

See this video for a Monte Carlo simulation showing how the multiplicity tends to increase.

As we have seen, the multiplicity  $\Omega$  of a material is of considerable interest, because the combined multiplicity of a system plus its surroundings tends to increase. We have also seen that for an Einstein solid the multiplicity tends to grow very rapidly (beyond exponentially) with system size for around  $10^{23}$  atoms (a few grams of any material), the multiplicity would be closer to  $10^{10^{20}}$ , which is a bit much. In addition, to combine the multiplicity of two systems, we have to multiply rather than add.

Instead of working with multiplicity, we far prefer the entropy  $S$

$$S \equiv (\text{constant}) \ln \Omega \quad (1)$$

where the constant is called Boltzmann's constant and in SI units is  $k_B = 1.38 \times 10^{23}$  J/K. (It is also possible to choose units such that temperature is expressed in energy units, and  $k_B = 1$ . I tend to do this in my own research.)

The natural log function ensures  $S$  is not astronomically large, and even more importantly it makes entropy an additive quantity. If we have two subsystems with multiplicity  $\Omega_1$  and  $\Omega_2$ , then the combined system has multiplicity

$$\Omega_{\text{combined}} = \Omega_1 \cdot \Omega_2 \quad (2)$$

$$S_{\text{combined}} = k_B \ln(\Omega_{\text{combined}}) \quad (3)$$

$$= k_B \ln(\Omega_1 \cdot \Omega_2) \quad (4)$$

$$= k_B \ln \Omega_1 + k_B \ln \Omega_2 \quad (5)$$

$$= S_1 + S_2 \quad (6)$$

If you're hazy on the behavior of logarithms, this wouldn't be a bad time to review those properties. Most crucially:

$$\ln(ab) = \ln a + \ln b \quad (7)$$

$$\ln\left(\frac{a}{b}\right) = \ln a - \ln b \quad (8)$$

$$\ln(a^b) = b \ln a \quad (9)$$

## 0.1 Analyzing a real system's entropy

Imagine dropping a hot block of metal into a room-temperature tub of water. How would you answer if I asked you to find  $\Omega_{\text{metal,initial}}$ ,  $\Omega_{\text{metal,final}}$ ,  $\Omega_{\text{water,initial}}$ , and  $\Omega_{\text{water,final}}$ ? You'd be stumped. I'd be stumped, if I tried to compute these multiplicities.

Does this mean that entropy is unhelpful in practice? Absolutely not! Entropy was actually discovered *before* the connection between it and multiplicity, and **changes in entropy are readily measurable!** We can't easily measure the absolute entropy (although it is possible and is actually done), but changes in entropy are often quite straightforward to measure.

The key is the property that

$$\Delta S = \frac{Q}{T} \quad (10)$$

where  $Q$  is the energy entering the object through heating (positive means it gains energy), and  $T$  is the temperature of the object we are considering, provided  $Q$  is small enough that we can neglect changes in temperature.  $T$  must be measured on an absolute scale (e.g. Kelvin).

Why does this equation work? It's related to the definition of temperature.