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WHAT IS THERMODYNAMICS AND WHAT IS IT FOR?

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ABSTRACT

Thermodynamics – contrary to its name – is not a dynamic theory. However, some relatively new developments, like finite time, endo-reversible or ordinary thermodynamics introduce time into thermostatics. In this framework the Second Law becomes a set of conditions ensuring the asymptotic stability of equilibrium. In this manuscript some examples are shown, how this basic conceptual change can lead to a profound understanding.

KEY WORDS

thermodynamics, thermostatics, time

CLASSIFICATION

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TIME IN THERMODYNAMICS

Equilibrium thermodynamics is sometimes called thermostatics [1,2] eliminating the contradiction in the name: a theory dealing with equilibrium states cannot be a dynamical one. According to the classical approach the basic concepts of equilibrium thermodynamics (entropy, temperature) are introduced and interpreted for equilibrium states only. Therefore dynamical problems in a thermodynamic theory can be treated only in one of the continuum frameworks. There we have well defined dynamical laws: partial differential equations of the different balances together with the corresponding constitutive functions. However, there is no time, there is no equation of motion in thermodynamics of discrete, homogeneous systems, which is therefore also called as equilibrium thermodynamics.

There are several reasons why one cannot simply restrict the continuum descriptions to a homogeneous one and get the analogous theory (e.g. by a spatial homogenization). The most important one is the lack of real processes in equilibrium thermodynamics, and the lack of clear operational distinction between the so called quasistatic and irreversible processes. To keep the universality, the First Law and the Second Law classically refer to starting and final states of thermodynamic systems. However, since only equilibrium is considered meaningful, the theory is a continuous struggle to avoid real dynamics. Our everyday experience shows that the description of the temperature change of a room, the cooling of a cup of coffee etc. do not always require the machinery of partial differential equations of continuum thermodynamics, because the bodies in the processes can be considered as homogeneous. This level of description exists and if necessary is somehow considered (e.g. Newton"s law of cooling). However, without the proper theoretical frame one does not know the conditions of validity, do not understand the role of the most important thermodynamic concepts (how the entropy changes in dry friction?), and most importantly, one cannot develop proper models for complex situations, when e.g. for several interacting thermodynamic bodies.

The birth of “finite time” and “endoreversible” thermodynamics can be connected to the conceptual vacuum created by the above mentioned situation. In the reality we have only finite time to get the work or the power from a machine but some ideal „equilibrium thermodynamic process“ need infinite time. What is the maximal power, that we can get, if we do not have enough time to operate with an „equilibrium machine“ [3,4,5]? This is a question related to the evolution of the system. The situation is similar with the endoreversible hypotheses: a part of the system is considered as an „equilibrium“ one, and the irreversibilities are usually supposed to occur between the „equilibrium part“ and the environment. This is a conceptualization of the meaning of “equilibrium” and “quasistatic” in the more conventional descriptions.

Therefore looking for processes in “finite time” it is worth to reconsider where the infinite times can occur in „equilibrium thermodynamics“. We can find at least three different ways:

- one may suppose that there are no „internal inhomogeneities“ in the body and no additional, „internal variables“ are necessary for the description of processes [6,7]. That is, the thermodynamic body is homogeneous and the equilibrium variables and equilibrium state functions (equations) properly characterize the system. This property is analogous to the hypotheses of „local equilibrium“ in continuum theories. The local equilibrium can be a good approximation, if the inhomogeneities and the internal variables vanish fast, compared to the characteristic times of the „equilibrium processes“.
- if a homogeneous thermodynamic body (without internal variables) is open to a single environment characterized by constant intensive variables, then the state of our body tends to equilibrium and this equilibration process frequently needs infinite time. A typical

example is a body thermally connected to an environment with constant temperature and obeying Newton"s law of cooling.

- infinite times appear also in idealized processes with constant intensive quantities. As an example let us see an isothermal process in our previous system, but now assume that there are more interactions between the body and the environment beyond the thermal one. Performing a little change in the non-thermal intensive parameters we wait for the temperature equilibration. Then step by step the temperature changes, a process is initiated and governed by this kind of „external control". This is the fiction of an "equilibrium" process as considered in some textbooks. Because of the infinitesimal steps one may naively expect that an ideal isothermal process requires infinite time. Is this what we see e.g. in a nuclear power plant? However, the power plants are designed by a theory operating with these concepts…

The first infinity can be excluded by the endoreversible hypothesis (the irreversibilities are at the interactions, they are not inside the body). The second one is not eliminated in this way, but from a practical point of view it is not a problem, but it is crucial for the right interpretation of the Second Law. In the following we will eliminate the third kind of infinity, give a dynamical understanding to the second one and weakening the endoreversible hypothesis we will show an example to deal with some „real" irreversible processes, too.

The concept of an "equilibrium process" – connected to the third type of infinities – deserves a closer look. Let us imagine the same in classical mechanics: a point mass is moving and is in an equilibrium at every instant. If our point mass represents an arrow, then we are at the contradictory concept of the motion of Zeno of Elea, we have formulated the arrow paradox. However, similar conceptual contradictions in mechanics were eliminated long time ago by the introduction of the velocity. Following the mechanical analogy we can easily realize, that an isothermal process between an environment and a homogeneous thermodynamic body requires a fast heat exchange. The faster is the heat exchange compared to the other processes in the system the more isotherm is the process. Anyway, we may recognize that the lacking concept of real dynamics reveals the original paradoxical statements of Zeno about the impossibility of – in our case – thermodynamic processes.

Let us stop her for a minute and look back to the previous sentences. In the previous reasoning several times we were speaking about thermodynamic quantities as time dependent functions. Therefore, we could not avoid to step out of equilibrium.

OPTIMIZATION REQUIRES A DYNAMIC THEORY

According to the endoreversible hypotheses, the thermodynamic quantities are time dependent, but we are in an „equilibrium theory", because only quasistatic processes are admitted, the equilibrium variables and state functions are properly characterize the time development of the system. Let us put aside the usual question about the existence of entropy and temperature. (In continuum theories it is not a problem at all.) Let us focus on a practical optimization question e.g. how could we get e.g. maximum power from a Carnot machine in finite time. What we need is an optimal solution. In their famous paper Curzon and Alhborn [3] (and before that Novikov [4]) suppose that during an isothermal process the temperature of a thermodynamic body is not equal to the temperature of the environment. Their calculation gives the value of that temperature to achieve a maximum power output in a Carnot engine. However, how can we fix a constant temperature for our machine? In an equilibrium process when the temperature of the body and the environment is equal the method is clear (but not very practical): wait for the equilibration. But what should we do in this clearly non-equilibrium situation? How can we accomplish an optimal process? The optimization theory gives clear answers, if and only if we know the dynamics of the system... Therefore with this disguised step time is already introduced in thermostatics. One may think that we are considering cycles only. However, why should we not start in another way, take the next step and try to understand the consequences and conditions of a thermodynamic description without cycles? If we want to optimize we need more, we have to introduce a real dynamics. To make real dynamics, we need a differential equation. If we have a differential equation and processes run according to its solutions, what is the meaning of the Second Law? Only a dynamic theory can provide a solid background for the optimization problem.

ORDINARY THERMODYNAMICS – QUASISTATIC PROCESSES

The theoretical need of a reinterpretation of thermostatics as a part of non-equilibrium thermodynamics is expressed clearly in [8]. The key of the reformulation is the understanding of the role of the Second Law as a stability requirement [9,10] and entropy as a Liapunov function of the equilibrium. Putting everything together one can solve the conceptual difficulties and get a firm mathematical framework [11,12].

The non-equilibrium approach to thermodynamics interprets the usual differentials as time derivatives and distinguishes static constitutive functions - the traditional equations of state, like the equation of state of an ideal gas – from the dynamic constitutive functions characterizing the interaction of a thermodynamic body with the environment – like the Fourier heat exchange law. The two kinds of equation of states are treated in a common framework. For example the First Law of thermodynamics is written as:

$$\frac{\mathrm{d}}{\mathrm{d}t} E = Q - W \,, \tag{1}$$

Here E is the energy of a thermodynamic body, Q is the heat exchange between the body and the environment and W is the mechanical work per unit time. (1) is a differential equation if the dynamic constitutive functions W and Q are given. A possibility is to introduce Newton's cooling law

$$Q = -\alpha(T - T_0), \tag{2}$$

and the classical form of work $W = p\mathrm{d}V/\mathrm{d}t$, where T and p are the pressure and the temperature of a thermodynamic body in an environment characterized by the temperature and pressure T_0 and p_0. V denotes the volume of the body and α is the nonnegative heat exchange coefficient. Then we can get a solvable set of differential equations for the energy and volume changes if we are able to specify a second differential equation for the volume.

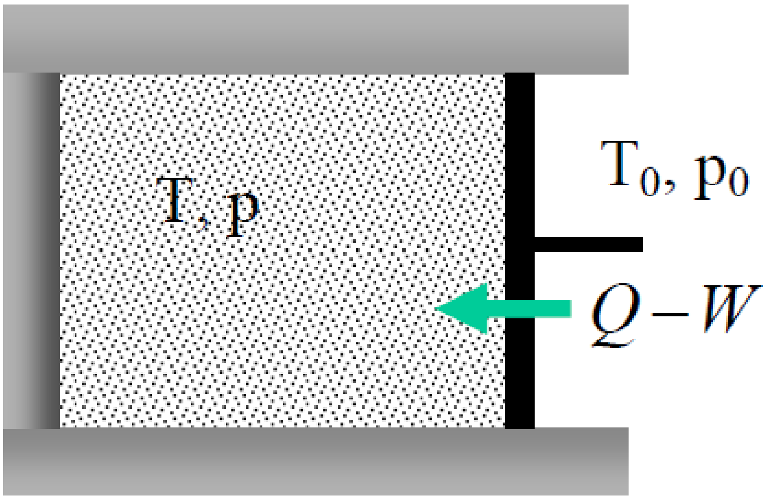

Figure 1. Sketch of relations accompanying expressions (1-3).

One can determine it in different ways, the simplest possibility may be assuming that the volume rate is proportional to the pressure difference with a positive coefficient β.

$$\frac{\mathrm{d}}{\mathrm{d}t}V = \beta(p - p_0). \tag{3}$$

In this way we can connect the mechanical and thermal interactions, and (1) and (3) is a solvable system of differential equations. We show a solution in case of van der Waals gas equation of state, where:

$$T = E + \frac{3}{V}, \; p = \frac{8T}{3V-1} - \frac{3}{V^2}, \tag{4}$$

Here the critical variables are applied, that is the thermodynamic quantities are given in critical point units. The exchange coefficients are α = 1, β = 1, and the environmental temperature and pressure are T_0 = 0,9 and p_0 = 0,5. A solution with different initial conditions is shown on figure 1. We may observe, that the integral curves first start to converge to a definite curve and then toward the equilibrium along that curve, as it is apparent at the right hand side of the figure. This behaviour indicates two different characteristic times of the equilibration. The dynamical law specified by the differential equations (1) and (2) corresponds to quasistatic processes, because if we change the environmental pressure and temperature in a way that corresponds to the actual temperature and pressure of the thermodynamic body, the process stops. This is a precise interpretation of this expected property of classical thermodynamics in our dynamic framework.

ORDINARY THERMODYNAMICS – BEYOND LOCAL EQUILIBRIUM

From a mechanical point of view the behaviour of the previous thermodynamic system seems to be unsatisfactory. In case of adiabatic conditions, when the exchange heat is zero (α = 0 in (2)), the above differential equations never give oscillatory behaviour. Therefore we may introduce a different dynamic law and instead of (3) we may assume, that

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}V = \gamma(p - p_0), \tag{5}$$

Applying the endoreversible hypothesis we can give a simple interpretation to γ. It can be connected to the exchange properties, therefore to the (reciprocal) mass of the cylinder. In more general situations γ can characterise also internal inertial effects.

A consequence of the theoretical assumptions is that now the state space of the thermodynamic body is larger. The time derivative of the volume $U = \dot{V}$ is a variable, in addition to the energy E and volume V. Hence it is possible to introduce damping effects. Therefore we assume, that the equation of state is given in a modified form as

$$T = E + \frac{3}{V}, \; p = \frac{8T}{3V-1} - \frac{3}{V^2} - \kappa U, \tag{6}$$

Here κ is the coefficient of damping that corresponds to the (bulk) viscosity in case of a continuum theory. Assuming the value κ = 100, the solution of (1) and (4) together with the equation of state (5) is shown on fig 2. We assumed that the gas starts form mechanical equilibrium, therefore the additional initial condition is $U(0) = 0$, but the other parameters and initial conditions are the same as they were in the previous calculations. A more detailed introduction of the above system, together with an analysis of the Second Law and stability properties is given elsewhere [12, 13].

CONCLUSIONS

“Finite time“ and “endoreversible thermodynamics“ introduces the time into thermostatics. Some conceptual problems require a differential equation governing the processes and a differential equation requires the reinterpretation of the role of some well known equilibrium concepts and theorems. A dynamic approach to equilibrium thermodynamics opens possibilities in modelling and optimization of processes and devices in engineering. This kind of development has been started already, independently of the above mentioned theoretical investigations [14] and goes far beyond the conventional exergy analyses.

Ordinary thermodynamics – the non-equilibrium interpretation of thermodynamics of discrete systems – gives a clear concept of the Second Law as conditions related to asymptotic stability of equilibrium. This approach gives a conceptual change also in case of continuum systems. The Gibbs-Duhem inequality, the inequality of the entropy production will be a source of constitutive functions, that ensure the tendency to a homogeneous equilibrium state. This attitude can lead to original approaches in some important and less understood continua like the stability properties of the Schrödinger-Langevin equations treated from the point of view of Madelung fluids [15] or a simple resolution to the famous generic instabilities in first order relativistic fluid theories [16].

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ŠTO JE TERMODINAMIKA I ČEMU SLUŽI?

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SAŽETAK

Termodinamika – suprotno svome imenu – nije dinamička teorija. Međutim, neki relativno novi pristupi, poput termodinamike konačnih procesa, endoreverzibilne ili ordinarne termodinamike, uvode vrijeme u termostatiku. U ovom pristupu drugi stavak termodinamike postaje skup uvjeta koji osiguravaju asimptotsku stabilnost ravnoteže. U radu su razmotreni primjeri koji pokazuju kako ova temeljna konceptualna promjena može dovesti do dubljeg razumijevanja.

KLJUČNE RIJEČI

termodinamika, termostatika, vrijeme