

Computational Material Science

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Outline

1. Introduction

- Simulation of Materials
- Characteristic lengths and times in materials
- Adiabatic approximation

2. Electronics Structure Calculation (T=0 K)

- Density Functional Theory (DFT), Hohenberg-Kohn Theo.
- Kohn-Sham Eqs., Local Density Approximation (LDA)
- Example: alumina

3. Moving the atoms

- Classical MD
- Ab-initio MD
- Example: germania

4. Conclusions

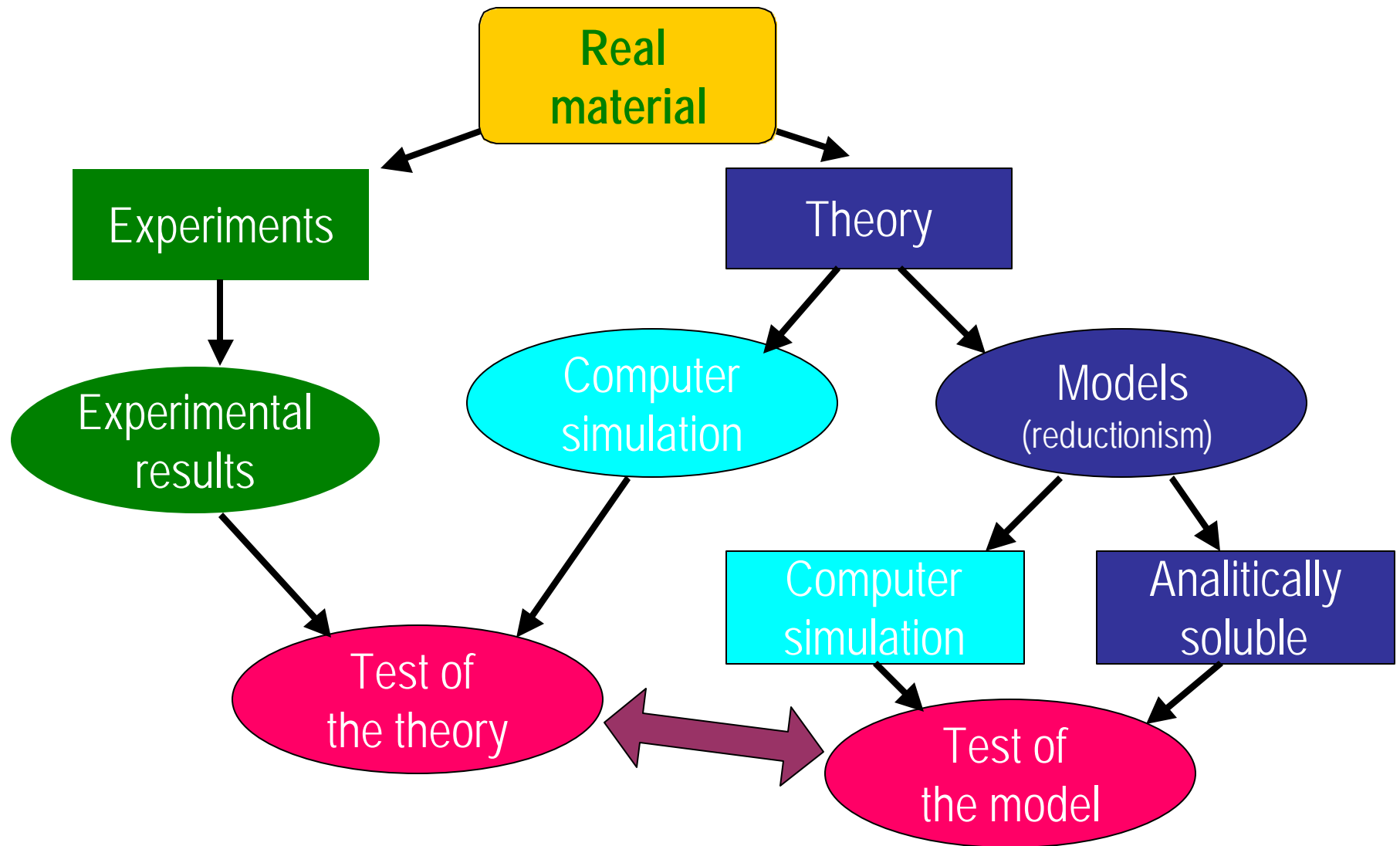
Tabla Periódica de los Elementos

H ¹																	He ²
Li ³	Be ⁴											B ⁵	C ⁶	N ⁷	O ⁸	F ⁹	Ne ¹⁰
Na ¹¹	Mg ¹²											Al ¹³	Si ¹⁴	P ¹⁵	S ¹⁶	Cl ¹⁷	Ar ¹⁸
K ¹⁹	Ca ²⁰	Sc ²¹	Ti ²²	V ²³	Cr ²⁴	Mn ²⁵	Fe ²⁶	Co ²⁷	Ni ²⁸	Cu ²⁹	Zn ³⁰	Ga ³¹	Ge ³²	As ³³	Se ³⁴	Br ³⁵	Kr ³⁶
Rb ³⁷	Sr ³⁸	Y ³⁹	Zr ⁴⁰	Nb ⁴¹	Mo ⁴²	Tc ⁴³	Ru ⁴⁴	Rh ⁴⁵	Pd ⁴⁶	Ag ⁴⁷	Cd ⁴⁸	In ⁴⁹	Sn ⁵⁰	Sb ⁵¹	Te ⁵²	I ⁵³	Xe ⁵⁴
Cs ⁵⁵	Ba ⁵⁶	La ⁵⁷	Hf ⁷²	Ta ⁷³	W ⁷⁴	Re ⁷⁵	Os ⁷⁶	Ir ⁷⁷	Pt ⁷⁸	Au ⁷⁹	Hg ⁸⁰	Tl ⁸¹	Pb ⁸²	Bi ⁸³	Po ⁸⁴	At ⁸⁵	Rn ⁸⁶
Fr ⁸⁷	Ra ⁸⁸	Ac ⁸⁹	Rf ¹⁰⁴	Db ¹⁰⁵	Sg ¹⁰⁶	Bh ¹⁰⁷	Hs ¹⁰⁸	Mt ¹⁰⁹	Uun ¹¹⁰								

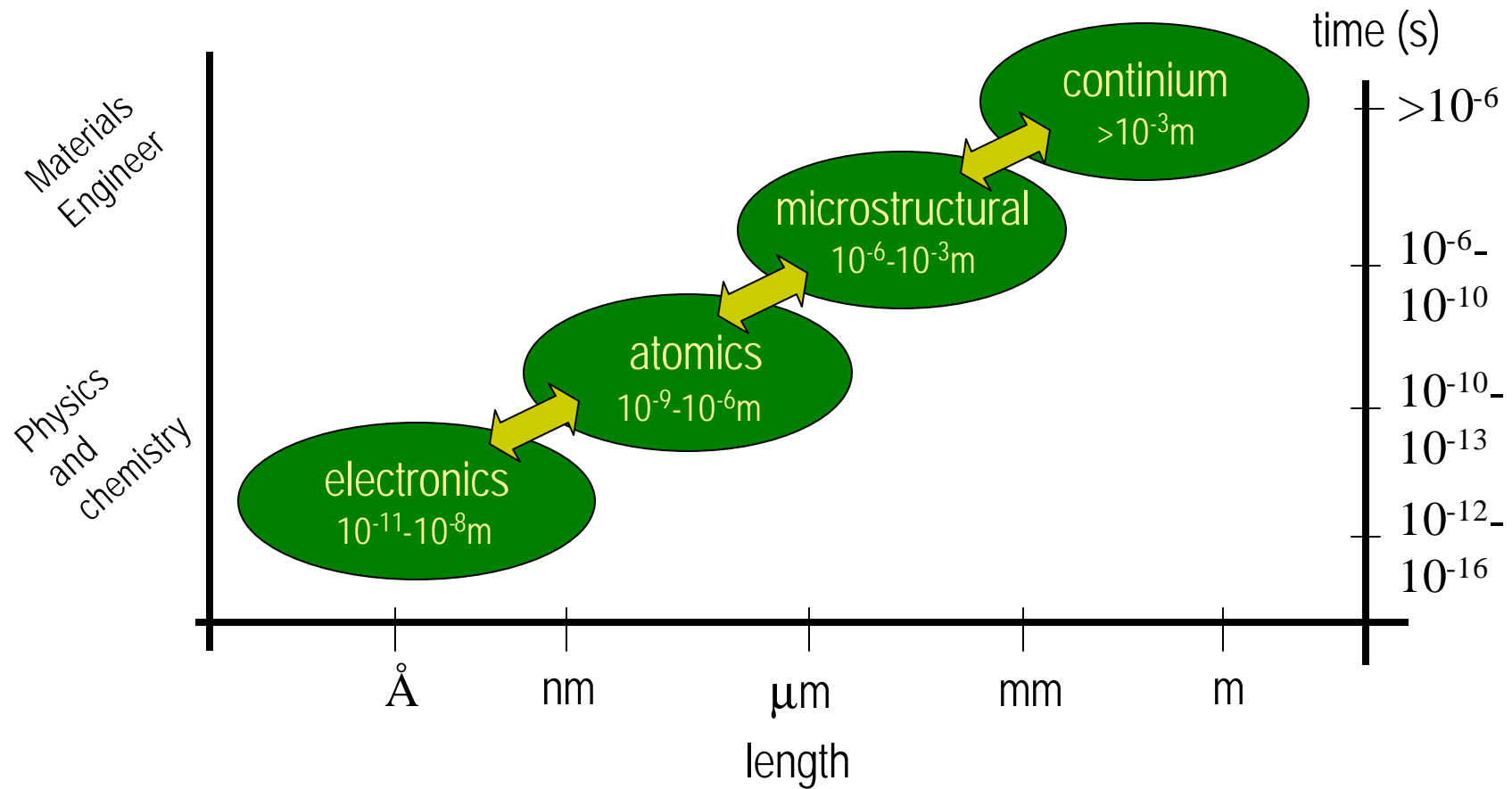
Ce ⁵⁸	Pr ⁵⁹	Nd ⁶⁰	Pm ⁶¹	Sm ⁶²	Eu ⁶³	Gd ⁶⁴	Tb ⁶⁵	Dy ⁶⁶	Ho ⁶⁷	Er ⁶⁸	Tm ⁶⁹	Yb ⁷⁰	Lu ⁷¹
Th ⁹⁰	Pa ⁹¹	U ⁹²	Np ⁹³	Pu ⁹⁴	Am ⁹⁵	Cm ⁹⁶	Bk ⁹⁷	Cf ⁹⁸	Es ⁹⁹	Fm ¹⁰⁰	Md ¹⁰¹	No ¹⁰²	Lr ¹⁰³

 Metales alcalinos	 Metales alcalinos terrosos	 Metales de transición	 Metales de tierras raras
 Otros metales	 Gases nobles	 haluros	 Otros no metales

Computer simulation



Space and time in materials



Splitting different characteristics time

- Equation of the system

$$H|\Psi\rangle = E|\Psi\rangle$$


- Solid state physics hamiltonian:


$$(T_{ion} + T_e + V_{e-e} + V_{e-ion} + V_{ion-ion})\Psi(r_1, \dots, r_N; R_1, \dots, R_M) = E\Psi(r_1, \dots, r_N; R_1, \dots, R_M)$$

- **Adiabatic approximation:** splitting of the ionics and electronics degree of freedom

$$M_{ion} \sim 2000-10000 m_e \Rightarrow \tau_{ion} \gg \tau_e$$

- **Writing** $\Psi(r;R) = \Phi(r) \chi(R)$, the problem split in two parts:

electron  $(T_e + V_{e-e} + V_{e-ion} + V_{ion-ion})\Phi(r_1, \dots, r_N; \{R\}) = \mathbf{e}(\{R\})\Phi(r_1, \dots, r_N; \{R\})$

ion  $(T_{ion} + \mathbf{e}(\{R\}))\mathbf{c}(R) = E \mathbf{c}(R)$

Electrons and ions

Electrons $(T_e + V_{e-e} + V_{e-ion} + V_{ion-ion})\Phi(r_1, \dots, r_N; \{R\}) = \mathbf{e}(\{R\})\Phi(r_1, \dots, r_N; \{R\})$

• **knowing $\mathbf{e}(R)$ we can have:**

- Ground state (T=0)
- Crystalline structure and PV diagram
- Elastic, optics, magnetics, etc, properties
- Potential energy surface
- Interatomic potential
- \Rightarrow **interatomic forces**

Iones $(T_{ion} + \mathbf{e}(\{R\}))\mathbf{c}(R) = E' \mathbf{c}(R)$

This is a quantum problem, but classical physics work pretty well!

- to look for an effective interatomic potential $\mathbf{e}(R)$
- to treat the ions as classical particles, i.e. obeying Newton Laws

Electrons : solution of the Schrödinger Eq.

- **Hamiltonian of a many electrons system:**

$$\left(\sum_{j=1}^N -\frac{\hbar^2}{2m} \nabla_j^2 + V_{e-e} + V_{ext} \right) \Phi(\vec{r}_1, \dots, \vec{r}_N) = E \Phi(\vec{r}_1, \dots, \vec{r}_N)$$

- To look for the GS by means of a variational method:

$$E_0[\Phi_0] = \text{Min}_{\tilde{\Phi}} \langle \tilde{\Phi} | H | \tilde{\Phi} \rangle$$

$$\tilde{\Phi}(\vec{r}_1, \dots, \vec{r}_N) \quad 3N \text{ dimensions trial function}$$

- **Approximate Methods** : one electron selfconsistent equations

Hartree: $\Phi(\vec{r}_1, \dots, \vec{r}_N) = \mathbf{f}_1 \dots \mathbf{f}_N$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Z}{r} + \int \frac{n(r')}{|r-r'|} dr' \right) \mathbf{f}_i = \mathbf{e}_i \mathbf{f}_i, \text{ con } n(r) = \sum_i |\mathbf{f}_i|^2$$

Hartree-Fock: $\Phi(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \det[\mathbf{f}_1 \dots \mathbf{f}_{N_i}]$

Density Functional Theory

The electronic density $n(r)$ as the basic variable

Hohenberg-Kohn (1964):

1. The external potential $v(r)$ is totally determined from the electronic density $n(r)$.

$$E[n] = \int n(r)v(r)dr + T[n] + V_{e-e}[n]$$

2. For the trial density $\tilde{n}(r)$ we obtain $E_0 \leq E[\tilde{n}]$

N.B. a) We had a $3N$ variables trial function $\Phi(r_1 \dots r_N)$, but now only a 3 variables trial function $\tilde{n}(r)$

b) DFT gives a strict formulaci3n of the search of the GS from the electronic density $\tilde{n}(r)$.

For example, Thomas-Fermi can be derived from DFT.

Electrons II: Kohn-Sham Eqs.

- Total energy reads as (Kohn & Sham, 1965)

$$E_{\{R\}}[\tilde{n}] = T_s[\tilde{n}] + E_{Hartree}[\tilde{n}] + E_{ext}[\tilde{n}] + E_{xc}[\tilde{n}]$$

- Minimization of $E_{\{R\}}[\tilde{n}]$ is equivalent to solve

Kohn-Sham Eqs.

Selfconsistent solution

$$\left\{ \begin{array}{l} \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\vec{r}) \right] \mathbf{j}_i(\vec{r}) = \mathbf{e} \mathbf{j}_i(\vec{r}) \\ v_{eff} = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{ext}(\vec{r}) + v_{xc}(\vec{r}) \\ n(\vec{r}) = \sum_{i=1}^N |\mathbf{j}_i(\vec{r})|^2 \end{array} \right.$$

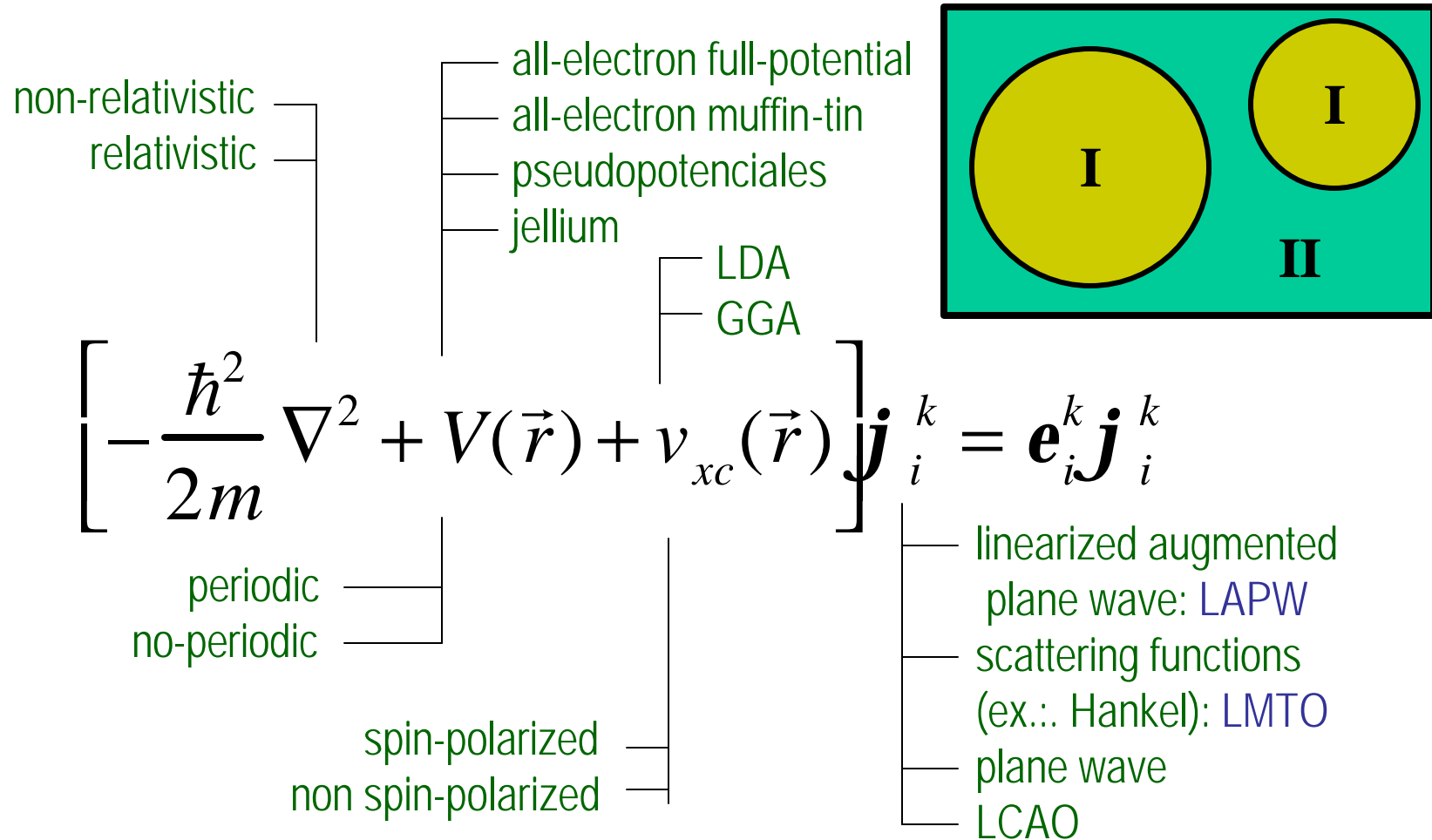
- LDA approximation: $E_{xc}[n] \approx \int n(\vec{r}) \mathbf{e}_{xc}(n(\vec{r})) d\vec{r}$

with

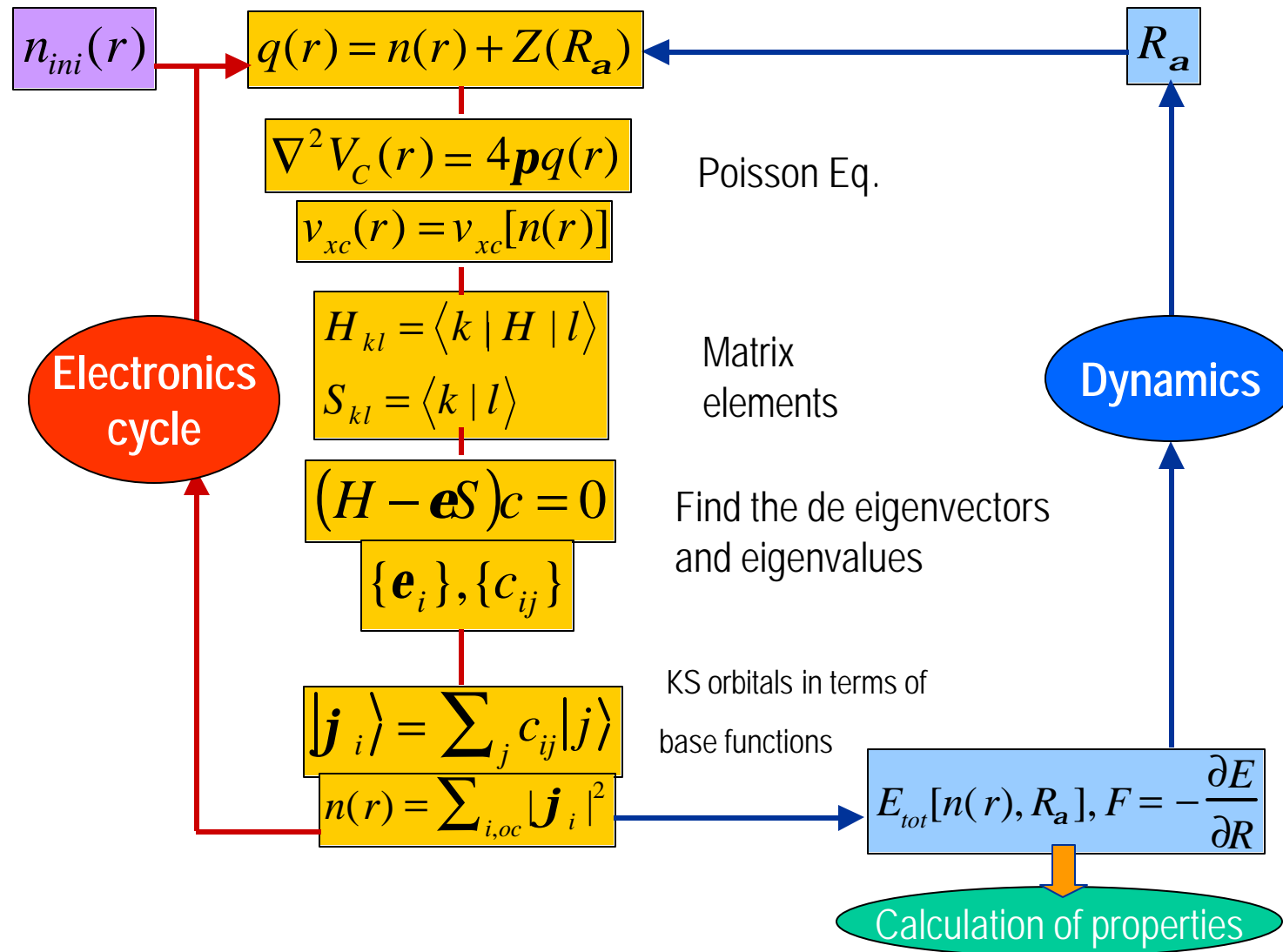
$$\mathbf{e}_{xc} = -\frac{0.458}{r_s} - \frac{0.44}{r_s + 7.8}$$

homogeneous
electron gas

Electrones III: implementation



Implementation: selfconsistent cycle



Technical issues

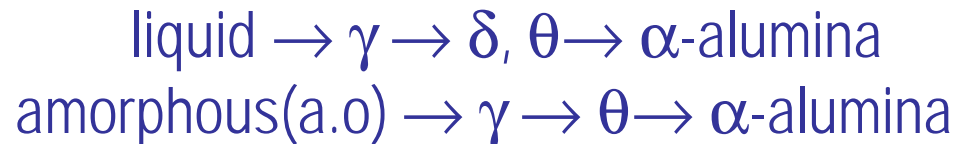
- Input: crystalline structure, atomic numbers
- Accuracy in energy, in forces
- Full potential calculation:
 - FPLAPW (Wien2k),
 - FPLMTO
- Pseudopotential calculation
 - PPPW method (VASP, CPMD, ABINIT)
 - Other expansion: Gaussian, SIESTA

Example: Al_2O_3

Importance:

- ceramic material important both in geosciences and technology
- many technological applications, because extreme hardness, high melting point, low electrical conductivity.

Structural phase transitions:



Transition aluminas are used as adsorbents, catalysts or catalyst support, coatings, etc, because of their fine particle size, high surface and catalytic activities of their surfaces.



**Ref: G. Gutiérrez et al: -PRB 65, 012101 (2002)
-to be submitted (2004)**

α and $\gamma\text{-Al}_2\text{O}_3$ are the most common phases,
but the structure of γ is still unknown.

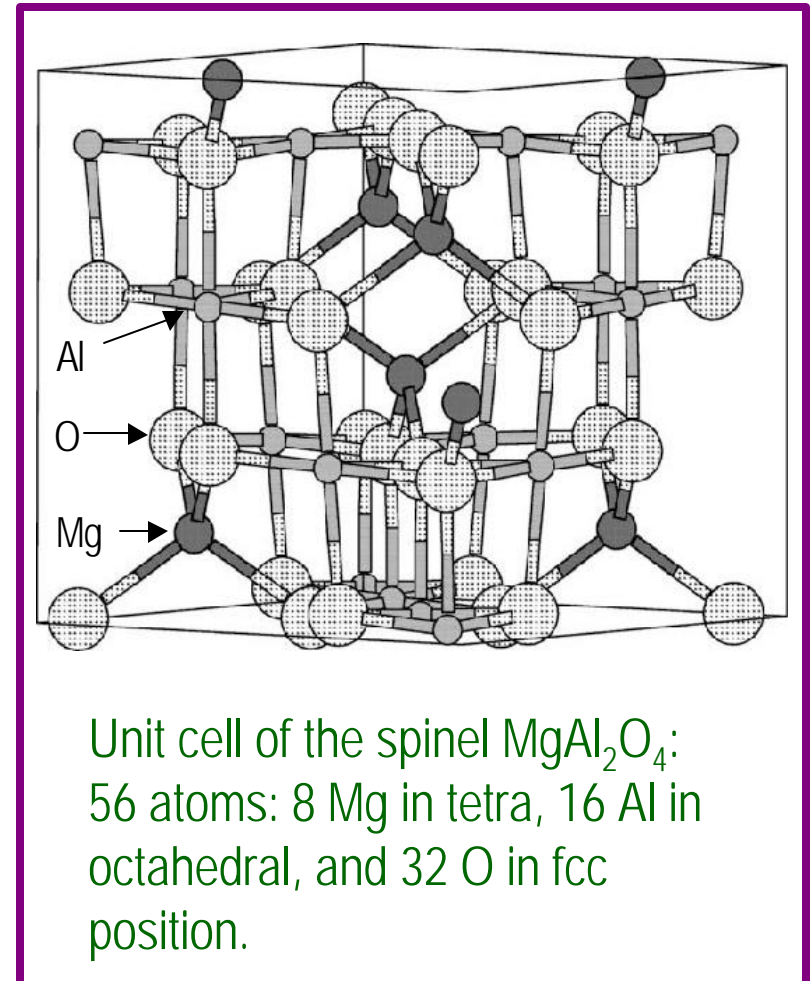
- Aluminum surface oxidize in the atmosphere, forming oxide films. Also, one can make a surface treatment to aluminum by anodic oxidation.
- How is the structure of such films?
- Are they amorphous-like, or they have a γ structure, as has been suggested because the low coordination that present Al atoms at the surface?
- The first step to answer these question is to determine the bulk $\gamma\text{-Al}_2\text{O}_3$ structure

$\gamma\text{-Al}_2\text{O}_3$: structure

• **Defective spinel:** cubic unit cell
 32 O in a fcc array, and $2\frac{1}{3}$ Al, placed in
 tetra- and octahedral positions at random.
 described by $\left[\right]_{2\frac{2}{3}}\text{Al}_{2\frac{1}{3}}\text{O}_{32}$

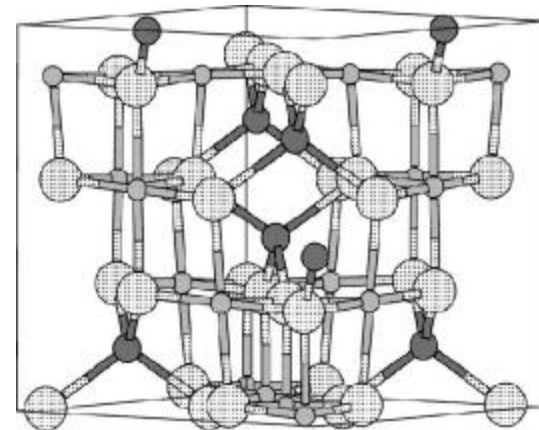
• This formula is deduced from the figure.
 An integer number of Al atoms is obtained
 if one enlarges this unit cell three times:
 160 at = $\left[\right]_8\text{Al}_{64}\text{O}_{96}$

*These Al vacancies occupy octahedral
 or tetrahedral cation sites?
 In what proportion?*



Situation so far

- **Experiments:** neutron, electron and x-ray diffraction has led to conflicting conclusions:
 - vacancies situated entirely in tetrahedral positions
 - octahedral
 - both, 63:37
- **Theoretical works:** not conclusive results either.
 - MD and MC 64% of vacancies in tetrahedral sites
 - Empirical pair pot+ab-initio, MD ('99): vacancies in octahedral positions.



Searching for the minimum energy structure

Total energies for a large number of configurations consistent with the crystallographic specifications need to be calculated

Two main ways:

- 1) In most MD simulations, authors have increased the unit cell
- 2) to consider as a tolerable stoichiometric approximation a unit cell with $56\text{at}=21\text{Al} + 32\text{O}$.

•Our approach: reduction of the unit cell

•Instead of considering a cubic unit cell, one can consider a primitive cell with less particles!

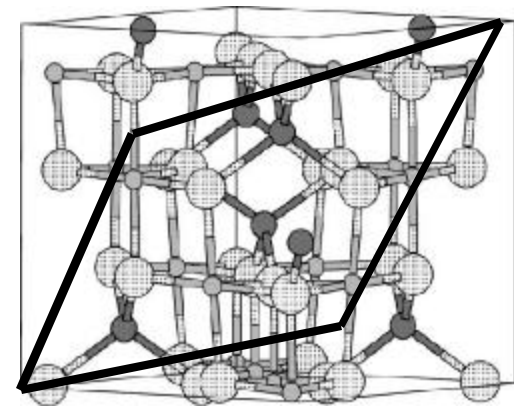
Noting that $(\text{Al}_8\text{O}_{24})/4 = \text{Al}_2\text{O}_6$ only 40 atoms

•In order to have it

•perfect spinel, Al_3O_4 , has 56 at., so the primitive has 14 at. Increase by three, remove 2 Al, and you get Al_2O_3

•There are two Al vacancies, which can be both tetrahedral, both octahedral, or one tetra and one octa.

•There are only 153 configurations for Al vacancies (in comparison to 10^{10} for the 160 at. unit cell).



Method

After a detailed structural analysis of the 153 configurations, one get only 14 non-equivalent config: 4 OO, 6 TO and 4 TT.

- We performed total-energy calculations for all these 14 configurations, allowing for relaxation.

Method: ab-initio total energy calculation

DFT within LDA and exchange-correlation functional of Ceperley and Alder

Plane wave pseudopotentials code (VASP)

Kinetic energy cutoff E_{cut} at 400 eV.,

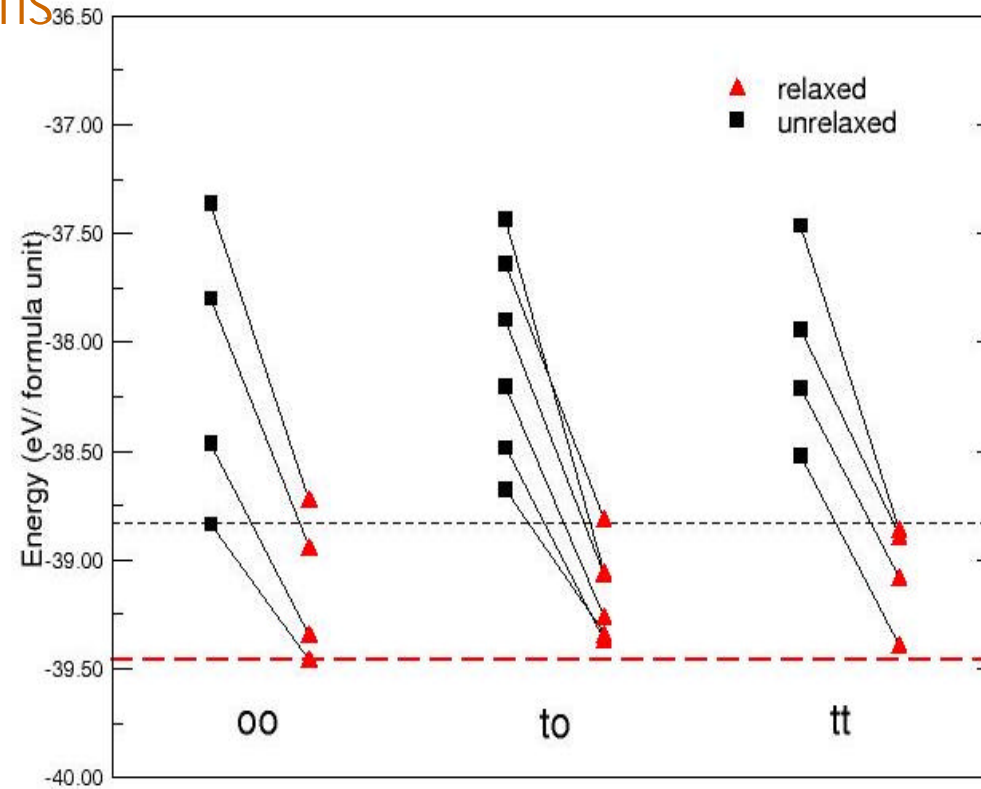
Two kind of k-point sampling, resulting two kind calculation

Low accuracy: only the g point, converged to 0.03 eV/(formula unit)

High accuracy, using a (3x3x9) k-point mesh, 0.004 eV/(formula unit)

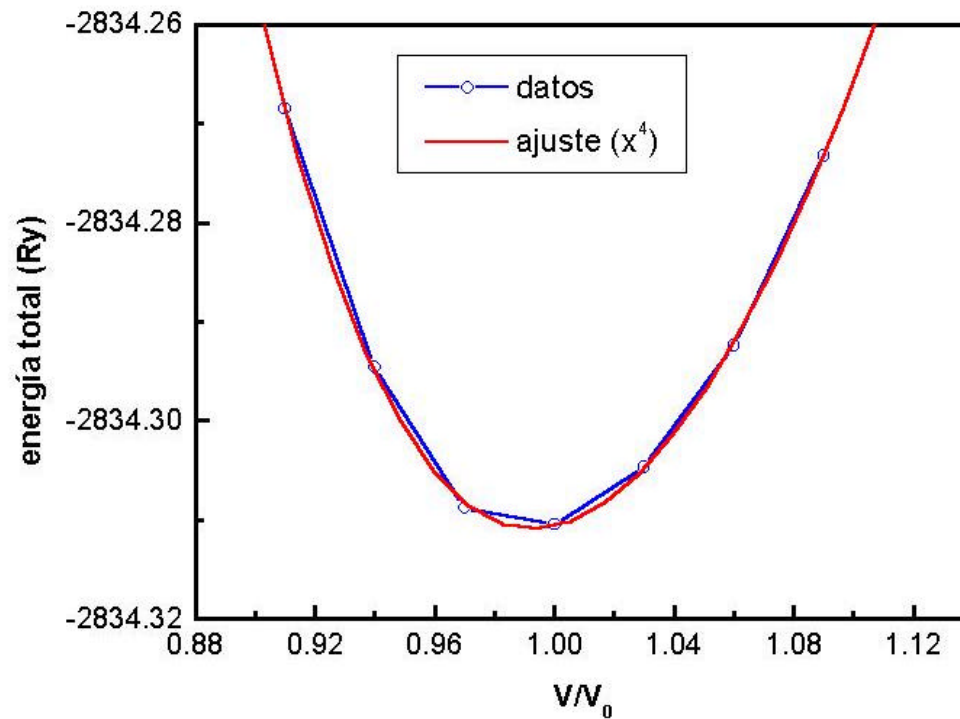
Total energy results

Total energy for the 14 minimum configurations

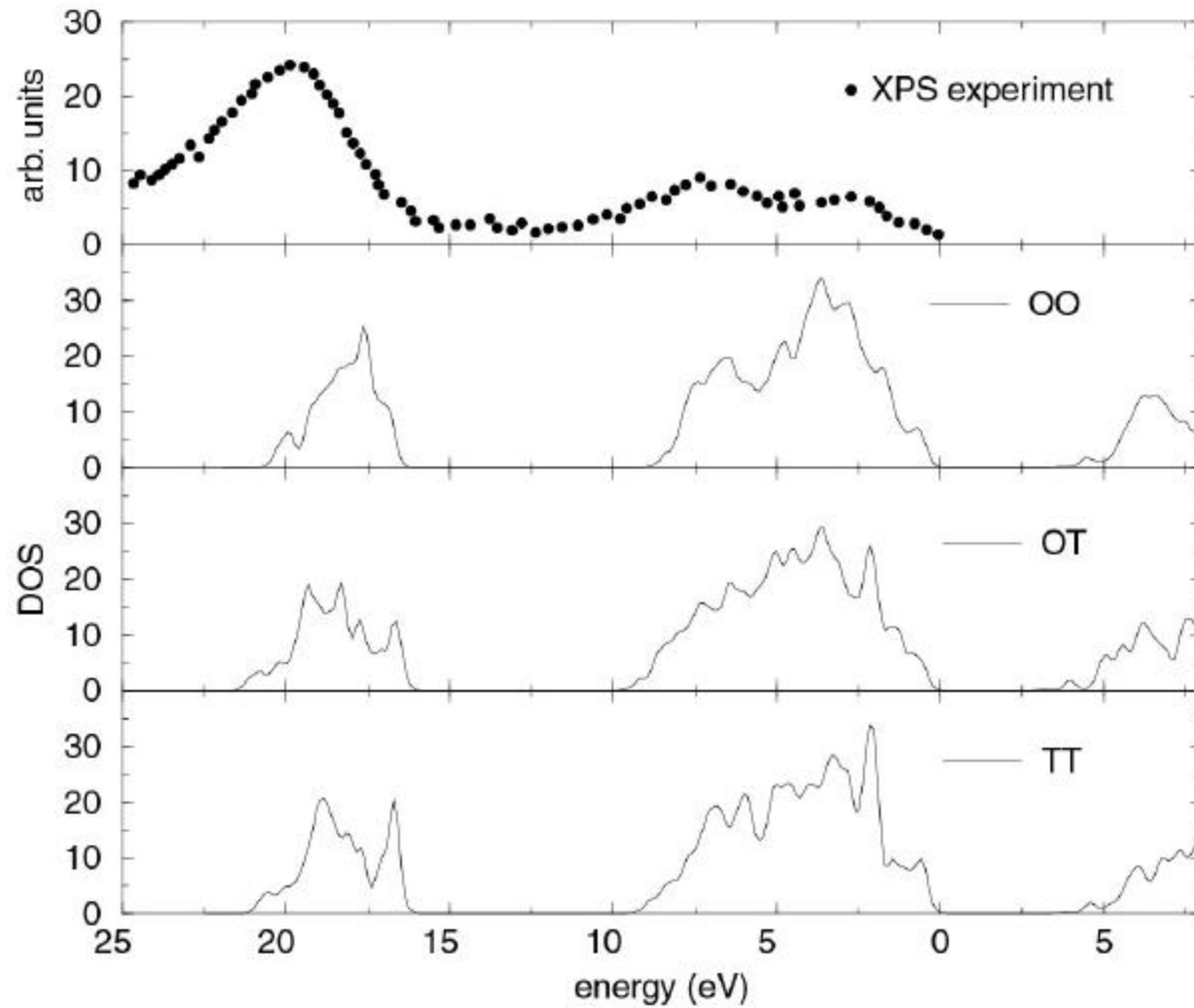


$\gamma\text{-Al}_2\text{O}_3$:total energy curve

Bulk modulus: 219 GPa



Density of states



Moving the atoms

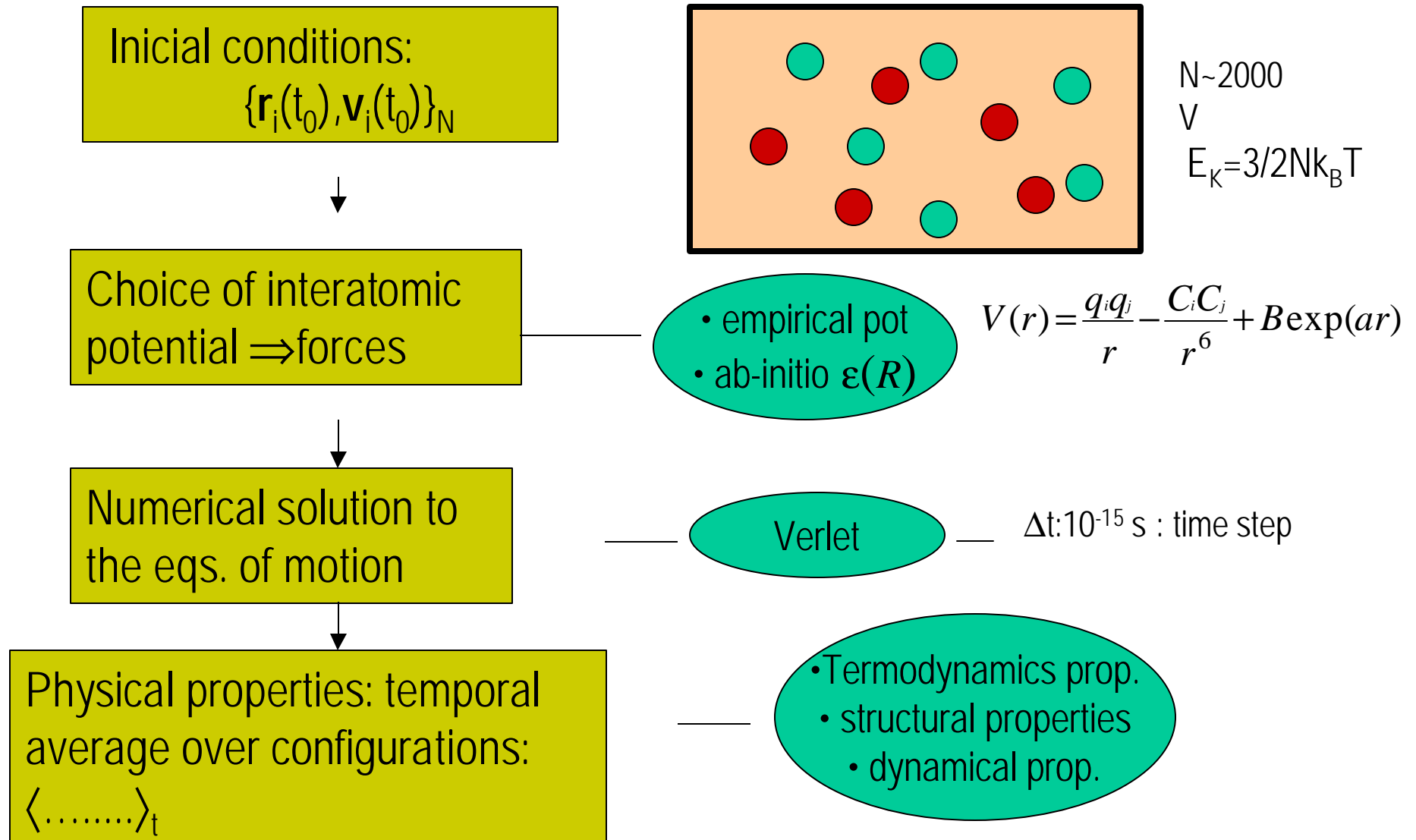
- **IDEA:** atoms “are” classical particles, they follow Newton laws

Interatomic potential $V(r)$ $F = -\nabla V(r_1, \dots, r_N)$

Temperature : equipartition theorem $T = \langle mv^2 / 3k \rangle$

- **Numerical solution** of the coupled ordinary differential equations
- **Results:** $r_1(t), \dots, r_N(t)$; $v_1(t), \dots, v_N(t)$
- **Physical properties:** average over configurations, like in statistical mechanics

Molecular Dynamic program



Interatomic potentials

A general expression for an interatomic potential should contain one-body, two body, three body,...and N body terms

$$V = \sum_{i=1}^N v_1(\vec{r}_i) + \sum_{i=1}^N \sum_{i \neq j}^N v_2(\vec{r}_i, \vec{r}_j) + \sum_{i=1}^N \sum_{i \neq j}^N \sum_{i \neq j \neq k}^N v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

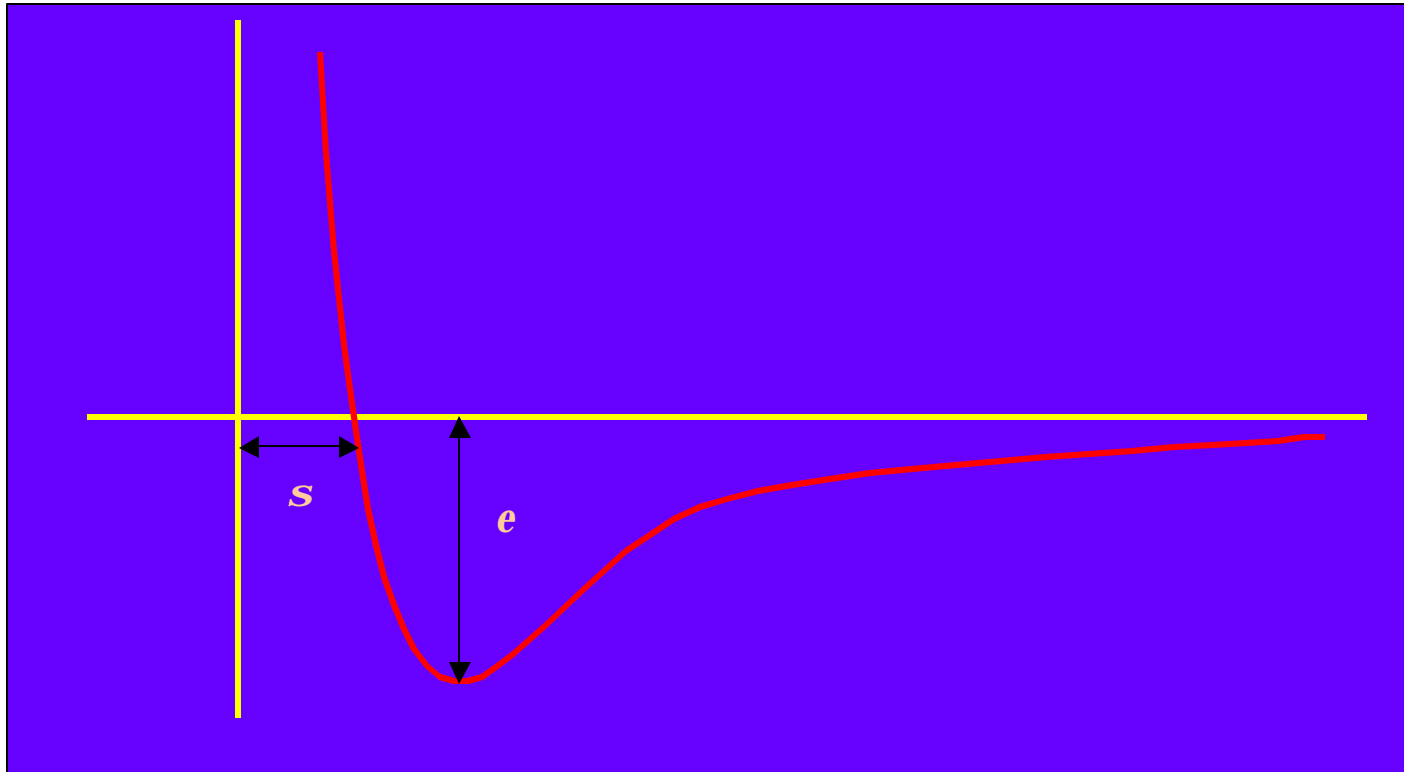
For simplicity, people in general use only two and three body terms.

The idea is to write a general functional form and to fit it according to some experimental data: elastic constants, vacancy energy, etc.

Simple interatomic potential

Ex: Lennard-Jones potential: good for noble gases

$$\Phi(r_{ij}) = 4e \left[\left(\frac{s}{r_{ij}} \right)^{12} - \left(\frac{s}{r_{ij}} \right)^6 \right]$$



Interatomic potential II

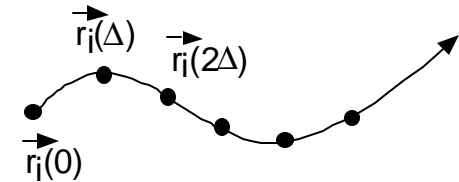
A good interatomic potential should have the following properties

- **FLEXIBILITY**
- 2. **PRECISION**
- 3. **TRANSFERABILITY**
- 4. **COMPUTATIONAL EFFICIENCY**

DM algorithm

Time discretization

$$\left\{ \begin{array}{l} \vec{r}_i(t + \Delta) = \vec{r}_i(t) + \vec{v}_i(t)\Delta + \frac{1}{2} \vec{a}_i(t)\Delta^2 \\ \vec{v}_i(t + \Delta) = \vec{v}_i(t) + \frac{\vec{a}_i(t) + \vec{a}_i(t + \Delta)}{2} \Delta \end{array} \right. \quad \vec{a}_i = -\frac{1}{m_i} \nabla \mathcal{V}(\vec{r}_i)$$



Time stepping: Velocity Verlet algorithm

Given $(\vec{r}_i(t), \vec{v}_i(t))$

1. Compute $\vec{a}_i(t)$ as a function of $\{\vec{r}_i(t)\}$
2. $\vec{v}_i(t + \frac{\Delta}{2}) \leftarrow \vec{v}_i(t) + \frac{\Delta}{2} \vec{a}_i(t)$
3. $\vec{r}_i(t + \Delta) \leftarrow \vec{r}_i(t) + \vec{v}_i(t + \frac{\Delta}{2})\Delta$
4. Compute $\vec{a}_i(t + \Delta)$ as a function of $\{\vec{r}_i(t + \Delta)\}$
5. $\vec{v}_i(t + \Delta) \leftarrow \vec{v}_i(t + \frac{\Delta}{2}) + \frac{\Delta}{2} \vec{a}_i(t + \Delta)$

Physical Properties

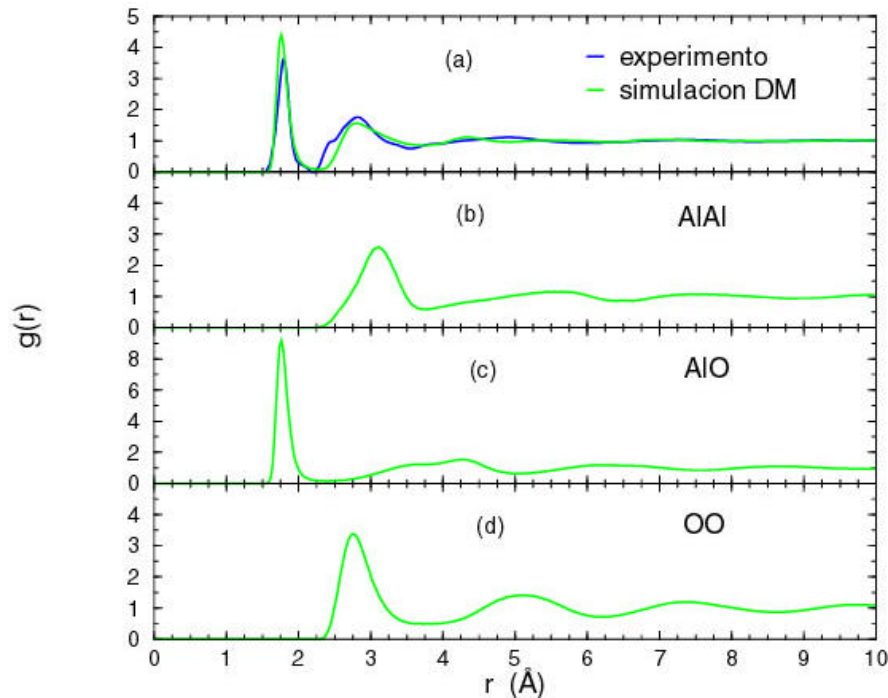
Structural properties: pair distribution function $g(r)$
static structure factor $S(q)$

Thermodynamics properties $pV = NkT + W$
heat capacity

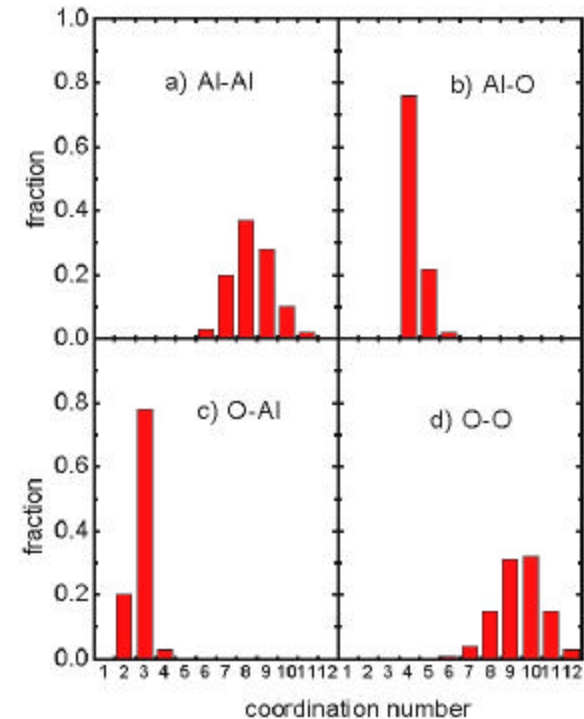
Dynamical properties diffusion coefficient D
Velocity autorrelation function $VACF(t)$
Vibrational density of states $D(\omega)$

Amorphous Al_2O_3 : results I

Pair distribution function

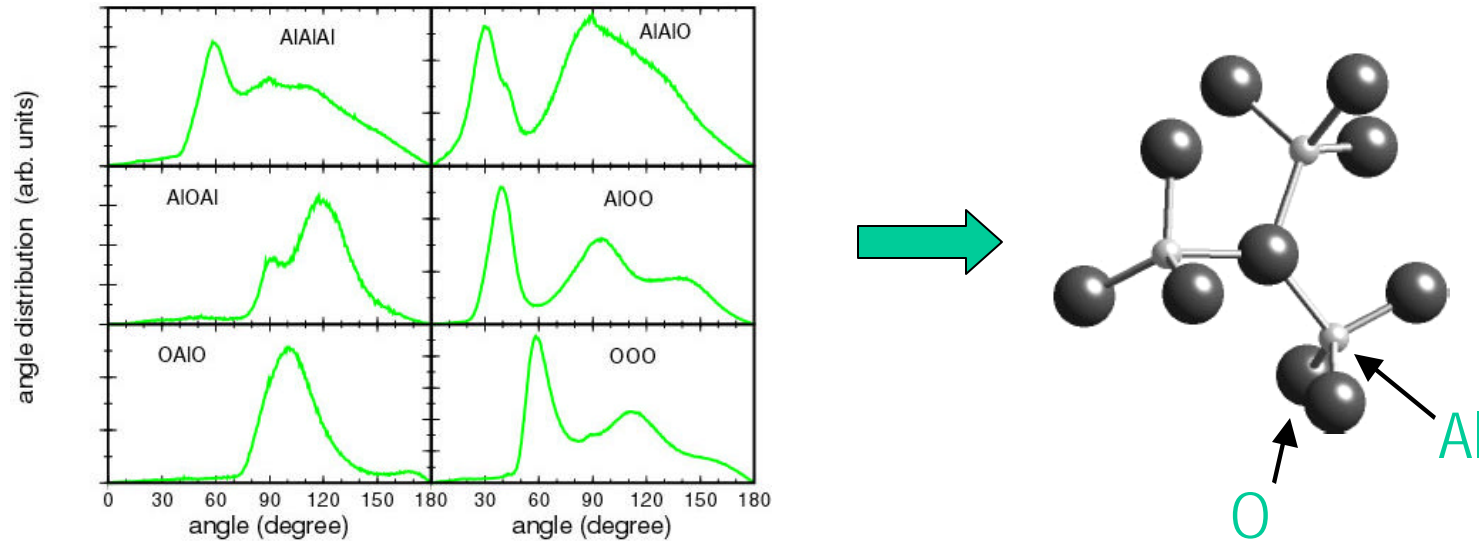


Coordination number



- Al-O distance: 1.76 Å (exp.=1.8 Å)
 - Coord. Nr: Al-O: 4.25, O-Al:2.83 (cutoff: 2.2 Å)
- Ref: G. Gutiérrez et al: PRB 65, 104202 (2002)

Amorphous Al_2O_3 : angle distributions



Summary:

- Short range order consists of AlO_4 tetrahedra.
- there are 3- and 4-fold rings, with planar 2- and 3-fold ring.

Structural transformation of amorphous Al_2O_3 under pressure

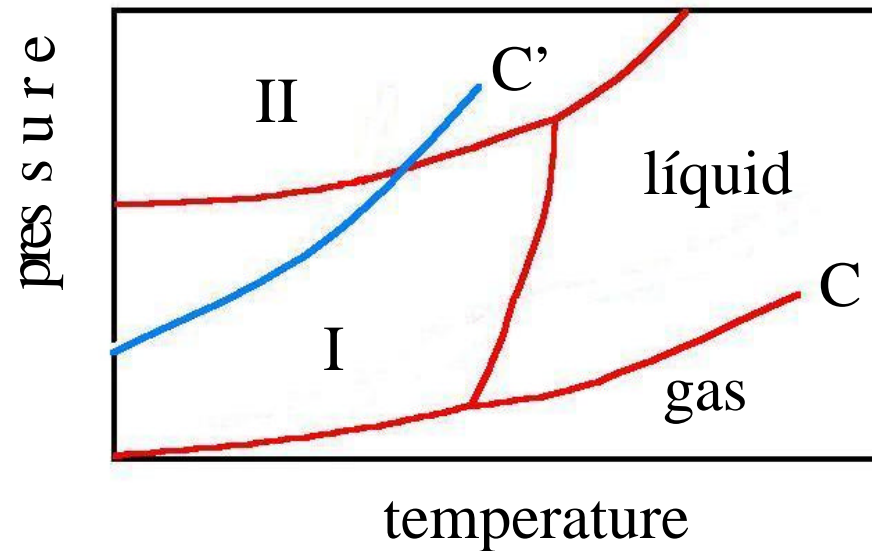
32

- In the Al_2O_3 - SiO_2 system (important in geoscience and ceramic) present a both a Si and Al coordination change, from tetrahedral to octahedral Coordination under pressure bajo.

In SiO_2 that change is wellknown. What does it happen in alumina?

- **Phase transformation in liquid and amorphous material:**

poli-amorphysm



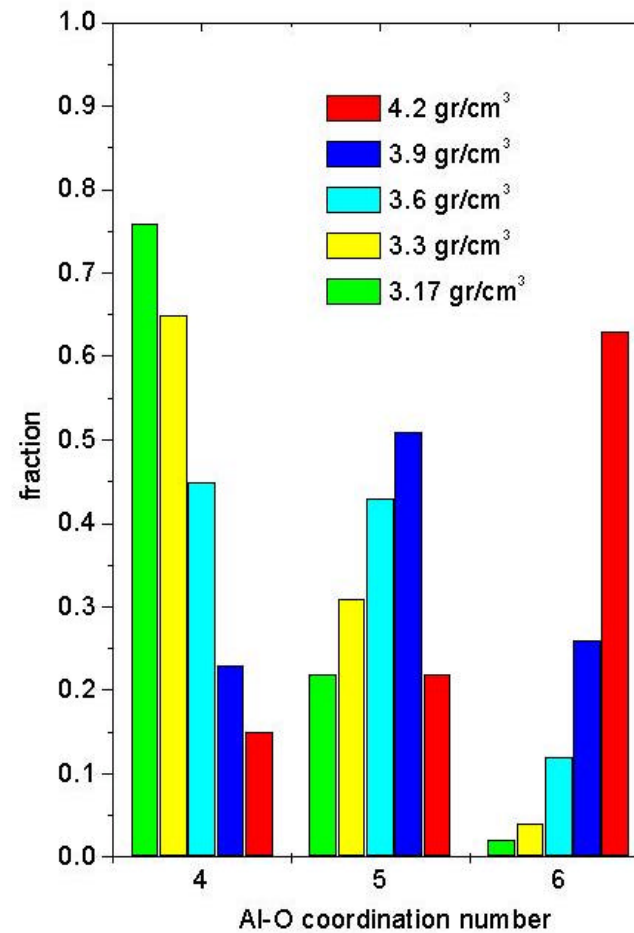
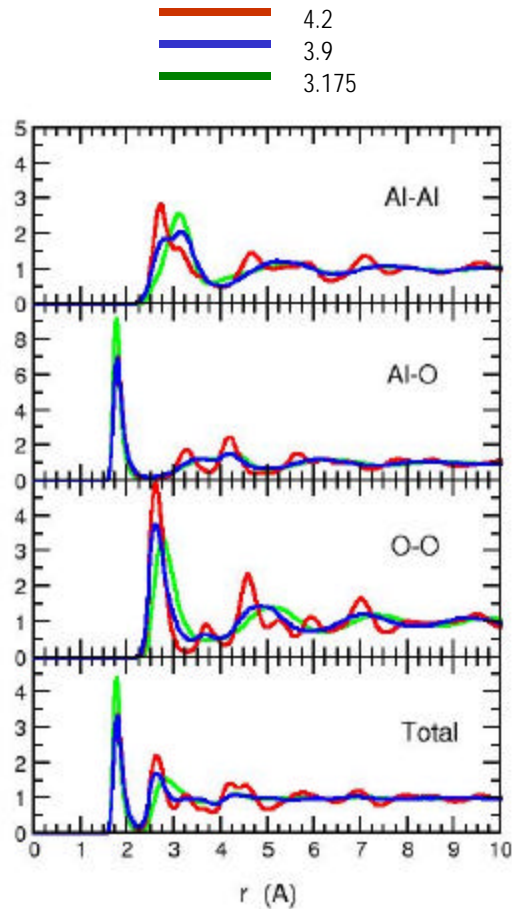
Observed in: H_2O !!

SiO_2 , GeO_2 , P,

Al_2O_3 - Y_2O_3

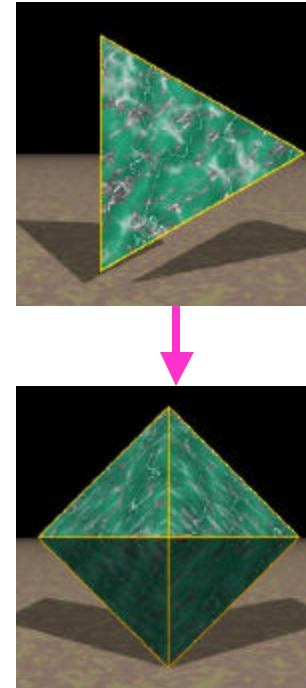
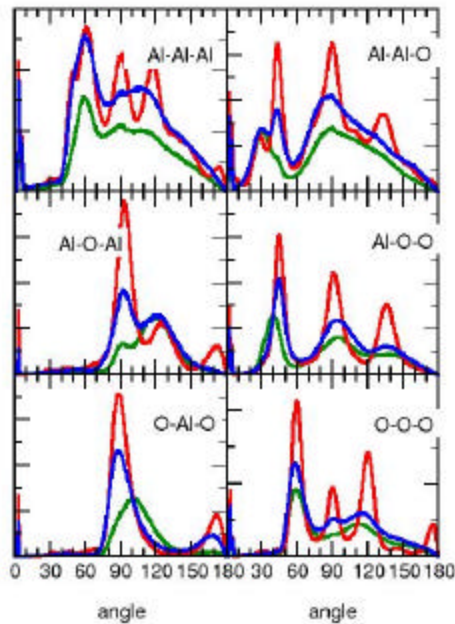
Amorphous Al_2O_3 under pressure: results

Ref: G. Gutiérrez, Submitted (2004)



Al₂O₃ under pressure II

Angular distribution



Coordination of Al changes according density **P** OK exp.

- a-a transformation in alumina: coord 4 **®** coord.6
- according our simulation, it does happen at pressure 15-25 Gpa.

Ions + electrons: ab-initio MD

The only interaction there exists is the Coulomb interactions!

The idea of ab-initio MD is to calculate everything from the solid state hamiltonian

1. **Electronic structure calculation** to obtain the total energy $e(\mathbf{R})$ in terms of the positions of the ions.
2. **Forces** for each Δt , forces are obtained from the electronic str. calc.

$$\begin{aligned}
 F_I &= -\frac{\partial}{\partial R_I} e(\{\mathbf{R}\}) = -\frac{\partial}{\partial R_I} E_{KS}(\{\mathbf{j}_i\}, \{\mathbf{R}_i\}) \Rightarrow \\
 &= -\frac{\partial}{\partial R_I} \sum_i \langle \mathbf{j}_i | H_{KS} | \mathbf{j}_i \rangle = -\sum_i \langle \mathbf{j}_i | \frac{\partial}{\partial R_I} H_{KS} | \mathbf{j}_i \rangle
 \end{aligned}$$

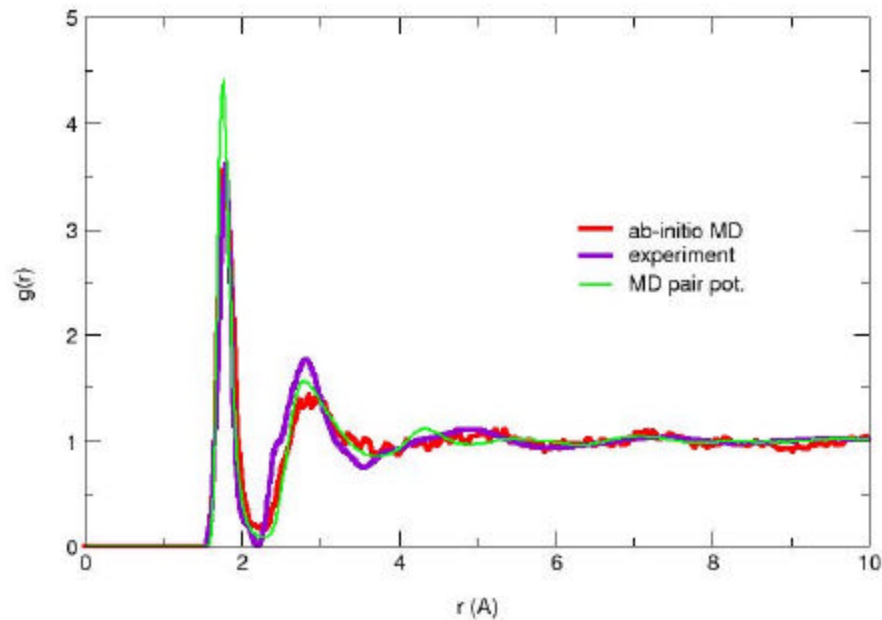
Teo.Hellman-Feynman

Amorphous Al_2O_3 : DM ab-initio

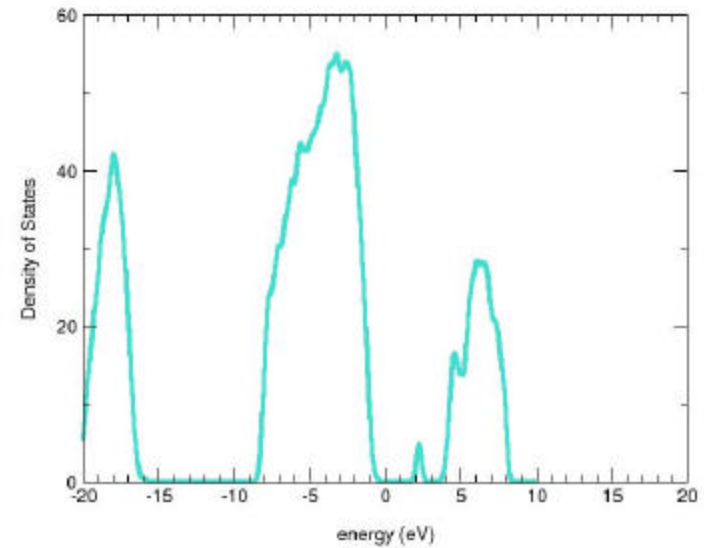
Preliminary Results

Ref: S. Davis & G. Gutiérrez, in progress

Pair distribution functions



Electronic Density of states



Detalles: Código VASP, 10 ps, 600 K, 80 at., (NVT), solo punto Γ , 5min/paso.