I) ROADMAP

4 PARTS to equilibrium STAT mech modeling ①

PART 1) Guess/work up a [Q. mech.] model of your system

8/27/23

A) so far, we've focused on NON-interacting systems [weak interparticle forces]

PART 2) Use model calc. quantum states/E_j for your system: energies

A) $\boxed{E_j}$ = j^{th} eigenenergy for N ptcl system

⊕ interacting & non-int systems

~~B) E~~

B) $\boxed{\epsilon_s}$ = s^{th} eigen energy for single ptcl.

⊕ non-int. sys.

WE'LL DO PTS 1 & 2 FOR N-ptcl system of non-interacting DIATOMIC molecules

~~PART~~ 3) ~~Derive statistical mech. model.~~

~~A) key objects/ QTYS~~

~~a) PARTIT.~~

PART 3 | DERIVE STAT mech model - NON-INTERACTING SYSTEMS ②

A)

A | compare

$$\boxed{l_{ptcl} = \left(\frac{V}{N}\right)^{1/3}}$$

to

$$\boxed{X_{S.B.} = \lambda_{\text{DeBroglie}} \sim \frac{h}{\sqrt{m k_B T}}}$$

to determine whether QUANTUM statistics or classical statistics reqd.

crucial diagnostic step

IF

$$\boxed{\frac{\left(\frac{V}{N}\right)^{1/3}}{\frac{h}{\sqrt{m k_B T}}} = \frac{l_{ptcl}}{X_{SB}} \gg 1}$$

⇒ QUANTUM effects small

⇒ use classical statistics

IF

$$\boxed{\frac{\left(\frac{V}{N}\right)^{1/3}}{\frac{h}{\sqrt{m k_B T}}} = \frac{l_{ptcl}}{X_{SB}} \ll 1}$$

⇒ QUANTUM effects DOMINANT → use QUANTUM statistics

3) equil. STAT mech model – noninteracting systems ~~config~~ ptcls of N INDISTINGUISH ptcls

B) KEY STATISTICAL PARAMETERS – QUANTUM STATISTICS

a) PARTITION FN = $\tilde{\Sigma}$

$$\tilde{\Sigma} = \sum_{j,N} e^{-\beta E_j} e^{\beta \mu N}$$

N = no. of ptcls in sys.
E_j = jth Q. state for system

b) AVG. NO. of ptcls in single ptcl. state ϵ_s:

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1} \quad \text{BOSONS}$$

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1} \quad \text{FERMIONS}$$

C) KEY STATISTICAL PARAMETER – CLASSICAL STATISTICS

a) PARTION FUNCTION

ptcls are id ass'd to be disting

~~takes~~ accts for ptcl indisting

$$Q_{\text{proper QUANTUM MODEL}} = \frac{Z_{\text{classical}}}{N!}$$

Lagrange mult

where:

i) $\boxed{Q_{\text{proper QUANTUM MODEL}}}$ (properly) ACCOUNTS FOR THE ESSENTIAL INDISTINGUISHABILITY OF THE PTCLS IN THE N-PTCL SYSTEM

ii) $\boxed{Z_{\text{classical}}}$ IS DERIVED BY (IMPLICITLY) ASSUMING THAT THE N-PTCLS ARE DISTINGUISHABLE

STEP 4 USE $\boxed{Q_{\text{proper quantum}}}$ (under condition where classical statistics apply) OR Σ (under conds where QUANTUM stats. apply) TO PREDICT MACROSCOPIC EQUIL. THERMO. OF YOUR SYSTEM

II) ~~III)~~ Details re. Hill's arg. that classical stat applies when $N_{Q\,\text{avail}} \gg N$ proof 5

$\frac{\Phi}{V} \sim \frac{\pi}{6}\left(\frac{k_B T\, 8\, m}{h^2}\right)^{3/2} = \frac{1}{m^3}$

no. of translational Q states w/ $\epsilon_s \lesssim k_B T$

$\epsilon = \epsilon(n_x, n_y, n_z) \Rightarrow \sim k_B T$

$m = \frac{30}{\cancel{24}\,\text{kg}}{6(10^{26})} \sim 5(10^{-26})\,\text{kg}$

MW = 30 kg/kgmol

$\frac{\text{kg}}{J^2 s^2} \doteq \frac{\text{kg}}{\left(\frac{\text{kg}\, m^2}{s^2}\right) s^2}$

$n_x, n_y, n_z \geq 1$

$\Phi \sim (0.5)(27)\left[\frac{\overbrace{(1.24)(10^{-23})}^{k_B}\, 3(10^2)\,(8)(5)(10^{-26})}{(36)(10^{-68})}\right]^{3/2}$ T = 300K

Likely similar situation for phonons

$(14)\left(\frac{20}{36}\right)^{3/2}(10^{21})^{3/2}$ $(1/2)^{3/2}$

true ⇓ $\frac{l_{\text{ptcl}}}{\lambda_{\text{sc}}} \gg 1$

$\frac{\Phi}{V} \sim (2)(30)(10^{30})\,(10^{3/2})(10^{38})$ $\frac{\text{translational states}}{m^3}$ @ T = 300K

N/V : a) $V = 1\,m^3$ b) T = 300K c) P = 1 atm

$\therefore \frac{\Phi/V}{N/V} \sim 2(10^6) \gg 1$

$\therefore \boxed{n = \frac{PV}{RT}} \sim \frac{(1\,\text{Atm})(1\,m^3)}{\cancel{0.082}\; 8.314\,\frac{\text{Nm}}{\text{mol K}}\; 300\text{K}}$ $10^5\,N/m^2$

$= \frac{10^5}{(24)(10^2)} \sim (0.04)10^3 \sim 40$ mol

e) $\therefore \frac{N}{V} = \frac{nN_A}{V} = \frac{(40)(6)(10^{23})}{1} = \boxed{2.4(10^{25})}$ ptcls / m³