⋆ Week 8 reading: Blundell+Blundell, chapters 21, 22, 29

• Continue where we left off last time. Consider distinguishable vs indistinguishable in the microcanonical description.

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

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

where $\omega(\{N_i\})$ is the number of microstates labeled by some N_i and 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 $N!$.

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

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. Discuss the answers:

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

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

The M.B., B.E., and F.D. cases all agree in the classical limit. 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.

- Next topic: the chemical potential, which applies when our system does not have a fixed N, but rather than exchange N with an external reservoir, e.g. for an open system. Applies in chemistry because molecules can combine to form other molecules via chemical reactions, so molecule numbers can change. The idea is to consider the change dU in the internal energy when $dN \neq 0$, and there is a new term: $dU = TdS - pdV + \mu dN$, so $\mu = (\partial U/\partial N)_{S,V}$. Let's switch to holding T instead of S fixed, using $F = U - TS$ or $G = U + pV - TS$: $\mu = (\partial F/\partial N)_{V,T}$ or $\mu = (\partial G/\partial N)_{p,T}$.

- $dS = T^{-1}(dU + pdV - \mu dN)$ so $T^{-1} = (\partial S/\partial U)_{N,V}$, and $p/T = (\partial S/\partial V)_{N,U}$, and $(\partial S/\partial N)_{U,V} = -\mu/N$. Let's now reconsider, including the chemical potential, the 2nd law and how two subsystems in contact approach thermal equilibrium. E.g. $dS = (\partial_{U_1} S_1)_{N,V} dU_1 + (\partial_{U_2} S_2)_{N,V} dU_2$ with $dU_1 = -dU_2 = dU$ gives $dS = (-T_1^{-1} + T_2^{-1})dU \geq 0$, which implies that energy flows from the hotter to the colder object. Likewise, with particle exchange, get $dS = (\mu_1 T_1^{-1} - \mu_2 T_2^{-1})dN \geq 0$ where dN is the gain in particle number by system 2. Taking e.g. $T_1 = T_2$ see that particles flow from 1 to 2 if $\mu_1 > \mu_2$.

- For the ideal gas we saw that $F = Nk_BT(\ln(N\lambda_{th}^3/V) - 1)$ so $\mu = (\partial F/\partial N)_{V,T} = k_BT\ln(N\lambda_{th}^3/V)$. Also $G = F + pV = N\mu$.

- Grand partition function: imagine that our small system, of energy ϵ and particle number N, is in contact with a huge reservoir with internal energy $U - \epsilon$ and particle number $\mathcal{N} - N$, and consider the number of states of the combined system plus reservoir, coming from the number of states in the reservoir. Taylor expand $S(U - \epsilon, \mathcal{N} - N) \approx S(U, \mathcal{N}) - (\epsilon - \mu N)/T$ and thus $P(\epsilon, N) \propto e^{S(U-\epsilon), \mathcal{N}-N)/k_B} \propto e^{\beta(\mu N - \epsilon)}$. So define the grand partition function as $\mathcal{Z}(T, \mu, V) \equiv \sum_i e^{\beta(\mu N_i - E_i)}$. Get $N = k_BT(\partial \ln \mathcal{Z}/\partial \mu)_{\beta,V}$. $U = -(\partial \ln Z/\partial \beta)_{\mu,V} + \mu N$. $S = -k_B \sum_i P_i \ln P_i = T^{-1}(U - \mu N + k_BT \ln \mathcal{Z})$. Taking $\Phi_G \equiv -k_BT \ln \mathcal{Z}$, show that $\Phi_G = F - \mu N$ and $S = -(\partial \Phi_G)/\partial T)_{V,\mu}$, $p = -(\partial \Phi_G/\partial V)_{T,\mu}$, $N = -(\partial \Phi_G/\partial \mu)_{T,V}$.