CPT INVARIA NCE AND ITS IMPLICATIONS FOR THERMODYNAMICS AND KINETICS

A. Y. Klimenko*, U. Maas**

*The University of Queensland, SoMME, QLD 4072, Australia, E-mail: klimenko@mech.uq.edu.au
**Karlsruhe Institut fur Technologie, ITT, 76131, Germany, E-mail: Ulrich.Maas@kit.edu

ABSTRACT
This work reviews the modern understanding of thermodynamics and kinetics while taking into account CPT (charge-parity-time) invariance. The CPT invariance is one of the key principles of modern physics and is linked to Lorentz invariance of special relativity. While CPT invariance has been proven in quantum mechanics as a theorem, we consider this principle as a general law applicable to the universe and not restricted to quantum mechanics. Consistency between two perspectives on the real world – that of thermodynamics and that of CPT invariance is the focus of our consideration. While extending thermodynamics from matter to antimatter and postulating that there is a fundamental similarity in physical laws controlling matter and antimatter, we show that there are two different extensions possible: CP-invariant thermodynamics, which is commonly implied in various applications, and CPT-invariant thermodynamics, which has not been explored yet. Since both thermodynamics are different only by 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 this stage. This work investigates the comparative properties of CP- and CPT-invariant thermodynamics and their implications for kinetic processes.

INTRODUCTION
Boltzmann’s time hypothesis

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 also involved a series of very interesting questions about 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]. One of these hypotheses identifies our perceived direction of time with the second law of thermodynamics. Another hypothesis links the second law to 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 [1]) 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. It seems, however, that while the low entropy conditions in the past of the Universe are important, there should be a more specific and more local mechanism that enacts asymmetry of time. Indeed, consider the following gedanken experiment. Figure 1 depicts a piston-cylinder device, which is placed in a very remote part of the Universe, surrounded by a perfect reflective mirror and, hence, is completely insulated from the rest of the Universe for a very long time. This removes any direct external influence of the Universe on the system with exception of the position of the piston. The piston is moved by an external force in a manner that is symmetric with respect to the past and the future. As we can guess, if the piston motion is sufficiently fast, the response of the system to this motion is not time symmetric: a compression shock wave appears when the piston is moving in, and a rarefaction wave is formed when the piston is moving out. Note that rarefaction shock waves do not violate the first law of thermodynamics but are prohibited by the second law, since entropy would decrease in these waves. The time asymmetry in this experiment is enforced not by the direct influence of the Universe but through the property of matter placed into the cylinder. The low-entropy initial conditions imposed on the Universe result in the formation of matter, which can exist for a very long time and, as it seems from the example of Figure 1, is not fully time-symmetric.

The time primer.

From the perspective of the ergodic theory, increase of entropy in dynamic systems of large dimensions is associated with ergodic mixing [2; 3]. 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 evolution of volumes in the extended phase space with mixing of fluids. This analogy was first introduced by Gibbs in his fundamental work [4], which laid the foundations of statistical physics. Ergodic mixing can be illustrates by Figure 2, 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 2(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 2: 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. This logic, however, encounters severe problems when states of the system are considered back in time [5]. 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 2, Ia). How can time-symmetric evolution (compare Ia and IIIa in Figure 2) be consistent with the second law?

The resolution of this apparent paradox in the process, which can be called the time primer. 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 2(IIIb). The time primer is a violation of both classical mechanics and quantum mechanics, but its magnitude 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 2(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 2(Ib). Hence entropy reduces back in time.

In spite of the overwhelming evidence for directional asymmetry of time around us, the 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 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. Penrose [5] believes that decoherence is linked to interactions of quantum mechanics and gravity (although gravity, classical or relativistic, is conventionally seen as time-symmetric). A few theories (see, for example, [6; 7]) are related to the process of quantum decoherence. 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 a special time-generating field. It is likely that generation of the time primer combines spontaneous (a) and induced (b) mechanisms. 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 entropy increase towards the common time direction.

The asymmetric nature of the time primer enacts causality: we see that future is determined by the past but not vice versa. Indeed, consider evolution of the phase volume schematically shown in Figure 3. 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: 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 backwards 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 to treat mechani-
physical evolutions (classical or quantum) as time-reversible, while replacing the temporal irreversibility by 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 causality are discussed by Price [8].

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 to 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 forecast the future but we cannot remember the future and cannot forecast the past.

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 for the phase volume to increase forward in time is dominant. We may observe some randomness forward in time (which, as the reader may notice, should be seen as causality backward 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.

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 [9]. 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 so called charge conjugation or (C-conjugation), the heat fluxes \( q \) can change according to the following linear operation \( \mathcal{C}(q) = \alpha q \), where \( q \) is a conventional vector and \( \alpha \) is a real constant. This operation takes us to antiuniverse with the same physical laws as ours but the constant \( \alpha \) is not necessarily 1 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

\[
q = \mathcal{C}(\mathcal{C}(q)) = \mathcal{C}(\alpha q) = \alpha^2 q \implies \alpha = \pm 1 \quad (1)
\]

We will show that these two values of \( \alpha \) correspond to different thermodynamics: CP-invariant (\( \alpha = +1 \)) and CPT-invariant (\( \alpha = -1 \)). Here, we refer to parity, which represents change of directions of spatial coordinates (\( P(x) = -x \)), as P and to time reversal, which represents change of directions of time (\( T(t) = -t \)), as T. These operations are known in quantum mechanics but here we follow Sakharov [10] and interpret them as general physical principles not confined to the field of quantum mechanics. Sakharov's principles that are necessary for explanation of the matter/antimatter bias are often quoted as:

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

This list, however, does not include the fourth important assumption made by Sakharov in the same work [10]: CPT invariance is a global property of the Universe. While CPT invariance is commonly known as a theorem in quantum mechanics, its more general interpretation is a hypothesis, not a theorem. Penrose [5] believes that CPT invariance will not hold if applied to the whole of the Universe due to action of the second law. In the terms used here, this view corresponds to CP-invariant thermodynamics. 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. The CP and T violations have been found in meson decays but are much less common than CP-preserving C and P violations. Note that CP violation combined with CPT invariance implies T violation [9].

Since thermodynamics mainly deals with macroscopic scalar quantities, parity transformations are not important for a thermodynamic analysis.\(^1\) In the following consideration we preserve conventional notations adopted in quantum mechanics and retain P in transformations. The implications of having positive and negative \( \alpha \) in (1) are shown in Figure 4, which illustrates an experiment conducted by placing matter and antimatter in the focuses of a perfectly reflective ellipsoid (Figure 4(A)). Heat is transferred by radiation between matter and antimatter. The direction of the heat transfer changes as the transformations are

\(^1\) Although particles with opposite chiralities may need to be treated as different species in thermodynamics and kinetics.
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 focuses 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.

In general, it is difficult 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. CP-invariant thermodynamics is conventional and thus does not need extensive analysis here. CPT-invariant thermodynamics, it seems, has not been considered in the past but it is linked to the status of the CPT invariance, which is commonly seen as fundamental, and to our existing knowledge that CP symmetry is not a universal property of the Universe.

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. In the case of CP-invariant thermodynamics (not considered in this section), the second principle is to be replaced by 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.**

The competing physical intuitions of CPT invariance and of conventional thermodynamics has been recently discussed by Downes et al [11]. The present approach should not be confused with the thermodynamic analysis conducted by Dunning-Davies [12] on the basis of Santilli isodualities and having physical outcomes and interpretations very different from ours. The reversible equivalence principle treats matter and antimatter as being the same with respect to mechanical laws, does not change the signs of energy and mass, and does not imply existence of antigravity and anti-photons that are associated with Santilli isodualities. A popular presentation of CPT-invariant thermodynamics is given in Ref.[13] from the perspective of a space traveller visiting world made of antimatter.

**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, while the systems 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

\[
S_i = k_B \ln(\Gamma_i)
\]  

linking the entropy \(S_i\) in the state \(i\) to the number of microstates \(\Gamma_i\) in this state. The number of microstates \(\Gamma_i\) 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 \(\Gamma_i\) to more manageable thermodynamic quantities.

Here, 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 inclusion of both the system and the antisystem.
Apparent temperatures. The temporal boundary conditions for the example shown in Figure 5 are: energy $U_m$ and entropy $S_m$ are specified for the system at $t = -t_1$ and $t = t_1$, while $\bar{U}_a$, $\bar{S}_a$ are specified for the antisystem at $t = -t_1$ and $t = t_1$. 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 transition of a small quantity of heat $\delta Q$ through exchange of radiation, occurs at $t = 0$ (and $\bar{t} = 0$). The time window is selected so that $|\delta Q|$ cannot exceed $\delta Q_{\text{max}}$ where $\delta Q_{\text{max}}$ is sufficiently small. According to the observer the thermal energy $\delta Q$ is transferred from the antisystem to the system as shown by the black solid arrow. According to the antiobserver, who interpret the same event in the opposite direction of time, the same thermal energy $\delta Q$ is transferred from the system to antisystem as shown by the red dashed arrow. Heat $\delta Q$ is assumed to be positive when transferred in the direction shown in Figure 5: from the antisystem to the system according to the observer and from the system to the antisystem according to the antiobserver. The total energy

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

(evaluated at any constant time $t = -\bar{t}$) is preserved in this example, as it should 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.\(^2\)

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 $\Gamma$) can be easily evaluated and these changes of intrinsic entropy are shown in Figure 5 for the states $m'$ and $\bar{m}'$.

$$\frac{\Gamma_{\text{tot}}(\delta Q)}{\Gamma_{\text{tot}}(0)} = \exp \left( \frac{\delta Q}{kB} \left( \frac{1}{\bar{T}_m} + \frac{1}{T_a} \right) \right) \tag{5}$$

where conventional definitions of the temperature

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

are used. (The quantity $\delta Q$ is assumed to be too small to affect the intrinsic temperatures of matter and antimatter, which remain $T_m$ and $T_a$ correspondingly.). From observer’s perspective, the conventional equilibrium condition is given by 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 $\Gamma_{\text{tot}}$. This occurs only when $T_m = -T_a$ indicating that the apparent temperature of antimatter is $T_a = -T_m$. In the same way, the antiapparent (i.e. perceived by the antiobserver) temperature of matter is $T_m = -T_a$. It is easy to see that thermodynamic quantities $S_m, T_a$, 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 (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 $T_a$ 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 $T_m = T_a$ does not correspond to equilibrium and, according to (5), transfer of heat from antisystem to system in 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

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\(^2\)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 Ref.[14]). The energy balance at the moment of contact is $U_{\text{tot}} = U_m + U_a + U_{\text{rad}}$ where $U_{\text{rad}}$ is the radiation energy and the subscript "0" indicates states taken at $t = 0$. 

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equilibrium with an antisystem 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 (7) is likely to have negative apparent heat capacities

\[ C_a = -\frac{1}{T_a^2} \left( \frac{\partial^2 S_a}{\partial T_a^2} \right)^{-1} = \frac{1}{T_a^2} \left( \frac{\partial^2 S_a}{\partial T_a^2} \right)^{-1} = -\tilde{C}_a \]  

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 \( -T_a = T_a \rightarrow +0 \). Note that stable thermodynamic equilibrium between a system and an antisystem is possible at \( T_m = T_a = T = \infty \).

Mass exchange between matter and antimatter. An antimatter system with a variable number of particles is characterised by the equation

\[ d\tilde{U}_a = \tilde{T}_a d\tilde{S}_a + \tilde{\mu}_a d\tilde{N}_a \]  

which remains the same as conventional as long as it is presented from the perspective of the antiobserver. From our perspective, this equation changes according to (7). The reversible equivalence requires 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 \( \mu \) coincide:

\[ N_a = N_a, \quad \mu_a = \tilde{\mu}_a \]  

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

We note first the at infinite temperatures \( T_m = T_a = T = \infty \), the same quantities of matter and antimatter \( N_a = N = N_m \), which are kept under the same conditions, are in both thermal and chemical equilibrium since \( \mu_a = \mu_m(\infty, N, ...) = \mu_m(\infty, N, ...) \). If, however, \( T_m < \infty \), then thermal equilibrium \( T_m = T_a = -T_a \) does not imply that matter and antimatter under similar conditions are in chemical equilibrium since \( \mu_a = \mu_m(-T, ...) \) is generally different from \( \mu_m = \mu_m(T, ...) \) 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 \( T_m = T_a = T < \infty \) (and the same other conditions), then \( \mu_a = \mu_m(T_a, N, ...) = \mu_m(T, N, ...) \). In this case, however, equality of chemical quantities does not ensure chemical equilibrium since there is no thermal equilibrium \( T_m \neq T_a = -T_a \). Consider the following example: matter and antimatter are confined to the system and antisystem correspondingly and can not mix (mixtures are considered in the following subsection). Matter and antimatter can react with each other \( n \equiv \bar{n} \) and can annihilate to produce radiation \( n + \bar{n} \equiv 2 \gamma \). These two reactions can be combined to result in conversion \( 2\gamma \equiv 2\gamma \equiv 2n \); that is antimatter is 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 \( T_m = T_a \) and intrinsic entropy per particle (or per mole) \( s_m = \tilde{s}_a \), where \( s = S/N \). The total apparent entropy \( S_{tot} = N_m s_m - N_a s_a \) clearly increases. We see that CPT-invariant thermodynamics strongly favours conversion of antimatter into matter (from observer’s perspective), even if the intrinsic properties of matter and antimatter are exactly the same. For an antiobserver, this process seems as conversion of matter into antimatter.

**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.

**Mixtures dominated by matter.** Consider a mixture of many particles \( n_m \) with very few antiparticles \( n_a \). The translational degrees of freedom are entangled to produce a dominant direction of thermodynamic time for the whole mixture. Since particles have the numbers, this direction must be forward in time. Presence of antiparticles may slightly increase the fluctuating components of the time primer without any noticeable effect on thermodynamic properties. If particles and antiparticles are considered as mechanical or quantum systems and the direct effect of the spontaneous time primer on the particles is below detection limits, the presence of antiparticles does not affect the thermodynamic properties of the mixture (we do not consider annihilations, of course).

A different situation appears when each particle (and each antiparticle) represents an autonomous thermodynamic subsystem (i.e. having a large number of comparable internal degrees of freedom). 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 intrinsic temperature of the antiparticles is negative (this is possible when internal energy levels of antiparticles are bounded — see [15]) 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. While techniques based on evaluating statistical sums can not be used for systems with negative heat capacity (see [15]), 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

$$Z = (Z_0)^{N_m+N_a} (Z_m)^{N_m} (Z_a)^{N_a} \frac{N_m!}{N_a!},$$  \hspace{1cm} (11)$$

$$Z_m = \sum_i \exp \left( - \frac{E_i}{k_B T} \right), \quad Z_a = \exp \left( - \frac{E_0}{k_B T} \right),$$  \hspace{1cm} (12)$$

where $Z_0$ is the partition function without considering internal degrees of freedom, $Z_m$ is partition function for particle internal energy levels and $Z_a$ is the partition function for antiparticles in their ground state. 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 [16]

$$\Delta \mu = \mu_a - \mu_m = \left( \frac{\partial A}{\partial N_a} - \frac{\partial A}{\partial N_m} \right)_T$$

$$= k_B T \left( \ln \left( \frac{N_a}{N_m} \right) + f_m(T) \right)$$  \hspace{1cm} (13)$$

where $A = -k_B T \ln(Z)$ is the Helmholtz potential and $f_m(T) = \ln(Z_m(T)) \geq 0$. 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 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 can not 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 equilibrium state in any direction of time. Any process that is irreversible (formation of a black hole, for example) is impossible in this mixture.

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 $T_m = T_a = T_0 = \infty$, then systems and antisystems are in equilibrium according to the analysis of the previous subsection. If, however, the intrinsic temperatures are high but finite, then (as also discussed in the previous subsection) thermodynamics favours 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 $\Delta \mu$ stimulates 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 another observer’s time; hence antimatter is converted into matter in our time.

**DISCUSSION AND CONCLUSIONS**

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 abundance of matter combined with absence of antimatter, while CP-invariant thermodynamics see these issues as separate. In the absence of appreciable quantities of antimatter in our world, it is very difficult to determine, which one of these thermodynamics is not only logically possible but also real: both versions give the same predictions for the matter and similar predictions for autonomous particles and antiparticles. If, however, baryons (neutrons and protons) can be treated as stochastic systems, then CP-invariant thermodynamics requires the similarity of particles and antiparticles, while CPT-invariant thermodynamics predicts differences in chemical potentials (and, possibly, other properties) between particles and their antiparticles. Is there experimental evidence to make a choice between the two versions of thermodynamics on this basis?

Recent experiments in high-energy accelerators, indicate that thermodynamics might be relevant to very small scales (within a hadron) and high energies [17]. Protons and neutrons seem to contain myriads of appearing and annihilating gluons and quarks. 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 $\mu_B$ — the chemical potential associated with the baryon number $B$, so that baryons ($B = +1$) and antibaryons ($B = -1$) have different chemical potentials [17]. This seems to confirm the CPT-invariant version of thermodynamics 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.

Hence, $\mu_B$ 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.

We 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 an arrow of time (presumably everywhere, including in remote and isolated systems), we still do not know its exact mechanism. Induced time priming, whose magnitude is amplified by thermodynamic surroundings, may be possible to detect in quantum systems. Interactions of a quantum system with time-priming process do not cause any detectable anomalous behaviour when the system is CP-symmetric. If, however, a quantum system displays a CP violation, its interactions with time priming induced by the environment are likely to produce an impression of a CPT violation. Two versions of thermodynamics differ in its interpretation. CP-invariant thermodynamics admits that CPT is violated. CPT-invariant thermodynamics insists that the world is CPT-invariant so that the CPT violation is only an apparent phenomenon created by asymmetrically dominant presence of matter in the Universe.

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1. One can compare this with assigning elements arbitrary chemical potentials in chemical reactions conserving the elements
The difference between CP- and CPT-invariant thermodynamics 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 (thermodynamics favours the latter over the former when observed forward in time). 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 very unstable state associated with negative apparent temperatures. The chaotic energy of random motions can then be converted to coherent light of high intensity in complete agreement with the laws of thermodynamics. CP-invariant thermodynamics, on the contrary, does not expect any dangerous thermodynamic instabilities in these experiments.

While CPT-invariant thermodynamics seems to be conceptually consistent with the invariance principles adopted in other branches of physics, making an experimentally justified choice between two versions of thermodynamics is not possible at present, since both of the versions give the same predictions for our world populated by matter. However, this may change as more and more substantial quantities of antimatter are produced in experiments by high-energy accelerators [18].

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NOMENCLATURE

- $k_B$: Boltzmann constant
- $t$: time
- $C$: heat capacity
- $N$: number of particles
- $Q$: heat energy
- $S$: entropy
- $T$: temperature
- $U$: energy
- $\Gamma$: number of microstates
- $\mu$: chemical potential
- $q$: heat flux
- $C$: charge conjugation
- $H$: Hamiltonian
- $P$: parity transformation
- $T$: time reversal

REFERENCES


Appendix A: Quantum Example

Consider a quantum system, which involves particles and antiparticles and is placed into environment filled by radiation (see Figure 6). The radiation is equilibrated by surroundings, which, of course, is made of matter prevalently present in the Universe. The system is quantum and not thermodynamic; hence its time priming is induced and not spontaneous. Note that we do not consider emission or adsorption but only very weak interactions of the system and radiation. We conduct our analysis within the framework of conventional quantum mechanics but the time-asymmetric nature of this process should be noted and taken into account as a selection rule. Radiation is understood as any field or interaction that can induce time priming, whose effect is related but not necessarily limited to quantum decoherence.

\[\langle \beta | \hat{H} | \beta \rangle = E_\beta | \beta \rangle.\]
In conventional quantum mechanics, the system wave functions \( \alpha \) and the reduced wave function of the system state.

The environment is large and not significantly affected by interactions with the system and remains in its maximally mixed state.

The state of the system can is characterized by a set of system ket states \( |s\rangle \) while the state of the supersystem, which involves the system and the radiation bath, are specified by the tensor product \( |s\rangle \otimes |\beta\rangle = |s\rangle |\beta\rangle \). The overall wave function \( \Psi \) and the reduced wave function of the system \( \Psi_S \) can be represented in form of the expansions:

\[
\Psi = \sum_{s, \beta} c_{s\beta} |s\rangle |\beta\rangle, \quad \Psi_S = \sum_{s, \beta} c_{s\beta} |s\rangle |\beta\rangle
\]

where \( \Psi_S \) is obtained by multiplying \( \Psi \) by the environmental bra state \( |\alpha\rangle \), noting orthonormality \( \langle \alpha|\beta\rangle = I_{\alpha\beta} \) and summing over all \( \alpha \). Here, \( I_{\alpha\beta} \) is the identity matrix \( I_{\alpha\beta} = 0 \) if \( \alpha \neq \beta \) and \( I_{\alpha\alpha} = 1 \), \( \alpha = \beta \). The random phase \( |\beta\rangle \) in \( \Psi_S \) indicates a mixture of states that correspond to different \( \beta \). This is similar to writing the overall state as \( |s\rangle |\beta\rangle \) and then assuming that states \( |\beta\rangle \) are not measurable and replacing \( |\beta\rangle \) by \( |\beta\rangle \). Since \( |\beta\rangle \) do not evolve in conventional quantum mechanics, the system wave functions \( \Psi_S^{(\beta)} \) that correspond to different \( \beta \) can be considered independently

\[
\Psi_S^{(\beta)} = \sum_s c_s^{(\beta)} |s\rangle, \quad c_s^{(\beta)} = \frac{c_{s\beta}}{p_\beta^{1/2}}, \quad p_\beta = \sum_s c_{s\beta}^* c_{s\beta}
\]

The overall Hamiltonian that corresponds to our assumptions is written in the form

\[
\hat{H} = \mathbb{H}_S \otimes I_B + I_S \otimes \mathbb{H}_B + \mathbb{H}_{SB}
\]

where \( \mathbb{H}_S \) is Hamiltonian of the system, \( \mathbb{H}_{SB} \) is the system/bath interaction Hamiltonian and \( I \) is the identity operator. Assume that

\[
\langle \alpha q | \mathbb{H}_{SB} | \beta \rangle = \delta_{q0} I_{\alpha\beta}
\]

The system/radiation bath interaction term can be approximated by \( h_{q0}^{(\beta)} = \delta_{q0} I_{\alpha\beta} \), where \( \delta_{q0} \) is the \( \beta \)-dependent intensity of coupling and \( h_{q0}^{(\beta)} \) is the associated Hamiltonian.

The interactions with radiation-induced time priming should be CP-invariant and T-asymmetric so that the corresponding properties of the Hamiltonian are

\[
\langle \alpha q | \mathbb{H}_{SB} | \beta \rangle = \langle \alpha q | \mathbb{H}_{SB} | \beta \rangle \Rightarrow h_{q0}^{(\beta)} = h_{q0}^{(\beta)}
\]

\[
\Delta h_{q0}^{(\beta)} = \langle \beta q | \mathbb{H}_{SB} | \beta \rangle - \langle \beta | \mathbb{H}_{SB} | q \beta \rangle \neq 0
\]

where the overbars denote anti-states. The property \( \beta = \bar{\beta} \) is taken into account for radiation (i.e., matter and antimatter interact with radiation in the same way). Note that \( \Delta h_{q0}^{(\beta)} \) is imaginary when \( \mathbb{H} \) is Hermitian. Equations (19) and (20) imply a CPT violation:

\[
\langle \beta q | \mathbb{H}_{SB} | \beta \rangle \neq \langle \bar{\beta} q | \mathbb{H}_{SB} | \bar{\beta} \rangle
\]

The different versions of thermodynamics, however, give different interpretations for this violation:

\begin{itemize}
  \item **CP-invariant thermodynamics** admits (21) as CPT violation;
  \item **CPT-invariant thermodynamics** sees (21) as apparent and induced by the fact that matter, which surrounds the experiment and is implicitly present in the interactions by equilibrating the radiation, is not replaced by antimatter.
\end{itemize}

Decay kinetics

Among the system states \( |s\rangle \), we distinguish two groups: the initial states \( |k\rangle \) (or \( |j\rangle \) when an alternative symbol is needed for the bra-space), and the final states, which are indexed by \( |f\rangle \). The system is initially placed into a pure state that spans over the \( k \)-states but then decays into one or several of the \( f \)-states. Both, the \( k \)-states and the \( f \)-states, are eigenstates \( \mathbb{H}_0 |f\rangle = E_f |f\rangle \), \( \mathbb{H}_0 |k\rangle = E_k |k\rangle \) of the undisturbed Hamiltonian \( \mathbb{H}_0 \); the initial states are degenerate: \( E_k = E_0 \) for all \( k \). The system Hamiltonian is given by \( \mathbb{H} = \mathbb{H}_0 + \mathbb{H}_1 \), where smaller component \( \mathbb{H}_1 \) is responsible for interactions of the initial and final states. After tracing out the state of the environment and denoting \( \mathbb{H}^{(\beta)} = \langle \beta | \mathbb{H} | \beta \rangle - E_{q0} I_{\alpha\beta} \) and \( h_{q0}^{(\beta)} = h_{q0}^{(\beta)} |k\rangle \langle f| \), we can write

\[
\mathbb{H}^{(\beta)} = \mathbb{H}_0 + \mathbb{H}_2^{(\beta)}, \quad \mathbb{H}_2^{(\beta)} = \mathbb{H}_1^{(\beta)} + h_{q0}^{(\beta)}
\]
The effective Hamiltonian $\Lambda_{kk}^{(B)}$ of the decaying $k$-states is obtained by using the Weisskopf-Wigner approximation [19], which plays in quantum decays the same role as kinetic equations in chemistry,

\[
\Lambda_{kk}^{(B)} = (j| \Xi^{(B)} |k) + \lambda_{kk}^{(B)}
\]

\[
\lambda_{kk}^{(B)} = \sum_f \frac{(j| \Xi^{(B)}_f |f) (f| \Xi^{(B)}_k |k)}{E_0 - E_f + i\varepsilon}
\]

where $\varepsilon \to 0$ and the sign of $\varepsilon$ is selected to produce decaying exponents required by causality. Approximation (23) is conventionally used to analyse decay of neutral kaons, $K^0$ and $\bar{K}^0$ [9]. We investigate the CPT-compliance of the decay, which requires that $\Theta^{(B)}_{kk} = \lambda^{(B)}_{kk} - \lambda^{(B)}_{kk} = 0$ [9].

The case of CP symmetry. Most quantum systems possess CP symmetry and relatively few CP violations are known in quantum mechanics. When the system Hamiltonian $\Xi^k$ is CP-invariant, we obtain

\[
H_{kf} = (k| \Xi^k |f) = \langle k | \Xi^k | f \rangle = H_{kf}
\]

\[
\Theta^{(B)}_{kk} = \lambda^{(B)}_{kk} - \lambda^{(B)}_{kk} = 0
\]

Here we use equations (19), (23), (24) to obtain (25) and conclude that the system appears to be CPT-compliant.

The case of CPT symmetry and CP violation. The system Hamiltonian $\Xi^k$ is CP-invariant provided

\[
H_{kf} = (k| \Xi^k |f) = \langle k | \Xi^k | f \rangle = H_{kf}
\]

We use equations (19), (23) and (26) and note that the first term in (23) does not contribute to $\Theta^{(B)}$ so that

\[
\Theta^{(B)}_{kk} = \lambda^{(B)}_{kk} - \lambda^{(B)}_{kk}
\]

\[
= \sum_f \left( H_{k'f} + h_{k'f}^{(B)} \right) \left( H_{k'f} + h_{k'f}^{(B)} \right) - \left( H_{k'f} + h_{k'f}^{(B)} \right) \left( H_{k'f} + h_{k'f}^{(B)} \right) \left( H_{k'f} + h_{k'f}^{(B)} \right)
\]

\[
= \sum_f \left( H_{k'f} + h_{k'f}^{(B)} \right) \left( H_{k'f} + h_{k'f}^{(B)} \right) - \left( H_{k'f} + h_{k'f}^{(B)} \right) \left( H_{k'f} + h_{k'f}^{(B)} \right)
\]

\[
= - \sum_f \frac{\Delta H_{k'f}^{(B)}}{E_0 - E_{f} + i\varepsilon} \Delta h_{k'f}^{(B)}
\]

where $H_{k'f} = (k| \Xi^k_1 |f), \Delta H_{k'f} = H_{k'f} - H_{k'f}$ . Hence, interactions with time priming can appear in CP-violating (but CPT preserving) systems as an apparent CPT violation. Absence of the time symmetry $\Delta H_{k'f}^{(B)} = 0$ and $\Delta h_{k'f}^{(B)} = 0$ is essential for this effect.

**Appendix B: Random Phase Notation**

This appendix explains the notations, which are used to distinguish pure and mixed states of quantum mechanics and are based on random phases. Let

\[
|\beta\rangle = \exp(i\theta_\beta)
\]

where $\theta_\beta$ is a random angle uniformly distributed between 0 and $2\pi$. The inner product is defined as averaging

\[
(\alpha|\beta) = \langle \exp(i(\theta_\beta - \theta_\alpha)) \rangle = I_{\alpha\beta}
\]

and different random phases are presumed to be stochastically independent so that the system of vectors $|\alpha\rangle$, $|\beta\rangle$, ... is orthonormal. These vectors can be seen as special quantum states that cannot be measured since only one operator — the identity operator $I$ — can be applied to these states: $(\alpha|\beta) = (\alpha|\beta) = I_{\alpha\beta}$.

Let $\psi$ be a wave function represented by the expansion

\[
\psi = \sum_{j,\beta} c_{j\beta} |j\rangle |\beta\rangle
\]

then the density matrix is evaluated by tracing out the random phases, that is

\[
\rho = \sum_{i,\alpha;\beta} c_{i\alpha} c_{j\beta} \langle i | \langle i | \alpha \rangle | \beta \rangle = \sum_{\beta} \sum_{i,j} c_{i\alpha} c_{j\beta} \langle i | \alpha \rangle | \beta \rangle \langle j | i \rangle
\]

As an example of using this notation, consider the following expressions

\[
\psi_1 = \frac{|1\rangle + |1\rangle}{\sqrt{2}}, \psi_{-1} = \frac{|1\rangle - |1\rangle}{\sqrt{2} |\beta\rangle}
\]

\[
\psi_2 = \frac{|1\rangle |\alpha\rangle + |1\rangle |\beta\rangle}{\sqrt{2}}, \psi_3 = \psi_1 + \psi_{-1}
\]

The first two expressions specify $\psi_{+1}$ and $\psi_{-1}$ as pure states (with arbitrary phases nominally given as $|\alpha\rangle$ and $|\beta\rangle$). The last two expressions indicate that $\psi_2$ is a mixture of two pure states $|1\rangle + |1\rangle$ with equal probability and that $\psi_3$ is a mixture of another two pure states $\psi_{+1}$ and $\psi_{-1}$ (since $\psi_1$ and $\psi_{-1}$ have different random phases $|\alpha\rangle$ and $|\beta\rangle$). Note that $\psi_3$ is different from $\psi_2$ and this difference is reflected by the random phase notation. The density matrices corresponding to these cases are evaluated according to (31):

\[
\rho_{+1} = \frac{1}{2} \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}, \rho_{-1} = \frac{1}{2} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}
\]

\[
\rho_{2} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \rho_{3} = \frac{1}{2} \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix}
\]

In conventional quantum mechanics, the random phase multipliers $|\alpha\rangle, |\beta\rangle$ are orthonormal and do not evolve in time. Spontaneous decoherence, however, corresponds to $|\alpha\rangle$ being the same as $|\beta\rangle$ initially but then evolving into stochastically independent quantities.