More accurate Debye model.

$$v \rightarrow \begin{cases} v_L & \text{longitudinal speed} \\ v_T & \text{transverse speed} \end{cases}$$

Density of states

$$D_{LA}(\omega) = \frac{V\omega^2}{2\pi^2 v_L^3} \; ; \; D_{TA}(\omega) = \frac{V\omega^2}{2\pi^2 v_T^3} \times \underset{\substack{\uparrow \\ \text{2 polarizations}}}{2}$$

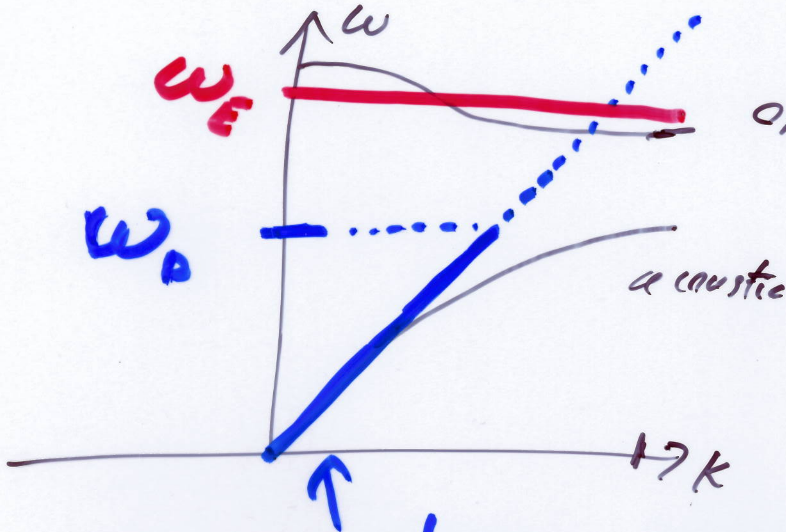
$$D_{tot}(\omega) = D_{LA}(\omega) + D_{TA}(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)$$

$$3N = \int_0^{\omega_D} \left[D_{LA}(\omega) + D_{TA}(\omega)\right] d\omega$$

$$\Longrightarrow \omega_D^3 = \frac{6\pi^2 N}{V}\left[\frac{3}{\frac{1}{v_L^3} + \frac{2}{v_T^3}}\right]$$

$$D_{tot}(\omega) = \frac{9N\omega^2}{\omega_D^3}$$

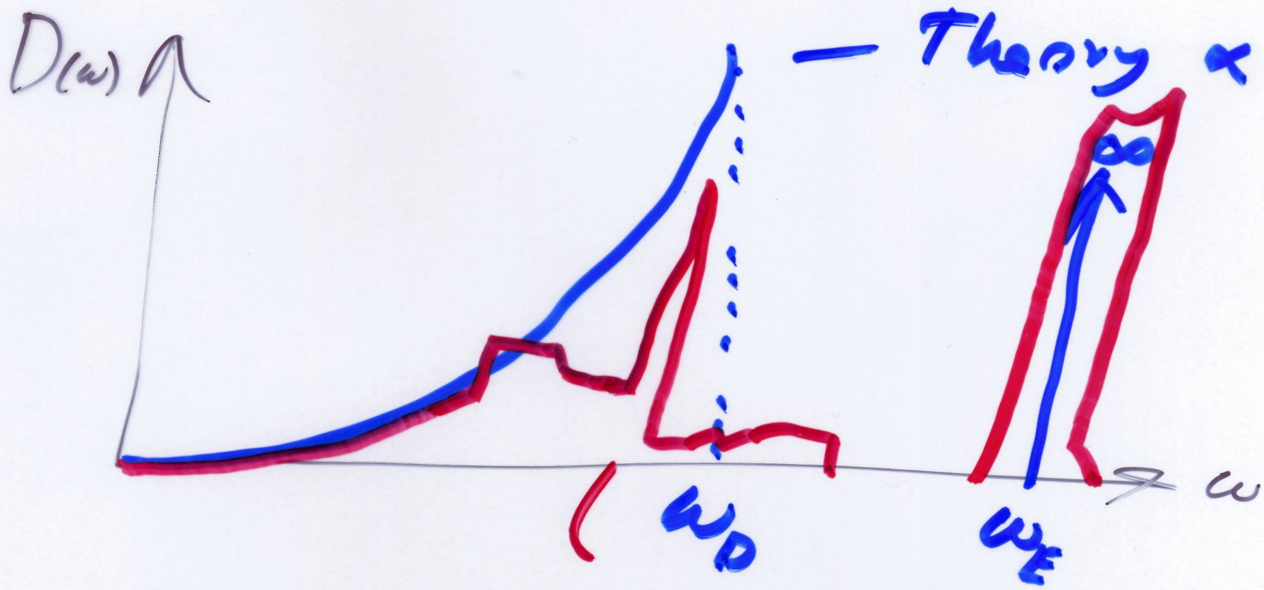
Dispersion Relations for a crystal with a polyatomic basis



Einstein
$\omega = \omega_E =$ constant

slope = speed of sound = v

Debye : $\omega = v k$



Data

Spikes in D(ω) occur when $v = 0$

Van Hove singularities

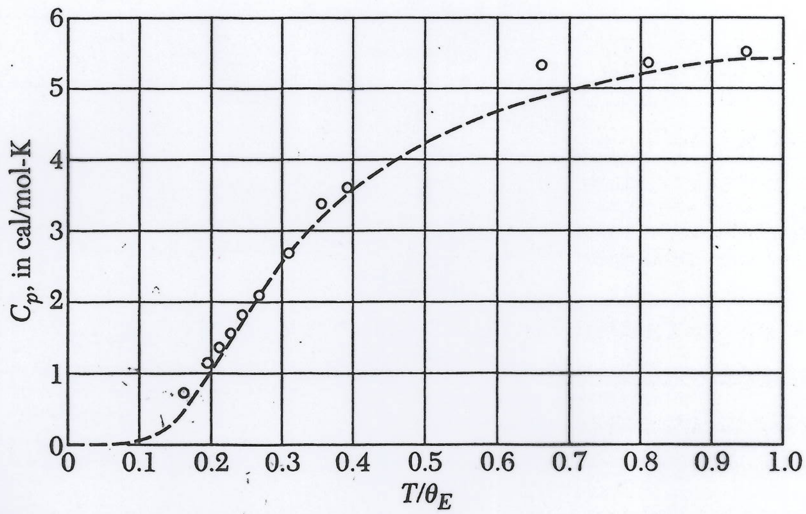


Figure 11 Comparison of experimental values of the heat capacity of diamond with values calculated on the earliest quantum (Einstein) model, using the characteristic temperature $\theta_E = \hbar\omega/k_B = 1320$ K. To convert to J/mol-deg, multiply by 4.186.

$$k_B T_E = \hbar \omega_E$$

$$\theta_E = T_E = \frac{\hbar \omega_E}{k_B}$$

Heat Capacity (Phonons)

p-atomic basis

$$C_V = C_{V_{Debye}} + C_{V_{Einstein}}$$

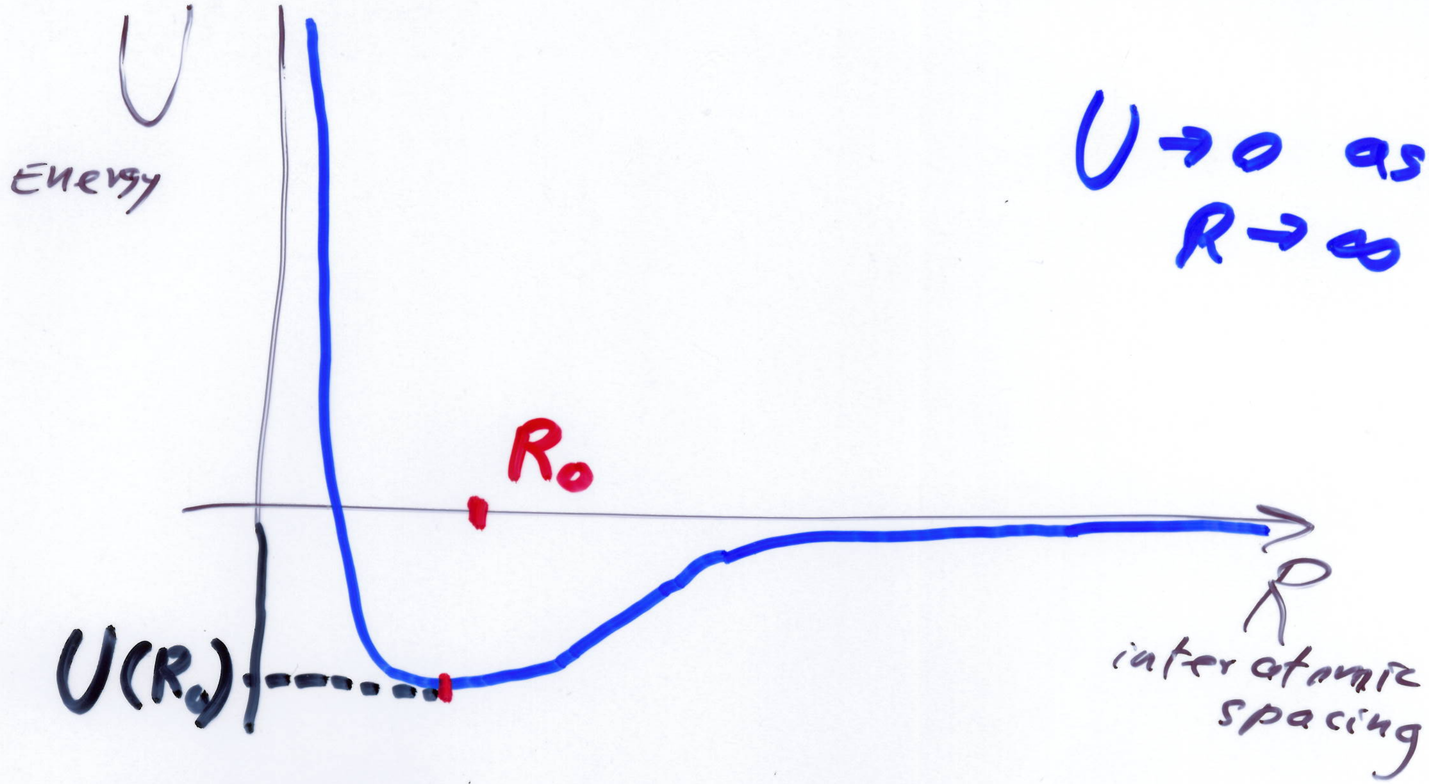
acoustic

1 Long + 2 Trans.

3 branches

optical

3p-3 optical branches



$U \to 0$ as $R \to \infty$

$$U(R) = U(R_0) + \underbrace{\cancel{\frac{dU}{dR}\Big|_{R_0}}}_{\to\, 0}(R-R_0)$$

$$+ \underbrace{\boxed{\frac{1}{2!}\frac{d^2U}{dR^2}\Big|_{R_0}}}_{c\,=}(R-R_0)^2 \quad \text{— harmonic}$$

$$+ \underbrace{\boxed{\frac{1}{3!}\frac{d^3U}{dR^3}\Big|_{R_0}}}_{-g\,=}(R-R_0)^3$$

$$+ \underbrace{\boxed{\frac{1}{4!}\frac{d^4U}{dR^4}\Big|_{R_0}}}_{-f\,=}(R-R_0)^4 + \dots$$

anharmonic

Define $x = R - R_0$ set $U(R_0) = 0$

$$U(x) = cx^2 - gx^3 - fx^4 + \cdots$$

Average Displacement

$$\langle x \rangle = \frac{\sum x\,P(x)}{\sum P(x)} = \frac{\int_{-\infty}^{+\infty} x\, e^{-\frac{U(x)}{k_B T}} dx}{\int_{-\infty}^{+\infty} e^{-\frac{U(x)}{k_B T}} dx}$$

Numerator

$$x\, e^{-\frac{cx^2 - gx^3 - fx^4}{k_B T}} = x\, e^{-\frac{cx^2}{k_B T}} \cdot e^{\frac{gx^3 + fx^4}{k_B T}}$$

Taylor expand last term

$$\approx x\, e^{-\frac{cx^2}{k_B T}} \left[1 + \frac{gx^3}{k_B T} + \frac{fx^4}{k_B T} + \cdots \right]$$

$$= e^{-\frac{cx^2}{k_B T}} \left[x + \frac{gx^4}{k_B T} + \frac{fx^5}{k_B T} + \cdots \right]$$

Denominator

$$e^{-\frac{U(x)}{k_B T}} = e^{-\frac{cx^2}{k_B T}} \cdot e^{\frac{gx^3 + fx^4}{k_B T}}$$

Taylor expand

$$\approx e^{-\frac{cx^2}{k_B T}}\left[1 + \cdots\right]$$

Num. $\displaystyle\int x\, e^{-\frac{U}{k_B T}}\,dx = \frac{3\sqrt{\pi}}{4}\,\frac{g}{(\sqrt{c})^5}\cdot\left(\sqrt{k_B T}\right)^3$

Den. $\displaystyle\int e^{-\frac{U}{k_B T}}\,dx = \sqrt{\frac{\pi k_B T}{c}}$

$$\langle x \rangle \approx \frac{3g}{4c^2}\cdot k_B T$$

$\langle x \rangle$ would be 0 without anharmonic terms.

Particle physics

momentum $= \hbar \vec{k}$

wavevector

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3$$

conserve momentum

Crystal

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{G}$$

Reciprocal lattice vector