6.730 Physics for Solid State Applications

Lecture 12: 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

March 1, 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*

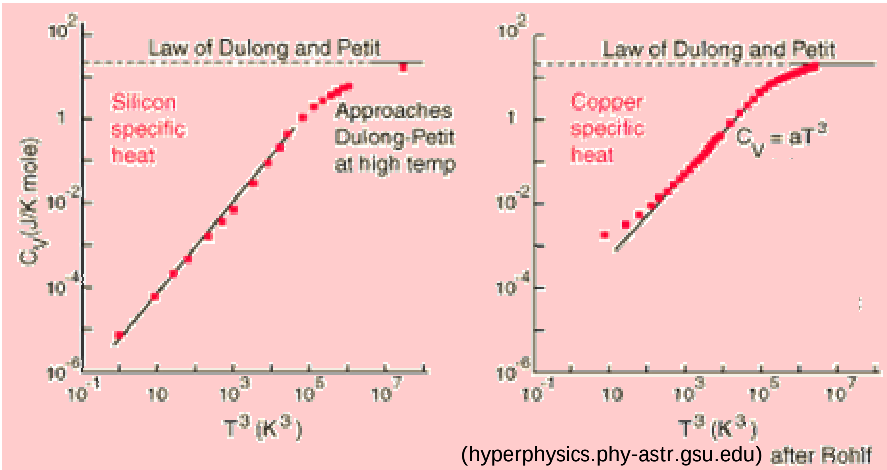
$$E = \sum_{\mathbf{k},\sigma} \hbar\omega_{\mathbf{k},\sigma} \left[\langle n_{\mathbf{k},\sigma} \rangle + \frac{1}{2} \right]$$

- 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:

$$V(\{u[\mathbf{R_s},\mathbf{t}]\}) = \mathbf{V_o} + \frac{1}{2}\sum_{\mathbf{i}}\sum_{\mathbf{j}}\sum_{\mathbf{R_p}}\sum_{\mathbf{R_m}} \mathbf{u_i}[\mathbf{R_p},\mathbf{t}]\,\widetilde{\mathbf{D}}_{\mathbf{i},\mathbf{j}}(\mathbf{R_p},\mathbf{R_m})\,\mathbf{u_j}[\mathbf{R_m},\mathbf{t}]$$

For single atom basis in 3-D, μ & ν denote x,y, or z direction:

$$H = \frac{M}{2}\sum_{\mathbf{R_j}}\sum_{\mu} \dot{\mathbf{u}}_\mu[\mathbf{R_j},\mathbf{t}]\,\dot{\mathbf{u}}_\mu[\mathbf{R_j},\mathbf{t}] + \sum_{\mathbf{R_j}}\sum_{\mathbf{R_k}}\sum_{\mu}\sum_{\nu} \mathbf{u}_\mu[\mathbf{R_j},\mathbf{t}]\,\widetilde{\mathbf{D}}_{\mu\nu}(\mathbf{R_j}-\mathbf{R_k})\,\mathbf{u}_\nu[\mathbf{R_k},\mathbf{t}]$$

$$[\widehat{x},\widehat{p}] = i\hbar \quad \Longrightarrow \quad M\left[\mathbf{u}_\mu[\mathbf{R_j},\mathbf{t}],\dot{\mathbf{u}}_\nu[\mathbf{R_k},\mathbf{t}]\right] = i\hbar\delta_{\mu,\nu}\,\delta_{R_j,R_k}$$

Hamiltonian for Discrete Lattice

Plane Wave Expansion

$$H = \frac{M}{2}\sum_{\mathbf{R_j}}\sum_{\mu} \dot{\mathbf{u}}_\mu[\mathbf{R_j},\mathbf{t}]\,\dot{\mathbf{u}}_\mu[\mathbf{R_j},\mathbf{t}] + \sum_{\mathbf{R_j}}\sum_{\mathbf{R_k}}\sum_{\mu}\sum_{\nu} \mathbf{u}_\mu[\mathbf{R_j},\mathbf{t}]\,\widetilde{\mathbf{D}}_{\mu\nu}(\mathbf{R_j}-\mathbf{R_k})\,\mathbf{u}_\nu[\mathbf{R_k},\mathbf{t}]$$

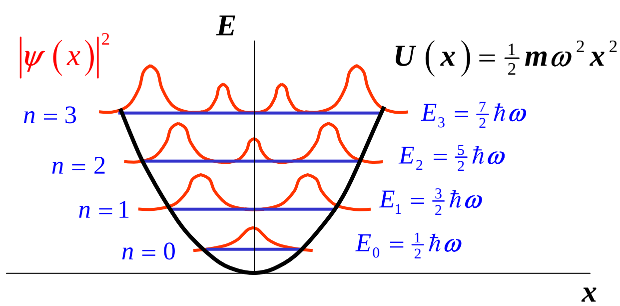
The lattice wave can be represented as a superposition of plane waves (eigenmodes) with a known dispersion relation (eigenvalues)….

$$\mathbf{u}[\mathbf{R_j},\mathbf{t}] = \sum_{\mathbf{k}}\sum_{\sigma} \mathbf{b_{k\sigma}}\,\mathbf{e^{ikR_j}}\,\tilde{\epsilon}_{\mathbf{k}\sigma} \qquad \sum_{\nu}\widetilde{\mathbf{D}}_{\mu\nu}\vec{\epsilon}_{\mathbf{k}\sigma\nu} = M\omega^2_{\mathbf{k}\sigma}\vec{\epsilon}_{\mathbf{k}\sigma\mu}$$

σ denotes polarization

$$H = \underbrace{\frac{MN}{2}\sum_{\mathbf{k}}\sum_{\sigma}\dot{\mathbf{b}}_{-\mathbf{k}\sigma}\,\dot{\mathbf{b}}_{\mathbf{k}\sigma} + \frac{MN}{2}\sum_{\mathbf{k}}\sum_{\sigma}\omega^2_{\mathbf{k}\sigma}\mathbf{b}_{-\mathbf{k}\sigma}\,\mathbf{b}_{\mathbf{k}\sigma}}_{\text{Sum of harmonic oscillators for each mode}}$$

Simple Harmonic Oscillator



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

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

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

Commutation Relation for Plane Wave Displacement

$$M\left[\mathbf{u}_\mu[\mathbf{R_j},\mathbf{t}],\dot{\mathbf{u}}_\nu[\mathbf{R_k},\mathbf{t}]\right]=i\hbar\delta_{\mu,\nu}\,\delta_{R_j,R_k}\qquad \mathbf{u}[\mathbf{R_j},\mathbf{t}]=\sum_{\mathbf{k}}\sum_\sigma \mathbf{b_{k\sigma}}\,\mathbf{e}^{\mathbf{ikR_j}}\,\tilde{\epsilon}_{\mathbf{k}\sigma}$$

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

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

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

…commute unless we have same polarization and k-vector

Creation and Annhilation Operators for Lattice Waves

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

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

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

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

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

Operators for the Lattice Displacement

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

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

$$\mathbf{u[R_j, t]} = \sum_{\mathbf{k}} \sum_{\mu} \mathrm{b}_{\mathbf{k}\mu}\, \mathrm{e}^{\mathbf{ikR_j}}\, \tilde{\epsilon}_{\mathbf{k}\mu}$$

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

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 $d\omega$: $g_{\sigma}(\omega) = \frac{\omega^2}{2\pi^2 c_{\sigma}^3}$

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

$$= \sum_{\sigma} \frac{\pi^2 k_B^4 T^4}{30 c_{\sigma}^3 \hbar^3}$$

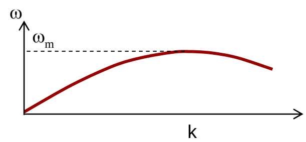
$$\boxed{C_V = \frac{\partial(E/V)}{\partial T} = AT^3}$$

Specific Heat with Discrete Lattice
Density of Modes from Dispersion

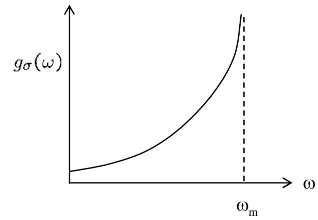
1-D continuum density of modes in $d\omega$: $g_\sigma(\omega)$

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

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



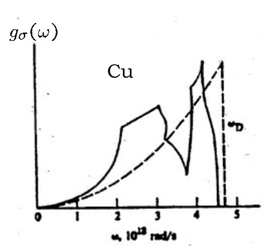
$$g_{1D}(\omega) = \frac{2}{a\pi}\frac{1}{\omega_m \cos\left(\frac{ka}{2}\right)} = \frac{2}{\pi a}\frac{1}{\sqrt{\omega_m^2 - \omega^2}}$$

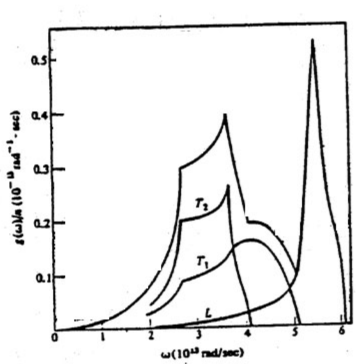


Specific Heat with Discrete Lattice
Density of Modes from Dispersion

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

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*

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

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

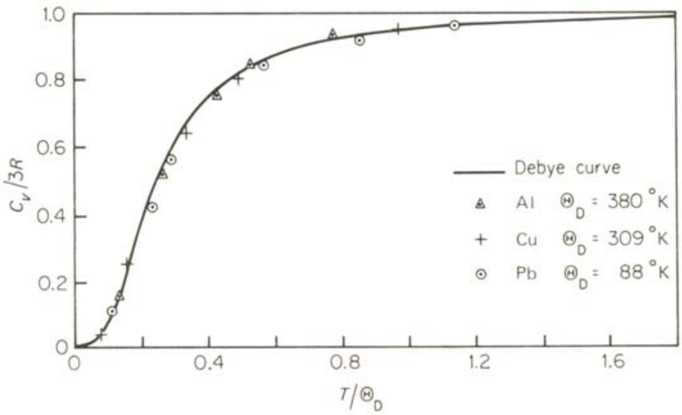
- Use Bose-Einstein statistics to determine the number of phonons in each mode

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

Specific Heat of Solid

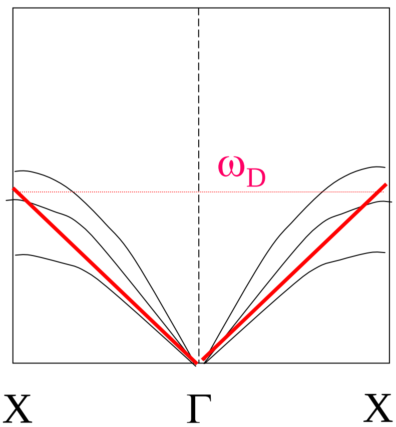
$$C_v = \frac{d}{dT} \sum_{\sigma} \int_{-\infty}^{\infty} \frac{\hbar\omega g_{\sigma}(\omega) d\omega}{e^{\hbar\omega/k_B T} - 1}$$

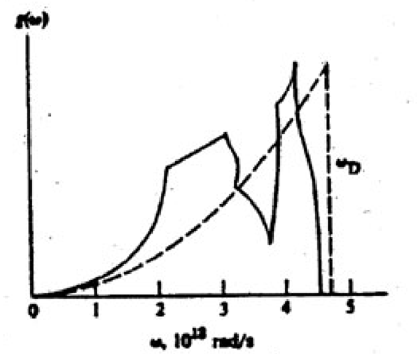
$$C_v = \frac{1}{4 k_B T^2} \sum_{\sigma} \int (\hbar\omega)^2 g_{\sigma}(\omega)\, \text{cosech}^2(\hbar\omega/2k_B T) d\omega$$



Approximate Models: The Debye Model

Replace exact phonon dispersion relation and the density of modes with the density of modes of an elastic continuum, but include a cut-off frequency, the Debye frequency ω_D





$$g(\omega) = \begin{cases} \frac{3\omega^2}{2\pi^2 v_s^3} & 0 < \omega < \omega_D \\ 0 & \omega > \omega_D \end{cases}$$

Determination of ω_D

The total number of modes of the system of N particles is 3N if there is one atom per primitive cell. The density of atoms per unit volume is then n = N/V.

The total density of modes is then

$$\int_{-\infty}^{\infty} g(\omega) d\omega = \frac{\omega_D^3}{2\pi^2 v_s^3} = 3n$$

Therefore,

$$\omega_D = (6\pi^2 n)^{1/3} v_s$$

Note: v_s can be the “real” or “weighted” or “model” velocity; that is one has the freedom to choose the ratio ω_D/v_s so long as n is correct.

Specific Heat in the Deybe Model

$$C_v = \frac{1}{4k_BT^2}\int_{-\infty}^{\infty}(\hbar\omega)^2 g(\omega)\,\mathrm{cosech}^2(\hbar\omega/2k_BT)d\omega$$

$$C_v = \frac{1}{4k_BT^2}\int_0^{\omega_D}(\hbar\omega)^2\left(\frac{3\omega^2}{2\pi^2 v_s^3}\right)\mathrm{cosech}^2\left(\frac{\hbar\omega}{2k_BT}\right)d\omega$$

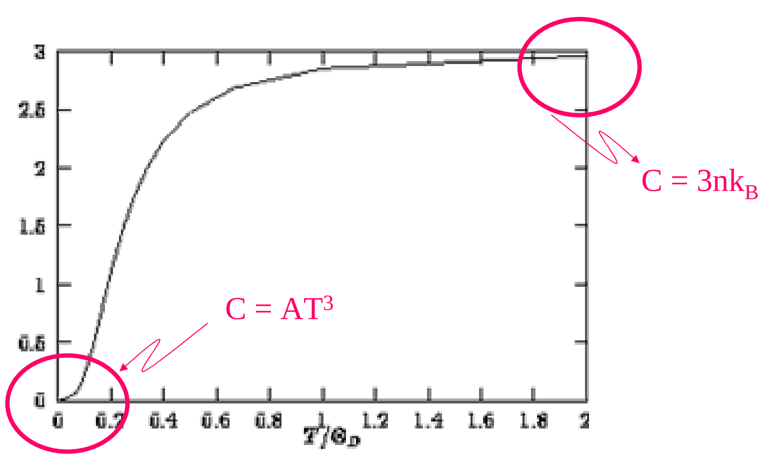
$$= \frac{3k_B^4T^3}{8\pi^2 v_s^3\hbar^3}\int_0^{\frac{\hbar\omega_D}{k_BT}} x^4\,\mathrm{cosech}^2(\frac{x}{2})dx$$

Define the Debye Temperature as $\theta_D = \hbar\omega_D/k_B$

$$C_v = 9nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4}{4}\mathrm{cosech}^2\frac{x}{2}dx$$

Debye Specific Heat

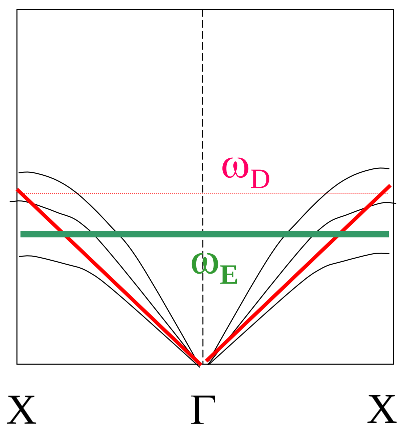
$$C_v = 9nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4}{4}\mathrm{cosech}^2\frac{x}{2}dx$$

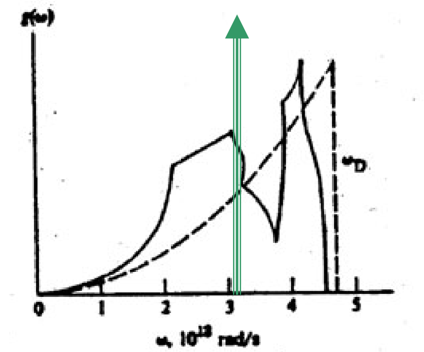


θ_D = 102 K for Pb, 343 K for Cu, and 1860 K for C.

Einstein Model

This is an even more simplistic model which approximates the dispersion relation by one frequency ω_E but demands that the number of modes per unit volume is correct.





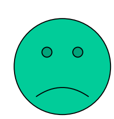
$$g(\omega) = 3n\,\delta(\omega - \omega_E)$$

Specific Heat in the Einstein Model

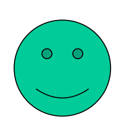
$$C_v = \frac{1}{4k_BT^2}\int_{-\infty}^{\infty}(\hbar\omega)^2 g(\omega)\,\mathrm{cosech}^2(\hbar\omega/2k_BT)d\omega$$

$$C_v = 3n\frac{\hbar^2\omega_o^2}{4k_BT^2}\,\mathrm{cosech}^2\frac{\hbar\omega_o}{2k_BT}$$

$C_V \approx 3n\frac{\hbar^2\omega_o^2}{k_BT^2}e^{-\hbar\omega_o/k_BT}$ for $\hbar\omega_o \gg k_BT$



$C_V \approx 3nk_B$ for $\hbar\omega_o \ll k_BT$



Combined Deybe and Einstein Models

Use Debye mode for acoustic modes and Einstein for optical mode.