Heat, atoms and fluctuations

from the covalent crystal to complex systems

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Outline

1 - Why studying heat-transfers at the nanoscale ?

2- Thermal physics from an atomistic point of view
fluctuation/dissipation and the linear response theory

3 - Selected examples and size effects :

(wave vs. particle nature of phonon)

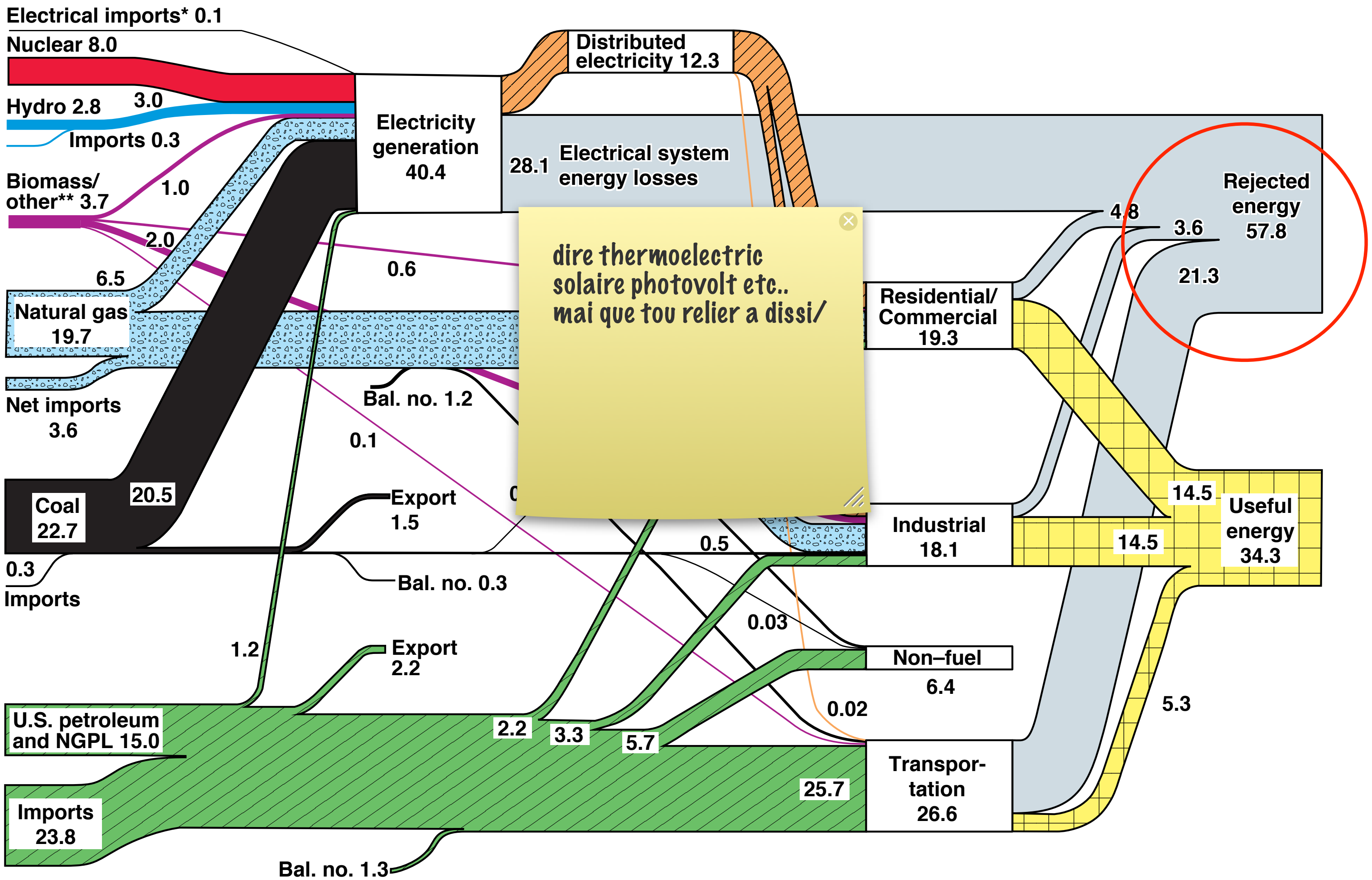
(A microscopic description of phonon transmission at interfaces)

(How classical electrodynamics fails at the nanoscale)

4 - Toward biological complex systems

Heat dissipation : A burning issue !

U.S. Energy Flow Trends – 2000
Net Primary Resource Consumption 98.5 Quads

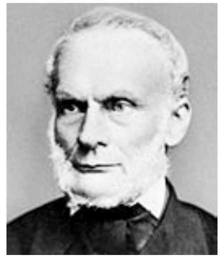


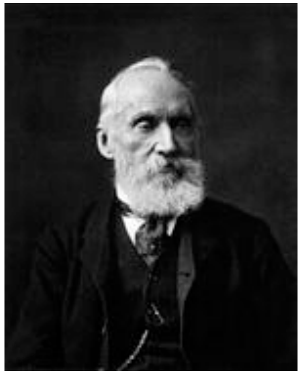
Source: Production and end-use data from Energy Information Administration, *Annual Energy Review 2000*
*Net fossil-fuel electrical imports
**Biomass/other includes wood and waste, geothermal, solar, and wind.

December 2001
Lawrence Livermore
National Laboratory
http://eed.llnl.gov/flow

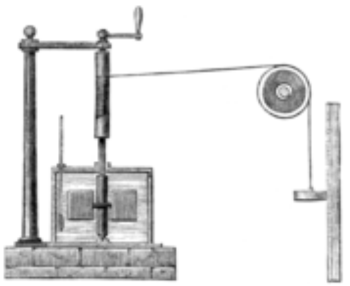
Source : annual energy review

Two centuries of scientific development around the concept of «heat»





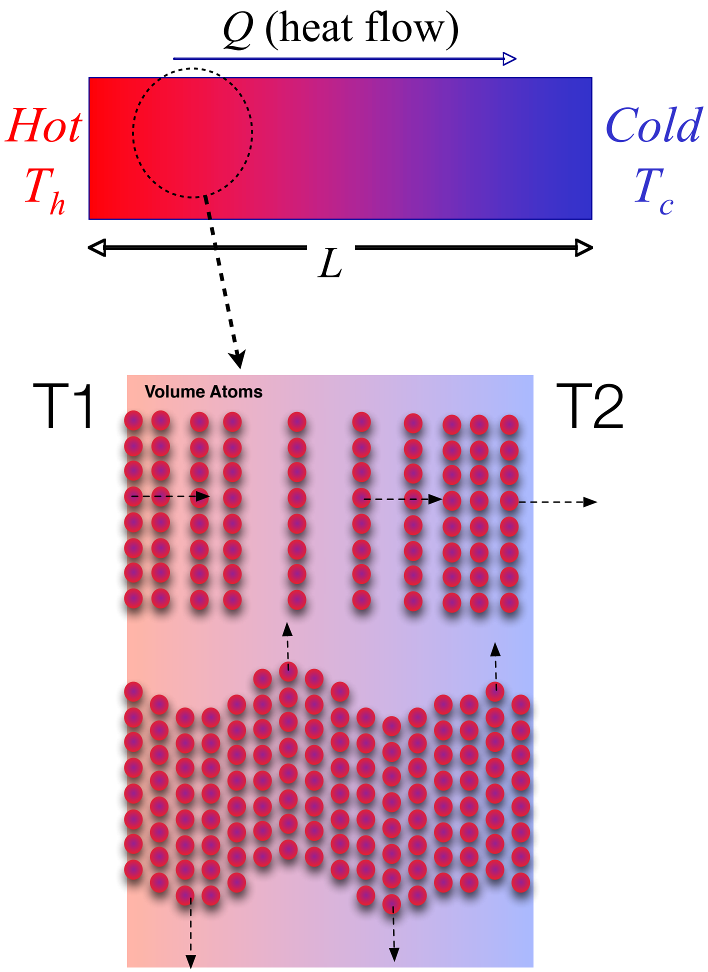
Fahrenheit	1724	Mercury thermometer
Bernoulli	1752	M/P
Lavoisier	1783	1st Calorimeter
Laplace	1789	M/P
Fourier	1807	**Differential eq. of conduction (T) in solids**
Joule & Waterson	1848	**Kinetics theory of gas**
Fourier	1822	**Analytic theory of heat**
Carnot	1828	Heat flux and work
Thomson	1842	Similarity bt/ heat eq, and electrostatic
Fick	1855	Fourrier eq. to diffusion
Clausius	1858	**Introduces the concept of «mean free path»**
Kirchoff	1859	Emission and absorption of radiation thermal Equilib.
Maxwell	1867	Diffusion eq. for gas, distribution functions.
Nernst	1888	Fick law : force and resistance.
Bachelier	1900	Betting in Finance and Heat eq.
Planck	1900	Theory of thermal radiation - concept of «quanta».
Einstein	1905	**Brownian motion**
Langevin	1908	stochastic eq.
Fermi	1936	Similarity bt/ Neutron Diffusion and heat eq.
Ritov	1960	Connection between radiation spectrum and current fluctuations.



source des images : wikipedia

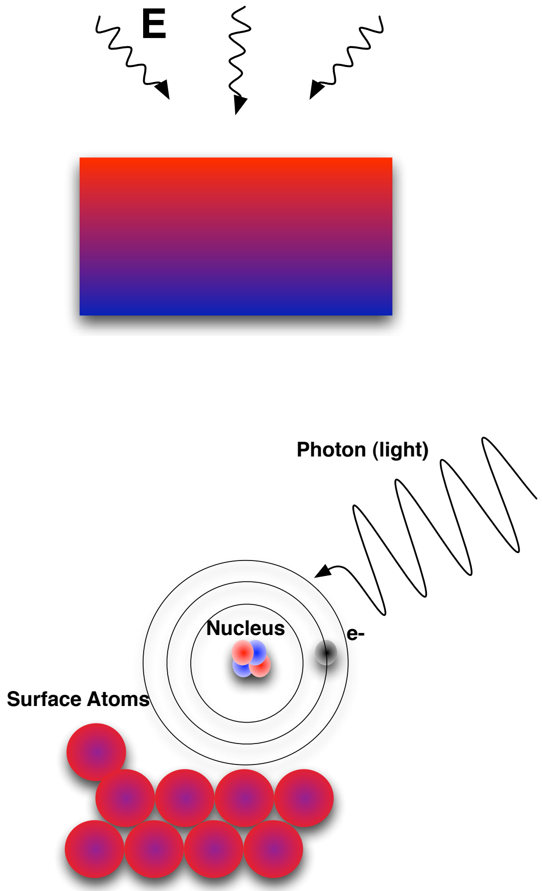
3 modes of heat transfers and their microscopic pictures :

Conduction



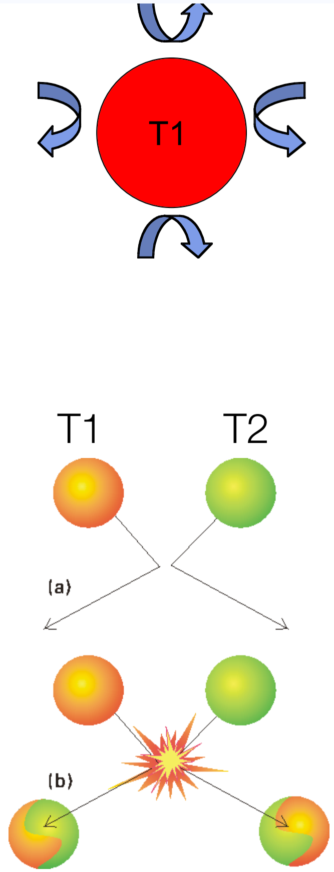
(Atomic Vibrations = **phonons**)

Radiation



(photons/electrons)

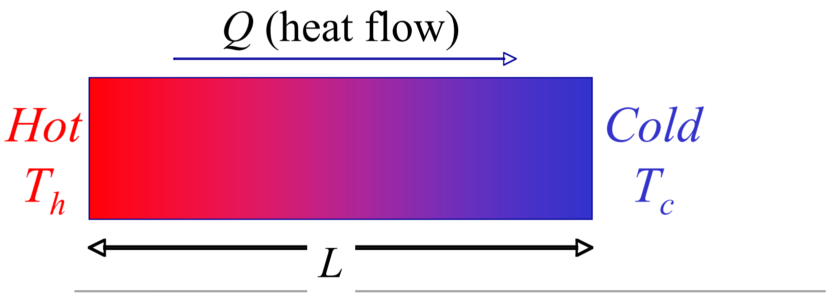
Convection/ diffusion



(molecules/ions)

Heat transfers and their caracteristic scales

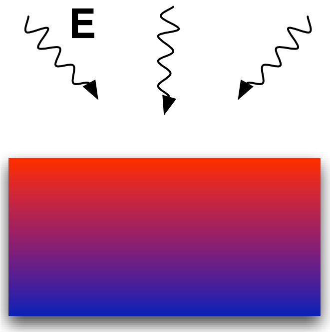
Conduction



$$\frac{\partial T}{\partial t} = \frac{k}{\rho C_p} \nabla^2 T$$

relaxation time (t ~ **10^{-12}s)**
Mean free path (L ~ **10^{-9}m)**

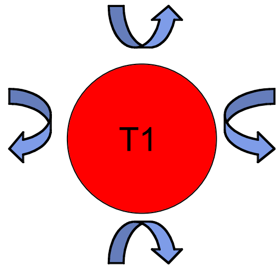
Radiation



$$P_{abs} = \frac{d\mathbf{P}}{dt} \cdot \mathbf{E}(t)$$

wavelength (L ~**10^{-6}-10^{-8}m)**
skin depth (L ~**10^{-9}m)**
screening length (L ~**10^{-10}m)**

Convection



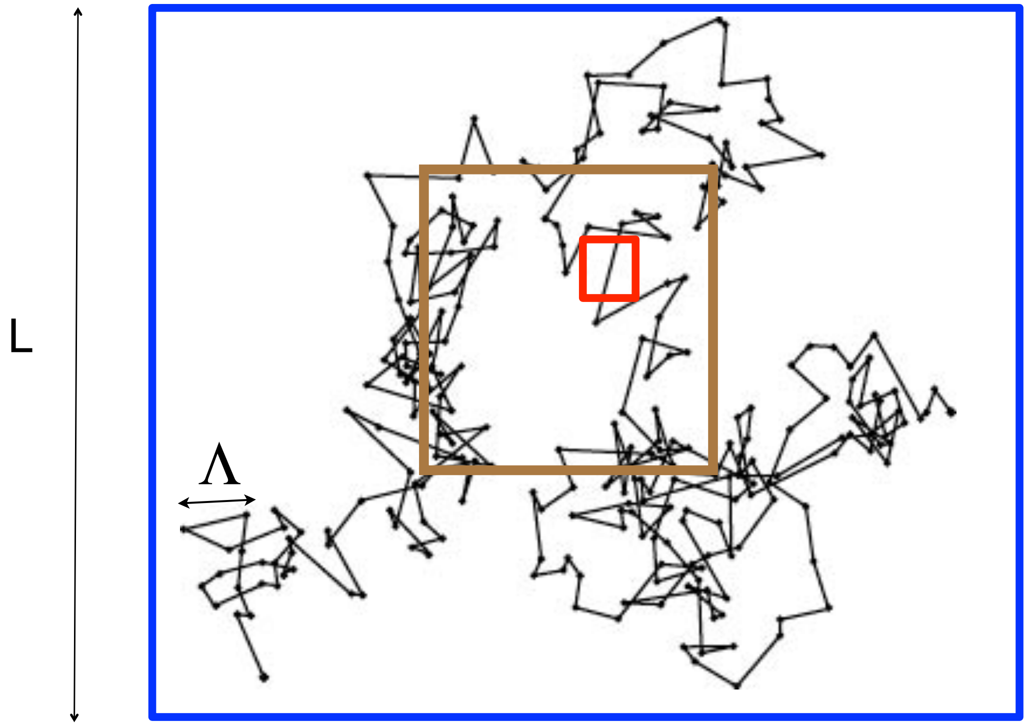
$$\frac{\partial T}{\partial t} = -\frac{hS}{\rho C_p V}(T_2 - T_1)$$

L ~ mean free path
t ~ time of flight

Nanoscale heat transfers = Thermal properties of materials bellow their caracteristic time and length scales !

e.g limit of a macroscopic description

$\lambda = 1/3\ C\ v\ \Lambda$



Dissusive vs. ballistic transport

e.g - The break down of the classical Fourier Law

Fourier Law

Heat flux — Temperature Gradient — thermal conductivity

$$\phi = -k\nabla T$$

energy conservation

$$\rho C_p \frac{\partial T}{\partial t} = -\nabla \cdot \phi$$

Heat Equation

$$\nabla^2 T = \frac{1}{a}\frac{\partial T}{\partial t}$$

$$a = k / \rho C_p$$

$$T(t,\mathbf{r}) = \frac{1}{(4\pi a t)^{3/2}} e^{-\frac{r^2}{4at}}$$

Instantaneous modification of the temperature field !

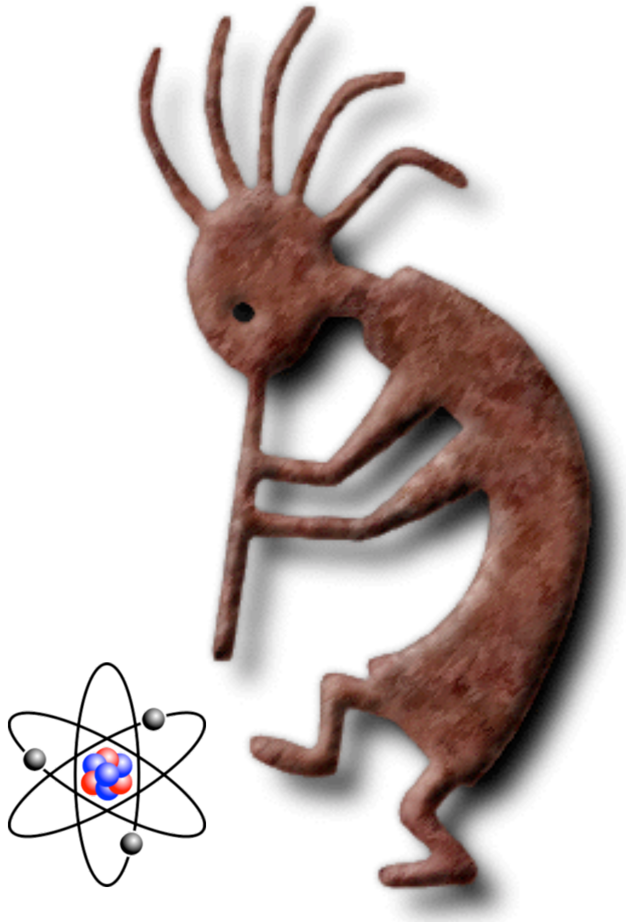
Modified Heat Eq.

$$\tau \frac{\partial \phi}{\partial t} + \phi = -k\nabla T$$

a microscopic dynamics of heat carriers !

Question

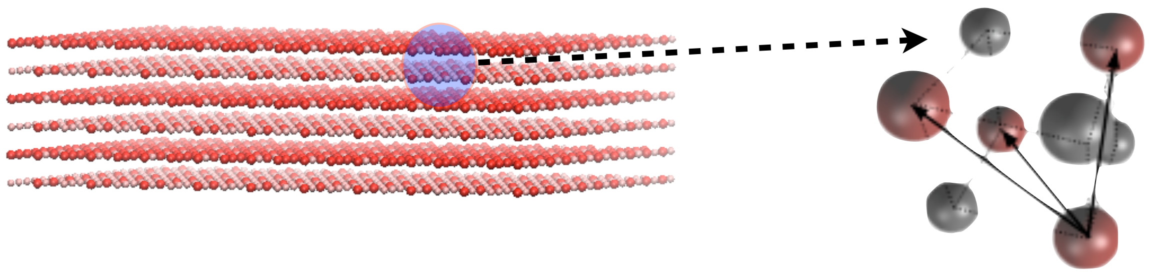
How possibly can we capture some thermal properties of matter at an atomic level ?



...e.g. with Molecular dynamics simulations

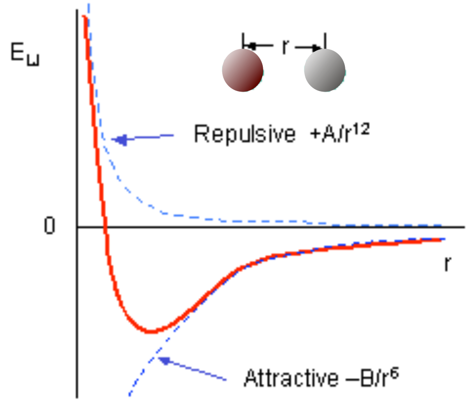
1) Cristallographic **STRUCTURE**

unit-cell e.g [CFC]



2) Atomic **INTERACTION**

$$\mathbf{F}_i = -\nabla \mathbf{r_i} \sum_{i \neq j} \frac{V(r_{ij})}{2}$$



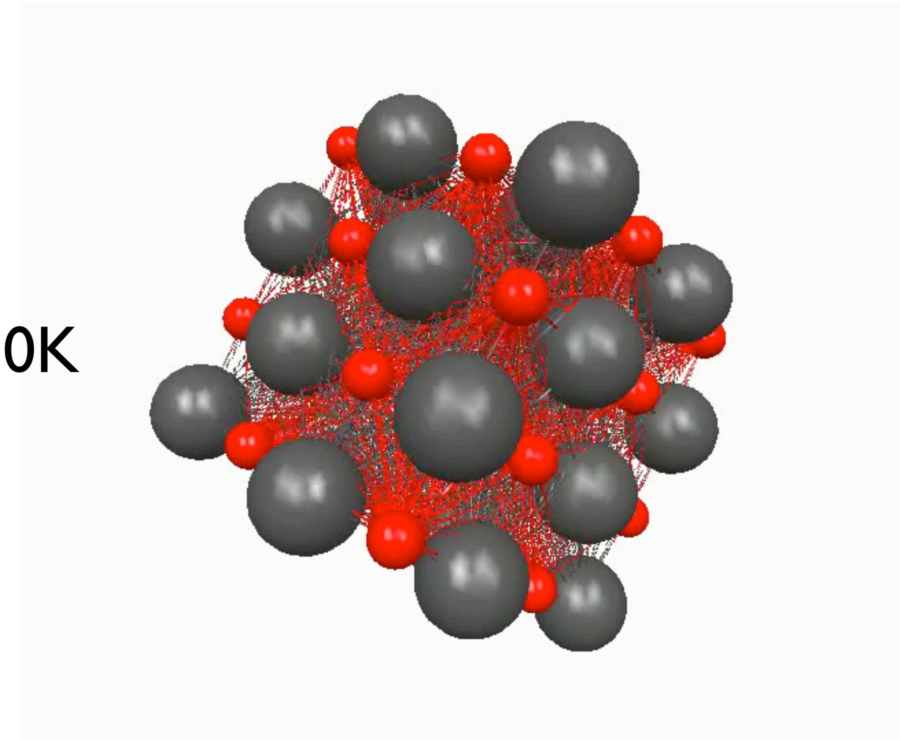
3) Time domain **DYNAMICS**

{X(t),V(t)}

$$m\ddot{\mathbf{r}}_i = \mathbf{F}_i(\{\mathbf{r}_j\})$$

Equilibrium Fluctuations
$\{x_i, p_i\}$ @ $t_1, t_2, t_3...$

T>0K



Phonon properties from equilibrium <u>fluctuations</u>
-> The quest of <u>correlation</u> functions

Physical properties and atomic fluctuations ?

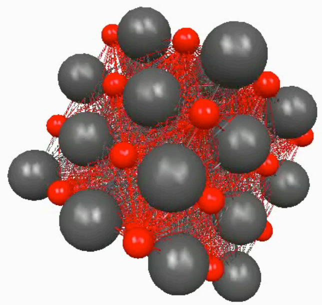
[Excitation] → Response function [Susceptibility] → [Reponse]

(e.g external force) (out of equilibrium)

$$R = \chi_e \cdot E_{ext}$$

Response — Susceptibility — Excitation

Macroscopic response arises from the Microscopic dynamics !!



GREEN-KUBO

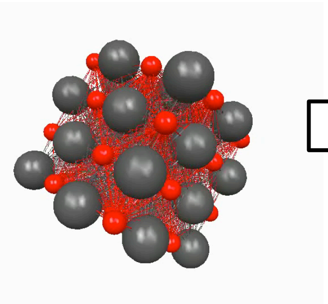
$$\chi_e \Rightarrow \chi(\omega) = \frac{1}{3}\left\{ \beta\left\langle R^2(0)\right\rangle + i\omega\int_0^{\infty} e^{i\omega t}\left\langle R(t=0)\cdot R(t)\right\rangle dt \right\}$$

Absorption (Dissipation)

Fluctuations

Static limit for T.C

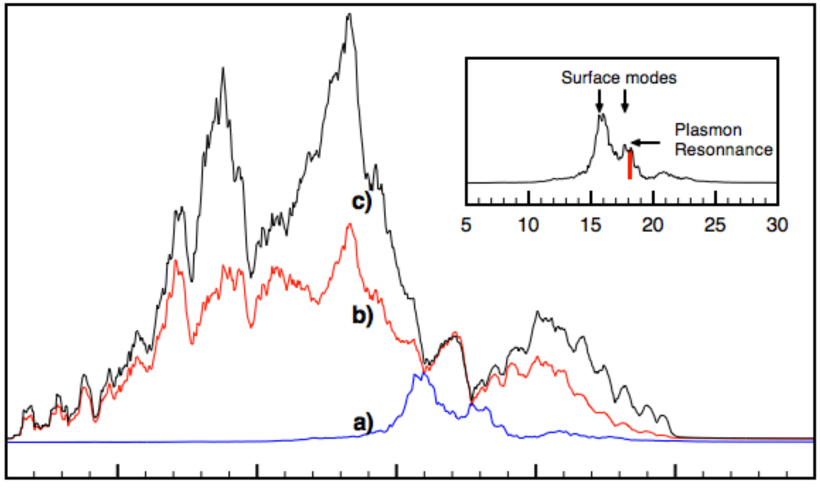
e.g #1 Phonon Properties from fluctuations



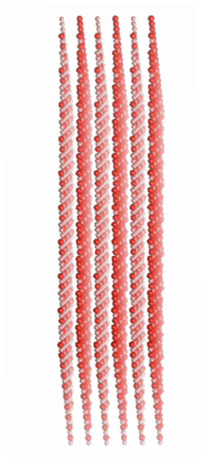
Phonon Density of states (LDoS)

$$g\frac{k_B\langle T\rangle}{2} = \frac{m}{2}\langle v(o)\cdot v(t)\rangle$$

$$g(\omega) \propto \beta\sum_i m_i \int_{-\infty}^{\infty} \langle v_i(0)v_i(t)\rangle e^{i\omega t}dt$$



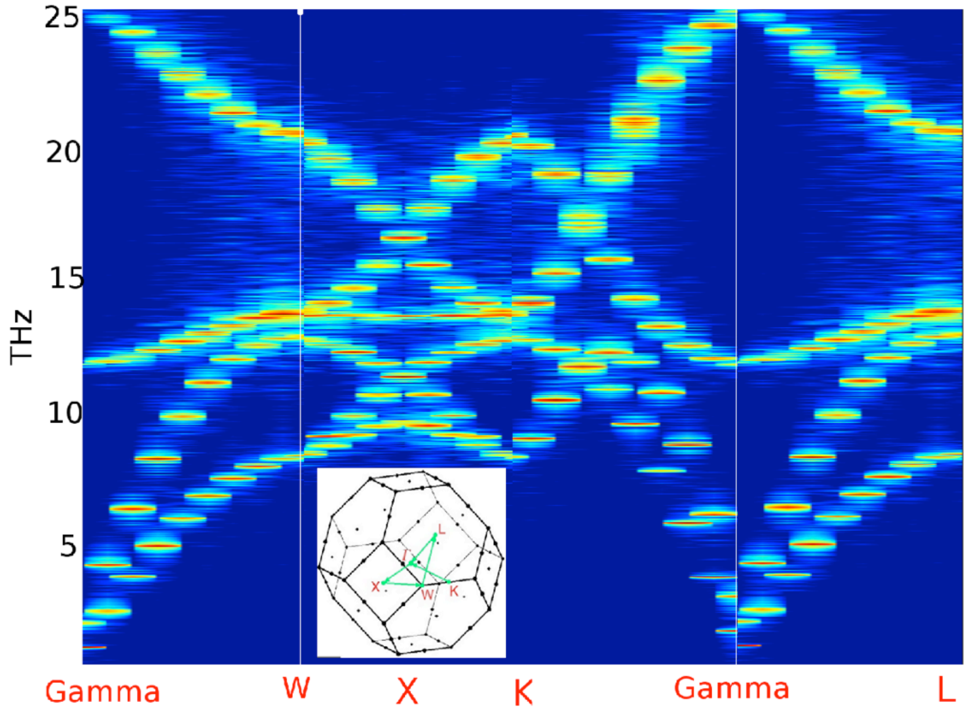
e.g MgO



Phonon Dispersion Relation

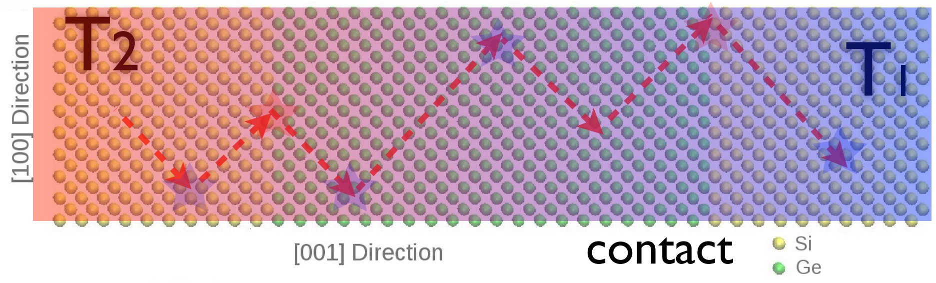
$$g(\omega,\mathbf{k}) \propto \beta\int_{-\infty}^{+\infty} \langle v(\mathbf{k},0)v(\mathbf{k},t)\rangle e^{i\omega t}dt$$

$$v_i(\mathbf{k},t) = \sum_{\mathbf{r}} v(\mathbf{r},t)e^{i\mathbf{kr}}$$



e.g #2 : The thermal conductivity

e.g semiconductor heterojunction



Heat flux and thermal conductivity

$$j = \kappa \cdot \nabla T$$

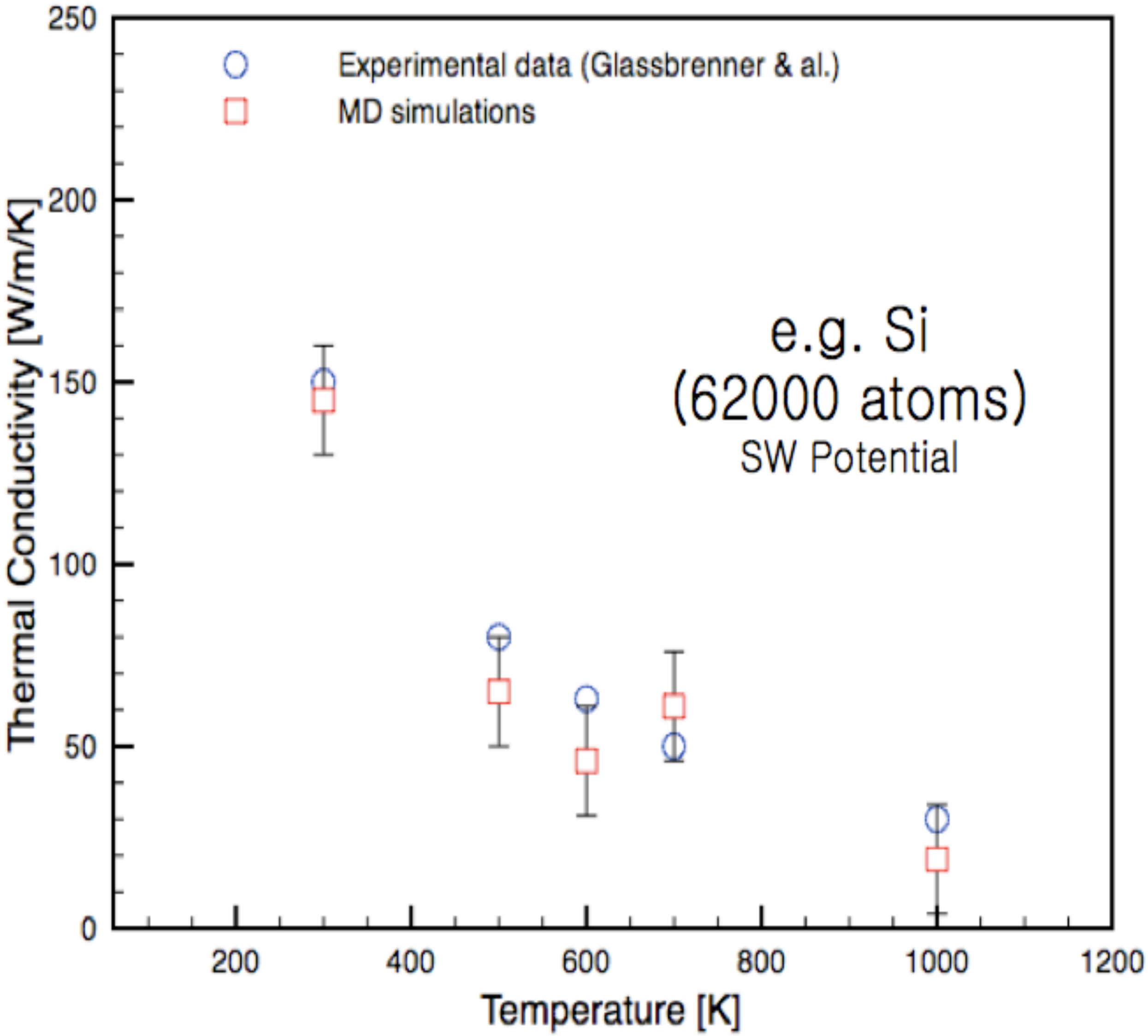
Equilibrium approach

(Green-Kubo thermal conductivity)

$$\kappa = \frac{\beta}{VT} \int dt \langle \mathbf{j}(0)\mathbf{j}(t) \rangle e^{i\omega t}$$

Equilibrium approach of thermal conductivity

$$\kappa = \frac{1}{Vk_B T_0^2} \int_0^\infty \langle q(0)q(t) \rangle dt$$



Putting some numbers

For one temperature

Time step ~ 1e-15s Time simulated ~ 1e-9s 1e6 integrations of :
1e-3 to 1-4 atomes / point in the brillouin zone x20 (20 points) x3 (3 dimensions)
x10 (ensemble average)

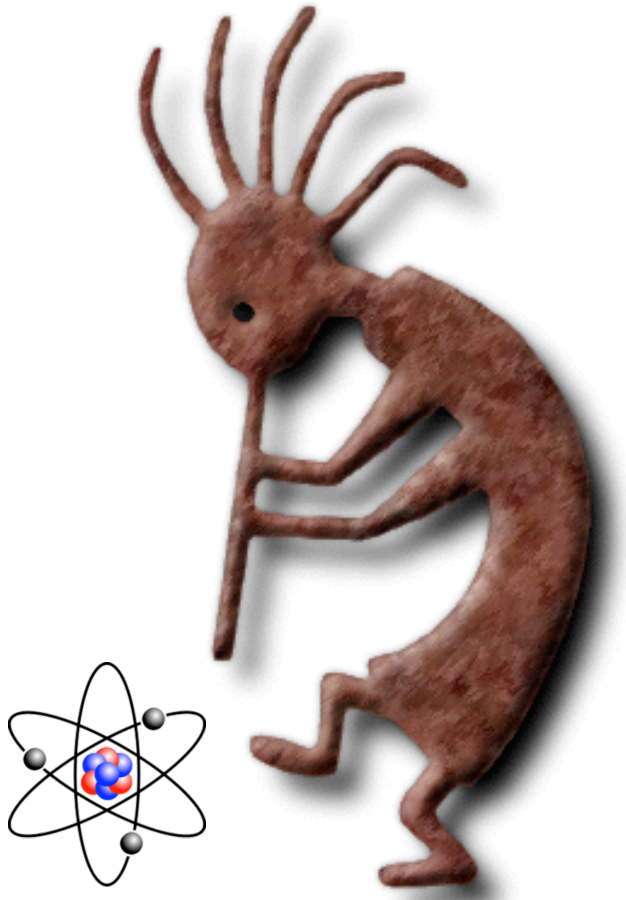
1e6 x 1e3 x 1000 = 1e12 operations for one temperature !

4 hours on 124 CPU / 100Mo HD

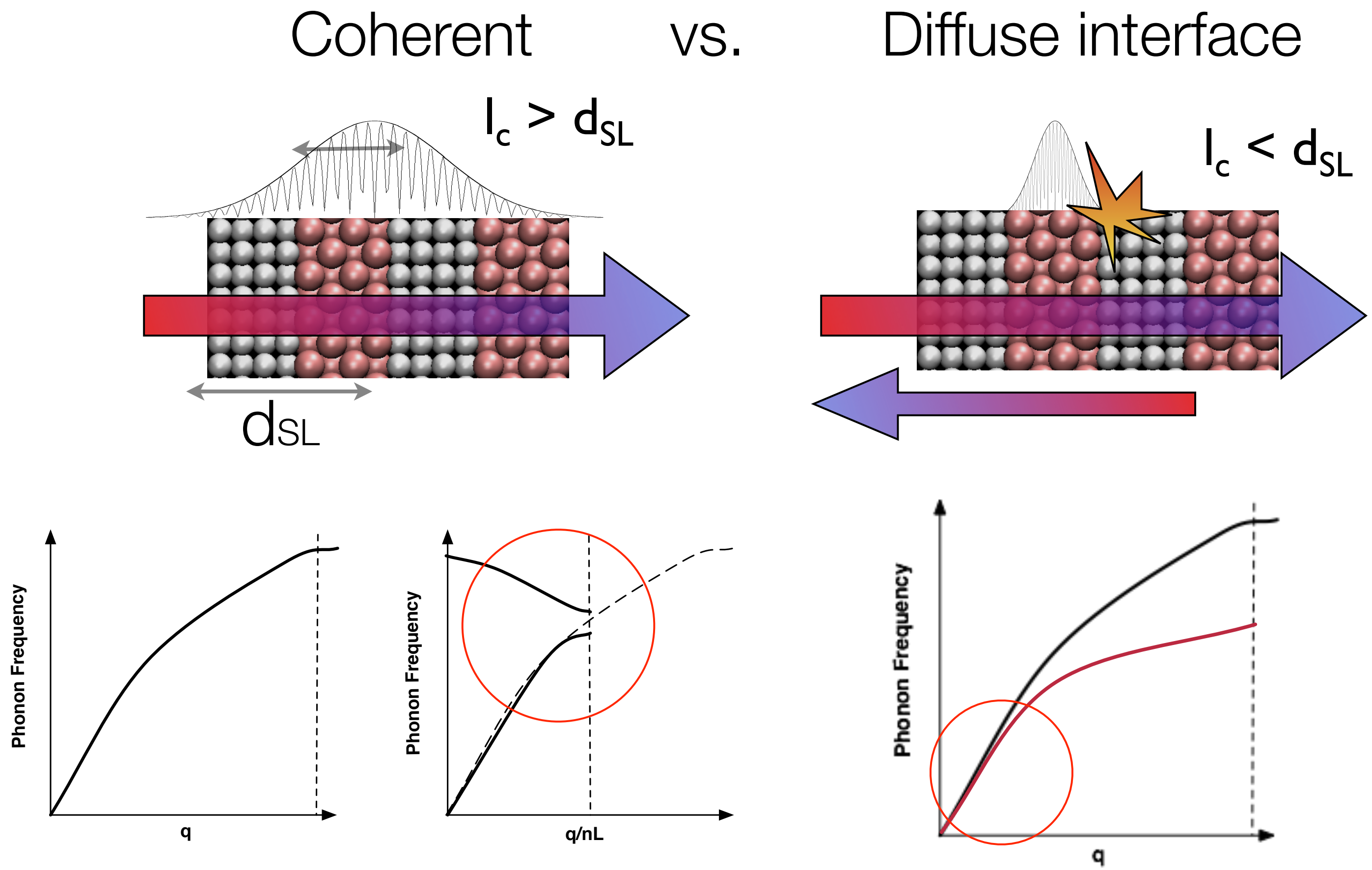
Before post-treatment...

Question :

Looking further than thermal conductivity : Can we caracterize particular transport effects ?

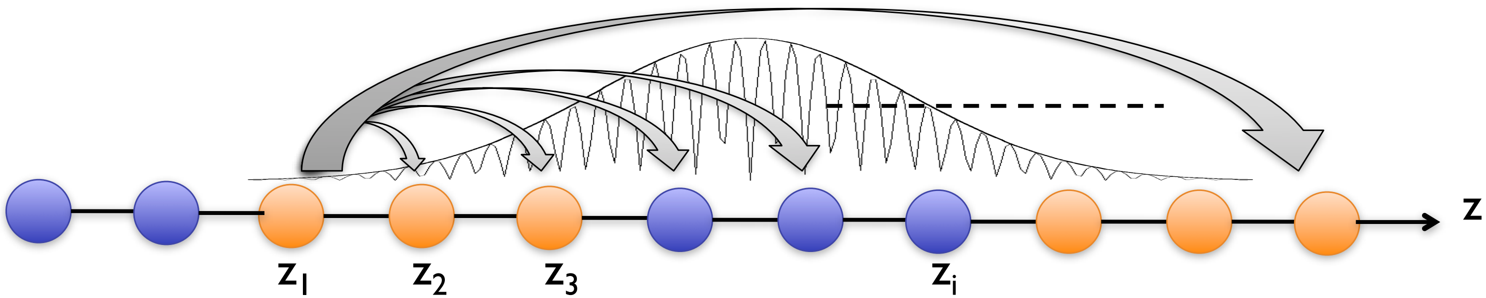


e.g #3 Toward a specific control of thermal properties : coherent vs diffuse phonon transport



Superlattice = Brillouin Zone folding

Coherence from fluctuations

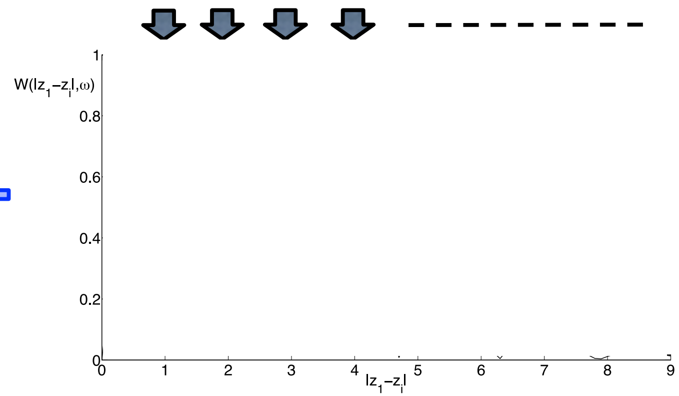


- spatial correlation of atomic displacement

$$v(z_1, t) * v(z_1 + \Delta z, t)$$

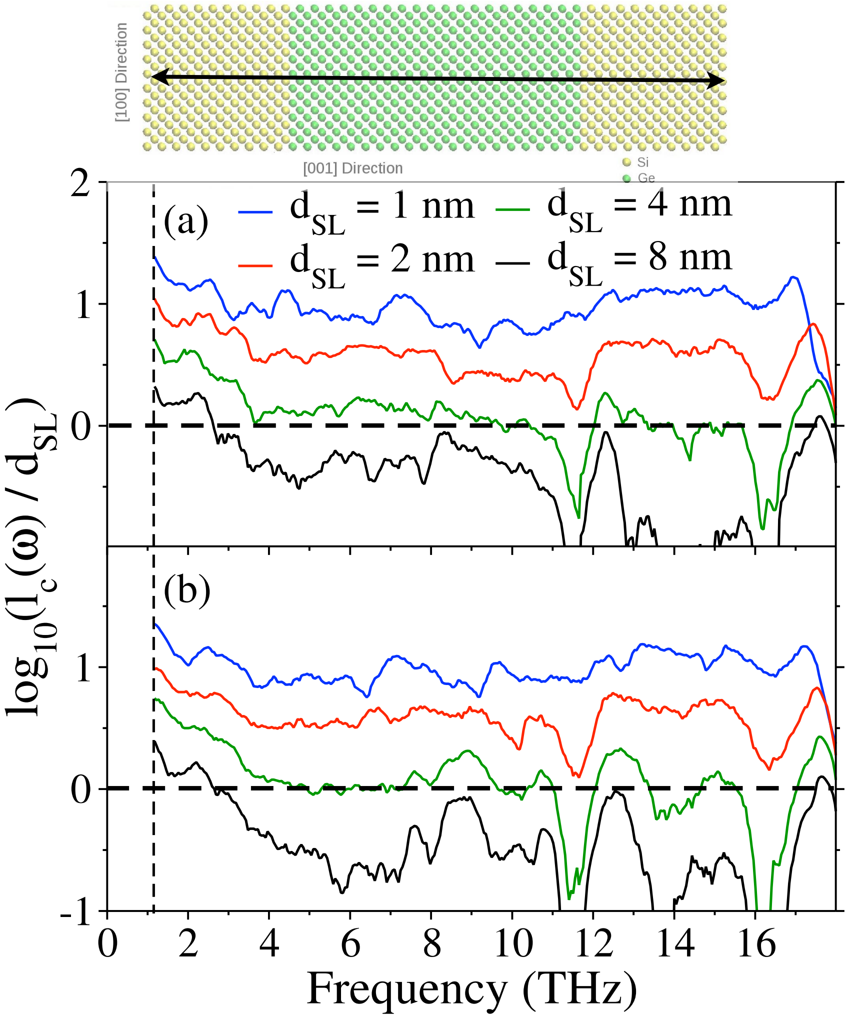
$$l_c(\omega)$$

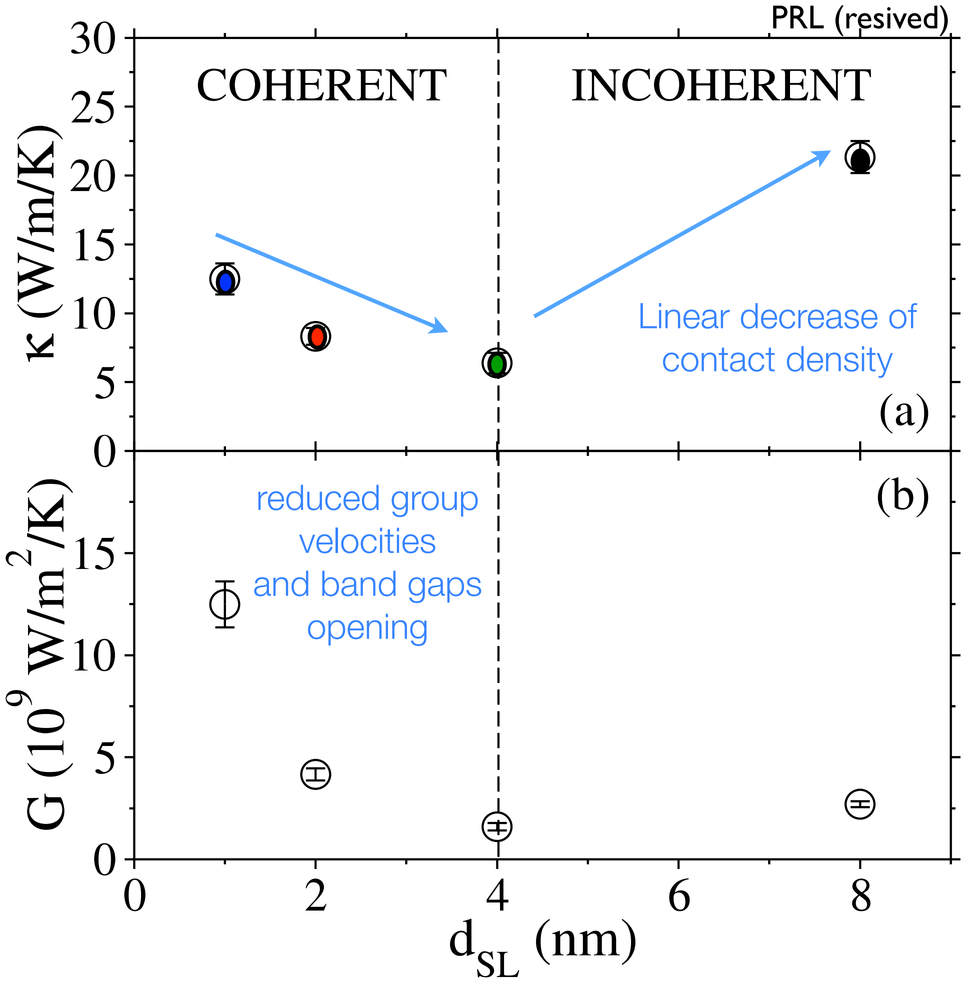
RMS of distribution



[1] Mandel L. and Wolf E., Optical coherence and quantum optics 1995

heat transport regime and the coherence length

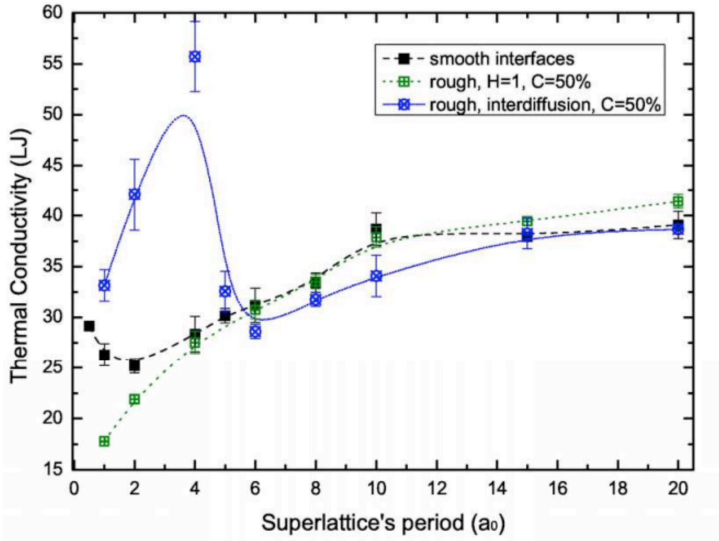


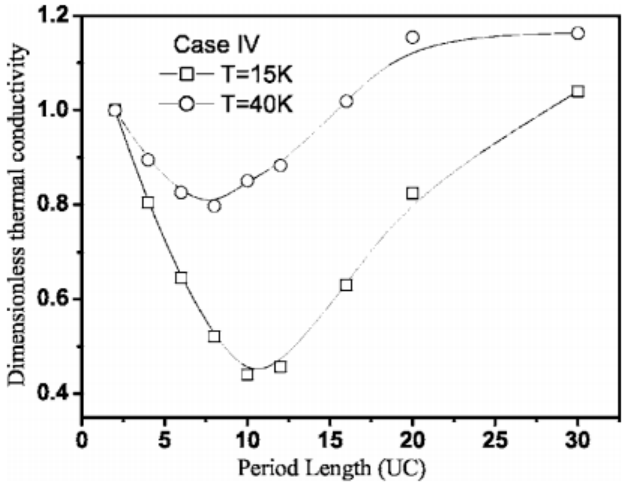


An important new caracteristic adimentioned parameter :
Lc/System length (wave vs particle !)

Simulations

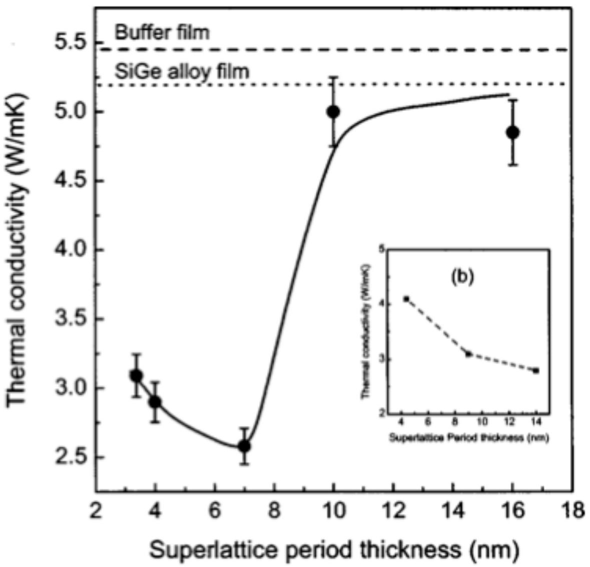
Simkin Mahan 2000
Daly 2002
Imamura 2003
Chen Y 2005
Landry 2009
Termentzidis 2010
Chalopin 2012
Lin KH 2013
Garg J 2013





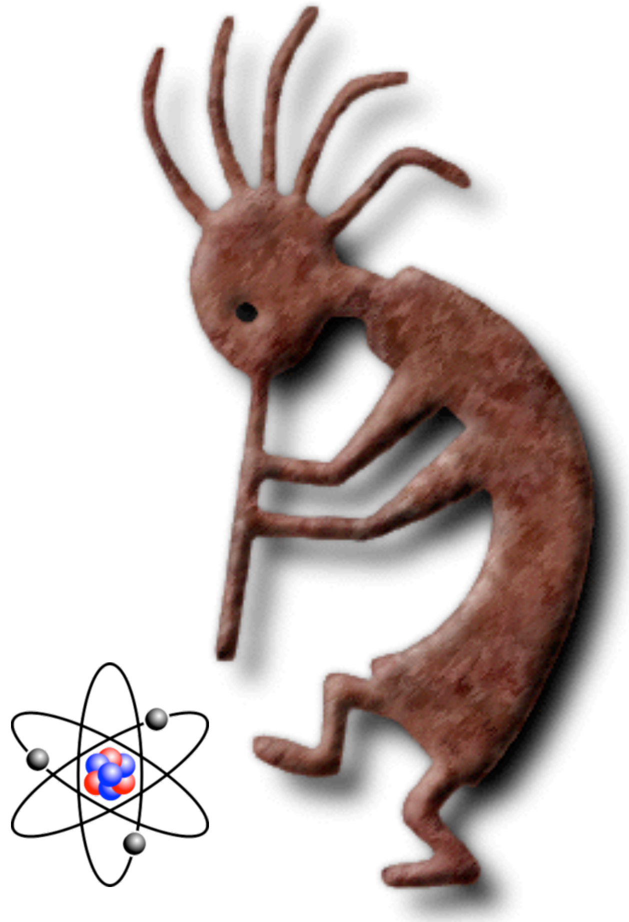
Experiments

Luckyanova 2012
Venkatasubramanian 2000
Borca-Tasciuc T 2000
Chakraborty 2003



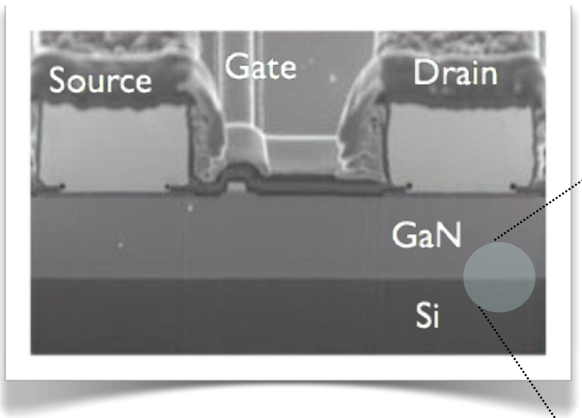
Question :

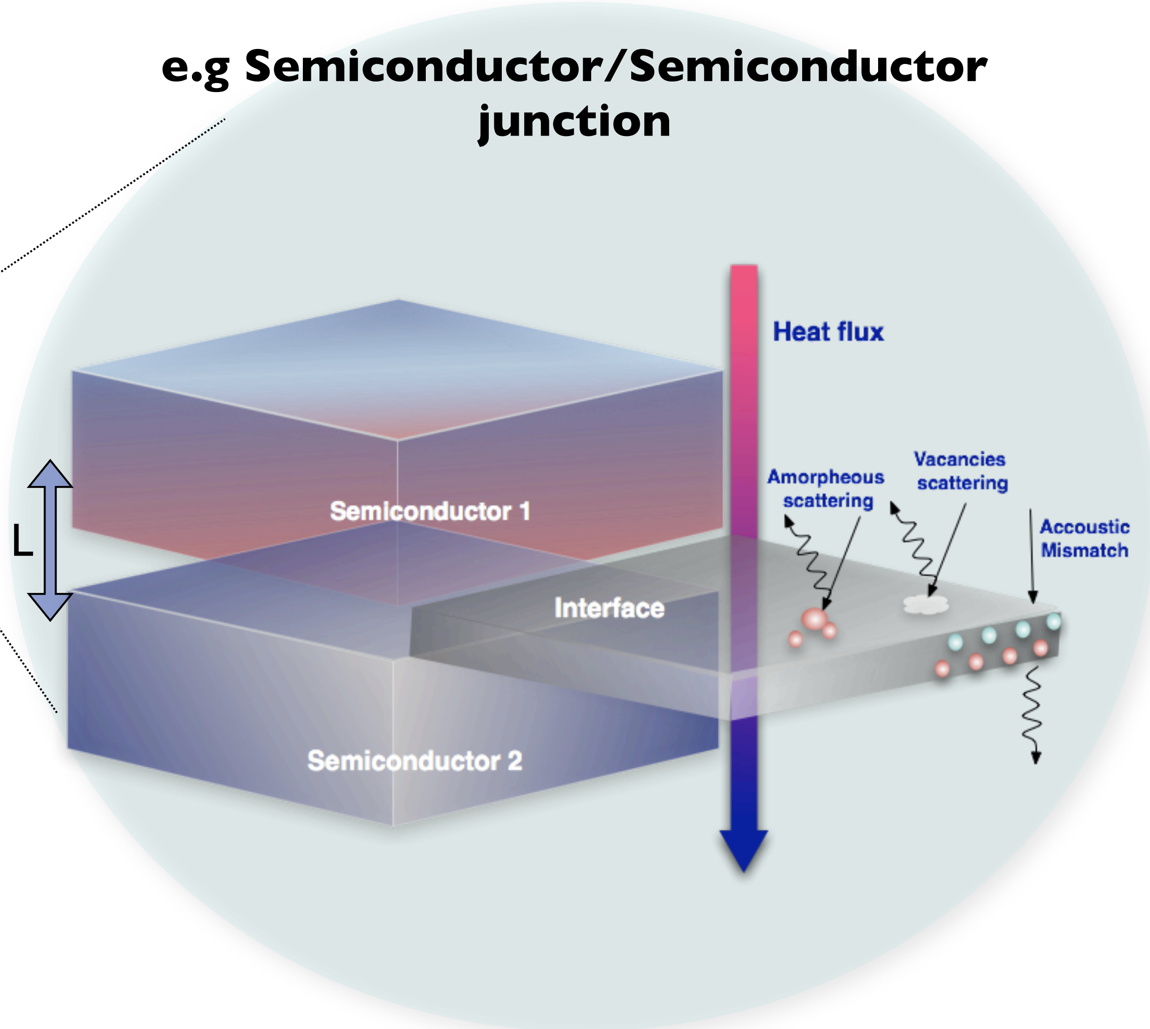
From coherent to **diffuse interface** : can we provide a microscopic description of what's a thermal interface ?



Question : Quantifying the phonon transport properties of a solid-solid interface ?

e.g Semiconductor/Semiconductor junction

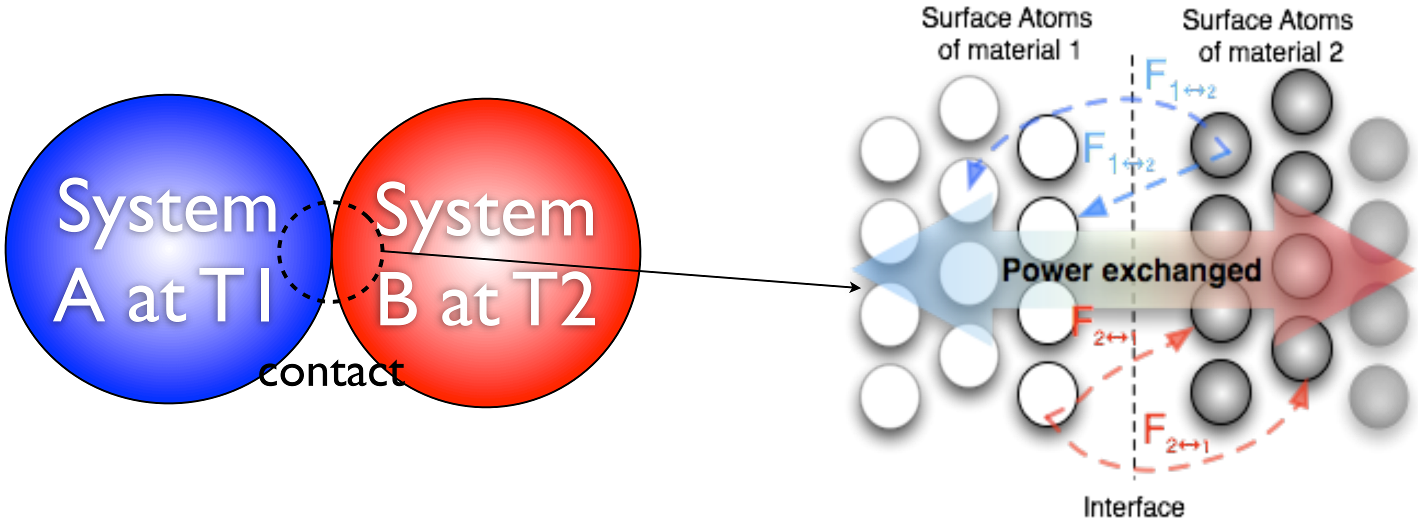




An interface affects the thermal transport due to its **atomic configuration**

- Kapitza effect
- intermixing / Roughness
- Vacancies and dislocations
- boundary scattering
- Inelastic scattering

e.g #4 : Interface Transmission from fluctuations



$$H = H_A + H_B$$

Heat Flux operator

$$H_i = \frac{1}{2}\left(\sum_{j,i} \nabla_x^2 U_{ij}(u_i - u_j) + m_i \dot{x}_i^2 \right)$$

$$J = -\langle \dot{H}_A \rangle = \langle [H, H_A] \rangle$$

<u>SPECTRAL HEAT FLUX</u>

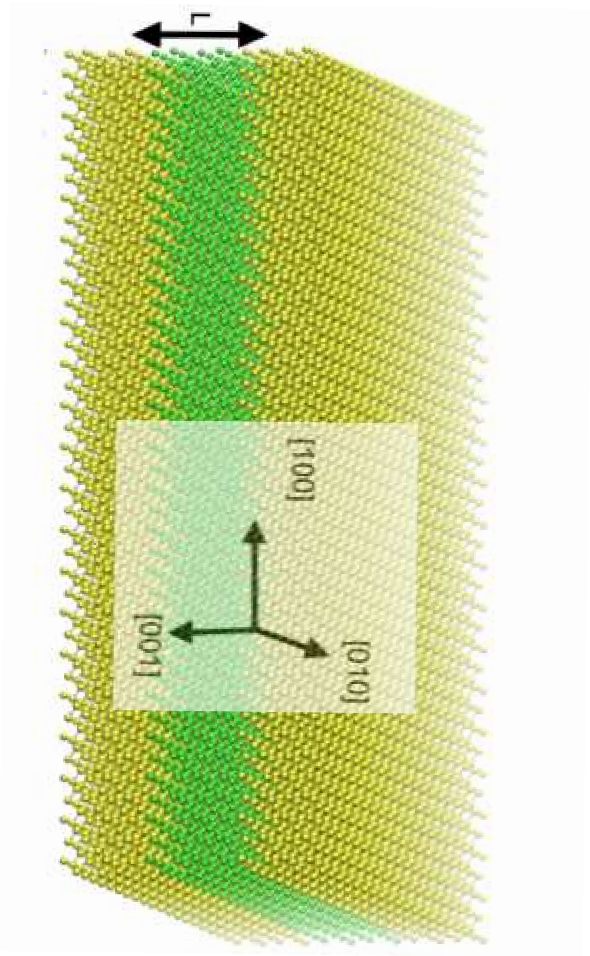
$$J(\omega) = -i\frac{\omega}{2} \sum_{i\in A, j\in B} k_{i,j}[u_i(\omega)u_j^*(\omega) - u_i^*(\omega)u_j(\omega)].$$

Chalopin et al.
PRB 2011

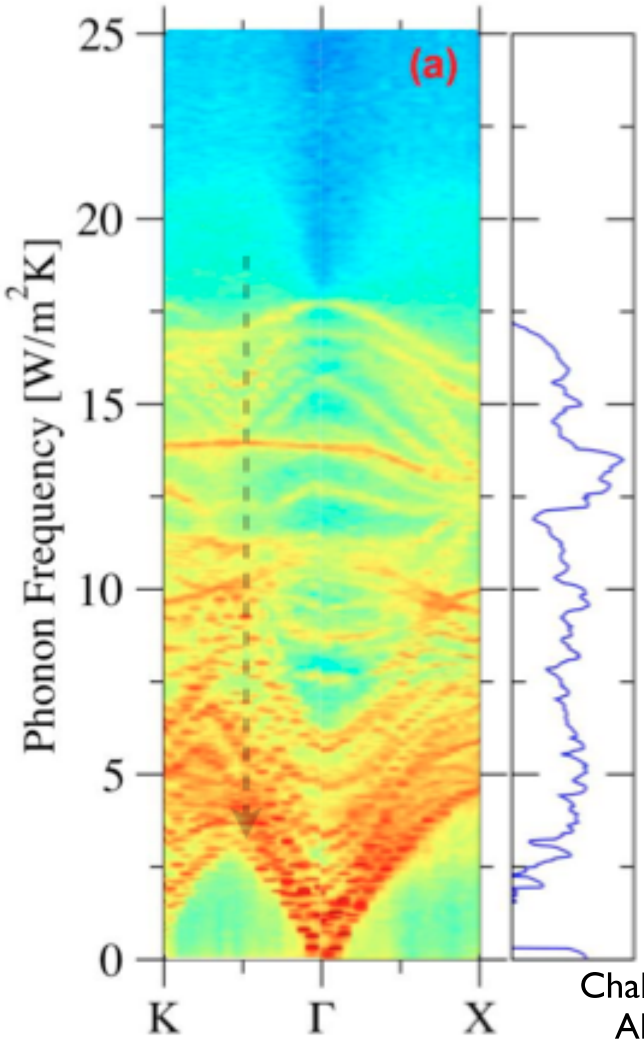
Chalopin et al.
APL 2012

e.g : Semiconductor (Si:Ge)interfaces

$$T(\omega, \mathbf{k}, \mathbf{k}') = \sum_{\substack{i \in A, j \in B \\ \alpha, \delta \in \{x,y,z\}}} \dot{u}_{\mathbf{k}}^{\alpha}(\omega) \dot{u}_{\mathbf{k}'}^{*\delta}(\omega) D_{i,j}^{\alpha,\delta}(\mathbf{k}, \mathbf{k}').$$



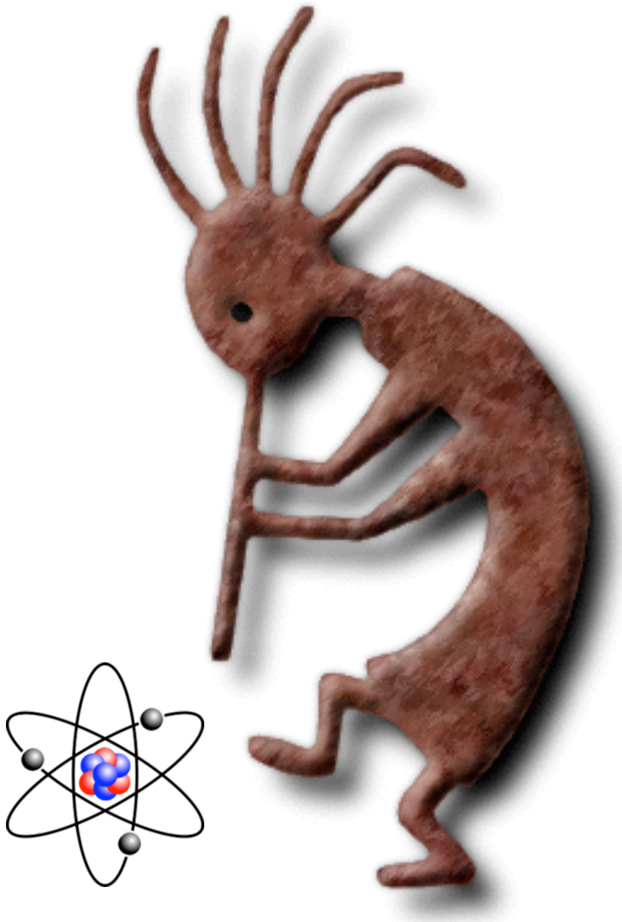
Interface Transmission (t)
«Selection rules» at the contact surface Brillouin Zone



Chalopin et al. APL 2013

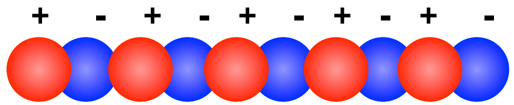
Question

phonon/phonon interface : OK
...but is there any things to look at for photons/phonons interface ?



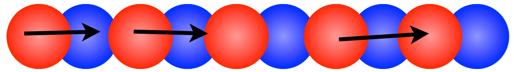
IR-Absorption and heat : the role of optical phonons

T=0K



Thermally activated dipole

T>0K



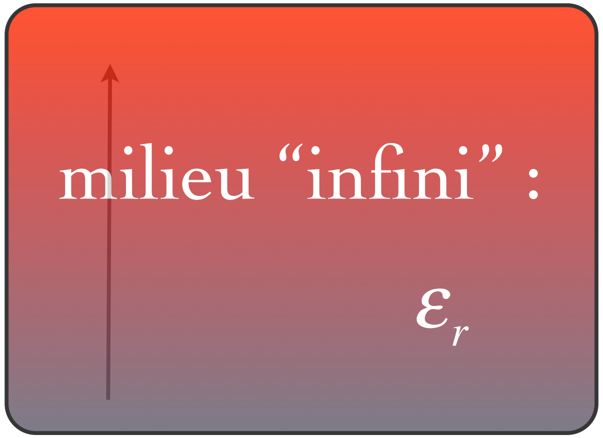
IR (THz) Aborption = Thermal activated **dipole**

Confinement and Microscopic mechanism of IR light absorption

Infinite Medium

(Averaged magnitudes, volumics, non-local...)

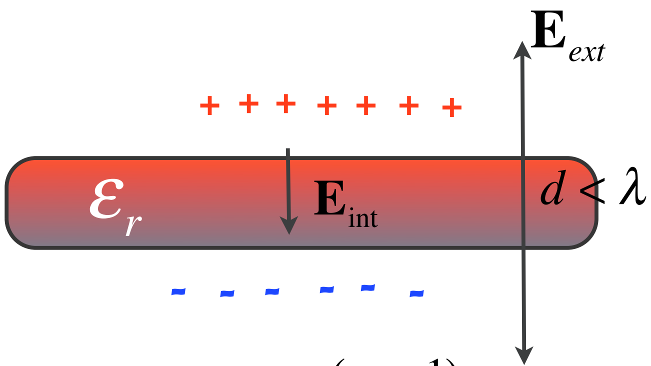
$$\mathbf{P} = \varepsilon_0(\varepsilon_r - 1)\cdot \mathbf{E}_m$$



Fresnel Coefficient well defined (interface of infinite thickness !)

Thin Films

$$\mathbf{P} = \varepsilon_0 \alpha \cdot \mathbf{E}_{\text{int}}$$

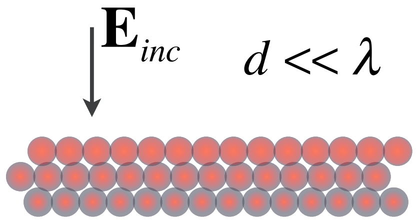


$$\mathbf{P} = \varepsilon_0 3V \cdot \frac{(\varepsilon_r - 1)}{\varepsilon_r + 1}\mathbf{E}_{ext}$$

Ns/Nv << 1

Polariton Resonnances predicted from Closius-Mossoty

Atomic Layers



Ns/Nv~1

?

e.g #5 : IR-Absorption properties from fluctuations

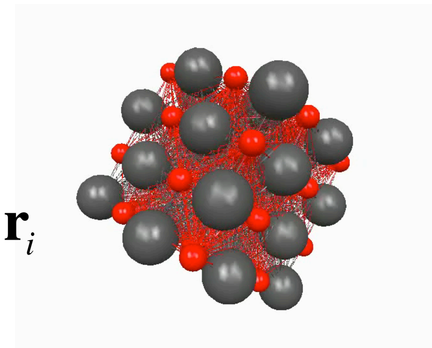
Dielectric Susceptibility

$$\mathbf{P} = \underbrace{\varepsilon_0 \alpha}\mathbf{E}_{\mathbf{ext}}$$

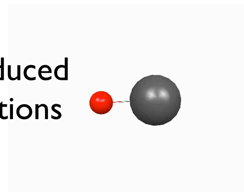
Wave-vector dependant dielectric Susceptibility

$$\chi(\omega,\mathbf{k}) = \frac{1}{3}\left\{\beta\left\langle P^2(0)\right\rangle + i\omega\int_0^\infty e^{i\omega t}\left\langle \mathbf{P}(t=0,\mathbf{k})\cdot\mathbf{P}(t,\mathbf{k})\right\rangle dt\right\}$$

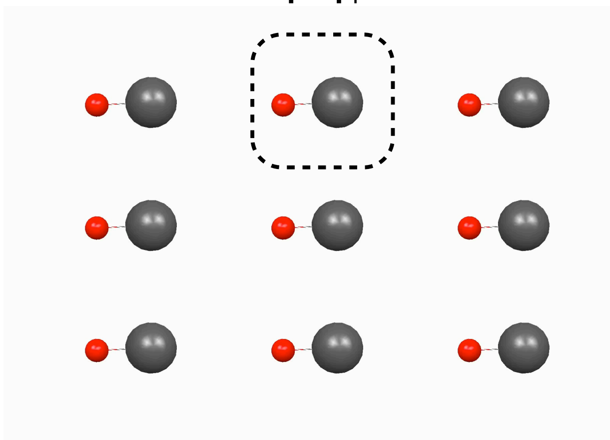
$$\mathbf{P} = \sum_i q_i \mathbf{r}_i$$



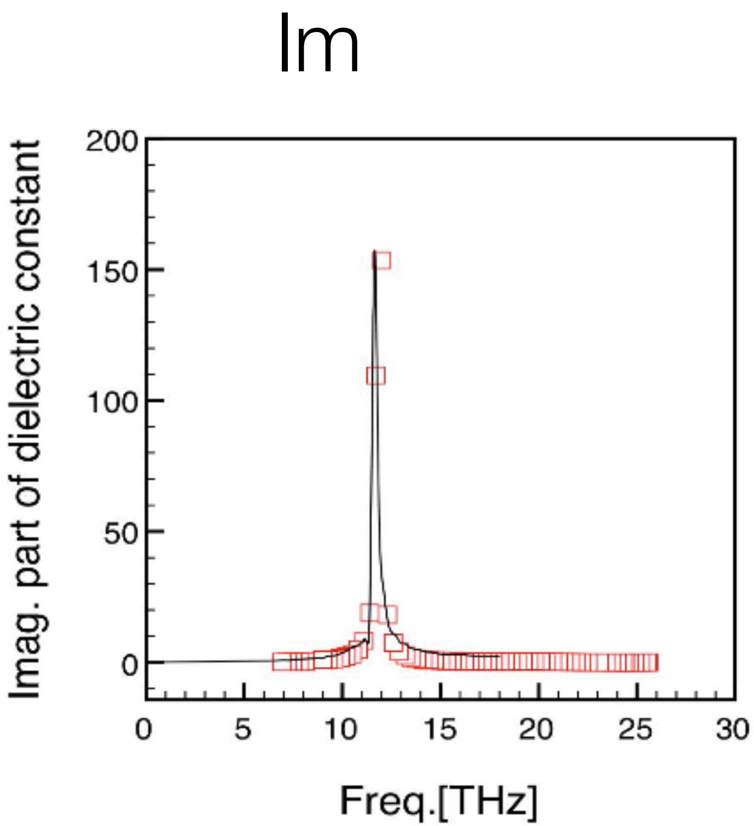
Thermal induced dipolar motions

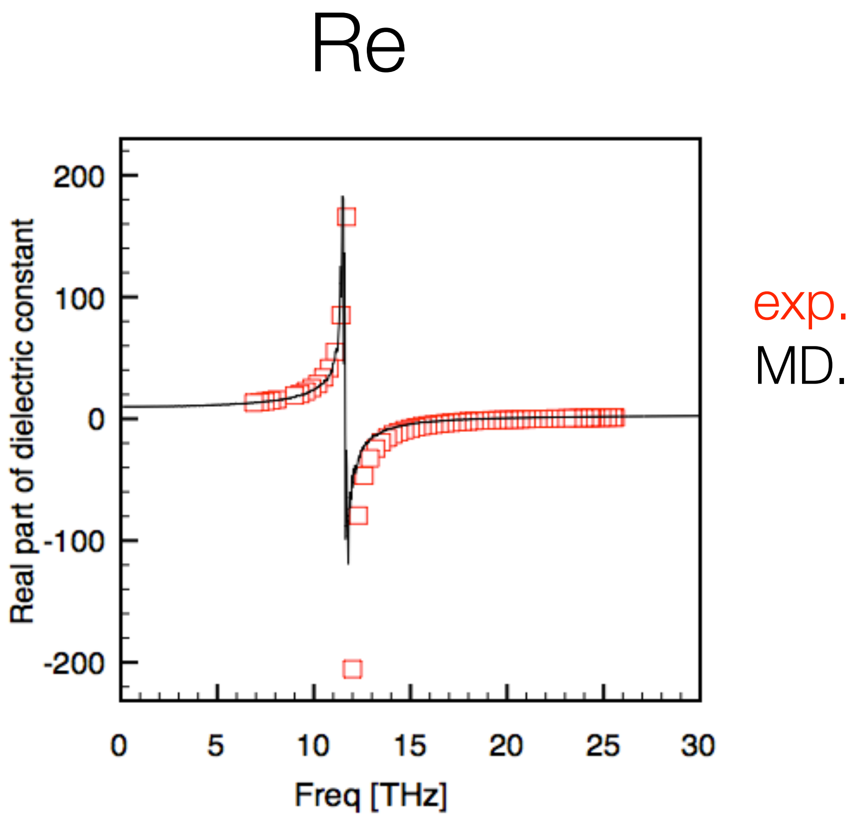


r=r$_i$

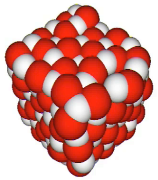


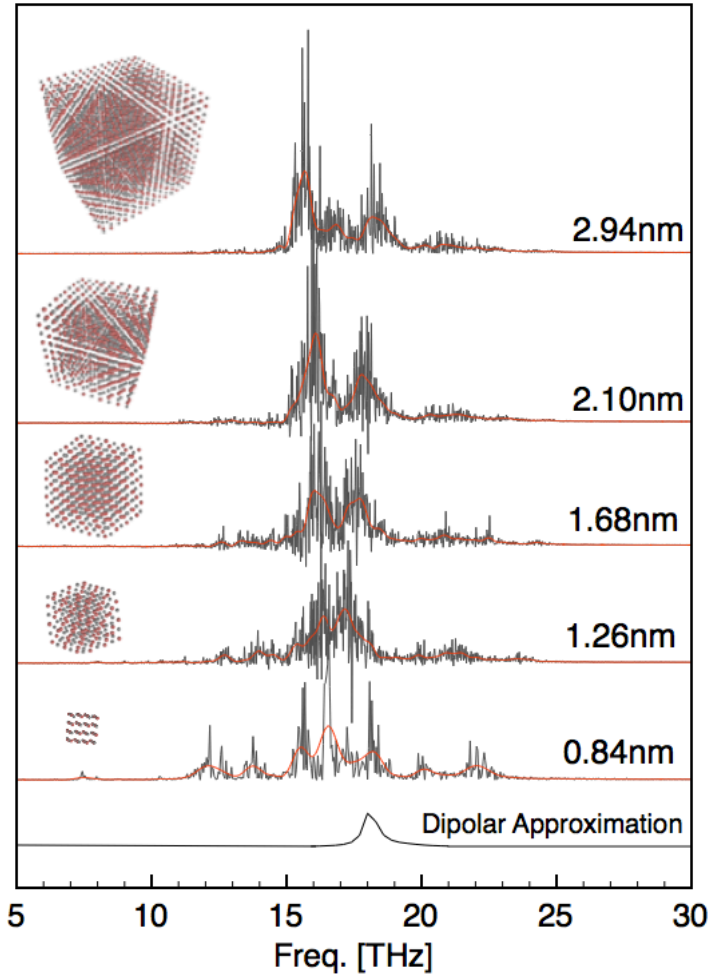
Validation with bulk



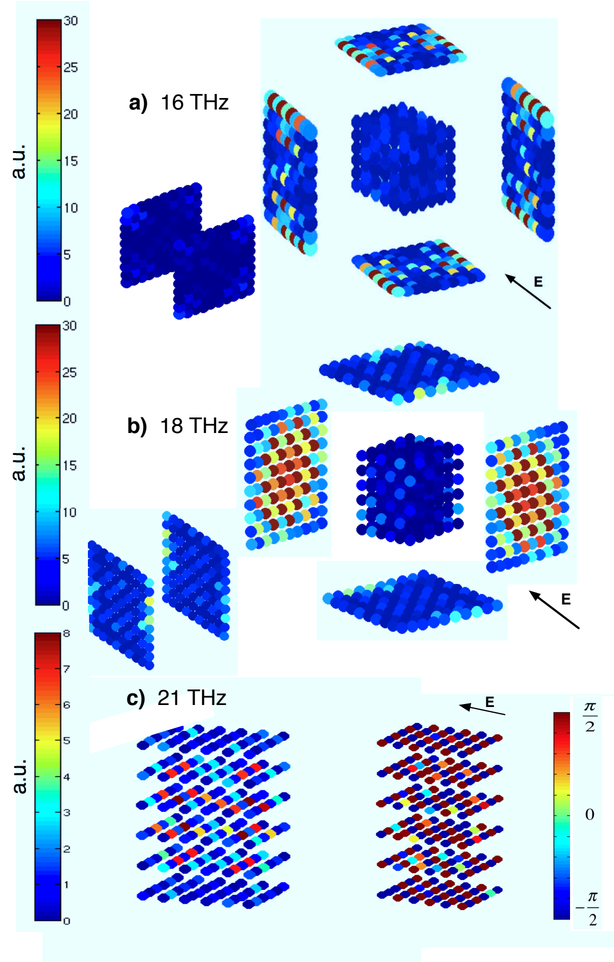


3D confinement and absorption mechanisms in clusters





surface modes !

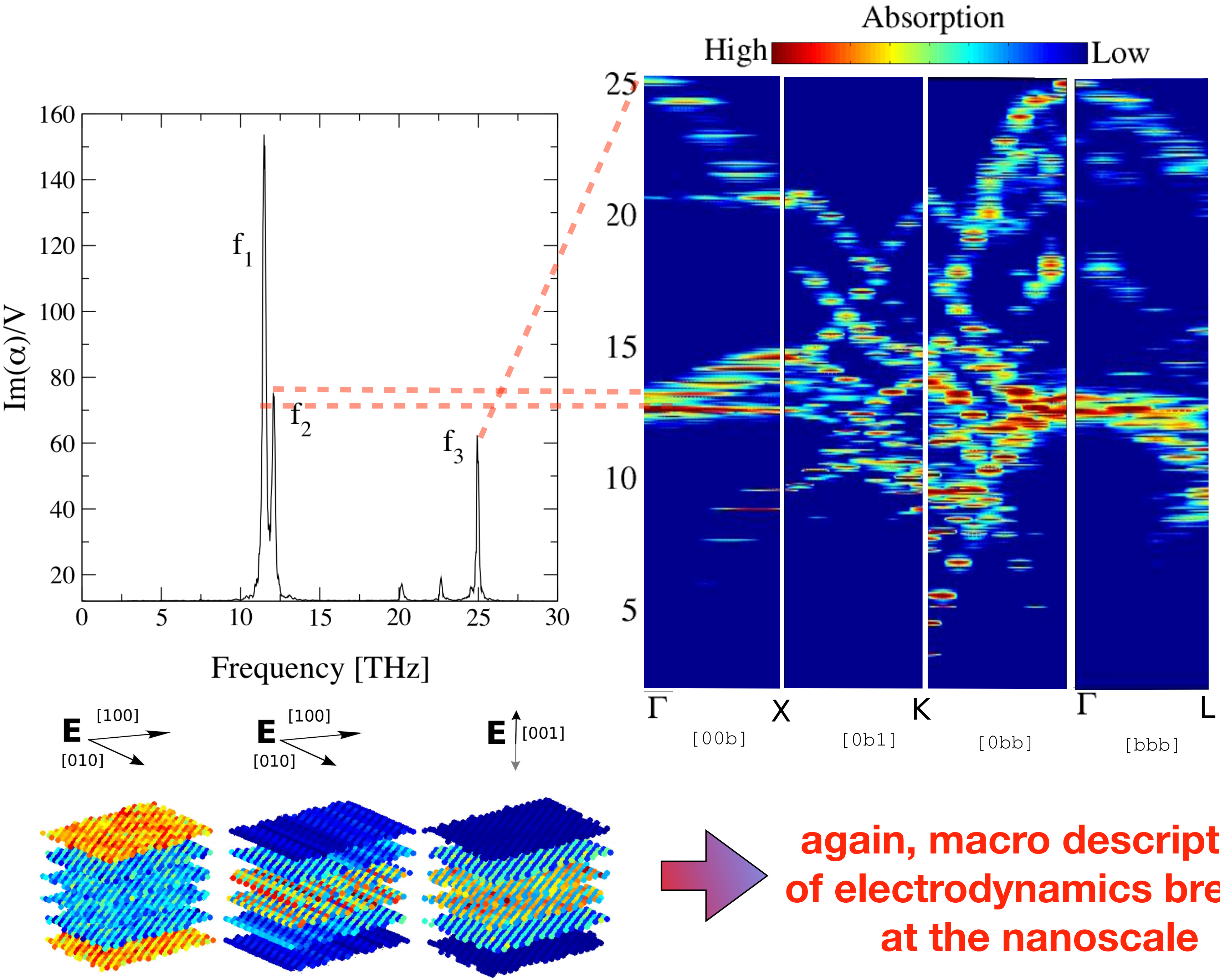


Chalopin et al.
APL 2011

Confinement = screening effects !

=> Surface-enhanced IR absorption

2D confinement and absorption mechanisms

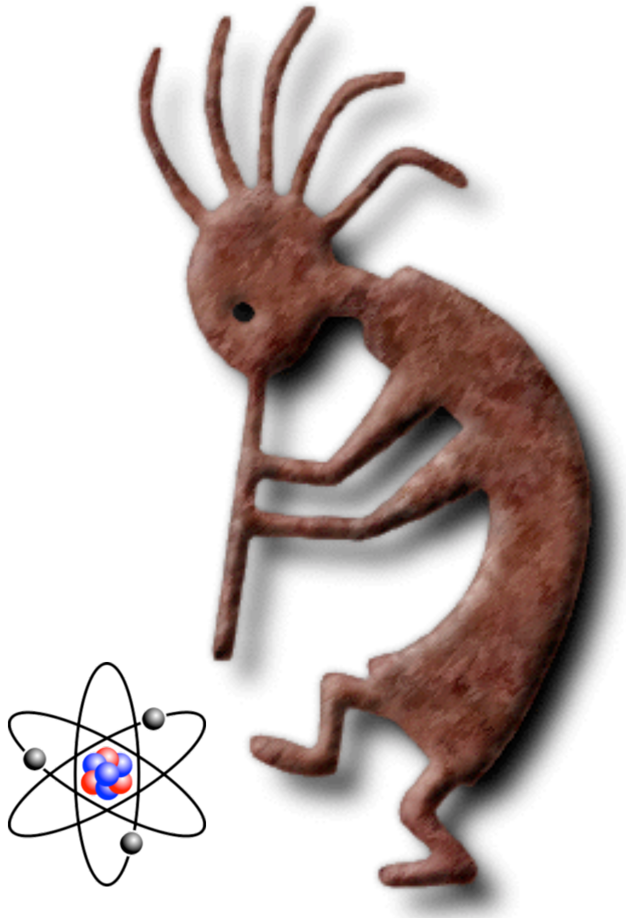


again, macro description of electrodynamics breaks at the nanoscale

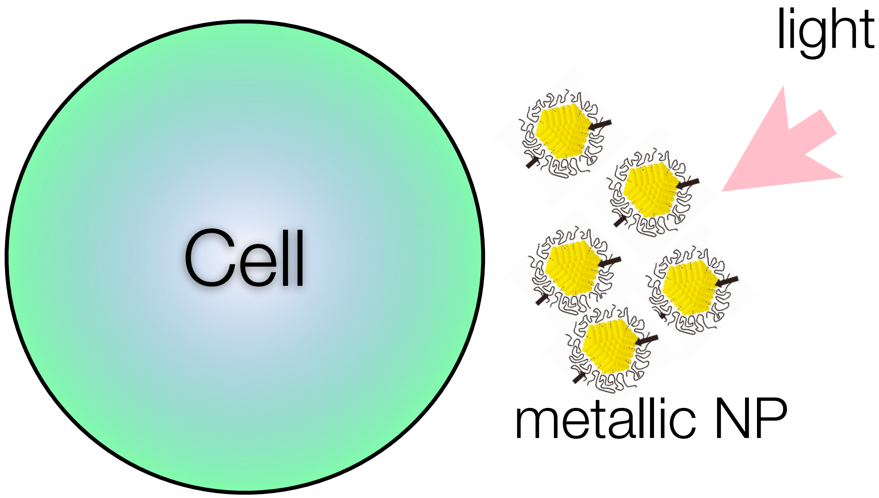
Question :

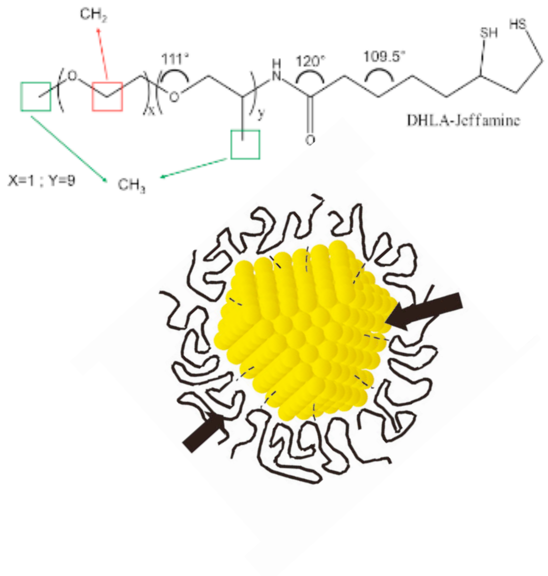
Heat properties of more complex systems (biological interest) :

Heat dissipation for therapeutic perspectives



e.g #1 :Laser (Plasmonic) induced hyperthermia in nanoparticles

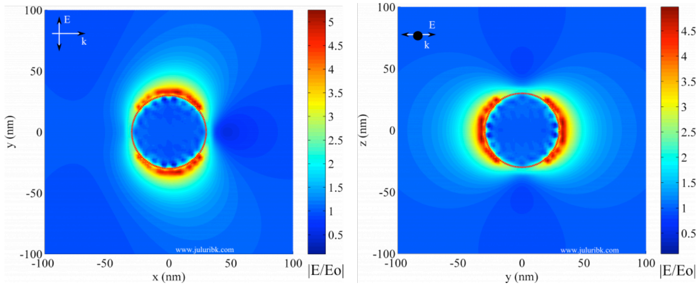




Heat deposited by the laser goes to the biological env. ?

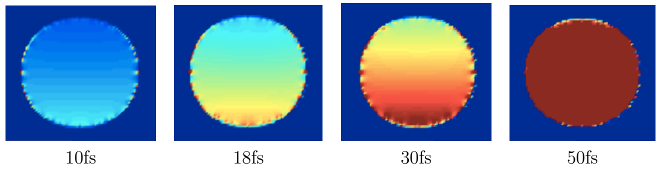
first step : Absorption properties and dynamics

1 - Electromagnetic calculation
(FDTD)

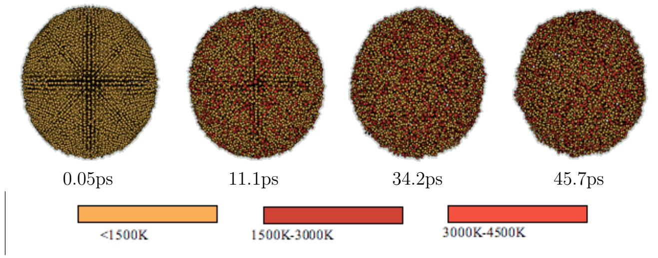


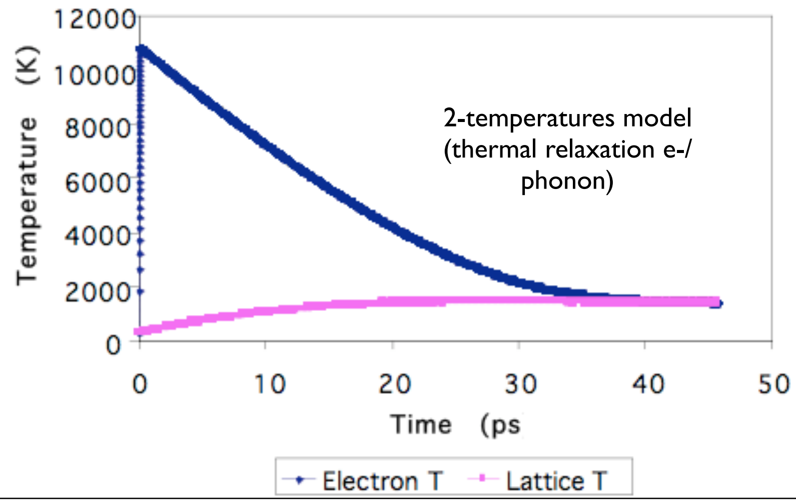
$$\mathbf{P} = \varepsilon_0 \alpha \mathbf{E}_{\mathbf{ext}}$$

2 - atomistic modeling

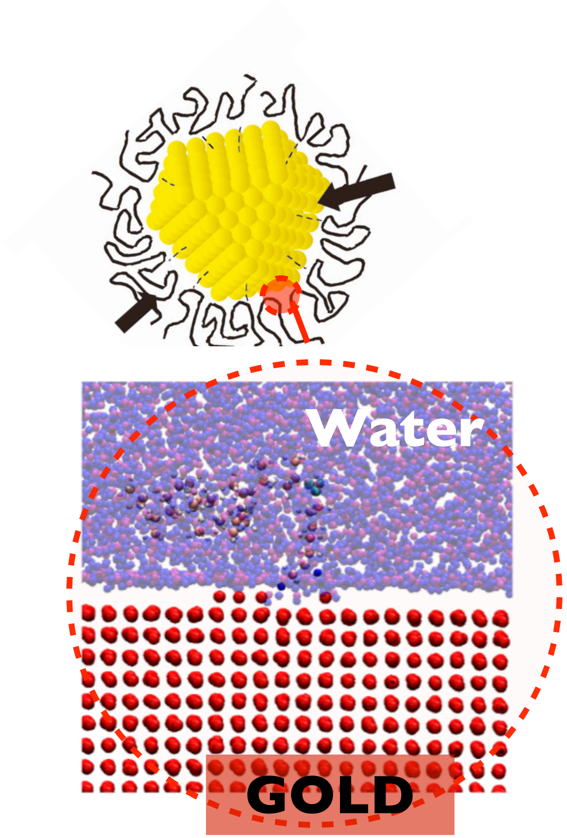


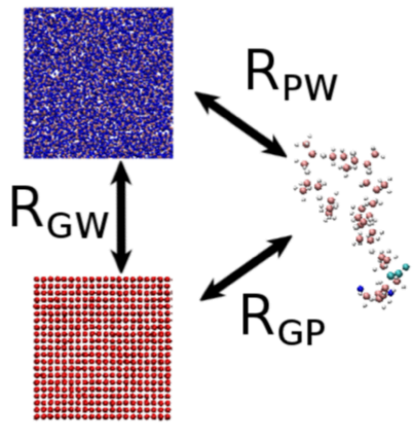
J.E

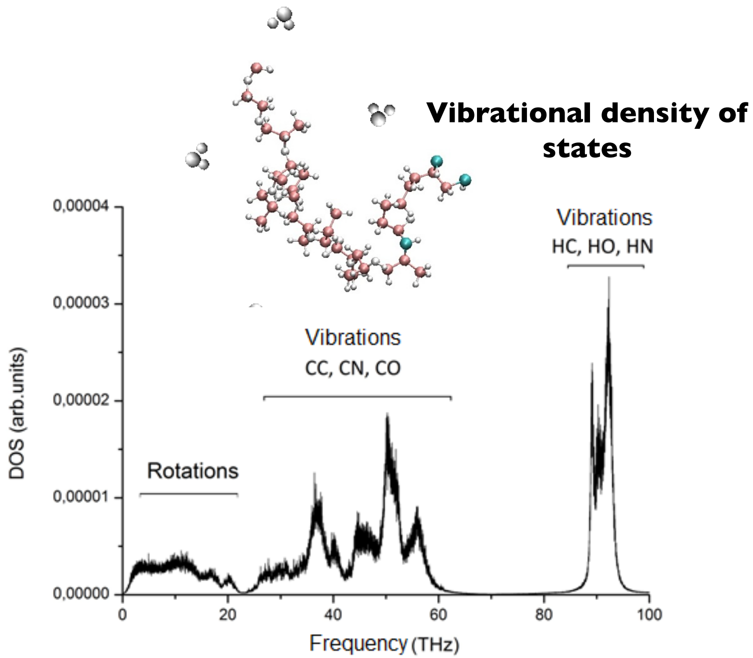




2nd step : Vibrational relaxation and interfaces





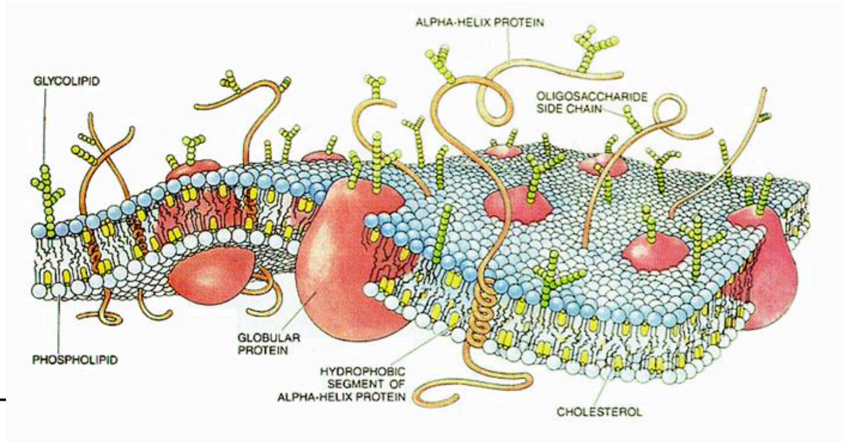


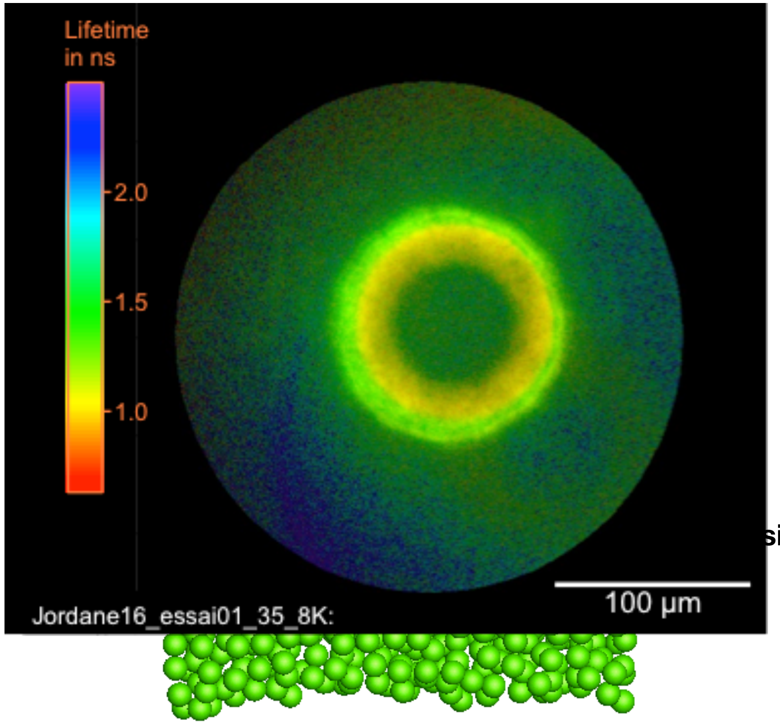
Polymer density	0	0.04	0.7
Thermal resistance (MK.W^{-1})	4.59	2.78	0.33

⇨ **Nanostructuration (polymer) + Confinement (plasmon) = Significant Exaltation of heat released**

e.g #2 - properties of biomembranes

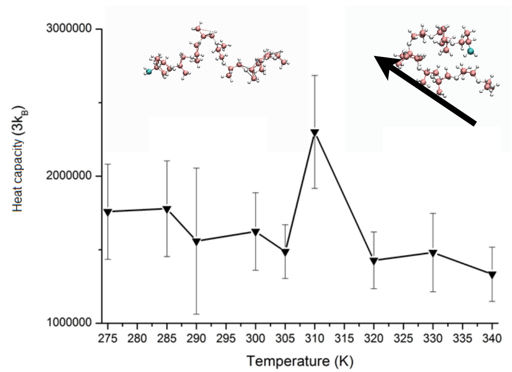
Molecular dynamics simulation of lipid bilayer

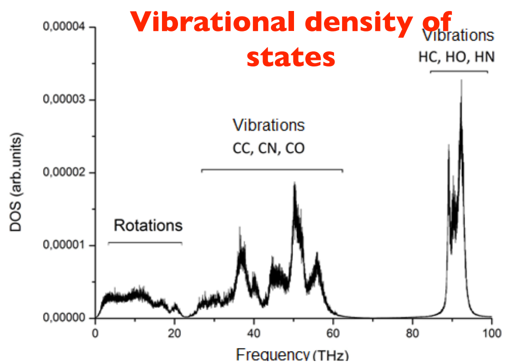


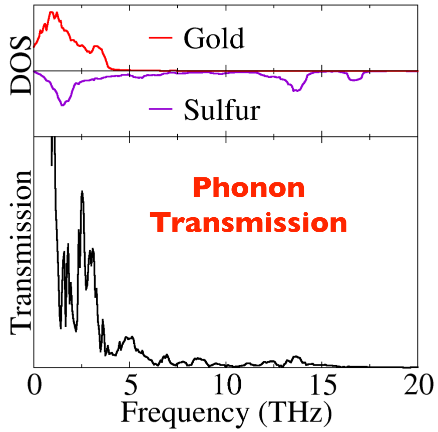


sis J Soussi)

Phase Transistion

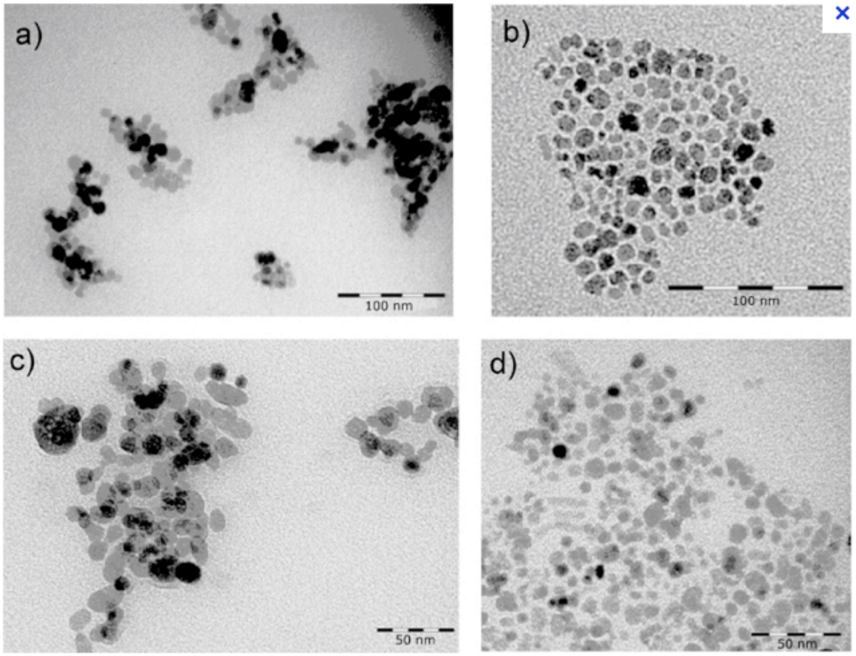


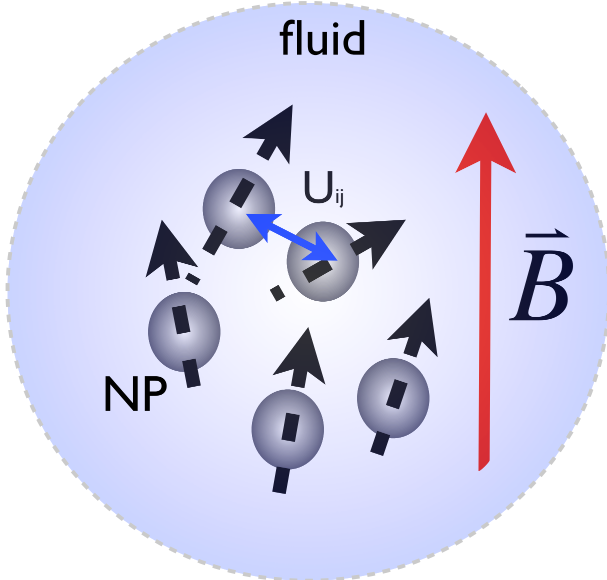


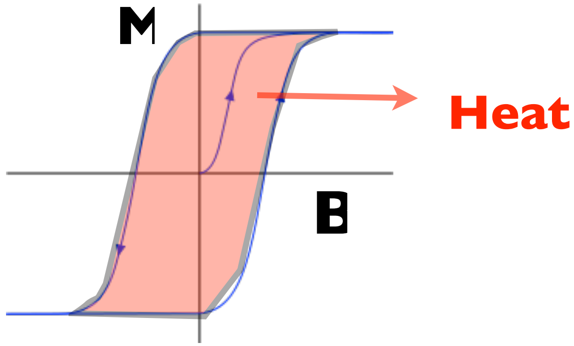


e.g #3 - Heat (Hyperthermia) with magnetic field

Tumor cell targeted by magnetic nanoparticles







<u>Problematic :</u>

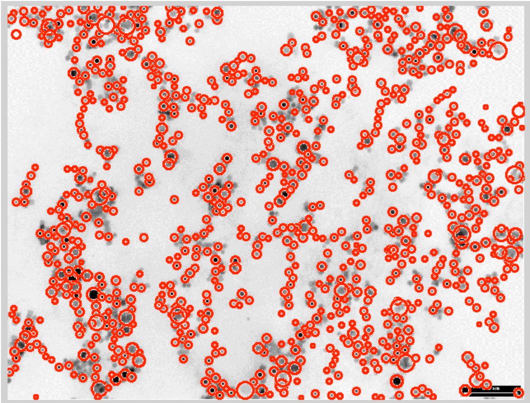
Dynamics and heat relaxation of a magnetic agregate subjected to **B**

Langevin Dynamics

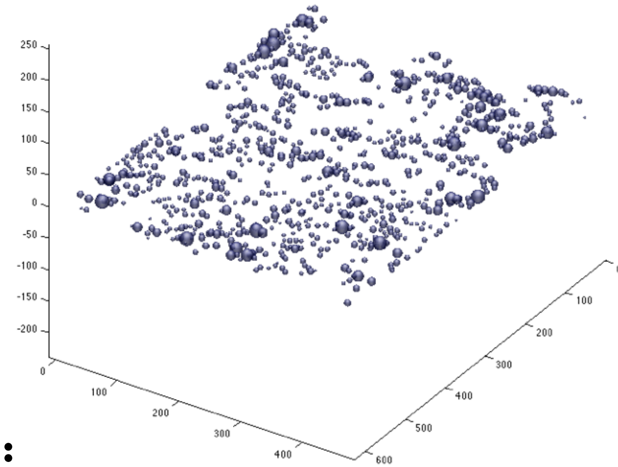
$$m\ddot{x}_i = \sum_j f(\mu_i,\mu_j) + g(B,\mu_j) + h(\eta,T) + i(\eta,T,\omega)$$

dipole/dipole — External field — brownian dissipation

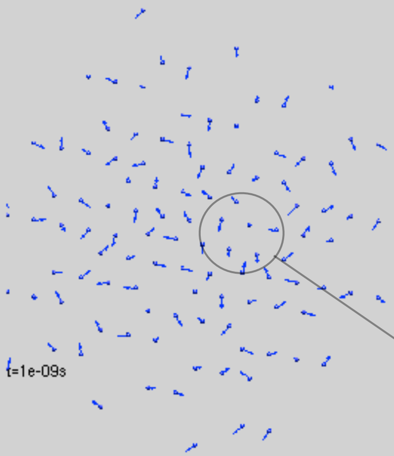
1- Image recognitions from experiments

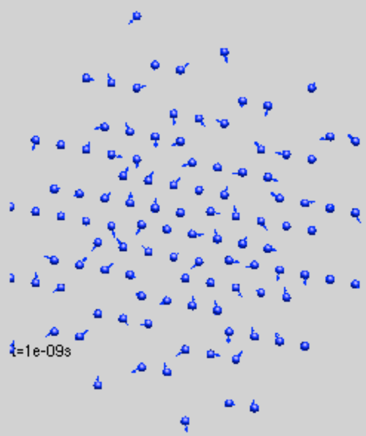


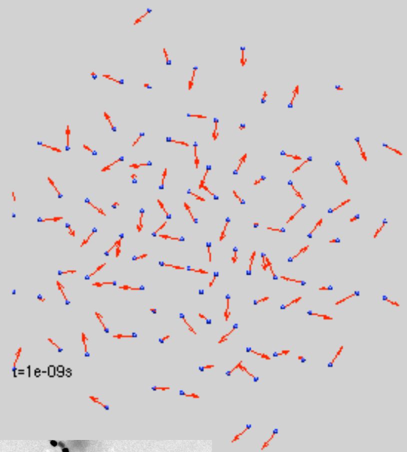
3D Configuration extraction



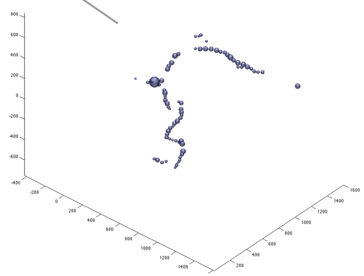
2 - Simulations by «Molecular dynamics» :

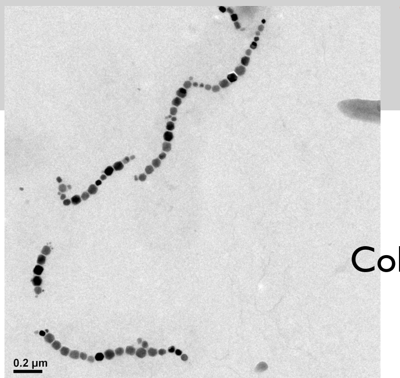






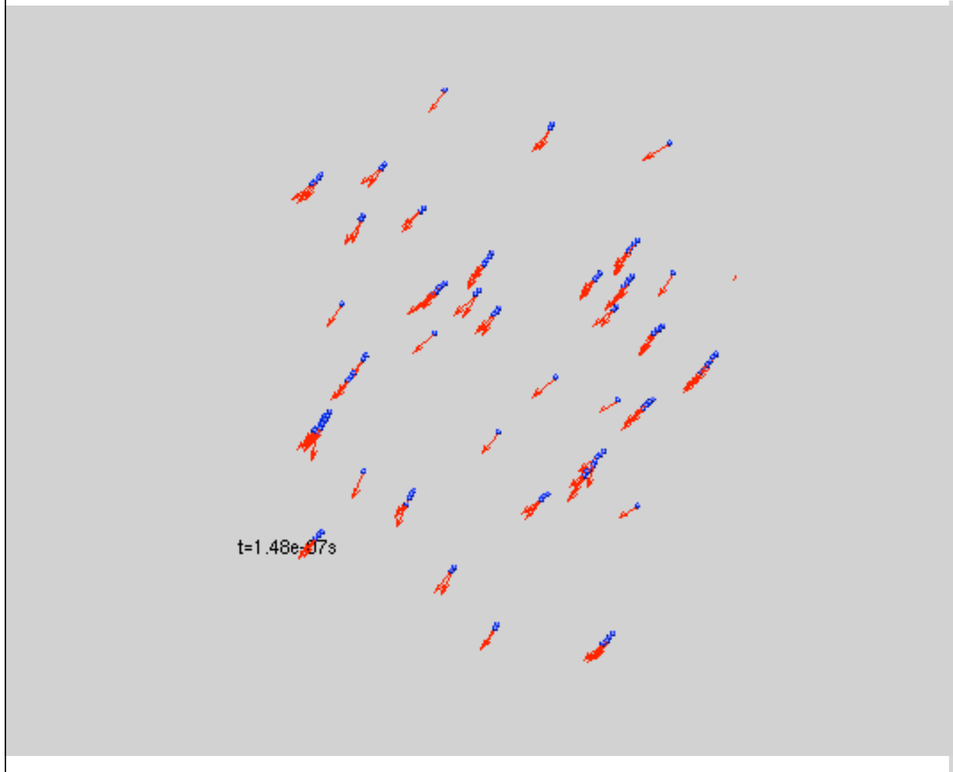
3 - Structural confrontation w/ experiments





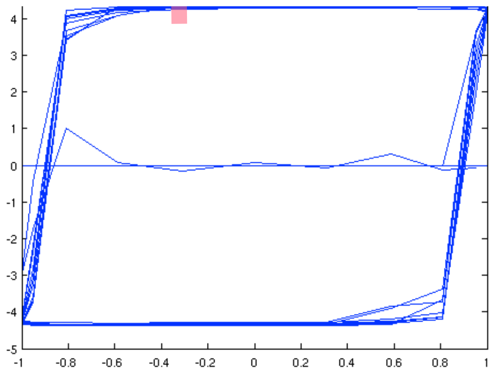
M.L Beoutis Thesis
Coll. F. Gazeau, M. Devaud.
MSC lab

Heat Dissipated under B field



$$H = \sum_i H_i = \frac{1}{2}\sum_{i,j} U_{ij} - \sum_i \vec{\mu}_i \cdot \vec{B}$$

M_{loc}

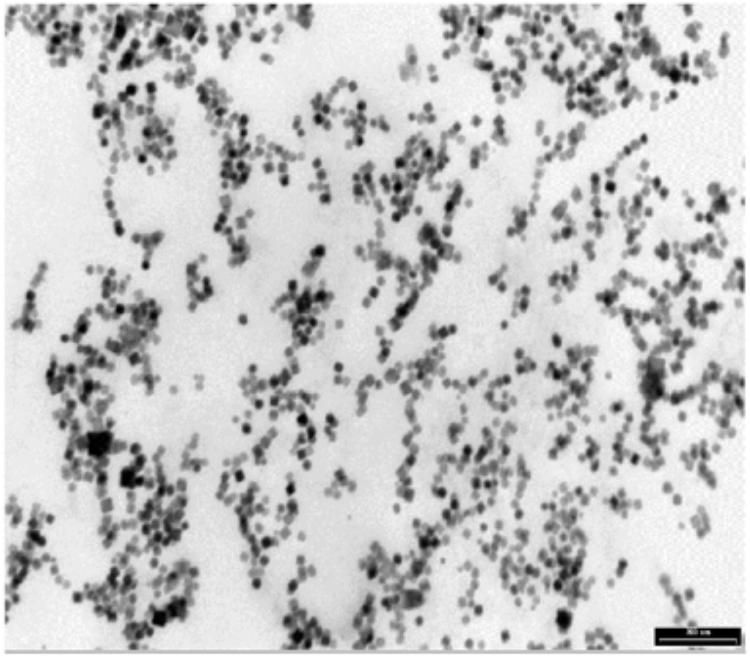


B_{ext}

Power dissipated

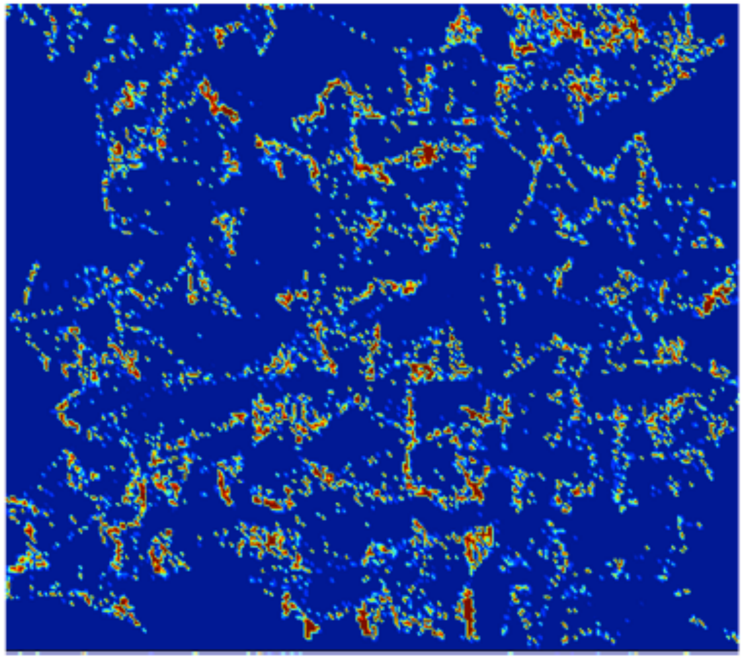
Example

a)



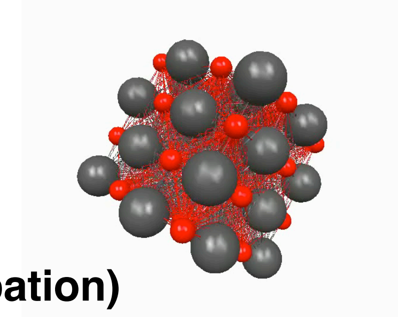
(TEM Image)

b)



(Thermal mapping at 500 KHz)

Conclusion / sum up



Heat = atomic/molecular motions

Vibrational relaxations ~ microscopic equilibrium fluctuations

MD good candidate to extract the correlations ! (Fluctuation/Dissipation)

Vibrational density of states

$$g \propto \beta \langle \dot{x}_i \dot{x}_i \rangle$$

Thermal conductivity

$$\kappa \propto \langle \mathbf{j}(0)\mathbf{j}(t) \rangle$$

Spatial coherence

$$C_{\mathbf{rr}'} \propto \langle x(\omega,\mathbf{r}) x(\omega,\mathbf{r}') \rangle$$

Phonon Transmission

$$\beta \langle u_i \dot{u}_j \rangle$$

Dynamical (Force constant) Matrix

$$D^{-1} \propto \beta \langle x_i x_i \rangle$$

Classical dynamics of nucleis in the time domain

Allow to Capture Particular Nanoscale/size effects

- Phonon Transport Channel (T/Kb)
  = cross PSD per atom

- Coherence/Diffuse interface Regime
  -> Period vs. Coherence length

- Surface Absorption in very thin-films
  -> screening length

Future orientation : Biological complexe materials, interaction w/ nanostructures

Memo !

At macroscale

Diffusion laws, geometrical optics

$$L \gg \lambda \quad L \gg \Lambda$$

- Incoherent summation of flux :
No phase relationship !

Physical properties are **local**

Solids = Bulk properties

at nanoscale

Statistical approach,
wave effects

Coherence and interference

$$L \ll l_{coh}$$

Non local effects

$$L \ll \lambda$$

Systems driven by surface and interface properties

$$L \ll \delta$$

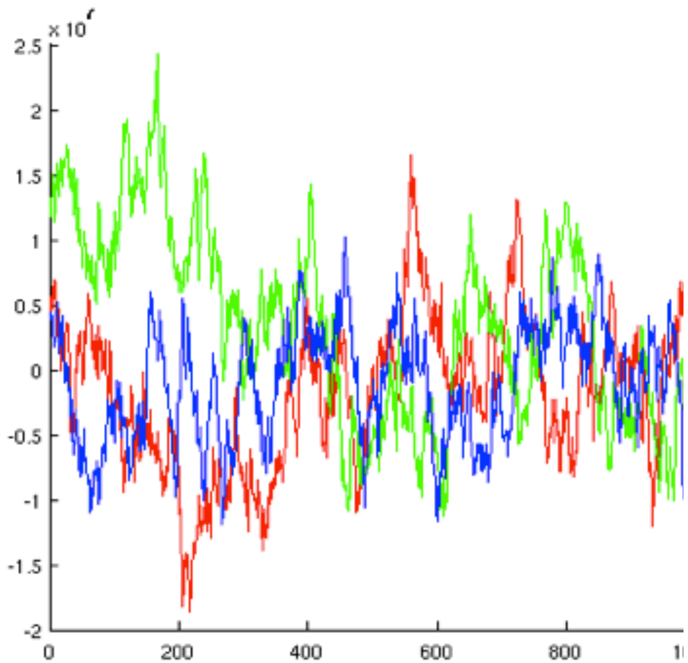
Aknowledgments/collaborators

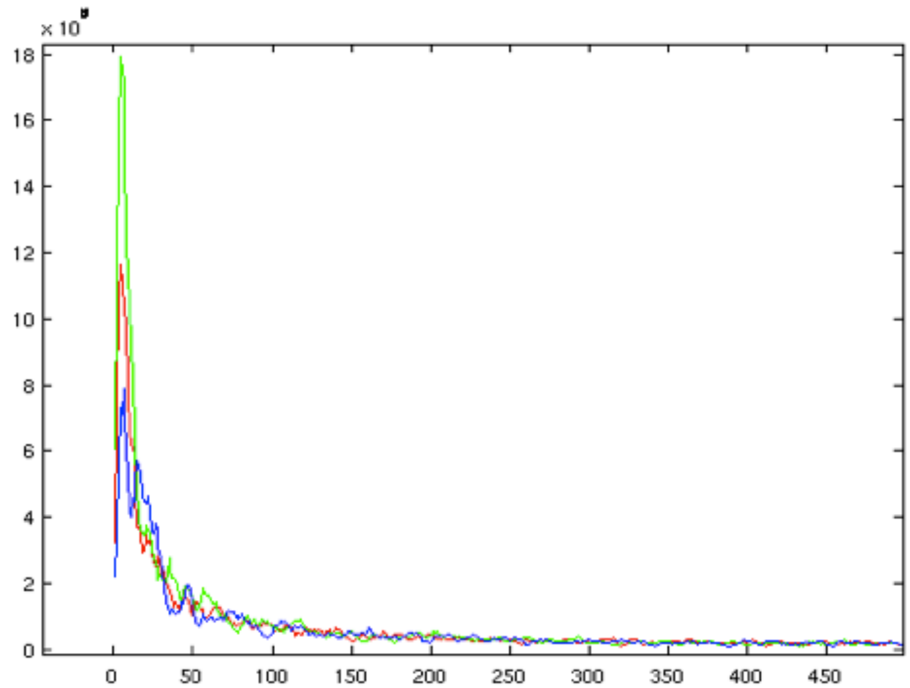
Conductance/Interface
S.Volz (CNRS - ECP)
B. Latour (Ph.D student ECP)
N. Mingo (CEA - Grenoble)

Heat transport in biological systems
B. Lepioufle (ENS Cachan)
R. Pansu (ENS Cachan)
J. Soussi (Ph.D student ECP)

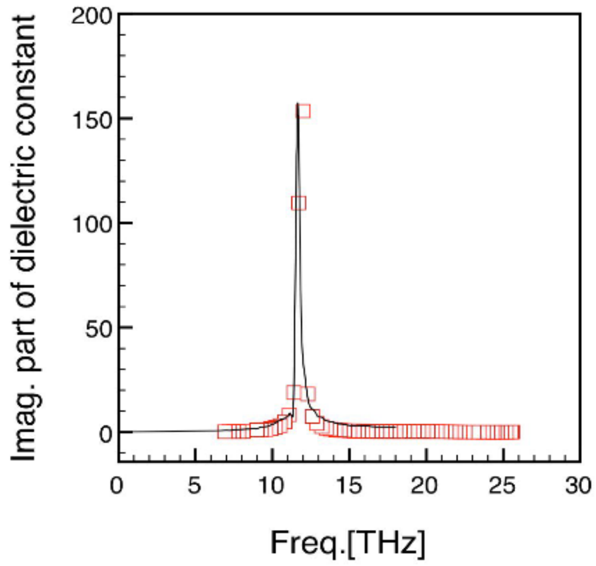
IR/ THz absorption
H. Dammak (Prof. ECP)
M. Hayoun (Ecole Polytechnic)
J. J. Greffet (prof. IOGS)

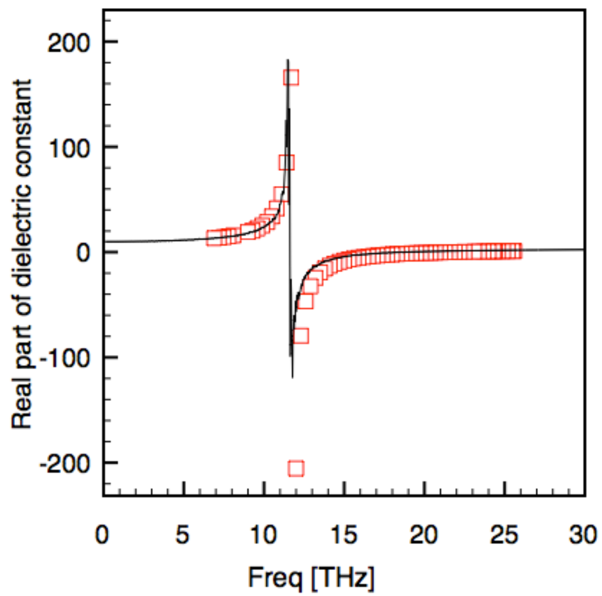
Magnetic Nanoparticles
F. Gazeau (CNRS - MSC, P7)
M. L. Beoutis (Ph.D student MSC)
M. Devaud (CNRS, MSC - P7)

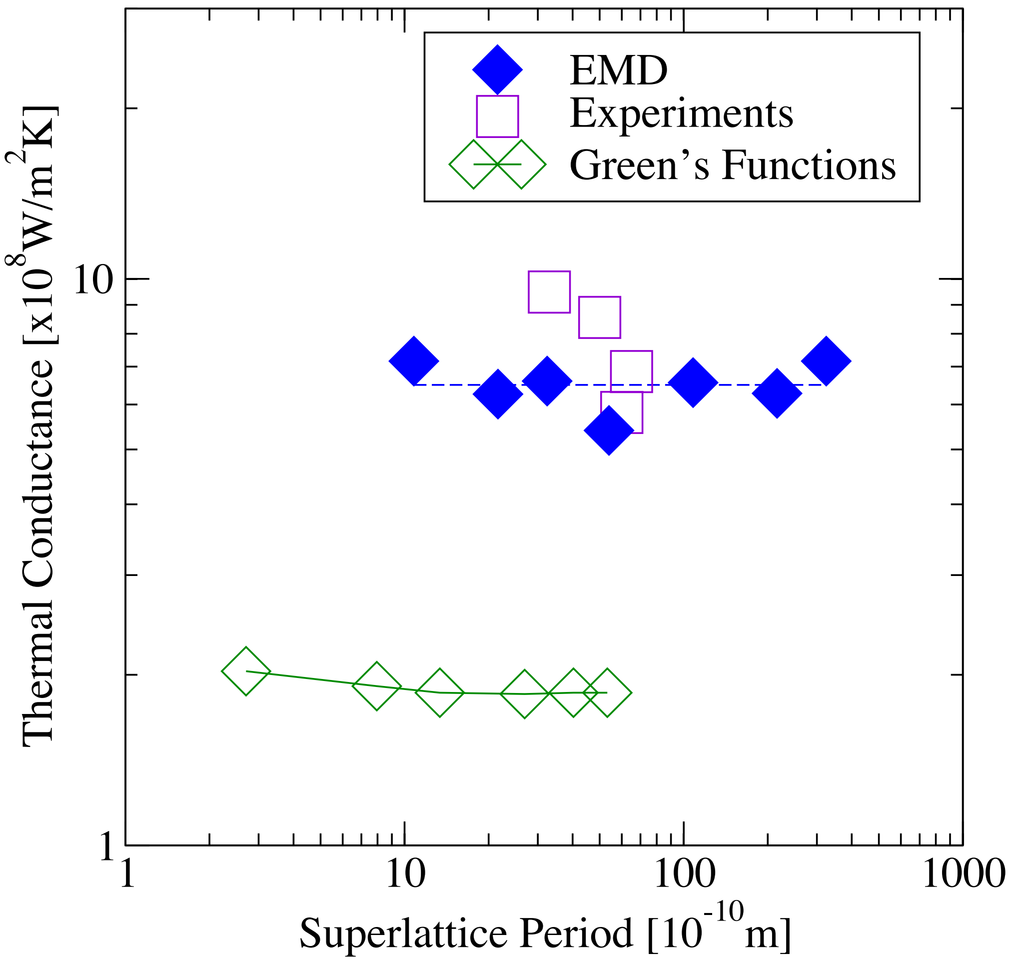

× 10
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0
200
400
600
800


× 10
18
16
14
12
10
8
6
4
2
0
0
50
100
150
200
250
300
350
400
450

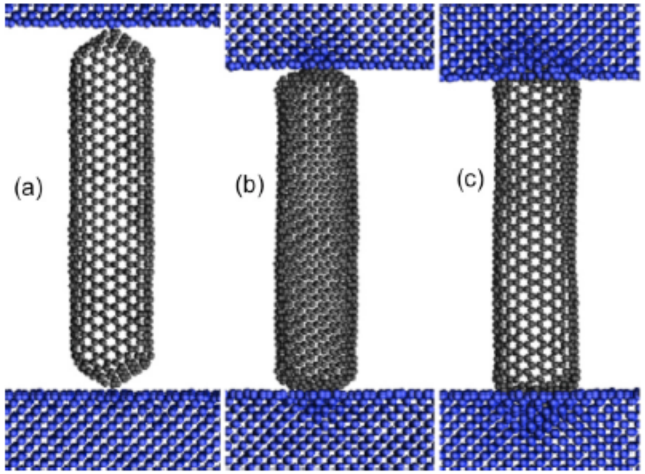
Validations







e.g #4: Phonon Transmission at Semiconductor Nanotube interfaces

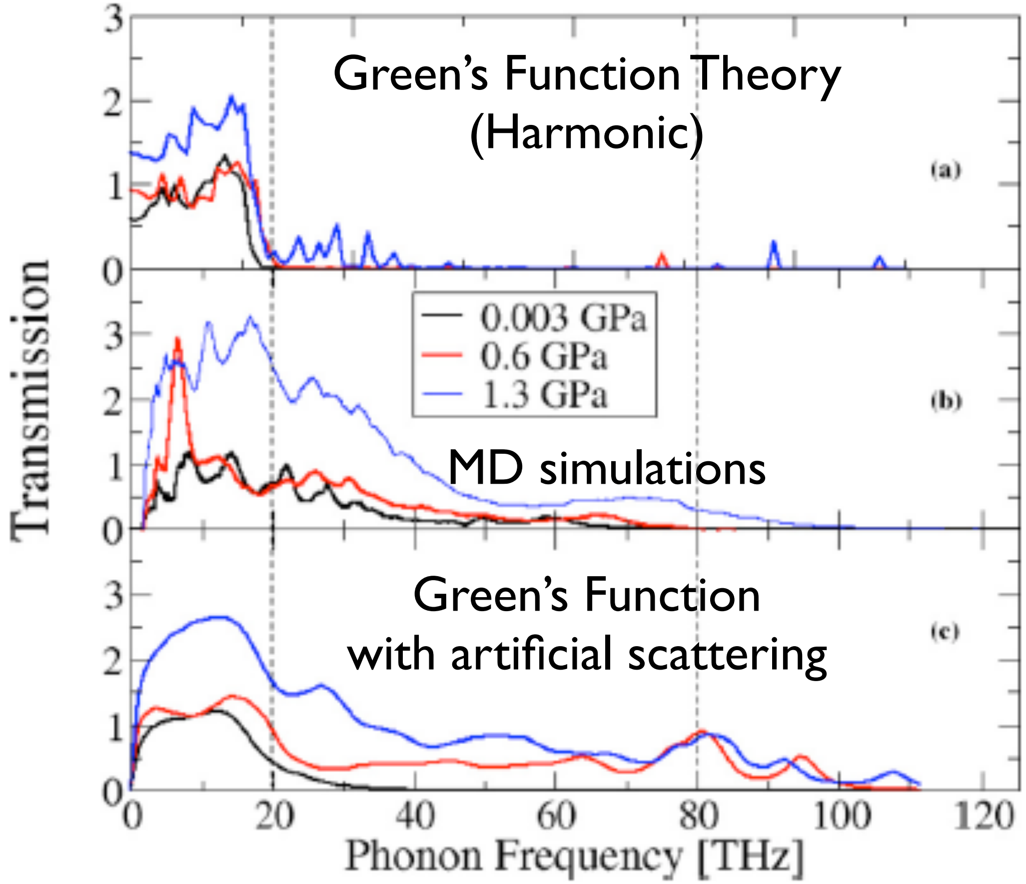


Chalopin et al.
APL 2012

$$G = \int_{FBZ} \hbar\omega_k \cdot n(\omega_k, T) \cdot t(\omega_k) d\omega_k$$

↓

Phonon Transmission



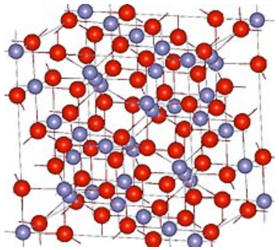
Chauffage magnéto-induit

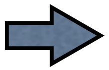
Approche «Atomistique»
relaxation vibrationelle :

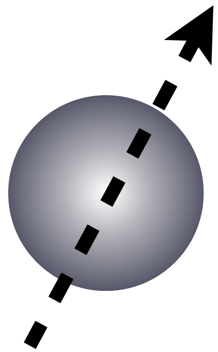
$\tau \sim 1_{-13}\, s$

dt=1$_{.15}$

N=6x1$_{.4}$



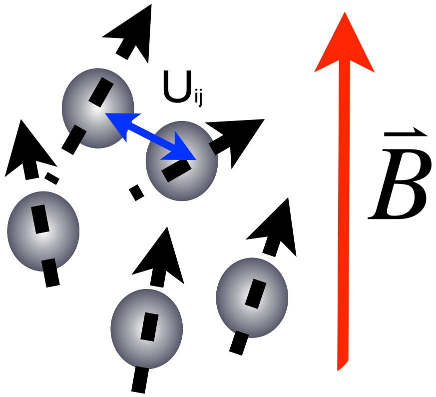




$\vec{\mu}$

relaxation Brown :

$\tau \sim 1_{-9} \,/\, 1_{-7}\, s$



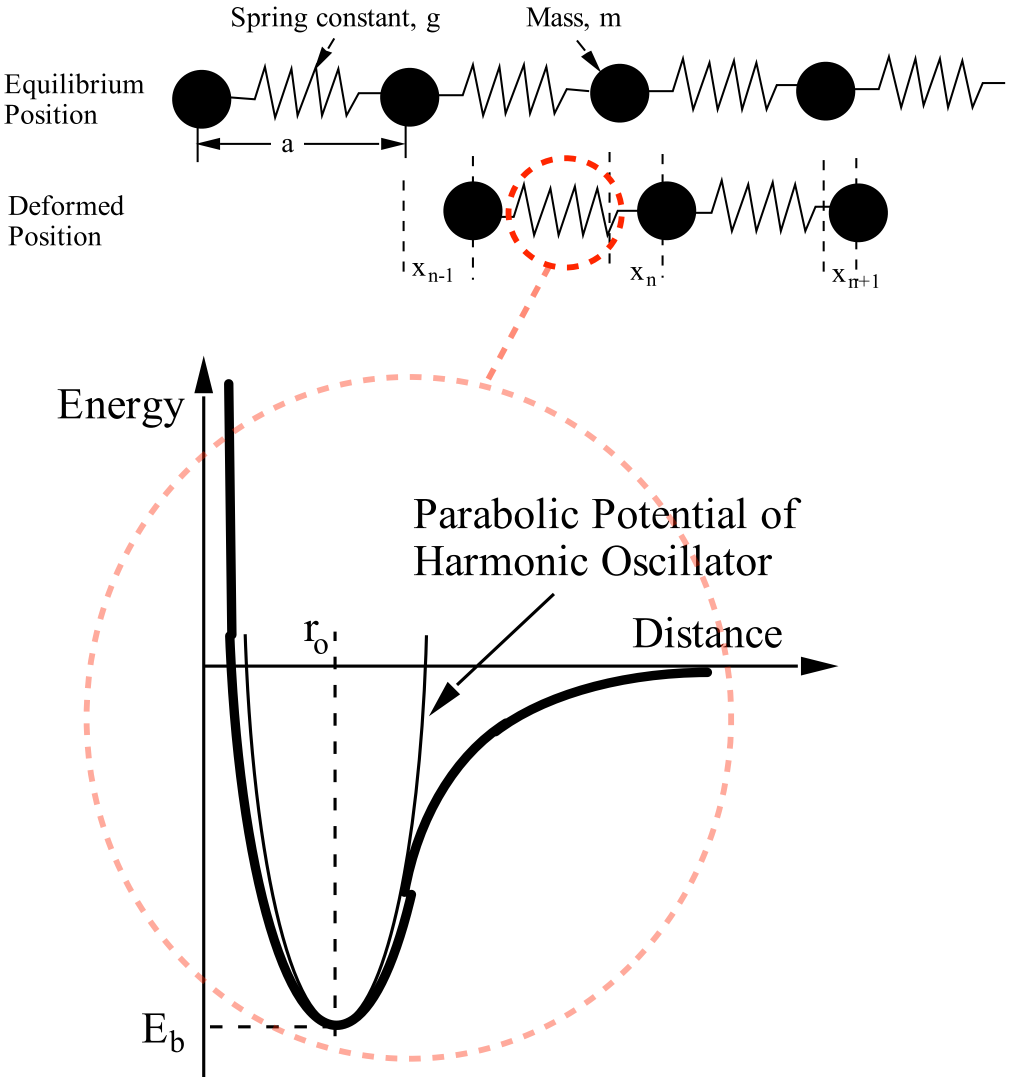
interaction dipolaire :

$$U_{ij} = \frac{\mu_0 \mu^2}{4\pi r^3_{ij}} \left[\vec{\mu}_i \cdot \vec{\mu}_j - 3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij}) \right] + r^{24}$$

$$H = \sum_i H_i = \frac{1}{2} \sum_{i,j} U_{ij} - \sum_i \vec{\mu}_i \cdot \vec{B}$$

Hamiltonien pour accéder à la dynamique :

Introducing Atoms and vibrations



Equation of motion

$$m\frac{d^2 x_n}{dt^2} = g\left(x_{n+1} + x_{n-1} - 2x_n\right)$$

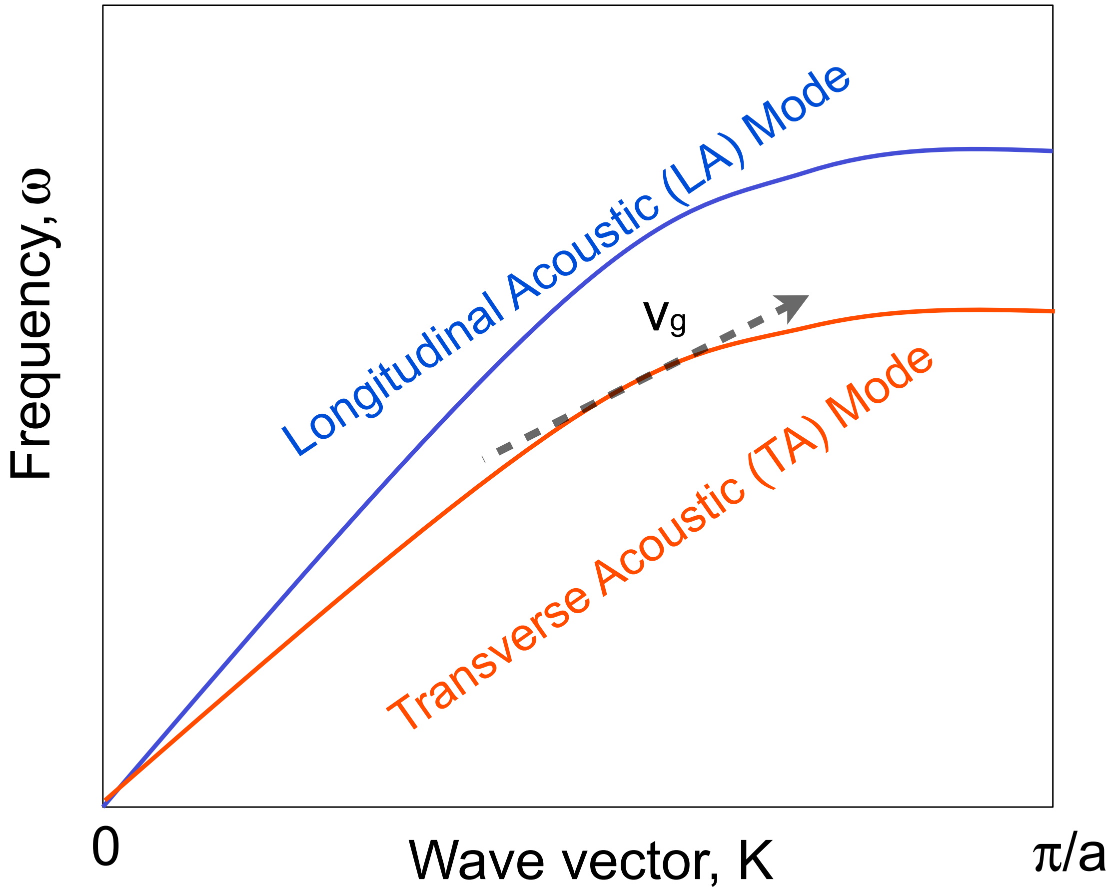
Solution

$$x_n = x_o \exp(-i\omega t)\exp(inKa)$$

Dispersion relation

$$\omega^2 m = g[2 - \exp(-iKa) - \exp(iKa)] = 2g(1 - \cos Ka)$$

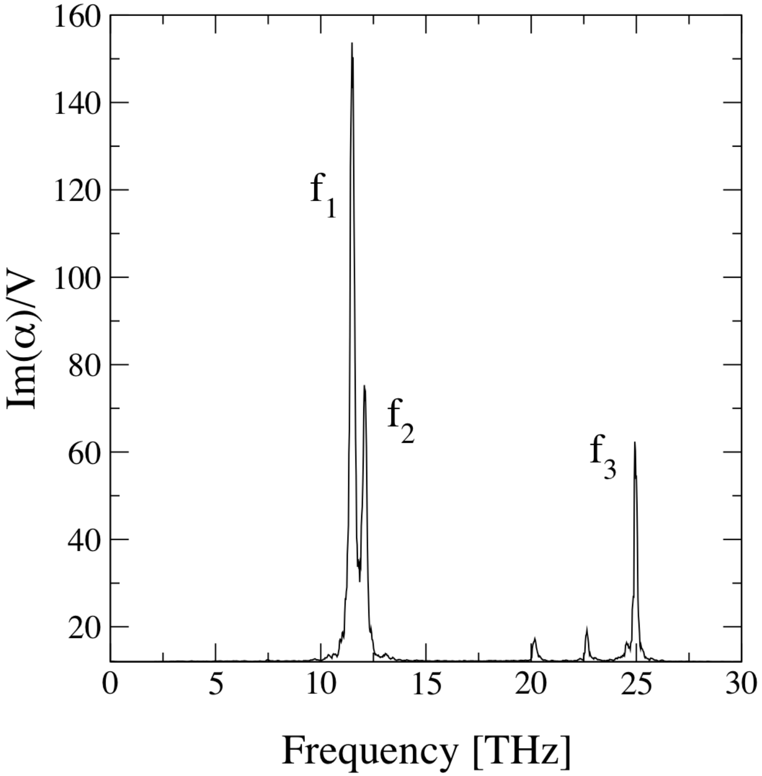
$$\omega = \sqrt{\frac{2g}{m}}(1 - \cos Ka)^{1/2}$$

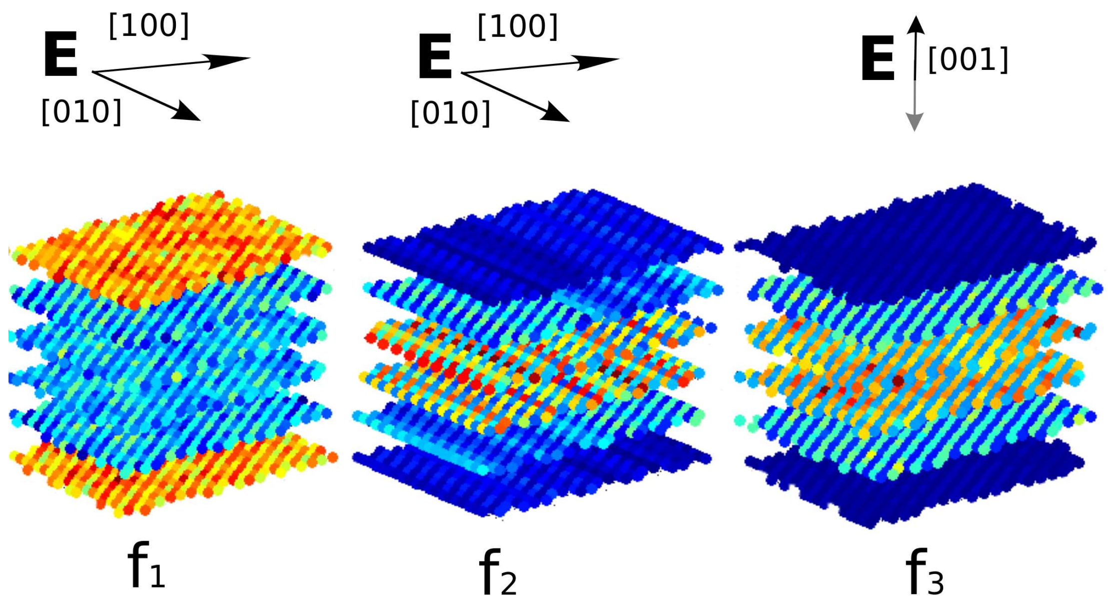


Group Velocity:

$$v_g = \frac{d\omega}{dK}$$

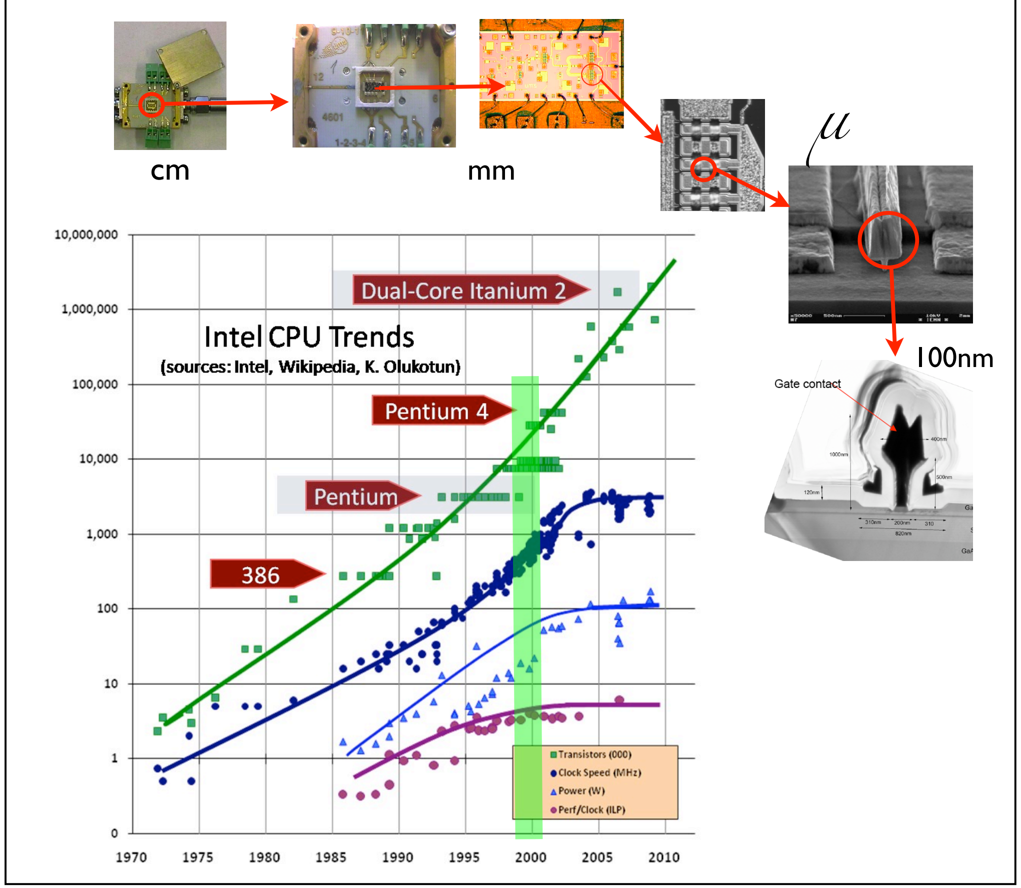
Origin of new modes



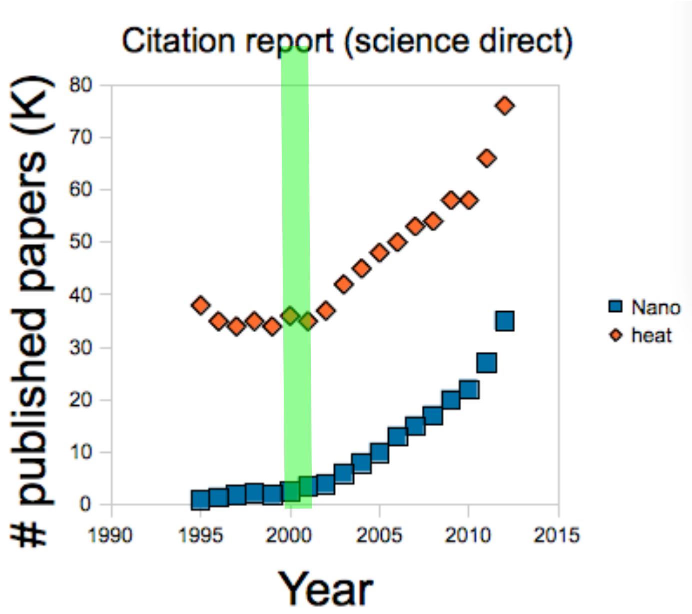


Heat dissipation : A burning issue for technology

e.g Scalling down in microelectronic

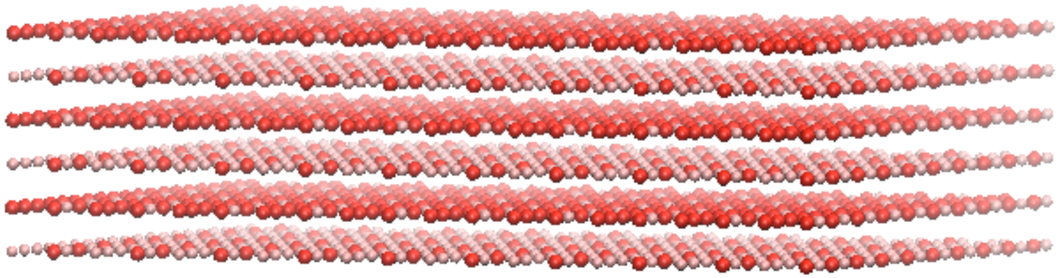


Industry needs for «new» modeling tools for designing and optimising systems at short scales

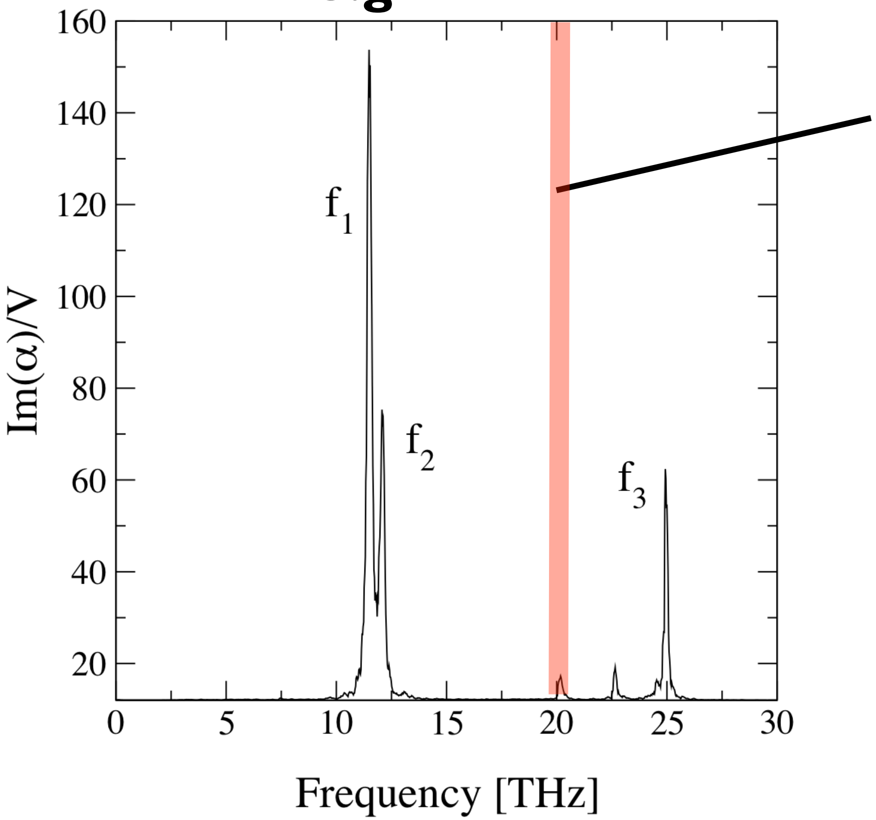


Emergence of short scales thermal energy transport !

Confinement effects in a Oxide (MgO) Thin Film



e.g L= 2nm



Mie resonnance predicted from Bulk dielectric constant !!

$$\frac{(\varepsilon_r - 1)}{\varepsilon_r + 1}$$

Other mode predominant !

Origin ?