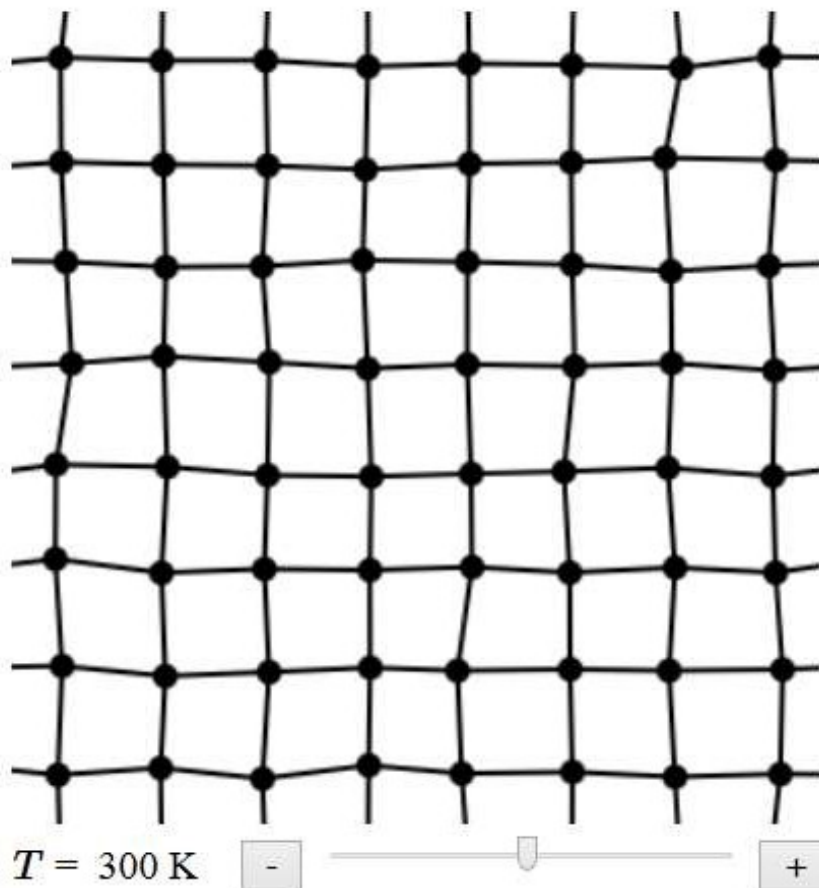


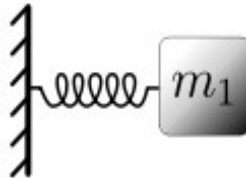
Phonons

Normal Modes and Phonons

At finite temperatures, the atoms in a crystal vibrate. In the simulation below, the atoms move randomly around their equilibrium positions.



Vibrations of a mass on a spring



$$m \frac{d^2 x}{dt^2} = -Cx$$

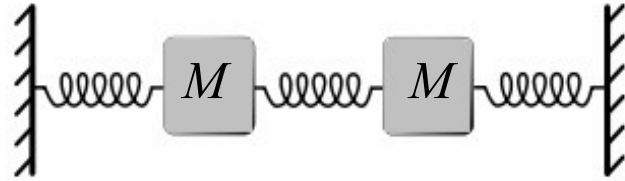
The solution has the form

$$x = Ae^{-i\omega t}$$

$$-\omega^2 m Ae^{-i\omega t} = -CAe^{-i\omega t}$$

$$\omega = \sqrt{\frac{C}{m}}$$

Coupled masses



Newton's law

$$M \frac{d^2 x_1}{dt^2} = -Cx_1 + C(x_2 - x_1)$$

$$M \frac{d^2 x_2}{dt^2} = -Cx_2 + C(x_1 - x_2)$$

assume harmonic solutions

$$x_1(t) = A_1 \exp(i\omega t)$$

$$x_2(t) = A_2 \exp(i\omega t)$$

$$-\omega^2 M A_1 e^{i\omega t} = -2C A_1 e^{i\omega t} + C A_2 e^{i\omega t}$$

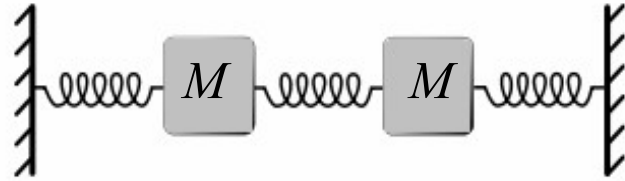
$$-\omega^2 M A_2 e^{i\omega t} = -2C A_2 e^{i\omega t} + C A_1 e^{i\omega t}$$

$$-\omega^2 M \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} -2C & C \\ C & -2C \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$$

Find the eigenvectors of this matrix

The masses oscillate with the same frequency but different phases

Coupled masses



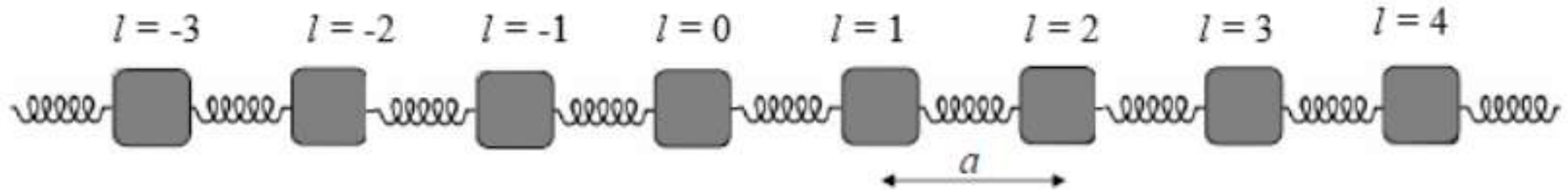
The normal modes are an in-phase mode where the masses move together,

$$\omega^2 M \begin{bmatrix} 1 \\ 1 \end{bmatrix} = C \begin{bmatrix} 1 \\ 1 \end{bmatrix} \rightarrow \omega = \sqrt{\frac{C}{M}},$$

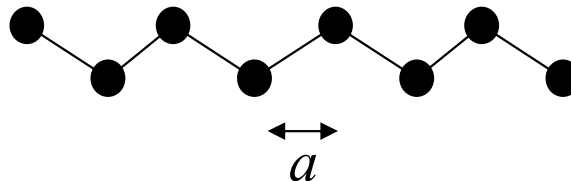
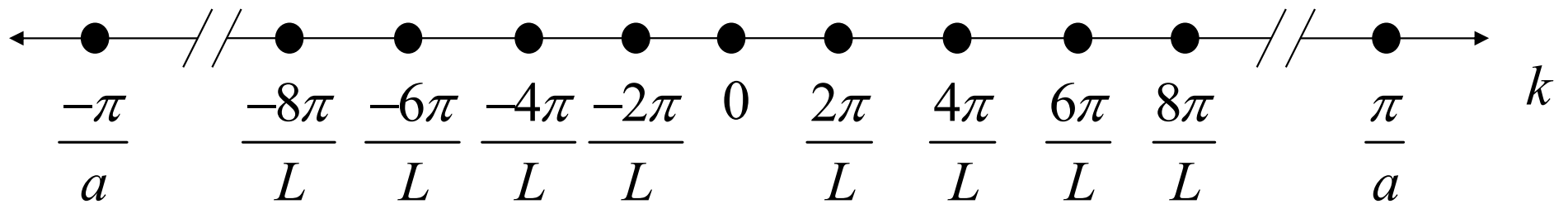
and an out-of-phase mode where the masses move in opposite directions,

$$\omega^2 M \begin{bmatrix} 1 \\ -1 \end{bmatrix} = 3C \begin{bmatrix} 1 \\ -1 \end{bmatrix} \rightarrow \omega = \sqrt{\frac{3C}{M}}.$$

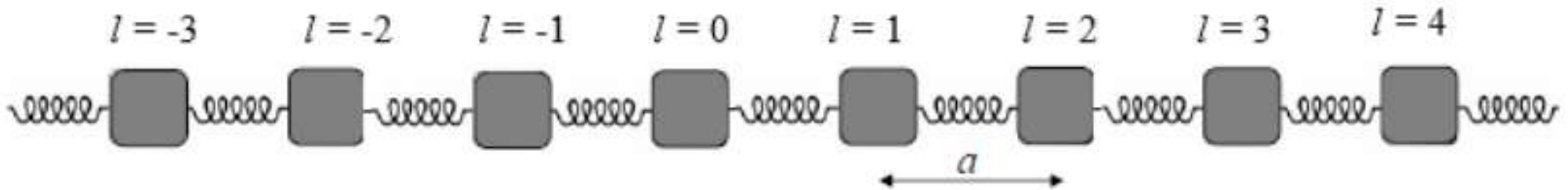
Linear Chain



solution: $u_l = A_k \exp(i(lka - \omega t))$



Linear Chain



$$M \frac{d^2 u_l}{dt^2} = C(u_{l-1} - u_l) + C(u_{l+1} - u_l).$$

$$\text{solution: } u_l = A_k \exp(i(lka - \omega t))$$

Substitute the solution in the equation:

$$\begin{aligned} -M\omega^2 A_k \exp(i(lka - \omega t)) &= C(A_k \exp(i((l-1)ka - \omega t)) - A_k \exp(i(lka - \omega t))) \\ &\quad + C(A_k \exp(i((l+1)ka - \omega t)) - A_k \exp(i(lka - \omega t))). \end{aligned}$$

Multiply by e^{-ilka}

$$-M\omega^2 = C(\exp(-ika) + \exp(ika) - 2)$$

$$\sin^2 \frac{ka}{2} = \frac{1}{2}(1 - \cos ka)$$

$$M\omega^2 = 2C(1 - \cos(ka))$$

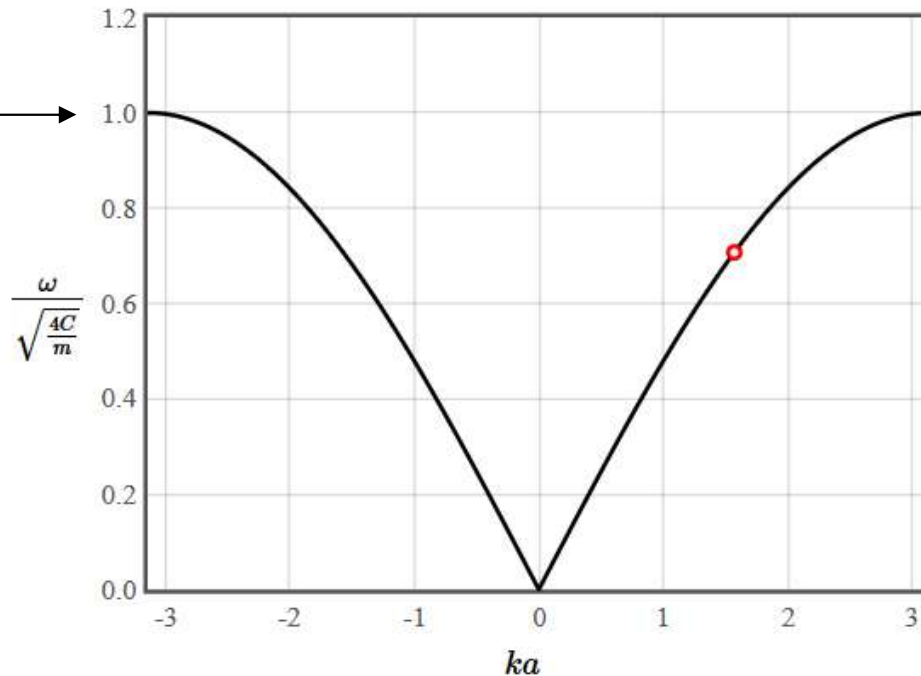
$$\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

Linear Chain - dispersion relation



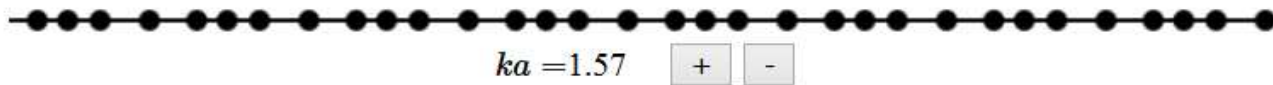
$$M \frac{d^2 u_l}{dt^2} = C(u_{l-1} - u_l) + C(u_{l+1} - u_l).$$

Max. freq. →



$$u_l = A_k \exp(i(lka - \omega t))$$

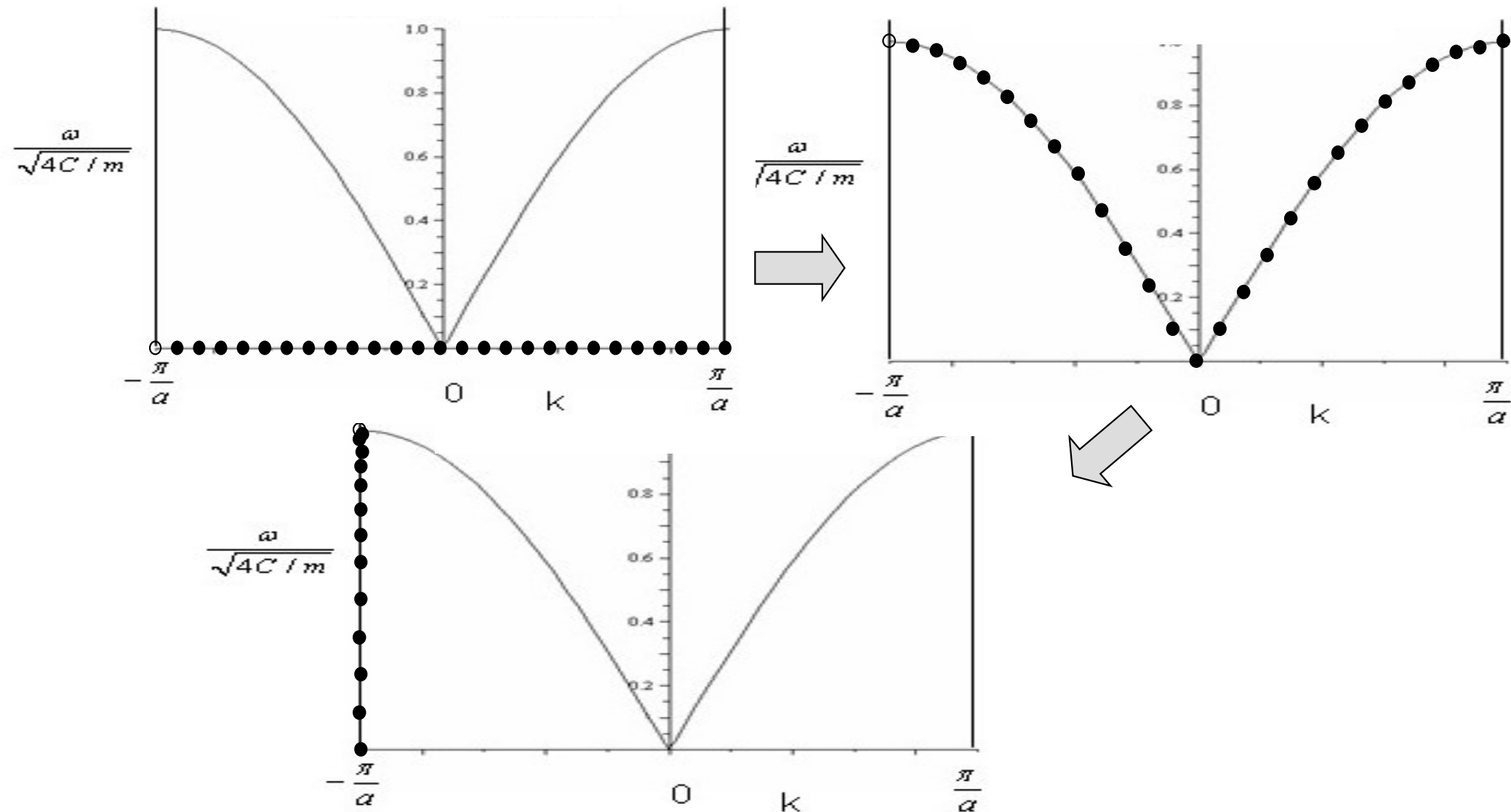
$$\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$



$$\text{speed of sound} = \sqrt{\frac{C}{m}} a$$

Linear Chain - density of states

Determine the density of states numerically $\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$



Linear Chain - density of states

This case is an exception where the density of states can be determined analytically.

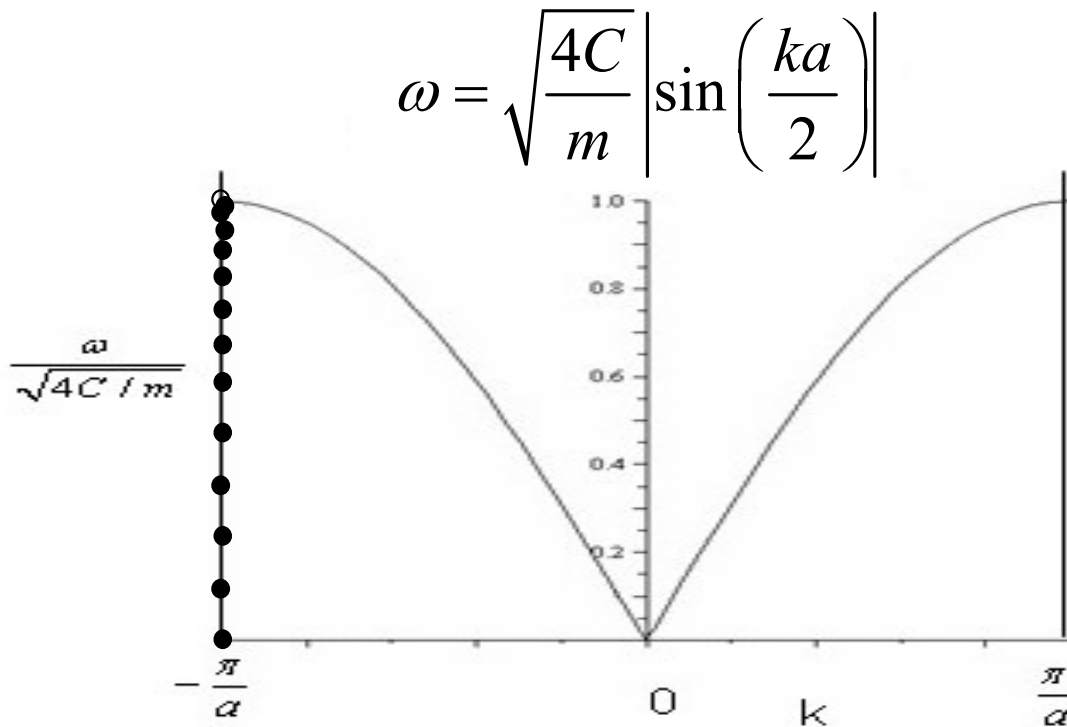
$$\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

$$D(k) = \frac{1}{\pi}$$

$$D(\omega) = D(k) \frac{dk}{d\omega}$$

$$d\omega = a \sqrt{\frac{C}{m}} \cos\left(\frac{ka}{2}\right) dk$$

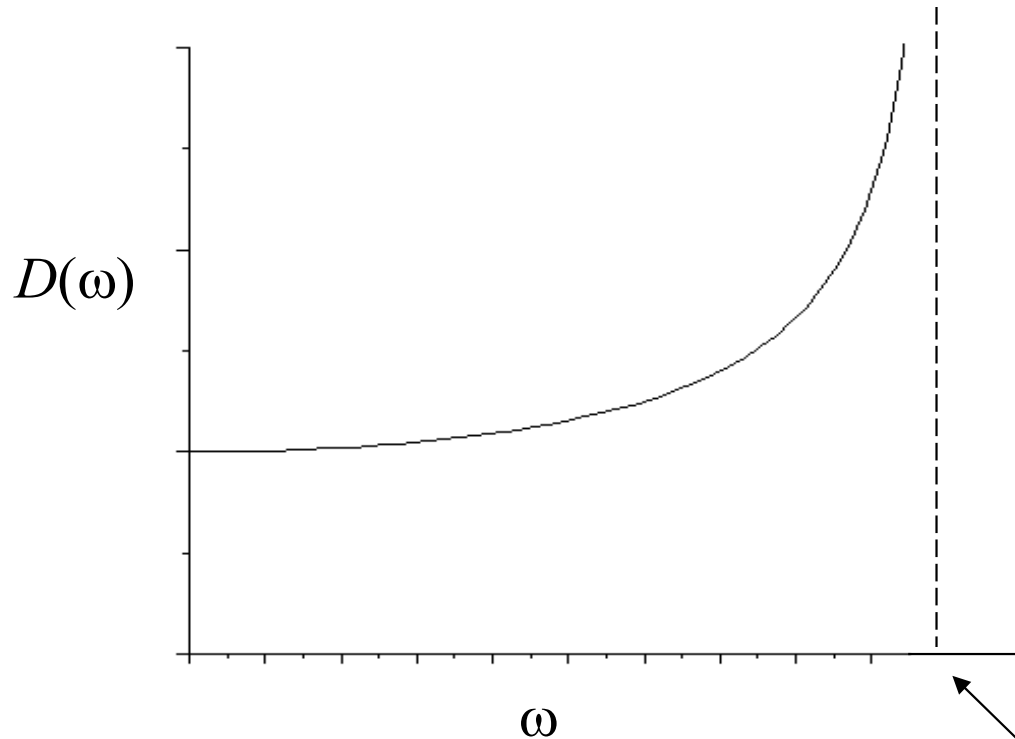
$$D(\omega) = \frac{1}{\pi a \sqrt{\frac{C}{m}} \sqrt{1 - \frac{\omega^2 m}{4C}}}$$



for every k calculate the frequency

density of states

van Hove singularity



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

$$D(k) = \frac{1}{\pi}$$

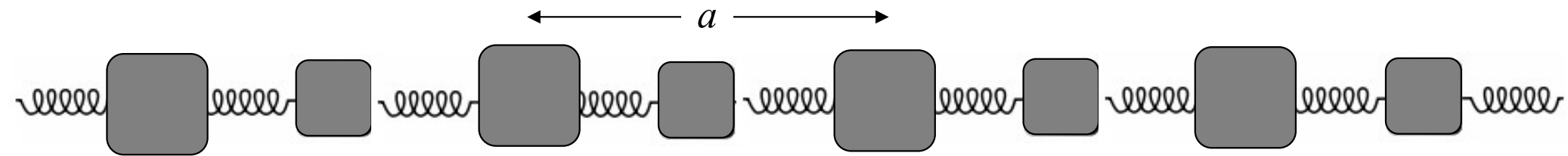
$$D(k)dk = D(\omega)d\omega$$

$$d\omega = a\sqrt{\frac{C}{m}} \cos\left(\frac{ka}{2}\right) dk$$

$$D(\omega) = \frac{1}{\pi a \sqrt{\frac{C}{m}} \sqrt{1 - \frac{\omega^2 m}{4C}}}$$

maximum frequency

Linear chain M_1 and M_2



Newton's law: $M_1 \frac{d^2 u_s}{dt^2} = C(v_{s-1} - u_s) + C(v_s - u_s)$

$2N$ modes $M_2 \frac{d^2 v_s}{dt^2} = C(u_s - v_s) + C(u_{s+1} - v_s)$

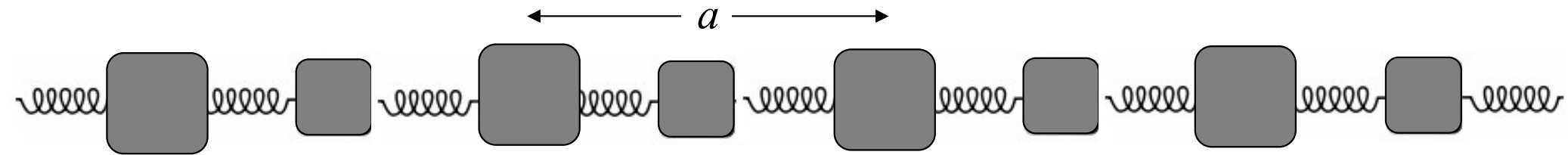
assume harmonic solutions $u_s = u_k e^{i(ksa - \omega t)}$

$v_s = v_k e^{i(ksa - \omega t)}$

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

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

Linear chain M_1 and M_2



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

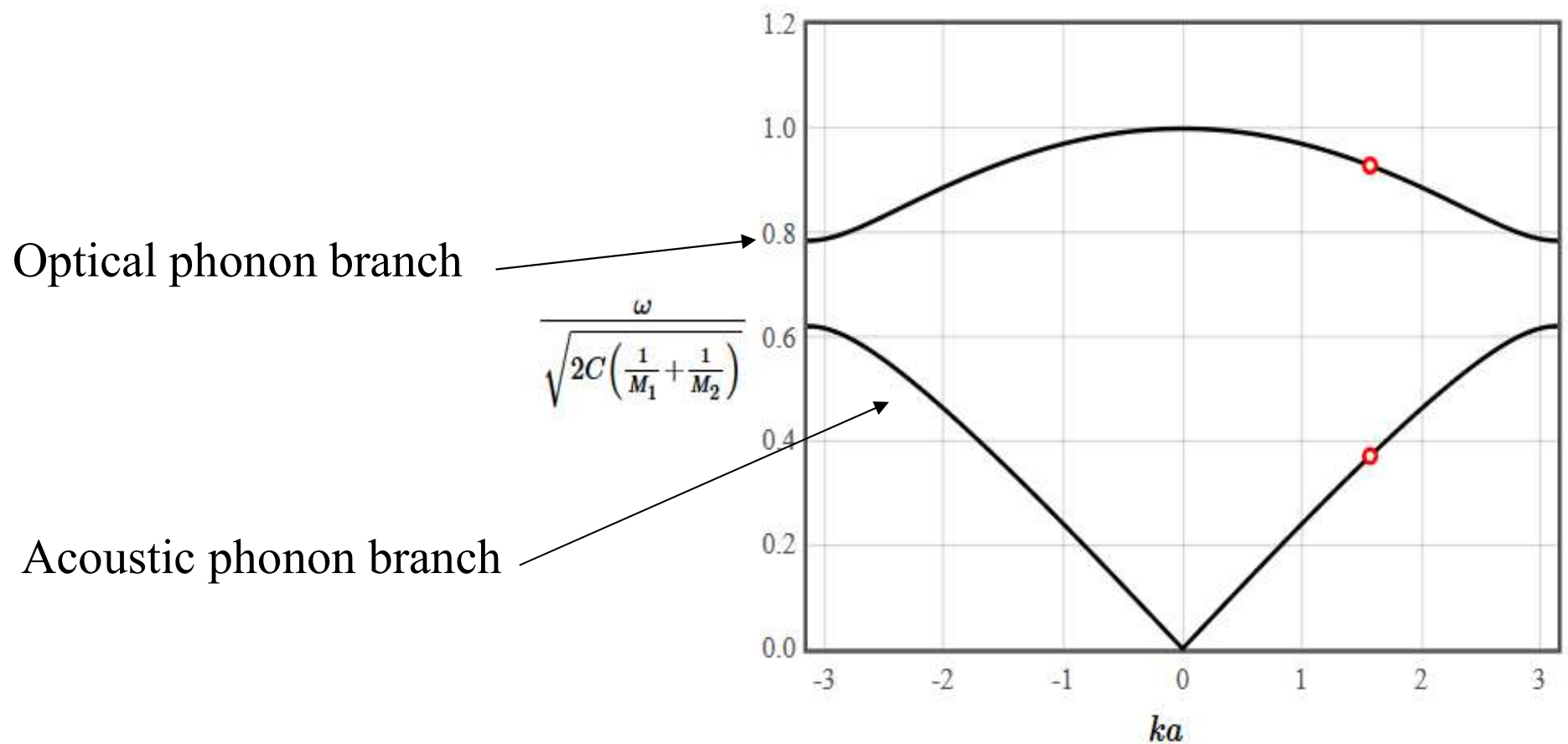
$$-\omega^2 M_2 v_k = C u_k (1 + \exp(ika)) - 2C v_k$$

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

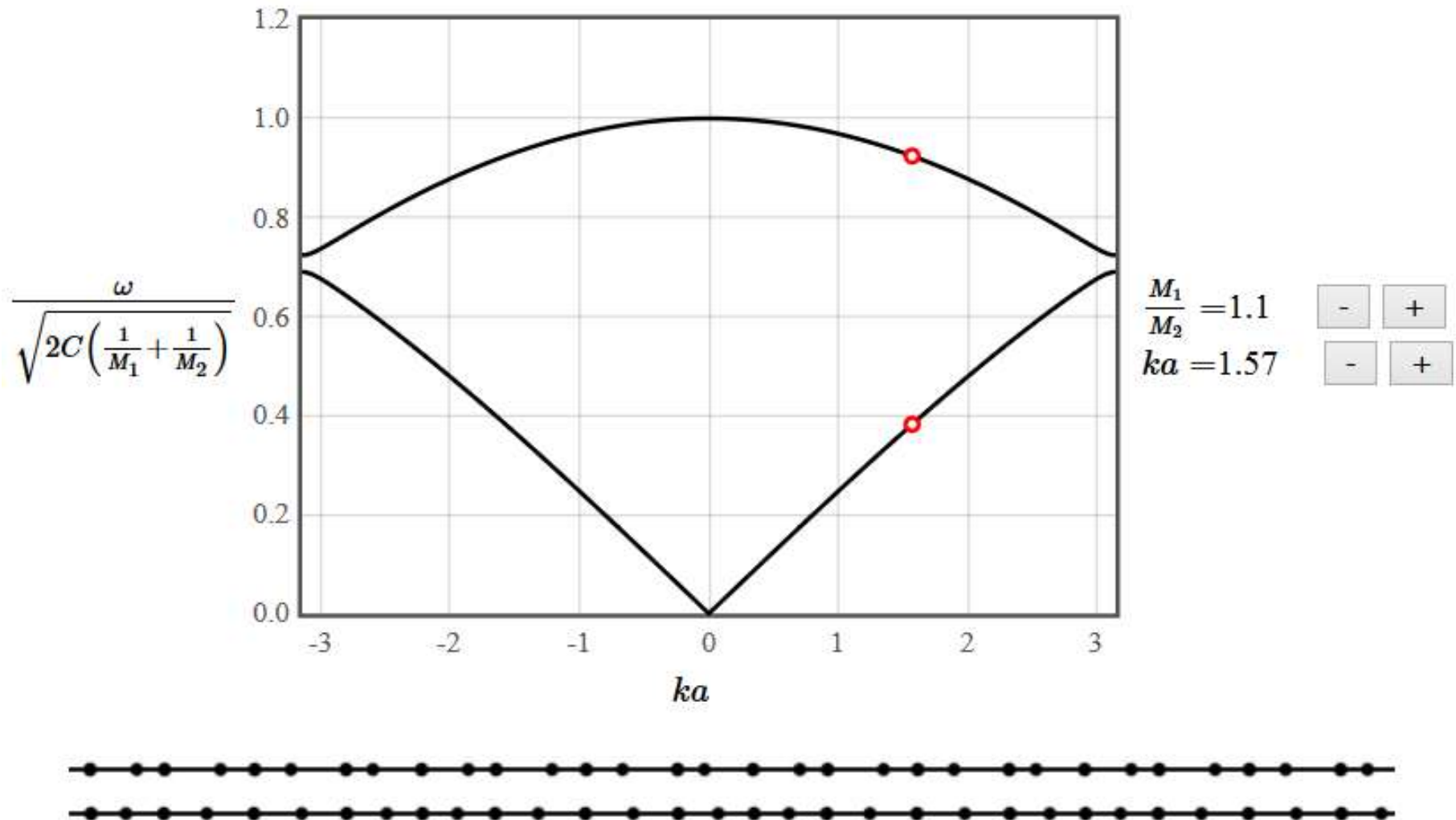
$$M_1 M_2 \omega^4 - 2C(M_1 + M_2) \omega^2 + 2C^2 (1 - \cos(ka)) = 0$$

dispersion relation

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

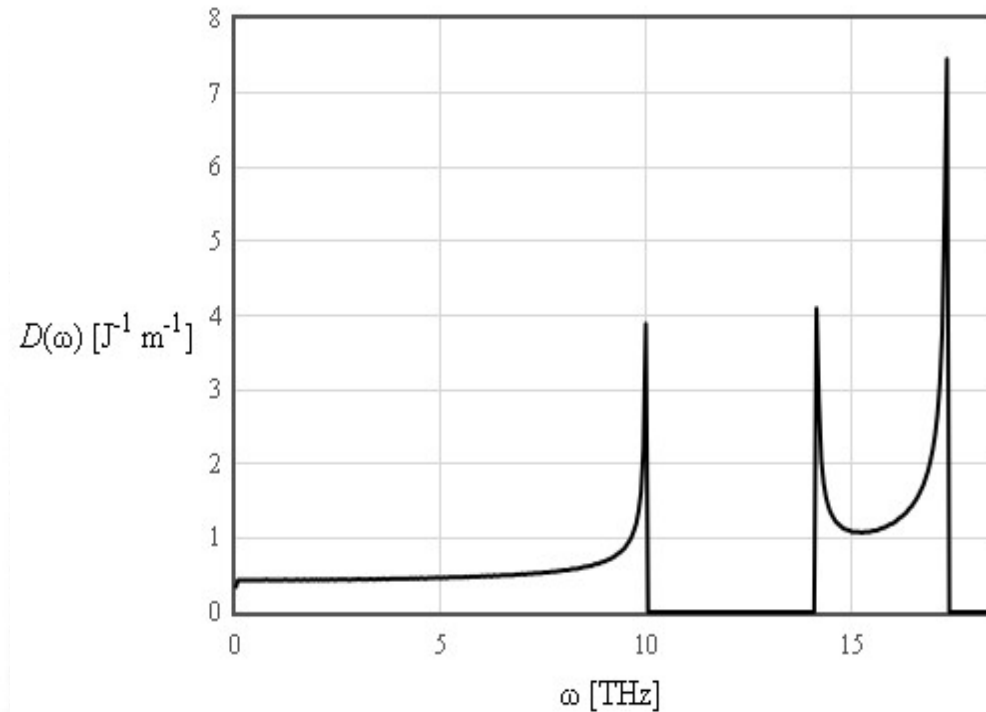
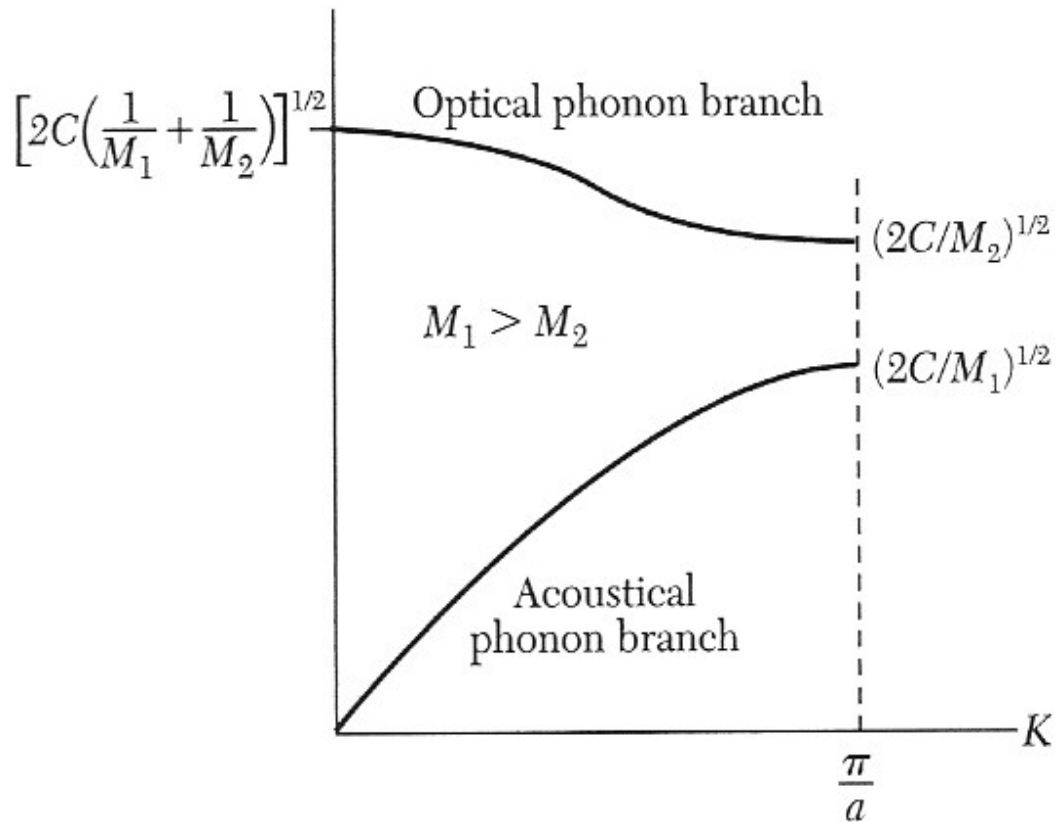


normal modes



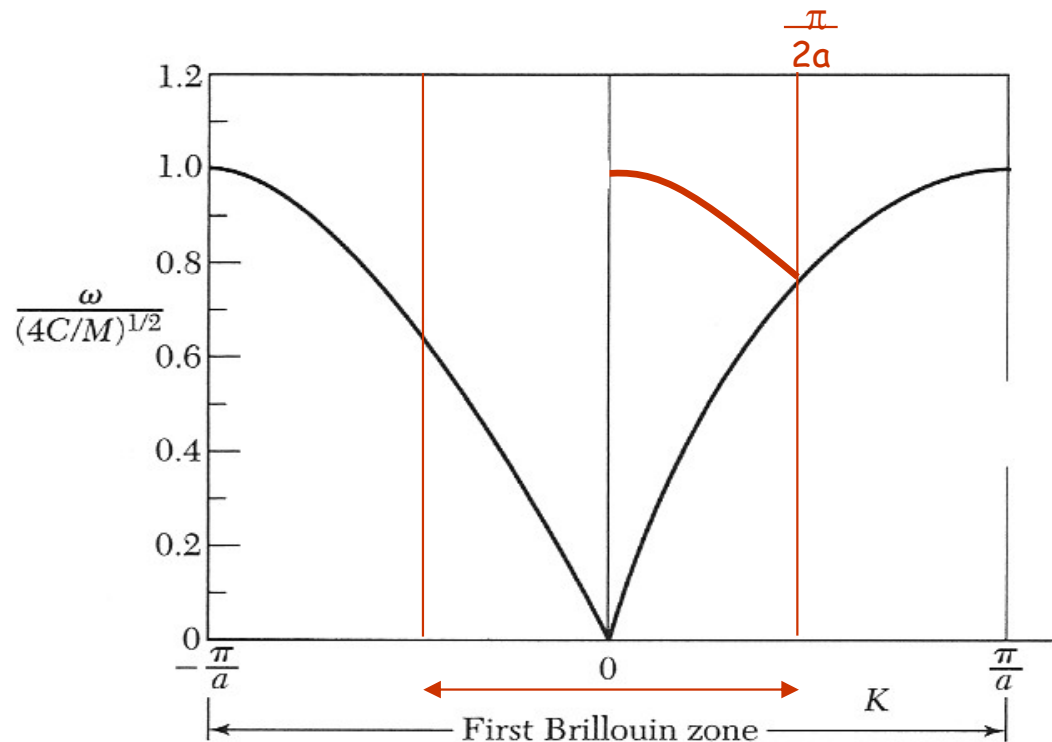
<http://lampx.tugraz.at/~hadley/ss1/phonons/1d/1d2m.php>

density of states

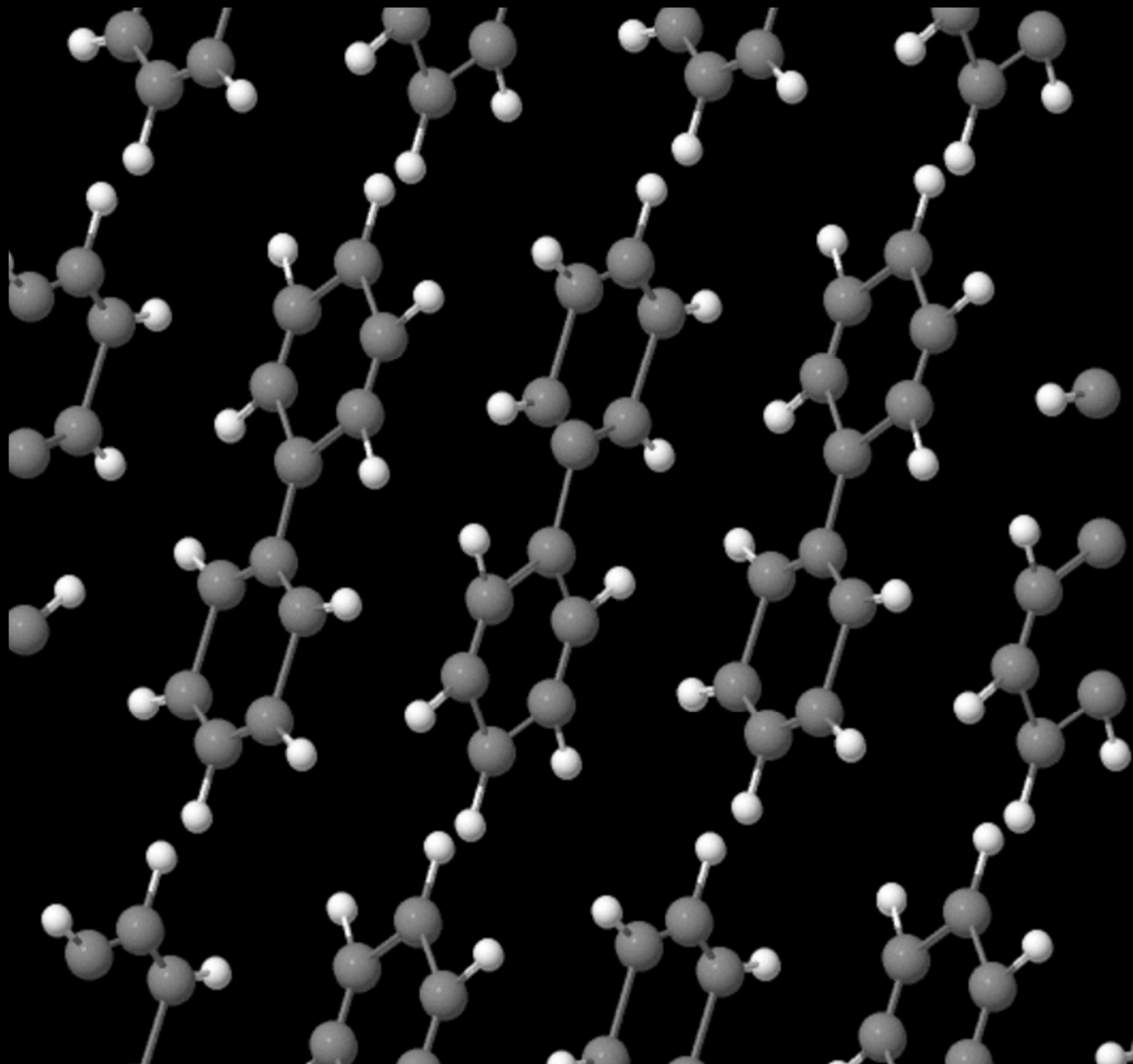


$$\omega^2 = C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm C \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2 ka}{M_1 M_2}}$$

Linear chain M_1 and M_2



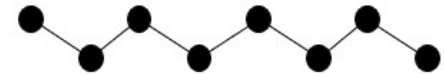
The branches of the dispersion curves can be translated by a reciprocal lattice vector $\vec{G}$.



Phonons in 3D crystals

Consider a simple cubic crystal with one atom in the basis, a lattice constant of a , and the dimensions $L \times L \times L$.

Periodic solutions satisfy



$$k_x, k_y, k_z = -\frac{\pi}{a} \cdots -\frac{6\pi}{L}, -\frac{4\pi}{L}, -\frac{2\pi}{L}, 0, \frac{2\pi}{L}, \frac{4\pi}{L}, \frac{6\pi}{L}, \cdots \frac{\pi}{a}$$

The allowed wavevectors for the phonon normal modes are only those wavevectors in the first Brillouin zone.

$$\left(\frac{2\pi}{a}\right)^3 \left(\frac{L}{2\pi}\right)^3 = N$$

The number of allowed $\mathbf{k}$ vectors in the first Brillouin zone is the number N of primitive unit cells in the crystal.

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

Normal modes are eigenfunctions of T

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

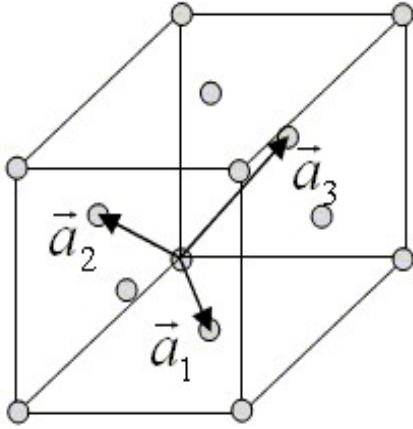
$$u_{lmn}^y = u_{\vec{k}}^y \exp\left(i\left(\vec{l}\vec{k} \cdot \vec{a}_1 + m\vec{k} \cdot \vec{a}_2 + n\vec{k} \cdot \vec{a}_3 - \omega t\right)\right)$$

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

These are eigenfunctions of T.

$$\begin{aligned} T_{pqr} u_{lmn}^x &= u_{\vec{k}}^x \exp\left(i\left(\vec{l}\vec{k} \cdot (\vec{a}_1 + p\vec{a}_1) + m\vec{k} \cdot (\vec{a}_2 + q\vec{a}_2) + n\vec{k} \cdot (\vec{a}_3 + r\vec{a}_3) - \omega t\right)\right) \\ &= \exp\left(i\left(lp\vec{k} \cdot \vec{a}_1 + qm\vec{k} \cdot \vec{a}_2 + rn\vec{k} \cdot \vec{a}_3\right)\right) u_{\vec{k}}^x \exp\left(i\left(\vec{l}\vec{k} \cdot \vec{a}_1 + m\vec{k} \cdot \vec{a}_2 + n\vec{k} \cdot \vec{a}_3 - \omega t\right)\right) \\ &= \exp\left(i\left(lp\vec{k} \cdot \vec{a}_1 + qm\vec{k} \cdot \vec{a}_2 + rn\vec{k} \cdot \vec{a}_3\right)\right) u_{lmn}^x \end{aligned}$$

fcc



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

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

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

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

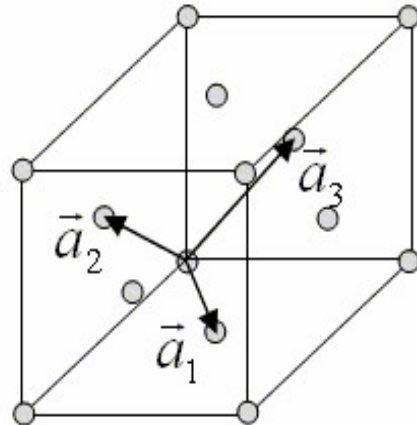
$$\vec{b}_2 = \frac{2\pi}{a} (\hat{k}_x - \hat{k}_y + \hat{k}_z)$$

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

$$\begin{aligned} m \frac{d^2 u_{lmn}^x}{dt^2} = & \frac{C}{2} \left[(u_{l+1mn}^x - u_{lmn}^x) + (u_{l-1mn}^x - u_{lmn}^x) + (u_{lm+1n}^x - u_{lmn}^x) + (u_{lm-1n}^x - u_{lmn}^x) \right. \\ & + (u_{l+1mn-1}^x - u_{lmn}^x) + (u_{l-1mn+1}^x - u_{lmn}^x) + (u_{lm+1n-1}^x - u_{lmn}^x) + (u_{lm-1n+1}^x - u_{lmn}^x) \\ & + (u_{l+1mn}^y - u_{lmn}^y) + (u_{l-1mn}^y - u_{lmn}^y) - (u_{lm+1n-1}^y - u_{lmn}^y) - (u_{lm-1n+1}^y - u_{lmn}^y) \\ & \left. + (u_{lm+1n}^z - u_{lmn}^z) + (u_{lm-1n}^z - u_{lmn}^z) - (u_{l+1mn-1}^z - u_{lmn}^z) - (u_{l-1mn+1}^z - u_{lmn}^z) \right] \end{aligned}$$

and similar expressions for the y and z motion

fcc



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

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

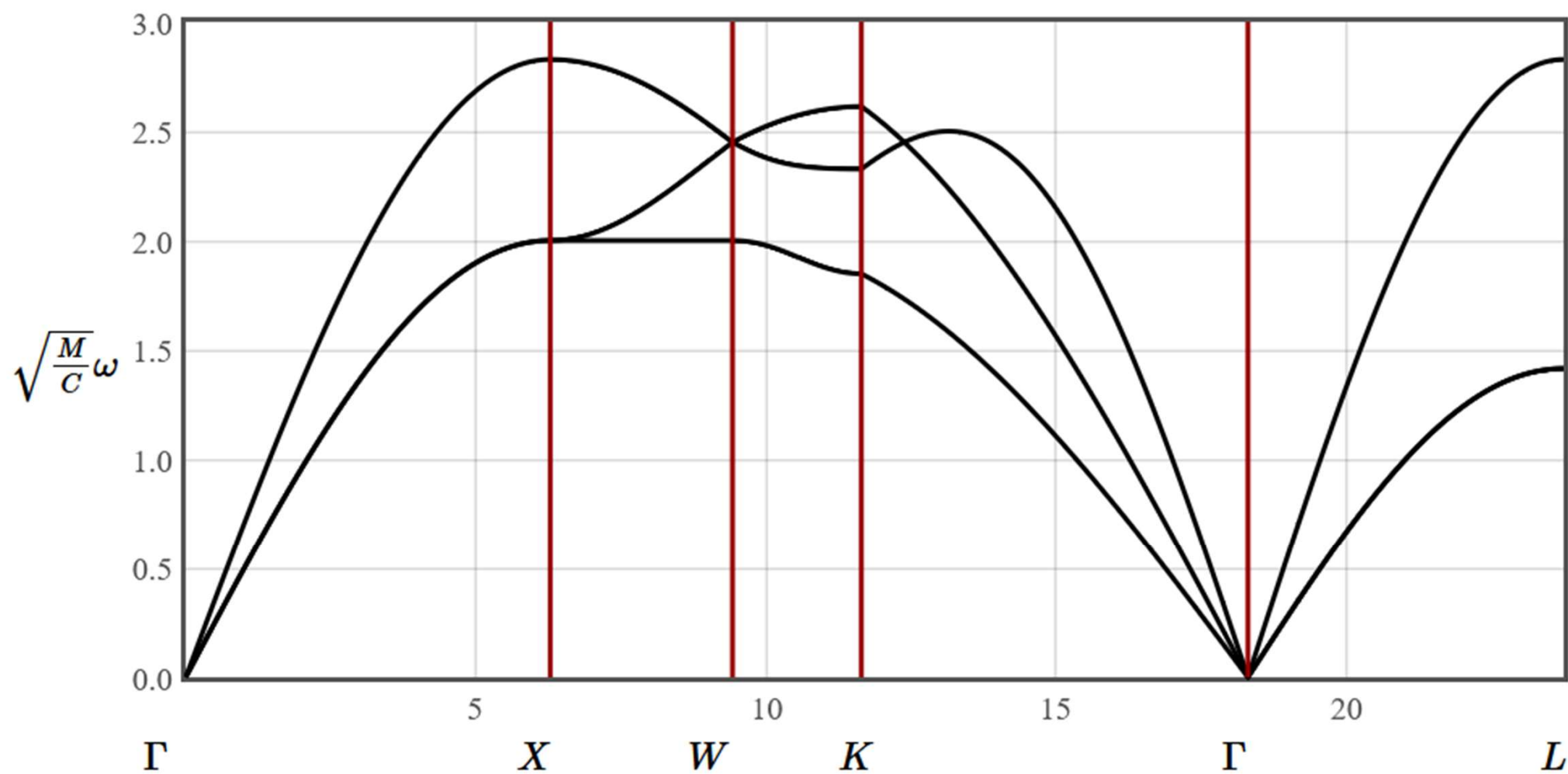
$$\vec{a}_3 = \frac{a}{2} \hat{y} + \frac{a}{2} \hat{z}$$

Substitute the eigenfunctions of T into Newton's laws.

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

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

For every k there are 3 solutions for ω .



Phonon dispersion Au

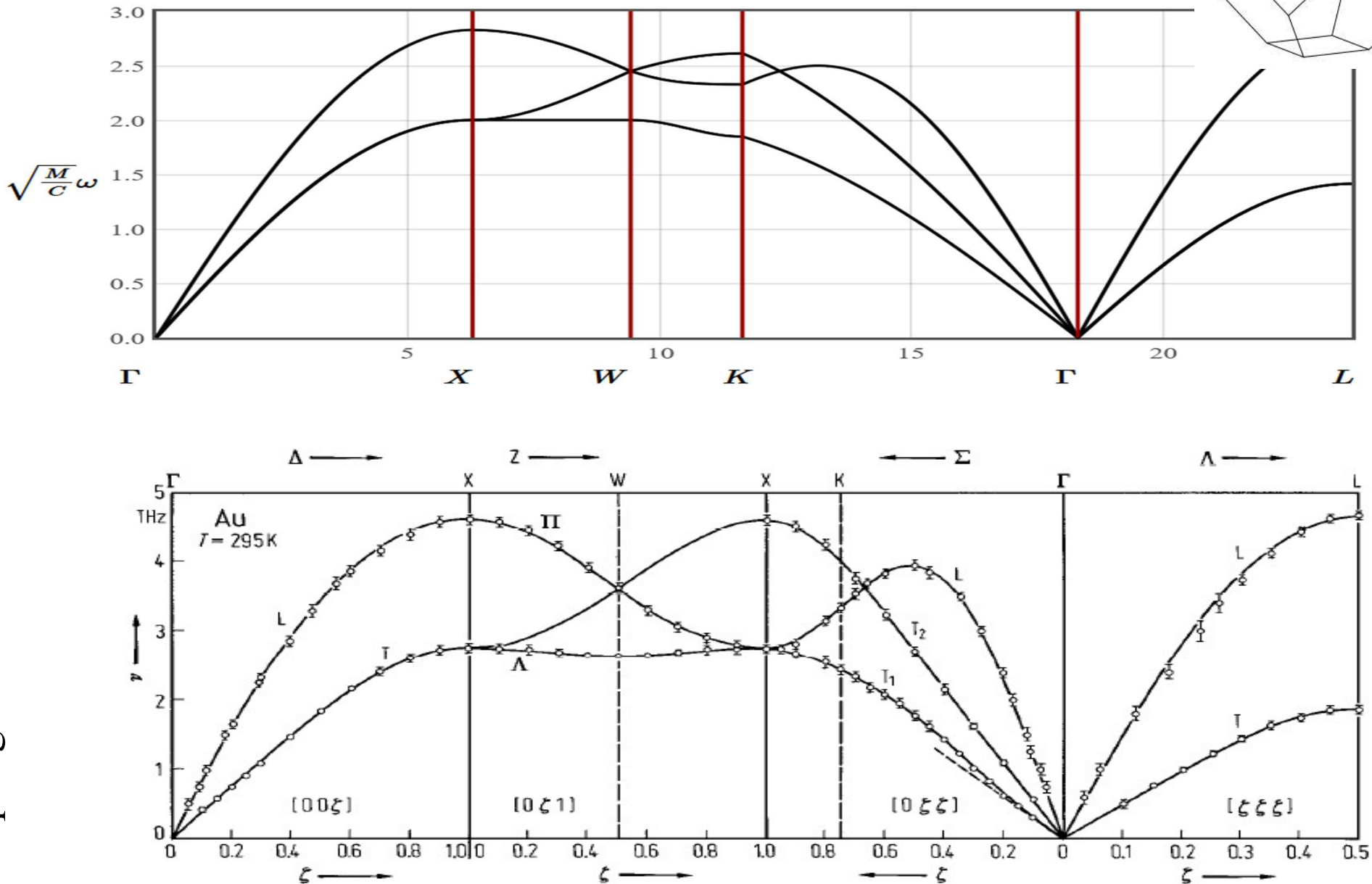
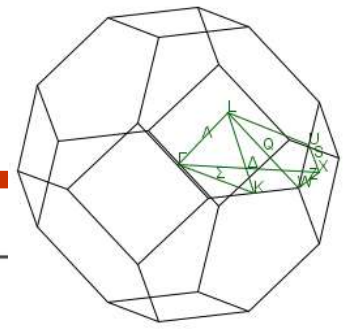
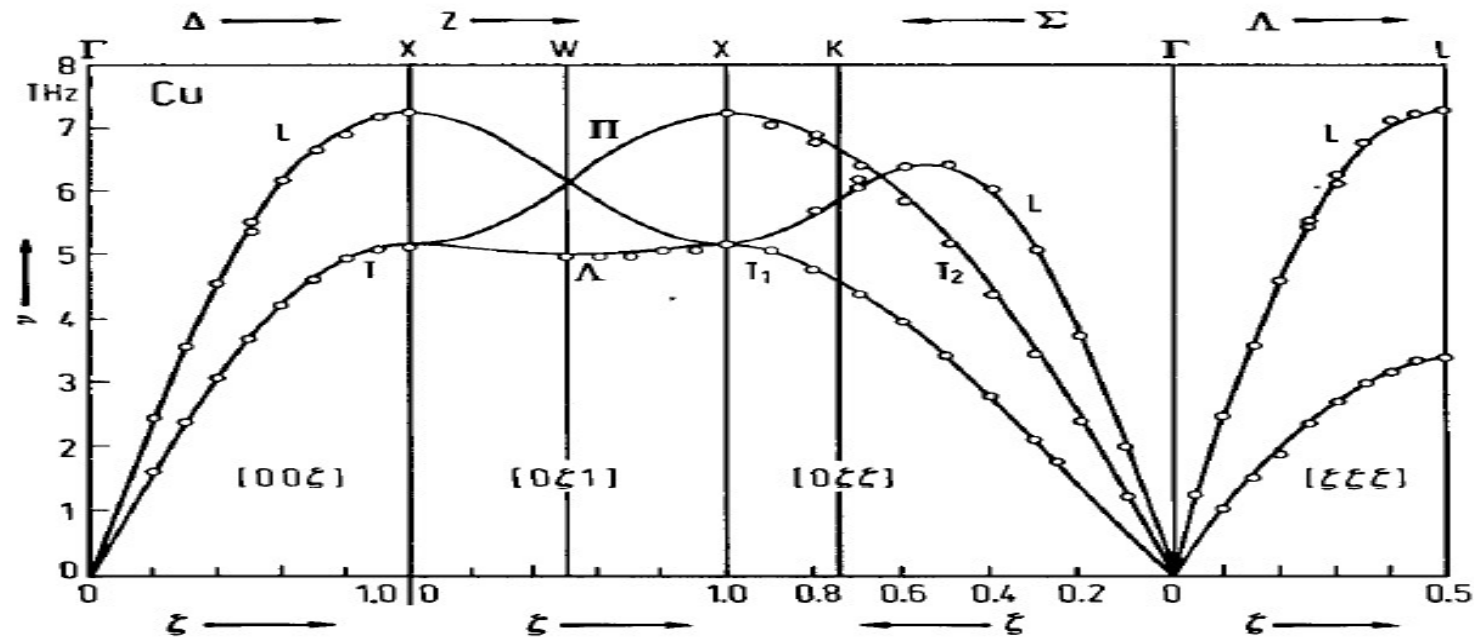
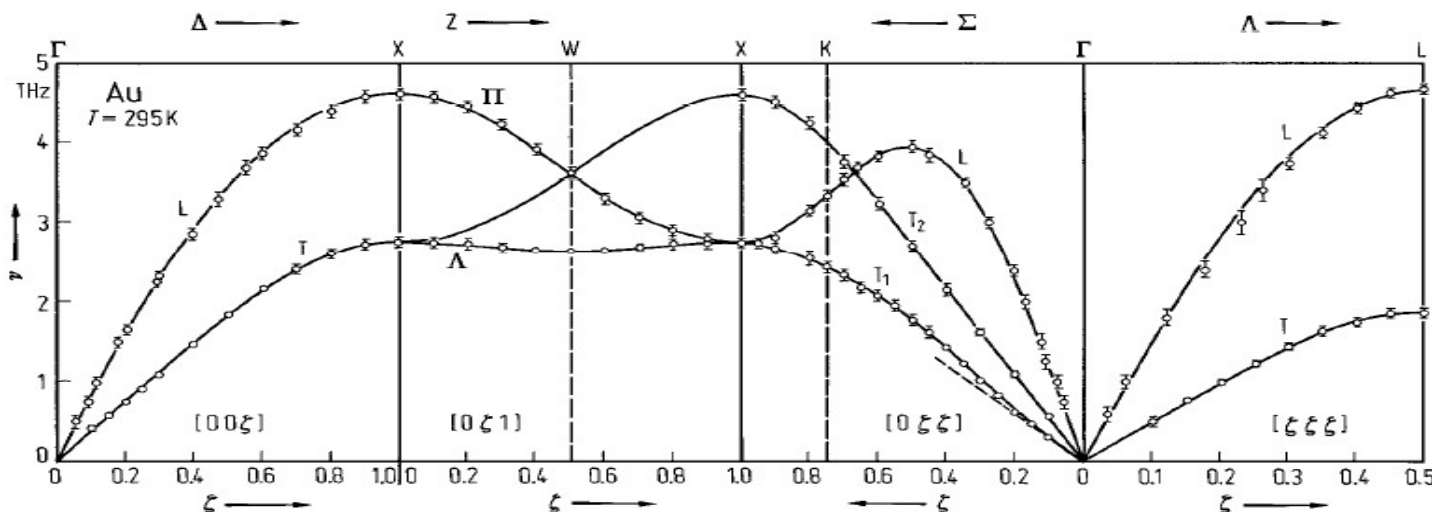


Fig. 1. Au. Phonon dispersion relations in the principal symmetry directions according to [73Ly1]. The solid curves represent both the fourth neighbour general force model (M1) and the fifth neighbour axially symmetric model (M2) of Table 3 Au. The dotted line in the Σ direction is corresponding to the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

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



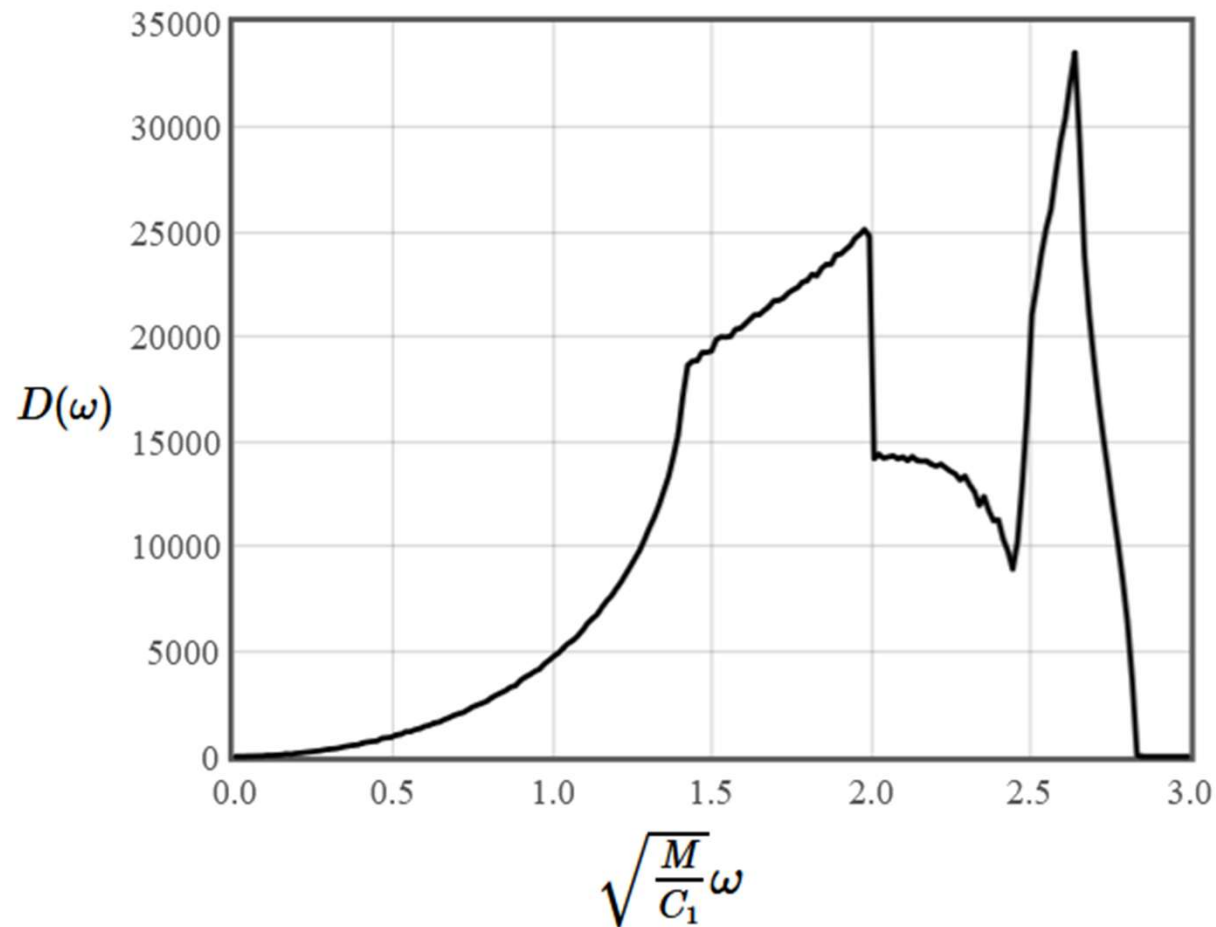
Cu



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 $\zeta\zeta$] T₁ branch.

Phonon density of states of a fcc crystal



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

Phonon DOS fcc

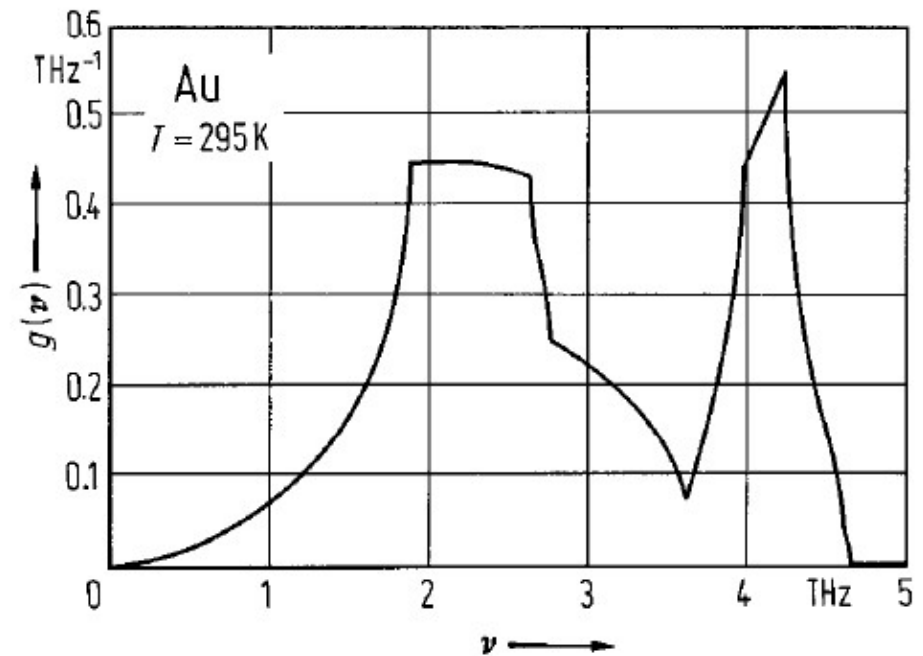
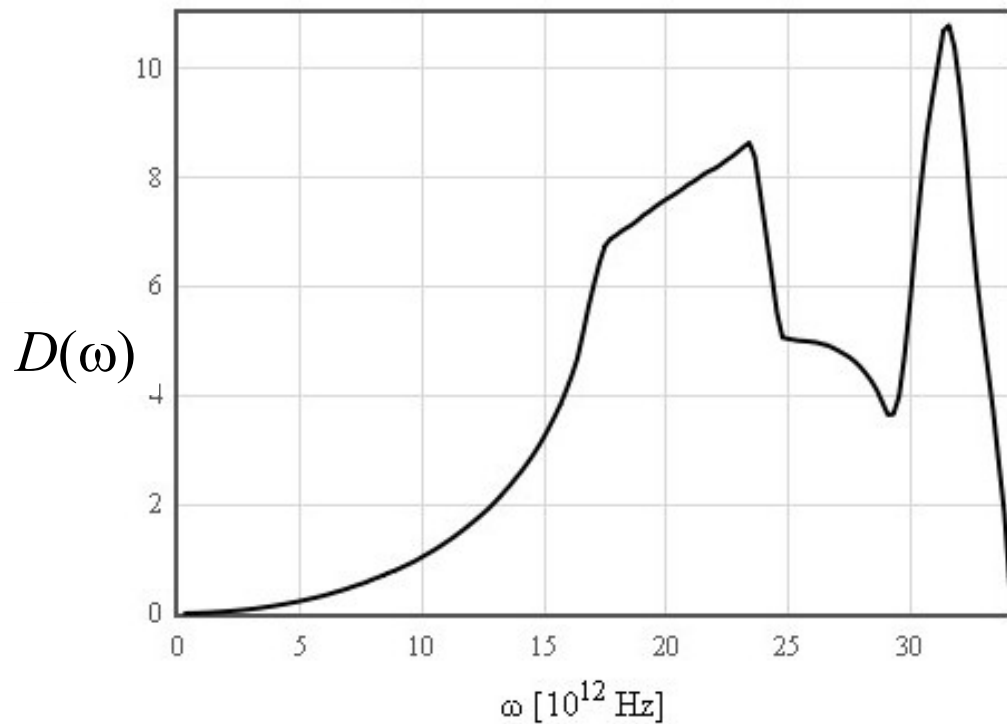
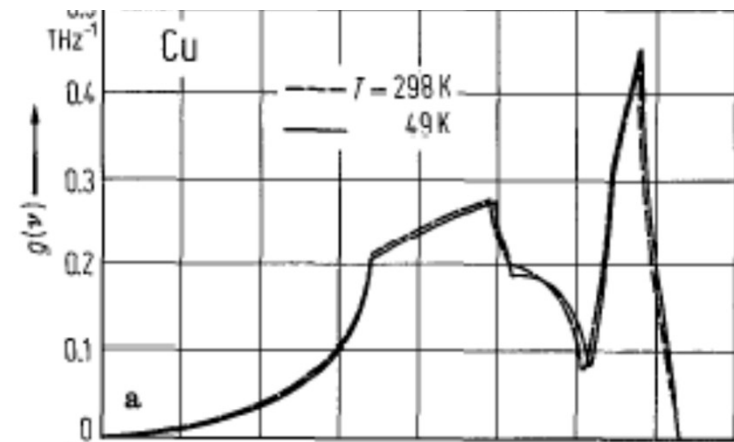
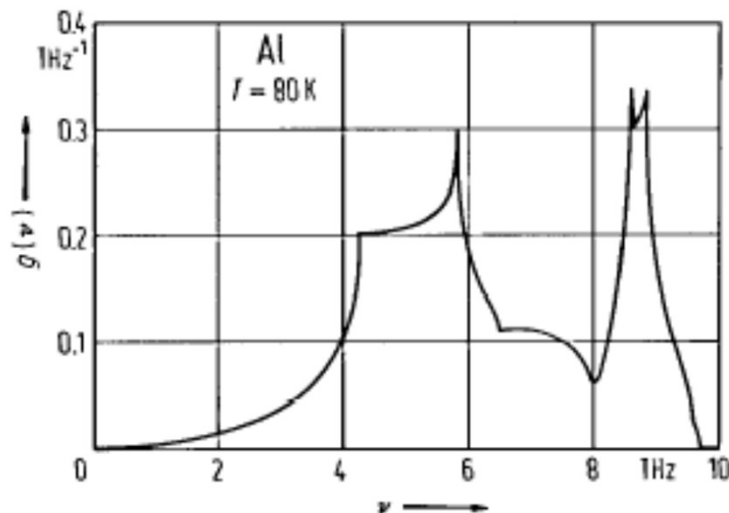
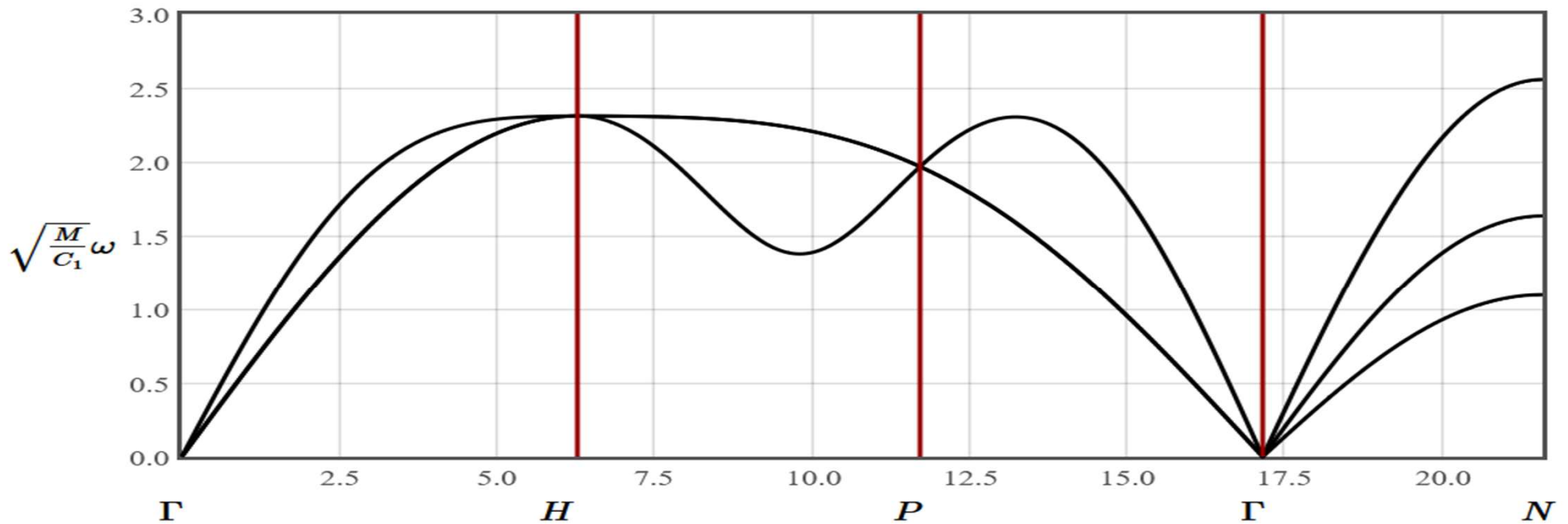
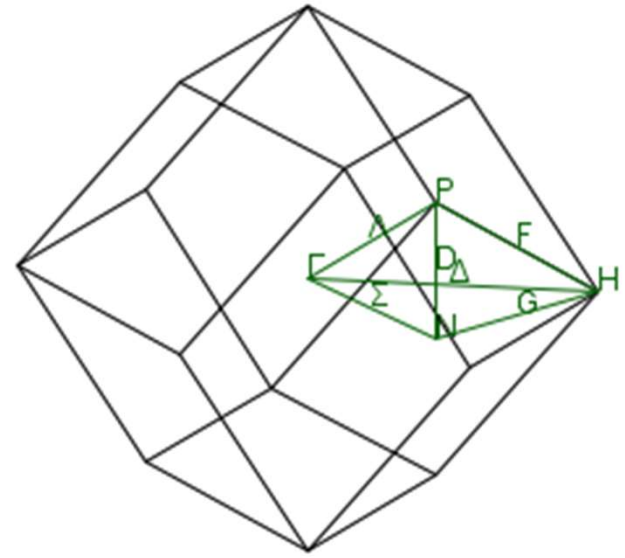
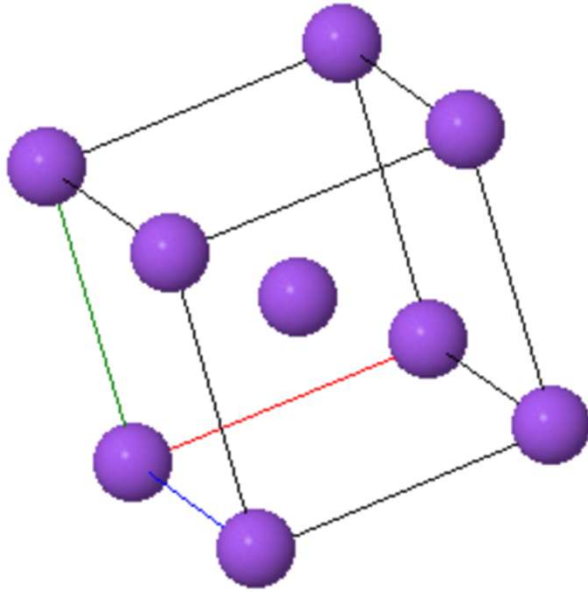


Fig. 2. Au. Frequency distribution calculated from the fourth neighbour general force constant model (M1) of Table 3 Au.



Phonon dispersion bcc



Phonon dispersion Fe

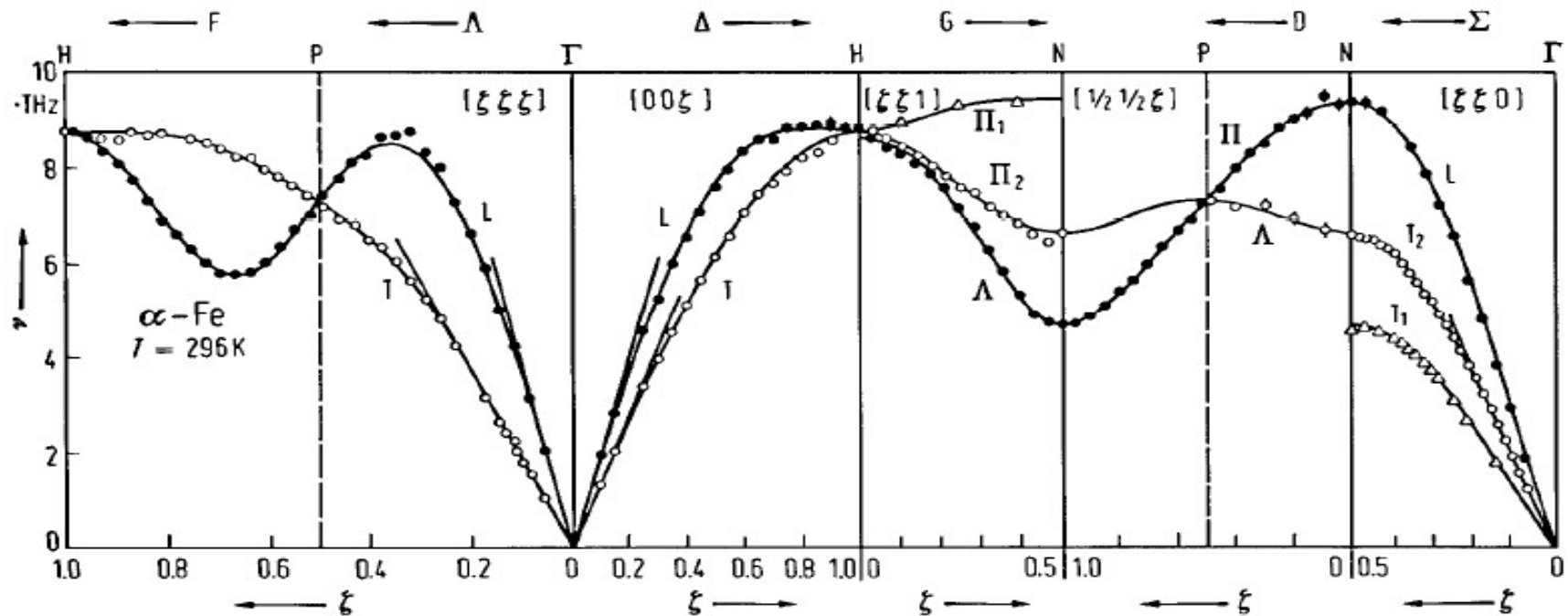
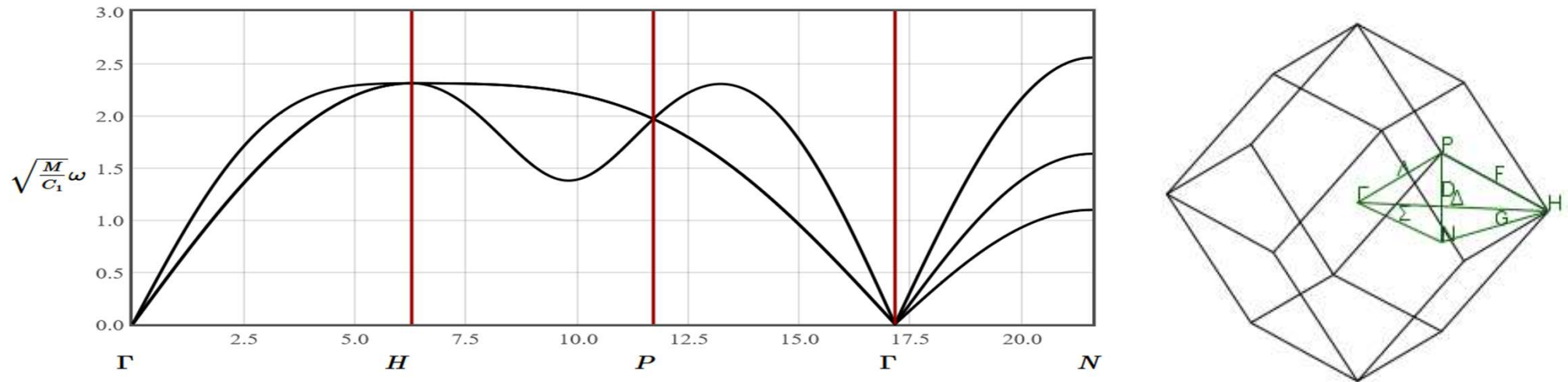


Fig. 2. Fe. Phonon dispersion curves in α -iron at 296 K. Experimental points: [68Va2]. Solid curve: fifth neighbour Born-von Karman model (Table 3 Fe [68Va2]).

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