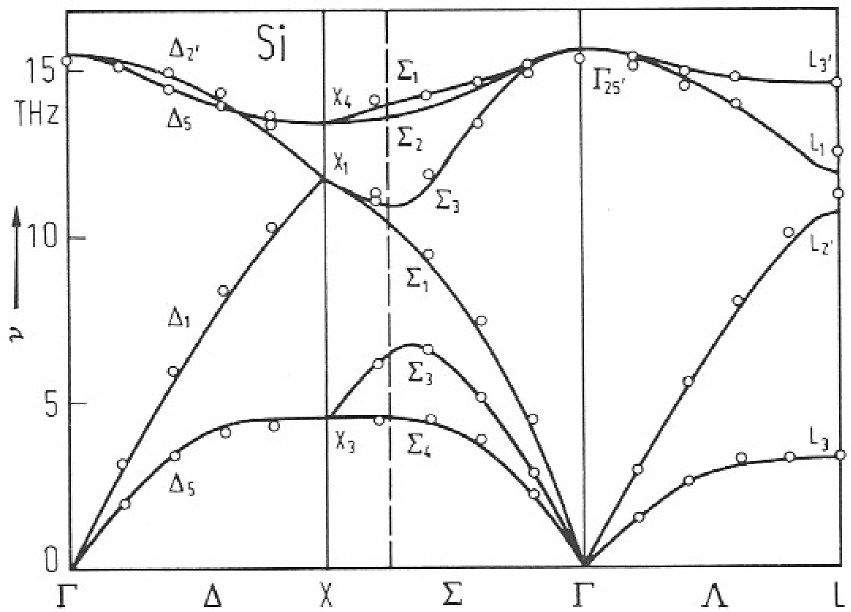
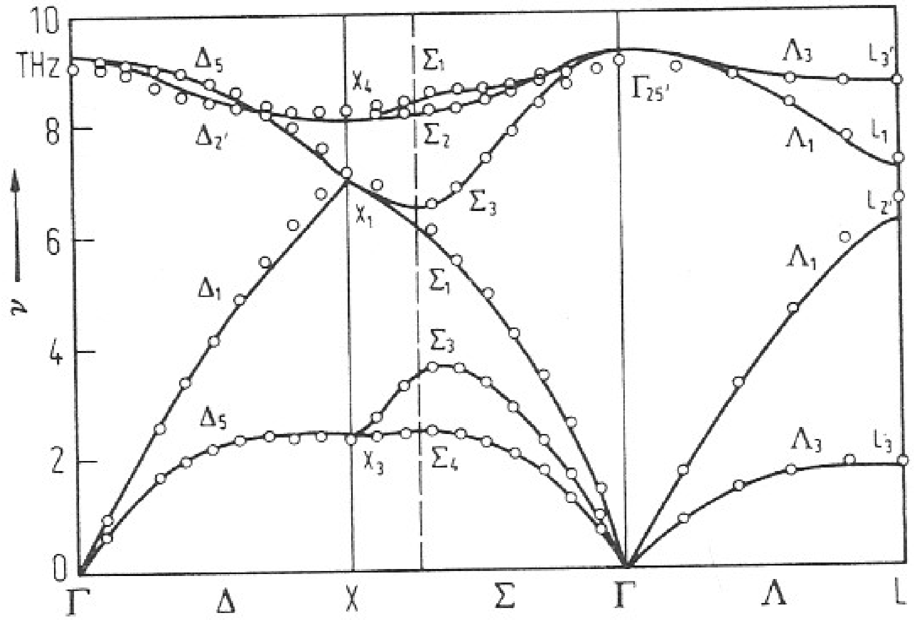
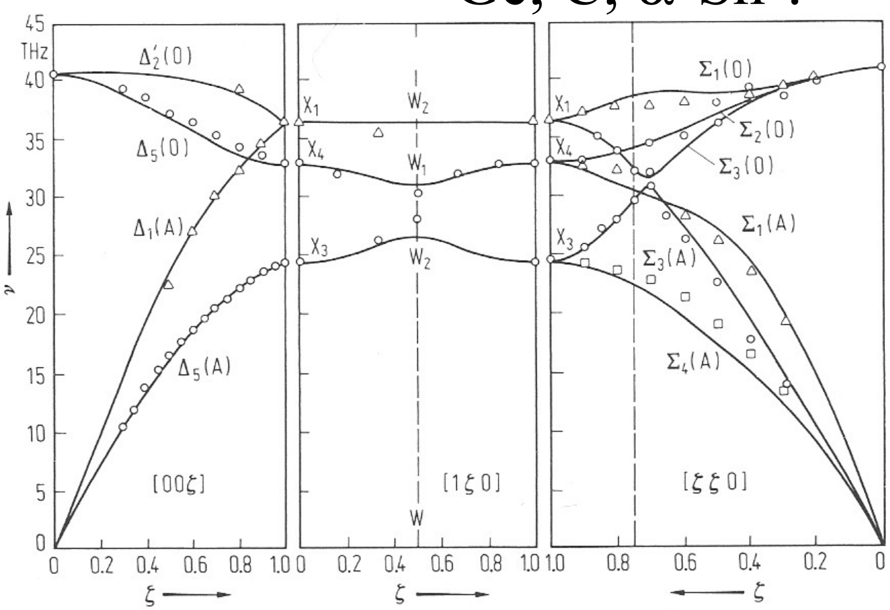
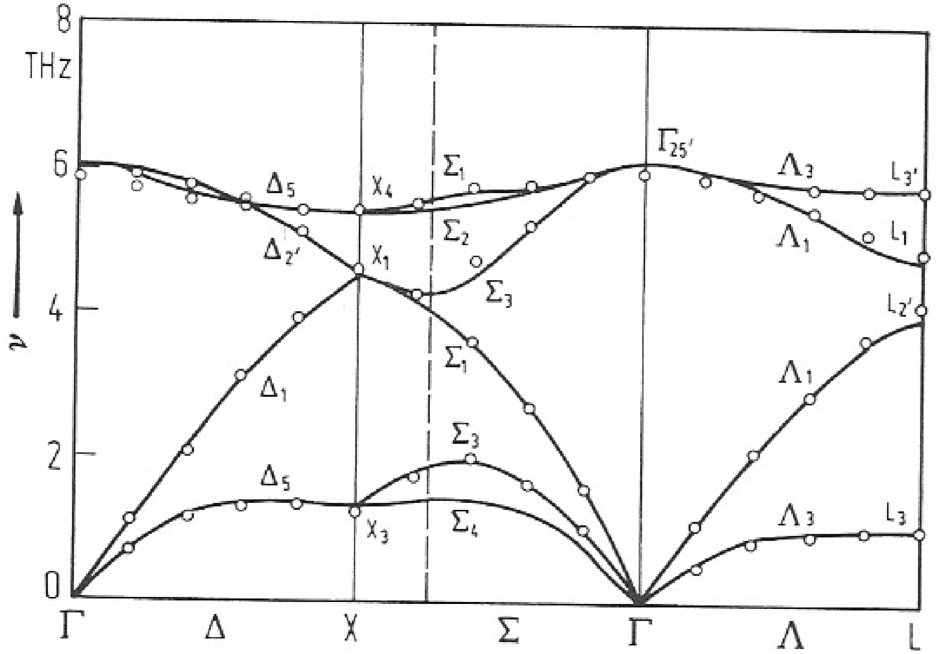
Phonons


Si
THz
ν
Γ Δ X Σ Γ Λ L
$\Delta_{2'}$ Δ_5 Δ_1 X_4 X_1 X_3 Σ_1 Σ_2 Σ_3 Σ_4 $\Gamma_{25'}$ $L_{3'}$ L_1 $L_{2'}$ L_3


THz
ν
Γ Δ X Σ Γ Λ L
Δ_5 $\Delta_{2'}$ Δ_1 X_4 X_1 X_3 Σ_1 Σ_2 Σ_3 Σ_4 $\Gamma_{25'}$ Λ_3 Λ_1 $L_{3'}$ L_1 $L_{2'}$ L_3

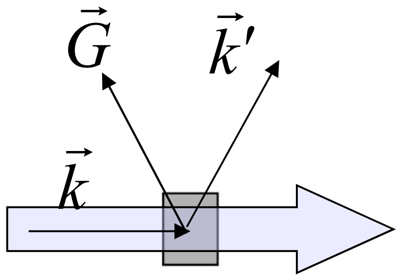
Ge, C, α-Sn ?


THz
ν
$\Delta_2'(0)$ $\Delta_5(0)$ $\Delta_1(A)$ $\Delta_5(A)$
X_1 X_4 X_3 W_2 W_1 W
$\Sigma_1(0)$ $\Sigma_2(0)$ $\Sigma_3(0)$ $\Sigma_1(A)$ $\Sigma_3(A)$ $\Sigma_4(A)$
[00ζ] [1ζ0] [ζζ0]
ζ


THz
ν
Γ Δ X Σ Γ Λ L
Δ_5 $\Delta_{2'}$ Δ_1 X_4 X_1 X_3 Σ_1 Σ_2 Σ_3 Σ_4 $\Gamma_{25'}$ Λ_3 Λ_1 $L_{3'}$ 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

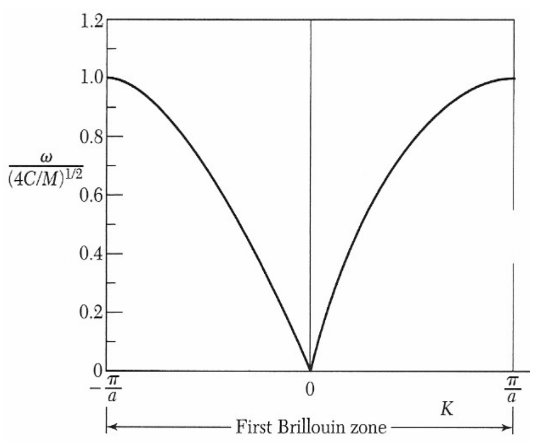
discrete version of wave equation

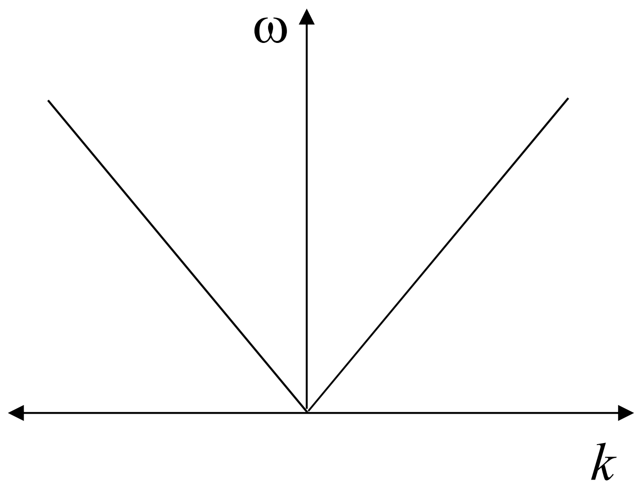
$$m\frac{d^2u_s}{dt^2}=C(u_{s+1}-2u_s+u_{s-1})$$

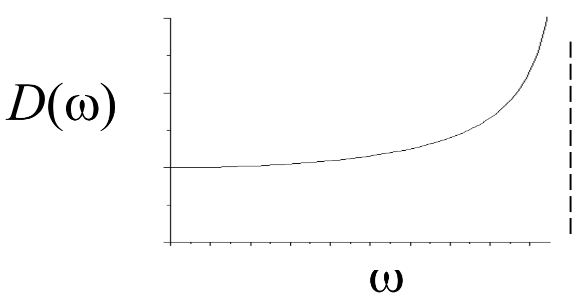
1-d wave equation

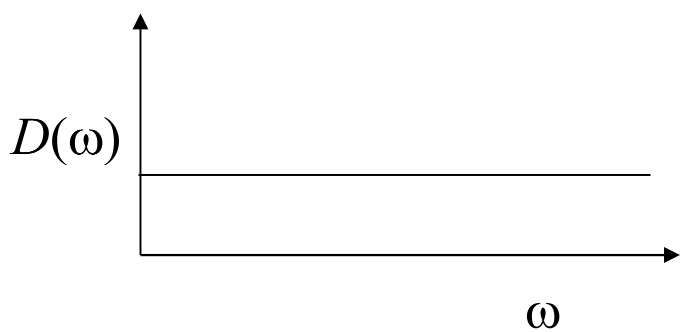
$$\frac{d^2u}{dt^2}=c^2\frac{d^2u}{dx^2}$$

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

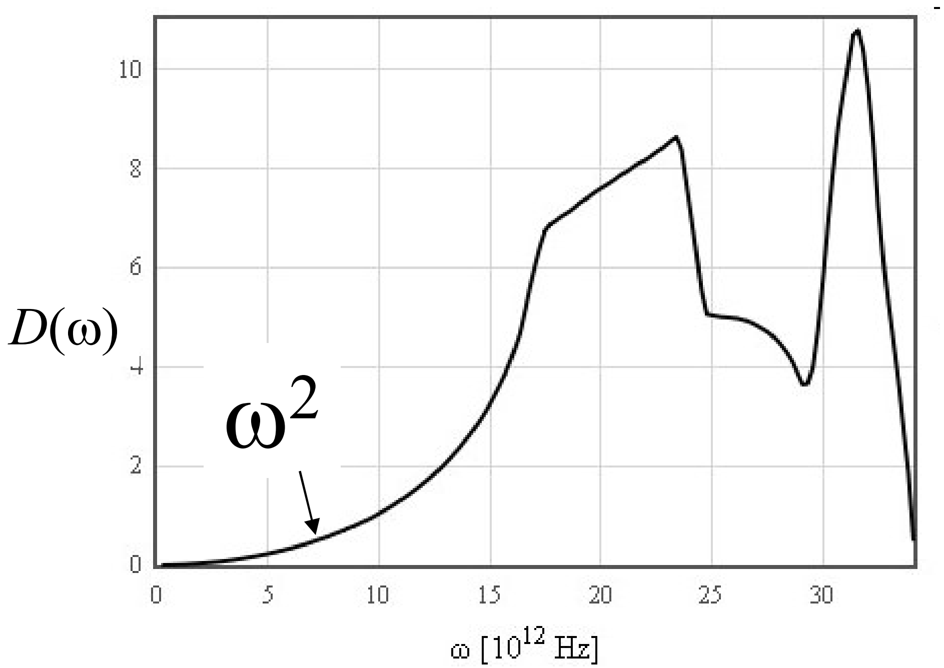


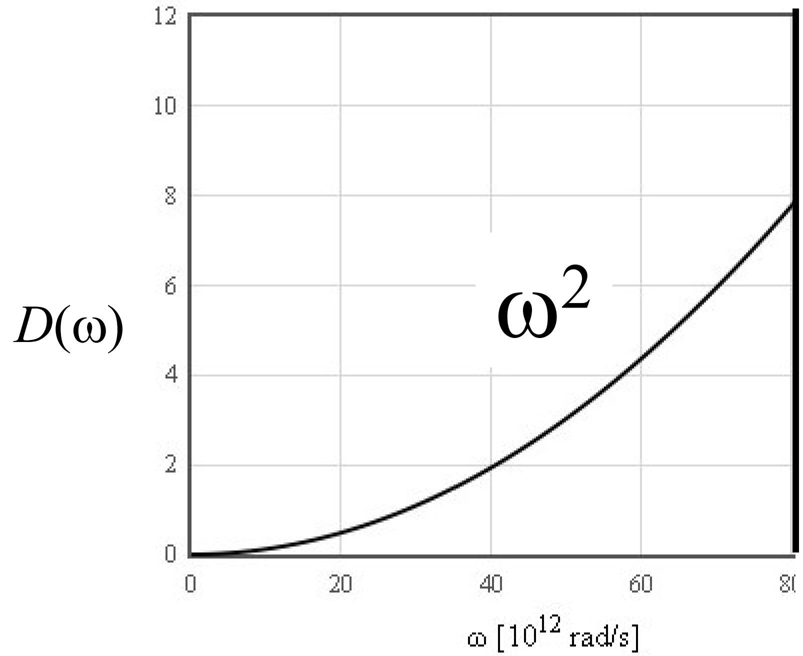






long wavelength, low temperature limit





Phonons - long wavelength, low temperature limit

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

3 polarizations

Density of states per polarization:

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

Specific heat of insulators at low temperatures per polarization

$$c_v = \frac{8\,\cancel{16}\sigma T^3}{c} \quad [\mathrm{J\,K^{-1}\,m^{-3}}]$$

Speed of sound

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

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

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

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

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

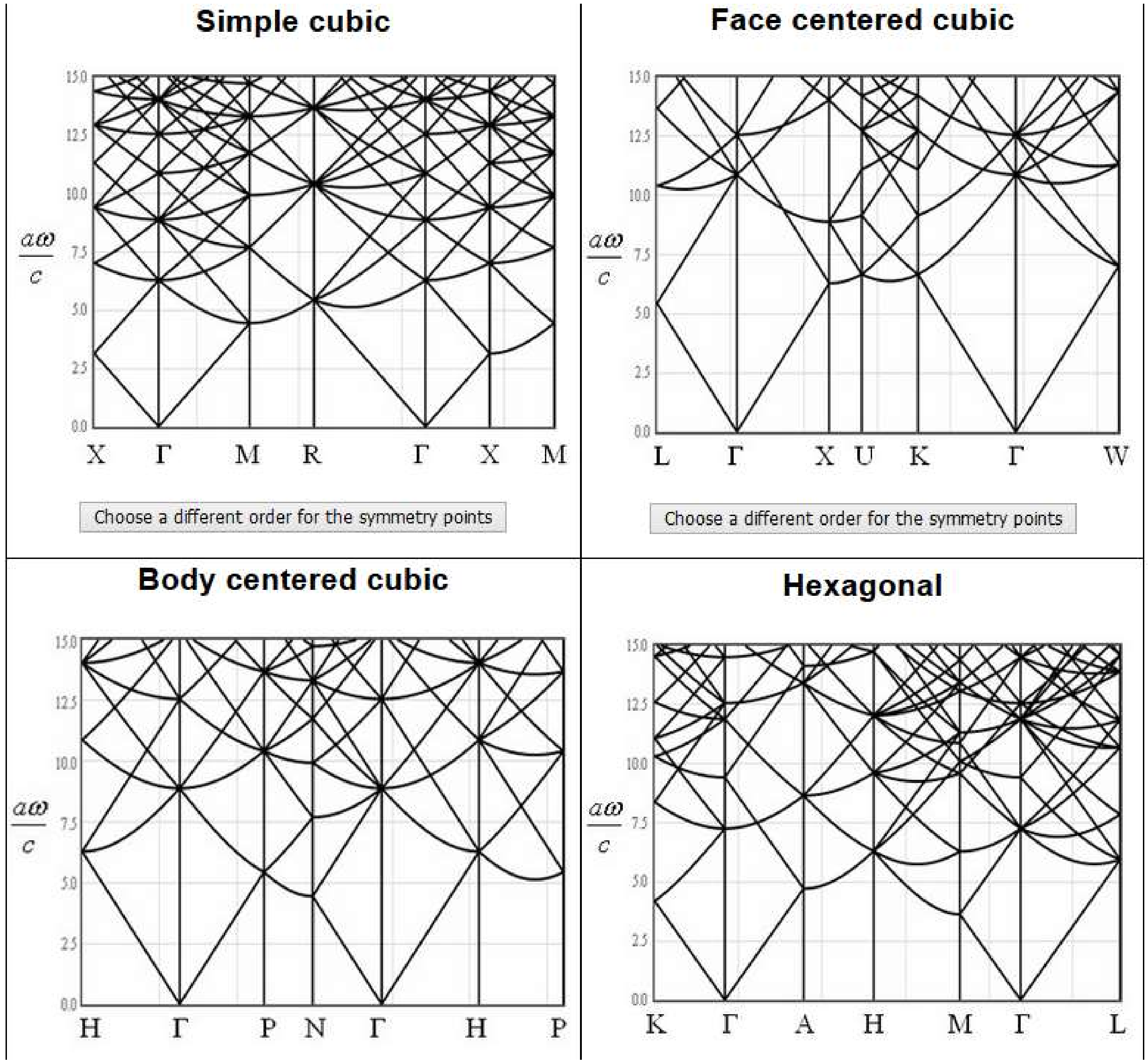
$$s = \frac{16\sigma T^3}{3c} \quad [\mathrm{J\,K^{-1}\,m^{-3}}]$$

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

Empty lattice approximation

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

3 acoustic branches
$3p$ - 3 optical branches



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.

Specific Heat

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

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

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

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

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.

Dulong and Petit (Classical result)

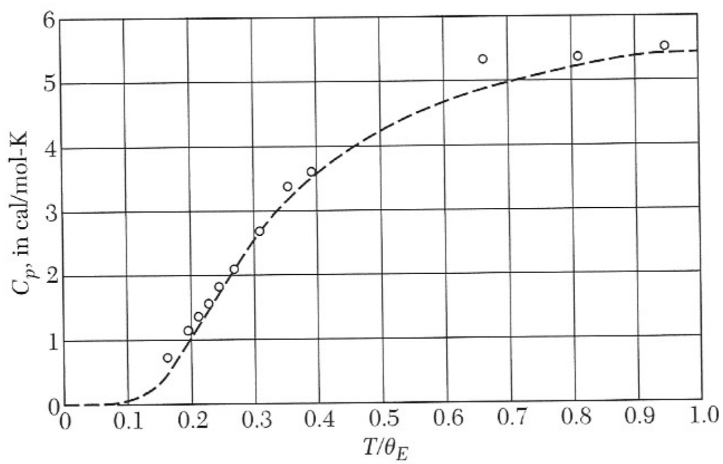
Equipartition: $\frac{1}{2}k_BT$ per quadratic term in energy

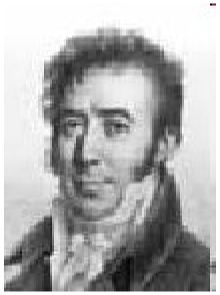
internal energy: $u = 3nk_BT$ n = atomic density

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

experiments: heat capacity goes to zero at zero temperature

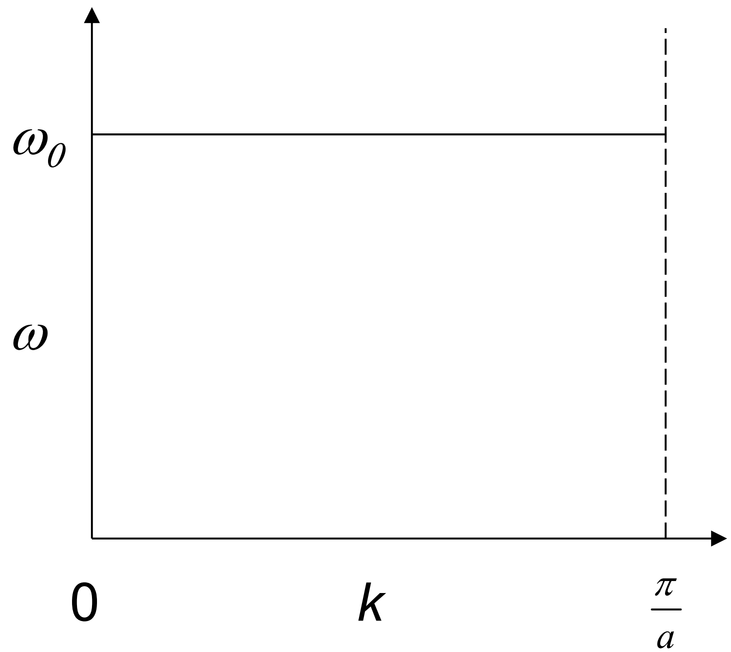
Pierre Louis Dulong

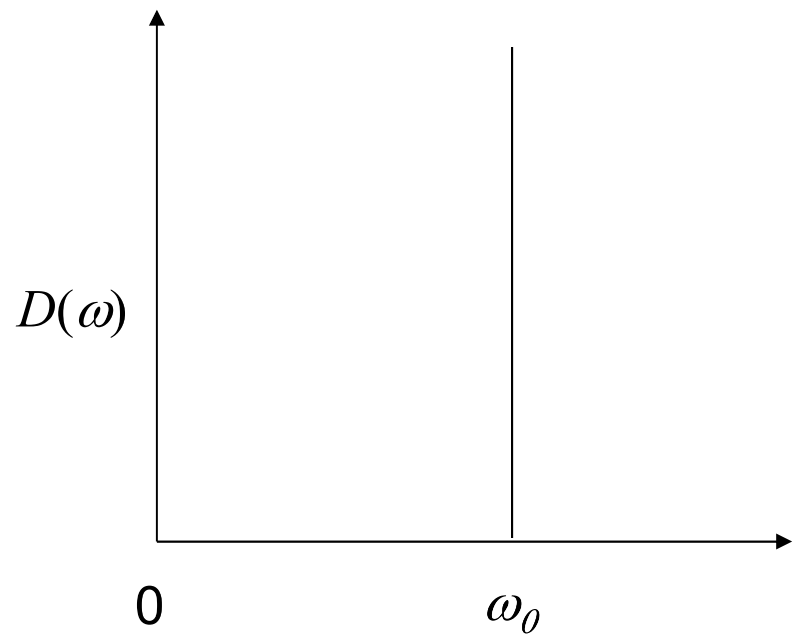




Alexis Therese Petit

Einstein model for specific heat





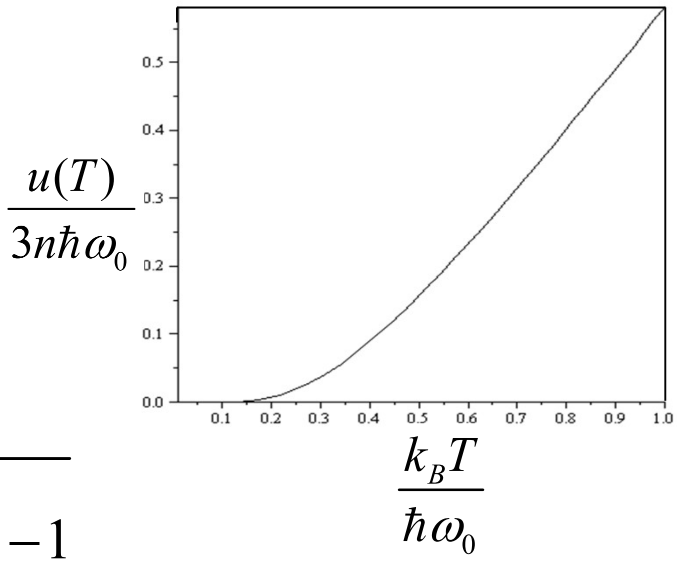
$$D(\omega) = 3n\delta(\omega - \omega_0)$$

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

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

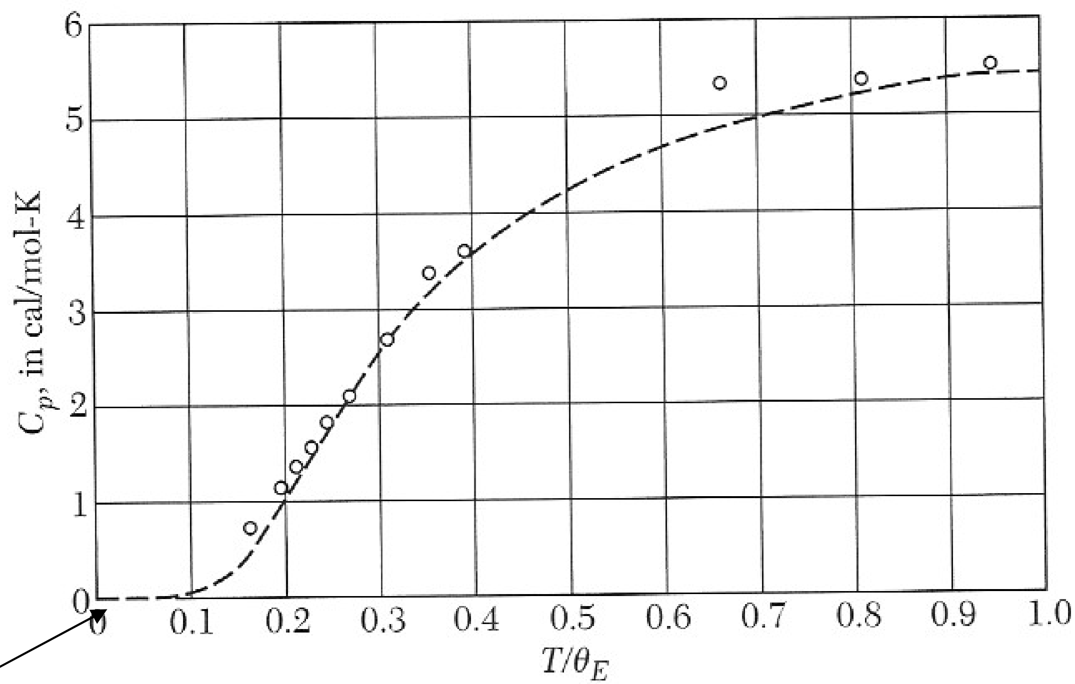


$$u = \int_0^\infty u(\omega)d\omega = \int_0^\infty 3n\hbar\omega \frac{\delta(\omega-\omega_0)d\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1} = \frac{3n\hbar\omega_0}{\exp\left(\frac{\hbar\omega_0}{k_B T}\right)-1}$$

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

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

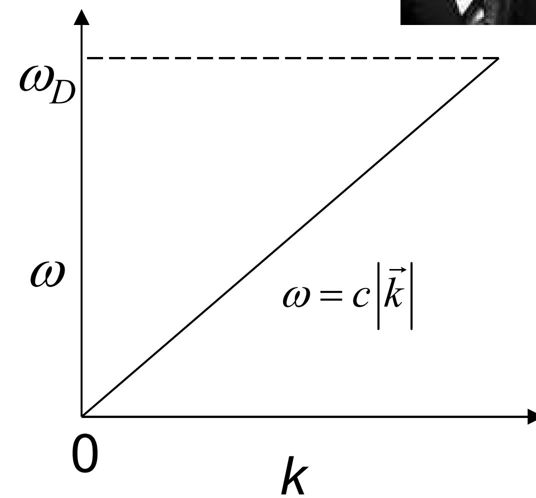
$$D(\omega) = \frac{3\omega^2}{2\pi^2 c^3}$$

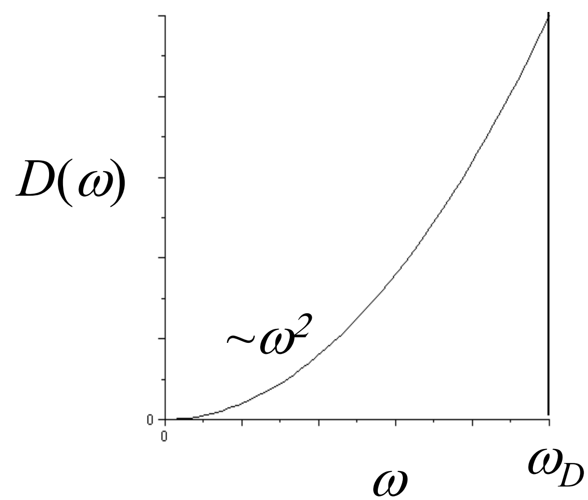
Like blackbody radiation up to a cutoff frequency.

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

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

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





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 $cm^{-1}K^{-1}$

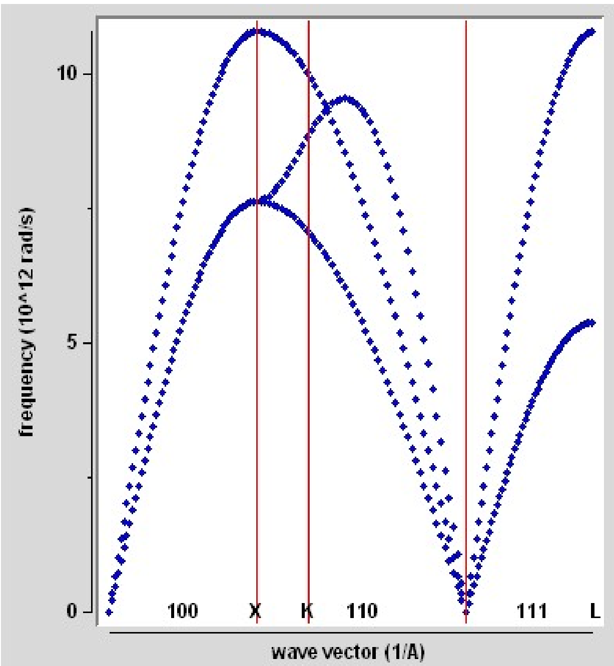
Li 344 0.85	Be 1440 2.00											B 0.27	C 2230 1.29	N	O	F	Ne 75
Na 158 1.41	Mg 400 1.56											Al 428 2.37	Si 645 1.48	P	S	Cl	Ar 92
K 91 1.02	Ca 230	Sc 360. 0.16	Ti 420 0.22	V 380 0.31	Cr 630 0.94	Mn 410 0.08	Fe 470 0.80	Co 445 1.00	Ni 450 0.91	Cu 343 4.01	Zn 327 1.16	Ga 320 0.41	Ge 374 0.60	As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

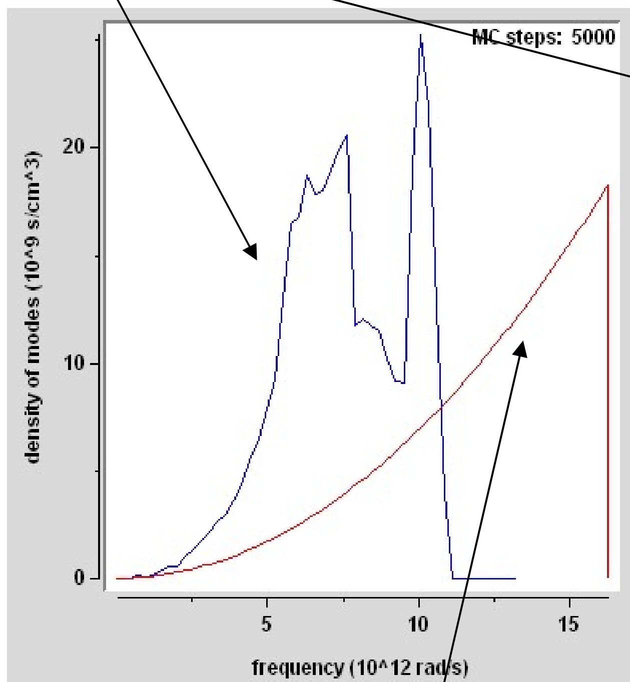
Ce 0.11	Pr 0.12	Nd 0.16	Pm	Sm 0.13	Eu	Gd 200 0.11	Tb 0.11	Dy 210 0.11	Ho 0.16	Er 0.14	Tm 0.17	Yb 120 0.35	Lu 210 0.16
Th 163 0.54	Pa	U 207 0.28	Np 0.06	Pu 0.07	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

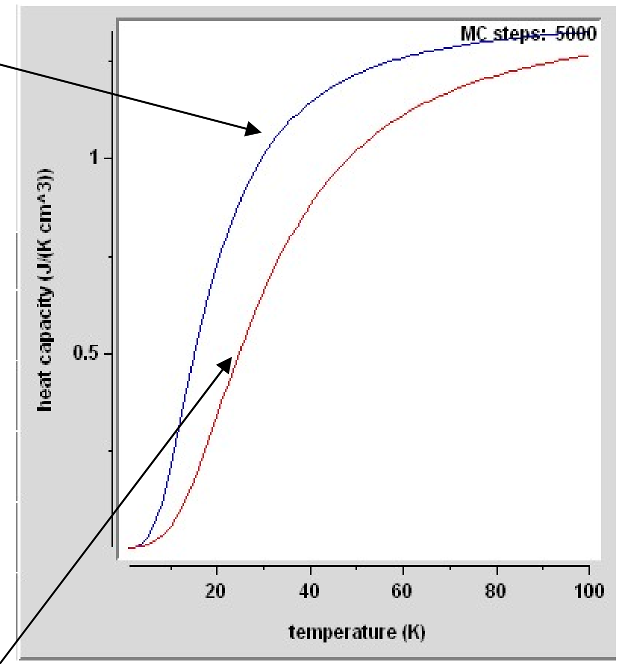
Kittel

Phonon density of states

fcc phonon density of states







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

Thermal properties

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

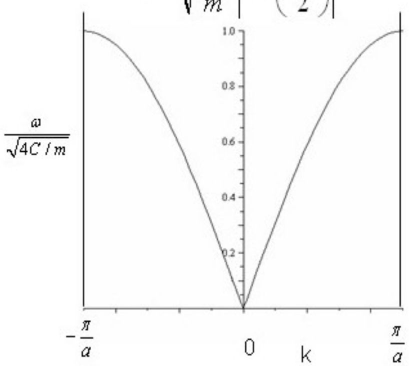
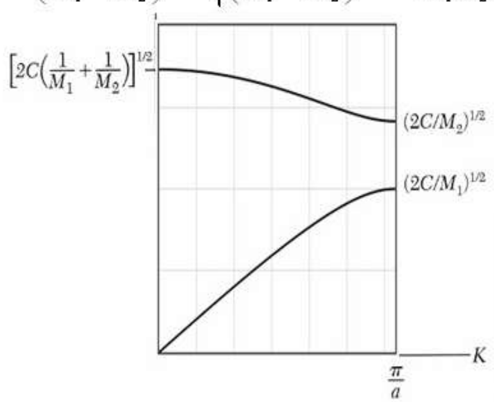
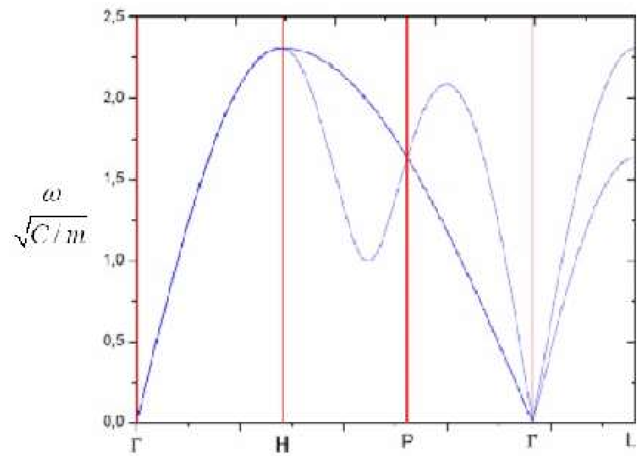
specific heat $$c_v = \frac{du}{dT} = \int \left(\frac{\hbar\omega}{T}\right)^2 \frac{D(\omega)\exp\left(\frac{\hbar\omega}{k_B T}\right)}{k_B\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} d\omega \quad [\text{J K}^{-1} \text{ m}^{-3}]$$

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
	$m\frac{d^2u_s}{dt^2}=C(u_{s+1}-2u_s+u_{s-1})$	$M_1\frac{d^2u_s}{dt^2}=C(v_{s-1}-2u_s+v_s)$ $M_2\frac{d^2v_s}{dt^2}=C(u_s-2v_s+u_{s+1})$	$\frac{d^2u^x_{lmn}}{dt^2}=\frac{C}{\sqrt{3}\,m}[(u^x_{l+1m+1n+1}-u^x_{lmn})+(u^x_{l-1m+1n+1}-u^x_{ln}$ $+(u^x_{l+1m-1n+1}-u^x_{lmn})+(u^x_{l+1m+1n-1}-u^x_{lmn})+(u^x_{l-1m+}$ $+(u^x_{l+1m-1n-1}-u^x_{lmn})+(u^y_{l+1m+1n+1}-u^y_{lmn})-(u^y_{l-1m+}$ $+(u^y_{l+1m-1n+1}-u^y_{lmn})-(u^y_{l+1m+1n-1}-u^y_{lmn})+(u^y_{l-1m+}$ $+(u^y_{l+1m-1n-1}-u^y_{lmn})+(u^z_{l+1m+1n+1}-u^z_{lmn})-(u^z_{l-1m+}$ $+(u^z_{l+1m-1n+1}-u^z_{lmn})-(u^z_{l+1m+1n-1}-u^z_{lmn})+(u^z_{l-1m+}$ $-(u^z_{l+1m-1n-1}-u^z_{lmn})]$ And similar expressions for the *y* and *z*
Eigenfunction solutions	$u_s=A_ke^{i(ksa-\omega t)}$	$u_s=ue^{i(ksa-\omega t)}$ $v_s=ve^{i(ksa-\omega t)}$	$u^x_{lmn}=u^x_{\vec{k}}e^{i(l\vec{k}\cdot\vec{a_1}+m\vec{k}\cdot\vec{a_2}+n\vec{k}\cdot\vec{a_3})}=u^x_{\vec{k}}e^{i(\frac{(-l-}{}}$ 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 $\Big[\; 4-cos(\frac{a}{2}(k_x+k_y+k_z))-cos(\frac{a}{2}(3k_x-k_y-k_z))$ $-cos(\frac{a}{2}(-k_x+3k_y-k_z))-cos(\frac{a}{2}(-k_x-k_y+3k_z))-\frac{m\omega^2}{\sqrt{3}C}$ $-cos(\frac{a}{2}(k_x+k_y$ $+cos(\frac{a}{2}(-k_x+3$ $-cos(\frac{a}{2}(k_x+k_y+k_z))+cos(\frac{a}{2}(3k_x-k_y-k_z))$ $+cos(\frac{a}{2}(-k_x+3k_y-k_z))-cos(\frac{a}{2}(-k_x-k_y+3k_z))$ $4-cos(\frac{a}{2}(k_x+$ $-cos(\frac{a}{2}(-k_x+3$ $-cos(\frac{a}{2}(k_x+k_y+k_z))+cos(\frac{a}{2}(3k_x-k_y-k_z))$ $-cos(\frac{a}{2}(-k_x+3k_y-k_z))+cos(\frac{a}{2}(-k_x-k_y+3k_z))$ $-cos(\frac{a}{2}(k_x+k_y$ $+cos(\frac{a}{2}(-k_x+3$ 
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

$\xrightarrow{573°C}$

β-Quartz
hexagonal
2.53 g/cm3

$\xrightarrow{870°C}$

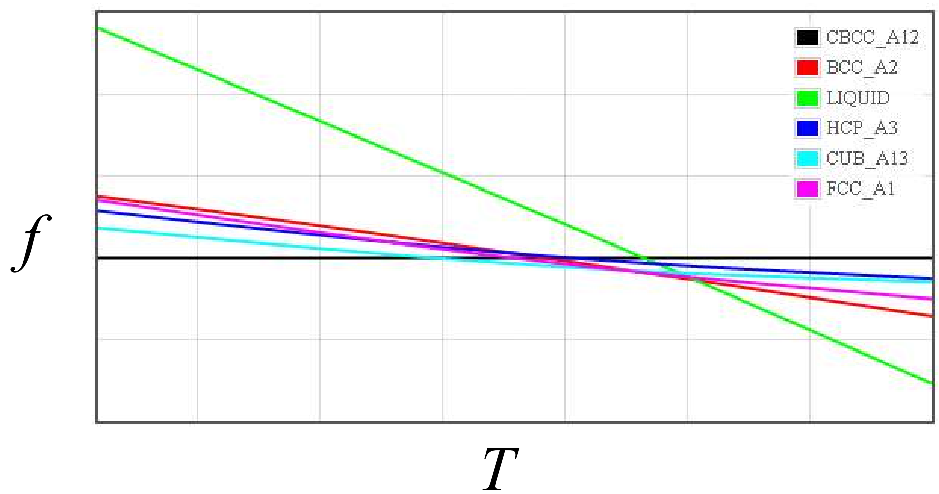
β-Tridymite
hexagonal
2.25 g/cm^3

1470°C ↓

β-Cristobalite
cubic
2.20 g/cm3

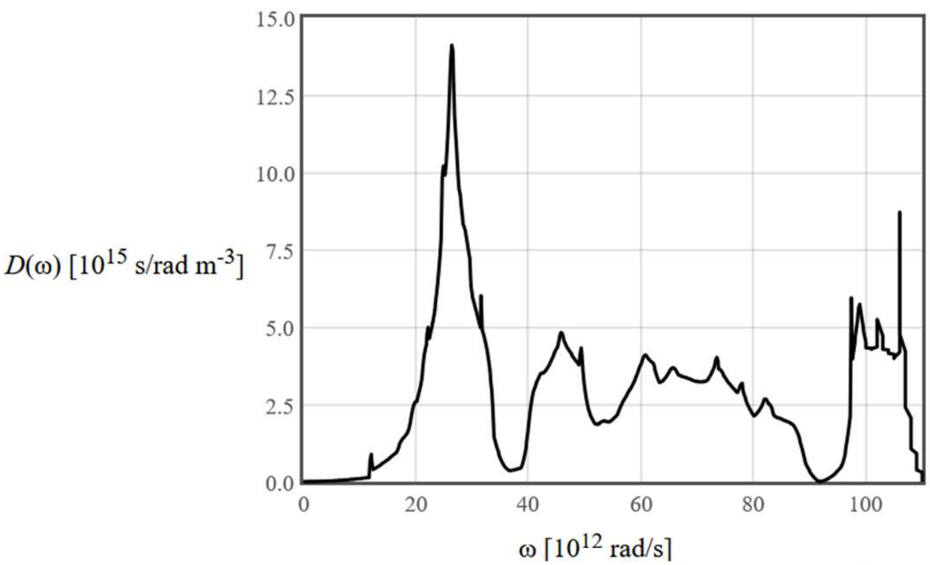
$\xleftarrow{1705°C}$

Silica Melt

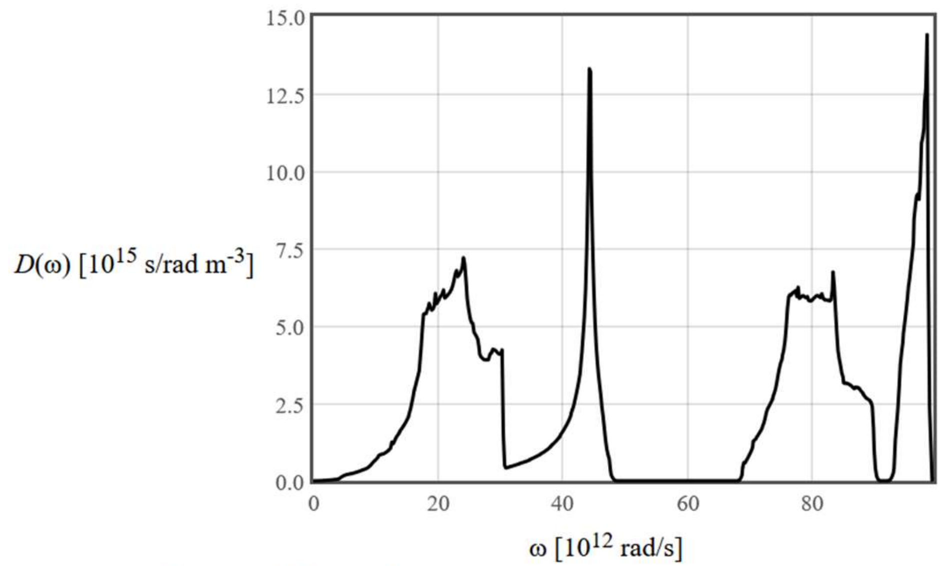


ZnO

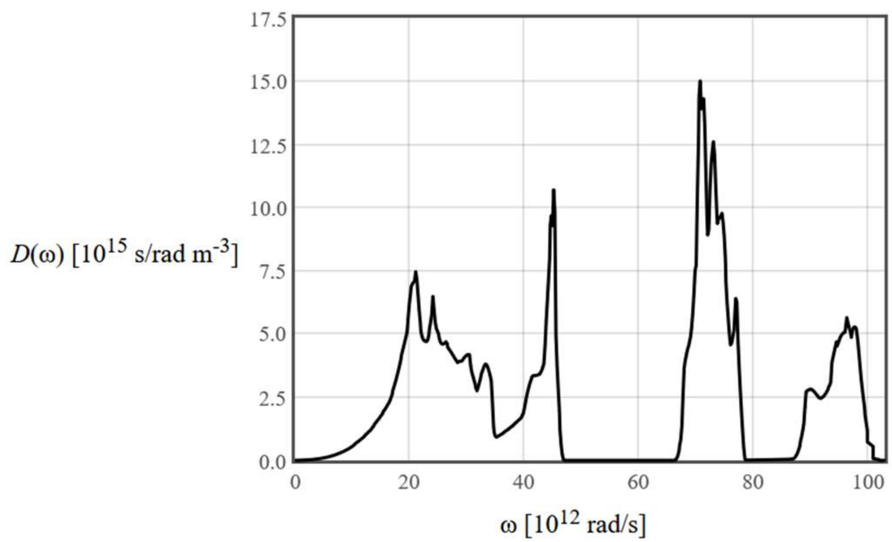
Phonon density of states for ZnO (Rocksalt)



Phonon density of states for ZnO (Zincblende)



Phonon density of states for ZnO (Wurtzite)



Waves and particles

The eigen function solutions of the wave equation are plane waves. The scattering time is one over the rate for scattering from a given plane wave solution to any other.

Phonons are particles. The scattering time is the time before the phonons scatter and randomly change energy and momentum.

$$E = \hbar\omega$$

$$\vec{p} = \hbar\vec{k}$$

The average time between scattering events is $\tau_{sc} = 1/\Gamma$

Phonon scattering

Scattering randomizes the momentum of the phonons.

$$H = H_{HO} + H_1$$

Transition rates determined by Fermi's golden rule

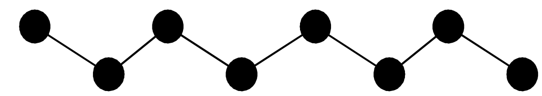
$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}\left|\left\langle \psi_f \left| H_1 \right| \psi_i \right\rangle\right|^2 \delta\left(E_f - E_i\right)$$

Any process (3 phonon, 4 phonon, 5 phonon. ...) that conserves energy and momentum is allowed.

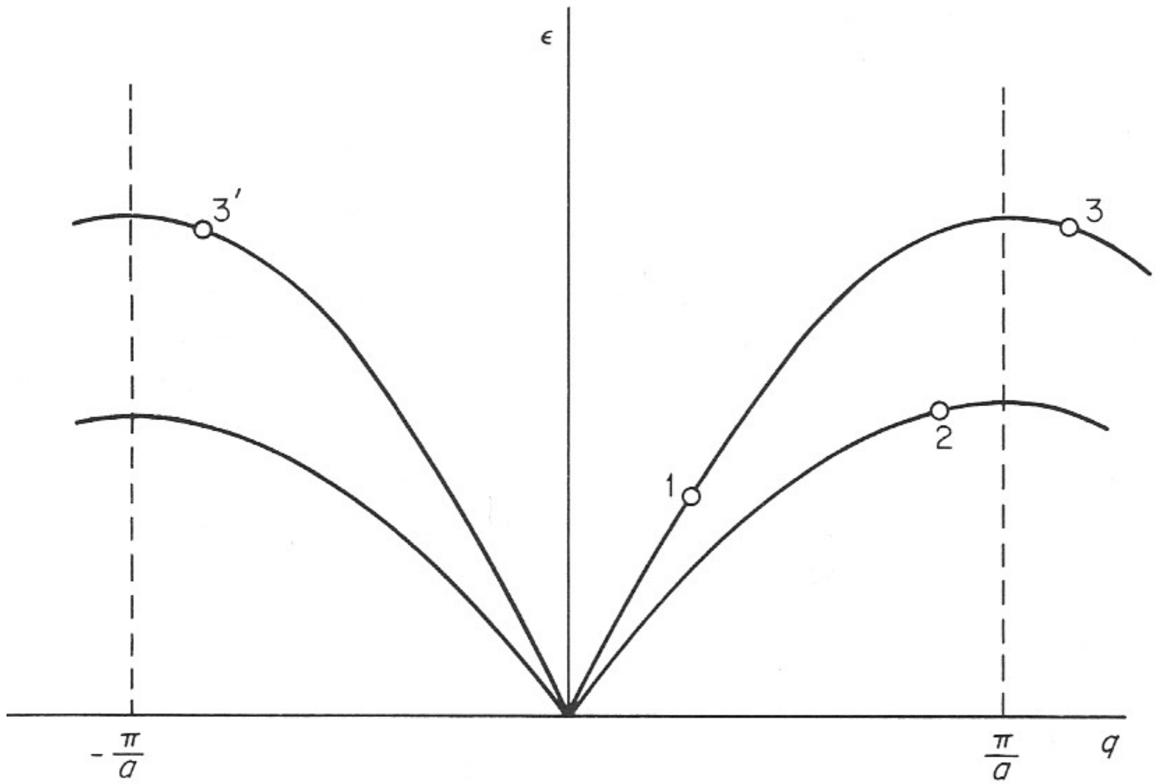
Results in attenuation of acoustic waves

Umklapp Processes

Three phonon scattering



$$\hbar\vec{k}_1 + \hbar\vec{k}_2 = \hbar\vec{k}_3 + \hbar\vec{G}$$

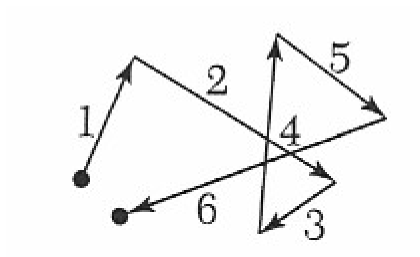


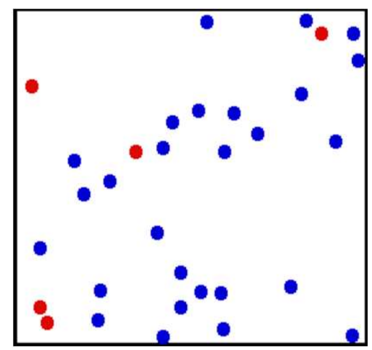
from: Hall, Solid State Physics

Heat transport (Kinetic theory)

Treat phonons as an ideal gas of particles that are confined to the volume of the solid.

Phonons move at the speed of sound. They scatter due to imperfections in the lattice and anharmonic terms in the Hamiltonian.





The average time between scattering events is τ_{sc}

The average distance traveled between scattering events is the mean free path: $\boldsymbol{l} = v\tau_{sc} \sim 10$ nm

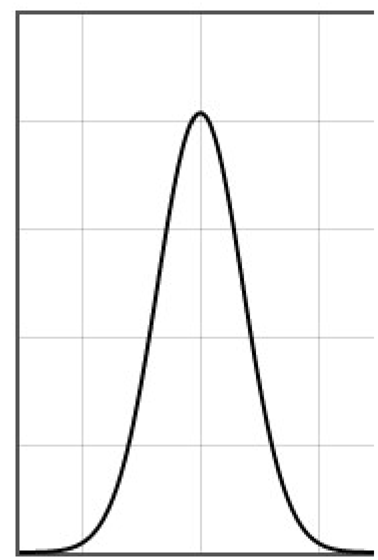
Diffusion equation/ heat equation

$$\frac{dn}{dt} = -D\nabla^2 n$$

Diffusion constant

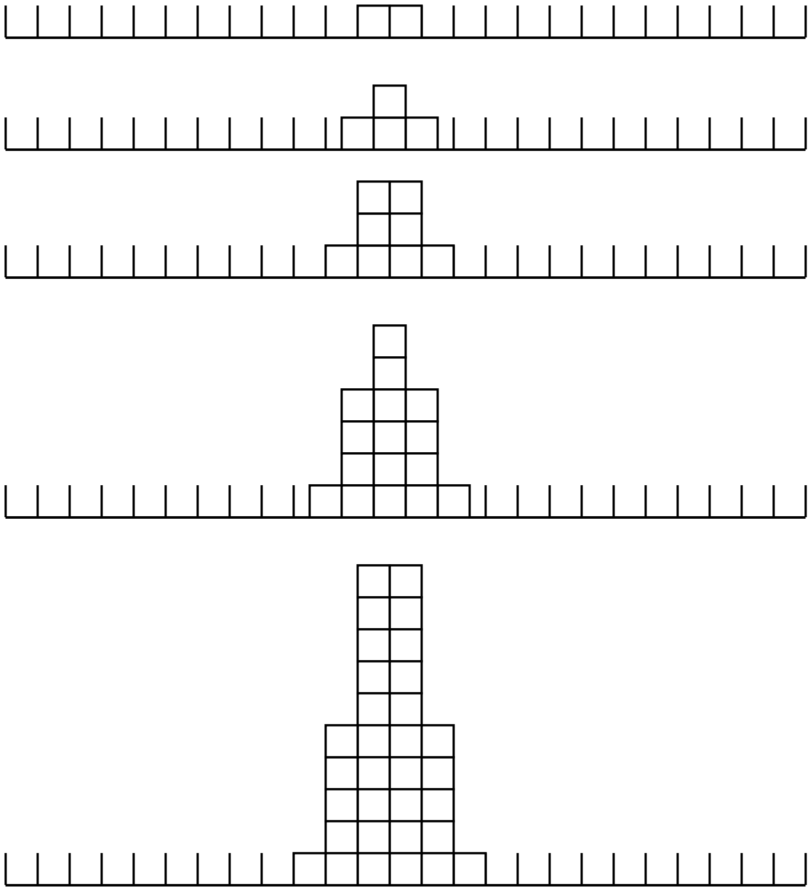
Fick's law $\quad \vec{j} = -D\nabla n$

Continuity equation $\quad \dfrac{dn}{dt} = \nabla \cdot \vec{j}$

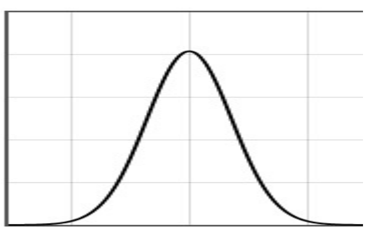


$$n = \frac{1}{\sqrt{4\pi Dt}} \exp\left(\frac{-r^2}{4Dt}\right)$$

Random walk



$$\frac{\Delta n_s}{\Delta t} = n_{s+1} - 2n_s + n_{s-1}$$



$$\exp\left(-x^2\right)$$

Central limit theorem: A function convolved with itself many times forms a Gaussian