11/14 Lecture outline

• Binomial distribution: recall

$$p(N_1) = \binom{N}{N_1} p^{N_1} q^{N_2},$$

$$\overline{N_1} = \sum_{N_1=0}^{N} N_1 p(N_1) = p\frac{\partial}{\partial p}(p+q)^N = Np$$

and

$$\overline{N_1^2} = \sum_{N_1=0}^{N} N_1^2 p(N_1) = \left(p\frac{\partial}{\partial p}\right)^2 (p+q)^N = (\overline{N_1})^2 + Npq.$$

So $\overline{(\Delta N_1)^2} = Npq$. I.e. $(\Delta N_1)_{RMS} = \sqrt{Npq}$. Define $x \equiv N_1/N$, so $\overline{x} = p$ and $\Delta x_{RMS} = (\Delta N_1)_{RMS}/N = \sqrt{(pq)}/\sqrt{N}$. Very sharply peaked around $x = \overline{x}$ for large N.

• For very large N, use Stirling's approximation:

$$n! \approx \sqrt{2\pi n}\left(\frac{n}{e}\right)^n \qquad \text{for } n \gg 1.$$

Use this to approximate $\binom{N}{N_1}$ when N and N_1 are both large. Write $x \equiv N_1/N$ and replace $p(N_1)$ with $p(x) = Np(N_1)$ (since $p(x)dx = p(N_1)\Delta N_1$, with $dx = \Delta N_1/N$). Using Stirling's approximation (along with a Taylor's series approximation) gives

$$p(x) \to \frac{1}{\sqrt{2\pi}\sigma}\exp(-(x-\overline{x})^2/2\sigma^2) \qquad \text{with} \quad \overline{x} = p \quad \text{and} \quad \sigma = \left(\frac{pq}{N}\right)^{1/2},$$

i.e. we get the Gaussian distribution. This is the law of large numbers: large samples become gaussian. Note that the gaussian has height $\sim \sqrt{N}$, and width $\sim 1/\sqrt{N}$. For $N \to \infty$, the probability distribution becomes a delta function: $p(x) \to \delta(x-p)$.

• Omit in class, but if you're interested here are the details of how to get the gaussian via Stirling's approximation (along with a Taylor's series approximation). Write $\ln\binom{N}{N_1} = \ln N! - \ln(Nx)! - \ln(N - Nx)!$. Using Stirling for each of the 3 terms, we have

$$\begin{aligned}\ln\binom{N}{N_1} &\approx N\ln N - N + \tfrac{1}{2}\ln N + \tfrac{1}{2}\ln(2\pi)\\ &\quad - [Nx\ln(Nx) + Nx + \tfrac{1}{2}\ln(Nx) + \tfrac{1}{2}\ln(2\pi)]\\ &\quad - [N(1-x)\ln(N(1-x)) + \tfrac{1}{2}\ln(N(1-x)) + \tfrac{1}{2}\ln(2\pi)].\end{aligned}$$

Expand this out and collect the terms. This function is peaked at $x = 1/2$, so Taylor expand it in x, around $x = 1/2$, and keep just the lowest order term involving x:

$$\ln \binom{N}{N_1} \approx N \ln 2 - \tfrac{1}{2} \ln N - \tfrac{1}{2} \ln(\pi/2) - 2N(x - \tfrac{1}{2})^2 + O(x - \tfrac{1}{2})^4,$$

where the last term means order $(x - \frac{1}{2})^4$ and higher, and we now drop those terms, because their coefficients are all tiny (i.e. the function is sharply peaked). Exponentiating the above then gives

$$\binom{N}{N_1} \approx 2^N \sqrt{\frac{2}{\pi N}} \exp(-2N(x - \tfrac{1}{2})^2).$$

This will give the quoted gaussian for the case $p = q = \frac{1}{2}$. For general p and q, when we multiply this by $p^{Nx} q^{N(1-x)}$, we get a function that is instead peaked at $x = p$. We should then Taylor expand $\ln \binom{N}{N_1}$ instead around $x = p$. Doing that, and multiplying by $p^{Nx} q^{N(1-x)}$, gives the gaussian quoted above.

• Multi-nomial distribution: fix $N = \sum_{i=1}^n N_i$; probability of a given set $\{N_i\}$ is

$$p(\{N_i\}) = N! \prod_{i=1}^n \frac{p_i^{N_i}}{N_i!},$$

where $\sum_{i=1}^n p_i = 1$. Note that these are properly normalized, since

$$\sum_{\{N_i\}}{}' p(\{N_i\}) = (\sum_i p_i)^N = 1,$$

where the $'$ means to sum over all N_i, subject to the constraint that $\sum_{i=1}^n N_i = N$.

• Statistical interpretation of entropy. Macro-state is specified by e.g. N and U. Micro-state is specified by e.g. $\{N_i\}$, with $N = \sum_{i=1}^n N_i$ and $U = \sum_{i=1}^n \epsilon_i N_i$. The number of micro-states associated with a given macro-state is $\Omega(N, U, \ldots)$. Boltzmann: the entropy is $S = f(\Omega)$ for some monotonically increasing function f. If system has isolated parts 1 and 2, then $\Omega = \Omega_1 \Omega_2$ and $S = S_1 + S_2$, so conclude that

$$S = k \ln \Omega.$$

For large N, we can also replace $\Omega \approx \omega_{max}$, where ω_{max} is the number of states in the most probable configuration. We will later justify the fact that the constant k is the same one appearing in the ideal gas law, $PV = NkT$. (Recall $n = N/N_A$ and $R = N_A k$, where $N_A = 6.02 \times 10^{26}$ particles/kilomole.)

• Each energy level in the quantum theory (or cell in the classical theory) has a degeneracy factor. E.g. consider a free particle in a cube, with sides of length L. To enumerate the available states, it's simpler to consider the quantum theory (otherwise must pixelize phase space by hand, as a regulator). The QM wavefunction is $\psi = A\sin(n_x \pi x/L)\sin(n_y \pi y/L)\sin(n_z \pi z/L)$, where $n_i = 1, 2, \ldots$, and energy is $\epsilon = \pi^2\hbar^2 n^2/2mL^2)$, where we define $n_j^2 \equiv n_x^2 + n_y^2 + n_z^2$. The groundstate has $n_j^1 = 3$, and there is a unique such state. The first excited state has $n_j^2 = 6$, and there are $g_j = 3$ such possibilities. The next excited state has $n_j^2 = 9$ and again $g_j = 3$. For large n, the number of states in the range from n to $n + dn$ is $N(n)dn \approx \frac{1}{8}4\pi n^2 dn$, where the 1/8 is because all $n_i > 0$. Let's use $d\epsilon = \pi^2\hbar^2 n dn/mL^2$ to get

$$g(\epsilon)d\epsilon = N(n)dn = \frac{1}{8}4\pi(2mL^2\epsilon/\pi^2\hbar^2)^{1/2}(mL^2 d\epsilon/\pi^2\hbar^2) = \frac{4\pi V\sqrt{2}}{(2\pi\hbar)^3}m^{3/2}\epsilon^{1/2}d\epsilon.$$

For fermions, we should multiply this by 2, for the possible two spin states (up or down).

• Boltzmann distribution: the number of energy states with a given set of $\{N_i\}$ is

$$\omega(\{N_i\}) = N! \prod_{i=1}^{n} \frac{g_i^{N_i}}{N_i!},$$

here i labels the energy levels, or cells, and g_i is the number of states with energy ϵ_i (or states in that cell). Later we will omit the $N!$. This is related to a question in class about entropy of mixing, upon removing a partition, when the particles on the two sides are the same (this is called Gibbs' paradox). Each factor is the number of ways of putting N_i out of the N particles in cell i. The total number of states is

$$\Omega(U, N) = \sum_{\{N_i\}}{}' \omega(\{N_i\}),$$

where the prime is a reminder that the $\{N_i\}$ must satisfy $\sum_i N_i = N$ and $\sum_i N_i \epsilon_i = U$.

Next lecture: we'll maximize $\omega(\{N_i\})$, and make contact with our results from thermodynamics.