H. How much excitation (phonons) at temperature T?

(a) Single Oscillator Statistical Physics

$$e_\omega = \underbrace{\langle n\rangle}_{\text{temperature dependent } \langle n\rangle}\hbar\omega + \frac{1}{2}\hbar\omega$$ = mean energy of an oscillator of characteristic freq. ω when it is at equilibrium at temperature T

$$\langle n\rangle(T) = \frac{1}{e^{\hbar\omega/kT}-1} \quad (31)$$

mean # phonons for a mode ω [$\omega(q)$] at temp. T

> **Remark:**
>
> single oscillator partition function → $$Z = \sum_{n=0}^{\infty} e^{-\beta\left(n\hbar\omega + \frac{\hbar\omega}{2}\right)} = e^{-\frac{\beta\hbar\omega}{2}}\sum_{n=0}^{\infty} e^{-n(\beta\hbar\omega)} = e^{-\frac{\beta}{2}\hbar\omega}\frac{1}{1-e^{-\beta\hbar\omega}}$$
>
> $$u = -\frac{\partial}{\partial\beta}\ln Z = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/kT}-1} = \frac{1}{2}\hbar\omega + \langle n\rangle\hbar\omega$$

high temperature behavior: ($kT \gg \hbar\omega$)

single oscillator energy $= \underbrace{\frac{1}{2}\hbar\omega}_{\text{G.S.}} + \underbrace{kT}_{\text{equipartition (two quadratic terms)}}$

$$\frac{\hbar\omega}{\left(1 + \frac{\hbar\omega}{kT}\right) - 1} = kT$$

<u>low temperature behavior</u>: ($kT < \hbar\omega$)

single oscillator energy $= \frac{1}{2}\hbar\omega + \underbrace{\hbar\omega\, e^{-\hbar\omega/kT}}_{\text{not much}}$

(b) All Branches and all modes

$$E = \underbrace{U_0}_{\text{G.S.}} + \sum_s \sum_{\vec{q}} \frac{\hbar\omega_s(\vec{q})}{e^{\hbar\omega_s(\vec{q})/kT} - 1} \qquad (32)$$

High temperature Limit: ($kT \gg$ all ω's)

$$E = U_0 + \underbrace{3r}\, N\, kT$$

r = # atoms/unit cell

$3r$ = # of branches [3 acoustic plus optical]

N = # unit cells in crystal

kT = "equipartition of energy"

$$C = \text{Heat capacity} = \frac{\partial E}{\partial T} = 3rNk \qquad (33)$$

per mole, then $N_A k = R$ ← gas constant

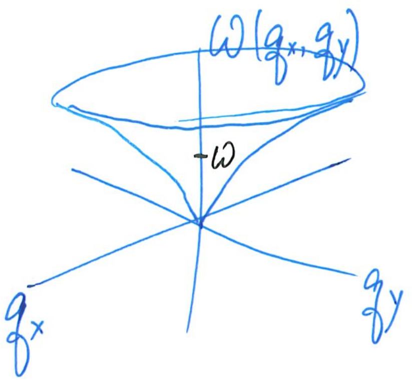
Called Dulong-Petit Law

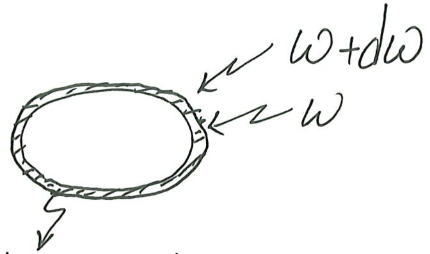
(c) Density of modes ($D(\omega)\,d\omega$)

- Similar to density of electronic states, want to count

$$\boxed{\#\text{ normal modes in interval } \omega \to \omega + d\omega}$$

- can do it branch by branch, then add results
- Cut at $\omega \Rightarrow$ Constant-ω surface [for a dispersion relation]





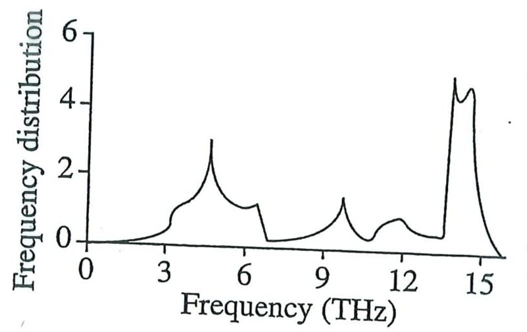
Area (Volume) enclosed $\propto \# \vec{q}$'s $\Rightarrow \propto \#$ modes

$$D(\omega) = \frac{V}{(2\pi)^3} \oint \frac{dS_\omega}{|\nabla_{\vec{q}}\, \omega(\vec{q})|}$$

for each branch, then add results

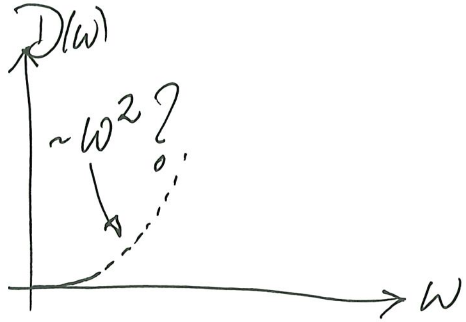
over surface (in $\vec{q}$-space) of constant-ω

Need numerical schemes to count $D(\omega)$



Frequency distribution function versus frequency for Si

- sharp features come from flatter parts of $\omega(\vec{q})$ and/or overlapping branches
- Critical points in $D(\omega)$ (places $|\nabla_{\vec{q}}\, \omega(\vec{q})| \approx 0$)
- Low frequency part

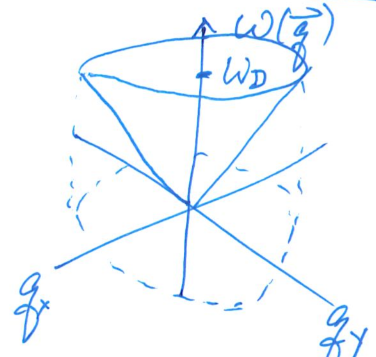


Debye approximation

Acoustic branches : $\underbrace{\omega \sim v_s q}$ $(q \to 0)$

- Keep $\omega \sim v_s q$ form beyond small q
- Keep N modes per branch

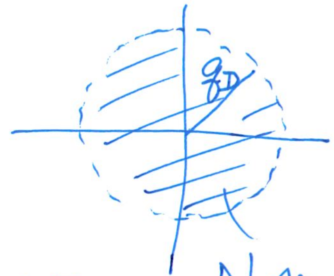
2D Picture



$$D(\omega)\,d\omega = \frac{V}{(2\pi)^3} \cdot 4\pi q^2\,dq = \frac{V}{2\pi^2} \cdot \frac{\omega^2}{v_s^3}\,d\omega$$

$$\therefore\ D(\omega) = \frac{V}{2\pi^2}\frac{1}{v_s^3} \cdot \omega^2$$

v_s ← slope of that branch

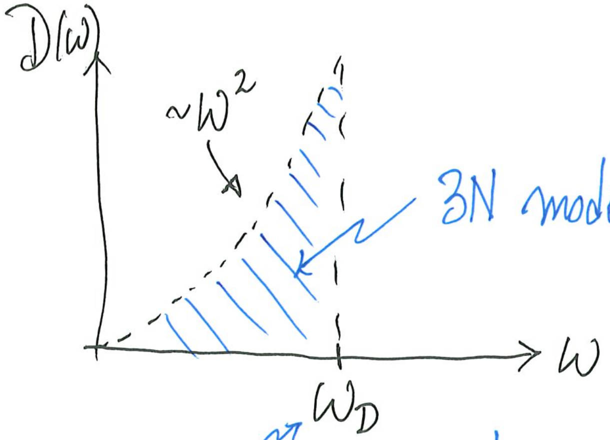


Two TA and One LA branches:

$$D(\omega) = \frac{V}{2\pi^2}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\omega^2 \equiv \frac{V}{2\pi^2}\frac{3}{v_0^3} \cdot \omega^2 \qquad (34)$$

3 identical ($\omega = v_0 q$) branches [equivalently]

N modes for the branch

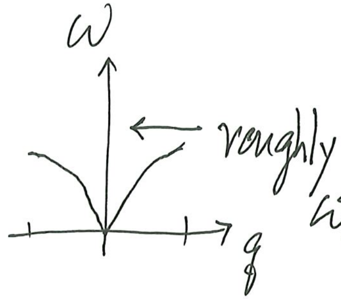


$$\int_0^{\omega_D} D(\omega)\,d\omega = 3N \;\Rightarrow\; \omega_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3} v_0$$

$$\equiv \underbrace{q_D}_{} \cdot v_0$$

meaning: Radius of sphere in q-space (from BZ center out) that contains N modes

ω_D is a property of material



ω_D characterizes extent of ω's

$\hbar\omega_D \equiv k\Theta_D$ ← Debye temperature [set temperature scale of lattice vibrations]

	Θ_D
Si	658 K
Ge	366 K
GaAs	345 K
InSb	200 K

} IR (just like molecular vibrational frequencies)

$\omega_D \leftrightarrow q_D \leftrightarrow \Theta_D$ (same thing expressed differently)

$$\boxed{D(\omega) = \frac{9N}{\omega_D^3} \cdot \underbrace{\omega^2}_{\sim\, \omega^{D-1}} \quad 0<\omega<\omega_D \quad \text{if expressed in } \omega_D}$$ Debye approximation

(D is dimension)

Now energy at temperature T becomes

$$E(T) = U_0 + \int D(\omega) \frac{\hbar\omega}{e^{\hbar\omega/kT}-1} d\omega$$

(exact) when $D(\omega)$ contains contributions from all branches

$$= \underbrace{U_0 + \frac{9N}{\omega_D^3}\int_0^{\omega_D} \omega^2 \frac{\hbar\omega}{e^{\hbar\omega/kT}-1} d\omega}_{\text{gives } 3NkT \text{ at } kT \gg \hbar\omega_D}$$

(Debye approximation) [acoustic branches]

(35)

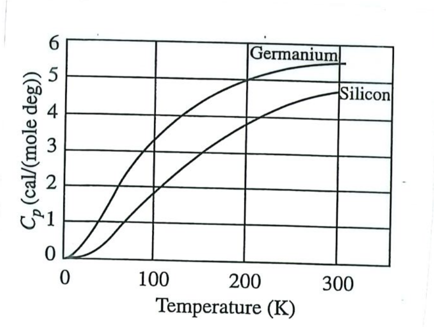
gives $\underbrace{3NkT}_{C\,\sim\, 3Nk}$ at $kT \gg \hbar\omega_D$ (high temp limit)

$C \sim 3Nk$ (observed)

$$E(T) = U_0 + a\underbrace{T^4}_{}$$

$kT \ll \hbar\omega_D$ (low temp.)

Hence $C \sim \left(\dfrac{T}{\Theta_D}\right)^3 \cdot Nk$ (low temp.) [observed] (36)

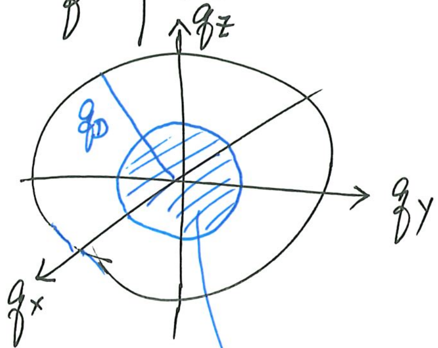


Specific heat of Si and Ge versus absolute temperature

Physical Picture

modes excited per branch at temp. T $\sim N \cdot \left(\dfrac{T}{\Theta_D}\right)^3$

or in q-space



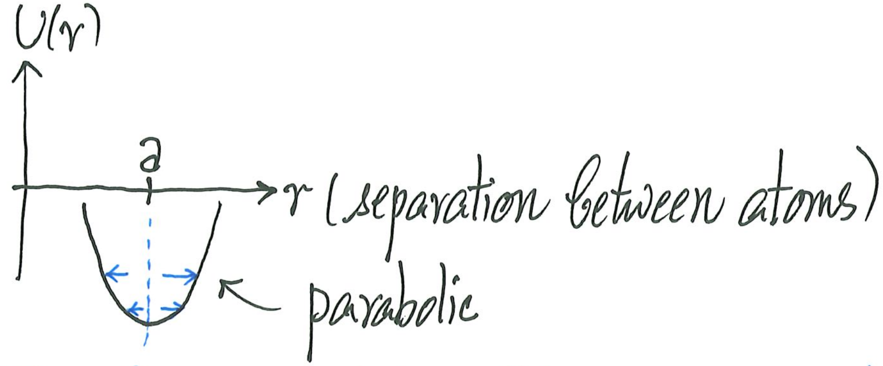
modes excited at temp. T

$q_{upper} \sim \left(\dfrac{kT}{\hbar v_0}\right)$

I. Anharmonic Effects

(a) Thermal Expansion

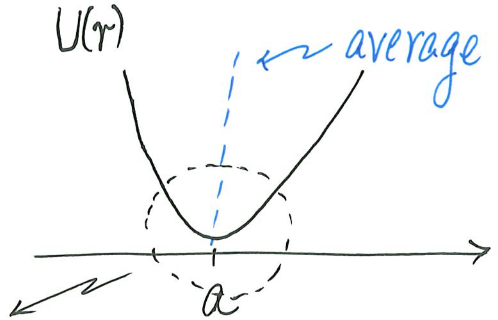
Harmonic Approximation



high T, large amplitude, but mean separation = a

$\Rightarrow$ no thermal expansion

Anharmonic



Consider $U = c\underbrace{(r-a)^2}_{x^2} - \gamma\underbrace{(r-a)^3}_{x^3}$

Average separation at $T = a + \frac{3\gamma}{4c^2}kT = a\Big(1 + \underbrace{\frac{3\gamma k}{4c^2 a}}_{\text{an estimate of thermal expansion coefficient}}\Big)T$

(b) Thermal Conductivity

$$\frac{dQ}{dt} = K \cdot A \cdot \underbrace{\left(-\frac{dT}{dx}\right)}_{\text{negative of temperature gradient (K/m)}} \qquad (36)$$

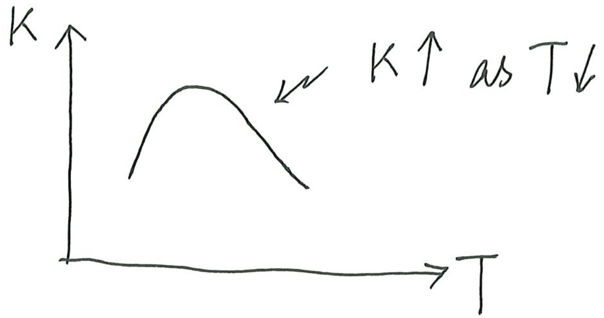
"−" sign: heat flows from high temp. to low temp.

$\frac{dQ}{dt}$: rate of heat flow (J/s or W)

K: $\boxed{\text{thermal conductivity } (W m^{-1} K^{-1})}$ ← a property of matter

A: cross sectional area across which heat flows (m^2)

Features for insulators/semiconductors (free carriers ignored)



This is a typical linear response idea.

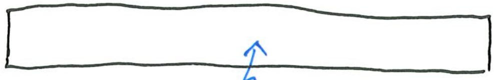
$$\underset{\text{response}}{\frac{dQ}{dt}} \propto \underbrace{\left(-\frac{dT}{dx}\right)}_{\text{cause}} \qquad K = \text{response function}$$

OR

$$\boxed{\underset{\substack{\text{heat flux} \\ \text{(heat flow per area per time)}}}{\vec{Q}} = -K \underbrace{\vec{\nabla} T}_{\text{gradient of temperature}} \qquad (36a)}$$

Physical Picture

smaller amplitude ((•)) — larger amplitude ((((•))))



cooler — $T(x)$ established — hotter

$n_{ph}(T)$ (less phonons) — (more phonons)

need to maintain T_{cooler} and T_{hotter}

(phonons tend to diffuse to cooler end and carry with them the higher energy of vibrations)

- Transport properties : Out of equilibrium ($T(x)$)

$$\boxed{K = \frac{1}{3}\, v_{ph} \cdot C_{ph} \cdot l_{ph}} \tag{37}$$

v_{ph}: an average speed of phonons

C_{ph}: heat Capacitor

l_{ph}: mean free path $(= v_{ph} \cdot \tau_{ph})$

τ_{ph}: mean free time

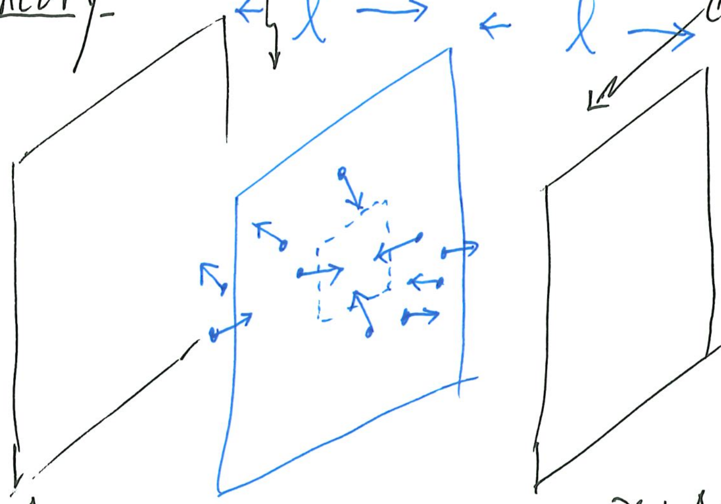
Phonon Gas plus kinetic theory

Kinetic Theory

start here can reach A

start here can reach A

$\leftarrow \ell \rightarrow \quad \leftarrow \ell \rightarrow$



$x-\Delta x$ (cooler, $T-\Delta T$)

plane at x (fictitious plane ⬚ ← Area A)

$x+\Delta x$ (hotter $T+\Delta T$)

ℓ = mean free path of $\underbrace{\text{particles}}_{\text{phonons in our context}}$

= distance travelled between collisions

$$\left(\frac{dQ}{dt}\right)_{hot \to cold} = a \cdot n(T+\Delta T) \cdot v \cdot A \cdot \overline{u}_{th}(T+\Delta T)$$

$\overline{u}_{th}$ ← average thermal energy of particles

Heat flow per time due to particles crossing A from hotter side at $\underbrace{x+\Delta x}_{\ell \text{ away}}$

$$\left(\frac{dQ}{dt}\right)_{cold \to hot} = a \cdot n(T-\Delta T) \cdot v \cdot A \cdot \overline{u}_{th}(T-\Delta T)$$

Heat flow per time due to particles crossing A from colder side at $x-\Delta x$

particles crossing unit area per second

$= a \cdot n \cdot v$

- a: O(1) constant
- n: particle number density ($n(T)$)
- v: some average speed

for phonons $v_{ph} \approx v_s$ ← doesn't vary with T

Net rate of energy flow

$$\frac{dQ}{dt} = \left(\frac{dQ}{dt}\right)_{hot\to cold} - \left(\frac{dQ}{dt}\right)_{cold\to hot} = a\cdot v\cdot A\left[\underbrace{\overline{n u_{th}}}_{\substack{\text{a representative}\\ \text{value of } n u_{th}\\ \text{at hotter side}\\ \text{at } T+\Delta T}}(T+\Delta T) - \overline{n u_{th}}(T-\Delta T)\right]$$

For small ΔT [across Δx]

$$\underbrace{\frac{dQ}{dt}}_{\text{to the left}} = 2avA\left[\frac{d}{dT}(n u_{th})\right]\Delta T$$

But ΔT = change in temperature over a distance $\Delta x = \ell$

$$\therefore \Delta T = \left|\frac{dT}{dx}\right|\cdot \ell$$

$$\therefore \frac{dQ}{dt} = A\cdot\underbrace{\left(2av\ell\frac{d}{dT}(\overline{n u_{th}})\right)}_{\kappa \,=\, \text{thermal conductivity}}\cdot\left(-\frac{dT}{dx}\right) \qquad (38)^{+}$$

+ This is typical of linear response, the response function κ is given in terms of quantities independent of $\left(-\frac{dT}{dx}\right)$.

$$K \propto \underset{\substack{\uparrow\\ \text{typical speed}\\ \text{of particles}}}{v} \cdot \underset{\substack{\nwarrow\\ \text{mean}\\ \text{free}\\ \text{path}}}{l} \cdot \underset{\substack{\nwarrow\\ \text{specific}\\ \text{heat}}}{C} \qquad (39)$$

$$C = \frac{d}{dT}\left(\overline{n u_{th}}\right)$$

n: # per volume

u_{th}: energy per particle

Prefactor "1/3" when things are done more carefully.

<u>Now our context is a Phonon Gas</u>

$v_{ph} \approx$ constant $(\omega = v_0 q)$

$l_{ph} = v_{ph} \cdot \tau_{ph}$ ← time between $\underbrace{\text{collisions}}$

<u>High temp</u>: phonon-phonon collisions dominant (many phonons, $n_{ph}(T)$)

<u>Low temp</u>: phonon-impurity, phonon-sample boundary scatterings

Phonon-phonon scattering

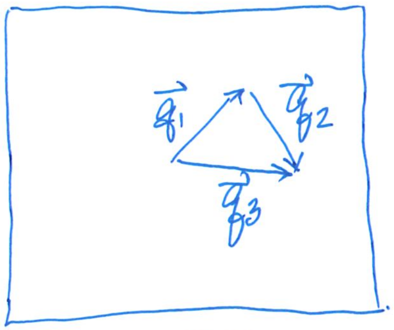
- Must due to anharmonic terms [harmonic ⇒ phonons are independent]
- terms $\sim u \cdot u \cdot u$ [recall: $u_{\vec{R}} \sim \sum_{\vec{q}} (\cdots) \left(\hat{b}_{\vec{q}} e^{i\vec{q}\cdot\vec{R}} + \hat{b}^{+}_{\vec{q}} e^{-i\vec{q}\cdot\vec{R}} \right)$]

$\therefore$ many terms involving $\vec{q}_1, \vec{q}_2, \vec{q}_3$ in exponential terms

$$\vec{q}_1 + \vec{q}_2 = \vec{q}_3 + \vec{G} \quad ; \quad \hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3$$

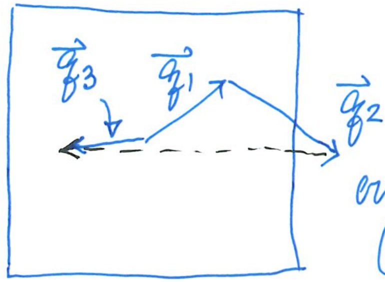
$(\hbar\vec{q}_1 + \hbar\vec{q}_2 = \hbar\vec{q}_3 + \hbar\vec{G})$ $\qquad$ $\omega_1(\vec{q}_1)$ $\quad$ $\omega_2(\vec{q}_2)$ $\quad$ $\omega_3(\vec{q}_3)$

$\vec{G} = 0 \Rightarrow$ Normal Processes $\qquad\qquad$ $\vec{G} \neq 0 \Rightarrow$ Umklapp Processes



B.Z.

destroying $\vec{q}_1, \vec{q}_2$ and creating $\vec{q}_3$



out of B.Z.
(translates back by a $\vec{G}$)

$\vec{q}_3 \sim$ in direction very different from $\vec{q}_1, \vec{q}_2$
(thermal resistance)

<u>K(T)</u> : $K \sim v_{ph} \cdot l_{ph} \cdot C_{ph}$

<u>High Temp.</u> : $C_{ph} \sim$ constant $\sim k$ (Dulong-Petit)

$l_{ph} \sim v_{ph} \cdot \tau_{ph}$; τ_{ph} dominated by Umklapp ph-ph scattering

$\sim \frac{1}{T}$ $\qquad \frac{1}{\tau_{ph}} \sim N_{phonon} \sim \frac{kT}{\hbar\omega_D} \sim T$

$K(T \gg \theta_D) \sim \frac{1}{T}$ $\qquad$ (sometimes observed to be $\sim \frac{1}{T^x}$ $(x > 1)$)

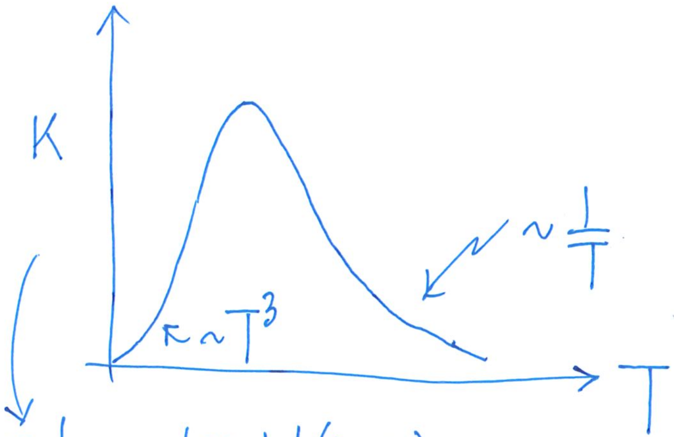
<u>Very low Temp</u>

$l_{ph} \sim$ very long for phonon-phonon scattering

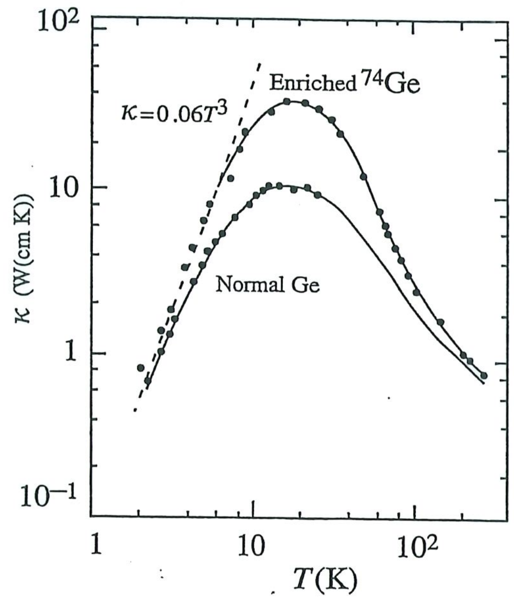
$\therefore$ other lengths take over, e.g. $l_{ph} \sim$ sample size

$C_{ph} \sim T^3$

$\Rightarrow K \sim T^3$



scale ~ 100 W/(m·K)
OR W/(cm·K)

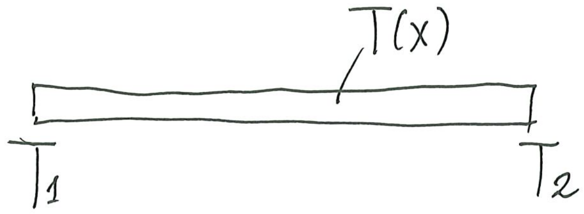


Thermal conductivity of isotopically enriched Ge versus temperature

Remark

- Proper treatment is to apply Boltzmann Equation for a generalized phonon distribution function.

Equilibrium $n(\vec{q}) = n_{\vec{q}} = \dfrac{1}{e^{\hbar\omega(\vec{q})/kT} - 1}$



$n(\vec{q}, x, t)\, d^3q\, dx$

= # phonons in d^3q at $\vec{q}$ and in x to x+dx at time t

Boltzmann Equation

Steady state $\left(\frac{\partial n}{\partial t}\right)_{\underbrace{\text{driven}}_{\text{e.g. } \vec{\nabla} T}} + \left(\frac{\partial n}{\partial t}\right)_{\text{scattering}} = 0$

Valid for weak or strong driving "forces" (both linear and nonlinear response)