

Review of: "On the statistical arrow of time"

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The paper by Henriksson [1] expresses the opinion that the concept of entropy which is the criterion that defines the direction of spontaneous processes, the arrow of time, is of subjective nature, because it depends on the perception of the observer. We are of course used to the fact that the perception of music, of a painting or another piece of art is subjective and depends entirely on the observer, and there is no objective measure of the quality of it. We also agree that some people may experience outdoor weather conditions on a given day as cold, whereas others may feel comfortable – but in this case we are glad to be able to measure temperature as an objective scientific criterion. Discussions about the role of the observer have a long tradition, most prominently in the early days of quantum mechanics when theories did not appear to have had the same reputation as today and were accepted only when they were supported by measurements, as the famous response by Einstein to Pais shows [2]: “Do you really believe that the moon only exists when I look at it?”

Indeed, today we believe that natural science is an exact discipline which is based on rigid facts. Personal interpretations may have some value as working hypotheses. Entropy has traditionally been a property of matter that was difficult to understand, in part because the term has been used colloquially for numerous situations of disorder such as for a messy desk, disordered dorm rooms or shuffling cards, and even for information entropy. As outlined in detail by Lambert [3] such type of disorder has nothing to do with thermodynamic entropy S , a property that has the dimension of an energy divided by a temperature. For clarity, it seems appropriate to first explain the characteristics of entropy and also its application for the determination of the direction of spontaneous processes, the *arrow of time*.

In simple systems, entropy has two main appearances. The first appearance can occur at constant temperature and relates to concentration or occupied volume. A drop of ink in a glass of water, or cigarette smoke in a room (which is equivalent to the example in the paper of a gas released in a room) spread spontaneously, a process driven by the concentration gradient and characterised by the mixing entropy. The process stops at equilibrium when a homogeneous distribution is reached. The change of entropy between the initial state with volume V_i or concentration c_i and final volume V_f is [4]

$$\Delta S = \int_{V_i}^{V_f} \frac{nR}{V} dV = nR \ln \left(\frac{V_f}{V_i} \right) = nR \ln \left(\frac{c_i}{c_f} \right)$$

For the second appearance we need to distinguish between a system of interest and its surrounding. For the system at

constant pressure, let's take a sample of highly ordered crystalline matter at absolute zero temperature, where S is assumed to be zero. The surrounding shall be a heat bath at high temperature. This heats up the system continuously and spontaneously by transfer of heat from the surrounding to the system so that its temperature increases. The arrow of time tells that heat flows only from hot to cold. At some point, the sample will melt without changing temperature T , then T will increase again until it approaches the boiling point where the sample evaporates. At all stages of this process the entropy of the sample increases, and we can indeed say that its disorder increases, in particular during the melting and the boiling phase transitions.

The criterion for a process to occur spontaneously is that the total entropy S of an isolated system (like the content of a thermo flask, or the entire universe) always increases, while it remains constant in equilibrium. In differential form it reads [4]

$$dS_{universe} = dS_{surrounding} + dS_{system} \geq 0$$

The important parameter is the heat dQ_{rev} that is exchanged reversibly between system and environment at their instant temperature

$$dS \geq \frac{\delta Q_{rev}}{T}$$

so that

$$dS_{universe} = \delta Q \left(\frac{1}{T_{surrounding}} - \frac{1}{T_{system}} \right)$$

For equal temperature of system and surrounding we have equilibrium, with

$$dS_{universe} = 0$$

If the system temperature is higher than that of the surrounding, the entropy change will be positive and the process spontaneous. If it is the other way around, the direction of heat flow is reversed, which changes the sign of dQ , so that the entropy change is still positive and the process spontaneous. Thus, the entropy of an isolated system (the universe) tends to a maximum value. It is of course cumbersome if one always has to include the entire universe in our calculation.

Therefore, an alternative but equivalent relation was derived for isobaric-isothermal processes, for which the universe cancels out. For these conditions, which are obeyed to a good approximation by most processes in our lab or in daily life,

$$\Delta G > 0$$

of the system alone is a much more convenient criterion for spontaneous behaviour.

It should be noted that we often have the impression that processes occur in the wrong direction and violate the arrow of time. For example, water in a pond freezes in a cold winter night, producing ice that is of lower entropy than water, or flowers seemingly grow spontaneously from seeds (living matter is thought to be of lower entropy than dead matter). These are driven processes. It is not forbidden for a system to show decreasing entropy as long as this entropy loss is offset by a larger positive contribution by the surrounding. And it is essential for life to occur that non-equilibrium situations are maintained. The main such process is photosynthesis, the production of sugar molecules from CO₂ and water, that is fuelled by solar energy.

A major misunderstanding of entropy originates in subjective views about order. Let us discuss this for the example of a checker board with its 32 white and 32 black fields (Figure 1, Ref. 4). Which arrangement of the fields is more ordered, the normal one with alternating black and white fields (Figure 1a) or one with all black fields on one side and the white ones on the other side? The answer is subjective. Objectively, the number W of distinguishable ways to arrange the $k = 32$ black fields over $n = 64$ fields is given by

$$W = \frac{n!}{k!(n-k)!} = \frac{64!}{32!32!}$$

which depends only on the number of black and white fields and is indistinguishable of their arrangement. Thus, all arrangements (e.g. that of Figure 1b) have the same probability $1/W$ as that of Figure 1a. However, this case has nothing to do with thermodynamic entropy since rearranging fields needs no energy, and there is not temperature. It therefore makes no sense to assign these probabilities to an energy divided by a temperature. This changes when we turn the system into a chemical one, for example by replacing black fields by positive sodium ions and white fields by negative chloride ions, which for a standard checker board gives a two-dimensional sodium chloride lattice (Figure 1c). Coulomb repulsion of equal and attraction of opposite charges leads to alternating occupation of fields as the single lowest energy arrangement. With increasing temperature, alternative arrangements of higher energy become increasingly populated, reflecting the aspect of entropy as a degree of thermal excitation, which distinguishes from disorder by concentration. Thermal population of the microstates is given by the Boltzmann distribution [5], and they are not equal in thermal equilibrium.

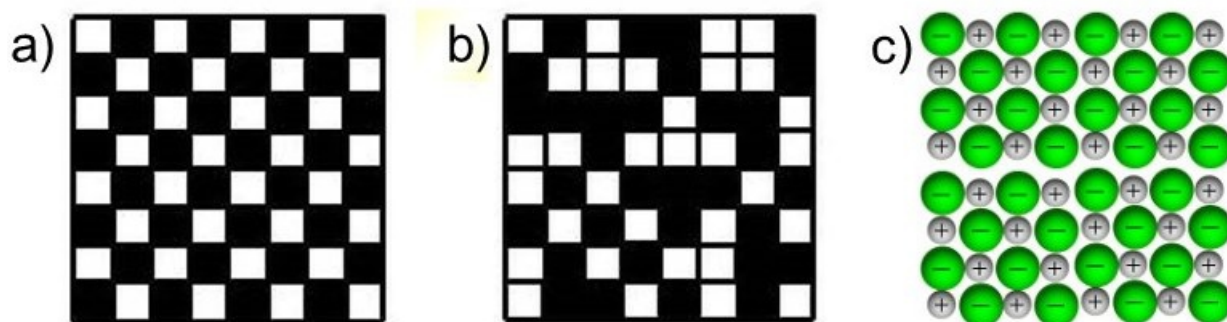


Figure 1: a) regular checker board, b) alternative arrangement has equal probability as a), c) regular arrangement as in a) but with cations and anions.

The criterion of increasing total entropy of system plus surrounding only gives the sign of a spontaneous process, but it says nothing about its rate. The rate is kinetics, and it is governed by activation barriers. As living organisms, we are glad that the process that takes us to equilibrium with our environment, which is when we have decomposed mainly to CO_2 and water, is not too fast. By daily eating our food we fuel the processes which keep us in flow-equilibria (steady states) away from equilibrium, and the rates of thousands of physiological processes are tediously adjusted by activation energies determined by enzymes, and by concentrations of reactants [6].

Another aspect concerns the origin of irreversibility of thermodynamic processes [4]. The equations of motion in Newton's classical mechanics, Maxwell's equations of electromagnetism, Einstein's equations of special and general relativity and Schrödinger's original equations of quantum mechanics are symmetric with respect to time-reversal. This means that if in the equation the variable time is replaced by negative time, as for a pendulum, the process will run exactly backward to its starting point, and it may oscillate. In contrast, a spontaneous process in thermodynamics proceeds only to a state that we call equilibrium, but not beyond, and it will not reverse unless it is forced to do so by supplying energy or spending work on it. Thus, there is only a forward direction, called the *arrow of time*. It turns out that the memory of the past is lost in all probabilistic processes, which do not occur at a precise time determined by the equation of motion. Even if a step in the reverse direction would occur it would not end up in the same previous state. Examples of probabilistic events are decays of radioactive elements or of excited states [5].

Overall, entropy in a thermodynamic sense is a well-defined property of matter that is objective and independent of an observer. In the interest of exact science, one should be careful to avoid association of the arrow of time to subjective, colloquial versions of the term entropy.

[1] A. Hendrikson, On the statistical arrow of time. *Qeios*, ID C9JOJ9 (2023).

[2] A. Pais, Einstein and the quantum theory, *Rev. Mod. Phys.* 51, 863-914 (1979).

[3] F.L. Lambert, Shuffled Cards, Messy Desks, and Disorderly Dorm Rooms - Examples of Entropy Increase? Nonsense! *J. Chem. Educ.* 76, 1385-1387 (1999).

- [4] E. Roduner, T.P.J. Krüger, The origin of irreversibility and thermalization in thermodynamic processes. *Phys. Rep.* 944, 1-43 (2022).
- [5] L. Boltzmann, Über die Beziehung zwischen dem zweiten Hauptsatz der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Wärmegleichgewicht. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wien, Mathematisch-Naturwissenschaftliche Classe. Abt. II*, 76 (1877) 373–435. Reprinted in *Wissenschaftliche Abhandlungen*, Vol. II, 164–223, Leipzig: Barth, 1909.
- [6] E. Roduner, S. Gayathri Radhakrishnan. In Command of Non-equilibrium. *Chem. Soc. Rev.*, 45, 2768–2784 (2016).