# Phonon Engineering: an introduction

## II. Phonon engineering and heat conduction


Dr P.-Olivier Chapuis

Institut Catala de Nanotecnolgia (ICN-CIN2)
Barcelona, Spain


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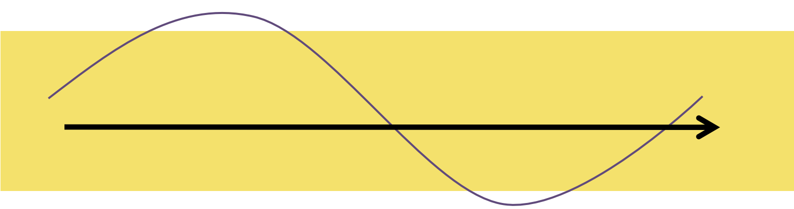
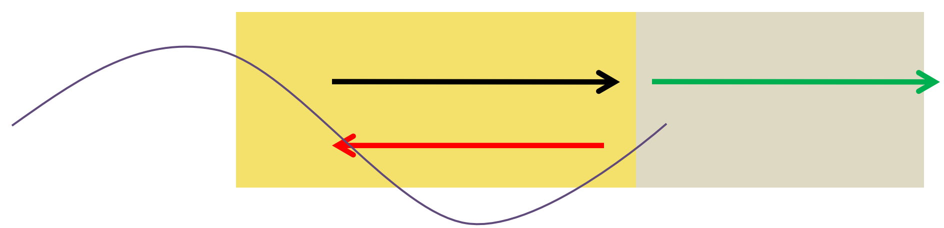
Avigliano Umbro TR, Italy, 1st-8th August 2010

## The Phononic heat conduction

- Phononic thermal conductivity → spectrum !
- Phonon scattering mechanisms → intrinisc
- Phonons at nanoscale → solve BTE
- Phonon transmission at interfaces → diffuse ?
- Phonons in novel materials → better transport ?
- Heat transfer phonons and measurements → techniques





# Contributions to the heat conduction…

Thermal conductivity ***k*** has different contributions:

$k = k_{phonon} + k_{electron}$

Wiedemann-Franz law for an approximation of electronic contribution in the thermal conductivity

$$L_0 = \frac{k_{el}}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.44 \cdot 10^{-8} W\Omega K^{-2}$$

Silicon (undoped)

$k_{Si}$= 149 $Wm^{-1}K^{-1}$

$\sigma_{Si}$= $10^{-3}$ $\Omega^{-1}m^{-1}$

$$\frac{k_{Si,e^-}}{k_{Si}} = \frac{L_0 T_{e^-} \sigma_{Si}}{\lambda_{Si}} << 1$$

Graphite

$k_{C\_graphite}$= 140 $Wm^{-1}K^{-1}$

$\sigma_{C\_graphite}$= 6.1 $10^4$ $\Omega^{-1}m^{-1}$

$$\frac{k_{C\_graphite,e^-}}{k_{C\_graphite}} = \frac{L_0 T_{e^-} \sigma_{C\_graphite}}{k_{C\_graphite}} \approx 0.3\%$$

# The model of the thermal conductivity

- Solution of a Boltzmann transport equation (Peierls)

$$\frac{\partial f}{\partial t}+\vec{v}\cdot\vec{\nabla}_{\vec{r}}f+\frac{\vec{F}}{m}\cdot\vec{\nabla}_{\vec{v}}f=\left.\frac{\partial f}{\partial t}\right)_{coll}=-\frac{f-f_0}{\tau(\omega)}$$

(Relaxation time approximation)

$$f=f_0-\tau(\omega).(\vec{v}\cdot\vec{\nabla}_{\vec{r}}f_0) \longrightarrow$$

$$\vec{\phi}=\sum_i E_i f_i \vec{v}_{i,x}=\sum_{pol}\int_{\omega=0}^{\infty} g(\omega,p)E(\omega)f(\omega)\vec{v}_{i,x}(\omega,p)d\omega$$

$$f_0(\omega,T)=\frac{1}{e^{\hbar\omega/k_BT}-1}$$

Bose-Einstein statistics

$$k=\sum_{pola.}\int_0^{+\infty}\frac{1}{3}\hbar\omega\cdot\frac{df_0}{dT}\cdot(v\tau)\cdot g(\omega)\cdot v\,d\omega$$

$$\vec{\phi}=k.\vec{\nabla}_{\vec{r}}T$$

NB: Isotropic approx. for v, τ,…

# The model of the thermal conductivity

- Solution of a Boltzmann transport equation (Peierls)

$$\frac{\partial f}{\partial t} + \vec{v}\cdot\vec{\nabla}_{\vec{r}} f + \frac{\vec{F}}{m}\cdot\vec{\nabla}_{\vec{v}} f = \left.\frac{\partial f}{\partial t}\right)_{coll} = -\frac{f - f_0}{\tau(\omega)}$$

(Relaxation time approximation)

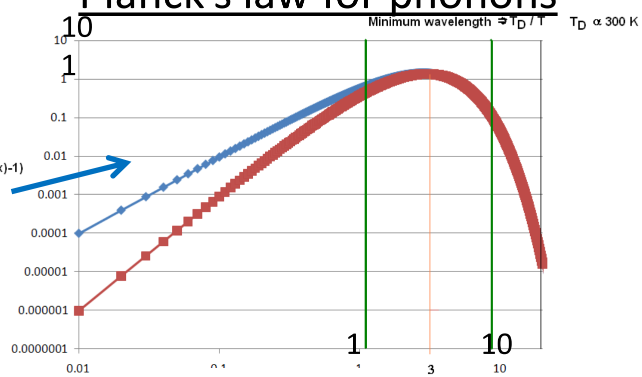
$$k = \sum_{pola.} \int_0^{+\infty} \frac{1}{3}\hbar\omega \cdot \frac{df_0}{dT} \cdot (v\tau) \cdot g(\omega) \cdot v\, d\omega$$

$$f_0(\omega, T) = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

Bose-Einstein statistics

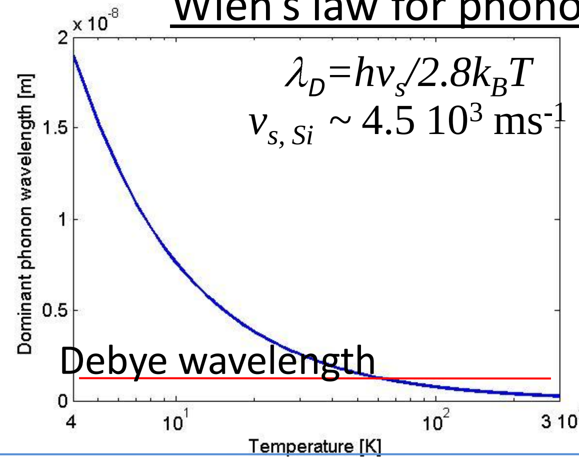
Planck's law for phonons

$$\frac{x^3}{e^x - 1}$$




$$x = hv_s / \lambda k_B T$$

Wien's law for phonons

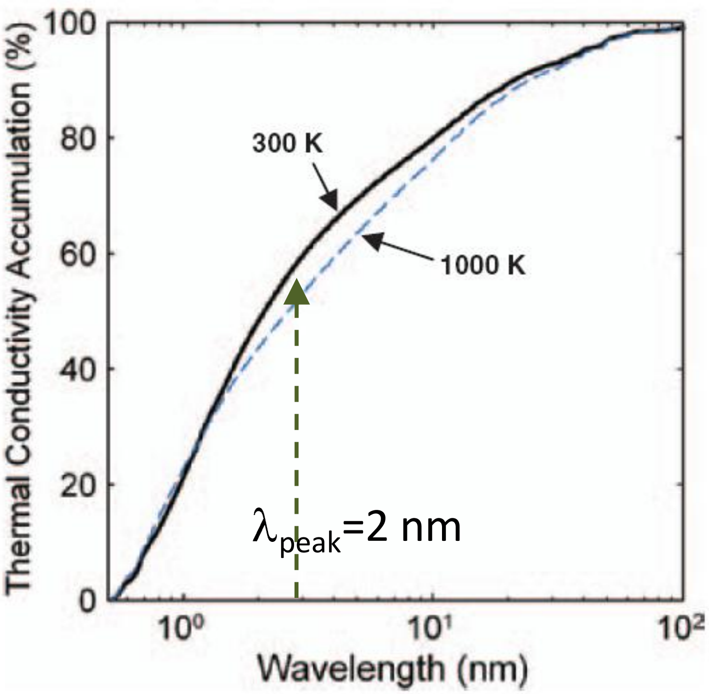



$f_0/dT$

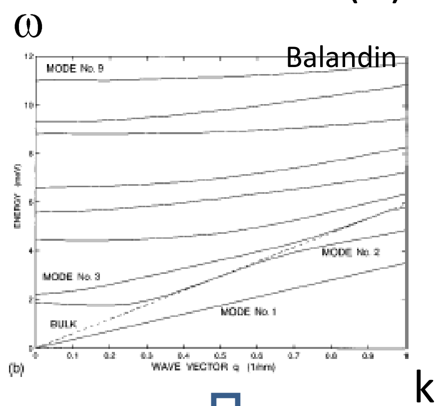
# Phonon spectrum

MD calculations with bulk Si

Calculated phonon density of states (D) in a e=37 nm Si nanowire

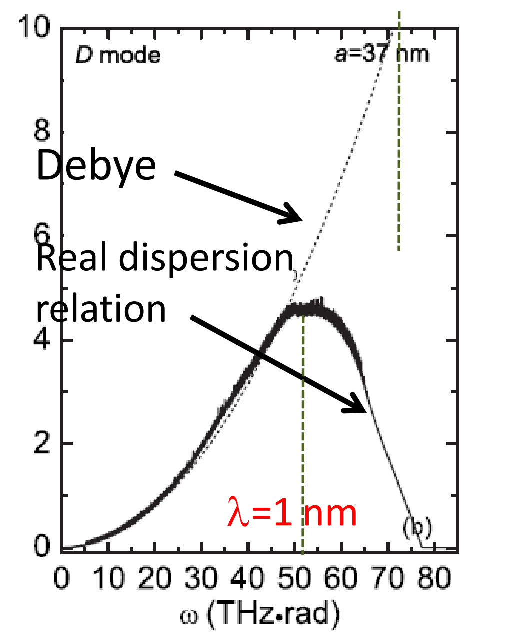



Henry and Chen,
J. Comp. Theo. Nanosci 5, 1 (2008)




⇩

← DOS →



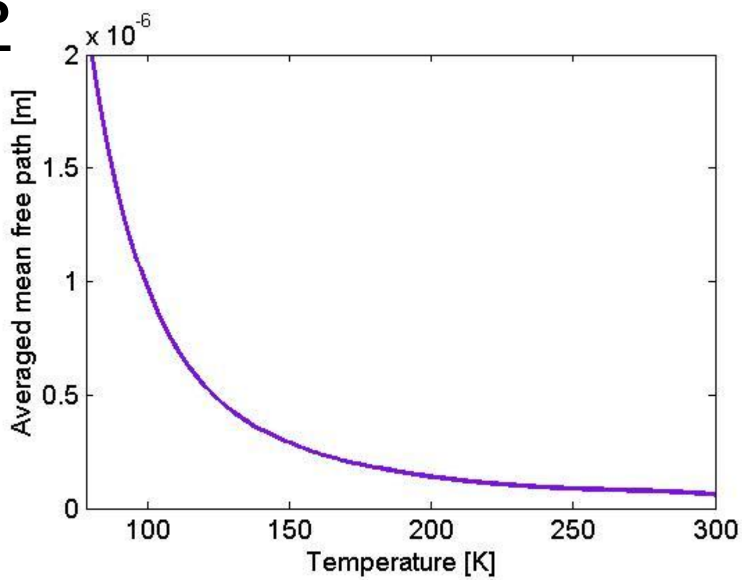

Lü, JAP 104, 054314 (2008)

## Which phonons ?

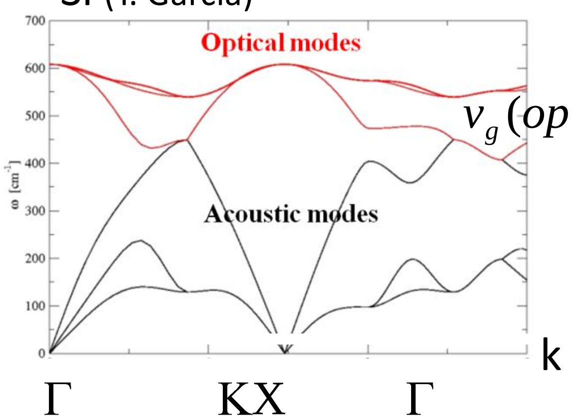
The acoustic phonons are carrying the heat.

$$k = \sum_{pola.} \int_0^{+\infty} \frac{1}{3} \hbar\omega \cdot \frac{df_0}{dT} \cdot (v\tau) \cdot g(\omega) \cdot v\, d\omega$$

$$= \int_0^{+\infty} \frac{1}{3} c_\omega v (v\tau) d\omega \longrightarrow k = \frac{1}{3} \rho c_p v_s \Lambda \longrightarrow$$

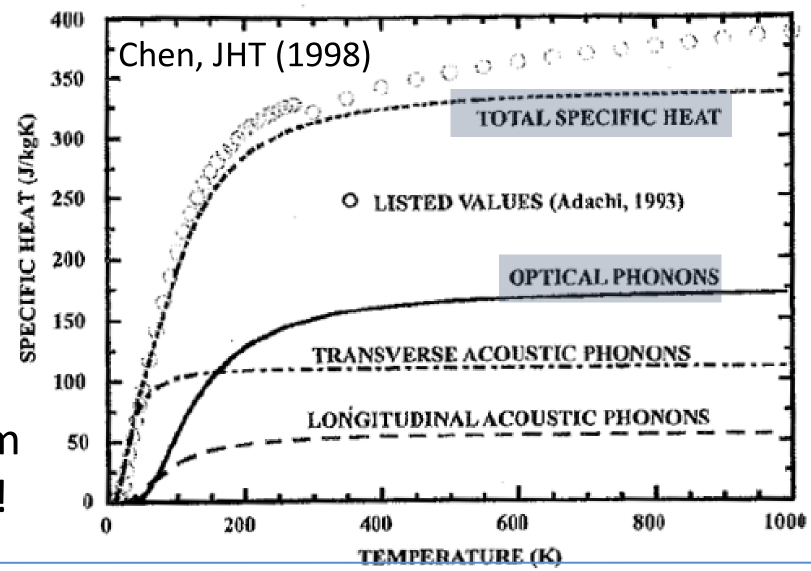



ω Si (Y. Garcia)




$$v_g(opt) = \frac{\partial\omega}{\partial k} \approx 0$$

NB: Different from the specific heat !



# Finiteness of the thermal conductivity..?

- Critical parameter: The phonon relaxation time

    as without it the propagation would be infinite !

In this absence of defects, it is due to the nonlinearity of the force field between atoms

NB: *k* has a 3D meaning…

→ FPI (Fermi Pasta Ulam) paradox of the atomic chain

*k* does not always exist when nonlinearity !

$k \sim L^{\alpha}$ , $\alpha$ not always $0$.

see Lepri etc.

# Scattering mechanisms

that do not conserve the momentum

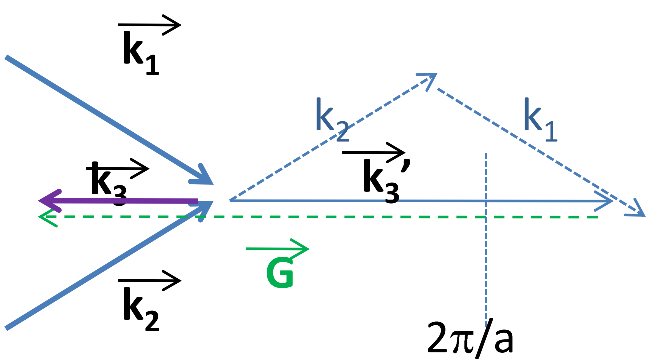
## Origin of the different terms in the mean free path

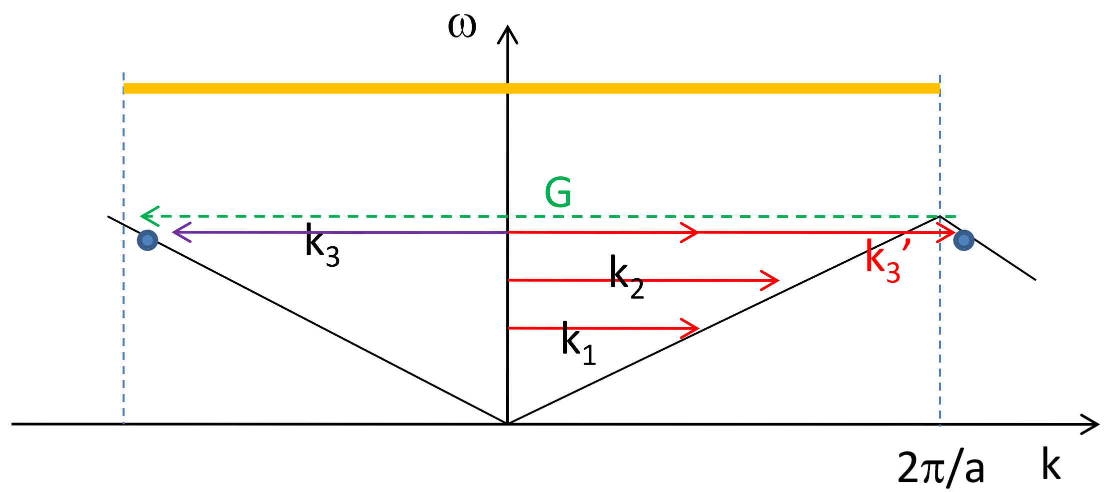
- Umklapp (Klemens model) $\tau_U(\omega)^{-1} \sim A_1 e^{-\theta_D/bT} T^n \omega^m$

  Origin: Nonlinearity=Anharmonicity !!

$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3$

$\vec{k}_1 + \vec{k}_2 = \vec{k}_3'$ but $\vec{k}_3$ in the end



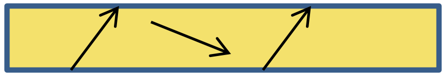



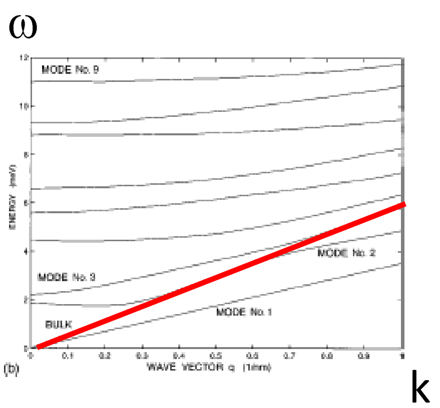

(Very schematic !!)

# Scattering mechanisms

## Origin of the different terms in the mean free path

- Umklapp (Klemens model) $\tau_U(\omega)^{-1} \sim A_1\, e^{-\theta_D/bT} T^3 \omega^2$
  Origin: Nonlinearity=Anharmonicity !!
- Boundary scattering of the particle $\tau_B(\omega)^{-1} \sim A_2\, v(\omega)/D$

D





To be taken into account only in crude model if dispersion relation have not been calculated !

# Scattering mechanisms

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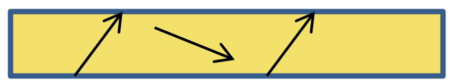
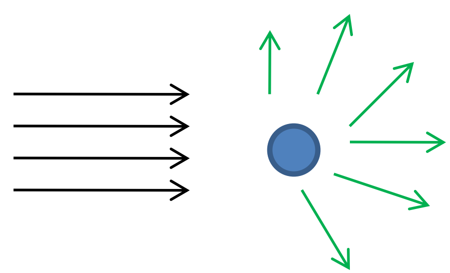
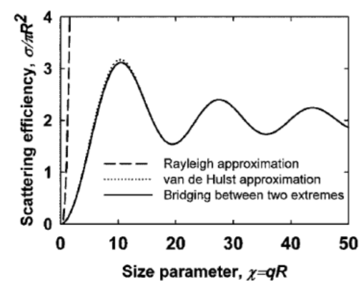


- 'Rayleigh' scattering due to impurities
  Similar to electromagnetics → Mie theory $\tau_I(\omega)^{-1} \sim A_3\, \omega^4$ ($d_{part} \ll \lambda$)





Majumdar, JAP (2005)

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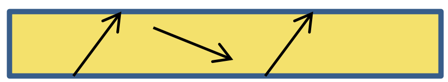
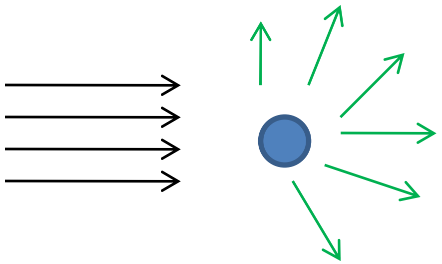
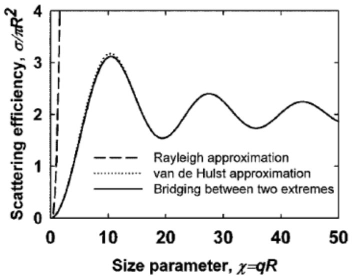


- 'Rayleigh' scattering due to impurities
  Similar to electromagnetics → Mie theory $\tau_I(\omega)^{-1} \sim A_3\, \omega^4$ ($d_{part} << \lambda$)

- Electron-phonon interaction
  $\tau_{e\text{-}ph}(\omega)^{-1} \sim T$





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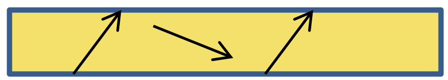

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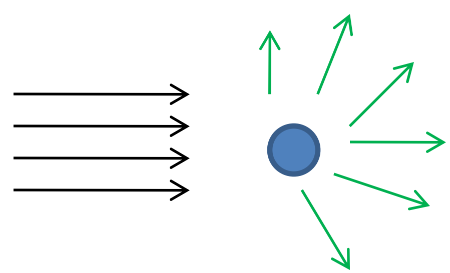
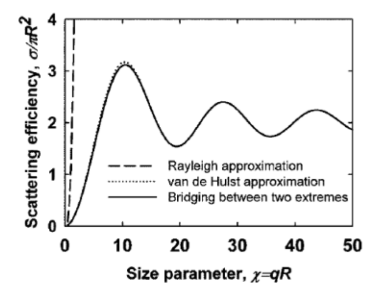





- Electron-phonon interaction
  $\tau_{e\text{-}ph}(\omega)^{-1} \sim T$

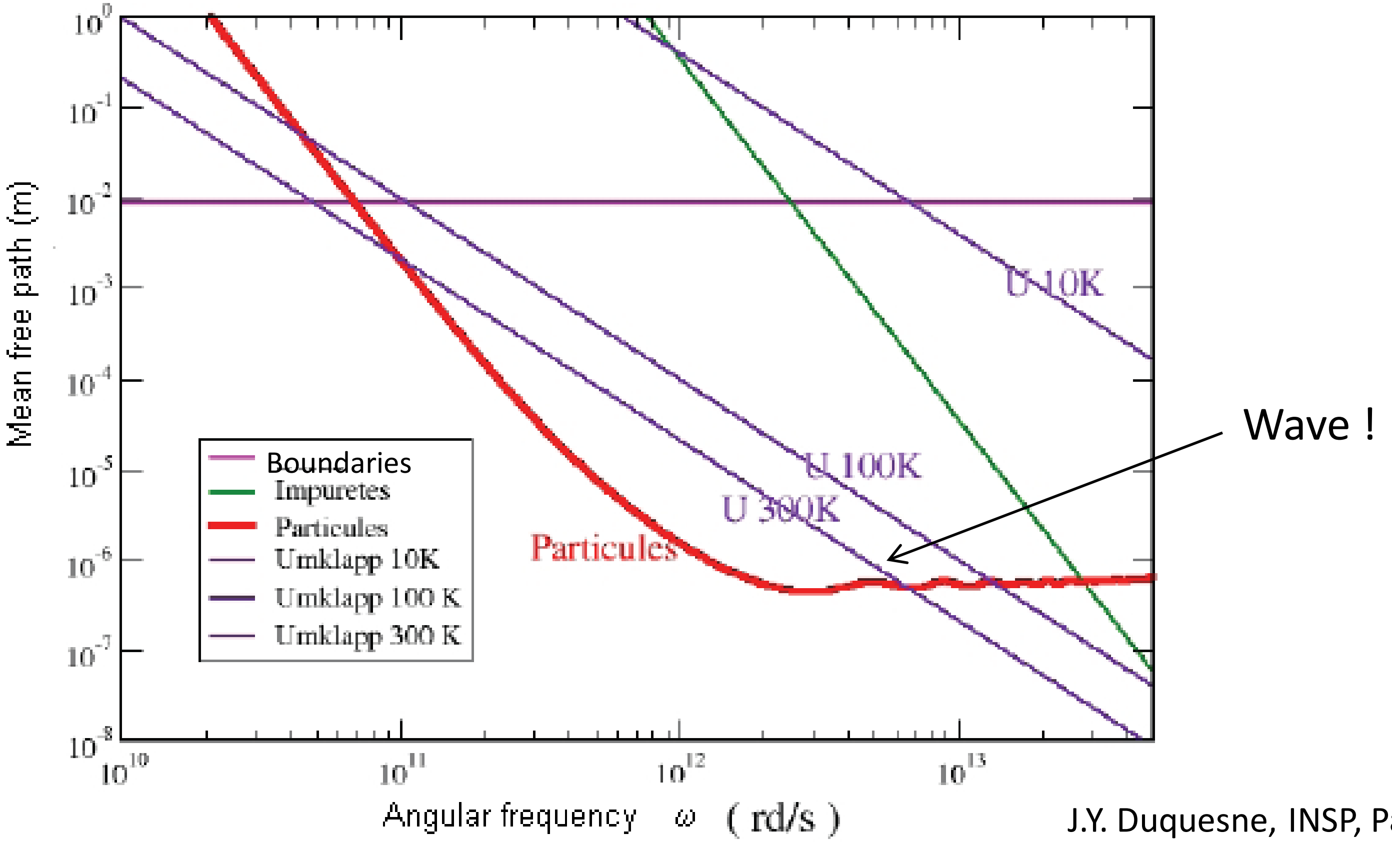
**Usually: Mathiessen rule of the relaxation time $\tau(\omega)^{-1} = \Sigma\, \tau_i(\omega)^{-1}$**

NB: Curious: Same treatment of elastic, inelastic etc. liftetime

# Scattering mechanisms (2)

Leading mean free paths…

$\Lambda = v_g \tau$



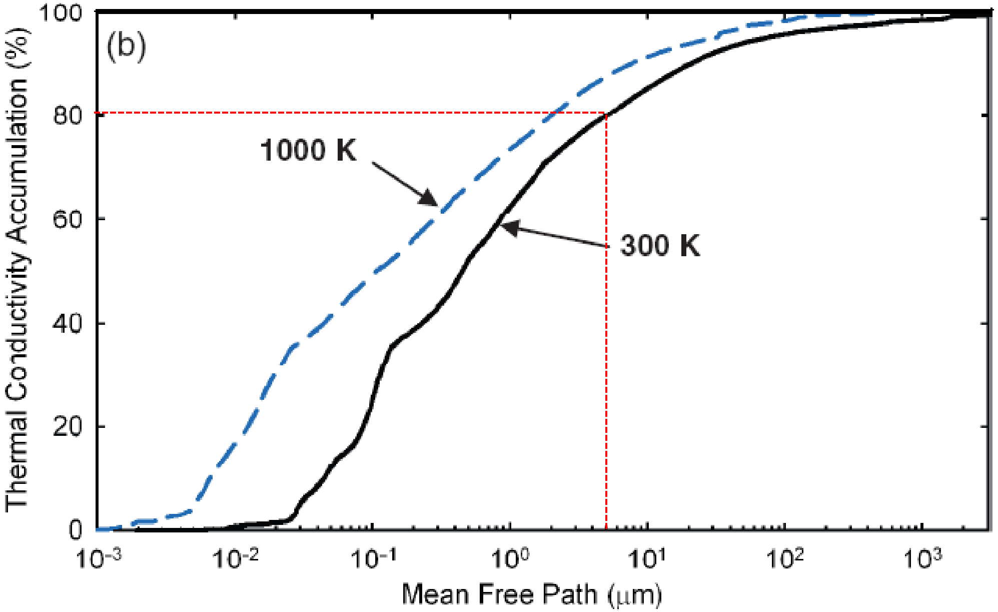

J.Y. Duquesne, INSP, Paris

10nm Si particles in a matrix of Ge

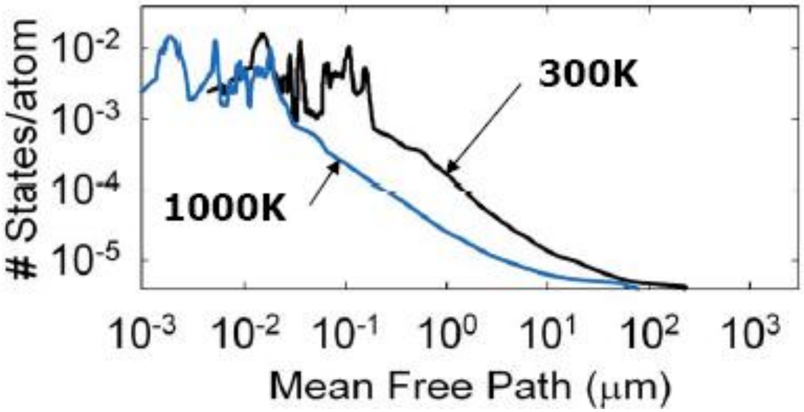
# Mean free path distribution

$$\Lambda = v_g \tau$$

MD calculations with bulk Si




Henry and Chen, J. Comp. Theo. Nanosci 5, 1 (2008)



# How to deal with BTE at low D ?

- At small scale (space/time), the Fourier approach breaks down !

Dispersion relation → wave effect

Phonon density of states

| | |
|---|---|
| Limitation of the approach: | L~$2\pi v/\omega$ [0–20nm] |
| (@RT) | L~$\Lambda$ [10–1000nm?] |

Phonon mean free path $\Lambda$

Particle transport effect

- One needs then or

| to solve the BTE (long !) | to use a simulation method |
|---|---|
| - Probabilistic: Monte-Carlo method<br><br>- Approx: Discrete ordinate (Radiation)<br>- Approx.: Ballistic-diffusive equation | at the atomic scale<br>- Molecular dynamics<br>- Lattice dynamics<br>- Atomistic Green's function method |

- 'Grey approximation' $\tau(\omega)=\tau$

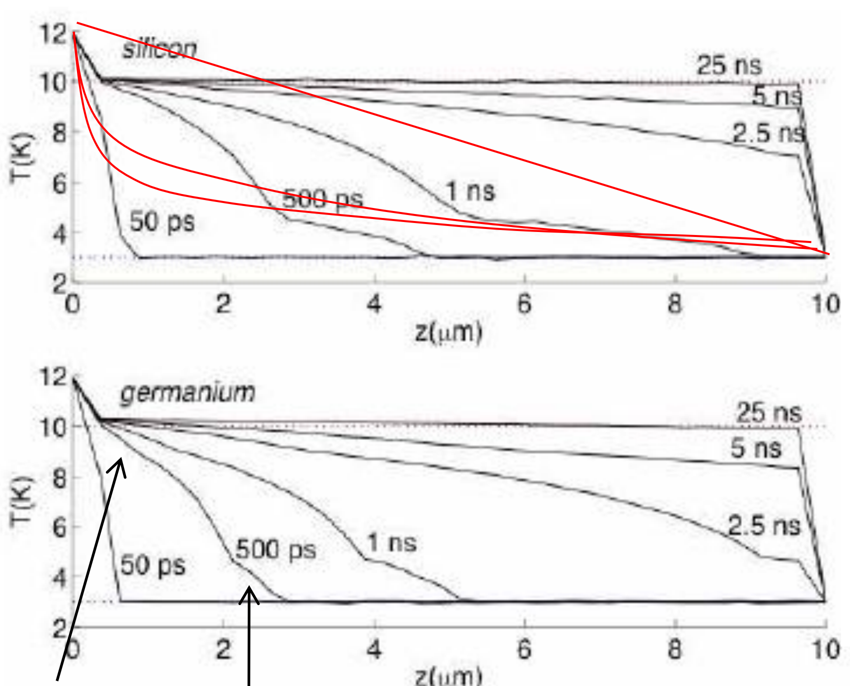
# Fourier vs BTE at nanoscale

Examples taken from Lacroix, Joulain, PRB (2005)

NB: Cattaneo-Vernotte

$$\frac{1}{\tau}\frac{\partial T}{\partial t}+\rho c\frac{\partial^2 T}{\partial t^2}=k\Delta T$$ also incomplete

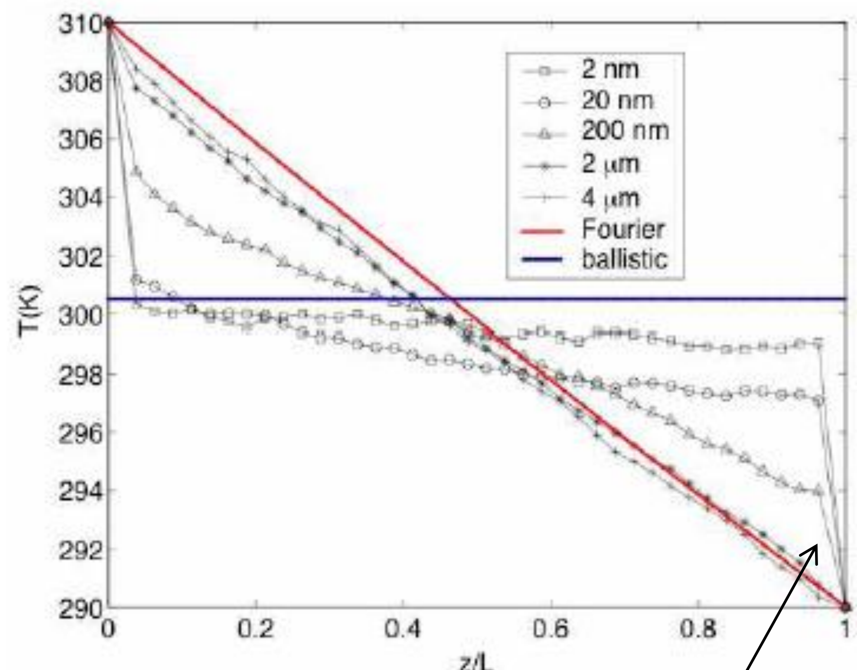
Propagation of heat




Transverse

Longitudinal

Stationary temperature profile between two parallel thermalized media




'Temperature jump'

# Reducing the thermal conductivity

Impurities or nanoparticles

- Useful for the generation of thermoelectricity !

Efficiency depends on figure-of-merit ZT

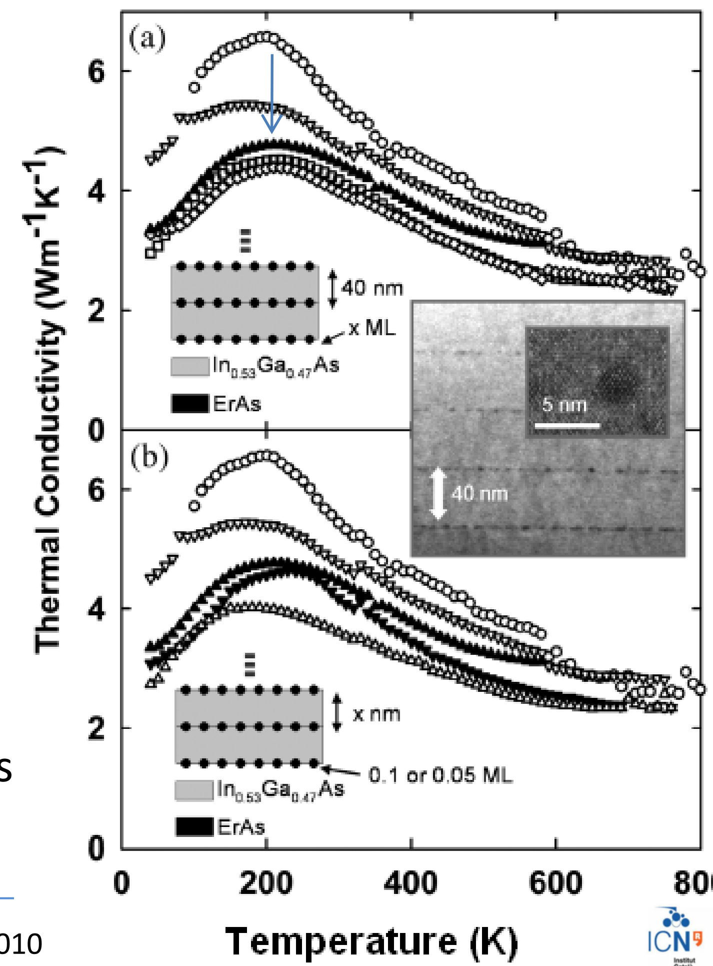
$$Z = S^2 \sigma / ( k_{el} + k_{ph} )$$

Strategies to decrease $k_{ph}$
(without impact on $\sigma$ and S )

**Adding impurities or nanoparticles !**

**→ impacts the high-frequency acoustic phonons**

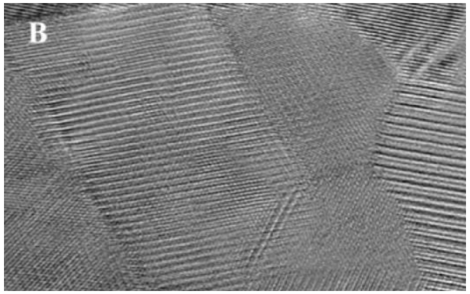
Majumdar, PRL (2007)




ErAs in InGaAs

# Reducing the thermal conductivity

## Boundaries

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Efficiency depends on figure-of-merit ZT

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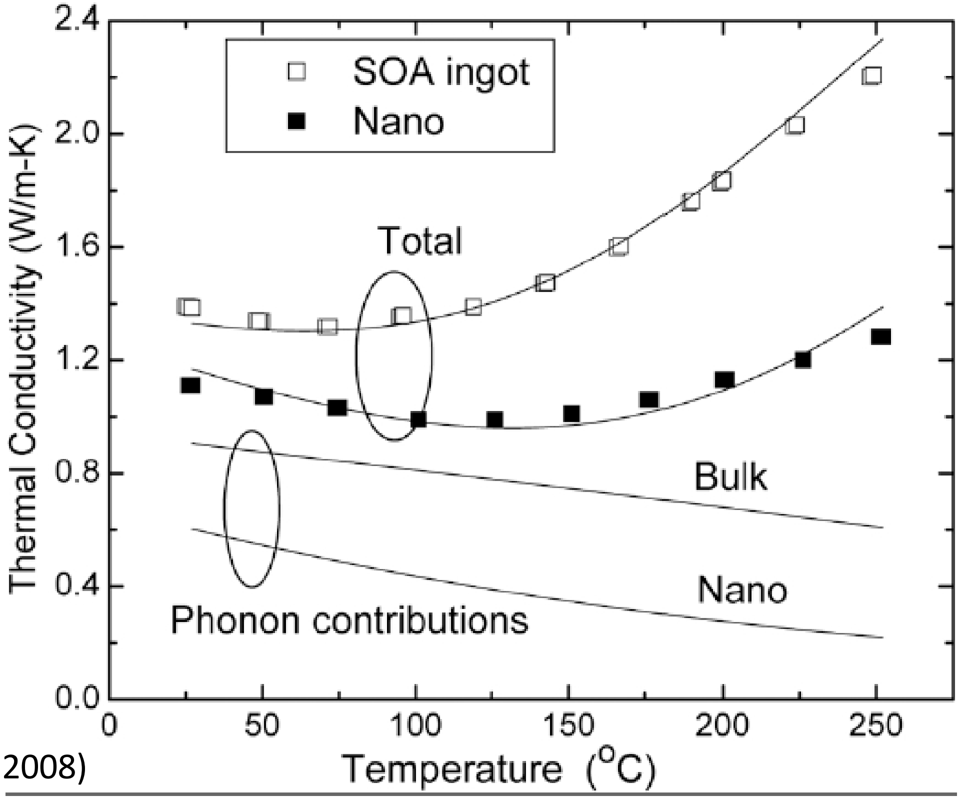
Strategies to decrease $k_{ph}$ (without impact on $\sigma$ and S )

**Adding boundaries**

**→ impacts all phonons**

Ball-milling




Chen and Ren, Science (2008)

# Reducing the thermal conductivity

Boundaries

- Useful for the generation of thermoelectricity !

Efficiency depends on figure-of-merit ZT

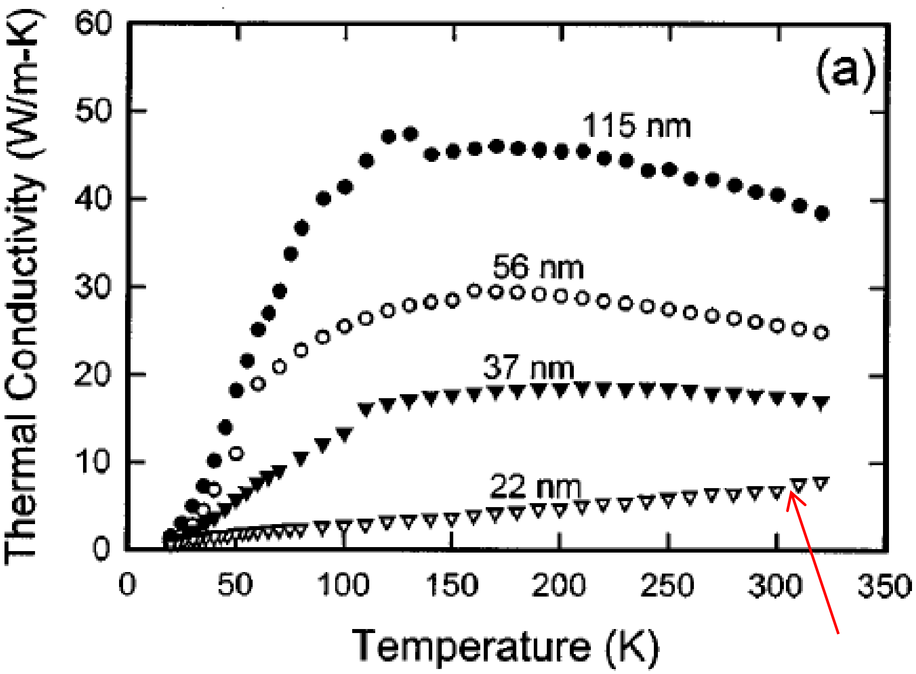
$Z = S^2 \sigma / ( k_{el} + k_{ph} )$

Strategies to decrease $k_{ph}$
(without impact on $\sigma$ and S )

**Adding boundaries**

**→ impacts all phonons**

**Here in nanowires**




Majumdar, APL (2003)

# Reducing the thermal conductivity

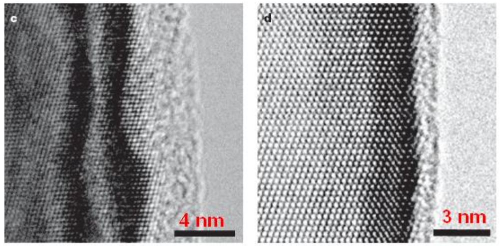
Roughness

- Useful for the generation of thermoelectricity !

Efficiency depends on figure-of-merit ZT

$Z = S^2 \sigma / ( k_{el} + k_{ph} )$

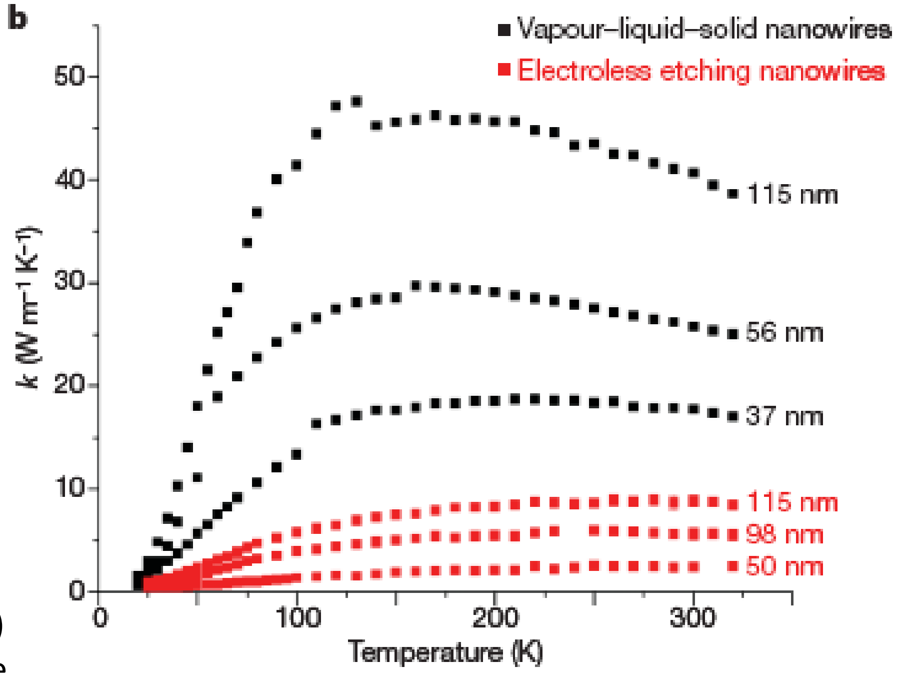
TEM




Strategies to decrease $k_{ph}$
(without impact on $\sigma$ and S )

**Adding amorphous layers at the boundaries**

**→ further reduces the thermal conductivity !**

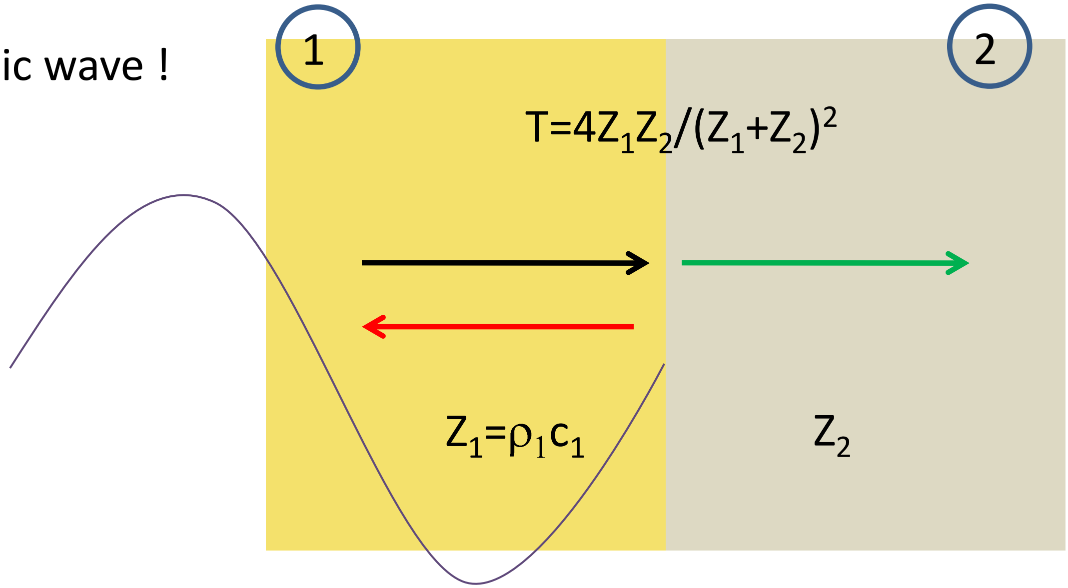



Majumdar, Nature (2009)
See also Heat, same issue

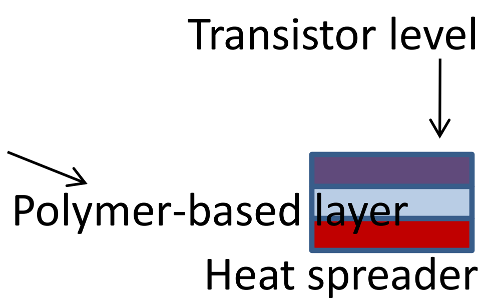
# Phonon transmission at interfaces ?

- Wave model for the low-frequency phonons

Acoustic wave !

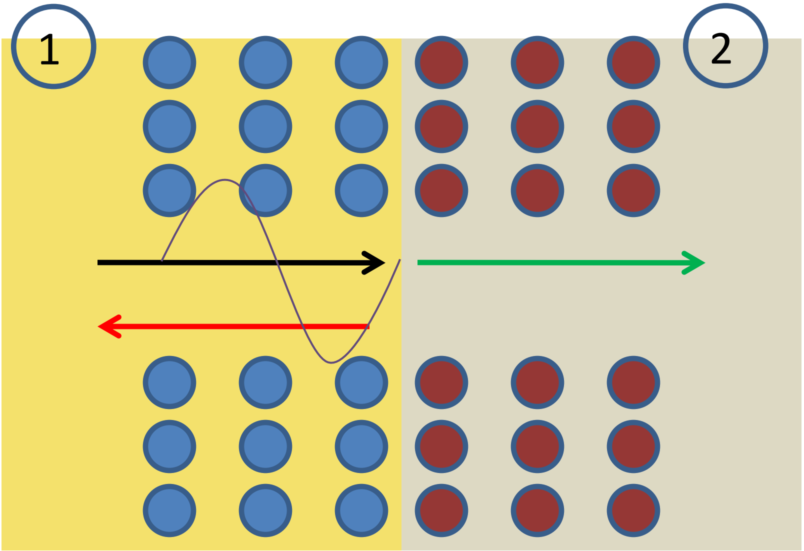



NB: Terminology issue: Kapitza resistance (fluid-solid)
Thermal interface resistance (thick interface)
**Thermal boundary resistance**
**surface**



# Phonon transmission at interfaces ? (2)

- More difficulty for the high frequency acoustic phonons




→ **Diffuse mismatch model**
**= limit of strong diffuse scattering**

# Acoustic mismatch and diffuse mismatch models

DMM: 'All correlations between ingoing and outgoing phonons are ignored'

$$t_{12}(\omega) = r_{21}(\omega) = 1 - t_{21}(\omega)$$

$$t_{12} = \frac{1/c_2^2}{1/c_1^2 + 1/c_2^2}$$ (With asssumption on the DOS)

$R_{Bd}T^3$ with units $K^4/(W/cm^2)$.

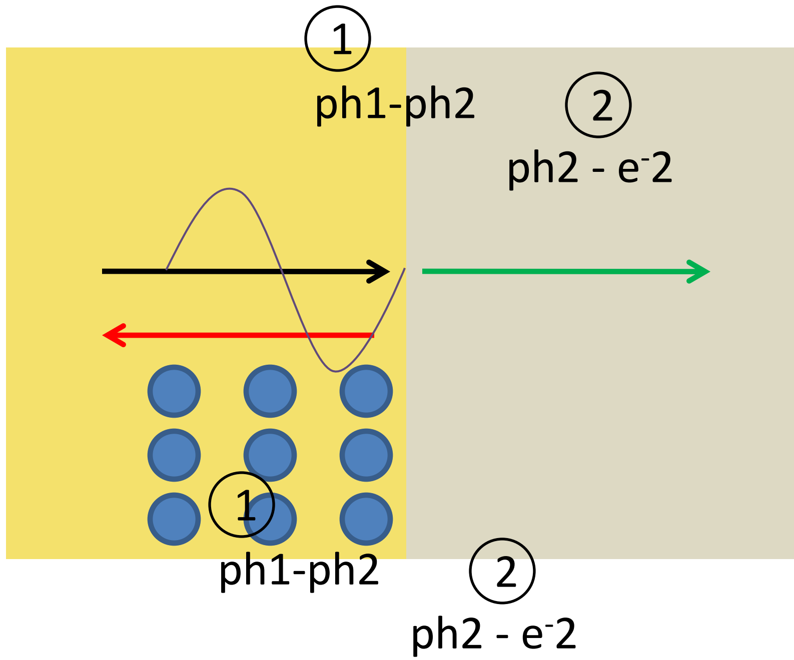
| | Sapphire | | | Quartz | | | Silicon | |
|---|---|---|---|---|---|---|---|---|
| | AMM | | DMM | AMM | | DMM | AMM | DMM |
| Aluminum | 21.0 | * | 21.4 | 6.50 | * | 10.8 | 11.8 | 15.9 |
| Chromium | 18.5 | | 24.4 | 9.77 | | 13.8 | 14.5 | 18.9 |
| Copper | 18.5 | | 20.1 | 8.66 | | 9.43 | 14.3 | 14.6 |
| Gold | 18.9 | * | 18.1 | 8.12 | | 7.48 | 15.8 | 12.6 |
| Indium | 20.4 | | 17.7 | 7.19 | | 7.10 | 12.1 | 12.2 |
| Lead | 18.8 | | 17.8 | 7.67 | | 7.14 | 12.8 | 12.3 |
| Nickel | 19.7 | | 21.1 | 9.32 | | 10.5 | 15.5 | 15.6 |
| Platinum | 20.8 | | 18.7 | 13.0 | | 8.10 | 21.3 | 13.2 |
| Rhodium | 20.8 | * | 23.6 | 13.0 | * | 13.0 | 19.2 | 18.1 |
| Silver | 18.2 | | 18.7 | 8.66 | | 8.06 | 13.8 | 13.2 |

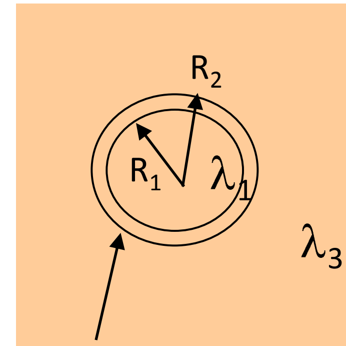
Swartz and Pohl, RMP (1987)

→ In bulk systems, the resistances with DMM and AMM are similar (30%)

# Metal dielectric interface

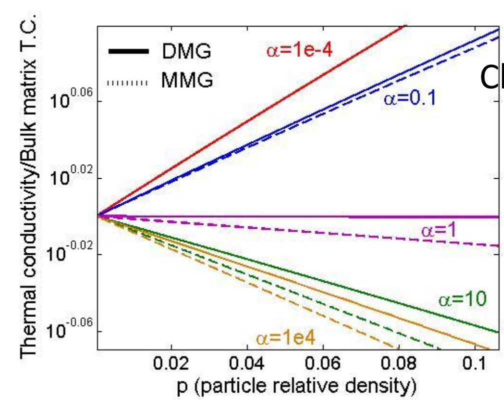
- Measured values higher than prediction




Thermal “surface resistance”

$\alpha=\lambda_3\,\rho_2/R$

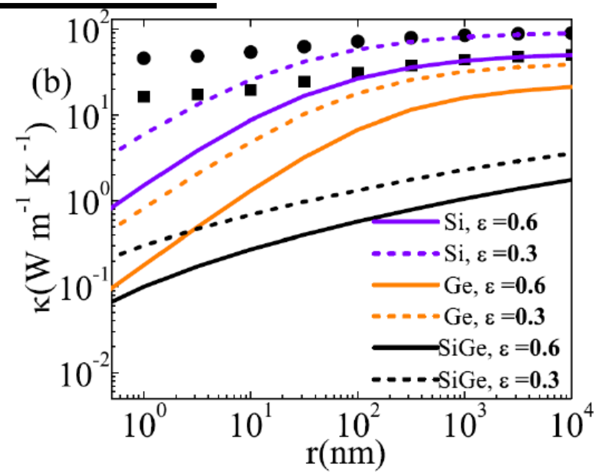



Chapuis

Maxwell-Garnett approximation

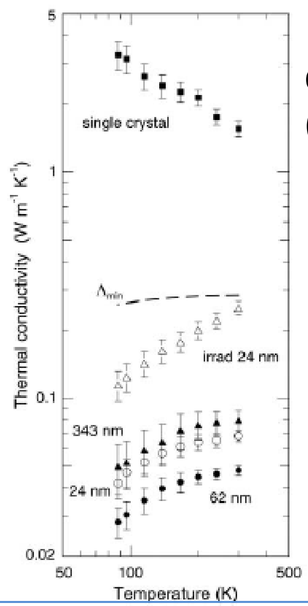
# Thermal conductivity of 'new' materials

Bera, PRL (2010)



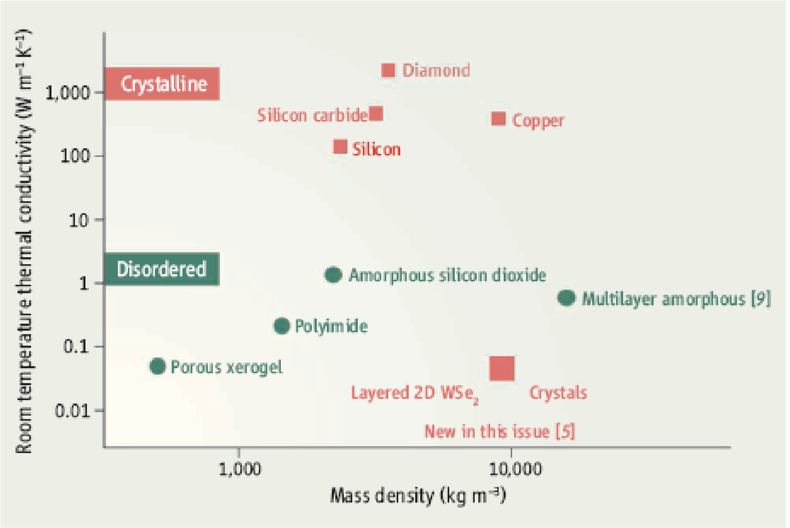

- Porous materials to harvest energy

- Other types of low-thermal conductivity materials (beating the 'Einstein limit' of amorphous materials)




Chiritescu, Science (2007)

Goodson, Science (2007)

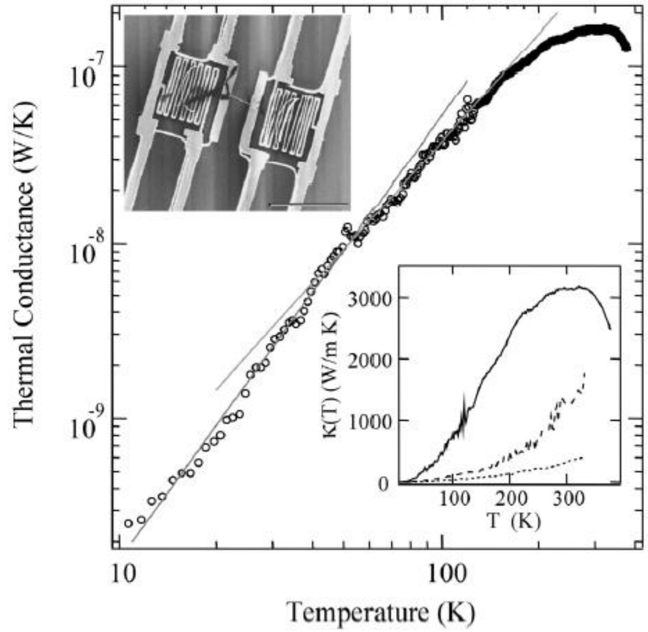



Disordered layered crystal

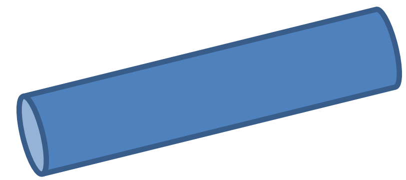
$k_{air}(300\ K)=0.025\ Wm^{-1}K^{-1}$

# Thermal conductivity of ‘novel’ materials

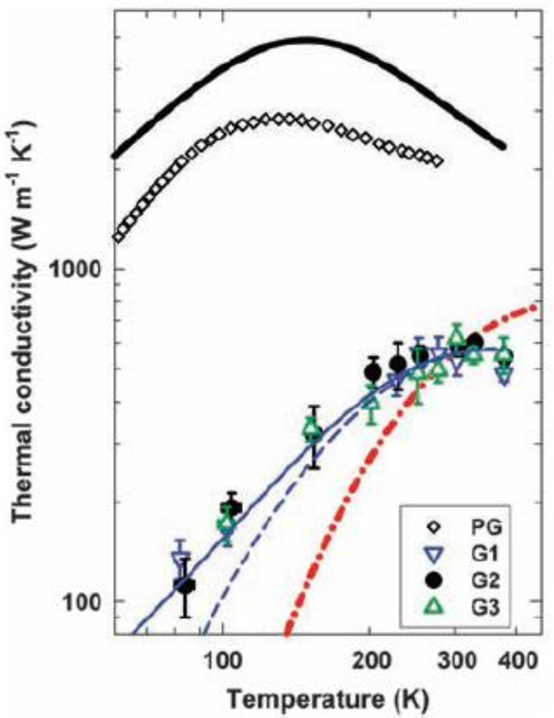
- Carbon nanotubes



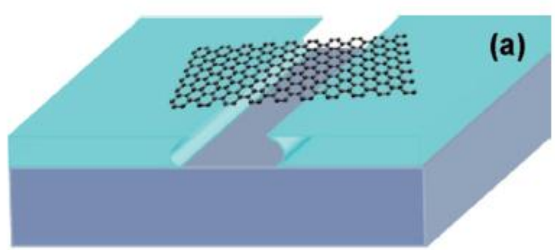

$k=3000\ Wm^{-1}K^{-1}$



MWCNT: Kim et al, PRL(2001)




Li Shi, Science (2010)



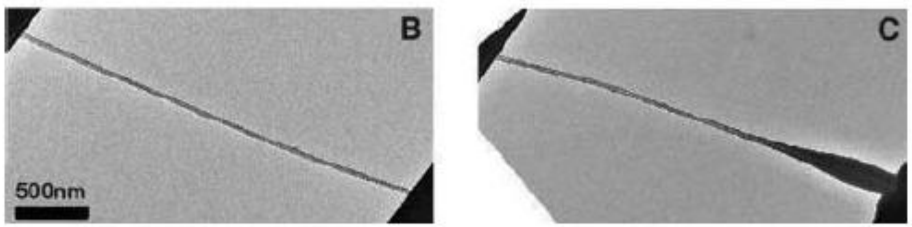

$k \sim 5 \times 10^3$ W/mK
Balandin, Nano Letters (2008)

- Graphene

# Other types of engineering

- Rectification ?

Carbon nanotubes loaded with gradient of molecule density

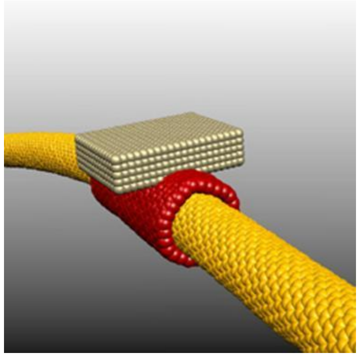



to low-mass ends, respectively. For the CNT in Fig. 2, the measured thermal conductivity was 305 W/(m·K), and the rectification effect at room temperature was 2%.

Figure 3, A to C, shows three BNNTs that were also mass-engineered with $C_9H_{16}Pt$. The respective thermal rectifications were found to be 7, 4, and 3%. The arrows in

Chang, ..,Majumdar, Zettl, Science 2006

- Phonon-based motor ?

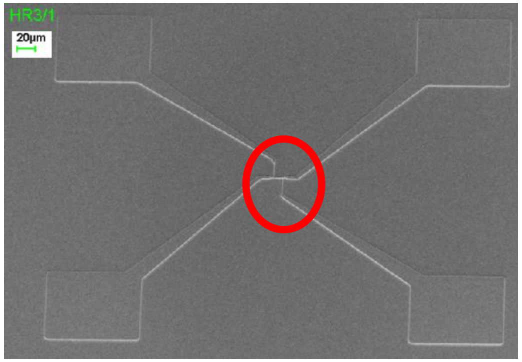


For the moment only due to the thermal gradient

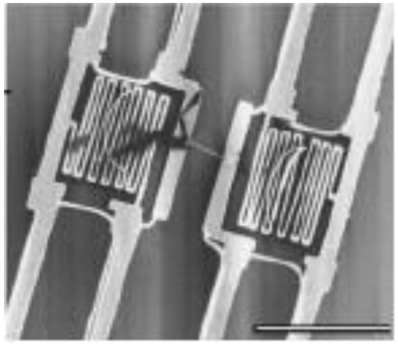
Bachtold, Science (2008)

# Usual methods for heat transport characterisation

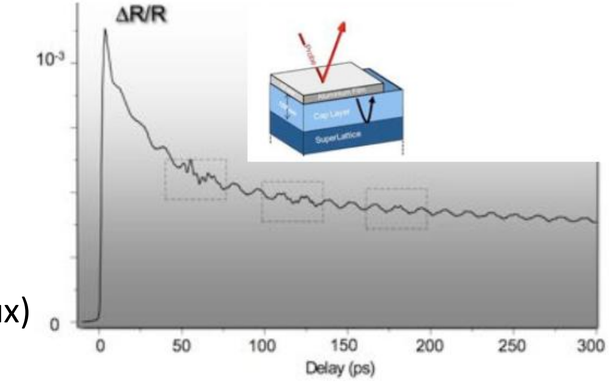
- $3\omega$ method (Cahill, RSI, 1989)
  Based on $R=R_0\,(1+\alpha\,\Delta T)$
  and $\Delta T \propto P=R\,[\,I_0 \cos \omega t\,]^2$
  $\longrightarrow \quad U_{3\omega}=\alpha/2\;R_0 I_0\,\Delta T_{2\omega}$
- Suspended microresistors (Shi and Majumdar)
- Ultrafast pump-probe spectroscopy




ICN and VTT



Shi and Majumdar



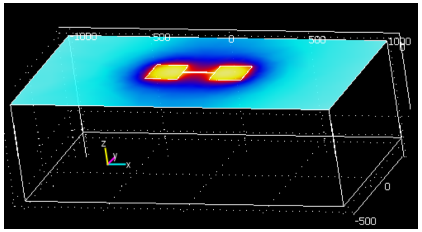

S. Dilhaire (Bordeaux)

## THE 3ω METHOD

- $R(T) = R_0 (1 + \alpha \Delta T)$ Resistance depends on temperature
- $I = I_0 \cos(\omega t) \rightarrow P(t) = R\, I(t)^2 = ½\, R\,(1 + \cos(2\omega t))$ Joule heating of an electric wire
  $\rightarrow T(t) = T_0 + T_{DC} + T_{2\omega} \cos(2\omega t+\phi_{2\omega})$
- $U = RI = R_0 I_0 [1 + \alpha(T_{DC} + T_{2\omega} \cos(2\omega t+\phi_{2\omega}))] \cos(\omega t)$

$= R_0\, I_0\, [(1+ \alpha T_{DC}) \cos(\omega t) + ½\, \alpha T_{2\omega} \cos(\omega t-\phi_{2\omega}) + ½\, \alpha T_{2\omega} \cos(3\omega t+\phi_{2\omega})\ ]$

$= U_\omega + ½\, \alpha R_0 I_0\, T_{2\omega} \cos(3\omega t+\phi_{2\omega})$



- Temperature of the wire = f(heat flux to the sample)

# Conclusions

- Wave behaviour superimposed to the quasiparticle behaviour
- Research driven by thermoeletric community and the quest for better insulator [lower k] or by microelectronics for better conductors [higher k]
- Still plenty of room…
  - Demonstration of the Boltzmann transport equation for phonons ?
  - Phonon relaxation time/mean free path
  - Degree of diffusivity at the interface
  - Filters and interference effects
  - Localization etc.
  - Amorphous materials… [not tackled here !]

# Useful references

- **Books**
- G. Chen, Nanoscale energy transport and conversion
- S. Volz (ed), Microscale and Nanoscale Heat Transfer
- S. Volz (ed), Thermal Nanosystems and Nanomaterials
- Z.M. Zhang, Nano/Microscale heat transfer
- …

**Reviews or interesting articles**

- A. Balandin, Phonon Engineering, J. Nanosc. & Nanotech 5, 1015 (2005)
- D. Cahill et al., Nanoscale thermal transport, J. Appl. Phys. 93, 793 (2003)
- A. Henry and G. Chen, J. Comp. Theo. Nanosci. 5, 1 (2008)
- …

# P2N group (June 2010)

Prof Clivia Sotomayor

Dr Francesc Alsina

Dr Vincent Reboud

Dr Nikolaos Kehagias

Dr Timothy Kehoe

Dr Damian Dudek

Dr Olivier Chapuis

Dr Yamila Garcia

Dr Lars Schneider

Ms Noemi Baruch

Mr John Cuffe

Mr Emigdio Chavez