140a Lecture 13, 2/21/19

$\star$ Week 7 reading: Blundell+Blundell, chapters 20, 21.

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

Example: the two-level system with $E_\pm = \pm\frac{1}{2}\Delta$: $Z = 2\cosh(\beta\Delta/2)$, then $U = -\frac{d}{d\beta}\ln Z = -\frac{\Delta}{2}\tanh(\beta\Delta/2)$, and $C_V = (dU/dT) = k_B(\beta\Delta/2)^2 \text{sech}^2(\beta\Delta/2)$ and $F = -k_BT\ln Z = -k_BT\ln(2\cosh(\beta\Delta/2))$ and $S = (U-F)/T = -(\Delta/2T)\tanh(\beta\Delta/2) + k_B\ln[2\cosh(\beta\Delta/2)]$. Note that $S(T\to 0)\to 0$ (i.e. $\Omega \to 1$ the groundstate) and $S(T\to\infty)\to k_B\ln 2$ (since $\Omega\to 2$, both states are equally likely at high T). Plot C_V/k_B as a function of k_BT/Δ: zero at low and high temperature, with maximum at $T \cong \Delta/k_B$ the "Schottky anomaly."

• Example: SHO: $Z = e^{-\frac{1}{2}\beta\hbar\omega}/(1 - e^{-\beta\hbar\omega})$ leads to $U = d\ln Z/d\beta = \hbar\omega(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1})$. Then $C_V = (dU/dT) = k_B(\beta\hbar\omega)^2 e^{\beta\hbar\omega}/(e^{\beta\hbar\omega}-1)^2$. Note that for high temperature U and C_V are approximately given by the equipartition result, $U \approx k_BT$. Also, $F = -k_BT\ln Z = \frac{1}{2}\hbar\omega + k_BT\ln(1 - e^{-\beta\hbar\omega})$ and then $S/k_B = (U-F)/k_BT = \beta\hbar\omega(e^{\beta\hbar\omega}-1)^{-1} - \ln(1-e^{-\beta\hbar\omega})$. Note that it obeys the third law, as expected since at $T\to 0$ the SHO goes to the non-degenerate groundstate. Also $S(T\to\infty)\to k_B\ln(k_BT/\hbar\omega)$.

• These examples illustrate general properties: for k_BT small compared to the energy level spacing, the system is approximate in the grounstate. If there are finite numbers of levels and k_BT is large compared with them, then the levels become occupied with equal probabilities in the high temperature limit. If there are an infinite number of energy levels (e.g. recovering classical physics at high energy according to the correspondence principle) then the high temperature limit is consistent with the equipartition theorem.

• Note that if one combines two decoupled systems then $E_{ij} = E_i^1 + E_j^2$ so $Z = Z_1Z_2$, fitting with $\ln Z$ being extensive.

• Spin 1/2 particle with magnetic moment μ_B in $\vec{B} = B\hat{z}$ has energy levels given by the two-state system, $E = \pm\mu_B B$, and thus $Z_1 = 2\cosh(\beta\mu_B B)$. A paramagnetic consists of N decoupled such spins, so $Z_N = Z_1^N$, and thus $F = -k_BT\ln Z_N = -Nk_BT\ln[2\cosh(\beta\mu_B B)]$ and the magnetic moment is $m = -(\partial F/\partial B)_T = N\mu_B\tanh(\beta\mu_B B)$. For $\beta\mu_B B$ large we see the spins aligned, for $\beta\mu_B B$ small they are random. For small $\beta\mu_B B$ use $\tanh(\beta\mu_B B)\approx\beta\mu_B B$ to get $M = m/V \approx N\mu_B^2 B/Vk_BT \approx \chi B/\mu_0$ so $\chi \approx N\mu_0\mu_B^2/Vk_BT \propto 1/T$ (Curie's law).

• Now let's compute the partition function for a free particle of mass m. Classically, we integrate over phase space $\int d^3\vec{r}\int d^3\vec{p}/h_0^3 e^{-\beta E}$, where h_0 is a phase space volume element. By translation invariance, this gives $Z = V\int d^3\vec{p}e^{-\beta E}/h_0^3$. In QM, we can relate this to counting Fourier modes, via $\vec{p} = \hbar\vec{k}$. We recover the above expression with $h_0 \to 2\pi\hbar = h$.

Recall that when we count modes in a box, we have a factor of $V\frac{d^3\vec{k}}{(2\pi)^3}$. For example take $\psi(\vec{x}) \sim e^{i\vec{k}\cdot\vec{x}}$ and impose periodicity in $x \to x + L$, etc to get $\vec{k} = 2\pi\vec{n}/L$ and then $\sum_{\vec{n}} \to V\frac{d^3\vec{k}}{(2\pi)^3}$. If we go to spherical coordinates and integrate over the solid angle associated with $\vec{k}$, we get $g(k)dk = Vk^2dk/2\pi^2$ for the density of states.

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

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

• 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 $\Delta S = Nk_B\ln(V_f/V_i)$. 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 $\Delta S = 2Nk_B\ln 2$. 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 $\Delta S = 2Nk_B\ln 2$. The indistinguishability is key to the resolution.