

Article

One Antimatter — Two Possible Thermodynamics

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Abstract: Conventional thermodynamics, which is formulated for our world populated by radiation and matter, can be extended to describe physical properties of antimatter in two mutually exclusive ways: CP-invariant or CPT-invariant. Here we refer to invariance of physical laws under charge (C), parity (P) and time reversal (T) transformations. While in quantum field theory CPT invariance is a theorem confirmed by experiments, the symmetry principles applied to macroscopic phenomena or to the whole of the Universe represent only hypotheses. Since both versions of thermodynamics are different only in their treatment of antimatter, but are the same in describing our world dominated by matter, making a clear experimentally justified choice between CP invariance and CPT invariance in context of thermodynamics is not possible at present. This work investigates the comparative properties of the CP- and CPT-invariant extensions of thermodynamics (focusing on the latter, which is less conventional than the former) and examines conditions under which these extensions can be experimentally tested.

Keywords: thermodynamic time; CPT-invariance; negative temperatures

1. Introduction

In the 1890s, the kinetic theory of Ludwig Boltzmann, which represents an important link between thermodynamics and classical mechanics, attracted both interest and criticism. The criticism was to some extent motivated by doubts about the atomic (molecular) structure of matter, which were quite persistent at that time, but which also involved a series of very interesting questions about the consistency of the reversibility of classical mechanics with the irreversible nature of thermodynamics. Some of these

questions (e.g., the exact physical mechanism determining the direction of time) are not fully answered even today. In response to his critics, Boltzmann put forward a number of hypotheses of remarkable originality and depth [1,2]. One of these hypotheses identifies our perceived direction of time with the second law of thermodynamics. Another hypothesis links the second law to a giant fluctuation and the temporal boundary conditions imposed on the Universe (or the observed part of it). The consequence of these hypotheses is the astonishing possibility (which was explicitly discussed by Boltzmann [2]) that, given different temporal boundary conditions, the perceived time may run in opposite directions in different parts of the Universe.

More than 100 years after, we still do not have a full explanation for the physical mechanism of the direction of time, and the second law of thermodynamics remains our key indicator for the time arrow. Our modern understanding of the Universe is, however, quite different from the views common in the late 19th century [3]. While giant thermodynamic fluctuations or radically different initial conditions imposed on different parts of the Universe seem rather unlikely, Boltzmann's thermodynamic time running in different directions might still be possible, due to the (potential) existence of antimatter. Since Feynman's theory of the positron [4], antiparticles are seen as particles moving backward in time. This gives us a hint that conventional thermodynamics, which is formulated for our world full of radiation and matter, but, as far as we know, free of assembled antimatter, can be extended to antimatter in two possible ways: CP (charge-parity)-invariant or CPT (charge-parity-time reversal)-invariant. Our discussion is aimed at the macroscopic properties, while the effect of thermodynamic interference on the invariant properties of quantum systems is discussed elsewhere [5].

While Sakharov [6] suggests that CPT symmetry can be a global property of the Universe, Penrose [3] believes that CPT symmetry does not hold on such scales, due to the action of the second law. The competing physical intuitions of CPT invariance and of conventional thermodynamics have been recently discussed by Downes *et al.* [7]. The present approach should not be confused with the analysis of isoduality of thermodynamic equations conducted by Dunning-Davies [8] on the basis of Santilli isodualities and having physical outcomes and interpretations very different from ours. Our work treats matter and antimatter as being the same with respect to the first law of thermodynamics (*i.e.*, all reversible and mechanical laws), does not change the signs of energy and mass and does not imply the existence of anti-gravity and anti-photons that are associated with Santilli isodualities. A popular presentation of CPT-invariant thermodynamics is given in [9] from the perspective of a space traveller visiting the world made of antimatter.

Quantum decoherence is commonly seen as the process initiating entropy increases, which are then reflected in macroscopic irreversibilities of temporal evolutions. Two approaches to decoherence can be distinguished: induced and spontaneous (intrinsic). The induced decoherence occurs within the unitary description of quantum systems, but involves the interference of the environment [10–12]. The spontaneous decoherence implies violations of unitarity that can be very small in magnitude for being detected directly, but the overall effect of these violations is amplified in quantum or mechanical systems of large dimensions and appears to be profound: the macroscopic increase in entropy [3,13–15]. Various possible causes and mechanisms of decoherence can be nominated, but, since the exact microscopic physical mechanisms enacting thermodynamic time are still not known, we use the term *time primer* as the place holder for these mechanisms without referring to any specific theory. It seems that both

mechanisms, induced and intrinsic, are likely to coexist in the real world and can be referred to here as the induced and intrinsic priming of time. Since our consideration pertains to the thermodynamic perspective, the details related to priming the direction of time are discussed in the Appendix. The two versions of thermodynamics considered here correspond to the intrinsic time priming having the same (CP-invariant thermodynamics) or opposite (CPT-invariant thermodynamics) temporal directions for matter and antimatter.

Microscopic symmetries have been repeatedly discussed in publications in the context of particle physics [16,17]. The current status of the experimental confirmation of quantum symmetry principles is that C, P, T and CP symmetries are broken by weak interactions, but the CPT symmetry, which is linked to the fundamental Lorentz invariance, is believed to be upheld [17]. The CP and T violations, however, are much less common than CP-preserving C and P violations. For many decades the CP violation observed in the decays of neutral K-mesons was deemed to be the only known exception [16,18]. The discoveries of CP violations for B-mesons by the BABAR[19], Belle [20] and LHCb[21] collaborations indicate that CP violations are rare, but not exceptional, although there is no reliable case of a CPT violation known in particle physics [17]. While CP violation combined with CPT invariance implies T violation, a direct confirmation of T violation has been obtained only very recently [22].

2. Symmetry of Matter and Antimatter

The Universe is populated mostly by radiation, has significant quantities of matter and, as far as we know, very small quantities of antimatter in the form of scattered elementary particles. Antimatter is not identical to matter, but there is a strong similarity between them [16]. We give this similarity a very broad interpretation: if our Universe were mostly composed from antimatter, we (also made of antimatter) would not be able to tell the difference, as the physical laws of the antimatter universe would be the same.

If we change matter to corresponding antimatter by s-called charge conjugation or (C-conjugation), the heat fluxes, \mathbf{q} , can change according to the following linear operation $\mathbb{C}(\mathbf{q}) = \alpha\mathbf{q}$, where \mathbf{q} is a conventional vector and α is a real constant. This operation takes us to an antiuniverse with the same physical laws as ours, but the constant, α , is not necessarily one, since we do not know the correspondence of space and time between the two universes, composed of matter and antimatter. Applying the charge conjugation again results in converting antimatter back to matter, *i.e.*, to going back to the original state. This means that:

$$\mathbf{q} = \mathbb{C}(\mathbb{C}(\mathbf{q})) = \mathbb{C}(\alpha\mathbf{q}) = \alpha^2\mathbf{q} \implies \alpha = \pm 1 \quad (1)$$

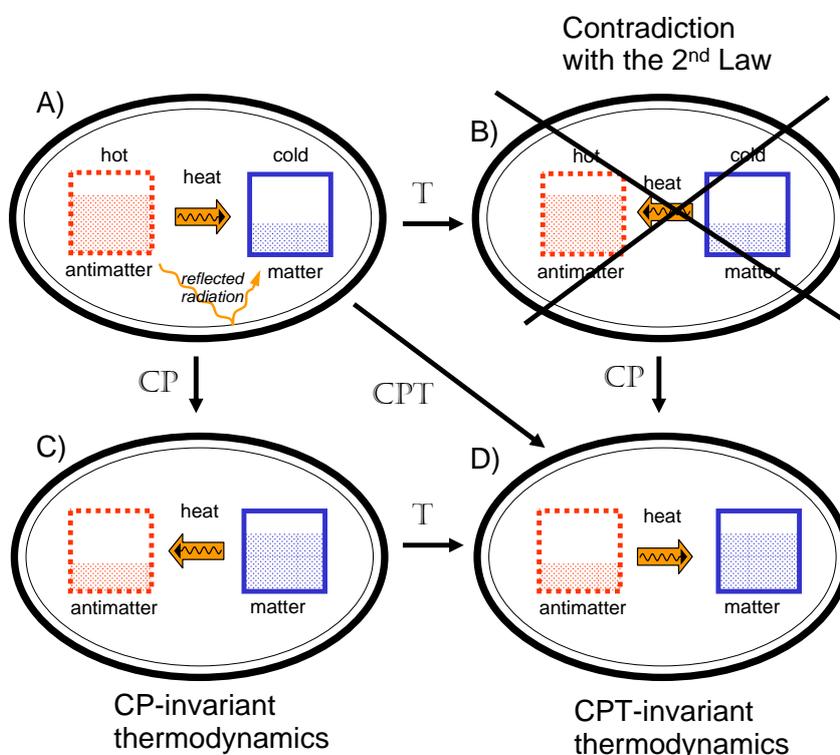
These two values of α correspond to different thermodynamics: C-invariant ($\alpha = +1$) and CT-invariant ($\alpha = -1$). Here, we refer to time reversal, which represents the change of directions of time ($\mathbb{T}(t) = -t$) and, thus, reverses the direction of \mathbf{q} , as T. Considering the parity transformation, which represents the change of directions of spatial coordinates ($\mathbb{P}(\mathbf{x}) = -\mathbf{x}$) and referred to as P, we follow accepted conventions and study CP-invariant and CPT-invariant versions of thermodynamics. These operations are commonly used in quantum mechanics, but here, we follow Sakharov [6] and interpret them as general physical principles not confined to the field of quantum mechanics. (Note that the quantum mechanical consistency requires only that $|\alpha^2| = 1$, *i.e.*, α^2 can be complex; the classical world deals

only with real quantities and $\alpha^2 = 1$.) Sakharov’s principles, which are necessary for the explanation of the matter/antimatter bias, are often quoted as:

- ◆ the existence of reactions violating baryon numbers;
- ◆ the violation of the C and CP symmetry;
- ◆ the deviation from thermodynamic equilibrium.

This list, however, does not include the fourth important assumption made by Sakharov in the same work [6]: CPT invariance is a global property of the Universe. While CPT invariance is commonly known as a theorem in quantum field theory (which, as mentioned in the Introduction, is supported by experiments conducted at the microscopic level), its application to macroscopic processes and/or to the whole of the Universe is a hypothesis, not a theorem. For example, Penrose [3] believes that CPT invariance would not hold if applied to the whole of the Universe; this view corresponds to the CP-invariant version of thermodynamics. The Universe, nevertheless, can be expected to be CPT invariant if the CPT-invariant version of thermodynamics is adopted (or if there are no irreversible processes taking place in the Universe, but this does not seem to be the case).

Figure 1. CP and T transformations of thermodynamics systems. The fill levels correspond to the intrinsic temperatures. Common-sense interpretation "cold" and "hot" are indicated when applicable.



Since thermodynamics mainly deals with macroscopic scalar quantities, parity transformations are, generally, not important for a thermodynamic analysis(although, particles with opposite chiralities may

need to be treated as different species in thermodynamics and kinetics). Here, we nevertheless preserve conventional notations adopted in quantum mechanics and retain P in transformations. The implications of having positive and negative α in Equation (1) are shown in Figure 1, which illustrates an experiment conducted by placing matter and antimatter in the foci of a perfectly reflective ellipsoid. One of many possible initial states, which is shown in Figure 1A, is subject to the C, P and T transformations. Heat is transferred by radiation between matter and antimatter, and the direction of the heat transfer changes as the transformations are applied. In simple terms, T reverses the direction of the heat transfer, C converts matter into antimatter and *vice versa*, while P swaps the systems located in the foci and reverses the heat flux accordingly. Since thermodynamic laws are not time-invariant, the T-transformation of Case (A) results in Case (B), prohibited by the second law. The other cases, (C) and (D), are possible and correspond to CP-invariant and CPT-invariant thermodynamics. Note that, since thermodynamics is not T-symmetric, it must also violate at least one of the symmetries, CP or CPT. The requirements of CP-invariant and CPT-invariant thermodynamics are thus incompatible, and only one of these thermodynamics corresponds to the real world. It is difficult, however, to determine how thermodynamics should be extended from matter to antimatter, due to the paucity of antimatter in the Universe. Both CP- and CPT-invariant thermodynamics give the same description for our current world populated by matter. While CP-invariant thermodynamics is conventional and does not need an extensive treatment here, it seems that CPT-invariant thermodynamics has not been considered in the past, and its implications need a detailed analysis.

3. CPT-Invariant Thermodynamics

Our previous discussion results in postulating the following key principles:

- ◆ *Reversible equivalence.* There is no distinction between matter and antimatter with respect to the first law of thermodynamics.
- ◆ *Inverted irreversibility.* Thermodynamically isolated antimatter can increase its entropy only backward in time (unlike any isolated matter, whose entropy increases forward in time).
- ◆ *Observational symmetry.* Antimatter and its interactions with matter are seen (*i.e.*, observed, experimented with or measured) by antiobservers in exactly the same way as matter and its interactions with antimatter are seen by observers.

These principles correspond to CPT-invariant thermodynamics, where the directions of thermodynamic time are opposite for matter and antimatter. In the case of CP-invariant thermodynamics (not considered in this section), the second principle is to be replaced by an entropy increase forward in time for both matter and antimatter. Hypothetical observers made of antimatter are called *antiobservers*, while the term *observers* refers only to us—observers made of matter. Properties of matter measured by us (the observers) and properties of antimatter measured by antiobservers are referred to as *intrinsic*. The properties of matter and antimatter measured by observers are referred to as *apparent*, while the properties of matter and antimatter measured by antiobservers are referred to as *antiapparent*.

3.1. The Interactions of Thermodynamic Systems and Antisystems

In this subsection, we consider thermodynamic interactions of two systems comprised of matter and antimatter (*i.e.*, a system and an antisystem). The interactions are limited by the maximal energy that is allowed to be transferred between the systems, which otherwise remain autonomous and isolated from the rest of the Universe. Due to autonomy, we can still apply causality in its modified form: the initial conditions for the matter system are set before and, for the antimatter system, are set after the interaction. Here, “before” and “after” refer to the observer’s time.

Thermodynamics is based on determining the direction of processes where states (*i.e.*, macrostates) can be realised by the largest possible number of microstates (given the constraints imposed on the system) and, thus, are overwhelmingly more likely than states encompassing fewer microstates. The logic of thermodynamics considers what is likely and neglects what is unlikely. The most likely state is called equilibrium. In conventional thermodynamics, unlikely states may be set as initial states, while the system tends to move towards its equilibrium as time passes. This is reflected by the well-known Boltzmann–Planck entropy equation:

$$S_i = k_B \ln(\Gamma_i) \quad (2)$$

linking the entropy, S_i , in the state, i , to the number of microstates, Γ_i , in this state. The number of microstates, Γ_i , is further referred to as the statistical weight of the thermodynamic state, i . The constant, k_B , is the Boltzmann constant that rescales very large changes in Γ_i to more manageable thermodynamic quantities. In practice, counting statistical weights of macrostates can be complicated by stochastic dependencies. For example, if the initial state is i_0 at $t = 0$, then the most likely state, $i_{\Delta t}$, at $t = \Delta t$, conditioned on the initial state of the system, may be different from the equilibrium state, i_e . We believe, however, that $i_{\Delta t}$ always becomes i_e when Δt is sufficiently large; *i.e.*, stochastic dependencies disappear for states separated by a substantial amount of time (and, possibly, space).

In this work, we do not discriminate the past and the future *a priori*: thermodynamic principles are applied by maximising the number of microstates associated with macroscopic evolutions, given spatial and temporal boundary conditions, as well as other physical constraints imposed on the overall system. The term “overall” stresses the inclusion of both the system and the antisystem, and the temporal boundary conditions may be applied in both the past and the future.

3.1.1. Apparent Temperatures

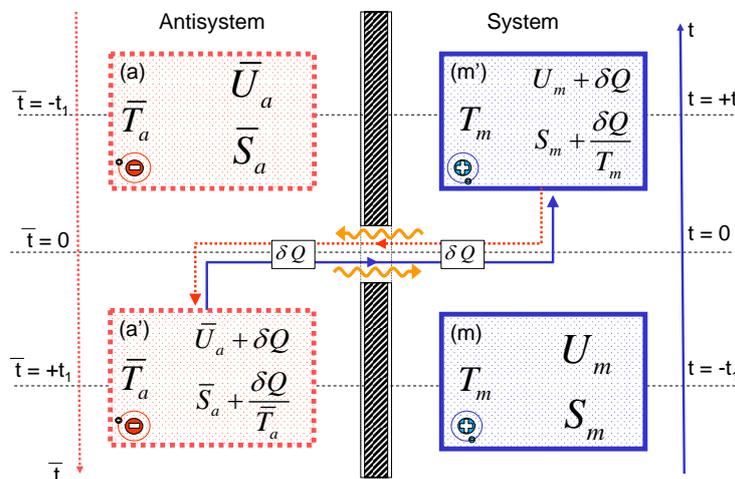
The temporal boundary conditions for the example shown in Figure 2 are: energy U_m and entropy S_m , which are specified for the system at $t = -t_1$ and $\bar{t} = t_1$; that is, in our past. According to inverted irreversibility, \bar{U}_a and \bar{S}_a are specified for the antisystem, at $\bar{t} = -t_1$ and $t = t_1$; that is, the antisystem’s thermodynamic past and our future. The overbar symbol indicates that the value is antiapparent, *i.e.*, evaluated from the perspective of an antiobserver, whose time $\bar{t} = -t$ goes in the opposite direction as compared to our time, t . The system and antisystem are isolated from each other for most of the time, but a limited thermodynamic contact of matter and antimatter, allowing for the transition of a small quantity of heat, δQ , through the exchange of radiation, occurs at $t = 0$ (and $\bar{t} = 0$). The time window is selected, so that $|\delta Q|$ cannot exceed δQ_{\max} , where δQ_{\max} is sufficiently small. According to the observer, the thermal energy, δQ , is transferred from the antisystem to the system, as shown by the

black solid arrow. According to the antiobserver, who interprets the same event in the opposite direction of time, the same thermal energy, δQ , is transferred from the system to the antisystem, as shown by the red dashed arrow. Heat, δQ , is assumed to be positive when transferred in the direction shown in Figure 2: from the antisystem to the system according to the observer and from the system to the antisystem according to the antiobserver. The total energy:

$$U_{tot} = U_m + (\bar{U}_a + \delta Q) = (U_m + \delta Q) + \bar{U}_a \tag{3}$$

(evaluated at any constant time $t = -\bar{t}$) is preserved in this example, as it should be, since the formulation of the first law of thermodynamics does not depend on the differences between matter and antimatter, due to the postulated reversible equivalence (interactions of matter and antimatter may include the third key component: coherent radiation. In thermodynamics, this would correspond to considering work reservoirs in addition to heat reservoirs (see, for example, the “weight process” of [23]). The energy balance at the moment of contact is $U_{tot} = U_{m0} + U_{a0} + U_{r0}$, where U_r is the radiation energy and the subscript “0” indicates states taken at $t = 0$) Note that $\bar{U}_a = U_a$, due to reversible equivalence. The entropy change of the system as observed by us and the entropy change of the antisystem as seen by the antiobserver (these are the entropies linked to Γ) can be easily evaluated, and these changes of intrinsic entropy are shown in Figure 2 for the states, m' and a' .

Figure 2. Thermodynamic interactions of a system (right) and antisystem (left) where a limited amount of thermal energy $\delta Q < \delta Q_{max}$ is allowed through the time window.



We now evaluate the overall statistical weight, Γ_{tot} , that corresponds to different trajectories that are allowed by the first law of thermodynamics. The overall state is related to the four sub-states: m , a , m' and a' . The overall statistical weight, Γ_{tot} , is linked to the product of the statistical weights of the sub-states, $\Gamma_m \Gamma_{m'} \Gamma_a \Gamma_{a'}$, and, according to Equation (2), becomes:

$$\Gamma_{tot}(\delta Q) \sim \Gamma_m \Gamma_{m'} \Gamma_a \Gamma_{a'} = \exp\left(\frac{S_m + S_{m'} + \bar{S}_a + \bar{S}_{a'}}{k_B}\right) \tag{4}$$

The value, Γ_{tot} , depends on δQ . Note that S_m and \bar{S}_a are fixed by the boundary conditions, and only $S_{m'}$ and $\bar{S}_{a'}$ depend on δQ . In this example, we should place the time moments $t = -t_1$ and $t = +t_1$

as far apart as needed to ensure the establishment of equilibriums within the system and the antisystem before and after the interaction, which is used in Equation (4) in the form of the stochastic independence of microstates that correspond to the macrostates, m and m' , a and a' . Two of the states, m and a , are fixed by the boundary conditions.

Equation (4) can be simplified through normalising Γ_{tot} by the value of Γ_{tot} at $\delta Q = 0$:

$$\frac{\Gamma_{tot}(\delta Q)}{\Gamma_{tot}(0)} = \exp\left(\frac{\delta Q}{k_B} \left(\frac{1}{T_m} + \frac{1}{\bar{T}_a}\right)\right) \tag{5}$$

where conventional definitions of the temperature:

$$\frac{1}{T_m} = \frac{\partial S_m}{\partial U_m}, \quad \frac{1}{\bar{T}_a} = \frac{\partial \bar{S}_a}{\partial \bar{U}_a} \tag{6}$$

are used. (The quantity δQ is assumed to be too small to affect the intrinsic temperatures of matter and antimatter, which remain T_m and \bar{T}_a , correspondingly.). From the observer’s perspective, the conventional equilibrium condition is given by the equivalence of apparent temperatures $T_m = T_a$. If the system and the antisystem are in thermodynamic equilibrium, both directions of heat transfer $\delta Q > 0$ and $\delta Q < 0$ must be equally likely and have the same statistical weight, Γ_{tot} . This occurs only when $T_m = -\bar{T}_a$, indicating that the apparent temperature of antimatter is $T_a = -\bar{T}_a$. In the same way, the antiapparent (*i.e.*, perceived by the antiobserver) temperature of matter is $\bar{T}_m = -T_m$. It is easy to see that thermodynamic quantities \bar{S}_a , \bar{T}_a and \bar{U}_a that characterise the intrinsic properties of antimatter are apparent as:

$$T_a = -\bar{T}_a, \quad S_a = -\bar{S}_a, \quad U_a = \bar{U}_a \tag{7}$$

from our perspective. The sign of U_a is selected to be consistent with the first law of thermodynamics Equation (3), while the sign of S_a is chosen to be consistent with the definition of temperature $T_a^{-1} = \partial S_a / \partial U_a$ and with Equations (6). The change of sign does not affect our interpretation of reversible transformations of antimatter, since S_a is constant whenever \bar{S}_a is constant, which is consistent with our assumption that matter and antimatter behave in the same way in reversible processes. The state of having the same positive (and finite) intrinsic temperatures $T_m = \bar{T}_a$ does not correspond to equilibrium and, according to Equation (5), the transfer of heat from antisystem to system in the observer’s time is strongly favoured by thermodynamics.

It appears that a system created in our world with negative temperatures can, at least in principle, be placed into thermal equilibrium with an antisystem held at positive intrinsic temperatures, or analogously, an antisystem at negative intrinsic temperatures can be in thermodynamic equilibrium with a system having a positive intrinsic temperature. This equilibrium state, however, would be predominantly unstable, since in most cases, the antimatter system according to Equation (7) is likely to have negative apparent heat capacities (see, for example, [24]):

$$C_a = \frac{-1}{T_a^2} \left(\frac{\partial^2 S_a}{\partial U_a^2}\right)^{-1} = \frac{1}{\bar{T}_a^2} \left(\frac{\partial^2 \bar{S}_a}{\partial \bar{U}_a^2}\right)^{-1} = -\bar{C}_a \tag{8}$$

This equation indicates that changing the sign of the entropy, S , changes the sign of the heat capacity, C , irrespective of the sign of the temperature, T . Hence, a thermodynamic contact of an antisystem and a system predominantly results not in reaching the corresponding thermal equilibrium state, but

in the antisystem losing energy (to the system) and further increasing its apparent temperature, until the temperature of the antisystem reaches its intrinsic ground state $-T_a = \bar{T}_a \rightarrow +0$. Note that a (neutrally) stable thermodynamic equilibrium between a system and an antisystem is possible at $T_m = T_a = \bar{T}_a = \infty$.

3.1.2. Mass Exchange between Matter and Antimatter

An antimatter system with a variable number of particles is characterised by the equation:

$$d\bar{U}_a = \bar{T}_a d\bar{S}_a + \bar{\mu}_a d\bar{N}_a \tag{9}$$

which remains the same as the conventional one as long as it is presented from the perspective of the antiobserver (the other conjugate thermodynamic variables, such as volume and pressure, can be added to this equation if needed). From our perspective, this equation changes according to Equation (7). The reversible equivalence requires the preservation of mass, which demands that the apparent and intrinsic numbers of particles composing antimatter are the same. Hence, the apparent and intrinsic values of the number of particles (or moles), N , and of the chemical potentials, μ , coincide:

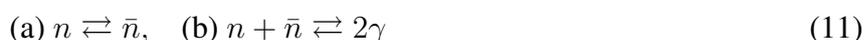
$$N_a = \bar{N}_a, \quad \mu_a = \bar{\mu}_a \tag{10}$$

Similar relations can be drawn for other thermodynamic quantities, such as volume and pressure. Due to the observational symmetry, $\mu_a = \bar{\mu}_a(\bar{T}_a, \bar{N}_a, \dots)$ is the same function as $\mu_m = \mu_m(T_m, N_m, \dots)$.

We note first that at infinite temperatures $T_m = T_a = \bar{T}_a = \infty$, the same quantities of matter and antimatter $N_a = N_m = N$, which are kept under the same conditions, are in both thermal and chemical equilibrium, since $\mu_a = \bar{\mu}_a(\infty, N, \dots) = \mu_m(\infty, N, \dots)$. If, however, $T_m < \infty$, then thermal equilibrium $T_m = T_a = -\bar{T}_a$ does not imply that matter and antimatter under similar conditions are in chemical equilibrium, since $\mu_a = \bar{\mu}_a(-T, \dots)$ is generally different from $\mu_m = \mu_m(T, \dots)$ for the same T . Hence, even if it might be possible to put an antisystem in thermal equilibrium with a system by using negative temperatures, this equilibrium does not extend to chemical stability between matter and antimatter.

If a system and an antisystem are kept at the same intrinsic temperatures $T_m = \bar{T}_a = T < \infty$ (and the same other conditions), then $\mu_a = \bar{\mu}_a(T, N, \dots) = \mu_m(T, N, \dots)$. In this case, however, equality of chemical potentials does not ensure chemical equilibrium, since there is no thermal equilibrium $T_m \neq T_a = -\bar{T}_a$.

Consider the following example: matter and antimatter are confined to the system and antisystem correspondingly and cannot mix (mixtures are considered in the following subsection). Assume that matter and antimatter can react with each other and can annihilate to produce radiation as reflected by the following reactions (We use hypothetical reactions with neutrons n and antineutrons \bar{n} to illustrate our point. The neutron/antineutron oscillation reaction $n \rightleftharpoons \bar{n}$ (or similar reactions converting antimatter into matter) is predicted by the first Sakharov condition, but has not been observed so far under current conditions prevailing in the Universe):



These two reactions can be combined to result in conversion $2\bar{n} \rightleftharpoons 2\gamma \rightleftharpoons 2n$; that is, antimatter can be moved from antisystem to system by radiation and converted to matter possessing the same energy.

Assuming that pressures are kept the same and constant in the system and antisystem; this transition does not affect intrinsic temperatures $T_m = \bar{T}_a$ and intrinsic entropy per particle (or per mole) $s_m = \bar{s}_a$, where $s = S/N$. The total apparent entropy $S_{tot} = N_m s_m - N_a \bar{s}_a$ clearly increases as N_a decreases and N_m increases. We see that CPT-invariant thermodynamics strongly favours the conversion of antimatter into matter (from the observer's perspective), even if the intrinsic properties of matter and antimatter are exactly the same. For an antiobserver, whose time is going backward, this process seems to be the conversion of matter into antimatter. Hence, from the antiobserver's perspective, thermodynamics favours the conversion of matter into antimatter.

3.2. Mixed Matter and Antimatter

When matter and antimatter are mixed, they do not form semi-autonomous thermodynamic systems with effectively independent directions of time. We shall distinguish two cases: when matter dominates antimatter in the mixture and when a 50 : 50 mixture is formed. Due to annihilations, radiation is also present in the mixture, but does not affect the direction of the thermodynamic time.

3.2.1. Mixtures Dominated by Matter

Consider a mixture of many particles, N_m , with very few antiparticles, N_a . The external degrees of freedom are entangled to produce a dominant direction of thermodynamic time for the whole mixture. Since particles dominate antiparticles in this mixture, this direction must be forward in time. The presence of antiparticles may slightly increase the fluctuating components of the time primer without any noticeable effect on the direction of thermodynamic time. If particles and antiparticles are considered as relatively simple mechanical or quantum systems, their thermodynamic behaviour is primed by the mixture, resulting in the analogous thermodynamic properties of the particles and antiparticles (the effect of thermodynamic interference with the invariant properties of quantum systems is discussed in [5]). The antiparticles, however, affect the thermodynamic state of the mixture by causing annihilations.

A different situation appears when each particle and each antiparticle represent an autonomous thermodynamic subsystem (*i.e.*, having a large number of comparable internal degrees of freedom, substantial ergodic mixing and Kolmogorov–Sinai entropy [25,26], dramatically amplifying the effect of time priming). In this case, the thermodynamic time runs in opposite directions within particles and antiparticles (and in the normal direction for the whole mixture). While the thermodynamic subsystems can, in principle, be placed in thermal equilibrium when the intrinsic temperature of the antiparticles is negative (this is possible when internal energy levels of antiparticles are bounded; see [24]), but this equilibrium is typically unstable, as discussed previously. Hence, antiparticle subsystems should fall into their ground state (which is nevertheless subject to fluctuations, significant for microscopic subsystems), while particle subsystems remain in conventional thermal equilibrium with the mixture. Although techniques based on evaluating statistical sums cannot be used for systems with negative heat capacity (see [24]), there is no contradiction in using these techniques when antiparticle systems are in their ground state. Let us see how the partition function, Z , should be evaluated in this case:

$$Z = (Z_0)^{N_m + N_a} \frac{(Z_m)^{N_m}}{N_m!} \frac{(Z_a)^{N_a}}{N_a!}, \quad (12)$$

$$Z_m = \sum_i \exp\left(-\frac{E_i}{k_B T}\right), \quad Z_a = \exp\left(-\frac{E_0}{k_B T}\right), \quad (13)$$

where Z_0 is the partition function without considering internal degrees of freedom, Z_m is the partition function for particle internal energy levels and Z_a is the partition function for antiparticles in their ground state. Classical statistics is assumed in this example. Note that Z_a can be made unity ($Z_a = 1$) without loss of generality by selecting E_0 as the reference energy level (*i.e.*, $E_0 = 0$). The difference in chemical potentials of particle and antiparticles can be evaluated by using standard techniques [27]:

$$\begin{aligned} \Delta\mu &= \mu_a - \mu_m = \left(\frac{\partial A}{\partial N_a} - \frac{\partial A}{\partial N_m} \right)_T \\ &= k_B T \left(\ln \left(\frac{N_a}{N_m} \right) + f_m(T) \right) \end{aligned} \quad (14)$$

where $A = -k_B T \ln(Z)$ is the Helmholtz potential and $f_m(T) = \ln(Z_m(T)) \geq 0$. Since $\Delta\mu > 0$, thermodynamics favours the conversion of antimatter into matter under these conditions. The asymmetry of the chemical potentials, $\Delta\mu$, tends to be higher at higher temperatures. Note that particles and antiparticles may have not only different chemical potentials, but also slightly different masses, as they have different average energies.

The system containing particles n , antiparticles \bar{n} and radiation γ , which are engaged in reactions specified by Equation (11), is now considered. Reactions Equation (11) require the following equilibrium conditions: (a) $\mu_m = \mu_a$ and (b) $\mu_m + \mu_a = 2\mu_\gamma$. Considering that photons should have zero chemical potential $\mu_\gamma = 0$ [27], we conclude that $\mu_m = \mu_a = 0$. Since, under conditions specified above, f_m is expected to be positive, Equation (14) indicates that particles dominate antiparticles $N_m > N_a$; this is consistent with the major assumption of this subsection.

3.2.2. The 50 : 50 Mixture

The case of having 50% particles and 50% corresponding antiparticles in the mixture is the most difficult case to analyse. The thermodynamic time cannot run in any direction, due to matter/antimatter symmetry. This generally means that only reversible processes can occur in this mixture, and there is no relaxation towards an equilibrium state in any direction of time. Any process that is irreversible forward or backward in time is impossible in this mixture. The mixture can also contain a large or small fraction of radiation, which does not affect the direction of time. CPT-invariant thermodynamics provides a thermodynamic perspective for Sakharov's hypothesis [6] of CPT invariance of the Universe (see also [9]) and changes interpretation of the third Sakharov condition listed in Section 2. The 50 : 50 mixture of matter and antimatter, which presumably existed after the initial singularity of the Big Bang, does not allow for gravitational collapses (such as formation of black hole or disappearance of a white hole) since these processes involve significant changes in entropy. This places constraints on the properties of the Universe at its origin.

Although there is no direction of thermodynamic time on average in this mixture, there are fluctuations in the system. The thermodynamic time might also fluctuate, moving slightly forward or backward, due to a minor local prevalence of one of the mixture components over the other. At this point, things get more complicated. The areas with a small excess of matter can be seen as forming systems, while the areas with a small excess of antimatter form antisystems. If all temperatures are infinite $T_m = T_a = \bar{T}_a = \infty$, then, according to the analysis of the previous subsection, systems and antisystems can be considered to be in equilibrium with respect to matter/antimatter conversion. If, however, the intrinsic temperatures are high, but finite, then (as also discussed in the previous subsection) thermodynamics favours the transfer of energy, volume and matter/antimatter from antisystems to systems. This process can be seen as thermodynamic instability, resulting in systems (with the forward-directed thermodynamic time) taking over and antisystems (with the backward-directed thermodynamic time) disappearing. In antisystem regions, matter and antimatter can unmix forward in time, reducing further the volume occupied by antisystems. Matter needs to retain its leading role over antimatter within the system regions, if the forward-time evolution is to continue in these regions. The asymmetry of chemical potentials Equation (14) stimulates the conversion of antimatter into matter within the systems. Note that the same mechanism converts matter into antimatter within the antisystems, but this happens in the forward direction of the antiobserver's time (*i.e.*, backward in our time). Hence, from the observer's perspective, antimatter is still converted into matter in this process.

4. Testing Invariant Properties of Thermodynamics

In our world, which is exclusively populated by radiation and matter, the CP-invariant and CPT-invariant versions of thermodynamics produce the same predictions, are not experimentally distinguishable and can be treated as different interpretations of the same physical theory. Specifically, CP-invariant thermodynamics treats the temporal irreversibility as CPT violation, while CPT-invariant thermodynamics sees CPT invariance as the fundamental property of nature and relates the arrow of time to the asymmetric presence of matter and the absence of antimatter in the Universe. The CP- and CPT-invariant versions of thermodynamics, however, represent different and experimentally distinguishable physical theories in interpreting the thermodynamic properties of antimatter, which (at least in principle) is possible to produce in high-energy colliders in statistically significant quantities [28,29].

On the face of the problem, making an experimentally justified choice between CP-invariant and CPT-invariant versions of thermodynamics is not too difficult; we just need to produce stochastically significant quantities of antimatter (whose intrinsic thermodynamic time runs backward in our time according to CPT-invariant thermodynamics) and insulate it from the time-generating interference of the surrounding matter. The antimatter system must be sufficiently complex and interacting to possess significant Kolmogorov–Sinai entropy and to amplify its intrinsic (spontaneous) time primer. If the physical reality is compliant with the CPT invariance, antimatter assembled in quantities exceeding a certain critical level would change the direction of its thermodynamic time. Note that under these conditions, the explosion of antimatter into a burst of coherent light directed at surrounding matter becomes thermodynamically possible, since antimatter has negative apparent temperatures in our

world. Besides creating and containing antimatter in sizeable quantities, the major difficulty with this experiment is that we do not know the mechanism of time priming, its amplitude and physical properties. We thus cannot be certain about the relative contributions of induced and intrinsic time priming in a particular experiment. Since the exact mechanism of time priming remains unknown, we cannot examine its invariant properties directly, without assembling thermodynamically significant quantities of antimatter.

Recent experiments in high-energy accelerators indicate that thermodynamics might be relevant to very small scales (within a hadron) and high energies [30]. Baryons (protons and neutrons) seem to contain myriads of appearing and annihilating gluons, quarks and antiquarks, as specified by so-called parton distribution [31]. Collisions involving protons and nuclei produce various particles and antiparticles with distributions strongly resembling a thermodynamic equilibrium. This equilibrium is characterised by a number of parameters, including μ_B —the chemical potential associated with the baryon number, B —so that baryons (*i.e.*, protons and neutrons having $B = +1$) and antibaryons (antiprotons and antineutrons having $B = -1$) have different chemical potentials [30]. This seems to confirm the CPT-invariant version of thermodynamics (since in CP-invariant thermodynamics, properties of matter and antimatter must be the same and $\mu_B = 0$), but in our opinion, this is probably not the case. In the absence of reactions violating B , true chemical potential associated with the baryon number is not revealed (This can be compared with chemical reactions, where elements can be assigned arbitrary chemical potentials; in the absence of nuclear reactions, true chemical potentials of the elements remain unknown). Hence, μ_B is likely to be an effective quantity reflecting initial conditions, although it does seem that thermodynamic equilibrium is achieved in these experiments with respect to the other parameters.

In spite of the difficulties in creating significant quantities of antimatter, thermodynamic antisystems may already exist in high-energy experiments. Here, we again refer to the parton distribution [31], describing the behavior of a large number of quarks, antiquarks and gluons in protons, neutrons and other hadrons. The parton distribution is biased towards two or three valent quarks that determine the properties of the particles. It is likely that at low temperatures (which can still be very high according to our common understanding of what is hot and what is cold), baryons are in their quantum ground state. In this case, thermodynamics does not play a role in the internal properties of these systems. If the temperature becomes extremely high (of order of $10^{12} K$), quarks, antiquarks and gluons break the confinement of hadrons and form the so-called quark-gluon plasma [30], which is a thermodynamic object and, thus, must be in a quantum mixed state. It is likely that at intermediate temperatures, such complex particles still remain intact, but are in a mixed state and display a thermodynamic behaviour. Hence, we might be able to treat baryons as thermodynamic systems (here, we refer to the particles themselves and not to various large thermodynamic systems that can be formed by these particles), implying the existence of small thermodynamic antisystems in our world in the form of antibaryons.

Let us investigate the thermodynamic implications of this assumption. We note first that the spontaneous time primer is then likely to exist within baryons and antibaryons: superposition of quantum states in neutrons would tend to lose coherence (de-coherence), while mixed states in antineutrons would tend to become pure superpositions (*i.e.*, en-coherence in our time). An analysis of the previous section indicates that in the environment dominated by matter, antisystems tend to remain in their ground

states (this does not exclude some level of thermodynamic fluctuations), while systems reach a quantum mixed state with a temperature similar to that of the environment. Since a large fraction of the energy of protons and neutrons is in the motions of quarks and gluons, a mass defect between particle and antiparticle is possible at a sufficiently high temperature. The particle possessing higher internal thermal energy should have a somewhat higher mass, as compared to their antiparticle counterparts. Let us turn to experimental evidence. While the equivalence of the masses of most particles and antiparticles (e.g., electrons and positrons, protons and antiprotons) has been confirmed with a very small relative error of around 10^{-6} – 10^{-7} percent [17], experimental confirmation of the equivalence of the neutron and antineutron masses is subject to a greater uncertainty. Measurements indicate that the neutrons are heavier than antineutrons by a small (and rather uncertain) fraction, which is estimated in [17] as $0.009 \pm 0.006\%$. CPT-invariant thermodynamics does not see this kind of discrepancies as violations of the fundamental CPT symmetry, but tends to relate them to thermodynamic interference with the measurements, resulting in different intrinsic temperatures of neutrons and antineutrons. Neutrons have higher internal thermal energy than antineutrons in our matter-populated environment, as expected from the analysis of the previous section. If assumptions about the thermodynamic state of neutrons introduced in this section are correct, this difference should decrease when neutrons are contained and cooled down before the experiments. Unlike the CPT-invariant version of thermodynamics, the CP-invariant version specifies exactly the same thermodynamic properties for both neutrons and antineutrons.

5. Discussion and Conclusions

Assuming a fundamental similarity of the intrinsic properties of matter and antimatter, conventional thermodynamics can be extended to include antimatter in two different ways: CP-invariant and CPT-invariant. Due to the time-directional nature of thermodynamics, its CP-invariant and CPT-invariant versions cannot be valid at the same time. Philosophically, CPT-invariant thermodynamics connects two major asymmetries in nature—the observed direction of time and the relative abundance of matter and the absence of antimatter—while CP-invariant thermodynamics sees these issues as separate. In the absence of appreciable quantities of antimatter in our world, it is very difficult to determine which version of thermodynamics is not only logically possible, but also real: both versions give the same predictions for the world dominated by matter.

The difference between CP- and CPT-invariant thermodynamics, however, is not limited to philosophical interpretations. CPT-invariant thermodynamics indicates that nature has difficulties in assembling substantial quantities of antimatter, due to its thermodynamic antagonism with matter. There is no thermodynamic antagonism between matter and antimatter according to CP-invariant thermodynamics. Collecting statistically significant quantities of antimatter at a sufficient density and insulating it from the dominant time priming influence of the environment should result, according to CPT-invariant thermodynamics, in changing the thermodynamic arrow of time and a thermodynamically unstable state associated with negative apparent temperatures. In this state, the transfer of energy and mass from antimatter to matter (forward in our time) is favoured by thermodynamics. Yet, these differences in apparent behaviour are consistent with the fundamental similarity between the intrinsic properties of matter and antimatter. CP-invariant thermodynamics, on the contrary, does not expect

any thermodynamic instabilities in such experiments and suggests that the apparent thermodynamic properties of matter and antimatter are the same.

We should assume that spontaneous time-priming processes are of very small magnitude and, thus, are not directly detectable in conventional experiments. This is plausible since, in spite of the clear presence of the arrow of time (presumably everywhere, including in remote and isolated systems), we still do not know its exact mechanism. The presence of some scattered elementary antiparticles in a world dominated by matter does not change the direction of thermodynamic time. If, however, baryons (neutrons and protons) can be treated as thermodynamic systems, due to the complexity of their parton distributions, then CP-invariant thermodynamics requires the exact similarity of the chemical potentials of baryons and antibaryons, while CPT-invariant thermodynamics predicts the differences in the effective chemical potentials between baryons and antibaryons in high-temperature environments.

While distinguishing two extensions of conventional thermodynamics (CP-invariant and CPT-invariant) can be quite difficult in the real world, which we are familiar with and which is essentially free from antimatter, this may change as more and more substantial quantities of antimatter are produced in experiments by high-energy accelerators [28,29].

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Conflicts of Interest

The authors declare no conflicts of interest.

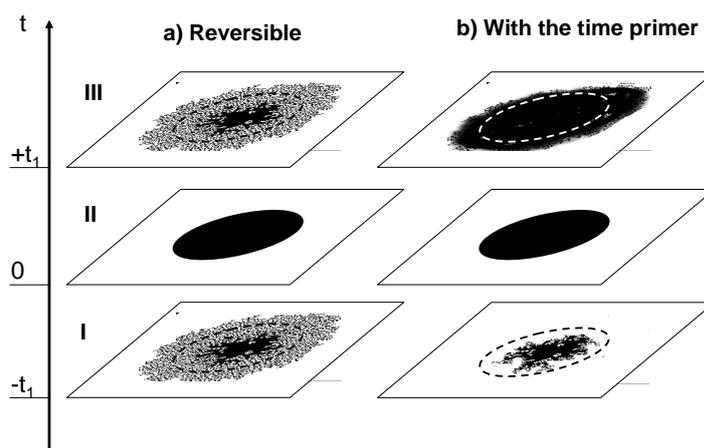
Appendix: Boltzmann's Time Hypothesis, the Direction of Time and the Time Primer

While this work is mostly interested in the macroscopic aspects of extending thermodynamics from matter to antimatter, it is difficult to stay within a macroscopic treatment of conventional thermodynamics when particles and antiparticles form mixtures rather than autonomous systems and antisystems. These cases are most complicated and need a working concept for the direction of thermodynamic time. This and other associated issues are briefly discussed below in the context of the Boltzmann time hypothesis, linking our perceived direction of time to the second law of thermodynamics. The temporal boundary conditions imposed on the Universe affect the direction of time directly and through the properties of matter.

From the perspective of the ergodic theory, the increase of entropy in dynamic systems of large dimensions is associated with ergodic mixing [25,26]. This perspective is based on classical mechanics, which is time-reversible and preserves volume measures in the extended phase space (whose dimension is very large and determined by the overall number of microscopic degrees of freedom in the system). Note that quantum mechanics possesses similar properties linked to the unitarity of quantum evolutions. Ergodic mixing can be understood through analogy between the evolution of volumes in the extended phase space with the mixing of fluids. This analogy was first introduced by Gibbs in his fundamental work [32], which laid the foundations of statistical physics. Ergodic mixing can be illustrated

by Figure A1, which depicts the extended phase space of a dynamic system. The ensemble of states is initially (at $t = 0$) confined to the black region in Figure A1(IIa). The evolution of the system changes the shape of the region, but does not alter its volume measure, so that after a sufficiently long period of time, t_1 , the trajectories become densely distributed in a larger and larger segment of the domain. Refer to Figure A1: the black areas have exactly the same measure (*i.e.*, the same number of black pixels) in IIa and IIIa, but the segment effectively occupied by the black spot is larger in IIIa. The increasing volume measure of this segment is conventionally associated with an increasing entropy, as required by the second law (in dynamic systems, the increase of the coarsened phase volume in time is characterised by the *Kolmogorov–Sinai dynamic entropy* [33]). This logic, however, encounters severe problems when states of the system are considered back in time [3]. Since the evolution of a dynamic systems is time-reversible, it can be extended back to negative times, and a state of the system similar to the state shown in IIIa should also be expected at $t = -t_1$ (see Figure A1, Ia). How can time-symmetric evolution (compare Ia and IIIa in Figure A1) be consistent with the second law?

Figure A1. Schematic for evolution of a selected volume in the phase space in case of a) reversible dynamics and b) under influence of the timer primer.

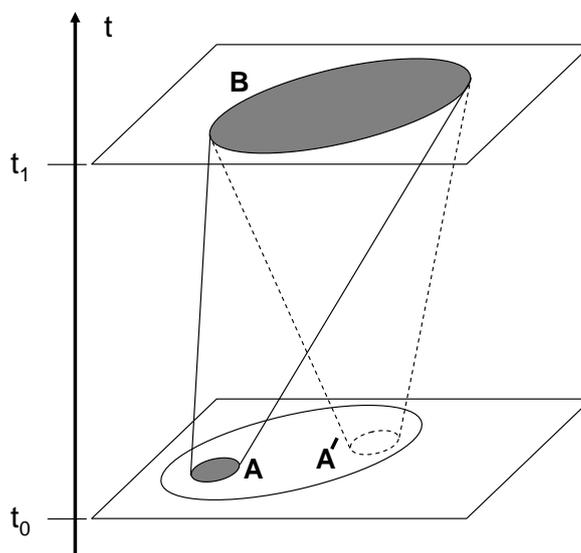


The resolution of this apparent paradox is commonly related to the set of ideas, which we call here the *priming of time*. We use this term to refer to a generic process that triggers or primes the mechanism of enacting the direction of thermodynamic time. This process causes a diffusion-like increase of the black volume into the white region, so that the state of the system at $t = t_1$ looks as shown in Figure A1(IIIb). The time primer does not refer to a specific theory or hypothesis, but is seen as a violation of classical mechanics and/or quantum mechanics; although the magnitude of these violations is so small that it is very difficult to detect the time primer directly. The influence of the time primer on the Universe is nevertheless profound. Due to ergodic mixing, the area of the black/white interface in Figure A1(IIIa) becomes so large that even very small coarsening of the distribution results in a large increase of the black volume. Hence, entropy increases forward in time. The time primer is not time-symmetric, and when we move back in time to $t = -t_1$, it acts to decrease the black volume, as depicted in Figure A1(Ib). Hence, entropy reduces back in time. According to Boltzmann's time hypothesis, our perceived direction of time is that of the thermodynamic time, which is linked to the

second law of thermodynamics. The direction of thermodynamic time is determined by the temporal direction of the time primer.

In spite of the overwhelming evidence for the directional asymmetry of time around us, the exact physical nature of the time primer still remains a mystery. In quantum mechanics, the time primer is linked with the process of decoherence, which is expected to violate the unitarity of quantum evolutions. Although time symmetry is broken in quantum mechanics by weak interactions, there is no evidence that the known T-violating processes are the ones enacting the direction of time. A few theories (see, for example, [14,15]) are related to the process of quantum decoherence, which increases the number of accessible quantum states. Penrose [3] believes that decoherence is linked to the interactions of quantum mechanics and gravity (although gravity, classical or relativistic, is conventionally seen as time-symmetric). We, however, do not link the time primer to any specific theory or mechanism. In principle, the time primer may be: (a) a spontaneously generated property of matter and antimatter; or (b) can be induced by interactions with the environment or, possibly, with a special time-generating field. It is likely that the generation of the time primer combines the *spontaneous* (a) and *induced* (b) mechanisms. In line with the adopted terminology, spontaneous time priming can also be called *intrinsic*. This means that the temporal irreversibility can be initially generated within matter (and also antimatter) and then propagate through interactions (for example, interactions by radiation). Even very small interactions, which have magnitudes below the detection limits, can be sufficient to tip the entropy increase towards the common direction of time.

Figure A2. Increase of the phase space volume in irreversible evolutions and causality.



The asymmetric nature of the time primer enacts the second law, which in its turn, enacts causality: we see that the future is determined by the past, but not *vice versa*. Indeed, consider the evolution of the phase volume schematically shown in Figure A2. If the initial state of the system is known as, say, Area A at $t = t_0$, the state of the system at any following moment can be predicted: for example, it is Area B at $t = t_1$. The converse statement is, however, incorrect, due to the action of the second law: knowing that the system is in State B at $t = t_1$ does not allow us to conclude that it was in State A at $t = t_0$,

since the system state at $t = t_0$ could well be A' , or many other states determined by various possible contractions of the phase volume measure. While moving backward in time, the choice between A and A' is seen as a random event. We interpret this by saying that A causes B , but B is not a cause for A . The causality principle allows one to treat mechanical evolutions (classical or quantum) as time-reversible, while replacing the temporal irreversibility by the requirement of setting the initial conditions before (and not after) the process under consideration. This principle provides a great simplification and works really well in many respects. The philosophical aspects of the time arrow and causality are discussed in a book by Price [34] and in a number of more recent publications [35–37].

The causality principle has another important implication: a non-equilibrium state must have its cause in the past, but not in the future. For example, footsteps on a beach will eventually reach equilibrium with the sand and disappear (no special effort is needed for this), but the footsteps could not appear without a reason (*i.e.*, someone walking across the beach), as this would contradict the second law. A system that evolves very slowly towards its equilibrium (a photograph, for example) is a testimony of a distant past when its initial state was created by an external disturbance. The main implication of causality is that we can remember the past and can predict the future, but we cannot remember the future and cannot retrodict the past (pure retrodiction is ill-posed, since many different pasts correspond to nearly the same future, but partial retrodiction combined with partial memory records can be much more feasible).

The time primer does not have to be a fully deterministic process, and the phase volume may fluctuate slightly from point to point, provided the overall trend of the phase volume to increase forward in time is dominant. We, nevertheless, may observe some randomness forward in time. The forward-time randomness can be seen as a minor fluctuation of the time primer process, which results in a small local reduction of the phase volume. For example, a rolling coin will finish on one of its sides, but it is impossible to predict if this is going to be “heads” or “tails”. When the outcome becomes known, the reduction of uncertainty in this single bit (*i.e.*, heads or tails) does not cause a global entropy decrease, since the falling coin dissipates energy, and this is accompanied by a large increase in molecular entropy. Another example of forward-time randomness is the collapse of the quantum wave function during measurements, which should be accompanied by offsetting the entropy increase somewhere in the measuring apparatus.

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