Phonon contribution to thermodynamic properties

Dulong and Petit (Classical result)

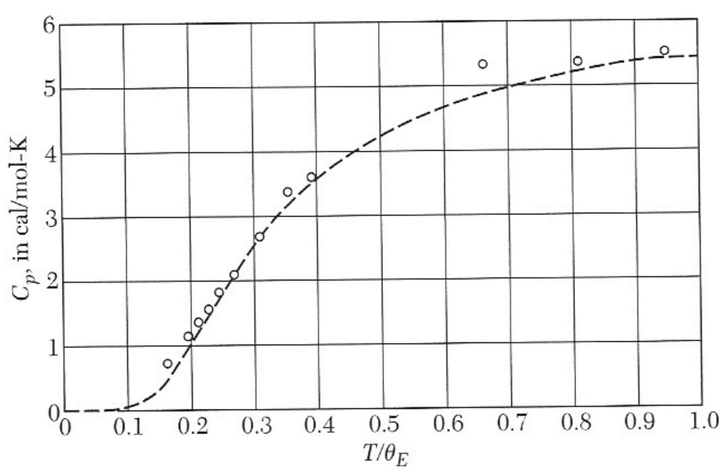
Equipartition: $\frac{1}{2}k_BT$ per quadratic term in energy

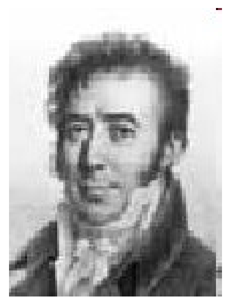
internal energy: $u = 3nk_BT$ n = atomic density

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

experiments: heat capacity goes to zero at zero temperature

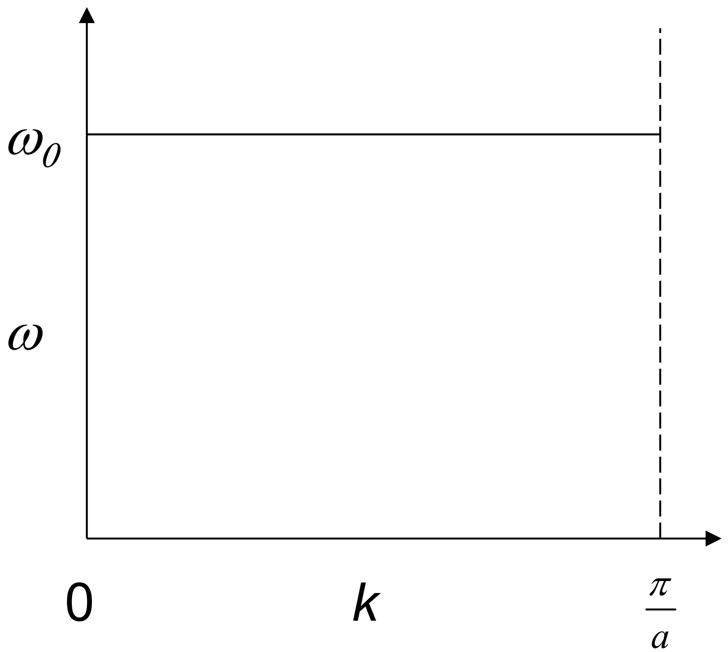
Pierre Louis Dulong

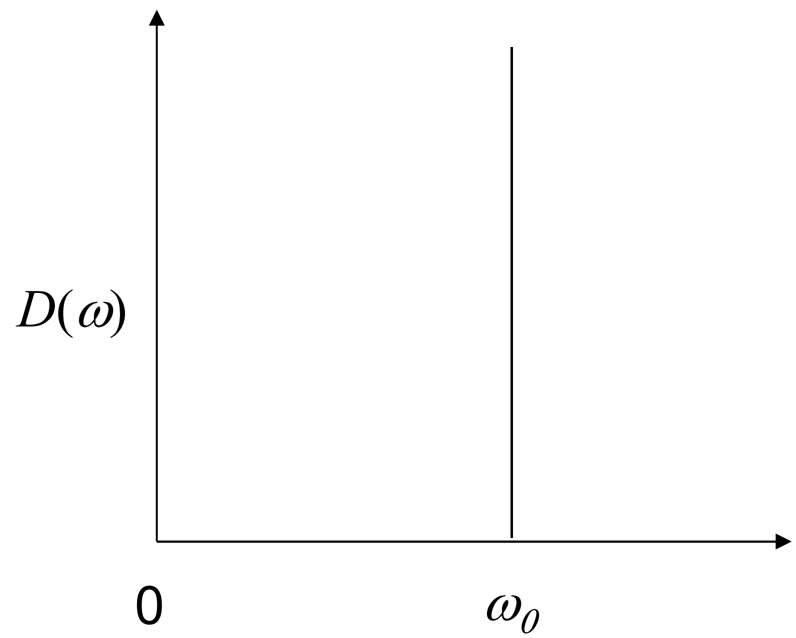




Alexis Therese Petit

Einstein model for specific heat





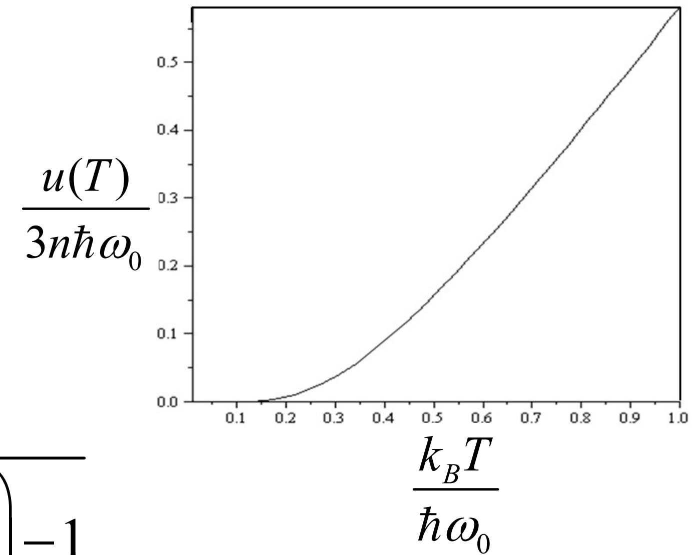
$$D(\omega) = 3n\delta(\omega - \omega_0)$$

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

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

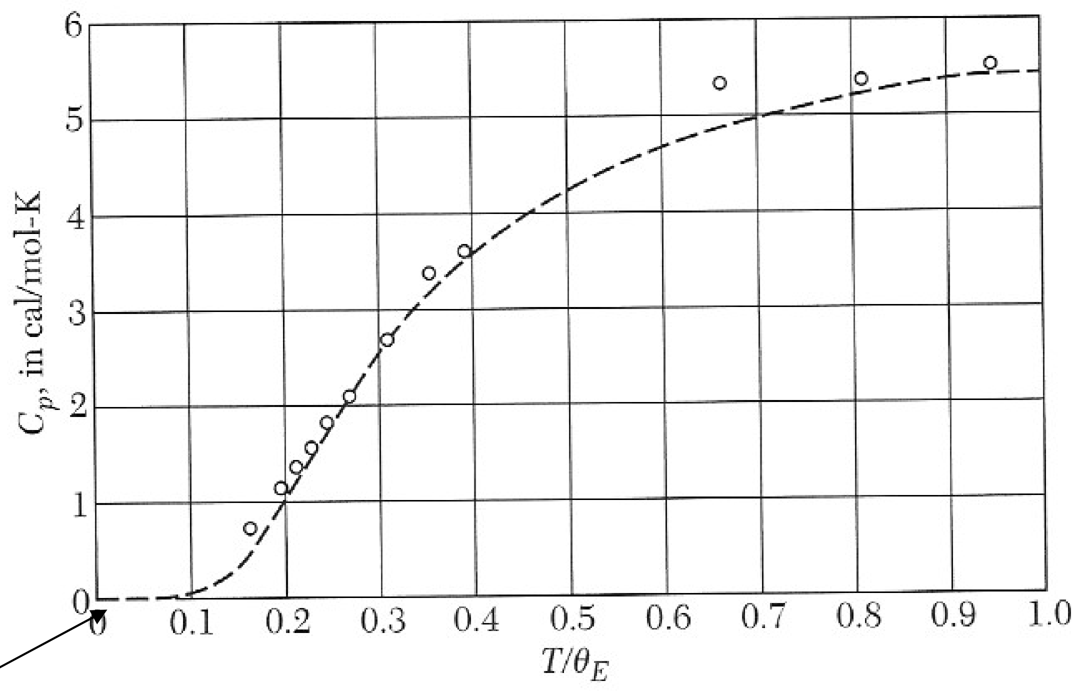


$$u = \int_0^\infty u(\omega)d\omega = \int_0^\infty 3n\hbar\omega \frac{\delta(\omega-\omega_0)d\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1} = \frac{3n\hbar\omega_0}{\exp\left(\frac{\hbar\omega_0}{k_B T}\right)-1}$$

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

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

$$c_v \approx 3nk_B$$

low T does not fit

$$\theta_E = \frac{\hbar\omega_0}{k_B}$$

Debye model for specific heat

Peter Debye

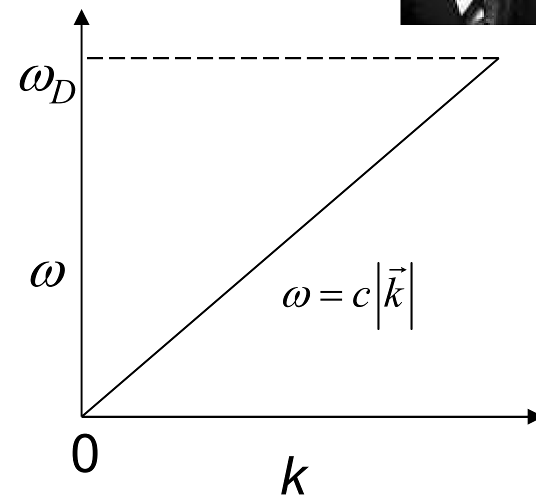
$$D(\omega) = \frac{3\omega^2}{2\pi^2 c^3}$$

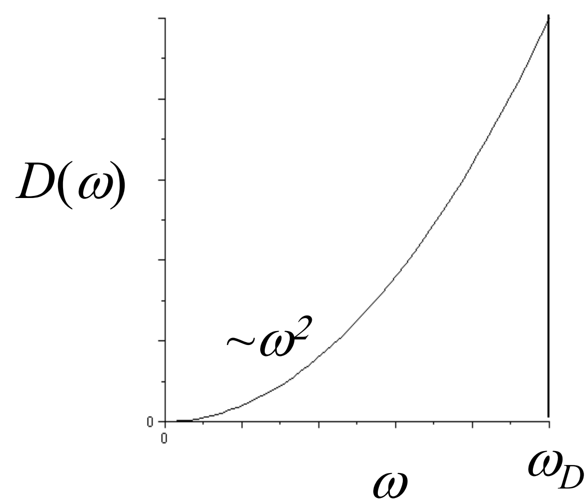
Like blackbody radiation up to a cutoff frequency.

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

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

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





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}

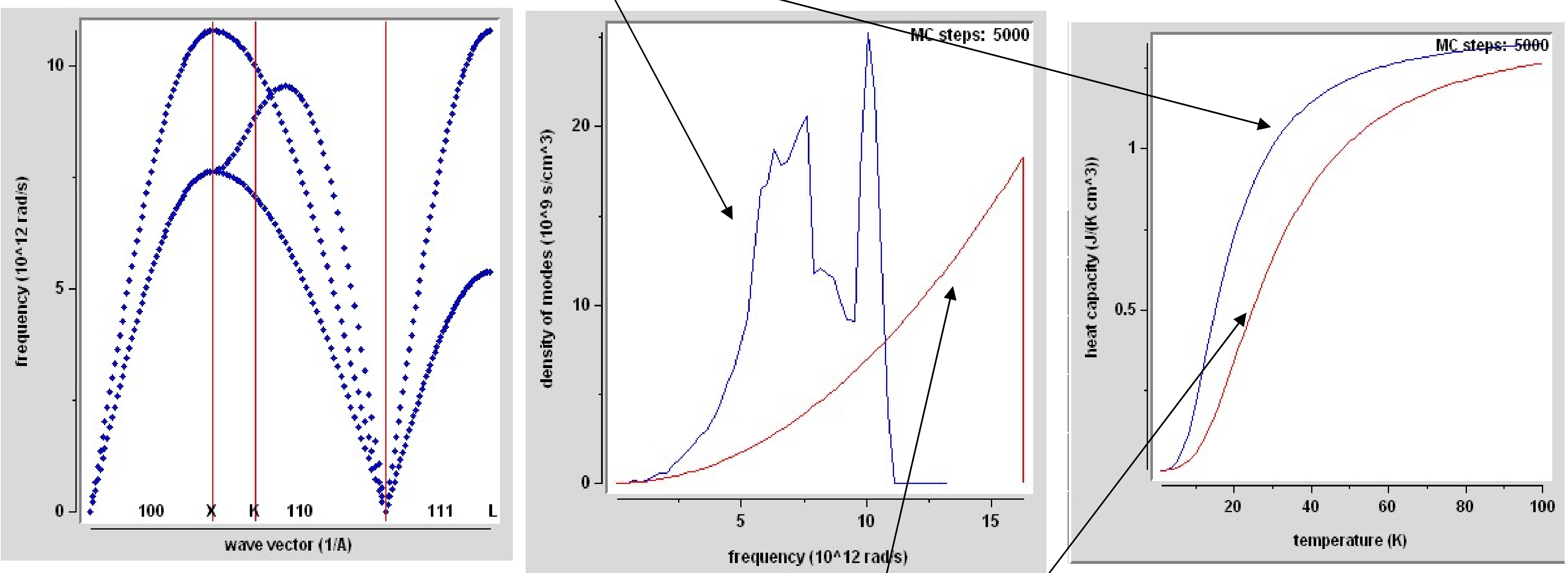
Li 344 0.85	Be 1440 2.00											B 0.27	C 2230 1.29	N	O	F	Ne 75
Na 158 1.41	Mg 400 1.56											Al 428 2.37	Si 645 1.48	P	S	Cl	Ar 92
K 91 1.02	Ca 230	Sc 360. 0.16	Ti 420 0.22	V 380 0.31	Cr 630 0.94	Mn 410 0.08	Fe 470 0.80	Co 445 1.00	Ni 450 0.91	Cu 343 4.01	Zn 327 1.16	Ga 320 0.41	Ge 374 0.60	As 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

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

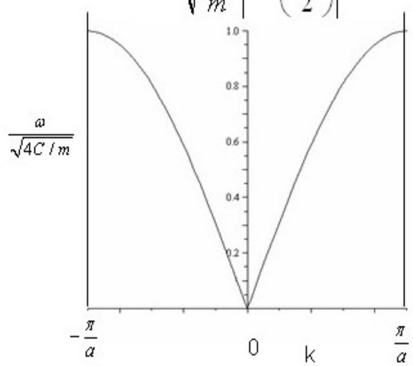
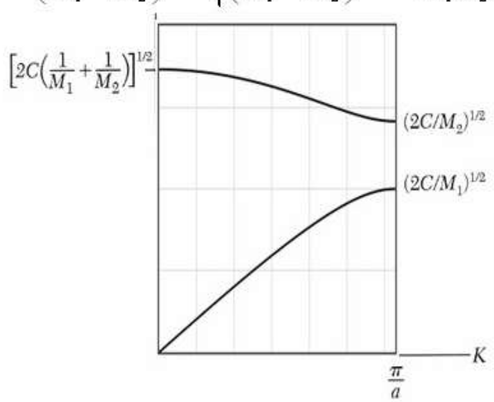
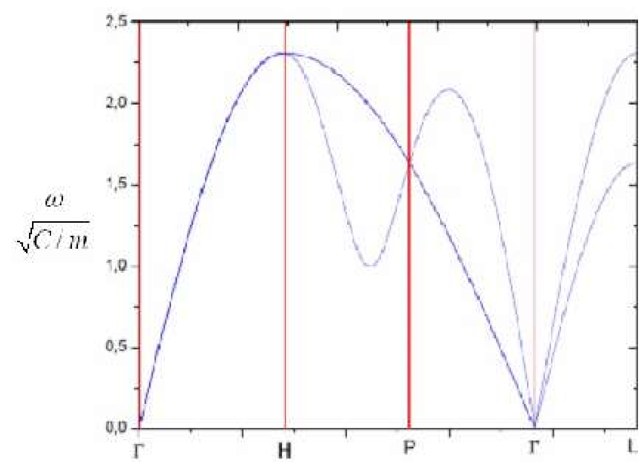
entropy density

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

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
	$m\frac{d^2u_s}{dt^2}=C(u_{s+1}-2u_s+u_{s-1})$	$M_1\frac{d^2u_s}{dt^2}=C(v_{s-1}-2u_s+v_s)$ $M_2\frac{d^2v_s}{dt^2}=C(u_s-2v_s+u_{s+1})$	$\frac{d^2u^x_{lmn}}{dt^2}=\frac{C}{\sqrt{3}\,m}[(u^x_{l+1m+1n+1}-u^x_{lmn})+(u^x_{l-1m+1n+1}-u^x_{l}$ $+(u^x_{l+1m-1n+1}-u^x_{lmn})+(u^x_{l+1m+1n-1}-u^x_{lmn})+(u^x_{l-1m+}$ $+(u^x_{l+1m-1n-1}-u^x_{lmn})+(u^y_{l+1m+1n+1}-u^y_{lmn})-(u^y_{l-1m+}$ $+(u^y_{l+1m-1n+1}-u^y_{lmn})-(u^y_{l+1m+1n-1}-u^y_{lmn})+(u^y_{l-1m+}$ $+(u^y_{l+1m-1n-1}-u^y_{lmn})+(u^z_{l+1m+1n+1}-u^z_{lmn})-(u^z_{l-1m+}$ $+(u^z_{l+1m-1n+1}-u^z_{lmn})-(u^z_{l+1m+1n-1}-u^z_{lmn})+(u^z_{l-1m+}$ $-(u^z_{l+1m-1n-1}-u^z_{lmn})]$ 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	$\omega=\sqrt{\frac{4C}{m}}\left\|\sin\left(\frac{ka}{2}\right)\right\|$ 	$\omega^2=C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2-\frac{4\sin^2\left(\frac{ka}{2}\right)}{M_1M_2}}$  Calculate ω(k)	The dispersi $\begin{bmatrix} 4-cos(\frac{a}{2}(k_x+k_y+k_z))-cos(\frac{a}{2}(3k_x-k_y-k_z)) -cos(\frac{a}{2}(-k_x+3k_y-k_z))-cos(\frac{a}{2}(-k_x-k_y+3k_z))-\frac{m\omega^2}{\sqrt{3}C} & -cos(\frac{a}{2}(k_x+k_y +cos(\frac{a}{2}(-k_x+3 \\ -cos(\frac{a}{2}(k_x+k_y+k_z))+cos(\frac{a}{2}(3k_x-k_y-k_z)) +cos(\frac{a}{2}(-k_x+3k_y-k_z))-cos(\frac{a}{2}(-k_x-k_y+3k_z)) & 4-cos(\frac{a}{2}(k_x+ -cos(\frac{a}{2}(-k_x+3 \\ -cos(\frac{a}{2}(k_x+k_y+k_z))+cos(\frac{a}{2}(3k_x-k_y-k_z)) -cos(\frac{a}{2}(-k_x+3k_y-k_z))+cos(\frac{a}{2}(-k_x-k_y+3k_z)) & -cos(\frac{a}{2}(k_x+k_y +cos(\frac{a}{2}(-k_x+3 \end{bmatrix}$ 
Density of states $D(k)$	$D(k)=\frac{1}{\pi}$	$D(k)=\frac{1}{\pi}$	$D(k)=\frac{3k^2}{2\pi^2}$

Quartz

α-Quartz
trigonal
2.65 g/cm³

573°C →

β-Quartz
hexagonal
2.53 g/cm3

870°C →

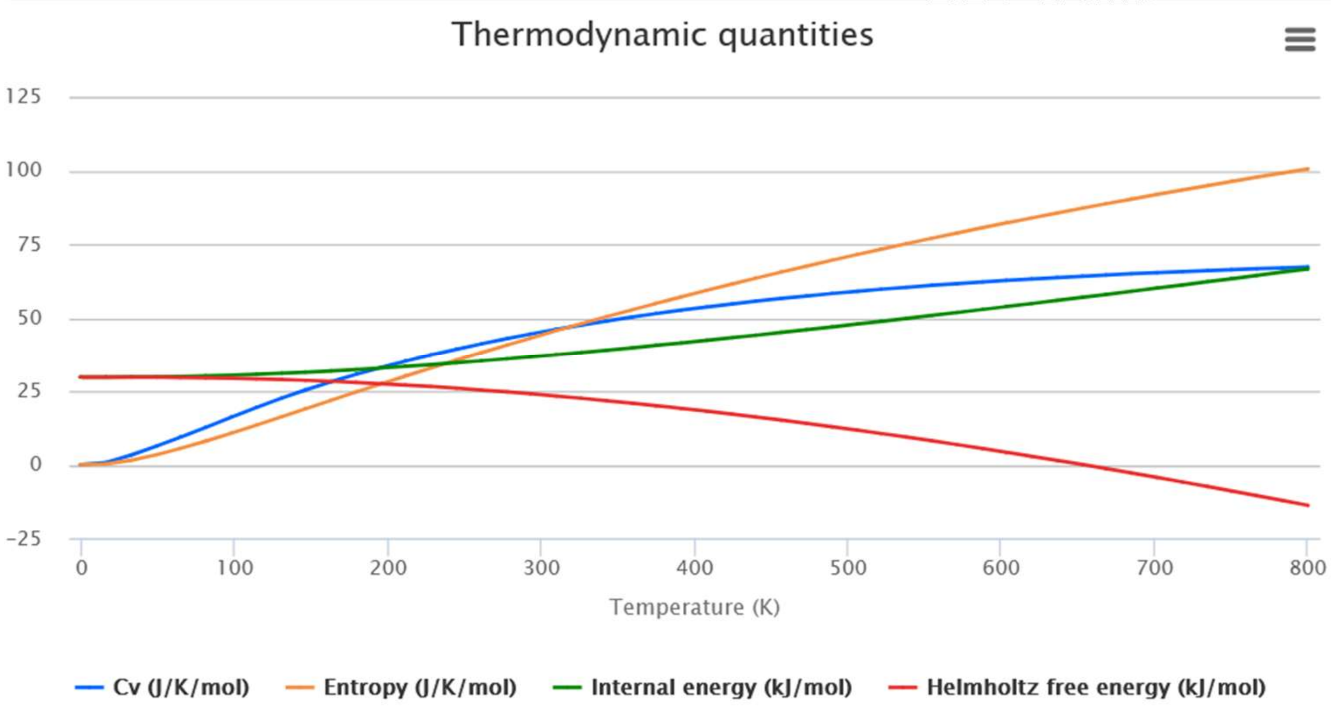
β-Tridymite
hexagonal
2.25 g/cm³

1470°C ↓

β-Cristobalite
cubic
2.20 g/cm3

1705°C ←

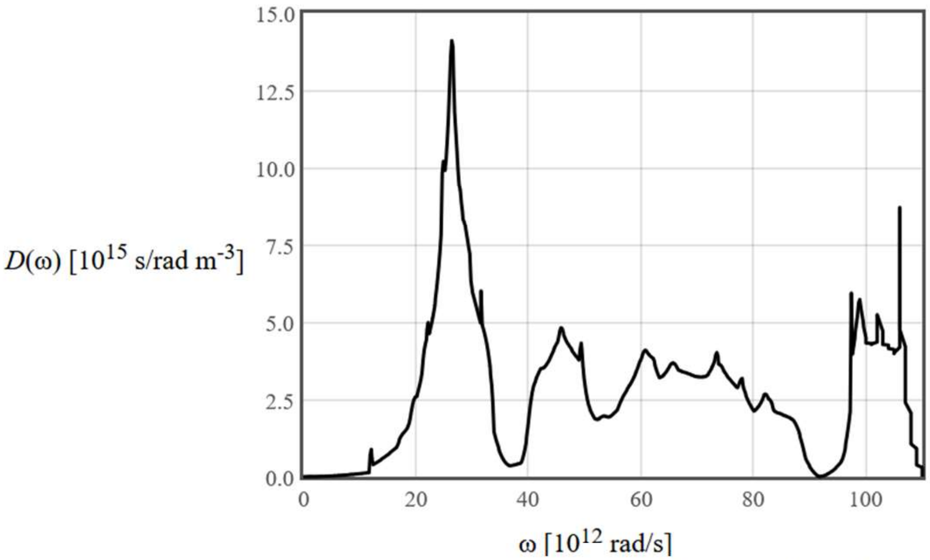
Silica Melt



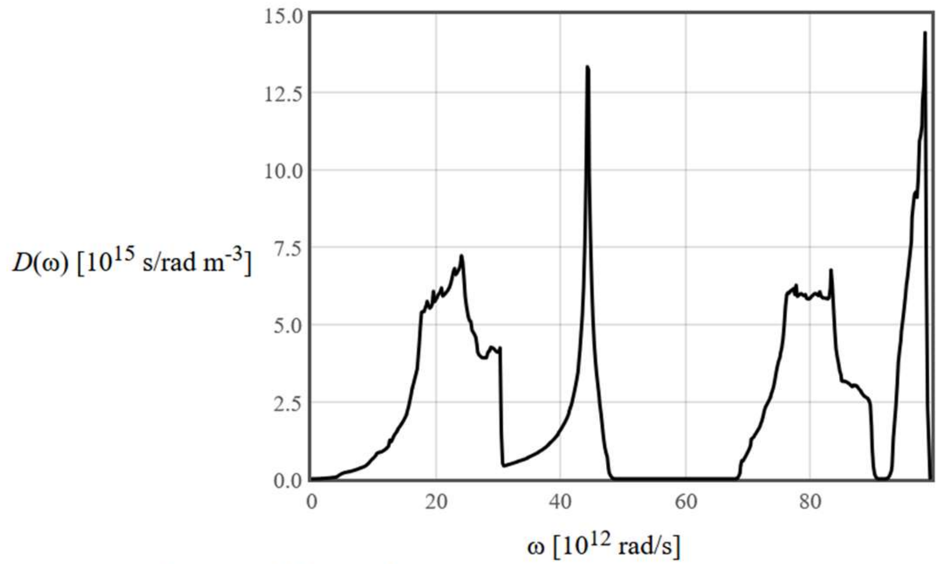
Materials project

ZnO

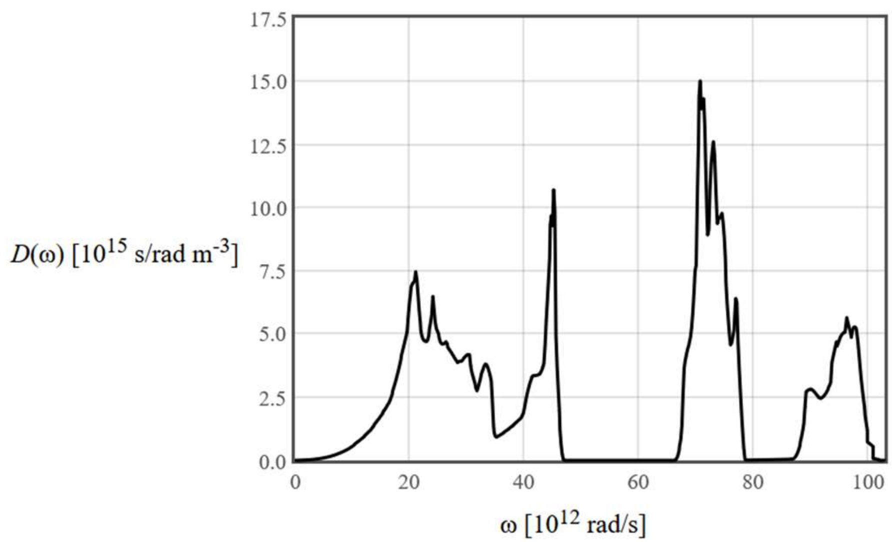
Phonon density of states for ZnO (Rocksalt)



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

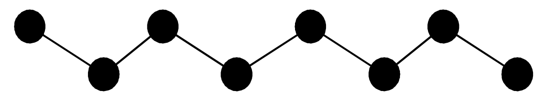
$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \left| \langle \psi_f | H_1 | \psi_i \rangle \right|^2 \delta\left(E_f - E_i\right)$$

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

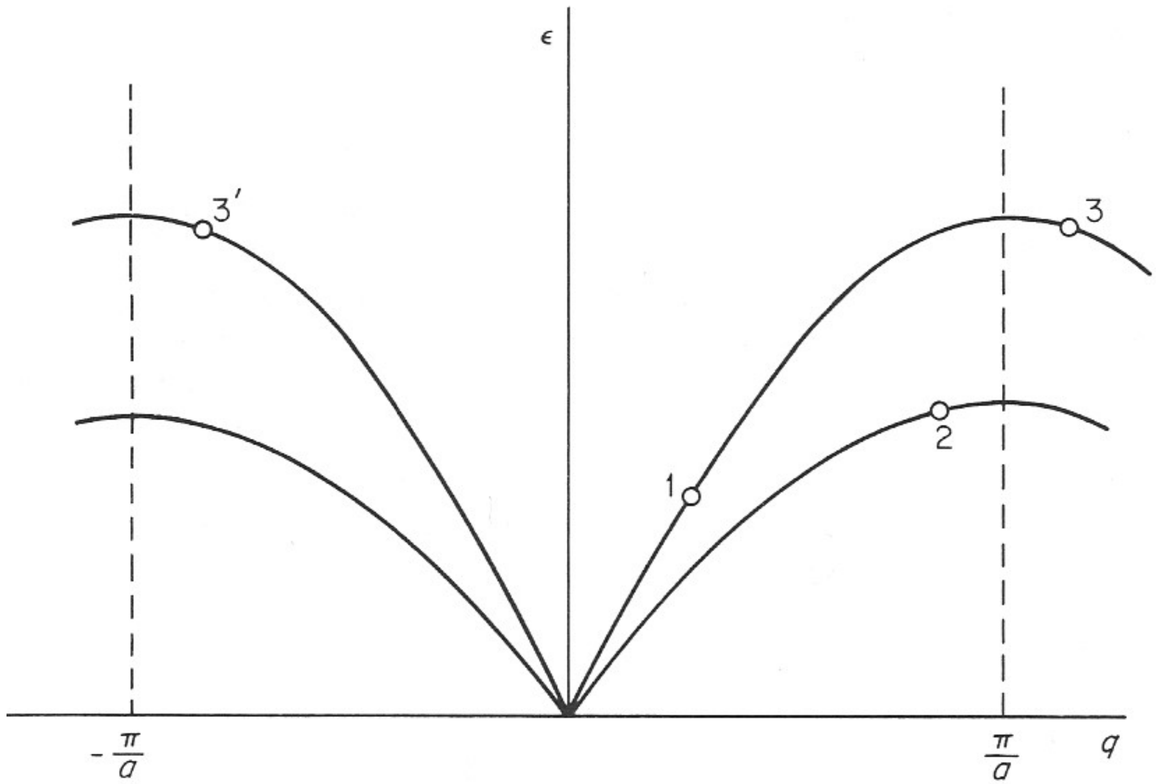
Results in attenuation of acoustic waves

Umklapp Processes

Three phonon scattering



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

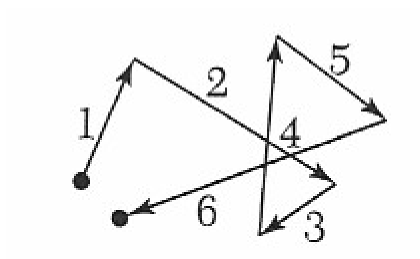


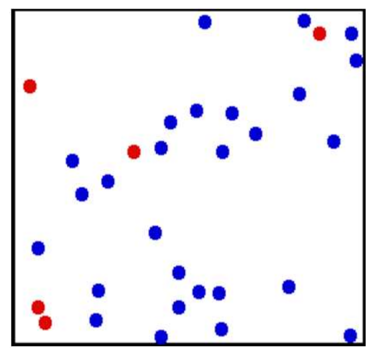
from: Hall, Solid State Physics

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

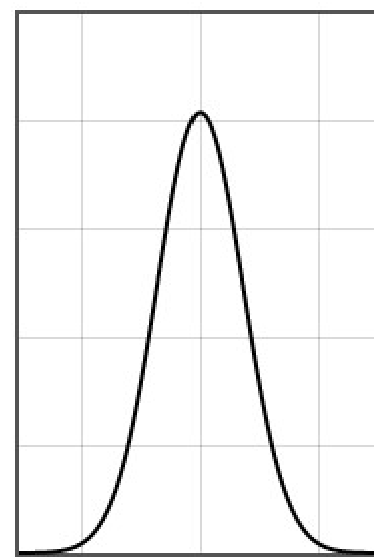
Diffusion equation/ heat equation

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

Diffusion constant → D

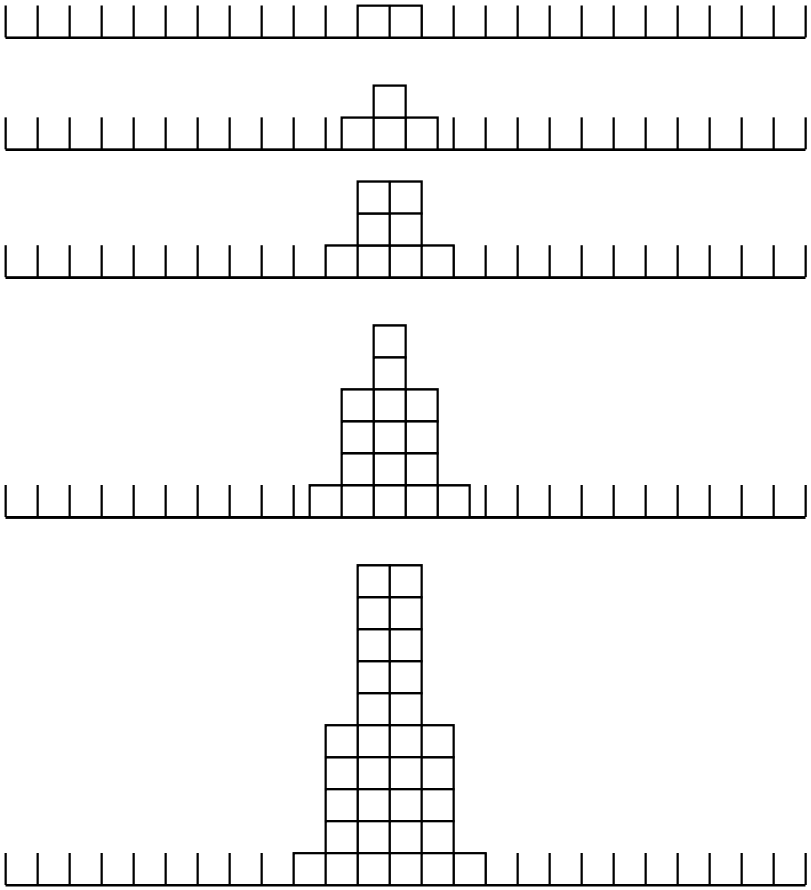
Fick's law $\vec{j} = -D\nabla n$

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



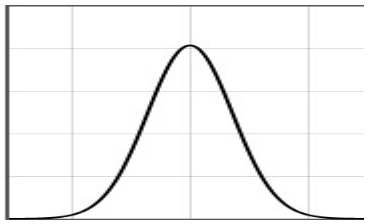
$$n = \frac{1}{\sqrt{4\pi Dt}} \exp\left(\frac{-r^2}{4Dt}\right)$$

Random walk



After N steps of size d, the distribution is

$$P = \frac{1}{\sqrt{\pi N d}} e^{-\frac{x^2}{Nd}}$$



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

Thermal conductivity

$$\vec{j}_U = \bar{E}\vec{j}$$

Average particle energy

$$u = \bar{E}n$$

internal energy density

$$\vec{j} = -D\nabla n$$

$$\vec{j}_U = -\bar{E}D\nabla n = -D\nabla u$$

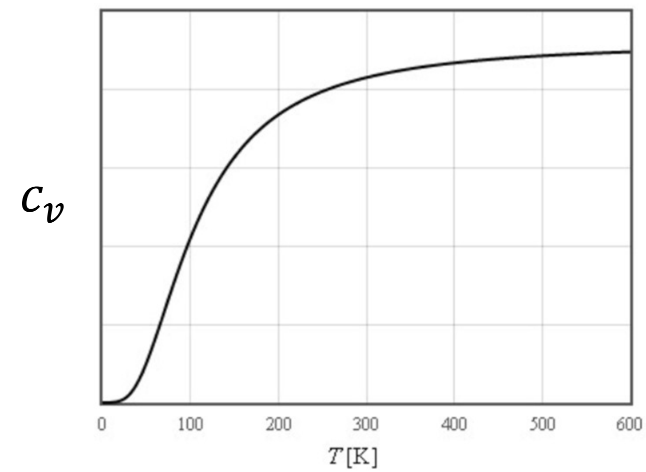
$$\vec{j}_U = -D\frac{du}{dT}\nabla T = -Dc_v\nabla T$$

$$\vec{j}_U = -K\nabla T$$

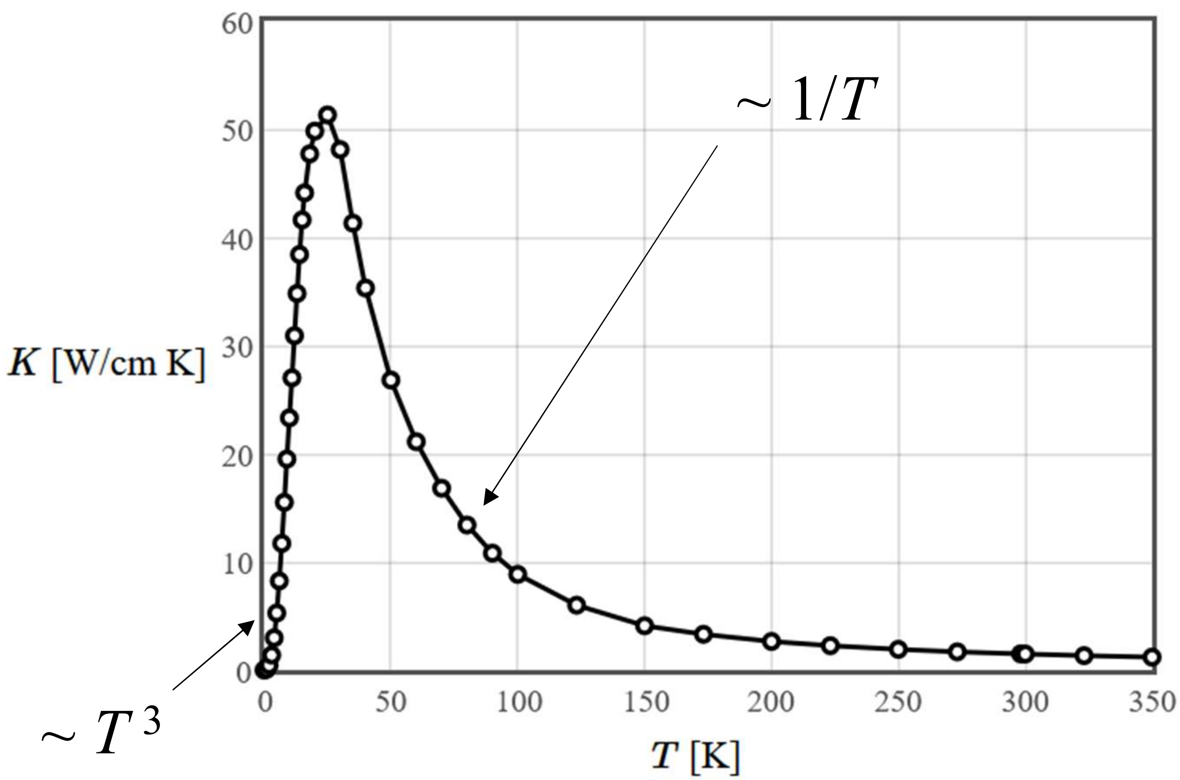
Thermal conductivity → K

$$K = Dc_v$$

$$K \to 0 \quad \text{as} \quad T \to 0$$



Thermal conductivity $\vec{j}_U = -K\nabla T$



The thermal conductivity of silicon.[1]

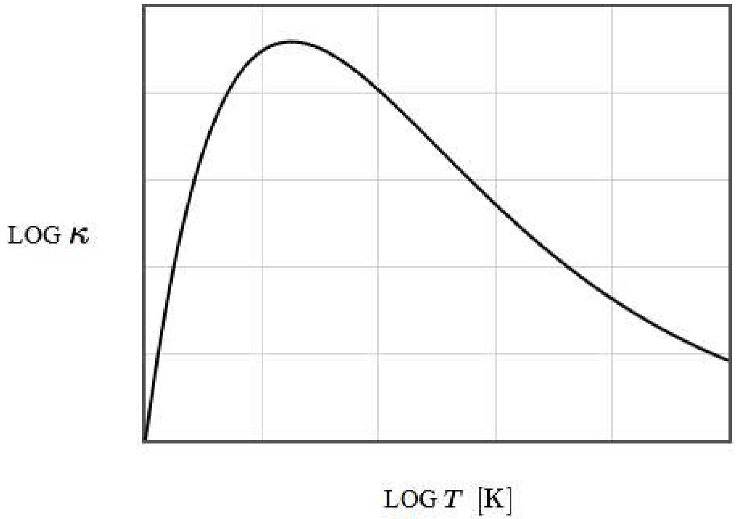
$$K = Dc_v$$

The diffusion constant decreases because of phonon-phonon scattering.

Thermal conductivity

$$\vec{j}_U = -K\nabla T$$

Material	**Thermal conductivity W/(m·K)**
Glass	1.1
Concrete, stone	1.7
Ice	2
Sandstone	2.4
Sapphire	35
Stainless steel	12.11 ~ 45.0
Lead	35.3
Aluminum	237
Aluminum alloys	120—180
Gold	318
Copper	401
Silver	429
Diamond	900 - 2320
Graphene	(4840±440) - (5300±480)



Phonon student projects

Calculate a dispersion relation for some other Bravais lattice.

Calculate one column of the phonon table: hcp, NaCl, CsCl, ZnS, diamond, ...

Calculate the temperatures at which ZnO goes through a phase transition.