Phys 425
Lecture 8

curvature : stiffness

Last time:

asymmetry → anharmonicity → thermal expansion

LCAO :

$$|\psi\rangle = C_1|1\rangle + C_2|2\rangle$$

anharmonic:

harmonic

similar to harmonic, but skewed.

Variational Solution

$$E = E_0 + V_{cross} \pm |t|$$

Reminders

- Pset in two weeks (#2)
- midterm in two weeks
  - notecard allowed

LCAO - way to model covalent bonds

→ combining two separate solutions = one two-part solution

UNIT 1: Microscopic Properties ⇒ UNIT 2: Thermal Properties

we're in unit 2 now!

Thermal Properties of Solids :

The early days: (Dulong - Petit Model) → The "classical" model or "limit" model

Heat Capacity (c) : energy required to raise temperature of 1 mol of a material by 1°K

Phys 142: gases have a heat capacity

constant volume heat capacity → $C_V = \frac{3}{2}k_B$ / atom

only works for gases

At the earliest stage: the prediction was:

↳ $\boxed{C = 3k_B \text{ per atom}}$ "Dulong - Petit Law"

↳ accurate for most solids @ room temp.

· Daimond $\frac{C}{R} \rightarrow R = N_A k_B \approx 0.735$ → not even close to 3.

Even for metals: C decreases with temperature

For Daimond, $C \rightarrow 3k_B$ for higher temps

Looking Ahead:

1st Attempt: Einstein Model – what if we use Quantum Mechanics?

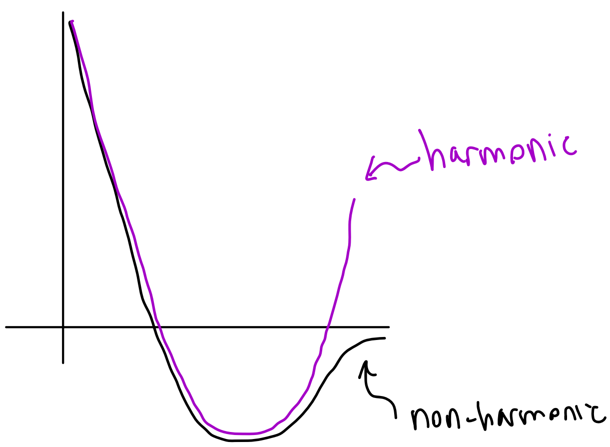
2nd Attempt: Debye Model

↳ what if vibrations behave like sound?

3rd Attempt: Normal Modes

↳ what if we don't ignore the lattice?

ASIDE: Harmonic Approximation: (211)



$\phi \approx \frac{1}{2}\gamma r^2 +$ gamma γ

where $\omega = \sqrt{\frac{\gamma}{m}}$

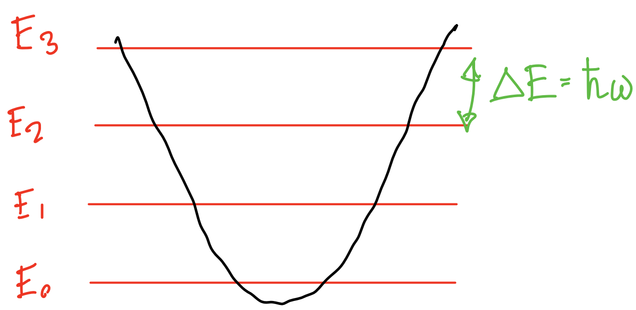
$$\underbrace{\ddot{x} = -\omega^2 x}_{\text{SHO}}$$

→ now quantize it

QSHO: potential $\hat{V} = \frac{1}{2}k\hat{x}^2$

solve schrodinger equations:

$$E_n = (n + \tfrac{1}{2})\hbar\omega$$



ASIDE 2 : Quantum Statistics (212) - Ch 9 of Modern Physics - Harris

- once we reach some thermodynamic limit, we can't track every particle (10^{23} particles potentially)
  - → we look at averages (average behaviours)

☆ We can have different probability distributions based on the system

For indistinguishable particles:

The likelihood that a particle occupies some energy state
- energy state = state with energy E

is known as the occupation #, $n(E,T)$

↳ Bosons (spin 0 particles) - integer spin
- can occupy the same state (Pauli Exclusion doesn't apply)

$$\boxed{\underbrace{n(E,T)}_{\text{occupation \#}} = \frac{1}{e^{E/k_B T} - 1}}$$

Bose - Einstein Distribution

↳ Fermions (spin $\frac{1}{2}$ particles)
- subject to Pauli exclusion principle

$$\boxed{n_{FD} = \frac{1}{e^{(E-\mu)/k_B T} + 1}}$$

μ = chemical potential

Fermi - Dirac Distribution

We define a density of states $g(E)$

$$g(E) = \frac{\#\text{ states between } E \text{ and } E+dE}{dE}$$

$$\text{or } g(\omega) = \frac{dN}{d\omega}$$

So the total # of particles

$$N = \int g(E)\, n(E)\, dE = \sum_n g(E_n)\, n(E_n)$$

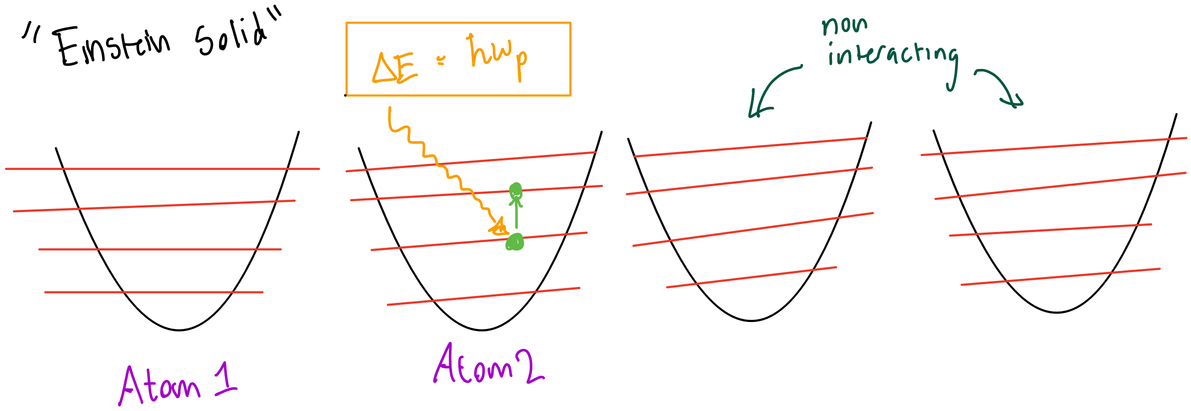
So a mean energy is obtained by computing:

$$\boxed{\langle E \rangle = \frac{\int E\, g(E)\, n(E)\, dE}{\underbrace{\int g(E)\, n(E)\, dE}_{N}}}$$

Einstein Model:

Treat each atom in the solid as a simple harmonic oscillator and quantize it.

"Einstein Solid"



$\longrightarrow$ discrete packets of energy (phonons)

$$E_{phonon} = \hbar\omega_p$$

Our goal:

Derive the total avg energy of the system.

↳ per atom, we have energy

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega$$

So to get $\langle E \rangle$, we average over all possible energies

$$\langle E \rangle = 3\left(\langle n \rangle + \tfrac{1}{2}\right) E_{phonon}$$

3D solid (degrees of freedom)

2D = 2

1D = 1

$\langle n \rangle$ is the average energy state that is occupied

↳ We will assume: phonons are Bosons

- in an actual calculation, Bosons fall out of the math

$$\langle n \rangle = \frac{1}{e^{E/k_BT} - 1}$$

$$\langle E \rangle = 3\left(\frac{1}{e^{E/kBT} - 1} + \frac{1}{2}\right) E_{phonon}$$

note: in statistical mechanics:

$$\underbrace{C = \frac{\partial \langle E \rangle}{\partial T}}_{\text{from thermodynamics}} = 3k_0 \left(\frac{\hbar\omega_p}{k_BT}\right)^2 \frac{e^{\hbar\omega_p/kBT}}{\left(e^{\hbar\omega/kBT} - 1\right)^2}$$