140a Lecture 12, 2/19/19

⋆ Week 7 reading: Blundell+Blundell, chapters 20, 21.

• Next topic: the partition function $Z = \sum_\alpha e^{-\beta E_\alpha}$, where $\beta \equiv 1/k_B T$. A powerful starting point for computing the various state variables of a system if you know the energy levels. In classical physics, the sum over energy levels is actually an integral over the (q, p) phase space – we will discuss this case shortly. For quantum systems that are bound, the sum is over the discrete energy levels of the Hamiltonian – we will discuss such cases first. We will first discuss the case of a single particle in thermal equilibrium with a heat bath at temperature T, and then extend to many particles. Note that if we have two decoupled systems, with energy levels E^1_α and E^2_β, then $Z_{tot} = Z_1 Z_2$, so $\ln Z$ is extensive.

• Example: two state system, with energy levels ϵ_0 and ϵ_1: $Z = e^{-\beta\epsilon_0} + e^{-\beta\epsilon_1} = e^{-\beta\epsilon_{ave}} 2\cosh(\beta\Delta/2)$, where $\epsilon_{ave} = \frac{1}{2}(\epsilon_0 + \epsilon_1)$ and $\Delta = \epsilon_1 - \epsilon_0$.

• Quantum SHO: $E_n = (n + \frac{1}{2}\hbar\omega)$ so $Z = e^{-\beta\hbar\omega/2}\sum_{n=0}^\infty e^{-n\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega}(1 - e^{-\beta\hbar\omega})^{-1}$. For low temperature, $\beta\hbar\omega \gg 1$, then $Z \approx e^{-\frac{1}{2}\beta\hbar\omega}$ i.e. the system is in the groundstate. For high temperature, $\beta\hbar\omega \ll 1$, get $Z \approx 1/\beta\bar{\omega} = Z_{cl}$. We compared to a classical SHO: $Z_{cl} = \int \frac{dxdp}{h} e^{-\beta(\frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 x^2)}$. So $Z_{cl} = h^{-1}\sqrt{2\pi mkT}\sqrt{2\pi kT/m\omega^2} = 1/\beta\hbar\omega$.

• N-level (equally spaced) system: $Z = \sum_{j=0}^{N-1} e^{-j\beta\hbar\omega} = (1 - e^{-N\beta\hbar\omega})/(1 - e^{-\beta\hbar\omega})$.

• Rotational energy levels $E_J = \hbar^2 J(J+1)$ with $2J+1$ degeneracy: $Z = \sum_{J=0}^\infty (2J+1)e^{-\beta\hbar^2 J(J+1)/2I}$.

• Show that $U = -d\ln Z/d\beta = k_B T^2 d\ln Z/dT$.

• $S = -k_B \sum_i P_i \ln P_i = k_B \sum_i P_i(\beta E_i + \ln Z) = (U/T) + k_B \ln Z$.

• $F = U - TS = -k_B \ln Z$, i.e. $Z = e^{-\beta F}$. Then $S = -(\frac{\partial F}{\partial T})_V = k_B \ln Z + k_B T(\frac{\partial \ln Z}{\partial T})_V$. Also $C_V = T(\frac{\partial S}{\partial T})_V = k_B T[2(\frac{\partial \ln Z}{\partial T})_V + T(\frac{\partial^2 \ln Z}{\partial^2 T})_V]$.

• $p = -(\frac{\partial F}{\partial V})_T = k_B T(\frac{\partial \ln Z}{\partial V})_T$.

• $H = U + pV = k_B T[T(\frac{\partial \ln Z}{\partial T})_V + V(\frac{\partial \ln Z}{\partial V})_T]$.

• $G = F + pV = k_B T[-\ln Z + V(\frac{\partial \ln Z}{\partial V})_T]$.

• Consider the two-level system with $\epsilon_{ave} = 0$. $Z = 2\cosh(\beta\Delta/2)$, 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 $F = -k_B T \ln Z = -k_B T \ln(2\cosh(\beta\Delta/2))$ 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 $k_B T/\Delta$: zero at low and high temperature, with maximum at $T \cong \Delta/k_B$ the "Schottky anomaly."