

Entropy and Temperature of a Thermodynamic System
(Atomic Scale Simulation)

Entropy and Temperature arise from the algebra of "big" numbers. The logarithm of the number of accessible states of the system is the entropy and of great importance to the thermal properties of a system. (This follows Kittel "Thermal Physics")

Consider two systems only in thermal contact. The systems have particle number, N_1 and N_2 , and energy, E_1 and E_2 . When in thermal contact the combined "new system" now has $N=N_1 + N_2$ particles and total energy $E_1 + E_2 = E'_1 + E'_2 = E$.

What is the degeneracy of states that are accessible? The degeneracy function is $g(N,E)$. For the combined system,

$$g(N, E) = \sum_{E_1}^{\leq E} g_1(N_1, E_1)g_2(N_2, E - E_1) \quad (1)$$

Sum is over all possible accessible states E_1 . The product g_1g_2 is the number of accessible state for the combined systems for energy E_1 .

For statistical mechanics, a very important feature of this product is that it must have a maximum for some value $E_1 = \bar{E}$, the most likely energy. It is an extremely sharply peaked. (Consider $g_1(x) = e^{-x^2}$ and $g_2(x) = e^{(8-x)^2}$. The product is basically zero except for a narrow region around $x=4$, and it is 10^{13} smaller than $g_1(0)$ and $g_2(8)$!!)

Consider the extremal properties of this distribution.

$$0 = dg = \left(\frac{\delta g_1}{\delta E_1} \right)_{N_1} g_2 dE_1 + g_1 \left(\frac{\delta g_2}{\delta E_2} \right)_{N_2} dE_2 \quad (2)$$

and we have $dE_1 + dE_2 = 0$. (We shall assume here that this is a maximum, which can be proved.) Then, the *most probable configuration* of the combined system (using $dE_1 = -dE_2$) gives

$$\frac{1}{g_1} \left(\frac{\delta g_1}{\delta E_1} \right)_{N_1} = \frac{1}{g_2} \left(\frac{\delta g_2}{\delta E_2} \right)_{N_2} \quad (3)$$

or

$$\left(\frac{\delta \ln g_1}{\delta E_1} \right)_{N_1} = \left(\frac{\delta \ln g_2}{\delta E_2} \right)_{N_2} \quad (4)$$

Let us define ENTROPY as $S(N, E) = \ln g(N, E)$ and INVERSE TEMPERATURE as $\left(\frac{\delta \ln g}{\delta E} \right)_N = T^{-1}$. We have for the maximal probability and equilibrium configuration the $T_1 = T_2$, the temperatures must be equal.

Note also that equilibrium is reach only when the number of accessible states are a maximum.

Note also that, in this maximal state, $S = \ln g_1g_2 = \ln g_1 + \ln g_2$ and the Entropy is Additive.

Gibbs and Boltzmann Distribution

For Statistical Mechanics or our simulation, we are interested in properties where one of the systems in contact is a very large thermal reservoir, i.e. $N_R \gg N_s$ and $E_R \gg E_s$. Let us even suppose that the systems are now in thermal and diffusive contact, so they exchange energy and particles.

What are the statistical properties of the system? We consider an ensemble consisting of identical copies of the "system + reservoir" having accessible states only.

What is the probability to find the system with N particles and in the state s of energy ϵ_s ? Clearly the probability $P(N_s, \epsilon_s)$ proportional to the number of accessible states of the RESERVOIR. Because when we specify the state of the system, i.e. N and ϵ_s , the number of accessible states can only arise from the reservoir: $g(sys + res) = g(sys)g(res) = g(res)$ as $g(sys) = 1$ (for it was specified). Therefore,

$$P(N_s, \epsilon_s) \propto g(N - N_s, E - E_s) \quad (5)$$

where $g(N, E)$ depends only on the reservoir. Notice that this relation is for the probability of the system, yet it appears to depend on the make up of the reservoir (strange indeed), but only (as we shall see) on the temperature, T , and chemical potential, μ , of the reservoir.

As we do not know the proportionality constant, let us consider the ratio of probabilities of two states:

$$\frac{P(N_1, \epsilon_1)}{P(N_2, \epsilon_2)} = \frac{g(N - N_1, E - E_1)}{g(N - N_2, E - E_2)} \quad (6)$$

Notice that $N - N_i \gg N_i$ and the $g(N, E)$ are extremely large numbers arising from the reservoir. So, to avoid big numbers we can define the Entropy as $S(N, E) = \ln g(N, E)$ and work with the logarithms.

$$\frac{P(N_1, \epsilon_1)}{P(N_2, \epsilon_2)} = e^{S(N - N_1, E - E_1) - S(N - N_2, E - E_2)} \quad (7)$$

Because the reservoir is very large compared to the system, we may expand to first-order (this can be verified as OK) to get ΔS in the exponent using Taylor's Series expansion.

$$\Delta S = -(N_1 - N_2) \left(\frac{\delta S}{\delta N} \right)_E - (E_1 - E_2) \left(\frac{\delta S}{\delta E} \right)_N \quad (8)$$

By defining

$$\frac{1}{T} = \left(\frac{\delta S}{\delta E} \right)_N \quad - \frac{\mu}{T} = \left(\frac{\delta S}{\delta N} \right)_E \quad (9)$$

We immediately get that

$$\frac{P(N_1, \epsilon_1)}{P(N_2, \epsilon_2)} = \frac{e^{-(E_1 - \mu N_1)/T}}{e^{-(E_2 - \mu N_2)/T}} \quad (10)$$

The numerator is the Gibbs' probability distribution for canonical ensemble, whereas for constant N the μN drops out and we have the Boltzmann distribution.

Gibbs and Principle of Maximum Entropy

Gibbs was actually more clever. He introduced the "index of probability" defined as $\ln g_N$ and its ensemble average $S = \int dV_{\Gamma} g_N \ln g_N$. Under the condition that $\langle E \rangle = \int dV_{\Gamma} E g_N$, microcanonical constraint, Gibbs showed that S was a maximum when $g_N = g_N^0 = e^{\beta(F-E)} = e^S$, so that $S = \ln g_N^0$ for equilibrium.

This is, in effect, Gibbs' principle of maximum entropy, a Laplacian-like view of probability (not a frequency or counting-occurrences-type viewpoint). Essentially, given any constraint, such as constant E , and the fact that the probability must sum to one, you can maximize the "entropy" $S = -K \sum_i P_i \ln P_i$ and obtain any of the distribution that we know, such as microcanonical for constant E , etc. The distributions such as Fermi-Dirac and Bose-Einstein occur because of how the states ϵ_i are occupied, like 1 or 0 for Fermions and 1,2,...infinity for Bosons.

More generally, this entropy $S = -K \sum_i P_i \ln P_i$ is called the Shannon Informational Entropy. With this general entropy and utilizing Maximum Entropy Method, you may find the most probable state for anything that has informational entropy: encryption, image analysis, etc. As an example, using the astronomical data provided by a friend, Laplace predict that Jupiter had to have an additional moon (not yet observed) to explain the deviation in the observed data. He even predicted it mass, being only off about 10% from today's value. (Ah, to be as amazing as Laplace!)

"Entropy" again results from the algebra of large numbers and what it means to be the most probable or average, whether it is thermodynamic state or something else. Using this Principle of Maximum Entropy and a few results from Probability Theory regarding correlated variables, most all of Statistical Mechanics can be derived in a few lines. While less straightforward, such an approach can also be used for non-equilibrium Statistical Mechanics (see "Introduction to Statistical Mechanics, vol 1: Equilibrium", Grandy, Jr. 1987)

An outstanding discussion of all these points, as well as Ergodicity, see "The Principle of Statistical Mechanics", R.C. Tolman, 1937.

Most importantly for simulation class is that if we pick the correct distribution function for our problem then we have gone quite far into be able to obtain averages via simulation. It is our concern later to learn how to choose the probability distribution for our ensemble cleverly. See Main notes.

Sept 1998, D.D. Johnson