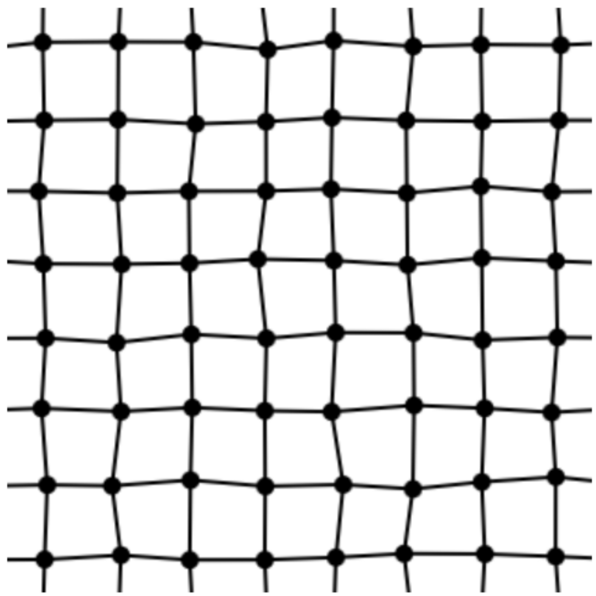
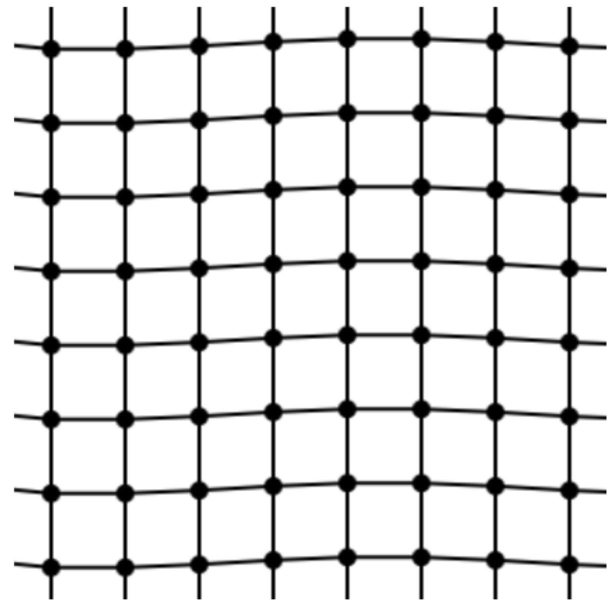
16. Phonons

May 17, 2018

Normal modes





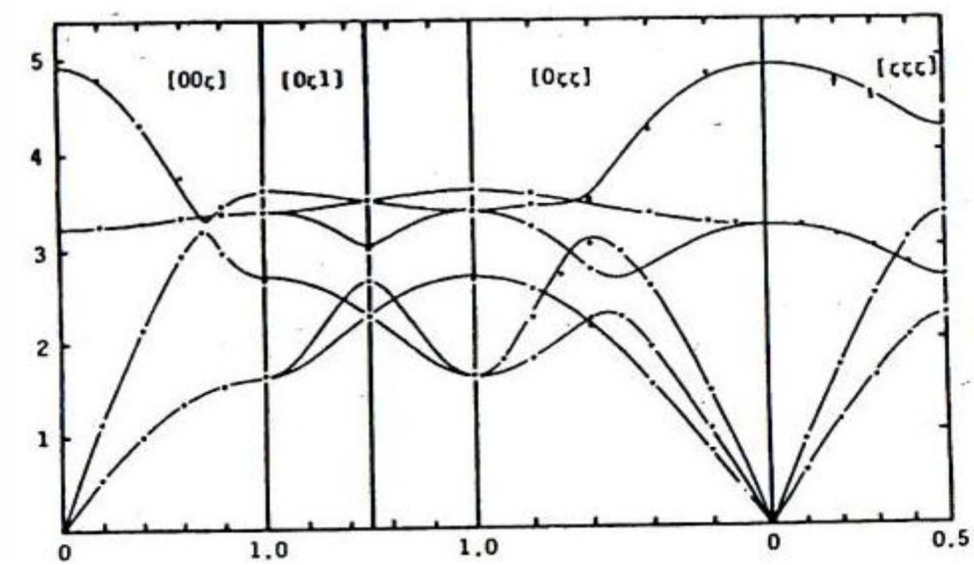
The motion of the atoms can be described in terms of normal modes.

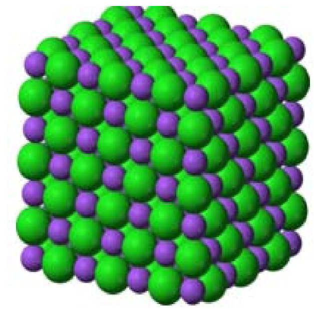
In a normal mode, all atoms oscillate at the same frequency ω.

The energy in a normal mode is quantized, $E = \hbar\omega(n + \frac{1}{2})$.

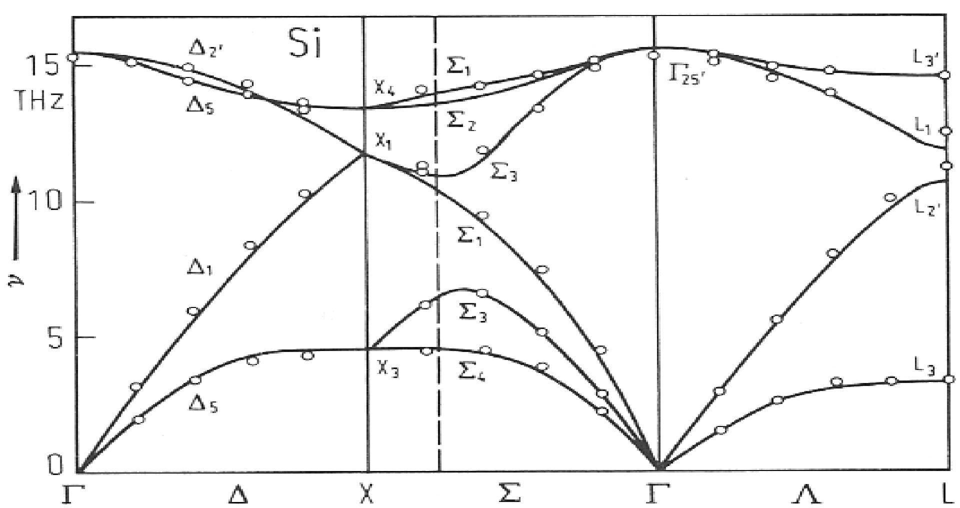
n is the number of phonons in that normal mode.

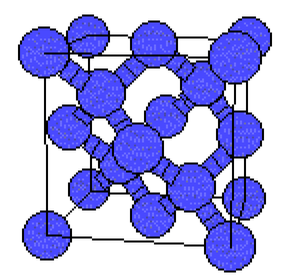
Two atoms per primitive unit cell





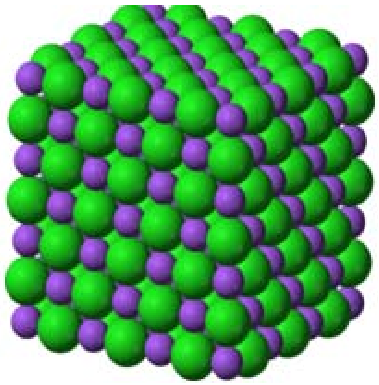
NaCl





Si

NaCl



2 atoms/unit cell

6 equations

3 acoustic and
3 optical branches

x - Richtung:

$$M_1 \frac{d^2 u^x_{nml}}{dt^2} = C\left(-2u^x_{nml} + v^x_{(n-1)m(l-1)} + v^x_{n(m-1)l}\right)$$

$$M_2 \frac{d^2 v^x_{nml}}{dt^2} = C\left(-2v^x_{nml} + u^x_{(n+1)m(l+1)} + u^x_{n(m+1)l}\right)$$

y - Richtung:

$$M_1 \frac{d^2 u^y_{nml}}{dt^2} = C\left(-2u^y_{nml} + v^y_{(n-1)(m-1)l} + v^y_{nm(l-1)}\right)$$

$$M_2 \frac{d^2 v^y_{nml}}{dt^2} = C\left(-2v^y_{nml} + u^y_{(n+1)(m+1)l} + u^y_{nm(l+1)}\right)$$

z - Richtung:

$$M_1 \frac{d^2 u^z_{nml}}{dt^2} = C\left(-2u^z_{nml} + v^z_{n(m-1)(l-1)} + v^z_{(n-1)ml}\right)$$

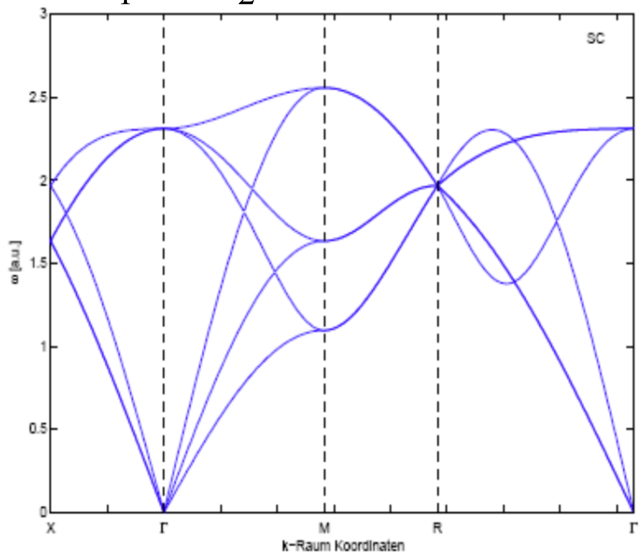
$$M_2 \frac{d^2 v^z_{nml}}{dt^2} = C\left(-2v^z_{nml} + u^z_{n(m+1)(l+1)} + u^z_{(n+1)ml}\right)$$

$$u^x_{nml} = u^x_{\vec{k}} \exp\left(i\left(\vec{k}\cdot\vec{a}_1 + \vec{k}\cdot\vec{a}_2 + \vec{k}\cdot\vec{a}_3 - \omega t\right)\right) \qquad v^x_{nml} = v^x_{\vec{k}} \exp\left(i\left(\vec{k}\cdot\vec{a}_1 + \vec{k}\cdot\vec{a}_2 + \vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

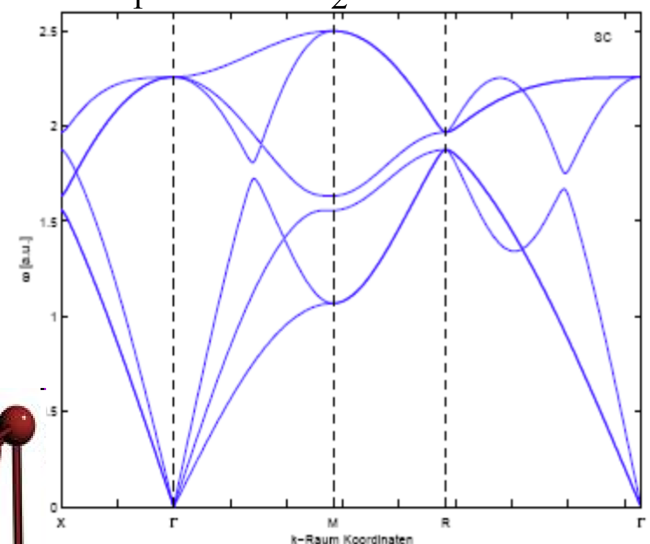
CsCl

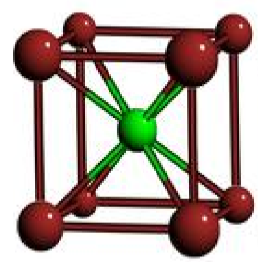
Hannes Brandner

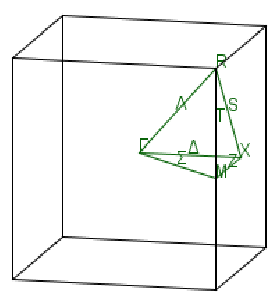
$M_1 = M_2$



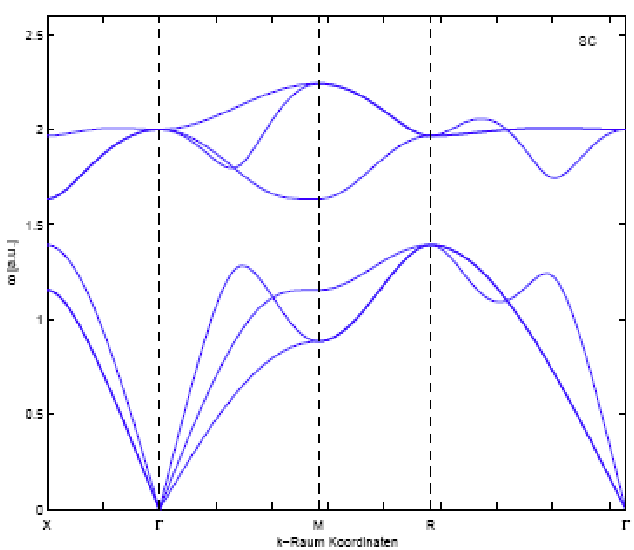
$M_1 = 1.1\ M_2$



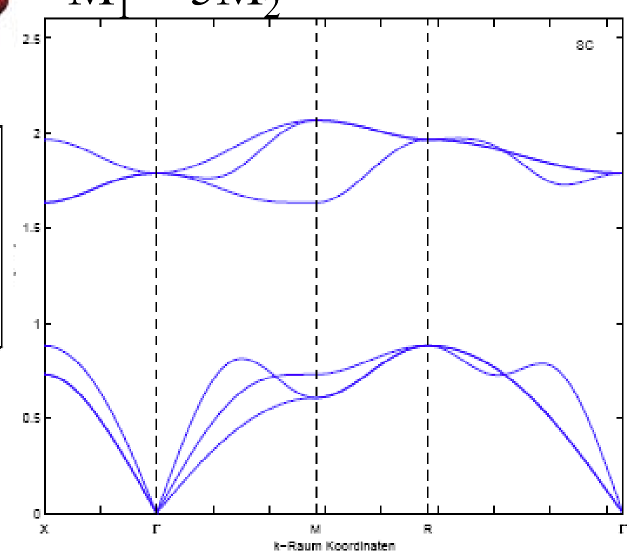




$M_1 = 2M_2$



$M_1 = 5M_2$



3 dimensions

p atoms per unit cell

3*p* branches to the dispersion relation

3 acoustic modes (1 longitudinal, 2 transverse)

3*p* - 3 optical modes

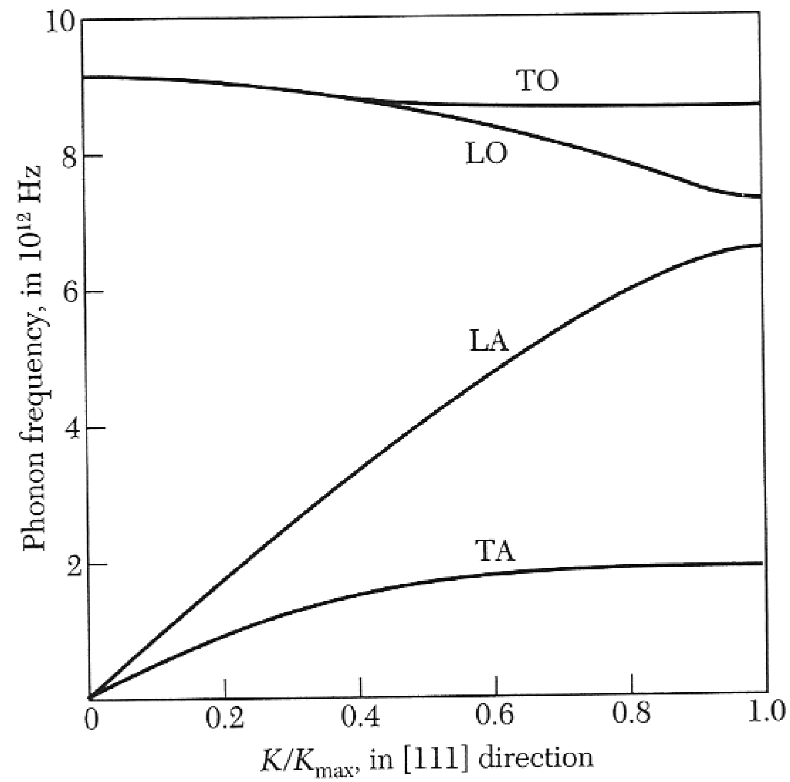
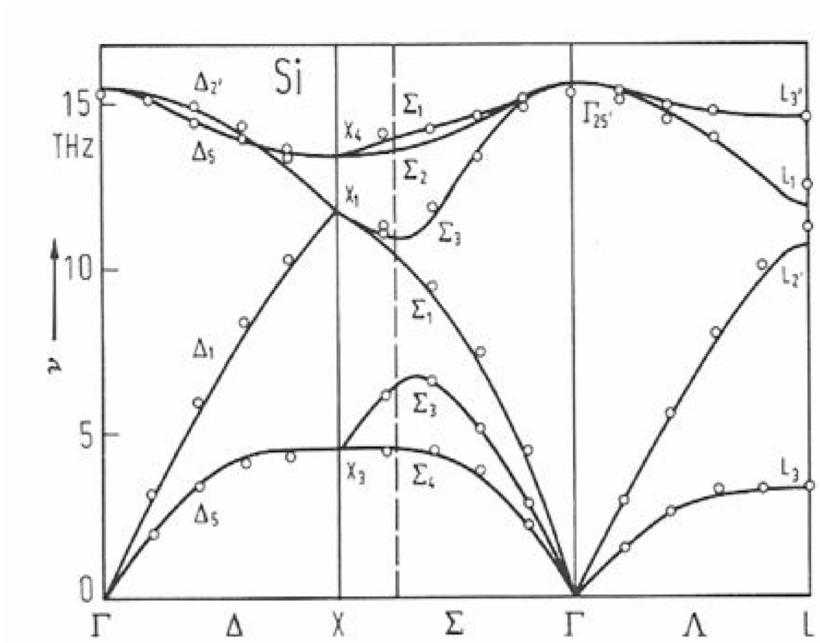
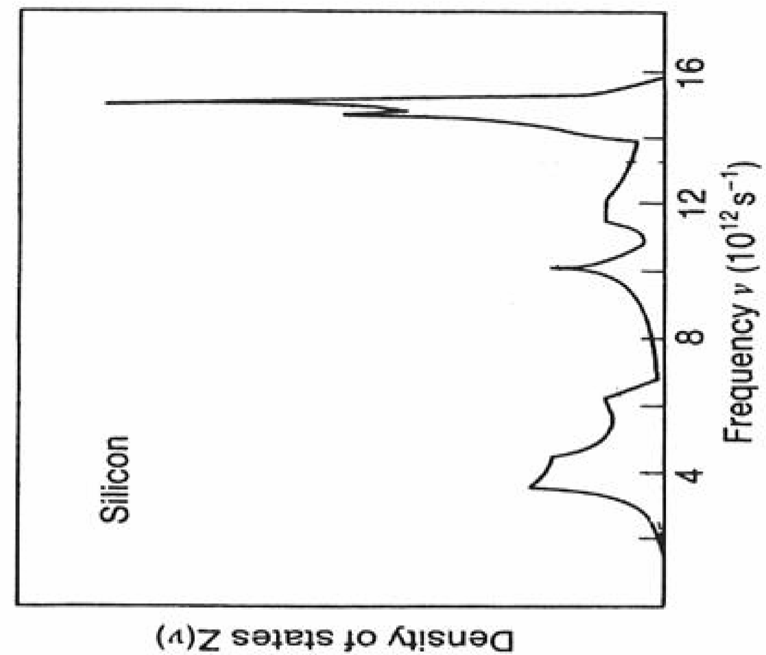


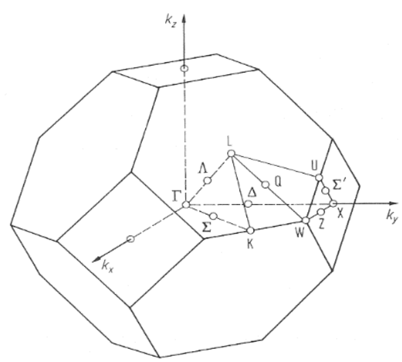
Figure 8a Phonon dispersion relations in the [111] direction in germanium at 80 K. The two TA phonon branches are horizontal at the zone boundary position, $K_{max} = (2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The LO and TO branches coincide at $K = 0$; this also is a consequence of the crystal symmetry of Ge. The results were obtained with neutron inelastic scattering by G. Nilsson and G. Nelin.

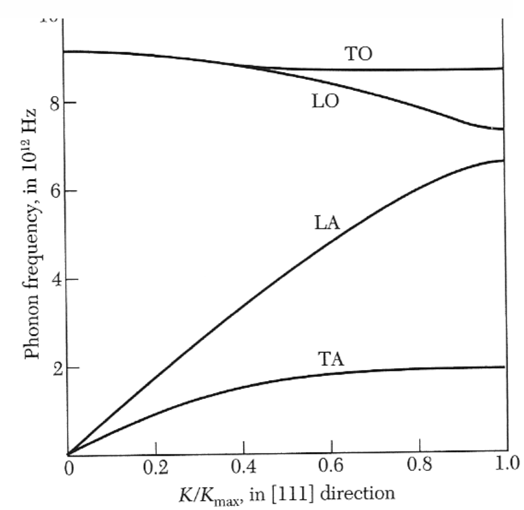
Silicon phonon dispersion, DOS



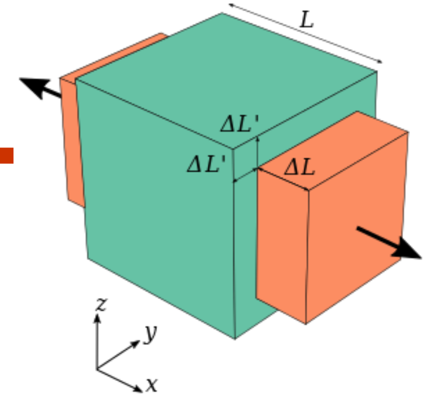


Different speeds of sound for different directions and polarizations causes dispersion of pulses.





Poisson's ratio



Wikipedia

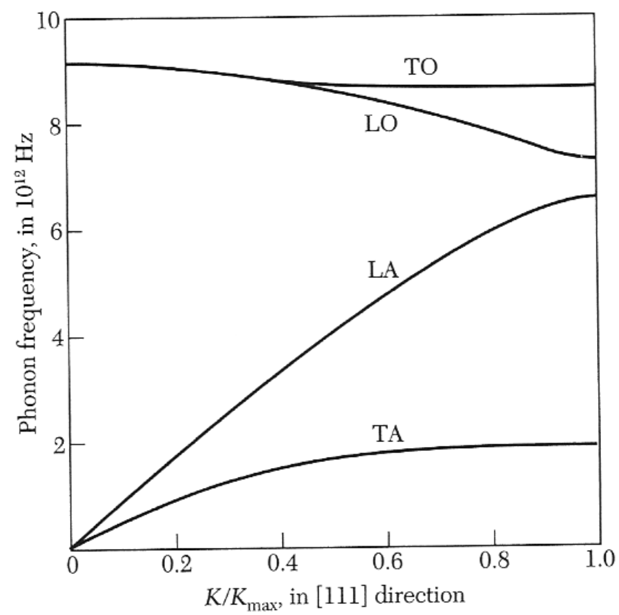
E - Elastic constant

ν - Poisson's ratio

ρ - density

$$c_T = \sqrt{\frac{E(1-\nu)}{\rho(1-\upsilon-2\upsilon^2)}}$$

$$c_L = \sqrt{\frac{E}{2\rho(1+\upsilon)}}$$



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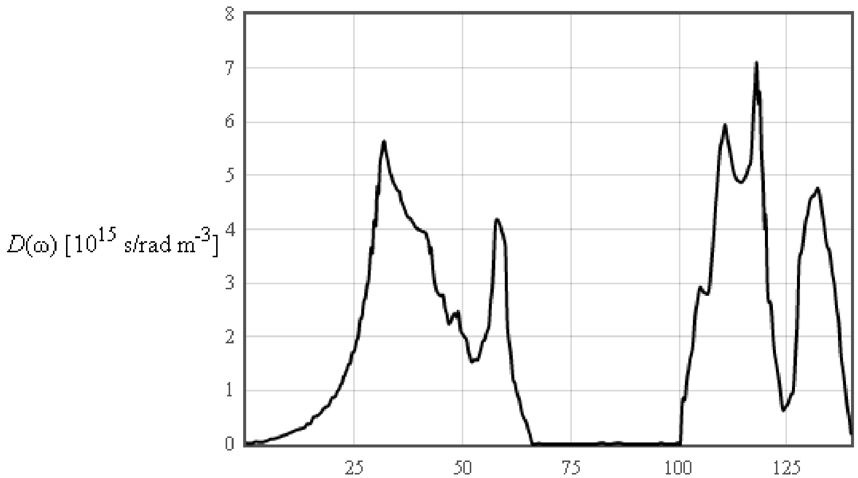
Kittel

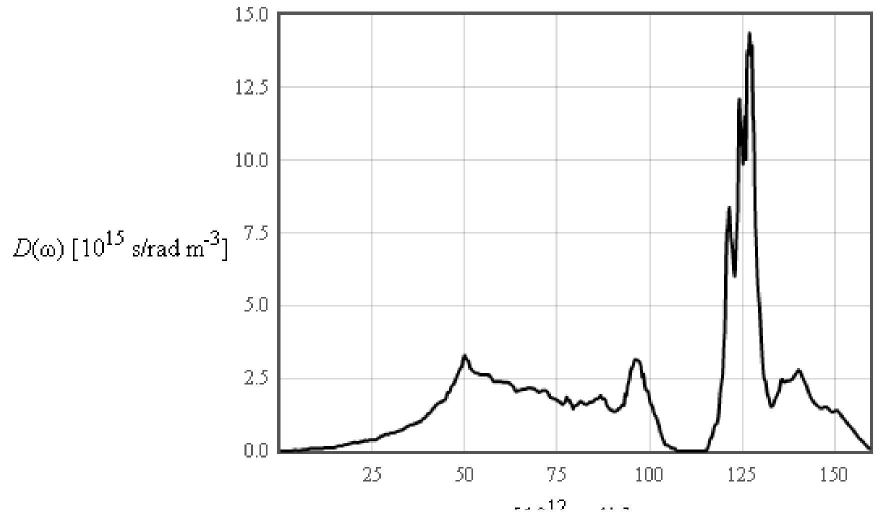
If the density is known, you can determine E and ν.

Two atoms per primitive unit cell

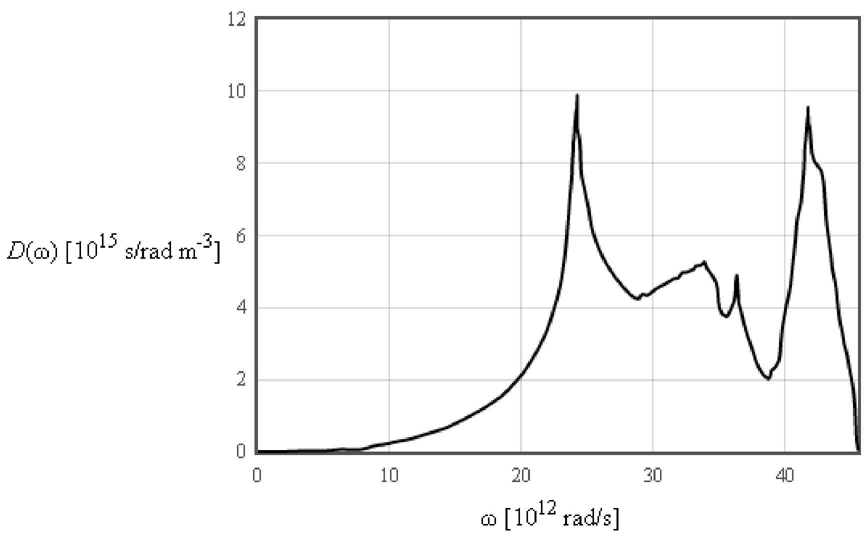
Phonon density of states for GaN



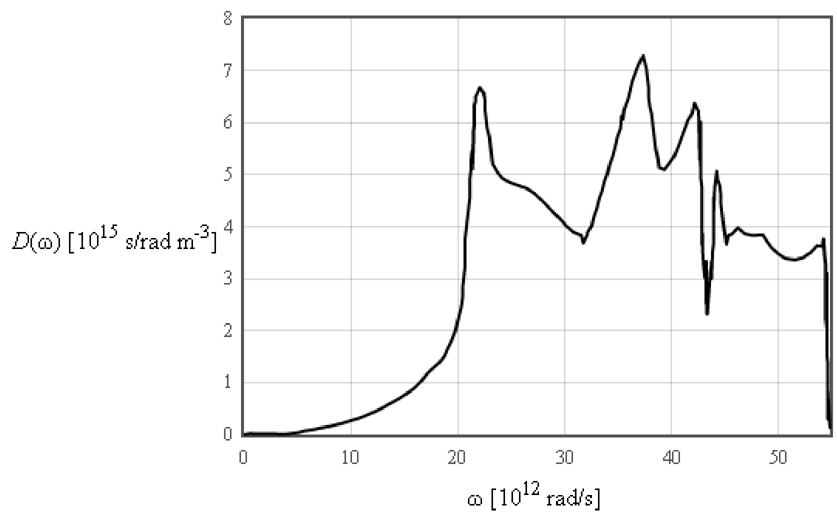
Phonon density of states for AlN

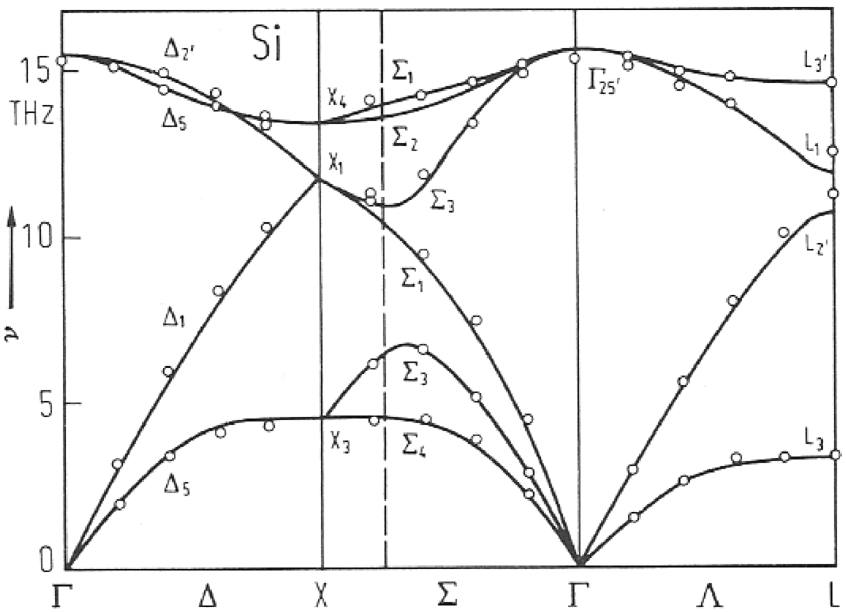


Phonon density of states for hcp magnesium



Phonon density of states for hcp titanium




Si
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$\Delta_{2'}$
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$\Gamma_{25'}$
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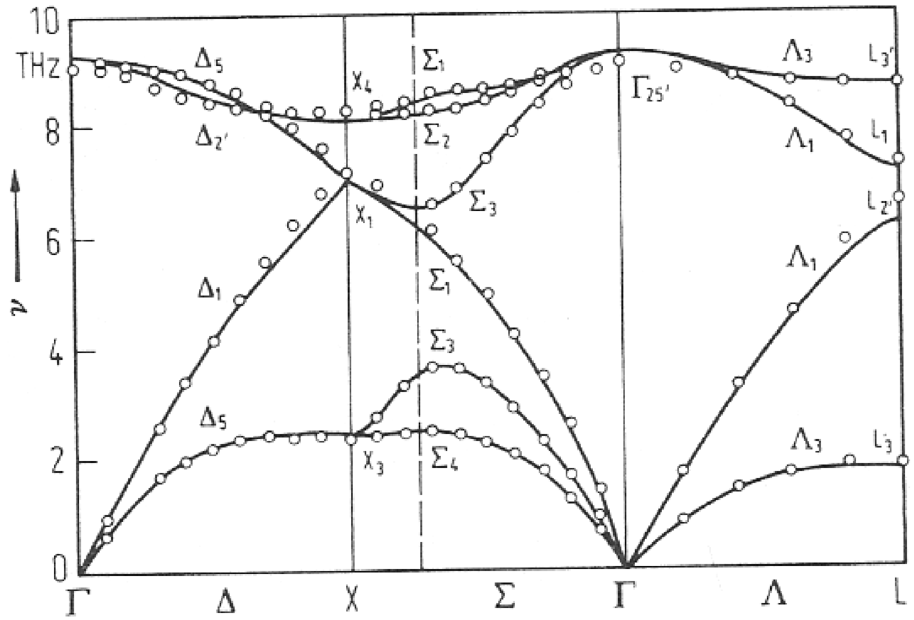
L_1
$L_{2'}$
L_3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L_1
$L_{2'}$
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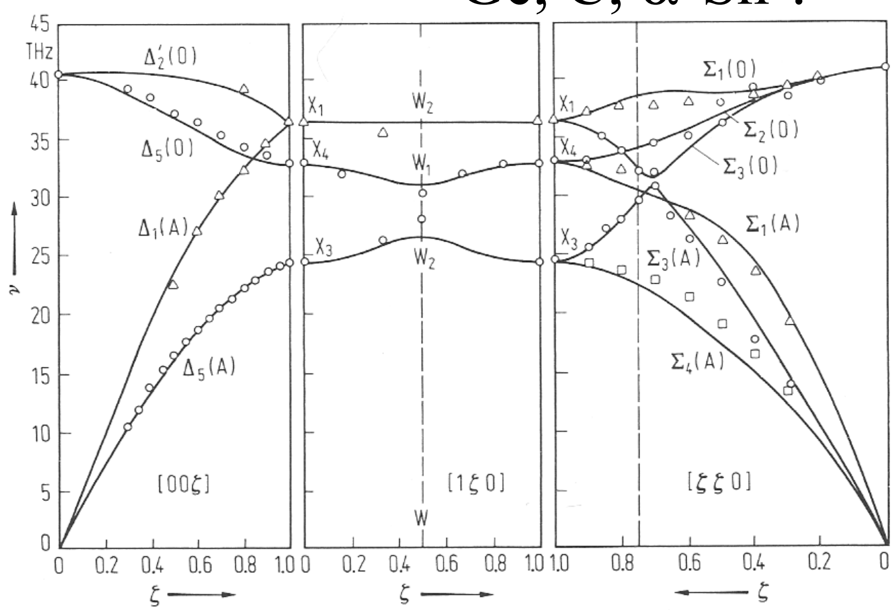
Ge, C, α-Sn ?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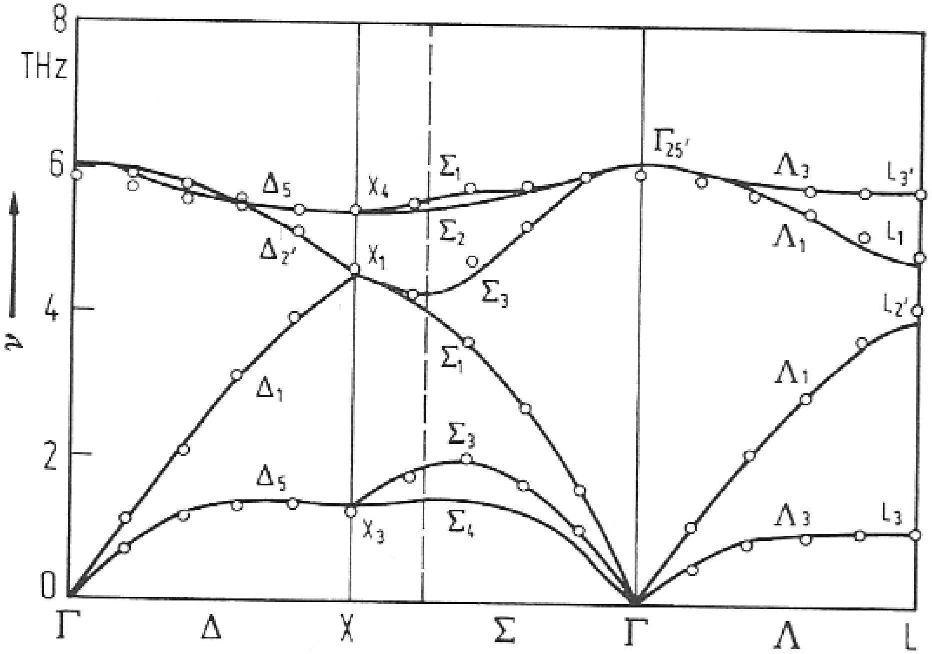
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$\Gamma_{25'}$
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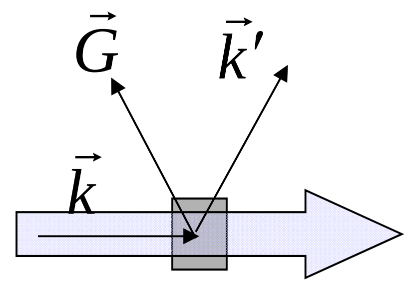
$L_{3'}$
L_1
$L_{2'}$
L_3

Inelastic neutron scattering

Diffraction condition for elastic scattering



$$\vec{k}' = \vec{k} + \vec{G}$$

The whole crystal recoils with momentum $\hbar\vec{G}$

Diffraction condition for inelastic scattering

$$\vec{k}' \pm \vec{K}_{ph} = \vec{k} + \vec{G} \qquad \frac{\hbar^2 k'^2}{2m_n} \pm \hbar\omega_{ph} = \frac{\hbar^2 k^2}{2m_n} + \cancelto{0}{\frac{\hbar^2 G^2}{2m_{crystal}}}$$

$\vec{K}_{ph}$ is the phonon momentum

Phonon dispersion relations are determined experimentally by inelastic neutron diffraction

long wavelength limit

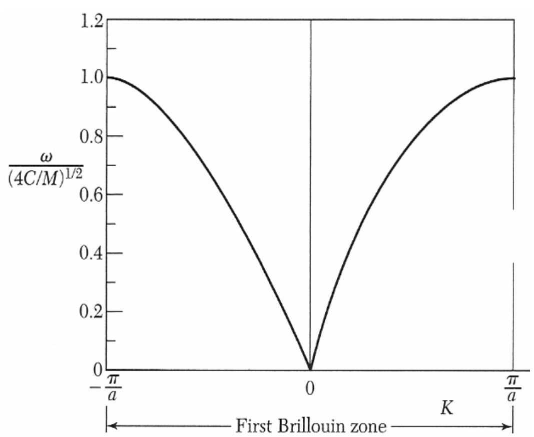
discrete version of wave equation

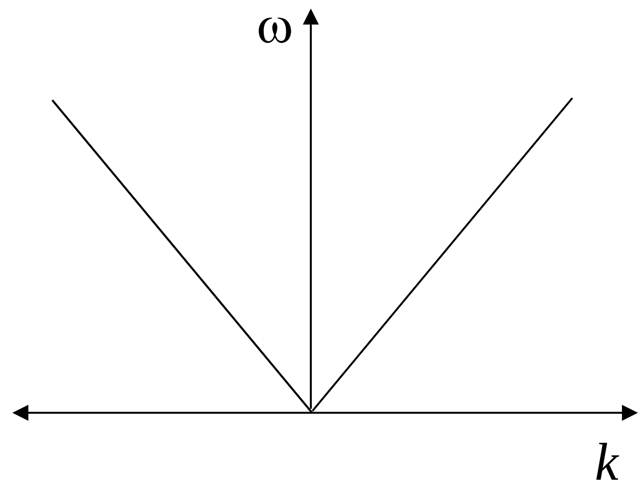
$$m\frac{d^2u_s}{dt^2} = C(u_{s+1} - 2u_s + u_{s-1})$$

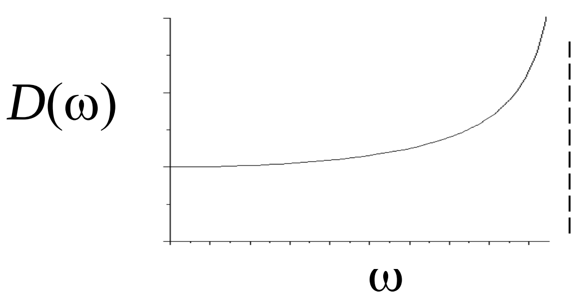
1-d wave equation

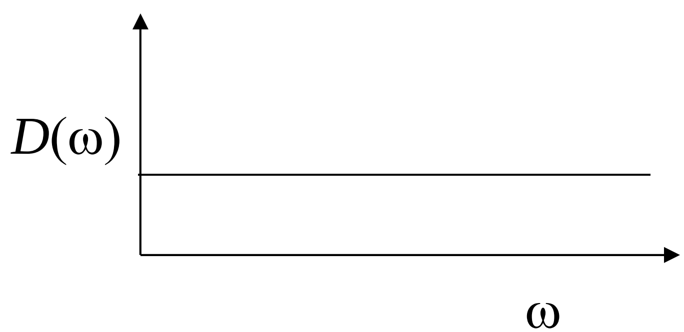
$$\frac{d^2u}{dt^2} = c^2\frac{d^2u}{dx^2}$$

The solutions to the linear chain are the same as the solutions to the wave equation for $|k| << \pi/a$.









Phonons - long wavelength, low temperature limit

At low T, there are only long wave length states occupied.

3 polarizations

Density of states: $$D(\omega)d\omega = \frac{3\omega^2}{2c^3\pi^2}d\omega.$$

Specific heat of insulators at low temperatures

$$C_v = \frac{24\sigma V T^3}{c}$$

Speed of sound

$$I = \frac{2\pi^5 k_B^4 T^4}{15c^2h^3} = \sigma T^4 \quad [\mathrm{J\ m^{-2}\ s^{-2}}]$$

$$u(\lambda) = \frac{8\pi hc}{\lambda^5\left(\exp\left(\frac{hc}{\lambda k_B T}\right) - 1\right)} \quad [\mathrm{J/m^4}]$$

$$u = \frac{4\sigma T^4}{c} \quad [\mathrm{J/m^3}]$$

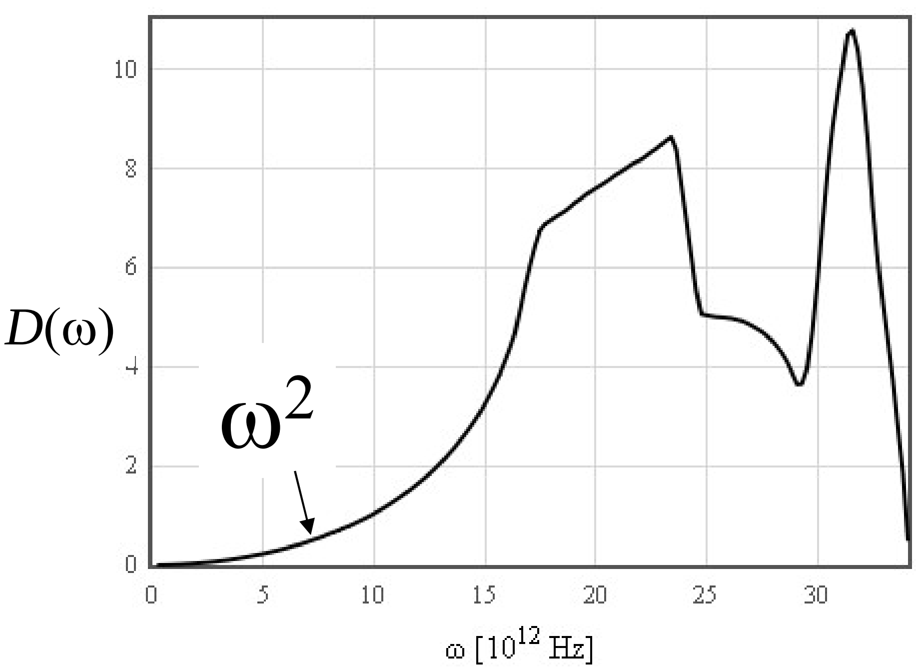
$$c_v = \frac{16\sigma T^3}{c} \quad [\mathrm{J\ K^{-1}\ m^{-3}}]$$

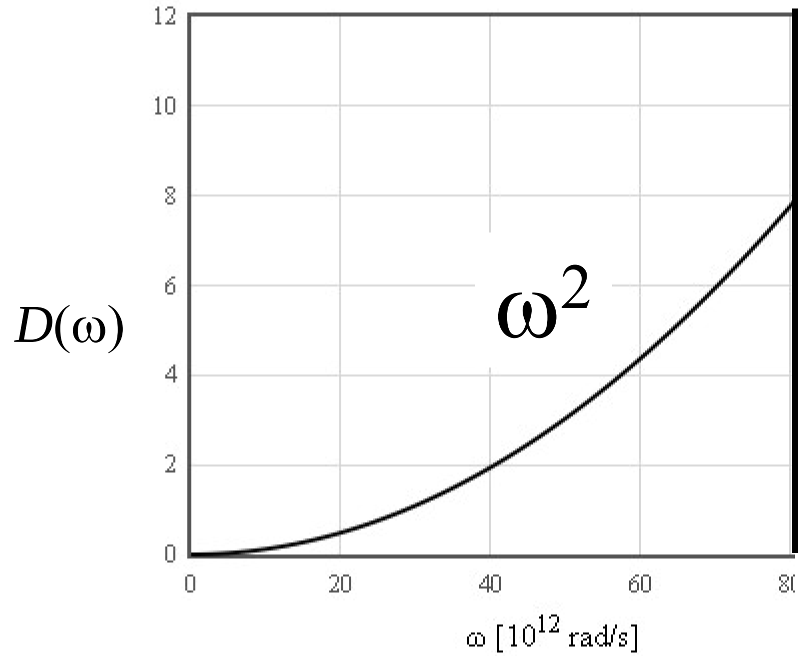
$$f = \frac{-4\sigma T^4}{3c} \quad [\mathrm{J/m^3}]$$

$$s = \frac{16\sigma T^3}{3c} \quad [\mathrm{J\ K^{-1}\ m^{-3}}]$$

$$P = \frac{4\sigma T^4}{3c} \quad [\mathrm{N/m^2}]$$

long wavelength, low temperature limit





Thermal properties

1. Determine the dispersion relation:

Write down the equations of motion (masses and springs).

The solutions to these equations will be eigen functions of T

$$\exp\left(i\left(\vec{k}\cdot\vec{a}_1+\vec{k}\cdot\vec{a}_2+\vec{k}\cdot\vec{a}_3-\omega t\right)\right)$$

Substitute the eigen functions of T into the equations of motion to determine the dispersion relation.

2. Determine the density of states numerically from the dispersion relation

$$D(\omega)$$

For every allowed *k*, find all corresponding values of ω.

long wavelength limit

discrete version of wave equation

$$m\frac{d^2u_s}{dt^2} = C(u_{s+1} - 2u_s + u_{s-1})$$

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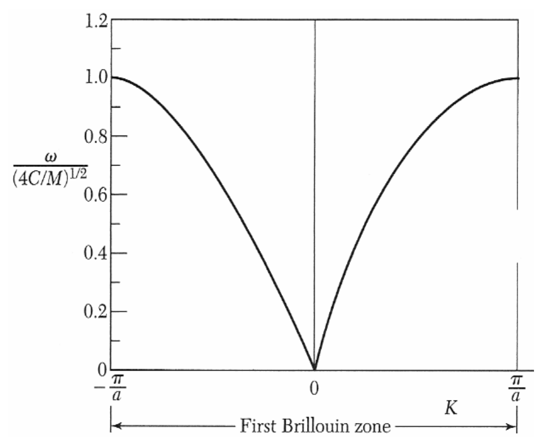

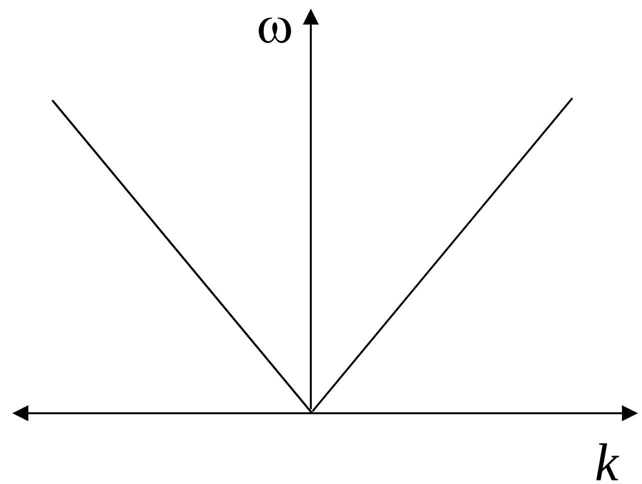

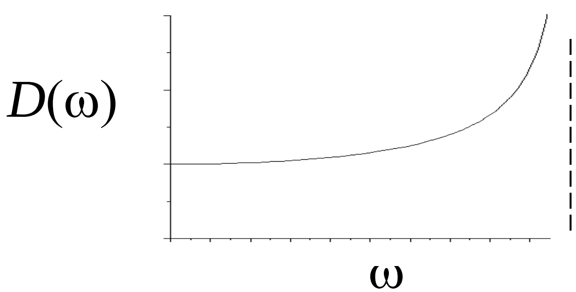

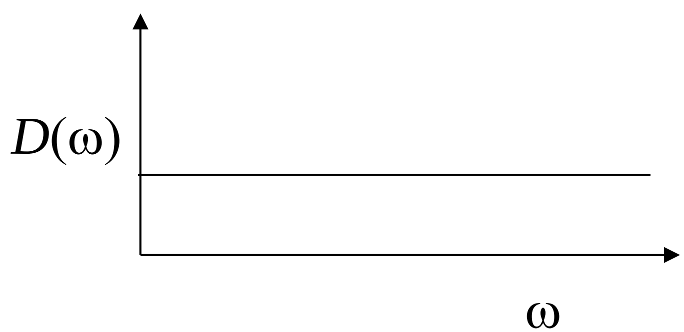

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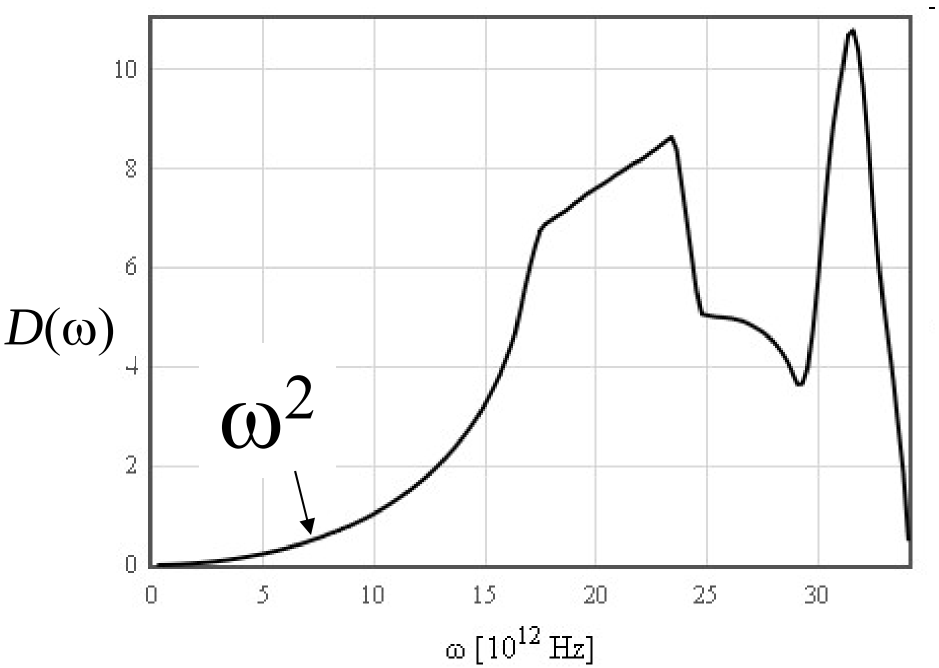
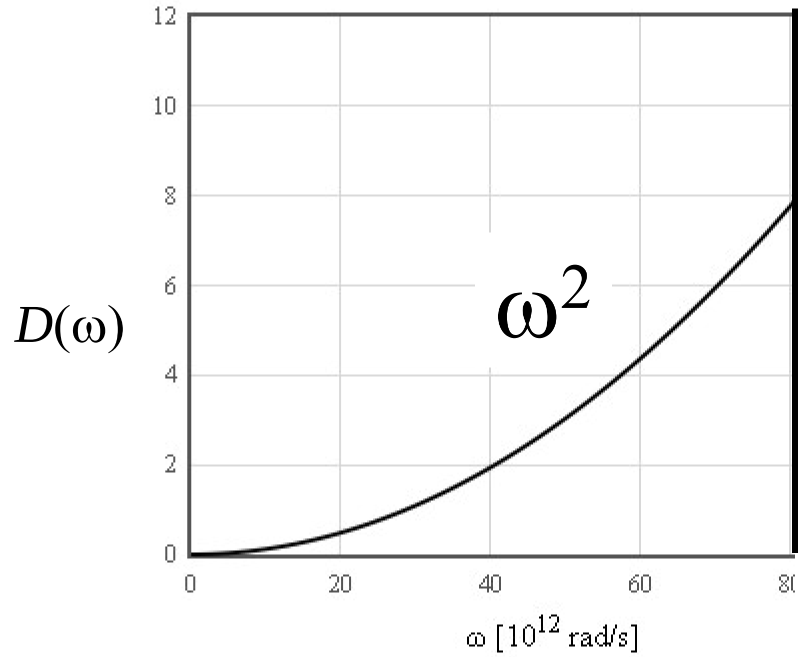
long wavelength, low temperature limit



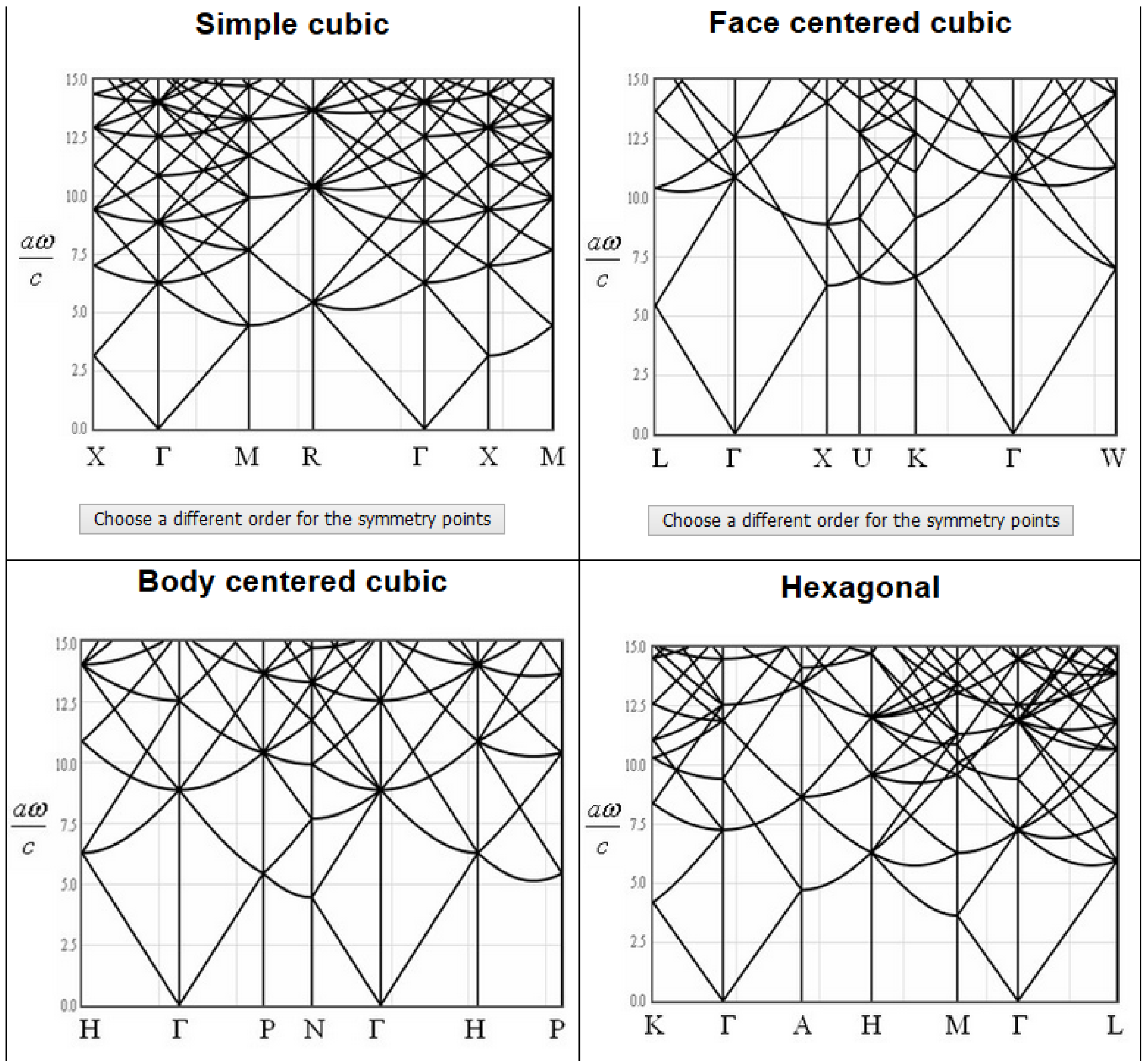


Empty lattice approximation

Use the speed of sound instead of the speed of light.

3 acoustic branches

$3p$ - 3 optical branches



Heat capacity / specific heat

Heat capacity is the measure of the heat energy required to increase the temperature of an object by a certain temperature interval.

Specific heat is the measure of the heat energy required to increase the temperature of a unit quantity of a substance by a certain temperature interval.

For solids, the heat capacity at constant volume and heat capacity at constant pressure are almost the same.

The heat capacity was historically important for understanding solids.

Dulong and Petit (Classical result)

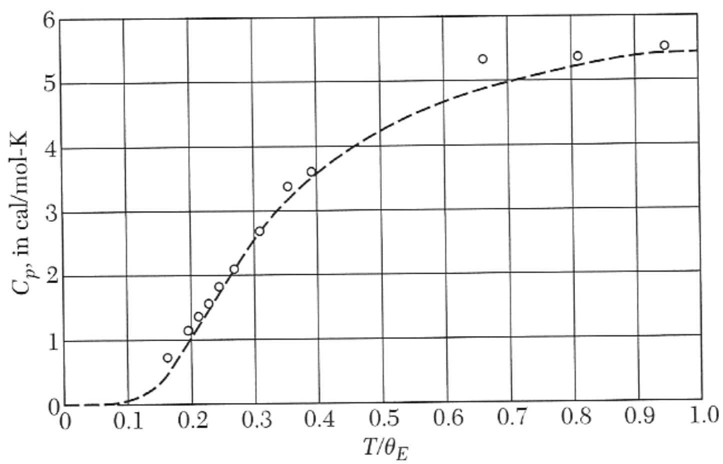
Equipartition: $\frac{1}{2}k_B T$ per quadratic term in energy

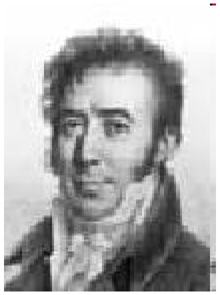
internal energy: $u = 3nk_B T$ N atoms of the crystal

specific heat: $c_v = \dfrac{du}{dT} = 3nk_B$

experiments: heat capacity goes to zero at zero temperature

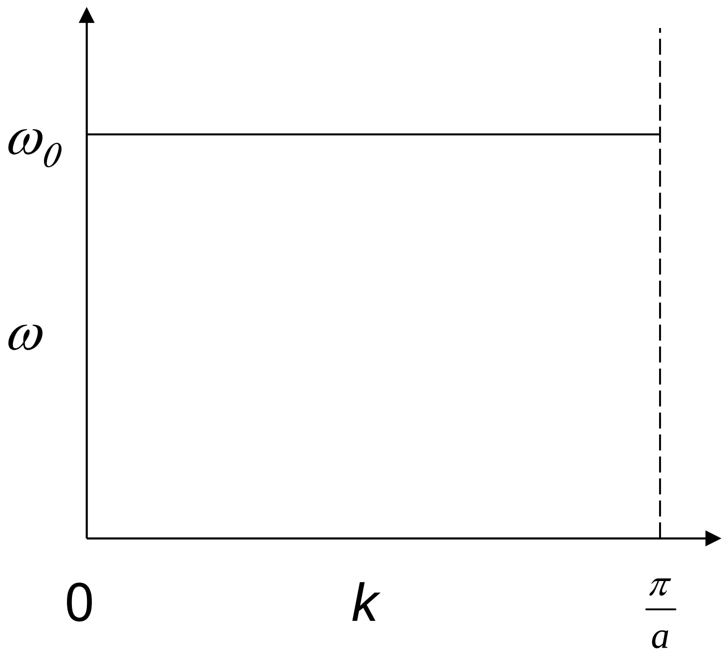
Pierre Louis Dulong

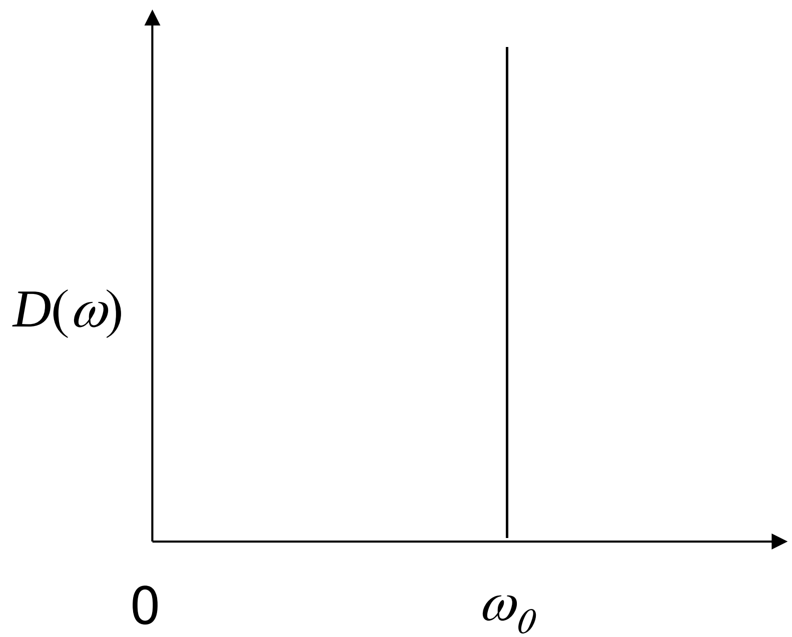




Alexis Therese Petit

Einstein model for specific heat





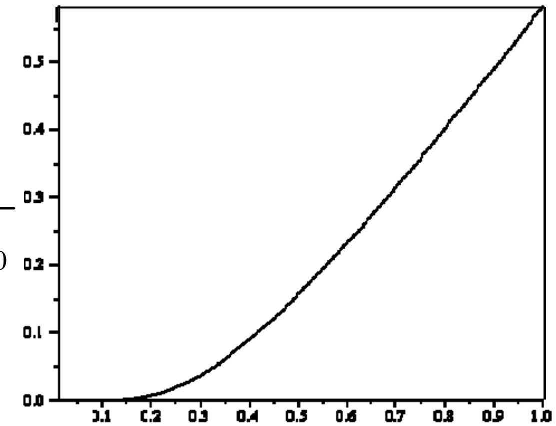
$$D(\omega) = 3n\delta(\omega - \omega_0)$$

n = density of atoms

$$u(\omega) = D(\omega)\hbar\omega \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} = \hbar\omega \frac{3n\delta(\omega - \omega_0)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

Einstein model for specific heat

$$u(\omega) = \hbar\omega \frac{3n\delta(\omega-\omega_0)}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1}$$

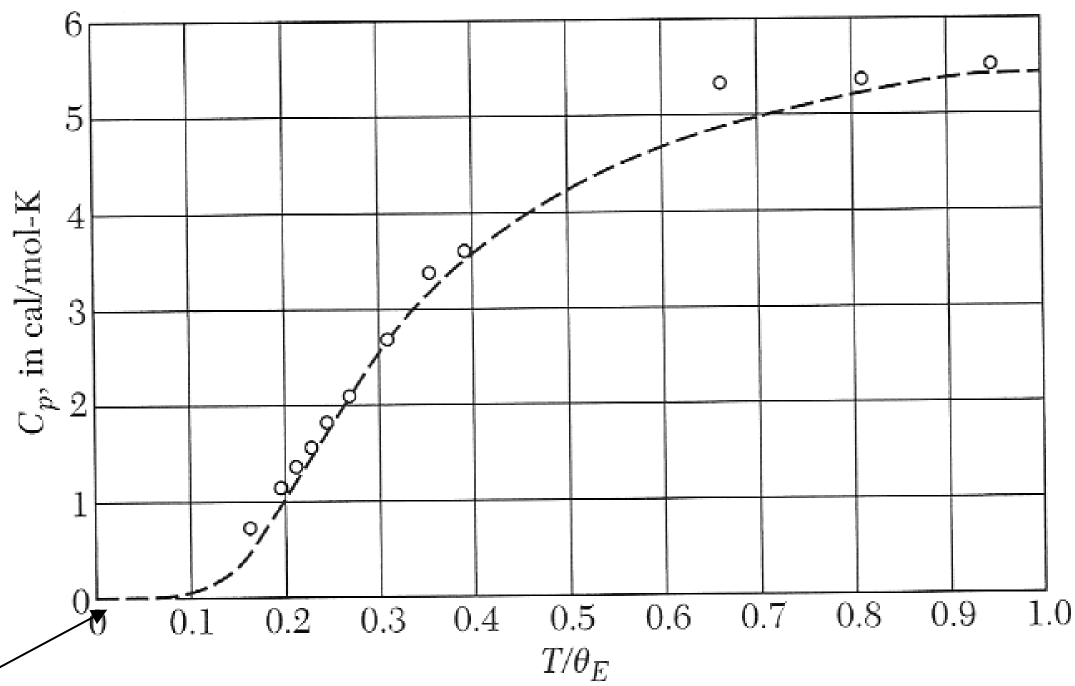


$$u = \int_0^\infty u(\omega)d\omega = \int_0^\infty 3n\hbar\omega \frac{\delta(\omega-\omega_0)d\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1} = \frac{3n\hbar\omega_0}{\exp\left(\frac{\hbar\omega_0}{k_B T}\right)-1}$$

$$c_v = \frac{du}{dT} = \frac{3n\hbar\omega_0 \frac{\hbar\omega_0}{k_B T^2}\exp\left(\frac{\hbar\omega_0}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega_0}{k_B T}\right)-1\right)^2} = \frac{3nk_B\left(\frac{\hbar\omega_0}{k_B T}\right)^2\exp\left(\frac{\hbar\omega_0}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega_0}{k_B T}\right)-1\right)^2}$$

Einstein model for specific heat

$$c_v = \frac{3nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \exp\left(\frac{\hbar\omega_0}{k_BT}\right)}{\left(\exp\left(\frac{\hbar\omega_0}{k_BT}\right)-1\right)^2}$$



High temperatures

$$c_v \approx 3nk_B$$

$$\theta_E = \frac{\hbar\omega_0}{k_B}$$

low T does not fit

Debye model for specific heat

Peter Debye

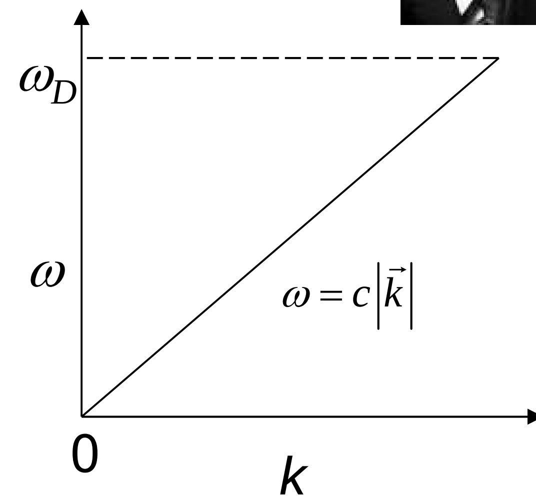
$$D(\omega) = \frac{3\omega^2}{2\pi^2 c^3}$$

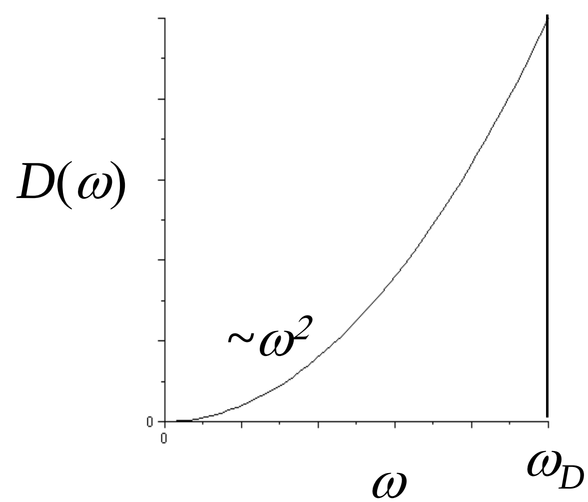
Like blackbody radiation up to a cutoff frequency.

$$V\int_0^\infty D(\omega)d\omega = 3N = Na^3 \int_0^{\omega_D} \frac{3\omega^2}{2\pi^2 c^3} d\omega = Na^3 \frac{\omega_D^3}{2\pi^2 c^3}$$

$$\omega_D = \left(\frac{6\pi^2 c^3}{a^3}\right)^{1/3}$$

Debye temperature $\hbar\omega_D = k_B \theta_D$





Debye model for heat capacity

$$u(\omega) = D(\omega)\hbar\omega \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} = \frac{3\omega^2}{2\pi^2 c^3} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

$$u = \int_0^{\omega_D} u(\omega) d\omega = \int_0^{\omega_D} \frac{3\omega^2}{2\pi^2 c^3} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega \approx \int_0^{\infty} \frac{3\omega^2}{2\pi^2 c^3} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega$$

for low T

$$\int_0^{\infty} \frac{x^3}{\exp(x) - 1} dx = \frac{\pi^4}{15}$$

$$u \approx \frac{3\pi^4}{5} n k_B \frac{T^4}{\theta_D^3} \qquad c_v \approx \frac{12\pi^4}{5} n k_B \left(\frac{T}{\theta_D}\right)^3$$

Table 1 Debye temperature and thermal conductivity

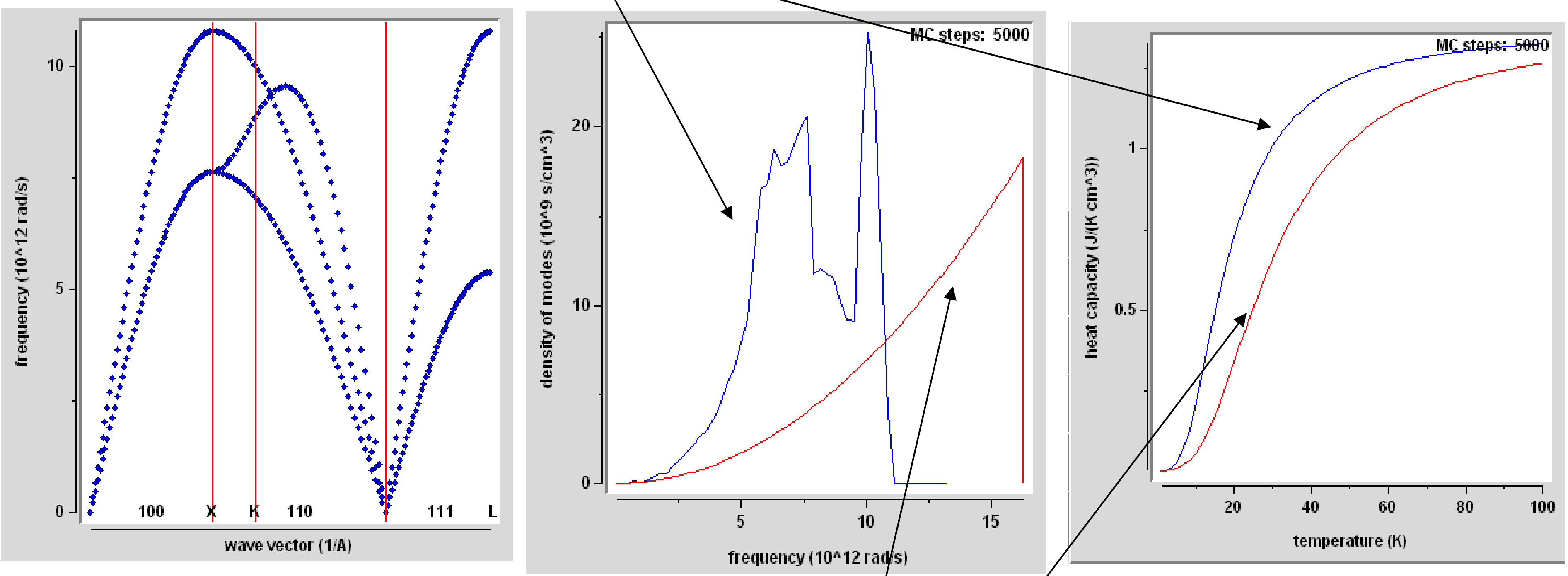
Low temperature limit of θ, in Kelvin
Thermal conductivity at 300 K, in W $cm^{-1}K^{-1}$

Li	Be											B	C	N	O	F	Ne
344	1440												2230				75
0.85	2.00											0.27	1.29				
Na	Mg											Al	Si	P	S	Cl	Ar
158	400											428	645				92
1.41	1.56											2.37	1.48				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
91	230	360.	420	380	630	410	470	445	450	343	327	320	374	282	90		72
1.02		0.16	0.22	0.31	0.94	0.08	0.80	1.00	0.91	4.01	1.16	0.41	0.60	0.50	0.02		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn w	Sb	Te	I	Xe
56	147	280	291	275	450		600	480	274	225	209	108	200	211	153		64
0.58		0.17	0.23	0.54	1.38	0.51	1.17	1.50	0.72	4.29	0.97	0.82	0.67	0.24	0.02		
Cs	Ba	La β	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
38	110	142	252	240	400	430	500	420	240	165	71.9	78.5	105	119			
0.36		0.14	0.23	0.58	1.74	0.48	0.88	1.47	0.72	3.17		0.46	0.35	0.08			
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
						200		210				120	210
0.11	0.12	0.16		0.13		0.11	0.11	0.11	0.16	0.14	0.17	0.35	0.16
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
163		207											
0.54		0.28	0.06	0.07									

Phonon density of states

fcc phonon density of states



Debye model (quantized wave equation with a cut-off frequency)

Thermal properties

internal energy density $$u = \int_0^\infty u(\omega)d\omega = \int_0^\infty \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1} d\omega \quad \left[\text{J/m}^3\right]$$

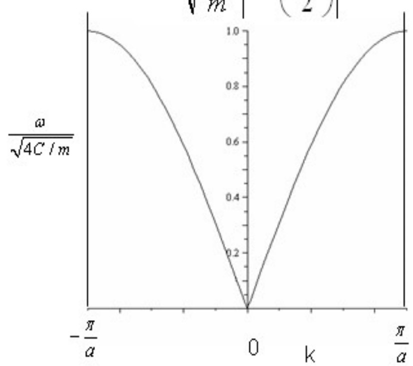
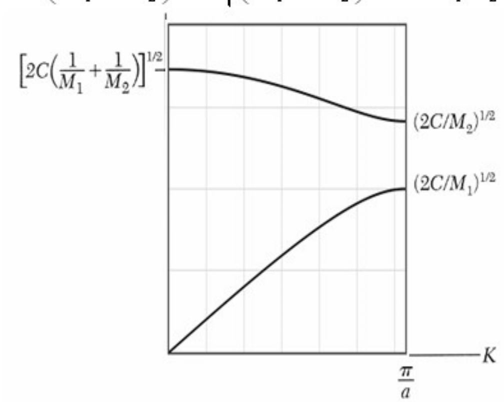
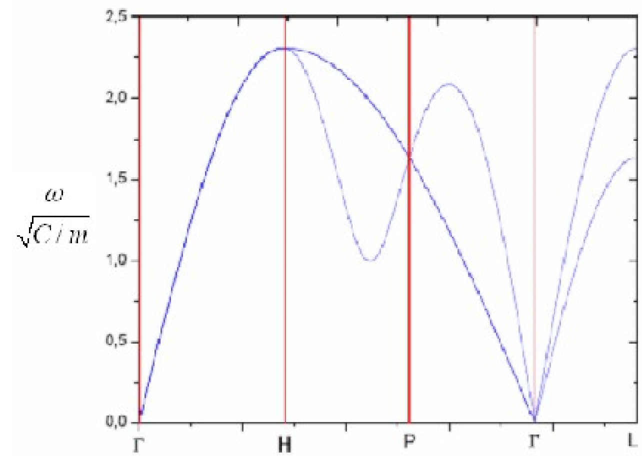
specific heat $$c_v = \frac{du}{dT} = \int \left(\frac{\hbar\omega}{T}\right)^2 \frac{D(\omega)\exp\left(\frac{\hbar\omega}{k_B T}\right)}{k_B\left(\exp\left(\frac{\hbar\omega}{k_B T}\right)-1\right)^2} d\omega \quad [\text{J K}^{-1}\ \text{m}^{-3}]$$

entropy density $$s(T) = \int \frac{c_v}{T} dT = \frac{1}{T}\int_0^\infty \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1} d\omega \quad [\text{J K}^{-1}\ \text{m}^{-3}]$$

Helmholtz free energy density

$$f(T) = u - Ts = k_B T \int_0^\infty D(\omega)\ln\left(1-\exp\left(\frac{-\hbar\omega}{k_B T}\right)\right) d\omega \quad \left[\text{J/m}^3\right]$$

Phonons

	Linear Chain	Linear chain 2 masses	body centered cubic
	$m\frac{d^2u_s}{dt^2}=C(u_{s+1}-2u_s+u_{s-1})$	$M_1\frac{d^2u_s}{dt^2}=C(v_{s-1}-2u_s+v_s)$ $M_2\frac{d^2v_s}{dt^2}=C(u_s-2v_s+u_{s+1})$	$\frac{d^2u^x_{lmn}}{dt^2}=\frac{C}{\sqrt{3}\,m}[(u^x_{l+1m+1n+1}-u^x_{lmn})+(u^x_{l-1m+1n+1}-u^x_{l\cdots}$ $+(u^x_{l+1m-1n+1}-u^x_{lmn})+(u^x_{l+1m+1n-1}-u^x_{lmn})+(u^x_{l-1m+\cdots}$ $+(u^x_{l+1m-1n-1}-u^x_{lmn})+(u^y_{l+1m+1n+1}-u^y_{lmn})-(u^y_{l-1m+\cdots}$ $+(u^y_{l+1m-1n+1}-u^y_{lmn})-(u^y_{l+1m+1n-1}-u^y_{lmn})+(u^y_{l-1m+\cdots}$ $+(u^y_{l+1m-1n-1}-u^y_{lmn})+(u^z_{l+1m+1n+1}-u^z_{lmn})-(u^z_{l-1m+\cdots}$ $+(u^z_{l+1m-1n+1}-u^z_{lmn})-(u^z_{l+1m+1n-1}-u^z_{lmn})+(u^z_{l-1m+\cdots}$ $-(u^z_{l+1m-1n-1}-u^z_{lmn})]$ And similar expressions for the *y* and *z* (
Eigenfunction solutions	$u_s=A_ke^{i(ksa-\omega t)}$	$u_s=ue^{i(ksa-\omega t)}$ $v_s=ve^{i(ksa-\omega t)}$	$u^x_{lmn}=u^x_{\vec{k}}e^{i(l\vec{k}\cdot\vec{a}_1+m\vec{k}\cdot\vec{a}_2+n\vec{k}\cdot\vec{a}_3)}=u^x_{\vec{k}}e^{i((-l\cdots}$ And similar expressions for the *y* and *z* (
Dispersion relation	$\omega=\sqrt{\frac{4C}{m}}\left\|\sin\left(\frac{ka}{2}\right)\right\|$  	$\omega^2=C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2-\frac{4\sin^2\left(\frac{ka}{2}\right)}{M_1M_2}}$  Calculate ω(k)	The dispersio $\begin{vmatrix} 4-\cos(\frac{a}{2}(k_x+k_y+k_z))-\cos(\frac{a}{2}(3k_x-k_y-k_z)) -\cos(\frac{a}{2}(-k_x+3k_y-k_z))-\cos(\frac{a}{2}(-k_x-k_y+3k_z))-\frac{m\omega^2}{\sqrt{3}C} & -\cos(\frac{a}{2}(k_x+k_y\cdots +\cos(\frac{a}{2}(-k_x+3\cdots \\ -\cos(\frac{a}{2}(k_x+k_y+k_z))+\cos(\frac{a}{2}(3k_x-k_y-k_z)) +\cos(\frac{a}{2}(-k_x+3k_y-k_z))-\cos(\frac{a}{2}(-k_x-k_y+3k_z)) & 4-\cos(\frac{a}{2}(k_x+\cdots -\cos(\frac{a}{2}(-k_x+3\cdots \\ -\cos(\frac{a}{2}(k_x+k_y+k_z))+\cos(\frac{a}{2}(3k_x-k_y-k_z)) -\cos(\frac{a}{2}(-k_x+3k_y-k_z))+\cos(\frac{a}{2}(-k_x-k_y+3k_z)) & -\cos(\frac{a}{2}(k_x+k_y\cdots +\cos(\frac{a}{2}(-k_x+3\cdots \end{vmatrix}$ 
Density of states $D(k)$	$D(k)=\frac{1}{\pi}$	$D(k)=\frac{1}{\pi}$	$D(k)=\frac{3k^2}{2\pi^2}$

Quartz

α-Quartz
trigonal
2.65 g/cm^3

573°C →

β-Quartz
hexagonal
2.53 g/cm3

870°C →

β-Tridymite
hexagonal
2.25 g/cm^3

1470°C ↓

β-Cristobalite
cubic
2.20 g/cm3

1705°C ←

Silica Melt