



The trouble with *microstates*

In which we take the dinghy ashore to look more closely at microstates, probabilities, moving entropy about—and then, back aboard, debrief by setting out the core principles of Nature's entropy law.

Sitting in the dinghy, rowing ashore to our entropy landfall, some of us are reviewing our first impressions of entropy.

“Surely”, one fellow says about our four-molecule gas in a two-chambered container, “there is a lot more than one *microstate* associated with all four molecules being in the left-hand side of the container. Even if they are all to the left, they could be at the top, middle, or bottom of the left—and they could have different energy levels and so on. Each of these conditions must constitute a different *microstate*, many more than the single *microstate* defined simply by saying ‘all molecules are in the left side of the container’”.

An incisive mind (now pulling the starboard oar) goes further to say, “What’s *really* troubling is that these molecules could be anywhere in an infinite continuum of locations, so what do we mean by ‘at the top?’ How close to the top must they be to be in the *topmost* location and not just *near* the top? So if both location—and for that matter energy levels—are continua, then the number of possible *microstates* must be infinite”.

A joker dragging his feet in the water snickers, “A four-molecule gas is nonsense. Even a very dilute gas will contain billions and billions of molecules”.

Excellent critiques. As we clamber up the shore we realize that resolution may lie in understanding a little more about Nature’s ways. It’s something strange, almost spooky, yet paradoxically it makes the idea of *microstates* and *macrostates* easier to accept—and therefore easier to understand.

Most of us have heard of quantum mechanics: the reality that Nature permits only discreet values for energy and location. While this is true for everything, it is usually of practical importance only for phenomena governed by extremely small dimensions or very few particles—like the inner workings of a light meter, a Geiger counter or the laser that reads your CD. In everyday life—like the way your car accelerates away from the stoplight—quantized behaviour is smeared into a continuum. There are so many *microstates* associated with the atomic and sub-atomic particles in your car that we consider the car’s speed to evolve smoothly. Imagine the luck you’d have if, standing before a judge defending yourself against a citation for a rolling stop, you claimed, “But Your Honour, I understand the officer may have *thought* my car didn’t come to a complete stop. However, for some quantum instant, my car might have stopped. And—I believe you’ll agree—I’m innocent until *proven guilty*”.

Quantum mechanics is the name we have given to this deeper way of watching Nature tick. It’s a good name. Still, since we have been paying attention to getting things by their right names, it will help our understanding if we know that this microscopic behaviour might have been called “probability mechanics” or “wave mechanics”. That’s because, at this microscopic level, Nature also decreed that location and energy states can *only* be defined probabilistically. Moreover, there is a strange duality between waves and particles—sometimes things appear as waves, other times as particles. I suspect the name “quantum mechanics” won because it’s less likely to mislead. “Wave mechanics” could be confused with the study of ocean waves—or violin strings. And “probability mechanics” might mean slot machines—or coin flipping. Still, for our purposes the name really doesn’t matter. What matters is knowing that there can only be a *finite* number of location and energy states available to *any* molecule in *any* material.¹

With these quantum ideas in mind, let’s return to our container, but now imagine it filled with a real gas containing a myriad of molecules. There are an extraordinarily large number of location-energy states available to each molecule and each sub-atomic particle. *But the number is still finite.* The number of *microstates* corresponding to the gas jammed into

¹ I’ve said “energy and location” as if they are independent of each other. In truth they are usually coupled. Take something most of us learned in high school: the energy level of electrons that orbit a nucleus depends upon *which* atomic electron shell.

left half of the container is uncountably large *but finite*. And when the same gas is uniformly distributed throughout the container, the number of *microstates* is uncountably larger, *but still finite*.

Indeed, there are an inconceivably large number of *microstates* corresponding to the *macrostate* of anything big enough for us to care about. Still there are differences in the largeness of the inconceivably large. And these differences give entropy differences.

Happily, to calculate entropy we don't need to actually know how many *microstates* exist. All we need to know is the logic, the principles—and (if we're purists) to have taken a good course in quantum statistical thermodynamics² to learn the calculation trickery. Moreover, there are easier ways yet—ways that allow us to calculate entropy from everyday properties like temperature and pressure. For this, all we need is an introductory thermodynamics course.

Fortunately, for our odyssey we need neither.

Now we're ready to use these ideas to link entropy *explicitly* to disorder, structure and probabilities. Ludwig Boltzmann, an Austrian physicist who, in the 19th century, anticipated that material was composed of molecules, used the symbol D for disorder. He then equated D with the number of different molecular *microstates* that would *all* yield the same *macrostate*.

But this brought a problem because D is a humongous number. Fortunately, there's an escape route from enormous numbers. They can be collapsed using the trick of logarithms—although the logarithm of an enormous number is still pretty damn large. So Boltzmann had gone further. He multiplied this large logarithm by a very small number. The number he chose came to be called the Boltzmann constant, $k = 1.38 \times 10^{-23} \text{ J/K}$.³ This allows the equation for entropy, using the historical symbol for entropy, S , to be written as

$$S = k \ln D.^4 \quad (1)$$

The symbol \ln means “*the natural logarithm of*” and so $\ln D$ is the natural logarithm of disorder. Clearly, as disorder, D , increases the entropy, S , also increases.

While tramping about ashore, we realize that there are several other paths to a feel for entropy.

For a start, there is Schrödinger's wonderful little book *What is Life* [1]. A good discussion of the remarkable yet tortuous path that led to the discovery of entropy can be found in *Maxwell's Demon* [2]. To learn more about Boltzmann's life and how it intercepted the lives of Maxwell and Gibbs—two other giant minds simultaneously struggling with the ideas of thermodynamics and whether material was made up of atoms—pick up a copy of *Boltzmann's Atom* [3].

By the way, when Boltzmann came up with Eq. (1) people knew nothing of quantum mechanics—let alone of the sub-atomic particles that are the building blocks of atoms and molecules. So Boltzmann's insights became even more stunning when people learned that we live in a universe of quantitized bits and pieces.

But we should be warned. If you want to dig further into entropy ideas because you find them incomplete or fascinating, be careful. After struggling with the ideas of entropy and the direction-of-time all his life, Boltzmann had essentially got it right when, holidaying at a seaside resort near Trieste with his wife and daughter he hanged himself. That was 1906. Then in 1933, Paul Ehrenfest, carrying on the ideas of Boltzmann, also died by his own hand. So if you find this article difficult, think back to distraught Boltzmann and don't take your difficulties too seriously.

Still, in spite of Boltzmann's sad end, we can still enjoy $S = k \ln D$, the simple, profound mathematical expression which is literally carved in stone—on his Vienna tombstone.

Back in “Entropy” [4], when we realized the entropy law is a probabilistic law, we promised to consider the possibility that a system might, spontaneously, jump from a high entropy state to one of lower entropy. Now is the time.

² Quantum statistical thermodynamics is much easier to understand than you'd guess by the length of its name.

³ As many readers know, 10^{-23} means a decimal point followed by twenty-three zeros until you finally put a “one”. Yup! It's a very small number.

⁴ For more insight, I offer the following. When thinking about how entropy should behave, Boltzmann realized that it should involve both a summation (because energy and entropy should be additive) and a product (because *microstate* probabilities are multiplicative). So, assigning the letter p_i to the probability of the i th *microstate*, he wrote S as a summation (over all *microstates*) of the product $p_i \ln p_i$ such that the expression for entropy came out as, $S = -k \{ p_1 \ln p_1 + p_2 \ln p_2 + p_3 \ln p_3 + \dots \text{ all the way up to } \dots + p_n \ln p_n \}$. Then, because each *microstate* is equally probable ($p_1 = p_2 = p_3 = \dots = p_n$), each $p_i = 1/n$. In turn, this means we can write this otherwise impossibly long equation as simply, $S = -kn \{(1/n) \ln (1/n)\} = -k \ln(1/n) = k \ln(n)$. (The last few steps came from observing that $n(1/n) = 1$, and that the logarithmic rule $-\ln(1/n) = \ln(n)$.) But disorder, D , is *defined* as the number of *microstates*, n . So our expression for entropy collapses to $S = k \ln D$. *Voilà!* A condition (*macrostate*) of perfect structure can result from only a single *microstate*. A single *microstate* means $n=1$. From high school we might recall that the logarithm of unity is zero. So for perfect structure, $S = k \ln(1) = k(0) = 0$. Another *Voilà!*

We already know that small, very quick and very localized fluctuations do occur. But for anything big enough to matter in everyday life,⁵ a significant spontaneous change to lower entropy is so rare that it's almost ridiculous to ponder. How rare? Well, the probability of a significant fluctuation decreases as the number of available *microstates* increase. And the number of available *microstates* increases rapidly as the number of molecules, atoms and the sub-atomic particles that make up the atoms increase. (Remember, for fluctuations we're talking about the *actual number* of microstates, not the *logarithm of the number* that we earlier used to shrink entropy.)

To keep our discussion of fluctuations as simple as possible, let's consider only molecules. Lord Kelvin gave us an everyday feeling for molecular numbers when he said: Suppose you could mark all the molecules in a glass of water and then pour that water in the ocean and (somehow) stir the ocean thoroughly. If you subsequently take a glass of water from anywhere in the world's oceans—surface, bottom, north or south—you'd find about one hundred of the marked molecules in your glass.

So if you are reading this article in your living room, worrying that *all* air molecules in the room might spontaneously jump into the south east corner—leaving you in breathless awe of this home-spun violation of the entropy law—you'll have a long, long wait. We need times longer than millions of universe lifetimes for this kind of fluke. You're in no danger of suffocating.

Let's walk round our entropic landfall to consider two last issues:

- How entropy changes can result from temperature and volume changes.⁶
- How entropy can be moved from place to place.

We'll first consider temperature and volume. Entropy increases as the number of *microstates* increase. So to understand how volume or temperature changes affect entropy, it's just a matter of understanding how these changes affect the number of *microstates*.

The quantum state for any gas particle is defined by specifying *both* the energy and location quantum states. So the number of *microstates* associated with a *macrostate* is the product of energy and location quantum states.

Let's start with the effect of changing the number of “location” quantum states. To do this, we'll use another *gedanken* experiment—this time imagining a gas container with a piston sliding in and out changing the gas volume.⁷ Our piston-cylinder device is much like you'd find in your car's engine—but without valves or sparkplugs. In this first *gedanken* experiment, we'll allow neither heat nor material to move between the gas and the cylinder's surroundings. Figs. 1A and B show our piston-cylinder divided into many small, equal size chunks, each of which we imagine represents a quantum *location*.

As the piston moves out, the gas volume increases the number of *available* location states increases proportionally. If we double the volume we double the quantum locations that can be occupied by any single gas particle—as seen by comparing Fig. 1A with Fig. 1B. Of course the number of *microstates* associated with a *macrostate* is proportional to the *square* of the number of available quantum locations—so by doubling the volume, the number of *microstates* associated with the new *macrostate* really jumps. But again we're saved by logarithms, when multiplication becomes addition. So as the volume increases the entropy increases in direct proportion—providing the number of possible energy states is unchanged.

Next we'll consider how changing total energy affects the number of energy quantum states. In this second *gedanken* experiment, we'll hold volume (and material) constant but allow heat to move between the gas and the cylinder's surroundings. Now imagine a four-molecule gas at a temperature of absolute zero. By definition, absolute zero means *each* molecule is in its *lowest possible* energy level. In turn, this means there is a single energy *microstate* associated with a *macrostate* of absolute zero. But if we add just a teensy bit of energy, just enough to raise any single molecule above its lowest energy level, then the number of energy *microstates* is four—because any one of particles #1, #2, #3 or #4 could be the particle having its energy one notch above the lowest. As we add more energy to the gas, it's easy to see that the number of available energy *microstates* rapidly grows. And so does entropy, but more slowly because, once again, its growth is logarithmic.

⁵ Fluctuations can, however, *trigger* everyday phenomena. Take a pint of your favourite. Microscopic fluctuations, assisted by surface roughness, cause CO₂ bubbles to start from the beer glass surfaces—most easily at the sharp curvature where the sides meet the bottom. The inverse of bubble nucleation is droplet nucleation—like in clouds or contrails, where small ice crystals or fine dust particles help fluctuation get the droplets started.

⁶ I didn't include other properties, like pressure, because *microstates* are set by energy and location only and these are tied to temperature and volume. One way or another, properties like pressure depend on temperature and volume.

⁷ *Gedanken* is the German word for “thought”. In science, the phrase “*gedanken experiment*” refers to the mental construct approach I'm using here.

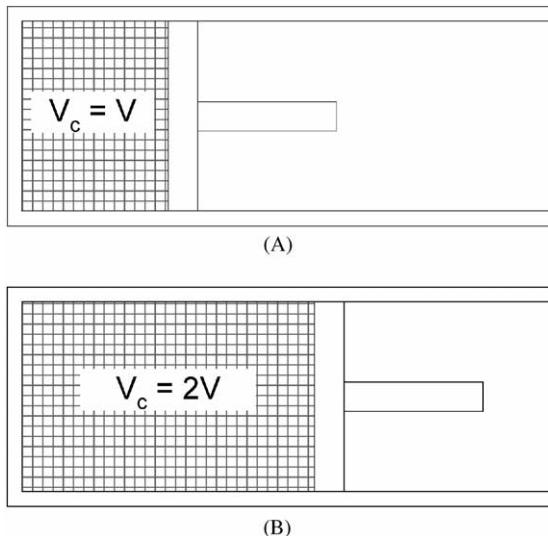


Fig. 1A. A Piston-cylinder of volume V , with space divided into equal size sub-volumes. (B) Same piston-cylinder, but with volume $2V$.

By the way, as the energy increases the temperature normally increases, because it's a manifestation of internal energy.⁸ In many real processes, volume and temperature change simultaneously. A volume increase will increase the location microstate component of entropy. While, a temperature increase, increases the energy-microstate component.⁹

Now let's think about Nature's methods for moving entropy about. From "Conservation, Confusion and Language", [5] we know Nature has three ways to move energy: via heat, work and material. Entropy transport is even simpler. That's because although heat and material carry entropy, work doesn't.

We'll begin with another *gedanken* experiment to illustrate why work doesn't move entropy—this time a lever rotating about a frictionless fulcrum. The work delivered to one end of the lever (force times the distance the lever moves at that end) is perfectly structured energy—and the work delivered to the other end (force times the distance the lever moves at the other end) is also perfectly structured. So while work moved energy from one end of the lever to the other it didn't move entropy. (Energy used to push down one end of the lever was transferred to a block lifted at the other end.)

We're left with material and heat as the only two mechanisms for entropy transport. We'll consider them in order.

(i) Entropy transport by *material*. When we move material we move anything that's inside the material—and entropy is inside it. That's all there is to it. I often use the symbol \mathbf{J} to represent the flow of commodities, with a subscript under the \mathbf{J} to indicate the commodity— \mathbf{J}_x symbolizes the flow of commodity "x".¹⁰ If we assign \mathbf{J}_s to entropy flow, \mathbf{J}_m to material flow and s to specific entropy (entropy stored per unit mass), the equation for entropy carried by material

⁸ The only time temperature doesn't change with an internal energy change is during phase transitions, like from ice to water.

⁹ Thermodynamics professors like to discuss reversible adiabatic processes. Let's consider an expanding "closed system" (material doesn't cross system boundary). "Adiabatic" means that no heat is transferred to or from the gas. "Reversible" means that no entropy is produced within the gas. Because entropy isn't produced and has no way in or out, the entropy is constant—and the process is called "isentropic".

How can this be? Well, it's just that the number of energy microstates and volume microstates evolve in synchrony to keep the total microstates (and therefore the entropy) constant. As the gas expands against, say, a piston, the volume increases causing the total number of location states to increase. However *simultaneously*, the gas loses energy by doing work to push the piston out, causing the gas's energy to decrease and therefore the number of energy microstates to decrease. As the number of volume microstates increase, the number of energy microstates decrease proportionally, so that the total remains constant—and the process is isentropic.

Engineering students can be tortured when trying to understand reversible adiabatic processes. Thinking of the process as simply one-for-one trading between energy and location microstates breaks the conceptual logjam. If it helps you too: wonderful! If it doesn't, don't worry. We already have more than enough to continue our odyssey.

¹⁰ I've used the word "flow". More precisely, I'm speaking of a "flux". Flux is *flow per unit area*, where the "area" is aligned perpendicular to the flow.

is simply

$$\mathbf{J}_s = s \mathbf{J}_m. \quad (2)$$

(ii) Entropy transport by *heat*. Heat is thermal energy moving from one place to another driven by a temperature difference. Moreover, temperature is a manifestation of random thermal motion within the material. So heat is the transport of disordered thermal energy. Therefore, whenever heat flows it carries entropy. It turns out that the amount of entropy transported by heat conduction is proportional to the heat itself divided by the local *absolute* temperature.¹¹ I won't twiddle the few equations to show why—you'll just have to trust me.

Once again, an equation can compress understanding, thereby (at least for some) making the relationship between heat and entropy flow easier to “see”. I'll first deal with conduction heat transfer. If heat flow by conduction is $\mathbf{J}_{q(c)}$ the associated entropy flow $\mathbf{J}_{s(c)}$ is

$$\mathbf{J}_{s(c)} = \mathbf{J}_{q(c)}/T. \quad (3)$$

Eq. (3) works for heat conduction.¹² When we talk about radiative heat transfer, it gets a little trickier. For radiation, the *shape* of Eq. (3) is unchanged, but we need to put a constant in front of the $\mathbf{J}_{q(r)}/T$. Typically, this constant is about 4/3, or slightly greater depending upon the distribution of radiation frequencies. So entropy transport by thermal radiation is simply¹³

$$\mathbf{J}_{s(r)} \cong 4/3 \mathbf{J}_{q(r)}/T. \quad (4)$$

Still for our voyage, it's only important to know that heat carries entropy, and the amount it carries is proportional to the amount of heat divided by the absolute temperature. Therefore, a fixed amount of heat, at say 600 K (327°C , 620°F) will carry half as much entropy as the same heat would carry at 300 K (23°C , 80°F).

Time to pull the dinghy off the beach and return to our vessel.

We're back aboard. We've weighed anchor and our entropy landfall is sinking below the horizon. During our visit we found many of entropy's features and nuances, which required that we became enmeshed in some rather deep arguments, perhaps too many to keep organized in our heads. So we should debrief—call out the essentials.

1. Entropy is *the* thermodynamic property that represents disorder, or lack of structure, or organizational randomness—or, if you like, anarchy.
 2. *All* real processes produce entropy. (This distinguishes the entropy law—a “growth” law—from *all* conservation laws.)
 3. The entropy of the universe is always increasing.
 4. Entropy can be moved from one location to another—carried by heat or material.
 5. Therefore, even when entropy is *produced* in one location, it need not increase in that location. (It can stay constant or even decrease *if* entropy is exported as fast or faster than it's produced.)
 6. If entropy decreases locally, somewhere else in the universe the entropy *must* increase by at least an equivalent amount.
- This debriefing is a visa for new landfalls. The next will be “The Arrow of Time”. [6]

This is the seventeenth in a series of articles by

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¹¹ This means the amount of entropy carried by heat down a thermal gradient *increases* as the heat slides down the gradient, even though the amount of heat remains the same. Consider heat being conducted at a constant rate down a metal rod from a higher to lower temperature. The heat flow, \mathbf{J}_q , is the same all along the rod, but the temperature, T , is dropping. Therefore Eq. (3) tells us the flow of entropy out the cold end must be greater than the flow into the hot end. This may seem strange, until we realize *entropy is being produced throughout the rod*—so more entropy *must* come out the cold end.

¹² In “Conservation, Confusion and Language” we viewed convection as energy carried by a moving fluid. Same thing for entropy. So we've already covered entropy transport by convection when we spoke of energy carried by material.

¹³ If you want to dig deeper into entropy transport by radiation, Adrian Bejan wrote an excellent book *Advanced Engineering Thermodynamics* that clarifies much. Nevertheless, unlike the expressions for conduction entropy transport (which has been well defined for some time) the formulation(s) for radiative entropy transport still have ragged edges.

References

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