

A CONCISE INTRODUCTION OF THE EXTROPY

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SUMMARY

The Clausian introduction of entropy is based on an unnecessary restriction, namely that diminishing circle integral leads to a unique state variable. Eliminating that restriction a family of entropy-like function is introduced. After we have chosen one, called extropy, which has better properties as the well known entropy.

KEY WORDS

thermodynamics, entropy, extropy

CLASSIFICATION

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INTRODUCTION

We used to describe processes with equilibrium states, and we do not ask if we can do it or not because we learned an equilibrium approach to the thermodynamics and we learned that it is the way to the non-equilibrium thermodynamics, too.

The equilibrium approach is a very good and sufficient way of teaching thermodynamics, and to give a simple skill to count with it. But there is a problem, when we want to make calculations for a process, and to describe the real world, we have to use processes in our calculations. Why aren't we able to describe a process with equilibrium states? Because process and equilibrium state are like the array and the point. With points we can only describe a line, without any direction and we can not describe an array.

Clausius did an equilibrium-approach, so he got less possibility as we can get with our non-equilibrium approach. How can we describe the processes without using formulas got from the equilibrium equations? We will show one of these methods.

To reach our goal, we have to introduce another state function, because we took advantage of the equilibrium equations in the introduction of entropy. It will be very similar to the entropy, this new state function, the difference will be, that we won't use any equilibrium equations in its deduction. The extropy was introduced and first used by Martínás et al. [1 – 3].

THERMODYNAMICAL DEDUCTION

We will use some axioms used in the equilibrium-approach of thermodynamics, but we will show, that these are true in non-equilibrium states, too.

The first axiom that we use is the first law of the thermodynamics, that

$$dU = dQ + dW. \quad (1)$$

where U is the internal energy, Q is the heat and W is the work. The energy change is equal to the sum of thermal flow and the work done. This equation is true in non-equilibrium circumstances because its roots are in the conservation of energy.

Our second axiom is that every system is keeping to the equilibrium state, which is the state of the environment (in case of equilibrium environment). This approach to equilibrium happens in a monotonous way, where the environment is large enough to take it as a reservoir.

The problem of thermodynamics that time was articulated by Kelvin in 1852, who wrote [4]:

If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat."

It leads to the Carnot-Kelvin-equation which is the following:

$$\oint dQ \cdot (1 - T_0/T) + dW \geq 0, \quad (2)$$

with dQ the heat transferred to the system at temperature T , and dW is the elementary work done by the system. From the citation follows, that this expression is equality in the reversible case and is an inequality in the irreversible case

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From the Carnot-Kelvin-expression, which is an equation in the reversible case, it follows that $dQ(1 - T_0/T) + dW$ is a state function because its circle integral is equal to zero in

reversible case, in the case when the original state is the same as the new. The definition of a state function is that “its value depends only on the current state of the system and is independent of how that state has been prepared. In other words, it is a function of the properties that determine the current state of the system.” [5].

If we integrate equation (2), we get the following expression:

$$dQ(1 - T_0/T) + dW = dA, \quad (3)$$

where T is the temperature of the environment, which is taken as a reservoir and T_0 is the temperature of the system, A is the *state function*, Q is the heat and the most important, W is the work.

For the definition of the expansion work there are two possibilities: (i) $dW = -pdV$ with meaning that work is done on the system, or (ii) $dW = (p - p_0)dV$ meaning the useful work done by the system, as the $-p_0dV$ part goes to the environment. In case there is only expansion type of work, we can write the following equation, considering dW as the useful work done by the system:

$$dW = -(p - p_0)dV, \quad (4)$$

where p is the pressure and V the volume of the system, while p_0 is the pressure of the reservoir, hence p_0 is a constant.

In addition, with the common transformation of the first law of the thermodynamics we get the following equation:

$$dQ = dU + pdV. \quad (5)$$

If we combine (3 – 5), we get the following:

$$(dU + pdV)(1 - T_0/T) - (p - p_0)dV = dA. \quad (6)$$

Dividing it by T_0 , the temperature of the environment, which is taken as a reservoir, the expression becomes

$$\left(\frac{1}{T_0} - \frac{1}{T}\right)dU + \left(\frac{p_0}{T_0} - \frac{p}{T}\right)dV = \frac{dA}{T_0}, \quad (7)$$

with T_0 a constant temperature of the reservoir. The quantity dA is a state function, as it depends on state variables (U , V , N), and as we know the difference between state variables and state function is that the independent variables are the state variables and the dependent is the state function. So, if a function depends on state variables, it is a state function. From this chain of thoughts comes that if we divide a state function with a constant or a state variable we will get another state function. So dA/T_0 is a state function as well as its integrate form. We will refer to it as the extropy and will denote it using the symbol Π for its integral.

$$d\Pi = \frac{dA}{T_0}, \quad (8)$$

$$\Pi = \frac{A}{T_0}. \quad (9)$$

If we write substitute (8) in (7), after integration we get:

$$\Pi = \left(\frac{1}{T_0} - \frac{1}{T}\right)U + \left(\frac{p_0}{T_0} - \frac{p}{T}\right)V. \quad (10)$$

That expression is valid for the blackbody radiation, as it has only two independent variables. In chemical systems the chemical potential difference also appears and the general form of extropy is

$$\Pi = \left(\frac{1}{T_0} - \frac{1}{T} \right) U - \sum_i \left(\frac{Y_{i,0}}{T_0} - \frac{Y_i}{T} \right) X_i. \quad (11)$$

where Y_i is the i -th intensive variable, and X_i is the i -th extensive one.

THE PROPERTIES OF EXTROPY

Let us show the similarities and differences between the entropy and the extropy. We begin with the similarities.

1. In the equilibrium state the extropy is equal to zero. Conversely, if the extropy is equal to zero then it is the equilibrium state.
2. The extropy of the system is always diminishing if the system is in a reservoir (for example in the environment). The proof is that if there is only a temperature difference, then the heat flows from hot to cold, so

$$\left(\frac{1}{T_0} - \frac{1}{T} \right) dU < 0, \quad (12)$$

while if there is only pressure difference, then

$$\left(\frac{p_0}{T_0} - \frac{p}{T} \right) dV < 0. \quad (13)$$

We can say that these differences are not a far cry, so we can keep the entropy, but the differences are significant in the following two cases.

The first case is that if the system is not in a reservoir then the energy and volume changes can be split into heat from the heat source (with temperature T) dQ^A and the spontaneous heat flow between the system and the environment, dQ^S . Similarly, the volume changes referring to useful work dV^A and to the equilibration process dV^S .

$$T_0 \frac{d\Pi}{dT} = \left(1 - \frac{T_0}{T} \right) dQ^A - dV^A + \left(1 - \frac{T_0}{T} \right) dQ^S + (p - p_0) dV^S. \quad (14)$$

The last two terms in (14) are always negative (see (11, 12)).

So using the extropy we can formulate the meaning of the Carnot-equation in this form: in a real cyclic process one has to compensate the extropy loss. The first two terms must compensate the dissipation.

The extropy is always positive or in equilibrium state equal to zero, so in non-equilibrium state we can write the following inequality,

$$\Pi > 0. \quad (15)$$

If we assemble the meaning of the inequalities we see that we can take the extropy as the distance to the equilibrium state.

The other case, where there is a big difference in the application is the case of the isolated system. In this case we know that the extropy is always diminishing. We can get a more comfortable description when with the choice of $1/T_0 = 0$ and $p_0 = 0$ we use the entropy.

CONCLUSION

For isolated systems entropy is the most appropriate form of the state function describing the irreversibility. For systems interacting with their environment (non-isolated) systems extropy is a more convenient form. So if we want to describe the real world, extropy is a better choice.

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UVOD U EKSTROPIJU

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SAŽETAK

Clausiusovo uvođenje entropije temelji se na nepotrebnim ograničenjima da iščezavajući konturni integral vodi na jedinstvenu varijablu stanja. Uklanjanjem tog ograničenja dolazi se do porodice funkcija sličnih entropiji. Među njima je izdvojena jedna, ekstropija, čija su svojstva u nizu procesa prikladnija od entropije.

KLJUČNE RIJEČI

termodinamika, entropija, ekstropija