

Part 2

MAIN PRINCIPLES, LAWS AND EQUATIONS OF FUNDAMENTAL DISCIPLINES

This section mainly aims at providing a unified description of fundamentals of a number of engineering and natural sciences from positions of energodynamics as a generalized theory of forces. Such a presentation is of great scientific, pedagogical and practical importance. The challenge is to obtain by deduction basic principles of as many fundamental disciplines as possible so as to give on their basis a uniform description of mechanical, thermal, electrical, magnetic, chemical, biological and the like properties and forms of the material world's motion. The author has made an attempt to offer the shortest way toward substantiating the basic statements of these disciplines, but excluding, at the same time, various historical accretions and zigzags associated with the origination and development of either of them. His latent intention has always been to make the interdisciplinary relations more explicit, the conceptual system more common and the mathematical body of the theory more available. He assumes that the implementation of the energodynamic method for investigating processes of any nature will facilitate the further self-study of specific subjects and the critical approach to analysis of the problems arising in various spheres of science and engineering/technology.

Chapter 3.

CLASSICAL MECHANICS

Mechanics was the first of natural sciences that reached maturity and became a theoretical basis of the technical civilization. Its object of investigation, viz. motion of macroscopic bodies, has long since been most demonstrative for investigators. This put mechanics in a special position among other natural sciences with its notional and conceptual system having up to date served as a basis for the majority of the natural science disciplines.

These merits of mechanics at the same time engendered some mechanicalism, viz. the intention to “bring all natural phenomena to attractive and repulsive forces, which value depends on their distance” (H. Helmholtz, 1847). However, it appeared impossible to create an exclusively mechanical vision of the world. On this understanding it is worth considering mechanics as an “equal partner” among other scientific disciplines dealing with non-mechanical forms of motion. In this connection the main attention will be focused on obtaining by deductive way fundamental principles of mechanics as a particular case of the unified theory of real processes named herein, for short, energodynamics.

3.1. Correction of Some Mechanical Concepts

Presentation of mechanics usually starts off with kinematics that deals with motion of bodies in space and time irrespective of physical nature of this motion. The notions of trajectory, the coordinate of a point lying on it, velocity and acceleration of this point are herein accepted “a priori” – before the background of motion and formulate the laws of motion have been clarified. Only then dynamics starts – with introducing the notion of material point, its mass and momentum. At the first glance, such a structure of mechanics (from simple to the difficult) seems quite natural. However, as L. De Broglie (1965) rightly noted, such an approach is rested upon an assumption that the results of abstract kinematical consideration may be applied, without an additional analysis, to the real motion of more complicated physical objects.

The corrections made from energodynamics when considering mechanics as its deduction start off with the object of investigation. In kinematics an abstract point is such an object, which has neither mass, nor the most important property of any material object – the extension. As a result, the state of this object, its displacement, acceleration, etc. are characterized by various-order derivative of the only coordinate – radius-

vector \mathbf{r} of the point. In energodynamics the object of investigation is the entire set of the interacting material points comprising a system. To define the state of such an object from the positions of kinematics requires the definition of a great (in case of continuum – infinite) number of coordinates of state and their derivatives. Such a description, while being generally received, contradicts, however, the state determinacy principle. According to this principle the number of variables conditioning the state of a system equals to that of independent processes running in the system. In case of solid body such processes are the translation motion of center of mass and the rotation of a body about the instantaneous center of inertia, as well as its acceleration. Besides, the variables pretending to being the coordinate of state of a system must be extensive values just like the energy of the system they describe. For the *quiescent* state (rest) such a variable is the moment of system mass distribution $\mathbf{Z}_m = M\mathbf{R}$, which derivatives with respect to time t define the motion of the system. According to the process distinguishability principle this motion is characterised by a system impulse

$$\mathbf{P} \equiv d\mathbf{Z}_m/dt = M\mathbf{v}. \quad (3.1.1)$$

In turn speed \mathbf{v} of the systems as whole can be spread out on two components: forward speed \mathbf{v}_0 the centre of mass M and speed of system as whole rotation $\boldsymbol{\omega} \times \mathbf{r}_\omega$, where \mathbf{r}_ω - instant radius of rotation (L.Landau, E.Livshits. T.I. Mechanics, 1972). According to it and systems impulse \mathbf{P} it is possible to spread out on an impulse of forward movement of a body

$$\mathbf{P}_0 \equiv M\mathbf{v}_0 = M d\mathbf{r}_0/dt, \quad (3.1.2)$$

and on an impulse of rotary movement:

$$\mathbf{P}_\omega \equiv \boldsymbol{\omega} \times M \mathbf{r}_\omega, \quad (3.1.3)$$

where $d\mathbf{r}_0 = \mathbf{e} dr_0/dt$ - a displacement vector; \mathbf{e} - an unity vector in a direction of speed \mathbf{v}_0 ; $r = |\mathbf{r}|$.

Instead of last expression is usually used as coordinate of rotary movement the moment of an impulse of system $\mathbf{L} = I \boldsymbol{\omega}$, in which I - the moment of body inertia). The variables \mathbf{P}_0 and \mathbf{L} characterize now the *motion* state. They are associated with the two independent terms in fundamental equation of energodynamics (2.3.5) and the two independent components of kinetic energy of the system corresponding to, respectively, its translation – $E^k = M\mathbf{v}^2/2$ and rotation – $E^\omega = I\boldsymbol{\omega}^2/2$. The time variations $d\mathbf{P}_0/dt$ and $d\mathbf{P}_\omega/dt$ of the coordinates \mathbf{P}_0 and \mathbf{P}_ω characterize two other independent processes (translation and rotation accelerations, respectively), i.e. the variation of the motion state, viz. its acceleration.

Although such a description of a set of the material points comprising a moving continuum looks like, from positions of continuum mechanics, approximate (lacking information on motion of each of the volume elements), within the framework of energodynamics this sufficiently characterizes the energy state of the system in whole. Transition to more detailed description of a moving continuum (material or spatial) is beyond of energodynamics. As noted in Chapter 1, such over-determination is fraught with the loss of some properties of the system as a whole. The over-determination is demonstrably instantiated with the concept of an “oriented point” introduced by Elie Cartan in the early 20th century, where the oriented point is endued with capability to rotate while moving along some trajectory. As a result, the state of the point needs to be defined by as many as six independent coordinates (three translation and three rotation ones), whereas a moving material point with no extension possesses only the translation kinetic energy so that its rotation coordinates do not characterize any real process. Naturally, the Cartan-Einstein gravitation theory based on the above will endue the space with properties really absent. G. Shipov (1997) goes still further in this direction enduing a material point with three more rotation coordinates in the space/time domain. As a result, the space of variables becomes neither more, nor less than 10-dimensional (including the time coordinate), and the theory of physical vacuum based on this foundation leads to a series of paralogsms (from God as entity up to perpetual motion as a real possibility).

Together with the above, the “under-determination” of mechanical systems may be also instantiated. This happens, e.g., when a material body is described without due consideration given to its density distribution over the space it occupies. Then the bodies with the different orientation of mass distribution moment \mathbf{Z}_m become indistinguishable, which excludes from consideration a whole series of the real processes of *reorientation* possible in heterogeneous systems. They take into consideration that the bodies differently space-oriented are not equivalent mechanically (L.D. Landau, E.M. Livshits, 2004).

The adequacy principle modifies also such fundamental notions of mechanics as mass, velocity and acceleration. Let us consider first the notion of mass M as the measure of body inertial properties. Such an interpretation of M was chronologically substantiated by the Newton-adopted method of introducing the notion of force $\mathbf{F} = M\mathbf{a}$ as a value directly proportional to the body acceleration \mathbf{a} , where the mass value M figured as a proportionality factor. Hence it followed that with the same force \mathbf{F} acting on a body the greater the body mass M , the lower its acceleration should be. The mass M thereby stood immediately for a measure of the body inertiality. With the special relativity theory and general rela-

tivity theory appeared such an interpretation of mass has been common in the notions of “inertial”, “gravitational”, “electromagnetic” mass, “rest mass”, etc.

A different situation arises with energodynamics where the notion of mass should be introduced long before the acceleration process has been considered, i.e. regardless of inertia. The mass here stands for a measure of extensive properties of any energy carriers Θ_i and the system energy U as their function, i.e. a quantity measure of matter contained in the system. Then such an interpretation is further supported with introducing the state parameter varying in the processes of matter exchange with the environment, i.e. the mass exchange coordinate.

The final difference of mass from the measure of system inertial properties is set with the transfer laws (2.6.11) formulated. With a single force \mathbf{F}_i applied to a system these laws become:

$$\mathbf{F}_i = \Sigma_i \bar{R}_i \mathbf{J}_i , \quad (3.1.4)$$

where the \bar{R}_i factor characterizes the resistance of the system to its state variation, i.e. its “inertiality” relative to the i th forces \mathbf{F}_i . As applied to the acceleration process its generalized rate \mathbf{J}_i is expressed by the time derivative of the system momentum $d\mathbf{P}/dt = M\mathbf{a}$. Substituting this expression to equation (3.1.4) gives:

$$\mathbf{F}_i = \bar{R}_i d\mathbf{P}/dt \quad (i,j = 1), \quad (3.1.5)$$

The factor \bar{R}_i is seen to appear as a function of the acceleration process, which characterizes the measure of the system inertial properties and has nothing to do with the mass M of the system as the function of its state and the quantity measure of matter therein. This becomes especially evident when comparing (3.1.5) with the Ohm law in electrical engineering, where \mathbf{F}_i – electromotive force; \mathbf{J}_i – current strength, and the to-current resistance factor \bar{R}_i does not depend on conductor mass at all. By the way, in the Newton’s second law of motion, with the \bar{R}_i factor adopted as unity, it does not depend on mass either. This means that the notions of mass as the measure of inertia and the quantity measure of matter are obviously distinguishable and their identification is inadmissible. Based on this, we will call \bar{R}_i as the “*inertia factor*” or *inertiality* for short.

Let's pass now to concept of acceleration. In kinematics velocity is construed as the total derivative of radius-vector of the point \mathbf{r} (or its component) with respect to time t , i.e. $\mathbf{v} \equiv d\mathbf{r}/dt$, while acceleration is

construed as the derivative of velocity with respect to time, i.e. $\mathbf{a} \equiv d\mathbf{v}/dt$. This derivative comprises both the variation of the particle velocity $\mathbf{v} = \mathbf{v}(\mathbf{r}, t)$ without variation of its direction $\mathbf{a} \equiv \mathbf{e}(dv/dt)$ and the variation of the particle velocity direction vde/dt without variation of the velocity value. As a result, *any rotation of a point appears to be the motion with acceleration*, whereas these processes cause motion state variations distinctive in kind and, from positions of ergodynamics, must be considered as *independent*. This means that the process of translation acceleration of a material point or a body with the coordinate $\mathbf{a} \equiv \mathbf{e}(dv/dt)$ should be distinguished from the process of *reorientation* of the body or the particle trajectory expressed, in particular, in a rotation of the body or the particle. The velocity of this process is expressed as vde/dt , while the coordinate of the process according to (3.4.5) is construed as the angular velocity vector $\boldsymbol{\omega} = d\boldsymbol{\phi}/dt$. The fact should be taken here in consideration that a particle can not be accelerated unless its spatial position (i.e. the \mathbf{r} coordinate) is changed. Therefore, the acceleration may be expressed in the developed form

$$\mathbf{a} \equiv d\mathbf{v}/dt = \mathbf{e}(\partial v/\partial t)_r + \mathbf{e}(\partial v/\partial \mathbf{r})d\mathbf{r}/dt = v\nabla v. \quad (3.1.6)$$

since the notion of the acceleration local component $\mathbf{e}(\partial v/\partial t)_r$ for the particle (with its position unvaried) does not make physical sense. This detail is a matter of no small consequence stressing the point that the acceleration process is inseparably associated with the locally heterogeneous velocity profile featuring the gradient $\nabla v \equiv (\partial v/\partial \mathbf{r})$ and generated in space. The generation of any heterogeneity demands time and energy consumption. This is the time delay that makes physical sense of the inertia conception.

The similar comments may be made on also the rotation acceleration $d\boldsymbol{\omega}/dt$. From a standpoint of ergodynamics, a uniform rotation of bodies with their kinetic energy $E^\omega = I\boldsymbol{\omega}^2/2$ remaining unvaried can not be classified as accelerated. This statement is even more right, because, the energy being constant, the rotation acceleration process does not demand work consumption as for the translation acceleration. Being considered from these positions, the uniform electron-around-nuclear rotation is non-accelerated, while the notion “centripetal acceleration” intrinsically inadequate. The correction of all these concepts will further impact many of the applications of mechanics.

3.2. Law of Inertia (Newton's First Law of Motion) and Its Generalization to Rotational Motion

Newton's first law is a statement of the law of inertia discovered by Galileo and reading that *"a body at rest remains at rest, and a body in motion continues to move in a straight line with a constant speed unless and until an external unbalanced force acts upon it"*.

For the mathematical substantiation of this law let us apply the fundamental identity of energodynamics (2.2.5)

$$dU \equiv \sum_i \Psi_i d\Theta_i - \sum_i \mathbf{F}_i \cdot \mathbf{e}_i dr_i - \sum_i \mathbf{M}_i \cdot d\boldsymbol{\varphi}_i. \quad (3.2.1)$$

to an arbitrary closed mechanical system (with no external forces \mathbf{F}_i or their moments \mathbf{M}_i exerted on). Thereby the system energy remains unvaried ($dU = 0$) and expression (3.2.1) will become:

$$\sum_i \Psi_i d\Theta_i = 0. \quad (3.2.2)$$

For a mechanical system not involved in rotational motion the momentum \mathbf{P} of the system as a whole associated with the velocity $\Psi_i \equiv \mathbf{v}$ is the only parameter Θ_i characterizing the state of motion of the system. From here the law of conservation of momentum directly ensues:

$$\mathbf{P} = M\mathbf{v} = \text{const} . \quad (3.2.3)$$

It becomes clear at the same time that the Galileo's principle of relativity stating that uniform and rectilinear motion of a closed system does not impact the processes running in the system is just a particular case of the "equilibrium self-non-disturbance principle" (the general law of thermodynamics). In fact, from positions of thermodynamics (and energodynamics too) the state of a mechanical system moving in a straight line is characterized by the only coordinate, viz. the momentum of the system. Therefore the only process is possible in it, viz. the acceleration of the system as a whole. The uniform motion means in this case the absence of such a process, i.e. partial equilibrium of the system. It is natural that only an external action can disturb such a state. However, the system being closed, neither of the processes is possible in it.

Let us consider now the additional consequences ensuing from treating mechanics as a particular case of energodynamics. This is first of all the law of conservation of momentum (Euler's law), which was absent in Newton's mechanics:

$$\mathbf{M} = I\boldsymbol{\omega} = \text{const}. \quad (3.2.4)$$

Both of these laws – (3.2.3) and (3.2.4) – may be unified in one statement reading that “any material body remains at rest or in motion unless and until some forces applied make it change this state”. It is easy to see that this statement generalizes Newton’s first law extending it to rotating systems and demanding the legitimation of the notion “coasting rotation”. It is significant that with such an approach the Galileo’s law of inertia appears to be valid irrespective of whatever theory of physical vacuum or assumption on homogeneity and isotropy of space and time (L. Landau, E. Livshits, 1973).

Thus Newton’s (3.2.3) and Euler’s (3.2.4) laws pertaining to, respectively, translation and rotation of bodies ensue from energodynamics as particular cases. One can not now assert that “free” motion of a closed system, i.e. “coasting”, is always rectilinear – it may also be rotational. It becomes clear at the same time that the Galileo’s principle of relativity stating that uniform and rectilinear motion of a closed system does not impact the processes running in the system is just a particular case of the “equilibrium self-non-disturbance principle” (the general law of thermodynamics). In fact, from positions of thermodynamics (and energodynamics too) the state of a mechanical system moving in a straight line is characterized by the only coordinate, viz. the momentum of the system. Therefore the only process is possible in it, viz. the acceleration of the system as a whole. The uniform motion means in this case the absence of such a process, i.e. equilibrium of the system. It is natural that only an external action can disturb such a state. However, the system being closed, neither of the processes is possible in it. This may be referred with the same degree of generality to also uniformly rotating bodies being in internal equilibrium.

Let us consider therefore a more general case of a mechanical system not being in internal equilibrium. In such a system, due to interaction (relative motion) of its macroscopic parts (subsystems), spontaneous redistribution processes ($d\mathbf{r}_i/dt \neq 0$) arise causing the variation of its ordered energy ($dE/dt \neq 0$). It becomes especially evident if to imagine the translation kinetic energy of such subsystems E^k as a sum of the kinetic energy of entire-system-center-of-mass motion $\frac{1}{2}\sum_k M_k \mathbf{v}^2$ and the kinetic energy of system-parts-relative motion $\frac{1}{2}\sum_k M_k \mathbf{w}_k^2$ (where \mathbf{v} , $\mathbf{w}_k = \mathbf{v}_k - \mathbf{v}$ – velocity of the center of mass of the system and relative displacement velocity of its parts in the center-of-mass system). This kinetic energy of the system-parts-relative displacement can both decrease (due to the viscous force action) and increase (due to the work done by forces of other nature when converting energy in a system with other degrees of freedom). The work of such kind is done, e.g., in oscillatory motions when converting kinetic energy into potential one and vice versa. Let us name this work as

useful internal, since the forces to be overcome in this process are internal with respect to the system as a whole. However, the internal work may also be dissipative if the oscillatory process is accompanied by damping of the relative motion among various parts (components) of the system.

The rotation kinetic energy of system parts $E^{\omega} = \frac{1}{2}\sum_k I_k \boldsymbol{\omega}_k^2$ behaves the same. It may also be represented as a sum of the kinetic energy of entire-system-rotation $\frac{1}{2}\sum_k I_k \boldsymbol{\omega}^2$ and the kinetic energy of system-parts-relative rotation $\frac{1}{2}\sum_k I_k (\boldsymbol{\omega}_k - \boldsymbol{\omega})^2$. The latter can also both decrease due to the rotational viscous force action and increase due to the other-nature-force action. Therefore when constructing a math model of such systems it is necessary to allow for the variation of not only the momentums $\mathbf{P}_k = M_k \mathbf{v}_k$ of the k^{th} components (parts) of the system, but also of their angular momentums $\mathbf{L}_k = I_k \boldsymbol{\omega}_k$ (where I_k – moments of their inertia). In this case expression (2.4.5) becomes for them:

$$\sum_k \mathbf{P}_k \cdot d\mathbf{v}_k/dt + \sum_k \mathbf{M}_k \cdot d\boldsymbol{\omega}_k/dt = \sum_k \mathbf{F}_k \cdot \mathbf{v}_k + \sum_k \mathbf{M}_k \cdot \boldsymbol{\omega}_k. \quad (3.2.5)$$

It follows that in case an isolated system contains the internal k^{th} forces $\mathbf{F}_k = -(\partial U/\partial \mathbf{P}_k) \neq 0$ and their moments $\mathbf{M}_k = -(\partial U/\partial \mathbf{L}_k) \neq 0$, it is only the sum of the translation and rotation kinetic energies of the k^{th} subsystem that remains unvaried even when the laws of conservation of momentum and angular momentum

$$\mathbf{F}_k = d\mathbf{P}_k/dt; \quad \mathbf{M}_k = d\mathbf{L}_k/dt \quad (3.2.6)$$

are valid separately for each of the k^{th} part of the system under consideration, i.e. the cross-impact of forces and moments is absent among various subsystems. However, since it is not so in general, the momentum of the system as a whole $\mathbf{P} = \sum_k M_k \mathbf{v}_k$ and its angular momentum $\mathbf{L} = \sum_k I_k \boldsymbol{\omega}_k$ are not bound to remain constant with variation of the system-parts-momentums $\mathbf{P}_k = M_k \mathbf{v}_k$ and their angular momentums $\mathbf{L}_k = I_k \boldsymbol{\omega}_k$. In fact, when the right side of equation (3.2.1) is equal to zero, only the sum of the translation and rotation energies is retained, but not each of them separately. Hence it is quite legitimate to assume the variation of not only the internal state of the system motion, but also its external state due to reciprocal conversion of the translation and rotation energies. This does not violate energy conservation since the energy of the system as a whole does not vary in this case.

Thus a fundamental deduction follows from energodynamics: what is valid for any homogeneous system (lacking redistribution processes) is not always valid for heterogeneous system. This statement is supported by results of the experiments conducted by N.V. Filatov (1969) followed by A.P. Gladchenko (1983) with inertoids. N.V. Filatov investigated col-

lision of two massive bodies installed on carts. One of the bodies comprised gyros fixed on the gimbal suspensions and having rotated in the opposite directions with the same angular velocity for mutual compensation of their moments. During the experiments the gyros collided with a usual mass installed on another cart. That process was recorded on a film with a speed of 2000 frames per second followed by a treatment to define center-of-mass velocity of the system pro- and post-collision. As a result of a great number of experiments, it was discovered that in case the gyros precession started post-collision, the center of mass of the system varied its velocity. Thus the possibility of reciprocal conversion of the translation energy into the kinetic energy of gyros precession was revealed.

The similar experiments were conducted by A.P. Gladchenko in 1983 with the B.N. Tolchin's inertioids – a gyro additionally equipped with a motor-brake to govern its center-of-mass velocity. Displacement of the cart with the gyro and the motor-brake was recorded on a film. Those experiments also revealed the possibility of displacing bodies due to partial conversion of the kinetic energy of system-parts-relative rotation into the system center-of-mass translation energy.

To more clearly explain the displacement of inertioid center of gravity against variation of kinetic energy pertaining to relative rotation of its parts, let us denote the inertia moments of two opposite-rotating parts and their angular velocities as I_1 , I_2 and $\boldsymbol{\omega}_1$, $\boldsymbol{\omega}_2$, respectively, while the radius vectors of their centers as \mathbf{R}_1 and \mathbf{R}_2 , respectively. Then, according to the general definition (1.5.7), the *rotational angular momentum distribution* in such a system is expressed as:

$$\mathbf{Z}_\omega = I_1 \boldsymbol{\omega}_1 \mathbf{R}_1 + I_2 \boldsymbol{\omega}_2 \mathbf{R}_2. \quad (3.2.7)$$

Since $\boldsymbol{\omega}_2 = -\boldsymbol{\omega}_1$ and $I_1 = I_2$, the above expression becomes:

$$\mathbf{Z}_\omega = I_2 \boldsymbol{\omega}_2 \Delta \mathbf{R}_\omega, \quad (3.2.8)$$

where $\Delta \mathbf{R}_\omega = \mathbf{R}_2 - \mathbf{R}_1$ – displacement of inertia center for a system containing rotating weights due to the opposite directions of the angular velocities $\boldsymbol{\omega}_1$ и $\boldsymbol{\omega}_2$. Since the forces causing this displacement are internal, the variations of the *rotational angular momentum distribution* \mathbf{Z}_ω they cause should be referred to internal wells or sinks $d_s \mathbf{Z}_\omega$ of this value. According to the wells–sinks balance equation (2.4.2) the corresponding wells or sinks $d_s \mathbf{Z}_w = Mvd\mathbf{R}_w$ should appear as pertaining to the *translational angular momentum distribution* \mathbf{Z}_w (because the inertioid does not have other degrees of freedom). This means that in the system of inertioid–environment their relative movement should appear and continue till the energy E_ω^k of relative rotation for inertioid parts is completely

converted into the energy E_w^k of their translational motion. As an example of the rotational-to/from-translational angular momentum interconversion may serve the conversion of laminar (translational) motion of liquid particles into their turbulent (vortical) motion and vortical motion into laminar one with obstacles appearing and disappearing in the flow.

It is significant that to obtain such conclusions, we did not have to resort to whatever models of physical vacuum of ether. That is why energodynamics is a theoretical base to explain the UFO flights and to create “free-of-any-support” vehicles.

3.3. Law of Force (Newton’s Second Law of Motion)

Newton’s second law introduces the force concept and usually has the form:

$$\mathbf{F} = M\mathbf{a}, \quad (3.3.1)$$

where \mathbf{F} – resultant mass force.

It is worth noting, however, that Newton’s acceleration coordinate is not the velocity \mathbf{v} , but the momentum (quantity of force) in the form¹⁾:

$$\mathbf{F} = d\mathbf{P}/dt . \quad (3.3.2)$$

I. Newton stated that law as follows: “*The rate of change of momentum of a body is directly proportional to the impressed force and takes place in the direction in which the force acts*”.

Force enters in expressions (3.3.1) and (3.3.2) as a reason of the acceleration process generation. However physics and natural sciences have generally to deal with forces causing also other processes (displacement, expansion, electrization, chemical and nuclear conversions, heat and mass transfer, etc.). Therefore (3.3.1) and (3.3.2) need to be considered as a particular case of force rather than its definition. Energodynamics gives a more general force definition by expression (3.2.1), wherefrom, in the absence of the reorientation processes, it follows:

$$\mathbf{F}_i \equiv - (\partial E / \partial \mathbf{r}_i) . \quad (3.3.3)$$

This expression reflects the unity of various-nature forces in their definition as itself. In particular, if \mathbf{r}_i is a vector characterising heteroge-

¹⁾ This form better complies with the requirement of energodynamics for the extensive character of generalized coordinates and will further take on fundamental significance in the context of the relativistic mass conversion

neity of mass distribution in space, force \mathbf{F}_i defines a gravitation field. If vector \mathbf{r}_i characterize displacement of free charges, force \mathbf{F}_i defines an electrostatic field, etc. Hence, *the force fields are generated not by masses, charges or currents, but rather by their heterogeneous distribution in space.* This statement is reasonable to be called for easy reference as **field-forming principle**.

It is easy to show that the expression for the acceleration force \mathbf{F} ensues from the above one as a particular case. Taking into consideration that this force causes deviation from equilibrium (so that its sign is opposite to that of the force \mathbf{F}_i) and based on (3.3.3) one can get:

$$\mathbf{F} \equiv (\partial E / \partial \mathbf{r}_m) = \partial(Mv^2/2) / \partial \mathbf{r}_m = Mv \nabla v = M\mathbf{a}, \quad (3.3.4)$$

where v , \mathbf{r}_m – magnitude of velocity and radius-vector of the center of mass of the system, respectively.

It is significant that the representation of acceleration in the form $\mathbf{a} = v \nabla v$ is exactly what allows representing the acceleration work dW_w^e in the same form (2.2.9) as for other kinds of work:

$$dW_w^e = \mathbf{F} \cdot d\mathbf{r} = Mv^2/2. \quad (3.3.5)$$

It is easy to show that definition (3.4.5) is applicable to also the centrifugal force concept:

$$\mathbf{F}_u \equiv (\partial E / \partial \mathbf{r}_u) = \partial(Mv^2/2) / \partial \mathbf{r}_u = M\omega^2 \mathbf{r}_u, \quad (3.3.6)$$

On this basis these are relationships (3.3.1) and (3.3.3) that ought to be considered the analytical expression of Newton's second law rather than the relation $\mathbf{F} = M\mathbf{a}$ referring only to acceleration process.

Let's discuss now specificity of "forces of inertia». Till now disputes have not ceased concerning the fact whether these forces are real or not, active or passive, external or internal, inherent in all processes or only acceleration, etc (G.I.Shipov, 1997).

The answer to this question is facilitated, if the entire set of interacting bodies is considered as a single whole. In that case all forces become internal. As shown above, such forces arise only in pairs and simultaneously. Therefore the question which of them is primary, disappears by itself. Both of them are real and a result of action of a force couple featuring another nature, which has caused process of energy conversion. In this sense both of them are reactions. At the same time they, like any forces, either cause or a stressed state of the system or generate a process. In the first case they become nonequilibrium state functions (like reaction of support), in the second case – process

functions. Forces of inertia relate to the latter. They exist only when a process is really running and disappear when the process has ceased. ($\mathbf{J}_i \neq 0$). It necessarily follows from Newton's law (3.1.1), according to which forces of inertia \mathbf{F} are absent in the absence of acceleration (at $\mathbf{a} = 0$). Such are Coriolis forces and the magnetic component of Lorentz's forces. Hence, force of inertia does not exist as a state function. Summarising the aforesaid, forces of inertia may be defined as a variety of reactions which are process functions. Therefore any statements about specific "fields" of these forces existing in nature (G.I.Shipov, 1997) are groundless.

This fact reveals a fallacy of the opinion that the concept of inertia cannot be generalized to nonmechanical processes. Such a narrowing of the concept of inertia contradicts the Le Chatelier–Braun principle according to which any external influence on a system causes changes in its state tending to weaken the result of this influence.

3.4. Extended Interpretation of Newton's Third Law of Motion (Principle of Action and Reaction)

I. Newton formulated his third law as the following statement: *“For every action force there is an equal, but opposite, reaction force”*.

This statement is most commonly written as:

$$\mathbf{F}^a = - \mathbf{F}^p, \quad (3.4.1)$$

where \mathbf{F}^a , \mathbf{F}^p – respectively, action forces and reaction forces. Thus it is meant, that active forces are enclosed to a body from the outside and have the same nature, as forces of reaction of a body.

However, I. Newton himself repeatedly emphasized, that besides the enclosed forces it is necessary to distinguish operating forces, and action of force should be estimated as product of enclosed force size \mathbf{F}_i for speed \mathbf{v} of the moving of object (A.P. Smirnov, 2002). In this connection Newton referred to Archimedes' law of leverage formulated as *“what we lose in velocity, we win in force”*. It is necessary therefore to clarify the statement of Newton's third law from the positions of energodynamics. For this purpose let us apply equation (2.3.5) to an arbitrary heterogeneous system doing mechanical work, the said Archimedes' lever being the simple example of it. The lever arms displace in the opposite directions with velocities \mathbf{v}_i and \mathbf{v}_j by the action of the forces \mathbf{F}_i и \mathbf{F}_j . Since all parameters Θ_i remain unvaried for such a system, equation (2.3.5) becomes:

$$\mathbf{F}_1 \cdot \mathbf{v}_1 + \mathbf{F}_2 \cdot \mathbf{v}_2 = 0. \quad (3.4.2)$$

This expression is nothing else but the law of conservation of energy (of power – to be more exact) in the context of mechanical phenomena. Just in a particular case, when $\mathbf{v}_1 = \mathbf{v}_2$ (e.g., when doing work is accompanied by displacement of the interface between two bodies, or the action is provided without whatever intermediate of the lever type), expression (3.4.2) goes over into (3.5.1). It is the relationship (3.4.2) that should be construed as a mathematical form of Newton’s third law rather than its particular case (3.4.1).

It also worth noting that the statement of Newton’s third law as per (3.4.2) does not demand the action force \mathbf{F}_i and the reaction force \mathbf{F}_j to be directed in the same straight line. This demand was quite evident for Newton’s mechanics that “unfiled” rotational motion of bodies. However, from the positions of energodynamics, allowing for torques caused just by offsetting the lines, in which counter-forces are acting, this demand is superfluous. Withdrawing this demand enables eliminating the contradiction with Newton’s third law in case of the interaction of, e.g., current-carrying conductors, when action and reaction forces appear to be directed not in the same line.

Further, as energodynamics operates not only external, but also internal forces, it is extremely important to show, that such forces arise and disappear only in steams. Internal forces any i^{th} nature have, as is known, no resultant \mathbf{F}_j . If \mathbf{f}_j (H/M²) - the specific force enclosed to unit of a surface f (M²) of any closed system in a direction of a normal \mathbf{n} for it, this resultant $\mathbf{F}_j = \int \mathbf{f}_j \cdot \mathbf{n} df$ is always equal to zero. Applying to this expression Gauss theorem, we have:

$$\mathbf{F}_j = \int \mathbf{f}_j \cdot \mathbf{n} df = \int \text{div} \mathbf{f}_j dV = 0. \quad (3.4.3)$$

It means, that if in any element dV volume of such system $\text{div} \mathbf{f}_j \neq 0$ (i.e. in it there is some volume force ($\partial \mathbf{F}_j / \partial V$) in other element of volume it should have an opposite sign (opposite direction). In other words, any internal force has counteracting, as followed prove. This statement is reasonable to be called for easy reference as the “**force couple principle**”: *internal forces in heterogeneous systems appear and disappear pairwise only*. Such forces often not without justification are called *as internal strain*. They also generate in spatially non-uniform systems internal processes of the energy transformation, studying being a subject of energodynamics. In the systems possessing several degrees of freedom, these strains have the different nature. It also causes the energy transformation which character depends by nature overcome

forces. In particular, if internal force has disorder character, there is a process of "energy dispersion», i.e. transformation of a part of the ordered internal energy into chaotic (thermal). The such phenomena will be considered later in the section devoted to thermodynamics of irreversible processes.

3.5. Theoretical Derivation of Law of Universal Gravitation

Based on Kepler's laws, I. Newton, from data available at that time on the masses of celestial bodies and the distances between them, calculated that the force of attraction of two point masses m and M was directly proportional to their product and inversely proportional to the squared distance r between them. Later Cavendish experimentally proved that the inverse-square law was valid for also terrestrial bodies while having calculated the mass of the Earth and the gravitational constant G_g . So the law of gravitation has come into being:

$$\mathbf{F}_g = G_g m M / r^2, \quad (3.5.1)$$

which impact on the science history can not be overestimated.

It is a matter of interest to derive this law from the first principles of ergodynamics. One of such principal statements is a declaration that the force fields are generated by neither masses nor charges¹⁾, but their non-uniform distribution in space. The gravitational field is known to be absent in the center of a massive homogeneous sphere. Thus the gravitational forces appear only where the attraction of the "test" body is unequal on different sides, i.e. the masses are distributed non-uniformly. In this case the heterogeneity is characterized by the distribution moment $\mathbf{Z}_m = M\mathbf{r}_m$, which is the product of the body mass M and the displacement of the radius-vector \mathbf{r}_m of the body center from its position at the homogeneous distribution. From the distribution moment definition (1.5.4) it follows that $d\mathbf{Z}_m = M d\mathbf{r}_m$, then the mass of any set of material points or bodies heterogeneously distributed is defined by the expression:

$$M = \partial \mathbf{Z}_m / \partial \mathbf{r}_m = \int \nabla \cdot \mathbf{Z}_{mV} dV, \quad (3.5.2)$$

where $\mathbf{Z}_{mV} = \rho \Delta \mathbf{r}_m = \partial \mathbf{Z}_m / \partial V$ – distribution moment density.

Changing over from the integral over volume into that over the closed surface f as based on the Gauss theorem the expression (3.6.2) becomes:

$$M = \int \mathbf{Z}_{mV} \cdot \mathbf{n} df. \quad (3.5.3)$$

This expression is valid for a body of any shape. Therefore let us take, for convenience, a spherical surface $f = 4\pi r_c^2$ (where r_c – radius of a sphere, filled with a mass M). Then instead of (3.5.3):

$$M = 4\pi \int \mathbf{Z}_{mV} \cdot \mathbf{n} dr_c^2. \quad (3.5.4)$$

The heterogeneity of mass distribution per unit volume of the system described by the vector \mathbf{Z}_{mV} generates the thermodynamic force \mathbf{x}_g , which in our case according to (2.3.8) is expressed by the negative gradient $-\nabla\psi_g$ of the gravitational potential ψ_g . This force is connected with the \mathbf{Z}_{mV} parameter through the general equation of state $\mathbf{Z}_{mV} = \mathbf{Z}_{mV}(\mathbf{x}_g)$. Assuming this relation proportional on the ground that both values (\mathbf{Z}_{mV} and \mathbf{x}_g) disappear simultaneously and denoting the proportionality factor as ε_g gives instead of (3.5.4):

$$M = 8\pi\varepsilon_g \int r_c \mathbf{x}_g \cdot \mathbf{n} dr_c. \quad (3.5.5)$$

The $\mathbf{x}_g \cdot \mathbf{n}$ product characterizes the absolute magnitude $x_g = |\mathbf{x}_g|$ of the specific force \mathbf{x}_g acting along the normal to the spherical surface. The field of this force is known to be heterogeneous. If the mass distribution in the volume V is homogeneous, the force \mathbf{x}_g inside the body is equal to zero and discontinues on the body surface. However, the Gauss formula is known to remain valid also in this case – it is just enough to change from $-\nabla\psi_g$ to the so-called surface divergence $\mathbf{x}_{g+}(r_c) - \mathbf{x}_{g-}(r_c)$, i.e. to the difference of forces on both sides of the sphere surface. In the case of the homogeneous mass distribution $\mathbf{x}_{g-}(r_c) = 0$, and instead of (3.5.5):

$$x_g = G_g M / r_c^2, \quad (3.5.6)$$

where $G_g = 1/4\pi\varepsilon_g$ – proportionality factor empirically defined and usually called the gravitational constant.

Since in the stationary field $\nabla\psi_g = d\psi_g/d\mathbf{r}$, it is easy to find the gravitational potential $\psi_g = -\int x_g dr$ in any point $r \geq r_c$. Integrating (3.5.6) within r_c to r gives:

$$\psi_g = G_g M (1/r_c - 1/r). \quad (r \geq r_c). \quad (3.5.7)$$

The gravitational potential ψ_g is known to be the force of gravity per unit mass m of a test body. Therefore the force $\mathbf{F}_g = m\psi_g$ found from this expression exactly complies with the gravity law (3.5.1). However, now this law of force was found theoretically from the condition of heterogeneous mass distribution. According to (3.5.7) the potential energy of

gravitating masses becomes zero not at their being infinitely apart from each other (as follows from (3.5.1)), but, on the contrary, when they occupy the same space (like components of a mixture), which complies with empirical facts. As a particular case, the fact follows from (3.5.7) that at homogeneous mass distribution (also inside a body with homogeneous density) the gravity force is equal to zero (constant potential ψ_g). Hence Newton's law of gravitation (3.5.1) does not work, i.e. the range of its validity is restricted to a provisional (equivalent) radius of the sphere confining the "field-forming" body M (area $r \geq r_c$). Unlike (3.5.1), the potential ψ_g and the gravity force \mathbf{F}_g in (3.5.7) do not become infinity at $r \rightarrow 0$. This eliminates the problem of "divergences" which, as appears now, is caused by the arbitrary extrapolation of the results obtained from observations on celestial bodies to dimensionless "point" objects. Taking into account the minimum distance r_c the test mass m can approach the mass M solves the problem. Indeed, whatever the value r_c could be, the potential $\psi_g = 0$ at $r = r_c$. Hence, intensity of gravitational interaction is defined not by the interaction constant, but rather by the force magnitude at the closest approach of the interacting objects. It is not less significant that despite the well-established conceptions the potential energy of gravitating masses can not be negative, which corresponds to the general definition of energy as the capability of a system comprising material bodies to do work¹.

One more correction to the law of gravitation will be needed if one desires to allow for the impact made on the gravitation from the relative orientation of celestial bodies with shape anisotropy. Different positions of bodies in space and their different orientation in the same are known to be not equivalent mechanically (L.D. Landau, E.M. Livshits, 2004). It is this fact that may explain the dependence recently discovered by astronomers of the gravitational constant G_g from the relative position of some celestial bodies. As a matter of fact, for a body of non-spherical form the value R_s varies, generally speaking, as a function of the angle φ , at which the other body is observed, i.e. $r_s = r_s(\varphi)$. In particular, for the Earth as a field-generating body the distance from its surface to the center of its mass is unequal at different latitudes and longitudes. This is allowed for by the gravitational potential written in the form

$$\psi_g(R) = (G_g M_1 / 4\pi) [1/r_s(\varphi) - 1/r], \quad (r \geq r_s). \quad (3.5.8)$$

¹ Positivity of energy in any form follows from the energy definition itself as a capability for doing work – which is either available or unavailable.

where the energy of interaction appears to be a function of the relative position of non-spherical bodies, e.g. the spiral galaxies. Such an approach is preferable to the assumption the gravitational constant is changeable. It better corresponds to the methodology of energodynamics demanding the orientation processes with the coordinate φ_i to be specifically classified.

Thus, mechanics consideration as one of branches of energodynamics allows not only to receive its main principles, laws and the equations as its consequence, but also to generalise the majority of them.

3.6. Substantiation of the Least Action Principle

The “least action principle” is considered as one of the fundamental principles of mechanics. As for the background, it is worth noting that the principle was stated at the time when such concepts as energy and the law of its conservation did not yet exist. The name “least action principle” was given by Maupertuis (1744). According to his statement of this principle regarding stationary conditions for real path of a material point in conservative force field the integral of particle momentum taken over the segment of a trajectory in-between two of its points is minimal as compared with the same integrals but taken over segments of other curves.

The above form of the principle, as well as its other forms, proceeded not from physical nature, but were based on the belief usual among scientists at that time that all natural processes occurred with a definite purpose. Natural philosophers treated that principle as the “elixir stone” to discover all natural laws. It only remained to find criteria for Nature to define that its target had been reached. Thus Laplace considered that “the real goal of Nature was saving of work-kinetic energy”. That was the viewpoint Lagrange adhered to, when he considered the above principle as “ought to be rather named the extreme work-kinetic energy”.

H. Helmholtz was the first, who legalized the least action principle as the most general law of mechanics. Having kept a principle in essence, the, unlike other researchers, took the Lagrange function of object under research $L = E^k - E^n$ as initial primary value, interpreting it as the difference between its kinetic E_k and potential E_n energy. This function was expressed through the generalized coordinates r_i and momenta p_i of all N system particles ($i = 1, 2, \dots, N$), which made the lagrangian $L[\mathbf{r}_i(t), \mathbf{p}_i(t), t]$ be time function t . According to it the least action principle is expressed in mechanics as functional:

$$\hat{S}(t) = \int L[\mathbf{r}_i(t), \mathbf{p}_i(t), t] dt = \min. \quad (3.6.1)$$

Helmholtz succeeded in deriving the laws of motion for a number of systems from the properties of this function extremum. After that principle had successfully been applied in electrodynamics and then also in the gravitation theory, a number of authoritative scientists started to consider it applicable to also those phenomena which are still to be studied. This Helmholtz' idea «to find wordings for the laws of new-class phenomena» has gradually led to attempts to transform physics into a science which would allow «to reduce all physical constants to mathematical ones».

Meanwhile till now have not yet succeeded not only attempts to substantiate the principle of the least action proceeding from whatever not less general and fixed laws, but even to understand the physical sense of the lagrangian. In this respect ergodynamics provides new possibilities. First of all, note that should (3.6.1) be integrated within the same interval of time $t_2 - t_1$, the action $\hat{S}(t)$ to within the constant $E\Delta t$ corresponds to the integral $\int 2Ek dt$ expressing action by Maupertuis. Expressing E_k in terms of mass m of a body under investigation and its velocity $v = dr/dt$ (where r – radius vector of its center of mass) the Maupertuis action may become:

$$\hat{S}(t) = \int m \mathbf{v} \cdot d\mathbf{r} = \min. \quad (3.6.2)$$

It is easy to notice, that the integrand in (3.5.2) is a special case of the more general expression for the increment $d\mathbf{Z}_i = \Theta_i d\mathbf{r}_i$ of the distribution moment pertaining to the carrier of the i th motion form Θ_i (1.5.4). In this case $\Theta_i \equiv \Theta_w$, i.e. represents the body momentum \mathbf{P} , while $\mathbf{r}_i = \mathbf{r}_w$ expresses the displacement of the inertia centre due to velocity field redistribution. The velocity profile in the liquid flow with the velocity in the flow core above the average value whereas in the boundary layer below it may serve an illustrative example of such a redistribution. In this case the least action principle becomes the condition of minimum increment for the translational angular momentum $\mathbf{Z}_w = \Theta_w \mathbf{r}_w$, caused by the deviation of the system from a dynamic equilibrium:

$$\hat{S}(t) = \mathbf{Z}_w = \int \Theta_w d\mathbf{r}_w = \min, \quad (3.6.3)$$

where the integral is taken of the state prior to starting motion.

Thus, the principle of the least action is reflexion of a condition of evolution of system to equilibrium (2.5.9). According to it, the decrease of ordered energy $E = E(\mathbf{Z}_i)$ is accompanied by reduction \mathbf{Z}_i to zero (owing to an opposite orientation of vectors \mathbf{X}_i and \mathbf{Z}_i). Thus, the

energodynamics opens physical sense of action as the compulsion deleting dynamic system from a condition of internal balance. About conservatism of systems (preservation the explanation and amazing universality of a principle of the least action, and its independence of a primary assumption finds in it the sums of potential and kinetic energy). Really, existence of the moments of distribution of impulse \mathbf{Z}_w as functions of a nonequilibrium condition does not depend on what the system has by come to this condition. On the other hand, thanking of dissipation the minimum of size \mathbf{Z}_w is reached. The undertaken substantiation eliminates obstacles to application of a principle of the least action in thermodynamics, hydroaerodynamics and electrodynamics.

Summarizing the chapter as a whole it may be concluded that considering classic mechanics as consequences from energodynamics allows not only substantiating all its fundamental statements, but also proceeding with their further generalization.

Chapter 4

CLASSIC THERMODYNAMICS

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 (thermodynamics) remote 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.

The escape from the situation may be found in obtaining basic statements of thermodynamics by deductive way as consequences of ergodynamics in order to avoid the extrapolation of classic thermodynamics beyond the framework strictly bounding the applicability of its initial concepts. This chapter is mainly dedicated to ascertaining the minimal scope of the corrections necessary to introduce into the fundamentals of thermodynamics from the positions of ergodynamics.

4.1. Principle of the Excluded Perpetuum Mobile of 1st Sort (the First Law of Thermodynamics)

R. Clausius, the founder of classic thermodynamics, presumed the principle of heat Q and work W equivalence generalizing the results of numerous experiments to be the only reliable basis to thermodynamics. He 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:

$$Q_c/W_c = 1, \tag{4.1.1}$$

or

$$\oint (dQ + dW) = 0 \tag{4.1.2}$$

where dQ , dW – elementary amounts of heat and work for particular parts of the cyclic process under consideration.

Clausius was the first who noticed that the above relationship did not depend on the nature of the cyclic process under consideration. According to a known curvilinear integral theorem the fact the integral along the contour within the space of variables x_1, x_2, \dots, x_n becomes zero is a sufficient evidence that the integrand represents the exact differential of some function of these variables $U(x_1, x_2, \dots, x_n)$.

Thus the principle of equivalence meant the existence of a specific function of state U , which variation was equal to the algebraic sum of heat and work of a process. Allowing for the rule of signs accepted in thermodynamics (the heat Q fed into a system and the work W done by the system being positive), the integrand may be expressed as:

$$dU = \bar{d}Q - \bar{d}W. \quad (4.1.3)$$

R. Clausius named the function U *the total heat of a body* (he meant the sum of the heat Q fed into a system and the “disregation” work of the dissipative nature, which replenished the “heat of the body” – the energy associated with heat motion in the system). Such an understanding reflected a known duality of the heat concept, which had historically been caused by consideration of the heat as a form of motion (in the same line with such phenomena as light, sound, electricity, magnetism). This duality means that heat shows in some cases as the state function (heat of a body), whereas in other cases – as the process function (heat of a process). Therefore from Clausius’ times on the function U has been referred to as the *internal energy* of a system. However, despite plenty discussions the said duality in using the term “heat” survives to this day. Accepting this fact as a historically preconceived reality, let us name the internal heat energy, for short, the “heat of a body”, whereas the quantitative measure of heat transfer – the “heat of a process” designating, for the avoidance of mishmash, the former through U_q and the latter through Q . In this case, to designate the infinitesimal increments of internal heat energy as a function of state, let us use the sign of exact differential d , whereas to designate the elementary amount of work W or heat Q as a process function – the sign \bar{d} ($\bar{d}W$, $\bar{d}Q$).

Equation (4.1.3) has been named the *first law of thermodynamics*. This reflects the constancy of energy of an isolated system ($U = \text{const}$ at $Q, W = 0$) and therefore is one of the statements of the *law of conservation of energy*. This law reflects the conservation of the internal energy U at its interchange among a system and the environment in the form of heat Q or work W . With regard to a cyclic process (cycle) expression (4.1.3) may be written as:

$$\oint \bar{d}Q = \oint dU + \oint \bar{d}W \quad \text{or} \quad Q_c = \oint dU + W_c, \quad (4.1.4)$$

where Q_c, W_c – total heat and work of the cyclic process.

Since the circuit integral of any state parameter, including the system energy U , is equal to zero, expression (3.1.4) directly gives that $W_c = Q_c$, i.e. the work done by working medium for a cycle is equal to the heat it expends in the cycle. In other words, *a cyclic machine is impossible, which would do work without heat expenditure*. This statement was named the *law of excluded perpetual motion of the first kind*.

At its early stages classic thermodynamics was restricted to the simplest thermo-mechanical systems, where expansion work was the only

kind of work. A system having been in equilibrium with the environment (equal pressures p), that work was determined from mechanical interpretation of pressure as a force and expressed by the relationship $dW_p = pdV$, where V – volume of the system. From there the so-called analytical expression for the first law of classic thermodynamics ensued in the form:

$$dQ = dU + pdV. \quad (4.1.5)$$

It may be said without exaggeration that the majority of methodological features intrinsic for thermodynamics, as well as its insufficiency, is caused by that specific form (4.1.5), in which it involves the law of conservation of energy. Expression (4.1.5) first of all involves only two forms of power interchange in a system, viz. heat Q and work W done by the equilibrium system¹⁾. Meanwhile, one more type of power interchange referred to neither heat transfer nor work take place in a great number of cases of practical interest. This is mass transfer associated with the k^{th} -substances interchange between a system and the environment. Such systems are called open ones. These types of power interchange are not covered by equation (4.1.5) describing the law of conservation of energy, therefore the principle of equivalency of heat and work can not serve as a basis for further generalization of this law to open systems. To do this, a more general approach is needed, which is exactly what ergodynamics puts forward.

Furthermore, equation (4.1.3), unlike (2.2.5), does not contain any forces \mathbf{X}_i causing the generation of the energy-conversion processes. Its terms on the right-hand side characterize energy interchange between a system and the environment in the form of heat and cubic strain work (confirming the principle that a system can only exchange what it really has). Therefore it describes only processes of energy *transfer*, but not *conversion*. In other words, the first law of thermodynamics characterizes the balance of energy only and has nothing to do with the law of conservation of energy at its conversion. It is even more true, because an internally equilibrium (homogeneous) system can not do useful work in the absence of other bodies (environment), with which it is not being in equilibrium. Besides, the energy balance itself described by equation (4.1.5) comes valid provided the system being in equilibrium with the environment. Actually, in the absence of, e.g., mechanical equilibrium between a system and the environment (when the pressure p in the system is not equal to the environmental pressure p_e , and the expression pdV does not

¹⁾ Such work will hereafter be referred to as “non-technical” unlike the useful external (technical) work done by various machines (by extended systems).

define the expansion work any more) the analytical expression of the first law of thermodynamics (4.1.5) goes over into inequality:

$$dQ \neq dU + pdV. \quad (4.1.6)$$

This is the reason why the first law in the form (4.1.5) is valid for only completely (both internally and externally) equilibrium systems.

One more reason of the insufficiency classic thermodynamics demonstrates is caused, strange though it may appear, by the notion of internal energy as itself. energy U belonging to, strictly speaking, entire set of the interacting (relatively moving) bodies is known to be far from being possibly attributed to one of the comprising parts considered as the object of investigation. This may be done to only that part which does not depend on position and motion of the system relative to other bodies and is defined by exclusively parameters of the system itself. That is exactly where the definition of the *internal energy* U is rooted in. However, it ensues from this definition that such a system can not do useful external work measured by the variation of external potential or kinetic energy of a system of interacting bodies. Therefore the internal energy of an equilibrium system is actually the *energy* (see Chapter 2).

The notion of internal energy is quite often extrapolated to systems lying in external fields of forces, which are, e.g., dielectric and magnetic materials. Their energy is known to be dependent on not only internal variables, but as well on intensities of these fields. However, these are often associated with the notion of magnetic and dielectric “internal self-energy” considering it sufficient to subtract the energy of electrical and magnetic fields from the total energy in the volume occupied with the system. This makes energodynamics consider a polarized medium along with a polarizing field as a whole and, generally, non-equilibrium system. Such an approach is substantiated by the fact that an attempt to isolate a dielectric or magnetic field from the surrounding fields of forces leads to change of their state (relaxation), which excludes a possibility of treating their energy as internal one (self-energy) and applying equation (4.1.3) to it.

There are also other serious and yet hardly perceived constraints for the equations operating with the notion of internal energy. In this sense the term “thermodynamic” may be applied only to the so-called “simple” media, where long-range and surface forces may be neglected since their energy can not be attributed to just one of the interacting bodies (Caratheodory, 1964). From this one more constraint ensues, viz. for size of a system. This exists not only “from above” (for galactic-size systems where long-range gravitational forces can not be neglected), but also “from below”, e.g., for usual continuums since when artificially splitting

them into elementarily small zones the surface energy of the continuum elements increases and may appear non-negligible (Putilov, 1971; Bazarov, 1983).

To exclude all these constraints, energodynamics considers as the object of investigation “extended systems” comprising such a set of interacting (relatively moving) bodies and fields, which energy, to enough degree of accuracy, may be considered as its “self-energy”. Such systems may be isolated not disturbing their internal state and energy. Furthermore, energodynamics offers an absolutely other (and in many ways oppositional) approach to stating the law of conservation of energy. This approach is notable for its basing the law of conservation not on the energy balance equation, which equation (4.1.3) is, but on the representation of the system energy as a function of a quite definite number of the system state parameters.

Suppose we deal with a thermo-mechanical system having only two (thermal and mechanical) degrees of freedom. These two degrees of freedom are described with two extensive state coordinates, which we formally designate as Θ_t and Θ_e . Their meaning will be explained hereafter. For now it is enough to know that the total energy of the system (consisting in this case exclusively of its internal energy U) as a function of state is expressed in the form of $U = U(\Theta_t, \Theta_p)$, whereas its exact differential may be written as:

$$dU = (\partial U / \partial \Theta_t) d\Theta_t + (\partial U / \partial \Theta_e) d\Theta_e. \quad (4.1.7)$$

Designating $\Psi_t \equiv (\partial U / \partial \Theta_t)$ и $\Psi_e \equiv (\partial U / \partial \Theta_e)$ gives a thermo-dynamic identity:

$$dU \equiv \Psi_t d\Theta_t + \Psi_e d\Theta_e. \quad (4.1.8)$$

According to this identity the energy of the system varies with variation of the said parameters Θ_t and Θ_e irrespective of what causes the variation – either energy interchange or internal processes in the system. Undoubtedly, in the latter case the terms $\Psi_t d\Theta_t$ and $\Psi_e d\Theta_e$ do not reflect any more heat exchange or cubic strain work. To define them, energodynamics offers other ways (see Chapter 2). That enabled energodynamics to refuse the classification of processes by the type of energy interchange. It was the said classification that engendered the problem of thermodynamic inequalities. As a matter of fact, the principle of classification by the type of energy interchange demands the availability of state coordinates that would remain unvaried in the absence of heat transfer processes and expansion work. However, this is excluded in a non-equilibrium system, where a number of its parameters can vary spontaneously. For this

reason classic thermodynamics is known to be restricted to equilibrium states and quasi-static processes not practically disturbing this equilibrium.

Unlike it, energodynamics classifies processes by exclusively those state variations they cause. Such a classification provides the fundamental equation of equilibrium thermodynamics in the form of (4.1.7) retains the nature of identity even in the case when the parameters Θ_i and Θ_p vary spontaneously, i.e. in the whole range of real processes.

4.2. Principle of Entropy Existence (Second Law for Reversible Processes)

Let us clarify the meaning of the variables Θ_i and Θ_e introduced above formally (by definition). Let us start off with the coordinate Θ_e of expansion work. It is considered quite natural to accept for this the volume V of a system. However, in this case the volume-correlated system potential $\Psi_e \equiv (\partial U/\partial V)$ according to relationship (2.2.2) takes on the meaning of pressure reversed in sign ($\Psi_p \equiv -p$). According to equation (2.3.2) this entails opposite-to-actual sign of the motive force of gas flow transfer process (as known from experience, gas flow is transferred by pressure-gradient force toward the lower-pressure zone – just like with potentials of other nature). Furthermore, the volume (positive or negative) does not comply with the requirement of energodynamics for potential and coordinate of some process simultaneously becoming zero. Lastly, the volume of a system can not serve as a cubic strain coordinate in open systems because it necessarily varies at mass transfer with the density ρ of the system remaining constant. For systems, where the processes of composition variation run (due to diffusion of the k^{th} substances across the borders of the system at constant mass M of the system), the cubic strain coordinate issue grows even more complicated since the system density $\rho = \sum c_k \rho_k$ can vary with constant density ρ_k of any of the k^{th} substances, but with the variation of the fractions c_k of their total masses. Therefore the cubic strain issue appears to be, in actual fact, not that plain.

From energodynamics any state coordinate Θ_i is considered as a quantitative measure of the corresponding form of energy in a system and therefore increases with increase of this energy. If, for the sake of simplicity, to be confined to only closed systems ($M = \text{const}$) of a constant composition ($c_k = \text{const}$), this demand is met by the difference between the theoretical compression limit $V_o = 0$ (this is the state corresponding to

zero of the cubic strain coordinate Θ_e) and the current value of the volume V , i.e.

$$\Theta_p = (V_o - V). \quad (4.2.1)$$

It is easy to see that Θ_e complies with all requirements for the cubic strain coordinate. In particular, $d\Theta_e = -dV$, and

$$\Psi_p \equiv (\partial U / \partial \Theta_p) = -(\partial U / \partial V) = p. \quad (4.2.2)$$

which provides further the concordance of signs for all potentials and forces of a system.

In equilibrium systems, where the reversible expansion work done by a system is the only reason of changing the volume of the system, according to (4.2.1) $dW_p = pdV$, which corresponds to expression (4.1.4). In more general case of non-equilibrium systems the term pdV characterizes the process of uniform compression or expansion of a system (its uniform cubic strain) irrespective of what causes it – either the compression (expansion) work done by the system or the energy dissipation (including that from overcoming frictional forces or from spontaneous expansion into void).

The next challenge R. Clausius, the founder of thermodynamics, faced on the way to representing the law of conservation of energy (4.1.3) in terms of state parameters was to find the heat transfer coordinate as a value remaining unvaried in adiabatic processes. R. Clausius found that coordinate thru splitting the arbitrary cycle of the heat engine by series of adiabatic and isothermal lines into a number of elementary reversible Carnot cycles. Designating the elementary amounts of heat being received and delivered in such elementary cycle at temperatures T' and T'' , respectively, thru dQ' и dQ'' gives the following form of the thermal efficiency η_i for each of such cycles:

$$\eta_i \equiv 1 - dQ''/dQ' = 1 - T''/T'. \quad (4.2.3)$$

From this it follows that the sum $dQ'/T' + dQ''/T''$ of the so-called “reduced heats” dQ'/T' and dQ''/T'' is equal to zero over all elementary cycles, i.e. the circuit integral, in its limit, of the reduced heat

$$\oint dQ/T = 0 \quad (4.2.4)$$

appears to be equal to zero irrespective of the cycle configuration. This means that the integrand dQ/T is the exact differential of some function of state, which Clausius named the entropy:

$$dS = dQ/T \text{ или } dQ = TdS. \quad (4.2.5)$$

It was thereby proved the existence of a reversible process coordinate, i.e. a state parameter which variation is a necessary and sufficient criterion of running the heat transfer process. That statement R. Clausius referred to the second law of thermodynamics as the law of entropy. The further investigations (Т.А. Afanasieva–Erenfest, 1928; А.А. Guhman, 1947; N. Petrov, J. Brankov, 1986) have shown that the law of entropy comprises two quite independent statements referred to, respectively, reversible and irreversible processes, viz. the laws of existence and increase of entropy. With all this going on, relationship (4.2.4) being the mathematical expression of the second law of thermodynamics for reversible processes has been proposed as the law of existence of entropy (А.А. Guhman, 1947).

With the lapse of time the concept of entropy has crossed the borders of not only thermodynamics, but also physics, and penetrated into the inmost of human brain. Therefore, many investigators have remained unsatisfied with the close connection between the concept of entropy and Carnot ideal gas cycles. Other ways have been tried for a long time to substantiate existence of entropy. The Caratheodory's system (Caratheodory, 1909) is commonly considered as the mathematically strictest and logically most consistent of all others. C. Caratheodory based his substantiation of existence of entropy and absolute temperature on an "axiom of adiabatic unattainability", according to which "in any vicinity of the initial state arbitrarily prescribed there are such ones which can not be however accurately approximated by adiabatic state variations". The implication of this axiom is most distinct from the Afanasieva–Erenfest's (1928) statement, "Provided $dQ = 0$ on infinitesimal way between two infinitely close states of a thermally homogeneous system, then none of mere adiabatic quasi-static ways is possible as bypass between these states". The "bare root" of the Caratheodory's axiom is thus growing from the evident ground that *reversible heat exchange results in such variations of state which can not be attained by any other way as well reversible*. It is easy to see that this statement is a particular case of the *process distinguishability principle (axiom)* we have embedded into the foundation of the process classification (Chapter 2). This axiom, as applied to heat exchange process, just logically results in a statement that a parameter exists, which variations reflect those specific state changes distinguishable in kind and non-reducible to each others, which the reversible heat ex-

change causes. However, Caratheodory was persistent in his intent to prove the existence of entropy not recurring to notions of non-mechanical nature (in particular, to the notions of heat and temperature). That was what engendered a known complexity and awkwardness of his entropy-existence substantiation. The main point of his approach offered consists in proving the holonomy of the expression $dQ = dU + pdV$, i.e. that this the so-called “Pfaffian” form contains the integrating factor $1/T$ converting the heat element dQ into the exact differential of some function of state, which Clausius has earlier named entropy. The fact is that the heat dQ and the work dW elements as themselves in the equation (4.1.3) of the first law of thermodynamics are not exact differentials since their values depend on the nature of a process. In particular, for adiabatic processes $dQ = 0$, for isochoric ones $dW = 0$. That is what required the representation of the elementary heat in terms of the exact differential of some function of state, i.e. per se the determination of the heat exchange coordinate.

As we’ll try to show hereafter, the one can avoid this complexity who classifies processes not by the energy exchange type, but by those specific state variations the processes cause. In this case it should be admitted a specific process exists dependable on a change of the system internal heat energy irrespective of what causes this change, either the external heat exchange Q or internal sources of the dissipative heat Q^d (from friction, chemical transformations, high-frequency or induction heating, etc¹⁾). Let us name this process, after K. Putilov (1971), the *thermal process*. Then it directly ensues from the theorem of degrees of freedom proven in Chapter 1 that a specific coordinate of the said process exists designated as Θ_i in the previous chapter. All we have to do now is to clarify the relationship between the thermal process coordinate and the heat exchange coordinate, viz. the Clausius’ entropy S . With this purpose let us use the equilibrium conditions determination method, which idea belongs to J. Gibbs (1885). Let us consider the conditions, at which the thermal equilibrium occurs between two parts (subsystems) of a system isolated in whole. The subsystems have intrinsically different empirical temperatures τ' and τ'' and are separated with a rigid diathermic (thermopeneable) partition. Since during the process of equilibrium setting the energy of such a system remains unvaried, the equilibrium condition ac-

¹⁾ Note that from the positions of equilibrium thermodynamics, where heat has been construed as a function of process, it would be incorrectly to qualify the “heat of a body” as a quantitative measure of the internal heat energy U_i . However, in energodynamics, like in thermal physics, the heat exchange is construed as a process of exchanging the internal heat energy U_i among bodies (confirming the principle that a system can only exchange what it really has). This considerably facilitates the comprehension of thermal process specificity.

ording to equation (4.1.4) is expressed as the absence of the energy variation dU for the system as a whole at any energy variations $\delta U'$ and $\delta U''$ for the subsystems (which is caused by the dynamic nature of thermal equilibrium):

$$\delta U = \delta U' + \delta U'' = \Psi_i' d\Theta_i' + \Psi_i'' d\Theta_i'' = 0. \quad (4.2.6)$$

Taking into account that in the thermal equilibrium state there are no any internal sources for the Θ_i' and Θ_i'' coordinates, while the system as a whole is isolated ($\Theta_i = \text{const}$), gives that possible variations Θ_i' and Θ_i'' in the subsystems obey the evident constraint:

$$\delta\Theta_i = \delta\Theta_i' + \delta\Theta_i'' = 0. \quad (4.2.7)$$

Considering (4.2.6) jointly with equation (4.2.7) of imposed constraints may lead to a conclusion that at thermal equilibrium the equality of potentials Ψ_i' and Ψ_i'' in both subsystems takes place:

$$\Psi_i' = \Psi_i''. \quad (4.2.8)$$

It is known from experience that thermal equilibrium is reached under equality of the empirical temperatures τ' and τ'' in subsystems measured in an arbitrary temperature scale (Celsius, Réaumur, Fahrenheit, etc.). Hence, the potentials Ψ_i' and Ψ_i'' are some functions of these temperatures, i.e. $\Psi_i' = \Psi_i'(\tau')$; $\Psi_i'' = \Psi_i''(\tau'')$. Since this statement is a generality and does not depend on the kind of substances in subsystems, the above functional dependence must be unified for all substances (*universal*)¹⁾. Furthermore, equality (4.2.7) is valid *as long as heat exchange between subsystems is possible*, i.e. until the heat motion in subsystems caused the particular type of energy exchange has ceased. From this it follows that the temperatures τ' and τ'' differ from zero *as long as heat exchange exists between any cogitable bodies*. This means that the potentials Ψ_i' and Ψ_i'' must be measured in the so-called absolute temperature scale, which zero *corresponds to the total degeneracy (disappearance) of heat motion*. It is the Kelvin scale that is known to meet these requirements. Designating the temperature in this scale thru T leads to a conclusion that the variation of the thermal process coordinate Θ_i in equilibrium

¹⁾ This chain of discourse makes quite evident the necessity to measure in absolute scale not only temperature, but also pressure, chemical, electrical and any other potential of a system under investigation. It is a matter for regret that this statement has not yet become common property of a great number of investigators.

systems is related to heat exchange via the same relationship as the Clausius' entropy:

$$d\Theta_t = \delta Q/T = dS. \quad (4.2.9)$$

From this it follows that the thermal process coordinate Θ_t coincides with the Clausius' entropy S to an accuracy of some constant (which may be set zero, though). This allows expressing thermodynamic identity (4.1.7) thru informal variables:

$$dU \equiv TdS - pdV. \quad (4.2.10)$$

Fundamental difference of this identity from the joint equation of the first and second laws of thermodynamics, where unequal sign figures instead of identity sign (for irreversible processes), lies in the fact that the former remains valid for also irreversible processes. Undoubtedly, in this case the terms of this identity do not characterize any more heat exchange and expansion work as it would be for reversible processes. The reason of this, as indicated above, is that entropy and volume have internal sources caused by dissipative processes running in heterogeneous systems. The variations of volume and entropy are, in this case, caused by not only the expansion work and the heat exchange, but by even more general processes, viz. cubic strain and thermal process both including an irreversible component. Such is the price that has to be paid for retaining the body of mathematics in thermodynamics in the form of equalities.

4.3. Principle of Entropy Rise (Second Law for Irreversible Processes)

In accordance with the law of existence of entropy the entropy means a state parameter, which variation in reversible processes is equal to the process heat Q related to the process average temperature T . However, the name of this parameter given by R. Clausius (entropy in Greek means "internal conversion") emphasized a quite other and unusual for science of that time property of entropy to increase also in the absence of heat exchange (due to a spontaneous conversion of ordered forms of energy into the heat energy). First S. Carnot in his "Réflexions..." (1824), then R. Clausius in "The Dynamic Theory of Heat" (1850) showed by different ways that if a heat engine was arranged so that in its reverse-direction operation all mechanical and heat effects were converted into their inverses, the engine would do the maximal amount of work. That meant that "the

mechanical energy thus expended might be returned to the initial state” (R. Clausius, 1950). Thus the concept of reversibility as a possibility to return a system to its initial state appeared immediately having taken the character of an initial postulate. From how this term was applied, the classicists construed it as a possibility to recover the “motive force of heat”. In particular, W. Tomson in his article “On Dynamic Theory of Heat” directly writes, “When heat or work is obtained with irreversible process, the dissipation of mechanical energy occurs and its complete return to the initial state is impossible”. Since the mechanical energy is measured by the amount of work that a body (system) can do, the irreversibility, as the founders of thermodynamics understood it, was a synonym for loss of capability to do work by the body (or, as we term it now – “dissipation” of energy).

Since all known thermodynamic systems being isolated are tending to equilibrium (where any macro-processes cease), the capability of such systems to do work decreases when spontaneous processes are running. To describe such a behavior mathematically, R. Clausius considered two “mating” heat engines – one engine working by direct cycle, while the other – by reverse cycle. He took for granted that the thermal efficiency η_t of any irreversible heat engine was less than in the reverse Carnot cycle (at the same temperatures of heat absorber and heat source). If so, then the equal sign in relationship (4.2.3) must be replaced by the unequal sign:

$$\eta_t \equiv 1 - \frac{dQ''}{dQ'} < \eta_t^k = 1 - T''/T. \quad (4.3.1)$$

In this case, repeating the same operations we immediately come to a conclusion that entropy of a system increases if any irreversible processes are running in the system:

$$dS > dQ/T, \quad (4.3.2)$$

Thus the law of increase of entropy appeared. It reflects the unilateral directivity of spontaneous processes and has acquired the status of the second law of thermodynamics. According to this law the entropy of an isolated system increases when any irreversible processes are running in it. R. Clausius, not having conceived restrictions to this law, extended it to the entire Universe. Such “absolutization” of the law of increase of entropy is best of all highlighted in his winged words, “The energy of the Universe is invariable. The entropy of the Universe is increasing”.

Clausius’s contemporaries immediately traced far-reaching effects in that conclusion – from “the Creation” up to inevitability of “heat death”

of the Universe. A good few of investigators even at that time treated such an extrapolation of the law of increase of entropy as extremely unconvincing (J.M. Gelfer, 1979). It is impossible to textually duplicate here even the least of the objections ensued. Under these circumstances the deduction of the law of increase of entropy from the positions of ergodynamics is a matter of great interest. The definition of the internal heat energy U_T given above makes quite natural and predictable its increase not only due to the heat exchange Q , but also due to internal sources of the dissipation heat Q^D :

$$dU_T = \bar{d}Q + \bar{d}Q^d. \quad (4.3.3)$$

Since the quotient obtained when the exact differential of any function of state (in this case – of U_i) is divided by any parameter Ψ_i (in this case – by absolute temperature T) is also the exact differential, the expression $d\Theta_T = dU_i/T$ does not demand the proof of holonomy and directly leads to the entropy balance equation I. Prigogine (1947) set forth:

$$dS = d_eS + d_sS. \quad (4.3.4)$$

Here $d_eS = \bar{d}Q/T \leq \geq 0$ – reversible part of the entropy variation caused by the external heat exchange $\bar{d}Q$; $d_sS = \bar{d}Q^d/T \geq 0$ – irreversible part of the entropy variation caused by internal sources of the dissipation heat $Q^d \geq 0$. Under this expression the entropy S of adiabatically isolated systems (where $\bar{d}Q = 0$) increases when any internal sources of the dissipation heat appear in them.

At the same time expressions (4.3.2) and (4.3.3) manifest clearly the inapplicability of the law of increase of entropy to irreversible processes, where the work counter the dissipation forces affects other components of the internal energy and does not initiate internal sources of the dissipation heat Q^d . In particular, metal cutting and material crushing processes involve changing the internal potential energy depending on the system structure. This is estimated in practice by the heat output ratio which is the dissipation heat Q^d related to the work expended W . For many processes the ratio Q^d/W is less than unit. Thus, from the positions of ergodynamics, it becomes absolutely evident that the thermodynamic entropy is not a measure of “each and either” irreversibility, but just reflects the fact of increasing the internal heat energy at the expense of other “non-entropy” forms of energy. The understanding of this circumstance is considerably facilitated by comparing the exact differential of the internal heat energy (4.3.3) $dU_i = TdS$ with the similar expression for the kinetic energy $dE^k = \mathbf{v}d\mathbf{P}$ (where \mathbf{v} – velocity of a system, \mathbf{P} – its momentum):

$$dU_{\tau} = TdS ; dE^k = \mathbf{v} \cdot d\mathbf{P} . \quad (4.3.5)$$

It is easy to notice that the entropy S behaves toward the internal heat energy U_i of a system in the same way as the momentum \mathbf{P} of the system toward its kinetic energy. In other words, *the entropy of a system is a thermo-momentum of a kind, i.e. the sum of momentum magnitudes of the particles comprising the system, which has lost its vector nature due to the randomness of heat motion.* It is natural therefore that the entropy as a thermo-momentum of a system increases not only at its transfer from the environment during heat exchange with the same, but at any dissipation processes involving the conversion of ordered forms of energy into the internal heat energy. The interpretation of the entropy as a thermo-momentum is a matter of no small consequence for conception of thermodynamics and its further generalizations. In particular, it becomes evident that the thermodynamic entropy can not serve as measure of the disorder not relating to heat motion, including the disorder of structure or uncertainty of information. In this respect the conversion of the *inergy* of a system into its *anergy* (see chapters 7, 8 and 14) is a much more general criterion of an isolated system evolving toward equilibrium. Such a conversion has an experimental confirmation, which may be, e.g. the so-called “effect of increasing heat content measured” (L. Brovkin, 1960, 1964). Those experiments revealed an increase of the mean integral temperature during the relaxation of gaseous or solid medium (paper, cardboard, rubber) with heterogeneous temperature field, whereas that temperature should seemingly have decreased. Characteristic are herein the experiments with a roll of paper, where throughout the length a resistance thermometer was inserted. After the tightly packed roll had been non-uniformly heated from an external source of heat, the system was lagged (heat insulated) and the resistance variation of such a “spread” thermometer was recorded. Series of such experiments revealed a considerable increase of the mean integral temperature of the roll for the initial period of its “cooling”, which amounted to 17.2% thru 36.4% depending on the degree of its heating. For rubber that effect appeared to have been even higher. That unambiguously evidenced the fact that the equilibrium component of the internal heat energy of the body (its anergy) $\bar{U}_i = TS$ increased whereas the U_i itself remained constant, i.e. that the thermal energy existed and transformed into the anergy during the relaxation of the system. Hereafter we will time after time advert to the concept of inergy as more “physic”, more informative and more general criterion of evolution than entropy.

4.4. Principle of Excluded Perpetual Motion of the Second Kind

Operation experience on heat engines and their theoretical investigation have led to the comprehension that there should exist in them, along with a heat source, also a heat absorber (or, to use the common locution – a “cold source”). Scientists have come to this conclusion by different ways: S. Carnot (1824) – from analogy of heat engines with hydraulic engines using the inlet-outlet water level differential; W. Thomson (1847) – from impossibility for working medium to be cooled below the ambient temperature; R. Clausius (1850) – from necessity of the “compensation” for converting heat into work as partial removal of this heat to surrounding bodies; W. Ostwald (1901) – from impossibility of using inexhaustible heat supply from the ocean. It was him, who offered to name engines lacking heat absorber the “perpetual motion of the second kind” (unlike the “perpetual motion of the first kind” lacking heat source and thus disturbing the first law of thermodynamics). The postulates stating impossibility of creating such engines make up an inseparable part of the second law of thermodynamics and are united by the “law of excluded perpetual motion of the second kind”.

However, the initial statements of this law referred to cyclic heat engines only and did not take into account the wide process variety of converting energy from one form into another. Therefore to many investigators the consideration of non-cyclic and non-heat engines has always seemed violating the “don’ts” of the mechanical theory for heat engines. This causes numerous discussions that have periodically arisen in scientific and popular press. In this context it is a matter of interest to clarify the limits of validity of the said postulates from the positions of a more general theory which energodynamics is.

Let us consider a heat source with a temperature of T_1 capable of heat exchange with the environment, but incapable of ceaseless mechanical work. In this case, to do work, a working medium has to be applied to capable of both heat-exchange and work, i.e. having both the thermal and mechanical degree of freedom. To avoid expenditure of working medium, let us make it perform a cyclic process (Fig.3-1). Providing such a working medium (e.g. steam or gas) is homogeneous in its physical properties (internally equilibrium), while the processes comprising the cycle are quasi-static (i.e. not disturbing this equilibrium), the joint equation of the first and second laws of energodynamics (2.2.5) becomes (4.1.5). According to (4.1.4) the work W_c of such a cycle is equal to the heat of the cycle:

$$W_c = Q_c = \oint TdS. \quad (4.4.1)$$

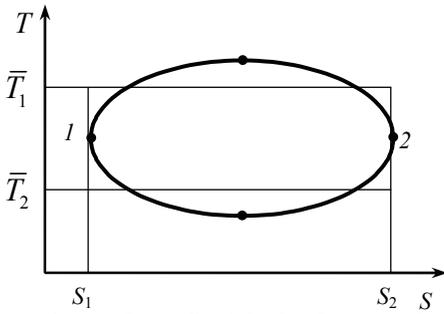


Fig.4.1. Generalized Cycle of Heat Engine

From this equation it follows that the work W_c in the cyclic process under consideration is other than zero only in the case, when the temperature T at various stages of the cycle accepts different values. Otherwise, factoring it outside the integral sign (4.4.1) and taking into account that the circuit integral

of entropy, like of any state parameter, is equal to zero, gives immediately $W_c=0$. Thus working medium in a cyclic engine must periodically contact with at least two heat sources having different temperatures T_1 and T_2 . In other words, both a “hot” and a “cold” heat sources are needed. However, it does not mean at all that the working medium can not take heat from both of them. To show that the cold source must be a heat absorber, let us note there is part 1–2 in the cycle, where the entropy increases and the heat $Q_1 = \int T_1 dS > 0$, i.e. is supplied to the working medium, and part 2–1, where the entropy decreases and the heat Q_2 is removed ($Q_2 = \int T_2 dS < 0$). Thus to run a cyclic process, both heat sources and absorbers are needed, which conceptualizes the law of excluded perpetual motion of the second kind. It is worth noting that this statement, as itself, directly ensues from the thermokinetic identity in the form of (2.2.5), where the terms of the addend sum characterize nothing but the useful work done by the system. These terms are structured as $\mathbf{X}_i d\mathbf{Z}_i$, which is a direct evidence that only heterogeneous systems ($\mathbf{X}_i \neq 0$) can do useful work, while this work itself involves transfer of energy carrier between the parts of such a system ($d\mathbf{Z}_i \neq 0$).

Following the chain of our discourse one can easily come to a concept of the degree of convertibility of heat into work. If to construe Q_1 and Q_2 as the heat, respectively supplied to and removed from the cycle, then according to (4.4.1) the work of an arbitrary cycle $W_c = Q_1 - Q_2$ and is expressed by the cyclic area, while the ratio η_t of the cyclic work W_c to the heat Q_1 supplied from a hot source is:

$$\eta_t \equiv W_c / Q_1 = 1 - Q_2 / Q_1 < 1. \quad (4.4.2)$$

This ratio was named the thermal efficiency of heat engine. According to (4.4.2) it is always less than unit. This fact is sometimes erroneously ascribed to shortcomings of heat engine leaving out of account the circumstance that removing a part Q_2 of the supplied heat Q_1 to the environment is not a loss, but the necessary provision to close the cycle. Only

that part Q_2 may be considered as losses, which is removed to heat absorber in excess of the minimum required. To define this minimum, let us represent Q_1 and Q_2 as:

$$Q_1 = \int T_1 dS_{1-2} = \bar{T}_1 (S_2 - S_1); \quad (4.4.3)$$

$$Q_2 = \int T_2 dS_{2-1} = \bar{T}_2 (S_1 - S_2), \quad (4.4.4)$$

where \bar{T}_1, \bar{T}_2 – the so-called mean thermodynamic temperatures of, respectively, heat supply and heat removal in a cycle. In Fig.4.1 those are expressed as the height of a rectangle equal in area to, respectively, the curvilinear trapeziums $S_1-1-2-S_2$ and $S_1-2-1-S_2$. This allows expressing the efficiency of any cycle thru these temperatures by the relationship:

$$\eta_t = 1 - \bar{T}_2 / \bar{T}_1 < 1. \quad (4.4.5)$$

From here it directly follows that the efficiency of the cycle under consideration will be maximal providing the temperatures of heat supplied and removed are constant and equal to, respectively, maximal and minimal temperature of the working medium in Fig.4.1. Such a cycle consisting of two isotherms and two adiabats was first set forth by S. Carnot and named after him. The removed heat Q_2 is there minimal and equal to Q_2^{min} . Hence only the heat difference $Q_1 - Q_2^{min}$ may be referred to as losses. It also ensues from (4.4.5) that the thermal efficiency of heat engine is defined by exclusively mean temperatures of heat supplied and removed in a cycle and, providing those are equal, does not depend on the working medium of the engine¹⁾. This statement is in substance equivalent to the Carnot theorem which he proved from the theory of thermogen and the assumption of reversibility (ideality) of his cycle. In our case we have come to all these statements without any assumptions regarding the cycle configuration and equilibrium of the processes comprising the cycle. From our consideration undertaken it also follows that the “compensation” for the Clausius-mentioned conversion of heat into work consists in removing the heat Q_2 into the environment (heat absorber) and in increasing its entropy by the value $(S_2 - S_1)$ theoretically equal to the decrease of the entropy of the heat source. In other words, to provide the

1) This fact means that the value of η_t does not depend on features of heat engine and its design perfection, but is defined by exclusively those resources that nature provides for the human, including the temperatures of heat source and heat absorber. Therefore some investigators have reasonably proposed to name η_t not “efficiency”, but “degree of reversibility” of the heat supplied.

heat conversion process, it is necessary to arrange a flow of entropy from the hot source to the cold one like the water flow in hydraulic engines. Yet S. Carnot noted this analogy between heat and hydraulic engines. Looking now back one can not choose but regret that after the theory of thermogen as the “indestructible fluid” failed this term has never been used to describe the carrier of the heat form of motion.

4.5. Principle of Unattainable Absolute Temperature Zero (Third Law of Thermodynamics)

This fact means that the value of η_r does not depend on features of heat engine and its design perfection, but is defined by exclusively those resources that nature provides for the human, including the temperatures of heat source and heat absorber. Therefore some investigators have reasonably proposed to name η_r not “efficiency”, but “degree of reversibility” of the heat supplied.

Thorough investigation tests on substances to study their low-temperature behavior were undertaken in the early 20th century. As a result of these studies it has been found (W. Nernst, 1929) that on approaching the absolute temperature zero *the entropy of any equilibrium system in isothermal processes ceases to depend on whatever thermodynamic state parameters Θ_i and in its limit at $T=0$ accepts a value the same for all system, which may be taken zero* (I.P. Bazarov, 1991). This is mathematically expressed by the relationship:

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial \Theta_i} \right)_T = 0 . \quad (4.5.1)$$

The validity of this statement named the third law of thermodynamics is presently substantiated for all equilibrium systems. Apparent deviation from this law revealed for some substances (glycerol, CO, NO, some alloys) appeared to have been attributed to a “freezing” of them in a metastable non-equilibrium state that passed off in some (sometimes very long) time.

Practical value of the third law consists in its advanced facilitation of calculating the thermodynamic functions. Before that law stated, to calculate entropy, it was necessary to know the dependence of heat capacity on temperature and the thermal state equation. Now this has become needless, since according to the heat capacity definition

$$C_v = T(\partial S / \partial T)_V; C_p = T(\partial S / \partial T)_P \quad (4.5.2)$$

integration of these equations gives:

$$S(T,V) = \int (C_v/T)dT ; S(T,p) = \int (C_p/T)dT , \quad (4.5.3)$$

where the integration is performed from the absolute temperature zero.

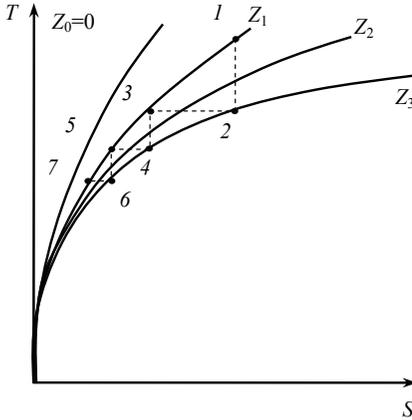


Fig.4.2. To the Law of Unattainability of Absolute Temperature Zero

Since according to the third law the entropy is finite at any temperature, the integrals (4.5.3) must be converging. From this it follows that the isochoric and isobaric heat capacities at $T \rightarrow 0$ tend to zero faster than the temperature (Einstein, 1966).

The availability of relationships (4.5.3) substantially facilitates calculating the entropy of bodies, when the dependence of their heat capacity on temperature is known.

At the same time the third law is a matter of no small theoretical consequence in the context of its interpretation as the law of unattainability of absolute temperature zero. From the positions of equilibrium thermodynamics such a conclusion may be drawn taking into consideration that on approaching the absolute temperature zero all isothermal processes are becoming simultaneously adiabatic. Hence at $T = 0$ heat exchange becomes impossible and this state can not be attained yet by the reversible heat exchange. This becomes even more evident taking into account the irreversibility of heat exchange, i.e. the provision that a temperature differential between a body and the environment is required to provide it. In this case, to attain the absolute temperature zero, bodies need to be available with a temperature below zero, which do not occur in nature. This is what W. Nernst, who did not welcome the notion of entropy, interpreted as the unattainability of absolute temperature zero.

From here it does not yet follows the impossibility of approaching the absolute temperature zero by whatever other way. It is possible to lower some potential Ψ_i (including temperature T) by varying one of the thermodynamic forces \mathbf{X}_i acting in a system. This, in particular, makes the basis for the method of attaining extremely low temperatures by the adiabatic demagnetization (V. Sychev, 1977). This method is based on the magneto-caloric effect, viz. on the phenomenon of decreasing the temperature T of magnetic material at its magnetization \mathbf{Z}_m depressing, the

decreasing rate being defined by the derivative $(\partial T/\partial \mathbf{H})_{S,p}$. At quite low temperatures this derivative reaches a noticeable value for a number of magnetic materials, which allows realizing the method offered by Debye and Gioque in 1926. Fig.4.2 explains the process by a T - S diagram. The diagram depicts a family of magnetization curves $\mathbf{Z}_m = \text{const}$. Since with the temperature decreasing, the entropy ceases depending on whatever parameters of magnetic material (including \mathbf{Z}_m), all curves at $T = 0$ converge to the same point. In this case the character of the curves themselves depends on the behavior of the heat capacity c_p of the magnetic material nearby the absolute temperature zero. Since with the temperature decreasing, the heat capacity c_p of a number of magnetic materials decreases even faster, the curves at $T=0$ have a common vertical tangent. Let point 1 ($S > 0$) on the T - S diagram characterizes the initial state of the magnetic material. Then running a single adiabatic demagnetization process (1-2) to the state $\mathbf{Z}_m = 0$ we are still quite far from the state $T=0$. However we can isothermally magnetize the material once again simultaneously removing the heat herein released to an intermediate coolant (2-3) and then repeat the adiabatic demagnetization. Iterating the process it is possible to become asymptotic to the absolute temperature zero. Temperatures of 0.001K have been reached by this way at present time. Thus one can only insist on unattainability of absolute temperature zero for a single process. In this context it is advisably to put forward one more, let us say, philosophical sanction. The unattainability of absolute temperature zero or any other generalized potential means the "indestructibility" of heat or any other form of energy at all and by whatever way. It follows from here that all known forms of energy either have always existed or were "created" for ever and aye by a disposition of Providence so that new forms of energy can not occur in nature. Antiscientific character of such a deduction is evident. Therefore, from the positions of energodynamics it is more preferable to adhere to the "asymptotic attainability" of absolute temperature zero as a result of infinite sequence of adiabatic-isothermal processes (1-2-3-4-5-6-7-etc.). From this viewpoint the heat or any other form of energy can "degenerate" under certain conditions. For the heat form of motion featuring a "symbiosis" of kinetic and potential energies of particles this can occur in two events – at infinitely high compression, when kinetic energy of all kinds of particle motion degenerates, and at infinite expansion (scattering) of particles, when potential energy of their interaction degenerates. Both events apparently occur in the Universe, which makes the extension of the thermodynamic laws to the Universe an impermissible extrapolation.

4.6. Principle of Entropy Maximum as Equilibrium Condition

The equilibrium self-non-disturbance principle is one of the primary postulates of classic thermodynamics. It reads that *an isolated system with time always comes to a state of thermodynamic equilibrium, and only an action from outside can make it out of this state*. Being a result of the experience accrued, this statement is a basis of thermodynamics as a whole and defines the limits of its applicability.

From the viewpoint of statistical physics internal equilibrium in a system corresponds to such a state of the incessantly moving micro-particles of the system which occurs most frequently and thus is most probable. From this it follows that the spontaneous transition of a system to equilibrium is not an absolute law of nature, but expresses just the most probable behavior of the system. Based on this principle, thermodynamics restricts the spectrum of the systems that may be considered as thermodynamic and leaves out of consideration the ones that develop missing equilibrium. Such systems, in particular, include microscopic objects, which never ceasing motion leads to their spontaneous deviation from the most probable state (system fluctuations). Here come also systems of galactic size, where, due to lag of interaction, instead of dying the fluctuations down their “build-up” may arise like in the regulation systems with positive (regenerative) feedback. Such systems become the subjects of energodynamics allowing for processes of “self-ordering” of a number of degrees of freedom against disordering of other ones and never coming to the total equilibrium state. However, this discipline is also rested on the statistical foundation of the collective behavior of a great number of particles (collective degrees of freedom) resulting in the macroscopic (observable) character which the microscopic motion acquires. From this it follows that the thermodynamic and statistical approaches are not alternative, but mutually complementary.

In accordance with its laws classic thermodynamics deals with transitions in-between two and more equilibrium states disregarding the kinetics of these transitions. Therefore the concept of equilibrium and equilibrium conditions are top-priorities in this theory.

The theory of system equilibrium and stability was first developed by Lagrange for mechanical systems. That was based on the virtual displacement principle. It says that a mechanical system at ideal constraints remains in equilibrium providing the sum of works done by all forces at any virtual (possible) displacement of the system is equal to zero. That theory was then extended by Gibbs to thermodynamic systems. The peculiarity of that principle as applied to thermodynamics was that depending on the conditions of the interface between a system and the environment there were several equilibrium conditions in thermodynamics instead of

one condition for mechanical systems. In particular, the condition of stable equilibrium for isolated systems means maximality of their entropy:

$$\delta S = 0, \delta^2 S < 0, \quad (4.6.1)$$

where δS , $\delta^2 S$ – respectively, first- and second-order variation of entropy. The equality of the first-order variation of entropy δS to zero means equilibrium, while the negativity of its second-order variation $\delta^2 S$ (maximality of entropy) characterizes the stability of equilibrium.

The general method of definition of equilibrium conditions set forth by Gibbs may be instantiated by a system that has, besides the thermal and the mechanical degrees of freedom, also some i^{th} degrees of freedom (related to, e.g., interchange of the k^{th} substances between the parts of the system). Let us consider a heterogeneous in whole system consisting of two homogeneous subsystems (phases or zones). Designating the parameters of these subsystems with correspondingly one or two primes let us express, according to (2.3.6), the variations of energy δS for both subsystems as:

$$\delta U' = T\delta S' - p'\delta V' + \Psi_i'\delta\Theta_i', \quad (4.6.2)$$

$$\delta U'' = T''\delta S'' - p''\delta V'' + \Psi_i''\delta\Theta_i''. \quad (4.6.3)$$

For the sake of simplicity we have only considered here one additional degree of freedom with the coordinate Θ_i and the potential Ψ_i , which, however, does not affect the generality of consideration. Since the system in whole is isolated, the variations of the extensive coordinates in (4.6.2) and (4.6.3) have the constraints imposed:

$$\delta U' + \delta U'' = 0; \delta S' + \delta S'' = 0; \quad (4.6.4)$$

$$\delta V' + \delta V'' = 0; \delta\Theta_i' + \delta\Theta_i'' = 0. \quad (4.6.5)$$

To use the principle of entropy maximality in equilibrium conditions, let us represent equations (4.6.2) – (4.6.3), allowing for (4.6.4) – (4.6.5), in the form:

$$\delta S = (1/T - 1/T'')\delta U' + (p'/T - p''/T'')\delta V' + (\Psi_i'/T - \Psi_i''/T'')\delta\Theta_i' = 0. \quad (4.6.6)$$

Since the variations $\delta E'$, $\delta V'$ and $\delta\Theta_i'$ caused by, respectively, possible heat exchange, increase of volume of one part at the expense of other and by transfer of the i^{th} energy carrier, do not depend on each other and

can take any values, the necessary and sufficient criteria of equilibrium assume the form:

$$T = T'' \text{ (thermal equilibrium);} \quad (4.6.7)$$

$$p' = p'' \text{ (mechanical equilibrium);} \quad (4.6.8)$$

$$\Psi_i' = \Psi_i'' \text{ (} i^{\text{th}} \text{- kind equilibrium).} \quad (4.6.9)$$

However the conditions of equilibrium of i^{th} sort found in such a way are fair only in the presence of thermal equilibrium (4.6.7) as otherwise they assume more difficult air $\Psi_i'/T' = \Psi_i''/T''$. It leads to a conclusion about a *special role* of thermal equilibrium. It is considered to be, that for lack of thermal balance can not come other kinds of equilibrium, for example, the material balance characterised by the termination of an exchange by k substances (R.Haaze, 1964). Meanwhile this conclusion does not prove to be true at use more the general power criteria of balance (V.Etkin, 1999). In particular, from an obvious condition (2.3.10) follows:

$$\mathbf{X}_i \equiv -(\partial E / \partial \mathbf{Z}_i) = 0. \quad (4.6.10)$$

That is equivalent to conditions (4.6.7) ... (4.6.9). Further this position will be confirmed on a number of concrete examples, testifying about discrepancy of this position to merits of case .

It is worth noticing in conclusion that the substantiation of the basic laws pertaining to equilibrium thermodynamics as consequences from thermokinetics allows to refuse their postulation and to expose the very gist of them. This makes the assumptions laid into the foundation of this theory clearer and the reasons of its inferiority more understandable. This allows outlining the ways how to generalize the classic theory and to overcome the difficulties revealed. These ways will be realized in subsequent chapters of the book.

Chapter 5

THERMODYNAMICS OF IRREVERSIBLE PROCESSES

The rise of engineering interest in phenomena at the interface between various disciplines and perception of their close relation with the phenomena of the energy dissipation led to creating, in the early 20th century, the thermodynamic theory of real process rate. This field in macroscopic physics of the 20th century was named the theory of irreversible processes (L. Onsager, 1931; I. Prigogine, 1947, 1955; H. Cazimir, 1945; K. Denbigh, 1951; S. De Groot, 1952, 1962; J. Meixner, 1954, I. Gyarmati, 1960, 1970; R. Haase, 1962, etc.). It has enriched the theoretical mind of the 20th century with a number of general physics principles and notably contributed to cognition of the in-depth interrelations between different-type phenomena. That contribution was appreciated by two Nobel prizes awarded in the field (Onsager, 1968; I. Prigogine, 1977).

However, the theory of irreversible processes (TIP) was constructed by extrapolating classic thermodynamics beyond the strict framework of applicability of its system equilibrium and process reversibility concepts. This has led the TIP to its losing the rigor and completeness intrinsic for the classic thermodynamic method. In this context it becomes a question of significant importance to provide a consistent thermodynamic substantiation of the TIP fundamentals from the more general positions of thermodynamics.

5.1. Linear Theory of Dissipation Processes Rate

More than centenary had passed before it became clear that “thermodynamics unaware of time” (to a Brian’s figurative locution) was substantially thermostatics wherein only Fourier’s, Navier’s, Ohm’s, Fick’s, Darcy’s, Newton’s, etc. equations prefigured the coming theory of non-static (running with finite rate) processes, viz. energodynamics. However, the development in that direction demanded introducing in thermodynamics the transfer concepts intrinsically extraneous for it. One of these belongs to N. Umov (1873), who wrote the law of conservation of energy in terms of the mass elements of resilient media as:

$$\partial\rho\varepsilon/\partial t + \nabla\cdot\mathbf{j}_e^0 = 0, \quad (5.1.1)$$

where ρ , ε – density of a system and its specific energy, respectively; \mathbf{j}_e^0 – local density of the energy flow across the stationary borders of the system; t – time.

The flow concept in application to entropy (G. Jaumann, 1911) became another stride. Note, that application was quite novel, because of the statistic-mechanical interpretation of entropy as a measure of state probability for which the transfer concept is absolutely senseless. G. Jaumann set forth the equation of entropy balance:

$$\partial(\rho\Sigma s)/\partial t + \nabla \cdot \mathbf{j}_s = \sigma_s, \quad (5.1.2)$$

where the specific entropy variation rate s (J/kg·K) is represented as a consequence, on the one hand, of its transfer across the system borders by the entropy flow with the density \mathbf{j}_s (W/m²·K), while, on the other hand, of availability of its internal sources with the volume density σ_s (W/m³·K). A little bit later De Donder (1927) related the entropy source σ_s with the rate of the r^{th} chemical reactions in the volume unit w_r of the system and with the affinity A_r of those reactions:

$$\sigma_s = \sum_r A_r w_r / T. \quad (5.1.3)$$

That was how the concepts of flow and process rate started their introduction into thermodynamics. The most decisive move in that direction was not, however, made, until 1931 (L. Onsager). Onsager built his theory of physicochemical process rate (he named it “quasi-thermodynamics”) based on the expression for the entropy generation rate, having thus emphasized the irreversible part of real phenomena. The entropy S of a closed adiabatic isolated system in equilibrium state is known to be maximal. If the parameters x_1, x_2, \dots, x_n (temperature T , pressure p , concentrations c_k of k^{th} substances, etc.) of non-equilibrium state differ from their equilibrium values $x_{10}, x_{20}, \dots, x_{n0}$ by a value of $\alpha_i = x_i - x_{i0}$, it is naturally to assume that the difference between the entropies of the current S and equilibrium S_0 states $\Delta S = S - S_0$ is a some function of $\alpha_1, \alpha_2, \dots, \alpha_n$. In this case the reason of the i^{th} scalar process generation (the scalar thermodynamic force X_i) and the generalized rate of this process (named by L. Onsager the flow J_i) could be found from the expression for the entropy generation rate:

$$dS/dt = \sum_i (\partial S / \partial \alpha_i) d\alpha_i / dt = \sum_i X_i J_i, \quad (5.1.4)$$

where

$$X_i = (\partial S / \partial \alpha_i); \quad J_i = d\alpha_i / dt . \quad (5.1.5)$$

Thus L. Onsager endowed the force X_i with a meaning quite different from that in Newton's mechanics and construed it as a parameter measuring the deviation of a system from internal equilibrium. At the same time L. Onsager postulated that for minor deviation from thermodynamic equilibrium any of the flows J_i obeyed the law of linear dependence on all the thermodynamic forces X_j active in the system:

$$J_i = \sum_j L_{ij} X_j . \quad (i, j = 1, 2, \dots, n) . \quad (5.1.6)$$

L. Onsager referred to those laws of relaxation processes, as well as the associated coefficients L_{ij} , as "phenomenological" (i.e. practice-based). The off-diagonal summands in expression (5.1.6) were introduced by Onsager to allow for various "superposition" (interrelation) effects of different-type irreversible processes running simultaneously in the same spatial zones.

The proof of reciprocity relationships between the "off-diagonal" phenomenological coefficients L_{ij} and L_{ji} ($i \neq j$) was most important in the L. Onsager's theory:

$$L_{ij} = L_{ji} . \quad (5.1.7)$$

These symmetry conditions are called the reciprocity relationships. They reduce the number of the coefficients L_{ij} to be experimentally defined from n (for mere empirical description) down to $n(n+1)/2$ (where n – a number of independent flows) and lead to setting up a before unknown relationship between the rates of different-type irreversible processes. L. Onsager was afterward awarded the Nobel Prize (1968) for his studies in that field. Those studies attributed to non-equilibrium thermodynamics just as much as the R. Clausius' studies to the making of classic thermodynamics. They have embodied the odds and ends of concepts and facts representing them in an accessible and understandable form. Their publication made a good start to the intensive development of the TIP in macroscopic and statistical physics. After Onsager, H. Cazimir (1945) extended the Onsager's theory to cover vector processes, having herein proved that in case the α - and β -type forces (even and odd time functions) acted simultaneously, the reciprocity relationships (6) would go over into the anti-symmetry conditions:

$$L_{ij} = -L_{ji} \quad (5.1.8)$$

A little bit later (1956-62) I. Prigogine (the 1977 Nobel prizewinner) based on Curie's symmetry law showed that in case the scalar and vector processes ran simultaneously, only the processes of the same (or even) tensor range could interact (superimpose). Insufficiency of the Onsager's postulate (see 5.1.6) was thus revealed. Besides, I. Prigogine showed that the stationary (unvaried with time) state of non-equilibrium systems was characterized by minimal rate of the entropy generation (minimal entropy production dS/dt) and corresponded to disappearance of the flows J_j subscript—similar to the non-fixed forces X_j . He also showed that the part of the entropy production $d_x S/dt$ associated with the force variation decreased as having approached the stationary state. That allowed further solving a number of problems associated with the evolution of non-equilibrium systems.

An especially rapid development of the TIP started post-World War II. The interest in that field of knowledge was caused not only by its general theoretical significance, but rather its important applications having been outlined in the forties and fifties and having involved the thermal diffusion isotope separation, the allowance for additional terms in the hydrodynamic equations for missile art and plasma physics, the development of membrane technique, biophysics, etc. Due to the resumptive studies of H. Cazimir (1945), I. Prigogine (1947, 1976), K. Denbigh (1951), S. De Groot (1952, 1962), J. Meixner (1954), I. Gyarmati (1960, 1970), R. Haase (1962), etc. this theory has become a separate field of thermodynamics with its own method and the certain spectrum of the problems to be solved.

Important investigations in this field have been carried out by domestic scientists. In particular, in 1947 M. Leontovich and L. Mandelshtamm developed a thermodynamic theory of acoustic relaxation distinguished from the Onsager's theory. L Landau and E. Livshits greatly contributed to the TIP, when showed in 1951 that under the symmetry conditions (5.1.7) the phenomenological coefficients in Onsager equation were terms of a substantially positive matrix and therefore had the constraint imposed:

$$(L_{ij} + L_{ji})^2 < 4L_{ii}L_{jj} . \quad (5.1.9)$$

Domestic scientists were among those, who much advanced practical applications of that theory to various processes, viz. chemical (Bakhareva, 1967; Bulatov and Lundin, 1984), metallurgical (Veinik, 1966; Gurov, 1978), biological (Rubin, 1984; Gladyshev, 1988, etc.), as well as a popularization of that field of knowledge (Zhukovsky, 1979; Burdakov, 1985, etc.). They especially contributed to having developed statistical methods of substantiation and construction of the linear and non-linear ir-

reversible process theory (Zubarev, 1971; Stratonovich, 1985, Kvasnikov, 1987; Bazarov, 1989, etc.).

The development of the phenomenological and statistical TIP has advanced the approximation of the heat-mass transfer theory to hydrodynamics, electrodynamics and continuum mechanics. It appeared to have been especially useful to study phenomena at interfaces between those disciplines. However, those theories never did eliminate the abovementioned line of demarcation between thermodynamics and the heat transfer theory. The reason is that the TIP is restricted to studying the dissipation processes like heat conductivity, electric conductivity, diffusion, as well as effects of their superposition, but does not deal with the processes of useful energy conversion, which are the main object of investigation in thermodynamics. This is the reason why the necessity appeared to call thermodynamics into being as a unified theory of energy transfer and conversion rate and capacity, which, unlike W. Thomson's "pseudothermostatics" and L. Onsager's "quasi-thermodynamics", would not "unfile" some part of a phenomenon, but would cover the entire spectrum of real processes.

5.2. Motive Forces and Generalized Rates of Transfer Processes

As it follows from expression (5.1.4), the selection of the motive forces X_i and the flows J_i in the TIP depends on how the expression for the entropy generation rate is broken up into separate components. The only demand herein is that the flows to be linearly independent and, at equilibrium, become zero along with the thermodynamic forces. Such arbitrariness was acceptable till the moment the different-type summands $X_i J_i$ characterized the power of the same energy dissipation processes. However, that arbitrary rule appeared to have been absolutely unacceptable in terms of the useful energy conversion processes, e.g. in biophysics, since that would lead to an equivocal assessment of the energy converter efficiency (see chapters 16, 17). Furthermore, expression (5.1.4) is inapplicable to evaluate the reversible component of the motive forces, since the reversible processes are known to have no influence on entropy (M.P. Vukalovich, I.I. Novikov, 1968; I.P. Bazarov, 1991). If, e.g., chemical reactions are described running in an ideal fuel cell (without entropy production due to thermodynamic irreversibility of chemical reactions), expression (4.1.4) gives zero value for these forces. For this reason it does not allow finding the true value of the motive forces including a reversible component. Moreover, in some instances expression (4.1.4) does not allow defining even the sign of these forces. If useful work is

done on a system, the product of the subscript-similar forces \mathbf{X}_i and flows \mathbf{J}_i appears to be always negative, whereas the value dS/dt in (4.1.4) being always positive. Furthermore, all summands of phenomenological laws (4.1.5) are always positive, whereas for useful energy conversion processes they are partly negative (the flow \mathbf{J}_i decreases as the forces \mathbf{X}_j being overcome increase). Besides, from relationship (5.1.7) some relative efficiency constraints ensue, which are alien for real energy converters. As a result of the said, the vastest spectrum of real processes with a relative efficiency above zero appeared to have been “extra vires” the TIP.

Thermodynamics allows avoiding this arbitrariness, when referring the forces \mathbf{X}_j and flows \mathbf{J}_i to the non-equilibrium state parameters, and enables finding them irrespectively of what causes them – either the dissipation or useful work done. As shown in chapter 2, any vector processes arise providing there is no internal equilibrium in a system, i.e. they are heterogeneous (M.P. Vukalovich, I.I. Novikov, 1968). This allows finding the thermodynamic forces of any nature \mathbf{X}_i as the derivatives of the system energy E with respect to the corresponding distribution moment

$$\mathbf{X}_i \equiv -(\partial E / \partial \mathbf{Z}_i), \quad (5.2.1)$$

while the flows \mathbf{J}_i – as the partial time derivatives with respect to these moments:

$$\mathbf{J}_i = \partial \mathbf{Z}_i / \partial t = \Theta_i \mathbf{v}_i. \quad (5.2.2)$$

Such a definition of thermodynamic forces univocally represents their local values \mathbf{x}_i in terms of negative gradients of the generalized potentials $\mathbf{x}_i \equiv -\nabla \psi_i$. This approach endues the thermodynamic forces with a concrete physical meaning as intensive measure of system heterogeneity. Their “global” (for a system in whole) analogs \mathbf{X}_i are herein the system-averaged values of these gradients. As shown in chapter 2, the forces \mathbf{X}_i mean the forces \mathbf{F}_i in their traditional (Newtonian) interpretation per a unit amount of the energy carrier $\mathbf{X}_i = \mathbf{F}_i / \Theta_i$, i.e. are analogs of the specific mass, volume, surface, etc. forces in hydrodynamics. Unlike them, the thermodynamic forces in the TIP may be represented as $\nabla \psi_i$, $T^{-1} \nabla \psi_i$, $\nabla(1/\psi_i)$, $\theta_i \nabla \psi / T$, etc. (De Groot, 1956). This, naturally, deprives them of an explicit physical meaning and impedes comprehension of the backbone of the phenomena occurring.

The said appertains as well to flows that may have different dimensionalities and meanings depending on the way the product $\mathbf{X}_i \cdot \mathbf{J}_i$ is broken up into cofactors. Besides, flows in the TIP are often construed (after

L. Onsager) as the generalized rates of scalar processes $v_i = d\Theta_i/dt$, e.g. of chemical reactions. Thermodynamics “restitutes” the general physical conception of flow as a vector value thus allowing to distinguish it from the generalized rate v_i of scalar process not only physically, but also analytically.

5.3. Entropy Balance Equation and Dissipation Rate

The core of the TIP comprises the balance equations for mass, momentum, charge, angular momentum and energy of multi-component systems, which allow further determining the entropy balance and finding from this the motive forces and generalized rates for a system under consideration. Setting up these balance equations is the most burdensome and laborious part of the TIP and its applications, especially taking into account that each of the equations mentioned has a local (spatial)

$$\partial \rho_i / \partial t + \nabla \cdot \mathbf{j}_i^{\circ} = \sigma_i \quad (5.3.1)$$

and a substantial (material) form :

$$\rho d\theta_i/dt + \nabla \cdot \mathbf{j}_i = \sigma_i, \quad (5.3.2)$$

where $\mathbf{j}_i^{\circ} = \rho\theta_i\mathbf{v}_i$, $\mathbf{j}_i = \rho\theta_i(\mathbf{v}_i - \mathbf{v}_o)$ – density, respectively, of local and substantial flow of the field value Θ_i ; \mathbf{v}_i , \mathbf{v}_o – transfer velocity, respectively, of the Θ_i value and selected volume element in the stationary (laboratory) coordinate system; σ_i – density of internal source for the value Θ_i .

To set up such balance equations for a particular field value Θ_i , thorough knowledge of an applicable scientific discipline is necessary, which should precede the associated TIP application. Naturally, one can hardly expect some corrections to such disciplines would be done.

Next step toward a TIP application denotes setting up energy balance equations – for both kinetic (translation and rotation) and potential (mechanical, electromagnetic, chemical, etc.) energies in some form or other (spatial or material). These equations are similar to expressions (5.3.1) and (5.3.2) except that θ_i , \mathbf{j}_i° , \mathbf{j}_i and σ_i are construed as specific values of a relevant energy form, densities of their flows and internal sources (if applicable). Since classic thermodynamics does not operate in terms of time as a physical parameter, the above data is also entirely taken from outside, viz. from applicable scientific disciplines. Only then thermodynamics proper starts off with using the joint equation of the first and sec-

ond laws of classic thermodynamics for open systems in the form of the Gibbs relationship (see 2.5.1). Using it for irreversible processes under investigation is based on the local equilibrium hypothesis which assumes this equation to be true locally (for continuum elements) despite the gradients of various potentials presenting in the elements and the irreversible processes running in them (internal sources of the entropy σ_s presenting there). From joint consideration of equation (2.5.1) and the abovementioned balance equations for mass, momentum, charge and angular momentum the energy balance equation is formulated, which, due to the above, now includes time and an irreversible part can be derived from it. This part formally looks like equation (2.5.1) that contains the sources of all actual values. This is the entropy balance equation that is formulated based on it relating the density of the entropy internal sources σ_s with the generalized rates of scalar and vector processes w_i and \mathbf{j}_i and their motive forces A_r and \mathbf{x}_i . Along with the entropy increase rate in a system the dissipation function $T\sigma_s$

$$T\sigma_s = \sum_i \mathbf{j}_i \cdot \mathbf{x}_i + \sum_r A_r w_r, \quad (5.3.3)$$

is often used, defining the energy dissipation rate in the system.

Next step denotes the formulation of Onsager's (5.1.6) kinetic equations (phenomenological laws) for particular processes under investigation. These equations are then considered jointly with Onsager's symmetry conditions (5.1.7) or (5.1.8) in order to define the relationship between the flows \mathbf{j}_i and \mathbf{j}_j arising from the static character of irreversible processes. The last investigation stage reveals the expressions for the so-called "stationary superposition effects" associated with disappearance of one of the actual flows \mathbf{j}_i while the system non-equilibrium state maintained.

As it follows from the above, the superposition effect definition based on the TIP is a quite complicated multi-stage problem involving the whole intellectual arsenal of special disciplines. This makes energetics even more attractive as a short cut method of finding a solution to the problem. This becomes possible due to the fact that the thermodynamic equations of (2.3.1) type already contain time, flows and thermodynamic forces and, therefore, do not need setting up complicated mass, charge, momentum, energy and entropy balance equations. These equations eliminate whatever arbitrariness in choosing the physical values defining motive forces and generalized rates of scalar and vector processes. Their meaning and analytical expression are unequivocally determined by choosing the coordinate Θ_i as a quantitative measure of a particular energy form carrier. In this case the thermodynamic forces, according to (2.2.8), are expressed in terms of negative gradients of the

generalized potential Θ_i -related, while the flows \mathbf{J}_i or \mathbf{j}_i – by the product of these values and the rate of their transfer under the action of the forces \mathbf{X}_i or \mathbf{x}_i . Applications of this method to various problems will be specifically instantiated in the chapters following hereafter. Other advantages of this approach will simultaneously become evident.

5.4. Phenomenological Laws of Transfer Processes

The Onsager's assumption that the around-equilibrium generalized rate of a relaxation process (he named this rate the flow J_i) is a linear function of all thermodynamic forces X_j acting in the system (L. Onsager, 1931) is one of the postulates lying in the TIP foundation. This statement named the linearity law is reflected in Onsager's phenomenological laws (see 5.1.6).

Such a (matrix) form of kinetic equations differed from Fourier's, Ohm's, Fick's, Darcy's, Newton's, etc. laws by the presence of additional (off-diagonal) terms (with subscripts $j \neq i$). L. Onsager introduced those terms to allow for the interrelation between different-type phenomena, which he had found experimentally and explained by the "superposition" of different-type flows. He expressed that interrelation in his well-known "reciprocity relationships" which stated the symmetry of the phenomenological coefficients matrix (see 5.1.7).

L. Onsager obtained those relationships based on a known statement of statistical mechanics regarding the reversibility of micro-processes in time under the assumption that the coefficients L_{ij} and L_{ji} were constant, while the subscript-dissimilar flows J_i and J_j were linearly independent and became zero with disappearance of the forces X_i and X_j .

The above postulate was not objected to for more than a half a century and was reproducible in all study guides on irreversible process thermodynamics but with a proviso that according to Curie's symmetry law only processes of the same (or even) tensor order could be interrelated. The question did not anyhow arise in that context how the flows J_i and J_j found to (5.1.4) as the time derivatives of the system independent state parameters $d\alpha_i/dt$ could be interrelated. There were no objections either to the fact that some (moreover the simplest) equations appeared to have been laid as a foundation of the thermodynamic theory which was known to have imported particular data on system properties (expressed in terms of state and transfer equations) "from outside" as uniqueness conditions of a kind while its body of mathematics itself was universal as based on the properties of exact differential of a number of functions of state. The investigators were not at all embarrassed either by the fact that the above postulate undermined the centuries-old buttress of mechanics

which stated that each independent process (movement, acceleration, tending to mechanical equilibrium, etc.) was associated with the only (resultant) force and ceased as soon as the force disappeared. Meanwhile, the existence of such a force followed from those equations of anisotropic heat conductivity and electric conductivity which, to Onsager's confession, prefigured his phenomenological laws. In fact, for anisotropic heat conductivity and electric conductivity the motive forces \mathbf{X}_j were components of the only force – the negative temperature gradient vector ∇T and the electric field intensity \mathbf{E} ($j = 1,2,3$), respectively. There were also other reasons to doubt the Onsager's postulate was adequate to the point. L. Onsager and his followers, based on equations (5.1.6), derived numerous thermo-mechanical, thermo-electrical, thermo-diffusive, etc. effects from the interrelations between the generalized rates of irreversible processes ran in the same spatial zones, i.e. from the “superposition of flows” or their “mutual entrainment” (N. Bulatov, A. Lundin, 1984). Meanwhile, the above effects are known to reach maximum in the so-called stationary states, when the flows not fixed by an external constraint disappear and, therefore, evidently can not superimpose on those remained. E.g., in electrolytic solutions, where electric conductivity and diffusion phenomena take place, the electric potential difference (Kwinke effect) is maximal whenever current ceases (R. Haase, 1967). This is the case with the Soret effect – arising gradient of the k^{th} substance concentration in a system initially homogeneous with the temperature gradient building up, the concentration gradient reaching maximum as soon as diffusion flows disappear. Hence the reason of such superposition effects should have been searched from the very first not in the interaction between independent flows, but in the superposition of unlike forces as it takes place in mechanics and electrodynamics. Furthermore, the laws (see 5.1.6) L. Onsager named “phenomenological” (i.e. practice-based) are really not so. First of all, the coefficients L_{ij} in Fourier's, Ohm's, Fick's, etc. laws depend on the state parameters of a system (its temperature, pressure, composition, etc.), i.e. are inconstant, whereas the requirement the coefficients L_{ij} to be constant is a substantial part of Onsager's linearity law and bears a principal character. In fact, the forces X_i in the Onsager's theory are functions of the system parameters (temperature T , pressure p , concentration c_k , etc.), therefore the dependence of the coefficients L_{ij} on them would mean their dependence on also the forces X_j , i.e. non-linearity of the phenomenological laws (5.1.6).

Furthermore, according to practice many phenomena arise only when the force reaches some “threshold” value \mathbf{F}_{j_0} depending on the activation energy for a process under consideration (see chapter 2). However, this circumstance can not be allowed for in Onsager's laws since in this case the flows J_i would disappear earlier than the forces X_i become zero.

Lastly, the terms of equation (5.1.6) not necessarily always have the same sign – in many cases the process rate (flow J_i) decreases with increase of the force X_j “being overcome” in this process. So are, as it will be hereafter shown, the phenomenological laws of all processes involving useful energy conversion.

All the said means that Onsager’s kinetic laws are not phenomenological, while his postulate itself does not hold water. This nothing but enhances interest toward finding their allowable form proceeding from the demands thermodynamics imposes on the uniqueness conditions of transfer processes. It is easy to show then that the so-called Onsager’s phenomenological laws are just a particular case of thermodynamic kinetic equations (2.6.10), when the coefficients K_{ij}^{cp} do not depend on the variables Θ_j, \mathbf{F}_j . As a matter of fact, introducing the thermodynamic force $\mathbf{X}_i \equiv \mathbf{F}_i/\Theta_i$ instead of \mathbf{F}_i and assuming $\mathbf{F}_{j0} = 0$ gives:

$$\mathbf{J}_i = \sum_j L_{ij} \mathbf{X}_j, \quad (i, j = 1, 2, \dots, n_j) \quad (5.4.1)$$

where $L_{ij} = \Theta_j K_{ij}$ – constant coefficients L. Onsager named “phenomenological”; \mathbf{j}_i – density of the flow \mathbf{J}_i ; \mathbf{x}_i – specific (per unit of the Θ_j value being transferred) thermodynamic forces \mathbf{X}_i in their “energy” representation (in terms of generalized potential).

The same laws may be expressed as functions of the flows \mathbf{J}_j и \mathbf{j}_j :

$$\mathbf{X}_i = \sum_j R_{ij} \mathbf{J}_j \quad \text{or} \quad \mathbf{x}_i = \sum_j R_{ij} \mathbf{j}_j, \quad (5.4.2)$$

where R_{ij} – resistance coefficients inverse to the conductivity coefficients L_{ij} .

As one can see, they actually integrate the thermal Θ_j and the kinetic K_{ij} factors. This is the reason why the coefficients L_{ij} or R_{ij} can be referred to neither state parameters nor mere kinetic coefficients (R. Haase, 1967, S.R. De Groot, R. Mazur, 1964, etc.). The values of these coefficients for a particular system are determined experimentally or, as the simplest case, based on statistical theories.

Representation of the phenomenological laws in the form of (5.4.2) allows generalizing the concept of inertia to non-mechanical processes. If to write Newton’s law $\mathbf{F} = M\mathbf{a} = d\mathbf{P}/dt$ in the same form of (5.4.2) substituting \mathbf{F}/M for \mathbf{x}_m and the acceleration $\mathbf{a} = d\mathbf{v}/dt$ for \mathbf{j}_m (i.e. to represent the acceleration of a body as the generalized rate of its momentum variation process), then Newton’s second law will appear to be a particular case of phenomenological laws (4.4.2), where the off-diagonal coefficient $R_{ji} = M$. In this case the mass M as a measure of inertia of a system takes a meaning of *one of the coefficients of resistance the system offers to running a relevant process (in this case the acceleration process)*. Thus

the concept of *inertia* as a measure of resistance a system offers to a process running in it acquires the general physics meaning.

5.5. Reciprocal Relation in Transfer Processes

As it has already been mentioned above, the substantiation of reciprocity relationships (5.1.7) was one of the most important statements of the Onsager's theory of irreversible processes (TIP). To substantiate them, he had to apply to the fluctuation theory, microscopic reversibility principle and additional postulate on linearity of the fluctuation damping laws. These three statements outstep the framework of thermodynamics. Therefore in the phenomenological TIP reciprocity relationships (5.1.7) are usually adopted as an additional primary postulate sometimes named (after D. Miller) the "forth law of thermodynamics".

At present statements often and often occur that these relationships do not need any thermodynamic proof since they are statistically substantiated. Discussions about the L. Boltzman's and J. Gibbs' statistical theories, "which grounds are obscure in many ways" (R. Cubo, 1970), are seemingly sunk into oblivion. So, one of the basic statements of statistical mechanics regarding the system ergodicity ¹⁾ has remained a hypothesis so far. By the early nineties of the 20th century as a result of the critical analysis conducted on the body of mathematics of statistical mechanics, as well as a result of digital experiments on high-performance computers, it became clear that only hypothetical systems of non-interacting particles might be ergodic. Interaction between particles (e.g. Coulomb or Van der Waals forces) leads to losing ergodicity, therefore the real systems of interacting particles should be described not by statistical, but dynamic methods.

The fact that these reciprocity relationships often vindicate their validity far beyond the restrictions imposed by the method itself of their substantiation evidences the means of proving the relationships L. Onsager offered are inadequate to the point. In fact, the microscopic reversibility principle with one of its statement about equal rates of any direct and reverse molecular processes is valid, strictly speaking, for only equilibrium states. This principle is indubitably inapplicable to the processes of transfer from one non-equilibrium state to other because a system returns to equilibrium state just because the frequency and amplitude of the

¹⁾ The system is referred to as ergodic, where space averaging of a physical value gives the same result as time averaging.

micro-processes running toward equilibrium dominate. Therefore the reciprocity relationships, providing these really vindicate the principle above, should have been valid in close proximity to the equilibrium state and violated more and more as the system was withdrawing from it. Meanwhile, as it will be instantiated for the helium and argon interrelated filtration and diffusion processes in graphite membranes, to vindicate the reciprocity relationships, just a partial equilibrium is enough, when just a part of the processes running in a system ceases.

Another weak point has been an assumption that the microscopic laws of fluctuation damping obey the same linear phenomenological laws (5.1.6) as the macroscopic processes of heat, substance, charge, etc. transfer. Meanwhile, the real laws of fluctuation damping demonstrate rather exponential character. Even kinetic equations (5.1.6) are, strictly speaking, non-linear. This is especially evident for Fourier's, Ohm's, Fick's, Darcy's, Newton's, etc. laws written in the integral form (in terms of the temperature T , pressure p , concentration c_k , etc. differentials), when the proportionality factors appear to be dependent on the temperature, pressure, concentration, etc. fields.

Lastly, should the linear laws be really necessary to prove the reciprocity relationships, the latter would be violated each time whenever the phenomenological laws cease to be linear. However, as it will be shown hereafter, the reciprocity relationships may be valid as well for the systems, where only the off-diagonal terms of equations (5.1.6) describing the superposition effects are linear. As a result, both the Onsager's theory and TIP in whole fail to reach those rigor and completeness which are intrinsic for the classic thermodynamic method. Therefore C. Truesdall (1975) was positively right, when confirmed that *"once the reciprocity relationships are valid, then the possibility of their merely phenomenological deduction should as well exist"*. Let us show that the Onsager's symmetry conditions ensue directly from the differential relationships of thermodynamics. It follows from independence of the second derivative of the system energy U with respect to the coordinates Z_i and Z_j :

$$(\partial Z_i / \partial X_j) = (\partial Z_j / \partial X_i). \quad (5.5.1)$$

These equalities remain valid as well after deriving the total derivatives of both parts with respect to the time t :

$$d(\partial Z_i / \partial X_j) / dt = d(\partial Z_j / \partial X_i) / dt. \quad (5.5.2)$$

In the stationary redistribution processes (at Θ_j , $X_i = \text{const}$) the time differentiation involves only the coordinates Z_i , Z_j . Their time derivatives

in the absence of the transfer (recharging) and reorientation processes ($\Theta_i, \varphi_i = \text{const}$) define the flows J_i and J_j . Allowing for this and changing in (5.5.2) the sequence of differentiation with respect to the time t and forces X_j, X_i , gives:

$$(\partial J_i / \partial X_j) = (\partial J_j / \partial X_i). \quad (5.5.3)$$

These equations may be well referred to the differential reciprocity relationships between flows and forces (V. Etkin, 1991, 1999). They state the cross-impact balance among different-type flows and their motive forces and therefore may be rather named the *reciprocal* relations than the symmetry conditions of phenomenological coefficients matrix (5.1.7). This statement is reasonable to be called for easy reference as the **reciprocal principle**: *dissimilar processes simultaneously running in the same domains of a space exert the equal influence on each other*.

Risselberghe (1962) was the first who postulated the existence of such-type relationships and proposed to name them the “generalized reciprocity relationships”. This is justified since the above Onsager’s symmetry conditions may be obtained as a corollary of these relationships for a particular case of linear systems. In fact, applying (5.5.3) to equations (5.1.6) one can obtain:

$$(\partial J_i / \partial X_j) = L_{ij} = (\partial J_j / \partial X_i) = L_{ji}. \quad (5.5.4)$$

Thus the Onsager’s reciprocal relations (symmetry conditions) ensue as a corollary of more general differential relationships of thermodynamics and do not need involving whatever statistic-mechanical considerations. Though attempts to substantiate these relationships were made time and again (Gyarmati, 1958, 1960; Li, 1958, 1988; Pitzer, 1961; Risselberghe, 1962), they failed till the lacking coordinates of redistribution processes were introduced. Note, relationships (5.5.3) do not impose any constraints on the process irreversibility degree and the system remoteness from equilibrium. They do not depend either on particular form of the state or transfer equations and, as it will be shown hereafter, are equally applicable to reversible and irreversible processes.

It is worth particular mentioning that from the positions of thermodynamics Onsager’s symmetry conditions (5.1.7) are valid as well in the case, when only additional (off-diagonal) terms of equations (5.1.6) are linear, i.e. only the “cross” coefficients L_{ij} or L_{ji} ($i \neq j$) are constant. This significantly extends the applicability of the differential reciprocity relationships once the diagonal terms of the matrix comprising the phenome-

nological coefficients L_{ii} or L_{jj} may remain herein any functions of the thermodynamic forces X_i or X_j subscript-similar to them. This is what Fourier's, Fick's, Ohm's, Darcy's and Newton's laws are. As for the additional (off-diagonal) terms, these describe less order infinitesimals and in a number of cases may be considered as linear. Thus approaching the problem from the positions of thermodynamics reveals excessiveness of the demand the coefficients L_{ii} or L_{jj} in equations (5.1.6) be constant, which is substantial in all preceding theories of irreversible processes. The demand of close proximity of the system to equilibrium Onsager has laid down in his theory appears to be the same excessive. In fact, the symmetry conditions (see 5.1.7) ensuing from the differential reciprocity relationships (see 5.5.3) are valid for arbitrary large values of the forces X_i or X_j in the diagonal terms of the phenomenological laws. This is what explains why the Onsager's theory appears to be applicable far beyond the restrictions imposed by the method itself of their substantiation.

Finally, according to (5.5.4) symmetry conditions (5.1.7) may give place to the anti-symmetry conditions $L_{ij} = -L_{ji}$ (named the Cazimir's relationships in the TIP) providing the terms in equation (4.1.6) have opposite signs. This occurs, when in a transfer process the flow J_i or J_j is directed against the forces X_j or X_i , i.e. "overcomes" them. Such are, in particular, all energy conversion processes, where energy source works against loads. This manifests itself in the occurrence of the so-called "no-load conditions", when with increase of the force X_j or X_i being overcome the flow J_i or J_j becomes zero. A demonstrative example to the case is loss of the secondary current in the welding transformer with arc extinction. The above statement as well outsteps the TIP, where laws (5.1.6) were postulated by Onsager with only the same sign for all terms.

Thus the reciprocity relationships do not need assumptions on close proximity of a system to equilibrium, constancy of all phenomenological coefficients and linearity of the fluctuation damping laws, which are laid in the foundation of their statistic-mechanical substantiation. According to the above, they ensue from the first laws of thermodynamics and, therefore, feature universal character. This enhances the heuristic value of these relationships and makes them a reliable tool to analyze the interrelations between different-type processes in the real world.

5.6. Law of Minimum Entropy Production

The insufficiency of formalism intrinsic for the linear TIP has caused numerous attempts to give other – variational statement of non-equilibrium thermodynamics. Calculus of variations is a quite universal

mathematical method that allows, subject to a suitable model selection, detailing a process under investigation and deriving the associated math laws (including the transfer equations) based on the only variational principle. However, these principles themselves need their substantiation, while their corollaries each time have to be experimentally checked.

L. Onsager set forth the first variational principle of non-equilibrium thermodynamics (1931). He took note of the fact that for the dissipation processes ($J_j = J_j^p$) his phenomenological laws

$$X_i = \sum_j R_{ij} J_j^p \quad (i, j = 1, 2, \dots, n), \quad (5.6.1)$$

(where $R_{ij} = L_{ij}^{-1}$ – resistance coefficients inverse to the phenomenological conductivity coefficients L_{ij}) along with the reciprocity relationships

$$R_{ij} = R_{ji} \quad (5.6.2)$$

are equivalent to the statement that the expression $\sum_j X_i dJ_j^p$ is the exact differential of some potential function $\Phi(J_i^p, J_j^p) = \frac{1}{2} \sum_j R_{ij} J_i^p J_j^p$, the first derivatives of which with respect to the flows J_j^p give linear phenomenological laws (5.6.1), while the mixed derivatives ($\partial^2 \Phi / \partial J_i^p \partial J_j^p$) give reciprocity relationships (4.6.2). The function $\Pi_X(X_i, X_j) = \frac{1}{2} \sum_j L_{ij} X_i X_j$ features the same properties, which leads to phenomenological laws (5.1.6) and reciprocity relationships (4.1.7). In linear systems the functions $\Phi(J_i, J_j)$ and $\Pi_X(X_i, X_j)$ are equal to half the dissipation function $P = T\sigma_s$,

$$\Phi_J(J_i^p, J_j^p) = \Pi_X(X_i, X_j) = \frac{1}{2} P \quad (5.6.3)$$

and are named the local dissipation potentials (expressed in terms of flows and forces, respectively).

It is easy to make sure that the variation of the potentials $\Phi_J(J_i^p, J_j^p)$ and $\Pi_X(X_i, X_j)$ with respect to flows at all forces X_j being constant gives the same value of X_j so that the extreme condition is met:

$$\delta[Y(X_j, J_j^p) - \Phi_J(J_i^p, J_j^p)]_{X_j} = 0, \quad (5.6.4)$$

where δ – variation symbol; the subscript to the function being varied denotes the value remaining constant at variation.

The extreme determined by (4.6.4) can be only the maximum owing to positive determinacy of the dissipation potentials. Therefore L. Onsager named statement (5.6.4) the “principle of least energy dissipation”.

Another form of the same principle was later offered by I. Gyarmati (1974) for the functional $Y(X_j, J_j^p) - \Pi_X(X_i, X_j)$ expressed in terms of forces at constant flows:

$$\delta(Y - \Pi_X) = \sum_j (J_j^p - \partial\Pi/\partial X_j) \delta X_j = 0. \quad (5.6.5)$$

I. Gyarmati further merged both forms of that principle in a single variational condition:

$$\delta(Y - \Phi_J - \Pi_X) = 0, \quad (5.6.6)$$

where variation may be conducted with respect to both forces and flows. This condition reflects the extremity of the so-called ‘‘Onsager-Machlup’s function’’ (the expression in brackets) and includes all statements of Onsager’s ‘‘quasi-thermodynamics’’.

A number of other variational principles convenient for particular applications were offered by G. Tzigler (1966). As I. Bakhareva then showed (1967), all the said variational principles could be obtained by simple transformations of the same expression:

$$\sum_j (\partial\Phi_J / \partial J_j^p - X_j) \delta\alpha_i = 0. \quad (5.6.7)$$

This eliminates the necessity to provide thermodynamic substantiation for each of the principles mentioned – it is enough to substantiate the validity of condition (5.6.7). This may be done based on some (linear or non-linear) phenomenological laws. In fact, whereas differential reciprocity relationships (5.5.3) do not depend on character of these laws, the differential form

$$\sum_j J_j^p dX_j = d\Pi_X \quad (5.6.8)$$

is always the exact differential of the dissipation function Π . Applying the Legendre transformation, it can be easily shown that the expression $\sum_j X_j dJ_j^p$ is as well the exact differential of other function of state of the non-equilibrium system Φ . From this it follows that $\partial\Phi/\partial J_j^p = X_j$. Expression (4.6.7) is thereby valid with the same generality degree, i.e. not only for linear systems, but also in a more general case, when the differential reciprocity relationships are valid. In this case $P = \Phi_J + \Pi$ even when $\Phi_J \neq \Pi_X$.

The law of *minimum entropy production* occupies a special place among the TIP extreme principles. Its first statement belongs to I. Prigogine (1947) and refers to discontinuous systems. According to the Prigogine-proven theorem the minimal production of entropy $\sigma_s = \min$ in a sta-

tionary-state system with the constant forces $\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_k$ ($k < m$) corresponds to the state, where flows with the indices $j = k+1, k+2, \dots, m$ disappear. The alternative statement of this law for continuum systems reads that in the stationary state compatible with the external constraints the dissipation function P is minimal:

$$P = \int T \sigma_s dV = \sum_j \int \mathbf{X}_j \cdot \mathbf{J}_j^p dV = \min; \quad \delta P = 0. \quad (5.6.9)$$

This statement is usually substantiated involving linear phenomenological laws (5.4.1) and the Onsager's reciprocity relationships and is, therefore, considered valid for only the systems being in close proximity to equilibrium. From the positions of thermodynamics this law acquires a more general character. According to the evolution criterion (see 4.6.6) it is quite evident that if an external force prevents a system from reaching equilibrium, the system comes to a halt in the minimal-dissipation state. Using flow balance equation (2.4.8) the condition of inergy constancy for a stationary-state system may be written in the form:

$$dU_i/dt = -\int \mathbf{x}_i \cdot (\mathbf{j}_i^e + \mathbf{j}_i^p) dV = 0, \quad (5.6.10)$$

From this it directly follows that if some of the external flows \mathbf{j}_i^e supporting the stationary state ($\mathbf{x}_i = \text{const}$) disappears ($\mathbf{j}_i^e = 0$), the subscript-similar relaxation flow \mathbf{j}_i^p also disappears along with the associated component of the dissipation function P . This statement does not depend on character of the phenomenological laws and is so evident that hardly needs some theorems to be proved.

Thus all basic statements of the current linear TIP may be obtained as deductions of thermodynamics without appeal to whatever postulates and hypotheses. This makes superfluous formulating complicated balance equations for mass, charge, momentum, energy and entropy, which has always been the most time-consuming part of the theory. It is not less important that such an approach excludes the necessity for preliminary and thorough knowledge of a number of fundamental disciplines to formulate the balance equations. This allows one to solve problems being not overburdened with hardened paradigms and dogmas associated with these problems. Furthermore, this approach opens up new possibilities to subsequently overcome the profound narrowness of non-equilibrium thermodynamics that is restricted to only linear systems and close-to-equilibrium states.

Chapter 6

HEAT-MASS TRANSFER THEORY

The development of the theory of irreversible processes (TIP) has created the prerequisites for a cardinal rapprochement between thermodynamics and the heat-mass transfer theory. Firstly, this theory has from the very beginning operated with the heat-mass transfer concepts: fields (both stationary and non-stationary), energy flows (including heat), gradients of potential (temperature), uniqueness conditions, etc. Secondly, energodynamics is based on the equations of a more general form, from which the equations of heat conductivity, electric conductivity, diffusion, etc. ensue as a particular case. Thirdly, it also uses the balance equations for extensive values and expresses their sources in terms of the measurable parameters of a system. In a word, the TIP already contains the whole arsenal of tools necessary to describe and investigate the heat-mass transfer processes. Energodynamics spreads still further and allows obtaining all statements of this theory essentially from thermodynamic. Therefore the TIP fundamental principles, laws and equations are most advisable to be stated from the positions of energodynamics.

6.1. Elimination of Strange Delimitation of Thermodynamics and the Heat Exchange Theory

No sooner had the heat theory appeared, it immediately separated into two directions. In 1822 a known J. Fourier's work appeared, which laid the foundation of the heat transfer theory; in 1824 not less famous S Carnot's work laid the foundation of thermodynamics. Both works were based on the afterward-rejected theory of thermogen as the indestructible fluid, both considered temperature as some potential which gradient conditioned the heat transfer direction or conversion of heat into ordered forms of energy. However only Fourier operated with time as a physical parameter, and that left an imprint on the whole further development of those theories. The concept of entropy introduced by R. Clausius in 1850-1865 as the coordinate of reversible heat exchange and the S. Carnot's method of reversible cycles widely used in thermodynamics connected thermodynamics for a long time with the concept of equilibrium and quasi-static character (infinitesimal rate) of processes under investigation as the condition of their reversibility. A lot of time had passed before it

became evident that “timeless” thermodynamics (to Brayan’s locution) was substantially thermostatics.

Meanwhile the J. Fourier’s ideas were running their course. Yet in 1822 the L. Navier’s work appeared having laid the foundation of hydrodynamics of viscous liquids, G. Ohm derived his famous law in 1827, A. Fick set forth the diffusion equation in 1855. Those equations and the like described kinetics of momentum, charge, substance, etc. transfer. However both directions mentioned developed quite independently without any points of contacts. Their difference showed not only in terminology, but it rather rooted in a basic methodological nature. Carnot-Clausius’ thermodynamics maintained aloofness from the transfer ideas and the heat exchange rate concept. The heat exchange theory, on the contrary, had nothing to do with the conversion of heat into other forms of energy and considered entropy as an extraneous concept. The so “fancy separation of two directions within the same area in macroscopic physics” (to K. Denbigh’s locution) was too hard to be overcome by the TIP as well. Even today the definition of heat concept remains different in thermodynamics and the heat exchange theory. In thermodynamics this is the part of energy exchange caused by exclusively the temperature difference between bodies and not associated with substance exchange between them (Thermodynamics. Terms, 1973). The heat exchange theory, on the contrary, considers heat as the part of internal energy associated with random motion (because a system can exchange just what it has) and studies, along with heat conductivity, the heat transfer carried out by substance and enabled by heterogeneity of the fields of other physical values (Heat Transfer. Terms, 1980). Such a situation demands searching more cardinal means to unify the two said fundamental disciplines.

6.2. Conductive Heat Exchange

The heat exchange processes may be classified into three classes: conductive, convective and radiant heat transfer. The conductive heat transfer (heat conductivity) features the absence of observable (macroscopic) motion in a heat conductive medium with direct contact between bodies or parts of a body having different temperatures. The basic law of heat conductivity was stated, as it has been already mentioned, by J. Fourier having proceeded from interpreting heat as the indestructible fluid. According to this law the heat flow density \mathbf{j}_q is directly proportional to the temperature gradient ∇T reversed in sign:

$$\mathbf{j}_q = -\lambda \nabla T, \quad (6.2.1)$$

where λ (W/m·K) – proportionality factor named coefficient of heat conductivity.

Classic thermodynamic interprets the heat flow as a conductive (not associated with the substance transfer) flow of the internal energy u with the density \mathbf{j}_q . Here the coordinate of a heat transfer process is construed as the entropy S . Therefore it is more correctly, from the positions of ergodynamics, to refer to rather the entropy flow with the density $\mathbf{j}_s = \mathbf{j}_q/T$ than to a heat flow. In this case Fourier's law for stationary heat conductivity directly ensues from kinetic equations (2.6.11) written down in the local form:

$$\mathbf{j}_s = L_s \mathbf{x}_s, \quad (6.2.2)$$

where $\mathbf{x}_s = -\nabla T$ – motive force of the process; $L_s = \lambda/T$ – coefficient that should be rather named coefficient of *entropy conductivity*. Note that the “thermokinetic” form of heat conductivity law representation (see 6.3.1) is much closer to the original form (see 6.3.1) than the one ensuing from Osager's laws, where the thermodynamic force is used in the form of $\mathbf{x}_q = T^{-1}\nabla T$ or $\mathbf{x}_q = \ln T$ even when choosing the heat flow \mathbf{j}_q as the generalized rate of the process.

The differential equation of non-stationary heat conductivity ensues from ergodynamics equally as directly. It is enough just to use the balance equation for the arbitrary field specific value θ_i of generalized form (6.3.1) assuming there $\theta_i \equiv u$ and $\sigma_i \equiv \sigma_q/T$. Using the definition of the specific heat at constant volume (isochoric) $c_v \equiv \partial u/\partial T$ in the absence of mass transfer and work (i.e. at constant ρ и c_v) one can find:

$$\rho c_v \partial T/\partial t + \nabla \cdot \mathbf{j}_q = \sigma_q. \quad (6.2.3)$$

This expression is the most general form of the differential equation of heat conductivity valid for both linear and non-linear processes. It is available in a more ordinary form if considered jointly with (6.2.1) assuming constant λ and introducing, to shorten the formula, the thermal diffusivity $\alpha_q = \lambda/c_v\rho$:

$$\partial T/\partial t = \alpha_q \nabla^2 T + \sigma_q/\rho c_v. \quad (6.2.4)$$

This equation relates the heating rate of a body directly proportional to the temperature field and heat sources in it. The latter is very important as allowing for chemical reactions running in a heat-conductive medium (see 6.1.3), high-frequency and induction (eddy-current) heating, friction, etc., i.e. the availability of any entropy sources σ_s .

Just like other differential equations of energodynamics, expressions (6.2.3) and (6.2.4) describe the entire group of the like phenomena. To extract a process under investigation from this entity and to completely describe it mathematically, it is necessary to take into consideration particular properties of the object. These are defined by uniqueness conditions including for a general case of non-stationary processes the initial, geometrical, physical and boundary conditions (including the initial temperature distribution, body configuration and size, body thermo-physical properties, surrounding relations, etc.). The problem thus stated is solved by either analytical, or numerical, or theoretical-experimental methods with an appeal to the heat exchange phenomena similarity theory. These methods are considered in special disciplines (A. Lykov, Y. Mikhailov, 1963).

6.3. Convective Heat Exchange and Transfer

Convective heat exchange (or heat transfer) is usually understood as a heat exchange between a moving medium and a stationary one without a substance exchange between them. This process is always accompanied by heat conductivity dominating nearby the stationary surface. Therefore the basic law of convective heat exchange may be derived based on the same kinetic equations of energodynamics in the form of (6.2.2) substituting herein the coefficient of heat conductivity λ for some empirical value α multiplied by the thickness $\delta_r = \Delta n$ of the thermal boundary layer of liquid (i.e. the liquid layer within which the liquid temperature varies from the wall temperature T_c to the temperature T_w of the bulk liquid flow). Taking into account that in stationary conditions $T_w = T_w(\mathbf{n})$, i.e. depends on only the normal coordinate \mathbf{n} to the heat exchange surface, and substituting on this basis $\nabla T \equiv \partial T_w / \partial \mathbf{n}$ for $dT_w / d\mathbf{n}$ expression (6.2.1) may be represented thru separation of variables in the form:

$$dT_w = (\mathbf{j}_q \delta_r / \alpha_q) d\mathbf{n}. \quad (6.3.1)$$

Integrating this with respect to δ_r one can find:

$$\mathbf{j}_q = \alpha_q \Delta T, \quad (6.3.2)$$

where $\alpha = \lambda / \delta_r$ (W/m²·K) – proportionality factor having been referred to as heat transfer coefficient; $\Delta T = (T_w - T_c)$ – thermal head. The further problem comes down practically to the definition of how this coefficient

depends on various factors, viz. liquid properties, liquid flow pattern, body configuration and streamline, etc.

Differential equation of convective heat exchange may be found in the same way as expression (6.2.3). It is only necessary to take into account that the temperature of a moving liquid is a function of not just time, but also the coordinate \mathbf{r} of this liquid, i.e. $T_w = T_w(\mathbf{r}, t)$. Therefore its total variation in the time domain dT_w/dt , along with the local variation $\partial T/\partial t$, includes the so-called convective variation $(\partial T/\partial \mathbf{r})d\mathbf{r}/dt = \nabla T \cdot \mathbf{v}$, defined by the flow velocity \mathbf{v} . Allowing for this component equation (6.2.3) assumes the form:

$$dT_w/dt = a_q \nabla^2 T + \sigma_q / \rho c_v. \quad (6.3.3)$$

This equation is usually named differential equation of energy in order to distinguish it from the other differential equation characterizing the heat exchange conditions at the wall–moving liquid interface. To derive this equation, let us heed the fact that there is a thin layer of stationary liquid nearby the wall ($n = 0$), wherein the heat transfer is provided by exclusively heat conductivity. Therefore, along with (6.3.2), one can write $\mathbf{j}_q = -\nabla T_{n=0}$, wherefrom it directly follows:

$$\alpha_q = -\lambda \nabla T_{n=0} / \Delta T. \quad (6.3.4)$$

This is the differential equation of heat exchange manifesting that convective heat exchange so many times exceeds heat conductivity in intensity, as temperature gradient in the boundary layer exceeds thermal head in value.

6.4. Radiant Heat Exchange

The radiant heat exchange is construed as a rather minor part of the radiant energy exchange that lies within the $0.8\mu\text{m}$ – 0.8mm wavelength spectrum and is perceived as heat, i.e. completely dissipates. The overwhelming part of the radiation responsible for such phenomena as photosynthesis, photoeffect, photoionization, photoluminescence, as well as for photoacoustic phenomena, photonuclear reactions, etc, is the ordered form of motion and by no means reducible to heat. Nevertheless, physicists of the XX century persistently ascribe a certain temperature to radiation as a whole (including the relict one). However, the question of definition of specific potentials which equality provides radiant equilibrium

between stars and relict radiation (or interstellar matter) has never been raised, as far as we know.

To realize the energodynamic approach (from the general to the particular), let's apply a known expression for density ρE_B of the wave energy E_B (F. Crawford, 1965):

$$\rho E_B = \rho A_B^2 v^2 / 2, \text{ Дж/м}^3 \quad (6.4.1)$$

where v – wave frequency, s^{-1} .

To further maintain generality in describing the energy of waves featuring any nature, which is built into equation (6.4.1), let's operate with not the medium density, but rather with the concentration of the wave motion form carrier. This concentration has a dimension of photon/ m^3 in the case the radiant energy flux is represented through the photon flux in void.

According to (6.4.1)

$$dE_B = A_B v d(A_B v). \quad (6.4.2)$$

Comparing (6.4.2) with the general expression for work of the i th kind dW_i (2.2.12) gives that for the wave form of motion

$$\psi_B = A_B v; \quad \mathbf{X}_B = -\nabla \psi_B. \quad (6.4.3)$$

The value ψ_B is to be reasonably called as the *amplitude-frequency wave potential*.

It will be shown hereafter (see Chapter 9) that based on these ideas the black body radiation law can be derived not resorting to the Planck's postulates, i.e. not disregarding the ensuing from (6.4.1) dependence of wave energy on its amplitude and the proportionality of wave energy to the second, but not the first power of frequency.

The further integration of the Planck's radiation law within the $0-\infty$ frequency spectrum is known to give the Stefan-Boltzmann law for the black body radiant exitance J [W/m^2]:

$$J = \sigma_{\pi} T^4, \quad (6.4.4)$$

where σ_{π} [$W/m^2 K^4$] – Stefan-Boltzmann constant. This expression relates, as required, the amplitude-frequency potential to the temperature for the particular case of thermal equilibrium between bodies. Note, however, that the mentioned “derivation” of the fourth-powers law (6.4.4) assumes the existing black body absorbing all the radiation dropping onto it

(regardless of the radiation frequency). This assumption contradicts experiment, too. Therefore purely experimental approaches are so critical in the radiant heat exchange theory. One of them is based on the ensuing from (6.4.3) necessity for the radiant energy to dissipate in not only bodies as themselves, but also in the medium separating them, i.e. the necessity of the available energy exchange motive force \mathbf{X}_b . From these positions the radiant energy exchange is appropriate to be considered as the “photonic conductivity” (G. Muchnik, I. Rubashov, 1974). In the last case the law may be written as:

$$\mathbf{j}_q = \lambda_f \nabla T, \quad (6.4.5)$$

where λ_f – coefficient of “photon heat conductivity”. For optically dense media this coefficient is defined by the Henzel equation:

$$\lambda_f = 16 k_{\bar{\sigma}} T^3 / 3 \bar{\alpha}_r, \quad (6.4.6)$$

where $\bar{\alpha}_r$ – absorption factor of a medium.

For the stationary heat exchange ∇T may be represented, as shown above, in the form of the fraction dT/dn . Separating on this basis the variables in (6.4.1) and integrating this expression with respect to the ray path length ℓ in-between the bodies with temperatures T_1 and T_2 , one comes to the radiant heat exchange law expressed as:

$$j_q = [k_{\bar{\sigma}} / (1 + \bar{\alpha}_r \ell)] (T_1^4 - T_2^4). \quad (6.4.7)$$

This expression is a good approximation for media with low optical density (weak absorption).

Thus all integral and differential equations of the heat exchange theory may be derived from energodynamics. This is what provides a methodologically unified approach to thermodynamics and the heat exchange theory.

6.5. Heat - Mass Exchange in Open Systems

Classic thermodynamics is known to have always distinguished only two kinds of system–environment energy exchange, viz. heat exchange and work. The former has been considered as a random form of energy supply, whereas the latter – as its ordered form. We owe the application of the thermodynamic method to open systems with mass transfer therein to J. Gibbs, who introduced the parameters M_k and N_k as additional inde-

pendent state variables and derived the joint equation of the first and second laws of thermodynamics for open systems in the form which can be more conveniently expressed in terms of the mole numbers of the k^{th} substances:

$$dU = TdS - pdV + \sum_k \mu_k dN_k, \quad (6.5.1)$$

where U, S, V – internal energy, entropy and volume of a system, respectively; T, p – absolute temperature and pressure, respectively; $\mu_k \equiv (\partial U / \partial M_k)_{S, V, N_m}$ – component potential determined at constant S, V and mole numbers of all other components N_m mass transfer process involving a variation of the system composition due to the k^{th} substances transfer across the system borders and from the mass transfer process involving the substance transfer without system composition variation.

The last term in this expression, by Gibbs' assumption, characterizes an independent process irreducible to heat exchange and cubic strain and involving a composition and mass variation for a system as a whole. He also assumed that the term TdS still (as in closed systems) characterized the elementary heat exchange $d\bar{Q}$. In fact, he writes, "...if a system consists of parts supposedly not thermally interconnected, then any entropy reduction in either of these parts should be deemed impossible since such variations can not occur without heat transfer". However, as investigators were striking into the issue, they clarified the necessity to exclude from the total entropy dS and volume dV variations for open systems a part caused by the k^{th} substance transfer. Despite the existing disagreement in identification of this part (S.R. De Groot, R. Mazur, R. Haase, 1967), the great majority of investigators have come to construing the heat exchange and work in open systems as the part of energy exchange caused by exclusively the temperature gradient and not associated with the substance transfer across the system borders. In the same way heat is understood and referred to in the collection of terms recommended by the Academy of Science, "Process heat is the energy transferred at interaction from a one body to another depending on exclusively temperature of the bodies and not associated with substance transfer between them" (Thermodynamics. Terms, 1973).

To confirm the validity of such an approach, let us proceed from the joint equation of the first and second laws of thermodynamics derived for one mole of the pure k^{th} substance and, therefore, valid for both closed and open systems. Designating the molar energy, entropy and pure substance volume as u_{ko}, s_{ko} and v_{ko} , respectively, and considering them as temperature and pressure functions ($s_{ko} = s_{ko}(p, T), v_{ko} = v_{ko}(p, T, r_k)$) the joint equation of the first and second laws of thermodynamics has the form:

$$du_{ko} = \bar{d}q_k - \bar{d}w_k = Tds_{ko} - pdv_{ko}. \quad (6.5.2)$$

Here $\bar{d}q = Tds_{ko}$, $\bar{d}w = pdv_{ko}$ – elementary neat and expansion work of an open system under consideration.

Multiplying all terms of this equality by the mole number of the k^{th} substance and applying the Legendre transformation $N_k du_{ko} = dU_{ko} - u_{ko} dN_k$, equation (6.2.2) may be modified as:

$$dU_{ko} = \bar{d}Q_k - \bar{d}W_k + u_{ko} dN_k, \quad (6.5.3)$$

where $\bar{d}Q_{ko} = N_k \bar{d}q_{ko} = N_k T ds_{ko}$ and $\bar{d}W_{ko} = N_k \bar{d}w_{ko} = N_k p dv_{ko}$ – respectively, elementary heat exchange and expansion work of the same pure k^{th} substance taken to the amount of the N_k moles if the heat and work concepts maintain their classic meaning. It is easy to see that once the terms TdS and $p dV$ in Gibbs' relationship (5.5.1) are still understood as the heat exchange $\bar{d}Q$ and expansion work $\bar{d}W$, then in a particular case of a single-component system ($s_k = s_{ko}$; $v_{ko} = v_{ko}$; $u_k = u_{ko}$ и $\mu_{ko} = u_{ko} - Ts_{ko} + pv_{ko}$) this relationship does not go over into (6.5.3) as should be expected. Hence the terms of (6.5.1) do not characterize independent processes as Gibbs assumed and the principle of effect distinguishability demands, while the term $\sum_k \mu_k dN_k$ does not determine the energy exchange caused by the k^{th} substance transfer across the system borders.

Thus there arises a problem in open systems how to distinguish the heat transfer, work and mass transfer. The decision to the problem supposes finding such coordinates of these processes which remain independent from processes of other kind simultaneously running. It is quite evident that the total entropy S and the total volume V of an open system are not any more coordinates of heat transfer and expansion work therein since they vary at mass transfer as well (variation of the total number of moles N at constant composition of the system). The specific entropy $s = \sum_k s_k r_k$ and specific volume of the mixture $v = \sum_k v_k r_k$ are not these coordinates either since they vary even at $N = \text{const}$ due to the system composition variation (variation of the mole fractions r_k of the k^{th} components). The partial molar entropies s_k and the volumes v_k of the k^{th} components can not either serve as coordinates of heat transfer and work in open systems since they vary with the variation of relationship between the mole numbers N_k of the k^{th} substances, i.e. $s_k = s_k(p, T, r_k)$ и $v_k = v_k(p, T, r_k)$ ¹⁾. Lastly, not quite adequate are the coordinates $s_{ko}(p, T)$ and $v_{ko}(p, T, r_k)$

¹⁾ Remember that partial molar function of the k^{th} substance means an increment in adequate extensive value when introducing into the system one mole of this substance at constant temperature, pressure and other potentials.

since they do not allow for the heat and bulk effects arising at the irreversible mixing of the introduced component with the substance of the system. Thus the concepts of “heat” and “work” loose their intrinsic meaning in the systems where diffusion takes place (M. Tribus, 1970). In this connection the classic division of the external energy exchange into heat transfer and work looses its heuristic value and should give place to other process classification having nothing to do with the energy exchange means. Such is, in particular, the “heat process” featuring a temperature variation in a system at constancy of its volume, mass and composition irrespective of what causes the process – external heat exchange or internal heat sources. A coordinate of this heating process may be the entropy of a mixture irreversibly composed $S^\circ = \sum_k N_k s_{k0}$ (in the absence of the heat mixing processes), where s_{k0} is considered a function of exclusively intensive parameters (temperature and pressure as the simplest case). Then:

$$\bar{d}Q = \sum_k N_k T ds_{k0} = T d_\Theta S^\circ, \quad (6.5.4)$$

where $d_\Theta S^\circ$ – part of the entropy variation caused by exclusively heating and not associated with the system volume and coordinate variation (including N_k). This heat keeps the same meaning as in classic thermodynamics, i.e. is defined by internal energy variation in the system at constancy of its volume V and the coordinates \mathbf{Z}_i of all other kinds of work ($\bar{d}Q = [dU]_{V, \mathbf{Z}_i}$). It is easily seen that the heat Q absorbed or released by the body is defined in this case in terms of the “isocoordinate heat capacity” $C_\Theta = (\partial U / \partial T)_{V, \mathbf{Z}_i}$ of the system, which is a conceptual generalization of the isochoric heat capacity C_V for the case of a polyvariant system. Since the derivatives of some parameters of the system (U in this case) with respect to its other parameters (T in this case) are also its state parameters, the system isocoordinate heat capacity C_Θ becomes state parameter (like C_V), while the heat $\bar{d}Q$ – measure of internal heat energy variation:

$$\bar{d}Q = dU_T = C_\Theta dT. \quad (6.5.5)$$

Similarly the expansion work for an open system $\bar{d}W_p$ may be found as:

$$\bar{d}W_p = \sum_k N_k p dv_{k0} = p d_\Psi V^\circ, \quad (6.5.6)$$

where $V^\circ = \sum_k N_k v_{k0}$ – volume of a reversibly composed mixture (in the absence of the bulk mixing effects); $d_\Psi V^\circ$ – volume variation due to ex-

clusively bulk deformation of the system components and not associated with the system intensive parameters' variation ψ_i (including p , T and c_k).

The above proposed definition of heat and work in open systems as notions keeping their classic meaning corresponds to the axiom of process distinguishability and allows to distinguish these processes as independent (irreducible to each other). In this case the heat-mass exchange process should be first of all distinguished from the diffusion process of the k^{th} substances across the system borders, which involves the variation of system composition with the system mass invariable. Accordingly, the *heat-mass exchange* will be construed as an exchange of internal heat energy between bodies if caused by the substance transfer across the system borders and having nothing to do with the variation of the system composition.

It is easy to see that the term TdS in relation (6.5.1) includes the component $\sum_k T s_{k0} dN_k$ caused by the transfer of the pure k^{th} substances across the system borders. This is the component that ought to be construed as the analytical expression of the heat-mass exchange dQ_m :

$$dQ_m = \sum_k T s_{k0} dN_k. \quad (6.5.7)$$

Similarly, the term $p dV$ in open systems, along with the usual expansion work $dW_p = \sum_k N_k p d\nu_{k0}$, also includes the so-called "input work" $dW_{in} = \sum_k p \nu_{k0} dN_k$:

$$dW_{in} = \sum_k p \nu_{k0} dN_k. \quad (6.5.8)$$

Substituting (6.5.7) and (6.5.8) into the Gibbs relation (6.5.1) gives:

$$dU = dQ + dQ_m - (dW_p + dW_m) + \sum_k \mu_k dN_k. \quad (6.5.9)$$

From this it follows that the term $\sum_k \mu_k dN_k$ in the Gibbs relation characterizes the heat-mass exchange with the diffusion of the k^{th} non-reacting substances across the system borders dU_d . This process should be called the *diffusion energy-mass exchange*¹⁾, unlike the diffusion in its exact meaning. In such a case the total energy-mass exchange $\sum_k \mu_{k0} dN_k$ can be represented as an algebraic sum of the heat-mass exchange dQ_m , the input work dW_{in} and the diffusion energy-mass exchange dU_d .

Thus the heat exchange in open systems includes the conductive and convective components of the heat flow caused by the heat conduc-

¹⁾ The term "diffusion" (from the Latin "diffusio" – spreading) relates, strictly speaking, to the other process – the equalization of the component concentrations all over the bulk of the system with its composition and mass invariable.

tion \mathbf{j}_q^c and the heat-mass exchange \mathbf{j}_q^k , respectively. The latter is inseparable from the density of the k^{th} substance flow across the system borders $\mathbf{j}_k = \rho_k \mathbf{v}_k$ (mol/m²·s) and according to (6.5.4) equals $\mathbf{j}_q^k = T_{S_{ko}} \mathbf{j}_k$. Then the basic law of heat exchange in open systems becomes:

$$\mathbf{j}_q = -\lambda \nabla T + \rho_k T_{S_{ko}} \mathbf{v}_k. \quad (6.5.10)$$

This expression fundamentally differs from that traditionally used in the heat-mass exchange theory because it contains not the enthalpy h_k of the k^{th} substance input having nothing to do with the internal heat energy of the substance, but the associated energy $T_{S_{ko}}$ of the substance input.

Summing up, it is possible to conclude, that the approach to the theory of heat exchange from energodynamic positions allows to eliminate strange delimitation of two directions of the theory of warmth and to receive the basic integrated and differential equations of the theory of heat exchange at the minimum volume of new concepts.

Chapter 7

HYDRO- AND AERODYNAMICS

In the late XIX century the liquid flow science disintegrated into two branches scarcely interconnected. On the one part, theoretical hydrodynamics, having proceeded from Euler's equation for ideal (frictionless) liquid, attained high perfection. On the other part, however, the results of this the so-called classic hydrodynamics sharply contradicted experiment, especially with regard to resistance the liquid offered to the bodies moving in it. Engineers were thus challenged to create their own liquid flow science in order to tackle practical problems. The science was named hydraulics. This discipline acquired a pronounced empirical character and sharply distinguished from theoretical hydrodynamics both in its goals and methods.

The theory of boundary layer L. Prandtl developed in the early XX century connected theory and practice and gave rise to a new direction that enabled to again merge the branches of the liquid flow science having hitherto drifted far apart. Nevertheless, up to the present a rational theory of mature turbulent flows has not yet existed (H. Schlichting, 1974). This explains the ever rising interest in the thermodynamic methods of calculating dissipation loss for compressible liquid flow, in the boundary layer stability, dynamic system evolution, etc. from the positions of the theory of irreversible processes (I. Prigogine, 1947, 1980, 1986; S.R. De Groot, R. Mazur, 1964; I. Gyarmati, 1974, and others). Hereafter we are going to consider the basic statements of hydro- and aerodynamics from the positions of energodynamics.

7.1. Basic Laws of Hydrodynamics

Whenever continuums are moving, the forms of energy are being converted into each other. To calculate these conversions, the energy balance equation serves as derived in thermodynamics. Therefore the deduction of basic statements of hydro- and aerodynamics is impossible without application to thermodynamics. The specific approach to studying the non-static processes of gas and liquid flows in classic thermodynamics was restricted to studying just steady flows, wherein the state of the gas/liquid elements in each point of the velocity or pressure fields remained unvaried. As the object of investigation the unit mass of gas/liquid was considered therein so that to reduce the flow as an open system to a closed one. All laws of thermodynamics were applied to such a system in the form of equalities despite the non-static character of the associated processes and heterogeneity of the unit mass of gas/liquid which occupied a certain part of the flow path with parameters having varied along its length and cross section. Additional simplifications meant the so-called “extended” systems under consideration, which comprised, along with the moving gas or liquid, also external force fields including the external pressure field. In that case the total energy E of the liquid or gas flow was represented as the sum of the internal energy of liquid U , its external kinetic energy $E^k = M\mathbf{v}^2/2$, the external potential energy of pressure $E^p = pV$ and the positional energy in gravity field $E^g = M\mathbf{g}\cdot\mathbf{r}_g$, where \mathbf{r}_g – distance to the surface of the Earth. The external potential energy of gas or liquid PV was therein measured by the “work to admit” the mass M into a medium with unvaried pressure and density ($p, v = \text{const}$) and was defined as the imaginary work $W_c = \int pdV = \int pvdM$ to compress the gas separated with an imaginary partition from the gas ad-

mitted (M.P. Vukalovich, I.I. Novikov, 1968; A.I. Andrushchenko, 1975, and others).

All those artificial procedures were applied in order to justify using the conceptual system and the body of mathematics for equilibrium thermodynamics of closed systems in the form of relationship (3.1.5). In that case the generalized equation of the first law of classic thermodynamics was supplemented with the components of the system external energy and with the new type of work $\bar{d}W_p'$, which different authors named “available”, “useful external”, “technical”, etc.

$$\bar{d}q = dh + d(v^2/2) + gdR_g + \bar{d}w_p', \quad (7.1.1)$$

where $h \equiv u + pv$ – enthalpy of liquid or gas.

One more simplification was that the analytical expression of specific work $\bar{d}w_p'$ was found by comparing (7.1.1) with the equation of the first law of thermodynamics for closed systems

$$\bar{d}q = dh - vdp, \quad (7.1.2)$$

wherefrom, if to neglect the gas gravitational energy variations ($gdR_g = 0$), it ensued $\bar{d}w_p' = -vdp$. However, the fact was missed that the gas-inflow work as a particular case of mechanical work $\mathbf{F} \cdot d\mathbf{r}$ characterized thereat not local variations of the system energy in the particular point of space (as all terms of 7.1.1), but rather the so-called convective variations of state due to the transport of the object in space. Thus the work $\bar{d}w_p'$ is defined in this case by the product of the pressure resultant force $\mathbf{F}_p = v\mathbf{X}_p$ and the gas displacement $d\mathbf{r}$ in the field of pressure with the gradient ∇p . Then $\bar{d}w_p' = -v\nabla p \cdot d\mathbf{r} = -vd_r p$, i.e. relates to the pressure variation $d_r p$ in the direction of the gas displacement, whereas in classic thermodynamics of stationary systems the dp means just a time variation of pressure in a particular point of space. Such “fitting to classic” by substituting the spatial variations of pressure $d_r p$ for the local ones dp did not, fortunately, tell on the calculation results, though considerably impeded comprehending that section of thermodynamics (A.F. Kotin, 1976).

Our goal is to obtain the same results not resorting to all these simplifying subterfuges. Energodynamics is properly equipped to do this. Let us apply its identity (2.3.9) to an arbitrary stream tube or a channel with a steady flow of compressible liquid within the gravity field of the Earth. The liquid flow under consideration receives generally the heat dQ° from the environment and does work against some j^{th} forces $\bar{d}W_j^\circ$. In this case the liquid has the thermal ($\Psi_T \equiv T$, $\Theta_T \equiv S$), mechanical ($\Psi_p \equiv p$, $\Theta_p \equiv V$), kinetic ($\Psi_w \equiv \mathbf{v}$, $\Theta_w \equiv \mathbf{P} = M\mathbf{V}$) and gravitational ($\Psi_g \equiv \Psi_g$, $\Theta_g \equiv M$) degrees of freedom. The system in a whole is heterogeneous (non-

equilibrium internally) and characterized by the available pressure gradient $\mathbf{X}_p = -\nabla p$ and gravitational potential $\mathbf{X}_g = -\nabla\Psi_g = \mathbf{g}$. These forces are the conjugate of the extensive state coordinates \mathbf{Z}_p , \mathbf{Z}_g и \mathbf{Z}_i which meaning has been earlier clarified. A new parameter is here the *moment of momentum distribution* $\mathbf{Z}_w = \mathbf{P}\mathbf{r}_w$ defined, like the other parameters of heterogeneity, by the product of the value being transferred (in this case the momentum \mathbf{P}) and the vector of center-of-inertia displacement \mathbf{r}_w for the body. The latter defines the center of system momentum being apart from the wall as far as just the *displacement thickness of boundary layer* (H. Schlichting, 1974). This makes superfluous such a specific parameter as the *displacement thickness of momentum*¹⁾ to be introduced into hydrodynamics. The moment of momentum distribution \mathbf{Z}_w is conjugated to the thermodynamic force \mathbf{X}_w defined by the value of the velocity gradient vector $\mathbf{x}_i \equiv -\nabla\mathbf{v} = \text{Grad}\mathbf{v}$ system-averaged. In this case the basic identity for the system under consideration becomes:

$$dU = TdS - pdV - \mathbf{X}_w \cdot d\mathbf{Z}_w - \mathbf{X}_p \cdot d\mathbf{Z}_p - \mathbf{X}_g \cdot d\mathbf{Z}_g - \mathbf{X}_i \cdot d\mathbf{Z}_i, \quad (7.1.3)$$

where $TdS = dQ^e + dQ^d$ – the sum of heats resulting from the system heat exchange dQ^e and the dissipation process dQ^d ; $\mathbf{X}_j \cdot d\mathbf{Z}_j = dW_j + dW_j^d$ – the sum of useful and dissipation works the system does; T, p – mass-average absolute temperature and pressure of the system in whole.

Since according to the law of heat and work equivalence the dissipation heat dQ^d released in a system is equal to the work done on the system against the dissipation forces in it ($dQ^d = -dW^d$), energy balance (7.1.3) remains valid in their absence:

$$dQ = dU + pdV + \mathbf{X}_w \cdot d\mathbf{Z}_w + \mathbf{X}_p \cdot d\mathbf{Z}_p + \mathbf{X}_g \cdot d\mathbf{Z}_g + dW_j, \quad (7.1.4)$$

To facilitate comparing with the results of classic thermodynamics, let us change to the scalar form of all terms in (7.1.4). At the same time we will use the energodynamics–associated law of parameter averaging when changing from local to global description of a system (see 2.5.11) construing Ψ_i as the generalized potentials of the system averaged over the stream tube (channel) cross section. Taking into account that the po-

¹⁾ As an example, let us find the moment of momentum distribution in a laminar flow within a tube with the radius R and the velocity vs. radius distribution law $v(r) = 2V_x(1 - r^2/R^2)$. Representing the bulk element dV as the product of the elementary ring square $2\pi r dr$ and the tube length ℓ one can find: $\mathbf{Z}_w = MV_x \Delta \mathbf{r}_w = 2\pi \ell M \int [2V_x(1 - r^2/R^2) - V_x] \rho r^2 dr = -\frac{2}{3}MV_x \mathbf{r}$ (the minus sign in this expression means the displacement occurring in the direction of tube axis).

tentials Ψ_i in a stationary flow vary only along the stream tube axis with the coordinate \mathbf{r} , i.e. $\Psi_i = \Psi_i(\mathbf{r})$, one can find :

$$\mathbf{X}_i \cdot d\mathbf{Z}_i = -\nabla \Psi_i \cdot \Theta_i d\mathbf{r} = -\Theta_i (d\mathbf{r}_i \cdot \nabla) \Psi_i = -\Theta_i d\Psi_i. \quad (7.1.5)$$

From here, in particular, $\mathbf{X}_p \cdot d\mathbf{Z}_p = -Vdp$ ¹⁾; $\mathbf{X}_g \cdot d\mathbf{Z}_g = -M_g dr_g$; $\mathbf{X}_w \cdot d\mathbf{Z}_w = -Mv \cdot dv = -Mdv^2/2$, so instead of (7.1.4) we have:

$$dQ = dH + Mdv^2/2 + Mgd r_g + dW_i, \quad (7.1.6)$$

where $H \equiv U + pV$ – enthalpy of liquid; $d(pV) = p dV + V dp$ – the sum of the local and spatial variations of the potential energy of pressure.

This equation corresponds to the first law of thermodynamics for moving gases and liquids (M.Vukalovich, I.Novikov, 1968; A. Andrushchenko, 1975). However, this is obtained without any assumptions about the equilibrium state of a system and the reversible (quasi-static) character of the processes running in it.

From this equation in a particular case of isothermal flow ($dU = 0$) of incompressible liquid ($\rho = \text{const}$) in the absence of heat exchange and work ($dQ, dW_i = 0$) Bernoulli law ensues:

$$p/\rho + v^2/2 + gr_g = \text{const}, \quad (7.1.7)$$

stating energy conservation for liquid moving along the stream-line.

In a more particular case of stationary liquid ($v = 0$) Archimedean principle ensues from (7.1.7):

$$p + \rho gr_g = \text{const}, \quad (7.1.8)$$

describing the conditions of liquid equilibrium.

In the same way other relationships of fluid thermodynamics and hydraulics can be found, which are, however, beyond the scope of this book. These are described in special literature, whereto we kindly refer all concerned readers.

¹⁾ It is taken into account here that $\Theta_i = -V < 0$ and $dR_p < 0$, i.e. the volume redistribution spreads into the overpressure zone.

7.2. Relationships between Thermodynamic and Geometrical Parameters in Gas Flows

To study energy conversion processes when compressible liquid is moving along channels of an arbitrary cross section, let us use the part of thermodynamic identity (2.3.9) directly characterizing such processes, i.e. describing reciprocal conversions of various forms of the system energy E . When such conversions run without losses,

$$dE = -\mathbf{X}_p \cdot d\mathbf{Z}_p - \mathbf{X}_w \cdot d\mathbf{Z}_w - \mathbf{X}_g \cdot d\mathbf{Z}_g = 0. \quad (7.2.1)$$

Neglecting in case of gas its position energy variation $\mathbf{X}_g \cdot d\mathbf{Z}_g$ and taking into account that $\mathbf{X}_p \cdot d\mathbf{Z}_p = -Vdp$; $\mathbf{X}_w \cdot d\mathbf{Z}_w = -Mvdv$ one can directly obtain after changing to specific values:

$$vdv = -vdp. \quad (7.2.2)$$

Note, this expression interrelates the spatial variations of the local parameters v and p . Integrating this relationship from the state $v_0 = 0$ one can easily come to the expression for theoretical velocity of gas outflow from nozzles v_t :

$$v_t = \int (-2vdp)^{0.5}. \quad (7.2.3)$$

In case of an outflow with friction (when internal sources of the dissipation heat $\bar{d}Q^d = -\bar{d}W_j^d$ appear in the system) the additional term $-\bar{d}W_j^d$ appears in the right part of (7.2.1), then expression (7.2.2) becomes:

$$v = (-2 \eta_{oi}^p vdp)^{0.5}, \quad (7.2.4)$$

where $\eta_{oi}^p = 1 - w_j^A/w_j^t$ – internal relative efficiency of the expansion process defined by the ratio of the dissipation work w_j^A of gas to its theoretically possible work w_j^t . The ratio of actual-to-theoretical outflow velocities v/v_t is usually named the *nozzle efficiency*. Designating this ratio as φ_c and comparing with (7.2.4) one can find that $\varphi_c^2 = \eta_{oi}^p$, i.e. depends on the dissipation loss share.

To ascertain the relationship between the flow parameters and the channel profile, let us play on the constancy of the liquid flow rate $I_i = \rho v f$ along the stream tube ($\rho v f = \text{const}$). After taking the logarithm of this expression ($\ln \rho + \ln v + \ln f = \text{const}$) followed by its differentiation we can find the steady flow continuity equation:

$$dv/v + df/f - dv/v = 0. \quad (7.2.5)$$

Considering the flow in channels as adiabatic and differentiating the adiabatic equation $p v^k = \text{const}$ the following relationship can be easily derived:

$$k(dv/v) = -dp/p, \text{ or } a_s^2 dv/v = -vdp = vdv, \quad (7.2.6)$$

where $a_s = (kp v)^{0.5}$ – sound velocity in gas.

Substituting dv/v from (7.2.5) into (7.2.4) followed by minor transformations we can obtain the so-called channel profile equation (Hugoniot's equation, 1880):

$$(M_s a_s^2 - 1)dv/v = df/f, \quad (7.2.7)$$

Here $M_s a_s \equiv v/a_s$ – Mach number characterizing the gas flow condition, viz. subsonic ($Ma < 1$) and supersonic ($M_s a_s > 1$).

Thus the application of energodynamics enables to obtain known results avoiding voluminous discourses justifying classic thermodynamics and omitting such notions referring to work as “input”, “push”, “available”, “technical”, useful external”, etc.

7.3. Law of Friction. Shear, Bulk and Rotational Viscosity

Now let us apply energodynamics to investigate such purely irreversible phenomena as viscosity. It is known from experience that if two selected layers of liquid are moving relative to each other in a direction x with a velocity v_x , surface friction forces (tangential stress) appear impeding this motion. Extracting from liquid an elementary volume dV with the faces dx , dy and dz and designating the specific forces (stress) acting along the x axis over the area $dx dy$ as τ_x each of these forces may be considered (in linear approximation) proportional to the velocity gradient dv_x/dy in the direction normal to the moving layers:

$$\tau_x = \mu_s dv_x/dy. \quad (7.3.1)$$

This expression has been named Newton's law of friction, while the associated proportionality factor μ_s – *absolute viscosity coefficient for liquid*.

However, Newton's law of friction allows for only one of the possible physical characteristics of liquid viscosity, viz. the coefficient of shear viscosity (see the subscript for μ). Meantime, when real (incom-

pressible) medium is moving, other sources of dissipation losses are available, e.g. those causing from the rapid (non-static) compression and expansion of the elementary volumes of the medium being strained, i.e. associated with a phenomenon of the so-called *bulk viscosity*. In this case the normal stress σ_n in compressible liquid should evidently differ from the thermodynamic (hydrostatic) pressure p by a value proportional, in a first approximation, to the liquid cubic strain velocity $\nabla \cdot \mathbf{v}$. Designating the proportionality factor η_v one can find the expression for any normal component of the stress tensor:

$$\sigma_n = -p + \mu_v \nabla \cdot \mathbf{v} . \quad (7.3.2)$$

Later on the value η_v was named the *coefficient of bulk (volume) viscosity* (S.P. De Groot, R. Mazur, 1964). The bulk viscosity is the second property of a liquid uniformly (isotropic) compressible, which should be taken into consideration in calculations and analyses.

G. Stokes in his intention to reduce the number of properties characterizing the stress field in compressible liquid to the same number as for incompressible one set forth in 1945 a hypothesis that $\mu_v = -\frac{2}{3} \mu_s$. Then instead of (7.3.2) one can write:

$$\sigma_n = -p - \frac{2}{3} \mu_s \nabla \cdot \mathbf{v} . \quad (7.3.3)$$

The laws of friction (7.1.1)...(7.1.3) allowed to introduce an additional “viscosity” term into the equation of the second law of motion and to obtain on this basis the law of viscous liquid motion known as the Navier-Stokes equation. However, before deriving this law as a deduction of energodynamics let us note that the dissipation losses may also appear from the rotation of the elements (“moles”) of liquid. Yet J. Boussinesq (1877) assumed that the “apparent” turbulent tangential stress τ_T was defined by a formula similar to Newton’s law of friction:

$$\tau_T = A_T d\bar{v}_x/dy , \quad (7.3.4)$$

where to instead of the actual velocity v_x the averaged velocity \bar{v}_x enters and instead of the coefficient μ_s – the turbulent exchange coefficient A_T . Unlike the coefficient of shear viscosity this coefficient is not a constant of liquid since depends on velocity and its distribution. This ensues, at least, from the fact that friction forces in turbulent motion are proportional to not simple velocity, but to approximately its squared value.

Considering the laws of friction (7.3.1), (7.3.2) and (7.3.4) from the position of energodynamics one can easily notice that these equations are

particular cases of the TIP linear kinetic laws of (5.6.5) type, wherein the flow motive force is expressed by a negative gradient of the generalized potential (velocity gradient vector $\mathbf{x}_i \equiv -\nabla\mathbf{v} = \text{Grad}\mathbf{v}$). This tensor characterizes the velocity field heterogeneity that causes internal processes of the momentum redistribution among various parts of the system. These processes feature shear and cubic strain as well as rotation of the bulk elements. From the position of energodynamics the shear strain process is irreducible to the cubic strain one, much less to the rotation of the liquid elements. Therefore all above processes are independent and possess their own coordinate and motive force. This demands resolution of the tensor $\nabla\mathbf{v} \equiv \text{Grad}\mathbf{v}$ per three components. One of them – the trace of the tensor – is the invariant scalar $\nabla\cdot\mathbf{v}$ composed of diagonal entries of the velocity matrix with the components $\partial v_\alpha/\partial x_\alpha$, where $\alpha, \beta = 1, 2, 3$ ¹⁾. This value characterizes strain velocity of continuum unit volume and is connected with normal stress arising in the liquid and described by expression (7.1.2). The associated stress deviator causes the force $\mathbf{x}_p = -\nabla p$ generating, in its turn, the bulk viscosity phenomenon (I. Gyarmati, 1974). The residuary non-diagonal part $\nabla\mathbf{v}$ may be resolved into the symmetrical $\nabla\mathbf{v}^s$ and anti-symmetrical $\nabla\mathbf{v}^a$ components. The former is defined by the expression $\nabla\mathbf{v}^s = 1/2(\partial v_\beta/\partial x_\alpha + \partial v_\alpha/\partial x_\beta)$ and characterizes the “slip” velocity of the liquid layers. The latter is defined by the expression $\nabla\mathbf{v}^a = 1/2(\partial v_\beta/\partial x_\alpha - \partial v_\alpha/\partial x_\beta) = 1/2\nabla \times \mathbf{v}$ and means an axial vector known in hydrodynamics as the *vortex* one. The symmetrical part of the velocity tensor characterizes the velocity of the shear strain and answers for the shear viscosity phenomenon. The anti-symmetrical part characterizes the rotational speed of the bulk element and generates the vorticity turbulent transfer process, i.e. the kinetic rotation energy exchange among various zones of the moving liquid.

All three phenomena, viz. bulk, shear and rotational (turbulent) viscosity may be described with generally the same non-linear kinetic equations (2.7.10) of energodynamics as other phenomena. Neglecting in (2.7.10) the threshold force \mathbf{F}_{j_0} and changing to the local form by substituting \mathbf{F}_j for the thermodynamic forces, as it done in (5.6.5), one can describe the phenomenon of, say, bulk viscosity by a kinetic equation in the form:

$$\mathbf{T}_n = \mu_v \nabla \cdot \mathbf{v} , \quad (7.3.5)$$

¹⁾ The velocity gradient toward the center of the bulk element within a compressible liquid arises because the velocity of the element-comprised particles decreases as they are approaching the center (wherein the velocity is zero).

where \mathbf{T}_n – normal component of the stress tensor \mathbf{T} .

Similarly the momentum transfer between the layers of a moving liquid (the shear viscosity phenomenon) may be described by expression (5.6.5), wherein the motive force of the process is represented via the symmetrical part $\mathbf{T}^s \equiv (\nabla \mathbf{v})^s$ of the tensor $\nabla \mathbf{v}$

$$\mathbf{T}^s = \mu_s (\nabla \mathbf{v})^s, \quad (7.3.6)$$

while the vorticity transfer (the turbulent viscosity phenomenon) – by the same equation, wherein the thermodynamic force is the anti-symmetrical part $\mathbf{T}^a \equiv (\nabla \mathbf{v})^a$ of the tensor $\nabla \mathbf{v}$ equal to half the so-called vortex vector $(\nabla \times \mathbf{v})$:

$$\mathbf{T}^a = \mu_t (\nabla \mathbf{v})^a, \quad (7.3.7)$$

wherein instead of the turbulent exchange coefficient A_t the coefficient of turbulent viscosity μ_t figures.

From the positions of ergodynamics the coefficients μ_v , μ_c and μ_t are neither pure thermodynamic, nor pure kinetic values and, as the other phenomenological coefficients $L_{ij} = \Theta_j K_{ij}$, depend in general on both the thermodynamic Θ_j , and the kinetic K_{ij} factors (chapter 2). Therefore equations (7.3.5 thru 7.3.7) are, strictly speaking, non-linear. This especially concerns equation (7.3.7), which at first sight does not reflect squared relationship between the losses in a mature turbulent liquid flow and the velocity of the main flow. It should, however, be taken into consideration that in ergodynamics the kinetic coefficient K_{ij} may be any function of motion state, i.e. $K_{ij} = K_{ij}(\nabla \mathbf{v})^a$. The nature of this relationship is defined from experiment. However, to explain the above peculiarity of a turbulent flow, it is no need to enter into details of the turbulence mechanism. The velocity \mathbf{v} of some point of rigid body is known to be possibly represented as the sum of the velocity of translational motion of its center of mass \mathbf{V} and the velocity of rotational motion $\boldsymbol{\omega} \times \mathbf{r} \equiv [\boldsymbol{\omega}, \mathbf{r}]$ (L.D. Landau, E.M. Livshits, 2004). The respective translational $M\mathbf{v}$ and rotational $\boldsymbol{\omega} \times M\mathbf{r}$ components of the system momentum \mathbf{P} are coordinates of two independent processes i.e. represent two independent degrees of freedom of the system. In the basic identity of ergodynamics (see 2.5.1) those are described by the two terms, which pertain to different types of processes, and by the two different components of system kinetic energy. In a laminar motion only one of the above degrees of freedom is “energized”, and the energy losses are proportional to the first power of \mathbf{v} . However, as the velocity is rising and the laminar flow loosing its stability, a rotational motion is energized in the flow, i.e. an additional degree of freedom appears. In a mature turbulent motion according to the law of uniform dis-

tribution of energy among degrees of freedom (L.D. Landau, E.M. Livshits, 2004) the total momentum of the translational and rotational motions is summed up increasing twofold so that the losses of the kinetic energy $Mv^2/2$ increase fourfold. In an immature turbulent motion the index of power for $(\nabla\mathbf{v})^a$ is expected to be from 1 to 2, which conforms to experiment.

However, it seems to be more valuable that the above explanation that the laws of shear, bulk and turbulent viscosity may be directly obtained from energodynamics as particular cases of its kinetic equations.

7.4. Derivation of Navier-Stokes' Generalized Equation

In the general case of a 3D-motion of the viscous compressible liquid the flow field is defined by five values, viz. the vector of the velocity \mathbf{v} with the components $v_\alpha, v_\beta, v_\gamma$; the pressure p and the density ρ . There are three equations to find these five values, viz. three equations of motion (law of momentum conservation), continuity equation (law of conservation of mass) and equation of thermodynamic state $p = p(\rho)$.

To formulate the equations of motion, let us proceed, as usual, from the second law of motion (see 3.3.2), reading that the rate of change of momentum of a body \mathbf{P} in time t is equal to the resultant \mathbf{F} of all forces acting on the body. According to (2.3.7) there are several categories of the thermodynamic forces $\mathbf{x}_i \equiv -\nabla\psi_i$ (2.3.8) acting on the liquid particles in a flow. Firstly, these are the mass forces \mathbf{F}_m comprising the gravitational forces, which specific values are expressed by a negative gradient of the gravitational potential ψ_g : $\mathbf{x}_g \equiv \mathbf{g} = -\nabla\psi_g$ (N/kg). Secondly, these are bulk forces, to which also the forces $\mathbf{x}_p = -\nabla p$ (N/m^2) should be attributed as caused by heterogeneity of the pressure fields ($\psi_p \equiv p$)¹⁾. Thirdly, these are surface forces comprising the shear stress arising in case of a body strain.

In continuum mechanics the forces from pressure and the tangential stresses are merged in a single mathematical object, viz. the stress tensor \mathbf{T} , wherein diagonal and non-diagonal components correspond to these forces. In this case the second law of motion directly adopts the most compact form of the Cauchy equation:

$$\rho d\mathbf{v}/dt = \rho\mathbf{F} + \nabla \cdot \mathbf{T}. \quad (7.4.1)$$

¹⁾ Note that in energodynamics pressure is construed not as a surface force (vector) with a dimension of N/m^3 , but rather as a concentration of potential energy with a dimension of J/m^3 (scalar).

Substituting all components of the tensor \mathbf{T} (7.3.5) thru (7.3.7) into (7.4.1) gives:

$$\rho d\mathbf{v}/dt = \rho \mathbf{F} - \nabla p + \nabla \cdot \{ \mu_c [(\nabla \mathbf{v})^s - \frac{2}{3} \mu_c \nabla \cdot \mathbf{v}] \} + \mu_t (\nabla \mathbf{v})^a. \quad (7.4.2)$$

This expression is the Navier-Stokes' equation generalized so as to allow for the turbulent viscosity phenomenon (I. Gyarmati, 1974). For incompressible liquids ($\nabla \cdot \mathbf{v}$) under an assumption that $\mu_s = \text{const}$ this equation may be simplified:

$$\rho d\mathbf{v}/dt = \rho \mathbf{F} - \nabla p + \mu_s \nabla^2 \mathbf{v} \quad (7.4.3)$$

Equations (7.4.2) and (7.4.3) make the foundation to all continuum mechanics, hydrodynamics and aerodynamics.

To complete the set of equations of hydrodynamics, it is necessary to supplement the equation of flow energy balance (7.4.2) with also the *continuity equation* for a more general case of non-stationary processes. The latter reflects the law of conservation of mass of a system and supports the statement that the sum of the masses flowing into and out of unit volume of a system per unit time is equal to the variation of mass of the system for the same time due to its density variation. This equation also directly ensues from the balance equation for the arbitrary field value Θ_i (2.4.8) in the absence of internal sources of mass ($\sigma_i = 0$). Substituting there $\Theta_i \equiv M$, $\mathbf{j}_i \equiv \mathbf{j}_m = \rho \mathbf{v}$ gives the integral form of the continuity equation:

$$dM/dt + \int \nabla \cdot \mathbf{j}_m dV = 0. \quad (7.4.4)$$

The differential form of this equation depends on the uniqueness conditions of processes under investigation. If a compressible liquid is considered, which bulk elements dV remain unvaried under its strain (such description of a continuum under strain is named spatial), then differentiation of mass with respect to time pertains to only the value $\rho = \rho(t)$. Then $dM/dt = \int (d\rho/dt) dV$, which leads to the so-called substantive equation of mass balance:

$$d\rho/dt + \nabla \cdot \mathbf{j}_m = 0, \quad (7.4.5)$$

where $\mathbf{j}_m = \rho \mathbf{v}$ – density of local mass flow.

If, on the contrary, the mass elements $dM = \rho dV$ of a continuum remain unvaried under its strain, then $\rho = \rho(M, t)$, and differentiating (7.4.4) gives:

$$\partial\rho/\partial t + \nabla\cdot(\rho\mathbf{v}) = 0. \quad (7.4.6)$$

In case of an incompressible liquid $\rho = \text{const}$, and the continuity equation becomes:

$$\nabla\cdot\mathbf{v} = 0. \quad (7.4.7)$$

Temperature variations in compressible fluids makes it necessary to supplement the equations of motion with additional thermodynamic relationships, e.g. the equation of gas state in aerodynamics or plasma state in magnetic hydrodynamics. In a more general case of flows aggravated with heat exchange or mass exchange the equations of the heat- and mass exchange theory should be taken into consideration. Therefore it is very important that energodynamics does not have to “import” these relationships from outside.

It is worth noting that due to great mathematical difficulties not a single general solution of the Navier-Stokes’ equation has been obtained up-to-date in its complete form, i.e. containing all terms allowing for viscosity, as well as the convective terms. The reason is that such a solution demands the knowledge of all stress tensor components for all continuum elements, which can not be measured or assigned by uniqueness conditions. Therefore it is quite important to consider those additional opportunities which energodynamics gives.

7.5. Momentum Transfer in Boundary Layer

It has been known for a long time that disagreement between classic hydrodynamics and practice arises from disregarding friction. Although Navier-Stokes’ equations for frictional flow were formulated yet in mid-19th century, it remained, nevertheless, beyond understanding for a long time why the minor frictional forces, which might be considered negligible in the classic theory, made a decisive impact on motion of bodies.

In 1904 L Prandtl showed the way that made the streamline problem with friction of multi-configuration bodies available for theoretical investigation. He showed from theoretical considerations and some simple experiments that a flow in the vicinity of a body might be divided into two zones, viz. a very thin boundary layer nearby the body, wherein friction dominated, and a zone outside that layer, wherein friction might be disregarded.

The Prandtl’s hypothesis about existence of a boundary layer appeared to have been very fruitful and gave a mighty impetus to the development of theoretical investigations. With the problems set in the early

last century by a boom in the aircraft technique the boundary layer theory has quite soon become a basis of the up-to-date fluid mechanics (along with other theories, viz. the airfoil theory and transonic flow theory).

L. Prandtl first defined the relationship between the turbulent exchange coefficient A_T and the averaged velocity in 1925 based on a notion of the *mixing path length* ℓ . The Prandtl's turbulent flow mechanism may be simplified to the following pattern: particular "moles" (particles) arising in liquid and having their own velocity are moving both in the longitudinal and transverse directions. While moving in this direction for some distance ℓ , the particle enters a zone of other velocity giving to (or taking from) it a corresponding momentum. This momentum is defined by the velocity transverse fluctuation, which allows interpreting the ℓ value as the path length the particle must cover in the transverse direction until the said velocity difference becomes equivalent to the velocity fluctuation in the longitudinal direction. This allows expressing the turbulent exchange coefficient A_T in terms of dv_x/dy by the relationship

$$A_T = \rho \ell^2 dv_x/dy, \quad (7.5.1)$$

and then obtaining the law of friction in the form:

$$\tau_r = \rho \ell^2 (dv_x/dy)^2. \quad (7.5.2)$$

J. Tailor derived (1935) the similar relationship from an assumption the "vorticity" dV_x/dy was constant. This relationship differs from (7.5.2) by only a factor of 0.5 added.

Equation (7.5.2) is successfully applied when calculating the flows alongside the walls and the free (not restricted to walls) turbulence. However, this is inapplicable to those flow zones, where $dv_x/dy = 0$, e.g. beyond the boundary layer or downstream of an obstacle equalizing the velocity. Alternative may be applying to the momentum transfer in the boundary layer the same semi-empirical kinetic equations as for other transfer processes.

When solving this problem, let us take into account that the forces entering into equations (7.3.7) thru (7.3.9) have different tensor order and kind. The bulk viscosity motive force \mathbf{x}_w^n – scalar, the shear viscosity motive force \mathbf{x}_w^s – tensor with a zero trace, the turbulent viscosity motive force \mathbf{x}_w^t – axial vector named in hydrodynamics the *vortex vector*. According to the Curie's principle (chapter 5) forces of different tensor order and kind can not interact. This means that Onsager's phenomenological laws (5.1.6) or (5.4.1), wherein the flows depend on simultaneously all forces acting in a system, are inapplicable to the boundary-layer momentum transfer and give place to the diagonal laws of (7.3.5) thru

(7.3.7) type. However, from the positions of energodynamics the stress tensor components \mathbf{T} must be replaced there by the momentum flow components \mathbf{j}_w which according to their general definition should be construed as the product of the value being transferred (momentum $\rho\mathbf{v}$) and its transfer velocity \mathbf{v}_w in the corresponding (stationary or concurrent) reference system $\mathbf{j}_w = \rho\mathbf{v}\mathbf{v}_w$. In this case from the positions of energodynamics the momentum flows \mathbf{j}_w^n which liquid layers exchange due to the shear viscosity phenomena should be distinguished from the momentum flows \mathbf{j}_w^s arising from the particle deceleration in the bulk strain processes (bulk viscosity phenomena), while the latter – from the rotational momentum flow \mathbf{j}_w^t caused by the vorticity turbulent transfer (turbulent viscosity phenomena). These three independent flows are supported in energodynamics by the three respective kinetic equations of momentum transfer in the boundary layer:

$$\mathbf{j}_w^n = -\mu_v \nabla \cdot \mathbf{v}, \quad (7.5.3)$$

$$\mathbf{j}_w^s = -\mu_c (\nabla \mathbf{v})^s, \quad (7.5.4)$$

$$\mathbf{j}_w^t = -\mu_r (\nabla \mathbf{v})^a, \quad (7.5.5)$$

where $\mathbf{x}_w^n \equiv -\nabla \cdot \mathbf{v}$, $\mathbf{x}_w^s \equiv -(\nabla \mathbf{v})^s$ и $\mathbf{x}_w^t \equiv -(\nabla \mathbf{v})^a = -\frac{1}{2}(\nabla \times \mathbf{v})$ – motive (thermodynamic) forces; η_v , η_s and η_r – phenomenological coefficients. Unlike the stress tensor components \mathbf{T} the flows \mathbf{j}_w^n , \mathbf{j}_w^s and \mathbf{j}_w^t are functions of process, but not state. Thus energodynamics makes logic free of violation when interpreting the stress tensor components (i.e. functions of state) as the momentum flows (S.P. De Groot, R. Mazur/ 1964; I. Gyarmati, 1974, and others).

Equations (7.5.3) thru (7.5.5) allow separately estimating the contribution each of the three said processes makes to energy dissipation caused by the boundary layer and to the associated flow kinetic energy loss. To facilitate the calculations, let us change to the integral form of these equations, where the intractable velocity gradients are replaced by the velocity differentials. For this let us divide the hydrodynamic boundary layer with a thickness of δ_w into sub-layers with a thickness of dn and introduce the integral thermodynamic force \mathbf{X}_{if} thru the expression:

$$\mathbf{X}_{if} = \int \mathbf{x}_i \cdot d\mathbf{n} = - \int (d\mathbf{n} \cdot \nabla) \psi_i = -\Delta \Psi_i, \quad (7.5.6)$$

where $-\Delta \Psi_i = \Psi_i' - \Psi_i''$ – difference in the generalized potentials between those apart from the wall and on the wall. In our case $\mathbf{x}_w^s \equiv -(\nabla \mathbf{v})^s = -dv_x/dy$, i.e. is defined by the velocity gradient in the normal direction to the boundary layer. Since due to adhesion the on-wall velocity $V_x = 0$,

then for the shear viscosity the integral force $\mathbf{X}_{wf}^s = \mathbf{v}$, i.e. is equal to the velocity of incident flow (or the main flow beyond the boundary layer). Similarly, taking into account that $(\nabla\mathbf{v})^a$ means the rotational speed $\boldsymbol{\omega}$ of the liquid element, which also becomes zero on the wall, one can find that $\mathbf{X}_{wf}^T = \boldsymbol{\omega}$, i.e. is defined by the main flow vorticity. It hardly needs proving that such (integral) forces are much more prone to measurement and imposition of boundary conditions.

Next step is to define the momentum flows \mathbf{J}_w^s and \mathbf{J}_w^T when streamlining a body with a surface of \mathbf{f} in whole. Assuming the liquid as incompressible ($\nabla\cdot\mathbf{v}$) for the sake of simplicity and construing η_s , η_T and δ_w as some values averaged over boundary layer length and thickness let us change to the “global” (integral) form of the boundary layer equations:

$$\mathbf{J}_w^s = \int \mathbf{j}_w^s \cdot \mathbf{x}_w^s df d\mathbf{n} = - \int (\mu_s/\delta_w) d\mathbf{v} df = \mu_s f \delta_w^{-1} \mathbf{v}, \quad (7.5.7)$$

$$\mathbf{J}_w^T = \int \mathbf{j}_w^T \cdot \mathbf{x}_w^T df d\mathbf{n} = - \int (\mu_T/\delta_w) d\boldsymbol{\omega} df = \mu_T f \delta_w^{-1} \boldsymbol{\omega}. \quad (7.5.8)$$

Knowing the momentum flows \mathbf{J}_w^s , \mathbf{J}_w^T and the motive forces of the energy dissipation processes \mathbf{V} and $\boldsymbol{\omega}$, the contribution of each of them to the power dissipation N^d may be easily calculated:

$$N_S^d = \mathbf{J}_w^s \cdot \mathbf{v}; \quad N_T^d = \mathbf{J}_w^T \cdot \boldsymbol{\omega}. \quad (7.5.9)$$

Since, on the other hand, the per-second work of frictional forces \mathbf{F}^d is defined by the expression $N^d = \mathbf{F}^d \cdot \mathbf{v}$, the tractive resistance of a body or the frictional losses in the channel may be found from the balance:

$$\mathbf{F}^d = \mathbf{J}_w^c + \mathbf{J}_w^T \cdot \boldsymbol{\omega}/\mathbf{v}. \quad (7.5.10)$$

These equations do not demand knowledge of the detailed pattern of velocity distribution in the boundary layer, its evolution along the surface being streamlined, the laws of viscosity coefficient variation against the thermodynamic state parameters, etc. Therefore in some instances, when their averaging is not too complicated, equations (7.5.10) can facilitate the streamline resistance calculation. Such an approach is intrinsically quite close to the wind-tunnel test results with regard to velocity fields upstream and downstream of the body under testing. In both cases not the boundary layer itself becomes the object of investigation, but the boundary layer-conditioned integral losses in the surrounding stream or the “wake” of the liquid being compressed. The advantage of such an approach lies in the rejection of whatever hypotheses and patterns of boundary layer behavior. Besides, particularly noticeable are simplicity, obviousness and conciseness of the math calculations leading to the re-

sults already known, whereas usually the statement of these problems covers hundreds of pages and the body of mathematics applied is far from everybody's comprehension. Furthermore, energodynamics abolishes the necessity to introduce a number of new notions, such as the "boundary layer displacement thickness", "momentum displacement thickness", etc. It is also quite understandable from the positions of energodynamics how the linear law of resistance goes over into the square law with the vortex motion evolving.

Chapter 8

ELECTRODYNAMICS

Despite indubitable achievements of the modern theory of electromagnetism and creating on its basis such directions as electrical engineering, radio engineering and electronics, this theory is certainly far from completion. This chapter is dedicated to corrections to be made to electrostatics and electrodynamics from the more general positions of energodynamics with the consecutive modifications to be imparted to our vision of the laws of motion and interaction between charged bodies.

8.1. Free, polarization and dipole Charges

As shown in Chapter 1 (Fig. 1.2), the redistribution of the density ρ_i for any field value Θ_i including the free charge Θ_e is associated with a displacement of its center position. As a result, some "moment of distribution" \mathbf{Z}_i appears with the arm $\mathbf{r}_i - \mathbf{r}_{i0}$ featuring the deviation of the system from homogeneous state. In the particular case of open conductors inserted into the electric field \mathbf{E} the parameter Θ_i is the free charge Θ_e so that the value \mathbf{Z}_i assumes a meaning of the electric displacement vector in the system as a whole, which density $\mathbf{Z}_{eV} = \partial\mathbf{Z}_e/\partial V = \rho_e(\mathbf{r}_e - \mathbf{r}_{e0})$ is identical in its sense to the electric displacement (induction) vector \mathbf{D} in unit volume of homogeneous dielectric:

$$\operatorname{div} \mathbf{D} = \operatorname{div} \mathbf{Z}_{eV} = \rho_e. \quad (8.1.1)$$

According to (2.4.10) the total time t derivative of the vector \mathbf{Z}_i defines the displacement flux $\mathbf{J}_i^c \equiv (\partial \mathbf{Z}_i / \partial t)_\phi = \Theta_i \mathbf{v}_i$, while the similar derivative of this moment density \mathbf{Z}_{eV} defines the density of this flux¹⁾ (8.1.2)

$$\mathbf{J}_i^c \equiv (\partial \mathbf{Z}_i / \partial t)_\phi = \Theta_i \mathbf{v}_i; \quad \mathbf{j}_i^c = (\partial \mathbf{Z}_{eV} / \partial t)_\phi = \rho_i \mathbf{v}_i. \quad (8.1.2)$$

This expression generalizes the Maxwell-introduced notion of flux to other-kind phenomena. According to energodynamics the displacement fluxes appear in the course of redistribution of any energy carrier Θ_i over the bulk of the system regardless of what caused that redistribution – either the system relaxation or non-uniform inflow of the energy carrier Θ_i across the borders of the system (flux divergence \mathbf{J}_i).

$$\mathbf{r}_i' = (\sum \mathbf{r}_i' d\Theta_i') / \Theta_i'; \quad \mathbf{r}_i'' = (\sum \mathbf{r}_i'' d\Theta_i'') / \Theta_i''. \quad (8.1.1)$$

The said approach is as well applicable to the processes of polarization and magnetization in dielectric and magnetic materials. Their unity may be more easily comprehended if imagining these processes as a result of creating dipoles with unlike (opposite in sign) elementary electric or magnetic “charges” (Ch. Coulomb, 1785). Marking them with single and double prime, respectively ($d\Theta_i' = \rho_i' dV$ and $d\Theta_i'' = \rho_i'' dV$), one can find the positions of their centers \mathbf{r}_i' and \mathbf{r}_i'' for the system as a whole:

$$\mathbf{r}_i' = (\sum \mathbf{r}_i' d\Theta_i') / \Theta_i'; \quad \mathbf{r}_i'' = (\sum \mathbf{r}_i'' d\Theta_i'') / \Theta_i''. \quad (8.1.3)$$

Since in the polarization processes the system in whole remains neutral ($\Theta_i' = -\Theta_i''$), its moment of polarization charge distribution $\mathbf{Z}_i = \Theta_i' \mathbf{r}_i' + \Theta_i'' \mathbf{r}_i''$ will be similar to (8.1.1):

$$\mathbf{Z}_i = \Theta_i'' (\mathbf{r}_i'' - \mathbf{r}_i'), \quad (8.1.4)$$

where $\mathbf{r}_i'' - \mathbf{r}_i'$ – mean value of dipole arm. The value \mathbf{Z}_i should be conveniently represented as the total moment of dipole both arms. To do this, let us express the dipole arm $\mathbf{r}_i'' - \mathbf{r}_i'$ as $(\mathbf{r}_i'' - \mathbf{r}_{i0}) - (\mathbf{r}_i' - \mathbf{r}_{i0}) = \Delta \mathbf{r}_i'' - \Delta \mathbf{r}_i'$, where $\mathbf{r}_{i0} = (\mathbf{r}_i' + \mathbf{r}_i'')/2$. With the sign of the dipole arms arbitrarily chosen; let us assume $\Delta \mathbf{r}_i' \leq 0$ и $\Theta_i' \leq 0$. Then the moments of the arms $\Theta_i' \Delta \mathbf{r}_i'$ and $\Theta_i'' \Delta \mathbf{r}_i''$ receive the same sign, and the total dipole moment of the system becomes equal to their sum $\mathbf{Z}_i = \Theta_i' \Delta \mathbf{r}_i' + \Theta_i'' \Delta \mathbf{r}_i''$. The derivative $\mathbf{Z}_{iV} \equiv (\partial \mathbf{Z}_i / \partial V) = \rho_i' \Delta \mathbf{r}_i' + \rho_i'' \Delta \mathbf{r}_i''$ defines the dipole moment in the unit volume of dielectric and magnetic: $\mathbf{Z}_{eV} = \rho_e' \Delta \mathbf{r}_e' + \rho_e'' \Delta \mathbf{r}_e''$ and $\mathbf{Z}_{mV} =$

$\rho_m' \Delta \mathbf{r}_m' + \rho_m'' \Delta \mathbf{r}_m''$, respectively, which corresponds to the notions of the polarization vector \mathbf{P} and the magnetization vector \mathbf{M} usually introduced by definition (L.D. Landau, E.M. Livshits, 1982). Hereafter we will be using these more common terms referring, however, to the unlike electric and magnetic charges Θ_i' and Θ_i'' as “dipole charges to clarify their origin, and the values ρ_e and ρ_m – densities of these charges.

According to the thermodynamic methodology the relationship between the extensive dipole moments \mathbf{Z}_e and \mathbf{Z}_m of dielectric and magnetic, their absolute temperature T and volume V , the electric and magnetic field intensities \mathbf{E} and \mathbf{H} , may be expressed by the state equations in the general form:

$$\mathbf{Z}_e = \varepsilon_0 \varepsilon_r(T) V \mathbf{E} ; \quad \mathbf{Z}_m = \mu_0 \mu_r(T) V \mathbf{H}, \quad (8.1.5)$$

where ε_0 , μ_0 – dielectric and magnetic permeability of “void”, respectively; $\varepsilon_r(T)$ and $\mu_r(T)$ – relative permeability of dielectric and magnetic as a function of their absolute temperature T . The known relationships below may be a modification of the above equations:

$$\mathbf{D} \equiv \varepsilon_0 \mathbf{E} + \mathbf{P} ; \quad \mathbf{B} \equiv \mu_0 \mathbf{H} + \mathbf{M}. \quad (8.1.6)$$

These equations define internal state of dielectrics and magnetics. In the particular case of conductors with no polarization the state equation becomes $\mathbf{D} = \varepsilon_0 \mathbf{E}$. The fact is quite important that according to the thermodynamic methodology it is the electric displacement vector \mathbf{D} that defines the sum of free and bound charges of imperfect dielectric rather than the external field \mathbf{E} existing, by the way, in vacuum, too (in the absence of any charges at all). Should it be otherwise, i.e. should the field \mathbf{E} characterize internal state of the system, one more state equation would evidently be needed to relate the \mathbf{E} with the external field. The same may be referred to the magnetic induction vector, too, which is often taken for the external field feature.

The introduction of the extensive parameters of heterogeneity \mathbf{Z}_i not only absolutely clarifies the problem, but also allows better visualizing the generation of polarization charges. If the boundaries of a system under consideration are marked correctly, i.e. do not “intersect” dipoles, the system contains a whole number of dipoles, which total charge $\Theta_i' + \Theta_i''$ is equal to zero:

$$\int (\rho_e' + \rho_e'') dV = 0 ; \quad \int (\rho_m' + \rho_m'') dV = 0. \quad (8.1.7)$$

This integral relationship holding true for a body of any volume means that the integrand $(\rho_e' + \rho_e'')$ or $(\rho_m' + \rho_m'')$ is expressed by diver-

gence of some vector values named the polarization vector \mathbf{P} and the magnetization vector \mathbf{V} (L.D. Landau, E.M. Livshits, 1982):

$$\operatorname{div}\mathbf{P} = \rho_e' + \rho_e''; \quad \operatorname{div}\mathbf{M} = \rho_m' + \rho_m'' \quad (8.1.8)$$

In a dielectric or magnetic homogeneously polarized these charges add up to zero, so that $\operatorname{div}\mathbf{P} = 0$ and $\operatorname{div}\mathbf{M} = 0$. However for the heterogeneous polarization (when the dipole arm being changed, a part of like dipole charges are “withdrawing” beyond the check bulk boundaries) the so-called “polarization” charges¹⁾ may appear (electric $\rho_e^p = -\operatorname{div}\mathbf{P}$ [2] and magnetic $\rho_m^p = -\operatorname{div}\mathbf{M}$ ones, respectively (K.M. Polivanov, 1982)). In distinction from ρ_e^p and ρ_m^p the dipole charges ρ_i' , ρ_i'' do not disappear with the homogeneous polarization of a dielectric or magnetic, and this fact plays, as we will see hereafter, an important part in formulating the Maxwell’s equations.

8.2. Thermodynamic Derivation of Maxwell’s Electrodynamic Equations

Let us consider, for generality, a stationary system being in the external electric \mathbf{E} and magnetic \mathbf{H} fields and adequately possessing the electric and magnetic degrees of freedom. The unit volume ordered energy E_v for such a system is a function of the electric \mathbf{D} and magnetic \mathbf{B} induction vectors which in their turn depend on the intensities \mathbf{E} and \mathbf{H} of these fields. The energodynamic relationship between them is

$$dE_v = \mathbf{E} \cdot d\mathbf{D} + \mathbf{H} \cdot d\mathbf{B} \quad (8.2.1)$$

The terms on the right side of the equation characterize, respectively, the elementary polarization $dW_{eV} = \mathbf{E} \cdot d\mathbf{D}$ magnetization $dW_{mV} = \mathbf{H} \cdot d\mathbf{B}$ works of the system.

Let us assume that in such a system the reciprocal conversions of electric and magnetic field energies run, which powers are

$$N_e = \mathbf{E} \cdot d\mathbf{D}/dt; \quad N_m = \mathbf{H} \cdot d\mathbf{B}/dt \quad (8.2.2)$$

Providing these processes do not change the system energy and entropy (i.e. the energy of the system entirely converts from a one ordered form into the other), the power balance $N_e = -N_m$ is evident. This directly leads to the following relationship:

$$\mathbf{E} \cdot (d\mathbf{D}/dt) = -\mathbf{H} \cdot (d\mathbf{B}/dt) \quad (8.2.3)$$

These simple relationships may be given the form offered by Maxwell. For this let us consider a system consisting of a closed electric circuit with an arbitrary length ℓ_e and variable (in general case) cross section f_e , which comprises an as well closed magnetic circuit with a length ℓ_m and cross section f_m variable thru the length. Taking this variability into consideration, (8.4.2) should be changed to the integral form:

$$N_e = \int \mathbf{E} \cdot (d\mathbf{D}/dt) dV_e; \quad N_m = \int \mathbf{H} \cdot (d\mathbf{B}/dt) dV_m, \quad (8.2.4)$$

The bulk elements may be represented in the form $dV_e = d\ell_e \cdot d\mathbf{f}_e$ and $dV_m = d\ell_m \cdot d\mathbf{f}_m$, where $d\ell_e$, $d\ell_m$ and $d\mathbf{f}_e$, $d\mathbf{f}_m$ – orthogonal vector elements of length and cross section, respectively, of the electric circuit and dielectric. The expressions (8.4.4) may be rewritten in terms of energodynamics as follows:

$$N_e = \int \mathbf{E} \cdot d\ell_e \int (d\mathbf{D}/dt) d\mathbf{f}_e = X_e J_e^d; \quad (8.2.5)$$

$$N_m = \int \mathbf{H} \cdot d\ell_m \int (d\mathbf{B}/dt) d\mathbf{f}_m = X_m J_m^d, \quad (8.2.6)$$

where $J_e^d = \int (d\mathbf{D}/dt) d\mathbf{f}_e$, $J_m^d = \int (d\mathbf{B}/dt) d\mathbf{f}_m$ – total fluxes of electric and magnetic displacements, respectively, sometimes named the “linkage fluxes” and traditionally represented by the number of the lines of force linking the cross section of the electric and magnetic circuits, respectively (K. Polivanov, 1982); $X_e = \int \mathbf{E} \cdot d\ell_e$, $X_m = \int \mathbf{H} \cdot d\ell_m$ – the so-called electromotive and magnetomotive forces (emf and mmf) defined by the circulation of the vectors \mathbf{E} and \mathbf{H} , respectively, along the closed electric and magnetic circuits.

Now the electromagnetic field equations may be given the form of phenomenological laws (5.1.6):

$$J_e^d = L_{ee} X_e + L_{em} X_m; \quad (8.2.7)$$

$$J_m^d = L_{me} X_e + L_{mm} X_m. \quad (8.2.8)$$

Here the terms $L_{ee} X_e$ and $L_{mm} X_m$ characterize the relaxation part of the displacement fluxes, which relates to the conduction current $I_e = L_{ee} X_e$ and its magnetic analog $I_m = L_{mm} X_m$ and is caused by, respectively, electric and magnetic energy dissipation; the terms $L_{em} X_m$ и $L_{me} X_e$, on the contrary, relate to overcoming the “extraneous” forces by the flow, i.e. to conversion of the electric energy into magnetic one and vice versa. Since $N_e = -N_m$ relationships (8.4.5)–(8.4.6) may take a more simple form:

$$J_e^d/X_M = -J_M^d/X_e . \quad (8.2.9)$$

Comparing this equation with phenomenological laws (8.2.7) and (8.2.8) one can find that the left-side part of (8.2.9) defines the coefficient L_{em} , while the right-side part $-L_{me}$. From this the Cazimir's anti-symmetry conditions (5.1.7)¹⁾ follow:

$$L_{em} = -L_{me} . \quad (8.2.10)$$

The value and dimensionality of these coefficients depend on the system of units chosen. In the international system of units (SI) $L_{em} = -L_{me} = 1$, therefore it may be written instead of (8.4.10):

$$X_e = -\int (d\mathbf{B}/dt) d\mathbf{f}_M , \quad (8.2.11)$$

$$X_M = \int (d\mathbf{D}/dt) d\mathbf{f}_e , \quad (8.2.12)$$

The first of these relationships represents Faraday's law (flux rule) reading that emf is equal in value, but opposite in sign to the variation rate of the electric circuit-linking flux. Let us now change, based on the Stokes theorem, in the force equation $X_e = \int \mathbf{E} \cdot d\mathbf{l}_e$ from the curvilinear integral taken over the closed electric circuit with a length of ℓ_e to the integral $\int \text{rot} \mathbf{E} \cdot d\mathbf{f}_M$ over the magnetic circuit cross section f_M . In the similar way one can change in the force equation $X_M = \int \mathbf{H} \cdot d\mathbf{l}_M$ from the curvilinear integral over the closed magnetic circuit with a length of ℓ_M to the integral $\int \text{rot} \mathbf{H} \cdot d\mathbf{f}_e$ over the surface f_e covering the electric circuit. Then (8.2.11) and (8.2.12) become:

$$\int \text{rot} \mathbf{E} \cdot d\mathbf{f}_M = -\int (d\mathbf{B}/dt) d\mathbf{f}_M . \quad (8.2.13)$$

$$\int \text{rot} \mathbf{H} \cdot d\mathbf{f}_e = \int (d\mathbf{D}/dt) d\mathbf{f}_e ; \quad (8.2.14)$$

Or in the differential form

$$\text{rot} \mathbf{E} = -d\mathbf{B}/dt, \quad (8.2.15)$$

$$\text{rot} \mathbf{H} = d\mathbf{D}/dt . \quad (8.2.16)$$

¹⁾ Availability of such relationships once again confirms that electricity and magnetism are two independent phenomena with interrelation between them seen only in dynamics.

These equations differ from the corresponding Maxwell's equations in that they contain the total time derivatives of electric and magnetic induction vectors. This is not a surprise since the primary equations of ergodynamics (see 8.4.1) as well contain the exact differentials of polarization and magnetization vectors. It is significant that Maxwell himself initially defined emf as well thru the total derivative $d\Phi/dt$ of magnetic flux Φ (K. Polivanov, 1982).

To form equations (8.4.15) and (8.4.16) into a more common shape, let us expand the derivatives $d\mathbf{B}/dt$ and $d\mathbf{D}/dt$ on the assumption that polarization and magnetization processes are absent in a system under consideration ($\mathbf{P}, \mathbf{M} = 0$). Since $(\partial\mathbf{E}/\partial\mathbf{r}) = \rho_e/\epsilon_0$, whereas magnetic analogs to the free charge ρ_e do not exist, we have:

$$d\mathbf{B}/dt = (\partial\mathbf{B}/\partial t); \quad d\mathbf{D}/dt = (\partial\mathbf{D}/\partial t) + \mathbf{j}_e. \quad (8.2.17)$$

Here $\mathbf{j}_e = (\partial\mathbf{D}/\partial\mathbf{r})\mathbf{v}_e = \rho_e\mathbf{v}_e$ – conduction current caused by the free charge transfer.

Thus finally:

$$\text{rot } \mathbf{E} = -(\partial\mathbf{B}/\partial t), \quad (8.2.18)$$

$$\text{rot } \mathbf{H} = \mathbf{j}_e + (\partial\mathbf{D}/\partial t). \quad (8.2.19)$$

As for another couple of Maxwell's equations:

$$\text{div } \mathbf{D} = \rho_e, \quad (8.2.20)$$

$$\text{div } \mathbf{B} = 0, \quad (8.2.21)$$

the first of them is a direct consequence from expression (8.1.1) written in the differential form since the electric displacement vector \mathbf{D} is identical by implication to the vector \mathbf{Z}_{eV} . Relationship (8.4.21) just states the fact of the absence of magnetic “monopolies” analogous to the electric charge ρ_e .

The thermodynamic derivation of electromagnetic field equations set herein forth rebuts the popular opinion that the Maxwell's equations are non-derivable from whatever primary laws. At the same time this derivation discloses a number of assumptions laid into their foundation. First of all, electromotive and magnetomotive forces have been defined in (8.2.11) and (8.2.12) for closed electric and magnetic circuits. Hence the Maxwell's equations are inapplicable to non-closed electric currents and their elements. This is what Maxwell himself stressed. Secondly, such processes as the re-polarization in semiconductors and the magnetic cir-

cuit re-magnetization were excluded from consideration. As a result, the losses from irreversibility of the electric-to-magnetic (and vice versa) field conversion were allowed for only the electric form of energy (due to conduction currents). The magnetic loss (re-magnetization, eddy currents, etc.) which lead to a magnetic analog of the conduction current was not taken into consideration in that case. It was assumed further that the electric and magnetic fluxes in equations (8.2.11) and (8.2.12) were homogeneous so that the power balance $N_e = N_m$ was observed for each of the local zones of a system under investigation (otherwise changing to the differential form (8.2.13)...(8.2.14) of the above equations becomes incorrect). These circumstances cause some incompleteness of the Maxwell's equations and disable interpreting on their basis a number of effects hardly prone to analysis.

8.3. Theoretical Derivation of Coulomb's Law

The theoretical substantiation of Coulomb's law (1785) usually proceeds from interpreting the "field flow" \mathbf{E} as something flowing "out from" a point charge and then "out into" a space just like it occurs with a gaseous mass or heat flow, i.e. preserved values (R. Feynman and others, 1979; L.D. Landau, E.M. Livshits, vol. 8, 1982).

However such analogy looks excessively artificial concerning electric field. It is a matter of interest thereby to derive Coulomb's law from more reliable data. According to (1.6.4) $\rho_e = \nabla \cdot \mathbf{Z}_{eV}$, so the electric charge Θ_e to area with volume V is equal

$$\Theta_e = \int \rho_e dV = \int \nabla \cdot \mathbf{Z}_{eV} dV, \quad (8.3.1)$$

where $\mathbf{Z}_{eV} = \partial \mathbf{Z}_e / \partial V$ – density of charge distribution moment meaning for electric phenomena the electric displacement vector in dielectric unit volume $\mathbf{Z}_{eV} \equiv \mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$. The Gauss' law (8.3.2) directly follows from here:

$$\nabla \cdot \mathbf{E} = \rho_e / \epsilon_0, \quad (8.3.2)$$

where ϵ_0 – vacuum inductive capacity.

The Gauss' law is seen to be a direct consequence of charge heterogeneous distribution. Substituting in (8.3.1) $\epsilon_0 \mathbf{E}$ for \mathbf{Z}_{eV} and changing as per the Gauss' theorem from the integral with respect to volume to the integral with respect to the closed surface $f=4\pi r_c^2$ of some sphere with the radius r_c encircling the charge Θ_e gives: (8.3.2).

$$\Theta_e = \varepsilon_0 \int \mathbf{E} \cdot \mathbf{n} df = 4\pi\varepsilon_0 \int E_e dr_c^2. \quad (8.3.3)$$

The Coulomb's law directly follows from here:

$$E_e = \Theta_e / 4\pi\varepsilon_0 r_c^2, \quad (8.3.4)$$

where $\mathbf{Z}_{eV} = \partial \mathbf{Z}_e / \partial V$ – density of charge distribution moment.

The value \mathbf{Z}_{eV} is one of the local measures of spatial heterogeneity, the thermodynamic force \mathbf{x}_e being another measure expressed according to (1.5.6) by the negative gradient ψ_e of electric potential, i.e. $\mathbf{x}_e = -\nabla\psi_e$. The parameters \mathbf{Z}_{eV} and \mathbf{x}_e are interrelated by the general equation of state $\mathbf{x}_e = \mathbf{x}_e(\mathbf{Z}_{eV})$. Assuming this relationship as linear with the proportionality factor $1/\varepsilon_0$ (i.e. $\mathbf{x}_e = \varepsilon_0^{-1} \mathbf{Z}_{eV}$), (8.3.2) may be rewritten as:

$$\Theta_e = \int \varepsilon_0 \mathbf{x}_e \cdot \mathbf{n} df. \quad (8.3.3)$$

Factoring some mean value of electric intensity $\mathbf{x}_e \cdot \mathbf{n} = x_e = |\mathbf{E}|$ outside the integral sign and integrating (8.1.3) with respect to spherical surface with a radius R_s enclosing the set of charges Θ_e under consideration gives an expression of the specific force acting on the unit (test) charge from the above set of charges:

$$x_e = \Theta_e / 4\pi\varepsilon_0 r_s^2. \quad (8.3.4)$$

This expression defines the force of attraction of a test charge opposite in sign lying on the surface of the sphere under consideration. Taking into consideration that $\mathbf{x}_e = \mathbf{E} = -\nabla\varphi$ the electric potential $\varphi = \varphi(\mathbf{r})$ in any field point $r \geq r_s$ may be found by integrating (8.3.4) between the limits r_s and r :

$$\varphi(\mathbf{r}) = (\Theta_e / 4\pi\varepsilon_0)(1/r_s - 1/r). \quad (r \geq r_s) \quad (8.3.5)$$

In this case the force $F_e = |\mathbf{F}_e|$ of attraction of the test charge Θ_e' defined by the derivative $\mathbf{F}_e / \Theta_e' = -\partial\varphi / \partial \mathbf{r}_e$ complies with Coulomb's law:

$$F_e = |\mathbf{F}_e| = \Theta_e \Theta_e' / 4\pi\varepsilon_0 R^2. \quad (8.3.6)$$

In accordance with (8.3.5) the applicability of this law is restricted to a conventional (equivalent) radius $r \geq r_s$ characterizing the sphere of the "field-forming" body, i.e. to the minimal distance two test charges can approach each other. This meets the Coulomb's experiment with a torsion

balance, where charged bodies were used, which had though small, but finite, dimensions. Each of the charged bodies used in the Coulomb's experiments also was a heterogeneous system due to the mutual repulsion of like charges therein.

Thus Coulomb law directly ensues from the heterogeneous distribution of charges in the system of "field-forming" bodies. The validity of this assumption is even more evident, because any set of interacting charges spatially separated already represents a heterogeneous system. From this it follows that the validity of Coulomb law is restricted to the minimal distance any two charged bodies can approach each other. This statement remains valid also in the case when charged bodies can interpenetrate. In fact, when two sets of charges are located concentric on each other (so that $R = 0$), then the potential of the body in the center of the charged sphere and its interaction force are equal to zero irrespective of values of the charges themselves (R. Feynman, and others, 1976).

It is significant that neither gravity \mathbf{F}_g , nor energy of the "field-forming" body (potential ψ_g) becomes infinite. Thereby a way opens toward a solution to the "divergence" problem arisen in quantum electrodynamics from treating the material particles as points lacking extent.

8.4. The Ohm's law and its generalisation

The Ohm's law experimentally discovered in 1827 for the case of stationary conductivity is known to be one of the most important laws which gave rise to electrostatics:

$$\mathbf{j}_e = -\sigma_e \nabla \varphi, \quad (8.4.1)$$

where σ_e – coefficient of electroconductivity; $\mathbf{E} = -\nabla \varphi$ – intensity of electrostatic field.

This law describes the electric charge motion under the action of the Coulomb's forces. In a more general case according to the laws of ergodynamics (5.4.2) the charge motion is affected by all other thermodynamic forces \mathbf{x}_i of the same tensor rank and kind available in the system. In particular, for the operation of electric engineering devices it is absolutely necessary that processes should run wherein negative charges move away from positive ones in defiance of the Coulomb's forces. To provide this, forces of "non-coulomb's nature" are needed called sometimes as "foreign" \mathbf{E}^{for} , "induced" \mathbf{E}^{ind} , etc (K.M. Polivanov, 1982). As a result, expression (8.4.1) takes the form of the Ohm's generalized law:

$$\mathbf{j}_e = \sigma_e (\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (8.4.2)$$

These “foreign” forces can be most easily found from equation (8.2.15) by substituting the total derivative $d\mathbf{B}/dt$ of magnetic field for the partial one. In this case $d\mathbf{B}/dt = (\partial\mathbf{B}/\partial t) + (\mathbf{v}_e \cdot \nabla)\mathbf{B}$, and according to (8.2.15) by vector analysis:

$$\text{rot } \mathbf{E} = [\mathbf{v} \times \text{rot} \mathbf{B}] - \partial \mathbf{B} / \partial t = \text{rot} [\mathbf{v} \times \mathbf{B}] - \text{rot} (\partial \mathbf{A}_e / \partial t). \quad (8.4.3)$$

Since in a closed electric circuit $\oint d\mathbf{l}_e \cdot \nabla \varphi = 0$, the motion of charges therein is provided by exclusively foreign forces \mathbf{E}^{for} so that (8.4.3) becomes:

$$\mathbf{E} = [\mathbf{v} \times \mathbf{B}] - (\partial \mathbf{A}_e / \partial t). \quad (8.4.4)$$

The first of these forces is the Lorentz’ force magnetic component $\mathbf{F}_n = \mathbf{v}_e \times \mathbf{B}$, while the other – the Ampere’s force $\mathbf{F}_A = I [\mathbf{l}, \mathbf{B}]$ found experimentally (1820) by the action of magnetic field \mathbf{B} on a conductor with a length of \mathbf{l} carrying current I and related here to the current density $\mathbf{j}_e = \rho_e \mathbf{v}_e$ of the charges moving through the conductor with a velocity of \mathbf{v}_e .

As a result the Ohm’s generalized law (8.4.2) takes the form: (8.4.5)

$$\mathbf{j}_e = \sigma_e (\mathbf{E} - \partial \mathbf{A}_e / \partial t + \mathbf{v} \times \mathbf{B}). \quad (8.4.5)$$

This expression is presently considered as most general. Meanwhile, according to TIP and energodynamics EMF is undoubtedly affected by also other physical, physicochemical, thermodynamic, etc processes. As will be ascertained hereafter, the Ohm’s law for systems with heterogeneous temperature field should be supplemented with the “thermo-electric” force \mathbf{X}_{er} expressed in terms of temperature gradient. In a more general case of electrochemical systems the motion of charged particles is caused by also the electrochemical forces \mathbf{X}_{ek} defined in terms of concentration gradients for the k th components of the system. Additional effects arise in also media with pressure gradients or differences, e.g., in electrolytic solutions. In this case one more EMF component appears in equation (8.3.5). Such an EMF representation will allow obtaining a whole number of the so-called superposition effects describing the interrelation between electric and non-electric phenomena.

The available foreign forces answer for introducing in electrical engineering the special scalar EMF \mathcal{E} . That notion was first applied with discovery of such a phenomenon as electromagnetic induction – EMF generation at variation in magnetic flux (Faraday, 1831). The electromagnetic induction formula as given by Faraday was very simple:

$$\mathcal{E} = -d\Phi_M/dt, \quad (8.4.6)$$

where \mathcal{E} – electromotive force (EMF); Φ_M – total magnetic flux which is by Faraday the number of magnetic lines “cut” by the magnetic circuit (or crossing it). Here each of the lines was associated with unit magnetic flux. Accordingly the EMF is evaluated by the work W_e the non-coulomb forces of “induction” \mathbf{E}^{ind} could do to transport unit charge in closed electric circuit with a length of \mathbf{l}_e :

$$\mathcal{E} = W_e/\Theta_e = \oint E^{\text{ind}} d\mathbf{l}_e. \quad (8.4.7)$$

In this case $d\mathcal{E} = (\mathbf{v} \times \mathbf{B})d\mathbf{l}_e$, i.e. is totally caused by the action of the Lorentz' force magnetic component. Nevertheless, Maxwell expresses the EMF in a more general form:

$$\mathcal{E} = \int (-\nabla\phi - \partial\mathbf{A}_e/\partial t + \mathbf{v} \times \mathbf{B})d\mathbf{l}_e. \quad (8.4.8)$$

Thus including also the potential gradient in the number of the non-coulomb's (foreign) forces though this gradient features all-electrical nature and disappears at closed-loop integration. Besides, the summand $-\partial\mathbf{A}_e/\partial t$ he also refers to the electric field intensity \mathbf{E} though, as shown above, it also features the non-coulomb's nature and, hence, should be referred to the “foreign” forces. This is what evidently explains the fact that this force has not had a definite interpretation and generally accepted name so far. All this evidences a certain imperfection of the force classification adopted in electrodynamics. This shows in the stereotyped statement that the Lorentz' force magnetic component does not do any work since it always acts along the normal to the electron path of motion ¹. Meanwhile, this conclusion is valid for just a current element, but not for the closed circuit as a whole, for which the Maxwell's equations apply. As follows from the above derivation of these equations, they describe the law of energy conservation at the conversion of the magnetic field energy into the electric field one and vice versa. As applied to the DC circuit, the rotation of a current loop in the magnetic field is the only kind of useful work done in the process. In energodynamics this fact is stressed through replacing the term $\mathbf{H} \cdot d\mathbf{B}$ in the law of energy conservation (8.2.1) by the more essentially adequate product of the torque (orientation mo-

¹ It means this force is not electromotive though referred to the “foreign” forces.

ment) \mathbf{M}_e the magnetic field generates and the angle of the current loop rotation $d\phi_e$ as done in the fundamental identity of energodynamics (2.2.5).

8.5. Flows of Electric and Magnetic Fields Energy. Poynting's Vector as their synthesis

As it follows from the law of conservation of energy (see 2.3.6), the rate of energy E variation in a system is equal to the total energy flux J_e across the borders of the system. In case of mechanical motion the density of this flux is defined by the Umov's vector he introduced in 1873. That vector defined the flux \mathbf{j}_u of internal energy the body transferred if had a mechanical stress. Ten years later (in 1884) an analogous expression for the electromagnetic energy flux $\mathbf{\Pi}$ was set forth by Poynting. To find this, let us use the expression for the per-second work (power) of the electric and magnetic energy reciprocal conversion process (8.2.1), (8.2.2).

Taking into account that according to (8.2.15) and (8.2.16) $d\mathbf{B}/dt = -\text{rot } \mathbf{E}$, $d\mathbf{D}/dt = \text{rot } \mathbf{H}$, (8.2.1) becomes:

$$dE_{\text{v}}/dt = \mathbf{E} \cdot \text{rot} \mathbf{H} - \mathbf{H} \cdot \text{rot} \mathbf{E} = -\text{div} \cdot (\mathbf{E} \times \mathbf{H}) = -\text{div} \mathbf{\Pi}. \quad (8.5.1)$$

From this it follows that the Poynting's vector is the external product of the electric and magnetic intensity vectors:

$$\mathbf{\Pi} \equiv \mathbf{E} \times \mathbf{H}, \quad (8.5.2)$$

and is oriented perpendicular to those in the direction of the electromagnetic energy propagation. That warranted the consideration of electromagnetic energy as a whole. Meantime, as it emerges from (8.5.1), the Poynting's vector reflects just a power balance of these processes. In particular, with equality of powers N_e and N_m (no losses) $dE_{\text{v}}/dt = 0$, so that $\text{div} \mathbf{\Pi} = 0$. This means that despite the vector $\mathbf{\Pi}$ differs from zero the electromagnetic energy as itself is not consumed by the system and not converted into other forms of energy. Only electromagnetic energy components are reciprocally convertible with their sum remaining unvaried in the absence of dissipation. This explains why the Poynting's vector is equal to zero in this case. Only whenever the electromagnetic energy converts into the dissipation heat that according to Ohm's law (8.3.4) is expressed by the product $\mathbf{E} \cdot \mathbf{j}_e = \mathbf{j}_e^2 / \sigma_e$, the Poynting's vector becomes equal to this loss value $N^d = N_e - N_m$. In a more general case when energy conversion in a system is accompanied by partial energy transformation

into the internal potential (mechanical) energy of its elastic deformation (strain energy), the right-hand side of the law of conservation of energy (see 8.4.1), along with the dissipative work dW^d , is supplemented with the mechanic work dW_{mech} , then equation (8.6.3) becomes:

$$dE_{\text{v}}/dt = N_e + N_M + N_{\text{mech}} + N^d = -\text{div}\mathbf{\Pi} - \text{div}\mathbf{j}_u + N^d. \quad (8.5.3)$$

Only then the conversion of electromagnetic energy into heat and mechanical ones may be referred to as the “conversion of Poynting’s vector into Umov’s vector” (K. Polivanov, 1982). Thus the Poynting’s vector reflects neither quantitatively nor qualitatively the reciprocal conversion of electric and magnetic energies. This disadvantage is avoided by energetics demanding the extensive coordinate to be found for each form of energy as a quantitative measure of this motion form carrier. In the instant case such are the distribution moments \mathbf{Z}_e and \mathbf{Z}_M , which time derivatives define the total fluxes of electric and magnetic displacements with the densities, respectively, \mathbf{j}_e^s and \mathbf{j}_M^s . This allows separate definition of the polarization and magnetization works done by electric and magnetic fields, respectively:

$$N_e = \mathbf{E} \cdot \mathbf{j}_e^c = \frac{1}{2} \varepsilon_0 \varepsilon_r d\mathbf{E}^2/dt; \quad N_M = \mathbf{H} \cdot \mathbf{j}_M^c = \frac{1}{2} \mu_0 \mu_r d\mathbf{H}^2/dt. \quad (8.5.4)$$

Thus electric and magnetic fields in dynamics as well are independent, though interrelated entities, which becomes especially evident only in statics. The found unity of the conversion processes for any forms of energy may appear to be quite useful to overcome difficulties in comprehension of electrodynamics.

Chapter 9.

QUANTUM MECHANICS

In this chapter we will consider appendices of ergodynamics to that area of the physical phenomena which is studied by the quantum (wave) mechanics. Quantum mechanics proceeded from the assumption that the laws the molecules and elementary particles (i.e. the objects of the microcosm) obey would radically differ from the classic laws regulating the behavior of macro-objects. One of the reasons to deny the classic wave theory of light were discovery the properties of light as particle (photoeffect, photoluminescence, Compton effect).

Other reason was the problem of atom stability. According to classical mechanics rotating electron should fall on a kernel in connection with continuously radiate of energy.

The above concept supported also Planck's formula of radiation (1900) based on the step-type behaviour of energy and being perfectly in agreement with experiment. However, is actual even today the question academician Vavilov put: has the wave theory really appeared to be helpless before the light quantum laws?

9.1. Planck Radiation Law Classic Derivation

In 1900 M. Planck known for his works in thermodynamics found a formula well describing the black body radiation density within the entire frequency spectrum. To do so, he had to put forward the hypothesis of oscillators' energy spectrum discreteness. According to Planck the radiation emission and absorption occurs by portions (quanta) later called the photons, which energy is proportional to the radiation frequency ν (M. Planck, 1935). The atoms of matter were interpreted as oscillator that could stay in only certain energy states with the energies $\varepsilon_n = nh\nu$, where $n = 1, 2, \dots$ – natural numbers series later called the quantum series. These energy levels of oscillator make up a discrete set of values forming an equidistant spectrum featuring the same difference between the energies $h\nu$ of any two neighboring levels.

It is easily seen that in this case the oscillator energy rises infinitely with the frequency ν increase, which leads to the so-called “violet catastrophe”. Therefore M. Planck assumed that with ν increasing the ratio of the number N_ν of oscillators featuring the energy $\varepsilon_n = nh\nu$ (i.e. the quan-

tum number n) to their total number N_0 decreases exponentially, thus, obeying the Boltzmann's classic statistics:

$$N_n = N_0 \exp(-\varepsilon_n/k_b T), \quad (9.1.1)$$

where k_b – Boltzmann's constant.

The mean statistical value of the oscillator energy $\langle \varepsilon_n \rangle$ M. Planck calculates here by changing from the integrals to the sums of natural numbers infinite series $n = 1, 2, \dots, \infty$:

$$\langle \varepsilon_n \rangle = \frac{\sum_n \varepsilon_n \exp(-\varepsilon_n/k_b T)}{\sum_n \exp(-\varepsilon_n/k_b T)}. \quad (9.1.2)$$

This mean value is equal to

$$\langle \varepsilon_n \rangle = \frac{\sum_n \varepsilon_n \exp(-\varepsilon_n/k_b T)}{\sum_n \exp(-\varepsilon_n/k_b T)}. \quad (9.1.2)$$

Planck assumes further that the spectral radiation density $u(\nu, T)d\nu$ within the frequency spectrum $d\nu$ is proportional to $\langle \varepsilon_n \rangle$ and to the number of stationary waves dN_ν confined within this frequency spectrum in the black body cavity:

$$dN_\nu = (8\pi\nu^2/c^3)d\nu. \quad (9.1.4)$$

In this case the product $\langle \varepsilon_n \rangle dN_\nu$ leads to his radiation law

$$u(\nu, T) = (8\pi h\nu^3/c^3)/[\exp(h\nu/k_b T) - 1] \text{ (Дж}\cdot\text{с/м}^3) \quad (9.1.5)$$

Although that formula perfectly well described experimental results, its derivation as itself was based on a number of rather arbitrary assumptions. Firstly, the oscillator energy quantization as its base came into obvious conflict with the concepts of classic mechanics regarding the energy spectrum continuity and the electron radiation process if the electron is permanently subjected to centripetal acceleration.

Secondly, the Planck's hypothesis assumed the radiation quantum energy to have been independent on the wave amplitude A_b . That contradicted the expression for plane progressive wave density (6.4.1) known from acoustics and hydrodynamics, according to which the wave energy is proportional to the squared wave frequency ν [s⁻¹] and to the wave amplitude A_b ¹.

¹ This expression is valid both for longitudinal and transverse waves in a medium where the oscillatory process involves at least one (kinetic or potential) component of its energy. It is also valid for electromagnetic waves where the value A_b

Thirdly, expression (9.1.5) tacitly assumes that the ratio of the number of photons the black body cavity emits to the number of stationary waves therein is always equal to unit. This assumption poorly complies with the photon interpreted as a wave_packet – it becomes absolutely incomprehensible how an entire train of waves is emitted during one period of stationary wave oscillation. Furthermore, it remains fuzzy at all how a stationary wave in the black body cavity, which is known not to carry energy, emits, nevertheless, the energy-carrying photons.

Fourthly, changing from (9.1.2) to (9.1.3) by Planck is based on the infinite geometric progression properties. Meanwhile, the series formed by the quantum numbers n is more than quite limited.

As a matter of fact, such questions arise in a great number. All attempts to derive from the primary principles the h value that L. De Broglie called a “mysterious constant” appeared to have failed. All this impels to searching another justification of the Planck’s radiation law not needing special quantum hypotheses.

For this purpose let’s consider not a single atom as an object of investigation (as in the N. Bohr’s model), but the whole set of the matter atoms in variable external force fields. According to the law of energy conservation the total energy of the atom considered as oscillator remains invariable providing the motion of orbital electrons occurs only under the action of internal (central) forces (L. Landau, E. Livshits, 1973). Hence, a body may be considered to radiate energy only in the case of the foreign (noncentral) forces \mathbf{F} from the surrounding electromagnetic fields acting on its atoms. When the force \mathbf{F} direction coincides with the moving direction of orbital electrons ($\mathbf{F} \cdot \mathbf{v} > 0$), the electrons accelerate. Otherwise ($\mathbf{F} \cdot \mathbf{v} < 0$), the electrons are subjected to short-term deceleration which duration is defined by the electromagnetic wave half-period. In this case the electromagnetic field unit disturbance appears, which propagates as a wave in the electromagnetic field. The sequence of such waves is what we call the radiation. Since the process of electron deceleration or acceleration is short, the associated process of electromagnetic energy emission or absorption by atoms is conditioned by the process character as itself and by no means contradicts classic mechanics.

When the field oscillation period exceeds the orbital electron circulation time, the deceleration occurs for two, three and more electron revolutions, on the average. Such orbits remain undisturbed (stable) for some time. However, as the frequency ν increases, the electrons will manage to successfully undergo not just one, but many (1,2,..., z_e) events of decel-

[m] is proportional to the intensities of electric \mathbf{E} and magnetic \mathbf{H} fields: $A_g = K_E \mathbf{E} = K_H \mathbf{H}$, where K_E, K_H – some factors depending on the system of units chosen.

eration or acceleration for one orbit turn. The acceleration of the electrons will occur as many times correspondingly, i.e. the electron path will change too (from apogee to apogee). For the circular orbit conditional radius of the order of 1\AA and the orbital electron velocity equal to $1/137$ of the light speed in vacuum the electron at the end of the X-ray frequency spectrum (10^{19} Hz) will manage to undergo about $8 \cdot 10^3$ events of acceleration or deceleration. This leads to the “fuzzy” path, which is interpreted as a consequence of the indeterminacy principle in the quantum theory.

As a result of the sequence of radiation and deceleration events of orbital electrons the equilibrium between radiation and matter gains dynamic character. Therefore the references to the inevitable drop of electron onto nucleus because of its energy emission as a base of rejecting the classic interpretations are also groundless.

The divergence between Rayleigh’s and Planck’s radiation is known to intensify with decreasing wave length. Therefore we are now interested in the case when $z_e > 1$. Then the radiation frequency ν of atom in any matter appears to be multiple to not only the number of revolutions the orbital electron undergoes, but also to the number z_e of its deceleration events per a turn of any (both closed and open) orbit¹.

The number of revolutions is known to be defined by the ratio of the electron mean velocity v_e on the orbit to the orbit length L so that for one “revolution” of the electron the radiation occurs $z_e n_e$ times:

$$\nu = z_e n_e = v_e / l_e = p_e / m_e l_e, \quad (9.1.6)$$

where $p_e = m_e v_e$ – mean momentum modulus for the electron on the orbit; $l_e = L / z_e$ – mean “braking length” for the electron.

According to (9.1.6) all the atoms, which orbits have the same “braking length” $l_e = L / z_e$ for electron, radiate energy at the same frequency ν . Such orbits will be hereafter called *similar* for short. Then the radiation frequency ν appears to be proportional to the mean momentum p_e for the electrons on all similar orbits. This complies with De Broglie’s ideas about a relation existing between wave frequency and particle momentum. What is more, according to (9.1.6) each kind of atoms with similar orbits corresponds to certain radiation (absorption) wave lengths. This

¹ The latter is confirmed by the fact known from the quantum theory that the length of the Bohr’s orbits appears to be multiple to the wave length by De Broglie.

also confirms the De Broglie's hypothesis that wave properties are inherent to all matters.

Furthermore, since the radiation frequency ν is connected with wave length λ by a simple relationship $\nu = c/\lambda$, it follows from (9.1.6):

$$c/\lambda = \nu_e/l_e. \quad (9.1.7)$$

Thus the length of the wave radiated is defined by the mean "braking length" l_e of electron and its mean velocity ν_e . This relationship explains why the orbit length L_e accommodates the whole number of De Broglie's waves with the length λ .

Let's now define the notion of radiant flux as a particular case of the any i th energy form flux carrier \mathbf{J}_i . In energodynamics any of such fluxes is expressed as the product of the value being transferred (mass M_k of the k th matter, its momentum $M_k\mathbf{v}_k$, charge Θ_e , entropy S , etc) and its transfer velocity \mathbf{v}_i . Accordingly, the density of this flux $\rho\mathbf{J}_i$ is defined as the product of the density $\rho\Theta_i$ and the same velocity. The value Θ_i can be found here from the expression for the elementary ordered work of the i th kind dW_i^e , which is equal to the decrease $-dE_i$ of this kind energy E_i , and can be expressed as the product of the value being transferred Θ_i and the variation of the potential ψ_i associated (2.2.12). The case of the wave form of energy ($E_i \equiv E_B$; $\Theta_i \equiv \Theta_B$; $\psi_i \equiv \psi_B$; $\mathbf{v}_i = c$) gives:

$$dW_B = -dE_B = -\rho\Theta_B d\psi_B = -\rho A_B v d(A_B v), \text{ Дж/м}^3. \quad (9.1.8)$$

It follows herefrom that $\rho\Theta_B = \rho A_B v$, so that

$$J_{\pi} = \rho V A_e c v = h_0 v, \text{ Дж}. \quad (9.1.9)$$

where $h_0 = \rho V A_e c$ (J·s) – some proportionality factor to be experimentally defined and meaning the action of the atom at a single event of its orbital electrons deceleration.

As seen, not the wave energy E_B is proportional to the first power of the frequency ν , but rather the radiant flux J_{π} having, according to (9.1.9) the dimensionality of energy and the meaning of radiant energy form flux carrier. The comprehension of this fact is significantly facilitated with the representation of radiation as a sequence of solitons. The soliton is usually construed as a nonlinear solitary wave featuring invariability of its form at motion and collision with the like waves. The properties of solitons are known to be much close to the properties of particles. In particular, when collided, two solitons do not pass through each other as usual linear waves, but rebound as if tennis balls. The sequence of solitary waves (solitons) is quite similar to the groups of waves, which move with

an overall velocity not depending on their amplitude. The radiation thus interpreted easily explains why the radiant flux J_{π} is proportional to its frequency ν since it gains in this case the meaning of soliton flux (soliton/s). Anyway, this fact of J_{π} proportional to ν does not contradict as itself to classic physics. Here the proportionality factor h_0 also gains a simple and clear sense of the energy being transferred by a solitary flux of solitons, while the frequency ν – the number of solitons radiated per unit time. In such a case the density ρ in expression (10) should be construed as the number N_{ν} of waves featuring the frequency ν and being “accommodated” in unit volume of the radiating body or radiation field. From the theory of waves this number is defined by the expression $N_{\nu} = (8\pi\nu^3/3c^3)$ so that their spectral density $\rho_{\nu} = dN_{\nu}/d\nu = 8\pi\nu^2/c^3$.

Representing sine wave as a triangle with a height of A_b and a base of $\lambda/2 = c/2\nu$ easily shows that as the wave frequency ν increases the wave amplitude A_b decreases subject to the wave form remains invariable. Therefore the Planck’s hypothesis (9.1.1) appears to be replaced by a quite substantiated statement that, according to (9.1.1), with ν increasing the number N_a of the oscillators with the same amplitude A_b decreases. Hence it follows that the oscillator energy ε_n drops with increasing ν not because an abstract quantum number n increases, but rather with the amplitude decreasing, which obeys the said Boltzmann’s statistics:

$$N_a = N_0 \exp(-h_0\nu/k_bT) . \quad (9.1.10)$$

In such a case the mean statistical value $\langle J_{\pi} \rangle$ of the radiant flux J_{π} will be defined similar to (9.1.2) as:

$$\langle J_{\pi} \rangle = \sum_z h_0\nu \exp(-h_0\nu/k_bT) / \sum_z \exp(-h_0\nu/k_bT), \quad (9.1.11)$$

and for the infinite series of natural numbers $z_e = 1, 2, \dots, \infty$ can be found by approximation of (9.1.11) to the same expression (9.1.3):

$$\langle J_{\pi} \rangle = \langle h_0 \rangle \nu / [\exp(\langle h_0 \rangle \nu / k_b T) - 1] , \quad (9.1.12)$$

where $\langle h_0 \rangle$ – mean statistical value of the factor h_0 .

However, this operation is now much more valid than that by Planck since the summation is done here for the series including many thousands of terms instead of a rather limited set of quantum numbers.

According to (9.1.9) the product of ρ_{ν} and the radiant flux mean statistical value $\langle J_{\pi} \rangle$ defines the spectral radiation density of black body $u(\nu, T)$, i.e. the spectral density of the energy radiated by the flux unit volume V at the frequency ν :

$$u(\nu, T) = \rho_{\nu} \langle J_{\text{fl}} \rangle = (8\pi \langle h_0 \rangle \nu^3 / c^3) [\exp(\langle h_0 \rangle \nu / k_b T) - 1] (D_{\text{JK}} c / M^3). \quad (9.1.13)$$

This expression differs from the Planck's radiation law (9.1.5) just because contains the mean statistical value $\langle h_0 \rangle$ of h_0 instead of the Planck constant h . Since both values, h and $\langle h_0 \rangle$, are defined experimentally based on the same equation (9.1.5), they may be considered identical. Then the Planck constant h gains a simple and clear sense of some function of the mean statistical amplitude value $\langle A_B \rangle$ for the wave radiated by black body:

$$h = \langle h_0 \rangle = \rho V \langle A_B \rangle c \quad (9.1.14)$$

This mean statistical character explains the rather exact fit of the h value found by different methods in experiments with real bodies (in particular, from the data on the black body radiation spectrum, from measurements of photoeffect in a number of metals, from the Josephson effect, etc).

When deriving the radiation law (9.1.14), we did not resort to whatever special postulates of quantum-mechanical character mentioned above. At the same time, it opens the possibility to interpret a number of known experimental facts in a new way. It becomes absolutely clear that these are the deceleration and acceleration of electron by non-central forces which cause the multiple process of radiation and absorption of electromagnetic waves by atom. From these positions the statement about an inevitable drop of electron onto nucleus looks like absolutely groundless since in the course of the events of "radiation" and "absorption" of electromagnetic energy following in turn a dynamic equilibrium state featuring constancy of electrons' mean energy can well occur. If considered from these positions, the Bohr's postulate of existing "stable" circular orbits looks like same groundless, because these are possible only in the absence of external forces \mathbf{F} acting on them. The N. Bohr's assumption regarding the possibility of nonradiative motion of electrons simultaneously becomes an intolerable idealization, too. From the energodynamic positions it becomes also clear that the radiation from atom is caused by not the electron "jump" from some stable orbit to another (as N. Bohr postulated), but rather by the multiple deceleration of electron on its orbit. Here the moving direction of orbital electrons also changes many times due to changing the relative positions of atoms, which contributes to the "fuzziness" of the orbit, as well.

Furthermore, the concept of the radiation energy quantum value also radically changes. The soliton energy ϵ_c can be found from dividing the density $\rho E_B = \rho A_B^2 \nu^2 / 2$ of wave energy with the frequency ν by the num-

ber of waves $N_\nu = (8\pi\nu^3/3c^3)$ with the same frequency, which are accommodated in unit volume:

$$\varepsilon_c = \rho E_B / N_\nu = 3\rho A_B^2 c^3 / 8\pi\nu, \text{ Дж.} \quad (9.1.15)$$

Unlike photons, the soliton energy *rises* with the wave amplitude increasing and *falls* with the wave frequency increasing. Comparing this value with the photon energy $\varepsilon_\phi = h\nu$ and defining the Planck constant as (9.1.14) gives that it appears to be $8\pi\nu^2/3A_B c^2$ times as much as the soliton energy (9.1.15). This explains why atom keeps its stability in the solitary event of soliton emission at any quantum numbers. The photon self-interference discovered yet in 1967 is explained in a natural way, too. Since soliton is a wave, though solitary, it should create, according to the wave theory, an interference pattern behind two slots or holes. Photon as a pack of ν solitons should create this pattern all the more.

The concept of electromagnetic wave as a sequence of solitons essentially facilitates the comprehension of the “wave-particle” dualism served as one of the reasons for rejecting the classic conceptions. The properties of solitons are known to be much close to the properties of particles. In particular, when collided, two solitons do not pass through each other as usual linear waves, but rebound as if tennis balls. Thus the solitons’ specific properties as themselves explain why the radiation in some cases features the wave properties (interference, diffraction, polarization), whereas in other cases – the particle properties (photoeffect, Compton effect).

9.2. Quantum Yield Consideration in Photoeffect Equation

In 1887 the German physicist H. Herz when having experimented the irradiation of electromagnetic waves with a discharger (a couple of metal balls placed into an evacuated glass chamber) revealed the intensification of the charge under the voltage $\Delta\phi$ applied to the balls when one of them was lighted by ultraviolet rays. So the external photoeffect was discovered.

The first investigations of the photoeffect A. Stoletov carried out (1888) ascertained the following its behavior:

1) The maximum kinetic energy of photoelectrons E^k demonstrates its linear increase with the light frequency ν and does not depend on the incident luminous flux J_{ph} ;

2) The number of electrons torn out from the metal surface per a second (photocurrent J_e) is directly proportional to the rate of luminous flow J_{ph} ;

3) The photoeffect does not occur if the light frequency ν is less than a certain minimum frequency ν_0 specific for a particular substance. In this case the voltage $-V_z = -\Delta\phi$ impeding the emission of photoelectrons (stopping potential) rises linearly with irradiation frequency ν and does not depend on the radiation rate J_{ph} . For alkali metals this “photoelectric threshold” lies within the visible light spectral band.

These regularities confirmed by subsequent studies of Lenard (1902), Richardson and Compton (1912), as well as Milliken (1916), did not keep within the frames of the wave theory of light. According to this theory the possibility itself to “tear” the electrons out from metal, as well as the energy of the electron torn out, should depend on the oscillation amplitude in the wave rather than on the oscillation frequency. Furthermore, the wave theory assumes the “swaying” of electron, which needs time and contradicts the observed instantaneousness of the photoeffect.

A. Einstein, while having developed the Planck’s concept of irradiation quantization, assumed that not only the irradiation process was quantized, but also the radiant energy itself contained within whatever closed space. The quantum of irradiation being the carrier of this energy has the properties of a particle (later called the photon). Based on that, Einstein in 1905 offered the first theoretical explanation of the photoeffect experimental relationships, which later made him the Nobel Prize winner (1922). He expressed the energy conservation law with reference to the photoeffect by the following relationship:

$$E^k = h\nu - W_e, \quad (9.2.1)$$

where E^k – photoelectron kinetic energy; $h\nu$ – photon energy ($h=1,0545887 \cdot 10^{-34}$ J·s – Planck constant; ν – irradiation frequency); W_e – photoelectric work function (atom ionization energy E_i).

According to this expression the photoeffect does not occur if the photon energy $h\nu < W_e$, i.e. is insufficient to ionize atom (to do photoelectric work). Furthermore, according to (9.2.1), as the frequency ν of the photons irradiating a photocathode increases, the kinetic energy E^k of the photoelectrons emitted from the photocathode rises linearly, which leads to increasing the stopping potential.

Such an explanation of the photoeffect looked so attractive that the investigators did not pay attention even to the some distinction of dimensions of the terms in relationship (9.2.1). It is found out, if in dimension somehow to consider the subject whom the given size concerns. In particular, terms E^k and W_e relate to one electron with the charge e

(J/electron), whereas the term $h\nu$ – to one photon (dimension J/photon). For alignment of dimensions of members of the equation (9.2.1) composed $h\nu$ should be divided into size Y_e , making sense relations of emitted electrons number to number of the absorbed quanta radiations - (elektron/photon). This value is known as the “quantum yield”. As experiments have shown, it depends on the properties of the body, state of its surface, temperature and energy of photons, and for the majority of photocathodes ranges from ~ 0.5 to 10^{-4} (Physical Encyclopedia, 1983). This means that to emit one photoelectron, 10^4 photons are required.

The necessity to allow for the quantum yield in the photoeffect equation (9.2.1) follows from the experiments themselves. Indeed, dividing all terms in (9.2.1) by the electron charge e gives (Millikan, 1916):

$$-V_z = h\nu/e - W_e/e. \quad (9.2.2)$$

Since the energy of a single photon $h\nu$ is the quotient of the radiant flux J_π (J) to the number of absorbed photons N_Φ and the electric charge e – the quotient of the photocurrent I_e to the number of emitted electrons N_e , expression (9.2.2) becomes:

$$-V_z = J_\pi N_e / N_\Phi I_e - W_e/e = Y_e J_\pi / I_e - W_e/e. \quad (9.2.3)$$

where $Y_e \equiv N_e / N_\Phi$ – quantum yield.

Thus the multiplier Y_e being absent in (9.2.1) leads to the energy balance disturbed. Therefore the relation (9.2.1) should be expressed as:

$$E^k = h\nu/Y_e - W_e, \quad (9.2.4)$$

or dividing by the electron charge e gives:

$$-V_z = h\nu/eY_e - W_e/e. \quad (9.2.5)$$

The necessity to allow for the quantum yield in (9.2.1) is demanded by other circumstances, too. As experience shows, the photocathode integral sensitivity, which is the ratio of the photocurrent I_e (A) to the incident radiant flux J_π (J), depends on matter properties. According to (9.2.4) this relation has the form:

$$(\partial E^k / \partial \nu)_{W_e} = h/Y_e, \quad (9.2.6)$$

i.e. for bodies with the same ionization energy depends on also the surface condition, body temperature, etc in complete agreement with ex-

periment. At the same time, this relation does not follow from the Einstein's formula (where $Y_e \equiv 1$).

Ultimately, to meet the balance equation (9.2.1), it is necessary that photon as particle, when "collided" with electron, gave the latter all its kinetic energy, which does not comply with the shock theory. All this means that the explanation of photoeffect by A. Einstein is not exhaustive.

Let's consider now the same phenomena, but from the positions of ergodynamics. In ergodynamics the Planck constant gains the meaning of some function of mean statistical amplitude for the wave a body absorbs. This means that the dependence of photocurrent on incident light amplitude following from the wave theory does not contradicts experimental data. The interpretation of photon as a flux of ν solitons does not contradict experiment either, which makes the dependence of photocurrent on radiation intensity quite understandable.

Replacing photon by a sequence of ν solitons enables somewhat other explanation of all the photoeffect mechanisms. In particular, (9.2.6) directly leads to linear growth of photoelectrons' kinetic energy with frequency for a photocathode featuring certain ionization energy (the Stoleto's first law). The same definitely (9.2.3) leads to direct proportionality of the photocurrent I_e to the light flux J_n for a particular photodiode ($W_e, Y_e = \text{const}$)

$$(\partial I_e / \partial J_n)_{W_e} = - Y_e / V_z, \quad (9.2.7)$$

which is the Stoleto's second law.

It directly follows from (9.2.5) that the stopping potential V_z rises linearly with the radiation frequency ν at the same conditions:

$$(\partial V_z / \partial \nu)_{W_e} = - h / e Y_e, \quad (9.2.8)$$

Ultimately, the above suggested idea of radiation as a flux of solitons terminates the contradiction between the photoeffect and the wave theory since the energy of solitary soliton according to (9.1.17) rises with its amplitude. The "zero-lag photoeffect" also finds its explanation – it is caused by the fact that the atom ionization occurs only at the moment when the number of absorbed solitons exceeds the ionization energy.

It is significant that with such an explanation you will not need to supplement physics with whatever specific "quantum" concepts, including assumptions of photon as particle, corpuscular interpretation of light, requirements for orbit discreteness, etc.

9.3. Alternative Description of Spectral Series

Quantum mechanics is known to aim not to reveal physical background of phenomena, but rather to exactly “precompute” experimentally found values, which are the spectral lines and their frequencies. An important role in this play belongs to the above-found dependence of the orbital constant h_0 on the orbit parameters and, natural at resonance conditions, the influence of interatomic electromagnetic field oscillation frequency on movement behavior of a certain group of orbital electrons in a system under consideration. This allows deriving formulas describing the Balmer, Lyman, Pashen series, etc, proceeding just from the character of their orbits.

As shown in paragraph 9.1, all the electrons radiate energy at the same frequency ν if their orbits are similar, i.e. obey the relation

$$l_e = L/z_e = \text{const}, \quad (9.3.1)$$

where L – orbit length (from apogee to apogee); z_e – number of deceleration or acceleration events for an electron per its one turn on the orbit.

Let’s assume that some electron is primordially moving under the action of only central force $F_u = -e^2/r_0^2$ on any closed orbit (no matter – circular, elliptic or parabolic) with a length of L_0 and equivalent radius of $r_0 = L_0/2\pi$. When some additional noncentral forces F_H are acting on the electron, its path changes, while the path conditional radius gains the value r corresponding to the new resultalt force $F = F_u + F_H$. In such a case the foreign forces are expressed by their difference $F_H = F - F_u$ which is defined as:

$$F_H = e^2(1/r_0^2 - 1/r^2) = (e^2/r_0^2)(1 - r_0^2/r^2) . \quad (9.3.2)$$

Since according to (9.3.1) $r_0/z_0 = r/z$, the relation (9.3.2) may be replaced by:

$$F_H = F_u(1 - z_0^2/z^2) . \quad (9.3.3)$$

Hence it follows that at $z = z_0$ radiation does not take place, which is natural. On the contrary, with noncentral forces acting the number of deceleration events for an electron in its orbital motion $z = z_0 + 1, 2, \dots$, i.e. rises relative to the primordial z_0 (typical for elliptic, parabolic, etc orbits) by the square law. Accordingly, the noncentral force field oscillation frequency ν also rises, which directly leads to the following relation:

$$\nu = \nu_0(1 - z_0^2/z^2), \quad (9.3.4)$$

where ν_0 – some constant value for a particular matter, which can be found experimentally.

Expression (9.3.4) is adequate to the law $\lambda = \lambda_0(1 - n_0^2/n^2)$ stated by Balmer in 1885 by experimental data on hydrogen spectrum. According to (9.3.4) radiation frequencies are discrete and reducible to their upper limit ν_0 with z increasing. Here z_0 defines the series name: Lyman's ($z_0=1$), Balmer's ($z_0=2$), Paschen's ($z_0=3$), Brackett's ($z_0=4$), Pfund's ($z_0=5$), etc. The two above statements perfectly comply with experiments (especially for hydrogen and hydrogen-like atoms).

However, now the existence of spectral series is explained by not the instantaneous electron “jump” from some stable orbit to another, but by electron deceleration or acceleration lasting for a finite time and forcing this electron to change its orbit. This eliminates a number of troubles in quantum mechanics. The most critical of them lies in the fact that the radiation frequency ν depends on the energy level of both start and finish orbits and, hence, remains uncertain until the electron reaches the latter. In such a case it should be acknowledged that the electron by some inconceivable way “knows” beforehand about its future work. That was one of the reasons which caused the negation of the cause-effect relations in the quantum theory. The said trouble does not arise if the radiation frequency is defined by current parameters of electron and orbit.

Another trouble which is usually missed relates to the problem of maintaining atom stability. If to be based on the known expression

$$h\nu = E_i (1 - n_i^2/n_j^2), \quad (9.3.5)$$

then, at least, with $n_i = 1$ and $n_j = 5$ the electron will lose 96% of its starting energy E_i for one radiation event. This casts doubt on the atom stability. Contrary to this fact, the number of acceleration or deceleration events for an electron on the orbit changes momentarily just by unit. In this case the energy loss is immediately replenished on some other portion of the same orbit. Naturally, this does not threaten the atom stability.

As seen, the formulas for calculation of Lyman's, Balmer's, Paschen's, etc spectral series, which have always been the “touchstone” of the quantum theory, can be explained from the positions of classic physics, too. The advantage of the suggested approach to study of spectral series lies in its physical clarity and obviousness. This relates, first of all, to the physical meaning of the values z and z_0 defining the orbit character. In the Bohr's model the relation between quantum numbers and orbit geometry is far from being obvious. In quantum mechanics this idea is rejected at all.

Noteworthy is the attractive simplicity in explanation of a number of observed regularities. In particular, it is quite natural that the electrons moving along the paths remoter from the nucleus have a longer orbital period. Therefore they have enough time to undergo the greater number of deceleration and acceleration events for this period and, respectively, have a higher radiation frequency. This explains why the electron radiation frequency in any spectral series rises with electron potential energy.

Furthermore, the number of electron acceleration (deceleration) events can not be fractional – from here comes the law of whole numbers (see (9.4.4)). In this order of ideas the fact that atoms of the same matter (including one-electron atoms) can have several series is explained by different character of the “central” orbits in different atoms of this matter (i.e. the paths appearing under the action of central forces). Note, such an explanation would be groundless if considering isolated one-electron atom in the Bohr’s conception. Somewhat worse results for alkali metals (principle, sharp, diffusional and bergman series available therein) may be explained in this order of ideas by approximate character of relation (9.3.2) for complex orbits.

The approach undertaken allows bringing the positions of classic and quantum mechanics together.

9.4. Energodynamic Analog of Schrödinger’s Equation

Many investigators are sharply dissatisfied with the tendency existing in modern physics and constituting a desire to “guess equations disregarding physical models or physical explanation” (R. Feynman, 1976). This relates in full measure to also the fundamental equation of quantum mechanics, which has appeared to be a product of its author’s intuition (E. Schrödinger, 1926). Therefore it is even more interesting to be able to derive the equation of such a type from the first laws of energodynamics.

As shown in Chapter 2, when some i^{th} process is running in a system, its generalized rate (flow \mathbf{J}_i) is defined by all thermodynamic forces \mathbf{X}_j ($i, j = 1, 2, \dots, n$) acting in the system. As applied to an “electron–nucleus” system, this means that at deceleration of the electron in its orbital movement along an arbitrary pathway its kinetic energy E_k is not only transforming into the potential energy of atom as a whole, but is also being consumed partly to overcome non-central forces from the electromagnetic fields external relative to this atom. As a result, each of the deceleration events leads to a solitary disturbance of this field arising and spreading in the field in the form of a solitary electromagnetic wave (soliton). As a result of joint action from the multitude of atoms, the total electromagnetic field of any substance will oscillate in phase with the

movement of the corresponding group of electrons predetermining, in its turn, the oscillation of their pathways. This is the way the various orbits of electrons of a particular group are synchronized with the oscillation frequency spectrum of the field itself. This oscillating process is described by a known spatial monochromatic wave equation (L. Landau, E. Livshits, 1973):

$$\nabla^2\Psi_v + (4\pi^2/\lambda^2)\Psi_v = 0, \quad (9.4.1)$$

where λ – wave length; ψ – “wave function”, i.e. some system parameter that is a function of spatial coordinates and deviates from its equilibrium value in oscillating process. In the classic sense Ψ_v may be construed as electromagnetic wave amplitude.

Using the above suggested mechanism of the oscillatory process appearing in the field of interatomic forces the relation between electron orbit parameters and the radiation wave length λ according to (9.1.7) gives:

$$\lambda = c/v = h_{op}/p_e, \quad (9.4.2)$$

where $h_{op} = m_e l_e c$ – experimental value that we call the orbital constant.

With $\lambda^2 = h_{op}^2/p_e^2$ and $p_e^2 = 2m_e E^k$, where $E^k = E - E^n$ – kinetic energy of electron defined as the difference between the external (ordered) energy E of atom (in our case, its hamiltonian \hat{H}) and its potential energy E^n . Then substitution in (9.4.1) and elementary transformations directly give the classic analog of the quantum mechanics stationary equation:

$$\nabla^2\Psi_v + (8\pi^2 m_e/h_{op}^2)(E - E^n)\Psi_v = 0. \quad (9.4.3)$$

From the formally mathematical positions this equation differs from the Schrödinger equation just because the Planck constant is therein replaced by the constant h_{op} . However, this equation can not be considered as the Schrödinger stationary equation derivation since the latter proceeds from the absolutely other considerations. Especially this applies to the physical sense of the function Ψ_v which is essentially unobservable value in quantum mechanics. In its interpretation the most eminent theoretical physicists have never been unanimous till now. The followers of the Copenhagen’s quantum mechanics interpretation in their majority interpret the Ψ_v function as a value, which square being multiplied by the bulk element dV describes the probability $\Psi_v^2 dV$ that the particle occupies the predetermined spatial domain. This concept assumes indeterminism even at the level of elementary processes, i.e. the lost capability for quantum

mechanics to predict events (to define subsequent parameter values from the previous ones).

We are interested basically in some mathematical properties of equation (9.4.3). It is proved in the theory of differential equations that the equations of such a kind have solutions fulfilling requirements of uniqueness, finiteness and continuity¹⁾ for only some “selected” negative values of the energy C called eigenvalues. In this case the solutions giving discrete levels of energy begin with some finite negative value of the difference $E - E^n$. The existing negative potential energy in principle contradicts energodynamics and, as shown in p. 3.6, results from the failure to allow in the Newtons laws for the minimal distance r_o to which two mutually attracting bodies or two particles like nucleus and electron can approach each other. Therefore the electron energy E^n is defined as $E^n = e^2(1/r_o - 1/r)$, i.e. is a value purely positive and becoming zero at $r = r_o$. In such a case $U > 0$ and the decisions of the equation (9.3.3) form a continuous spectrum. Hence, according to energodynamics not the total energy of some system is quantized, but only the part relating to the energy level of the electron orbit in the central force field and varying discretely because of the process specificity as itself. This statement is reasonable to be called for easy reference as the **quantization principle**: *the part of energy, which changes in the discrete process of energy exchange, is subject to the quantization.* This eliminates the apparent contradiction between quantum and classic mechanics. The example is once again appropriate here regarding the ocean that could hardly be considered as consisting of drops despite the rain falls in the form of drops onto the ocean surface.

Anyway, the classic derivation of equation (9.4.3) allows solving, by methods of quantum mechanics, the same problems as by the Schrödinger stationary equation which is considered to be the fundamental equation of quantum mechanics. It remains now to see the relation between the Planck constant h which meaning has been found earlier by (9.1.15) and the constant $h_{op} = m_e l_e c$ (9.4.2). Comparing them gives their identity providing

$$\rho V \langle A_v \rangle = m_e l_e. \quad (9.4.4)$$

As mentioned above, the electron braking length is connected with the radiated wave length λ which, in its turn, is defined through the wave amplitude by the wave form factor. Therefore relation (9.4.4) does not contradict the facts known. However, there is no rigorous proof of this relation. It is evidently not needed since the values h , h_o and h_{op} are experimental ones.

9.5. Orbital Electrons Parameters Definition

The determinism inherent to ergodynamics in approach to macro- and microworld objects shows in the possibility to define mean statistical parameters of orbital electrons and electron orbits themselves, which out-steps the possibilities of quantum mechanics. These additional possibilities were the consequence of another interpretation of radiation as a process which duration is defined by the time of electron orbital deceleration caused by noncentral forces from the electromagnetic fields surrounding the atom.

The resulting dependence of the radiation frequency ν and the radiated wave length λ on the electron momentum p_e and braking length l_e (9.1.7) allows finding these parameters from the specified radiation frequency ν or, on the contrary, precalculating the whole spectrum of these frequencies for the electrons with a known mean momentum.

In particular, it is possible to find the length L and radius r of the conventional circular "orbit" for the electrons radiating at this frequency from the known radiation wave length λ (or the wave number c/λ). Let's use for this purpose relation (9.1.7) which evidences the unique relationship existing between the radiation frequency ν , electron velocity v_e and electron braking length l_e . Since the length L of an arbitrary orbit is connected with the radius r_e of the length-equivalent circular orbit with the number of deceleration portions z_e through the simple relation

$$L = 2\pi z_e r_e, \quad (9.5.1)$$

the radiation frequency ν becomes a function of the relation (v_e/r_e) according to (9.1.7). Let's find the form of this function $\nu = \nu(v_e/r_e)$ for the case when undisturbed motion of the electron occurs along a circumference with the radius r_e , i.e. only under the action of central forces. Then the electron attractive force \mathbf{F}_e according to the Coulomb law is equal to:

$$\mathbf{F}_e = \Gamma Z_A e^2/r_e^2, \quad (9.5.2)$$

where $\Gamma = 8,98756 \cdot 10^9$ – electric constant; Z_A – atomic number of the element corresponding to the number of protons in its nucleus; $e = 1,602 \cdot 10^{-19} \text{C}$ – electron charge.

At uniform motion of the electron on circular orbit this force is balanced by the centrifugal force

$$\mathbf{F}_H = m_e v_e^2/r_e, \quad (9.5.3)$$

so that the electron orbital velocity v_e appears to be connected with the circular orbit radius r_e through the relation:

$$v_e = e(Z_A \Gamma / m_e r_e)^{1/2}. \quad (9.5.4)$$

Considering (9.5.1) and (9.1.7) jointly gives:

$$r_e = (Z_A \Gamma e^2 z_e^2 / 4\pi^2 v^2 m_e)^{1/2} = C_A (z_e / v)^{2/3}, \quad (9.5.5)$$

where $C_A = (Z_A \Gamma e^2 / 4\pi^2 m_e)^{1/2}$ – constant value for a particular atom, which may be called “orbital constant”. This relation allows finding for each radiation spectrum frequency ν the radii of electron orbits with a known number of deceleration portions z_e for different atoms, the electron mean momentum modulus

$$p_e = m_e v_e = e(Z_A \Gamma m_e / r_e)^{1/2} \quad (9.5.6)$$

and the electron mean kinetic energy

$$E^k = p_e^2 / 2m_e. \quad (9.5.7)$$

It is significant that the radii of orbits for different atoms radiating at the same frequency ν form, according to (9.5.5) the power series depending on the number of deceleration portions z_e

$$r_z / r_0 = C_A z_e^{2/3}, \quad (9.5.8)$$

where r_z , r_0 – current radius and the 1st orbit radius with $z_e = 1$, respectively.

Let's consider now, it is how much real the offered dependences for atom of hydrogen ($Z_A = 1$; $m_e = 9,109534 \cdot 10^{-31}$ кг), radiating on frequency of the argon laser $\nu = 2,379 \cdot 10^{15}$ Hz (length of a wave $\lambda = 1,261 \cdot 10^{-7}$). In this case we have according to (9.5.8) $C_A = 1,858$ so $r_0 = 1,04 \cdot 10^{-10}$ m. This size, naturally, more than 1st Bohr's (not radiating) radius $r_0 = 0,529 \cdot 10^{-10}$ m, but have with it оди an order. Corresponding average speed of orbital movement of electron is equal $v_e = 1,56 \cdot 10^6$ м/с, that corresponds to an average impulse электрона $p_e = 1,421 \cdot 10^{-24}$ кг·м/с with and its average kinetic energy $E^k = 1,108 \cdot 10^{-18}$ J.

The possibility to find these parameters lies outside the scope of problems quantum mechanics solves since quantum mechanics excludes the unobservable parameters (position of electron on orbit, electron velocity, type of orbit, etc) from its consideration.

Summing up to this chapter, it is possible to notice, that specificity of quantum mechanics consists not in its equations, and in that ideology which accompanies their conclusion. This makes us hope that other deductions of quantum mechanics will also appear to be deduced from a correct generalization of classic physics to the microcosmic objects.

Conclusion to Part 2

As shown in this section, distribution of a thermodynamic method of research on other fundamental disciplines «building a bridge» between classical and quantum mechanics; classical and nonequilibrium thermodynamics, heat- and mass transfer theories, hydrodynamics and electro-dynamics.

It became possible thanks to orientation of ergodynamic conceptual system direct on spatially non-uniform systems and to generalisation of a mathematical apparatus of the theory on nonstatic processes proceeding in such environments. A special role has played thus the expansion of space of variables with introduction of spatial heterogeneity parameters of investigated systems.

Created such theory has allowed to argue the fundamental principles of these disciplines, to prove their main laws and to deduce their basic equations as mathematical and logic consequences of ergodynamics, not resorting thus to any hypotheses, postulates or modelling representations about the molecular mechanism of investigated processes.

It is rather important, that such (deductive) statement of fundamental disciplines has allowed not only to present an essence of the matter in the most compressed and compact form, but also to release these disciplines from set of the historical stratifications accompanying their formation. It does ergodynamics by a real integration tool of sciences and realisation of the program of interdisciplinary preparation of experts of various trades.

The big number of experimental acknowledgement above mentioned principles, laws and the equations of fundamental disciplines testifies that ergodynamics can serve as the reliable base to construction of modern natural sciences conceptual base .

Special value of ergodynamics is shown that she has allowed to prove the laws which were considered not deduced from first principles. Among them a “least action principle” by Maupertuis; Newton’s, Coulomb’s and

Maxwell's laws; Maxwell's and Schrödinger's equations. Not less important that it changes many developed representations, concerning energy and entropy, force and acceleration, mass and inertia, warmth and work, quantum of radiation and the reasons of its step-type behaviour, etc.

At the same time ergodynamics has allowed to find out reserves of further development in variety disciplines. It was expressed in generalisation of all three Newton's laws and principles of the excluded perpetuum mobile, in a finding of characteristic functions of the nonequilibrium state, expanding possibilities of a classical thermodynamic method of potentials, in generalisation of reciprocity relations of the irreversible processes theory on nonlinear systems, in elimination of historically developed strange division of the heat exchange theory with thermodynamics etc.

All of this does the ergodynamics as the interdisciplinary theory keeping the basic advantage of a classical thermodynamic method - immutable justice of its consequences.