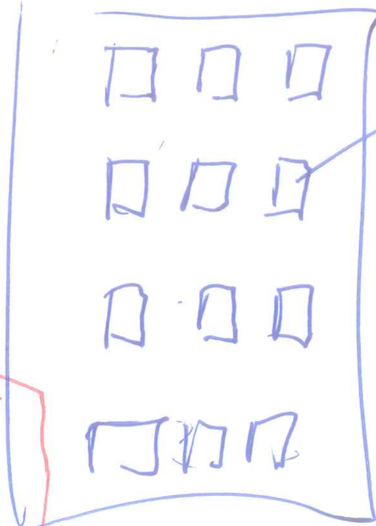
In class 4/17/23 (1)

solids

Derivation of Discrete Q_{sys} for phonons in solid

A)



$\tilde{N}$ replica

Last time:

OBJ 1: Derive exact discrete Q_{sys}

OBJ 2: reexpress (1) as an approx integral form

Q ; Ξ_{sys}

Q en states ; E_{sys} =

B) each sample → N atoms different masses

C) canonical ensemble:

$$p(E_{sys_j}) = \frac{n(E_{sys_j})}{\boxed{Q_{sys}}}$$

d) ~~Q_{sys}~~

$$\boxed{E_{sys_j} = V_0 + \sum_{s=1}^{3N}\left[\frac{1}{2} + n_s\right]\epsilon_s} \quad (1.1)$$

(i) $\epsilon_s = \hbar\omega_s$

ω_s = s^{th} avail. phonon freq.

(ii) V_0 = ~~potent.~~ base potential energy solid

e) Given (1.1)

$$\boxed{Q_{sys} = \sum_{j=1}^{M} e^{-\beta E_{sys_j}}} \quad (1.2)$$

e) $Q_{sys} = \sum e^{-\beta \left[\underbrace{V_0 + \frac{1}{2}\sum_{s=1}^{3N} \hbar\omega_s}_{E_0} + n_1\epsilon_1 \right.}$

$+ n_2 \epsilon_2$

$+ n_3 \epsilon_3$

$\vdots$

$\left. + n_{3N} \epsilon_{3N} \right]$

$n_1, n_2 = 0, 1, 2, \ldots \infty$

$E_0 = 3N(\epsilon_0)$

$\epsilon_s = \hbar \omega_s$

$\omega_s = \nu_s =$ s th eigenvalue in coord xformn from xyz coord. to uncoupled normal coord

= fixed set of freqs

f) $\therefore$

$$\boxed{Q_{sys} = \sum_{\{n\}} e^{-\beta [(\epsilon_0 + n_1\epsilon_1) + (\epsilon_0 + n_2\epsilon_2) + (\epsilon_0 + n_3\epsilon_3) + \cdots + (\epsilon_0 + n_{3N}\epsilon_{3N})]}}$$

$$\epsilon_0 = \frac{E_0}{3N}$$

3

g) $\cancel{A}$ ∴ (3.1) $\boxed{Q_{sys} = q_{phonon_1} \cdot q_{phonon_2} \cdots q_{phonon_{3N}}}$

(3.2) $\boxed{q_{phonon_s} = \sum_{s=0}^{\infty} e^{-\beta(\epsilon_0 + n_s \epsilon_s)} = (e^{-\beta\epsilon_0}) \sum_{s=0}^{\infty} e^{-\beta n_s \epsilon_s}}$

$\boxed{\epsilon_s = \hbar \omega_s}$

h) $Q_{sys} = e^{-\beta \overbrace{3N\epsilon_0}^{E_0}} \tilde{q}_1 \cdot \tilde{q}_2 \cdots \tilde{q}_{3N}$ (3.3)

$\boxed{\text{Geom. series}} \rightarrow \boxed{\tilde{q}_s = \sum_{s=0}^{\infty} e^{-\beta n_s \epsilon_s} = \boxed{\frac{1}{1-e^{-\beta\epsilon_s}}}}$

i) $S_n = A + Af + Af^2 + \ldots + Af^n$

$\boxed{\underline{\text{Reif}}}$

$A = 1$

$f = e^{-\beta\epsilon_s} = e^{-\beta\hbar\omega_s}$

$fS_n = Af + Af^2 + Af^3 + \ldots + Af^{n+1}$

∴ $\boxed{S_{n_{\infty}} = \frac{1}{(1-f)}} = \frac{(A - A\cancel{f^{n+1}})^0}{(1-f)}$

j) : $\boxed{Q_{sys} = e^{-\beta E_0} \prod_{s=1} (1-e^{-\beta E_s})^{-1}}$ (+)

k) $\boxed{\ln Q_{sys} = -\beta E_0 - \sum_{s=1}^{3N} [\ln(1-e^{-\beta\hbar\omega_s})]}$

(+) exact ~~QU~~ system = ~~Solids~~ (N atom solid) partition fn

(+) Q.M.

(+) discrete ⇐ hard to evaluate

II) anytime ~~since~~ ~~diff~~ ~~energy~~ we have a discrete partition fn $\boxed{Q_n}$ in which indiv. energy levels are close, try re-expressing $\boxed{Q}$ as $\boxed{\int}$.

Idea: replace sum over discrete $\vec{n}$'s by ~~binning~~ grouping Q en. levels into **bins**;

equivalently, define a **degeneracy** fn.:

$$\boxed{g(\omega)\,d\omega \equiv \text{no. of phonon modes in } V_{sys} \text{ w/ frequencies } \omega \text{ in } [\omega, \omega + d\omega]}$$

THUS, Let

$$(6.1)\quad \boxed{\sum_{s=1}^{3N} \ln(1-e^{-\beta\hbar\omega_s}) \stackrel{AS}{=} \int_0^{\infty} \ln(1-e^{-\beta\hbar\omega})\, g(\omega)\, d\omega}$$

III) ~~Rigor~~ Follow, Debye and derive an expr'n. for $\boxed{g(\omega)\, d\omega}$

A) $\cancel{g(\omega)\,d\omega}$ $\boxed{g(k)\,dk = \cancel{B}\; 4\pi k^2 dk \frac{V}{(2\pi)^3}}$

B) where does $\boxed{\frac{V}{(2\pi)^3}}$ come from?

$$\boxed{\Delta n_{\underline{k}} \equiv \frac{L_x L_y L_z}{(2\pi)^3}}$$

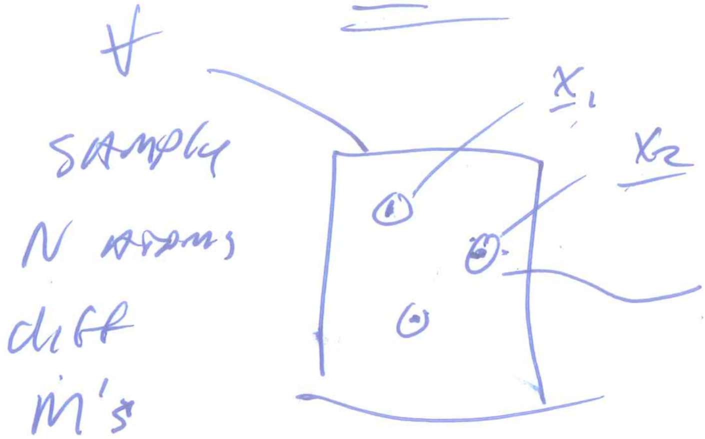
$\underline{\Delta k} = [dk_x, dk_y, dk_z] \equiv$ ~~no of phonons in~~ no of waves, per phonon, in V w/ $\underline{k}$ in $[\underline{k}, \underline{k}+\underline{\Delta k}]$

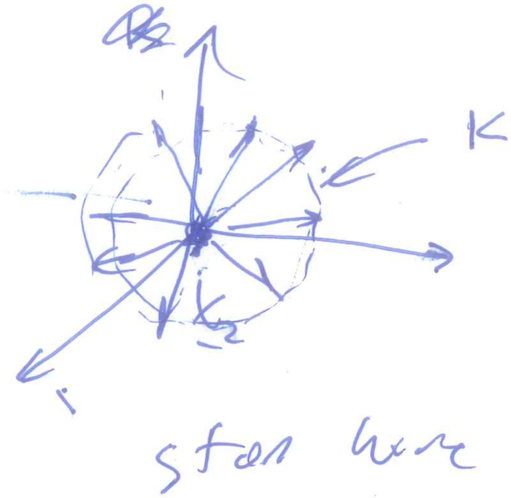
∴ III c) Debye Ass'n ⑦

@ any $\underline{x}$ in V

the distribn of phonon

wave no.s is isotropic





prep notes

(1)

1) S. E. ⇒ $E_{solid} = V_0 + \sum_{j=1}^{3N} \left(\frac{1}{2} + n_j\right) \hbar\omega_j$

2) $E_{s_j} = \underbrace{V_0 + \sum_j^{3N} \frac{1}{2}\hbar\omega_j}_{\begin{subarray}{c} E_0 \\ = 3N\epsilon_0 \end{subarray}} + n_1\hbar\omega_1 + n_2\hbar\omega_2 + \ldots$

$n_1 \in 0, 1, 2 \ldots$; same ; $n_{3N}\hbar\omega_{3N}$

~~a) $p(\epsilon_1, \epsilon_2, \epsilon_3 \ldots) = p(\epsilon_1)p(\epsilon_2)\ldots$~~

~~$p(\epsilon_s) = e^{-\beta n_s \epsilon_s}$~~

~~$= \sum p(\epsilon_1)$~~

~~b) $p(\epsilon_s)$~~

3) $E_{s_j} = (\epsilon_0 + n_1\hbar\omega_1) + (\epsilon_0 + n_2\hbar\omega_2) + \ldots (\epsilon_0 + n_{3N}\hbar\omega_{3N})$

4) ∴ Can. ens. of $\tilde{N}$ replica solids, leads to

$$Q = \sum_{j=1} e^{-\beta E_j}$$

$$= \sum_{j=1} e^{-\beta[(\epsilon_0 + n_1\epsilon_1) + (\epsilon_0 + n_2\epsilon_2) + (\epsilon_0 + n_3\epsilon_3) \ldots (\epsilon_0 + n_{3N}\epsilon_{3N})]}$$

$$= \sum_{\{n\}} e^{-\beta[\ ]}$$

4a) $\epsilon_\alpha = \hbar\omega_\alpha$

5) ∴ $Q = q_1 \cdot q_2 \cdot \varepsilon_3 \cdot \cdots \varepsilon_{3N}$

(ptn fn for phonon 1) (" 2) (" 3) ... (3N)

6) $$q_s = \sum_{n_s=0}^{\infty} e^{-B(\epsilon_0 + n_s \epsilon_s)}$$

$$= e^{-B\epsilon_0} \sum_{n_s=0}^{\infty} e^{-B n_s \epsilon_s} \qquad \epsilon_s = \hbar\omega_s$$

7) $$\sum_{n_s=0}^{\infty} e^{-B n_s \epsilon_s} \quad S_n = A + Af + Af^2 + \cdots + Af^n$$

$$fS_n = f + Af^2 + Af^3 + \cdots + Af^{n+1}$$

$A=1 \quad f = e^{-B\epsilon_s}$

$$\Rightarrow S_n = \frac{(1 - Af^{(n+1)})}{(1-f)}$$

$$= \frac{1}{(1 - e^{-B\epsilon_s})}$$

8) ∴ $$q_s = e^{-B\epsilon_0}(1 - e^{-B\epsilon_s})^{-1}$$

9) ∴ $$Q = e^{-B\epsilon_0 3N} \prod_{s=1}^{3N} (1 - e^{-B\epsilon_s})^{-1}$$

10) ∴ $$\left[\ln Q = -BE_0 - \sum_{s=1}^{3N} \ln(1 - e^{-B\epsilon_s}) \right.$$

10a) OBT. TURN Σ in 10) to $\int$

11) Let $g(\omega)\,d\omega$ = no. of phonons in V_{solid} w/ ω in $[\omega, \omega + d\omega]$

12) $$\sum_s f(\omega_s) = \sum_{s'} f(\omega_{s'}) \tilde{g}(\omega_{s'}) \approx \sum_{s'} f(\omega_{s'}) N$$

degen of phonon en. level $\hbar\omega_s$; = no. of phonons of energy range

3

[3] or $\sum_s f(\omega_s) = \sum_{s'} f(\omega_{s'}) \tilde{g}(\omega_{s'})$

$$= \sum_{s'} f(\omega_{s'}) \underbrace{g(\omega_{s'}) \Delta\omega_{s'}}$$

no. of phonons in k w/ energy in $[\hbar\omega_{s'}, \hbar(\omega_{s'} + \Delta\omega_{s'})]$

$$= \int_0^\infty f(\omega)\, g(\omega)\, d\omega$$

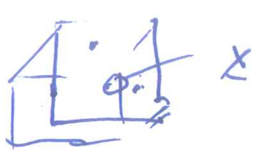
[4] [5] models for $g(\omega)$:

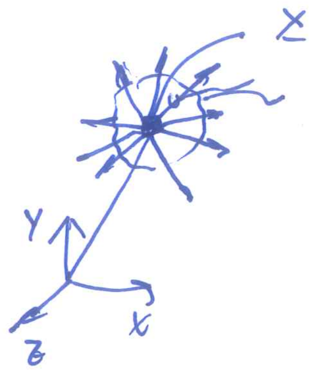
in V:

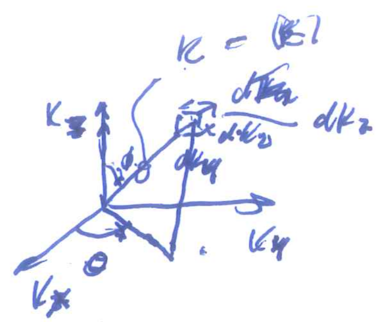
1) no. of phonon modes within $\underline{k}$ & $\underline{k} + dk_x dk_y dk_z$

$$= \frac{V}{(2\pi)^3} dk_x dk_y dk_z$$

2) Assume @ any locn w/in V phonon wave nos are isotropic







3) $\therefore$ no. of phonon modes in

$$d\underline{K} = K\sin\phi\, d\theta\, K\, d\phi\, dK$$

$$= \frac{V}{(2\pi)^3} K^2 \sin\phi\, d\phi\, d\theta\, dK$$

4) $\therefore$ <u>total</u> phonon modes w/ $|\underline{K}|$ ~~dK~~ in $[K, K + dK]$

@ any $\underline{x}$ in V $\Leftarrow$ $N_{K_{TOT}}$

$$N_{K_{TOT}} = \frac{V}{(2\pi)^3} \int_0^{\pi}\int_0^{2\pi} K^2\, dK\, d\theta\, \sin\phi\, d\phi$$

$$\cos\phi\Big|_{\pi}^{0} = 2$$

$$\cancel{\frac{V(2\pi)}{(2\pi)^3}\left(\frac{1}{3}\right)K^3(2)} = \frac{V(2\pi)(2)K^2\, dK}{(2\pi)^3}$$

5) $\cancel{N_{K_{TOT}} = \frac{V}{(2\pi)^2}\left(\frac{2}{3}\right)K^3}$

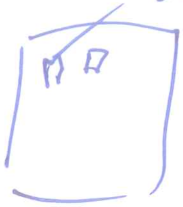
a) $C_l = \frac{\omega}{K_l} \Rightarrow \boxed{K = \frac{\omega}{c}}$

b) $\therefore$ $d\omega = c\, dK$

c) $N_{TOT} = \frac{V\, 4\pi\, \omega^2}{(2\pi)^3 (c^2)} \frac{d\omega}{(c)}$ = no. of phonon modes in V w/ freqs between $[\omega, \omega + d\omega]$

$= g(\omega)\, d\omega$

d) $\therefore$ $\boxed{g(\omega) = \frac{V(4\pi)\omega^2}{(2\pi)^3(c^3)} d\omega}$

1) 

solid 1

$\tilde{N}$

(1)

prev notes 2

2) $\Rightarrow \quad \dfrac{n(v_{s\omega_j})}{\tilde{N}} = \dfrac{e^{-\beta\epsilon_j}}{\sum_j e^{-\beta\epsilon_j}}$

3) $\epsilon_j = V_0 + \sum_{s=1}^{3N}\left(\frac{1}{2} + n_s\right)\hbar\omega_s$

$+ \quad \sum$

$= \underbrace{\left[V_0 + \sum_{s=1} \frac{1}{2}\hbar\omega_s\right]}_{\epsilon_0} + \underbrace{n_1}_{0,1,2}\epsilon_1 + n_2\epsilon_2 \ldots$

$= (\epsilon_0 + n_1\epsilon_1) + (\epsilon_0 + n_2\epsilon_2) + (\epsilon_0 + \quad) + \ldots$

$(\epsilon_0 + n_{3N}\epsilon_{3N})$

4) $\therefore \quad Q = \sum_{\{n\}} e^{-\beta(\epsilon_0 + n_1\epsilon_1 + \epsilon_0 n_2\epsilon_2 + \ldots + \epsilon_0 n_{3N}\epsilon_{3N})}$

$= q_1 \cdot q_2 \cdot \ldots \quad q_{3N}$

$= \left(\sum_{n_1=0}^{\infty} e^{-\beta(\epsilon_0 + n_1\epsilon_1)}\right)\left(\qquad\right)$

5) $= e^{-\beta\epsilon_0 3N}\left(\sum_{n_1=0}^{\infty} e^{-\beta n_1\epsilon_1}\right)\left(\qquad\right)$

6) $\sum_{n_s=0}^{\infty} e^{-\beta n_s\epsilon_s} = \left(1 - e^{-\beta\epsilon_s}\right)^{-1}$

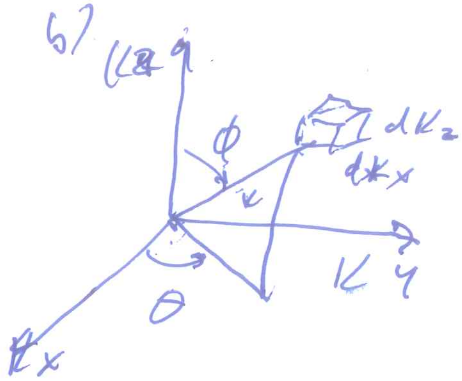
7) $$\boxed{\ln Q = -\beta E_0 \; \sum_{s=1}^{3N} \ln(1 - e^{-\beta \epsilon_s})}$$

7a) $$\ln Q = -\beta \epsilon_0 + \int_0^\infty \ln(1 - e^{-\beta \hbar \omega})\, g(\omega)\, d\omega$$

8) no. of phonons $\forall$ w/ $\underline{K}$ $\boxed{g(\omega)\, d\omega}$

in $(\underline{K}, \underline{K} + dK_x\, dK_y\, dK_z) = \frac{V}{(2\pi)^3}$

9) ass. isotropic $\underline{K}$:



$\Rightarrow \quad dV_K = K'^2 \sin\phi \, d\phi \, d\theta \, dK'$

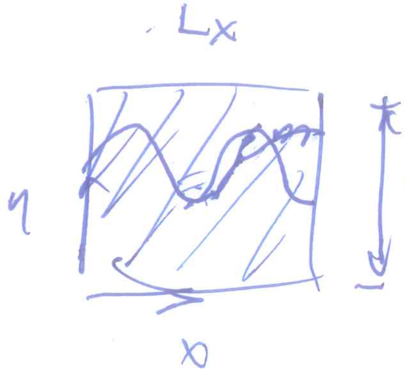
$\therefore$ no of phonons in $\forall$ w/

$|\underline{K}|$ in $[K, K + dK]$:

$$\iiint_0 K'^2 \sin\phi \, d\theta \, dK'$$

$$K^2 dK \, 2\pi \cos\phi \Big|_\pi^0 = \underline{4\pi K^2 dK}$$

10) Disp. $c_\ell = \frac{\omega_\ell}{K_\ell} \Rightarrow \boxed{K = \omega / c} \Rightarrow \boxed{dK = \frac{d\omega}{c}}$



a) n_{λ_x} = no ~~phonon~~ waves in x-dir of sample ~~for~~ for single phonon phon

$= \dfrac{L_x}{\lambda_x}$

b) $\underline{\underline{n_{\lambda_x + d\lambda_x}}} = \boxed{\dfrac{L_x}{\lambda_x + d\lambda_x} = \dfrac{L_x}{\lambda_x}\left(1 - \dfrac{d\lambda_x}{\lambda_x}\right)}$

$\parallel \quad = \dfrac{L_x}{\lambda_x\left(1 + \dfrac{d\lambda_x}{\lambda_x}\right)}$

c) Δn_{λ_x} = no. of waves per phonon in sample w/ λ's in $[\lambda_x, \lambda_x + d\lambda_x]$

f) ∴ $\Delta n_{\Delta k} = V\, dk_x dk_y dk_z$

= no of waves per phonon w/ $\underline{k}$ in $[\underline{k}, \underline{k} + \Delta k]$

$= \dfrac{V}{(2\pi)^3}$

$\Delta n_x = n|_{\lambda_x + d\lambda_x} - n_{\lambda_x}$

$= -\dfrac{L_x}{\lambda_x}\left(1 - \dfrac{d\lambda_x}{\lambda_x}\right) + \dfrac{L_x}{\lambda_x}$

$= \boxed{\dfrac{L_x\, d\lambda_x}{\lambda_x^2}}$

d) ~~λ_x~~ But $k_x = \dfrac{2\pi}{\lambda_x}$

$\Rightarrow \boxed{\begin{aligned} \lambda_x &= 2\pi/k_x \\ d\lambda_x &= -2\pi/k_x^2\, dk_x \end{aligned}}$

$[k_x, k_x + dk_x]$ e) ∴ $\Delta n_x = \dfrac{L_x (2\pi)\, dk_x\, \cancel{k_x^2}}{(\cancel{k_x^2})(2\pi)^2}$

no of waves per phonon in $\overline{V}$ $\overline{w/}$ k_x in $= \boxed{\Delta n_x = \dfrac{L_x}{2\pi} dk_x}$

(3)

(1) SW $g(\omega)\,d\omega = (4\pi k^2 dk)\dfrac{V}{(2\pi)^3}$

(2) $= (4\pi)\left(\dfrac{\omega^2}{c^2}\right)\left(\dfrac{d\omega}{c}\right)\dfrac{V}{(2\pi)^3}$ ✓

$\square \rightarrow$ P waves

(3) $\boxed{g_{\text{ext}}(\omega)\,d\omega = (3)\left(\dfrac{\omega^2}{c_s^3}\right)\dfrac{V}{(2\pi)^3}}$

(4) $\boxed{\dfrac{3}{c_{\text{eff}}} = \dfrac{1}{c_l^2} + \dfrac{2}{c_t^2}}$