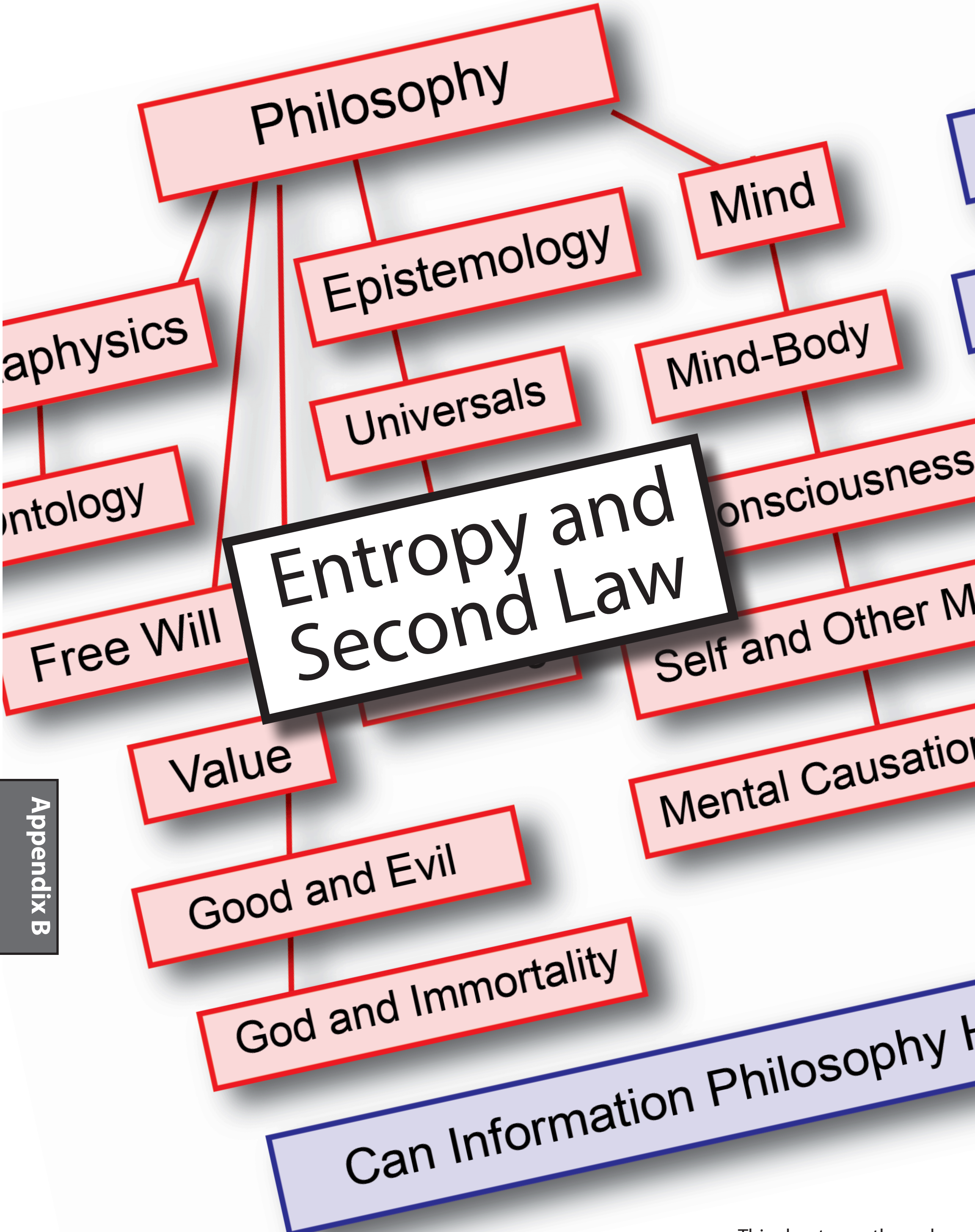
Entropy and Second Law



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Entropy and the Second Law

Every scientist who made a major contribution to the probabilistic nature of the world had some doubts as to whether the use of probability implies that chance is real. Is the appearance of randomness just a consequence of the limits on human knowledge and merely epistemological? Or is randomness a fundamental part of the external world and thus ontological? Quantum physics says chance is ontological and the laws of physics are statistical.

In 1860, James Clerk Maxwell was the first physicist to use statistics and probability. He discovered the distribution of velocities of atoms or molecules in a gas. Although there was no real evidence for the existence of atoms until Albert Einstein's work on Brownian motion in 1905, Maxwell and Ludwig Boltzmann showed that the macroscopic laws of thermodynamics could be explained if gases consist of microscopic atoms in motion. They used the *calculus of probabilities* to reduce thermodynamics to statistical mechanics.

This is despite the fact that they knew next to nothing about the details of processes at the atomic level.

Paradoxically, ignorance of microscopic details is overcome by the power of averages over large numbers of cases. The average value of any property gets more and more accurate as the number of independent events gets large. The number of gas particles in a cubic centimeter of air is truly astronomical, close to the number of stars in the observable universe. For this reason, thermodynamic gas laws like $PV = NkT$ derived from statistical mechanics are highly accurate, well beyond experimental error. This accuracy suggests the laws are deterministic. But they are only adequately or *statistically* deterministic. Determinism is an illusion.[1]

Discrete Particles

To refine a famous comment by Richard Feynman, if there is just one fact that could survive the destruction of knowledge, so as to give future scientists the fastest recovery of physics, it would be

1 See chapter 19.

that the contents of the universe are made up of discrete particles, not fields. This is now the standard model of particle physics. It grew out of the study of ordinary gases.

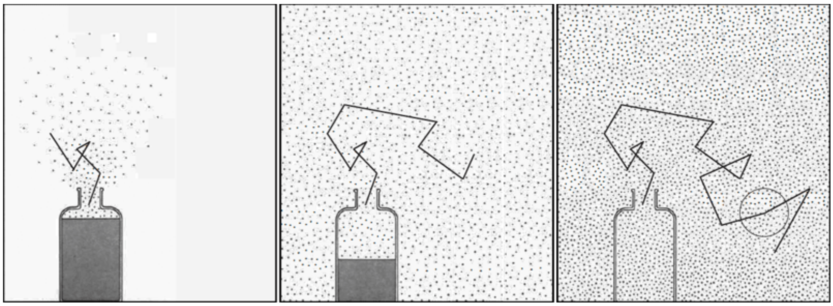


Figure 30-5. The perfume molecules dissipate until they are uniformly distributed. Classical statistical physics mistakenly claims that if the velocities of all the particles were reversed at an instant, the molecules would return to the bottle. It assumes that the complete path information needed to return to the bottle is preserved. But information is not conserved. It can be created and it can be destroyed. We shall show why such microscopic reversibility is extremely unlikely.

Gas particles are distributed in ordinary coordinate space *(x, y, z)* and in a conjugate momentum ($p = mv$, mass times velocity) space (p_x, p_y, p_z).

These two spaces are combined to form a six-dimensional space called a "phase space," one element of which is $\Delta x\ \Delta y\ \Delta z\ \Delta p_x\ \Delta p_y\ \Delta p_z$. At equilibrium, when average density is the same everywhere, particles are found distributed in proportion to the volume of those spaces. But phase space elements are weighted by an exponential factor that reduces the probability of particles being found in higher energy spaces. The factor is

$e^{-p2/2mkT} = e^{-E/kT,}$ today known as the "Boltzmann factor," though it was first found by Maxwell.

E is the particle energy, *p* is the particle momentum, *T* is the absolute temperature (in degrees Kelvin), *e* is the base of natural logarithms, and *k* is Boltzmann's constant (so named by MAX PLANCK). As *E* increases, the probability of finding particles with that energy decreases exponentially. But as the temperature *T* rises, the probability of finding particles with any given energy *E* increases.

Appendix B

With the hindsight of quantum physics, we can envision the distribution of particles as the integer number ("occupation number") of particles in the smallest possible volumes of this 6-dimensional "phase space" allowed by quantum mechanics. These have the dimensions of h^3, where h is Planck's constant. h has the dimensions of action (momentum times position). It's called the "quantum of action."

This minimum phase space volume of h^3 can be understood as the result of Heisenberg's uncertainty principle for each dimension, $\Delta p\ \Delta x = h$. It is as if space itself is divided into these small "cells." But space is continuous, like time. Space and time are abstract tools for assigning numbers to particle properties like location and motion. The minimum volume h^3 corresponds to locations and momenta where there is a non-zero probability of finding a discrete particle.

Although classical statistical mechanics did not include these quantum volumes, Boltzmann did divide phase space into discrete "coarse-grained" volumes for calculation purposes. This important new insight of classical statistical mechanics was accepting the radical idea of the ancient Greeks Democritus and Leucippus that matter comes in indivisible discrete discontinuous lumps.

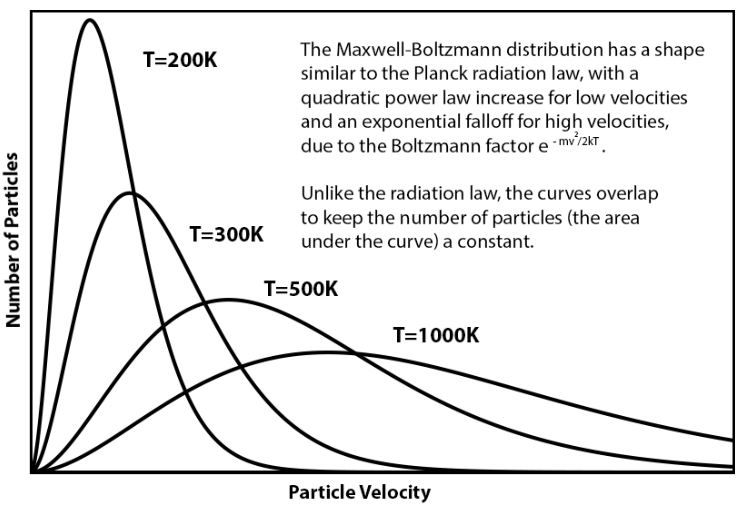


Figure 30-6. The number of particles with a given velocity at different temperatures.

Maxwell not only accepted the idea of atoms and molecules, he deduced their distribution among different velocities,

$N(v) = (2\pi mkT)^{-3/2}\, 4\pi v^2\, e^{-mv^2/2kT}$

When heat is added and the temperature rises, the average velocity gets higher and there are fewer particles with low velocities, since the total number of molecules is a constant. Note that it was Maxwell who first found the exponential decay at higher energies $e^{-mv^2/2kT}$, now called the "Boltzmann factor."

Maxwell did not know about the future Boltzmann's constant k and its relationship to temperature, but he knew that the exponential term is a measure of the average velocity squared, and so of the average energy ($mv^2/2$).

The Maxwell-Boltzmann velocity distribution has two distinct regions which were critically important in MAX PLANCK's attempt to discover the distribution of electromagnetic radiation. For very low energies, the number rises as the square of the velocity. It turns around at a maximum near the average velocity. It then declines slowly like the long exponential tail of the normal distribution of errors because of the Boltzmann factor.

Boltzmann explained that probabilities can give definite results because of the large number of particles in a gas, but that the use of probabilities does not imply any uncertainty. He wrote:

> The mechanical theory of heat assumes that the molecules of a gas are not at rest, but rather are in the liveliest motion. Hence, even though the body does not change its state, its individual molecules are always changing their states of motion, and the various molecules take up many different positions with respect to each other. The fact that we nevertheless observe completely definite laws of behaviour of warm bodies is to be attributed to the circumstance that the most random events, when they occur in the same proportions, give the same average value. For the molecules of the body are indeed so numerous, and their motion is so rapid, that we can perceive nothing more than average values.

Boltzmann refers to the social statistics of Buckle and Quételet

> One might compare the regularity of these average values with the amazing constancy of the average numbers provided by statistics, which are also derived from processes each of which is determined by a completely unpredictable inter-

> action with many other factors. The molecules are likewise just so many individuals having the most varied states of motion, and it is only because the number of them that have, on the average, a particular state of motion is constant, that the properties of the gas remain unchanged. The determination of average values is the task of probability theory. Hence, the problems of the mechanical theory of heat are also problems of probability theory.
>
> It would, however, be erroneous to believe that the mechanical theory of heat is therefore afflicted with some uncertainty because the principles of probability theory are used. One must not confuse an incompletely known law, whose validity is therefore in doubt, with a completely known law of the calculus of probabilities; the latter, like the result of any other calculus, is a necessary consequence of definite premises, and is confirmed, insofar as these are correct, by experiment, provided sufficiently many observations have been made, which is always the case in the mechanical theory of heat because of the enormous number of molecules involved.[2]

In the 1870's, Boltzmann clearly saw probability as completely deterministic.

The Second Law of Thermodynamics

Beyond his ability to visualize the above "liveliest states of motion" for atoms, Boltzmann's greatest work was his attempt to prove the second law of thermodynamics. The second law says that isolated systems always approach thermal equilibrium. Entropy or disorder always increases. Boltzmann showed that if the velocities of gas molecules were initially not in the Maxwell distribution above, they would always approach that distribution, and do it rapidly at standard temperatures and pressures (as we all know from experience).

Boltzmann then developed a mathematical expression for entropy (he called it *H*), the quantity in classical thermodynamics that is a maximum for systems in thermal equilibrium.

At first Boltzmann tried to do this with the dynamical theories of classical mechanics. The particles in his system would move around in phase space according to deterministic Newtonian laws. They collide with one another as hard spheres (elastic collisions). He included only two-particle collisions, assuming three-particle collisions are rare. As it turns out, three-particle collisions are essential for proving Boltzmann's insights, but calculations are difficult.

2 "Further Studies on the Thermal Equilibrium of Gas Molecules," Vienna Academy of Sciences, 1872

But Boltzmann's mentor, Josef Loschmidt, criticized the results. Any dynamical system, he said, would move in reverse if all the particles could have their velocities reversed. Apart from the practical impossibility of doing this, Loschmidt had shown that systems could exist for which the entropy should decrease instead of increasing. This is called Loschmidt's Reversibility Objection, or the problem of microscopic reversibility.[3]

Loschmidt's criticism forced Boltzmann to reformulate his proof of the second law with purely statistical considerations based on probability theory.

He looked at all the possible distributions for particles in phase space consistent with a given total energy. Since phase space is continuous, there is an infinity of positions for every particle. So Boltzmann started by limiting possible energy values to discrete amounts ε, 2ε, 3ε, etc. He thought he would eventually let ε go to zero, but his discrete "coarse-graining" gets him much closer to modern quantum physics. He replaced all his integrals by discrete sums (something the "founders of quantum mechanics" in the nineteen-twenties would do).

Boltzmann then found the following expression that when summed over all the possible discrete energy states has the desired property of irreversible statistical increase,

$\Sigma f(E) \log f(E)$, where $f(E)$ is the fraction of states with energy E.

In 1948, Claude Shannon found a similar expression to describe the amount of information, $\Sigma_i p_i \log p_i$, thus connecting his communication of information to Boltzmann's entropy

Today scientists identity Boltzmann's expression with the thermodynamic entropy S, defined as the change of heat Q added to a system, divided by the temperature T,

$dS = dQ/T.$

3 See chapter 25 on irreversibility.

In terms of a sum over possible states, S is now written as the logarithm of the total number of possible states W multiplied by Boltzmann's constant,

$$S = k \log W.$$

Boltzmann was discouraged to find that a group of scientists, who still hoped to deny the existence of atoms, continued to criticize his "*H*-Theorem." They included Henri Poincaré, an expert on the three-body problem, Max Planck, who himself hoped to prove the second law is not statistical but *absolute*, and a young student of Planck's named Ernst Zermelo who was an extraordinary mathematician, later the founder of axiomatic set theory.

Poincaré's work on the three-body problem suggested that, given enough time, a bounded world, governed only by the laws of mechanics, will always pass through a state very close to its initial state. Zermelo accepted Boltzmann's claim that a system will most likely be found in a macrostate with the largest number of microstates, but he argued that given enough time it would return to a less probable state. Boltzmann's *H*-Theorem of perpetual increase of entropy would therefore be incorrect sometime in the long run.

Information physics has shown that, when quantum physics and the interaction of electromagnetic radiation with matter are taken into account, Loschmidt's reversibility objection and Zermelo's recurrence objection fail to prevent entropy from increasing indefinitely in our open universe.[4]

Unfortunately for Boltzmann, he died just before the significance of radiation and the quantum were appreciated, and just as Einstein proved the existence of his atoms. And ironically, it was Max Planck, Zermelo's mentor and one of those strongly opposing both Boltzmann's ideas of atoms and his use of statistics, who was to correctly guess the distribution law for electromagnetic radiation.

Adding to the injustice, to develop his radiation law, Planck used Boltzmann's own statistical ideas, his assumption about discrete

4 See chapter 25 on irreversibility and 26 on the recurrence problem.

energies, coarse graining, and his ideas about entropy. The radiation distribution has almost exactly the same shape as the Maxwell-Boltzmann distribution for particle velocities. You can see the initial rise as the square of the radiation frequency *ν*, and after the maximum the decline according to the Boltzmann factor $e^{-h\nu / kT}$, where the energy $E = h\nu$ is Planck's new constant *h* times the radiation frequency. The reason for the similarity is profound, electromagnetic radiation - light is also made of particles, as Einstein brilliantly hypothesized in 1905.

$$B(\nu) = 8\pi h\nu^3 / c^3 \, (e^{h\nu/kT} - 1)^{-1}$$

Figure 30-5 shows the number of photons with a given frequency at different temperatures. When heat is added and the temperature rises, the average energy gets higher at all frequencies. The frequency at which energy is a maximum moves to higher frequencies. Unlike the Maxwell-Boltzmann distribution above (Figure 30-4), where the total number of molecules is a constant, additional heat shows up as more photons at all frequencies. The number of photons is not conserved. So the area under the radiation curve grows with temperature, where the area under the particles curve is a constant.

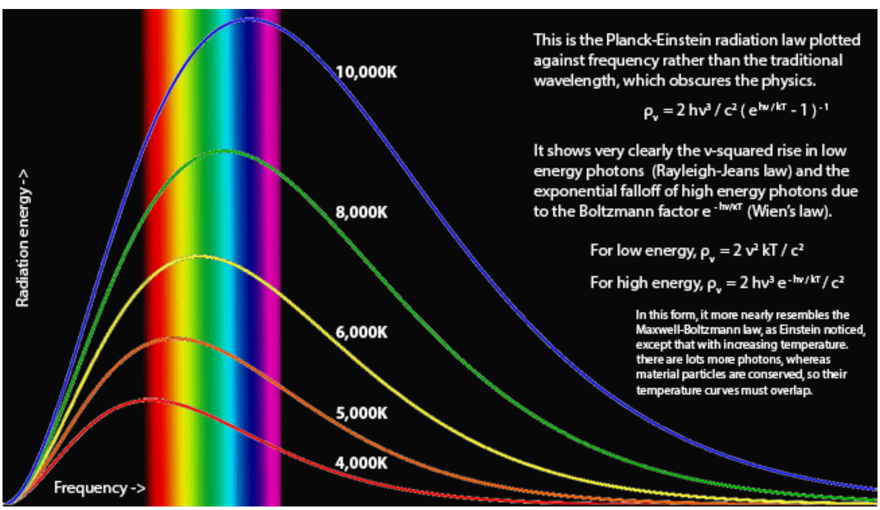


Figure 30-7. Planck's radiation distribution law is often presented as a function of wavelength rather than frequency, but this masks the similarity with the Maxwell-Boltzmann distribution of particles.

Compounding the irony and injustice for Boltzmann still further, Planck, who was long the opponent of discrete particles and statistical mechanics, used Boltzmann's assumption that energies come in discrete amounts, ε, 2ε, 3ε, etc. Planck called them *quanta* of energy $h\nu$, $2h\nu$, $3h\nu$, proportional to frequency ν, where h is a new constant, now named for Planck. He thereby named and launched the twentieth-century development of quantum mechanics, without really understanding the full implications of quantizing the energy. Planck thought quantization was just a mathematical trick to get the right formula for the blackbody radiation law.

Albert Einstein said that "the formal similarity between the curve of the chromatic distribution of thermal radiation and the Maxwellian distribution law of velocities for gas particles is so striking that it could not have been hidden for long." But for over twenty years few others than Einstein saw so clearly the implication that light itself is a localizable quantized discrete particle just as any particle of matter! Planck refused to believe this for many years.

So did Niels Bohr, despite his famous 1913 work that quantized the energy levels for electrons in his Bohr model of the atom.

Bohr postulated two things, 1) that the energy levels in the atom are discrete and 2) that when an electron jumps between levels it emits or absorbs energy $E = h\nu$, where the radiated energy E is the difference between the two energy levels in the atom, $E = E_n - E_m$.

After independently developing the theory of statistical mechanics in 1902-1904, extending it well beyond Boltzmann, Einstein hypothesized in 1905 that light comes in bundles of localized energy that he called light quanta (now known as photons). Although it is hard to believe, Bohr denied the existence of discrete photons well into the nineteen-twenties, although today's textbooks teach that quantum jumps in the Bohr atom emit or absorb photons (a grave this case an injustice to Einstein. Bohr insisted until the middle 1920's that the radiation in his discrete quantum jumps is a *continuous* wave. He was most reluctant to accept Einstein's work, to depart from Maxwell's classical laws of electromagnetism.

Einstein had told friends that his hypothesis of light quanta was more revolutionary than his theory of special relativity published the same year. It was Einstein, not Planck or Bohr or Heisenberg, who should be recognized as the *father of quantum theory*. He first saw mysterious aspects of quantum physics like wave-particle duality, nonlocality, entanglement, and the ontological nature of chance, perhaps more deeply than any other physicist has ever seen them.

Einstein famously abhorred chance ("God does not play dice"), but he did not hesitate to tell other physicists that chance seems to be an unavoidable part of quantum theory.

Entropy Flows in the Universe

Creation of information structures means that in parts of the universe the local entropy is actually going down. Creation of a low entropy system is always accompanied by transfer of positive entropy away from the local structures to distant parts of the universe, into the night sky for example.

My Harvard colleague Eric Chaisson studied energy rather than entropy. He saw energy consumption or production per gram a better measure of complexity in cosmic evolution. He wrote,

> When examined on a system-by-system basis, information content can be a slippery concept full of dubious semantics, ambivalent connotations, and subjective interpretations. Especially tricky and controversial is meaningful information, the value of information...The conceptual idea of information has been useful, qualitatively and heuristically, as an aid to appreciate the growth of order and structure in the Universe, but this term is too vague and subjective to use in quantifying a specific, empirical metric describing a whole range of real-world systems. [5]

But information philosophy sees matter and energy as conserved quantities that need information concepts to explain how they do what they do. As the universe expands, both positive and negative entropy are generated.[6] The normal thermodynamic entropy is known as the Boltzmann Entropy. The negative entropy, often called the Shannon Entropy, is a measure of the free energy content, energy that is available to do useful work or become information.

5 *Cosmic Evolution: The Rise of Complexity in Nature*, p.132.
6 As shown by our common mentor at Harvard, David Layzer.

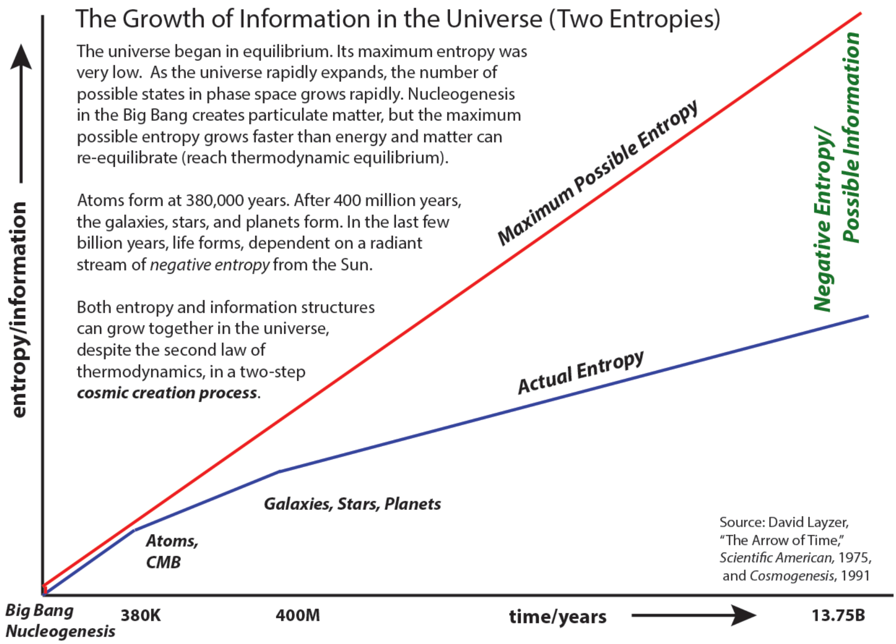


Figure 30-8. David Layzer's growth of information in the universe

"Negative entropy" is simply the difference between the maximum possible entropy (where all the particles in a physical system would be in a maximum state of disorder, there would be no visible structure or available free energy) and the actual entropy.

For matter in thermodynamic equilibrium, there is only motion of the microscopic constituent particles ("the motion we call heat"). The existence of macroscopic structures, such as the stars and planets, and their motions, is a departure from thermodynamic equilibrium. And that departure we call the "negative entropy."

The second law of thermodynamics says that the entropy (or disorder) of a *closed* physical system increases until it reaches a maximum, the state of thermodynamic equilibrium. It requires that the entropy of the universe is now and has always been increasing. This established fact of increasing entropy led many scientists and philosophers to assume that the universe we have is "running down" to a "heat death." They think that means the universe began in a very high state of information, since the second law requires that any organization or order is susceptible to decay. The information that remains today, in their view, has always been here.

But Harvard cosmologist DAVID LAYZER showed that the universe is not a closed system (see Figure 30-4). It is in a dynamic state of expansion that is moving away from thermodynamic equilibrium faster than entropic processes can keep up. The maximum possible entropy is increasing much faster than the actual increase in entropy. The difference between the maximum possible entropy and the actual entropy is potential information.

Positive and Negative Flows

There are two information/entropy flows. In any process, the positive entropy increase is always at least equal to, and generally orders of magnitude larger than, the negative entropy in any created information structures, to satisfy the second law of thermodynamics.

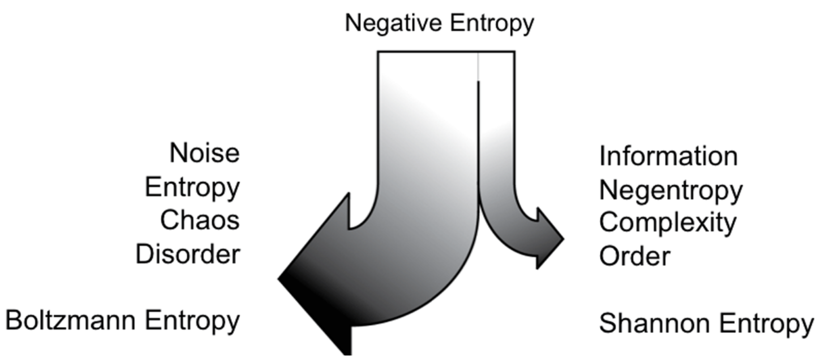


Figure 30-9. Information flows into Boltzmann and Shannon Entropy.

Material particles are the first information structures to form in the universe from the primordial quarks and gluons. They are baryons, the protons and neutrons of atomic nuclei, which combine with electrons to form atoms and eventually molecules, when the temperature is low enough. After hundreds of millions of years, these particles are attracted by the force of gravitation to form the gigantic information structures of the galaxies, stars, and planets.

The stars are a special and very important case. The weak but universal force of gravitation pulls vast quantities of atomic material to collapse, heating it up again. Extraordinary pressures and temperatures in stellar interiors initiate themonuclear reactions that convert matter to a supply of energy that is stable for billions of years, a necessary condition for the emergence of life.

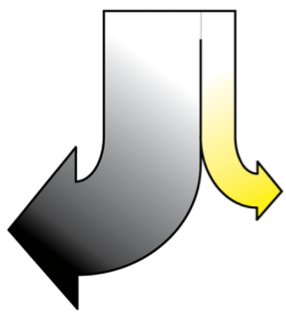


Figure 30-10. Cosmological information flows.

Microscopic quantum mechanical particles and huge self-gravitating systems are stable and have extremely long lifetimes, thanks in large part to quantum stability.

Stars are a second source of radiation, after the original Big Bang cosmic source, which today has cooled down to 3 degrees Kelvin (3K) and shines as the cosmic microwave background radiation.

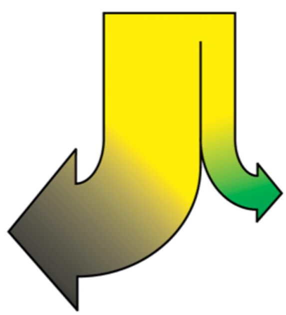
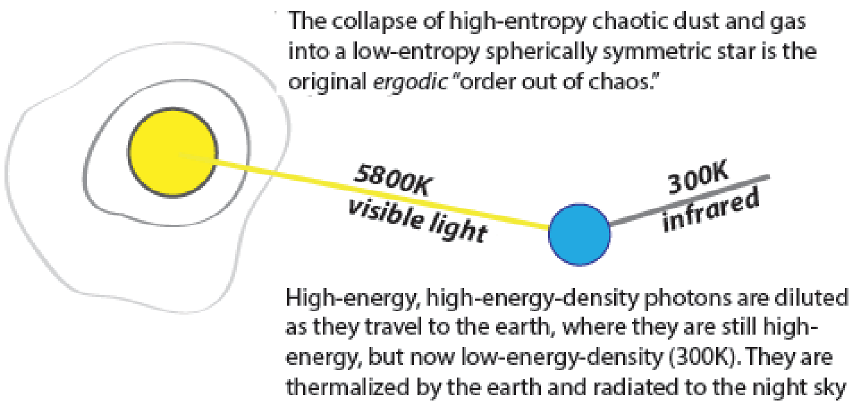


Figure 30-11. Sun to Earth information flow.

Our solar radiation has a high color temperature (5000K) and a low energy-content temperature (273K). It is out of equilibrium and it is the source of free energy - the information-generating negative entropy that drives biological evolution on the Earth. Note that the fraction of the light falling on Earth is less than a billionth of that which passes by and is lost in space.



Just a tiny fraction of the solar energy falling on the earth gets converted into the information structures of plants and animals. Most solar energy is radiated away as waste energy to the night sky.

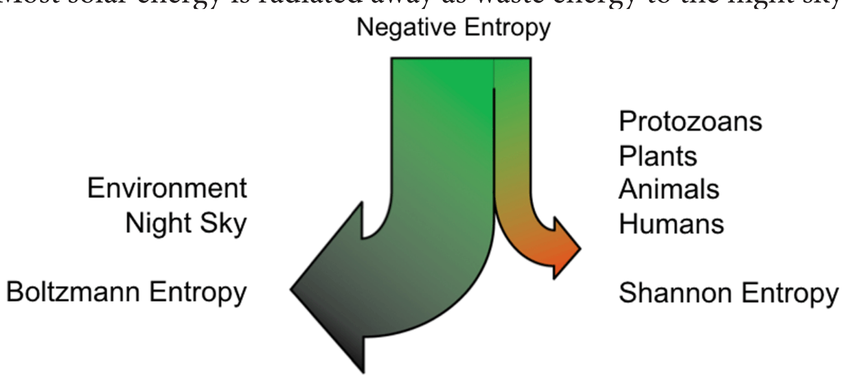


Figure 30-12. Information flows into life.

Every biological structure is a quantum mechanical structure. DNA has maintained its stable information structure over billions of years in the constant presence of chaos and noise.

The extraordinarily stable information content of a human being, from the DNA in every cell to the memories in the *Experience Recorder and Reproducer*,[7] survives many changes in the material content of the body during a person's lifetime. The body is an information structure through which matter and energy flow. Only with death does the mental information (spirit, soul) dissipate totally - unless it is saved somewhere external to the body. [8]

7 See appendix E for the ERR
8 See chapter 2 for identity over time.

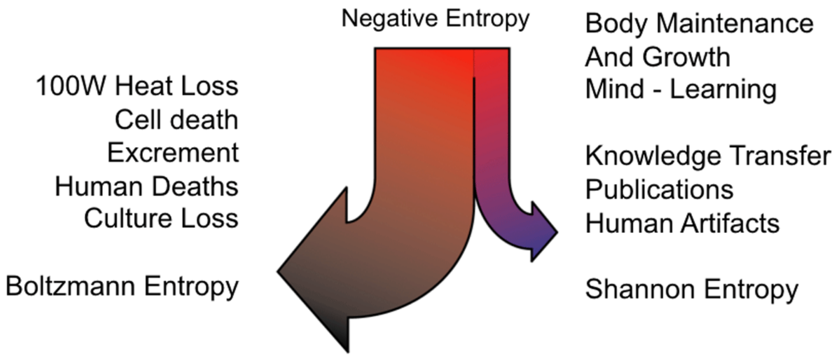


Figure 30-13. Information flows in a human being.

The total mental information in a living human is orders of magnitude less than the information content and information processing rate of the body. But the information structures created by humans outside the body, in the form of external knowledge like this book, and the enormous collection of human artifacts, rival the total biological information content of one individual human.

Information increases and we are co-creators of the universe. Creation of information structures means that today there is more information in the universe than at any earlier time. This fact of increasing information fits well with an undetermined universe that is still creating itself. In this universe, stars are still forming, biological systems are creating new species, and intelligent human beings are co-creators of the world.

All this creation is the result of the two-step core process that creates all information.[9] It is a combination of two distinct physical processes, one quantum mechanical, the other thermodynamic.

Understanding this core creative process is as close as we may come to understanding the reality behind the popular but primitive idea of an anthropomorphic creator of the universe, a still-present divine providence, the cosmic source of everything good and evil.

Information philosophy hopes to replace beliefs with knowledge. The "miracle of creation" is happening now, in the universe and in you and by you.

9 See appendix F on the cosmic creation process.