11/16 Lecture outline

• Last time:

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

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

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

• For distinguishABLE particles, the number of states 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). This is the number of ways of putting N_i out of the N particles in cell i.

• But Gibbs tells us to get rid of 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). 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 $N^N \approx N!$.

• So

$$\omega(\{N_i\})_{M.B.} = \prod_{i=1}^{n} \frac{g_i^{N_i}}{N_i!}.$$

Now let's briefly discuss QM and identical particles. For identical particles, we should replace the configuration number

$$N! \prod_i \frac{1}{N_i!} \to 1,$$

since they different orderings of the particles are now meaningless. But we're not finished! We also need to replace the $\prod_i g_i^{N_i}$ factor with something more appropriate, and that depends on whether the particles are bosons or fermions. We then get

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

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

Discuss why. As we'll discuss, the M.B., B.E., and F.D. cases all agree in the classical limit (which we'll see is when $(\epsilon_i - \mu) \gg kT$). This is the justification for studying the M.B. distribution: it's physically wrong, but it's a bit simpler and it gives approximately right answers in some appropriate limit.

• Back to the M.B. distribution. Maximize it over microstates, subject to the constraints that we reproduce the macroscopic U and N. Using Stirling's approximation (taking all N_i large) we have

$$\ln \omega_{M.B.}(\{N_i\}) = \sum_{i=1}^{n} N_i \ln g_i - \ln N_i! \approx \sum_i N_i \left[\ln\left(\frac{g_i}{N_i}\right) + 1 \right].$$

We want to maximize this, over all N_i, subject to the constraints $N = \sum_i N_i$ and $U = \sum_i N_i \epsilon_i$. Use Lagrange mulipliers to enforce these constraints. So maximize

$$\sum_i N_i \left[\ln\left(\frac{g_i}{N_i}\right) + 1 + \alpha + \beta\epsilon \right],$$

over all N_i, where α and β are Lagrange multipliers. Get that ω is maximized for $N_i = N_i^*$, given by

$$N_i^* = g_i \exp(\alpha + \beta\epsilon_i),$$

$$\ln \omega_{max} \approx -\alpha N - \beta U + N.$$

Recall from thermodynamics that

$$U - TS + PV \equiv G = \mu N,$$

so

$$S = -\frac{\mu}{T}N + \frac{1}{T}U + \frac{PV}{T}$$

Compare with

$$k \ln \omega_{max} \approx k\alpha N - k\beta U + kN.$$

Fits with

$$PV = NkT$$

$$\alpha = \mu/kT$$

$$\beta = -1/kT$$

- So

$$N_i^* = g_i e^{(\mu-\epsilon_i)/kT} \equiv g_i e^{\alpha+\beta\epsilon_i},$$

and we still need to enforce

$$N = \sum_i N_i^* = e^\alpha \sum_i g_i e^{\beta\epsilon_i}$$

$$U = \sum_i N_i^* \epsilon_i = e^\alpha \sum_i g_i \epsilon_i e^{\beta\epsilon_i}.$$