Phonons

Phonon dispersion

1. **Determine the dispersion relation:**

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

   The solutions to these equations will be

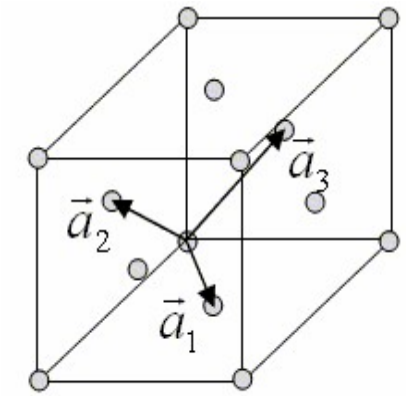
$$A_k \exp\left(i\left(\vec{k}\cdot\vec{a}_1 + \vec{k}\cdot\vec{a}_2 + \vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

   Substitute the solutions 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.

fcc



$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}$$

$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}$$

$$\vec{a}_3 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$

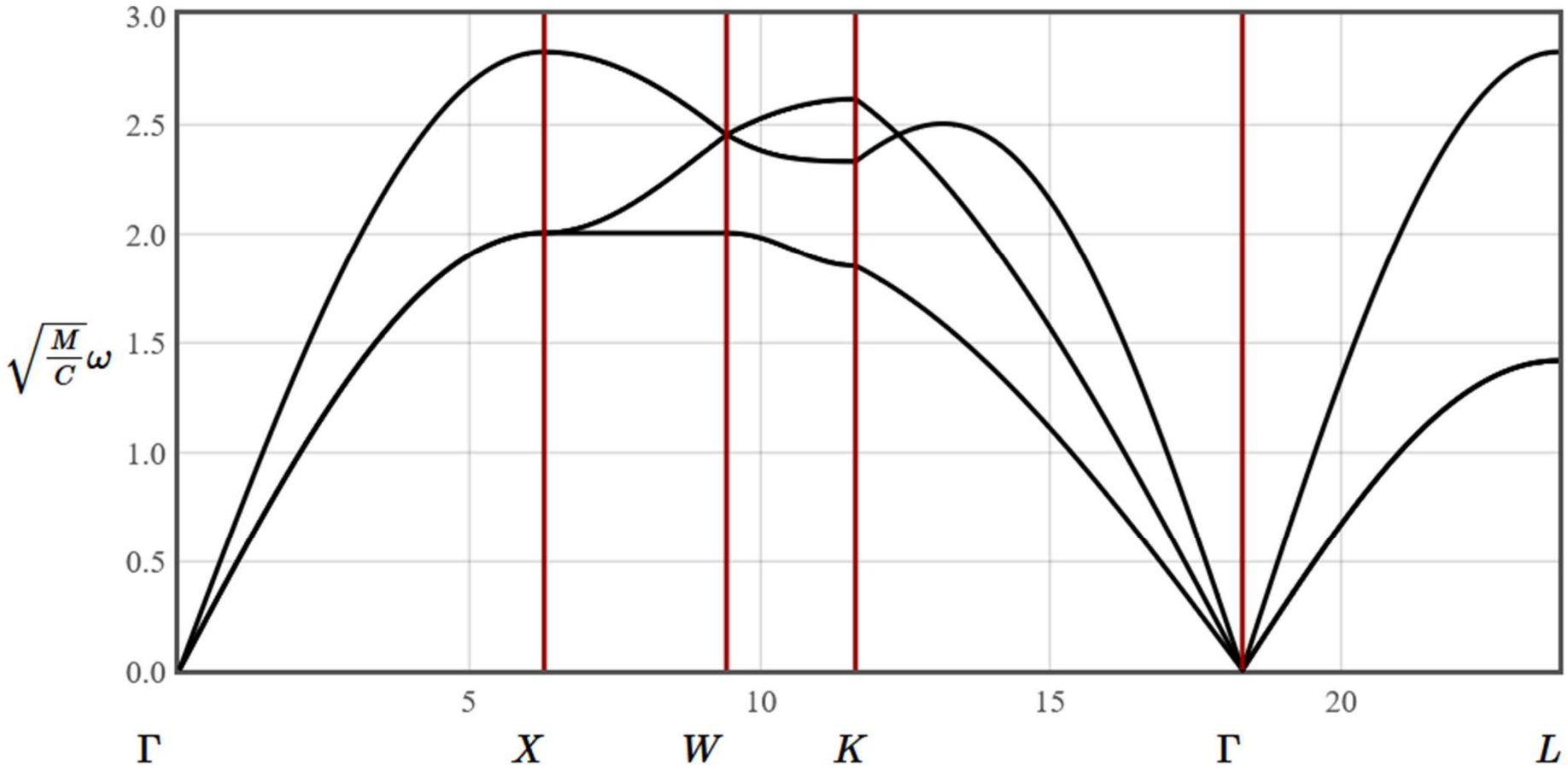
Substitute the eigenfunctions of T into Newton's laws.

$$u^x_{lmn} = u^x_{\vec{k}} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3\right)\right) = u^x_{\vec{k}} \exp\left(i\left(\frac{(l+m)k_x a}{2} + \frac{(l+n)k_y a}{2} + \frac{(m+n)k_z a}{2}\right)\right).$$

$$\begin{vmatrix} 4-\cos\left(\frac{k_x a}{2}+\frac{k_y a}{2}\right)-\cos\left(\frac{k_x a}{2}+\frac{k_z a}{2}\right)-\cos\left(\frac{k_x a}{2}-\frac{k_y a}{2}\right)-\cos\left(\frac{k_x a}{2}-\frac{k_z a}{2}\right)-\frac{m\omega^2}{\sqrt{2}C} & -\cos\left(\frac{k_x a}{2}+\frac{k_y a}{2}\right)+\cos\left(\frac{k_x a}{2}-\frac{k_y a}{2}\right) & -\cos\left(\frac{k_x a}{2}+\frac{k_z a}{2}\right)+\cos\left(\frac{k_x a}{2}-\frac{k_z a}{2}\right) \\ -\cos\left(\frac{k_x a}{2}+\frac{k_y a}{2}\right)+\cos\left(\frac{k_x a}{2}-\frac{k_y a}{2}\right) & 4-\cos\left(\frac{k_y a}{2}+\frac{k_z a}{2}\right)-\cos\left(\frac{k_y a}{2}+\frac{k_x a}{2}\right)-\cos\left(\frac{k_y a}{2}-\frac{k_x a}{2}\right)-\cos\left(\frac{k_y a}{2}-\frac{k_z a}{2}\right)-\frac{m\omega^2}{\sqrt{2}C} & -\cos\left(\frac{k_y a}{2}+\frac{k_z a}{2}\right)+\cos\left(\frac{k_y a}{2}-\frac{k_z a}{2}\right) \\ -\cos\left(\frac{k_x a}{2}+\frac{k_z a}{2}\right)+\cos\left(\frac{k_x a}{2}-\frac{k_z a}{2}\right) & -\cos\left(\frac{k_y a}{2}+\frac{k_z a}{2}\right)+\cos\left(\frac{k_y a}{2}-\frac{k_z a}{2}\right) & 4-\cos\left(\frac{k_z a}{2}+\frac{k_x a}{2}\right)-\cos\left(\frac{k_z a}{2}+\frac{k_y a}{2}\right)-\cos\left(\frac{k_z a}{2}-\frac{k_y a}{2}\right)-\cos\left(\frac{k_z a}{2}-\frac{k_y a}{2}\right)-\frac{m\omega^2}{\sqrt{2}C} \end{vmatrix} = 0$$

http://lamp.tu-graz.ac.at/~hadley/ss1/phonons/fcc/fcc.html

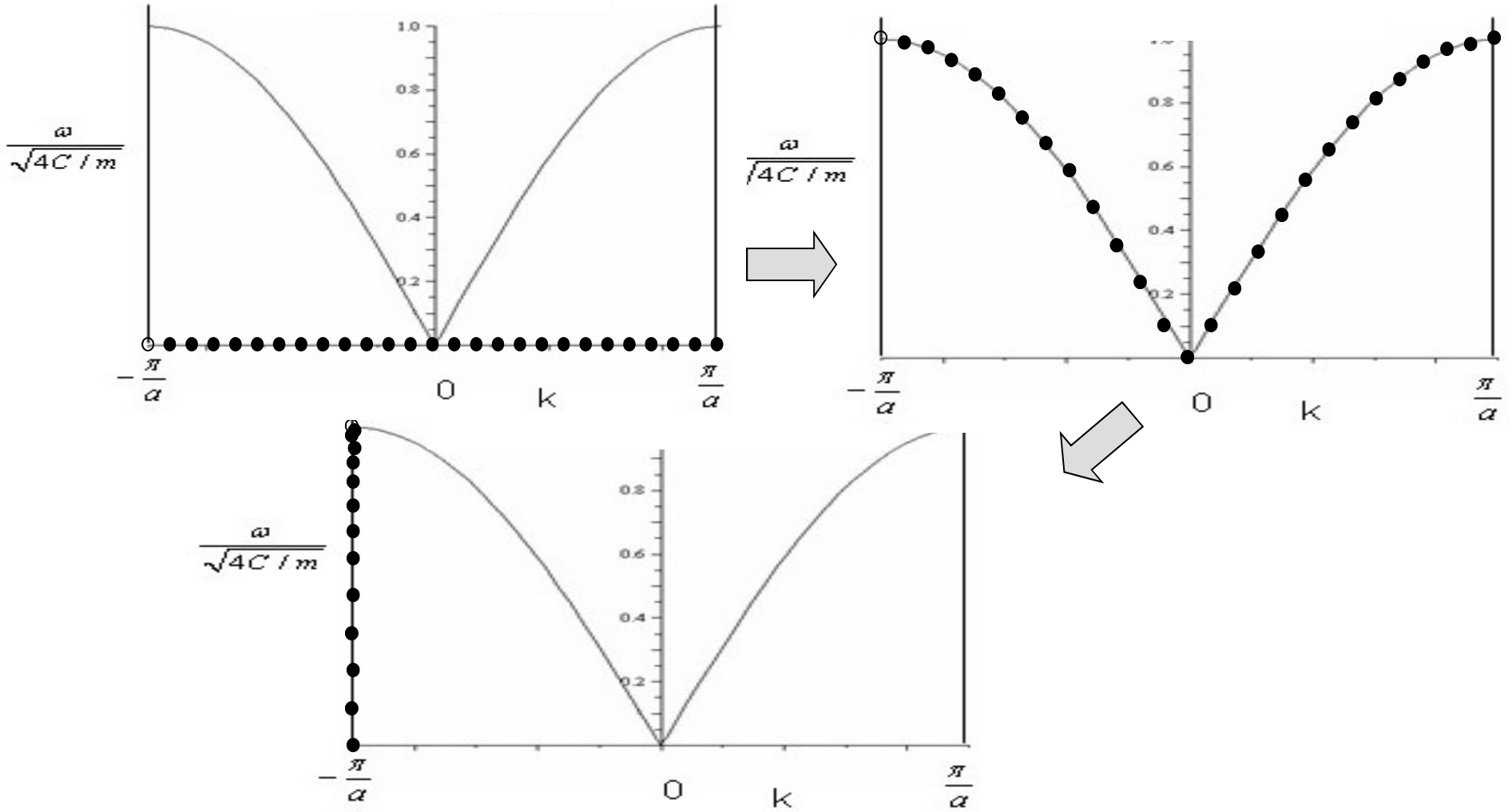
For every k there are 3 solutions for ω.



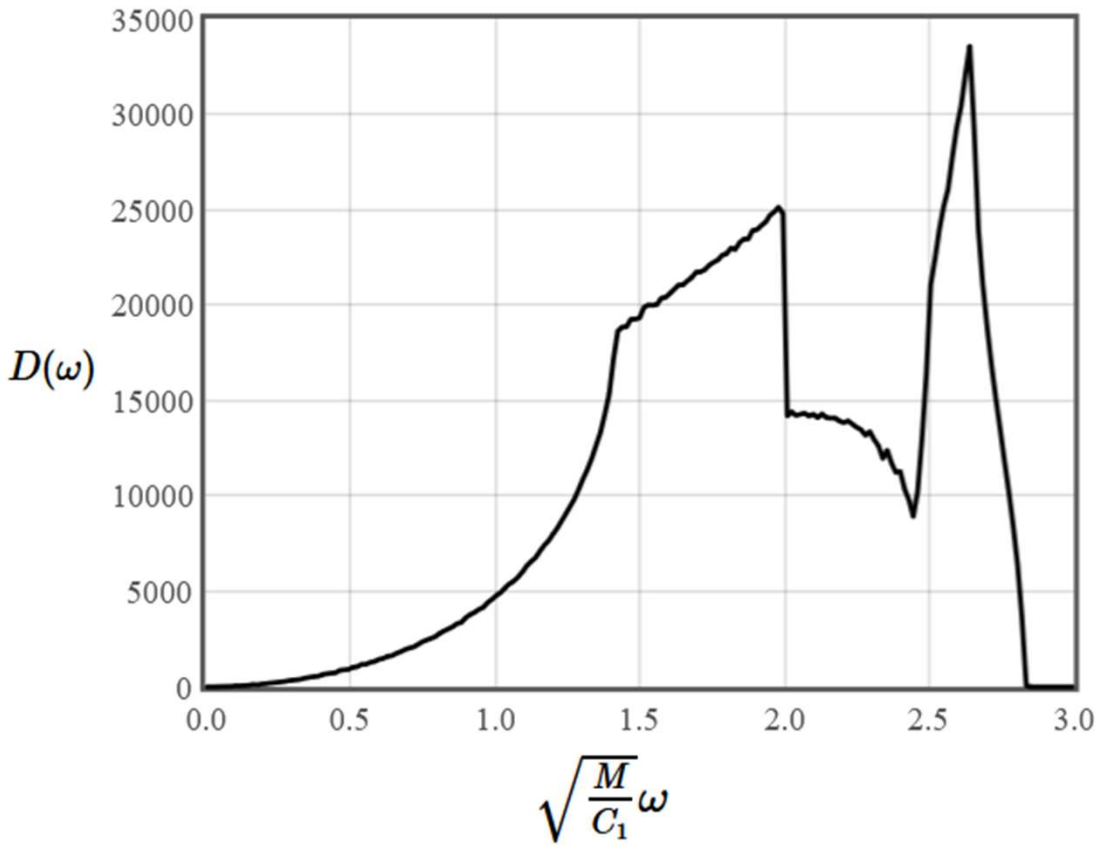
Linear Chain - density of states

Determine the density of states numerically

$$\omega = \sqrt{\frac{4C}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

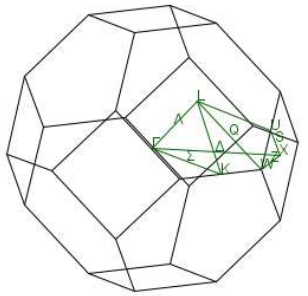


Phonon density of states of a fcc crystal



http://lampx.tugraz.at/~hadley/ss1/phonons/fcc/fcc_dos.php

Phonon dispersion Au



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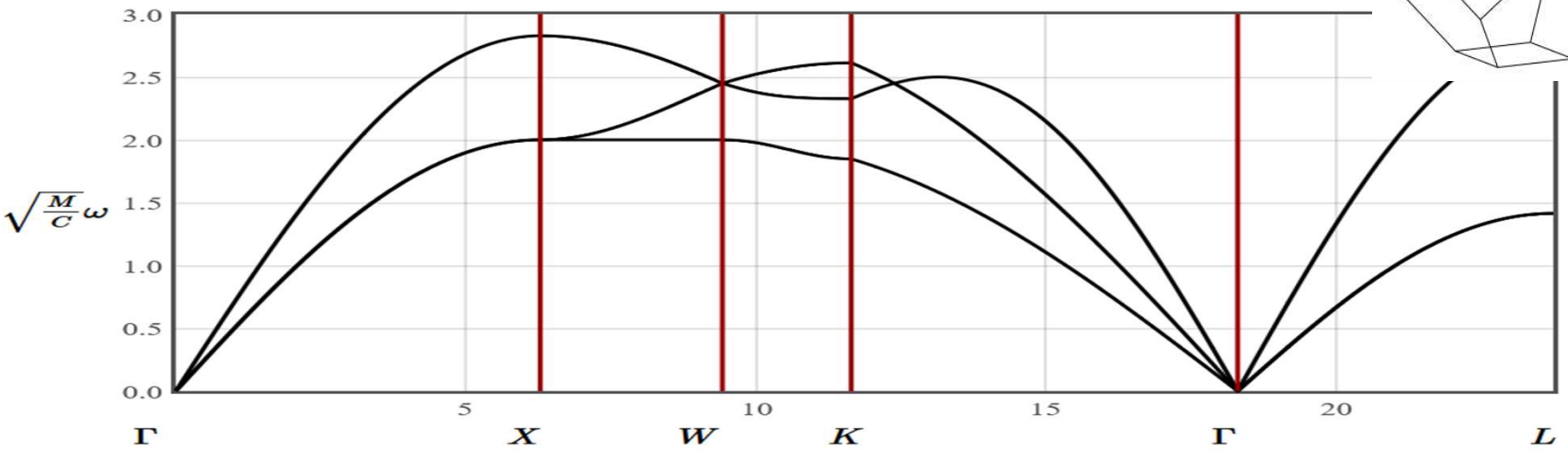


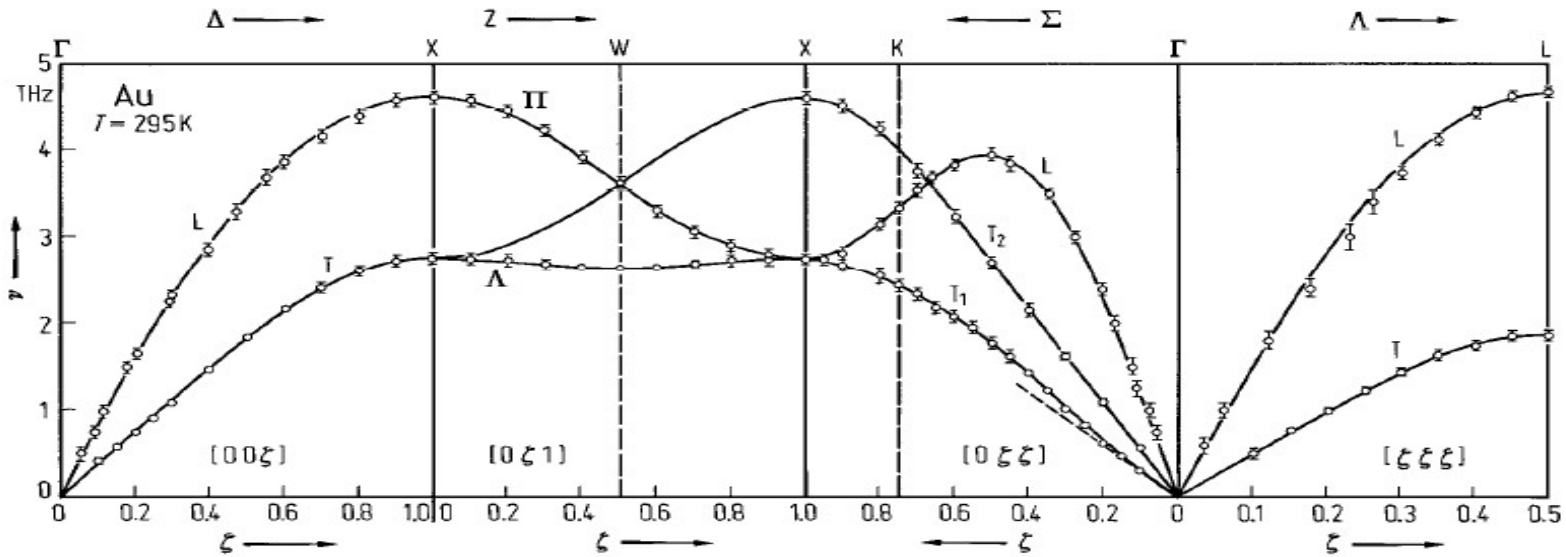
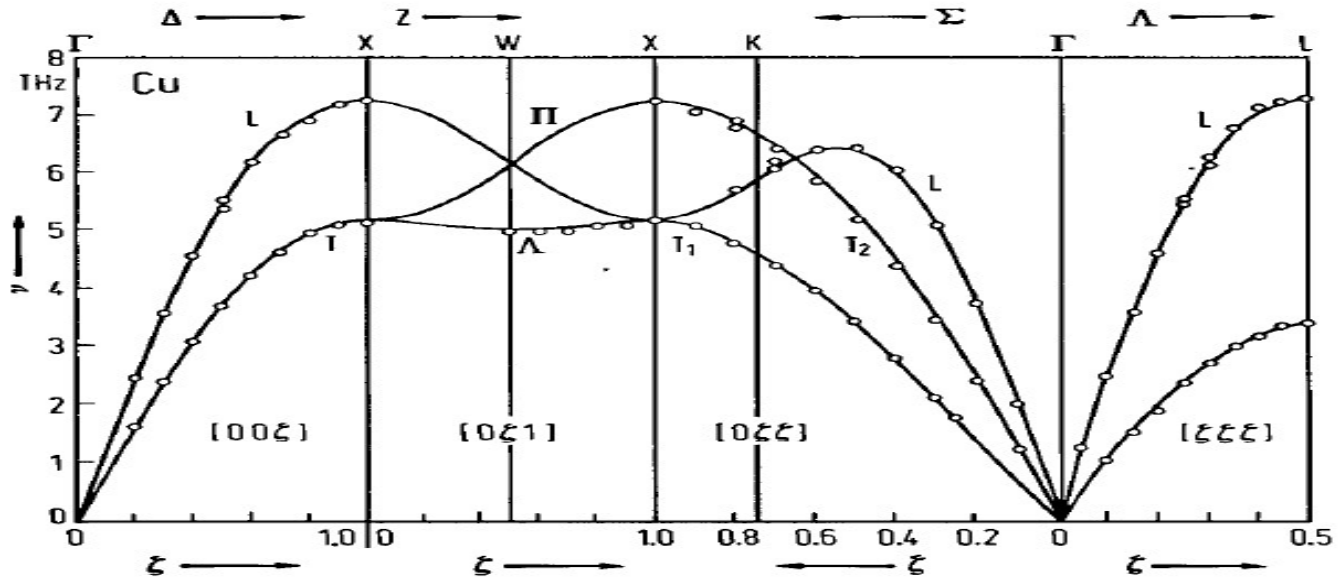
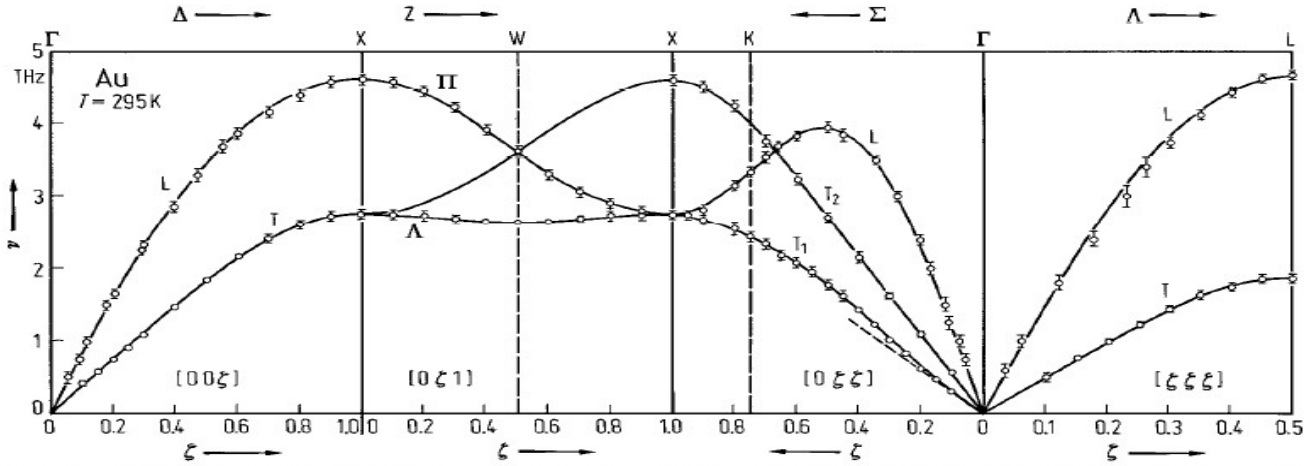


Fig. 1. Au. Phonon dispersion relations in the principal symmetry directions according to [73Ly1]. The solid curves represent both the fourth neighbour general force model (M1) and the fifth neighbour axially symmetric model (M2) of Table 3 Au. The dotted line in the Σ direction is corresponding to the velocity of sound appropriate to the [0ζζ] T_1 branch.

Materials with the same crystal structure will have similar phonon dispersion relations



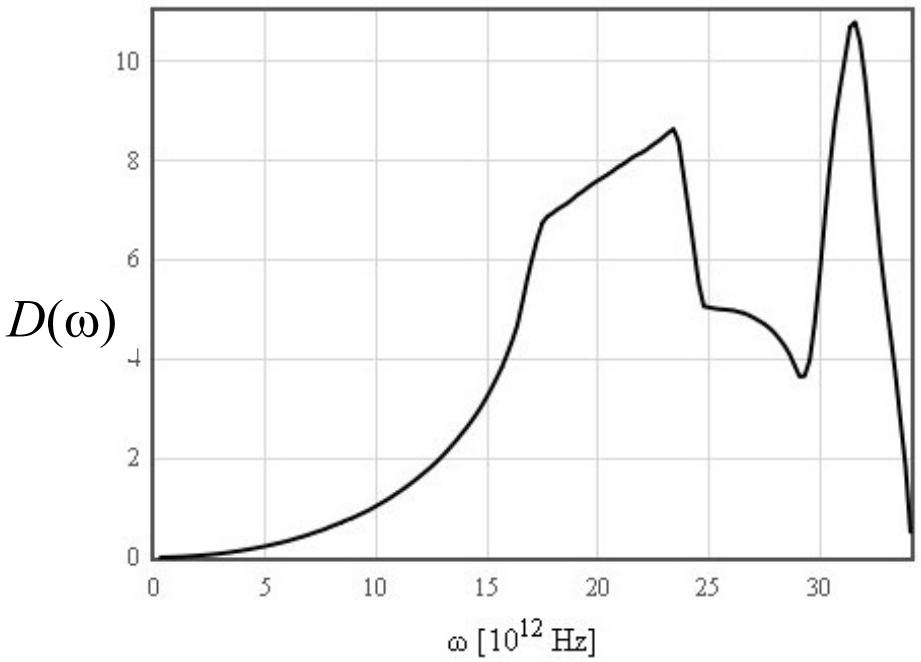
Cu



Au

Fig. 1. Au. Phonon dispersion relations in the principal symmetry directions according to [73Ly1]. The solid curves represent both the fourth neighbour general force model (M1) and the fifth neighbour axially symmetric model (M2) of Table 3 Au. The dotted line in the Σ direction is corresponding to the velocity of sound appropriate to the $[0\zeta\zeta]$ T_1 branch.

Phonon DOS fcc



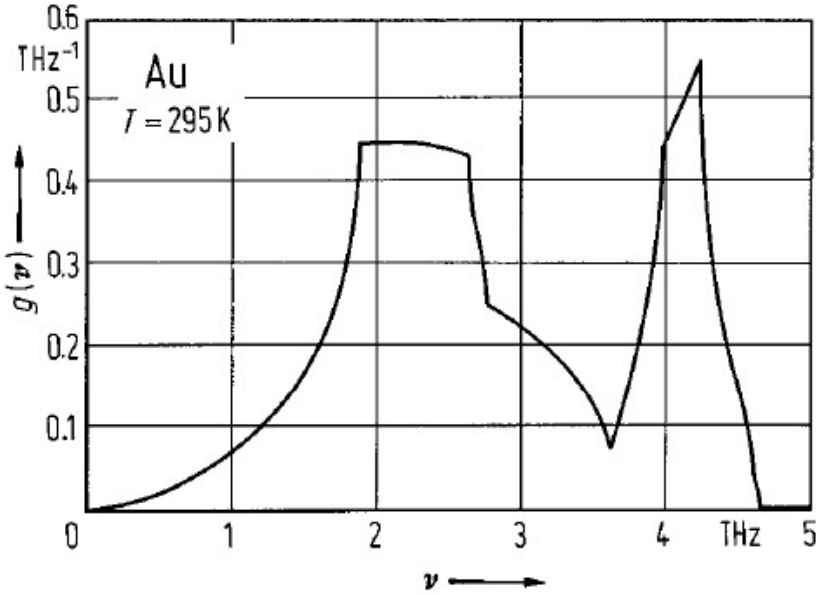
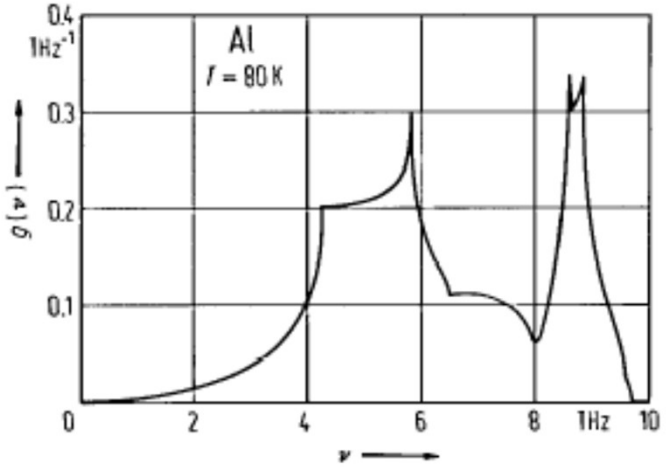
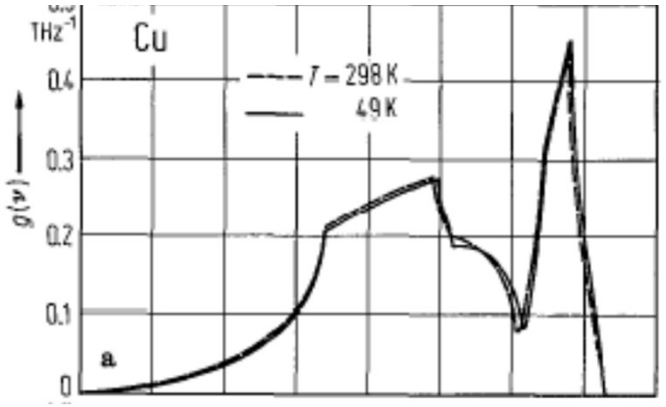


Fig. 2. Au. Frequency distribution calculated from the fourth neighbour general force constant model (M1) of Table 3 Au.





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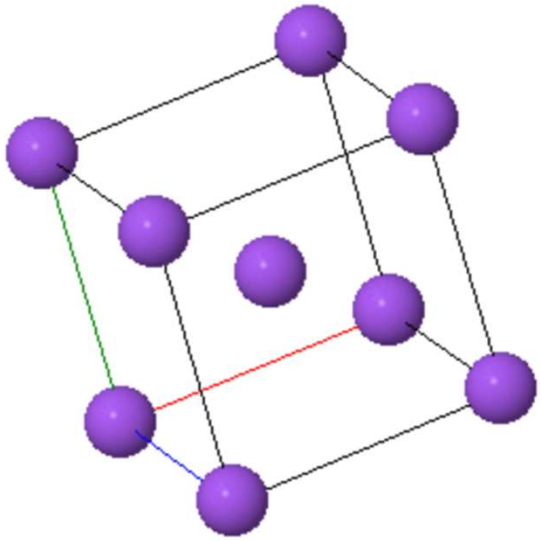
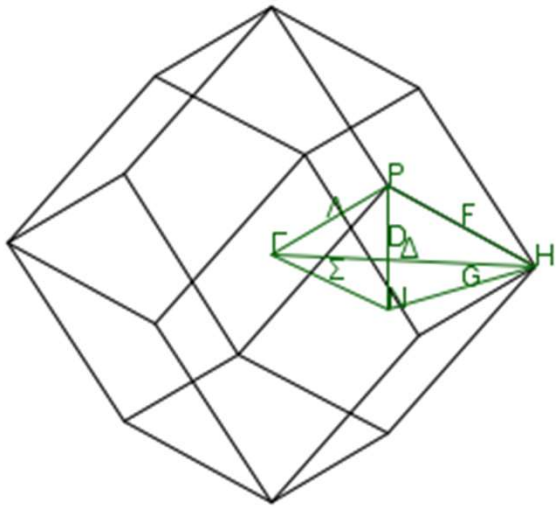
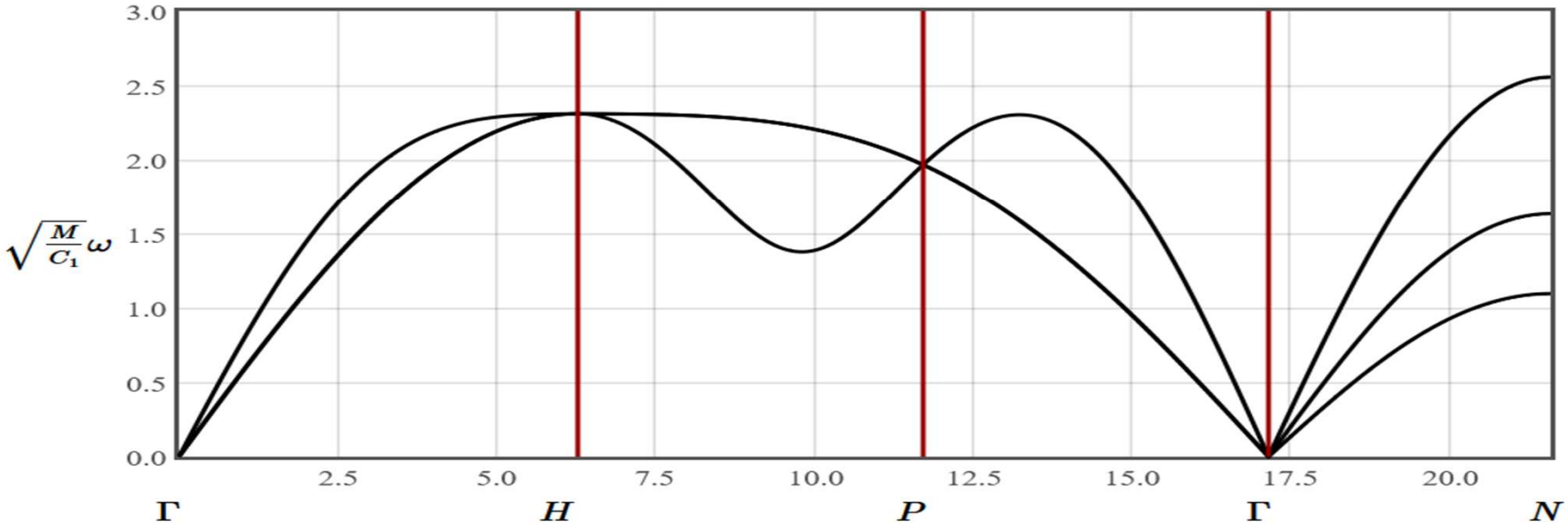
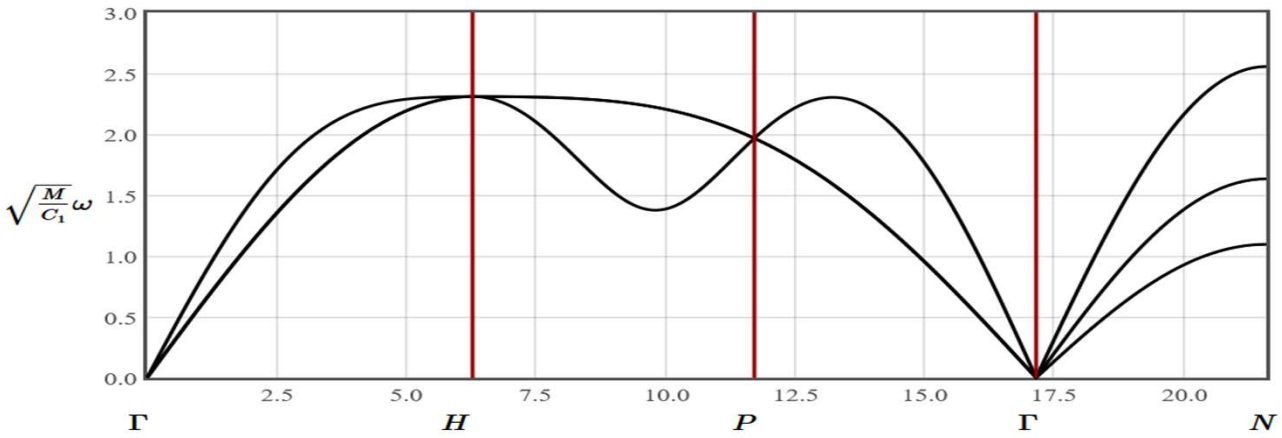
Phonon dispersion bcc

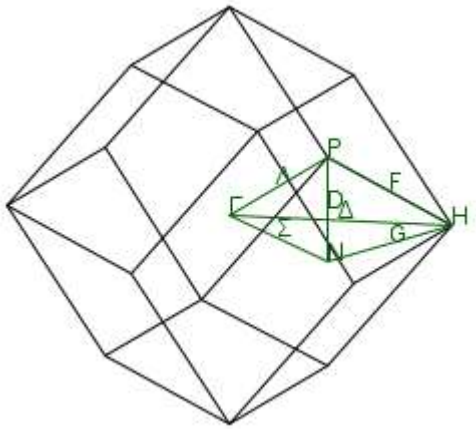






Phonon dispersion Fe





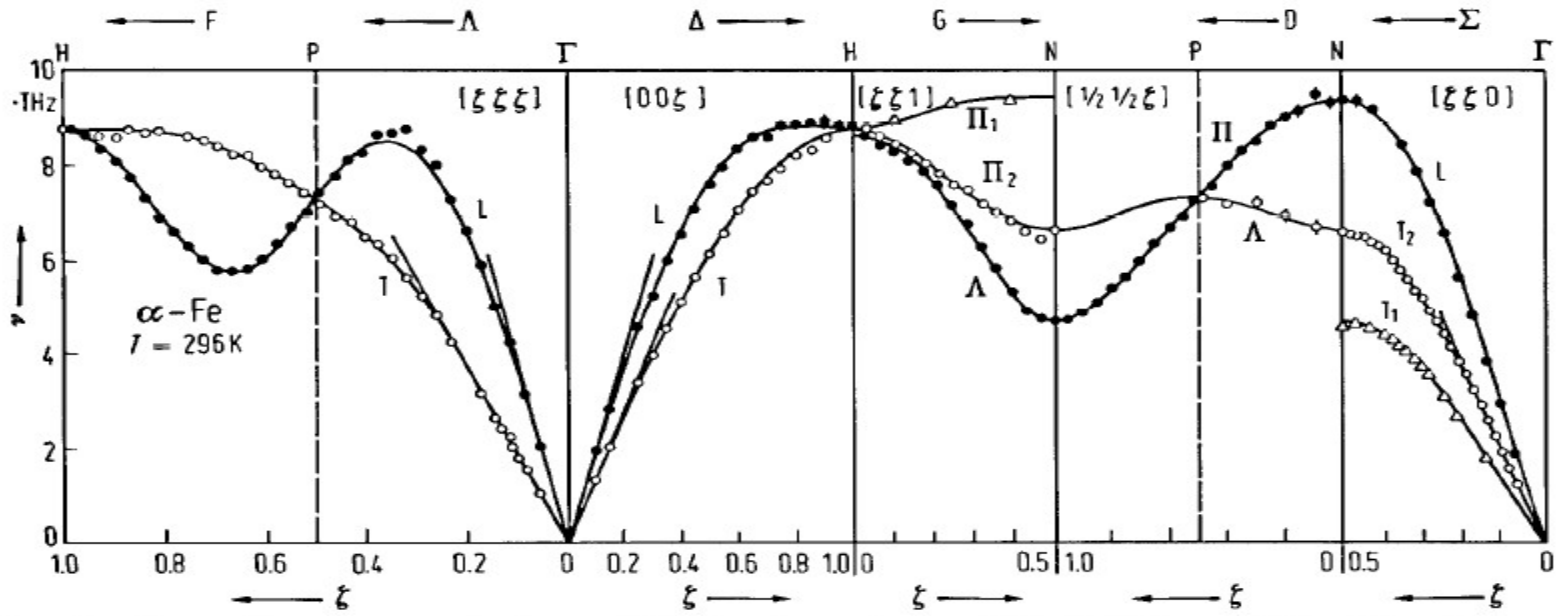


Fig. 2. Fe. Phonon dispersion curves in α-iron at 296 K. Experimental points: [68Va2]. Solid curve: fifth neighbour Born-von Karman model (Table 3 Fe [68Va2]).

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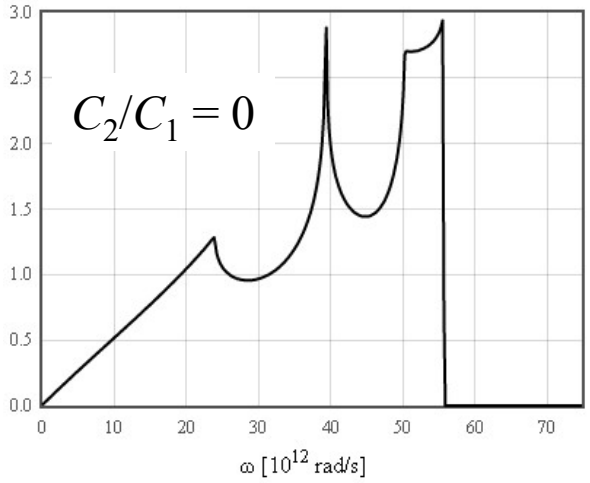
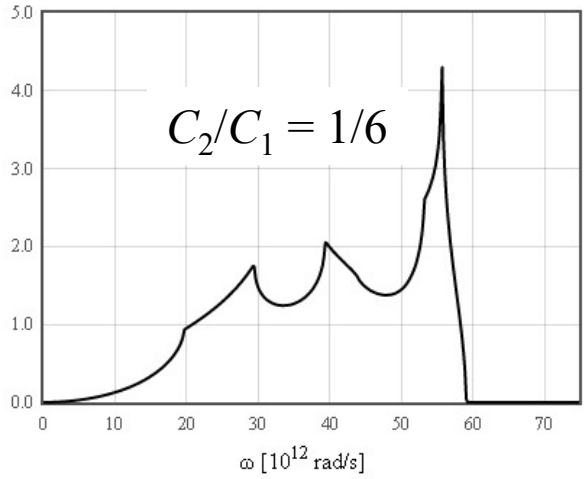
Phonon DOS Fe





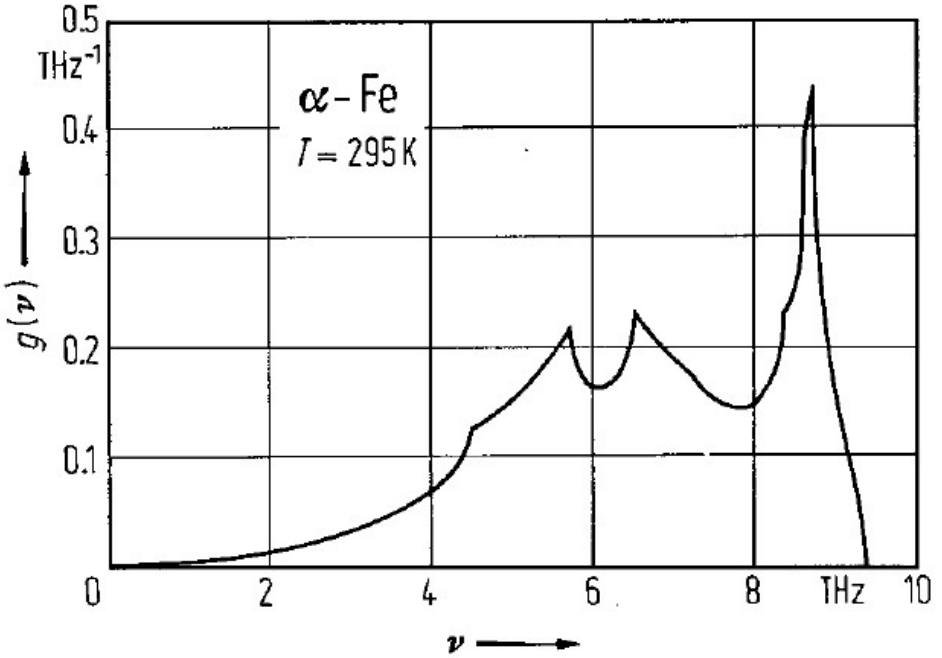


Fig. 3. Fe. Frequency spectrum of α-iron at 295 K calculated from the Born-von Karman force constants of Table 3 Fe [67Mi1].

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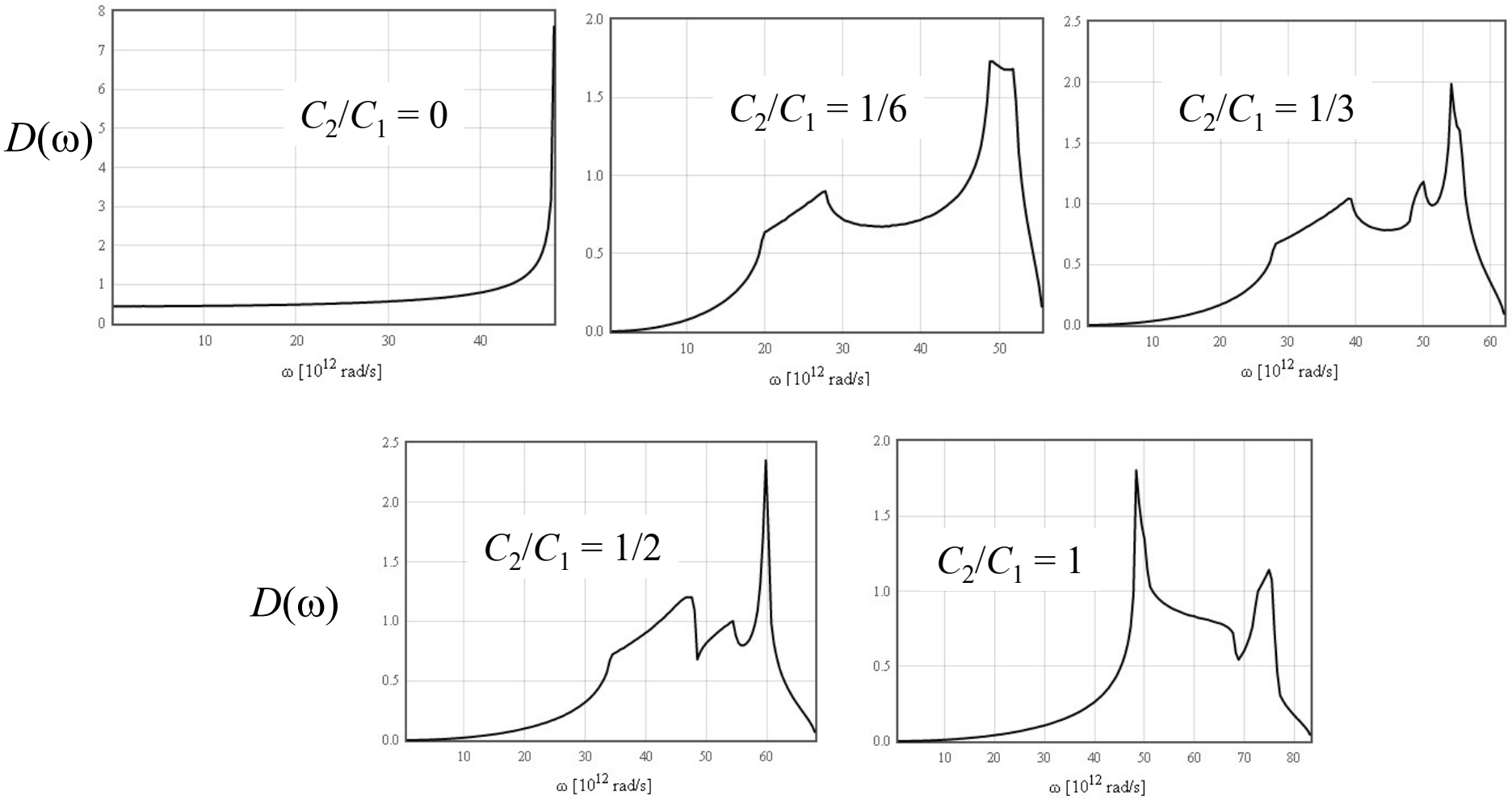
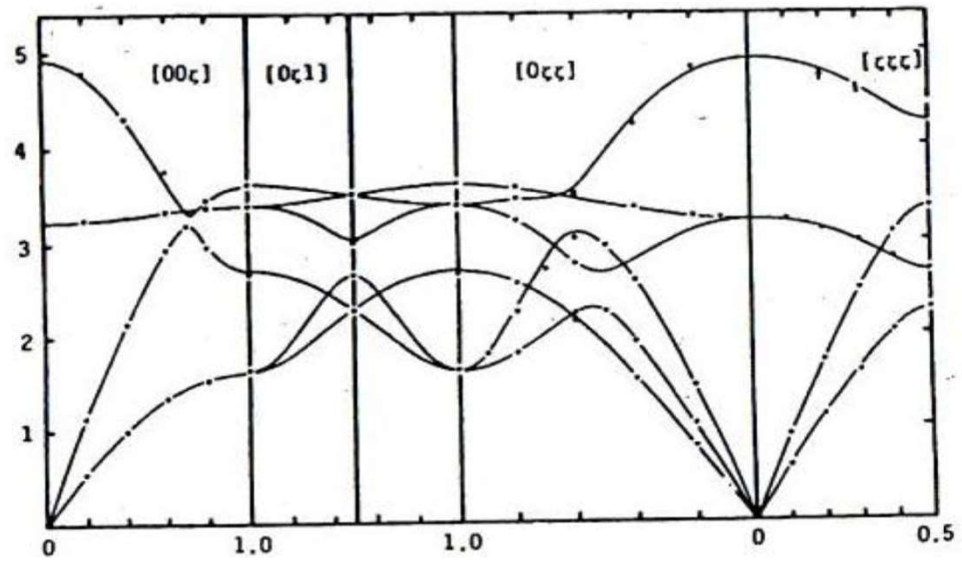
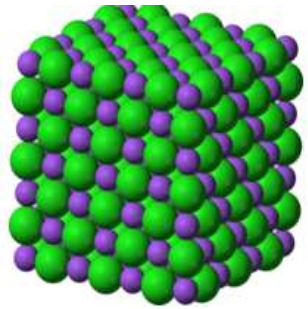
Next nearest neighbors (simple cubic)



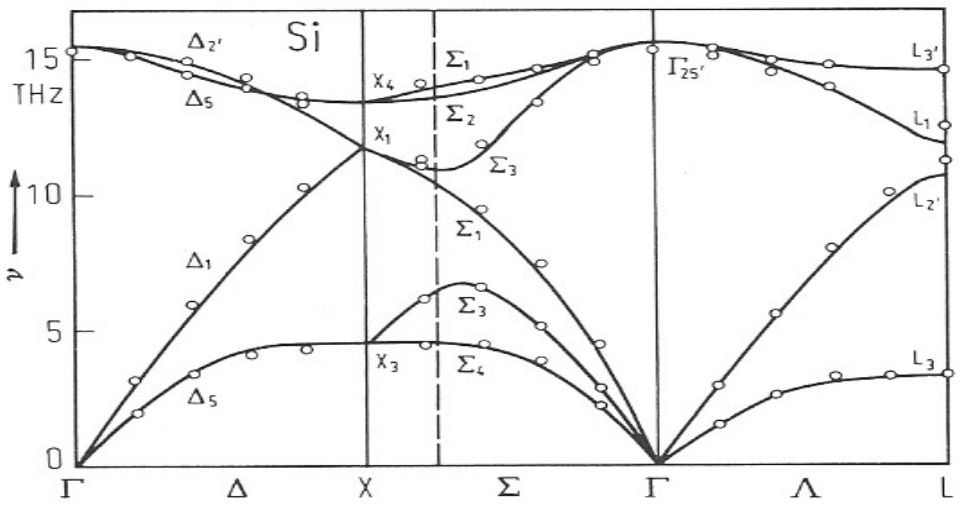
Sometimes the 5th neighbors are included.

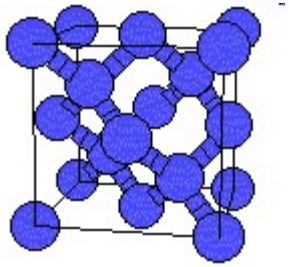
Two atoms per primitive unit cell





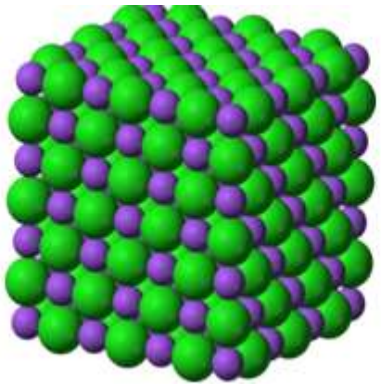
NaCl





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:

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

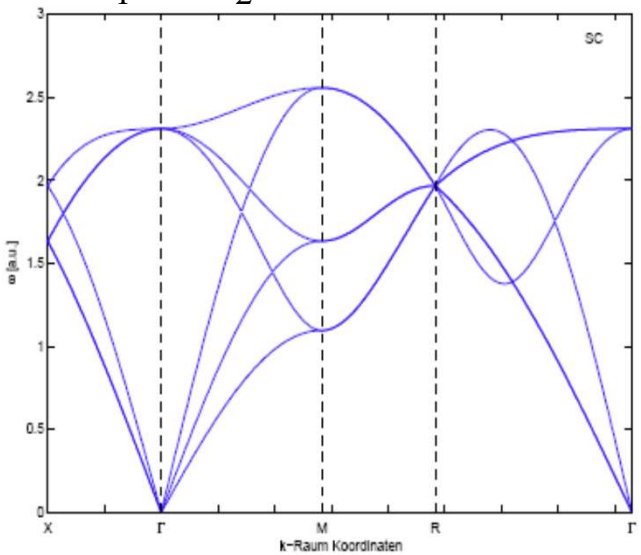
$$M_2 \frac{d^2 v^z_{nml}}{dt^2} = C\left(-2v^z_{nml} + u^z_{n(m+1)(l+1)} + u^z_{(n+1)ml}\right)$$

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

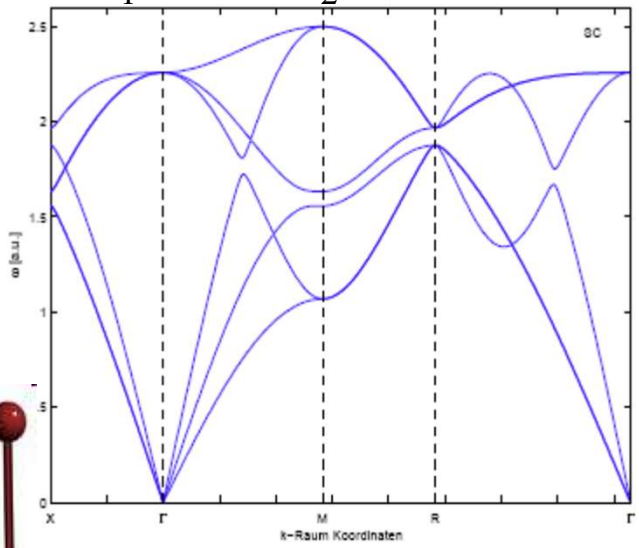
CsCl

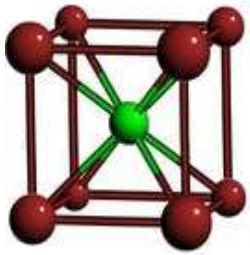
Hannes Brandner

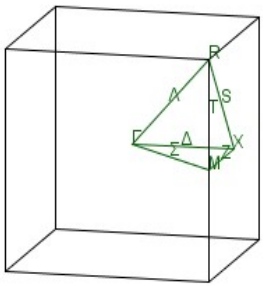
$M_1 = M_2$



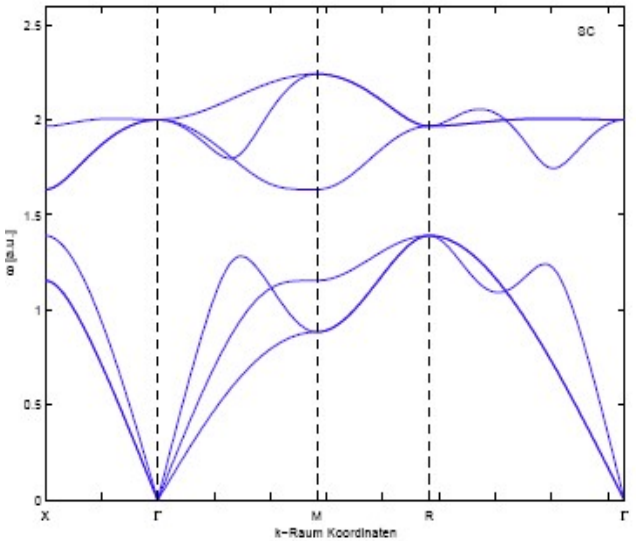
$M_1 = 1.1\ M_2$



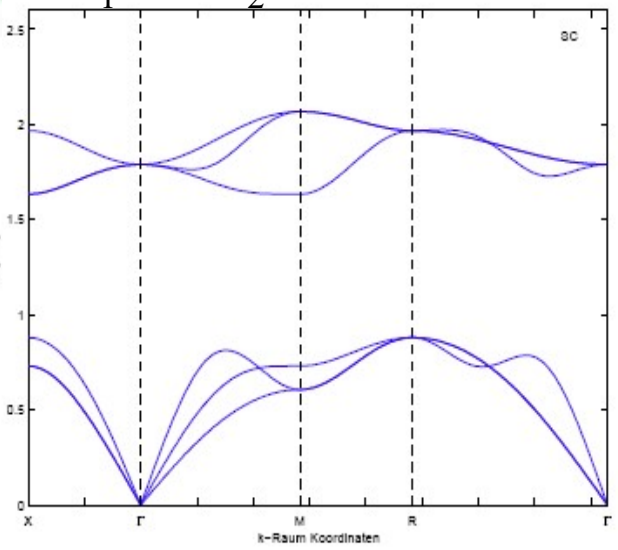




$M_1 = 2M_2$



$M_1 = 5M_2$



3 dimensions

N atoms

3*N* normal modes

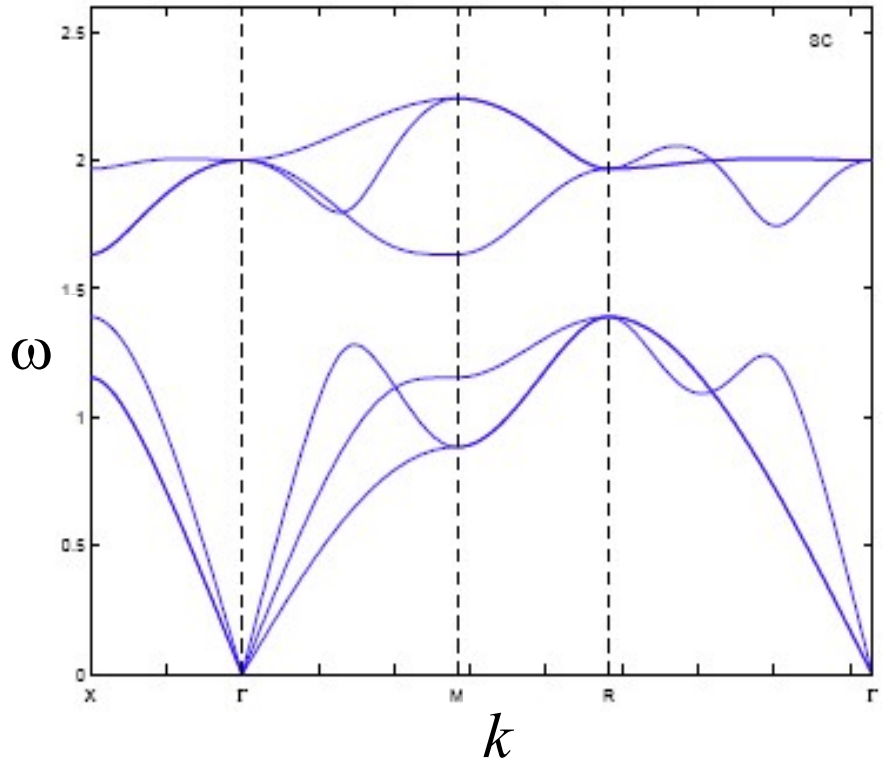
p atoms per unit cell

N/p unit cells = *k* vectors

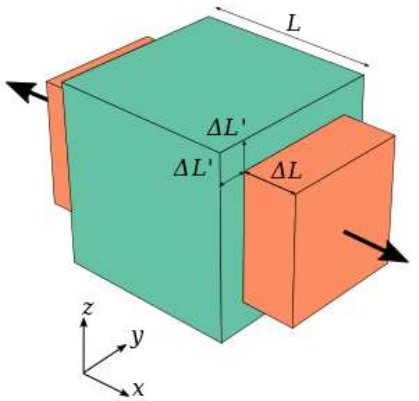
3*p* branches to the dispersion relation

3 acoustic modes (1 longitudinal, 2 transverse)

3*p* - 3 optical modes



Poisson's ratio



Wikipedia

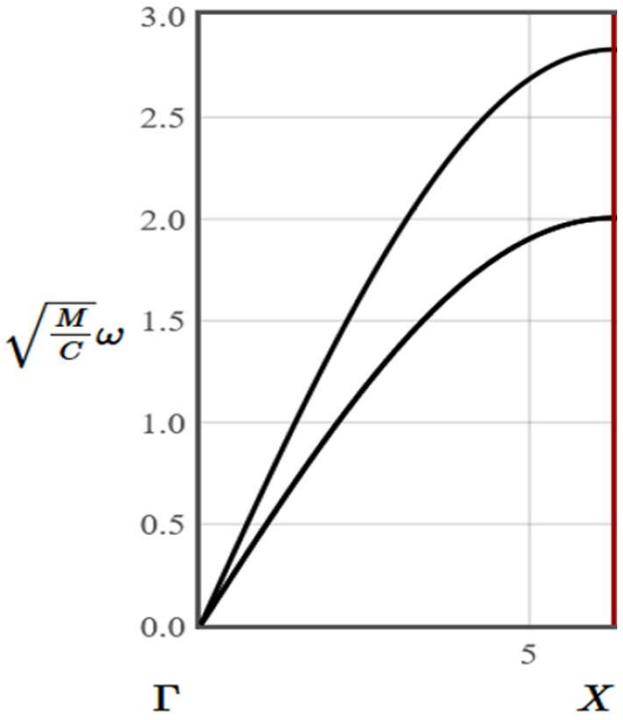
E - Elastic constant

ν - Poisson's ratio

ρ - density

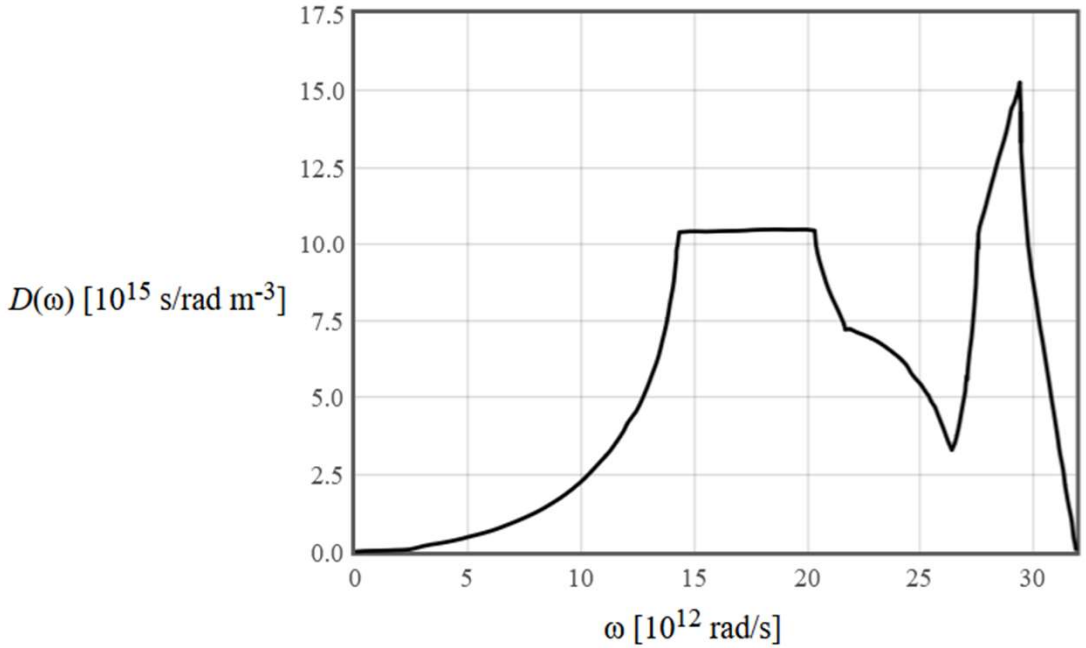
$$c_T = \sqrt{\frac{E(1-\nu)}{\rho(1-\upsilon-2\upsilon^2)}}$$

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



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

Phonon density of states for fcc silver



The atomic density is taken to be 5.86×10^{28} m^{-3}. Each atom has three degrees of freedom so the integral over all frequencies is $3\times5.86\times10^{28}$ m^{-3}. The data is from doi: 10.1007/b19988.

T = 296 K

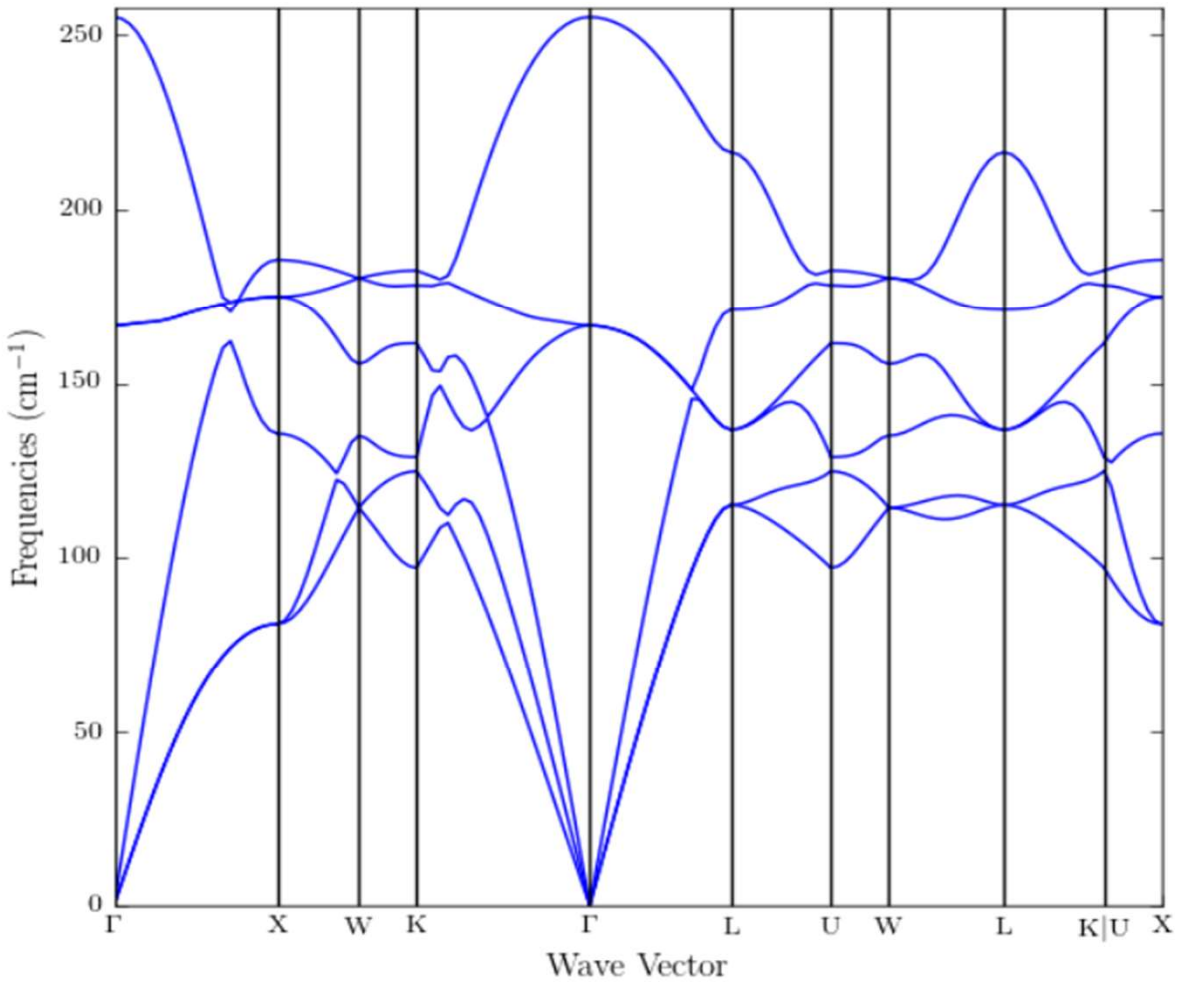
ω [rad/s]	$D(\omega)$ [s $rad^{-1}m^{-3}$]
0.0000	0.0000
5.7327e+10	6.8161e+12
4.0123e+11	2.3856e+13
7.4510e+11	3.0672e+13
1.0890e+12	3.4080e+13
1.4233e+12	4.0897e+13
1.7624e+12	5.1121e+13
2.0967e+12	5.7937e+13
2.4120e+12	7.4977e+13
2.7177e+12	1.2610e+14
3.0379e+12	1.8744e+14
3.3723e+12	2.3516e+14
3.7163e+12	2.7264e+14

Vibrational Properties

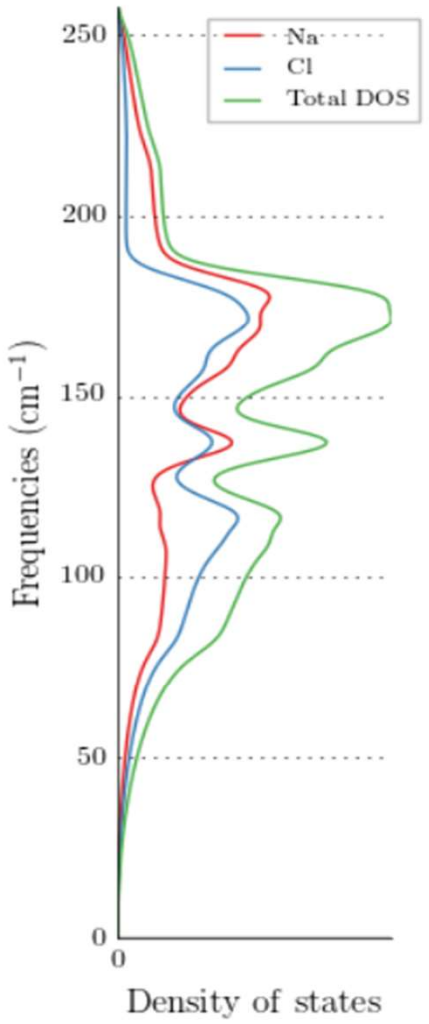
Reference for phonon calculations and visualization:

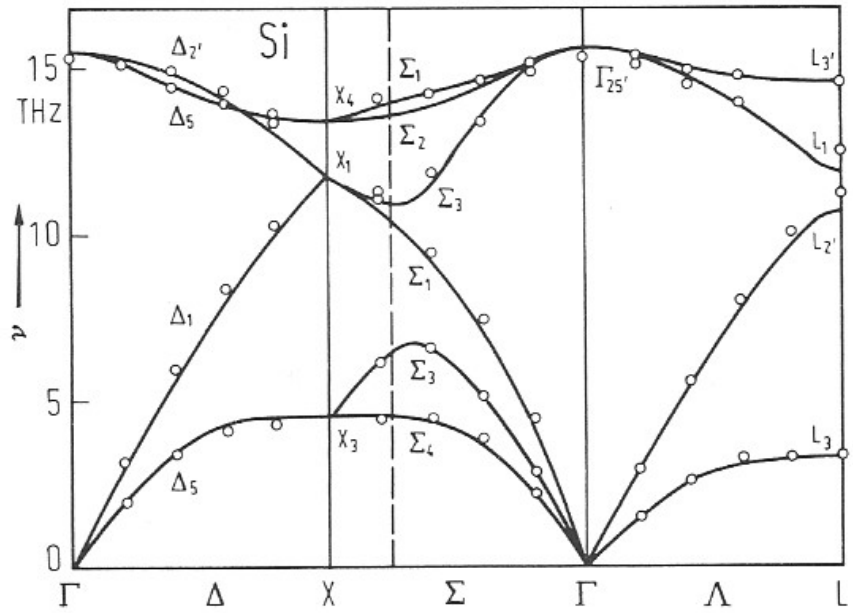
Visualize with phononwebsite

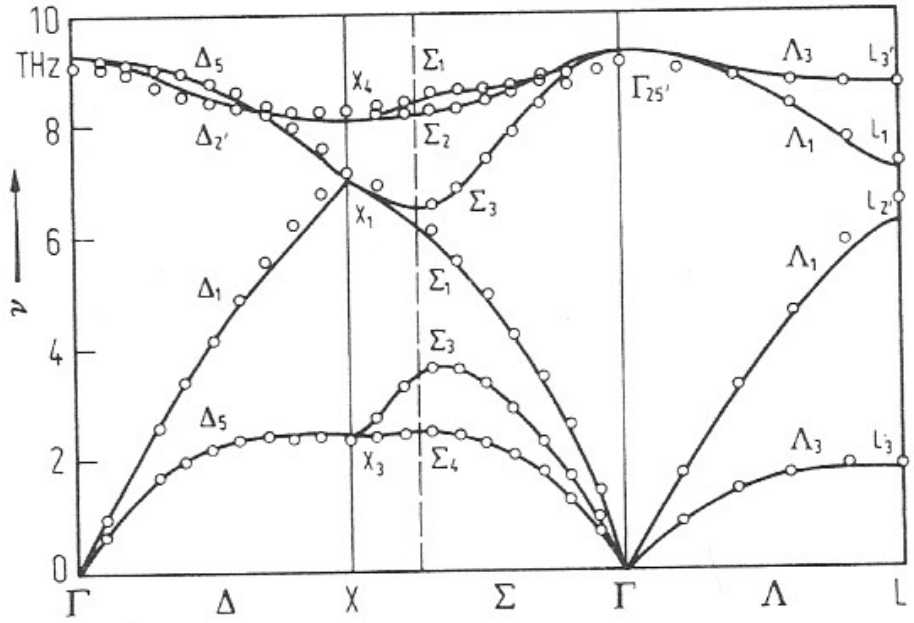
Phonon dispersion



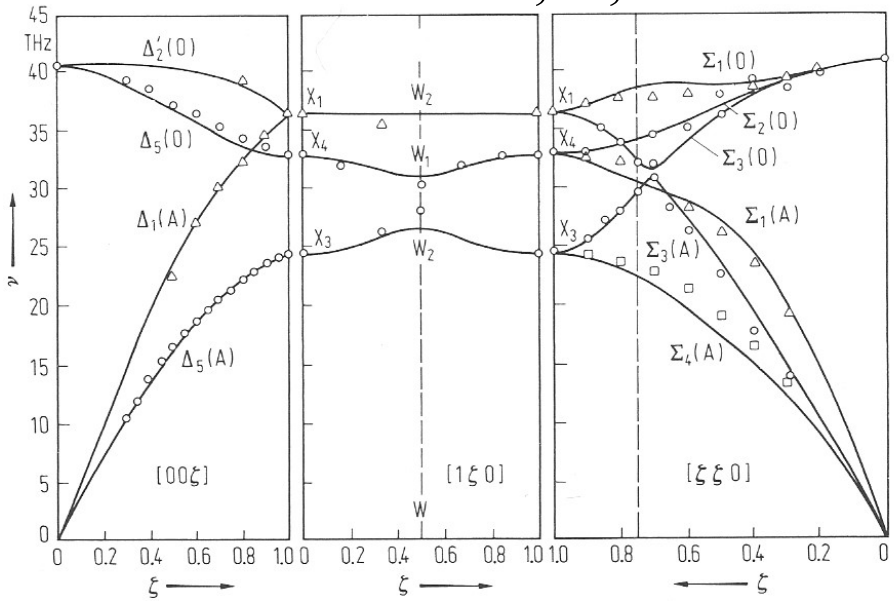
Density of States

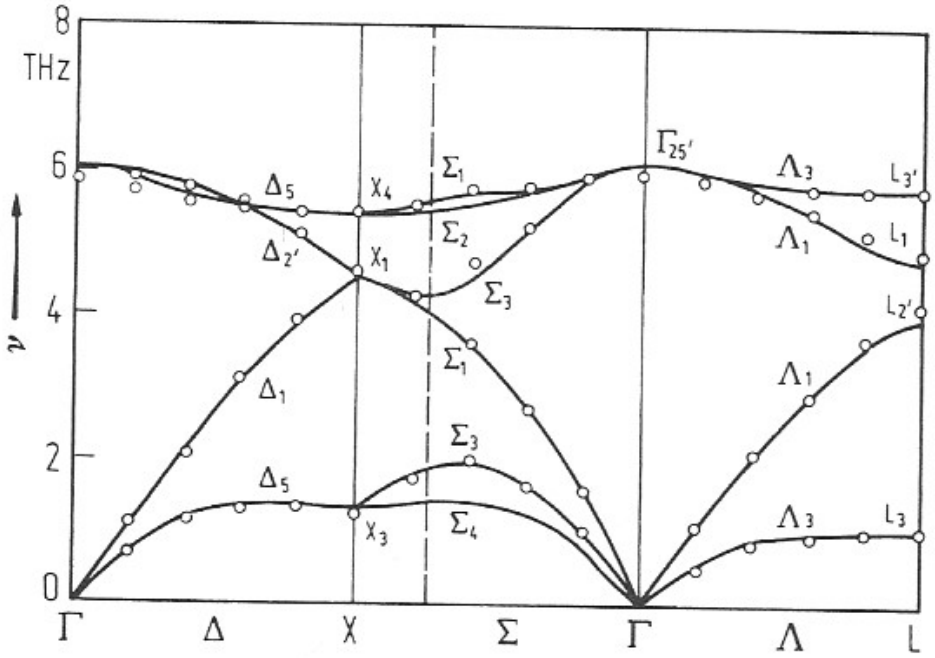



Si
15
THz
10
5
0
ν
Γ
Δ
X
Σ
Γ
Λ
L


10
THz
8
6
4
2
0
ν
Γ
Δ
X
Σ
Γ
Λ
L

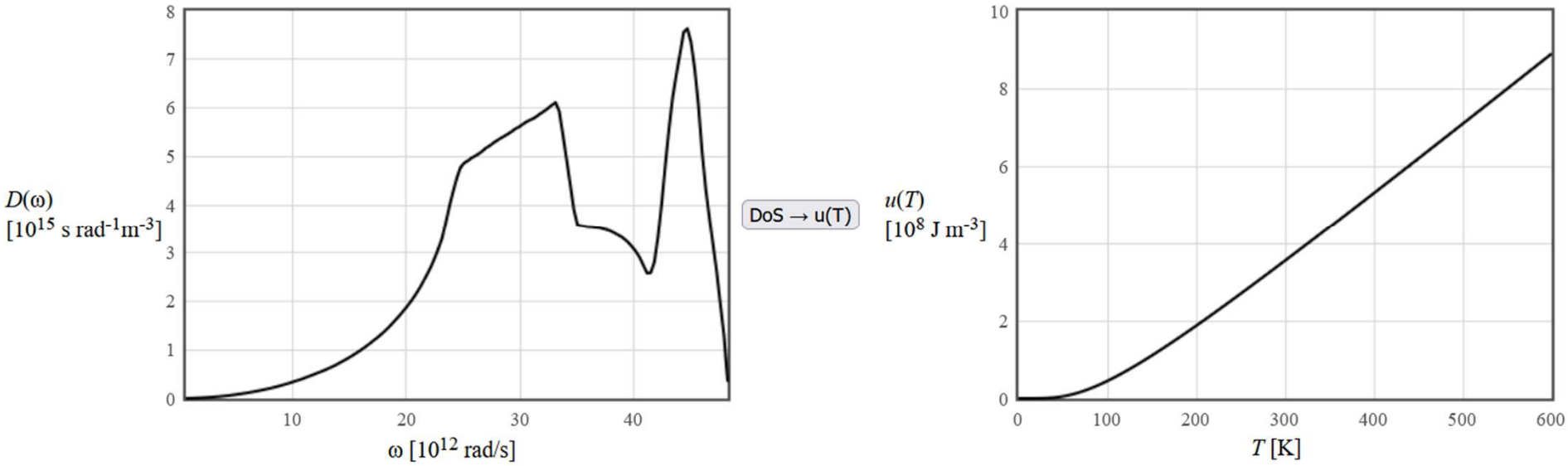
Ge, C, α-Sn ?


45
THz
40
35
30
25
20
15
10
5
0
ν
[00ζ]
[1ζ0]
[ζζ0]
W
ζ


8
THz
6
4
2
0
ν
Γ
Δ
X
Σ
Γ
Λ
L

Density of states → Internal energy density

$$u(T) = \int_0^\infty \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}\, d\omega$$



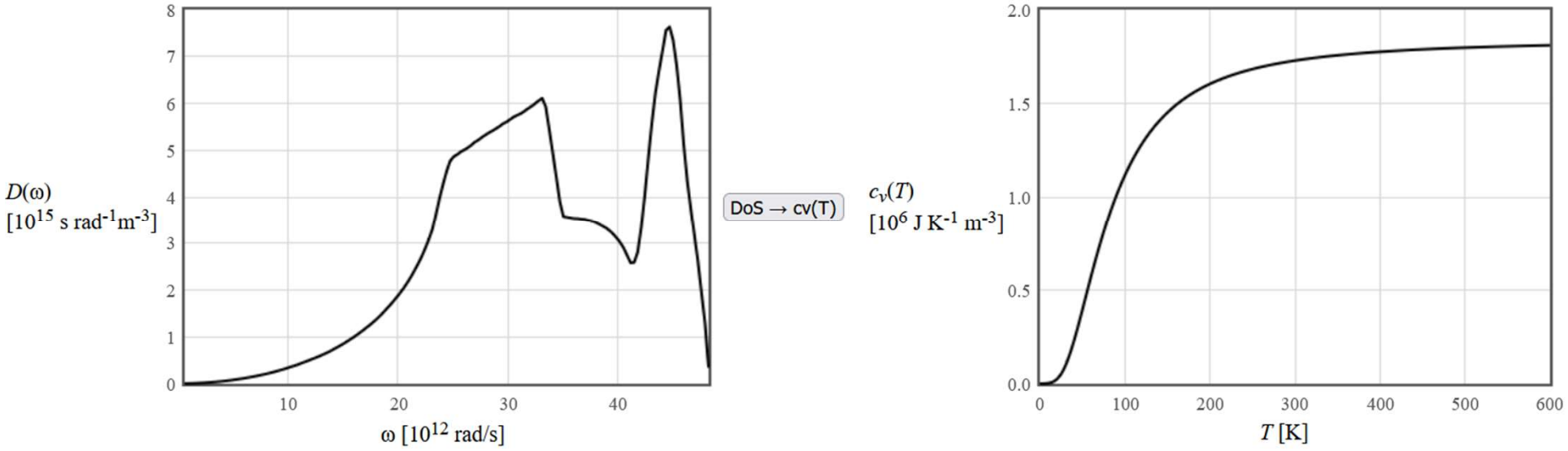
http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2ut.html

Specific Heat

$$c_v = \left(\frac{\partial u}{\partial T}\right)_{N,V}$$

$$c_v = \int \hbar\omega D(\omega) \frac{\partial}{\partial T}\left(\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\right) d\omega$$

$$c_v = \int \left(\frac{\hbar\omega}{T}\right)^2 \frac{D(\omega) e^{\frac{\hbar\omega}{k_B T}}}{k_B \left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2} d\omega$$



http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2cv.html

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.

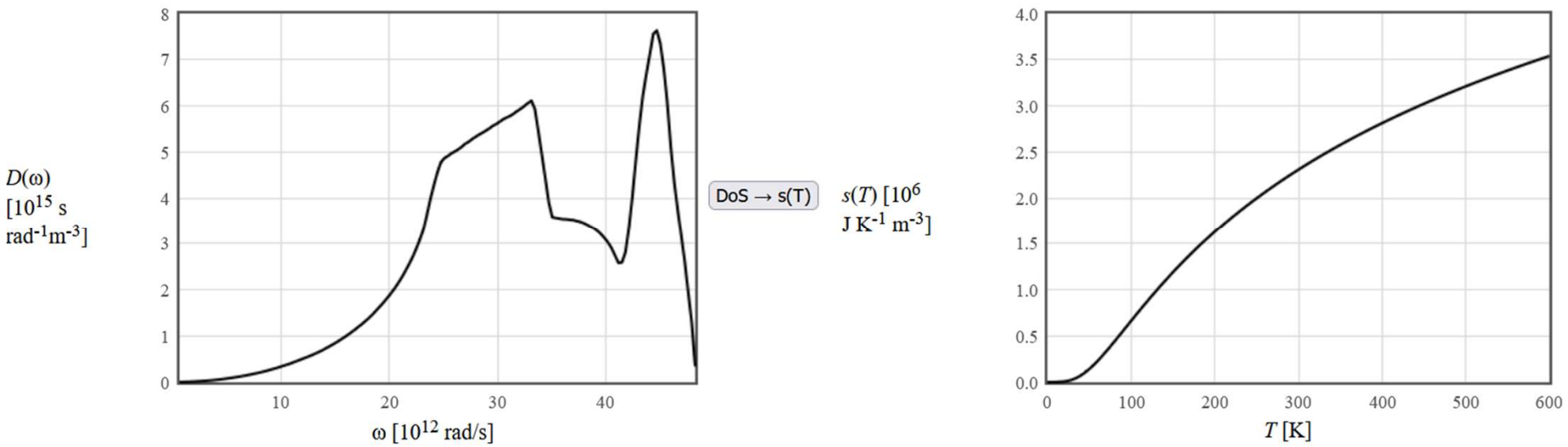
For solids, the heat capacity at constant volume and heat capacity at constant pressure are almost the same.

The heat capacity was historically important for understanding solids.

Density of states → entropy density

$$s = \int \frac{c_v}{T} dT$$

$$s = -\frac{\partial f}{\partial T} = -k_B \int_0^\infty D(\omega) \left(\ln\left(1 - e^{-\hbar\omega / k_B T}\right) + \frac{\hbar\omega}{k_B T \left(1 - e^{\hbar\omega / k_B T}\right)} \right) d\omega$$

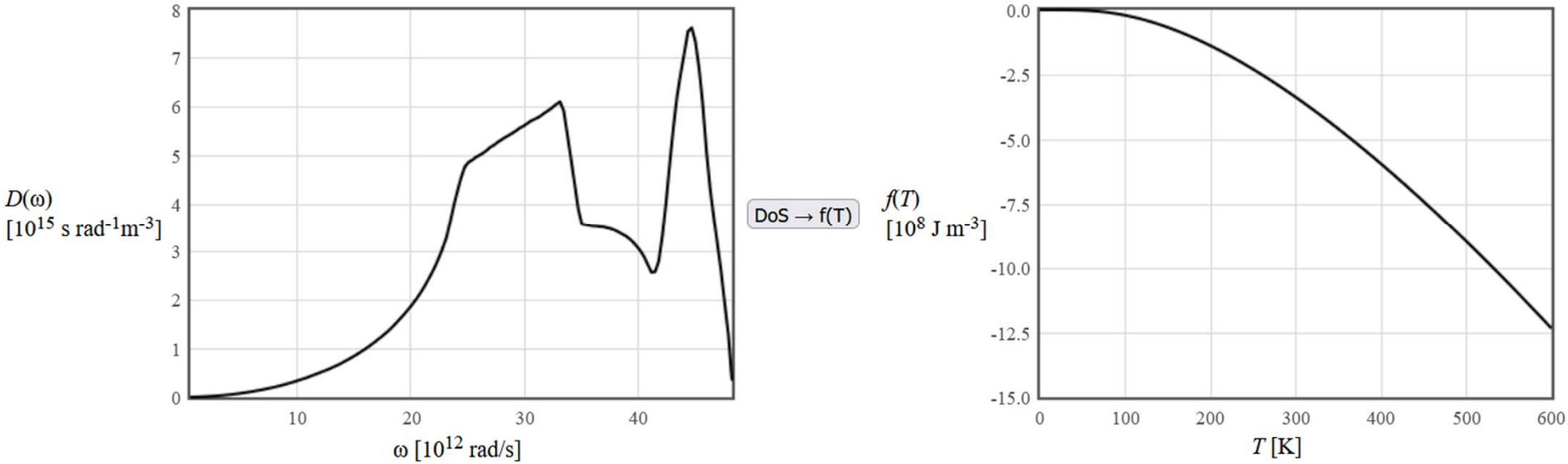


http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2s.htmll

Density of states → Helmholtz free energy density

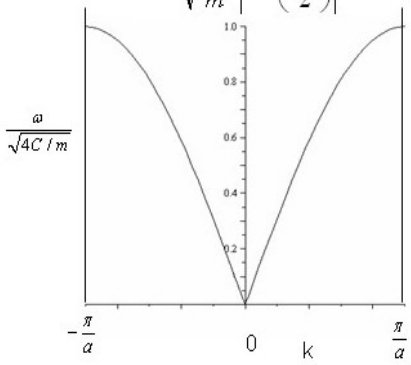
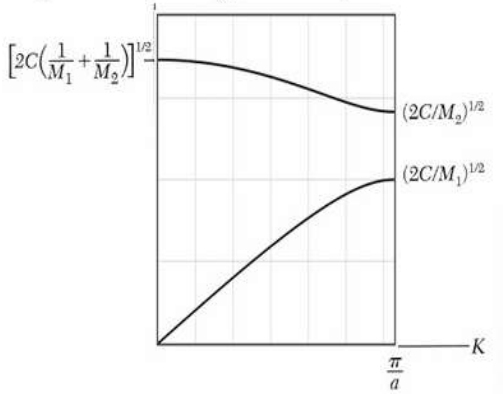
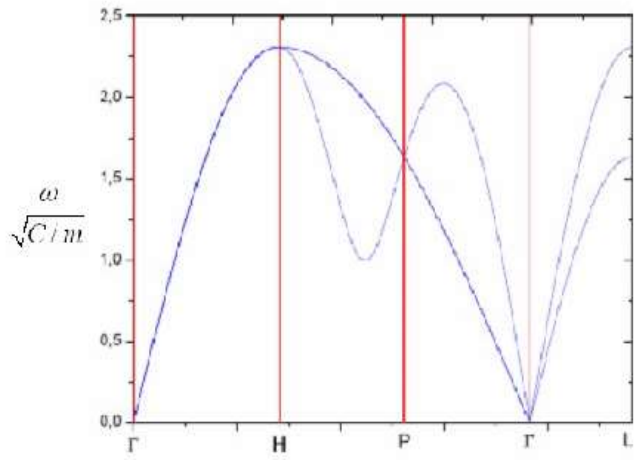
$$f(T) = k_B T \int_0^\infty D(\omega) \ln\left(1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)\right) d\omega$$

$$f = u - Ts$$



http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2h.html

Phonons

	Linear Chain	Linear chain 2 masses	body centered cubic
	$m\frac{d^2u_s}{dt^2} = C(u_{s+1} - 2u_s + u_{s-1})$	$M_1\frac{d^2u_s}{dt^2} = C(v_{s-1} - 2u_s + v_s)$ $M_2\frac{d^2v_s}{dt^2} = C(u_s - 2v_s + u_{s+1})$	$\frac{d^2u^x_{lmn}}{dt^2} = \frac{C}{\sqrt{3}\,m}[(u^x_{l+1m+1n+1} - u^x_{lmn}) + (u^x_{l-1m+1n+1} - u^x_{lr}$ $+(u^x_{l+1m-1n+1} - u^x_{lmn}) + (u^x_{l+1m+1n-1} - u^x_{lmn}) + (u^x_{l-1m+}$ $+(u^x_{l+1m-1n-1} - u^x_{lmn}) + (u^y_{l+1m+1n+1} - u^y_{lmn}) - (u^y_{l-1m+}$ $+(u^y_{l+1m-1n+1} - u^y_{lmn}) - (u^y_{l+1m+1n-1} - u^y_{lmn}) + (u^y_{l-1m+}$ $+(u^y_{l+1m-1n-1} - u^y_{lmn}) + (u^z_{l+1m+1n+1} - u^z_{lmn}) - (u^z_{l-1m+}$ $+(u^z_{l+1m-1n+1} - u^z_{lmn}) - (u^z_{l+1m+1n-1} - u^z_{lmn}) + (u^z_{l-1m+}$ $-(u^z_{l+1m-1n-1} - u^z_{lmn})]$ And similar expressions for the y and z
Eigenfunction solutions	$u_s = A_k e^{i(ksa - \omega t)}$	$u_s = ue^{i(ksa - \omega t)}$ $v_s = ve^{i(ksa - \omega t)}$	$u^x_{lmn} = u^x_{\vec{k}} e^{i(l\vec{k}\cdot\vec{a_1} + m\vec{k}\cdot\vec{a_2} + n\vec{k}\cdot\vec{a_3})} = u^x_{\vec{k}} e^{i(\frac{(-l-}{}}$ And similar expressions for the y and z
Dispersion relation	$\omega = \sqrt{\frac{4C}{m}}\left\lvert\sin\left(\frac{ka}{2}\right)\right\rvert$ 	$\omega^2 = C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4\sin^2\left(\frac{ka}{2}\right)}{M_1M_2}}$  Calculate ω(k)	The dispersic $\begin{bmatrix} 4 - cos(\frac{a}{2}(k_x + k_y + k_z)) - cos(\frac{a}{2}(3k_x - k_y - k_z)) & -cos(\frac{a}{2}(k_x + k_y \\ -cos(\frac{a}{2}(-k_x + 3k_y - k_z)) - cos(\frac{a}{2}(-k_x - k_y + 3k_z)) - \frac{m\omega^2}{\sqrt{3}C} & +cos(\frac{a}{2}(-k_x + 3 \\ -cos(\frac{a}{2}(k_x + k_y + k_z)) + cos(\frac{a}{2}(3k_x - k_y - k_z)) & 4 - cos(\frac{a}{2}(k_x + \\ +cos(\frac{a}{2}(-k_x + 3k_y - k_z)) - cos(\frac{a}{2}(-k_x - k_y + 3k_z)) & -cos(\frac{a}{2}(-k_x + 3 \\ -cos(\frac{a}{2}(k_x + k_y + k_z)) + cos(\frac{a}{2}(3k_x - k_y - k_z)) & -cos(\frac{a}{2}(k_x + k_y \\ -cos(\frac{a}{2}(-k_x + 3k_y - k_z)) + cos(\frac{a}{2}(-k_x - k_y + 3k_z)) & +cos(\frac{a}{2}(-k_x + 3 \end{bmatrix}$ 
Density of states $D(k)$	$D(k) = \frac{1}{\pi}$	$D(k) = \frac{1}{\pi}$	$D(k) = \frac{3k^2}{2\pi^2}$

Thermal properties

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

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

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

Helmholtz free energy density

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

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