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IN-CLASS NOTES 3/29/23

EXAMPLE N-monatomic molecules in Heated BOX

Ref: 4.4 Hill's

I) FIRST MODEL ⇒ NO INTERNAL D.O.F.

II) (I) 2nd " MODEL 2 ⇒ ATOMS; taking into account nuclear Q. Dynamics ⊕ Q. electron dynamics ~~atomic~~ about nuclei

M

⊕ translational Quantum energy of Atom C.O.M

we've done this

B) 1) $H_{ATOM} = H_{nucleus} + H_{el.} + H_{translation\ c.o.m}$

a) RANDOM DYNAMICS of 3 modes statistical ~~[struck]~~ indep.

C) Temp of BOX/GAS is high enough and/or N/V small enough that Quantum stat mechs ~~can~~ approx'd by classical limit

D) For GC. high T / low den

$Q_{QUANTUM}$ (rigorous) $= \frac{Q_{classical}}{N!}$

(2,3) Q_{sys} (master) $\Leftarrow$ ~~Q~~ $Q_{classical} = \frac{(q_{ATOM})^N}{N!}$

(+) N exponent ⇔ random

ASSUMP 2? dynamics of each atom is stat. indep

(+) N! → proven in upcoming lecture

(+) Hill

(+) GIBB'S correction

(3) q_{ATOM}

a) since (3.1) $M_{ATOM} = M_{nuclear} + M_{elect} + M_{trans\ C.o.m}$

(b) then (3.2) $\hat{H}_{ATOM} |\psi_{ATOM}\rangle = E_{ATOM} |\psi_{ATOM}\rangle$

c) ~~(b) to~~ (3.1) allows factoring (3.2):

S.G. nucleus (c1) $\hat{H}_{nuc} |\psi_{nuc}\rangle = \epsilon_{nuc} |\psi_{nuc}\rangle$??

S.G. electron (c2) $\hat{H}_{elec} |\psi_{elec}\rangle = \epsilon_{elec} |\psi_{elec}\rangle$ ← Bienetroder

" C.o.M. (c3) $\hat{H}_{trans} |\psi_{trans}\rangle = \epsilon_{trans} |\psi_{trans}\rangle$ ← Done!

d) (c1) ⇒ $\epsilon_{N_1}, \epsilon_{N_2} \ldots$

(c2) ⇒ $\epsilon_{e_1}, \epsilon_{e_2} \ldots$

(c3) → $\epsilon_{t_1}, \epsilon_{t_2} \ldots$

F) $$\epsilon_{ATOM_{ijk}} = \epsilon_{n_i} + \epsilon_{e_j} + \epsilon_{t_k} \quad (4.1)$$

H) ALSO, BECAUSE we're assuming stat. indep. dynamics

$$q_{ATOM} = q_{NUC}\, q_{elec}\, q_{tran}$$

$$q = q_n\, q_e\, q_t \quad (4.2)$$

III q_n = partition fn nuclear dynamics

A) $$q_n = \sum_{s=1}^{\Lambda} \omega_{n_s} e^{-\beta\epsilon_{n_s}} \quad (4.3)$$

B) $^1H,\ ^2H$

① ω_{n_s} = no. of distinct nuclear quantum states having Q. energy ϵ_{n_s}

B] Hill: preliminary guess:

assume ground state energy for a ptcl = ptcl en. @ T = 0K

B] Hill:

i) $\epsilon_{n_1} \cong 0$

iii) $S(0K) = k_B \ln \Omega_N$ ⇓ ω_{n_1} ⇓ $S_{nuclei}(0K) \neq 0$

∴ nuclei's mod/n.

ii) ω_{n_1} = not 0

AS, DS perfect crystals

have 0 degeneracy

@ 0K ⇐ there's only

1 unique Q state

@ 0K $(T = 0K)$

∴ $S_{crystals} = k_B \ln \Omega_{gs} = \underline{0}$

nuclei cont'd (Mill)

$$\epsilon_{n_2} = O(10^6 \, eV)$$

$$1 \, eV \cong 10^4 \, K$$

To get nuclei excited from $\epsilon_{n_1} (\approx 0)$ to ϵ_{n_2} thermally / collisionally reqs $T \sim O(10^{10} K)$!!

∴ a) $$q_n = \sum_{s=1} w_{n_s} e^{-\beta \epsilon_{n_s}}$$

(c(1)) b) $$q_{nuclear} = w_{n_1} e^{-\beta \epsilon_{n_1}} + w_{n_2} e^{-\beta \epsilon_{n_2}} + \ldots$$

$\beta \epsilon_{n_2} \sim \frac{k_B (10^{10} K)}{k_B (10^3 K)}$

e^{-10^7}

c) For temps $\lesssim 10^4 K$

$$p_n(\epsilon_{n_2}) \Leftrightarrow P_{Boltzmann}(\epsilon_{n_2})$$

(7)

where $P_{Bottom}(\epsilon_{n_2}) = \frac{e^{-\beta \epsilon_{n_2}}}{\xi_{full}}$. (→ tiny)

(f) $= \frac{e^{-10^7}}{\omega_{n_1}}$

$p(\epsilon_{n_2}) \to 0$

(f) $P_{Boltz}(\epsilon_{n_1}) = \frac{e^{-\beta \epsilon_{n_1}}}{\sim e^{-\beta \epsilon_{n_1}}} = 1$

(e) Temps $\Rightarrow \ll 10^{10}$ K
all atomic nuclei
are in their
ground state

IV) q_e

A) physical factoids

Alkali Atoms K, Li, etc

$\Delta\epsilon_e = \epsilon_{e_2} - \epsilon_{e_1}$

first exci (↑ ϵ_{e_2})

ground state elec. cloud con. (↑ ϵ_{e_1})

$\Delta\epsilon_e \sim 1.5\,eV \Leftrightarrow 15000K$

Halogens Ar, Kr, Xe, Ne

$\Delta\epsilon = 10-20\,eV \Leftrightarrow$

$10^5 - 2(10^5)\,K$

Halogens F, Cl, etc

$\Delta\epsilon = 0.05\,eV - 1\,eV$

$0.05\,eV \Updownarrow 600K$

$1\,eV \Updownarrow 10^4\,K$

PREP NOTES V.1

(A1)

1) $H_{atom}^{mill} = H_{nuc} + H_{ele} + H_{trans}$

~~$= H_t + H_{n\cdot}$~~

2) classical limit

$Q_{proper} = \frac{Q_{classical}}{N!}$

3) $Q = (q_{atom})^N$

4) $q_{atom} = q_t \, q_n \, q_e$

Boltzmann

$q_e = \sum_{s=0}^{w_{e_s}} e^{-\beta \epsilon_{e_s}}$

$q_t = \sum_{s=0}^{w_{t_s}} e^{-\beta \epsilon_{t_s}}$

$q_n = \sum_{s=0}^{w_{n_s}} e^{-\beta \epsilon_{n_s}}$

$\Leftrightarrow O(10^{10} K)$

$10^6 eV \Leftrightarrow$

5) $|\epsilon_{n_1} - \epsilon_{n_0}| \Leftrightarrow 10^{10} K \Leftrightarrow$ nucleus stays in GS, temps for lnuc

5a) ⊕ THERE'S A NON UNIT degeneracy → w_n

6) MANY ATOMS

ALKALI metals Li, K etc

$|\epsilon_{e_1} - \epsilon_{e_0}| \Leftrightarrow O(1.5eV) \Leftrightarrow O(15,000K)$ normal $\Leftrightarrow 10^3 K \Leftrightarrow$

Alkali metals

~~⊕ : q_n =~~

Inert gases Ar, Ne, Kr, Xe

$\epsilon_{e_1} - \epsilon_{e_0} \Leftrightarrow O(10-20 eV) \Leftrightarrow T = 10-20K$

$\epsilon_{e_1} - \epsilon_{e_0} \sim O(0.05eV$ to $1eV)$

$\Updownarrow$ 500K $\quad \Updownarrow$ $10^4 K$

Halogens

#2

$q_n = w_n$

ASIDE on degeneracy: when multiple distinct states have same energy

~~microscopic~~ system = part. can

example: see

translational

$$q = e^{-\beta\epsilon_0} + e^{-\beta\epsilon_1}$$

$$= [e^{-\beta\epsilon_1} - e^{-\beta\epsilon_0}] + [e^{-\beta}$$

1) $q_{states} = \sum_{s=0} e^{-\beta\epsilon_s}$

2) $q_{levels} = \sum w(\epsilon_s) e^{-\beta\epsilon_s}$

3) $w(\epsilon_s)$ = degcy of m

4) $p_{states}(\epsilon_s) = \frac{e^{-\beta\epsilon_s}}{q}$

5) $p_{levels}(\epsilon_s) = \frac{w(\epsilon_s) e^{-\beta\epsilon_s}}{\sum_{s'} w(\epsilon_{s'}) e^{-\beta\epsilon_{s'}}}$

for small $\Delta\epsilon$'s

6) $\underset{\sim}{\Sigma} = \sum_{s'} w(\epsilon_{s'}) e^{-\beta\epsilon_{s'}} = w(\epsilon_1) e^{-\beta\epsilon_1} \Delta\epsilon_M + w(\epsilon_2) e^{-\beta\epsilon_2} \Delta\epsilon_M + \ldots$

from calc Σ's for small $\Delta\epsilon \Rightarrow \underset{\sim}{\Sigma} = \int w(\epsilon) e^{-\beta\epsilon} d\epsilon$

$$q_t \frac{\Delta\epsilon_{tor}}{M} = \{ w(\epsilon_1) e^{-\beta\epsilon_1} + w(\epsilon_2) e^{-\beta\epsilon_2} + \quad \} \left(\frac{\epsilon_{max}-\epsilon_{min}}{M}\right)$$

$$q_t = \left[\frac{w(\epsilon_1) e^{-\beta\epsilon_1}}{\Delta\epsilon_{tor}/M} + \frac{w(\epsilon_2) e^{-\beta\epsilon_2}}{\Delta\epsilon_{tor}/M}\right] \frac{\Delta\epsilon_{tor}}{M} \; \Delta\epsilon$$

$$= \left[\frac{w(\epsilon_i) e^{-\beta\epsilon_i}}{\Delta\epsilon} \Delta\epsilon \right]$$

$$= \sum_i \tilde{w}(\epsilon_i) e^{-\beta\epsilon_i} \Delta\epsilon = \int_0^\infty \tilde{w}(\epsilon) e^{-\beta\epsilon'} d\epsilon$$

$$\tilde{w}(\epsilon_i) = \frac{w(\epsilon_i)}{\Delta\epsilon} = \frac{\text{no. of molecular states w/ energy } \epsilon_i}{(\text{unit energy interval})}$$

$$= \int \tilde{w}(\epsilon) e^{-\beta\epsilon} d\epsilon$$

$=$

$\Phi =$

$\Phi(\epsilon) =$

diatomic molecule

degcy (A4)

$^2P_{3/2} \Rightarrow \tilde{S} = 1/2$

$L = 1$ $\rightarrow g = 4$ form

$J = \tilde{S} + L = 3/2$

term symbol

$^2P_{1/2} \Rightarrow \tilde{S} = 1/2$

$L = 1$

$J = \tilde{S} + L =$

g = no integers between

+J and −J

(+) $^2P_{3/2} \Rightarrow g = -1,$

TOTAL $g = 2J+1$

$\therefore$ $^2P_{3/2} \rightarrow g = 2(3/2) + 1$

$= 4$

$^2P_{1/2} \rightarrow g = 2(1/2) + 1$

⑥

$q_{atom} = q_t \, q_e \, q_n$

PRD Notes V.2

10^6 eV

q_n : (a) $\epsilon_{n_2} - \epsilon_{n_1} \sim 10^{10}$ K

⇓

⊕ atomic nuclei remain in their ground state

⊕

⊕ $q_n = \sum_{s_1}^{n_s} \omega e^{-\beta \epsilon_{n_1}}$

$= \omega_{n_1}$

choose ~~define~~

$\epsilon_{n_1} = 0$

q_e

$\epsilon_2 - \epsilon_1 \simeq k_B T$; $\epsilon_3 - \epsilon_1 \gg k_B T$

(1)

$$p(\epsilon_2) \simeq \frac{w_2 e^{-\beta \epsilon_2}}{w_1 e^{-\beta \epsilon_1} + w_2 e^{-\beta \epsilon_2}}$$

= Halogens F, Cl, Br, I:

$\Delta \epsilon_e = \epsilon_2 - \epsilon_1$ ⇓ ⇓ ⇓ ⇓

0.05 0.11 0.46 0.94 eV

~500K ~100K ~5000K ~10^4K

$$\boxed{w_{\epsilon_1} = 4 \quad , \quad w_{\epsilon_2} = 2}$$

See $\left({}^{2S+1}L_J\right)$ ← term symbols

$J = L + S$ (L: orb ang mom e's; S: total electron spin)

$2S+1 = 2 \Rightarrow \boxed{S = 1/2}$

$L = S = 0 \Rightarrow \boxed{J = 1/2}$

L	symbol
0	S
1	P
2	D
3	

$$\boxed{g = 2J+1}$$

$P(\epsilon_2)$

②

II) a/ Q or in terms of discrete molecular quant. ϵ_n

$$q \text{ or } Q = \sum_s e^{-\beta \epsilon_s}$$

b/ q in terms of molec en. levels and degeneracy w

$$q_{mol, or nuclear or elect or Trans} = \sum_s w_{s\, mol, e, t} e^{-\beta \epsilon_s}$$

w_s

⊕ w_s = no of q. states having energy = to ~~[illegible]~~ or ~~w_s~~ ϵ_s

c) when ϵ's are close together q or Q can be expressed as integral.

FOR $k_B T << \epsilon_2 - \epsilon_1$

$$q_{el} = \sum_{s=1} e^{-\beta\epsilon_s} = e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}$$

elkasn

$$\epsilon = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z)$$

$$\epsilon =$$

$$\frac{\hbar^2 2\pi^2}{mL^2} = \frac{h^2 \, 2\pi^2}{2\pi^2 \, m \, L^2}$$

a) $n_x^2 + n_y^2 + n_z^2 = R^2$

$$R = \sqrt{\epsilon_{xyz}\left(\frac{8mV^{2/3}}{h^2}\right)}$$

b) $\Phi(\epsilon_{xyz} \leq k_B T) =$ vol.

$$= \frac{4}{3}\frac{\pi R^3}{8}$$

$$= \left(\frac{\pi}{6}\right)(k_B T)^{3/2}\left(\frac{8mV^{2/3}}{h^2}\right)^{3/2}$$

$\Downarrow$
ϵ

c)

d) i) $q_t = \sum_{i=1} w(\epsilon_{t_i}) e^{-\beta \epsilon_{t_i}}$

⊛ $\epsilon_{t_i} \ominus \epsilon_{xyz} =$ x y z

⊛

ii) $$q_t = \sum_i \frac{w(\epsilon_{t_i})}{\Delta\epsilon} e^{-\beta \epsilon_{t_i}} \Delta\epsilon$$

$$\Delta\epsilon = \frac{\epsilon_{t\,max} - \epsilon_{t\,min}}{M}$$

$$= \sum \tilde{w}(\epsilon_t) e^{-\beta \epsilon_t} \Delta\epsilon$$

⊛ $\tilde{w}(\epsilon_m) \doteq \dfrac{\text{no. of distinct states having } \epsilon = \epsilon_i}{(\text{per unit } \Delta\epsilon)}$ ~~interval~~

$$\therefore q_t = \int_0^\infty \tilde{w}(\epsilon_t) e^{-\beta\epsilon_t} d\epsilon_t$$

e) $\tilde{w}(\epsilon_t)$: a) $\Phi \simeq \frac{\pi}{6} (k_B T)^{3/2} \left(\frac{8 m V^{2/3}}{h^2}\right)^{3/2}$ ($k_BT \leftrightarrow \epsilon$)

= no of trans. states less than $\epsilon \simeq k_B T$

(5)

b) $\tilde{w} = \frac{d\phi(\epsilon)}{d\epsilon} \doteq \frac{\left(\begin{array}{c}\text{no. of Q states} \\ \epsilon \text{ having } \epsilon = \epsilon\end{array}\right)}{\Delta\epsilon}$

or $\tilde{w}(\epsilon_t) = \frac{d}{d\epsilon}\left[\left(\frac{8m V^{2/3}}{h^2}\right)^{1/2} \epsilon^{1/2}\right]$

$= \frac{1}{2}(\;)^{1/2} \frac{1}{\epsilon^{1/2}}$

c) $\therefore$ $q_t(V,T) = \frac{1}{2}(\;)^{1/2} \int_0^\infty \epsilon^{-1/2} e^{-\beta\epsilon} d\epsilon$

b) $\tilde{w}(\epsilon) = \frac{d\phi(\epsilon)}{d\epsilon} = \frac{d}{d\epsilon}\left[\left(\frac{8m}{h^2}\right)^{3/2}(V)\left[\frac{\pi}{6}\right]\epsilon^{3/2}\right]$

$= \left[\left(\frac{3}{2}\right)\left(\frac{8m}{h^2}\right)^{3/2}\left(\frac{\pi}{6}\right) V\right]\epsilon^{1/2}$

c) $\therefore$ $q_t(V,T) = [\;] \int_0^\infty \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon$