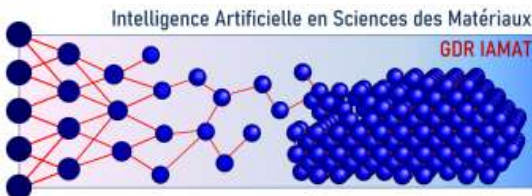


(Elements of) Molecular Dynamics and Density Functional Theory

A. Serva (MD) – A. Marco Saitta (DFT)



PROGRAMME
DE RECHERCHE
MATÉRIAUX
ÉMERGENTS

École internationale DIADEM

25-29 août 2025 Paris (France)

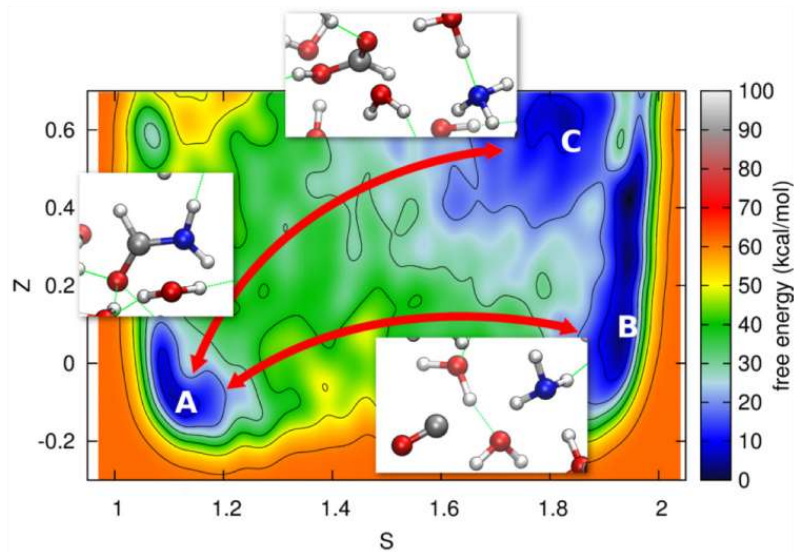


IA et physique des matériaux

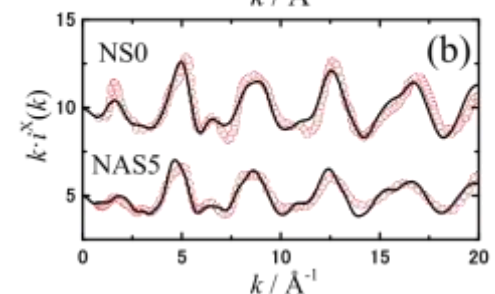
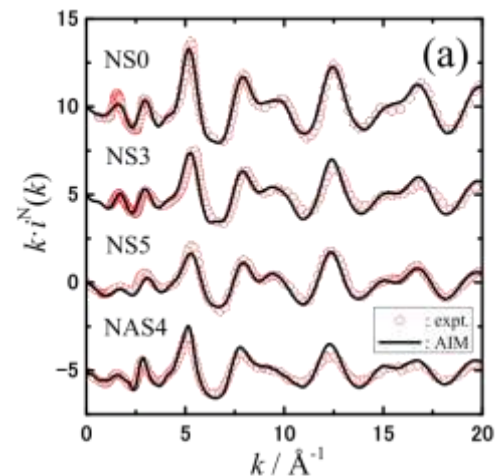
Objectives of molecular simulations



Visualization



Prediction



Interpretation

Statistical mechanics



Choice of statistical ensemble

$$(N, V, T)$$

$$(N, P, T)$$

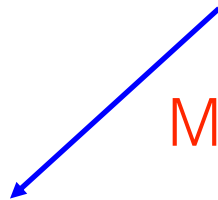
...



Partition function

$$Q = \sum_i \exp\left(\frac{-E_i}{kT}\right)$$

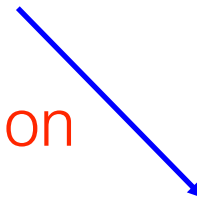
Molecular simulation



Sampling phase space

=

+



Evaluating the energy

$$Q = \sum_i \dots$$

$$\dots \exp\left(\frac{-E_i}{kT}\right)$$

Statistical mechanics



Choice of statistical ensemble

$$(N, V, T)$$

$$(N, P, T)$$

...



Partition function

$$Q = \sum_i \exp\left(\frac{-E_i}{kT}\right)$$

Molecular simulation

=

+

Sampling phase space

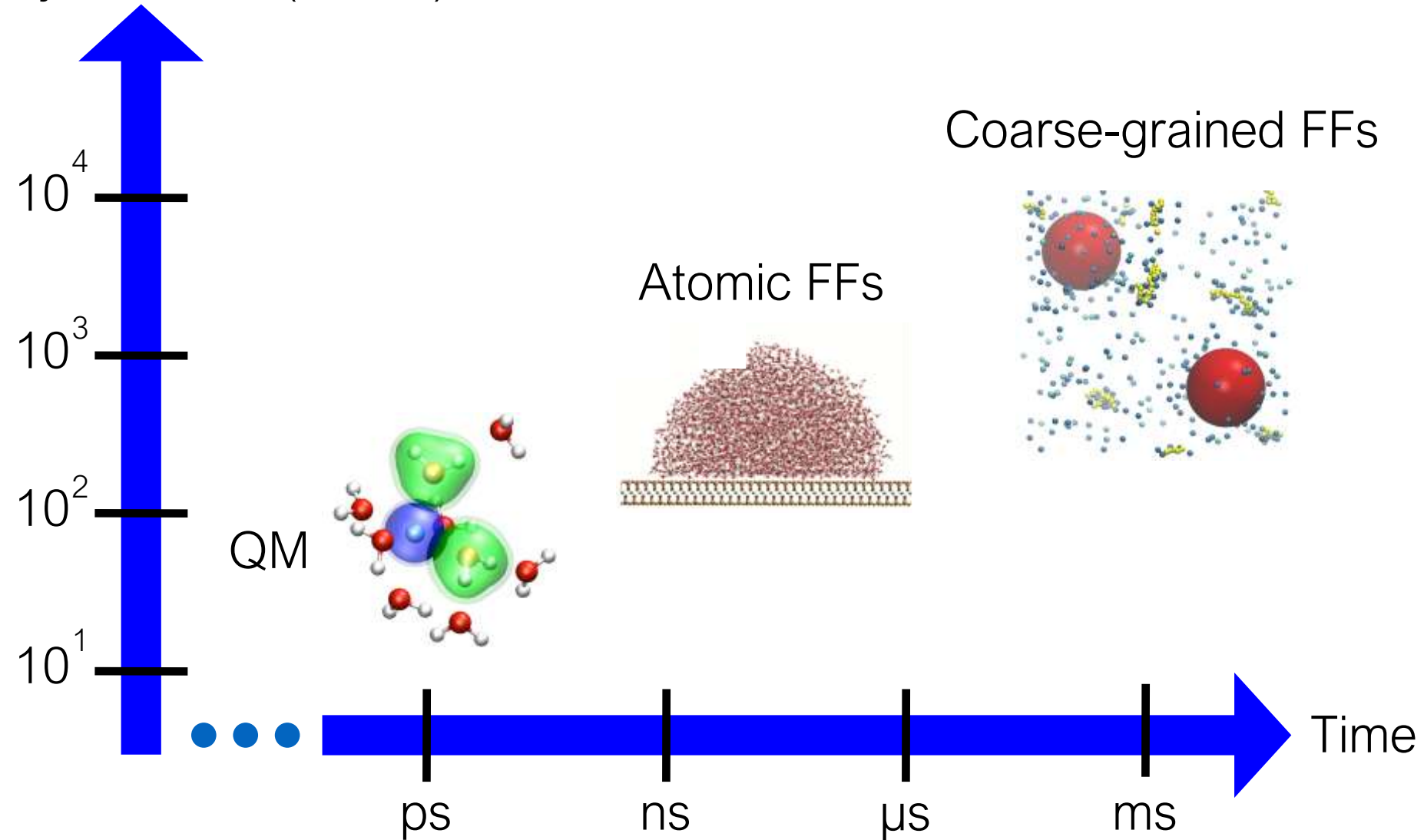
Evaluating the energy

- Single-point calculation
- Energy minimization
- Integrating Newton's equation (molecular dynamics = MD)
- Stochastic sampling (Monte Carlo = MC)

- Quantum methods (QM)
 - Hartree-Fock & post HF
 - Density Functional Theory
 - Quantum Monte Carlo
- Classical force fields (FF)

Time and length scales

System size (atoms)



Sampling phase space

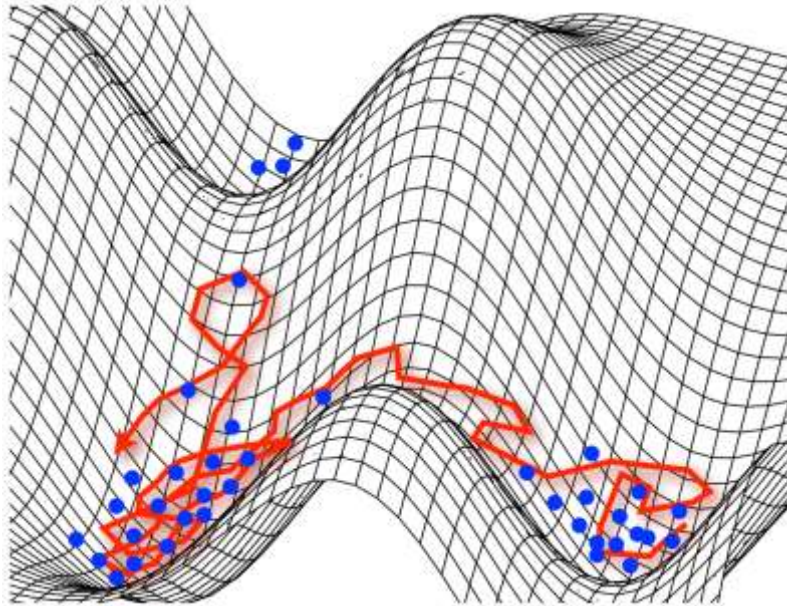
Molecular dynamics

$$m\ddot{\mathbf{r}} = -\frac{\partial \mathcal{U}}{\partial \mathbf{r}}$$

Trajectories

Dynamical
processes

Collective moves



Monte Carlo

$$\mathcal{P} \propto \exp\left(-\frac{E}{kT}\right)$$

Random moves

Many statistical
ensembles

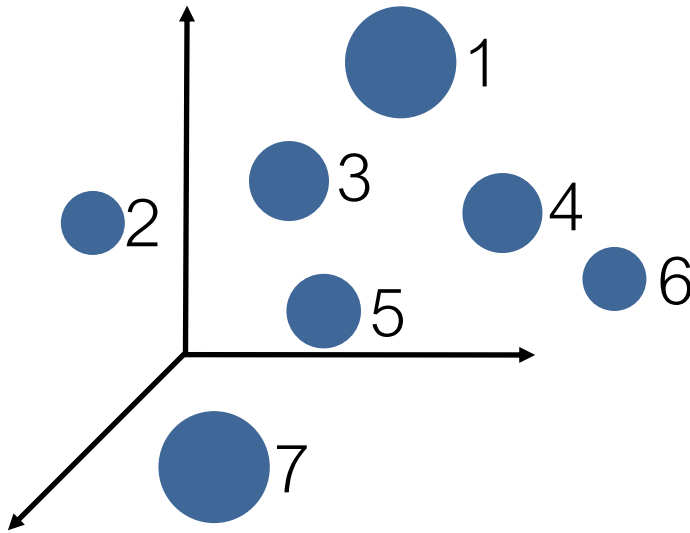
Non local sampling

Molecular dynamics

- ✓ Propagation of motion

Propagation of motion

$$\mathbf{r}_1 = (x_1, y_1, z_1); \dot{\mathbf{r}}_1 = (\dot{x}_1, \dot{y}_1, \dot{z}_1)$$



Newton's equation of motion: $m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i = -\frac{\partial \mathcal{U}}{\partial \mathbf{r}_i}$

Impossible to solve analytically

→ Solved numerically at discrete intervals of time

Propagation of motion: Verlet algorithm

Taylor expansion of the positions at $t + \Delta t$

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \dot{\mathbf{r}}(t)\Delta t + \frac{1}{2!}\ddot{\mathbf{r}}(t)\Delta t^2 + \frac{1}{3!}\dddot{\mathbf{r}}(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

$\mathbf{r}(t)$, $\dot{\mathbf{r}}(t)$ are known

$\ddot{\mathbf{r}}(t)$ calculated using Newton's equation

$\dddot{\mathbf{r}}(t)$ unknown

————→ error of order $\mathcal{O}(\Delta t^3)$

Propagation of motion: Velocity Verlet algorithm

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \dot{\mathbf{r}}(t)\Delta t + \frac{1}{2!}\ddot{\mathbf{r}}(t)\Delta t^2 + \mathcal{O}(\Delta t^4)$$

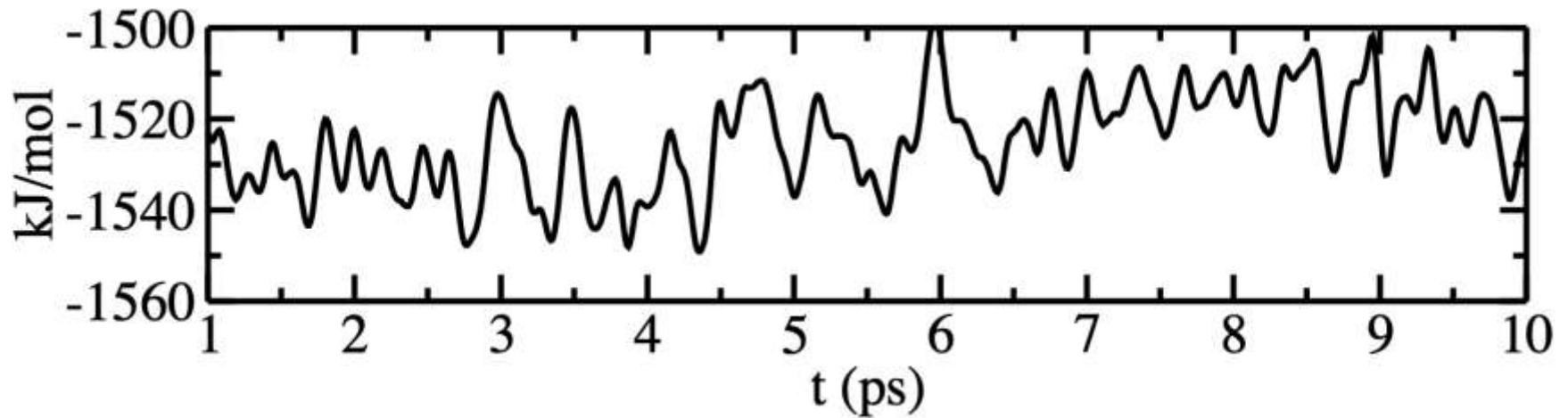
$$\dot{\mathbf{r}}(t + \Delta t) = \dot{\mathbf{r}}(t) + \frac{\ddot{\mathbf{r}}(t) + \ddot{\mathbf{r}}(t + \Delta t)}{2}\Delta t + \mathcal{O}(\Delta t^2)$$

We only need to know quantities at time t

Most widely used algorithm in MD packages

Energy conservation

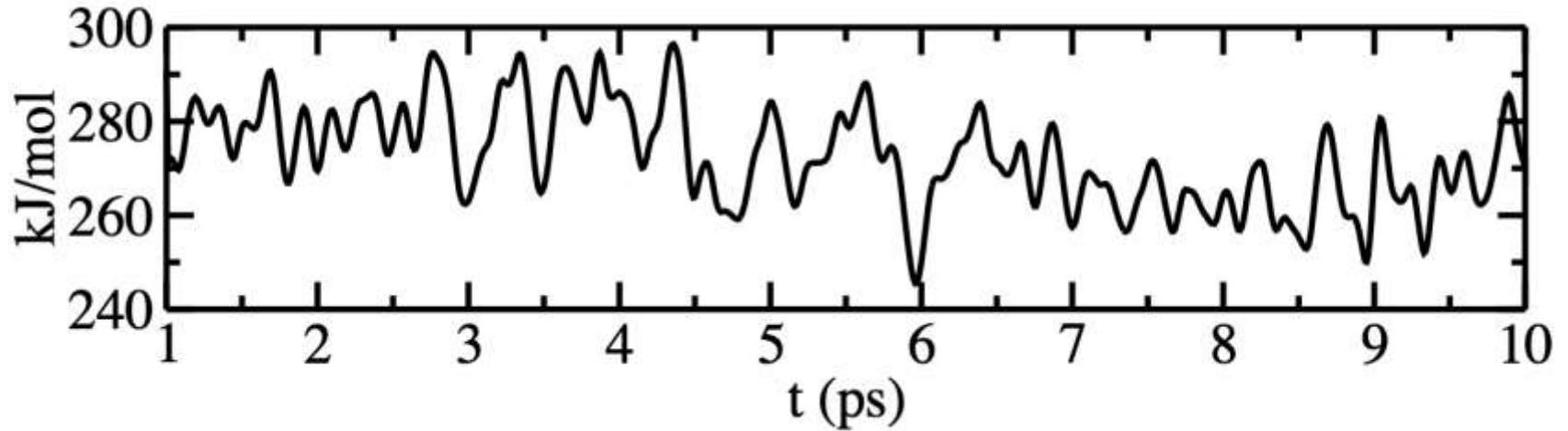
Potential energy $\mathcal{U}(\mathbf{r}^N)$



System: 256 Argon atoms

Energy conservation

Kinetic energy $\mathcal{K}(\dot{\mathbf{r}}^N) = \sum_{i=1}^N \frac{1}{2} m_i \dot{\mathbf{r}}_i^2$



System: 256 Argon atoms

Energy conservation

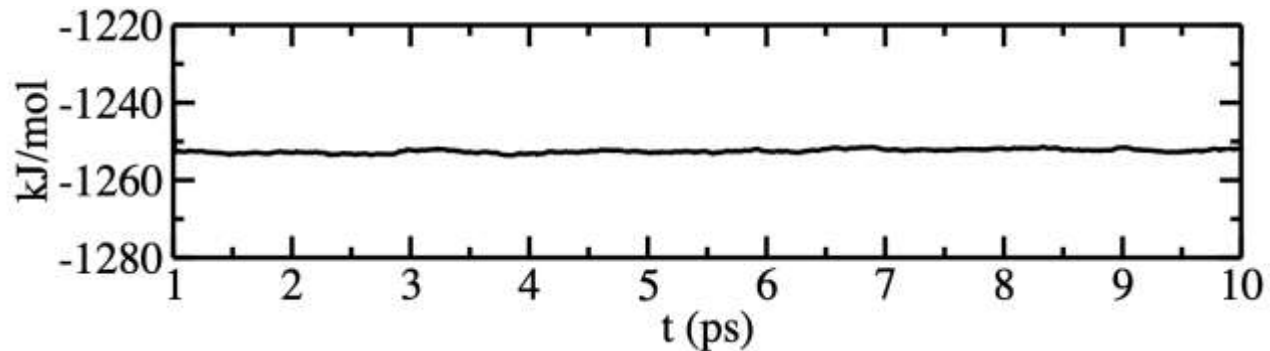
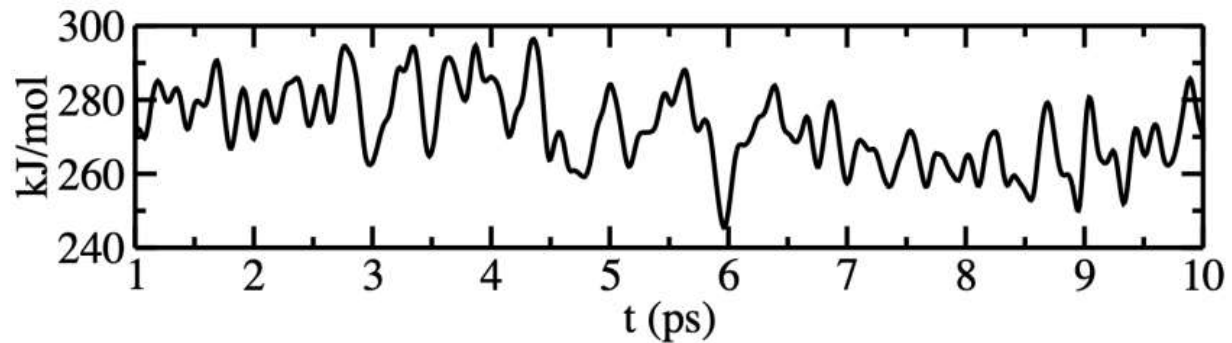
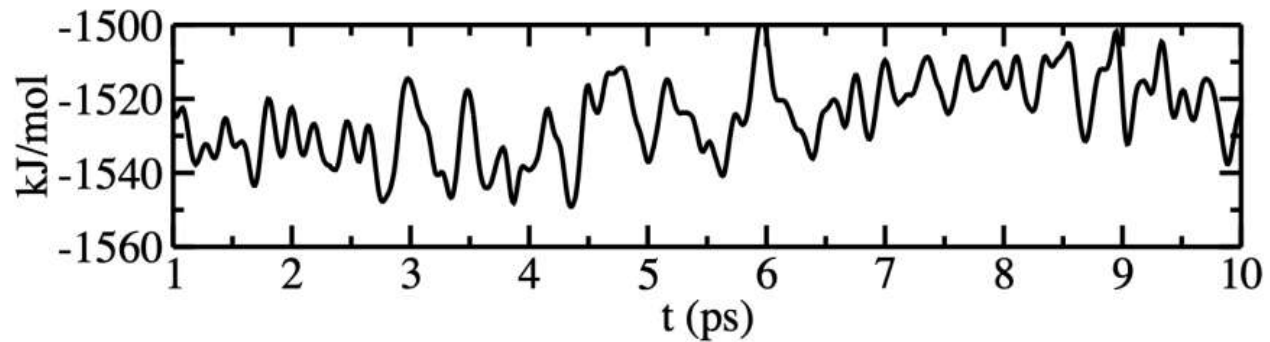
Potential energy

+

Kinetic energy

=

Total energy



Molecular dynamics

- ✓ Propagation of motion
 - Verlet algorithm
 - Velocity Verlet algorithm
- ✓ Thermodynamic ensemble

Thermodynamic ensembles

(N, V, E) Straightforward

(N, V, T) With a thermostat

(N, P, T) With a barostat

~~(μ, V, T)~~ Impossible

Berendsen thermostat

Instantaneous temperature: $\mathcal{T}(t) = \frac{1}{3kN} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2$

External heat bath at fixed temperature: $\frac{d\mathcal{T}}{dt} = \frac{1}{\tau} (T_0 - \mathcal{T}(t))$

Velocities scaled at each step: $\dot{\mathbf{r}}_{\text{new}}(t) = \lambda \dot{\mathbf{r}}_{\text{old}}(t)$

Scaling factor: $\lambda = \left[1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{\mathcal{T}(t)} - 1 \right) \right]^{1/2}$

Does not sample correctly the canonical ensemble
(does not allow fluctuations in temperature)

————→ Useful for equilibration

Nosé-Hoover thermostat

Add friction term to Newtonian equations of motion

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{F}_i}{m_i} - \chi \dot{\mathbf{r}}_i$$

which is dynamical and responds to temperature fluctuation

$$\dot{\chi} = \frac{1}{Q} \left[\sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2 - 3NkT \right]$$

—————→ Q is an effective mass(inertia) for the friction

Total energy for the extended system:

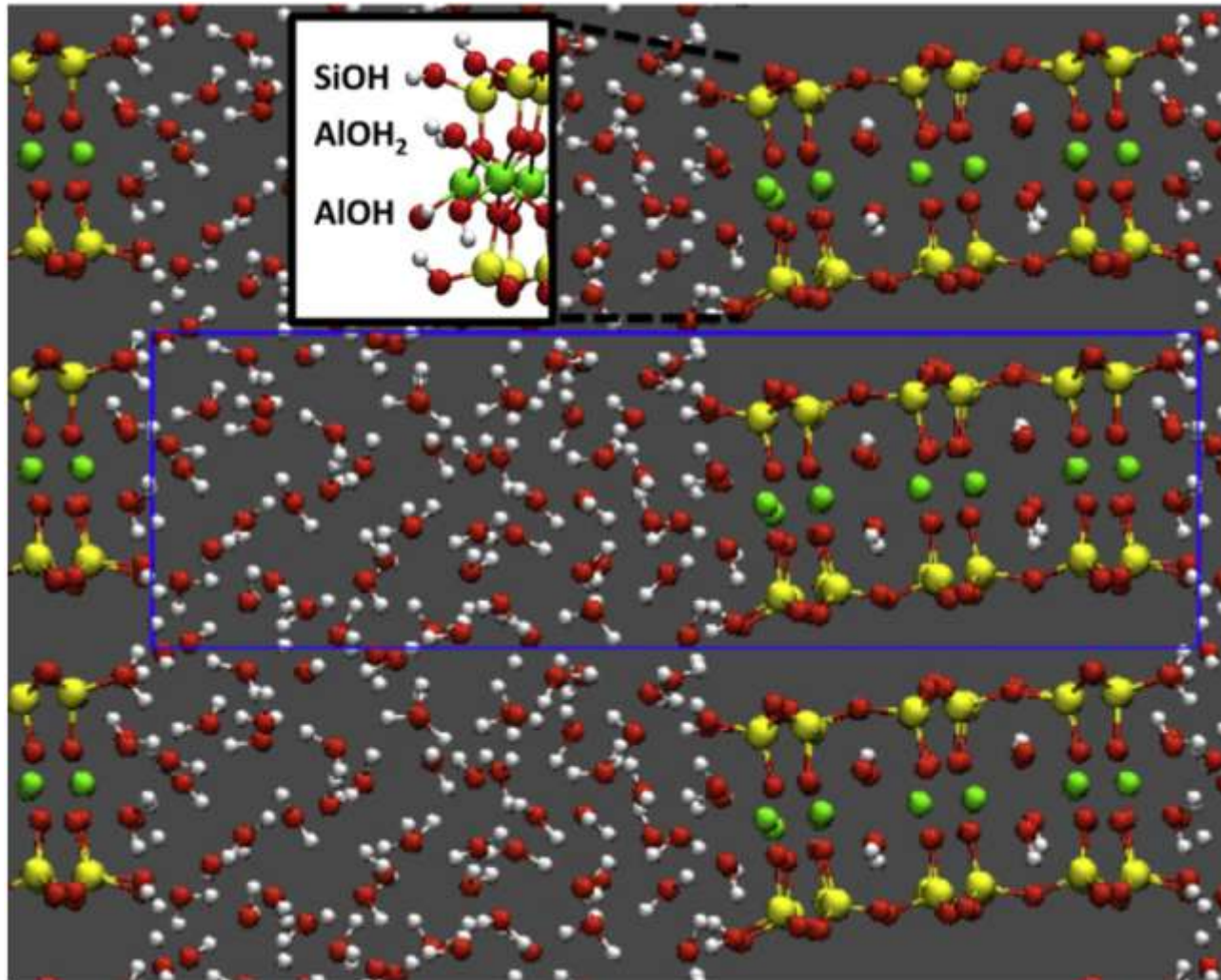
$$\mathcal{H}_{\text{NH}} = \mathcal{H} + \frac{Q}{2} \chi^2 + 3NkT \int \chi dt$$

It is a conserved quantity: $\frac{d\mathcal{H}_{\text{NH}}}{dt} = 0$

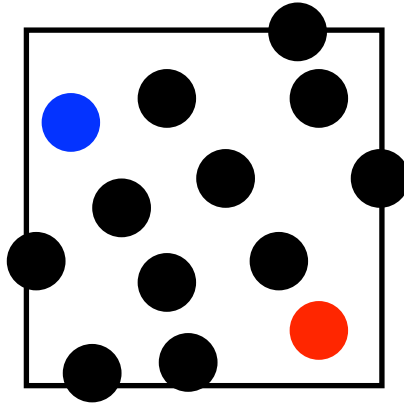
Molecular dynamics

- ✓ Propagation of motion
 - Verlet algorithm
 - Velocity Verlet algorithm
- ✓ Thermodynamic ensembles
 - Berendsen and Nosé-Hoover thermostat
 - Barostat
- ✓ Periodic boundary conditions

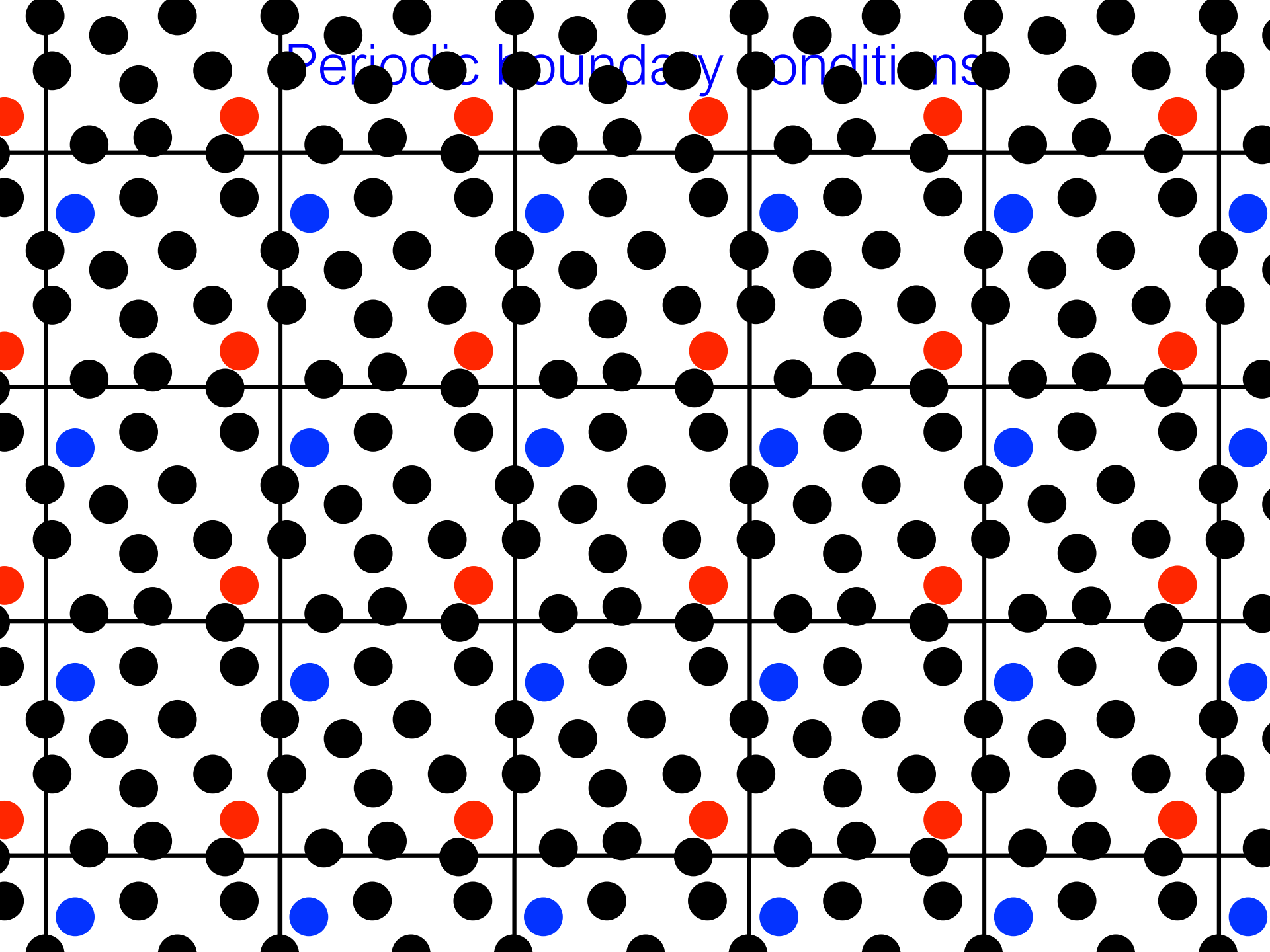
Periodic boundary conditions



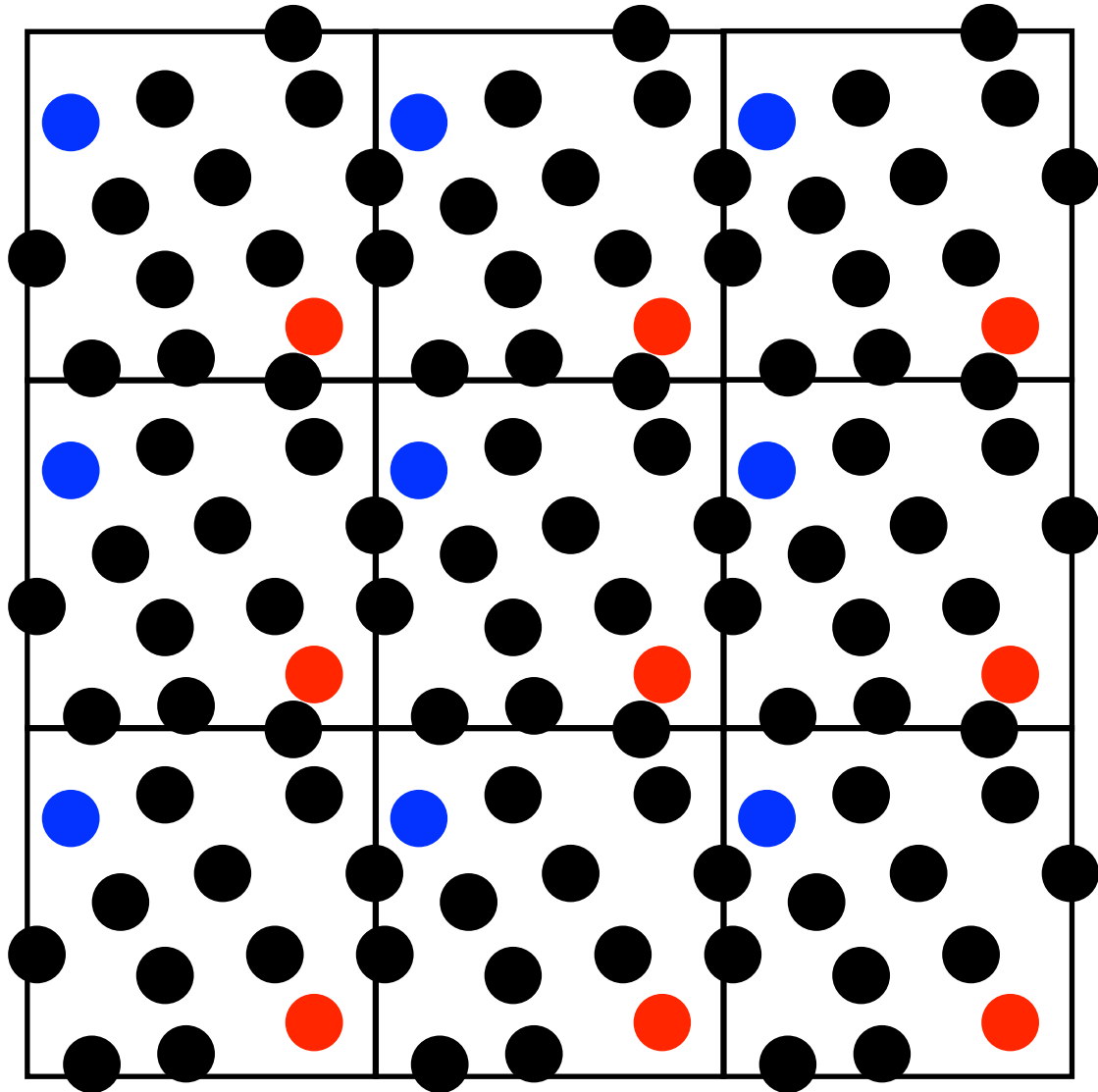
Periodic boundary conditions



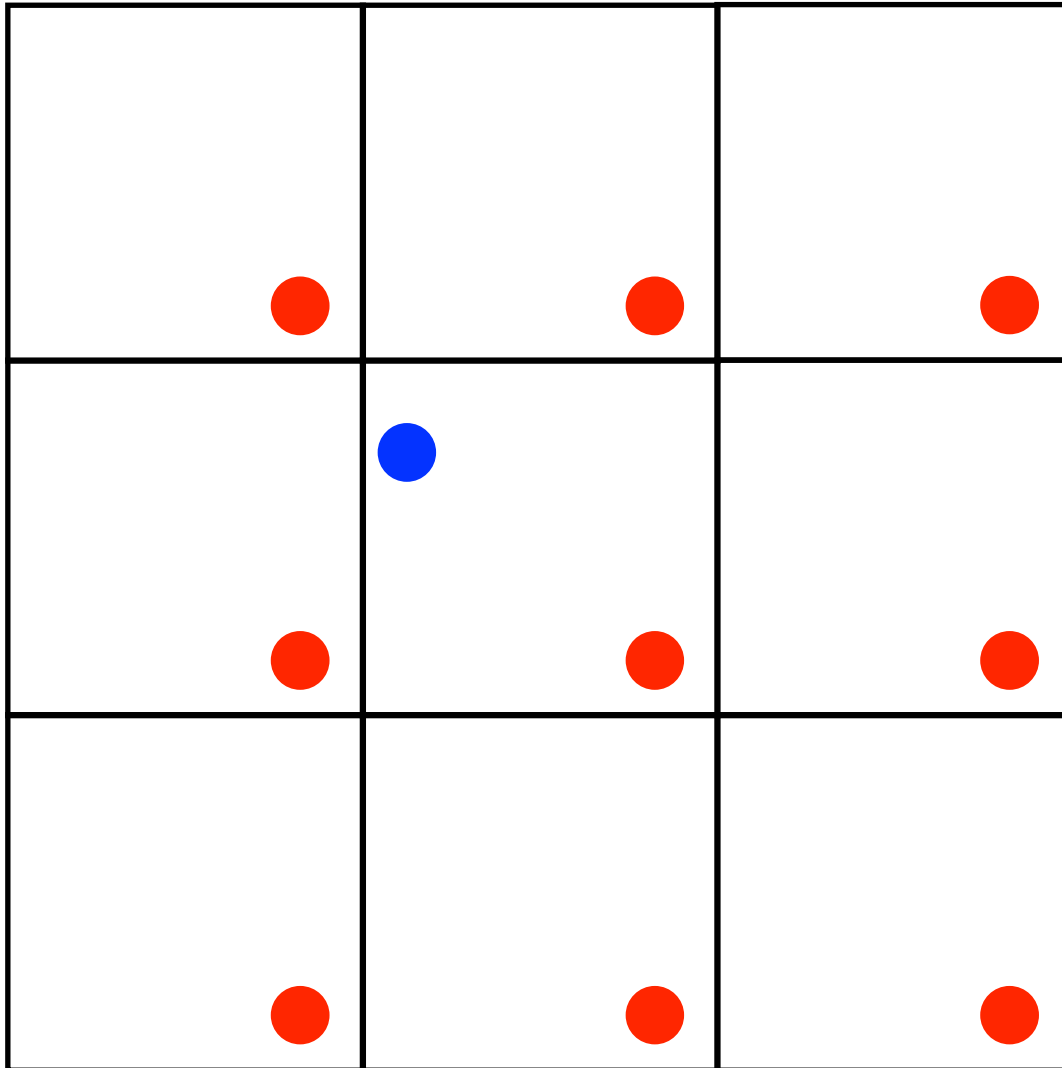
Periodic boundary conditions



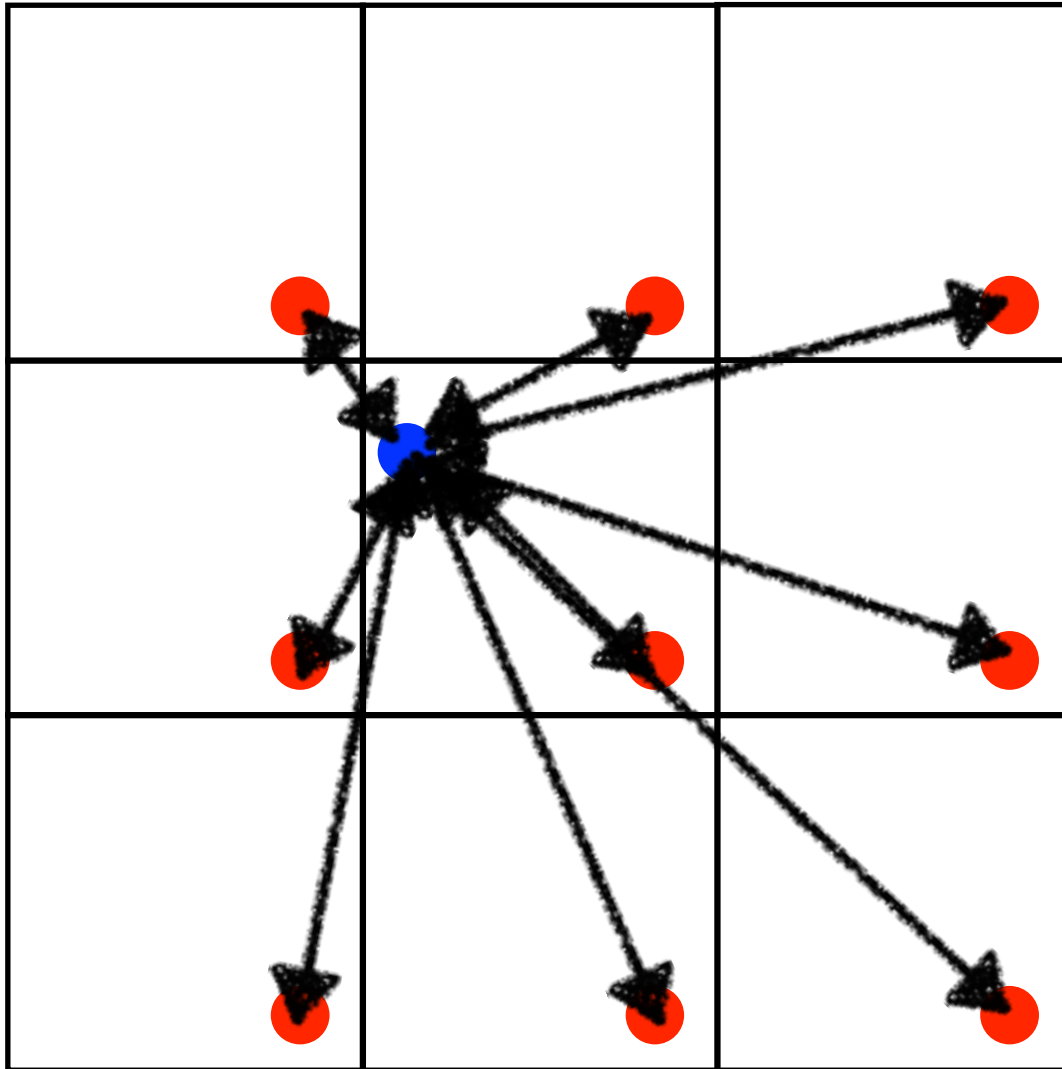
Periodic boundary conditions



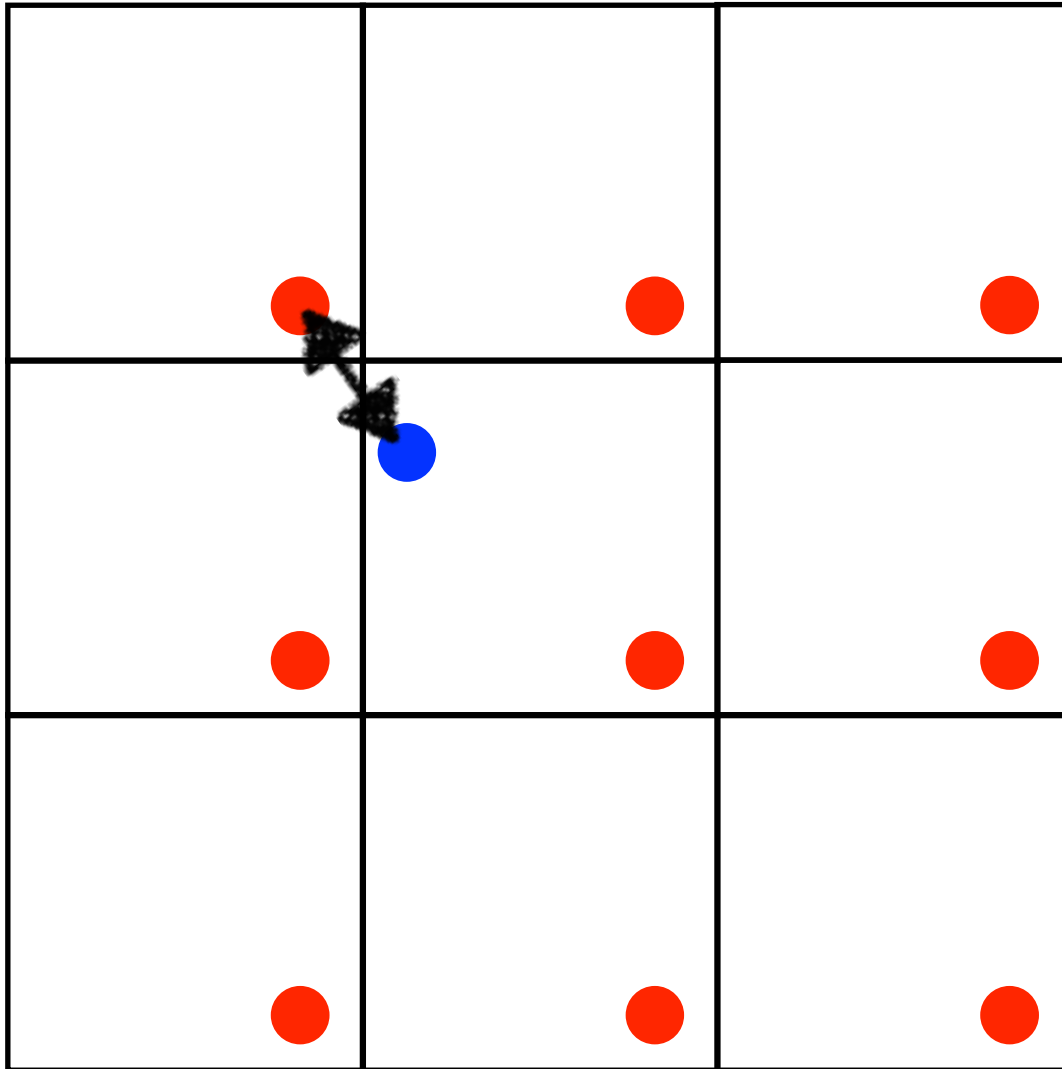
Periodic boundary conditions



Periodic boundary conditions

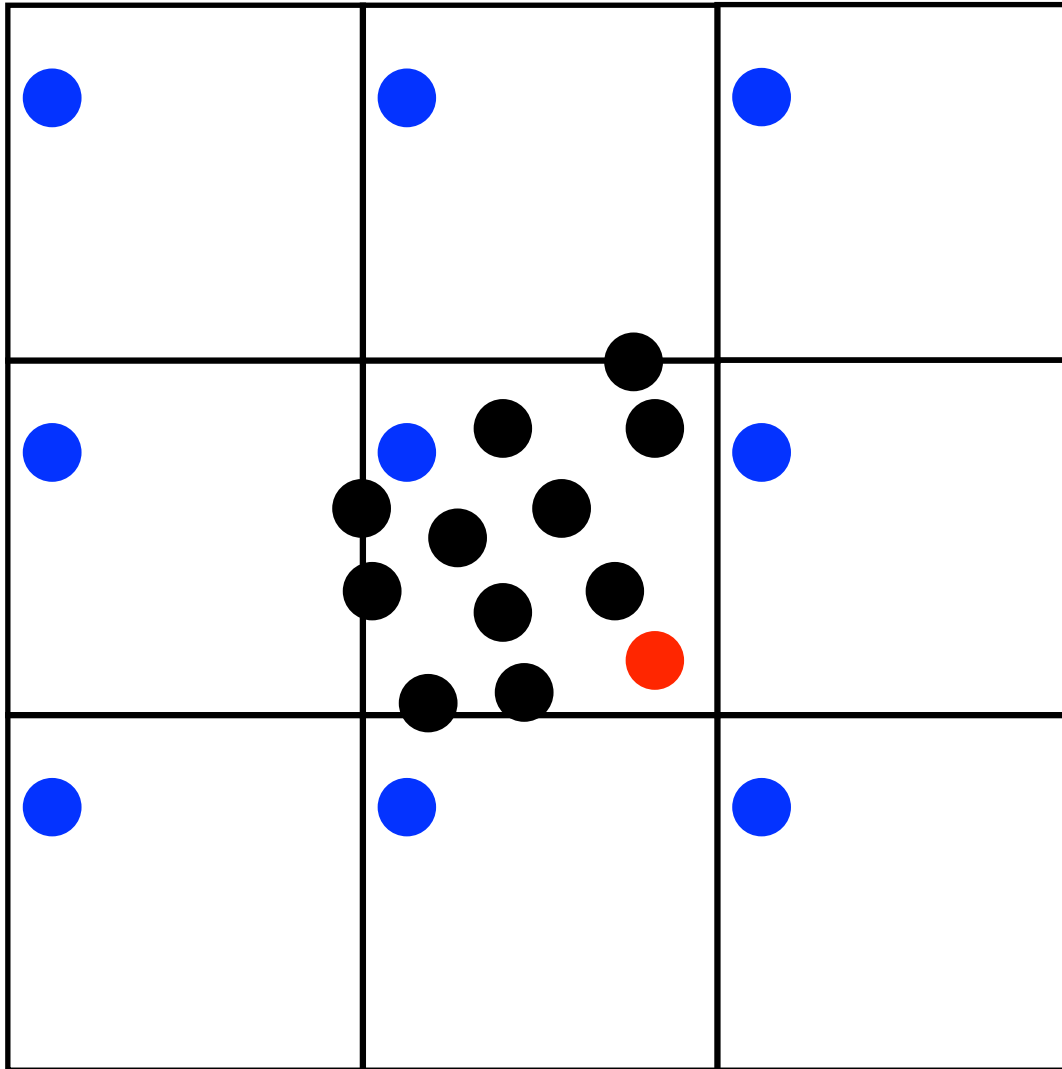


Periodic boundary conditions

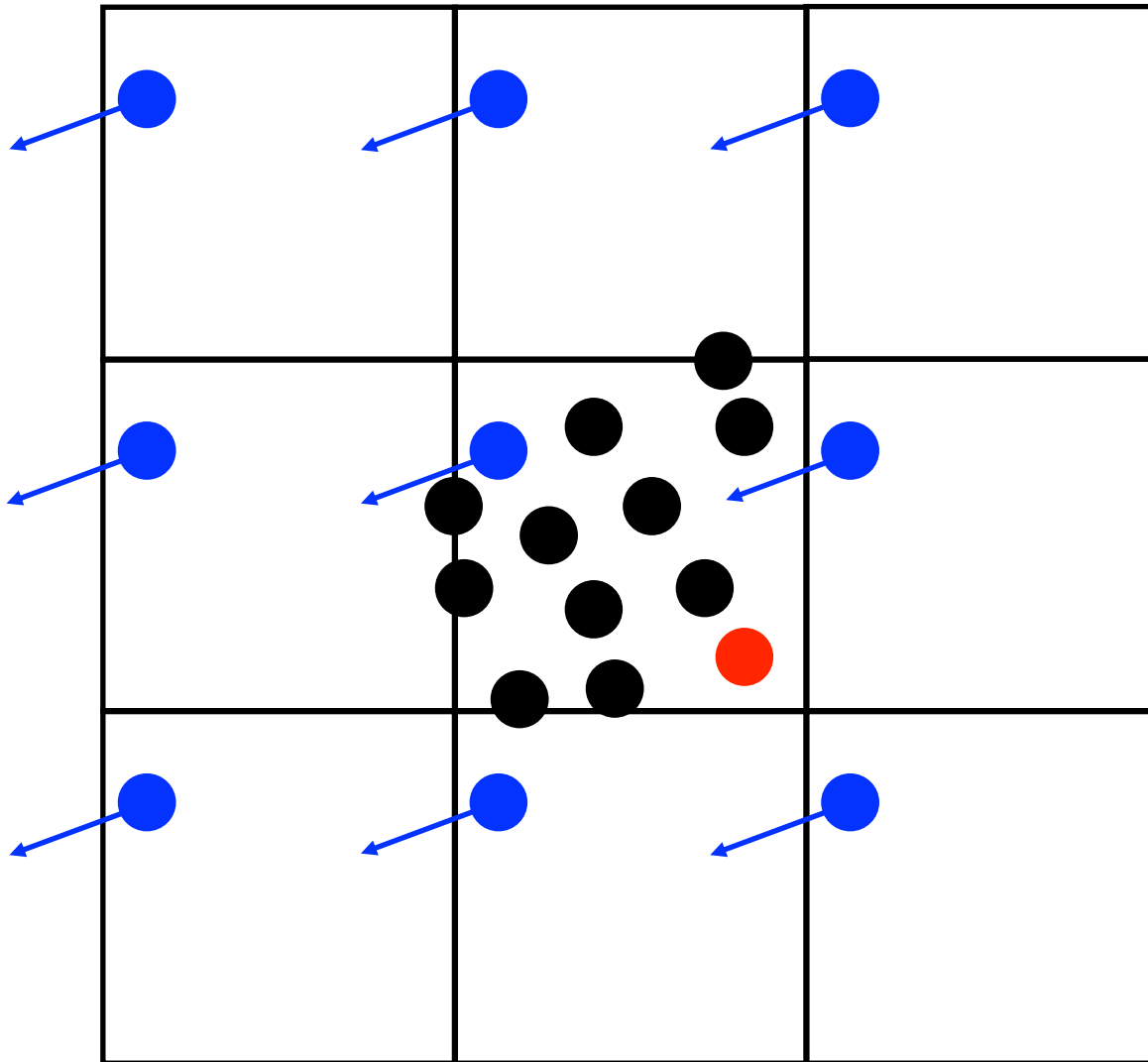


Minimum image convention

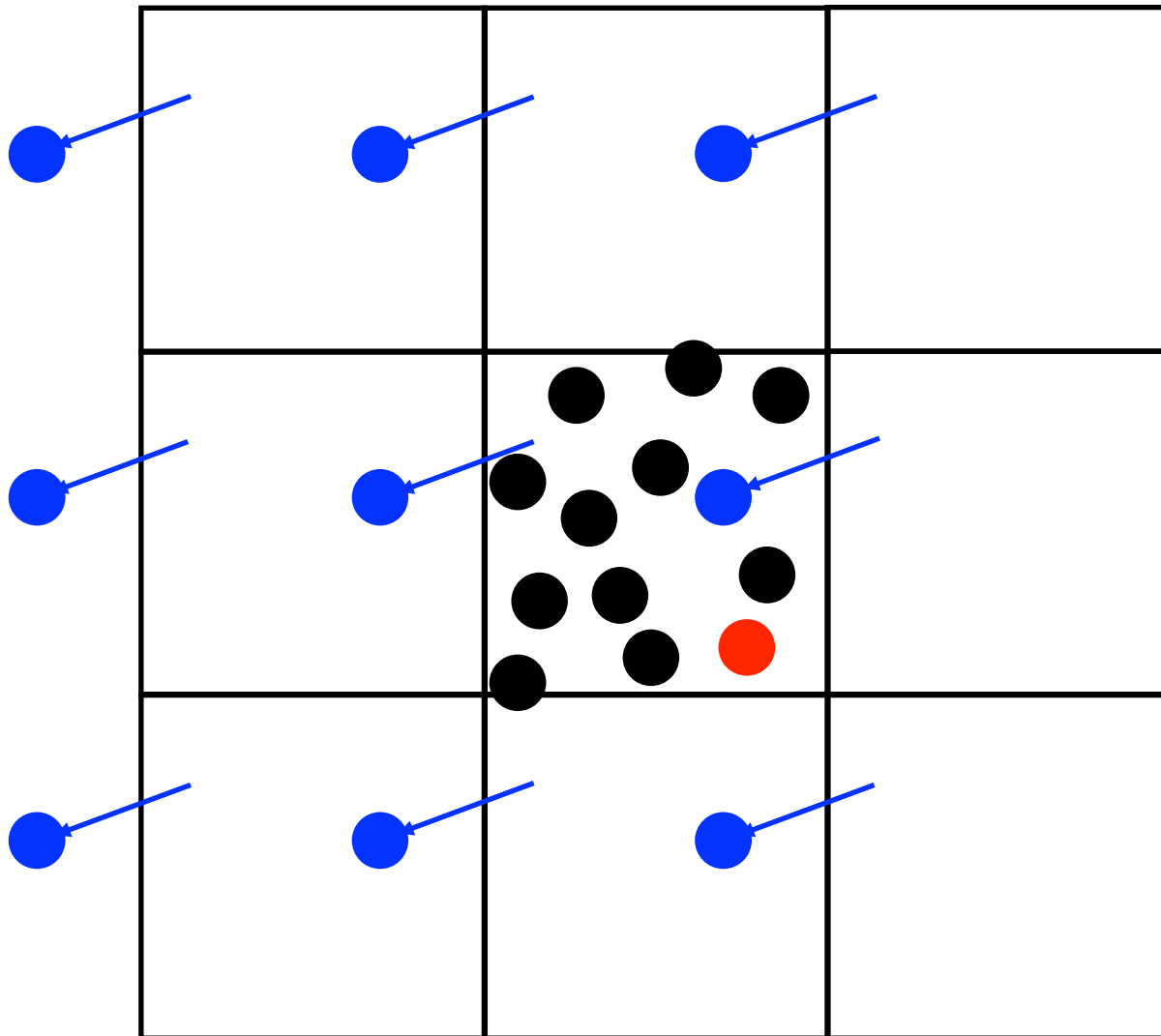
Periodic boundary conditions



Periodic boundary conditions



Periodic boundary conditions



Constant number of atoms in the cell

Molecular dynamics

- ✓ Propagation of motion
 - Verlet algorithm
 - Velocity Verlet algorithm
- ✓ Thermodynamic ensembles
 - Berendsen and Nosé-Hoover thermostat
 - Barostat
- ✓ Periodic boundary conditions
 - Minimum image convention
 - Constant number of atoms

Statistical mechanics



Choice of statistical ensemble

$$(N, V, T)$$

$$(N, P, T)$$

...



Partition function

$$Q = \sum_i \exp\left(\frac{-E_i}{kT}\right)$$

Molecular simulation

=

+

Sampling phase space

Evaluating the energy

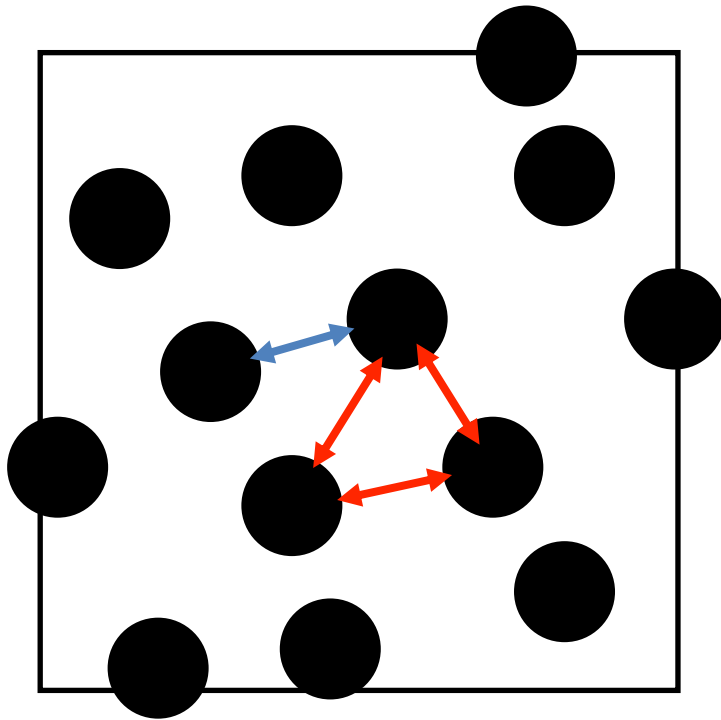
- Single-point calculation
- Energy minimization
- Integrating Newton's equation (molecular dynamics = MD)
- Stochastic sampling (Monte Carlo = MC)

- Quantum methods (QM)
 - Hartree-Fock & post HF
 - Density Functional Theory
 - Quantum Monte Carlo
- Classical force fields (FF)

Interactions in condensed matter

- Electron sharing (chemical bonds, metals)
- Coulomb
- Electronic clouds overlap repulsion
- Long-range dispersion
- Induction (polarisation)

Interactions in condensed matter

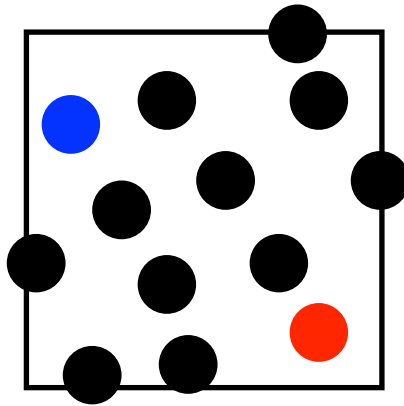


$$\begin{aligned}\mathcal{U}(\mathbf{r}^N) &= \sum_{i < j} U_{ij}^{2\text{-body}}(\mathbf{r}_i, \mathbf{r}_j) \\ &+ \sum_{i < j < k} U_{ijk}^{3\text{-body}}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \\ &+ \dots\end{aligned}$$

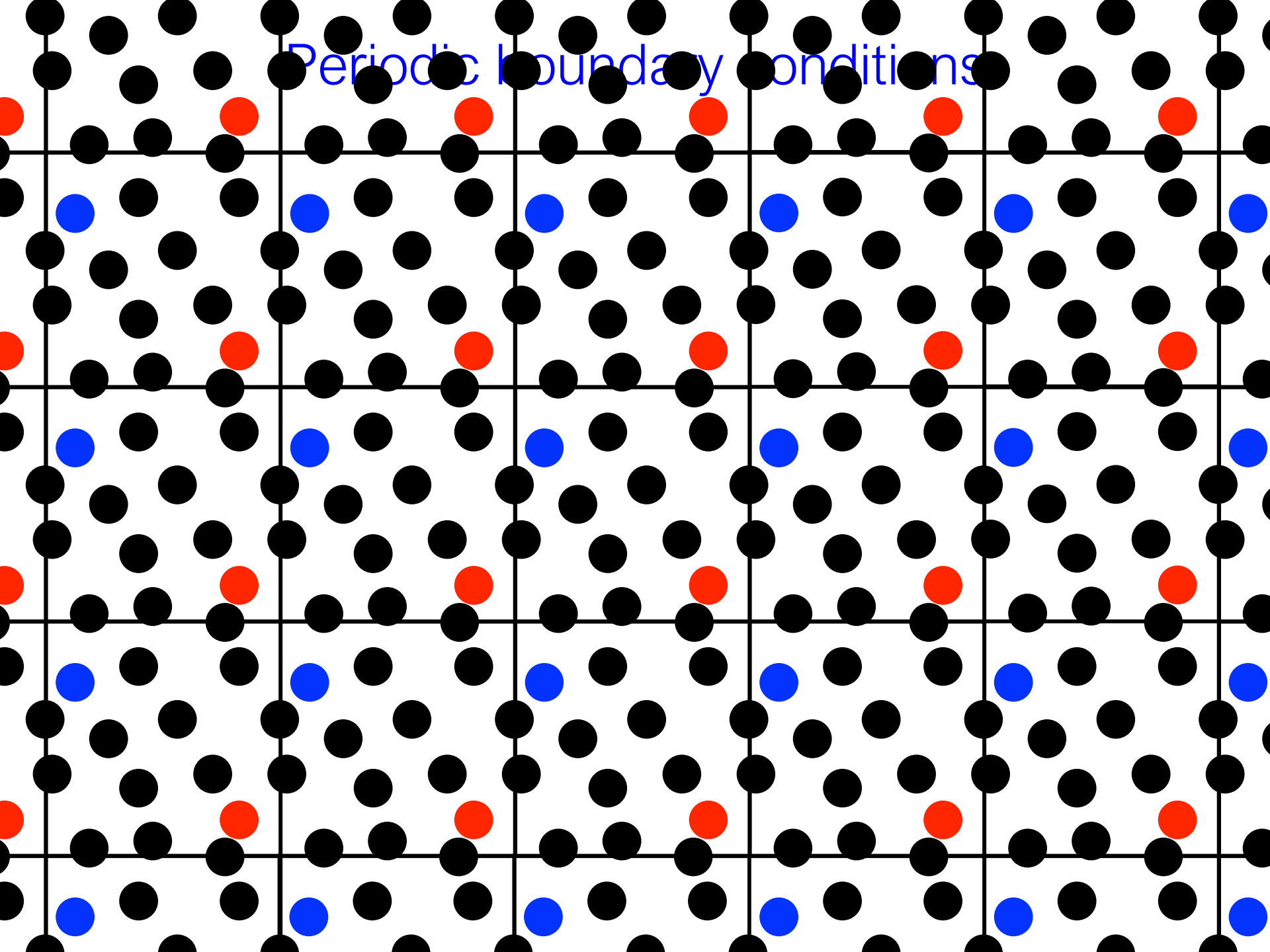
$$\mathcal{U}(\mathbf{r}^N) \approx \sum_{i < j} U_{ij}^{2\text{-body}}(r_{ij}) \quad \text{with} \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$$

Force field = Expression for $\mathcal{U}(\mathbf{r}^N)$ + Parameters

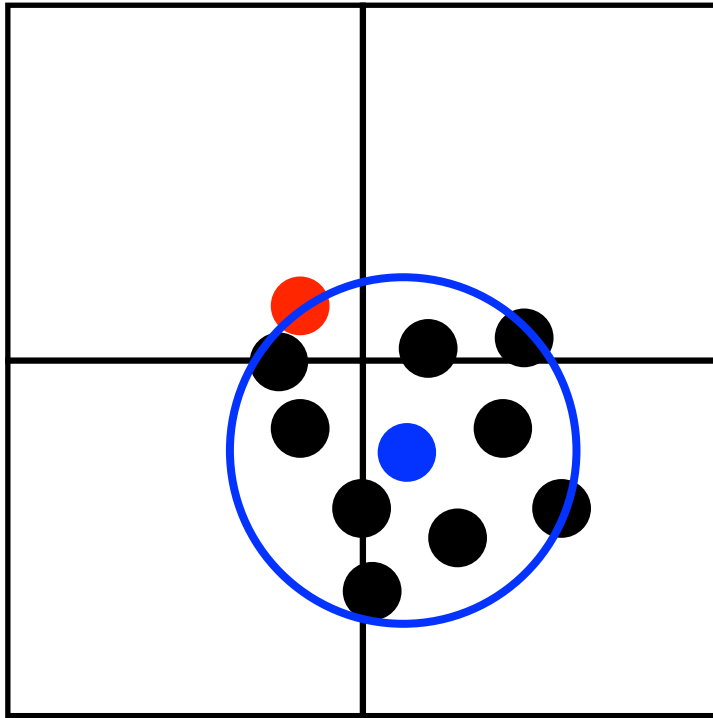
Periodic boundary conditions



Periodic boundary conditions



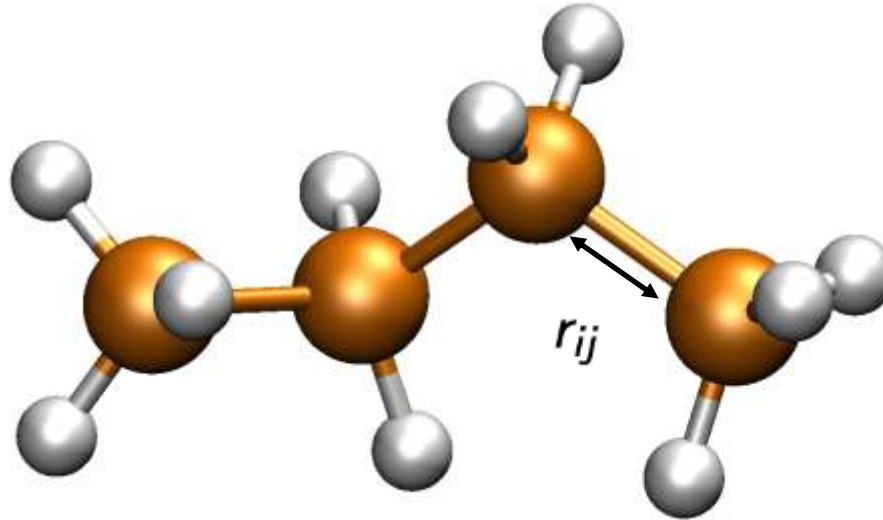
Periodic boundary conditions



Short-ranged potentials: spherical cut-off

Long-ranged potentials: numerical tricks (e.g. Ewald)

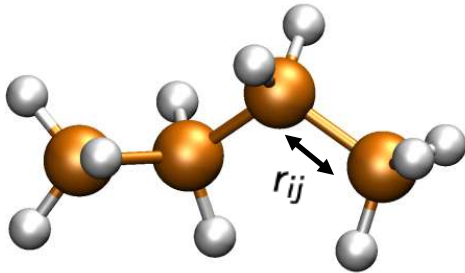
Intramolecular contributions



Spring-like term for the bonds:

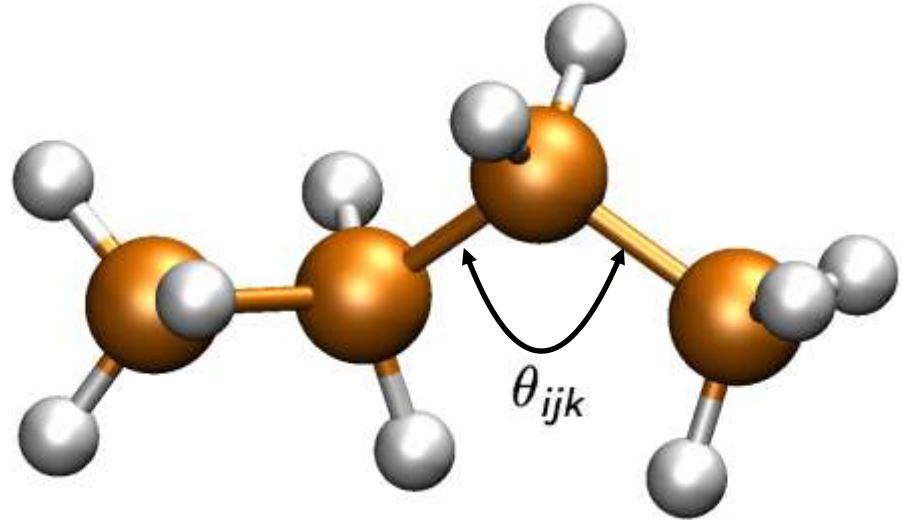
$$U_{ij}^{\text{bonds}}(r_{ij}) = \frac{k_{ij}^r}{2} (r_{ij} - r_{ij}^0)^2$$

Intramolecular contributions



Spring-like term for the bonds:

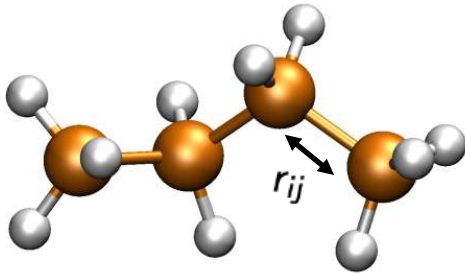
$$U_{ij}^{\text{bonds}}(r_{ij}) = \frac{k_{ij}^r}{2} (r_{ij} - r_{ij}^0)^2$$



Spring-like term for the angles:

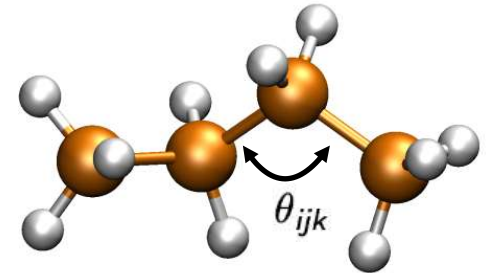
$$U_{ij}^{\text{angles}}(\theta_{ijk}) = \frac{k_{ijk}^\theta}{2} (\theta_{ijk} - \theta_{ijk}^0)^2$$

Intramolecular contributions



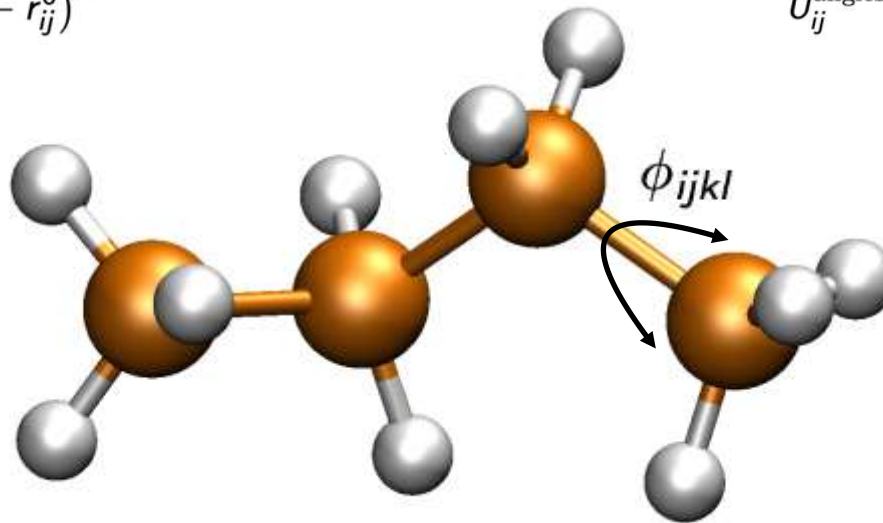
Spring-like term for the bonds:

$$U_{ij}^{\text{bonds}}(r_{ij}) = \frac{k_{ij}^r}{2} (r_{ij} - r_{ij}^0)^2$$



Spring-like term for the angles:

$$U_{ij}^{\text{angles}}(\theta_{ijk}) = \frac{k_{ijk}^\theta}{2} (\theta_{ijk} - \theta_{ijk}^0)^2$$

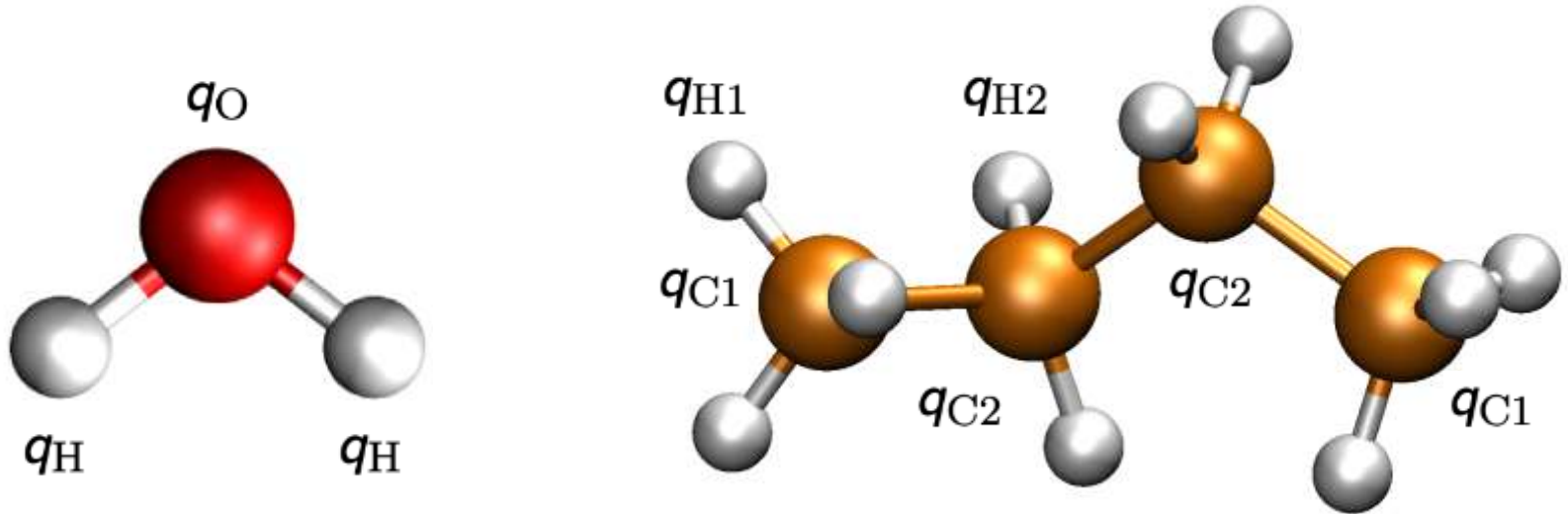


Contribution due to torsions:

$$U_{ijkl}^{\text{dihedrals}}(\phi_{ijkl}) = \sum_{m=1}^4 \frac{V_{ijkl}^m}{2} [1 + (-1)^m \cos(m\phi_{ijkl})]$$

Intermolecular contributions

Coulomb interaction

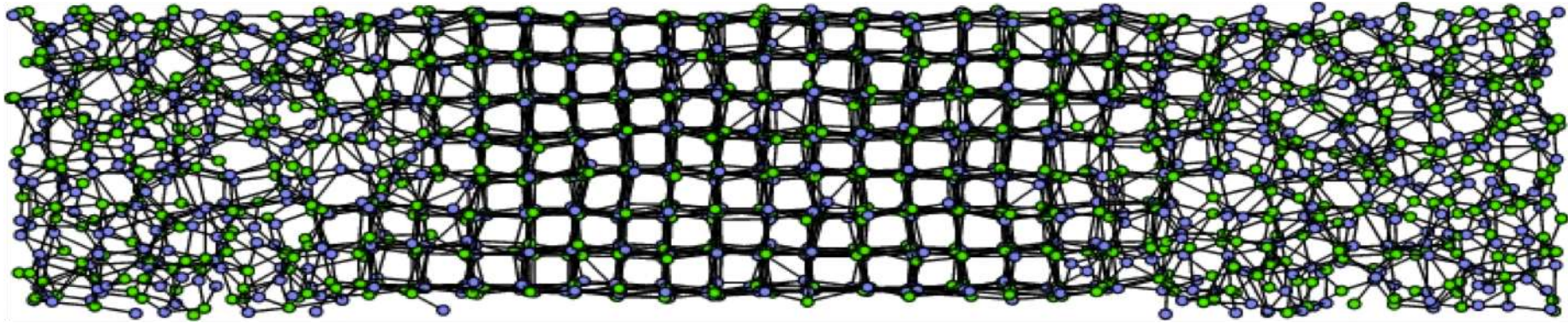


For a neutral molecule $\sum_i q_i = 0$

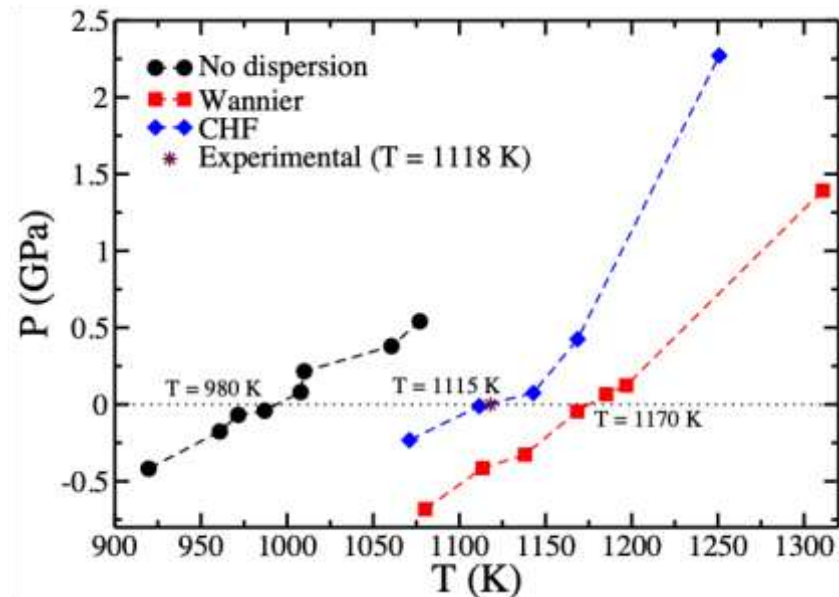
Pair potential
$$U_{ij}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j e^2}{r_{ij}} \equiv \frac{q_i q_j}{r_{ij}}$$

Intermolecular contributions

Dispersion interaction



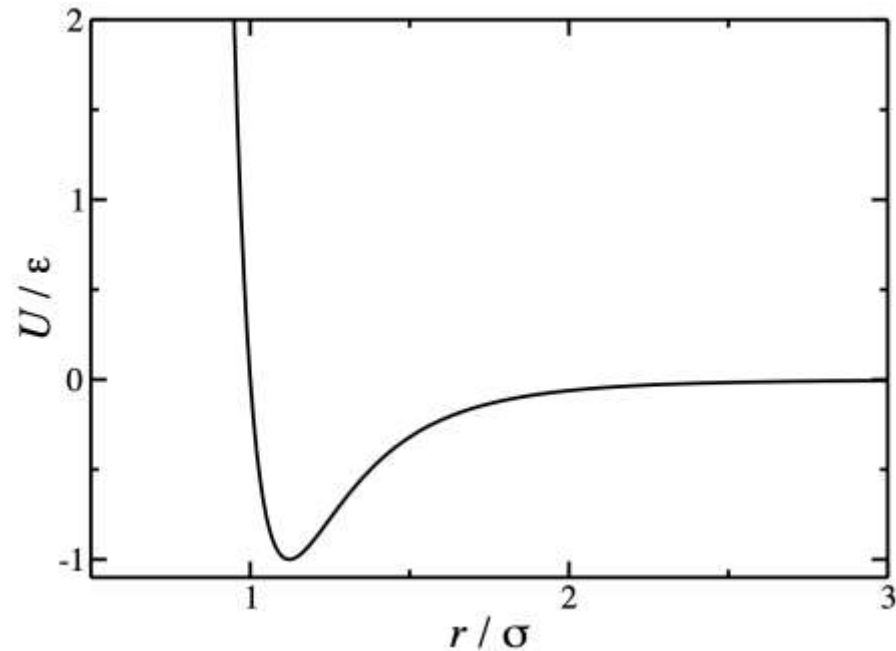
Melting point of LiF:



Lennard-Jones potential

$$U_{ij}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

repulsion dispersion



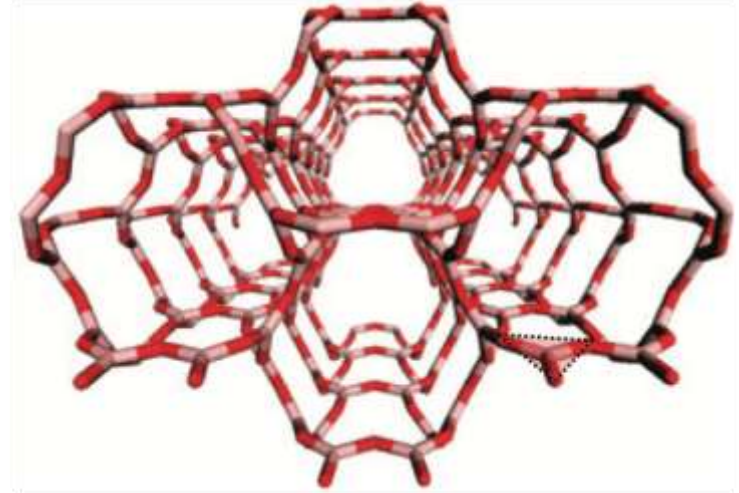
Widely used in the simulation of organic molecules,
biomolecules: OPLS, AMBER, CHARMM

Born-Huggins-Mayer potential

$$U_{ij}(r_{ij}) = A_{ij} \exp(-b_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8}$$

repulsion

dispersion



Widely used in the simulation of oxides
and ionic materials (Tosi-Fumi)

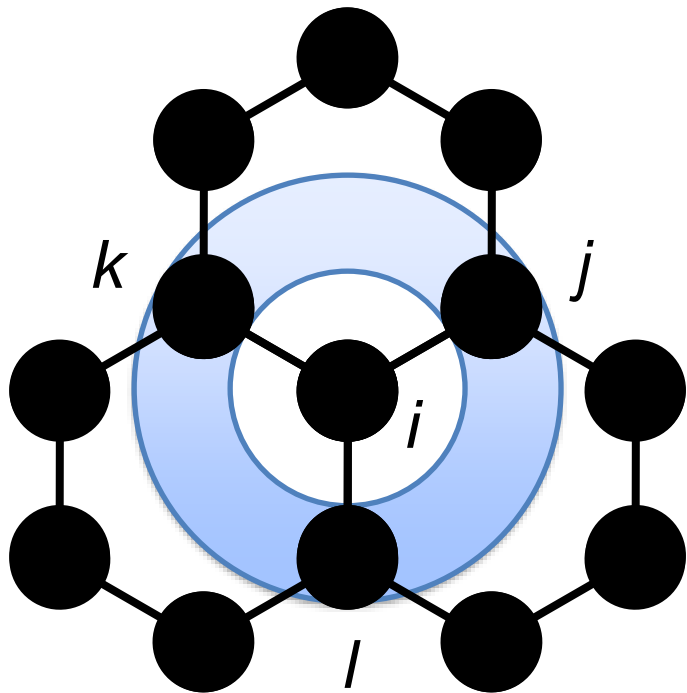
Tersoff potential

$$U_{ij}(\mathbf{r}^N) = f_c(r_{ij}) \left(A_{ij} \exp(-\lambda_1^{ij} r_{ij}) - b_{ij}(\mathbf{r}^N) B_{ij} \exp(-\lambda_2^{ij} r_{ij}) \right)$$

cut-off

repulsion

attraction (covalency)



Here $b_{ij}(\mathbf{r}^N)$ depends on:

- 3 distances:

r_{ij}

r_{ik}

r_{il}

- 2 angles:

θ_{ijk}

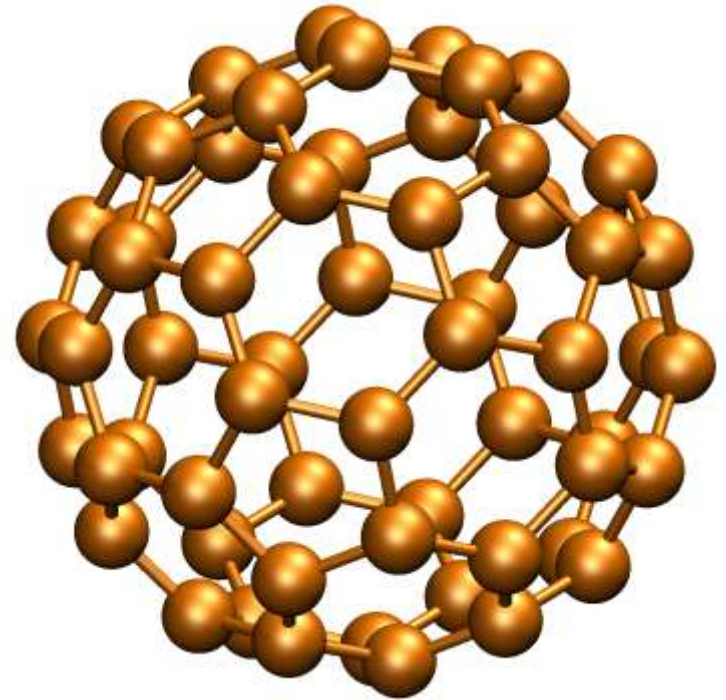
θ_{ijl}

$$U_{ij}(\mathbf{r}^N) \neq U_{ji}(\mathbf{r}^N)$$

Family of bond order potentials

Bond-order potentials

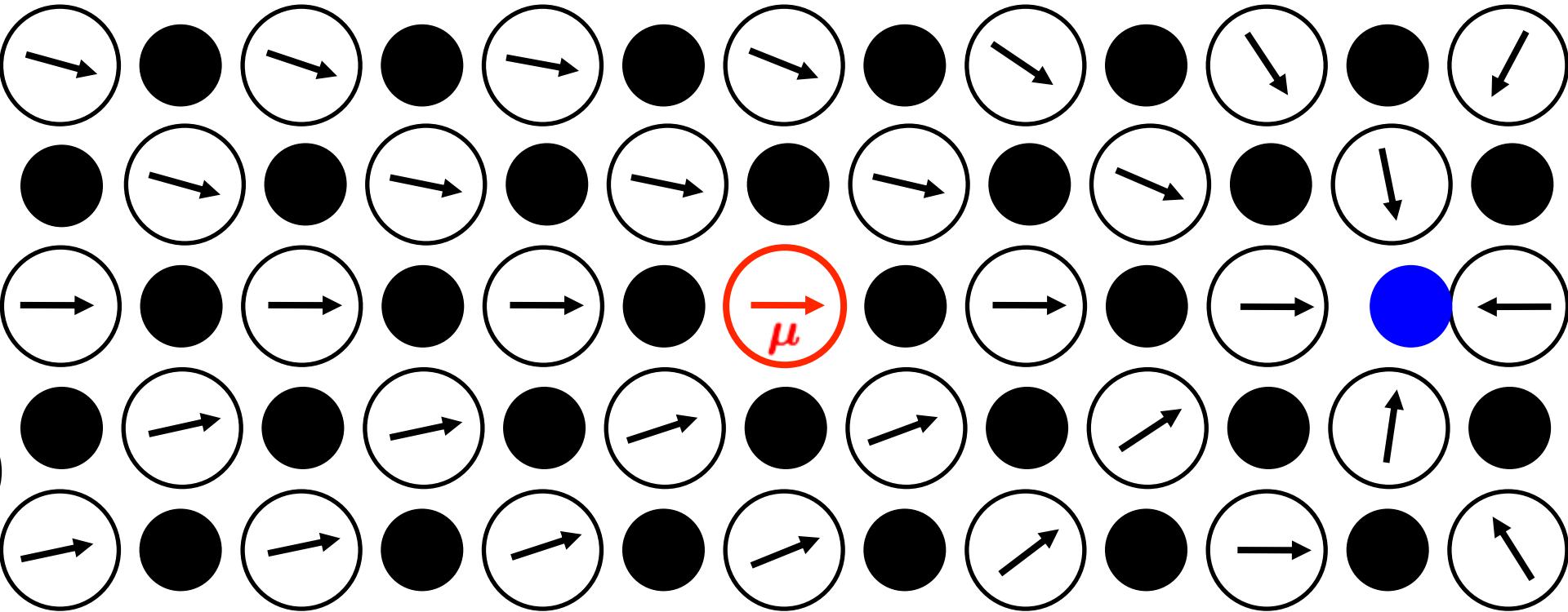
- Tersoff
- Brenner
- Finnis-Sinclair
- Embedded Atom Model
- ReaxFF
- ...



Widely used for carbon, silicon, ...
ReaxFF for chemical reactions

Intermolecular contributions

Induced dipoles



All the induced dipoles change the local electric field

They also act on the induced dipole

$$\mu = \alpha \mathbf{E}(q^N, \mu^N)$$

Induced dipoles have to be calculated self-consistently

1. For each polarizable atom, calculate the electric field due to the charges:

$$\mathbf{E}_i^{(0)}(q^N) = \sum_{j \neq i} -q_j \nabla_i \frac{1}{r_{ij}} = \sum_{j \neq i} q_j \frac{\mathbf{r}_{ij}}{r_{ij}^3}$$

2. Calculate a first set of dipoles:

$$\boldsymbol{\mu}^{(0)} = \alpha \mathbf{E}^{(0)}$$

3. Electric field with the dipoles:

$$\mathbf{E}_i^{(1)}(q^N, (\boldsymbol{\mu}^{(0)})^N) = \mathbf{E}_i^{(0)}(q^N) + \sum_{j \neq i} \left[\frac{3\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}}{r_{ij}^5} - \frac{1}{r_{ij}^3} \mathbf{I} \right] \boldsymbol{\mu}_j^{(0)}$$

4. Update the dipoles:

$$\boldsymbol{\mu}^{(1)} = \alpha \mathbf{E}^{(1)}$$

Induced dipoles have to be calculated self-consistently

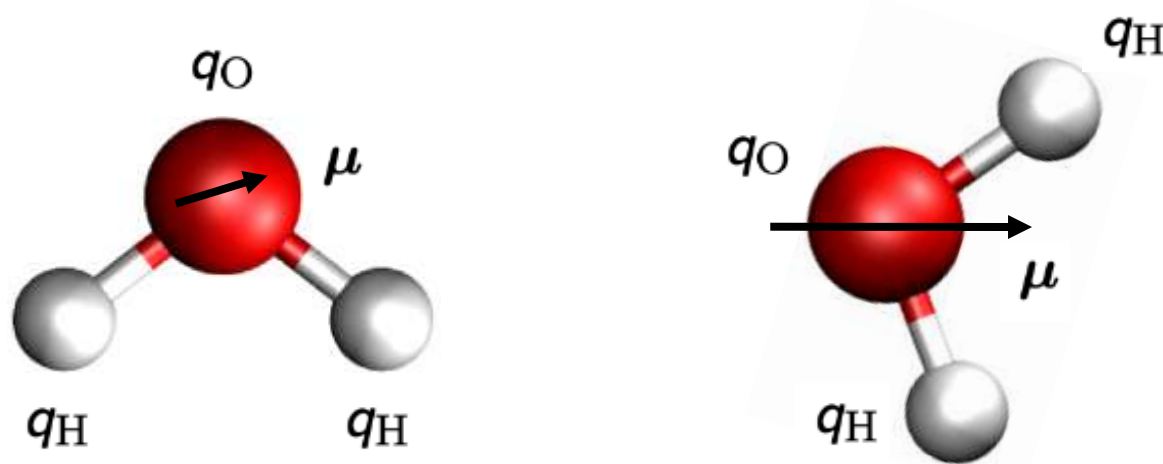
5. Convergence?

$$| \boldsymbol{\mu}^{(i)} - \boldsymbol{\mu}^{(i-1)} | < \epsilon$$

6. If not update the electric field and the dipoles:

$$\mathbf{E}_i^{(i+1)} \left(q^N, (\boldsymbol{\mu}^{(i)})^N \right) = \mathbf{E}_i^{(0)}(q^N) + \sum_{i \neq j} \left[\frac{3\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}}{r_{ij}^5} - \frac{1}{r_{ij}^3} \mathbf{I} \right] \boldsymbol{\mu}_j^{(i)}$$
$$\boldsymbol{\mu}^{(i+1)} = \alpha \mathbf{E}^{(i+1)}$$

Once the induce dipoles are known,
the computational overhead is small



Charge-dipole:
$$U_{ij}^{q\mu}(\mathbf{r}_{ij}, \mu_i, \mu_j) = \frac{q_i \mathbf{r}_{ij} \cdot \mu_j}{r_{ij}^3} - \frac{q_j \mathbf{r}_{ij} \cdot \mu_i}{r_{ij}^3}$$

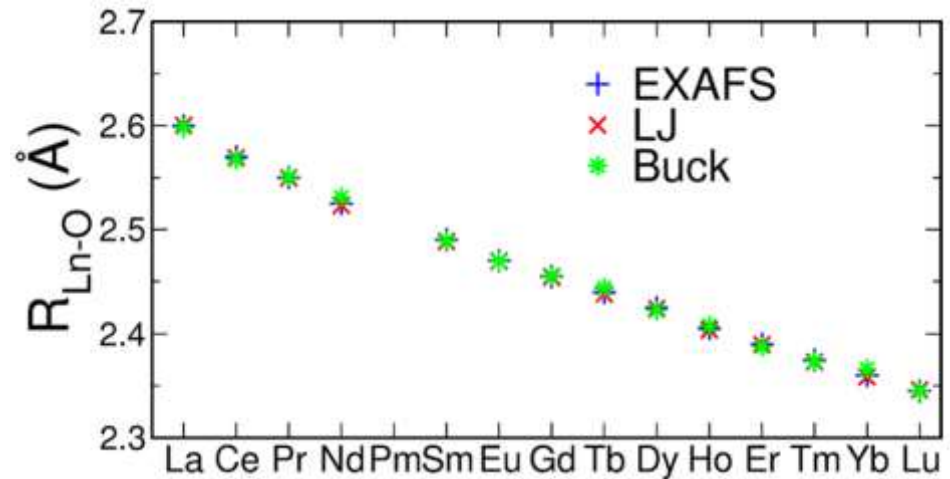
Dipole-dipole:
$$U_{ij}^{\mu\mu}(\mathbf{r}_{ij}, \mu_i, \mu_j) = \frac{\mu_i \cdot \mu_j}{r_{ij}^3} - \frac{\mu_i (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}) \mu_j}{r_{ij}^5}$$

Self energy:
$$U_i^{\mu}(\mu_i) = \frac{1}{2\alpha_i} |\mu_i|^2$$

1- and 2-body but the dipoles depend on the N positions!

Force field parameterization from experiments

- Basic structure (bond length, etc)
- Advanced structure (xray/neutron diffraction)

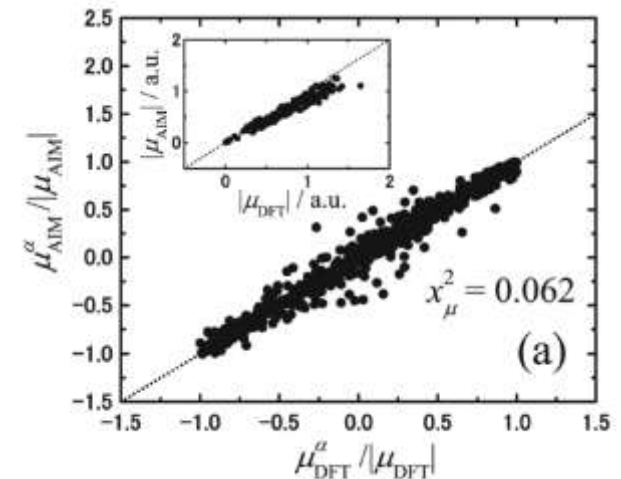
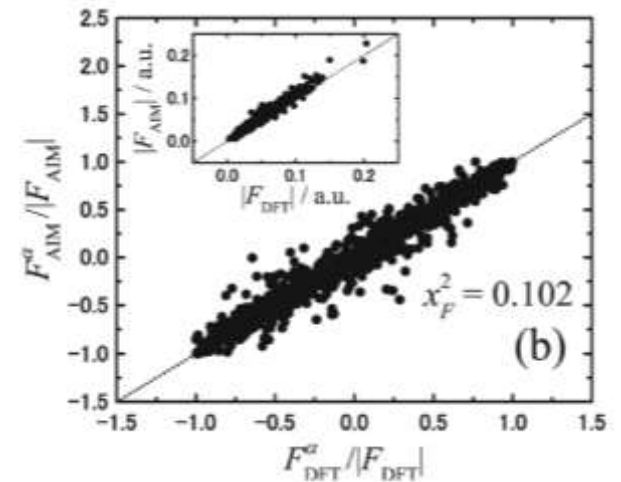


- Lattice parameters, density
- Vibrational spectroscopy (phonons, infrared,...)
- ...

Not very predictive!

Force field parameterization from *ab initio*

- Energies (total or decomposition)
- Forces
- Dipoles (multipoles)
- Stress tensors
- ...

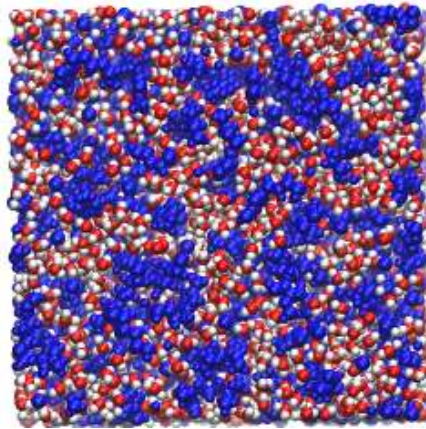
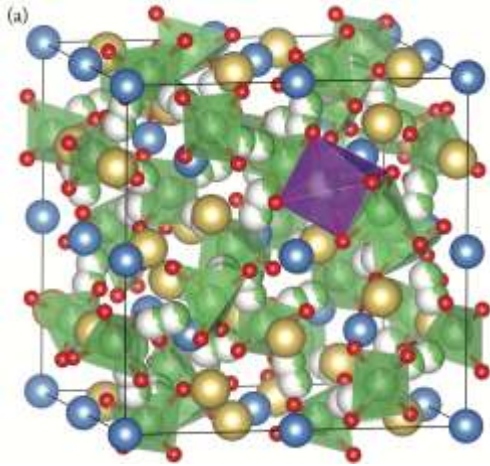


Garbage in = Garbage out!

Typical (raw) output

- Positions (trajectory)
- Velocities
- Stress tensor
- Pressure tensor
- Temperature
- Energy and its decomposition
- (Potential)
- (Electric field)
- (Dipole moments)

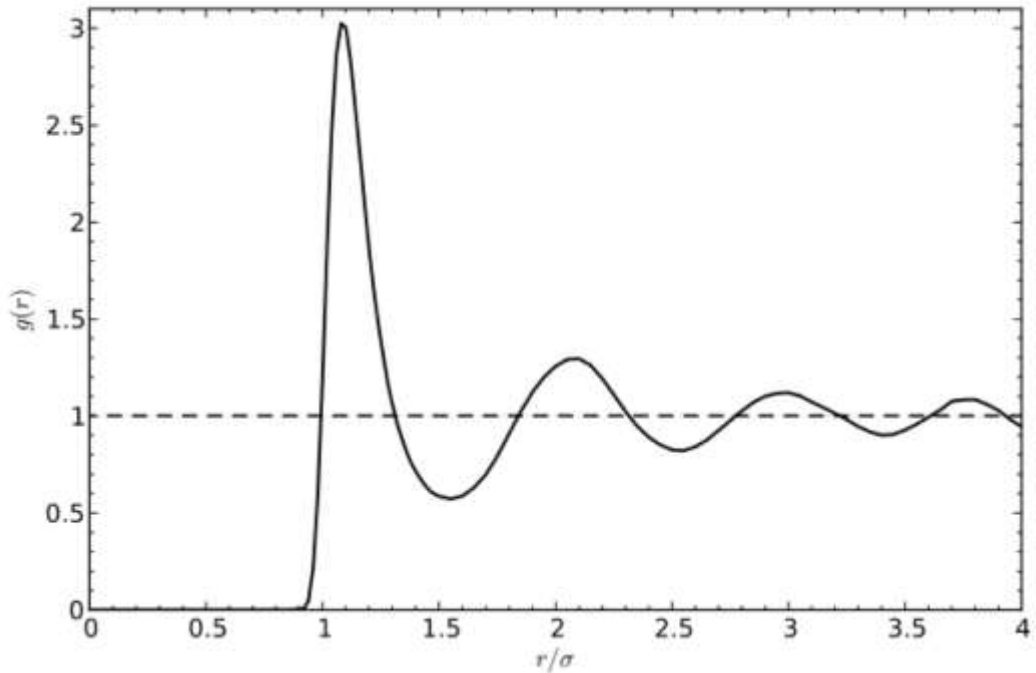
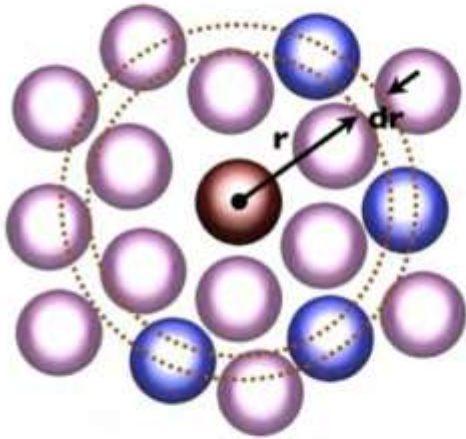
Structure: trajectory visualization



Good but not quantitative

Structure: Radial distribution functions

$$g_{ab}(r) = \frac{\langle \rho_b(r) \rangle}{\rho_b^{ave}} = \frac{1}{N_a \rho_b^{ave}} \sum_{i \in a} \sum_{j \in b} \frac{\delta(r_{ij} - r)}{4\pi r^2}$$



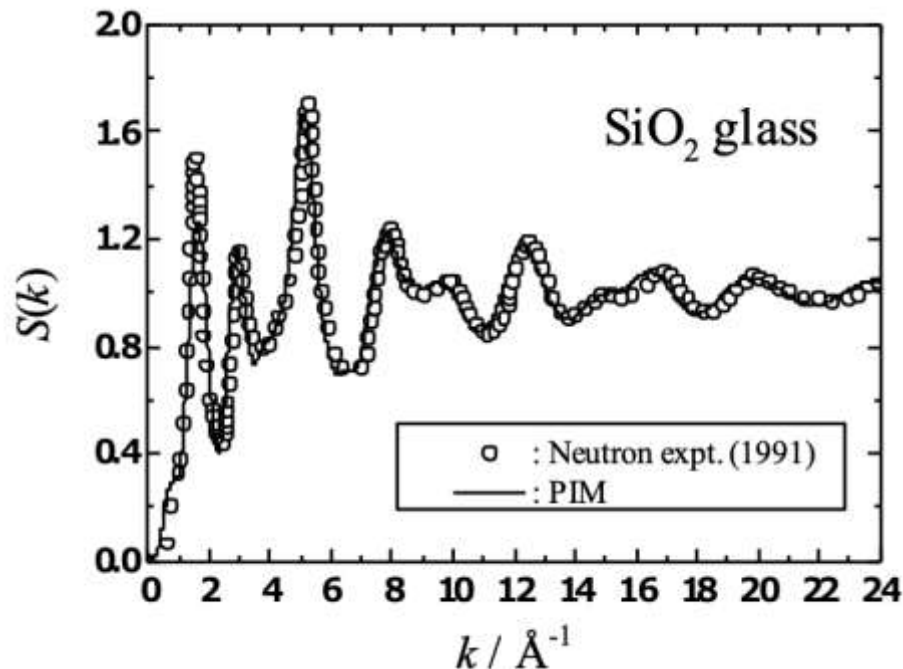
$$N_b = 4\pi\rho_b \int_0^{R_{min}} g_{ab}(r)r^2 dr$$

Coordination
numbers

X-ray/neutron diffraction: structure factors

$$S(k) = 1 + \frac{1}{|\langle w(k) \rangle|^2} \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} w_{\alpha}(k) w_{\beta}^*(k) [S_{\alpha\beta}(k) - 1]$$

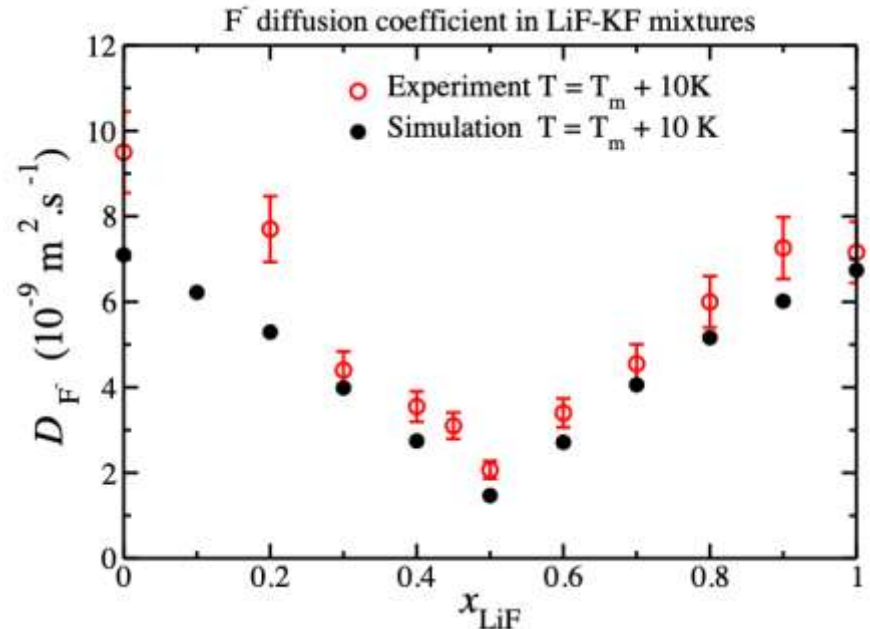
where $S_{\alpha\beta}(k) = 1 + \frac{4\pi\rho}{k} \int_0^{\infty} dr r [g_{\alpha\beta}(r) - 1] \sin(kr)$



Transport properties

Diffusion coefficients:
Mean-squared displacements

$$D_i^{\text{PBC}} = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\delta \mathbf{r}_a(t)|^2 \rangle$$



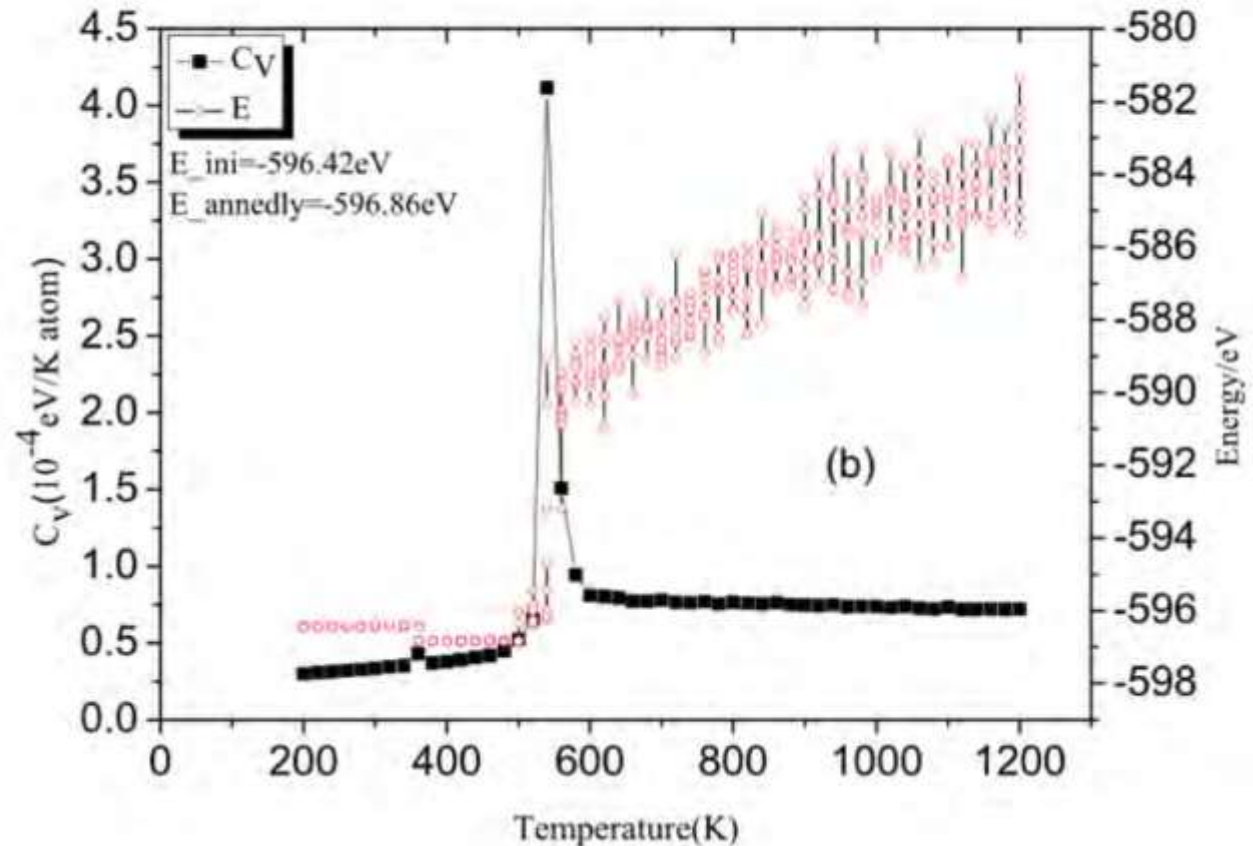
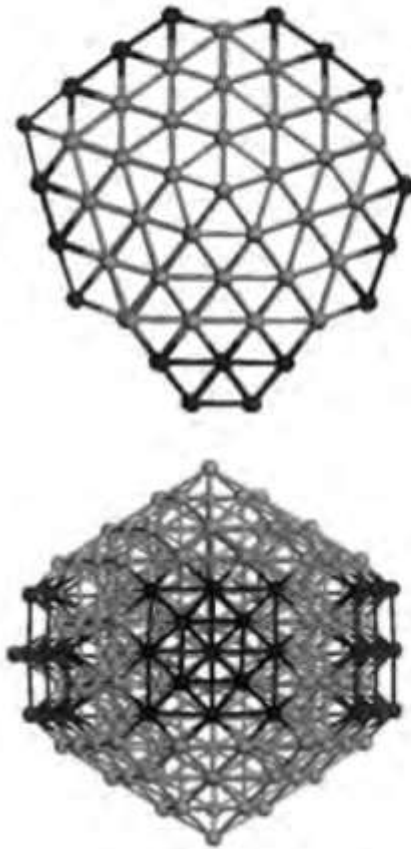
Viscosity: stress tensor auto-correlation function

Ionic conductivity: displacements of charged species

Thermodynamic properties

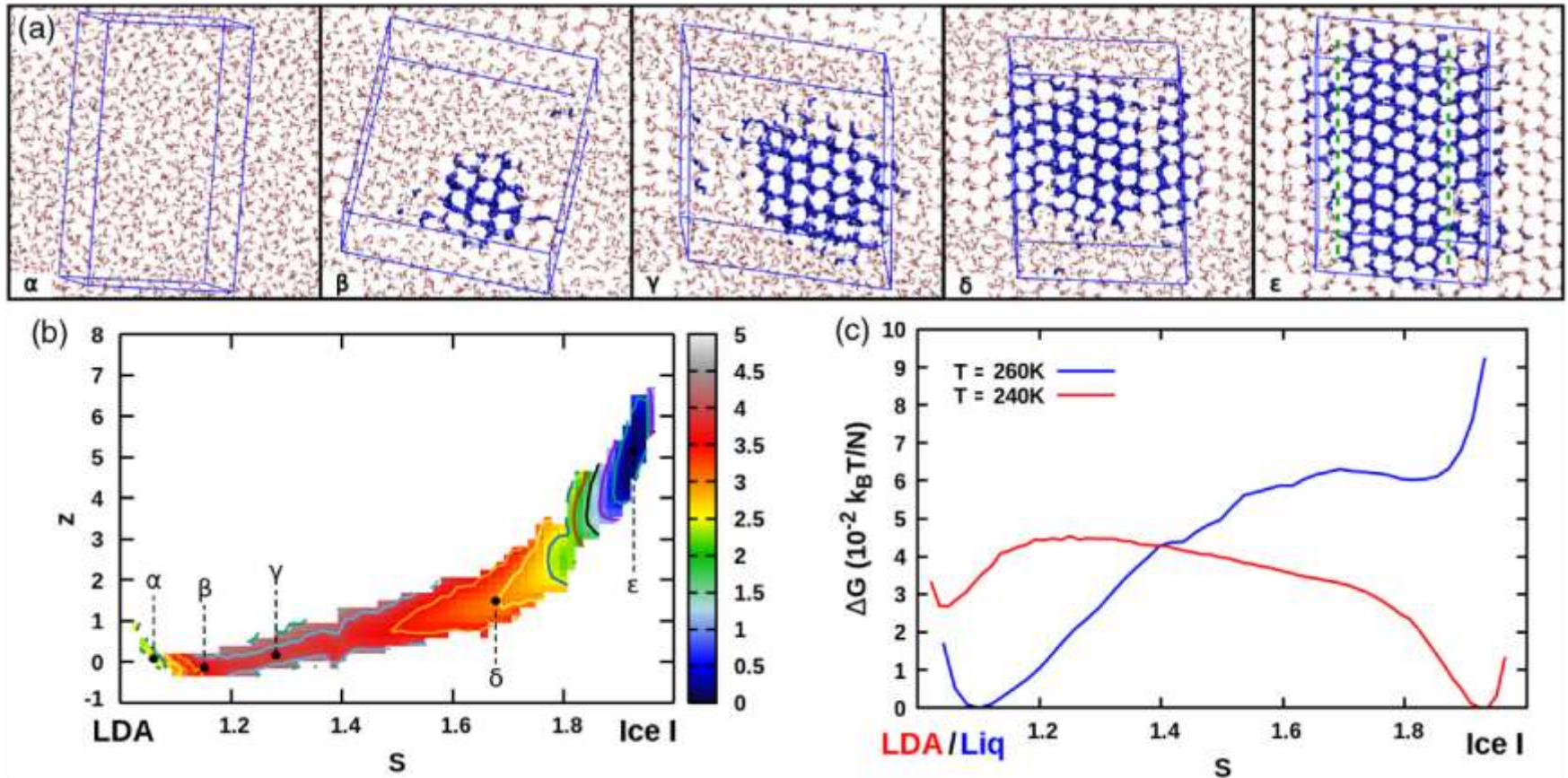
Melting of Al_{196} nanoparticle

C. L. Li, M. Kailaimu, and H. M. Duan / J. At. Mol. Sci. 4 (2013) 367-374



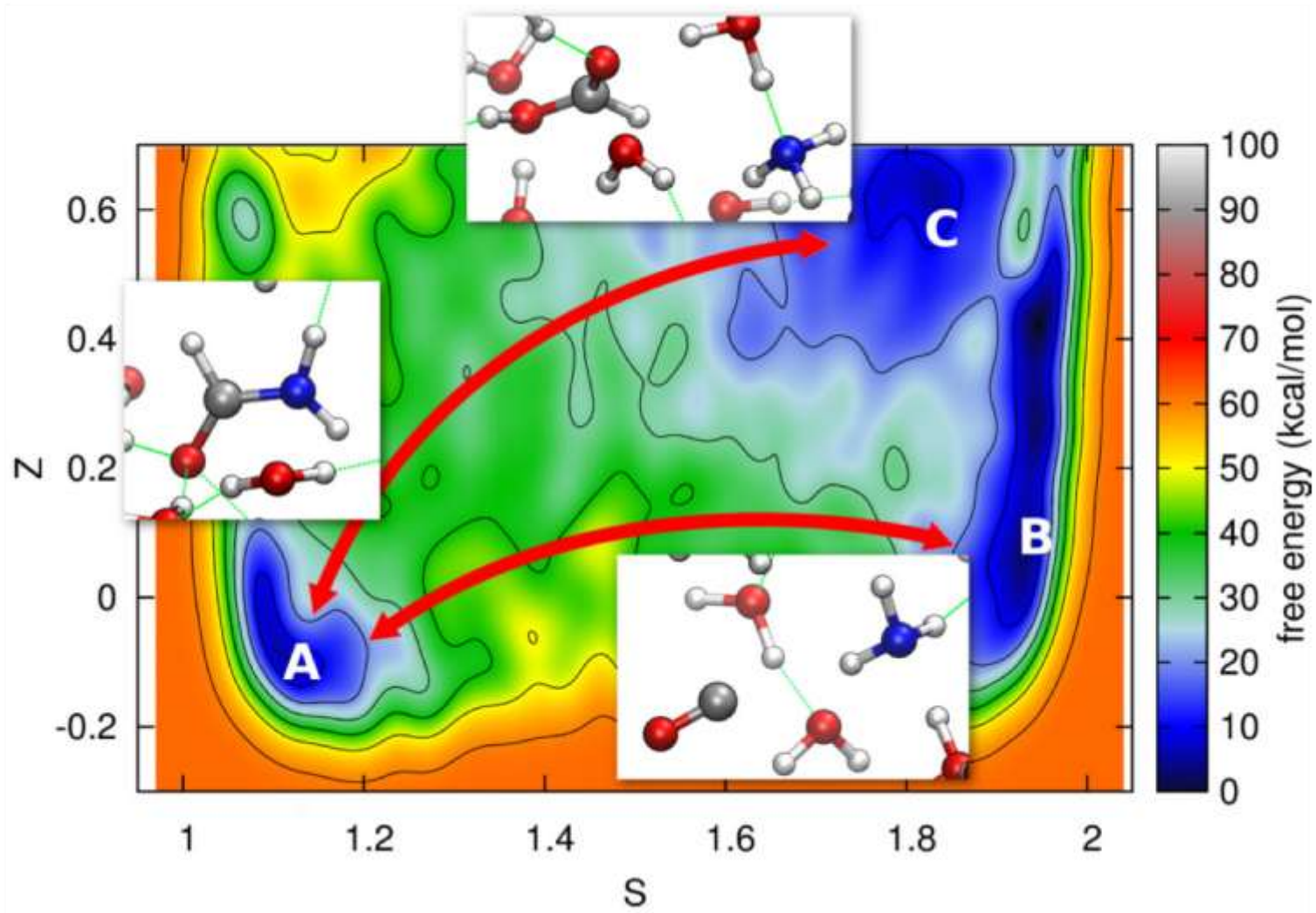
Heat capacity, phase diagram, compressibility, etc

Free energy: physical transformation



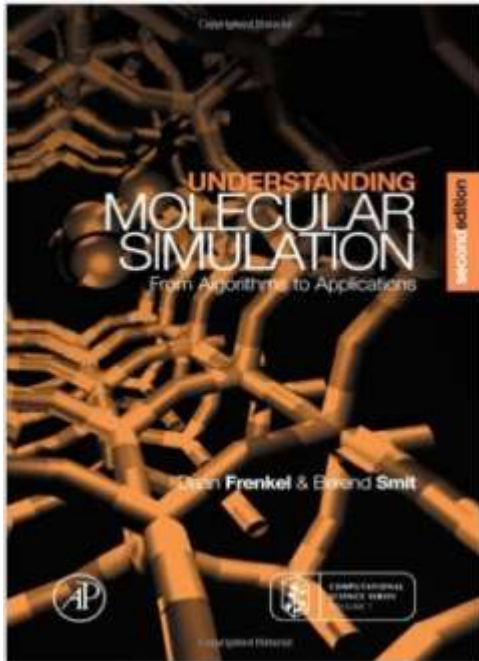
Crystallization of liquid water

Free energy: chemical transformation

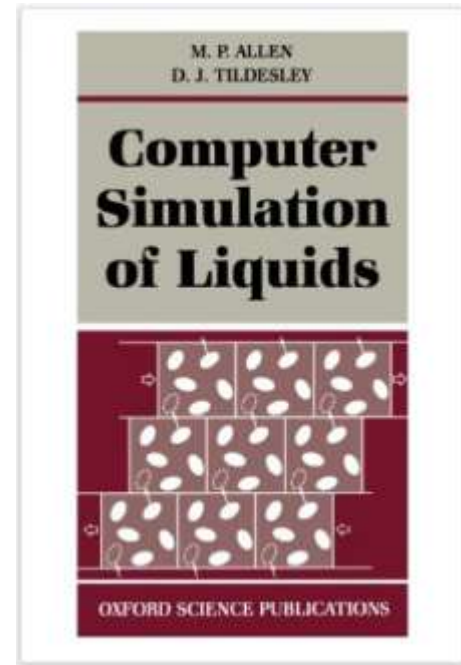


Generally requires ab initio molecular dynamics

Further reading



Frenkel & Smit

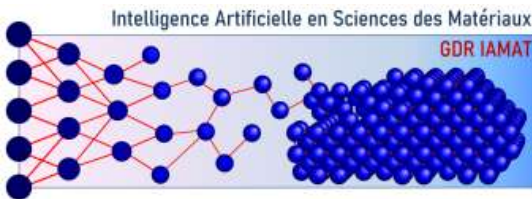


Allen & Tildesley

Simulations: The Dark Side, D. Frenkel, arXiv:1211.4440

(Elements of) Density Functional Theory

A. Marco Saitta



PROGRAMME
DE RECHERCHE
MATÉRIAUX
ÉMERGENTS

École internationale DIADEM

25-29 août 2025 Paris (France)



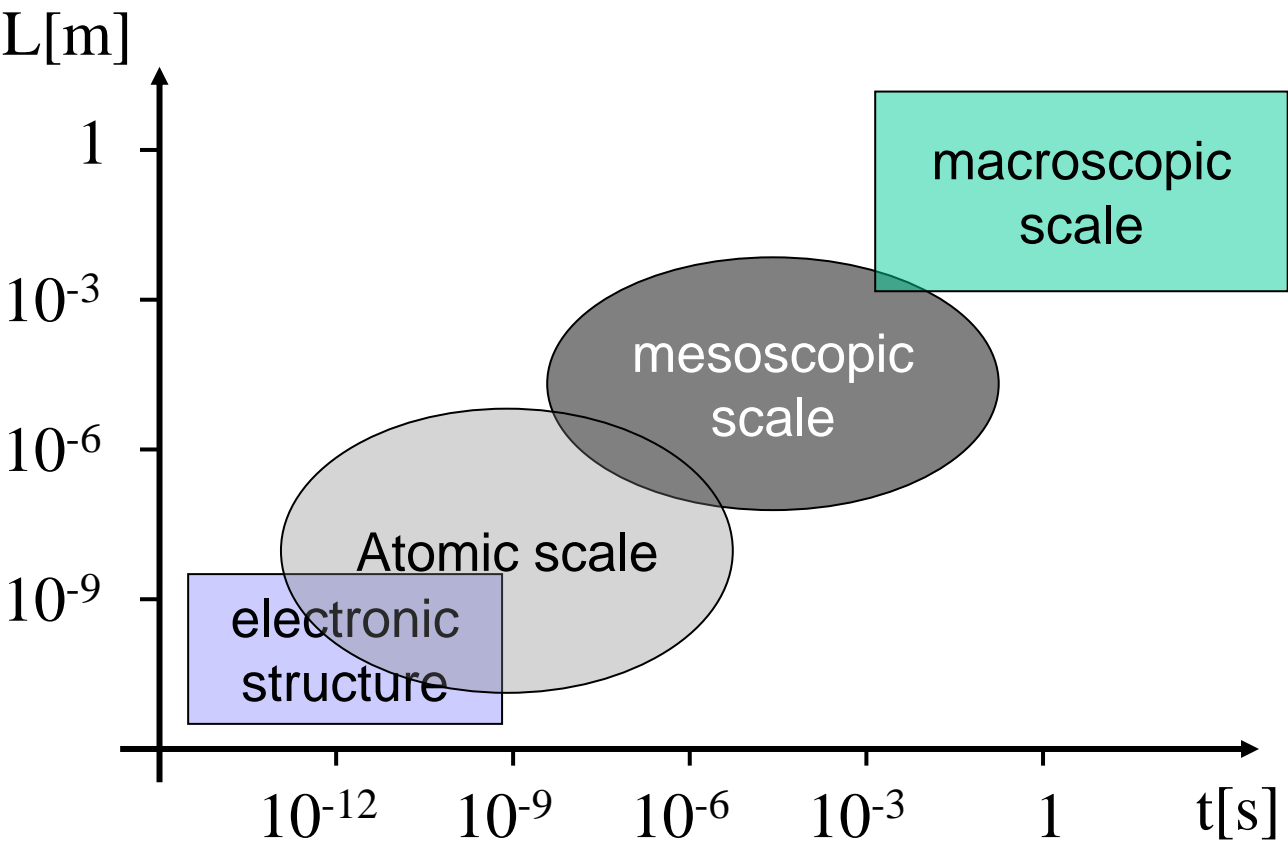
IA et physique des matériaux

Outline

- Time and length scales
- Why ab initio calculations?
- The electron density as the fundamental quantity
- Formalism, theorems, and the Kohn-Sham equations
- Approximations for the exchange-correlation functional
- Pseudopotentials
- Plane-wave expansion, Brillouin zone sampling
- Basic properties with DFT

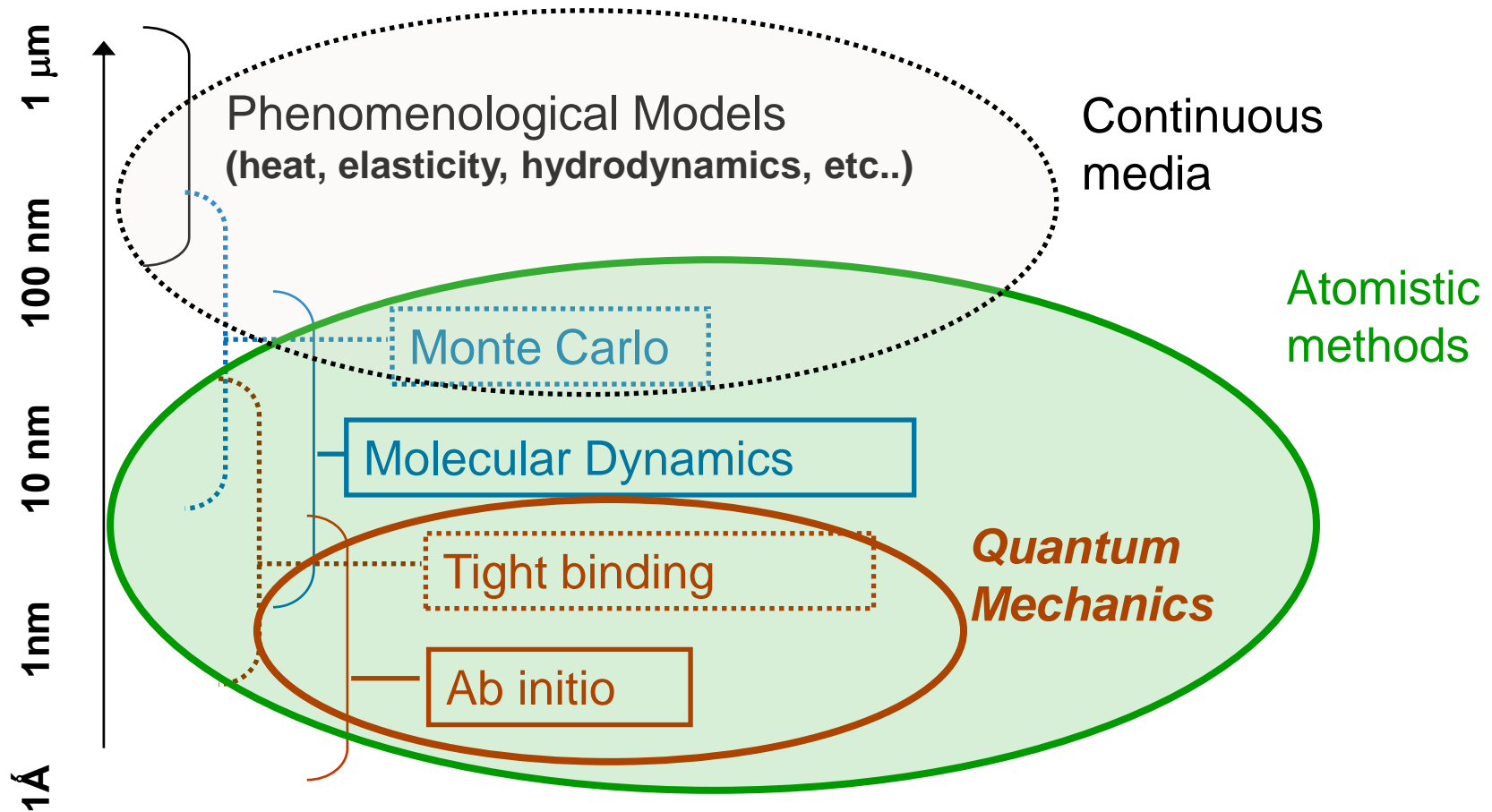


Length/time scales, methods

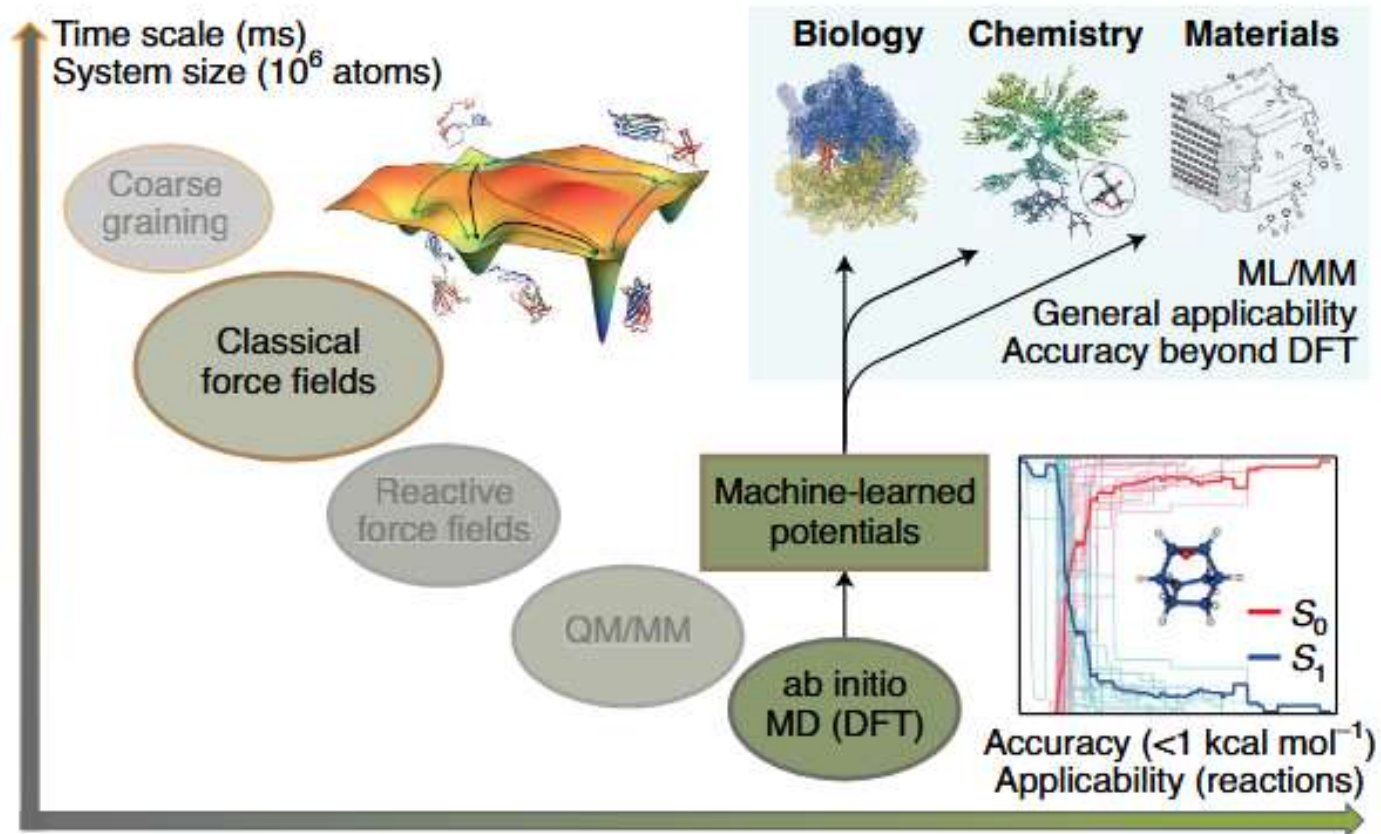




Length/time scales, methods

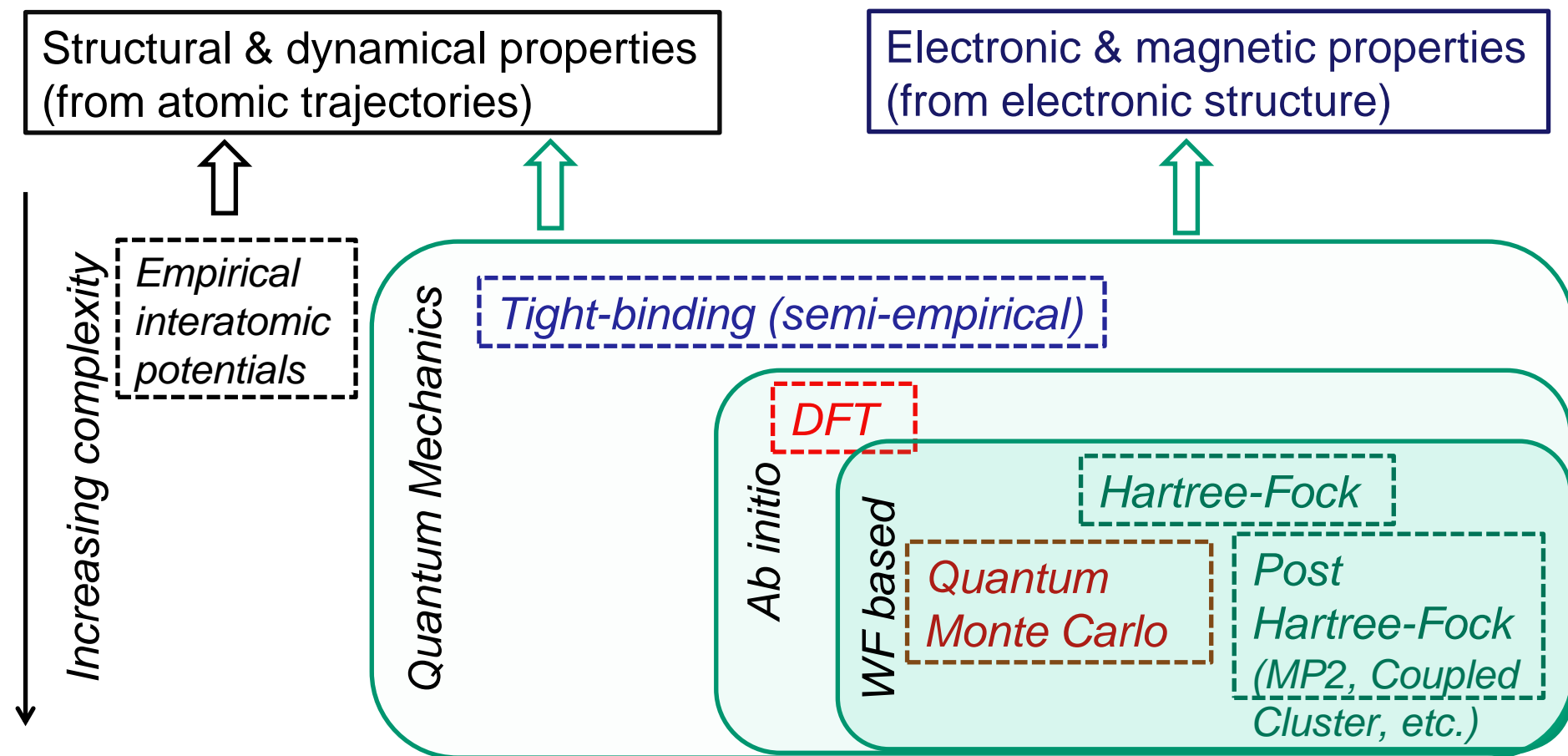


Length/time scales, methods





Length/time scales, methods



Classical methods: major drawbacks

- Potential tailored on specific properties of the system
- Potential parameters taken from experiments
- Classical potentials not transferable
- Chemical reactions, change of bonding properties and in general electronic properties not described
- Ab initio calculations: treating explicitly the electronic degrees of freedom

Ab initio vs classical calculations

- Ab initio interactions solely determined by the electronic structure of atoms
- Solution of the quantum mechanical EOM of the electrons: energy and forces
- Atomic number the only “external” input: transferability
- However, a special theoretical framework is needed

Ab initio calculations: why?

- Same approach from biology to planet interiors
- Electronic structure and properties, chemical reactions, change of coordination
- Accuracy at the (sub)nano scale
- Directly simulate experimental spectra (x-ray, Raman, infrared, NMR,...)



Ab initio calculations: why?

Generality (« transferability »): all atoms from periodic table

Desired accuracy (« predictive » theory):

- | | |
|------------------------------|-------------------------------------------------------|
| ▪ crystallographic positions | $\pm 0.005 \text{ \AA}$ |
| ▪ bonding energies | $\pm 40 \text{ meV/atom } (\cong 1 \text{ kcal/mol})$ |
| ▪ vibrational frequencies | $100 \text{ GHz} \sim 3.3 \text{ cm}^{-1}$ |
| ▪ dipolar moments | $\pm 0.02 \text{ D}$ |
| ▪ magnetic moments | $\pm 0.1 \mu_B$ |
| ▪ spectra (visible, UV, X) | $\pm 0.1 \text{ eV}$ |

Typical system size: $< 10^3$ atomes

Typical time scale: $\sim 10^{-11} \text{ s}$

Computational efficiency: parallel algorithms, modularity

The many-electron problem

Time-independent, non-relativistic, spinless, Schrödinger equation for N electrons interacting with fixed nuclei

$$H\Psi(\vec{r}_1, \dots, \vec{r}_N) = \varepsilon\Psi(\vec{r}_1, \dots, \vec{r}_N)$$

$$H = \sum_{i=1}^N \left[-\frac{\hbar^2 \nabla_i^2}{2m} + V_{\text{ext}}(\vec{r}_i) \right] + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

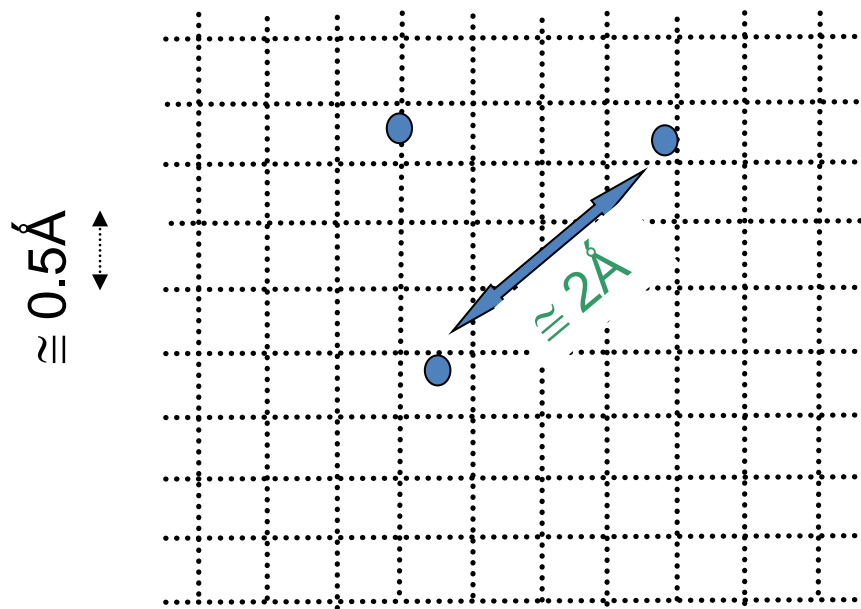
sum of N one-electron operators
(kinetic operator + Coulomb
potential from the nuclei)

Long range $e^- - e^-$ interaction
(the big problem!)

Can we solve it numerically by brute force?

The many-electron problem by brute force?

Example: Li_3 cluster



9 electrons

Solve the Schrödinger equation
on a $M \times M \times M$ grid for each
spatial coordinate

For $M=10 \rightarrow 10^{27} \times 2^9$
independent variables

$\rightarrow \sim 5 \times 10^{29}$ operations just to
evaluate $\langle \Psi | H | \Psi \rangle$!

On a Tflops computer this would need $\sim 10^{11}$ years!
(unfeasible even if computer speed increases by a factor ~ 4 every ~ 2 yrs)

Adiabatic (Born-Oppenheimer) approximation

- Electrons much lighter & faster than nuclei, their timescales much shorter
- Quantum EOM for electrons, classical ones for ions
- Solution of the electrons QM: global many-body wavefunction, whose size grows exponentially

The electronic density

$$n(\vec{r}) = \langle \Psi | \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) | \Psi \rangle = N \int d^3r_2 \dots \int d^3r_N |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2$$

- Is a function of 3 spatial coordinates, independently of N
- Is measurable
- Many physical quantities can be inferred from it

Can we reformulate the many-body electron problem in terms of $n(r)$?

The Hohenberg-Kohn theorem (aka Density Functional Theory)

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

*École Normale Supérieure, Paris, France and Faculté des Sciences, Orsay, France
and*

University of California at San Diego, La Jolla, California

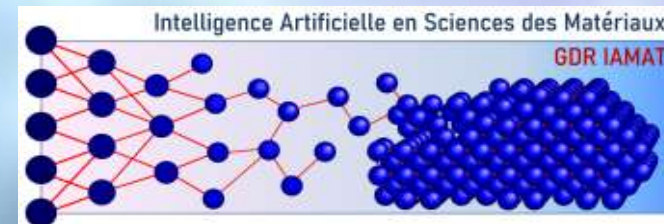
(Received 18 June 1964)



PROGRAMME
DE RECHERCHE
MATÉRIAUX
ÉMERGENTS

École internationale DIADEM

25-29 août 2025 Paris (France)



The Hohenberg-Kohn theorem (aka Density Functional Theory)

1) For non-degenerate ground states: one-to-one correspondence between Hamiltonians H and ground-state electron densities $n_0(r)$

the ground-state energy is a functional of $n(r)$: $E = E[n]$

2) We consider a large class of “physically sensible” electron densities $n(r)$; $E[n]$ is minimal when $n(r)$ is the actual ground-state density $n_0(r)$:

$$\min E[n] = E[n_0]$$

Can we thus “just” minimize $E[n]$?

The energy functional

$$H = \sum_{i=1}^N \left[-\frac{\hbar^2 \nabla_i^2}{2m} + V_{\text{ext}}(\vec{r}_i) \right] + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$E[n] = T[n] + E_{\text{ext}}[n] + U[n]$$

$$E_{\text{ext}}[n] = \int d^3r V_{\text{ext}}(\vec{r}) n(\vec{r})$$

$$U[n] = E_{\text{H}}[n] + \Delta U[n] \quad E_{\text{H}}[n] = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

Kohn-Sham: map onto a non-interacting system

- Separate, in $T[n]$, the kinetic energy of N non-interacting electrons but not necessarily homogeneous $T_s[n]$

$$T[n] = T_s[n] + T_c[n],$$

- Add the term E_{xc} that describe quantum effects (exchange and correlation) and the difference between $T[n]$ and $T_s[n]$

$$E_{xc}[n] = T_c[n] + \Delta U[n]$$

The energy functional rewritten

$$E[n] = T[n] + E_{\text{ext}}[n] + U[n]$$

$$U[n] = E_{\text{H}}[n] + \Delta U[n]$$

$$T[n] = T_{\text{s}}[n] + T_{\text{c}}[n]$$

$$E_{\text{xc}}[n] = T_{\text{c}}[n] + \Delta U[n]$$

$$E_{\text{ext}}[n] = \int d^3r V_{\text{ext}}(\vec{r}) n(\vec{r})$$

$$E_{\text{H}}[n] = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$E[n] = T_{\text{s}}[n] + \int d^3r V_{\text{ext}}(\vec{r}) n(\vec{r}) + E_{\text{H}}[n] + E_{\text{xc}}[n]$$

The Kohn-Sham equations

- Regroup all “potential” terms into a single-particle effective potential

$$V_s(\vec{r}) = V_{\text{ext}}(\vec{r}) + e^2 \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{\text{xc}}(\vec{r}; [n])$$

$$V_{\text{xc}}(\vec{r}; [n]) = \delta E_{\text{xc}}[n] / \delta n(\vec{r})$$

- Rewrite Schrödinger equation in terms of (solvable) independent single-particle equations

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_s(\vec{r}) \right] \psi_j(\vec{r}) = \varepsilon_j \psi_j(\vec{r}) \quad n_s(\vec{r}) = \sum_j f_j |\psi_j(\vec{r})|^2$$

The exchange-correlation term

- Contains everything we do not know

$$T[n] = T_s[n] + T_c[n]$$

$$U[n] = E_H[n] + \Delta U[n]$$

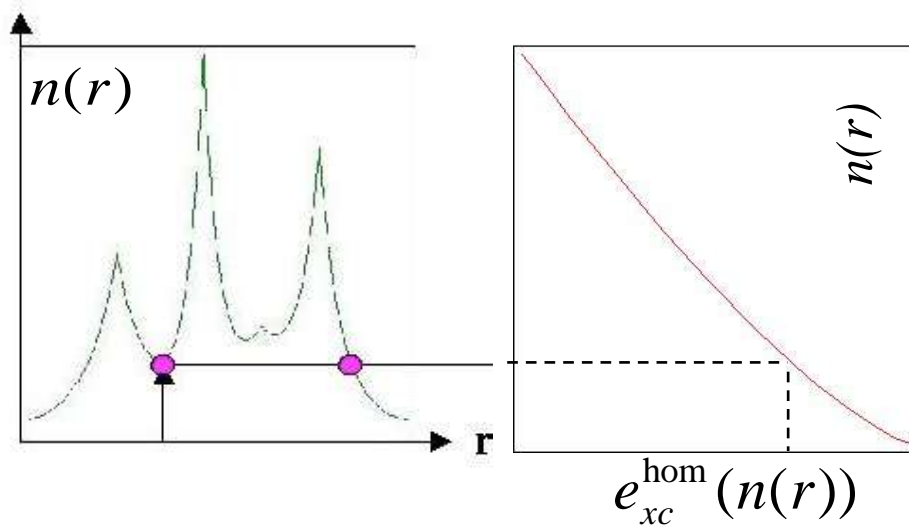
$$E_{xc}[n] = T_c[n] + \Delta U[n]$$

- The kinetic energy difference between the interacting and non-interacting systems at the same density $n(r)$
- Quantum effects on e-e interactions: exchange, Coulomb correlation, self-interaction correction

DFT and the local density approximation (LDA)

- Unknown electron-electron interaction confined in the exchange-correlation term
- DFT is an exact and useless ground state theory, no analytical form of this $E_{XC}[n]$ functional
- LDA: the XC term described as a function $E_{XC}(n)$ of the density
- Its numerical expression through exact quantum Monte Carlo simulations of the homogenous electron gas

DFT and the local density approximation (LDA)



Ceperley & Alder, PRL 1980

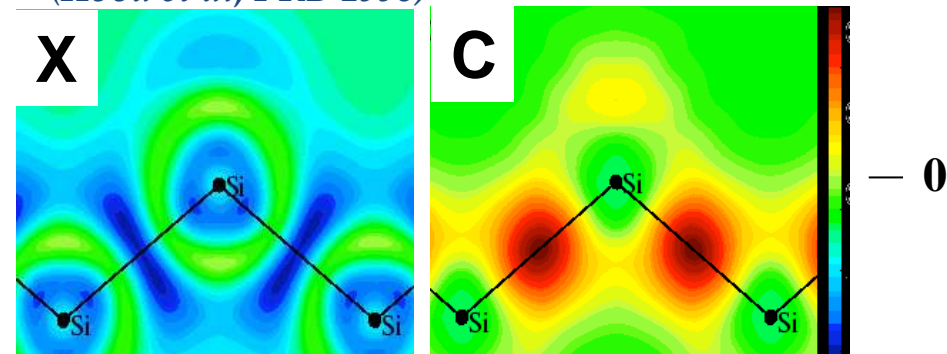
- The inhomogeneous system is considered as locally homogeneous
- The XC energy per particle is the same as in the homogeneous electron gas

DFT and the local density approximation (LDA)

- Despite its simplicity, LDA works surprisingly well
- Sum rule: the XC hole contains exactly one electron
- Error compensation: LDA is exact in the limit $N/V \rightarrow \infty$

Difference between the exact XC energy and LDA energy in c-Si

(Hood et al, PRB 1998)





LDA drawbacks

- Electrons not enough localized (not too surprising, because the LDA is exact only for completely delocalized electrons in the HEG)
- Strongly correlated electron systems are very badly described
- Self-interaction problem
- Over-binding in most cases (bonding energy is often overestimated, bond distance underestimated)
- “Weak” interactions: H-bonds, van der Waals

E_{xc} : the Generalized Gradient Approximation (GGA)

- GGA: improving LDA by including the derivatives (gradients) in the XC functional

$$E_{xc}^{GGA}[n, \sigma] = E_{xc}^{LDA}[n, \sigma] + \int d^3r e_{xc}^{GGA}(n(\vec{r}), \nabla n(\vec{r}))$$

- Many available recipes:
 - Becke (exchange) – Perdew (correlation): BP86
 - Becke (X) – Lee-Yang-Parr (correlation): BLYP
 - Perdew-Burke-Ernzerhof: PBE

E_{XC} : the Generalized Gradient Approximation (GGA)

- GGAs tend to overcorrects LDA: bond lengths $\sim 0-2\%$ larger than experimental values, cohesive energy 10-20% too small
- GGAs cannot describe long-range (wan der Waals) effects; H-bonds are usually well accounted for
- GGAs describe XC effects in small-density regions of space much better than LDA; usually employed for atoms, molecules, surfaces
- Strongly correlated electron systems are still out of reach

E_{XC} : the Jacob's ladder of XC functionals

E_{XC} depends on:

Hybrid Functionals

$$n(r), \nabla n(r), \{\varphi_i(r)\}$$

Meta-GGA

$$n(r), \nabla n(r), \{\nabla^2 \varphi_i(r)\}$$

DFT-vdW including dispersion via the response function to perturbations

$$n(r), \nabla n(r), \frac{\delta n(r)}{\delta V(r')}$$

Generalized Gradient Approximations (GGA)

$$n(r), \nabla n(r)$$

Local Density Approximations (LDA, LSDA)

$$n(r)$$

DFT and excitations

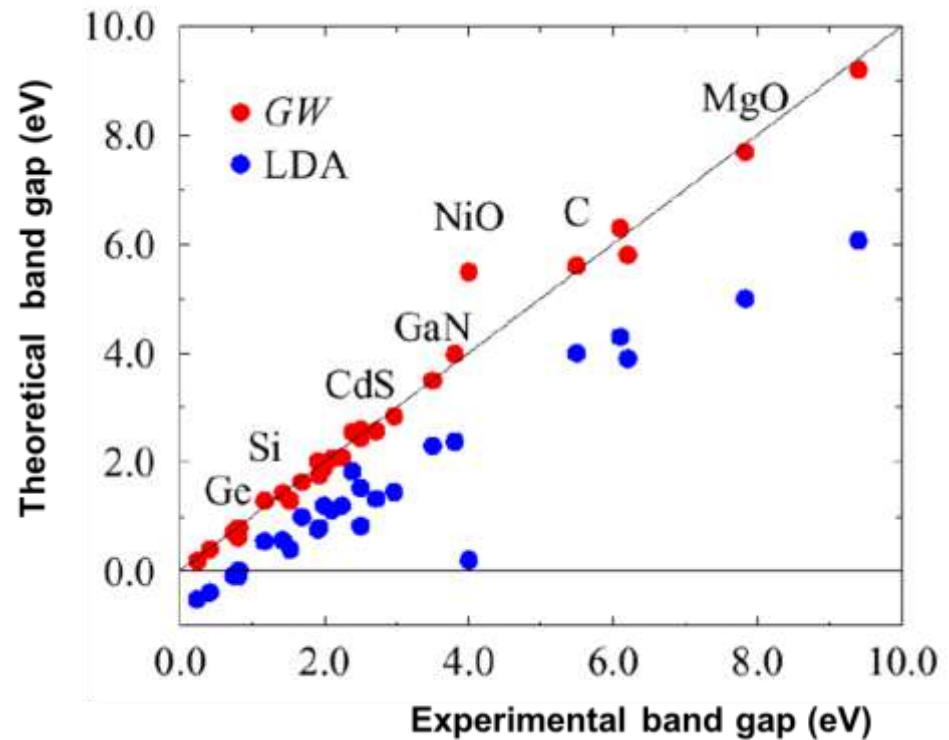
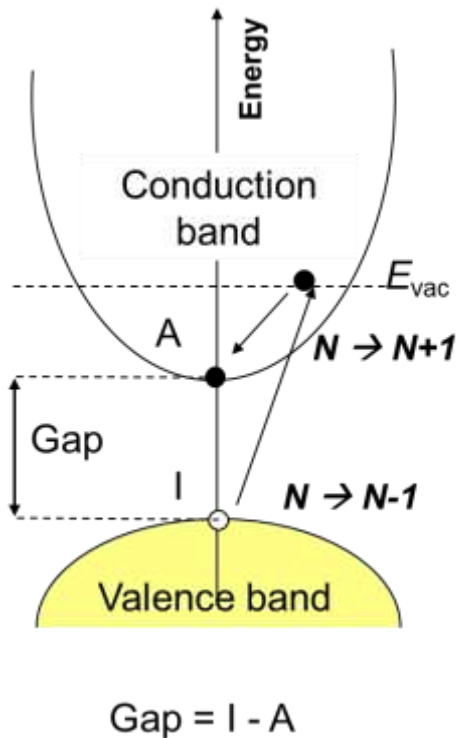
- DFT (no matter which XC functional is used) is a ground-state theory
- Kohn-Sham eigenvalues of the independent-particle equations are NOT the interacting-electrons values

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_s(\vec{r}) \right] \psi_j(\vec{r}) = \varepsilon_j \psi_j(\vec{r})$$

- They usually reproduce quite well the valence electronic bands
- They are badly, badly wrong in describing excited states, for example the conduction bands

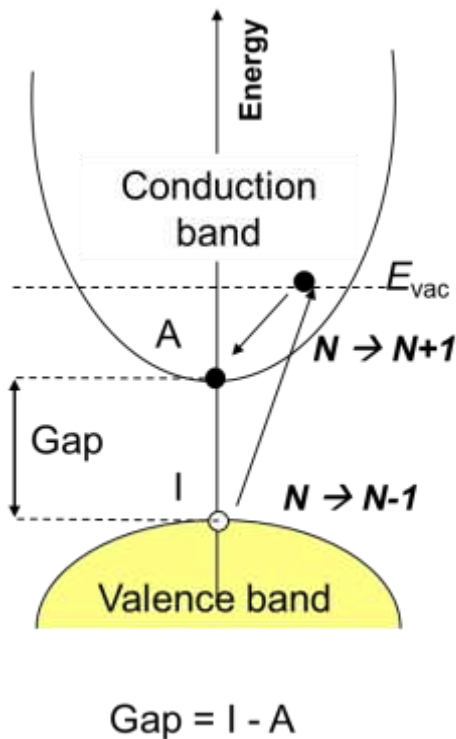
DFT and excitations

The band gap problem: most approximations to the exact functional systematically underestimate band gaps



DFT and excitations

The band gap problem: most approximations to the exact functional systematically underestimate band gaps



$$E_{gap} = I - A = (E_{vac} - \epsilon_N^{(N)}) - (E_{vac} - \epsilon_{N+1}^{(N+1)}) = \epsilon_{N+1}^{(N+1)} - \epsilon_N^{(N)} = \boxed{\epsilon_{N+1}^{(N+1)} - \epsilon_{N+1}^{(N)}} + \boxed{\epsilon_{N+1}^{(N)} - \epsilon_N^{(N)}}$$

This is the variation of $(N+1)^{th}$ eigenvalue when changing the number of electrons. Cannot be obtained straightforwardly within a theory that is devised for fixed N

This is the « DFT » gap: LUMO-HOMO at constant number N of electrons

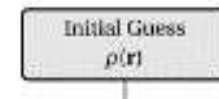
DFT: synthesis and take-home messages

- An effective theory for ground-state properties, through the minimization of the energy, which is a functional of the electron density
- A way to recast the interacting many-electron problem into a set of self-consistent one-electron equations
- In principle based only on the electron density; actually, single-particle orbitals are used in the determination of the electron density
- Exact in principle, but necessarily approximated (the exact $E_{XC}[n]$ is unknown)
- Unfit to study excited-state properties; usually a starting point for more sophisticated approaches

DFT: practical implementation

A. Initialization

- Set up the basic parameters (unit cell, atomic positions, k points, cutoff energy, atom types with the corresponding pseudo-potentials, XC approximation, etc.)
- Choose a starting electron density (ex: superposition of atomic-like densities)



B. Self-consistent cycle

Numerically solve the Kohn-Sham equations

- **Kohn-Sham equations**

$$\begin{aligned} h^{\text{KS}}[n] \psi_j(\vec{r}) &= \varepsilon_j \psi_j(\vec{r}) & h^{\text{KS}}[n] &= -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{ext}}(\vec{r}) + e^2 \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{\text{xc}}(\vec{r}; [n]) \\ n(\vec{r}) &= \sum_j f_j |\psi_j(\vec{r})|^2 \end{aligned}$$

- **Wavefunctions are expanded on a basis**

$$\psi_j(\vec{r}) = \sum_{\alpha} c_{j,\alpha} f_{\alpha}(\vec{r}) \qquad h^{\text{KS}}[n] \sum_{\alpha} c_{j,\alpha} f_{\alpha}(\vec{r}) = \varepsilon_j \sum_{\alpha} c_{j,\alpha} f_{\alpha}(\vec{r})$$

- **The problem becomes a linear algebra one**

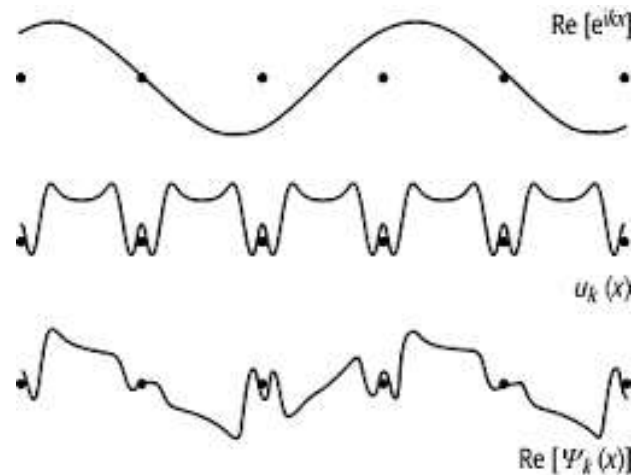
$$\begin{aligned} \sum_{\alpha} c_{j,\alpha} \int d^3r f_{\beta}^*(\vec{r}) h^{\text{KS}}[n] f_{\alpha}(\vec{r}) &= \sum_{\alpha} c_{j,\alpha} \varepsilon_j \int d^3r f_{\beta}^*(\vec{r}) f_{\alpha}(\vec{r}) \\ \sum_{\alpha} c_{j,\alpha} [h_{\alpha,\beta}^{\text{KS}} - \varepsilon_j S_{\alpha,\beta}] &= 0 \qquad \text{Det} [\mathcal{H}^{\text{KS}} - \varepsilon_j \mathcal{S}] = 0 \end{aligned}$$

Periodic crystals/cells: plane-wave expansion

- Wave-functions must have the same periodicity of the crystal (Bloch's theorem)

$$\psi_{m,\vec{k}}(\vec{r} + \vec{r}_l) = e^{i\vec{k} \cdot \vec{r}_l} \psi_{m,\vec{k}}(\vec{r})$$

$$\psi_{m,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N\Omega_0}} e^{i\vec{k} \cdot \vec{r}} u_{m,\vec{k}}(\vec{r})$$



Periodic crystals/cells: plane-wave expansion

- Wave-functions must have the same periodicity of the crystal (Bloch's theorem)

$$\psi_{m,\vec{k}}(\vec{r} + \vec{r}_l) = e^{i\vec{k}\cdot\vec{r}_l} \psi_{m,\vec{k}}(\vec{r}) \qquad \psi_{m,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N\Omega_0}} e^{i\vec{k}\cdot\vec{r}} u_{m,\vec{k}}(\vec{r})$$

- They can be expanded over the reciprocal lattice

$$u_{m,\vec{k}}(\vec{r}) = \sum_{\{\vec{G}\}} e^{i\vec{G}\cdot\vec{r}} \tilde{u}_m(\vec{k} + \vec{G})$$

- Plane-wave form an infinite set: a cutoff must be chosen

$$u_{m,\vec{k}}(\vec{r}) = \sum_{\{\vec{G}\}: \frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m} \leq E_{\text{cut}}} e^{i\vec{G}\cdot\vec{r}} \tilde{u}_m(\vec{k} + \vec{G})$$

Numerically solve the Kohn-Sham equations

- KS wave-functions are expressed in terms of plane-waves

$$\psi_{m,\vec{k}}(\vec{r}) = \sum_{\{\vec{G}\}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \tilde{u}_m(\vec{k} + \vec{G})$$

- The electron density reads

$$n(\vec{r}) = 2 \sum_m \sum_{\vec{k}} w_{\vec{k}} f_{m,\vec{k}} |\psi_{m,\vec{k}}(\vec{r})|^2$$

- Integrals in the k -space are replaced by a sum of finite special symmetry points (see later)

$$\bar{f} = \frac{\Omega}{(2\pi)^3} \int_{\text{BZ}} d^3k f(\vec{k}) \simeq \sum_{i=1}^{N_{\vec{k}}} w_{\vec{k}_i} f(\vec{k}_i)$$

Numerical solutions: making us of direct and reciprocal spaces and Fast Fourier Transforms

$$n(\mathbf{r}) = 2 \sum_{\mathbf{m}, \mathbf{k}} f_{\mathbf{m}} w_{\mathbf{k}} |\Psi_{\mathbf{m}\mathbf{k}}(\mathbf{r})|^2 \quad \Psi_{\mathbf{m}\mathbf{k}}(\mathbf{r}) \sim \sum_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} u_{\mathbf{m}, \mathbf{k}+\mathbf{G}}$$

Naively: $n(\mathbf{r}) \sim 2 \sum_{\mathbf{m}, \mathbf{k}} f_{\mathbf{m}} w_{\mathbf{k}} \sum_{\mathbf{G}, \mathbf{G}'} e^{i(\mathbf{G}-\mathbf{G}')\mathbf{r}} u_{\mathbf{m}, \mathbf{k}+\mathbf{G}} u_{\mathbf{m}, \mathbf{k}-\mathbf{G}}^*$

convolution: double sum on \mathbf{G} space $\rightarrow \mathcal{O}(N M_{\text{PW}}^2) !!$

Instead:

$$u_{\mathbf{m}, \mathbf{k}+\mathbf{G}}$$

$$\downarrow \text{FFT}^{-1} \mathcal{O}(N M_{\text{PW}} \log M_{\text{PW}})$$

$$u_{\mathbf{m}\mathbf{k}}(\mathbf{r}) \rightarrow |u_{\mathbf{m}\mathbf{k}}(\mathbf{r})|^2$$

.... sum up on \mathbf{k} -points and states

$$\dots \rightarrow n(\mathbf{r})$$

$$\downarrow \text{FFT}$$

$$n(\mathbf{G})$$

Numerically calculate the energy functional DFT terms

- The DFT functional

$$E[n] = T_s[n] + \int d^3r V_{\text{ext}}(\vec{r}) n(\vec{r}) + E_H[n] + E_{\text{xc}}[n]$$

- The (non-interacting) kinetic energy

$$T_s[n] = 2 \sum_m \sum_{\vec{k}} w_{\vec{k}} f_{m,\vec{k}} \int d^3r \psi_{m,\vec{k}}^*(\vec{r}) \left[-\frac{\hbar^2 \nabla^2}{2m} \psi_{m,\vec{k}}(\vec{r}) \right]$$

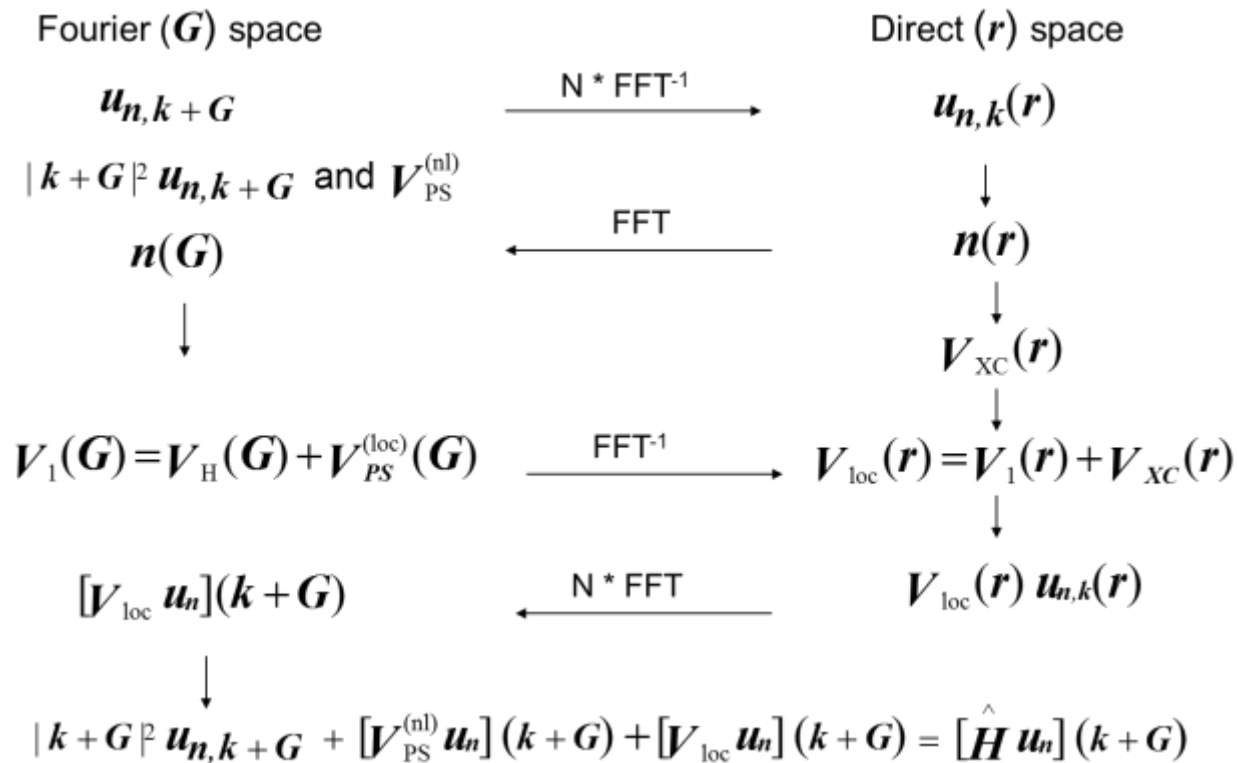
- The electrostatic (Hartree+pseudopotential) terms

$$E_H[n] = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} = 2\pi\Omega_0 \sum_{G \neq 0} \frac{|\tilde{n}(\vec{G})|^2}{G^2}$$

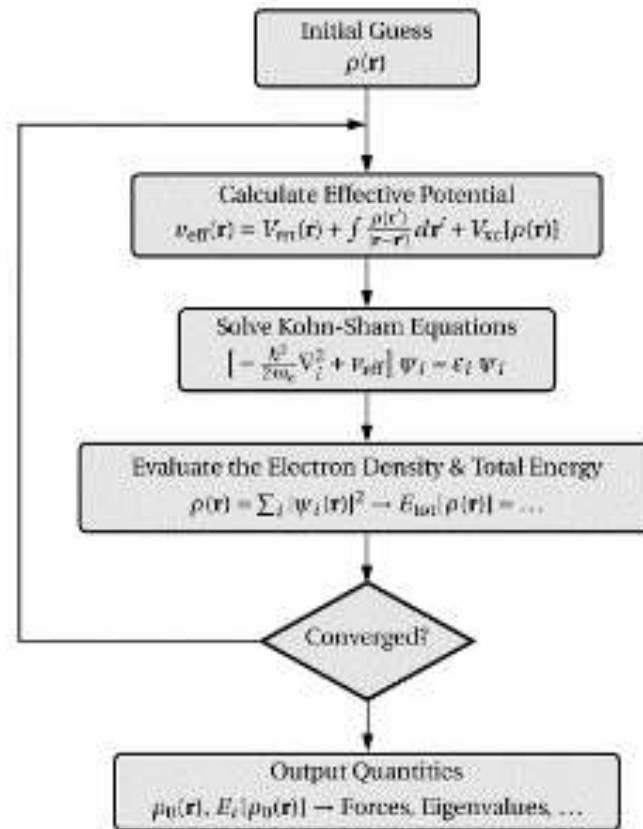
- The XC term

$$E_{\text{xc}}[n] \simeq E_{\text{xc}}^{\text{LDA}}[n] = \int d^3r n(\vec{r}) e_{\text{xc}}^{\text{HEG}}(n(\vec{r}))$$

Numerical solutions: making us of direct and reciprocal spaces and Fast Fourier Transforms



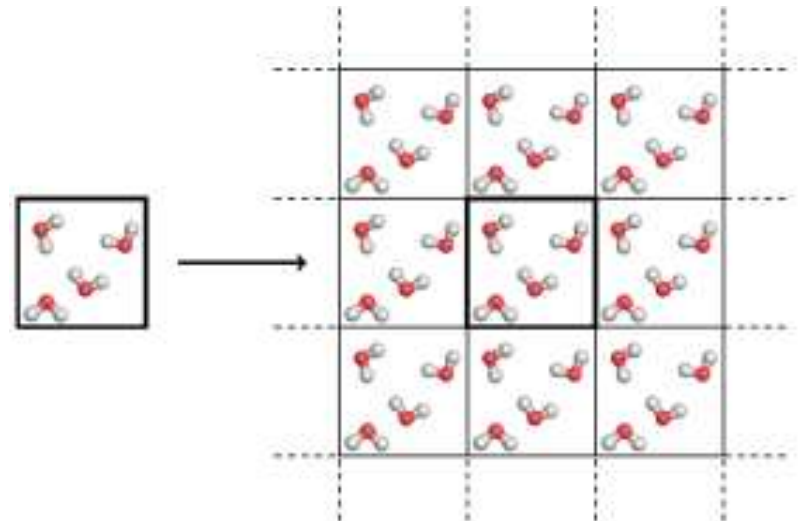
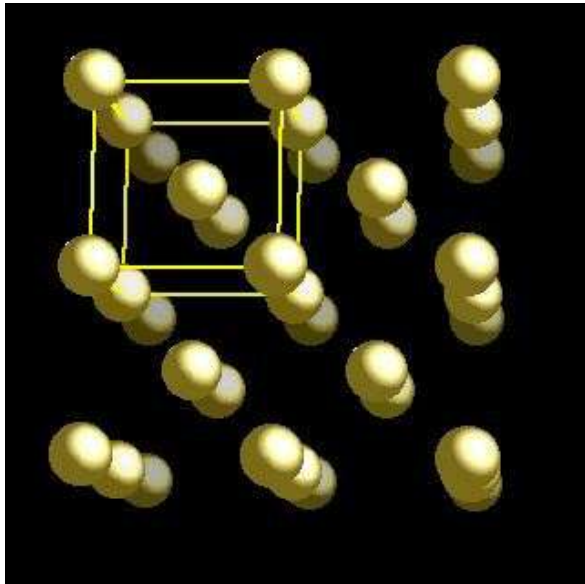
Numerical solutions: DFT flowchart (again)



$$V_{\text{new}} = \beta V_{\text{new}} + (1 - \beta) V_{\text{old}}$$
$$\beta < 1; \beta \approx 0.7$$

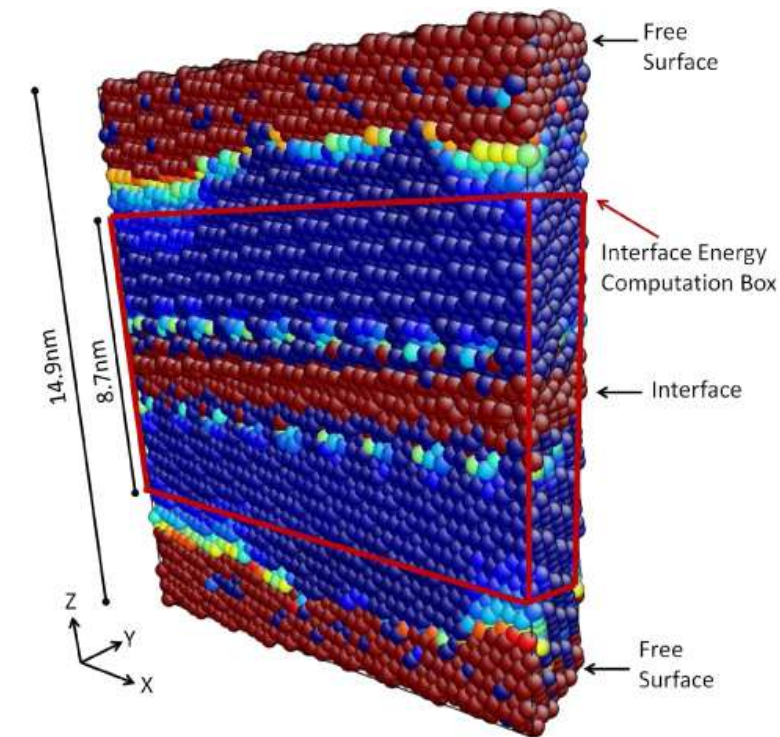
A word on periodic boundary conditions

- DFT codes make large use of PBC, but their use in non 3D-bulk/non-crystalline systems is tricky



A word on periodic boundary conditions

- DFT codes make large use of PBC, but their use in non bulk/non-crystalline systems is tricky



A word on periodic boundary conditions

- DFT codes make large use of PBC, but their use in non bulk/non-crystalline systems is tricky

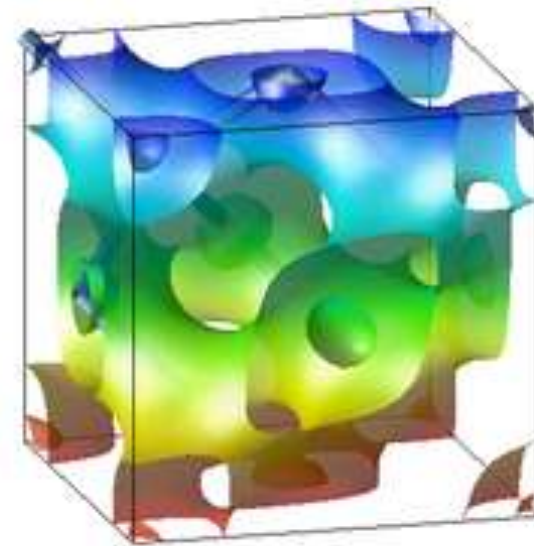
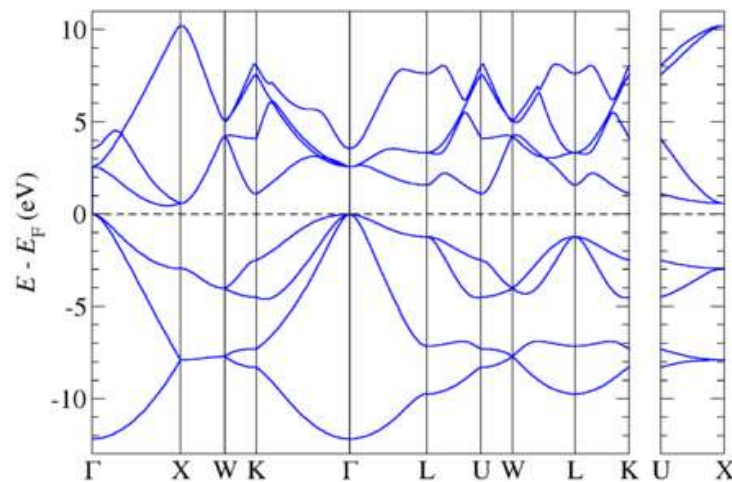


Plane-waves: take-home message

- Take advantage of crystal symmetry and periodicity
- Independent of atomic positions
- Same precision everywhere/useless accuracy in void space
- Formulae are easy to implement
- Choice between R and G spaces/Take advantage of fast Fourier transforms
- Many PW's ($\sim 10^2 - 10^3$ /atom): cutoff choice needed, easy to check/improve convergence
- Generally used in conjunction with pseudopotentials (no all-electron calculations just using PW's)

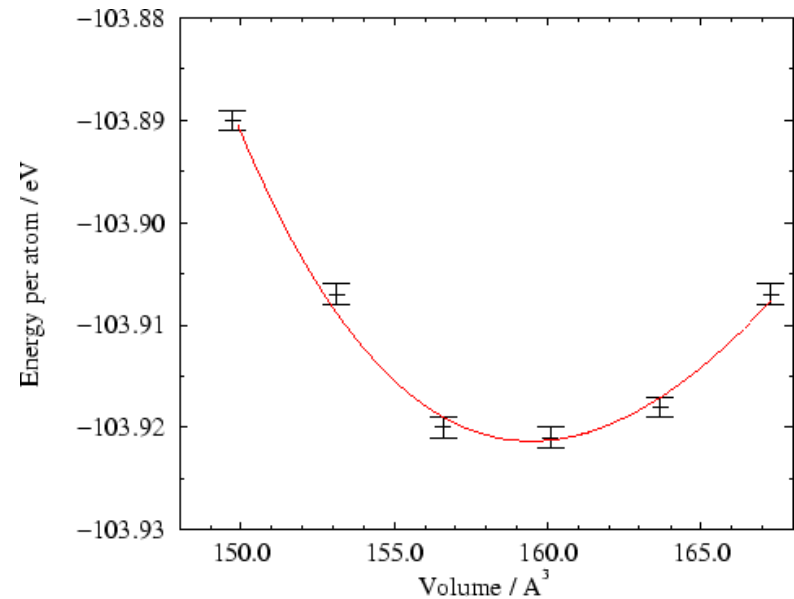
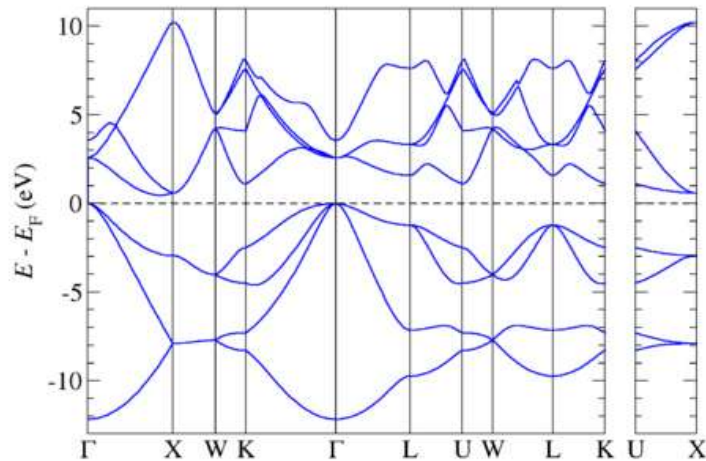
“Total energy” basic properties

- Electronic band structure and charge density map



“Total energy” basic properties

- Energy-volume equations of state

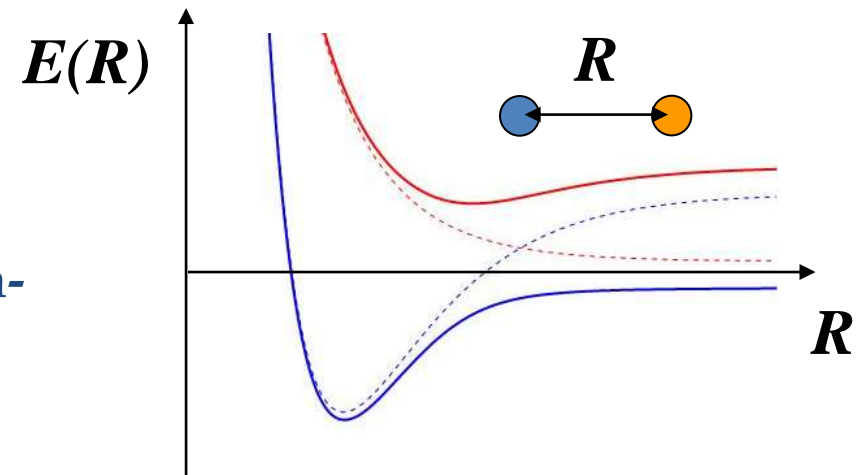


Derivatives of DFT energy: forces and pressure (stress)

- Forces

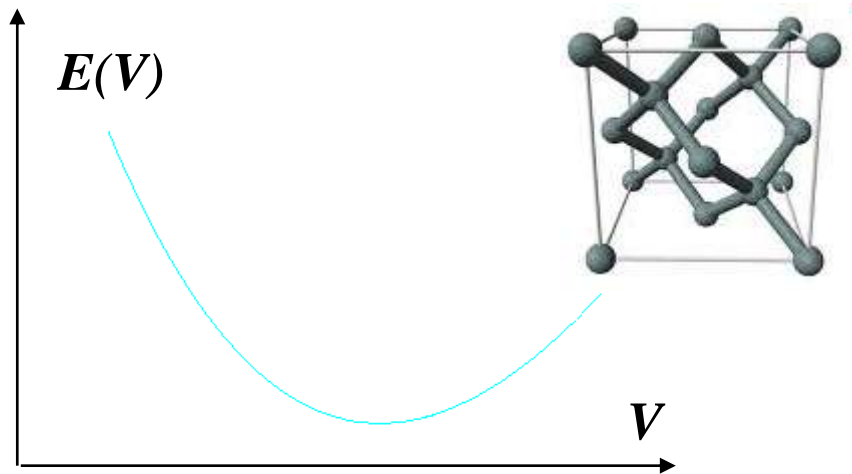
$$F = -\frac{\partial E}{\partial R}$$

Forces on the nuclei, within the Born-Oppenheimer approx. → find the optimal bond length R_0



Derivatives of DFT energy: forces and pressure (stress)

- Pressure



$$P = -\frac{\partial E}{\partial V}$$

Pressure \rightarrow find the optimal volume V_0 of the unit cell

Derivatives of DFT energy: forces and pressure (stress)

- Hellmann-Feynman theorem

$$\frac{dE_\lambda}{d\lambda} = \frac{d}{d\lambda} \langle \psi_\lambda | \hat{H}_\lambda | \psi_\lambda \rangle = \left\langle \psi_\lambda \left| \frac{d\hat{H}_\lambda}{d\lambda} \right| \psi_\lambda \right\rangle$$

$$\frac{dE}{d\vec{R}_J} = \frac{\partial E}{\partial \vec{R}_J} + \int d^3r \frac{\delta E}{\delta n(\vec{r})} \frac{\partial n(\vec{r})}{\partial \vec{R}_J} = \frac{\partial E}{\partial \vec{R}_J}$$

Roots for catalysis and synthesis

Materials for Li batteries

HPC for materials science



High T_c superconductors

Perovskites

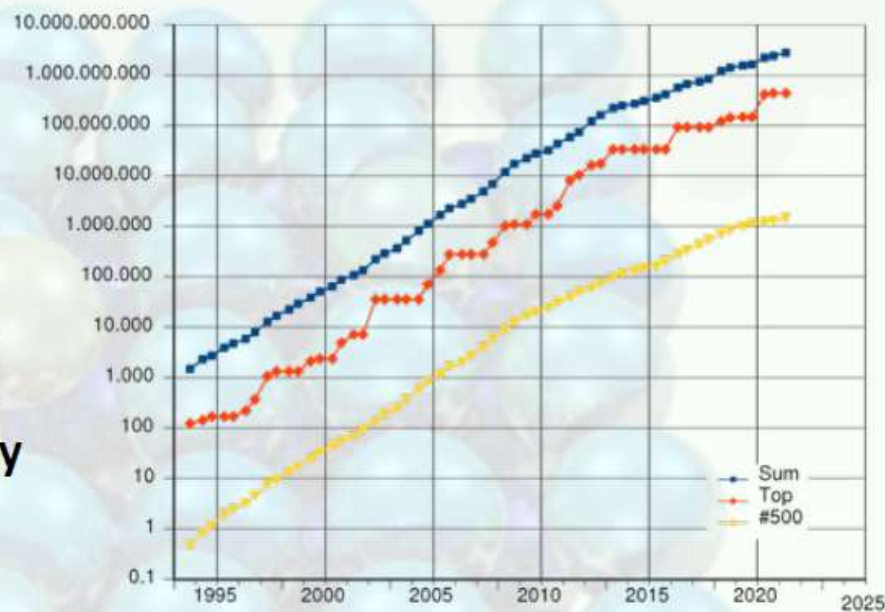


HPC for materials science

THE RISE OF COMPUTATIONAL SCIENCE

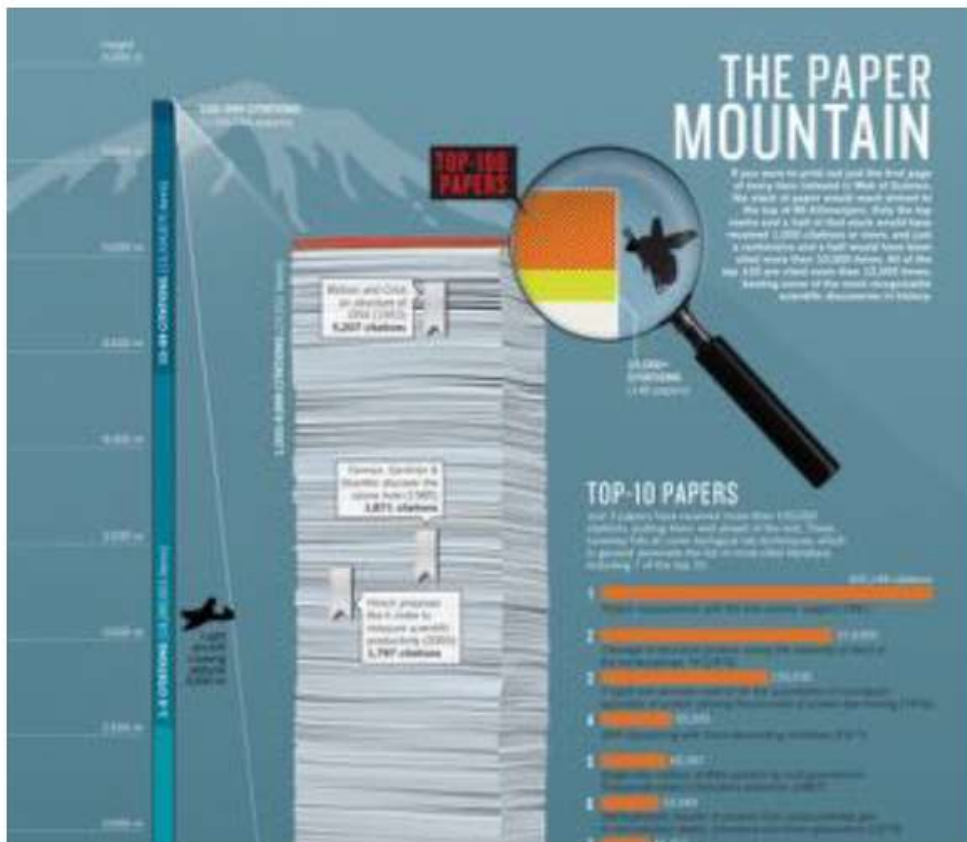
A calculation that took
one year in 1993 takes
30 seconds in 2022
(1-million-fold increase).

And this is just with bits: neurons
are in, and qubits on the horizon.
21st-century science and discovery
will be driven by computational
science.



HPC for materials science

IMPACT OF COMPUTATIONAL QUANTUM MECHANICS



THE TOP 100 PAPERS:
12 papers on density-functional theory in the top-100 most cited papers in the entire scientific-medical-engineering literature, ever.

NATURE, OCT 2014



Courtesy of Nicola Marzari, EPFL

HPC for materials science

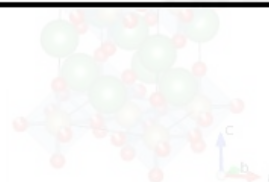
MATERIALS ARE KEY TO SOCIETAL WELL BEING

We need novel materials for:

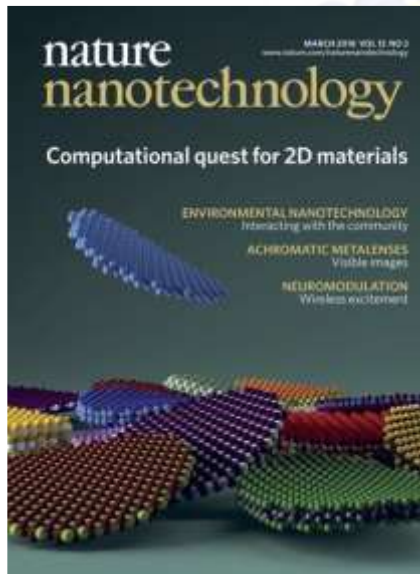
- **Energy harvesting, conversion, storage, efficiency**
- **Environmental protection and reparation**
- **High-tech and high-value industries**
- **Information and communication technologies**
- **Health care and biomedical engineering**
- **Pharmaceuticals** (crystallization, stability, polytypes)
- **Monitoring, provenance, and safety of foods**
- **Fundamental science** (graphene and 2D materials, topological insulators, entangled spins for quantum computing, high- T_c)
- **Experimental science** (detectors, sensors, magnets)



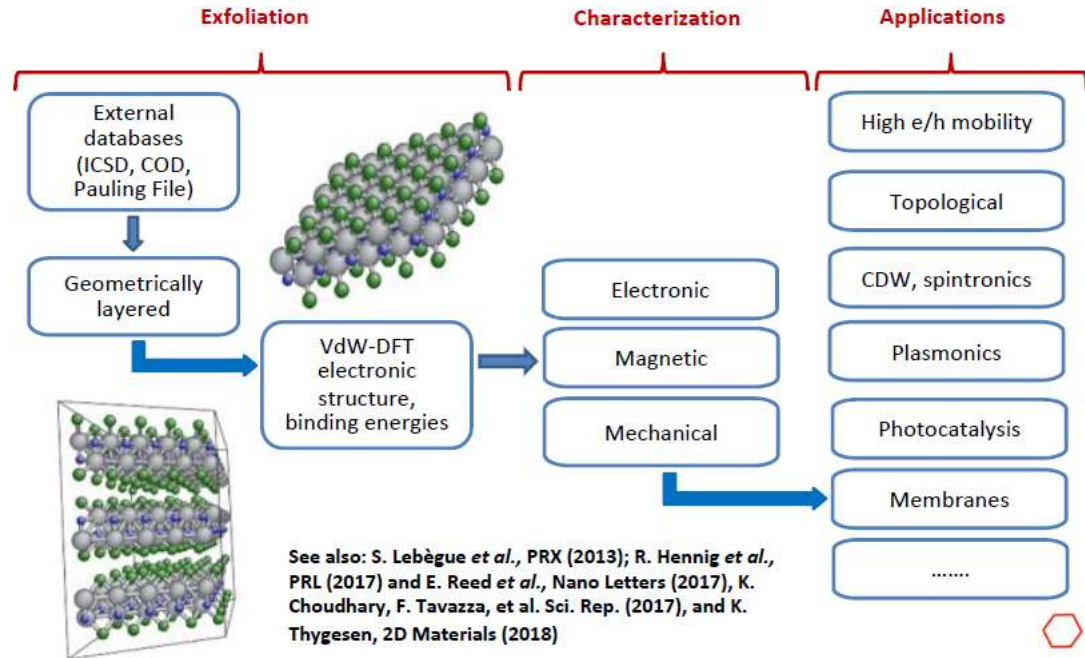
Courtesy of Nicola Marzari, EPFL



HPC for materials science

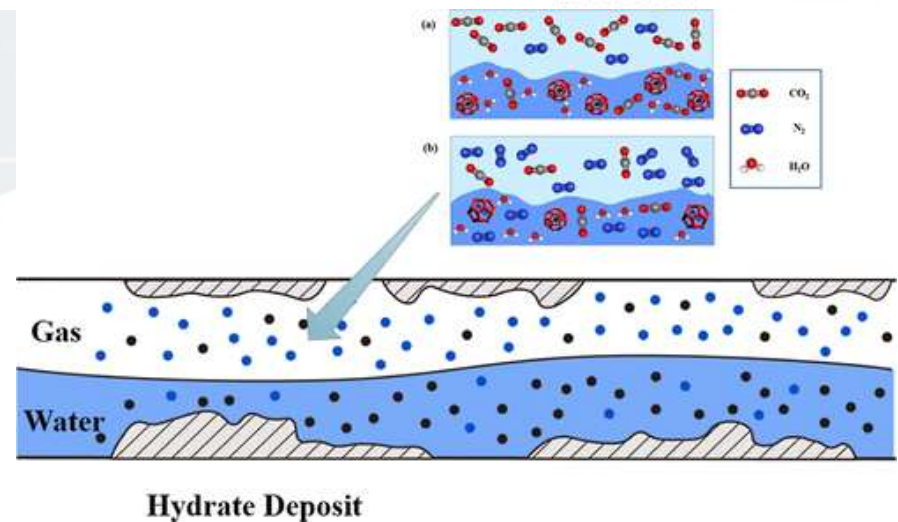
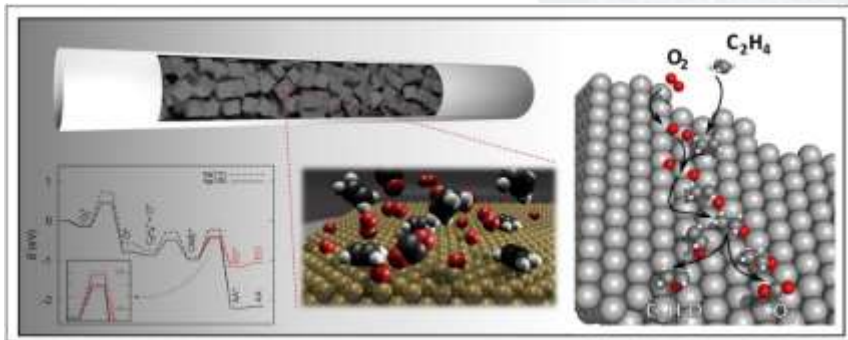
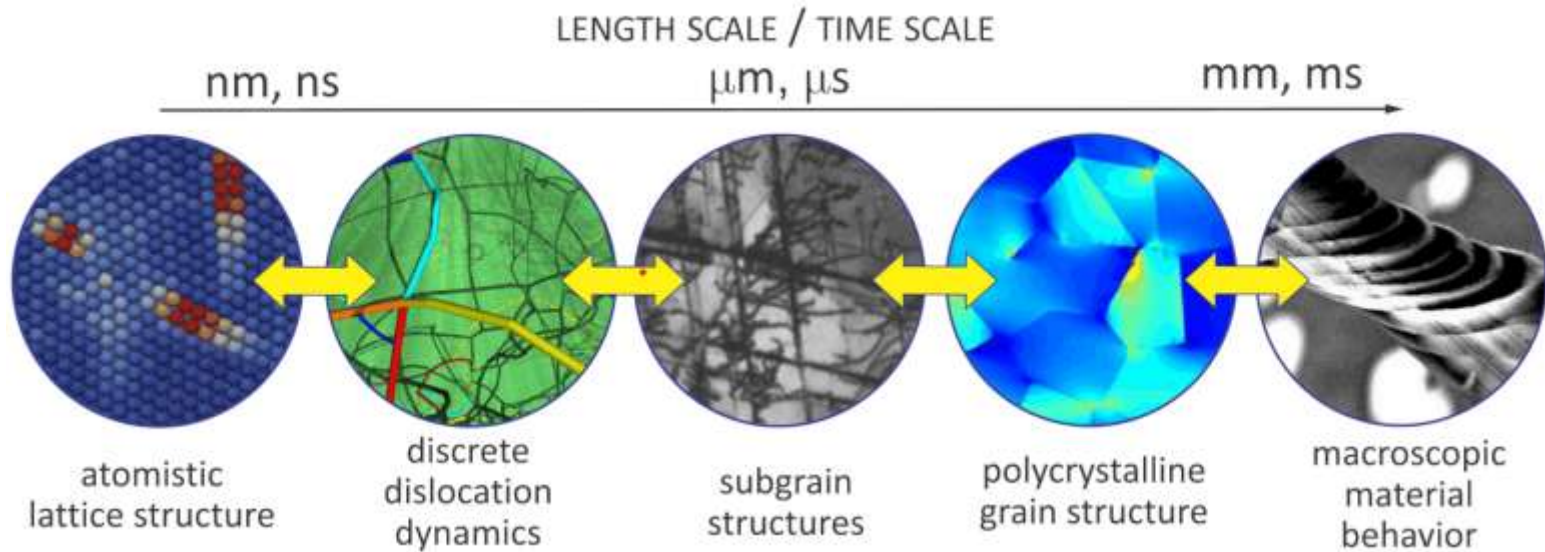


HIGH-THROUGHPUT COMPUTATIONAL EXFOLIATION

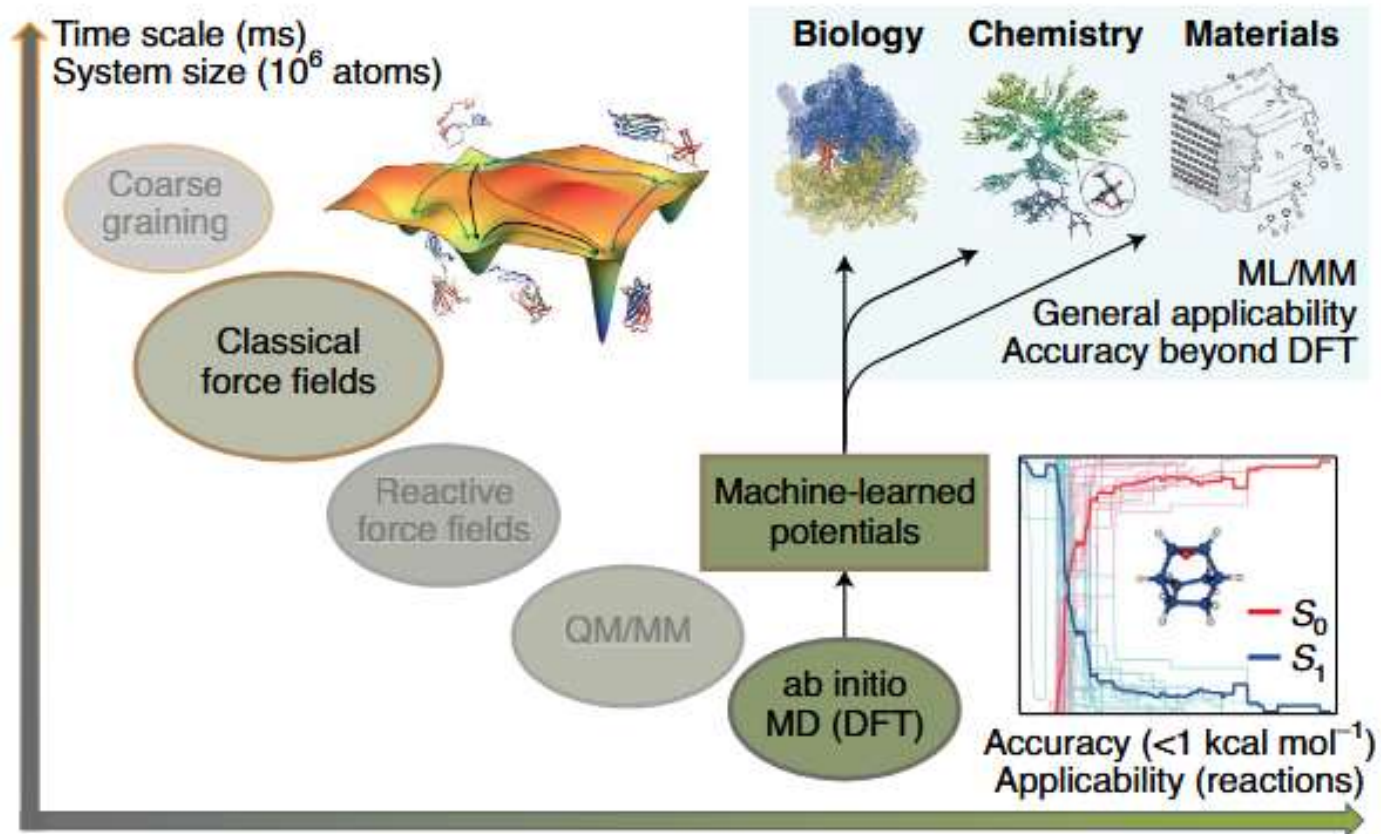


Courtesy of Nicola Marzari, EPFL

«Real» materials science

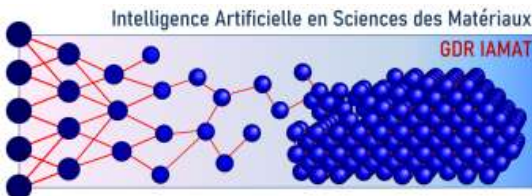


Length/time scales, methods



(Elements of) Molecular Dynamics and Density Functional Theory

A. Serva (MD) – A. Marco Saitta (DFT)



PROGRAMME
DE RECHERCHE
MATÉRIAUX
ÉMERGENTS

École internationale DIADEM

25-29 août 2025 Paris (France)



IA et physique des matériaux