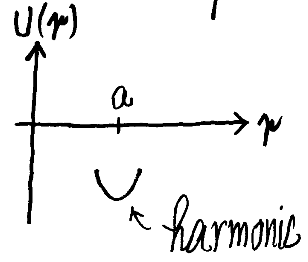
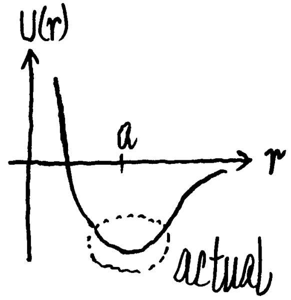
Appendix : Anharmonic Effects

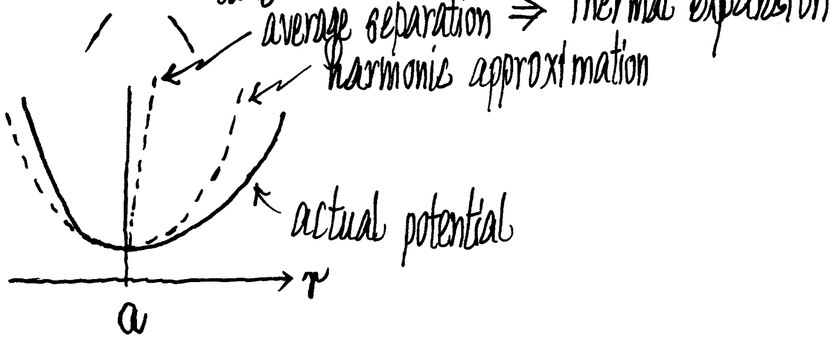
(a) Thermal Expansion



Mean position is always at $r=a$

⇒ No thermal expansion!





$\Delta V = V_0 \beta \Delta T$ $\quad$ β = coefficient of volume expansion

$\beta = 3\alpha$ $\quad$ α = coefficient of linear expansion

$\alpha(Cu)$: 16.7×10^{-6} °C^{-1}

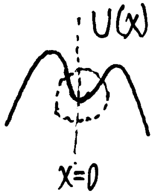
$\alpha(Au)$: 13×10^{-6} °C^{-1} $\quad$ (~ room temperature)

$\alpha(Zn)$: 30×10^{-6} °C^{-1}

To illustrate the idea, let

$$U(x) = cx^2 - \overbrace{gx^3}^{\text{gives asymmetry between } x<0 \text{ and } x>0} - fx^4 , \quad c,g,f>0$$

$$\underbrace{- gx^3 - fx^4}_{\text{anharmonic terms}}$$



Classical approach

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx\, x\, e^{-\beta U(x)}}{\int_{-\infty}^{\infty} dx\, e^{-\beta U(x)}} \qquad \beta \equiv \frac{1}{kT}$$

$$\int_{-\infty}^{\infty} dx\, x\, e^{-\beta c x^2} e^{+\beta g x^3 + \beta f x^4}$$

$$\approx \int_{-\infty}^{\infty} dx\, x\, e^{-\beta c x^2} (1 + \beta g x^3 + \beta f x^4) \qquad \text{small displacement}$$

$$= \int_{-\infty}^{\infty} dx\, \beta g x^4 e^{-\beta c x^2} = \beta^{-3/2} g c^{-5/2} \int_{-\infty}^{\infty} dy\, y^4 e^{-y^2}$$

$$= \frac{3\pi^{1/2}}{4} g c^{-5/2} \beta^{-3/2}$$

$$\int_{-\infty}^{\infty} dx\, e^{-\beta U(x)} \approx \int_{-\infty}^{\infty} dx\, e^{-\beta c x^2} = \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} dy\, e^{-y^2} = \sqrt{\frac{\pi}{c}}\, \beta^{-1/2}$$

$$\therefore \underset{\substack{\uparrow \\ \text{average separation}}}{\langle x \rangle} = \frac{3g}{4c^2} k_B \underset{\substack{\nwarrow \\ \text{increase with } T}}{T}$$

∴ Anharmonic effect is needed to explain thermal expansion

(b) Thermal Conductivity : Electrical Insulators

$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dx}$$

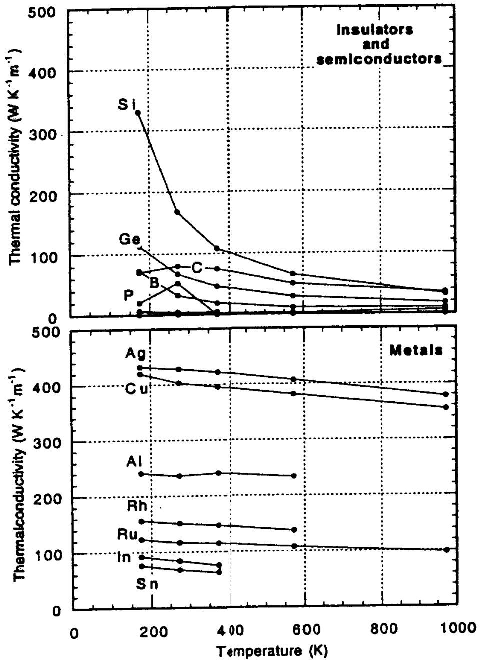
$\frac{dQ}{dt}$: rate of heat flow (W)

κ: thermal conductivity ($W m^{-1} K^{-1}$)

A: cross-sectional area across which heat is flowing (m^2)

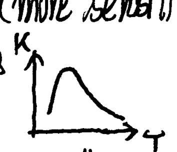
$\frac{dT}{dx}$ ← temperature gradient ($K m^{-1}$)

"−" ⇒ heat flows from heat temperature to low temperature
(κ so defined is positive)



← Electrical insulators

- $\kappa\uparrow$ as $T\downarrow$ (more sensitive)
- some systems



- In general, κ smaller than electrical conductors.

← Electrical conductors

- $\kappa\uparrow$ as $T\downarrow$ (gradually)

+ More formally, $\vec{J}_Q = -\kappa \vec{\nabla} T$, where $\vec{J}_Q$ = heat current density

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κ of common materials

Thermal conductivity of a variety materials ($WK^{-1} m^{-1}$). The tables refer to metallic alloys, refractory materials, i.e. those suitable for use in high temperatures without degradation, and a selection of everyday materials.

	173.2K	273.2K	373.2K	573.2K	873.2K	973.2K	1473.2K
Brass (Cu70%,Zn30%)	89	106	128	146	—	—	—
Bronze (Cu90%,Sn10%)	—	53	60	80	—	—	—
Carbon steel	48	50	48.5	54.5	—	30.5	—
Silicon steel	—	25	28.5	31	—	28	—
Stainless steel	—	24.5	25	25.5	—	24.8	—
Alumina (Al_2O_3)	—	40	28	—	9.2	—	5.7
Beryllia (BeO)	—	300	213	—	61	—	22
Fire brick	—	—	—	—	1.1	—	1.3
Silica (SiO_2) fused quartz	—	1.33	1.48	—	2.4	—	—
Zirconia (ZrO_2)	—	—	1.8	—	2.0	—	2.2

Substance	κ ($WK^{-1} m^{-1}$)	Substance	κ ($WK^{-1} m^{-1}$)	Substance	κ ($WK^{-1} m^{-1}$)
Brick wall	≈1	Porcelain	1.5	Glass wool	0.037
Plaster	≈0.13	Rubber	≈0.2	Cotton wool	0.03
Timber	≈ 0.15	Polystyrene	≈0.1	Sheep's wool	0.05
Balsa wood	≈0.06	Glass (crown)	1.1	Nylon	0.25
Paper	0.06	Glass (flint)	0.85	Epoxy resins	≈0.2
Cardboard	0.21	Glass (pyrex)	1.1	Cellular polystyrene	≈0.04

$$\underbrace{\kappa(\text{metal})}_{\text{Two contributions}} > \underbrace{\kappa(\text{electrical insulator})}_{\text{ONE contribution}}$$

Two contributions

{ lattice vibrations (phonons)
+
electrons }

⇓

a gas of phonons
+
a gas of electrons

ONE contribution

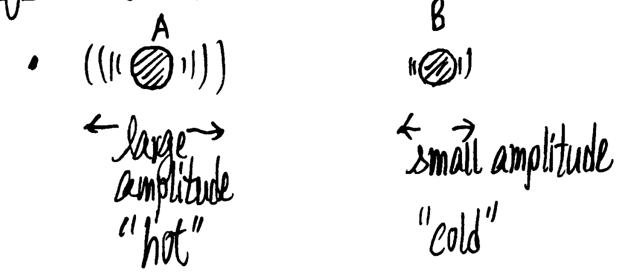
lattice vibrations (phonons)

⇓

a gas of phonons

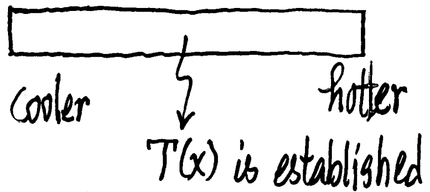
Since lattice vibrations contribute in both kinds of materials, κ (insulator) is somewhat smaller than κ (metal).

Physical Picture

- 

- couple them together

  ⇒ A tends to lose energy until the average energies per degree of freedom of A and B are equal (equilibrium)



In terms of phonons,

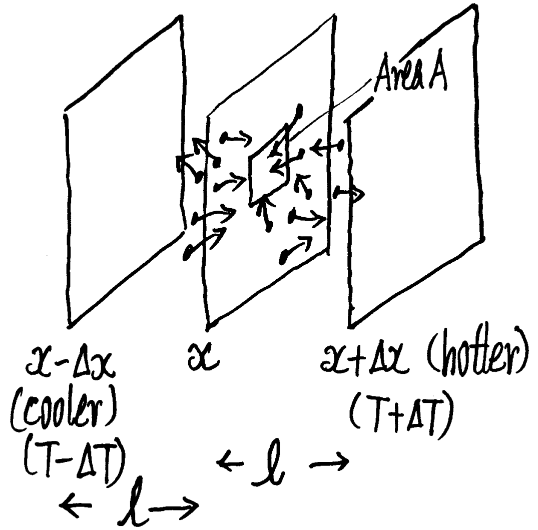
$\because n_{ph} = n_{ph}(T) \Rightarrow$ more phonons at hotter places than cooler places

and phonons tend to diffuse to the cooler end and carry with them the excess energy of vibrations from the hotter side.

$\ell =$ mean free path of particles (phonons)

= distance travelled between collisions

Let's analyse the rate of energy flow due to particles crossing a fictitious area A perpendicular to $\frac{dT}{dx}$



"Kinetic theory"

Assume:

- average speed of particles v does not vary much with temperature (e.g. $v_{phonon} = \underset{\text{speed of sound}}{v_{sound}}$)
- # particles crossing unit area per second

$$= \underset{\substack{\text{constant}\\ \text{of order one}}}{a} \cdot \underset{\substack{\text{number}\\ \text{density of}\\ \text{particles}}}{n} \cdot \underset{\text{average speed}}{v} \quad (n = n(T))$$

- Each particle brings with it on average a small amount of energy, which may be passed on to other particles in a collision.

Rate of energy flow due to particles crossing A from the hotter side at $x+dx$ (ℓ away from x):

$$\left.\frac{dQ}{dt}\right|_{H\to C} = a\cdot n(T+\Delta T)\cdot v\cdot A\cdot \underset{\substack{\uparrow\\ \text{average thermal energy}\\ \text{of particles}}}{\overline{u}_{th}}(T+\Delta T)$$

Rate of energy flow due to particles crossing A from the cooler side at $x-dx$ (ℓ away from x):

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

<u>Net rate of energy flow</u>

$$\frac{dQ}{dt} = \left.\frac{dQ}{dt}\right|_{H\to C} - \left.\frac{dQ}{dt}\right|_{C\to H}$$

$$= a\,v\,A\left[\overline{n\,u_{th}}(T+\Delta T) - \overline{n\,u_{th}}(T-\Delta T)\right]$$

$\therefore$ We need a gradient in n and/or a gradient in $\overline{u}$ to get $\frac{dQ}{dt}\neq 0$, and $-\frac{dT}{dx}$ serves to provide the gradients

- For small ΔT, expand to $(\Delta T)^1$:

to the left $\rightsquigarrow$ $$\frac{dQ}{dt} = 2\,a\,v\,\frac{d}{dT}(n\,u_{th})\,\Delta T$$

- ΔT is the change in temperature over a distance $\Delta x = \ell$

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

Finally,

$$\frac{dQ}{dt} = -A\cdot\Big(2a\,v\cdot\ell\cdot\underbrace{\frac{d}{dT}(\overline{n\,u_{th}})}_{\substack{\text{heat capacity}\\ \text{per volume}}}\Big)\frac{dT}{dx}$$

$$\therefore K \propto v\cdot\ell\cdot\frac{d}{dT}(\overline{n\,u_{th}})$$

$$\propto \underset{\substack{\uparrow\\ \text{speed}\\ \text{of particles}}}{v}\cdot\underset{\substack{\uparrow\\ \text{mean}\\ \text{free path}}}{\ell}\cdot\underset{\substack{\nwarrow\\ \text{specific heat}}}{C}$$

More complete theory shows:

$$K = \frac{1}{3}\,v\cdot\ell\cdot C$$

Apply to gas of phonons:

$$\boxed{K = \frac{1}{3}\, \underset{\substack{\uparrow\\ \sim \text{constant}}}{v_{ph}} \cdot \underset{\substack{\uparrow\\ C_{ph} = \text{const } (T > \theta_D)\\ \sim T^3 \ (T \ll \theta_D)}}{C_{ph}} \cdot \ell_{ph} \leftarrow \ell_{ph} = v_{ph} \cdot \tau_{ph} \text{ governed by collisions}}$$

Debye: $\omega = v \cdot q$ (same v for all q)

$$\underset{\substack{\uparrow\\ \text{mean free path}}}{\ell_{ph}} = v_{ph} \cdot \underset{\substack{\uparrow\\ \text{time between collisions}}}{\tau_{ph}}$$

- When there are many entities around to collide with phonons, τ_{ph} is short $\Rightarrow$ ℓ is small

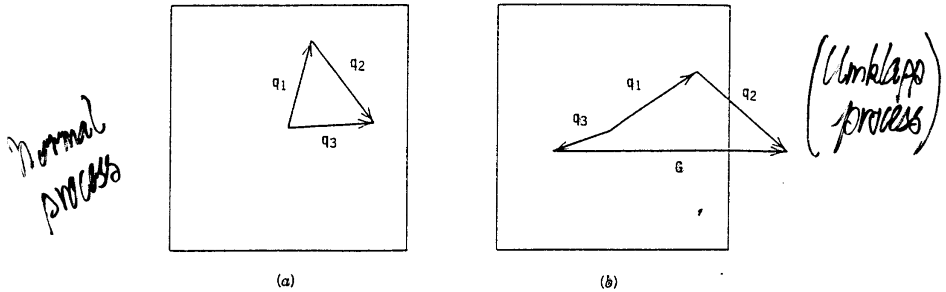
<u>High temperatures</u>: Many phonons around (all modes are fully excited)

$\Rightarrow$ phonon-phonon collisions are important

<u>Low temperatures</u>: not much ph-ph collisions and ℓ_{ph} is due to phonon scatterings off impurities and sample boundary

<u>Phonon-phonon scattering</u> (anharmonic effect)$^+$

<u>Normal Processes</u>	<u>Umklapp Processes</u>
• involves phonons of short q's	• involves phonons of longer q's
• <u>not</u> leading to <u>thermal resistivity</u>.	• $\vec{q}_3 \sim$ not in directions of $\vec{q}_1, \vec{q}_2$
	• lead to thermal resistivity.



Phonon-phonon scattering events. Phonons with propagation vectors q_1 and q_2 disappear and a phonon with propagation vector q_3 appears. All three propagation vectors are in the Brillouin zone. (a) A normal event: $q_1 + q_2 = q_3$. (b) An Umklapp event: $q_1 + q_2 = q_3 + G$, where G is a reciprocal lattice vector.

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

$$\vec{G} = 0 \text{ (normal process)} \ ; \ \vec{G} \neq 0 \text{ (Umklapp process)}$$

Thermal conduction: Net phonon flow and more phonons at hot end.

$^+$ Recall that within harmonic approximation, the normal modes are independent of each other. We need anharmonic effect to cause phonon-phonon scattering.

K(T) for insulators

- at high temperatures ($T \gg \theta_D$)

$$\kappa \sim \underset{\text{constant}}{v_{ph}} \cdot \underset{\frac{1}{T}}{l_{ph}} \cdot \underset{\text{constant}}{C_{ph}}$$

- C_{ph} ~ temperature-independent ($\sim k_B$)

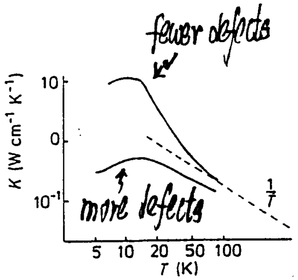
$$l_{ph} = \underset{\approx \text{ constant (Debye)}}{v_{ph}} \cdot \tau_{ph}$$

$\frac{1}{\tau_{ph}}$ ~ rate of effective ph-ph (Umklapp) scatterings

$\sim N_{phonon} \sim T \quad \Rightarrow l \propto \frac{1}{n_{ph}(T)}$

$\therefore \tau_{ph} \sim \frac{1}{T} \quad \Rightarrow \boxed{l_{ph} \sim \frac{1}{T}}$

and $K(T \gg \theta_D) \sim \frac{1}{T}$ $\qquad n_{ph} = \frac{1}{e^{\hbar\omega/k_BT} - 1}$



K of quartz

- approaches $\frac{1}{T}$ behavior at high T

Sometimes, $K(T \gg \theta_D) \sim \frac{1}{T^x}$ with $\underbrace{x > 1}$

involving collisions related to more than 3 phonons

- at intermediate temperatures

- $T \lesssim \theta_D$

K stills increases with $\underbrace{\text{falling temperature}}$

despite C drops with temp.

$\downarrow$

fewer Umklapp processes to limit thermal conduction

N_{ph} ~ # phonons that could create Umklapp processes

~ drops with temp. as $\sim e^{-\theta_D/bT}$

$\uparrow$ some parameter $\hookrightarrow$ (~2 or 3) in real data

K shows a behaviour of

$\sim e^{\theta_D/bT}$

at intermediate temperatures

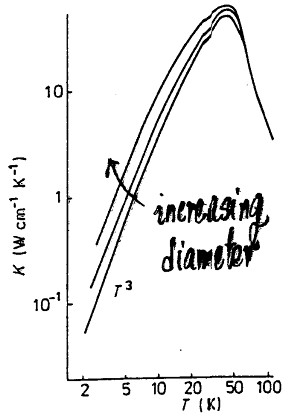
- <u>at very low temperatures</u>

  - $l_{ph} \sim$ very long ($\tau_{ph} \sim$ very long)

For pure samples[+], $l_{ph} \sim$ sample size

$\Rightarrow K$ may show size effect

Recall: C has a T^3 temp. dependence at low T (recall: Debye model)



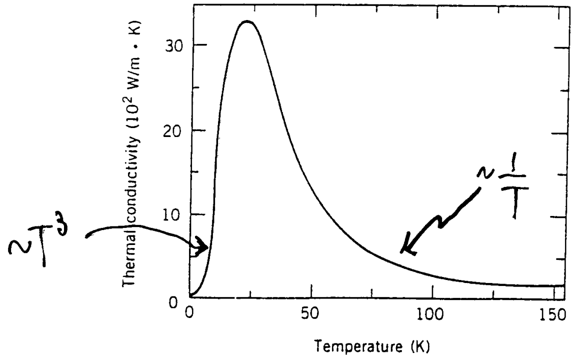
K of sapphire rods of different diameters (shows size effect)

$\sim T^3$ behaviour at low T comes from the heat capacity C.

$$K \sim \underset{\text{constant}}{v_{ph}} \cdot \underset{\text{constant}}{l_{ph}} \cdot \underset{\sim T^3}{C_{ph}}$$

[+] often, there are imperfections such as dislocations, grain boundaries and impurities, which could lead to phonon scatterings and limit l_{ph}.

MgO (insulator)



Thermal conductivity of magnesium oxide as a function of temperature. At low temperature the curve is nearly proportional to T^3, while at high temperature it is proportional to $1/T$.

$K \sim T^3$ low T (T-dependence from heat capacity)

$K \sim \frac{1}{T}$ high T (T-dependence from ph-ph scattering through τ).