GDR NAME

Atelier n.2

Transport at the nanoscale

Presenters: Valentina GIORDANO, Marc BESCOND, Riccardo MESSINA, Lorenzo PAULATTO

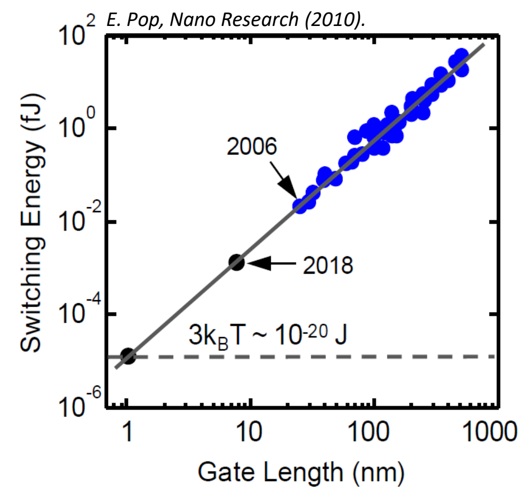
Fundamental Physics: Panoramic shot on

1) Transport at the nanoscale and energy applications

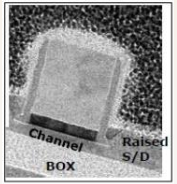
2) Phonons, Electrons, Photons, Ions: Transport regimes at the nanoscale, coupling and effect of nanostructure

3) Theoretical and experimental techniques

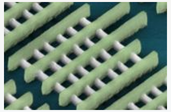
Transport at the nanoscale


E. Pop, Nano Research (2010).

FD SOI
28 nm

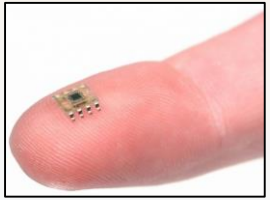


Intel nœud
22 nm



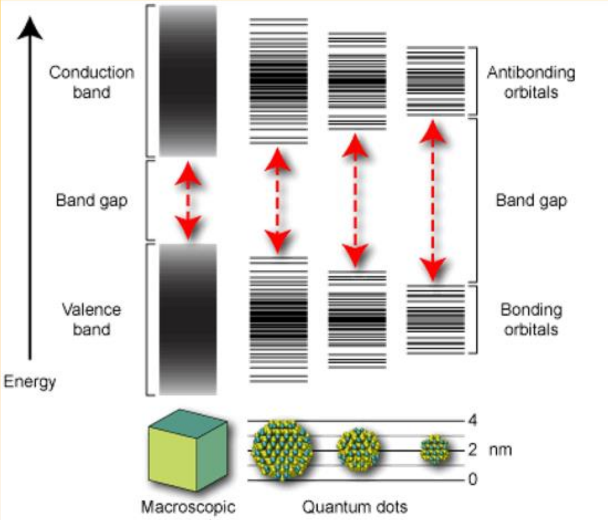
Why it is important?

Global miniaturization:	**(Quasi)particles involved**
1) Nano-devices in micro-electronics	⇨ *Electrons*
2) Photo-catalysis	⇨ *Electrons, photons*
3) Third generation solar cells	⇨ *Photons, electrons, phonons*
4) Nanostructure in thermoelectricity to increase yield	⇨ *Electrons, phonons*
5) Thermal insulation (ex. radiative heat transport at sub-wavelength in complex insulating materials under vacuum (glass wool)	⇨ *Photons, phonons, electrons*
6) The ubiquitous thermal management problem	⇨ *Phonons, electrons, photons*
7) New materials and technologies for ion separation and water desalination	⇨ *Ions*

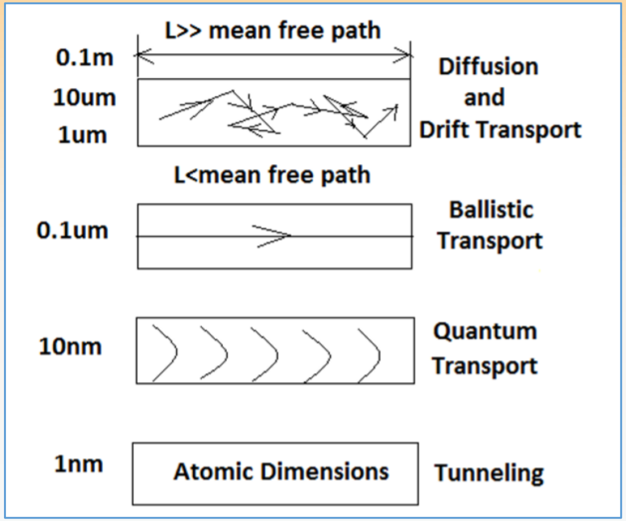


The specificity of nano-scale effects

1) **Importance of surface vs bulk**
2) **Interface and size effects**
3) **Quantum effects (energy levels quantization, tunneling, interference)**
4) **Near-field contribution to radiative transfer**

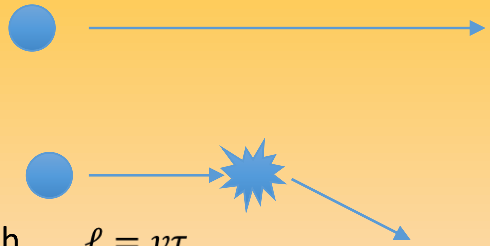


Ex: electrons



When the typical size becomes smaller than characteristic lengths such as carriers mean free path or coherence length, new effects and new transport regimes arise

Transport regimes at the nanoscale: focus on electrons and phonons



E/e

Mean Free Path $\ell = v\tau$

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

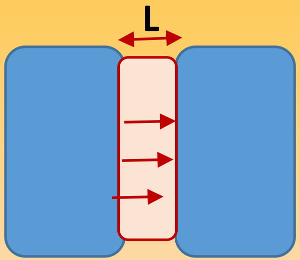
$$\ell = distance\ between\ 2\ scattering\ events$$

At the nanoscale different sources of scattering may arise, which modify the mean free path and thus the capacity of the particle to transport energy or charge, leading to different transport regimes

G. Fugallo, V. Giordano

Phonon Transport Regimes

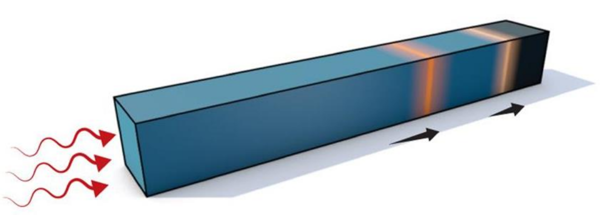
BALLISTIC



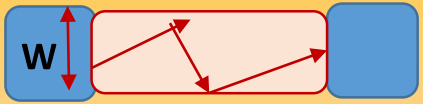
L << mfp

Dimensions much smaller than mean free path

- The dominant scattering events are extrinsic (border)
- Quantum of thermal conductance



ZIMAN/CASIMIR

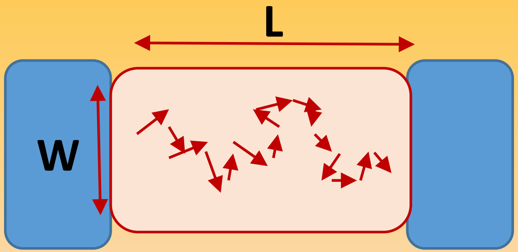


W << mfp, L ∼mfp

Dimension perpendicular to the heat-flux much smaller than mean free path

- Guided waves and Surface dominated Transport
- Phonons of different polarizations/group velocities move towards the right-end

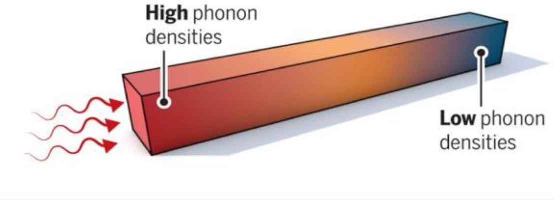
DIFFUSIVE



L,W >> mfp

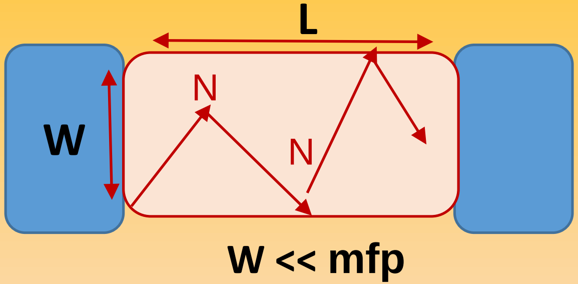
All dimensions much larger than mean free path

- Scattering sources intrinsic to the material (anharmonicity, defects, isotopes etc)
- Phonon density / temperature decreases with distance from the left-end



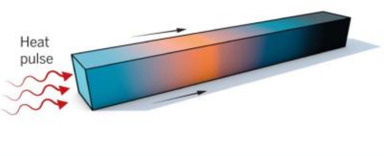
Phonon Transport Regimes

Hydrodynamic/Poiseuille



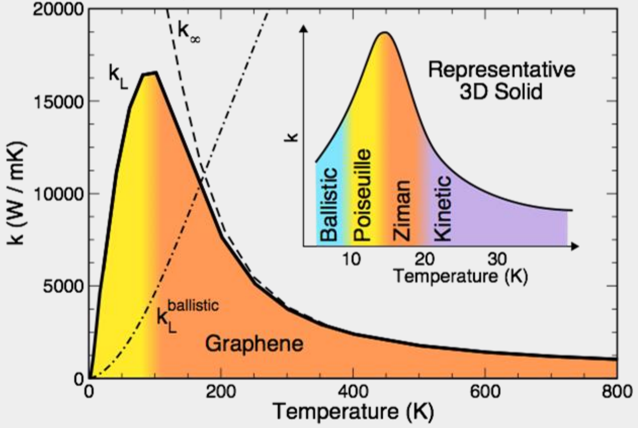
Dimension perpendicular to the heat-flux much smaller than mean free path

- **Surface scattering +** **Predominance of momentum-conserving processes (Normal)** which preserve the direction of the energy flow.
- Phonon transport similar to fluid flow: A single temperature pulse formed by interactive phonons propagates as a wave packet (**Second Sound)** from the left to the right.



Shi L. Science. 3**64**, 6438 (2019)

Cepellotti. A. et al, *Nat. Commun.* **6**, 7400 (2015)



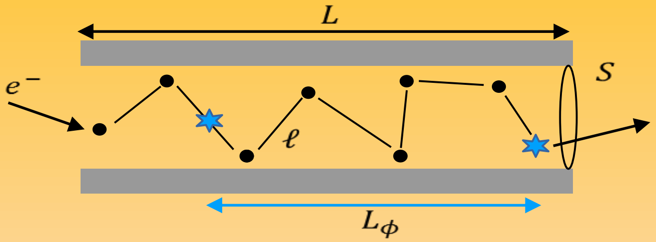
Hydrodynamic phonon-transport has been observe (in few 3D materials) at **cryogenic temperatures**. **in 2D and layered materials it can be observed even room temperature.**

(GRAPHITE: SECOND SOUND OBSERVED ABOVE 100K)

Huberman et al. Science **364**, 375. (2019)

Electron Transport Regimes

For Si mfp~10 nm@RT, 500nm@77K



L – system's length

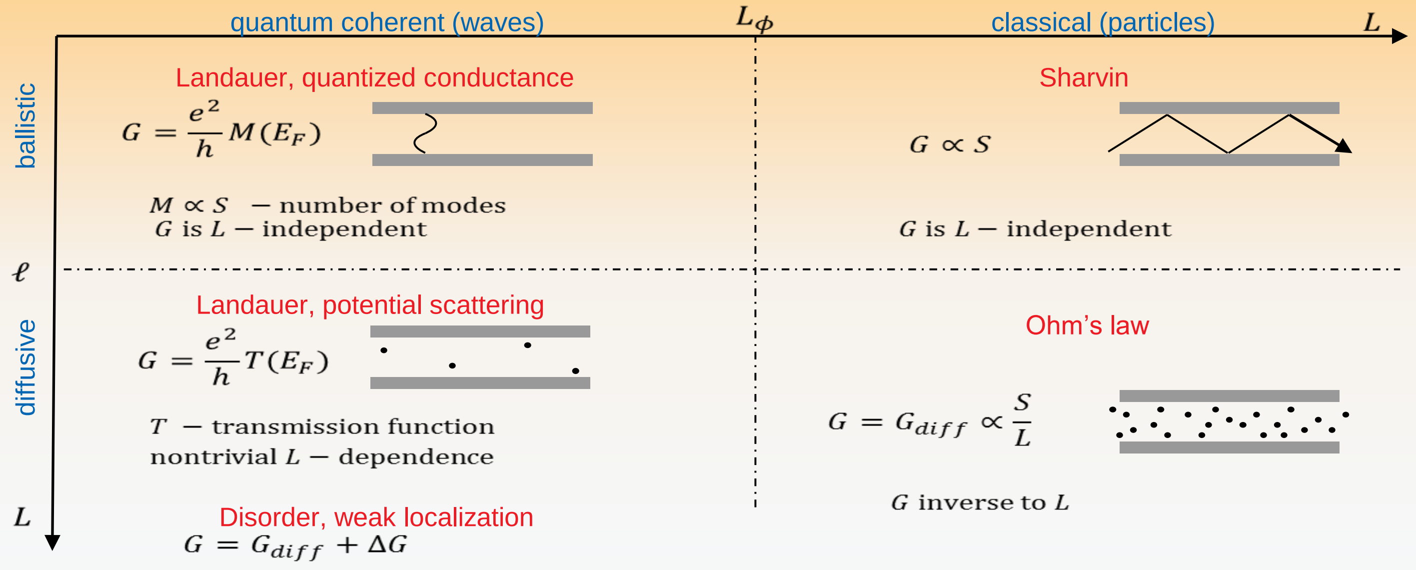
S – system's cross-section

ℓ – mean free path, *elastic* (conserving energy) scattering:

- static impurities, structural defects, boundaries, etc.

L_φ – phase coherence length, *inelastic* scattering:

✵ electron-phonon, magnetic impurities, etc.



Landauer, quantized conductance

$$G = \frac{e^2}{h} M(E_F)$$

$M \propto S$ − number of modes
G is L − independent

Sharvin

$$G \propto S$$

G is L − independent

Landauer, potential scattering

$$G = \frac{e^2}{h} T(E_F)$$

T − transmission function
nontrivial L − dependence

Ohm's law

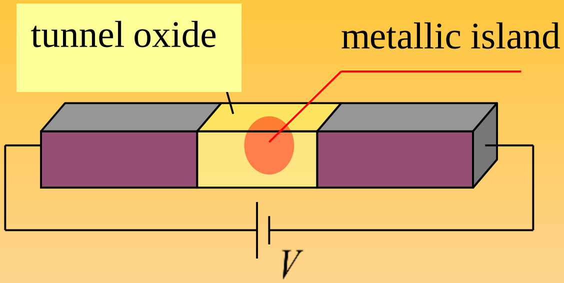
$$G = G_{diff} \propto \frac{S}{L}$$

G inverse to L

Disorder, weak localization

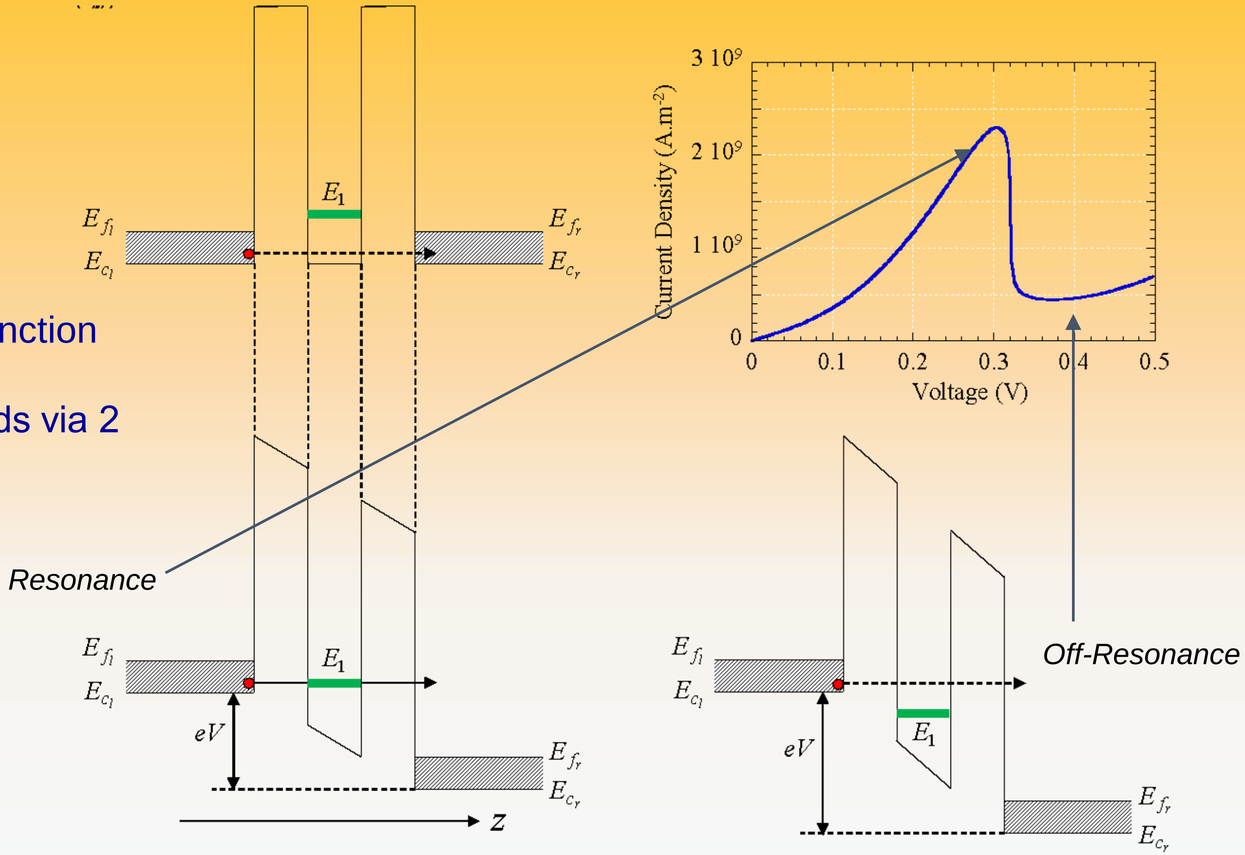
$$G = G_{diff} + \Delta G$$

Quantum transport exemple (1): Resonant Tunneling



Basic structure: The double tunnel junction

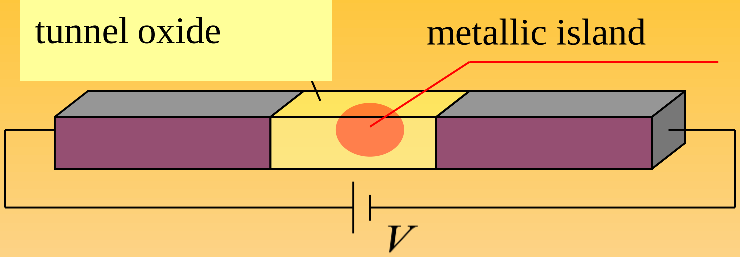
→ conducting island coupled to 2 leads via 2 tunnel junctions

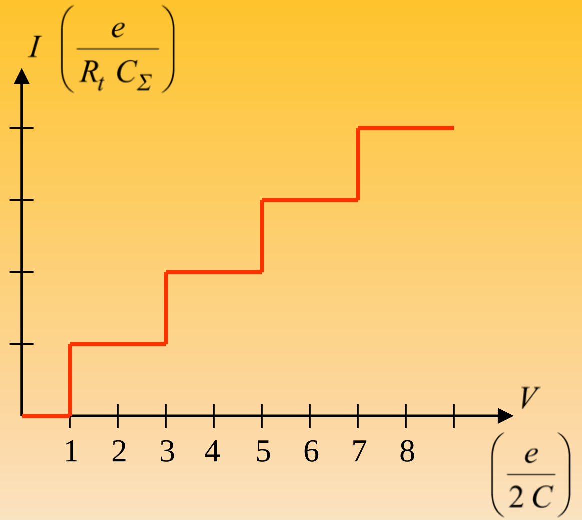


Resonance

Off-Resonance

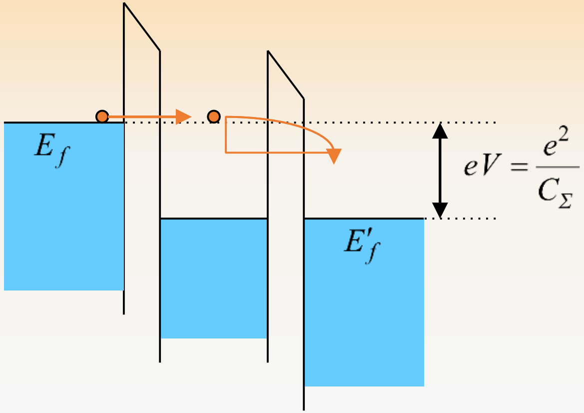
Quantum transport exemple (2): the Coulomb blockade





Basic structure: The double tunnel junction, one lead is weakly coupled to the dot

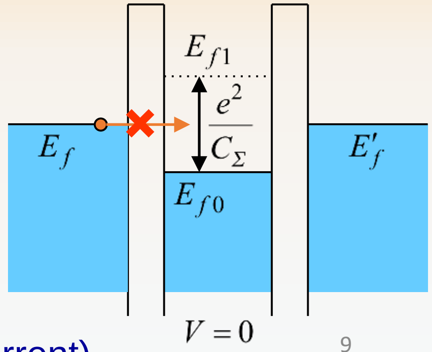
→ sequential tunneling



Charging energy :

$$E_{ch} = \frac{e^2}{C_\Sigma}$$

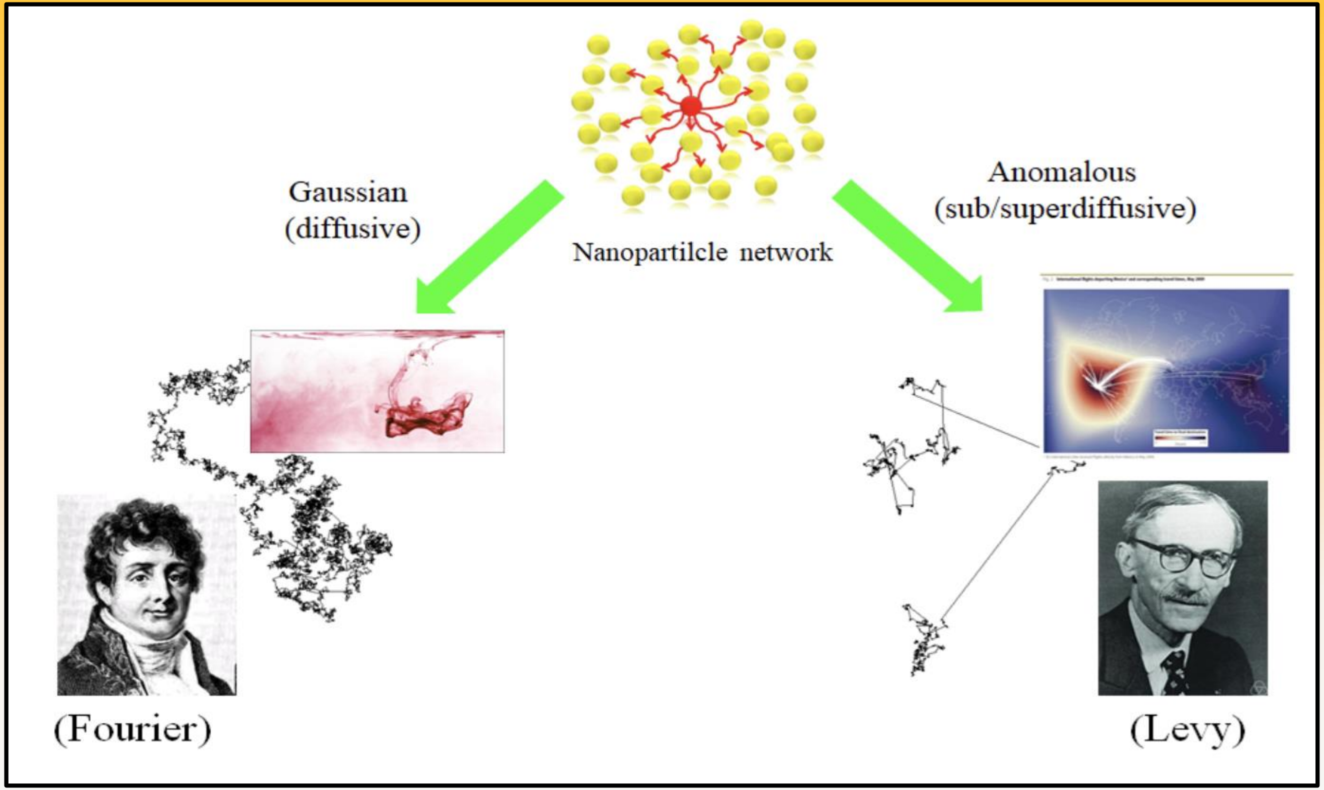
Additional energy in the island for 1 additional electron
=> electrostatic energy
(Coulombic effect)



Coulomb blockade: the number of electron in the dot is quantized (and thus the current)

R. Messina,
P. Ben-Abdallah,
Y. De Wilde

Photons: transport regimes in many-body systems

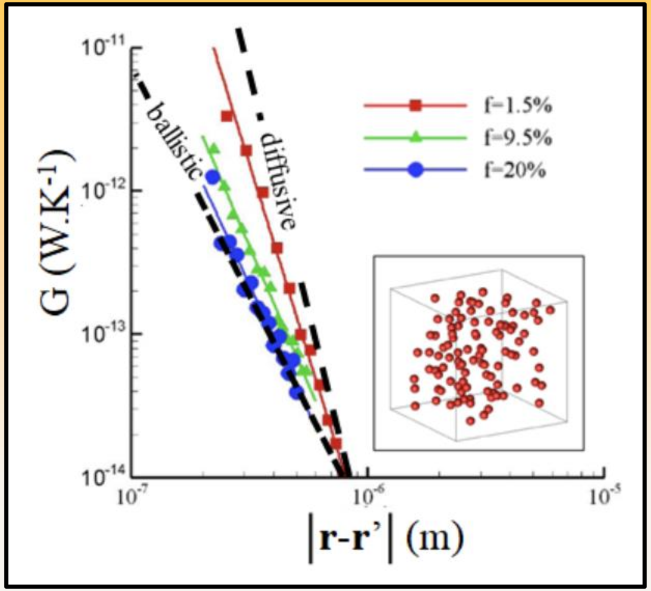


Which are the possible transport regimes for radiative heat transfer?

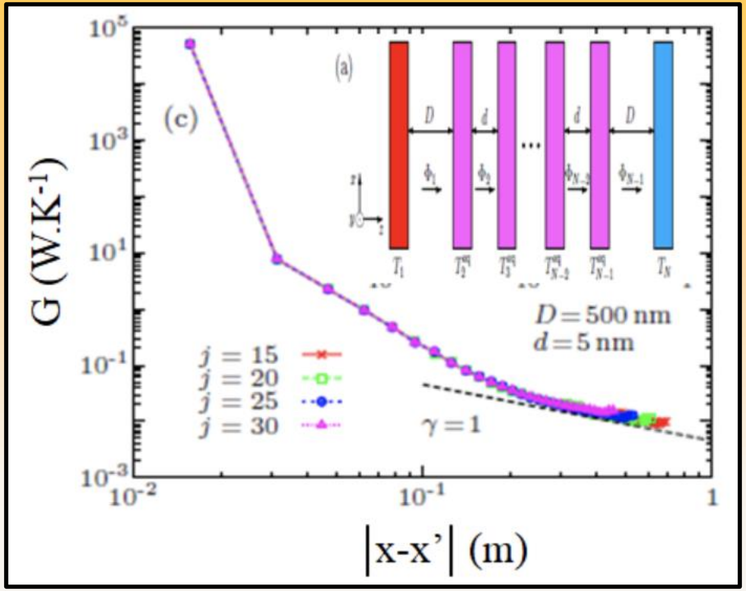
R. Messina,
P. Ben-Abdallah,
Y. De Wilde

Anomalous radiative heat transport regimes

The regime can be identified by analyzing the scaling law for the thermal conductance



P. Ben-Abdallah et al., Phys. Rev. Lett. **111**, 174301 (2013)



I. Latella et al., Phys. Rev. B **97**, 035423 (2018)

Superdiffusive regime in diluted networks

Transition to ballistic regime in dense networks

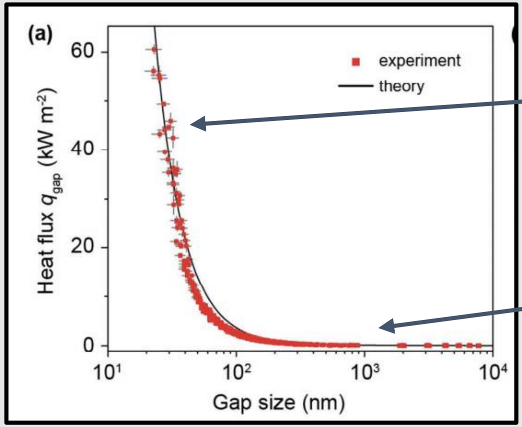
R. Messina,
P. Ben-Abdallah,
Y. De Wilde

Local density of energy above a polar material

$$U\left(\mathbf{r},\omega,T\right)=\underline{\underline{\rho\left(\mathbf{r},\omega\right)}}\theta\left(\omega,T\right)$$

Local density of states (EM-LDOS)

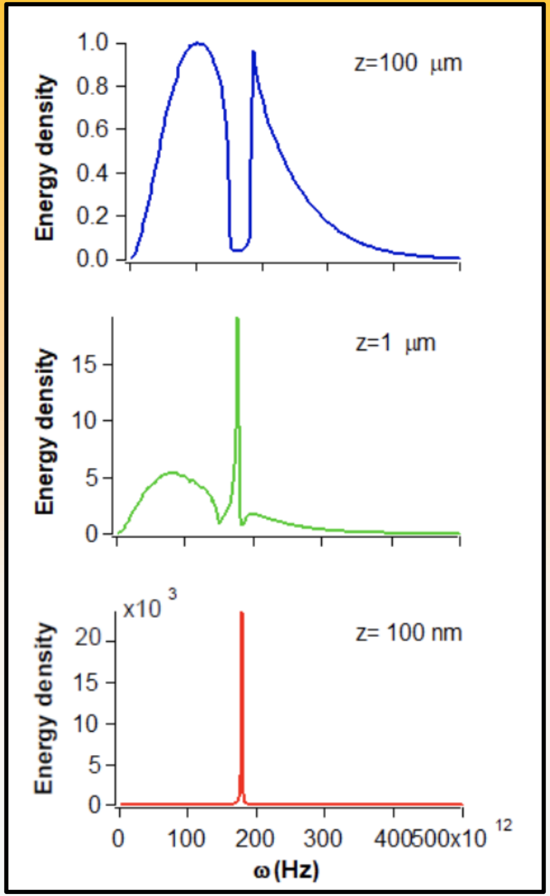
Impact on radiative heat transfer



Near field
Photon
tunneling

Far field
Propagative
photons

A. Fiorino et al. Nano Lett. **18**, 3711 (2018)



V. Shchegrov et al.,
Phys. Rev. Lett. **85**, 1548 (2000)

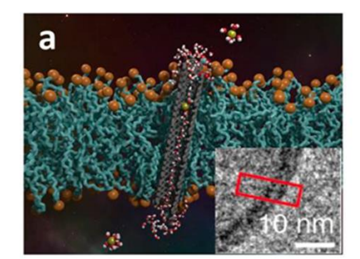
Near field
Contribution from
surface energy
→ divergent LDOS

L. Boquet

Ions: nanofluidics

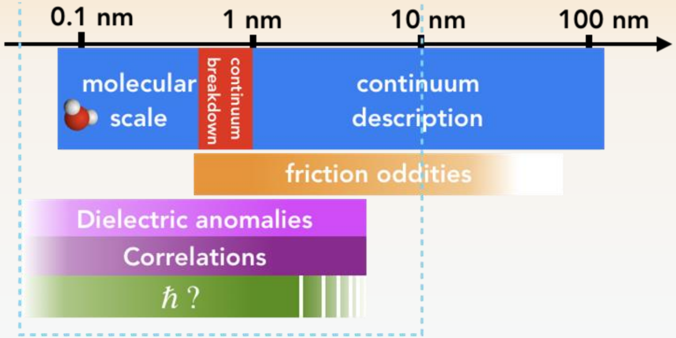
The exploration of transport of fluids and ions at the nanoscales is an emerging field

Nanoengineering → progress in nanofluidic studies



Noy et al. Science (2017)

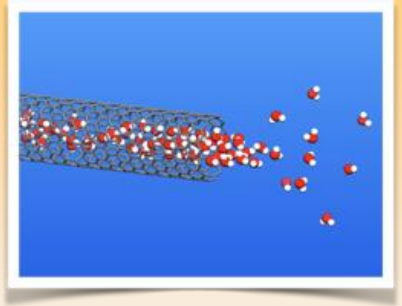
- Small dimensions: Breakdown of continuum transport (diffusion/convection)
- A wealth of exotic phenomena occuring below 10nm confinement
  - Frictionless flows, fluctuations, dielectric anomalies, many-body ion transport, strong correlation, quantum effects...



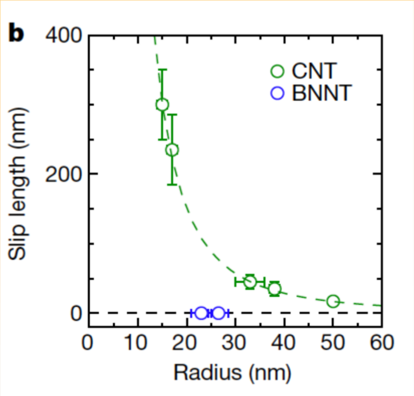
Kavokine et al. ARFM (2021)

Examples

Ultralow water friction at carbon surfaces

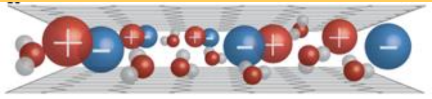


Surface friction ~ 1/(slip length)

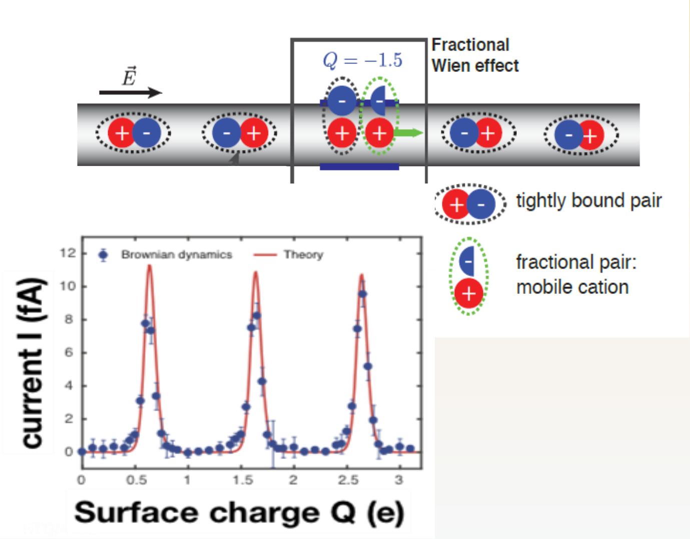


Secchi et al., Nature (2016)

Strong ionic correlations --> non-linear transport.



Ionic Coulomb blockade: quantized transport



Kavokine et al., Nature Nano (2019)

Carriers coupling:
a useful strategy for energy applications

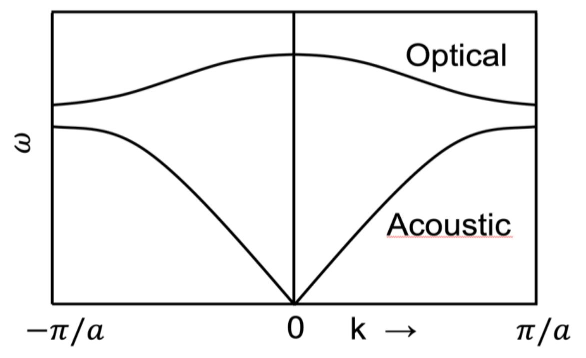
Electron-Phonon scattering

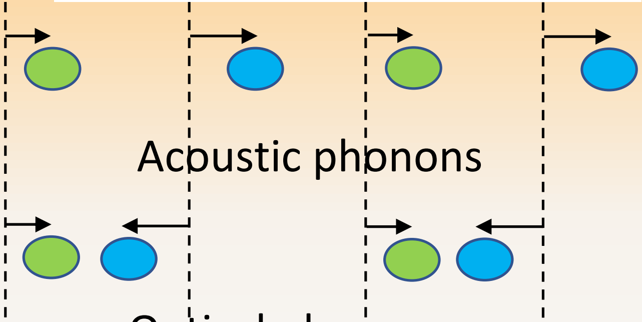
- Non-polar materials (Si,Ge)
  - Scattering with acoustic phonons:
    - Acoustic branch linear at small k.

➡ Elastic interactions at room temperature .

  - Scattering with non-polar phonons:
    - Optical phonons appear at higher energy

➡ Inelastic interactions at room temperature. (amount of energy needed to excite this mode: usually few tens of meV)





Optical phonons

✓ e-ph coupling is usually higher for the optical phonons.

J. Appl. Phys. **118**, 045713 (2015); doi: 10.1063/1.4927530

→ Non-polar electron-phonon interactions: defined by a deformation potential

- Electronic band structure modification under a small (linear response regime) lattice constant deformation.

Electron-Phonon scattering

- Polar materials (GaAs)
  - Additional scattering due to the polarity of the material (usually dominant)
    - Deformation of the lattice by phonons modifies this dipole between two atoms.

      → Long-range electric field that scatters the electrons.

    - Acoustic phonons.

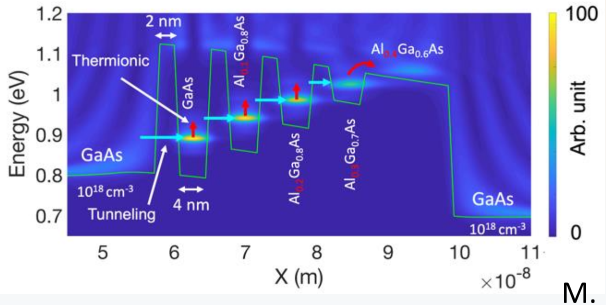
      → "piezoelectric" scattering.

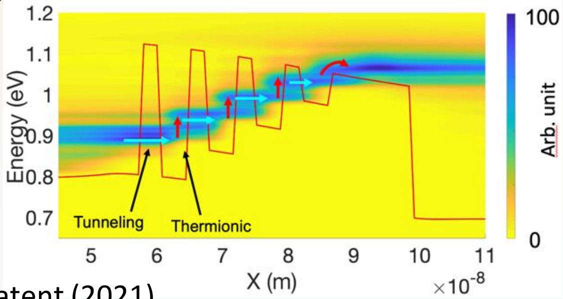
    - Optical phonons.

      → "polar optical phonon scattering".

      (dominant at room temperature over the other types of phonon scatterings.

Ex: Effect of the polar optical phonon scattering in « Quantum cascade cooler »





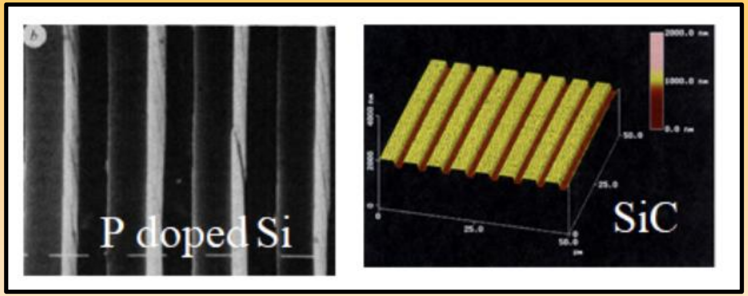
M. Bescond & K. Hirakawa, patent (2021)

R. Messina,
P. Ben-Abdallah,
Y. De Wilde

Coupling: Phonon-Polariton, an example of directional thermal emission (spatial coherence)

Surface gratings

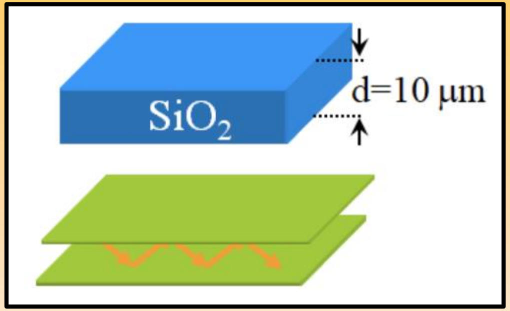
(Diffraction of surface waves)



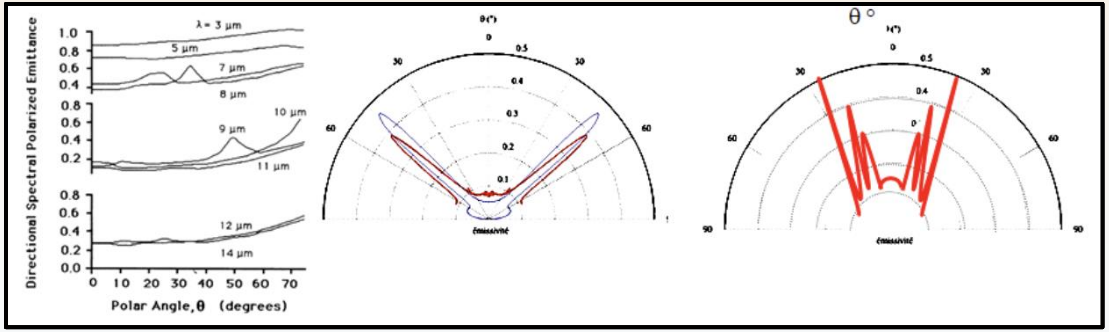
Hesketh et al., Phys. Rev. B **27**, 10803 (1988)
Greffet et al., Nature **416**, 61 (2002)

Thin films

(Interferences)



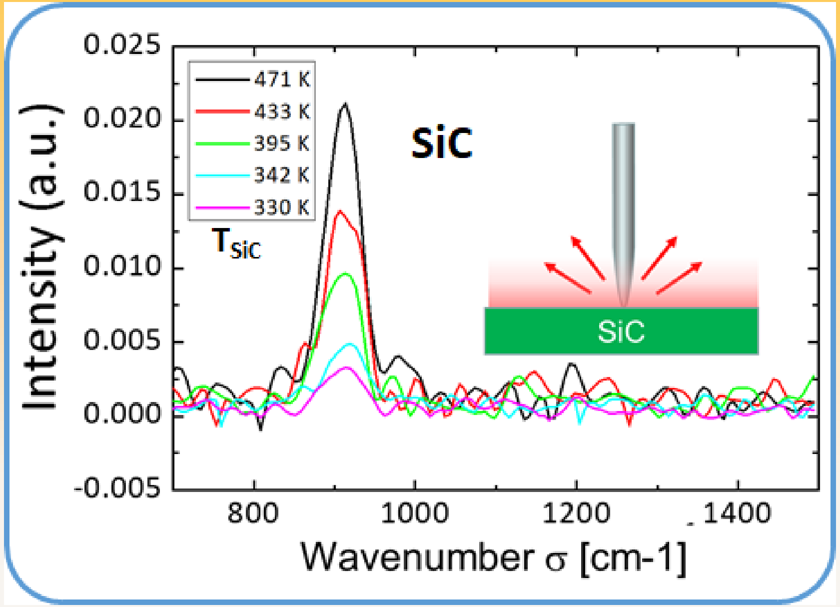
Kollyukh et al., Opt. Commun. **225**, 349 (2003)
P. Ben-Abdallah, JOSA A **21**, 1368 (2004)

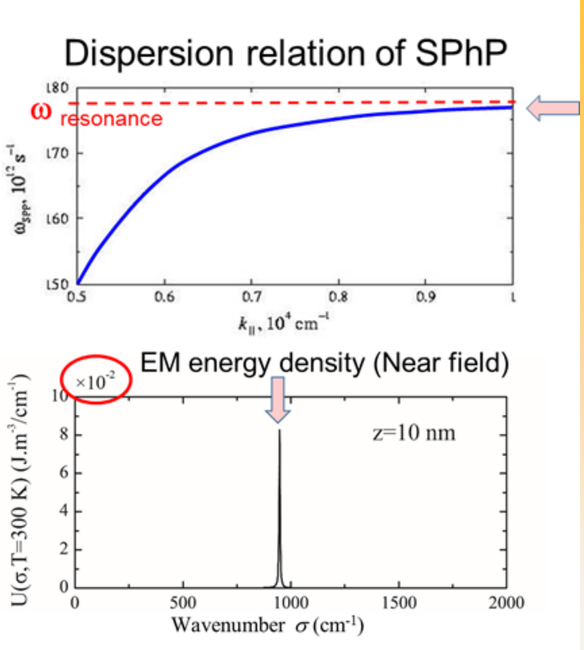


R. Messina,
P. Ben-Abdallah,
Y. De Wilde

Quasi-monochromatic thermal emission (temporal coherence)

TRSTM spectra on Silicon Carbide





<u>Prediction</u>: Shchegrov et al.,
Phys. Rev. Lett. **85**, 7 (2000)

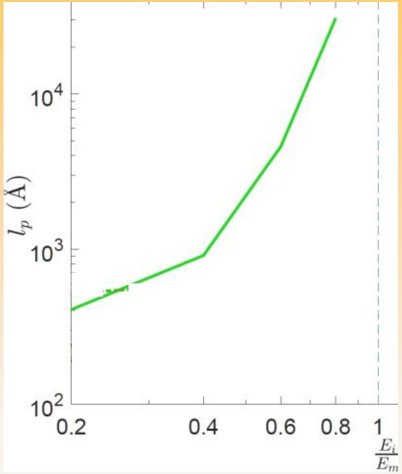
<u>Observation</u>: Babuty et al.,
Phys. Rev. Lett. **110**, 146103 (2013).

Non-planckian spectrum observed in the near field due to peak in EM-LDOS (surface phonon polaritons).

Effect of a nanostructure on carriers propagation

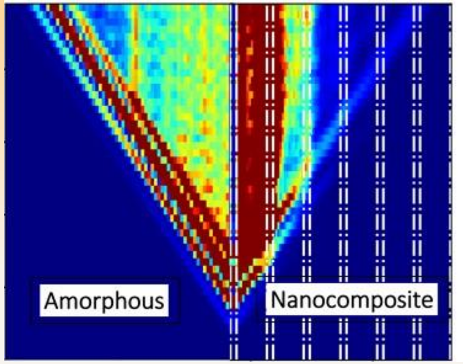
Effect of nanostructure on phonon propagation

Phonon mean free path reduction



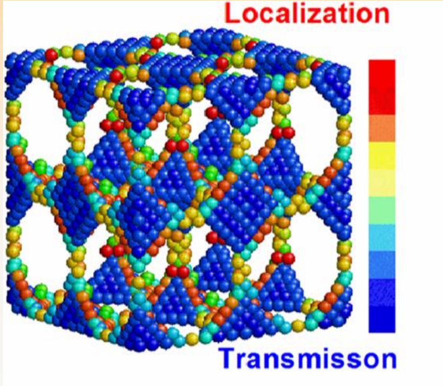
Luo, Nanomaterials 9, 1471 (2019)

Change of transport regime: From propagatif to diffusive



Tlili, Nanoscale, 11, 21502 (2019)

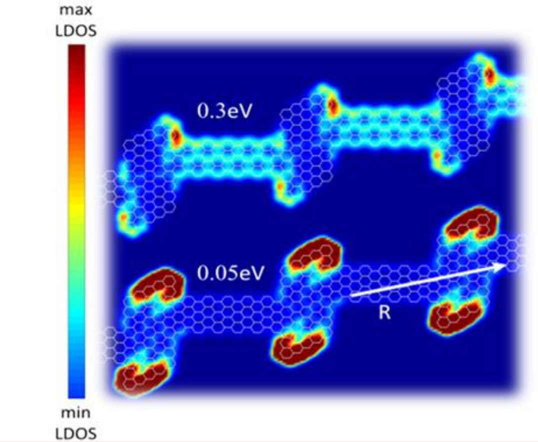
Periodic nanostructure: Coherent effects such as phonon localization



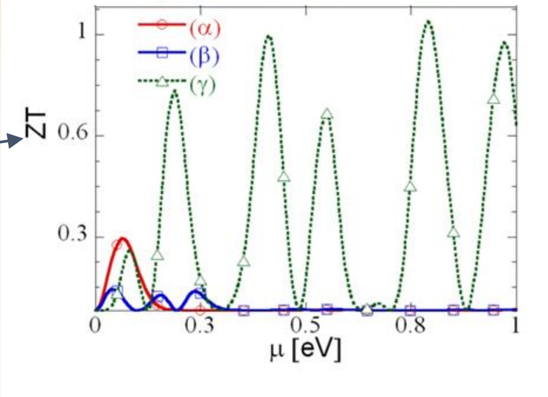
Yang, NanoLett. 14,1734 (2014)

Effect of nanostructure on electron transport

The discretization of electronic levels in nanostructures leads to an **energy filtering of electrons** during transport through tunneling
Ex: graphene nanostructure to improve *S* by resonant tunneling



F. Mazzamuto et al. , Phys. Rev. B (2011)



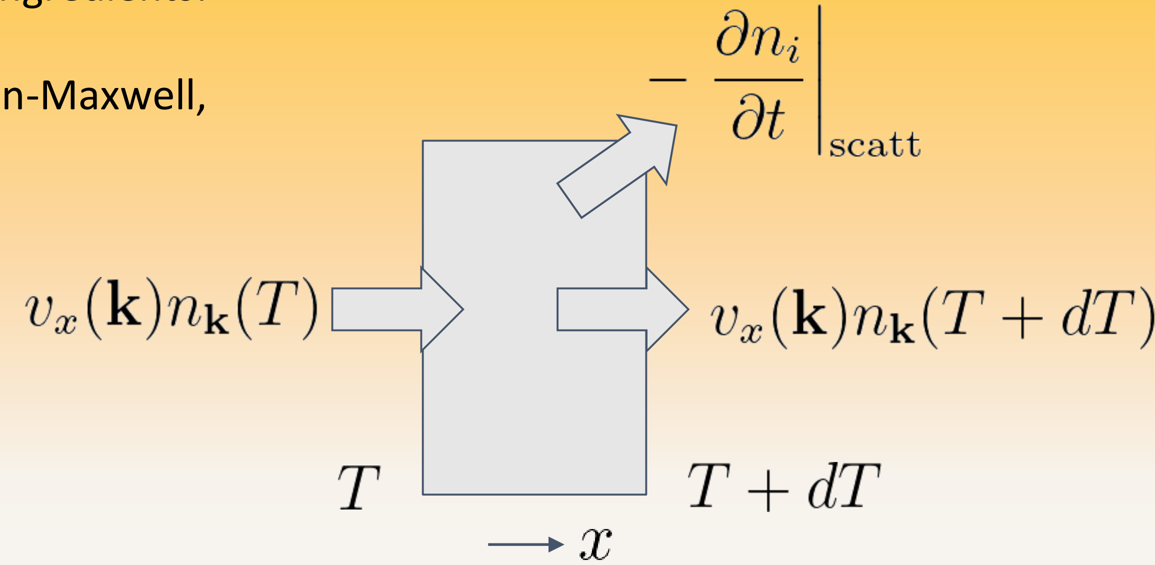
ZT= thermoelectric figure of merit

Theoretical approaches to carriers transport

Electrons & Phonons: Boltzmann transport equation

Describes transport **by particles** in a gradient (voltage, temperature, pressure, chemical…) with only three ingredients:

1. Equilibrium population (Boltzmann-Maxwell, Fermi-Dirac, Bose-Einstein)
2. Scattering rate (intrinsic vs. extrinsic)
3. Group velocity



$$-v(\mathbf{k})\nabla T\left(\frac{\partial n_{\mathbf{k}}}{\partial T}\right)+\left.\frac{\partial n_{\mathbf{k}}}{\partial t}\right|_{\mathrm{scatt}}=0$$

Electrons & Phonons: Boltzmann transport equation

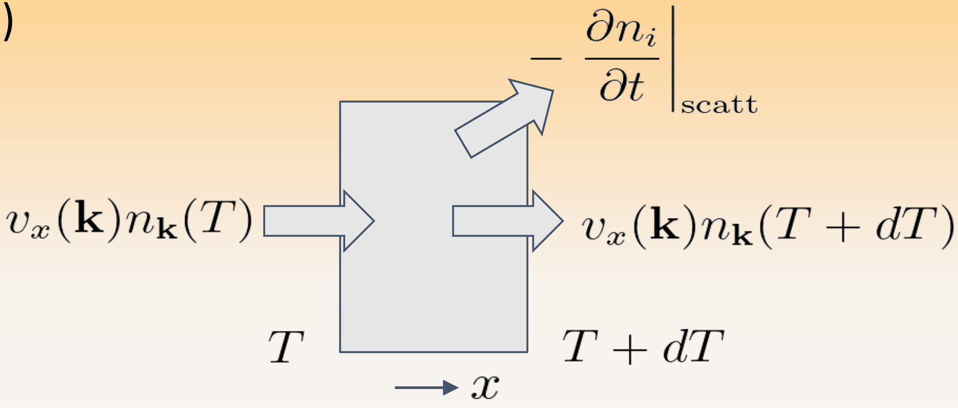
In practice, approximation of small gradient, or almost equilibrium (single-mode approximation) are typically employed.

It fails when:

1. No collisions (ballistic)
2. No group velocity (amorphous materials)
3. No particles (strong interactions)

What is difficult/expensive:

1. Calculation of scattering probability
2. Strong perturbation (linearization fails)
3. Mesoscopic systems
4. Multiple carriers
5. External fields



Electrons: From classic to quantum transport

- **Boltzmann (1D) : slowly variable potential** V

$$\frac{\partial f}{\partial t} + v\cdot\nabla_x f = \boxed{\frac{1}{\hbar}\nabla V\cdot\nabla_k f} + \hat{C}\, f$$

local effect of potential V

QUANTUM TRANSPORT

- **Wigner function** derived from density matrix
- **Wigner (1D) : potential**

$$\frac{\partial f_w}{\partial t} + v\cdot\nabla_x f_w = \boxed{\hat{Q}_V\, f_w} + \hat{C}\, f_w$$

non local of potential V

$$\hat{Q}_V\, f_w = \frac{1}{2\pi}\int dk'\; V_w(x,k-k')\, f_w(x,k')$$

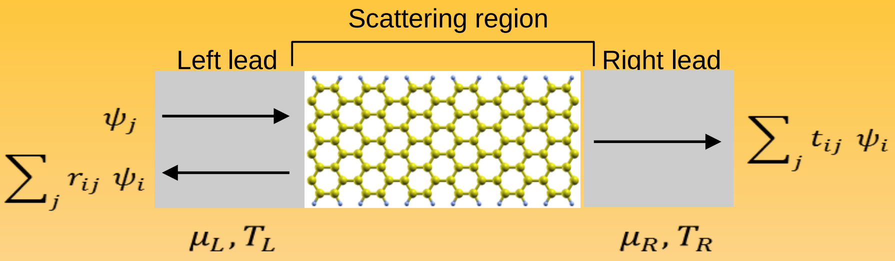
Wigner Potential : $$V_w(x,k)=\int dx'\sin(kx')\left[V\left(x+\frac{x'}{2}\right)-V\left(x-\frac{x'}{2}\right)\right]$$

- **$f_w \longrightarrow$ f if « classic » V** *D. Querlioz et al. Physical Review B (2008)*

- **Classic Boltzmann transport is a special case of quantum transport**

A. Smogunov

Coherent transport: Landauer and NEGF



t_{ij}/r_{ij} – transmission/reflection amplitudes for propagating Bloch states

Landauer-Buttiker formula :

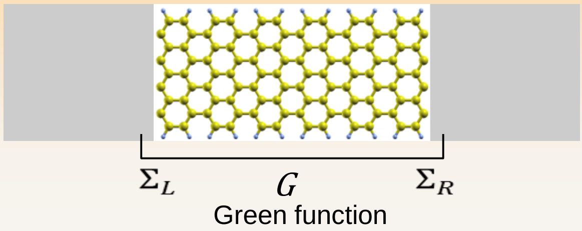
$$I = \frac{e}{h}\int T(E)[f_L(E) - f_R(E)]dE$$

T – electron transmission function

$f_{L/R}$ – Fermi–Dirac distribution functions

$$T = \Sigma_{ij}|\,t_{ij}\,|^2$$

Widely-used Non-Equilibrium Green Functions (NEGF) formalism:



$$T = \mathrm{Tr}\,[\Gamma_L G \Gamma_R G^\dagger]$$

$$\Gamma_{L/R} = i[\Sigma_{L/R} - \Sigma^\dagger{}_{L/R}]$$

$\Sigma_{L/R}$ – contact selfenergies

Valid for other carriers, *e.g.*, for thermal current *Q* of *phonons* :

$$Q = \frac{1}{h}\int \tau(E)[n_L(E) - n_R(E)]\,E\,dE$$

τ – phononic transmission function

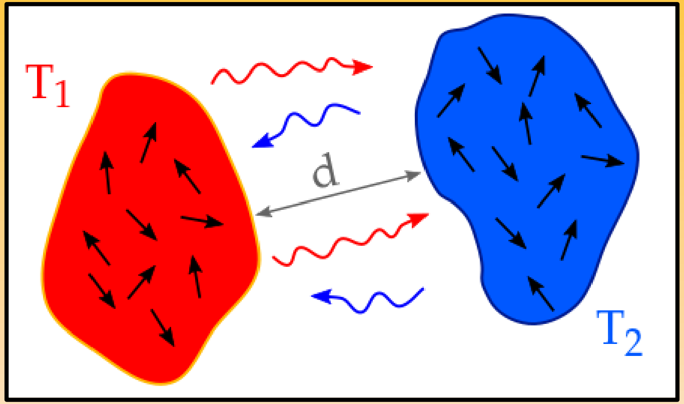
$n_{L/R}$ – Bose–Einstein distribution functions

Interactions between carriers within the Scattering region:

$$\Sigma = \Sigma_L + \Sigma_R \rightarrow \Sigma_L + \Sigma_R + \Sigma_{\text{int}}$$

R. Messina,
P. Ben-Abdallah,
Y. De Wilde

Radiative Transport: Fluctuational electrodynamics



Far field (d>>λ): Radiometry theory

$$\frac{\varphi}{S} \leq \sigma(T_1^4 - T_2^4)$$

Stefan-Boltzmann's law

- Set the upper bound to radiative transfer in far-field
- No wave phenomena are taken into account

Near-field (d<λ): Linear response theory (**Rytov**, **Polder** and **van Hove**)

- Fluctuating currents inside each body
- Fluctuation-dissipation theorem

⇨ Radiative heat flux (Landauer-like expression)

Temperature

$$\langle J_i(\mathbf{r})J_k(\mathbf{r}')\rangle \propto N(\omega,T)\mathrm{Im}(\varepsilon)$$

Material properties

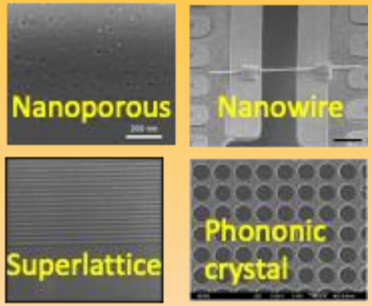
$$\varphi(T_1,T_2) = \sum_{\text{EM modes}} \hbar\omega[N(\omega,T_1) - N(\omega,T_2)]\mathcal{T}^{\alpha}$$

Transmission coefficient

D. Lacroix

Numerical methods:
Monte Carlo method for solving the BTE

Nanostructures



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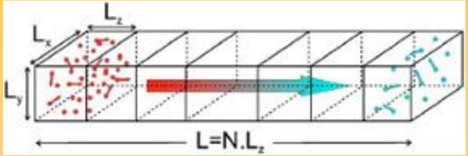
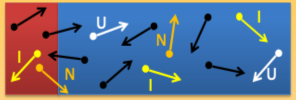


$$+\quad \frac{\partial f}{\partial t}+\nabla_K\omega\cdot\nabla_r f+F\cdot\nabla_p f=\left.\frac{\partial f}{\partial t}\right|_{scat}$$

Drift

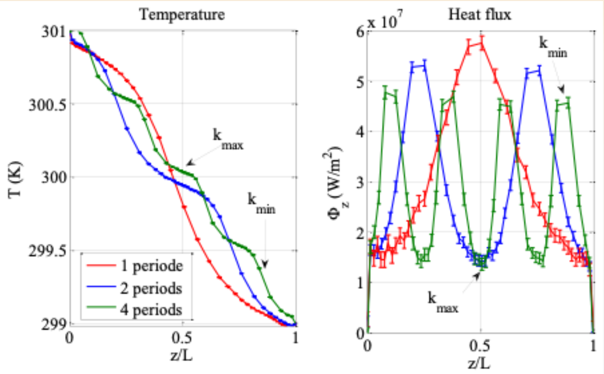
$$r(t+\delta t)=r(t)+v_g(\omega,p)\,\delta t$$

Scattering

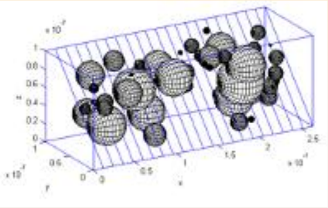


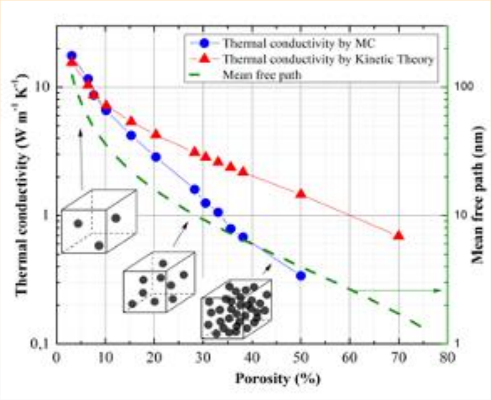
$$P_{scat}=1-\exp\left[\frac{-\delta t}{\tau(\omega,p,T)}\right]$$

Modulated nanowire

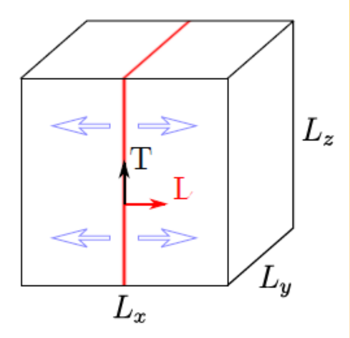


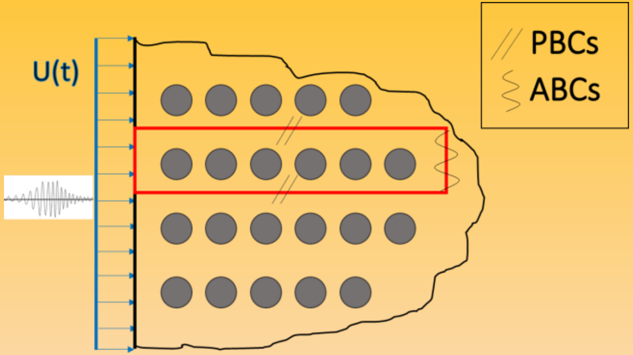
Nanoporous film





Simulation Methods: Wave Packet Dynamics





A wave-packet is generated and its propagation in the material investigated by MD or FEM

Different regimes can be evidenced

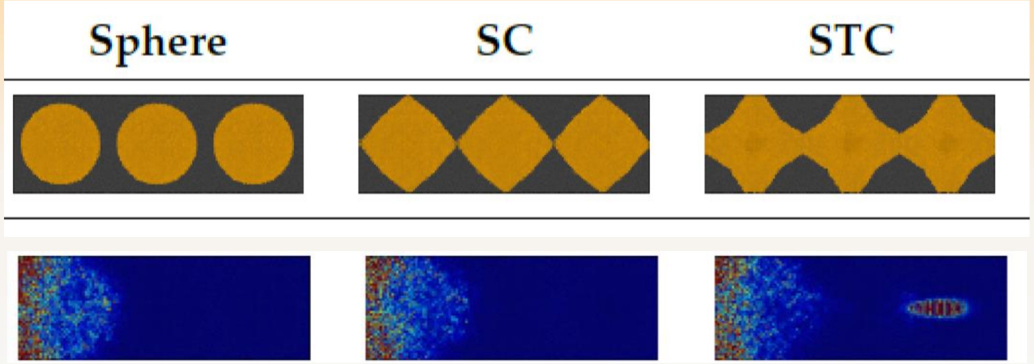
propagatif

propagating+diffusif

localization

H. Luo et al. (2020)

Effect of the nanostructure geometry



10 THz

P. Desmarchelier et al. (2021)

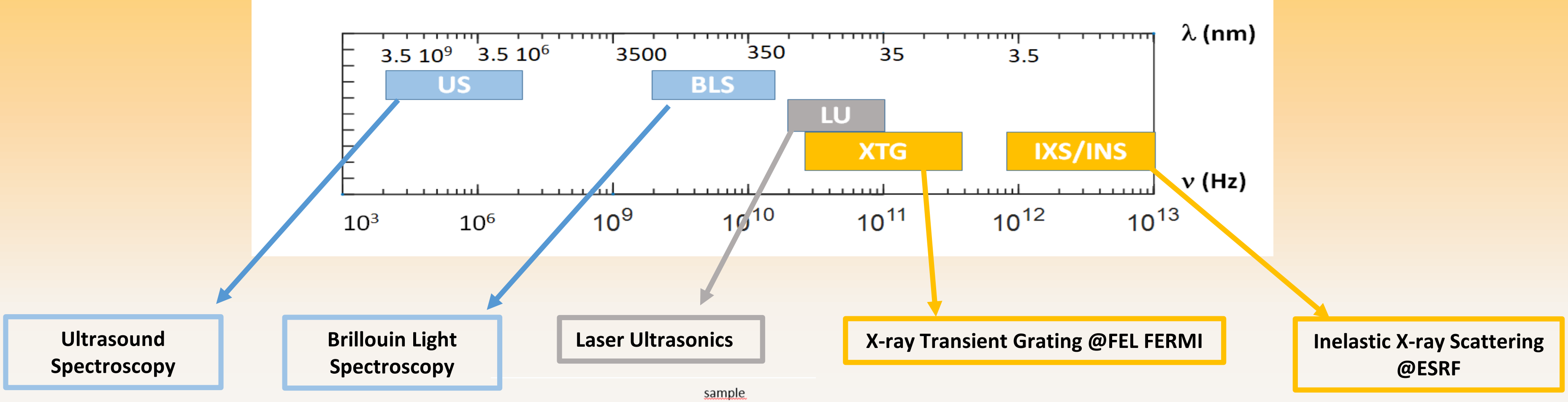
Experimental techniques to access individual carriers properties

Phonon measurements

Heat transport is mainly assured by acoustic phonons, with a distribution centered at the dominant wavelength

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

→ Depending on T we want to access phonons with wavelengths from macroscopic to sub-nanometric.



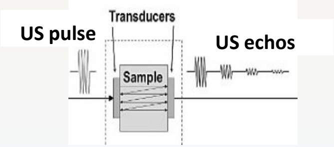
Ultrasound Spectroscopy

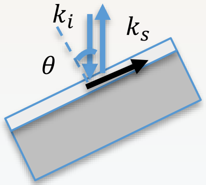
Brillouin Light Spectroscopy

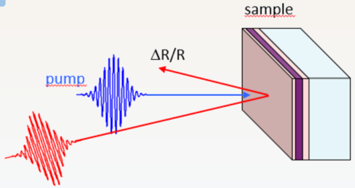
Laser Ultrasonics

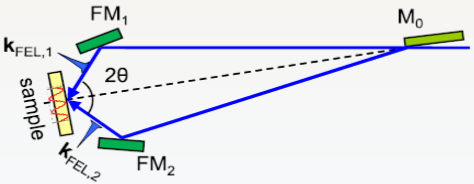
X-ray Transient Grating @FEL FERMI

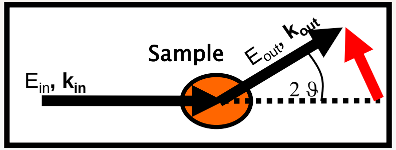
Inelastic X-ray Scattering @ESRF







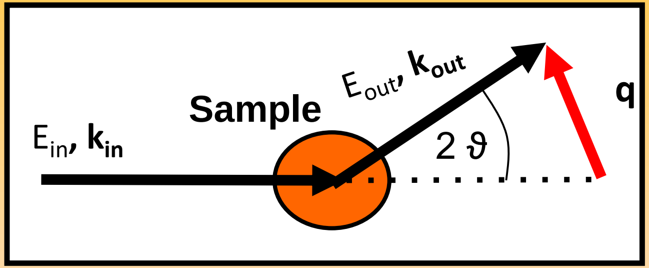




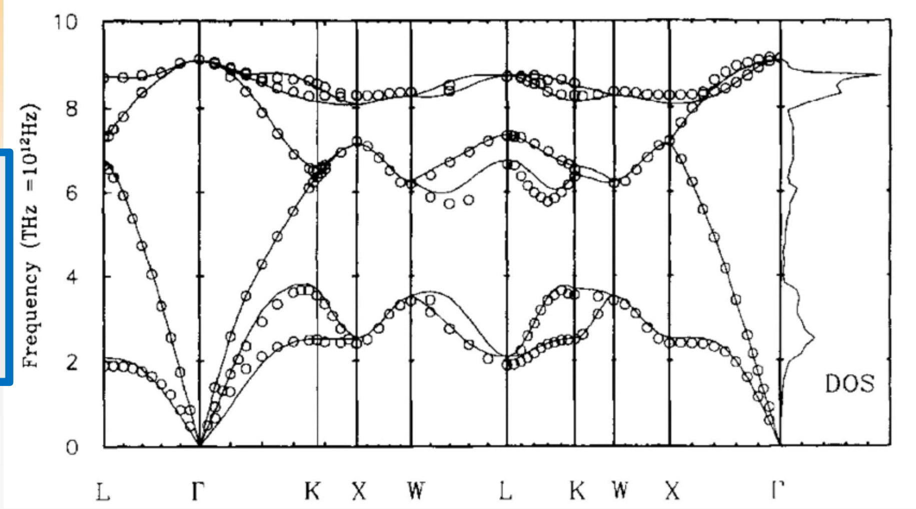
V. Giordano

From nm to sub-nm wavelengths: Inelastic neutrons and x-ray Scattering

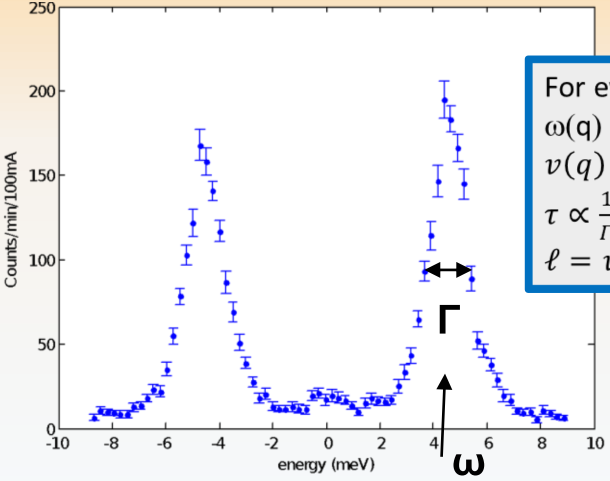
Neutron Reactors, 3rd generation synchrotron sources



Acoustic and optic modes
in the whole Brillouin
Zone



Ge Transverse Mode at a given q



For every direction:

$\omega(q)$ → energy

$v(q) = {}^{\partial\omega}/_{\partial q}$ → velocity

$\tau \propto \frac{1}{\Gamma}$ → lifetime

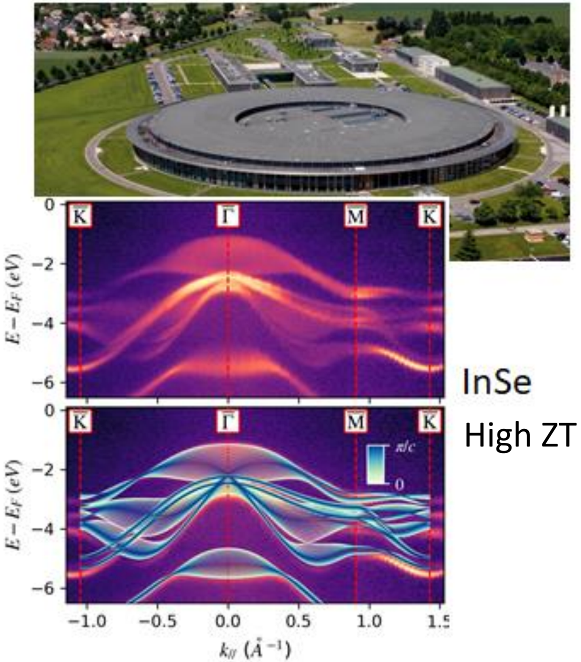
$\ell = v\tau$ → Mean Free Path

Electronic band structure and phonons

Nano Angle resolved photoemission spectroscopy (Nano ARPES)

Band structure

ARPES at synchrotron SOLEIL



InSe

High ZT

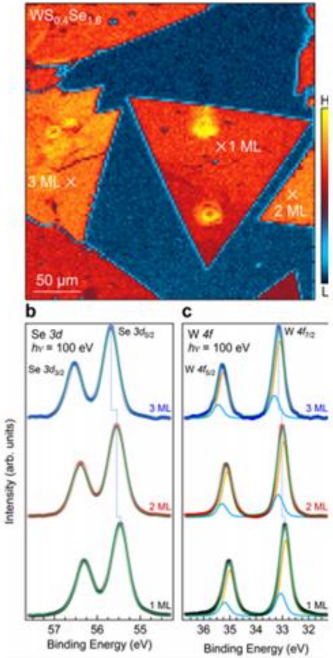
Henck, H et al. (2019),
Physical Review Materials, 3(3), 034004.

Measurement of the electronic band structure (valence band) of material with high ZT or interesting for thermoelectricity

Sub micrometer spatial resolution
5mV-50mV of energy resolution

Band structure

Nano XPS on $WS_{2(1-x)}Se_{2x}$ alloys



Novels
2D
materials

Ernandes, C et al. (2021). *npj 2D Materials and Applications*, 5(1), 1-7..

The Atelier 2 team

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