

- ① Phonons
- ② X-Ray
- ③ Electronic properties

**RESPONSE FUNCTION** → how ob measurements

P	R	F
X	X	S
✓	J	0
Ω	≡	
H	B	
Q	T	$c_v$

$$\xrightarrow{P} \boxed{\quad} \xrightarrow{R} R = F(P)$$

GOAL = what is F?

Builds a model  
that give the  
response

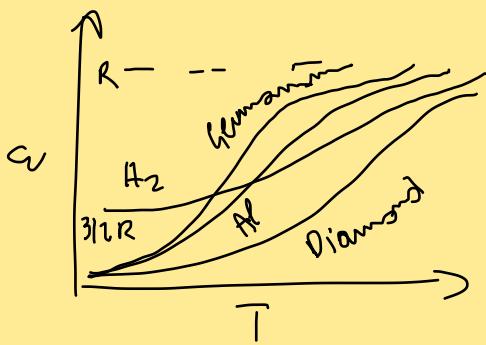
In principle we can do everything with quantum mechanics.  
TASK → build models for  $R = F(P) = A_P$   $A \approx \frac{R}{P}$  **LINEAR APPROXIMATION**

$c_v \xrightarrow{Q} \boxed{?} \xrightarrow{T}$  what is inside the box? Model

### TERMODYNAMICS

- axiomatic theory
- not based on a model
- ergothes law → connection the macroscopic behavior with the micro

WHAT IS THE CONNECTION BETWEEN Q-T?



### ZERO PRINCIPLE

Something hot - something cold in contact → reach equilibrium

STATE →  $U, V, M_1, M_2, \dots, M_f$

↓  
internal energy  
# partial of chemical components

I need to make a choice = U or S, then the other variables are correlated

THE RUMAL CONTACT → two materials in contact exchange heat

THE RUMAL EQUILIBRIUM → The state does not change (dynamical eq.)

T → in Kelvin

$$\boxed{A} T_A \rightarrow \boxed{A} \boxed{B} T_{AB} \quad T_A \leq T_{AB} \leq T_B$$

## FIRST PRINCIPLE

Perpetuum motion does not exist  $\rightarrow$  GENERALIZATION OF ENERGY CONSERVATION

$$\exists U: \alpha, \beta \text{ at equilibrium } E = U(\beta) - U(\alpha)$$

$\uparrow$

INTERNAL ENERGY

$$E = W + Q$$

$W$  work done  
 $Q$  heat supplied

$$W + Q = \Delta U \quad \text{or} \quad \delta U = \delta W + \delta Q$$

e.g.  $\delta W = -P\delta V \quad \delta W = E \cdot \delta P \quad \delta V = \frac{1}{P} \delta H$

## SECOND PRINCIPLE

heat flows spontaneously from high-T to low-T  
it is not possible the opposite.

$\exists S$ , ENTROPY, extensive variable

- showing arbitrary ADIABATIC process (no heat exchange)

$$Q_{\alpha \rightarrow \beta} = 0 \rightarrow S(\beta) \geq S(\alpha)$$

$$\delta Q = 0 \rightarrow dS \geq 0$$

$$\text{CANNOT occur} \quad dS \geq \frac{\delta Q}{T}$$

$$\text{if transformation reversible} \quad dS = \frac{\delta Q}{T}$$

## THIRD PRINCIPLE

Related to QM

"The S of all perfect crystal at T=0 is always the same = a constant that we assume to be 0"

QUESTION = HOW TO CONNECT T WITH Q

$$\xrightarrow{\frac{\delta Q}{\delta T}} \boxed{?} \xrightarrow{\frac{T}{\delta T}} \left( \frac{\delta Q}{\delta T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V = C_V$$

$$\delta Q + \delta W = \delta U$$

$$\delta Q - P\delta V = \delta U$$

Principle of TD one at constant V?

STATE VARIABLE

REALITY  $\rightarrow$  not constant V  
 $C_V \rightarrow C_P$

$$\text{e.g., } \Delta Q = I^2 R \Delta t$$

- $C_p \sim C_v$
  - CM phase space
  - SM Boltzmann
  - SM Equipartition
  - Duulang - Petit
- } Classical physics
- 

$$\xrightarrow{P} \boxed{\quad} \xrightarrow{R} \left( \frac{dQ}{dT} \right)_{V,N} = C_{V,N}$$

$$F(P) = R \qquad dQ + dW = dU$$

LINEAR APPROXIMATION  $dQ = TdS$

Let's be little bit more precise on the  $C_V$  definition: in principle I can also define  $C_{P,N}$  and relates it with  $C_{V,N}$

$$\left( \frac{dQ}{dT} \right)_{P,N} = C_{P,N}$$

$$C_{P,N} = C_{V,N} + \left( \frac{\partial V}{\partial T} \right)_{P,N} \left[ \left( \frac{\partial U}{\partial V} \right)_{T,N} + \frac{P}{V} \right]$$

ISOTHERM. COMPRESSIBILITY  $\kappa_{P,N} = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N}$

Thermal expansivity  $\alpha_{P,N} = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,N}$

We can combine all together and we obtain:

$$K_{T,N} (C_{P,N} - C_{V,N}) = TV \alpha_{P,N}^2 \rightarrow C_V \sim C_P$$

NB Water has very high specific heat = 'in' is the reason of life on earth  
I feel cold when I touch metal because conduction is high

MODEL = Box full of particle

What we know for moving from mechanics (one system at the time) to statistical mechanics (average number of some systems)? Clarify the concept of phase space.

## PHASE SPACE

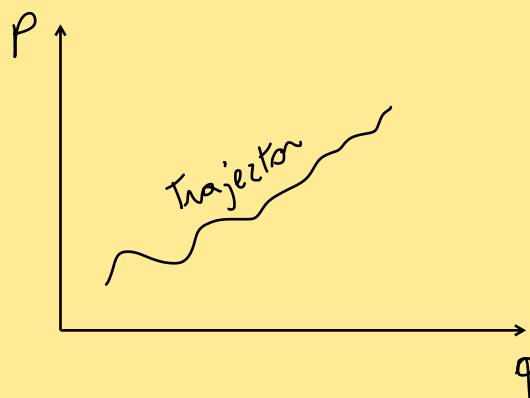
Hamiltonian mechanics allow to go from CLASSICAL to QUANTUM mechanics -

HM → position and momenta as INDEPENDENT VARIABLES

$$\begin{array}{l} \underbrace{\underline{x}_1, \underline{x}_2, \dots, \underline{x}_N}_{\text{POSITIONS}} \\ \underbrace{\underline{p}_1, \underline{p}_2, \dots, \underline{p}_N}_{\text{MOMENTA}} \end{array}$$

In HM I need only momenta = first order differential equation

$$(\underline{q}_1, \underline{q}_2, \dots, \underline{q}_{3N}, \underline{p}_1, \underline{p}_2, \dots, \underline{p}_{3N}) \rightarrow \text{PHASE SPACE}$$



$$\dim \Gamma = 2N_f \quad N_f \text{ degree of freedom}$$

Which equation do I have? No forces, ENERGY

$$H(\underline{q}_1, \underline{q}_2, \dots, \underline{q}_{3N}, \underline{p}_1, \underline{p}_2, \dots, \underline{p}_{3N}, t)$$

not all system

$$H = T + V$$

$$\begin{cases} \dot{\underline{q}}_i = \frac{\partial H}{\partial \underline{p}_i} \\ \dot{\underline{p}}_i = -\frac{\partial H}{\partial \underline{q}_i} \end{cases}$$

HAMILTON EQUATIONS

Kinetic energy is not related to the positions  $\frac{1}{2}mv^2 = \frac{\underline{p}^2}{2m} = T$

$$\dot{\underline{p}}_i = -\frac{\partial H}{\partial \underline{q}_i} = -\frac{\partial V}{\partial \underline{q}_i} \rightarrow \text{Nothing less than the second law of Newton}$$

$$\{f, g\} = \sum_i \left( \frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right)$$

POISSON BRACKETS

I can use poisson brackets to rewrite the Hamilton equations

$$\dot{q}_i = \{q_i, H\}$$

$$\dot{p}_i = \{p_i, H\}$$

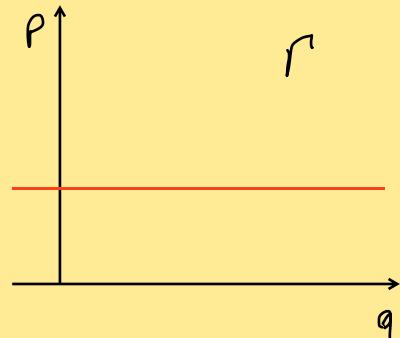
- useful when we will do harmonic oscillator
- quantization

### Ex = FREE PARTICLE

$$H = \frac{p^2}{2m} = \frac{p_1^2 + p_2^2 + p_3^2}{2m}$$

$$N=1 \quad \text{dim } \Gamma = 6$$

$$(q_1, q_2, q_3, p_1, p_2, p_3)$$



$$\begin{cases} \dot{q}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{m} \rightarrow p_i = m \dot{q}_i \\ \dot{p}_i = -\frac{\partial H}{\partial q_i} = 0 \rightarrow \text{Momentum is conserved: no forces!} \end{cases}$$

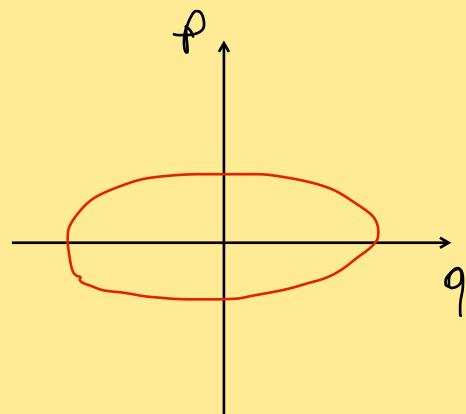
### Ex = HARMONIC OSCILLATOR

$$H = \frac{p^2}{2m} + \frac{1}{2} \kappa q^2$$

$$\omega^2 = \frac{\kappa}{m}$$

$$\begin{cases} \dot{q}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{2m} \\ \dot{p}_i = -\frac{\partial H}{\partial q_i} = -\kappa q \end{cases} \rightarrow \begin{aligned} q &= q_0 \cos \omega t \\ p &= p_0 \sin \omega t \end{aligned}$$

choice free

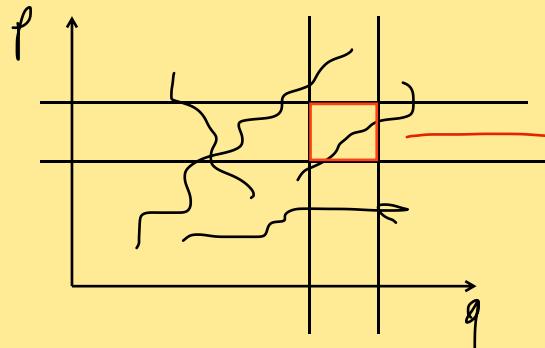


I have phase space now.

Now I have to introduce the concept of ENSEMBLE

ENSEMBLE → each particle different initial conditions

To moving particle  $\rightarrow$  I need to consider averages



$$H(q_1, q_2, \dots, q_{3N}, p_1, p_2, \dots, p_{3N})$$

N particles in total  
 $m_i$  particles in each cell

EQUILIBRIUM  $\rightarrow$  something that maximize the probability to find a particle

ONLY ONE  
 CELL

$$\binom{N}{m_i} = \frac{N!}{m_i!(N-m_i)!}$$

ALL THE  
 COMBINATION  
 FOR ALL CELLS

$$P = \binom{N}{m_1} \binom{N-m_1}{m_2} \binom{N-m_1-m_2}{m_3} \dots = \frac{N!}{m_1! m_2! m_3! \dots}$$

I have to maximize  $P$ , if at EQUILIBRIUM

there is something missing :

- $N$  remain the same  $\sum_i m_i = N$  } TWO CONSTRAINT
- Energy conservation  $\sum_i m_i \bar{E}_i = \bar{E}$  } TO IMPOSE

TRICK: I work on  $\ln P$  instead of  $P$

$$F[\{m_i\}, \alpha, \beta] = \ln P - \alpha (\sum_i m_i - N) - \beta (\sum_i m_i \bar{E}_i - \bar{E})$$

Lagrange  
 mult.

I need to compute  $\frac{\partial F}{\partial m_i} = 0$ .

NB.  $\ln P = \ln(N!) - \sum_i \ln(m_i!)$

$$\ln m! = \sum_1^m \ln m \sim \int_1^m \ln x dx =$$

$$\ln P = N \ln N - N - \sum_i (m_i \ln m_i - m_i)$$

STEARIAN  
 APPROX.

$$\frac{\partial F}{\partial n_i} = 0 = -\ln m_i \nabla + \nabla - \alpha - \beta E_i; \quad \boxed{m_i = \exp(-\alpha - \beta E_i) \\ = A e^{-\beta E_i}}$$

This is a discrete formulation, I can do also the continuous formulation

$$dm = A e^{-\beta H(q, p)}$$

BOLTZMANN  
DISTRIBUTION  
FUNCTION

$$\int dm = N$$

$$A = \frac{1}{\int e^{\beta H} dp_1 dp_2 \dots dp_N dq_1 dq_2 \dots dq_N}$$

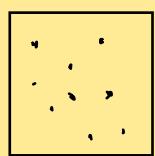
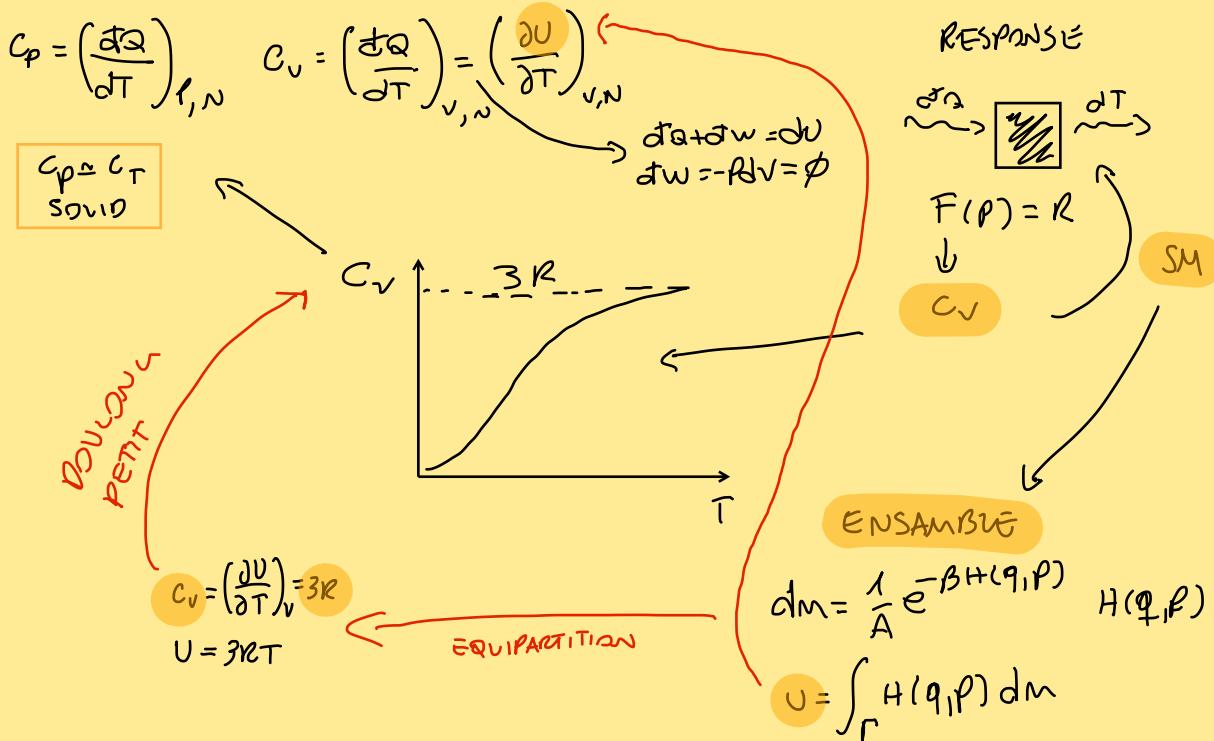
What is  $\beta$ ?  $\beta = \frac{1}{k_B T}$ , interpreted a posteriori

We need to count what happens to  $m_i$  when  $H$  is quadratic in  $T$  and  $V$ : we can derive the EQUIPARTITION THEOREM.

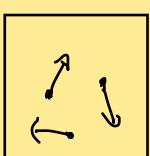
- CM
- CM + SM + TD
- Tutorial**
- Equipartition
- CM
- QM

**Next**

- QM Revision
- Article on Einstein



$$H = \frac{p^2}{m}$$



SOLID

$$\sum_i \frac{p_i^2}{m} + \frac{1}{2} \sum_i q_i^2$$

BOTH QUADRATIC HAMILTONIANS

$$H = H(q_1, q_2, q_3, \dots, p_1, p_2, \dots) = \sum_i (b_j p_j^2 + \alpha_j q_j^2)$$

$$U = \langle H \rangle \longrightarrow \frac{\int b_j p_j^2 dm}{\int dm} = \frac{\int b_j p_j^2 e^{-\beta H} dq_1 dq_2 \dots dp_1 dp_2 \dots}{\int e^{-\beta H} dq_1 dq_2 \dots dp_1 dp_2 \dots}$$

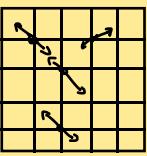
$$\text{NB } \prod_{k+j} \frac{\int e^{-\beta H} dp_k dp_{k+j}}{\int e^{-\beta H} dp_k p_{k+j}^2} = 1$$

$$\int e^{-(\alpha x)^2} x^3 dx = \frac{\sqrt{\pi}}{4\alpha^3}$$

$$\int e^{-(\alpha x)^2} dx = \frac{\sqrt{\pi}}{2\alpha}$$

$$= b_j \frac{1}{2\beta b_j} = \frac{1}{2\beta} = \frac{1}{2} k_B T$$

EQUIPARTITION THEOREM OF ENERGY



$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} = \frac{3}{2} k_B T$$

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_i q_i^2 = 6N_A \frac{1}{2} k_B T = 3RT$$

I can observe this for every quadratic Hamiltonian that I know.

$$\frac{\int \alpha_j q_j^2 dm}{\int dm}$$

$C_V$  is not a function of  $T$ ! PROBLEM!

I am not so off ...  $T \rightarrow 0$ ,  $C_V \rightarrow 3R$

For now the approximations one: quasistatic Hamiltonian

$$C_V = \left( \frac{\partial U}{\partial T} \right)_N = 3R \quad \text{DULONG - PETIT MODEL}$$

Classically we cannot explain the  $T$  dependence of  $C_V$  = we introduce QUANTUM MECHANICS.

1<sup>o</sup> POSTULATE → the wave function  $\psi$  describes the state of the system

$$\psi(r_1, r_2, \dots, r_f, t)$$

$$\psi^* \psi d\tau = \psi^* \psi dr_1 dr_2 \dots dr_f \rightarrow \int \psi^* \psi d\tau = 1$$

2<sup>o</sup> POSTULATE → From classical physics to quantum  
classically we can always define an operator as function of positions and momenta.

ARE THE  
SAME THING

$$\begin{cases} r_i \rightarrow \hat{r}_i \\ p_i \rightarrow i\hbar \frac{\partial}{\partial r_i} = -i\hbar \nabla_i \end{cases} \quad t_i = \frac{\hbar}{2m}$$

Ex.  $H = \frac{p^2}{2m} \rightarrow \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$

$H = \frac{p^2}{2m} \rightarrow \hat{H} = -\frac{\hbar^2}{2m} \nabla^2$

$\{f, g\} \rightarrow \frac{1}{i\hbar} [\hat{f}, \hat{g}]$

$$\{q, p\} = \frac{\partial q}{\partial \theta} \frac{\partial p}{\partial P} - \frac{\partial q}{\partial P} \frac{\partial p}{\partial \theta} = 1$$

$$[\hat{q}, \hat{p}] = i\hbar \quad (\hat{q}\hat{p} - \hat{p}\hat{q})\psi = \left( -x \left( i\hbar \frac{\partial}{\partial x} \right) - \left( -i\hbar \frac{\partial}{\partial x} \right)x \right) \psi$$

$$= -i\hbar x \frac{\partial \psi}{\partial x} + i\hbar \frac{\partial}{\partial x} (x\psi)$$

$$= -i\hbar \cancel{x} \frac{\partial \psi}{\cancel{\partial x}} + i\hbar \frac{\partial x}{\partial x} + i\hbar \cancel{\frac{\partial \psi}{\partial x}} = i\hbar$$

3° POSTULATE  $\rightarrow$  Eigenvalue problem

$$\hat{\mu} \psi = m \psi \quad m \text{ are the possible value that } \hat{\mu} \text{ can assume apply on } \psi$$

$$\hat{\mu} = \left( r; -i\hbar \frac{\partial}{\partial r}; t \right)$$

$E \cdot \hat{H} \psi = E \psi$  Schrödinger equation at the stationary state

4° POSTULATE  $\rightarrow$  The time evolution of the system is determined by the Schrödinger equation

$$H\psi = i\hbar \frac{\partial}{\partial t} \psi$$

### FREE-PARTICLE MODEL

$$H = \frac{p^2}{2m} \quad H\psi = i\hbar \frac{\partial}{\partial t} \psi$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = i\hbar \frac{\partial \psi}{\partial t} \quad \psi(x, t) = \varphi(x)\phi(t)$$

Solved by separate the variable

$$-\frac{\hbar^2}{2m} \phi(t) \frac{\partial^2 \psi}{\partial x^2} = i\hbar \varphi(x) \frac{\partial \phi}{\partial t}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = i\hbar \frac{\partial \phi}{\partial t} \quad \rightarrow \quad -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E \psi \quad \psi(x) = B e^{ikx}$$

$$i\hbar \frac{\partial \phi}{\partial t} = E \phi \quad \phi(t) = A e^{-i\omega t}$$

$$\omega: i\hbar(-i\omega) = E$$

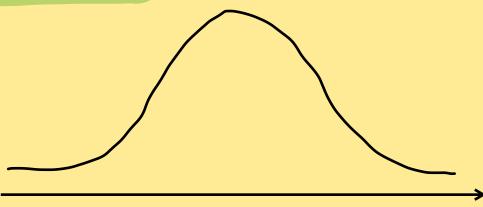
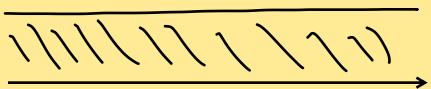
$$E = \hbar\omega = \frac{h}{8\pi} 8\pi v = h\nu \quad \text{EINSTEIN RELATION}$$

$$E = \frac{\hbar^2}{2m} k^2 \quad k = \frac{n\pi}{\lambda}$$

$$\hbar k = p = \frac{h}{8\pi} \frac{n\pi}{\lambda} = \frac{h}{\lambda} \rightarrow \frac{p\lambda}{\lambda} = \frac{h}{p}$$

**PROBLEM** Free-electron model gives a  $\psi$  that is NOT NORMALIZABLE

→ SOLUTION = WAVE-PACKETS



(D)  $\rightarrow$  +QM Einstein model

Coupled  $\rightarrow$  normal modes

TODAY

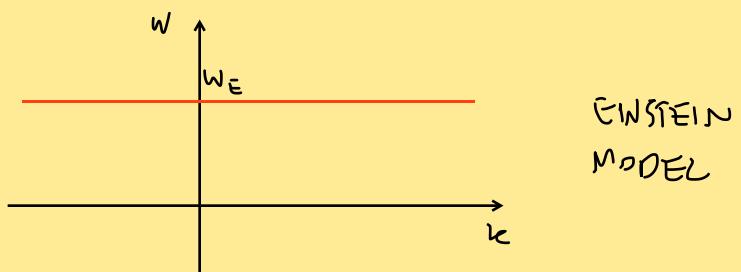
QM

Quasi particles

DOS

$$U = \hbar \omega_e \left( m_{BE} (\omega_1 T) + \frac{1}{2} \right) 3 N_A$$

↑  
this point



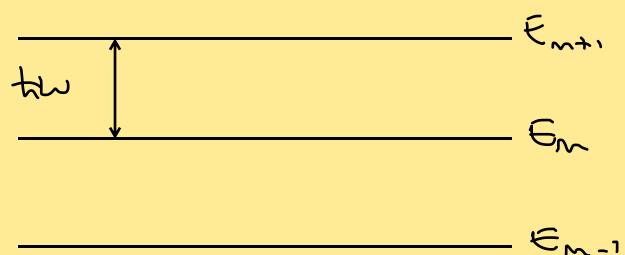
$$U = \sum_{m, \kappa} \hbar \omega_m(\kappa) \left( m_{BE} + \frac{1}{2} \right)$$

$$\psi_m(x, t) = |m\rangle \quad H|m\rangle = E_m |m\rangle \quad H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

$$[\hat{x}, \hat{p}] = i\hbar \quad [\hat{x}, \hat{H}] = \frac{i\hbar}{m} \hat{p}$$

$$\begin{cases} (E_m - E_n) \langle \kappa | \hat{x} | m \rangle = \frac{i\hbar}{m} \langle \kappa | \hat{p} | m \rangle \\ (E_m - E_n) \langle \kappa | \hat{p} | m \rangle = -im\hbar\omega^2 \langle \kappa | \hat{x} | m \rangle \end{cases}$$

$$E_n = \hbar\omega(n + c)$$



$$E_{m-1} \quad E_m \quad E_{m+1}$$

## II QUANTIZATION

NB. In a non-relativistic regime, it does not add anything - it is only another notation -

$-im\omega$

$$\begin{cases} (\epsilon_m - \epsilon_n) \langle k | \hat{x} | m \rangle = \frac{i\hbar}{m} \langle k | \hat{p} | m \rangle \\ (\epsilon_m - \epsilon_n) \langle k | \hat{p} | m \rangle = -im\hbar\omega^2 \langle k | \hat{x} | m \rangle \end{cases} +$$

$$(-im\omega)(\epsilon_m - \epsilon_n) \langle k | \hat{x} | m \rangle + (\epsilon_m - \epsilon_n) \langle k | \hat{p} | m \rangle = (-im\omega) \frac{i\hbar}{m} \langle k | \hat{p} | m \rangle - im\hbar\omega^2 \langle k | \hat{x} | m \rangle$$

$$(\epsilon_m - \epsilon_n) \underbrace{\langle k | \hat{p} - im\omega x | m \rangle}_{\alpha} = \hbar\omega \underbrace{\langle k | \hat{p} - im\omega x | m \rangle}_{\alpha}$$

$\alpha \rightarrow$  electrons excitations (quasi particles)

$\alpha^+ \rightarrow$  odds excitations

$\left. \begin{array}{l} (\hat{p} - im\omega x)^* = (\hat{p} + im\omega x) \\ \alpha \neq \alpha^+ \rightarrow \text{not observable} \end{array} \right\}$  (2nd postulate QM)

Let's see some properties of  $\alpha$

$$\langle m-1 | \alpha | m \rangle = \lambda_m = \sqrt{m}$$

$$\alpha | m \rangle = \sqrt{m} | m-1 \rangle$$

lowering and

$$\langle m | \alpha^+ | m-1 \rangle = \lambda_m^* = \sqrt{m}$$

$$\alpha^+ | m-1 \rangle = \sqrt{m} | m \rangle$$

raising operators

In II quantization each excitation corresponds to a quantum of energy -

Let's understand the ZERO-POINT ENERGY.

$$\alpha | 0 \rangle = (\hat{p} - im\omega x | 0 \rangle = 0 | 0 \rangle \longrightarrow (\hat{p} + im\omega x)(\hat{p} - im\omega x) | 0 \rangle = (\hat{p}^2 + im\omega[\hat{x}, \hat{p}] + m^2\omega^2\hat{x}^2) | 0 \rangle$$

by definition

$$im\left(\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 - \frac{1}{2}\hbar\omega\right) | 0 \rangle = 0$$

$$H | 0 \rangle = \frac{1}{2}\hbar\omega | 0 \rangle$$

The absence of excitation have an energy because of indeterminism principle -

$$\text{NB. } \epsilon_m = \hbar\omega \left(m + \frac{1}{2}\right)$$

In order to simplify how we write it

$$(p - im\omega x) \frac{1}{\sqrt{2m\hbar\omega}} = \sqrt{\frac{m\omega}{2\hbar}} x + i \frac{p}{\sqrt{2m\hbar\omega}} = \alpha \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

$$(p + im\omega x) \frac{-i}{\sqrt{2m\hbar\omega}} = \sqrt{\frac{m\omega}{2\hbar}} x - i \frac{p}{\sqrt{2m\hbar\omega}} = \alpha^+ \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

$$[\alpha, \alpha^+] = 1$$

$$H = (\alpha^\dagger \alpha + \frac{1}{2}) \hbar \omega$$

$\hat{N} = \alpha^\dagger \alpha \rightarrow$  how many excitations I have in the system

$$\hat{N}|M\rangle = \alpha^\dagger \alpha |M\rangle = M|M\rangle$$

$$\alpha = \begin{pmatrix} 0 & 1 & & & \\ 0 & 0 & \sqrt{2} & & \\ & 0 & 0 & \sqrt{3} & \\ & & 0 & 0 & \sqrt{4} \\ & & & \ddots & \end{pmatrix} \quad \alpha^\dagger = \begin{pmatrix} 0 & & & & \\ 1 & 0 & & & \\ & \sqrt{2} & 0 & & \\ & & \sqrt{3} & 0 & \\ & & & \sqrt{4} & \dots \\ & & & & \ddots \end{pmatrix} \quad N = \begin{pmatrix} 1 & & & & \\ & 2 & & & \\ & & 3 & & \\ & & & 4 & \\ & & & & \ddots \end{pmatrix}$$

Now I want to write H for more than one oscillator = a family of oscillators

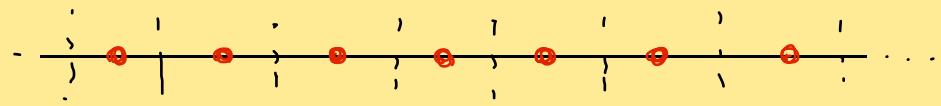
$$H = \sum_{m,k} \hbar \omega_{mk} (\alpha_{mk}^\dagger \alpha_{mk} + \frac{1}{2})$$

Now I have to count the particles differently

$$|M_1, M_2, M_3, \dots \rangle = \sum (a_1^\dagger)^{M_1} (a_2^\dagger)^{M_2} \dots |0\rangle \quad \text{FOCK SPACES} \rightarrow \text{direct product of H spaces}$$

## LINEAR CHAIN OF OSCILLATIONS

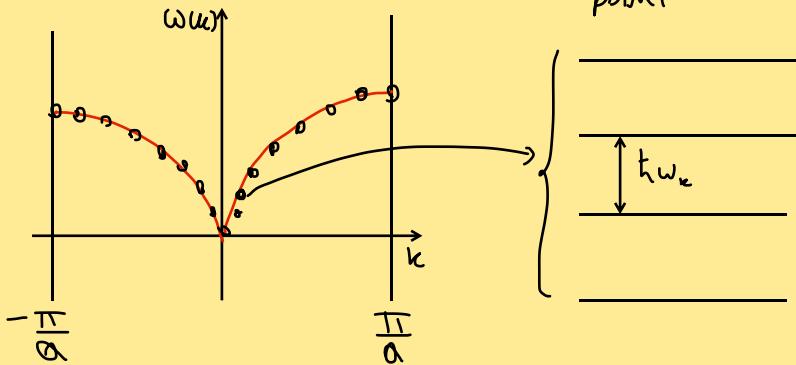
$$H = \sum_m \frac{p_m^2}{2m} + \frac{1}{2} J (2\omega_m^2 - \omega_m \omega_{m+1} - \omega_m \omega_{m-1})$$



$$\alpha_k = \frac{1}{\sqrt{N}} \sum_m e^{-im\alpha} \left[ \left( \frac{m\omega(k)}{2\pi} \right)^{1/2} \omega_m + i \sqrt{\frac{1}{2\pi m \omega(k)}} p_m \right]$$

$$\alpha_k^+ = \frac{1}{\sqrt{N}} \sum_m e^{im\alpha}$$

We have a ladder  
for each  $\omega$   
point



$$[\alpha_k, \alpha_{k'}^+] = \delta_{kk'} i$$

$$[\alpha_k, \alpha_k] = [\alpha_k^+, \alpha_k^+] = 0$$

$$H = \sum_k \hbar \omega(k) (\alpha_k^+ \alpha_k + \frac{1}{2})$$

$$E(k') = \underbrace{\langle 0 | \alpha_{k'} | H | \alpha_{k'}^+ | 0 \rangle}_{\langle k' |} \underbrace{\langle 0 |}_{\langle k' |}$$

Now, instead of do a sum I want to do an integral

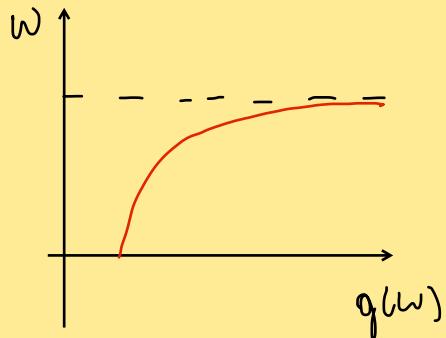
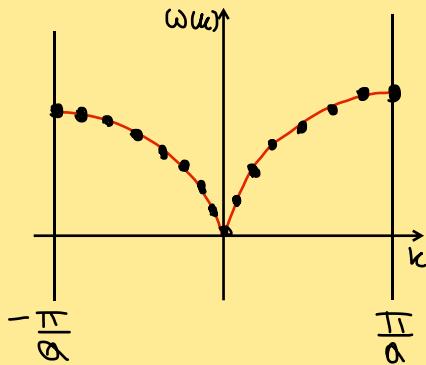
$$U \sim \int \hbar \omega(g(\omega)) n_{BE}(\omega T) d\omega \rightarrow \int d\omega \text{ DOS} \quad \begin{matrix} \text{How many states} \\ \text{have for each } \omega \end{matrix}$$

$\downarrow \sqrt{\left(\frac{dw}{dk}\right)^{-1}}$

$$\omega(k) = \left( \frac{J}{m} \right)^{1/2} \sin \left( \frac{ka}{2} \right) \quad k = \frac{2\pi}{a} \frac{m}{N} \quad \rho(k) = \frac{N}{2\pi} = \frac{Na}{2\pi}$$

$$\begin{cases} dm = \rho(k) dk \\ dm = \frac{1}{2} g(\omega) d\omega \end{cases} \rightarrow \frac{Na}{2\pi} dk = \frac{1}{2} g(\omega) d\omega \quad \rightarrow \quad g(\omega) = \frac{1}{\pi a} \left( \frac{m}{J} \right)^{1/2} \frac{1}{\cos(\frac{ka}{2})}$$

$$g(\omega) = \frac{1}{\pi a} \left( \frac{m}{J} \right)^{1/2} \frac{1}{\cos(\frac{ka}{2})}$$



February 27, 2020

## SUMMARY

- QUASI-PARTICLE = PHONONS (BOSONS)  
(QUASI-MOMENTUM  $\underline{k}$ )
- DP  $\rightarrow$  Einstein  $\rightarrow$  Normal modes  $\rightarrow$  anelastic phonons  $\rightarrow$   
 $\rightarrow$  Debye Interpolation scheme

$$\begin{matrix} \text{CM} & \text{QM} \\ \text{SM} & \text{SM} \end{matrix} \left\{ \begin{matrix} \text{FD} \\ \text{BE} \end{matrix} \right.$$

$$\begin{matrix} \text{CM} & \omega_n(\underline{k}) \\ \text{Periodicity} \\ \text{PBC} \\ (\text{WS/BZ}, \text{RL}) \\ \text{DOS: } g(\omega) \end{matrix}$$

$$\omega(\underline{k}) = v_s(\underline{k})$$

$$\int_0^{\omega_D} g(\omega) d\omega = 3N$$

$C_V \rightarrow$  the only vibrations that I can have at low T are the anelastic ones

$$U_0 = \int \hbar \omega g(\omega) M_{BE}(\omega, T) d\omega + U_0 \quad g(\omega) = \text{DOS}$$

$$\rightarrow \underline{k} = \frac{2\pi}{a} \frac{m}{N} \quad g(\underline{k}) = \left( \frac{\frac{2\pi}{a}}{N} \right)^{-1} = \frac{Na}{2\pi m}$$

$$\rightarrow \frac{Na}{2\pi} dk = \frac{1}{2} g(\omega) d\omega \quad g(\omega) = \frac{Na}{\pi} \left( \frac{d\omega}{dk} \right)^{-1} = \frac{2L}{\pi a} \left( \frac{4J}{m} - \nu^2 \right)^{1/2}$$

We have to develop the theory for  $k \rightarrow 0$  = we want to see if when  $T \rightarrow 0$  the  $C_V \rightarrow 0$  in a cube way = in order to not lose everything, I have to introduce Debye model.

## DOS

We want to generalize the DOS

$$\sum_{\mathbf{k}} f_m(\mathbf{k}) \frac{V}{(2\pi)^3} \sum_m \int d\mathbf{k} f(\mathbf{k}) \rightarrow \int g(\omega) d\omega f(\omega)$$

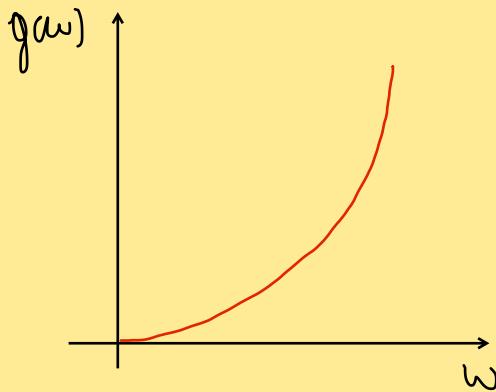
Mathematically = use the property of Dirac delta -

$$\int_{BZ} \delta(\omega' - \omega(\mathbf{k})) g(\mathbf{k}) d\mathbf{k} \doteq g(\omega') \quad \delta(\omega' - \omega(\mathbf{k})) = \begin{cases} \infty & \omega' = \omega(\mathbf{k}) \\ 0 & \omega' \neq \omega(\mathbf{k}) \end{cases}$$

$$f(\mathbf{k}) = \frac{V}{(2\pi)^3} \quad g(\omega') = \int_{BZ} \delta(\omega' - \omega(\mathbf{k})) f(\mathbf{k}) d\mathbf{k} \quad |\mathbf{k}| = \omega = \sqrt{k_1^2 + k_2^2 + k_3^2}$$

$$k^2 = \frac{\omega^2}{\sigma_s^2} \quad 2k dk = \frac{2\omega d\omega}{\sigma_s^2} \rightarrow dk = \frac{d\omega}{\sigma_s}$$

$$dm = g(\omega) d\omega = \frac{V}{(2\pi)^3} 4\pi k^2 dk = \frac{V}{(2\pi)^3} 4\pi \frac{\omega^2}{\sigma_s^3} d\omega = \frac{V}{2\pi^2} \frac{\omega^2}{\sigma_s^3} d\omega$$



$$g(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{\sigma_s^3}$$

Now we want to compute the Cv

$$x = \frac{\hbar\omega}{k_B T} \quad dx = \frac{\hbar}{k_B T} d\omega$$

$$U = U_0 + \frac{V}{2\pi^2} \frac{1}{\sigma_s^3} \int_0^\infty \frac{1}{\tau \omega^3} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} d\omega$$

$$\hbar^3 \omega = \frac{1}{k^2} (k_B T)^3 x^3$$

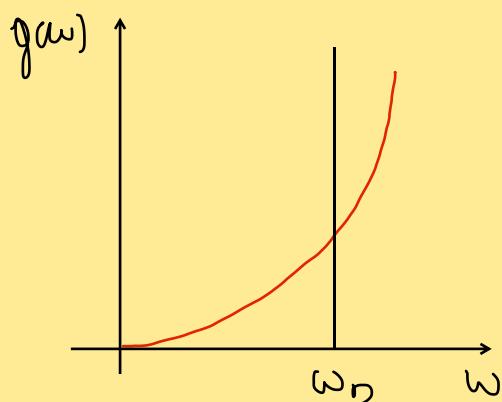
$$= U_0 + \frac{V}{2\pi^2} \frac{1}{\sigma_s^3} \frac{(k_B T)^2}{\hbar^3} \underbrace{\int_0^\infty \frac{x^3}{e^x - 1} dx}_{\frac{\pi^4}{15}}$$

$$U = U_0 + \frac{V}{2\pi^2} \frac{1}{\nu_s^3} \frac{(k_B T)^4}{\hbar^3} \frac{\pi^4}{15}$$

$\left(\frac{\partial U}{\partial T}\right)_V = C_V \sim T^3 \rightarrow$  fixed problem at lower T  
 $\rightarrow$  new problem at high T

NB. I have to interpolate between this model and Einstein = this is the contribution of Debye-

$\omega_D \rightarrow$  cutoff frequency when you have enough energy



$\omega_D \rightarrow$  I know how many vibrations I have in the system =  $3N$

$$U = U_0 + \frac{V}{2\pi^2} \frac{1}{\nu_s^3} \int_0^{\omega_D} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} d\omega$$

$$3 \cdot \frac{1}{\nu_s^3} \rightarrow \frac{2}{\nu_T^3} + \frac{1}{\nu_L^3} \quad g(\omega) = \frac{V}{2\pi^2} \left( \frac{2}{\nu_T^3} + \frac{1}{\nu_L^3} \right) \omega^2$$

$$\int_0^{\omega_D} \omega^2 d\omega = \left[ \frac{V}{2\pi^2} \left( \frac{2}{\nu_T^3} + \frac{1}{\nu_L^3} \right) \right]_{3N} = \frac{\omega_D^3}{3} \rightarrow \omega_D = \left( 9N \left[ \frac{V}{2\pi^2} \left( \frac{2}{\nu_T^3} + \frac{1}{\nu_L^3} \right) \right] \right)^{1/3}$$

$$g(\omega) = \frac{9N}{\omega_D^3} \omega^2$$

$$U = U_0 + \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\frac{\hbar\omega}{k_B T}} - 1} d\omega$$

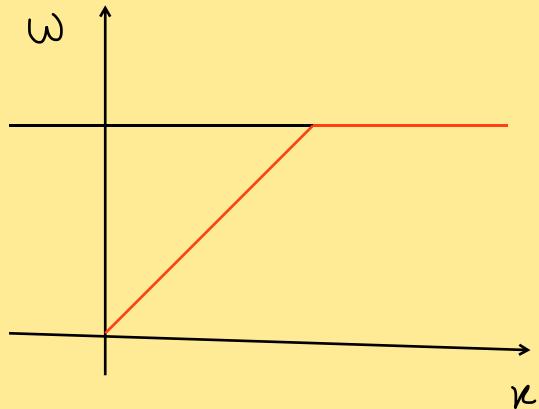
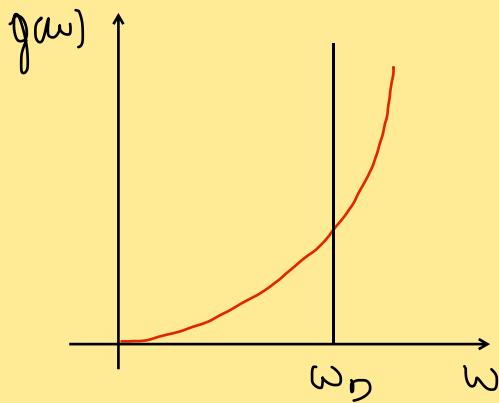
$$\frac{\Theta_D}{T} = \frac{\hbar\omega_D}{k_B T} \rightarrow \Theta_D = \frac{\hbar\omega_D}{T} = \text{DEBYE TEMPERATURE}$$

$$\frac{\partial U}{\partial T} = \frac{gN}{\omega_D^3} \int_0^{\omega_D} \frac{tw e^{\frac{tw}{k_B T}} \frac{tw}{k_B T} \frac{1}{T^2}}{\left(e^{\frac{tw}{k_B T}} - 1\right)^2} dw$$

$$= \frac{gN}{\omega_D^3} \frac{k_B^3 T^2}{\hbar^2} \frac{k_B T}{\hbar} \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx = C_V$$

$$\int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx \underset{T \rightarrow \infty}{\sim} \int_0^{\frac{\theta_D}{T}} \frac{x^4 (1+x)}{x^2} dx \sim \int_0^{\frac{\theta_D}{T}} x^2 dx \sim \left(\frac{\theta_D}{T}\right)^3 \frac{1}{3}$$

$$C_V \underset{T \rightarrow \infty}{\sim} \left(\frac{\theta_D}{T}\right)^3 \frac{1}{3} \frac{gN}{\omega_D^3} \frac{k_B^3 T^2}{\hbar^2} \frac{k_B T}{\hbar} \sim \text{const} = 3R$$



**NB.** Now we close the story = we are able to catch the two limits ( $T \rightarrow 0$ ,  $T \rightarrow \infty$ ), but not in the middle -  
We studied only harmonic oscillations, not anharmonic -  
a solid will never melt only with harmonic oscillations

