

Extended thermodynamics in a discrete-system approach

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Received 9 February 2005, in final form 11 April 2005

Published 21 June 2005

Online at stacks.iop.org/EJP/26/769

Abstract

The foundation of non-equilibrium thermodynamics is discussed. The behaviour of thermodynamic systems is described with the help of internal variables. It is shown that the requirement that a thermodynamic system cannot fulfil any work via internal variables is equivalent to the conventional formulation of the second law of thermodynamics. This work has to be included into the balance energy equation (the first law of thermodynamics). These statements, in line with axioms introducing internal variables, can be considered as basic principles of non-equilibrium thermodynamics. The statements do not affect equilibrium thermodynamic functions, but allow one to obtain consistent definitions of non-equilibrium functions. On some examples, it is demonstrated that the developed formalism provides the known results for non-equilibrium functions in a direct way, which encourages us to investigate and apply the formalism further.

1. Introduction

While studying and teaching thermodynamics, one can be confused with some discrepancy when the thermodynamic functions are introduced for a non-equilibrium system. Indeed, the energy balance for a thermodynamic system

$$dE = dQ - \sum_{i=1}^n X_i dx_i, \quad (1)$$

where E is the internal energy, Q is the incoming heat and the last term represents the work of the system via the basic variables x_i , can be written through entropy S . During reversible processes

$$T dS = dQ, \quad (2)$$

so that

$$dE = T dS - \sum_{i=1}^n X_i dx_i, \quad (3)$$

and one can consider internal energy as a function of entropy and constitutive variables, $E = E(S, x_1, x_2, \dots, x_n)$. However, during irreversible processes

$$T dS \geq dQ, \quad (4)$$

and one has

$$dE \leq T dS - \sum_{i=1}^n X_i dx_i. \quad (5)$$

Is the internal energy a function of any arguments in this case? Or has one to consider that internal energy is a function of entropy and constitutive variables x_i , which means that one has to accept relation (3) both for reversible and irreversible processes, and define a function of entropy in a proper way? The solution of the problem seems to lie in a proper generalization of thermodynamic functions for non-equilibrium states, which ought to be characterized with some internal variables—fluxes, for examples, or gradients, vanishing in the equilibrium situation. Though some hints at the internal variables can be traced [1] in works of the beginning of the last century, the first example of the use of internal variables in a modern way was apparently presented in the paper by Mandelstam and Leontovich [2], in which they considered the effect of relaxation of chemical composition on the fading of sound. The results are reproduced by Landau and Lifshits in the monograph [3]. Another example, in which tensor internal variables are used, is the description of viscoelasticity of both fluid and solid bodies [4]. Now there are different approaches to the problem; the two well-known distinctive approaches are: extended irreversible thermodynamics [5], which postulates the existence of a generalized, dependent on the fluxes as non-equilibrium quantities, entropy, and the internal-variables theory [1], which is classical thermodynamics of irreversible processes with additional state variables and the appropriate axiom of local equilibrium state. Plenty of results of explicit application of internal variables to a wide variety of physical problems convincingly demonstrate the usefulness of the introduction of internal variables for the description of complex thermodynamic systems [5, 6]. Nevertheless, a general appraisal is that up to now ‘there is no formal consensus on how to formulate a thermodynamics of non-equilibrium’, according to [1, p 219]. The confirmation of this appreciation can also be found in other works, for example, one can read in paper [7]: ‘... the thermodynamics of irreversible processes has not yet achieved a phenomenological formulation and a methodology which can be considered satisfactory’. In this situation, one has to be encouraged to investigate the very foundation of non-equilibrium thermodynamics.

In this paper, we shall try to discuss the foundation of non-equilibrium thermodynamics, introducing internal variables into the principles (section 2). The changes do not affect equilibrium thermodynamic functions, but allow us to obtain a consistent generalization of non-equilibrium functions. On some examples, it is demonstrated that the developed formalism provides the known results for non-equilibrium functions in a direct way (section 3), which encourages us to investigate and apply the formalism further.

2. The concept of a thermodynamic system

2.1. Macroscopic description

We consider an open thermodynamic system at temperature T which is regarded as a characteristic (a variable) of a state. One assumes that the chemical composition of the system is given by the concentrations of different substances

$$c_1, c_2, \dots, c_N. \quad (6)$$

The macroscopic state of the thermodynamic system is assumed to be given by a set of the macroscopic variables

$$x_1, x_2, \dots, x_n; \xi_1, \xi_2, \dots \quad (7)$$

The first n variables x_i , $i = 1, 2, \dots, n$, are basic variables which are chosen to characterize and determine the thermodynamic system. One can say that a thermodynamic system is given, if a set of basic variables is given, so that one can also call them *constitutive variables*. In the simplest case, the constitutive variable is the volume V which contains a certain part of substance in a gas or liquid phase.

An indefinite number of other variables ξ_i , $i = 1, 2, \dots$, has to be added to the set of constitutive variables to describe the macroscopic state of the system in more detail. When a limited list of n constitutive variables is fixed, the other variables are called *internal variables*. Among the internal variables, one can find variables which determine the deviations of concentration from equilibrium ones, the gradients of concentrations, temperature, velocity and many others. Though in some cases these variables are not used explicitly, one usually keeps in mind that there is something that allows non-equilibrium states of a thermodynamic system to be distinguished from equilibrium ones. The internal variables change their values according to internal laws of evolution of the system, which, in a general form (but disregarding diffusion processes), can be written as

$$\frac{d\xi_i}{dt} = f_i(T, x_1, x_2, \dots, x_n; \xi_1, \xi_2, \dots), \quad i = 1, 2, \dots \quad (8)$$

It is assumed, in accordance with empirical evidence, that, having been allowed to be on their own, internal variables are tending to their unique steady-state values, so that the system tends to its *equilibrium macrostate*, which is specified by stating that values of the internal variables are determined by temperature and values of constitutive variables

$$\xi_j^0 = \xi_j^0(T, x_1, x_2, \dots, x_n), \quad j = 1, 2, \dots \quad (9)$$

At small deviations from the equilibrium and at the given values of the constitutive variables, the law of changes can be written to the first approximation with respect to deviations as

$$\frac{d\xi_i}{dt} = -\frac{1}{\tau_i}(\xi_i - \xi_i^0), \quad i = 1, 2, \dots \quad (10)$$

where $\tau_i = \tau_i(T, x_1, x_2, \dots, x_n)$ are relaxation times of corresponding variables. The agitation has disappeared over time, which is described as relaxation of the variables to their equilibrium values that can be conveniently taken as zeros. In other words, equilibrium states of a thermodynamic system are assumed to be stable. Equation (10) is a description of the simplest behaviour of internal variables; the examples of more complicated dynamics can be found in works [1, 6].

If one assumes that a process of transition from one state to another is occurring in such a slow fashion that all characteristic times of the processes $t \gg \tau_i$, all variables practically have their equilibrium values. Otherwise, some of the relaxation times appear to be greater than a characteristic time of process. In this case some of the internal variables appear to be agitated, and one has to include these variables implicitly or explicitly into the description.

2.2. The principles

A change of state of a thermodynamic system is induced by interactions with the environment, which are usually described as heat flux, work and exchange of matter:

- The heat flux to the system ΔQ , while we use the symbol Δ to show a change of the amount of a quantity which is not a function of a state of the system.

- Work of the system via change of the constitutive variables x_1, x_2, \dots, x_n of the system

$$\Delta A = \sum_{i=1}^n X_i \Delta x_i,$$

where $X_i, i = 1, 2, \dots, n$, are thermodynamic forces which depend on the process of transition from one state to another.

- Changes of concentrations of substances in the system bring the change of energy

$$\Delta G = \sum_{j=1}^N \mu_j \Delta c_j,$$

where c_j is the concentration of substance j in the system, μ_j is a change of energy of the considered system due to an addition of unity of the substance labelled j —the quantity called *chemical potential*.

2.2.1. The law of conservation. So, energy in the amount $\Delta Q - \Delta A + \Delta G$ is being received by the system from the environment. Incoming fluxes change the state, while one has to take into account that, during a process of interaction with the environment via work, transfer of heat and/or fluxes of matter, some of the internal variables $\xi_i, i = 1, 2, \dots$, can be agitated in the process, as an extra result of the interaction¹. Incoming energy provides the increase in internal energy ΔE and work done by the system via internal variables

$$\Delta Q - \Delta A + \Delta G = \Delta E + \sum_{i=1}^{\infty} \Xi_i \Delta \xi_i.$$

Using the above definitions, one can write the law of conservation of energy in the form

$$\Delta E = \Delta Q - \sum_{i=1}^n X_i \Delta x_i - \sum_{i=1}^{\infty} \Xi_i \Delta \xi_i + \sum_{j=1}^N \mu_j \Delta c_j. \quad (11)$$

This form of *the first principle of thermodynamics* takes into account the processes of reallocation of energy due to the work of the internal variables. The law of conservation of energy in the form of relation (11) is written for a general case, when there are exchanges of matter and energy in the form of heat between the system and surroundings, that is, for open systems. For a system with constant composition—closed system, when there are neither chemical reactions inside the system, nor fluxes of substances in or out of the system, the last term in (11) disappears. In a case of an isolated system, when there are neither work nor fluxes of heat and substances, internal energy is changing only due to the work of internal variables

$$\Delta E = - \sum_{i=1}^{\infty} \Xi_i \Delta \xi_i. \quad (12)$$

To avoid misunderstanding, note that the total energy of an isolated system, which is the sum of thermodynamic internal energy E and potential energy of agitated internal variables, does not change, of course, in accordance with the law of conservation of energy.

One can note that the internal variables can be agitated by external influences, but the system cannot fulfil any positive work via the internal variables, which means

$$\sum_{i=1}^{\infty} \Xi_i \Delta \xi_i \leq 0. \quad (13)$$

¹ For example, if a system is brought into contact with another system at a different temperature, the temperature gradients emerge in the systems.

Potential energy of agitated internal variables is entirely dissipated inside the system instead of being developed against the exterior. Statement (13) can be considered as a formulation of *the second principle of thermodynamics*, which, as will be shown below, is equivalent to the formulation of the principle in terms of entropy.

2.2.2. The concept of internal energy. One has no other definition of a thermodynamic quantity—internal energy E apart from the balance equation for energy. Clearly, this quantity is the same internal energy considered in equilibrium thermodynamics. However, in the case of irreversible processes, to take explicitly into account the processes of reallocation of energy due to the work of the internal variables, it is convenient to define thermodynamic internal energy in the above way, by equation (11). It leads to a definition of internal energy that is different from the total energy of the system; the latter is usually used as the thermodynamic internal energy of the system in the generalizations of equilibrium thermodynamics. Total energy and internal energy differ by the potential energy of the work of internal variables, which is absent for the reversible processes. If definition (11) is accepted, the change of internal energy of an isolated system, in virtue of equations (12) and (13), due to the internal processes is always non-negative

$$\Delta E \geq 0.$$

This amount of energy is coming into internal energy at relaxation of the agitated internal variables, which are considered as a memory of past exterior influences. The total energy of the isolated system, which is the sum of thermodynamic internal energy and potential energy of agitated internal variables, does not change, of course, in accordance with the law of conservation of energy.

Indeed, generalizations of equilibrium thermodynamics can be different. So as there are no compulsory requirements how to define the concept of internal energy in non-equilibrium thermodynamics, we have to investigate the advantages and disadvantages of different definitions. One of the advantages of definition (11) is the possibility of explicitly including internal processes in the framework of non-equilibrium thermodynamics, thus, incorporating our knowledge about internal processes into a macroscopic framework.

2.3. Thermodynamic characteristic functions

2.3.1. Free energy and internal energy. Balance equation (11) defines a change of internal energy due to external and internal influences, but one has to turn this equation into an expression for the total differential to define internal energy as a function of variables of state. The problem, as is well known, is solved for reversible processes by postulating the existence of such a variable S , called entropy, that the total differential of internal energy can be written as

$$dE = T dS - \sum_{i=1}^n X_i dx_i. \quad (14)$$

In another aspect entropy is a function of temperature and constitutive variables—a function of state. The scheme works well for reversible processes, and we shall show in this section that it also works perfectly well for irreversible processes, if the balance equation includes work of internal variables.

There are different ways of introduction of thermodynamic characteristic functions. It is convenient to start by postulating the existence of one of the characteristic functions, accepting that the temperature T is a parameter (a variable) of state. In accordance with tradition, one

can assume that in line with characteristic quantity—internal energy E , one can introduce another characteristic quantity—a function of temperature and basic variables, so-called *free energy*

$$F = F(T, x_1, x_2, \dots, x_n).$$

The total differential of free energy in a process of changing state can be written as

$$dF = -S dT - \sum_{i=1}^n X_i dx_i. \quad (15)$$

The thermodynamic forces are defined as partial derivatives of the potential function

$$X_i = -\frac{\partial F}{\partial x_i}, \quad \text{at } T = \text{const},$$

and appear to be functions of temperature and constitutive variables.

The well-known thermodynamic quantity—entropy, as a function of temperature and constitutive variables, has emerged here

$$S = -\frac{\partial F}{\partial T}, \quad \text{at } x_1, x_2, \dots, x_n = \text{const}. \quad (16)$$

To define a thermodynamic function of internal energy and clarify the meaning of entropy, one can add zero in the form $T dS - T dS$ to the right-hand side of equations (15) and, by combining the terms, find

$$d(F + TS) = T dS - \sum_{i=1}^n X_i dx_i. \quad (17)$$

One can note that relations (11) and (17) can be identified. So, one has

$$E = F + TS, \quad T dS = \Delta Q - \sum_{i=1}^{\infty} \Xi_i \Delta \xi_i + \sum_{j=1}^N \mu_j \Delta c_j. \quad (18)$$

The last relation determines that entropy of the system, as an independent (in this case) variable, changes when the quantities Q , ξ_i and/or c_j change.

The total differential of thermodynamic internal energy of the system can be written in the form (14), so that we return to the conventional definition of thermodynamic internal energy of the system as a function of entropy S and constitutive variables

$$E = E(S, x_1, x_2, \dots, x_n).$$

The concept of entropy here and in equation (18) is the same as in the conventional theory of irreversible processes, which does not include internal variables in the definition of entropy, and one has to write for irreversible processes, instead of equation (18), the inequality

$$T dS \geq \Delta Q + \sum_{j=1}^N \mu_j \Delta c_j. \quad (19)$$

This equation in couple with equation (14) is the conventional form (see, for example, [1, equation (3.5)]) of the equation for the rate of entropy. The last relation shows that a change of entropy in a real process is more than a change of entropy in a reversible process, and internal production of entropy was invented to compensate the deficiency. Equation (18) introduces an explicit description of internal production of entropy that can be considered as one of the advantages of definition of internal energy by relation (11).

2.3.2. Entropy. A variable—entropy S —is introduced by relation (18), while the presence of internal variables is taken into account. The total change of entropy in the system dS is split into the two components

$$dS = d_e S + d_i S. \quad (20)$$

The external component of the entropy change $d_e S$ is connected with flows of heat and substances through the boundaries of the system

$$d_e S = \frac{1}{T} \left(\Delta Q + \sum_{j=1}^N \mu_j \Delta c_j \right), \quad (21)$$

where c_j is the concentration of the substance j in the system, μ_j is the chemical potential. Entropy S changes if there are fluxes of heat and/or substances in or out of the system. One can consider the fluxes to be fluxes of entropy in or out of the system but, nevertheless, the real flux is a flux of heat or a flux of substance and the real function of state is entropy. One can see that the fluxes of substances are interpreted similar to the heat fluxes. Both the heat and the fluxes of substances bring a positive or negative change of energy into the system. The quantity $d_e S$ can be both positive (the flux of heat and/or substances into the system) and negative (the flux of heat and/or substances out of the system). In an *isolated* system, when there are neither heat fluxes nor matter fluxes between the system and environment, $d_e S = 0$.

Entropy also changes if there are some internal processes. The internal part of entropy production $d_i S$ is connected with some internal processes within the system

$$d_i S = -\frac{1}{T} \sum_{j=1}^{\infty} \Xi_j \Delta \xi_j, \quad d_i S \geq 0. \quad (22)$$

In virtue of equation (13), $d_i S$ can only be positive or zero and this is a conventional expression of the second law of thermodynamics. One can use the dynamic equation (8) or (10) for internal variables to rewrite the expression for production of entropy. For small deviations from equilibrium, one has

$$\frac{d_i S}{dt} = \frac{1}{T} \sum_{k=1}^{\infty} \frac{1}{\tau_k} \Xi_k \xi_k. \quad (23)$$

At reversible processes, when the process is committing in such a slow fashion (characteristic time of the process $t \gg \tau_i$) that all internal variables practically have their equilibrium values, the internal production of entropy is equal to 0, $d_i S = 0$.

3. Complex thermodynamic systems

The functions of free energy and internal energy, discussed in the previous section, are functions of constitutive variables x_1, x_2, \dots, x_n , and do not depend on the internal variables, which have non-specified values in a non-equilibrium state, as is assumed in classical thermodynamics [9]. However, there are situations in which some of the internal variables $\xi_1, \xi_2, \dots, \xi_s$ are noticeable and play a distinctive role in the description of the system [1, 6]. Such variables can be called *complexity variables* and the system is considered complex. One can also say that one deals with a *complex* system. A complex system is a thermodynamic system in a non-equilibrium state, it returns eventually to equilibrium, if external forces supporting the non-equilibrium state have disappeared.

3.1. Characteristic functions

As characteristics of the system, complexity variables can be considered equally with constitutive variables, so that similar to the classical thermodynamic functions (see section 2.3), one can introduce characteristic functions which depend also on the complexity variables—extended characteristic functions: internal energy, free energy and entropy

$$\begin{aligned} E(S, \mathbf{x}, \boldsymbol{\xi}) &= E(S, x_1, x_2, \dots, x_n; \xi_1, \xi_2, \dots, \xi_s), \\ F(T, \mathbf{x}, \boldsymbol{\xi}) &= F(T, x_1, x_2, \dots, x_n; \xi_1, \xi_2, \dots, \xi_s), \\ S(T, \mathbf{x}, \boldsymbol{\xi}) &= S(T, x_1, x_2, \dots, x_n; \xi_1, \xi_2, \dots, \xi_s), \end{aligned} \quad (24)$$

while, in virtue of the way of introduction of the functions,

$$E = F + TS, \quad S = -\frac{\partial F}{\partial T}, \quad T = \frac{\partial E}{\partial S}. \quad (25)$$

Note that, according to the above relations, one can write the total differential of internal energy as

$$dE = T dS - \sum_{i=1}^n X_i dx_i - \sum_{i=1}^s \Xi_i d\xi_i, \quad (26)$$

where the change of entropy, as an independent variable in the above equation, is defined as

$$T dS = \Delta Q - \sum_{i=s+1}^{\infty} \Xi_i \Delta \xi_i + \sum_{j=1}^N \mu_j \Delta c_j. \quad (27)$$

The above equations represent the basic equations of thermodynamics with internal variables [1]. Expression (26) coincides exactly with equation (4.11) from work [1], though the notions of internal energy and entropy for non-equilibrium states in this work and in work [1] are somewhat different. However, equation (26) is an exact equation for any irreversible process, while equation (4.11) in [1] is postulated as an approximate equation for ‘the local accompanying state’. Apparently, there is no need in the axiom of the local accompanying state in this place, if one accepts the first law of thermodynamics in form (11). Equations (24)–(27) have to be completed with dynamic equations for the internal variables $\xi_1, \xi_2, \dots, \xi_s$, for example, in the form

$$\frac{d\xi_i}{dt} = f_i(T, x_1, x_2, \dots, x_n; \xi_1, \xi_2, \dots), \quad i = 1, 2, \dots, s.$$

The right-hand side of these equations depends also on internal variables with the label numbers which are bigger than s , so that the set of equations is not closed and one has to introduce some approximations, which are apparently equivalent to the axiom of the local accompanying state, to solve a problem. The set of internal variables and the choice of approximation are specific for each physical situation. The examples of application of internal-variables thermodynamics for solution of some physical problems are well known [5, 6, 8].

3.2. Entropy

To determine the entropy of a complex system as a function of complexity variables, one can consider a process of relaxation of the system from a non-equilibrium state with the complexity variables $\xi_1, \xi_2, \dots, \xi_s$ to the equilibrium state. If entropy S is considered to be a function of state, the result does not depend on the path of transition. One can assume that there is

neither work of the system, nor external fluxes, so that the change of entropy is connected with changes of internal variables and, according to equations (20)–(22), can be expressed as

$$dS = -\frac{1}{T} \sum_{j=1}^s \Xi_j d\xi_j \geq 0. \quad (28)$$

Now, one can consider a process of transition from a non-equilibrium state with some particular values of the internal variables $\xi_1, \xi_2, \dots, \xi_s$ to an equilibrium one to obtain the difference between values of entropy in equilibrium and non-equilibrium states. The result can be symbolically written as

$$S(T, \mathbf{x}, \boldsymbol{\xi}) - S(T, \mathbf{x}, 0) = -\frac{1}{T} \int_0^{\xi_1, \xi_2, \dots, \xi_s} \sum_{j=1}^s \Xi_j d\xi_j \leq 0. \quad (29)$$

Relation (29) can be considered as a definition of the entropy of a non-equilibrium state of a thermodynamic system. One can assume that the thermodynamic forces $\Xi_1, \Xi_2, \dots, \Xi_s$ are known as functions of the internal variables $\xi_1, \xi_2, \dots, \xi_s$, so that entropy, as a function of internal variables, exists, if a solution of expression (29) exists. One can see from relation (29) that the value of entropy of a complex system (a system in a non-equilibrium state) is less than the value of entropy of the same system in the equilibrium state, assuming that the values of temperature and constitutive variables are the same. Examples of calculation of entropy for some simple complex systems are considered in the next section.

3.3. The simplest complex systems

For illustration, we consider some simple complex systems in situations when there is no work done by the systems. At given constant fluxes of matter and heat, the system can be considered to be in a steady-state situation, that is

$$dE = 0, \quad dS = 0.$$

It means that, in virtue of relations (20), (21) and (23), one has

$$d_i S = -d_e S, \quad \frac{d_i S}{dt} = \frac{1}{T} \sum_{k=1}^s \frac{1}{\tau_k} \Xi_k \xi_k, \quad d_e S = \frac{1}{T} \left(\Delta Q + \sum_{j=1}^N \mu_j \Delta c_j \right), \quad (30)$$

where c_j is the concentration of substance j in the system, μ_j is the chemical potential.

The above formulae allow one to determine thermodynamic forces, if the situation is given and a set of internal variables is set up, and due to relation (29), calculate entropy of the system.

3.3.1. Gradient of temperature. One can consider a portion of matter in a small volume $\Delta x \Delta y \Delta z$ as a thermodynamic system with a flux of heat q along the axis x induced by the temperature gradient $\nabla_x T$

$$q = \frac{1}{\Delta y \Delta z} \frac{\Delta Q}{\Delta t}, \quad \nabla_x T = \frac{\Delta T}{\Delta x}.$$

The flux and gradient are always connected with each other locally at the same point of the system. In the simplest case one has the relation

$$q = -\lambda \nabla_x T. \quad (31)$$

We consider the gradient of temperature $\nabla_x T$ to be an internal complexity variable². In this case, mean velocities of thermal motion of molecules in different layers are different and this can be registered in other ways.

Without external influences, the gradient of temperature always tends to decrease, and the decrease of gradient, if the above equation is valid, is determined by the equation

$$\frac{\partial \nabla T}{\partial t} = \lambda \frac{\partial^2 \nabla T}{\partial x \partial x},$$

which can be rewritten as

$$\frac{d \nabla T(x)}{dt} = -\lambda (\nabla T(x - \Delta x) - 2 \nabla T(x) + \nabla T(x + \Delta x)).$$

It means that relaxation of the temperature gradient at one point is not independent of the relaxation of the temperature gradient at other points of the system. However, normal modes, which relax independently of each other, can be introduced in this case. We simplify the situation and consider a relaxation equation for a gradient of temperature in the form

$$\frac{d \nabla_x T}{dt} = -\frac{1}{\tau} \nabla_x T, \quad (32)$$

where τ is the time of relaxation of the temperature gradient which is considered as an internal complexity variable.

We consider a steady-state situation, when equation (31) is valid and the flux of heat, according to the last equation from (30), determines the flux of entropy

$$\frac{d_e S}{dt} = \frac{1}{\Delta x} \left(\frac{q}{T} - \frac{q}{T + \Delta T} \right) \approx \frac{q}{T^2} \nabla_x T. \quad (33)$$

The thermodynamic state of the volume does not change in a steady-state situation. So according to the first equation from (30), internal production of entropy is

$$\frac{d_i S}{dt} = -\frac{d_e S}{dt} = \frac{\lambda}{T^2} (\nabla_x T)^2. \quad (34)$$

One can see that the gradient of temperature $\nabla_x T$ is an origin of the permanent internal production of entropy which, according to the second equation from (30), can also be presented as

$$\frac{d_i S}{dt} = \frac{1}{T} \frac{1}{\tau} \Xi \xi, \quad \xi = \nabla_x T, \quad (35)$$

where τ is the time of relaxation of the internal variable, that is a temperature gradient in this case. Now we can compare relations (34) and (35) to find the thermodynamic force

$$\Xi = \frac{\lambda \tau}{T} \xi, \quad \xi = \nabla_x T.$$

Eventually, formula (29) brings us the known [5] result—entropy of the system

$$S - S_0 = -\frac{1}{T} \int_0^{\nabla_x T} \Xi d\xi = -\frac{\lambda \tau}{2T^2} (\nabla_x T)^2. \quad (36)$$

² Some scholars [5] prefer to use the fluxes as internal variables, instead of the gradients, which provides formally equivalent results.

3.3.2. Gradient of concentration. Quite similar, one can consider a situation in a small volume $\Delta x \Delta y \Delta z$ with a permanent flux of a substance

$$q = \frac{1}{\Delta y \Delta z} \frac{\Delta m}{\Delta t} = -D \nabla_x c \quad (37)$$

coming through along the axis x due to the concentration gradient

$$\nabla_x c = \frac{\Delta c}{\Delta x}.$$

The system is characterized by a chemical potential, which depends on concentration

$$\mu = \mu(c), \quad \frac{\partial \mu}{\partial c} \geq 0.$$

According to formulae (30), the flux of substance is accompanied by the flux of entropy

$$\frac{d_e S}{dt} = \frac{q}{T} \frac{\mu(c + \Delta c) - \mu(c)}{\Delta x} = \frac{q}{T} \frac{\partial \mu}{\partial c} \nabla_x c = -\frac{1}{\kappa T} (D \nabla_x c)^2, \quad D = \kappa \frac{\partial \mu}{\partial c}, \quad (38)$$

which, in a steady-state situation, is compensated by the internal production of entropy

$$\frac{d_i S}{dt} = -\frac{d_e S}{dt} = \frac{1}{\kappa T} (D \nabla_x c)^2. \quad (39)$$

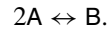
One can see that there is permanent internal production of entropy, which is connected with gradient of concentration $\nabla_x c$. The further speculations are quite similar to those in the previous subsection, so that one can define the thermodynamic force

$$\Xi = \frac{\tau}{\kappa} D^2 \xi, \quad \xi = \nabla_x c,$$

and get the known [5] result—entropy of the system

$$S - S_0 = -\frac{\tau}{2\kappa T} (D \nabla_x c)^2. \quad (40)$$

3.3.3. Chemical transformations. As a simple example, one can consider a reaction of association–dissociation that can be represented by the symbolic equation



It means that two molecules of substance A (mass m each) can unite into one molecule of substance B (mass $2m$), whereas a molecule of substance B can split into two molecules of substance A, so that the changes of concentrations of substances are connected with each other

$$2dN_A = -dN_B, \quad dc_A = -dc_B.$$

Each substance in the system is characterized by chemical potential, so that the condition of equilibrium, due to the above relations, can be written as

$$\mu_A(c_A, c_B) = \mu_B(c_A, c_B).$$

This equation determines the equilibrium concentrations of substances c_A^0 and c_B^0 , if, for example, the total mass of substances is given. To consider approaching the equilibrium state, one has to refer to equations of chemical kinetics. We can imagine that there is a reactor with the incoming flux J of substance A which transforms into substance B in the reaction, while the substance B permanently goes out of the reactor, so that equations for concentrations of substances, due to the rules of chemical kinetics, can be written as

$$\frac{dc_A}{dt} = J - \kappa_{[A \rightarrow B]} c_A^2 + \kappa_{[B \rightarrow A]} c_B, \quad \frac{dc_B}{dt} = \kappa_{[A \rightarrow B]} c_A^2 - \kappa_{[B \rightarrow A]} c_B - J. \quad (41)$$

Under the equilibrium situation ($J = 0$), the time derivatives are equal to zero, and one can find the relation between the kinetic constants $\kappa_{[A \rightarrow B]}$ and $\kappa_{[B \rightarrow A]}$ and the equilibrium concentrations

$$\kappa_{[B \rightarrow A]}c_B^0 = \kappa_{[A \rightarrow B]}(c_A^0)^2.$$

The differences between non-equilibrium and equilibrium concentrations $\Delta c_A = c_A - c_A^0$ and $\Delta c_B = c_B - c_B^0$, while $\Delta c_A = -\Delta c_B$, can be chosen to describe deviation of the state of the system from equilibrium, and equations (41) are followed

$$\frac{dc_A}{dt} = J - \frac{1}{\tau} \Delta c_A, \quad \frac{1}{\tau} = \kappa_{[A \rightarrow B]}c_A^0 \left(2 + \frac{c_A^0}{c_B^0} \right). \quad (42)$$

In a steady-state situation, the left-hand sides of the kinetic equations are equal to zero, so that one can see that the deviation of concentration from equilibrium is determined by the flux of substances through the reactor

$$\Delta c_A = \tau J. \quad (43)$$

In virtue of equation (30), the change of entropy in units of time due to the flux of the substances is determined as

$$\frac{d_e S}{dt} = \frac{1}{T} (\mu_A - \mu_B) J.$$

It is convenient to use an expansion of chemical potentials and write the difference as

$$\mu_A - \mu_B = -B \Delta c_A, \quad B = \left(\frac{\partial \mu_A}{\partial c_A} - \frac{\partial \mu_A}{\partial c_B} - \frac{\partial \mu_B}{\partial c_A} + \frac{\partial \mu_B}{\partial c_B} \right).$$

In the steady-state situation, the external flux of entropy is compensated by the internal production of entropy

$$\frac{d_i S}{dt} = -\frac{d_e S}{dt} = \frac{1}{T} \frac{B}{\tau} (\Delta c_A)^2. \quad (44)$$

One can see that there is a permanent internal production of entropy that is connected with the deviation of concentration from equilibrium Δc_A . The further speculations are quite similar to those in the previous subsections, so that one can define the thermodynamic force

$$\Xi = \frac{1}{T} \frac{B}{\tau} \Delta c_A, \quad \xi = \Delta c_A,$$

and calculate entropy of the system in the non-equilibrium state

$$S - S_0 = -\frac{B}{2\tau T} (\Delta c_A)^2. \quad (45)$$

One can use relation (43) to write result (45) in the form derived by Fort *et al* [10]. Note that some assumptions of their derivation can be avoided, if one uses the proposed formalism.

4. Conclusion

The introduction of internal variables, which characterize deviations of a thermodynamic system from the equilibrium state, into the principles of thermodynamics helps us to overcome the discrepancy in the description of behaviour of non-equilibrium systems and to obtain a consistent formulation of non-equilibrium thermodynamics. To formulate an universal methodology, work of internal variables ought to be considered explicitly, and it was taken into account in balance equation (11)—this is a crucial modification of the form of the first law of thermodynamics. Entropy is defined through internal variables, and the second law

of thermodynamics is formulated as a requirement that a thermodynamic system cannot fulfil any positive work via internal variables. The last sentence is equivalent to the conventional formulation of the second law of thermodynamics through entropy, but deprives the concept of entropy of its mystique flavour. All these statements allow us to define entropy for a non-equilibrium state and to assert that internal energy for both equilibrium and non-equilibrium systems is a function of entropy and constitutive parameters x_i , so that relation (3), in which E is internal energy (not total energy!), is valid for non-complex systems in any case, while the internal energy of a complex system depends additionally on the complexity variables ξ_j . The discussed suggestions do not change the relations of equilibrium thermodynamics at all and do not urge to change the conventional practice of usage of thermodynamics in non-equilibrium situations. The paper can be considered as a sketch of a scheme that might be followed for teaching non-equilibrium thermodynamics to provide a clear and consistent set of definitions of thermodynamic quantities. The discipline ought to be formulated on its own principles independently of microscopic foundations; although microscopic approaches are essential, the state of the art is not completely satisfactory until the corresponding macroscopic thermodynamic theory is consistently formulated.

Acknowledgments

The author is grateful to the anonymous referees of the paper for helpful and constructive comments.

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