

Some Appendices to the book:

Entropy: The Greatest Blunder in the History of Science.

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Appendix C*: Some mathematical details about SMI

We provide here very briefly some mathematical details about the properties of the SMI. More details may be found in Ben-Naim (2017a).

The existence of a single maximum of the SMI for two outcomes can be shown as follows:

We take the two derivatives of $H(p)$ (note that $\log_2 p = \ln p / \ln 2$, where \ln is the natural logarithm).

$$(\ln 2) \frac{dH}{dp} = \ln \frac{1-p}{p} \quad (\text{C.1})$$

$$(\ln 2) \frac{d^2H}{dp^2} = \frac{-1}{p(1-p)} \quad (\text{C.2})$$

The condition for an extremum is:

$$\frac{dH}{dp} = 0 \quad (\text{C.3})$$

or equivalently

$$p = (1 - p) \quad (\text{C.4})$$

Thus, $H(p)$ has a *single* solution at:

$$p = \frac{1}{2} \quad (\text{C.5})$$

Clearly, the extremum at $p = \frac{1}{2}$ is a maximum since the second derivative, Eq. (C.2) is always negative in the range $0 < p < 1$.

The value of the function of $H(p)$ at the maximum is:

$$H_{max} = H\left(p = \frac{1}{2}\right) = 1 \quad (\text{C.6})$$

The Shannon Measure of Information for a finite number of outcomes

Originally, Shannon assumed that a measure of uncertainty or a measure of information must have certain properties. Through the years, various modifications of these properties have been suggested. One convenient list of properties (sometimes referred to as axioms) is the following:

1. The function $H(p_1, \dots, p_n)$ is a continuous function of all the variables p_i , where $0 \leq p_i \leq 1$ and $\sum_{i=1}^n p_i = 1$.
2. When $p_i = p = \frac{1}{n}$ for all $i = 1, 2, \dots, n$, the function $H(p_1, \dots, p_n) = f(n)$ is a monotonically increasing function of n .
3. The function $f(n)$ has the property.

$$f(n \times m) = f(n) + f(m) \quad (\text{C.7})$$

4. The function $H(p_1, \dots, p_n)$ fulfills the equality:

$$H(p_1, \dots, p_n) = H(p_A, p_B) + p_A H\left(\frac{p_1}{p_A}, \dots, \frac{p_r}{p_A}\right) + p_B H\left(\frac{p_{r+1}}{p_B}, \dots, \frac{p_n}{p_B}\right) \quad (\text{C.8})$$

where we denoted by $p_A = \sum_{i=1}^r p_i$ and $p_B = \sum_{i=r+1}^n p_i$. This property is referred to as the grouping or the consistency property.

Shannon proved that there exists a unique function which fulfills these assumptions.

The maximum of the SMI over all possible discrete distributions

This is a generalization of the existence of a single maximum of the SMI for the case of a game (or a random variable, or an experiment) having n outcomes with a distribution p_1, \dots, p_n . The function $H(p_1, \dots, p_n)$ has a *single maximum* over all possible distributions with the same n . Detailed proof in Ben-Naim (2017a).

The mathematical problem is to find the maximum of the function:

$$H(p_1, \dots, p_n) = -\sum_{i=1}^n p_i \log p_i \quad (\text{C.9})$$

subject to the constraint (or the closure condition):

$$\sum_{i=1}^n p_i = 1 \quad (\text{C.10})$$

The result is that there is a single maximum of H when all the probabilities are equal (uniform distribution):

$$p_i^* = \frac{1}{n}, \text{ For all } i \quad (\text{C.11})$$

This is an important result. It states that the maximum value of H , subject to only the condition (C.10), is obtained when the distribution is *uniform*.

The value of H at the maximum is:

$$H_{max} = -\sum_{i=1}^n p_i^* \log p_i^* = -\sum_{i=1}^n \frac{1}{n} \log \frac{1}{n} = \log n \quad (\text{C.12})$$

Clearly, when there are n equally likely events, the value of H is larger, the larger the number of possible outcomes.

The case of infinite number of outcomes

The definition of the SMI for the case of discrete infinite number of possibilities is straightforward. For the continuous distribution there might be some mathematical problems. Formally, we can follow Shannon's treatment for a continuous distribution for which a density function $f(x)$ exists. In analogy with the definition of the H function for discrete probability distribution, we define the quantity H for a continuous distribution. Let

$f(x)$ be the density distribution, i.e. $f(x)dx$ is the probability of finding a particular value of the random variable between x and $x + dx$.

We defined the H function in the form:

$$H = - \int_{-\infty}^{\infty} f(x) \log f(x) dx \quad (\text{C.13})$$

Note carefully that in this definition, $f(x)dx$ is a pure number. In general, $f(x)$ itself is not a pure number (e.g. if dx has units of length, then $f(x)$ has units of 1/length). Therefore, one must be careful in using this definition of H . See also Ben-Naim (2017b).

Three extremum theorems on the SMI

Here we quote without proofs three important theorems proved by Shannon (1948). They are important for three reasons: First, they show how three fundamental distributions in probability theory and statistics arise; second, they shed new light on the meaning of equilibrium state in thermodynamics; and third, they are essential to the understanding of both entropy and the Second Law of thermodynamics.

The uniform distribution of locations

Consider a particle that is confined to a one-dimensional “box” of length L , we seek the maximum of H defined in (C.13), but with limits $(0, L)$, subject to the conditions that:

$$\int_0^L f(x) dx = 1 \quad (\text{C.14})$$

One applies the Lagrange method of undetermined multiplier, then take the functional derivative with respect to the component $f(x')$. One finds that the probability density $f^*(x)$ which maximizes H , subject to the condition (C.14), is:

$$f^*(x) = \frac{1}{L} \quad (\text{C.15})$$

We refer to this distribution as the *equilibrium distribution* and use the notation $f_{eq}(x)$ instead of $f^*(x)$.

Thus, the equilibrium density distribution is *uniform* over the entire length L . The probability of finding the particle at any interval, say between x and $x + dx$ is:

$$f_{eq}(x)dx = \frac{dx}{L} \quad (C.16)$$

which is independent of x . This result is of course in accordance with our expectations. Since no point in the box is preferred, the probability of being found in an interval dx is simply proportional to the length of that interval.

The SMI associated with equilibrium density (C.16) is:

$$H_{max} = - \int_0^L f_{eq}(x) \log f_{eq}(x) dx = - \frac{1}{L} \log \frac{1}{L} \int_0^L dx = \log L \quad (C.17)$$

Clearly, the larger L the larger the SMI, or the larger the uncertainty in the location of a particle within the range $(0, L)$. Note carefully that L has units of length. Therefore, the only meaningful application of (C.17) is for *differences* in H .

The Normal distribution

The second theorem we present here is the following: Of all the continuous distribution densities $f(x)$ for which the second moment (or the standard deviation) is finite and constant, the Gaussian (or the normal) distribution maximizes the SMI in (C.13). The mathematical problem is to maximize H as defined in (C.13) subject to the two conditions:

$$\int_{-\infty}^{\infty} f(x) dx = 1 \quad (C.18)$$

$$\int_{-\infty}^{\infty} x^2 f(x) dx = \sigma^2 (= \text{constant}) \quad (C.19)$$

The result is the equilibrium density:

$$f^*(x) = f_{eq}(x) = \frac{\exp[-x^2/2\sigma^2]}{\sqrt{2\pi\sigma^2}} \quad (C.20)$$

The maximum value of the SMI is:

$$H_{max} = - \int_{-\infty}^{\infty} f^*(x) \log f^*(x) dx = \frac{1}{2} \log(2\pi e \sigma^2) \quad (\text{C.21})$$

The exponential, or the Boltzmann distribution

Another theorem proved by Shannon is that the Boltzmann distribution is obtained by maximizing H defined in (C.13), subject to the two conditions:

$$\int_0^{\infty} f(x) dx = 1 \quad (\text{C.22})$$

$$\int_0^{\infty} x f(x) dx = a \quad , \quad \text{with } a > 0 \quad (\text{C.23})$$

The result is that the density function that maximized H , is:

$$f^*(x) = \frac{1}{a} \exp\left(\frac{-x}{a}\right) \quad (\text{C.24})$$

$f^*(x)$

Appendix D*: An example of a process in an isolated system for which entropy increases

For the process described in Figure 2.4, the total volume of the system, the total number of particles, and the total energy of the system are fixed. For this system we have the two equalities:

$$V = \sum_{i=1}^c V_i \quad (\text{D.1})$$

$$N = \sum_{i=1}^c n_i^{(in)} \quad (\text{D.2})$$

We also assume that each compartment can accommodate any number of particles $0 \leq n_i \leq N$. The vector $\mathbf{n}^{(in)} = (n_1^{(in)}, n_2^{(in)}, \dots, n_c^{(in)})$ may be referred to as a *partition* of the number N into c numbers $n_i^{(in)}$ such that the sum of $n_i^{(in)}$ is equal to N . In this Appendix we use the word *partitions* for the barriers separating between the compartments, and the vector $\mathbf{n}^{(in)}$ describes the initial equilibrium state of the system.

Initially, we have a *constrained equilibrium state*. The entropy of the system as a whole is given by:

$$S_{Total}^{(in)} = \sum_{i=1}^c S_i^{(in)} \quad (D.3)$$

where $S_i^{(in)}$ is the entropy of the compartment i .

We now show that whenever we remove all the partitions between the compartments the total entropy of the system will increase. This will be the basis on which we shall establish the entropy formulation of the Second Law for the isolated system.

The process is shown in Figure 2.4. Initially, we have a constrained equilibrium state (before the removal of the partitions). Immediately after the removal of the partitions, the system is shown in Figure 2.4b. At this point the system is not in an equilibrium state. It is still characterized by the vector $(n_1^{(in)}, n_2^{(in)}, \dots, n_c^{(in)})$. After some time, the system shall reach a new (unconstrained) equilibrium state, Figure 2.4c. We denote by $(n_1^{(f)}, n_2^{(f)}, \dots, n_c^{(f)})$ the final equilibrium state. It should be noted that $n_i^{(f)}$ is the final number of particles in the compartment i , in the *absence* of the partitions (shown as dashed lines in figure 2.4).

As we saw in Chapter 1, the locational SMI for each particle is maximum for the uniform distribution, i.e. the probability of finding a *specific* particle in any element of volume dV at a point \mathbf{R} , is:

$$f(\mathbf{R})dV = \frac{dV}{V} \quad (D.4)$$

$f(\mathbf{R})$ is independent of the locational vector \mathbf{R} .

If we choose dV to be small enough so that at most one center of a particle can be accommodated in this volume, the probability of finding *any* particle in dV is NdV/V . We denoted by $\rho = \frac{N}{V}$ the density of particles at the final equilibrium state. The average number of particles in each compartment of volume V_i (in the absence of the partitions) is thus:

$$n_i^{(f)} = \rho V_i = \frac{NV_i}{V} \quad (D.5)$$

Thus, when we remove the partitions separating all the compartments, the system will move to a new equilibrium state. At this equilibrium state, the uniform locational distribution has the largest probability. Uniform distribution implies that the average number of particles in any compartment is proportional to the volume of that compartment, i.e. $n_i^{(f)} = \rho V_i$, or $x_i^{(f)} = \frac{n_i^{(f)}}{N} = \frac{V_i}{V}$, where $x_i^{(f)}$ is the molar fraction of particles in compartment i . The corresponding change in entropy can be calculated from the entropy function, see Chapter 1. The difference in entropy in the process in Figure 2.4, is:

$$\begin{aligned} \Delta S &= S(E, V, N) - \sum_{i=1}^c S(E_i, V_i, n_i^{(in)}) \\ &= Nk_B \ln\left(\frac{V}{N}\alpha\right) - \sum N_i k_B \ln\left(\alpha \frac{V_i}{n_i^{(in)}}\right) \end{aligned} \quad (\text{D.6})$$

In eq. (D.6) we included in α all the factors which do not change in the process, in particular $E_i/n_i^{(in)}$ which is proportional to the temperature T . Denoting the *mole fractions* as:

$$x_i^{(in)} = \frac{n_i^{(in)}}{N} \quad , \quad x_i^{(f)} = \frac{n_i^{(f)}}{N} \quad (\text{D.7})$$

We can rewrite eq. (D.6) as:

$$\begin{aligned} \Delta S &= Nk_B \sum_{i=1}^c x_i^{(in)} \ln\left[\frac{Vn_i^{(in)}}{NV_i}\right] \\ &= Nk_B \sum_{i=1}^c x_i^{(in)} \ln\left[x_i^{(in)}/x_i^{(f)}\right] \geq 0 \end{aligned} \quad (\text{D.8})$$

The equality holds if, and only if $x_i^{(in)} = x_i^{(f)}$ for all i . The inequality in (D.8) follows from the fact that apart from the Boltzmann constant and the change in the base of the logarithm, this is the Kullback-Leibler [see Ben-Naim(2017a)] distance between the two distributions $\mathbf{x}^{(in)}$ and $\mathbf{x}^{(f)}$.

Let us repeat a similar experiment as follows: Suppose we start with a system having fixed values of E , V , N . We divide it into c compartments of equal volumes, V/c each having different number of particles n_i , such that $\sum n_i = N$. The initial entropy of each compartment is denoted by $S_i^{(in)}$ and the total entropy of the system, assuming that each compartment is macroscopic and at equilibrium is:

$$S^{(in)}(E, V, N; \mathbf{x}^{(in)}) = \sum_{i=1}^c S_i^{(in)} \quad (\text{D.9})$$

where $\mathbf{x}^{(in)}$ is the distribution defined by its components $x_i^{(in)}$.

When we remove all the partitions between the compartments keeping E , V , N constant, the system will evolve into a new equilibrium state with an entropy value which is *larger* than the initial entropy, and for which the distribution of particles is uniform, i.e. $\mathbf{x}_i^{(f)}$ and:

$$S^{(f)}(E, V, N; \mathbf{x}^{(f)}) \geq S^{(in)}(E, V, N; \mathbf{x}^{(in)}) \quad (\text{D.10})$$

We emphasize that the reason for the evolution of the system from the initial to the final state:

$$\mathbf{x}^{(in)} \rightarrow \mathbf{x}^{(f)} \quad (\text{D.11})$$

is probabilistic, and the change in entropy is always positive (under the condition that the system is isolated).

Note that in this example starting from *any* initial distribution $\mathbf{x}^{(in)}$, the system will always evolve towards the *uniform distribution* $\mathbf{x}^{(f)}$. The reason is that the uniform distribution is the one that maximizes the probability $\text{Pr}(\mathbf{x})$, or equivalently, the corresponding SMI. A more general formulation is discussed in Ben-Naim (2017a).

We can now state the probability formulation of the Second Law as follows: We first write the relationship between the entropy difference in the process, and the probability ratio:

$$\frac{\text{Pr}(final)}{\text{Pr}(initial)} = \exp\left[\frac{S(final) - S(initial)}{k}\right] \quad (\text{D.12})$$

Thus, in an isolated system since $\Delta S = S(\text{final}) - S(\text{initial}) > 0$, the probability ratio is very large, of the order of $\text{Exp}[N]$. Note that the states “*final*” on the two sides of eq. (D.12) are the same state. The states “*initial*” on the two sides of the equation are different. The state “*initial*” on the right-hand side of the equation is the state *before* the removal of the constraints (Figure 2.4a), whereas the state “*initial*” on the left-hand side of the equation, is the state right *after* the removal of the constraints (Figure 2.4b).

Appendix H*: Callen’s formalization of the definition of “disorder”

Callen’s excellent book on “Thermodynamics (1961) introduced the concept of entropy axiomatically. In the first edition of the book Callen does not even mention “disorder” in connection with entropy. Surprisingly, in the second edition of his book (1985), Callen tried to formalize the “disorder interpretation of entropy.” He starts by recognizing Shannon’s measure of information.

“In fact, the conceptual framework of “information theory,” erected by Claude Shannon in the late 1940s, provides a basic interpretation of the entropy in terms of Shannon’s measure of *disorder*.”

Then he postulated several requirements of a “measure of disorder.”

The problem solved by Shannon is the definition of a *quantitative measure of the disorder* associated with a given distribution $\{f_j\}$.

- (a) *The measure of disorder should be defined entirely in terms of the set of numbers $\{f_j\}$.*
- (b) *If any of the f_j is unity (and all the rest consequently are zero) the system is completely ordered. The quantitative measure of disorder should then be zero.*
- (c) *The maximum disorder corresponds to each f_j being equal to $1/\Omega$ - that is, to the child showing no preference for any of the rooms in the house, among which he wanders totally randomly.*
- (d) *The maximum disorder should be an increasing function of Ω (being greater for a child wandering randomly through a large house rather than a small house).*

- (e) *The disorder should compound additively over “partial disorders.” That is, let f^1 be the fraction of the time the child spends on the first floor, and let Disorder⁽¹⁾ be the disorder distribution over the first floor rooms. Similarly, for f^2 and Disorder⁽²⁾. Then the total disorder should be*

$$\text{Disorder} = f^1 \times \text{Disorder}^{(1)} + f^2 \times \text{Disorder}^{(2)}$$

These qualitatively reasonable attributes uniquely determine the measure of disorder. Specifically,

$$\text{Disorder} = -k \sum_j f_j \ln f_j$$

where k is an arbitrary positive constant.

For a closed system the entropy corresponds to Shannon’s quantitative measure of the maximum possible disorder in the distribution of the system over its permissible micro-states.

Thus, we recognize that the physical interpretation of the entropy is that the entropy is the quantitative measure of the disorder in the relevant distribution of the system over its permissible micro-states.”

The list above are essentially the requirements that Shannon postulated for a *measure of information, not a measure of disorder*. Here, Callen fell into two pitfalls. First, Shannon never discussed *disorder* or a measure of *disorder*. Second, Shannon’s postulated plausible properties of a measure of *information*, not plausible properties of a “measure of disorder.” Therefore, I must conclude that what Callen did is either misleading or even deceiving.

I take this opportunity to venture into the explanation of the reasons for Callen’s lamentable definition of disorder. Callen clearly recognized, and probably admired Shannon’s approach to information theory. This is clear from his discussion in Chapter 17 of his book (1985). However, Callen probably confused the SMI with the general concept of information, see section 3.4. The latter, but not the former, could be subjective. Callen, could not accept the “subjective” character that unjustifiably stuck to the SMI. He therefore wanted to eat the cake of SMI, and at the same time rejecting SMI which reeked of subjectivity. So he embraced the SMI, but pretended that it is something else, in this case “disorder.”

Callen defined “Shannon’s disorder” by:

$$disorder = -\sum p_i \log p_i$$

The right-hand-side of this equation is a well-defined quantity. What Callen has defined is not “Shannon’s disorder” but “Shannon’s measure of information.” Therefore, the positioning of “disorder” on the left-hand-side of the equation is unwarrantable and unjustifiable.

Shannon sought a quantity that was not known; a measure of information. He asked himself: suppose that such a measure exists, what properties must it have? Shannon assumed that if a measure of information exists, it must have some plausible properties. Then he showed that there exists a unique quantity which will have these properties. Clearly, if he wanted to derive a measure of *disorder*, he would not have assumed that it will have the same properties presumed for a measure of information. Therefore, it is unlikely that he would have obtained a “measure of disorder” as defined by Callen. For more details, see Ben-Naim (2012).

Appendix J*: Leff’s procedure to derive a spreading function

Leff (2007) made a serious attempt to formalize the spreading and sharing metaphor. His procedure has elements from Callen’s procedure to axiomatization of thermodynamics, (see Appendix K), as well as elements of Callen’s attempt to formalize “disorder,” (see Appendix H). Leff listed the properties that a *bona fide* “spreading function” must possess and are deemed to be “reasonable.” Here they are with my comments:

1. *For a homogenous body, J is a function of the system’s energy E , volume V , and particles N . Rationale: These are common thermodynamic variables, for one-component systems.*

Comment: Perhaps it is a function of these variables, but it does not say what the function is, as we have seen the function of SMI and the entropy are functions of these variables.

2. *At uniform temperature, J is an increasing function of energy E . Rationale: More energy means there is more energy to spread and thus more spreading.*

Comment: This is potentially misleading. Obviously if there is more energy there will be more energy to spread. However, changes in entropy are not larger the more energy there is. See example discussed in section 3.3.

3. *For a body made of the same material, but with twice the volume and energy, the value J is double that of the original body; i.e. $J(2E, 2V, 2N) = 2J(E, V, N)$. This requires the degree of spreading to double when twice the energy spreads over twice the number of particles occupying twice the volume. A generalization is that for any real $\beta \geq 0$, $J(\beta E, \beta V, \beta N) = \beta J(E, V, N)$, which is the property called extensivity. Rationale: Clearly, there should be more spreading for $\beta > 1$, and it is reasonable that, for example, doubling E, V, N doubles $J(E, V, N)$. Having E, V, N would give half as much spreading, and so forth.*

Comment: This is a property of entropy, not necessarily a property of spreading function.

4. *For two systems, labeled a and b , $J_{a+b} = J_a(E_a, V_a, N_a) + J_b(E_b, V_b, N_b)$. Rationale: We require that the spreading function be additive, as are internal energy, volume, and particle number themselves. This is based on the belief that spreading effects on boundaries of systems a and b are negligible, being overwhelmed by the spreading over volumes. It is assumed that particles interact via short-range interatomic and intermolecular forces.*

Comment: Again, this is a property belonging to entropy which is assumed to be a property of the spreading function.

5. *The J_{a+b} is maximal at equilibrium. Rationale: Spreading continues until equilibrium is reached and cannot become larger. This will become more clear in the following example.*

Comment: This is the most serious mistake. Here, Leff takes a property which is erroneously assigned to entropy, then quite arbitrarily assign it to the spreading function. Spreading may change until it reaches equilibrium, but entropy does not! Entropy is defined only at equilibrium.

To conclude, in my opinion, what Leff did was nothing but assign properties of the entropy to the concept of “spreading.” Therefore, as expected he concluded that the symbol S used for entropy should be viewed as a shorthand for “spreading.” I beg to differ. First, because these properties are artificially assigned to the Spreading. Second, even if one

could justify all these properties of the Spreading function, it does not follow that the entropy is spreading. Therefore, the whole procedure is invalid.

Appendix K*: Callen's procedure to axiomatization of thermodynamics

Callen in his admirable book (1961), developed thermodynamics from a few postulates. These postulates play the same role as the axioms in any mathematical theory. What Callen did was to “invert” the traditional historical development of thermodynamics. The few postulates he chose are essentially the properties of entropy that we already know from thermodynamics. As Callen correctly stated in his book's preface (1961):

“The postulatory formulation of thermodynamics features states, rather than processes, as fundamental constructs.”

“The conventional method proceeds inversely from processes to state functions...”

The four postulates he proposed are:

Postulate I: There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U , the volume V , and the mole numbers N_1, N_2, \dots, N_r of the chemical components.

Postulate II: There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

Callen repeatedly stresses that the postulate of existence of entropy applies only for equilibrium states! With which I fully agree.

Postulate III: The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.

Postulate IV: The entropy of any system vanishes in the state for which

$$\left(\frac{\partial U}{\partial S}\right)_{V, N_1, \dots, N_r} = 0 \quad (\text{That is, at zero temperature})$$

The essential point I would like to stress here is that Callen did not introduce a new concept but used the known concept of entropy, and known properties of entropy to build up the entire edifice of thermodynamics with a minimal number of postulates.

Although lacking a definition of entropy (within thermodynamics), I wholeheartedly accept this property of entropy.

Interestingly, Callen does not even mention Clausius' definition of entropy, nor Clausius' formulation of the Second Law. In later chapters on statistical mechanics, Callen introduces Boltzmann's definition of entropy. It is in those chapters where Callen did a serious mistake in attempting to interpret entropy in terms of disorder. This is further discussed in Appendix H.

In Appendix B of his book (1961) he also summarizes “the significance of the entropy” by using essentially Boltzmann's definition of entropy $S = k_B \ln \Omega$, and states that “The entropy of any macro-state is proportional to the logarithm of the number of micro-states *associated* with the macro-state.”

In his second edition (1985) Callen clarifies the meaning of Ω as the “number of *available* micro-states” and then as “the number of micro-states *consistent* with the macroscopic constraint. He did not fall into the pit of replacing the “number of micro-states” by one word; “availability,” “consistency,” “accessibility” or “spreading.”

Appendix O*: Example of an expansion process in 1D system

Consider the case of one-dimensional (1D) systems of N (non-interacting and simple) particles in “volume” V . See Figure O.1a

When we remove the *partition* in Figure O.1a, and let the particles expand from $V/2$ to V , the entropy change is $Nk_B \ln 2$. The interpretation of this change in entropy in terms of SMI is quite simple. Apart from the constant factor $k_B \ln 2$, we lost one bit per particle, hence N bits of information for N particles.

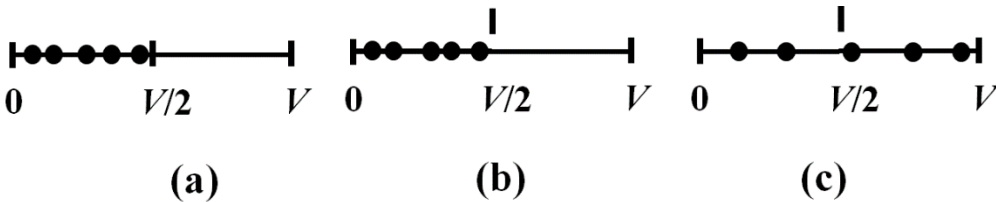


Figure O.1 (a) N particles in a 1D system of “volume” $V/2$.
 (b) The same system as in (a) but the partition is removed.
 (c) The system reached a new equilibrium state, the particles occupying the entire volume V .

Next, we ask about the probability of finding the “initial” state in Figure O.1. Now, read carefully the following probabilities:

Before the removal of the partition:

1. The probability of the “initial” state (a) (here, state, *means* macro-state) is *one*.

After the removal of the partition:

2. The probability of the “initial” state (a) is *zero*.

3. The probability of the “initial” state (b) is very small: $\left(\frac{1}{2}\right)^N$.

This is an extremely small number, which for all practical purposes, can be considered as zero for N of the order 10^{23} .

Take note of the extreme difference between the probabilities of the same (macro) states, *before* and *after* the removal of the partition. The probability of the state (a) changes from *one* to *zero*; once we remove the partition, we can *never* obtain the state (a) spontaneously. On the other hand, the “state” (b) is the state at the very instant we remove the partition, just before any of the particles have started to move out of the initial region. The probability of the state (b) is extremely small. See discussion of conditional probability in Appendix F.

Let us stay in the *physical* one-dimensional system as shown in Figure O.1, but change the number of particles in the system. Here we discuss only the *configurational volume* in

PS, i.e. we exclude the momentum part of the PS, which is presumed to be unchanged in this process.

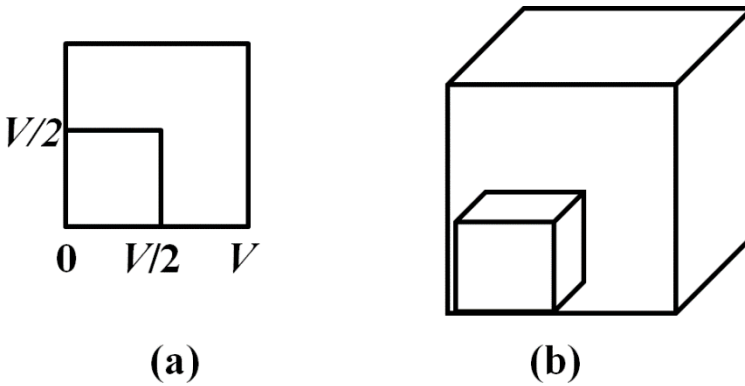


Figure O.2 The configurational volume in PS for two particles, (a) and for three particles (b).

For $N = 1$, the probability of finding the particle anywhere in the “volume” V is one. The probability of finding the particle in the interval between zero to $\frac{1}{2}V$ is $Pr(N = 1) = \frac{1}{2}$. In this case, the PS-volume is the same as the physical volume V .

For $N = 2$, the physical volume is still V but the phase-space volume is now V^2 . See Figure O.2a. Clearly, if we restrict the particles to be in the physical volume $\frac{1}{2}V$, the corresponding volume in the phase-space is now $\left(\frac{1}{2}V\right)^2$. Thus, while the ratio of the physical volumes is $\frac{2V}{V} = 2$, the corresponding ratio of the volumes in the phase-space is now $\left(\frac{2V}{V}\right)^2 = 4$. For $N = 3$, the ratio of the volumes in phase-space, is now $\left(\frac{2V}{V}\right)^3 = 8$, Figure O.2b.

For $N = 10$ particles, the ratio of the *physical volumes* is the same $\frac{2V}{V} = 2$, but the ratio of the volumes in the phase space becomes $\left(\frac{2V}{V}\right)^{10} = 2^{10}$. This is already a very large number.

For $N = 10^{23}$ the ratio of the physical volume available for each particle is again, $\left(\frac{2V}{V}\right) = 2$. The entropy change per particle is $k_B \ln 2$, and for the N particles is $k_B N \ln 2$. Thus, for the calculation of the entropy change all we need is the change in the *physical* volume. The “volumes” in PS (here we need only the configurational PS, ignoring the momenta PS) are irrelevant.

The probability of finding each particle in the physical volume $V/2$ is now extremely small; it is $2^{-10^{23}}$. Let us not forget that this probability is a *conditional* probability, i.e. *given that the entire probability spaces* Ω . In our case, the probability space Ω is the entire volume of the (configurational) PS. The probability of the event “*all particles in physical volume V ,*” is one. The probability of the event “*all particles in physical volume $V/2$* is extremely small, it is $2^{-10^{23}}$, which may be considered to be practically zero.

To conclude, the entropy change is determined by the ratio of the *physical volumes* of the system. The probability ratio is sometimes, but not always determined by the ratio of volumes in PS.

Appendix S*: On the fundamental assumptions of non-equilibrium thermodynamics

This Appendix is dedicated to discussing the main assumptions made in the theory of non-equilibrium thermodynamics, Ben-Naim (2018a, 2018d). It will focus mainly on Prigogine’s book (1961). Prigogine wrote a short and very influential book: **Thermodynamics of Irreversible Processes (1961)**.

This book starts with the assertion that:

A serious limitation of classical thermodynamics as a general tool for the macroscopic description of physicochemical processes lie in the fact that its method is based on such concepts as “reversible processes” and “true equilibrium states.”

The author claims that since the majority of the phenomena started in biology, meteorology, astrophysics, and other subjects are irreversible, there is an urgent need for an extension of the methods of thermodynamics to include irreversible processes.

As we shall see, in developing the “extension” of thermodynamics the author “sneaks in” some assumptions without providing any justification. The unwary reader might not notice those assumptions and accept the results uncritically just like many others did.

Chapters 1 and 2 are standard presentations of thermodynamics and the first law. The third chapter is on “**Entropy Production – The Second Principle of Thermodynamics.**”

It should be said that the word “production” used in the title of the chapter (as well as in many other publications) might be misleading in the following sense; entropy is not *produced*. It might increase or decrease for specific systems. The word “produced” might indicate an *active production* of a quantity. When we remove a partition, say in the process of Figure 2.15, and the gas expands from V to $2V$, we do not say that volume was *produced*; the volume of the system has *increased* in this process. The same is true for the entropy. In this process entropy *increased* by $R\ln 2$, it was not *produced* by anyone or by anything. The second potentially misleading point in the title is similar to a very common formulation of the Second Law (or second principle), as the “*law of increasing entropy.*” Entropy, by itself does not increase or decrease. It may increase or decrease for some specific processes in some specific systems.

Although the above comments are semantic in nature, they are important when one wants to interpret either entropy or the Second Law.

As we have discussed in Chapter 2, entropy changes abruptly either at the moment of removing the partition, or when the system reaches a new equilibrium state. On page 14 Prigogine defines “reversible and irreversible processes,” see Appendix A. As an example of an irreversible process, Prigogine discusses the “*The irreversible approach to thermal equilibrium.*”

Clearly, this “*irreversible approach to equilibrium*” in general, does not follow from his own definition of irreversibility simply because there is no equation which is not invariant under the transformation $(t) \rightarrow (-t)$, which describe the general approach to equilibrium.

We believe that any isolated system will reach equilibrium, and that this process is irreversible. However, this irreversibility is not absolute, but only “in practice” or with high probability.

On page 15 the author says:

Most of the usual physicochemical processes like diffusion, conduction of heat or electricity, chemical reactions, etc., are irreversible processes and the major progress in thermodynamics during the last twenty years is related to the extension of macroscopic methods to such processes.

Indeed, we believe that physicochemical processes are irreversible, but this irreversibility is not defined by an equation, such as equation 3.2 on page 14, which is invariant under $(t) \rightarrow (-t)$.

Next, on page 15, the author defines entropy as:

The second principle of thermodynamics postulates the existence of a function of state, called entropy (from the Greek $\epsilon\nu\tau\rho\omega\pi\eta$ meaning “evolution”) which possesses the following properties:

a) The entropy of the system is an extensive property. If a system consists of several parts, therefore the total entropy is equal to the sum of the entropies of each part.

b) The change of entropy dS can be split into two parts. Denoting by d_eS the flow of entropy, due to interactions with the exterior, and by d_iS the contribution due to changes inside the system, we have

$$dS = d_eS + d_iS \quad (3.3)$$

As we have discussed in Chapters 1 and 2, entropy can be defined without reference to the Second Law, and the Second Law may be formulated without mentioning entropy.

Historically, it is true that entropy and the Second Law were intertwined, but this is not a necessity. Note carefully that the statement $d_iS > 0$ for irreversible processes is true for processes in isolated systems. In neither (a), nor in (b), in the quotation above is the condition of an “isolated system” mentioned. Therefore, this statement of the “second principle” is not true. It is only later in equation (3.6) that the condition “isolated system” is introduced, and for which he writes the equation:

$$dS = d_i S \geq 0 \quad (\text{isolated system}) \quad (3.6)$$

It must also be emphasized that the very *concept* of “flow of entropy” cannot be introduced at this stage before one defines entropy. Unfortunately, the author raises Clausius’ “definition” of entropy only two pages later. On page 18, he writes:

We shall consider first a closed system containing a single component, an irreversible process being excluded ($d_i S = 0$). We shall then define the entropy by the explicit formula

$$dS = \frac{dQ}{T} \quad (3.7)$$

where T is a positive quantity called absolute temperature, which satisfies the following requirements...”

As we pointed out in Chapter 1, this “definition” does not *define* entropy, but an entropy-change for a specific process. Therefore, what the author calls a “definition” of entropy by an “explicit formula” is not a definition of entropy, and certainly not an explicit definition of the entropy function as we have done in Chapter 1.

An example of “entropy production” is provided on pages 19-20. Although the example is correct, it is represented in a very sloppy manner.

First, *the system* consists of two subsystems I and II. Therefore, it is true that if this (entire) *system* is isolated, then the entropy of the process that occurs should involve an increase in entropy. Unfortunately, the author does not say that the system is isolated.

Second, and most important, the author claims that the two subsystems (or “phases”) are maintained at uniform temperatures T^I and T^{II} but he does not tell us how these subsystems are “maintained at uniform temperature.” If the entire system is isolated and the temperature difference is finite, and a finite quantity of heat is transferred between the two phases, the temperatures of the two-phases will change. Unfortunately, the author “forgot” to tell us that his definition of entropy is valid for a system at constant T , when an infinitesimal quantity of heat is exchanged between two phases. This is what we refer to as a quasi-static process. Thus, his calculation of the change in entropy is correct either when $T_1 - T_2$ is very small, or, when $T_1 - T_2$ is finite, and we exchanged a very small quantity

of heat. In both cases this process will be referred to as quasi-static process. The whole argument is not valid when the entire system is not isolated, or when both $T_1 - T_2$, and dQ are finite quantities.

Finally, on page 20 he concludes:

“Further on, we shall often make use of the entropy production per unit time

$$\frac{d_i S}{dt} = \frac{d_i^l Q}{dt} \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) > 0 \quad (3.16)$$

This equation is of a simple form which is of great importance.”

Writing a derivative of S with respect to time (t) is misleading. It suggests that entropy is a function of time. Equation (3.16) quoted above is true for an infinitesimally small quantity of heat added during the time interval dt . The ratio $d_i S/dt$ is *not* a *derivative*, but simply a ratio of a small quantity of heat (dQ) transfer during an arbitrary period of time, denoted here as dt , suggesting a derivative.

Thus, what he calls an equation of “great importance” is, in fact, a greatly misleading equation. In order to understand why, consider a simpler example. We assume that there are two compartments containing ideal gas at different pressures, such that $P_1 - P_2 > 0$ is infinitely small. The entire system is isolated. We now let the partition move from left to right. Since $P_1 - P_2$ is very small the change of volume of each subsystem is small too, thus we can calculate the change in entropy for this process as:

$$TdS = P_1 dV - P_2 dV = (P_1 - P_2) dV$$

Since dV , is by definition positive, the entropy change for this process is also positive.

Clearly, this change of entropy took some time, let us call it Δt . We could have made the transfer at any duration Δt we wanted (we could also simply calculate the difference in entropy between the initial and the final states without mentioning time at all. It would be misleading to write the ratio:

$$\frac{d(TS)}{\Delta t} = (P_1 - P_2) \frac{dV}{\Delta t}$$

and to refer to $dS/\Delta t$ as the rate of the entropy production, or to suggest that this is time derivative of the entropy.

More generally, one can use the Gibbs relationship:

$$dS = \frac{dE}{T} + \frac{P}{T} dV - \sum_{i=1}^c \frac{\mu_i}{T} dN_i$$

This is valid for any infinitesimal change in either E, V , or N_i . One can change, say, the volume during a time interval Δt keeping E and all N_i constant and write:

$$\frac{dS}{\Delta t} = \frac{P}{T} \frac{dV}{\Delta t}$$

Δt can be any arbitrary interval of time, it could also be zero, by simply comparing two systems, at the same time ($\Delta t = 0$), in which case the change of entropy is $dS = \frac{P}{T} dV$. One cannot view the ratio $dS/\Delta t$ as a derivative of S with respect to t , simply because there is no such function $S(t)$.

Next, comes the example of chemical reaction which we write in the form:

$$\sum v_i M_i = 0$$

where M_i is the compound i , and v_i is its stoichiometric coefficient (positive for product and negative for reactants). The change in the number of moles of the i th component is dn_i .

And the extent of the reaction is defined by:

$$dn_i = v_i d\zeta$$

The rate of the chemical reactions is thus:

$$v = \frac{d\zeta}{dt}$$

For a process at constant temperature and volume we have:

$$\begin{aligned} dS &= \frac{dE}{T} - \sum \frac{\mu_i}{T} dn_i = \frac{dQ}{T} - \sum v_i n_i d\zeta \\ &= \frac{dQ}{T} + \frac{A}{T} d\zeta \end{aligned}$$

Where the affinity of the reaction is defined by:

$$A = - \sum v_i n_i$$

Thus, the entropy change may be written as:

$$dS = \frac{dQ}{T} + \frac{A}{T} d\zeta$$

This change is due to flow of heat (dQ) and the chemical reaction provided the chemical reaction is carried out in a quasi-static manner.

On page 24 Prigogine writes the “entropy production per unit of time as:

$$\frac{d_i S}{dt} = \frac{A}{T} v > 0$$

The problem with this equation is that the v is the reaction rate, i.e. the *derivative* $\frac{d\zeta}{dt}$, but on the left-hand-side the ratio $d_i S/dt$ is *not a derivative*. It is simply the ratio of the change in the entropy in a quasi-static process where dt can be an arbitrary time interval. Thus, if we start at time $t = 0$ with only a reactant, and let the chemical reaction proceed spontaneously, the rate of the reaction, v is well-defined experimentally. However, the entropy of the system is defined only at the initial and the final equilibrium state, and not in the intermediate state.

Of course, if we do the same passage from the initial to the final state quasi-statically the entropy will be *defined* at each intermediate state, but now the “rate of reaction” is not v but is the arbitrary rate at which we decide to perform the reaction from the initial to the final state. In this case, $d_i S$ at each interval of time Δt is well-defined but the ratio of $d_i S/\Delta t$ is not the derivative of the entropy function, and $d\zeta/\Delta t$ is not the measurable *rate* of the reaction.

Thus, in general, for any spontaneous process from equilibrium state A to equilibrium state B the entropy change is well-defined:

$$\Delta S = S(B) - S(A)$$

If the process is spontaneous, going through non-equilibrium states, then entropy is not defined at any intermediary point.

If we do the same process from A to B quasi-statically, then the time intervals Δt is arbitrary, and the ratio $dS/\Delta t$ cannot be regarded as the rate of entropy production.

On page 32 the author discusses the “Entropy production in Continuous System.” I believe it is at this point where the author (as well as many others) introduces an equation which is well-defined for the density (as well for electric charges), but not for the entropy. This is the *continuity equation* for the entropy.

Starting from the principle of conservation of mass which may be written as:

$$\frac{\partial \rho}{\partial t} = -\text{div}(\rho w)$$

where ρ is the density, and w is the velocity of the mass. This equation simply means that the change in the number of particles (or the density) in a small element of volume can come about by mass flowing through the boundaries of that volume. If there is a chemical reaction, then there are two terms to the change in the density of each component:

$$\frac{\partial \rho_i}{\partial t} = -\text{div}(\rho_i w) + \rho_i M_i v_v \quad (3.66)$$

The first term on the right-hand-side of equation (3.66) is due to the flow of component i , through the boundaries of the element of volume. The second term is due to the “production” of the chemical component (i), which can either be positive or negative. (Here, M_i is the molecular mass of component i , and v_v is the rate of the chemical reaction per unit of volume). On page 34 the author states:

An equation similar to (3.66) can be established for every variable having the properties of a generalized “density,” like ρ or ρ_i .

Thus, he writes for the “entropy per unit volume s_v ,” the equation:

$$\frac{\partial s_v}{\partial t} = -\text{div}\phi + \sigma \quad (3.69)$$

where ϕ is the “flow of entropy” and σ is the entropy production per unit volume and unit of time.

This is a grave mistake. Entropy is not a generalized “density” like ρ . In facts one *cannot* define an entropy density for systems far from equilibrium. The entropy of a system at equilibrium is the sum of the entropy of all macroscopic subsystems. If one takes the entropy of the system and divide it by the volume V , one may call it entropy per unit of volume S/V , but this quantity is *not* the entropy of a small element of volume. It is here that the author sneaks in the “entropy per unit volume s_v ,” without any justification. This unjustified error appears in almost every book on thermodynamics of irreversible processes. Furthermore, the quantity σ , referred to as “entropy productions per unit volume and per unit of time, *cannot be defined* for a system far from equilibrium. Therefore, one cannot obtain the “entropy production” of the whole system by integrating (the undefinable) quantity σ , over the entire volume of the system either for systems at equilibrium or not at equilibrium. It follows that the “postulate” stating that (p-34):

$$\sigma = 0 \text{ (reversible processes)} \quad (3.70)$$

$$\sigma > 0 \text{ (irreversible processes)} \quad (3.71)$$

is a meaningless postulate!

We conclude this Appendix by pointing out that many authors repeat the same assumptions without ever giving any justification for these assumptions (e.g. de Groot and Mazur (1962), Glansdorff and Prigogine (1971), Kondepudi and Prigogine (1999), Kreuzer (1981), see also criticism of these in Ben-Naim (2018a, 2018b))

Conclusion

To the best of our knowledge the assumption of "local equilibrium," followed by the definition of entropy-density function in a system far from equilibrium has never been founded either within thermodynamics, or from statistical mechanical arguments.

Furthermore, we argued that an entropy density function, even if it could be defined would not have the same functional dependence on the local energy, volume, and number of particles (u, v, n) as the entropy of a macroscopic system at equilibrium $S(U, V, N)$. These findings shed serious doubts on the thermodynamics of systems far from equilibrium.

Appendix T*: Prigogine's Book: "*From Being to Becoming*"

In his book, "From Being to Becoming," Prigogine extends some of his earlier ideas on self-organization [published earlier by Nicolis and Prigogine (1977)] and non-equilibrium phenomena.

The Preface starts with the following statement about the aims of Prigogine's book:

This book is about time. I would like to have named it Time, the Forgotten Dimension, although such a title might surprise some readers. Is not time incorporated from the start in dynamics, in the study of motion? Is not time the very point of concern of the special theory of relativity?

While reading the above quotations from the Prigogine's book I wondered which "time" is the "forgotten dimension." The answer to this question becomes clear in the rest of the book. This is the time that has been misconstrued with entropy and the Second Law by so many authors. The fact is that this "time" that was *never forgotten*; It should have been forgotten!

On page xii we find:

Physicists and chemists know that a description in which past and future play the same roles does not apply to all phenomena. Everybody observes that two liquids put into the same vessel generally diffuse toward some homogenous mixture. In this experiment the direction of time is essential. We observe progressive homogenization, and the one-sidedness of time becomes evident in the fact that we do not observe spontaneous phase separation of the two mixed liquids.

It is not true that two liquids will always mix, and when they do it has nothing to do with “the one-sidedness of time.”

This description does not leave any doubt as to the “forgotten dimension” of time. From this “innocent example” of mixing, which seems to evolve in one *direction* of time, he continues to the concept of evolution:

The concept of evolution seems to be central to our understanding of the physical universe. It emerged with full force in the nineteenth century. It is remarkable that it appeared almost simultaneously in physics, biology, and sociology, although with quite different specific meanings. In physics it was introduced through the Second Law of thermodynamics, the celebrated law of increase of entropy, which is one of the main subjects of this book.

Here, Prigogine clearly misconstrued the evolution in physics, biology, and sociology with the Second Law of Thermodynamics. The fact is that the Second Law does not have anything to do with evolution; not in biology, sociology, and not in most processes in physics. It is also not true that the concept of evolution...*emerges with full force...through the Second Law of thermodynamics.* It is clear that Prigogine intends to apply thermodynamics to biology and sociology:

How can we relate these various meanings of time – time as motion, as in dynamics; time related to irreversibility, as in thermodynamics; time as history, as in biology and sociology? It is evident that this is not as easy matter.

Here, it is also clear that Prigogine confuses the direction of time with the apparent irreversibility in thermodynamics.

On page xiii, the author explains the main thesis of his book as follows:

First, irreversible processes are as real as reversible ones; they do not correspond to supplementary approximations that we of necessity superpose upon time-reversible laws.

Second, irreversible processes play a fundamental constructive role in the physical world; they are at the bases of important coherent processes that appear with particular clarity on the biological level.

Third, irreversibility is deeply rooted in dynamics. One may say that irreversibility starts where the basic concepts of classical or quantum mechanics (such as trajectories or wave functions) cease to be observables. Irreversibility corresponds not to some supplementary approximation introduced into the laws of dynamics but to an embedding of dynamics within a vaster formalism.

In my view, the three points cited above are the utmost embodiment of the greatest blunder in the history of science.

Irreversible processes are only apparent irreversible, not absolute, and have nothing to do with “time’s direction.”

Although life seems to consist of some irreversible processes, there is no real evidence that they have a fundamental *constructive role* in the physical world. Certainly, not on the “*biological level.*”

Later in the preface the author mentioned Jacques Monod :

“Jacques Monod has called living systems “these strange objects,” and they are very strange indeed compared with the “nonliving” world (Monod 1970). Thus, one of my objectives is to try to disentangle a few general features of these objects.”

This promise of disentangling a few general features of living systems is not fulfilled, neither in this book, nor in any other publications.

Although Prigogine is aware of the fact that living systems are “far from equilibrium,” he still uses the assumption of “*local equilibrium,*” which is justified nowhere (see also Appendix S).

I disagree with most of the book’s contents. Here, I will provide one more quotation from page 6 of Prigogine’s book with which I do not agree with:

The Second Law of thermodynamics, then, states that irreversible processes lead to a kind of one-sidedness of time. The positive time direction is associated with the increase of entropy. Let us examine how strongly and specifically the one-sidedness of time appears

in the Second Law. It postulates the existence of a function having quite specific properties such that in an isolated system it can only increase in time.

Nothing is true in this paragraph! Note that Prigogine does not provide an entropy which is a function of time. Instead, he claims that such a function is only *postulated*. As I have discussed in the Appendix S and in Ben-Naim (2019a) this postulate may be traced back to the assumption of “local equilibrium” which cannot be justified for systems which are far from equilibrium.

Appendix X*: Perutz on Physics of Life

In 1987 Perutz wrote an article in *Nature* on “**Physics and the riddle of life.**” In this article Perutz admitted that Schrödinger “drew several of the brightest physicists into molecular biology.” However, he added:

“But the book’s chief merit lies in its rescue from obscurity and popularization of an earlier paper by Timoféef, Zimmer and Delbrück.”

This comment refers to Schrödinger’s ideas about “*The Nature of Genetic Mutations and the Structure of the Gene*” which was the title of the article by Timoféef – Ressovsky, Zimmer, and Delbrück. Perutz claims that most of the ideas discussed by Schrödinger on genetics were lifted from the article in *Nature*.

Regarding the question of “*Order, Disorder, and Entropy,*” Perutz writes:

Schrödinger's last two chapters do contain his own thoughts on the nature of life. In "Order, Disorder and Entropy" he argues that "the living organism seems to be a macroscopic system which in part of its behavior approaches to that purely mechanical (as contrasted with thermodynamical) conduct to which all systems tend, as the temperature approaches the absolute zero and the molecular disorder is removed". He comes to this strange conclusion on the ground that living systems do not come to thermodynamic equilibrium, defined as the state of maximum entropy. They avoid doing so, according to Schrödinger, by feeding on negative entropy. I suspect that Schrödinger got that idea from a lecture by Boltzmann on the Second Law, delivered before the Imperial Austrian Academy of Sciences in 1886.

Thus, Perutz does not criticize the main idea of “Negative entropy,” but instead says that this is a “strange idea,” and that it was apparently taken from Boltzmann who wrote in 1886:

Hence the general battle for existence of living organisms is not one for the basic substances these substances are abundant in the air, in water and on the ground - also not for energy that everybody contains abundantly, though unfortunately in a non-available form, but for entropy which becomes available by the transition of energy from the hot sun to the cold earth.

Another interesting comment by Perutz is that living systems are not isolated systems. Therefore, the entropy formulation does not apply. Instead, if one wants to apply the Second Law it should be the Gibbs-energy formulation. Next, he quotes Simon's comment as follows:

Franz (later Sir Francis) Simon, then at Oxford, pointed out to Schrödinger that we do not live on $-T\Delta S$ alone, but on free energy. Schrödinger deals with that objection in the second edition of his book; he writes that he had realized the importance of free energy, but had regarded it as too difficult a term for his lay audience; to me this seems a strange argument, because the meaning of entropy is surely harder to grasp. Schrödinger's postscript did not satisfy Simon who pointed out to him in a letter that: The reactions in the living body are only partly reversible and consequently heat is developed of which we have to get rid to the surroundings. With this irreversibly produced heat also flow small amounts (either + or -) of reversibly produced heat $-T\Delta S$, but they are quite insignificant and therefore cannot have the important effects on life processes which you assign to them.

As a result of this comment, Schrödinger added a footnote on page 79. His argument is making use of the meaningless “negative entropy” instead of “free energy” because the latter is a “highly technical term,” is strange, to say the least. The “entropy” is as “highly technical term” as “free energy.”

In 1987, Schneider also wrote a short note to Nature, entitled “Schrödinger's grand theme shortchanged.”

SIR – Perutz's critical review of Schrödinger's “What is Life?” focused only on the leaves and not only missed the forest but the trees as well. His review sifted through reductionist references of the past and dismissed the important themes developed by Schrödinger, who noted that living systems displayed two fundamental processes. One he called “order from order,” and the other “order from disorder.” Schrödinger synthesized and characterized the existing physical knowledge of the soon to be discovered DNA with the former and then proceeded to integrate the laws of thermodynamics with biology with the latter.

Then he adds:

Schrödinger's most important and least studied observation was his "order from disorder" premise which links all biological systems with the expanded fundamental theorems of thermodynamics.

Schneider adds to this the common nonsense that "entropy should be maximized, and disorder should reign at equilibrium.

Living systems, however, are the antithesis of disorder as they display marvelous levels of order made from disorder. Schrödinger solved this dilemma by turning to 'non-equilibrium thermodynamics.'

Life is a far-from-equilibrium dissipative structure that maintains its local level of organization, or negentropy, at the expense of the large global entropy budget.

Finally, he concludes:

Perutz contends that Schrödinger's essay was not original work, and its chief merit was the popularization of the Timoféef paper. I am sorry that Perutz missed Schrödinger's grand theme of the possible description of biologic processes within the framework of modern physics.

This whole note, as well as the chapter Schneider and Kay contributed to the "50 years after..." is unfortunate. The truth is that Schrödinger did *nothing*, absolutely nothing to describe biological processes within the framework of modern physics. In my opinion, Perutz did not miss any of the "grand themes" in Schrödinger's book. Instead, Perutz was right in criticizing Schrödinger's strange and meaningless ideas about life and negative entropy. It is Schneider who failed to see that nonsensical ideas which he calls "grand theme."

Perutz concluded:

When I was invited to review the influence of What is Life? I accepted with the intention of doing honor to Schrödinger's memory. To my disappointment, a close study of his book and of the related literature has shown me that what was true in his book was not original, and most of what was original was known not to be true even when it was written.

I like this truly great comment!

Appendix Z*: Bill Nye’s “Undeniable” book

Nye’s book “Undeniable” is a short and very interesting book on evolution. The only problem I have with this book is his erroneous application of the Second Law. In Chapter 3 on “Creationism and the Second Law of Thermodynamics,” Nye identifies at least two “reasons” for not believing in evolution. One is an argument of “incredulity.”

It cannot be true, because I find it so hard to believe that it’s true. But sometimes creationists take a more interesting, science-inspired line of attack and insist that evolution is not physically possible, because no system can naturally become more complex over time. More specifically, they cite evolution for violating one of the most well-established principles in science, the Second Law of Thermodynamics.

Nye correctly rejects this argument; the Second Law cannot be involved in connection with evolution, see section 4.3. Unfortunately, Nye uses the wrong argument to do it:

In commonsense terms, the Second Law is this: Given the chance, balls roll downhill; they never roll uphill on their own. Put another way, energy tends to spread out: Heat spreads out, and lakes never spontaneously freeze on a warm summer day.

This is *not* the Second Law; balls roll downhill because of gravity, not the Second Law. In short, the Second Law cannot be used in connection with life or with evolution.

Then, he cites a quotation from Eddington:

The following quotation is irresistible; it’s from the renowned twentieth-century astronomer Arthur Stanley Eddington:

“The law that entropy always increases – the Second Law of Thermodynamics – holds, I think, the supreme position among the Laws of Nature.”

As a mechanical engineer who took a lot of physics, I am fascinated by this particular creationist argument, because it is both scientifically subtle and completely misinformed. Here’s the most important thing to know: The Second Law applies only to closed systems, like a cylinder in a car engine, and Earth is not even remotely a closed system. Transfers of matter and energy are constantly taking place. Life here is nothing like a perpetual motion machine, but neither is it like a ball rolling inexorably downhill.

Of course, it is true that the Second Law in its entropy-formulation applies to an isolated system (which he refers to as “closed” system). Nye correctly points out that a living system exchanges energy, and materials with its environment, and therefore, the “entropy law does

not apply.” Unfortunately, the author fails to tell the readers of his excellent book that no other formulation of the Second Law applies to any living system.

From here on the author is wrong in almost everything he says about the Second Law. The reader is urged to read carefully the following quotations from pages 21-23 of Nye’s book, and count the number of wrong statements on the Second Law:

The Second Law sets the boundaries; it’s the rule we all have to play by. Starting with energy to study evolution is a great way to understand life. What do living things do with all this energy? We use it to drive chemical systems that obey the Second Law. But the Second Law comes into play everywhere in your life. When you pedal a bicycle, there’s a little bit of friction in the chain joints and the bearings that hold the pedal and cranks.

The tendency for energy to spread out in natural systems might also explain how a kid’s room becomes such a mess.

Now back to those creationists who go all crazy insisting that since disorder always increases, and heat spreads out, Earth and everything on it must be getting more and more disordered. They are completely wrong that the Second Law puts a lid on complexity, because of their confusion (or deception?) about closed versus open systems. But it turns out that the analysis of the flow of energy, especially with the Second Law in mind, is a wonderful way to approach evolution. It provides a useful way to understand the way that living things use the energy that’s available.

The reader is urged to read carefully the above quotations and make notes about each of the errors that he or she encounters.

Here is another meaningless statement connecting “evolution” with the “Second Law.”

Far from violating the Second Law of Thermodynamics, evolution is a powerful validation of the law. Embracing the idea that life adheres to the Second Law is akin to saying that evolution is not random; living things are directed and selected by competition. Life runs on energy, and likewise evolution runs on energy. A system that makes use of energy almost serves as a definition of life.

Finally, in the last paragraph of this chapter the author writes:

That’s what makes the creationists viewpoint not just staggeringly wrong, but sadly impoverished. In twisting around the Second Law of Thermodynamics, they take a powerful tool for understanding the world and try to make it into a barrier to understanding instead. But there is a silver lining here. By inspiring people to learn the fundamental features of nature described by the Second Law of Thermodynamics, creationists can actually inspire a richer appreciation of the mechanism of evolution.

Again, these are wonderful words. I fully agree with the author's rejection of the creationists using (or rather misusing) the Second Law. Unfortunately, the author himself fails in using the Second Law against the creationists' argument. Instead, he could have simply said that neither entropy, nor the Second Law apply to any living system, and certainly not to evolution!

Appendix ZB*: Pinker's outstanding messing "Entropy" with "*human condition*" and "*human affairs*"

Here, another writer who joins the bandwagon and writes whatever comes to his mind on entropy. I am familiar with several excellent books written by Pinker, and I must admit I admire his writings. Unfortunately, this book is exceptionally dull and a scientifically misleading book.

In February 2017, I read an article by Steven Pinker entitled:

What Scientific term or concept ought to be more widely known?

I did not like most of what was written in this article. Since I know that Pinker is a psychologist not a physicist, I thought it would be helpful to point out some errors and misconceptions in his article.

On Feb 8th I sent him an email:

Dear Steven,

I read several of your books, on Blank Slate, Mind Works etc., and I admire your writings. I read some paragraphs that you wrote on the Second Law. I found that what you wrote is the very common erroneous view of entropy and the Second Law, which is propagated in the literature, both in text books and popular science books.

All the best,

Arieh

On Feb 9th Pinker replied:

Dear Arieh,

Thanks for your note, If it is possible to identify the sentences in the newspaper article that you found erroneous and explain what you feel is wrong with them, that would be more helpful.

Best,

Steve Pinker

I did as he requested and sent him his own article and noted where he was wrong. I never heard from him again.

Here are a few excerpts from Pinker's article along with my comments:

The title:

WHAT SCIENTIFIC TERM OR CONCEPT OUGHT TO BE MORE WIDELY KNOWN?

The subtitle:

The Second Law of Thermodynamics

Although it is not said explicitly, it is clear that the subtitle is meant to be the answer to the question posed in the title.

The opening sentence:

The Second Law of Thermodynamics states that in an isolated system (one that is not taking in energy), entropy never decreases.

This is correct, except that the characterization of an isolated system is deficient. An isolated system is a system with fixed energy, volume and number of particles. Also, one can add that such a system does not interact with its surroundings. Note also that Pinker does not bother to define entropy.

Clearly, if one accepts this formulation of the Second Law, it is far from clear why this law should be “more widely known.” The answer to this question is contained in the rest of Pinker’s article. In short, entropy and the Second Law are viewed as the most powerful driving force underlying everything that happens. Accepting this distorted view of entropy and the Second Law, it becomes obvious that the Second Law should be known by everyone.

Here are a few incorrect statements which I found in the article that I marked them in my letter to Pinker:

“Now order could be characterized in terms of the set of all microscopically distinct states of a system: Of all these states, the ones that we find useful make up a tiny sliver of the possibilities, while the disorderly or useless states make up the vast majority. It follows that any perturbation of the system, whether it is a random jiggling of its parts or a whack from the outside, will, by the laws of probability, nudge the system toward disorder or uselessness. If you walk away from a sand castle, it won’t be there tomorrow, because as the wind, waves, seagulls, and small children push the grains of sand around, they’re more likely to arrange them into one of the vast number of configurations that don’t look like a castle than into the tiny few that do.”

“Scientists appreciate that the Second Law is far more than an explanation for everyday nuisances; it is a foundation of our understanding of the universe and our place in it.”

As I pointed out in my letter to Pinker, nothing is true in these statements, see below for more details.

Then, Pinker quotes the lecture by Snow from 1959:

“In his famous 1959 lecture “The Two Cultures and the Scientific Revolution,” the scientist and novelist C. P. Snow commented on the disdain for science among educated Britons in his day:

Below are two more paragraphs from Pinker’s article which at best can be said to be plain nonsense.

“To start with, the Second Law implies that misfortune may be no one’s fault. The biggest breakthrough of the scientific revolution was to nullify the intuition that the universe is saturated with purpose: that everything happens for a reason. In this primitive understanding, when bad things happen—accidents, disease, famine—someone or something must have wanted them to happen. This in turn impels people to find a defendant, demon, scapegoat, or witch to punish. Galileo and Newton replaced this cosmic

morality play with a clockwork universe in which events are caused by conditions in the present, not goals for the future. The Second Law deepens that discovery: Not only does the universe not care about our desires, but in the natural course of events it will appear to thwart them, because there are so many more ways for things to go wrong than to go right. Houses burn down, ships sink, battles are lost for the want of a horseshoe nail.”

The Second Law does not imply “that misfortune may be no one’s fault...”

And the Second Law does not “deepen that discovery...”

I will stop discussing Pinker’s article at this point since the same statements in the article appeared later in his book titled “*Enlightenment Now*” which I will discuss below.

First, I would like to make a comment regarding C.P. Snow’s article:

“The two Cultures and the Scientific Revolution:

Although a well-known and well-quoted article, I believe it is sometimes over-interpreted and sometimes misinterpreted. Personally, I did not find the idea of “two cultures” interesting. There are far more than two cultures, and I do not think that a “culture” – any culture – may be characterized by people’s ability to quote Shakespeare, the Second Law or any other law. Thus, the title of Snow’s article might be misleading.

Note that Snow did not talk about *quoting* the Second Law, but about “*describing*” the Second Law. I also take the liberty to say that either “quoting” or “describing” the Second Law does not mean much. The question is whether people can *quote* or *describe* or *state* the Second Law correctly!

In this respect, I doubt whether Snow himself could quote or describe the Second Law *correctly*. Atkins (2007), who also “quotes” Snow’s article, expressed doubts about Snow’s knowledge of the Second Law. Unfortunately, Atkins himself did not quote the Second Law correctly! For details see Ben-Naim (2017b)

In 2018, Pinker published a new book: “**Entitlement Now.**” In this book Pinker repeats the same nonsenses and meaningless statements on entropy and the Second Law, completely ignoring my letter and my comments to his article.

In the book's preface the author begins with a few quotations by people who have a "dark vision" of the state of the world (poverty, crimes, etc.), and then promises:

In the pages that follow, I will show that this bleak assessment of the state of the world is wrong. And not just a little wrong – wrong wrong, flat-earth wrong, couldn't-be-more wrong...I will present a different understanding of the world, grounded in fact and inspired by the ideals of the Enlightenment: reason, science, humanism, and progress. Enlightenment ideals, I hope to show, are timeless, but they have never been more relevant than they are right now.

I doubt that this promise is fulfilled. In the following I will focus only on Pinker's usage of *entropy* and the *Second Law* in discussing topics that have nothing to do with entropy and the Second Law. I will show that Pinker is: "not just a little wrong – wrong wrong, flat-earth wrong, couldn't-be-more wrong."

Pinker is an example of a non-physicist who quotes what physicists say about entropy and the Second Law, and takes the liberty in extending the applicability of these concepts to realms in which they cannot be applied.

In Chapter 2, titled: "Entro, Evo, Info" (short for Entropy, Evolution and Information), the author first introduces entropy and the Second Law:

The first keystone in understanding the human condition is the concept of entropy or disorder, which emerged from 19th-century physics and was defined in its current form by the physicist Ludwig Boltzmann. The Second Law of Thermodynamics states that in an isolated system (one that is not interacting with its environment), entropy never decreases.

Take note that the author correctly states the Second Law (for isolated systems), but does not define entropy. In the first sentence we find "entropy or disorder" as if these two concepts are synonymous.

Interestingly, the references to the "definition" of entropy and the Second Law do not include any textbook on thermodynamics. Instead, we find references to Atkins (2007), Carroll (2016), and Lane (2015). The first two references were already discussed in chapter 4 and Ben-Naim (2016a, 2017b, 2018c). The last two reference contains the same nonsensical ideas about entropy as discussed in Pinker's book.

Unfortunately, neither entropy nor disorder is a “keystone” in understanding the “human condition.” In fact, entropy was never defined for “human conditions.” This introductory statement is a harbinger of fictitious and nonsensical ideas involving entropy and the Second Law.

After the opening statement the author asks the question:

“How is entropy relevant to human affairs?”

This question should have been asked by the author *before*, and not *after* stating that entropy (or order) is a keystone in understanding the human condition. The correct answer to this question is simple: **Entropy is totally irrelevant to any living system, and certainly irrelevant to “human affairs.”**

Pinker does not answer this question. Instead, he describes how “*life and happiness*” depends on “*an informational sliver of orderly arrangements of matter amid astronomical number of possibilities.*” This, of course is a typical echo of numerous statements we find about life which are commonly written in popular science books. Perhaps, the only “original” contribution of Pinker to this nonsensical idea about “life” is the inclusion of “happiness” in his discussion of the Second Law. I have no idea wherefrom the author got the idea that “happiness” depends on the “*orderly arrangements of matter.*” I wonder whether sorrow and sadness depend on “disorderly” arrangement of matter.

On page 16 the author reveals to the reader how entropy is involved in everyday life:

The law of entropy is widely acknowledged in everyday life in sayings such as “Things fall apart,” “Rust never sleeps,” “Shit happens,” “Whatever can go wrong will go wrong,” and (from the Texas lawmaker Sam Rayburn) “Any jackass can kick down a barn, but it takes a carpenter to build one.”

Of course, it goes without saying that none of these phenomena have anything to do with the Law of Entropy (perhaps with the exception of “shit happens?”). It is true that such statements are very common in popular science books. But this fact does not make such statements true.

Next, the author quotes Eddington's statement on the Second Law which we have discussed in Section 4.2. The unwary reader might get the impression that the quotation from Eddington which was raised here supports the claims of the author. Unfortunately, the quotation from Eddington is totally irrelevant to the author's statement.

Before doing so he claims:

Scientists appreciate that the Second Law is far more than an explanation of everyday nuisances. It is a foundation of our understanding of the universe and our place in it.

The Second Law *does not* explain any of our "everyday nuisances," and it *is not* the foundation of understanding the universe (whatever that means – see section 4.4), and certainly not "our place in it" (wherever we may be in the universe). This trick is quite common in popular science books: You make an unfounded statement, then either provide a reference to, or provide a quotation from some famous scientist which is totally irrelevant to your statement. This is similar to Shermer's book, see Appendix W.

Next, he quotes the (misleading) title of Atkin's book "Four Laws That Drive the Universe." As I have discussed in my book "*The Four Laws that do not Drive the Universe*," Atkin's book is totally misleading, not only in claiming that the Laws of Thermodynamics drive the universe (whatever that means), but also in assigning all kinds of fancy attributes to entropy. Unfortunately, Atkin's book is still widely quoted, and continues to mislead and confuse scientists and non-scientists alike about entropy and the Second Law.

From Atkin's quotation the author continues to even more pompous but meaningless statements by the evolutionary psychologists Tooby, Cosmides, and Barrett:

"The Second Law of Thermodynamics is the First Law of psychology"

The Second Law has nothing to do with psychology! This is pure Kishkush! Citing this quotation makes the whole discussion of the author in this chapter a great Kishkush!

Following this, Pinker adds his own statement (which begs the question as to whether it is original) to the chorus of pompous and ignominious contribution:

Why the awe for the Second Law? From an Olympian vantage point, it defines the fate of the universe and the ultimate purpose of life, mind, and human striving: to deploy energy and knowledge to fight back the tide of entropy and carve our refugees of beneficial order.

It is remarkable how much nonsense can be jammed into one sentence. The Second Law *does not define* the fate of the universe (whatever that means), *it does not define* the ultimate purpose of life (whatever that means), *not* the mind, *not* the human striving to deploy energy and knowledge... A string of beautiful words, poetic even which makes a vacuous sentence!

Before he moves on to discuss the second “keystone in understanding human condition” we find two more “original” meaningless ideas about entropy and life:

“The fact that we find these configurations beautiful, incidentally, suggests that beauty may not just be in the eye of the beholder. The brain’s aesthetic response may be a receptiveness to the counter-entropic patterns that can spring forth from nature.”

“Living things are made of organs that have heterogenous parts which are uncannily shaped and arranged to do things that keep the organism alive (that is, continuing to absorb energy to resist entropy).”

Highly graded pure nonsense!

The second “keystone” is “Evo,” short for evolution. Just before he attacks creationists who use the Second Law in criticizing evolutionists, the author explains the basic elements of the evolution mechanism. One central element is the occurrence of mutations. Sometimes, these mutations occur as a result of errors in copying the information contained in the DNA. Contrary to what the author says such errors have nothing to do with the “Law of Entropy.”

It is true that invoking the Second Law by creationists is ridiculous. This has already been criticized by Dawkins and by many others. However, the invalidity of the creationists argument is not due to the fact that living organisms are not isolated systems (or closed systems as the author claims), but simply because the Second Law *does not apply* to any living system.

Having done with the second keystone the author moves on to the third: Info, short for information. On page 19, we find:

Information may be thought of as a reduction in entropy – as the ingredient that distinguishes an orderly, structured system from the vast set of random, useless ones.

Here, the author echoes the common confusion between entropy, Shannon’s measure of information, and information.

On page 21 we find another involvement of entropy:

“Getting back to evolution, a brain wired by information in the genome to perform computations on information coming in from the senses could organize the animal’s behavior in a way that allowed it to capture energy and resist entropy. It could, for example, implement the rule “If it squeaks, chase it; if it barks, flee from it.”

Capturing energy may be meaningful. Resisting entropy is meaningless as resisting volume, resisting time, or resisting the number of holes in a pretzel. See prologue for clarification.

A similar idea about entropy is expressed on page 23:

Energy channeled by knowledge is the elixir with which we stave off entropy, and advances in energy capture are advances in human destiny.

“Staving off entropy” is a reflection of Seife’s ideas (see Appendix L) about the “ravages of entropy.” As I mentioned several times in this book, including in the Preface, *entropy does not do anything to anything*. It certainly does not ravage anything. Therefore, it is pointless in “resisting entropy” or “staving off entropy.” See also Shermer’s ideas in Appendix W. It is better to embrace entropy as a beautiful, well-defined, well-interpreted, and totally harmless concept. Yes, as harmless as the number of holes in a pretzel!

As many before him, Pinker proceeds to discuss the involvement of entropy in personal “*human condition*,” and “*human affairs*” to social phenomena, See also Appendix ZC.

“Poverty, too, needs no explanation. In a world governed by entropy and evolution, it is the default state of humankind.”

Indeed, poverty needs no explanation. What does it have to do with Entropy that does not govern anything? Of course, this is not Pinker's original idea: Atkins and many others have said it before, see Appendix ZC.

Unlike the cells in a body or the individuals in a colonial organism, humans are genetically unique, each having accumulated and recombined a different set of mutations that arose over generations of entropy-prone replication in their lineage.

Perhaps, "Entropy-prone replication" is an original idea, but it is still as meaningless as all the other ideas about the involvement of entropy in human affairs and evolution. See also the end of section 4.3.

Here is another irrelevant "implication" of the Law of Entropy:

Another implication of the Law of Entropy is that a complex system like an organism can be easily disabled, because its functioning depends on so many improbable conditions being satisfied at once.

This statement is not only wrong, it also insinuates the erroneous implication on probability, see section 3.6. Towards the end of the chapter, we find yet another comment which elicits a smile from me:

Yet another implication of the Law of Entropy; harms are easier to inflict and have larger effects than benefits.

One can argue whether it is true or not that it is easier to inflict harm, and have a larger or smaller effect than benefits. In fact, one cannot make such general a statement without specifying which harm and which effect are involved. One thing is clear however, the harms caused by Pinker's book are certainly greater than its benefits.

In any case, one should *never* even mention the Law of Entropy in connection with such an argument, as well as in all other topics discussed in the whole book on "Enlightenment." The above quoted sentence turns from a legitimate debatable question into a plain silly and meaningless Kishkush!

By the way, if you insist in having an explanation of why *“harms are easier to inflict... than benefits”* you should consider the implication of the Pretzel-Second Law, as discussed in the Prologue.

The next chapter is about “Counter-Enlightenments.” There is not much about entropy except two repetitions about entropy being the greatest villain that is our “enemy” and should be resisted. Here are the two quotations from page 32:

“The romantic Green movement sees the human capture of energy not as a way of resisting entropy and enhancing human flourishing but as a heinous crime against nature, which will exact a dreadful justice in the form of resource wars, poisoned air and water, and civilization-ending climate change.”

“Our greatest enemies are ultimately not our political adversaries but entropy, evolution (in the form of pestilence and the flaws in human nature), and most of all ignorance – a shortfall of knowledge of how best to solve our problems.”

In my opinion, neither “evolution” nor “ignorance” are our greatest “enemies.” As for “entropy” it is as harmless as a lamb and cannot hurt anyone. I personally consider entropy as my best and dearest friend. I suggest to the author to read my book “Entropy for Smart Kids” and I am sure he will never see entropy as his enemy, ever again (Ben-Naim (2019)). As an alternative “enemy” I would suggest to consider the number of holes in the pretzels discussed in the Prologue. These are really *“Our greatest enemies.”*

The next chapter on “Life” starts with the beautiful words:

“The struggle to stay alive is the primal urge of animate beings, and humans deploy their ingenuity and conscious resolve to stave off death as long as possible.”

“Staving off death as long as possible” is, of course an important goal; something everyone will agree with. This chapter presents some statistical data on “life expectancy,” “child mortality,” and “maternal mortality.” Then he discusses the question of extending life-expectancy, and perhaps even “immortality.”

The fact is that life expectancy of humans have steadily increased during the past two centuries (see Figure 5.1 on page 54 of Pinker’s book). It is also plausible that this trend will continue in the future. Whether or not we shall achieve immortality is a question we

cannot answer. Not even Ray Kurzweil can forecast that “*those of us who make it to 2045 will live forever.*” This is impossible to predict. Even if you live for hundreds, thousands, or millions of years you will never be able to say that you shall live forever. You will *have to live forever*, first, before you can claim that you *lived forever!* This is, of course an absolute impossibility.

Setting aside the question of the achievability of immortality, I can categorically say that there exists no law of physics, chemistry, or biology that precludes that possibility. I had a similar comment about immortality in section 4.3 in connection with Shermer’s book discussed in Appendix W. Therefore, I strongly object to two of the statements made by the author on page 61:

“Lacking the gift of prophecy, no one can say whether scientists will ever find a cure for mortality. But evolution and entropy make it unlikely.”

“And even if we were fitted with perfectly tuned biological hardware, the march of entropy would degrade it.”

Either “evolution” or entropy do not, and cannot affect anything associated with longevity or immortality, and there is no such thing as “*the march of entropy.*” Entropy, as volume of a specific system, never marches!

The chapter concludes with two meaningless, and silly quotations: The first is Stein’s Law: “*Things that cannot go on forever don’t.*”

The second by Davies: “*Things that can’t go on forever can go on much longer than you think.*”

Personally, I think that it is shameful to quote these *shameful* (nonexistent) “laws.” These are “laws” as meaningful as the Pretzel-Second Law, discussed in the Prologue.

In Chapter 22 on “Science” the author quotes a statement by Sean Carroll who argues in his book, “The Big Picture” [see a review of this book in Ben-Naim (2018b)], that the laws of physics underlying everyday life are “*completely known.*” This is not true. In fact, it is not clear what one means by “everyday life.” Is there any known law of physics

underlying my thinking, my feelings, and my writing this book? No one knows such laws of physics. I have no idea why Pinker raises this topic in a book on Enlightenment.

I will conclude my partial review of Pinker's book with one quick quotation from pages 414-415:

As I mentioned in Chapter 2 (following an observation by John Tooby), the Law of Entropy sentences us to another permanent threat. Many things must all go right for a body (and thus a mind) to function, but it takes just one thing going wrong for it to shut down permanently – a leak of blood, a constriction of air, a disabling of its microscopic clockwork.

It is quite evident by now that Pinker, as scores of others has been “indoctrinated” by popular science books written by irresponsible authors who do not understand entropy, but audaciously and irresponsibly “invent” all kinds of powers which are ascribed to the innocent and harmless concept of entropy. See also my Epilogue for my own contribution to “enlightenment.”

Appendix ZC*: Kafri and Kafri's contribution to misleading the public on the unlimited powers of the Second Law

I will start with the description of the content of the book: **Entropy: God's Dice Game**, as it appears in Amazon.com and on the back cover of the book by Kafri and Kafri (2013):

“Why do we want more and more money regardless of how much we already have? Why do we hate to be manipulated and to lose? Why do twenty percent of the people own eighty percent of the wealth? Why in most languages, the most common word appears twice as often as the second most common word? Why the digit “1” appears in company balance sheets six and a half times more often than the digit “9?” Why does nature hate “bubbles?”

The cause for all these phenomena is the very same law that makes water flow from high to low, and heat – from hot place to a cold one. This law, which for historical reasons is called the Second Law of thermodynamics, states that there is a never-decreasing and always increasing quantity called “entropy.”

The entropy represents the uncertainty of a system in hypothetical equilibrium state in which everybody and everything have equal opportunities but slim chances to win; or in other words - the majority have little and a few have a lot. The book describes the historical

evolution of the understanding of entropy, alongside the biographies of the scientists who contributed to its definition and exploration of its effects in exact sciences, communication theory, economy and sociology. The book is of interest to wide audience of scientist, engineers, students and the general public alike.

I agree with only half of a sentence in cited paragraph “*Entropy represents the uncertainty of a system.*” This is true provided one specifies “uncertainty.” The question is; uncertainty, with respect to what? This topic is discussed in section 1.4, where I explained the uncertainty-interpretation of the Shannon’s measure of information.

The second part of this sentence: “Where everybody and everything have equal opportunities but slim chances to win.” This is a meaningless sentence which has nothing to do with entropy.

Oded Kafri is a friend of mine. He gave me a copy of his book. I read the entire book and I was convinced that the authors are totally wrong about everything they wrote in their book. What I will write below, I also said in private conversation with Oded Kafri.

The book starts with a wrong “definition” of entropy, then proceeds to discuss all kinds of imaginary powers assigned to entropy and the Second Law. In the book’s prologue, the authors write: “*Entropy’s tendency to increase is the source of all changes in our universe,*” and then: “*The Second Law is actually something of a super law, governing nature as it does.*”

The truth is that Entropy has no tendency to increase, it is not the source of any change, and the Second Law *does not govern anything!*

After reading their book I wrote to Oded Kafri to ask him whether making love and having children are also results of the Second Law. His answer was:

“Of course, everything that happens in the universe is a result of the Second Law. Read my book and you will be convinced.”

I read their book, I was convinced that they have no idea what entropy is and what the Second Law states!

In the book’s prologue they write:

Entropy is a physical quantity, yet it is different from any other quantity in nature. It is definite only for systems in a state of equilibrium, and it tends to increase: in fact, entropy's tendency to increase is the source of all changes in our universe.

It is true that entropy is defined for systems at equilibrium. This is the meaning of a *state function*. Once entropy is defined for a system at equilibrium, it does not change, it does not tend to increase and it is not the *source of all changes*!

Here is another paragraph from the Prologue:

“The main quantity behind the Second Law of thermodynamics is entropy – which is a measure of uncertainty. The forces deployed by entropy are not as strictly determined as those described by other laws of nature. They are expressed as a tendency of changes to occur, in a manner somewhat analogous to human will. In order for entropy to increase, energy must flow; and any flow of energy that leads to change, increases entropy. This means that any action in nature – whether “natural” or man-made – increases entropy. In other words, entropy’s tendency to increase is the tendency of nature, including us humans, to make energy flow.”

“Measure of uncertainty,” as explained in section 1.4, is meaningless unless one specifies “uncertainty with respect to what.” Not every action in nature increase entropy!

An original idea appears on page 21:

But as we shall see, part of the difficulty inherent in understanding the Second Law and its accompanying evasive quantity, entropy, stems from the difficulty in properly understanding the concept of temperature (or, alternatively, from actually misunderstanding its nature).

Temperature is relatively easy to understand. Its understanding has nothing to do with the understanding of entropy or the Second Law!

Regarding the choice of the title of the book, the authors write:

So, it seems that contrary to Einstein’s famous quote that “God does not play dice with the world,” logical entropy and its expression in probability distributions proves that God does, indeed, play dice, and actually plays quite fairly.

This is, of course, a charmingly silly and misleading statement, first because there is no such a thing as “logical entropy.” Second, what the authors means by “logical entropy” is SMI, and SMI does not prove that God plays dice, let alone the claim that God plays dice

“quite fairly.” Contrary to what the authors say in the quotation above, one can conclude that this book is not “*contrary to Einstein’s famous quote,*” but in fact it proves one of Einstein’s famous quotes! See quotation- page of this book.

On pages 144 and 145,

During this journey, we came to realize that there is a significant difference between entropy and most the other physical quantities in nature.

They explain that unlike mass, time length, etc. which are measurable quantities, entropy is not measurable:

But there is no “entropy meter.”

Concluding that:

The fact that entropy cannot be measured directly is of great help for scientists in the field: they can write about entropy almost anything that comes to mind. At the same time, it demonstrates the fact that entropy is different from all these other physical quantities.

Ironically, the authors do exactly just that; they write about entropy and the Second Law with *whatever comes to their minds!*

Most of the book discusses many other interesting topics from “Bedford’s Law” to “Zipf’s Law” to “Pareto Principle,” and all of these are not laws of science, and they have nothing to do with either entropy or the Second Law. In addition, the authors claim that the tendency of entropy to increase is the powerful machine that drives everything, including our decisions to do things, to reproduce, and even social changes associated with our culture. All these topics do not belong to physical science and certainly not to the Second Law.

Regarding the “scientific part,” the author starts with a *definition*, or better said an ill-definition of entropy. None of the phenomena discussed in their book follow from the entropy, or from what they *define* as entropy.

While reading this book, I exchanged a few emails with Oded Kafri where I expressed my disagreement with what they wrote.

Interestingly, Oded wrote back and told me that if only I read their books carefully, and with an open mind, I will *change* my mind.

I read carefully their book and I still disagree with almost everything they wrote.

To conclude, Kafri and Kafri's book contains some short biographical notes on people who contributed to the Second Law of Thermodynamics. Scientifically, it contains nothing true on either entropy or the Second Law.

Appendix ZD*: Bekenstein on Black-Hole Entropy

In section 4.4 we discussed the inapplicability of the concept of entropy to black holes. In this Appendix we present some quotations from Bekenstein on black-hole entropy.

In a paper titled: "Black-Holes and Entropy", Bekenstein (1973) starts from the following observations:

There are a number of similarities between black-hole physics and thermodynamics. Most striking is the similarity in the behaviors of black-hole area and of entropy: Both quantities tend to increase irreversibly.

Then the author continues:

"We show that it is natural to introduce the concept of black-hole entropy as a measure of information about a black-hole interior which is inaccessible to an exterior observer."

In my view, the existence of "similarity" between black-hole physics and thermodynamics does not necessarily mean that there should be a connection between the two. From these similarities, Bekenstein suggested that *"we already have a concept of energy in black-hole physics, and the above observation suggests that something like entropy may play a role in it."*

What could that something *like* entropy be?

"The physical content of the concept of black-hole entropy derives from the following generalized version of the Second Law: When common entropy goes down a black hole,

the common entropy in the black-hole exterior plus the black-hole entropy never decreases. The validity of this version of the Second Law is supported by an argument from information theory as well as by several examples.”

Here, common entropy means the thermodynamic entropy. There is no such thing as “*the common entropy in the black-hole exterior plus the black-hole entropy...*”

The main point of the article is:

“It is clear that changes of a black hole generally take place in the direction of increasing area. This is reminiscent of the Second Law of thermodynamics which states that changes of a closed thermodynamic system take place in the direction of increasing entropy. The above comparison suggests that it might be useful to consider black hole physics from a thermodynamic viewpoint: We already have the concept of energy in black-hole physics, and the above observation suggests that something like entropy may also play a role in it. Thus, one can hope to develop a thermodynamics for black holes -at least a rudimentary one. In this paper we show that it is possible to give a precise definition of black-hole entropy. Based on it we construct some elements of a thermodynamics for black holes.”

“In Sec. II we point out a number of analogies between black-hole physics and thermodynamics, all of which bring out the parallelism between black-hole area and entropy. In Sec. III, after a short review of elements of the theory of information, we discuss some features of black-hole physics from the point of view of information theory.”

As I noted in section 4.4.3 the analogy between entropy and some properties of black holes is not sufficient for justifying the introduction of the concept of black-hole entropy. It is also clear that Bekenstein misuses Information theory in order to establish the concept of black-hole entropy.

Indeed, in section III of his article he makes it clear that:

“The connection between entropy and information is well known. The entropy of a system measures one's uncertainty or lack of information about the actual internal configuration of the system. Suppose that all that is known about the internal configuration of a system is that it may be found in any of a number of states with probability p_n for the n th state. Then the entropy associated with the system is given by Shannon's formula...”

Since nothing is known about the “internal configuration of the system,” there is no way to define the Shannon measure of information on any distribution of black-holes.

“It is then natural to introduce the concept of black-hole entropy as the measure of the inaccessibility of information (to an exterior observer) as to which particular internal configuration of the black hole is actually realized in a given case.”

In my opinion it is also clear that Bekenstein confuses the concept of SMI with the general concept of information. See also section 4.4.3. In fact, Bekenstein admits that the BH entropy is not the “thermal entropy”:

At the outset it should be clear that the black-hole entropy we are speaking of is not the thermal entropy inside the black hole. In fact, our black-hole entropy refers to the equivalence class of all black holes which have the same mass, charge, and angular momentum, not to one particular black hole. What are we to take as a measure of this black-hole entropy?

To conclude, it is clear that black-hole entropy is not entropy!

First, one can rule-out the thermodynamic entropy as defined by Clausius. One cannot make any measurements on a black-hole, specifically one cannot determine its heat capacity.

Second, it is not possible to define the Boltzmann entropy for black-holes. This requires some knowledge of the total number of accessible states, W . Unfortunately, it is not clear how to calculate the energy-states of a black-hole, or which other states to include in W . Therefore, the Boltzmann entropy is ruled out.

What remains is the entropy derived from the Shannon’s measure of information (SMI). To do so, one needs to evaluate the relevant distributions which maximize the SMI. These were referred to as the equilibrium distributions in Chapter 2. It is only for these equilibrium distributions that the value of the SMI becomes identical (up to a multiplicative constant) with the entropy of the system.

Since we do not know what these equilibrium distributions in black-holes are, this approach is ruled out too. In fact, Bekenstein uses arguments from information theory, and uses the SMI to which he referred to as Shannon entropy. As we have noted in Section 1.4, the SMI is, in general not entropy. Indeed, Bekenstein alluded to this by stating:

Although there can be little doubt that black-hole entropy corresponds closely to a phenomenological entropy, its deeper meaning has remained mysterious.

Does it stand for information lost in the transcendence of the hallowed principle of unitary evolution? I would claim that at this stage the usefulness of any proposed interpretation of black-hole entropy turns on how well it relates to the original “statistical” aspect of entropy as a measure of disorder, missing information, multiplicity of micro-states compatible with a given macrostate, etc.

In my view, all these interpretations of the entropy should *follow* the definition of black-hole entropy, not precede it. Since the thermodynamic entropy is not definable for black holes, there is no justification to speculate about the *information* of black holes, information *lost* in black holes, or information *swallowed* by black holes, etc. as is common in popular science books.

Appendix ZF*: Bridgman’s book on “The Nature of Thermodynamics”

Bridgman’s (1961) introduction to his book, “The Nature of Thermodynamics,” emphasizes that thermodynamics apply to well-defined equilibrium states.

But all these analyses are subject to the essential restriction that the states of the system with which the analysis deals are states for which the entropy must be defined in classical terms, that is, they are states for which some reversible path exists connecting them with the fiducial state, although the actual process may be one for which the path is irreversible.

He specifically mentions the applicability of entropy of living systems:

“For example, all living systems are of this nature and technically the concept of entropy may not be applied to such systems.”

On page 148 he also expressed doubts regarding the application of the concept of entropy to the entire universe.

Another question to which we are led naturally...is as to the meaning of the “entropy of the entire universe.” Of course our original definitions have no application, for they were limited to reversible processes in isolated systems, and the universe is not isolated, nor its processes reversible.

Later, he further elaborates on the question of whether the universe is finite or infinite. Although Bridgman is wrong in stating that the definitions of entropy apply to “reversible

processes,” it is clear that he expresses serious doubts about the application of the concept of entropy to either living systems or to the entire universe.

I should also add a comment regarding Bridgman’s view on “entropy as disorder.” On page 166 we find:

It is not easy to give a logically satisfying definition of what one would like to cover by “disorder,” and it has been a favorite topic for discussion... “disorder” is therefore not an absolute, but has a meaning only in context.

Appendix ZG*: Earman on the Past hypothesis

Here is an article by Earman (2006), On: *The “Past Hypothesis”: Not even false.*

I like and agree with the title of Earman’s article, but I do not agree with much of what is said in the article itself.

In the Abstract Earman writes:

It has become something of a dogma in the philosophy of science that modern cosmology has completed Boltzmann’s program for explaining the statistical validity of the Second Law of thermodynamics by providing the low entropy initial state needed to ground the asymmetry in entropic behavior that underwrites our inference about the past. This dogma is challenged on several grounds. In particular, it is argued that it is likely that the Boltzmann entropy of the initial state of the universe is an ill-defined or severely hobbled concept.

I agree that “*it has become a dogma...*,” however, I do not agree with the assertion that the entropy of the universe (at any stage) is “ill-defined.” I simply claim that the entropy of the universe *is not definable* either at the present or in the “initial state.”

Then, he continues to describe the “Low entropy” of the universe at the initial state:

It is also argued that even if the entropy of the initial state of the universe had a well-defined, low value, this would not suffice to explain why thermodynamics works as well as it does for the kinds of systems we care about.

Needless to say, since the entropy of the initial state of the universe is not defined, it is pointless to argue “*why thermodynamics works as well as it does....*”

Later in the article he writes:

...so a living being that finds itself in such a world at a certain period of time can define the time direction as going from the less probable [lower entropy] to the more probable [higher entropy] states (the former will be the “past” and the latter will be the “future”) and by virtue of this definition he will find that this small region, isolated from the rest of the universe, is “initially” always in an improbable [low entropy] state. (Boltzmann, 1897b, p. 242) It is not clear how seriously Boltzmann took this proposal for a define-your-way solution to the asymmetry problem.

There is no way any living system “can define the time direction as going from the less probable [lower entropy] to the more probable [higher entropy] states.”

Moreover, the identification of “less probable state” with “lower entropy,” and the “more probable state” with “higher entropy” is meaningless! See section 3.6.

Finally, in the article’s conclusion he repeats what he had mentioned in the abstract:

Moreover, there are good reasons for thinking that the alleged solutions to these problems that invoke the Past Hypothesis is badly flawed.

Thus, although I agree with the general “critical tone” of Earman’s article, I do not agree with his arguments, and not with his conclusion. The “Past Hypothesis” is a meaningless hypothesis mainly because it involves the undefinable concept of “entropy of the universe” as well as the meaningless assertion that the entropy of the universe is increasing!

In the same article, Earman (2006) states the “*Boltzmannian version of the Second Law...*” as follows: If at $t=0$ the Boltzmann entropy $S(0)$ of the system is low; then for some appropriate t , it is highly probable that, $S(t) > S(0)$.

I disagree! In my view, if the entropy of a system is defined, then it does not change with time. On the other hand, when the state of the system changes with time, the entropy is not defined. In other words, entropy of a specific system is either defined or not. When it is defined it has a fixed value and it is not a function of time.

In another article, Earman (2002) writes:

Abstract: *David Albert’s Time and Chance (2000) provides a fresh and interesting perspective on the problem of the direction of time. Unfortunately, the book opens with a highly non-standard exposition of time reversal invariance that distorts the subsequent discussion. The present article not only has the remedial goal of setting the record straight*

about the meaning of time reversal invariance, but it also aims to show how the niceties of this symmetry concept matter to the problem of the direction of time and to related foundation issues in physics.

I agree with his general criticism of the Past Hypothesis” but for very different reasons. See Appendices Q and R.

Appendix ZH*: Gleick’s book on “Time Travel, A History”

This book is on Time Travel written by an excellent writer of popular science books. Here is the book’s content as described in the jacket-cover.

From the acclaimed author of the Information and Chaos, here is a mind-bending exploration of time travel: its subversive origin in literature and science, and its influence on our understanding of time itself.

Indeed, as his book on “Information” and “Chaos,” it is a good, well-written history of the evolution of the concept of entropy in the literature. Both books are better described as *concept-bending*, rather than “mind-bending.” In this appendix I will discuss only the “entropy-aspect” of his book. Therefore, this appendix is not a review of Gleick’s book, nor is it a criticism of the author’s writing. Instead, it is only an example of the “mechanism of propagation,” a wrong idea in some popular science books.

Specifically, as I wrote several times in my present book, any book on time should not mention entropy as much as any book on thermodynamics should not mention time. Gleick’s book has a particularly amusing aspect of the relationship between entropy and time.

Normally, when you look at the index of a book you expect to find information on the pages in which certain concepts are discussed.

Usually, in a book on *time* I would not expect to find an entry on entropy or the Second Law. As much as I would not look for the entry “entropy” or Napoleon’s biography in a book on “geometry.”

Take a look at page 326 of the Index where you will find:

Entropy, 97, 115, 116-121, 174, 310

Arrow of time, 116-121, 130

Thermodynamic equilibrium (heat death), 120-121, 157

On pages 97, 115, 116, 174, 310, 119-120, 157 the word entropy is mentioned; we shall soon discuss how “entropy” is misrepresented on all these pages. Before doing so I should mention that in pages 130 and 268 “entropy” is not mentioned. I went over the text of both pages thoroughly, and even asked my wife to check, and the word “entropy” was never mentioned on these pages. Were these two pages, featured in the Index under “entropy” by mistake? Probably not, according to the author’s view (more precisely, according to what numerous authors have written before about entropy). The mysterious non-appearance of “entropy” on pages 130 and 268 is quite simple; the erroneous association of “entropy” with the “arrow of time.” This association is so deeply entrenched in the minds of physicists (hence, in the author’s mind as well), that the two concepts “entropy” and “arrow of time” are considered as synonyms. Thus, the fact that on these two pages “arrow of time” is discussed is sufficient enough reason for the author to include pages 130 and 268 under the entry of “entropy” in the index.

Having done with the pages on which entropy is not discussed (yet appear in the Index under the entry “entropy,”) let us briefly look at what the author has to say about entropy. As you will see nowhere in the book is “entropy” defined, and nowhere in the book will you find a correct statement about entropy. Instead, you find a lot of nonsense, irrelevant to, and sometimes silly statements about, entropy.

On pages 115 to 121, there is a long discussion of the “Arrow of Time,” where the standard baloney about Eddington’s ideas are discussed (see also Appendix P). Specifically, Eddington’s book: “The Nature of the Physical World” is quoted.

On page 118 there is also a quotation from Maxwell on the Second Law.

Moral: The 2nd law of Thermodynamics has the same degree of truth as the statement that if you throw a tumblerful of water into the sea, you cannot get the same tumblerful of water out again.

I have criticized this erroneous statement in my earlier books; Ben-Naim (2012, 2016b). Here, I will just comment that this quotation is totally irrelevant to “time” or to “time travel.” I have no idea why it was mentioned in Gleik’s book.

On page 120 is another standard misinterpretation of the Second Law.

The universe tends toward maximum entropy, the condition of ultimate disorder from which there is no return.

On page 157, perhaps another original, non-standard meaningless discussion of eternity and entropy.

Since this Eternity is created not only by theologians but by technocrats, it does have a beginning and an end. It begins in the twenty-seventh century, after the development of the necessary machinery (“temporal fields” and whatnot), and ends in the “unplumbable entropy death ahead.

I have no idea what this entire paragraph means.

On page 174, perhaps another original idea:

They travel through time in parallel with the rest of us, at our standard velocity of one second per second, one day per day. Only we go about our business of living and decaying, while time capsules try, ostrich like, to evade entropy.

I do not know of anyone, not even an ostrich, who tried to “evade entropy.”

Finally, on the last pages of the book you will read some (perhaps original?) silly discussion of “time travel,” “death,” and of course, “entropy.”

Enjoy the following meaningless, but amusing ideas:

Why do we need time travel? All the answers come down to one. To elude death.

Time is a killer. Everyone knows that. Time will bury us. I wasted time, and now doth time waste me. Time makes dust of all things. Time’s winged chariot isn’t taking us anywhere good.

Entropy can be held off only here and there, now and then. Every life lapses into oblivion. Time and the bell have buried the day.

Appendix ZJ*: On Wheeler's book: *At Home in the Universe*

Wheeler has a whole chapter in his book (1996) titled:

“It from bit,”

which briefly means, in his words:

Every particle, every field of force, even the spacetime continuum itself – derives its function, its meaning, its very existence entirely – even if in some context indirectly – from the apparatus-elicited answers to yes or no questions, binary choice, bits.

Then he continues:

It from bit symbolizes the idea that every item of physical world has at bottom – at a very deep bottom, in most instances – an immaterial source and explanation. In short, all things physical are information-theoretical in origin and this is a participatory universe.

I believe that Wheeler was carried away, way too far in fact with these statements. I certainly cannot agree with such an exaggerated, distorted and partially meaningless view of the physical world. In one part he says *“in most instances,”* but then says later that *“all things physical are information.”*

In my opinion, it is (almost) meaningless to claim that “every particle,” its function,” and “its meaning” can be reduced to “bits.”

In fact, I do not think that any information (in the colloquial sense) can be reduced to bits, let alone physical things, their function, and their meaning.

Towards the end of the book Wheeler lists six issues that *“invite exploration,”* the last one which is particularly baffling:

...celebrate the absence of a clean clear definition of the term “bit” as an elementary unit in the establishment of meaning.

In my view the “bit” is a well-defined quantity, as much as, and perhaps even better than the centimeter, the gram, and the second. However, Wheeler claims that there is no clear definition of the term “bit.” This, in itself undermines the definition of his doctrine *“It from bit.”*

Besides, a “bit” is not a unit in the establishment of meaning.” A “bit” has nothing to do with meaning. Associating the “bit” with “meaning” casts doubts about the meaning of what Wheeler means by: ***“It from bit.”***

Finally, it should be said that not only not every “it” is a “bit,” but also not every information can be measured in bits. As noted in section 1.4, only a very limited class of information can be assigned a measure, and the units of that measure are the bits.

In conclusion, Wheeler confuses the colloquial notion of “information” with Shannon’s measure of information, then confuses the SMI with the “units of information,” and finally makes a silly-to-meaningless statement: **It from Bit!**

Appendix ZK*: Some quotations from Barnett’s book *“The Universe and Dr. Einstein”*

In his excellent book *“The Universe and Dr. Einstein,”* Lincoln Barnett discusses mainly relativity. However, there are some comments which are relevant to thermodynamics.

On page 64 we find:

Prior to Relativity scientists had pictured the universe as a vessel containing two distinct elements, matter and energy – the former inert, tangible, and characterized by a property called mass, and the latter, active, invisible and without mass. But Einstein showed that mass and energy are equivalent; the property called mass is simply concentrated energy. In other words, matter is energy and energy is matter, and the distinction is simply one of temporary state.

Regarding the various theories about the “fate” of the Universe, we find in page 102:

The universe is thus progressing toward an ultimate “heat-death,” or as it is technically defined a condition of “maximum entropy.” When the universe reaches this state, some billions of years from now all processes of nature will cease. All space will be at the same temperature. No energy can be used because all of it will be uniformly distributed through the cosmos. There will be no light, no life, no warmth – nothing but perpetual and irrevocable stagnation. Time itself will come to an end. For entropy points the direction of time. Entropy is the measure of randomness. When all system and order in the universe have vanished, when randomness is at its maximum, and entropy cannot be increased, when there no longer is any sequence of cause and effect, in short when the universe runs down, there will be no direction to time – there will be no time. And there is no way of avoiding this destiny. For the fateful principle known as the Second Law of

Thermodynamics, which stands today as the principal pillar of classical physics left intact by the march of science, proclaims that the fundamental processes of nature are irreversible. Nature moves just one way.

It is not clear whether the author is expressing Einstein's views in this paragraph, or is reiterating the prevailing views of physicists. I do not agree with the following assertions:

The "ultimate heat death" of the universe", "reaching "maximum entropy," "time itself will come to an end," "for entropy points the direction of time."

These are simply not true. Entropy points at no direction. Entropy is an *innocent scalar*, having a fixed value for a well-defined thermodynamic system.

In the last part of the paragraph the author alludes to Einstein's statement about thermodynamics. However, even when one accepts the view that thermodynamics – the pillar of classical physics is left intact in spite of the two great revolutions – it does not follow that Nature moves just one way.

However, Barnett adds a comment about "contemporary theorists who propose a different "fate" of the universe.

There are a few contemporary theorists, however, who propose that somehow, somewhere beyond man's meager ken the universe may be rebuilding itself. In the light of Einstein's principle of the equivalence of mass and energy, it is possible to imagine the diffused radiation in space congealing once more into particles of matter – protons, neutrons, and electrons – which may then combine to form larger units, which in turn may be collected by their own gravitational influence into diffuse nebulae, stars, and, ultimately, galactic systems. And thus the life cycle of the universe may be repeated for all eternity.

In my view, this is as speculative as the prediction of the "heat death" of the universe.

Appendix ZL*: Ohanian's book on: "Einstein's Mistakes"

Ohanian (2008) starts his book "Einstein's Mistakes" with the words:

This book is a forensic biography that dissects Einstein's scientific mistakes. It deals only tangentially with the mistakes in his personal life.

In this Appendix, we quote only a few paragraphs from Ohanian's book which are relevant to entropy and the Second Law.

In Chapter 5 of his book titled: *“Motions of inanimate, small, suspended bodies,”* the author describes Einstein’s work on Brownian motion which contributed decisively to the recognition of the atomic constituency of matter. On page 111, while discussing Boltzmann’s advocacy of the “atomic theory of physics,” he writes:

Perhaps his greatest discovery was the proportionality between probability and entropy, with a constant of proportionality called “Boltzmann’s constant.” The thermodynamic entropy is a measure of the disorder in a physical system, and thus Boltzmann’s proportionality says that when a system is in a state of high probability, it is in a state of high disorder (for instance, for a more or less uniform distribution of air molecules over the volume of a room, the probability and the disorder are high; but for a nonuniform distribution, with an unusually large concentration of molecules in one corner of the room, the probability and the disorder are lower).

Nothing is true in this paragraph! First, Boltzmann did not discover that entropy is not proportional to probability. Second, entropy is not a measure of disorder. Third, state of high probability is not necessarily a state of high disorder. See Section 3.6 and Appendix V.

Clearly, these erroneous statements are not “original” as they have already been featured in many books and articles. These statements are, of course, not relevant to “Einstein’s mistakes.”

On page 116, the author discusses Einstein’s effort to *“deduce the Second Law of Thermodynamics from the laws of mechanics.”*

Then, he writes:

To deduce this law from mechanics, Einstein introduced the assumption that in any physical system the probability of the configuration always increases. For a room left to itself, the concentration of heat in one corner of the room has low probability, whereas the distribution of the heat all over the room has a higher probability, and Einstein’s assumption of an increase of probability “explains” the flow of heat demanded by the Second Law. But his argument fails to relate the change of probability to the laws of mechanics - there is nothing in mechanics to prevent a reversed flow of heat, that is, a flow of heat from the cold regions of the room into one hot corner.

Note that the author makes an error similar to Brillouin’s error (see Appendix ZI) when he writes that; *“the probability of the configuration always increases.”*

The correct statement is that the probability of the configuration does not increase or decrease, it is the configuration which changes towards the one having larger probability. It is not clear whether this error was made by Einstein, or by the author.

The author correctly states that it is impossible to “deduce” the Second Law of thermodynamics from the laws of mechanics. But then he adds:

It is somewhat of a mystery why he [*Einstein*] *opened this can of worms, because the derivation of the Second Law of Thermodynamics from the laws of mechanics had already been formulated by Boltzmann in his celebrated H theorem.*”

The truth is that Boltzmann *did not* derive the Second Law from the law of mechanics!

Appendix ZM*: Clark’s book on “The Unknown Universe.”

This Appendix provides a few quotations from Clark (2016) regarding entropy which feature in a book on: “*The Unknown Universe.*” These quotations are commonplace in numerous popular science books where distorted views of entropy are expressed.

On page 276 the author discusses common irreversible processes and comments:

By the middle of the nineteenth century, this behavior had been linked to a concept called entropy. It can be thought of as a measure of the disorder in a system, and it never decreases. A smashed plate is at higher entropy than a whole one. To put that plate together would require the expenditure of energy that increases the entropy in our surroundings. It is a no-win situation. You can never decrease the overall entropy of the Universe because everything that happens is driven by the one-way flow of energy from hot to cold. This certainly makes it look as if time is flowing in a single direction, but it still doesn’t answer the basic question: what is time?

Nothing in this paragraph is true! Entropy is not a measure of disorder, entropy can decrease, a smashed plate does not have higher entropy than a whole one, it is not clear what is meant by “no-win situation,” no one knows anything about the entropy of the universe, not everything that happens is driven by the flow of energy from hot to cold, and the whole discussion has nothing to do with time!

Then, on page 277 we find more of the same nonsense:

Time is clearly linked to the concept of entropy, the measure of the disorder in a system. But entropy is more than that. It crops up in the relatively modern field of information theory.

Time is clearly not link to entropy! At this point the author discusses Shannon's measure of information, and then states:

Shannon called the amount of information a message can hold its "entropy," and people soon started noticing that thermodynamic entropy and information theory entropy were closely related, perhaps even exactly the same thing. One of those people was Steven Hawking.

This is just one example of confusing entropy with Shannon's measure of information (see Ben-Naim 2016a and 2017a). One of those people who propagated the confusion between entropy and time is Hawking (1988) Then, the author continues to discuss BH entropy which is anything but entropy. See Appendix ZD.

Appendix ZO*: Sommerfeld's book on "Thermodynamics"

Sommerfeld's book (1956) on Thermodynamics is a classical well written book. In this Appendix I present only a few quotations relevant to the Entropy and the Second Law. On page 19, the author discusses reversible and irreversible processes:

Reversible processes are not, in fact, processes at all, they are sequences of states of equilibrium. The processes which we encounter in real life are always irreversible processes, processes during which disturbed equilibria are being equalized. Instead of using the term "reversible process," we can also speak of infinitely slow, quasi-static processes during which the system's capacity for performing work is fully utilized and no energy is dissipated. In spite of their not being real, reversible processes are most important in thermodynamics because definite equations can be obtained only by considering reversible changes; irreversible changes can only be described with the aid of inequalities when equilibrium thermodynamics is used.

Notes: First, the term "reversible" is defined here as a sequence of equilibrium states." Sommerfeld does not explain why it is called reversible, see Appendix A. He also does not explain why an irreversible process is *irreversible*. Second, it states that all real processes are irreversible simply because there exists no "reversible" process as described here, i.e. there is no idealized process which is an infinite sequence of equilibrium states. Third, all

“definite equations” in thermodynamics apply to reversible processes, i.e. to the sequence of equilibrium states.

At this stage, the term reversible means only that the *path* through which the process proceeds can be reversed since all the intermediate states are equilibrium states.

Thus, although the concept “reversible process” as a sequence of equilibrium states is well-described in this paragraph it does not follow that:

The actual criterion for a process to be reversible states that during its course there are no lasting changes of any sort in the surroundings if the process is allowed to go forward and then back to the original state.

On page 22, the author has a footnote stating:

A reversible process must be carried out infinitely slowly. The reverse is, however, not true, as an infinitely slow process need not be reversible. Example illustrating the latter case: Discharging a condenser through a very large resistance.

Note that reversible is defined as a process of a sequence of equilibrium states. It does not necessarily have to be infinitely slow. It only requires that the process be slow enough so that the equilibrium in the system follows. In other words, the system is well-defined thermodynamically at each step. The second sentence in the note is not true. If you do the process infinitely slow, then one can expect that the *system*, say the gas within the container will be at equilibrium throughout the process, this is true provided that you start with an equilibrium state.

Of course, one can do an infinitely slow process in which a piston is moved creating friction with the walls. In this case the process within the system is quasi-static, i.e. a sequence of equilibrium state, hence, reversible according to our definition. Here, the term reversible applies to the system.

Therefore, to avoid this kind of confusion it is preferable to define: A quasi-static process – a sequence of equilibrium states (this is usually equivalent from the point of view of the description of the system, *if, and only if*, the process is infinitely slow).

On page 26 he introduces the Second Law:

All thermodynamic systems possess a property which is called entropy. It is calculated by imagining that the state of the system is changed from an arbitrarily selected reference state to the actual state through a sequence of states of equilibrium and by summing up the quotients of the quantities of heat dQ introduced at each step and the “absolute temperature.” T ; the latter is to be defined simultaneously in this connection.

During real (i.e. non-ideal) processes the entropy of an isolated system increases. (Second part of the Second Law).

What Sommerfeld calls the “first part of the Second Law” is only a part of the *definition* of entropy, or rather, the *existence* of such a state function. It is not part of the Second Law. However, I do agree that entropy is defined only for states of equilibrium.

The second part introduces a “real” process which is nothing but a *spontaneous* process, and it states that in such a process in an isolated system the entropy increases.

If we combined the two parts in this formulation of the Second Law it is clear that the entropy changes in a *real process* and a spontaneous process refers to two states of a system; initial and final, which are equilibrium states.

On page 27:

Heat cannot pass spontaneously from a lower to a higher temperature level (Clausius). The following postulate, due to Kelvin, is equivalent to that due to Clausius: It is impossible continuously to produce work by cooling only one body down to a temperature below the coldest part of its surroundings.

We have Clausius’ and Kelvin’s equivalent formulations of the Second Law. The equivalence between these two formulations can easily be shown.

The most important statement which is relevant to the universe is on page 38:

We shall refrain here from discussing the application to the universe which was already given by Clausius and which predicts its “thermal death.” The increase in entropy is supposed to equalize all temperature differences so that the performance of work will supposedly become impossible. We think that the nature of the universe, i.e. whether it is open or closed, expanding (even pulsating!) or stationary is still too much in doubt to enable us to discuss this problem.

On page 47 Sommerfeld discusses the “maximum of entropy.” Although he does not state that entropy of a system increases until it reaches a maximum, he introduces the idea that:

An isolated system will tend to a final state at which the entropy has a maximum if all constraints within the system are removed. We shall call this a state of unconstrained thermodynamic equilibrium.

He does not explain what a constrained system is. Here, the concept of an “unconstrained equilibrium state” is used to define equilibrium. However, on the next page he clearly states that no spontaneous process can occur in an “unconstrained equilibrium.”

Finally, it is appropriate to bring a most quoted statement by Sommerfeld:

Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two points. The third time you go through it, you know you don't understand it, but by that time you are so used to the subject, it doesn't bother you anymore...

My addition to this statement is that if you have been writing and teaching thermodynamics for a long time, you might have only a delusion, not a real understanding of thermodynamics.

Appendix ZP*: Campbell's book on “Grammatical Man”

Campbell's book (1982) is mainly on Information, Information Theory and Life. The first time I read this book I enjoyed it very much. This was the very first time I read about the application of the Shannon measure of Information (SMI) for life processes. In this appendix I will critically examine only a few statements from this book where entropy and the Second Law were misused and confused with the SMI.

If you look at the Index of Campbell's book, you will find that the “*definition of entropy*” is discussed on page 11. Here is how entropy is “defined” on page 11:

Biologists as well as philosophers have suggested that the universe, and the living forms it contains, are based on chance, but not on accident. To put it another way, forces of chance and of antichance coexist in a complementary relationship. The random element is called

entropy, the agent of chaos, which tends to mix up the unmixed, to destroy meaning. The nonrandom element is information, which exploits the uncertainty inherent in the entropy principle to generate new structures, to inform the world in novel ways.

Clearly, there is no *definition* of entropy here. Hence, the Index of the book is misleading! Instead, this paragraph contains a mixture of concepts such as entropy, chance, antichance (?), information, randomness, and chaos. In short, a chaotic *mélange* of concepts which are supposed to “define entropy,” but in fact confuse the readers with all these vague concepts which are totally irrelevant to entropy.

The first sentence is vague, to say the least. What does it mean by “the universe, and the living forms it contains are based on chance?” This statement does not make any sense. One can claim that some *processes*, or even all processes occur by chance. However, it is meaningless to claim that an object – the universe, including you, and I – are “based on chance.” See also section 3.6.

The second sentence is supposed to explain the meaningless first sentence, but in fact it only deepens the confusion. I do not know what the “forces of chance” are. I have no idea what the forces of “antichance” mean, and I do not have any idea about their coexistence in a complementary relationship.

The third sentence introduces (according to the Index) the “definition” of entropy which again is supposed to clarify the meaning of the meaningless first sentence. But now it is very clear that the author himself does not have any idea about the meaning of the first sentence, and certainly not about the meaning of entropy.

The “random element” of what is called entropy? I read many claims about entropy being a measure of “disorder,” “chaos” etc. but I have never heard of entropy being an “*agent of chaos*.” Is this supposed to be a “definition” of entropy?

I also have no idea what the author means by entropy “destroying meaning.” What I could conclude from this paragraph are two things; first, it does not contain any definition of entropy, and second, whatever the meaning of entropy is, it has already been *ruined* this paragraph.

On page 46 the author presents Boltzmann's entropy; $S = k \log W$ and explains:

S stands for entropy, k is a universal constant known as Boltzmann's constant, and W has to do with the number of ways in which the parts of the system can be arranged. The entropy S reaches a maximum when all parts of the system are so thoroughly mixed up and random that there is no reason to expect it to favor one particular arrangement over any of the colossal number of other possible arrangements.

This description of Boltzmann's entropy is anything but a "definition" of Boltzmann's entropy! Here, the author confuses the first postulate of statistical mechanics which simply states that all micro-states of an isolated system are presumed to be equally probable, with "S reaches a maximum when all parts of the system are so thoroughly mixed up and random..." See Chapter 1 for a definition of Boltzmann's entropy and why that definition has nothing to do with entropy reaching a maximum (with respect to what?).

Having done with the two *non-definition* of entropy let us examine some other uses, or rather misuses of entropy.

In fact, the confusion between entropy and information theory is already revealed in the book's foreword.

On page 12 we find:

Information theory shows that there are good reasons why the forces of antichance are as universal as the forces of chance, even though the entropy has been presented as the overwhelmingly more powerful principle.

I have no idea what the author means by relating Information Theory with "forces of chance" and "forces of antichance," and what the latter forces have anything to do with entropy. Information theory *does not* deal with any "forces," certainly not with the meaningless "forces of chance" or "forces of antichance."

I know that entropy has been presented as a powerful concept (see preface). However, when the author says "more powerful" he must explain: More than what? See also my Preface and Epilogue.

The confusion reaches its peak in the last paragraph on page 12:

Sense and order, the theory says, can prevail against nonsense and chaos. The world need not regress toward the simple, the uniform, and the banal, but may advance in the direction of richer and more complex structures, physical and mental. Life, like language, remains “grammatical.” The classical view of entropy implied that structure is the exception and confusion the rule. The theory of information suggests that instead that order is entirely natural: grammatical man inhabits a grammatical universe.

I do not know of any theory (certainly neither Information Theory nor thermodynamics) which *states* that “sense and order...” prevails against “nonsense and chaos.” To the best of my knowledge there exists no theory which deals with “sense and order,” or with “nonsense and chaos.” Therefore, the most straightforward meaning that I can assign to this sentence is that “nonsense and chaos” *prevails* in Campbell’s entire book.

I also do not know anything about the “classical view” of entropy implying that “structure is the exception and confusion the rule.” Here, the author clearly confuses the “classical view of entropy” with the content of his book. It is only in the latter that “confusion is the rule!”

The last sentence of the quoted paragraph proves my view; the theory of information *does not suggest* anything about order or disorder, being either natural or unnatural.

On pages 32 and 33 the author correctly points out that “order” and “disorder” are subjective concepts, but then uses the erroneous association of entropy with disorder. From this it also follows that entropy must have some degree of subjectivity (see section 3.2).

Part of the trouble arises because while entropy refers to the physical state of a physical system, it is a measure of the disorderliness of that system, and disorder is not a wholly objective property. The human observer cannot be excluded completely, because the idea of order is inextricably linked to the mind’s awareness. Muddle, to some extent, is in the brain of the beholder. One person’s disorder may be another’s order, depending on how much knowledge that person possesses about the details of the apparent confusion.

On page 48, we find more nonsense ideas:

Entropy is a protean concept. It measures a physical property, the transformation of energy from an accessible to an inaccessible state. It has to do with probability, since the most probable state of a system in constant, random motion is for all its contrasts to be smoothed out.

Entropy is also an irreversible process. It does not decrease unless some extra source of energy intervenes to push it back “uphill.” It is thus a physical index of the one-way, irreversible flow of time.

Entropy is not a “transformation of energy...” Entropy is not probability (see section 3.6), and entropy is not an irreversible process (whatever that means, see section 3.8).

Please read the last quotation again. “Entropy is also an irreversible process.” Entropy *is not a process*; either reversible or irreversible! This statement is worse than the interpretation of entropy as a “measure of irreversibility.” See section 3.8. This statement clearly proves that the author is an “irreversible process”! Perhaps it also contributes another proof of Einstein’s conjecture.

More entertaining nonsense may be found on page 50:

Entropy is closer to the untidiness and variety of life than previous physical laws. Oswald Spengler, in The Decline of the West, singled out entropy as the concept most typical of the downfall of modern science from its classical purity and certainty. He chose it because entropy is a statistical rather than an exact principle and has more to do with living things and with history than the timeless, abstract equations of the old mechanics.

Entropy is physical quantity; it is not a “principle.” Entropy is not closer (nor farther) to “untidiness and variety of life.” These are beautiful words, combined to a meaningless grammatical sentence.

On page 83, the author discusses the “Arrow of Time” and its relationship with the “entropy principle.” He adds an “original” idea that the distinction between past and future is “independent of consciousness.”

The “arrow of time” is a metaphor invented by Sir Arthur Eddington to express the idea that there exists a purely physical distinction between past and future, independent of consciousness. Such a distinction is based on the entropy principle, which asserts that as time goes on energy tends to be transformed from an orderly into a less orderly form. In Eddington’s view, earlier is different from later because earlier energy is more highly organized.

The idea of entropy being associated with orderly or disorderly energy, is of course, not original. See Appendix P.

On page 83 we find another beautiful nonsense:

Only the “one-wayness” of time insures that “the world makes sense,”

Why the “one-wayness” of time insures that “the world makes sense”?

This is not explained either here or in Eddington’s book (see Appendix P). As I have explained in Appendix P, nothing said in Eddington’s book on entropy makes sense. This *ensures* that Eddington’s book, as well as Campbell’s makes no sense at all!

On page 99 we find another interesting, but meaningless, association of language, living systems and the Second Law.

Language and living systems, it is clear, have at least one thing in common: they are complex and stable at the same time, and they achieve this by means of internalized rules. They do not surrender to the randomizing effects decreed by the Second Law of thermodynamics, and they depend less than might have been expected on chance and accident. Their complexity is self-regulating.

Beautiful, impressive but totally devoid of any meaning!

Appendix ZQ*: Feynman on the Second Law

Feynman’s Lectures (1963) is one of the best books for beginners in physics.

In volume I, Feynman starts with one of the particular formulation of the Second Law:

Carnot assumed that heat cannot be taken in at a certain temperature and converted into work with no other change in the system or the surroundings.

This is known as the Kelvin formulation of the Second Law. Another particular formulation is due to Clausius; heat does not spontaneously flow from a cold to a hot body.

On page 44-10 Feynman introduces entropy. First, after discussing Carnot cycle he refers to the quantity Q/T as entropy:

This Q/T is called entropy, and we say “there is no net change in entropy in a reversible cycle.”

This is a mistake. Q/T is not entropy (though quite often is “called” entropy) but a change in entropy for a specific process. See Chapter 1.

Following the particular example of the Carnot cycle, he concludes that entropy is “a function of the condition,” later explaining:

We can, therefore, say that there is a certain function, which we call entropy of the substance, that depends only on the condition, i.e. only on the volume and temperature.

Today, we would say that the entropy is a “state function,” where the “state” of the system could be characterized by any set of thermodynamic variables at equilibrium; “volume and temperature” are only one possibility.

It should be noted that soon after Feynman calls the quantity Q/T , entropy, he uses Clausius’ definition as $dS = dQ/T$. Feynman does not elaborate on the meaning of the quantity Q/T . If Q is the quantity of heat transferred into the system at constant T , then Q/T is not the entropy of the system, but the *change* of the entropy of the system due to the heat transferred.

Feynman continues with a specific example described on page 44-12:

Another example of irreversibility is this: If we put together two objects that are at different temperatures, say T_1 and T_2 , a certain amount of heat will flow from one to the other by itself. Suppose, for instance, we put a hot stone in cold water. Then when a certain heat ΔQ is transferred from T_1 to T_2 , how much does the entropy of the hot stone change? It decreases by $\Delta Q/T_1$. How much does the water entropy change? It increases by $\Delta Q/T_2$. The heat will, of course, flow only from the higher temperature T_1 to the lower temperature T_2 so that ΔQ is positive if T_1 is greater than T_2 . So the change in entropy of the whole world is positive, and it is the difference of the two fractions:

$$\Delta S = \frac{\Delta Q}{T_2} - \frac{\Delta Q}{T_1}$$

So the following is true: in any process that is irreversible, the entropy of the whole world is increased.”

Unfortunately, Feynman was not careful in both his calculation and his conclusion.

If the two objects are *finite* and a *finite amount* of heat is transferred from the hot to the cold object, then it is not true that the entropy change of the hot body is $-\Delta Q/T_1$, and it is not true that the entropy change of the cold body is $\Delta Q/T_2$. The reason is that while the

(finite) amount of heat is transferred, both the temperatures T_1 and T_2 will change and will not be constant.

The correct statement is that for large objects at T_1 and T_2 , and an infinitesimal transfer of heat dQ , such that the temperatures T_1 and T_2 are not affected as a result of the heat transfer. Hence, the entropy change is:

$$dS = \frac{dQ}{T_2} - \frac{dQ}{T_1} = \frac{(T_1 - T_2)dQ}{T_1 T_2}$$

Since $T_1 - T_2 > 0$, dS is positive.

Feynman's conclusion that the entropy of the "whole world" increased is also not correct. The entropy of the two sub-systems increase. Nothing may be concluded about the entropy of the whole world.

It seems that Feynman somehow "corrected" his conclusion later. After quoting Clausius' formulation of the Second Law in the form:

The entropy of the universe is always increasing.

Feynman comments:

That is not a very good statement of the Second Law; it does not say, for example, that in a reversible cycle the entropy stays the same, and it does not say exactly what the entropy is.

In my opinion this is not a good formulation of the Second Law not because it does not "say exactly what the entropy is" but rather because the entropy of the universe is not defined!

On page 46-5 Feynman discussed the question of the source of irreversibility of some process and asks the question:

Where does irreversibility come from?

As so many authors wrote, Feynman also seems to view the irreversibility of processes we see around us (such as the scrambling of an egg) as an *absolute* irreversibility. See also

Ben-Naim (2018a) and Appendix A. If this is the case, then there exists a conflict between the reversibility of the equations of motion and the apparent irreversibility of processes in macroscopic objects. See also section 4.2.

Feynman concludes that:

It is the change from an ordered arrangement to a disordered arrangement which is the source of the irreversibility.

In fact, Feynman adopts here the “disorder” interpretation of entropy, by saying:

First, the entropy measures the disorder. Second, the universe always goes from “order” to “disorder,” so entropy always increases. Order is not order in the sense that we like the arrangement, but in the sense that the number of different ways we can hook up it up, and still look the same from the outside, is relatively restricted.

It seems to me that Feynman was not so sure about the meaning of “disorder” when he said: “Order is not order in the sense that we like the arrangement.” Nevertheless, it is still not correct that “entropy always increases,” and that the universe always goes from disorder to disorder – in whatever sense one interprets the term order and disorder. See also section 3.2.

Appendix ZR*: Planck’s book on “Treatise on Thermodynamics”

Part III of Planck’s book (1017) on “The Second Fundamental Principle of Thermodynamics” starts with these words:

The Second Law of thermodynamics is essentially different from the first law, since it deals with a question in no way touched upon by the first law, viz. the direction in which a process takes place in nature. Not every change which is consistent with the principle of the conservation of energy satisfies also the additional conditions which the Second Law imposes upon the processes, which actually take place in nature. In other words, the principle of the conservation of energy does not suffice for a unique determination of natural processes.

On page 88, he introduces the entropy:

The Second Law of thermodynamics states that there exists in nature for each system of bodies a quantity, which by all changes of the system either remains constant (in reversible processes) or increases in value (in irreversible processes). This quantity is called, following Clausius, the entropy of the system. The exposition in the following chapter aims

at obtaining a mathematical expression for the entropy of a system, and proving its properties.

Note that Planck emphasizes “*entropy of a system*” not as an abstract concept of entropy detached from a specific system. The formulation of the Second Law follows:

It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat-reservoir.

On page 97 after he formulates the Second Law he continued to say that:

It must not be supposed that the entropy of a gas has a meaning only for states of equilibrium. We may assume each sufficiently small particle, even of a gas in turmoil, to be homogenous and at a definite temperature, and must, therefore, according to (...), assign it to a definite value of the entropy. M , v , and T are then the mass, specific volume, and temperature of the particle under consideration. A summation extending over all the particles of the mass – within which the values of v and T may vary from particle to particle – gives the entropy of the whole mass of the gas in a particular state.

This is strange because he seems to propose that entropy may be assigned even to non-equilibrium states. The justification for this is not clear; it is not clear what is meant by assigning entropy to “each sufficiently small particle.” Does he mean entropy for each particle, or entropy for a small volume or small mass of a system?

Then he also assumes that these entropies can be summed (or integrated?) over all the system. In Appendix S, I discuss these assumptions which are the basis in any theory of irreversible processes.

Planck comments on Clausius’ formulation of the Second Law stating:

The energy and the entropy of the world have no meaning, because such quantities admit no accurate definition.

Right after stating the above he adds that those propositions by Clausius can be given a meaning but he does not explain how (pages 104-105).

Perhaps the most important statement of Planck which is relevant to our discussion in this book may be found on page 106.

It would be absurd to assume that the validity of the Second Law depends in any way on the skill of the physicist or chemist in observing or experimenting. The gist of the Second

Law has nothing to do with experiment; the law asserts briefly that there exists in nature a quantity which changes always in the same sense in all natural processes.

It is clear from this quotation that Planck believes that entropy and the Second Law are objectively independent of the observer. I concur with this statement. What I do not agree with is that “*there exists in nature a quantity...*” Perhaps, the author was not careful in this statement. He should have added that this quantity always increases in a natural process in isolated system!

Appendix ZS*: Kubo on “*Thermodynamics*”

In his book, Kubo (1968) states that he will mostly limit himself to discuss equilibrium states.

In Chapter 1, the author defines a system and its environment. Both are *macroscopic* (i.e. system containing large number of particles) systems at *equilibrium*. It is very clear that “environment” here is not the *entire universe* but a well-defined thermodynamic system at *equilibrium* such as a thermostat.

On page 4, the author defines the quasi-static process as:

Quasi-static process: This is an ideal process during which it may be assumed that both the system and its surroundings maintain thermal equilibrium. Such a process is approximately realized by making the change sufficiently slow.

In the limit these two processes follow the same path in opposite directions. Thus a quasi-static process is reversible. The following are the important quasi-static processes.

It is clear here that “reversible” means reversing the process along the same path, i.e. the process and its reverse are along a sequence of well-defined equilibrium states. See Appendix A.

In Chapter 2, the Second Law is introduced. Before doing so he defined a reversible process as:

Reversible process: Suppose that when a system under consideration changes from a state, α , to another state, α' , the environment changes from β to β' . If in some way it is possible to return the system from α' to α and at the same time return the environment from β' to β , the process $(\alpha, \beta) \rightarrow (\alpha', \beta')$ is said to be reversible.

Remember that the “environment” was defined as a thermodynamic system. Therefore, it is meaningful to talk about change of states $\alpha \rightarrow \alpha'$ for the *system*, and change of state for the *environment* $\beta \rightarrow \beta'$.

If one defines the environment as the entire universe, then it becomes meaningless to specify the states β and β' .

Then the author makes a distinction between “reversibility,” in the broadest sense, as defined in the quotation above, and a *narrower* definition as:

A given process is reversible if it can be reversed in each step by infinitesimal changes of the conditions of the environment. A reversible process in this sense is none other than the quasi-static process explained in 1.5. A quasi-static process can be reversed in this sense. A reversible process in the broader sense is not necessarily reversible in this strict sense.

Clearly, since $\alpha, \alpha', \beta, \beta'$ are all equilibrium states, the system and the environment can be reversed (not necessarily along the same path) from (α', β') to (α, β) .

Note that this reversal will not be spontaneous. One can reverse the process by using the environment.

The example of reversible process in the narrower sense is the same as an expansion of an ideal gas, but through a very small hole between the two compartments. In this case, the process is again spontaneous. It will go from α to α' , but the process can be reversed along the *same path*.

Thus, it is clear that a reversible process in the broader sense is not necessarily reversible in this strict (or narrower) sense.

Then, the author states the following:

Real physical processes proceed at finite speeds and are necessarily irreversible, since they always involve some kind of friction. A reversible process is an idealization.

Here, the “friction” enters for the first time. However, the example above is a quasi-static process, therefore, it is reversible in the narrow sense. Thus, this is a real process which is reversible (also, there is no friction involved).

Note: In this “broadest sense” it is only required that the system and its environment can be returned to its initial states α and β , respectively. It does not say anything about the path of the reversal process, it does not say anything about the “state” of the rest of the universe (remember that in his definition, the environment is also a well-defined thermodynamic system. This excludes the interpretation of the environment as the entire universe).

It is unclear why the author adds “at the same time.” Does it mean that both the system and the environment should be reversed simultaneously?

It seems to me that this additional requirement is superfluous.

In my view, setting aside the additional “at the same time,” this definition of reversible is altogether superfluous. Every process in such a system and its environment can be reversed in this sense.

The stricter sense is the reversal along the *same path*. This definition is identical with a quasi-static process. It only requires that the state of the system be well-defined at each step along the path.

On page 63 we find the two most famous “principles.”

Clausius principle: A process which involves no change other than the transfer of heat to a hotter to a cooler body is irreversible; or, it is impossible for heat to transfer spontaneously from a colder to a hotter body without causing other changes.

Kelvin’s principle: A process in which work is transferred into heat without other changes, is irreversible; or, it is impossible to convert all the heat taken from a body of uniform temperature into work without causing other changes.

It is easy to show that these two principles are equivalent.

On page 83, the author describes a “reversible” process of mixing for which the entropy does not change.

It should be said that here, “reversible” means quasi-static process. Although this specific process of mixing is not a “real” or a spontaneous process, it involves no entropy

change. This comment is important in connection with the “disorder” interpretation of entropy which is discussed in section 3.2.

Appendix ZT*: Münster on “Classical Thermodynamics”

Münster’s book (1970) is one of the best books on thermodynamics. In the book’s introduction the author makes it clear that:

Thermodynamics actually deals with only some of these phenomena. It confines itself to the considerations of equilibrium states and to those changes of state which may be represented by a continuous series of equilibrium states (quasi-static changes of state). Such changes of state can, strictly speaking, only to be imagined as being infinitely slow. They can, therefore, not to be represented as a function of time.

To remove any doubts, he emphasizes again:

Time is never a factor in thermodynamic considerations.

The author lists a few milestones in the history of thermodynamics. Interestingly, the author points out that the formulations of the Second Law in terms of entropy in 1854 is *new* formulation which follows earlier formulations which do not involve entropy.

The author also quotes Clausius’ famous statement:

The energy of the universe is constant.

The entropy of the universe tends towards a maximum.

At this point the author does not comment on the use of the entropy for the universe. On page 6, the author describes equilibrium states as:

A considerable simplification is caused by thermodynamics being limited to equilibrium states and quasi-static processes. Since the existence and properties of equilibrium are closely connected with the Second Law, we can, at the moment, define equilibrium merely as that state towards which a system tends spontaneously; alternatively, equilibrium may be defined as that state in which the thermodynamic quantities of the system are no longer time dependent.

On page 17, after discussing the Second Law for an isolated system as:

$$\Delta S \geq 0 \text{ (for an adiabatic isolated system)}$$

He refers to the Clausius' formulation and comments:

If the universe is regarded as a closed system, the theorem of Clausius mentioned in I follows.

This is a very important comment: First, it is not clear whether the universe is isolated, or a closed system. But the author seems to have forgotten his own statement regarding the applicability of thermodynamics to equilibrium states. Thus, regardless whether the universe is adiabatic, closed or isolated, it is certainly not in an *equilibrium state*, therefore, the above formulation of the Second Law cannot be applied.

I will conclude by saying that nowhere in the book does Münster discuss any interpretation of entropy. This clearly shows that thermodynamics does not need and does not depend on any molecular interpretation of entropy.

Appendix ZU*: Fermi's book on "*Thermodynamics*"

Fermi (1937) first states the Second Law as stated by Kelvin and Clausius:

A transformation whose only final result is to transform into work heat extracted from a source which is at the same temperature throughout is impossible. (Postulate of the Lord Kelvin).

A transformation whose only final result is to transfer heat from a body at a given temperature to a body at higher temperature is impossible.

Both of these statements are about *impossibilities*. Next, he proves the equivalence of the two formulations. Only in Chapter IV does Fermi introduce the concept of entropy. On page 50, he explains that we arbitrarily choose a certain equilibrium state *O* of our system and call it the *standard state*. Let *A* be some other equilibrium state, and consider the integral:

$$S(A) = \int_0^A \frac{dQ}{T}$$

taken over a *reversible transformation*.

Clearly, Fermi defines entropy only for equilibrium states. Interestingly, in a footnote on the same page Fermi writes that it is possible to define the entropy even for non-equilibrium states. Here, we quote the relevant part of the footnote on page 50:

In many cases, however, it is possible to define the entropy even for non-equilibrium states. Let us consider, for example, a system composed of several homogenous parts at different temperatures and pressures. Let each part, have a uniform temperature and pressure. If the different parts are in direct contact with each other the system will evidently not be in equilibrium, since heat will flow from the hotter to the colder parts, and the differences of pressure will rise to motion. If, however, we enclose each part in a thermally insulating rigid container, our system will be in equilibrium, and we shall be able to determine its entropy.

If you read the footnote carefully you will realize that Fermi describes a system at a *non-equilibrium state*, but the assignment of entropy is actually made only when the parts of the system are at *equilibrium*. Note that even in his description of the non-equilibrium state, he requires uniform temperature and pressure. This is not a general non-equilibrium state!

Although Fermi does not use the concept of “constrained equilibrium state” he in fact, *does not* define entropy for any non-equilibrium state, but only for a “constrained equilibrium states” which are nothing but equilibrium states.

There is one more important point raised by Fermi which is relevant to the possibility or impossibility of extending the concept of entropy to non-equilibrium states. On page 58, he writes about the additivity of the entropy. He then adds that this is true only for macroscopic systems for which one can neglect the “*surface energy*.”

The surface energy can generally be neglected only if the two substances are not finely subdivided; otherwise, it can play a considerable role.

This is a very important comment. Further discussion of this aspect of entropy in Appendix S. Fermi also discusses the Boltzmann entropy, but as far as I know he never adapted any of the interpretations of entropy in terms of order-disorder, etc.

Appendix ZV*: What are Entropic Forces?

“Entropic-forces” are neither “entropic” nor “forces.” Yet, you can read about the entropic-forces, entropic mood, entropic dreams, and a plethora of “entropic ideas.” What one usually means by “entropic” is an adjective derived from “disorder.” If one accepts the “disorder” interpretation of entropy (see section 3.2), then it makes sense to refer to any tendency towards more disorder as “entropic.”

Below is what you will find in Wikipedia regarding Entropic forces:

In physics, an entropic-force acting in a system is an emergent phenomenon, resulting from the entire system's statistical tendency to increase its entropy, rather than from a particular underlying force on the atomic scale. The entropic force can be considered as an emergent of the entropic interaction. The concept of entropic interaction was usually used in a subjunctive mood. For example: "macromolecule links, as if, entropically repulse from each other at a short distance and entropically are attracted to each other at a long distance". In a modern view, the entropic interaction is considered to be a real-life interaction, and it is viewed as a mutual influence of open thermodynamic systems on each other by means of transferring information about their states, changing their entropies and translation of these systems into more probable conditions. The entropic interaction is a quintessential physical interaction that is realized by well-known basic interactions (gravitational, electromagnetic, nuclear strong and weak) through the processes that occur elsewhere in the universe including the solar system, our planet Earth, and living organisms. The basic interactions are considered to be daughter of the entropic interaction.

Nothing in the above paragraph is correct. The general idea is that since “entropy tends to increase,” and since this tendency causes some change, and if there is a change, there must be a “force” that causes that change.

Consider the expansion of an ideal gas as an example. You remove a constraint (a partition, as in Figure 2.1a), and you observe a change; the gas *expands*, and moves from the smaller compartment of volume V into a larger volume of $2V$. This “motion” of the gas must be due to some “force” which is referred to as entropic-force.

In physics, a force is something that operates on a particle. In a thermodynamic system, the forces acting on each particle is due either to intermolecular interactions, or to some external source such as gravity. ***Entropy does not exert any force on any particle!***

Hoffmann (2012) has a whole section on “Entropic Force” in which he discusses biochemical processes such as self-assembly of biomolecules, protein folding, etc. In describing this process of self-association (page 108) he claims that while the binding of large molecules is associated with decrease in entropy (or increase in “order”), there is also another process involving an *increase* in entropy of the smaller molecule. Then, he concludes:

What we end up with a force that is not the result of decreasing energy, but of increasing entropy. Such strange forces which can only exist at a molecular scale, are called entropic forces.

Unfortunately, it is not true that the process of self-assembly involves an increase in entropy of “the small molecules,” and the forces between the larger molecules do not necessarily arise from “increasing entropy.” Hoffmann also describes “hydrophobic forces” as an example of “entropic force.” (page 111) This is also not correct. Hydrophobic forces can be associated with a decrease or increase in entropy. This topic is discussed at great length in Ben-Naim (2011a, 2016c).



Figure ZV1. Two spherical particles are brought from infinite separation to a distance R .

Here, I will explain in what sense one can associate a force to change in entropy. Consider two particles at fixed positions in a solvent, say water, Figure ZV1. We now bring these two particles from infinite separation to some small distance R , where R is of the order of molecular diameter of the solute molecules.

We associate with this process, carried out at constant temperature and pressure, a change in Gibbs energy which we write as:

$$\Delta G(\infty \rightarrow R) = \Delta H(\infty \rightarrow R) - T\Delta S(\infty \rightarrow R)$$

Here, ΔH is essentially the *energy* change in the process [see Ben-Naim (2011a), and ΔS is the corresponding change in the entropy.

In general, whenever $\Delta G(A \rightarrow B) < 0$, for any process $A \rightarrow B$, people say that there is a *thermodynamic force* that derives the process $A \rightarrow B$. This is true for processes at constant temperatures and pressures; when the process $A \rightarrow B$ occurs, the Gibbs energy decreases. However, this Gibbs energy change is not a *force* in the normal sense used in physics. It is also not true when we discuss a molecular process such as hydrophobic interaction or protein folding.

For a macroscopic process, $A \rightarrow B$, when $|\Delta H| > |T\Delta S|$ the process is said to be driven by the energy (or enthalpy), while when $|\Delta H| < |T\Delta S|$ the process is said to be driven by entropy.

The function $\Delta G(\infty \rightarrow R)$ is often called as the potential of mean force (PMF). Its gradient with respect to R given an average force exerted on one particle, at the origin, given another particle at distance R , and averaged over all configurations of the solvent molecules. This average force could be either attractive or repulsive, and could be associated with either positive or negative change in entropy. If the two particles are simple spherical, and they move along the x -axis, then the force is given by:

$$F = -\frac{\partial}{\partial x} \Delta G(\infty \rightarrow x)$$

$$= -\frac{\partial}{\partial x} [\Delta H(\infty \rightarrow x)] + \frac{\partial}{\partial x} [T\Delta S(\infty \rightarrow x)]$$

The first term on the right-hand-side of this equation, may be referred to as a force associated with the gradient of the energy (or the enthalpy) function, and the second, as forces associated with the gradient of the entropy change. One should be careful in using the term “entropic force” for the second term on the right-hand-side equation.

Another way of splitting the Gibbs energy change is obtained by writing the Gibbs energy change in the process of Figure ZV1 as:

$$\Delta G(R) = \Delta U(R) + \delta G(R)$$

The first term on the right-hand-side is the *direct interaction* between the two particles, at distance R in vacuum (figure ZV1). The second term is the solvent induced contribution to the Gibbs energy change. Taking the gradient of this equation we get a *direct force* between the two particles and an *indirect force*, or the *solvent induced forces*. For details, see Ben-Naim (2011a, 2016c). Note that the second force may both have an enthalpy and an entropy component.

A common misconception about the Gibbs energy function $G(R)$ is that once we release the constraint on a fixed distance, the two solute particles will move to such a distance R^* for which the function $G(R)$ has a minimum. This kind of argument about the Gibbs energy is often featured in a discussion of protein folding, where the constraint is about the angles of rotations, see Ben-Naim (2016c).

Consider again the two solute particles as in Figure ZV1. Starting from any initial distance R and releasing the constraint on a constant distance, the two particles will not move to a new distance, say R_{min} for which the Gibbs energy function, $G(R)$ has a minimum. Instead, the system will move to a state for which the *distribution* of distances $\text{Pr}(R)$ is the distribution that minimizes the Gibbs energy functional $G(T, P, N; \text{Pr}(R))$.

Similarly, suppose we have a protein and we start with a fixed conformation defined by the vector $\alpha = (\alpha_1, \dots, \alpha_n)$, where α_i is the i th internal rotational angle.

When we release the constraint on a fixed conformation, the system will move to a distribution of angles $\text{Pr}(\alpha)$ which minimizes the Gibbs energy functional $G(T, P, N; \text{Pr}(\alpha))$. Unfortunately, most people who discuss the protein folding problem would say that the system will proceed from the initial conformation α to a final conformation α_{min} for which the Gibbs energy is minimum. For more details, see Ben-Naim (2011a, 2016c).