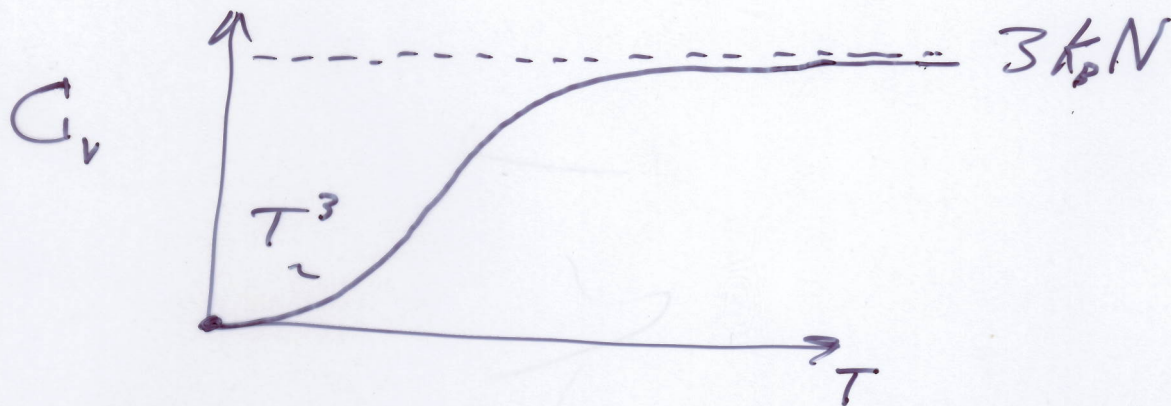
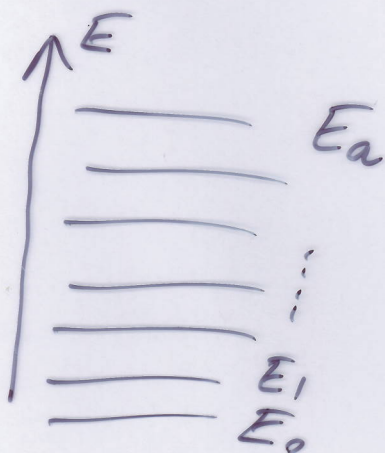


We want a lattice heat capacity at constant volume $C_v \equiv \left(\frac{\partial U}{\partial T}\right)_v \sim C_p$ for solids
 $C_v = C_p$ as $T \rightarrow 0$. Need $U(T)$



(Classically, use equipartition (valid at high T) $\Rightarrow \frac{1}{2}k_B T$ per degree of freedom
 Nature, 3 dimensions, Kinetic or Potential energy

$$U = 3Nk_B T \quad \Rightarrow \quad C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3Nk_B$$



Probability system has energy

E_a is

$$P_a \propto e^{-\frac{E_a}{k_B T}}$$

$$\sum_{a=0}^{\infty} P_a = 1 \quad \Rightarrow \quad \sum_{a=0}^{\infty} e^{-\frac{E_a}{k_B T}}$$

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

Denominator

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

partition function

Simple Harmonic Oscillator

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

N_a = # phonons in state a
 fraction of phonons in state a is

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

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

Average excitation quantum number, occupation number

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

$$\text{Define } x = \frac{-\left(\frac{h\nu}{k_B T}\right)}{e^{\left(\frac{h\nu}{k_B T}\right)}}$$

$$\sum_1 = \sum_{b=0}^{\infty} x^b = \frac{1}{1-x}$$

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

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

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

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

$$f''(0) = \left. \frac{+2}{(1-x)^3} \right|_0 = 2$$

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

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

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

$$= 1 + x + x^2 + x^3 + \dots$$

$$-x - x^2 - x^3 - \dots = 1 \quad \checkmark$$

$$|x| < 1$$

$$\text{Denominator} = \sum_+ = \frac{1}{1-x}$$

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

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

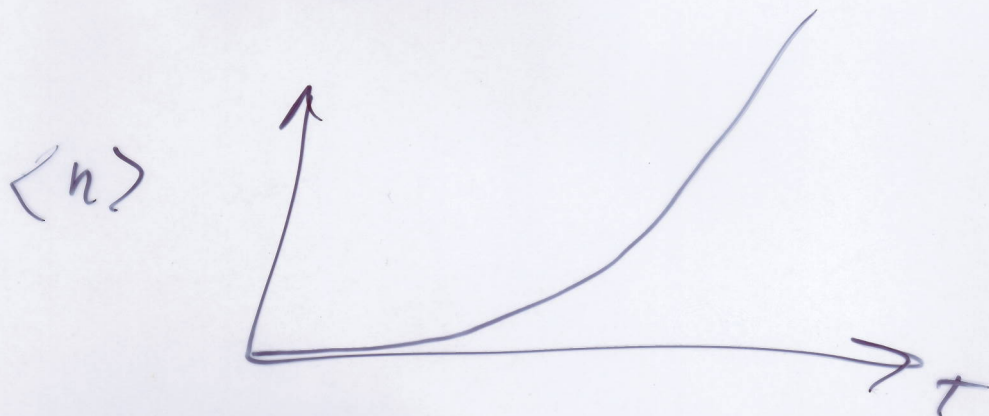
$$\begin{aligned} x \frac{d}{dx} \sum_+ &= \sum_{a=0}^{\infty} a x^a = x \frac{d}{dx} \left(\frac{1}{1-x} \right) \\ &= \frac{x}{(1-x)^2} = \text{Numerator} \end{aligned}$$

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

$$x = e^{-\frac{h\nu}{k_B T}}$$

$$\langle n \rangle = \frac{1}{e^{\frac{h\nu}{k_B T}} - 1}$$

Planck distribution



Average energy of an oscillator at temp T

$$\langle u \rangle = \langle (n + \frac{1}{2}) \hbar \omega \rangle = \hbar \omega \langle n \rangle + \frac{1}{2} \hbar \omega$$

$$= \frac{\hbar \omega}{e^{\frac{\hbar \omega}{k_B T}} - 1} + \frac{1}{2} \hbar \omega$$

high temperature $T \gg \frac{\hbar \omega}{k_B}$

$$\langle u \rangle = k_B T$$

3 dimensions, N atoms

$$U = 3N k_B T$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3N k_B \\ = 3R \times (\# \text{ moles})$$

$$U = \sum_k \sum_{p=1}^3 \langle n_{kp} \rangle \hbar \omega_{kp}$$

\uparrow wave vector \leftarrow polarization

For N atoms, there are $3N$ wave numbers

easier to replace \sum_k by integral

$$U = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{e^{\frac{\hbar \omega}{k_B T}} - 1}$$

\uparrow density of states

$D_p(\omega)$ is the number of vibrational modes (states) of polarization p in the frequency range ω to $\omega + d\omega$

$$D(\omega) = \frac{dN}{d\omega} \leftarrow \# \text{ of states}$$

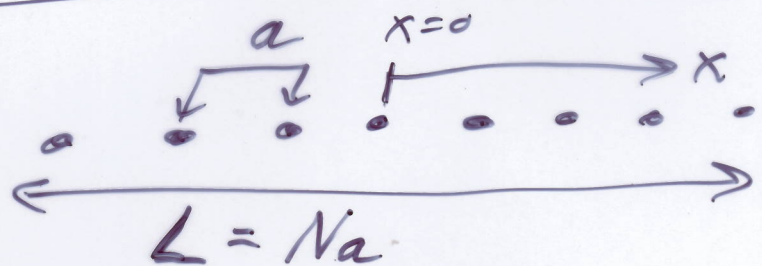
$$\int D(\omega) d\omega = \int \frac{dN}{d\omega} d\omega = \int dN = N$$

If $N(k)$ is the total number of states (modes) with wave number less than k .

$$D(\omega) = \frac{dN}{d\omega} = \frac{dN}{dk} \cdot \frac{dk}{d\omega} = \frac{dN}{dk} \left(\frac{1}{\frac{d\omega}{dk}} \right)$$

$$= \frac{dN}{dk} v_{\text{group}}$$

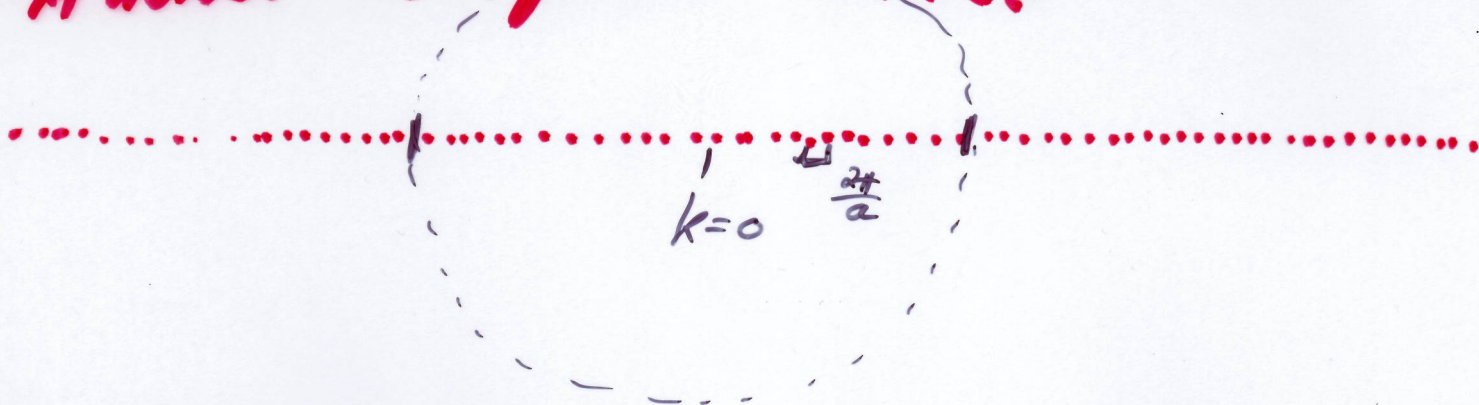
one dimension
direct lattice



Reciprocal lattice



Another reciprocal lattice



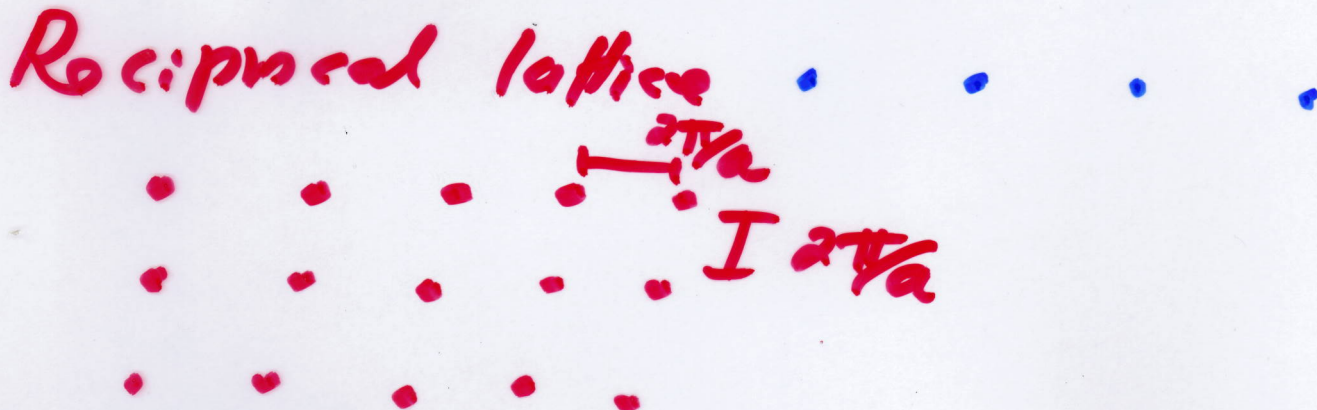
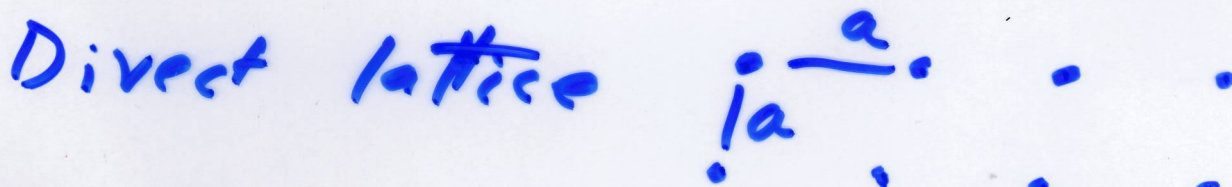
$N(k)$ = # of dots (wavenumbers) in the interval.

$$N = \frac{L}{a} = \frac{Lk}{\pi} = \frac{2Lk}{2\pi} = 2k \left(\frac{L}{2\pi} \right)$$

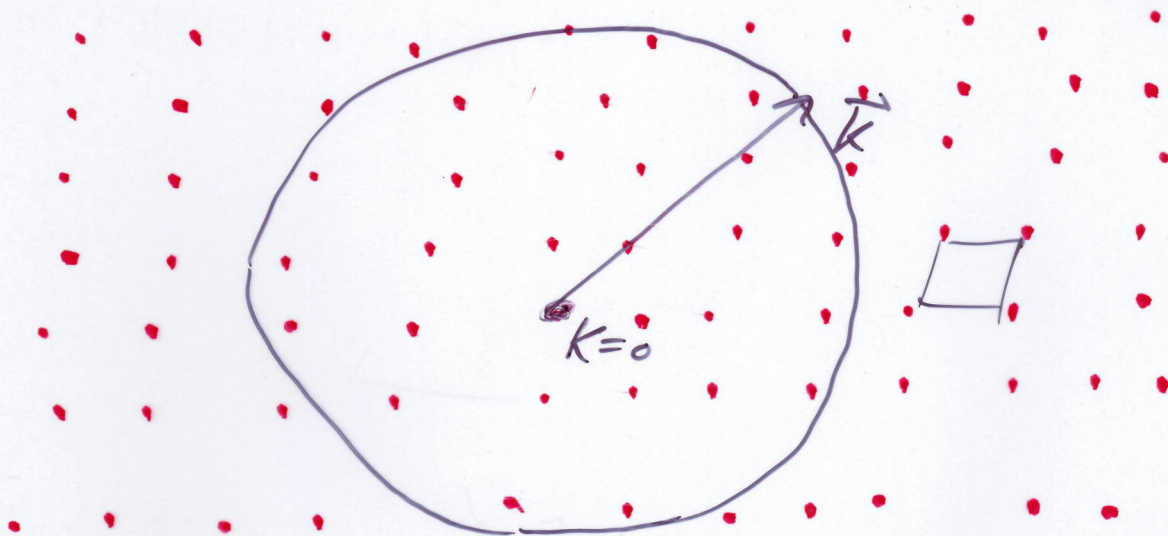
$$\frac{dN}{dk} = 2 \left(\frac{L}{2\pi} \right)$$

$$D(\omega) = \frac{dN}{dk} \frac{1}{v_{group}} = 2 \left(\frac{L}{2\pi} \right) \frac{1}{v_{group}}$$

Two dimensions



Reciprocal Lattice



$$N(k) = \pi k^2 \left(\frac{L}{2\pi}\right)^2$$

$$\frac{dN}{dk} = 2\pi k \left(\frac{L}{2\pi}\right)^2$$

Three dimensions

$$N(k) = \frac{4}{3}\pi k^3 \left(\frac{L}{2\pi}\right)^3$$

$$\frac{dN}{dk} = 4\pi k^2 \left(\frac{L}{2\pi}\right)^3$$