

RESEARCH IN ENTROPY WONTERLAND: A REVIEW OF THE ENTROPY CONCEPT

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The entropy concept was introduced in the mid-nineteenth century by Clausius and has been continually enriched, developed and interpreted by researchers in many scientific disciplines. The use of entropy in a wide range of fields has led to inconsistencies in its application and interpretation, as summarized by von Neuman “No one knows what entropy really is.” To resolve this problem, thermodynamics and other scientific disciplines face several crucial questions concerning the entropy concept: (1) What is the physical meaning of entropy? (2) Is entropy a subjective or an objective property? (3) How to apply entropy to living organisms? To answer these questions, this paper describes the roots, the conceptual history of this important concept, as well as the path of development and application in various scientific disciplines, including classical thermodynamics, nonequilibrium thermodynamics, statistical mechanics and life sciences.

Keywords: Thermal entropy; Residual entropy; Shannon entropy; Total entropy; Negentropy; Equilibrium thermodynamics; Nonequilibrium thermodynamics; Statistical mechanics; Life sciences.

“I intentionally chose the word Entropy as similar as possible to the word Energy.”

Rudolf Clausius [1]

“The law that entropy always increases holds, I think, the supreme position among the laws of nature...”

Sir Arthur Eddington [2]

“Classical thermodynamics is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts” Albert Einstein [3]

1. Introduction

The entropy concept is frequently used in many scientific disciplines, including equilibrium and non-equilibrium thermodynamics [4, 5], statistical mechanics [6-9], cosmology [10], life sciences [11-15], chemistry and biochemistry [4, 16], geosciences [17], linguistics [18], social sciences [19, 20] and

information theory [21]. The use of entropy in a diverse range of disciplines has led to inconsistent application and interpretation of entropy [22-25], summarized in von Neumann's words: "*Whoever uses the term 'entropy' in a discussion always wins since no one knows what entropy really is, so in a debate one always has the advantage*" [24]. The situation has even been described as "*unbelievable confusion*" [22]. The problem stems from a lack of consensus in the scientific community on key aspects of entropy, including its physical meaning, philosophical nature and application to living organisms.

(1) *What is the physical meaning of entropy?* The physical meaning of entropy has been interpreted in various ways. Entropy has been related to information: "*The mathematical definition of Shannon entropy has the same form as entropy used in thermodynamics, and they share the same conceptual root in the sense that both measure the amount of randomness*" [26]. Another definition is the chemical thermodynamic definition: "*Qualitatively, entropy is simply a measure of how much the energy of atoms and molecules becomes more spread out in a process*" [27]. This definition is in line with Clausius' original intention to relate *Entropy* and *Energy*.

(2) *Is entropy a subjective or an objective property?* The philosophical nature of entropy is an open question, the problem being a lack of consensus whether entropy is a subjective or an objective property. A significant part of the scientific community considers entropy as a subjective property [23, 28-30]. Others insist that entropy is an objective property [31-34]. So, von Neumann was right – no one knows what entropy really is (subjective or objective, energy or something else, arrangement of particles or realization of microstates, negentropy, many kinds of entropy...). The following von Neumann-Shannon anecdote expresses the frustration over two different quantities being given the same name. Shannon and his wife had a new baby. Von Neumann suggested they name their son after the son of Clausius "entropy". Shannon decides to do so, to find out, in the years to follow, that people continually confuse his son with Clausius' son and also misuse and abuse the name [23].

(3) *How to apply entropy to living organisms?* There is disagreement on how entropy should be applied to living organisms. Schrödinger introduced "negentropy" as entropy taken with a negative sign [35], a concept still in use today [36-39]. However, negentropy has been criticized recently [15, 40-42].

2. Roots and Genesis of the Entropy Concept

This section reviews entropy as used in classical and nonequilibrium thermodynamics, in statistical mechanics, and in life sciences.

2.1. Entropy in Classical Thermodynamics

A thermodynamic system is the material content of a macroscopic volume in space (the rest of the Universe being its surroundings) and is categorized as an isolated (constant mass, constant energy), closed (constant mass, exchanges energy with the surroundings) or open system (exchanges both mass and energy

with the surroundings) [4]. A thermodynamic system is in a state defined by state variables, such as the amount of matter, volume, temperature, entropy, enthalpy, energy and pressure. Of particular importance to thermodynamics is the state of thermodynamic equilibrium, a state where there is no macroscopic flow of energy or matter between systems or between parts of a single system. All three kinds of thermodynamic systems can be in or out of a state of thermodynamic equilibrium [43]. Thermodynamic states define thermodynamic processes: any change of state of a thermodynamic system represents a thermodynamic process [4]. Thermodynamic processes are categorized based on whether the system is in or out of equilibrium during the process, resulting in two categories: reversible and irreversible processes. In a reversible process, the system is infinitesimally out of equilibrium during the entire process [4]. The infinitesimal driving force enables the process to be reversed by an infinitesimal change in some property of the system or the surroundings. [4, 44]. Because true equilibrium is a limiting state that takes an infinite amount of time to form, there are no truly reversible processes in nature [8, 45]. The second class are the irreversible processes, processes during which the system is out of equilibrium.

Entropy was discovered in the 19th century in an attempt to improve the efficiency of heat engines. In 1803, Lazarus Carnot wrote that any natural process has an inherent tendency to dissipate energy in unproductive ways [46]. In 1824, His son, Sadi Carnot, introduced the concept of heat-engines, producing work from heat flow, with a limiting maximum efficiency [47]. Clausius [1, 48, 49] realized that the Carnots had found an early statement of the Second Law of Thermodynamics, also known as the entropy law [20], and was the first to explicitly state the basic idea of entropy and the second law of thermodynamics [1]. Entropy was introduced with the following summary statements of the first and second laws of thermodynamics “*The energy of the universe is constant; the entropy of the universe tends to a maximum.*” [1].

The modern concept of thermodynamic entropy as a property of a material is related to the heat capacity of the material at constant pressure. Thermodynamic entropy S at a temperature τ is calculated from the equation

$$S = S_0 + \int_{T=0}^{\tau} \frac{C_p}{T} dT \quad (1)$$

C_p is heat capacity at constant pressure, T is temperature as an integrating variable, τ is temperature at which the entropy S is determined and S_0 is the zero-point or residual entropy of the material at absolute zero. Note that the thermodynamic entropy equation contains two conceptually different types of entropy:

- a) *Thermal entropy*, $S_{Therm} = \int (C_p / T) dT$, due to thermally induced motion of particles.
- b) *Residual entropy*, S_0 due to the arrangement of particles in a crystal lattice (section 2.4).

The *Third Law of Thermodynamics* defines a reference state for entropy as a perfect crystal at zero Kelvins with $S_0(\text{perfect crystal}) = 0$, which allows determination of absolute values of entropy. Thermal entropy S_{Therm} and residual entropy S_0 are thus defined as non-negative properties ($S_{Therm} \geq 0$; $S_0 \geq 0$), since entropy S is defined to be zero for an ideal crystal at absolute zero.

Thermodynamic entropy is a conserved property in a reversible process [4, 5, 50], however, thermodynamic entropy is not conserved in an irreversible process [4, 5, 50]. Entropy for the first time gave a quantitative difference between reversible and irreversible processes. A reversible process generates no entropy [4, 5, 50]. Since all natural processes are irreversible, the entropy of the universe always increases (section 2.2.) [8, 45].

Thermal entropy is caused by thermal motion of particles and is quantified by temperature. Thus, differentiating equation (1) with respect to temperature and substituting $dQ_{rev} = C_p dT$, where dQ_{rev} is heat exchanged in a reversible process, gives thermal entropy, S_{Therm} , which is defined in classical thermodynamics as a state function,

$$dS_{Therm} = \frac{dQ_{rev}}{T} \quad (2)$$

Thus, more thermal energy at a given temperature implies greater entropy, and $T dS_{Therm}$ is a measure of thermal energy at a given temperature. In any process where the system gives up energy ΔU , and its entropy falls by ΔS_{Therm} , a quantity of heat at least $Q = T \Delta S_{Therm}$ must be given up to the system's surroundings. From a macroscopic perspective, i.e. in classical thermodynamics, entropy is interpreted as a state function, that is, a property depending only on the current state of the system. According to Clausius [1, 48, 49], thermal entropy is a part of the total energy content and represents a fraction of energy that cannot be converted into the mechanical work.

Entropy can be determined directly by low temperature calorimetry [4], using equation (1). Alternatively, entropy changes can be measured indirectly from measured Gibbs energy changes, ΔG , and enthalpy changes, ΔH , using the Gibbs equation:

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

Gibbs energy is a thermodynamic property that measures the maximum amount of non-expansion or non-mechanical work that may be performed by a thermodynamic system at a constant temperature and pressure (e.g. electrical work) [4]. Gibbs [51] and Helmholtz [52] assumed two types of energy: available energy ΔG that can be converted into work at constant pressure, and unavailable energy that cannot be converted into work, $T\Delta S$. An analogous quantity to Gibbs energy is the Helmholtz energy, A , defined as the maximum expansion or mechanical work that a system can perform

$$\Delta A = \Delta U - T\Delta S \quad (4)$$

U is internal energy [4]. Again, entropy is a measure of the fraction of internal energy that cannot be converted into useful expansion work.

2.2. Entropy in nonequilibrium thermodynamics

The entropy equations discussed above hold for closed and isolated thermodynamic systems. Prigogine extended the use of entropy to open thermodynamic systems. Prigogine's equation for total entropy change of an open system is

$$dS = d_e S - d_i S \quad (5)$$

$d_e S$ denoting entropy exchange with the surroundings, $d_i S$ the production of entropy due to irreversible processes in a system, e.g. chemical reactions, diffusion, and heat transport. The term $d_i S$ is always positive, according to the second law; $d_e S$, however, may be negative as well as positive [5, 50, 53]. To determine the value of $d_i S$, one needs to consider the ways in which an open system can exchange energy with its surroundings: work, heat flow and mass transfer. Exchange of energy as work does not lead to entropy exchange [50]. Heat flow does lead to entropy exchange, the relationship being

$$d_e S_Q = \int_{\Sigma} \frac{\dot{q}}{T_b} dB dt \quad (6)$$

$d_e S_Q$ is entropy exchange due to heat transfer, $\dot{q} = d^2 Q / dB dt$ is the heat exchange rate per unit surface area, B is the surface area of the system, T_b is the temperature at the boundary between a system and its surroundings and the integral is over the boundary surface area Σ [50]. If \dot{q} and T_b are constant during the process over the entire surface area, the equation simplifies to: $d_e S_Q = (\dot{Q}/T_b) dt$, where \dot{Q} is heat exchange rate. Mass transfer leads to entropy exchange, because entropy is a fundamental property of all substances, and substances that enter the system bring their entropy in, while those exiting take their entropy out of the system

$$d_e S_m = \sum_{in} s \dot{m} dt - \sum_{out} s \dot{m} dt \quad (7)$$

$d_e S_m$ is entropy exchange due to mass transfer, \dot{m} is the mass flow rate and s is specific entropy (entropy per unit mass) [50]. The first summation is over all matter entering the system, while the second summation is over all matter exiting the system. The entropy exchange with the surroundings is the sum of the heat and mass flow contributions: $d_i S = d_i S_Q + d_i S_m$ [50]. Notice the way entropy exchange is estimated: through the processes that transfer matter and energy. However, not all forms of energy transfer can lead to entropy exchange. Entropy can be exchanged by heat transfer but not by doing work.

Entropy production of a thermodynamic system $d_i S$ can be estimated through the equation

$$d_i S = \int_V \sigma \, dV dt \quad (8)$$

The integral is over the volume of the system. The parameter σ is the entropy production rate density, also known as the entropy source strength [5, 50]. Entropy production rate density σ is defined as a product of conjugate thermodynamic flows J and forces X :

$$\sigma = \sum_i J_i X_i \quad (9)$$

The summation is over all flows and forces acting on the system [5]. Each thermodynamic force X_i acting on a system has its conjugate flow J_i . For example, temperature gradient is a thermodynamic force and its conjugate flow is heat transfer. Processes that lead to entropy production are irreversible heat transfer, mass transfer, viscous dissipation and chemical reactions [5]. Whenever possible it is convenient to express flows as functions of forces, using phenomenological equations of the form:

$$J_i = \sum_j L_{ij} X_j \quad (10)$$

where the summation is over all forces, and L_{ij} 's are constants known as phenomenological coefficients. Notice that a flow can be influenced by forces other than its conjugate force. For example, a chemical reaction can cause mass diffusion across biological membranes, catalyzed by K-Na-ATPase [5].

Nonequilibrium thermodynamics is of particular importance in life sciences [54, 55]. Living organisms are open systems out of equilibrium [54-56] and, thus, analyzing biological processes requires nonequilibrium thermodynamics [54, 55]. Balmer's *Modern engineering thermodynamics* [50] gives a good introduction into nonequilibrium thermodynamics, along with its applications. For a detailed description of nonequilibrium thermodynamics, see Demirel's *Nonequilibrium thermodynamics* [5].

2.3. Entropy in Statistical Mechanics

Statistical mechanics describes the behavior of thermodynamic systems starting from the behavior of their constituent particles. To describe the motion of a particle, it is necessary to know six parameters – the position and velocity components along the x, y and z axes. The number of independent parameters needed to completely describe a physical system is the *number of degrees of freedom* of that system. Thus, the number of degrees of freedom of a particle is 6. Since $6 \cdot 10^{23}$ particles make one mole of a monoatomic ideal gas, the number of degrees of freedom is $36 \cdot 10^{23}$. Obviously, dealing with each particle individually is impossible in practice and statistics is used to simplify the problem through the concepts of microstates and their probabilities. Imagine a system made of an ideal gas at equilibrium with its many atoms moving randomly. Now take a snapshot of that system in a single instant, remembering the position and velocity of each particle. You just determined the system's microstate at that point in time. Since the particles move

and collide, a snapshot of the gas made at some other moment will differ. The microstates change in time, even though the gas is at macroscopic equilibrium. So, many microstates constitute one macrostate, the state which can be described through a small number of thermodynamic parameters, like temperature and pressure. While only two parameters are required to describe a macrostate, describing a microstate requires knowing each degree of freedom, typically of the order of 10^{23} . A way out is offered by the ergodic theorem, which says that the macroscopic properties of a system can be found as the probability weighed average of the values for microstates [6, 7]. This rule is also known as the Gibbs postulate [7] or second postulate of statistical thermodynamics [6]. For example, internal energy is

$$U = \sum_i p_i \varepsilon_i \quad (11)$$

p_i is the probability of microstate i and ε_i is its energy [6-8]. Therefore, it is not necessary to evaluate all 10^{23} particle positions and velocities for the microstates to find the internal energy of the system. All that is needed is their probabilities and energies. The probability of a microstate as a function of its energy is given by the Boltzmann distribution

$$p_i = \frac{e^{-\varepsilon_i/k_B T}}{\sum_i e^{-\varepsilon_i/k_B T}} \quad (12)$$

T is temperature and k_B is the Boltzmann constant. The Gibbs entropy equation relates the entropy of a system to the probability distribution of the microstates [6, 8]

$$S = -k_B \sum_i p_i \ln p_i \quad (13)$$

Consider a system in a macrostate which corresponds to a set of microstates of equal energy, volume and number of particles. Since there is nothing that would make any single microstate more probable than the others, each microstate is equally probable [6, 7, 29, 57]. This is known as the Laplace principle [29, 57], principle of equal *a priori* probabilities [7] or the first postulate of statistical thermodynamics [6]. Because of this and the fact that probabilities of all states add up to 1, for all states, $p_i = 1/\Omega$, where Ω is the total number of microstates [6, 57]. When this is substituted into the Gibbs entropy equation and summed over all Ω possible states [6, 57], it leads to

$$S = -k_B \sum_{i=1}^{\Omega} p_i \ln p_i = -k_B \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k_B \cdot \Omega \cdot \left(\frac{1}{\Omega} \ln \frac{1}{\Omega} \right) = k_B \ln \Omega \quad (14)$$

which is the Boltzmann equation. The Boltzmann equation, also known as the Boltzmann-Planck equation, in its more well-known form is

$$S = k_B \ln W \quad (15)$$

W is the number of accessible microstates in a system [4, 8]. The Boltzmann equation is still applicable if more than one macrostate is available to a system. The entropy of a macrostate j , S_j , is

$$S_j = k_B \ln W_j \quad (16)$$

W_j is the number of microstates corresponding to that macrostate [9]. The total number of microstates available to the system W is equal to the sum of W_j 's for all the macrostates. However, the number of microstates corresponding to the equilibrium macrostate W_{eq} is much larger than that of all other macrostates, so its logarithm is approximately equal to that of the total number of microstates W [8, 9]

$$S_{eq} = k_B \ln W_{eq} \approx k_B \ln W \quad (17)$$

Note that it is the logarithms of W and W_{eq} that are approximately the same, while their values may differ greatly [8, 9]. This equation enabled Boltzmann to define entropy for both equilibrium and nonequilibrium systems [9]. Alternative ways to derive the Boltzmann equation are given in [4, 6, 7].

The Gibbs (13) and Boltzmann entropy (15) equations define entropy of a system based on two parameters: probabilities and number of accessible microstates, respectively. Both equations are applicable to any problem in statistical mechanics. However, since their approaches differ, one will usually be easier to manipulate mathematically than the other. So the approach that gives the simplest analysis is usually chosen. For example, the Gibbs equation is used to determine thermal entropy of an ideal gas, while the Boltzmann equation is used to determine residual entropy or entropy of mixing.

The Gibbs and Boltzmann entropy equations give an understanding of entropy at the level of particles. The Boltzmann equation shows that entropy is proportional to the number of microstates available to a system. Boltzmann viewed entropy as a measure of disorder. In particular, it was his attempt to reduce the second law to a stochastic collision function, or a law of probability following from the random mechanical collisions of particles. Particles, for Boltzmann, were gas molecules colliding like billiard balls in a box. Each collision brings more disorder to the nonequilibrium velocity distributions, leading to a final state of macroscopic uniformity and maximum microscopic disorder - the state of maximum entropy. Maximum entropy and the second law, he argued, are simply the result of the fact that in a world of mechanically colliding particles disordered states are the most probable [58]. Because there are so many more possible disordered states than ordered ones, a system will almost always be found either moving towards or being in the state of maximum disorder – the macrostate with the greatest number of accessible microstates, such as a gas in a box at equilibrium. On the other hand, a dynamically ordered state, one with molecules moving "*at the same speed and in the same direction*", Boltzmann concluded, is thus "*the most improbable case*"

conceivable...an infinitely improbable configuration of energy" [58]. Thus, Boltzmann interpreted entropy as disorder in a thermodynamic system.

Except as disorder, entropy has also been interpreted as information missing to completely specify the microstates of a system, based on information theory [23, 29, 30]. In 1948, Shannon [21] discovered a quantitative measure of information in a message, called Shannon entropy \check{S}

$$\check{S} = -K \sum_k p_k \ln p_k \quad (18)$$

K is a constant and p_k is probability of symbol k occurring in a message. The similarity of equations (13) and (18) has been a basis for a new interpretation of entropy: entropy is information missing to completely specify the microstate of a system [23, 29, 30]. In the beginning of this section, it was noted that statistics has been used to decrease the number of variables that describe a system from the order of 10^{23} to a few key thermodynamic parameters, such as U and S . Entropy has been interpreted as information lost in this process.

An excellent and intuitive explanation of entropy from the viewpoint of statistical mechanics is offered by Dugdale's *Entropy and its Physical Meaning* [8]. McQuarrie's *Statistical Mechanics* [7] is a good and comprehensive text on theory of statistical mechanics in general. An account of statistical mechanics, with a particular focus on its applications is given in Sandler's *An Introduction Applied to Statistical Thermodynamics* [6].

2.4. Negentropy and Living Organisms

Based on Boltzmann's reasoning that entropy is a measure of disorder, Schrödinger introduced a quantitative measure of order: negentropy. Negentropy was proposed as entropy taken with a negative sign: $-S$ ($S < 0$). Disorder D and order O in living organisms were considered by Schrödinger [35] to be reciprocals $D = 1/O$. Setting D equal to W , Schrödinger rearranged the Boltzmann equation into

$$-S = k_B \ln(1/D) \quad (19)$$

Schrödinger argued that, since $O=1/D$, negentropy $-S$ is a measure of order. Thus, Schrödinger [35] postulated a local decrease of entropy in living organisms, quantified with negentropy and explained through order of biological structures. Negentropy is often used in biothermodynamics - thermodynamics of living organisms, describing their orderliness and explaining the general patterns of metabolism.

What exactly is negentropy? Boltzmann predicted that organisms decrease their entropy during life: "The general struggle for existence of animate beings is not a struggle for raw materials, but a struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth" [58]. Schrödinger followed his lead: "(An organism) feeds upon negative entropy, attracting, as it were, a stream

of negative entropy upon itself, to compensate the entropy increase it produces by living and thus to maintain itself on a stationary and fairly low entropy level” [35]. Thus, thermodynamic entropy of a cell or an organism is predicted to decrease during its life span, paralleled by an accumulation of information [50]. Balmer argued in 2006 that: “one characteristic that seems to make a living system unique is its peculiar affinity for self-organization” [50]. As the system lives, it grows and ages and generally becomes more complex. So, “living systems are uniquely characterized by decreasing their entropy over their life spans” [50]. However, Schrödinger pointed out a potential conflict between the second law and life processes, because the direction of change in entropy tends to its maximum, and the direction of change in life process seemed to be toward greater order, decreasing thermodynamic entropy and accumulating information [35]. Schrödinger explained this “apparent” contradiction by suggesting that the very existence of living systems depends on increasing the entropy of their surroundings [35]. The second law is not violated but only locally circumvented at the expense of global increase in thermodynamic entropy, concluded Morowitz [59]. It seems obvious that there is at least an apparent contradiction between the second law and life processes. The decrease of thermodynamic entropy of living systems during their life spans was predicted by Boltzmann and Schrödinger and is represented by the following equation of entropy rate balance of a living system, derived by combining equations (5), (6) and (7) and assuming constant heat exchange rate \dot{q} and temperature T_b over entire surface area of the organism [50]

$$\frac{dS}{dt} = \frac{\dot{Q}}{T_b} + \sum_{in} \dot{m}s - \sum_{out} \dot{m}s + \frac{d_i S}{dt} \quad (20)$$

$\dot{Q} = dQ / dt$ is metabolic heat transfer rate, \dot{m} is the mass flow rate, $d_i S$ is the organisms’ internal entropy production, S is the total entropy of the organism and t is time. The term $d_i S / dt$ must always be positive, according to the second law [50]. In order for the organism to maintain itself at a high level of order, it is necessary that $dS/dT \leq 0$ [50], which together with equation (20) implies

$$\left| \frac{\dot{Q}}{T_b} + \sum_{in} \dot{m}s - \sum_{out} \dot{m}s \right| \geq \frac{d_i S}{dt} \quad (21)$$

Living organisms release metabolic heat into their surroundings $\dot{Q} < 0$ and the entropy of incoming food is lower than the entropy of outgoing wastes: $\sum_{in} \dot{m}s - \sum_{out} \dot{m}s < 0$ [50]. Since the left-hand side of equation (21) represents entropy exchange with the surroundings, this view implies that an organism imports negentropy from its environment. The negentropy concept has been supported by Mahulikar and Herwig [36], Davis and Rieper [37], Ho [38, 39] and others [60-63]. However, recent studies [15, 40-42] have been casting doubt on validity of negentropy (section 3). Negentropy has been found in many cases to be misleading.

Negentropy in the discussion above was interpreted using nonequilibrium thermodynamics [53]. Nonequilibrium thermodynamics was applied to living organisms by Garbi and Larsen [64], yielding a detailed analysis of metabolic processes. On the other hand, Gladyshev [65] proposes an alternative method of analysis of living organisms.

2.5. Residual Entropy

Residual entropy (S_0) was introduced in the first half of 20th century and is a property of a thermodynamic system near absolute zero, appearing as a consequence of random arrangement of asymmetric atoms or molecules in a crystal lattice [27, 66-70]. Molecules can be symmetric (Figure 1a) or asymmetric (Figure 1b). They can be unaligned, as in gasses, or aligned in arrays in crystals. Arrays of aligned molecules can be monotonic or nonmonotonic. In a monotonic array all molecules are aligned in the same way (Figure 1d). A nonmonotonic array is made of molecules that are not aligned in the same way (Figure 1c). Asymmetrical molecules can align nonmonotonically to form an imperfect crystal resulting in residual entropy. Residual entropy represents a difference in entropy between an imperfect crystal and an equilibrium state at zero Kelvins - a perfect crystal. Thus, the total entropy of an imperfect crystal at absolute zero is equal to its residual entropy. Residual entropy is a consequence of molecular arrangement in a crystal lattice and does not result from any form of molecular motion, including the “zero-point energy” of vibration or rotation [8]. The “zero-point energy state” is the same for both perfect and imperfect crystals [8]. Residual entropy ($3\text{--}12 \text{ J mol}^{-1} \text{ K}^{-1}$) is present near absolute zero in some crystals composed of asymmetric atoms and molecules, for example, H, CO, N_2O , FCIO_3 , and H_2O . [66]. Water ice is one of the first discovered examples of residual entropy, first pointed out by Pauling [71].

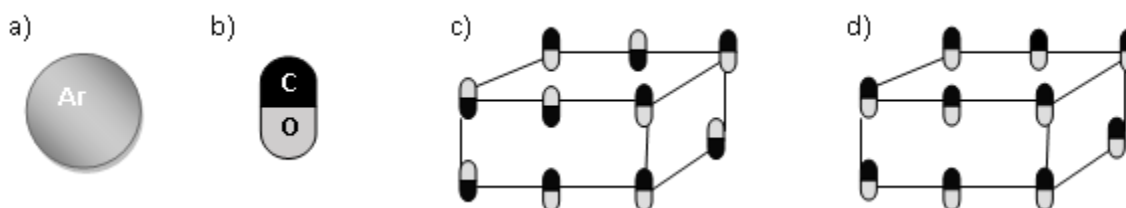


Figure 1: (a) A symmetric particle: in this case an argon atom, which can have only one orientation in a crystal lattice. (b) An asymmetric particle: in this case CO, which can have two orientations in a crystal lattice: either C or O can point upwards. (c) An imperfect crystal of CO: each CO molecule in the crystal lattice can point either up or down. Therefore, there is randomness and thus uncertainty in molecular orientation, leading to residual entropy. (d) A perfect crystal of CO: all molecules in the lattice are oriented in the same direction. There is no randomness nor uncertainty and, thus, residual entropy is zero.

Residual entropy is experimentally determined using calorimetry to measure the difference in heat capacity between an imperfect and a perfect crystal. However, calorimetry can measure only the change in

entropy by adding known amounts of heat. The situation is similar to a problem where one has two vessels, the first is empty and the second is partly filled with water. The task is to determine how much water is in the second vessel only by adding known amounts water. The solution is to fill both vessels completely and subtract the amounts of water added to them. Similarly, one adds known amounts of heat until both the perfect and the imperfect crystals melt. Since in the liquid there is no residual entropy [69, 72, 73], the entropies of both samples are equal. However, since the entropies of the starting crystals were not equal, the heat added was not equal. The difference in heat needed to reach the liquid state is then converted into the difference in entropy, i.e. the residual entropy. An example of such a measurement is the determination of residual entropy of glycerol by Gibson and Giauque [72], who measured the heat capacity difference between a perfect and an imperfect crystal of glycerol. In the case of glycerol [72] there were both a perfect and an imperfect crystal available, so the residual entropy was found directly as the difference in their experimental entropies. On the other hand, in the case of CO only an imperfect crystal was available [68]. In order to circumvent this problem, the entropy measurement for the hypothetical perfect crystal of CO was replaced by a statistical mechanical calculation based on spectroscopic measurements [68]. The calculation yielded the entropy change from a perfect crystal of CO at absolute zero to gaseous CO. The entropy change from the available imperfect crystal was determined by calorimetric measurements of heat capacity and enthalpies of phase changes from 0 K to the temperature of the gas [68]. The difference between the measured heat capacity of the imperfect crystal and the calculated perfect crystal value gave the residual entropy as $4.602 \text{ J mol}^{-1} \text{ K}^{-1}$ [68].

Residual entropy can also be calculated from theory, without any experiments. Kozliak [66] described four ways to calculate residual entropy. The informational or “*combinatoric method*”, derived using the “*coin tossing model*”, is traditionally used in textbooks to illustrate residual entropy [66]. Residual entropy is the difference in entropy between a non-equilibrium imperfect crystal state and the equilibrium perfect crystal state of a substance. The entropy difference between the two states can be found by applying the Boltzmann–Planck equation:

$$S_0 = k_B \ln \left[\frac{W_{2,random}}{W_{1,perfect}} \right] \quad (22)$$

W_2 and W_1 are the numbers of microstates of the imperfect and perfect crystal state, respectively [66]. The perfect crystal state has only one microstate– all molecules are aligned monotonically in the same way, so $W_1 = 1$. The quantity W_2 is related to the number of distinct orientations a molecule can have in an imperfect crystal, m , and the number of molecules that form the crystal, N , by the relation $W_2 = m^N$. This way to find W_2 is equivalent to tossing a coin or an m -sided die N times, thus the name “*coin tossing model*.” The residual entropy of imperfect crystalline CO calculated using equation (22) is $5.76 \text{ J mol}^{-1} \text{ K}^{-1}$, slightly higher than the experimentally determined $4.602 \text{ J mol}^{-1} \text{ K}^{-1}$ [68].

3. Theoretical Analysis

The entropy concept has a 150-year long history. Entropy represents a very abstract concept both scientifically and philosophically, and the use of entropy in diverse scientific disciplines has led to inconsistencies in its application and interpretation. [22-25]. To resolve this problem, this section answers the three questions in the abstract.

What is the physical meaning of entropy? From the work of Clausius (section 2.1.) entropy is a measure of energy in a system that cannot be converted into work. Thermodynamic entropy is a part of the total energy content, in the form of chaotic motion (translation, rotation, vibration...) of the particles in a system. The physical meaning of thermodynamic entropy can be seen from the Helmholtz energy equation

$$A = U - TS \quad (23)$$

A is Helmholtz energy, U is internal energy, T is temperature and S is thermodynamic entropy [4]. Thus

$$1 = \frac{A}{U} + \frac{TS}{U} \quad (24)$$

Helmholtz energy is equal to the maximum amount of expansion work that can be extracted from a system w_{max} [4]. Thus equation (24) can be rewritten as

$$1 = \frac{w_{max}}{U} + \frac{TS}{U} \quad (25)$$

The first term w_{max}/U (or A/U) represents the maximum fraction of the internal energy of a system that can be extracted as work. The second term TS/U represents the fraction of the internal energy of a system that is “trapped” as thermal energy and cannot be extracted as work. So, equation (25) becomes

$$x_w + x_Q = 100\% \quad (26)$$

where $x_w = w_{max} / U$ and $x_Q = TS / U$, and S is in that case

$$S = \frac{U}{T} x_Q \quad (27)$$

Therefore, the term TS/U represents the minimum fraction of internal energy that is trapped as heat and cannot be converted into work. In that sense, entropy is a measure of the part of internal energy that cannot be converted into work, or in practical terms is useless energy.

Is entropy from the philosophical perspective a subjective or an objective property? Denbigh [28] stated: “*there remains at the present time a strongly entrenched view to the effect that entropy is a **subjective** concept precisely because it is taken as a measure of missing information*”. Jaynes’ insight also suggests

that entropy is subjective [29]. However, Singh and Fiorentino [31] introduced four interpretations of the entropy concept. First, “*entropy as a measure of system property assumed to be an **objective** parameter*” [31]. Second, “*entropy assumed as a probability for measure of information probability*” [31]. Third, “*entropy assumed as a statistic of a probability distribution for measure of information or uncertainty*” [31]. Fourth, “*entropy as a Bayesian log-likelihood functions for measure of information*” [31]. The second, third and fourth are assumed to be **subjective** parameters [31]. However, Clausius [1], and after him Boltzmann [74] and Gibbs [75], clearly stated: “*the entropy of the universe tends to a maximum*” [1]. Heat represents energy and is thus an objective parameter, and temperature represents a measure of molecular chaotic motion and thus is also an objective parameter. Energy is an objective property. Because these quantities define thermodynamic entropy, it is also an objective property. Stars would explode in supernovae (and increase the entropy of the universe) independently of our ability to measure the phenomenon. Entropy change in chemical reactions occurs with or without observers. Bunge was explicit: “*Thermodynamic probabilities are objective property... used to calculate another system property namely its entropy*” [33]. Hintikka wrote: “*Boltzmann and Gibbs were somewhat closer to the objective end of the spectrum of entropy as a physical objective to entropy as nonphysical property*” [34]. Further, Carnap wrote: “*Entropy in thermodynamics is asserted to have the same general character as temperature and heat all of which serve for quantitative characterization of some objective property of a state of a physical system*” [34]. Indeed, the thermodynamic entropy of the universe tends to a maximum independently of human knowledge or even existence. To claim that thermodynamic entropy is subjective is anthropocentric. Bohm and Peat wrote “*Entropy now has a clear meaning that is independent of subjective knowledge or judgement about details of the fluctuation*” [32], and explicitly “*entropy is an objective property*” [32]. Thus, the thermal entropy should be considered as an objective parameter. At absolute zero asymmetrical molecules of CO, H₂O or H atoms would align in a crystal lattice spontaneously by a physical process, creating an imperfect crystal containing some residual entropy without an observer. Thus, the residual entropy should also be considered as an objective parameter. The experimental determination of glycerol entropy shows that residual entropy (S_0) is an objective parameter, since two crystals take different amounts of heat for an equal change in their temperatures [72].

How to apply entropy to living organisms? The root of the negentropy concept is the assumption that living organisms continuously decrease their entropy during their lifespans: $(dS/dt)_{Organism} < 0$ (section 2.4.). Notice that $(dS/dt)_{Organism} < 0$ does not imply a negative absolute value of entropy (-S). However, several recent studies are revealing an increase in entropy during life processes, thus questioning the negentropy concept. Hayflick [12-14] reported a change in entropy during the aging process. Silva [15] found an increase in entropy during the lifespan of an average human individual to be 11.4 kJ/K per kg of body mass. Gems and Doonan [11] reported that the entropy of the *C. elegans* pharynx tissues increases as the animal ages. Cells and organisms grow as a consequence of internal accumulation of matter, a process shown to increase their entropy [42, 54]. Thermodynamic entropy increases proportionally to mass of an organism

during growth [54]. Hansen concluded that entropy of an organism “*doesn’t have to decrease*” when biological molecules are synthesized from non-live matter [40, 41]. In section 2.4. possible contradictions involving the negentropy concept were mentioned. Instead of negative entropy change ($\Delta S < 0$) Schrödinger introduced entropy taken with a negative sign ($S < 0$) [35]. However, entropy itself cannot have a negative sign according to the third law of thermodynamics [4, 8]. The equation for negentropy results from a mathematically correct manipulation of the Boltzmann equation [76]. However, it has no physical sense, since entropy (just as energy) cannot have a negative value [76]. Entropy is a thermodynamic property, resulting from motion of particles in a system. Motion of particles cannot be negative. Therefore, thermodynamic entropy represents a non-negative property. However, entropy change (ΔS) can be negative.

Finally, is life really associated with a *continuous* decrease of entropy? Both unicellular and multicellular organisms are open thermodynamic systems according to von Bertalanffy [56]. A living organism is an open thermodynamic system because it exchanges both energy and matter with its surroundings. It grows from the single cell - zygote to an adult organism and increases its mass. Thus, it accumulates matter. Mass is related to entropy by the equation

$$\Delta S = s\Delta m \quad (28)$$

m is mass. Since an organism grows, its mass increases or $\Delta m > 0$. According to the third law of thermodynamics $s > 0$ for all matter. Therefore, for a growing organism, ΔS is positive. The accumulation of matter and increase in mass cause an increase in internal energy U and thermal entropy S_{Therm} . Moreover, cell division and nucleic acid replication increase the total number of chromosomes in an organism. Thus, the total length of the chromosomes in an organism as a whole increases during its life. Therefore, the information content and Shannon entropy also increase. In conclusion, accumulation of matter (macroscopically observed as a growth) leads to an increase in both thermal and information entropy during life. Life is just an ordinary phenomenon proceeding in accordance with the second law of thermodynamics. After death an organism decomposes (a process opposite to growth), loses matter and decreases its entropy.

4. Conclusions

The entropy concept is unavoidable in many scientific disciplines, resulting in inconsistencies in its application and interpretation. To resolve this problem, the three questions from the abstract were analyzed. The analysis showed that:

- (1) The physical nature of thermal entropy is represented by the statement: Thermal entropy represents a measure of **useless energy** stored in a system at a given temperature, resulting from thermal motion of particles. Residual entropy represents a measure of disorder of arrangement of aligned asymmetrical particles in a crystal lattice (string). The sum of residual and thermal entropy represents the total entropy content of a thermodynamic system.
- (2) Entropy is a non-negative objective property.

- (3) The negentropy concept, while mathematically correct, is physically misleading. Both theoretical considerations and experimental evidence suggest that entropy of living organisms increases during their lifespans, as a consequence of mass accumulation.

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Nomenclature

A	– Helmholtz energy	S_j	– Entropy of macrostate j
B	– Surface area	S_{Therm}	– Thermal entropy
C_p	– Heat capacity at constant pressure	\check{S}	– Shannon entropy
D	– Disorder	T	– Temperature
G	– Gibbs free energy	T_b	– Boundary temperature
H	– Enthalpy	U	– Internal energy
J	– Thermodynamic flow	W	– Number of microstates of equal energy available to a system
K	– Shannon equation constant	W_{eq}	– Number of microstates corresponding to the equilibrium macrostate
k_B	– Boltzmann constant	W_j	– Number of microstates corresponding to macrostate j
m	– Mass	w_{max}	– Maximum amount of expansion work that can be extracted from a system
\dot{m}	– Mass flow rate	X	– Thermodynamic force
p_i	– Probability of microstate i	x_Q	– Fraction of internal energy that is trapped as heat
p_k	– probability of symbol k	x_w	– Fraction of internal energy available to do work
Q	– Heat exchange	ε_i	– Energy of microstate i
Q_{rev}	– Heat exchange in a reversible process	σ	– The entropy production rate density
\dot{q}	– Heat exchange rate per unit surface area	Σ	– Boundary surface area
\dot{Q}	– Heat exchange rate	Ω	– Total number of microstates of equal energy
S	– Thermodynamic entropy		
s	– Specific entropy		
S_0	– Residual entropy		
$d_e S$	– Entropy exchange with the surroundings		
$d_e S_Q$	– Entropy exchange due to heat transfer		
$d_e S_m$	– Entropy exchange due to mass transfer		
$d_i S$	– Entropy production due to irreversible processes		

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