Lecture 10

Equipartition Thm: (Classical systems) (1)

Consider Quadratic Hamiltonian:

$$H = p_{x,1}^{(1)2}/2m + \text{rest} \equiv p_x^2/2m + \tilde{H}$$

$\tilde{H}$ is indep. of $p_{x,1}^{(1)}$

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \frac{\frac{1}{2m}\int \frac{d^{3N}p\, d^{3N}q}{h^{3N}} \left(p_x^{(1)}\right)^2 \exp\left[-\beta\left(\frac{p_x^{(1)2}}{2m} + \tilde{H}\right)\right]}{\int \frac{d^{3N}p\, d^{3N}q}{h^{3N}} \exp\left[-\beta\left(\frac{p_x^{(1)2}}{2m} + \tilde{H}\right)\right]}$$

$$= \frac{1}{2} kT$$

$\therefore$ similarly, any quadratic form $H = \alpha x_i^2 + \tilde{H}$

$$\langle \alpha x_i^2 \rangle = \frac{1}{2} kT$$

So if $H = \sum_{i=1}^{N} |\vec{p}_i|^2/2m$

$$\langle E \rangle = 3N\left(\frac{kT}{2}\right) \Rightarrow \varepsilon = \frac{\langle E \rangle}{N} = \frac{3}{2} kT$$

The Canonical Partition function can be simplified when the system can be subdivided into independent subsystems

$$Z = \sum_j e^{-\beta E_j}; \text{ if } j = \{k, l\}; \quad E_j = E_k + E_l$$

$$Z = \sum_k \sum_l e^{-\beta(E_k + E_l)} = Z_1 \cdot Z_2$$

$$= \left(\sum_k e^{-\beta E_k}\right)\left(\sum_l e^{-\beta E_l}\right), \quad j = \{k, l\}$$

$\Rightarrow$ distinguishable

Example: Translational, rotational + vibrational degrees of freedom of molecules in a gas, or magnetic spin system and thermal vibrations of a magnetic crystal

Revisit the spin $\frac{1}{2}$ system: $E_j = \sum_{i=1}^{N} m_i \, \varepsilon_B$

$$Z = \sum_{\{E_j\}} g(E_j)\, e^{-\beta E_j}, \quad g(E_j) = \# \text{ of ways of } \cancel{\text{finding}}$$

distributing the spins in $N_+ \uparrow$ and $N_- \downarrow$

$$= \sum_{\{N_+, N_-\}} \frac{N!}{N_+!\, N_-!}\, e^{-\beta \varepsilon_B (N_- - N_+)}$$

$$= \sum_{N_+ = 0}^{N} \frac{N!}{N_+!\,(N - N_+)!}\, e^{2\beta \varepsilon_B N_+}\, e^{-\beta \varepsilon_B N}$$

(Binomial sum)

$$Z = e^{-\beta \varepsilon_B N}\left[1 + e^{2\beta \varepsilon_B}\right]^N$$

$$Z = 2^N (\cosh \beta \varepsilon_B)^N$$

or we could have written Z as ~~#~~ if each spin was connected to an independent energy reservoir.

$$E_j = \sum_{i=1}^{N} \varepsilon_i \quad ; \quad Z = \sum_{\{j\}} e^{-\beta E_j} = \sum_{\{\varepsilon_1\},\{\varepsilon_2\},\dots\{\varepsilon_N\}} e^{-\beta \varepsilon_1} e^{-\beta \varepsilon_2} \dots e^{-\beta \varepsilon_N}$$

$$= \prod_{i=1}^{N} \left[e^{-\beta \varepsilon_B} + e^{+\beta \varepsilon_B} \right] = 2^N (\cosh \beta \varepsilon_B)^N$$

$$-\frac{F}{T} = k \ln Z = Nk \ln 2 + Nk \ln(\cosh \beta \varepsilon_B)$$

$$U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{N \varepsilon_B \sinh \beta \varepsilon_B}{\cosh \beta \varepsilon_B} = -N \varepsilon_B \tanh \beta \varepsilon_B$$

$$S = -\frac{\partial F}{\partial T}\bigg|_{V,N} = Nk \ln 2 + Nk \ln[\cosh(\beta \varepsilon_B)] + kT \left[\frac{N \sinh \beta \varepsilon_B}{\cosh \beta \varepsilon_B} \left(-\frac{\varepsilon_B}{kT^2} \right) \right]$$

$$\therefore \frac{S}{Nk} = \ln[2 \cosh \beta \varepsilon_B] - \frac{\varepsilon_B}{kT} \tanh \beta \varepsilon_B$$

Paramagnetism (Quantum Treatment)

dipoles in a magnetic field tend to align w/ field. Thermal fluctuations inhibits that.

$\mathcal{H} = -\vec{\mu}\cdot\vec{B} = -g\frac{\mu_B}{\hbar}\vec{J}\cdot\vec{B}$, where $\vec{J} = \vec{L}+\vec{S}$

$\mu = \mu_S + \mu_L = \frac{\mu_B}{\hbar}(2S + L)$ (total Magnetic moment)

Aligning z-direction to that of $\vec{B}$, we find,

$$\varepsilon_m = -g\mu_B B_z m, \quad \text{with } m = -J, -J+1, \ldots, J-1, J$$

where $g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$ is Landé's g-factor accounts for the projection of magnetic moment along $\vec{J}$.

$$Z = \sum_{\{\varepsilon_{n_i}\}} e^{-\beta\sum_{i=1}^{N}\varepsilon_{n_i}}$$

$$= \prod_{i=1}^{N}\sum_{\{\varepsilon_{n_i}\}} e^{-\beta\varepsilon_{n_i}} = \prod_{i=1}^{N}\sum_{m=-J}^{J} e^{+\beta g\mu_B B_z\cdot m}$$

define $\varepsilon_0 = g\mu_B B$

$$= \prod_{i=1}^{N}\sum_{m=-J}^{J} e^{\beta\varepsilon_0 m} = \left[\sum_{m=-J}^{J} e^{\beta\varepsilon_0 m}\right]^N$$

$$\sum_{m=-J}^{J} e^{\beta\varepsilon_0 m} = e^{-\beta\varepsilon_0 J}\sum_{m=0}^{2J} e^{\beta\varepsilon_0 m}$$

$$\sum_{m=0}^{2J} X^m = \frac{1 - X^{2J+1}}{1 - X}$$

$$\therefore Z = e^{-\beta N\varepsilon_0 J}\frac{\left[1 - e^{\beta\varepsilon_0(2J+1)}\right]^N}{\left(1 - e^{+\beta\varepsilon_0 J}\right)^N}$$

$$Z = \frac{e^{-\beta N \varepsilon_0 J} \, e^{(2J+1)\beta\varepsilon_0 N/2}}{e^{+\beta\varepsilon_0 J/2 \, N}} \left[\frac{\sinh\left(\frac{2J+1}{2}\beta\varepsilon_0\right)}{\sinh \beta\varepsilon_0/2} \right]^N$$

$$-\beta N\varepsilon_0 J + \beta N \varepsilon_0 J + \beta N \varepsilon_0 \frac{J}{2} - \beta N \varepsilon_0 \frac{J}{2} = 0$$

$$\therefore Z = \left[\frac{\sinh \frac{2J+1}{2}\beta\varepsilon_0}{\sinh \beta\varepsilon_0/2} \right]^N, \text{ a function of } T, N \text{ and } B$$

To find the magnetization, we do the same tricks as before: [$Z(B)$, not $Z(M)$]

$$S' = S + \frac{\vec{B}\cdot\vec{M}}{T}, \quad -\frac{F'}{T} = -\frac{F}{T} + \frac{\vec{B}\cdot\vec{M}}{T}$$

$$d\left(-\frac{F'}{T}\right) = -U' d\left(\frac{1}{T}\right) + M \cdot d\left(\frac{B}{T}\right) - \frac{\mu}{T} dN + \frac{P}{T} dV$$

$$\therefore M : \left.\frac{d(-F'/T)}{d(B/T)}\right|_{\frac{1}{T}, N, V} \quad \text{vary } \beta B \text{, holding } \beta \text{ constant.}$$

define $X = \beta\varepsilon_0 = \beta B_z g \mu_B$, so

$$M_z = \frac{\partial \ln Z}{\partial (B/T)} = \frac{\partial \ln Z}{\partial (\beta B)} = \left.\frac{\partial \ln Z}{\partial x}\right|_{\frac{1}{T}} \frac{\partial x}{\partial (\beta B)}$$

$$= \left.\frac{\partial \ln Z}{\partial x}\right|_{\frac{1}{T}} g \mu_B$$

$$M_z = N g \mu_B \frac{\partial}{\partial x} \ln \left[\frac{\sinh \frac{2J+1}{2} x}{\sinh \frac{x}{2}} \right]$$

$$= N g \mu_B \frac{\sinh \frac{x}{2}}{\sinh \frac{2J+1}{2} x} \left\{ \frac{\left(\frac{2J+1}{2}\right) \mathrm{ch} \frac{2J+1}{2} x}{\mathrm{sh}\, x/2} - \frac{\frac{1}{2} \mathrm{ch} \frac{x}{2} \mathrm{sh} \frac{2J+1}{2} x}{(\mathrm{sh}\, x/2)^2} \right\}$$

$$M_z = \frac{N g \mu_B}{2} \left\{ (2J+1) \mathrm{ch} \frac{2J+1}{2} x - \coth\left(\frac{x}{2}\right) \right\}$$

$$= N g \mu_B J \, B_J(x)$$

"Brillouin function" $B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2} x - \frac{1}{2J} \coth \frac{x}{2}$

Define the magnetic susceptibility $\chi = \frac{\partial M}{\partial B_z}$

$$\chi = -N g \mu_B \left\{ \left(\frac{2J+1}{2}\right)^2 \mathrm{cosech}^2 \frac{2J+1}{2} x - \left(\frac{1}{2}\right)^2 \mathrm{cosech}^2 \frac{x}{2} \right\} \frac{\partial x}{\partial B_z}$$

$$= -\frac{N (g \mu_B)^2}{kT} \left\{ \left(\frac{2J+1}{2}\right)^2 \mathrm{cosech}^2 \frac{2J+1}{2} x - \left(\frac{1}{2}\right)^2 \mathrm{cosech}^2 \frac{x}{2} \right\}$$

We can expand χ for small fields: x small:

$\mathrm{cosech}\, \epsilon = \frac{1}{\epsilon} - \frac{\epsilon}{6} + \dots$ $\left(\mathrm{cosech} = \frac{1}{\sinh}\right)$

$$\chi \to -\frac{N (g \mu_B)^2}{kT} \left\{ \cancel{\frac{1}{x^2} - \frac{1}{x^2}} - \frac{1}{3}\left(\frac{2J+1}{2}\right)^2 + \frac{1}{3}\left(\frac{1}{2}\right)^2 \right\}$$

$$\simeq + \frac{N (g \mu_B)^2}{kT} \left\{ \frac{1}{4.3} \left[4J^2 + 4J + 1 - 1 \right] \right\}$$