VALUE: Economics, Psychology, Life

Appendix Two: **Physical Entropy and the Second Law of Thermodynamics**[1]

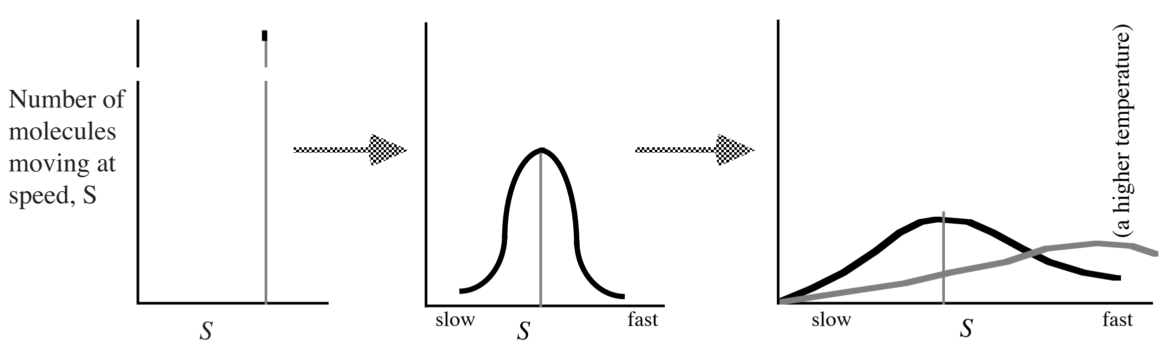
First enunciated by Rudolf Clausius in 1848 in connection with heat engines, and given a statistical-mechanical description by Ludwig Boltzmann in the 1870s, the Second Law of Thermodynamics states that in a completely isolated physical system, *entropy* cannot diminish over time; it can only stay constant or—far more likely—increase.

What is "entropy?" The following, idealized experiment brings us closer to an understanding of this much-referred-to but little-understood concept.

Imagine a completely closed vessel filled with an *ideal gas*. An "ideal" gas consists of a vast number of identical mono-atomic molecules flying about freely, bouncing off each other and off the walls of vessel like tiny, perfectly elastic billiard balls—without energy-loss to internal friction, to intra-atomic vibration, or to change in rotational (angular) momentum. With every collision, kinetic energy is passed along from one molecule to the other, their motion never stops, and the total amount of energy (heat) in the vessel stays constant. Under normal atmospheric pressure and below, many real gases closely approximate ideal ones.

Now imagine that we could instantaneously start all the molecules off *at the same speed* but from random starting positions and headed in random directions. Almost instantaneously many would collide with each other. Before too long, most of the molecules will have collided with many others many times and at many different degrees of obliquity. As with billiard balls, glancing collisions cause the striking molecule and the struck molecule both to emerge from the collision with altered course and speed, with the result that the range and variety of actual molecule speeds and directions soon covers the gamut. The randomness of starting positions and starting directions-of-motion will have "invaded" the realm of speed distribution.

Diagrammatically, what will have happened is this:



STARTING | INTERMEDIATE STATE | FINAL STATE (Maxwell-Boltzmann Distribution)

If we were to start the molecules off not only at the same speed but also in the same *direction* and from (say) a planar grid of starting *positions*, the very slightest perturbation or irregularity (say, in the vessel geometry) would quickly propagate through the entire population of molecules and set them on the path of history shown above, that is, towards a spreading-out in the distribution of speeds, the only global constraints being that the sum of the squares of the speeds of all the molecules, $\sum S_i^2$, would remain a constant and that the starting speed would remain the average value.[2]

The number of molecules moving at a *particular* small speed range, ΔS, divided by the total number of molecules in the vessel gives us the *probability* that a given molecule, spied upon at random, would be found to be travelling at that particular speed. With the gas in the final state called "thermal equilibrium" and characterized, necessarily, by a Maxwell-Boltzmann (M-B) speed distribution curve, we could not know less about the speed of particular molecules. We could say that they were as disorganized—as "disordered"—as they physically can be *for an ideal gas at that temperature*. But note: *maximum possible* statistical *disorder is something different* and higher. It would occur with our ideal gas only at infinitely high temperature. For at infinitely high temperature the M-B curve would be flat and horizontal, meaning that *every* molecule-speed between zero and the speed of light would be equally likely. (In reality however, long before this temperature is reached, the gas will have broken down into an white-hot plasma of subatomic particles, a miniature star—indeed, a black hole—embodying infinite energy. Scientists are uncertain as to how, or even whether, the Second Law holds up under these circumstances.) From a purely information-theoretical point of view, then, any closed physical system at finite temperature and at thermal equilibrium has *some* degree of organization, $R \leq \log N$, where N is the number of possible speed distributions measured with a certain precision—indeed the greater degree of organization, R, as its temperature is lower.[3]

Now, there *is* a chance that at some time in the future all the molecules in the vessel will once again, for an instant, have the same, identical distribution of speeds that they started with, i.e., the *same* speed in our thought experiment. But the probability of this occurring is very, very small. So too is the probability that they will all again occupy any original starting position set or motion-direction set.[4] Indeed, the chances of them all falling into *any* pattern *we* would recognize as "organized" is very small indeed. The overwhelming probability of states of maximum physically-possible disorder-of-parts in closed systems (of given temperatures) is the claim that the Second Law of Thermodynamics is making. "Entropy" is just a measure of this disorder, and, similar to our complexity measure, it takes a maximum value of k ln(W), where W is proportional to the number of combinations of individual molecule-speeds that could give the system its known total energy, k is a constant (the "Boltzman constant"whose numerical value depends on the units used to measure energy and temperature), and "ln" denotes the natural logarithm function.[5]

What is true of gases is also true of liquids and solids, although the time it takes for the isolated system to reach its maximally disordered, most entropic state (for a given temperature) is greater in each case. It is not without significance that living organisms are largely *liquid* and *gelatinous*: these phases of matter inhabit the region between gases and solids, between the very rapid passage to maximum entropy typical in gases and the very slow passage to maximum entropy typical in solids.[6] Biological life establishes itself in this middling state: unlike a cloud, stable enough to persist and hold in its structure; unlike a stone, "gaseous" enough to move and rearrange its parts.

The reader may remember that in Chapter One I was reluctant to rely heavily on the concept of *entropy* and its association with the Second Law of Thermodynamics in order to explain complexity in biological and human-psychological terms. Since Erwin Schrödinger's famous essay *What is Life* ?,[7] so much has been written about entropy in so many literatures, and with such little agreement, that it was a term I thought best circumvented.

Our theoretical machinery, however, has progressed to the point that I would now offer the following definition of entropy and, with it, of the Second Law of Thermodynamics: *Of the many possible sets of trajectories (in the space of complexity and organization as we have defined it) from some level of organization to chaos,* "*increasing entropy in closed systems*" *consists in the set of quarter-circle trajectories shown in Figure 2.5.*

In other words, *entropy*-change is a particular "style" of change in both complexity *and* organization. Specifically: the increasing entropy of closed systems spoken of in the Second Law of Thermodynamics *is the increase of C and the simultaneous decrease of R under the constraint of potential complexity,* C_{pot}*, remaining constant*. (Again, one must specify at what *scale(s)* this is or is not happening).

Of course, many other trajectories, and dozens of different fields of trajectories through the space of complexity and organization are possible—*but not for closed systems* which can neither import nor export energy, matter, or information, by definition. These other trajectories thus would not be describing the Second Law, nor, properly, the concept of entropy which now stands forward not as the general measure of complexity (or disorganization) that it is usually taken to be, but as a *particular* vector field in the space of complexity and organization tied to, and descriptive of, the Second Law of Thermodynamics.

This restricted definition of entropy has not to my knowledge been suggested before. In the literature of physics and physical chemistry, entropy, denoted *S*, is just what we have been calling complexity and applies only to physical systems that are in thermodynamic equilibrium (or that are changing in state so gradually that close-to-equilibrium conditions are maintained). Indeed, in thermodynamic theory the very concept "temperature" is defined only for systems at thermal equilibrium—which is to say, systems that have already reached maximum entropy, or $C = C_{pot} = C_{max}$ for that temperature, pressure, and volume, as we learned earlier.

Finally, let us remember that the maximum entropy that a closed system of finite size can reach spontanseously is finite. It is limited not only by the actual temperature, pressure, and volume of the system, but by the *number* of particles and states (speeds, positions, spin energies, etc.) of which the system is comprised at that temperature; and this depends in turn upon its chemical composition at the outset. For example, *ice* which is highly organized and simple melts at 0^0C to form *water*, which is less organized and more complex. Water boils at 100^0C to form *steam* which is a very complex and disorganized gas, but, at higher temperatures yet, steam breaks down into independent hydrogen and oxygen *atoms* (and there are 3 times as many of these than there were molecules of H_2O). At still-higher temperatures, even these atoms each fly apart into myriad subatomic particles each doing largely "its own thing" at an immense range of velocities.

Does *R* ever go to zero or *C* go to infinity? As close as they come, it seems not. Outside of a black hole, it seems that *R* and *C* are always positive and finite at all scales.[8]

Notes:

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[1] My thanks to Professor Martin Goldstein of Yeshiva University for his valuable comments on this Appendix, and to Professor Francisco Arumi-Noé of the University of Texas at Austin for his help at various times, over many years, in understanding the mathematics of entropy.

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[2] The total energy of the vessel of gas is determined by the sum of squares of the speeds of the molecules, so if the energy remains constant (because the system is isolated or open and energy input equals energy output), this sum must also remain constant. If the sum of squares of the speeds is divided by the number of molecules, and then the square root is taken, the result is called the "root mean square" and it is not very different from the average speed of a molecule. Strictly speaking, the root-mean-square speed is what is preserved in closed systems, not the average.

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[3] One implication of this fact is that the universe—which is the only *really* closed system—is *not* increasing in total entropy, as is widely proffered to be the case. This is because, in expansion, it is cooling, and in cooling all element speeds are not equally probable. The highest possible information-theoretical or statistical entropy for a given, finite, number of particles, can only be a feature of closed systems of infinitely high temperature (and that are therefore of infinite mass, pace Einstein), and the only candidate for this "reality" is/was the Big Bang. Ever since the Big Bang, organization has abounded. True, the universe might be forever getting closer the maximum entropy *it can have* for the temperature it is getting to be as it approaches thermal equilibrium at a less-than-infinite "temperature" (which is a magnitude defined only on a Maxwell-Boltzman speed distribution of elements in a gas). But this entropy is nowhere near the entropy it once had when it was "an infinitely hot and dense dot" (Mark Leyner's phrase)—at least not on the prevailing Big Bang scenario of cosmogenesis which says

the universe *was* once an infinitely hot and dense dot.

But I suspect that all talk of *The Universe*—its temperature, its entropy, its information content, mass, origin, fate, etc., etc.—even by proverbial "top scientists," is deeply flawed at the logical, conceptual level. (I include my own amateur offerings in this area, of course!) Can it make any sense to say that "the universe" is a closed system, that it has a size, or that it had a beginning? Closed off from what? Smaller than what? Before which, what? The very concept "universe" is fraught with presumption. Better science, it seems to me, comes from reducing the scope of one's investigations to the merely immense.

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[4] Indeed, on a closer analysis, an isolated ideal body of gaseous, liquid, or solid matter has not one but three molecular entropies or realms of order-disorder: one with respect to molecular *position*, one with respect to molecular *direction* (of-motion), and one with respect to molecular *speed*. Only the last is typically considered because of its direct implications for energy and its availability for work, which is, of course, the very subject matter of "thermodynamics." The first two, position-entropy and direction-entropy, may or may not follow speed-entropy. Certainly they can both reach statistical maxima at finite temperatures, which speed-entropy cannot.

Moreover, in "non-ideal" closed systems, yet further dimensions for entropy open up: there is the statistical variety of molecular *weights* and also *shapes* (both of which may change with chemical interactions over time); there is molecular spin, intra-molecular motions, intra-atomic energies, and so on and so forth all the way down to quantum level interactions between quarks. Entropy in any one of these dimensions can "leak into" or infiltrate one of more of the others dimensions, making even a closed and isolated system quasi-open internally as Roger Penrose points out.

Many writers mistakenly characterize a system that is at its maximum entropy as being "simple." Lee Smolin for example, in marvelling at the harmony of universal physical constants and productive they have been of our hugely various, non-simple, and life-supporting universe, writes:

> To see this, all we need to do is compare our actual universe to one that is really simple. Imagine, for example, a homogenous gas of neutrons, filling the universe at some constant temperature and density. That would be simple. Compared to that possibility, our universe is extraordinarily complex and varied. (*The Life of the Cosmos* [Oxford University Press, 1997] p. 44.)

On my view, this conclusion is at least terminologically quite wrong. What our universe is is remarkably *organized*. A neutron gas is "simple" only because "temperature" and "pressure" are macroscopic measurements. No individual neutron has a temperature or a pressure. Specifying the quantum state of every single neutron—which is what would be required to characterize the state of the universe at any moment—would involve information in effectively infinite amount. And where would we store *that* inforfmation, even it we could arrange to have it? Highly entropic systems are "simple" only if, and when, and because, we have (perhaps wisely) abandoned explaining them in detail. They are "simple" because we have better things to do than be defeated by their real complexity.

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[5] Note that "temperature" is a measure of energy density that is defined only for bodies presumed to be in thermal equilibrium, i.e. to have the M-B curve of a "final state." Bodies that are not at thermal equilibrium do not have *a* temperature. If they are large enough, they might have several local temperatures within them. These systems, if they are identifiable at all (i.e. persist, have boundaries, display order, etc.), are stable at far-from-(thermal-)equilibrium conditions. All living systems are far-from-equilibrium systems in this sense. The reader of this footnote is no doubt aware of the enormous literature, popular and technical, that has come out of Ilya Prigogine's pioneering work in this area in the last twenty years.

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[6] Again certain constraints enter this statement. Radioactive materials are apt to decay

into other elements, with further entropy increase, before or after maximum entropy is reached in the Maxwell-Boltzman classical sense.

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[7] New York, The Macmillan Company, [1946] 1945.

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[8] There are many technical, and many more anecdotal. expositions of the concept of entropy and of the Second Law in the physical sciences. My chief technical source has been David W. Oxtoby and Norman H. Nachtreib, *Principles of Modern Chemistry* (Chicago, Holt, Rinehart and Winston, 1987).