

ON ONE METHOD OF THE ANALYSIS OF THERMOPHYSICAL PROCESSES

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Abstract: We present the conception of phenomenological approach to the description of notions and laws of thermophysical processes. We point out the principles of application of the phenomenological theory to the analysis of phase transitions and the laws of nonequilibrium thermodynamics.

Each scientific investigation uses a certain collection of notions and concepts. Some of them require explanations and definitions, but other are interpreted as obvious. These notions, having a physical essence, which often are considered as obvious but, in some cases, cannot be deduced from more profound cognition, represent phenomenological notions.

In the phenomenological description of a certain physical phenomenon, an important stage is connected with the choice of quantities that can describe this phenomenon or its properties. For example, for the conception of exergy-economic optimization, which was recognized and developed recently, special terminology was proposed: fuel exergy, product exergy, exergy loss and destruction, and exergy-economic factor.

Among the phenomenological notions, we should mention the notion of causality, which represents one of the most general principles, determining the allowable limits of influence of a certain event. The causality principle is confirmed by experiments in the macroscopic region and by practice common to all mankind.

In the apparatus of physical theory, the causality principle is used, first of all, for the choice of boundary conditions to the corresponding equations of dynamics, which guarantees the uniqueness of their solution. In addition, the causality principle enables one to establish the general properties of the quantities that describe the response of a physical system to external action on it.

Phenomenological thermodynamics deals with macroscopic quantities, which represent the result of averaging. Strictly speaking, all the thermodynamic quantities fluctuate. One can evaluate the level of fluctuations thermodynamically, without considering the macroscopic processes taking place in the system under study.

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The phenomenological theory begins from the choice of quantities for the description of a certain phenomenon or its properties. For determining the relations between the chosen quantities, it is customary to use experimental data or their consequences. A substantial feature of this method lies in the possibility to attract the general laws of nature (energy conservation law, entropy increase law, time reversibility, etc.). We may say that phenomenological description formulates the problem for the analysis of macroscopic phenomena.

Much attention should be given to the processes related to phase transitions. These processes are usually analyzed by the principles of the phenomenological theory [1].

As is well known, there are phase transitions of the first and second kinds.

Specific phenomena observed near the critical points (e.g., the point of liquid–vapor equilibrium) and points of phase transitions of the second kind are called critical phenomena.

The critical point represents a special case of the point of phase transition and is characterized by the loss of thermodynamic stability as to the density or composition of the substance.

In a more narrow sense, the phenomena whose origin is connected with the growth of fluctuations of density, concentration, and other quantities near the points of phase transitions belong to the critical phenomena.

The critical parameters have the property of universality; they are independent of the physical nature of the substance. The similarity of critical phenomena in the fields of different nature enables one to consider them from a common position. It has been established that all objects possess identical temperature dependences of their physical properties near the points of phase transitions, which can be expressed as a power function of reduced temperature.

The critical phenomena are determined by the properties of the entire assemblage of components, but not by the individual properties of each component. This means that, at the point of phase transition, changes in any part of the system under consideration correspond to changes in its other parts. On the contrary, far from the point of phase transition, fluctuations become statistically independent, and random changes in the state of a certain substance do not affect the properties of other substances.

Much attention is given in recent years to the principles of nonequilibrium thermodynamics.

In studying macroscopic nonequilibrium processes, the system is considered as a continuous medium, and the parameters of its state as field variables, i.e., continuous functions of coordinates and time. The analysis of nonequilibrium processes is based on the phenomenological postulates. It is assumed that, in the case of small deviations of the system from thermodynamic

equilibrium, the arising flows depend linearly on the thermodynamic forces and are described by

$$I_i = \sum_k L_{ik} X_k, \quad (1)$$

where L_{ik} are kinetic (phenomenological) coefficients.

Relation (1) is a consequence of the Onsager theorem, which represents one of the fundamental postulates of the thermodynamics of nonequilibrium processes [2].

The thermodynamic forces X_k can cause a resulting action in the case of $i \neq k$ as well. For example, temperature gradient can cause a flow of substance in multicomponent media, i.e., thermodiffusion, etc. Such effects imposed one onto another are characterized in nonequilibrium thermodynamics by the coefficient X_i , $i \neq k$.

The thermodynamic forces and flows can be scalars (in the case of volume viscosity), vectors (heat conduction, diffusion), and tensors (shear viscosity).

As follows from the Onsager theorem, if there are no magnetic fields and rotation of the system as a whole, then

$$L_{ik} = L_{ki}. \quad (2)$$

This is connected with the fact that the Lorentz and Coriolis forces remain invariable with change in the direction of velocities.

Relation (2) expresses the principle of symmetry of kinetic coefficients. According to the Curie theorem, for an isotropic medium, linear relations can connect only the thermodynamic forces and flows of equal tensor dimension.

As follows from nonequilibrium thermodynamics, the value of entropy generation σ is given by

$$\sigma = \sum_i I_i X_i. \quad (3)$$

Based on the Onsager reciprocal relations, Prigogine has formulated the well-known theorem of the minimum of entropy generation [3].

Deriving the laws of the thermodynamics of irreversible processes from the laws of mechanics (classic and quantum) and obtaining expressions for the kinetic coefficients via the parameters characterizing the structure of substance are the problems of nonequilibrium statistical thermodynamics, which relates to the thermodynamics of nonequilibrium processes as statistical thermodynamics to classic thermodynamics.

REFERENCES

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