

SOLEIL THEORY DAY

6 MAY 2014

DENSITY FUNCTIONAL THEORY

A PRIMER

GIORGIA FUGALLO

OUTLINE



WHY?



WHO? WHEN?



WHAT?



HOW?



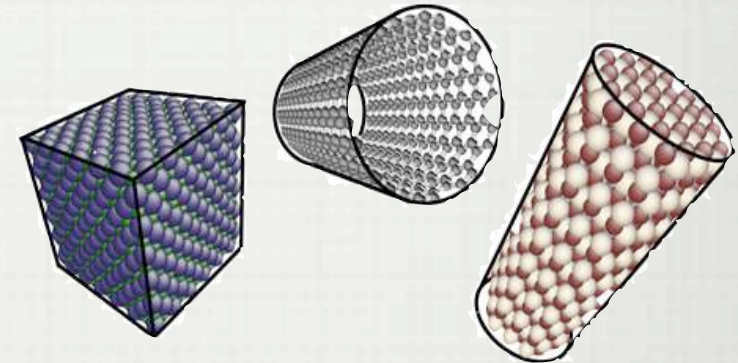
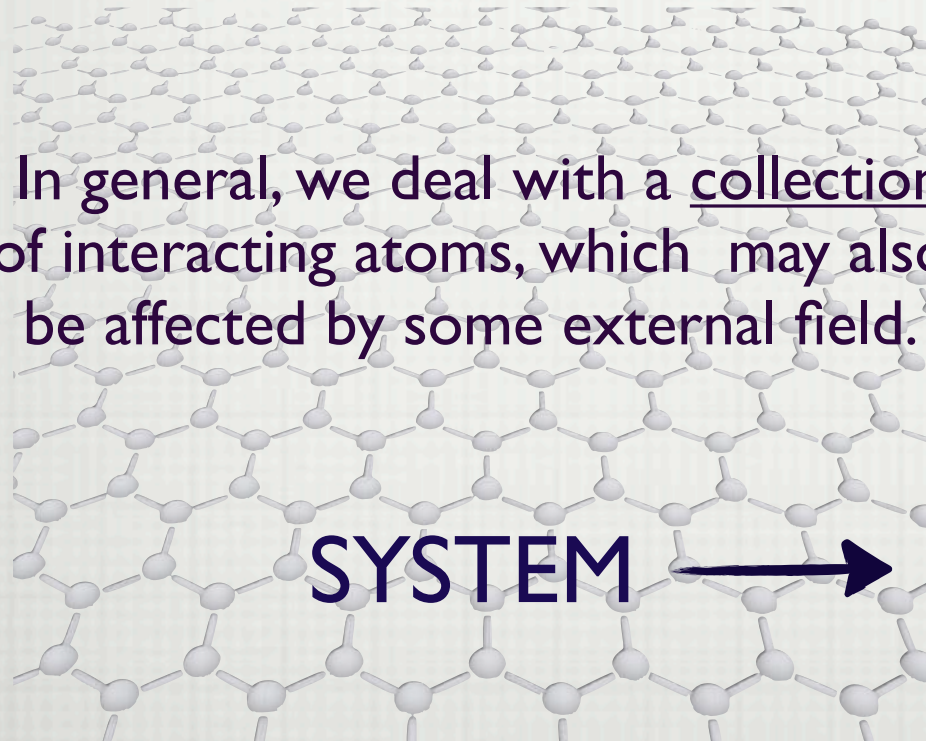
... APPLICATIONS!

WHY?

WE HAVE A PROBLEM!
(A COMPLEX ONE)

Microscopic description of the physical and chemical properties of matter

In general, we deal with a collection of interacting atoms, which may also be affected by some external field.



Number of Nuclei and
Electrons
interacting through
Coulombic (electrostatic)
forces

WHY?

MANY BODY PROBLEM

Formally....

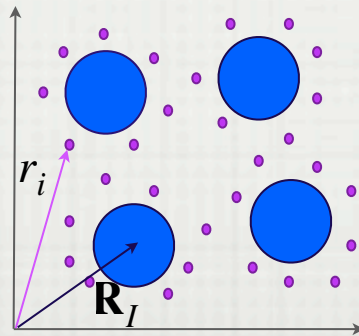
$$\begin{aligned}\hat{H} = & -\sum_{I=1}^P \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 \\ & + \frac{e^2}{2} \sum_{I=1}^P \sum_{J \neq I}^P \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{e^2}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{|r_i - r_j|} \\ & - e^2 \sum_{I=1}^P \sum_{i=1}^N \frac{Z_I}{|\mathbf{R}_I - r_i|}\end{aligned}$$

all ingredients are known
so simply solve the

$$\hat{H}\Psi_i(\mathbf{r}, \mathbf{R}) = E_i\Psi_i(\mathbf{r}, \mathbf{R})$$

Many Body

Schroedinger Equation



PROBLEM SOLVED

LET'S GO HOME!

WHY?

MANY BODY PROBLEM

actually.....

- This problem is almost impossible to treat in a full quantum-mechanical framework
- Only in a few cases a complete analytic solution is available and numerical solutions are also limited to a very small number of particles.

APPROXIMATIONS

(large majority of calculation presented in literature)

- Adiabatic separation of nuclear and electronic degrees of freedom.
- Classical Treatment of the nuclei

APPROXIMATIONS

MANY BODY PROBLEM

- ADIABATIC APPROXIMATION (BORN-OPPENHEIMER)

MOTION TIME SCALE:

NUCLEI \ll ELECTRONS

Electrons can be adequately described as following instantaneously the motion of the nuclei, staying always in the same stationary state of the electronic Hamiltonian.



DECOUPLING
THE 2 DYNAMICS

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \Theta_m(\mathbf{R}, t) \Phi_m(\mathbf{R}, \mathbf{r})$$

Electrons

Nuclei

APPROXIMATIONS

MANY BODY PROBLEM

Still formidable task but in a large variety of cases of interest

THE QUANTUM TREATMENT FOR NUCLEI
IS *NOT* NECESSARY

- CLASSICAL NUCLEI APPROXIMATION

WHY?

MANY BODY PROBLEM
(AND THE ELECTRONS???)

the exact solution is known only in the cases:

- i) Uniform electron gas;
- ii) Atoms with a small number of electrons;
- iii) A few small molecules.

These exact solutions are
always numerical.

At the analytic level  APPROXIMATIONS

THOMAS FERMI (1927)
HARTREE (1927)
HARTREE-FOCK (1930)
CONFIG. INTER. (1930)
MP2-MP4(1934)
DFT (1964)

DFT!

(NOBEL LAUREATE)

Hohenberg, P. and Kohn, W. (1964) *Phys. Rev.*, **136**, B864.

Kohn, W. and Sham, L.J. (1965) *Phys. Rev.*, **140**, A1133.



The Nobel Prize in Chemistry 1998

Walter Kohn - Facts



Walter Kohn

Born: 9 March 1923, Vienna, Austria

Affiliation at the time of the award: University of California, Santa Barbara, CA, USA

Prize motivation: "for his development of the density-functional theory"

Field: theoretical chemistry

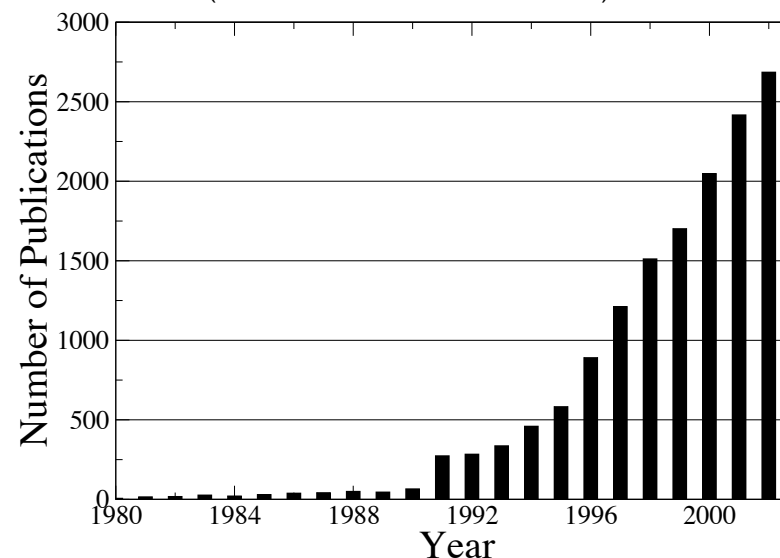
Prize share: 1/2



1. Hohenberg-Kohn (1964): ~ 4000 citations

2. Kohn-Sham (1965): ~ 9000 citations

Number of publications where the phrase "density functional theory" appears in the title or abstract (taken from the ISI Web of Science).



WHO? WHEN?

DFT

Hohenberg, P. and Kohn, W. (1964) *Phys. Rev.*, **136**, B864.

□ 1964: HOHENBERG-KOHN THEOREM

ELECTRONIC DENSITY
 $\rho(\mathbf{r})$
BASIC VARIABLE

ALL MICROSCOPIC AND
MACROSCOPIC QUANTITY
DEPEND ON $\rho(\mathbf{r})$

$$E = F[\rho(\mathbf{r})] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

universal functional of electron density

external potential due to atomic nuclei

- 1) The total energy of a system of interacting electrons is a functional of the density.
- 2) The energy takes its minimum at the ground state density.

HOW?

DFT

Hohenberg, P. and Kohn, W. (1964) *Phys. Rev.*, **136**, B864.

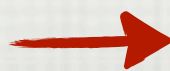
Using DFT, one can determine the electronic ground state density and energy exactly, provided that $F[\rho]$ is known!

$$F[\rho] = \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle$$

kinetic energy

electron-electron interaction potential

BIG Problem



expressing $T[\rho]$

HOW?

DFT

Kohn, W. and Sham, L.J. (1965) *Phys. Rev.*, **140**, A1133.

□ 1965: KOHN-SHAM

REPLACE THE SYSTEM OF INTERACTING ELECTRONS
by A FICTITIOUS SYSTEM OF NON-INTERACTING
ELECTRONS WITH THE SAME DENSITY

$$F[\rho] = T_R[\rho] + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{XC}[\rho]$$

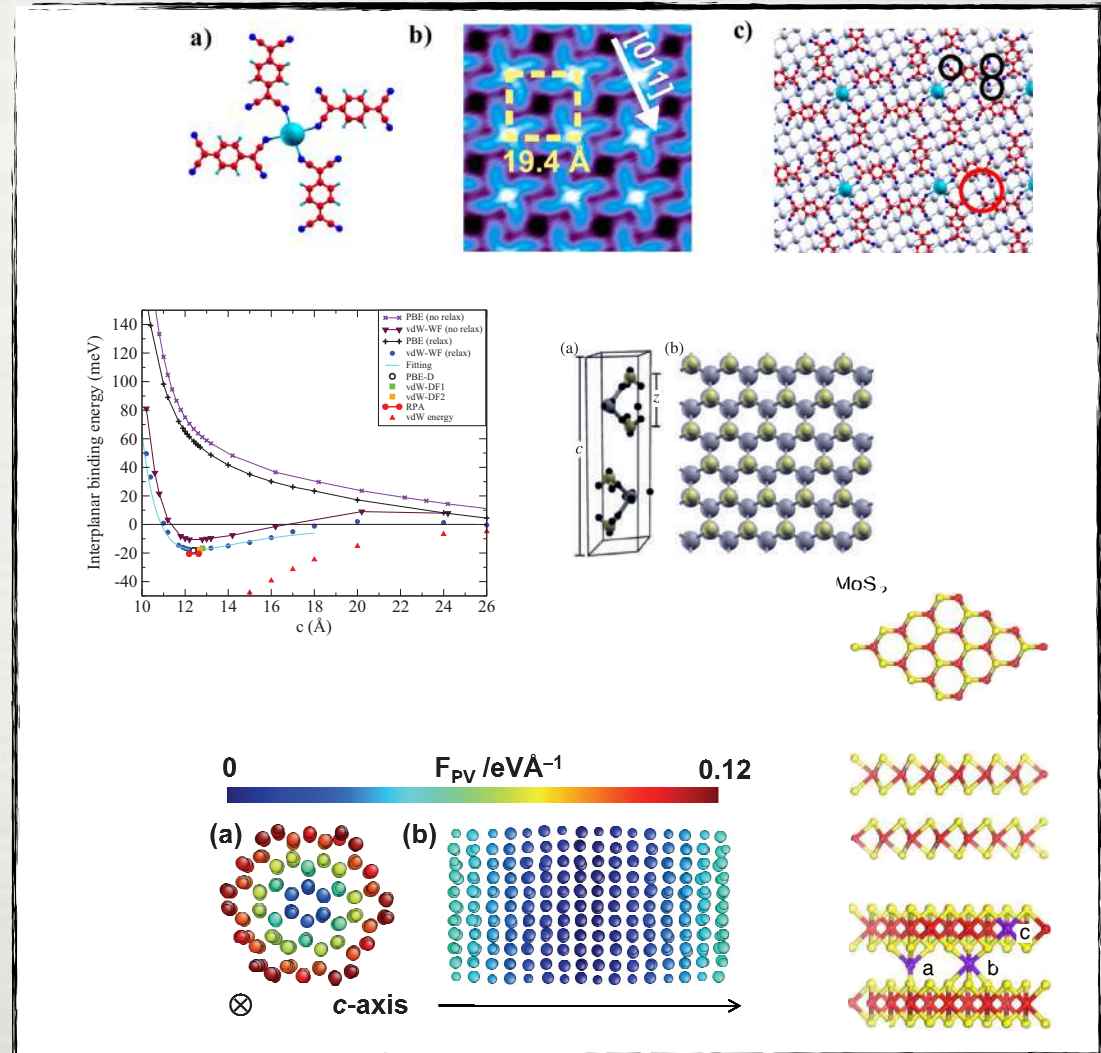
The explicit form of the functional $F[\rho]$ is the major challenge of DFT.

WHAT?

(TO BE PRAGMATICS: WHAT CAN BE CALCULATED?)

• STRUCTURAL PROPERTIES

- LATTICE PARAMETER
- ELASTIC CONSTANTS
- ATOMIC FORCES
- SURFACE RELAXATION
- DEFECT STRUCTURES

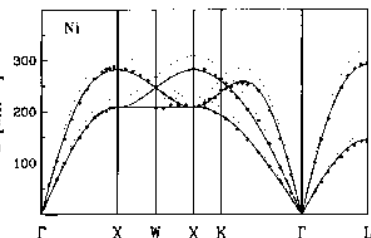
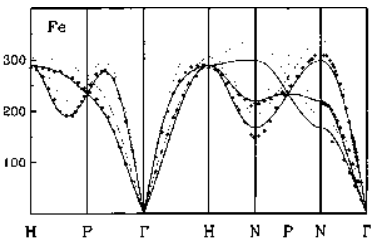
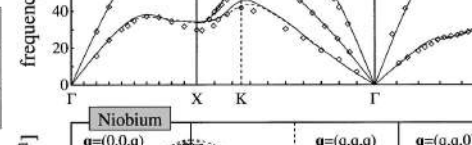
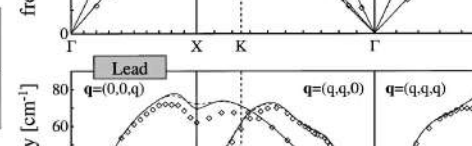
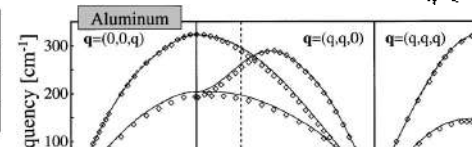
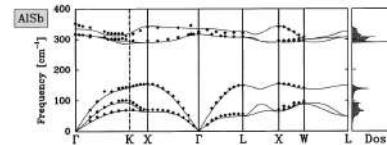
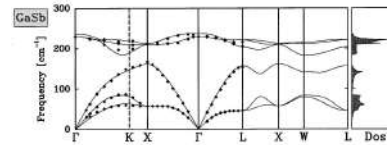
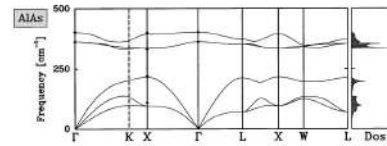
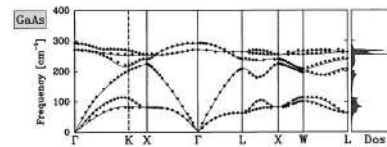
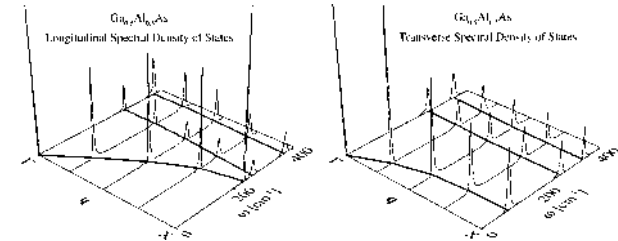
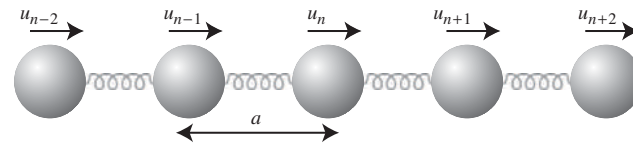


WHAT?

(TO BE PRAGMATIC: WHAT CAN BE CALCULATED?)

• LATTICE DYNAMICS

- VIBRATIONAL FREQUENCIES
- PHONON DENSITY OF STATES
- PHONON GROUP VELOCITIES
- PHONON RELAXATION TIMES



Baroni *et al.*: Phonons and related crystal properties from DFPT
Rev. Mod. Phys., Vol. 73, No. 2, April 2001

WHAT?

(TO BE PRAGMATICS: WHAT CAN BE CALCULATED?)

- ELECTRONIC PROPERTIES

and

- SPECTROSCOPY

- BAND STRUCTURE

- PHOTOEMISSION

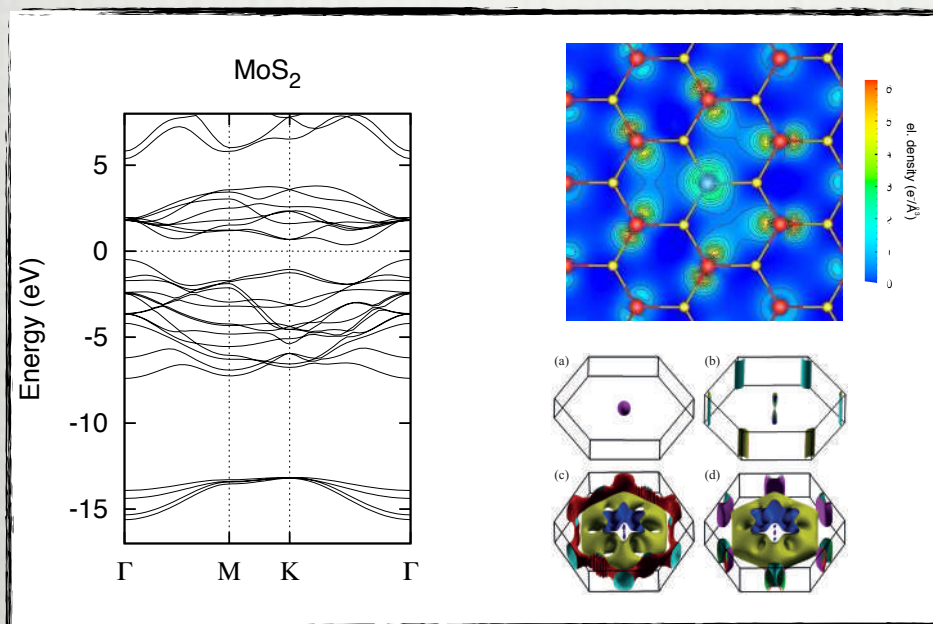
- CHARGE DENSITY

- ELECTRON ENERGY LOSS /
ABSORPTION DIELECTRIC
FUNCTION

- DENSITY OF STATES

- CORE LEVEL SPECTROSCOPIES
RAMAN SCATTERING

- COMPTON SCATTERING
POSITRON ANNIHILATION



CODES?

(LONG LIST)

abinit



CPMD

exciting




CASTEP



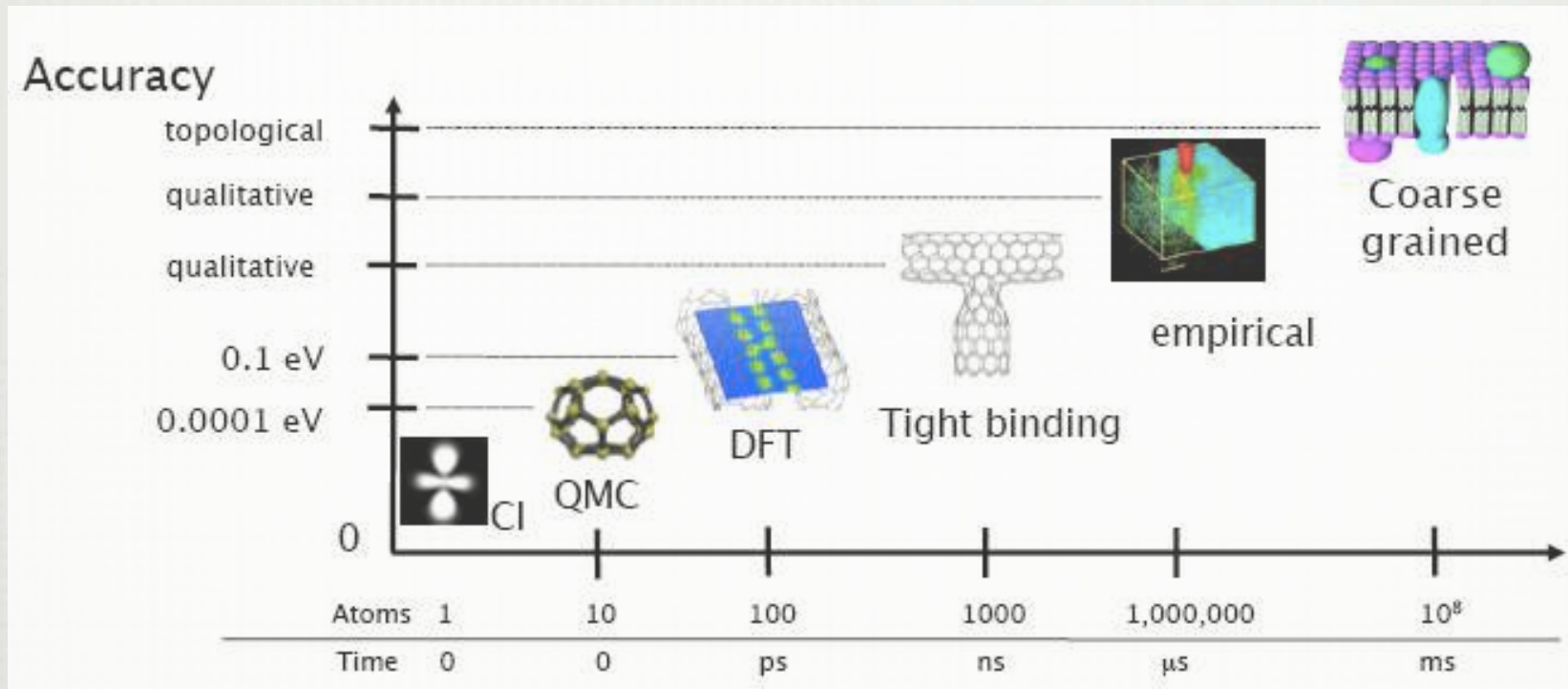
ONETEP

b-initio
VASP
Vienna
package
simulation

Yambo. 

COMPUTATIONAL PHYSICS

(GENERAL OVERVIEW)

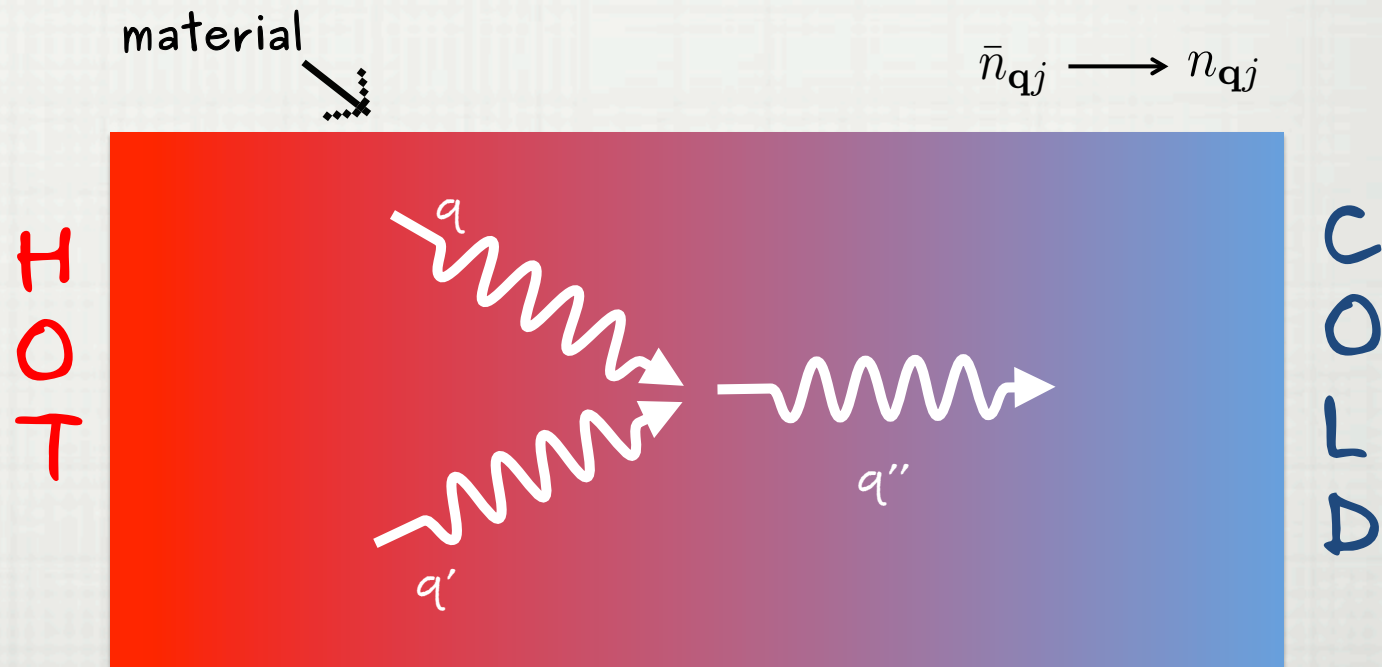


SOME APPLICATIONS

(DFT VS CLASSICAL)

Thermal transport

Boltzmann Transport Equation



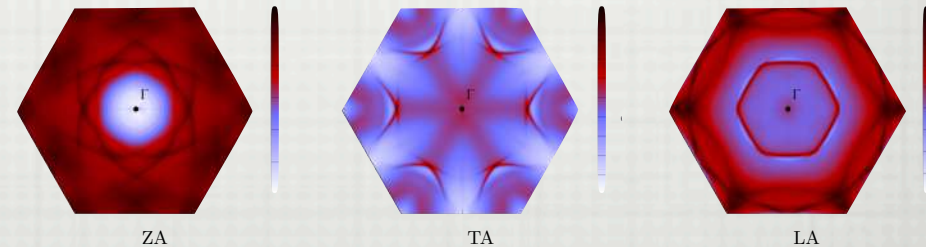
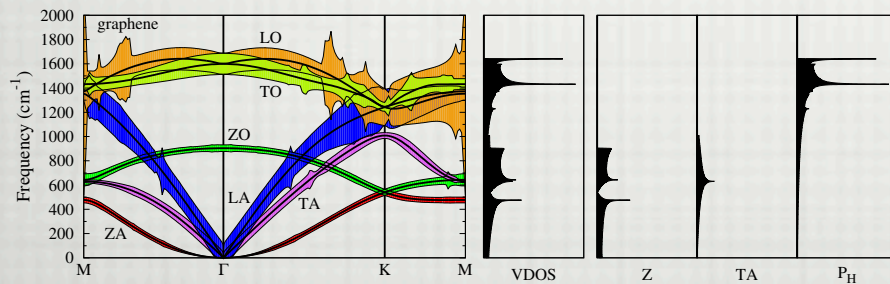
Fourier Law \rightarrow
$$Q = \frac{1}{N_0 \Omega} \sum_{q,j} \hbar \omega_{q,j} n_{q,j} \mathbf{v}_{q,j} = -k \nabla T$$

THERMAL TRANSPORT

(FUNDAMENTAL INGREDIENTS)

- PHONON FREQUENCIES
- GROUP VELOCITIES
- BOSE EINSTEIN POPULATIONS

- PHONON SCATTERING RATES
- PHONON LINEWIDTH AND RELAXATION TIMES



THERMAL TRANSPORT

(FUNDAMENTAL INGREDIENTS)

G.Fugallo et al. *Phys. Rev. B*, **88**, 045430 (2013).

L. Paulatto et al. *Phys. Rev. B* **87**, 214303 (2013).

- PHONON FREQUENCIES
- GROUP VELOCITIES
- BOSE EINSTEIN POPULATIONS

- PHONON SCATTERING RATES
- PHONON LINEWIDTH AND RELAXATION TIMES

HARMONIC INTERATOMIC FORCE CONSTANTS (IFCS)

ANHARMONIC INTERATOMIC FORCE CONSTANTS (IFCS)

$$\frac{\partial^2 \mathcal{E}^{tot}}{\partial u_{\mathbf{q}_1} \partial u_{\mathbf{q}_2}}$$

$$\frac{\partial^3 \mathcal{E}^{tot}}{\partial u_{\mathbf{q}_1} \partial u_{\mathbf{q}_2} \partial u_{\mathbf{q}_3}}$$

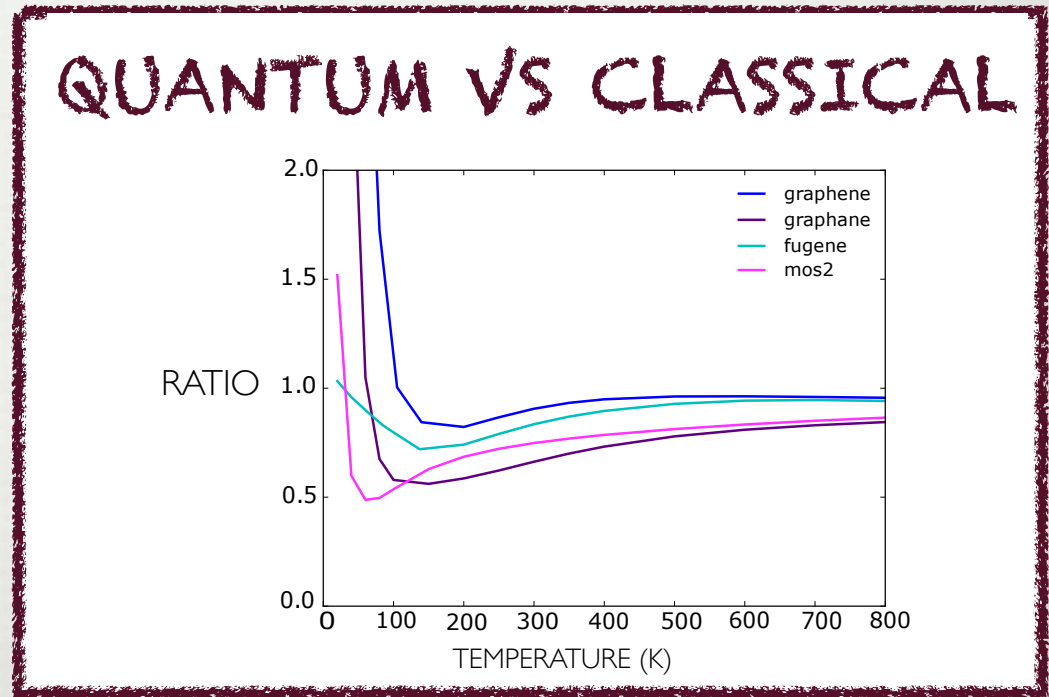
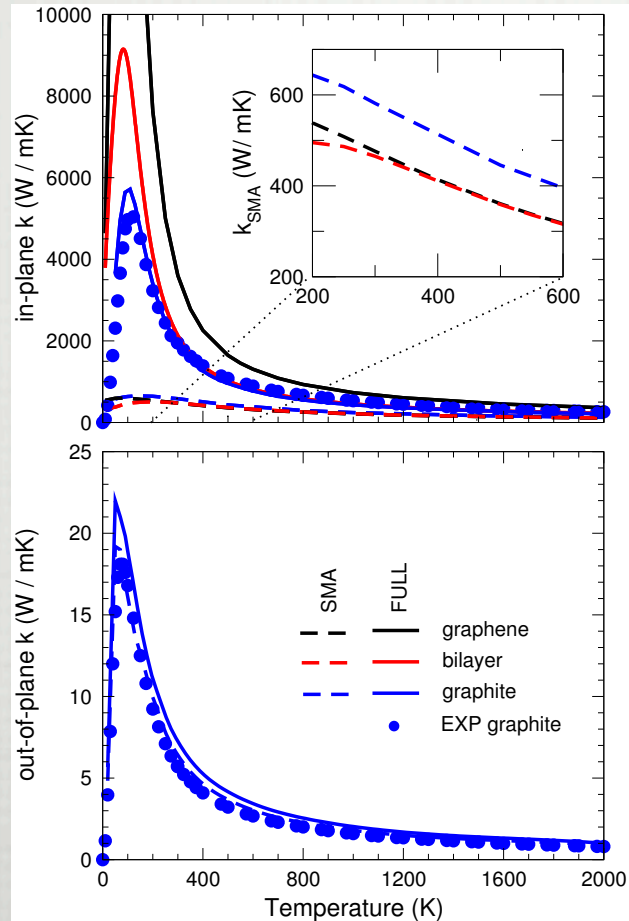
FROM DFPT

THERMAL TRANSPORT

G. Fugallo et al *Phys. Rev. B*, **88**, 045430 (2013)

G. Fugallo et al . Thermal transport driven by collective excitations in Graphene (2014)/ Thermal transport in 2D materials (2014), in preparation

GRAPHITE, GRAPHENE AND RELATED 2D



STRUCTURAL CHARACTERIZATION

Bottem, Fugallo, Molteni PLoS ONE 8, 7, e70556 (2013)

GREEN TEA POLYPHENOL INTERACTIONS WITH CARDIAC PROTEIN TROPONIN C

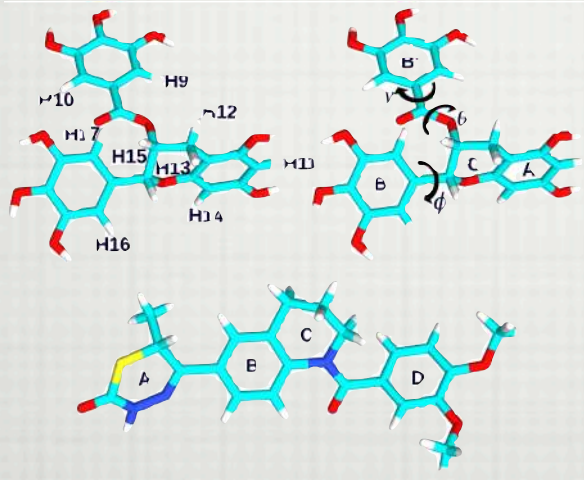


FIG. (top) The structures of green tea polyphenol EGCg and the (bottom) calcium sensitizer EMD 57033.

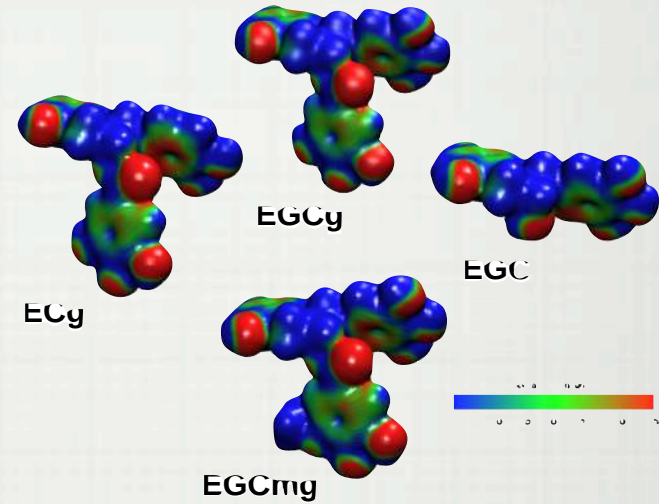


FIG. Electrostatic energy potential mapped onto an electronic isosurface for the four polyphenols

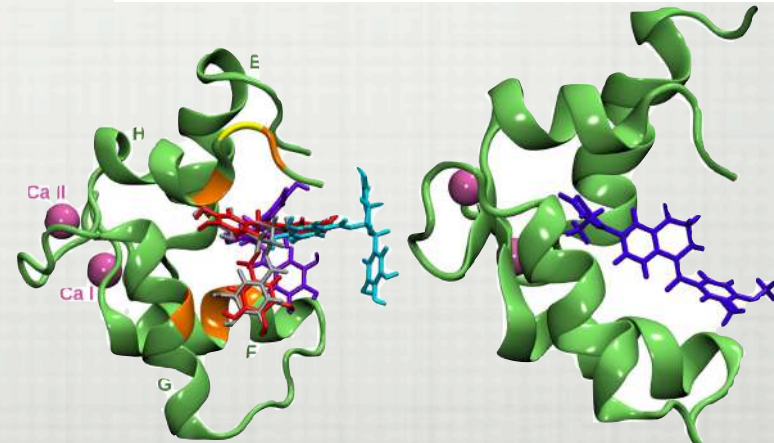


FIG: The C terminal domain of troponin C in complex with EGCg and EMD 57033.

STRUCTURAL CHARACTERIZATION

(DFT VS CLASSIC)

Bottem, Fugallo, Molteni PLoS ONE 8, 7, e70556 (2013)

QUANTUM VS CLASSICAL

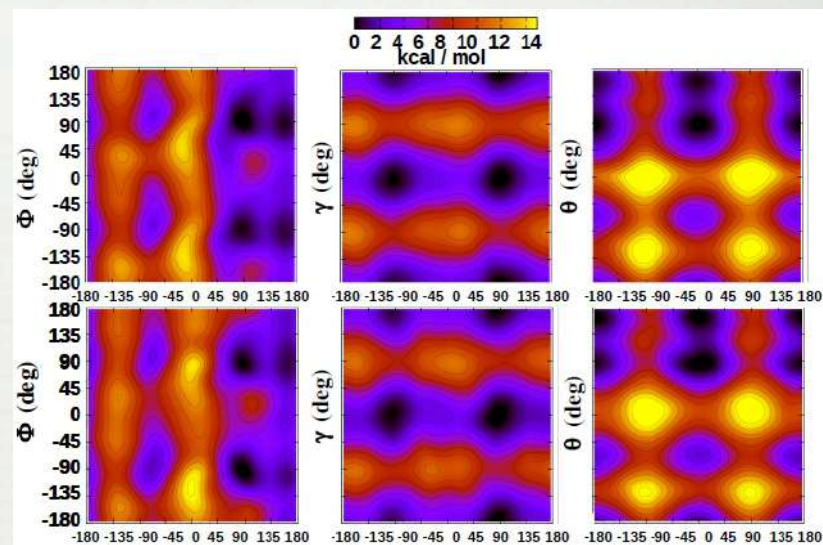
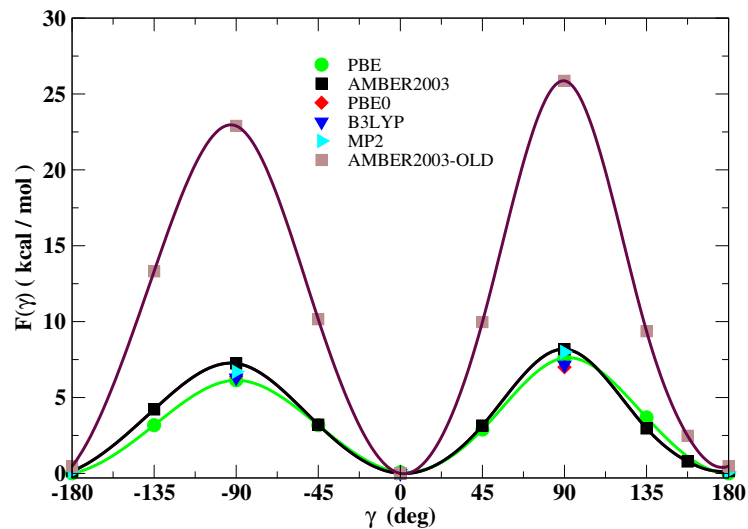


FIG. Free energy maps of the EGC torsional angle in water

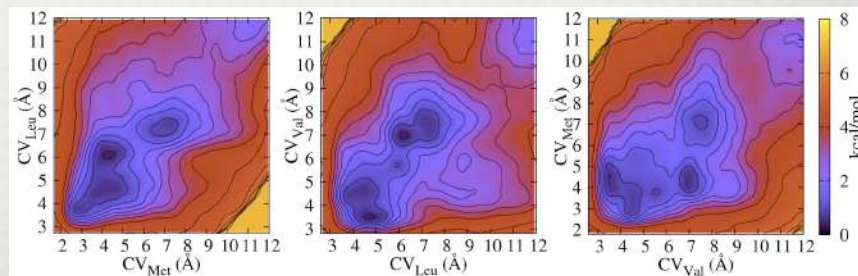


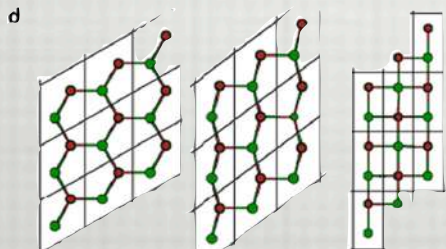
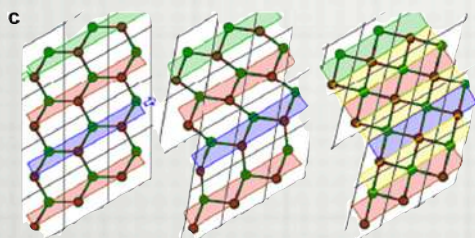
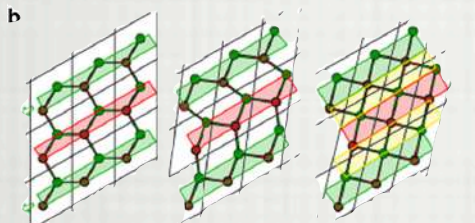
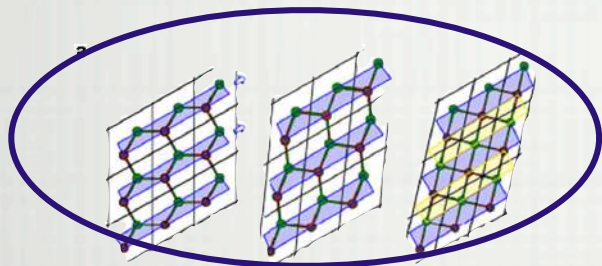
FIG. Free energy maps of the EGC binding site in cTnC

CRYSTAL PREDICTION

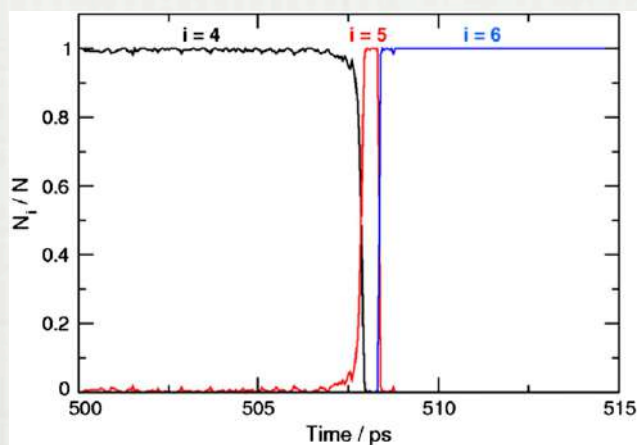
(AIMD + METADYNAMICS)

Bealing, Fugallo . Martonak, Molteni, **Phys. Chem. Chem. Phys.**, 12 , 8542 - 8550 (2010)

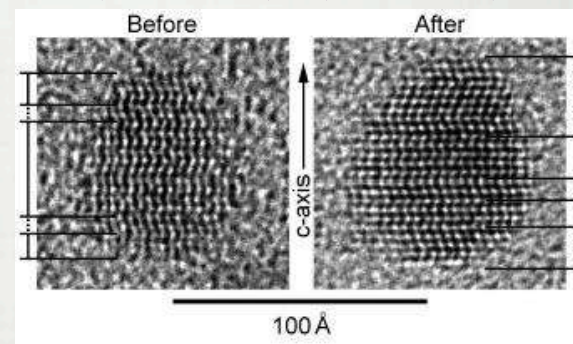
Wurtzite to Rock Salt transition in CdSe under pressure



STANDARD ABMD



Transition Pressure
2.5 GPa



RARE EVENTS

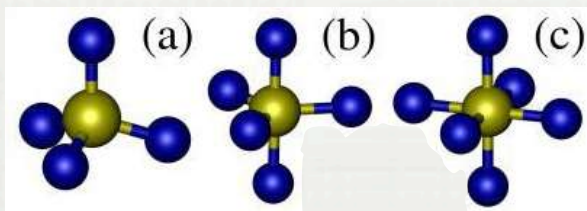
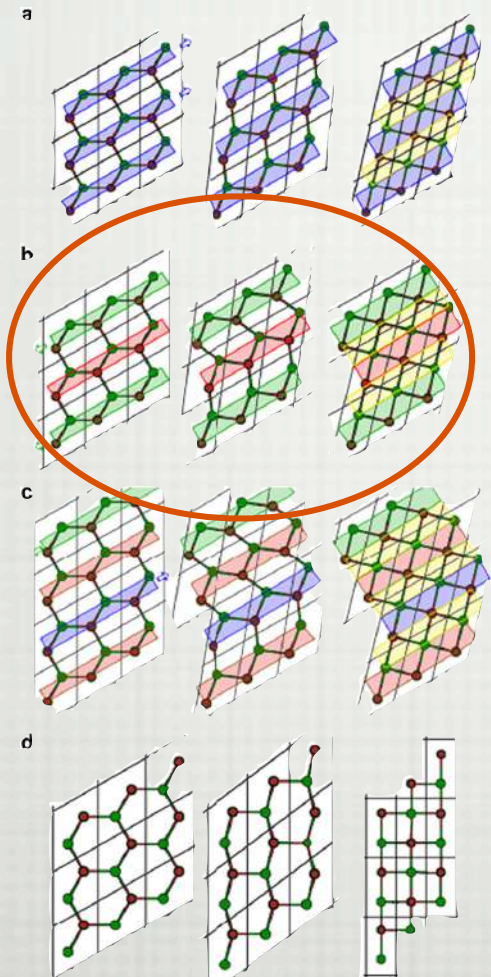
Transition at
10.5 GPa

CRYSTAL PREDICTION

(DFT-MD + METADYNAMICS)

Bealing, Fugallo . Martonak, Molteni, **Phys. Chem. Chem. Phys.**, 12 , 8542 - 8550 (2010)

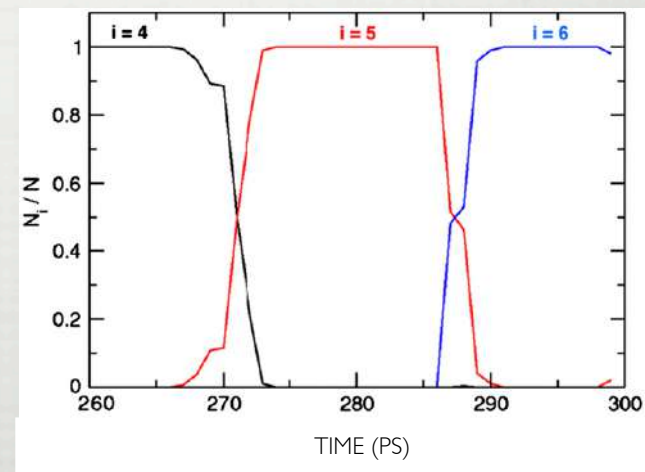
Wurtzite to rock salt transition in CdSe under pressure



Transition
Pressure
2.5 GPa

Transition at
2.5 GPa

ABMD
+
METADYNAMICS



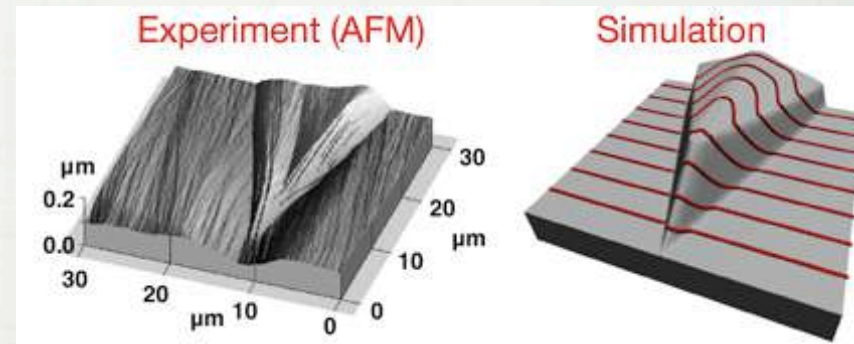
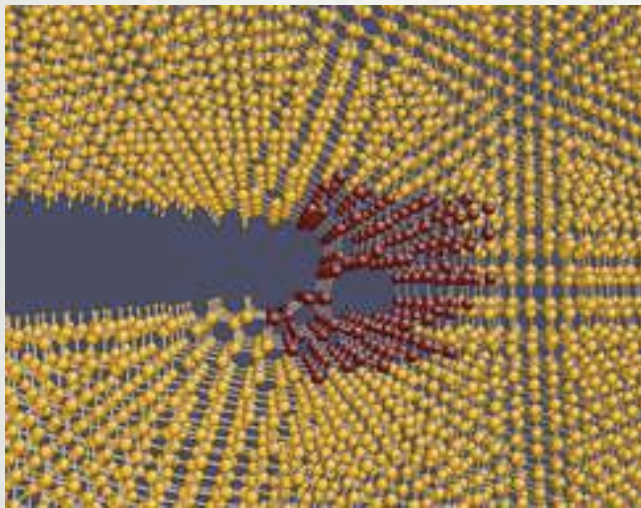
BRITTLE FRACTURE

(MULTI-SCALE APPROACH)

"Learn on the fly": a hybrid classical and quantum-mechanical molecular dynamics simulation

Physical Review Letters **93** p. 175503 (2004) ([PDF](#) [626 KB])

BRITTLE FRACTURE IN SILICON



At least 200,000 atoms are necessary to describe the long range stress and strain fields of the crack tip.

The description of the cracks tips area require accurate DFT calculations

HYBRID-APPROACH
MULTI-SCALE

THANK YOU

...SEE YOU AT THE
EXPERIMENTS DAY
AT THE LSI :-)