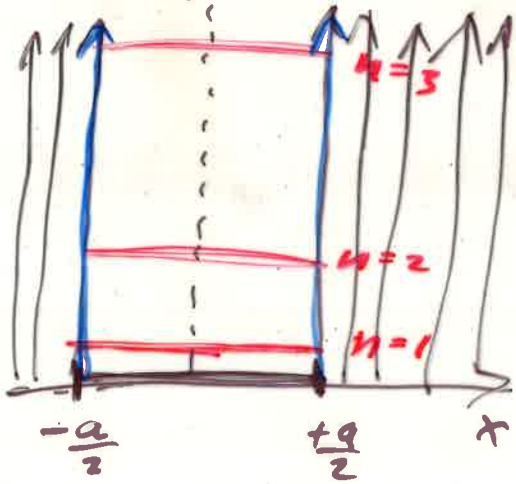
New Quantum Mechanics

Recall Bound states → Energy is quantized.

∞ Square Well



$$U(x) = \begin{cases} 0, & -\frac{a}{2} < x < \frac{a}{2} \\ \infty, & \text{elsewhere} \end{cases}$$

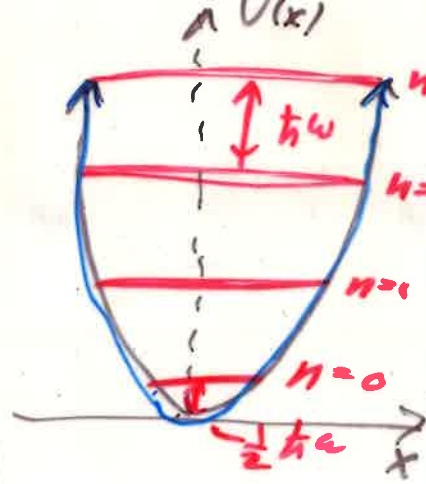
$$E_n = \frac{n^2 \hbar^2 \pi^2}{2ma^2} \propto n^2$$

$(n \geq 1)$

Generalize to 3-dim

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Simple Harmonic oscillator



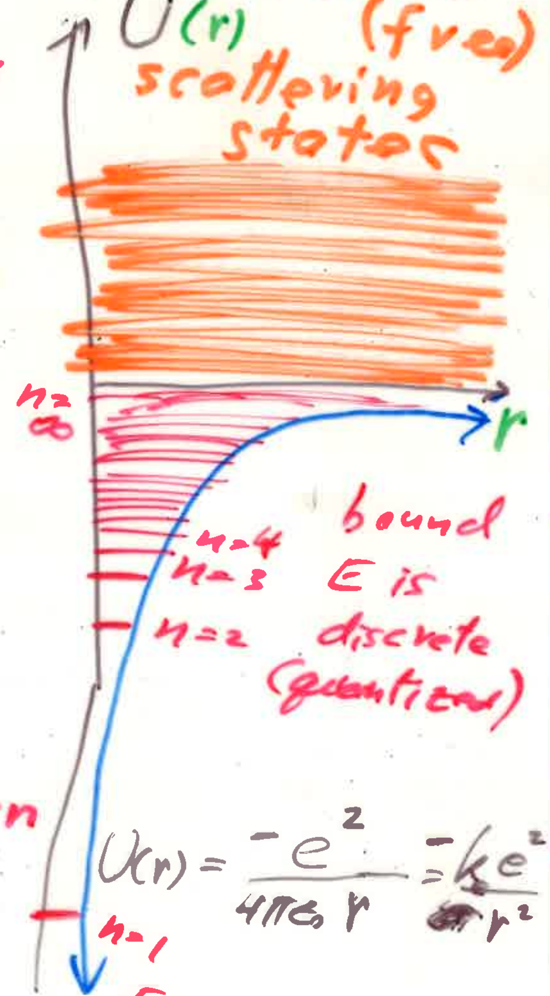
$$U(x) = \frac{1}{2} m \omega^2 x^2 = \frac{1}{2} k x^2 = \frac{1}{2} C x^2$$

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

$n \geq 0$

$$E_n = (n_x + n_y + n_z + \tfrac{3}{2})\hbar\omega$$

H-atom (Kepler)
only 3-dimensions



bound E is discrete (quantized)

$$U(r) = \frac{-e^2}{4\pi\epsilon_0 r} = \frac{-ke^2}{r}$$

$$E_1 = -13.6\,\text{eV}$$

$$E_n = \frac{-m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} \propto \frac{1}{n^2}$$

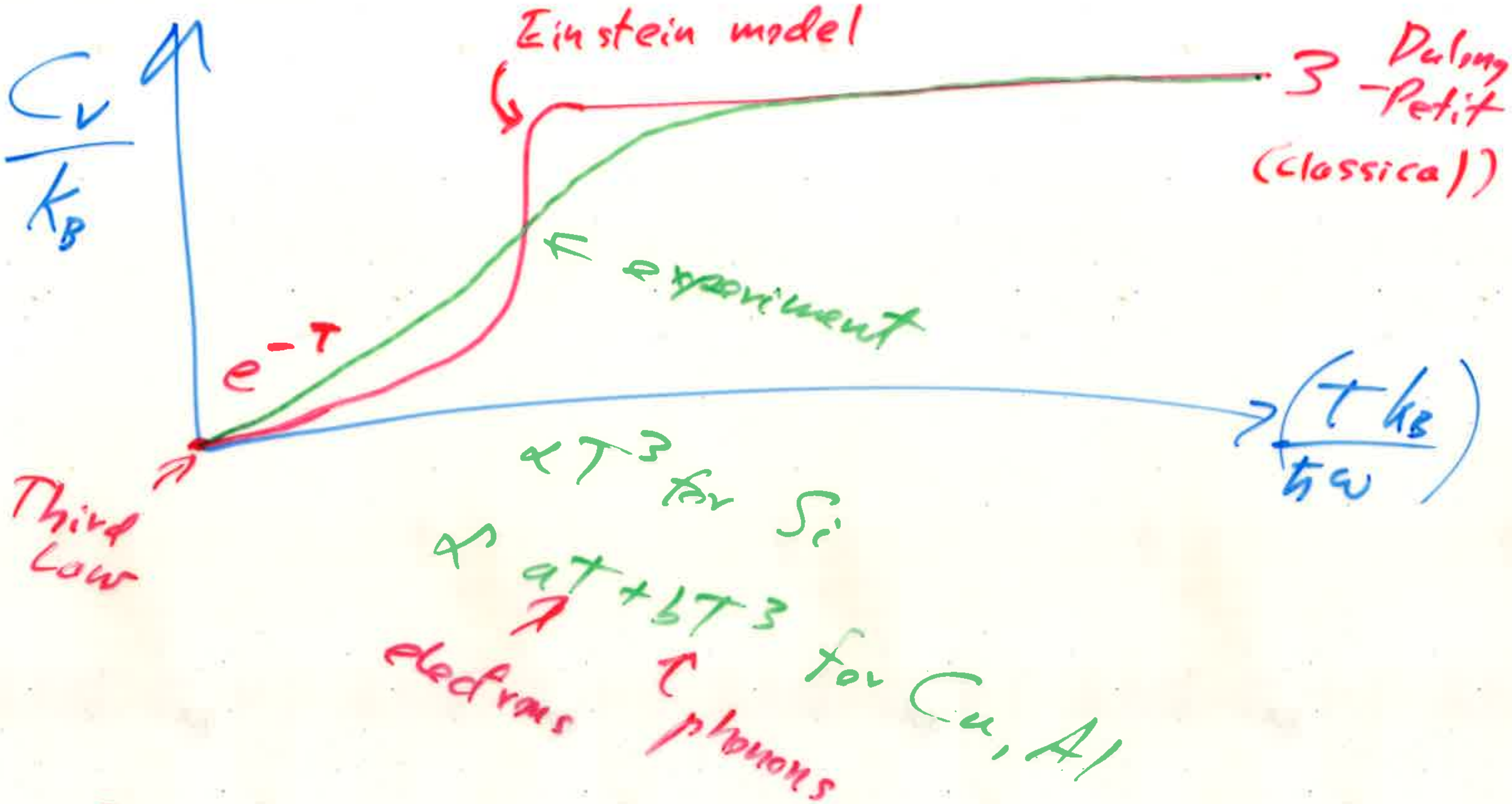
Phonon Energy

$\hbar\omega$

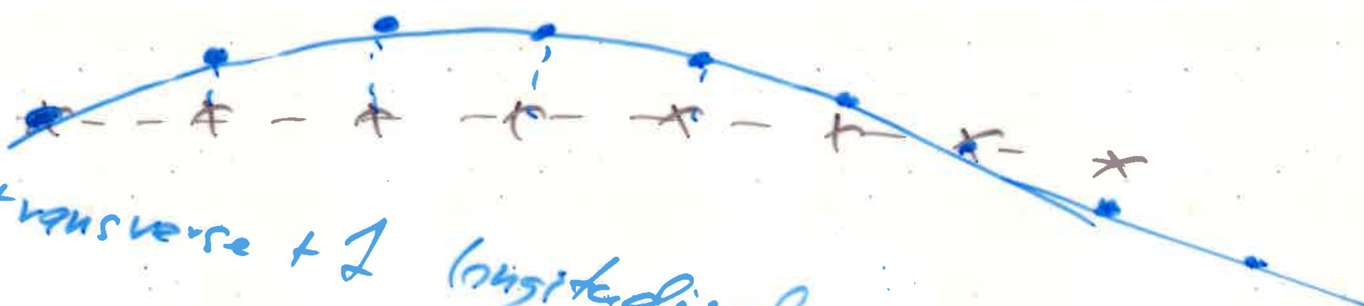
Phonon Momentum

$\hbar k$

$\omega(k)$ from dispersion relation



By concentrating on one site in crystal, we have ignored long-wavelength oscillations

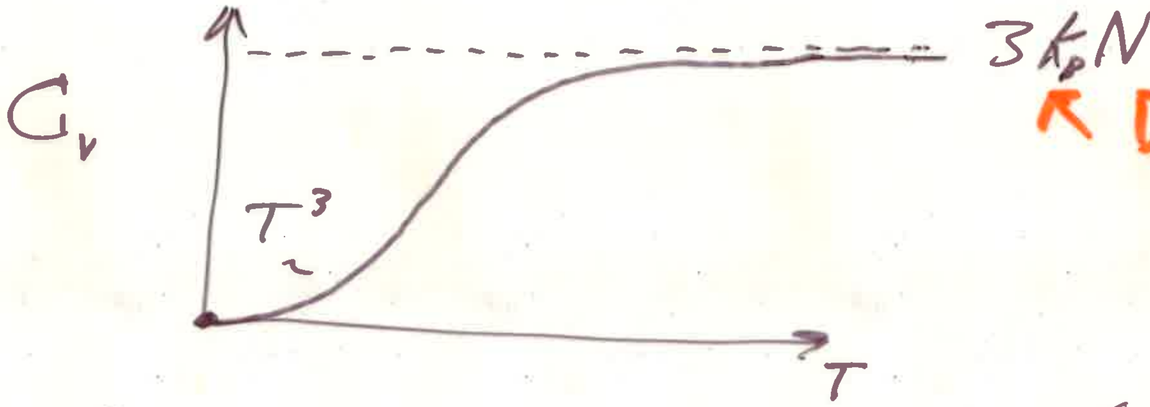


2 transverse + 1 longitudinal wave

100s or 1000s of sites

We want a lattice heat capacity at constant volume $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \sim C_p$ for solids

$C_V = C_p$ as $T \to 0$. Need $U(T)$



Classically, use equipartition (valid at high T) $\Rightarrow \frac{1}{2}k_BT$ per degree of freedom

N atoms, 3 dimensions, Kinetic or Potential energy

$$U = 3Nk_BT \quad \Rightarrow \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B$$

Probability system has energy E_a is

$$P_a \propto e^{-\frac{E_a}{k_BT}} \quad \text{Boltzmann}$$

$$\sum_{a=0}^{\infty} P_a = 1 \Rightarrow \cancel{\sum_{b=0}^{\infty} e^{-\frac{E_b}{k_BT}}}$$

Unitarity

$$P_a = \frac{e^{-\frac{E_a}{k_B T}}}{\sum_{b=0}^{\infty} e^{-\frac{E_b}{k_B T}}}$$

Denominator

$$Z = \sum_{b=0}^{\infty} e^{-\frac{E_b}{k_B T}}$$

partition function

Simple Harmonic Oscillator

$$E_a = (a + \tfrac{1}{2})\hbar\omega$$

N_a = # phonons in state a

fraction of phonons in state a is

$$\frac{N_a}{\sum_{b=0}^{\infty} N_b} = P_a = \frac{\exp\left[-(a+\frac{1}{2})\hbar\omega/k_B T\right]}{\sum_{b=0}^{\infty} \exp\left[-(b+\frac{1}{2})\hbar\omega/k_B T\right]}$$

$$= \frac{\exp\left[-a\hbar\omega/k_B T\right]}{\sum_{b=0}^{\infty} \exp\left[-b\hbar\omega/k_B T\right]}$$

Average excitation quantum number, occupation number

$$\langle n \rangle = \sum_{a=0}^{\infty} a P_a = \frac{\sum_{a=0}^{\infty} a \exp\left[-a\hbar\omega/k_B T\right]}{\sum_{b=0}^{\infty} \exp\left[-b\hbar\omega/k_B T\right]}$$

Define $x = e^{-\left(\frac{\hbar\omega}{k_B T}\right)}$

$$Z = \sum_{b=0}^{\infty} x^b = \frac{1}{1-x}$$

Proof ① $f(x) = \frac{1}{1-x}$ Taylor (Maclaurin) expansion

$$f(x) = f(0) + \left.\frac{df}{dx}\right|_0 x + \frac{1}{2!}\left.\frac{d^2f}{dx^2}\right|_0 x^2 + \cdots$$

$$f(0) = \frac{1}{1-0} = 1$$

$$f'(0) = \left.\frac{+1}{(1-x)^2}\right|_0 = 1$$

$$f''(0) = \frac{+2}{(1-x)^{-3}} = 2$$

$$f(x) = 1 + x + x^2 + \cdots \sum_{b=0}^{\infty} x^b$$

Proof② $\frac{1}{1-x} \stackrel{?}{=} 1 + x + x^2 + x^3 + \cdots$

$$1 \stackrel{?}{=} (1-x)(1 + x + x^2 + x^3 + \cdots)$$

$$= 1 + x + x^2 + x^3 + \cdots - x - x^2 - x^3 - \cdots = 1$$

$|x| < 1$

$$\text{Denominator} = Z_1 = \frac{1}{1-x}$$

$$\text{Numerator} = \sum_{a=0}^{\infty} a\,x^{a}$$

$$\frac{d}{dx} Z_1 = \frac{d}{dx}\sum_{a=0}^{\infty} x^{a} = \sum_{a=0}^{\infty} a\,x^{a-1}$$

$$x\frac{d}{dx} Z_1 = \sum_{a=0}^{\infty} a\,x^{a} = x\frac{d}{dx}\left(\frac{1}{1-x}\right)$$

$$= \frac{x}{(1-x)^2} = \text{Numerator}$$

$$\langle n\rangle = \frac{\left[\frac{x}{(1-x)^2}\right]}{\left[\frac{1}{1-x}\right]} = \frac{x}{1-x} = \frac{1}{\frac{1}{x}-1}$$

$$x = e^{-\frac{\hbar\omega}{k_B T}}$$

$$\langle n\rangle = \frac{1}{e^{\frac{\hbar\omega}{k_B T}}-1}$$ Planck distribution