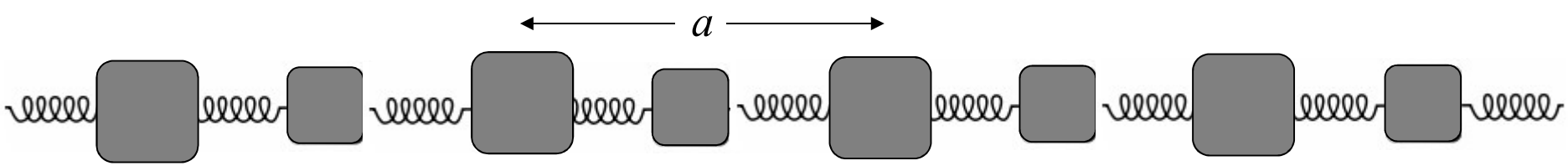
Phonons

Linear chain M_1 and M_2



$$-\omega^2 M_1 u_k = C v_k (1+\exp(-ika)) - 2C u_k$$
$$-\omega^2 M_2 v_k = C u_k (1+\exp(ika)) - 2C v_k$$

$$\begin{bmatrix} \omega^2 M_1 - 2C & C(1+\exp(-ika)) \\ C(1+\exp(ika)) & \omega^2 M_2 - 2C \end{bmatrix} \begin{bmatrix} u_k \\ v_k \end{bmatrix} = 0$$

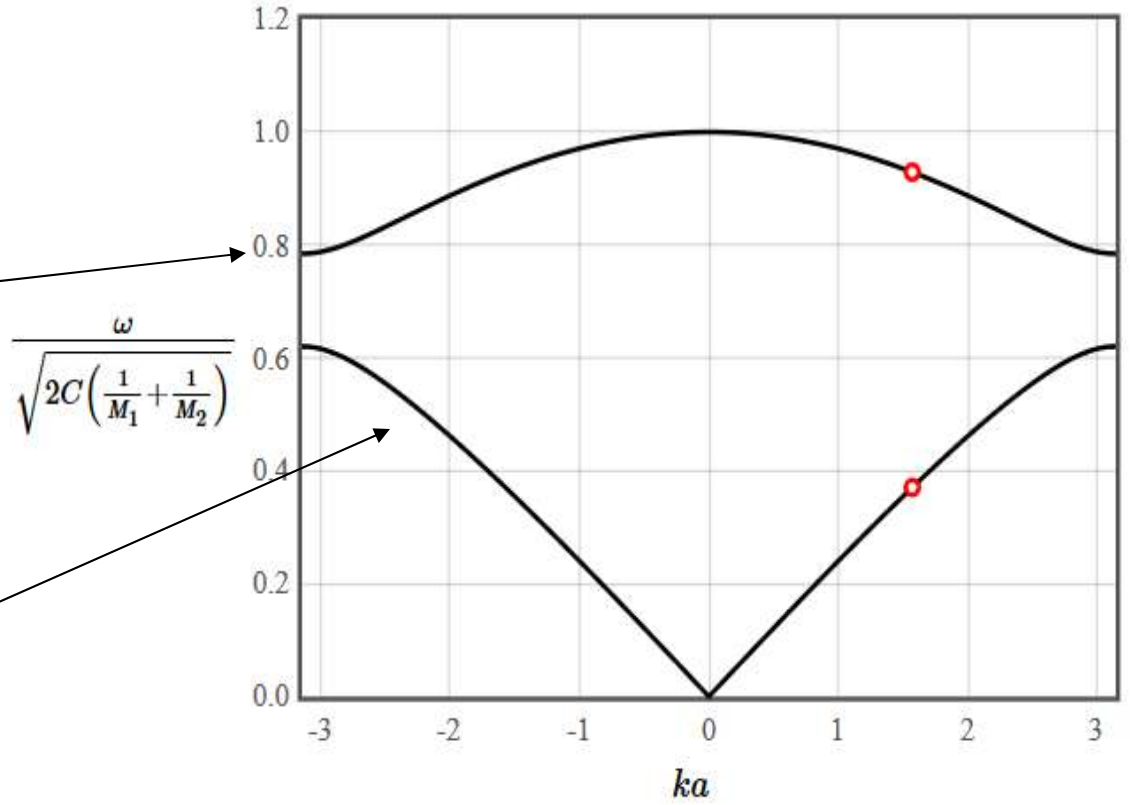
$$M_1 M_2 \omega^4 - 2C\left(M_1 + M_2\right)\omega^2 + 2C^2\left(1-\cos(ka)\right) = 0$$

dispersion relation

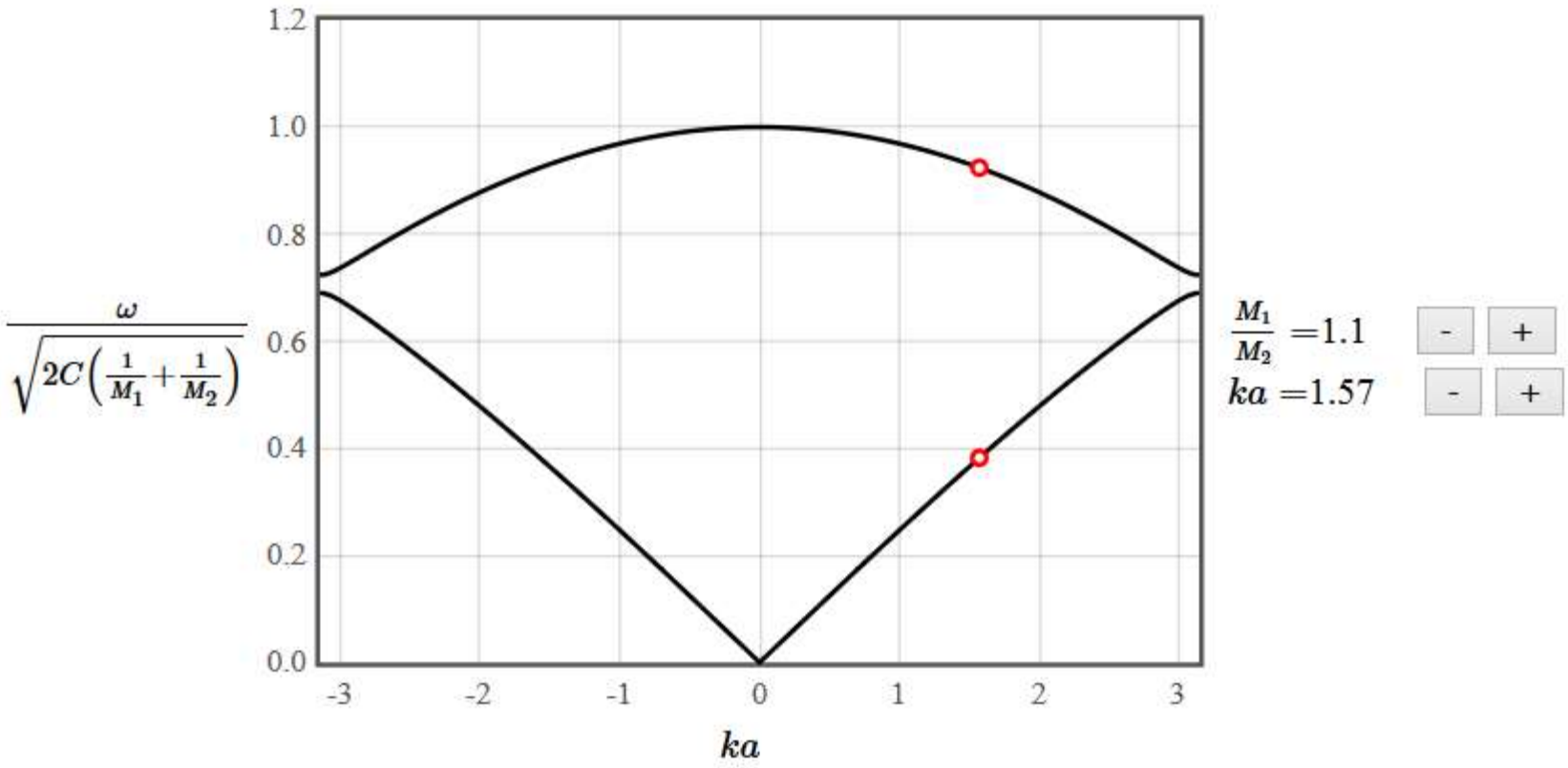
$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2\left(\frac{ka}{2}\right)}{M_1 M_2}}$$

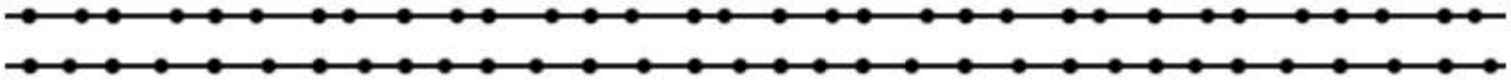
Optical phonon branch

Acoustic phonon branch



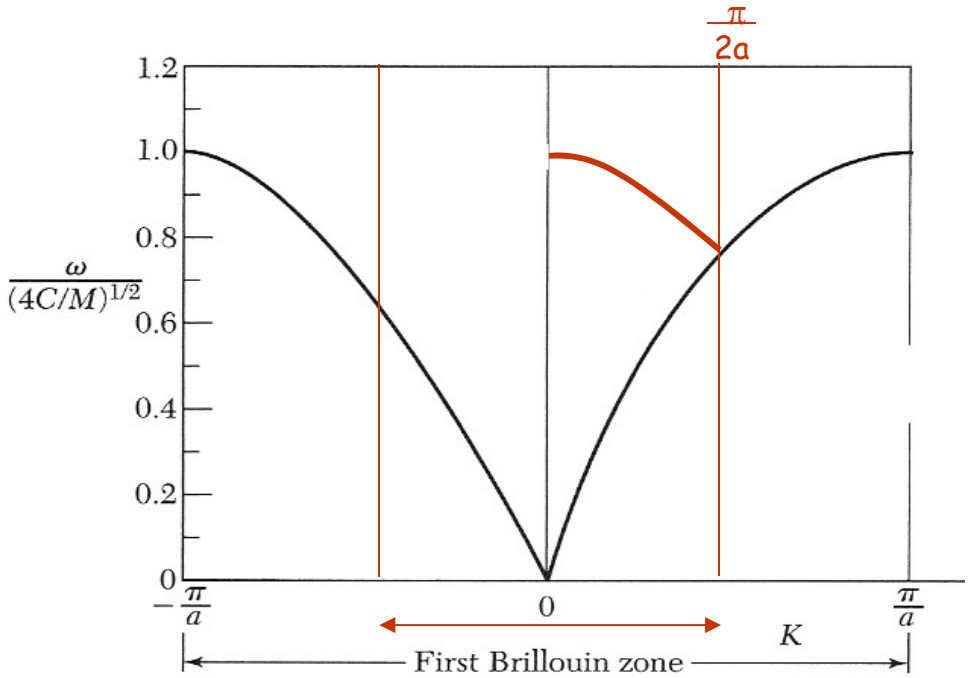
normal modes





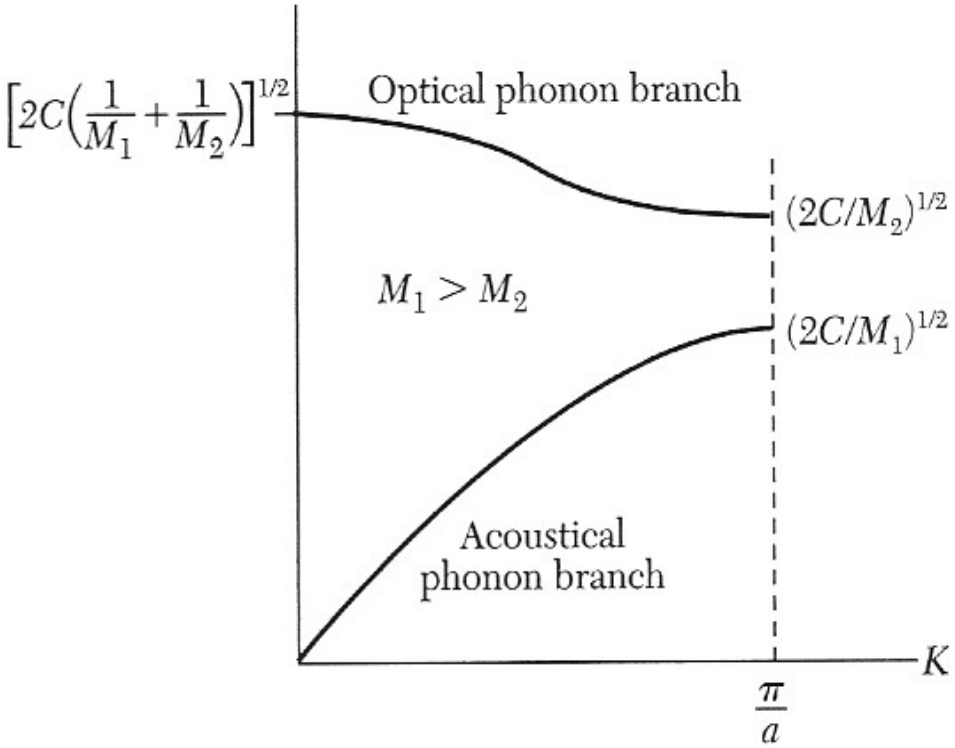
http://lampx.tugraz.at/~hadley/ss1/phonons/1d/1d2m.php

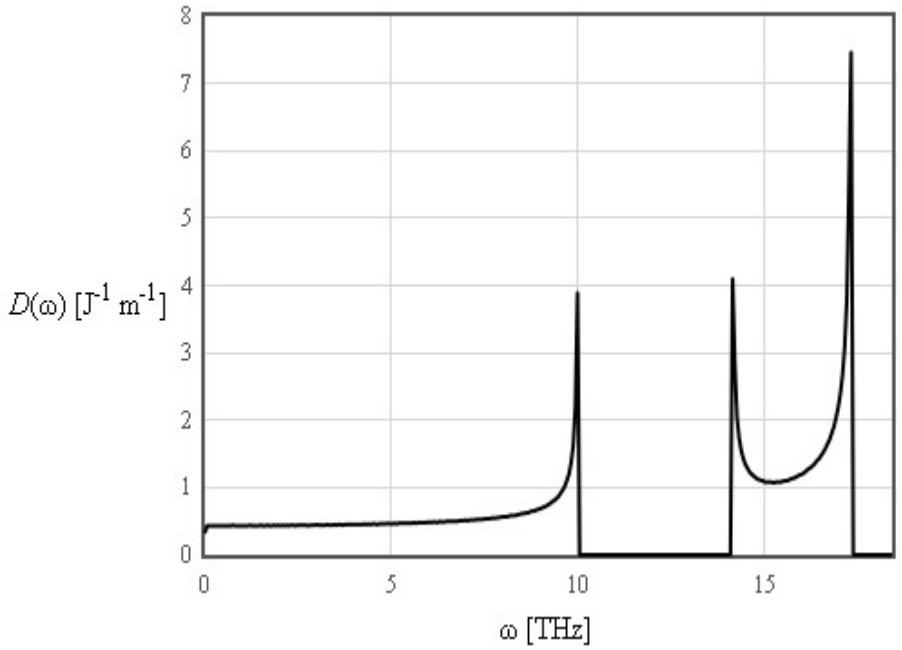
Linear chain M_1 and M_2



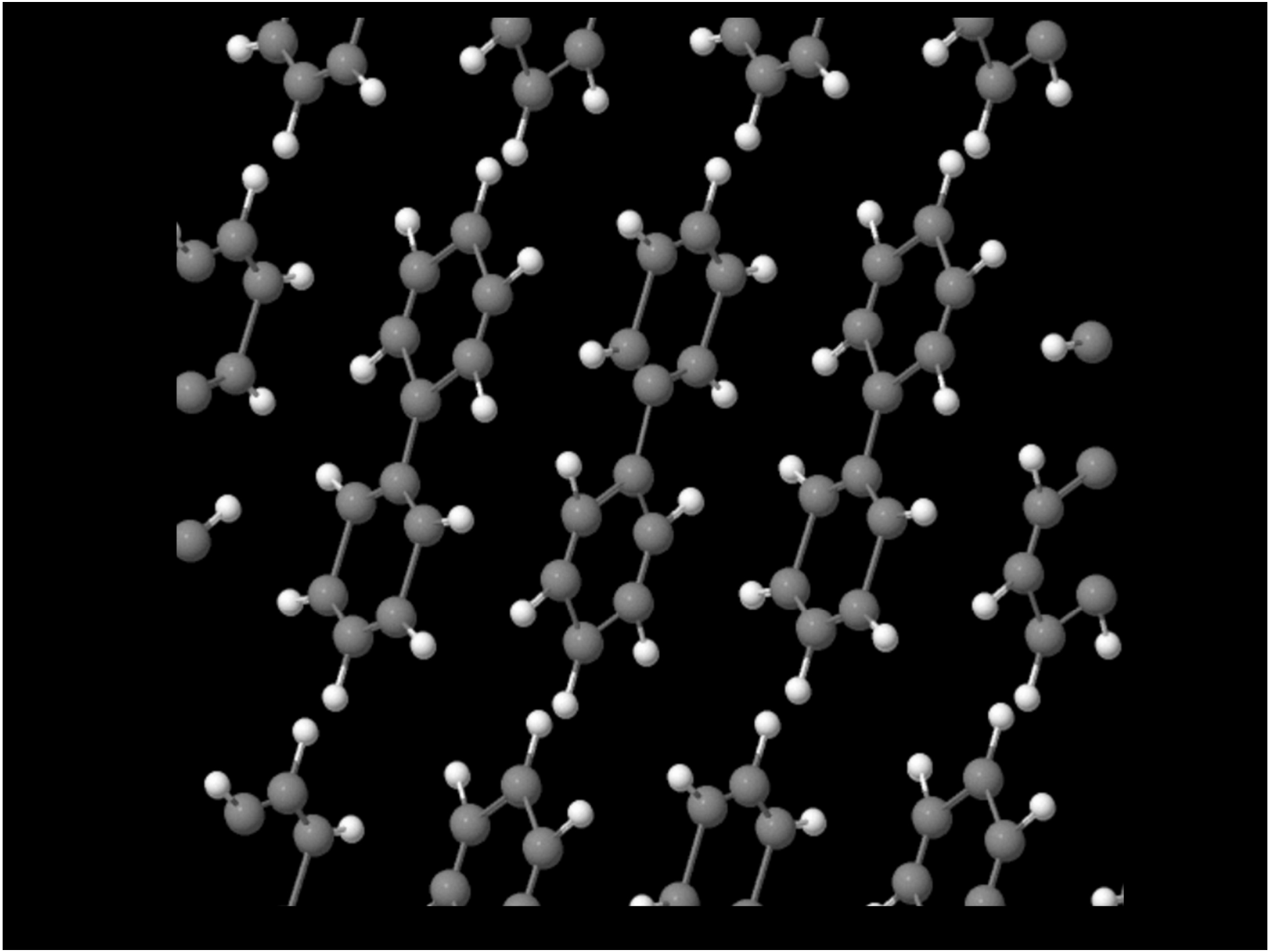
The branches of the dispersion curves can be translated by a reciprocal lattice vector $\vec{G}$.

density of states

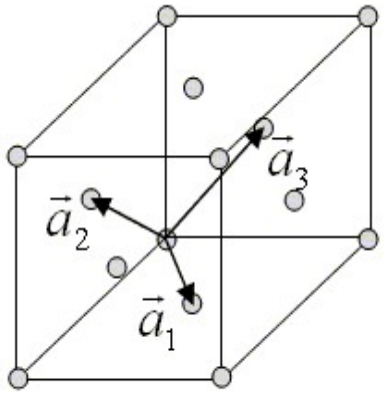




$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2 ka}{M_1 M_2}}$$



fcc



$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y} \qquad \vec{b}_1 = \frac{2\pi}{a}\left(\hat{k}_x + \hat{k}_y - \hat{k}_z\right)$$

$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z} \qquad \vec{b}_2 = \frac{2\pi}{a}\left(\hat{k}_x - \hat{k}_y + \hat{k}_z\right)$$

$$\vec{a}_3 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z} \qquad \vec{b}_3 = \frac{2\pi}{a}\left(-\hat{k}_x + \hat{k}_y + \hat{k}_z\right)$$

$$m\frac{d^2u^x_{lmn}}{dt^2} = \frac{C}{2}\Big[\left(u^x_{l+1mn} - u^x_{lmn}\right) + \left(u^x_{l-1mn} - u^x_{lmn}\right) + \left(u^x_{lm+1n} - u^x_{lmn}\right) + \left(u^x_{lm-1n} - u^x_{lmn}\right)$$
$$+ \left(u^x_{l+1mn-1} - u^x_{lmn}\right) + \left(u^x_{l-1mn+1} - u^x_{lmn}\right) + \left(u^x_{lm+1n-1} - u^x_{lmn}\right) + \left(u^x_{lm-1n+1} - u^x_{lmn}\right)$$
$$+ \left(u^y_{l+1mn} - u^y_{lmn}\right) + \left(u^y_{l-1mn} - u^y_{lmn}\right) - \left(u^y_{lm+1n-1} - u^y_{lmn}\right) - \left(u^y_{lm-1n+1} - u^y_{lmn}\right)$$
$$+ \left(u^z_{lm+1n} - u^z_{lmn}\right) + \left(u^z_{lm-1n} - u^z_{lmn}\right) - \left(u^z_{l+1mn-1} - u^z_{lmn}\right) - \left(u^z_{l-1mn+1} - u^z_{lmn}\right)\Big]$$

and similar expressions for the *y* and *z* motion

Normal modes are eigenfunctions of T

$$u^x_{lmn} = u^x_{\vec{k}} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

$$u^y_{lmn} = u^y_{\vec{k}} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

$$u^z_{lmn} = u^z_{\vec{k}} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

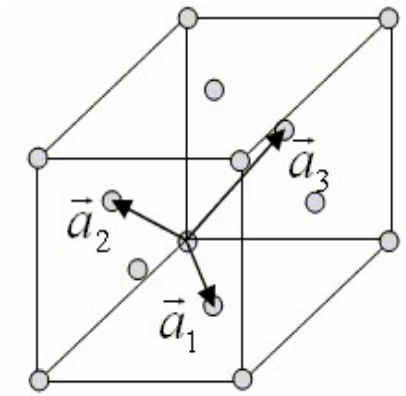
These are eigenfunctions of T.

$$T_{pqr}u^x_{lmn} = u^x_{\vec{k}} \exp\left(i\left(l\vec{k}\cdot\left(\vec{a}_1 + p\vec{a}_1\right) + m\vec{k}\cdot\left(\vec{a}_2 + q\vec{a}_2\right) + n\vec{k}\cdot\left(\vec{a}_3 + r\vec{a}_3\right) - \omega t\right)\right)$$

$$= \exp\left(i\left(lp\vec{k}\cdot\vec{a}_1 + qm\vec{k}\cdot\vec{a}_2 + rn\vec{k}\cdot\vec{a}_3\right)\right)u^x_{\vec{k}} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

$$= \exp\left(i\left(lp\vec{k}\cdot\vec{a}_1 + qm\vec{k}\cdot\vec{a}_2 + rn\vec{k}\cdot\vec{a}_3\right)\right)u^x_{lmn}$$

fcc



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

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

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

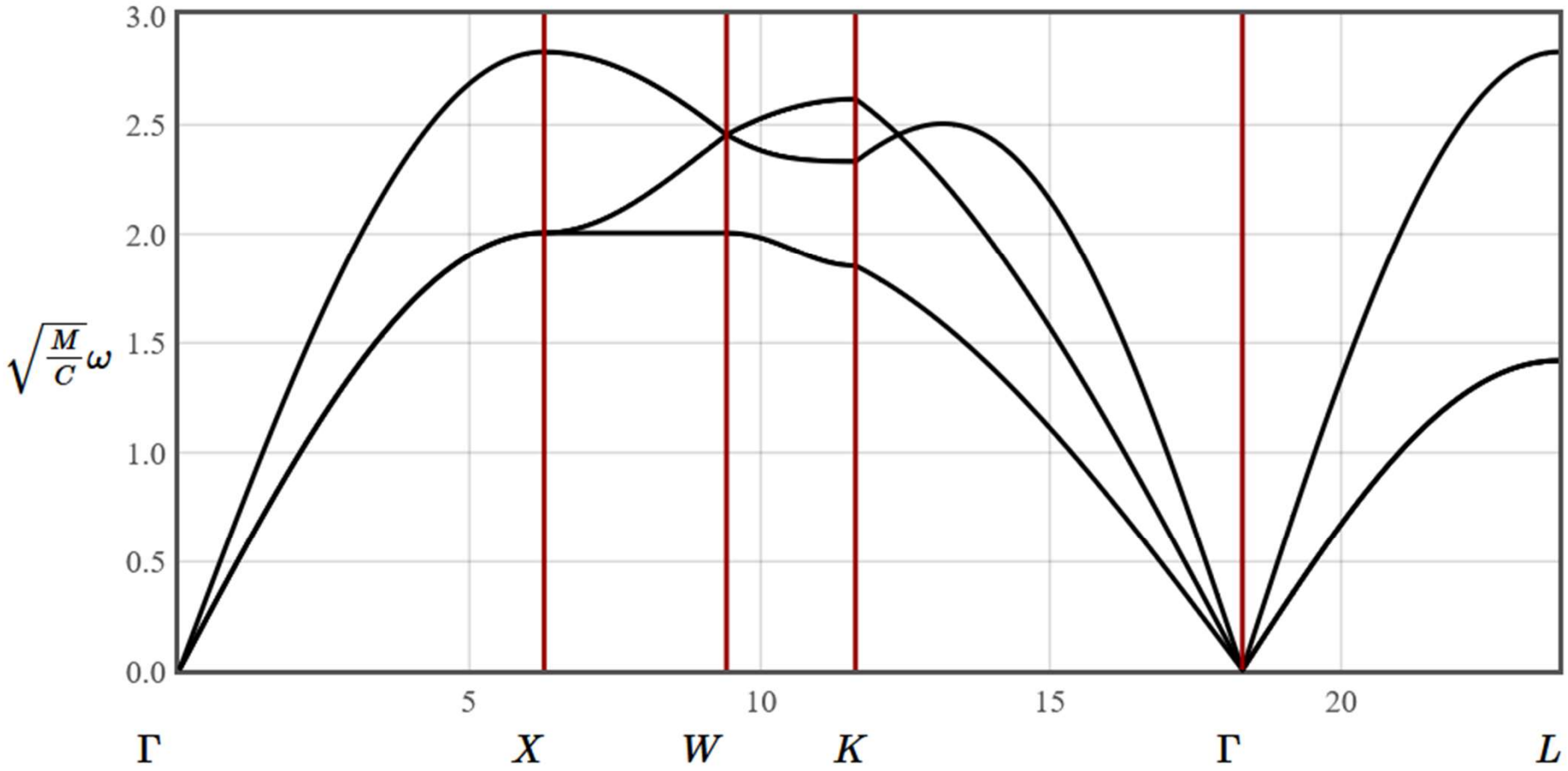
Substitute the eigenfunctions of T into Newton's laws.

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

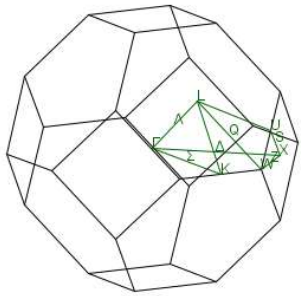
$$\begin{vmatrix} 4-\cos\left(\frac{k_x a}{2}+\frac{k_y a}{2}\right)-\cos\left(\frac{k_x a}{2}+\frac{k_z a}{2}\right)-\cos\left(\frac{k_x a}{2}-\frac{k_y a}{2}\right)-\cos\left(\frac{k_x a}{2}-\frac{k_z a}{2}\right)-\frac{m\omega^2}{\sqrt{2}C} & -\cos\left(\frac{k_x a}{2}+\frac{k_y a}{2}\right)+\cos\left(\frac{k_x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

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

For every k there are 3 solutions for ω.



Phonon dispersion Au



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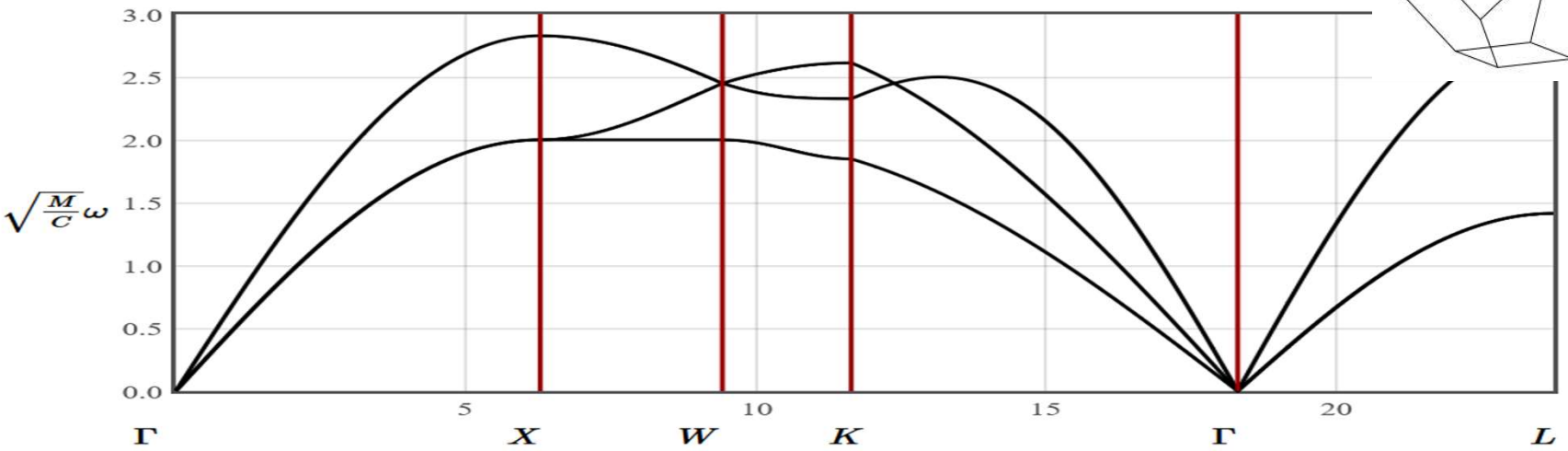


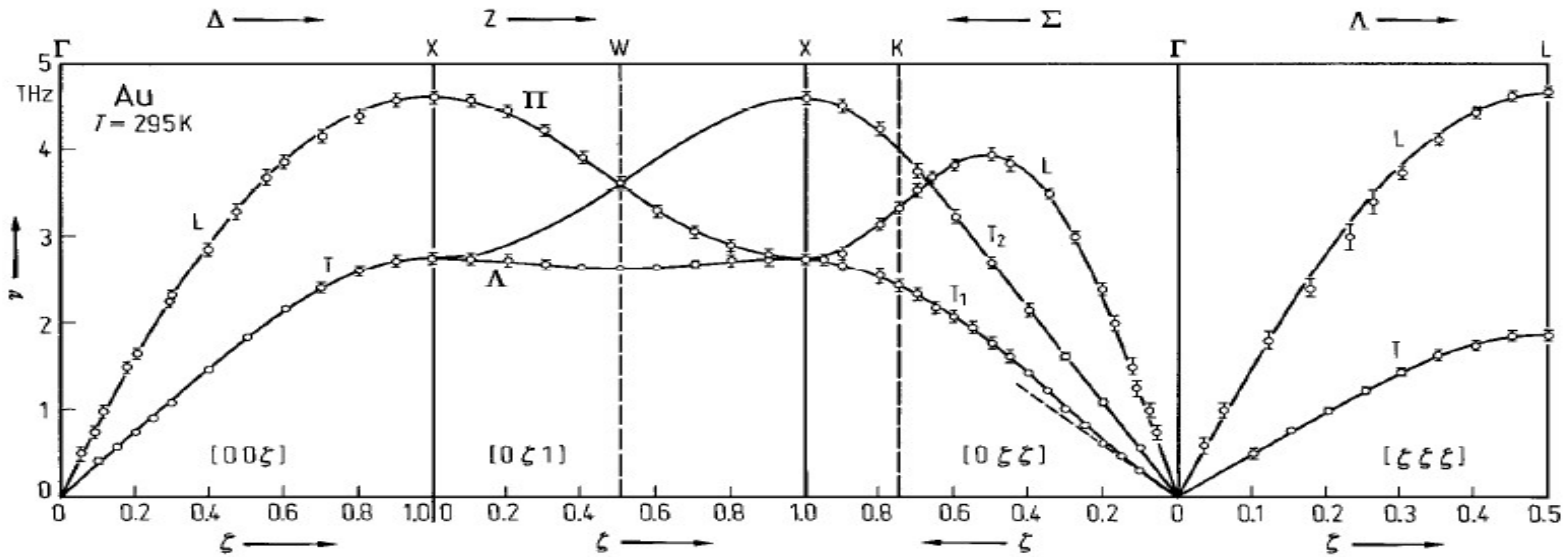
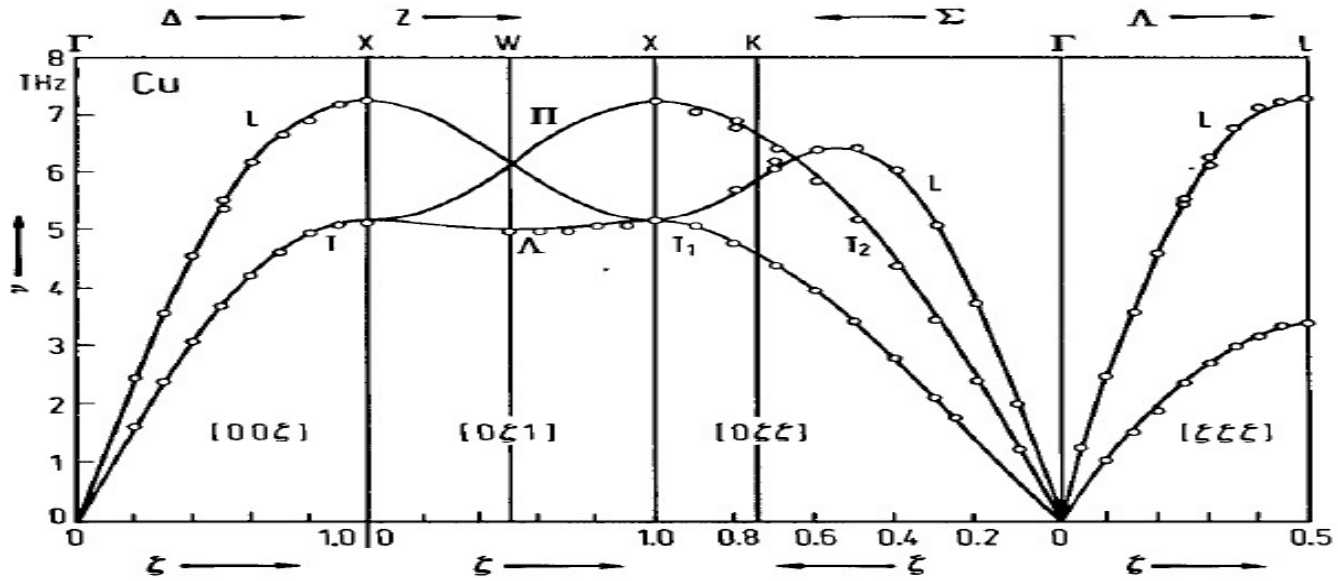
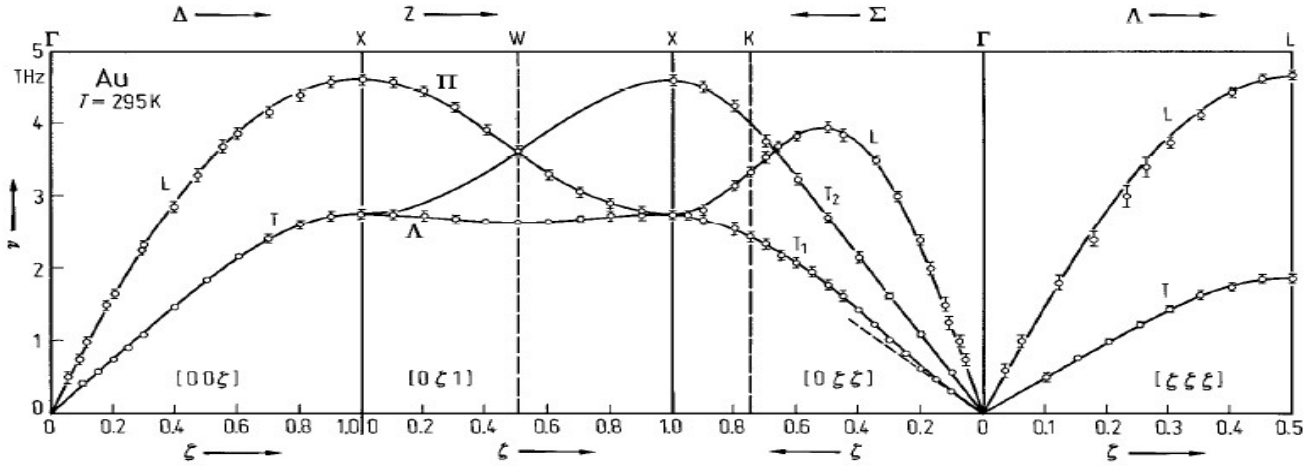


Fig. 1. Au. Phonon dispersion relations in the principal symmetry directions according to [73Ly1]. The solid curves represent both the fourth neighbour general force model (M1) and the fifth neighbour axially symmetric model (M2) of Table 3 Au. The dotted line in the Σ direction is corresponding to the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

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



Cu



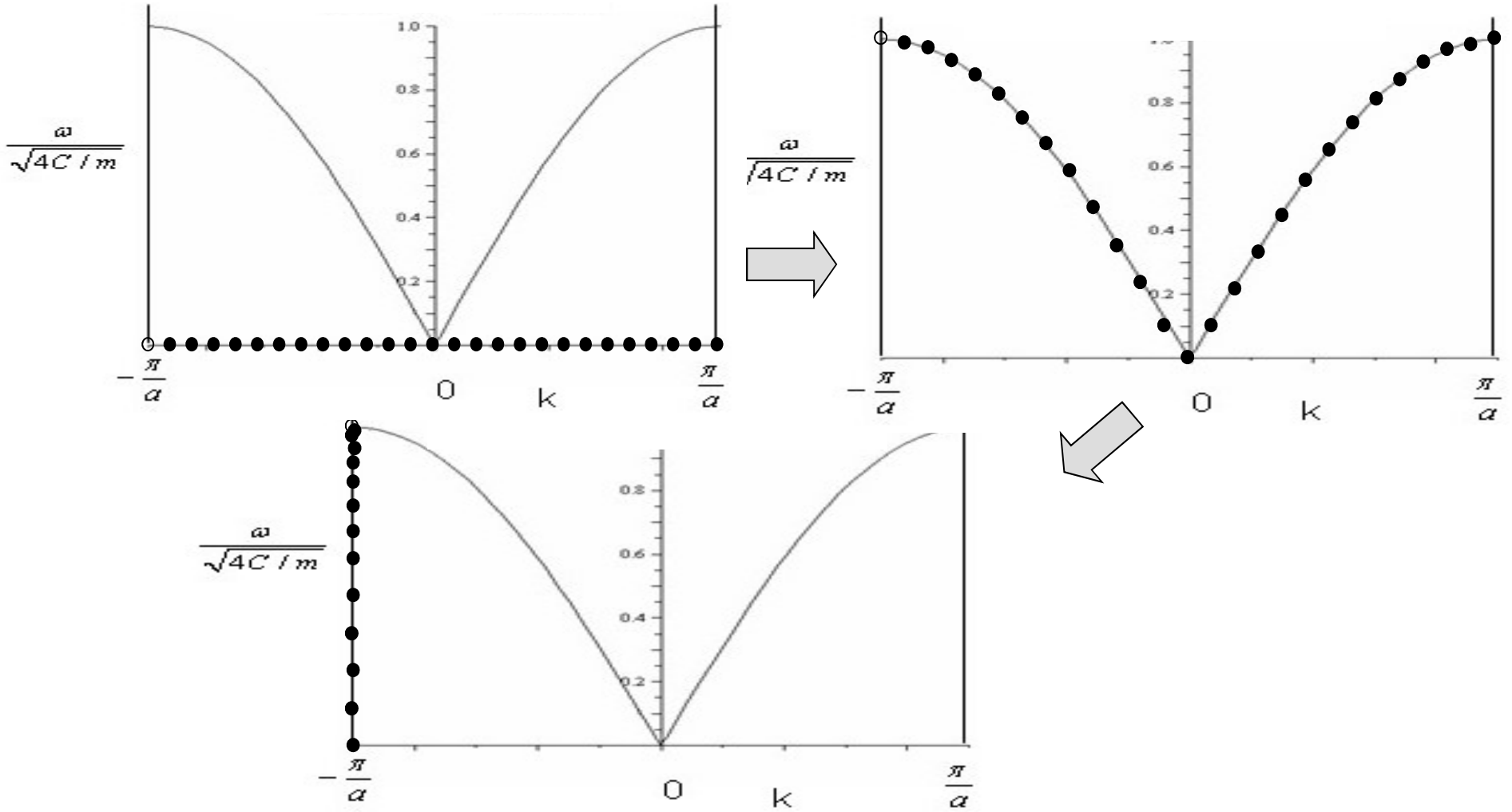
Au

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.

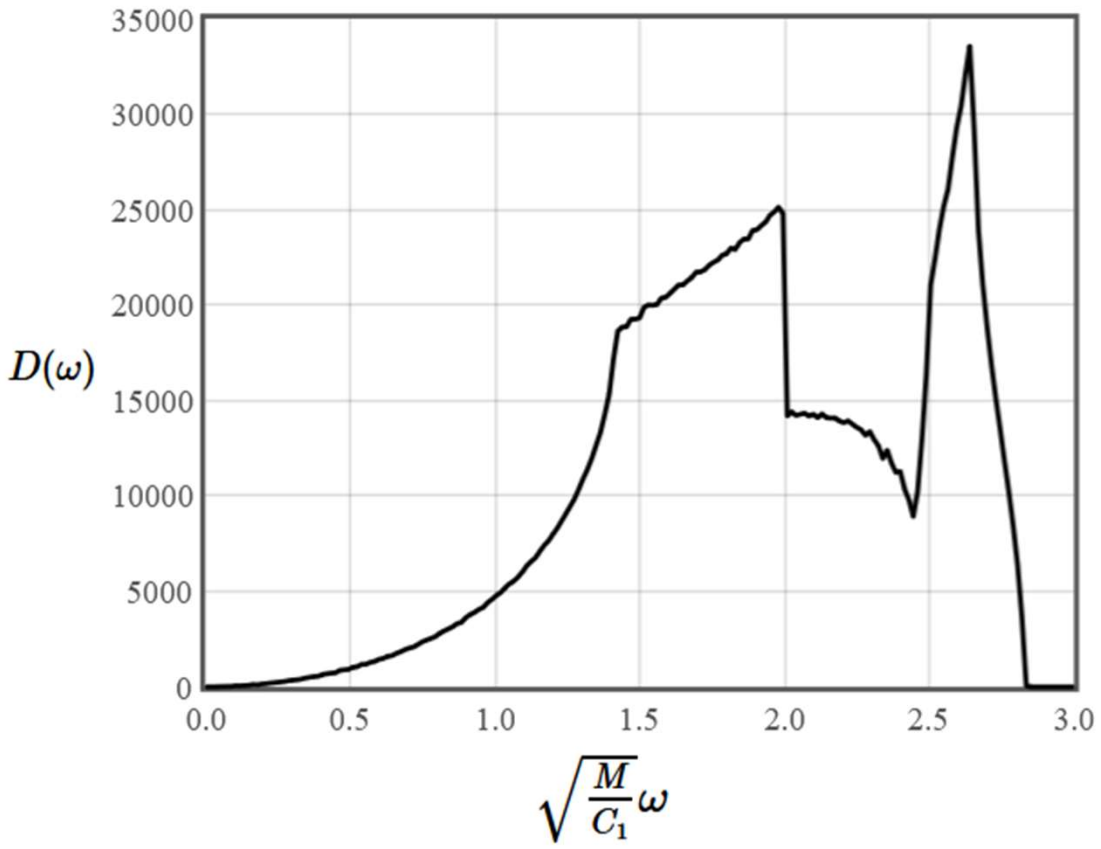
Linear Chain - density of states

Determine the density of states numerically

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

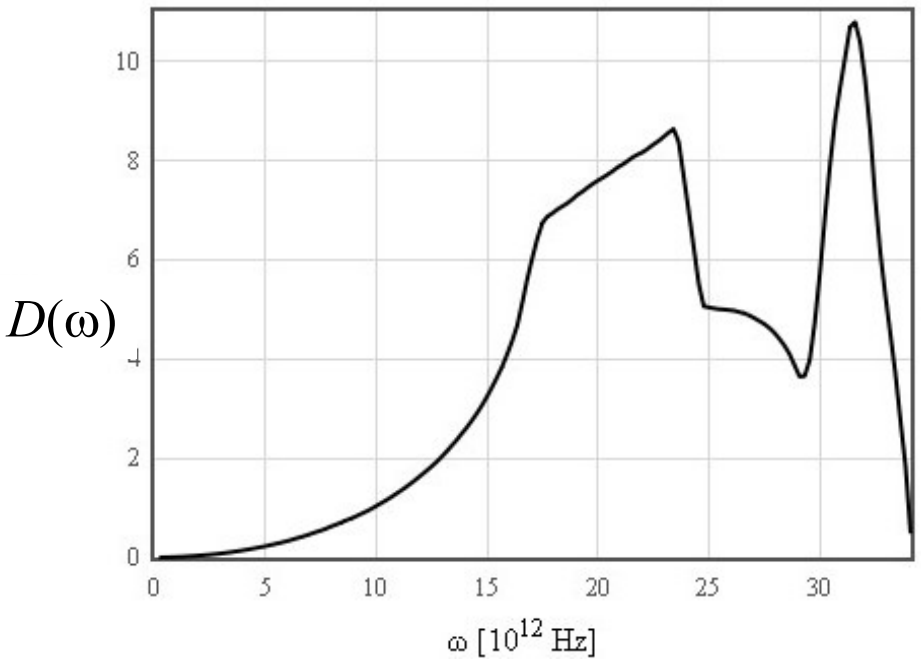


Phonon density of states of a fcc crystal



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

Phonon DOS fcc



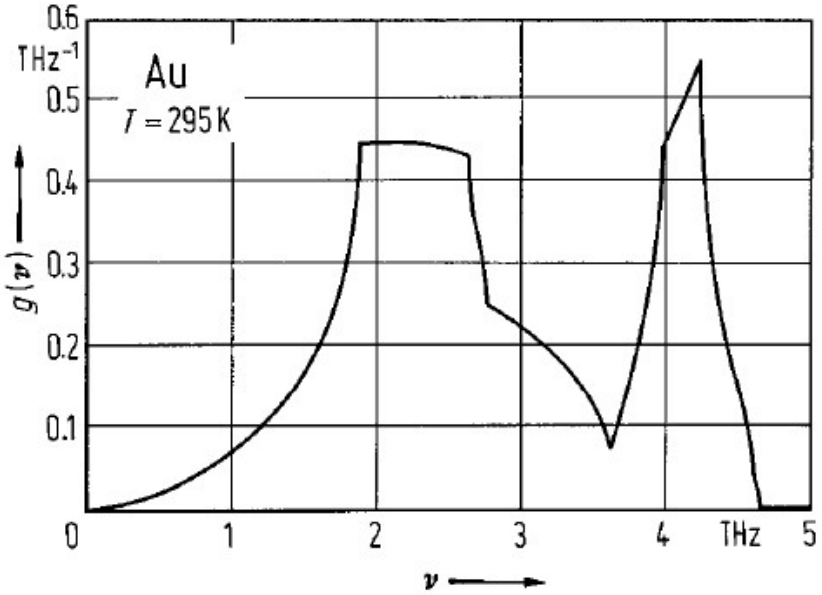
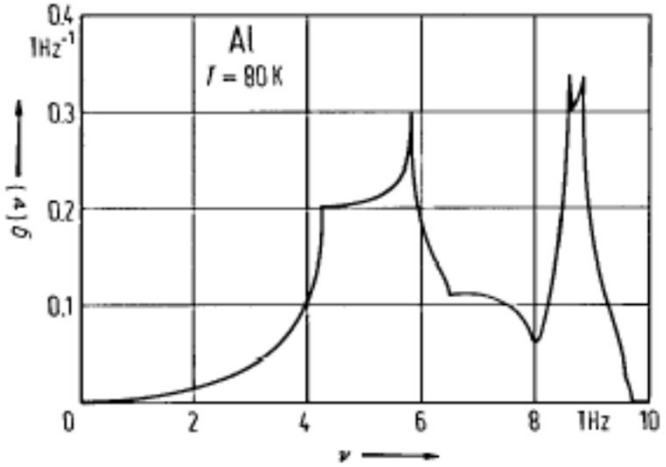
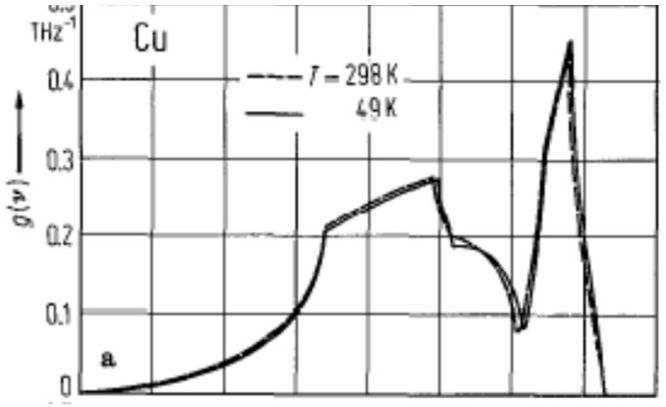


Fig. 2. Au. Frequency distribution calculated from the fourth neighbour general force constant model (M1) of Table 3 Au.





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Phonon dispersion

1. **Determine the dispersion relation:**

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

   The solutions to these equations will be

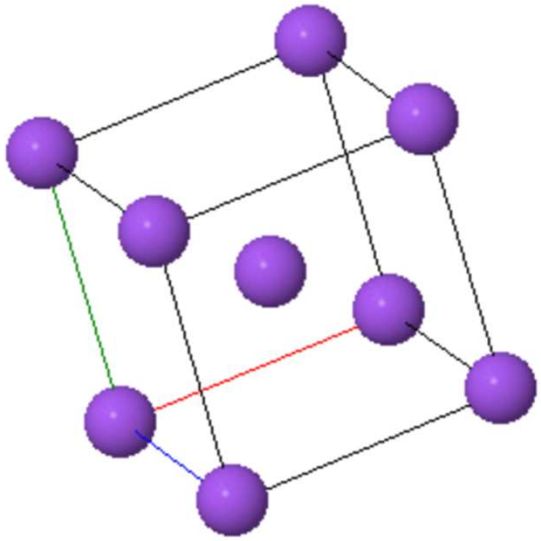
$$A_k \exp\left(i\left(\vec{k}\cdot\vec{a}_1 + \vec{k}\cdot\vec{a}_2 + \vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

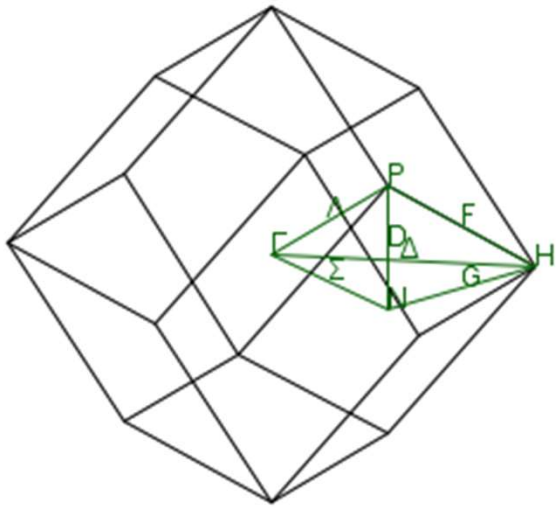
   Substitute the solutions into the equations of motion to determine the dispersion relation.

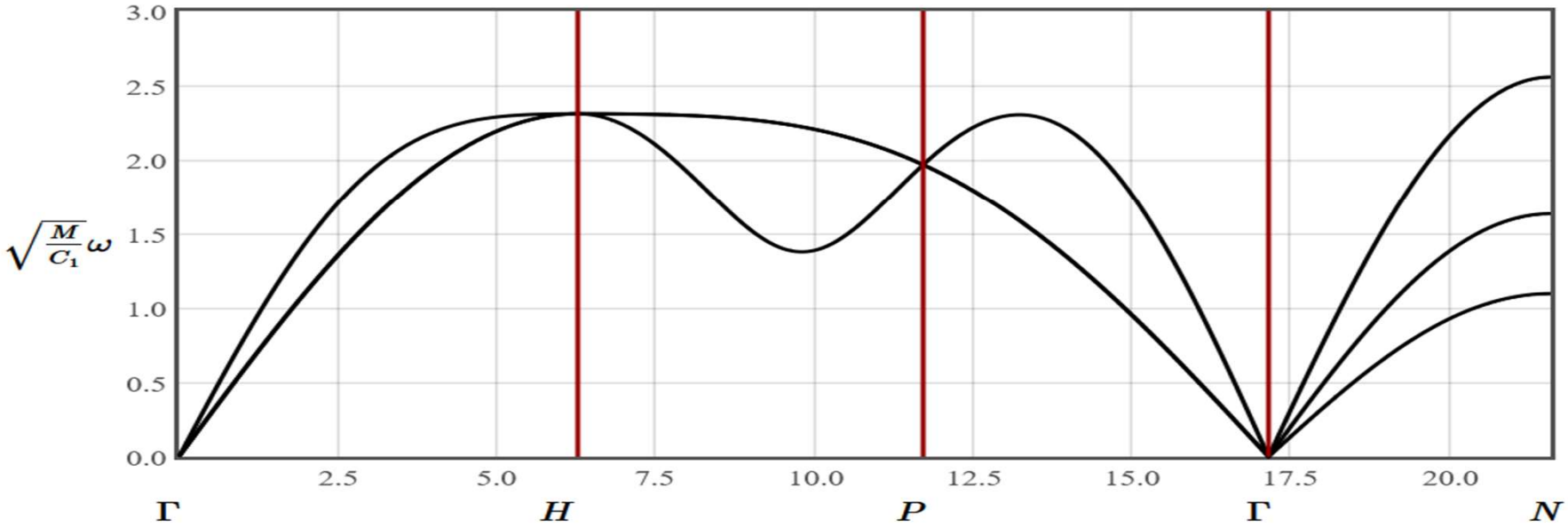
2. **Determine the density of states numerically from the dispersion relation** $D(\omega)$

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

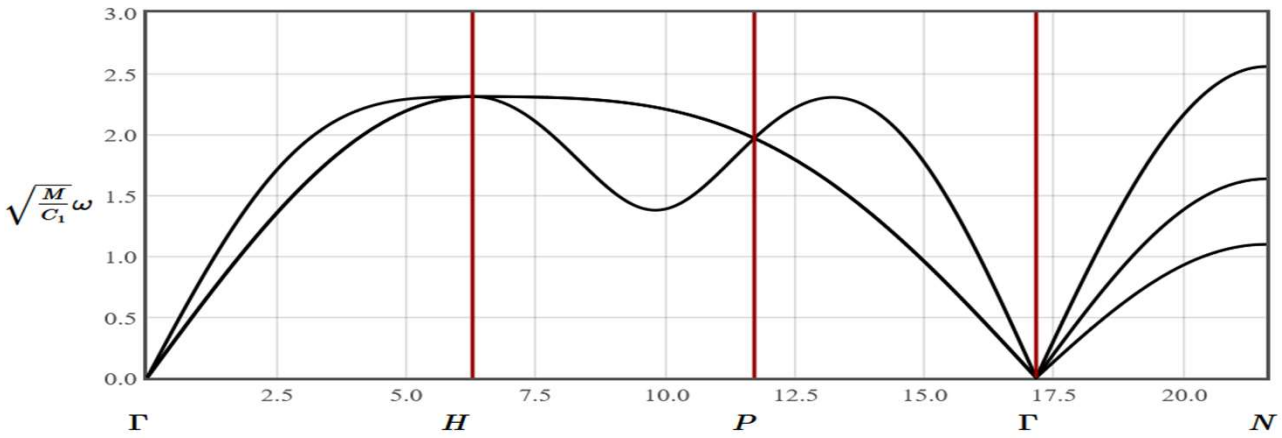
Phonon dispersion bcc

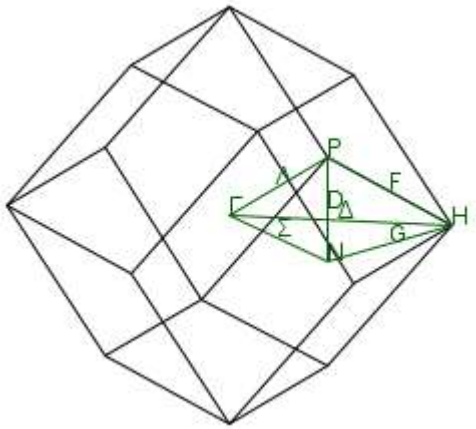






Phonon dispersion Fe





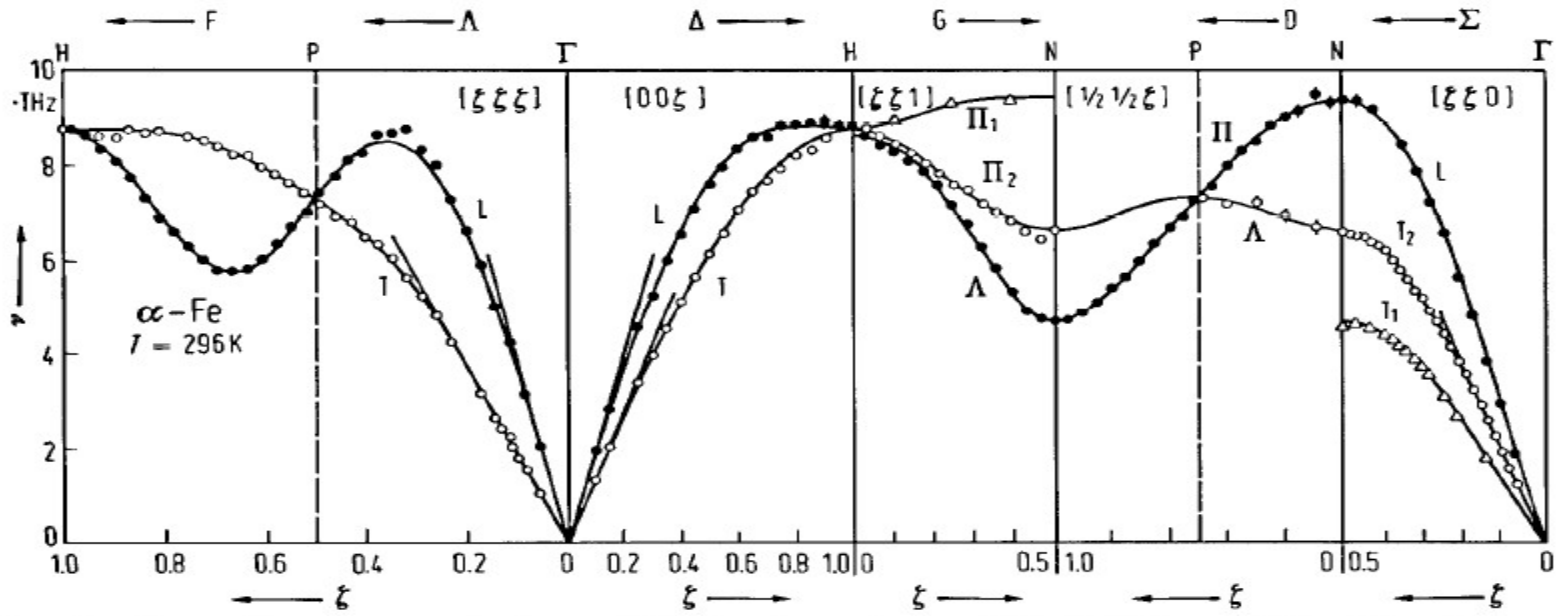


Fig. 2. Fe. Phonon dispersion curves in α-iron at 296 K. Experimental points: [68Va2]. Solid curve: fifth neighbour Born-von Karman model (Table 3 Fe [68Va2]).

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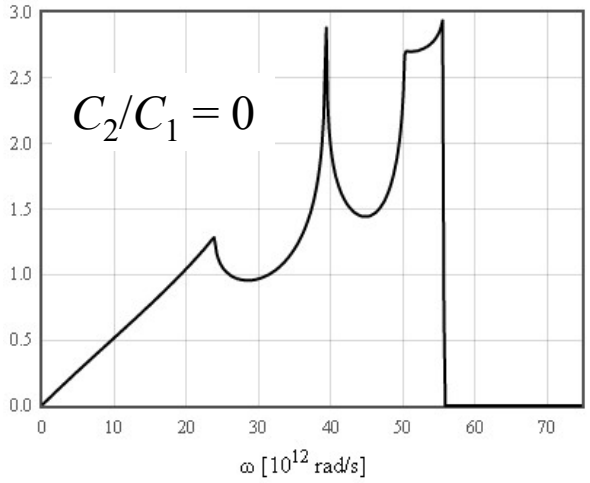
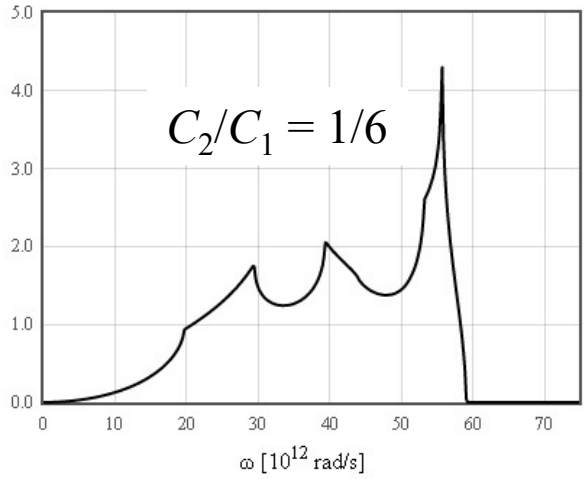
Phonon DOS Fe





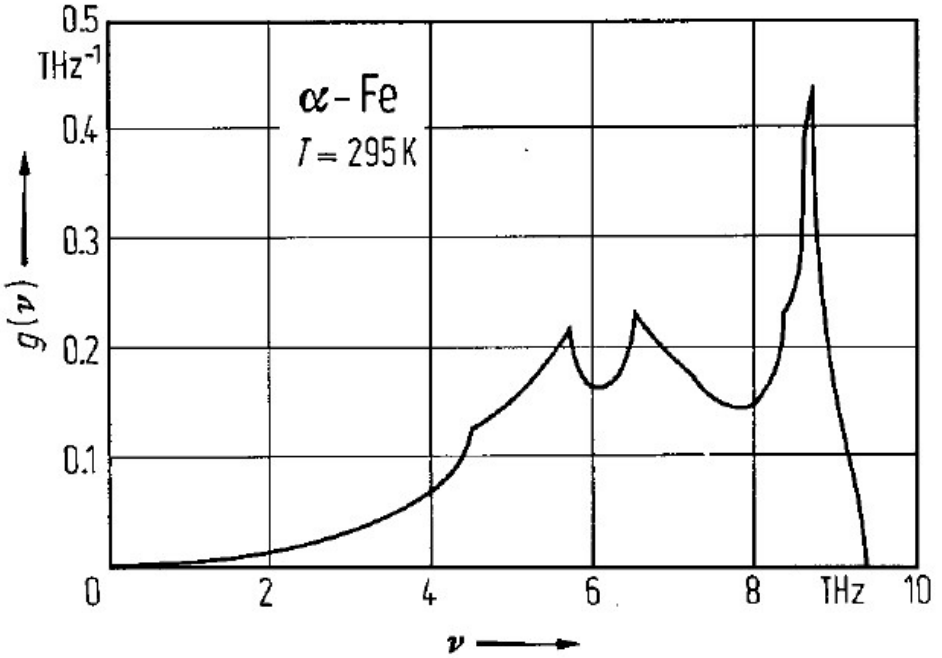


Fig. 3. Fe. Frequency spectrum of α-iron at 295 K calculated from the Born-von Karman force constants of Table 3 Fe [67Mi1].

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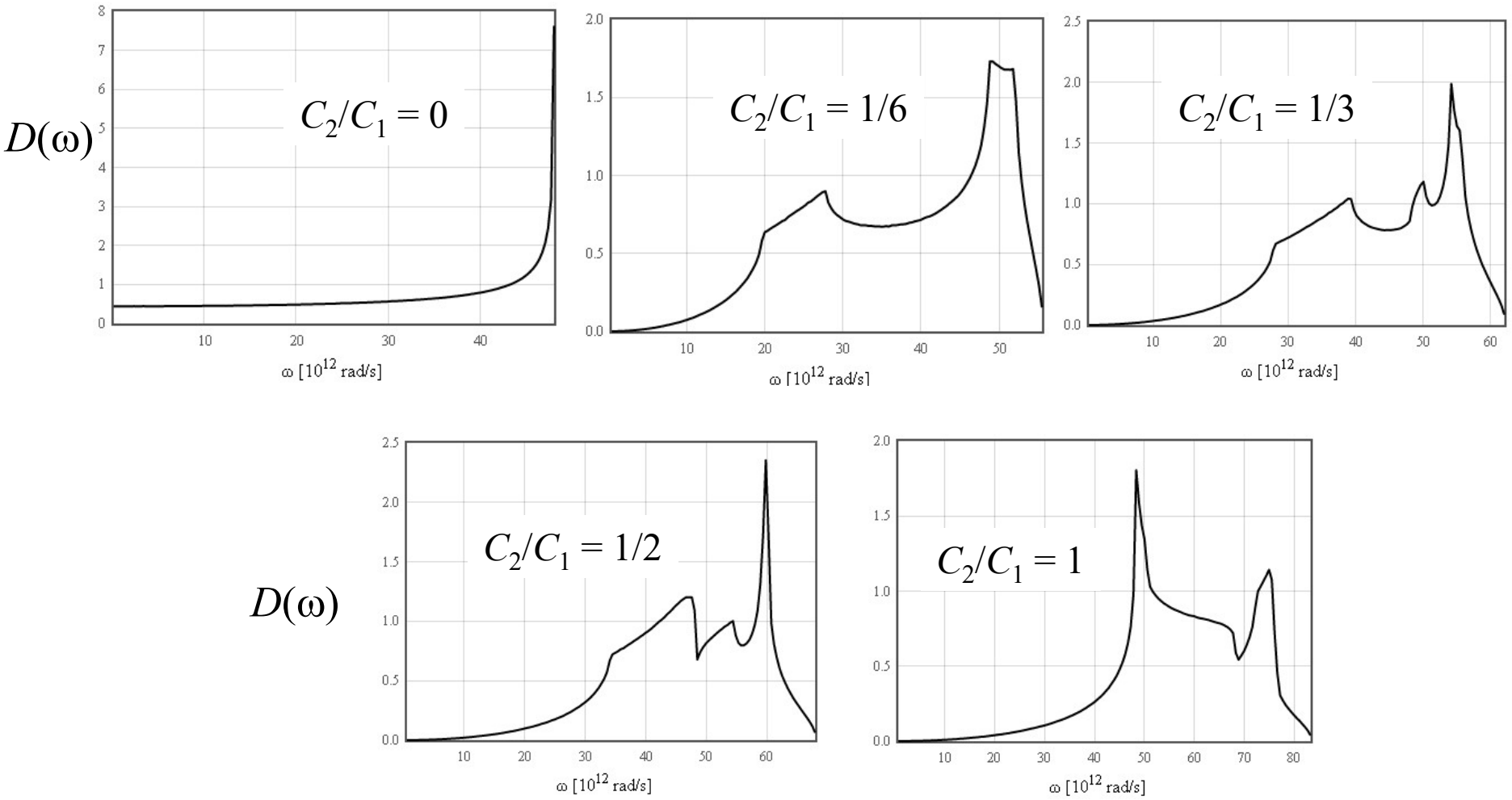
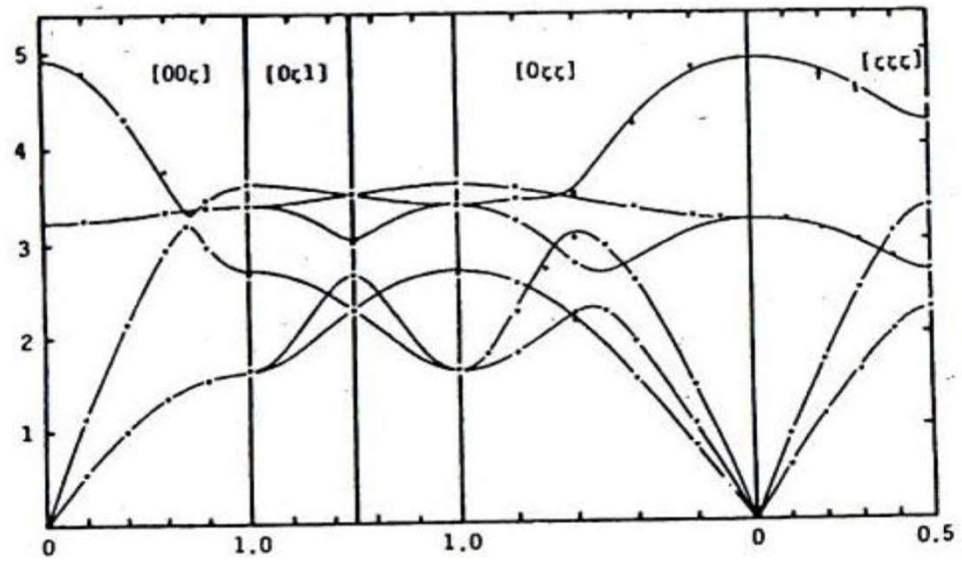
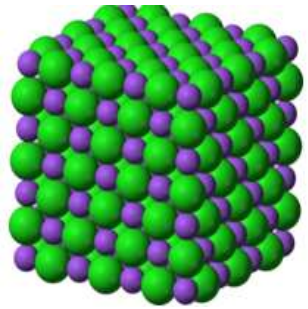
Next nearest neighbors (simple cubic)



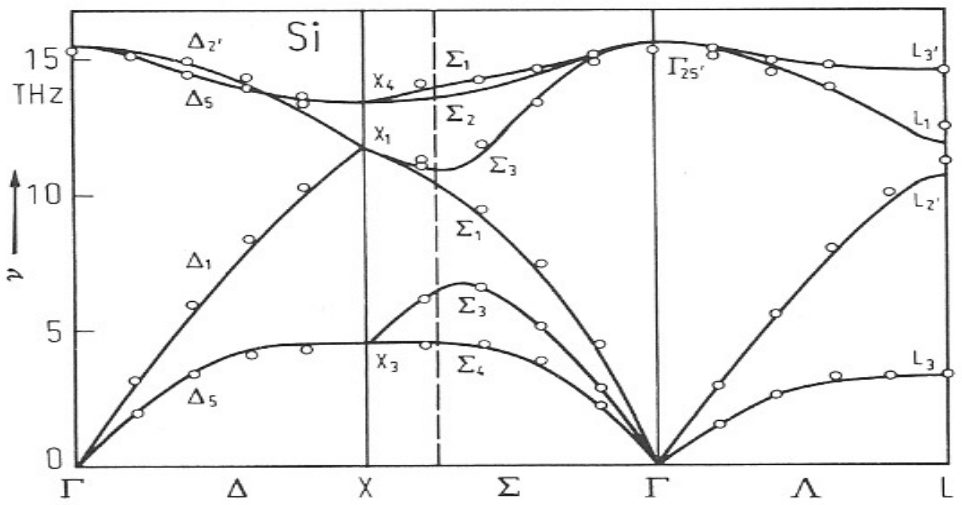
Sometimes the 5th neighbors are included.

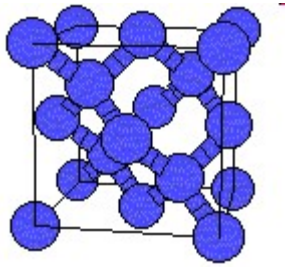
Two atoms per primitive unit cell





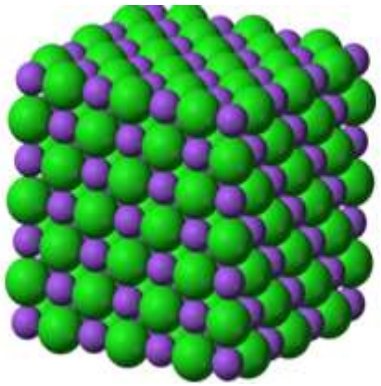
NaCl





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:

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

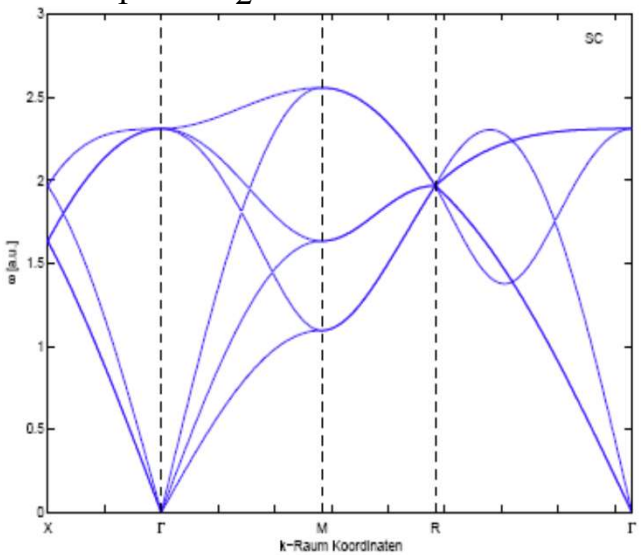
$$M_2 \frac{d^2 v^z_{nml}}{dt^2} = C\left(-2v^z_{nml} + u^z_{n(m+1)(l+1)} + u^z_{(n+1)ml}\right)$$

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

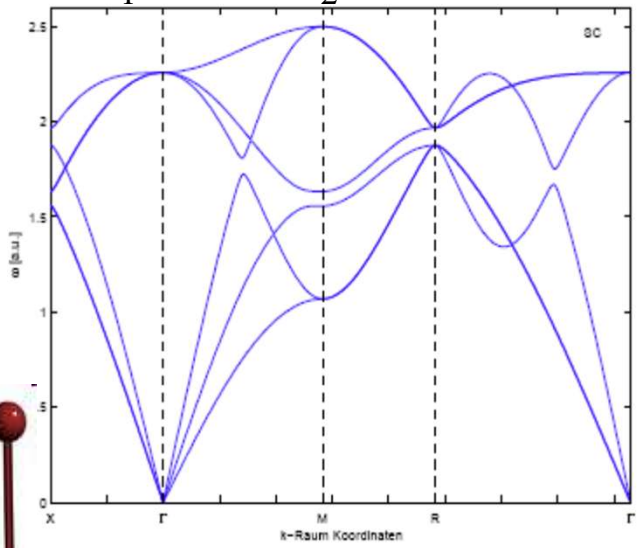
CsCl

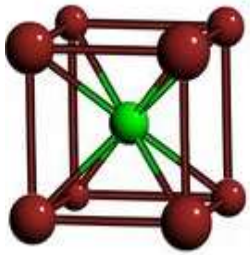
Hannes Brandner

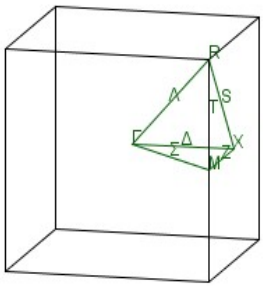
$M_1 = M_2$



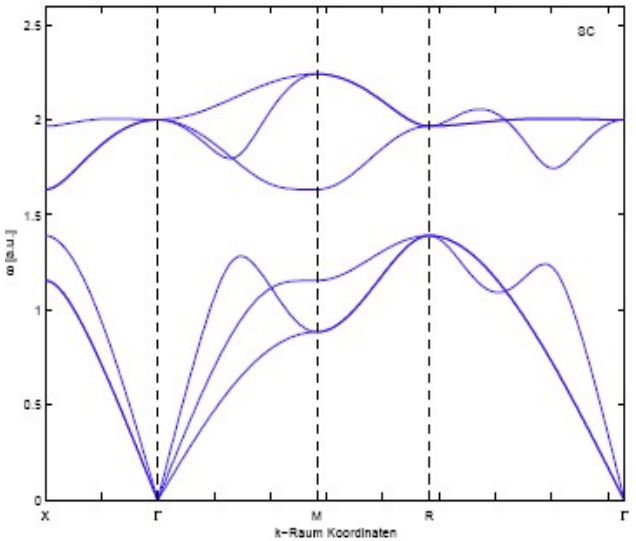
$M_1 = 1.1\ M_2$



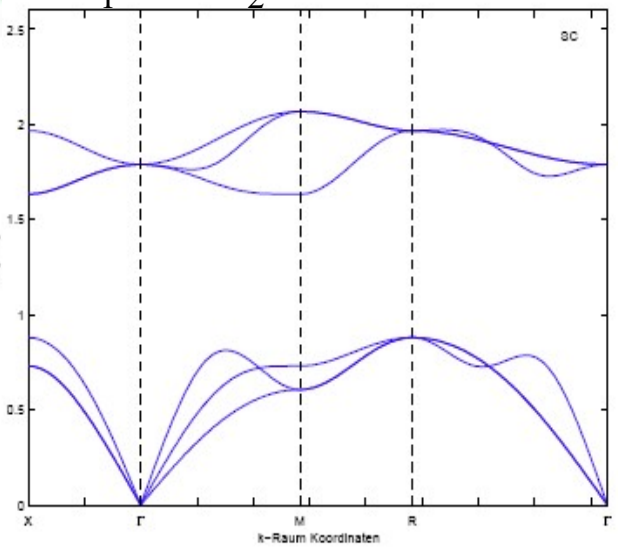




$M_1 = 2M_2$



$M_1 = 5M_2$



3 dimensions

N atoms

3*N* normal modes

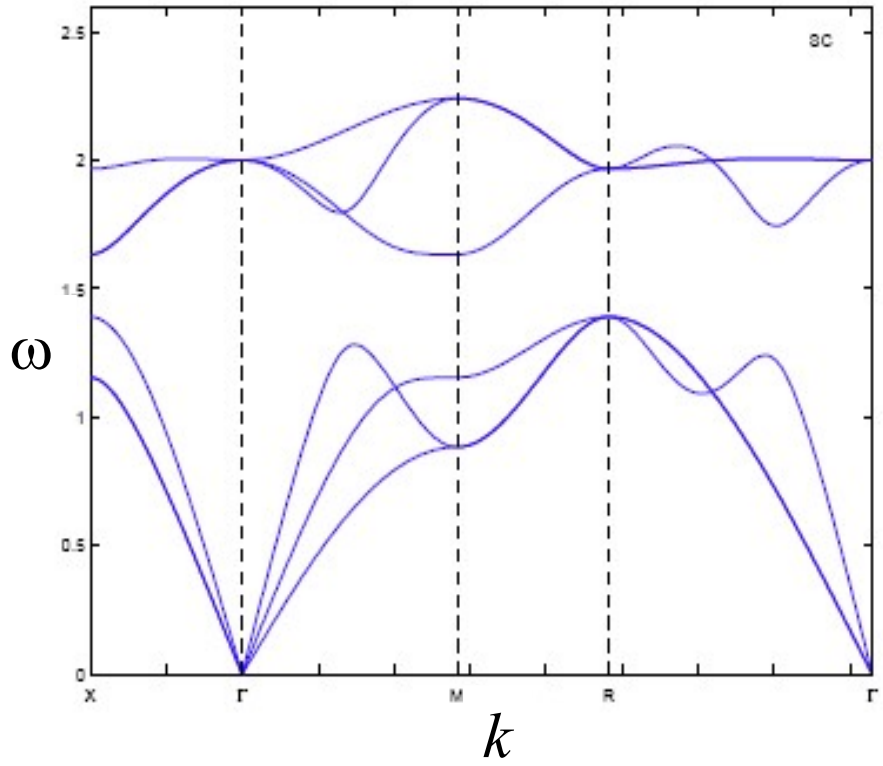
p atoms per unit cell

N/p unit cells = *k* vectors

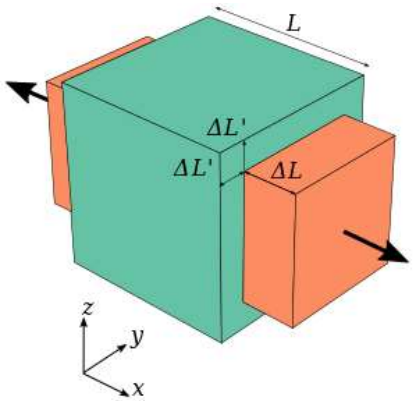
3*p* branches to the dispersion relation

3 acoustic modes (1 longitudinal, 2 transverse)

3*p* - 3 optical modes



Poisson's ratio



Wikipedia

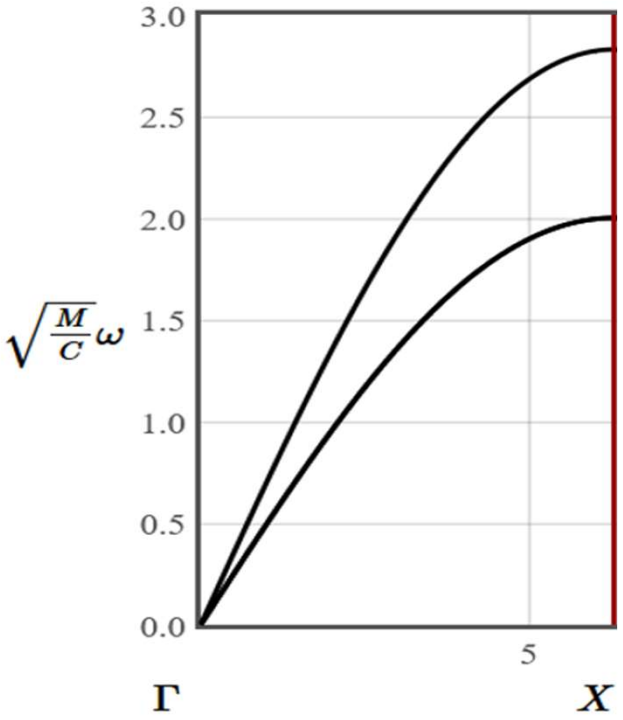
E - Elastic constant

ν - Poisson's ratio

ρ - density

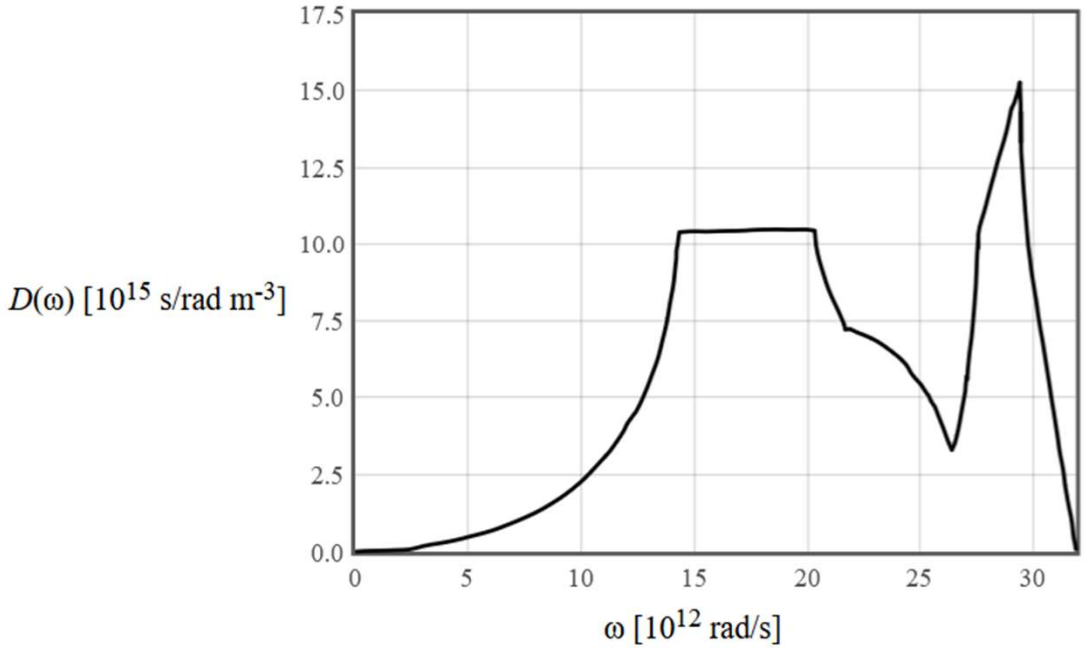
$$c_T = \sqrt{\frac{E(1-\nu)}{\rho(1-\upsilon-2\upsilon^2)}}$$

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



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

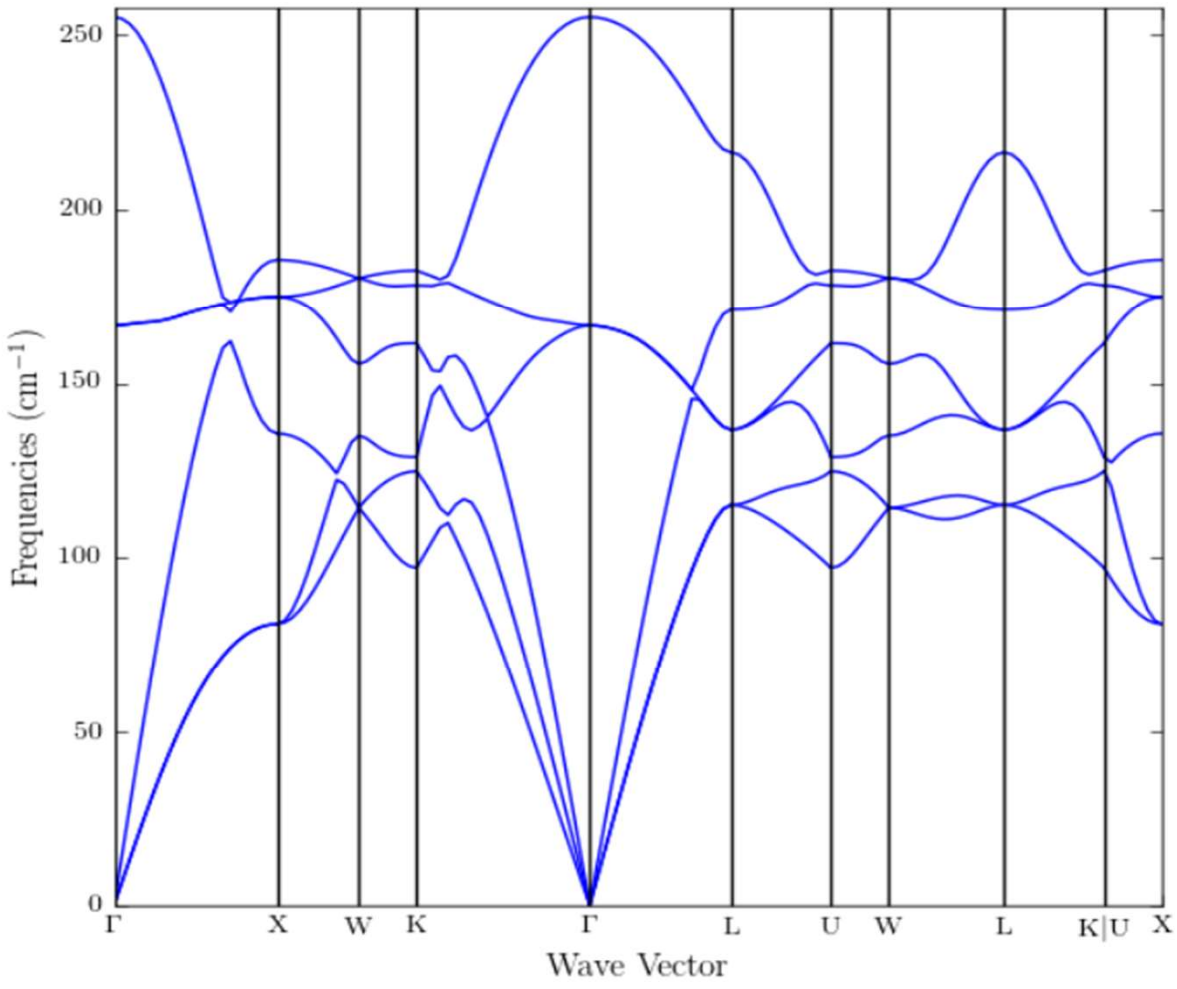
ω [rad/s]	$D(\omega)$ [s $rad^{-1}m^{-3}$]
0.0000	0.0000
5.7327e+10	6.8161e+12
4.0123e+11	2.3856e+13
7.4510e+11	3.0672e+13
1.0890e+12	3.4080e+13
1.4233e+12	4.0897e+13
1.7624e+12	5.1121e+13
2.0967e+12	5.7937e+13
2.4120e+12	7.4977e+13
2.7177e+12	1.2610e+14
3.0379e+12	1.8744e+14
3.3723e+12	2.3516e+14
3.7163e+12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

Vibrational Properties

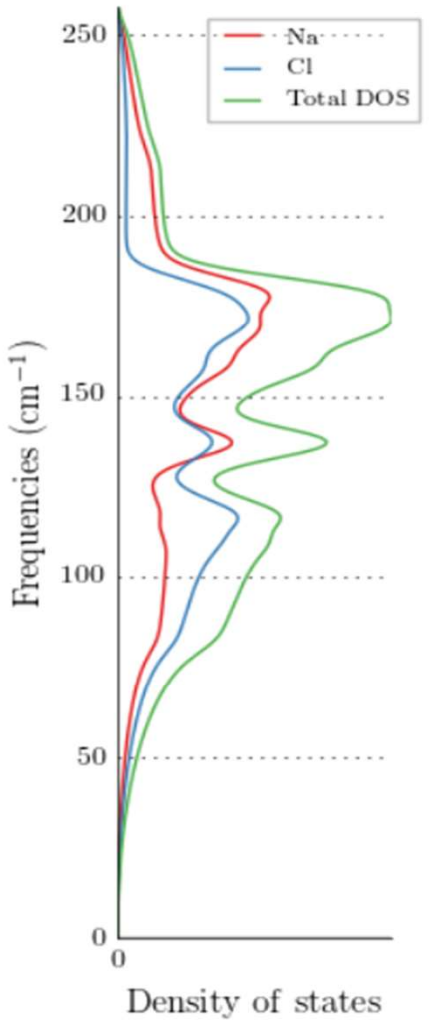
Reference for phonon calculations and visualization:

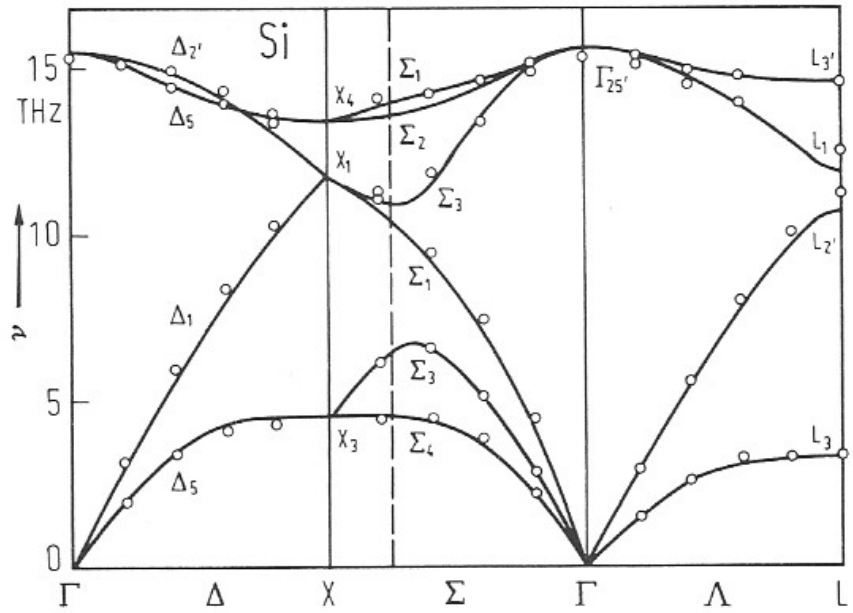
Visualize with phononwebsite

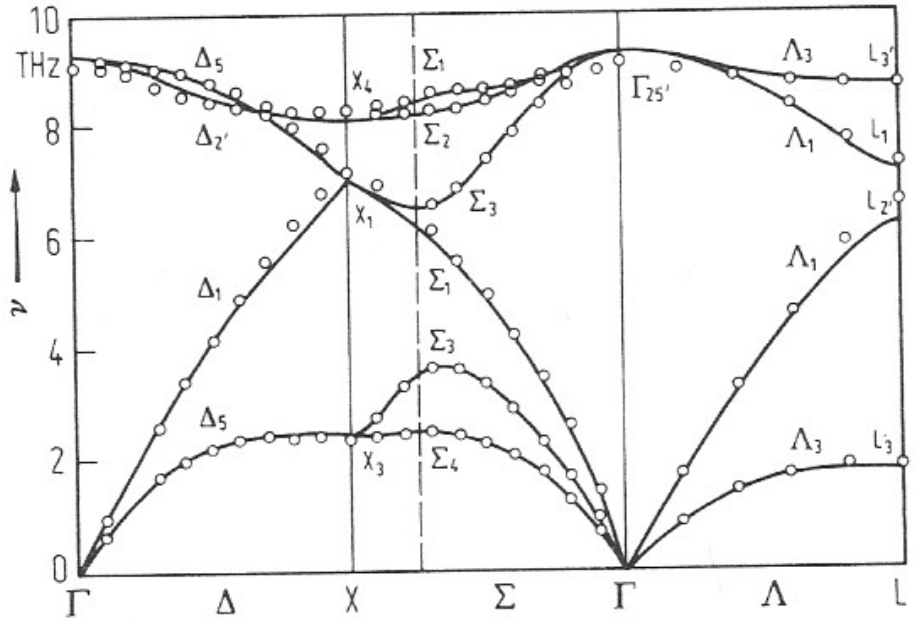
Phonon dispersion



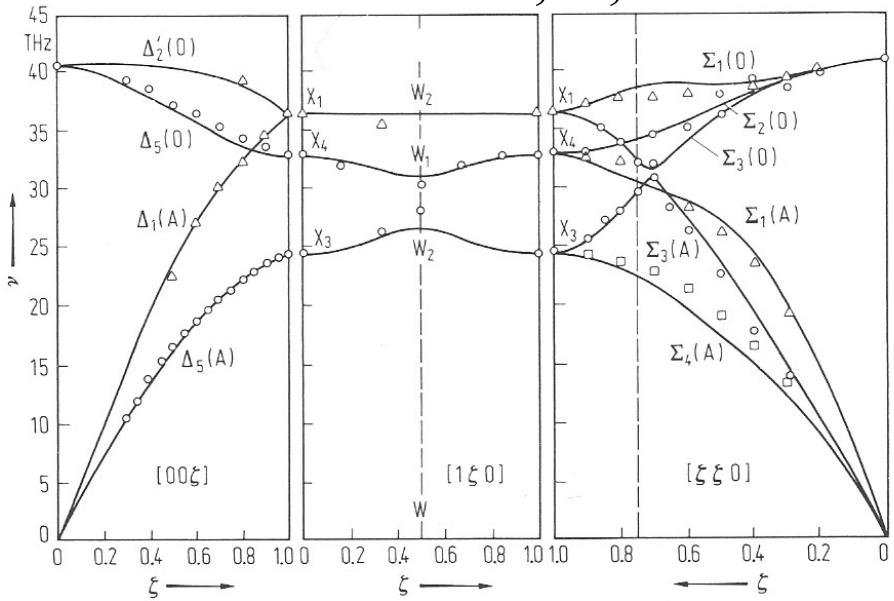
Density of States

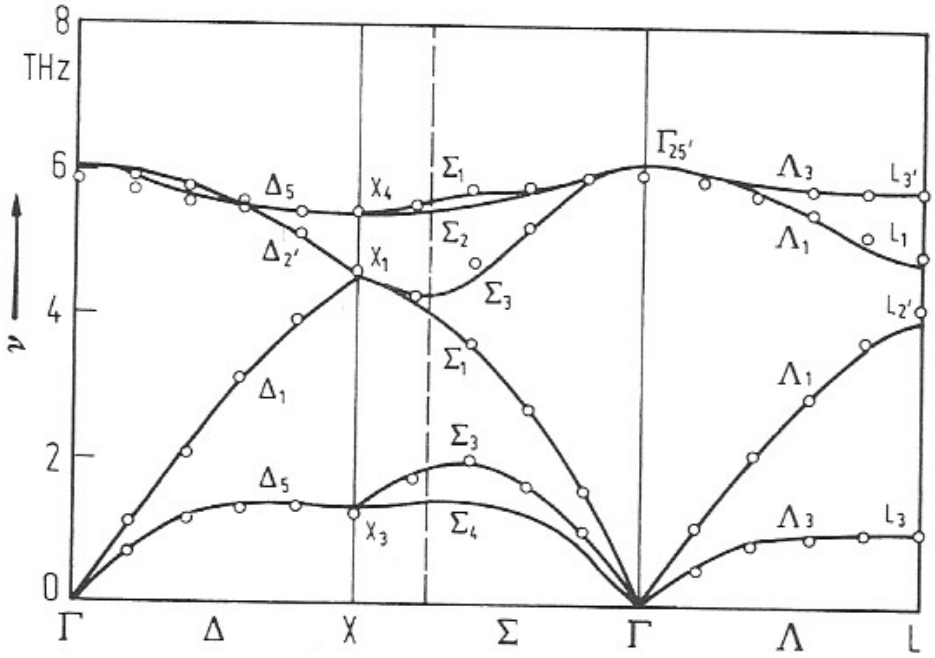



Si
15
THz
10
5
0
ν
Γ
Δ
X
Σ
Γ
Λ
L


10
THz
8
6
4
2
0
ν
Γ
Δ
X
Σ
Γ
Λ
L

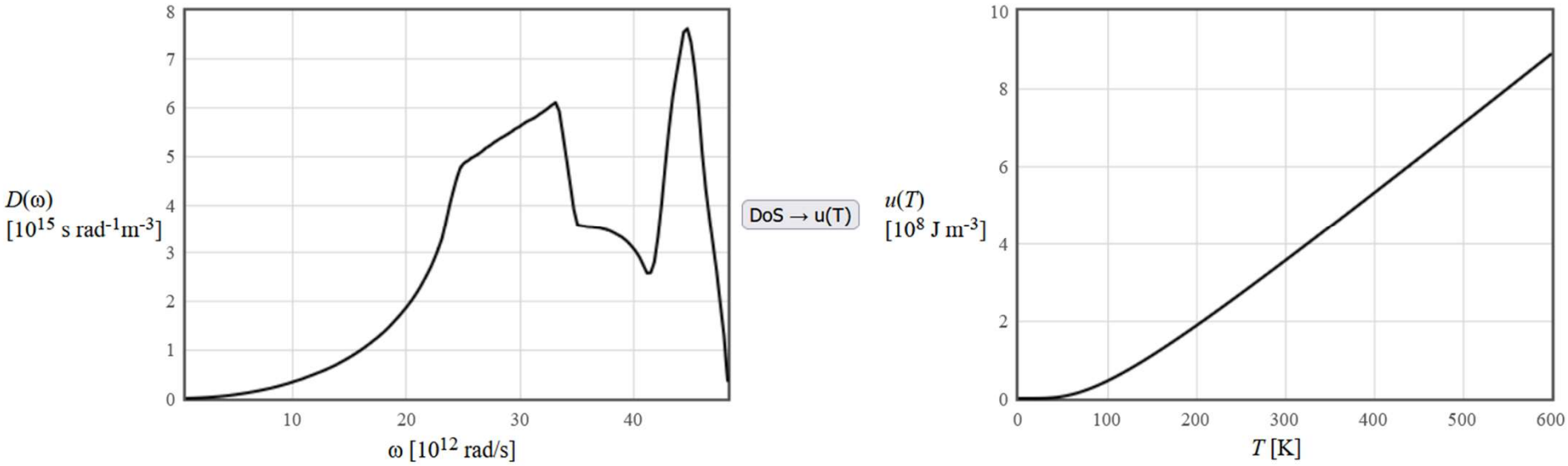
Ge, C, α-Sn ?


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