

1.) particle in a box (3D)

eigenfunctions: $\Psi(\vec{n}; \vec{r}) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$

eigenenergies: $E_{\vec{n}} = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$

density matrix (modifying results of derivation in book section 5.5)

$$\begin{aligned} \text{def } \rho &= \langle \vec{r}_1, \vec{r}_2, \vec{r}_3 | \hat{\rho} | \vec{r}'_1, \vec{r}'_2, \vec{r}'_3 \rangle \\ &= \sum_E \langle \vec{r}_1, \vec{r}_2, \vec{r}_3 | E \rangle e^{-\beta E} \langle E | \vec{r}'_1, \vec{r}'_2, \vec{r}'_3 \rangle \\ &= \sum_{\vec{N}} \langle \vec{r}_1, \vec{r}_2, \vec{r}_3 | E(\vec{N}) \rangle e^{-\beta E(\vec{N})} \langle E(\vec{N}) | \vec{r}'_1, \vec{r}'_2, \vec{r}'_3 \rangle \\ \vec{N} &= n_x^{(1)} n_y^{(1)} n_z^{(1)} \dots n_x^{(3)} n_y^{(3)} n_z^{(3)} \\ E(\vec{N}) &= E_{\vec{n}_1} + E_{\vec{n}_2} + E_{\vec{n}_3} \\ &= \frac{1}{3!} \sum_{\vec{N}} \left[\begin{matrix} \psi(\vec{n}_1, \vec{r}_1) \dots \psi(\vec{n}_1, \vec{r}_3) \\ \vdots \\ \psi(\vec{n}_3, \vec{r}_1) \dots \psi(\vec{n}_3, \vec{r}_3) \end{matrix} \right] e^{-\beta(E_{\vec{n}_1} + E_{\vec{n}_2} + E_{\vec{n}_3})} \\ &\quad \left[\begin{matrix} \psi(\vec{n}_1, \vec{r}'_1) \dots \psi(\vec{n}_1, \vec{r}'_3) \\ \vdots \\ \psi(\vec{n}_3, \vec{r}'_1) \dots \psi(\vec{n}_3, \vec{r}'_3) \end{matrix} \right] \end{aligned}$$

sum over $\vec{N} \Rightarrow$ sum over distinct energies

switch to $\sum_{\vec{n}_1, \vec{n}_2, \vec{n}_3}$

$$= \frac{1}{(3!)^2} \sum_{\vec{n}_1, \vec{n}_2, \vec{n}_3} \left[\begin{matrix} \dots \end{matrix} \right] e^{-\beta(E_{\vec{n}_1} + E_{\vec{n}_2} + E_{\vec{n}_3})} \left[\begin{matrix} \dots \end{matrix} \right]$$

for fermions $\left[\begin{matrix} \dots \end{matrix} \right] \Rightarrow$ determinant

for bosons $\left[\begin{matrix} \dots \end{matrix} \right] \Rightarrow$ permanent

$$= \frac{1}{3!} \left[\begin{matrix} \langle \vec{r}_1 | \psi^{(1)} | \vec{r}'_1 \rangle \dots \langle \vec{r}_1 | \psi^{(n)} | \vec{r}'_3 \rangle \\ \vdots \\ \langle \vec{r}_3 | \psi^{(1)} | \vec{r}'_1 \rangle \dots \langle \vec{r}_3 | \psi^{(n)} | \vec{r}'_3 \rangle \end{matrix} \right]$$

where: $\langle \vec{r}_i | \psi^{(n)} | \vec{r}'_j \rangle = \langle \vec{r}_i | e^{-\beta \hat{H}} \psi^{(n)} | \vec{r}'_j \rangle = \sum_{\vec{n}} \langle \vec{r}_i | \vec{n} \rangle e^{-\beta E_{\vec{n}}} \langle \vec{n} | \vec{r}'_j \rangle$

in the high-T limit sum over $\vec{n}$ becomes an integral

$$\langle \vec{r} | S^{(1)} | \vec{r}' \rangle = \int_{-L}^L \int_{-L}^L \int_{-L}^L dx_y dz \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_x \pi x'}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_y \pi y'}{L}\right) \\ \sin\left(\frac{n_z \pi z}{L}\right) \sin\left(\frac{n_z \pi z'}{L}\right) \exp\left[-\frac{\beta \hbar^2 \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)\right]$$

$$= \mathcal{V} S_x(x, x') S_y(y, y') S_z(z, z')$$

$$S_x(x, x') = \frac{2}{L} \int_{-\infty}^{\infty} dn_x \left(\frac{e^{\frac{i n_x \pi x}{L}} - e^{-\frac{i n_x \pi x}{L}}}{2i} \right) e^{-A n_x^2} \left(e^{\frac{i n_x \pi x'}{L}} - e^{-\frac{i n_x \pi x'}{L}} \right)$$

$$= f(x+x') + f(-x-x') - f(x-x') - f(x'-x)$$

$$f(x) = -\frac{1}{2L} \int_{-\infty}^{\infty} \exp\left(-A n_x^2 + \frac{2i n_x \pi y}{L} + \frac{i^2 \pi^2 y^2}{4L^2} - \frac{i^2 \pi^2 y'^2}{4L^2}\right) dn_x \\ \left(A = \frac{\beta \hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \right)$$

$\Rightarrow$

$$= -\frac{1}{2L} \int_{-\infty}^{\infty} dx_x \exp\left[-A \left(n_x^2 - \frac{2i n_x \pi y}{L} + \frac{i^2 \pi^2 y^2}{4L^2} - \frac{i^2 \pi^2 y'^2}{4L^2}\right)\right]$$

$$= -\frac{1}{2L} \exp\left[-\frac{\pi^2 y^2}{4L^2 A}\right] \sqrt{\frac{\pi}{A}}$$

$$= -\frac{1}{2L} \sqrt{\frac{2\pi m}{\beta \hbar^2}} \exp\left[-\frac{\pi^2 y^2 2m}{4L^2 \beta \hbar^2}\right]$$

$$= -\frac{1}{2L}$$

$$= -\frac{4 \sqrt{2\pi m}}{h \beta} \exp\left[-\frac{m y^2}{2\beta \hbar^2}\right]$$

$$S_x(x, x') = \frac{2}{h} \sqrt{\frac{2\pi m}{\beta}} \left[\exp\left[-\frac{m(x-x')^2}{2\beta \hbar^2}\right] - \exp\left[-\frac{m(x+x')^2}{2\beta \hbar^2}\right] \right]$$

$$\langle \vec{r} | S^{(1)} | \vec{r}' \rangle = S_x(x, x') S_y(y, y') S_z(z, z')$$

partition function

~~Q~~

for bosons: $- \beta [\epsilon(\vec{n}_1)] \times 3$ $- \beta [\epsilon(\vec{n}_1) 2 + \epsilon(\vec{n}_2)]$

$$Q_B = \sum_{\vec{n}_1} e^{-\beta [\epsilon(\vec{n}_1)] \times 3} + \sum_{\vec{n}_1 \neq \vec{n}_2} e^{-\beta [\epsilon(\vec{n}_1) 2 + \epsilon(\vec{n}_2)]}$$

$$+ \sum_{\vec{n}_1 \neq \vec{n}_2 \neq \vec{n}_3} e^{-\beta [\epsilon(\vec{n}_1) + \epsilon(\vec{n}_2) + \epsilon(\vec{n}_3)]}$$

for fermions

$$Q_F = \sum_{\vec{n}_1 \neq \vec{n}_2 \neq \vec{n}_3} e^{-\beta [\epsilon(\vec{n}_1) + \epsilon(\vec{n}_2) + \epsilon(\vec{n}_3)]}$$

high T limit

$\beta \rightarrow 0 \rightarrow Q_B = Q_F$ since states which are missing from Q_F and present in Q_B will have vanishingly small weight

6.2 Bose-Einstein

6.2

$$Q = \sum_n e^{-\beta(E + \mu)n}$$

$$P(n) = \frac{e^{-\beta(E + \mu)n}}{Q}$$

$$\langle n \rangle = \sum_n P(n)n = \frac{1}{\beta Q} \frac{\partial Q}{\partial \mu}$$

$$\langle n^2 \rangle = \sum_n P(n)n^2 = \frac{1}{\beta^2 Q} \frac{\partial^2 Q}{\partial \mu^2}$$

$$\langle n^2 \rangle - \langle n \rangle^2 = \frac{1}{\beta^2 Q} \frac{\partial^2 Q}{\partial \mu^2} - \frac{1}{\beta^2 Q^2} \left(\frac{\partial Q}{\partial \mu} \right)^2$$

$$\frac{1}{\beta} \frac{\partial \langle n \rangle}{\partial \mu} = \frac{1}{\beta^2 Q} \frac{\partial^2 Q}{\partial \mu^2} - \frac{1}{\beta^2 Q^2} \left(\frac{\partial Q}{\partial \mu} \right)^2 = \langle n^2 \rangle - \langle n \rangle^2$$

expression for $\langle n^2 \rangle - \langle n \rangle^2$ for Bosons

$$Q = \frac{1}{1 - e^{-\beta(E + \mu)}}$$

$$\langle n \rangle = \frac{1}{\beta} \frac{1}{Q} \frac{\partial Q}{\partial \mu} = \frac{1}{\beta} \frac{(1 - e^{-\beta(E + \mu)})(-1)(-e^{-\beta(E + \mu)})}{(1 - e^{-\beta(E + \mu)})^2}$$

$$= \frac{e^{-\beta(E + \mu)}}{1 - e^{-\beta(E + \mu)}} = \frac{1}{e^{\beta(E + \mu)} - 1}$$

$$\begin{aligned} \langle n^2 \rangle - \langle n \rangle^2 &= \frac{1}{\beta} \frac{\partial}{\partial \mu} \left[\frac{1}{e^{\beta(E + \mu)} - 1} \right] = \frac{1}{\beta} \frac{+1}{(e^{\beta(E + \mu)} - 1)^2} e^{\beta(E + \mu)} (-1) \\ &= \frac{e^{\beta(E + \mu)}}{(e^{\beta(E + \mu)} - 1)^2} \end{aligned}$$

Fermi-Dirac

$$P(0) = \frac{1}{1 + e^{-\beta(E-\mu)}}$$

$$Q = 1 + e^{-\beta(E-\mu)}$$

$$P(1) = \frac{e^{-\beta(E-\mu)}}{1 + e^{-\beta(E-\mu)}}$$

$$\langle n \rangle = \sum_{n=0}^1 n P(n) = \frac{e^{-\beta(E-\mu)}}{1 + e^{-\beta(E-\mu)}} = \frac{1}{e^{\beta(E-\mu)} + 1}$$

$$\langle n^2 \rangle = \sum_{n=0}^1 n^2 P(n) = \frac{e^{-\beta(E-\mu)}}{1 + e^{-\beta(E-\mu)}} = \frac{e^{-\beta(E-\mu)}}{1 + e^{-\beta(E-\mu)}} = \frac{1}{e^{\beta(E-\mu)} + 1}$$

$$\langle n^2 \rangle - \langle n \rangle^2 = \frac{1 - (e^{\beta(E-\mu)} + 1)}{(e^{\beta(E-\mu)} + 1)^2} = \frac{e^{-\beta(E-\mu)}}{(e^{\beta(E-\mu)} + 1)^2}$$

$$\langle n \rangle = \frac{1}{\beta} \frac{\partial \ln Q}{\partial \mu} = \frac{1}{\beta} \frac{1}{1 + e^{-\beta(E-\mu)}} e^{-\beta(E-\mu)} \beta = \frac{1}{e^{\beta(E-\mu)} + 1}$$

$$\langle n^2 \rangle - \langle n \rangle^2 = \frac{1}{\beta} \frac{\partial \langle n \rangle}{\partial \mu} ?$$

$$\frac{1}{\beta} \frac{\partial \langle n \rangle}{\partial \mu} = \frac{1}{\beta} - \frac{(-1) e^{-\beta(E-\mu)}}{(e^{\beta(E-\mu)} + 1)^2} = \frac{e^{-\beta(E-\mu)}}{(e^{\beta(E-\mu)} + 1)^2}$$

M.B.

$$P(n) = \frac{e^{-\beta(E-\mu)n} / n!}{\exp[e^{-\beta(E-\mu)}]}$$

$$\sum_{n=0}^{\infty} P(n) n = \sum_{n=0}^{\infty} \frac{e^{-\beta(E-\mu)n}}{(n+1)!} \frac{1}{\exp[e^{-\beta(E-\mu)}]}$$

$$= e^{-\beta(E-\mu)} \sum_{n=0}^{\infty} \frac{e^{-\beta(E-\mu)(n-1)!}}{(n-1)!} = \frac{e^{-\beta(E-\mu)}}{\exp[e^{-\beta(E-\mu)}]}$$

$$\begin{aligned}
 \sum_{n=0}^{\infty} f(n) n^2 &= \sum_{n=0}^{\infty} \frac{e^{-\beta(E-\mu)n}}{n!} n^2 \frac{1}{\exp[\beta(E-\mu)]} \\
 &= \sum_{n=1}^{\infty} \frac{e^{-\beta(E-\mu)n}}{(n-1)!} + \sum_{n=1}^{\infty} \frac{e^{-\beta(E-\mu)n}}{(n-1)!} \\
 &\quad \frac{1}{\exp[\beta(E-\mu)]} \quad \frac{1}{\exp[\beta(E-\mu)]} \\
 &= \frac{e^{-\beta(E-\mu)}}{\exp[\beta(E-\mu)]} \sum_{n=2}^{\infty} \frac{e^{-\beta(E-\mu)(n-1)}}{(n-2)!} + \frac{e^{-\beta(E-\mu)}}{\exp[\beta(E-\mu)]} \sum_{n=1}^{\infty} \frac{e^{-\beta(E-\mu)(n-1)}}{(n-1)!} \\
 &= e^{-2\beta(E-\mu)} + e^{-\beta(E-\mu)}
 \end{aligned}$$

$$\begin{aligned}
 \langle n^2 \rangle - \langle n \rangle^2 &= e^{-\beta(E-\mu)} \\
 \frac{1}{\beta} \frac{\partial \langle n \rangle}{\partial \mu} &= e^{-\beta(E-\mu)} \quad \checkmark
 \end{aligned}$$

6.3

derive partition function

$$Q = \sum_{n=0}^l e^{-\beta(E-\mu)n}$$

$$Q = \frac{1-x^{l+1}}{1-x} \quad x = e^{-\beta(E-\mu)}$$

$$\langle n \rangle = \frac{1}{\beta} \frac{\partial \ln Q}{\partial \mu}$$

$$= \frac{1}{\beta} \frac{\partial \ln Q}{\partial x} \frac{\partial x}{\partial \mu}$$

$$\frac{\partial x}{\partial \mu} = e^{-\beta(E-\mu)} \quad \beta = x\beta$$

$$\langle n \rangle = x \frac{\partial \ln Q}{\partial x} = \tau \frac{1}{Q} \frac{\partial Q}{\partial x}$$

$$= \frac{x(1-x)}{1-x^{l+1}} \left[\frac{-(l+1)x^l}{1-x} + \frac{(1-x^{l+1})}{(1-x)^2} \right]$$

$$= \left[\frac{x}{1-x} - \frac{(l+1)x^{l+1}}{1-x^{l+1}} \right]$$

$$= \frac{1}{x^{-1}-1} - \frac{(l+1)}{(x^{-1})^{l+1}-1}$$

$$= \frac{1}{e^{\beta(E-\mu)}-1} - \frac{(l+1)}{e^{\beta(E-\mu)(l+1)}-1}$$

$$l=1 \quad \langle n \rangle = \frac{1}{e^{\beta(E-\mu)}-1} - \frac{2}{e^{2\beta(E-\mu)}-1} = \frac{e^{\beta(E-\mu)}-1}{(e^{\beta(E-\mu)}-1)(e^{\beta(E-\mu)}+1)} = 2$$

$$= \frac{1}{e^{\beta(E-\mu)}+1} \quad \text{Fermi-Dirac} \checkmark$$

$$l \rightarrow \infty \quad \langle n \rangle = \frac{1}{e^{\beta(E-\mu)}-1} \quad \text{Bose-Einstein} \checkmark$$

$$\sum_{n=0}^l x^n = F$$

$$\sum_{n=0}^l x^{n+1} = xF$$

$$\sum_{n=1}^{l+1} x^n = xF$$

$$x^{l+1} - 1 + F = xF$$

$$F(1-x) = 1-x^{l+1}$$

$$F = \frac{1-x^{l+1}}{1-x}$$

G.21

$$K(T) = \frac{q_{HD}^2}{q_{H_2} q_{D_2}}$$

$$q_{HD} = \left(\frac{2\pi m_{HD} kT}{h^2} \right)^{3/2} \left(\frac{T}{\Theta_{r,HD}} \right) \left(\frac{e^{-E_{v,HD}/2T}}{1 - e^{-E_{v,HD}/T}} \right) e^{D_e/kT}$$

$$q_{H_2} = \left(\frac{2\pi m_{H_2} kT}{h^2} \right)^{3/2} \left(\frac{T}{2\Theta_{r,H_2}} \right) \left(\frac{e^{-E_{v,H_2}/T}}{1 - e^{-E_{v,H_2}/T}} \right) e^{D_e/kT}$$

$$q_{D_2} = \left(\frac{2\pi m_{D_2} kT}{h^2} \right)^{3/2} \left(\frac{T}{2\Theta_{r,D_2}} \right) \left(\frac{e^{-E_{v,D_2}/T}}{1 - e^{-E_{v,D_2}/T}} \right) e^{D_e/kT}$$

J

~~K(T)~~ Θ_{r_2} = rotational temperature

$$\frac{h^2}{8\pi^2 I k_B}$$

$$I = \mu r_0^2$$

↑
reduced mass

Θ_v = vibrational temperature

$$\Theta_v = \frac{h\nu}{k_B}$$

$$\begin{aligned} K(T) &= \frac{\left(\frac{2\pi m_{HD} kT}{h^2} \right)^3}{\left(\frac{2\pi m_{H_2} kT}{h^2} \right)^{3/2} \left(\frac{2\pi m_{D_2} kT}{h^2} \right)^{3/2}} \frac{\left(\frac{T}{\Theta_{r,HD}} \right)^2}{\left(\frac{T}{\Theta_{r,H_2}} \right) \left(\frac{T}{\Theta_{r,D_2}} \right)} \frac{\left(\frac{e^{-E_{v,HD}/T}}{1 - e^{-E_{v,HD}/T}} \right)^2}{\left(\frac{e^{-E_{v,H_2}/T}}{1 - e^{-E_{v,H_2}/T}} \right) \left(\frac{e^{-E_{v,D_2}/T}}{1 - e^{-E_{v,D_2}/T}} \right)} \\ &= \frac{(m_{HD})^3}{m_{H_2}^{3/2} m_{D_2}^{3/2}} \frac{4 \Theta_{r,H_2} \Theta_{r,D_2}}{\Theta_{r,HD}^2} \times \left(\frac{e^{-\Theta_{v,HD}/2T}}{1 - e^{-\Theta_{v,HD}/2T}} \right) \left(\frac{1 - e^{-\Theta_{v,H_2}/T}}{e^{-\Theta_{v,H_2}/T}} \right) \left(\frac{1 - e^{-\Theta_{v,D_2}/T}}{e^{-\Theta_{v,D_2}/T}} \right) \end{aligned}$$

$$m_{D_2} = 2m_{H_2}$$

$$m_{HD} = \frac{3}{2}m_{H_2}$$

$$K(T) = \left(\frac{3}{2}\right)^3 \frac{1}{2^{3/2}} \times \frac{4 \Theta_{r,H_2} \Theta_{r,D_2}}{\Theta_{r,HD}^2} e^{-\frac{1}{kT} [2G_{v,HD} - G_{v,H_2} - G_{v,D_2}]} \\ \times \frac{[1 - e^{-G_{v,H_2}/kT}][1 - e^{-G_{v,D_2}/kT}]}{[1 - e^{-G_{v,HD}/kT}]^2}$$

$$\Theta_{r,H_2} = \frac{h^2}{2k_B \mu_{H_2} r^2}$$

equilibrium bond-lengths (r) are the same for H_2 , D_2 , HD
(within Born-Oppenheimer approximation)

$$\frac{\Theta_{r,H_2} \Theta_{r,D_2}}{\Theta_{r,HD}^2} = \frac{\mu_{HD}^2}{\mu_{H_2} \mu_{D_2}} = \frac{24}{9} \frac{m_H^2}{m_H^2} = \frac{8}{9}$$

$$\mu_{HD} = \frac{m_H(2m_H)}{m_H + 2m_H} = \frac{2}{3}m_H$$

$$\mu_{D_2} = \frac{(2m_H)(2m_H)}{2m_H + 2m_H} = m_H$$

$$\mu_{H_2} = \frac{m_H^2}{2m_H} = \frac{m_H}{2}$$

$$K(T) = \left(\frac{9}{8}\right)^{3/2} \times \frac{8}{9} 4 e^{-\frac{1}{kT} [2G_{v,HD} - G_{v,H_2} - G_{v,D_2}]} \\ \times \frac{[1 - e^{-G_{v,H_2}/kT}][1 - e^{-G_{v,D_2}/kT}]}{[1 - e^{-G_{v,HD}/kT}]^2}$$

$$\Theta_{v,HD} = h\omega$$

$$\omega = \sqrt{\frac{k}{\mu}}$$

$$= \frac{h\sqrt{k}}{\sqrt{\mu}}$$

$$\omega \uparrow \rightarrow \frac{9}{8} K(T) \rightarrow 9 \cdot \left(\frac{9}{8}\right)^{1/2}$$

$$\omega \rightarrow T \rightarrow \infty$$

$$K(T) = \left(\frac{g}{8}\right)^{3/2} \times \frac{8}{g} \times 4 \times \frac{\Theta_{v,H_2} \Theta_{v,D_2}}{\Theta_{v,HD}^2}$$

$$\Theta_{v,H_2} = h \sqrt{\frac{h}{\mu_{H_2}}}$$

$$K(T) = \left(\frac{g}{8}\right)^{3/2} \left(\frac{8}{g}\right) \times 4 \sqrt{\frac{\mu_{HD}^2}{\mu_{H_2} \mu_{D_2}}}$$

$$= 4$$