11/29 Lecture outline

• Basic idea of statistical mechanics: 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

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

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 soon 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.) Summary:

$$S(U, N, ...) = k \ln \Omega(U, N, ...) \approx k \ln \omega_{max}.$$

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

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

• Suppose that there are energy levels ϵ_i, and that each has a degeneracy factor g_i. Suppose that we put N_i particles into the energy level ϵ_i, and that there are N particles total. If the particles are all distinguishable, and there is no restriction on them occupying the same state, then the number of configurations with a given set of $\{N_i\}$ is

$$\omega_{M.B.}(\{N_i\}) = N! \prod_{i=1}^n \frac{g_i^{N_i}}{N_i!},$$

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). If we set all $g_i = 1$, this is simply the multinomial distribution (Recall a HW problem about a case where all $g_i = 1$). The $g_i^{N_i}$ accounts for the extra configurations coming from the degeneracies of energy levels (or cells).

• The above result is problematic. The basic problem is that it describes distinguishable objects. 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). The correct answer is a replacement of the above with a quantum answer. But, pre-quantum, Gibbs found a simple modification of the above. Recall from thermodynamics $\Delta S = Nk\ln(V_f/V_i) + \frac{3}{2}Nk\ln(T_f/T_i)$ for monatomic ideal gas. This tells us

$$S = Nk\ln V + \frac{3}{2}Nk\ln T + f(N).$$

Soon we will see what the $f(N)$ is. It is reasonable to expect $f(N) = aN + b$ for constants a and b, since entropy is extensive, and that is indeed what we'll find. Gibb's paradox is that if we then have N_1 atoms in volume V_1 and N_2 in volume V_2 and then take away the partition, all the atoms are now in the larger volume $V = V_1 + V_2$. If it's free expansion, the energies are unchanged, and

$$\Delta S = kN_1\ln(V/V_1) + kN_2\ln(V/V_2) > 0,$$

which is correct if the atoms are different. But this is incorrect if they're of the same type and the process is reversible (which requires that $P_1 = P_2$ and $T_1 = T_2$, so $N_1/V_1 = N_2/V_2 = (N_1 + N_2)/(N_1 + V_2)$; in this case we should instead get $\Delta S = 0$. Gibb's recipe to fix this has to do with the $f(N)$. He says that

$$S = Nk\ln(V/N) + \frac{3}{2}Nk\ln U + aN + b$$

for constants a and b. This amounts to dividing Ω by $N^N \approx N!$.

- Summary: Gibbs tells us to get rid of the $N!$, so replace above with

$$\omega_{M.B.G.}(\{N_i\}) = \prod_{i=1}^{n} \frac{g_i^{N_i}}{N_i!},$$

- Quantum statistical mechanics. Main point is that each electron is identical with every other electron. Likewise every photon is identical with every other photon. Switching two identical particles does not count as a new state. Also even (or odd) statistics of the wavefunction for bosons (or fermions): $\psi_{B/F}(\vec{x}_1, \vec{x}_2) = \pm\psi_{B/F}(\vec{x}_2, \vec{x}_1)$. Gives Pauli exclusion principle for fermions. So, for identical particles,

$$\omega(\{N_i\})_{B.E.} = \prod_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} \qquad \text{bosons}$$

$$\omega(\{N_i\})_{F.D.} = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!} \qquad \text{fermions.}$$

For the fermion case, each g_i level can be filled at most once (Pauli exclusion principle), and the factor counts the number of choices of which N_i out of the g_i possibilities will be filled, with $g_i - N_i$ left unfilled. Picture the g_i states as g_i boxes, and the N_i particles as N_i balls, and we want to count how many ways the balls can be put in the boxes if at most one ball fits in each box. In the boson case, there is no restriction on how many times each of the g_i possibilities can be filled. We again have a picture of N_i balls and g_i boxes, but now there is no restriction on how many balls can go in each box. The combinatoric factor can then be understood in terms of different configurations of N_i balls and $g_i - 1$ separators.

- Illustrate the g_i degeneracy factors. 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).