

## 6.730 Physics for Solid State Applications

### Lecture 11: Specific Heat of Discrete Lattice

#### Outline

- Review Continuum Specific Heat Calculation
- Density of Modes
- Quantum Theory of Lattice Vibrations
- Specific Heat for Lattice
- Approximate Models

February 27, 2004

### Specific Heat of Solid How much energy is in each mode ?

Approach:

- Quantize the amplitude of vibration for each mode
- Treat each quanta of vibrational excitation as a bosonic particle, *the phonon*

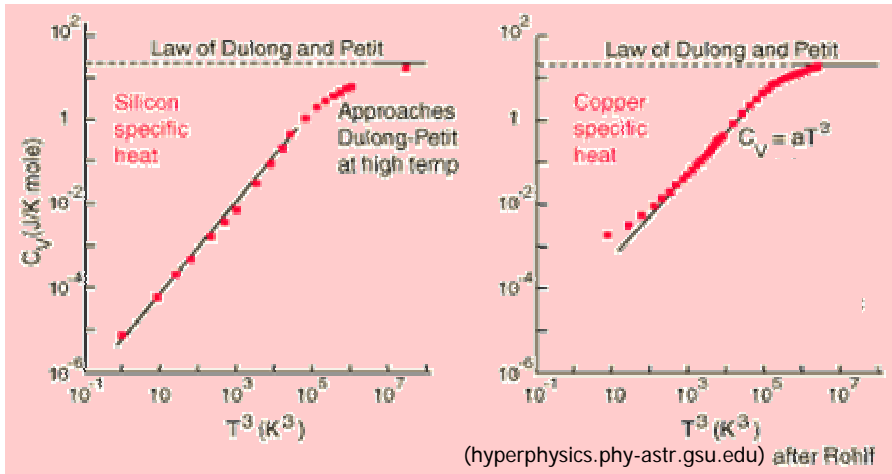
$$E = \sum_{\mathbf{k}, \sigma} \hbar \omega_{\mathbf{k}, \sigma} \left[ \langle n_{\mathbf{k}, \sigma} \rangle + \frac{1}{2} \right]$$

- Use Bose-Einstein statistics to determine the number of phonons in each mode

$$\langle n_{\mathbf{k}, \sigma} \rangle = \frac{1}{e^{\hbar \omega_{\mathbf{k}, \sigma} / k_B T} - 1}$$

$$\frac{E}{V} = \sum_{\sigma} \int \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} g_{\sigma}(\omega) d\omega$$

## Specific Heat Measurements



$$C_v = C_{el} + C_{phonon} = \gamma T + AT^3$$

## Hamiltonian for Discrete Lattice

Potential energy of bonds in 3-D lattice with basis:

$$V(\{u[\mathbf{R}_s, t]\}) = V_0 + \frac{1}{2} \sum_i \sum_j \sum_{\mathbf{R}_p} \sum_{\mathbf{R}_m} u_i[\mathbf{R}_p, t] \tilde{D}_{i,j}(\mathbf{R}_p, \mathbf{R}_m) u_j[\mathbf{R}_m, t]$$

For single atom basis in 3-D,  $\mu$  &  $\nu$  denote x,y, or z direction:

$$H = \frac{M}{2} \sum_{\mathbf{R}_j} \sum_{\mu} \dot{u}_{\mu}[\mathbf{R}_j, t] \dot{u}_{\mu}[\mathbf{R}_j, t] + \sum_{\mathbf{R}_j} \sum_{\mathbf{R}_k} \sum_{\mu} \sum_{\nu} u_{\mu}[\mathbf{R}_j, t] \tilde{D}_{\mu\nu}(\mathbf{R}_j - \mathbf{R}_k) u_{\nu}[\mathbf{R}_k, t]$$

$$[\hat{x}, \hat{p}] = i\hbar \quad \longrightarrow \quad M [u_{\mu}[\mathbf{R}_j, t], \dot{u}_{\nu}[\mathbf{R}_k, t]] = i\hbar \delta_{\mu,\nu} \delta_{\mathbf{R}_j, \mathbf{R}_k}$$

## Hamiltonian for Discrete Lattice Plane Wave Expansion

$$H = \frac{M}{2} \sum_{\mathbf{R}_j} \sum_{\mu} \dot{\mathbf{u}}_{\mu}[\mathbf{R}_j, t] \dot{\mathbf{u}}_{\mu}[\mathbf{R}_j, t] + \sum_{\mathbf{R}_j} \sum_{\mathbf{R}_k} \sum_{\mu} \sum_{\nu} \mathbf{u}_{\mu}[\mathbf{R}_j, t] \tilde{\mathbf{D}}_{\mu\nu}(\mathbf{R}_j - \mathbf{R}_k) \mathbf{u}_{\nu}[\mathbf{R}_k, t]$$

The lattice wave can be represented as a superposition of plane waves (eigenmodes) with a known dispersion relation (eigenvalues)....

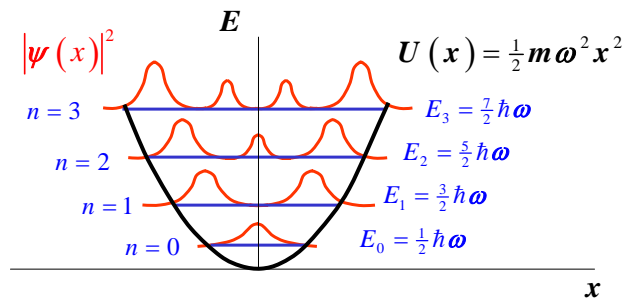
$$\mathbf{u}[\mathbf{R}_j, t] = \sum_{\mathbf{k}} \sum_{\sigma} \mathbf{b}_{\mathbf{k}\sigma} e^{i\mathbf{k}\mathbf{R}_j} \tilde{\mathbf{e}}_{\mathbf{k}\sigma} \quad \sum_{\nu} \tilde{\mathbf{D}}_{\mu\nu} \tilde{\mathbf{e}}_{\mathbf{k}\sigma\nu} = M\omega_{\mathbf{k}\sigma}^2 \tilde{\mathbf{e}}_{\mathbf{k}\sigma\mu}$$

$\sigma$  denotes polarization

$$H = \frac{MN}{2} \sum_{\mathbf{k}} \sum_{\sigma} \dot{\mathbf{b}}_{-\mathbf{k}\sigma} \dot{\mathbf{b}}_{\mathbf{k}\sigma} + \frac{MN}{2} \sum_{\mathbf{k}} \sum_{\sigma} \omega_{\mathbf{k}\sigma}^2 \mathbf{b}_{-\mathbf{k}\sigma} \mathbf{b}_{\mathbf{k}\sigma}$$

Sum of harmonic oscillators for each mode

## Simple Harmonic Oscillator



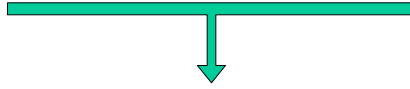
$$\hat{a} = \sqrt{\frac{M\omega^2}{2\hbar}} \hat{x} + i\sqrt{\frac{1}{2M\hbar\omega}} \hat{p} \quad \hat{a}^\dagger = \sqrt{\frac{M\omega^2}{2\hbar}} \hat{x} - i\sqrt{\frac{1}{2M\hbar\omega}} \hat{p}$$

$$[\hat{x}, \hat{p}] = i\hbar \quad \longrightarrow \quad [\hat{a}, \hat{a}^\dagger] = 1$$

$$H = \hbar\omega \left[ \hat{a}^\dagger \hat{a} + \frac{1}{2} \right]$$

## Commutation Relation for Plane Wave Displacement

$$M [\mathbf{u}_\mu[\mathbf{R}_j, t], \dot{\mathbf{u}}_\nu[\mathbf{R}_k, t]] = i\hbar \delta_{\mu,\nu} \delta_{R_j, R_k} \quad \mathbf{u}[\mathbf{R}_j, t] = \sum_{\mathbf{k}} \sum_{\sigma} b_{\mathbf{k}\sigma} e^{i\mathbf{k}\mathbf{R}_j} \tilde{\epsilon}_{\mathbf{k}\sigma}$$



$$M \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{\sigma} \sum_{\sigma'} [b_{\mathbf{k}\sigma}, \dot{b}_{\mathbf{k}'\sigma'}] e^{i\mathbf{k}\mathbf{R}_j + i\mathbf{k}'\mathbf{R}_k} \epsilon_{\mu, \mathbf{k}\sigma} \epsilon_{\nu, \mathbf{k}'\sigma'} = i\hbar \delta_{\mu,\nu} \delta_{R_j, R_k}$$

$$\sum_{\mu} \epsilon_{\mu, \mathbf{k}\sigma} \epsilon_{\mu, \mathbf{k}\sigma'} = \delta_{\sigma, \sigma'}$$

$$\sum_{\sigma} \epsilon_{\mu, \mathbf{k}\sigma} \epsilon_{\nu, \mathbf{k}\sigma} = \delta_{\mu, \nu}$$

$$M [b_{\mathbf{k}\sigma}, \dot{b}_{\mathbf{k}'\sigma'}] = i\hbar \delta_{\sigma\sigma'} \delta_{\mathbf{k}, -\mathbf{k}'}$$

...commute unless we have same polarization and k-vector

## Creation and Annihilation Operators for Lattice Waves

$$\hat{a}_{\mathbf{k}\sigma} = \sqrt{\frac{MN\omega_{\mathbf{k}\sigma}}{2\hbar}} b_{\mathbf{k}\sigma} + i\sqrt{\frac{MN}{2\hbar\omega_{\mathbf{k},\sigma}}} \dot{b}_{\mathbf{k}\sigma}$$

$$\hat{a}_{\mathbf{k}\sigma}^\dagger = \sqrt{\frac{MN\omega_{\mathbf{k}\sigma}}{2\hbar}} b_{-\mathbf{k}\sigma} - i\sqrt{\frac{MN}{2\hbar\omega_{\mathbf{k},\sigma}}} \dot{b}_{-\mathbf{k}\sigma}$$

$$[\hat{a}_{\mathbf{k},\sigma}, \hat{a}_{\mathbf{k}',\sigma'}^\dagger] = \delta_{\mathbf{k},\mathbf{k}'} \delta_{\sigma,\sigma'}$$

$$H = \sum_{\mathbf{k}} \sum_{\sigma} \frac{\hbar\omega_{\mathbf{k}\sigma}}{2} [a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} + a_{-\mathbf{k}\sigma} a_{-\mathbf{k}\sigma}^\dagger]$$

$$H = \sum_{\mathbf{k}} \sum_{\sigma} \hbar\omega_{\mathbf{k}\sigma} \left[ a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} + \frac{1}{2} \right]$$

## Operators for the Lattice Displacement

$$\hat{a}_{\mathbf{k}\sigma} = \sum_{\mathbf{R}_j} \frac{e^{-i\mathbf{k}\mathbf{R}_j}}{\sqrt{N}} \tilde{\epsilon}_{\mathbf{k}\sigma} \left( \sqrt{\frac{M\omega_{\mathbf{k}\sigma}}{2\hbar}} \mathbf{u}[\mathbf{R}_j, t] + i\sqrt{\frac{1}{2M\hbar\omega_{\mathbf{k}\sigma}}} M\dot{\mathbf{u}}[\mathbf{R}_j, t] \right)$$

$$\hat{a}_{\mathbf{k}\sigma}^\dagger = \sum_{\mathbf{R}_j} \frac{e^{i\mathbf{k}\mathbf{R}_j}}{\sqrt{N}} \tilde{\epsilon}_{\mathbf{k}\sigma} \left( \sqrt{\frac{M\omega_{\mathbf{k}\sigma}}{2\hbar}} \mathbf{u}[\mathbf{R}_j, t] - i\sqrt{\frac{1}{2M\hbar\omega_{\mathbf{k}\sigma}}} M\dot{\mathbf{u}}[\mathbf{R}_j, t] \right)$$

$$\mathbf{u}[\mathbf{R}_j, t] = \sum_{\mathbf{k}} \sum_{\mu} b_{\mathbf{k}\mu} e^{i\mathbf{k}\mathbf{R}_j} \tilde{\epsilon}_{\mathbf{k}\mu}$$

$$\mathbf{u}[\mathbf{R}_j, t] = \sum_{\mathbf{k}\sigma} \sqrt{\frac{\hbar}{2MN\omega_{\mathbf{k}\sigma}}} (\hat{a}_{\mathbf{k}\sigma} e^{i\mathbf{k}\mathbf{R}_j} + \hat{a}_{\mathbf{k}^\dagger\sigma} e^{-i\mathbf{k}\mathbf{R}_j}) \tilde{\epsilon}_{\mathbf{k}\sigma}$$

We will use this for electron-phonon scattering...

## Specific Heat with Continuum Model for Solid

$$\frac{E}{V} = \sum_{\sigma} \int \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} g_{\sigma}(\omega) d\omega$$

3-D continuum density of modes in  $d\omega$ :  $g_{\sigma}(\omega) = \frac{\omega^2}{2\pi^2 c_{\sigma}^3}$

$$\begin{aligned} \frac{E}{V} &= \sum_{\sigma} \int \frac{\hbar\omega^3}{2\pi^2 c_{\sigma}^3 (e^{\hbar\omega/k_B T} - 1)} d\omega \\ &= \sum_{\sigma} \frac{\pi^2 k_B^4 T^4}{30 c_{\sigma}^3 \hbar^3} \end{aligned}$$

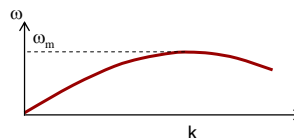
$$C_V = \frac{\partial(E/V)}{\partial T} = AT^3$$

## Specific Heat with Discrete Lattice Density of Modes from Dispersion

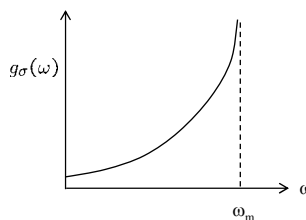
1-D continuum density of modes in  $d\omega$ :  $g_{\sigma}(\omega)$

$$\frac{dk}{2\pi} = g(\omega) d\omega \quad \longrightarrow \quad g_{1D}(\omega) = 2 \frac{1}{2\pi} \frac{1}{|\partial\omega/\partial k|}$$

$$\omega = \omega_m \left| \sin\left(\frac{ka}{2}\right) \right| \quad \text{for} \quad \omega_m = 2\sqrt{\alpha/M}$$



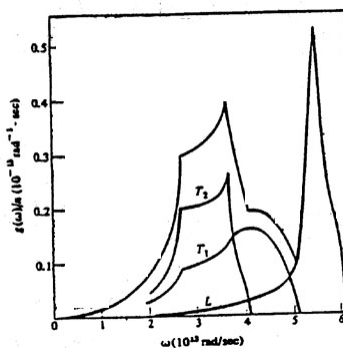
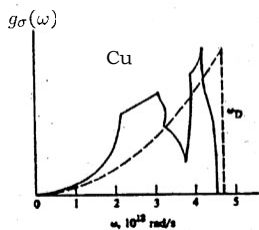
$$g_{1D}(\omega) = \frac{2}{a\pi \omega_m \cos\left(\frac{ka}{2}\right)} = \frac{2}{\pi a \sqrt{\omega_m^2 - \omega^2}}$$



## Specific Heat with Discrete Lattice Density of Modes from Dispersion

$$\frac{E}{V} = \sum_{\sigma} \int \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} g_{\sigma}(\omega) d\omega$$

3-D continuum density of modes in  $d\omega$ :  $g_{\sigma}(\omega)$



## Specific Heat of Solid How much energy is in each mode ?

Approach:

- Quantize the amplitude of vibration for each mode
- Treat each quanta of vibrational excitation as a bosonic particle, *the phonon*

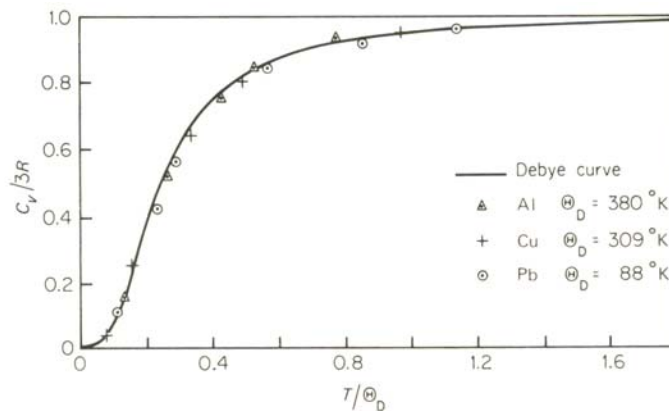
$$H = \sum_{\mathbf{k}} \sum_{\sigma} \hbar \omega_{\mathbf{k}\sigma} \left[ a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma} + \frac{1}{2} \right]$$

$$E = \sum_{\mathbf{k},\sigma} \hbar \omega_{\mathbf{k},\sigma} \left[ \langle n_{\mathbf{k},\sigma} \rangle + \frac{1}{2} \right]$$

- Use Bose-Einstein statistics to determine the number of phonons in each mode

$$\langle n_{\mathbf{k},\sigma} \rangle = \frac{1}{e^{\hbar \omega_{\mathbf{k},\sigma}/k_B T} - 1} \quad \frac{E}{V} = \sum_{\sigma} \int \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1} g_{\sigma}(\omega) d\omega$$

## Specific Heat of Solid How much energy is in each mode ?



And we are done...