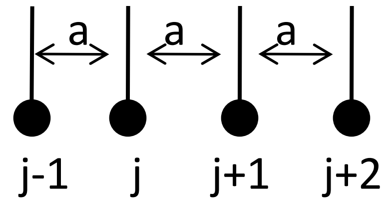
Chapter 11 – McQuarrie – Crystals

don't have to worry about transl. or rotation of entire crystal

monotonic crystals – 1D case



$$U = U(0,0,\ldots 0) + \sum_{j=1}^{N} \left(\frac{\partial U}{\partial \zeta_j} \right)_0 \zeta_j + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 U}{\partial \zeta_i \partial \zeta_j} \right)_0 \zeta_i \zeta_j + \ldots$$

U(0, 0, 0) – all atoms at equilibrium positions

Taylor series about the equilibrium structure

$$U = \underbrace{U(0,0,\ldots 0)}_{\text{Depends on } V/N} + \frac{1}{2} \sum_{i,j} k_{ij} \zeta_i \zeta_j + \ldots$$

first derivates vanish because we are expanding about a minimum

force constants (depend on *V/N*)

Apply normal mode analysis (find coordinates that eliminate off-diagonal terms)

$$\nu_j = \frac{1}{2\pi}\sqrt{\frac{k_j}{\mu_j}}, \quad j = 1, 2, \ldots, 3N$$

(for 3D case)

$$Q\left(\frac{V}{N}, T\right) = e^{-U(0,\rho)/kT} \prod_{j=1}^{3N} q_{vib_j}$$

lattice points can be labeled. Hence no *N!* factor

$$Q = \prod_{j=1}^{3N} \left(\frac{e^{-h\nu_j/2kT}}{1 - e^{-h\nu_j/kT}} \right) e^{-U(0,\rho)/kT}$$

Let $g(\nu)d\nu =$ # frequencies between ν and $\nu + d\nu$

$$-\ell n Q = \frac{U(0,\rho)}{kT} + \int_0^\infty \left[\ell n\left(1 - e^{-h\nu/kT}\right) + \frac{h\nu}{2kT} \right] g(\nu)\, d\nu$$

$$\int_0^\infty g(\nu)\, d\nu = 3N$$

total # of vibrations

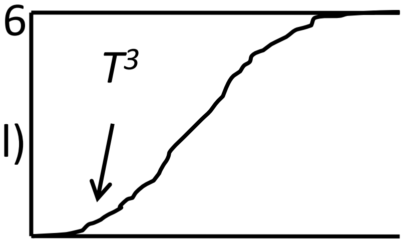
$$E = U(0,\rho) + \int_0^\infty \left[\frac{h\nu e^{-h\nu/kT}}{\left(1 - e^{-h\nu/kT}\right)} + \frac{h\nu}{2} \right] g(\nu)\, d\nu$$

$$C_{\mathrm{v}} = k \int_0^\infty \left(\frac{h\nu}{kT} \right)^2 \frac{e^{-h\nu/kT}}{\left(1 - e^{-h\nu/kT}\right)^2} g(\nu)\, d\nu$$

But how do
we find *g(ν)*?

Einstein assumed all oscillators had frequency ν_E

$$g(\nu) = 3N\delta(\nu - \nu_E)$$



$$C_v = 3Nk\left(\frac{h\nu_E}{kT}\right)^2 \frac{e^{-h\nu_E/kT}}{\left(1-e^{-h\nu_E/kT}\right)^2} = 3Nk\left(\frac{\theta_E}{T}\right)^2 \frac{e^{-\theta_E/T}}{\left(1-e^{-\theta_E/T}\right)^2}$$

$$\rightarrow 0, \quad T \rightarrow 0$$

$$\rightarrow 3Nk, \quad T \rightarrow \infty$$

but fails to give observed T^3 behavior at low T

law of corresponding states – C_v *vs.* T curve same for all materials if plotted as a function of $\frac{T}{\theta_E}$

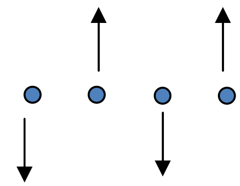
Debye theory

Debye: vibrations with λ >> lattice spacing can be treated by assuming the crystal is a continuous elastic substance

$$g(\nu)\,d\nu = \left(\frac{2}{\mathrm{v}_t^3} + \frac{1}{\mathrm{v}_\ell^3}\right) 4\pi V \nu^2 d\nu$$

Let $\dfrac{3}{\mathrm{v}_0^3} \equiv \dfrac{2}{\mathrm{v}_t^3} + \dfrac{1}{\mathrm{v}_\ell^3}$

$$g(\nu)\,d\nu = \frac{12\pi V}{\mathrm{v}_0^3}\nu^2 d\nu$$

t = transverse 

ℓ = longitudinal 

v_t and v_ℓ are the transverse and longitudinal velocities

$$\int_0^{\nu_D} g(\nu)\,d\nu = \frac{4\pi V}{\mathrm{v}_0^3}\nu_D^3 = 3N \Rightarrow \nu_D = \left(\frac{3N}{4\pi V}\right)^{1/3} \mathrm{v}_0$$

$$g(\nu)\,d\nu = \frac{9N}{\nu_D^3}\nu^2 d\nu \qquad 0 \le \nu \le \nu_D$$

$$= 0 \qquad \nu > \nu_D$$

Lattice dynamics

consider the 1D case

$$H = \sum_{j=1}^{N} \frac{m}{2} \dot{\zeta}_j^2 + \sum_{j=2}^{N} \left(\zeta_j - \zeta_{j-1}\right)^2 \frac{f}{2}$$

$$\mathrm{m}\,\ddot{\zeta}_j = f\left(\zeta_{j+1} + \zeta_{j-1} - 2\zeta_j\right)$$

let $\zeta_j = e^{i\omega t} y_j$

Assumes the time dependence is harmonic

$$-m\omega^2 y_j = f\left(y_{j+1} + y_{j-1} - 2y_j\right)$$

difference equation

try $y_j = e^{ij\phi}$

$$-m\omega^2 = f[2\cos\varphi - 2] \rightarrow \omega^2 = \frac{4f}{m}\sin^2\left(\frac{\phi}{2}\right)$$

$$\zeta_j(t) = e^{i(\omega t + j\phi)}$$

repeats every $\Delta j = \frac{2\pi}{\phi}, \quad \lambda = a\Delta j = \frac{a2\pi}{\phi}$

$$\phi = \frac{2\pi a}{\lambda} = ka, \qquad k = \text{wave vector}$$

a = lattice spacing

$\hbar k$ = momentum of phonon.

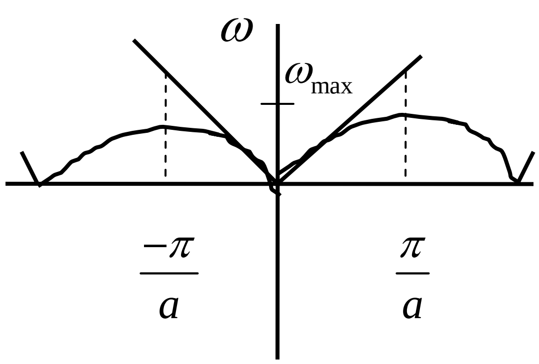
$$\zeta_j(t) = e^{i(jka + \omega t)}$$

wavelength = $\frac{2\pi}{k}$

freq = ω

$$\omega = \omega_{\max}\left|\sin\left(\frac{ka}{2}\right)\right|$$

$k \rightarrow k + \frac{2\pi n}{a}, \quad n = \pm 1, \pm 2, \ldots$ leaves ζ_j uncharged



So we need only $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$

Periodic boundary conditions

$$\zeta_j(t) = \zeta_{j+N}(t) \longleftarrow$$

ends of chain connected to give a circle

$$e^{iNka} = 1 \Rightarrow k = \frac{2\pi j}{Na}, \quad j \text{ an integer} \qquad \Rightarrow j = \pm 1, \pm 2, \ldots, \pm \frac{N}{2}$$

$$E = \sum_j \frac{\hbar\omega_j}{\left(e^{\beta\hbar\omega_j} - 1\right)} = \frac{Na}{\pi}\int_0^{\pi/a} \frac{\hbar\omega(k)dk}{e^{\beta\hbar\omega(k)} - 1}$$

$$dk = \frac{dk}{d\omega}d\omega = \frac{d}{d\omega}\left[\frac{2}{a}\sin^{-1}\left(\frac{\omega}{\omega_{\max}}\right)\right]d\omega$$

$$= \frac{2d\omega}{a\left(\omega_{\max}^2 - \omega^2\right)^{1/2}}$$

$$\Rightarrow g(\text{v}) = \frac{2N}{\pi}\frac{1}{\sqrt{v_{\max}^2 - v^2}}$$

For one-dimensional crystal

$$g(\nu) = \frac{Na}{\pi}\frac{1}{d\nu/dk}$$

dv/dk = group velocity
= constant for a continuum