

140a Lecture 14, 2/26/19

★ Week 8 reading: Blundell+Blundell, chapters 21, 22.

• Last time: $Z = \sum_{\alpha} e^{-\beta E_{\alpha}}$, where $\beta \equiv 1/k_B T$. $P(E_{\alpha}) = e^{-\beta E_{\alpha}}/Z$. $U = -d \ln Z/d\beta = k_B T^2 d \ln Z/dT$. $S = k_B \sum_i P_i(\beta E_i + \ln Z) = (U/T) + k_B \ln Z$. $F = U - TS = -k_B \ln Z$. $C_V = T(\frac{\partial S}{\partial T})_V = k_B T[2(\frac{\partial \ln Z}{\partial T})_V + T(\frac{\partial^2 \ln Z}{\partial T^2})_V]$. $p = -(\frac{\partial F}{\partial V})_T = k_B T(\frac{\partial \ln Z}{\partial V})_T$. $H = U + pV = k_B T[T(\frac{\partial \ln Z}{\partial T})_V + V(\frac{\partial \ln Z}{\partial V})_T]$. $G = F + pV = k_B T[-\ln Z + V(\frac{\partial \ln Z}{\partial V})_T]$.

The single particle partition function is, in terms of the thermal wavelength λ_{th} :

$$Z_1 = \int_0^{\infty} e^{-\beta \hbar^2 k^2 / 2m k_B T} g(k) dk \equiv V/\lambda_{th}^3, \quad \lambda_{th} \equiv h/\sqrt{2\pi m k_B T}.$$

Distinguishable vs indistinguishable particles. If we have N copies of a system that are distinguishable and non-interacting, then $Z_N = Z_1^N$. But if the N copies are identical and indistinguishable, then $Z_N \neq Z_1^N$. Mention Gibbs' paradox and resolution. Gibbs noticed a paradox, and he also figured out the resolution. Consider free expansion of ideal gas from V_i to $V_f > V_i$. Then $\Delta S = N k_B \ln(V_f/V_i)$. Suppose that $V_f = 2V_i$ and that there were two distinguishable gasses (say nitrogen and oxygen) on the two sides of the partition, with N molecules of each, and then the partition is removed. Then $\Delta S = 2N k_B \ln 2$. Now suppose that the gas on the two sides is the same and indistinguishable. Then we should find $\Delta S = 0$ upon removing the partition, since the gas doesn't much notice the partition (which could also be a pretend partition). But just applying our formulae suggests instead that $\Delta S = 2N k_B \ln 2$. The indistinguishability is key to the resolution.

• For N non-interacting particles, we would have $Z_{N,naive} = Z_1^N$. This is called naive because it applies only if each of the N particles is distinguishable, whereas molecules are indistinguishable. Anyway, it leads to $\ln Z_{N,naive} = N \ln(V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln(2\pi m/h^2))$. Then

$$S_{naive} = Nk(\ln V + \frac{3}{2} \ln T + \sigma_{naive}), \quad \sigma_{naive} = \frac{3}{2}(1 + \ln(2\pi m k_B/h^2)).$$

We know from our earlier calculations of ΔS that

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

so S_{naive} agrees with that, for a specific $f(N)$, and recall that S_{naive} is in conflict with the 3rd law since $S(0) \neq 0$. But S_{naive} is not really extensive: if we take $V \rightarrow \alpha V$ and $N \rightarrow \alpha N$ we do not get $S \rightarrow \alpha S$. This is related to the Gibbs paradox mentioned last time. Gibbs understood the resolution: molecules are identical.

- Consider e.g. a system of two two-state systems that are distinguishable we have $Z = 1 + 2e^{-\beta\epsilon} + e^{2\beta\epsilon} = Z_1^2$ whereas if they are indistinguishable we have $Z = 1 + e^{-\beta\epsilon} + e^{2\beta\epsilon} \neq Z_1^2$.

For large N there is a simplification in the indistinguishable case, $Z_N \approx Z_1^N/N!$. If the states are sparsely populated, so it is unlikely to have various energy levels occupied by multiple particles, and $N \gg 1$, then $Z_N \approx Z_1^N/N!$. The condition for this to hold is $n \ll n_Q \equiv 1/\lambda_{th}^3$. This is the ideal gas limit, where the identical gas molecules are interacting but are widely separated compared to their thermal wavelength. Then $Z_N \approx (V/\lambda_{th}^3)^N/N!$.

- This leads to $\ln Z = N \ln V + \frac{3}{2}N \ln T + \text{const.}$. $U = -d \ln Z / d\beta = \frac{3}{2}Nk_B T$, $C_V = \frac{3}{2}Nk_B T$. $F = -k_B T \ln Z = -k_B T N \ln V - k_B \frac{2}{2} N T \ln T - k_B T x \text{const.}$. So $p = -(\partial F / \partial V)_T = Nk_B T / V$, recovering the ideal gas law. $H = U + pV = \frac{5}{2}Nk_B T$. To compute S , use Stirling's approximation $N! \approx (N/e)^N$ to get $\ln Z \approx N \ln(Ve/N\lambda_{th}^3)$ so $F \approx -Nk_B T \ln(Ve/N\lambda_{th}^3)$ so $S = (U - F)/T = \frac{5}{2}Nk_B - Nk_B \ln(N\lambda_{th}^3/V)$. Also $G = H - TS = Nk_B T \ln(N\lambda_{th}^3/V)$.

- Improved ideal gas expression is thus $S = \frac{5}{2}Nk_B - Nk_B \ln(N\lambda_{th}^3/V)$. The $1/N!$ leads to replacing V with V/N inside the \ln , which makes S properly extensive.

- Example: diatomic gas. Since $E = E_{trans} + E_{vib} + E_{rot}$ and each involves decoupled, independent sums, get $Z = Z_{trans}Z_{vib}Z_{rot}$. As before, $Z_{trans} = V/\lambda_{th}^3$ and $Z_{vib} = e^{-\frac{1}{2}\beta\hbar\omega} / (1 - e^{-\beta\hbar\omega})$ and $Z_{rot} = \sum_{J=0}^{\infty} (2J+1)e^{-\beta\hbar^2 J(J+1)/2I}$. Then $C_V = (\frac{dU}{dT})_V = C_{V,trans} + C_{V,vib} + C_{V,rot}$, since $U = -\frac{d}{d\beta} \ln Z = U_{trans} + U_{vib} + U_{rot}$. This reproduces the observed behavior of plateaus in $C_V/Nk_B \sim \frac{1}{2}f$: for $k_B T$ large enough that the ideal gas approximation is OK, but $k_B T < \hbar^2/2I$ and $\hbar\omega$, get $f = 3$ from the translation d.o.f., the next plateau is for $\hbar^2/2I < k_B T < \hbar\omega$, when the vibrational d.o.f. are also excited, get $f = 5$. Then, for $k_B T > \hbar\omega$ get $f = 7$. This was observed before QM, or molecules(!), were understood; it was a big hint (in retrospect).

- Consider distinguishable vs indistinguishable in the microcanonical description.

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

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

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 $\sum_i N_i \epsilon_i = U$. Continue from here....