An introduction to MOLECULAR DYNAMICS simulations : basic principles and examples

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PREAMBLE

- I’m a researcher, not a teacher, so this will not be a standard lecture like in master classes, but rather the point of view of a molecular dynamics (MD) fan
- I’ve learned molecular dynamics by myself, by reading the litterature and writing a code (MODYC) using the routines by F. Ercolessi, author of « A molecular dynamics primer »
- Afterwards I’ve used DL_POLY then CPMD
- I have applied MD to
  - Study the diffusion of a dopant atom in crystalline silicon
  - Study the solid phase epitaxy of amorphous silicon
  - Calculate thermal conductivities and interface resistances
  - Model disordered materials

→ You will see illustrations issued from these topics in the following slides…

« If atoms don’t move we are not happy »
Slogan of the small group of MD fans @IEMN

MD is a simulation technique aimed at describing the time evolution of a set of interacting atoms

MD simulations are carried out in 3 steps:

1. Build an initial system, i.e. affect positions and type (species) to atoms
2. Calculate the atomic trajectories
3. Perform an analysis

in a way that we can qualify of « experiment on a computer »

How do we calculate the atomic trajectories ?

We solve the Newton equation* for each atom I of mass M_I at position $\boldsymbol{R}_I$ (bold → vector)

$$M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I$$

*Or Euler-Lagrange equation of motion

where $\boldsymbol{F}_I$ is the force acting upon atom I

→ The MD method is based on an iterative algoritm:

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From $t = t_{init}$ to $t_{final}$
    calculate $\boldsymbol{F}_I$
    integrate to obtain $\boldsymbol{R}_I$
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Verlet algorithm (based on a Taylor expansion):

$$\boldsymbol{R}_I(t + \Delta t) = \boldsymbol{R}_I(t) + \Delta t \cdot \dot{R}_I(t) + \frac{1}{2}\frac{\boldsymbol{F}_I(t)}{M_I}$$

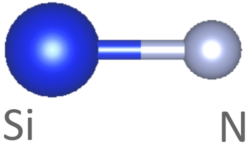
→ result in the classical trajectory of atom I

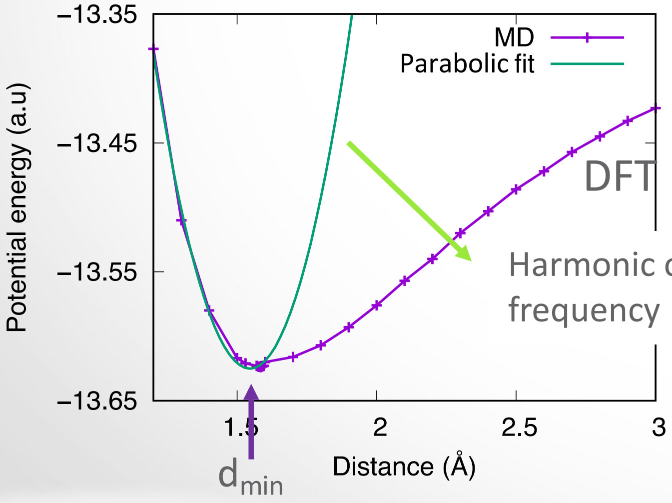
Time step Δt: fs range

How do we get the force $\boldsymbol{F}_I$?

From the gradient of the potential energy E_p ($\boldsymbol{F}_I=-\nabla E_p$)

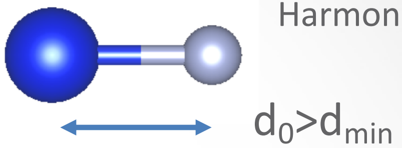
Example: The Si-N dimer:



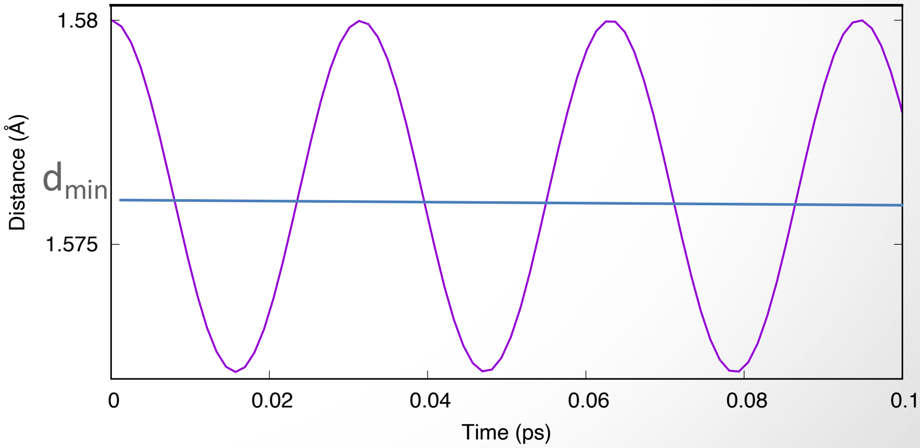


Harmonic oscillator of frequency 1058 cm^{-1}

Harmonic regime



If Si and N are initially set at a distance d_0 slightly larger than d_{min} we observe oscillations of period 0.0316ps ie 1054 cm^{-1}



→ Atomic motion and potential energy are closely related

Empirical interatomic potentials (used in Classical Molecular Dynamics)

In this case, the potential energy has an analytical formulation and involves parameters

Example: The Stillinger-Weber* potential for Si-Si

* Stillinger et al, Phys. Rev. B 1985

Two-body term:

$$f_2(r)=\begin{cases} A\,(Br^{-p}-r^{-q})\exp[(r-a)^{-1}]\,, & r<a \\ 0\,, & r\geq a \end{cases}$$

→ Fixes the equilibrium distance

Three-body term:

$$h(r_{ij},r_{ik},\theta_{jik})=\lambda\exp[\gamma(r_{ij}-a)^{-1}+\gamma(r_{ik}-a)^{-1}] \times(\cos\theta_{jik}+\tfrac{1}{3})^2\,;$$

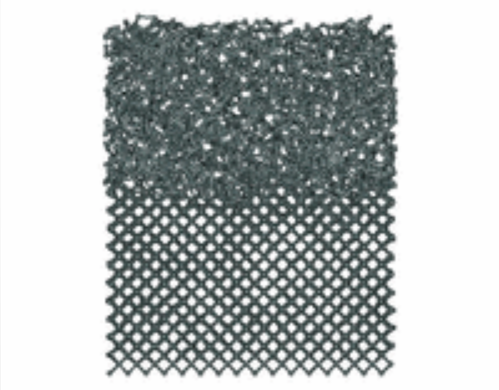
→Fixes the angle to achieve the tetrahedral configuration of the diamond crystal lattice

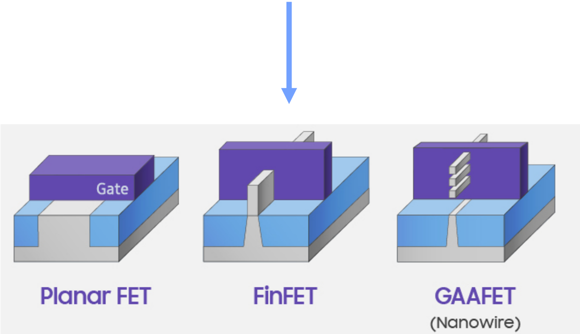
Parameters A,B,a,p,q,λ and γ are fitted on diamond structure, melting point and liquid structure

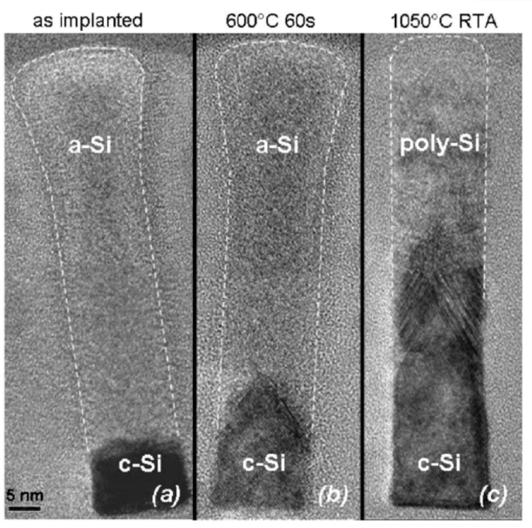
1st example of Classical Molecular Dynamics simulations

The recrystallization of preamorphized silicon:

Motivation : impact of size/orientation/geometry… to optimize the technology of devices (FinFET)





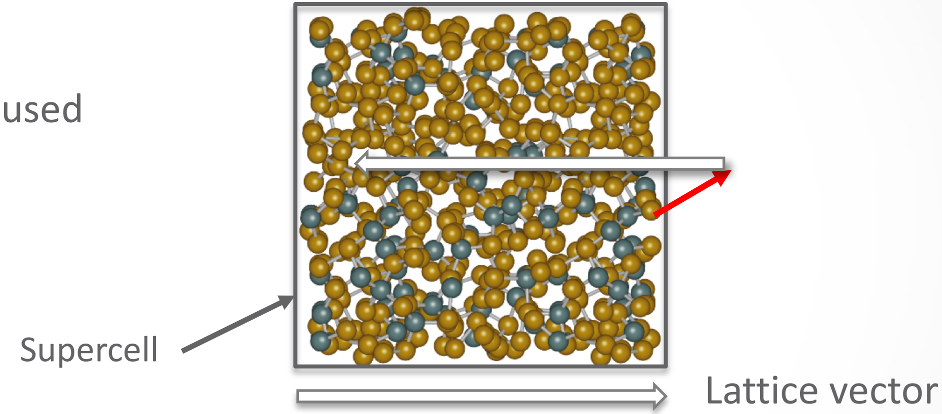


→ Incomplete recrystallization / presence of twins and grains evidenced by microscopy (TEM)

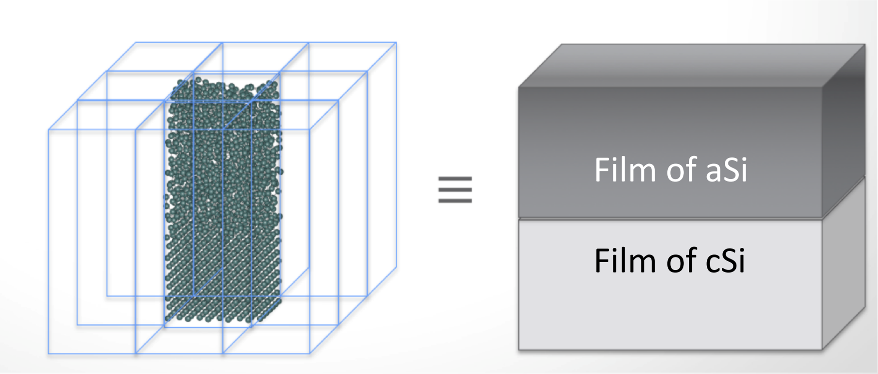
J. Appl. Phys. 101, 123506 (2007); J. Appl. Phys. 106, 063519 (2009); J. Appl. Phys. 109, 123509 (2011).

Bulk, films, …, clusters : periodic boundary conditions (PBC)

→ Periodic boundary conditions can be used to circumvent the effect of limited size

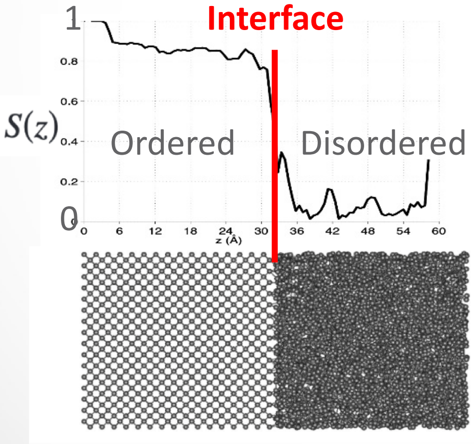


→ For the study of the recrystallization of a Si film, we have used PBC in 2 directions

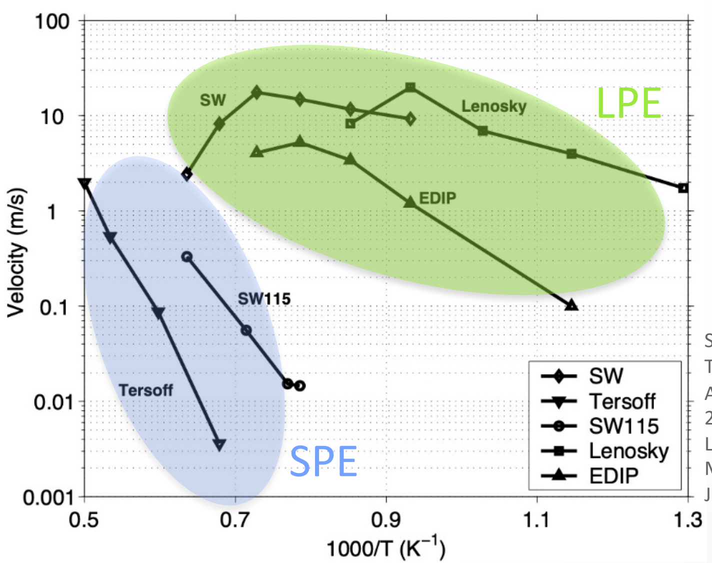


Position of the interface determined from a 1D structure factor:

$$S(z) = \left| \frac{1}{N_z} \sum_{z<z_i<z+dz} \exp(j\vec{k}\cdot\vec{r}_i) \right|$$



Velocity of recrystallization :



Stillinger et al, PRB 1985
Tersoff, PRB 1988
Albenze et al, Mol Simul 2005
Lenosky et at, Model Simul Mater Sci Eng 2000
Justo et al PRB 1998

→ Strong dependence on the interatomic potential

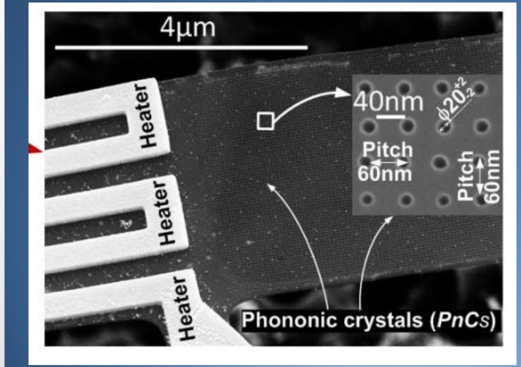
→ **Solid phase epitaxy** vs **liquid phase epitaxy** depending on the tendency of the potential to describe the amorphous phase (Tersoff, SW115) or the liquid one (SW, Lenosky, EDIP)

2nd example of Classical Molecular Dynamics simulations

The thermal conductivity at nanoscale

Motivation : identify impact of size, defects, interfaces, …

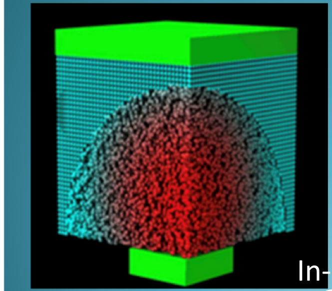
Applications : Heat management of nanodevices →
Thermoelectric devices ↓

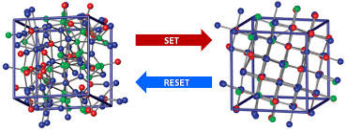


Route for energy harvesting

@IEMN

Ex: Phase Change Memories





In-memory computing
@IBM

Temperature, thermostats and Molecular Dynamics

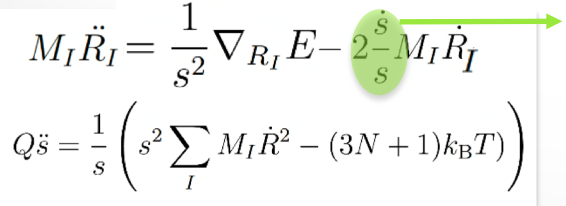
- Temperature is a direct output of a MD simulation via the atomic velocities $\boldsymbol{v}_I = \dot{\boldsymbol{R}}_I$:

$$\frac{3}{2}Nk_{\mathrm{B}}T=\sum_{I=1}^{N}\frac{1}{2}M_I\,\dot{\boldsymbol{R}}_I^2$$

(Equipartition theorem)

- The « natural » ensemble of MD simulations is the microcanonical (NVE)

- Options to set a target temperature T_g :
  1. velocity rescaling : a factor $\lambda=\sqrt{\frac{T_g}{T(t)}}$ is applied to the velocities
  2. Nosé-Hoover thermostat, i.e. add a (single) degree of freedom *s* coupled to the system and acting as a heat reservoir :



$$M_I\ddot{R}_I = \frac{1}{s^2}\nabla_{R_I}E - 2\frac{\dot{s}}{s}M_I\dot{R}_I$$

$$Q\ddot{s} = \frac{1}{s}\left(s^2\sum_I M_I\dot{R}^2 - (3N+1)k_{\mathrm{B}}T\right)$$

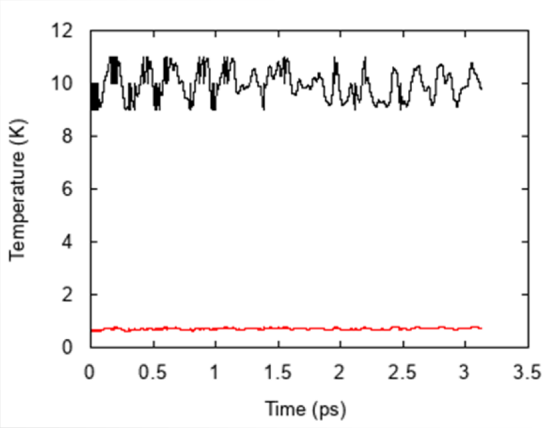
Q: mass of the thermostat

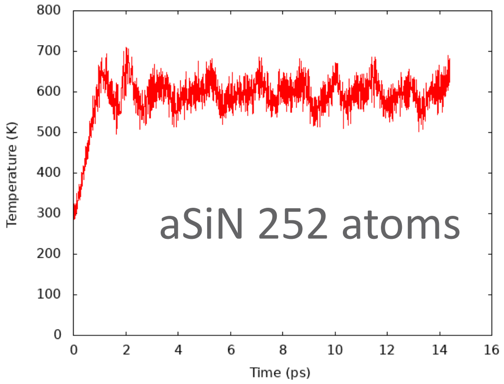
Dynamic friction coefficient: acceleration or damping of the ions, i. e. heating or cooling, depending on the sign of $\dot{s}$

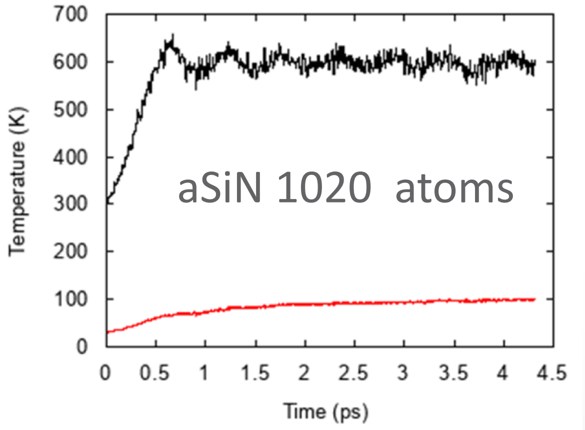
Nose Mol. Phys. 1984; Hoover Phys Rev A 1985

Nosé-Hoover @ 600K

Velocity scaling to 10 K +/-1
(aSiN 1020 atoms)







Fluctuations of the temperature decrease when the number of atoms increases

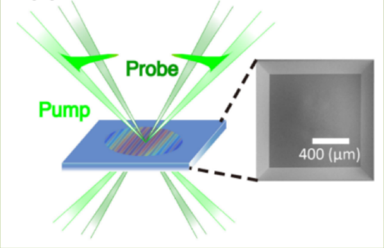
(*T* constant @ infinite number i.e. thermodynamic limit)

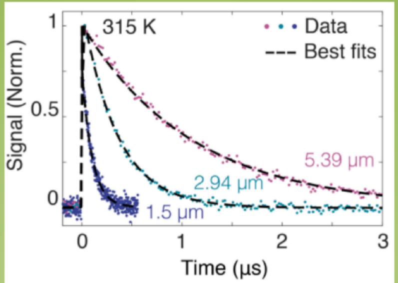
Thermal conductivity by AEMD (Approach-to-Equilibrium Molecular Dynamics)

Lampin et al JAP 2013; Zaoui et al PRB 2016; Palla et al, IJHMT 2019

Equivalent on computer of the thermal transient grating experiment*:

*Minnich, PRL 2012

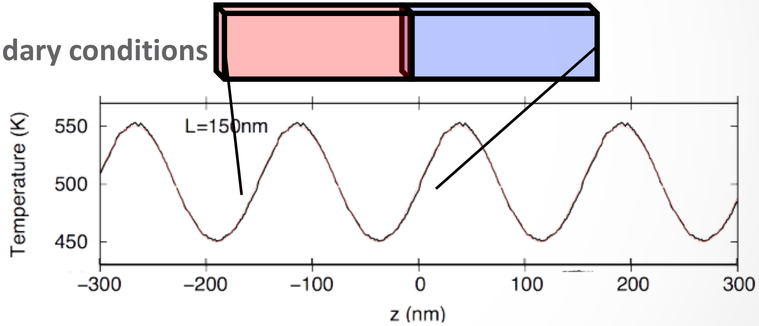




Phase 1: establishment of a hot/cold periodic signal

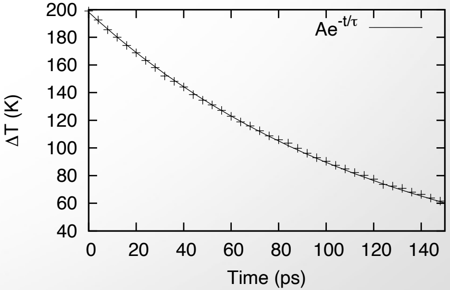
2 local thermostats: **Hot** **Cold**

+ periodic boudary conditions



Phase 2: monitoring of the transient to equilibrium

$$\Delta T = T_{hot} - T_{cold}$$



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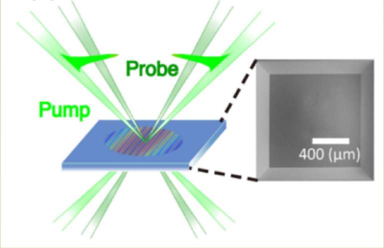

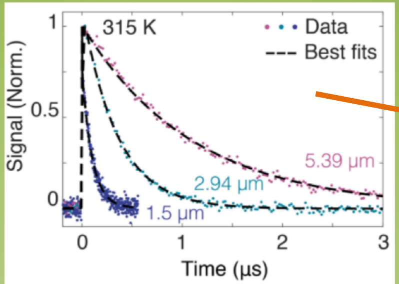

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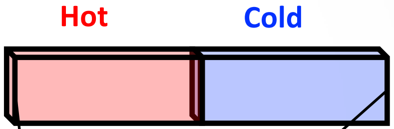
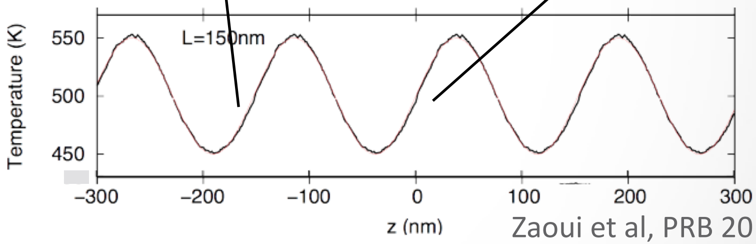


+ periodic boudary conditions



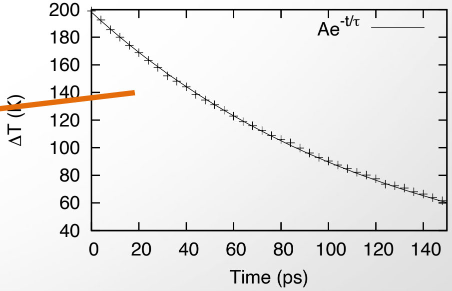
Zaoui et al, PRB 2017

Phase 2: monitoring of the transient to equilibrium

Transient time τ

Thermal diffusivity $\alpha=L^2/(4\pi^2\tau)$

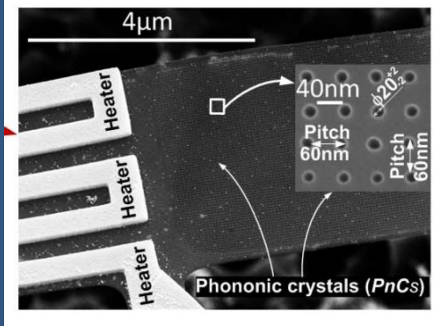
Thermal conductivity $\kappa=\rho C\alpha$

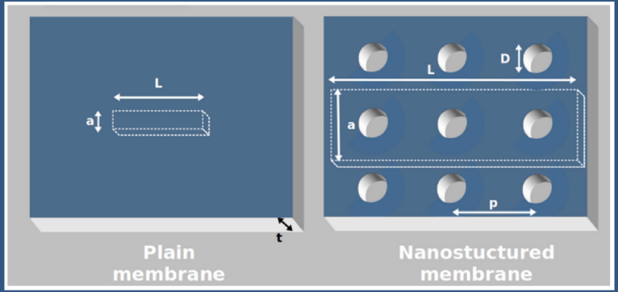


Thermal conductivity by AEMD
(Approach-to-Equilibrium Molecular Dynamics)

Advantage of the AEMD:

- Only requires to apply thermostats and monitor temperatures
  Easily feasible with all MD codes
- Transient → less time to wait to get κ
  → larger supercells can be studied, i. e. closer to real systems
  Record : more than 6 millions atoms, Si membrane with holes:



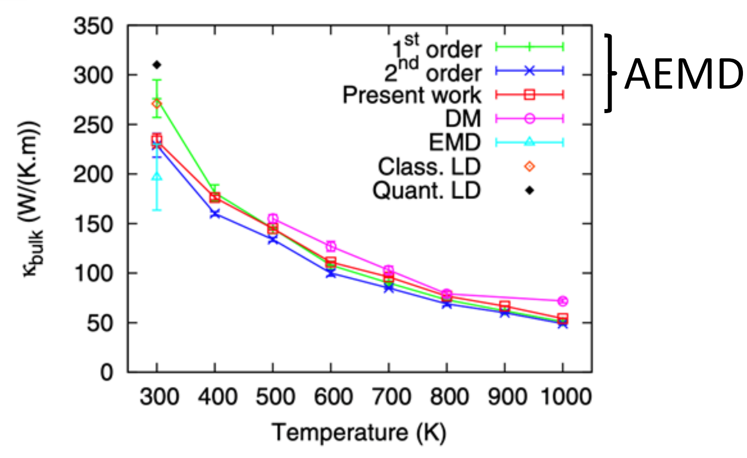


Thickness ~8nm
a= 60 nm
L =300 nm

Zaoui et al IJHMT2018

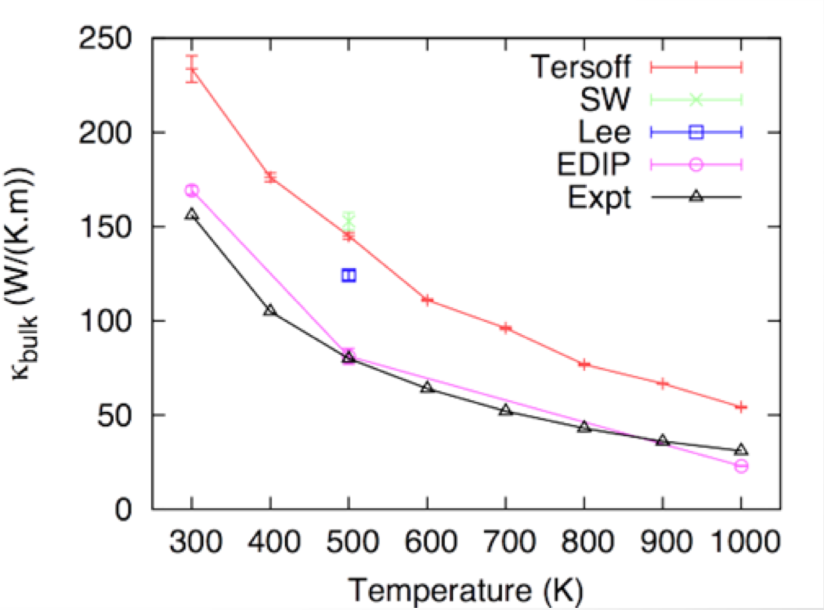
Thermal conductivity of silicon

The results do not depend on the method used to calculate the thermal conductivity:



DM: direct method (Schelling et al, PRB 2002)
EMD : Green-Kubo (Zwanzig, Annu Rev Phys Chem 1965)
LD : lattice dynamics (He et al, PCCP 2012)

But the thermal conductivity depends on the interatomic potential



Zaoui et al, PRB 2016

To summarize, so far we have seen that:

1. Molecular dynamics deals with the solution of the equation of motion:

$$M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I$$

2. Periodic boundary conditions enable to handle finite size supercells (nearly) without impact of the surfaces

3. The temperature can be easily obtained (velocities) and can be controlled by thermostats

4. In classical MD,
   - empirical interatomic potentials
   - number of atoms : up to millions
   - timescale : hundreds of ns

5. Quantitative modeling requires to go beyond empirical interatomic potentials

First-Principal Molecular Dynamics (FPMD)

i.e. the potential energy is obtained from the density-functional theory (DFT)

In the Born-Oppenheimer scheme, the most « straightforward »:

At each time step, the electronic ground state is determined by minimising the DFT or Kohn-Sham hamiltonian H_e for the ionic positions R_I:

$$H_e\phi_0 = E_0\phi_0$$

Before propagating the ions in the corresponding potential :

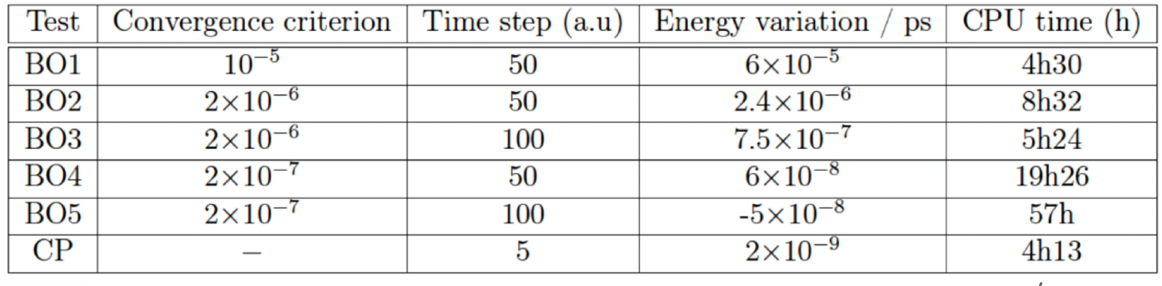
$$M_I\ddot{R}_I(t) = -\nabla_I \mathrm{min}_{\phi_0}\{\langle\phi_0|\, H_e \,|\phi_0\rangle\}$$

Pros and cons of the Born-Oppenheimer Molecular Dynamics

Pros :

Time step same order than in CMD since given by the ion kinetics (100 a.u. = 2.4 fs)

Principles quite « simple » : controlled by convergence level of the H_e minimization



Test	Convergence criterion	Time step (a.u)	Energy variation / ps	CPU time (h)
BO1	10^{-5}	50	6×10^{-5}	4h30
BO2	2×10^{-6}	50	2.4×10^{-6}	8h32
BO3	2×10^{-6}	100	7.5×10^{-7}	5h24
BO4	2×10^{-7}	50	6×10^{-8}	19h26
BO5	2×10^{-7}	100	-5×10^{-8}	57h
CP	–	5	2×10^{-9}	4h13

/ps

aSiN
252 atoms
100 K

CP: 10^{-5}

Cons :

Computational cost is high due to H_e minimisation at each time step

Energy is less well conserved compared to other schemes, in particular the Car-Parrinello

The Car-Parrinello approach for FPMD

Main idea: the electronic orbitals $\{\phi_i\}$ are considered as classical variables that evolve with the ions dynamics

→ Lagrangian

Fictitious mass

$$L_{\text{CP}} = \frac{1}{2}\sum_I M_I \dot{R}_I^2 + \sum_i \frac{1}{2}\int \mu \dot{\phi}_i^*(r)\dot{\phi}_i(r)dr - E^{\text{DFT}}(\{\phi_i\},\{R_I\}) + \sum_{ij}\lambda_{ij}\left(\int \phi_i^*\phi_j dr - \delta_{ij}\right)$$

Kin. energy ions

Fictitious electronic kin. energy

Potential energy

Lagrange multiplier for orthonormality

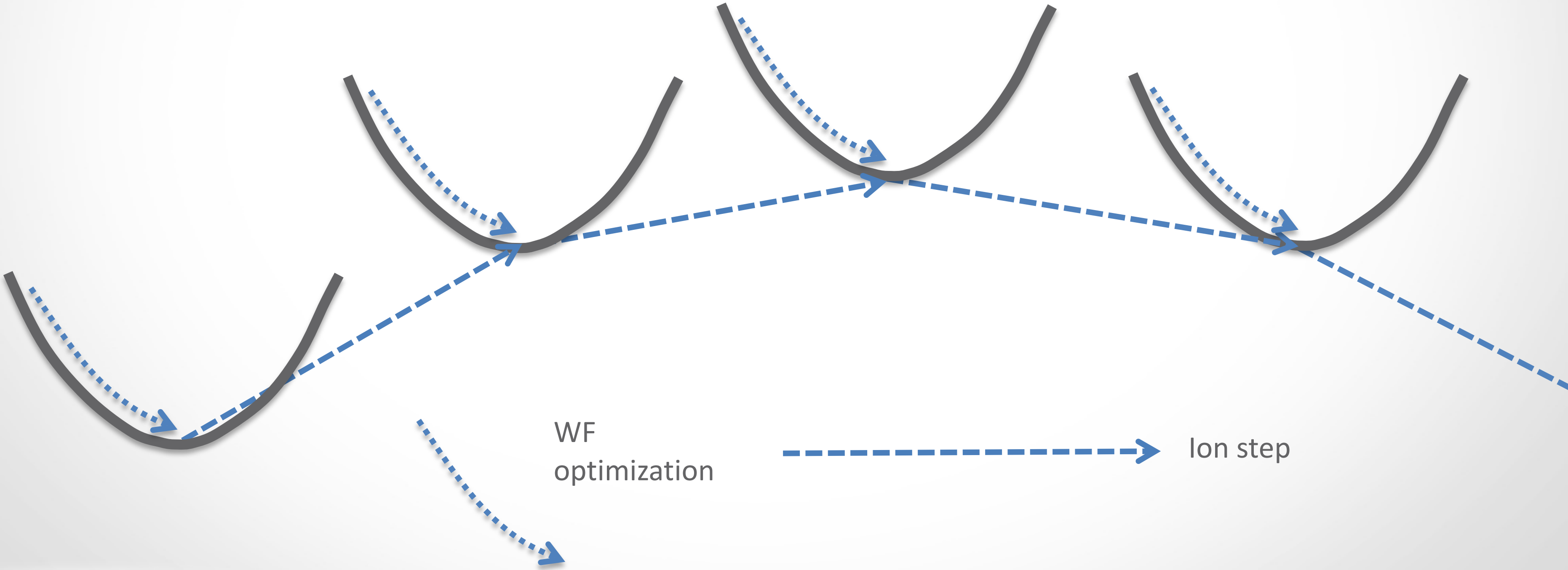
→ Euler-Lagrange equation for the CP:

$$\mu\ddot{\phi}_i = -\frac{\partial E\left(\{\phi_i\},\{R_I\}\right)}{\partial \dot{\phi}_i^*} + \sum_j \lambda_{ij}\phi_j$$

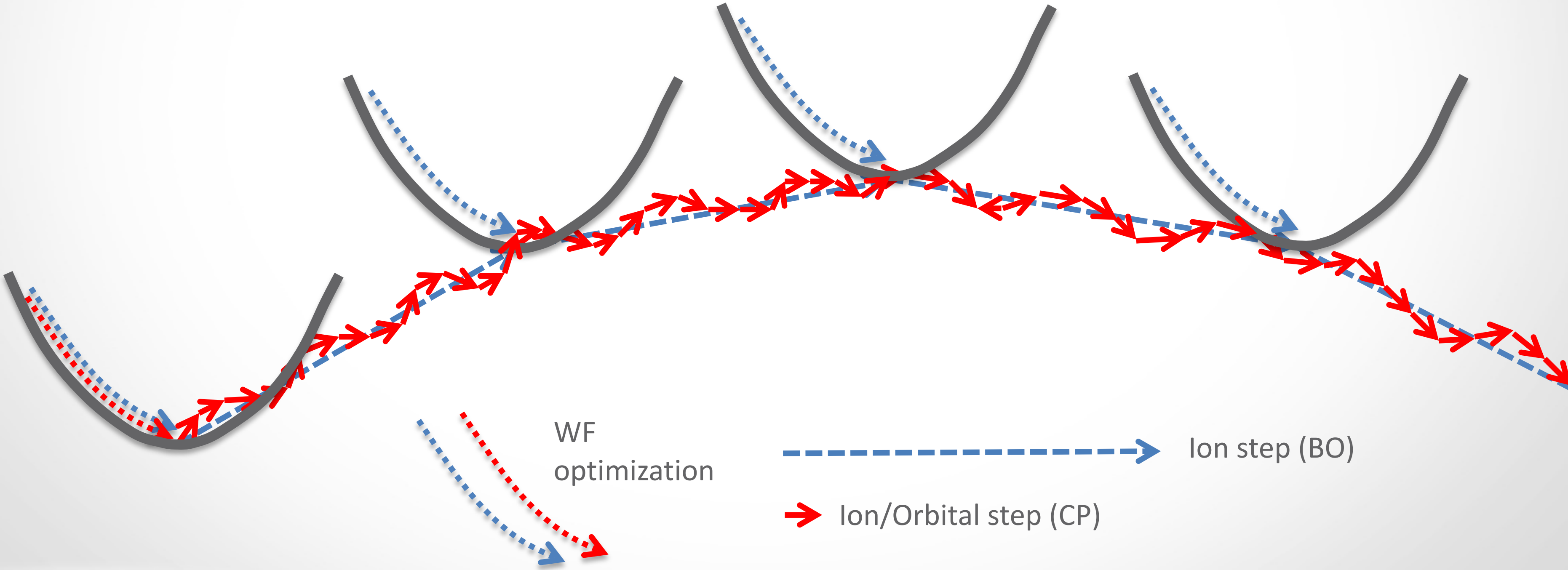
$$M_I\ddot{R}_I = -\frac{\partial E\left(\{\phi_i\},\{R_I\}\right)}{\partial R_I}$$

Available in the code cpmd (cpmd.org)

Born-Oppenheimer Molecular Dynamics



Car-Parrinello Molecular Dynamics



WF
optimization

Ion step (BO)

Ion/Orbital step (CP)

Fictitious mass in CP molecular dynamics

μ is a critical parameter since :

→ It must be large enough to enable a significant dynamics of the electronics orbitals/ the use of a reasonable time step, typically 5 a.u = 0.12 fs

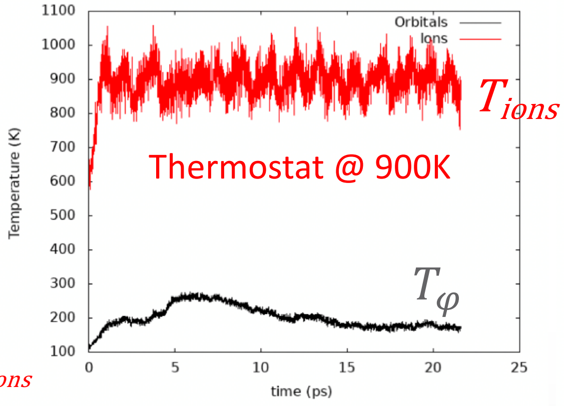
→ But if it is too large the departure from the BO trajectory increases / non-adiabatic coupling of the ionic and electronic subsystem

→ Temperature of orbitals T_φ

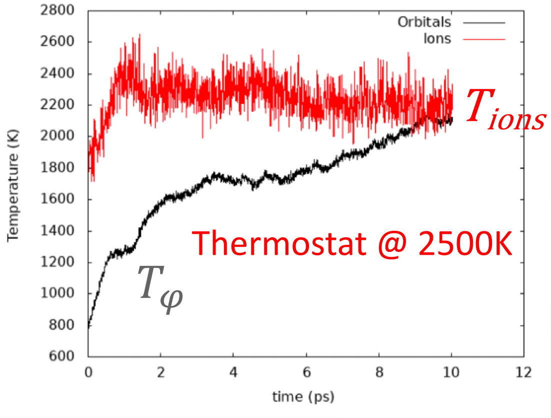
$\frac{N_\varphi}{2} k_B T_\varphi = E_{Fict}^{Kin}$

low compared to ionic temperature T_{ions}

YES



NO



→ Temperature ions and orbitals egal

→ Ionic temperature decreases/unable to thermostat

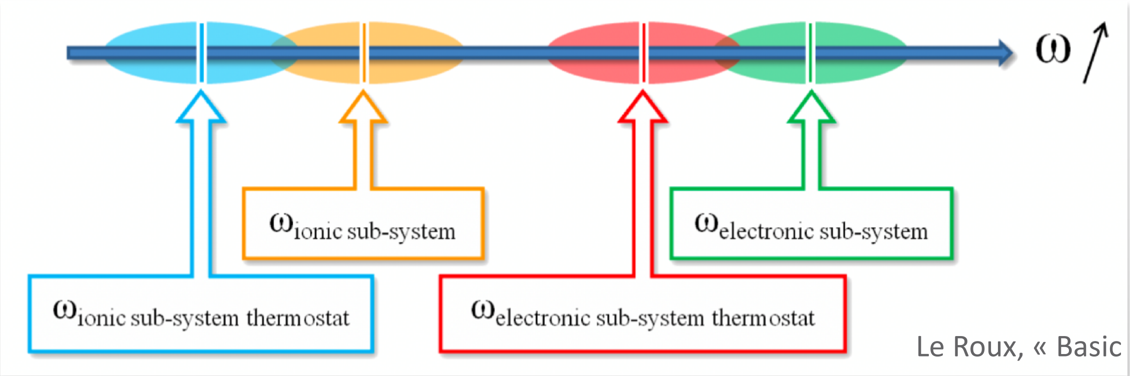
Control of the adiabadicity in the CP approach

Thermostat on the electronic orbitals

$$Q_e\ddot{\xi} = \frac{2}{\xi}\left(\xi^2\sum_i \mu|\dot{\phi}_i(x)|^2 - E_e^{\mathrm{kin}}\right) \qquad \mu\ddot{\phi}_i(x) = -\frac{\partial E^{\mathrm{DFT}}}{\partial \dot{\phi}_i^*} + \sum_j \lambda_{ij}\phi_j - \frac{\dot{\xi}}{\xi}.\mu.\phi_i$$

$$Q\ddot{s} = \frac{1}{s}\left(s^2\sum_I M_I\dot{R}_I^2 - (3N+1)k_{\mathrm{B}}T\right) \qquad M_I\ddot{R}_I = \frac{1}{s^2}\nabla_{R_I}E^{\mathrm{DFT}} - 2\frac{\dot{s}}{s}M_I\dot{R}_I$$

→ Parameters of thermostats :



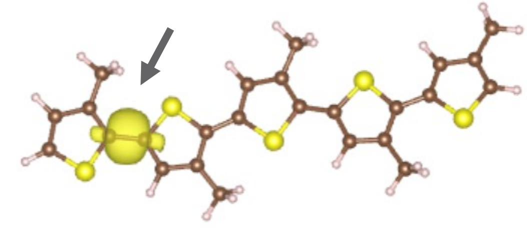
Le Roux, « Basic tutorial to CPMD calculations »

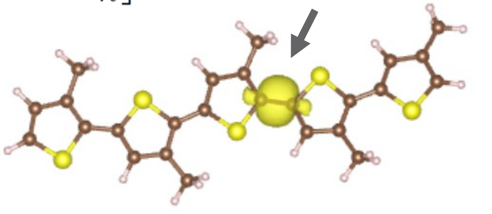
1st example : Orbitals and analysis of chemical bonding

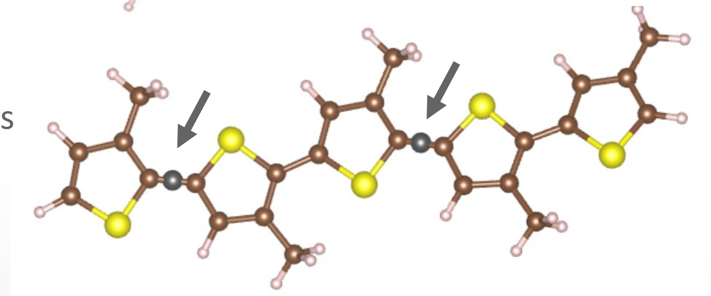
Molecule P3MT (penta(3-methylthiophene))

Representation of two wave functions (transformed from Kohn-Sham orbitals, which are not necessarily localised, to the localized Wannier*) :

→ minimise the quadratic spread : $\Omega = \sum_n \left[\langle r^2\rangle_n - \bar{\mathbf{r}}_n^2\right]$



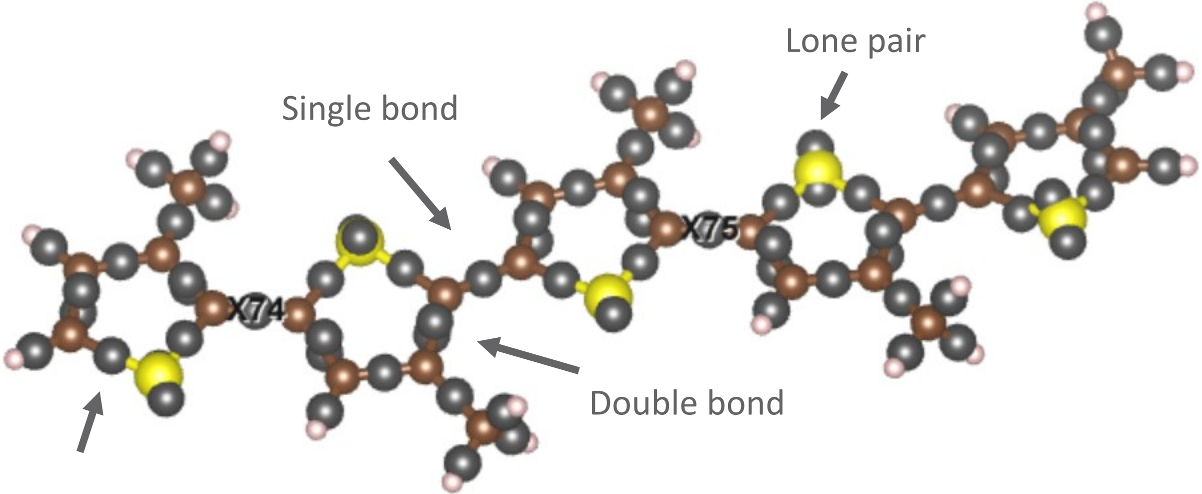




Corresponding Wannier centers

*Marzari et al, Rev. Modern Phys (2011)

1st example : Orbitals and analysis of chemical bonding



Lone pair

Single bond

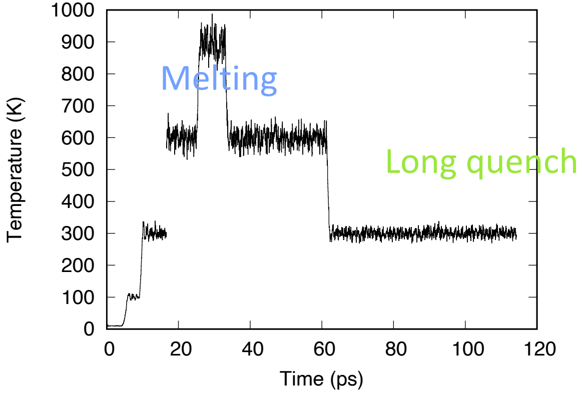
Double bond

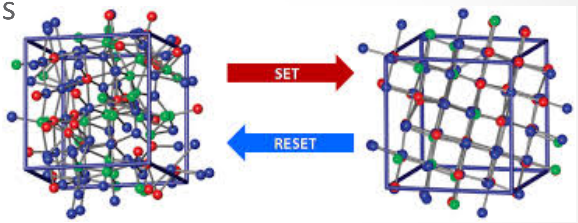
Electronegativity

2nd example : disordered materials

The case of $Ge_2Sb_2Te_5$, a phase-change material used in memories

Structure of
the amorphous phase ?



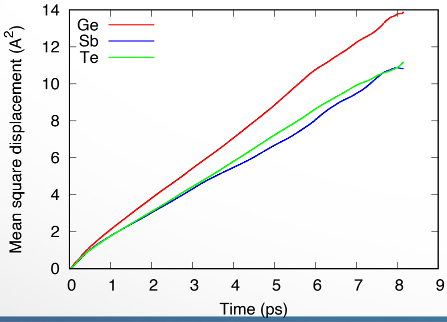


Amorphous phase

Crystalline phase

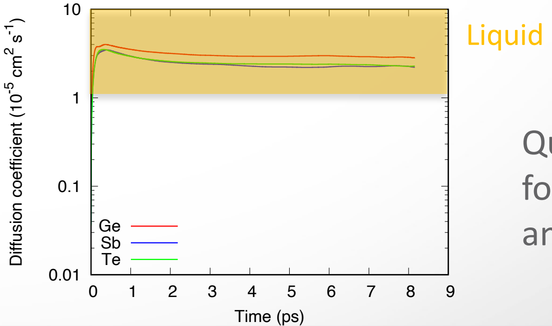
Monitoring of the diffusion
(liquid state ?) :

$$MSD(t) = \left\langle \frac{1}{N}\sum_I \left(R_I(t) - R_I(t_O)\right)^2 \right\rangle_{t0}$$



$\equiv$

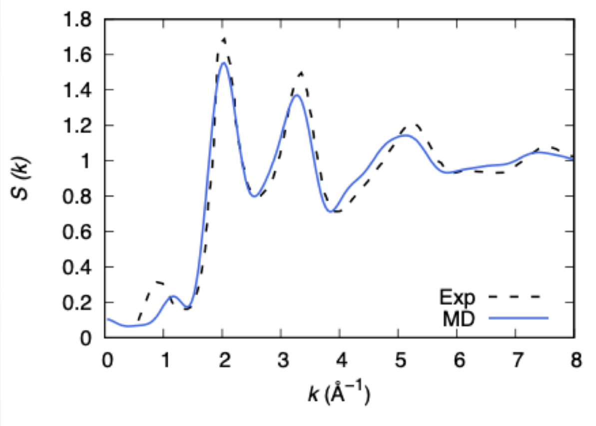
$$D(t) = \frac{MSD(t)}{6t}$$



Quench → model ready
for the structural
analysis…

Analysis of the structure

Neutrons structure factor of a$Ge_2Sb_2Te_5$:



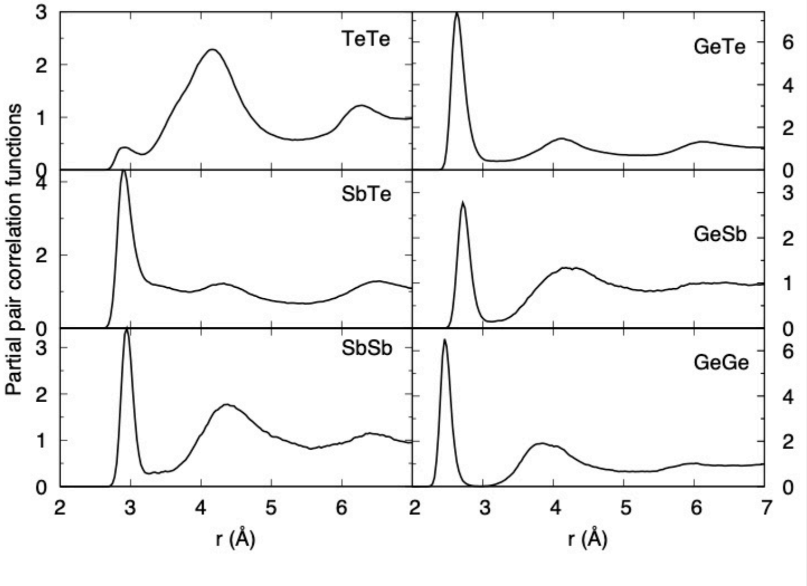
→ Quantitative agreement with experiment

Legitimate model as a basis to analysis the bond distances, coordination number, identify structural units (tetrahedra, octohedra…)

Bouzid et al, Phys Rev B (2017)

Partial pair correlation functions
= Number of atoms of species *i* at a distance *r* of an atom of species **j**

$$g_{ij}(r) = \frac{dn_{ij}}{4\pi r^2 dr \rho_i}$$

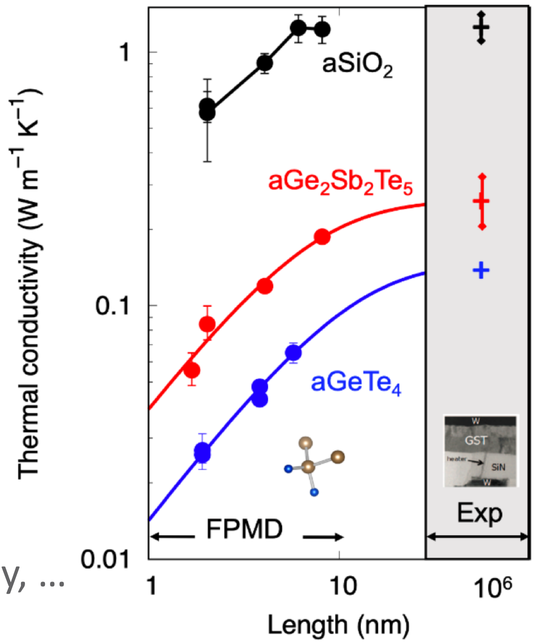


Thermal conductivity

Obtained by applying the AEMD

Extrapolation* or value at saturation in quantitative agreement with measurements (bulk)

→ Open the way to the analysis of the reduction at short *L* in real amorphous materials :
origin, consequences for nanotechnology, …



* Alvarez and Jou APL 2007

- Bouzid et al, Phys Chem Chem Phys 2017
- Martin et al, J. Non-Cryst. Solids 2018
- Duong et al, Phys. Rev. Mat. 2019
- Duong et al, Comp. Mater. Sc. 2020
- Duong et al, RSC Advances 2021
- Martin et al, J. Non-Cryst. Solids 2022

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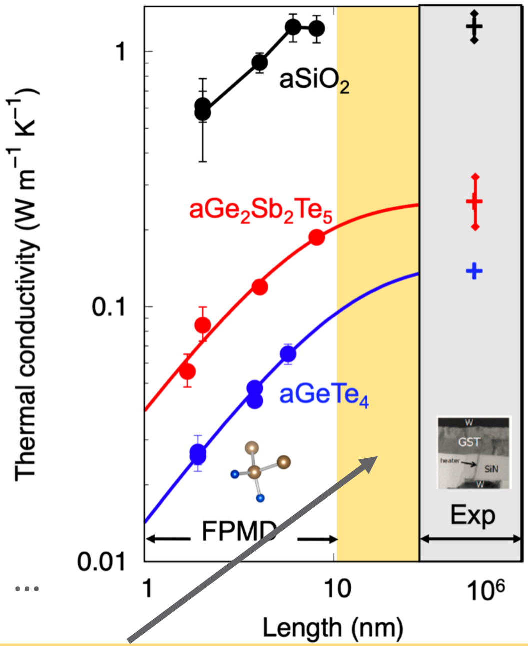

- Bouzid et al, Phys Chem Chem Phys 2017
- Martin et al, J. Non-Cryst. Solids 2018
- Duong et al, Phys. Rev. Mat. 2019
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- Duong et al, RSC Advances 2021
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Fill the gap FPMD /Exp keeping the FPMD predictivity ?
→ Machine learning potentials ?

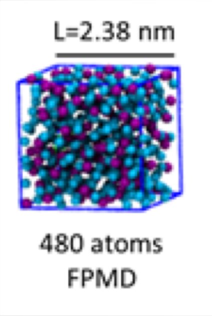
Potential energy & machine learning

Basic idea : training of a potential on a FPMD database (atomic configurations, energies, …)

Example : a$GeSe_2$, GAP* approach (G. Ori et al, private communication)

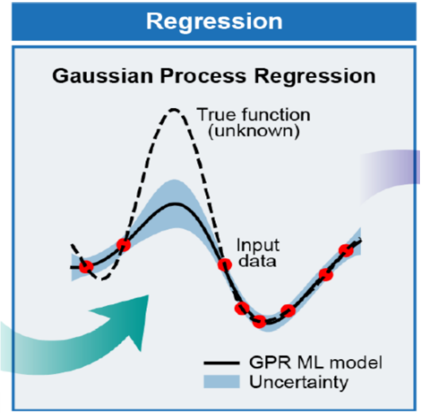
*Gaussian Approximation Potential, Bartok PRL 2010

Melt/quench
by FPMD

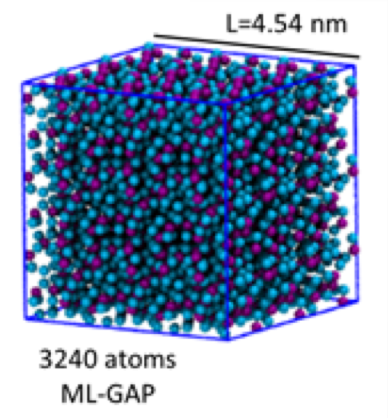


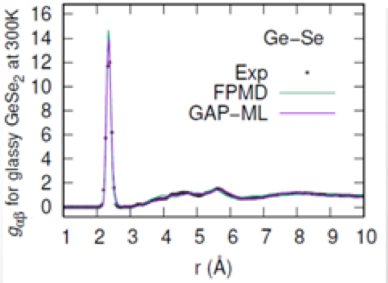
Generation
of the ML
potential

(Gaussian
Process
Regression)



Generation of a
larger model
using the ML
potential in
LAMMPS to
melt/quench





→ Same structure, 7x number of atoms

To go further:

M. Meyer and V. Pontikis, « Computer Simulation in Materials Science » 1991

M. Tuckerman, « Statistical Mechanics: Theory and Molecular Simulation », Oxford U. Press (2010)

D. Marx and J. Hutter, « Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods », Cambridge U. Press (2012)

C. Massobrio, « The structure of amorphous materials by Molecular Dynamics: from methodology to achievements », IOP publishing, in press

The present lecture has been enriched by the illustrations of Achille Lambrecht (M2) and Cheick Diarra (PhD) @ ICube

It has been improved thanks to the critical reading of Carlo Massobrio, Guido Ori & Mauro Boero @ IPCMS

Thank you for listening and enjoy molecular dynamics simulations !