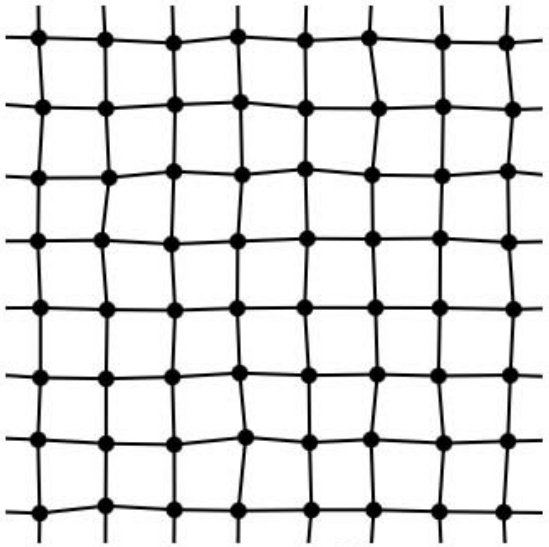
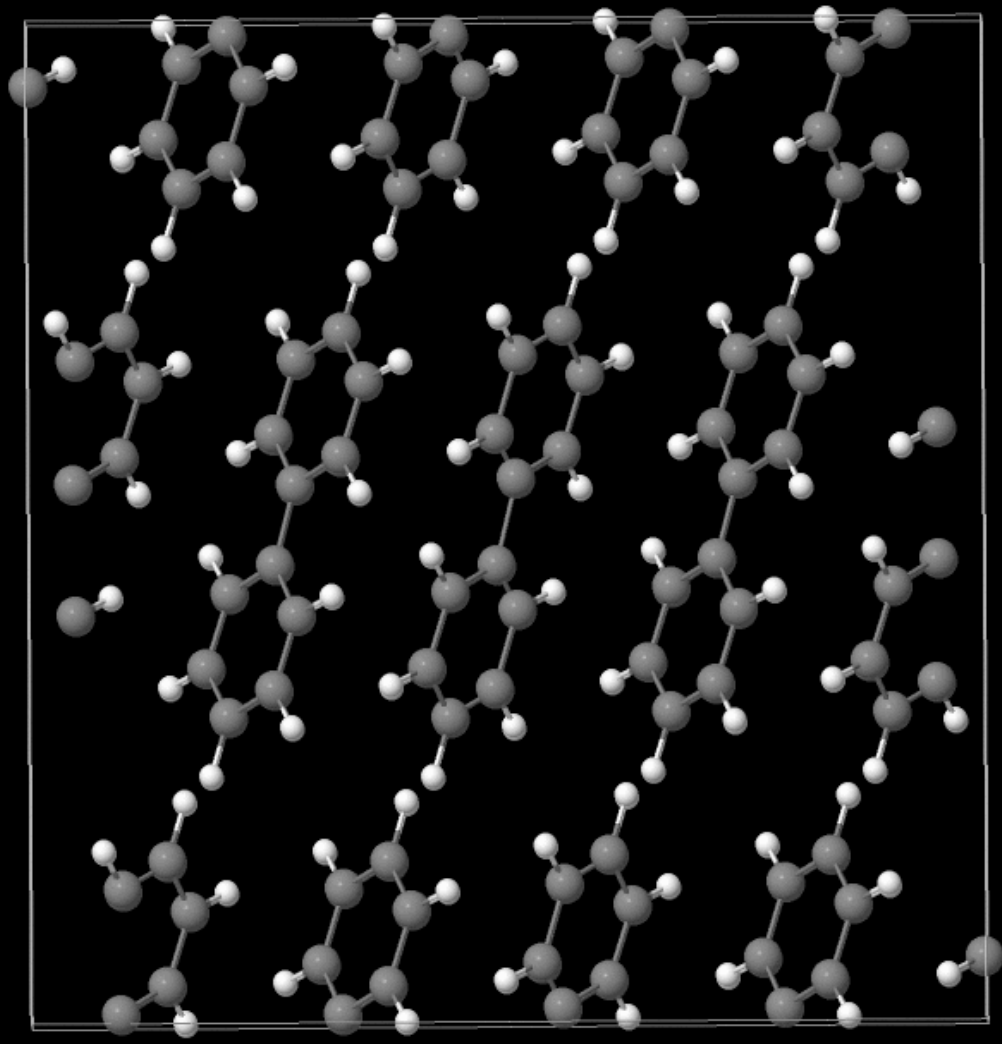
Phonons

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.

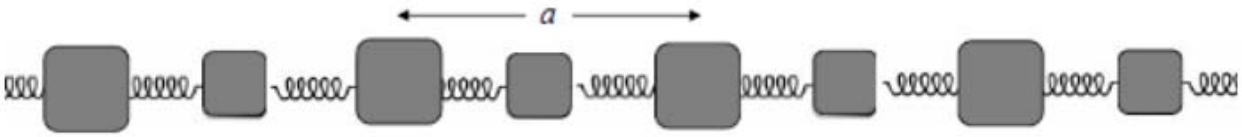




Natalia Bedoya

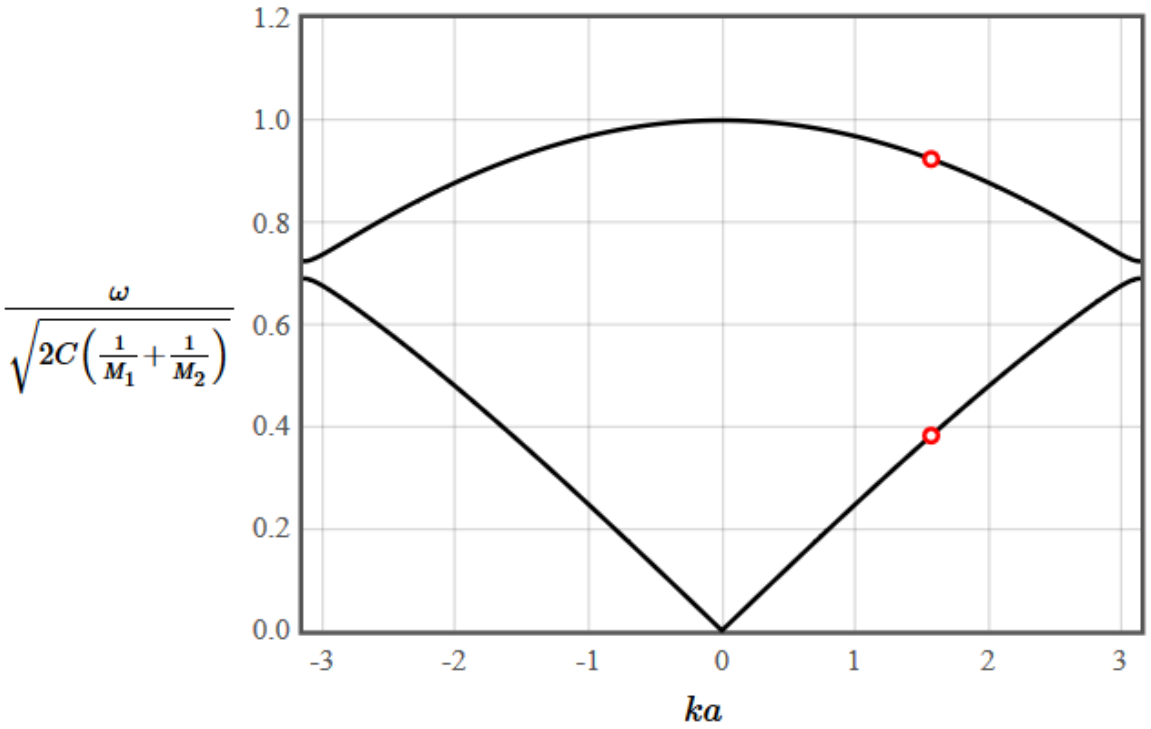
In a normal mode, all of the atoms oscillate at the same frequency.

1-d chain of atoms with two different masses



$$M_1 \frac{d^2 u_l}{dt^2} = C(v_{l-1} - 2u_l + v_l)$$

$$M_2 \frac{d^2 v_l}{dt^2} = C(u_l - 2v_l + u_{l+1})$$



Phonons

N_{atom} atoms in crystal
$3N_{atom}$ normal modes
p atoms in the basis
N_{atom}/p unit cells
N_{atom}/p translational symmetries
N_{atom}/p k-vectors
$3p$ modes for every k vector
3 acoustic branches and $3p$-3 optical branches

Normal modes are eigenfunctions of T

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

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

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

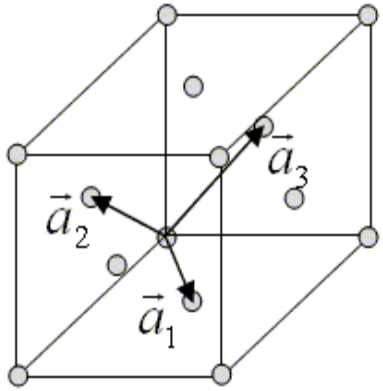
These are eigenfunctions of T.

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

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

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

fcc



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

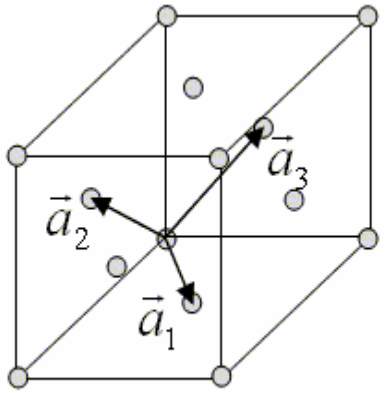
$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z} \qquad \vec{b}_2 = \frac{2\pi}{a}\left(\hat{k}_x - \hat{k}_y + \hat{k}_z\right)$$

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

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

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

fcc



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

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

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

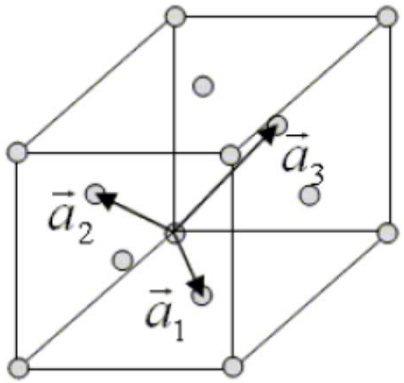
Substitute the eigenfunctions of T into Newton's laws.

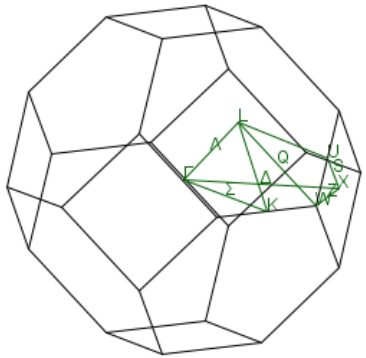
$$u^x_{lmn} = u^x_{\vec{k}} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3\right)\right) = u^x_{\vec{k}} \exp\left(i\left(\frac{(l+m)k_x a}{2} + \frac{(l+n)k_y a}{2} + \frac{(m+n)k_z a}{2}\right)\right).$$

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

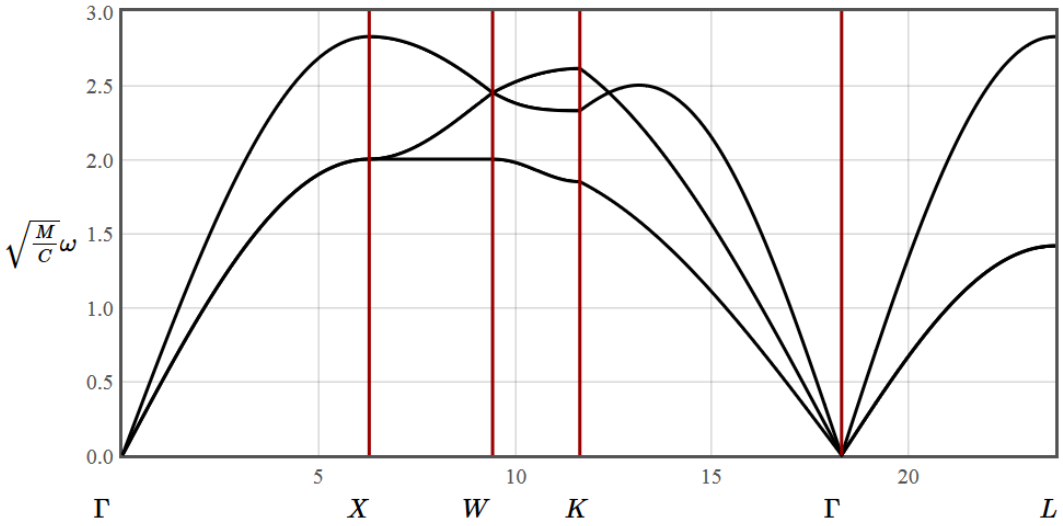
http://lamp.tu-graz.ac.at/~hadley/ss1/phonons/fcc/fcc.html

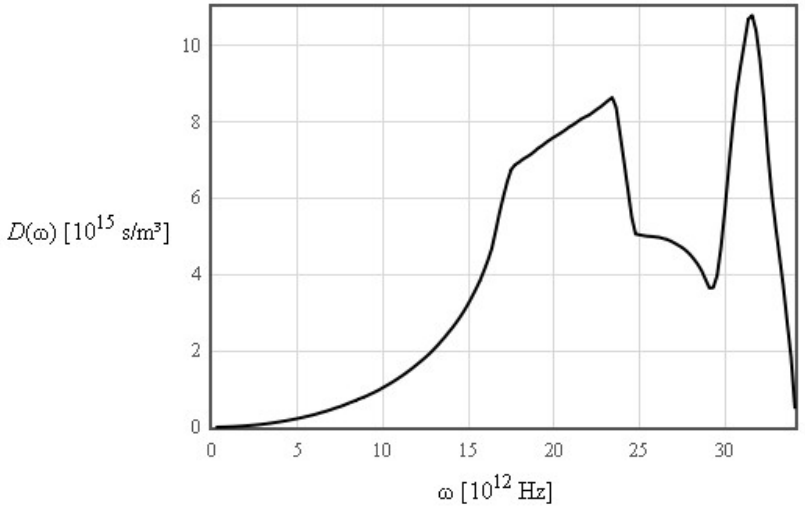
fcc phonons





$3N$ degrees of freedom





Phonon dispersion Au

From Springer Materials: Landholt Boernstein Database

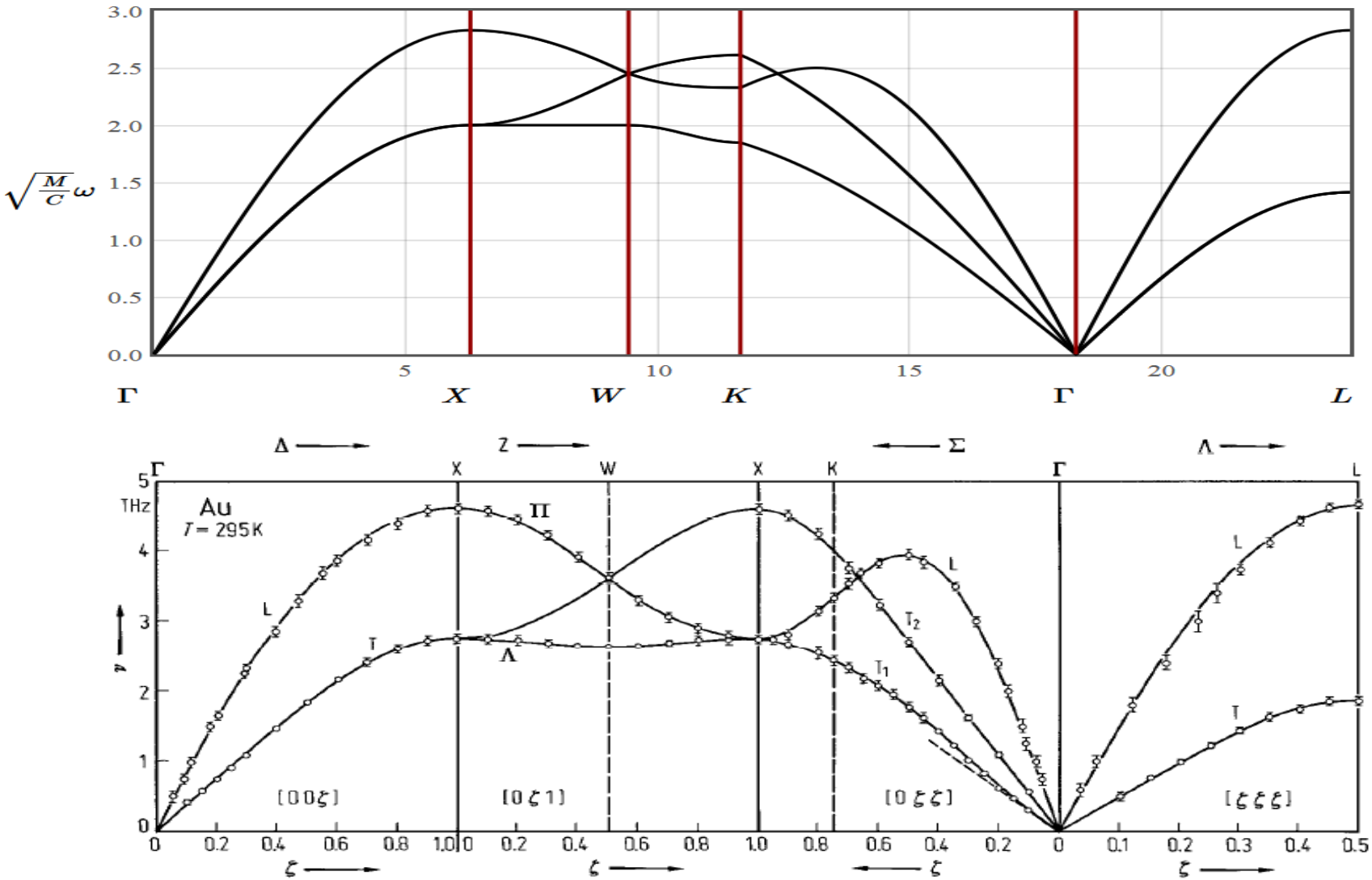
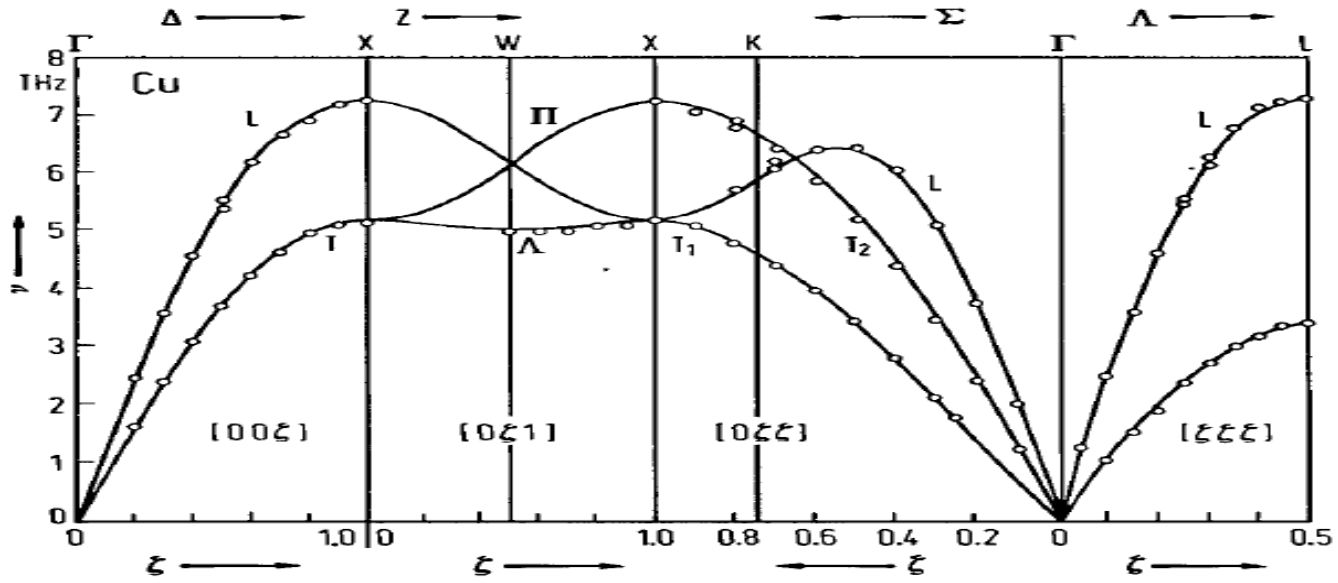
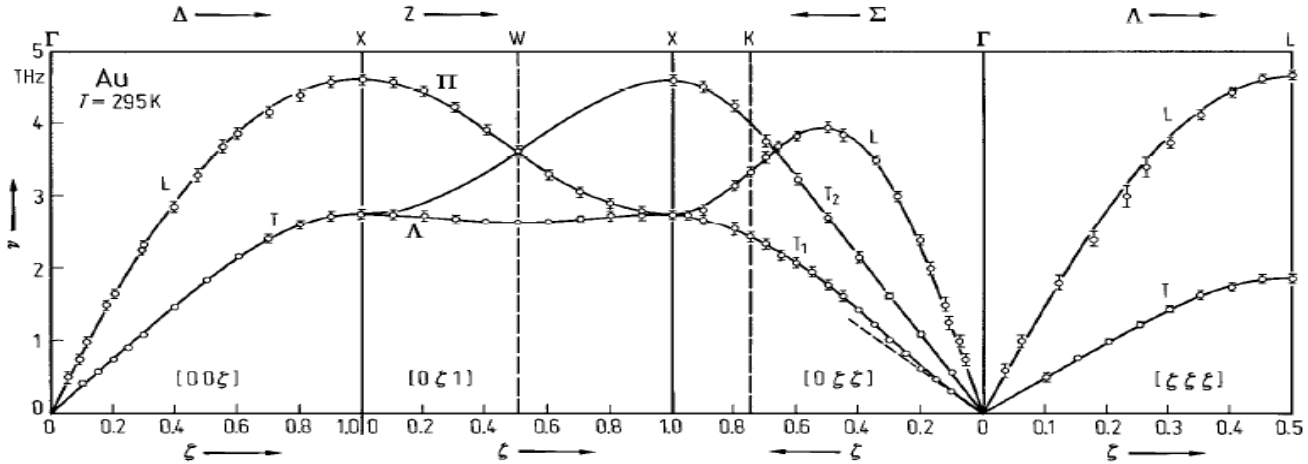


Fig. 1. Au. Phonon dispersion relations in the principal symmetry directions according to [73Ly1]. The solid curves represent both the fourth neighbour general force model (M1) and the fifth neighbour axially symmetric model (M2) of Table 3 Au. The dotted line in the Σ direction is corresponding to the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

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



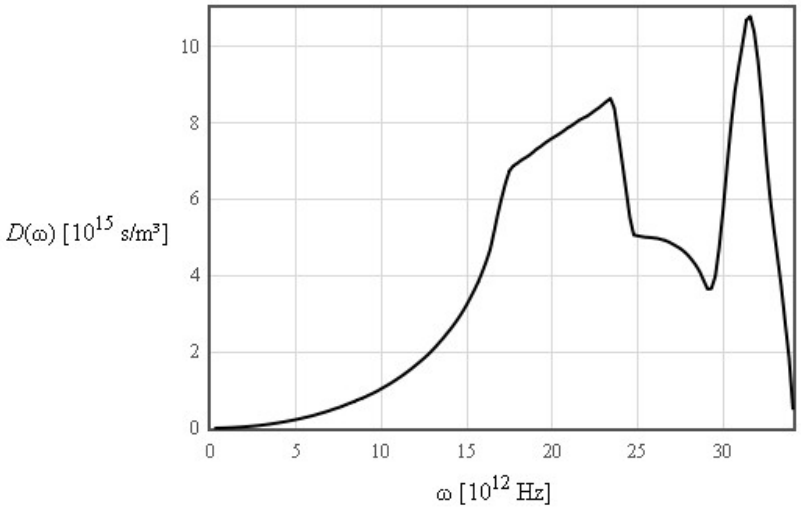
Cu

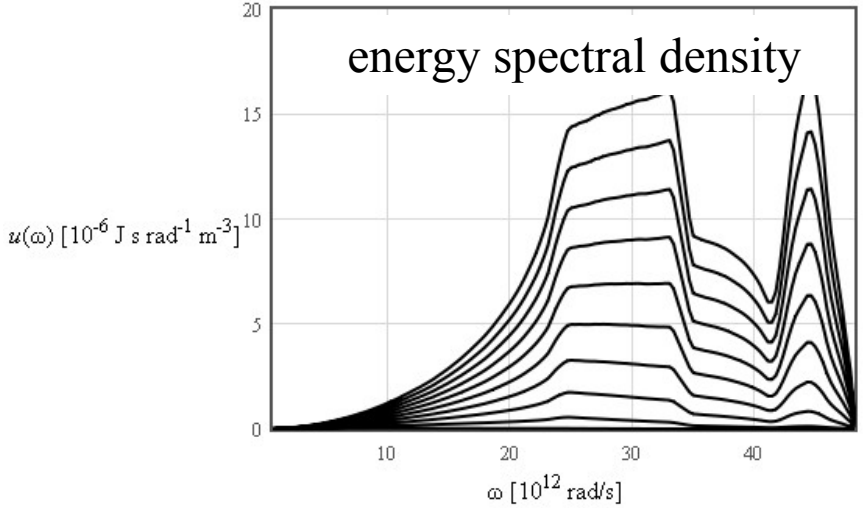


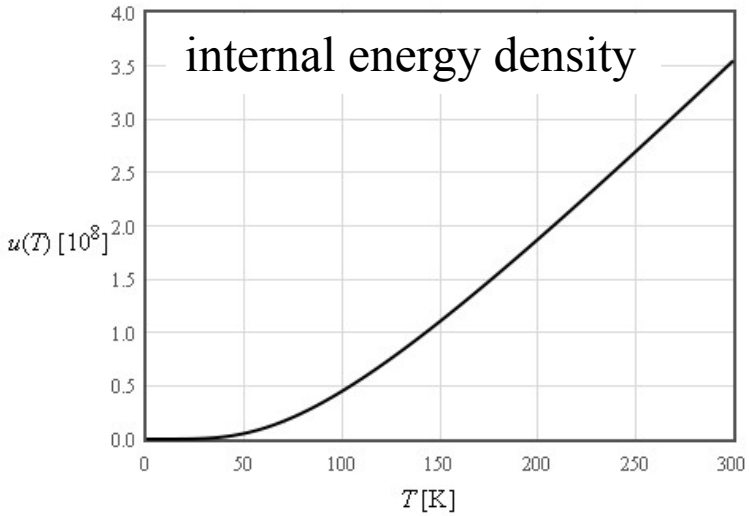
Au

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.

fcc phonons


$D(\omega)$ [10^{15} s/m^3]
0
2
4
6
8
10
0
5
10
15
20
25
30
ω [10^{12} Hz]


energy spectral density
$u(\omega)$ [10^{-6} J s rad^{-1} m^{-3}]
0
5
10
15
20
10
20
30
40
ω [10^{12} rad/s]


internal energy density
$u(T)$ [10^8]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
50
100
150
200
250
300
T [K]

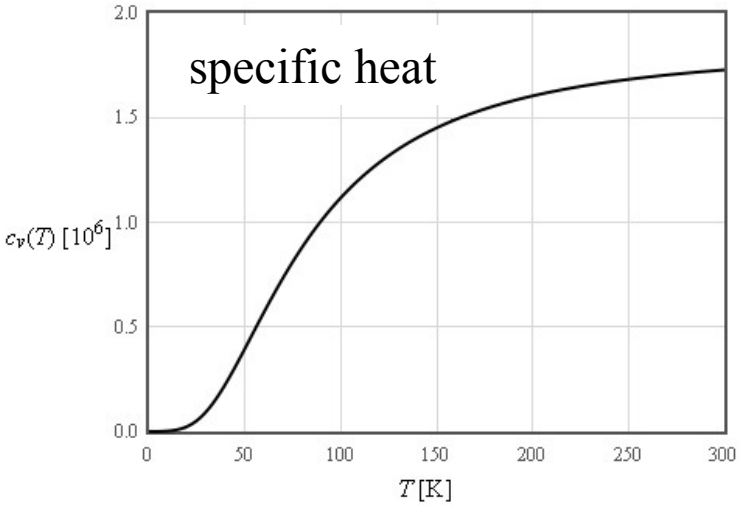
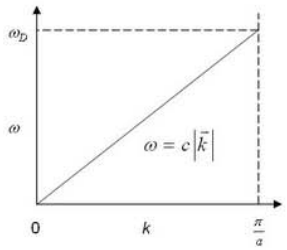
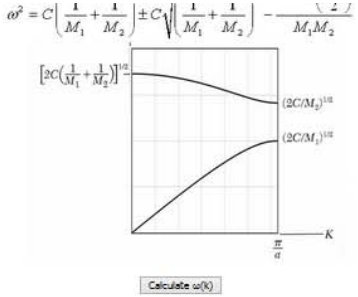
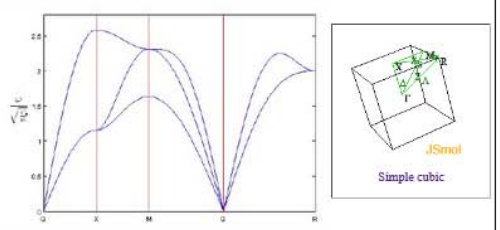
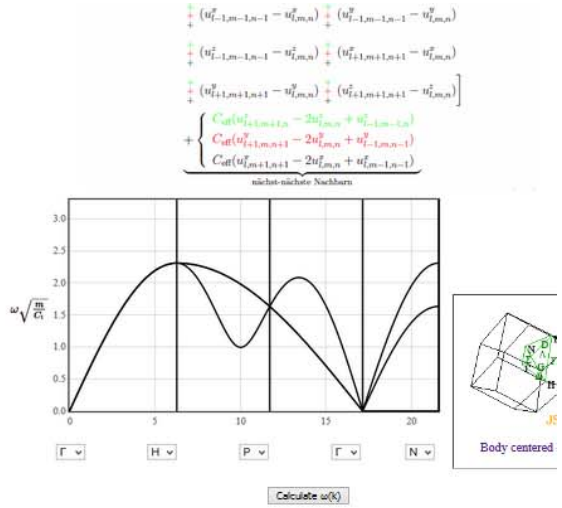
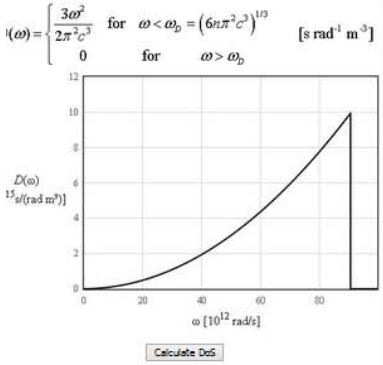
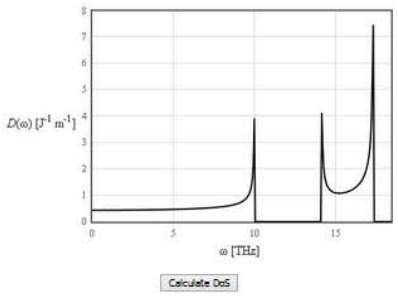
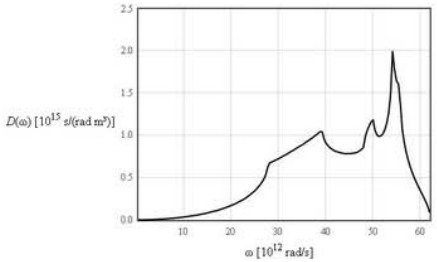
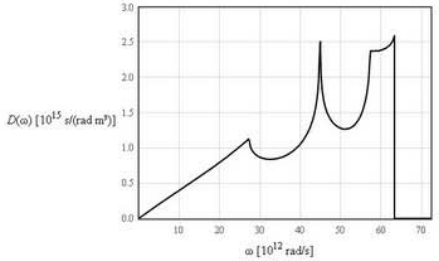
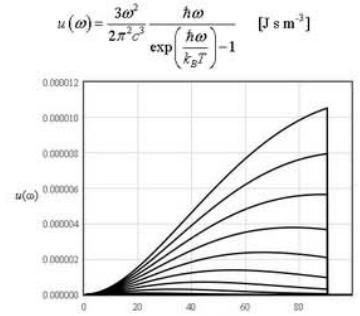
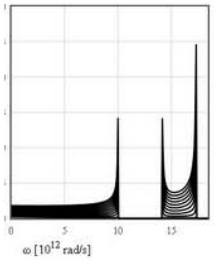
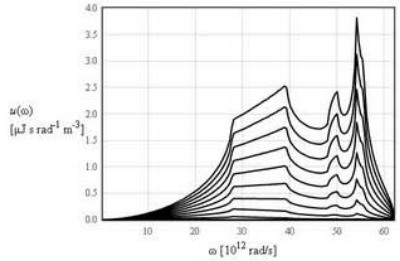
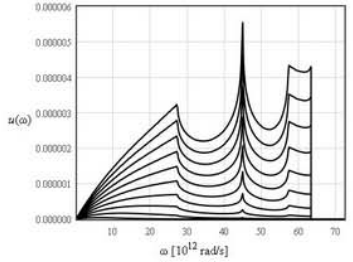

specific heat
$c_v(T)$ [10^6]
0.0
0.5
1.0
1.5
2.0
0
50
100
150
200
250
300
T [K]

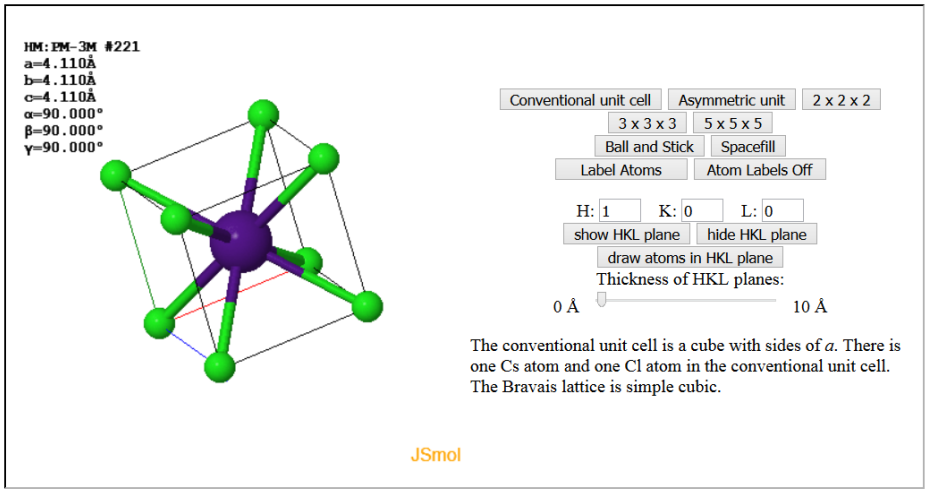
Table summarizing the thermodynamic properties of phonons

			
$D(k) = \frac{3k^2}{2\pi^2}$	$D(k) = \frac{1}{\pi}$	$D(k) = \frac{3k^2}{2\pi^2}$	$D(k) = \frac{3k^2}{2\pi^2}$
			
			

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

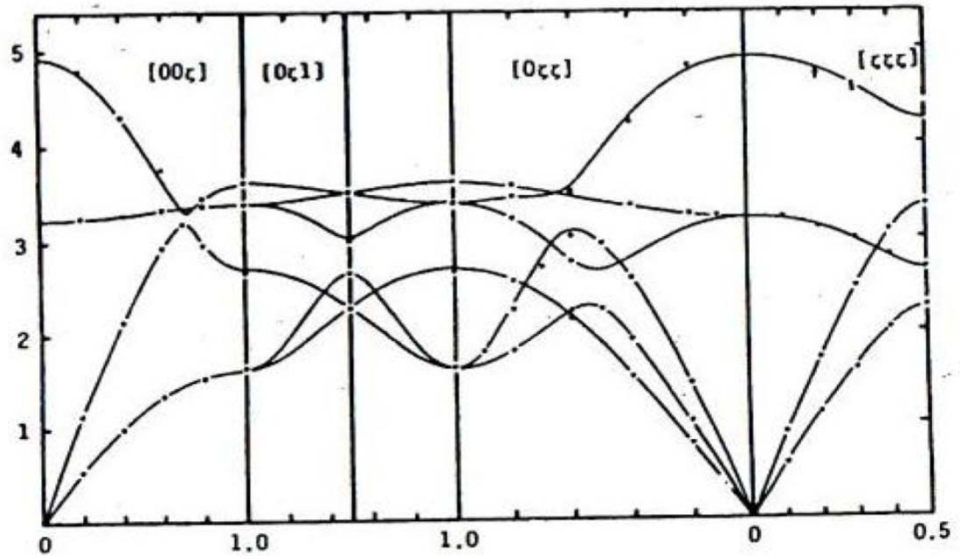
- **Phonons**
  - Normal modes and phonons
    - Using complex numbers to represent sinusoidal oscillations
    - Linear chain
    - Linear chain with two different masses
    - fcc with linear springs to nearest neighbors
    - bcc with linear springs to nearest neighbors
    - CsCl
  - Thermodynamic properties of non-interacting bosons
    - Density of states
      - simple cubic, bcc, fcc
      - Ag-fcc, Al-fcc, AlN, Au-fcc, Fe-bcc, GaN, Mg-hcp, Mo-bcc, Si-diamond, α-Sn, β-Sn, Ta-bcc, Tb-hcp, Ti-hcp, W-bcc, ZnO (rocksalt), ZnO (zincblende), ZnO (wurtzite), Zr-hcp
    - Energy spectral density $u(\omega,T)$
    - Internal energy density $u(T)$
    - Specific heat $c_v(T)$
    - Helmholtz free energy density $f(T)$
    - Entropy density $s(T)$
    - Table summarizing the thermodynamic properties of phonons

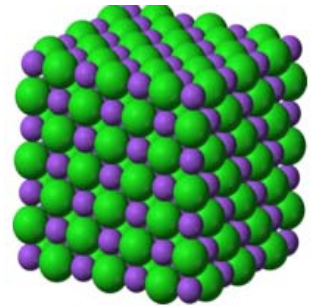
Phonon dispersion of CsCl



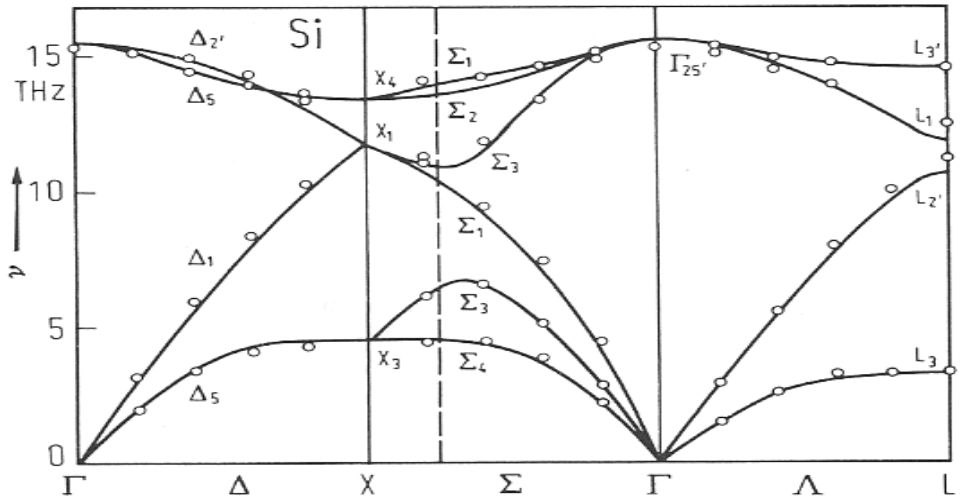
$$
\begin{aligned}
M_{\mathrm{Cs}}\frac{d^2u^x_{lmn}}{dt^2} = \frac{C_{\text{Cs-Cl}}}{3}\Big[&+ (v^x_{lmn} - u^x_{lmn}) + (v^y_{lmn} - u^y_{lmn}) + (v^z_{lmn} - u^z_{lmn}) \\
&+ (v^x_{(l-1)mn} - u^x_{lmn}) - (v^y_{(l-1)mn} - u^y_{lmn}) - (v^z_{(l-1)mn} - u^z_{lmn}) \\
&+ (v^x_{(l-1)(m-1)n} - u^x_{lmn}) + (v^y_{(l-1)(m-1)n} - u^y_{lmn}) - (v^z_{(l-1)(m-1)n} - u^z_{lmn}) \\
&+ (v^x_{l(m-1)n} - u^x_{lmn}) - (v^y_{l(m-1)n} - u^y_{lmn}) + (v^z_{l(m-1)n} - u^z_{lmn}) \\
&+ (v^x_{lm(n-1)} - u^x_{lmn}) + (v^y_{lm(n-1)} - u^y_{lmn}) - (v^z_{lm(n-1)} - u^z_{lmn}) \\
&+ (v^x_{(l-1)m(n-1)} - u^x_{lmn}) - (v^y_{(l-1)m(n-1)} - u^y_{lmn}) + (v^z_{(l-1)m(n-1)} - u^z_{lmn}) \\
&+ (v^x_{(l-1)(m-1)(n-1)} - u^x_{lmn}) + (v^y_{(l-1)(m-1)(n-1)} - u^y_{lmn}) + (v^z_{(l-1)(m-1)(n-1)} - u^z_{lmn}) \\
&+ (v^x_{l(m-1)(n-1)} - u^x_{lmn}) - (v^y_{l(m-1)(n-1)} - u^y_{lmn}) - (v^z_{l(m-1)(n-1)} - u^z_{lmn})\Big] \\
&+ C_{\text{Cs-Cs}}\left(-2u^x_{lmn} + u^x_{(l-1)mn} + u^x_{(l+1)mn}\right),
\end{aligned}
$$

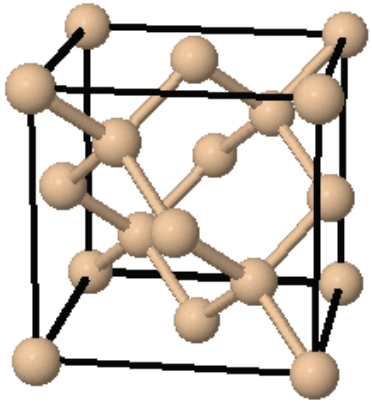
Two atoms per primitive unit cell





NaCl

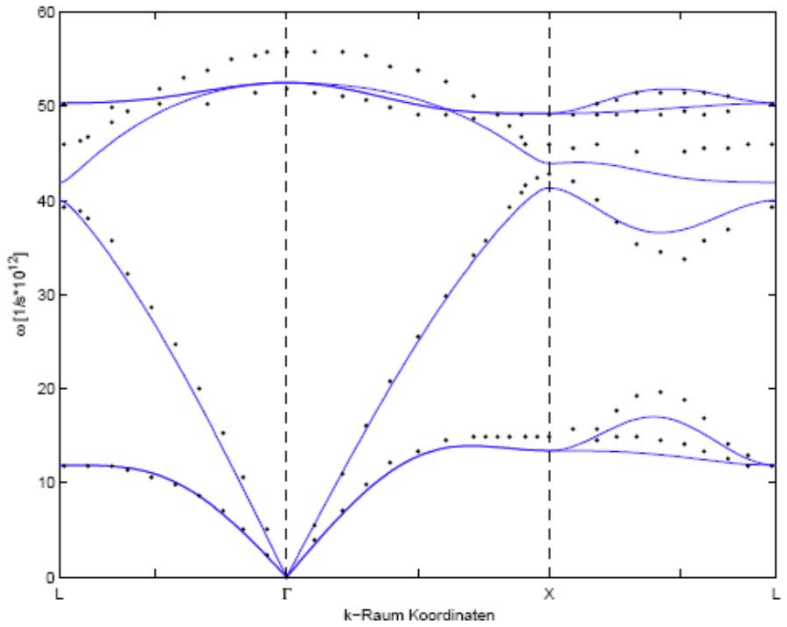


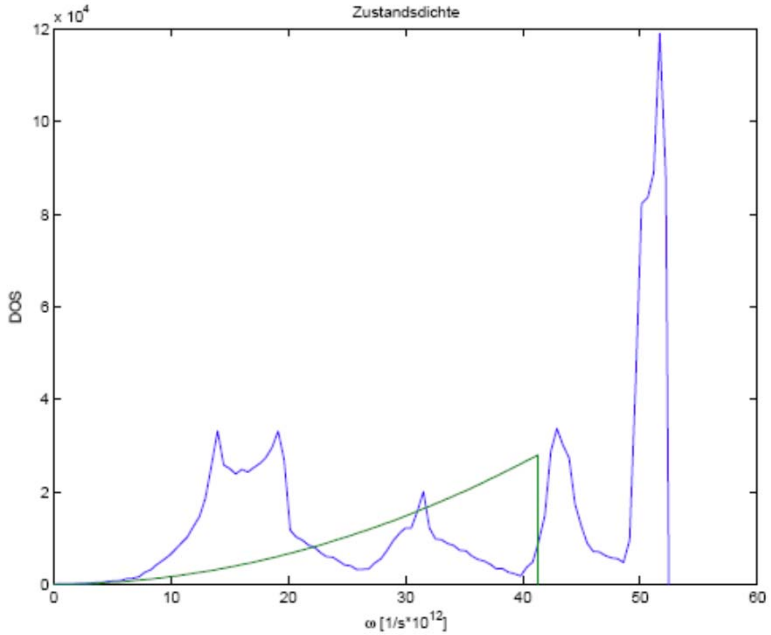


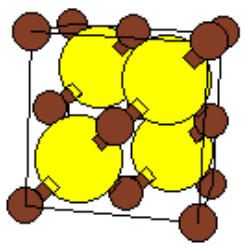
Si

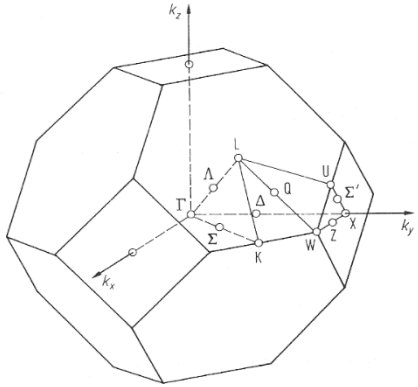
GaAs

Hannes Brandner









Phonon quasiparticle lifetime

Phonons are the eigenstates of the linearized equations, not the full equations.

Phonons have a finite lifetime that can be calculated by Fermi's golden rule.

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}\left|\langle f \left| H_{ph-ph} \right| i\rangle\right|^2 \delta\left(E_f - E_i\right)$$

Occupation is determined by a master equation (not the Bose-Einstein function).

$$\begin{bmatrix} \frac{dP_0}{dt} \\ \frac{dP_1}{dt} \\ \vdots \\ \frac{dP_N}{dt} \end{bmatrix} = \begin{bmatrix} -\sum_{i\neq 0}\Gamma_{0\to i} & \Gamma_{1\to 0} & \cdots & \Gamma_{N\to 0} \\ \Gamma_{0\to 1} & -\sum_{i\neq 1}\Gamma_{1\to i} & \cdots & \Gamma_{N\to 1} \\ \vdots & \vdots & \ddots & \vdots \\ \Gamma_{0\to N} & \Gamma_{1\to N} & \cdots & -\sum_{i\neq N}\Gamma_{N\to i} \end{bmatrix} \begin{bmatrix} P_0 \\ P_1 \\ \vdots \\ P_N \end{bmatrix}$$

Acoustic attenuation

The amplitude of a monocromatic sound wave decreases as the wave propagates through the crystal as the phonon quasiparticles decay into phonons with other frequencies and directions.

Welcome to phonopy

Phonopy is an open source package for phonon calculations at harmonic and quasi-harmonic levels.

Phono3py is another open source package for phonon-phonon interaction and lattice thermal conductivity calculations. See the documentation at http://atztogo.github.io/phono3py/

Phonon database: A collection of first principles phonon calculations is available as open data at http://phonondb.mtl.kyoto-u.ac.jp/ , where the raw data of phonopy & VASP results are downloaded.

The following features of phonopy are highlighted:

- Phonon band structure, phonon DOS and partial-DOS
- Phonon thermal properties: Free energy, heat capacity (Cv), and entropy
- Phonon group velocity
- Thermal ellipsoids / Mean square displacements
- Irreducible representations of normal modes
- Dynamic structure factor for INS and IXS
- Non-analytical-term correction: LO-TO splitting (Born effective charges and dielectric constant are required.)
- Mode Grüneisen parameters
- Quasi-harmonic approximation: Thermal expansion, heat capacity at constant pressure (Cp)
- Interfaces to calculators: VASP, VASP DFPT, ABINIT, Quantu ESPRESSO, SIESTA, Elk, FHI-aims, WIEN2k, CRYSTAL, LAMMPS (external)
- Phonopy API for Python

A presentation in pdf for introduction to phonopy is downloaded ***here***.