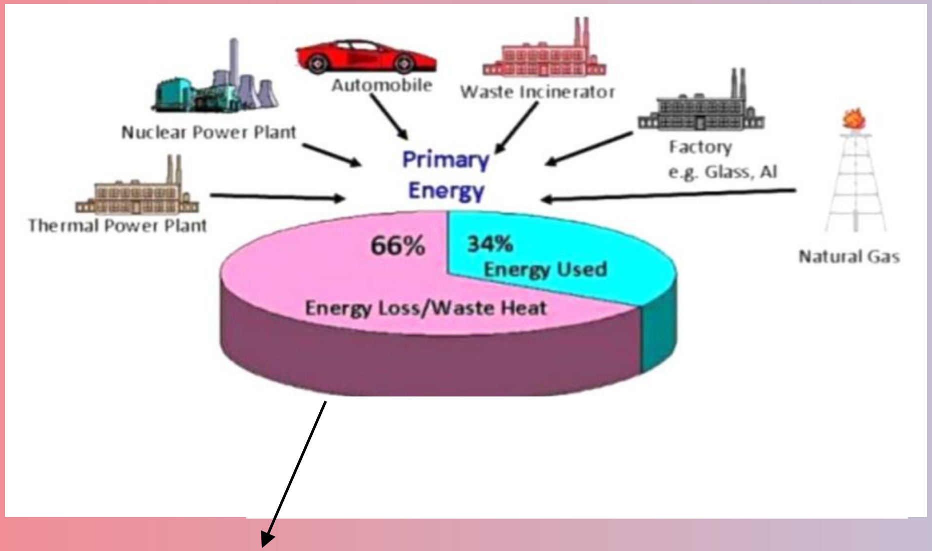
# Nanostructuration for thermoelectric applications

# Outline

- Introduction
- Basics of phonons
- Scattering mechanisms, strategies
- Nanostructuration: why it works and how it works
- Nanostructured: interface thermal resistance: AMM, DMM models
- Nanostructuration and power factor
- Nanophononics

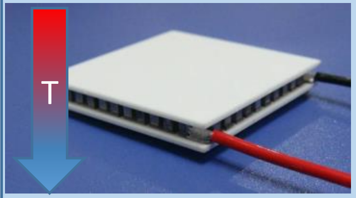
# Thermal management:
# a key challenge in modern society



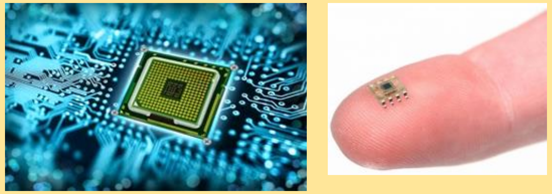

**Heat dissipation reduction**

*K. Zeb et al., Renewable and Sustainable Energy Reviews, 75, 1142 (2017)*

**Thermoelectricity**




**Microelectronics**



Size reduction

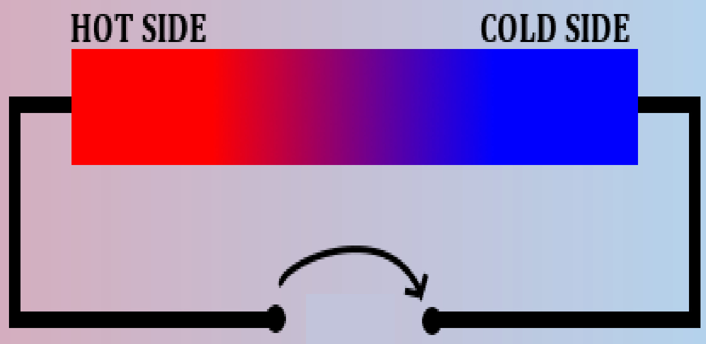
Higher current density

Joule heating

Need:
**Low $k_T$** to increase thermal confinement and reduce heat dissipation

# Thermoelectricity

A thermoelectric material is a material able to generate an electric potential when subjected to a temperature gradient




$$\Delta V = S\Delta T$$

Figure of merit

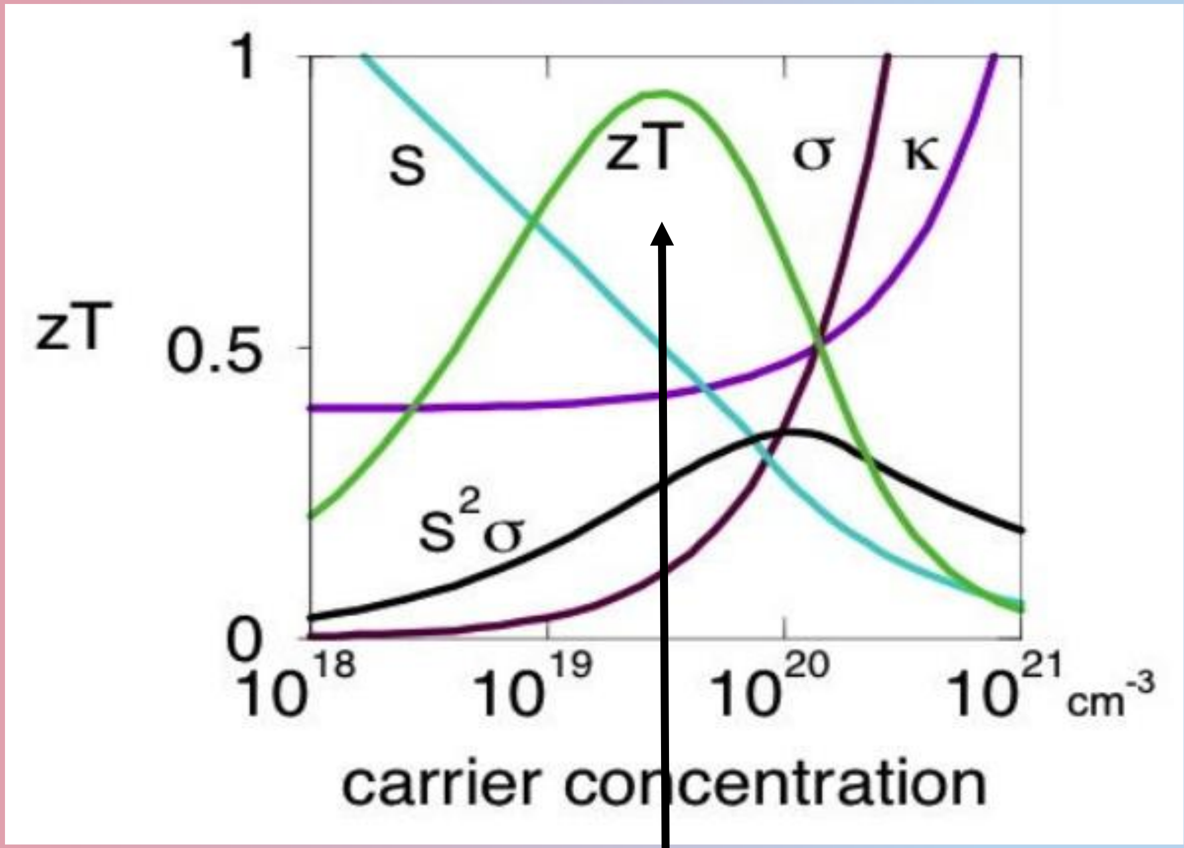
$$\boldsymbol{ZT = \frac{S^2\sigma}{\kappa}T}$$

$\boldsymbol{S}$ = Seebeck coefficient
$\boldsymbol{\sigma}$ = electrical conductivity
$\boldsymbol{\kappa}$ = thermal conductivity

Optimization strategies:
1) Acting on the electronic transport
2) Reducing the thermal conductivity by phonon engineering

# The puzzle of entangled quantities

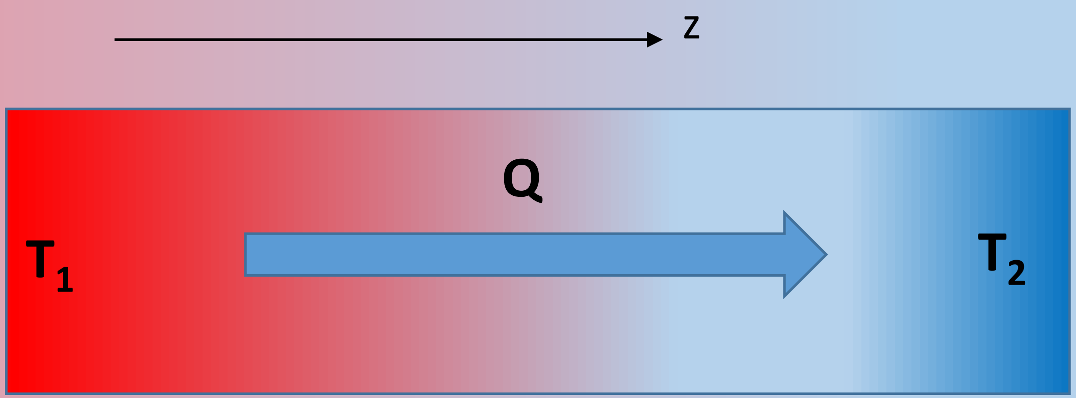
$$ZT = \frac{S^2\sigma}{\kappa}T$$

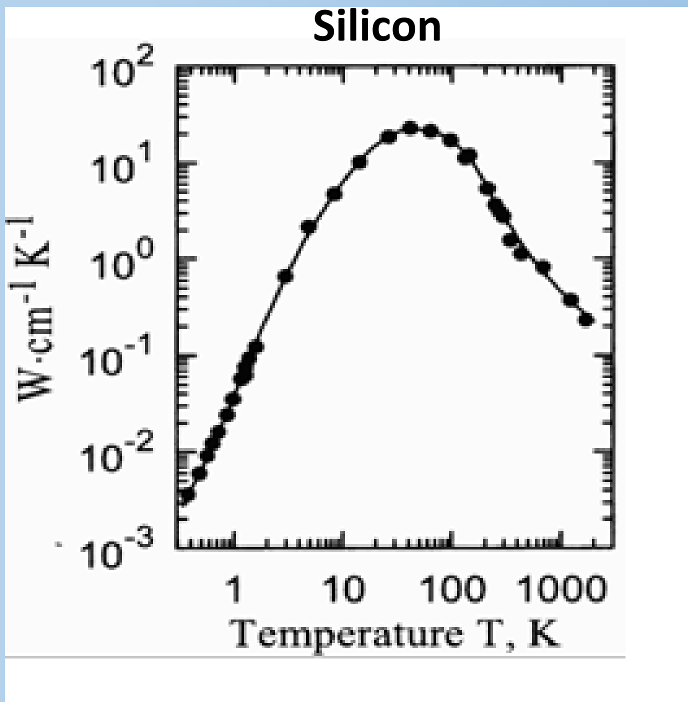



Heavily doped semiconductors

To improve the power factor, electronic engineering is possible tipically through doping. What about thermal transport?

# Heat transport in solids




Macroscale: Fourier Law: diffusive heat transport

The Heat flux (per unit area and unit time) is proportional to the temperature gradient

$$\frac{Q}{\Delta t S} = -k\nabla T$$

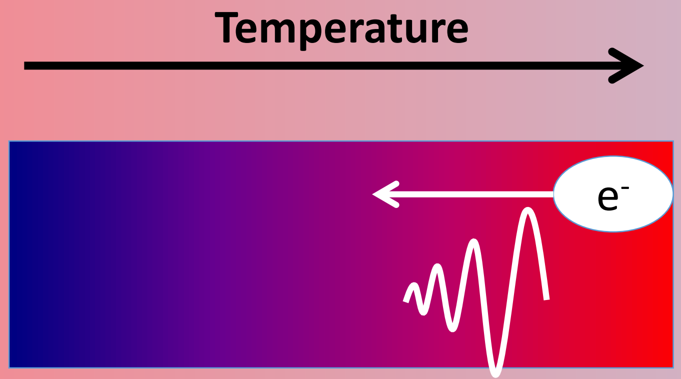
Where S is the area perpendicular to $\nabla T$, thus a surface of constant T. Remembering $\nabla T = \frac{\Delta T}{\Delta z} = \frac{\Delta T}{L}$

$$\frac{Q}{\Delta t} = -k\frac{\Delta T}{L}S$$

Here L is the length of propagation (length of the thin film, of the quantum wire)
S= cross section of the guide

$K = \frac{Sk}{L}$ thermal conductance along the direction z.

# Heat transport in solid materials: A microscopic understanding




2 heat carriers: electrons and atomic vibrations (phonons)

$$k_T = k_T^{el} + k_T^{ph}$$

Electrons:
Wiedemann-Franz law $k_{T,el}$

L = Lorenz Number ~ 2.44 1

dominant electrons

dominant phonons

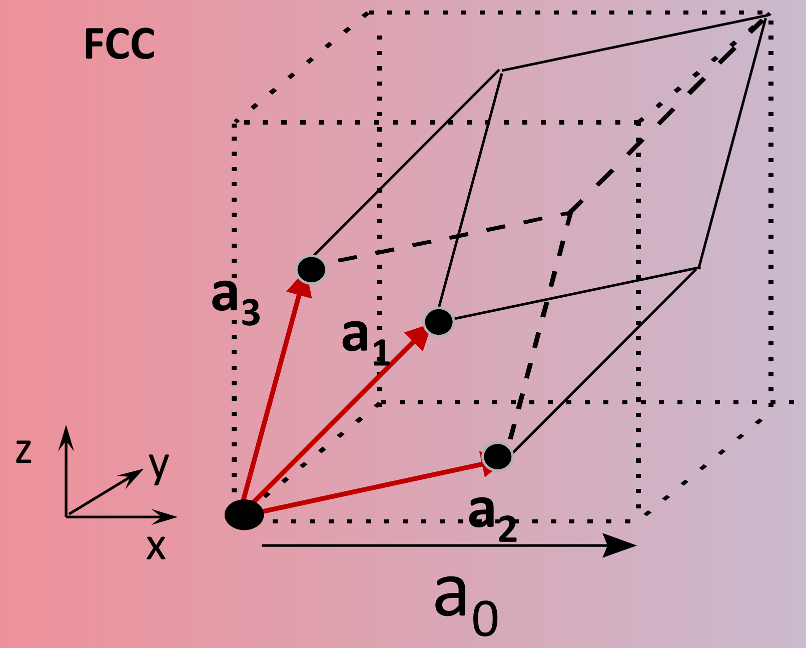
$$ZT = \frac{S^2\sigma}{k_{ph} + L\sigma T}T$$

Playing on the phonon contribution to reduce thermal transport preserving the electronic one

# Phonons: a reminder

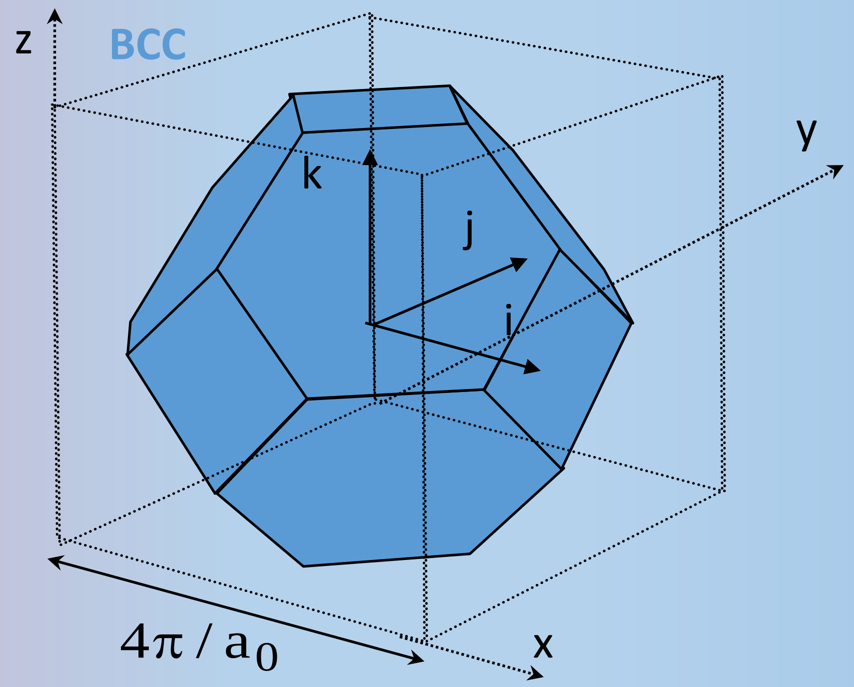
**Crystal**

In the real space, the structure is defined starting from a unit cell and its basis vectors $a_1$,$a_2$,$a_3$



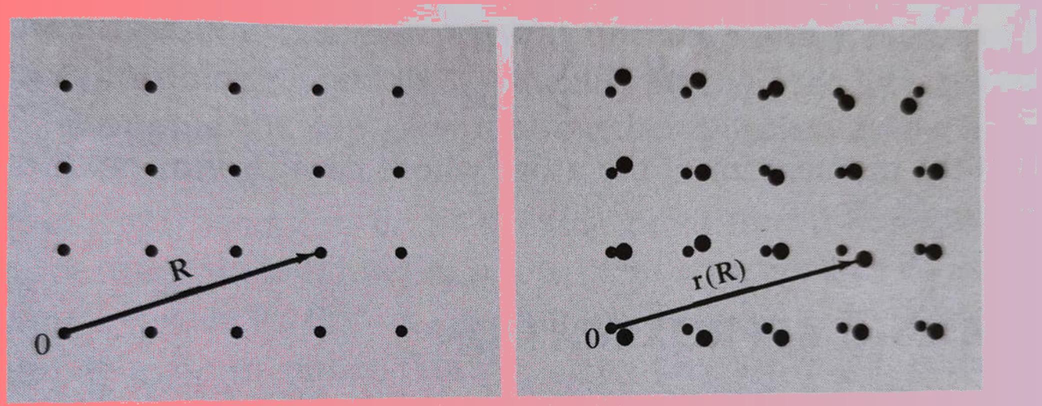

**Reciprocal lattice**

In the reciprocal space the first Brillouin zone is described by the reciprocal vectors $b_1$, $b_2$, $b_3$




$$b_i \cdot a_i = 2\pi\delta_{ij}$$

$$b_1 = 2\pi \frac{a_2 \otimes a_3}{a_1 . a_2 \otimes a_3} \qquad b_2 = 2\pi \frac{a_3 \otimes a_1}{a_1 . a_2 \otimes a_3} \qquad b_3 = 2\pi \frac{a_1 \otimes a_2}{a_1 . a_2 \otimes a_3}$$




$$\boldsymbol{r}(\boldsymbol{R}) = \boldsymbol{R} + \boldsymbol{u}(\boldsymbol{R})$$

$$H = \sum_{R} \frac{P(R)^2}{2M} + U$$

For N atoms, we have 3N equations of motions

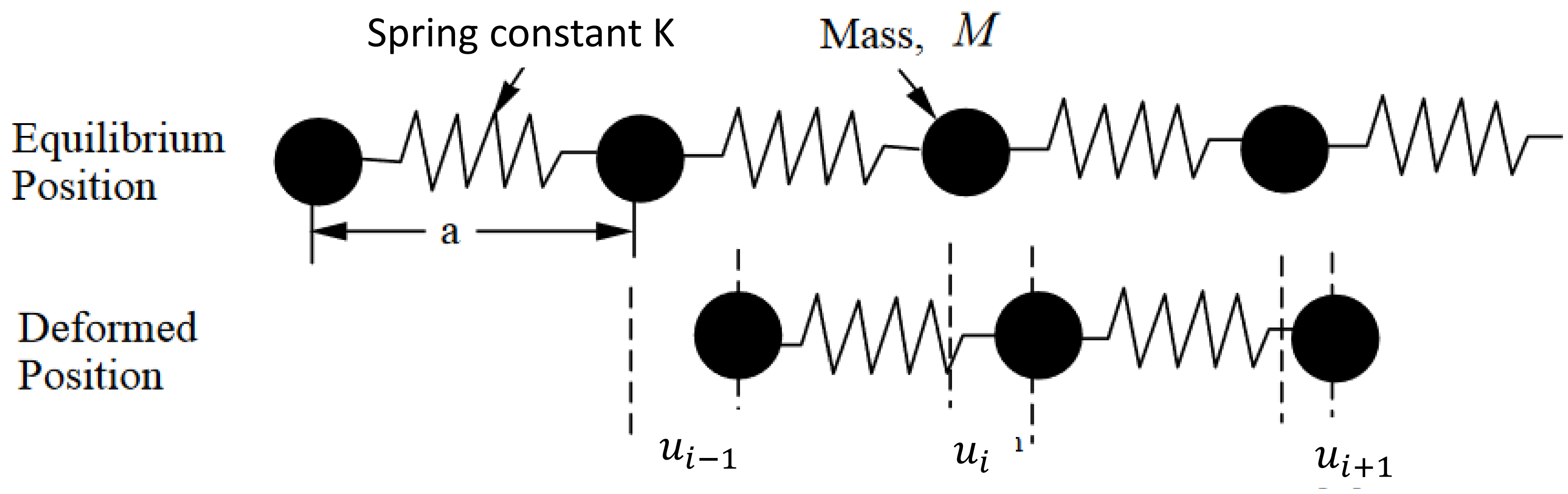
$$\mathrm{M}\ddot{u}_i(R) = -\frac{\partial U}{\partial u_i(R)}$$

For 3N atoms, 3N equations (coupled through the inter-atomic potential $U(r_i(R))$

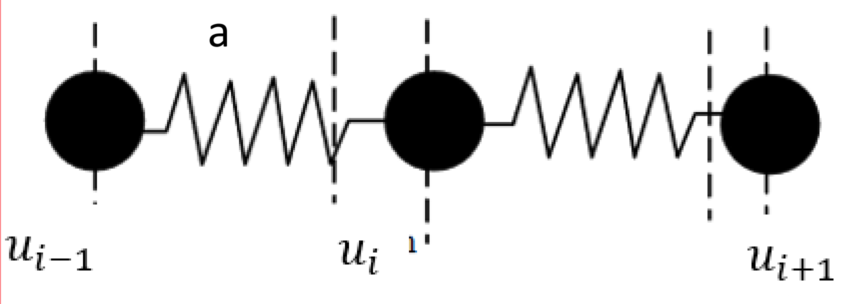
Let's look to a simple case

# The monoatomic chain: 1D system

Longitudinal wave of a 1-D Array of Spring Mass System




$u_i$ displacement of the i[th] atom from its equilibrium position



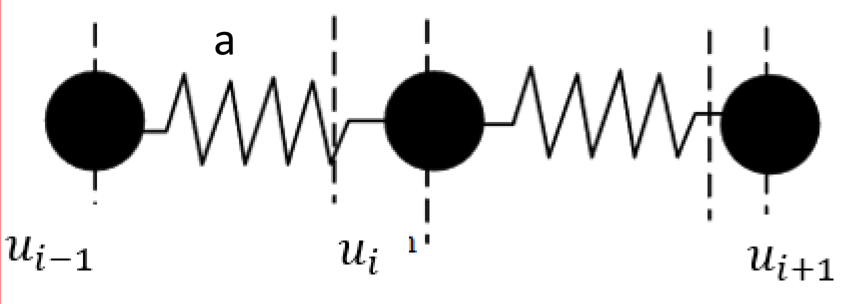

$$\mathrm{U} = U^0 + \frac{1}{2}\sum_{i=1}^{N} K(\boldsymbol{u}_i - \boldsymbol{u}_{i+1})^2 + K(\boldsymbol{u}_i - \boldsymbol{u}_{i-1})^2$$

$$F_i = m_i \frac{\partial^2 u_i}{\partial t^2} = -\frac{\partial U}{\partial u_i} =$$

$$= -\frac{1}{2}\left(2K(\boldsymbol{u}_i - \boldsymbol{u}_{i+1}) + 2K(\boldsymbol{u}_i - \boldsymbol{u}_{i-1})\right) =$$

$$= -K\ (2u_i - u_{i+1} - u_{i-1})$$

$$\boxed{\frac{\partial^2 u_i}{\partial t^2} = -\frac{K}{m_i}\ (2u_i - u_{i+1} - u_{i-1})}$$




$$\frac{\partial^2 u_i}{\partial t^2} = -\frac{K}{m_i}\,(2u_i - u_{i+1} - u_{i-1})$$

Let’s try a wave solution $u_s = Ae^{i\omega t - iq\cdot r_s}$

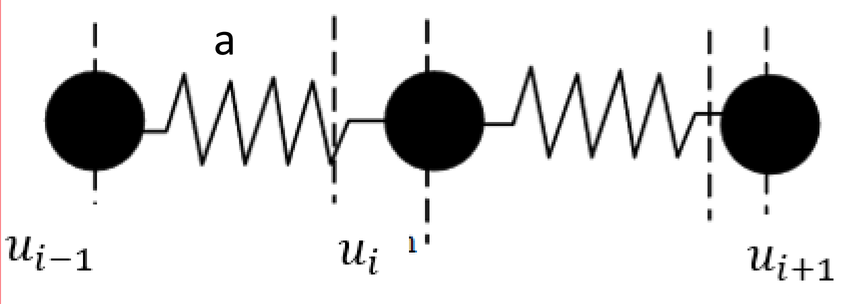
Remembering that $r_s = \mathrm{sa}$

$$u_s = Ae^{i\omega t - iqsa}$$

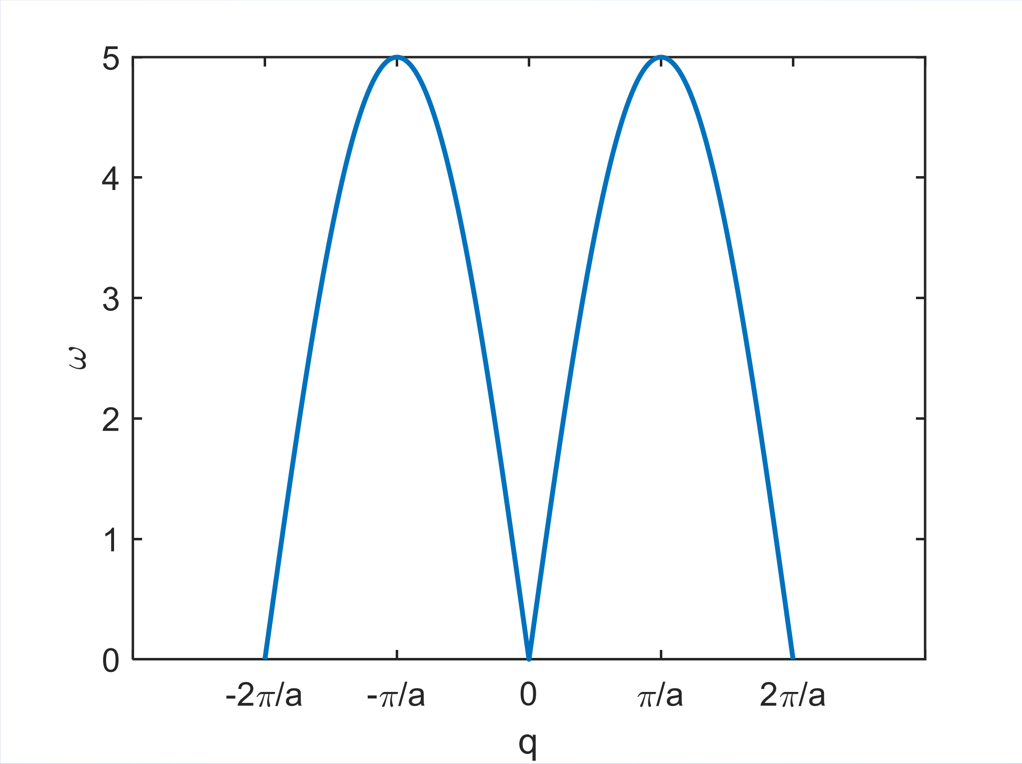
$$-m_s\omega^2\left(e^{iqsa} - e^{-iqsa}\right) = -K\left(e^{iqsa}\left(2 - e^{iqa} - e^{-iqa}\right) - e^{-iqsa}\left(2 - e^{iqa} - e^{-iqa}\right)\right)$$

$$m_s\omega^2 = K\left(2 - e^{iqa} - e^{-iqa}\right) = K(2 - 2\cos(qa)) = 4K\sin^2\left(\frac{qa}{2}\right)$$

$$\omega = 2\sqrt{\frac{K}{m_s}}\left|\sin\left(\frac{qa}{2}\right)\right|$$




$$\omega = 2\sqrt{\frac{K}{m_s}}\left|sin\left(\frac{qa}{2}\right)\right|$$




Thanks to the periodicity of the chain,
It is

$$Ae^{i\omega t-iqsa} = Ae^{i\omega t-iq(sa+Na)}$$

$$1 = e^{-iqNa} \rightarrow q = \frac{2\pi}{Na}n, n = 1 \ldots N-1$$

The wavevector has values only between 0 and $\frac{\pi}{a}$:
beyond this, it just repeats itself because of periodicity: this is the Brillouin zone limit

# Phonons: a reminder

A phonon (*i.e.* a lattice wave) is described by :

- a wave vector, **q** : determines the direction of propagation
- a dispersion relation, $\boldsymbol{\omega_q = f(q)}$,

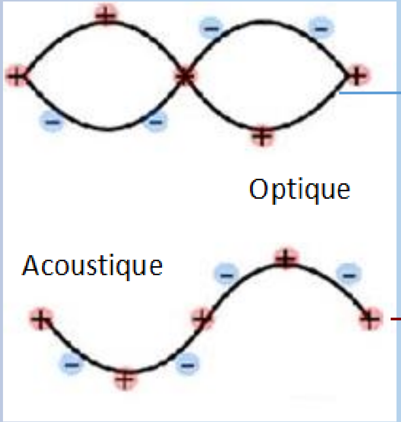
relating wave vector **q** and energy $\boldsymbol{\omega_q}$

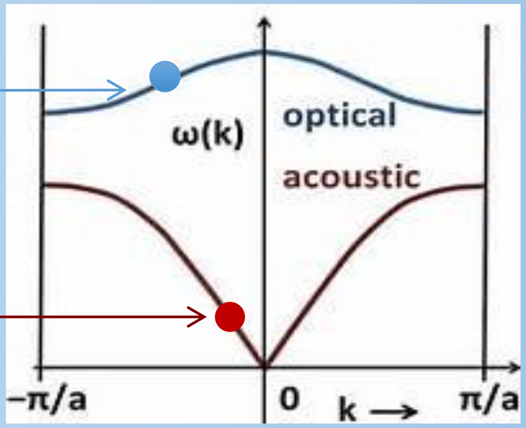
- a polarization vector, $\boldsymbol{e_q}$ :

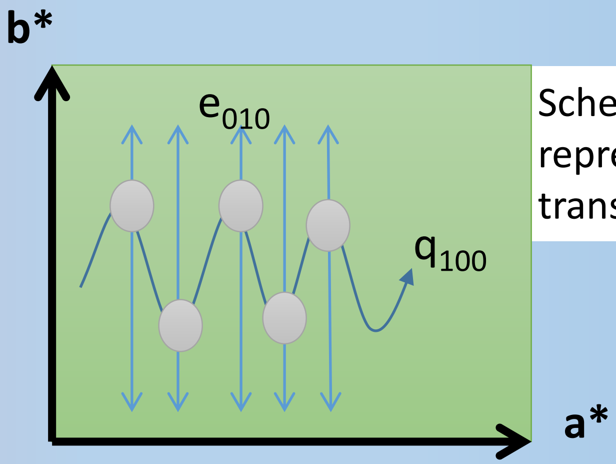
gives the direction of atomic

displacements: three types of waves :

  - 1 longitudinal (compressional) for $\boldsymbol{e_q // q}$
  - 2 transverse (shear) $\boldsymbol{e_q \perp q}$



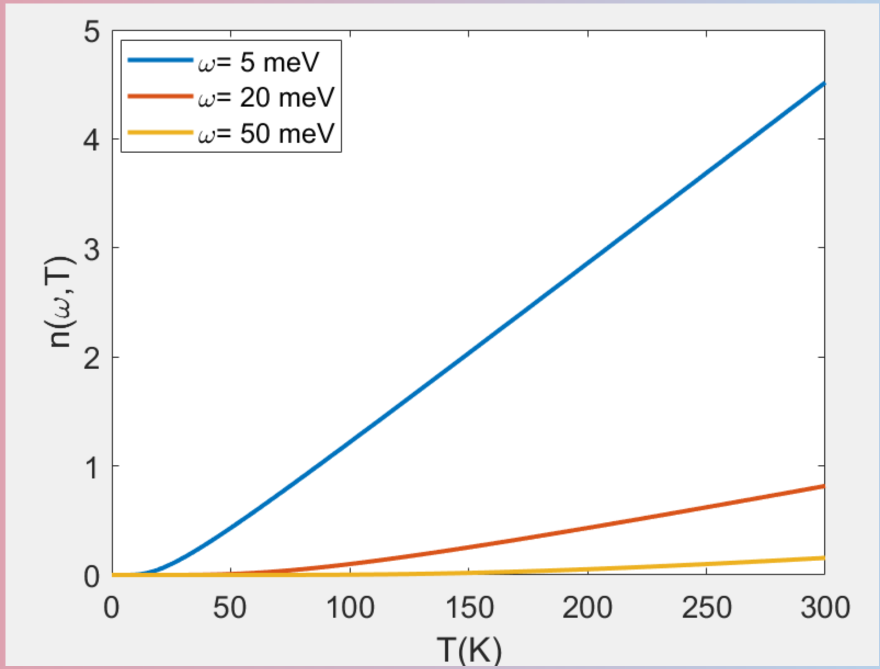




Schematic representation of a transverse wave

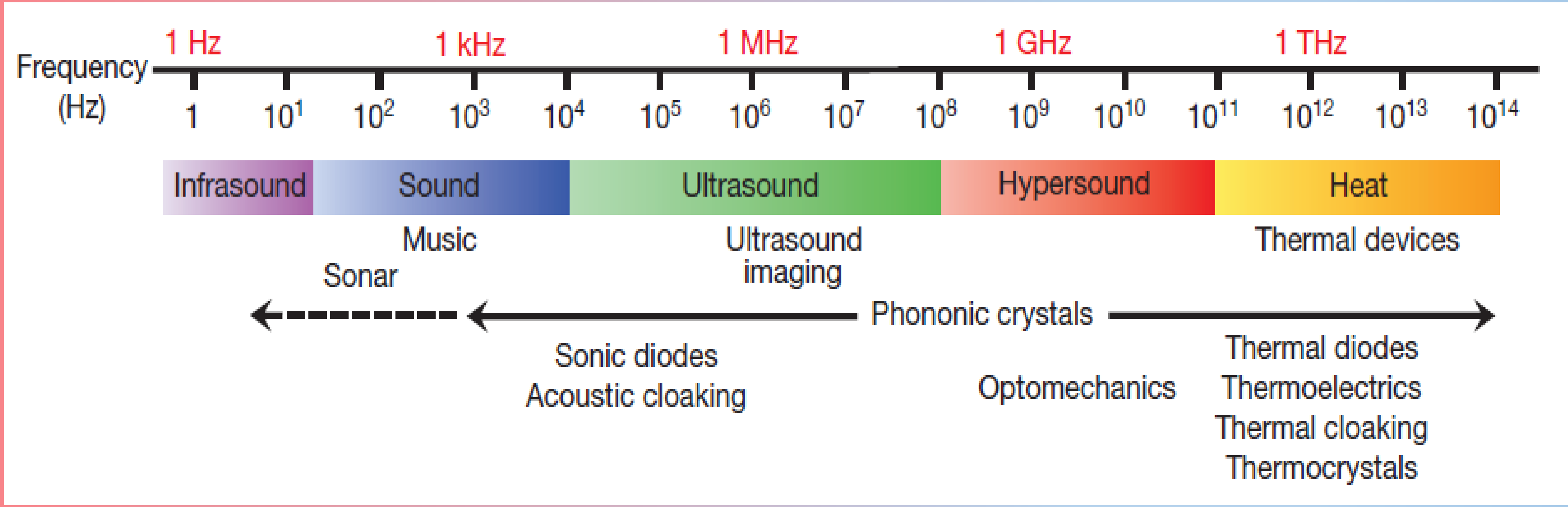
# Phonons: a reminder

A phonon is described by :

- A density of states $g(\omega) = \frac{1}{V}\frac{dN}{d\omega}$: number of phonons modes per unit volume between $\omega\ \ and\ \omega + d\omega$
    - 3D: Debye model $\omega = vq, g(\omega) = \frac{3\omega^2}{2\pi^2 v^3}$
- an occupation number given by the Bose-Einstein distribution : $n\left(\omega_{\boldsymbol{q},j}\right) = \frac{1}{\left(exp\left(\hbar\omega_{\boldsymbol{q},j}/k_B T\right) - 1\right)}$



# Phonon: responsible for sound and heat transport




*M. Maldovan, Nature 503,209 (2013)*

# Phonons and Thermal transport

Phonon: think of it as a particle

$v, \omega, \tau(\omega), \ell(\omega)$

$\tau = time\ between\ 2\ scattering\ events$

$\ell = distance\ between\ 2\ scattering\ events$

$\ell = v\tau$

thermal conductivity depends on:

- Energy transported by the carrier
- Velocity of the carrier
- Distance travelled
- How many carriers participate

$$k_T = \frac{1}{3}\int C_v(\omega)v(\omega)\ell(\omega)g(\omega)d\omega$$

$$\kappa_{ph} = \frac{1}{3}\int C_V(\omega)v^2(\omega)\tau(\omega)g(\omega)d\omega$$

**Boltzmann transport equation**

$C_v = \frac{\partial E}{\partial T}$ Phonon specific heat

$v(\omega) = \left(\frac{\partial \omega}{\partial q}\right)$ Phonon velocity

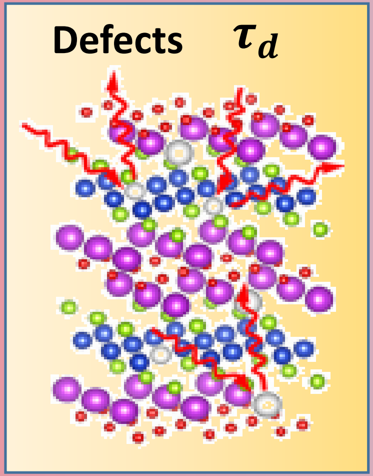
Depends only on the energy dispersion ω(q)

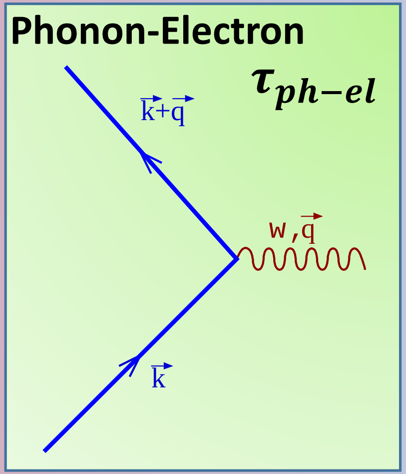
$\tau(\omega)$ Phonon Lifetime

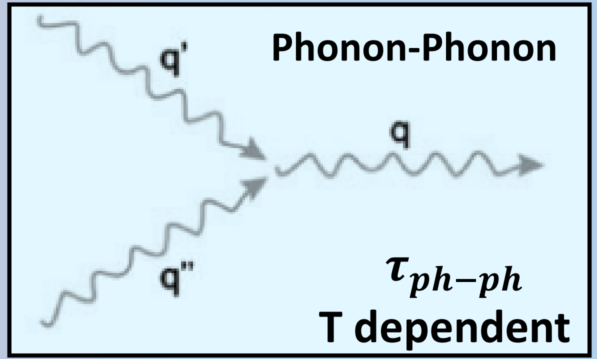
➡ Related to phonon attenuation $\Gamma = \frac{2}{\tau}$

$g(\omega)$ Phonon Density of States

# Intrinsic Scattering processes



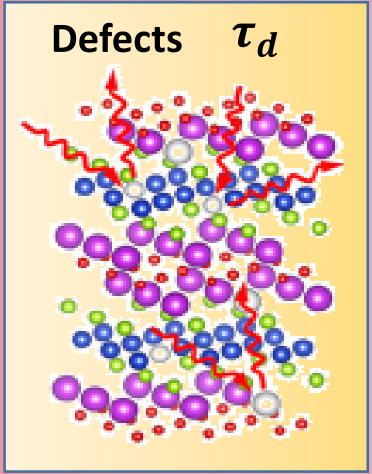



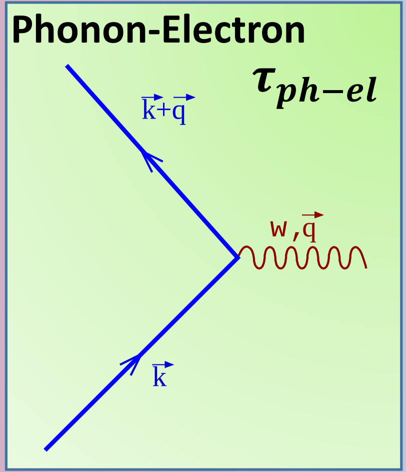



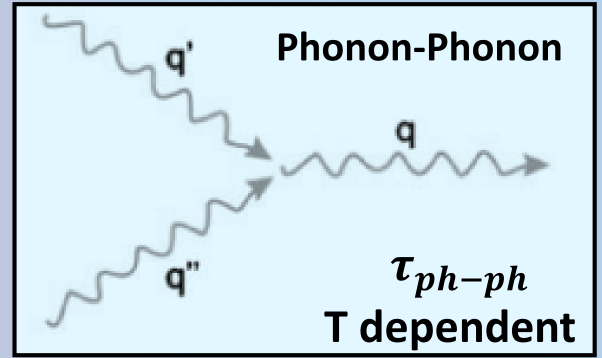

Matthiessen rule

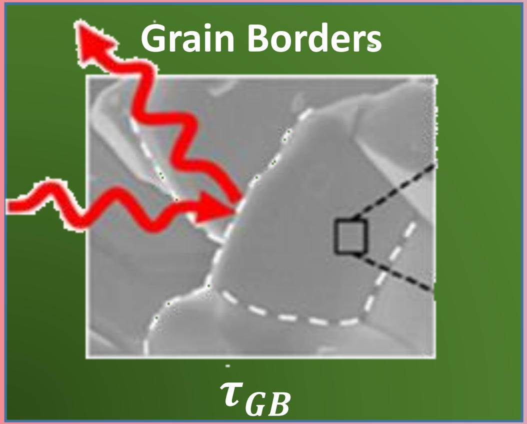
$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i}$$

# Extrinsic Scattering processes

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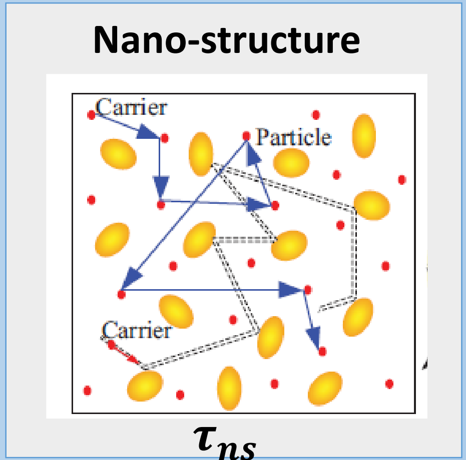
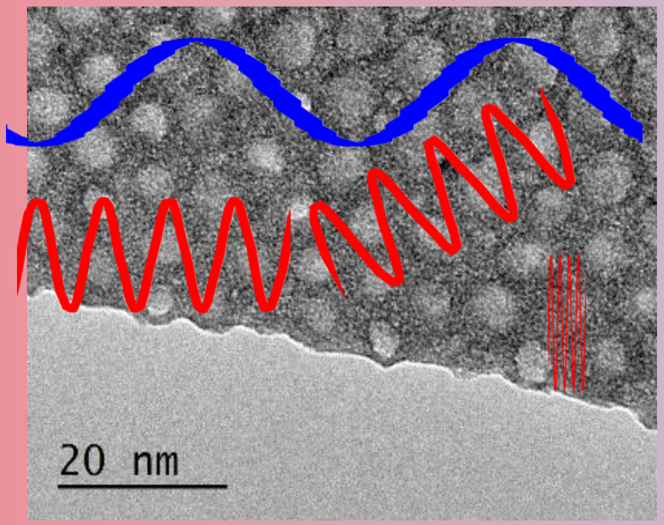


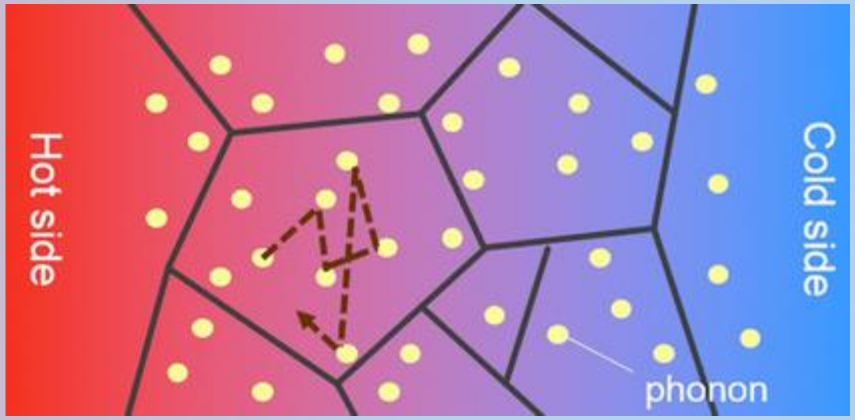

**A given scattering process will become important only at wavelengths such that the wave “sees” the obstacle, and energies such that the conservation of energy is respected**

# When nanostructuration is relevant ?




**When nanostructure matters ?**
Lengthscale vs phonon wavelength

Lengthscale vs phonons mean free path




**Nanostructure efficient for lengthscale < MFP and lengthscale ~phonon wavelength**

# Thermal transport: which phonons, which wavelength?

Phonon gaz internal energy in the Debye model: $\omega = v_s q, g(\omega) = \frac{3\omega^2}{2\pi^2 v_s^3}$

$$U = \sum_q (\hbar\omega_q) n(\hbar\omega_q) = 3\frac{a^3\hbar}{\pi^2 v_s^3}\int_0^{\omega_D} \boxed{\frac{\omega^3}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}} d\omega \rightarrow$$

Single phonon energy

# Thermal transport: which phonons, which wavelength?

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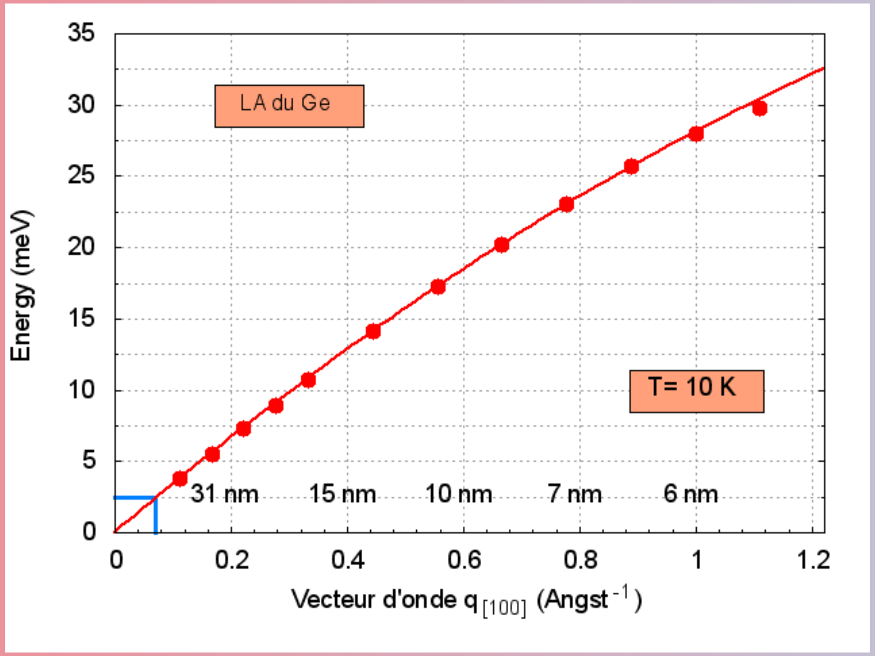
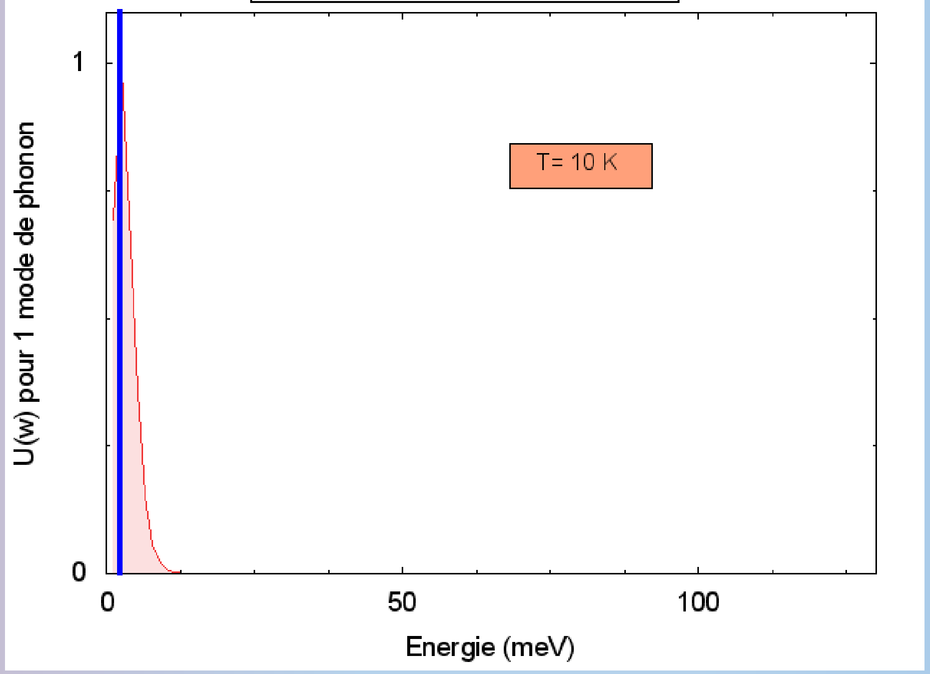
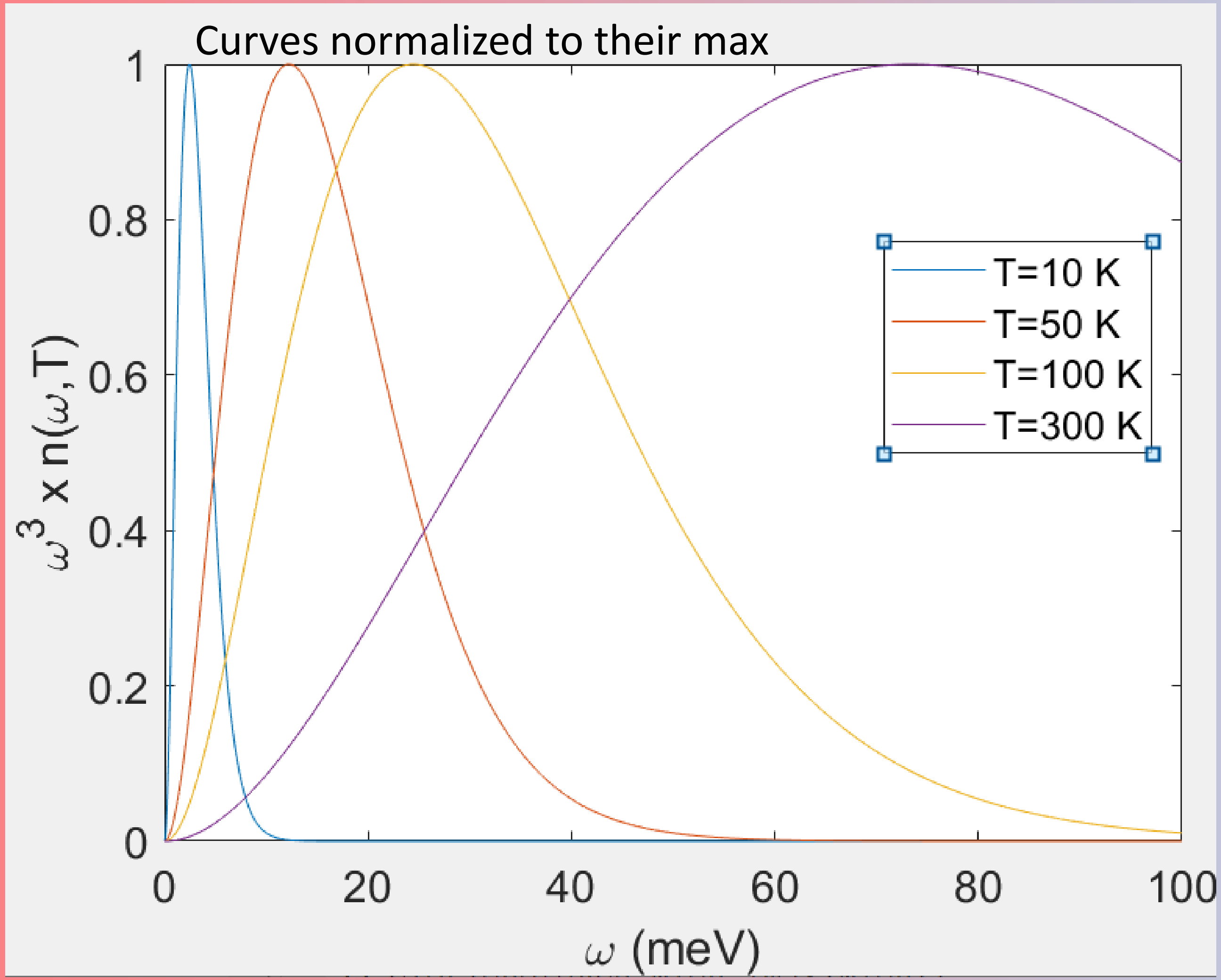
*1Thz=$10^3$GHz~4meV~48K*




The phonon energy distribution is peaked at higher and higher energies with temperature
All populated phonons participate to heat transport, but the major contribution at a given temperature comes from the center of mass of this distribution at that temperature

# The pertinent wavelength




Silicon: $v_L$=8945 m/s

T = 300 K
$\omega_{max} \sim 74\ meV$
$\lambda \sim 0.5$ nm

T = 10 K
$\omega_{max} \sim 2.5\ meV$
$\lambda \sim 15$ nm

T = 1 K
$\omega_{max} \sim 0.25\ meV$
$\lambda \sim 150$ nm

The lower the temperature, the larger the wavelength at which this distribution is centered

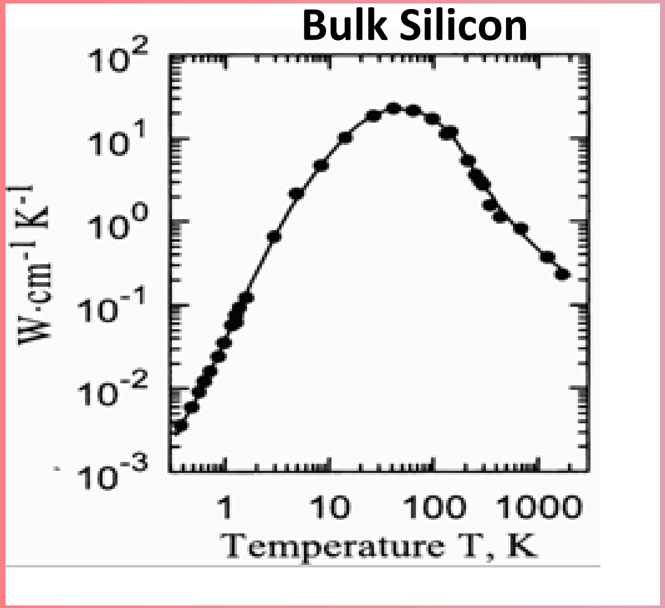
$$\lambda_{dom}(T) = \frac{h v_s}{2.82\ K_B T} \propto \frac{1}{T}$$

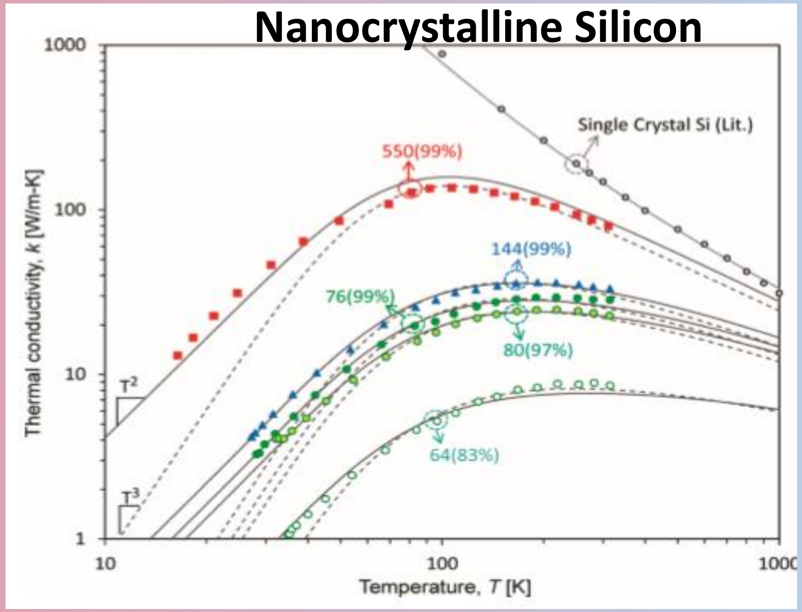
Depending on the application temperature, different phonons dominate heat transport

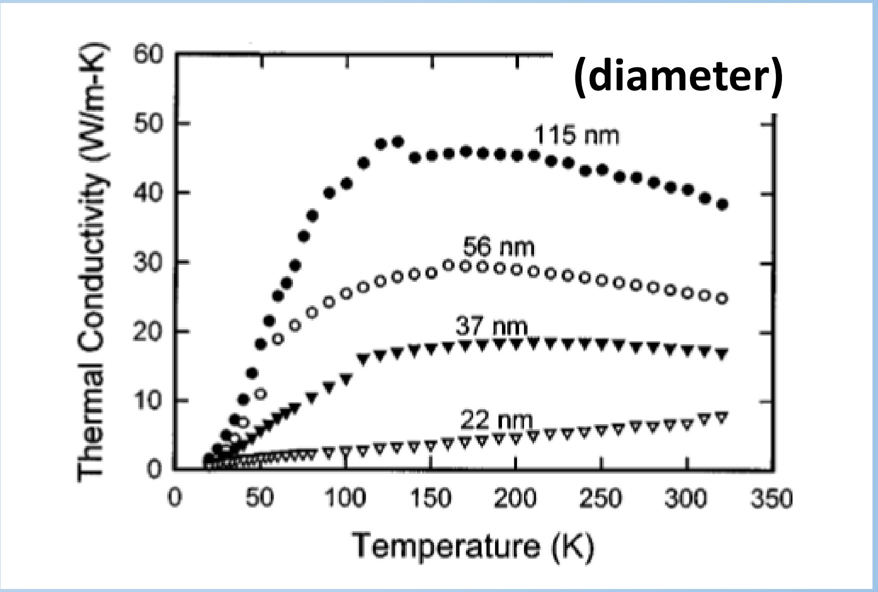
To control heat transport, the nanostructure needs to be adapted to the phonon wavelength pertinent for thermal transport at that temperature

Still, the nanostructure will be efficient only if smaller than the intrinsic mean free path

# Nano-scale thermal transport




*Nano Lett. 2011, 11, 2206–2213* *Appl. Phys. Lett., Vol. 83, 2934, 2003*

$$k_T = \frac{1}{3}\int c_v(\omega) v_g^2(\omega)\tau(\omega) g(\omega) d\omega$$

$\tau(\omega)$ depends on the sources of scattering: their relevance depends on phonon wavelength, temperature and lengthscale

$g(\omega)$ depends on the dimensionality

$\omega(q)$ is modified in nano-objects due to confinement, so are $c_v(\omega)$ *and* $v_g^2(\omega)$

# Mean free path and cumulative thermal conductivity

$$k_T = \frac{1}{3}\int C_v(\omega)v(\omega)\ell(\omega)g(\omega)d\omega$$

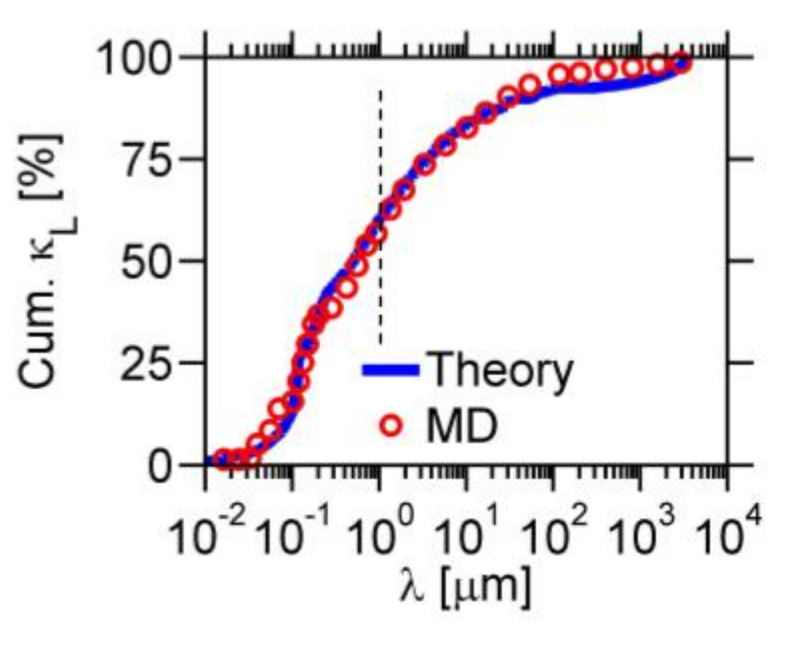
I use the mean free path as variable for integration

$$k_T = \int_0^{\infty} k_\lambda d\lambda_{ph}$$

$$k_\lambda = \frac{1}{3}C_v(\omega)v(\omega)\ell(\omega)g(\omega)\frac{d\omega}{d\lambda_{ph}}$$

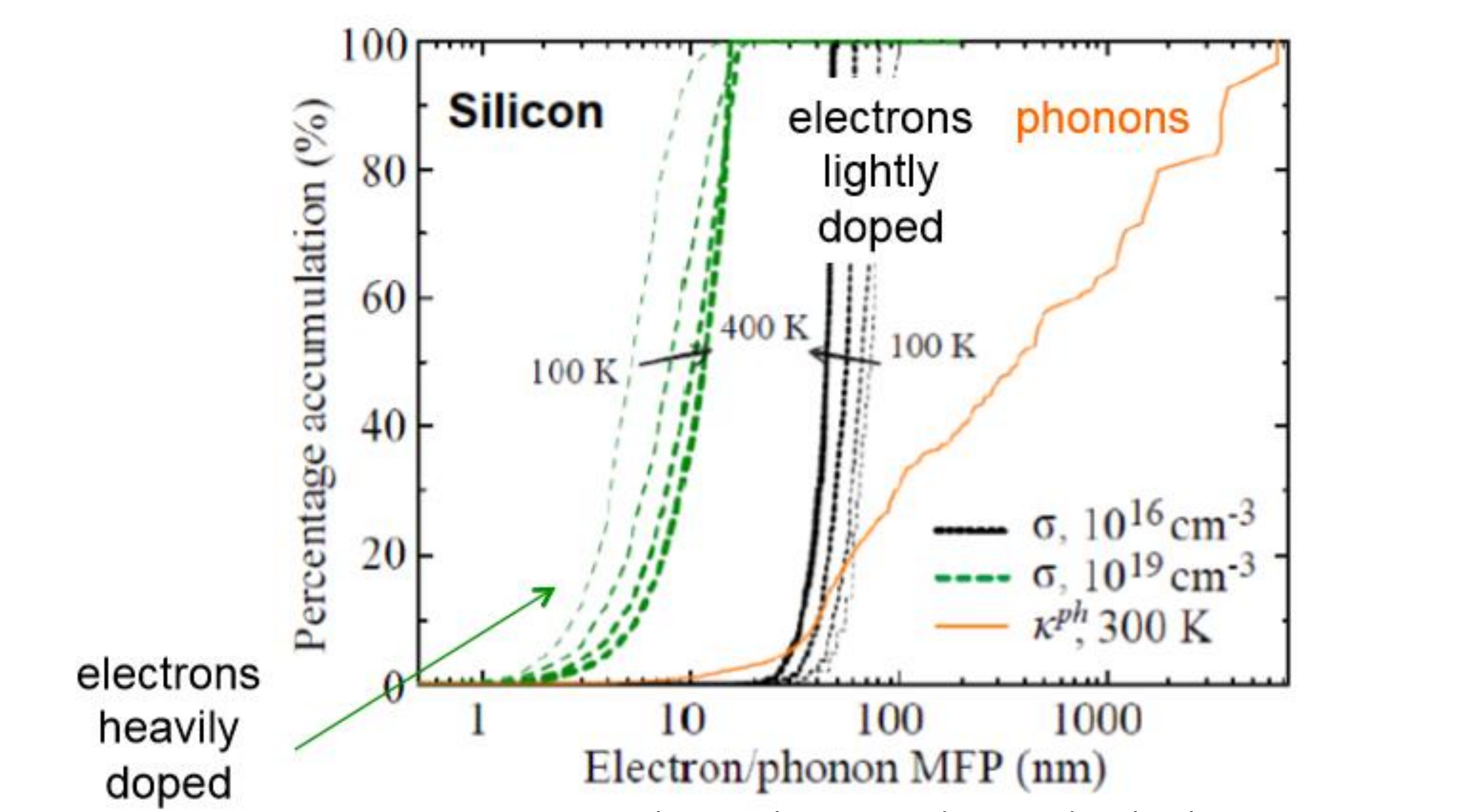
I define the cumulative thermal conductivity as a function of the mean free path:

$$k_T(\lambda_{ph}) = \frac{\int_0^{\lambda_{ph}} k_\lambda d\lambda_{ph}}{k_T}$$




MD: J. Comput. Theor. Nanosci. **5**, 141 (2008)

# The cumulative thermal conductivity




J. Zhou et al., Semicond. Sci. and Technol., 31, 043001, 2016

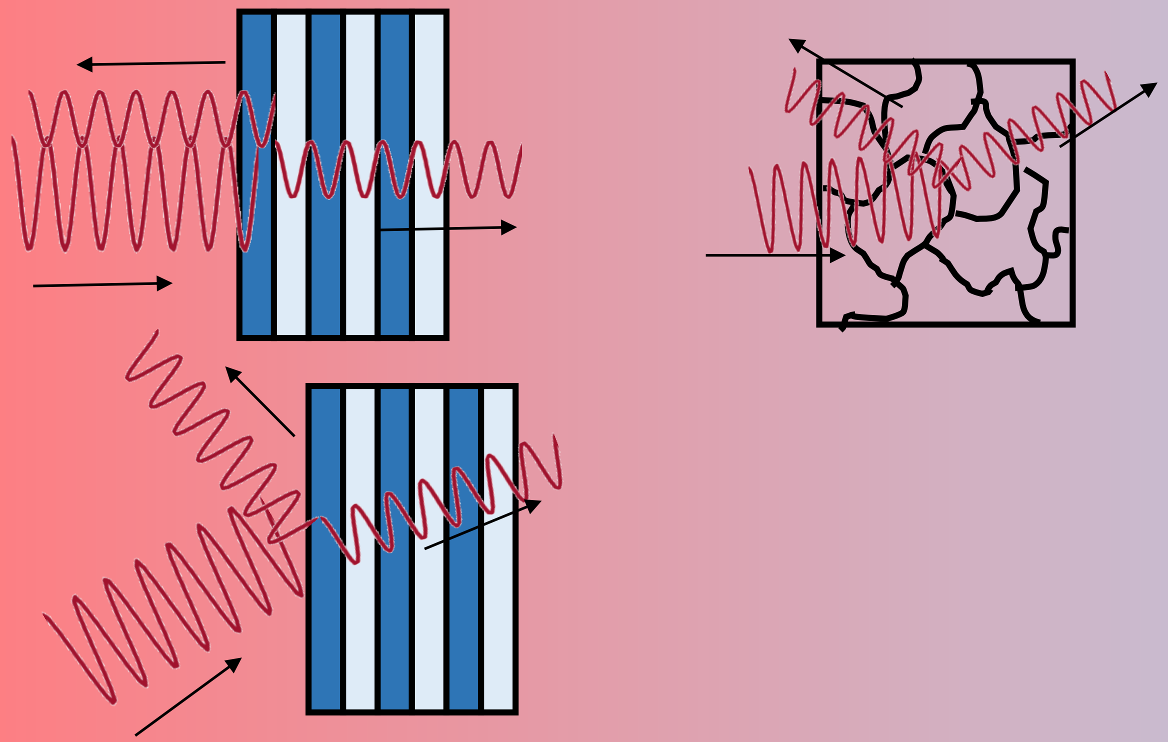
A much broader distribution of mfp with respect to electrons

It is clear that we can think of a nanostructuration impacting thermal but not electrical conductivity
That’s the key point for nanostructured thermoelectric materials

# Thermal transport in nanostructured materials

## Interfaces and Kapitza thermal resistance

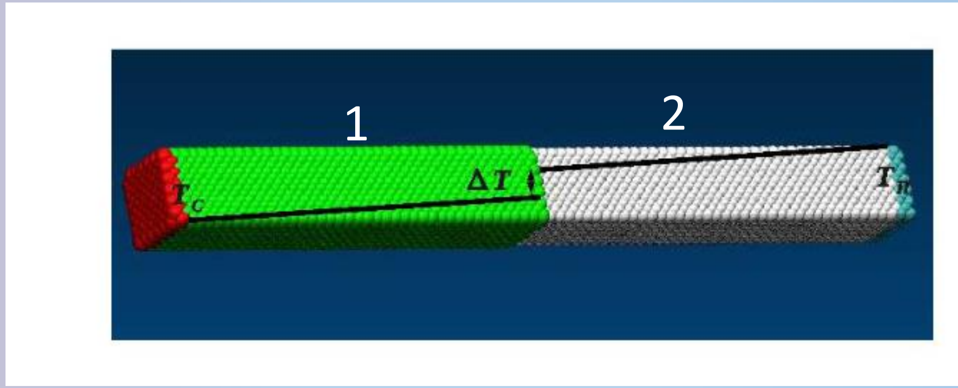
***Swartz, Reviews of Modern Physics, 61, (1989) p. 617-624***



Interfaces diffuse phonons: these are deviated or reduced in their transmission. As such, the presence of interfaces is very useful for hindering thermal transport

**Nanostructured materials (nanocomposites, Multilayers):** Phonons will go through interfaces, meeting a thermal resistance (Kapitza), which reduces thermal transport, depending on the contrast of acoustic properties between the materials

## Let's calculate the heat flux across a surface




The net heat flux across an interface per unit time from 1 to 2 is:

$$\frac{\dot{Q}_{1\rightarrow 2,net}}{S} = \frac{\dot{Q}_{1\rightarrow 2} - \dot{Q}_{2\rightarrow 1}}{S} = -k_B(T_2 - T_1)$$

The boundary thermal conductivity will thus be

$$k_B = \frac{\dot{Q}_{1\rightarrow 2} - \dot{Q}_{2\rightarrow 1}}{S(T_1 - T_2)}$$

If $T_2 = T_1$ , $\dot{Q}_{1\rightarrow 2,net} = 0 \rightarrow \dot{Q}_{1\rightarrow 2} = \dot{Q}_{2\rightarrow 1}$

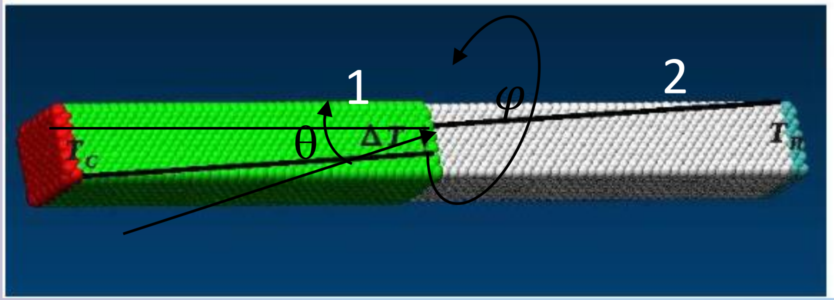
This means that in the general case I can always use one single direction in the flux calculation:

$$\dot{Q}_{1\rightarrow 2,net} = \dot{Q}_{1\rightarrow 2}(1 = T_1, 2 = T_2) - \dot{Q}_{1\rightarrow 2}(1 = T_2, 2 = T_1)$$

This is a great simplification

Let's calculate the flux: we need the energy contained in the unit volume touching the surface

The number of phonons with a given energy ω incident on the unit surface S per unit time and from a direction identified by θ and ϕ is:




*Component of the velocity perpendicular to the surface*

$$N = n(T_1)\mathrm{D}(\hbar\omega)\mathrm{S}\underbrace{\mathrm{v}\cos\theta}dt\,\underbrace{\frac{d\Omega}{4\pi}}$$

*solid angle element* $d\Omega = sin\theta d\theta d\varphi$*: I take from the total volume the portion in this little* $d\Omega$*:* $d\Omega/4\pi$

The gross heat current density from side 1 to side 2, is the **sum over all frequencies and incident angles** of this number times the phonon energy, times the transmission probability for each phonon

$$\frac{\dot{Q}_{1\to2}(1=T_1,2=T_2)}{S} = \frac{1}{4\pi}\sum_j \int_0^\infty \int_0^{\frac{\pi}{2}} \hbar\omega\, t_{1\to2}(\theta,j,\omega) n(T_1)\, D_j(\hbar\omega) v_j \cos\theta sin\theta d\theta\; d\omega \int_0^{2\pi} d\varphi =$$

$$=\frac{1}{2}\sum_j \int_0^\infty \int_0^{\frac{\pi}{2}} \hbar\omega\, t_{1\to2}(\theta,j,\omega) n(T_1)\, D_j(\hbar\omega) v_j \cos\theta sin\theta d\theta\; d\omega$$

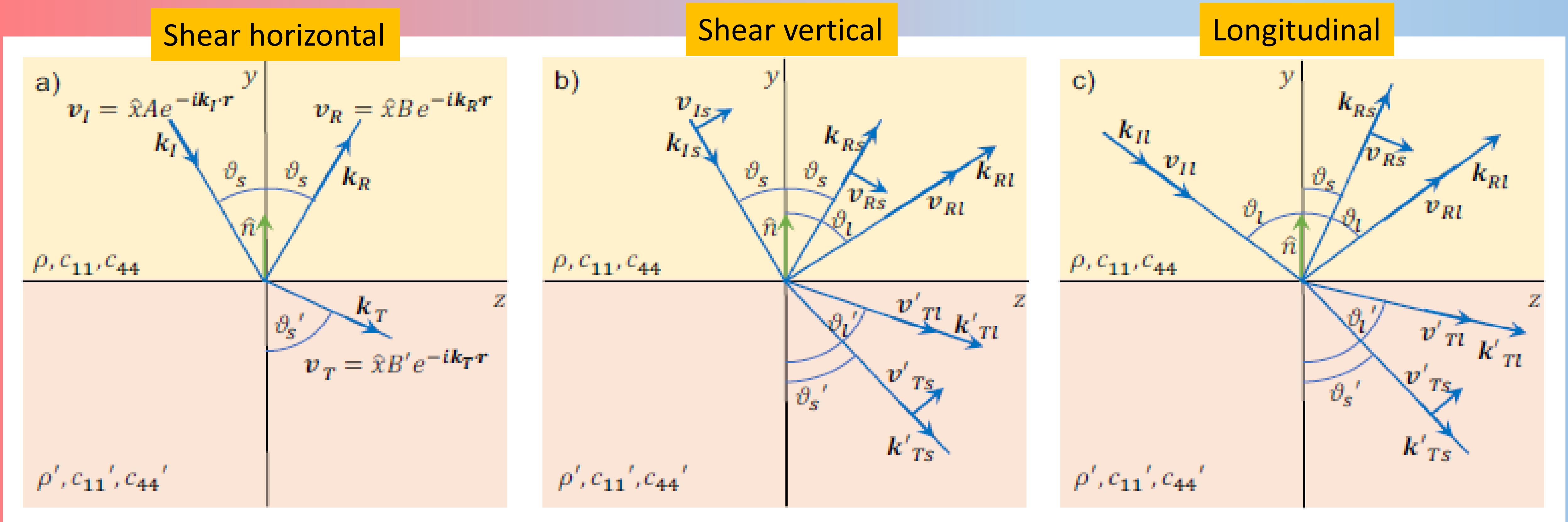
$D_j(\omega)$: density of states per unit volume and polarization,
$t_{1\to2}(\theta,j,\omega)$ transmission coeff depending on angle, polarization and energy

Now we « only » need an expression for the transmission coefficient

# Acoustic Mismatch Model (AMM)

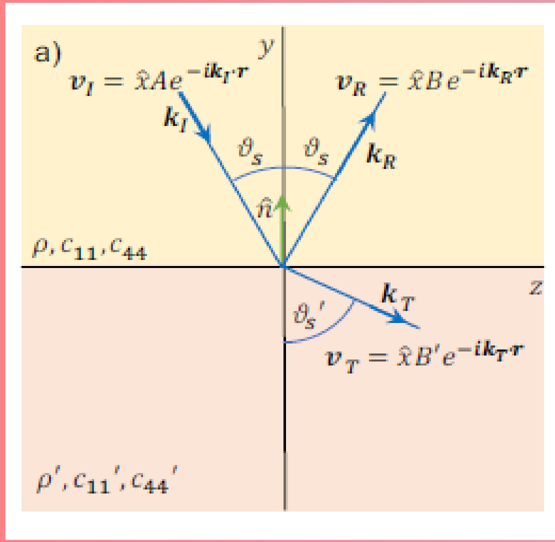
This model is based on continuum theory and reflection/transmission coefficients.

It holds for long wavelengths phonons and specular reflection/transmission




The transmission coefficients depend on angle, polarization and the acoustic impedence of the two media

# Example: Shear horizontal




Acoustic impedence

$$Z_s = \sqrt{\rho C_{44}} = \rho v_s$$

$$Z_s' = \sqrt{\rho' C_{44}'} = \rho' v'_s$$

$$\frac{\sin\theta_s}{\sin\theta_s'} = \frac{v_s}{v_s'}$$ Snell law $$\theta_s^{cr} = sin^{-1}\frac{v_s}{v_s'}$$

If $v_s < v_s$, *there exists a critical angle*

$$R = \frac{B}{A} = \frac{Z_s cos\theta_s - Z_s' cos\theta_s'}{Z_s cos\theta_s + Z_s' cos\theta_s'}$$ Reflection coefficient

$$T = \frac{B\prime}{A} = \frac{2Z_s cos\theta_s}{Z_s cos\theta_s + Z_s' cos\theta_s'}$$ Transmission coefficient

We can introduce the dependence of $\Gamma_s$ on phonon energy by using the phonon group velocity $v_s = \frac{\partial\omega}{\partial k}$

Only phonons impinging within the critical cone $\theta < \theta_s^{cr}$ have a chance to be transmitted

$$\dot{Q}_{1\to 2}(1 = T_1, 2 = T_2) - \dot{Q}_{1\to 2}(1 = T_2, 2 = T_1)$$

$$I = \frac{1}{2}\sum_j \int_0^\infty \int_0^{\frac{\pi}{2}} \hbar\omega\ t_{1\to 2}(\theta, j, \omega)(n(T_1) - n(T_2))\ D_j(\hbar\omega) v_j \cos\theta \sin\theta d\theta\ d\omega =$$

$$K_B = \frac{1}{2}\sum_j \int_0^\infty \int_0^{\frac{\pi}{2}} \hbar\omega\ t_{1\to 2}(\theta, j, \omega) \frac{\partial n}{\partial T} D_j(\hbar\omega) v_j \cos\theta \sin\theta d\theta\ d\omega$$

I define the average transmission coefficient $\Gamma_{1,j}(\omega) = \int_0^{\frac{\pi}{2}} t_{1\to 2}(\theta, j, \omega)\ \cos\theta \sin\theta d\theta$

$$\Longrightarrow\quad K_B = \frac{1}{2}\sum_j \int_0^\infty v_j \Gamma_{1,j}(\omega)\ \hbar\omega D_j(\hbar\omega)\ \frac{\partial n}{\partial T} d\omega$$

$$K_B = \frac{1}{2}\sum_j \int_0^\infty v_j \Gamma_{1,j}(\omega)\hbar\omega D_j(\hbar\omega)\ \frac{\partial n}{\partial T} d\omega$$

Let' use Debye (long wavelengths, low T)

$\omega = vk\ (v\ constant\ per\ polarization)\ ,\ thus\ also\ \Gamma_{1,j}$ constant

$$D_j(\omega) = \frac{\omega^2}{2\pi^2 {v_j}^3} \rightarrow D(\omega) = \sum_j \frac{\omega^2}{2\pi^2 {v_j}^3}$$

$$\omega_D = v\sqrt[3]{6\pi^2 n}$$

$$K_B = \frac{1}{2}\sum_j \int_0^{\omega_D} \hbar\omega\Gamma_{1,j} \frac{\omega^2}{2\pi^2 {v_j}^2}\ \frac{\partial n}{\partial T} d\omega$$

$$x = \frac{\hbar\omega}{K_B T}; \frac{\partial n}{\partial T} = -\frac{\partial n}{\partial x}\frac{x}{T}$$

$$d\omega = \frac{K_B T}{\hbar}\,\mathrm{dx}$$

$$K_B = \frac{1}{4\pi^2}\frac{K_B^4 T^3}{\hbar^3}\sum_j \frac{\Gamma_{1,j}}{{v_j}^2} \int_0^\infty (-x^4 \frac{\partial n}{\partial x})\ dx = \frac{4\pi^4}{15}$$

$$\Rightarrow \quad K_B = \frac{\pi^2}{15}\frac{K_B^4 T^3}{\hbar^3}\sum_j \frac{\Gamma_{1,j}}{{v_j}^2}$$

# AMM

$$\Gamma_{1,j}(\omega) = \int_0^{\frac{\pi}{2}} t_{1\rightarrow 2}(\theta, j, \omega)\ \cos\theta sin\theta d\theta$$

If the two media are identical, $t_{1\rightarrow 2} = 1$, $\Gamma_{1,j} = \frac{1}{2}$

$$K_B = \frac{\pi^2}{15}\frac{K_B^4 T^3}{\hbar^3}\sum_j \frac{\Gamma_{1,j}}{{v_j}^2}$$

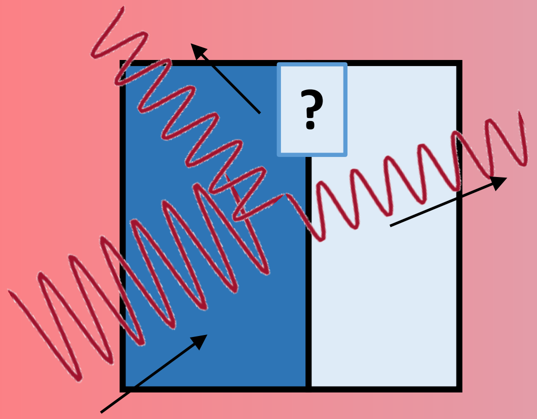
Goes as $T^3$, depends on the transmission coefficient $\Gamma_{1,j}$ from 1 to 2 and on velocities in medium 1

# Diffuse Mismatch Model (DMM)

Acoustic Mismatch Model: no scattering at the interface: perfect specularity

Diffuse Mismatch Model: all phonons are scattered at the interface: zero specularity

Assumption:
acoustic correlations at interfaces are assumed to be completely destroyed by diffuse scattering: no memory of incident direction and velocity is kept. Elastic scattering: only energy is conserved.




A phonon impinging on the interface will be completely absorbed. The re-emitted phonon will go to medium 1 or 2 with a certain probability, which will not depend on the incoming direction (medium and angle) but only on the availability of states with its energy in one medium (density of states) and the detailed balance.

By construction for two identical media $t_{1\to2}^{Diff} = 0.5$ vs $t_{1\to2}^{Acoust} = 1$

Assumption:
no memory of incident direction, phonon branch nor velocity is kept. Elastic scattering: only energy is conserved.

$$t_{1\to2}^{Diff}(\theta, j, \omega) = t_{1\to2}^{Diff}(\omega) = 1 - t_{2\to1}^{Diff}(\omega)$$

The number of phonons of energy $\hbar\omega$ per unit area per unit time leaving side 1 is

$$\frac{1}{4\pi}\sum_j \int_0^{\frac{\pi}{2}} \hbar\omega\, t_{1\to2}(\theta, j, \omega) n(T_1)\, D_j(\hbar\omega) v cos\theta sin\theta d\theta \int_0^{2\pi} d\varphi$$

I can already integrate angles, as there is no angular dependence in the integrand

$$\frac{1}{4\pi}\sum_j \int_0^{\frac{\pi}{2}} \hbar\omega\, t_{1\to2}(\theta, j, \omega) n(T_1)\, D_j(\hbar\omega) v cos\theta sin\theta d\theta \int_0^{2\pi} d\varphi = \frac{1}{4}\sum_j t(\omega) v_{j,1} \hbar\omega n(T_1) D_{j,1}(\hbar\omega)$$

For detailed balance, this must be equal to the number of phonons of energy $\hbar\omega$ per unit area per unit time leaving side 2

$$\frac{1}{4}\sum_j t(\omega) v_{j,1} \hbar\omega n(T_1) D_{j,1}(\hbar\omega) = \frac{1}{4}\sum_j (1 - t(\omega)) v_{j,2} \hbar\omega n(T_2) D_{j,2}(\hbar\omega) \quad \Rightarrow \quad t(\omega) = \frac{\sum_j v_{j,2} n(T_2) D_{j,2}(\hbar\omega)}{\sum_{a=1,2,j} v_{j,a} n(T_1) D_{j,a}(\hbar\omega)}$$

Let's write down the heat flow

$$\dot{Q}_{1\to 2}(1 = T_1, 2 = T_2) - \dot{Q}_{1\to 2}(1 = T_2, 2 = T_1)$$

$$I = \frac{1}{2}\sum_j \int_0^{\infty} \int_0^{\frac{\pi}{2}} \hbar\omega\, t_{1\to 2}(\theta, j, \omega) \frac{\partial n}{\partial T} D_j(\omega) v_{j,1} \cos\theta sin\theta d\theta\, d\omega =$$

$$K_B = \frac{1}{4}\sum_j \int_0^{\infty} d\omega \frac{\sum_j v_{j,2} n(T_2) D_{j,2}(\hbar\omega)}{\sum_{j,a=1,2} v_{j,a} n(T_1) D_{j,a}(\hbar\omega)}\; D_{j,1}(\hbar\omega) v_{j,1} \frac{\partial n}{\partial T} \hbar\omega$$

Using the same definition as for AMM, the average transmission coefficient will now be:

$$\Gamma_{1,j}(\omega) = \int_0^{\frac{\pi}{2}} t_{1\to 2}(\theta, j, \omega)\; \cos\theta sin\theta d\theta = \frac{1}{2}\; \frac{\sum_j v_{j,2} n(T_2) D_{j,2}(\hbar\omega)}{\sum_{j,a=1,2} v_{j,a} n(T_1) D_{j,a}(\hbar\omega)}$$

$$K_B = \frac{1}{4}\sum_j \int_0^\infty d\omega \frac{\sum_j v_{j,2} n(T_2) D_{j,2}(\hbar\omega)}{\sum_{j,a=1,2} v_{j,a} n(T_1) D_{j,a}(\hbar\omega)} \; D_{j,1}(\omega) v_{j,1} \frac{\partial n}{\partial T} \hbar\omega$$

$$\omega = vk \; (v \; constant \; per \; polarization)$$

$$D_j(\omega) = \frac{\omega^2}{2\pi^2 v_j{}^3}, \; \omega_D = v\sqrt[3]{6\pi^2 n}$$

Let's use Debye, and assume $T_1 \sim T_2$

$$\Gamma_{1,j}(\omega) = \frac{1}{2}\frac{\sum_j v_{j,2} n(T_2) D_{j,2}(\hbar\omega)}{\sum_{j,a=1,2} v_{j,a} n(T_1) D_{j,a}(\hbar\omega)} = \frac{1}{2}\frac{\sum_j v_{j,2} \frac{\omega^2}{2\pi^2 v_{j,2}^3}}{\sum_{j,a=1,2} v_{j,a} \frac{\omega^2}{2\pi^2 v_{j,a}^3}} \frac{n(T_2)}{n(T_1)} \sim \frac{1}{2}\frac{\sum_j v_{j,2}^{-2}}{\sum_{j,a=1,2} v_{j,a}^{-2}}$$

To calculate the boundary conductance, the passages are the same as for the acoustic mismatch model, we will have only to use the proper average transmission coefficient

$$x = \frac{\hbar\omega}{K_B T}; \frac{\partial n}{\partial T} = -\frac{\partial n}{\partial x}\frac{x}{T}$$

**AMM**

$$K_B = \frac{\pi^2}{15}\frac{K_B^4 T^3}{\hbar^2}\sum_j \frac{\Gamma_{1,j}}{v_{j,1}{}^2}$$

$\Rightarrow$

**DMM**

$$K_B = \frac{\pi^2}{15}\frac{K_B^4 T^3}{\hbar^2}\frac{1}{2}\frac{\sum_j v_{j,2}^{-2} \sum_j v_{j,1}^{-2}}{\sum_{j,a=1,2} v_{j,a}^{-2}}$$

Note that $\sum_j v_{j,1}^{-2}$ appears in the numerator from the integral of $D_{j,1}(\omega) v_{j,1}$

**AMM**

$$K_B = \frac{\pi^2}{15}\frac{K_B^4 T^3}{\hbar^2}\sum_j \frac{\Gamma_{1,j}}{{v_{j,1}}^2}$$

**DMM**

$$K_B = \frac{\pi^2}{15}\frac{K_B^4 T^3}{\hbar^2}\frac{1}{2}\frac{\sum_j v_{j,2}^{-2}\sum_j v_{j,1}^{-2}}{\sum_{j,a=1,2} v_{j,a}^{-2}}$$

Notes:

1) for higher T Debye breaks down and the exact phonon group velocities and density of states must be used
2) AMM depends on both mass density and phonon velocity ($t_{1\to2}$ depends on acoustic impedence)
3) DMM does not depend on mass density.
4) In both models I have $T^3$ dependence

For very similar media (similar acoustic impedences and velocities):

$$\Gamma_{1,j}(\omega) = \int_0^{\frac{\pi}{2}} t_{1\to2}(\theta, j, \omega)\ \cos\theta \sin\theta d\theta$$

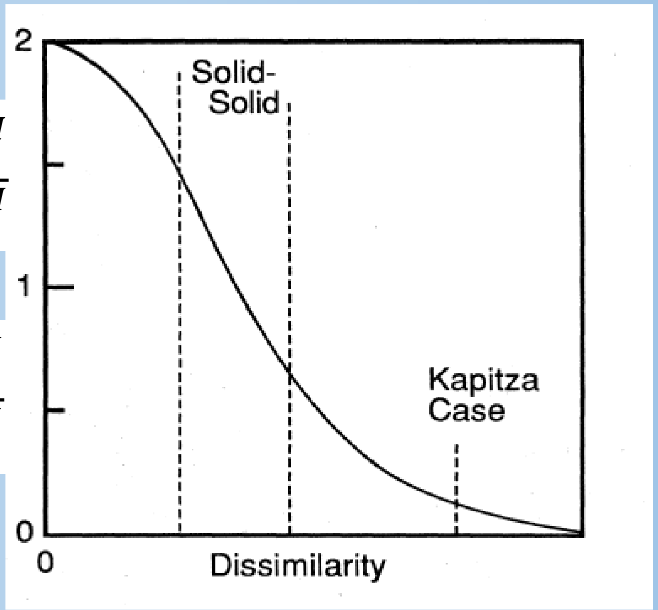
AMM: t=1 $\Gamma = \frac{1}{2}$

DMM: t=0.5 $\Gamma = \frac{1}{4}$

DMM predicts half thermal flux

$\frac{K_B^{AMM}}{K_B^{DMM}}$

$\frac{R_K^{DMM}}{R_K^{AMM}}$




**Kapitza resistance:** $R_K = \frac{1}{K_B}$

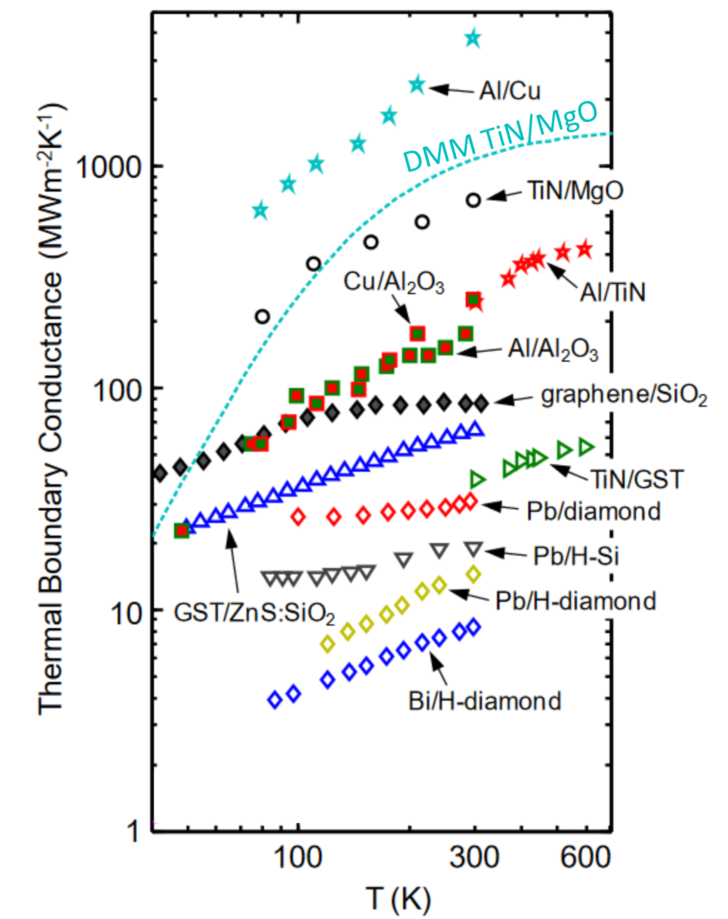
Decreases with $T^{-3}$ : more important at low T

CAVEAT

Both AMM and DMM completely disregard the effects of inelastic scattering and multiple phonon interactions.
For example, the models only allow for a phonon occupying a particular mode frequency to interact with another phonon occupying a mode of exactly the same frequency. In reality, this is not the case.

Neither model is very effective for predicting the thermal interface resistance (with the exception of very low temperature), but rather for most materials they act as upper and lower limits for real behavior.

# Some experimental values

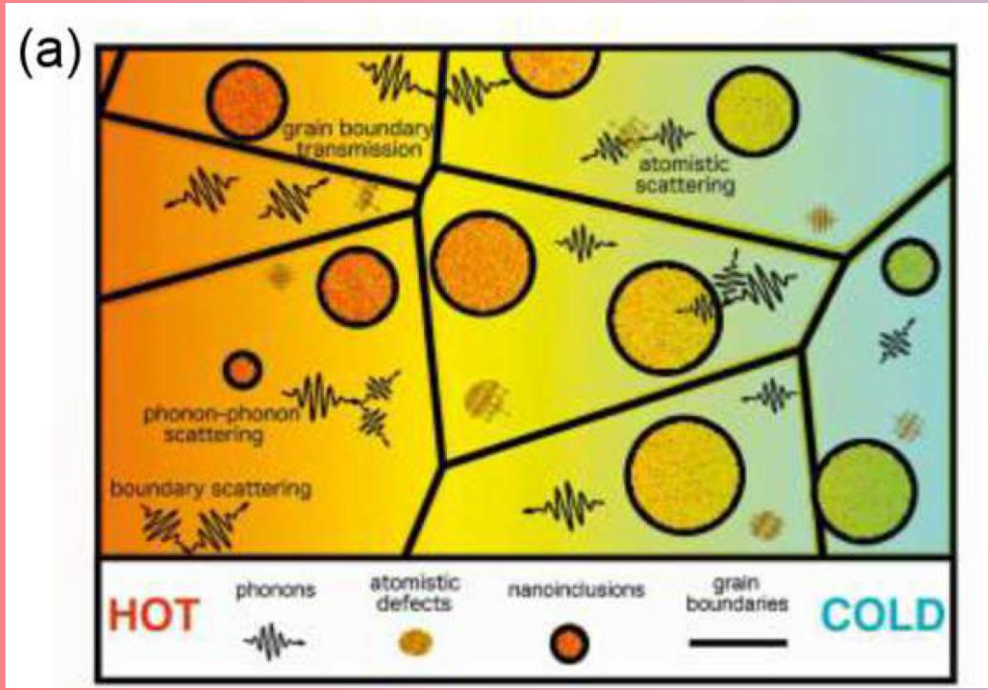



*E. Pop, Nano Research 3, 147 (2010)*

- Typical range: 1-1000 MW/m2K
- The highest known conductance is at good metal interfaces (Al/Cu) where electrons dominate the thermal exchange
- The lowest known conductance is between materials with highly mismatched phonon density of states and velocities (Bi/H-diamond)

G = 10 MW/m$^2$K is equivalent to the thermal impedance of a 140 nm film of SiO2 (k = 1.4 W/mK)
G = 100 MW/m$^2$K is equivalent to 14 nm of SiO2.
This comparison highlights the importance of interfaces in all nanometer scale devices and structures

# Hierarchical nanostructuration for thermoelectric applications

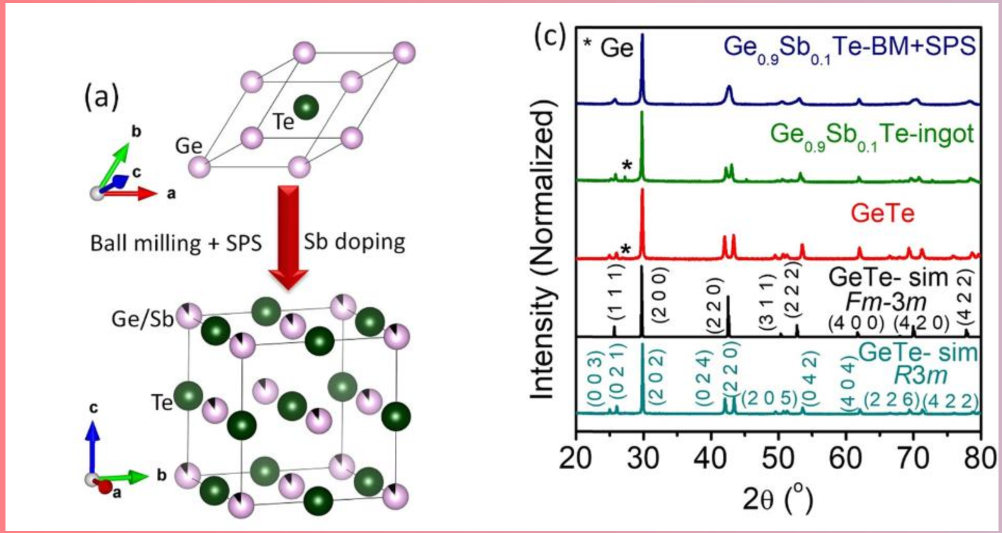



*N. Neophytou, Eur. Phys. J. B (2020) 93: 213*

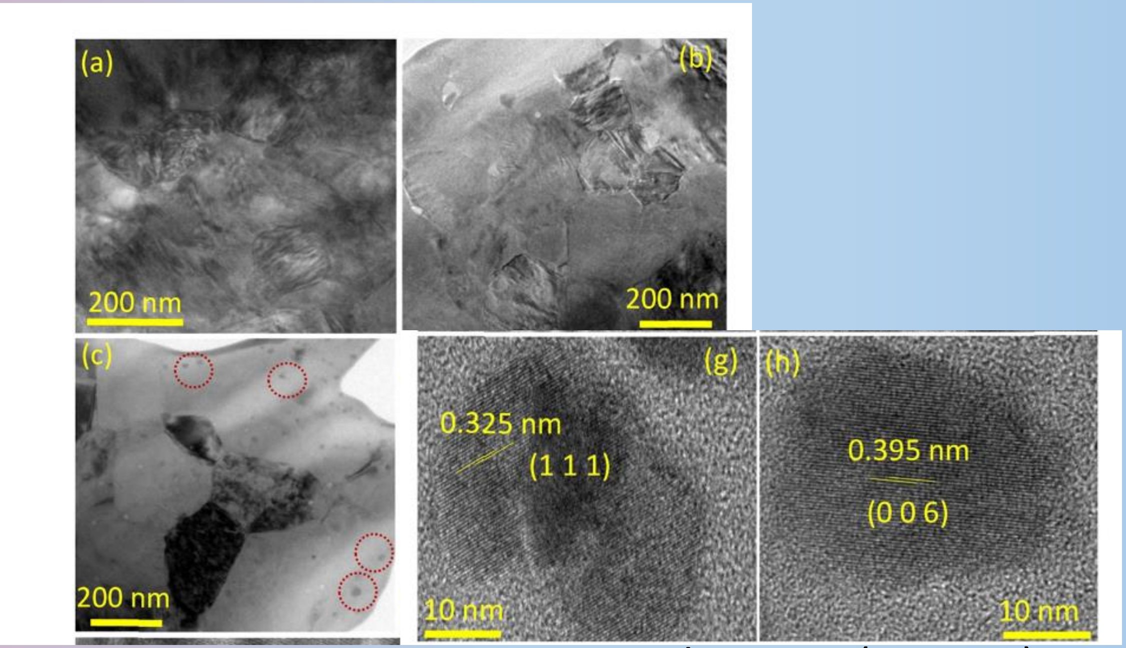
Phonon scattering in a large wavelength range:
Defect scattering (Angstrom)
Scattering from inclusions (nanoscale)
Scattering from grain boundaries (mesoscale)

# Example: hierarchical nanostructuration in GeTe

10 mol% Sb-doped GeTe upon ball-milling (BM) followed by spark plasma sintering (SPS)

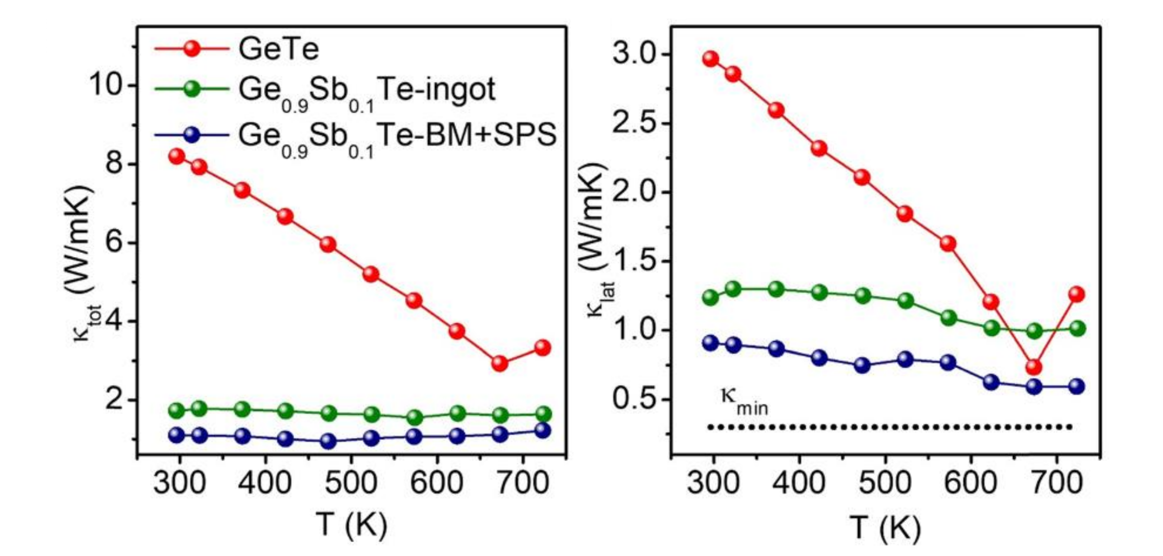



Mesoscale grains (80-200nm)




Nanoscale grains (5-20nm)

Strong thermal conductivity reduction

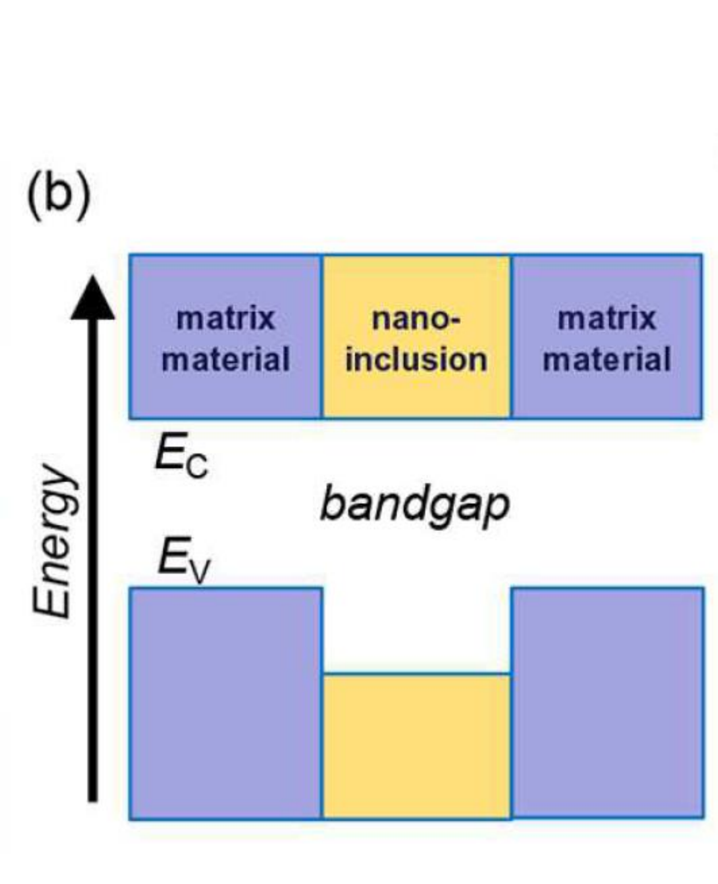



Quid of the Power Factor?



*D. Sarkar, Energy Environ. Sci., 15, 4625 (2022)*

# Nanostructuration and power factor




Inclusions/grain boundaries:
formation of potential barriers: this increases electrical resistivity

The goal is to have nanoinclusions or grain boundaries for which the band edge discontinuity is as small as possible, or even zero (see figure), such that the majority electrons (or holes) experience as little resistance to their path as possible.

A compromise is needed for a nanostructuration dense enough to affect phonons, but with the least possible effect on electrons.
In this way, we can benefit from the reduction of the thermal conductivity with minimal penalty in the electrical conductivity.

*N. Neophytou, Eur. Phys. J. B (2020) 93: 213*

# Energy filtering

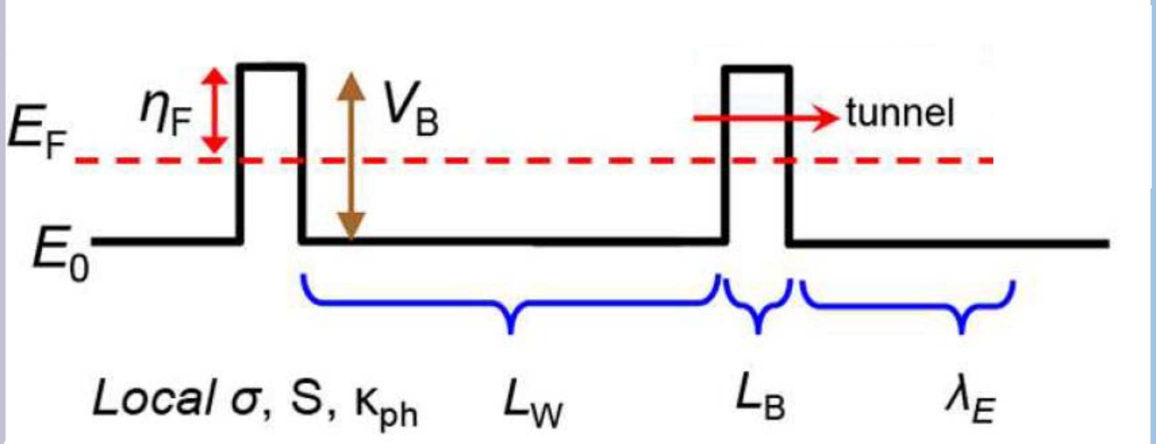
Potential barriers can block the low energy, cold carriers and let through only the high energy, hot ones, producing an energy filtering.

$$S \propto \frac{< E > - E_F}{T}$$

$< E >$= average energy of the current flow. If cold carriers are blocked, $< E >$ will increase

The barrier needs to be not too thin otherwise low energy carriers could tunnel and reduce the effect of the energy filtering

Next to the barrier, a carrier can absorb an optic phonon and gain energy to overcome the barrier And then release energy emitting an optic phonon. As such after the barrier, it will have a higher energy than in equilibrium conditions, and will loose it within 20-30 nm usually ( a few inelastic electron mean free paths). The Seebeck will result increased thanks to this higher energy in a region with high conductivity → large PF

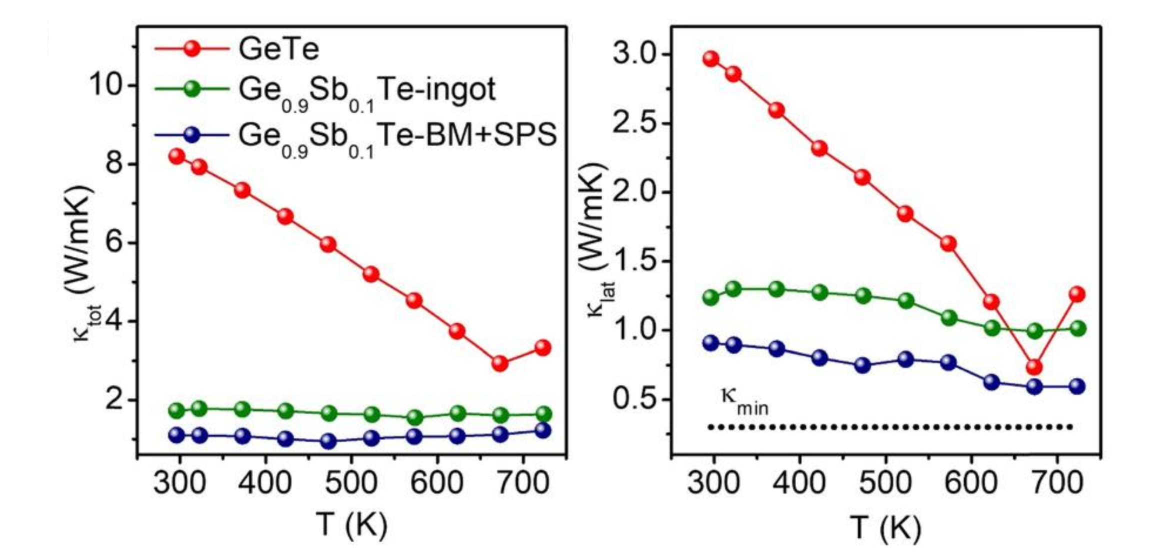


The engineering of the potential barriers is even more complex than this and other phenomena can appear and need to be taken into account

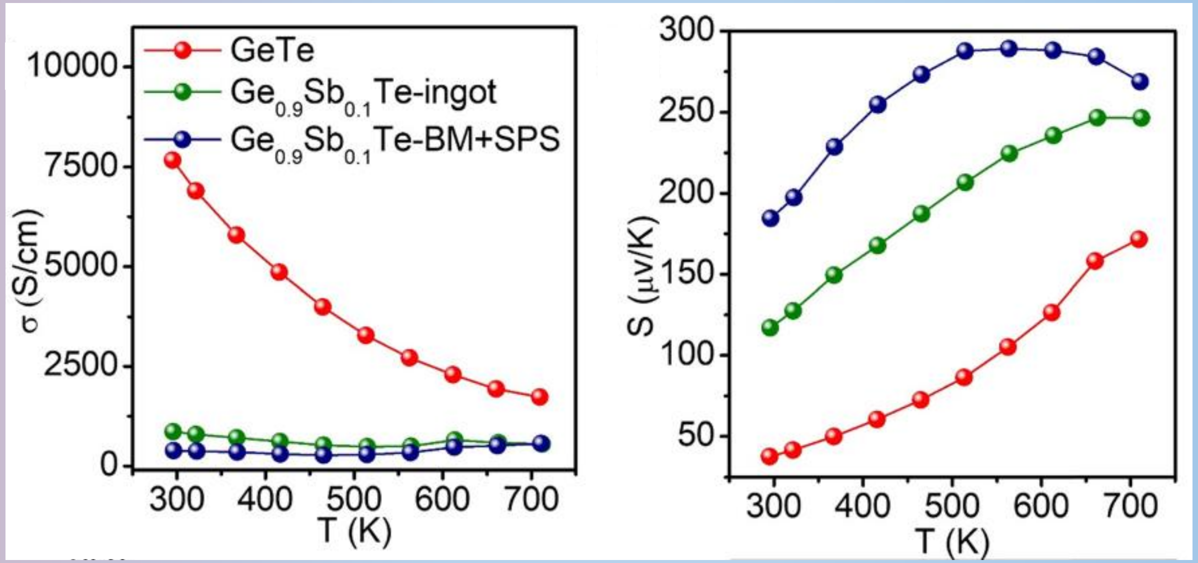
Generally speaking, nanostructuration is meant to reduce thermal transport with the smallest possible effect on power factor. It's rare than this latter is improved. Normally, even with an improvement in the Seebeck, the electrical conductivity reduction compensates it so that the power factor remains almost constant.

# Back to our example: hierarchical nanostructuration in GeTe

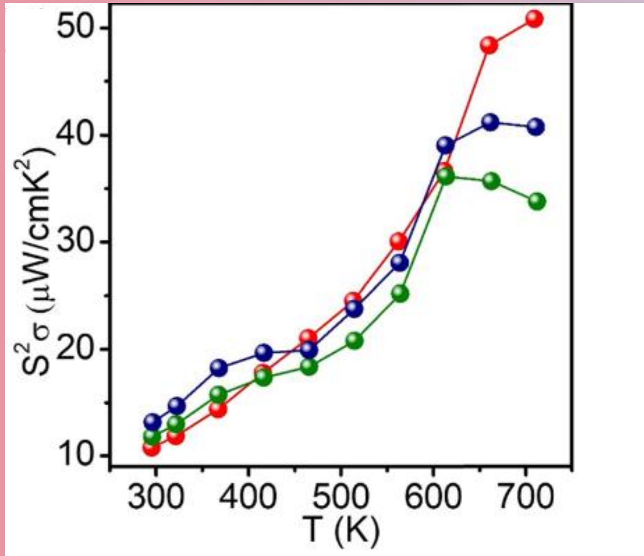
Strong thermal conductivity reduction



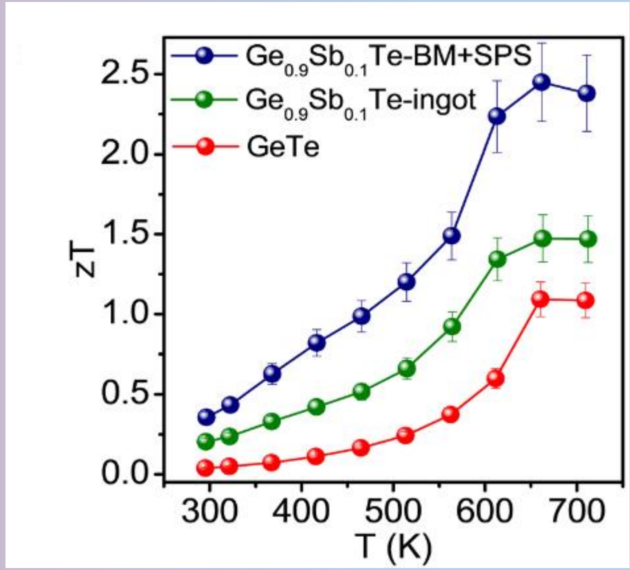

Strong electrical conductivity reduction but Seebeck improvement




Almost no effect on power factor




2-fold ZT improvement

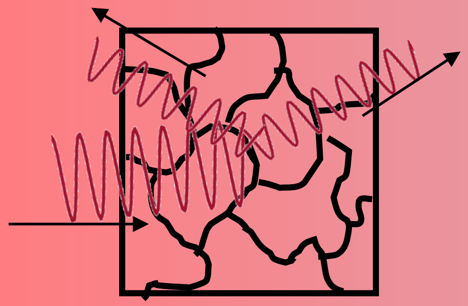


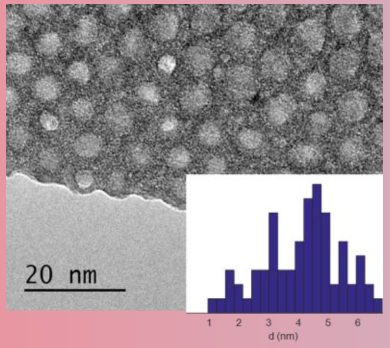



*D. Sarkar, Energy Environ. Sci., 15, 4625 (2022)*

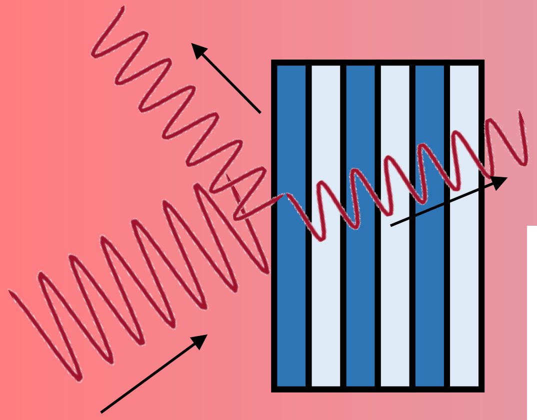
# Phononic Crystals

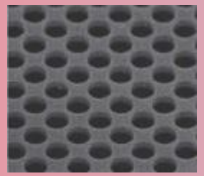
Confined material: boundary conditions for long wavelength waves

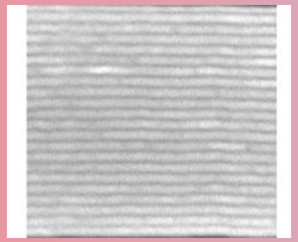





Composite material: transmission coefficients at interfaces affect wave propagation







Periodic composite materials?

We expect scattering from interfaces and possible coherent reconstruction of scattered waves such as in confined materials: new boundary conditions

Phononic materials

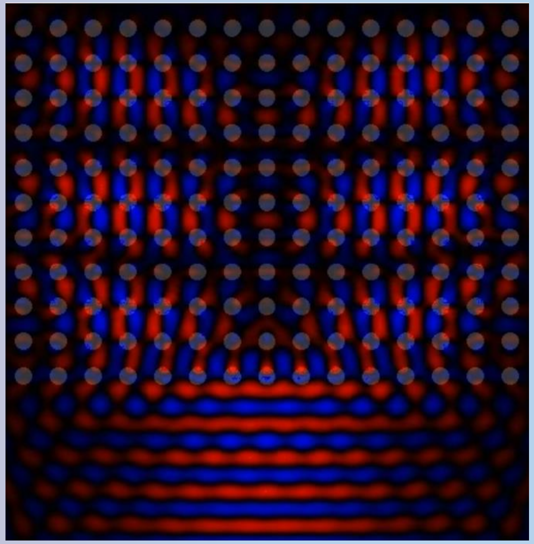
# Phononic crystals for acoustic applications

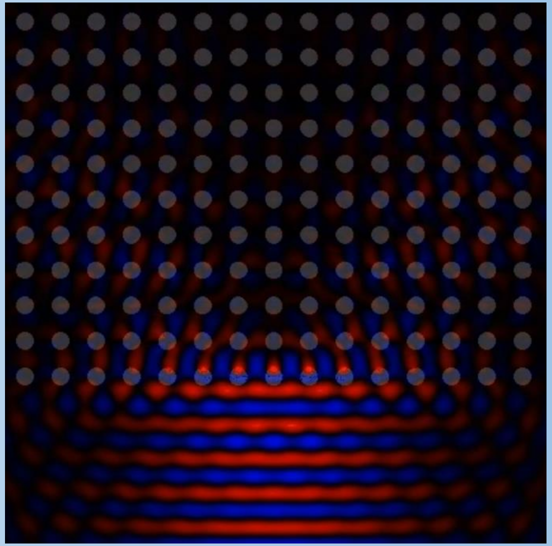
## The inspiration: photonic crystals

Photonic crystals have been studied in one form or another since 1887, but no one used the term *photonic crystal* until over 100 years later

Photonic crystals are composed of periodic dielectric microstructures that affect electromagnetic wave propagation in the same way that the periodic potential in a crystal affects electrons, defining allowed and forbidden electronic energy bands.

https://en.wikipedia.org/wiki/Photonic_crystal

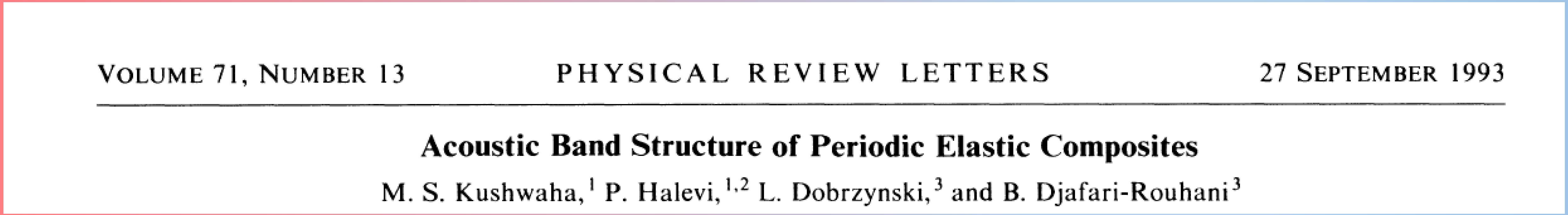




Depending on the refraction index contrast and the wavelength the wave can or cannot go through

# Can we do the same for elastic waves?

The question arose in the 90s. One of the first studies:


VOLUME 71, NUMBER 13 PHYSICAL REVIEW LETTERS 27 SEPTEMBER 1993

**Acoustic Band Structure of Periodic Elastic Composites**

M. S. Kushwaha,[1] P. Halevi,[1,2] L. Dobrzynski,[3] and B. Djafari-Rouhani[3]

From electrons to optics to acoustics

Forbidden gaps: acoustic filters

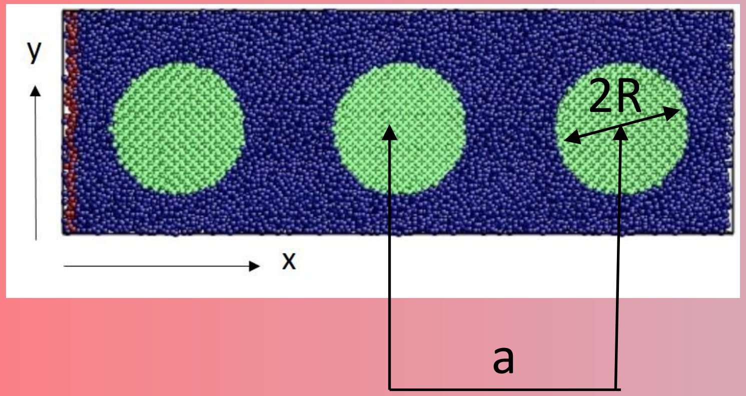
Only few propagation directions: acoustic guides

Phonon localization

# From electrons to optics to acoustics

TABLE I. Band-structure-related properties of three periodic systems.

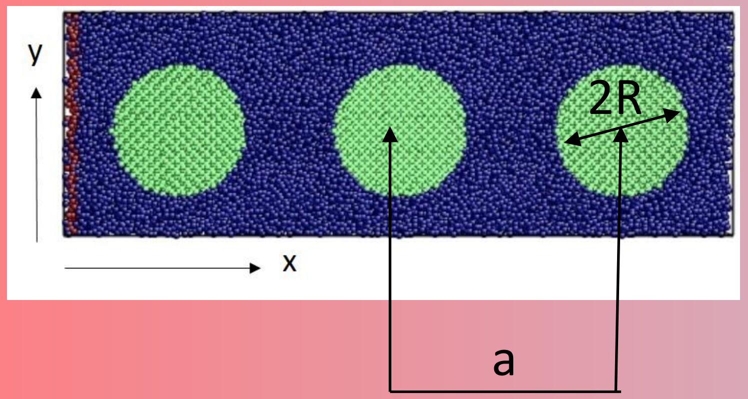
| Property | "Electronic" crystal | "Photonic" crystal | "Phononic" crystal |
|---|---|---|---|
| Materials | Crystalline (natural or grown) | Constructed of two dielectric materials | Constructed of two elastic materials |
| Parameters | Universal constants, atomic numbers | Dielectric constants of constituents | Mass densities, sound speeds $c_l, c_t$ of constituents |
| Lattice constant | 1–5 Å (microscopic) | 0.1 $\mu$m–1 cm (mesoscopic or macroscopic) | Mesoscopic or macroscopic |
| Waves | de Broglie (electrons) $\psi$ | Electromagnetic or light (photons) $\mathbf{E}, \mathbf{B}$ | Vibrational or sound (phonons) $\mathbf{u}$ |
| Polarization | Spin $\uparrow, \downarrow$ | Transverse: $\nabla \cdot \mathbf{D} = 0$ ($\nabla \cdot \mathbf{E} \neq 0$) | Coupled trans.-longit. ($\nabla \cdot \mathbf{u} \neq 0, \nabla \times \mathbf{u} \neq 0$) |
| Band gap | Increases with crystal potential; no electron states | Increases with $\|\epsilon_a - \epsilon_b\|$; no photons, no light | Increases with $\|\rho_a - \rho_b\|$, etc. no vibration, no sound |
| Spectral region | Radio wave, microwave, optical, x ray | Microwave, optical | $\omega \lesssim 1$ GHz |




Case 2D: matrix wih periodically embedded infinitely long cylinders with axis // z

Symmetry breaking: polarization //z will behave differently than polarizations //x and //y

What does it change in the equations of motion?



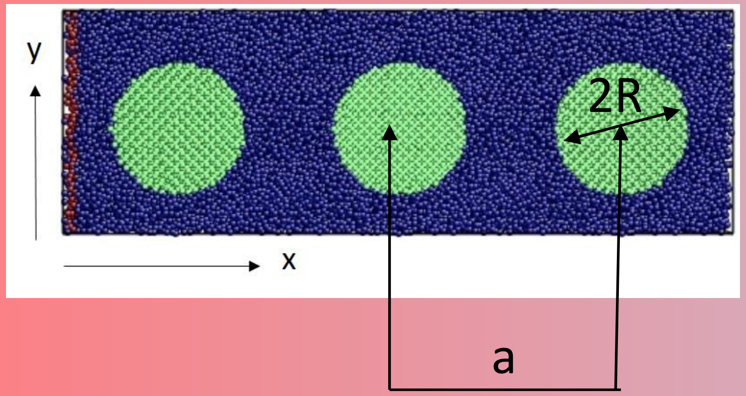

Case 2D: matrix wih periodically embedded infinitely long cylinders with axis // z

Symmetry breaking: polarization //z will behave differently than polarizations //x and //y

What does it change in the equations of motion?

1) Inhomogeneity of density and elastic constants
2) Additional periodicity

Which parameters will play a role?




Case 2D: matrix wih periodically embedded infinitely long cylinders with axis // z

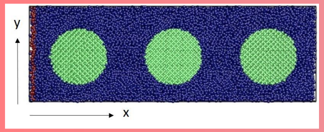
Symmetry breaking: polarization //z will behave differently than polarizations //x and //y

What does it change in the equations of motion?

1) Inhomogeneity of density and elastic constants
2) Additional periodicity

Which parameters will play a role?

1) Periodicity a
2) geometry. Definition of filling fraction $f = \frac{\pi R^2}{a^2}$
3) Acoustic impedences (contrast)



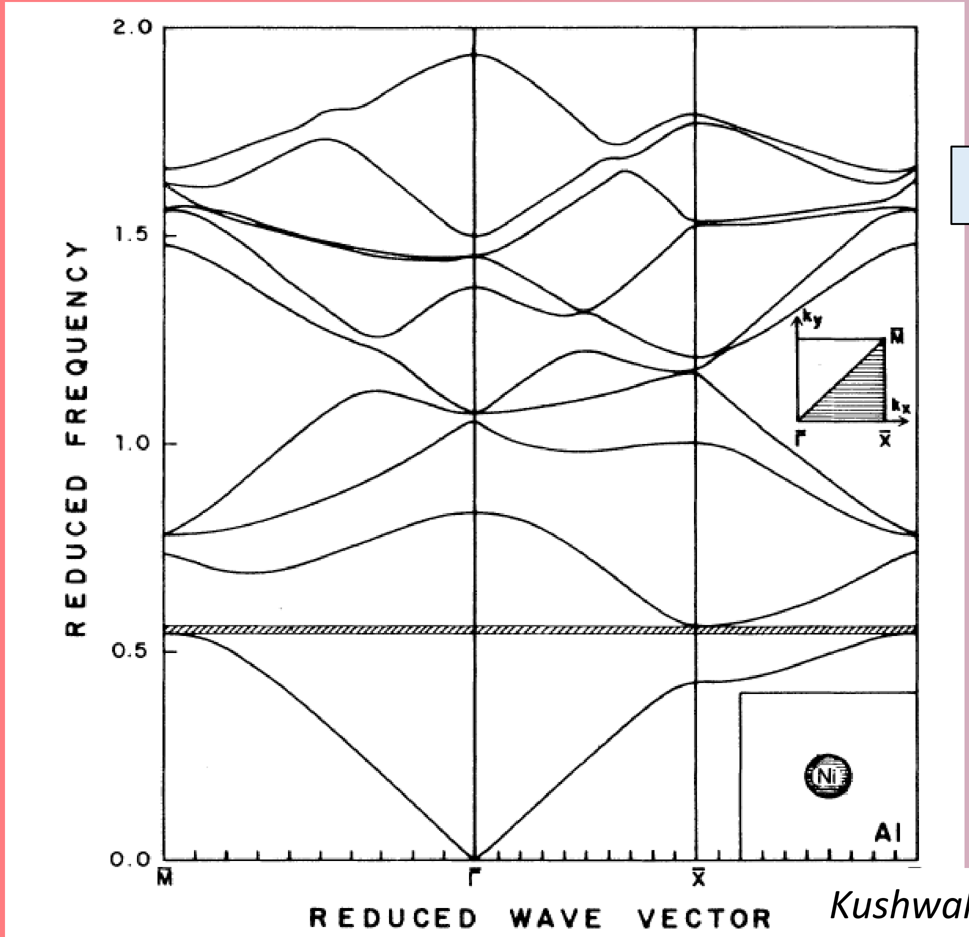

Nickel in Aluminium: hard in soft
Filling fraction f=0.1

Calculation for a transverse mode with z-polarization//cylinders

| | Ni | Al |
|---|---|---|
| ρ (g/cm3) | 8.936 | 2.697 |
| $v_T$ (m/s) | 3000 | 3040 |
| Z | 26808 | 8004 |

Aluminiun in Nickel : soft in hard
Filling fraction f=0.75

Calculation for a transverse mode with z-polarization//cylinders

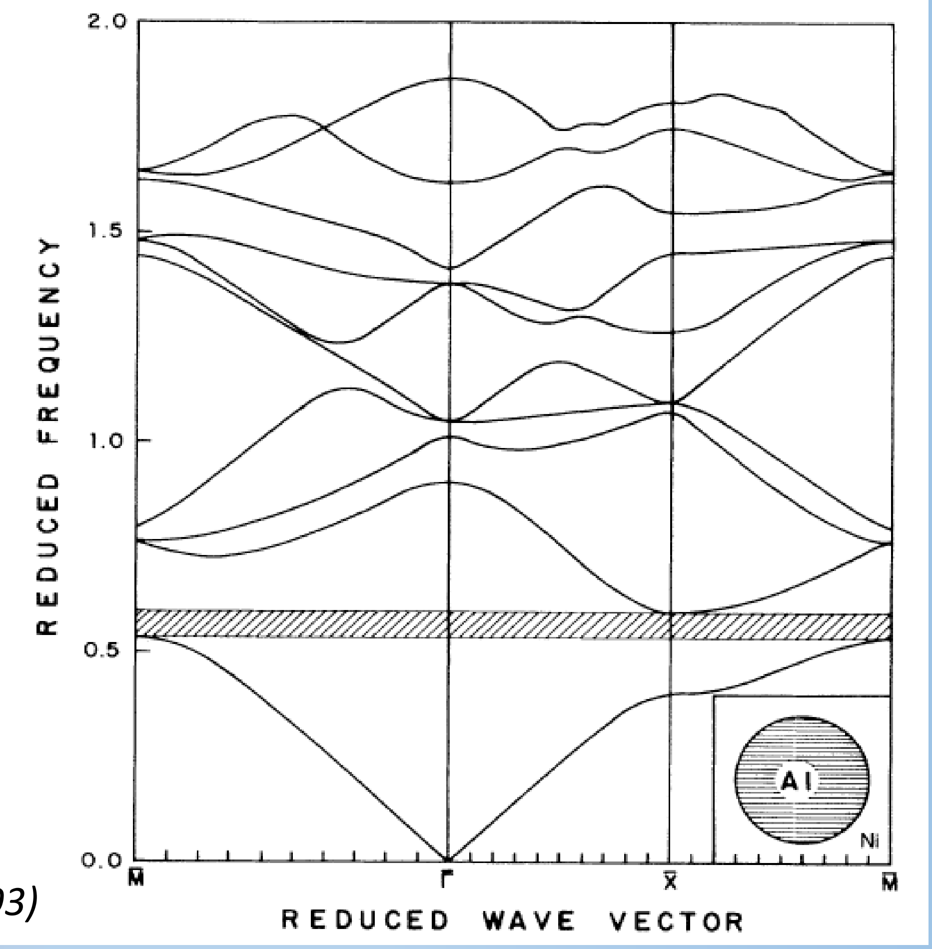



$$\omega_{red} = \frac{\omega a}{2\pi v_m}$$

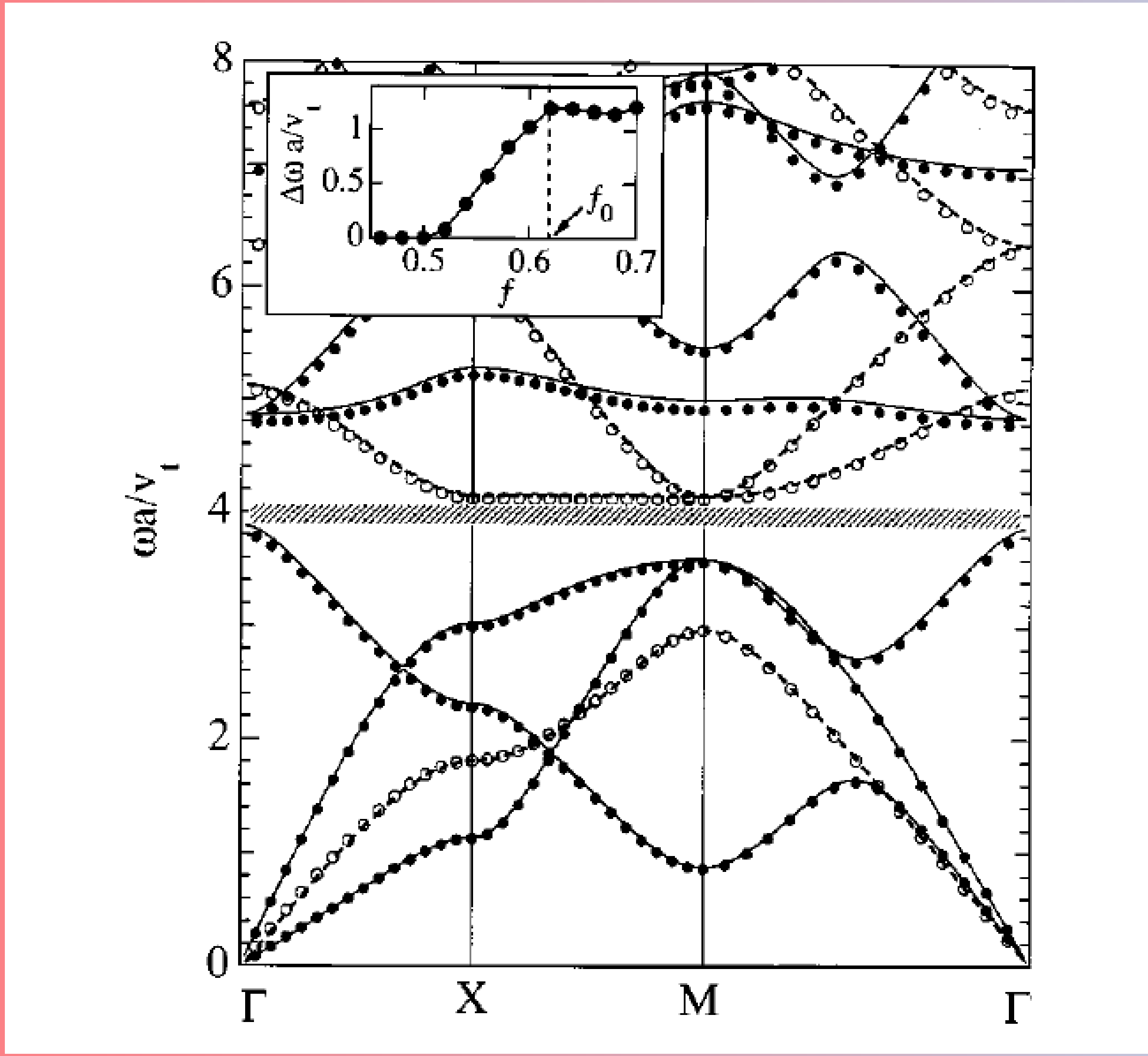
$v_m$=velocity of the matrix

$$k_{red} = \frac{ka}{2\pi}$$

Forbidden band gap




*Kushwaha et al., Phys. Rev. Lett. 71, 2022 (1993)*




Empty pores in Al : extreme soft in hard f=0.55

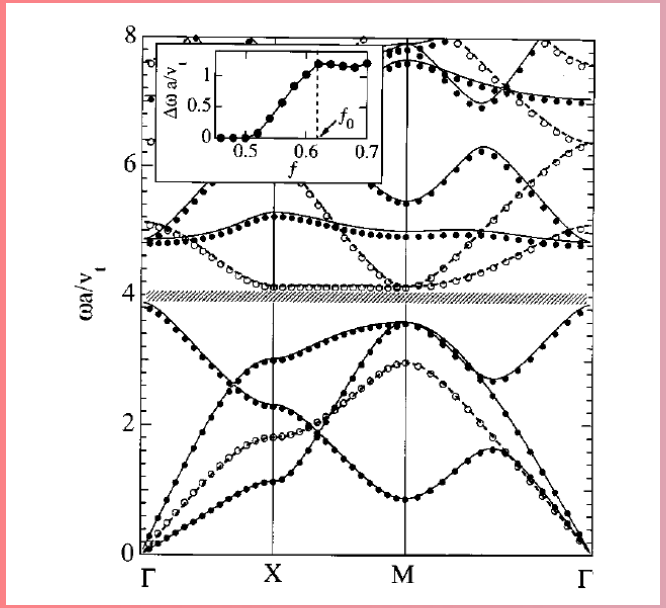
L+T (x,y) polarization: dots
T (z) polarization: circles

| | PE | Al |
|---|---|---|
| ρ (g/cm3) | 0 | 2.697 |
| $v_T$ (m/s) | 0 | 3040 |
| Z | 0 | 8004 |

A full-gap opens and its width increases with the filling factor

*Tanaka et al., Phys. Rev. B 62, 7387 (2000)*

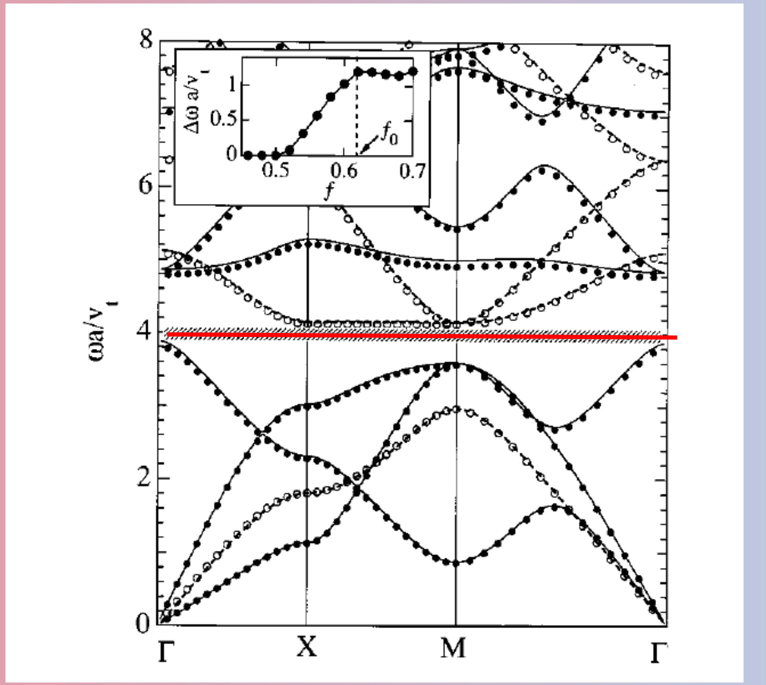
# Dispersions modifications and applications




Full gap:
No acoustic wave can propagate in that frequency range, independent on polarization and propagation direction

⇩

Acoustic barrier/ shield




If I have local resonances, flat modes, and one within the gap: That frequency can propagate in all directions.
It can be nicely isolated

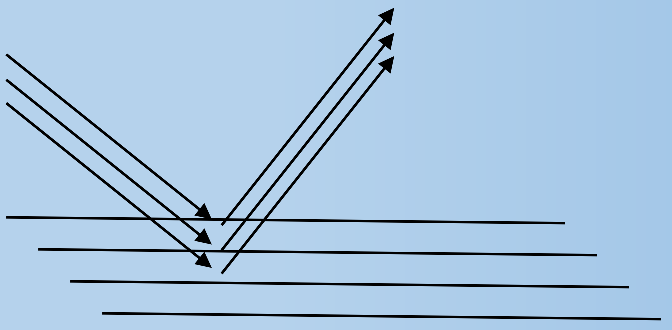
⇩

Acoustic selector, filter

# Phononic Crystals and coherence

The modification of dispersions, the appearance of band gaps, of localization are a consequence of Bragg diffraction on the inclusions, or perfect specularity

Only wavelengths long enough to act coherently are affected

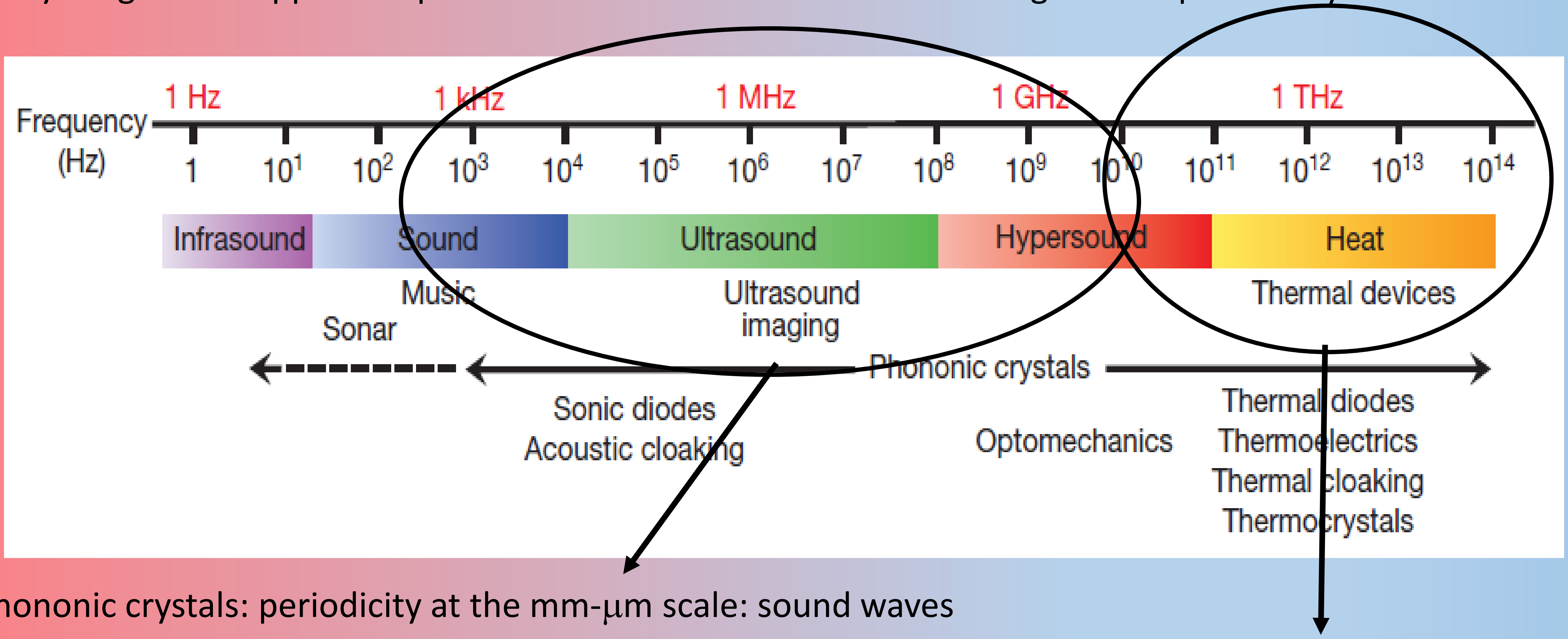


2 key parameters:

1) Periodicity P to select the affected wavelenght range $\lambda \sim P$
2) Roughness $\eta$ to select the wavelengths for which there is specularity $\lambda \gg \eta$

# From Phononic to Nanophononic

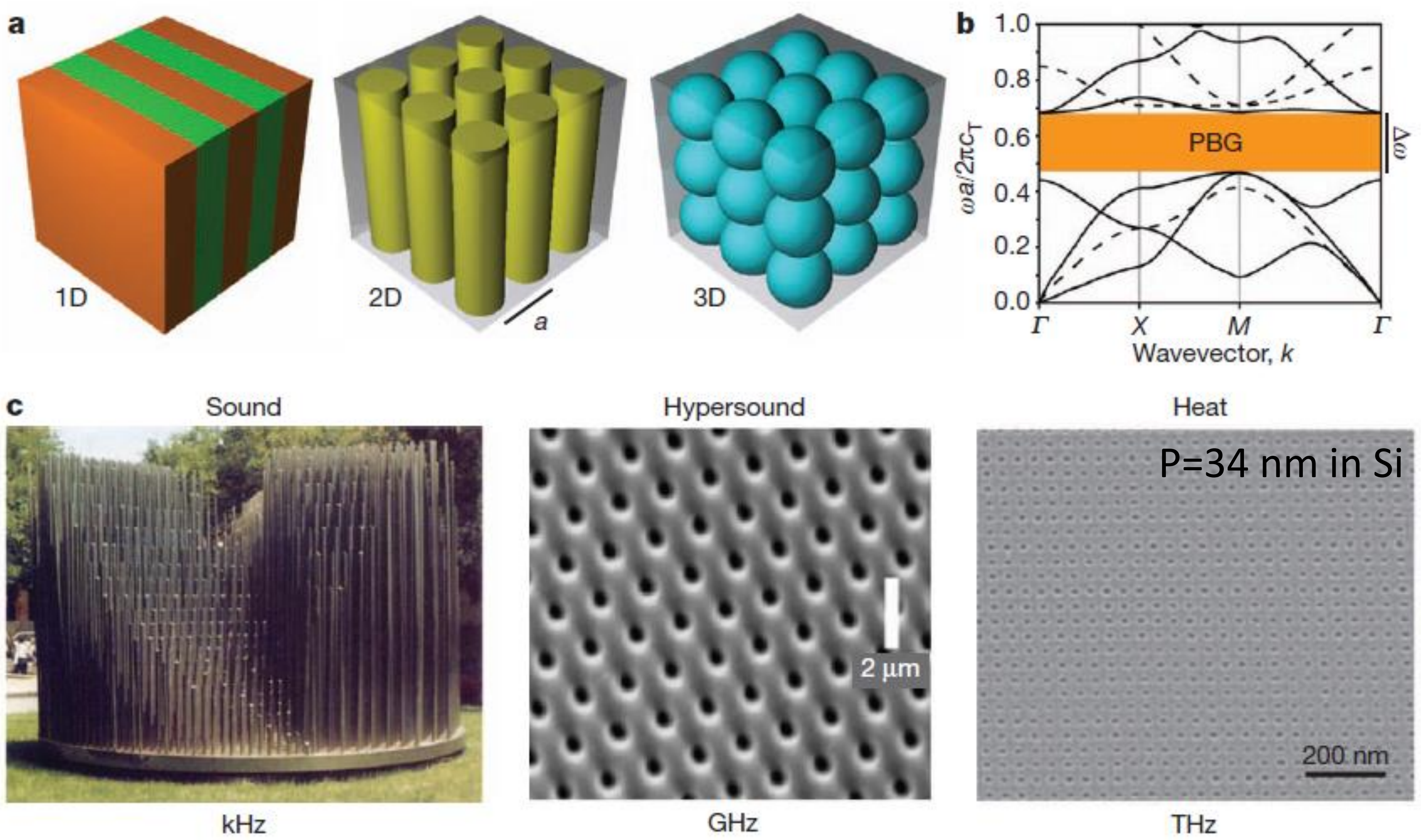
Everything can be applied to phonons with nanometer-scale wavelength if the periodicity is at the nanoscale




Phononic crystals: periodicity at the mm-μm scale: sound waves

Nanophononic crystals: periodicity at the nm scale: main heat carriers at RT

*M. Maldovan, Nature 503,209 (2013)*




P=1,36μm
Gap at 1 GHz

Thermal conductivity reduction
by 2 orders of magnitude!

*M. Maldovan, Nature 503,209 (2013)*

# Quality of the interface: coherence

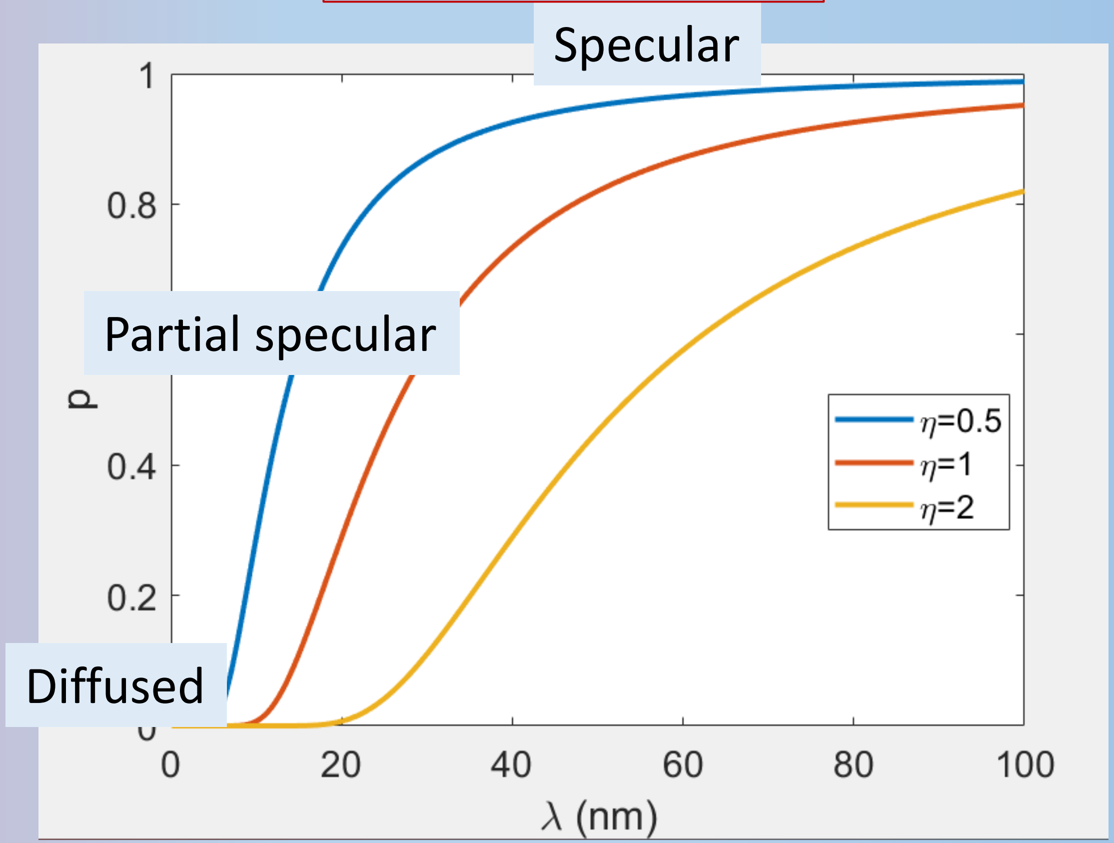
**Specular parameter** $p = e^{-\frac{16\pi^2\eta^2 \cos^2\theta_1}{\lambda^2}}$

The roughness must be good enough for having coherent phenomena at the wavelength we want to affect

⇩

nm to sub-nm roughness is required for nanophononics

For normal incidence



# From micro to nanostructure

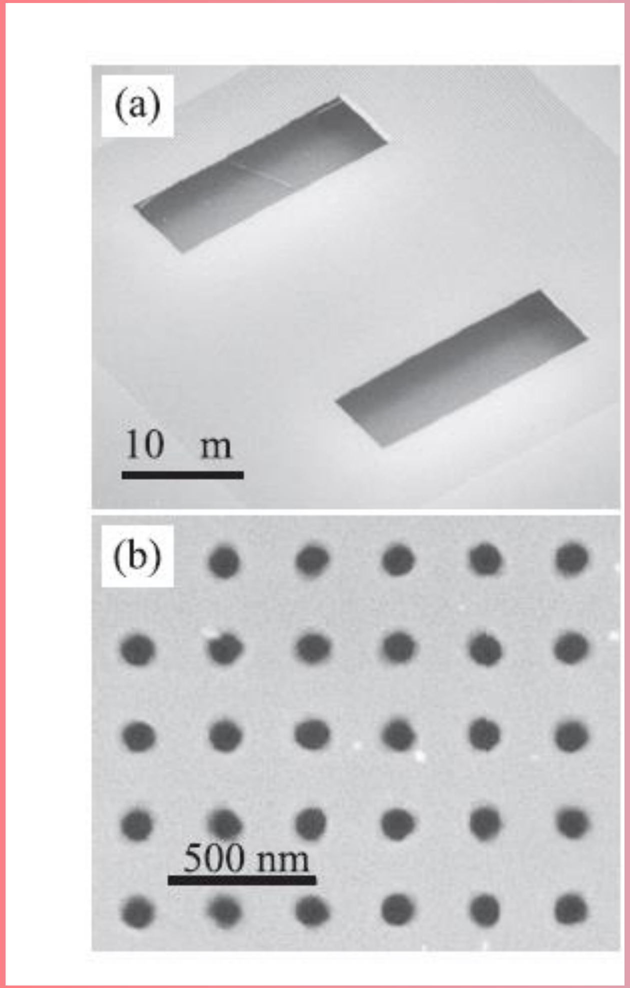
Gaps around $\boxed{\omega_{red} = \dfrac{\omega a}{2\pi v_m} \approx 0.5}$

With $\boxed{v_m = 4000 \text{ and a=1mm}}$ $\Rightarrow$ $\omega = 10\ MHz$

$\boxed{v_m = 4000 \text{ and a=100nm}}$ $\Rightarrow$ $\omega = 125\ GHz$

$\boxed{v_m = 4000 \text{ and a=10nm}}$ $\Rightarrow$ $\omega = 1\ THz$ $\Rightarrow$ Typical phonons dominating heat transport at RT

# Is it only the effect of the gap?




In fact it is more the effect of modified phonon dispersions, velocities and density of states

$$k_T = \frac{1}{3} \int c_v(\omega) v_g^2(\omega) \tau(\omega) g(\omega) d\omega$$

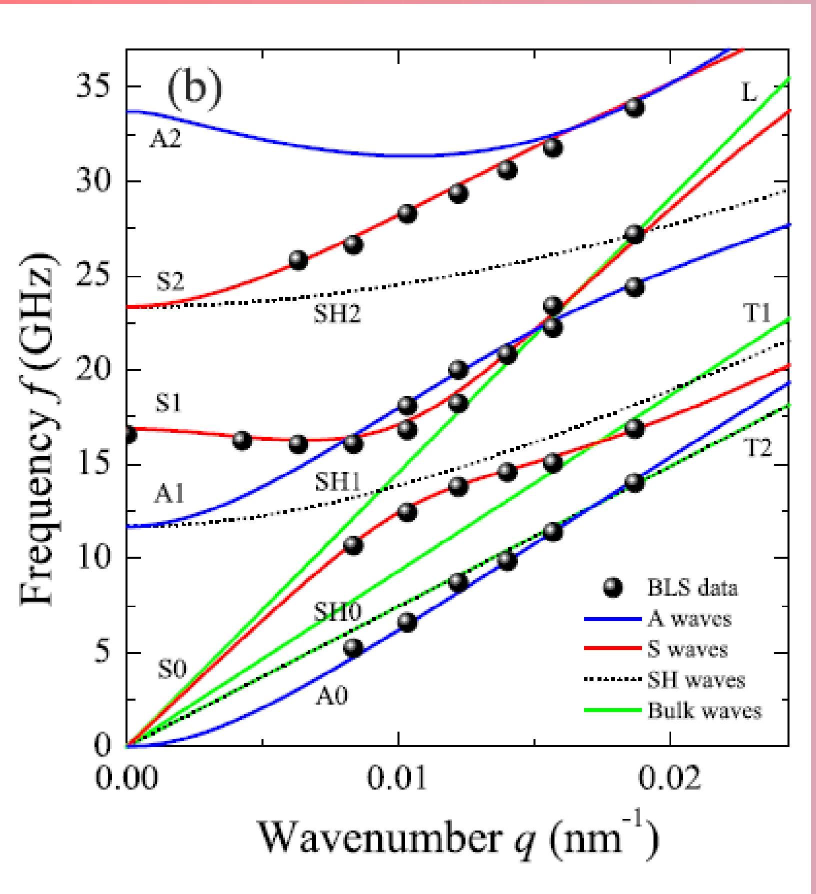
Example:
Si 250 nm thick membrane

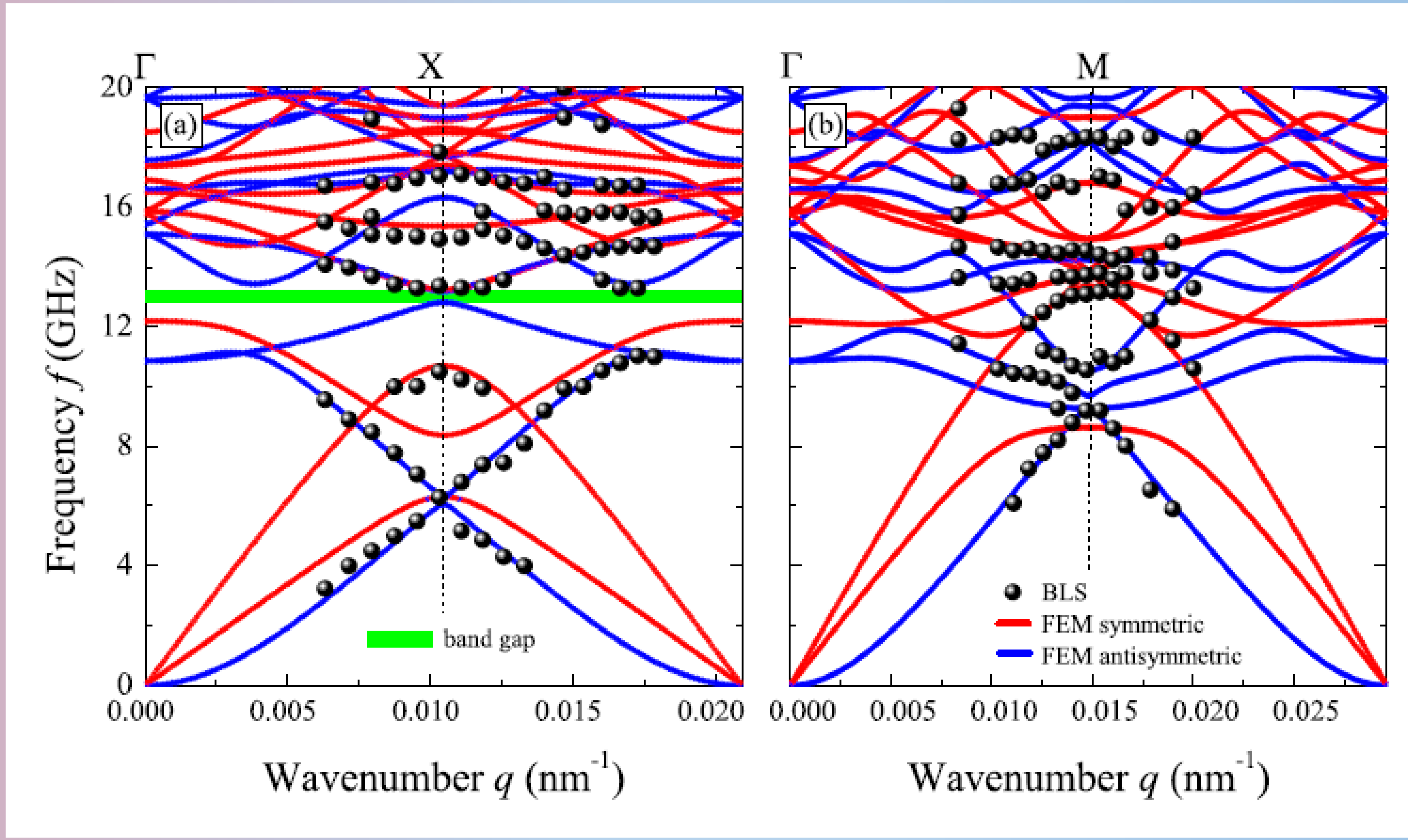
a) Full
b) Nanophononic.

*Hole diameter d* = 100 nm
*periodicity a* = 300 nm

*B. Graczykowski et al. Phys. Rev. B* ***91****, 075414 (2015)*

# Strongly modified acoustic dispersions



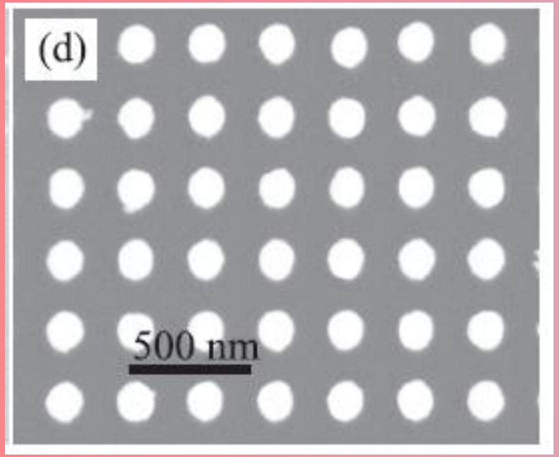



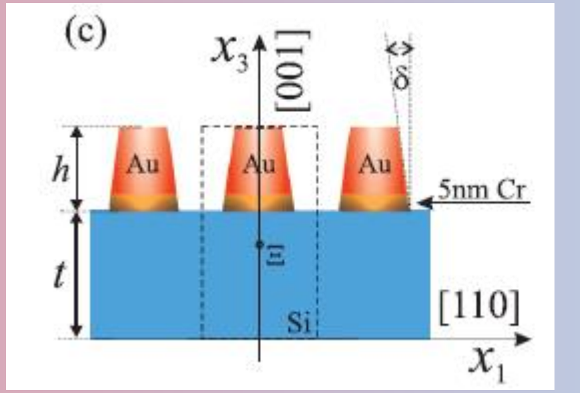

Note that $k_0 = \frac{\pi}{a} = 0.0105\ nm^{-1}$ becomes a mirror axis: it is the BZ border, inducing folding

Note the presence of a band gap along ΓX

Plenty of optic flat modes at higher energy in the nanophononic: less contributing to thermal transport

# Nanophononic on the surface: from holes to pillars

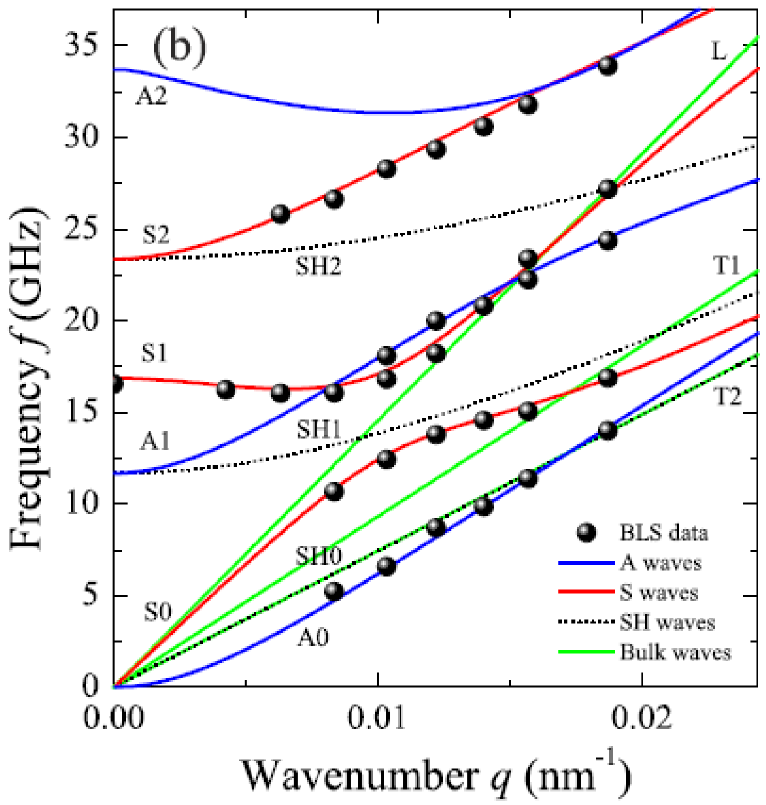


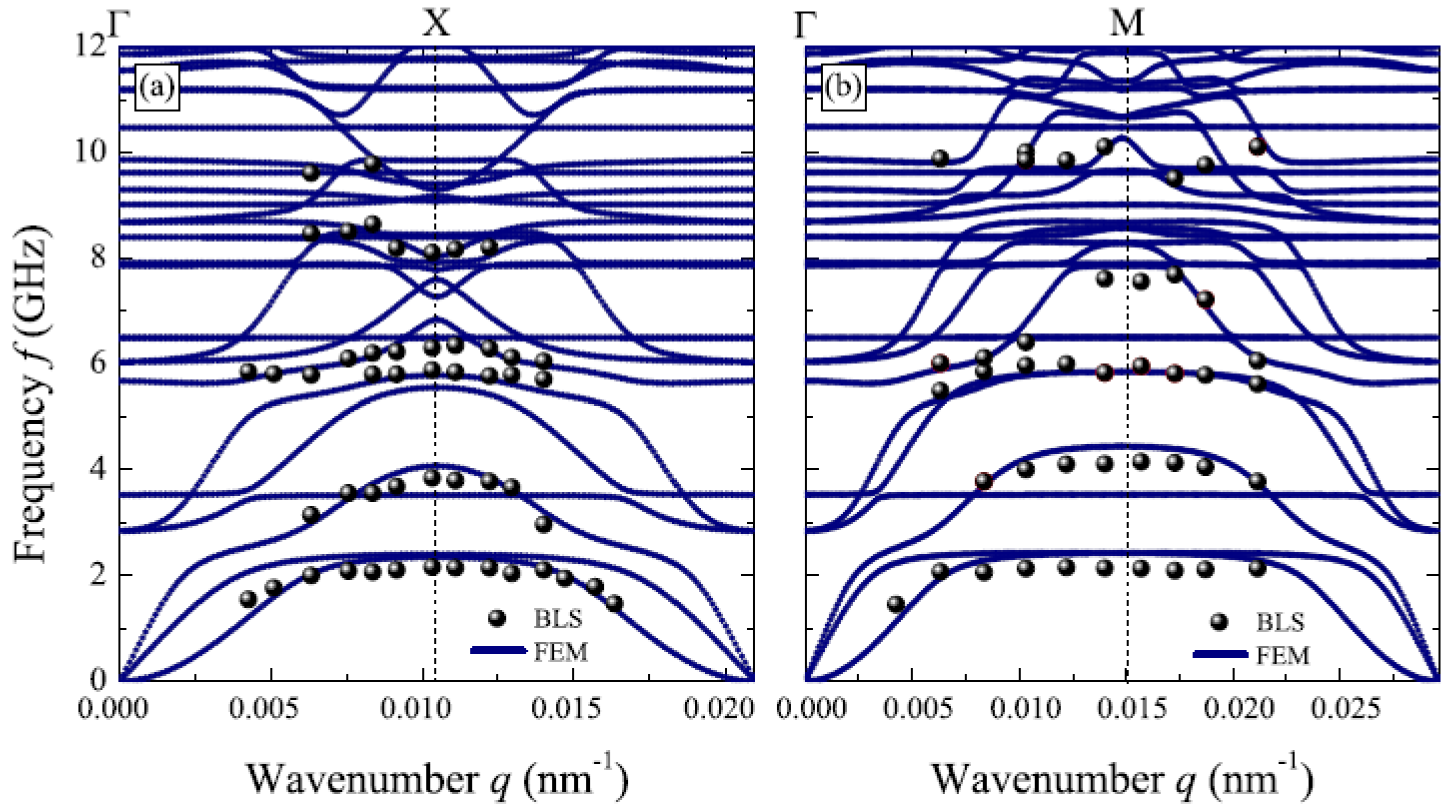




Uniforme membrane with periodic Au nanopillars on the top

What would you expect?

1) To see nanopillars modes and uniforme Si membrane modes
2) Modified modes due to interference between nanopillars and membrane




Plenty of flat bands: Au local resonances
Strong velocity reduction for acoustic modes

# Going further nano: shifting the bandgap from GHz to THz

Gaps around $\boxed{\omega_{red} = \frac{\omega a}{2\pi v_m} \approx 0.5}$

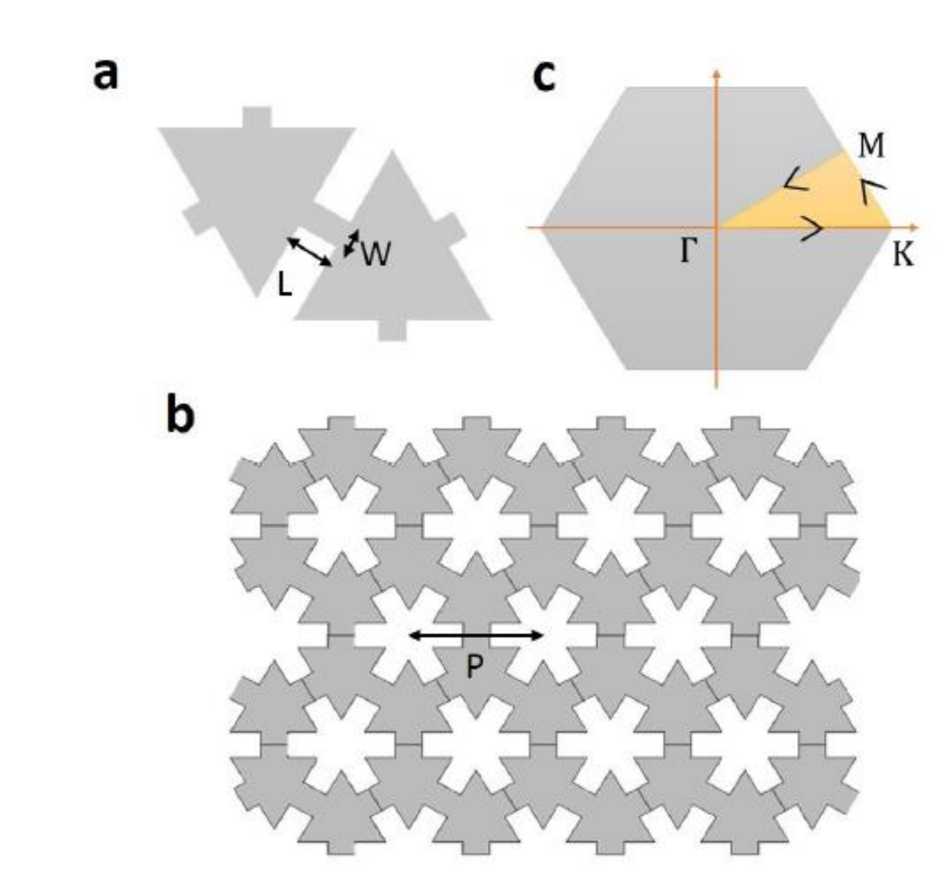
With $v_m = 4000$ and a=1mm $\Rightarrow$ $\omega = 10\ MHz$

$v_m = 4000$ and a=100nm $\Rightarrow$ $\omega = 125\ GHz$

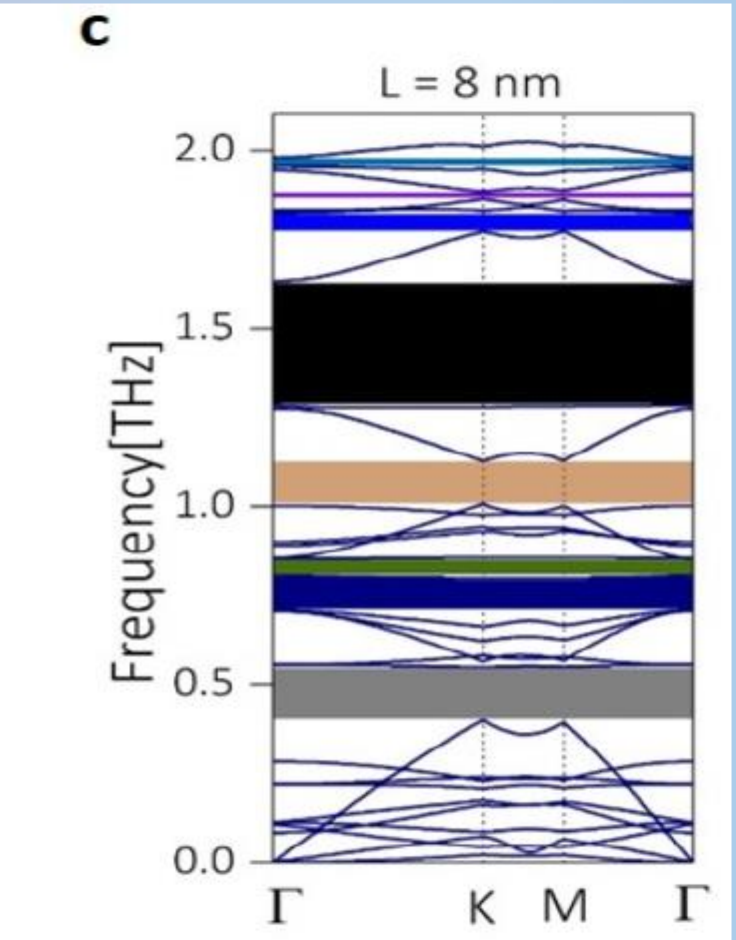
$v_m = 4000$ and a=10nm $\Rightarrow$ $\omega = 1\ THz$

*Masrura et al., Micromachines 11, 655 (2020)*

# Nanophononic graphene: a promising material for microelectronics




p=25 nm
L=8 nm
Hexagonal symmetry

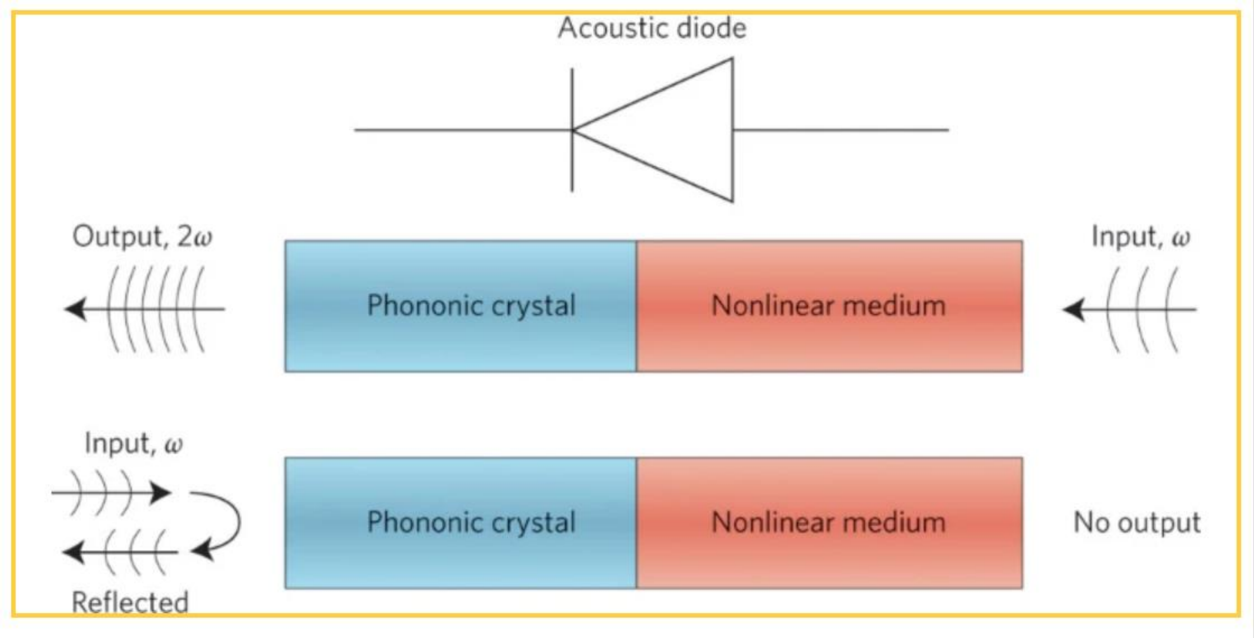



Several full gaps in the THz range: no phonon transmission there

*Masrura et al., Micromachines 11, 655 (2020)*

# Phononic engineering: fancy applications

# One way sound: the acoustic diode




If $\omega$ is in the gap, it won't go through the phononic crystal  (from left to right)
However, if it goes through a nonlinear medium prior to enter the phononic crystal, it will be partially converted in its overtones: they can go through the phononic crystal (form right to left).

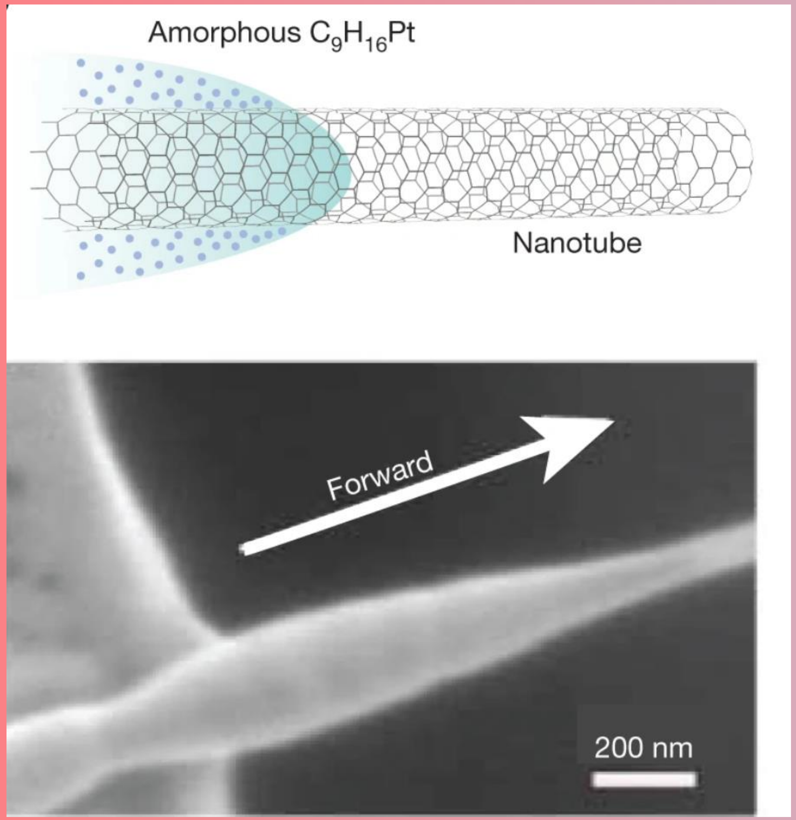
Other strategies have been explored to create acoustic diodes.

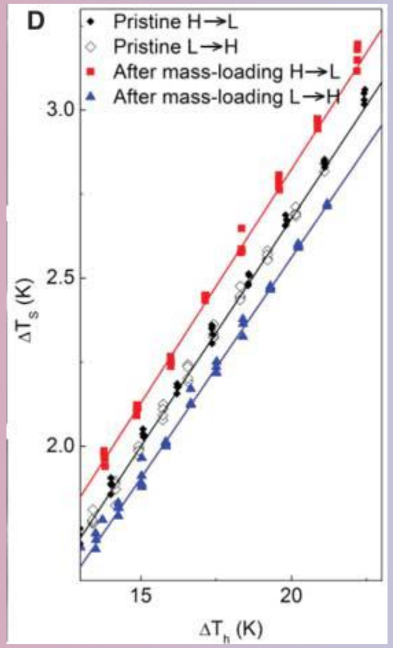
The challenge is to create thermal diodes, as thermal transport implies a large phonon energy spectrum. Realizing a thermal diode is the necessary condition for realizing thermal circuits and use thermal flow as we use electrical flow in microelectronics

*Li et al., Nature Mater* **9**, 962–963 (2010).

# Thermal diode

A boron nitride nanotube with asymmetric deposition of amorphous $C_9H_{16}Pt$.




$\Delta T_s = temperature\ change\ after\ the\ nanotube$

$\Delta T_h = temperature\ change\ before\ the\ nanotube$

For asymmetric nanotubes, higher thermal conductances are measured when heat flows from a high-mass region to a low-mass region

Note 1) C9H16Pt has negligible thermal conductance: does not contribute
Note 2) BN is insulating: it's a phonon effect

*Chang et al., Science* **314**, 1121–1124 (2006)

# Thanks for your attention !

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