THERMODYNAMIC MEASURE FOR NONEQUILIBRIUM PROCESSES

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SUMMARY

One of the most fundamental laws of Nature is formulated by the Second Law of Thermodynamics. At present, in its usual formulation the central concept is entropy characterized in terms of equilibrium state variables. We point out that because thermodynamic changes arise when systems are out of equilibrium and because entropy is not a natural state variable characterizing non-equilibrium states, a new formulation of the Second Law is required. In this paper, we introduce a new, more general, but still entropic measure that is suitable in non-equilibrium conditions as well. This new entropic measure has given a name extropy. The introduction of extropy allows us to formulate the Second Law in a more suitable and precise form, and it resolves some conceptual difficulties related to the interpretation of entropy. We point out that extropy has a fundamental significance in physics, in biology, and in our scientific worldview.

KEY WORDS

entropy, thermodynamics, extropy, irreversibility

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INTRODUCTION

One of the most fundamental laws of nature is Second Law of Thermodynamics. This law tells that changes during any adiabatic transition of any system proceeds toward the equilibrium, and in this process a certain thermodynamic quantity - called entropy - is never less than that of its initial value [1]. The point is that macroscopic changes do not occur without the presence of non-equilibrium and non-equilibrium processes are not necessarily adiabatic. We attempt here to reformulate the second law with the help of a more general thermodynamic state variable measuring the distance from equilibrium. This distance is not symmetric like geometrical distance just because thermodynamic changes have a preferred direction towards the equilibrium. We call this more general thermodynamic state variable measuring the distance form equilibrium as extropy [2 – 5].

Let us mention some of the characteristic problems related to entropy that we are aware of at present. In the highly popular website "The Second Law of Thermodynamics" (http://www.secondlaw.com – #1 in the Google search list of information under the search term "thermodynamics" and also #1 under "second law"; the site won the Internet Guide Award of The Encyclopedia Britannica) Lambert [6] claims that the idea of the Second Law is "the biggest, most powerful, most general idea in all of science". The concept of entropy, together with the concept of energy, is of central importance for science. Unfortunately, there seems to be wide-ranging confusion regarding this fundamental concept. Recently a new impetus is given to clarify the concept of entropy [7 – 12]. It is pointed out that entropy is not a measure of 'disorder' since 'disorder' is a highly qualitative and not precisely defined concept that sometimes contradicts to the characterization offered by an entropic measure. Instead, Leff [7] and Lambert [6] proposed that entropy is a measure of energy dispersion: "Energy spontaneously tends to flow only from being concentrated in one place to becoming diffused or dispersed and spread out". This formulation is a significant improvement in comparison to the older one regarding entropy as a measure of disorder. Moreover, it could be very much helpful also due to its metaphoric power. The physical content is also valid at least in cases when only one gradient is present. We point out that in more general cases this formulation still requires further improvement. For example, friction is a basic thermodynamic process in which kinetic energy is transformed into heat. Now it is an everyday experience to observe that when someone applies the brakes of a car all of a very sudden, the part of the wheel of the car in contact with the road is suddenly heated to large temperatures. The point is that the process of energy transfer from the car's global kinetic energy to a small region of its wheel is not "energy spreading". More generally, the phenomenon of "spontaneous energy focusing" (www.physics.ucla.edu/Sonoluminescence/page2.html) like sonoluminescence, spark generation, turbulence etc. (e.g. [13 – 17]) seems to indicate that either the concept of spontaneity in Lambert's formulation of the Second Law is problematic in some cases or the validity of Lambert's formulation is not universal. In this paper, we will present a more general and more precise formulation of the Second Law.

ENTROPY IN ISOLATED, CLOSED, AND OPEN SYSTEMS

For *isolated* systems, standard entropy is a good measure of the direction of changes relative to thermodynamic equilibrium. The positive sign of entropy change indicates the direction towards equilibrium state having the highest entropy. For *closed* systems - the difference from the isolated ones is that they are able to exchange energy (heat) with their surroundings – entropy is already not always a good measure of the direction of changes. Equilibrating processes (shortly: e-processes) are the ones occurring in a system that interacts only with its equilibrium environment. In contrast, processes in which the system exchanges matter/energy

not only with its environment will be termed as not-necessarily-equilibrating processes or n-processes. For example, the Earth can be regarded as a closed system when we neglect mass transfer with its cosmic environment. The Earth receives a varying amount of solar radiation corresponding to the varying phase of solar activity. Clearly entropy cannot tell the direction of global changes of the Earth in each and every instant.

For *open* systems, i.e. systems that exchange not only energy but matter with their surroundings, entropy is even less good indicator of changes to occur. For example, when we have two systems from the same material, and we know that one having smaller entropy than the other, what do we know about the relation of these systems? One possibility is that the system with smaller entropy is in a larger distance from the thermodynamic equilibrium than the other. Another is that the system with smaller entropy is in the same distance from equilibrium but it has a smaller amount of mass. Entropy in itself does not tell which the case is. The point is that entropy can increase (or decrease) in two types of processes: in e-processes or in n-processes. For example, in the case of biological growth the mass of the given system increases, accompanied by the extensive increase of entropy.

Moreover, not only changes within the system can lead to changes relative to the equilibrium, but also changes in its relations to its environment. Therefore, environmental changes can also induce changes in a system. In order to obtain a general law telling the direction of system's changes, we will need a thermodynamic quantity that is based not only in the thermodynamic parameters of the system, but also on the parameters of its environments. The simplest of all these thermodynamic measures, as we will show here, is the thermodynamic distance from thermodynamic equilibrium as measured in entropic units. Entropic units make it possible that entropy can be a special case of the new, more general thermodynamic variable. How can we obtain such a highly desired variable?

THE INTRODUCTION OF EXTROPY: THE STATE VARIABLE CHARACTERIZING THE ENTROPIC DISTANCE FROM EQUILIBRIUM

We want to characterize the distance of nonequilibrium states from the state of thermodynamic equilibrium (distance from equilibrium, D_e). One immediate idea is to measure the distance of our system from the equilibrium by the temperature difference between it and its environment,

$$D_e = |T - T_0|.$$

This seems to be a good measure in many cases, and, in everyday life, we measure the degree of nonequilibrium with it in many cases well. This subjective guess proposes the measure, which is larger for larger systems, so we need the distance as the extent of non-equilibrium,

$$D_e = U|T - T_0|.$$

Nevertheless, the temperature is not a universal measure, since in many cases the system is not in pressure equilibrium with its environment. For pressure the extent of non-equilibrium is

$$V|p - p_0| = V\Delta p.$$

With the measure $D_e = U|T - T_0|$ we have $U\Delta T$ and $V\Delta p$ in the same units, as it is shown by the First Law of Thermodynamics which states that the work W has the same unit as the internal energy U. It means that if there is a measure for the extent of non-equilibrium, it has the form

$$D_e = K\left[\frac{U}{T}\Delta T + V\Delta p\right],$$

where K is a parameter. This is still not a general measure, since in many cases there is a difference in chemical composition between the system and its environment, and so in the corresponding thermodynamic parameter μ; we have add also $N\Delta\mu$ to D_e. Similarly, in case of electric potential difference can be important; in case of a difference in gravitational potential energy a term $mg\Delta h$ should be added, and so on. In general, the measure of the distance from thermodynamic equilibrium will be

$$D_e = \Delta U + \Delta W + \ldots \ . \tag{1}$$

After a simple transformation of (1), with the choice $K = 1$

$$D_e = U\left|1 - \frac{T_0}{T}\right| + \Delta(Vp) + \Delta(N\mu) + \ldots \ . \tag{2}$$

In this way, we obtain a measure for the distance from thermodynamic equilibrium in energy units. This is a good measure of the distance from thermodynamic equilibrium, if it is

(i) zero in equilibrium,

(ii) positive in nonequilibrium,

(iii) always decreasing in equilibration processes.

We can see that D_e fulfils (i), since in equilibrium $\Delta t = \Delta p = \Delta\mu = \ldots = 0$. In general, it is easy to see that D_e (ii) fulfils, since in nonequilibrium $\Delta t, \Delta p, \Delta\mu \ldots > 0$.

From these two requirements, it arises that $D_e > 0$ in nonequilibrium, D_e decreases to zero as we proceed towards equilibrium. The larger the Δt, Δp, Δm etc., the larger is the distance from equilibrium, and the larger is D_e. Regarding (iii), it is important to note that in thermodynamics it is crucial to consider processes in which the various differences (Δt, Δp, Δm etc.) are transformed into each other. For such processes, our measure D_e sums up the contributions of the various differences to the arising distance from equilibrium. Until now, the concept "equilibration" is not characterized quantitatively. If we characterize equilibration by D_e, we find the D_e is not only a suitable measure of the distance from equilibrium, but it is a quantitative measure of equilibration as well. Unfortunately, the absolute value in the formula of D_e makes it difficult to handle.

Now we will show how to obtain thermodynamics from equations $(1 - 3)$. Equation (1) was written on the basis of intuitive notion of the distance from equilibrium. Let us notice that (1) has a remarkable violation of symmetry. All the terms (except the thermal ones) are written in the form extensive×intensive difference. Volume, mole numbers are extensive variables – proportional to the extension of the system), while pressure and chemical potentials are the intensives (they are the same in equilibrium, and their difference is related to the degree of non-equilibrium). On the other hand in the thermal term, energy is extensive, but $1 - T_0/T$ is not a difference of the intensive parameter, it is only a number, not a physical state variable, as all physical variable has a measuring unit, and it is not only a number.

Formally the problem can be solved in two ways - and they lead to different, but concise thermodynamic measures.

a) Instead of energy, an other physical quantity with the dimension energy/temperature is used. It is the entropy. The point we note is that while energy can be measured and determined, it is overly complicated to obtain the exact value of entropy for real systems. With this selection, the measure of distance from equilibrium will be the quantity known as exergy B.

$$B = S(T - T_0) + \Delta Vp + \Delta N\mu + \ldots \ .$$

b) The other way is the modification of the intensives

$$B = S(T - T_0) + \Delta V p + \Delta N \mu + ... \quad \Pi = U \left| \frac{1}{T_0} - \frac{1}{T} \right| + V \left(\frac{p_0}{T_0} - \frac{p}{T} \right) + N \left(\frac{\mu_0}{T_0} - \frac{\mu}{T} \right) + ...$$

For the first sight it may seem clumsier than necessary. But imagine such a physics where instead of Kelvin scale $T^* = 1/T$ is used. The third law would change to the statement - infinite temperature is the lowest, and one never can reach it. Similarly, if in this physics $p^* = p/T$ is used, then the ideal gas equation would be $p^* = R \, N/V$. It would be simpler, naturally other expressions would be more complicated, but it can be done. In that case

$$\Pi = U(T^* - T_0^*) + V(p^* - p_0^*) + N(\mu^* - \mu_0^*) + ... \; .$$

Formally this relation has the same structure as exergy, but it is an entropic measure. Π is called extropy.

An important remark is that in the formula (2) defining D_e the first term $U|1 - T_0/T|$ is the product of U, the internal energy, and $|1 - T_0/T|$, a term without physical meaning because it is dimensionless. We point out that if we write this term into a form $T_0 * U |1/T_0 - 1/T|$, the last factor $|1/T_0 - 1/T|$ has a physical meaning measuring the distance from equilibrium in terms of $\Delta(1/T)$. If we transform all the other terms correspondingly, this transformation yields an entropic measure, and it has the advantage that entropy does not appear.

$$\Pi = U \left(\frac{1}{T_0} - \frac{1}{T} \right) + V \left(\frac{p_0}{T_0} - \frac{p}{T} \right) + N \left(\frac{\mu_0}{T_0} - \frac{\mu}{T} \right) + ... \; . \tag{3}$$

In the present paper we derive an entropic-like measure for the extent of non-equilibrium. Now we return to Carnot principle, and we show that Clausius made some (allowed) but not needed simplification, that is why he introduced entropy as the only measure for non-equilibrium.

EXTROPY AS A MEASURE OF THE DISTANCE FROM EQUILIBRIUM

We want to consider whether extropy is a monotonous decreasing function of time for equilibration processes. We already had shown that extropy can be written as

$$\Pi = \sum_i Y_i X_i \; .$$

where X_i is for the extensive, $X_1 = U$, $X_2 = N$, …… $X_n = V$, and Y_i for the related intensive $Y_1 = 1/T_0 - 1/T$, …, $Y_n = p_0/T_0 - p/T$, variables. Now we show that the properties of extropy flows from the zeroth and the first law.

The Zeroth Law constraint tells that Π is a homogeneous linear function of U, V, and N. Doubling the system leads to double its extropy.

Proof: Let us make the following transformation: $U \rightarrow kU$, $V \rightarrow kV$, $N \rightarrow kN$, where $k > 0$.

Variables T, p, and μ do not depend on the size of the system,

$$T(U,V,N) = T(kU,kV,kN),$$
$$p(U,V,N) = p(kU,kV,kN),$$
$$\mu(U,V,N) = \mu(kU,kV,kN).$$

That is,

$$Y(kU,kV,kN) = Y(U,V,N),$$

telling that they are homogeneous zeroth order function of U, V, N, in agreement with the Zeroth law of thermodynamics.

The effect of transformation k for Π is

$$\Pi(k) = \sum_i Y_i(k) X_i(k) = \sum_i Y_i X_i(k) = k \sum_i Y_i X_i = k\Pi \; . \tag{4}$$

Now, differentiating both sides by k,

$$\frac{\mathrm{d}\Pi}{\mathrm{d}k} = \sum_{ij} Y_i X_i \ . \tag{5}$$

But considering Π as the function of k, then

$$\frac{\mathrm{d}\Pi}{\mathrm{d}k} = \sum \frac{\partial \Pi}{\partial(kX_i)} \mathrm{d}(kX_i)\mathrm{d}k = \sum \frac{\partial \Pi}{\partial(kX_i)} X_i \ . \tag{6}$$

Comparing (5) and (6) for $k = 1$, we get

$$\frac{\partial \Pi}{\partial X_i} = Y_i \ ,$$

so

$$\mathrm{d}\Pi = \sum_i Y_i \mathrm{d}X_i \ . \tag{7}$$

The extropy change of the system is, from eq. (7),

$$\mathrm{d}\Pi = \left(\frac{1}{T_0} - \frac{1}{T}\right)\mathrm{d}U + \ldots$$

Extropy is additive function, so in case of non-equilibrium systems, when the intensives can depend on the spatial coordinates r, then extropy is the sum of the local extropies defined as densities that can vary in space, and so we can work with extropy as a variable depending on variables r, $Y = Y(r)$ and $\rho_i(r) = X_i/V$. With this notation,

$$\Pi = \int \sum_i Y_i \rho_i \mathrm{d}V \ ,$$

and from eq. (7)

$$\mathrm{d}\Pi = \int \sum_i Y_i \mathrm{d}\rho_i \mathrm{d}V \ , \tag{8}$$

now we have a balance equation for the densities and so we can determine the time dependence of extropy.

TIME DEPENDENCE OF EXTROPY

The time derivative is (it follows from eq. 8)

$$\frac{\mathrm{d}\Pi}{\mathrm{d}t} = \int \sum_i Y_i \frac{\mathrm{d}\rho_i}{\mathrm{d}t} \mathrm{d}V \ . \tag{9}$$

The first law of thermodynamics expresses the conservation of energy. Now the continuity equation for the energy density ρ_1 tells that

$$\frac{\partial \rho_i}{\partial t} + \mathrm{div}j_i = 0 \ ,$$

and for the mole numbers ρ_j if there is no chemical reaction, in case of chemical reactions

$$\frac{\partial \rho_j}{\partial t} + \mathrm{div}j_j = s_j \ ,$$

where s_j is the source/sink of the mole numbers. Inserting these continuity equations into eq. (9), after straightforward manipulations (see Appendix) we obtain for the change of extropy the relation

$$\frac{\mathrm{d}\Pi}{\mathrm{d}t} = \int \sum_i Y_i J_i \mathrm{d}f + \int \sum_i \mathrm{grad}(Y_i)J_i \mathrm{d}V \ ,$$

where the first integral is for the surface of the system. We split the flows into to parts: flows to the environment, these are always equilibrating flows, J_{i0}, and J_{ie} flows going to/or coming from other systems being in the environment. We obtain

$$\frac{\mathrm{d}\Pi}{\mathrm{d}t} = \int \sum_i Y_i J_{ie} \mathrm{d}f + \int \sum_i Y_i J_{io} \mathrm{d}f + \int \sum_i \mathrm{grad}(Y_i) J_i \mathrm{d}V$$

Formally,

$$\frac{\mathrm{d}\Pi}{\mathrm{d}t} = J_\Pi - \Sigma,$$

where

$$J_\Pi = \int \sum_i Y_i J_{ie} \mathrm{d}f.$$

Now

$$\Sigma = -\left(\int \sum_i Y_i J_{io} \mathrm{d}f + \int \sum_i \mathrm{grad}(Y_i) J_i \mathrm{d}V \right),$$

where J_Π is the extropy carried to the system, and Σ contains the effect all the other processes. It contains the effect of processes within the system and processes between the system and its reservoir.

We will prove the following Thesis: The Carnot –Principle ensures that in real processes Σ is always positive. In a complete cycle the extropy does not change, so

$$\int \frac{\mathrm{d}\Pi}{\mathrm{d}t} \mathrm{d}t = \int J_{ie} \mathrm{d}t - \Sigma(t) \mathrm{d}t = 0.$$

This equation tells that for a complete cycle

$$\int \Sigma(t) \mathrm{d}t = \int J_{ie} \mathrm{d}t = I_e. \tag{10}$$

Lemma : In a real cycle, the following requirement will be always fulfilled:

$$I_e \geq 0. \tag{11}$$

Actually, for any part of the cycle, the relevant part of I_e can be negative for a certain period. The point is that, for the complete cycle, I_e in (11) is always positive. It can be zero for the imaginary reversible process, and never can be negative in a complete cycle.

Now we will show the proof of the above formulated Thesis. Classical thermodynamics was built from Carnot on the concept of cycle. First, let us calculate the extropy flow in a cyclic process to the system. Now our system is a heat engine that runs cyclically. It makes contact successively with n reservoirs at temperatures T_i, exchanging from them $\mathrm{d}U_i$ energies, and it has contact with pressure reservoirs with pi pressures, and the relevant volume changes are $\mathrm{d}V_i$.

Then

$$J_{ie} = \sum_{cycl} \mathrm{d}U_i \left(\frac{1}{T_0} - \frac{1}{T_i} \right) + \mathrm{d}V_i \left(\frac{p_0}{T_0} - \frac{p_i}{T_i} \right). \tag{12}$$

The Second Law states (see the Appendix) that $Q(1 - T_2/T_1) - W \geq 0$. Now we show that $Q(1 - T_2/T_1) - W$ is just the extropy flow. Then utilising again the First Law, $\mathrm{d}Q = \mathrm{d}U + p\mathrm{d}V$, and the relation telling that the useful work is

$$W = (p_2 - p_1)\mathrm{d}V, \tag{13}$$

where p_2 is the pressure of the environment, we obtain

$$U\left(\frac{1}{T_2} - \frac{1}{T_1} \right) + \mathrm{d}V\left(\frac{p_2}{T_2} - \frac{p_1}{T_1} \right) \geq 0. \tag{14}$$

A simple generalization is then obvious; we may consider a more complicated heat engine that runs cyclically, making contact successively with n reservoirs at temperatures T_i. Then the first law is $W = \Sigma_i W_i$, and Carnot's principle becomes

$$\Sigma_{cycl}\left[dQ_i\left(1 - \frac{T_0}{T_i}\right) - dW_i \right] \geq 0, \tag{15}$$

Utilizing the First Law and substituting (13) into (15), it yields

$$\Sigma_{cycl}\left[dQ_i\left(1 - \frac{T_0}{T_1}\right) - dW_i \right] = \Sigma_{cycl}\, dU_i\left(\frac{1}{T_0} - \frac{1}{T_i}\right) + dV_i\left(\frac{p_0}{T_0} - \frac{p_i}{T_i}\right) \geq 0 \tag{16}$$

It is easy to see that

$$\Sigma_{cycl}\, dU_i\left(\frac{1}{T_0} - \frac{1}{T_i}\right) + dV_i\left(\frac{p_0}{T_0} - \frac{p_i}{T_i}\right) = \int J_{ie}\, dt = I_e,$$

is the total extropy flow to the system during the cycle that must be positive for every cyclic process, and so we proved our Lemma telling that $I_e > 0$ is always valid for real processes.

Our Lemma implies that in real circumstances a process is always present which consumes the extropy. As it is valid for any type (imaginary or real) cycle, it implies that

$$\Sigma(t) \geq 0. \tag{16}$$

The result we obtained tells that in any real cycle extropy Π is consumed.

We utilized the Carnot principle for showing that Π has a special property: in real processes it is always decreasing. Therefore we proved that extropy fulfils our requirement (iii). Only extropy inflow can increase the amount of extropy and to realize a complete cycle in which every state variable regains its original value. The production of extropy from nothing is not allowed.

Simple manipulations yield, that

$$\Pi = \sum_i \int_{Y_i}^{Y_{io}} (Y_{io} - Y_i)\, dX_i$$

or introducing the entropy matrix:

$$g_{ik} = -\frac{\partial^2 S}{\partial X_i \partial X_k}$$

and $s_{ik} = g_{ik}^{-1}$, we can write $dX_i = -s_{ik} dY_k$, so

$$\Pi = \sum_i \int_{Y_i}^{Y_{io}} (Y_{io} - Y_i) s_{ik}\, dY_k$$

Extropy is zero in the equilibrium state with the environment. Expression $\Pi = 0$ means that the system is not distinguishable from its environment. There is no way to get energy from it. There is no order.

Extropy is a function of the parameters of the reservoir, and the parameters of the system being this reservoir.

We note that Π is a non-equilibrium potential function measuring the thermodynamic distance from thermodynamic equilibrium in entropic units. It is a thermodynamic distance, and it is not symmetric, at variance with geometric distance.

The geometric distance d between two point A and B $d(A,B)$ has the properties:
1. $d(A, B) \geq 0$
2. $d(A, A) = 0$
3. symmetry: $d(A, B) = d(B, A)$
4. triangle inequality $d(A, B) + d(A, C) \leq d(A, C)$

In contrast, extropy as a thermodynamic distance is asymmetric, since it is measured from the equilibrium state E to the actual state A or B. Its properties are
$$d(E, A) \geq 0,$$
$$d(E, E) = 0.$$
Instead of the triangle inequality it is subadditive
$$d(E, A) + d(E, B) \leq d(E, A + B)$$
where A + B is the symbol of the unified A and B systems. Subadditivity follows from the superaddivity of entropy.

Now let us estimate the thermodynamic distance Π from the equilibrium state in the case of the human body. In a simplest approach, we can keep the dominant term in eq. (16), and so we can approximate the value of extropy of the human body as

$$\Pi \approx dN\left(\frac{\mu}{T} - \frac{\mu_0}{T_0}\right). \tag{25}$$

Equation (25) is similar to the Gibbs potential $G = \mu N$. In chemistry, the chemical potential is not calculated relatively to the environment of the system. Nevertheless, if someone regards G as measured relative to the environment (e.g. [18]), and redefine the chemical potential in a way that $\mu_0 = 0$, than a simple relation will be found between the Gibbs potential and the extropy:

$$\Pi \approx \frac{G}{T}. \tag{26}$$

Now a simple method to determine the value of extropy is available through estimating G. To determine the Gibbs free energy, we can use the formula $G = H - TS$. In human organisms, the processes are isothermal at $T \sim 310$ K. The fuel content of a 70 kg person is given as triacylgcerols (fat), 15,6 kg; proteins, 9,5.kg; carbohydrates, 0,5 kg. The combustion heat of fat is 38,9 kJ/g, therefore the chemical entropy of fat of the human body is 606,8 MJ. The combustion heat of protein and carbohydrate is 17,2 kJ/g, all together 172 MJ. The enthalpy present in the chemical bonds of the 70 kg human body H = 778,8 MJ. The entropy of glucose is 212,13 $J \cdot K^{-1} \cdot mol^{-1}$ = 1,18 $J \cdot K^{-1} \cdot g^{-1}$ and that of liquid water 69,94 $J \cdot K^{-1} \cdot mol^{-1}$ = 3,88 $J \cdot K^{-1} \cdot g^{-1}$. Approximating the entropy content of living matter with that of glucose, the 9,5 kg protein will give 11,21 $kJ \cdot K^{-1}$, the 15,6 kg fat 18,4 $kJ \cdot K^{-1}$, and the 0,5 kg carbohydrates 0,59 $kJ \cdot K^{-1}$, all together 30,20 $kJ \cdot K^{-1}$. The 44,4 kg water has an entropy of 172,25 $kJ \cdot K^{-1}$. In this way, the estimated entropy of the material of the 70 kg human body is found to be $S_h \approx 202,4$ $kJ \cdot K^{-1}$. With $T \approx 310$ K, $T_S \approx 62,6$ MJ, and so $G \approx 716,2$ MJ. Therefore extropy, or thermodynamic distance from equilibrium, will be $\Pi \approx G/T \approx 2,31$ $MJ \cdot K^{-1}$, an order of magnitude higher than entropy, $S_h \approx 0,20$ $MJ \cdot K^{-1}$. In this way, we obtained that

$$\Pi(\text{human organism}) \approx 2,31 \text{ MJ} \cdot K^{-1} >> S(\text{human organism}) \approx 0,20 \text{ MJ} \cdot K^{-1} \tag{27}$$

The fact that the extropy of the human organism is much larger than its entropy corresponds to the general experience of the ultimate easy to move our fingers, hands or foots.

FORMULATION OF THE SECOND LAW WITH THE HELP OF EXTROPY

The second law of thermodynamics, in a concise form, states that any thermodynamically *isolated* system tends to equilibrate with its environment:

<div align="center">"Isolated systems seek the dead level" (I)</div>

But this formulation seems to be clearly restricted. Attempting to obtain a formulation of the Second Law as a general law of Nature, it is highly desirable to expand its range of application. Now it is easy to expand the range of this law to more general type of systems by regarding the system plus its equilibrium environment *together* as representing an isolated system.

The Second Law of Thermodynamics can be formulated in a precise form telling:

"In cases when the considered material system A is governed by its equilibrating interactions with its equilibrium environment B, α_i, the thermodynamic parameters of A, will tend toward β_i, the thermodynamic parameters of its environment B." (II)

We can observe that (II) does not apply in cases when friction, sparkling or other spontaneous energy focusing processes are present. For example, in the case of a braking car the temperature of the car can increase, heat goes from a colder to a hotter place, and so the thermodynamic parameter of the system T_A does not tend toward the temperature of the environment T_B during the process of braking. At the same time, we may observe that the kinetic energy decreases drastically in the process of braking; therefore, if a thermodynamic parameter could be construed that involves somehow the sum of thermal, kinetic, chemical, electric etc. processes, in a way that this new thermodynamic parameter measures the distance from the equilibrium, this new parameter could work well characterizing the direction of changes.

A simple formulation of the Second Law is available formulated with extropy:

In cases when the considered material system A is governed by its equilibrating interactions with its equilibrium environment B, the decrease of extropy of the system $\Pi_A \leq 0$ determines the direction of changes relative to thermodynamic equilibrium. (III)

Certainly, our formulation (III) surpasses previous formulations of the Second Law like (I) and (II) in the sense that it can be applied to a wider set of phenomena, and so it may be regarded as a better and as a more general formulation of the Second Law.

The biosphere – or the biological organisms are embedded in the environment, but they interact with each other (and with the Sun). In the present (extropic approach) first we characterize the systems with the extropy – that is they are in the equilibrium environment, and after we describe their interaction. As in the interactions material and energy may go from one system to the other, extropy flow also appears.

Living system can maintain themselves, because they acquire extropy from their environment.

THE DIFFERENCES AND SIMILARITIES OF EXTROPY WITH ITS PREDECESSORS: ENTROPY, GIBBS FREE ENERGY, NEGENTROPY AND EXERGY

Entropy is measured from zero degree (0 K) instead from the equilibrium with the actual environment, and this circumstance leads to hardly tractable complications. One point is that entropy in general cannot be simply calculated, since heat capacity variations with temperature influences its value when obtaining by extrapolations from zero degree, and variations of heat capacities around zero degree involve complicated quantum processes.

Therefore, in general, it is simply not possible to determine the exact value of entropy theoretically. Moreover, it is not easy to obtain empirical determination of such complex materials that exist in our environment and in biological organisms. Another point is that entropy does not have any convenient interpretation.

Unfortunately, there are many problems with the interpretation of entropy, and therefore it is not always easy to obtain quantitative insights on the relation of these two quantities of overall importance.

Let us take two examples. We have two piles of apples, and you have to tell which pile you prefer: the pile with higher or lower entropy. If you select the pile with lower entropy, in the hope that the apples of this pile will be not rotten, and this is why their entropy is lower, you can receive less number of apples, but they can be all rotten. Now if you select the pile of higher entropy, it can contain more apples; but you cannot know in advance if they are rotten or not. Therefore, entropy is not a good measure in itself for a selection of apples if you are hungry. The situation became confused because the apples can change their entropy content, depending on their state. We can assume that a fresh apple has smaller entropy than the old one. On the other hand two apples have twice as much entropy as one apple has.

Another quantity closely related to extropy is the Gibbs free energy. Haynie [18: pp.85-86] defines the free energy through the change of the chemical potential $\mu_A - \mu_A^0$ relative to the standard state corresponding to $T = 298,16$ K and $p = 1$ bar. At the same time, Haynie claims [18: p.74] that the Gibbs free energy measures the maximum amount of work that can be done by a process going from a non-equilibrium state to an equilibrium state (at constant temperature and pressure). We point out that there is a hidden awkwardness or ambiguity in the different uses of the term Gibbs energy. The introduction of the concept of extropy sheds light to this awkwardness and, at the same time, it resolves the problem lying in the background. Work can be made only relatively to the environment. The same compressed gas can make different amount of work in different environment. Therefore, if one wants to interpret G as the maximum amount of work that can be done by a process going from a non-equilibrium state to an equilibrium state (at constant temperature and pressure), one has to define the zero point of chemical potential to the environment. Extropy is a concept that rules out such awkwardness, it is a precise and exact thermodynamic state potential, and it can be applied generally.

Another closely related concept to the concept of extropy is Brillouin's negentropy $N = S_0 - S$, where S_0 is the entropy of the system in the corresponding equilibrium and S is its entropy content in its actual state. In many cases, the concept of negentropy is very useful in describing and understanding nonequilibrium system's behaviour. But from a thermodynamic viewpoint negentropy does not have the property frequently attributed to it, namely, measuring the distance from the equilibrium, since equilibrium is always referring to the actual environment, and mass and energy exchange with this environment always introduces conditions not taken into account by the system's parameters only. For example, the Brillouin negentropy N does not change when the same system is in different environment, like room once in a summertime, once in a wintertime environment; N(wintertime) = N(summertime). Certainly, the same room with the same degree of temperature 20 C is farther from thermodynamic equilibrium in winter ($T = 0$ ^{o}C) than in summer ($T = 15$ ^{o}C). Extropy performs better in this respect, too, since it is equivalent with

$$\Pi \approx \left(S_{syst} + S_{env}\right)_0 - \left(S_{syst} + S_{env}\right). \tag{28}$$

This equations shows that for an isolated system extropy is equal with Brillouin's negentropy, but in the case of closed and open systems the two entropic measure is different; Brillouin's negentropy does not measure the distance from equilibrium while extropy does.

SUMMARY AND CONCLUSIONS

We found that extropy as an indicator of direction of changes performs better, since it is simpler, more general and elegant than entropy. Simplicity and universality are one of the most fundamental aspects of scientific theories. The Second Law of thermodynamics is one of the most fundamental laws of Nature. Therefore, extropy has an even more fundamental role in physics than entropy.

The fact that extropy as a driver of processes is based on differences presents an unexpected and fundamental challenge for us physicists accustomed to the preconceptions based on Newtonian physics. In modern physics, it is generally regarded that the basic drivers of physical processes are forces. The four fundamental forces of physics, gravitation and electromagnetism, weak and strong nuclear forces are forces corresponding to the properties of the objects themselves. In contrast, our finding is that the basic driver of thermodynamic processes is not a physical factor corresponding to the properties of the objects themselves, but to the relation between the objects and their environments. Modern physics regards as Aristotelian the view that the factor driving natural processes depends on the relation between the objects and their environments. The force beyond thermodynamic changes is not of a Newtonian type, because it is based on differences and not the material properties of the objects themselves. We learned that this thermodynamic force is originated from the fact that the system is not in thermodynamic equilibrium. This thermodynamic force is not symmetric, not fulfilling Newton's third law. It seems that we have to change our basic preconceptions regarding the nature of physical world and learn to be accustomed to a new worldview based on the extropic aspects of thermodynamic.

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TERMODINAMIČKA MJERA ZA NERAVNOTEŽNE PROCESE

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SAŽETAK

Jedan od temeljnih zakona prirode iskazan je kao drugi zakon termodinamike. U današnje vrijeme, u njegovom uobičajenom iskazu središnji pojam je entropija određena putem varijabli ravnotežnog stanja. Ističemo da je, zbog toga što termodinamičke promjene nastupaju kad je sustav van ravnoteže i zbog toga što entropija nije prirodna varijabla za opis neravnotežnih stanja, potreban novi iskaz drugog zakona termodinamike. U ovom radu uvodimo novu, općenitiju mjeru, i dalje entropijsku, prikladnu za neravnotežen uvjete – ekstropiju. Uvođenje ekstropije omogućava nam iskzivanje drugog zakona termodinamike u prikladnijem i preciznijem obliku te razrješava neke konceptualne nejasnoće povezane s interpretacijom entropije. Ističemo fundamentalno značenje ekstropije u fizici, biologiji i znanstvenom pogledu na svijet.

KLJUČNE RIJEČI

entropija, termodinamika, ekstropija, ireverzibilnost