1 April 4 - FASM

For a closed system, all accessible microscopic states are equally likely. Then, given the multiplicity g of a state s, the probability of thate state is $P(s) \propto \frac{1}{g}$, such that $\sum P = 1$. If we then have for example, a binomial distribution of multiplicities $g(N, s) = \frac{N!}{N_1!N_2!}$ where N is the total number of particles and $1, 2$ are the respective states, the Stirling approximation gives that $g(N, s) \approx \sqrt{\frac{2}{\pi N}} 2^N e^{-2s^2/N}$, a Gaussian, as we expect. We note that the width of this Gaussian is $\propto \sqrt{N}$. This was discussed last week.

We then investigate a system of temperature flow. We construct a pair of systems of certain particles N_1, N_2 of energies U_1, U_2 yielding multiplicities g_1, g_2. The total multiplicity of the combined system is then $g = g_1 g_2$. We then consider the transfer of energy when $U = U_1 + U_2$ energy is conserved; note that we will not allow particles to transfer. We then note that the new g' after transfer is given by $g' = \sum g_1(N_1, U_1) g_2(N_2, U - U_1)$, where we sum over all values of U_1. In general, $g' > g$. Note that $g' = g_1 g_2$ is a Gaussian centered at some energy $\hat{U}_1$, which is denoted the most probable configuration or the equilibrium configuration. We can then solve for this peak. We differentiate $g_1 g_2$:

$$\begin{aligned}
0 &= dg \\
&= \left(\left. \frac{\partial g_1}{\partial U_1} \right|_{N_1} \right) g_2 dU_1 + g_1 \left(\left. \frac{\partial g_2}{\partial U_2} \right|_{N_2} \right) dU_2 \\
&= \left(\left. \frac{\partial g_1}{\partial U_1} \right|_{N_1} \right) g_2 - g_1 \left(\left. \frac{\partial g_2}{\partial U_2} \right|_{N_2} \right) \\
\frac{\partial}{\partial U_1} \left(\ln g_1|_{N_1} \right) &= \frac{\partial}{\partial U_2} \left(\ln q_2|_{N_2} \right)
\end{aligned}$$

where we take advantage of the fact that $dU_1 = -dU_2$. We then define entropy $\sigma(N, U) = \ln g(N_U)$. Note that entropies are additive: $g = g_1 g_2 \cdots g_n$, $\sigma = \sigma_1 + \sigma_2 + \cdots + \sigma_n$. We then note that the equilibrium condition from the last line then becomes

$$\left.\frac{\partial \sigma_1}{\partial U_1}\right|_{N_1} = \left.\frac{\partial \sigma_2}{\partial U_2}\right|_{N_2}$$

This then shows that when the two terms are not equal, energy flows. If the left term is larger, then energy flows from system 1 to system 2, and if the right term is larger, then vice versa. We then define temperature $\tau = \left.\frac{\partial \sigma}{\partial U}\right|_N$. This then gives the following expression: $d(\sigma_1 + \sigma_2) = \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) dU_1$. At equilibrium then, it is clear that $\tau_1 = \tau_2$. But if $\tau_2 \neq \tau_1$, then heat will flow from the higher τ to the lower.

We then note that $\tau = k_B T$ where T is the conventional temperature in $^\circ K$ and $k_B = 1.4 \times 10^{-23}$J/K is the Boltzmann constant.

We then note that we can write $g(N,s) = g(N,0)e^{-2s^2/N}$. We can also find that $\sigma = \ln(g_1 g_2) = C - \frac{2s_1^2}{N_1} - \frac{2s_2^2}{N^2}$ and so substituting $s_2 = s - s_1$ and forcing our constaint $\frac{\partial \sigma}{\partial s_1} = -\frac{4s_1}{N_1} + \frac{4(s-s_1)}{N_2}$, we find that the equilibria $\hat{s}$ give $\frac{\hat{s}_1}{N_1} = \frac{\hat{s}_2}{N_2} = \frac{s}{N}$.

We then investigate the likelihood of fluctuations $s_1 = \hat{s}_1 + \delta$. This gives $\sigma = C - \frac{2}{N_1}(\hat{s}_1 + \delta)^2 - \frac{2}{N_2}(s - \hat{s}_1 - \delta)^2$, which if we group the $\hat{s}_1$ terms into the C gives $\sigma = C + 0\delta - \frac{2}{N_1}\delta^2 - \frac{2}{N_2}\delta^2$, where we know that the coefficient is 0 because we have minimized σ. Then $g_1 g_2 = e^{\sigma_1 + \sigma_2} = Ce^{-2\left(\frac{1}{N_1} + \frac{1}{N_2}\right)\delta^2}$. Then when $N_1 = N_2$, we find $g_1 g_2 = Ce^{8\delta^2/N}$. We finally find that $\delta \sim \sqrt{N}$.

If we perform a back-of-the-envelope calculation, giving $N \sim 10^{22}$, we find that $\delta \sim 10^{11}$. We then ask the probability that δ varies as high as 10^{12}? It can easily be calculated that given $\delta = 10^{12} \Rightarrow g_1 g_2 \sim e^{-400} = 10^{-174}$. In comparison, the age of the universe is 10^{61} planck times.

The second law of thermodynamics can then be seen here, because entropy never decreases when two systems are brought into contact. This means that almost all processes are irreversible.