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Arkady BEREZOVSKY\* and Victor ROSENBLUM\*\*

## BASIC CONCEPTS OF THERMODYNAMICS OF COMPLEX SYSTEMS

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**Abstract.** For the description of complex systems the classical thermodynamics needs the supplementation and the refinement of its basic concepts in order to apply them in the more general situation. In the paper the basic principles supplementing the thermodynamic laws are formulated explicitly, the mathematical expression of these principles is obtained and the consequences from them are analysed. It is shown that the current thermodynamical equilibrium of complex interacting systems is characterized by more general conditions than the classical conditions of equilibrium of isolated systems. These conditions permit to link the properties of a complex system to those of its simple constituents.

### 1. Introduction

One of the powerful resources of scientific research is the idealization of the subject of inquiry. The discarding of insignificant factors permits to expose the distinguishing features of a process or a phenomenon and to understand the basic relationships. In essence, idealization may mean the reduction of the dimension of the problem which makes it available to substantial analysis. Idealization is deliberate simplification of a real situation which is too complex for full description and is thus a necessary step in the shaping of every theory. However, ideal models do not exhaust all the aspects of the processes and phenomena. There are always phenomena and processes a necessary condition of the existence of which is complexity [1]. Obvious cases are the biological organisms and processes [2]. The investigation of inorganic nature gives also more and more examples of complex behaviour that is not reduced to simple schemes. First, there are the self-organization and cooperative phenomena in dissipative systems such as Benard's cells, Taylor's vortices, Belousov-Zhabotinsky's reaction process [3-5], etc. Secondly, there are the phenomena and processes described by solutions having strange attractors in the phase space [3-7]. Such examples show that a description of complex behaviour of the subject of inquiry is just as necessary as its idealization. In H. Haken's opinion "complexity is a new challenge to investigators" [8].

\* Eesti Teaduste Akadeemia Küberneetika Instituut (Institute of Cybernetics, Estonian Academy of Sciences). Akadeemia tee 21, EE-0026 Tallinn, Estonia.

\*\* Санкт-Петербургский государственный технический университет (St. Petersburg State Technical University). Политехническая 29, 195251 Санкт-Петербург, Россия.

It is probably necessary to define more exactly the notion of "complexity". This notion can be defined only with regard to the notion of "simplicity". As a rule, every theory introduces in the consideration ideal objects which are supposed to be "simple". A process or phenomenon is said to be "complex" if its description is impossible in the framework of relationships established for simple objects. In other words, "complexity" is that which cannot be reduced to "simplicity". At the same time, the properties of complex objects must be dependent on the properties of their simple constituents. Thus, simplicity and complexity supplement each other in the description of real processes and phenomena.

All the abovestated bears immediate relation to such a traditional branch of science as thermodynamics. Successful idealizations of investigated objects such as "isolated system" and "ideal gas" led to impressive theoretical achievements and numerous applications of thermodynamics. At the same time the tendency to reduce the properties of real systems to the properties of isolated systems and the ideal gas led to the absence of the concept of complexity.

The present paper is to some degree an endeavour to make up for this deficiency. Basing on the results of existing theories, the authors propose a new approach to thermodynamic analysis that uses the concept of complexity.

The basis of the theory is the excellently developed and logically unexceptionable classical thermodynamics of simple systems in its axiomatic form [9]. For the description of complex systems it is supplemented by the following principles:

1. Principle of composition.  
Complex systems are composed of a sequence of simple subsystems.
2. Principle of interaction.  
Simple systems forming a complex system interact with each other and with the surrounding medium. Non-interacting systems cannot compose a simple whole.
3. Principle of invariance.  
The first and the second laws of thermodynamics are valid for systems at every complexity level and do not change their form in transition from simple systems to complex ones.
4. Principle of duality.  
The extensive form of the first and the second laws determines the behaviour of the system as a continuous medium. Their intensive form describes the behaviour of the system as an assemblage of discrete particles. Both forms of the first and the second laws are fulfilled independently and simultaneously.

For simple systems empiric information is given by two-parametrical equations of state. It is assumed that such equations also remain valid for simple systems in a compound of a complex system. It appears that such information is sufficient for the description of the properties of a complex system in the framework of postulates 1—4.

In this paper the basic notions are specified and conclusions from postulates 1—4 are drawn. Special consideration is given to the additivity and homogeneity of extensive functions of state. The notion of the equilibrium of interacting systems is defined more accurately. The conditions of the current equilibrium of homogeneous systems are given as a result. The difference between homogeneous and heterogeneous equilibria is established.

In the second part the common notions used in conventional thermodynamics are presented in order to explain the meaning of several concepts which are essential for understanding the resulting formalism. The next part of the paper is devoted to the discussion of the problem of compatibility of empiric equations of state with thermodynamic laws. Mathematical expression of the principles supplementing the classical laws of thermodynamics in the description of complex systems is obtained in the fourth part. In the last part of the paper the general conditions assuring the consistency of thermodynamic properties of both simple subsystems and a complex system as a whole are established.

## 2. Thermodynamic approach

**Thermodynamic systems.** Thermodynamics deals with the notion "thermodynamic system", that is an idealization of the description of a physical body [10-14]. From the thermodynamic point of view, every part of the material world which can exchange energy and matter with other parts can be considered a thermodynamic system. Thus, every thermodynamic system has mass  $M$ , internal energy  $U$ , and occupying volume  $V$ , and is characterized by temperature  $T$  and pressure  $p$ . The absence of any one of these attributes takes the object out of the frame of thermodynamic systems.

Thermodynamic systems can be joined and divided into parts. Such operations will result also in thermodynamic systems if the mass, internal energy, volume, temperature and pressure do not lose their value. In particular, there exist no thermodynamic systems with zero mass, zero volume, zero internal energy, zero temperature or zero pressure.

Mass, volume, internal energy, temperature and pressure are examples of parameters of a system. A certain sequence of the values of parameters characterizes the state of the system. As a rule, the state of the system is associated with the notion "state of equilibrium". The attainment of equilibrium is conditioned by the isolation of the system from external actions. For interacting systems such an isolation is impossible in principle. Therefore, the term "state of the system" here always means the current state caused by the interaction of the system with its surrounding medium. It is assumed that the state of the system is determined by a finite set of parameters. A parameter is called a function of state if its value is independent of the way by which the corresponding state is attained. Mass, volume, internal energy, temperature and pressure are functions of state.

**Equations of state.** The functions of state are not independent of each other. Current values of the functions of state are bound up with the thermal and caloric equations of state [11]

$$U=U(p, T, M), \quad V=V(p, T, M), \quad (1)$$

which express individual properties of a certain thermodynamic system. The equations of state of a real system are elaborated on the basis of experimental data and correspond to observed relations.

The existence of mutual relations between functions of state in the form of equations of state leads to the concept of discrete particles that compose the thermodynamic system under consideration. More exactly, there exists a subsystem of a certain minimal size, the mass of which cannot vary without changing the nature of this subsystem.

**Homogeneity.** The use of equations of state actually supposes homogeneity of thermodynamic systems [15]. The additive functions of state, such as volume and internal energy, will be extensive, i.e. proportional

to the mass of such a system. The intensive functions of state, such as temperature and pressure, have the same value for each part of a system.

As a rule, the real physical bodies are inhomogeneous. They can be homogeneous only in the absence of external fields of forces. Homogeneous systems are the simplest model of physical bodies.

**Interaction.** All that is not included in the thermodynamic system under consideration, is its surrounding medium. The interaction of a thermodynamic system with other systems or with the surroundings as a whole is expressed in the appearance of relations between the parameters of the interacting systems. It is assumed that the interaction of thermodynamic systems does not change the properties of homogeneity. The interaction of thermodynamic systems always supposes the transfer of energy in the form of heat and work. The values of parameters of interacting systems vary in correspondence to changes in the surrounding medium. Every variation of a thermodynamic system corresponds to a certain thermodynamic process.

**The first law.** The basic principle of thermodynamics maintains that energy transfer proceeds in correspondence to the law of energy conservation in its thermodynamic form [10-14]

$$\delta Q = dU + \delta L + \delta E, \quad (2)$$

where  $\delta Q$  is heat,  $\delta L$  is work,  $\delta E$  is energy transferred by matter.

The law of energy conservation is universal. It must be fulfilled in each process in every thermodynamic system. In particular, for discrete particles the first law has the form

$$\delta q_p = du_p + \delta l_p.$$

Here  $\delta q_p$ ,  $\delta l_p$ ,  $u_p$  are heat, work and internal energy of a discrete particle, respectively.

By multiplying both parts of the last equation by the molecular mass of the considered substance we obtain the expression of the first law for the unit of mass

$$\delta q = du + \delta l. \quad (3)$$

Here  $\delta q$ ,  $\delta l$ ,  $u$  are heat, work and internal energy per unit mass, respectively.

Forms (2) and (3) of the first law, expressing different aspects of the behaviour of a thermodynamic system, should be noted. The extensive form (2) of the first law determines the behaviour of the system as a certain continuous medium, while its intensive form (3) characterizes the properties of the system as an assemblage of discrete particles. Therefore, we have duality of continuity and quantity of the thermodynamic system. Both forms of the first law must be satisfied simultaneously and independently.

**Thermodynamic approach.** The concepts of heat and work are formulated by the generalization of immediate sensations associated with the everyday human activity. The expression of such concepts in the terms of quantitative relations between the parameters of thermodynamic systems is essential. Heat and work depend on the path of the realization process, and they are called functions of the process. These functions, generally speaking, depend not only on the parameters of the thermodynamic system under consideration, but also on the parameters of a certain different system or on the parameters of the surroundings as a whole. The heart of the thermodynamic approach is the expression that describes

functions of the process only in the terms of functions of state of the considered thermodynamic system. The realization of the thermodynamic approach led to the generalization of empiric facts and to the formulation of the postulates of thermodynamics.

**The second law.** The principle of the existence of entropy, which is the first part of the second law of thermodynamics [10-12, 14], binds heat with the differential of the new additive function of state  $S$ , named entropy

$$\delta Q = TdS. \quad (4)$$

The importance of this principle in thermodynamics is directly related to the definition of entropy, that has no analogs in human activity. The introduction of such a function of state is induced by the demands of the thermodynamic approach only.

As it was in the case of the first law, the principle of the existence of entropy is valid for each discrete particle of the system [11, 12]

$$\delta q_p = Tds_p.$$

Here entropy  $s_p$  characterizes the state of a discrete particle. For the unit mass we can write

$$\delta q = Tds, \quad (5)$$

where entropy  $s$  corresponds to the unit mass.

**Work of expansion.** The variation of volume under the influence of external forces determines the work of expansion [10, 11]

$$\delta L = p dV. \quad (6)$$

The work of expansion corresponding to a discrete particle is represented in the form

$$\delta l_p = p d v_p.$$

Here volume  $v_p$  also determines the volume of the discrete particle.

By virtue of the molecular mass we obtain the expression for the work of expansion for the unit mass

$$\delta l = p d v. \quad (7)$$

Here volume  $v$  also corresponds to the unit mass. Relations (4)–(7) must be satisfied simultaneously and independently for every thermodynamic system, as well as with regard to the first law.

**Energy transport by matter.** The increment of energy transferred by matter is assumed to be proportional to mass variation [10, 11]

$$\delta E = -\varphi dM. \quad (8)$$

The formulated postulates (2)–(8) realize the thermodynamic approach completely, i.e. they express functions of the process in terms of functions of state. Together with the first law they form the basis of classical thermodynamics [9].

Substituting expressions (4), (6), and (8) into (2), we obtain the fundamental equation of the first and the second laws in terms of functions of state

$$TdS = dU + p dV - \varphi dM. \quad (9)$$

The intensive form of the fundamental equation is expressed as

$$Tds = du + p dv, \quad (10)$$

because relations (3), (5), and (7) are fulfilled.

**Homogeneous functions.** Extensive functions of state are in the mathematical sense homogeneous functions relative to the mass [15]. This permits to connect the specific functions of state such as specific internal energy  $u$ , specific volume  $v$ , and specific entropy  $s$ , with the extensive functions by means of relations which follow from Euler's theorem of homogeneous functions [15]

$$u = \frac{U}{M} = \left( \frac{\partial U}{\partial M} \right)_{p,T}, \quad v = \frac{V}{M} = \left( \frac{\partial V}{\partial M} \right)_{p,T}, \quad s = \frac{S}{M} = \left( \frac{\partial S}{\partial M} \right)_{p,T}. \quad (11)$$

Relations (11) are actually definitions of specific functions of state.

The coefficient of proportionality in the right-hand side of (8) can be expressed in the terms of introduced functions of state. For this the first law will be represented in the form

$$d(TS) - SdT = dU + d(pV) - Vdp - \Phi dM. \quad (12)$$

Hence, for the fixed values of  $p$  and  $T$  we obtain

$$\Phi = \left( \frac{\partial \Phi}{\partial M} \right)_{p,T}, \quad (13)$$

where  $\Phi = U + pV - TS$  is Gibbs's function.

Gibbs's function is a linear combination of extensive functions of state and, therefore, it is also an extensive function of state.

Relation (13) determines a specific function of state called the chemical potential of a thermodynamic system.

**Simple systems.** The homogeneity properties of thermodynamic functions of state (11), (13) ensure consistency between the extensive (9) and intensive (10) forms of the fundamental equation of the first and the second laws. In addition, the properties of homogeneity permit to represent the equations of state of pure substance (1) in the form

$$v = v(p, T), \quad u = u(p, T). \quad (14)$$

Thus, the intensive state of the system in this case is fully determined by the values of two independent variables.

Thermodynamic systems, the intensive state of which is determined by means of equations of state in the form (14), are usually called simple systems [12]. The classical thermodynamics of simple systems supplemented by the conditions of compatibility between equations of state (14) and thermodynamic laws (9), (10), is a self-consistent theory [9].

The realization of the thermodynamic approach for simple systems illustrated by equations of state for ideal gas composes the basic content of textbooks of thermodynamics. In addition, the relations of the thermodynamics of simple systems are the basis of numerous applications of thermodynamics which show the advantage of the thermodynamic approach.

Unfortunately, in practice it is impossible to deal with simple systems only. Such a circumstance induces the development of more general thermodynamic theories [16-20].

### 3. Compatibility of equations of state with thermodynamic laws

The empiric nature of equations of state requires that the form of an equation of state should be compatible with the mathematical structure of the thermodynamic theory. Arbitrary relations between the parameters of state cannot play the role of equations of state.

**Entropy as a function of state.** Considering entropy as a function of state we suppose that by the representation of the total differential of specific and full entropy by means of the fundamental equations of the first and the second laws of thermodynamics (9) and (10), respectively,

$$ds = \frac{1}{T} du + \frac{p}{T} dv, \quad (15)$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\Phi}{T} dM, \quad (16)$$

we must in the right-hand sides actually obtain integrated expressions, i. e. the conditions

$$\left( \frac{\partial s}{\partial u} \right)_v = \frac{1}{T}, \quad \left( \frac{\partial s}{\partial v} \right)_u = \frac{p}{T}, \quad (17)$$

$$\left( \frac{\partial S}{\partial U} \right)_{v,M} = \frac{1}{T}, \quad \left( \frac{\partial S}{\partial V} \right)_{u,M} = \frac{p}{T}, \quad \left( \frac{\partial S}{\partial M} \right)_{u,v} = -\frac{\Phi}{T} \quad (18)$$

must be fulfilled.

It is usually assumed that the aforementioned relations are always automatically satisfied in simple systems without dependence on a concrete form of the equations of state (14), because the integrability of the right-hand sides (15) and (16) is evident by virtue of mathematical properties of functions on two independent variables [21].

**Conditions of compatibility for simple systems.** However, there are also certain restrictions for simple systems. Such restrictions are connected with the method of the input of empiric information into the thermodynamic theory. As in every thermodynamic theory, the information about the properties of the substance in simple systems is embedded in equations of state

$$v = v(p, T), \quad (19)$$

$$u = u(p, T), \quad (20)$$

which must be specified for each concrete thermodynamic system in an explicit form. When such a way of introducing empiric information is used, parameters  $v$  and  $u$  immediately become functions of state. Hence it cannot be concluded that specific entropy  $s$  is also a function of state as demanded by the second law. In order to reach definitely this conclusion, it is necessary to examine the consistency of the method of specification of empiric information in the form (19), (20) with the conditions of identity of the differential form in the right-hand side of expression (15) with the total differential of entropy. In the case of two independent variables, the following condition must in addition be fulfilled [9]

$$\left( \frac{\partial u}{\partial v} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_v - p. \quad (21)$$

Other forms of the condition of the existence of the total differential of entropy in this case are Maxwell's equations [22]

$$\begin{aligned} \left( \frac{\partial s}{\partial v} \right)_T &= \left( \frac{\partial p}{\partial T} \right)_v, & \left( \frac{\partial s}{\partial v} \right)_p &= \left( \frac{\partial p}{\partial T} \right)_s, \\ \left( \frac{\partial s}{\partial p} \right)_T &= -\left( \frac{\partial v}{\partial T} \right)_p, & \left( \frac{\partial s}{\partial p} \right)_v &= -\left( \frac{\partial v}{\partial T} \right)_s. \end{aligned} \quad (22)$$

Hence it follows that the demand of compatibility with the conditions of the existence of the total differential of entropy imposes restrictions on the form of state equations also for two independent variables. In practice it means that in the case of the specification of the thermal equation of state (19) in the form of an arbitrary approximation of experimental data, the rest of empiric information is introduced into the thermodynamic model in a form compatible with (19) and (21).

**Procedure of consistency for simple systems.** The method of obtaining consistency will be described on the example of the specification of experimental data on heat capacity

$$c_v = c_v(T, v). \quad (23)$$

Internal energy immediately becomes a function of state, therefore the expression of the total differential of internal energy

$$du = \left( \frac{\partial u}{\partial T} \right)_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv, \quad (24)$$

by using (21), can be represented in the form

$$du = c_v dT + \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right] dv. \quad (25)$$

The form of the empiric equation for heat capacity (23) is selected so that the condition of the existence of the total differential for the right-hand side of expression (25) would be fulfilled

$$\left( \frac{\partial c_v}{\partial v} \right)_T = \left( \frac{\partial \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right]}{\partial T} \right)_v. \quad (26)$$

After integrating (25), using equation of state (19) and the condition of the existence of the total differential of entropy (26), the explicit form of the caloric equation of state (20) can be obtained.

Specific entropy is definitely a function of state by such a way of handling the consistency of empiric information with thermodynamic laws, and the relations of homogeneity (11), (13) ensure such a property also for full entropy.

Thus, even for a simple thermodynamic system the input of empiric information must be compatible with the restriction of the existence of entropy as a function of state. The described procedure of guaranteeing the consistency of equations of state with thermodynamic laws is applied in practice, for example, in the calculation of the surface of states of pure substances.

**Problem of compatibility in complex systems.** The compatibility of the empiric information specified by equations of state with the mathematical structure of the thermodynamic theory for complex systems is certainly much more complicated.

Complex systems, in contrast to simple ones, cannot be characterized by the equations of state dependent on only two variables. It is known that the functions of state for complex systems depend on more than two independent variables [10, 15]

$$\begin{aligned} V_c &= V_c(p_c, T_c, M_1, \dots, M_n), \\ U_c &= U_c(p_c, T_c, M_1, \dots, M_n), \end{aligned} \quad (27)$$

where  $n$  is the number of constituents and the index  $c$  corresponds to the value of a parameter characterizing the system as a whole.



In addition, observations show that intensive functions of state of a complex system do not depend on the total mass. The empiric equations of state in this case can be written in the form [21]

$$\begin{aligned} v_c &= v_c(p_c, T_c, x_1, \dots, x_n), \\ u_c &= u_c(p_c, T_c, x_1, \dots, x_n), \end{aligned} \quad (28)$$

where  $x_i = M_i/M_c$ .

While the intensive state of a complex thermodynamic system is determined by  $n+2$  independent variables, the total differentials of such functions of state as specific and full entropy are represented in the form corresponding to empiric equations of state (27), (28)

$$ds_c = \left( \frac{\partial s_c}{\partial p_c} \right)_{T_c, (x_i)} dp_c + \left( \frac{\partial s_c}{\partial T_c} \right)_{p_c, (x_i)} dT_c + \sum_{i=1}^n \left( \frac{\partial s_c}{\partial x_i} \right)_{p_c, T_c, (x_l)} dx_i, \quad (29)$$

$$dS_c = \left( \frac{\partial S_c}{\partial p_c} \right)_{T_c, (M_i)} dp_c + \left( \frac{\partial S_c}{\partial T_c} \right)_{p_c, (M_i)} dT_c + \sum_{i=1}^n \left( \frac{\partial S_c}{\partial M_i} \right)_{p_c, T_c, (M_l)} dM_i. \quad (30)$$

Expressions (29), (30) are quite independent of each other in complex systems because in contrast to simple systems the relations of homogeneity in the form (11), (13) do not solve the problem of the mutual transformation of intensive and extensive forms of the total differential of entropy. As a rule, in the textbooks of thermodynamics considerations about the problem of the consistency of differential expressions (29) and (30) are not given.

The conditions of the existence of entropy as a function of state impose  $n(n-1)/2$  supplementary restrictions on the function  $s$ . Consequently, in the selection of the form or structure of equations of state (27) allowance must be made for all conditions of compatibility. Any other method of creating empiric equations of state leads to the necessity of breaking the law of energy conservation. Herein lies the problem of the compatibility of empiric information with thermodynamic laws for complex thermodynamic systems.

In theoretical works [10-12, 17-21] it is assumed that the equations of state for complex systems have just such a form which ensures the existence of entropy as a function of state. On the other hand, in practical manuals [23, 24] it is considered that the theoretical relations can be used without dependence on the explicit form of the existing equations of state. The problems are solved by means of the introduction of new variables such as, for example, affinity [25], or by the reduction of the properties of the complex system to the relations characteristic of ideal gas by means of coefficients of activity, fugacity, etc. [26].

If a complex system is considered a simple one because one need not know that it is a complex one, then the equations of state are represented in the form which does not contain the masses of the constituents. For example,

$$\begin{aligned} v_c &= v_c(p_c, T_c), \\ u_c &= u_c(p_c, T_c). \end{aligned} \quad (31)$$

Often it is done just like that, considering, for example, air a one-component substance [26]. However, the information on the influence of the compound on the properties of the complex system is then lost. An attempt to preserve such information again leads to the equations of state in the form (27).

If the empiric equations of state for a complex system in the form (27) or (28) were compatible with the conditions of the existence of entropy as a function of state, then it would be possible to use the thermody-

dynamic description of complex systems. However, such demands are not fulfilled for purely empiric equations of state. Therefore, it is necessary to find such a method of analysis of the thermodynamic structure of complex systems which will permit to expose the connection between the compound and the properties of complex systems by the retention of the compatibility of empiric information with the thermodynamic laws.

The remaining part of the paper is dedicated to the description of such a method with regard to complex systems. Special consideration is given to mutual relations between the methods of the input of empiric information into the system by means of equations of state and mathematical relations of the thermodynamic theory. The consequences of restrictions of homogeneity, compatibility, and the possibility of dual representation of a thermodynamic system as a continuous medium and as an assemblage of discrete particles are analysed carefully.

#### 4. Complex systems. Additivity and homogeneity

**Composition.** A method for describing complex thermodynamic systems is proposed that does not use the empiric equations of state for complex systems. The system of axioms of classical thermodynamics [9] is supplemented by principles 1—4 expressing the relations between a complex whole and its simple parts.

Let us consider a complex system as a composition of simple subsystems. The intensive state of each simple subsystem is determined by two parameters of state, for example,  $p_i$  and  $T_i$ . The equations of state for simple subsystems are assumed to be known in the form

$$v_i = v_i(p_i, T_i), \quad u_i = u_i(p_i, T_i), \quad i = 1, \dots, n, \quad (32)$$

where  $n$  is the number of simple subsystems. These equations of state are also suggested to be satisfied in the compound of a complex system.

For every thermodynamic process in each of the interacting subsystems, the first and the second laws of thermodynamics are valid in both the intensive and the extensive form according to the principle of duality

$$\delta Q_i = dU_i + \delta L_i + \delta E_i, \quad \delta q_i = du_i + \delta l_i, \quad (33)$$

$$\delta Q_i = T_i dS_i, \quad \delta q_i = T_i ds_i, \quad (34)$$

$$\delta L_i = p_i dV_i, \quad \delta l_i = p_i dv_i, \quad (35)$$

$$\delta E_i = -\varphi_i dM_i, \quad i = 1, \dots, n. \quad (36)$$

**Invariance.** Following the principle of invariance, we must also write for the complex system

$$\delta Q_c = dU_c + \delta L_c + \delta E_c, \quad \delta q_c = du_c + \delta l_c, \quad (37)$$

$$\delta Q_c = T_c dS_c, \quad \delta q_c = T_c ds_c, \quad (38)$$

$$\delta L_c = p_c dV_c, \quad \delta l_c = p_c dv_c, \quad (39)$$

$$\delta E_c = -\varphi_c dM_c. \quad (40)$$

The difference between the description of complex and simple systems consists in the fact that the equations of state for a complex system in the form (27) or (28) are inconvenient and they will not be used. Consequently, the quantities used in relations (37)—(40), generally speaking, do not immediately become functions of state.

From relations (37)—(40) the possibility of the presentation of the fundamental equation of the first and the second laws of thermodynamics in the form of the total differential of specific and full entropy of a complex system as a whole follows:

$$ds_c = \frac{1}{T_c} du_c + \frac{p_c}{T_c} dv_c, \quad (41)$$

$$dS_c = \frac{1}{T_c} dU_c + \frac{p_c}{T_c} dV_c - \frac{\Phi_c}{T_c} dM_c. \quad (42)$$

Relations (33)—(42) do not yet determine the interaction between the subsystems of a complex system. However, they must be satisfied in every way of interaction. The interaction must be such that the thermodynamic parameters in expressions (37)—(40) would remain functions of many variables and they would really be functions of state.

**Interaction.** The imposing of conditions (41) and (42) on the processes of transfer of energy in subsystems results in the set of subsystems composing a simple whole. Consequently, the mass and volume of a complex system must be additive

$$M_c = \sum_{i=1}^n M_i, \quad (43)$$

$$V_c = \sum_{i=1}^n V_i. \quad (44)$$

Equality (43) expresses the law of mass conservation and (44) follows from the geometrical properties of physical space.

Additivity is a property of the extensive quantity which is related to the fact that the value of this quantity corresponding to the object as a whole is equal to the sum of values of the same quantity corresponding to the parts of such a whole. However, the relations of the part and the whole appear only as a result of interaction between the parts of such a whole.

The concept of quanticity permits to identify the notion of the extensive quantity of a discrete particle with that of the intensive quantity of a simple subsystem as a whole. This means that specific quantities are connected with each other as follows:

$$M_c dv_c = \sum_{i=1}^n M_i dv_i, \quad M_c du_c = \sum_{i=1}^n M_i du_i, \quad M_c ds_c = \sum_{i=1}^n M_i ds_i. \quad (45)$$

In order that specific heat and work determined by relations (38) and (39) for a complex system and by (34) and (35) for a simple one were consistent with each other, we suppose that the sum of specific heats absorbed by the mass of each discrete particle is equal to the value of specific heat absorbed by their total mass. An analogous assumption is true for the works

$$M_c \delta q_c = \sum_{i=1}^n M_i \delta q_i, \quad (46)$$

$$M_c \delta l_c = \sum_{i=1}^n M_i \delta l_i. \quad (47)$$

The obtained relations can be presented in terms of functions of state. In fact, expressions (46) and (47), by means of the thermodynamic laws, can be transformed into the form

$$M_c p_c dv_c = \sum_{i=1}^n M_i p_i dv_i, \quad (48)$$

$$M_c T_c ds_c = \sum_{i=1}^n M_i T_i ds_i. \quad (49)$$

The additivity of specific heat and work permits to identify the sum of the fundamental equations of the first and the second laws for subsystems (33) with the fundamental equation for the system as a whole (37), and to obtain conditions for the satisfaction of the postulates of thermodynamics simultaneously for both simple subsystems and the system as a whole.

Let us assume that in the absence of phase transitions and chemical reactions the interaction of subsystems with each other and with the surroundings proceeds in such a way that the internal energy as well as entropy, volume and bounded energy are additive

$$U_c = \sum_{i=1}^n U_i, \quad S_c = \sum_{i=1}^n S_i, \quad (50)$$

$$p_c V_c = \sum_{i=1}^n p_i V_i, \quad (51)$$

$$T_c S_c = \sum_{i=1}^n T_i S_i. \quad (52)$$

Let us show that the relations follow from formulated conditions

$$\frac{dv_c}{v_c} = \frac{dv_i}{v_i}. \quad (53)$$

Consider first the case of two constituents. By multiplying both parts of the first equation (45) and (44) by  $p_c$  we obtain

$$p_c M_c dv_c = p_c M_1 dv_1 + p_c M_2 dv_2, \quad (54)$$

$$p_c v_c M_c = p_c v_1 M_1 + p_c v_2 M_2. \quad (55)$$

Term-by-term subtraction of equation (54) from (48) and equation (55) from (51) yields

$$(p_c - p_1) M_1 dv_1 = -(p_c - p_2) M_2 dv_2, \quad (56)$$

$$(p_c - p_1) M_1 v_1 = -(p_c - p_2) M_2 v_2. \quad (57)$$

As a result of term-by-term division of equations (56) and (57), we obtain

$$\frac{dv_1}{v_1} = \frac{dv_2}{v_2}. \quad (58)$$

Analogously we can deduce the following relation:

$$\frac{dv_1}{v_1} = \frac{dv_c}{v_c}. \quad (59)$$

The full proposition (53) can be proved by the method of mathematical induction.

**Homogeneity.** A common property of thermodynamic systems, for the description of which equations of state are used, is the homogeneity of extensive functions of state in respect to mass [15]. The property of homogeneity for simple thermodynamic subsystems

$$\begin{aligned}
 (81) \quad u_i &= \frac{U_i}{M_i} = \left( \frac{\partial U_i}{\partial M_i} \right)_{p_i, T_i}, & v_i &= \frac{V_i}{M_i} = \left( \frac{\partial V_i}{\partial M_i} \right)_{p_i, T_i}, \\
 (82) \quad s_i &= \frac{S_i}{M_i} = \left( \frac{\partial S_i}{\partial M_i} \right)_{p_i, T_i}, & i &= 1, \dots, n,
 \end{aligned}
 \tag{60}$$

ensures the compatibility of intensive and extensive forms of the fundamental equation of the first and the second laws.

Extensive functions of state are in the mathematical sense homogeneous functions of the first degree. This circumstance allows us to write

$$\begin{aligned}
 kU_c &= U_c(T_c, p_1, \dots, p_n, kM_1, \dots, kM_n), \\
 kU_c &= U_c(T_c, p_c, kM_c).
 \end{aligned}
 \tag{61}$$

Extensive and intensive functions of state for a complex system as a whole are connected by relations analogous to (60)

$$\begin{aligned}
 (83) \quad u_c &= \frac{U_c}{M_c} = \left( \frac{\partial U_c}{\partial M_c} \right)_{p_c, T_c}, & v_c &= \frac{V_c}{M_c} = \left( \frac{\partial V_c}{\partial M_c} \right)_{p_c, T_c}, \\
 (84) \quad s_c &= \frac{S_c}{M_c} = \left( \frac{\partial S_c}{\partial M_c} \right)_{p_c, T_c}.
 \end{aligned}
 \tag{62}$$

By virtue of Euler's theorem about homogeneous functions [15] for each of the extensive functions of state of a complex system the following relations are valid in addition to (62)

$$U_c = \sum_{i=1}^n M_i \left( \frac{\partial U_c}{\partial M_i} \right)_{p_c, T_c, M_j}, \quad i \neq j.
 \tag{63}$$

Thus, homogeneity in complex systems is displayed in two ways. The extensive functions of state of a complex system show the properties which are analogous to those of simple systems in respect to total mass.

Full heat and work can be expressed in terms of functions of state, taking into account the remaining parts of equalities (34), (35), (38), (39), in the form

$$p_c dV_c = \sum_{i=1}^n p_i dV_i - \sum_{i=1}^n p_i v_i dM_i + p_c v_c dM_c,
 \tag{64}$$

$$T_c dS_c = \sum_{i=1}^n T_i dS_i - \sum_{i=1}^n T_i s_i dM_i + T_c s_c dM_c.
 \tag{65}$$

For closed systems expressions (64) and (65) are reduced to the common form of additivity of heat and work.

The properties of additivity and homogeneity of energetic characteristics of a complex system do still not give an unambiguous description of the state of a complex system. At the same time, the representation of a complex thermodynamic system as a composition of simple subsystems permits to describe the state of a complex system without empiric equations of state. A complete description of the state of a complex system supposes that the values of the masses of the constituents as well as the values of two intensive parameters of each constituent and the values of two intensive parameters of the system as a whole are known. The whole number of these values is  $3n+2$ . In correspondence with Gibbs's phase rule  $n+2$  of them are independent and can be given arbitrarily. The rules for determining the values of  $2n$  more parameters are needed.

## 5. Conditions of equilibrium in complex systems

**Conditions of interaction.** The interaction of subsystems with each other and with the surroundings is exposed in the existence of mutual relations between the parameters of the subsystems in question. The method of interaction must not contradict thermodynamic laws nor the properties of homogeneity and additivity.

At least two kinds of relations between intensive parameters of state of subsystems satisfy such restrictions. The first of them says that the temperatures of subsystems retain the same value

$$T_i = T_j = T_c, \quad i, j = 1, \dots, n, \quad (66)$$

and the second preserves equal values of pressures

$$p^{(i)} = p^{(j)} = p^{(c)}, \quad i, j = 1, \dots, n. \quad (67)$$

Relations (66) and (67) determine two different ways of interaction of subsystems which are called the homogeneous and the heterogeneous equilibrium, respectively.

Conditions of interaction (66) and (67) allow to determine the value of one intensive parameter for each of  $n$  subsystems. The value of the second parameter can be obtained from the compatibility of the existence of entropy as a function of state in both a complex system and each of the subsystems with the properties of additivity of heat and work. The relations which express the necessary conditions are called the equilibrium conditions.

**Homogeneous equilibrium without phase transitions.** Let us represent the expression for the total differential of entropy in a sequence of independent variables  $T, v, M$ . In absence of phase transitions the masses of the constituents as well as temperature  $T_c$  and volume  $v_c$  of the complex system are independent variables

$$M_i = M_i(t), \quad i = 1, \dots, n, \quad (68)$$

$$T_c = T_c(t), \quad v_c = v_c(t), \quad (69)$$

where  $t$  is an external parameter, for example, time.

In the conditions of homogeneous equilibrium the temperatures of the constituents are identical, i.e. the conditions of interactions (66) are valid.

The expressions for the total differentials of entropy of simple constituents multiplied by the corresponding masses have the form

$$M_i ds_i = M_i \left( \frac{\partial s_i}{\partial T_i} \right)_{v_i} dT_i + M_i \left( \frac{\partial s_i}{\partial v_i} \right)_{T_i} dv_i, \quad i = 1, \dots, n. \quad (70)$$

Summing up in respect of  $i$ , relation (70) yields

$$\sum_{i=1}^n M_i ds_i = \sum_{i=1}^n M_i \left( \frac{\partial s_i}{\partial T_i} \right)_{v_i} dT_i + \sum_{i=1}^n \left( \frac{\partial s_i}{\partial v_i} \right)_{T_i} \frac{M_i}{p_i} p_i dv_i. \quad (71)$$

On the other hand, the total differential of entropy for the complex system multiplied by its mass has the form

$$M_c ds_c = M_c \left( \frac{\partial s_c}{\partial T_c} \right)_{v_c} dT_c + M_c \left( \frac{\partial s_c}{\partial v_c} \right)_{T_c} dv_c. \quad (72)$$

By virtue of the additivity of specific heat and work (48), (49), expression (72) can be represented in the form

$$\sum_{i=1}^n M_i ds_i = M_c \left( \frac{\partial s_c}{\partial M_c} \right)_{v_c} dT_c + \sum_{i=1}^n \left( \frac{\partial s_c}{\partial v_c} \right)_{T_c} \frac{M_i}{p_c} p_i dv_i. \quad (73)$$

**Conditions of equilibrium.** In the case of independent actions the coefficients in the right-hand sides of expressions (71) and (73) must be the same, i. e.

$$\left(\frac{\partial s_c}{\partial T_c}\right)_{v_c} = \sum_{i=1}^n \frac{M_i}{M_c} \left(\frac{\partial s_i}{\partial T_i}\right)_{v_i}, \quad (74)$$

$$\frac{1}{p_c} \left(\frac{\partial s_c}{\partial v_c}\right)_{T_c} = \frac{1}{p_i} \left(\frac{\partial s_i}{\partial v_i}\right)_{T_i}, \quad i=1, \dots, n. \quad (75)$$

Relations (74), (75) give the concrete expressions of the remaining part of conditions of the interaction of subsystems in the compound of a complex system. It is natural to call them the conditions of equilibrium of interacting homogeneous systems, such as multi-component mixtures and solutions. Condition (74) is the definition of total heat capacity. Condition (75) makes it possible to determine the values of pressure for each subsystem.

Consider now the features of the behaviour of a complex system in which the properties of the continuous medium are displayed. The method of separation into subsystems must not play the main role in the homogeneous system. Every part of the homogeneous system must make its own contribution to the interaction of the system as a whole with the surroundings at the given  $T_c$  and  $p_c$ . Retaining the separation of the complex system into subsystems made up by pure constituents, we will assume that the parameters of each constituent are a function of the total pressure  $p_c$ .

The expression for the total differentials of entropy for the constituents in the set of variables  $p_c, v_i$  has the form

$$ds_i = \left(\frac{\partial s_i}{\partial p_c}\right)_{v_i} dp_c + \left(\frac{\partial s_i}{\partial v_i}\right)_{p_c} dv_i, \quad i=1, \dots, n. \quad (76)$$

It must be noted that relations (51) and (64) determine the complex expression for the differential of total pressure

$$V_c dp_c = \sum_{i=1}^n V_i dp_i - \sum_{i=1}^n p_i v_i dM_i + p_c v_c dM_c. \quad (77)$$

The derivation of entropy with regard to volume at fixed total pressure is calculated in correspondence to relation (53) as follows

$$\left(\frac{\partial s_i}{\partial v_i}\right)_{p_c} = \frac{V_i}{V_c} \left(\frac{\partial s_i}{\partial v_i}\right)_{p_i}, \quad i=1, \dots, n. \quad (78)$$

After the summing up of equations (76) multiplied by the corresponding masses with regard to  $i$  by virtue of (78) we obtain

$$\sum_{i=1}^n M_i ds_i = \sum_{i=1}^n M_i \left(\frac{\partial s_i}{\partial p_c}\right)_{v_i} dp_c + \sum_{i=1}^n \frac{M_i V_i}{V_c} \left(\frac{\partial s_i}{\partial v_i}\right)_{p_i} dv_i. \quad (79)$$

Substituting the expression for the differential of specific volume of constituent (53) we can write

$$\sum_{i=1}^n M_i ds_i = \sum_{i=1}^n M_i \left(\frac{\partial s_i}{\partial p_c}\right)_{v_i} dp_c + \sum_{i=1}^n \frac{V_i^2}{V_c v_c} \left(\frac{\partial s_i}{\partial v_i}\right)_{p_i} dv_c. \quad (80)$$

At the same time, the total differential of entropy for the complex system has the form

$$M_c ds_c = M_c \left(\frac{\partial s_c}{\partial p_c}\right)_{v_c} dp_c + M_c \left(\frac{\partial s_c}{\partial v_c}\right)_{p_c} dv_c. \quad (81)$$

The left-hand sides of expressions (80) and (81) are equal. Consequently, independent variables' coefficients in the right-hand sides must be identical

$$\left(\frac{\partial s_c}{\partial p_c}\right)_{v_c} = \sum_{i=1}^n \frac{M_i}{M_c} \left(\frac{\partial s_i}{\partial p_c}\right)_{v_i} = \sum_{i=1}^n \frac{v_i}{v_c} \left(\frac{\partial s_i}{\partial p_i}\right)_{v_i} \quad (82)$$

$$\left(\frac{\partial s_c}{\partial v_c}\right)_{p_c} = \sum_{i=1}^n \frac{V_i^2}{V_c^2} \left(\frac{\partial s_i}{\partial v_i}\right)_{p_i} \quad (83)$$

Relations (82) and (83) determine the behaviour of a complex system as a continuous medium.

Conditions of equilibrium (74), (75), (82) and (83) ensure the mutual transformation of the extensive and the intensive forms of the fundamental equation. The parameters of a complex system as a whole become really functions of state by such a way of attaining the compatibility between the properties of simple constituents and a complex system as a whole.

## 6. Conclusion

The conditions of current equilibrium in interacting systems are different from the classical equilibrium conditions. The classical conditions of equilibrium express the identity of state of each part of the isolated system. The obtained conditions of equilibrium are more general. Different parts of a complex system can have distinct states, but the variation of these states can proceed only by strict satisfaction of thermodynamic laws both for every subsystem and for the complex system as a whole.

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Arkadi BEREZOVSKI, Viktor ROSENBLUM

#### KEERUKATE SÜSTEEMIDE TERMODÜNAAMIKA PÕHIMÕISTED

Keerukate süsteemide kirjeldamise üldisemal juhul vajavad klassikalise termodünaamika põhimõisted täiendamist ja täpsustust. Artiklis on formuleeritud keerukate süsteemide kirjeldamise põhiprintsiibid, mis täiendavad termodünaamika seadusi, on saadud nende printsiipide matemaatilised avaldised ja analüüsitud neist tulenevaid järeldusi. On näidatud, et keerukate, üksteist vastastikku mõjutavate süsteemide hetkelist termodünaamilist tasakaalu seloomustavad isoleeritud süsteemide klassikalistest tasakaalutingimustest keerukamad tingimused, mis võimaldavad siduda keerukate süsteemide omadusi neid moodustavate lihtsate osasüsteemide omadustega.

Аркадий БЕРЕЗОВСКИЙ, Виктор РОЗЕНБЛУМ

#### ОСНОВНЫЕ ПОНЯТИЯ ТЕРМОДИНАМИКИ СЛОЖНЫХ СИСТЕМ

При описании сложных систем классическая термодинамика нуждается в дополнении и уточнении основных понятий для их применения в более общей ситуации. В статье сформулированы основные принципы описания сложных систем, дополняющие термодинамические законы, получено математическое выражение этих принципов и проанализированы выводы из них. Показано, что текущее термодинамическое равновесие сложных взаимодействующих систем характеризуется более общими условиями, нежели классические условия равновесия изолированных систем. Эти условия позволяют связать свойства сложных систем со свойствами их простых составляющих.