

27/1/06

Quantum Statistical Mechanics of ideal gas in a periodic box of lengths (L_1, L_2, L_3)

Single particle energy eigenstates:

$$e^{2\pi i(k_1 x/L_1 + k_2 y/L_2 + k_3 z/L_3)}, \quad k_1, k_2, k_3 \text{ integers}$$

$$\text{Energy} = \frac{\hbar^2}{2m} \cdot 4\pi^2 \left(\frac{k_1^2}{L_1^2} + \frac{k_2^2}{L_2^2} + \frac{k_3^2}{L_3^2} \right)$$

$$\text{Momentum } \vec{p} = (p_x, p_y, p_z)$$

$$= \left(\frac{2\pi\hbar k_1}{L_1}, \frac{2\pi\hbar k_2}{L_2}, \frac{2\pi\hbar k_3}{L_3} \right)$$

$$e(\vec{p}) = \frac{\vec{p}^2}{2m}$$

Basis of N -particle state

→ (Antisymmetrized product of the basis of single particle states

Specify the occupation number $n(\vec{p})$ for each \vec{p} .

$$n(\vec{p}) = 0, 1 \text{ for fermions}$$

$$= 0, 1, 2, 3, \dots \text{ for bosons}$$

$$\sum_{\vec{p}} n(\vec{p}) = N \rightarrow \text{total no. of particles}$$

$$\text{e.g.} \rightarrow \psi_{\vec{p}_1}(\vec{x}_1) \psi_{\vec{p}_2}(\vec{x}_2) \pm \psi_{\vec{p}_2}(\vec{x}_1) \psi_{\vec{p}_1}(\vec{x}_2)$$

$$n(\vec{p}_1) = 1$$

$$n(\vec{p}_2) = 1$$

$$n(\vec{p}) = 0$$

if $\vec{p} \neq \vec{p}_1, \vec{p}_2$

which particle has momentum \vec{p} is not relevant once you specify $n(\vec{p})$ because you have symmetrized or antisymmetrized the wave fns

$$\sum_{\vec{p}} n(\vec{p}) e(\vec{p}) = E$$

$$\sum_{\{\vec{p}\}} \rightarrow \text{quantum states}$$

$$\sum_{\vec{p}} \rightarrow \sum_{n(0,0,0)} \sum_{n(\frac{2\pi k_1}{L_1}, 0, 0)} \sum_{n(0, \frac{2\pi k_2}{L_2}, 0)} \dots$$

this sum is without the constraint $\sum_{\vec{p}} n(\vec{p}) = N$

Microcanonical ensemble (for small ΔE)

infinite sum

Kronecker delta

$$\Omega(E, N) \Delta E = \sum_{\{n(\vec{p})\}} \left[\delta_{\sum_{\vec{p}} n(\vec{p}), N} \Theta\left(\sum_{\vec{p}} n(\vec{p}) e(\vec{p}) - E\right) \Theta\left(E + \Delta E - \sum_{\vec{p}} n(\vec{p}) e(\vec{p})\right) \right]$$

$$S(E, N) = k \ln \Omega(E, N)$$

→ Difficult to calculate

Canonical ensemble

the sum is diff. to perform bco of the constraint

$$Z(\beta, N) = \sum_{\{n(\vec{p})\}} \sum_{\vec{p}} e^{-\beta \sum_{\vec{p}} n(\vec{p}) e(\vec{p})}$$

$$F(\beta, N) = -kT \ln Z(\beta, N)$$

$$\beta = 1/kT$$

Grand canonical ensemble

$$\mathcal{Q}(\beta, \mu) = \sum_{\{n(\vec{p})\}} e^{\beta \mu \sum_{\vec{p}} n(\vec{p}) - \beta \sum_{\vec{p}} n(\vec{p}) e(\vec{p})}$$

$$= \sum_{\{n(\vec{p})\}} \prod_{\vec{p}} e^{\beta \mu n(\vec{p}) - \beta e(\vec{p}) n(\vec{p})}$$

