

In Search of Time Lost: Asymmetry of Time and Irreversibility in Natural Processes

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Abstract

In this survey, we discuss and analyze foundational issues of the problem of time and its asymmetry from a unifed standpoint. Our aim is to discuss concisely the current theories and underlying notions, including interdisciplinary aspects, such as the role of time and temporality in quantum and statistical physics, biology, and cosmology. We compare some sophisticated ideas and approaches for the treatment of the problem of time and its asymmetry by thoroughly considering various aspects of the second law of thermodynamics, nonequilibrium entropy, entropy production, and irreversibility. The concept of irreversibility is discussed carefully and reanalyzed in this connection to clarify the concept of entropy production, which is a marked characteristic of irreversibility. The role of boundary conditions in the distinction between past and future is discussed with attention in this context. The paper also includes a synthesis of past and present research and a survey of methodology. It also analyzes some open questions in the feld from a critical perspective.

Keywords Asymmetry of time · Irreversibility · Arrow of time · Second law of thermodynamics · Quantum mechanics · Quantum entropy · Entropy production

1 Introduction

"The physical world is constituted by changing things" (Bunge and Maynez [1976](#page-42-0)). Paradoxically, this conclusion follows from an analysis of physical space: "...construction of space involves the notions of event and event composition, and the latter allows one to define a time order of events" (Bunge and Maynez [1976](#page-42-0)).

The problem of time (Denbigh [1981;](#page-43-0) Landsberg [1984;](#page-45-0) 't Hooft and Vandoren [2015;](#page-47-0) Anderson [2012,](#page-42-1) [2017](#page-42-2), [2010\)](#page-42-3) is a complicated conceptual problem in various branches of science, and in physics and cosmology in particular. Like the universe, which has many faces (or facets) (Hoyle [1977](#page-45-1)), time is a many-faceted notion (Denbigh [1981;](#page-43-0) Horwitz et al. [1988\)](#page-45-2). Entropy, like time, is also a many-faceted concept (Grad [1961\)](#page-44-0). There is an apparent

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close relationship between entropy and time, which is discussed below. It has sometimes been said that time appears in thermodynamics not as a quantity but only as an indicator of the sense of a quantity, the change of entropy. This is why the concepts of time, entropy, and irreversibility, which is also a many-faceted notion (Denbigh [1989a](#page-43-1), [b](#page-43-2)), are tightly related (Popper [1965](#page-47-1)).

In this context, the interest in the problem of time and its directionality that has become apparent in recent decades is understandable. Many difficult questions regarding the problems of time and the directionality (arrow) of time in classical and quantum physics are now under intensive study by various researchers (Horwich [1987;](#page-45-3) Liu [1993;](#page-46-0) Halliwell et al. [1996;](#page-44-1) Savitt [1995;](#page-47-2) Denbigh [1996](#page-43-3); Price [1996](#page-47-3); Penrose [2005;](#page-46-1) Zeh [2007;](#page-48-0) Boyarsky and Gora [2009;](#page-42-4) Lineweaver et al. [2013](#page-46-2); 't Hooft and Vandoren [2015;](#page-47-0) Anderson [2012](#page-42-1), [2017;](#page-42-2) Kuzemsky [2018](#page-45-4)). However, no complete resolution of these problems has yet been accomplished.

Indeed, the problem of time includes a rather wide spectrum of philosophical issues (de Bianchi [2012](#page-43-4); Heylighen [2010\)](#page-44-2). There is no sharp dividing line between the foundational issues of physics and the philosophy of time. The literature on this subject is vast (Kuzemsky [2018](#page-45-4); Callender [2011;](#page-43-5) Wuppuluri and Ghirardi [2017;](#page-48-1) Hsu [1992](#page-45-5); Birx [2009\)](#page-42-5).

The basic unsolved problem is the relationship between physical time and time as we experience it; For example, Halvorson [\(2010](#page-44-3)) remarked that: "...there are good arguments that we should expect time to emerge as a parameter (a classical, superselected quantity) because of decoherence processes... But these arguments indicate that time belongs more to the realm of appearances than to the realm of being."

In his book *Physics and Philosophy*, Heisenberg ([1958\)](#page-44-4) devoted a special chapter entitled "Language and Reality in Modern Physics" to a discussion of the ability of language to express the complicated concepts of modern physics: Physics has recently opened up vast new felds of knowledge, making it necessary for us to modify some of our most basic philosophical notions ...The improved experimental technique of our time brings into the scope of science new aspects of nature which cannot be described in terms of the common concepts ...However, "one has not yet found the correct language with which to speak about the new situation" (see also Ref. Rosenfeld [1960\)](#page-47-4). The notions of time and space are the marked examples of the interdependence of physics and philosophy (Wuppuluri and Ghirardi [2017](#page-48-1); Sklar [1977;](#page-47-5) Smolin [2013;](#page-47-6) Unger and Smolin [2014](#page-48-2)).

Such debates on the reality and signifcance of time have raged in both the scientifc and philosophical communities from the high antiquity and continue to the present day (Whitrow [1988;](#page-48-3) Callender [2011](#page-43-5); Wuppuluri and Ghirardi [2017](#page-48-1)).

One of the most important questions concerning the foundations of physics, especially from the point of view of astrophysics, cosmology, nonequilibrium statistical thermodynamics, chemical physics, and biology, is the role of time in natural processes (Kuzemsky [2018;](#page-45-4) Callender [2011](#page-43-5); Wuppuluri and Ghirardi [2017;](#page-48-1) Hsu [1992;](#page-45-5) Birx [2009\)](#page-42-5). Intuition tells us that time is a continuous dimension along which events occur and that it is complementary to position in space. Hence, time is the dimension of the physical universe which, at a given place, orders the sequence of events (Bunge and Maynez [1976;](#page-42-0) Sklar [1977](#page-47-5)).

The question of why time has an arrow is an especially controversial subject matter and is still under intense debate (Halliwell et al. [1996](#page-44-1); Savitt [1995](#page-47-2); Denbigh [1996](#page-43-3); Price [1996;](#page-47-3) Penrose [2005;](#page-46-1) Zeh [2007](#page-48-0); Boyarsky and Gora [2009](#page-42-4); Lineweaver et al. [2013](#page-46-2); 't Hooft and Vandoren [2015;](#page-47-0) Anderson [2012,](#page-42-1) [2017;](#page-42-2) Kuzemsky [2018\)](#page-45-4). As formulated by Anderson ([2012\)](#page-42-1), "the problem of time occurs because the *time* of general relativity and of quantum theory are *mutually incompatible* notions," a point that was formulated earlier by Macias and Gamacho ([2008\)](#page-46-3)

The origin of time asymmetry (the arrow of time) and the interrelation between past and future are the most fundamental questions regarding temporal evolution (Kuzemsky [2018;](#page-45-4) Horwich [1987](#page-45-3); Lineweaver et al. [2013](#page-46-2)). Time-asymmetric behavior is the most characteristic feature of irreversible processes, being related to changes of state in various thermodynamic processes, substances, and materials. The very defnition of time essentially includes the notion of irreversibility. Indeed, "time is the measurement by which it is possible to judge how quickly or slowly a change occurs." An inseparable feature of time is thus to pass from past to future *irreversibly*. Irreversible change means that it cannot be changed back to what it was before.

In nature, there exist systems whose interaction with their surroundings consists only in the exchange of work and heat. These are termed "thermodynamic systems." As a rule, it was assumed that a system is initially at rest with its surrounding if there are no external applied forces. There are *isolated*, *closed*, and *open* systems. The frst type can exchange neither energy nor matter with its surroundings. The second is a less isolated system and can exchange energy but not matter with its surroundings. An open system can exchange both energy and matter with its surroundings. Note that the strictly isolated system is an idealization.

Irreversible thermodynamics, which describes these phenomena, is a well-developed subject (Kuzemsky [2018;](#page-45-4) Denbigh [1958](#page-43-6); Kreuzer [1981;](#page-45-6) Muller [2007](#page-46-4); Muller and Muller [2009;](#page-46-5) Muller and Weiss [2012;](#page-46-6) Demirel [2014\)](#page-43-7); in particular, linear irreversible thermodynamics (Garcia-Colin [1995](#page-44-5)) is widely used.

Common wisdom states that entropy production (Kuzemsky [2018;](#page-45-4) Denbigh [1958;](#page-43-6) Kreuzer [1981](#page-45-6); Denbigh and Denbigh [1985;](#page-43-8) Velasco et al. [2011](#page-48-4); Dewar et al. [2014\)](#page-43-9) is the main component of irreversibility, even though many natural processes which are irrevers-ible do not appear to result in significant entropy production (Denbigh [1989a,](#page-43-1) [b](#page-43-2)).

However, such a formulation of the laws of nature from the point of view of a change of entropy of real systems is only a particular case and as such has certain limitations. In addition, the thermodynamic criterion for the production of entropy (Kuzemsky [2018](#page-45-4)) characterizes only spontaneous heat processes in simple systems but does not apply to the nonentropic processes which may take place in real complex systems. The second law of thermodynamics is applicable to closed systems. This law summarizes the results of observations and states that, in natural processes which are thermally isolated from their surroundings, systems evolve from a more ordered to a less ordered state. This fact is equivalent to the assertion that, in irreversible processes subject to adiabatic constraints, there is a tendency for thermal energy to be distributed uniformly among the basic elements of matter.

Similar directionality principles can be used in evolutionary biology (Blum [2016;](#page-42-6) Demetrius [1997](#page-43-10)). Indeed, the directionality in populations of replicating organisms can be parameterized in terms of a statistical concept known as "evolutionary entropy." This parameter, which is a measure of the variability in the age of reproducing individuals in a population, is isometric with the macroscopic variable body size. Evolutionary trends in entropy due to mutation and natural selection fall into patterns that are modulated by ecological and demographic constraints (Demetrius [1997\)](#page-43-10).

In this regard, some authors (Denbigh [1996,](#page-43-3) [1989a](#page-43-1), [b](#page-43-2); Denbigh and Denbigh [1985](#page-43-8)) have claimed that it is possible to make a distinction between *entropy production* and *irreversibility* in the nonequilibrium thermodynamics of natural processes. A more appropriate name for this kind of process is *quasistatic*. Statistical mechanics formulates a suitable approach that successfully describes the stationary macroscopic behavior of many-particle systems such as fuids, gases, and solids. The aim of statistical mechanics (Kuzemsky

[2018;](#page-45-4) Zubarev [1974;](#page-48-5) McLennan [1989](#page-46-7); Wu [1969;](#page-48-6) Keizer [1987](#page-45-7); Dougherty [1993,](#page-43-11) [1994;](#page-44-6) Lebowitz [1993](#page-46-8), [1999](#page-46-9); Kuzemsky [2007](#page-45-8), [2016](#page-45-9), [2017](#page-45-10), [2018](#page-45-11)) is to provide a consistent workable formalism for a microscopic description of the macroscopic behavior of thermodynamic systems. It also clarifes basic thermodynamic concepts such as heat, temperature, and entropy based on the underlying microscopic laws. It is important to emphasize that equilibrium statistical mechanics is based on the postulate of the equiprobability of all the microstates of a macroscopic *N*-particle system under study. The probability of the realization of a given microstate is thus proportional to the number of available microstates, and the state of equilibrium is the most probable state for a system.

Nonequilibrium statistical physics describes irreversible processes starting from the underlying, time-symmetric dynamics of many-particle systems (Kuzemsky [2018](#page-45-4); Zubarev [1974;](#page-48-5) McLennan [1989;](#page-46-7) Wu [1969;](#page-48-6) Keizer [1987;](#page-45-7) Dougherty [1993](#page-43-11), [1994;](#page-44-6) Lebowitz [1993](#page-46-8), [1999;](#page-46-9) Kuzemsky [2007](#page-45-8), [2016](#page-45-9), [2017](#page-45-10), [2018](#page-45-11)). Beyond its practical purposes, the statistical physics of out-of-equilibrium open systems aims to reveal the real physical origins of irreversibility in complex many-particle systems.

The aim of the present paper is to discuss concisely and attempt to provide an account of the physical concept of time and its asymmetry in quantum theory and statistical physics, mainly from the point of view of nonequilibrium statistical thermodynamics. We outline some relevant notions and facts that may help to understand better what time means from diferent points of view. We do not aim for complete generality. Rather, we try to discuss qualitatively several aspects of the subject and refer to the literature for more detailed considerations.

2 Quantum Evolution and the Time Parameter in Quantum Theory

The spectral theory of linear operators in Hilbert spaces is the most important tool in the mathematical formulation of quantum mechanics; in fact, linear operators and quantum mechanics have a deep relationship (Jauch [1968](#page-45-12); Piron [1976](#page-47-7)). The quantization of physical systems includes a correct defnition of physical observables (such as the Hamiltonian and the momentum) as self-adjoint operators (Jauch [1968;](#page-45-12) Piron [1976\)](#page-47-7) in an appropriate Hilbert space H and their proper spectral analysis. A solution of this problem is not a straightforward and unambiguous procedure for nontrivial quantum systems (systems on nontrivial manifolds, in particular on manifolds with boundaries or singular interactions).

The problems with time, in general, and quantum evolution in particular, have been discussed extensively in literature (Bayfeld [1999;](#page-42-7) Tannor [2007\)](#page-48-7). Time *t* does not correspond to a dynamical variable (operator); rather, it drives the evolution of a system. It is of essence that measurements are made *at an instant of time*; histories are not measurable (Jauch [1964](#page-45-13), [1968](#page-45-12)). The Pauli ([1980\)](#page-46-10) theorem says that the existence of a self-adjoint time operator that is canonically conjugate to a Hamiltonian is impossible, since this would imply that both operators possess completely continuous spectra spanning the entire real line.

To emphasize the importance of the Pauli statement, we briefy discuss the role of the *time parameter* in quantum theory following the analysis in his book (Pauli [1980](#page-46-10)) literally.

Pauli made his statement on the impossibility of considering time as a dynamical variable when studying the general form of the laws of motion. Pauli pointed out that, in matrix quantum mechanics, in addition to the commutation relations, an important role is played by the prescription that the energy matrix, namely the Hermitian matrix H_{nm} , should be in diagonal form:

$$
H_{nm} = E_n \delta_{nm}.
$$
 (1)

Heisenberg added a further condition concerning the dependence of the matrix elements on time. He stipulated that the time dependence of the matrix elements of quantities that do not explicitly contain the time variable should be given by

$$
F_{nm}(t) = F_{nm}(0) \exp\left[\frac{i}{\hbar}(E_n - E_m)t\right].
$$
 (2)

On introducing the unitary diagonal matrix,

$$
U_{nm}(t) = \delta_{nm} \exp\left[\frac{i}{\hbar}E_n\right],\tag{3}
$$

we should have

$$
F(t) = U(t)F(0)U^{-1}(t) = U(t)F(0)\tilde{U}(t).
$$
\n(4)

If the Hamiltonian does not contain time explicitly, Eq. ([4\)](#page-4-0) with $F = H$ indicates that Eq. ([1\)](#page-4-1) remains true for all *t*. The relation [\(2\)](#page-4-2) can also be replaced by the diferential equation

$$
\frac{\hbar}{i}\dot{F}_{nm} = F_{nm}[E_n - E_m]
$$
\n(5)

or

$$
\frac{\hbar}{i}\dot{F} = HF - FH,\tag{6}
$$

if H is taken to be the diagonal matrix (1) (1) . On account of (1) (1) (1) , the form (2) (2) again follows from [\(6\)](#page-4-3). Relation ([2\)](#page-4-2) is nothing but the relation for the calculation of the matrix elements with the functions u_n replaced by the functions

$$
\psi_n(t) = u_n \exp\left[\frac{i}{\hbar}E_n\right].\tag{7}
$$

These satisfy the wave equation

$$
\frac{\hbar}{i}\dot{\psi}_n = H\psi_n \tag{8}
$$

because then

$$
F_{kn} = \int \psi_k^*(F\psi_n) dq = \exp\left[\frac{i}{\hbar}(E_k - E_n)t\right] \int u_k^*(Fu_n) dq = \exp\left[\frac{i}{\hbar}(E_k - E_n)t\right] F_{kn}(0).
$$
\n(9)

We can now generalize this idea by introducing an arbitrary orthogonal system φ_n , as the basis for the matrices, without their necessarily having to possess the special form [\(7](#page-4-4)), although we impose the essential requirement that all the functions $\varphi_n(t)$ should satisfy the wave equation

$$
\frac{\hbar}{i}\dot{\varphi}_n = H\varphi_n.
$$
\n(10)

It immediately follows from the fact that, for all solutions of ([10](#page-5-0)) the integral $\int \psi^* \psi dq$ is constant in time, for any solution of the form $(c_n\varphi_n + c_m\varphi_m)$ with arbitrary coefficients c_n, c_m , we have

$$
\frac{d}{dt} \int \varphi_n^* \varphi_m dq = 0; \tag{11}
$$

i.e., the orthogonality and normalization of the set of functions remain unaltered in time. Hence, from the defnition

$$
F_{nm} = \int \varphi_n^*(F\varphi_m)dq,\tag{12}
$$

we obtain, on diferentiating, the following relation which is valid for any Hermitian operator *F not containing time explicitly*:

$$
\frac{\hbar}{i}\dot{F}_{nm} = \int \left[(H\varphi_n)^* (F\varphi_m) - \varphi_n^* (FH\varphi_m) \right] dq
$$
\n
$$
= \int \left[\varphi_n^* (HF\varphi_m) - \varphi_n^* (FH\varphi_m) \right] dq = (HF - FH)_{nm}.
$$
\n(13)

Thus, we recover Eq. ([6](#page-4-3))

$$
\frac{\hbar}{i}\dot{F} = HF - FH,\tag{14}
$$

but now without any special assumption about the matrices. On account of this rule, every set of commutation relations (which are mutually compatible and do not contain time explicitly) remains unchanged in time if it is satisfied for $t = 0$.

At this stage, Pauli [\(1980](#page-46-10)) made a remarkable note:

In the older literature on quantum mechanics, we often fnd the operator equation

$$
Ht - tH = \frac{\hbar}{i}I,\tag{15}
$$

which arises from Eq. ([6\)](#page-4-3) formally by substituting *t* for *F*. It is *generally not possible*, however, to construct a Hermitian operator (e.g., as a function of *p* and *q*) which satisfes this equation. This is so because, from the commutation relations written above, it follows that *H* possesses continuously all eigenvalues from $-\infty$ to $+\infty$, whereas discrete eigenvalues of *H* can be present. We, therefore, conclude that the introduction of an operator *t* is *basically forbidden* and the time *t* must necessarily be considered as an ordinary number ("*c*-number") in quantum mechanics. As opposed to this, operators are usually called "q-numbers." There are numerous works that try to "bypass" the Pauli theorem (Isidro [2005](#page-45-14)) or generalize the Hilbert space to avoid Pauli's restrictions. Due to lack of space, we have no possibility to discuss this here.

3 In Search of Time Lost

As discussed above, the notion of time is very difficult to define precisely. Numerous attempts have been made to give such a unifed defnition, for example: time may be considered as the indefnite continued progress of existence and events in the past, present, and future regarded as a whole. Such a defnition is a wording only and should be considered as a null hypothesis. In spite of the fact that time is hard to defne, it is also not an easily discussable subject. However, it should be discussed in many regards and with competing hypotheses to treat the subject. To introduce this subject, a number of complementary (or contradictory) approaches are frst described briefy to emphasize the very diferent character of various theories.

Ellis ([2013](#page-44-7); [2014](#page-44-8)) summarized the existing data, including the results of the Planck team, for the present age of the universe. Precision cosmology (Jones [2017](#page-45-15)) supports the point that space–time is an evolving block universe, with the present being the future boundary of a space–time that steadily extends into the future as *time progresses*. In this picture, the present separates the past (which already exists) from the future (which does not yet exist, and is indeterminate because of foundational quantum uncertainty). There are some technical aspects to this, namely: (1) simultaneity has no physical import, and it is a purely psychological construct; (2) one can defne unique surfaces of constant time in a nonlocal geometric way; (3) this proposal solves the chronology protection problem (it prevents the existence of closed time-like lines); and in this context, (4) the *arrow of time* is distinguished from the *direction of time*, which is nonlocally defned in the evolving block universe context. Ellis concludes that "time fows on and the universe is now older than it was then. But this view contradicts what many scientists claim."

Indeed, in recent decades, numerous works that categorically deny the physical signifcance of the notion of time have been published (Ellis [1974](#page-44-9); Barbour [1999](#page-42-8), [2004;](#page-42-9) Butterfeld [2002](#page-43-12); Rovelli [2004](#page-47-8), [2011](#page-47-9), [2018](#page-47-10)). An extremely radical point was presented by Ellis ([1974](#page-44-9)), who claimed that a rigorous analysis of time will provide understanding of the unity of gravity and electromagnetism. The reconcilability of gravitational with electromagnetic clocks may suggest that time can be considered to be a fundamental property of elementary particles, and only derivatively a property of clocks. A declaration was made that the fow of an elementary particle's time is the change of its radius, and that time is therefore illusory. The author speculated that "the de Sitter expanding universe was derived from this principle by treating elementary particles as spheres in Euclidean space. The hyperspheres of de Sitter space call up a fve-dimensional metric manifold whose geometry models gravity, electromagnetism, and other phenomena tied to the structure of matter; neutrinos are provided for. Distance in this manifold was related to a secondary time, not correlated to primary time, but just as illusory. A particle's inertial rest mass was treated as the relative rate of its two proper times; mass and charge are jointly, not individually, conserved." In this connection, it is worth noting that de Sitter space is a maximally symmetric space–time with constant curvature that does not have the degrees of freedom required to model any phenomena except the gravity feld of a cosmological constant.

At a later date, Boyarsky and Gora ([2009](#page-42-4)) investigated similar questions in the modern context. A defnition of time based on the fundamental Planck scale was formulated. In other words, they presented a defnition of time based on a particle's interaction with the Higgs feld. Just as a particle acquires mass by interacting with the Higgs feld, their model proposes that time is acquired via the energy of virtual particles participating in

the quantum exchange interactions with Higgs particles. It was shown that, for *macroscopic time*, this defnition accords with the Lorentz transformation of special relativity.

In his book *The End of Time*, Barbour [\(1999](#page-42-8)) formulated his vision in the following way: "I now believe that time does not exist at all, and that motion itself is pure illusion. What is more, I believe there is quite strong support in physics for this view." Indeed, the book *The End of Time* is highly provocative and formulates its basic ideas in a radical form. Barbour analyzes what time really is. According to him, the answer is "nothing." In other words, the basic facts of classical dynamics show that time, or precisely duration, is redundant as a fundamental concept. Duration and the behavior of clocks emerge from a timeless law that governs change.

In fact, the roots for Barbour's conclusions are based on a new approach to the dynamics of the universe (Barbour [2004\)](#page-42-9). In this approach, the only kinematics presupposed is the spatial geometry needed to defne confguration spaces in purely relational terms. For this aim, a new formulation of the principle of relativity based on Poincaré's analysis of the problem of absolute and relative motion (Mach's principle) was given. The entire dynamics was based on shape and nothing else. This may lead to much stronger predictions than the standard Newtonian theory. For the dynamics of Riemannian 3-geometries on which matter felds also evolve, implementation of the new principle of relativity establishes unexpected links between special relativity, general relativity, and the gauge principle. They all emerge together as a self-consistent complex from a unifed and completely relational approach to dynamics. A connection between time and scale invariance was also established. In particular, the representation of general relativity as the evolution of the shape of space leads to a unique dynamical defnition of *simultaneity*. This opens up the prospect of a solution to the problem of time in quantum gravity on the basis of a fundamental dynamical principle.

Butterfeld [\(2002](#page-43-12)) thoroughly discussed Barbour's Machian theories of dynamics and his proposal that a Machian perspective enables one to solve the problem of time in quantum geometrodynamics (by saying that there is no time). This study shed light on the somewhat semiprophetic ideas of Barbour.

The problem of time in physics and in quantum gravity in particular was analyzed by Rovelli ([2004,](#page-47-8) [2011](#page-47-9), [2018](#page-47-10)). According to his point of view, "...we conventionally think of time as something simple and fundamental that fows uniformly, independently from everything else, from the past to the future, measured by clocks and watches. In the course of time, the events of the universe succeed each other in an orderly way: pasts, presents, futures. The past is fxed, the future open. . . . And yet all of this has turned out to be false. One after another, the characteristic features of time have proved to be approximations, mistakes determined by our perspective, just like the fatness of the Earth or the revolving of the sun. The growth of our knowledge has led to a slow disintegration of our notion of time. What we call *time* is a complex collection of structures, of layers. Under increasing scrutiny, in ever greater depth, time has lost layers one after another, piece by piece... The physics on which I work—quantum gravity—is an attempt to understand and lend coherent meaning to this extreme and beautiful landscape. To the world without time."

Thebault ([2012\)](#page-48-8) summarized the three denials of time in the interpretation of canonical gravity. He carried out an analysis of the temporal structure of canonical general relativity, and the connected interpretational questions with regard to the role of time within the theory both rest upon the need to respect the fundamentally dual role of the Hamiltonian constraints found within the formalism. In his opinion, any consistent philosophical approach towards the theory must pay dues to the role of these constraints in both generating dynamics, in the context of phase space, and generating unphysical symmetry transformations, in

the context of a hypersurface embedded within a solution. A frst denial of time in terms of the position of reductive temporal relationalism can be shown to be troubled by failure on the frst count, and a second denial in terms of Machian temporal relationalism can be found to be hampered by failure on the second. A third denial of time, consistent with both of the roles of Hamiltonian constraints, is constituted by the implementation of a scheme for constructing observables in terms of correlations and leads to a radical Parmenidean timelessness. The motivation for and implications of each of these three denials were investigated carefully.

In their study, Gryb and Thebault ([2016\)](#page-44-10) expressed a point of view opposed to that of Rovelli. In their opinion, on one popular view, the general covariance of gravity implies that change is relational in a strong sense, such that all that it is for a physical degree of freedom to change is for it to vary with regard to a second physical degree of freedom. At a quantum level, this view of change as relative variation leads to a fundamentally timeless formalism for quantum gravity. Gryb and Thebault ([2016\)](#page-44-10) found a way by which one may avoid this acute "problem of time." Under their view, duration is still regarded as relative but *temporal succession* is taken to be absolute. In their opinion, following that approach (Gryb and Thebault [2014\)](#page-44-11), it is possible to conceive of a genuinely dynamical theory of quantum gravity within which time, in a substantive sense, remains.

Gryb and Thebault ([2016\)](#page-44-10) clarifed their statements by pointing out that "a key feature of Einstein's theory of gravity is its invariance under arbitrary transformations of the space–time manifold. This difeomorphism symmetry implies that only the coordinatefree information contained in the geometry has a physical basis within the theory. Foliation symmetry further implies that any observable quantity within the theory must not be dependent upon the local temporal labelling of space–time. This leads us directly to the question of how we should understand the change in physical quantities? In addition to not having a representation of time, we seem also to have lost a clear methodology for representing change! Our conceptual machinery appears in need of retooling. According to the correlation, or partial observables, view of time in general relativity, the radical moral one should draw from difeomorphism invariance is that change is relational in a strong sense, such that all that it is for a physical degree of freedom to change is for it to vary with respect to a second physical degree of freedom; and there is no sense in which this variation can be described in absolute, non-relative terms. This radical relationalist view of time implies that there is no unique parameterization of the time slices within a space–time, and also that there is no unique temporal ordering of states. Furthermore, it implies a fundamentally diferent view of what a degree of freedom actually is: such parameters no longer have distinct physical signifcance since they can no longer be understood as being free to change and be measured independently of any other degree of freedom". For an additional discussion see also Gryb and Thebault [\(2014](#page-44-11)) and Thebault [\(2012](#page-48-8)).

Anderson ([2012,](#page-42-1) [2017\)](#page-42-2) additionally clarifed that the problem of time in quantum gravity occurs because "time" is taken to have a diferent meaning in each of general relativity and ordinary quantum theory (Jauch [1968;](#page-45-12) Piron [1976\)](#page-47-7). This incompatibility creates serious problems when trying to replace these two branches of physics with a single framework in regimes in which neither quantum theory nor general relativity can be neglected, such as in black holes or in the very early universe. Anderson [\(2012](#page-42-1), [2017](#page-42-2)) states that strategies for resolving the *Problem of Time* have appeared somewhat since the early 1990s only. Anderson [\(2010](#page-42-3)) proposes the following divisions: "I) time before quantization, such as hidden time or matter time. II) Time after quantization, such as emergent semiclassical time. III) Timeless strategies of Type 1: naive Schrödinger interpretation, conditional probabilities interpretation and various forms of records theories and Type 2: 'Rovelli'—in

terms of evolving constants of the motion, complete observables and partial observables. IV) Anderson argued that for histories theories should be a separate class of strategy. Additionally, various combinations of these strategies have begun to appear in the literature, e.g. the loop quantum gravity, supergravity and string/M-theory from the problem of time perspective."

In their paper "Time: a constructal viewpoint and its consequences," Lucia and Grisolia ([2019\)](#page-46-11) considered the complicated problem of the irreversibility of the electromagnetic interaction with atoms and molecules. In the environment, there exists a continuous interaction between electromagnetic radiation and matter. So, atoms continuously interact with photons of the environmental electromagnetic felds. In their opinion, this electromagnetic interaction is the consequence of the continuous and universal thermal nonequilibrium, which introduces an element of randomness into atomic and molecular motion. Consequently, the decrease of path probability required for microscopic reversibility of evolution occurs. Recently, an energy footprint has been theoretically proven in the atomic electron–photon interaction, related to the well-known spectroscopic phase shift efect, and results on the irreversibility of the electromagnetic interaction with atoms and molecules obtained experimentally in the late 1960s. The authors tried to show how this quantum footprint is connected with the "*origin of time*." The result obtained also represents a response to the question introduced by Einstein on the analysis of the interaction between radiation and molecules when thermal radiation is considered; he highlighted that, in general, one restricts oneself to a discussion of the energy exchange, without taking the momentum exchange into account. The result of Lucia and Grisolia was obtained by just introducing the momentum into the quantum analysis. In addition, the authors underpinned their speculations with the hypothesis that time is the consequence of constructal considerations (Bejan and Lorente [2011\)](#page-42-10) of the *H* which is the Hamiltonian of the photon–atomic electron interaction, i.e., from a macroscopic point of view.

It is evident that a well-developed theory of time (whatever it may be) is still in thick fog. This opinion was expressed by Le Bihan ([2015\)](#page-45-16): Is time fowing? A-theorists say yes, B-theorists say no. But both take time to be real. It means that B-theorists accept that time might be real, even if lacking a property usually ascribed to it ...I want to ask what are the diferent properties usually ascribed to time in order to draw the list of diferent possible kinds of realism and anti-realism about time. Le Bihan ([2015\)](#page-45-16) attempted to argue that there are three main kinds of antirealism. He claimed that, if time is defned as the universe's fourth dimension, there is no way time could be unreal.

Clear analyses of the present status of the problem of time have been carried out by Smolin ([2013\)](#page-47-6), Unger and Smolin ([2014\)](#page-48-2), and Smolin ([2009,](#page-47-11) [2015](#page-47-12)), who considered the subject in a broad perspective.

4 The Arrows of Time and Asymmetry of Time

The basic laws of physics are time symmetric (Kuzemsky [2017;](#page-45-10) Belinfante [1975](#page-42-11); Sachs [1987\)](#page-47-13). In technical terms, this can be formulated as the statement that a physical theory, which describes a specifc law, is time-reversal invariant. This means that the full set of solutions of the corresponding diferential equations satisfes the diferential equations under time reversal of the solution, i.e., on replacement of (t) by $(-t)$.

Indeed, symmetry plays a very big role in the natural sciences (Sachs [1987;](#page-47-13) Kuzemsky [2010;](#page-45-17) Lewis [1930;](#page-46-12) Schwichtenberg [2018;](#page-47-14) Geru [2018](#page-44-12)). At the same time, there are many asymmetrical things and phenomena around us. In the course of the derivation of the second law of thermodynamics, Penrose ([2016\)](#page-47-15) poses the following question: "What we seem to have deduced is a time-asymmetrical law when the underlying physics may be taken to be symmetrical in time. How has this come about?"

Indeed, asymmetry arises in the real world and in physics in a number of diferent situations. Asymmetry is the absence of, or a violation of, symmetry (the property of an object being invariant to a transformation, such as refection). Symmetry is an important property of both physical and abstract systems in mathematics. The absence of or violation of symmetry can lead to various consequences for concrete systems. Remarkably, a most striking asymmetry is encountered in the realm of biology (Wagniere [2008;](#page-48-9) Meierhenrich [2008;](#page-46-13) Kuzemsky [2010\)](#page-45-17). Living organisms contain proteins built almost exclusively from L -amino acids, and nucleic acids derived from D-sugars only. Yet a mirror-image biochemistry, based on D-amino acids and L-sugars is, from a purely chemical standpoint, entirely conceivable. It is still not fully clear where this extraordinary natural selectivity comes from. The most intriguing question is whether it is directly, or indirectly, connected to the universal violation of parity. The answer may imply that the universe displays handedness, or chirality, and that it is fundamentally asymmetric. We present here the problem of handedness to emphasize that there is no evident mechanism of selection of the preferred chirality.

Penrose [\(1968](#page-46-14), [1979](#page-46-15), [1989,](#page-46-16) [1994](#page-46-17), [2016](#page-47-15)) gives the following formulation: "All the successful equations of physics are symmetrical in time. They can be used equally well in one direction in time as in the other...". Davies addresses the questions on the nature of time in numerous publications (Davies [1977](#page-43-13), [2005\)](#page-43-14). "It is a basic property of nature that our world possesses a structural distinction between past and future; in physics this is known as time asymmetry, and it is a controversial and obscure area of study. Can the asymmetry in time of the everyday world be accounted for on the basis of conventional physics? If so, what is the nature of asymmetry? What is its origin? Are there other, less conspicuous asymmetric processes?" The thermodynamic arrow of time and the role of cosmic infation were considered by Albrecht ([2004\)](#page-42-12), who discussed the connection between these two topics from a variety of angles. A useful account of cosmology and infation theory was presented by Mukhanov [\(2005](#page-46-18)).

Hence, asymmetry of time is a very broad notion which deserves thorough research and clarifcation. Indeed, Penrose in numerous publications (Penrose [1968](#page-46-14), [1979](#page-46-15), [1989,](#page-46-16) [1994](#page-46-17), [2016\)](#page-47-15) has advocated the statement that one of the long-standing mysteries of physics is the origin of the *arrow of time*. Penrose [\(1968](#page-46-14), [1979,](#page-46-15) [1989](#page-46-16), [1994](#page-46-17), [2016\)](#page-47-15) pointed out that one should distinguish a number of diferent "*arrows of time*" that express the time asymmetry of the universe.

The arrow of time is intimately related to the second law of thermodynamics (Penrose [1994\)](#page-46-17). The second law of thermodynamics says, in efect, that the extent to which any natural process can occur is limited by the dispersion of thermal energy (the increase in entropy). This process of weakening of energy accompanies it, and once the change has occurred, it can never be reversed without spreading even more energy around. In other words, the entropy of the world only increases and never decreases.

In this connection, Penrose [\(1994](#page-46-17)) pointed out that "the second law of thermodynamics has two distinct aspects to its foundations. The frst concerns the question of why entropy goes up in the future, and the second, of why it goes down in the past. Statistical physicists tend to be more concerned with the frst question and with careful considerations of defnition and mathematical detail. The second question is of quite a diferent nature; it leads into areas of cosmology and quantum gravity, where the mathematical and physical issues are ill understood". Penrose's ([2016\)](#page-47-15) book *The Road to Reality* provides a comprehensive account of our knowledge about the physical universe and the possibility of describing it by appropriate mathematical theory. In that book he also summarizes his thoughts about the concept of entropy and the foundations of the second law of thermodynamics, which deserve the most meticulous attention and discussion.

It was long-standing opinion that there is no asymmetry between the two directions of time in the general laws of nature. However, many phenomena in the real world display an evident asymmetry of time (Arntzenius [1995](#page-42-13)). The theoretical description of such phenomena will entail that time has a direction, the *arrow of time*, and that such asymmetry may be an internal feature of the real world. Asymmetry of time is a wider notion than is the arrow of time.

It is difficult to give a single-valued and fully clearly definable sense to the term "arrow" of time" (Gold [1962](#page-44-13); Gal-Or [1972;](#page-44-14) Coveney and Highfeld [1991](#page-43-15); Mackey [1992](#page-46-19); Price [1996,](#page-47-3) [2010;](#page-47-16) Mersini-Houghton and Vaas [2012;](#page-46-20) Albeverio and Blanchard [2014;](#page-42-14) Savitt [1996;](#page-47-17) Maudlin [2002;](#page-46-21) Ridderbos [2003](#page-47-18); Wallace [2013\)](#page-48-10). The arrow of time could be denoted as a phenomenological fact of nature, since real-world events always proceed in the direction of increasing entropy, even though the laws of physics do not require this.

The very term "time's arrow" was coined by Eddington in 1935 (Price [2010;](#page-47-16) Eddington [1935\)](#page-44-15) to answer the question of why time fows as it does, despite the lack of a temporal direction in our scientifc laws. He wrote: "The great thing about time is that it goes on ...The events are there in their proper spatial and temporal relation ..."

Eddington seems to have believed that only the second law of thermodynamics clearly indicates a direction of time (Eddington [1935;](#page-44-15) Callender [2001\)](#page-43-16) : "The law that entropy always increases,—the second law of thermodynamics—holds, I think, the supreme position among the laws of Nature". This kind of arrow of time is called (Callender [2011\)](#page-43-5) the *thermodynamic arrow of time*. Investigations on the problem of what is the source of time asymmetry in thermodynamics and in various sciences are continued in numerous papers (Kuzemsky [2018](#page-45-4); Callender [2011;](#page-43-5) Gold [1962;](#page-44-13) Gal-Or [1972](#page-44-14); Coveney and Highfeld [1991;](#page-43-15) Mackey [1992;](#page-46-19) Price [1996,](#page-47-3) [2010](#page-47-16); Mersini-Houghton and Vaas [2012;](#page-46-20) Albeverio and Blan-chard [2014](#page-42-14); Savitt [1996;](#page-47-17) Maudlin [2002](#page-46-21); Ridderbos [2003;](#page-47-18) Wallace [2013;](#page-48-10) Brown and Uffink [2001\)](#page-42-15).

There are diverse *arrows of time*: the thermodynamic arrow, cosmological arrow, electromagnetic arrow, gravitational arrow, information arrow, biological arrow, psychological arrow, etc.

It is widely believed that entropy is the only physical quantity in the natural sciences that seems to imply a particular direction of progress, called an arrow of time. As time progresses, the second law of thermodynamics states that the entropy of an isolated system never decreases. This forces us to connect the notion of entropy with time fow. Thus, the notion of the thermodynamic arrow of time (Coveney and Highfeld [1991](#page-43-15); Mackey [1992;](#page-46-19) Price [1996;](#page-47-3) Wallace [2013;](#page-48-10) Callender [2001;](#page-43-16) North [2002](#page-46-22)) is based on classical thermodynamics; it states that there is an extensive state function *S*, called entropy, which leads to the second law in all natural processes:

$$
\Delta S \ge \int \frac{\delta Q}{T}.
$$

Here *Q* is the heat and *T* is the temperature.

The electromagnetic arrow of time appears in classical electrodynamics (Gal-Or [1972](#page-44-14)). It is known that an accelerated electric charge loses energy to its surroundings, whereas incoming radiation is never seen. The classical equations of electrodynamics are symmetric under time reversal. There are two types of solution, for time (*t*) and for (−*t*). These solutions are the retarded solution and advanced solution (Kuzemsky [2017\)](#page-45-10), both of which are valid in principle. The retarded solution only is chosen, to ft experimental observations. This is motivated by the desire to be in accord with the principle of *causality*.

Another intriguing problem is the cosmological arrow of time (Penrose [1968,](#page-46-14) [1979](#page-46-15), [1989,](#page-46-16) [1994,](#page-46-17) [2016](#page-47-15); Gold [1962;](#page-44-13) Gal-Or [1972](#page-44-14); Davies [1977,](#page-43-13) [2005;](#page-43-14) Hawking [1985;](#page-44-16) Mukhanov [2005](#page-46-18)). The cosmological asymmetry in time should be discussed with special care (Gal-Or [1972](#page-44-14); Ridderbos [2003;](#page-47-18) Wallace [2013\)](#page-48-10).

In some way, the time arrow of cosmology (Gold [1962;](#page-44-13) Gal-Or [1972;](#page-44-14) Ridderbos [2003;](#page-47-18) Jejjala et al. [2012\)](#page-45-18) imposes the thermodynamic arrow. It has been suggested that thermodynamic irreversibility may be due to cosmological expansion. The *cosmological arrow of time* is understood in connection with the expanding universe (Gold [1962;](#page-44-13) Gal-Or [1972;](#page-44-14) Coveney and Highfeld [1991](#page-43-15); Mackey [1992;](#page-46-19) Price [1996](#page-47-3), [2010](#page-47-16); Mersini-Houghton and Vaas [2012](#page-46-20); Albeverio and Blanchard [2014](#page-42-14); Savitt [1996](#page-47-17); Maudlin [2002;](#page-46-21) Ridderbos [2003;](#page-47-18) Jejjala et al. [2012](#page-45-18); Wallace [2013\)](#page-48-10).

The gravitational arrow of time is a complicated notion and has various aspects (Liu [1993;](#page-46-0) Gal-Or [1972;](#page-44-14) Ridderbos [2003;](#page-47-18) Jejjala et al. [2012](#page-45-18)). It is generally believed that there are still two very basic fundamental concepts that have challenged the real explanation, namely time and gravity. Barbour et al. ([2014\)](#page-42-16) proposed a new direction for understanding the concept of time in their paper entitled "Identifcation of a gravitational arrow of time." They pointed out that: "Many diferent phenomena in the Universe are time asymmetric and defne an arrow of time that points in the same direction everywhere at all times. Attempts to explain how this arrow could arise from time-symmetric laws often invoke a 'past hypothesis': the initial condition with which the Universe came into existence must have been very special." In other words, time flows definitively in one direction and the arrow of time certainly points into the future. Barbour et al. ([2014\)](#page-42-16) conjectured a completely diferent sort of explanation than was used before. They supposed that "the origin of time's arrow is not necessarily to be sought in initial conditions but rather in the structure of the law which governs the Universe." Their suggestion is that initial conditions do not necessarily need to be imposed on a time-symmetric law when attempting to describe solutions to behaviors that defne an *arrow of time*. It is widely believed that special initial conditions must be imposed on any time-symmetric law if its solutions are to exhibit behavior of any kind that defnes an arrow of time. Barbour, Koslowski, and Mercati showed that this is not so. The simplest nontrivial time-symmetric law that can be used to model a dynamically closed universe is the Newtonian *N*-body problem with vanishing total energy and angular momentum. Because of the special properties of this system (likely to be shared by any law of the universe), its typical solutions all divide at a uniquely defned point into two halves. In each, a well-defned measure of shape complexity fuctuates but grows *irreversibly* between rising bounds from that point. Structures that store dynamical information are created as the complexity grows and act as *records*. Barbour, Koslowski, and Mercati argued that each solution can be viewed as having a single past and two distinct futures emerging from it. Any internal observer must be in one half of the solution and will only be aware of the records of one branch and deduce a unique past and future direction from inspection of the available records. In essence, the gravitational arrow of time is the direction of time in which gravitational radiation propagates to the future rather than the past.

There is also the biological arrow of time, mainly related to the phenomenon of evolution (Blum [2016](#page-42-6)). The informational arrow is connected with the probability of the intrinsic time arrow from information losses, as it was explained by Diosi ([2004\)](#page-43-17).

The psychological arrow of time has many facets also. One must always distinguish between physical time and psychological time. What we call time is partially connected with the phenomenon of consciousness. Time is sought as a universal steady fux, the feeling that there is a lapse of time. The psychological arrow of time is connected with the fact that we remember events in the past but not in the future. There is an opinion that the universal steady fux of time is an idea and not a physical fact; our conscience uses this idea and projects it into the external world around us. Gold [\(1966](#page-44-17)) posed the following question: "...the central problem is: why it is that we live with this frm impression of the passage of time, and how the physical world around us has given us the possibility of forming such an impression." However, a detailed consideration of these questions (Bunge and Ardila [1987](#page-42-17)) lies beyond the scope of the present review.

There are other asymmetries in nature, and their studies are in progress. The principal possibilities of the occurrence of time reversal are discussed from various points of views in literature. Uncovering the origin of the "arrow of time" remains a fundamental scientifc challenge. Recently, Lesovik et al. ([2019\)](#page-46-23) confrmed that the fundamental question of the origin of the irreversibility of time, which emerged from classical statistical physics, remains a subject deserving meticulous attention. Within the framework of statistical physics, this problem is inextricably associated with the second law of thermodynamics, which declares that entropy growth proceeds from the system's entanglement with the environment. This poses a question of whether it is possible to develop protocols for circumventing the irreversibility of time and if so to practically implement these protocols. The authors showed that, while in nature the complex conjugation needed for time reversal may appear exponentially improbable, one can design a quantum algorithm that includes complex conjugation and thus reverses a given quantum state. Using this algorithm on an IBM quantum computer, the authors were able to experimentally demonstrate a backward-time dynamics for an electron scattered on a two-level impurity. The authors' fndings suggest several directions for investigating time reversal and backward time fow in real quantum systems.

It is useful to summarize the various arrows of time in the form of Table [1.](#page-13-0) Numerous attempts have been made to elaborate a new sophisticated view on time. A remarkable attempt was made by t'Hooft (2018) (2018) . He stated that: "It is brought forward that viable theories of the physical world which have no variable at all that can play the role of time,

The time asymmetry	Description
The thermodynamic arrow	The direction of time in which entropy increases
The electrodynamic arrow	The preference of retarded solutions of the field equations
The psychological arrow	We remember events in the past but not in the future
The biological arrow	Irreversibility and direction in evolution (Blum 2016)
The informational arrow	Probability of an intrinsic time arrow from information loss (Diosi 2004)
The time asymmetry of particle physics	Decay of K^0 meson (Sachs 1987)
The cosmological arrow	The direction in time in which the universe is expanding
Gravitational arrow of time	Barbour et al. (2014)

Table 1 Diferent arrows of time

do not exist; some notion of time is one of the very frst ingredients a candidate theory should possess. Almost by defnition, time has an arrow. In contrast, time reversibility, or even the possibility to run the equations of motion backwards in time, is not at all a primary requirement. This means that the direction of the arrow of time may well be uniquely defned in the theory, even locally. It is explained that a rigorous defnition of time, as well as a formulation of the causality and locality concepts, can only be given when one has a model for the physical phenomena described. The only viable causality condition is one that is symmetric under time reversal. We explain these statements in terms of the author's favored deterministic cellular automaton interpretation of quantum mechanics, also to be referred to as "vector space analysis," and expand on these ideas. It is also summarized how our more rigorous causality condition afects Bell's theorems. What distinguishes quantum systems from classical ones is our fundamental inability to control the microscopic details of the initial state when phenomena are studied in the light of some theoretical model."

In his paper, Lopez [\(2018](#page-46-24)) shed some doubts on a widely held claim: standard quantum mechanics is time-reversal invariant and, thereby, blind to the direction of time. Building bridges between physics and philosophy, Lopez argued that such a claim features some puzzling assumptions that are frequently overlooked in literature. In particular, Lopez frst argued that the claim involves some methodological and metaphysical commitments that should be evaluated more prudently from the points of view of philosophy and physics. Second, he pointed out that the common inference that goes from symmetry to metaphysical conclusions needs some correction and refnement to be acceptable in discussions about time symmetry and the debate around the arrow of time.

In a complementary paper, Garcia-Pintos et al. [\(2017](#page-44-18)) addressed the problem of understanding, from frst principles, the conditions under which a quantum system equilibrates rapidly with respect to a concrete observable. On the one hand, previously known general upper bounds on the time scales of equilibration were unrealistically long, with times scaling linearly with the dimension of the Hilbert space. These bounds proved to be tight since particular constructions of observables scaling in this way were found. On the other hand, the computed equilibration time scales for certain classes of typical measurements, or under the evolution of typical Hamiltonians, are unrealistically short. However, most physically relevant situations fall outside these two classes. In their paper, the authors provided a new upper bound on the equilibration time scales which, under some physically reasonable conditions, give much more realistic results than previously known. In particular, the authors applied this result to the paradigmatic case of a system interacting with a thermal bath, where they obtained an upper bound for the equilibration time scale independent of the size of the bath. In this way, they found general conditions that singled out observables with realistic equilibration times within a physically relevant setup.

5 Entropy and the Second Law

It was generally recognized that energy and entropy are the most important concepts in physics and the natural sciences (Carnap [1977;](#page-43-18) Jaynes [1965;](#page-45-19) Grandy [2008](#page-44-19); Muller [2007;](#page-46-4) Starzak [2010](#page-47-19); Thess [2011](#page-48-12); Tame [2019](#page-47-20)). Thermodynamics is usually understood as the branch of science which deals with the study of thermal processes and energy transformations (Planck [2010](#page-47-21); Guggenheim [1933,](#page-44-20) [1985](#page-44-21); Fermi [1956](#page-44-22); Schrödinger [1946](#page-47-22); Pauli [1973;](#page-46-25) Muller [2007;](#page-46-4) Muller and Muller [2009](#page-46-5); Beattie and Oppenheim [1979](#page-42-18); Honig [1991;](#page-45-20) Kondepudi [2008\)](#page-45-21). The thermodynamic properties of macroscopic systems can be derived through appropriate thermodynamic functions of state (or thermodynamic variables). The concept of *entropy* was introduced into thermodynamics by Clausius in 1876 (Muller [2007;](#page-46-4) Tame [2019](#page-47-20)). During the decades since, great progress has been made in our understanding of the concept of entropy in various branches of science, including chemistry, biology, information theory, cosmology, climate theory, economics, etc. In the quantum domain, entropy can be considered as a measure of the intrinsic dispersion, i.e., degree of mixing, impurity, uncertainty, lack of information, or amount of chaos of a quantum state.

Entropy is a basic physical quantity which has led to various and conficting interpretations; entropy is a multifaceted notion (Wehrl [1978](#page-48-13); Lef [2007](#page-46-26)). The number of publications on the subject is huge (Grad [1961](#page-44-0); Carnap [1977](#page-43-18); Starzak [2010;](#page-47-19) Thess [2011](#page-48-12); Tame [2019;](#page-47-20) Beattie and Oppenheim [1979](#page-42-18); Honig [1991;](#page-45-20) Muller and Muller [2009;](#page-46-5) Jaynes [1965](#page-45-19)). Grad ([1961\)](#page-44-0) formulated an explanation of the workability of the entropy concept: "...there is a large choice of macroscopic quantities (functions of state variables) called entropy, on the other hand, a variety of microscopic quantities, similarly named, associated with the logarithm of a probability or the mean value of the logarithm of a density. Each one of these concepts is suited for a specifc purpose ...The fertility of this concept is in large part due to its fexibility and multiple meanings. On the other hand, much of the confusion in the subject is traceable to the ostensibly unifying belief (possibly theological in origin!) that there is only one entropy."

The frst law, the principle of the conservation of energy, asserts that energy can only be transformed but not created. The second law of thermodynamics is mainly concerned with the transformation of work into heat.

Clausius formulated the second law (Muller [2007](#page-46-4); Muller and Muller [2009](#page-46-5)) in the following words: "Heat cannot, of itself, pass from a colder to a hotter body." Hence, the second law of thermodynamics states in fact that the extent to which any natural process can occur is limited by the dispersal of thermal energy. Due to this energy dispersion, an accompanying increase in entropy occurs. These changes are impossible to reverse without spreading even more energy around. This is why the second law of thermodynamics is sometimes not called a law of conservation but a law of waste.

As discussed in literature (Kuzemsky [2018](#page-45-4); Muller [2007](#page-46-4); Muller and Muller [2009;](#page-46-5) Planck [2010](#page-47-21); Guggenheim [1933](#page-44-20), [1985](#page-44-21); Fermi [1956;](#page-44-22) Schrödinger [1946](#page-47-22); Pauli [1973;](#page-46-25) Honig [1991;](#page-45-20) Kondepudi [2008\)](#page-45-21), the time directionality of physical processes is deeply related to the second law of thermodynamics. The physical meaning of the second law of thermodynamics states that the entropy of an isolated system increases with time (or remains constant, for a reversible transformation).

In thermodynamics, there are two basic types of thermodynamic variables: *intensive* and *extensive*. The entropy of a system of bodies is equal to the sum of the entropies of the individual bodies and hence is an extensive property of the thermodynamic system. Note, that the notion of extensivity should be used with care (Riek and Sobol [2016](#page-47-23)) for small systems, even in the thermodynamic limit (Kuzemsky [2014\)](#page-45-22).

Let us consider a system in contact with a thermal bath (heat reservoir) during a reversible process. If heat Q is absorbed by the reservoir at temperature T , the change in entropy of the reservoir is $\Delta S = Q/T$. In general, reversible processes are accompanied by heat exchanges that occur at diferent temperatures. It is convenient to represent a reversible process in terms of infnitesimal portions of the cycle. The total entropy change of the system plus surroundings will be

$$
dS_{\text{tot}} = dS_{\text{sys}} + dS_{\text{res}} = 0.
$$

Hence, for a reversible process, no change occurs in the total entropy, i.e., the entropy of the system plus the entropy of the surroundings.

Planck ([2010\)](#page-47-21) formulated the following inequality connecting diferentials of energy *U*, temperature *T*, and entropy *S* with the work *W*:

$$
dU - TdS \le W. \tag{16}
$$

Speaking generally, the entropy of a system is a measure of its disorder and/or of the unavailability of energy to do work. In this context, Planck referred to time rates in actual processes in a system. In this approach, these should include the rate of increase of energy through nonmechanical efects such as heat conduction and radiation.

There are tens of formulations of the second law of thermodynamics (Muller [2007](#page-46-4); Muller and Muller [2009](#page-46-5); Planck [2010](#page-47-21); Guggenheim [1933,](#page-44-20) [1985](#page-44-21); Fermi [1956;](#page-44-22) Schrödinger [1946](#page-47-22); Pauli [1973](#page-46-25); Beattie and Oppenheim [1979;](#page-42-18) Honig [1991](#page-45-20); Kondepudi [2008](#page-45-21)); For example, Guggenheim ([1933,](#page-44-20) [1985](#page-44-21)) insisted that the best formulation was given by Planck [\(2010\)](#page-47-21). Fermi ([1956\)](#page-44-22) discussed the second law in an operational form. A body, no matter what its temperature may be, can always be heated by friction, receiving an amount of energy in the form of heat exactly equal to the work done. Contrary to the frst law, which places no limitations on the possibility of transforming energy from one form into another, there are very defnite limitations on the possibility of transforming heat into work. It is impossible for any device that operates in a cycle fashion to receive heat from a single thermal reservoir and produce some amount of work. In other words, no heat engine can have a thermal efficiency of 100%, except if the temperature of the lower reservoir is 0 K.

Fermi [\(1956\)](#page-44-22) used the formulations of Kelvin and Clausius (which are equivalent): A transformation whose only fnal result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible.

In this connection, it is useful to remember that, in order to realize an entropy increase in a system, heat (or a fux of heat) should be provided in some way for the system itself. However, there are examples of isothermal processes in which there are heat fuxes but the temperature does not change (Denbigh [1996](#page-43-3), [1989a](#page-43-1), [b;](#page-43-2) Denbigh and Denbigh [1985](#page-43-8)).

The general expression for the entropy diference between two states is

$$
\Delta S = \int_{A}^{B} \frac{dQ}{T}.
$$
\n(17)

This expression states that the diference in entropy between two equilibrium states *A* and *B* of a physical system can be determined by measuring the heat flow ΔQ over an arbitrary reversible path connecting the states. To establish a connection between the empirical (macroscopic) and statistical (microscopic) description of complex many-particle systems, it was necessary to make an important step and write down the connection between thermodynamic entropy *S* and statistical entropy. According to Boltzmann,

$$
S = k_{\rm B} \ln \Omega,\tag{18}
$$

where k_B is the Boltzmann constant and Ω is the number of distinct microscopic states available to the system given the macroscopic constraints (e.g., fxed total energy *U*). The Boltzmann constant may be considered as a scaling factor which connects the macroscopic (thermodynamic temperature) and microscopic physics of the thermal motion of atoms and molecules.

Let us briefy consider the dimension of entropy. Certainly, it depends on the units selected for the purpose (Guggenheim [1933](#page-44-20), [1985](#page-44-21); Buckingham [1914;](#page-42-19) Bridgman [1963;](#page-42-20) Leff [1999;](#page-46-27) Borde [2005](#page-42-21); Gibbings [2011;](#page-44-23) Sparavigna [2015](#page-47-24); Bich [2019](#page-42-22)). The Boltzmann constant is equal to the ratio of the gas constant *R* to the Avogadro number N_A

$$
k_{\rm B} = \frac{R}{N_{\rm A}} = 1.380 \times 10^{-23} \frac{\rm J}{\rm K} = 8.617 \times 10^{-5} \frac{\rm eV}{\rm K}.
$$
 (19)

Hence, the Boltzmann constant is a *derived* physical constant, since its value is determined by other physical constants.

It is clear that thermodynamic entropy in the dynamical units of measurement has dimensionality (Guggenheim [1933](#page-44-20), [1985](#page-44-21); Buckingham [1914](#page-42-19); Bridgman [1963;](#page-42-20) Leff [1999](#page-46-27); Gibbings [2011;](#page-44-23) Sparavigna [2015](#page-47-24)) which coincides with the dimensionality of energy divided by temperature: $[S] = [E/\theta] = L^2 T^{-2} M \theta^{-1}$. The dimension of entropy started to be discussed long ago (Guggenheim [1933](#page-44-20), [1985;](#page-44-21) Buckingham [1914;](#page-42-19) Bridg-man [1963;](#page-42-20) Leff [1999](#page-46-27); Gibbings [2011;](#page-44-23) Sparavigna [2015;](#page-47-24) Bich [2019\)](#page-42-22). Thermodynamic entropy has the dimensions of energy per temperature; in SI units, it is joules per kelvin (J/K), i.e. coinciding with the dimension of the Boltzmann constant.

When using natural units (Guggenheim [1933](#page-44-20), [1985](#page-44-21); Buckingham [1914;](#page-42-19) Bridgman [1963](#page-42-20); Leff [1999;](#page-46-27) Borde [2005](#page-42-21); Gibbings [2011](#page-44-23); Sparavigna [2015](#page-47-24); Bich [2019](#page-42-22)), one sets each of the constants \hbar , k_B , and c equal to unity. It is still possible to check the dimensions of a given equation, but one then has to understand that quantities such as those associated with velocity are dimensionless and that things such as length and time have the same dimensions. One can write every quantity in terms of powers of a single unit, e.g., GeV (= 10^9 eV). The conversion factors to SI units are: Energy: 1 GeV = 1.6 $\times 10^{-10}$ J; Temperature : 1 GeV = 1.16 $\times 10^{13}$ K.

It is unclear why entropy does not have a derived unit name. One reason for this may be the fact that entropy's dimensions are linked to the defnition of the Kelvin temperature scale (Lef [1999\)](#page-46-27). Obviously, entropy can be defned to be dimensionless when temperature θ is defined as an energy.

Landau and Lifshitz ([1980](#page-45-23)) selected a defnition of entropy which leads to the dimensionless expression. They considered the derivation of the "quantum microcanonical distribution" and supposed (Landau and Lifshitz [1980](#page-45-23)) that the energy spectra of macroscopic bodies are "almost continuous." They also used the concept of the number of quantum states of a closed system which "belong" to a particular infnitesimal range of values of its energy. Landau and Lifshitz (1980) (1980) (1980) denoted this number by $d\Gamma$; it plays a part analogous to that of the phase volume element $\Delta p \Delta q$ in the classical case. When deriving the expression for entropy, they denoted as $\Gamma(E)$ the number of quantum states with energy less than or equal to E. Then, the required number of states with energy between E and $E + dE$ will be

$$
\frac{d\Gamma(E)}{dE}\Delta E.\tag{20}
$$

The energy probability distribution is

$$
W(E) = \frac{d\Gamma(E)}{dE} w(E),\tag{21}
$$

where $w(E)$ denotes the distribution function for subsystems (Landau and Lifshitz [1980](#page-45-23)). The function $W(E)$ has a very sharp maximum at $E = \overline{E}$, being appreciably different from zero only in the immediate neighborhood of this point.

They considered the quantity $\Delta\Gamma$, which is the statistical weight of the macroscopic states of the subsystem

$$
\Delta \Gamma = \frac{d\Gamma(\bar{E})}{dE} \Delta E. \tag{22}
$$

Here, ΔE is the "width" of the curve $W = W(E)$. The interval ΔE is equal in order of magnitude to the mean fluctuation of energy of the subsystem. The quantity $\Delta\Gamma$ thus defined may be said to represent the *degree of broadening* of the macroscopic state of the subsystem with respect to its microscopic states. The logarithm of the statistical weight

$$
S = \log \Delta \Gamma \tag{23}
$$

can be called the *entropy* of the subsystem (Landau and Lifshitz [1980](#page-45-23)). Hence, entropy is a logarithmic measure of the number of states with a signifcant probability of being occupied (Kuzemsky [2016;](#page-45-9) Landau and Lifshitz [1980\)](#page-45-23). Like the statistical weight itself, the entropy is dimensionless. Statistical entropy is the logarithm of the probability p_k that a microstate *k* will be occupied

$$
S = -k_{\rm B} \sum_{k} p_k \log p_k. \tag{24}
$$

Hence, this expression for entropy may be interpreted as a *measure* of the spread of the probability distribution. Indeed, when a distribution is narrow, we have near certainty (entropy is low). For a widely spread distribution, the uncertainty is greater (entropy is high). In this context, it is of interest to recall the original approach to the foundation of equilibrium thermodynamics proposed by Jauch ([1972\)](#page-45-24). This was stimulated by certain ideas of Ehrenfest. Jauch's method was based on the conservation of energy for reversible adiabatic processes. The main result is the proof of the existence of entropy as a consequence of the conservation of energy for conservative thermal systems. Jauch noted that so-called classical thermodynamics deals exclusively with equilibrium states and "quasistatic" processes. Indeed, for any given system, there is a state, which is called the *equilibrium state*, for which the entropy has the largest possible value (Kuzemsky [2016,](#page-45-9) [2018;](#page-45-4) Jaynes [2003](#page-45-25)).

It is worth noting that it is possible to associate an entropic value with any probability distribution. In a general sense, entropy can also be understood as a measure of the disorder or randomness of a closed system; the lower the entropy of the system, the higher its state of order. This is why the concept of entropy plays a central role in information theory (Kuzemsky [2018,](#page-45-4) [2016,](#page-45-9) [2017](#page-45-10); Wright [1970](#page-48-14); Jaynes [2003;](#page-45-25) Kozlov and Smolyanov [2006;](#page-45-26) Diosi [2004](#page-43-17); Short and Wehner [2010](#page-47-25); Zurek [2018\)](#page-48-15). Information plays an important role in our understanding of the physical world (Kuzemsky [2017](#page-45-10), [2016\)](#page-45-9). Indeed, the most fundamental concept of information theory is entropy. The entropy of a random variable *Q* is defned by

$$
H(Q) = \sum_{q} p_q \log \frac{1}{p_q}.\tag{25}
$$

The entropy is *nonnegative*, and is zero when the random variable can be predicted with certainty.

Short and Wehner ([2010\)](#page-47-25) proposed an *entropic measure of information* for any physical theory that admits systems, states, and measurements. In the quantum and classical worlds, this kind of measure reduces to the von Neumann and Shannon entropy, respectively. It can even be used in a quantum or classical setting, where we are only allowed to perform a limited set of operations. In a world that admits superstrong correlations in the form of nonlocal boxes, their measure may be useful for analyzing protocols such as superstrong random-access encodings and the violation of "*information causality*." It was shown that, in such a world, no entropic measure can exhibit all the properties we commonly accept in a quantum setting; For example, there exists no "reasonable" measure of conditional entropy that is subadditive. Short and Wehner [\(2010](#page-47-25)) also proved a coding theorem for some theories that is analogous to the quantum and classical settings, providing us with an appealing operational interpretation.

It is worth mentioning that entropy is a concept in thermodynamics and statistical physics and in information theory (Kuzemsky [2017](#page-45-10), [2016;](#page-45-9) Jaynes [2003](#page-45-25); Kozlov and Smolyanov [2006\)](#page-45-26). The concept of information was formulated in the context of the mathematical theory of communication. However, its connection to statistical mechanics became apparent very soon because of the fact that statistical mechanics is a theory in which predictions are made on the basis of incomplete information about the system under consideration (Jaynes [2003\)](#page-45-25). The close connection between both theories is evident, as emphasized by Jaynes and others (Jaynes [2003;](#page-45-25) Zubarev [1974;](#page-48-5) Kuzemsky [2017;](#page-45-10) Kozlov and Smolyanov [2006](#page-45-26)). These two concepts, viz. information entropy and thermodynamic entropy, do actually have much in common (Jaynes [2003;](#page-45-25) Kozlov and Smolyanov [2006](#page-45-26)). Shannon's defnition of entropy is closely related to thermodynamic entropy as defned by physicists and many chemists. In information theory, entropy is conceptually the actual amount of (information-theoretic) information in a piece of data. The central physical concept in statistical thermodynamics is energy. However, entropy is not to be considered as merely an auxiliary function but more appropriately as a chief factor in all of the major natural processes. Extremum principles play an important role in various branches of physics, especially mechanics. The maximum-entropy principle plays a similar role in thermal physics (Kuzemsky [2017\)](#page-45-10). The maximum-entropy principle can be formulated in a concise form as follows: When one has only partial information about the possible outcomes of a random process, one should choose the probabilities so as to maximize the uncertainty about the missing information (Jaynes [2003](#page-45-25); Zubarev [1974](#page-48-5); Kuzemsky [2017\)](#page-45-10). In other words, it is necessary to use all the available information on the relevant parameter. Moreover, any information that is irrelevant should be avoided. Therefore, one should be as uncommitted as possible about missing information.

Studies on the extremum of thermodynamic functions (e.g., the maximum-entropy algorithm) can be traced back way to Boltzmann, Gibbs, and Shannon. In general form, the maximum-entropy approach to thermodynamics was initiated by Jaynes ([1965,](#page-45-19) [2003](#page-45-25), [1957a,](#page-45-27) [b](#page-45-28)), based on probability theory and Bayesian inductive inference. Jaynes termed it "the principle of maximum entropy." The extremization of an appropriate entropic functional may yield probability distribution functions that maximize the respective entropic structure. This procedure is known in statistical mechanics and information theory as Jaynes' formalism (Jaynes [2003](#page-45-25)) and has been up to now a standard methodology for deriving the aforementioned distributions. The Gibbs theorem states that the canonical equilibrium distribution, of all the normalized distributions having the same mean energy, is the one with maximum entropy. The notion of entropy is expressed in terms of the probability

of various states. Entropy treats the distribution of energy. For any given system, the equilibrium state is the state with the largest possible entropy, due to the fact that all the available states may be equally probable, as for an isolated system in equilibrium. Thus, a principle may be guessed that the most probable condition is that in which the energy in a system is as uniformly distributed as permitted by physical constraints (Kuzemsky [2017;](#page-45-10) Jaynes [2003](#page-45-25), [1957a](#page-45-27), [b\)](#page-45-28).

It was noticed in recent decades that statistical distributions observed in nature show great diversity. However, the principle of maximum entropy works well for a wide diversity of systems, including biological systems. An interesting problem was considered by Buskermolen et al. [\(2019](#page-43-19)). They studied contact guidance, i.e., the widely known phenomenon of cell alignment induced by anisotropic environmental features, which is an essential step in the organization of adherent cells. However, the mechanisms by which cells achieve such orientational ordering remain unclear. Buskermolen et al. ([2019\)](#page-43-19) seeded myofibroblasts on substrates micropatterned with stripes of fbronectin and observed that contact guidance emerged at stripe widths much greater than the cell size. To understand the origins of this surprising observation, they combined morphometric analysis of cells and their subcellular components with a novel statistical framework for modeling nonthermal fuctuations of living cells. This modeling framework was shown to predict not only the trends but also the statistical variability of a wide range of biological observables, including cell (and nucleus) shapes, sizes, and orientations, as well as stress-fber arrangements within the cells with remarkable fdelity using a single set of cell parameters. By comparing observations and theory, the authors identifed two regimes of contact guidance: (1) guidance on stripe widths smaller than the cell size ($w \le 160 \mu m$), which is accompanied by biochemical changes within the cells, including increasing stress-fber polarization and cell elongation; and (2) *entropic guidance* on larger stripe widths, which is governed by fuctuations in the cell morphology. Overall, their fndings suggest an entropy-mediated mechanism for contact guidance associated with the tendency of cells to *maximize* their morphological entropy through shape fuctuations. This is a really nice example of the workability of the principle of maximum entropy even in such complex systems.

In nature, the tendency of thermal energy to disperse as widely as possible is what drives all spontaneous processes, which are accompanied by changes of entropy. Contrary to the frst law, which places no restriction on the direction of a process, the second law of thermodynamics may be interpreted in the sense that processes occur in a certain direction. This is the so-called principle of increasing entropy (Sheehan [2006](#page-47-26); Toretti [2007;](#page-48-16) Drory [2008;](#page-44-24) Wallace [2015\)](#page-48-17). However, this statement should be taken with a reservation. Indeed, a process can occur when and only when it satisfes both the frst and second laws of thermodynamics.

Phenomenological thermodynamics was formulated as asymmetrical in time. It was conjectured that entropy in an isolated system can only increase with time. This was derived from the second law. Equilibrium statistical mechanics, which is based on Hamiltonian dynamics, is symmetric in time. Nonequilibrium statistical mechanics (Zubarev [1974;](#page-48-5) Dorfman [1999;](#page-43-20) Zwanzig [2001;](#page-48-18) Gallavotti [2014\)](#page-44-25) states that a normal system which is below its maximum entropy tends to evolve towards higher entropy.

From the mechanical point of view, taking into consideration dissipative forces, e.g., those which depend on velocity, may lead to an explicit time direction on the Hamiltonian. To resolve the problem of entropy increase and the approach to equilibrium, a few diferent schemes have been used (Zubarev [1974](#page-48-5); Dorfman [1999;](#page-43-20) Zwanzig [2001;](#page-48-18) Gallavotti [2014;](#page-44-25) Kuzemsky [2017](#page-45-10)). One of the possible treatments employs a coarse-graining method. The

other methods are based on the derivation of generalized master equations, etc. (Zubarev [1974;](#page-48-5) Kuzemsky [2017;](#page-45-10) Landau and Lifshitz [1980](#page-45-23); Breuer and Petruccione [2002](#page-42-23)).

A sharp debate concerning the nature of the concept of entropy and its physical meaning still persists in literature to the present day.

In particular, Penrose [\(1968](#page-46-14), [1979](#page-46-15), [1989](#page-46-16), [1994](#page-46-17), [2016](#page-47-15)) insists that the very notion of entropy should be carefully reanalyzed. "Entropy is, very roughly speaking, a measure of the 'randomness' in the system" (Penrose [2016](#page-47-15)). He asks: "But what precisely is the entropy of a physical system?...In order to make the notion of entropy precise, we require a concept of what is called coarse graining...But for the ...formula for *S* to represent something physically precise, it would be necessary to have a clear-cut prescription for the coarse graining." Penrose's states "My own position concerning the physical status of entropy is that I do not see it as an 'absolute' notion in present-day physical theory, although it is certainly a very useful one...There is a common view that the entropy increase in the second law is somehow just a necessary consequence of the expansion of the universe...There are many ways to see that this viewpoint cannot be correct." Penrose insists on the necessity of taking into account "gravitational degrees of freedom ...With gravitation, the clumping of material can represent a much higher entropy than ordinary thermal motions. "In his opinion (Penrose [1989](#page-46-16)), "...the entropy concept could not really be a very clear-cut scientific quantity ...entropy is a concept that may be bandied about in a totally cavalier fashion!".

It should be mentioned here that there is undivided attention to the problems of the validity and universality of the second law (Lieb and Yngvason [1999;](#page-46-28) Callender [2001;](#page-43-16) Brown and Uffink [2001](#page-42-15); Sheehan [2007;](#page-47-27) Duncan and Semura [2007](#page-44-26); D'Abramo [2012](#page-43-21); Henderson [2014;](#page-44-27) Dewar et al. [2014](#page-43-9)). The bounds of applicability of the second law have been carefully reexamined from various sides (Dewar et al. [2014](#page-43-9); Czapek and Sheehan [2005](#page-43-22)). It is remarkable that even a "quest for its violations" was announced (D'Abramo [2012](#page-43-21)). In addition, as demonstrated by Czapek and Sheehan [\(2005](#page-43-22)) and Sheehan [\(2006](#page-47-26)), there are over two dozen theoretical challenges to the second law, many of them laboratory testable. These facts may have cast some doubt on the continued universality of that law. Shee-han [\(2006](#page-47-26)) reviewed some representative challenges and considered the possibility that the thermodynamic arrow of time might be reversed on local or global scales. Experiments have been proposed to test the connections between retrocausation and a reversed thermodynamic arrow. Nevertheless, the second law of thermodynamics is still holding frm in its domain of validity.

6 Irreversibility

The observed phenomena of nature force us to conclude that the macroscopic processes of nature exhibit irreversible behavior. By "process" we usually understand a continuous change made up of a connected and related series of events. What is important is that a process has a beginning in time and a completion, when the process stops. There are reversible and irreversible changes of the state of a system (Denbigh [1989a](#page-43-1), [b;](#page-43-2) Zubarev [1974;](#page-48-5) McLennan [1989;](#page-46-7) Lebowitz [1993](#page-46-8), [1999](#page-46-9); Kuzemsky [2007;](#page-45-8) Planck [2010](#page-47-21); Fermi [1956;](#page-44-22) Dorfman [1999;](#page-43-20) Zwanzig [2001;](#page-48-18) Gallavotti [2014](#page-44-25); Breuer and Petruccione [2002;](#page-42-23) Prigogine [1999;](#page-47-28) Petrosky and Prigogine [2000](#page-47-29); Karakostas [1996;](#page-45-29) Bishop [2004;](#page-42-24) Perez-Madrid [2004](#page-47-30), [2005;](#page-47-31) Baldovin et al. [2019\)](#page-42-25). A change is said to occur reversibly when it can be carried out

in a series of infnitesimal steps, each of which can be undone by making a reverse change to the conditions that bring the change about. The majority of natural processes involve an increase of entropy in the system. The second law applies to irreversible processes that cannot be made reversible, such as a frictional process transforming mechanical energy into work, the process of the evaporation of a liquid, etc.

It was argued above that a general measure of the preference of nature for a given state is characterized by a physical quantity called the *entropy*. An increase in entropy is associated with dissipation of heat. This type of process is classifed as *irreversible*; it also imposes a limit on the amount of heat that can be transformed into energy or work, as discussed above.

The earlier attempts to resolve the problem of explaining macroscopic irreversibility from reversible microscopic equations can be traced back to Boltzmann's ideas of molecular chaos and his *H*-theorem (Muller [2007](#page-46-4); Brown et al. [2009\)](#page-42-26). The problem of Boltzmann's entropy and the arrow of time was considered lucidly by Lebowitz ([1993](#page-46-8), [1999](#page-46-9)). Boltzmann attempted to develop a statistical approach to explain the observed irreversible behavior of macroscopic systems in a manner consistent with their reversible microscopic dynamics (Sklar [1993](#page-47-32)). Lebowitz ([1993,](#page-46-8) [1999](#page-46-9)) pointed out very clearly that "Boltzmann statistical theory of time-asymmetric, irreversible nonequilibrium behavior assign to *each microscopic state* of a macroscopic system ...a number S_B , the *Boltzmann entropy* of that state." Contrary to the Gibbs entropy S_G , which is defined not for an individual state but for a statistical ensemble and which does not change in time, describing a system in equilibrium, S_B may show increasing behavior and thus explain (at least partially) the evolution toward equilibrium of such systems. What is important (Lebowitz [1993](#page-46-8), [1999\)](#page-46-9) is the fact that, in a physical sense, S_B coincides with S_G and agrees (in the thermodynamic limit; Kuzemsky [2014\)](#page-45-22) with the thermodynamic entropy of Clausius when the system is in equilibrium.

Boltzmann's *H*-theorem, in essence, states (Cercignani [1982;](#page-43-23) Brown et al. [2009](#page-42-26)) that a gas starting in a nonequilibrium state will evolve towards equilibrium. This is an evident contradiction to the classical (Newtonian) dynamical laws, which are invariant under time reversal (Sklar [1993](#page-47-32); Brown et al. [2009;](#page-42-26) Wu [1969](#page-48-6); Hofman and Green [1965](#page-45-30); Lee and Wu [1973;](#page-46-29) Wu [1975;](#page-48-19) Cercignani [1982](#page-43-23), [1988,](#page-43-24) [2006](#page-43-25)), and raised intense debate. It is instructive to mention here very briefy the formulation of Boltzmann's *H*-theorem (Sklar [1993;](#page-47-32) Brown et al. [2009](#page-42-26); Wu [1969;](#page-48-6) Hoffman and Green [1965;](#page-45-30) Lee and Wu [1973](#page-46-29); Wu [1975;](#page-48-19) Cercignani [1982](#page-43-23), [1988,](#page-43-24) [2006\)](#page-43-25). The *H*-theorem (Sklar [1993;](#page-47-32) Brown et al. [2009](#page-42-26)) associated with the Boltzmann equation (Sklar [1993;](#page-47-32) Brown et al. [2009](#page-42-26); Wu [1969;](#page-48-6) Hofman and Green [1965;](#page-45-30) Lee and Wu [1973;](#page-46-29) Wu [1975](#page-48-19); Cercignani [1982](#page-43-23), [1988,](#page-43-24) [2006](#page-43-25))

$$
\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial r} + \frac{F_{\text{ext}}}{m} \frac{\partial f}{\partial v} = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}},\tag{26}
$$

extends the definition of thermodynamic entropy to nonequilibrium states. Here, $f(r, v, t)$ is the distribution function. The theorem was formulated under the assumptions that only binary collisions occur and that the distribution function for pairs of particles factorizes in the form

$$
f^{(2)}(r_1, v_1, r_2, v_2, t) = f(r_1, v_1, t)f(r_2, v_2, t).
$$
\n(27)

This assumption is called the hypothesis of *molecular chaos*, which states that the pair of molecules are uncorrelated (Bogoliubov [1962\)](#page-42-27). The function *H* was introduced by Boltz-mann (Brown et al. [2009](#page-42-26)) in the form

$$
H = \int \int f(r, v, t) \ln f(r, v, t) dr dv.
$$
 (28)

In Boltzmann's approach, the arrow of time was expressed by the *H*-theorem (Brown et al. [2009\)](#page-42-26):

$$
\frac{dH}{dt} \le 0.\tag{29}
$$

Note that

$$
\frac{dH}{dt} = 0, \quad \text{if} \quad f(r, v, t) = f_0(r, v), \tag{30}
$$

where $f_0(r, v)$ is the thermal equilibrium distribution. It is known that Boltzmann's original defnition of the entropy

$$
S = k_{\text{B}} \ln W,\tag{31}
$$

was written in terms of the probabilities of available microscopic states of composite systems. Here, *W* is the number of microstates which correspond to a macrostate of the system (*the thermodynamical probability of the macrostate*). In spite of its popularity, the Boltz-mann approach led to hot discussion (Jaynes [1965;](#page-45-19) Kuzemsky [2018\)](#page-45-4).

The Boltzmann formula has been analyzed from various sides in general form by Jaynes [\(1965\)](#page-45-19), Zubarev ([1974](#page-48-5)), and Wehrl ([1978](#page-48-13)) to characterize it uniquely using physically plausible properties. In spite of this, it should be considered as a kind of postulate. In particular, the Boltzmann formula has been criticized in literature on the grounds that it gives a nonsufficient dynamical foundation in view of the thermal motion of the particles of which a physical system consists. It follows from the Boltzmann defnition that the entropy is larger if ρ is smeared out, where ρ is the probability density in phase space. The microscopic defnition of entropy given by Boltzmann does not, by itself, explain the second law of thermodynamics, even in classical physics.

It is worth noting that, in the general case, the Boltzmann entropy may also be for-mally defined by formula ([18\)](#page-16-0). It can be shown that, if the function $f_1(p_1, q_1, t)$ satisfies the Boltzmann kinetic equation, then the Boltzmann entropy increases. In the case of statistical equilibrium, it is constant. What is most important in this context is the fact that the Boltzmann defnition of entropy is adequate for a strongly rarefed gas only (Desvillettes and Villani [2005\)](#page-43-26). It is less adequate in the general case.

Special care should be taken when discussing the possibilities of the application of the concept of entropy to the universe as a whole (Tolman [1931](#page-48-20); Patel and Lineweaver [2017](#page-46-30)). This is important in the light of the prediction made by James Jeans long ago: "The second law of thermodynamics compels materials in the universe to move ever in the same direction along the same road which ends only in death and annihilation" (Jeans [1929](#page-45-31)).

However, Boltzmann's derivation works equally well in **both** directions of time. Thus, the *H*-theorem cannot be established in full measure on the basis of the dynamical laws. This subject is well explored, and we refer to the literature (Sklar [1993;](#page-47-32) Mackey [1992](#page-46-19); Brown et al. [2009](#page-42-26); Wu [1969](#page-48-6); Hofman and Green [1965;](#page-45-30) Bogoliubov [1962;](#page-42-27) Lee and Wu [1973](#page-46-29); Wu [1975](#page-48-19); Cercignani [1982](#page-43-23), [1988](#page-43-24), [2006\)](#page-43-25) for further reading.

In 1950, Schrödinger published a remarkable article entitled "Irreversibility" (Schrödinger [1950\)](#page-47-33). It may be considered as an addendum to his notable short book (Schrödinger [1946\)](#page-47-22). The article (Schrödinger [1950\)](#page-47-33) contains an interesting discussion of the concept (or notion) of irreversibility. Schrödinger writes: It may seem an audacity if one undertakes to profer new arguments in respect of a question about which there has been for more than eighty years so much passionate controversy, some of the most eminent physicists and mathematicians siding diferently or favouring opposite solution...It is sometimes believed that only quantum mechanics, or some processes of thought borrowed from it, give the fnal clue to the problem. I wish to show here that this is wrong and that the solution given previously can be defended against the last objection...I do not wish to derive irreversibility at all. I wish to reformulate the laws of phenomenological irreversibility, thus certain statements of thermodynamics, in such a way, that the logical contradiction any derivation of these laws from reversible models seems to involve ...will be removed and ...in what manner you have to reformulate the law of entropy—or for that matter all other irreversible statements—so that they be capable of being derived from reversible models.

Schrödinger pointed out the essence of the discussion: "This objection, in short, is this: a proof that a reversible model shows an irreversible behavior, i.e. that it *nearly always* exhibits a temporal succession of observable states which it *almost never* passes through in the reverse order of time—such a proof needs must be at fault some where. The problem before us here is not actually to derive irreversibility say, the increase of entropy with time—from any kind of general or special reversible model. Not from a general one: for it is hardly possible to devise a model general enough not only to comprise all kinds of physical events but also to anticipate all changes the reversible theories of physics may undergo in future, and to be inviolable to any such change...No such derivation can avoid introducing right at the outset a *time variable t*...if the model is reversible, any general behavior you rightfully infer for increasing *t*, must also hold for decreasing *t*. In other words it must be an invariant of the transformation $t' = -t$. Hence our task is to formulate all statements about irreversibility in such a fashion that they are invariant to the said transformation. At frst sight it would seem that phenomenological time can have nothing to do with the variable *t*. It could not be defned by *t*. And it could not be defned by −*t*. This is true. And if you unite these statements and say it can be defned neither as *t*, nor as −*t*, that is also true. We shall see however that it can be defned as "either *t* or -*t*."

What is important is that Schrödinger discusses the problem of irreversibility as a characteristic common to quantum mechanics, thermodynamics, and statistical mechanics. Schrödinger formulated it as: "...the very spirit of quantum mechanics, combined with that of thermodynamics, forbids us even to think of such observations taking place, if—as has often to be assumed—the system is isolated from the rest of the world in the interval between the two observations." It is of interest to compare this statement with the conclusions of well-known notable works (Einstein et al. [1931](#page-44-28); Aharonov et al. [1964](#page-42-28)).

Denbigh devoted close attention to the work of Schrödinger ([1950\)](#page-47-33) in his essay review (Denbigh [1996](#page-43-3)) of the book *Time's Arrows Today* (Savitt [1995](#page-47-2)). Denbigh pointed out that the second law can be formulated in a way which makes no separate reference to "earlier than" or "later than." This was done by Schrödinger when he worked in Dublin ...He considers the limit $dS/dt \geq 0$, which is usually understood as the statement of the second law.

And it also expresses time's arrow in terms of entropy increase. Denbigh concludes with the statement that it is the parallelism of the *entropy changes* that provides an objective statement of the second law, just as much as that higher-entropy states occur later in consciousness. In his opinion, the concept of entropy is *less signifcant* than that of irreversibility, for there are several processes that are irreversible without being entropic with any certainty (Denbigh [1989a](#page-43-1), [b](#page-43-2)). Also it is the notion of irreversibility that directs our attention to where the "*arrow*" of time is really to be seen. It lies in the fact that no processes exist that can be completely reversed when all efects on the environment, however small, are allowed for, and when exceedingly improbable fuctuations are disregarded. In short, *there is a prevailing irreversibility in the world*.

In Denbigh's [\(1996](#page-43-3), [1989a](#page-43-1), [b](#page-43-2)) opinion, irreversibility is a much broader concept than is entropy increase, as is shown by the occurrence of certain processes which are irreversible without seeming to involve any intrinsic entropy change. These processes are of different kinds; they include, for example, the spreading outwards into space of particles, or of radiation, and they also include certain biological and natural phenomena (Roduner and Radhakrishnan [2016;](#page-47-34) Zurek [2018](#page-48-15)); For example, Davis [\(1994](#page-43-27)) studied RNA replication in the bacteriophage $Q\beta$ system. It can, in principle, transmit sequence complexity at a higher rate than it increases entropy. He found that expanding the variety of nucleotides, through novel base-pair interactions, would move the threshold at which synthesis produces more complexity than entropy away from near equilibrium while accelerating the system approach to equilibrium. A decrease in sequence complexity during polymerization, leading to a many-to-one correspondence between monomer and template, cannot be reversed, owing to symmetry restrictions. In terms of the kinetic mechanism, uncertainty was associated with the path of depolymerization, which yields a path entropy which selectively prolongs the reverse reaction. He concluded that, together with an elevation in thermodynamic entropy, therefore, there are two possible sources of irreversibility in a physical process. Some implications of kinetic irreversibility were considered in relation to the second law of thermodynamics and to the processing and translation of mRNA.

It is worth recalling (England [2013](#page-44-29)) that every species of living thing can make a copy of itself by exchanging energy and matter with its surroundings. One feature common to all such examples of spontaneous "self-replication" is their statistical irreversibility. Self-replication is a capacity common to every species of living thing, and simple physical intuition dictates that such a process must invariably be fueled by the production of entropy. In the paper by England ([2013\)](#page-44-29), this process was investigated quantitatively by deriving a lower bound for the amount of heat that is produced during a process of self-replication in a system coupled to a thermal bath. It was found that the minimum value for the physically allowed rate of heat production is determined by the growth rate, internal entropy, and durability of the replicator, and the implications of this fnding for bacterial cell division were discussed, as well as for the prebiotic emergence of self-replicating nucleic acids.

Zivieri et al. [\(2017](#page-48-21)) pointed out that, in living systems, it is crucial to study the exchange of entropy that plays a fundamental role in the understanding of irreversible chemical reactions. However, no works that can describe the rate of entropy production associated with irreversible processes in a systematic way are available. The authors developed a theoretical model to compute the rate of entropy production in the minimum living system. In particular, they applied the model to the most interesting and relevant case of a metabolic network, namely glucose catabolism in normal and cancer cells. The authors showed that: (i) the rate of internal entropy is mainly due to irreversible chemical reactions, and (ii) the rate of external entropy is mostly correlated with the heat fow towards the intercellular environment. The future applications of their model could be of fundamental importance for a more complete understanding of self-renewal and physiopathologic processes and could potentially provide support for cancer detection.

However, irreversibility has some common features; namely, it develops in the temporal direction towards the future. In other words, irreversibility is the spreading out of all forms of trajectories, new entities, or new states in one direction.

It is instructive to discuss this matter in the context of previous observations regarding irreversibility with an emphasis on the mixing partial order for macrostates. This was performed by Denbigh [\(1989a](#page-43-1), [b](#page-43-2)) in his paper "The many faces of irreversibility." He observed that "What appears to be the common feature of irreversibility is the fanning out of trajectories, new entities or new states, in the temporal direction towards the future." Grad discussed some aspects of these general ideas in his paper "The many faces of entropy" from a mathematical point of view. Denbigh also suggested that there are three distinct forms for the *divergent quality* of the trajectories: (a) a branching towards a greater number of distinct kinds of entities, (b) a divergence from each other of particle trajectories or of sections of wavefronts, and (c) a spreading over an increased number of states of the same entities.

Denbigh [\(1996](#page-43-3), [1989a](#page-43-1), [b\)](#page-43-2) conjectured that any efect in nature is always the result of the dynamic balances of the interactions between the open systems and their environment, and the exchange of energy drives some behavior of natural systems; i.e., their evolution is driven by the decrease of their free energy in the least time. *Exergy* is defned as the maximum amount of work obtainable by a system as it comes to equilibrium with its reference environment. It thus represents a measure of the ability of a system to cause changes, due to its noncomplete stable equilibrium, in relation to the reference environment. From the other side, *entropy production* may be thought of as the standard gauge of irreversibility. However, as keenly noted by Denbigh, many processes are irreversible but apparently do not result in signifcant entropy production. In this regard, it should be kept in mind that it is possible to make a distinction between entropy production and irreversibility in nonequilibrium thermodynamics.

There are a diversity of approaches to the description of irreversibility (Zubarev [1974;](#page-48-5) Kuzemsky [2017;](#page-45-10) Dorfman [1999](#page-43-20); Zwanzig [2001](#page-48-18); McLennan [1989;](#page-46-7) Gallavotti [2014](#page-44-25)). It is important to mention the fundamental works of Prigogine and his group (Prigogine [1999;](#page-47-28) Petrosky and Prigogine [2000;](#page-47-29) Karakostas [1996](#page-45-29); Bishop [2004](#page-42-24)) on the microscopic origin of irreversibility. Using extensions of the traditional Hilbert space and Poincaré's nonintegrability, new formulations of the laws of dynamics which can be expressed only in terms of probabilities (and not in terms of trajectories or wavefunctions) and which include time symmetry breaking were obtained. The fundamental problem on which Prigogine and his group have focused can be stated briefy as follows: Our observations indicate that there is an *arrow of time* in our experience of the world (e.g., decay of unstable radioactive atoms like uranium, etc.) Most of the fundamental equations of physics are time reversible, however, presenting an apparent confict between our theoretical descriptions and experimental observations. Many have thought that the observed arrow of time was either an artifact of our observations or due to very special initial conditions. An alternative approach, followed by the Prigogine and his group, is to consider the observed direction of time to be a *basic physical phenomenon* due to the dynamics of physical systems. The fundamental concerns are the same as in their earlier approaches (subdynamics, similarity transformations), but the contemporary approach utilizes rigged Hilbert space (whereas the older approaches used Hilbert space). While the emphasis on nonequilibrium statistical mechanics remains the same, their more recent approach addresses the physical features of large Poincaré systems, nonlinear dynamics, and the mathematical tools necessary to analyze them.

Hao Ge ([2014\)](#page-44-30) investigated the nonequilibrium thermodynamics of a general secondorder stochastic system. He showed that, at a steady state, under inversion of velocities, the condition of time reversibility over the phase space is equivalent to the antisymmetry of spatial fux and the symmetry of velocity fux. He then showed that the condition of time reversibility alone cannot always guarantee the Maxwell–Boltzmann distribution. The author compared the two conditions together and found that the frictional force naturally emerges as the unique odd term of the total force at a thermodynamic equilibrium, and is followed by the Einstein relation. The two conditions respectively correspond to two previously reported diferent entropy production rates. In the case where the external force is only position dependent, the two entropy production rates become one. Hao Ge concluded that such an entropy production rate can be decomposed into two nonnegative terms, expressed respectively by the conditional mean and variance of the thermodynamic force associated with the irreversible velocity fux at any given spatial coordinate. In the small inertia limit, the former term becomes the entropy production rate of the corresponding overdamped dynamics, while the anomalous entropy production rate originates from the latter term. Furthermore, regarding the connection between the frst law and second law, Hao Ge found that, in the steady state of such a limit, the anomalous entropy production rate is also the leading order of the Boltzmann-factor weighted diference between the spatial heat dissipation densities of the underdamped and overdamped dynamics, while their unweighted diference always tends to vanish.

An interesting aspect of the problem of irreversibility was considered by Baldovin et al. [\(2019](#page-42-25)). With the aid of simple analytical computations for the Ehrenfest model, they clarifed some basic features of macroscopic irreversibility. The stochastic character of the model allowed them to give a nonambiguous interpretation of the general idea that *irreversibility is a typical property*: for the vast majority of the realizations of the stochastic process, a single trajectory of a macroscopic observable behaves irreversibly, remaining "very close" to the deterministic evolution of its ensemble average, which can be computed using probability theory. The validity of the above scenario was checked through simple numerical simulations, and a rigorous proof of the typicality was provided in the thermodynamic limit (Kuzemsky [2014](#page-45-22)).

Biological systems open new perspectives for studying entropy and irreversibility (Strong et al. [1998;](#page-47-35) Buskermolen et al. [2019\)](#page-43-19). The interaction between the open system and its environment, and the exchange of energy drives some specifc behavior of natural systems (Zurek [2018\)](#page-48-15). As a result of such interaction, the temporal direction towards the future, i.e., irreversibly, may be developed. Biological systems and processes are open systems with mass, energy, entropy, and information fuxes across their boundaries, for example, the evolution of a population (Demetrius [1997\)](#page-43-10) and other similar complex systems in which irreversible phenomena are not accompanied by changes of entropy. The use of traditional approaches is not so obvious in living systems. Time irreversibility, a fundamental property of nonequilibrium systems, should be important in assessing the status of physiological processes that operate over a wide range of scales. However, measurements of these properties in living systems are rather limited. Costa et al. ([2005\)](#page-43-28) considered the problems of the broken asymmetry of the human heartbeat and the loss of time irreversibility in aging and disease. They provided a computational method derived from basic physics assumptions to quantify time asymmetry over multiple scales and applied it to the human heartbeat time series in health and disease. They found that the multiscale time asymmetry index is highest for a time series from young subjects but decreases with aging or heart disease. Loss of time irreversibility may provide a new way of assessing the functionality of living systems that operate far from equilibrium.

Lineweaver and Egan ([2008\)](#page-46-31) investigated the global (and controversial) problem of the cosmic evolution of entropy and the gravitational origin of the free energy required by life. All dissipative structures in the universe, including all forms of life, owe their existence to the fact that the universe started in a low-entropy state and has not yet reached equilibrium. The low initial entropy was due to the low gravitational entropy of the nearly homogeneously distributed matter and has, through gravitational collapse, evolved gradients in density, temperature, pressure, and chemistry. These gradients, when steep enough, give rise to far from equilibrium dissipative structures (e.g., galaxies, stars, black holes, hurricanes, and life) which emerge spontaneously to hasten the destruction of the gradients which spawned them. This represents a paradigm shift from "we eat food" to "food has produced us to eat it."

7 Quantum Systems and Quantum Entropy

Symmetries play a fundamental role in our understanding of physics and, in particular, in quantum mechanics. The problem of time invariance and time asymmetry (Kuzemsky [2017;](#page-45-10) Lewis [1930;](#page-46-12) Sachs [1987;](#page-47-13) Schwichtenberg [2018](#page-47-14); Geru [2018;](#page-44-12) Einstein et al. [1931;](#page-44-28) Aharonov et al. [1964](#page-42-28)) in quantum mechanics has stood for a long time. Common wisdom says that quantum systems are developed in time by unitary evolution, so no arrow of time appears. However, measurement is time asymmetric, and information is lost. Penrose ([1979\)](#page-46-15) remarked that "...in my attitude to quantum mechanics ...it contains no manifest arrow, and the solution to the problem of macroscopic time asymmetry must be sought elsewhere." The debates on this problem still persist (Peres [1994](#page-47-36); Aharonov et al. [2010;](#page-42-29) Nauenberg [2011;](#page-46-32) Kastner [2011](#page-45-32)).

In quantum mechanics (Jauch [1968;](#page-45-12) Piron [1976;](#page-47-7) Kuzemsky [2017](#page-45-10)), the state of a system is characterized by a state vector in Hilbert space H that contains all the relevant information. The states that can be represented as state vectors are called pure states. However, not all states can be represented in this way. In practice, there are situations in which the information is incomplete and one has resort to the notion of a mixed ensemble in which we do not know the state vector of each member; in this case, the density matrix (or density operator ρ) formalism (ter Haar [1961](#page-48-22)) is appropriate. A mixed ensemble can be set up in terms of the eigenfunctions of any observable, but usually it was assumed that they are the energy eigenfunctions. This mixed ensemble is the quantum-mechanical analog of the classical distribution in energy. Thus, the expectation value of an observable, *A*, given the density operator ρ , is

$$
\langle A \rangle = \text{Tr}(A\rho). \tag{32}
$$

The density operator is particularly important for the treatment of open systems. Indeed, when a system interacts with others systems, a description with a state vector is impossible. It is convenient to separate a selected subsystem H_1 which is of primary interest from the entire system *H*. In such a case, we are interested in only a part of the total system. This can be done, for example, with the aid of the projection technique (Kuzemsky [2017\)](#page-45-10).

Aharonov, Bergmann, and Lebowitz in their paper "Time symmetry in the quantum process of measurement" (Aharonov et al. [1964](#page-42-28)) declared that "One of the perennially challenging problems of theoretical physics is that of the 'arrow of time'...all the "microscopic" laws of physics ever seriously propounded and widely accepted are entirely symmetric with respect to the direction of time; they are form-invariant with respect to time reversal."

Aharonov et al. ([1964\)](#page-42-28) examined the assertion that the "reduction of the wave packet," implicit in the quantum theory of measurement, introduces into the foundations of quantum physics a time-asymmetric element, which in turn leads to irreversibility. They argued (Aha-ronov et al. [1964](#page-42-28)) that this time asymmetry is actually related to the manner in which statistical ensembles are constructed. If one constructs an ensemble time symmetrically by using both initial and fnal states of the system to delimit the sample, then the resulting probability distribution turns out to be time symmetric as well. According to the authors (Aharonov et al. [1964](#page-42-28)), the conventional expressions for prediction as well as those for "*retrodiction*" may be recovered from the time-symmetric expressions formally by separating the fnal (or the initial) selection procedure from the measurements under consideration by sequences of "coherence destroying" manipulations. We can proceed from this situation, which resembles prediction, to true prediction (which does not involve any postselection) by adding to the time-symmetric theory a postulate which asserts that ensembles with unambiguous probability distributions may be constructed on the basis of preselection only.

The authors (Aharonov et al. [1964\)](#page-42-28) argued that, if the validity of this postulate and the falsity of its time reversal result from the macroscopic irreversibility of our universe as a whole, then the basic laws of quantum physics, including those referring to measurements, are as completely *time symmetric* as the laws of classical physics. As a by-product of their analysis, it was also shown that, during the time interval between two noncommuting observations, one may assign to a system the quantum state corresponding to the observation that follows with as much justifcation as it was assigned, ordinarily, the state corresponding to the preceding measurement. Additional discussion of time reversal, symmetry violation, and the *H*-theorem was carried out by Aharony [\(1971](#page-42-30)).

Jacobs and Maes ([2005](#page-45-33)) pointed out that the discussion on time reversal in quantum mechanics has continued at least since Wigner's "Über die Operation der Zeitumkehr in der Quantenmechanik" paper in 1932. If and how the dynamics of the quantum world is timereversible has been the subject of many controversies. Some have seen quantum mechanics as fundamentally time-irreversible (see, for example, von Neumann), while some have seen in that the ultimate cause of time's arrow and second law behavior. Penrose [\(1989](#page-46-16)) argued similarly and concluded that "our sought-for quantum gravity must be a time-asymmetric theory."

There is a project (Jacobs and Maes [2005](#page-45-33)) to extend quantum mechanics into new fundamentally irreversible equations, thus proposing a new theory giving "... une description fondamentale irréversible de tout système physique." Jacobs and Maes [\(2005](#page-45-33)) carried out a review of a number of general points on this difficult problem that were less emphasized in existing literature. They also described the emergence of thermodynamic irreversibility.

When a state in quantum systems is described by a density operator ρ , on a Hilbert space H, then for a state $\rho \in \mathfrak{S}(\mathcal{H})$, the quantum entropy (Breuer and Petruccione [2002](#page-42-23)) will be given by the expression

$$
S(\rho) = -\text{tr}\rho \log \rho. \tag{33}
$$

The main properties of entropy $S(\rho)$ can be summarized in the following form: For any density operator $\rho \in \mathfrak{S}(\mathcal{H})$, the following hold:

- $-$ Positivity: $S(\rho) \geq 0$
- *→* Symmetry: Let $\rho' = U^{-1} \rho U$ for an invertible operator U , → $S(\rho') = S(\rho)$
- Additivity: *S*($ρ_1 ⊗ ρ_2$) = *S*($ρ_1$) + *S*($ρ_2$) for any $ρ_i ∈ ℤ(H)$
- $-$ Concavity: *S*($λρ_1 + (1 λ)ρ_2$) ≥ $λS(ρ_1) + (1 λ)S(ρ_2)$ for any $ρ_1, ρ_2 \in \mathfrak{S}(\mathcal{H})$

 $-$ Subadditivity: For the reduced states $ρ₁, ρ₂$ of $ρ ∈ \mathfrak{S}(H \otimes H₂)$, $S(ρ) ≤ S(ρ₁) + S(ρ₂)$.

The introduction of entropy into quantum mechanics gives in a compact form all the classical defnitions of entropy. The temporal evolution of the von Neumann entropy is governed by the Liouville–von Neumann equation (Zubarev [1974;](#page-48-5) Kuzemsky [2017\)](#page-45-10) for isolated quantum systems. A detailed discussion of the von Neumann entropy and its properties was summarized by Kuzemsky ([2015\)](#page-45-34) in the context of variational principles for the free energy of complex many-particle interacting systems. This paper (Kuzemsky [2015\)](#page-45-34) also discusses the variational inequalities, including Klein's inequality. The corresponding theo-rem (Kuzemsky [2015\)](#page-45-34) states that, for $A, B > 0$,

$$
Tr A(\log A - \log B) \ge Tr(A - B),\tag{34}
$$

with equality if and only if $(A = B)$.

In a more general form, the Klein inequality may be formulated in the following way:

For all $A, B \in \mathbf{H}_n$ and all differentiable convex functions $f : \mathbb{R} \to \mathbb{R}$, or for all $A, B \in \mathbf{H}_{n}^{\dagger}$ and all differentiable convex functions $f : (0, \infty) \to \mathbb{R}$,

$$
\operatorname{Tr}\left(f(A) - f(B) - (A - B)f'(B)\right) \ge 0.
$$
\n(35)

In either case, if *f* is strictly convex, there is equality if and only if $A = B$.

Actually, $S(\rho)$ is not only a strictly concave function of the eigenvalues of ρ ; it is also a strictly concave function of ρ itself. The concavity property is useful in various problems of statistical thermodynamics (Prestipino and Giaquinta [2003\)](#page-47-37).

It is well known that many difculties with the probabilistic interpretation of quantum theory are related to the of-diagonal elements of the density operator. The irreversible *state reduction* to the diagonal form is a fundamental problem in statistical mechanics and in measurement theory. In 1929, von Neumann claimed to have proved the *H*-theorem in quantum mechanics without the assumptions necessary in classical physics.

Whether or not irreversibility may be an element common to quantum dynamics and the quantum-mechanical measurement process (Belinfante [1975](#page-42-11); Wheeler and Zurek [1983;](#page-48-23) Schulman [1997;](#page-47-38) Omnes [2002](#page-46-33); Schlosshauer [2004](#page-47-39), [2007\)](#page-47-40) is still disputable. Farinelli and Gamba [\(1956](#page-44-31)) considered further the problem of explaining macroscopic irreversibility from reversible microscopic laws. They carried out a critical discussion from a physical standpoint of the proof of the second principle of thermodynamics in quantum mechanics given by von Neumann. It was shown how information theory allows a much more satisfactory physical interpretation. They considered the problem from the beginning, starting from the point of view that entropy is nothing but a measure of our ignorance of the state of a system.

Bonifacio ([1983\)](#page-42-31) demonstrated that a proper coarse-grained description of time evolution leads to a finite-difference equation with step τ for the density operator. This implies state reduction to the diagonal form in the energy representation and a quasiergodic behavior of quantum-mechanical ensemble averages. An intrinsic time–energy relation $\tau \Delta E \ge \hbar/2$ was proposed, and its equivalence to a time quantization discussed.

Indeed, in the von Neumann approach, the process of measurement can be described as a determination of statistical correlations between the state of the object and that of the measuring apparatus. The measurement process (Belinfante [1975;](#page-42-11) Wheeler and Zurek [1983;](#page-48-23) Schulman [1997](#page-47-38)) in quantum mechanics involves a system and the apparatus, which interact at some time and should then be separated. Hence, the system under consideration

is not isolated, i.e., is open, whereas the von Neumann entropy is invariant under the unitary dynamics. In other words, the changes in the entropy of the system during the measurement process should be estimated very carefully (Wheeler and Zurek [1983;](#page-48-23) Omnes [2002;](#page-46-33) Schlosshauer [2004](#page-47-39), [2007](#page-47-40)). Even if the quantum measurement process is irreversible, such irreversibility is not quantifed by an increase of the von Neumann entropy; For example, any nondegenerate rank-one projective quantum measurement over an initial mixed state (hence, with strictly positive von Neumann entropy) reduces the fnal state (conditional on the known measurement result) to a pure state, which has zero von Neumann entropy. Even if one compares the initial von Neumann entropy with the weighted fnal entropy (corresponding to performing a measurement and ignoring the result), the latter can be lower then the former, as follows from the concavity property. The simplest relation that can be put forward between the von Neumann entropy and a quantum measurement process can be obtained by means of Klein's inequality, which allows one to prove that the Shannon entropy corresponding to the probabilities pertaining to the measurement outcomes of a nondegenerate observable is always larger or equal to the von Neumann entropy. The equality is achieved by the measurement on the basis which diagonalizes the input state. Hence, the von Neumann entropy just measures the uncertainty of the initial state, which coincides with the indeterminacy of the best possible measurement.

Does von Neumann's entropy correspond to thermodynamic entropy? This question has arisen in some papers in connection with von Neumann's expression $-kTr(\rho \ln \rho)$.

von Neumann's defnition of entropy was analyzed thoroughly by Lebowitz and collaborators (Goldstein et al. [2010](#page-44-32)) in the context of quantum statistical mechanics. They pointed out that, in his article of 1929, von Neumann studied the long-time behavior of macroscopic quantum systems and proved a theorem, which he called the "quantum ergodic theorem." According to Lebowitz et al. (Goldstein et al. [2010\)](#page-44-32), it expresses a fact which they called "normal typicality" and which can be summarized as follows: for a "typical" finite family of commuting macroscopic observables, every initial wavefunction ψ_0 from a microcanonical energy shell evolves such that, for most times *t* in the long run, the joint probability distribution of these observables obtained from ψ_t is close to their microcanonical distribution.

The approach to thermal equilibrium of macroscopic quantum systems has been studied recently by many authors (Goldstein et al. [2010](#page-44-33); Reimann [2010\)](#page-47-41). Lebowitz et al. (Goldstein et al. [2010\)](#page-44-33) considered an isolated macroscopic quantum system. They proved a theorem asserting that, for a sufficiently large quantum system with a typical Hamiltonian and an arbitrary initial state ψ_0 , the system's state ψ_t spends most of the time, in the long run, in thermal equilibrium. In other words, for "*typical*" Hamiltonians with given eigenvalues, all the initial state vectors ψ_0 evolve in such a way that ψ_t is in thermal equilibrium for most times *t*. This result is closely related to von Neumann's quantum ergodic theorem of 1929.

Reimann [\(2010](#page-47-41)) studied a related problem: how to derive the equilibrium statistical mechanics, namely the canonical ensemble, from quantum mechanics in combination with certain, very weak assumptions regarding the preparation, observables, and Hamiltonian of the system, i.e., in the context of *canonical thermalization*. The quantum-mechanical time evolution generated by the Hamiltonian was not to be touched in any way, neither by heuristically modifying it to account for small remnant external perturbations, nor by introducing any kind of approximation. In other words, the well-known time-inversion invariance of quantum mechanics was fully and rigorously maintained. For quantum systems that are weakly coupled to a much "bigger" environment, thermalization of possibly far from equilibrium initial ensembles was demonstrated. This means that, for sufficiently long times, the ensemble is for all practical purposes indistinguishable from a canonical density

operator under conditions that are satisfed under many, if not all, experimentally realistic conditions.

Deville and Deville ([2013\)](#page-43-29) thoroughly discussed the above-mentioned debate about the link of the von Neumann or statistical entropy with the entropy of phenomenological thermodynamics. Referring to Gibbs's and von Neumann's founding texts, they placed von Neumann's 1932 contribution in its historical context, after Gibbs's 1902 treatise and before the creation of the information entropy concept, which places boundaries on the debate. Reexamining von Neumann's reasoning, they stressed that the part of his reasoning implied in the debate mainly uses thermodynamics, not quantum mechanics, and identifed two implicit postulates. Deville and Deville ([2013\)](#page-43-29) thoroughly examined the critical papers, insisting upon the presence of open thermodynamical subsystems, imposing the use of the chemical potential concept. The authors briefy mentioned Landau's approach (Landau and Lifshitz [1980](#page-45-23)) to the quantum entropy. On the whole, it was shown that von Neumann's viewpoint is right, and the claim that von Neumann entropy "is not the quantum-mechanical correlate of thermodynamic entropy" cannot be retained.

Lesovik et al. [\(2016](#page-46-34)) analyzed the *H*-theorem in quantum physics from the point of view of the theory of information. Indeed, remarkable progress on quantum information theory allowed the formulation of mathematical theorems for conditions where data transmission or processing occurs with a nonnegative entropy gain. However, the relation of these results formulated in terms of entropy gain in quantum channels to the temporal evolution of real physical systems was not fully understood. The authors used the mathematical formalism provided by quantum information theory to formulate the quantum *H*-theorem in terms of physical observables. They discussed the manifestation of the second law of thermodynamics in quantum physics and uncovered special situations where the second law may be violated. They further demonstrated that the typical evolution of energy-isolated quantum systems occurs with nondiminishing entropy. For further discussion, see Gudder [\(2006](#page-44-34)).

These studies clearly show that the concepts of thermodynamic entropy, quantum entropy, and information entropy are tightly interrelated and should be used with great care (Zubarev [1974](#page-48-5); Kuzemsky [2016](#page-45-9), [2018](#page-45-11); Kozlov and Smolyanov [2006](#page-45-26); Jaynes [1957a,](#page-45-27) [b;](#page-45-28) Landauer [1975](#page-45-35); Maes and Netocny [2003](#page-46-35)). This is of special importance in the connection with the problem of time asymmetry from the quantum viewpoint.

In his detailed survey, Zeh ([2007\)](#page-48-0) investigated diverse irreversible phenomena and their foundation in classical, quantum, and cosmological settings. The latter aspect includes a discussion of the meaning of probabilities (Kuzemsky [2016](#page-45-9)) in a cosmological context. The irreversible aspects of quantum computers, and various consequences of the expansion of the universe, were considered as well. In particular, the book contains an analysis of the physical concept of time, a detailed treatment of radiation damping, as well as extended sections on quantum entanglement and decoherence (see also Omnes [2002;](#page-46-33) Elze [2004;](#page-44-35) Schlosshauer [2004,](#page-47-39) [2007\)](#page-47-40), arrows of time hidden in various interpretations of quantum theory, and the emergence of time in quantum gravity. Zeh conjectures that *time asymmetry* lies in the initial (or fnal) conditions rather than in the dynamical laws. He also considered the controversial issue of "the quantization of time" in the context of quantum cosmology.

Zurek ([2018\)](#page-48-24) recently carried out a deep analysis of related questions. According to Zurek, a system in equilibrium does not evolve—time independence is its telltale characteristic. However, in Newtonian physics, the microstate of an individual system (a point in its phase space) evolves incessantly in accordance with its equations of motion. Ensembles were introduced in the 19th century to bridge this chasm between the continuous motion of phase space points in Newtonian dynamics and the stasis of thermodynamics: While states of individual classical systems inevitably evolve, a phase space distribution of such

states—an ensemble—can be time-independent. Zurek conjectured that entanglement (e.g., with the environment) can yield a time-independent equilibrium in an individual quantum system. This allows one to eliminate ensembles—an awkward stratagem introduced to reconcile thermodynamics with Newtonian mechanics—and use an individual system interacting and therefore entangled with its heat bath to represent equilibrium and to elucidate the role of information and measurements in physics. Thus, according to Zurek, in our quantum universe, one can practice statistical physics without ensembles—hence, in a sense, without statistics. The elimination of ensembles uses ideas that led to the recent derivation of Born's rule from the symmetries of entanglement. Zurek ([2018\)](#page-48-24) also discussed difculties related to the reliance on ensembles and illustrated the need for ensembles with the classical Szilard engine. A similar quantum engine—a single system interacting with the thermal heat bath environment (see Kuzemsky [2017,](#page-45-10) [2018\)](#page-45-11)—is enough to establish thermodynamics. The role of Maxwell's demon (which in this quantum context resembles Wigner's friend) was also discussed.

Zurek's conclusions suggested a few questions. First of all, it should be noted that similar problems were discussed by Blokhintsev ([1977\)](#page-42-32) from a complementary point of view (Kuzemsky [2008](#page-45-36)). Blokhintsev studied the same questions: What is the origin of those phenomenological, deterministic laws that approximately control the quasiclassical region of our everyday experience in a universe controlled at the fundamental level by quantummechanical laws characterized by uncertainty and probability distribution? What characteristic features and limits of applicability of these classical laws can be traced to underlying quantum-mechanical concepts.

A detailed analysis of the ensemble approach to the probabilistic postulates of quantum mechanics was performed by Blokhintsev ([1977\)](#page-42-32) in the context of the description of quantum measurements.

Note that it was believed that the Gibbs distribution can be deduced asymptotically from the general principles of mechanics under the assumption that the system is ergodic. However, no rigorous derivation, except for the case of a vanishingly small interaction, has been obtained. It was shown rigorously by Kozlov ([2000\)](#page-45-37) that the Gibbs canonical distribution (Gibbs ensemble) is the only *universal* one whose density depends on energy and that is compatible with the axioms of thermodynamics.

In this context, it is worth mentioning the approach of Galgani and collaborators (Carati and Galgani [2001;](#page-43-30) Carati et al. [2006\)](#page-43-31). Carati, Galgani, and Giorgilli formulated their approach to the reconciliation of thermodynamics with mechanics in their paper "Dynamical systems and thermodynamics." In connection with the foundations of statistical mechanics, the relations between thermodynamics and dynamics were considered in the context of the fact that, in quantum mechanics, equipartition should be replaced by Planck's law (Carati and Galgani [2001](#page-43-30); Carati et al. [2006\)](#page-43-31).

It was argued above that irreversibility is one of the most complicated concepts in thermodynamics and statistical physics. Microscopic physical laws are symmetric in time, but macroscopic average behavior has in many cases a preferred direction of time. According to the second law of thermodynamics, this asymmetry of time is associated with a positive mean entropy production.

Entropy and entropy generation in the nonequilibrium steady state have been treated in a number of papers on nonequilibrium statistical thermodynamics (Kuzemsky [2018;](#page-45-4) Zubarev [1974](#page-48-5); Kuzemsky [2007,](#page-45-8) [2017](#page-45-10)). This quasi-Gibbs approach assigns entropy the same role as in equilibrium statistical mechanics; however, entropy represents a lack of information, and is maximized subject to constraints imposed on the system (Jaynes [1957a](#page-45-27), [b\)](#page-45-28).

The laws of classical mechanics are independent of the direction of time, but whether the same is true in quantum mechanics has been a subject of long debate. While it is agreed that the laws that govern isolated quantum systems are time-symmetric, measurement changes the state of a system according to rules that only seem to work forward in time, and there is diference in opinion about the interpretation of such efects. Oreshkov and Cerf ([2015\)](#page-46-36) attempted to formulate a time-symmetric version of quantum theory which establishes a close link between this asymmetry and the fact that we can remember the *past* but not the *future*, i.e., a phenomenon that has sometimes been called the *psychological arrow of time*. The idea that our choices at present can infuence events in the future but not in the past is refected in the rules of standard quantum theory as the principle of causality. The study ofers some new insights into the concepts of *free choice* and *causality*, and conjectures that causality may not be considered as a basic principle of physics. It also extends a theorem in quantum mechanics due to Wigner (Kuzemsky [2017](#page-45-10)), pointing to new directions for the search for physics beyond the known models.

Oreshkov and Cerf [\(2015](#page-46-36)) reconsidered the operational formulation of time reversal in quantum theory. It was widely believed that the most general symmetry transformations in quantum theory correspond to unitary or anti-unitary transformations on the Hilbert space (Kuzemsky [2017](#page-45-10); Belinfante [1975;](#page-42-11) Sachs [1987\)](#page-47-13), with symmetries involving time reversal being anti-unitary. This has profound implications for many phenomena, such as the classifcation of possible elementary particles. The joint transformation of charge conjugation, parity inversion, and time reversal, defned according to this principle, is considered an exact symmetry of all known physical laws. However, it has been recognized that Born's rule, which describes the probabilities for the outcomes of future measurements conditional on past preparations, does not apply for events in the reverse order. This is in confict with the very defnition of symmetry underlying the above assertions. Moreover, because the operational interpretation of a quantum state is directly linked to Born's rule, this raises doubts about whether the commonly accepted notion of a time-reversed state makes physical sense. Oreshkov and Cerf [\(2015](#page-46-36)) addressed this problem from a rigorous operational perspective, using the circuit framework for operational probabilistic theories, which has been shown to successfully formalize the informational foundations of quantum theory. The authors argued that reconciling time reversal with the probabilistic rules of the theory requires a generalized notion of operation, defned without assumptions on whether the implementation of an operation involves pre- or postselection. In this approach, operations are not expected to be up to the "*free choices*" of agents, but merely describe knowledge about the possible events taking place in diferent regions, conditional on information obtained locally. The authors developed the generalized formulation of quantum theory that stems from this approach and showed that it has a new notion of state space that is not convex. They formulated a precise defnition of time-reversal symmetry, taking into account the diferent nature of states and efects, which had been overlooked in previous treatments. As a result, the authors succeeded in proving an analog of Wigner's theorem, which characterizes all possible symmetry transformations in this time-symmetric formulation of quantum theory.

The irreversible behavior of a quantum-mechanical system was confrmed experimentally for the frst time by Batalhao et al. ([2015\)](#page-42-33). They found that thermodynamic irreversibility *persists in a quantum system*. Physicists have performed an experiment confrming that thermodynamic processes are irreversible in a quantum system—meaning that, even on the quantum level, you cannot reverse the process back. In the experiment, a sample of liquid chloroform $(CHCl₃)$ was placed at the center of a superconducting magnet inside a nuclear magnetic resonance magnetometer. Using a nuclear magnetic resonance setup, forward and reverse magnetic pulses were applied to the sample, which drives the carbon nuclear spins out of equilibrium and produces irreversible entropy. The authors measured the nonequilibrium entropy produced in an isolated spin-1/2 system following fast quenches of an external magnetic feld. It was demonstrated experimentally that it is equal to the entropic distance, expressed by the Kullback–Leibler divergence (Kuzemsky [2018\)](#page-45-4), between a microscopic process and its time reversal. These results may have implications for understanding thermodynamics in quantum systems and may be useful for quantum information technologies.

8 Boundary Conditions and Asymmetry of Time

It is known that diferent choices of boundary conditions imply diferent physical models and their solutions; For example, the Hamiltonian of a quantum particle confned to a box involves a choice of boundary conditions at the box ends. Similarly, in a concrete system, the arrow of time may be the result of the form of the Hamiltonian (an explicit time dependence of the Hamiltonian) and the initial (or boundary) conditions (e.g., the choice of an initial equilibrium state). This will lead to the breakage of time symmetry and specifying the direction of that arrow. As regards the cosmological arrow of time, there is consensus that its origin lies in the primordial singularity. This statement provides an appropriate formal framework. However, in the literature, discussion continues on the *natural boundary conditions* that may lead to the observed arrows of time. Zeh ([2007\)](#page-48-0) conjectures that *time asymmetry* lies in the initial (or fnal) conditions rather than in the dynamical laws.

Don Page ([1985](#page-46-37)) formulated his view on the asymmetry of time in the following words: "The temporal asymmetry of arrow of time of our world is one of the most striking facts of everyday experience and yet it is one of the deepest mysteries of physics ...It would be seem very to give a physical *explanation* for the asymmetry, because all of the fundamental dynamical law of physics discovered so far are time asymmetric in the sense of being CPT invariant ...Physics has given a description of the arrow of time in the form of the second law of thermodynamics: the entropy of the universe or of any of its subsystems which become approximately isolated increases with time ...However, it is generally agreed that this is not a fundamental dynamical law governing the microscopic evolution of the Universe but is rather a restriction on the boundary conditions which select the actual state for the universe from the many presumably allowed by the dynamical laws."

The previous discussion shows that boundary conditions play an important role in the microscopic description of the evolution of quantum-mechanical and statisticalmechanical systems. The *retarded solutions* play the special role in mathematical physics. Here we recall this by considering the formal scattering theory in quantum mechanics, which was formulated by Gell-Mann and Goldberger ([1953\)](#page-44-36). The formal scattering theory elucidates the very important question of how the limiting processes (making the dimensions $\mathcal L$ of the system go to infinity and making the parameter ϵ characterizing the switching on of the interaction go to zero) should be performed. What is remarkable is that the result depends on the order in which these limits are taken. The order of the same limits is also of a great importance in nonequilibrium statistical mechanics (Zubarev [1974;](#page-48-5) Kuzemsky [2007](#page-45-8), [2017\)](#page-45-10).

According to Gell-Mann and Goldberger ([1953\)](#page-44-36), in the quantum-mechanical description of scattering, the total Hamiltonian *H* of the colliding particles is divided into two parts *K* and *V*, where *K* is the Hamiltonian of the noninteracting particles and *V* is the interaction between them. It is assumed that V tends sufficiently rapidly to zero as the particles move apart. The quantity which should be calculated is the transition probability per unit time from one free state to another.

The complete system is described by the Schrödinger equation

$$
i\hbar \frac{\partial \Psi(t)}{\partial t} = (K + V)\Psi(t). \tag{36}
$$

An important feature of the problem is that the interaction *V* exists at *every moment of time*, although the scattering process occurs between states without interaction. In the absence of the interaction, the Schrödinger equation has the form

$$
i\hbar \frac{\partial \Phi(t)}{\partial t} = K \Phi(t),\tag{37}
$$

and its stationary solutions are

$$
\Phi_i(t) = \Phi_i e^{-\frac{iE_i t}{\hbar}}.
$$
\n(38)

It is necessary to calculate the diferential efective cross section of scattering from the state Φ_j to the state Φ_i under the influence of the interaction *V*. The initial state Φ_j is used for the characteristics of the true state Ψ_j of the real system. Knowing Ψ_j , we can find the probability that the system undergoes a transition to one of the final states Φ_i by the time t.

It is important to discuss the question of how to formulate correctly the scattering boundary conditions to the Schrödinger equation. Let one observe the scattering process at time $t = 0$. Then a physical procedure for preparing the quantum-mechanical state Φ_j up to time $t = 0$ when the transition occurs, i.e. for $t < 0$, must be formulated mathematically.

The most convenient boundary condition is that the wavefunction Φ_j for $t < 0$ is put equal to

$$
\Psi_j^{(\varepsilon)}(t) = \varepsilon \int_{-\infty}^0 e^{\varepsilon \tau} e^{-\frac{iH(t-\tau)}{\hbar}} \Phi_j(\tau) d\tau,
$$
\n(39)

where $\varepsilon \rightarrow +0$ at the end of the calculations. In the above formula a *time-smoothing* procedure was performed, since

$$
\varepsilon \int_{-\infty}^{0} e^{\varepsilon \tau} d\tau = 1, \tag{40}
$$

but the factor $e^{\epsilon\tau}$ distinguishes the *past*, and so the averaging [\(40\)](#page-36-0) has a "*causal*" character. In addition to the limit $\varepsilon \to +0$ another limiting process $\mathcal{L} \to \infty$ must also be performed (the functions Φ_i are normalized to unity in the large volume \mathcal{L}^3). The time \tilde{t} of switching-on the interaction is ε^{-1} on order of magnitude and cannot be greater than the time of propagation of the wave packet over a distance \mathcal{L} , i.e., than the quantity \mathcal{L}/v , where *v* is the group velocity,

$$
\varepsilon^{-1} \ll \mathcal{L}/v.
$$

Thus, when $\mathcal{L}^{-3} \to 0$ and $\varepsilon^{-1} \to \infty$, the quantity $\varepsilon^{-1} \mathcal{L}^{-3}$ must tend to zero. This means that we must first take the limit $\mathcal{L}^3 \to \infty$, and *then* $\epsilon \to +0$. Together with this rule for the limits $\mathcal{L} \to \infty$ and $\epsilon \to +0$, the condition [\(39\)](#page-36-1) ensures the *selection of the correct retarded causal solutions* of the Schrödinger equation. In fact, if $\varepsilon^{-1} < \mathcal{L}/v$, then waves reflected from the boundaries of the system, i.e., incoming waves, are excluded, since the extent of the wave train in time, ε^{-1} , is shorter than the time necessary for it to propagate over the distance \mathcal{L} . The great convenience of the boundary condition [\(39\)](#page-36-1) lies in the fact that the causality condition is imposed more automatically, without a detailed analysis of the outgoing waves. It is clear that its meaning also consists in the selection of the *retarded solutions*. It can be shown (Gell-Mann and Goldberger [1953](#page-44-36)) that the boundary conditions for the quantum-mechanical collision problem can be formulated by means of the introduction of infnitesimally small sources selecting the *retarded* solutions of the Schrödinger equation. The boundary conditions selecting the retarded solutions of the Schrödinger equation in formal scattering theory (Gell-Mann and Goldberger [1953](#page-44-36)) can be obtained if one introduces into it, for $t \leq 0$, an infinitesimally small source violating the symmetry of the Schrödinger equation with respect to time reversal

$$
\frac{\partial \Psi_{\varepsilon}(t)}{\partial t} - \frac{1}{i\hbar} H \Psi_{\varepsilon}(t) = -\varepsilon (\Psi_{\varepsilon}(t) - \Phi(t)),\tag{41}
$$

where $\epsilon \rightarrow +0$ after the volume of the system tends to infinity, and $\Phi(t)$ is the wavefunction of the free motion of the particles, with Hamiltonian *K*. The infnitesimally small source has been introduced in such a way that it is equal to zero when $\Psi(t) = \Phi(t)$, i.e., in the absence of the interaction. It does indeed violate the symmetry of the Schrödinger equation with respect to time reversal, since in this transformation the left-hand side of Eq. ([41](#page-37-0)) changes sign while the right-hand side remains unchanged. The sign of ϵ is chosen so that we obtain the *retarded* rather than *advanced* solutions.

It is possible to rewrite Eq. (41) (41) in the form

$$
\frac{d}{dt}\left(e^{\varepsilon t}\Psi_{\varepsilon}(t,t) = \varepsilon e^{\varepsilon t}\Phi(t,t)\right),\tag{42}
$$

where

$$
\Psi_{\varepsilon}(t,t) = e^{-Ht/i\hbar} \Psi_{\varepsilon}(t), \, \Phi(t,t) = e^{-Ht/i\hbar} \Phi(t). \tag{43}
$$

Integrating this expression from $-\infty$ to *t*, we have

$$
\Psi_{\varepsilon}(t) = \varepsilon \int_{-\infty}^{t} d\tau e^{\varepsilon(\tau - t)} e^{-H(\tau - t)/i\hbar} \Phi_{\varepsilon}(\tau)
$$
\n
$$
= \varepsilon \int_{-\infty}^{t} d\tau e^{\varepsilon \tau} e^{-H\tau/i\hbar} \Phi((t + \tau)).
$$
\n(44)

Putting $t = 0$, we obtain the scattering-theory boundary condition in the Gell–Mann–Goldberger form

$$
\Psi_{\varepsilon}(0) = \varepsilon \int_{-\infty}^{t} d\tau e^{\varepsilon \tau} e^{-H\tau/i\hbar} \Phi(\tau). \tag{45}
$$

A boundary condition analogous to Eq. ([45](#page-37-1)) may be applied to the Liouville equation for the description of nonequilibrium processes (Zubarev [1974](#page-48-5); Kuzemsky [2007,](#page-45-8) [2017](#page-45-10)). The

quantum Liouville equation, like the classical one, is symmetric under time-reversal transformation. However, the solution of the Liouville equation is unstable with respect to small perturbations violating this symmetry of the equation. Let us consider the Liouville equation with an infnitesimally small source on the right-hand side

$$
\frac{\partial \rho_{\varepsilon}}{\partial t} + \frac{1}{i\hbar} [\rho_{\varepsilon}, H] = -\varepsilon (\rho_{\varepsilon} - \rho_q) \tag{46}
$$

or equivalently

$$
\frac{\partial \ln \rho_{\varepsilon}}{\partial t} + \frac{1}{i\hbar} [\ln \rho_{\varepsilon}, H] = -\varepsilon (\ln \rho_{\varepsilon} - \ln \rho_{q}), \tag{47}
$$

where ($\epsilon \to 0$) after the thermodynamic limit. Equation [\(46\)](#page-38-0) is analogous to the corresponding equation of quantum scattering theory. The introduction of infnitesimally small sources into the Liouville equation is equivalent to the boundary condition

$$
e^{\left(\frac{iHt_1}{\hbar}\right)}\left(\rho(t+t_1) - \rho_q(t+t_1)\right)e^{\left(\frac{-iHt_1}{\hbar}\right)} \to 0,\tag{48}
$$

where $t_1 \rightarrow -\infty$ after the thermodynamic limiting process. It was shown (Zubarev [1974;](#page-48-5) Kuzemsky [2007,](#page-45-8) [2017](#page-45-10)) that the operator ρ_{ε} has the form

$$
\rho_{\varepsilon}(t,t) = \varepsilon \int_{-\infty}^{t} dt_1 e^{\varepsilon(t_1-t)} \rho_q(t_1,t_1) = \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \rho_q(t+t_1,t+t_1).
$$
 (49)

Here the first argument of $\rho(t, t)$ is due to the indirect time dependence via the parameters $F_m(t)$, while the second one is due to the Heisenberg representation. The required nonequilibrium statistical operator is defned as (Zubarev [1974;](#page-48-5) Kuzemsky [2007,](#page-45-8) [2017\)](#page-45-10)

$$
\rho_{\varepsilon} = \rho_{\varepsilon}(t,0) = \overline{\rho_q(t,0)} = \varepsilon \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} \rho_q(t+t_1,t_1)
$$
\n(50)

Here, ρ_a is the quasiequilibrium statistical operator. Hence, the nonequilibrium statistical operator can then be written in the form (Zubarev [1974;](#page-48-5) Kuzemsky [2007](#page-45-8), [2017](#page-45-10))

$$
\rho = Q^{-1} \exp \left(- \sum_{m} \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \left(F_m(t + t_1) P_m(t_1) \right) \right)
$$

= $Q^{-1} \exp \left(- \sum_{m} F_m(t) P_m + \sum_{m} \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \left[\dot{F}_m(t + t_1) P_m(t_1) + F_m(t + t_1) \dot{P}_m(t_1) \right] \right).$ (51)

The method of the nonequilibrium statistical operator is a very useful tool to analyze and derive generalized transport and kinetic equations (Zubarev [1974;](#page-48-5) Kuzemsky [2017,](#page-45-10) [2007](#page-45-8), [2018\)](#page-45-11). In the work of Kuzemsky [\(2017](#page-45-10), [2007](#page-45-8), [2018](#page-45-11)), the generalized kinetic equations for the system weakly coupled to a thermal bath have been derived. The aim was to describe the relaxation processes in two weakly interacting subsystems, one of which is in the nonequilibrium state and the other is considered as a thermal bath. We took the quasiequilibrium statistical operator ρ_q in the form

$$
\rho_q(t) = \exp(-S(t, 0)), \quad S(t, 0) = \Omega(t) + \sum_{\alpha \beta} P_{\alpha \beta} F_{\alpha \beta}(t) + \beta H_2.
$$
 (52)

Here, $F_{\alpha\beta}(t)$ are the thermodynamic parameters conjugated with $P_{\alpha\beta}$, and β is the reciprocal temperature of the thermal bath; $\Omega = \ln \text{Tr} \exp(-\sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) - \beta H_2)$. The nonequilibrium statistical operator in this case has the form

$$
\rho(t) = \exp(-\overline{S(t,0)}); \quad \overline{S(t,0)} = \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \left(\Omega(t+t_1) + \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) + \beta H_2 \right).
$$
\n(53)

The parameters $F_{\alpha\beta}(t)$ are determined from the condition $\langle P_{\alpha\beta} \rangle = \langle P_{\alpha\beta} \rangle_a$.

In the derivation of the kinetic equations, we used the perturbation theory in a *weakness of interaction*. The kinetic equations for $\langle P_{\alpha\beta} \rangle$ were derived in the form (Kuzemsky [2017](#page-45-10), [2007,](#page-45-8) [2018\)](#page-45-11)

$$
\frac{d\langle P_{\alpha\beta}\rangle}{dt} = \frac{1}{i\hbar}(E_{\beta} - E_{\alpha})\langle P_{\alpha\beta}\rangle - \frac{1}{\hbar^2} \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} \langle \left[[P_{\alpha\beta}, V], V(t_1) \right] \rangle_q.
$$
 (54)

The last term on the right-hand side of Eq. [\(54\)](#page-39-0) can be called the generalized *collision integral*. Thus, we can see that the collision term for the system weakly coupled to the thermal bath has the convenient form of a double commutator. It should be emphasized that the assumption about the model form of the Hamiltonian of a system (H_1) interacting with a thermal bath (H_2) $H = H_1 + H_2 + V$ is not essential to the derivation (Kuzemsky [2017,](#page-45-10) [2007,](#page-45-8) [2018\)](#page-45-11). Equation ([54](#page-39-0)) will be fulflled for a general form of the Hamiltonian of a small system weakly coupled to a thermal bath.

The change of the entropy during the evolution of the small subsystem to equilibrium has the form

$$
S = -\langle \ln \rho_q \rangle = \beta \langle H_2 - \mu_2 N_2 \rangle + \sum_{\alpha \beta} F_{\alpha \beta}(t) \langle P_{\alpha \beta} \rangle - \ln Q_q. \tag{55}
$$

After diferentiation with respect to time *t*, we obtain

$$
\frac{dS}{dt} = \beta \langle J_2 \rangle + \sum_{\alpha \beta} F_{\alpha \beta}(t) \frac{d \langle P_{\alpha \beta} \rangle}{dt}.
$$
 (56)

Now, we substitute into this equation the expression

$$
J_2 = \frac{1}{i\hbar} [(H_2 + V), H].
$$
\n(57)

We then obtain

$$
\frac{dS}{dt} = \sum_{\alpha\beta} X_{\alpha\beta}(t) \frac{d\langle P_{\alpha\beta} \rangle}{dt},\tag{58}
$$

which is the standard expression for the entropy production in terms of the thermodynam-ics of irreversible processes (Zubarev [1974;](#page-48-5) Kreuzer [1981;](#page-45-6) Keizer [1987](#page-45-7)). Here, $X_{\alpha\beta}$ is the generalized "*thermodynamic force*."

9 Concluding Remarks

We have presented a concise review of some sophisticated ideas and approaches to treat the problem of time and its asymmetry in thermodynamics, statistical mechanics, and quantum mechanics. We have brought together various points of view on the problems of time and its asymmetry, presented from the standpoint of their consistency and universality. Because of the nature of such a burning issue, various preliminary and complementary sections were added to ensure a self-contained presentation. The aim is to show the inseparable connections between the notions of time and its asymmetry, entropy and its production, and the second law of thermodynamics. We devoted close attention to the important concept of the *t*−invariance of a process, since it connects with the notions of irreversibility and the arrow of time.

In spite of the great progress in the area of nonequilibrium statistical mechanics (Bogoliubov [1962](#page-42-27); Zubarev [1974;](#page-48-5) Kuzemsky [2017](#page-45-10); Lebowitz [1999;](#page-46-9) Goldstein et al. [2010](#page-44-33); Dorfman [1999;](#page-43-20) Zwanzig [2001](#page-48-18); Gallavotti [2014](#page-44-25); Mackey [1989](#page-46-38), [1992](#page-46-19); Sklar [1993;](#page-47-32) Kuzemsky [2018,](#page-45-11) [2019](#page-45-38)), we are still unable to trace irreversibility back to its root origin. Landau and Lifshitz ([1980\)](#page-45-23) expressed it in these words: "...it is not at present clear if ...it is possible to deduce the law of entropy increase from classical mechanics." However, the second law of thermodynamics still holds frm in its domain of validity (Bogoliubov [1962](#page-42-27); Mackey [1989;](#page-46-38) Coveney and Highfeld [1991;](#page-43-15) Mackey [1992](#page-46-19); Sklar [1993;](#page-47-32) Callender [2004](#page-43-32); Henderson [2014\)](#page-44-27).

We also tried to manifest that a solid proving ground for a sophisticated discussion on the problem of time and its asymmetry is highly desirable, since we do not yet have a "universal theory of time." Denbigh, in his essay review (Denbigh [1996\)](#page-43-3) in the book *Time's Arrows Today* (Savitt [1995](#page-47-2)), attracted the reader's attention to Wittgenstein's statement in his *Tractatus*: "The description of the temporal sequence of events is only possible if we support ourselves on another process." It is important to note that the second law of thermodynamics allows such "another process," viz. the process of entropy increase. Hence such a thermodynamic variable, i.e., the entropy, may be used to indicate the lapse of time.

In this context, it is worth mentioning that time is the form of our sentient being; we know no other. Indeed, language as the human method of communication of knowledge, ideas, feeling, etc. sues a system of sound (or other) symbols. Language thus implies in a deepest sense the notion of time. Time is an inherent component of grammatical structure and is the immanent quality of language. A grammar is impossible without verbs and starts with a defnition what a verb is. Verb is a word showing what a person or thing does, what state he or it is in, or what is *becoming* of him or it. According to context, verbs can be described as words denoting *action*. The term "action" embraces the meaning of activity, process, relation, etc. Action is the process of doing things. It is a way of using *energy*, infuence, etc. The expression "the time has come for action" means a signal to begin to act. English verbs fall into two groups: the *dynamic* verbs and the *static* verbs.

In physics, action is a basic concept related with motion. Classical mechanics describes how a mechanical system evolves in time *t*. To achieve this aim, it is useful to defne the state of a given system as a set of variables that completely specifes the condition of the considered system at a moment in time. Thus, the state of a system in symbolic form is {state} = { q, \dot{q} } = {position, velocity}. For a system of *N* particles, the Lagrangian can be written as

$$
\mathcal{L} = \mathcal{L}(q_k, \dot{q}_k, t) = \frac{1}{2} \sum_{k} m_k \dot{q}_k^2 - U(q_1, q_2, \dots q_k, \dots q_N, t).
$$
 (59)

The generalized coordinates can have diferent physical meanings (length, angle, etc.), but the Lagrange function always has the dimension of energy. The number of generalized coordinates equals the number of degrees of freedom of the system. Note that, in classical mechanics, time *t* and the Hamiltonian *H* are not canonically conjugate variables.

Dynamics operates based on a fundamental notion of classical mechanics, viz. the action function A, which is defned as

$$
\mathcal{A} = \int_{t_1}^{t_2} \mathcal{L}(q_k, \dot{q}_k, t) dt.
$$
 (60)

Thus, the action is an integral associated with the trajectory of a system in confguration space, equal to the sum of the integrals of the generalized momenta of the system with respect to their canonically conjugate coordinates. The action functional $A[q(t)]$ is symmetric with respect to time because the Lagrangian $\mathcal L$ does not depend explicitly on t . This symmetry in time implies energy conservation. It is worth noting that the action function has the dimension of energy times time.

The simplest dimensional analysis (Bridgman [1963](#page-42-20); Gibbings [2011\)](#page-44-23) yields the relation

$$
t \sim \frac{\text{Action}}{\text{Energy}}.
$$

As a simplest illustration, we take the minimal possible action, the Planck constant *h*, and obtain

$$
t \sim \frac{h}{h\nu} \sim \frac{\hbar}{\hbar\omega} \sim \frac{1}{\omega}.
$$

Hence, in physics, time in a way is a manifestation of a *cyclic* process.

We demonstrated above that there are numerous natural processes that manifest nontrivial temporal behavior and irreversibility. However, the ontological nature of time remains unknown, although its infuence and consequences are evident. What we can carry out are measurements of time with the aid of universal cyclic processes using various advanced methods.

Bunge ([1972\)](#page-42-34) discussed long ago "the alleged reduction of thermodynamics to statistical physics." He concluded that: "Thermodynamics as a whole, and particularly the 2nd law, which is its most distinctive feature, has not been reduced to particle mechanics—nor, for that matter, have been fuid dynamics, the mechanics of deformable bodies, and other branches of continuous physics. *The reduction of thermodynamics is not a fact but a programme*." This conclusion coincides with the author's position. For a complementary point of view, see the paper by Callender ([1999\)](#page-43-33).

Although our study may be incomplete (because of lack of space), it is hoped that the reader with a keen interest in the problem will consult the papers cited to fnd references to works and opinions omitted here.

In summary, our analysis shows that there are a number of important and interesting questions concerning the nature of time, its asymmetry, and irreversibility. *The time has come for action*.

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