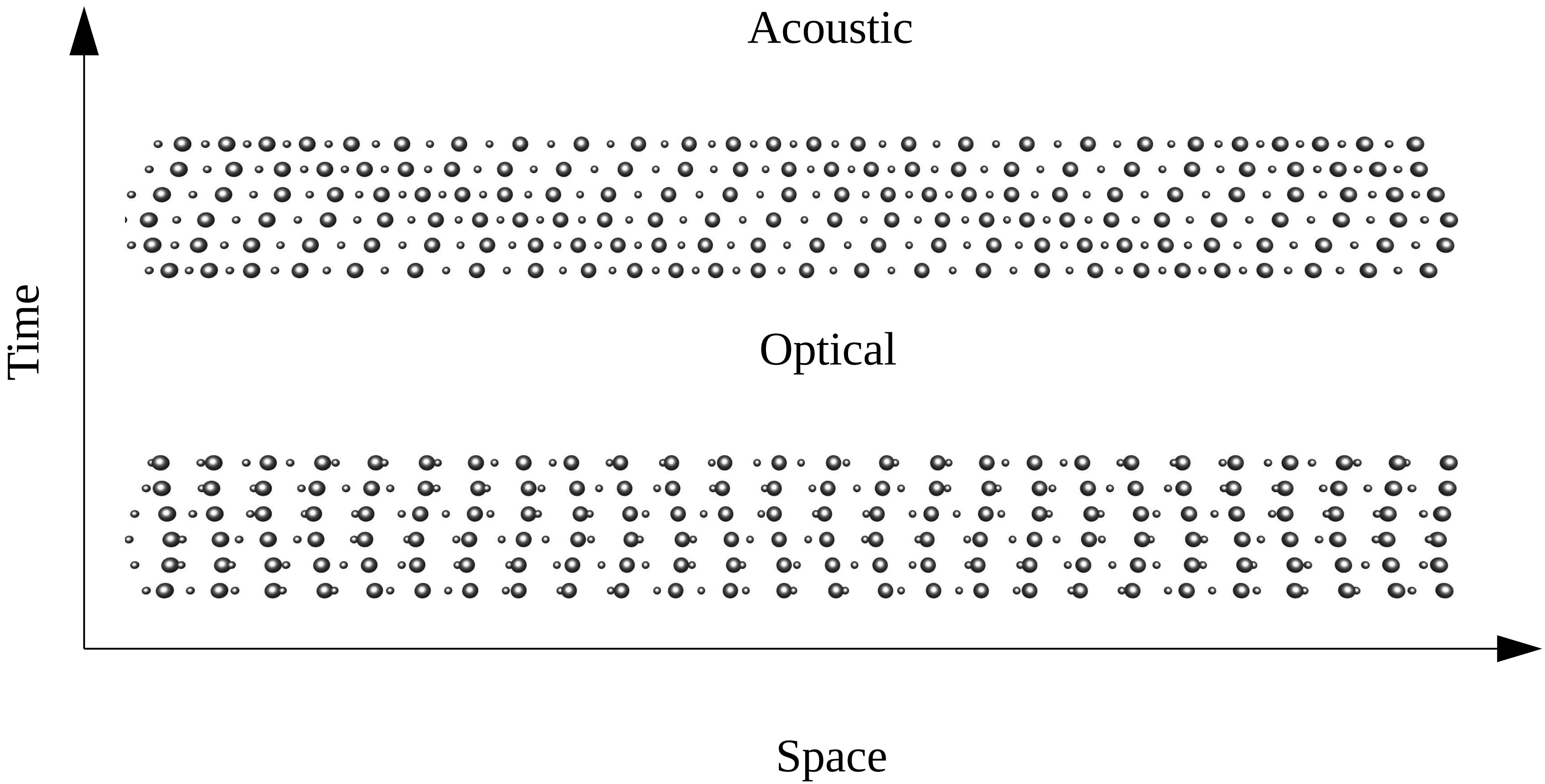
Phonons



Definitions

- Phonons
- Goldstone modes
- Acoustic branch
- Optical branch
- Density of phonon states
- Einstein model
- Debye model, Debye frequency, Debye temperature
- Grüneisen parameter
- Inelastic scattering, scattering length, inelastic structure factor
- Debye–Waller factor
- Kohn anomalies
- Mössbauer effect

Vibrations of a Classical Lattice

Find energy when atoms move small distances from equilibrium. Must keep changes to second order.

$$\mathcal{E}(\vec{u}^1, \vec{u}^2 \dots \vec{u}^N), \tag{L1}$$

$$\mathcal{E} = \mathcal{E}_c + \sum_{\substack{\alpha \\ l}} \frac{\partial \mathcal{E}}{\partial u^l_\alpha} u^l_\alpha + \frac{1}{2} \sum_{\substack{\alpha\beta \\ ll'}} u^l_\alpha \Phi^{ll'}_{\alpha\beta} u^{l'}_\beta + \dots. \tag{L2}$$

$$\Phi^{ll'}_{\alpha\beta} = \frac{\partial^2 \mathcal{E}}{\partial u^l_\alpha \partial u^{l'}_\beta} \tag{L3}$$

$$M\ddot{\vec{u}}^l = -\sum_{l'} \Phi^{ll'} \vec{u}^{l'}. \tag{L4}$$

In a crystal, because of translational invariance,

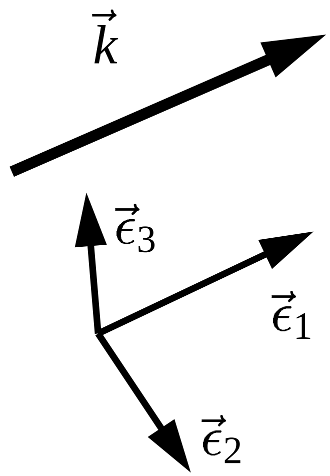
$$\sum_{l'} \Phi^{ll'} = 0. \tag{L5}$$

Polarization $\vec{\epsilon}$

$$\vec{u}^l = \vec{\epsilon} e^{i\vec{k}\cdot\vec{R}^l - i\omega t}. \tag{L6}$$

$$M\omega^2\vec{\epsilon} = \sum_{l'} \Phi^{ll'} e^{i\vec{k}\cdot(\vec{R}^l - \vec{R}^{l'})}\vec{\epsilon} \tag{L7a}$$

$$= \Phi(\vec{k})\vec{\epsilon}, \text{ with } \Phi(\vec{k}) = \sum_{l'} e^{i\vec{k}\cdot(\vec{R}^l - \vec{R}^{l'})}\Phi^{ll'}. \tag{L7b}$$



Normal Modes

$$\omega^2_{\vec{k}\nu} = \frac{\Phi_\nu(\vec{k})}{M}. \tag{L8}$$

$$\Phi(\vec{k}+\vec{K}) = \Phi(\vec{k}), \tag{L9}$$

- ☞ Can restrict $\vec{k}$ to the first Brillouin zone.
- ☞ Phonons, like electrons, are waves in a periodic potential.
- ☞ $\vec{k}$ in Brillouin zone completely exhausts all phonon states.

Example in One Dimension

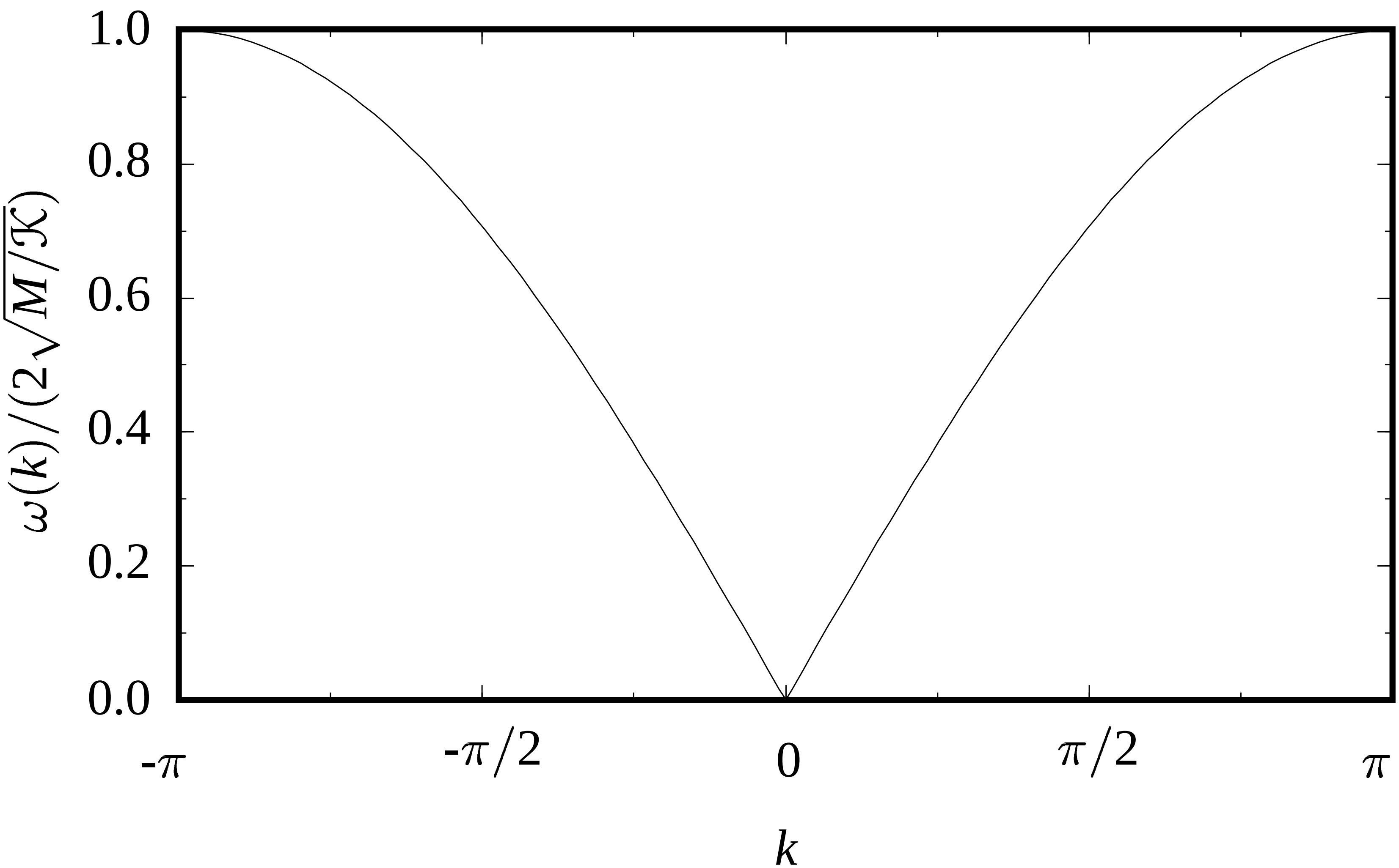
$$M\ddot{u}^l = \mathcal{K}(u^{l+1} - 2u^l + u^{l-1}). \tag{L10}$$

Substituting $u \propto \exp(ikl - i\omega t)$ gives

$$M\omega^2 = ? \quad ? \tag{L11}$$

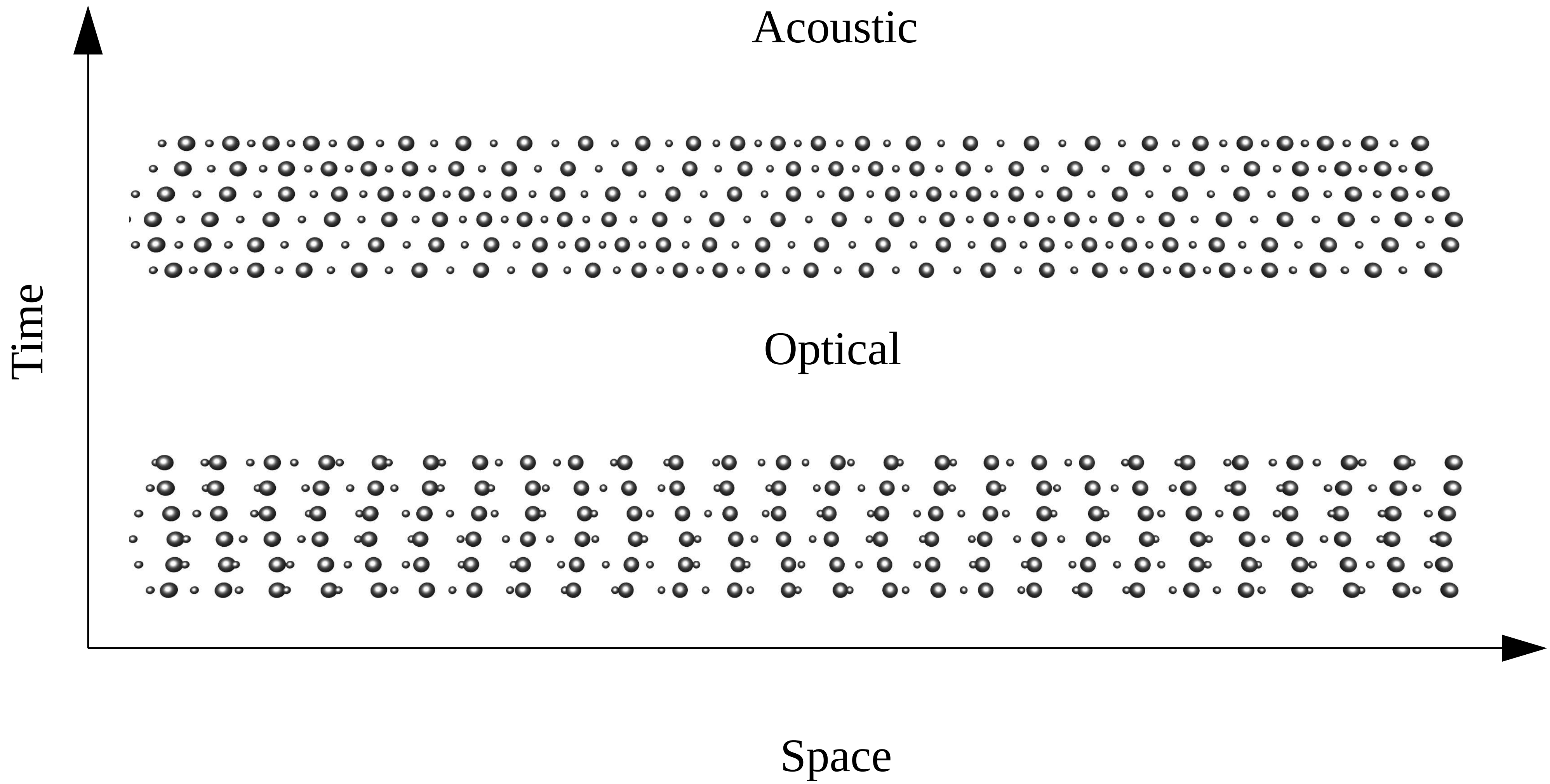
$$\Rightarrow \omega = ? \quad ? \tag{L12}$$

Example in One Dimension



Linear dispersion as $\vec{k} = \to 0$ is generic, example of Goldstone mode.

Lattice with a Basis



$$M_n \ddot{\vec{u}}^{ln} = -\sum_{l'n'} \Phi^{lnl'n'} \vec{u}^{l'n'}, \qquad \text{(L13)}$$

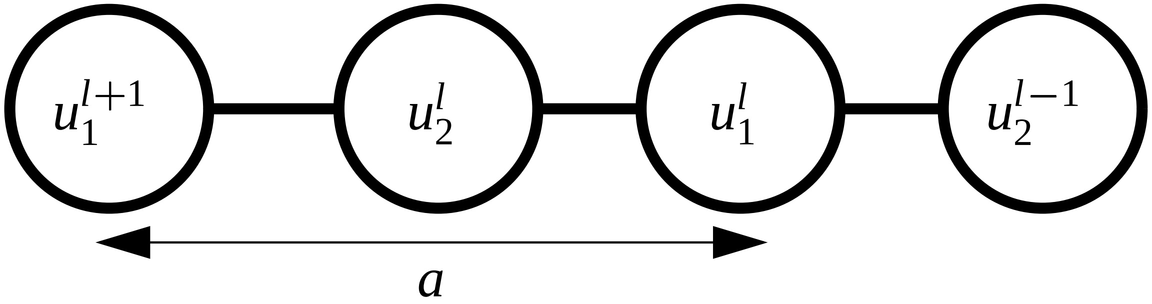
Lattice with a Basis

$$\vec{u}^{ln} = \vec{\epsilon}^{n} e^{i\vec{k}\cdot\vec{R}^{ln} - i\omega t}, \tag{L14}$$

$$\Rightarrow M_n \omega^2 \vec{\epsilon}^{n} = \sum_{n'} \Phi^{nn'}(\vec{k}) \vec{\epsilon}^{n'}. \tag{L15}$$

$$M_p \omega^2 \epsilon_p = \sum_{p'}^{3N} \Phi_{pp'}(\vec{k}) \epsilon_{p'}. \tag{L16}$$

One–dimensional example with basis



$$M_1\ddot{u}_1^l = \mathcal{K}(u_2^l - 2u_1^l + u_2^{l-1}) \quad \text{(L17a)}$$

$$M_2\ddot{u}_2^l = \mathcal{K}(u_1^{l+1} - 2u_2^l + u_1^l) \quad \text{(L17b)}$$

$$\Rightarrow -\omega^2 M_1\epsilon_1 e^{ikla} = \mathcal{K}(\epsilon_2 - 2\epsilon_1 + \epsilon_2 e^{-ika})e^{ikla} \quad \text{(L18a)}$$

$$-\omega^2 M_2\epsilon_2 e^{ikla} = ? \qquad ? \quad \text{(L18b)}$$

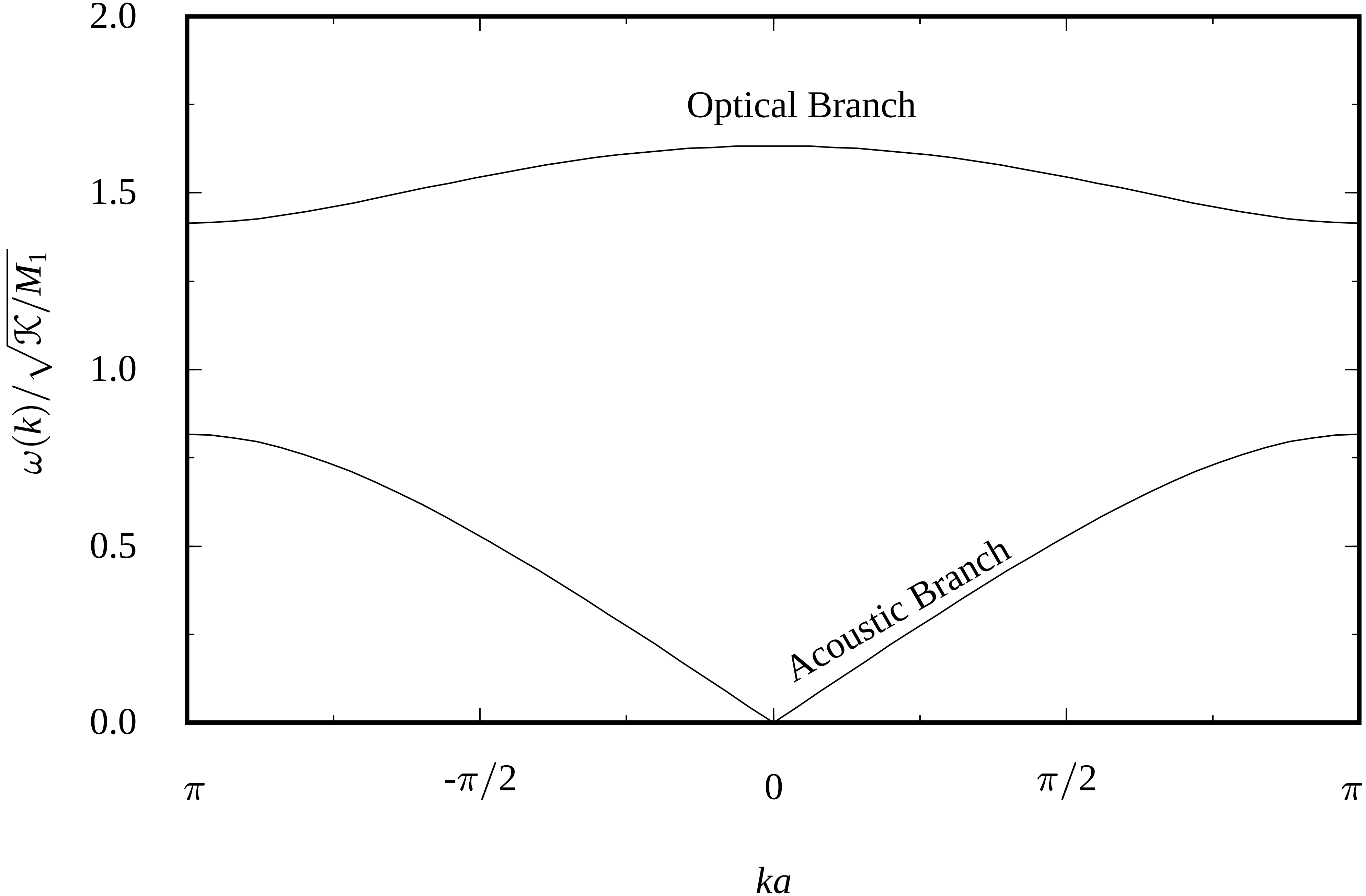
$$\Rightarrow \omega = \sqrt{\mathcal{K}}\sqrt{\frac{M_1 + M_2 \pm \sqrt{M_1^2 + 2M_1M_2\cos ka + M_2^2}}{M_1M_2}}. \quad \text{(L19)}$$

One–dimensional example with basis

$$\omega(k) = \sqrt{\frac{\mathcal{K}}{2(M_1+M_2)}}ka, \qquad \epsilon_1 = 1;\, \epsilon_2 = 1+ika/2, \tag{L20a}$$

$$\omega(k) = \sqrt{\frac{2\mathcal{K}(M_1+M_2)}{M_1M_2}}, \qquad \epsilon_1 = M_2;\, \epsilon_2 = -M_1(1+ika/2). \tag{L20b}$$

One–dimensional example with basis



$$U = \frac{1}{2}\sum_{lnl'n'} \phi_{nn'}(|\vec{u}^{ln} + \vec{R}^{ln} - \vec{u}^{l'n'} - \vec{R}^{l'n'}|). \tag{L21}$$

$$U \approx \frac{1}{4}\sum_{lnl'n'} [\vec{u}^{ln} - \vec{u}^{l'n'}]\mathbf{f}^{lnl'n'}[\vec{u}^{ln} - \vec{u}^{l'n'}], \tag{L22}$$

$$\mathbf{f}^{lnl'n'}_{\alpha\beta} = \frac{\partial^2}{\partial r_\alpha r_\beta}\phi_{nn'}(|\vec{r}|)\Big|_{\vec{r}=\vec{R}^{ln}-\vec{R}^{l'n'}} \tag{L23}$$

$$= \left\{\frac{r_\alpha r_\beta}{r^2}[\phi''_{nn'}(r) - \frac{1}{r}\phi'_{nn'}(r)] + \frac{\delta_{\alpha\beta}}{r}\phi'_{nn'}(r)\right\}\Big|_{\vec{r}=\vec{R}^{ln}-\vec{R}^{l'n'}}. \tag{L24}$$

$$\sum_{l'n'} \frac{\vec{r}}{r}\phi'_{nn'}(r)\Big|_{\vec{r}=\vec{R}^{ln}-\vec{R}^{l'n'}} = 0. \tag{L25}$$

$$\Phi^{lnl'n'} = \sum_{l''n''} \mathbf{f}^{lnl''n''}(\delta_{ll'}\delta_{nn'} - \delta_{l'l''}\delta_{n'n''}). \tag{L26}$$

$$f_1 - f_2 = \phi''(d) - \frac{1}{d}\phi'(d) \tag{L27}$$

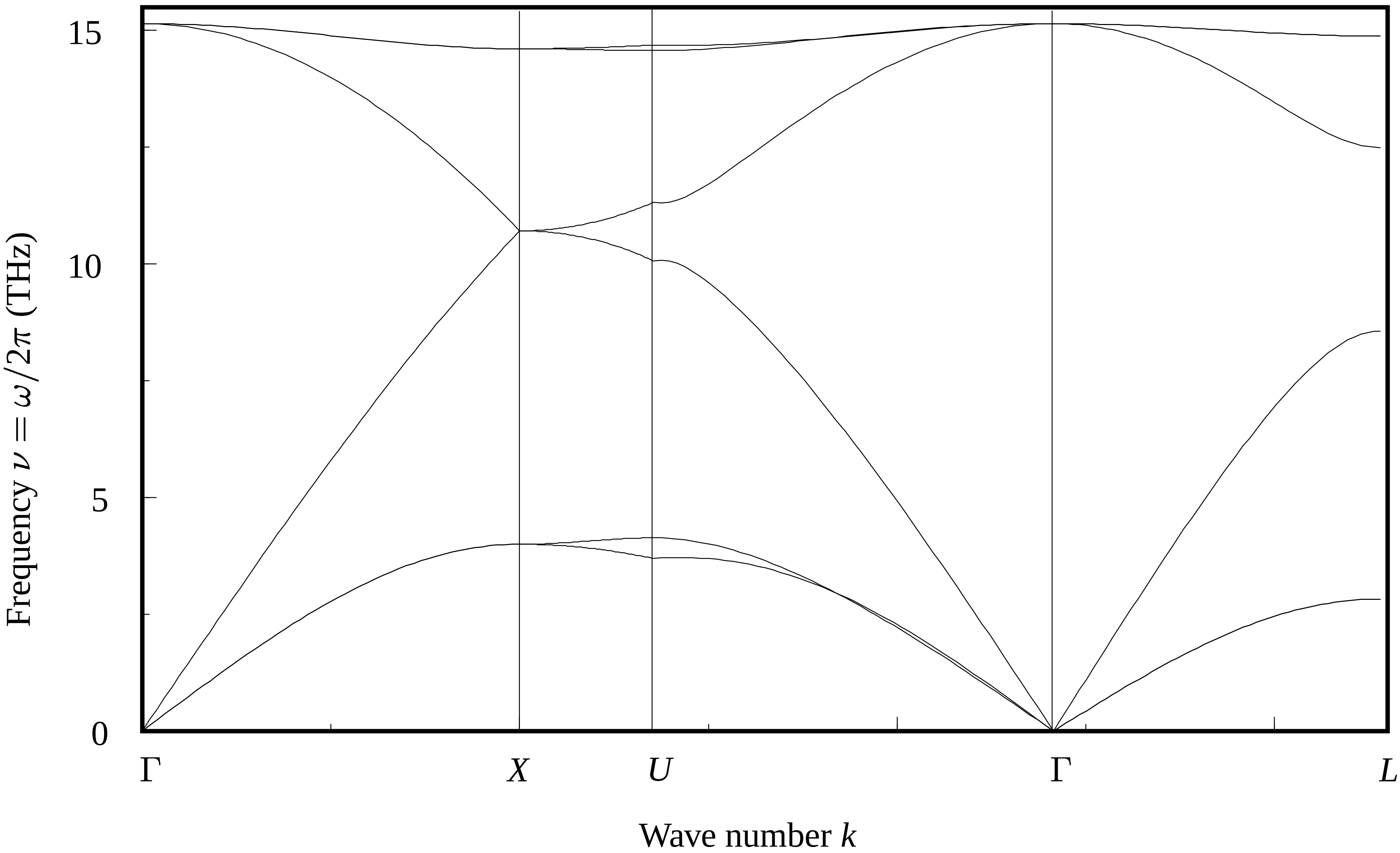
and

$$f_2 = \frac{1}{d}\phi'(d) \tag{L28}$$

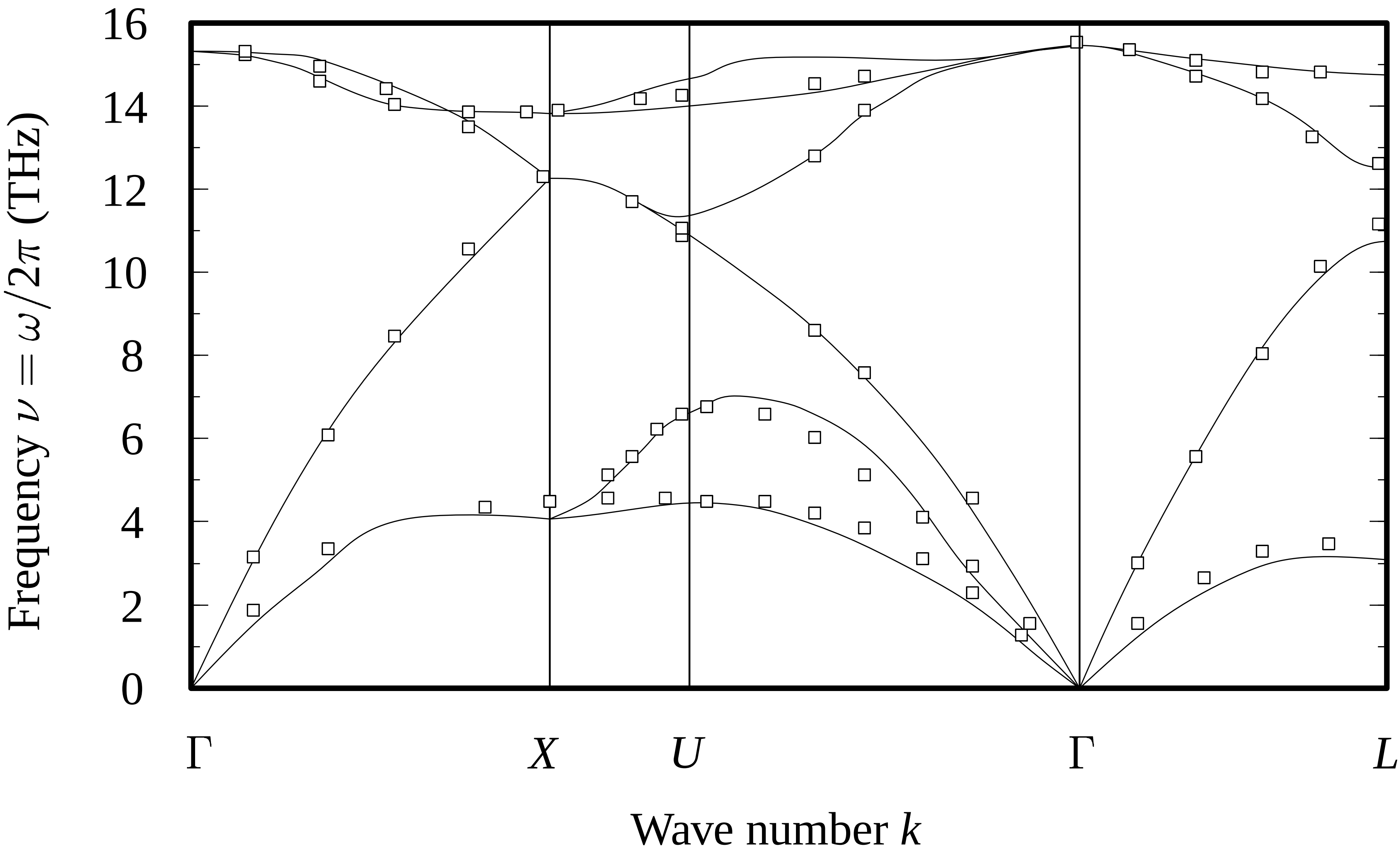
$$\Rightarrow \mathbf{f}_{\alpha\beta}^{lnl'n'} = \frac{r_\alpha r_\beta}{r^2}[f_1 - f_2] + \delta_{\alpha\beta} f_2 \Big|_{\vec{r}=\vec{R}^{ln}-\vec{R}^{l'n'}}. \tag{L29}$$

$$\Phi^{nn'}(\vec{k}) = \sum_{l'} \Phi^{0nl'n'} e^{i\vec{k}\cdot(\vec{R}^{0n}-\vec{R}^{l'n'})} \tag{L30}$$

Comparison with Experiment



Comparison with Experiment



$$\hbar\omega_{\vec{k}\nu}(n+\tfrac{1}{2}); \tag{L31}$$

$$\hat{\mathcal{H}} = \frac{\hat{P}^2}{2M} + \frac{1}{2}M\omega^2\hat{R}^2 \tag{L32}$$

Raising and lowering operators

$$\hat{a}^\dagger = \sqrt{\frac{M\omega}{2\hbar}}\hat{R} - i\sqrt{\frac{1}{2\hbar M\omega}}\hat{P} \tag{L33a}$$

$$\hat{a} = \sqrt{\frac{M\omega}{2\hbar}}\hat{R} + i\sqrt{\frac{1}{2\hbar M\omega}}\hat{P}. \tag{L33b}$$

$$\hat{\mathcal{H}} = \hbar\omega\left(\hat{a}^\dagger a + \tfrac{1}{2}\right) = \hbar\omega\left(\hat{n} + \tfrac{1}{2}\right) \tag{L34}$$

$$\hat{R} = \sqrt{\frac{\hbar}{2M\omega}}(\hat{a} + \hat{a}^\dagger). \tag{L35}$$

$$\hat{\mathcal{H}} = \sum_l \frac{\hat{P}^{l\,2}}{2M} + \tfrac{1}{2}\sum_{ll'} \hat{u}^l \Phi^{ll'} \hat{u}^{l'} \ldots . \tag{L36}$$

$$\hat{a}_{\vec{k}\nu} = \frac{1}{\sqrt{N}} \sum_{l=1}^{N} e^{-i\vec{k}\cdot\vec{R}^l} \vec{\epsilon}^{\,*}_{\vec{k}\nu} \cdot \left[\sqrt{\frac{M\omega_{\vec{k}\nu}}{2\hbar}}\hat{u}^l + i\sqrt{\frac{1}{2\hbar M\omega_{\vec{k}\nu}}}\hat{P}^l\right] \tag{L37a}$$

$$\hat{a}^\dagger_{\vec{k}\nu} = \frac{1}{\sqrt{N}} \sum_{l=1}^{N} e^{i\vec{k}\cdot\vec{R}^l} \vec{\epsilon}_{\vec{k}\nu} \cdot \left[\sqrt{\frac{M\omega_{\vec{k}\nu}}{2\hbar}}\hat{u}^l - i\sqrt{\frac{1}{2\hbar M\omega_{\vec{k}\nu}}}\hat{P}^l\right]. \tag{L37b}$$

$$\hat{u}^l = \frac{1}{\sqrt{N}} \sum_{\vec{k}\nu} \left[\hat{u}_{\vec{k}\nu} e^{i\vec{k}\cdot\vec{R}^l} + \hat{u}^\dagger_{\vec{k}\nu} e^{-i\vec{k}\cdot\vec{R}^l}\right] \text{ with } \hat{u}_{\vec{k}\nu} \equiv \sqrt{\frac{\hbar}{2M\omega_{\vec{k}\nu}}}\vec{\epsilon}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu} \tag{L38a}$$

and

$$\hat{P}^l = \frac{1}{\sqrt{N}} \sum_{\vec{k}\nu} \left[\hat{P}_{\vec{k}\nu} e^{i\vec{k}\cdot\vec{R}^l} + \hat{P}^\dagger_{\vec{k}\nu} e^{-i\vec{k}\cdot\vec{R}^l}\right] \text{ with } \hat{P}_{\vec{k}\nu} = -i\sqrt{\frac{\hbar M\omega_{\vec{k}\nu}}{2}}\vec{\epsilon}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}. \tag{L38b}$$

$$[\hat{P}^l, \hat{R}^l] = -i\hbar$$

$$[\hat{a}_{\vec{k}\nu}, \hat{a}^{\dagger}_{\vec{k}\nu}] = 1. \tag{L39}$$

$$\omega_{\vec{k}\nu} = \omega_{-\vec{k}\nu}. \tag{L40}$$

$$\sum_{l} \frac{\hat{P}^{l\,2}}{2M} = \sum_{\vec{k}\nu} \frac{\hbar\omega_{\vec{k}\nu}}{4} \left\{ \begin{array}{llll} [& \hat{a}_{\vec{k}\nu} & \hat{a}^{\dagger}_{\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}] & \\ -[& \hat{a}_{\vec{k}\nu} & \hat{a}_{\vec{k}\nu}\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{\epsilon}_{-\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}^{\dagger}_{\vec{k}\nu}\vec{\epsilon}^{*}_{\vec{k}\nu}\cdot\vec{\epsilon}^{*}_{-\vec{k}\nu}] & \end{array} \right\} \tag{L41a}$$

$$\sum_{ll'} \tfrac{1}{2}\hat{u}^{l}\Phi^{ll'}\hat{u}^{l'} = \sum_{\vec{k}\nu} \frac{\hbar\omega_{\vec{k}\nu}}{4} \left\{ \begin{array}{llll} [& \hat{a}_{\vec{k}\nu} & \hat{a}^{\dagger}_{\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}] & \\ +[& \hat{a}_{\vec{k}\nu} & \hat{a}_{\vec{k}\nu}\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{\epsilon}_{-\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}^{\dagger}_{\vec{k}\nu}\vec{\epsilon}^{*}_{\vec{k}\nu}\cdot\vec{\epsilon}^{*}_{-\vec{k}\nu}] & \end{array} \right\} \tag{L41b}$$

Don't assume $\vec{\epsilon}^{*}_{\vec{k}\nu} = \vec{\epsilon}_{-\vec{k}\nu}$, as it leads to problems for longitudinal modes.

$$\hat{\mathcal{H}} = \sum_{\vec{k}\nu} \frac{\hbar\omega_{\vec{k}\nu}}{2}[\hat{a}_{\vec{k}\nu}\hat{a}^{\dagger}_{\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}] = \sum_{\vec{k}\nu} \hbar\omega_{\vec{k}\nu}(\hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu} + \tfrac{1}{2}). \tag{L42}$$

$$\hat{\mathcal{H}} = \sum_i \hbar\omega_i(\hat{n}_i + \tfrac{1}{2}). \tag{L43}$$

$$\hat{a}_{\vec{k}\nu}(t) = e^{i\hat{\mathcal{H}}t/\hbar}\hat{a}_{\vec{k}\nu}e^{-i\hat{\mathcal{H}}t/\hbar} \tag{L44}$$

so that

$$\frac{\partial \hat{a}_{\vec{k}\nu}(t)}{\partial t} = e^{i\hat{\mathcal{H}}t/\hbar}i[\hat{\mathcal{H}},\hat{a}_{\vec{k}\nu}]e^{-i\mathcal{H}t/\hbar}/\hbar \tag{L45}$$

$$= -i\omega_{\vec{k}\nu}\hat{a}_{\vec{k}\nu} \tag{L46}$$

$$\Rightarrow \hat{a}_{\vec{k}\nu}(t) = \hat{a}_{\vec{k}\nu}e^{-i\omega_{\vec{k}\nu}t}. \tag{L47}$$

$$\hat{u}^l(t) = \frac{1}{\sqrt{N}}\sum_{\vec{k}\nu}[\hat{u}_{\vec{k}\nu}e^{i\vec{k}\cdot\vec{R}^l - i\omega_{\vec{k}\nu}t} + \hat{u}^\dagger_{\vec{k}\nu}e^{-i\vec{k}\cdot\vec{R}^l + i\omega_{\vec{k}\nu}t}]. \tag{L48}$$

Testing ground for quantum mechanics

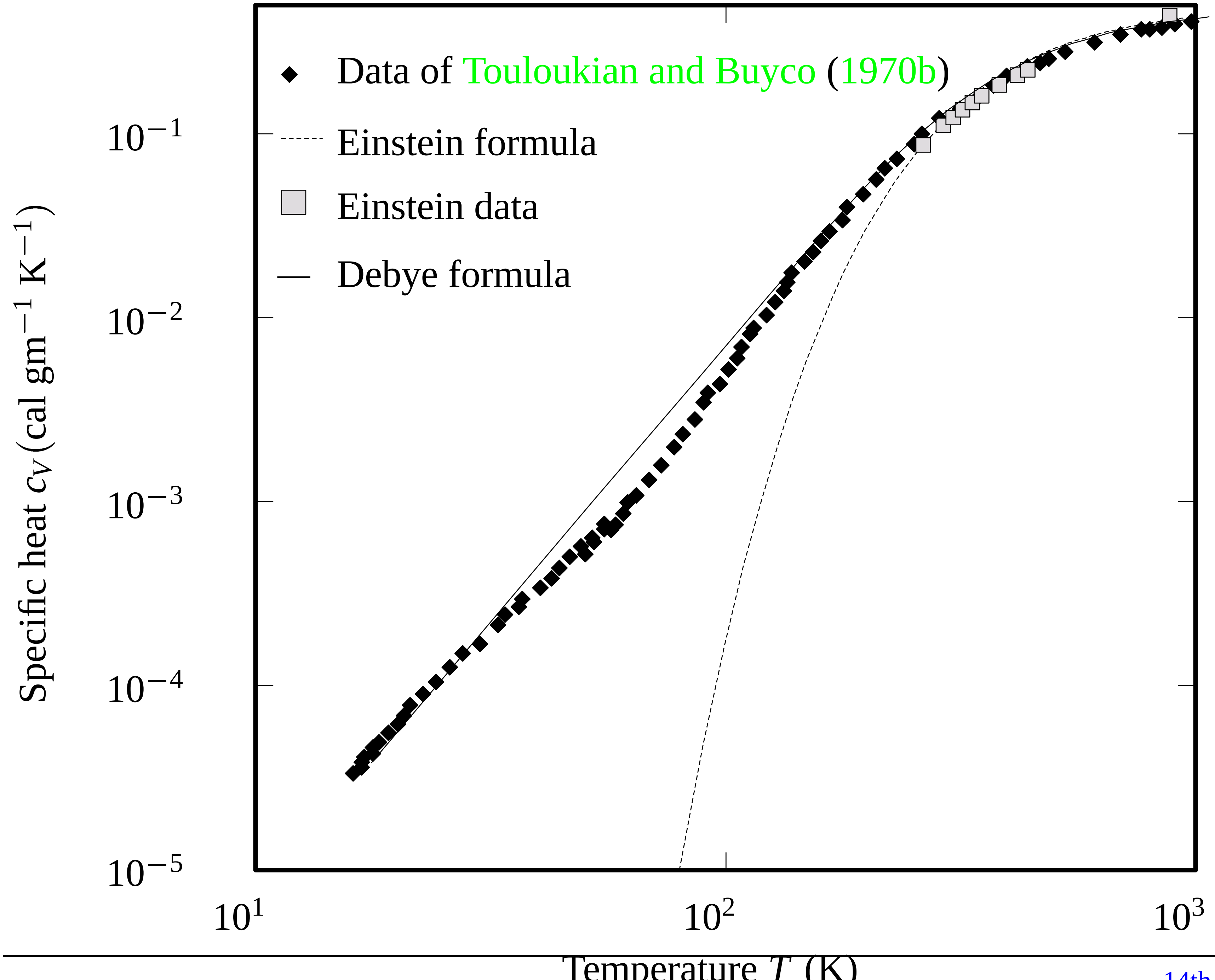
Einstein model

$$\mathcal{E} = \frac{3N\hbar\omega_0}{e^{\hbar\beta\omega_0} - 1} \quad \text{(L49)}$$

$$\Rightarrow C_{\mathcal{V}} = \frac{\partial \mathcal{E}}{\partial T}\Big|_{\mathcal{V}} = \frac{3N(\hbar\omega_0)^2 e^{\hbar\beta\omega_0}/(k_B T^2)}{[e^{\hbar\beta\omega_0} - 1]^2}. \quad \text{(L50)}$$

Residual ray of diamond $\omega_0 = 1.71 \cdot 10^{14}\mathrm{s}^{-1}$ leads to

Phonon Specific Heat



$$\mathcal{E} = \sum_i \hbar\omega_i(l_i + \tfrac{1}{2}). \tag{L51}$$

$$Z = \sum_{l_1=0}^{\infty}\sum_{l_2=0}^{\infty}\ldots e^{-\beta\sum_i \hbar\omega_i(l_i+1/2)} \tag{L52}$$

$$= \prod_{i=1}^{\infty}\left\{\sum_{l=0}^{\infty} e^{-\beta\hbar\omega_i(n+1/2)}\right\} \tag{L53}$$

$$= \prod_{i=1}^{\infty}\left\{\frac{e^{-\beta\hbar\omega_i/2}}{1-\exp(-\beta\hbar\omega_i)}\right\} \tag{L54}$$

$$\Rightarrow \mathfrak{F} = -k_B T \ln Z = \sum_i \frac{\hbar\omega_i}{2} + k_B T \ln(1-e^{-\beta\hbar\omega_i}) \tag{L55}$$

$$\Rightarrow \mathcal{E} = \frac{\partial\beta\mathfrak{F}}{\partial\beta} = \sum_i \frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1} = \sum_i \hbar\omega_i(n_i + \tfrac{1}{2}) \tag{L56}$$

with

$$n_i \equiv \frac{1}{e^{\beta\hbar\omega_i}-1} \tag{L57}$$

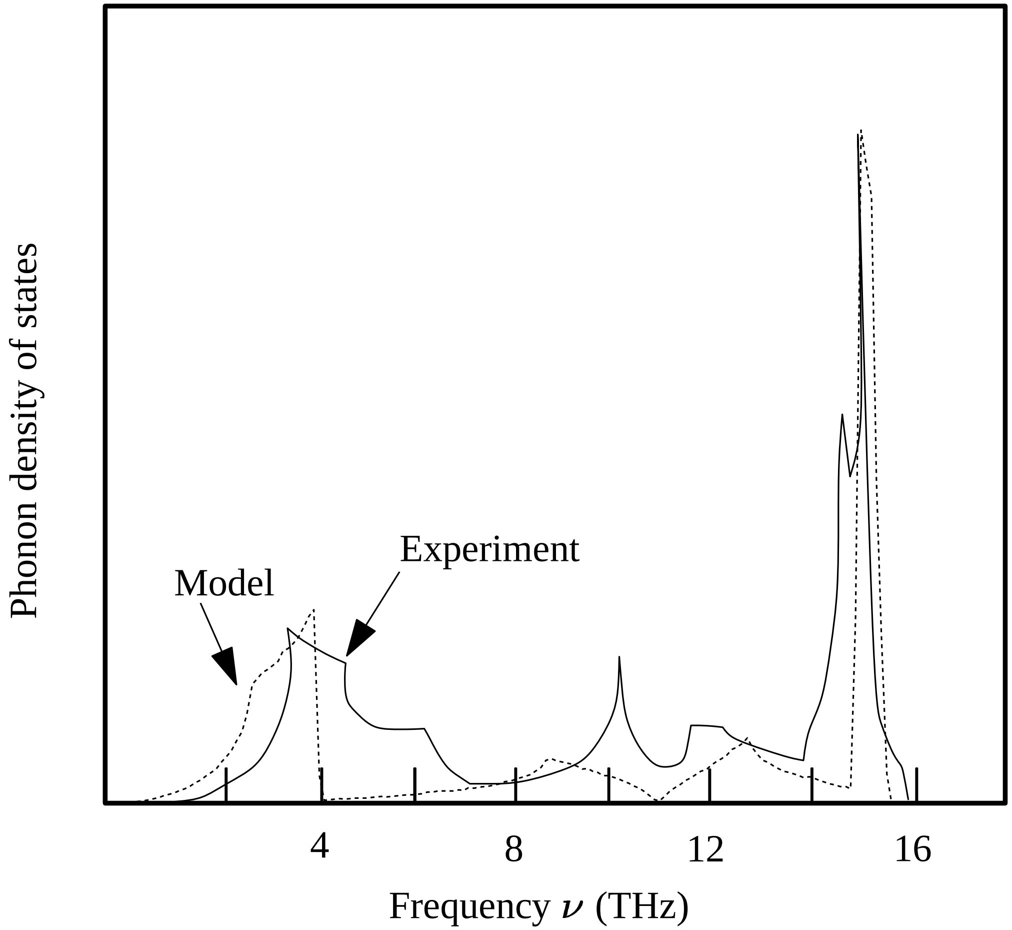
Phonon Specific Heat

$$\Rightarrow C_{\mathcal{V}} \quad = \quad \frac{\partial \mathcal{E}}{\partial T}\,|_{\mathcal{V}} = \sum_i C_i = \sum_i \hbar\omega_i \frac{\partial n_i}{\partial T}. \tag{L58}$$

$$D(\omega) = \sum_i \delta(\omega - \omega_i) = \sum_{\vec{k}\nu} \delta(\omega - \omega_{\vec{k}\nu}) = \int \frac{d\vec{k}}{(2\pi)^3} \sum_\nu \delta(\omega - \omega_{\vec{k}\nu}), \tag{L59}$$

$$C_{\mathcal{V}} = \mathcal{V} \int_0^\infty d\omega\, D(\omega) \frac{\partial}{\partial T} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}. \tag{L60}$$

Phonon Specific Heat



- Characteristic frequency of 16 THz
- Cusps are van Hove singularities (Section 7.2.1)

Phonon Specific Heat

Dulong and Petit

$$C_{\mathcal{V}} = Nk_B \quad \text{(L61)}$$

$$\begin{aligned} D(\omega) &= \int \frac{d\vec{k}}{(2\pi)^3} \sum_\nu \delta(\omega - c_\nu(\hat{k})k) && \text{(L62)} \\ &= \frac{3\omega^2}{2\pi^2 c^3} \text{ with } \frac{1}{c^3} = \frac{1}{3}\sum_\nu \int \frac{d\Sigma}{4\pi} \frac{1}{c_\nu^3(\hat{k})} && \text{(L63)} \\ \Rightarrow C_{\mathcal{V}} &= \mathcal{V} \frac{\partial}{\partial T} \frac{3(k_B T)^4}{2\pi^2 (c\hbar)^3} \int_0^\infty dx \frac{x^3}{e^x - 1} && \text{(L64)} \\ &= \mathcal{V} \frac{2\pi^2}{5} k_B \left[\frac{k_B T}{\hbar c}\right]^3. && \text{(L65)} \end{aligned}$$

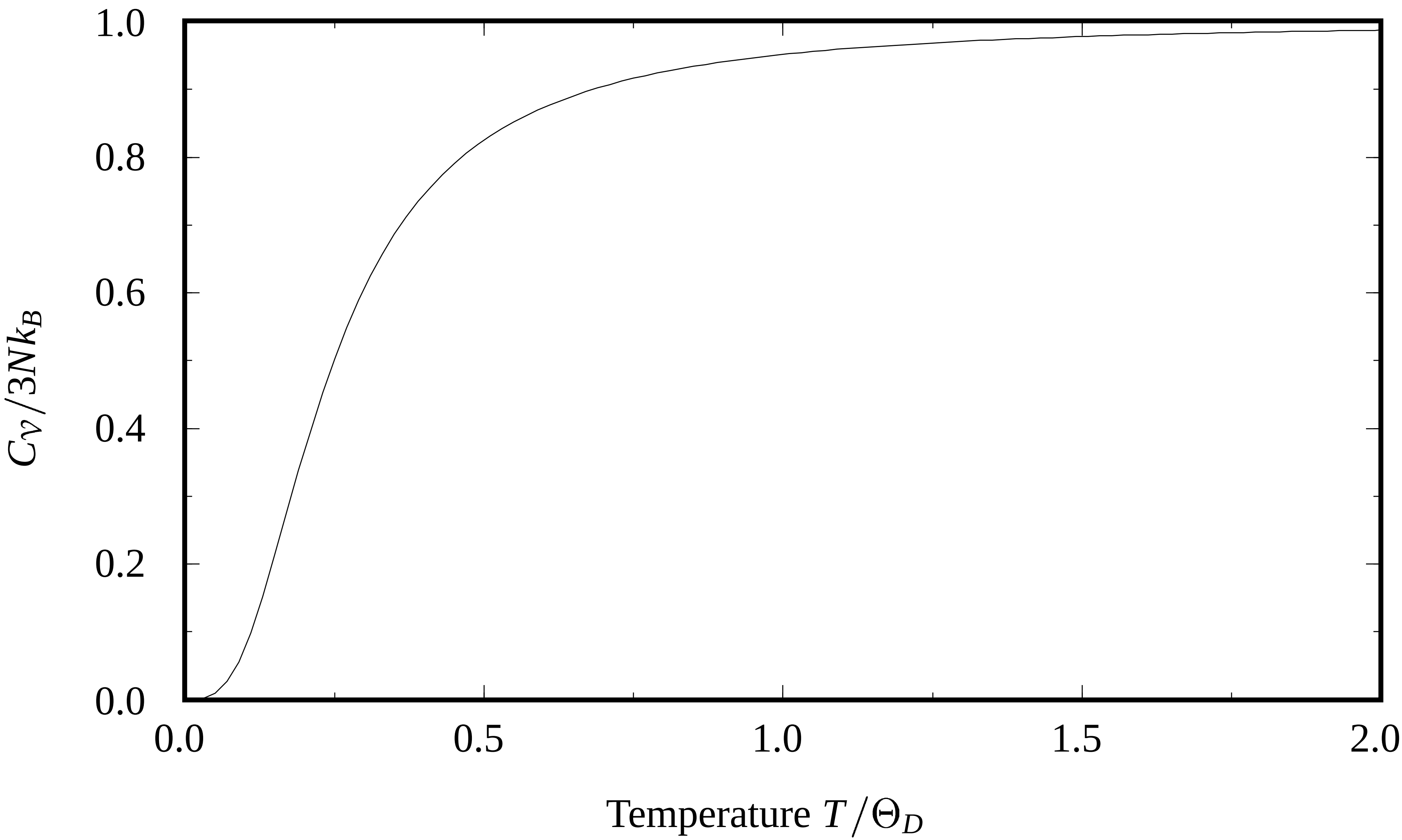
Einstein and Debye Models

☞ Einstein Model

$$D(\omega) = \frac{3N}{\mathcal{V}}\delta(\omega-\omega_0), \quad \text{(L66)}$$

☞ Debye Model

$$D(\omega) = \frac{3\omega^2}{2\pi^2 c^3}\theta(\omega_D-\omega) \quad \text{(L67)}$$



[Data, Dolling and Cowley (1966)]

Einstein and Debye Models

Total number of modes

$$3N = \mathcal{V}\int_0^\infty d\omega\, D(\omega) \Rightarrow n = \frac{\omega_D^3}{6\pi^2 c^3}. \tag{L68}$$

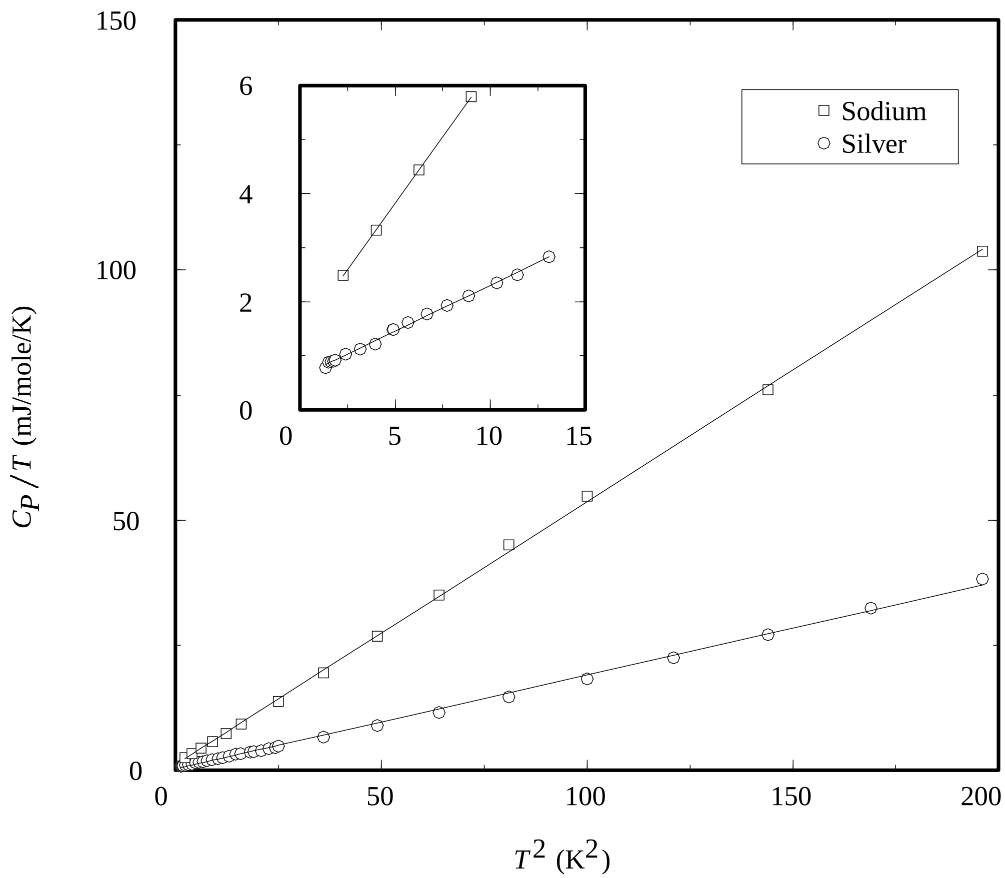
Debye temperature:

$$k_B\Theta_D \equiv \hbar\omega_D \tag{L69}$$

$$C_\mathcal{V} = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x-1)^2} \tag{L70}$$

Form of specific heat

$$C_P \approx \gamma T + \beta T^3, \tag{L71}$$

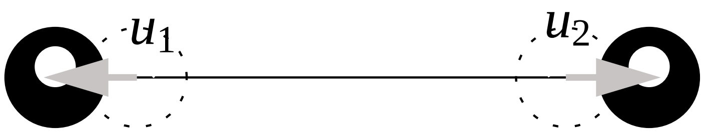


[Data, Touloukian et al (1975)]

Phonon and electron specific heats comparable when $T \approx \Theta_D \sqrt{\Theta_D / T_F}$, 10 K

Debye Temperatures

El.	Θ_D	El.	Θ_D	El.	Θ_D	El.	Θ_D
Am	121	Eu	118	Na	157	Sm	169
Ar	92	Fe	477	Nb	276	Sn	199
Ag	227	Ga	325	Nd	163	Sr	147
Al	433	Ge	373	Ne	74.6	Ta	245
As	282	Gd	182	Ni	477	Tb	176
Au	162	H	122	Np	259	Te	152
Ba	111	He	34-108	Os	467	Th	160
Be	1481	Hf	252	Pa	185	Ti	420
Bi	120	Hg	72	Pb	105	Tl	78.5
B	1480	Ho	190	Pd	271	Tm	200
C(gr)	412	I	109	Pr	152	U	248
C(dia)	2250	In	112	Pt	237	V	399
Ca	229	Ir	420	Pu	206	W	383
Cd	210	K	91.1	Rb	56.5	Xe	64.0
Ce	179	Kr	71.9	Re	416	Y	248
Co	460	La	150	Rh	512	Yb	118
Cr	606	Li	344	Ru	555	Zn	329
Cs	40.5	Lu	183	Sb	220	Zr	290
Cu	347	Mg	403	Sc	346		
Dy	183	Mn	409	Se	153		
Er	188	Mo	423	Si	645		



$$\mathcal{E} = \frac{1}{2}\mathcal{K}x^2. \quad \text{(L72)}$$

$$\mathcal{E}(x) = \mathcal{E}_0 + \frac{1}{2}\mathcal{K}x^2 + \ldots \quad \text{(L73)}$$

$$\bar{x} = \frac{\int dx\, x e^{-\beta\mathcal{E}(x)}}{\int dx e^{-\beta\mathcal{E}(x)}} = \frac{\partial}{\partial A}\left(\ln \int dx e^{Ax-\beta\mathcal{E}(x)}\right)\Big|_{A=0} \quad \text{(L74)}$$

$$\approx \frac{\partial}{\partial A} \ln \int dx e^{Ax-\beta\mathcal{E}(x_0)-\beta\mathcal{E}'(x_0)(x-x_0)-\beta\mathcal{E}''(x_0)(x-x_0)^2/2}\big|_{A=0}. \quad \text{(L75)}$$

$$A = \beta\mathcal{E}'(x_0) = \beta\mathcal{K}x_0 \quad \text{(L76)}$$

$$\Rightarrow \bar{x} = \frac{\partial}{\partial A}\left[\ln\sqrt{\frac{2\pi}{\beta\mathcal{E}''(x_0)}}e^{Ax_0-\beta\mathcal{E}(x_0)}\right]\Big|_{A=0} \quad \text{(L77)}$$

$$= \frac{k_B T}{\mathcal{K}} \frac{\partial}{\partial x_0} \left[\ln \sqrt{\frac{2\pi}{\beta \mathcal{E}''(x_0)}} e^{\beta \mathcal{K} x_0^2/2 - \beta \mathcal{E}_0} \right] |_{x_0=0} \quad \text{(L78)}$$

$$= -\frac{k_B T}{\mathcal{K}\omega} \frac{\partial \omega}{\partial x}|_{x=0}, \text{ with } \mu\omega^2(x) \equiv \mathcal{E}''(x). \quad \text{(L79)}$$

$$\mathcal{V}\beta_T \equiv \frac{\partial \mathcal{V}}{\partial T}|_P = \frac{\partial P/\partial T|_{\mathcal{V}}}{-\partial P/\partial \mathcal{V}|_T} \quad \text{(L80)}$$

$$= -\frac{\mathcal{V}}{B} \frac{\partial^2 \mathcal{F}}{\partial \mathcal{V} \partial T}, \quad \text{(L81)}$$

$$\frac{\partial \mathcal{F}}{\partial \mathcal{V}}|_T = \sum_i (n_i + \tfrac{1}{2}) \frac{\partial \hbar \omega_i}{\partial \mathcal{V}} \quad \text{(L82)}$$

$$\Rightarrow \frac{\partial^2 \mathcal{F}}{\partial \mathcal{V} \partial T} = \sum_i \frac{\partial n_i}{\partial T} \frac{\partial \hbar \omega_i}{\partial \mathcal{V}}. \quad \text{(L83)}$$

Thermal Expansion

Main results

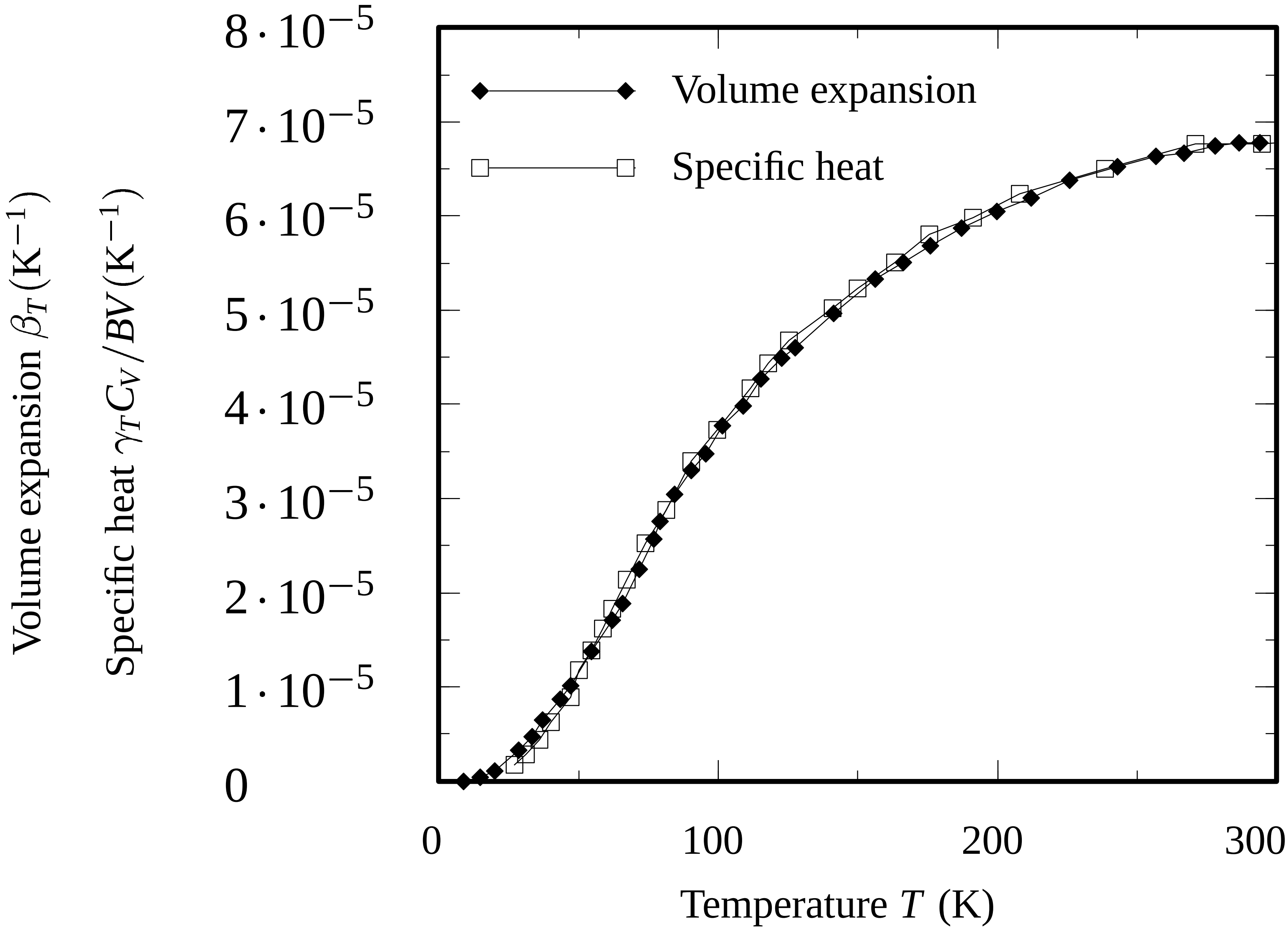
- No thermal expansion until anharmonic effects are taken into account.
- Grüneisen parameter relates thermal volume expansion to specific heat

$$\gamma_T = \frac{\sum_i \frac{\partial n_i}{\partial T}\left(-\mathcal{V}\frac{\partial \hbar\omega_i}{\partial \mathcal{V}}\right)}{\sum_i \hbar\omega_i \frac{\partial n_i}{\partial T}} \tag{L84}$$

$$\Rightarrow \quad -\frac{\partial^2 \mathcal{F}}{\partial \mathcal{V}\partial T} = \frac{\gamma_T C_{\mathcal{V}}}{\mathcal{V}} \tag{L85}$$

$$\Rightarrow \quad \beta_T = \frac{\gamma_T C_{\mathcal{V}}}{B\mathcal{V}}. \tag{L86}$$

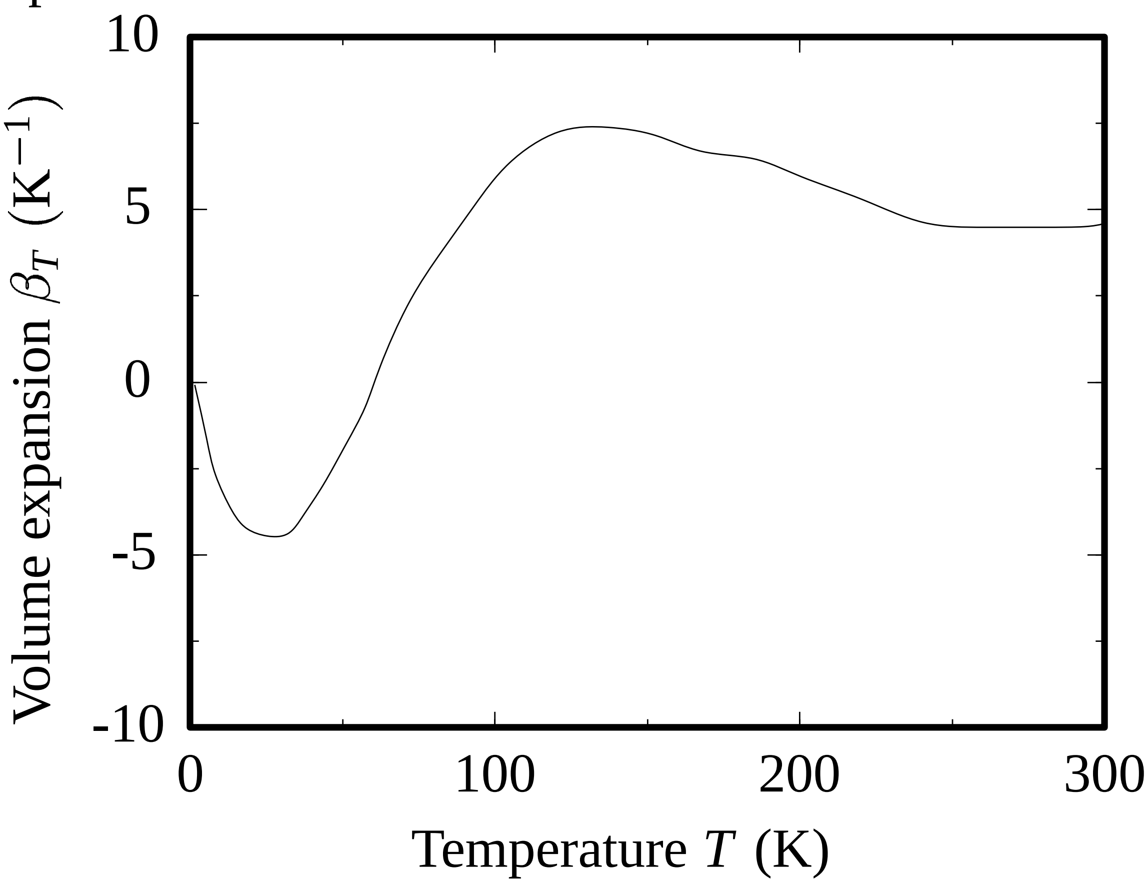
Thermal Expansion



[Data from Touloukian (1970a) and (1975) for aluminum]

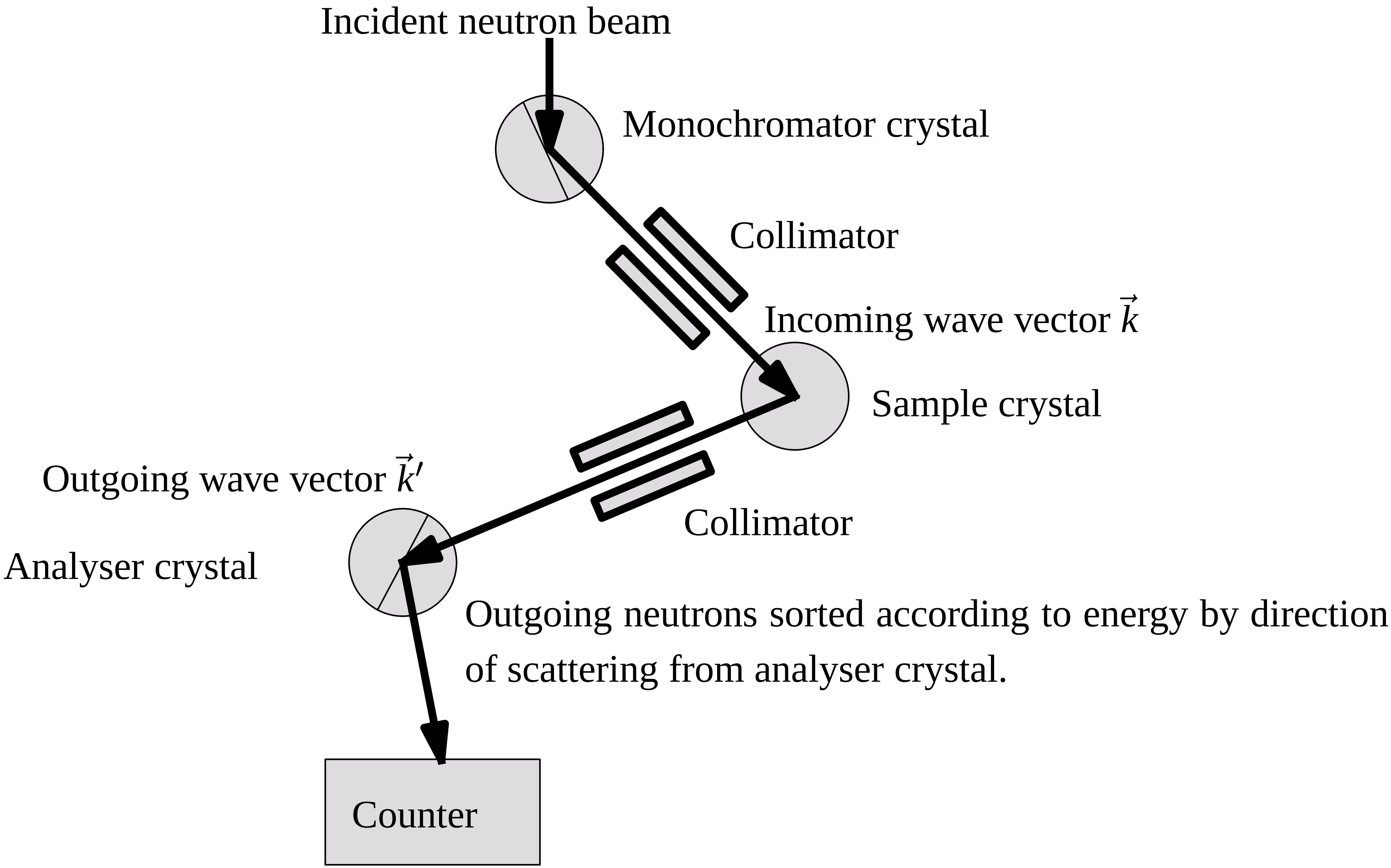
Thermal Expansion

Invar, won a Nobel prize!



[Data from Touloukian (1975)]

Inelastic Neutron Scattering



Scattering can be understood from conservation laws

Energy

If neutron creates a phonon, then

$$\frac{\hbar^2 k^2}{2m_{\rm n}} = \frac{\hbar^2 (k')^2}{2m_{\rm n}} + \hbar\omega_{\vec{q}\nu}. \tag{L87a}$$

If, on the other hand, passage of the neutron destroys a phonon and steals its energy, then

$$\frac{\hbar^2 k^2}{2m_{\rm n}} = \frac{\hbar^2 (k')^2}{2m_{\rm n}} - \hbar\omega_{\vec{q}\nu}. \tag{L87b}$$

Momentum

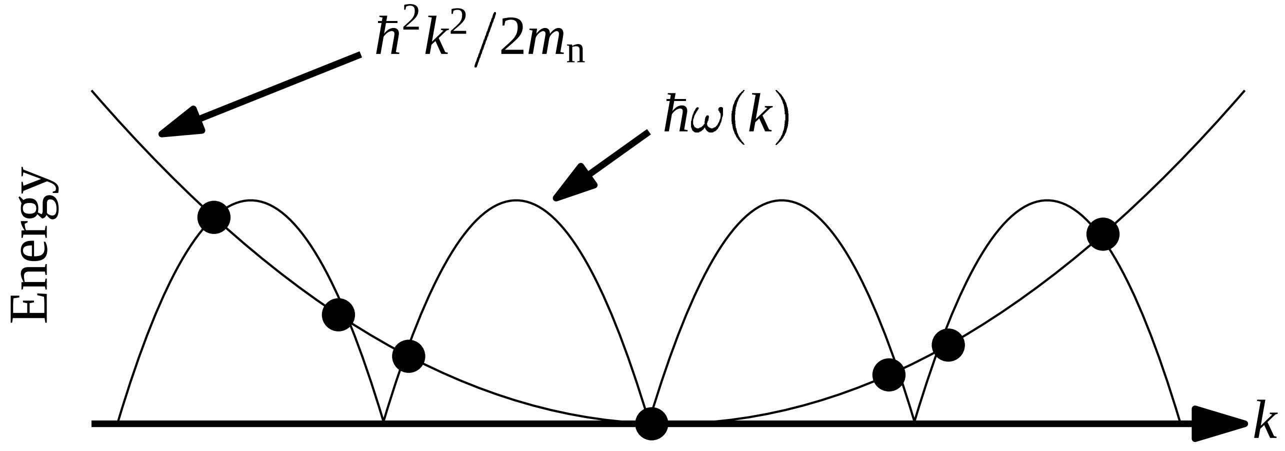
$$\vec{k}' + \vec{q} = \vec{k} + \vec{K} \tag{L88a}$$

for some reciprocal lattice vector $\vec{K}$, and when a phonon is absorbed,

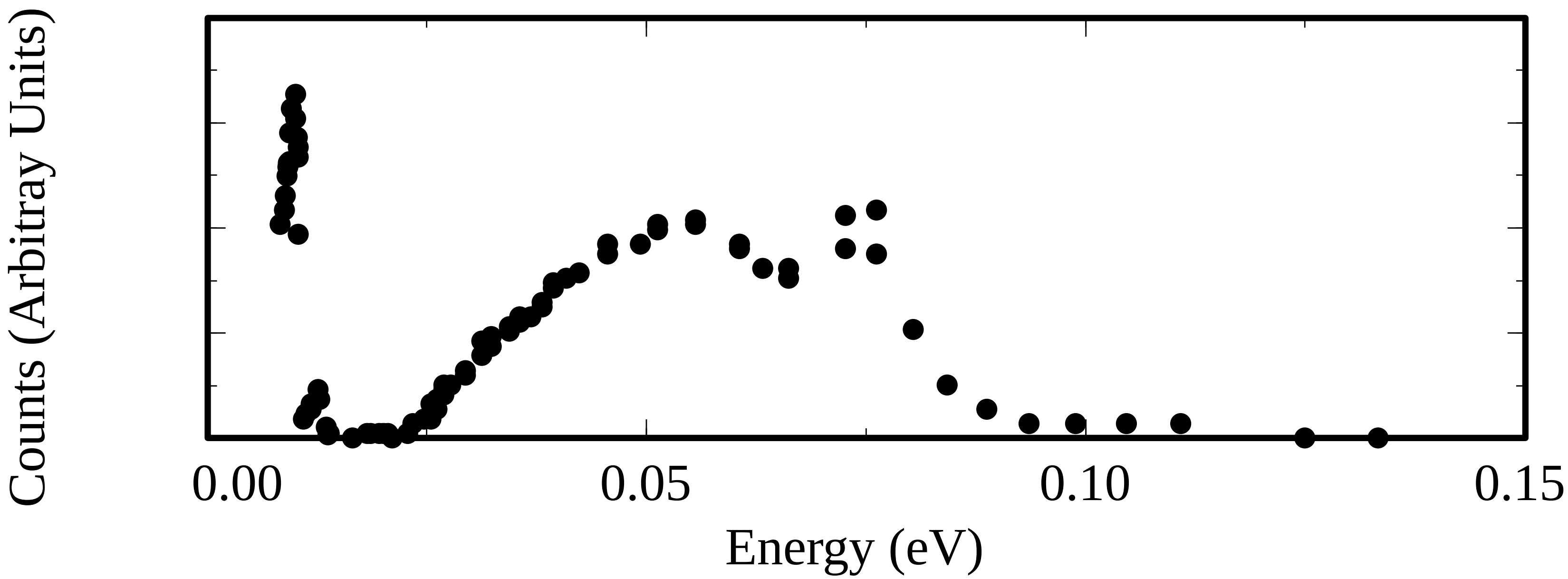
$$\vec{k}' - \vec{q} = \vec{k} + \vec{K}. \tag{L88b}$$

$$\frac{\hbar^2 k^2}{2m_{\mathrm{n}}} \pm \hbar\omega_{(\vec{k}-\vec{k}'),\nu} = \frac{\hbar^2 (k')^2}{2m_{\mathrm{n}}}, \qquad \text{(L89)}$$

Graphical criterion

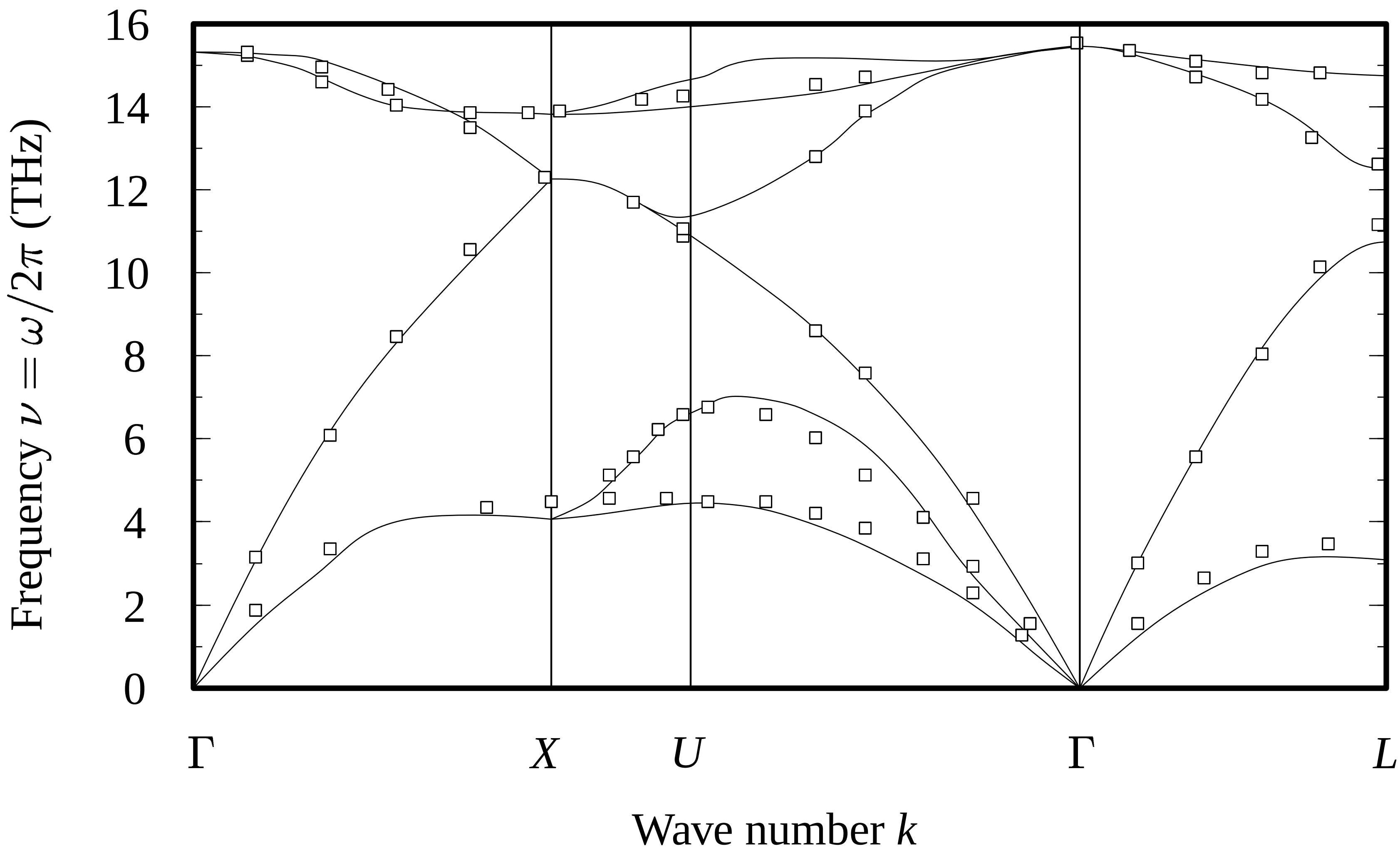


Results



[Data, Mozer et al (1965)]

Results



[Data Dolling and Cowley (1972), Nilsson and Nelin (1972), density functional computations We and Chou (1994)]

Nuclear scale is 10^{-13} cm

$$\hat{U} = \frac{2\pi\hbar^2 a}{m_\mathrm{n}} \sum_l \delta(\hat{R}_\mathrm{n} - \vec{R}^l - \hat{u}^l). \tag{L90}$$

$$\frac{\mathcal{P}\mathcal{V} d\vec{k}'}{(2\pi)^3} \tag{L91}$$

$$\frac{\mathcal{P}\mathcal{V} m_\mathrm{n} \hbar k' d\mathcal{E}_\mathrm{n} d\Omega}{(2\pi\hbar)^3}. \tag{L92}$$

$I = \hbar k / \mathcal{V} m_\mathrm{n}$

$$\frac{d\sigma}{d\Omega d\mathcal{E}_\mathrm{n}} = \frac{k'}{k} \frac{(\mathcal{V} m_\mathrm{n})^2}{(2\pi\hbar)^3} \mathcal{P}(\vec{k} \to \vec{k}'). \tag{L93}$$

$$\mathcal{P}(\vec{k} \to \vec{k}') = \sum_{\text{final states f}} \frac{2\pi}{\hbar} \delta(\mathcal{E}^\mathrm{f} - \mathcal{E}^\mathrm{i}) |\langle \Psi^\mathrm{f} | \hat{U} | \Psi^\mathrm{i} \rangle|^2. \tag{L94}$$

$$\begin{aligned}\langle\Psi^{\rm f}|\hat{U}|\Psi^{\rm i}\rangle &= \int d\vec{r}\langle\vec{k}'|\vec{r}\rangle\langle\vec{r}|\langle\Phi^{\rm f}|\sum_l \frac{2\pi\hbar^2 a}{m_{\rm n}}\delta(\hat{R}-\vec{R}^l-\vec{u}^l)|\vec{k}\rangle|\Phi^{\rm i}\rangle &\text{(L95)}\\ &= \int \frac{d\vec{r}}{\mathcal{V}}e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}\langle\Phi^{\rm f}|\frac{2\pi\hbar^2 a}{m_{\rm n}}\sum_l \delta(\vec{r}-\vec{R}^l-\vec{u}^l)|\Phi^{\rm i}\rangle &\text{(L96)}\\ &= \frac{1}{\mathcal{V}}\frac{2\pi\hbar^2 a}{m_{\rm n}}\sum_l\langle\Phi^{\rm f}|e^{i(\vec{k}-\vec{k}')\cdot(\hat{u}^l+\vec{R}^l)}|\Phi^{\rm i}\rangle. &\text{(L97)}\end{aligned}$$

$$\hbar\omega_{\rm n} = \frac{\hbar^2k^2}{2m_{\rm n}} - \frac{\hbar^2k'^2}{2m_{\rm n}} \qquad \text{(L98)}$$

$$\mathcal{P}(\vec{k}\to\vec{k}') = \frac{(2\pi\hbar)^3}{(m_{\rm n}\mathcal{V})^2}a^2\sum_{\rm f}\delta(\mathcal{E}^{\rm f}_{\rm ph}-\mathcal{E}^{\rm i}_{\rm ph}+\hbar\omega_{\rm n})\left|\sum_l\langle\Phi^{\rm f}|e^{i(\vec{k}-\vec{k}')\cdot(\hat{u}^l+\vec{R}^l)}|\Phi^{\rm i}\rangle\right|^2. \qquad \text{(L99)}$$

$$\frac{d\sigma}{d\Omega d\mathcal{E}_{\rm n}} = \frac{k'}{k}\frac{Na^2}{\hbar}S^{\rm i}(\vec{k}-\vec{k}',\omega_n), \qquad \text{(L100)}$$

$$S^{\rm i}(\vec q,\omega) = \frac{1}{N}\sum_{\rm f}\delta([\mathcal{E}^{\rm f}_{\rm ph}-\mathcal{E}^{\rm i}_{\rm ph}]/\hbar+\omega)\Big|\sum_l\langle\Phi^{\rm f}|e^{i\vec q\cdot(\hat u^l+\vec R^l)}|\Phi^{\rm i}\rangle\Big|^2. \quad \text{(L101)}$$

$$S^{\rm i} = \frac{1}{N}\sum_{\rm f}\int\frac{dt}{2\pi}e^{it\left([\mathcal{E}^{\rm f}_{\rm ph}-\mathcal{E}^{\rm i}_{\rm ph}]/\hbar+\omega\right)}\sum_{ll'}e^{i\vec q\cdot(\vec R^l-\vec R^{l'})}\,[\langle\Phi^{\rm i}|e^{-i\vec q\cdot\hat u^{l'}}|\Phi^{\rm f}\rangle \times\langle\Phi^{\rm f}|e^{i\vec q\cdot\hat u^l}|\Phi^{\rm i}\rangle] \quad \text{(L102)}$$

$$= \frac{1}{N}\sum_{\rm f}\int\frac{dt}{2\pi}e^{it\omega}\sum_{ll'}e^{i\vec q\cdot(\vec R^l-\vec R^{l'})}\,[\langle\Phi^{\rm i}|e^{-i\vec q\cdot\hat u^{l'}}|\Phi^{\rm f}\rangle \times\langle\Phi^{\rm f}|e^{i\hat{\mathcal{H}}_{\rm ph}t/\hbar}e^{i\vec q\cdot\hat u^l}e^{-i\hat{\mathcal{H}}_{\rm ph}t/\hbar}|\Phi^{\rm i}\rangle] \quad \text{(L103)}$$

$$= \frac{1}{N}\sum_{\rm f}\int\frac{dt}{2\pi}e^{it\omega}\sum_{ll'}e^{i\vec q\cdot(\vec R^l-\vec R^{l'})}\langle\Phi^{\rm i}|e^{-i\vec q\cdot\hat u^{l'}}|\Phi^{\rm f}\rangle\langle\Phi^{\rm f}|e^{i\vec q\cdot\hat u^l(t)}|\Phi^{\rm i}\rangle \quad \text{(L104)}$$

$$= \frac{1}{N}\int\frac{dt}{2\pi}e^{it\omega}\sum_{ll'}e^{i\vec q\cdot(\vec R^l-\vec R^{l'})}\langle\Phi^{\rm i}|e^{-i\vec q\cdot\hat u^{l'}}e^{i\vec q\cdot\hat u^l(t)}|\Phi^{\rm i}\rangle. \quad \text{(L105)}$$

$$\langle\hat A\rangle = \frac{\sum_{\rm i}\langle\Phi^{\rm i}|e^{-\beta\hat{\mathcal{H}}}\hat A|\Phi^{\rm i}\rangle}{\sum_{\rm i}\langle\Phi^{\rm i}|e^{-\beta\hat{\mathcal{H}}}|\Phi^{\rm i}\rangle}. \quad \text{(L106)}$$

$$S(\vec{q},\omega) = \frac{1}{N}\sum_{ll'} e^{i\vec{q}\cdot(\vec{R}^l - \vec{R}^{l'})}\int \frac{dt}{2\pi} e^{i\omega t}\langle e^{-i\vec{q}\cdot\hat{u}^{l'}} e^{i\vec{q}\cdot\hat{u}^l(t)}\rangle \tag{L107}$$

$$= \frac{1}{N}\int d\vec{r}d\vec{r}'\frac{dt}{2\pi} e^{i\vec{q}\cdot(\vec{r}-\vec{r}')} e^{i\omega t}\sum_{ll'}\langle\delta(\vec{r}-\vec{R}^l-\hat{u}^l)\delta(\vec{r}'-\vec{R}^{l'}-\hat{u}^{l'}(t))\rangle. \tag{L108}$$

Averaging Exponentials

$$\mathcal{S} \equiv \langle e^{\hat{A}} \rangle \qquad \text{(L109)}$$

$$\mathcal{S} = \langle 1 + \hat{A} + \frac{1}{2}\hat{A}^2 + \ldots \rangle. \qquad \text{(L110)}$$

$$\mathcal{S} = 1 + \frac{1}{2}\langle \hat{A}\hat{A} \rangle + \frac{1}{4!}\langle \hat{A}\hat{A}\hat{A}\hat{A} \rangle + \ldots. \qquad \text{(L111)}$$

Wick's theorem

$$\begin{aligned} \mathcal{S} &= 1 + \frac{1}{2}\langle \hat{A}\hat{A} \rangle + \frac{1}{2!}\frac{1}{2^2}\langle \hat{A}\hat{A} \rangle^2 + \ldots + \frac{1}{2^l}\frac{1}{l!}\langle \hat{A}\hat{A} \rangle^l \ldots. && \text{(L112)} \\ &= \exp[\frac{1}{2}\langle \hat{A}^2 \rangle]. && \text{(L113)} \end{aligned}$$

$$\langle e^{\hat{A}} e^{\hat{B}} \rangle = e^{\frac{1}{2}\langle \hat{A}^2 + 2\hat{A}\hat{B} + \hat{B}^2 \rangle}. \qquad \text{(L114)}$$

$$\mathfrak{M} \equiv \langle e^{-i\vec{q}\cdot\hat{u}^{l'}} e^{i\vec{q}\cdot\hat{u}^{l}(t)} \rangle. \qquad \text{(L115)}$$

Debye-Waller factor

Quantitative account of how thermal fluctuations degrade scattering peaks

$$\mathfrak{M} = \exp[-\langle(\vec{q}\cdot\hat{u}^l)^2\rangle]\exp[\langle(\vec{q}\cdot\hat{u}^{l'})(\vec{q}\cdot\hat{u}^l(t))\rangle]. \quad \text{(L116)}$$

$$\begin{aligned} 2W &\equiv \langle(\vec{q}\cdot\hat{u}^l)^2\rangle \\ &= \frac{1}{N}\sum_{\substack{\vec{k}\vec{k}' \\ \nu\nu'}}\langle(\vec{q}\cdot[\hat{u}_{\vec{k}\nu}e^{i\vec{k}\cdot\vec{R}^l}+\hat{u}^\dagger_{\vec{k}\nu}e^{-i\vec{k}\cdot\vec{R}^l}])(\vec{q}\cdot[\hat{u}_{\vec{k}'\nu'}e^{i\vec{k}'\cdot\vec{R}^l}+\hat{u}^\dagger_{\vec{k}'\nu'}e^{-i\vec{k}'\cdot\vec{R}^l}])\rangle. \quad \text{(L117)} \end{aligned}$$

$$\begin{aligned} 2W &= \sum_{\vec{k}\nu}\frac{1}{N}\frac{\hbar^2|\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{q}|^2}{2M\hbar\omega_{\vec{k}\nu}}\langle\hat{a}^\dagger_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}+\hat{a}_{\vec{k}\nu}\hat{a}^\dagger_{\vec{k}\nu}\rangle \quad \text{(L118)} \\ &= \sum_{\vec{k}\nu}\frac{1}{N}\frac{\hbar^2|\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{q}|^2}{2M\hbar\omega_{\vec{k}\nu}}\left(2n_{\vec{k}\nu}+1\right). \quad \text{(L119)} \end{aligned}$$

Low temperature

Debye-Waller factor

$$2W = \sum_{\vec{k}\nu} \frac{1}{N} \frac{\hbar^2 (\vec{\epsilon}_{\vec{k}\nu} \cdot \vec{q})^2}{2M\hbar\omega_{\vec{k}\nu}}. \tag{L120}$$

In Debye approximation

$$2W = \frac{3}{4} \frac{q^2\hbar^2}{M\hbar c k_D}. \tag{L121}$$

Evaluation of Structure Factor

$$S(\vec{q},\omega) = \sum_{ll'} \frac{1}{N} e^{i\vec{q}\cdot(\vec{R}^l - \vec{R}^{l'})} \int \frac{dt}{2\pi} e^{i\omega t} e^{-2W} e^{\langle \vec{q}\cdot\hat{u}^{l'} \vec{q}\cdot\hat{u}^l(t)\rangle}. \tag{L122}$$

$$S^{(0)}(\vec{q},\omega) = \sum_l e^{i\vec{q}\cdot\vec{R}^l} \int \frac{dt}{2\pi} e^{i\omega t} e^{-2W} \tag{L123}$$

$$= \delta(\omega) N e^{-2W} \sum_{\vec{K}} \delta_{\vec{q}\vec{K}}. \tag{L124}$$

$$S^{(1)}(\vec{q},\omega) = \sum_{ll'} \frac{1}{N} e^{i\vec{q}\cdot(\vec{R}^l - \vec{R}^{l'})} \int \frac{dt}{2\pi} e^{i\omega t} e^{-2W} \langle \left(\vec{q}\cdot\hat{u}^{l'}\right) \left(\vec{q}\cdot\hat{u}^l(t)\right)\rangle. \tag{L125}$$

$$\mathfrak{M}' = \langle \left(\vec{q}\cdot\hat{u}^{l'}\right) \left(\vec{q}\cdot\hat{u}^l(t)\right)\rangle$$

$$= \frac{1}{N} \sum_{\substack{\vec{k}\vec{k}' \\ \nu\nu'}} \begin{array}{l} \langle(\vec{q}\cdot[\hat{u}_{\vec{k}\nu} e^{i\vec{k}\cdot\vec{R}^{l'}} + \hat{u}^\dagger_{\vec{k}\nu} e^{-i\vec{k}\cdot\vec{R}^{l'}}]) \\ \times(\vec{q}\cdot[\hat{u}_{\vec{k}'\nu'} e^{i\vec{k}'\cdot\vec{R}^l - i\omega_{\vec{k}'\nu'} t} + \hat{u}^\dagger_{\vec{k}'\nu'} e^{-i\vec{k}'\cdot\vec{R}^l + i\omega_{\vec{k}'\nu'} t}])\rangle \end{array} \tag{L126}$$

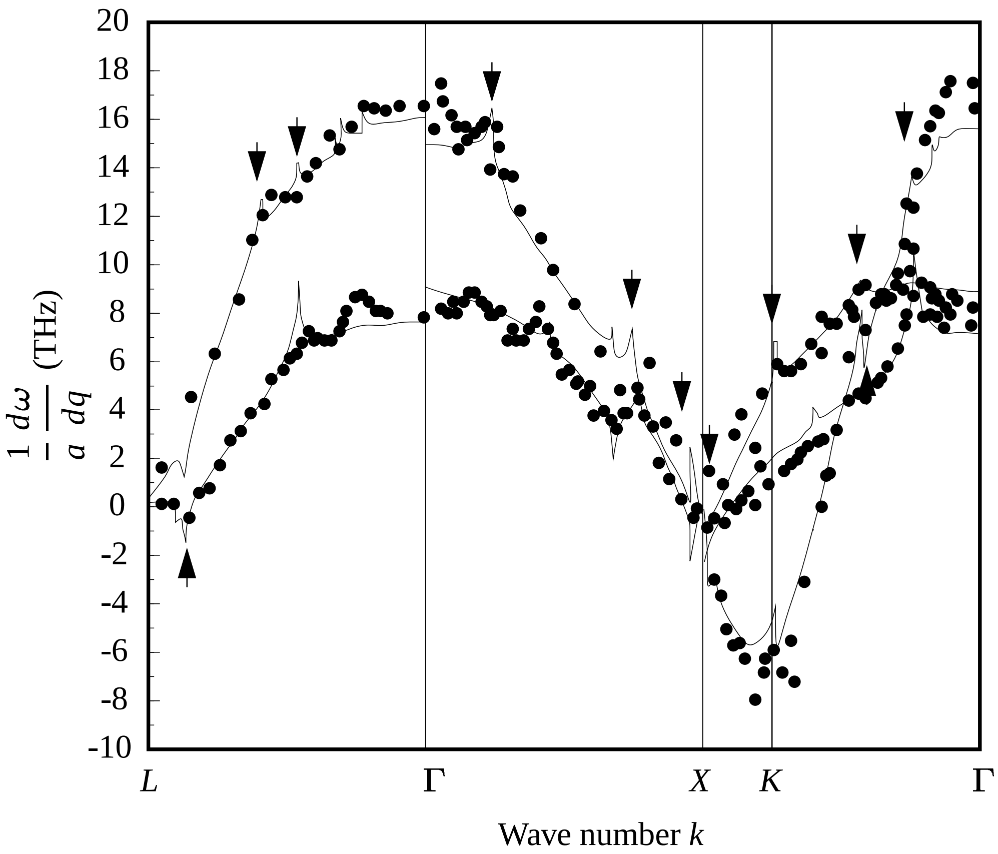
$$= \sum_{\vec{k}\nu} \frac{1}{N} \frac{\hbar^2 (\vec{\epsilon}_{\vec{k}\nu} \cdot \vec{q})^2}{2M\hbar\omega_{\vec{k}\nu}} \langle \hat{a}^\dagger_{\vec{k}\nu} \hat{a}_{\vec{k}\nu} e^{-i\omega_{\vec{k}\nu} t} + \hat{a}_{\vec{k}\nu} \hat{a}^\dagger_{\vec{k}\nu} e^{i\omega_{\vec{k}\nu} t} \rangle e^{i\vec{k}\cdot(\vec{R}^{l'} - \vec{R}^{l})} \quad \text{(L127)}$$

$$= \sum_{\vec{k}\nu} \frac{1}{N} \frac{\hbar^2 (\vec{\epsilon}_{\vec{k}\nu} \cdot \vec{q})^2}{2M\hbar\omega_{\vec{k}\nu}} \left([n_{\vec{k}\nu} + 1] e^{i\omega_{\vec{k}\nu} t} + n_{\vec{k}\nu} e^{-i\omega_{\vec{k}\nu} t} \right) e^{i\vec{k}\cdot(\vec{R}^{l'} - \vec{R}^{l})}, \quad \text{(L128)}$$

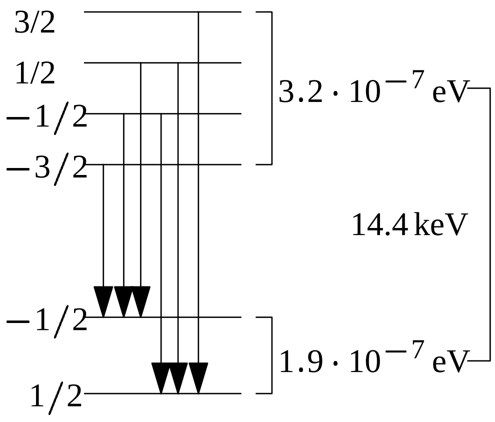
$$S^{(1)}(\vec{q},\omega) = e^{-2W} \sum_{\nu} \frac{\hbar^2 [\vec{q} \cdot \vec{\epsilon}_{\vec{q}\nu}]^2}{2M\hbar\omega_{\vec{q}\nu}} [(1 + n_{\vec{q}\nu})\delta(\omega + \omega_{\vec{q}\nu}) + n_{\vec{q}\nu}\delta(\omega - \omega_{\vec{q}\nu})]. \quad \text{(L129)}$$

Kohn Anomalies

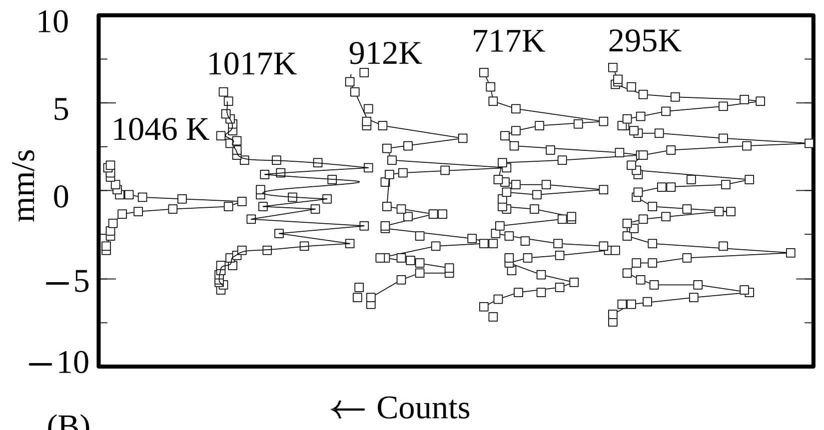
$q = 2k_F$



The Mössbauer Effect



(A)



(B)

$$S(\vec{q}) = \frac{1}{N}\sum_{ll'} e^{i\vec{q}\cdot(\vec{R}^{l}-\vec{R}^{l'})}\int_0^\infty \frac{dt}{2\pi}\left[e^{i(\Delta\mathcal{E}/\hbar+i\Gamma)t}+e^{-i(\Delta\mathcal{E}/\hbar-i\Gamma)t}\right]\langle e^{-i\vec{q}\cdot\hat{u}^{l'}}e^{i\vec{q}\cdot\hat{u}^{l}(t)}\rangle. \quad \text{(L130)}$$

$$\frac{2\Gamma}{(\Delta\mathcal{E}/\hbar)^2+\Gamma^2} \quad \text{(L131)}$$

$$f = \exp\left[-\frac{3}{4}\frac{q^2\hbar^2}{M\hbar c k_D}\right]. \quad \text{(L132)}$$