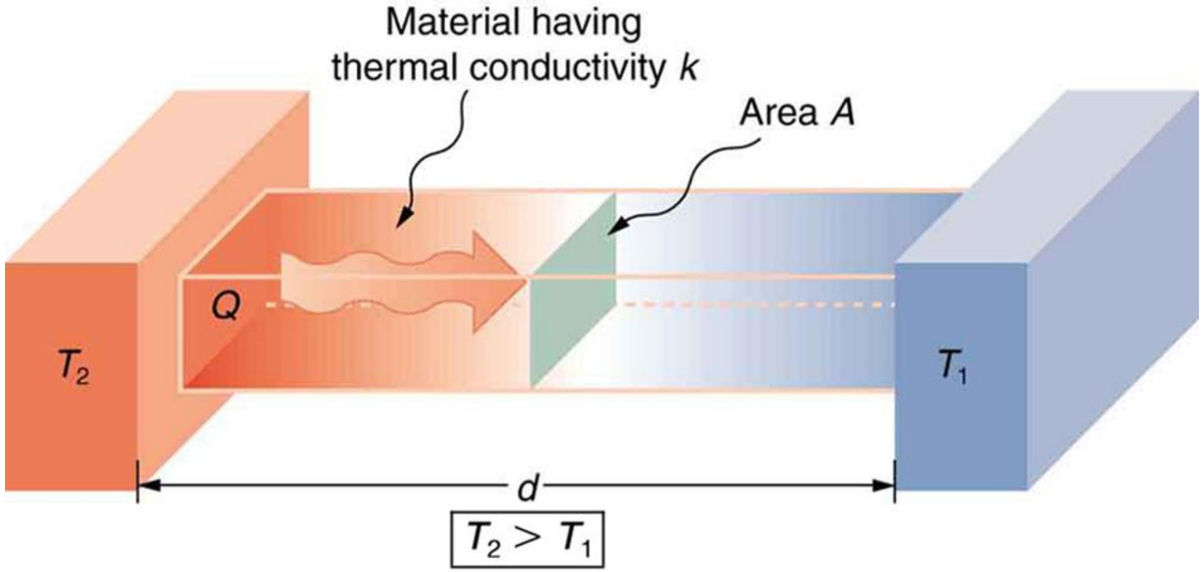
Phonons: Thermal properties

Kittel Chapter 5



Material having
thermal conductivity k
Area A
Q
T2
T1
d
T2 > T1

Thermal properties - Goals

- Introduction: Why do we care?
- **Debye’s Model for heat capacity**
- **Einstein’s Model for heat capacity**
- **Thermal conductivity**

Heat capacity

Heat capacity is the measure of how much energy it takes to raise the temperature of a unit of mass of an object a certain amount

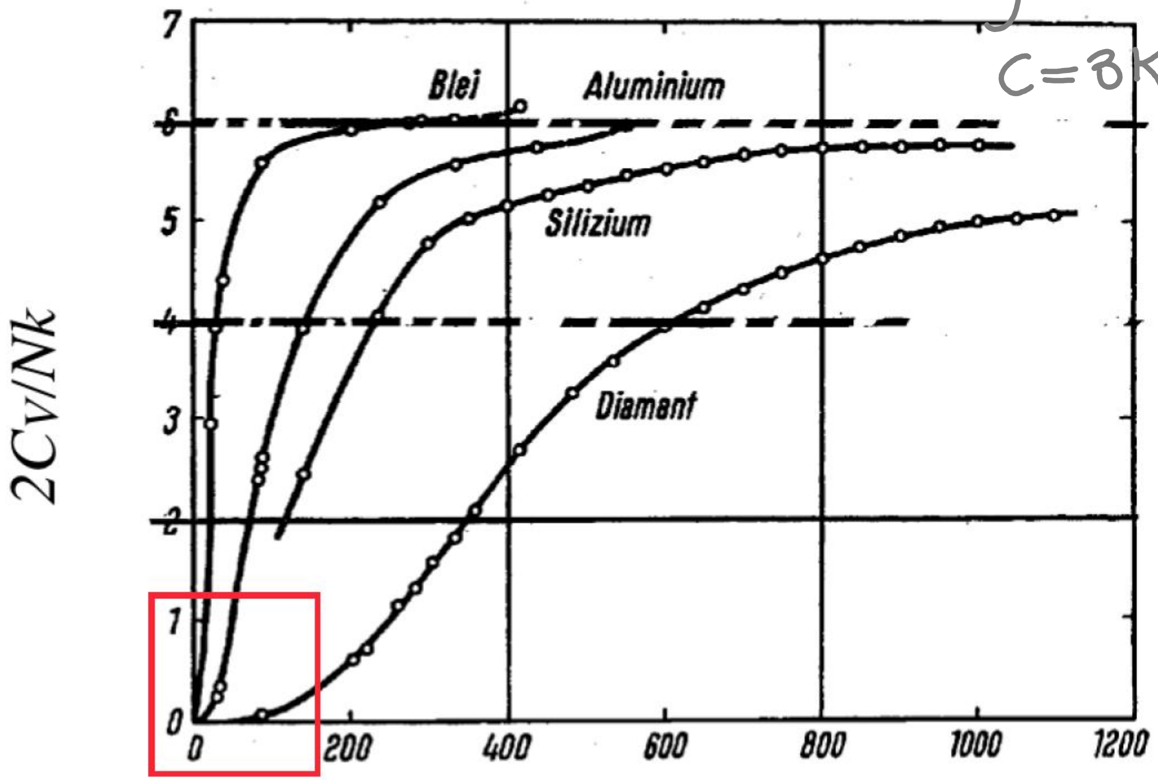
at constant volume $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

U = energy

LATTICE HEAT CAPACITY = contribution of phonons to C of a crystal

Dulong Petit Law

$C = 3k_B$ per atom



C_v(Gitter) prop. T^3

Phonons Energy

$$U_{LATT} = \sum_{K} \sum_{p} u_{K,p} = \sum_{K} \sum_{p} \langle n_{K,p} \rangle \hbar\omega_{K,p}$$

polarization

Thermal Equilibrium occupancy of phonons of wavector K and polarization p

We cannot determine the number of phonons at given T, but we can know the probability of having n phonons

Planck distribution

Bose-Einstein distribution

$$\langle n_{Kp} \rangle = \frac{1}{\exp\left(\frac{\hbar\omega}{K_B T}\right) - 1}$$

(see Kittel for more details)

K_B : Boltzmann constant

Planck distribution

$$\langle n_{K,p} \rangle = \frac{1}{\exp(\frac{\hbar\omega}{k_B T}) - 1}$$

number of phonons ↓
as temperature ↓

at fixed frequency:

```
Plot[{1/(Exp[1/x] - 1)}, {x, 0, 3}, PlotRange → {{0, 3}, {0, 3}},
 PlotStyle → Thick, AxesLabel → {"T/(ℏω/k_B)", "⟨n⟩"}, LabelStyle → Medium]
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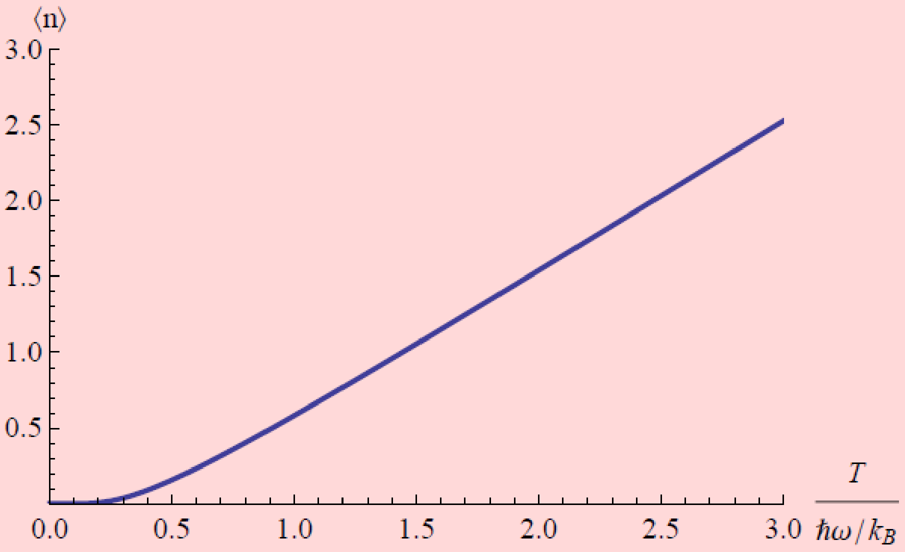
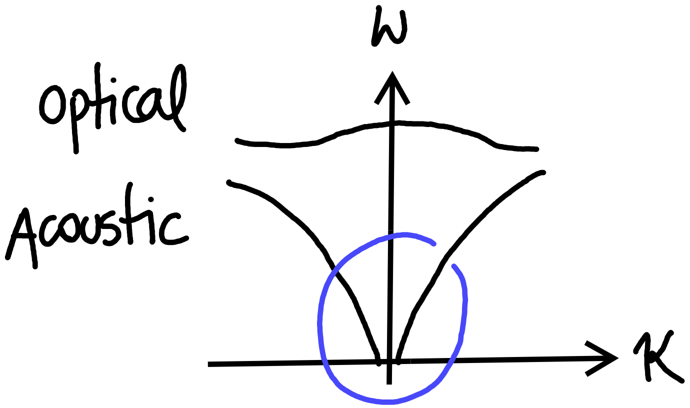


Planck distribution

$$\langle n_{K,p}\rangle = \frac{1}{\exp(\frac{\hbar\omega}{k_B T}) - 1}$$

Low ω-modes have more phonons than high ω modes



at very low T, we mainly need to consider acoustic modes

at fixed temperature:

```
Plot[{1/(Exp[x] - 1)}, {x, 0, 3}, PlotRange → {{0, 3}, {0, 10}},
 PlotStyle → Thick, AxesLabel → {"ω/(k_B T / ħ)", "⟨n⟩"}, LabelStyle → Medium]
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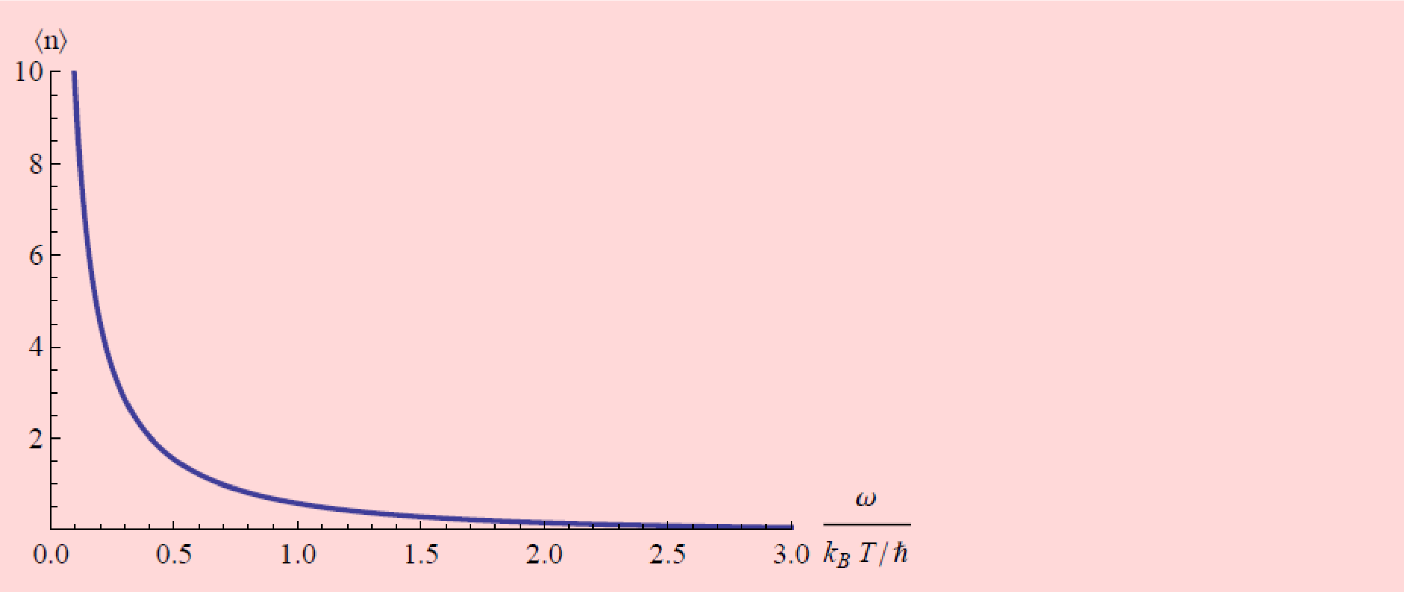
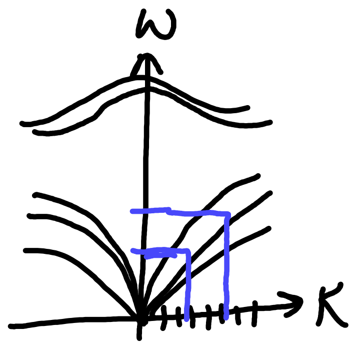


Phonons Energy



$$\mathcal{U} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar\omega_{Kp} = \sum_K \sum_p \frac{\hbar\omega_{K,p}}{\exp\left(\frac{\hbar\omega_{Kp}}{K_B T}\right) - 1}$$

Replace $\sum_K$ by $\int$:

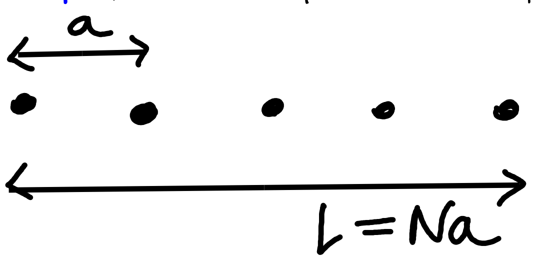
$$\mathcal{U} = \sum_p \int d\omega\, D_p(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{K_B T}\right) - 1}$$

number of modes per unit fegcency range
(Density of modes; density of states)

$$C = \frac{\partial \mathcal{U}}{\partial T}\Big]_V \Rightarrow C_{LATT} = K_B \sum_p \int d\omega\, D_p(\omega) \frac{x^2 \exp x}{(\exp x - 1)^2} \quad \text{with } x = \frac{\hbar\omega}{K_B T}$$

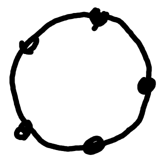
Density of states in 1D

Recap: How many different phonon modes we have?



$$s_n = A\exp(-i\omega t + iKx_{eq})$$
$$= A\exp(-i\omega t + iKna)$$

in 1D:



periodic boundary conditions $s(na) = s(na+L)$

$$s(na+L) = A\exp(-i\omega t + iK(na+L)) = s(na)\cdot\underbrace{\exp(iKL)}_{=1}$$

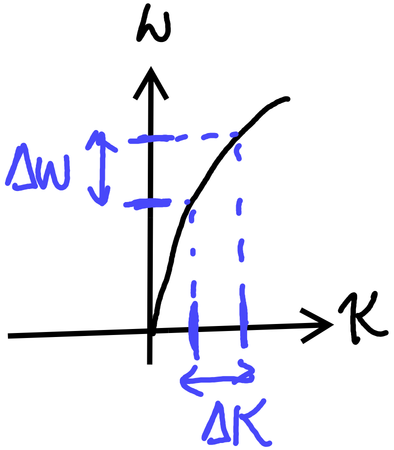
$$\exp(iKL) = 1 \Rightarrow K = \pm\frac{2\pi}{L}p = \pm\frac{2\pi}{a}\frac{p}{N}$$

p: integer

→ Notice than K and $K+G$ gives the same result (check it!)

⇒ we only need to consider $-\frac{\pi}{a} \leq K \leq \frac{\pi}{a}$; so, $K = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L} \dots \frac{N\pi}{L}$

$D_1(\omega)$ Number of modes per unit frequency range for a given polarization



$$D_1(\omega) = \frac{\text{number of modes}}{\Delta\omega}$$

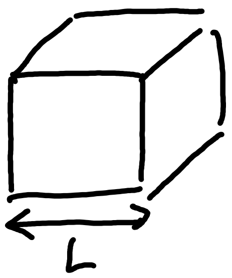
$$\#\text{ of modes} = 2\,\frac{\Delta K}{2\pi/L} = 2\,\frac{\frac{dK}{d\omega}\,\Delta\omega}{2\pi/L}$$

$$\Rightarrow D_1(\omega) = \frac{L}{\pi}\,\frac{1}{\underbrace{\frac{d\omega}{dK}}}$$ in 1D

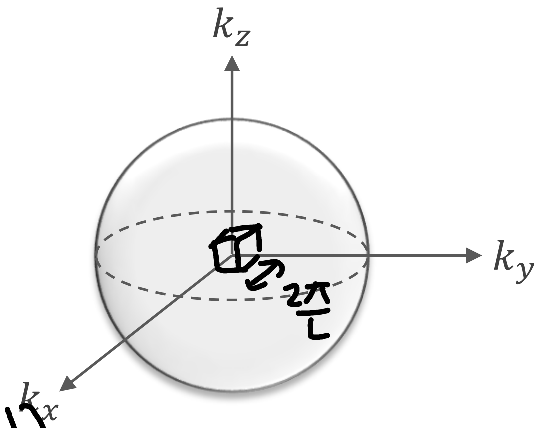
group velocity can be obtained from $\omega(K)$

(! singularities at $v_g = 0$)

Density of states in 3D



N^3 primitive unit cells within cube of side L



Periodic boundary conditions $\Rightarrow \vec{K}$ is determined by the condition:

$$\exp(i(K_x x + K_y \cdot y + K_z \cdot z)) = \exp(i(K_x(x+L) + K_y(y+L) + K_z(z+L)))$$

as before, it requires: $K_x, K_y, K_z = 0, \pm\frac{2\pi}{L}, \frac{4\pi}{L} \ldots \frac{N\pi}{L}$

there is one allowed K value per $\left(\frac{2\pi}{L}\right)^3$ in K space

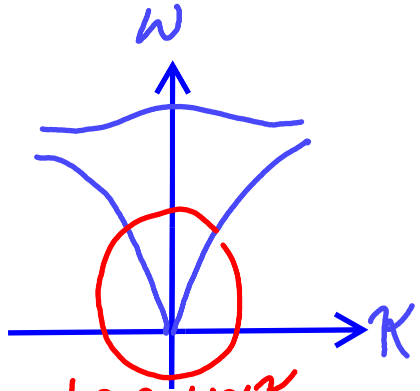
$\left(\frac{L}{2\pi}\right)^3 = \frac{V}{8\pi^3}$ allowed values of $\bar{K}$ per unit K-space for each polarization and for each branch

$$N = \frac{4/3\,\pi K^3}{\left(2\pi/L\right)^3} = \frac{V}{2\pi^2}\frac{K^3}{3} \Rightarrow \boxed{D_3(\omega) = \frac{dN}{d\omega} = \frac{V}{2\pi^2}K^2\frac{dK}{d\omega}}$$

for each polarization type

Debye model

In this approx. $\boxed{v_{sound} = ct}$ for each polarization type
(as it would be for a classical elastic continuum)



here $\omega \propto K$
$\Rightarrow$ Debye model
$\Rightarrow$ Acoustic Phonons

Dispersion relation $\omega = v K$ ⟶ $K = \dfrac{\omega}{v}$

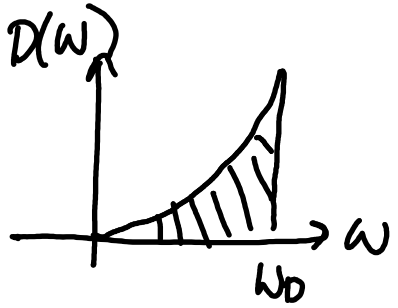
(v: velocity of sound)

⟶ there is a <u>cutoff frequency</u> given by the max. occupied K

from before: $N = \dfrac{V}{2\pi^2}\dfrac{K^3}{3} = \dfrac{V}{6\pi^2}\left(\dfrac{\omega^3}{v}\right) \Rightarrow \omega_D^3 = 6\pi^2 \dfrac{N}{V} v^3$

to this ω_D, it corresponds a cutoff wavevector K $\Rightarrow K_D = \dfrac{\omega_D}{v} = 6\pi^2\left(\dfrac{N}{V}\right)^{1/3}$

$$D(\omega) = \frac{dN}{d\omega} = \frac{V}{6\pi^2}\frac{\omega^2}{v^3}$$



In this model, K larger than K_D are not allowed thermal energy: $U = \sum_K \int d\omega\, D(\omega) \langle n_{\omega,K} \rangle \hbar\omega = \sum_K \int_0^{\omega_D} d\omega \left(\frac{V\omega^2}{2\pi^2 v^3} \right) \frac{\hbar\omega}{e^{\frac{\hbar\omega}{K_B T}} - 1}$

assuming phonon velocity independent of polarization

$\Rightarrow$ we multiply $\times 3$ (LA, TA$\times$2)

$$U = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\frac{\hbar\omega}{K_B T}} - 1} = \frac{3V K_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1}$$

$$x \equiv \frac{\hbar\omega}{K_B T} \ ; \ x_D = \frac{\hbar\omega_D}{K_B T} = \frac{\Theta}{T}$$

Definition: <u>Debye Temperature</u>: Θ $\longrightarrow$ $\Theta = \frac{\hbar v}{K_B} \cdot \left(\frac{6\pi^2 \cdot N}{V} \right)^{1/3}$

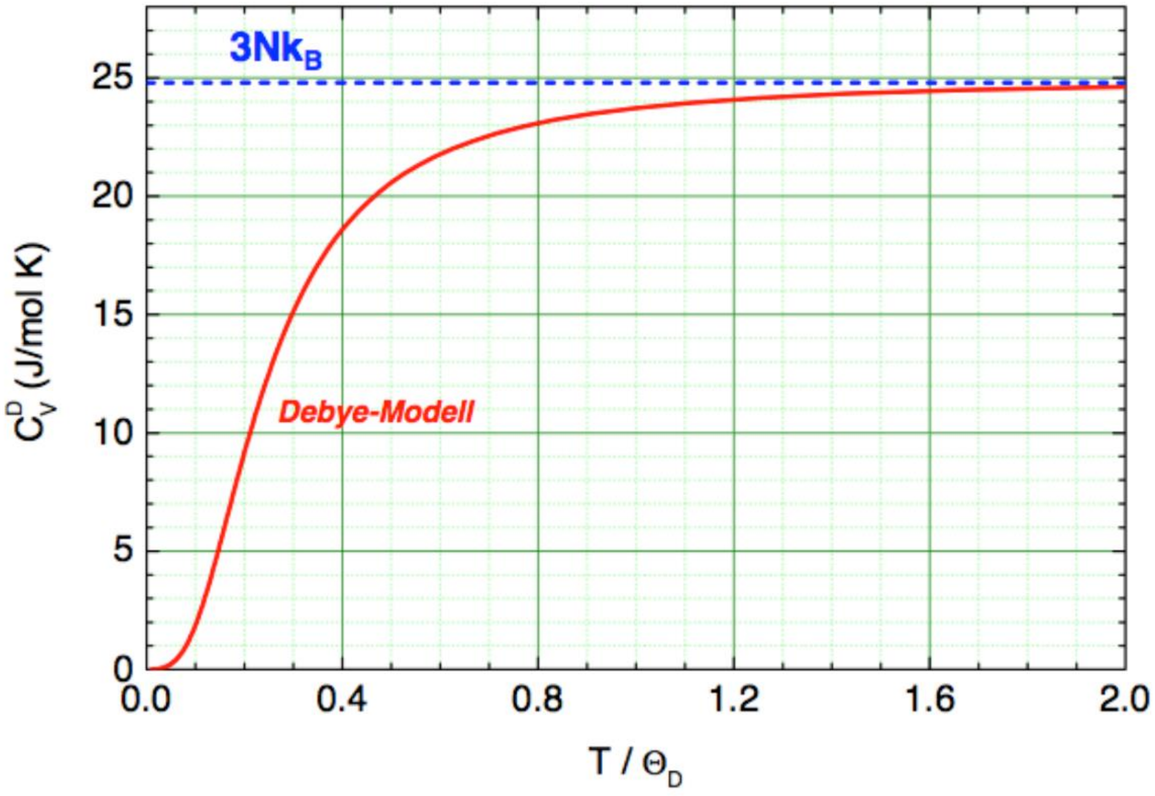
$$K_B \Theta_D \equiv \hbar\omega_D$$

total phonon energy: $U = 9NK_B T \left(\frac{T}{\Theta} \right)^3 \int_0^{x_D} \frac{x^3}{e^x - 1} dx$

Heat Capacity: $C = \frac{3V\hbar^2}{2\pi^2 v^3 K_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\frac{\hbar\omega}{K_B T}}}{\left(e^{\frac{\hbar\omega}{K_B T}} - 1 \right)^2} = 9NK_B \left(\frac{T}{\Theta} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$

Debye approximation

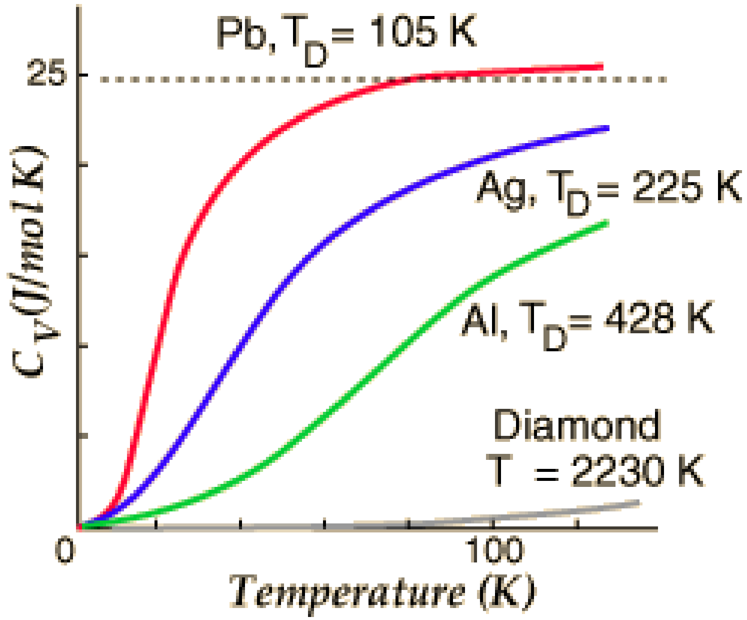
$$C_v = 9Nk_B\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx\, \frac{x^4 e^x}{(e^x - 1)^2}$$

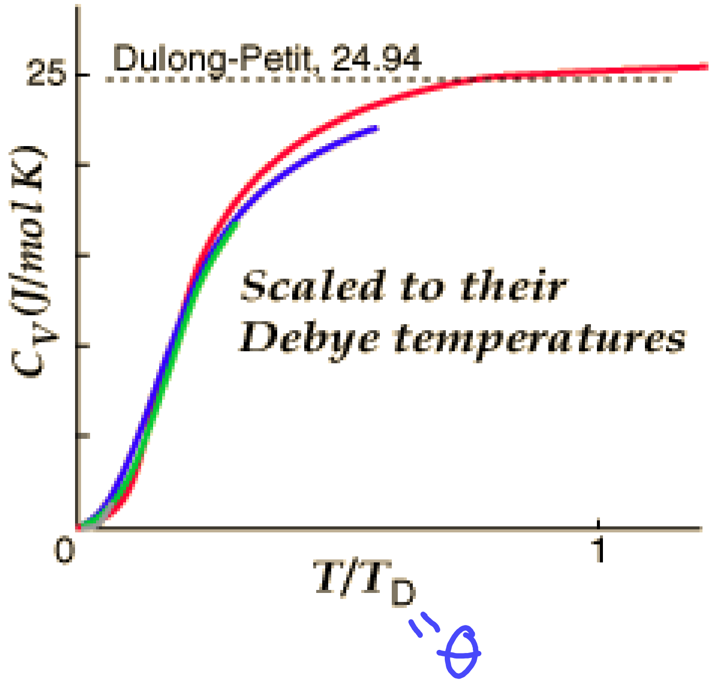


Heat capacity for different elements

$$C_v = 9Nk_B\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

Debye Model $\rightarrow$ C_V is a universal function of the variable T/θ





High and low temperature limits of Debye heat capacity

$$U = 9Nk_BT\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1}$$

$$C_v = 9Nk_B\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

with $\theta = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$ and $x = \frac{\hbar\omega}{k_B T}$

at high T $\quad x = \frac{\theta}{T}$ is very small : $e^x \simeq 1 + x$

$\Rightarrow C_v = \cdots = 3NK_B$ classical result

at low T $\quad x = \frac{\theta}{T} \longrightarrow \infty \quad : \quad \int dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$

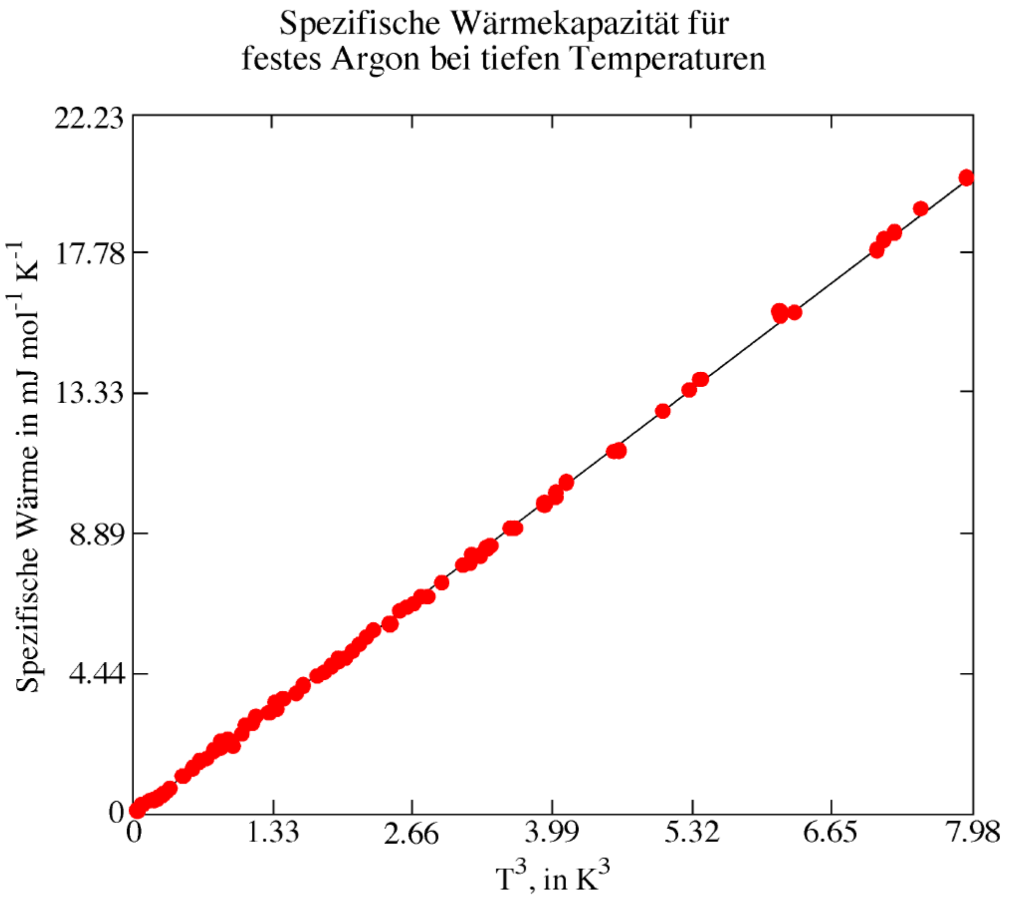
$U = \frac{3}{5}\pi^4 NK_B \frac{T^4}{\theta^3}$ for $T \ll \theta$

$C = \frac{12\pi^4}{5} NK_B \left(\frac{T}{\theta}\right)^3 \Longrightarrow \boxed{C \propto T^3}$

It is a good approx. at low T

Debye approximation

$$C_v = 9Nk_B\left(\frac{T}{\theta}\right)^3\int_0^{x_D}dx\,\frac{x^4e^x}{(e^x-1)^2}$$



$$\theta = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

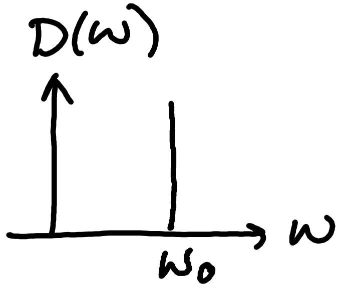
	$\Theta_D(K)$		$\Theta_D(K)$
Li	344	**Cu**	343
Na	158	**Ag**	225
Rb	56	**Au**	165
Be	1440	**Fe**	470
Ca	230	**LiF**	620
Al	428	**NaCl**	280
Diamant	2230	**KCl**	230
Si	645	**KBr**	175
Pb	105	**RbBr**	130

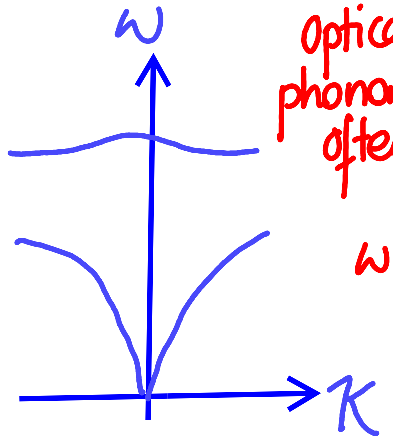
Einstein model

$\boxed{N \text{ oscillators of same frequency } \omega_0}$

1D

Density of states: $D(\omega) = N\,\delta(\omega - \omega_0)$





Optical Branch phonon band is often very flat
⇓
$\omega \sim$ ct.

Thermal energy: $\mathcal{U} = N\langle n\rangle \hbar\omega = \dfrac{N\hbar\omega}{e^{\frac{\hbar\omega}{K_BT}} - 1}$

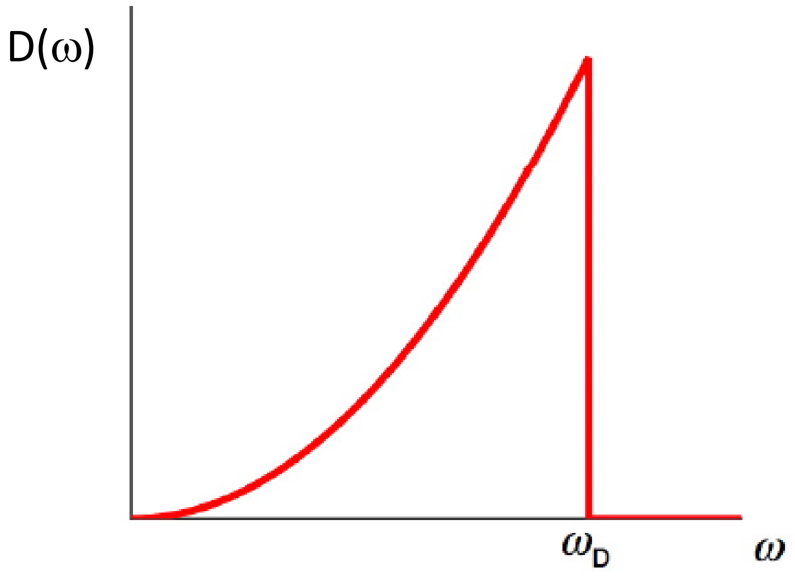
Heat Capacity $C_V = \left.\dfrac{\partial \mathcal{U}}{\partial T}\right)_V = N K_B \left(\dfrac{\hbar\omega}{K_BT}\right)^2 \dfrac{e^{\hbar\omega/K_BT}}{\left(e^{\frac{\hbar\omega}{K_BT}} - 1\right)^2}$

- 3D $\Rightarrow$ 3N oscillators
- at high T $\Rightarrow$ $C_V = 3NK_B$

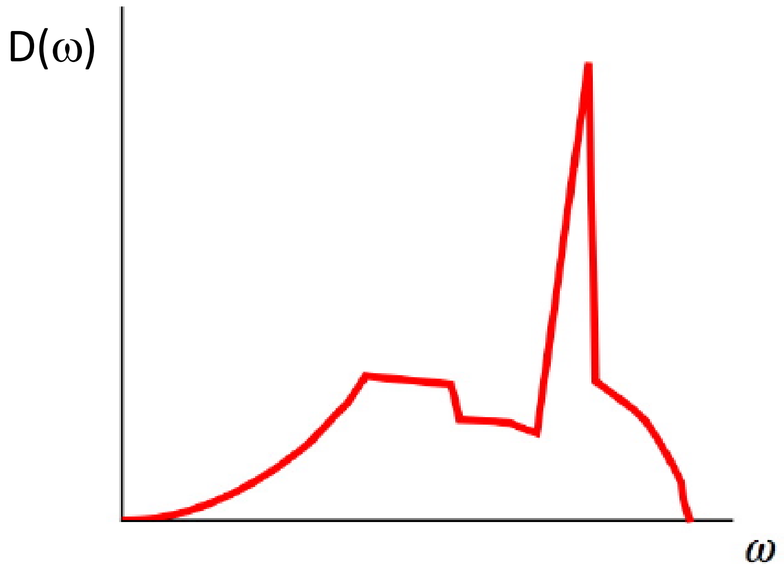
  at Low T $\Rightarrow$ C_V decreases as $\exp\left(-\dfrac{\hbar\omega}{K_BT}\right)$

It is Known that $C_V \propto T^3$ at Low T, but Einstein approx. is often used for optical phonons

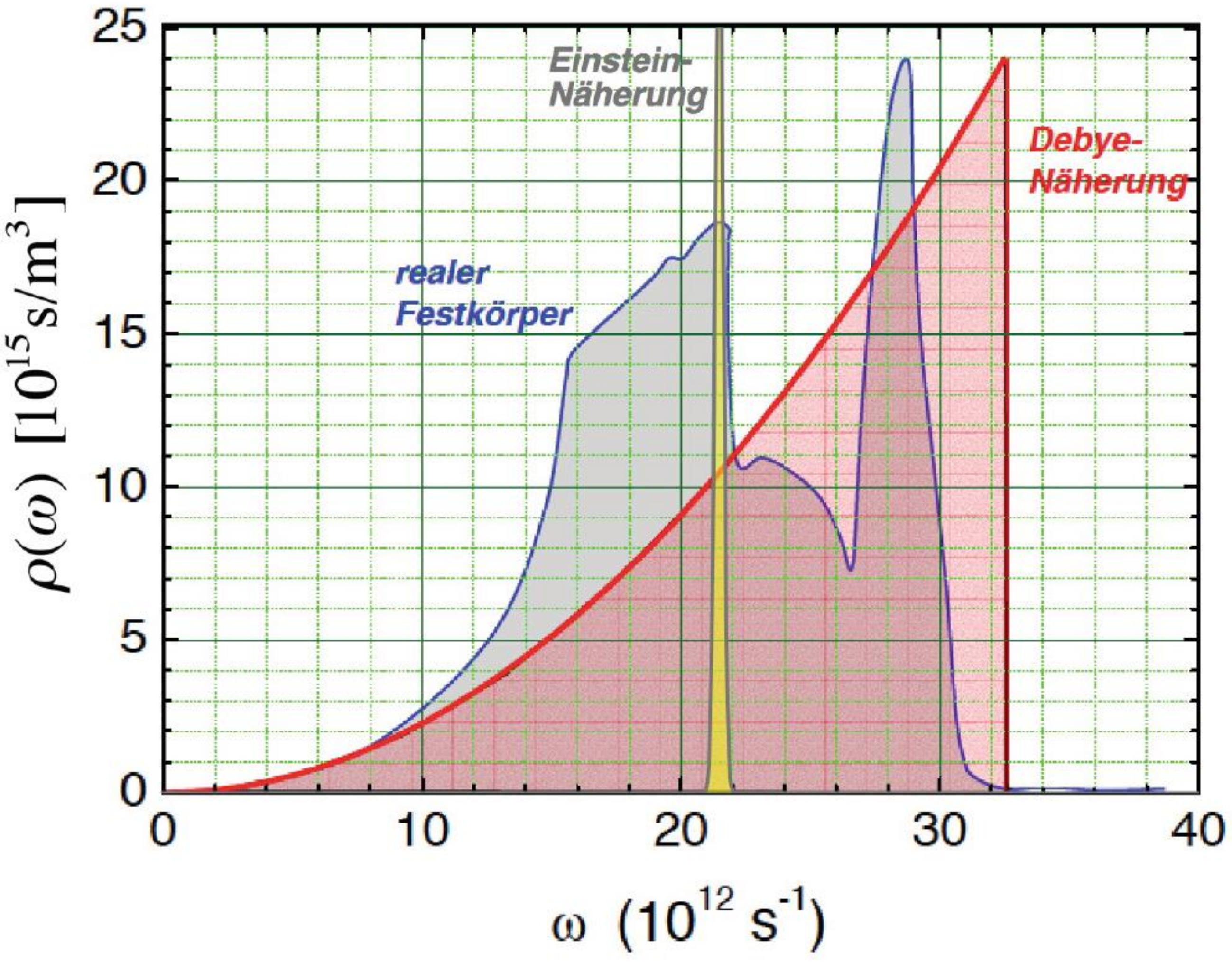
Real solid



Debye solid

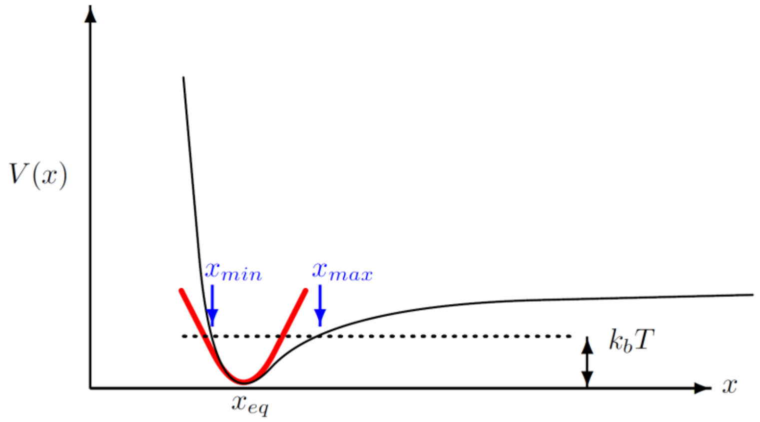


Real crystal structure



Einstein-
Näherung
Debye-
Näherung
realer
Festkörper
$\rho(\omega)$ [10^{15}s/m^3]
ω (10^{12} s^{-1})
0
5
10
15
20
25
0
10
20
30
40

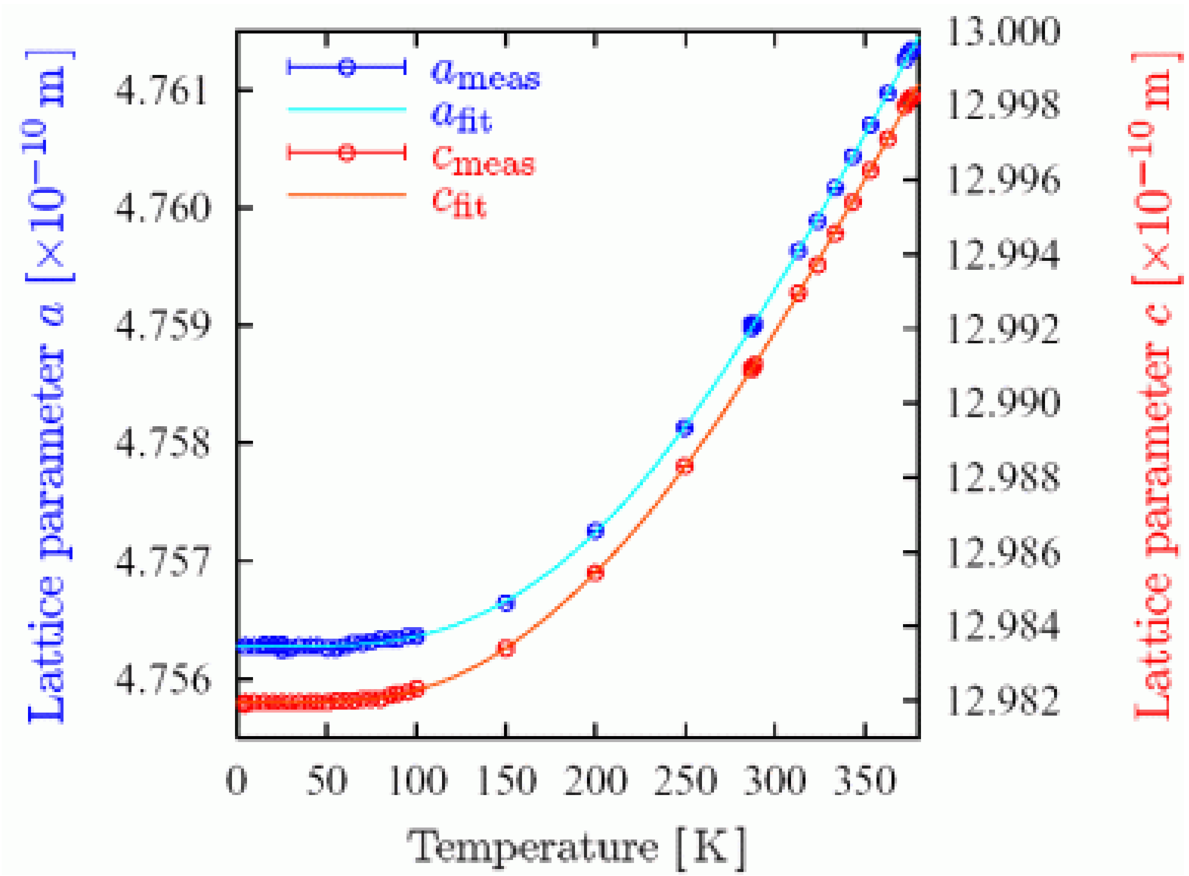
Anharmonic crystal interactions



Limitations Harmonic approximation:

- There is no thermal expansion
- Two lattice waves do not interact
- The heat capacity becomes constant at high temperatures
- Adiabatic and isothermal elastic constants are equal
- The elastic constants are independent of pressure and temperature

Lattice parameters of sapphire



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Sapphire: aluminum oxide (α-Al_2O_3) with trace amounts of elements such as iron, titanium, chromium, copper, or magnesium.