

# The origin of irreversibility and thermalization in thermodynamic processes

Emil Roduner\*, Institute of Physical Chemistry, University of Stuttgart, D-70569 Stuttgart, Germany, and  
Department of Chemistry, University of Pretoria, Pretoria 0002, Republic of South Africa  
(e.roduner@ipc.uni-stuttgart.de)

Tjaart P. J. Krüger, Department of Physics, University of Pretoria, Pretoria 0002, Republic of South Africa

## ABSTRACT

Understanding the origin of irreversibility in thermodynamics has been a fundamental scientific challenge and puzzle for nearly a century. Initially, the discussions related to classical thermodynamic systems, but recently quantum systems became the main focus. Explanations have often been sought by reference to classical equations of motion, which are time-reversible. We conjecture that the origin of irreversibility lies in energy dissipation, a term that is at the core of the Second Law of thermodynamics. However, thermodynamic irreversibility is distinct from time-irreversibility. A system in thermodynamic equilibrium may have reached this state via a deterministic, integrable and therefore time-reversible process, or, alternatively, via an irreversible route, both resulting in thermodynamically indistinguishable states. The process with time-reversible history may become irreversible by a process called thermalization, which occurs when the system loses memory of its history without the necessity of energy dissipation. Quantum systems do this by losing phase coherence; for classical systems the decoherence is at zero frequency, due to loss of time correlation. More generally, not only equilibrium systems may have lost memory of their history. A common cause of memory loss are probabilistic/stochastic events, which are not deterministic and take place only with a certain probability at any given time. In contrast to thermalization, equilibration involves energy dissipation within a system or to the surroundings or by decrease of concentration of the system. Time-reversibility is not related to system size, and the fluctuation theorem is a probabilistic and not a deterministic phenomenon and therefore not suited to provide an understanding of the irreversibility of time in thermodynamic systems. There are also processes which are both dissipative and probabilistic, such as the radiative or non-radiative decay of electronically excited states. Dissipation of a given energy into multiple smaller energy quanta (heat) is by itself not fully reversible for kinetic reasons. It is kinetically a first-order probabilistic process, whereas the reverse is a second- or higher-order process. Thermodynamics provides empirical laws, developed for conventional matter as we know it on planet Earth and in our laboratories. Of relevance here is the Second Law, also called the arrow of time, stating that spontaneous processes take place for isolated systems with increasing entropy. It is assumed to hold also for the universe as a whole. However, over the distances of individual galaxies, self-gravitation leads to conditions where the kinetic energy of the system decreases while the total energy increases, pretending negative heat capacity, and it allows the formation of black holes. This requires an extension of the Second Law. This review aims at presenting an overarching tutorial clarification of the subject.

Keywords:

Thermodynamic equilibration is independent of time-reversibility;

Equilibration and the arrow of time are related to dissipation of heat or the decrease of concentration;

Thermalization is distinct from equilibration and reflects the loss of memory and thus of time-reversibility;

A common cause of the loss of time-reversibility are probabilistic events;

Time-irreversibility is reflected by quantum decoherence and by classical loss of spatial correlations;

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## 1. Introduction

The equations of motion in Newton's classical mechanics are symmetric with respect to time reversal. Maxwell's equations of electromagnetism, Einstein's equations of special and general relativity and Schrödinger's original equations of quantum mechanics are also time-reversible, and therefore deterministic and (time)integrable, meaning that for a known equation of motion the system is fully defined for each point in the future and in the past.

Such a picture may be useful for simplified model systems but is clearly incompatible with the real world. Thus, these time-reversible equations provide an incomplete description of real processes.

In the absence of friction, a pendulum will interconvert potential and kinetic energy infinitely in an oscillatory manner. The pendulum can be seen as a classical analogue of a quantum coherence. In contrast, any thermodynamic process occurs in a single direction towards equilibrium where it comes to rest, although non-linear (auto-catalytic) feedback in the kinetic equations may lead to transient oscillating concentrations [1,2] while the free energy of the entire system nevertheless approaches its equilibrium value monotonously.

Irreversible thermodynamic processes, whether spontaneous or driven (forced), are dictated by the Second Law, also called the “arrow of time”, based on the entropy of an isolated system that never decreases but increases until equilibrium is reached, while the total energy is nevertheless conserved within the range given by the Heisenberg uncertainty relation. Surely, there must be a smooth transition from a reversible classical or quantum-mechanical description to an irreversible thermodynamic description of a system, but how this happens has puzzled generations of scientists [3-6]. Implying that reversibility has to do with the size of the system, Jarzynski [7] formulated the core question similar to Lebowitz [6] as follows: “How can microscopic equations of motion that are symmetric with respect to time reversal give rise to macroscopic behavior that clearly does not share this symmetry?” We suggest here that this is perhaps not the adequate question, and that one should instead ask, “Why are dissipation and decoherence not time-reversible?” Ever since Eddington coined the term “arrow of time” to describe the direction of dissipation [8] numerous investigators who were possibly misled by this term have focused on the mathematical description of the original time-reversible equations in their search for an explanation of irreversibility of thermodynamic systems [9-11] and they ignored the nature of dissipation and decoherence, which are the true cause of thermodynamic irreversibility.

*Dissipation of heat* that occurs spontaneously from a warmer to a colder part of the system or to the surrounding is the key term in the Second Law. The Newtonian equations of motion are based on very general concepts of distance, time and mass, essentially pretending to first principles. To accommodate irreversibility, one can add empirical terms that represent dissipation. This seems an adequate strategy to build a bridge to the real world, since the laws of thermodynamics are also fully empirical and not based on first principles.

The aim of this review is to bring various floating aspects on the topic together under an overarching view and in a didactical manner, without attempting to be comprehensive. We suggest that the focus should not be on the mathematical treatment of time-reversal symmetry and the arrow of time but more directly on the nature of decoherence and dissipation and the low probability to reverse them. To develop the picture, we shall in Chapter 2 first revisit a number of fundamentals, introducing the main concepts and some nomenclature. Chapter 3 compares two descriptions of an equilibrium system of a monoatomic gas, the kinematic Maxwell-Boltzmann (MB) ensemble of a monoatomic gas and the photonic system of Planck’s hollow black body. Since such a system has only a single equilibrium that must be conserved during both collisional energy transfer and photon absorption and emission, the two pictures are complementary. This is the origin of the equivalence of energy in the form of heat and of photons. Chapter 4 outlines two variants of a Gedankenexperiment in which two MB systems at different temperatures are equilibrated, one under retention of time-reversibility of a Newtonian system and the other one with broken time-reversibility. This reveals that equilibration depends neither on time-reversibility nor on the size of the system. The conclusion is supported by a discussion of two further processes,

the expansion of an ideal gas into empty space and the interdiffusion of different particles upon removal of a partition. Both processes are spontaneous but occur without heat dissipation. Chapter 5 deals with dissipation, heat death and the entropy of the universe, including the surprising finding that the Second Law needs an extension for the description of systems with negative heat capacities. Chapter 6 discusses the probabilistic and irreversible nature of dissipation. Chapter 7 concentrates explicitly on irreversibility and thermalization in real and in isolated quantum systems. Biological evolution of life, introduced in Chapter 8, also appears to be to a large extent a directed, irreversible process, although not related to the thermodynamic Second Law. The final Chapter summarizes the main take-home messages.

## 2. Fundamentals

### 2.1 Tools for the description of matter and processes

Neglecting electromagnetism, the prominent traditional tools for the description of matter are classical Newtonian mechanics, thermodynamics and quantum mechanics. They are based on fundamentally different concepts and related to each other only to a limited extent. It may be possible to describe a small sample of matter by all of these tools. Each of them provides different insight that is complementary to that of the others, but there is often no seamless transition between them.

#### 2.1.1. Newtonian mechanics

*Classical mechanics* describes the motion of macroscopic objects under the influence of forces. Solving Newton's equations of motion requires knowledge of the initial coordinates and velocity (or momentum) vectors of all involved bodies as well as all interacting forces between them and all external forces, e.g. gravity. An important parameter is time but usually not temperature.

*Molecular dynamics (MD)* and *molecular mechanics (MM)* is a numerical simulation method that is mainly based on classical Newtonian mechanics. The vast development of computer capacity and speed of calculations allows calculating large systems consisting of billions of particles [12] based on Newtonian mechanics and empirical, classical, time-independent force fields describing interatomic and intermolecular interactions [13]. The positions of all particles and the corresponding energy are calculated iteratively over hundreds of nanoseconds in time steps of typically one femtosecond from a chosen starting configuration until equilibrium is reached. The method has a broad range of applications. For example, it can be used to visualize the dynamics of liquids, and the structure of biomolecules. MD is a numerical version of classical mechanics for a multi-body system, but it is not so much the dynamics of the individual bodies that is of interest; rather, one would like to know the structure (coordinates) at equilibrium and the thermodynamic parameters at different temperatures which are also accessible. MD thus has the advantage that it provides bulk properties based on an atomic or molecular picture.

#### 2.1.2. Thermodynamics (TD)

Exact solutions of the classical equations of motion are possible for two-body systems; more bodies can be treated approximately. However, knowing the initial conditions of all participating bodies and handling their individual motion becomes extremely complex already for very few bodies. Macroscopic amounts of atomic or molecular matter in a solid, liquid or gaseous state are therefore described by means of *classical thermodynamics*. It neglects the information of the individual particles and describes only their ensemble average in thermal equilibrium. Parameters describing

the systems are the state functions pressure, volume, temperature (reflecting kinetic energy of thermal random motion), composition, internal energy, and entropy, but time is normally excluded.

*Statistical thermodynamics* builds a bridge between bulk thermodynamic properties of materials and the properties of its constituting atoms or molecules. In *quantum statistical thermodynamics* the properties are based on molecular data derived from spectroscopy or calculated by quantum chemical methods. It accepts that the bulk material consists of atoms and molecules and assumes that the bulk properties can also be found as the sum of molecular properties plus their interactions. Each molecule can occupy dynamically a large number of translational, rotational, vibrational and electronic states. This assumes that there is a most probable state in the ensemble average that dominates the behavior to an extent that other states can be neglected already for a relatively small system. The probability that this state is occupied is given by the Boltzmann distribution, or at low temperature by the Fermi-Dirac or the Bose Einstein distributions. Statistical thermodynamics assumes that the system changes its microstate energy stochastically, spontaneously or prompted by collisions. Like classical thermodynamics, it is also not time-reversible.

The *ergodicity theorem lies at the basis of statistical mechanics*. It states that the long-time average of a randomly fluctuating property of an individual subsystem (atom, molecule) is identical to the ensemble average of a large number of identical subsystems at any given time. The mismatch between the two expectation values decreases exponentially with time while the degree of equilibration increases. It is commonly expected that the ergodic theorem holds for most interacting systems. However, it should be stressed that many exceptions are known [5]. For example, a one-dimensional chain of anharmonic oscillators shows no or extremely slow equilibration.

Also central is the *H-theorem* that goes back to Boltzmann and requests a tendency of the ensemble of states to evolve towards maximum entropy, as required by the Second Law [6,14].

### 2.1.3. Quantum mechanics (QM)

A Hamiltonian containing exact coordinates is typically defined for single electrons in the effective field of the other electrons and the nuclei of the system, and then extended to many-electron systems. The *Schrödinger equation* (SE) is solved for single-electron wave functions in the effective potential of the other particles. However, since it is impossible to know the initial coordinates and velocity (or momentum) vectors simultaneously, the time dependence is usually separated off, and only the *time-independent Schrödinger equation* is solved for a set of eigenenergies  $E_i$  (for bound systems) and wave functions,  $\psi_i$ . This reduces the number of variables per particle from six to three.  $|\psi_i|^2$  is the observable property, a time-averaged distribution function, called the probability distribution of particle  $i$ . Historically, the interpretation of the wave function caused intense debates. Einstein called it *incomplete* [15]. It was Bohm who resolved the issue, regarding the systems as ensembles with unknown position and momentum of individual particles, which he termed "hidden variables" [16].

It is often overlooked that already Heisenberg pointed out that in analogy to classical theories "as long as the phase of the atom is not known the position of an electron can be given only as a probability" [17]. The unknown phase is equivalent to Bohm's "hidden" variable. Nevertheless, von Neumann claimed to have disproved the

necessity of hidden variables [18], but Hermann [19], and later Bell trashed this attempt on the ground of a faulty assumption [20]. Non-local hidden variables, represented by random numbers for the phase constants of wave packets, are still promoted [21].

For sufficiently simple systems where the initial conditions of position and momentum are known and which can even be prepared experimentally, the full solution can be calculated exactly as a trajectory. With this aim, Dirac and later Feynman formulated an alternative view of quantum mechanics, the *path integral method*, stating “A probability amplitude is associated with an entire motion of a particle as a function of time, rather than simply with a position of the particle at a particular time.” [22]. The time integral of the classical Lagrangian along the path is a function of velocity and position of a point-like quantum particle and is an explicit function of time. Feynman demonstrated that considering *all possible paths* that a particle can take between two given positions leads to a description that satisfies the Schrödinger equation.

The above methods view matter from quite different angles. It is a dream to put them all on the same foundation and obtain a unified theory for the description of matter. The most important impediment to this is the understanding of how time-reversible systems transform into time-irreversible ones. Classical mechanics and quantum mechanics in their original forms, i.e. in the absence of added dissipative terms (Section 2.4), are time-reversible and therefore deterministic. Thermodynamics is by definition not time-reversible due to the dissipative term that is included in the Second Law (see Section 2.5).

Originally, *statistical thermodynamics* was formulated by Gibbs as a landmark new theory describing the relation between the macroscopic and the microscopic point of view of complex *classical* systems [23]. However, as soon as quantum mechanical descriptions had been established, the theory was extended by von Neumann to *quantum statistical thermodynamics* [24].

A rough overview of the main methods and their typical parameters is given in Table 1. The methods are being developed further in various directions. A hybrid method that has become quite valuable for complex systems treats the center of interest, e.g. a catalytic center, and its immediate surrounding by high accuracy QM methods and the remaining environment by less accurate MM.

Table 1: Typical parameters, reversibility and equilibration properties of common methods for the description of matter near equilibrium

Method	Typical parameters		Time-reversible	Equilibration
	Few body systems	Many body ensembles		
<b>Newtonian mechanics</b> <sup>a)</sup>				
Classical mechanics	$\mathbf{r}_i(t), \mathbf{v}_i(t)$		✓	--
Molecular dynamics		$\langle E(t) \rangle, \langle S(t) \rangle$	✓	✓
<b>Thermodynamics (TD)</b>				
Classical TD (bulk)		$p, V, T, E, S$	--	✓
Statistical TD (ensemble)		$\langle p \rangle, \langle V \rangle, \langle T \rangle, \langle E \rangle, \langle S \rangle$	--	✓
<b>Quantum mechanics</b> <sup>a)</sup>				
Time-independent SE <sup>b)</sup>	$\langle E_i \rangle, \langle  \psi_i ^2 \rangle$		✓	--
Time-dependent SE <sup>c)</sup>	$\mathbf{r}_i(t), \mathbf{v}_i(t), E(t)$		✓	--

<sup>a)</sup> No empirical dissipating term included

<sup>b)</sup> Time separated off. Coordinates and velocities are “hidden variables”.

c) Path integral method

## 2.2 Reversibility and system size

Classical mechanics was historically restricted to treat small systems consisting of two particles or by approximate methods to very few-body cases, such as the solar planetary system. Thermodynamics, on the other hand, was defined for bulk matter. Time was not one of the central parameters, and reversibility was not used with respect to time but to energy. Already in 1852, William Thomson (later knighted and entitled Baron Kelvin of Largs) reported an imbalance in the transformation of energies and in this context coined the term “dissipation” [25]. He expressed this as follows: “When heat is created by any unreversible process (such as friction), there is a dissipation of mechanical energy, and a full restoration of it to its primitive condition is impossible”, a fact that was confirmed by Carnot and Clausius.

In attempts to pin down the reversibility problem, the focus has often been on the size of the system, inferring that microscopic systems are time-reversible, while macroscopic ones are not [6,26,27]. The emphasis on the importance of size for the Second Law of Thermodynamics goes back to as far as Maxwell who pointed out that it is continually being violated in small groups of molecules [28]. On the same ground, this aspect has been discussed more recently using the fluctuation theorem that permits short time reversals away from equilibrium, and statistical thermodynamics predicts that this is more likely to occur in small systems since the probability of a short time reversal decreases exponentially with the number of degrees of freedom in the system [7,29-31]. Einstein was the first to investigate fluctuation phenomena which must exist if the statistical interpretation of the Second Law is sound [32]. Thermodynamic equilibria are generally dynamic, with equal rates for the forward and the backward reactions. This implies a stochastic, microscopic kinetic reversibility and is inconsistent with a deterministic and full reversibility.

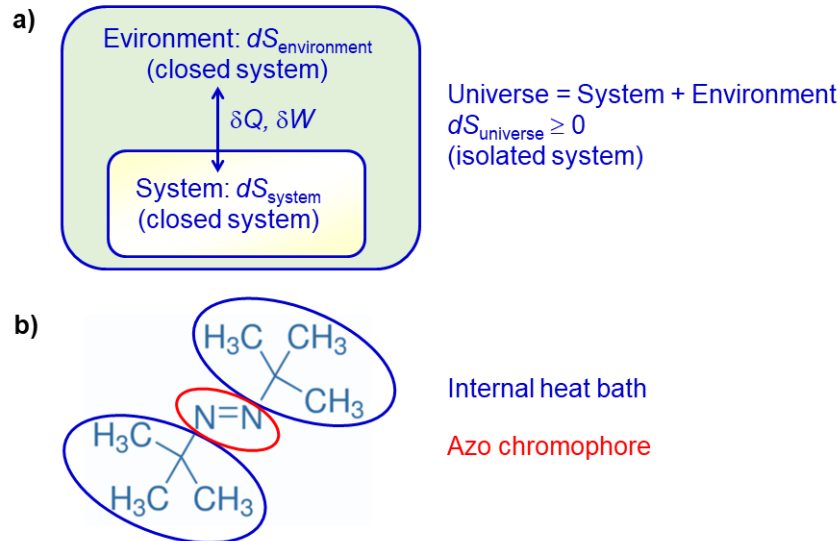
The more recent field of quantum thermodynamics tries to reconcile the 200 years old laws of thermodynamics with the laws of quantum mechanics, with the intention to build macroscopic (bulk) systems from small systems of quantum nature. The question is “whether the fundamental laws that govern heat and energy on large scales also dictate the behavior of nanoscale systems – or whether new laws are needed” [33]. The independence of system size will be further addressed in Section 4.2.

## 2.3 Thermodynamic systems and ensembles

It is customary in thermodynamics to define a *system*, which is the minimum part of the universe that is sufficient to describe the issues of interest in the given context. It may be as small as a molecule or just a particle. It is embedded in its *environment*, consisting of the entire “universe” with the exception of the system (Figure 1a). The universe is an *isolated system* that can change neither its mass nor its energy content, while its entropy is constant in equilibrium but increases for any spontaneous process in conventional, non-self-gravitating systems. In contrast, a system that can exchange energy but not mass with its environment is called *closed*, and a system that can exchange both energy and mass is called *open*. The environment is a heat bath with an infinite capacity so that it does not change its temperature when it absorbs heat from the system or delivers heat to it. Distinguishing properly between a closed system and the universe is essential for avoiding confusions that are frequent in literature.

Of high current interest to reach an understanding of the origin of irreversibility are quantum many-body systems which can still be handled theoretically and serve as models, bridging the size between small analytically integrable Newtonian and bulk thermodynamic systems (Figure 1b).





**Figure 1:** a) A thermodynamic system is embedded in its environment. Together they form an isolated system, commonly called the universe. b) Isolated quantum many body system, represented here by the 2,2'-azobis-(2-methyl-propan) molecule, where the azo group is a chromophore that may be excited and the two isopropyl groups act as the internal heat bath. (color online)

In statistical descriptions of matter the systems are described from the viewpoint of a collection of  $N$  individual particles, called ensembles. The analog of the isolated system is the *microcanonical ensemble*  $Z(NVU)$ , which is defined to be at a fixed internal energy  $U$  and volume  $V$ . Its equilibrium state corresponds to its maximum entropy  $S$ . Alternatively, one talks about *canonical ensembles*  $Z(NVT)$ , which are the analog of closed systems at constant temperature because of their embedding in a large heat bath. A third system is the *grand canonical ensemble*  $Z(\mu VT)$ , which is open and can exchange particles with the surrounding. Instead, its chemical potential  $\mu = G/N$  is fixed, where  $G$  is the Gibbs free energy, and its equilibrium state is defined by the minimal value of  $\mu$ .

#### 2.4 The origin of dissipation

No physical system can be completely isolated from its surrounding environment and therefore exchanges energy and/or particles with its environment. This exchange of energy often occurs during processes involving partial interconversion of different forms of energy, for example between heat and work, or the unwanted heat generated in an electrical circuit (Joule heating). Usually, the heat is transferred to or from a heat bath, and since it is accompanied with a loss, it is an irreversible process that is called *dissipation*. The increase of the entropy of the universe is the driving factor of all irreversible, spontaneous and driven processes, and it is the key to understanding irreversibility in thermodynamic systems.

Dissipation can also relate to the nonradiative relaxation of an excited electronic state of a molecule by redistributing the excitation energy among vibrational and rotational states of the electronic ground state. Recently, a non-contact cryogenic scanning probe microscopy technique based on a superconducting quantum interference device (SQUID) positioned on a sharp tip has been reported to provide thermal sensing for imaging of dissipation in quantum systems with nanoscale resolution at four orders of magnitude higher sensitivity than previous devices [34].

The entropy of an isolated system can also increase without dissipation of heat. Entropy increases with decreasing concentration (increasing volume) or by mixing/interdiffusion of

different compounds. In analogy with dissipation of heat this may be called dissipation of matter, where the system particles are redistributed in a broader volume. Since this type of dissipation is to a good approximation, the part of the universe surrounding the system is not involved (see also the discussion below in context with eqns. 7 and 8).

In classical mechanics, the magnitude of the force,  $f$ , on a particle or a body may be closely represented, over a limited range of velocities by a power law,  $f = av^\nu$ , where  $v$  is the velocity of the particle or body and  $a$  and  $\nu$  are constants. Depending on the value of  $\nu$  we have the following types of dissipative forces [35]:

- *Frictional force.* This force is usually required to slide one surface over another. Once the motion is started the magnitude of the force is independent of the speed. Thus, in this case,  $\nu = 0$ . It is highly complex to understand this phenomenological continuum behavior at the atomic scale, but recent MD simulations have been able to shine some light on the fundamental nature of friction by evaluating the averaged forces and the contact area of atomically rough surfaces as a function of applied pressure [36].
- *Viscous force.* When the force is proportional to the speed of the particle, i.e.,  $\nu = 1$ , we call the force a viscous force.
- *Newtonian dissipative force.* For high speed motion of an object in the air, the force is proportional to the square of the velocity, i.e.,  $\nu = 2$ .

Friction, diffusion, Joule heating due to electricity flowing through a resistance and heat flow through a thermal resistance are also relevant for dissipation in thermodynamically treated systems. Moreover, dissipation occurs on freezing of a liquid, in chemical reactions, and in probabilistic events like radioactivity and photon emission.

### 2.5 The Second law of Thermodynamics

One of the pillars of physics is conservation of energy. Various forms of energy can be completely interconverted, the total energy remaining constant. This holds also when mass is added as a form of energy according to Einstein's mass-energy equivalence relation ( $E = mc^2$ ). The First Law of thermodynamics is a representation of energy conservation. Mayer, and independently only slightly later Joule, expressed this by determining the mechanical equivalent of heat [37,38]. However, it did not take long to find that while mechanical energy can be transformed completely into heat, the reverse is not true (see Section 2.2). Energy conservation is still in place, but a fraction of it is not convertible and dissipated as "waste heat". Heat is therefore often called an inferior, degraded or fragmented form of energy.

The above observations by Thomson, Carnot and Clausius led to the formulation of the Second Law of thermodynamics,

$$dS_{universe} = dS_{system} + dS_{environment} \geq 0, \quad (1)$$

stating that the entropy  $S$  of the universe increases in all real processes (Clausius inequality), and in equilibrium it is constant. Unlike in Chapter 5 where we discuss the real universe, the term "universe" stands here only symbolically for an ideal isolated system. Entropy depends on various parameters, and the driving factor can be a gradient in any of these. A spontaneous process will always aim at a reduction of this gradient. Most commonly, eqn. (1) is expressed in terms of a temperature gradient between the system and environment, so that

$$dS_{universe} = \frac{\delta Q_{system}}{T_{system}} + \frac{\delta Q_{environment}}{T_{environment}} \quad (\text{temperature gradient}), \quad (2)$$

where  $\delta Q$  is the infinitesimal heat that is dissipated from a closed system to its environment at temperature  $T_{environment}$ . The heat that is dissipated by the system (by definition a negative quantity) is absorbed by the environment, i.e.  $-\delta Q_{system} = \delta Q_{environment}$ , and  $\delta Q = C_p dT$  for a process at constant pressure and  $\delta Q = C_v dT$  at constant volume. The inequality in eqn. (1) holds for  $T_{system} > T_{environment}$ , which is equivalent to stating that spontaneous flow of heat is always from hot to cold. The equality holds for  $T_{system} = T_{environment}$ . Such processes are also called “reversible” (this is thermodynamic reversibility, not to be confused with time-reversibility). However, when the temperature gradient disappears the driving force is lost, and in reality, such processes therefore do not proceed.

Alternative options to heat dissipation as indicators of the origin of irreversibility are lowering of gas pressure, or, equivalently, lowering of the concentration of the system:

$$dS_{universe} = C_v \frac{dp_{system}}{p_{system}} + C_v \frac{dp_{environment}}{p_{environment}} \quad (\text{pressure gradient, } T, V = \text{const.}) \quad (3)$$

$$dS_{universe} = C_v \frac{dc_{system}}{c_{system}} + C_v \frac{dc_{environment}}{c_{environment}} \quad (\text{concentration gradient, } T, V = \text{const.}) \quad (4)$$

Figure 1a makes clear that the entropy of a system can decrease when the entropy of the environment increases by at least the same amount so that the Second Law is not violated. Such a non-equilibrium situation that leads to a gradient between system and environment is in fact essential for many processes occurring in daily life in the laboratory and in nature. Work has to be spent or heat transferred against a gradient to create this situation, and energy barriers prevent that it relaxes too quickly back to equilibrium [39].

Classically, there are two distinct uses of the term entropy: (i) the *thermodynamic entropy* is obtained by performing macroscopic thermodynamic measurements, and (ii) entropy as a measure of the lack of information about a system’s state [40]. Boltzmann introduced a statistical measure of entropy by expressing it in terms of the number of accessible microstates,  $W$  corresponding to a particular macrostate of the system:  $S_B = k \ln W$ , with  $k$  being the Boltzmann constant. The basic assumption of this formulation is that all microstates are equally probable and thus have the same energy, a description that holds for a microcanonical ensemble of identical, non-interacting classical particles. Gibbs generalized the definition of the classical statistical entropy to that of a canonical ensemble to allow for non-equal energies of the microstates:  $S_G = -k \sum_i p_i \ln p_i$ , where  $p_i$  is the probability for the system to be in microstate  $i$ . The Gibbs expression was extended to quantum-mechanical systems by von Neumann in terms of the density matrix  $\rho$ , giving the von Neumann expression,  $S_{vN} = -\text{Tr}(\rho \ln \rho)$ , in units of the Boltzmann constant  $k$ . Of particular recent interest has been the emergence of the macroscopic thermodynamic entropy from microscopic systems. For an isolated system consisting of a single pure state,  $S_{vN} = 0$ , which is consistent with the usual assumption of thermodynamic entropy at absolute zero temperature as expressed by the Third Law of thermodynamics.

For quantum systems, another type of entropy is introduced, called the *entanglement entropy*. It is described by dividing the system into two (partly) entangled subsystems  $A$  and  $B$  and considering a pure quantum state,  $\varphi$ , of the composite system. Reducing  $\varphi$  to one of the subsystems by introducing  $\rho_A = \text{Tr}_B(\varphi)$ , the reduced density matrix of  $\varphi$  on  $A$ , the entanglement entropy is defined as the von Neumann entropy of  $\rho_A$ , i.e.,  $S_E(\rho_A) = -\text{Tr}(\rho_A \ln \rho_A)$  [41]. Similarly, we can define  $S_E(\rho_B) = -\text{Tr}(\rho_B \ln \rho_B)$ , where  $\rho_B = \text{Tr}_A(\varphi)$ . It can be proven that  $S_E(\rho_A) = S_E(\rho_B)$  [41], i.e., it is sufficient to define the entanglement

entropy considering the subsystem with the fewest degrees of freedom. Hence, entanglement entropy describes the degree of entanglement between  $A$  and  $B$ .

Entropy is often associated with a degree of order. This is a problematic analogy. A messy desk or shuffled cards have nothing to do with thermodynamic entropy [42]. We regard the normal distribution of alternating black and white fields of a checkerboard as a highly ordered state, but randomizing these fields does not change the thermodynamic entropy because there is no energy change (no dissipation) involved in this process. The thermodynamic entropy of the checkerboard is related to the number  $W$  of distinguishable ways to arrange  $k = 32$  black fields over  $n = 64$  fields, which is given by

$$W = \frac{n!}{k!(n-k)!} = \frac{64!}{32!32!} \quad (5)$$

which depends only on the number of black and white fields and is indistinguishable of their arrangement. However, we can define a local entropy within a given frame of e.g. 4 by 4 fields. All fields of the same color in a frame correspond to the highest order and gives the lowest possible value,  $W=1$ , and thus the lowest entropy, whereas the highest entropy is reached with an equal number of black and of white fields. For two neighboring frames with unequal numbers of black and white fields this will lead to a driving force for mixing due to information theoretic (Shannon type, see Section 4.1) entropy in the absence of energy dissipation. This is the expected behavior for diffusion in the presence of inhomogeneous concentrations. Furthermore, if we assign to the black fields a positive charge and to the white fields a negative charge, this introduces an energetic interaction between the fields, which makes the entropy dependent on the arrangement of the fields [39].

It should be noted that the Second Law as described above with the entropy of isolated systems increasing for spontaneous processes (eqn.1) holds for conventional thermodynamic systems, i.e. for matter in our laboratory and more generally on the Earth or on planets. However, as will be described in Section 5.5, matter with astronomical dimensions experience a long-range attraction by gravitation, an interaction that is fully negligible for the conventional systems. It has the consequence that for ensembles of stars there are conditions under which the specific heat is negative, which causes heat to flow from cold to hot and spontaneous processes generally occur with decreasing entropy.

### 2.6 The Carnot cycle: a reversible process in a non-equilibrium environment

The Carnot cycle is a Gedankenexperiment that represents an idealized reversible process to rationalize the function of a steam or combustion engine. The process converts a fraction of heat  $Q_h$  supplied by a heat bath at a high temperature  $T_h$  to work  $W$  under dissipation of the remaining fraction of heat  $Q_c$  to a cooler heat bath at temperature  $T_c$  (Figure 2).

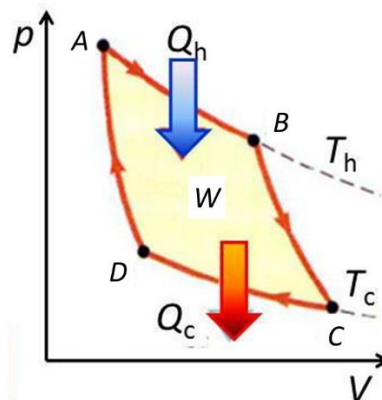


Figure 2: Carnot cycle with isothermal expansion  $A-B$  at temperature  $T_h$ , followed by adiabatic (isentropic) expansion  $B-C$ , isothermal compression  $C-D$  at temperature  $T_c$ , and adiabatic compression  $D-A$ . In this  $p-V$  plot, the area of the cycle corresponds to the work  $W$ , that is of equal magnitude but opposite sign compared with the converted amount of heat,  $Q_h - Q_c$ . (color online)

The Carnot process is well documented in textbooks and will not be discussed further here, but the heat and entropy terms related to each leg of the cycle are collected in Table 2. Since the entropy is a state function, the round-trip value of the system entropy is always zero. For given temperatures, this defines which net fraction of heat  $Q_c$  is dissipated from the upper to the lower heat bath, even for a process in which all four legs are thermodynamically reversible. However, in the reversible case there is no temperature gradient for the heat transfer; the process is therefore infinitely slow. In the irreversible case, the temperature of the heat bath and system are different. This does not affect the round-trip entropy change of the system, only that of the environment (Table 2). Also, the two legs which in the reversible case were adiabatic can be irreversible if there is a pressure gradient between the system and environment. The work  $W$  of the overall cycle is represented by the area of the cycle in a  $p - V$  plot,  $W = \oint p dV$ . This area shrinks for an irreversible cycle with the same corner points  $A, B, C, D$ . To compensate for this loss, an irreversible amount of heat  $Q'_c$  is dissipated in addition to the reversible amount  $Q_c$ .

Table 2: Balance of heat and entropy of the Carnot cycle and its environment

Changes	Leg $A-B$	Leg $B-C$	Leg $C-D$	Leg $D-A$	Total of cycle
System heat	$+Q_h$	0	$-Q_c$	0	$Q_h - Q_c$
Heat bath $T_h$	$-Q_h$	0	0	0	} $Q_c - Q_h$
Heat bath $T_c$	0	0	$+Q_c$	0	
System entropy	$+Q_h/T_h$	0	$-Q_c/T_c$	0	$Q_h/T_h - Q_c/T_c \equiv 0$ ( $S$ is state function)
Entropy of environment	$-Q_h/T_h$	0	$+Q_c/T_c$	0	0 (reversible case)
Entropy of the environment <sup>a)</sup>	$-Q_h/T'_h$	0	$+Q_c/T'_c$	0	$Q_h/T'_h - Q_c/T'_c > 0$ (irreversible case)

<sup>a)</sup> Irreversible case,  $T'_h < T_h, T'_c > T_c$

Eqn. (1) defines the arrow of time, but only its direction; there is no timescale on the arrow. The rate is determined by kinetic criteria such as flow rates in the presence of activation barriers. Such barriers are common but often ignored in thermodynamic treatments. In the Carnot cycle, the work  $W$  provides a step-like energy barrier. In an experiment, it is the fuel that provides the non-equilibrium conditions by creating the high temperature of the upper heat bath.

### 2.7 The Arrow of Time for systems near equilibrium

The Second Law (eqn. 1) states that the entropy of the universe never decreases; rather, it increases monotonically at all times, or it stays constant at equilibrium or equilibrium-like conditions. This implies a time-dependence of entropy [43]:

$$dS_{universe}/dt = \Pi - \Phi \geq 0, \quad (6)$$

where  $\Phi$  is the *entropy flux rate* from the system to the environment, and  $\Pi$  is the *entropy production* in the system per unit time. The Carnot cycle may serve as an example (Figure 2). Entropy is a state function; its change over the complete cycle is  $\Delta\Pi = 0$ . The entropy flux rate to the environment is given by  $\Phi = Q_h/T_h - Q_c/T_c$  (Table 2). For  $\Phi = 0$ , there is no driving force for the overall Carnot cycle.

Like time, the entropy of the universe cannot run backward. It may be represented by an arrow that always points to the future. The Second Law is therefore also called the *arrow of time* [8,44]. For gases, entropy is mainly a function of temperature and volume. For conventional matter, an increasing volume and temperature is consistent with an increasing entropy during its development toward *heat death*, although this does not hold for an expanding universe (see Section 5.4).

For chemical or biological systems, the spatial coordinates  $q$  are replaced by the thermodynamic state variables like volume, pressure, temperature, and concentration of constituent molecules. Here, the equilibrium state no longer corresponds to the most stable state (i.e, the lowest internal energy or enthalpy). The situation is displayed schematically in Figure 3. For an equilibrium state, the Second Law requires a plateau or maximum in the entropy, i.e.  $dS_{universe}/dq = 0$ . The entropy of the universe (or of any isolated system) increases monotonically for any process of non-zero rate since they are all irreversible. However, it is impractical to include the whole universe in all calculations. Since most processes in liquid or solid states occur at approximately constant temperature and pressure, the Second Law (eqn. 1) is rewritten in a way that the environment cancels out. For the isothermal-isobaric constraints, the new but equivalent criterion for spontaneity of a process in a closed system is given by the free enthalpy or Gibbs free energy  $G = H - TS$  (the Gibbs-Helmholtz equation) as

$$dG_{system} = dH_{system} - TdS_{system} \leq 0. \quad (7)$$

Similarly, for isothermal isochoric gaseous systems the Helmholtz free energy  $F = U - TS$  can be used to obtain

$$dF_{system} = dU_{system} - TdS_{system} \leq 0. \quad (8)$$

Here,  $H$  is the enthalpy and  $U$  is the internal energy. In short,  $dG_{system}$  and  $dF_{system}$  of a spontaneous process in a closed system decrease and approach zero at equilibrium.

Self-organization and self-assembly are processes that lead to higher order, which obviously represents a state of lower entropy. Examples are crystallization, the formation of self-assembled monolayers on surfaces and a rich variety of structures, among them micelles, bilayers, and vesicles, derived from aqueous solutions of surfactants or other amphiphilic molecules. These processes appear to be spontaneous, so that one is tempted to call them a violation of the Second Law. However, it is only an example of the situation shown in Figure 1a. These processes occur in an open system which is coupled to its environment that acts as a heat bath. It is driven by the enthalpy of formation, supported or hindered by entropic effects. Its complexity derives from the fact that it is often carried out in solution. In the initial, dispersed state, the solute molecules have enthalpic interaction (heat of solvation) with the solvent. The hydrophobic interaction causes partial order of solvent molecules in the first solvation shell, and thus often a negative entropy of solvation. On aggregation, these enthalpic contributions are replaced by solute-solute and solvent-solvent terms, and the reduced surface of the aggregate diminishes strongly the entropy of solvation, but instead we have a negative entropy term due to the order in the aggregate. The entropy term,  $-T\Delta S$ , enters the stability criteria (eqns. 3 and 4). Positive reaction entropy of the process gives

preference to the dispersed form at high temperature. However, the entropy term may cross zero at a certain temperature, which leads to more complex behavior. Micelle formation in water is clearly driven by a positive entropy of formation [45].

### 2.8 Pseudo-equilibria and steady states

Self-assembled structures have many applications and are of great importance in materials science. Here, we only briefly mention vesicles, which are hollow spherical bilayer aggregates derived from surfactants, with an aqueous medium outside and inside. They form either as equilibrium or out-of-equilibrium metastable structures. Since the bilayers are close analogs of biological cell membranes which consist of phospholipids, the vesicles are simple models of biological cells. The thermodynamics and kinetics of their formation have been reviewed competently by Guida [46].

From classical mechanics we are used to classify equilibria by judging the potential energy hypersurface. The absolute energy minimum corresponds to the global equilibrium (within the considered range of coordinates  $q$ ). There are often non-global (local) minima at higher energy, and plateaus are called metastable equilibria.

For thermodynamic closed systems, the criterion of equilibration is a minimum in the Gibbs free energy,  $G = H - TS$ , consisting of an enthalpic and an entropic term (eqn. 7). The behavior of an enthalpy-neutral process along some coordinate  $q$  is displayed schematically in Figure 3. Point A represents a global minimum in  $G$  and hence thermodynamic equilibrium, while points C and E depict local minima in  $G$  close or far from equilibrium [47]. D is at a plateau where the slope of  $\Delta G$  is zero, thus there is no time evolution. It represents a *pseudo-equilibrium*.

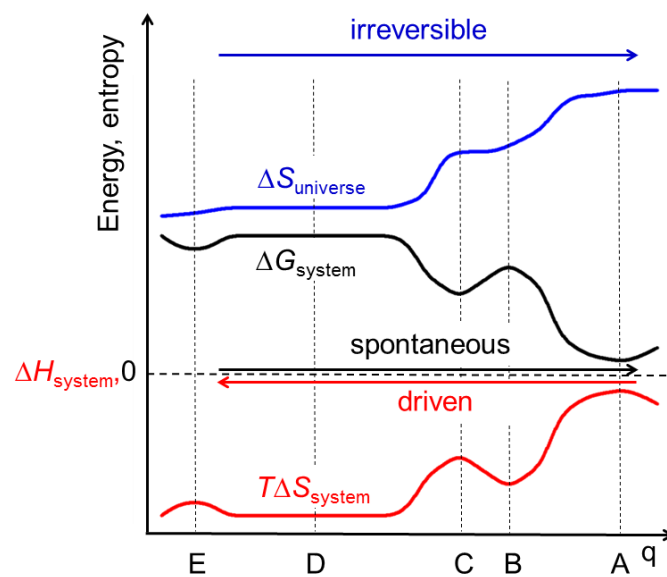


Figure 3: Schematic one-dimensional example of the change of thermodynamic parameters for a process along some coordinate  $q$ . For any process, the entropy of the universe increases monotonously with a slope given by the degree of non-equilibrium. The more familiar system parameter for the free enthalpy,  $\Delta G_{\text{system}}$ , has a global minimum, non-global (local) minima and plateaus, resembling the case of classical mechanics. If  $\Delta H_{\text{system}}$  is assumed to be zero or constant,  $T\Delta S_{\text{system}}$  shows a complementary behavior to  $\Delta G_{\text{system}}$ . (color online)

Equilibria look static but are always dynamic, meaning that the forward and backward rates are equal. This distinguishes pseudo-equilibria from *steady states* in which forward and backward rates are not equal, but the influx from the left equals the outflux to the right, and

vice-versa, so that the system is stable at point D. Finally, B represents a barrier that slows down the flux from C to A to maintain a given population or concentration at C. For example, the molecules formed in photosynthesis are of high energy and must be protected by barriers from reacting too quickly to equilibrium in the oxygen atmosphere of oxygenic organisms. Much of what chemists do has to do with tuning the height of such barriers. Decreasing barriers accelerates the process, which is called catalysis. Increasing the barrier slows the process down, which is called corrosion inhibition. The barriers are also crucial in living systems. Their height is adjusted by dedicated enzymes to tune the fluxes of reactants of a complex network of physiological processes so that they all occur at the needed rates within a narrow temperature range, the body temperature [39]. Living systems are typical steady-state systems which require that energy of molecular fuels is continuously added to keep the processes going. Life is motion on a bumpy slope of the free energy surface.

Systems at or near a local equilibrium can be treated as if they were near a global equilibrium. Although being far from equilibrium globally, they are near equilibrium locally [48]. Near-equilibrium states are predictable systems. Linear steady states near equilibrium are the result of gradients of one or more extensive properties, e.g. temperature, which create fluxes of extensive quantities, e.g. thermal energy [47]. In linear systems, the fluxes are proportional to the gradients (i.e. the forces), and since the gradients decrease with time the systems relax exponentially to equilibrium. This result derives from the assumption of small perturbations so that only terms linear in the deviation from equilibrium are retained. The vast majority of problems addressed in non-equilibrium thermodynamics are for near-equilibrium conditions, and the solutions are consistent with the Second Law [48].

As drawn in Figure 3, the process in the closed system is spontaneous ( $\Delta G < 0$ ) from the left to the right, and a driven process in the reverse direction. Both processes will always increase the entropy of the universe.

Figure 1a is misleading in the sense that it may suggest that a “system” is a well-defined, homogeneous, spatially confined part of the universe. If we want to judge a sample of a mixture of chemical or biological molecules that looks stable, it may in fact represent a mixture of systems that are in different equilibrium states. The system may, for example, be in its global equilibrium as regards pH since proton exchange reactions are fast, but it may be only in a local equilibrium regarding other reactions, like oxidation by molecular oxygen in air.

### *2.9 Systems far from equilibrium*

Isolated systems far from equilibrium are those where the proportionality of entropy production to a gradient is no longer valid and deviations from linearization of the perturbed entropy near its local maximum value,  $dS = S_0 + \delta S + \frac{1}{2}\delta^2 S$ , lead to qualitatively new effects. Prominent examples are the pressure, temperature and humidity patterns in hurricanes, or chemical reactions with oscillating concentrations of reactants [1,2,49,50]. Systems at equilibrium are not expected to oscillate since this would contradict the Second Law. Thermodynamically, such systems are described as being far from equilibrium since, obviously, at equilibrium there would be no concentration gradient. Furthermore, even off equilibrium, the concentration gradients are often monotonic, which leads us to conclude that the non-monotonic concentration distribution with the concomitant emerging dynamic, self-organized pattern represents a state even more remote from equilibrium and of even lower entropy. Kinetically, these systems lead to non-linear rate equations. Examples are autocatalytic reactions, where one of the reaction products is also a catalyst of the reaction, in the simplest case,  $A + B \rightleftharpoons 2B$ , where B serves as a catalyst, which leads to the coupled non-linear rate equations



$$d[A]/dt = -k_f[A][B] + k_b[B]^2, \quad d[B]/dt = k_f[A][B] - k_b[B]^2, \quad (9)$$

where  $k_f$  and  $k_b$  are the rate constants of the forward and the backward reaction, respectively. This does not lead to any oscillations, just to a monotonically but initially exponentially increasing concentration of [B] that saturates in a sigmoid-shaped curve when [A] is used up. This type of growth curve is quite abundant and universal [51,52].

The simplest and famous example of a far-from-equilibrium process leading to oscillations is that of the populations (conventionally given in square brackets, in analogy to chemical concentrations) of rabbits [R] and foxes [F], also called the predator-prey or *Lotka-Volterra* system. The rabbits reproduce at a rate  $r^*[R]$  and are eaten up by the foxes at a rate  $r^\dagger[R][F]$ , while the foxes reproduce at a rate  $f^*[F][R]$  and die in the absence of rabbits at  $f^\dagger[F]$ . The corresponding set of coupled non-linear differential equations is

$$d[R]/dt = (r^* - r^\dagger[F])[R], \quad d[F]/dt = (f^*[R] - f^\dagger)[F]. \quad (10)$$

When the population of rabbits is high, the foxes reproduce well and their population grows, but this causes the population of rabbits to go down. In the absence of rabbits, the population of foxes decreases as well, so the population of rabbits will flourish again. Thus, the two populations oscillate out of phase (Figure 4a).

As long as the populations in eqn. (10) depend only on time but not on spatial coordinates, i.e. as long as the populations/concentrations are homogeneous, possibly due to stirring, the oscillations are only temporal. For the special conditions where the eqns. (10) are set to zero, i.e. for  $r^* = r^\dagger[F]$  and  $f^*[R] = f^\dagger$ , the system becomes stationary. Alternatively, if the concentrations are inhomogeneous at some time, they oscillate (Figure 4a). However, the undamped oscillations remind more of a classical time-reversible Newtonian system, not of a thermodynamic chemical or biological system that is not supposed to oscillate about equilibrium. The reason is that the scheme of eqns. (10) is incomplete. Rabbits are born from somewhere, and foxes die to something. By comparison with a chemical system, the oscillating populations [R] and [F] represent intermediates, and there is a background process that drives the system. In this case, rabbits live on grass that itself is a product of photosynthesis and solar energy. Grass fuels growth and reproduction, rabbits are then the fuel for foxes, leaving dead matter at the end. The entire process is accompanied by dissipation of heat, water and carbon dioxide.

Somewhat more complex examples of oscillating chemical reactions are the *Brusselator*, discussed in detail by the Prigogine group in Brussels [48], and the *Oregonator*, involving 11 reactions and 12 chemical species [53]. It is a truncated form of the famous Belousov-Zhabotinsky reaction containing 21 different chemical species [54].

On a surface or in a thin layer, these systems can develop macroscopic spatiotemporal patterns. The maxima and minima propagate like the fronts of wildfires. This can also happen in three dimensions, but it is more difficult to visualize. The novel patterns far from equilibrium are called *dissipative structures*. The term was coined by Prigogine who obtained the Nobel Prize in Chemistry (1977) for his work on non-equilibrium thermodynamics [49].

Rabbits and foxes digest food and dissipate heat, chemical reactions also exchange heat. As for any dynamic situation, the entropy of the universe must increase monotonously without oscillation. Entropy is an inverse logarithmic function of concentration. Therefore, for a dynamic, inhomogeneous system in time and space the local entropy will oscillate while the overall entropy will increase monotonically.

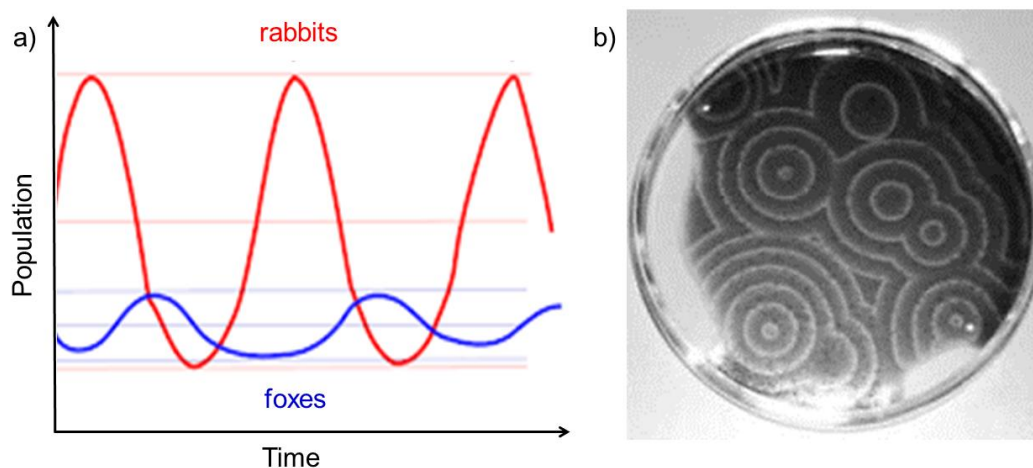


Figure 4: a) Time dependence of homogeneous Lotka-Volterra system of two-component non-linear kinetics with oscillating populations of rabbits and foxes, or of equivalent chemical systems (adapted from abiweb.de, [www.abiweb.de/biologie-oekologie/populationsoekologie-und-wachstum/raeuber-und-beute-lotka-volterra.html](http://www.abiweb.de/biologie-oekologie/populationsoekologie-und-wachstum/raeuber-und-beute-lotka-volterra.html)). b) Spatiotemporal dissipative structure of concentrations in the Belousov-Zhabotinsky reaction in a thin layer in a petri dish (reprinted from Ref. 50 (open access) (color online)

A rod that is suspended flexibly at one end represents a simple undamped oscillator with well-defined reversible Newtonian motion. A double-rod pendulum, which has a second rod attached end-to-end to the first rod, is a much more complex dynamic system. It shows a non-periodic motion with trajectories of the tip that depend strongly on the initial conditions. They are deterministic and reversible, i.e. exactly the same initial condition will always lead to the same trajectory. However, near certain values, an infinitesimal change in the initial condition may lead to a vastly different trajectory. Such systems are said to be chaotic, and this minute change is called the *butterfly effect*, meaning symbolically that a butterfly flapping with its wing can have a big effect at a large distance, for example in the weather on the other side of the Earth. This term, and chaos theory in general, goes back to Edward Lorenz, a mathematician [55,56]. The parameter set at which stable periodic motion switches to chaotic behavior is called a *bifurcation point*. The sharp transition between a disordered and a structured regime reminds of a phase transition. However, the bifurcation occurs far from equilibrium while the phase transition is near equilibrium.

Chaos theory has applications in a variety of disciplines, including chemistry [1]. The deterministic (time-reversible) motion, whether periodic or chaotic, is driven by an irreversible background reaction. This reveals an interesting double nature of chemical or biological systems, which can be simultaneously time-reversible and thermodynamically irreversible, albeit at different length and timescales. Many aspects of these phenomena far from equilibrium are not yet fully understood and still issues of active research. Of interest is for example the symmetry breaking that allows coherent motion to emerge spontaneously from a homogeneous solution, perhaps by spontaneous fluctuations. Also, periodic events in daily life like the beating of hearts, menstruation cycles, or rhythmic firing of neurons may be based on oscillating chemical reactions.

Single molecule off-equilibrium states can be generated in biological systems. It has been shown that the free energies of the folding and unfolding process of an RNA hairpin can be measured using optical tweezers or atomic force microscopes [57]. The work distributions of pulling the molecule from the folded equilibrium to the unfolded off-equilibrium structure was measured for a large number of repetitions of the experiment and analyzed based on Crooks' fluctuation theorem. At the same time, this served as a verification of the theorem.

### 3. A system in equilibrium represented by the Maxwell-Boltzmann distribution and by Planck's hollow black body

#### 3.1 The Maxwell-Boltzmann distribution of molecular speeds

The Maxwell-Boltzmann distribution of the speeds of atoms or molecules of mass  $m$  in the gas phase in equilibrium at temperature  $T$  (Figure 5a, b) is given by

$$f(v, T) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 \left[\exp\left(\frac{mv^2}{2kT}\right)\right]^{-1}, \text{ or equivalently}$$

$$f(\varepsilon, T) = 2 \left(\frac{\varepsilon}{\pi}\right)^{\frac{1}{2}} \left(\frac{1}{kT}\right)^{3/2} \left[\exp\left(\frac{\varepsilon}{kT}\right)\right]^{-1}, \quad (11)$$

where  $\varepsilon = mv^2/2$  is the translational kinetic energy and  $d\varepsilon = \sqrt{2m\varepsilon} dv$  [58,59].

#### 3.2 Planck's black body radiation

Wilhelm Wien (1896) was the first to propose an analytical solution for the spectrum of black body radiation by relating the frequency of emitted radiation to the thermal energy of the emitting molecules as given by the Maxwell-Boltzmann (MB) distribution of molecular speeds [60]. Interestingly, the concept of a "finite quantum of energy" often ascribed to Planck, appears already in 1893 in Wien's paper on the displacement law [58]. Wien's law gave an excellent match with the observed black-body radiation at high energies but deviated at low values (compare Figure 5d). Shortly thereafter, Lord Rayleigh derived a different relation based on standing waves in a black-body cavity, and he applied the equipartition theorem [60], assigning a thermal energy of  $kT$  to *all* states instead of populating them according to Boltzmann. His distribution law matched well at low energies but missed out the exponential decay term that reflects Bose-Einstein population for the photons (see eqn. (12) below). This led to an unlimited increase at high energy, a behavior that was later dubbed the "ultraviolet catastrophe". Planck derived his distribution law first on thermodynamic grounds, but after a discussion with Boltzmann about the number of ways of distributing discrete equal energy quanta among a number of molecules, he saw the similar structure of the resulting expression with his distribution. By setting the energy quanta proportional to the photon frequency,  $\varepsilon = h\nu$ , where the "Planck constant"  $h$  entered as a proportionality factor, he obtained the number density of photons as a function of frequency that provided a perfect match with experiment [61,62]:

$$f(\nu, T) = \frac{\rho(\nu, T)}{h\nu} = \frac{8\pi\nu^2}{c^3} \left[\exp\left(\frac{h\nu}{kT} - 1\right)\right]^{-1}, \text{ or}$$

$$f(\varepsilon, T) = \frac{8\pi}{h^2c^2} \varepsilon^2 \left[\exp\left(\frac{\varepsilon}{kT} - 1\right)\right]^{-1}, \quad (12)$$

where  $\rho(\nu, T)$  is the spectral energy density and  $c$  the velocity of light. Eqn. (12) differs from Wien's formula only by the "-1" in the exponential term in the square bracket, but becomes identical for  $h\nu \gg kT$  [61]. Photons are bosons and have integer spin equal to 1. The square-bracket expression reflects properly the Bose-Einstein statistics, and the high-energy limit and Wien's formula represent the approximate Boltzmann distribution.

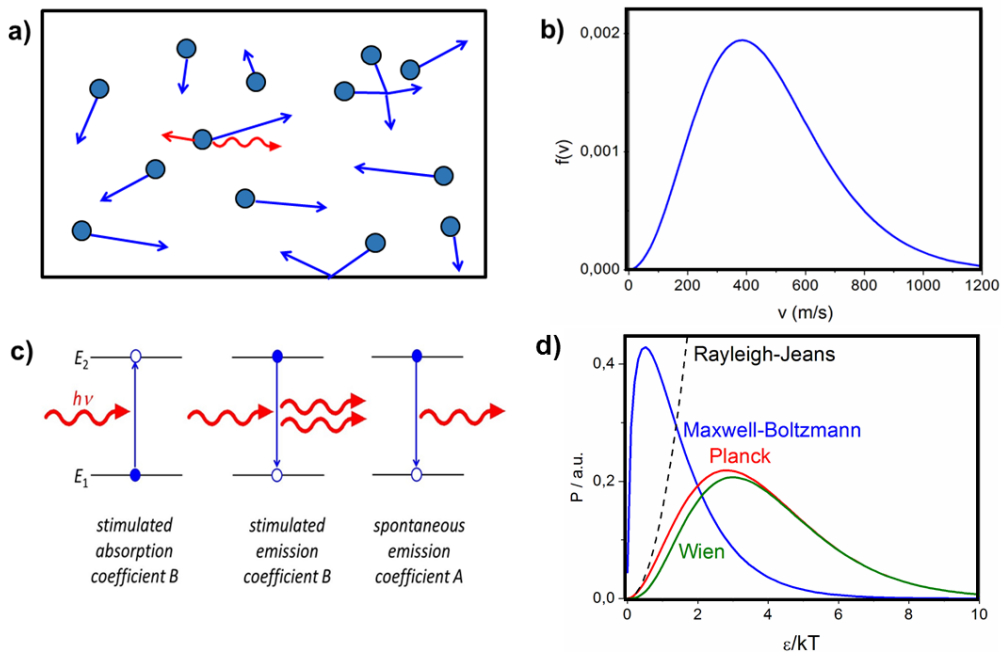


Figure 5: a) Schematic presentation of a system of gas phase particles with vectors of their speeds (blue arrows) and emitted photon in random direction with corresponding recoil vector (red). The walls of the box are ideally reflecting for particle energy and for photons. b) Maxwell-Boltzmann distribution function of molecular speeds of system (a) in equilibrium. c) Process of stimulated absorption and emission in a radiation field, and of spontaneous emission in the absence of interaction with a radiation field. d) Comparison of Wien's, Rayleigh-Jeans' and Planck's distribution of black-body radiation with Maxwell-Boltzmann's distribution law for molecular speeds, here converted to the energy scale using  $\epsilon = \frac{1}{2} mv^2$  for particles of mass  $m$  and speed  $v$ , while the photon energy equals  $h\nu$ . (color online)

### 3.3 Einstein's absorption and emission kinetics

A more systematic derivation was given later by Einstein [63]. In this derivation (see below), Wien's formula corresponds to the absence of induced emission [64]. Atoms absorbing or emitting a photon experience a recoil effect that changes the velocity and thus the kinetic energy of the atom. A central requirement in the derivation of Planck's law is therefore that these processes do not change the equilibrium energy distribution of the emitting and absorbing matter at the given temperature. Absorption and emission rates in a steady state were therefore matched to the expression of the Boltzmann distribution of a gas [63]. Thereby, it was recognized that the Boltzmann distribution of the population of states of a given energy is much more fundamental and not restricted to a gas but valid for all systems in thermodynamic equilibrium. The success of this treatment underlines the equivalence of the description of heat as kinetic energy of particles interacting with the black-body radiation field.

Figure 5d compares the number densities of molecular speeds in the MB distribution as a function of energy with that of photons from Wien's, Planck's and Rayleigh-Jeans' distributions. Despite the fact that Planck's curve was derived from the MB distribution and represents the same equilibrium, the two curves differ markedly. The initial increase of Planck's distribution is quadratic in energy, while the MB curve starts off with square-root dependence. The origin of this apparent mismatch reveals a fundamental difference in the nature of the two equilibration processes. In the MB picture, a single process, the energy exchange during mostly bimolecular elastic collisions, governs the distribution of particle speeds. In contrast, radiative equilibration is based on two processes (Figure 5c) [63]: at low energies, it is dominated by *stimulated photon absorption and emission*, which are both

proportional to the energy density  $\rho$  of the black-body radiation field at the resonant transition frequency  $\nu = (E_2 - E_1)/h$  and a constant  $B$  (the Einstein coefficient for induced transitions):

$$B_{12} = B_{21} = 4\pi^2 |\boldsymbol{\mu}_{12}|^2 / 6\epsilon_0 h, \quad A_{21} = B_{21} \cdot 8\pi h \nu^3 / c^2, \quad (13)$$

where 
$$\boldsymbol{\mu}_{12} = \int \psi_2^* \boldsymbol{\mu} \psi_1 d\tau = -e \int \psi_2^* \mathbf{r} \psi_1 d\tau \quad (14)$$

is the transition dipole moment, calculated as the expectation value of the electric dipole operator  $\boldsymbol{\mu} = -e\mathbf{r}$  with the electronic wave functions of the initial and the final states,  $\psi_i$  and  $\psi_f$ . The symbol  $e$  stands for the electrical charge and  $\mathbf{r}$  is the position vector of the electron.

*Spontaneous emission* is a first-order process, proportional to the Einstein coefficient  $A_{21}$  and independent of the radiation field. It dominates stimulated emission at high energies due to the  $\nu^3$  dependence. The *induced transitions* (absorption and stimulated emission) are bidirectional and occur with the same rate constant, but the spontaneous transition occurs only in emission, reflecting the broken symmetry that is at the origin of irreversibility. The subtlety of the phase relations between stimulated and spontaneously emitted photons has been discussed recently by Pollnau [65].

In thermodynamic equilibrium the rate of emission between any two states equals the rate of absorption:

$$A_{21}n_2 + B_{21}n_2\rho(\nu) = B_{12}n_1\rho(\nu). \quad (15)$$

For two singly degenerate levels the ratio of populations  $n_2$  and  $n_1$  is given by the Boltzmann distribution

$$\frac{n_2}{n_1} = \exp - \left( \frac{E_2 - E_1}{kT} \right). \quad (16)$$

For a gas phase ensemble of atoms in thermal equilibrium, i.e. a MB ensemble (Figure 5a), eqn. (16) also gives the ratio of the number of atoms with kinetic energy  $E_2$  and  $E_1$ , and analogously for other pairs of energies. Therefore, it is irrelevant whether the atoms possess kinetic energy or electronic excitation, a form of potential energy. The two forms are interconvertible, and neither the exchange of photons nor any collisional energy exchange affects the overall distribution function. The MB distribution and the energy distribution of Planck's black body are equivalent and do not change as long as equilibrium is maintained. Off-equilibrium situations represent the case where the populations in eqns. (11) and (12) are represented by the system temperature being different from the temperature of the environment, which acts as a heat bath. This leads to collisional and/or radiative energy exchange between system and bath until equilibrium is restored. Equilibration is a spontaneous and irreversible process in which energy is conserved but entropy is not. The degree of irreversibility is characterized by an amount of energy that is *dissipatively* redistributed. The nature of this process is at the origin of thermodynamic irreversibility and is the subject of the following chapters.

## 4. Isolated time-reversible and time-irreversible systems in thermodynamic equilibrium

### 4.1 Equilibration versus thermalization

The occurrence of dissipative structures in systems far from thermodynamic equilibrium (Section 2.9) is an example of equilibration far from a thermal state. It is essential for an understanding of the origin of irreversibility to distinguish between the terms *equilibration* and

*thermalization*. *Equilibration* refers to a process whereby one or more observables or properties of the system evolve toward their microcanonical expectation value and exhibit only exponentially small temporal fluctuations around that average value for a prolonged period of time [5, 14]. *Thermalization* is a more restrictive process than equilibration. It means that the local memory about the initial conditions is at least partly lost, whereas thermodynamic equilibration does not necessarily involve memory loss, in which case it is time-reversible [66]. The term *thermalization* is not used consistently in literature and may be somewhat misleading; we would prefer to express it synonymously as *memory loss*. Equivalent expressions to the absence of thermalization are time-reversibility and, for most systems, also (time)-integrability. Equilibration and thermalization of quantum systems are discussed in Chapter 7.

A thermalizing time-irreversible process and a non-thermalizing time-reversible process can reach the same thermodynamic equilibrium. This means that the final states of both processes are characterized by the same thermodynamic parameters; in particular, they also have the same thermodynamic entropy for an isolated system or the same free energy for a closed system (Figure 6). This has the important consequence that time-irreversibility is not related to the Second Law of thermodynamics, which determines the arrow of time; it represents merely a decoherence of information (a loss of memory, i.e. a loss of correlation between different parts of the system) without any energy dissipation or change in concentration. In agreement with this, Santos et al. state that the entropy flux (eqn. 6) has thus no contribution arising from quantum coherences: entropy (and energy) will only flow due to imbalances in the populations. Any loss of coherence contributes only to the entropy production rate and has no associated flux [43]. It has been suggested that the local non-equilibrium free energy rate of Markovian open quantum systems (which represent most systems in nature) requires the presence of information-related contributions to complement the Second Law [67]. It is believed that the potential contribution of decoherence on chemical equilibria needs further attention.

*Quantum dissipation* is the process of spontaneous energy transfer from the quantum system into the environment. During this process, the system transitions into lower energy states, akin to transitions to inferior forms of heat in a classical system, which requires an energy input to be reversed. The heat transferred into the environment is distributed among its large number of degrees of freedom and is thus lost in the environment. Considering an infinite number of environmental degrees of freedom, the environment's temperature is unaffected and the environment thus serves as a thermal bath or heat reservoir.

*Decoherence* or *dephasing* is a quantum-mechanical phenomenon that describes the gradual decay of oscillations in quantum systems. It is due to interaction with the system's environment, during which the quantum correlations, initially confined to the quantum system, get delocalized among a large number of degrees of freedom in the bath. In other words, as the system evolves, information about its initial state becomes increasingly entangled with environmental degrees of freedom. The system's memory of its initial state is therefore hidden or lost in the system-bath correlations, indicating that this process is a quantum-mechanical version of thermalization. Reversibility of this process would require full knowledge of the many new correlations, which would introduce new irreversible processes, for example by means of measurements to determine all global operators of the entangled system. Each such measurement will result in an apparent collapse of the wave function, when the values of all variables are determined at the time of collapse (see Section 2.1.3 about the hidden variables). Decoherence leads to the transition from quantum to classical phenomena and is the inevitable consequence of interaction between a quantum system and its surrounding environment [68]. Decoherence is typically measured by the von Neumann entropy,  $S(\rho) = -\text{Tr}(\rho \ln \rho)$ , where  $\rho$  is the density matrix of the quantum system.  $S(\rho)$  is

closely related to the information theoretic Shannon entropy and to the entropy of entanglement [69]. The classical analog is a correlation function, for example the position-position time correlation  $\langle x(0) x(t) \rangle$  [70].

The distinction between equilibration and thermalization in a closed system is shown schematically in Figure 6. The off-equilibrium state can be near or far from equilibrium, and the thermodynamic equilibrium state can be a local or global equilibrium. In the scheme, we have split the Arrow of Time into an Arrow of Dissipation that is driven by energy dissipation according to the conventional Second Law, and an Arrow of Thermalization that is separated off, in agreement with Ptaszyński [67], representing memory loss. The Arrow of Thermalization has often been ignored or subsumed into the thermodynamic Arrow of Time, which is the origin of the confusion about time-reversibility and thermodynamic irreversibility. The Arrow of Thermalization has no energetic component. For quantum systems with coherent motion it is driven by the von Neumann entropy and for classical systems by the Gibbs entropy. However, classical and quantum systems in random motion can also be time-reversible if the motion is deterministic, e.g. if a classical system is governed by Newtonian processes (see Gedankenexperiment in Section 4.2). The loss of memory in this classical case and also in quantum systems is measured by the loss of time correlation between different particles.

The Arrow of Dissipation can be reversed by spending work on the system, as discussed in the context of Figure 1a. This reverse dissipation in the system must then be more than balanced by dissipation in the environment, so that the Second Law is nevertheless obeyed. Deterministic motion can be reversed at zero energetic cost in a thought experiment. In a real experiment it is technically possible by inversion of the magnetization in a spin system in a magnetic field.

Any probabilistic (or stochastic) event, the time of which cannot be accurately predicted, in contrast to that of deterministic processes, is suitable to disturb or destroy time-reversibility of the correlations. This will be discussed in detail in Chapter 6.

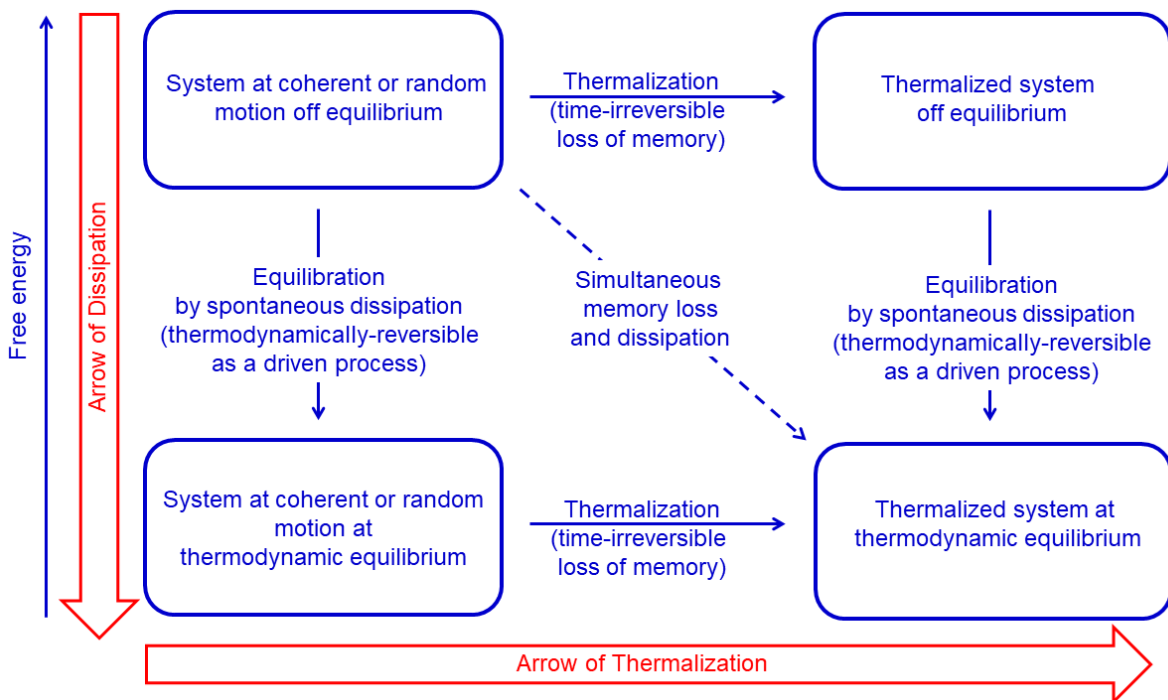


Figure 6: Schematic description of the difference between dissipation and thermalization in a closed thermodynamic system. The Arrow of Time is split into an Arrow of Dissipation,



representing the conventional equilibration process, and an Arrow of Thermalization that so far has been implied to be part of equilibration. (color online)

#### 4.2 Illustration for equilibrated Maxwell-Boltzmann equilibria

Here we discuss a Gedankenexperiment that is outlined in Figure 7 for an isolated system with perfectly elastic walls. It consists of two subsystems, for simplicity each of  $n$  mol of the same mono-atomic gas in identical volumes  $V$ , but with subsystem 1 at initial temperature  $T_1$ , while subsystem 2 is at  $T_2$  (Figure 7a). A heat-conductive wall separates the two subsystems, each of which is equilibrated and characterized by the MB distribution of atomic speeds at the given initial temperatures. We now perform two different experiments to reach an equilibrated final state of the overall system (Figure 7b).

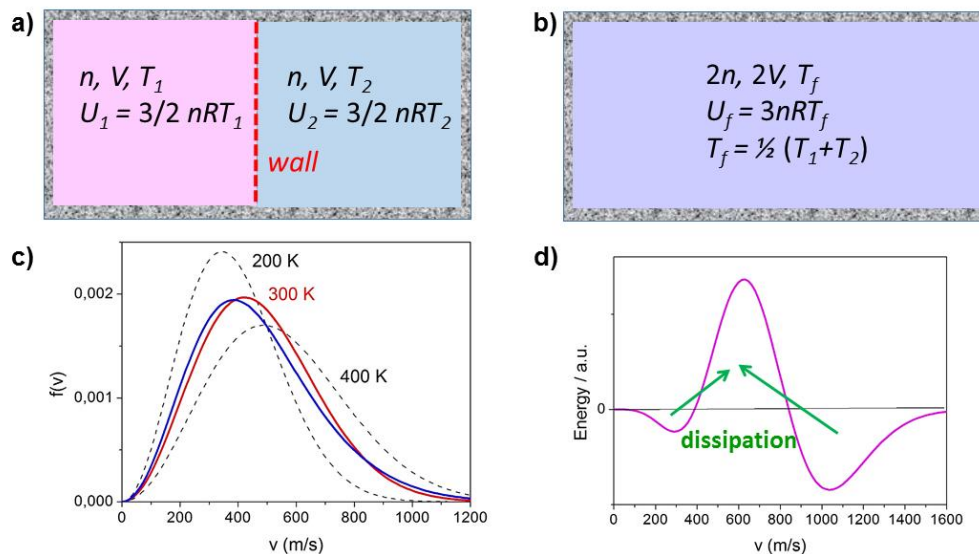


Figure 7: a) Isolated system with two subsystems separated by a heat-conducting wall, containing identical equilibrated amounts of the same gas in the same volume but initially at different temperature. b) Final state after equilibration by heat exchange through the wall or alternatively by removing the wall. c) Maxwell-Boltzmann distributions for a gas with mass 40 a.u. at 200 K at 400 K (black broken lines), their 1:1 superposition (blue) and the equilibrated state at 300 K (red). d) Energy (i.e. velocity square) weighted difference between blue and red curve of c), showing that during equilibration, energy dissipates from high-energy gas atoms to a more central range, and also the fraction at very low energy diminishes. (color online)

In the first experiment we remove the partitioning wall so that all atoms can collide and interdiffuse. Energy is conserved, but heat flows from the part at higher temperature to the one at lower temperature so that the overall entropy increases. In the absence of velocity-dependent forces we have Newtonian systems with elastic collisions that are time-reversible, i.e. the motion of collision partners before and after a collision is correlated. The process can be simulated by molecular dynamics (MD) using equations of motion based on a time-independent Hamiltonian. Disregarding numerical inaccuracies, reversing all the velocity or momentum vectors at the same instant will cause the molecules to retrace their trajectories back to their initial values. [5,13]. This time-reversibility is independent of the size of the system.

The second experiment leaves the wall in, but since it is heat conductive, the two subsystems will nevertheless equilibrate at the same final state characterized by the MB distribution at  $T_f$ . The difference from the first experiment is that energy is now transferred indirectly, mediated by the wall, which prevents the correlation of the atoms between the two



subsystems; the overall time-reversibility is lost. Nevertheless, the final equilibrium and velocity distributions are identical in the two experiments. Since the memory of the initial conditions is lost in the second experiment, the final state is called not only equilibrated but also thermalized [66].

Figure 7c shows the initial MB distributions of the gases in the two subsystems, assumed to be at 200 K and 400 K, and the equilibrated final state at 300 K (red). Also shown is a 1:1 superposition of the two initial states (blue), which is basically bimodal although this is not resolved. The difference between the blue and the red curves shows the change in the fractions of atoms at a given speed during equilibration. More telling is the energy difference (i.e. velocity square weighted difference) shown in Figure 7d. As a plausible microscopic interpretation of the heat transfer from high to low temperature it shows that the atoms from the fast end of the initial 400 K gas dissipate energy, and the ones from the slow end of the initial 200 K gas become warmer, which concentrates the energy in a more central range corresponding to 300 K.

The difference between the two experiments is fundamental and reminds of the early work by Boltzmann in which he derived the velocity distribution of equilibrated gases based on his “molecular chaos” assumption (H-theorem, uncorrelated velocity vectors of colliding particles independent of position), intended to derive the Second Law of thermodynamics from reversible microscopic mechanics [71]. He later admitted that the velocity vectors are no longer uncorrelated after collisions, and that his result was a consequence of assumptions about initial conditions. The two Gedankenexperiments of Figure 7 conceivably lead to identical equilibrium conditions, independent of whether they were conducted in the presence of a wall and thus without any correlation between the two subsystems, or by removal of the wall that leads to a fully correlated equilibration process. This means that the loss of correlation and thus of time-reversal symmetry is not fundamental for reaching thermodynamic equilibrium. The loss of correlation goes beyond equilibration and is called thermalization (see Section 4.1).

Secondly, time-reversibility is not limited to small systems. However, the MB distribution is the result of a statistical evolution. For a small number of member atoms of the ensemble it may therefore be advisable to take advantage of the ergodic theorem and evaluate an extended time average instead of an instantaneous ensemble average that is susceptible to large fluctuations [7,29]. To account for the loss of time coherence, modern versions of MD simulation programs may include a friction term that is velocity-dependent (non-Newtonian), and/or empirical stochastic kicks (thermal noise) to generate time-irreversible behavior [12].

Reversing time is easy to carry out in a computer simulation but difficult in experiments. It is possible in nuclear magnetic resonance (NMR) when a defined spin state is constructed by a preparative electromagnetic pulse in resonance with a spin transition. Because of the fundamental difference between the  $T_1$  and  $T_2$  relaxation times, spin systems are also ideal examples to explain the difference between time-irreversibility and thermodynamic irreversibility. This will be discussed in Section 6.3.

#### *4.3 Rapid expansion of an ideal gas upon removal of a partition*

The next experiment starts with a setup such as the one shown in Figure 7a, but with the gas confined to the left compartment. When we remove the partitioning wall, the gas will expand rapidly into the second compartment, reaching a final state at half the initial pressure and, for an ideal gas, at the same temperature as the initial state. This is obviously a spontaneous process in which the initial and the final states are equilibrium states. There is no heat flow, but the entropy increases by an amount  $nR \ln 2$  due to a decrease in concentration of atoms by a factor 2, similar to the cases described in eqns. 3 and 4. To revert the system in a real

experiment to the initial state it has to be compressed, which corresponds to spending work. Alternatively, in a Gedankenexperiment that may be done in an MD simulation, the velocity vectors of all particles can be reversed simultaneously. If all collisions between the atoms and between the atoms and the walls are fully elastic and in the absence of numerical inaccuracies, all atoms will retrace their trajectories from the expansion phase, and the system will return to the initial state (and continue beyond if we do not stop it). Thus, although the state after the expansion is an equilibrium state that is thermodynamically not reversible, it is kinematically time-reversible [13] because the entire dynamics follows Newton's laws. Thermodynamic irreversibility has nothing to do with kinematic time-irreversibility.

#### 4.4 Time-reversible and time-irreversible interdiffusion

Consider again the setup represented by Figure 7a but now with two different ideal gases at the same pressure and temperature, one gas confined to each compartment. When we remove the partitioning wall the two gases will mix by diffusion in a spontaneous process, reaching a fully mixed final state without a change in temperature or pressure. The increase in entropy is given by the mixing entropy of the gases,  $2nR \ln 2$ . There is no spontaneous unmixing of the gases back to the lower entropy state. However, in an MD simulation we can again simultaneously reverse all velocity vectors, which causes the gases to unmix. The system has kept the memory of its kinematic history and is kinematically time-reversible but thermodynamically irreversible.

We now repeat the experiment with the two gases solvated in the same liquid. There will again be spontaneous mixing with the same mixing entropy. However, diffusion in a liquid is accompanied by friction. This is a non-Newtonian interaction that erases the memory of the trajectory, which causes time-reversibility to be lost. This outcome is in full agreement with the example by Lebowitz of mixing two fluids (Figure 2 of Ref. 6).

#### 4.5 The fluctuation theorem in its failure to reverse the arrow of time

The probabilistic nature of entropy is reflected by the statistical entropy formulations  $S_B$ ,  $S_G$ ,  $S_{vN}$ , and  $S_E$  defined in Section 2.5. Hence, the smaller an isolated system, the smaller are the number of microstates and degrees of freedom of the system and the more prominent statistical fluctuations of the system's entropy become around its average value. The entropy of sufficiently small isolated systems will therefore be frequently found to decrease or increase spontaneously for transient periods, a phenomenon that has been demonstrated through various experiments (see, e.g. [57,72-74]). Based on the relationship between the thermodynamic parameters, the same statistical fluctuations are manifested by the other thermodynamic parameters of microscopic isolated systems. By definition, for microscopic systems, the thermodynamic laws are only valid for long time averages because thermodynamic parameters have a clear physical meaning only when averaged over a sufficiently large ensemble. For example, in this context, the Second Law of thermodynamics is only valid when expressed as  $\langle dS \rangle \geq 0$ , where the angular brackets denote an ensemble average over all realizations of a thermodynamic process of the microscopic system, assuming ergodicity. Similarly, although nanomachines are able to spontaneously extract heat from the environment at random times and for durations determined by exponential probabilities (see below), such behavior does not violate the Second Law because thermal dissipation is positive *on average*. With the exception of the gravitational systems described in Section 5.5, claims of violations of the Second Law are therefore erroneous.

The stochastic fluctuations of a microscopic system's thermodynamic parameters are quantified by the so-called fluctuation theorem, which is a set of theorems sharing a common form and describing different parameters of a non-equilibrium time-symmetric

thermodynamic process [75]. The general form of the (transient) fluctuation theorem considers any entropy-producing, time-reversible process described by the trajectory  $x(t)$  in phase space for a time duration  $t$ . The time-reversal of this trajectory,  $x'(t)$ , corresponds to a negative amount of entropy change. The ratio of the probabilities of the forward and backward trajectories then results in [76]:

$$\frac{P[x(t)]}{P[x'(t)]} = e^{\sigma_{x(t)}}, \quad (17)$$

where  $\sigma_{x(t)}$  is the amount of entropy produced by the forward trajectory  $x(t)$ . This equation states that the forward, entropy-producing trajectory is exponentially more likely to occur than the backward, entropy-consuming trajectory, and the longer the trajectory (i.e. the longer the time over which changes in the entropy are averaged), the less likely the backward trajectory becomes. This expression can be simplified into an expression in terms of the entropy production  $\sigma(t)$  of a non-equilibrium, stochastic microscopically reversible process over time  $t$ , giving [31]  $\frac{P_F[\sigma(t)]}{P_R[-\sigma(t)]} = e^{\sigma(t)}$ , where  $P_F$  and  $P_R$  denote the probability of the forward and time-reversed processes, respectively, and  $-\sigma(t)$  denotes entropy consumption. In terms of the change in the system's total entropy during the process,  $\Delta S$ , expressed in units of the Boltzmann constant, the inverse probability ratio is given by  $\frac{P_R[-\Delta S]}{P_F[\Delta S]} = e^{-\Delta S}$ , indicating that the probability for an *apparent* violation of the Second Law decreases exponentially.

One of the notable successes of the fluctuation theorem is its use as a basis to derive an integral fluctuation theorem for the so-called dissipation function  $\Omega_t$  [29,77,78], expressed as  $\langle e^{-\Omega_t} \rangle = 1$ . Given that the extended time average of  $\Omega_t$  is equal to the average entropy production, an integral fluctuation theorem for  $\Delta S$  can similarly be derived, i.e.  $\langle e^{-\Delta S} \rangle = 1$ , representing a mathematical generalization of the Clausius inequality. Furthermore, the fluctuation theorem provides an elegant explanation of the transition between time-reversible dynamics, which occurs stochastically in microscopic systems, and thermodynamically irreversible dynamics (i.e. equilibration) in macroscopic systems by expressing thermodynamic parameters as ensemble averages.

Despite this and in contrast to numerous claims in literature [79], the fluctuation theorem is the wrong framework for investigations into the thermodynamic arrow of time and does not provide a basis for the Second Law. Firstly, the arrow of time is defined by the direction of spontaneous entropy increase of an isolated system, where entropy is a macroscopic state function defined for a system at equilibrium, while the fluctuation theorem deals with microscopic systems out of equilibrium for which the notion of entropy is ill-defined [80-82]. One of the main assumptions of non-equilibrium thermodynamics is that the system is in local thermodynamic equilibrium, while experimental demonstrations of time-reversals are for systems driven out of equilibrium. Secondly, even if the concept of entropy can be extrapolated to a non-equilibrium microscopic system, time-reversibility requires a deterministic description, in contrast to the stochastic description provided by the fluctuation theorem. We therefore clearly contradict the notion expressed in literature [79] that "the second Law is deeply rooted in the time-reversal symmetry of the laws of microscopic dynamics." Instead, the deeper, more fundamental question can be formulated as, Why does a transition occur between stochastic time-reversible dynamics at the microscale and thermodynamic irreversibility at the macroscale? Or, expressed mathematically, Why is a forward trajectory in phase space exponentially more likely to occur than the time-reversed trajectory? This review clarifies that it is due to the nature of thermal dissipation, which is not time-reversible due to kinetic reasons, as outlined, e.g., in Sections 3.3, 5.1 and 6.1. Built on this foundational aspect, the fluctuation theorem then gives a measure of the probability of

stochastic time-reversible processes, considering that the more degrees of freedom a system has, the smaller this probability becomes.

As pointed out in Section 4.1, time-reversals are fundamentally unrelated to reversals in the arrow of time: time-reversibility is the result of system-bath statistical correlations (or phase coherences in quantum systems), while thermodynamic irreversibility, which establishes the thermodynamic arrow of time, is the result of energy dissipation. Decoherence and dissipation are distinct processes, indicating that time-irreversibility cannot be directly related to the arrow of time, even though the two processes often occur together.

## 5. Dissipation and the entropy of the universe

### 5.1 *Maxwell's demon reversing the direction of spontaneous heat flow*

At this point, we may make use of a variant of the thought experiment presented in Figure 7. We replace the wall in Figure 7a by a fully elastic wall that does not absorb any energy, but the wall should have a hole that allows particles from the left and the right compartments to exchange. If initially the gas in the left compartment is at a higher energy ( $T_1 > T_2$ ), the particles traveling from the left to the right carry on average a higher kinetic energy. The number of particles is initially the same in both compartments, but since the particles at the left have a higher kinetic energy, more particles are expected to travel from the left to the right than in the reverse direction. This net particle flow will be progressively countered by the increasing density gradient between the right and the left until the gradient vanishes. Eventually, the probability of particles to cross from the left to the right will be the same as in the reverse direction. However, the higher kinetic energy of the particles traveling from the left to the right than in the reverse direction gives rise to a situation where we have zero net particle flow but non-zero (positive) net heat flow from the hot to the cold compartment. When equilibrium is reached at  $T_1 = T_2$ , particles will still exchange, but there is no longer any net heat flow. We have a dynamic equilibrium. It is plausible that this process is not reversible. This would be inconsistent with experience that one of the compartments will heat up spontaneously at the cost of the other one. To make this possible, we would have to place *Maxwell's famous demon* at the hole. His job is to select the particles passing the hole, leaving the more energetic particles to pass only from the left to the right, and the low energy particles in the reverse direction [83]. It may be imagined that a small machine can be constructed to do the job of the demon. This has inspired scientists, and the construction of a nanodevice based on a *Brownian ratchet* was reported 2007 by Leigh [84]. However, the device needs to be powered by an external source and therefore does not violate the Second Law of thermodynamics.

It is significant that  $\delta Q$  in eqn. (1) is consistently expressed as “heat”, not more generally as “energy”. This is explained conveniently by means of the Carnot cycle, a thermodynamic process of a gas in which the end point is identical to the starting point and which is at all times conducted reversibly, meaning that the temperature and pressure of the closed system are at all times identical to the temperature and pressure of the environment. Since the end point of the process is identical to the starting point, all state functions like temperature  $T$ , pressure  $p$ , volume  $V$ , and the internal energy  $U$  or the entropy  $S$  of the system are unchanged after the full cycle, although they vary in between. However, heat  $Q$  and work  $W$  are not state functions; they depend on the path of the process.

### 5.2 *Spontaneous and driven processes of a closed system*

In a reversible heat engine, following a clockwise direction of the Carnot cycle in a  $p - V$  diagram (Section 2.6, Figure 2), heat is absorbed from the environment during the high temperature (isothermal) leg of the process, partly converted into work that the engine

provides, while the remaining fraction is dissipated as reversible “waste heat” during the lower temperature (isothermal) leg. No thermal energy is lost, but there is no way to convert it completely into work. The dissipated heat is absorbed in full by the environment that acts as a bath (a thermal reservoir with infinite capacity) at the same temperature. If we reverse the direction of the process, we obtain a heat pump in which the environment has to provide work to the system so that more heat can leave the system at the high temperature leg than is absorbed at the low temperature. Although we talk about “processes”, reversible processes are infinitely slow.

Processes occur *spontaneously* down a gradient, but they can also be *driven* to occur uphill. Real processes are always irreversible, with temperature and/or pressure of the system being different from those of the environment. For the case of the heat engine, a chemical fuel provides the heat during the high temperature leg. In addition to the reversibly dissipated heat  $Q_c$  there is now an irreversible fraction of heat that is dissipated to the environment, resulting in an increase of  $S_{universe}$ , as required by the Second Law (eqn. 1).

The heat pump represents a driven process in which the environment exerts work on the system, resulting in heat flow from the lower temperature system to the higher temperature environment. This leads to a reduction of the system’s entropy, but in an entropy increase of the environment. The latter fraction is larger for the irreversible process so that there is also a net increase of the entropy of the universe. The rate of entropy production,  $dS_{universe}/dt$ , (eqn. 6) is the driving force of a real process. Energy is always conserved, but entropy is conserved only in reversible processes. The entropy of the universe as the prototypical isolated system never decreases.

Specifically, the Second Law does not forbid the entropy of a partial (closed) system to decrease. In fact, many processes in daily life, like driving a car uphill, chemical synthesis of large molecules, crystallization, distillation, and other separation processes in the laboratory, lead to lower entropy in a partial system. Importantly, also biological processes such as the growth of plants (driven by photosynthesis) or replication of organisms (driven by adenosine triphosphate – ATP – the energy currency of living organisms) represent vital processes which seemingly contradict the Second Law since they lead to partial systems at lower entropy [39]. Even the transformation of single cells to complex forms of life according to the evolutionary theory of life is not in contradiction with the Second Law (see Chapter 8).

Kelvin recognized the importance of these processes not only for individual organisms but also for the development of life on our planet. He concluded with stunning clarity that “within a finite period of time past, the earth must have been, and within a finite period of time to come the earth must again be unfit for the habitation of man as at present constituted” [24]. This can be seen as an early and remarkable statement of the “arrow of time” and of the development of the universe towards “heat death” [39].

### 5.3 Dissipation of energy as photons and as heat

A question that remains is whether the Second Law also applies to the case where energy dissipation is in the form of photons instead of heat. Colloquially, we identify radiation in the UV-visible range as photons and in the infrared as heat, but this distinction relies on human perception and places an arbitrary limit on a continuous energy scale. Energy is a state function, and the energy of  $n$  photons amounts to  $n h \nu$ , but the heat  $Q$  is not a state function. A didactical comparison of a monoatomic ideal gas and a photon gas has been provided by Leff [85]. He points out the fundamental differences of the two systems. The MB distribution is based on classical physics or the semi-classical limit of a quantum ideal gas and hence does not provide insights on quantum or relativistic phenomena. Its internal energy is independent of volume, which for real gases holds only in the low-density limit. It therefore

gives also no insight into phase changes such as the vapor-liquid transition. In contrast, the photon gas is a quantum-mechanical system of particles with zero rest mass. Photons move with the speed of light so that the photon gas is a relativistic system. This leads to many differences in thermodynamic properties of the two systems, but interestingly, and most significantly in the present context, the comparison reveals that both systems have the same efficiency in a reversible Carnot cycle, and furthermore,  $Q = H$  for the photon gas, i.e. the heat is equivalent to the enthalpy of a gas of  $n$  photons [85]. This is the basis for the fundamental equivalence of dissipation of heat of a MB system with dissipation of photons from a black body.

A second question relates to the type of matter. An MB ensemble of a monoatomic ideal gas seems to be a rather special type of matter. It was confirmed, however, that the distribution function of the black-body radiation matches any type of matter, also solids, and even the distribution of the cosmic radiation background [86]. This demonstrates that the radiative and the collisional body pictures are fully equivalent. Dissipation of heat and dissipation of photons are therefore also equivalent. Moreover, heat dissipation must also be time-irreversible, just as photon dissipation, which was justified by the probabilistic nature of spontaneous photon emission, i.e. by the asymmetry of absorption and emission discussed in Section 3.3.

Planck's formula for radiation inside a hollow black body gives the maximum possible rate of absorption and emission in thermal equilibrium [87]. It holds for emission across a vacuum gap in the far-field limit, i.e. over distances that exceed thermal wavelengths [88]. Between two bodies out of equilibrium, the processes are the same, but the intensity of emission of the hot body exceeds that of absorption so that there is net dissipation. Wien's law gives the maximum of the radiative energy distribution at 300 K from  $T \cdot \lambda_{\max} = 2.898 \times 10^{-3} \text{ m} \cdot \text{K}$  in the infrared around  $10 \text{ } \mu\text{m}$ , or  $1000 \text{ cm}^{-1}$ , not too far from the bending vibration of the water molecule ( $1648 \text{ cm}^{-1}$ ). However, the energy density in this spectral range corresponds to a single exchanged photon per nm in 2.5 hours, which is not a sufficiently efficient process that could explain radiative heat transfer in the bulk of condensed matter. By comparison with a 90 nm wide fluorescence band with a typical fluorescence lifetime of 1 ns it falls short by 11 orders of magnitude at 300 K.

Recent work has reported a hundred-fold enhancement of radiative heat transfer over separations greater than the Wien wavelength [89]. Of more interest is work that finds giant heat transfer, over distances shorter than the Wien wavelength [90]. Although this heat flux is more than five orders of magnitude larger than predicted by Planck's black-body radiation of equilibrated systems and requires new models of heat transfer across a vacuum gap, it still falls short for an explanation of typical deactivation rates near room temperature. However, this does not matter, since the radiative and collisional mechanisms represent the same equilibrium. It just means that the collisional mechanism is more efficient and dominates equilibration at not too high energies.

#### 5.4 Heat death and the entropy of the universe

The universe is homogeneous on a scale above  $\sim 100$  million light years. It is therefore generally assumed that thermodynamics is valid also for the description of the universe, starting with the *Big Bang*. The Second Law requires the entropy  $S_{\text{universe}}$  to increase monotonically with all non-zero rate processes. Nothing flows, nothing blows and nothing grows without this increasing entropy. It will not go to infinity but reach a maximum value at equilibrium, where all processes come to rest. This state is called *Heat Death*, or also *Big Chill* or *Big Freeze*, and for a system with an effective radius  $R$  the upper limit of entropy

scales with its total energy  $E$  and is given as  $S_{universe} \leq 2\pi RE/\hbar c$ , where  $c$  is the vacuum speed of light and  $\hbar$  is Planck's constant [91].

A common chemical reaction, the combustion of 1 mol of glucose to carbon dioxide and water, may serve as a simple model system to help understand what heat death means (Figure 8) [39]. First, we look at the reaction in an isothermal and isobaric closed system. It is exothermic, with  $\Delta H_R^0 = -2805$  kJ. This energy is dissipated as heat. The reaction is also strongly exergonic and therefore spontaneous, with  $\Delta G_R^0 = -2883$  kJ, but it is endentropic with  $\Delta S_R^0 = +262$  J K<sup>-1</sup>. Although the reaction is thermodynamically favored, it does not readily occur at room temperature because it is kinetically hindered by an activation barrier  $E_a$  (Figure 8b). Nature routinely reverses this reaction by a process called photosynthesis and restores the situation where the less stable glucose molecule is trapped behind the barrier in a side minimum of the energy hypersurface. The trapping of matter behind an energy barrier in a metastable state is a common situation in daily life [39].

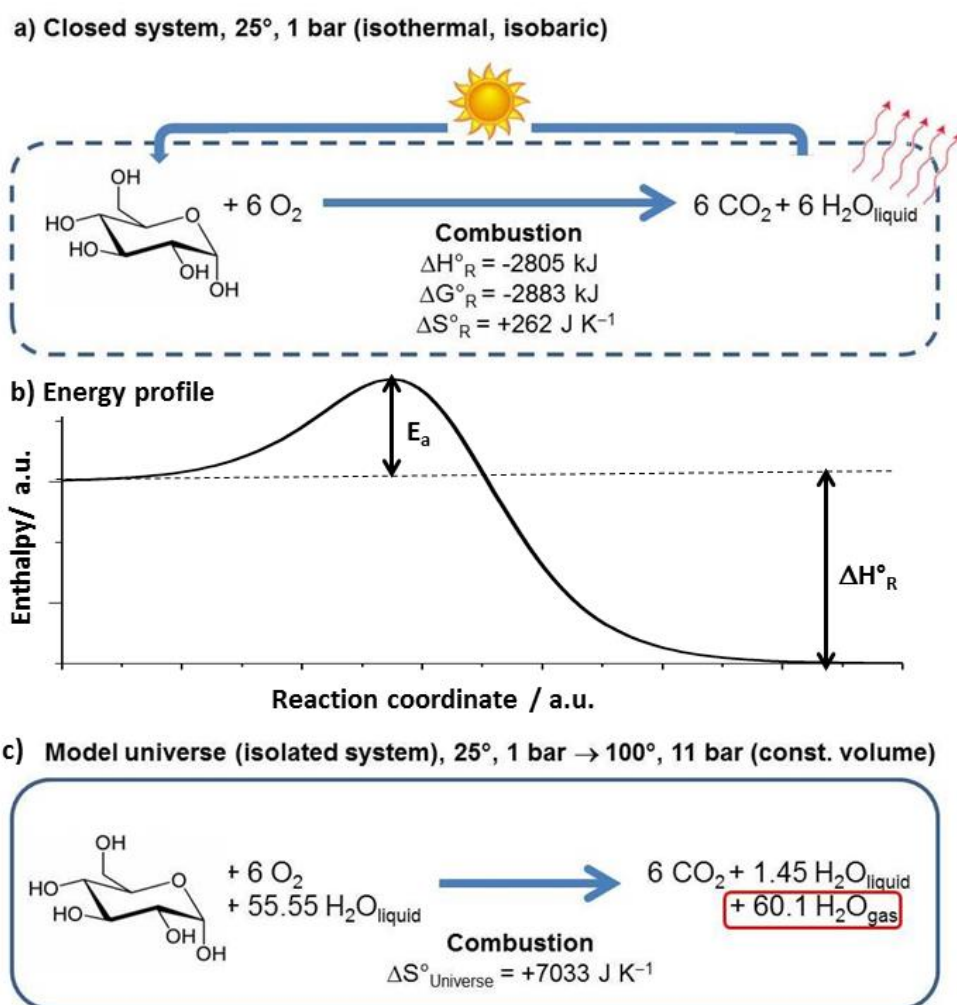


Figure 8: a) Oxidation reaction of glucose with oxygen to water and carbon dioxide, with thermodynamic parameters for the reaction at standard pressure and temperature in a closed system. b) Schematic energy profile of the reaction. c) The same reaction in an isolated system with 1 L added water serving as a model universe to illustrate heat death. (Adapted with permission from [39], published by the Royal Society of Chemistry (open access, color online))

Figure 8c shows the same reaction, but now in an isolated system at constant volume. To cope with the process heat, which can no longer be dissipated, we have added 1 L of liquid water. The reaction is still spontaneous, as revealed by the entropy increase,  $\Delta S_{universe} = +7033 \text{ J K}^{-1}$  per mol of glucose. But the heat of reaction heats up the water to its boiling point and evaporates most of it. Thus, this model reaction tells us that heat death means a much higher temperature and lots of water vapor in the atmosphere of our planet.

Photosynthesis also creates molecular oxygen. The high oxygen concentration in the Earth's atmosphere is unique among the planets in our solar system, and it is taken as a measure of the deviation from equilibrium conditions [92]. It is generally assumed that all of the molecular oxygen in our atmosphere originates from photosynthesis and that before the first photosynthetic organisms existed, the Earth had a reducing atmosphere consisting mostly of nitrogen, carbon dioxide and water vapor, similar to that of the other planets that have not lost it.

It has been known since 1929 that the universe is expanding [93], implying that the distance between galaxies increases, while gravitation holds together the stars within the shorter length scale of a given galaxy. The entropy of an ideal gas that expands freely into space increases (see Section 4.3). However, the expansion of the universe is isentropic on the ground that entropy of relativistic particles such as photons, gravitons and neutrinos is only proportional to the number of such particles and does not increase with volume expansion [93]. Nevertheless, a monotonic increase of the entropy of the universe is often assumed (Figure 9).  $S_{universe}$  has various contributions which can be estimated. By far the most important one is the entropy of the black holes, amounting to ca.  $3.1 \times 10^{104}$  in units of the Boltzmann constant  $k$  [93]. It is followed by the contributions of the cosmic microwave background, the cosmic neutrinos, dark matter, the cosmic graviton background, the interstellar and intergalactic medium, and only in seventh position the contribution of all stars, 24 orders of magnitude less than that of the black holes.

On a scale below a million light-years, the universe is very inhomogeneous, as evidenced by our solar system. Considering the tiny fraction that the Earth takes in the entire universe, it is a brave and momentous assumption to generalize the laws of thermodynamics, which were derived empirically from observations of conventional matter on Earth, to hold for the entire universe, including objects like black holes. In this context it is perhaps significant that the low value of the initial entropy of the universe after the Big Bang that left matter in the form of a hot plasma is an unresolved issue of cosmology [93, 94]. However, the entropy of the entire universe did not have to be low in order for our part of the universe to have low entropy [93]. There are hot stars and cold objects, so the universe is not only inhomogeneous as regards to mass distribution but despite its age certainly also not in thermal equilibrium. Feynman discussed whether the low entropy part of the universe could represent an entropy fluctuation [95]. Reverting to Figure 8, the products of photosynthesis (a miniature analog of the Big Bang) are left at lower entropy, trapped behind a barrier, we suggest that the initial state is perhaps a *trapped* low-entropy fluctuation.

The universal validity of the thermodynamic formalism is generally accepted [88,93]. In particular, Einstein praised it as "the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic concepts, it will never be overthrown." [32]. It is agreed that thermodynamics is a valuable and self-consistent theory. It works well in its application to ideal systems like noble gases, which have negligible interaction between particles. It also works for condensed matter where the interparticle interaction is constant if we disregard short-time oscillations or fluctuations. However, for systems with a pronounced dynamic variability of interactions, such as for ionic, van der Waals or Lennard-Jones interactions at varying concentration, e.g. near phase transitions,



the ideality is lost, and empirical fudge factors (fugacity, activity, virial van der Waals, or Lennard-Jones coefficients) have to be introduced to match experiment and theory.

There are also alternative cosmological hypotheses for the fate of the ultimate universe. The factors to be considered for proposals of the ultimate fate include its structure and shape (which is generally assumed to be flat), the amount of dark energy that it contains, and how this energy density responds to the expansion of the universe. The *Big Rip* describes a situation of infinite expansion in which all matter disintegrates into elementary particles and radiation. The model has been criticized to rest on implausible physical properties [97]. The *Big Crunch* proposes that the expansion slows down, reverting to a contraction that ends up in a collapsed universe of extremely high density that leads to a new Big Bang. Such a repeatedly cyclic model would be in contradiction with the Second Law of Thermodynamics [98].

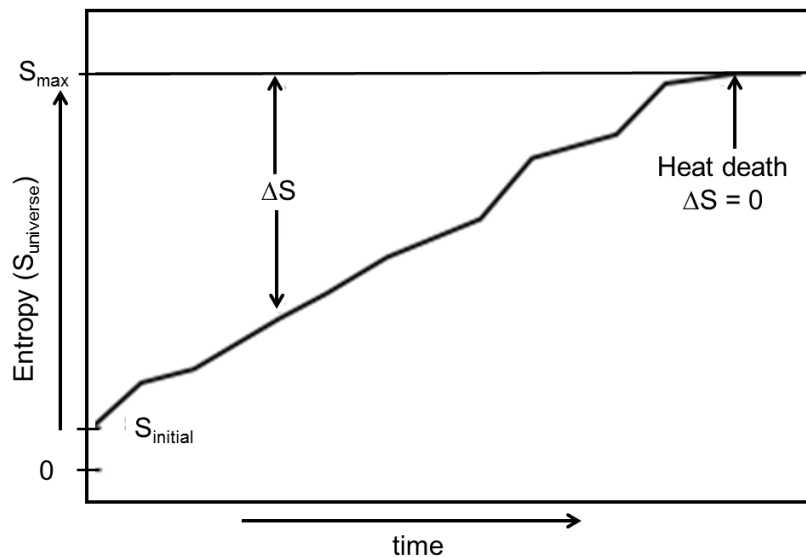


Figure 9: Schematic drawing of the monotonically increasing overall entropy of the universe with time, from its initial value after the big bang to heat death [90]. The entropy of an ensemble of stars in a given galaxy is known to decrease spontaneously, because of the negative specific heat (see Section 5.5). (Reprinted with permission from [99]).

### 5.5 Stellar galaxies: the gravitational potential requiring an extension of the Second Law

We are used to believe that the heat capacity of matter must be positive, i.e. that the temperature of a sample increases when heat is added to it. However, astronomers have known for more than a century that adding energy to a star or a star cluster makes it expand and cool down [100]. This explains the absence of a local entropy maximum, called the gravothermal catastrophe, for stellar systems of a given energy and mass within a rigid sphere [101].

The virial theorem (from Latin *vis*, meaning “force” or “energy”) describes the evolution of the kinetic energy of particles under a potential gradient. If the expectation value of the system’s total potential energy scales with distance  $r$  as  $\langle V \rangle \sim r^{-n}$ , the virial theorem takes on the form  $\langle 2K \rangle + n\langle V \rangle = 0$ , where  $\langle K \rangle$  is the expectation value of the total kinetic energy of the system. For non-interacting particles such as an ideal gas,  $n = 0$ , yielding zero kinetic energy. This is not correct since it is well known that the thermal kinetic energy of an

ensemble of  $N$  particles is  $\langle K \rangle = \frac{3}{2} Nk\langle T \rangle$  ( $k$  being the Boltzmann constant and  $T$  the temperature). The kinetic energy derived from the virial theorem for  $n \neq 0$  represents the monotonic evolution of the kinetic energy under the influence of the potential gradient when potential and kinetic energy are interconverted. It is thus of a different characteristic than the kinetic energy from random thermal motion. It may be debatable whether the kinetic energy of monotonic origin should also be counted as heat, but it is not debatable that an attractive interaction as it occurs under gravitation ( $n = 1$ ) must have severe consequences for the state of matter and for the direction of spontaneous processes. These effects are subject to the following discussion.

Considering the proper  $r^{-1}$  distance scaling of the gravitational potential, the properties of a cluster of stars is typically treated thermodynamically like an ensemble of gas particles. It follows from the virial theorem for  $n = 1$ , given the total energy  $\langle E \rangle = \langle K \rangle + \langle V \rangle$ , that  $\langle K \rangle = -\langle E \rangle$  in the absence of random thermally related kinetic energy. Gravitational systems are bound systems since  $\langle E \rangle$  is negative because  $\langle K \rangle$  is always positive. Therefore,  $\langle K \rangle$  decreases when  $\langle E \rangle$  increases, which, provided that  $\langle K \rangle$  corresponds to heat (see previous paragraph), means that the system has a negative heat capacity. This is the basis for the claim of *negative heat capacities*, and Lynden-Bell arrives at this conclusion using a slightly different justification [100]. For Sections 5.5 and 5.6 we shall adopt this nomenclature that has been established in the referenced literature, but we recommend to use it with caution. For a system at constant energy, the potential energy depends on particle density in the opposite direction than the kinetic energy, and temperature becomes a function of density.

There are notable consequences of the  $r^{-1}$  scaling of the (unscreened, contrasting with the screening of the Coulomb potential in multi-particle systems) gravitational potential. Because of the puzzling phenomena, isolated, self-gravitating systems represent a long-held puzzle that has not been successfully resolved for nearly 50 years [102]. If the  $N$  particles of energy  $E$  are placed in a spherical box of radius  $r_e$ , the most probable distribution deviates from the homogeneous case that we have for non-interacting gas atoms. The most probable radial distribution function with the gravitational potential determined self-consistently assumes a local maximum – where the Boltzmann entropy is highest – whenever  $r_e$  is not too large. In addition, as  $r_e$  increases, the density at the edge,  $\rho_e$ , drops compared with the density at the center,  $\rho_c$ , due to gravity [100]. As determined first by Antonov [103], this maximum occurs at a point A (the Antonov point) where the density contrast between the center and edge,  $\rho_c/\rho_e = 709$  (Figure 10a). At values of  $\rho_c/\rho_e$  greater than A, the distribution becomes unstable and develops further local maxima with increasing  $\rho_c/\rho_e$  [100]. The most probable distribution at A corresponds to the most stable situation with the most negative dimensionless binding energy of the system,  $-Er_e/(GM^2)$ , where  $M = N \cdot m$  is the total mass of the system and  $G$  is the gravitational constant (Figure 10a). The figure also shows that the dimensionless binding energy of an equilibrium gravitational gas sphere never exceeds a value of 0.335 for any size of the sphere.

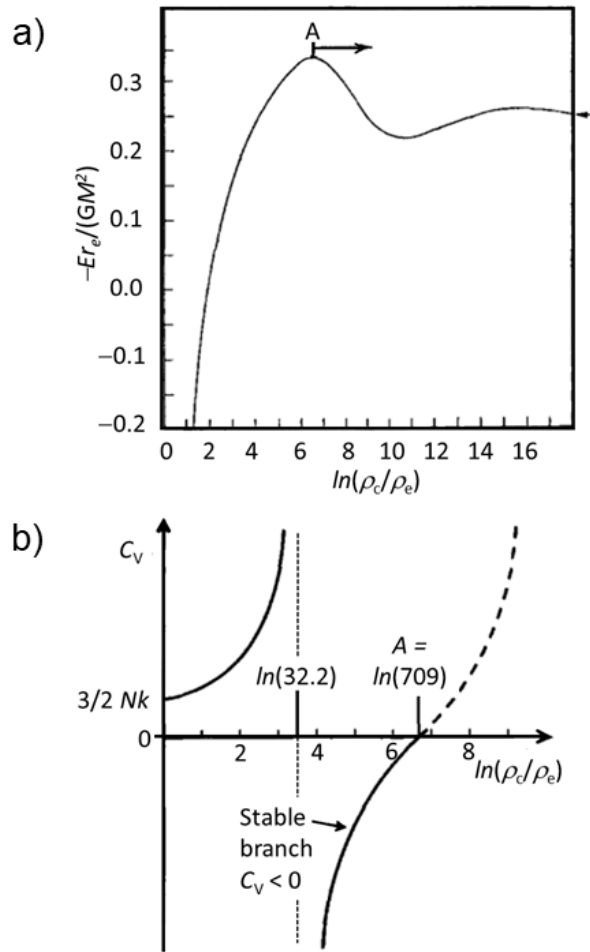


Figure 10: a) Dimensionless binding energy,  $-Er_e/(GM^2)$ , for a self-gravitating sphere in a spherical container as a function of the natural logarithm of the density contrast between center and edge,  $\ln(\rho_c/\rho_e)$ , and b) its specific heat,  $C_V = dE/dT$ . Instability sets in at the Antonov point A where  $\rho_c/\rho_e = 1/709$ . Redrawn and adapted from [100].

The calculations were made for an isolated system with constant energy. For further understanding, the heat capacity at constant volume is calculated by adding an infinitesimal amount of heat. The result, displayed in Figure 10b, is spectacular. For  $\rho_c = \rho_e$ , i.e. at zero gravity,  $C_V = 3/2 Nk$ , as expected for a non-interacting monoatomic gas. Switching on more and more gravity increases  $C_V$  until the edge density is a factor 32.2 less than the density at the center, at which point there is a discontinuity where  $C_V$  flips to negative values, followed by an increase until it crosses zero from below at the Antonov point A [100]. The negative heat capacity occurs in the stable range of Figure 10a (between  $\ln 32.2$  and  $\ln 709$ ). Theory predicts in particular that under very general assumptions, stable thermal equilibrium configurations of isolated systems near instability always have negative heat capacities, which turn to be positive when systems become unstable! In classical thermodynamics a small thermally stable subsystem of an ensemble has always a positive heat capacity [104]. For classical thermodynamic systems with negative heat capacity we refer to Section 5.6.

Thus, thermodynamic equilibrium of a self-gravitating system enclosed within a box exists only above a critical energy  $E_c = -0.335 GM^2/r_c$  or above a critical temperature  $T_c = GM/2.52kR$  and is at most a metastable state, i.e., a *local* maximum of a relevant thermodynamic potential, i.e. the entropy in the microcanonical ensemble and the free energy in the canonical ensemble. For  $T < T_c$  or  $E < E_c$ , the system is expected to collapse, which is called the gravothermal catastrophe [105,106].

Some of the stunning consequences of negative heat capacity systems are the following [96]:

- (i) Two negative  $C_V$  sub-systems in thermal contact at slightly different temperatures cannot evolve to thermal equilibrium. The hotter part gives away energy, getting hotter, while the colder one gets even colder by absorbing this energy. Heat flows from cold to hot, in apparent contradiction to the Second Law, and the slight initial deviation from equilibrium is amplified, even by small fluctuations. In reality, the Second Law is still correct, but Clausius' formulation that "heat can never pass from a colder to a warmer body without some other change" [107] is restricted to the classical case of positive  $C_V$  and thus to matter that is not ruled by the  $r^{-1}$  dependence of self-gravitational interaction.
- (ii) A negative  $C_V$  system cannot equilibrate with a heat bath. When it is initially hotter than the bath, heat that flows to the bath will cause the system to heat up further. Stable isolated systems near instability are necessarily unstable if put in a heat bath. This well-known "non-equivalence of ensembles" has no analog in classical thermodynamics [104].
- (iii) Most interestingly, a stable equilibrium can be achieved between two sub-systems if one of them has positive  $C_V$  and the other one negative  $C_V$  provided the sum of the two is negative. The negative  $C_V$  system is initially hotter, and heat will flow to the cooler sub-system, which will also get hotter, but by a smaller amount since the combined heat capacity is negative.

Isothermal gravitating spheres with a density contrast greater than 709 are internally unstable and develop spontaneously a temperature gradient with a hotter center and a cooler edge. This is of important consequence for stellar systems, called the gravothermal catastrophe, in which the central part gets hotter and denser compared with the more sluggish outer part. It leads to the formation of *black holes*, as confirmed by Hawking's calculations [108].

A remarkable and seminal conclusion about the entropy principle and its consequence for the Second Law of self-gravitating systems was drawn by He and Kang [102]. They expressed it as seemingly paradoxical, but actually complementary. The conventional Clausius inequality for an isolated system states that entropy never decreases spontaneously, but for the long-range interaction of self-gravitating systems, the entropy never increases. This does not conflict with the standard Second Law of thermodynamics, since the latter is only valid for systems dominated by short-range relaxation mechanisms. The result merely generalizes the Second Law to accommodate the different behavior of long-range, self-gravitating systems. However, the presence of regions in the universe where entropy increases and others where it decreases spontaneously complicates greatly the question about the initial state of the universe, in particular its entropy and the distribution of matter [94].

He and Kang [102] illustrate the result by a thought experiment: Take a sample of an ideal gas confined in an adiabatic container that resides in vacuum. Then remove the container walls. The gas expands into vacuum in order to increase its entropy. Next, a long-range attractive potential (the gravitational potential) is switched on. It initiates a time-reversal and pulls the gas back toward the initial location, which is accompanied by a decrease in entropy. Finally, the container walls are put back in place and the long-range potential is switched off, restoring the initial low-entropy conditions.

We now have two different signs for the entropy change in spontaneous processes in isolated systems:  $\delta S < 0$  for the thermodynamics of conventional matter in the absence of a long-range self-gravitating potential, and  $\delta S > 0$  for self-gravitating systems. This suggests

that there must be a transition from one to the other behavior where the two behaviors are in equilibrium with  $\delta S = 0$ . It was found that this condition exists, but the entropy function is neither a maximum nor a minimum but a saddle point [109]. This is consistent with Antonov's conclusion [103] that equilibrium states of self-gravitating systems are not maximum entropy states.

On a remote but interestingly related matter, it has been pointed out that an interesting analogy exists between self-gravitating Brownian particles and bacterial populations. This biological context describes the chemotactic aggregation of bacterial colonies that can develop a finite time singularity [110].

### 5.6 Cluster physics: negative specific heat of evaporative ensembles

Negative specific heat is a property not only of long-range self-gravitating systems but also of species with short-range attractive interactions as described, for example, by the Lennard-Jones potential of atoms or molecules forming nanoclusters. Potentially, the phenomenon must occur for any process where kinetic energy is converted to potential energy and the loss of kinetic energy is equivalent to cooling.

Serving as an instructive example, cyclic  $S_8$  molecules can spontaneously ring-open above  $\sim 430$  K to form linear  $S_8$  and longer polymeric chains. The potential energy needed to break the bond originates in the excitation energy of vibrational degrees of freedom. The RRK theory of unimolecular reactions according to Rice, Ramsperger and Kassel assumes that energy can flow freely between vibrational modes within a molecule. The more vibrational modes are available in a molecule, the higher is the probability to realize a fluctuation that locates the required fraction of available vibrational quanta in one specific bond that allows it to break. [111,112].

An example from cluster physics is the *evaporative ensemble* shown in Figure 11. One or more atoms can evaporate off an isolated cluster in the gas phase, again by conversion of kinetic to potential energy [113]. If the initial temperature is just above the melting point, the remaining cluster may crystallize when it spends some of its kinetic energy to dissociate off a fragment. The experiment can also be conducted in a closed system that allows the addition of heat, for example via infrared laser pulses. Microcanonical calculations as a function of energy revealed a negative heat capacity for an  $Al_{147}$  cluster [114].

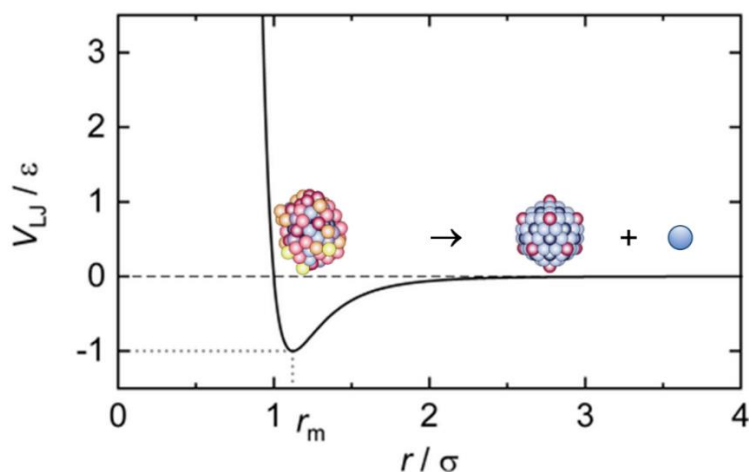


Figure 11: Evaporative ensemble with negative heat capacity. The isolated cluster is initially equilibrated just above the melting point. Converting some of the kinetic energy to potential energy permits one or more atoms to dissociate off, leaving the cluster at a lower temperature,

possibly below the melting point. This is a metastable rather than an equilibrated state. (color online)

A systematic analysis of caloric curves with negative heat capacities in two- and three-dimensional Lennard-Jones-like systems has been given by Ison et al. [115]. The occurrence of negative heat capacities has been criticized as an artefact of applying equilibrium thermodynamics to small systems trapped in a metastable state [116], but this was denied using microcanonical calculations for the heat capacity of equilibrated  $\text{Na}_{147}$  clusters [117], which is the experimental system of Schmidt et al. [113]. The results are displayed in Figure 12. These authors agreed that S-shaped caloric curves (lower left inset of Figure 12) can also give arise to non-ergodic macroscopic systems, but that this effect is rare in small clusters. The negative specific heat and the associated S-shaped entropy curves in these systems originate in the attractive shape of the Lennard-Jones potential and the interconversion of kinetic into potential energy when the bond length increases. As discussed in Section 5.5, this type of monotonic kinetic energy should perhaps not be termed “heat”.

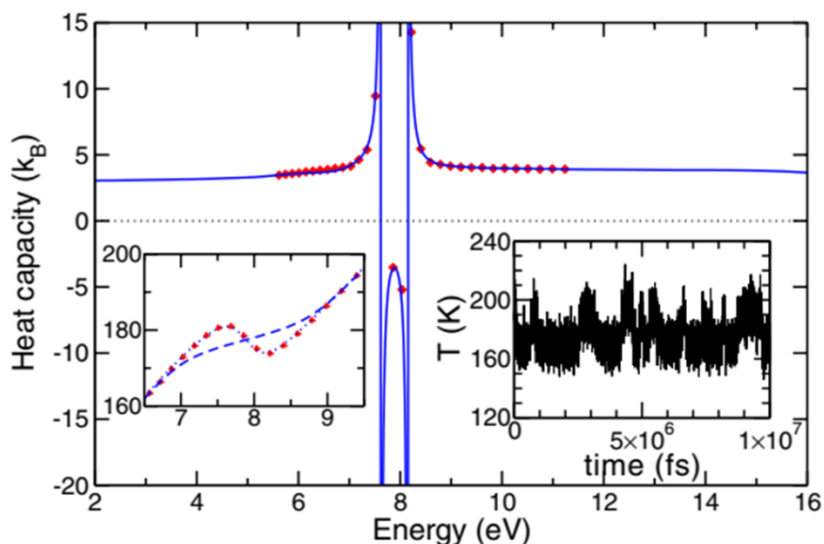


Figure 12: Microcanonical heat capacity of  $\text{Na}_{147}$ . The red dots and blue line correspond to values obtained from microcanonical total energy densities of states calculated using microcanonical and canonical parallel tempering MC, respectively. The microcanonical temperature is shown in the lower left inset, along with the canonical curve as a dashed line. The lower right inset shows the variation of the kinetic temperature along an MD trajectory in the coexistence energy range. (reprinted with permission from F. Calvo et al. [117]. Color online)

The short-range attractive interactions between atoms and molecules play a central role also in phase transitions, notably in liquefaction of gases. Phenomenologically, this phase transition is described, for example, by the van der Waals equation, in which the effective pressure is reduced from the ideal gas pressure as a result of the attraction by a term that is called *internal pressure*. Interestingly, using the formalism developed for self-gravitating systems, Kang derived an equation that is analogous to the van der Waals equation [118] and already Lynden-Bell showed that an element that obeys the full curve of the van der Waals equation inevitably has a negative  $C_p$  while  $C_v$  remains positive [100]. He furthermore suggested that perhaps *all* first-order phase transitions could be viewed as due to negative specific heat systems of molecular size. Just as in the thought experiment of Section 5.5, a condensing gas follows the attractive forces to reduce its volume to that of the liquid, accompanied with a lowering of the system entropy, but the heat of condensation is

dissipated to the surrounding bath to an extent that the increase in entropy of the surrounding is greater than the decrease by the system. The Second Law thus remains valid in the conventional form.

## 6. Irreversibility of dissipation: a probabilistic phenomenon

### 6.1 Photon emission from excited states: a first-order probabilistic process

While the black-body radiation model addresses equilibrium systems, we now focus on excited electronic states for which there is a net dissipation of energy (Figure 13). The essential point for loss of time-reversibility is to account for probabilistic events. These are found typically in the interaction with radiation, as recognized early on by Einstein: “The process of emission of light does not have the character of reversibility” [119]. The radiative decay of excited states may be spontaneous or induced by collisions with other particles or with photons. Both types occur at a random time, and photon emission breaks the deterministic nature of Newtonian mechanics. Their probability is a manifestation of Heisenberg’s uncertainty principle, giving rise to the “natural linewidth” of a particular transition [120]. The transitions follow first-order kinetics, i.e. the rate is proportional to the concentration of the reactant, as in a radioactive decay. Calculation of their probability is based on Fermi’s Golden Rule that goes back to a perturbation theory approach by Dirac [121]. They invoke the transition moment for electric dipole allowed transitions (eqn. 14). The finite lifetime of a discrete state is a truly quantum mechanical effect that is not found in a classical energy continuum. Furthermore, the photon is emitted not only at a random time but also normally in a random direction as long as it is compatible with the direction of the transition moment. The recoil effect of the emitted photon kicks the emitting species out of its initial trajectory, which erases the path information in an irreversible way, as described by Doyle [122].

Fluorescence is the spontaneous emission of a single photon that carries away most of the excitation energy (Figure 13a). It is a probabilistic process akin to radioactive decay, and it therefore shows first-order kinetics. Typical fluorescing molecules are planar, rigid and contain delocalized and aromatic motifs, and the fluorescence lifetimes in liquid solution ( $1/k_F$  in Figure 13a) are about 1–20 ns [123]. This is a few orders of magnitude longer than the collision-free time in condensed matter and therefore suitable to destroy the collisional reversibility. Collisions may also shorten the lifetime of excited states because they cause a transient distortion of the wave functions and thus influence the transition moment that governs photon emission. Forbidden transitions may therefore become partly allowed.

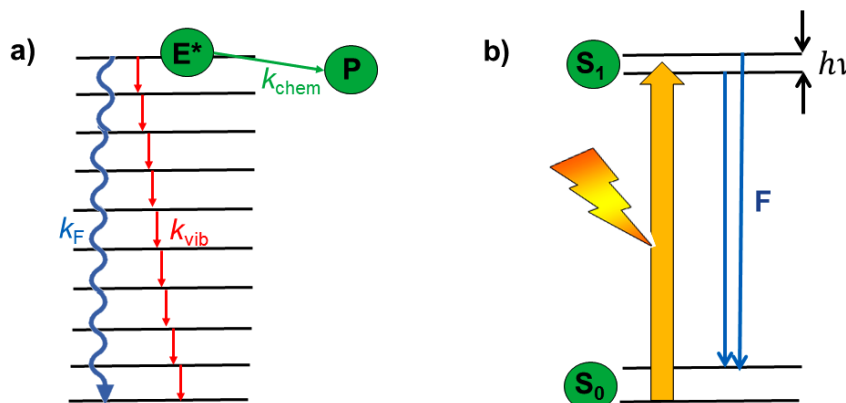


Figure 13: a) Schematic representation of energy dissipation from an excited quantum state  $E^*$ . Excitation may have taken place by absorption of a photon, by a collision, or the molecule may have been created with excess energy in a chemical reaction. Shown are three



deactivation processes: (i) fluorescence emission of a photon at a rate  $k_F$ , if the transition is electric dipole allowed [124], (ii) vibrational relaxation at a rate  $k_{vib}$ , also called non-radiative relaxation, via excited vibrational (and rotational) states of the ground state, and (iii) chemical reaction to a product state P by molecular fission or electron transfer that occurs at a rate  $k_{chem}$ . b) Schematic 4-level system with ground state  $S_0$  that is excited with a short laser pulse that is wide enough to excite coherently two sublevels of the electronic excited state  $S_1$  that is a superposition of the two substates and oscillates at the frequency  $\nu$  corresponding to their energy difference. This oscillation leads to modulation of the fluorescence intensity at the frequency  $\nu$  of the quantum coherence. (color online)

Also non-radiative energy dissipation like vibrational deactivation is a probabilistic process that obeys first-order kinetics. It occurs on the picosecond or sub-picosecond timescale ( $1/k_{vib}$  in Figure 13a) [125]. Vibrational energy is dissipated as heat. Ultrafast electron-transfer or molecular fission reactions may proceed on a similar timescale ( $1/k_{chem}$  in Figure 13a). Both of these mechanisms are thus often more efficient than radiative processes. The fluorescence lifetime  $\tau_{E^*}$  is given by the inverse sum of the individual rates, which are all of first order (or possibly pseudo-first order in the case of  $k_{chem}$ ) and therefore probabilistic:

$$\tau_{E^*} = (k_F + k_{vib} + k_{chem})^{-1} \quad (18)$$

Vibrational deactivation is not directly observable, and its rate,  $k_{vib}$ , can only be determined from variations of  $\tau_{E^*}$  in eqn. (18) if  $\tau_F$  and  $k_{chem}$  can be varied independently via quencher concentrations (Stern-Volmer kinetics).

Behavior with an extended excited-state lifetime is possible only in an energy-quantized and thus quantum-mechanical system but not in an energy continuum. Classical mechanics is continuous, deterministic and does not lead to the emission of discrete light. The quantum world is discontinuous (energy-quantized). Only discrete states show probabilistic, finite lifetimes and emission. In this sense, irreversibility is a direct consequence of quantum mechanics.

### 6.2 Quantum coherences: damped and undamped oscillatory behavior

Figure 13b shows the case where two vibrational sublevels of an electronic state are excited instantaneously and therefore coherently (i.e. in phase) with a laser pulse that is sufficiently short and, following Heisenberg's uncertainty principle, energetically sufficiently broad so that it can excite both sublevels. The excited state is then in general a non-eigenstate, i.e. a superposition of two or more eigenstates that oscillates between these states. This oscillating behavior is called "quantum beating" or "quantum coherence" [126]. It is recorded conveniently as intensity oscillations of the cross-correlation between the two coherent states, with an oscillating frequency equal to the energy difference between the two coherent states, which is revealed after Fourier transformation. For how long a quantum coherence survives and oscillatory behavior is observable obviously depends on the rate of dissipation of the excited state energy. For example, remarkably long-lived (660 fs and longer) quantum coherences following excitation with an ultrashort, energetically broad laser pulse were observed in various large photosynthetic light-harvesting chromophore-binding proteins [127] and explained to originate mainly from Raman-active vibrational substates of the electronic ground state [128]. Observing the molecules in a supersonic expansion of a buffer gas allows cooling them to typically 5 and 50 K for rotational and vibrational temperatures, respectively, which dramatically reduces spectral congestion [126]. Instead of being between substates of the same electronic state, the oscillations can also be between degenerate singlet and triplet manifolds and represent intersystem crossing. This is basically a spin-forbidden process and therefore only weakly allowed and slow but it can be made strongly allowed by hyperfine



interaction. Coherent oscillations between the singlet and triplet spin states of a radical pair in a photoexcited molecule in the eyes of birds and various other organisms are likely at the basis of magnetoreception in these animals [129,130], allowing them to orient themselves and navigate long distances.

More important in biological systems than the vibrational coherence explained in Figure 13b would be vibronic (mixed vibrational-electronic) and electronic coherences where two coupled adjacent electronic states are involved. The long-lived quantum coherences in photosynthetic macromolecular systems were originally thought to be mainly electronic coherences that could markedly enhance the organisms' biological functions [131,132], but more recent evidence shows that these coherences are only vibrational in nature [128]. Although evidence for some vibronic coherent contributions was also found [133], the overall presence of quantum coherences in these photosynthetic systems offers no obvious functional benefit to the organisms [134].

Inelastic collisions can also change the population of quantum states to higher or lower states without involving an exchange of photons. However, by far not every collision is successful in this. Success depends on the impact parameter, the relative orientation of collision partners and on the phase of vibrations at the instant of collision. The success may be captured by a probability, and this is how it is normally represented [135,136]. In contrast to the probabilistic events represented by first-order kinetics as discussed earlier, collisional deactivation is a process of second-order kinetics where the time of each deactivation process is defined by the precise collision time between the two collision partners, not by a probability.

In summary, bound quantum systems such as atoms or molecules possess discrete energy eigenstates which are populated on a probabilistic basis. They have lifetimes which are determined by first- or second-order kinetics and are therefore probabilistic, not deterministic. There are plenty of mechanisms that influence the lifetime of these states and contribute to the loss of time-reversibility. However, we maintain that time-reversibility is not the relevant criterion for thermodynamic irreversibility as described by the Second Law.

The Second Law, as all laws of thermodynamics, represents an empirical finding. Since no serious reports of violations have become known it is generally considered valid [32]. On the other hand, it is difficult to justify on a microdynamic basis this macroscopic phenomenon that heat cannot be converted completely to higher forms of energy without dissipation. Further below we will discuss this in two ways, first considering the up-conversion of lower- to higher-energy photons (Section 6.4), and then by considering the Carnot cycle (Section 6.6). This reminds of the equivalence of photons with conventional heat (particle kinetic energy) as expressed in Planck's relation of black-body radiation.

### 6.3 Experimental time-reversal and relaxation of a spin system

In nuclear magnetic resonance (NMR) and electron spin resonance (ESR), spin systems are routinely prepared in non-eigenstates by flipping the angle of the magnetization away from the z-axis, which coincides with the direction of the magnetic field  $B_0$ . A free spin- $\frac{1}{2}$  system, such as a proton or an electron, in a magnetic field may serve as an example (Figure 14). The energy of an electron in a magnetic field  $B_0$  is  $E_{\alpha,\beta} = m_S g_e \mu_B B_0$ , where  $m_S = \pm\frac{1}{2}$  is the spin quantum number of the two eigenstates  $|\alpha\rangle$  and  $|\beta\rangle$ ,  $g_e$  the electron  $g$ -value, and  $\mu_B$  the Bohr magneton. A general state  $|\Psi\rangle$  is written as a superposition of the two eigenstates:

$$|\Psi\rangle = c_1|\alpha\rangle + c_2|\beta\rangle, \quad (19)$$

with  $c_1^2 + c_2^2 = 1$ , and its time evolution is given by

$$\Psi(\mathbf{r}, t) = \Psi(\mathbf{r}_0, 0) \exp\left(\frac{iEt}{\hbar}\right), \quad (20)$$

$$\text{i.e., } \Psi(t) = c_1 |\alpha\rangle \exp(\frac{1}{2}i\omega t + \varphi_\alpha) + c_2 |\beta\rangle \exp(-\frac{1}{2}i\omega t + \varphi_\beta), \quad (21)$$

for  $\omega = (E_\alpha - E_\beta)/\hbar = g_e \mu_B B_0/\hbar$ , and the initial phases are  $\varphi_\beta = \varphi_\alpha - \pi/2$ .

First, for a flip angle of  $90^\circ$ ,  $c_1^2 = c_2^2 = 1/2$ , and the magnetization lies in the x-y-plane and rotates about the z-axis. For this transverse initial polarization, the  $M_z$  component of the magnetization,  $\langle M_z \rangle$ , is zero at all times, while  $\langle M_x \rangle$  and  $\langle M_y \rangle$  are time-dependent and oscillate between  $\pm |M|$ , so only their time-averages are equal to zero. If an exponential damping term is introduced in eqns. 20 and 21, this represents a phase decoherence that in magnetic resonance is conventionally called transverse relaxation rate  $1/T_2$  (where  $T_2$  is the phase memory time). It does not change the eigenstate populations, does not influence the energies and thus does not lead to equilibration. Decoherence may be due to spatial inhomogeneity of the magnetic field. In this case, a  $180^\circ$  pulse along x or y after a period  $\Delta t$  inverts the direction of time evolution and leads to an unchanged echo of the signal after an additional period  $\Delta t$ , indicating that phase memory is not lost (Figure 14c, see also Figure 4 of Ref. 6 for a historical illustration of this time-reversal experiment). However, if the effective Hamiltonian changes in time, for example due to diffusion in an inhomogeneous magnetic field, the echo amplitude will be diminished since memory of the phase coherence is partly lost. In any case, the  $T_2$  process has no energetic component since it does not change the population of spin states. It has no effect on the thermodynamic entropy and does not lead to equilibration.

We next look at the case of a non-eigenstate with longitudinal polarization, with non-zero magnetization along z, following a flip angle between  $90^\circ$  and  $180^\circ$ . A two-state system in a non-eigenstate oscillates between the two states, and the difference in population probabilities,  $c_1^2 - c_2^2$ , develops with time as  $\cos^2(\omega t + \varphi)$  (Figure 14b). The energy is equivalent to heat because the system does not do any work. It oscillates with  $\pm \Delta E = \pm \frac{1}{2} \hbar \omega$ . We identify  $\omega$  as  $1/\tau$  or  $1/\Delta t$ , which allows us to rewrite this equality as

$$\Delta E \cdot \Delta t = \frac{1}{2} \hbar, \quad (22)$$

which is the uncertainty relation [137], but as an equality, not an inequality. This is because energy and time represent a Fourier pair of parameters, i.e. their variances  $\langle \Delta E^2 \rangle^{1/2}$  and  $\langle \Delta t^2 \rangle^{1/2}$  are not independent; rather, they are related by Fourier transformation and are therefore inversely proportional, with their product obeying eqn. (22). This means that a system violates conservation of energy by an amount  $\pm \Delta E$  that is proportional to the inverse time increment  $1/\Delta t$  of this violation. The shorter the duration of a violation of energy conservation the larger the violation may be. In the time average, however, energy is conserved. Thus, while thermodynamic systems may violate energy conservation by statistical fluctuations, free quantum-mechanical systems do so by regular oscillations. Any statistical external perturbation such as inelastic collisions by Brownian motion contributes to dephasing of the oscillations and thus to a transition from quantum to thermodynamic characteristics (see Chapter 7).

We can again introduce a damping term in eqns.19 and 20. In this case it affects the longitudinal polarization and is therefore called the longitudinal relaxation rate,  $1/T_1$ . It damps the oscillations shown in Figure 14b, diminishes the population difference of the two eigenstates by dissipation of energy until equilibrium is achieved (Figure 14d). The fundamental difference between the two relaxation times,  $T_1$  and  $T_2$ , is well established in the

magnetic resonance communities, and the two relaxation times can adopt very different numerical values.  $T_2$  stands for decoherence and thus for loss of time reversibility without achieving thermodynamic equilibrium, while  $T_1$  represents relaxation into thermodynamic equilibrium by energy dissipation.

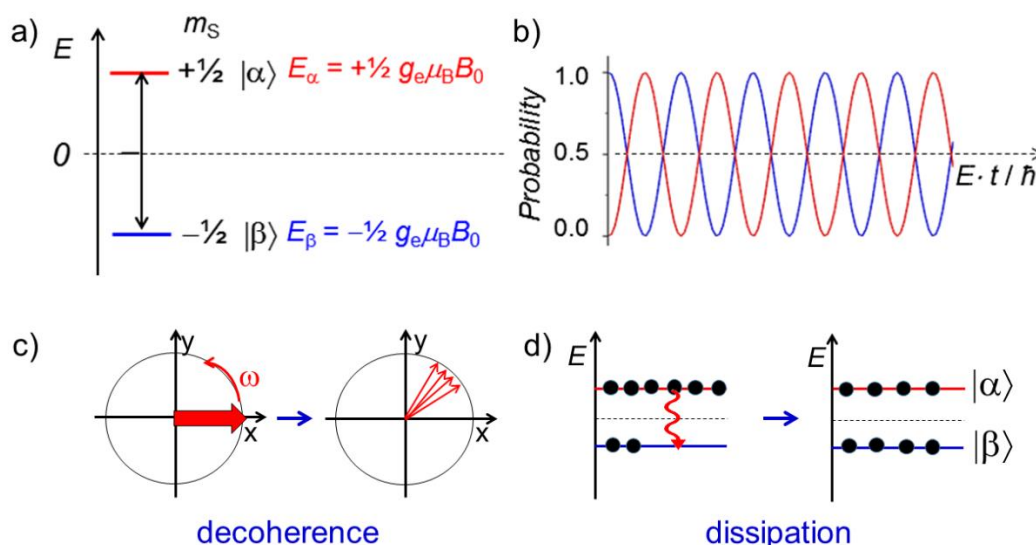


Figure 14: a) Two-state magnetic energy level of an electron spin and b) evolution of the wave function (in terms of the  $m_s = \pm\frac{1}{2}$  eigenstates) of a non-eigenstate prepared at the intermediate energy. The probability of occupancy of the two states oscillates at angular frequency  $\omega = (E_\alpha - E_\beta)/\hbar$ . c) Decoherence of an ensemble of spins in the x-y plane. d) Energy dissipation to equilibrium populations. (color online)

We furthermore note that the full solution of the time-dependent Schrödinger equation is a time-dependent wave function that has no hidden variables provided that the initial state is well-defined. It represents what is often called a “collapsed wave function”. There are no uncertainties of any observables described by the wave function at any time. Uncertainties appear only in the solutions to the time-independent Schrödinger equation, which are partial solutions representing the time average of the full wave function. The Heisenberg uncertainty principle applies only to the wave functions of the time-independent Schrödinger equation.

#### 6.4 Reversal of photon dissipation: a higher-order process

It has been known since Einstein’s explanation of the photoelectric effect that the threshold energy for ejection of a photoelectron from a metal surface has to be provided by a single photon, and that an increased number of lower energy photons, i.e. a higher intensity, cannot compensate for this [138].

Similarly, if an excited molecular state emits a single photon, why can this process not be reversed by reabsorption of two (non-resonant) photons which add up to the initial excitation energy? The answer was given by Maria Goeppert Mayer in her PhD thesis. She showed that the simultaneous absorption of two photons by an atom is proportional to the product of light intensity at each of the two frequencies. For two photons of the same frequency it is proportional to the square of the light intensity. This is thus a second-order non-linear process and therefore highly improbable at normal light intensities [139]. By analogy, the phenomenon can be extended to the absorption of several non-resonant photons, which is a higher-order process and increasingly less probable.

The effect was exemplified later by the molecule rhodamine B, which is an excellent 1- or 2-photon absorber that absorbs in bright sunlight a single photon about once every second, a

photon pair by 2-photon absorption only once every 10 million years, while no 3-photon absorption is expected throughout the entire age of the universe [140].

Frequency doubling (second harmonic generation) is a process where a selected non-linear optical material is excited by a given frequency. A fraction of the total energy is converted and emitted as photons of double the excitation frequency. This is also a second-order process that requires high laser intensities for efficient conversion [141].

The effect of simultaneous absorption of two photons within the interaction time of absorption has to be distinguished from sequential resonant absorption of two photons via a sufficiently long-lived intermediate state, a process that is called upconversion [142].

### *6.5 Heat flow from cold to hot without external intervention*

In Section 5.5 it was explained that the Second Law of thermodynamics has to be amended for the treatment of self-gravitating systems in the context of astrophysics, and that these systems provide conditions where heat flows spontaneously from cold to hot. This does not affect the Second Law for conventional matter for which thermodynamics was developed. However, there have been several recent reports about spontaneous heat flow from cold to hot, without violating the Second Law and reversing the arrow of time [143-145].

Schilling et al. [143] described a system that they called a “thermal inductor”. The device is an oscillating thermal circuit consisting of an electrical inductor, which is coupled to a Peltier element that creates a heat flux across a junction of two different electrically conducting materials when a dc voltage is applied. The two materials are initially at different temperatures. The process starts with heat flowing from hot to cold, but depending on the system parameters, this heat flow can overshoot, going from cold to hot without any driving force from an external source, before it reverses again. There can be several oscillations, passing through a quasi-equilibrium state, while the entropy was shown to increase monotonously. Thus, the process conforms entirely with Clausius’ postulate of the Second Law, stating that a flow of heat from cold to hot must be associated with “some other change, connected therewith, occurring at the same time” [107]. It is comparable with oscillating chemical reactions (Section 2.9) which are also explained based on coupled differential equations.

Micadei et al. [144] demonstrate experimentally, using a nuclear magnetic resonance setup, the reversal of heat flow for two quantum-correlated spins- $\frac{1}{2}$ , prepared in local thermal states at different effective temperatures, associated with the population of the two energy levels. The specific system consisting of a  $^{13}\text{C}$ -labelled  $\text{CHCl}_3$  liquid sample is prepared in an initially correlated state by application of  $\pi/2$  radio frequency pulses at the resonance frequencies of the  $^1\text{H}$  and  $^{13}\text{C}$  spins. The free induction decay of the coupled spin system that follows these preparatory pulses represents an oscillatory repopulation of the energy levels. Since no work on the spin system is involved, the oscillatory change in energy was interpreted as being equal to a change in heat. The characteristic transverse decoherence time and dissipation given by the transverse and the longitudinal relaxation time, respectively, are on the order of one to several seconds for such a small system. The system is analogous to the one described in Section 6.3 and in our view does not violate the Second Law but instead takes advantage of the Heisenberg uncertainty relation between energy and time (see Figure 14).

Latune et al. [145] elaborated further on the system reported by Micadei et al. [144]. They conclude that the heat flow reversal depends only on internal coordinates of the system and does not need any access to a heat bath. Furthermore, heat flow reversal can happen without reversal of the arrow of time. Surprisingly, indistinguishability and correlations

between subsystems can reverse the heat flow between an ensemble and its bath. This type of heat flow reversal has no classical counterpart [145].

### 6.6 Converting heat to higher forms of energy

The Carnot cycle representing an internal combustion engine converts heat from a high-temperature heat bath at  $T_h$  to work (Section 2.6). The process requires that a fraction of the absorbed heat is dissipated as waste heat to a low-temperature heat bath  $T_l$ . Its reversible efficiency,  $\eta_r^c = 1 - (T_l/T_h)$ , depends only on the temperatures, and it never reaches 100% (i.e. nothing is lost, but the “waste heat” is not counted) [146]. Carnot machines are independent of the working medium [147]. The reversed cycle represents a driven process that uses an energy source (e.g. sunlight, fuel/heat, food) to operate intelligent machines or life-maintaining cycles in an entropy-reducing process to produce mechanical work, chemical synthesis of higher energy compounds, separation of mixtures, or biological self-assembly, but they work only when waste heat is dissipated to a heat sink, the environment. The reversible efficiency of the inverse Carnot process, a heat pump or refrigerator, is the inverse of the efficiency of the forward Carnot process given above. It is always greater than one, but this does of course not represent a *perpetuum mobile*; it merely uses energy that is free because it is taken from a heat bath. The generalized scheme was called the “machinery of life” [39].

Low-grade heat, even if called “waste”, can nevertheless be of good use, either directly for heating purposes in a scheme called co-generation, or it can be converted back to higher-grade energy such as electricity, but never to 100%. Recently, a highly interesting option has been demonstrated that generates electrical power “from the coldness of the universe”. The method is akin to the principle of a solar cell but uses the negative illumination effect when a semiconductor diode faces the sky at night. A Shockley-Queisser analysis predicts a maximum power density of  $4 \text{ W m}^{-2}$  when the diode is at a temperature of 293 K. This is several orders of magnitude more than has been reached in first experiments [148].

Other possible options have recently been summarized by Rahimi et al. [149]. An organic Rankine cycle is the analogue of a steam engine, but it operates with an organic liquid of low boiling point and high vapor pressure. It converts low-grade heat into work that is used to produce electrical power. A second option is the solid-state thermoelectric generator (Seebeck generator). It uses the thermoelectric effect between p- and n-type semiconductors or of semimetals with high electrical conductivity and thermoelectric sensitivities. It produces a thermo-electrical voltage of the order of  $\mu\text{V K}^{-1}$  based on a temperature difference on two sides of a device without the need of any moving parts. Both methods are well investigated but have not been used for large-scale conversion of low-grade heat because of low power densities and too large costs.

A more promising option are thermo-electrochemical cells, which consist of a redox couple in an electrolyte that separates two (often identical) electrodes at different temperatures so that oxidation occurs at one electrode and reduction at the other one. Potential differences on the order of  $\text{mV K}^{-1}$  have been generated, making them an interesting alternative to solid-state thermoelectric generators [150]. A power density of  $6.6 \text{ W m}^{-2}$  with an efficiency near 4% of the Carnot efficiency was obtained [149].

A further option is thermo-osmotic energy conversion. Water from the hot compartment evaporates into a hydrophobic porous membrane with air bubbles and condenses into the cold compartment, where it generates a pressure that drives a turbine to generate electricity. In theory, hydraulic pressures of 400 bar can be generated by a minor temperature

difference of only 5°C. Efficiencies of 34% of the Carnot value (4.1% absolute) can be obtained with operating temperatures at 60°C and 20°C [149].

The above processes of harvesting low-grade heat to convert it to superior forms of energy, most desirably electricity, all operate between two temperatures. They can be rationalized on the basis of the Carnot cycle, and they only work because a fraction of the harvested energy is dissipated in the form of even lower-grade heat, in full compatibility with the Second Law. Temperature and heat are thermodynamic concepts. A microscopic interpretation must draw from the equality of heat as the expectation value of kinetic energy. This is done by reference to collision dynamics outlined in Figure 5, which requires that total energy and momentum of two collision partners are conserved in an elastic collision.

## 7. Irreversibility in quantum processes

### 7.1 Real systems in a heat bath

For quantum statistical systems, an *open quantum systems* approach is a widely used framework to describe the time evolution of the quantum system as a result of its interaction with the environment that allows the exchange of energy and particles (cf. Figure 1), a characteristic of any real-life system. This interaction leads to *quantum dissipation* and *quantum decoherence*, the quantum-mechanical analogs of classical energy dissipation (such as friction) and Brownian motion. Both quantum dissipation and decoherence are irreversible processes (see Section 4.1).

### 7.2 Isolated quantum systems

Most isolated quantum systems can be treated in the framework of open quantum systems by considering that each small subsystem, which contains a small fraction of the full system's degrees of freedom, interacts with the rest of the system, the latter of which is treated as a thermal bath (Figure 1b). Hence, the full, isolated system can act as its own thermal bath. Isolated quantum systems can be created in the laboratory where the system of interest is isolated for all practical purposes for the duration of the experiment, which typically spans nanoseconds to microseconds, a few orders of magnitude longer than thermalization of open many-body quantum systems. Although isolated systems are synthetic and not representative of real systems, they are excellent testbeds for theories. In reality, weak coupling of the system with the external world cannot be completely eliminated, even in the dilute gas phase, and the system will eventually thermalize. Thermalization can therefore be at best delayed or slowed down. Here we discuss thermalization and equilibration characteristic of different classes of quantum systems which have so far received attention in literature, and the results are collated in Table 3.

#### 7.2.1 Eigenstate thermalization hypothesis

Thermalization of an isolated quantum system initially in a non-equilibrium state can be well-explained by the *eigenstate thermalization hypothesis* (ETH) [151-153] by considering that the system behaves according to the *ergodicity theorem*. The ETH assumes that any initial state of the system is an energy eigenstate of the system's Hamiltonian and is a thermal state. As a result, all subsystems – each of which is related to a different eigenstate – thermalize and hence the whole system thermalizes. A thermal state describes a state of a system in thermal equilibrium with a large heat bath at a finite temperature, while thermalization refers to memory loss of the system's initial conditions. The notion that a thermal state can thermalize is therefore no contradiction in terms. Rigol and coworkers [153] explain this by considering that the initial state of a quantum-mechanical system can be described as a superposition of thermal eigenstates, i.e. coherences between these states

make the system appear to be non-thermal. As the system evolves, dephasing sets in, giving rise to thermalization.

The condition that all eigenstates of the system are thermal is more rigorously expressed as the condition that all diagonal matrix elements of the associated observables in the energy basis must be smooth functions of the energy and must evolve to the microcanonical expectation values of the associated observables. Another necessary assumption is that the off-diagonal matrix elements must evolve at an exponential rate to values that are exponentially smaller than the diagonal matrix elements [5,14,154,155], i.e., all quantum coherences are rapidly destroyed. Although the ETH has not yet been proven, it has been successfully applied in various numerical studies [153,156,157] and is therefore a widely accepted hypothesis. Examples of systems that thermalize but do not obey the ETH have been given by Shiraishi and Mori [158,159].

During recent years, four classes of isolated quantum systems have been introduced that exhibit non-ergodic behavior and do not thermalize. These processes are at the frontier of current research in quantum thermodynamics and non-equilibrium statistical mechanics. Each process will be briefly introduced here. It is worth noting that experimental advances in the last two decades have allowed the realization of many of these quantum systems to a remarkably good degree. For example, laser beams can be used to confine ultracold atoms in virtually any desired geometry and to measure the states of the atoms with unprecedented precision [160]. These systems are, therefore, not mere academic curiosities but real systems, albeit under highly artificial conditions.

### 7.2.2 Quantum integrable systems

The first class of systems is called *integrable* [161], which implies time-reversibility in most cases. Although there is to date no consensus on a rigorous, inclusive definition of integrability in quantum systems [162,163], the definition of *classical integrability* provides a good basis. Classical integrability is based on Liouville's theorem, stating that the equations of motion of a dynamical system can be solved implicitly by direct integration of known functions. This is possible due to a number of time-invariant quantities (also called integrals of motion), each of which imposes constraints on the system's time-evolution. A classical system with  $N$  degrees of freedom is integrable when it possesses  $N$  functionally independent conserved quantities that are pairwise Poisson-commuting. To define *quantum integrability*, the classical definition is commonly translated word-by-word to a quantum context but suffers from ill-defined concepts such as the degrees of freedom of a quantum system (the hidden variables, see Section 2.1.3) and the manner of independence of the conserved quantities [14,162,1663].

A sufficiently small number of conserved quantities (i.e., a sufficiently limited number of constraints) allows a classical system to explore every part of phase space, making the ergodic principle a reasonable assumption. In contrast, an extended number of conserved quantities will impose constraints preventing the system from sampling the entire phase space during its time evolution and the long-time average will not be equal to the microcanonical ensemble average, i.e., the ergodic principle breaks down. Similarly, thermalization is precluded in a quantum integrable system when it contains extensively many conserved quantities that prevent the system from adopting all the allowed configurations in Hilbert space [164,165]. Conversely, when an initially integrable system thermalizes, it loses integrability and therefore cannot be fully solved anymore.

According to the Kolmogorov–Arnold–Moser (KAM) theorem [166], a classical system that is nearly integrable can also violate the ergodic principle. This can be understood as follows. Integrable classical systems are characterized by periodic motions. The KAM theorem

dictates that a weak perturbation transforms this motion into a quasi-periodic orbit, preserving most of the system's conserved quantities but destroying some. If the system, after the perturbation, still contains an extended number of conserved quantities, it remains integrable and thermalization is (temporarily) prevented. This has been demonstrated in a pioneering experiment where a condensate of ultracold rubidium atoms was trapped along one dimension [167]. After a small perturbation, the gas failed to thermalize for an unusually long time, despite thousands of collisions between the individual atoms. The explanation offered for this phenomenon was that a perturbed integrable system can relax to an equilibrium state predicted by the generalized Gibbs ensemble (GGE) instead of to a thermal state [168], a process known as prethermalization for which Gogolin & Eisert give numerous experimental examples [14]. Based on the initial finding from numerical studies that a few other integrable systems similarly equilibrate to the GGE, it was proposed that this phenomenon may be a generic property of far-from-equilibrium quantum integrable systems [169]. In addition, by selecting energy eigenstates of the system's Hamiltonian with similar conserved quantities, relaxation of the system proceeds in a manner akin to the ETH. Since the ETH applies typically to non-integrable systems, while the new hypothesis applies to integrable systems, the latter can be considered a generalization of ETH to integrable systems, hence the term *generalized (eigenstate) thermalization* was coined [169]. It is now widely believed that integrable systems equilibrate to the GGE and that generalized thermalization is the best explanation for this phenomenon [170,171], provided that appropriate conserved quantities are identified, which is not a trivial task for integrable systems [5].

Most commonly-studied thermalizing systems are non-integrable. It is, therefore, generally assumed that all non-integrable systems thermalize while integrable systems by definition do not thermalize but equilibrate to the GGE. However, there are systems for which this correlation is not true [172]. Moreover, the fate of an integrable system often depends sensitively on the initial conditions: special initial conditions may still cause thermalization of an integrable system [169].

Only a small fraction of many-body quantum systems have an exact solution, i.e., a unique set of quantum numbers can be found for every eigenstate of such a system. One of the first examples of an exactly solvable system was introduced by Bethe using a specific form of the wavefunctions, known as the Bethe Ansatz, applied to the one-dimensional spin-1/2 Heisenberg anti-ferromagnetic chain [173]. This chain consists of an array of electrons, each with a spin quantum number of  $\frac{1}{2}$ , with uniform exchange interaction between nearest neighbors and periodic boundary conditions. The Bethe Ansatz has been generalized and applied to numerous other one-dimensional integrable quantum many-body systems to make them exactly solvable. One paradigmatic example is the integrable Lieb-Liniger model, which describes a one-dimensional interacting Bose gas. This system cannot be mapped to a non-interacting system and is also a rare example of an integrable system that does not relax to the GGE. Based on the latter result, it was proposed that relaxation to the GGE may be prohibited by any continuum integrable systems with contact interactions undergoing a sudden perturbation [174,175].

### 7.2.3. Many-body localization

A second type of system that violates ETH is one displaying the phenomenon of *many-body localization* (MBL) [176,177]. In the past few years, this phenomenon has been demonstrated and investigated in various experimental settings (see, e.g. [178-181]). MBL describes an unusual process by which a many-body quantum system at high energy equilibrates but does not thermalize. It occurs when the system is subject to sufficiently strong disorder or quasi-periodic potentials [182] that prevent efficient exchange of information (i.e. entanglement) between subsystems. As a result, the information of some of the subsystems



remains localized and those subsystems preserve memory of their local initial conditions. In the context of ETH, some of an MBL system's eigenstates do not obey ETH and, hence, the complete system fails to thermalize. The presence of quasi-local conserved quantities (also called quasi-local integrals of motion) is considered to be one of the key characteristics of MBL systems, giving these a different type of integrability [155], as opposed to the existence of only global integrals of motion in other integrable systems. In contrast to (other) integrable systems, an MBL system is robust to weak perturbations [183].

MBL is characterized by a logarithmic growth in the entanglement entropy as a function of time, as opposed to a linear entropy growth in thermalizing systems [155]. This represents a relatively small rate of entropy growth but nevertheless a positive rate, indicating that MBL is an irreversible process, despite the reversibility of some of its subsystems. Due to the (logarithmic) entanglement spreading amongst the thermalizing subsystems, some quantum decoherence occurs, forming the basis of the irreversible time evolution. Since a pure MBL system is isolated, no energy transfer to an external environment can take place and thus no quantum dissipation occurs.

#### 7.2.4 Quantum scars

A *quantum scar* is a third type of system that disobeys ETH. Quantum scarring refers to enhancements in the probability amplitude of a system's wavefunction near the trajectories of classical periodic orbits, giving rise to a few non-thermal eigenstates that weakly break ergodicity in the system. Scarring is an example of a non-integrable process that does not thermalize. The phenomenon was predicted in 1984 for closed single-particle dynamic billiard systems [184], and a few years later verified experimentally for microwave cavities [185], quantum dots [186], and semiconductor quantum wells [187]. A recent, influential experiment was the observation of long-lived, coherent oscillations in a chain of ultracold interacting rubidium Rydberg atoms, representing a disorder-free many-body quantum system [188]. Instead of remaining entangled, the atoms oscillated between entangled and disentangled states for an extended period of time, a behavior indicative that the system retained memory of its initial state and which was found to occur only when the initial configuration of the system was a particular product state. This unusual behavior was attributed to quantum scarring [189] using a model with a few non-thermalizing eigenstates, and slow equilibration of the rest of the eigenstates to the GGE values of the associated observables [190].

#### 7.2.5 Hilbert space fragmentation/shattering

Very recently, a fourth type of ETH-violating system was introduced, called Hilbert space fragmentation [191] or shattering [192]. In these two studies, it was shown that when both charge and dipole moment are conserved in a many-body quantum system, the Hilbert space breaks up into exponentially many disconnected subsectors, each of which corresponds with a non-thermal eigenstate that retains memory of the initial local structure, preventing the system from thermalizing. The non-thermal eigenstates equilibrate to finite values while the remaining eigenstates at the same energies are thermal [191]. This behavior is similar to the phenomenon known as Krylov fracturing [193], where a Krylov subspace coincides with the GGE, which may indicate that a Hilbert space fragmented system similarly equilibrates to the GGE. The equilibration characteristics of Hilbert space fragmentation is still under investigation [193]. This phenomenon can be generalized to quantum systems with a finite number of constraints, a distinctive property of integrable systems. Some dynamics of these integrable systems are similar to those of MBL or quantum scarring systems, for example the strong dependence of the systems on the initial product state, a key feature of quantum scarring, while some other properties are different; for example, the fragmentation is robust to disorder, unlike MBL [191, 192]. Two numerical studies published shortly before

[191,192] have attributed a similar phenomenon to a special type of MBL. However, the unique characteristics of Hilbert space fragmentation places the phenomenon in a different class and the two said numerical studies have been reinterpreted instead as Hilbert space fragmentation [192]. It is predicted that these systems may be realized in the near future in ultracold atom experiments [192].

Table 3: Equilibration and thermalization characteristics of different classes of quantum systems

Quantum System	Equilibration?	Thermalization?
Open quantum system	Yes	Yes
ETH	Yes	Yes
(Near-)integrable quantum system	Yes (to GGE)	No
MBL	Yes	No
Quantum scarring	Partly (to GGE)	No
Hilbert space fragmentation	Yes	No

It stands out that all classes of systems represented in Table 3 show at least partial equilibration, but only some of them thermalize and ETH is the only type of isolated quantum system that thermalizes. There is no open or isolated quantum system that thermalizes without equilibration. This may have been the reason for overlooking thermalization as a process that is distinctly different from equilibration, and it may have led to statements in literature like “Equilibration is generally considered a necessary condition for thermalization.” [14]. Equilibration is a consequence of the Second Law and takes place by coincidence along with thermalization, but we do not see a causality. For quantum systems, this is seen best by the difference between the independent longitudinal (dissipation) and transverse (decoherence) relaxation processes in spin systems, as discussed in Section 6.3. For classical systems, the difference between the two processes is obvious from MD simulations which equilibrate without losing time-reversibility [13] and by the two Gedankenexperiments described in Section 4.2 and Figure 7. Furthermore, thermalization is often defined as equilibration to a thermal state [5,14], which is also inconsistent and is only true if both decoherence and dissipation take place.

## 8. Irreversibility of biological evolution

Life exists in an environment that is governed by chemical thermodynamics, and biological processes such as replication are accompanied with dissipation in order to maintain a low-entropy living system [196]. Marchettini et al. [197], by reference to Wicken and Prigogine [198,199], interpret biological cells as dissipative structures, but with a higher degree of complexity than simple reaction-diffusion systems.

Vesicles reflect the concept of compartmentalization of biological systems, which is important for securing concentration of metabolic intermediates. They are therefore often seen as simple inanimate analogs of living cells. We accept that they can be understood as a result of dissipative structures. However, the origin of life is marked by the transition from inanimate to

living matter, from chemistry to biology, increasing simultaneously order and complexity [200], and this goes along with additional principles beyond those of spontaneous thermodynamic processes [201]. We do not see any rigorous evidence that living cells are simply collective autocatalytic systems, which maintain themselves as entities capable of reproducing themselves and evolving. Sexual reproduction, genetically programmed structures and processes as well as their evolution, let alone the spiritual aspects of life, are on quite a different level than what can be explained by the thermodynamics of inanimate matter.

Biological evolution starts with prebiotic chemical molecular evolution of inanimate building blocks to produce the first and probably simplest living cell that exhibits metabolism, replication and the ability to change further in an evolutionary manner. These building blocks are moderately complex organic molecules including amino acids, peptides, ribose sugars, nucleobases, fatty acids, nucleotides, and oligonucleotides [202]. The fatty acids are soap-like amphiphilic molecules that self-assemble in aqueous environments into double layers, eventually leading to spherical vesicular structures that are commonly regarded as models of living cells because of their structural analogy [203]. This evolutionary process has been suggested to have taken place in channels and cracks of tectonic fault zones of the earth crust at a depth near 1000 m [204]. During periodic pressure changes due to geyser activity the carbon dioxide in mixtures with water oscillates between its gaseous and supercritical state, giving rise to different solubility of the organic solutes. The cyclic change in chemical potential imposed by the pressure oscillations periodically leads to aggregation by self-assembly of the vesicles without violating the Second Law of Thermodynamics. These processes are reversible, but a fraction of the lower entropy ordered products can be stabilized by escaping the reactive zone. Experiments also yielded clear evidence for vesicle-induced accumulation of membrane-interacting peptides [203]. Catalytic self-reproduction of vesicle protocells by dissipative self-assembly was achieved via a process fueled by a hydrolysis step that was introduced to destroy the surfactant [205].

Biological evolution consists of several distinct steps. It is generally believed that once the first living single cell organism had stabilized, the evolutionary process followed a different mechanism. The Darwinian principle, *Survival of the Fittest*, can be considered to be the analog of the Second Law of Thermodynamics for living systems. However, the Second Law requires an increase in the entropy of isolated systems, while living organisms are open systems far from equilibrium, which increase complexity and therefore lower their entropy during the evolutionary process, fed to a large extent either directly by photosynthesis or indirectly by the energetic molecules formed in this process.

It is unimaginable that dinosaurs will resurrect or fossils will come back to life. We would not be enthusiastic about the prospect that humans evolve back to earlier forms, which work with flint tools and create rock paintings. The view of irreversible evolution was expressed as early as 1890 in Dollo's Law [206]. In contrast to this, a fairly high reversibility of mutations in *Drosophila*, often caused by a chain of reactions (such as the exchange of individual DNA base units, or the deletion or insertion or the rearrangement of larger sections of genes or chromosomes) was reported later by Muller [207], and a limited reverse evolution is attested also in more recent work [208]. Viruses with a single-strand RNA genome show much higher mutation rates than life forms based on the double-stranded DNA, which is stabilized by the interactions in the helix.

When cereal seeds are sowed on the field, the sprouts will grow and the entire field of cornstalks will have approximately the same height. All grains have the same chance and the same success rate, apart from some that do not make it. This is programmed growth and in stark contrast to evolution of life that is estimated to have started over 4 billion years ago with simple single-celled organisms under anaerobic conditions. *Survival of the fittest* may be a

conceivable concept viewed from the proud throne of human beings or insects like bees, or other representatives of the animal kingdom that are sophisticated organisms with what we call intelligence, and with societal behavior. However, many modern-day living organisms are unicellular and can therefore be considered to have remained at a single cell stage, much closer to the Last Universal Common Ancestor (LUCA, see Figure 15). All of the roughly  $5 \pm 3$  million named creatures of life on Earth [209] are based on the same genetic code represented in DNA and RNA and are therefore thought to have a single common ancestor, the LUCA. The large number of single-celled species like bacteria, archaea and some groups of algae and fungi have by far not reached the high sophistication over the same 4-billion-year time span, despite high mutation rates, and they nevertheless proved to be sufficiently fit to survive. Since they are often considered to represent early stages of life they are sometimes called *living fossils*. They reveal that Darwinian evolution is not to the same extent compulsory and predictable for all species as in the programmed growth or in the evolution of chemical matter according to the Second Law.

Trees of life are instant images representing the state-of-the-art knowledge of evolution, but this knowledge evolves so that trees of life have to be revised frequently. Furthermore, the branches of these trees are not so cleanly separated as it is often suggested. In particular among the bacteria, there is a frequent horizontal gene transfer between the branches which blurs the distinct lineages [210]. However, the generally accepted evolution of humans from the LUCA, the first single living cell species, represents a complex path with many key evolutionary steps. It is difficult to investigate, in particular its early stages, because we are missing numerous fossils of sufficient quality, and we cannot repeat evolution in the laboratory. Dying is not the reverse of getting to life, so studying the biology of dying does not help. A more promising approach may be based on the recognition that each human being starts off from a single cell, and intermediate fetal stages show organs which resemble earlier forms of life along the phylogenetic branch of evolution. One could therefore hypothesize that the evolution of an individual human being traces the phylogenetic evolution of humans in the sense of a fast time lapse, and that studying the evolution of an individual organism may reveal the phylogeny. A serious limitation to this undertaking is that individual evolution is a linear process, while the phylogenetic tree has many branching points. A fertilized human egg will after successful growth and multiplication end up in a human organism, but never in a fig tree or a dinosaur. Securing the linearity of embryonic and fetal development is obviously due to the genes, which prevent to a large extent any branching off. The genetic information reduces the large entropy represented by the many species in the phylogenetic tree to that of a single target species.

The long-term coexistence of simple and complex forms of life, and furthermore the fact that in a pandemic a simple organism like a Malaria bacterium or a coronavirus can eradicate large fractions of human populations, raises questions about the validity of the principle of Darwinian evolution. For example, which of the creatures is fitter, the complex or the simple one? Obviously, fitness cannot be equated with complexity. The formulation of Darwinism has concentrated on the lineage to the complex forms of life among the Eukarya in the tree of life and offers a plausible explanation for an evolution that contains several key steps of increasing complexity. It has, however, neglected to a large extent the fact that the major number of species that are currently living consist of a single cell with a complexity near that of the LUCA. What does this mean for the *survival of the fittest* principle as the arrow of the evolution of life?

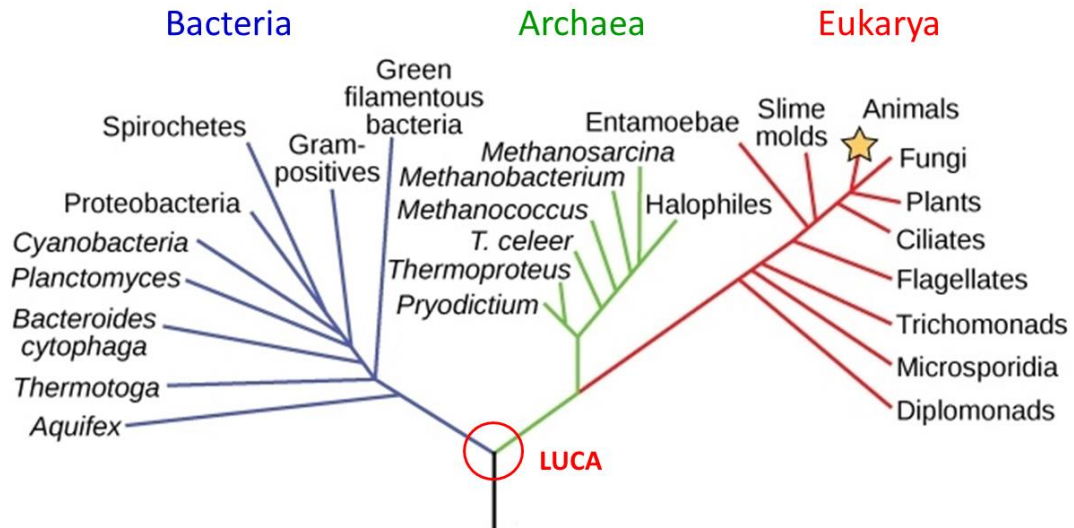


Figure 15: Phylogenetic tree of life after Woese et al. [211]. Human beings are subsumed under the Animals kingdom, together with other mammals, birds/reptiles, fish, insects, and roundworms. LUCA stands for the Last Universal Common (Cellular) Ancestor. (color online) [212 (open source).]

## 9. Conclusions

Exact or approximate solutions of the coupled Newtonian equations of motion are available for relatively few atoms only. They are complicated by the need of  $3N$  coordinates and a three-component velocity vector for each of the  $N$  particles. In molecular dynamics and molecular mechanics calculations, today's fast and large computers permit numerical solutions of these equations for much larger numbers of particles. In this way they bridge the gap to thermodynamic treatments which ignore the knowledge of all  $6N$  parameters and consider only ensemble averages. Quantum-mechanical treatments take in most cases an intermediate approach by separating off the time dependence, which reduces the number of parameters to the  $3N$  spatial nuclear coordinates but instead requires also the coordinates of all or at least the valence electrons. Also, these calculations rely in an essential way on the power of fast computers. Ignoring the time dependence has the consequence that the solution is incomplete and consists merely of a time-averaged wave function.

The attempt to understand thermodynamic irreversibility and the arrow of time from the viewpoint of loss of time-reversibility of equations of motion has misled generations of scientists. In fact, the two irreversibilities have nothing in common. Loss of time-reversibility is defined as loss of memory of the past and is reflected by the loss of phase correlations of the components of quantum systems, and by loss of statistical time correlations in classical systems. Thermodynamic irreversibility, on the other hand, is related to dissipation, i.e. to a change in energy distributions, reflected by populations of energy levels, or by a change in concentration.

The following statements serve as take-home messages that summarize the essence of the subject:

- Time-irreversibility of the equations of motion and thermodynamic irreversibility are two separate subjects which are not directly related to each other. A thermodynamic equilibrium is attained by maximizing the entropy of an isolated system (or by minimizing the free energy of a closed system) and may be reached via time-irreversible and also time-reversible processes. It involves redistribution of energy, i.e.

changes of the populations of energy levels or changes in concentrations. Time-irreversibility involves the loss of memory of previous states, represented, e.g., by dephasing of coherent oscillations in quantum states or by the loss of time correlations between different parts of a classical system. In contrast to equilibrated states, systems that have lost memory of their past are called thermalized.

Probabilistic events are a common cause of memory loss. In mathematical descriptions, the populations relate to diagonal and the decoherence to off-diagonal elements of the density matrix of a quantum state in the energy basis.

- An equilibrated ensemble of matter is characterized by the Boltzmann distribution, described by statistical thermodynamics. This equilibrium distribution is neither changed by elastic collisional energy exchange (as in a Maxwell-Boltzmann ensemble) nor by photon exchange (as in Planck's black body), except for temporary fluctuations. This results in the fundamental equivalence of heat in the form of energy and in the form of photons.
- All thermodynamic equilibria are dynamic, with equal rates of forward and backward reactions indicating microscopic reversibility. The fluctuation theorem describes spontaneous random deviations of thermodynamic properties from equilibrium. The probability of a deviation of a certain amplitude decreases exponentially with this amplitude, and in a statistical ensemble it decreases with the size of the system. Since thermodynamics is defined for macroscopic systems, these fluctuations do not contradict the Second Law, and since they are random and not deterministic, they are also not suitable to explain time-irreversibility.
- Off-equilibrium ensembles approach equilibrium by dissipation of heat, either in the form of kinetic energy and/or of photons, as described by the Second Law of Thermodynamics. Equivalent to the dissipation of heat is a lowering of concentration or gas pressure of the system.
- Other forms of energy can be converted quantitatively into heat, but the reverse is not true. Heat is therefore often called an inferior form of energy.
- Spontaneous thermodynamic processes in closed subsystems can be reversed by driving them. This decreases the entropy of the subsystem, while the entropy of the universe nevertheless increases. Driven processes are among the most important in daily life and in nature.
- The main characteristics of time-irreversibility lies in the probabilistic nature of processes which lead to the loss of memory (quantum decoherence and loss of spatial correlations), not the dissipation of energy, and it is not fundamentally dependent of the size of a system. Only deterministic processes are time-reversible and therefore integrable.
- The finite, non-zero lifetime of a discrete energetic state is a truly quantum-mechanical effect that is not found in a classical energy continuum. The quantum nature is thus an important origin of both equilibration and thermalization. The main phenomenon that prevents a system to reverse to an excited state is the low probability of the simultaneous non-resonant absorption of two or several low-energy photons or collisional energy quanta since these are second- or higher-order kinetic processes.
- Both time-irreversible and time-reversible systems equilibrate, as evidenced by Maxwell-Boltzmann ensembles of elastically colliding particles and by standard molecular-dynamics calculations. Equilibration is therefore not a criterion for irreversibility. Otherwise we could ask why we do not observe reversible systems returning from equilibrium to the initial non-equilibrium state. This is just because it is in many systems experimentally not possible to reverse all trajectories of an ensemble coherently, whereas it can be done in molecular-dynamics simulations.

- Magnetic resonance, manipulating and monitoring the evolution of spin systems in an applied external magnetic field provides the best example for experimental time reversal, and at the same time it demonstrates the fundamental difference between the loss of time-reversibility and thermodynamic irreversibility. Coherent precession of a spin ensemble is initiated by a preparative pulse that tilts the equilibrium magnetization vector away from the direction of the magnetic field, defined to lie along the z-axis. The perpendicular component precesses in the x-y plane. This motion can be reversed after a time period  $\tau$  and refocused to produce an echo after another period  $\tau$ . This precession does not affect entropy, but the echo amplitude may be diminished after repeated sequences, characterized by the transverse or spin memory relaxation time  $T_2$ , reflecting dephasing and thus the loss of time reversibility without changing the extent of deviation from thermodynamic equilibrium. The relaxation of the magnetization vector back to its equilibrium orientation is described by the longitudinal relaxation time  $T_1$ , independent of the state of phase coherence.
- Isolated quantum systems can temporarily violate the First Law, as described by the energy-time interval uncertainty relation. This may be of stochastic origin (fluctuations) or due to the oscillatory evolution of non-eigenstates.
- Unlike the Coulomb force between charges of equal and opposite signs, the gravitational force is not shielded. This leads to conditions where matter has a negative heat capacity so that heat flows spontaneously from cold to hot, which is in contradiction with the arrow of time for conventional (non-gravitational) matter and requires an amendment of the Second Law. Internal coupling in a thermal inductor or in coupled spin systems can lead to heat flowing temporarily from cold to hot without external intervention. Nevertheless, the entropy of the isolated system does not reverse so that the Second Law is not violated in these cases.
- Quantum coherences reveal the quanticity (quantum nature) of biological systems. This is more than just a characteristic of the matter but is of relevance to energy and charge transfer between coupled neighboring chromophores, thus providing a mechanism for energy and charge transport and eventually to charge separation. Interaction of the coherent electronic states with vibrational modes in the thermal bath gives rise to equilibration and thermalization.
- The evolution of living subsystems occurs in a thermodynamic environment, but it requires additional principles beyond the Second Law of thermodynamics, like Darwin's principle of the *survival of the fittest* (which has some serious limitations). Since biological evolution also seems to be not fundamentally reversible, this principle provides an arrow of evolution that is complementary to the arrow of time.
- A proper treatment of dissipation and thermalization may be able to link classical Newtonian, quantum-mechanical, statistical and thermodynamic descriptions of the dynamics of matter. This may potentially lead to a unified theory of matter.

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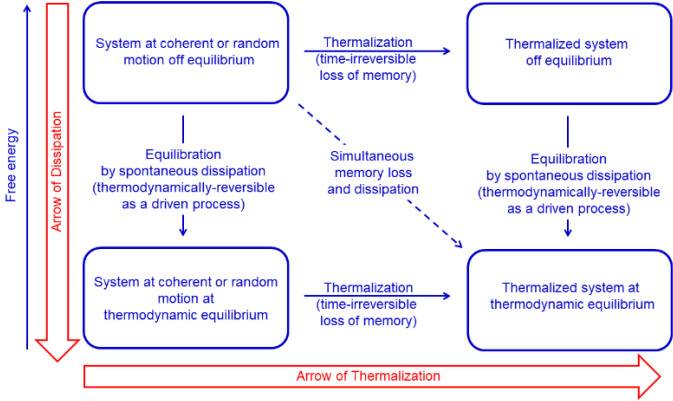


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# Graphical abstract



The arrow of time splits into an arrow of dissipation that leads to thermodynamic equilibrium and an arrow of thermalization that leads to the loss of time-reversibility.