

This content has been downloaded from IOPscience. Please scroll down to see the full text.

Download details:

IP Address: 46.39.56.134

This content was downloaded on 03/08/2020 at 10:25

Please note that [terms and conditions apply](#).

Part I

Principles of non-equilibrium thermodynamics

Chapter 1

The concept of a thermodynamic system

To define a *thermodynamic system* means, first of all, to allocate some portion of the substance or matter, on which our attention is focused. This portion should not be too small; we assume also that the system consists of many separate cooperating particles (atoms and molecules), moving in a certain field. The laws of movement of the particle can be known, though we do not need to know them to formulate the macroscopic principles; moreover, a detailed microscopic description of the system appears to be possible in principle only. To describe gross characteristics, or large scale properties of the system, one has to introduce a set of new variables. To provide a macroscopic description, the thermodynamics solves, first of all, the problem of development of the methods of the description of behaviour of the assembly of many particles, as a whole system under various influences.

1.1 Composition of a thermodynamic system

The thermodynamic system is considered as an assembly of molecules of various chemical substances, the quantity and some characteristics of which sometimes (but not always) are known. The evidence of complex composition of macroscopic bodies was observed during many years¹. We assume that the numbers of molecules (numbers of moles) of various substances in the considered system can be set

$$n_1, n_2, \dots, n_k. \quad (1.1)$$

¹For an illustration it is possible to consider some volume of water. Since ancient times it is known that properties of water do not change if the given volume is divided into two parts. Anything from these two volumes can be also divided into two parts, while water remains water. We can recognize properties of water in each portion, but a question arises: how long is it possible to continue the process of division? Philosophers of ancient Greece believed that division cannot last indefinitely long. Finally, one can reach an indivisible particle named an atom (*ατομος*—not capable to be cut, indivisible), up to the last portion of volume, which still possesses the properties of water. Now, after many centuries, we know that a glass of water, for example, contains approximately 6×10^{24} molecules of water H_2O and this quantity (approximately 180 g) can be divided in two only 82 or, possibly, 83 times to reach the limit of division.

One has an equivalent description, when the concentrations of substances are given

$$c_1 = \frac{n_1}{n}, c_2 = \frac{n_2}{n}, \dots, c_k = \frac{n_k}{n}, \quad n = \sum_{\alpha=1}^k n_{\alpha},$$

where n is a total of molecules in the system². Considering the thermodynamic system, the complete chemical composition of the system appears to be unknown; one is interested in the description of changes of composition, which are occurring due to internal chemical reactions or fluxes of substances from the environment of the system.

As a system, obeying the laws of classical or quantum mechanics³, the assembly of particles is characterized by a certain quantity of *energy*, one speaks about *internal energy* U , assuming the system in the rest, and this quantity remains one of the main characteristic of thermodynamic system. The value of internal energy depends on the composition of the system and changes under external influences on the system. The change of composition provokes the change of the internal energy of the system that can be written as

$$\Delta U = \sum_{\alpha=1}^k h_{\alpha} \Delta n_{\alpha}. \quad (1.2)$$

The quantity h_{α} presents the change of internal energy that is occurring in the system with coming of a particle (mole) of substance. The quantity is introduced by equation (1.2) as intensive quantity, so that it can depend on the ratios of extensive quantities, that is on the concentrations $c_{\alpha} = n_{\alpha}/n$

$$h_{\alpha} = h_{\alpha}(c_1, c_2, \dots, c_n). \quad (1.3)$$

The energy, obtained by the system at variation of composition, depends, apparently, on the conditions at which the process occurs and, consequently, the specific enthalpy depends also, except for concentration, on other characteristics of the thermodynamic system, which will be discussed in the subsequent sections (see section 2.9).

Note that the change of number of particles in the system can occur due to both internal transformations and external fluxes of substance. A system, in which there are external fluxes of substances, is considered an *open system*. The numbers of particles in fluxes in and out the system ought to be specified. Otherwise, if there are

²One can use also the mass concentration, defined by equation

$$c_{\alpha} = \frac{m_{\alpha}}{V} n_{\alpha}.$$

³The microscopic specification of a system is used for the introduction of a statistical description of the thermodynamic system. In greater detail, it is possible to see, for example, the fifth chapter (section 5.1.2) for classic mechanics.

no fluxes of substances at all, the system is regarded as *closed* or even *isolated*. We shall return to the classification later.

1.2 Fundamental variables and work

We are concentrating on a collection of matter, which is considered as a *thermodynamic system* and must be specified further by introducing some characteristics of the state of the system. Everything external to the selected portion of matter is called *the surroundings* or the environment (thermostat), so that certain *borders* of the thermodynamics system exist. If we consider the system of stable composition, the borders are non-penetrable for matter and there are no fluxes of substances into or out of the system. The borders are fixed by a set of variables, and for the certain thermodynamic system the set of the parameters allocating the system from the environment is usually known from experiments. In the following we shall name such parameters as *fundamental variables* and designate x_1, x_2, \dots, x_n . The specified variables allocate the thermodynamic system, defining its borders. In the simplest case, the set of fundamental variables reduces to the only variable—to volume V , containing the certain quantity of substance in a gas or liquid phase.

The interaction between the system and its surroundings is considered to be performed via work of the fundamental variables x_1, x_2, \dots, x_n , and therefore is a form of energy in transit. An expression for work of the system has to be written as

$$\Delta A = \sum_{i=1}^n X_i \Delta x_i \quad (1.4)$$

where $X_i, i = 1, 2, \dots, n$ are thermodynamic forces which depend on the process of crossover from one state to another. The expression (1.4) will be everywhere used to represent work done by the system. The work done on the system has the opposite sign, however, it is not equal, in the general case, to the work done by the system. As a convention of sign, the quantity (1.4) is considered positive, while work done on the system is considered negative. The quantity ΔA stands for a small part of work. In the simplest case, when a system is characterized by the only fundamental variable—by volume V , work of the system is presented in the form

$$\Delta A = p \Delta V$$

where V is a volume of the system, p is internal pressure within the system, which need not be equal to the external pressure.

The work fulfilled by the system leads to variation of the internal energy of the system. In the simple case, when the reduction of energy is equal to the work, $\Delta U = -\Delta A$, the thermodynamic system can be considered as an *isolated* system, though usually it is not allowed work for an isolated system. However, there are cases, when $\Delta U \neq -\Delta A$. The inequality is connected with the possibility of exchange of energy between the system and environment in the form of thermal energy. In this case, the system is named a *closed* one, assuming the composition of the system is unchanged. The closed system has, generally speaking, no certain value of energy. The clarification of the role of thermal interaction was the basic difficulty, and the

proper solution (Clausius 1865) has led to the modern formulation of thermodynamics.

1.3 Entropy and absolute temperature

The energy passed from one system to another because of the temperature distinction between the two systems is named *heat energy*, which can be identified only at crossing of the border of the system and, consequently, it is a form of energy in transit. As an agreement of a sign, the quantity of heat received by a system ΔQ is considered positive, while the quantity of heat given by the system, is considered negative. If borders of the closed system do not allow exchange of heat between the system and the environment, the closed system is named *isolated*.

The change of internal energy U is provoked by the exchange of energy between the system and the surroundings⁴. The internal energy of the system U is increasing due to the flux of heat coming into the system ΔQ and decreasing due to the work of the system ΔA ; the energy coming with the fluxes of substances (1.2) is considered as a positive contribution, so that the change of the energy of the system can be written as

$$\Delta U = \Delta Q - \sum_j X_j \Delta x_j + \sum_\alpha h_\alpha \Delta n_\alpha. \quad (1.5)$$

This expression represents the standard form of the first law of thermodynamics, as it is stated in any text-book on thermodynamics. All quantities in equation (1.5) are characteristics of the thermodynamic system (not the environment), and the written relation is valid for any processes (reversible or irreversible) and situations.

There appears a difficulty, when one intends to define internal energy as a function of variables of a state. The matter is that the heat Q cannot be an argument of a function of state, this quantity is not a characteristic of the system, it is not a property of the system, it is heat obtained by the system. The designation ΔQ stands for a small part of heat, while we use the symbol Δ to show a change of the amount of a quantity which is not a function of system.

In the earlier days of development of the science of heat, it was supposed, that the stream of heat is connected with a stream of a special substance—phlogiston that flows in and out the thermodynamic system. Phlogiston had not been detected, and the problem, as it is well known, was solved by Clausius (1865) by postulating the existence of a such quantity S , called entropy and defined as

⁴ It was experimentally shown that energy is a measure of equivalence of the various macroscopic phenomena. The steam engines of Newcomen (from 1712) and Watt (from 1774) demonstrated that heat performs mechanical work. On the other side, work can produce heat. The historically most important experiment illustrating the reverse transformation of work into heat was performed in Munich by Count Rumford (1798): he caused water to boil, when a cannon barrel was being bored. In 1843 through his famous experiments Joule was led to the postulate that heat and work were equivalent in some sense. Mechanical work and heat are interchangeable, i.e. heat may be converted into mechanical work as in a steam engine, or mechanical work can be converted into heat which occurs as the barrel of a cannon is bored.

$$dS = \frac{\Delta Q}{T},$$

where T is an absolute temperature that will be discussed later.

Generalizing the concept of entropy for the systems with variable composition, one can write the total differentials of the total internal energy and entropy (in a reversible process) as

$$dU = T dS - \sum_j X_j dx_j + \sum_\alpha \mu_\alpha \Delta n_\alpha, \quad (1.6)$$

$$dS = \frac{\Delta E}{T}, \quad \Delta E = \Delta Q + \sum_\alpha \eta_\alpha \Delta n_\alpha. \quad (1.7)$$

When determining the entropy S , we are forced to divide the total contribution of chemical energy h_α , brought to the system by particles of substances, into two parts $h_\alpha = \eta_\alpha + \mu_\alpha$. One part with the chemical potential μ_α , contributes to the potential internal energy, as defined by Gibbs (1875); the other part with the specific value η_α is converted immediately into the thermal energy of the system⁵; it is convenient to introduce in the expression (1.7) the symbol E for internal thermal energy of the system.

In contrast to equation (1.5), which is valid for any situations, equations (1.6) and (1.7) are valid for the specific processes, when there is no need to introduce extra variables, apart from fundamental ones, so-called reversible processes. Note that, while equation (1.6) defines internal total energy as a function of variables S , \mathbf{x} and \mathbf{n} , equation (1.7) does not define entropy as a function⁶; arguments of the function of entropy will be discussed later (see section 2.5).

The notion of entropy, as a measure of internal heat energy, was firmly integrated by science, and the attempts to find phlogiston were abandoned. Simultaneously with entropy S , the absolute temperature T with an absolute thermodynamic scale of temperature (see any text-book on thermodynamics) is defined. The absolute temperature T is always positive and has a constant reference point. The temperature can be interpreted in terms of other physical quantities and is measurable, or,

⁵ The definition of the quantities will be done in section 2.8. The quantity μ_α is chemical potential and η_α is entropy contribution to thermal energy by a particle (mole) of the α th substance; due to equation (2.27), the sum $\eta_\alpha + \mu_\alpha$ denotes specific enthalpy of the substance. Researchers use, in line with concepts of chemical potential and partial enthalpy, a notion of ‘partial molar entropy of the exchanged chemical species under the conditions of the system boundary’ (von Stockar and Liu 1999) that is identical to the quantity η_α/T . Having in mind to develop the theory of open systems, which could be applied to biological objects, we cannot allow omitting the important quantity η_α .

⁶ Some researchers (see, for example, Sommerfeld 1952, chapter 2, section 14) do define the function by the expression

$$TdS = dU + \sum_j X_j dx_j - \sum_\alpha \mu_\alpha \Delta n_\alpha.$$

One can note, taking equation (1.6) into account, that the written relation is not a definition of function, but an uncertain differential equation for quantity S . Usage of this relation brings some inconsistency.

one can say, that it has physical meaning and empirical justification for its existence, as an intensive characteristic of the system. The temperature is usually measured in degrees, but, according to the connection with other physical quantities, it is energy. To omit the factor of transition from degrees to energy, it is convenient to agree that the temperature is measured in power units, as was proposed by Landau and Lifshitz (1986, p 52), which is accepted further at the writing of all equations. If the temperature is measured in degrees, to recalculate to power units, the factor of transition k , named the Boltzmann constant, is used. It has value

$$k = 1.38 \times 10^{-16} \text{ erg/grad} = 1.38 \times 10^{-23} \text{ J/grad.}$$

It is assumed that the values of *entropy* and *temperature* can be attributed to every thermodynamic system, as to the object consisting of many ‘particles’. Let us notice, however, that these specific quantities have been introduced by equation (1.6) for the reversible processes, which means that the processes of transition from one state to another are being fulfilled so slowly⁷, that in each point in time the state of the thermodynamic system is unambiguously defined by its unique set of fundamental variables, which means that the system remains in the state that is referred to as *an equilibrium state*. The equilibrium macrostate is unique, it is a certain idealization of the reality, similar to an idealized motion of a body with constant velocity in mechanics, and in this sense, it is a natural state of a thermodynamic system. The thermodynamic system cannot go out of the equilibrium macrostate without external influences (from the environment).

1.4 The fluxes and thermodynamic forces

The situation of equilibrium is a certain idealization of the reality; the real thermodynamic system is an object of various influences of the environment that causes variations of thermodynamic system as far as it is allowed by the borders of the system. In the most general case we should admit that borders of the system allow an exchange not only of heat, but also substances. In this general case, the system is named *open*; we recall, the system is named *closed* if the borders are impenetrable for substances, but allow transit of energy in the form of heat, and *isolated*, if there is no exchange of heat and substances.

1.4.1 Fluxes of heat

Let us consider a system consisting of two adjacent subsystems with various temperatures, T_1 and T_2 , which are incorporated in a combine system considered isolated. When two systems at different temperatures are brought in thermal contact

⁷More exactly, the slow fashion means that all characteristic times of the processes are much greater than corresponding relaxation times, $t \gg \tau_i$, and all variables practically have their equilibrium values. Such slow processes, when a state of thermodynamic system is determined only by fundamental variables, are called *reversible*. Otherwise, some of the relaxation times appear to be greater than a characteristic time of the process, which is called in this case *irreversible*. During such a process the interior of the system is permuted, and one needs in some extra variables (called internal ones) to describe the macrostate of the system more completely.

with each other, the combined system appears to be in a non-equilibrium state. It is known from evidence that there is a flux of heat from the system with higher temperature to the system with lower temperature, which appears to diffuse the difference in temperatures. The total energy of the combined system is constant, so that in any case, the change of heat within system 1 due to the flux from system 2 is the same (with the reverse sign) as the change of heat within system 2 due to the flux from system 1

$$\Delta Q_1 = -\Delta Q_2.$$

The heat fluxes provoke the changes of entropy in the compartments that, according to definition (1.7), can be written as

$$\Delta S_1 = \frac{\Delta Q_1}{T_1}, \quad \Delta S_2 = -\frac{\Delta Q_1}{T_2}.$$

In contrast to heat, the change of entropy in one compartment does not correspond to the change of entropy in the other department

$$\Delta S_1 \neq -\Delta S_2$$

and the change of entropy of the combined system can be estimated as

$$\Delta S = \frac{T_2 - T_1}{T_1 T_2} \Delta Q_1. \quad (1.8)$$

The change of entropy in this process is always non-negative and the trend to equilibrium can be interpreted as the trend of entropy to the highest value.

The results of the heat fluxes are the changing of values of temperatures of either system, so that a single value of temperature is established through the combined system. Equality of temperatures is a condition for thermal equilibrium between two systems or between two parts of a single system.

The inequality of temperatures in different points of the system provokes a flux of heat from the point with higher value to the point with lower value of temperature, so that one can write a local relation, for example, in the simplest form

$$\mathbf{J}_T = -\lambda \nabla T, \quad \lambda > 0, \quad (1.9)$$

where coefficient of proportionality is named coefficient of conductivity of temperature (conductivity of heat).

1.4.2 Fluxes of substances

In a similar way we shall consider the system consisting of two adjacent subsystems with different concentrations of substances. If subsystems are separated by an impenetrable-for-substances partition, no variations in the system and subsystems is observed. After removal of the partition, changes of concentration of substances in both subsystems occur, and, if the compound system as a whole is isolated, the total energy of the system and number of particles in it do not change, so that the following relation, based on (1.2), can be written

$$\sum_{\alpha} (h_{\alpha}(c^{(1)}) - h_{\alpha}(c^{(2)})) \Delta n_{\alpha}^{(1)} = 0. \quad (1.10)$$

In an initial state, $\Delta n_{\alpha}^{(1)} \neq 0$ and therefore $h_{\alpha}(c^{(1)}) - h_{\alpha}(c^{(2)}) = 0$. This means that the quantity h_{α} , which is called the specific heat content of the substance α and is represented as the sum of two quantities $h_{\alpha} = \mu_{\alpha} + \eta_{\alpha}$ (see section 1.3), does not depend on the concentration.

From the recorded parity it does not follow that there is any preferential distribution of concentration, or any fluxes of substances, when the partition is removed. Mechanics can tell nothing about variations of concentration in subsystems; it does not follow from the laws of mechanics that the flow of matter is directed from a system with a higher concentration to a system with a lower concentration; we accept this as an empirical fact, which ought to be explained. To do this, we refer to the two quantities introduced by the relations (1.6) and (1.7): potential energy and entropy, the changes of which for each of the subsystems are defined as

$$\begin{aligned} \Delta(U_1 - E_1) &= \sum_{\alpha} \mu_{\alpha}(c^{(1)}) \Delta n_{\alpha}^{(1)}, \quad \Delta(U_2 - E_2) = - \sum_{\alpha} \mu_{\alpha}(c^{(2)}) \Delta n_{\alpha}^{(1)}, \\ \Delta S_1 &= \frac{1}{T} \sum_{\alpha} \eta_{\alpha}(c^{(1)}) \Delta n_{\alpha}^{(1)}, \quad \Delta S_2 = - \frac{1}{T} \sum_{\alpha} \eta_{\alpha}(c^{(2)}) \Delta n_{\alpha}^{(1)}. \end{aligned}$$

We believe that both chemical potential μ_{α} and the specific entropy flow η_{α}/T depend on concentration, and the changes in the quantities in one compartment do not correspond to changes in these values in another compartment.

The changes in the potential energy and entropy of the combined system after a certain amount of substance $\Delta n_{\alpha}^{(1)}$ has moved from subsystem 2 to subsystem 1 can be estimated as

$$\begin{aligned} \Delta(U - E) &= \sum_{\alpha} (\mu_{\alpha}(c^{(1)}) - \mu_{\alpha}(c^{(2)})) \Delta n_{\alpha}^{(1)}, \\ \Delta S &= \frac{1}{T} \sum_{\alpha} (\eta_{\alpha}(c^{(1)}) - \eta_{\alpha}(c^{(2)})) \Delta n_{\alpha}^{(1)}. \end{aligned} \quad (1.11)$$

We believe that the potential energy of the entire system cannot spontaneously increase, it can only decrease, and therefore the entropy of the combined system does not decrease with alignment. We can see, as in the previous example with heat, that the tendency to equilibrium can be interpreted as the tendency of entropy to the highest value. It follows also from the above speculations that the specific entropy η_{α}/T decreases with increasing concentration. In this case, the chemical potential μ_{α} is an increasing function of the concentration of the substance.

If concentration of a substance in the environment differs from concentration of a substance in the open system, there are processes of alignment of concentration. There is a flux of substances through the border of the system \mathbf{J}_c ; it is convenient to reduce the situation to local consideration: the inequality of concentration in adjacent points of the system leads to a stream of substance from a point with

higher value to a point with smaller value of concentration, so that it is possible to record for the flux of substance

$$\mathbf{J}_c = -D\nabla c, \quad D > 0, \quad (1.12)$$

where D is the coefficient of diffusion. The process of alignment of composition is running until concentrations of substances appear equal in all points of the compound system—one speaks of the system coming to equilibrium. Equality of concentration is a condition of equilibrium of two systems or parts of a united system. The specific thermodynamic characteristics in various parts of the system also appear equal.

1.5 Non-equilibrium thermodynamics

Macroscopic behaviour of the thermodynamic system does not reduce to any principles of mechanics, and a phenomenological theory, based on the specific thermodynamic principles, has been developing. It was understood that specific quantity—entropy—plays, in line with energy, a prominent role in description of macroscopic behavior of the system. Evidence of this kind is considered in section 1.4, which shows that for the description of non-equilibrium phenomena one needs concepts of thermodynamic forces and fluxes. To describe the state of a thermodynamic system that deviates from the equilibrium state, one needs to introduce special quantities that are called *internal variables*.

1.5.1 Internal variables

Among internal variables, as we can see in the above examples, one can find variables which determine the local deviations of concentrations and temperature from equilibrium ones

$$\Delta c_\alpha = c_\alpha - c_\alpha^0, \quad \alpha = 1, 2, \dots, n, \quad \Delta T = T_1 - T_2, \quad (1.13)$$

and the gradients of concentrations and temperature

$$\nabla c_\alpha, \quad \alpha = 1, 2, \dots, n; \quad \nabla T. \quad (1.14)$$

These quantities have various values at various points of the thermodynamic system and characterize the non-equilibrium state of the system. Apart from these quantities, many other internal variables can appear during processes of transition from one state to another. Generally, one needs in a set of internal variables ξ_1, ξ_2, \dots , to describe deviation of the state of thermodynamic system from the equilibrium one.

The internal variables emerge, when the thermodynamic system is undergone with influences from the environment. The rate of emergence is connected with the history of fluxes \mathbf{J} into the system

$$\frac{d\xi_i}{dt} = \mathcal{B}_i \frac{\infty}{s=0} [\mathbf{J}(t-s)], \quad i = 1, 2, \dots \quad (1.15)$$

Having been allowed to be on their own, the internal variables are tending to their unique equilibrium values, so that the system is tending to its stable equilibrium state. The local law of disappearing can be written as the relaxation equation for each internal variable

$$\frac{d\xi_i}{dt} = -\frac{1}{\tau_i} (\xi_i - \xi_i^{(0)}), \quad i = 1, 2, \dots, \quad (1.16)$$

where $\tau_i = \tau_i(T, x_1, x_2, \dots, x_n)$ is a relaxation time of corresponding variables. It is convenient to consider the initial value ξ_i^0 is equal to zero. The tending of the internal variables to disappear means that the equilibrium state is stable⁸.

To investigate the non-equilibrium situation, one has to consider the two simultaneous processes: the emerging and disappearing of the internal variables. The first one is connected with external influences, the disappearing is a process obeying the internal laws. In the situations that are close to equilibrium, the disappearing is described by equation (1.16). The dynamics of the emerging and relaxation of internal variables in an arbitrary situation is considered in chapter 3.

Let us note that, when some of the times of relaxation of internal variables are very big as compared with times of external processes, the corresponding internal variables appear to be constant, thus constituting a metastable structure of the system. In the general case, the internal variables in the system represent fading memory about past interactions.

1.5.2 The problem of formulation

The thermodynamic description of equilibrium situations is fulfilled perfectly. However, it cannot be said about non-equilibrium situations: according to authoritative experts on *non-equilibrium thermodynamics* (Maugin and Muschik 1994, p 219), to date ‘there is no formal consensus on how to formulate a thermodynamics of non-equilibrium’. The confirmation of this assessment can also be found in other works, for example, it is possible to read in the article (Mesquita *et al* 1999): ‘... the thermodynamics of irreversible processes has not yet achieved a phenomenological formulation and a methodology which can be considered satisfactory’.

To consider the complex system, the principles of non-equilibrium thermodynamics ought to be formulated first of all, and, further on, in this part, an attempt is made to present, following previous investigation by the author (Pokrovskii 2005, 2013), the consequent formulation of the theory, in which we use an extra set of variables, so-called internal variables, for the fixation of a non-equilibrium state of a thermodynamic system. It leads to a foundation and some justification of the known

⁸Note that the reversible process can now be defined more accurately. The process of transition of a thermodynamic system from one macrostate to another is called *reversible* if the relaxation times of all internal variables τ_i are much smaller than the characteristic times of the transition process t ; in this case, all fundamental variables actually have equilibrium values, and the internal variables are zero values. Otherwise, some of the relaxation times are greater than the characteristic time of the process, which, in this case, is called *irreversible*. In this case, some of the internal variables are excited and must be taken into account implicitly or explicitly.

(see, for example, Kondepudi and Prigogine 1999) parities of non-equilibrium thermodynamics. Turning to the regular description of non-equilibrium behaviour of a thermodynamic system, we are keeping in the mind the open thermodynamic system that intensively exchanges heat and substances with the environment. We shall notice, that use of internal variables is a universal method of considering of non-equilibrium situations, it is not a special ‘thermodynamics with internal variables’.

Perhaps, the first, who used internal variables for the consecutive formulation of thermodynamics, was Leontovich (1983)⁹. An independent development of the theory is presented in the work (Maugin and Muschik 1994) where authors understand the internal variables as only the complexity internal variable (see further chapter 3), and interpret the theory, as classical thermodynamics of irreversible processes with additional variables of state and an appropriating axiom of local balance. There is an alternative version of the theory in which not the internal variables, but fluxes are used for the description of non-equilibrium situations. Such a description named ‘the expanded irreversible thermodynamics’ (Jou *et al* 2001) appears equivalent to the description by means of the internal variables in stationary cases, so as in these cases there is an algebraic correspondence between streams and internal variables. In general case there is no such correspondence: it is possible to imagine the case when the fluxes are absent, but the system is in a non-equilibrium state with nonzero internal variables, and descriptions do not appear equivalent. The usage of fluxes as characteristics of the state cannot be proved in a conclusive way, and the version with the internal variables remains preferential.

References

- Clausius R 1865 Ueber verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie *Ann. Phys. Chem.* **125** 353–400
- Gibbs J W 1875 On the equilibrium of heterogeneous substances *Trans. Conn. Acad. Arts Sci.* **III** 108–248 343–524
- Gibbs J W 1928 *Equilibrium of Non-Homogenous Substances, 1895–1898: Collected works* (New York: Longman Green)
- Jou D, Casas-Vázquez J and Lebon G 2001 *Extended Irreversible Thermodynamics* 3rd edn (Berlin: Springer)
- Kondepudi D and Prigogine I 1999 *Modern Thermodynamics: From Heat Engines to Dissipative Structures* (Chichester: Wiley)
- Landau L D and Lifshitz E M 1986 *Statistical Physics* vol 1 3rd edn (Oxford: Pergamon)
- Leontovich M A 1983 *Vvedenie v termodinamiku. Statisticheskaya fizika [Introduction to Thermodynamics. The Statistical Physics]* (Moskva: Nauka, Glavnaya redaktsiya fiziko-matematicheskoy literatury)
- Maugin G A and Muschik W 1994 Thermodynamics with internal variables part I. General concepts *J. Non-Equil. Thermodyn.* **19** 217–49

⁹The first Russian edition of *Introduction to Thermodynamics*, based on his pre-war and war-time lectures, appeared, as a separate book, in 1950.

- Mesquita M V, Vasconcellos A R and Luzzi R 1999 Irreversible processes in the context of a non-equilibrium statistical ensemble formalism *Phys. Scr.* **59** 257–65
- Pokrovskii V N 2005 A derivation of the main relations of non-equilibrium thermodynamics *Eur. J. Phys.* **26** 769–81
- Pokrovskii V N 2013 A derivation of the main relations of non-equilibrium thermodynamics *ISRN Thermodyn.* **2013** 906136
- Sommerfeld A 1952 *Thermodynamik und Statistik—Vorlesungen über theoretische Physik Band 5* ed F Bopp and J Meixner (Wiesbaden: Diederichsche Verlagsbuchhandlung) Translation: Sommerfeld A 1964 *Thermodynamics and Statistical Mechanics—Lectures on Theoretical Physics Volume V* ed F Bopp and J Meixner (New York: Academic) translated by J Kestin
- von Stockar U and Liu J-S 1999 Does microbial life always feed on negative entropy? Thermodynamic analysis of microbial growth *Biochim. Biophys. Acta* **1412** 191–211