

Entropy

Keith Andrew

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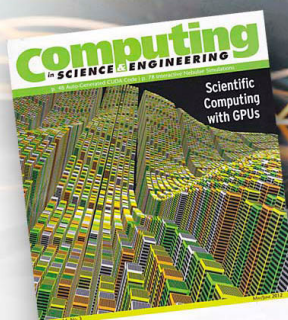
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Entropy

Keith Andrew

Physics Department, University of Arkansas, Fayetteville, Arkansas 72701

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Several different conceptualizations of entropy are examined: thermal, probabilistic, quantum-mechanical, information theoretic, black-hole, and chaotic. The unifying nature of entropy in all physical processes and recent cosmological advances are discussed.

I. INTRODUCTION

Entropy offers a means of perceiving unity in physics. It is a common denominator in the evolution of all physical processes and thus serves as a fundamental unifying feature. Yet as fundamental as entropy is, it does not appear in any of the basic equations of motion. Classically it is treated as a phenomenological property of all systems. Systems evolve in the direction of increasing entropy. This is a dynamic condition subject to the constraint that there exists an initial low-entropy state; this state serves as a boundary condition. Classically entropy is clearly expressed in terms of phase space, partition functions, and probability distributions. Quantum mechanically, entropy is also a clear and well-defined concept. The normal tools of quantum mechanics—Hilbert space, wave functions, observables, and the density matrix—suffice to yield a totally unambiguous concept of entropy.¹⁻⁴

Ultimately one hopes to understand entropy well enough to perceive the unity it provides to diverse areas of physics. An understanding of entropy is founded upon concepts such as probability, reversibility, information content,⁵ black holes,⁶ chaos,⁷ geometry,⁸ and time asymmetry.^{9,10} Some of these concepts strike deeply into basic problems with our present understanding of nature—the meaning of having “knowledge” of a system, a generalized second law of thermodynamics, a possible boundary condition on the cosmological evolution of the universe, the arrow of time, and the CPT theorem. Here we investigate each area in turn to help illuminate the underlying unity provided by entropy.

II. ENTROPY

A. Classical macroscopic entropy

We are concerned with finding an extensive state variable which is capable of telling whether an isolated system, which has undergone a change to a new equilibrium configuration, has done so reversibly or not. This is to be done without any reference to the possible microstates of the system. This quantity provides a means for separating processes that can occur from those that cannot even though they satisfy the first law of thermodynamics. Such a variable is the entropy S , where

$$\int_i^f dS = S_f - S_i \geq 0 \quad (1)$$

for any thermally isolated system, and

$$dS = \frac{\delta Q}{T} \quad (2)$$

for any quasistatic infinitesimal process which absorbs heat δQ . The equality of Eq. (1) only holds for isentropic processes, these being reversible. As such the second law of

thermodynamics states that the entropy of an isolated system never decreases. The power in this law is that it provides a key to understanding the motion of all isolated classical macroscopic systems. It does not, however, describe any mechanism responsible for the creation of the initial low-entropy state.

B. Microscopic entropy: Accessible states

We may directly relate our microscopic knowledge of the system to the entropy of the system by the relation

$$S = k \ln W, \quad (3)$$

where k is Boltzmann's constant and $W = W(E, V, \mathbf{m}, \dots)$, which is the number of quantum states which have the same values on all macroscopic extensive variables: energy, volume, magnetization, etc. Knowing the nature of the particles making up the system and the interactions between them one can in principle calculate W . The difference in entropy after completing a process is

$$\Delta S = S_f - S_i = k \ln \frac{W_f}{W_i}. \quad (4)$$

The condition for reversibility is now $W_f = W_i$. The number of quantum states accessible to the system remains unchanged by the process. From the point of view of accessible states all physical quantities of interest can be expressed in terms of the fundamental quantity $\ln W$. This represents the microcanonical approach; the system is distributed with equal probability over all accessible states of fixed extensive macroscopic variables: energy E and particle number N .

C. Microscopic entropy: Statistics

Instead of treating $\ln W$ as the fundamental quantity we may treat the partition function,

$$Z = \sum_r e^{-E_r/kT}, \quad (5)$$

where k is Boltzmann's constant and E_r is the energy of state r , as such a quantity. Thus all physical quantities may be expressed in terms of $\ln Z$. The entropy of a system is then

$$S = k (\ln Z + \bar{E}/kT), \quad (6)$$

where \bar{E} is the average energy of the system. With the aid of a probability argument one can now show¹¹ that this is equivalent to $S = k \ln W$. Here one says that the system remains in the state of maximum entropy. This represents the canonical approach: the system is distributed over all states with a fixed number of particles but with different energies.

The statistical approach reproduces all the results of

thermodynamics and goes beyond. The theory is adept at dealing with systems for which quantum effects are negligible and the information is less than complete. Such incomplete states are known as mixed, otherwise one has a pure state.¹² In terms of the canonical probability distribution ρ the entropy is

$$S(E, N) = -k \int \rho(x) \ln[\alpha \rho(x)] dx, \quad (7)$$

where $\rho(x) = Z^{-1} e^{-H/kT}$; $H = H(q_1 \dots p_N)$, the Hamiltonian of the system; $\alpha = h^{3N} N_1! \dots N_k!$; $dx = d^3 q_1 \dots d^3 p_N$; x is the phase space point of the system $(q_1 \dots p_N)$; and h^{3N} is the phase-space volume.

The time development of ρ is given by Liouville's equation,

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0, \quad (8)$$

where

$$\{\rho, H\} = \sum_i \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right)$$

is the Poisson bracket.

Thus far several points are worth noting. First, we may use Eq. (7) to express entropy as a function of ρ : $S = S(\rho)$. For the time rate of change of entropy we have

$$\frac{dS}{dt} = \frac{\partial S}{\partial \rho} \frac{d\rho}{dt} = 0 \quad (9)$$

since $d\rho/dt = 0$ by Liouville's equation. Thus one concludes that $S(\rho(t)) = S(\rho(0))$; the entropy of the system is time independent. This result has a corresponding quantum analog to be taken up in Sec. II D.

Next we shall consider the H theorem first proposed by Boltzmann in 1872. Given a well-defined quantity H , which is a function of the system's probability distribution, the H theorem states that the time rate of change of this quantity is such that

$$\frac{dH}{dt} \leq 0, \quad (10)$$

where the condition $dH/dt = 0$ only occurs at equilibrium. Proofs of the theorem for a gas vary but they require some assumptions concerning randomness and lack of correlations between collisions. One immediately observes that the H theorem is the negative of the second law of thermodynamics; as entropy increases H decreases.

Finally we mention the Poincaré recurrence theorem with regards to fluctuations and the statement "entropy never decreases." Poincaré's recurrence theorem states that in an isolated system any state the system has gone through will be revisited to arbitrary closeness an infinite number of times. This seems to be in direct contradiction to the H theorem and the second law statement "entropy never decreases." However, the entropy of the system, even if in equilibrium, is constantly undergoing fluctuations. Some of these fluctuations are such that they reduce the system's entropy to the original low-entropy state in accordance with the theorem of Poincaré. However, the recurrence times for such states of a macroscopic system are of such a large order of magnitude that experimentally they never occur.

It is important to notice that changes in thermodynamic entropy can be measured in the laboratory just as energy change and position change can be measured. The abstract

analogies to be introduced in later sections do not have this property. They merely exploit the mathematical characteristics of the Boltzmann definition in terms of symmetry, convexity, etc. With this in mind we now make the natural extension of this formalism to the quantum regime, enabling one to understand entropy from the more fundamental rules of quantum mechanics.

D. Quantum mechanics and entropy

Recall that in quantum mechanics observables correspond to self-adjoint operators in Hilbert space while states, mixed and pure,¹² can be characterized by a density matrix $\rho = \sum_i c_i |i\rangle \langle i|$. The expectation value of an observable A in state ρ is $\langle A \rangle = \text{Tr}(\rho A)$. Entropy is not an observable, it is a function of a mixed state defined as¹³

$$S(\rho) = -k \text{Tr}(\rho \ln \rho). \quad (11)$$

Notice that for any pure state $S(\rho) = 0$. The time evolution of ρ is given by quantum Liouville equation

$$\frac{d}{dt} \rho - \frac{i}{\hbar} [\rho, H] = 0, \quad (12)$$

where $[\rho, H] = \rho H - H \rho$.

A problem now arises as to the application of the Schrödinger equation and the second law of thermodynamics as expressed in Sec. II A: Entropy must never decrease. The entropy of a system obeying the Schrödinger equation, with a time-independent Hamiltonian, always remains constant. The time evolution of the density matrix is given by

$$\rho(t) = e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar}. \quad (13)$$

Since $e^{iHt/\hbar}$ is a unitary operator, the eigenvalues of $\rho(t)$ are the same as $\rho(0)$; therefore $S(\rho(t)) = S(\rho(0))$, even for irreversible process.¹⁴ One way to avoid this difficulty is to abandon the Schrödinger equation in statistical mechanics and use instead the master equation, Boltzmann equation, etc. These equations are not time invariant and it is a great challenge to show that all time invariant equations follow from them. Another means of reconciling this discrepancy between macroscopic and microscopic concepts is to retain the Schrödinger equation and use an information theoretic approach to calculate the entropy; this is the subject of Sec. II E.

E. Entropy and information

The connection between entropy and information is well known.^{5,15,16} The entropy of a system is a measure of one's lack of information about the internal configuration of the system. To see how this comes about let us review the basics of information theory. Any message can be represented by a sequence of binary digits, which we shall consider to be finite in length. If the length of a "word" is n then one needs n such digits. The set E_n of all words of length n contains 2^n elements, thus the amount of information needed to characterize one element is \log_2 of (the number of elements of E_n) = $\log_2 N = n$ where $N = 2^n$. Let $E = \bigcup E_i$ of all pairwise disjoint sets, N_i = number of elements in each E_i , $p_i = N_i/N$, and $N = \sum N_i$. Thus the information required to determine a word is which E_i it is in and $\log_2 N_i$ bits to characterize the word completely. The average amount of information needed to determine an element, given which

E_i it is in, is

$$\begin{aligned} \sum (N_i/N) \log_2 N_i &= \sum p_i \log_2 N p_i \\ &= \sum p_i \log_2 p_i + \log_2 N. \end{aligned}$$

Where $\log_2 N$ is the information needed if one does not know to which E_i a given element belongs, the corresponding lack of information is

$$I = - \sum p_i \log_2 p_i. \quad (14)$$

This is Shannon's formula.¹⁶ Physically, the set E is a set of N measurements and p_i are the probability of finding the system in the pure state $|i\rangle$. Then, to within a constant, Shannon's formula gives an expression for the entropy of the system. This is a classical expression and great care must be exercised in arriving at a quantum-mechanical expression due to commutation rules.¹⁷

Whenever new information becomes available this imposes constraints on some of the p_i which decreases the entropy,¹⁸

$$\Delta I = - \Delta S. \quad (15)$$

A thermodynamic system not in equilibrium increases its entropy since information about the internal configuration of the system is lost during its time evolution.¹⁹ This is the basic significance of the second law of thermodynamics.

Herein we may use the Schrödinger equation to analyze the time evolution of entropy $S(t)$.^{20,21} Assume the system's macroscopic variables are energy, $\langle \hat{H} \rangle$, and magnetization, $\langle \hat{m} \rangle$. Given $\langle \hat{H} \rangle_{t=0}$ and $\langle \hat{m} \rangle_{t=0}$ one can find $S(t=0)$ by maximizing $-k \text{Tr} \hat{\rho}(0) \ln \hat{\rho}(0)$ subject to the constraints due to $\langle \hat{H} \rangle_0$ and $\langle \hat{m} \rangle_0$. Now use the Schrödinger equation to find $\langle \hat{H} \rangle_t$, and $\langle \hat{m} \rangle_t$, i.e., $\hat{\rho}(t) = e^{-i\hat{H}t} \rho(0) e^{-i\hat{H}t}$. Now maximize $-k \text{Tr}(\hat{\rho}_t \ln \hat{\rho}_t)$ subject to the predicted values of $\langle \hat{H} \rangle_t$ and $\langle \hat{m} \rangle_t$. Notice that this procedure is different from calculating $\hat{\rho}(t)$ from the Liouville equation. Thus the macroscopic entropy at time t is the maximum of

$$S(t) = -k \text{Tr}(\hat{\rho}_t \ln \hat{\rho}_t) = S(\langle \hat{H} \rangle_t, \langle \hat{m} \rangle_t). \quad (16)$$

This entropy is the maximum uncertainty about the microscopic state, given the macroscopic observables $\langle \hat{H} \rangle_t$ and $\langle \hat{m} \rangle_t$ as predicted by the Schrödinger equation. This technique provides the most natural means of overcoming the discrepancy between microscopic and macroscopic conceptualizations. It has the further advantage of direct interpretation as information loss of the microscopic state of the system. Such connections between microscopic and macroscopic domains are powerful guides to understanding nature.

F. Black holes and entropy

Recently entropy and thermodynamics have led to surprising discoveries in understanding gravitation, thereby uniting general relativity to thermodynamics. The detailed studies of black-hole dynamics have led to an interesting law: Changes in a black hole generally take place in the direction of increasing its horizon surface area.^{22,23} The surface area of a black hole is interpreted as a measure of the inaccessibility of information about its internal configuration. This directly yields an expression for black-hole entropy⁶:

$$S = \frac{1}{4} \frac{kc^3}{\hbar G} A, \quad (17)$$

where k is Boltzmann's constant, c is the speed of light, \hbar is the Planck's constant, G is the gravitational constant, and A is the surface area of the horizon. For a system of several black holes the black-hole entropy is additive. Black-hole entropy is not the thermodynamic entropy of the system inside the event horizon. To get a feeling for how irreversible the process of black-hole formation is, notice that the entropy of a one solar mass black hole is 10^{60} ergs/K; in contrast the entropy of the sun is 10^{42} ergs/K.

Another means of understanding the motivation for Eq. (17) is by direct analogy to classical thermodynamics. Two neighboring black-hole equilibrium states are related by the first law of black-hole dynamics:

$$dm = \frac{g}{8\pi G} dA + \frac{\Omega}{c^2} dJ, \quad (18)$$

where g is the surface gravity of the black hole, A is the surface area of the black hole, Ω is the angular velocity of the black hole, J is the angular momentum of the black hole, G is the gravitational constant, and m is the mass of the black hole. Comparing this to the first law of thermodynamics,

$$dU = Tds + pdV, \quad (19)$$

one sees that if some multiple of A is regarded as entropy, then some multiple of g is analogous to temperature. Therefore not only is there an entropy associated with black holes but also a finite temperature.

$$T = \hbar g / kc\pi. \quad (20)$$

One result of black-hole entropy is a generalized second law of thermodynamics: The common entropy in the black-hole exterior plus the black-hole entropy never decrease. Black-hole entropy is regarded as a genuine contribution to the entropy of the universe.

Black holes also represent limits to the applicability of physical laws. Thus Eq. (17) can be used to put restrictions on several "everyday" quantities, i.e., the ideal digital computer cannot perform more than 10^{15} elementary operations per second and there exists an upper bound on the number of quarks.²⁴

G. Dynamical entropy and chaos

It has been shown that very simple dynamical systems with regular data exhibit completely unpredictable behavior.²⁵ As an example, consider $\theta_{n+1} = 2\theta_n \pmod{2\pi}$ on the unit circle. Then $\delta\theta_n = 2^n \delta\theta_0$ for some initial θ_0 . Any small uncertainty in θ_n will eventually fill the entire phase space available to it, the total circumference. Although the equation is completely deterministic after a sufficient number of iterations, all knowledge of the initial datum is lost, as well as predictive power, provided there exists an uncertainty in the initial datum.

We are led to a quantity which indicates a measure of the degree of disorder in the phase-space trajectories traced out by the solutions of the system. Such a quantity is the metric entropy (or Kolmogorov entropy).^{26,27}

Consider iterative mappings of the type

$$x_{n+1} = T(x_n). \quad (21)$$

We wish to know if the solutions exhibit any stationary behavior as $n \rightarrow \infty$. If there exists a sufficiently sensitive

dependence on initial conditions then neighboring solutions diverge exponentially under iteration. Thus the knowledge of the initial conditions is lost at an exponential rate. Neighboring solutions may diverge less than exponentially. Then initial knowledge is still lost, but the metric entropy is zero and the system is not truly random. Where the trajectories diverge as e^{S_n} then the metric entropy is S defined, for one-dimensional maps,⁸ as

$$S = \left\langle \log \left| \frac{d}{dx} T(x) \right| \right\rangle = \int_0^1 \log \left| \frac{dT(x)}{dx} \right| \mu(x) dx, \quad (22)$$

where $\mu(x)dx$ is the relative number of iterates between x and $x + dx$.

Formal chaos will exist for $S > 0$. Such systems are macroscopically deterministic but not predictive. The knowledge of initial conditions is lost after $\approx S^{-1}$ iterations. The system will be predictive only if $S = 0$.

A crucial feature of metric entropy is its stable character. It is a slowly varying function in chaotic dynamical systems and thus a preferred means of stable description. It is the metric entropy for solutions to the Einstein field equations that leads to cosmological implications.

III. DISCUSSION

There is nothing more suggestive in the classical descriptions of entropy than the existence of a connection between entropy and the "arrow of time." Time appears to be asymmetric; one can recall the past but not the future. In the classical description this asymmetry manifests itself as irreversibility, heat does not flow from cold to hot bodies. This asymmetry is revealed in the boundary conditions of the system and not in the dynamical equations describing the evolution of the system.

Turning to the more fundamental rules of quantum mechanics to formulate a microscopic description of entropy is helpful. Using the information theoretic approach entropy increase is understood as the loss of information about the internal configuration of the system during its time evolution. One associates this loss of information with an increased randomness of the system, i.e., irreversibility. Although there does not exist a satisfactory microscopic time asymmetric equation of motion this approach provides a consistent means of bridging the gap between microscopic and macroscopic phenomena. Until recently this would have appeared sufficient. However, a dynamic time asymmetric event has been discovered: the CP violating K^0 decay. By virtue of the *CPT* theorem this implies a *T* invariance violation; a breakdown of microscopic reversibility. Any time asymmetric microscopic equation of motion must be capable of describing the K^0 decay. If such an equation is to be successful one expects the time invariant equations to be derivable from it.

The concept of black-hole entropy adds another insight to understanding reversibility. It is difficult to imagine an event more graphically irreversible than gravitational collapse. Yet Hawking has proposed a mechanism capable of dismantling a black hole: quantum-mechanical evaporation.²⁸ This mechanism describes the black hole as emitting particles until the final naked singularity state violently explodes. As a result, black-hole evaporation provides a means of producing a high entropy per baryon ratio for the universe. Herein lies a problem.

The theory of black-hole evaporation weaves together aspects of general relativity and quantum mechanics; it is

an essential ingredient on the path to a quantum theory of gravitation. However, it is perfectly time symmetric and leads to no distinguishable difference between a black hole and its time reversed counterpart, a white hole. Furthermore, it leads to an estimated value of the entropy per baryon ratio many orders of magnitude above the observed value. In addition, the theory incorporates an observer-dependent space-time geometry as a quantum aspect.

There is a somewhat more radical approach to this problem due to Penrose.^{29,30} One maintains a difference between black and white holes by invoking the Weyl curvature hypothesis as the necessary constraint on singularities. This highly time asymmetric hypothesis states that the Weyl conformal curvature vanishes as the singularity is approached. This leads to a search for new laws of physics which are time asymmetric, the possibility that quantum linear superposition fails when space-time geometry is involved, and a search for a time asymmetric theory of gravity. Both views provide clear evidence of the need for further work in understanding entropy and the second law.

There are other considerations for the description of microscopic phenomena in the presence of a gravitational field. If one follows the general rule that the weaker the interaction the more symmetry conditions it violates, then one may abandon *CPT* invariance. Furthermore, space-time may not be smooth on a microscopic scale. The structure may be more reminiscent of a fractal geometry.^{31,32} These kinds of ideas are difficult to handle and are in need of further investigation. The concept of metric entropy goes much farther than just chaos. It is responsible for introducing the concept of gravitational turbulence, in analogy to hydrodynamic turbulence, as a new avenue of development.⁸ Perhaps more interesting is the idea of gravitational entropy of a cosmological space-time.^{8,29} This manifests itself as a function of the Weyl conformal curvature; thus it is a purely general relativistic effect having no Newtonian analog. As a result, the evolution of the universe is endowed with a significant time asymmetry. Analyzing the features of gravitation and entropy has led Davies to conclude³³:

The origin of *all* thermodynamic irreversibility in the real universe depends ultimately on gravitation. *Any* gravitating universe that can exist and contains more than one type of interacting material *must* be asymmetric in time, both globally in its motion, and locally in its thermodynamics.

The concept of entropy takes one from macroscopic irreversibility through statistical and quantum-mechanical microstates to quantum gravity and time asymmetry. Such pervasiveness speaks for the power and unity of entropy as a means of understanding all physical phenomena.

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¹²A pure state corresponds to a complete description of the system. A mixed state is an incomplete description. Classically, a pure state is given by the phase space point $x = (q_1 \dots q_f, p_1 \dots p_f)$ for all q_j and p_j available to a system of f degrees of freedom. Quantum mechanically a state is described by $\psi(q_1 \dots q_f)$ or by the density matrix ρ . A necessary and sufficient condition for this to be a pure state is $\rho = \rho^2$. The uncertainty in a mixed quantum state is not the quantum uncertainty of the state.
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Stirling's cycle and the second law of thermodynamics

Raul A. Simon

Universidad de Magallanes, Casilla 113-D, Punta Arenas, Chile

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In order to prove the general validity of the second law of thermodynamics, several instances of the Stirling cycle are studied, especially in relation to their efficiency.

I. INTRODUCTION

Some time ago, the Sociedad Científica de Chile sponsored a series of conferences at the Biblioteca Nacional in Santiago, with the engineer, Froimovich, about the second law of thermodynamics. At the first of these lectures, the author of the present paper was given the mission of defending the truth of the second law against the unorthodox views of Froimovich. The whole occurrence was rather unsuccessful because, while the debate took place, a very noisy jazz concert was going on across the hallway. Apparently, no one thought that the two events might interfere!

The argument presented by the author at the time will be repeated here, with some improvements, in Sec. II. In Sec. III we perform a similar calculation for a more general type of gas, i.e., one obeying a virial-type equation of state. In Sec. IV we study a Stirling cycle in the vicinity of a change of phase (e.g., between liquid and vapor). In Sec. V, we study the same kind of cycle for a magnetic substance. Finally, in Sec. VI, some comments of a general nature are advanced.

II. THE STIRLING CYCLE

The Stirling cycle—nowadays rather forgotten—is depicted in Fig. 1. It is composed of two isothermals, ab and cd , and two isochores, bc and da . In Ref. 1 Froimovich considers such a cycle. Starting from the correct formula

$$\eta = 1 - p_a/p_d, \quad (1)$$

he states that if p_a be kept fixed and p_d lowered by using a substance with a different "expansion coefficient," then the efficiency of the cycle can be brought infinitesimally close to unity.

Before deriving Eq. (1), and seeing that $\eta \leq 1 - (T_1/T_2)$, we must point out that the expansion coefficient mentioned by Froimovich is irrelevant in this context; what he probably means is $(\partial p/\partial T)_v$.

The substance considered by Froimovich as undergoing a Stirling cycle is a so-called "harmonic gas," i.e., one that satisfies the following conditions:

(i) Its internal energy depends only on temperature:

$$u = u(T). \quad (2)$$