume V and surface f of the body. This category also includes the Lorenz force $\mathbf{F}_{\mathrm{e}}$ related to the electric charge Θ_{e} transferred. In the theory of irreversible processes such forces are termed the *thermodynamic forces in their energy representation* (Gyarmati, 1974). Using them enables representation of work by two equivalent expressions:

$$đW_i^{\mathrm{e}} = \mathbf{F}_i \cdot d\mathbf{r}_i = \mathbf{X}_i \cdot d\mathbf{Z}_i. \qquad (2.2.9)$$

The work described by expression (2.2.9) may be mechanical, thermal, electrical, chemical, etc (depending on nature of the forces to overcome); external or internal (depending on where the forces arise – either in the system itself or outside); useful or dissipative (depending on what the work involves – either purposeful conversion of energy or its dissipation).

Lastly, the terms of the third sum in (2.2.5) correspond to the reorientation processes running with constant Θ_i and R_i. In this case $\mathbf{F}_i \cdot d\mathbf{r}_i = \mathbf{F}_i \cdot [d\boldsymbol{\varphi}_i, \mathbf{r}_i]$, and the parameter $\mathbf{M}_i$ acquires the meaning of a torque from the force $\mathbf{F}_i$:

$$\mathbf{M}_i = \mathbf{F}_i \times \mathbf{r}_i \qquad (2.2.10)$$

This "torsion" torque is advisable to be called the "orientation" torque in the case it becomes zero when the direction of the force $\mathbf{F}_i$ coincides with the direction of the displacement vector $\mathbf{r}_i$.

The fundamental identity of energodynamics thus obtained is valid regardless of what causes the variation of the parameters Θ_i, $\boldsymbol{r}_i$ and $\boldsymbol{\varphi}_i$ – either the external heat exchange or the internal (including relaxation) processes. Therefore it is applicable to *any processes* (both reversible and irreversible). At the same time it is most detailed of all the relationships connecting the parameters of spatially heterogeneous systems since it allows for *any possible categories of processes* running in such systems.

Let us pay attemtion now to the fundamental difference between ordered and unordered works described in this expression by the variables of scalar and vector character. For this let us consider first some heterogeneous system consisting of two subsystems with the parameters Ψ_i', Θ_i' and Ψ_i'', Θ_i''. If such a system is homogeneous as a whole (($\mathbf{X}_i$,$\mathbf{M}_i$ = 0) and isolated (dU = 0), expression (2.2.5) for it takes the form:

$$dU = \Psi_i' d\Theta_i' + \Psi_i'' d\Theta_i'' = 0. \qquad (2.2.11)$$

Hence it follows that in the process of redistribution of the energy carrier Θ_i between the parts of such a system $d\Theta_i' = - d\Theta_i''$ the value of the *i*th energy form U_i therein remains invariable, i.e. only a transfer of energy occurs in this form across the border between these parts. We called such an energy exchange running without energy form variation as the *energy transfer* for short.

Another kind are the processes described by the terms of $\mathbf{X}_i \cdot d\mathbf{Z}_i$ type or $\mathbf{M}_i \cdot d\boldsymbol{\varphi}_i$ as their variety. If a system is heterogeneous, i.e. $\mathbf{X}_i = - \nabla\Psi_i \neq 0$ and $d\mathbf{Z}_i = \Theta_i d\mathbf{R}_i \neq 0$, then

$$\mathbf{X}_i \cdot d\mathbf{Z}_i = - \Theta_i (d\mathbf{r}_i, \nabla)\, \Psi_i = - \Theta_i\, d\Psi_i (\mathbf{r}_i), \qquad (2.2.12)$$

where $\Psi_i(\mathbf{r}_i)$ is the potential of some part in the heterogeneous system, which varies with part-to-part transfer within the system, i.e. should be considered as a function of system position $\mathbf{R}_i$ in the field of the Ψ_i potential. Thus the terms $\mathbf{X}_i \cdot d\mathbf{Z}_i$ describe the *i*th energy form variations caused by the above redistribution of the energy carrier Θ_i if kept in the system as a whole. In accordance with the energy conservation law this is possible only as a result of other energy forms converted into the *i*th form. Therefore ordered work is always associated with the *energy conversion* process.

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2.3. Differentiation between Ordered and Unordered Parts in Internal Energy (Inergy and Anergy)

The fact energy lost its primary meaning as a measure of capacity for work after the notions of internal and dissipation energy have been introduced engendered the problem to find a measure of motion or interaction, which would characterize such an important property of energy as its capacity for ordered (useful) work. The notion of external energy should have seemingly got the goals. The external energy was construed as that part of the energy of a system which did not depend on its internal state and was defined by exclusively the motion or position of the system as a whole relative to other bodies. As in mechanics, the external energy was defined by the useful external work a system could do when transiting from one configuration into another (adopted for a reference frame). The internal energy was accordingly construed as another part of the energy which did not depend on the position or motion of a system relative to other bodies and was defined by exclusively the internal (latent) motion and interaction of particle comprising the system. Since in equation (1.3.4) the internal energy played the role of dissipation energy, i.e. the energy that lost its capacity for work, it was equivalent to its division into workable and unworkable parts. However, later it became clear that a part of external energy, nevertheless, depends on the internal state of the system. E.g., in dielectric and magnetic materials the resulting electrical and magnetic field depends on the temperature of these bodies. In this case the polarization and magnetization work of these bodies involves a work done against external fields, i.e. changes both the external and internal energies. In some particular cases the situation could be simplified by introducing an additional notion of “internal self-energy of such bodies without field energy in vacuum” (I. Bazarov, 1991 et al). However, this energy, strictly speaking, is not anymore a “self-energy” since the external field has already been changed by the polarized or magnetized bodies available therein. Furthermore, with the advent of the specific theory of relativity it was revealed moving bodies did not feature at all a whatever part of energy which would not depend on the rate of their motion. (R. Tolman, 1974).

As a result, the energy irreversibility and dissipation phenomena – most fundamental for thermodynamics and natural science – have become non-interpretable in whole as resulting from the conversion of *external* energy into *internal.* The way out of the situation was seen for a long time as the idea offered by H. Helmholtz and consisted in the division of energy into a “free” part” $\Gamma = U - TS$ and a “bound” (to heat motion) part TS. As will be shown in Chapter 4, the decrease of the Helmholtz free energy F under certain conditions actually defines the capacity of systems for reversible work. However, with the arbitrariness classic thermodynamics tolerates in choosing the internal energy reference frame the bound energy value *TS* appears in many cases to be in excess of the internal energy itself (K. Putilov, 1974). Under these conditions this may not be considered as a part of internal energy. The same may be also said of the Gibbs' "free enthalpy" $G = H - TS$ (where $H = U + pV$ is enthalpy). Furthermore, in open systems these state functions do not define anymore the work a particular system does (G. Gladyshev, 1988; I. Bazarov, 1991). In this connection the division of energy into "free" and "bound" loses its heuristic value in many respects.

The situation was not saved with the notion of *exergy* subsequently introduced (Z. Rant, 1955) as the maximal work a system can do before complete thermodynamic equilibrium with the environment has been obtained. The remainder unworkable part of the system energy Rant termed as *anergy*. The exergy and the anergy of a system define its *technically usable* and *unusable* parts, respectively. However, their values depend on not only the parameters of a system itself, but on the parameters of the environment as well so that the exergy is not the function of state of a system itself. Furthermore, the exergy does not at all define the capacity of a system itself to do work since depends on the amount of heat supplied to the system from outside in the process of its work. And what is more, the exergy may even be a negative value (unlike the energy) if the intensive parameters of the system (e.g., its temperature) are below the same of the environment. We say nothing of the difficulties in calculating the exergy under inconstant environmental conditions, as well as of the arbitrariness in choosing its reference point under the conditions when environmental parameters substantially differ for different points of the planet. As a result, the division of energy into exergy and anergy has not either gained a wide spread.

A solution to the said problem becomes possible when changing over to studying non-equilibrium systems and introducing additional non-equilibrium state parameters of spatially heterogeneous media $\mathbf{X}_i$ and $\mathbf{Z}_i$.

Let us assume that we deal with a spatially homogeneous medium ($\mathbf{X}_i = 0$) where the generalized potential values Ψ_i are the same for all points, i.e. equal to their equilibrium values $\bar{\Psi}_i$. For such a system in the form of (2.2.9) instead of identity (2.2.6) the following equation is available:

$$d\bar{U} = \Sigma_i \, \Psi_i d\Theta_i, \tag{2.3.1}$$

where $\bar{U}$ – equilibrium part of the energy in non-equilibrium system.

The right-hand terms of this equation characterize the equilibrium heat exchange between the system and the environment. The term "equilibrium" means that at $\mathbf{X}_i \to 0$ processes are running infinitely slowly (quasi-statically) and, therefore, do not disturb the spatial homogeneity of the system ($\mathbf{Z}_i \rightarrow 0$). The work of these processes refers to the *unordered* category due to the absence of a resultant of the forces to be overcome in homogeneous systems. The work of such a kind involves introducing the k^{th} substance across the system borders (when not only the cubic strain occurs, but the interparticle interaction forces are also overcome), electrical charge introduced, uniform compression, mass transfer, momentum convective transfer along with the mass introduced, and heat exchange we attribute to the "micro-work" category on the grounds that heating of a body accelerates the chaotic motion of particles.

Applying the Legendre transformation to the above summands $\Psi_i d\Theta_i = d\Psi_i\Theta_i - \Theta_i d\Psi_i$ gives:

$$d(\bar{U} - \Sigma_i \Psi_i\Theta_i) = - \Sigma_i \Theta_i d\Psi_i = 0. \tag{2.3.2}$$

This expression refers to a system with no work done on, which could disturb it from equilibrium. Hence, according to the self-non-disturbance axiom both parts of (2.5.2) become zero. From this it follows that the equilibrium part of system energy $\bar{U}$ up to a constant (which could be assumed equal to zero) is defined as:

$$\bar{U} = \Sigma_i \bar{U}_i = \Sigma_i \Psi_i\Theta_i, \tag{2.3.3}$$

and

$$- \Sigma_i \Theta_i d\Psi_i = 0, \tag{2.3.4}$$

According to (2.3.3) the unordered energy of a system $\bar{U}$ is the sum of the system component energies $\Sigma_i\Psi_i\Theta_i$ (by the number of degrees of freedom), each being defined as the product of the momentum (interaction) of a particular kind Θ_i by the potential Ψ_i as a measure of its intensity. The value $\bar{U}_i$ characterizes the part of the non-equilibrium system energy left after the completion of all relaxation processes in the system (equalization of all potentials and completion of all chemical and the like internal transformations) and unable to do useful (ordered) work. Therefore we will call it after Z.Rant for brevity ***anergy*** (from Greek αν – "not" and εργον – "action")$^{1)}$.

$^{1)}$ Herein, to conveniently represent the inergy, we have changed over to its scalar form in order to avoid the (-) symbol otherwise needed because the vectors $\mathbf{X}_\text{i}$ and $\mathbf{Z}_\text{i}$, as well as $\mathbf{F}_\text{i}$ и $\mathbf{R}_\text{i}$ are counter-directed, while the value *E* is always non-negative.

The expression (2.3.4) generalizes a known Gibbs-Duhem's relationship (I. Bazarov, 1991) to the polyvariant equilibrium systems with any finite number of degrees of freedom.

Subtracting (2.3.1) from (2.2.6), we will find, that other part E of internal energy of the system, capable to make the ordered work, it is defined by expression:

$$dE \equiv \Sigma_i\, d(U_i - \bar{U}_i) = -\,\Sigma_i\, \mathbf{F}_i \cdot d\mathbf{r}_i, \qquad (2.3.5)$$

This part of internal energy $E = (U - \bar{U})$ we will name for brevity *ordered energy* or is even more short ***inergy***2). Owing to the equations of balance (2.3.2) decrease инергии defines the sum of all kinds useful W_i^e and dissipative W_i^{d} works of the given sort, made by system:

$$-\,dE = \Sigma_i\, \mathbf{F}_i \cdot d\mathbf{r}_i = \Sigma_i\, đW_i^{\mathrm{e}} + \Sigma_i\, đW_i^{\mathrm{d}}. \qquad (2.3.6)$$

It allows to define the ordered energy (*inergy*) as the maximum useful external work which the system to an establishment in it of internal balance can make at non-dissipative character of this process. It makes related concept of the ordered energy with *external energy* in the mechanic, and also with concepts of *free energy* and exergy in thermodynamics. However in view of noted above inapplicability of these concepts generally the objects including all set of co-operating bodies or parts of a body, division of energy on ordered and disorder is represented good alternative.

The ordered energy of non-equilibrium systems should also be complemented with chemical, atomic, nuclear, etc types of system energy. These types as well have the capacity for work and dissipation just as the energy of motion and interaction between macroscopic parts of the system. Chemically reacting media, spontaneously fissionable nuclear fuels, optically excited and ionized gases, etc are *non-equilibrium* even if spatially homogeneous. The non-equilibrium of such a kind existing in each of the system bulk elements and not associated with the spatial heterogeneity of the system as a whole will hereinafter be called *local*. Such environments as we will be convinced further, also are non-uniform. However the scale of this heterogeneity is that, that it does not give in to the account by means of such macroscopical parametres, as gradients or differences of potentials. Therefore such heterogeneity followed to name *local or microheterogeneity*.

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2) In contrast to the anergy, this term reflects the capacity of a system for *internal* work, i.e. for transmutations of energy (including the dissipation character). It is evident that a system not having this ability can not either participate in the energy exchange involved in these processes, i.e. can not do *useful internal work*.

To describe the state of locally non-equilibrium systems, it is also necessary to introduce special parameters of non-equilibrium. Here comes, in particular, the *completeness degree (intensity, range*, etc) of the r^{th} chemical reaction ξ_r. The similar coordinates may be introduced for phase transitions (V. Etkin, 1991). As will be clearly shown hereinafter, the scalar nature of such state coordinates will impose certain constraints on the possible conversion of such forms of energy into ordered work.

As seen, the energodynamic approach makes superfluous such notions as external and internal, free and bound energies, Gibbs' energy and exergy superseding them by the intuitively comprehensible terms of ordered and unordered energies. Another nontrivial consequence of such an approach consists in the conclusion there is an ordered and unordered component in any of the i^{th} forms of matter motion including the internal thermal energy U_{T} that in thermal physics has always been entirely attributed to the chaotic form of motion and, therefore, considered as an entirely depreciated (degraded) energy. Meanwhile, thermal energy has also an ordered part that depends on the temperature gradients or drops in a system. In itself the fact a thermally heterogeneous system is able to do useful work has been known yet since S. Carnot (1824) who expressed it as, "all over where a temperature difference is available, the "living force" (i.e. the thermal "motive force" *(author's note)*) may also appear". In thermal relaxation processes this ordered part of thermal energy dissipates (degrades) just as other ordered forms of energy. This phenomenon may be experimentally confirmed by, e.g., the so-called *measurable heat content rise effect* (L. Brovkin, 1960, 1964).

In series of his experiments Brovkin discovered a phenomenon unexplainable from the classic thermodynamic standpoint and consisting in increasing mean-integral temperature in the process of thermal relaxation of an isolated thermally heterogeneous system. The experiments were conducted as follows. A resistance temperature detector sensing element was inserted into the gap of a closely packed roll of paper, cardboard, rubber tape or other sheet materials all over their length. Then the roll was subjected to irregular heating from an external heat source followed by the spontaneous process of thermal relaxation. In that process the resistance variation for such a "distributed" thermometer was registered. Surprising was the fact that for all of the materials tested a considerable (up to 17%) rise of the mean-integral temperature was observed. That rise had continued for tens of minutes until the temperature fall due to cooling of the specimen not quite thermally protected became dominating. The experimental results were attempted to have been explained by the dependence of thermal capacity of the materials on the temperature gradients therein and were construed as a rise of "measurable" (i.e. different from actual) heat content (enthalpy) of the system. Meanwhile, the experimental results directly demonstrated the rise of unordered part of internal thermal energy (analog of the Helmholtz's "bound" energy) due to the decrease in its ordered part (analog of his "free" energy).

The fact the ordered E and unordered $\bar{U}$ energies belong to the non-equilibrium state functions with the exact differential properties incident to them in this connection makes it possible to generalize the classic method of characteristic functions to spatially heterogeneous (in their properties) systems with an arbitrary number of degrees of freedom. The characteristic functions are construed in thermodynamics as such state functions of a system, mathematical operations on which allow direct definition of fundamental properties of this system. In itself the term *characteristic function* was introduced by Massier (1869), who first realized those functions as convenient to be used in finding the system parameters as their derivatives. One of such characteristic functions is the system energy U itself, which complete variation in any processes is represented by (2.2.5). In accordance with (2.2.5) and (2.2.3) the reason why any of the i^{th} non-equilibrium processes arises – the generalized force $\mathbf{F}_i$ – may be found as the derivative of system energy with respect to the displacement vector $\mathbf{R}_i$ under the constancy of other similar vectors $\mathbf{R}_j$ and all "thermostatic" coordinates Θ_i.

In the similar way the derivatives of the system anergy $\bar{U}$ with respect to the "thermostatic" coordinates Θ_i under the constancy of other similar coordinates Θ_i and all displacement vectors $\mathbf{R}_i$ allow finding the generalized potentials for the non-equilibrium state of the system:

$$\Psi_i = (\partial\bar{U}/\partial\Theta_i). \tag{2.3.7}$$

Due to the breakdown of energy into the ordered and unordered components we receive in addition to it two more characteristic functions $E = \Sigma_i E_i$ and $\bar{U} = \Sigma_i \bar{U}_i$, where E_i, $\bar{U}_i$ – components of E and $\bar{U}$, which we will hereinafter call the *partial* energies (of the i^{th} kind). These functions known allow to solve the same problems as the energy under less strict constraints. In particular, the forces $\mathbf{F}_i$ can be found as the derivatives of ordered energy

$$\mathbf{F}_i = -(\partial E/\partial\mathbf{r}_i) = -(\partial E_i/\partial\mathbf{r}_i), \tag{2.3.8}$$

omitting in the first case the constancy requirement for all thermostatic variables Θ_i and in the second case – the constancy requirement for all other displacement vectors $\mathbf{r}_j \neq \mathbf{r}_i$. Furthermore, U replaced by E_i allows finding the internal forces $\mathbf{F}_i$ acting within isolated systems (where $dU=0$). In mechanical systems, where the ordered energy E is identical to the potential energy of the system, the above expression goes over into the standard force expression in mechanics (L. Landau, E. Livshits, 1973).

The advantage of representing thermodynamic potentials in terms of ordered and unordered energy becomes apparent when allows finding the ordered W_i^{e} and unordered $W_i^{\text{н}}$ work for each of its i^{th} forms. In this respect they stand out from the Gibbs and Helmholtz free energies in classic thermodynamics, which decrease characterizes just their sum of W^{e} and $W^{\text{н}}$. It is significant that in this case the energy components introduced herein can be found for *any current state of the system* by known fields or distribution function for the energy carrier Θ_i and known equations of system state in the general form as $\psi_i = \psi_i\,(\theta_1, \theta_2, \ldots, \theta_n)$. In particular, the potentials Ψ_i can be found as mean-mass values of the local potential ψ_i .

Allocation of the ordered part of system energy yields researchers the major concept of system orderliness degree, a characterising parity of inergy and energy in it:

$$\text{æ}_{\text{c}} = E/U. \tag{2.3.9}$$

One of advantages of allocation in system of the ordered and disorder part of internal energy is possibility in intuitively clear image to reflect a unilateral orientation of natural processes (their irreversibility). In the isolated systems external work is not made ($\text{đ}W_i^{\text{e}} = \Sigma_i\, \mathbf{F}_i{\cdot}d_e\mathbf{r}_i = 0$), and according to (2.3.2) $d_s\mathbf{r}_i = d\mathbf{r}_i,$ i.e. all work against forces $\mathbf{F}_i$ is internal. As dissipation forces there are always in any real system, dissipative work $\text{đ}W_i^{\text{д}} = \Sigma_i\, \mathbf{F}_i{\cdot}d_s\mathbf{r}_i > 0$. According to a parity (2.3.3) it means, that inergy E in isolated systems decreases and becomes equal to zero in equilibrium:

$$dE_{izol} = -\,\Sigma_i\, \text{đ}W_i^{\text{d}} \leq 0. \tag{2.310}$$

Under the maintenance this result is equivalent to known position of 2-nd beginning of classical thermodynamics for irreversible processes. This statement is reasonable to be called for easy reference as the **energy devaluation principle**: *the capability of any systems for work in spontaneous processes of ordered-to-unordered energy transition decreases.* However it becomes clear now, that some of works can be directed in isolated system against an establishment of internal balance (i.e. to be useful). Such processes play a main role in the theory of evolution of live and lifeless systems.

2.4. Rate and Productivity of Real Processes as Allowed for in Equations of Energodynamics

Due to the fact that energodynamics rejects in its grounds the process idealization expressed in such notions as "quasi-static" (infinitely slow), "equilibrium" and "reversible" a possibility appears to introduce time as a logically consistent physical parameter into its equations. For that it is enough to rewrite identity (2.2.5) in the form containing total derivatives of the state parameters earlier introduced with respect to time t:

$$dU/dt \equiv \Sigma_i \Psi_i \, d\Theta_i/dt - \Sigma_i \mathbf{F}_i \cdot \mathbf{v}_i - \Sigma_i \mathbf{M}_i \cdot \boldsymbol{\omega}_i \,. \qquad (2.4.1)$$

Here $\mathbf{v}_i \equiv \mathbf{e}_i dr_i/dt$ – translation velocity of the energy carrier Θ_i; $\boldsymbol{\omega}_i \equiv d\boldsymbol{\varphi}_i/dt$ – angular velocity of its reorientation (or rotation). In the particular case, when the parameter Θ_i means mass of a system, the values $\mathbf{v}$ and $\boldsymbol{\omega}$ characterize its linear and angular velocity as a whole. For the future it is quite important to obtain the local statement of this identity true for any element of the continuum. For this purpose let us apply equation (2.2.5) first to the system where redistribution processes are absent. Then the second and the third sums in (2.2.5) disappear, and the identity becomes:

$$dU/dt \equiv \Sigma_i \Psi_i \, d\Theta_i /dt. \qquad (2.4.2)$$

In the systems this equation represents the variation of the Θ_i[1)] parameters is caused by exclusively the transfer of some amount of energy carrier across the system borders. This allows representing the behavior of these parameters in the time domain by a known expression:

$$d\Theta_i/dt = -\int \mathbf{j}_i^{\mathrm{e}} \cdot d\mathbf{f} \,, \qquad (2.4.3)$$

where $\mathbf{j}_i^{\mathrm{e}} = \rho_i \mathbf{v}_i$ – local density of flow of the energy carrier Θ_i through a vector element $d\mathbf{f}$ of the closed surface f in the direction of external normal $\mathbf{n}$; $\mathbf{v}_i$ – velocity of energy carrier transfer through the system surface element $d\mathbf{f}$ in stationary reference frame (Fig. 2.1).

Substituting (2.4.3) into (2.4.2) gives:

[1)] From the physical standpoint the value Θ_i that is actually the extensive measure of particular kind interaction (Energy) carrier is advisable to be called for short the *Energy carrier*. This will facilitate the understanding of many processes under investigation.

$$dU/dt = -\Sigma_i \Psi_i \int \mathbf{j}_i^{\mathrm{e}} \cdot d\mathbf{f}. \qquad (2.4.4)$$

This equation is evidently a particular case of the more general expression

$$dU/dt = -\Sigma_i \int \psi_i \mathbf{j}_i^{\mathrm{e}} \cdot d\mathbf{f}, \qquad (2.4.5)$$

when the local value ψ_i of generalized potential Ψ_i is the same for all system points and may therefore be factored outside the integral sign. The product $\psi_i \mathbf{j}_i$ is the i^{th} component of the energy flow density $\mathbf{j}_{\mathrm{e}} = \Sigma_i\ \psi_i \mathbf{j}_i$ through an element $d\mathbf{f}$ of the system surface f. Therefore changing in (2.4.4) to the integral taken over system volume as based on the Gauss-Ostrogradsky’s theorem we come to the expression for the law of energy conservation for an arbitrary continuum area, which was proposed by N. Umov in 1873:

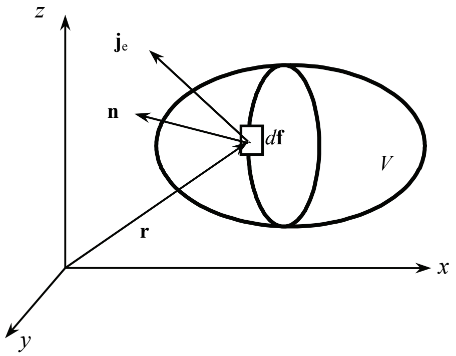

Fig. 2.1. Energy Flow across System Borders

$$dU/dt = -\int \nabla \cdot \mathbf{j}_{\mathrm{e}} dV. \qquad (2.4.6)$$

According to this expression the system energy variation equals the amount of energy having passed across the system borders for that particular time. Or according to Umov himself, “energy flow…is caused by energy admission or release a medium provides across its borders”. It should be noted that the validity of this statement is by no means restricted to the mechanical energy N. Umov meant.

This equation may be developed by representing the energy flow divergence $\nabla \cdot \mathbf{j}_{\mathrm{e}} = \Sigma_i \nabla \cdot (\psi_i \mathbf{j}_i^{\mathrm{e}})$ as a sum of two summands $\Sigma_i\ \psi_i\ \nabla \cdot \mathbf{j}_i^{\mathrm{e}} + \Sigma_i \mathbf{j}_i^{\mathrm{e}} \cdot \nabla \psi_i$:

$$dU/dt = -\Sigma_i \int \psi_i\ \nabla \cdot \mathbf{j}_i^{e}\, dV + \Sigma_i \int \mathbf{x}_i \cdot \mathbf{j}_i^{e}\, dV, \qquad (2.4.7)$$

where

$$\mathbf{x}_i \equiv -\nabla \psi_i \qquad (2.4.8)$$

is a local motive force of the i^{th} process expressed as negative gradient of generalized potential and named in the theory of irreversible processes as the "thermodynamic force in its energetic representation" (I. Gyarmati, 1974).

Equation (2.4.7) enables clarifying the meaning of the "global" variables Ψ_i and $\mathbf{X}_i$ introduced earlier for a system in whole. Taking into account that volume or mass elements in continuums do not change their spatial orientation ($d\boldsymbol{\varphi}_i = 0$) identity (2.2.6) may be expressed in the form:

$$dU/dt \equiv \Sigma_i \Psi_i\, d\Theta_i/dt - \Sigma_i\, \mathbf{X}_i \cdot \mathbf{J}_i\,, \tag{2.4.9}$$

where

$$\mathbf{J}_i \equiv (\partial \mathbf{Z}_i/\partial t)_\varphi = \Theta_i \mathbf{e}_i dr_i/dt = \Theta_i \mathbf{v}_i\,, \tag{2.4.10}$$

i.e. are total flows of displacement (transfer) of the i^{th} energy carrier Θ_i.

These flows at $d\boldsymbol{\varphi}_i = 0$ may be expressed in terms of their densities $\mathbf{j}_i \equiv \rho_i d\mathbf{r}_i/dt$ through the evident relationship:

$$\mathbf{J}_i \equiv \Theta_i d\mathbf{r}_i/dt = \int (d\mathbf{r}_i/dt) d\Theta_i = \int \mathbf{j}_i\, dV\,. \tag{2.4.11}$$

It is easy to see that the flows $\mathbf{J}_i$ differ in their dimensions from the more usual notion of flow rate and in their meaning as per (2.3.10) are closer to the "generalized momentum" $\mathbf{P}_i = \Theta_i \mathbf{v}_i$ of the i^{th} energy carrier Θ_i for a system in whole. Such flows play an important role in many phenomena. These are, e.g., the vector flows of electric displacement in a system with the volume V defined by the product of the system free charge Θ_e and the velocity of its center displacement in the free charge redistribution processes. This is the value, to which the following parameters are proportional: magnetic field induction vector (Biot-Savart's law), Thomson–Joule heats in conductors and thermo-elements, electromagnetic force driving a conductor with current (Ampere's law), etc. We will hereinafter be referring to them time and again when dealing with the transfer and conversion of energy in any forms, which will confirm the necessity and usefulness of generalizing the Maxwell's displacement current concept to phenomena of other nature.

To find the relation between the "global" (pertaining to a system in whole) and the local thermodynamic forces $\mathbf{x}_i$, let us take into account that the parameters Ψ_i in identity (2.3.5) are defined for the coordinates $\mathbf{Z}_i$ being constant, i.e. for the difference $\rho_i(\mathbf{r},t) - \overline{\rho}_i(t)$ invariable in all points of the system volume V. From this it follows that in the expression

$$d\Theta_i/dt = \int (d\theta_i/dt)\, \rho dV\,, \tag{2.4.12}$$

the specific parameters θ_i vary uniformly in all parts of the system, so that $d\theta_i/dt$ may be factored outside the integral sign. Hence,

$$\Psi_i = M^{-1}\int \psi_i dM\,, \tag{2.4.13}$$

being the system mass-averaged value of the local potential ψ_i. Similarly proceeding from the invariance of the process power $N_i = \mathbf{X}_i{\cdot}\mathbf{J}_i$ when representing it in terms of the local and global parameters

$$\mathbf{X}_i = \mathbf{J}_i^{-1}\int \mathbf{x}_i{\cdot}\mathbf{j}_i\, dV, \tag{2.4.14}$$

gives that the "global" thermodynamic force $\mathbf{X}_i$ is some averaged value of the local thermodynamic force $\mathbf{x}_i \equiv -\nabla\psi_i$.

The relationship thus obtained between the local variables the field theories operate with and the thermodynamic parameters characterizing the state of a continuum in whole opens the possibility of describing their properties from the positions of energodynamics. In this case particular importance is attached to introducing in thermodynamic equations the most significant for natural science in whole concepts of flows $\mathbf{J}_i$,$\mathbf{j}_i$ as generalized rates of the transfer processes and the concept of power (capacity) of the energy conversion process in a whole system $N_i = \mathbf{X}_i{\cdot}\mathbf{J}_i$ and in its unit volume $\mathbf{x}_i{\cdot}\mathbf{j}_i$. It should be noted that the notion of capacity refers to only the useful energy conversion processes and, therefore, could not appear in the depths of the theory of irreversible processes restricted to consideration of exclusively dissipative phenomena. On the contrary, all basic relationships of this theory will hereinafter be obtained as a consequence from energodynamics (Chapter 4).

2.5. Irreversibility in Energy Balance Equations

In non-equilibrium systems the majority of the state parameters Θ_i and $\mathbf{R}_j$ vary due to not only energy interchange between the systems and the environment, but also in relaxation processes running in them, i.e. spontaneously. In particular, the system volume may increase with no work done, but due to expansion into void, the mass M_k of the k^{th} substances – due to chemical reactions running in the system, the entropy S – due to conversion of ordered forms of energy into chaotic (thermal) form, the displacement vectors $\mathbf{R}_i$ – due to equalization of distributing the above parameters over the system. This fact is usually taken into account by the so-called balance equations, which integral form looks like:

$$d\Theta_i = d_e\Theta_i + d_s\Theta_i\,, \tag{2.5.1}$$

$$d\mathbf{r}_i = d_\mathrm{e}\mathbf{r}_i + d_s\mathbf{r}_i\,. \tag{2.5.2}$$

Here $\mathrm{d}_e\Theta_i$ – two-sided variations of the Θ_i coordinates caused by external energy exchange (heat transfer, expansion work, mass transfer, etc.); $\mathrm{d}_e\mathbf{r}_j$ – similar variations of the $\mathbf{r}_j$ coordinates caused by useful work of the i^{th} kind; $d_s\Theta_i$, $d_s\mathbf{r}_j$ – one-sided spontaneous variations of the same parameters caused by running internal (relaxation) processes and, depending on sign, named usually either "wells" or "sinks" of corresponding parameters.

Expression (2.4.2) may be more conveniently represented as the flow balance equation:

$$\mathbf{J}_i = -\,\mathbf{J}_i^e + \mathbf{J}_i^p\,, \tag{2.5.3}$$

where $\mathbf{J}_i^\mathrm{e} = -d_e\mathbf{r}_i/dt$; $\mathbf{J}_i^p = d_s\mathbf{r}_i/dt$ – useful and relaxation components of the $\mathbf{J}_\mathrm{i}$ flow, respectively. Here the positive direction of the flow, just as the forces $\mathbf{F}_i$ and $\mathbf{X}_i$, is construed as the direction toward equilibrium, which corresponds to the rule of signs accepted in thermodynamics, viz. the external work $\mathbf{F}_i{\cdot}d_e\mathbf{R}_i$ is positive if done by a system.

To derive the differential form of balance equation (2.5.1), let us represent the equation in the form:

$$d\Theta_i/dt = -\int \nabla{\cdot}\mathbf{j}_i^e\,dV + \int \sigma_i\,dV, \tag{2.5.4}$$

where the augend corresponds to the term $d_e\Theta_i/dt$ and the addend – to $\mathrm{d}_s\Theta_i/dt$; σ_i – density of internal wells or sinks Θ_i.

To change over from the integral form of (2.5.4) to the differential one, let us represent the Θ_i as the integral $\int\rho_i dV$, where $\rho_i = (\partial\Theta_i/\partial V) = \rho_i(V,t)$ – density of the Θ_i value. We are going to consider a continuum, which mass elements $dM{=}\rho dV$ remain invariable during its deformation (such a description is named spatial or Lagrangian). Then $d\Theta_i/dt = \int(d\theta_i/dt)\rho dV$, and one can write instead of (2.5.3):

$$\rho d\theta_i/dt + \nabla{\cdot}\mathbf{j}_i^e = \sigma_i\,. \tag{2.5.5}$$

where $\mathbf{j}_i^e = \rho_i\mathbf{w}_i$ – density of the energy carrier flow across the borders of the system elements; $\mathbf{w}_i = \mathbf{v}_i - \mathbf{v}$ – velocity of the value Θ_i transfer relative to the moving border of a system element. Equation (2.4.5) is called the substantial equation describing balance of some field value Θ_i.

In the similar way one can change over to the differential form of balance equation (2.5.3) allowing for relationship (2.5.3):

$$\mathbf{j}_i = -\,\mathbf{j}_i^e + \mathbf{j}_i^p\ . \qquad (2.5.6)$$

Substituting balance equations (2.5.5) and (2.5.6) into (2.4.7) and considering that, as in (2.4.12), $d\theta_i/dt$ is constant all over the bulk of the system and factoring the mean-mass potential Ψ_i and the force $\mathbf{X}_i$ out of the integral sign gives according to (2.4.14):

$$dU/dt = \Sigma_i\!\int\!\psi_i\,(d\theta_i/dt)\rho dV - \Sigma_i\!\int\!\mathbf{x}_i\cdot\mathbf{j}_i dV - \Sigma_i\!\int\!\psi_i\sigma_i dV + \Sigma_i\!\int\!\mathbf{x}_i\cdot\mathbf{j}_i^p dV =$$

$$= \Sigma_i\Psi_i\,d_e\Theta_i/dt - \Sigma_i\mathbf{X}_i\cdot\mathbf{J}_i - \Sigma_i\!\int\!\psi_i\sigma_i dV + \Sigma_i\!\int\!\mathbf{x}_i\cdot\mathbf{j}_i^p dV. \qquad (2.5.7)$$

Comparing this expression with (2.4.9) gives that the last two of its terms containing wells and sinks of various coordinates mutually balance. From here the relation ensues between the wells and the sinks of various state coordinates:

$$\Sigma_i\,\psi_i\sigma_i = \Sigma_i\,\mathbf{x}_i\cdot\mathbf{j}_i^p\ , \qquad (2.5.8)$$

which will hereinafter (Chapter 5) directly lead to the dissipative function expression as fundamental for the theory of irreversible processes.

Due to the mutual balance between the wells and the sinks of various coordinates energodynamic identity (2.2.9) remains valid even when the variation of its terms is caused by internal (irreversible) processes. In other words, the thermodynamic identity *remains valid within the entire spectrum of real processes* – from “quasi-reversible” to critically irreversible.

2.6. Predicting General View for Equations of State and Transfer

The above-developed body of mathematics is in itself insufficient for the investigation of particular processes. For that uniqueness conditions are required enabling to complete the set of the energodynamic equations. Although energodynamics imports these uniqueness conditions from outside it, nevertheless, dictates certain requirements for the number, general form and character of such uniqueness conditions.

The equations of state describing systems under investigation are the fundamental component of the uniqueness conditions. They reflect the relationship between the variables entering into thermodynamic identity (2.2.5) or (2.2.6). The total number of such equations is defined by the number of the independent variables entering into this identity, i.e. by the number of the independent processes really running in a system being described. Particular form of these equations is found by experimental or theoretically experimental way based on the simulation procedures including those of statistically mechanical character.

To go on with, let us restrict the consideration to an ample spectrum of systems lacking the reorientation processes. Let us assume the experimental investigation of such a system has revealed n transfer or redistribution processes running in it ($i = 1, 2, \dots, n$). Then according to identity (2.2.5) or (2.2.9) the total number of variables characterizing the state of the system and its energy E is generally equal to $2n$. However, due to the constraints imposed some number of the processes of one of these categories may be absent. Let us assume the number of the transfer processes is n_i ($i = 1, 2, ..., n_i$), while the same of the redistribution processes – n_j ($j = 1, 2, ..., n_j$). Then the total number of the variables entering into identity (2.2.9) is equal $2(n_i + n_j)$. Since only $(n_i + n_j)$ of them are independent, there must exist for such a system n_i equations interconnecting the variables Ψ_i and Θ_i and having the general form as:

$$\Psi_i = \Psi_i(\Theta_i, \mathbf{r}_j)\,, \tag{2.6.1}$$

and n_j equations interconnecting the variables $\mathbf{X}_i$ and $\mathbf{Z}_i$ and having the general form as:

$$\mathbf{X}_i = \mathbf{X}_i(\Theta_i, \mathbf{r}_j)\,. \tag{2.6.2}$$

Relations (2.6.1) may be instantiated by Clapeyron-Mendeleev's law and Van der Waals' law for gases, while relations (2.6.2) – by Hooke's law for elastic bodies, Curie-Weiss' law for dielectrics, etc. The fact itself such equations exist enables definition of a number of relations between physicochemical properties of the systems under investigation. These are, e.g., the relations between thermal coefficients of expansion for gases or isothermal compression coefficients and coefficients of elasticity in thermodynamics of solid bodies (Bazarov I.P., 1991).

When studying non-static processes, together with the equations of state it is necessary to know those relating velocity of some process with its motive forces. These equations include the laws of transfer of heat, charge, the k^{th} substance, momentum, etc. (Fourier's, Ohm's, Fick's, Newton's laws, etc.). They relate the generalized velocity of vector processes of heat conduction, electric conduction, diffusion and viscous friction. Arrenius' law relating the velocity of some r^{th} homogeneous chemical reaction w_r with its affinity A_r is an example of the scalar process equation. Fundamental equations of energodynamics (2.2.5) and (2.2.6) without such empirical laws are equally as barren as the unified equation of the first and second laws of thermodynamics in the absence of the equations of state of the systems under investigation. The particular form of the transfer equations is derived *a posteriori* (from experience). However, energodynamics makes certain demands on the number and general form of such equations imposing some constraints on the character of the interrelation between the state parameters these equations contain. In fact, having equations of state (2.6.1) and (2.6.2) at our disposal, let us represent the displacement vectors $\mathbf{R}_j$ as a function of n_i coordinates Θ_i and n_j motive forces $\mathbf{F}_j$:

$$\mathbf{r}_i = \mathbf{r}_i\,(\Theta_i, \mathbf{F}_j) \quad (i = 1,2,..., n_i; j = 1,2,..., n_j). \tag{2.6.3}$$

Taking total derivative of both parts of this expression with respect to time and keeping in mind that in stationary processes (where Ψ_i, $\mathbf{F}_j$ =const) these derivatives refer to the value $\mathbf{r}_i$ only and characterize velocity of the i^{th} transfer process $\mathbf{v}_i = d\mathbf{r}_i/dt$, gives:

$$\mathbf{v}_i = \mathbf{v}_i\,(\Theta_i, \mathbf{F}_j) \quad (i = 1,2,..., n_i; j = 1,2,..., n_j). \tag{2.6.4}$$

Respectively, the displacement flow $\mathbf{J}_i \equiv \Theta_i d\mathbf{r}_i/dt$ may be defined as:

$$\mathbf{J}_i = \mathbf{J}_i\,(\Theta_i, \mathbf{F}_j)\,. \tag{2.6.5}$$

This relationship reflects the general form of the transfer laws ensuing from the equations of state of the system under investigation. The particular form of these equations is derived *a posteriori*. However, the fact itself of existing equations for the flows $\mathbf{J}_i$ as a function of the state parameters describing a non-equilibrium system is a good ground to attribute these flows to the state functions of such systems[1]. Note that this statement could by no means ensue from the existing theory of irreversible processes since this theory, according to the local equilibrium hypothesis, has never treated the thermodynamic forces as system state variables. Functional relationship (2.6.5) allows writing the exact differential of the flow J_i as:

$$dJ_i = \Sigma_i\,(\partial J_i/\partial\Theta_i)d\Theta_i + \Sigma_j(\partial J_i/\partial F_j)dF_j\ (j \neq i). \tag{2.6.6}$$

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[1] This statement is especially evident for isolated systems: all processes running therein are defined by exclusively the properties of a system as itself.

Now, to find the displacement flows, this expression should be integrated between the limits from the equilibrium state (where all $J_i = 0$) to the current state:

$$J_i = \Sigma_i \int(\partial J_i/\partial\Theta_i)d\Theta_i + \Sigma_j\int(\partial J_i/\partial F_j)dF_j \quad (j \neq i). \tag{2.6.7}$$

Note that the equilibrium state with $J_i = 0$ is attained for the so-called "memory-possessing media" (viscoelastic and viscoplastic materials, hysteresis phenomena, etc.) generally at some the so-called "threshold" force value $\mathbf{F}_{j0}$ other than zero. Therefore the integration with respect to $\mathbf{F}_j$ will be started from exactly this value $\mathbf{F}_{j0}$. Taking into account the fact that the value of any parameter does not depend on the integration path, let us, for convenience's sake, integrate (2.6.7) first with respect to Θ_i at $F_j - F_{j0} = 0$ and then with respect to $\mathbf{F}_j$ at Θ_i = const. In this case the integral of the first sum in this expression does not at all contribute to the flow $\mathbf{J}_i$ since at equilibrium state ($F_j - F_{j0} = 0$) none of the coordinate Θ_i variations can cause the flow $\mathbf{J}_i$. As for the terms of the second sum, they may be represented more compactly by designating

$$K_{ij} \equiv (\partial J_i/\partial F_j) \quad (j \neq i). \tag{2.6.8}$$

Then expression (2.6.7) becomes:

$$J_i = \Sigma_i \int K_{ij}\, dF_j\,. \tag{2.6.9}$$

Let us consider the most general case, when the phenomenological coefficients L_{ij} explicitly depend on the forces F_j and thermostatic variables Θ_j, i.e. $K_{ij} = K_{ij}(\Theta_j,F_j)$, and. the dependence of J_i on F_j is non-linear. Then this relation may be represented in the pseudo-linear (linearized) form. Factoring some values of the functions $\overline{K}_{ij} = \overline{K}_{ij}\,(\Theta_j,\mathbf{F}_j)$ averaged between the limits from F_{j0} to F_j outside the integral sign the above expression becomes:

$$J_i = \Sigma_i\, \overline{K}_{ij}\,(F_j - F_{j0}), \quad (i, j = 1, 2, ..., n_j)\,, \tag{2.6.10}$$

or in vectorial form

$$\mathbf{J}_i = \Sigma_i\, \overline{K}_{ij}\,(\mathbf{F}_j - \mathbf{F}_{j0}), \quad (i, j = 1, 2, ..., n_j)\,, \tag{2.6.11}$$

This expression is the most general form of the equations describing the transfer of heat, substance, charge, momentum, etc. In many of phenomena the threshold value $\mathbf{F}_{j0}$ of the force $\mathbf{F}_j$ may be neglected. Then the transfer laws in the form of 2.6.10 can be rewritten in a simpler form:

$$\mathbf{J}_i = \Sigma_i \bar{K}_{ij} \mathbf{F}_j \text{ или } \mathbf{F}_i = \Sigma_i \bar{R}_{ij} \mathbf{J}_j , \qquad (2.6.12)$$

where $\bar{R}_{ij}$ – the coefficient, inversely to $\bar{K}_{ij}$.

Thus energodynamics suggests for an investigator a self-consistent form of representing the results of experiments on finding the transfer equations. As for the proportionality factors $\bar{K}_{ij}$ themselves, their finding is the problem for physical kinetics that uses for this, along with experiment, also considerations of the molecular-kinetic and statistical-mechanical theories.

The differential relationships between the state parameters and their functions enable solution of also other problems. In particular, they allow calculating by experimental data the fundamental state functions of a system. Although these relationships can not describe the mechanism of processes under investigation, they impose the restricting conditions that should be met for each of models. This always clarifies the models because allows neglecting redundant or non-existent constraints. Therefore, the differential relationships are a very effective tooling of mathematical analysis conducted on an object of investigation.

Conclusions to Part 1

One of the most attractive features of the thermodynamic method has always consisted in its possibility to obtain on the basis of a small number of the primary principles (beginnings) having in relation to thermal processes character of axioms, a great number of consequences covering various phenomena.

The energodynamics goes further away, putting in the basis only such principles general physics values (determinancies of a state, distinguishability of processes, them contra direction and conservation of energy) which do not demand additional experimental check. On their basis it builds mathematical model of the real processes, allowing to describe processes of transfer and transformation of any forms of energy in their indissoluble communication with the thermal form of movement. Thus energy its simple and clear initial sense of ability of system to accomplish any (ordered and disorder) works comes back.

Passing to consideration of all set of co-operating material bodies or particles interesting the researcher as uniform non-equilibrium whole, energodynamics prevents loss of the integrated properties, caused by traditional crushing of systems on elementary areas and particles for the purpose of simplification of their research. Thanks to introduction of missing parametres of spatial heterogeneity of investigated systems it allows to develop a mathematical apparatus of theory, in an equal measure suitable to research of processes with any degree of dissipation. This device is not beyond programs of mathematics of technical colleges and is based basically on properties of full differential of some characteristic functions of a non-equilibrium state. All other data on properties of investigated objects energodynamics involves «from the party» as some kind of unambiguity conditions. It gives to consequences of the theory character of indisputable truths in all cases when unambiguity conditions are not required or are not beyond experiment.

The system approach to objects of research, the obvious account of their spatial heterogeneity, refusal of idealisation of processes and systems, an exception of postulates and hypotheses from the bases of the theory and a deductive method of reception of all its consequences gives to energodynamics not passing heuristic value. Therefore it is necessary to expect, that distribution of a thermodynamic method on other fundamental sciences, changing methodology of their research, opens new possibilities of knowledge of the Nature.