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Appendix VIII. Statistical entropy difference

Abstract

With the aim to refine the existing entropy concept, an expression for a microscopically applicable entropy difference is derived on the basis of recent theoretical findings in the field of statistical mechanics. Some similarities and differences between the resulting formula and the detailed fluctuation theorem are identified. Subsequently, the Second Law of Thermodynamics is derived from the new entropy formula and a crude estimate of its limits of application is calculated. Theoretical and empirical implications are considered and the new concept of *statistical entropy difference* is applied to the single-particle decay process of the neutral K-meson.

1 Introduction

Entropy has a unique status in physics, since it is the only physical quantity that varies monotonically with time: the entropy of an isolated system either remains constant or increases. The entropy concept has been a subject of controversies ever since it was developed in the middle of the nineteenth century, and the issue has not been settled yet.[1] A central issue is how to derive the time asymmetry, intrinsic to the entropy concept, from assumed time symmetric fundamental laws. Furthermore, entropy concept has only limited application in microscopic and nonequilibrium process.[2]

A crucial leap forward in these respects was taken by Ludwig Boltzmann through his statistical interpretation of the entropy quantity, S,[3]

$$S = k_B \cdot \ln W \ , \tag{1}$$

[1] For an account of historical controversies, see Brown et al. (2009), while Uffink (2001, 2007), Nikulov & Sheehan (2004), and te Vrugt (2021) describe more recent issues.

[2] Several authors (Earman, 1974, 2006; Denbigh, 1989; Uffink, 2007) have pointed out the lack of generality of the entropy concept. However, Batalhâo et al. (2015) and Rossnagel et al. (2016) have demonstrated microscopic entropy differences empirically, and microscopic applications of entropy is described by fluctuation theorems (see Section 4).

[3] According to Swendsen (2006), it was Max Planck rather than Boltzmann who formulated this equation, even if it is inscribed in the tombstone of the latter.

where W denotes the number of equally probable microstates of the macrostate in question and k_B is Boltzmann's constant. However, even this entropy concept has several limitations. First, statistical entropy, thus defined, can only be measured for systems for which it is possible to identify a limited number of equally probable microstates; for example, it cannot measure the time asymmetric evolution in disequilibrium chemical processes or radioactive decay. Second, a derivation of the macroscopic time asymmetrical aspect of entropy from some fundamental principles of physics has still not been established. Third, it is unclear what entropy actually measures - disorder, energy dispersal, probability or information.

The aim of the present article is to extend the concept of entropy to overcome these limitations. In Section 2, some basic concepts are defined. In Section 3, an expression for statistical entropy difference is derived and in Section 4 it is compared with the detailed fluctuation theorem. The derived expression constitutes a foundation for a derivation of the Second Law of Thermodynamics in Section 5. The theoretical implications of these results are considered in Sections 6, and in Section 7 and 8 macroscopic and microscopic applications are described. Finally, in Section 9, further development of the entropy concept is discussed.

2 Basic concepts

In a previous article, Skoruppa (2022d) proposes a physical law which is verified to some extent in Skoruppa (2022b) and more thoroughly in Skoruppa (2022f):

> **Law of statistical mechanical time asymmetry**
> Assume that $A[t_1, t_2]$ and $B[t_3, t_4]$, where $t_1 \leq t_2 \leq t_3 \leq t_4$ and $t_1 < t_4$, are macroscopic states, defined by the same quantities and the same degree of coarse graining in an isolated disequilibrium process. Then $p(B[t_3, t_4]|A[t_1, t_2])$ is always, while $p(A[t_1, t_2]|B[t_3, t_4])$ is never, time translation invariant through the entire evolution from disequilibrium to an enduring equilibrium.

The law thus states that, in time translation invariant conditional probabilities that correctly describe a physical process evolving from equilibrium to disequilibrium, the outcome always *follows* the condition, while the outcome never *precedes* the condition in these probabilities.[4] The two kinds of conditional probabilities that is expressed in the law can be defined in the following ways.

[4] This can be considered as a precise physical expression for the time asymmetry that Evans & Searles (2002) describe in terms of the unphysical *Axiom of Causality* (also mentioned in Section 4 in the present article).

Definition 1 *Future-directed probability:*

$$p(B[t_2]|A[t_1]) = \frac{p(A[t_1] \wedge B[t_2])}{p(A[t_1])} ,$$

where $t_1 < t_2$.

Definition 2 *Past-directed probability:*

$$p(A[t_1]|B[t_2]) = \frac{p(A[t_1] \wedge B[t_2])}{p(B[t_2])} ,$$

where $t_1 < t_2$.

3 Derivation of statistical entropy difference

As a point of departure, let the entropy of equation (1) describe a difference between well-defined entropies of two macrostates, A and B, between which the system in question can evolve spontaneously if kept in isolation. The system is assumed to be isolated in a container with a constant and finite volume and with no heat exchange with the environment. Furthermore, the entropies of A and B are assumed to be defined by the same macroscopic quantities, which are measured by means of the same degree of coarse-graining, i.e. the same size of cells in phase space.[5] Then, equation (1) implies

$$S_A - S_B = k_B \cdot \ln\, W_A - k_B \cdot \ln\, W_B = k_B \cdot \ln\, \frac{W_A}{W_B} \, . \tag{2}$$

A good reason for analysing entropy in terms of *difference* is the difficulty to ascribe an absolute entropy value to a physical state, since it depends on the method of coarse-graining and on which aspects of the entropy value that is estimated. For example, the entropy of a gas in a closed container is dependent on whether the measure is based on the velocity distribution or the spatial distribution of the molecules; the entropy is also dependent on how fine-grained the categorization of the velocity and spatial measures are. Yet another entropy value could be the result if it was also taken into account that the entropy of an isolated system, in the long run, will increase as a result of nuclear reactions, e.g. the spontaneous decay of protons and neutrons from which the system is built.

A significant characteristic of thermodynamical processes is their unique possible *future* state of equilibrium, if they evolve in isolation

[5]Since the probabilities in the derivation are defined in terms of Gibbs' ensemble concept, coarse-graining is defined in terms of Gibbs' phase space concept as well.

in a vessel of constant and finite volume.[6] Since W stands for equally probable microstates, this means that

$$\lim_{t\to\infty} p(X[t]) = \frac{W_X}{W_{tot}} \;, \tag{3}$$

where W_{tot} denotes the total number of equally probable microstates, and where $p(X[t])$ denotes the unconditional probability of the statistically described arbibrary state X to occur at the point in time t. This tendency towards a future equilibrium can be considered a consequence of the *law of statistical mechanical time asymmetry*, presented in Section 2, since a stable future equilibrium state requires translation invariant *future-directed* probabilities.[7]

Thus, A and B are assumed to be two possible states in an isolated physical process that can be correctly described as a homogeneous stochastic process with a unique possible equilibrium probability distribution. Since the future-directed probabilities are time translation invariant in accordance with the *law of statistical mechanical time asymmetry*, the following relation is implied for two arbitrary states, A and B, two arbitrary points in time, t and t', and an arbitrary time interval τ, where $\tau > 0$,

$$p(A[t'+\tau]|B[t']) = \lim_{t\to\infty} p(A[t+\tau]|B[t]) \;. \tag{4}$$

Furthermore, if the spontaneous evolution under study is evolving for an infinite time, it can be assumed to end in a state of equilibrium restricted to *detailed balance*.[8] Detailed balance is defined as equilibrium with no circular probability currents, and thus,

$$\lim_{t\to\infty} p(A[t]\wedge B[t+\tau]) = \lim_{t\to\infty} p(B[t]\wedge A[t+\tau]) \;. \tag{5}$$

[6]Uffink (2007, p. ∼1029) writes: "In fact, I will argue that this discussion of irreversible behaviour as derived from the Markov property suffers from an illusion. It is due to the habit of studying the prediction of future states from a given initial state, rather than studying retrodictions towards an earlier state. As we shall see, for a proper description of irreversibility in stochastic dynamics one needs to focus on another issue, namely the difference between backward and forwards transition probabilities."

[7]This tendency towards a *future* equilibrium state can be proven in terms of linear algebra, where a stable steady-state vector is derived on the basis of time translation invariant future-directed probabilities, and where the time direction of the probabilities usually is implicit (see e.g. Lay (1994)). The assertion is also proven for a simple model of the universe in Section 5 of Skoruppa (2022c).

[8]The concept of detailed balance originates from Lewis (1925) and is expressed by Bacciagaluppi (2010) in a form that is equivalent to equation (5), except for the limit to infinity. The limit does not influence the validness of the expression. The assumption of detailed balance can be considered as a reasonable postulate, which the following derivation is built upon.

It is now possible to rewrite the entropy difference in equation (2), given that the involved probabilities are non-zero (i.e. that an evolution between A and B is possible in the time interval τ), and given that t'' is another arbitrary point in time:

$$\begin{aligned} S_A - S_B &= k_B \cdot \ln \frac{W_A/W_{tot}}{W_B/W_{tot}} = \{(3)\} \\ &= \lim_{t\to\infty} k_B \cdot \ln \frac{p(A[t])}{p(B[t])} \\ &= \lim_{t\to\infty} k_B \cdot \ln \left[\frac{p(A[t])}{p(B[t])} \cdot \frac{p(A[t] \wedge B[t+\tau])}{p(A[t] \wedge B[t+\tau])} \right] = \{(5)\} \\ &= \lim_{t\to\infty} k_B \cdot \ln \left[\frac{p(A[t])}{p(B[t])} \cdot \frac{p(B[t] \wedge A[t+\tau])}{p(A[t] \wedge B[t+\tau])} \right] = \{\text{definition}\} \\ &= \lim_{t\to\infty} k_B \cdot \ln \frac{p(A[t+\tau]|B[t])}{p(B[t+\tau]|A[t])} = \{(4)\} \\ &= k_B \cdot \ln \frac{p(A[t'+\tau]|B[t'])}{p(B[t''+\tau]|A[t''])} , \end{aligned} \tag{6}$$

where $\tau > 0$. This is an expression for what from now on is named *statistical entropy difference*, and it denotes the entropy difference between two states in an isolated spontaneous evolution by means of future-directed transition probabilities.

The above derivation, in addition to the assumed detailed balance, is dependent on Boltzmann's assumption that the system in question can be measured in terms of number of equally probable states, W, according to the formula (1). However, it seems reasonable to assume that the relation

$$S_A - S_B = \lim_{t\to\infty} k_B \cdot \ln \frac{p(A[t])}{p(B[t])} \tag{7}$$

to be generally valid also in processes where the microscopic states are not equally probable, e.g. chemical processes. The general validity of the relation (7) is therefore postulated and hence the formula (6) for statistical entropy difference can be considered as generally valid for all kinds of isolated processes contained in constant and finite volumes.

In conclusion, the derivation above is based on three crucial assumptions apart from the characteristics of the system and the states in question: (a) the validness of *the law of statistical mechanical time asymmetry*, (b) that an isolated system finally reaches a state restricted to detailed balance, and (c) the validness of the assumption expressed by equation (7).

4 Relation between the obtained formula and the detailed fluctuation theorem

Thirty years ago Evans et al. (1993) derived a *fluctuation theorem* that expresses the probability of fluctuations in the shear stress of a fluid in a nonequilibrium steady state far from equilibrium. It gives an analytical expression for the probability of observing Second Law violating dynamical fluctuations in thermostatted dissipative non-equilibrium systems, especially for short time intervals and in systems with few particles.

Derivation of various fluctuation theorems has since become a fruitful area of research. In the "detailed" version, the quotient between the probability of the positive entropy production Σ, when a system runs according to the Second Law of Thermodynamics, and the probability of the negative entropy production $-\Sigma$, when the same system is run in reverse, equals the exponential of the entropy production. As Salazar (2021) puts it:

> Particularly, the strong Detailed Fluctuation Theorem (DFT) is a relation about the asymmetry of the probability density function of the entropy production,
>
> $$\frac{p(\Sigma)}{p(-\Sigma)} = e^{\Sigma} \tag{8}$$
>
> indicating that positive values of entropy production are more likely to be observed than the negative counterparts. It arises, for instance, in time symmetric protocols in the exchange fluctuation framework. The most known consequence of (8) is the integral fluctuation theorem (IFT), $\langle e^{-\Sigma} \rangle = 1$, which results in the second law of thermodynamics, $\langle \Sigma \rangle \geq 0$, from Jensens inequality. (Salazar, 2021, p. 062101:1)

If the involved entropies are interpreted as being expressed in nats (i.e. natural units) in accordance with Crooks (1999) and England (2013), equation (8) can be rewritten as

$$\Sigma = k_B \cdot \ln \frac{p(\Sigma)}{p(-\Sigma)} \ , \tag{9}$$

where Σ denotes an entropy distribution according to e.g. Crooks (1999). Equation (9) looks quite similar to equation (6), but the author of the present article is admittedly not schooled enough in this field of physics to decide *how* similar the two expressions actually are. However, some differences can be brought out:

- While equation (6) describes a relation between probabilities of developments in an isolated system, equation (9) describes a relation between probabilities of developments between summed exchanges with a heat bath (i.e. the *entropy production*) of an insulated system.
- While equation (6) describes a relation between the probabilities of two single trajectories in phase space, equation (9) describes the probabilities between two *distributions* of trajectories.
- While it is clear that the time asymmetry of equation (6) originates from the proposed physical *Law of statistical mechanical time asymmetry*, it is unclear where the time asymmetry of equation (9) originates from; Evans & Searles (2002) refer it to the metaphysically flavoured *Axiom of Causality*, which Pietsch (2005) correctly opposes to.

5 Derivation of the Second Law of Thermodynamics on the basis of the statistical entropy difference formula

Assume that two macroscopic states **I** and **II** can evolve to each other in both directions in an isolated thermodynamic process (at least theoretically, as a result of an extremely improbable fluctuation) at a given place. Moreover, assume that both these states have well defined entropies, and that the entropy of state **I**, $S_{\mathbf{I}}$, is measurable smaller than the entropy of state **II**, $S_{\mathbf{II}}$. In order to provide wide margins for the following derivation of the Second Law of Thermodynamics, "measurable smaller" is defined by an entropy difference that is greater than $10^{-10}J/K$ (a larger value makes the derivation even more convincing). This limit is applied to the formula of *statistical entropy difference* (6), and thus:

$$\begin{aligned}
&S_{\mathbf{II}} - S_{\mathbf{I}} = k_B \cdot \ln \frac{p(\mathbf{II}[t' + \tau]|\mathbf{I}[t'])}{p(\mathbf{I}[t'' + \tau]|\mathbf{II}[t''])} > 10^{-10}J/K \\
\Rightarrow &\frac{p(\mathbf{II}[t' + \tau]|\mathbf{I}[t'])}{p(\mathbf{I}[t'' + \tau]|\mathbf{II}[t''])} > e^{\frac{10^{-10}J/K}{k_B}} \approx 10^{10^{12.5}} \Rightarrow \{\text{definition}\} \\
\Rightarrow &\frac{p(\mathbf{II}[t' + \tau] \wedge \mathbf{I}[t'])}{p(\mathbf{I}[t'' + \tau] \wedge \mathbf{II}[t''])} > \frac{p(\mathbf{I}[t'])}{p(\mathbf{II}[t''])} \cdot 10^{10^{12.4}}\ , \qquad (10)
\end{aligned}$$

where $\tau > 0$.

The right side of the inequality (10) expresses a lower limit for how much more probable it is for the lower entropy state **I** to evolve to the higher entropy state **II** than the reverse evolution. Hence, if we want to establish a lowest possible *numerical* limit for the probability of the evolution $\mathbf{I} \to \mathbf{II}$, we must find the lowest possible numerical limit for $p(\mathbf{I}[t'])$ and the highest possible limit for $p(\mathbf{II}[t''])$.[9] Since it is impossible to calculate an empirically motivated upper limit for any state of a given system to appear at a given place at a specific point of time, the latter limit is set to unity, i.e. $max\big[p(\mathbf{II}[t''])\big] = 1$.

To obtain the lowest possible numerical limit for $p(\mathbf{I}[t'])$, assume that state **I** is *empirically realistic*, which here means that the state has a reasonably large statistical likelihood to appear at the given place at the time when it is measured.[10] Accordingly, state **I** is defined as empirically realistic if it has an unconditional probability, $p(\mathbf{I}[t'])$, that would allow it to occur at the given place at least once during the time of existence of the universe up to now. A very low limit (which is meant to be extremely inclusive) for state **I** to be empirically realistic, is that it has an unconditional probability that is larger than the shortest physically possible time interval of occurrence divided by the largest possible time interval of occurrence in the life time of the universe up to now. Therefore, the limit is decided to be the Planck time divided by the age of the universe.[11] Hence,

$$\left.\begin{array}{l} min\big[p(\mathbf{I}[t'])\big] = \dfrac{\text{Planck time}}{\text{Age of the universe}} \\ max\big[p(\mathbf{II}[t''])\big] = 1 \end{array}\right\}$$

$$\Rightarrow \frac{p(\mathbf{I}[t'])}{p(\mathbf{II}[t''])} > \frac{\text{Planck time}}{\text{Age of the universe}} \approx \frac{5.39 \cdot 10^{-43}\ \text{s}}{1.84 \cdot 10^{16}\ \text{s}} > 10^{-59}. \qquad (11)$$

The equations (10) and (11) combine to

$$\frac{p(\mathbf{I}[t']) \wedge \mathbf{II}[t'+\tau])}{p(\mathbf{II}[t''] \wedge \mathbf{I}[t''+\tau])} > 10^{-59} \cdot 10^{10^{12.4}} > 10^{10^{12.3}}\,, \qquad (12)$$

where $\tau > 0$. This means that if the entropy of the state **II** is measurably greater than the entropy of the state **I**, and if both states have unconditional probabilities that allow them to have a reasonable chance

[9]The derivation implicitly relies on the existence of objective probabilities, especially with respect to the value of $p(\mathbf{I}[t'])$. This, in turn, depends on the assumption that the universe is stochastic in an objective sense, which is a reasonable interpretation of the quantum mechanical description.

[10]The concept of *empirical realism* is motivated by the fact that the unconditional probabilities of the universe as a whole and most of its subsystem at the current time prove to be far much greater than it would be in a state of equilibrium (i.e. in the case of heat death) – otherwise these disequilibrium states would have probabilities so low that they would not occur in practice.

[11]The derivation is not dependent on the Planck time being the shortest possible time interval, but rather on the mere *existence* of a shortest possible time interval greater than $\sim 10^{-10^{10}}$ seconds.

to occur in the process in question, at a given place, at least once during the existence of a universe up to now, the probability of the entropy increase $\mathbf{I} \rightarrow \mathbf{II}$ is enormously much greater than the probability of the entropy decrease $\mathbf{II} \rightarrow \mathbf{I}$ (if the two states are separated by the same arbitrary time interval). Expressed in other words, this is a version of the *Second Law of Thermodynamics*:

> In an isolated evolution between two empirically realistic macroscopic states with a measurable entropy difference, the entropy will, in practice, always increase.

Moreover, it is possible to estimate the approximate limits of applicability of the Second Law on the basis of the above derivation and the reasonable assumptions that it is built upon. First, the derivation is built on the assumption that the system is isolated and macroscopic, where the latter assumption motivates a minimum entropy differences of $10^{-10} J/K$. For microscopic systems, where the entropy difference comes close to the Boltzmann constant, $1,38 \cdot 10^{-23} J/K$, it can easily be shown that the derivation is no longer valid (as an example, a microscopic entropy difference is calculated in Section 8).

Second, the limit for the state $\mathbf{I}$ to be empirically realistic is defined as a fraction with the age of the universe as the denominator. The age of the universe has to be less than $10^{10^{12.4}}$ years for the probability $p(\mathbf{I}[t']) \wedge \mathbf{II}[t' + \tau])$ to necessarily be larger than the probability $p(\mathbf{II}[t''] \wedge \mathbf{I}[t'' + \tau])$ in accordance with equation (12). However, the universe is predicted to expand forever and, therefore, the derivation is valid only in the infinitesimal part of the history of the universe that happens to be the case right now, when the predicted "heat death" has not yet prevailed. Later on, the Second Law of Thermodynamics can not be expected to hold.

6 Other theoretical implications of statistical entropy difference

A characteristic of the statistical entropy difference formula is that the quotient of the transition probabilities is independent of the length of the time interval τ between the two states. It is also noteworthy that the formula (6) incorporates both probabilities and time asymmetry into the same entropy formula, with the time asymmetry represented by the *future-directed* (in contrast to past-directed) probabilities in the quotient. This time asymmetry is essential in the derivation of second law of thermodynamics in accordance with the line of reasoning in Section 5.

The statistical entropy difference concept also has a wider domain of applicability than the formula (1), since it is no longer dependent on the existence of countable and equally probable microstates as a consequence of the postulate expressed by equation (7) in the end of Section 3. This opens the possibility to generalize the entropy concept to a wider range of physical phenomena, e.g. chemical disequilibrium, which is the subject of Skoruppa (2022e).

The most profound theoretical implication of the statistical entropy difference concept emanates from the relationship with the widely discussed symmetry that is considered to be the criterion for *time reversal invariance*, expressed in terms of probabilities:[12]

$$p(B[t+\tau]|A[t]) = p(A^T[t+\tau]|B^T[t]) \ , \tag{13}$$

where $\tau > 0$, and where the superscript '^{T}' denotes time reversal of the state with respect to quantities such as velocity, spin and angular momentum. If it were not for these superscripts, the symmetry implies equal entropy value according to equation (6).

However, in macroscopic thermodynamics, the relevant quantities are not influenced by time reversal, since they express macroscopic conditions of a system, such as temperature, volume and weight, which are independent of the time direction. Hence, formula (6) would have the same meaning even if the superscripts on right side of equation (13) were present and, consequently, the symmetry (13) is possible to interpret in terms of equal entropies in microscopic as well as macroscopic process.

In two recent articles,[13] analyses have shown that it is deeply questionable to define symmetry (13) as a criterion for *time reversal invariance* – partly because the symmetry is time asymmetric in itself – and therefore two alternative names have been suggested by the authors of these articles: *orthodox criterion for reversal symmetry* and *criterion for future-directed process reversal invariance*, respectively. It is now possible, in accordance with the discussion above, to propose a more comprehensible label for this important symmetry:

Definition 3 Criterion for entropy equality
In an isolated process, two states A and B have equal entropy value if

$$p(B[t+\tau]|A[t]) = p(A^T[t+\tau]|B^T[t]) \ , \tau > 0 \ ,$$

given an arbitrary time interval τ, and given that the conditional probabilities are time translation invariant and not zero.

[12] This probabilistic symmetry is discussed by Holster (2003).
[13] Holster (2003) and Skoruppa (2022g).

Consequently, this is a criterion for entropy equality between two states that can appear in succession in the same isolated system (in Section 8 it will become clear that this criterion is applicable also to microscopic processes).

7 Macroscopic applications

The derivation of the entropy concept represented in equation (6) is built on the assumptions that the states in question are macroscopically well-defined and that the process in question can be correctly described as a homogeneous stochastic process with a unique equilibrium probability distribution. The latter assumption is valid if the system is isolated in a constant and finite volume. Hence, the following formal definition can be formulated by means of equations (2), (3) and (6):

Definition 4 Statistical entropy difference (macroscopic version)
Assume that two macroscopically states, A and B, defined by the same degree of coarse graining, have non-zero probabilities to spontaneously evolve to each other in an arbitrary time interval $[t, t+\tau]$ in an isolated system with a constant and finite volume. Then the entropy difference between A and B is

$$S_A - S_B = k_B \cdot \ln \frac{p(A[t'+\tau]|B[t'])}{p(B[t''+\tau]|A[t''])} = \lim_{t\to\infty} k_B \cdot \ln \frac{p(A[t])}{p(B[t])} \, , \tag{14}$$

where $\tau > 0$, and where t' and t'' denote arbitrary points in time.

Statistical entropy difference, as defined in the present work, has a considerable potential for empirical applications in macroscopic systems. As an example, is shown in Skoruppa (2022e) that the concept can play a crucial role in the derivation of entropy differences in disequilibrium chemical systems.

It seems plausible that a corresponding derivation can be applied also to quasi-stationary systems, such as radioactive decay and spontaneous emission, which also can exhibit states of equilibrium and disequilibrium. If this kind of systems appears in a large reservoir, the future-directed probability of the decay or the emission is much larger than the future-directed probability of the reversed process (in fact, the latter probability is zero if the reservoir is ideally empty space). As a consequence, the entropy of the quasi-stationary state is decidedly less than the entropy of the dispersed state following the decay or the emission.[14]

[14]Hopefully, this approach has potential to overcome some of the difficulties con-

The statistical entropy difference concept also makes way for a new understanding in the troublesome field of gravitation entropy.[15] The apparent contradiction between the evolution towards denser matter concentration in the creation of galaxies and stars and the spreading out of matter in expanding gases (which are both considered entropy increasing processes) is reconciled if the entropy difference between a dense and dilute state is expressed in terms of the future-directed probabilities of the transition between the two states.[16]

A concrete example of a macroscopic application is provided if the formula for *statistical entropy difference* (14) is combined with the well known formula for entropy increase of an ideal gas expanding as a function of the number of molecules and the volume of the gas. The entropy difference between the two equilibrium states are (n denotes the number of moles and N denotes the number of molecules in the gas; R and k_B denote the molar gas constant and Boltzmann's constant, respectively):

$$\begin{aligned} S_{\mathbf{II}} - S_{\mathbf{I}} = n \cdot R \cdot \ln \frac{V_{\mathbf{II}}}{V_{\mathbf{I}}} = \{(14)\} = k_B \cdot \ln \frac{p(\mathbf{II}[t' + \tau]|\mathbf{I}[t'])}{p(\mathbf{I}[t'' + \tau]|\mathbf{II}[t''])} \\ \Rightarrow \frac{p(\mathbf{II}[t' + \tau]|\mathbf{I}[t'])}{p(\mathbf{I}[t'' + \tau]|\mathbf{II}[t''])} = \left(\frac{V_{\mathbf{II}}}{V_{\mathbf{I}}}\right)^{\frac{n \cdot R}{k_B}} \\ \Rightarrow \frac{p(\mathbf{II}[t' + \tau]|\mathbf{I}[t'])}{p(\mathbf{I}[t'' + \tau]|\mathbf{II}[t''])} = \left(\frac{V_{\mathbf{II}}}{V_{\mathbf{I}}}\right)^{N} , \end{aligned} \tag{15}$$

where $\tau > 0$. It should be emphasized that this relation is independent of the size of the time interval τ between the two states. Since N usually is in the magnitude of 10^{20} or larger, the quotient between the probabilities normally represents, to say the least, a huge number. An alternative derivation of the formula (15) is presented in Skoruppa (2022a).

The widest potential area of empirical application of statistical entropy difference is probably the field of non-equilibrium thermodynamics, where it opens up for a definition of entropy in systems far from equilibrium. Up to now, the difficulties in this field of physics have, in their turn, obstructed scientific study of self-organization and living organisms from a perspective of statistical mechanics.

8 Microscopic applications

In accordance with the hypothetisised Definition 3, the scope of the statistical entropy difference can be widened also to include microscopic

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nected with the application of the entropy concept to quantum unstable systems and nuclear reactions that e.g. Civitarese & Gadella (2015) and Tosti (2021) describe.

[15] See e.g. Mann (2003) and Earman (2006) for accounts of some of the troubles.

[16] A sketchy account of statistical time asymmetry of gravitational aggregation of matter is given in the end of Chapter 20 in Skoruppa (2022f).

systems. A slightly modified version of Definition 4 can, as a consequence of the analysis in Section 6, be proposed as follows:

Definition 5 Statistical entropy difference (general version)
Assume that an evolution between two states, $A \to B$, as well as an evolution $B^T \to A^T$, has a non-zero probability to spontaneously evolve in an arbitrary time interval $[t, t+\tau]$ in an isolated system with a constant and finite volume. If the states in question are defined by the same degree of coarse graining, the entropy difference between the two pair of states is

$$S_A - S_B = S_{A^T} - S_{B^T} = k_B \cdot \ln \frac{p(A^T[t'+\tau]|B^T[t'])}{p(B[t''+\tau]|A[t''])} \,, \quad (16)$$

where $\tau > 0$, and where t' and t'' denote arbitrary points in time.

As a peripheral but significant microscopic example, the statistical entropy difference now can be calculated for a single decay of the neutral K-meson. Accurate experiments have given the following result (with the experimental limits $1 \cdot 10^{-10}$ s $< \tau < 2 \cdot 10^{-9}$ s):[17]

$$\frac{p(K^0[t+\tau]|\bar{K}^0[t]) - p(\bar{K}^0[t+\tau]|K^0[t])}{p(K^0[t+\tau]|\bar{K}^0[t]) + p(\bar{K}^0[t+\tau]|K^0[t])} = (6.6 \pm 1.3) \cdot 10^{-3}$$
$$\Rightarrow \frac{p(K^0[t+\tau]|\bar{K}^0[t])}{p(\bar{K}^0[t+\tau]|K^0[t])} = 1.0133 \pm 2.6 \cdot 10^{-3} \,.$$

Since the K-meson decay correctly can be described by probabilities and since the two states K^0 and $\bar{K}^0$ are unchanged under time reversal, the formula (16) describes the entropy difference in a single particle decay:

$$\begin{aligned} S_{K^0} - S_{\bar{K}^0} &= k_B \cdot \ln(1.0133 \pm 2.6 \cdot 10^{-3}) \\ &= (1.82 \pm 0.36) \cdot 10^{-25} \text{ J/K} \,. \end{aligned} \quad (17)$$

Hence, the statistical entropy difference formula gives a very small but measurable value for the entropy difference between the neutral K-meson and its antiparticle.

In Skoruppa (2022e) statistical entropy difference is applied to chemical systems, where it describes statistical time asymmetry on the molecular level in terms of entropy. Another area, where statistical entropy difference is presumably useful, is in the derivations and applications of various fluctuation theorems (see Section 4).

[17] Angelopoulos et al. (1998).

9 Discussion

The concept of the statistical entropy difference hopefully has a potential to give a significant contribution to the field of thermodynamics, since it seems to provide answers to some of the foundational problems in this realm. It is especially noteworthy that the statistical entropy difference formula (14) explicitly expresses both time direction and probability through the quotient of future-directed probabilities. Thereby the connection with the asserted time asymmetry of the second law of thermodynamics becomes overt, which makes it possible to derive the second law on the basis of the formula of statistical entropy difference as is demonstrated in Section 5.

It should be noted that the implications of the statistical entropy difference, derived in the present article, is restricted to a certain condition: one of the two states in question must be potentially able to spontaneously evolve to the other in an isolated system. As a consequence of this limitation, it is for example not possible to use the formula (14) to decide the entropy difference between two states with different masses. Another noteworthy consequence of this formula is that the entropy difference in a deterministically evolving system, e.g. the expanding universe, is not defined, since the quotient in the formula (6) is not defined if either of the two probabilities is zero.

Hopefully, the new entropy formula will shed light over some of the issues associated with the entropy concept. For example, both the recurrence and the reversible objections, raised against Boltzmann, have less validity when raised against an entropy concept where the time asymmetry of the entropy concept is outspoken. The statistical entropy difference also clarifies what entropy actually measures; loosely speaking, the entropy difference between two states, A and B, is a measure of how much larger the future-directed probability is for B to evolve, given A, than the future-directed probability for A to evolve, given B.

Moreover, the statistical entropy difference can be used to demonstrate some important relations between fundamental physical concepts. Surprisingly, the probabilistic symmetry that has previously been used as a criterion for *time reversal invariance* should rather, in the light of the present analysis, be interpreted as a criterion for entropy equality between states. Therefore, the so called T violation, first observed in the decay of the neutral K-meson, is better interpreted as a sign of entropy difference between an evolution and its time reverse in a spontaneous quantum processes than as a sign of a fundamental time asymmetry. It is also clear that the statistical entropy difference concept is in accordance with the *law of statistical mechanical time asymmetry*, which is described in Section 2.

Another point to be noted is that the statistical entropy difference concept is not in opposition with Boltzmann's entropy formula, but rather extends his statistical interpretation of entropy beyond the estimation of the number of configurations that represents the state in question. This opens the possibility to calculate entropy differences in a single-particle system, which is demonstrated in Section 8. It also opens possibilities to estimate entropy values of non-equilibrium states in some cases, where the number of configurations is not possible to calculate or where this number is not comparable for different microscopically defined states, e.g. in chemical processes.

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