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Entropy and the Second Law

Various formulations of the second law and entropy are reviewed. Longstanding foundational issues concerned with their definition, physical applicability and meaning are discussed.

1.1 Early Thermodynamics

The origins of thermodynamic thought are lost in the furnace of time. However, they are written into flesh and bone. To some degree, all creatures have an innate ‘understanding’ of thermodynamics — as well they should since they are bound by it. Organisms that display thermotaxis, for example, have a somatic familiarity with thermometry: zeroth law. Trees grow tall to dominate solar energy reserves: first law. Animals move with a high degree of energy efficiency because it is ‘understood’ at an evolutionary level that energy wasted cannot be recovered: second law. Nature culls the inefficient.

Human history and civilization have been indelibly shaped by thermodynamics. Survival and success depended on such things as choosing the warmest cave for winter and the coolest for summer, tailoring the most thermally insulating furs, rationing food, greasing wheels against friction, finding a southern exposure for a home (in the northern hemisphere), tidying up occasionally to resist the tendencies of entropy. Human existence and civilization have always depended implicitly on an understanding of thermodynamics, but it has only been in the last 150 years that this understanding has been codified. Even today it is not complete.

Were one to be definite, the first modern strides in thermodynamics began perhaps with James Watt's (1736-1819) steam engine, which gave impetus to what we now know as the Carnot cycle. In 1824 Sadi Nicolas Carnot (1796-1832), published his only scientific work, a treatise on the theory of heat (*Réflexions sur la Puissance Motice du Feu*) [1]. At the time, it was not realized that a portion of the heat used to drive steam engines was converted into work. This contributed to the initial disinterest in Carnot's research.

Carnot turned his attention to the connection between heat and work, abandoning his previous opinion about heat as a fluidum, and almost surmised correctly the mechanical equivalent of heat[1]. In 1846, James Prescott Joule (1818-1889) published a paper on thermal and chemical effects of the electric current and in another (1849) he reported mechanical equivalent of heat, thus erasing the sharp boundary between mechanical and thermal energies. There were also others who, independently of Joule, contributed to this change of thinking, notably Hermann von Helmholtz (1821-1894).

Much of the groundwork for these discoveries was laid by Benjamin Thompson (Count of Rumford 1753-1814). In 1798, he took part in boring artillery gun barrels. Having ordered the use of blunt borers – driven by draught horses – he noticed that substantial heat was evolved, in fact, in quantities sufficient to boil appreciable quantities of water. At roughly the same time, Sir Humphry Davy (1778-1829) observed that heat developed upon rubbing two pieces of metal or ice, even under vacuum conditions. These observations strongly contradicted the older fluid theories of heat.

The law of energy conservation as we now know it in thermodynamics is usually ascribed to Julius Robert von Mayer (1814-1878). In classical mechanics, however, this law was known intuitively at least as far back as Galileo Galilei (1564-1642). In fact, about a dozen scientists could legitimately lay claim to discovering energy conservation. Fuller accounts can be found in books by Brush [2] and von Baeyer [3]. The early belief in energy conservation was so strong that, since 1775, the French Academy has forbidden consideration of any process or apparatus that purports to produce energy *ex nihilo*: a *perpetuum mobile* of the first kind.

With acceptance of energy conservation, one arrives at the first law of thermodynamics. Rudolph Clausius (1822-1888) summarized it in 1850 thus: "In any process, energy may be changed from one to another form (including heat and work), but can never be produced or annihilated." With this law, any possibility of realizing a *perpetuum mobile* of the first kind becomes illusory.

Clausius' formulation still stands in good stead over 150 years later, despite unanticipated discoveries of new forms of energy — *e.g.*, nuclear energy, rest mass energy, vacuum energy, dark energy. Because the definition of energy is malleable, in a practical sense, the first law probably need not ever be violated because, were one to propose a violation, energy could be redefined so as to correct it. Thus, conservation of energy is reduced to a tautology and the first law to a powerfully convenient accounting tool for the two general forms of energy: heat and work.

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[1] Unfortunately, this tract was not published, but was found in his inheritance in 1878.

In equilibrium thermodynamics, the first law is written in terms of an additive state function, the internal energy U, whose exact differential dU fulfills

$$dU = \delta Q + \delta W. \tag{1.1}$$

Here δQ and δW are the inexact differentials of heat and work added to the system. (In nonequilibrium thermodynamics, there are problems with introducing these quantities rigorously.) As inexact differentials, the integrals of δQ and δW are path dependent, while dU, an exact differential is path independent; thus, U is a state function. Other state functions include enthalpy, Gibbs free energy, Helmholtz free energy and, of course, entropy.

1.2 The Second Law: Twenty-One Formulations

The second law of thermodynamics was first enunciated by Clausius (1850) [4] and Kelvin (1851) [5], largely based on the work of Carnot 25 years earlier [1]. Once established, it settled in and multiplied wantonly; the second law has more common formulations than any other physical law. Most make use of one or more of the following terms — entropy, heat, work, temperature, equilibrium, *perpetuum mobile* — but none employs all, and some employ none. Not all formulations are equivalent, such that to satisfy one is not necessarily to satisfy another. Some versions overlap, while others appear to be entirely distinct laws. Perhaps this is what inspired Truesdell to write, "Every physicist knows exactly what the first and second laws mean, but it is my experience that no two physicists agree on them."

Despite — or perhaps because of — its fundamental importance, no single formulation has risen to dominance. This is a reflection of its many facets and applications, its protean nature, its colorful and confused history, but also its many unresolved foundational issues. There are several fine accounts of its history [2, 3, 6, 7]; here we will give only a sketch to bridge the many versions we introduce. Formulations can be catagorized roughly into five catagories, depending on whether they involve: 1) device and process impossibilities; 2) engines; 3) equilibrium; 4) entropy; or 5) mathematical sets and spaces. We will now consider twenty-one standard (and non-standard) formulations of the second law. This survey is by no means exhaustive.

The first explicit and most widely cited form is due to Kelvin[2] [5, 8].

> **(1) Kelvin-Planck** No device, operating in a cycle, can produce the sole effect of extraction a quantity of heat from a heat reservoir and the performance of an equal quantity of work.

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[2] William Thomson (1824-1907) was known from 1866-92 as Sir William Thomson and after 1892 as Lord Kelvin of Largs.

In this, its most primordial form, the second law is an injunction against *perpetuum mobile* of the second type (PM2). Such a device would transform heat from a heat bath into useful work, in principle, indefinitely. It formalizes the reasoning undergirding Carnot's theorem, proposed over 25 years earlier.

The second most cited version, and perhaps the most natural and experientially obvious, is due to Clausius (1854) [4]:

> **(2) Clausius-Heat** No process is possible for which the sole effect is that heat flows from a reservoir at a given temperature to a reservoir at higher temperature.

In the vernacular: Heat flows from hot to cold. In contradistinction to some formulations that follow, these two statements make claims about strictly *nonequilibrium* systems; as such, they cannot be considered equivalent to later equilibrium formulations. Also, both versions turn on the key term, *sole effect*, which specifies that the heat flow must not be aided by external agents or processes. Thus, for example, heat pumps and refrigerators, which do transfer heat from a cold reservoir to a hot reservoir, do so without violating the second law since they require work input from an external source that inevitably satisfies the law.

Other common (and equivalent) statements to these two include:

> **(3) Perpetual Motion** *Perpetuum mobile* of the second type are impossible.

and

> **(4) Refrigerators** Perfectly efficient refrigerators are impossible.

The primary result of Carnot's work and the root of many second law formulations is Carnot's theorem [1]:

> **(5) Carnot theorem** All Carnot engines operating between the same two temperatures have the same efficiency.

Carnot's theorem is occasionally but not widely cited as the second law. Usually it is deduced from the Kelvin-Planck or Clausius statements. Analysis of the Carnot cycle shows that a portion of the heat flowing through a heat engine must always be lost as waste heat, not to contribute to the overall useful heat output[3]. The maximum efficiency of heat engines is given by the Carnot efficiency: $\eta = 1 - \frac{T_c}{T_h}$, where $T_{c,h}$ are the temperatures of the colder and hotter heat reservoirs between which the heat engine operates. Since absolute zero ($T_c = 0$) is unattainable (by one version of the third law) and since $T_h \neq \infty$ for any realistic system, the Carnot efficiency forbids perfect conversion of heat into work (*i.e.*, $\eta = 1$). Equivalent second law formulations embody this observation:

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[3] One could say that the second law is Nature's tax on the first.

(6) Efficiency All Carnot engines have efficiencies satisfying: $0 < \eta < 1$.

and,

(7) Heat Engines Perfectly efficient heat engines ($\eta = 1$) are impossible.

The *efficiency* form is not cited in textbooks, but is suggested as valid by Koenig [9]. There is disagreement over whether Carnot should be credited with the discovery of the second law [10]. Certainly, he did not enunciate it explicitly, but he seems to have understood it in spirit and his work was surely a catalyst for later, explicit statements of it.

Throughout this discussion it is presumed that realizable heat engines must operate between two reservoirs at different temperatures. (T_c and T_h). This condition is considered so stringent that it is often invoked as a litmus test for second law violators; that is, if a heat engine purports to operate at a single temperature, it violates the second law. Of course, mathematically this is no more than asserting $\eta = 1$, which is already forbidden.

Since thermodynamics was initially motivated by the exigencies of the industrial revolution, it is unsurprising that many of its formulations involve engines and cycles.

(8) Cycle Theorem Any physically allowed heat engine, when operated in a cycle, satisfies the condition

$$\oint \frac{\delta Q}{T} = 0 \tag{1.2}$$

if the cycle is reversible; and

$$\oint \frac{\delta Q}{T} < 0 \tag{1.3}$$

if the cycle is irreversible.

Again, δQ is the inexact differential of heat. This theorem is widely cited in the thermodynamic literature, but is infrequently forwarded as a statement of the second law. In discrete summation form for reversible cycles ($\sum_i Q_i/T_i = 0$), it was proposed early on by Kelvin [5] as a statement of the second law.

(9) Irreversibility All natural processes are irreversible.

Irreversibility is an essential feature of natural processes and it is the essential thermodynamic characteristic defining the direction of time[4] — *e.g.*, omelettes do

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[4] It is often said that irreversibility gives direction to time's arrow. Perhaps one should say irreversibility *is* time's arrow [11-17].

not spontaneously unscramble; redwood trees do not 'ungrow'; broken Ming vases do not reassemble; the dead to not come back to life. An irreversible process is, by definition, not quasi-static (reversible); it cannot be undone without additional irreversible changes to the universe. Irreversibility is so undeniably observed as an essential behavior of the physical world that it is put forward by numerous authors in second law statements.

In many thermodynamic texts, *natural* and *irreversible* are equated, in which case this formulation is tautological; however, as a reminder of the essential content of the law, it is unsurpassed. In fact, it is so deeply understood by most scientists as to be superfluous.

A related formulation, advanced by Koenig [9] reads:

> **(10) Reversibility** All normal quasi-static processes are reversible, and conversely.

Koenig claims, "this statement goes further than [the irreversibility statement] in that it supplies a necessary and sufficient condition for reversibility (and irreversibility)." This may be true, but it is also sufficiently obtuse to be forgettable; it does not appear in the literature beyond Koenig.

Koenig also offers the following orphan version [9]:

> **(11) Free Expansion** Adiabatic free expansion of a perfect gas is an irreversible process.

He demonstrates that, within his thermodynamic framework, this proposition is equivalent to the statement, "If a [PM2] is possible, then free expansion of a gas is a reversible process; and conversely." Of course, since adiabatic free expansion is irreversible, it follows *perpetuum mobile* are logically impossible — a standard statement of the second law. By posing the second law in terms of a particular physical process (adiabatic expansion), the door is opened to use any natural (irreversible) process as the basis of a second law statement. It also serves as a reminder that the second law is not only *of* the world and *in* the world, but, in an operational sense, it *is* the world. This formulation also does not enjoy citation outside Koenig [9].

A relatively recent statement is proposed by Macdonald [18]. Consider a system Z, which is closed with respect to material transfers, but to which heat and work can be added or subtracted so as to change its state from A to B by an arbitrary process $\mathcal{P}$ that is not necessarily quasi-static. Heat ($H_{\mathcal{P}}$) is added by a *standard heat source*, taken by Macdonald to be a reservoir of water at its triple point. The second law is stated:

> **(12) Macdonald** [18] It is impossible to transfer an arbitrarily large amount of heat from a standard heat source with processes terminating at a fixed state of Z. In other words, for every state B of Z,

$$\mathrm{Sup}[H_{\mathcal{P}} : \mathcal{P} \text{ terminates at } B] < \infty,$$

where Sup[...] is the supremum of heat for the process $\mathcal{P}$.

Absolute entropy is defined easily from here as the supremum of the heat $H_{\mathcal{P}}$ divided by a fiduciary temperature T_o, here taken to be the triple point of water (273.16 K); that is, $S(B) = \mathrm{Sup}[H_{\mathcal{P}}/T_o : P \text{ terminates at } B]$. Like most formulations of entropy and the second law, these apply strictly to closed equilibrium systems.

Many researchers take equilibrium as the *sine qua non* for the second law.

> **(13) Equilibrium** The macroscopic properties of an isolated nonstatic system eventually assume static values.

Note that here, as with many equivalent versions, the term *equilibrium* is purposefully avoided. A related statement is given by Gyftopolous and Beretta [19]:

> **(14) Gyftopolous and Beretta** Among all the states of a system with given values of energy, the amounts of constituents and the parameters, there is one and only one stable equilibrium state. Moreover, starting from any state of a system it is always possible to reach a stable equilibrium state with arbitrary specified values of amounts of constituents and parameters by means of a reversible weight process.

(Details of nomenclature (*e.g.*, weight process) can be found in §1.3.) Several aspects of these two equilibrium statements merit unpacking.

- *Macroscopic* properties (*e.g.*, temperature, number density, pressure) are ones that exhibit statistically smooth behavior at equilibrium. Scale lengths are critical; for example, one expects macroscopic properties for typical liquids at scale lengths greater than about 10^{-6}m. At shorter scale lengths statistical fluctuations become important and can undermine the second law. This was understood as far back as Maxwell [20, 21, 22, 23].

- There are no truly *isolated* systems in nature; all are connected by long-range gravitational and perhaps electromagnetic forces; all are likely affected by other uncontrollable interactions, such as by neutrinos, dark matter, dark energy and perhaps local cosmological expansion; and all are inevitably coupled thermally to their surroundings to some degree. Straightforward calculations show, for instance, that the gravitational influence of a minor asteroid in the Asteroid Belt is sufficient to instigate chaotic trajectories of molecules in a parcel of air on Earth in less than a microsecond. Since gravity cannot be screened, the exact molecular dynamics of all realistic systems are constantly affected in essentially unknown and uncontrollable ways. Unless one is able to model the entire universe, one probably cannot exactly model any subset of it[5]. Fortunately, statistical arguments (*e.g.*, molecular chaos, ergodicity) allow thermodynamics to proceed quite well in most cases.

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[5] Quantum mechanical entanglement, of course, further complicates this task.

- One can distinguish between *stable* and *unstable* static (or equilibrium) states, depending on whether they "persist over time intervals significant for some particular purpose in hand." [9]. For instance, to say "*Diamonds are forever.*" is to assume much. Diamond is a metastable state of carbon under everyday conditions; at elevated temperatures (∼ 2000 K), it reverts to graphite. In a large enough vacuum, graphite will evaporate into a vapor of carbon atoms and they, in turn, will thermally ionize into a plasma of electrons and ions. After 10^{33} years, the protons might decay, leaving a tenuous soup of electrons, positrons, photons, and neutrinos. Which of these is a stable equilibrium? None or each, depending on the time scale and environment of interest. By definition, a *stable* static state is one that can change only if its surroundings change, but still, time is a consideration. To a large degree, equilibrium is a matter of taste, time, and convenience.

- Gyftopoulos and Beretta emphasise *one and only one stable equilibrium state.* This is echoed by others, notably by Mackey who reserves this caveat for his *strong form* of the second law [24].

Thus far, entropy has not entered into any of these second law formulations. Although, in everyday scientific discourse the two are inextricably linked, this is clearly not the case. Entropy was defined by Clausius in 1865, nearly 15 years after the first round of explicit second law formulations. Since entropy was originally wrought in terms of heat and temperature, this allows one to recast earlier formulations easily. Naturally, the first comes from Clausius:

> **(15) Clausius-Entropy** [4, 6] For an adiabatically isolated system that undergoes a change from one equilibrium state to another, if the thermodynamic process is reversible, then the entropy change is zero; if the process is irreversible, the entropy change is positive. Respectively, this is:
>
> $$\int_i^f \frac{\delta Q}{T} = S_f - S_i \tag{1.4}$$
>
> and
>
> $$\int_i^f \frac{\delta Q}{T} < S_f - S_i \tag{1.5}$$

Planck (1858-1947), a disciple of Clausius, refines this into what he describes as "the most general expression of the second law of thermodynamics." [8, 6]

> **(16) Planck** Every physical or chemical process occurring in nature proceeds in such a way that the sum of the entropies of all bodies which participate in any way in the process is increased. In the limiting case, for reversible processes, the sum remains unchanged.

Alongside the Kelvin-Planck version, these two statements have dominated the scientific landscape for nearly a century and a half. Planck's formulation implicitly cuts the original ties between entropy and heat, thereby opening the door for other versions of entropy to be used. It is noteworthy that, in commenting on the possible limitations of his formulation, Planck explicitly mentions the *perpetuum mobile*. Evidently, even as thermodynamics begins to mature, the specter of the *perpetuum mobile* lurks in the background.

Gibbs takes a different tack to the second law by avoiding thermodynamic processes, and instead conjoins entropy with equilibrium [25, 6]:

> **(17) Gibbs** For the equilibrium of an isolated system, it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.

In other words, thermodynamic equilibrium for an isolated system is the state of maximum entropy. Although Gibbs does not refer to this as a statement of the second law, *per se*, this *maximum entropy principle* conveys its essential content. The maximum entropy principle [26] has been broadly applied in the sciences, engineering economics, information theory — wherever the second law is germane, and even beyond. It has been used to reformulate classical and quantum statistical mechanics [26, 27]. For instance, starting from it one can derive on the back of an envelope the continuous or discrete Maxwell-Boltzmann distributions, the Planck blackbody radiation formula (and, with suitable approximations, the Rayleigh-Jeans and Wien radiation laws) [24].

Some recent authors have adopted more definitional entropy-based versions [9]:

> **(18) Entropy Properties** Every thermodynamic system has two properties (and perhaps others): an intensive one, absolute temperature T, that may vary spatially and temporally in the system $T(x,t)$; and an extensive one, entropy S. Together they satisfy the following three conditions:
> (i) The entropy change dS during time interval dt is the sum of: (a) entropy flow through the boundary of the system d_eS; and (b) entropy production within the system, d_iS; that is, $dS = d_eS + d_iS$.
> (ii) Heat flux (not matter flux) through a boundary at uniform temperature T results in entropy change $d_eS = \frac{\delta Q}{T}$.
> (iii) For reversible processes within the system, $d_iS = 0$, while for irreversible processes, $d_iS > 0$.

This version is a starting point for some approaches to irreversible thermodynamics.

While there is no agreement in the scientific community about how best to state the second law, there is general agreement that the current melange of statements, taken en masse, pretty well covers it. This, of course, gives fits to mathematicians, who insist on precision and parsimony. Truesdell [28, 6] leads the charge:

> Clausius' verbal statement of the second law makes no sense.... All that remains is a Mosaic prohibition; a century of philosophers and journalists have acclaimed this commandment; a century of mathematicians have shuddered and averted their eyes from the unclean.

Arnold broadens this assessment [29, 6]:

> Every mathematician knows it is impossible to understand an elementary course in thermodynamics.

In fact, mathematicians have labored to drain this "dismal swamp of obscurity" [28], beginning with Carathéodory [30] and culminating with the recent *tour de force* by Lieb and Yngvason [31]. While both are exemplars of mathematical rigor and logic, both suffer from incomplete generality and questionable applicability to realistic physical systems; in other words, there are doubts about their empirical content.

Carathéodory was the first to apply mathematical rigor to thermodynamics [30]. He imagines a state space Γ of all possible equilibrium states of a generic system. Γ is an n-dimensional manifold with continuous variables and Euclidean topology. Given two arbitrary states s and t, if s can be transformed into t by an adiabatic process, then they satisfy *adiabatically accessibility* condition, written $s \prec t$, and read *s precedes t*. This is similar to Lieb and Yngvason [31], except that Lieb and Yngvason allow sets of possibly disjoint ordered states, whereas Carathéodory assumes continuous state space and variables. Max Born's simplified version of Carathéodory's second law reads [32]:

> **(19a) Carathéodory (Born Version)**: In every neighborhood of each state (s) there are states (t) that are inaccessible by means of adiabatic changes of state. Symbolically, this is:

$$(\forall s \in \Gamma, \forall U_s) : \exists t \in U_s s \nprec t, \tag{1.6}$$

where U_s and U_t are open neighborhoods surrounding the states s and t.

Carathéodory's originally published version is more precise [30, 6].

> **(19b) Carathéodory Principle** In every open neighborhood $U_s \subset \Gamma$ of an arbitrarily chosen state s there are states t such that for some open neighborhood U_t of t: all states r within U_t cannot be reached adiabatically from s. Symbolically this is:

$$\forall s \in \Gamma \forall U_s \exists t \in U_s \& \exists U_t \subset U_s \forall r \in U_t : s \nprec r. \tag{1.7}$$

Lieb and Yngvason [31] proceed along similar lines, but work with an set of distinct states, rather than a continuous space of them. For them, the second law is a theorem arising out of the ordering of the states via adiabatic accessibility. Details can be found in §1.3.

In connection with analytical microscopic formulations of the second law, the recent work by Allahverdyan and Nieuwenhuizen [33] is noteworthy. They rederive and extend the results of Pusz, Woronowicz [34] and Lenard [35], and provide an analytical proof of the following equilibrium formulation of the Thomson (Kelvin) statement:

> **(20) Thomson (Equilibrium)** No work can be extracted from a closed equilibrium system during a cyclic variation of a parameter by an external source.

The Allahverdyan-Niewenhuizen (A-N) theorem is proved by rigorous quantum mechanical methods without invoking the time-invariance principle. This makes it superior to previous treatments of the problem. Although significant, it is insufficient to resolve most types of second law challenges, for multiple reasons. First, the A-N theorem applies to equilibrium systems only, whereas the original forms of the second law (Kelvin and Clausius) are strictly nonequilibrium in character and most second law challenges are inherently nonequilibrium in character; thus, the pertinence of the A-N theorem is limited. Second, it assumes that the system considered is isolated, but realistically, no such system exists in Nature. Third, it assumes the Gibbs form of the initial density matrix. While this assumption is natural when temperature is well defined, once *finite* coupling of the system to a bath is introduced, this assumption can be violated appreciably, especially for systems which purport second law violation (*e.g.*, [36]).

The relationships between these various second law formulations are complex, tangled and perhaps impossible to delineate completely, especially given the muzziness with which many of them and their underlying assumptions and definitions are stated. Still, attempts have been made along these lines [2, 6, 7, 9] [6]. This exercise of tracing the connections between the various formulations has historical, philosophical and scientific value; hopefully, it will help render a more inclusive formulation of the second law in the future.

In addition to academic formulations there are also many folksy aphorisms that capture aspects of the law. Many are catchphrases for more formal statements. Although loathe to admit it, most of these are used as primary rules of thumb by working scientists. Most are anonymous; when possible, we try to identify them with academic forms. Among these are:

- Disorder tends to increase. (*Clausius, Planck*)
- Heat goes from hot to cold. (*Clausius*)
- There are no perfect heat engines. (*Carnot*)
- There are no perfect refrigerators. (*Clausius*)
- Murphy's Law (and corollary) (*Murphy* $\sim$ 1947)

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[6] See, Table I in Uffink [6] and Table II (Appendix A) in Koenig [9]

  1. If anything can go wrong it will.
  2. Situations tend to progress from bad to worse.

- A mess expands to fill the space available.
- The only way to deal with a can of worms is to find a bigger can.
- Laws of Poker in Hell:
  1. Poker exists in Hell. (*Zeroth Law*)
  2. You can't win. (*First Law*)
  3. You can't break even. (*Second Law*)
  4. You can't leave the game. (*Third Law*)
- Messes don't go away by themselves. (*Mom*)
- Perpetual motion machines are impossible. (*Nearly everyone*)

Interestingly, in number, second law aphorisms rival formal statements. Perhaps this is not surprising since the second law began with Carnot and Kelvin as an injunction against perpetual motions machines, which have been scorned publically back to times even before Leonardo da Vinci (∼ 1500). Arguably, most versions of the second law add little to what we already understand intuitively about the dissipative nature of the world; they only confirm and quantify it. As noted by Pirruccello [37]:

> Perhaps we'll find that the second law is rooted in folk wisdom, platitudes about life. The second law is ultimately an expression of human disappointment and frustration.

For many, the first and best summary of thermodynamics was stated by Clausius 150 years ago [4]:

1. Die Energie der Welt ist konstant.
2. Die Entropie der Welt strebt einem Maximum zu.

or, in English,

1. The energy of the universe is constant.
2. The entropy of the universe strives toward a maximum.

Although our conceptions of energy, entropy and the universe have undergone tremendous change since his time, remarkably, Clausius' summary still rings true today — and perhaps even more so now for having weathered so much.

In surveying these many statements, one can get the impression of having stumbled upon a scientific Rorschauch test, wherein the second law becomes a reflection of one's own circumstances, interests and psyche. However, although there is much disagreement on how best to state it, its primordial injunction against *perpetuum mobile* of the second type generally receives the most support and the least dissention. It is the gold standard of second law formulations. If the second law is the flesh of thermodynamics, this injunction is its heart.

If the second law should be shown to be violable, it would nonetheless remain valid for the vast majority of natural and technological processes. In this case, we propose the following tongue-in-cheek formulation for a post-violation era, should it come to pass:

> **(21) Post-Violation** For any spontaneous process the entropy of the universe does not decrease — except when it does.

1.3 Entropy: Twenty-One Varieties

The discovery of thermodynamic entropy as a state function is one of the triumphs of nineteenth-century theoretical physics. Inasmuch as the second law is one of the central laws of nature, its handmaiden — entropy — is one of the most central physical concepts. It can pertain to almost any system with more than a few particles, thereby subsuming nearly everything in the universe from nuclei to superclusters of galaxies [38]. It is protean, having scores of definitions, not all of which are equivalent or even mutually compatible[7]. To make matters worse, "perhaps every month someone invents a new one," [39]. Thus, it is not surprising there is considerable controversy surrounding its nature, utility, and meaning. It is fair to say that no one *really* knows what entropy is.

Roughly, entropy is a quantitative macroscopic measure of microscopic disorder. It is the only major physical quantity predicated and reliant upon wholesale ignorance of the system it describes. This approach is simultaneously its greatest strength and its Achilles heel. On one hand, the computational complexities of even simple dynamical systems often mock the most sophisticated analytic and numerical techniques. In general, the dynamics of n-body systems ($n > 2$) cannot be solved exactly; thus, thermodynamic systems with on the order of a mole of particles (10^{23}) are clearly hopeless, even in a perfectly deterministic Laplacian world, sans chaos. Thus, it is both convenient and wise to employ powerful physical assumptions to simplify entropy calculations — *e.g.*, equal *a priori* probability, ergodicity, strong mixing, extensivity, random phases, thermodynamic limit. On the other hand, although they have been spectacularly predictive and can be shown to be reasonable for large classes of physical systems, these assumptions are known not to be universally valid. Thus, it is not surprising that no completely satisfactory definition of entropy has been discovered, despite 150 years of effort. Instead, there has emerged a menagerie of different types which, over the decades, have grown increasingly sophisticated both in response to science's deepening understanding of nature's complexity, but also in recognition of entropy's inadequate expression.

This section provides a working man's overview of entropy; it focuses on the most pertinent and representative varieties. It will not be exhaustive, nor will

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[7] P. Hänggi claims to have compiled a list of 55 different varieties; here we present roughly 21.

it respect many of the nuances of the subject; for these, the interested reader is directed to the many fine treatises on the subject.

Most entropies possess a number of important physical and mathematical properties whose adequate discussion extends beyond the aims of this volume; these include additivity, subadditivity, concavity, invariance, insensitivity, continuity conditions, and monotonicity [24, 31, 39]. Briefly, for a system A composed of two subsystems A_1 and A_2 such that $A = A_1 + A_2$, the entropy is additive if $S(A) = S(A_1) + S(A_2)$. For two independent systems A and B, the entropy is subadditive if their entropy when joined (composite entropy) is never less than the sum of their individual entropies; *i.e.*, $S(A + B) \geq S(A) + S(B)$. (Note that for additivity the subsystems (A_1, A_2) retain their individual identities, while for subadditivity the systems (A, B) lose their individual identities.) For systems A and B, entropy demonstrates concavity if $S(\lambda A+(\lambda-1)B) \geq \lambda S(A)+(1-\lambda)S(B)$; $0 \leq \lambda \leq 1$.

A workingman's summary of standard properties can be extracted from Gyftopoulous and Beretta [19]. Classical entropy must[8]:

a) be well defined for every system and state;
b) be invariant for any reversible adiabatic process ($dS = 0$) and increase for any irreversible adiabatic process ($dS > 0$);
c) be additive and subadditive for all systems, subsystems and states.
d) be non-negative, and vanish for all states described by classical mechanics;
e) have one and only one state corresponding to the largest value of entropy;
f) be such that graphs of entropy versus energy for stable equilibria are smooth and concave; and
g) reduce to relations that have been established experimentally.

The following are summaries of the most common and salient formulations of entropy, spiced with a few distinctive ones. There are many more.

(1) Clausius [4] The word *entropy* was coined by Rudolf Clausius (1865) as a thermodynamic complement to energy. The *en* draws parallels to *energy*, while *tropy* derives from the Greek word $\tau\rho o\pi\eta$, meaning *change*. Together *en-tropy* evokes quantitative measure for thermodynamic change[9].

Entropy is a macroscopic measure of the microscopic state of disorder or chaos in a system. Since heat is a macroscopic measure of microscopic random kinetic energy, it is not surprising that early definitions of entropy involve it. In its original and most utilitarian form, entropy (or, rather, entropy *change*) is expressed in terms of heat Q and temperature T. For reversible thermodynamic processes, it is

$$dS = \frac{\delta Q}{T}, \tag{1.8}$$

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[8] Many physical systems in this volume do not abide these restrictions, most notably, additivity.

[9] Strictly speaking, Clausius coined *entropy* to mean *in transformation.*

while for irreversible processes, it is

$$dS > \frac{\delta Q}{T} \tag{1.9}$$

These presume that T is well defined in the surroundings, thus foreshadowing the zeroth law. To establish fiduciary entropies the third law is invoked. For systems "far" from equilibrium, neither entropy nor temperature is well defined.

(2) Boltzmann-Gibbs [40, 41] The most famous classical formulation of entropy is due to Boltzmann:

$$S_{BG,\mu} = S(E,N,V) = k \ln \Omega(E,N,V) \tag{1.10}$$

Here $\Omega(E,N,V)$ is the total number of distinct microstates (complexions) accessible to a system of energy E, particle number N in volume V. The Boltzmann relation provides the first and most important bridge between microscopic physics and equilibrium thermodynamics. It carries with it a minimum number of assumptions and, therefore, is quite general. It applies directly to the microcanonical ensemble (fixed E, N, V), but, with appropriate inclusion of heat and particle reservoirs, also to the canonical and grand canonical ensembles. In principle, it applies to both extensive and nonextensive systems and does not presume the standard thermodynamic limit (*i.e.*, infinite particle number and volume [$N \to \infty$, $V \to \infty$], finite density [$\frac{N}{V} = C < \infty$]) [38]; it can be used with boundary conditions, which often handicap other formalisms; it does not presume temperature. However, ergodicity (or quasi-ergodicity) is presumed in that the system's phase space trajectory is assumed to visit smoothly and uniformly all neighborhoods of the (6N-1)-dimensional constant-energy manifold consistent with $\Omega(E,N,V)$ [10].

The Gibbs entropy is similar to Boltzmann's except that it is defined via ensembles, distributions of points in classical phase space consistent with the macroscopic thermodynamic state of the system. Hereafter, it is called the Boltzmann-Gibbs (BG) entropy. Like other standard forms of entropy, $S_{BG,\mu}$ applies strictly to equilibrium systems.

Note that Ω is not well defined for classical systems since phase space variables are continuous. To remedy this, the phase space can be measured in unit volumes, often in units of $\hbar$. This motivates *coarse-grained* entropy. Coarse-graining reduces the information contained in Ω and may be best described as a kind of phase space averaging procedure for a distribution function. The coarse-grained distribution leads to a proper increase of the corresponding statistical (information) entropy. A perennial problem with this, however, is that the averaging procedure is not unique so that the rate of entropy increase is likewise not unique, in contrast to presumably uniquely defined increase of the thermodynamic entropy.

Starting from $S_{BG,\mu}$, primary intensive parameters (temperature T, pressure P, and chemical potential μ) can be calculated [42-46]:

---

[10] Alternatively, ergodicity is defined as the condition that the ensemble-averaged and time-averaged thermodynamic properties of a system be the same.

$$(\frac{\partial S}{\partial E})_{N,V} \equiv \frac{1}{T} \tag{1.11}$$

$$(\frac{\partial S}{\partial V})_{E,N} \equiv \frac{P}{T} \tag{1.12}$$

$$(\frac{\partial S}{\partial N})_{V,E} \equiv -\frac{\mu}{T}. \tag{1.13}$$

If one drops the condition of fixed E and couples the system to a heat reservoir at fixed temperature T, allowing free exchange of energy between the system and reservoir, allowing E to vary as $(0 \leq E \leq \infty)$, then one passes from the microcanonical to the canonical ensemble [41-46].

For the canonical ensemble, entropy is defined as

$$S_{BG,c} \equiv k\left[\ln(Z) + \beta\overline{E}\right] = k\left[\frac{\partial}{\partial T}(T\ln(Z))\right]. \tag{1.14}$$

Here $\beta \equiv \frac{1}{kT}$ and Z is the partition function (*Zustandsumme* or "sum over states") upon which most of classical equilibrium thermodynamic quantities can be founded:

$$Z \equiv \sum_i e^{-\beta E_i}, \tag{1.15}$$

where E_i are the constant individual system energies and $\overline{E}$ is the mean (average) system energy:

$$\overline{E} \equiv \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \sum_i E_i p_i. \tag{1.16}$$

The probability p_i is the Boltzmann factor $\exp[-E_i/kT]$. One can define entropy through the probability sum

$$S_{BG} = -k\sum_i p_i \ln p_i, \tag{1.17}$$

or in the continuum limit

$$S_{BG} = -k\int f \ln f dv, \tag{1.18}$$

where f is a distribution function over a variable v. This latter expression is apropos to particle velocity distributions.

If, in addition to energy exchange, one allows particle exchange between a system and a heat-particle reservoir, one passes from the canonical ensemble (fixed T, N, V) to the grand canonical ensemble (fixed T, μ, V), for which entropy is defined [41-46]:

$$S_{BG,gc} \equiv \frac{1}{\beta}(\frac{\partial q}{\partial T})_{z,V} - Nk\ln(z) + kq = k[\frac{\partial(T\ln(\mathcal{Z})}{\partial T}]_{\mu,V}. \tag{1.19}$$

Here q is the q-potential:

$$q = q(z, V, T) \equiv \ln[\mathcal{Z}(z, V, T)], \tag{1.20}$$

defined in terms of the grand partition function:

$$\mathcal{Z}(z, V, T) \equiv \sum_{i,j} \exp(-\beta E_i - \alpha N_j) = \sum_{N_j=0}^{\infty} z^{N_j} Z_{N_j}(V, T). \tag{1.21}$$

Here $z \equiv e^{-\beta\mu}$ is the fugacity, Z_{N_j} is the regular partition function for fixed particle number N_j, and $\alpha = -\frac{\mu}{kT}$. The sum is over all possible values of particle number and energy, exponentially weighted by temperature. It is remarkable that such a simple rule is able to predict successfully particle number and energy occupancy and, therefrom, the bulk of equilibrium thermodynamics. This evidences the power of the physical assumptions underlying the theory.

(3) von Neumann [47] In quantum mechanics, entropy is not an *observable*, but a *state* defined through the density matrix, ρ:

$$S_{vN}(\rho) = -kTr[\rho \ln(\rho)]. \tag{1.22}$$

(Recall the expectation value of an observable is $\langle A \rangle = Tr(\rho A)$.) Roughly, $S_{vN}(\rho)$ is a measure of the quantity of chaos in a quantum mechanical mixed state. The von Neumann entropy has advantage over the Boltzmann formulation in that, presumably, it is a more basic and faithful description of nature in that the number of microstates for a system is well defined in terms of pure states, unlike the case of the classical continuum. On the other hand, unlike the Boltzmann microcanonical entropy, for the von Neumann formulation, important properties like ergodicity, mixing and stability strictly hold only for infinite systems.

The time development of ρ for an isolated system is governed by the Liouville equation

$$i\frac{d}{dt}\rho(t) = \frac{1}{\hbar}[H, \rho(t)] \equiv \mathcal{L}\rho(t). \tag{1.23}$$

Here H is the Hamiltonian of the system and $\mathcal{L}\ldots = \frac{1}{\hbar}[H, \ldots]$ is the Liouville superoperator. It follows that the entropy is constant in time. As noted by Wehrl [39],

> ... the entropy of a system obeying the Schrödinger equation (with a time-independent Hamiltonian) *always remains constant* [because the density matrix time evolves as] $\rho(t) = e^{-iHt}\rho e^{iHt}$. Since e^{iHt} is a unitary operator, the eigenvalues of $\rho(t)$ are the same eigenvalues of ρ. But the expression for the entropy only involves the eigenvalues of the density matrix, hence $S(\rho(t)) = S(\rho)$. (In the classical case, the analogous statement is a consequence of Liouville's theorem.)[11]

---

[11] This statement holds if H is a function of time; *i.e.*, $\rho(t) = \mathcal{U}\rho(0)\mathcal{U}^\dagger$, where $\mathcal{U} = T\exp(-\frac{i}{\hbar}\int_0^t H dt)$.

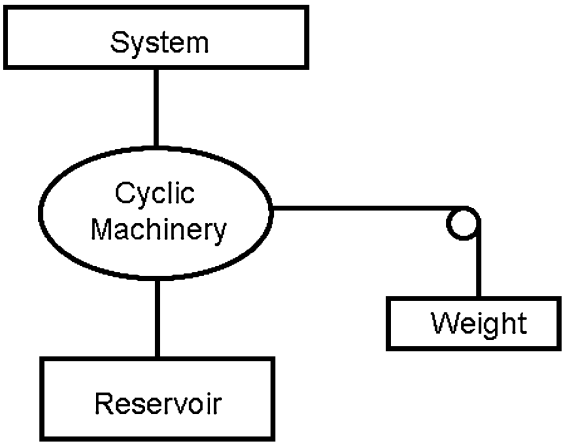

Figure 1.1: S_{GHB} is based on *weight processes.*

Since the Schrödinger equation alone is not sufficient to motivate the time evolution of entropy as normally observed in the real world, one usually turns to the Boltzmann equation, the master equation, or other time-asymmetric formalisms to achieve this end [43, 48, 49, 50]. Finally, the von Neumann entropy depends on time iff ρ is coarse-grained; in contrast, the fine-grained entropy is constant. (This, of course, ignores the problematic issues surrounding the non-uniqueness of the coarse graining process.)

(4) Gyftopoulous, et al. [19, 51] A utilitarian approach to entropy is advanced by Gyftopoulos, Hatsopoulos, and Beretta. Entropy S_{GHB} is taken to be an intrinsic, non-probabilistic property of any system whether microscopic, macroscopic, equilibrium, or nonequilibrium. Its development is based on *weight processes* in which a system A interacts with a reservoir R via cyclic machinery to raise or lower a weight (Figure 1.1). Of course, the weight process is only emblematic of any process of pure work. S_{GHB} is defined in terms of energy E, a constant that depends on a reservoir c_R, and *generalized available energy* Ω^R as:

$$S_{GHB} = S_0 + \frac{1}{c_R}[(E - E_0) - (\Omega^R - \Omega_0^R)], \tag{1.24}$$

for a system A that evolves from state A_1 to state A_0. E_0 and Ω_0^R are values of a reference state and S_0 is a constant fixed value for the system at all times. Temperature is not ostensibly defined for this system; rather, c_R is a carefully defined reservoir property (which ultimately can be identified with temperature). *Available energy* Ω^R is the largest amount of energy that can be extracted from the system A-reservoir combination by weight processes. Like S_{GHB}, it applies to all system sizes and types of equilibria.

At first meeting, S_{GHB} may seem contrived and circular, but its method of weight processes is similar to and no more contrived than that employed by Planck and others; its theoretical development is no more circular than that of Lieb and Yngvason [31]; furthermore, it claims to encompass broader territory than either by applying both to equilibrium and nonequilibrium systems. It does not, however, provide a microscopic picture of entropy and so is not well-suited to statistical mechanics.

(5) Lieb-Yngvason [31] The Lieb-Yngvason entropy S_{LY} is defined through the mathematical ordering of sets of equilibrium states, subject to the constraints of monotonicity, additivity and extensivity. The second law is revealed as a mathematical theorem on the ordering of these sets. This formalism owes significant debt to work by Carathéodory [30], Giles [52], Buchdahl [53] and others.

Starting with a space Γ of equilibrium states X,Y,Z ..., one defines an ordering of this set via the operation denoted $\prec$, pronounced *precedes.* The various set elements of Γ can be ordered by a comparison procedure involving the criterion of *adiabatic accessibility.* For elements X and Y, [31]

> A state Y is adiabatically accessible from a state X, in symbols X $\prec$ Y, if it is possible to change the state X to Y by means of an interaction with some device (which may consist of mechanical and electrical parts as well as auxiliary thermodynamic systems) and a weight, in such a way that the device returns to its initial state at the end of the process whereas the weight may have changed its position in a gravitation field.

This bears resemblance to the GHB weight process above (Figure 1.1). Although superficially this definition seems limited, it is quite general for equilibrium states. It is equivalent to requiring that state X can proceed to state Y by *any* natural process, from as gentle and mundane as the unfolding of a Double Delight rose in a quiet garden, to as violent and ultramundane as the detonation of a supernova.

If X proceeds to Y by an irreversible adiabatic process, this is denoted X $\prec\prec$ Y, and if X $\prec$ Y and Y $\prec$ X, then X and Y are called *adiabatically equivalent*, written X $\overset{A}{\sim}$ Y. If X $\prec$ Y or Y $\prec$ X (or both), they are called *comparable.*

The Lieb-Yngvason entropy S_{LY} is defined as [31]:

> There is a real-valued function on all states of all systems (including compound systems), called **entropy** and denoted by S such that
> a) *Monotonicity*: When X and Y are comparable states then
>
> $$\mathrm{X} \prec \mathrm{Y} \text{ if and only if } \mathrm{S(X)} \leq \mathrm{S(Y)}.$$
>
> b) *Additivity and extensivity*: If X and Y are states of some (possibly different) systems and if (X,Y) denotes the corresponding state in the composition of the two systems, then the entropy is additive for these states, *i.e.*,
>
> $$\mathrm{S(X,Y)} = \mathrm{S(X)} + \mathrm{S(Y)}$$

> S is also extensive, *i.e.*, for each $t > 0$ and each state X and its scaled copy tX,
>
> $$\mathrm{S}(t\mathrm{X}) = t\mathrm{S}(\mathrm{X}).$$

The monotonicity clause is equivalent to the following:

$$\mathrm{X} \overset{A}{\sim} \mathrm{Y} \Longrightarrow \mathrm{S}(\mathrm{X}) = \mathrm{S}(\mathrm{Y}); \text{ and}$$
$$\mathrm{X} \prec\prec \mathrm{Y} \Longrightarrow \mathrm{S}(\mathrm{X}) < \mathrm{S}(\mathrm{Y}).$$

The second of these says that entropy increases for an irreversible adiabatic process. This is the Lieb-Yngvason formulation of the second law.

The existence and uniqueness of S_{LY} can be shown to follow from assumptions surrounding adiabatic accessibility and the comparsion process. In this formalism, temperature is not a primitive concept; rather, it is defined via S_{LY} as $\frac{1}{T} := (\frac{\partial S_{LY}}{\partial U})_V$, where U is energy and V is volume. The mathematical details of these results are beyond the scope of this discussion; the intrepid reader is directed to [31].

(6) Carathéodory Historically preceding S_{LY}, Carathéodory also defined entropy in a formal mathematical sense [30, 6].

> For simple[12] systems, Carathéodory's principle is equivalent to the proposition that the differential form $\delta Q := dU - \delta W$ possesses an integrable divisor, *i.e.*, there exists functions S and T on the state space Γ such that
>
> $$\delta Q = TdS.$$
>
> Thus, for simple systems, every equilibrum state can be assigned values for entropy and absolute temperature. Obviously these functions are not uniquely determined by the relation [$\delta Q = TdS$].

Carathéodory's entropy was not widely accepted by working scientists during his lifetime, but it has grown in significance during the last 40 years as thermodynamic foundations have been shored up.

(7) Shannon [54] Various information-relevant entropies have been proposed over the last six decades, the most prominent of which are the Shannon entropy and algorithmic randomness [55, 56, 57]. These are especially salient in considerations of sentient Maxwell demons [21], which have helped expose the deep relationships between physics and information theory.

Let p_j be probabilities of mutually exclusive events, say for instance, the probabilties of particular letters in an unknown word. The uncertainty (entropy) of the information about this situation is the Shannon entropy:

---

[12] Consult the literature for the requirements of a *simple* system [6, 30]

$$S_{Sh} = -\sum_{j} p_j \log(p_j) \tag{1.25}$$

The logarithm may be taken to any fixed base, but base 2 is standard, giving entropy in bits. Shannon entropy can be seen to be a discrete form of the classical Boltzmann-Gibbs entropy, (1.17).

(8) Fisher Shannon entropy is defined over a space of unordered elements, for instance, letters. For a space of ordered elements, for example, a continuous parameter (*e.g.*, the length or brightness of meteor trails), Fisher information is appropriate. For a probability distribution $f(x;\phi)$ in the random variable x dependent on the unobservable variable ϕ, the Fisher information (entropy) is

$$S_F(\phi) = K[\frac{\partial}{\partial\phi}\log f(x;\phi)]^2 = -K[\frac{\partial^2}{\partial\phi^2}\log f(x;\phi)] \tag{1.26}$$

Clearly, the sharpness of the support curve is proportional to the expection of $S_F(\phi)$, thus high information content (low entropy) corresponds to a sharp distribution and a low information content (high entropy) to a broad distribution.

(9) Algorithmic Randomness [55, 56, 57] Algorithmic randomness (algorithmic complexity, Kolmorgorov complexity) of a string of elements is defined as the minimum size of a program (*e.g.*, in bits) executed on a universal computer that yields the string. Strings are relatively simple or complex depending on whether its program length is relatively short or long, respectively. For example, the string of 60,000 digits (121223121223121223...) is relatively simple and has relatively low algorithmic randomness since it can be programmed as 10,000 repeating blocks of (121223), whereas a completely *random* string of 60,000 digits cannot be compressed this way and thus has a relatively large algorithmic randomness. Most strings cannot be compressed and, to leading order in binary notation, their algorithmic randomness is given by their lengths in bits. By example, a random natural number N, if it can be expressed as $N \sim 2^s$, has algorithmic randomness $\sim log_2 N = s$.

Algorithmic complexity, in contrast to other standard definitions of entropy, does not rely on probabilities. However, the randomness of a string is not uniquely determined and there is no general method to discern a simple string from a complex one; this is related to Gödel's undecidability [59]. For example, the sequence (22459157718361045473427152) may appear completely random, but it is easily generated from π^e. Or, the letter sequence FPURCLK might seem random until it is unscrambled and considered in an appropriate context. Apparently, order can be in the eye of the beholder.

Zurek suggests that *physical entropy* "is the sum of (i) the missing information measured by Shannon's formula and (ii) of the [algorithmic content] in the available data about the system" [58].

(10) Tsallis [60, 61] Tsallis entropy is a controversial generalization of Boltzmann-Gibbs entropy and is an heir to the Rényi and Daróczy entropies below. It is defined as

$$S_{Ts} = \frac{1}{q-1}\left[1 - \int f^q(x)dx\right], \tag{1.27}$$

where q is a real number *entropic index* and $f(x)$ is a probability distribution function. For $q = 1$, S_{Ts} reduces to the Boltzmann-Gibbs entropy.

Primary virtues of the Tsallis entropy include its mathematical simplicity and descriptiveness of nonextensive systems. A physical quantity is extensive if its value scales linearly with the size of the system [13]. The extensive Boltzmann-Gibbs entropy of two independent systems A and B is $S_{BG}(A+B) = S_{BG}(A) + S_{BG}(B)$, while for the Tsallis entropy it is $S_{Ts}(A+B) = S_{Ts} + S_{Ts}(B) + (1-q)S_{Ts}(A)S_{Ts}(B)$. The parameter q can be taken as a measure of nonextensivity[14].

Tsallis entropy has been applied to numerous disparate physical phenomena that are deemed beyond the reach of equilibrium thermodynamics. Notably, these include systems with long-range nonextensive fields (*e.g.*, gravitational, electrostatic) such as plasmas and multi-particle self-gravitating systems (*e.g.*, galaxies, globular clusters). It has been applied to the behaviors of self-organizing and low-dimensional chaotic systems and processes far from equilibrium; examples include financial markets, crowds, traffic, locomotion of microorganisms, subatomic particle collisions, and tornados. Unfortunately, its underlying physical basis has not been well established, leading critics to label it *ad hoc* and its successes little more than "curve fitting." Its elegant simplicity and adaptability, however, cannot be denied.

The entropic index (nonextensivity parameter) q is taken to be a measure of the fractal nature of a system's path in phase space. Whereas under Boltzmann-Gibbs formalism, a system on average spends equal time in all accessible, equal-sized volumes of phase space (equal *a priori* probability), under the Tsallis formalism the phase space path is fractal, thereby allowing it to model chaotic, nonequilibrium systems, and display rapid and radical changes in behavior and phase.

(11-21) Other Entropies There are a number of other entropy and entropy-like quantities that are beyond the scope of this discussion. These include (with ρ the density matrix, unless otherwise noted):

Daróczy entropy [62]:

$$S_D = \frac{1}{2^{1-\alpha} - 1}(Tr(\rho^\alpha) - 1), \tag{1.28}$$

with $\alpha > 0$ and $\alpha \neq 1$.

Rényi entropy [63]:

$$S_R = \frac{k}{1-\alpha}\ln[Tr(\rho^\alpha)], \tag{1.29}$$

again with $\alpha > 0$ and $\alpha \neq 1$.

---

[13] Extensivity is a traditional requirement for thermodynamic quantities like energy and entropy.

[14] Notice that if $q \rightarrow 1$, then $S_{Ts} \rightarrow S_{BG}$.

Hartley entropy [64]:

$$S_H = k \ln[N(\rho)], \tag{1.30}$$

where $N(\rho)$ is the number of positive eigenvalues of ρ.

Infinite norm entropy:

$$S_{In} = -k \ln \|\rho\|_\infty, \tag{1.31}$$

where $\|\rho\|_\infty = p_{max}$ is the largest eigenvalue of ρ.

Relative entropy (classical mechanics) [65, 66]:

$$S_{Rel,c} = -\int \rho(\ln \rho - \ln \sigma) d\tau, \tag{1.32}$$

where ρ and σ are probability distributions and τ is the phase space coordinate.

Relative entropy (quantum mechanics):

$$S_{Rel,q}(\sigma|\rho) = Tr[\rho(\ln \rho - \ln \sigma)], \tag{1.33}$$

where ρ and σ are distinct density matrices. It is non-negative [67].

In addition to these, there is Segal entropy [68], which subsumes many of the quantum mechanical entropies mentioned above; Kolmogorov-Sinai (KS) entropy, which describes dynamical systems undergoing discrete time evolution; Kouchnirenko A entropies, close relatives to KS entropy; skew entropy [69]; Ingarden-Urbanik entropy [70]; Macdonald entropy [18]. For completeness, you may add your own personal favorite here: .

1.4 Nonequilibrium Entropy

There is no completely satisfactory definition of entropy. To some degree, every definition is predicated on physical ignorance of the system it describes and, therefore, must rely on powerful *ad hoc* assumptions to close the explanatory gap. These limit their scopes of validity. Let us review a few examples. The Boltzmann-Gibbs entropy assumes equal *a priori* probability either of phase space or ensemble space. While this is a reasonable assumption for simple equilibrium systems like the ideal gas and Lorentz gas, it is known to fail for large classes of systems, especially at disequilibrium; the molecular chaos ansatz (Boltzmann's Stosszahlansatz) is similarly suspect. It is not known what the necessary conditions are for ergodicity. The thermodynamic limit, which is presumed or necessary for most quantum and classical thermodynamic formalisms, on its face cannot be completely realistic, particularly since it ignores boundary conditions that are known to be pivotal for many thermodynamic behaviors. Extensivity, also presumed for most entropies, is ostensibly violated by systems that exhibit long-range order and fields — these include systems from nuclei up to the largest scale structures of the universe [38]. Information entropies are hobbled by lack of general definitions of order, disorder

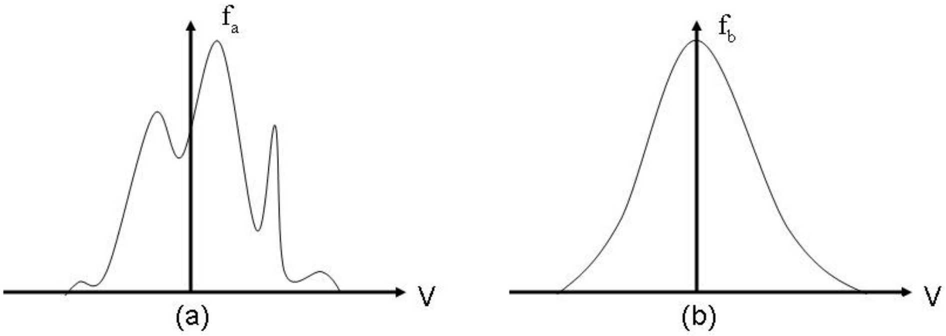

Figure 1.2: One-dimensional velocity distribution functions: (a) non-Maxwellian; (b) Maxwellian.

and complexity. Finally, as it is deduced from thermodynamics, the notion of entropy is critically dependent on the presumed validity of the second law.

Among the many foundational issues thwarting a general definition of physical entropy, none is more urgent than extending entropy into the nonequilbrium regime. After all, changes in the world *are* primarily irreversible nonequilibrium processes, but even the most basic nonequilibrium properties, like transport coefficients, cannot be reliably predicted in general[15].

The prominent classical and quantum entropies strictly apply at equilibrium only. As a simple example, consider the two one-dimensional velocity distributions in Figure 1.2. Distribution f_a is highly nonequilibrium (non-Maxwellian) and does not have a well-defined temperature, while f_b is Maxwellian and does have a well-defined temperature. Let's say we wish to add heat δQ to f_a to transform it into f_b and then calculate the entropy change for this process via $\int_i^f \frac{\delta Q}{T} = \Delta S$. This presents a problem in this formalism because T is not properly defined for f_a or any other other intermediate distribution on its way to the Maxwellian f_b [16].

While small excusions into near nonequilibrium can be made via the Onsager relations [71] or fluctuation-dissipation theorems [43, 72], in general, far nonequilibrium systems are unpredictable. Only recently has theory begun to make significant headway into these regimes. Excursions are limited to idealized systems and carry with them their own questionable baggage, but results are heartening [73]. Notable past and present exponents of nonequilibrium thermodynamics include Onsager, Prigogine, Meixner, Green, Kubo, Ruelle, Hoover, Evans, Cohen, Gallavotti, Lebowitz, Nicolis, Gaspard, Dorfmann, Maes, Jou, Eu and many others [71-89]. Notable recent advances in the microscopic descriptions of nonequilib-

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[15] Some entropies, like S_{GHB} and S_{Ts}, are claimed to apply at nonequilibrium, but they do not have compelling microscopic descriptions.

[16] On the other hand, one might aver that, since $S = -k \int f \ln f dv$, one could calculate $\Delta S = -k \left[\int f_b \ln f_b dv - \int f_a \ln f_a dv\right]$.

rium entropy have proceeded largely through study of nonequilibrium steady states (NESS), especially in fluids (gases) [73]. This formalism is apropos to many of the challenges in this volume.

For NESS, classical phase space volumes ($dx = dqdp$) are often replaced by more general measures, perhaps the best known of which is the Sinai-Ruelle-Bowen (SRB) measure. It is especially useful in describing chaotic systems whose phase space development is hyperbolic; that is, stretching in some dimensions while contracting in others. Phase space stretching gives rise to the hallmark of chaos: sensitivity to initial conditions. The separation rate of initially proximate phase space trajectories is given by Lyapounov exponents λ, one for each dimension. Negative λ indicates convergence of trajectories, while positive λ indicates exponential separation of nearby trajectories — and chaos.

Although a general definition of entropy in NESS is lacking, entropy production can be expressed as

$$\dot{S}(\rho) = \int (-\nabla_x \mathcal{X}) \rho(dx), \tag{1.34}$$

where divergence is with respect to the phase space measure coordinate and the nonequilibrium time development of x is determined via

$$\frac{dx}{dt} = \mathcal{X}(x), \tag{1.35}$$

where $\mathcal{X}(x)$ is a vector field denoting physical forces. Using SRB measures, the second law demands that $\dot{S}(t) \geq 0$; for dissipative systems (those producing heat) $\dot{S}(t) > 0$. This is possible because SRB measures break time reversal symmetry, rendering the system non-Hamiltonian, thus allowing $\nabla_x \mathcal{X} \neq 0$.

Within the chaotic dynamics paradigm, NESS exist at nonequilibrium attractors in phase space. An example of NESS attractors among second law challenges can be inferred from Figure 6.6 in §6.2.4.3, pertaining to a gravitator that circulates at a steady-state angular velocity within a gas-filled cavity, driven by spontaneous pressure gradients. The primary difference between this and standard NESS is that, while traditional NESS are dissipative (turn work into heat), second law challenges are regenerative (turn heat into work), thus admitting $\dot{S}(t) < 0$.

Nonequilibrium, irreversibility and dissipation are the triumvirate that rules the natural thermodynamic world. Second law challenges obey the former two, but not the third. As such, much of the formalism already developed for nonequilibrium thermodynamics should be directly applicable to the challenges in this volume, the chief proviso being sign reversal for heat and entropy production. By turning this considerable theoretical machinery on the challenges, they may be either further supported or resolved in favor of the second law.

It is now commonly held that the second law arises as a consequence of the interaction between a quantum system and its thermal environment [90, 91, 92]. While this might be true, it should be noted that system-bath interactions can also take an active role in *violations* of specific formulations of this law in specific situations, as will be shown in Chapter 3.

1.5 Entropy and the Second Law: Discussion

Entropy and the second law are commonly conflated — for example, the nondecrease of entropy for a closed system is an oft-cited version — but many formulations of the second law do not involve entropy at all; consider, for instance, the Clausius and Kelvin-Planck forms. Entropy is surely handy, but it is not essential to thermodynamics — one could hobble along without it. It is more critical to statistical mechanics, which grapples with underlying dynamics and microstates, but even there its utility must be tempered by its underlying assumptions and limitations, especially when treating chaotic, nonlinear, and nonequilibrium systems (See §2.3.2.).

The majority of second law challenges are phrased in terms of heat and work, rather than in terms of entropy. This is largely because entropy *per se* is difficult to measure experimentally. Heat, temperature, pressure, and work are measured quantities, while entropy is usually inferred. Thus, entropy, the second law, and its challenges are not as intimate as is often assumed. Entropy is a handmaiden of the second law, not its peer.

At the microscopic level an individual molecule doesn't know what entropy is and it couldn't care less about the second law. A classical system of N particles is also oblivious to them insofar as its temporal trajectory in a (6N-1)-dimensional phase space is simply a moving point to which an entropy cannot be ascribed and to which entropy increases are meaningless. (In this context, for ensemble theory, entropy cannot be strictly defined since f is singular.) Entropy is a global property of a system, measurable in terms of the surface area of the constant energy manifold on which the system's phase space point wanders, but this assumes conditions on the motion of the phase space point that, by definition, are either not measured or not measurable and, hence, might not be valid.

In its very conception, entropy presumes ignorance of the microscopic details of the system it attempts to describe. In order to close the explanatory gap, one or more far-reaching assumptions about the microscopic behavior or nature of that system must be made. Many of these provisos — *e.g.*, ergodicity, strong mixing, equal *a priori* probability, extensivity, thermodynamic limit, equilibrium — allow accurate predictions for large and important classes of thermodynamic phenomena; however, *every* formulation of entropy makes assumptions that limit the parameter space in which it is valid, such that *no* known formulation applies to *all* possible thermodynamic regimes[17]. It is doubtful that any formulation of entropy can be completely inclusive since there will probably always be special cases outside the range of validity of any proviso powerful enough to close the explanatory gap. The best one can hope to do is to identify when a particular type of entropy will or will not apply to a particular case — and even the criteria for this hope are not known. Insofar as complex systems — and most realistic thermodynamic systems are complex — can display chaotic and unpredictable behavior (unpredictable to the experimenter and perhaps even to the system itself), it seems unlikely that any single form of entropy will be able to capture all the novelty Nature can produce.

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[17] Systems are known for which one, many, or all the above provisos fail.

Entropy formulations vary across disciplines, from physics to engineering, from chaos theory to economics, from biology to information theory. Even within a single discipline (physics) there are numerous versions between classical and quantum regimes, between utilitarian and formal approaches. Not all are equivalent, or even compatible. Most become problematic at nonequilibrium, but this is where physics becomes the most interesting. Most entropies blend seemlessly into others, making clear distinctions nearly impossible. One could say the subject of entropy is well-mixed and somewhat disordered. This state of affairs is intellectually unsatisfying and epistemologically unacceptable.

It is the opinion of one of the authors (d.p.s.) that, despite its singular importance to thermodynamics and statistical mechanics, entropy will never have a completely satisfactory and general definition, nor will its sovereign status necessarily endure. Rather, like the *calorique*, which was useful but not intellectually persuasive enough to survive the 19^{th} century, entropy could well fade into history[18]. In the end, each thermodynamic system (particularly nonequilibrium ones) should be considered individually and microscopically with respect to its boundary conditions, constraints, and composition to determine its behavior[19]. Considered classically, it is the 6N-dimensional phase space trajectory that truly matters and the various approximations that currently expedite calculations are too simplistic to capture the true richness of dynamic behaviors. Thus, each system should be considered on a case by case basis. If entropy is defined at the microscopic level of detail necessary to make completely accurate predictions about phase space trajectories, however, it loses its utility — and meaning [20].

Entropy remains enigmatic. The more closely one studies it, the less clear it becomes. Like a pointillisme painting whose meaning dissolves into a collection of meaningless points when observed too closely, so too entropy begins to lose meaning when one contemplates it at a microscopic level. Insofar as our definition of entropy is predicated on what is presumed unknown or unknowable about a system, it is epistemologically unsatisfactory and must ultimately be surpassed. As our understanding of the underlying dynamics of complex systems brightens, so must the utility of entropy dim and, perhaps, entirely disappear. Fortunately, the second law can survive without its handmaiden.

1.6 Zeroth and Third Laws of Thermodynamics

The first law is the skeleton of thermodynamics; the second law is its flesh. The first gives structure; the second gives life. By comparison, the zeroth and

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[18] In the near term, however, this will surely not be the case.

[19] A few simple cases, like the ideal gas, will be predictable due to their thermodynamic simplicity, but realistically complex nonequilibrium systems that possess significant thermodynamic depth — like life — will defy tidy description in terms of entropy, or easy prediction in terms of behavior. In the most interesting cases, *chaos rules.*

[20] On the other hand, perhaps if a completely general definition of *order* and *complexity* is discovered, this will lead to a general definition of physical entropy.

third laws are mere hat and slippers. Since one should not go about undressed, let us briefly consider the latter two.

Zeroth Law The zeroth law pertains to the transitivity of equilibrium. It can be stated:

> If system A is in equilibrium with systems B and C, then system B is in equilibrium with system C.

More commonly, it is expressed in terms of temperature, because temperature is the easiest equilibrium property to measure experimentally:

> If the temperature of system A is equal to the temperature of system B, and the temperature of system B is equal to the temperature of system C, then the temperature of system A is equal to the temperature of system C. (If $T_A = T_B$ and $T_B = T_C$, then $T_A = T_C$.)

Or, to put it succinctly:

> Thermometers exist.

The role of this law is far-reaching since it allows one to introduce, within axiomatic thermodynamics, integral intensive characteristics of mutually equilibrium systems, such as temperature, pressure, or chemical potential. It is therefore unsettling that quantum mechanical models exist that predict its violation (§3.6.7).

Third Law[21] The third law of thermodynamics pertains primarily to establishing fiduciary entropies. Like the second and zeroth, it can be stated in various ways. The first, the Nernst-Planck form states:

> **Nernst-Planck** Any change in condensed matter is, in the limit of the zero absolute temperature, performed without change in entropy. (Nernst 1906)

Planck supplemented this in 1912 (in modern form):

> **Planck** The entropy of any pure substance at $T = 0$ is finite, and, therefore, can be taken to be zero.

The third law says that any substance that has a unique stable or metastable state as its temperature is reduced toward absolute zero can be taken to have zero entropy at absolute zero [93]. In fact, at $T = 0$ most substances will have residual *zero point entropies* associated with such things as mixed isotopic composition, randomly oriented nuclear spins, minor chemical impurities, or crystal defects, but if these do not affect the thermodynamic process for which entropy is pertinent, they can be safely ignored since "they just go along for the ride." In some sense, the entropy depends on the knowledge or opinion of the observer. Ideally, if the

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[21] M.O. Scully maintains, "The third law has all the weight of an Italian traffic advisory."

number of microstates that describes this perfect substance at $T = 0$ is $\Omega = 1$, then its entropy via the Boltzmann formula is $S = k \ln[\Omega = 1] = 0$ exactly. This law has far reaching consequences like the zero-temperature vanishing of specific heats, thermal expansion coefficients, latent heats of phase transitions.

The third law can also be stated as impossibilities, for instance:

> It is impossible to reduce the temperature of a system to absolute zero via any finite sequence of steps.

or,

> *Perpetuum mobile* of the third type are impossible.

The first of these can be argued formally [93] and has not been violated experimentally; the current lower limit of experimentally achieved temperatures is about 10^{-9}K. The second of these has been effectively violated by a number of non-dissipative systems, notably superfluids in motion and supercurrents, whose theoretical decay time exceeds 10^5 years.

In summary, the laws of thermodynamics are not as sacrosanct as one might hope. The third law has been violated experimentally (in at least one form); the zeroth law has a warrant out for its arrest; and the first law can't be violated because it's effectively tautological. The second law is intact (for now), but as we will discuss, it is under heavy attack both experimentally and theoretically.

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