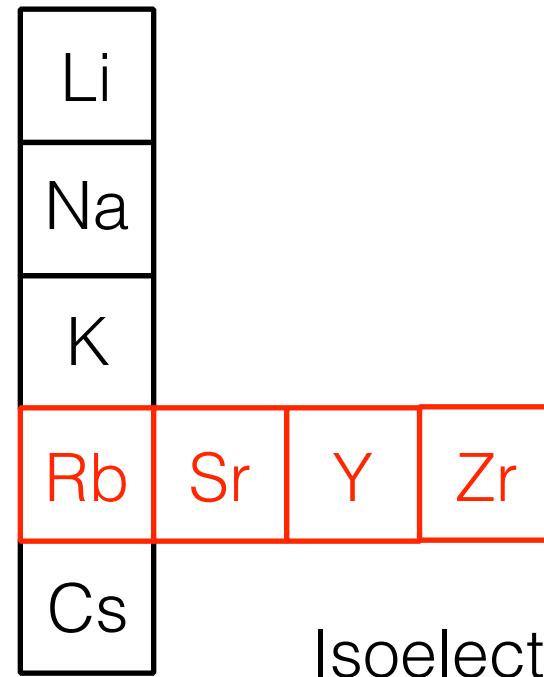
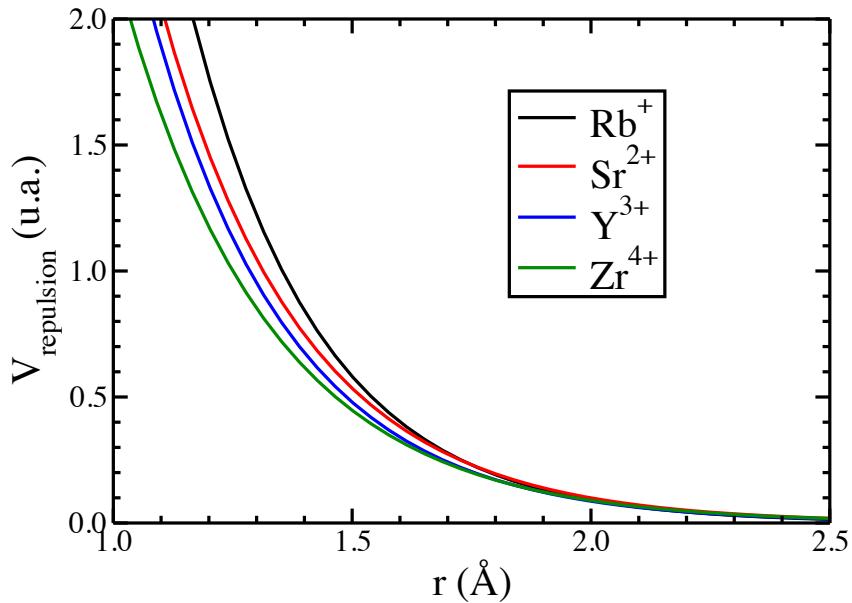


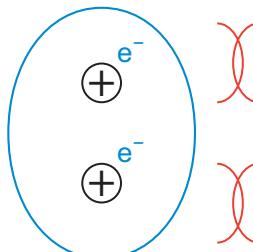
# Overlap repulsion interaction



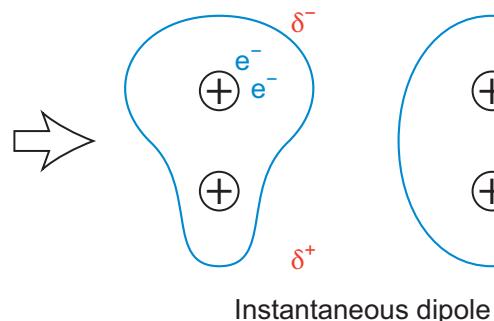
Repulsion depends on the atomic radii

# Dispersion interaction

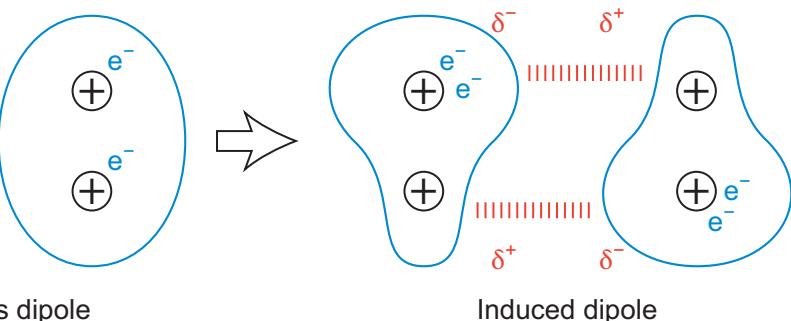
a Electrostatic repulsion



b



c Attractive London dispersion interaction



Small contribution to  
the overall interaction

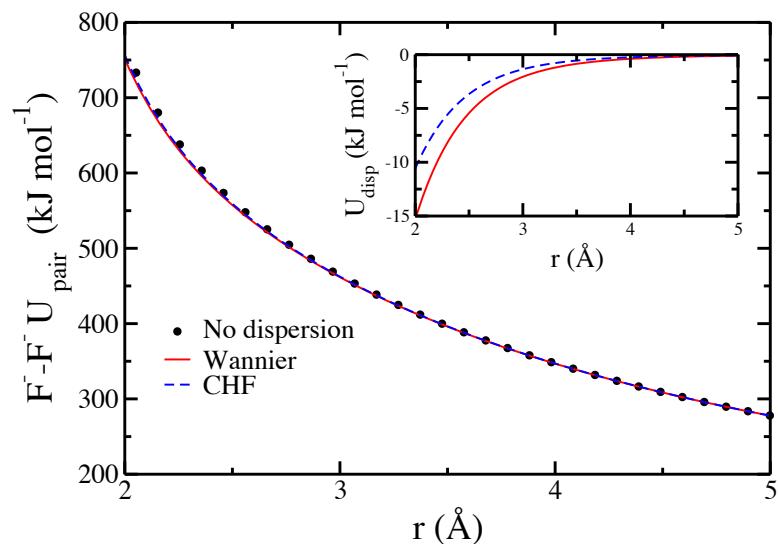
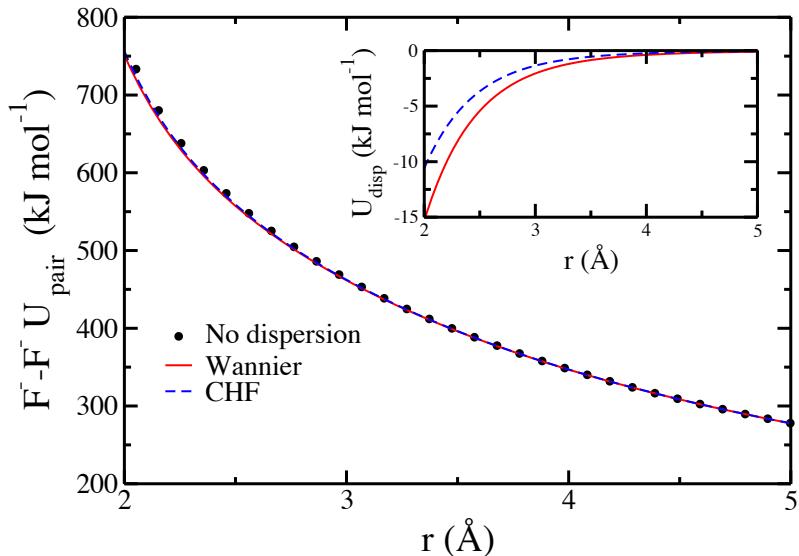


Figure from Shimizu, Nat. Chem., 2013

# Dispersion interaction

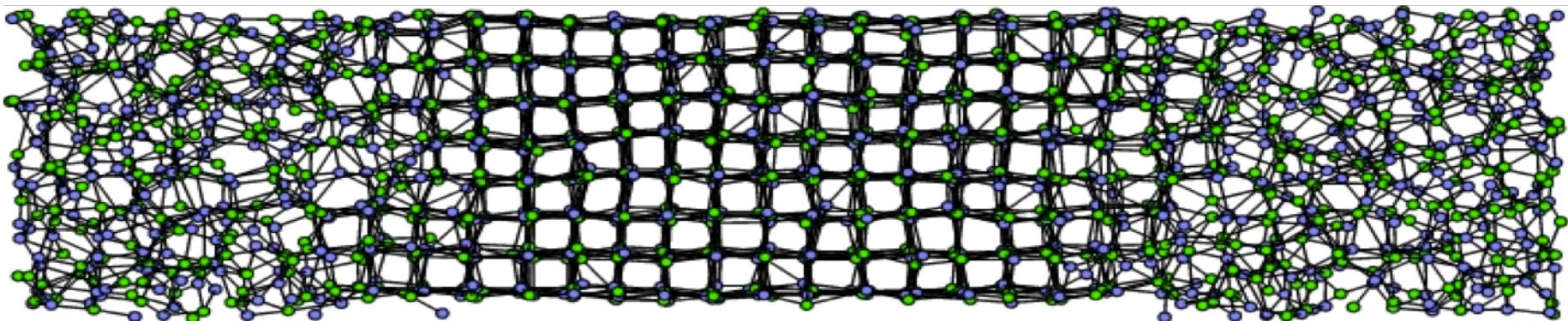


Density of LiF

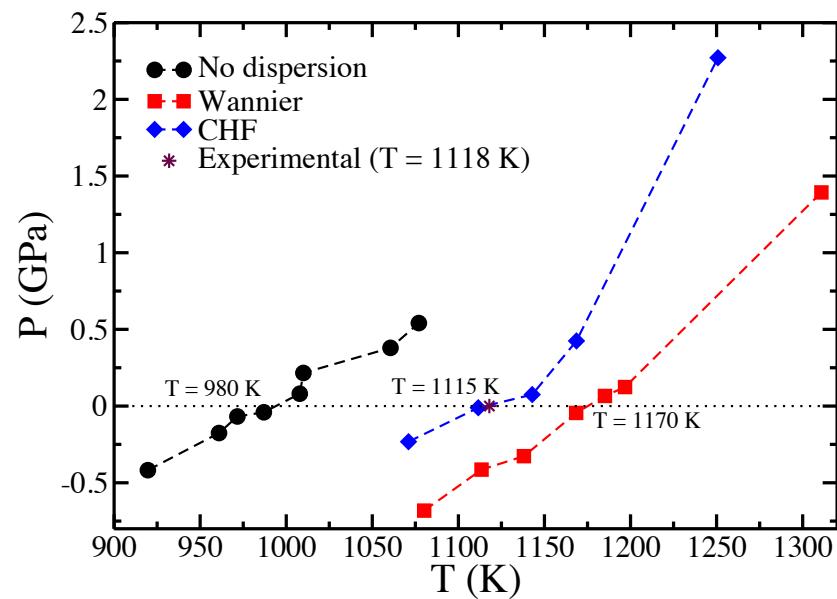
Setup	$\rho^{\text{sol}}$ (g cm <sup>-3</sup> )	$\rho^{\text{liq}}$ (g cm <sup>-3</sup> )
Experiment	2.64	1.77
No dispersion	2.32	1.50
CHF	2.38	1.62
Wannier	2.42	1.69

No changes on the structure/dynamics at fixed volume!

# Dispersion interaction



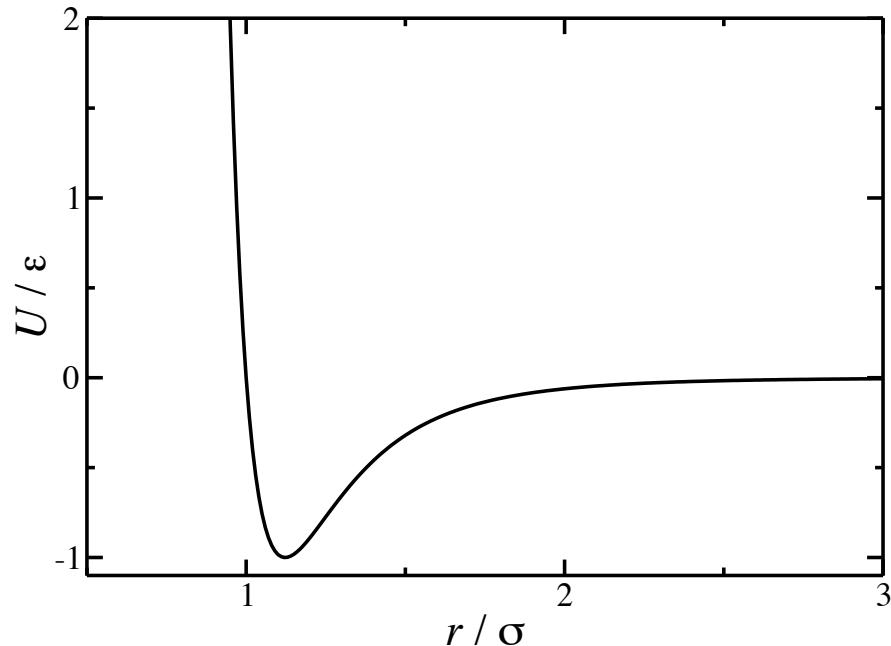
Melting point of LiF:



# 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



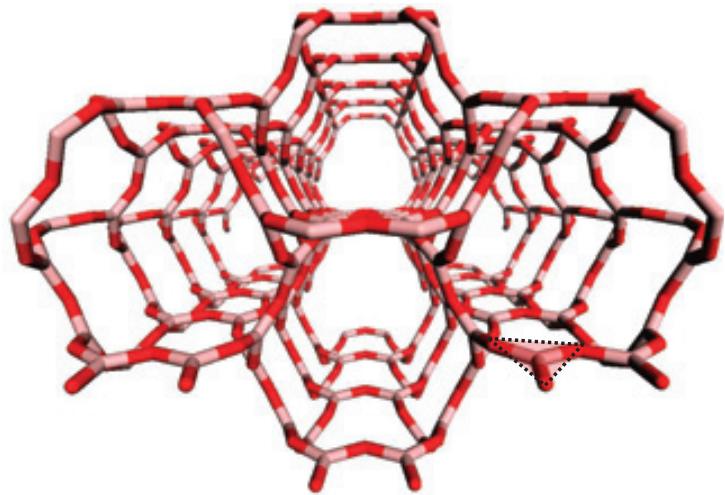
Widely used in the simulation of biomolecules:  
AMBER, CHARMM

# 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

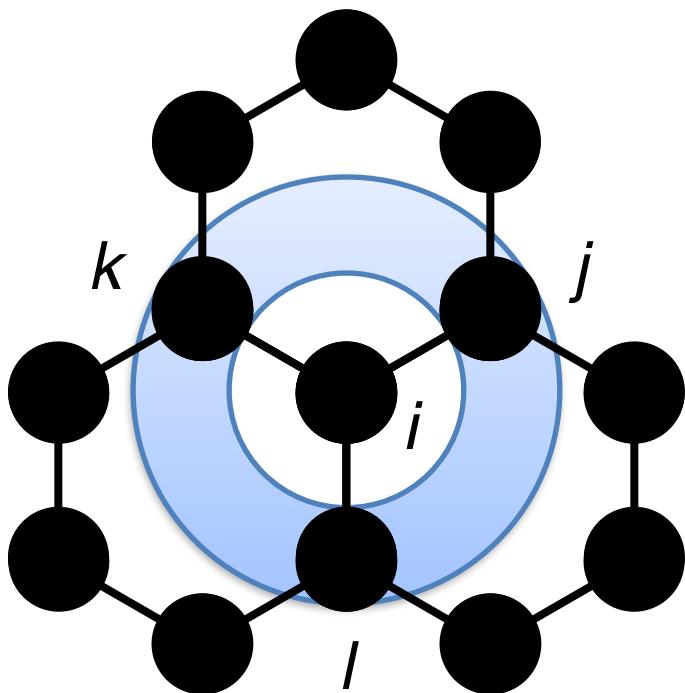


Widely used in the simulation of oxides  
and ionic materials (Tosi-Fumi)

# 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:

$$r_{ij} \quad r_{ik} \quad r_{il}$$

- 2 angles:

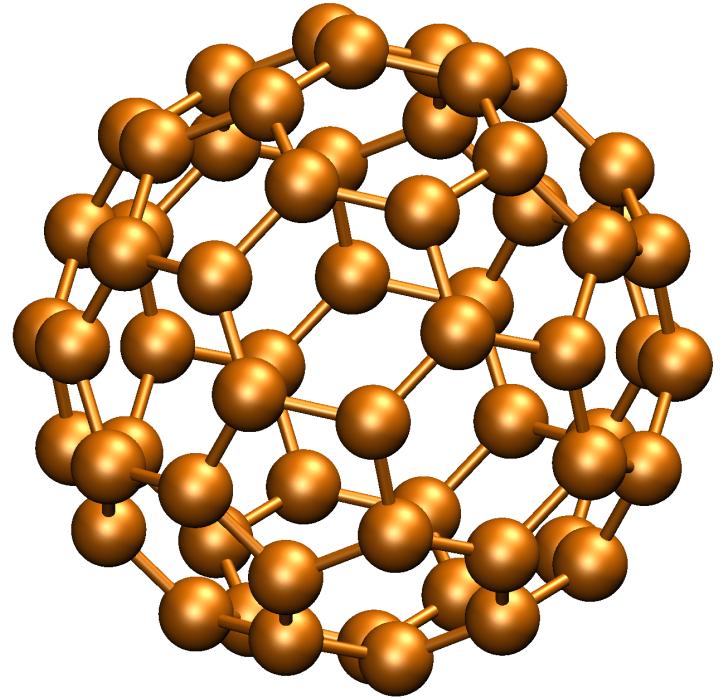
$$\theta_{ijk} \quad \theta_{ijl}$$

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

Family of bond order potentials

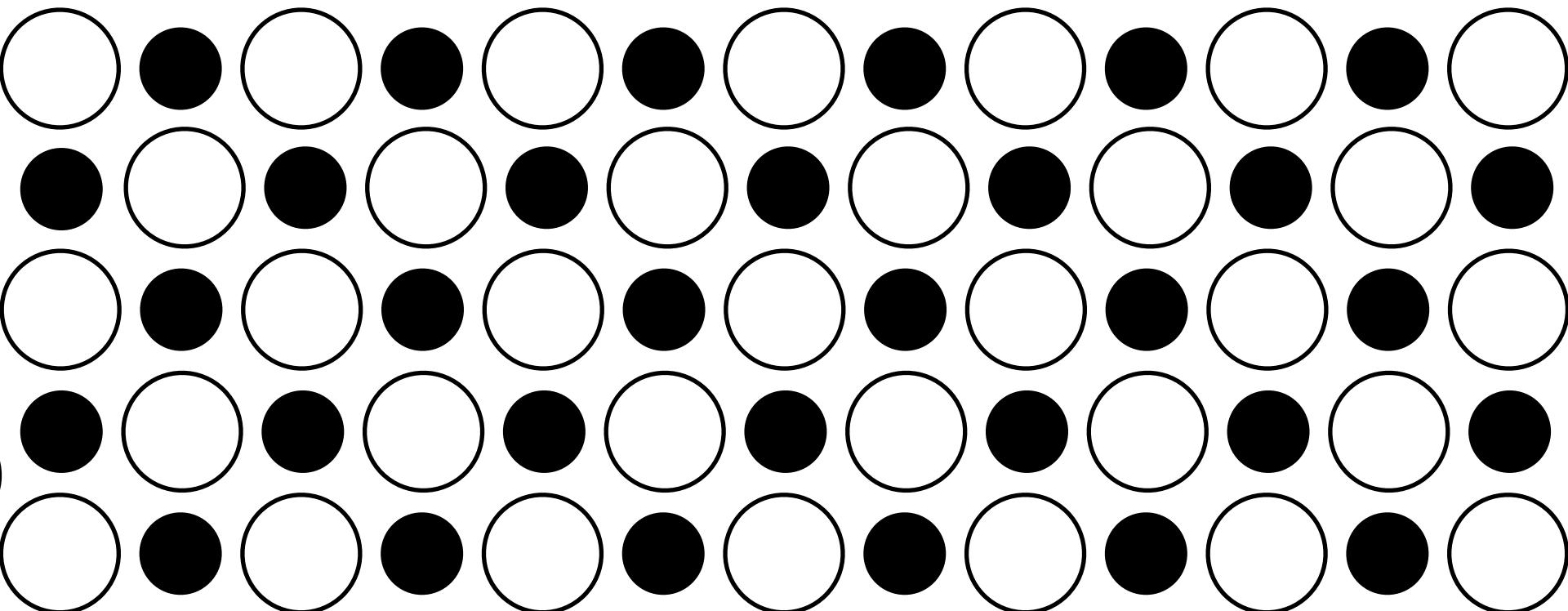
# Bond-order potentials

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

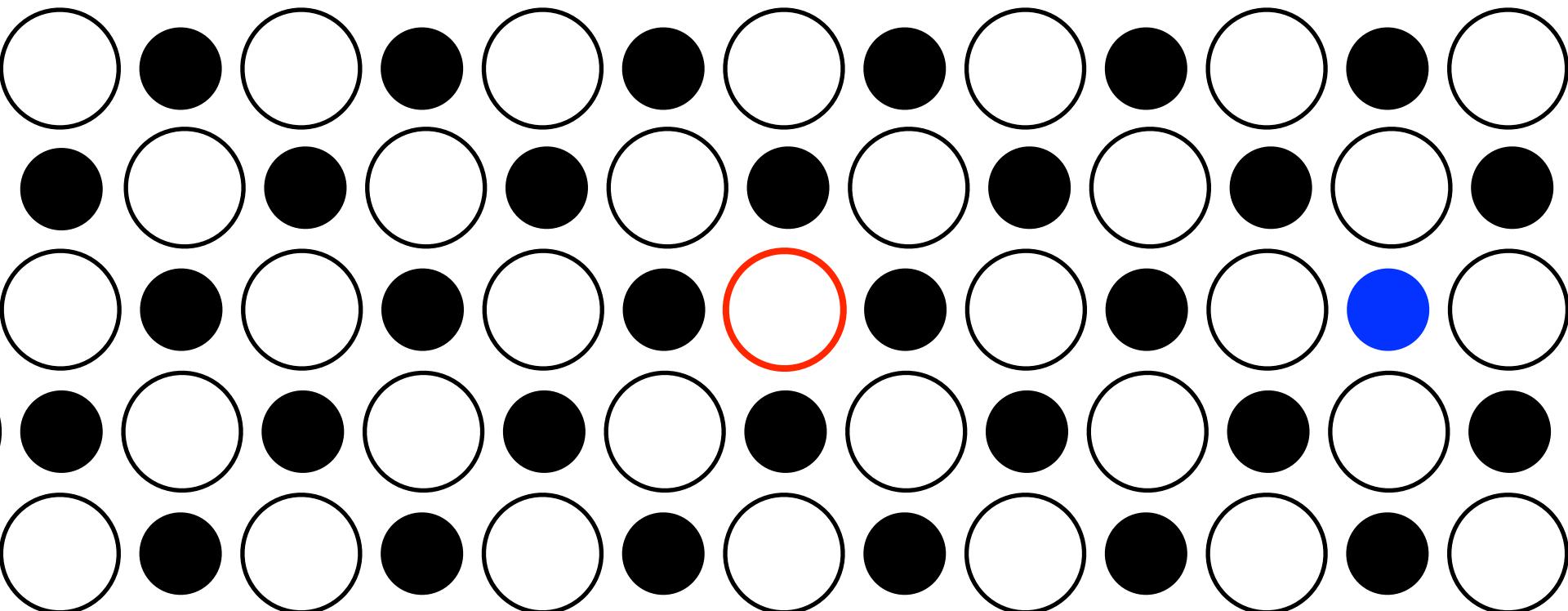


Widely used for carbon, silicon, ...  
ReaxFF for chemical reactions

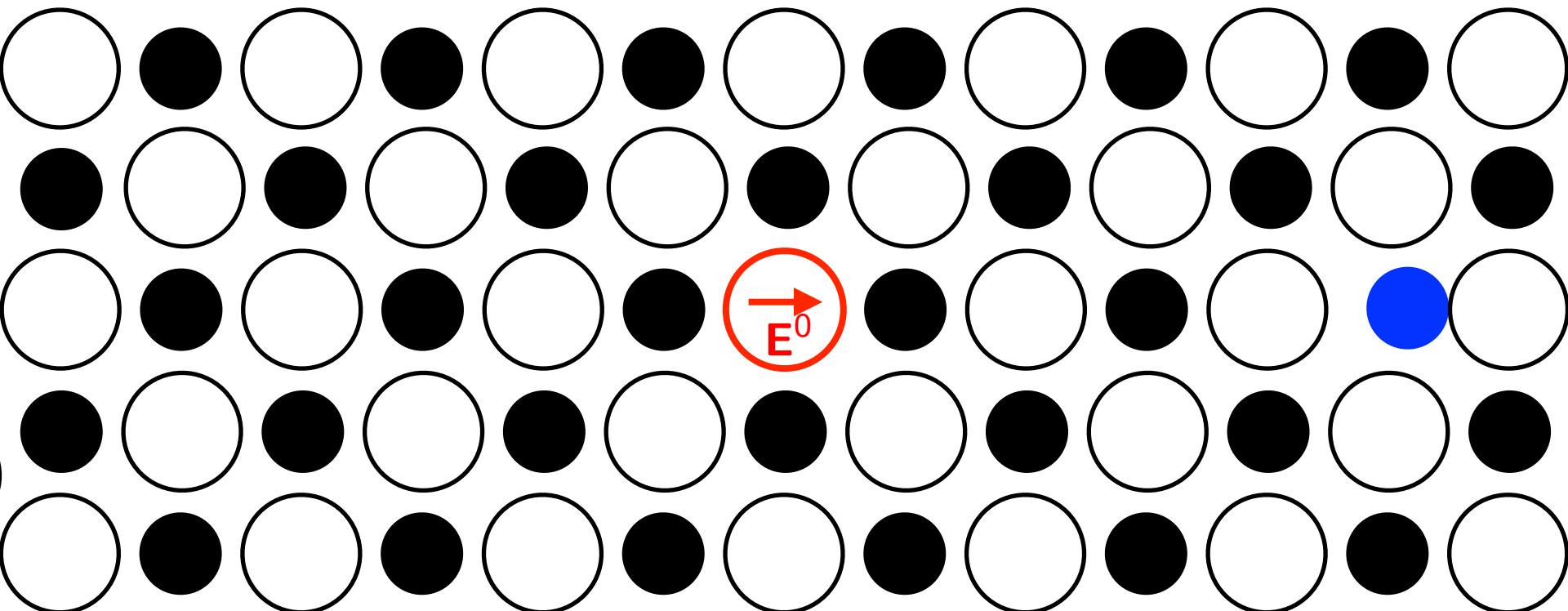
# Induced dipoles



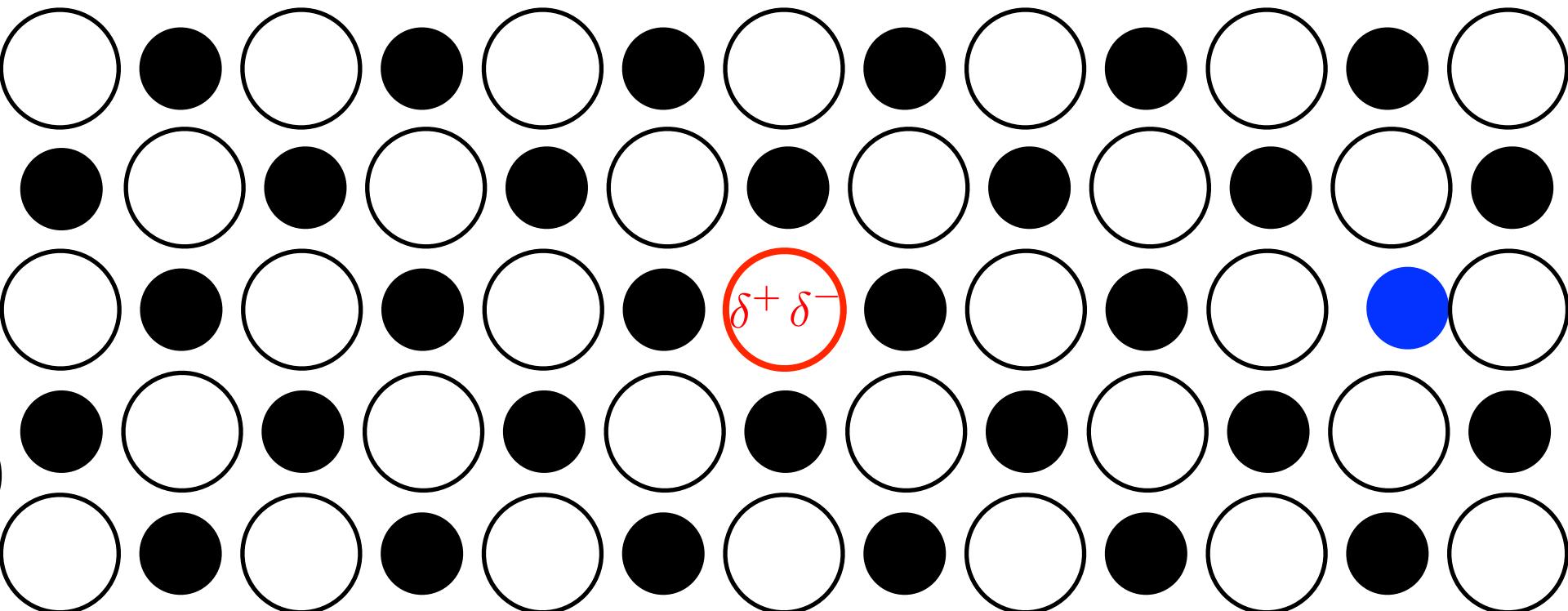
# Induced dipoles



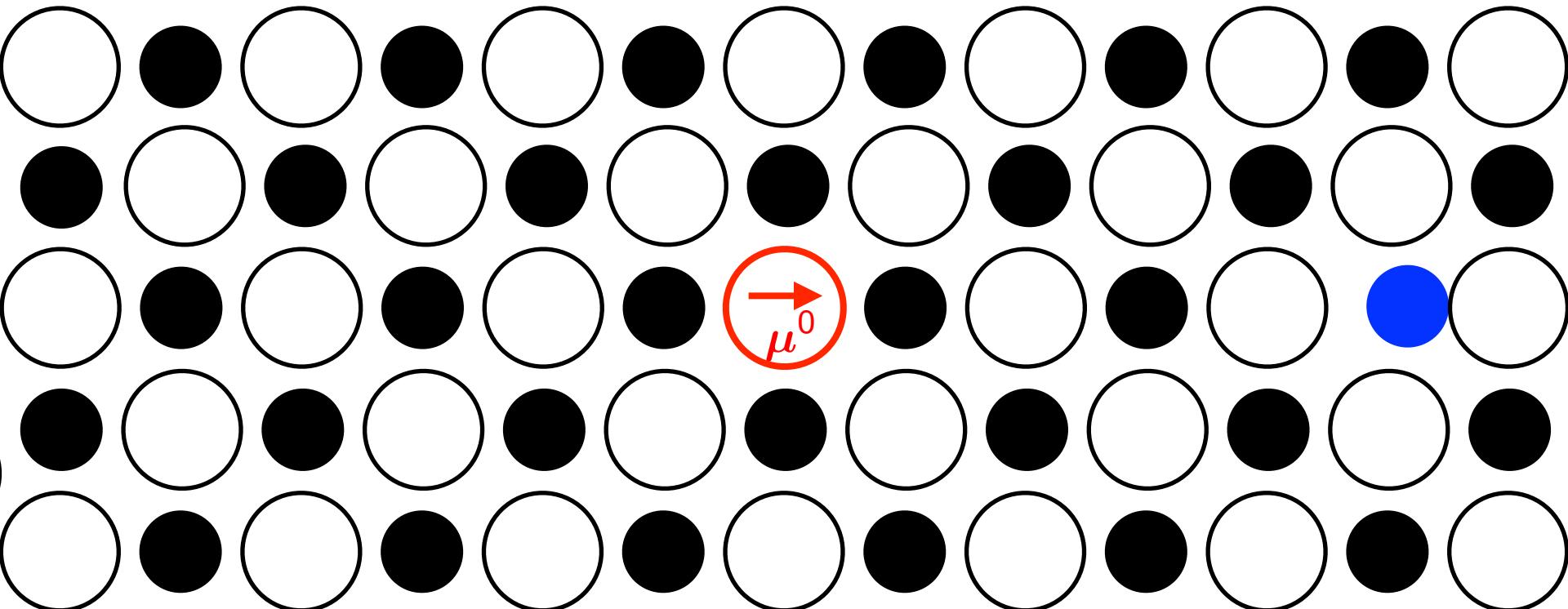
# Induced dipoles



# Induced dipoles

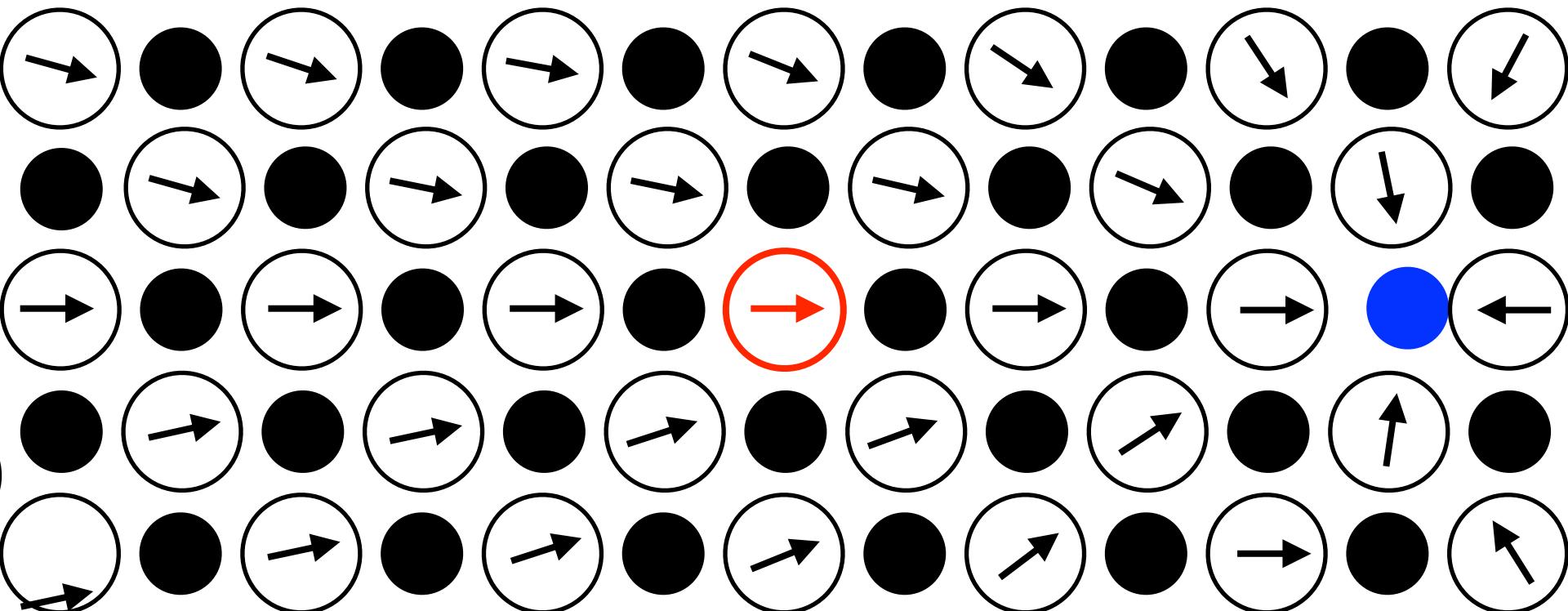


# Induced dipoles

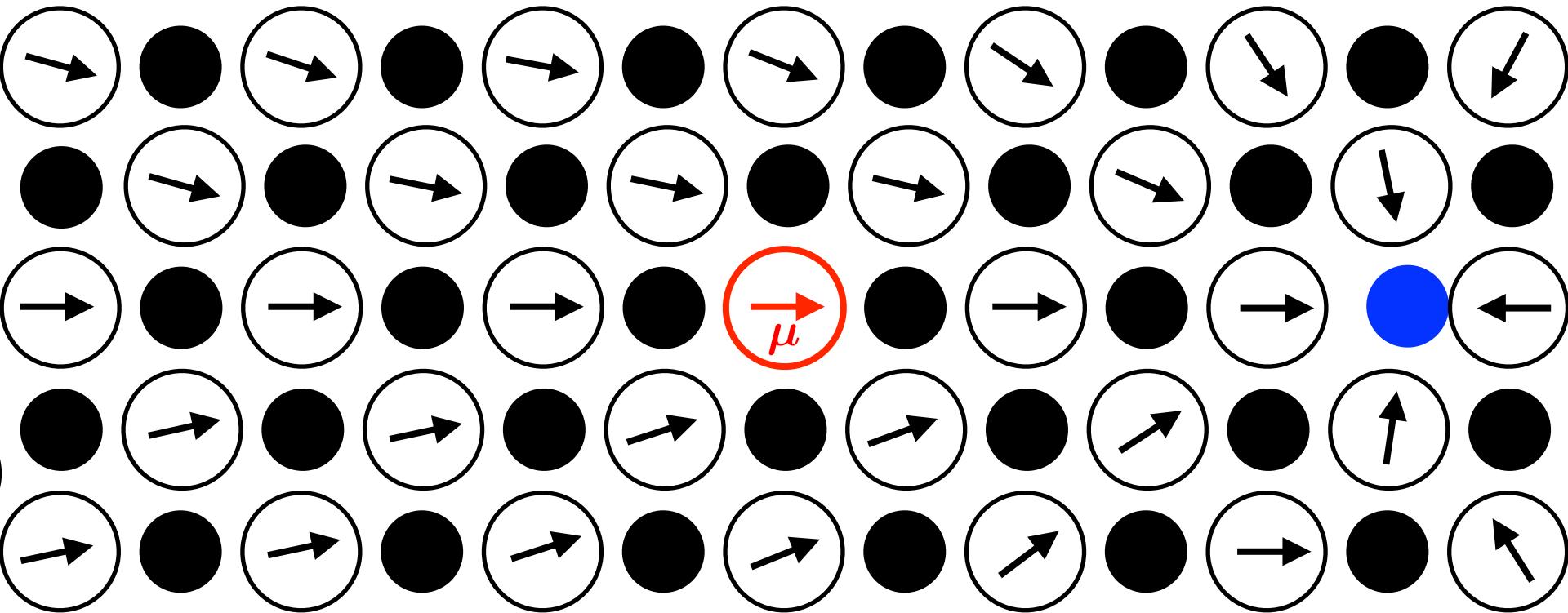


$$\mu^0 = \alpha \mathbf{E}^0(q^N)$$

# Induced dipoles



# 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

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:

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

4. Update the dipoles:

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

# Induced dipoles

5. Convergence?

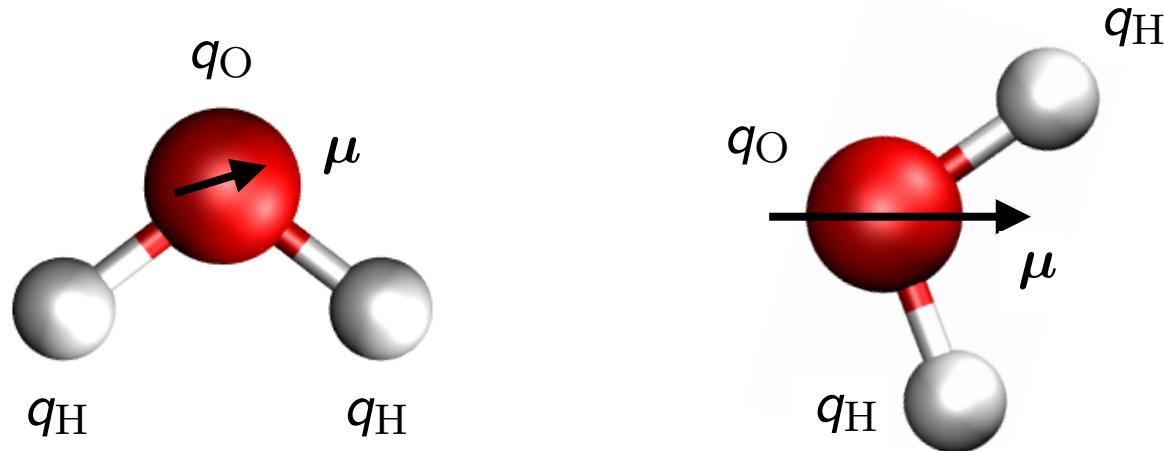
$$| \boldsymbol{\mu}^{(i)} - \boldsymbol{\mu}^{(i-1)} | < \epsilon$$

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

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

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

# Polarization interaction



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

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

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

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

# Polarization interaction

Total contribution due to the dipoles:

$$\mathcal{U}^{\text{pol}}(\mathbf{r}^N, \boldsymbol{\mu}^N) = \sum_{i < j} U_{ij}^{q\mu}(\mathbf{r}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) + U_{ij}^{\mu\mu}(\mathbf{r}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) + \sum_i U_i^\mu(\boldsymbol{\mu}_i)$$

It is easy to show that:

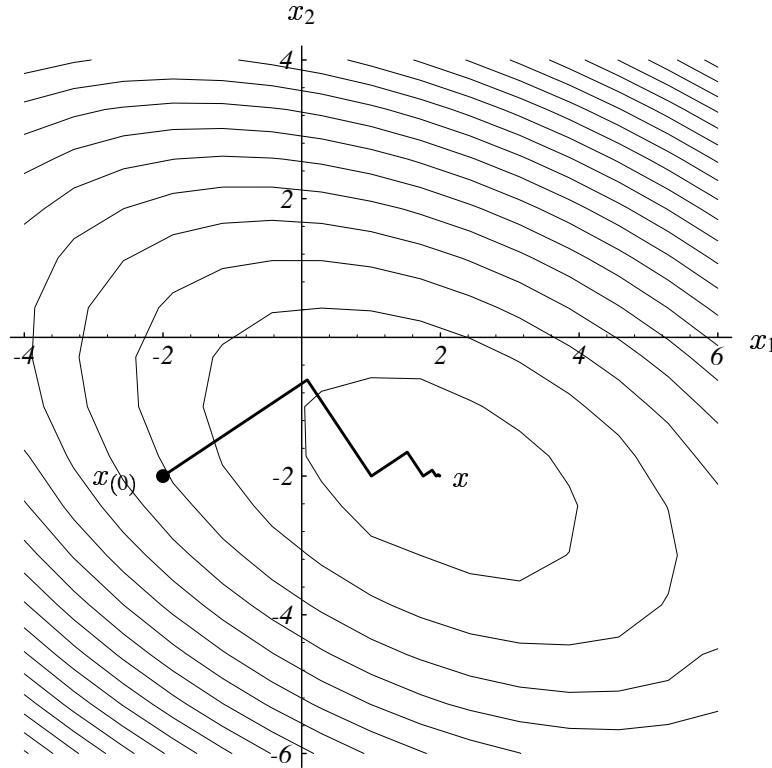
$$\frac{\partial \mathcal{U}^{\text{pol}}}{\partial \boldsymbol{\mu}_i} = 0 \quad \equiv \quad \boldsymbol{\mu}_i = \alpha_i \mathbf{E}_i$$

Induced dipoles can be treated as  
additional degrees of freedom

which take their adiabatic value at each step

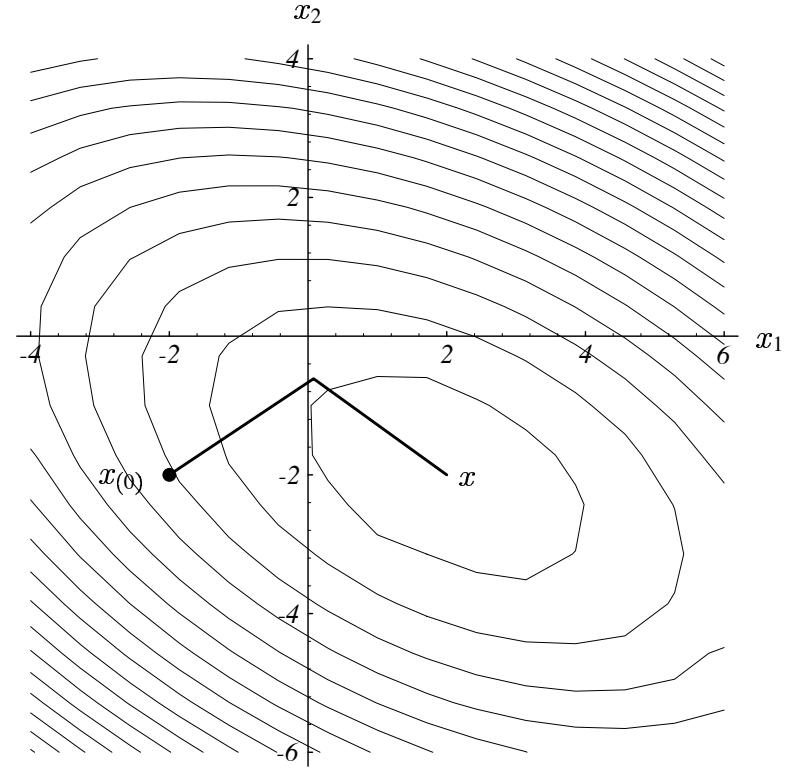
# Polarization interaction

Objective: minimize  $\mathcal{U}^{\text{pol}}$  w.r.t. the dipoles



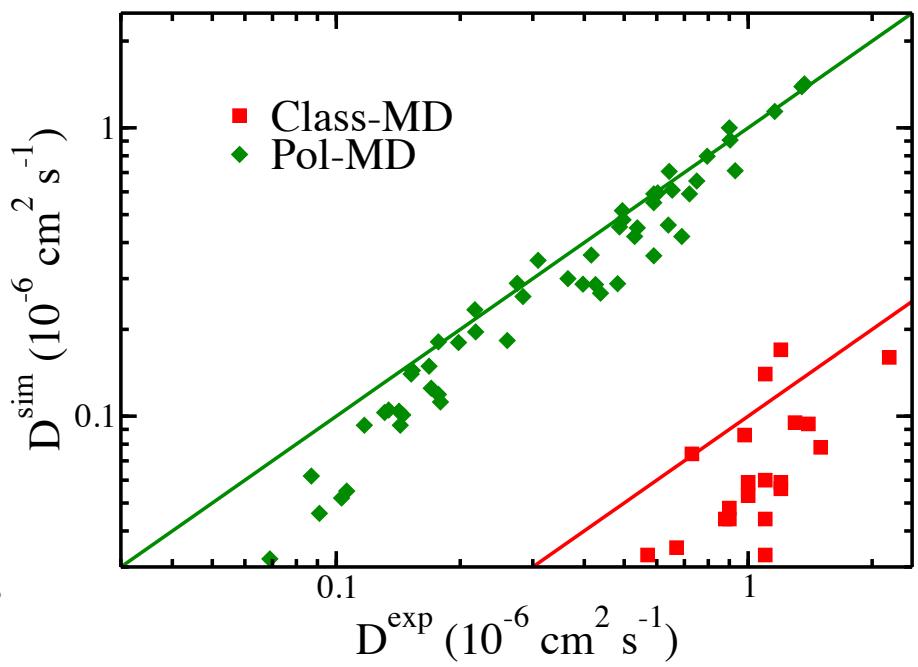
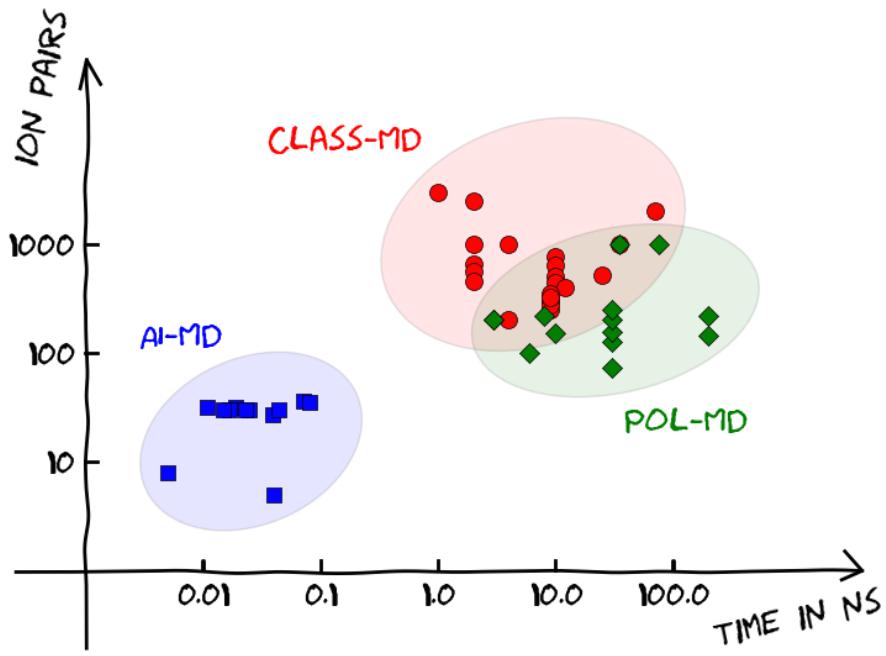
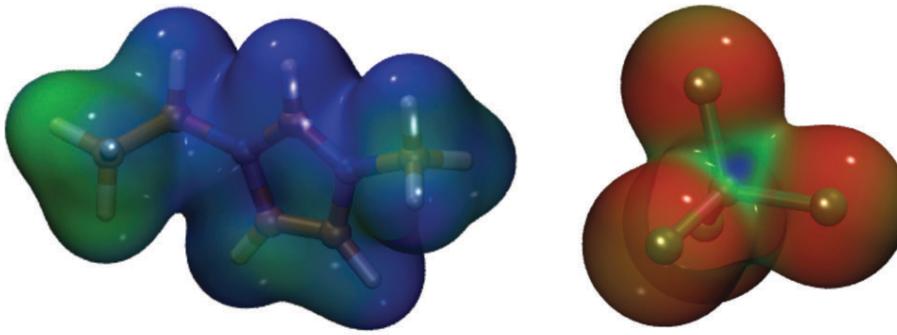
Steepest descent

Cost x5 compared to conventional MD



Conjugate gradients

# Polarization in ionic liquids



Figures from Salanne, PCCP, 2015

# Parameterization from experiments

- Basic structure (bond length, etc)
- Advanced structure (xray/neutron diffraction)
- Lattice parameters, density
- Vibrational spectroscopy (phonons, infrared,...)
- ...

Not very predictive!

# Parameterization from *ab initio*

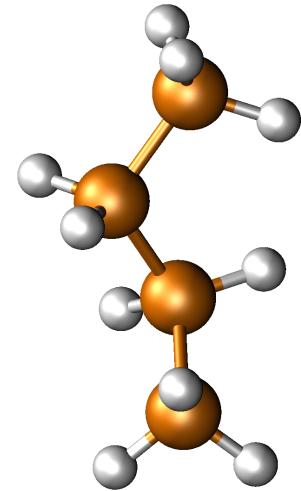
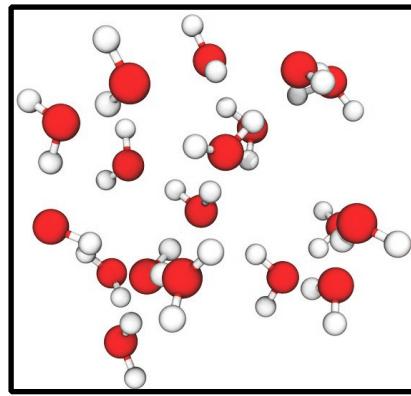
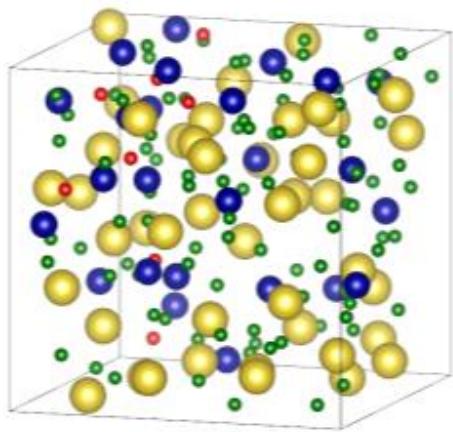
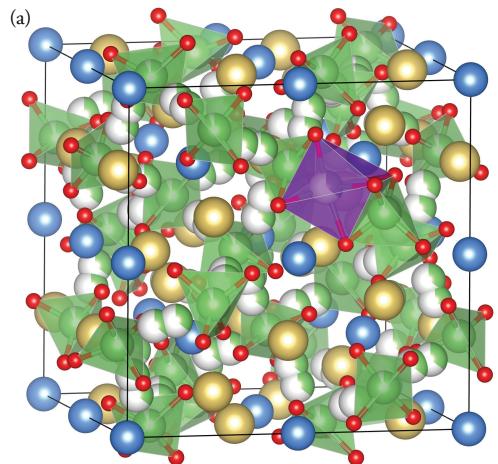
- Energies (total or decomposition)
- Forces
- Dipoles (multipoles)
- Stress tensors
- ...

Garbage in = Garbage out!

# Typical (raw) output

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

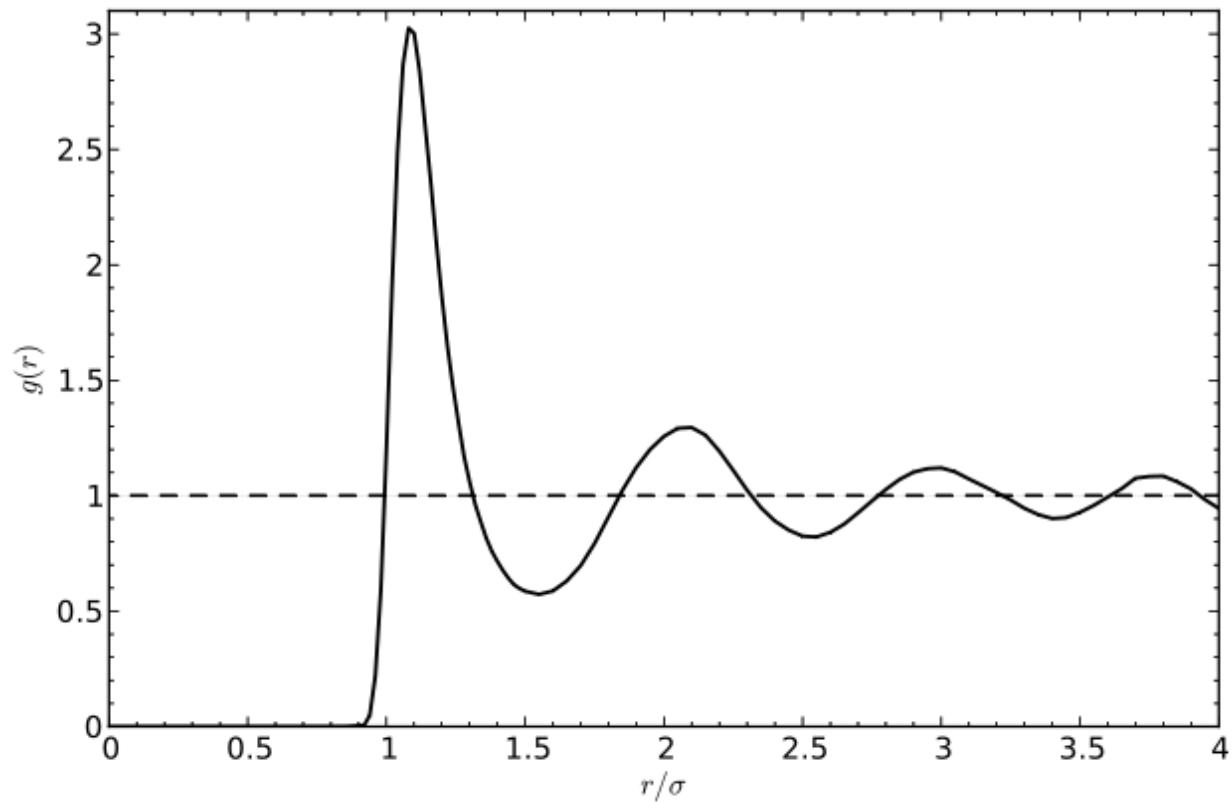
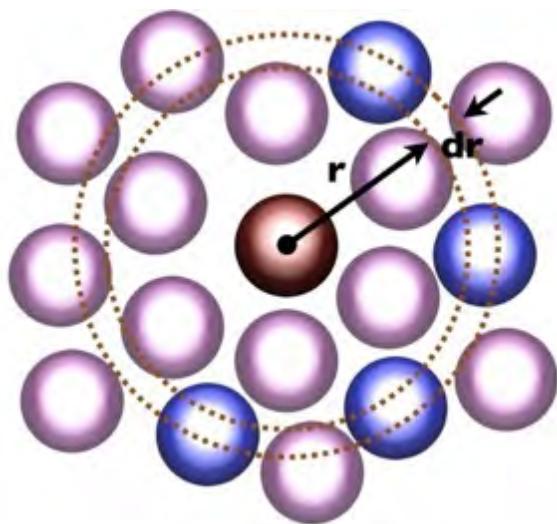
# Structure



Good for visualization but not quantitative

# Radial distribution functions

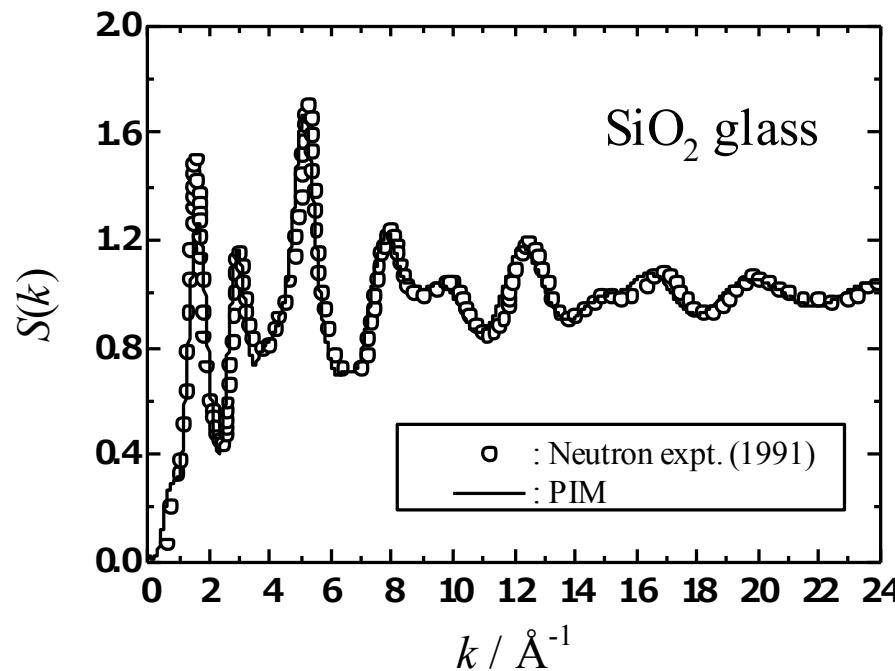
$$g_{\alpha\beta}(r_{ij}) = \frac{\rho_{\alpha\beta}^{(2)}(\mathbf{r}_i, \mathbf{r}_j)}{\rho_{\alpha}^{(1)}(\mathbf{r}_i) \times \rho_{\beta}^{(1)}(\mathbf{r}_j)}$$



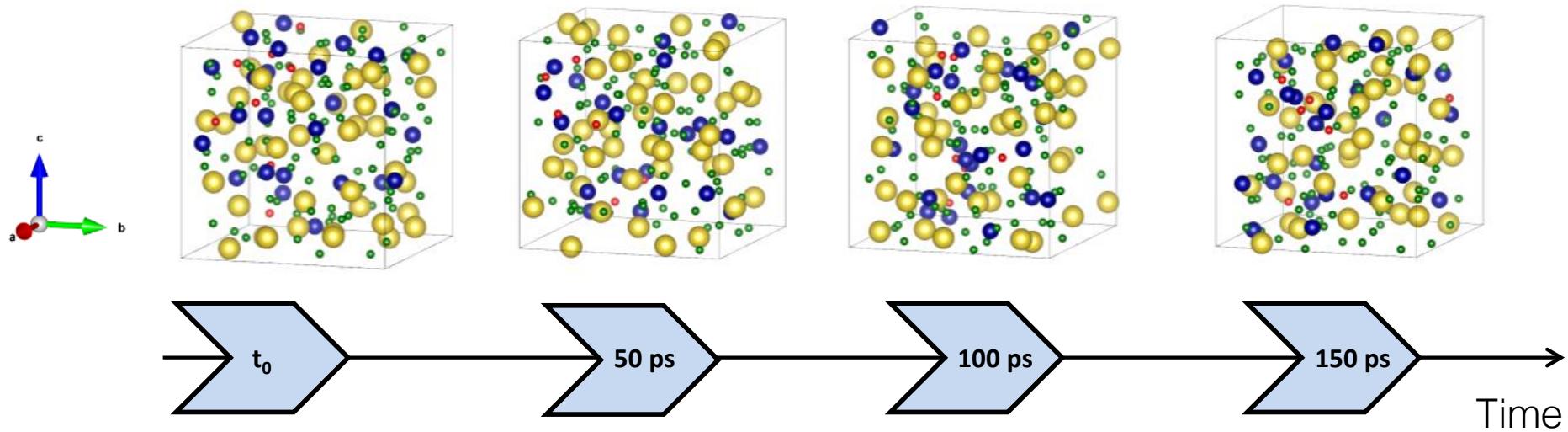
# X-ray/neutron diffraction: structure factors

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

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

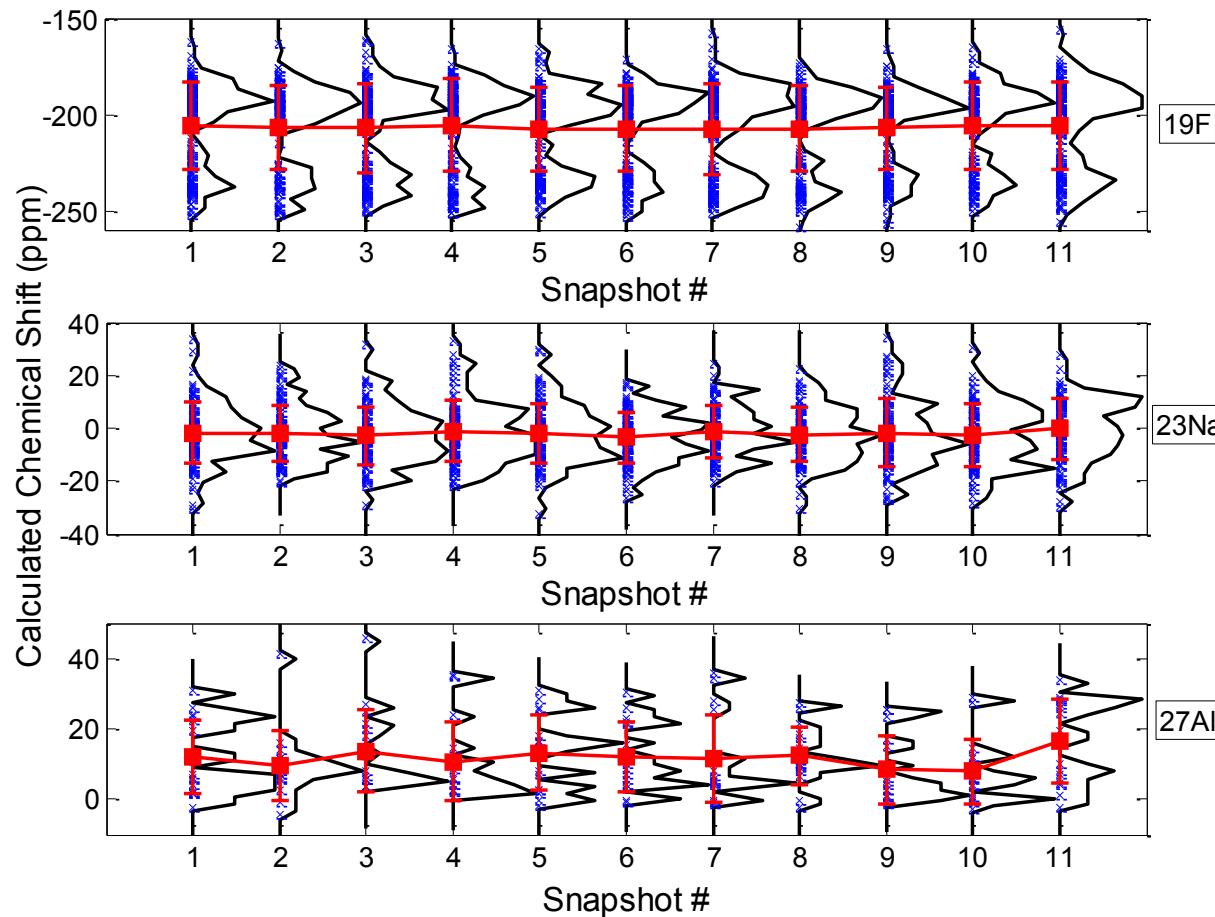


# NMR: GIPAW calculations



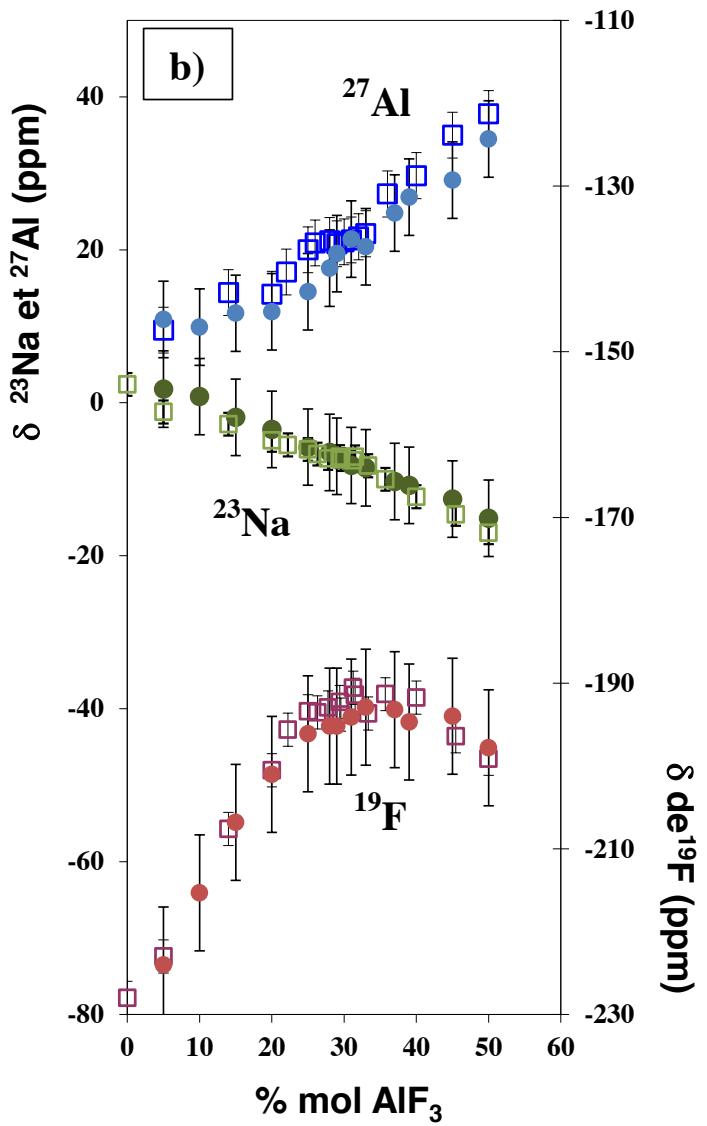
Extraction of snapshots along a trajectory  
(system = high temperature liquid cryolite NaF-AlF<sub>3</sub>)

# NMR: GIPAW calculations



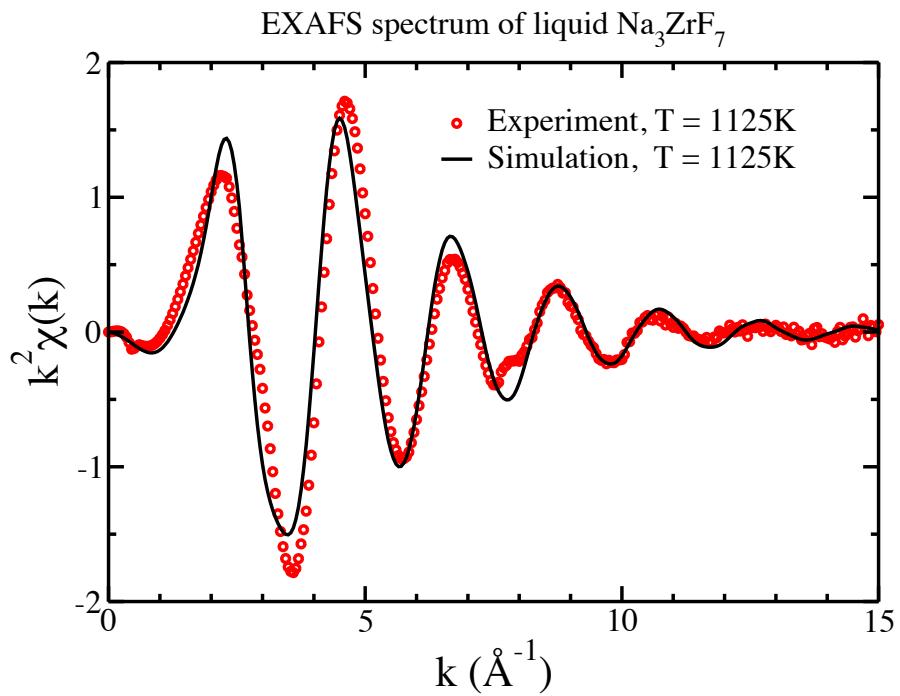
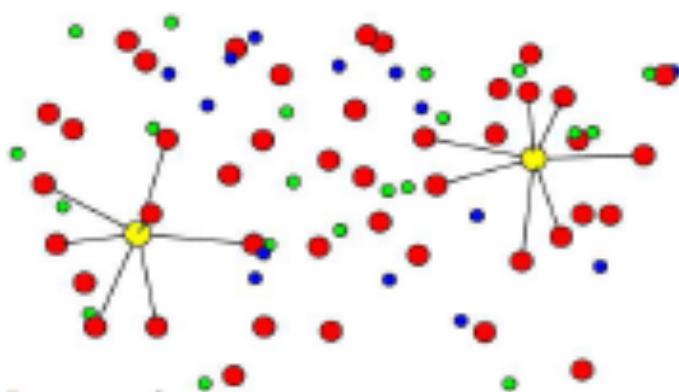
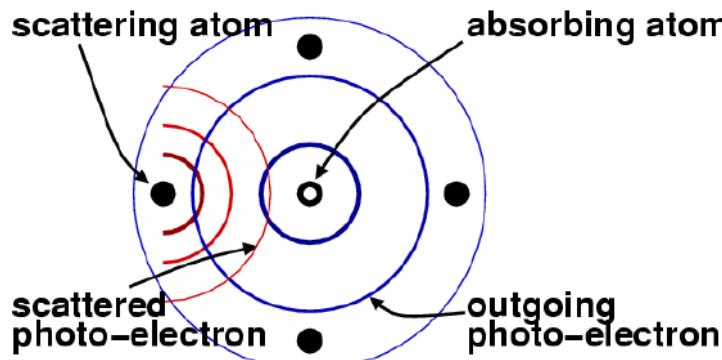
Determination of all chemical shifts for a composition

# Comparison with experiments



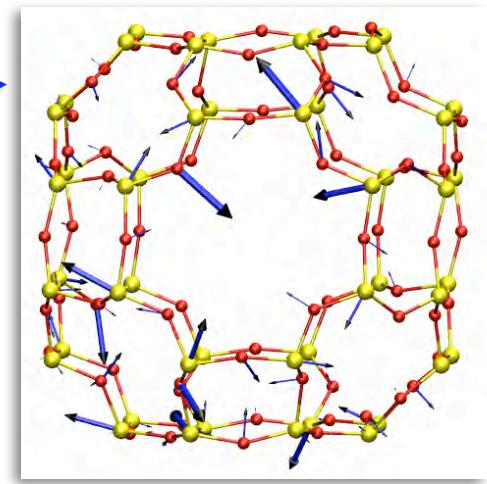
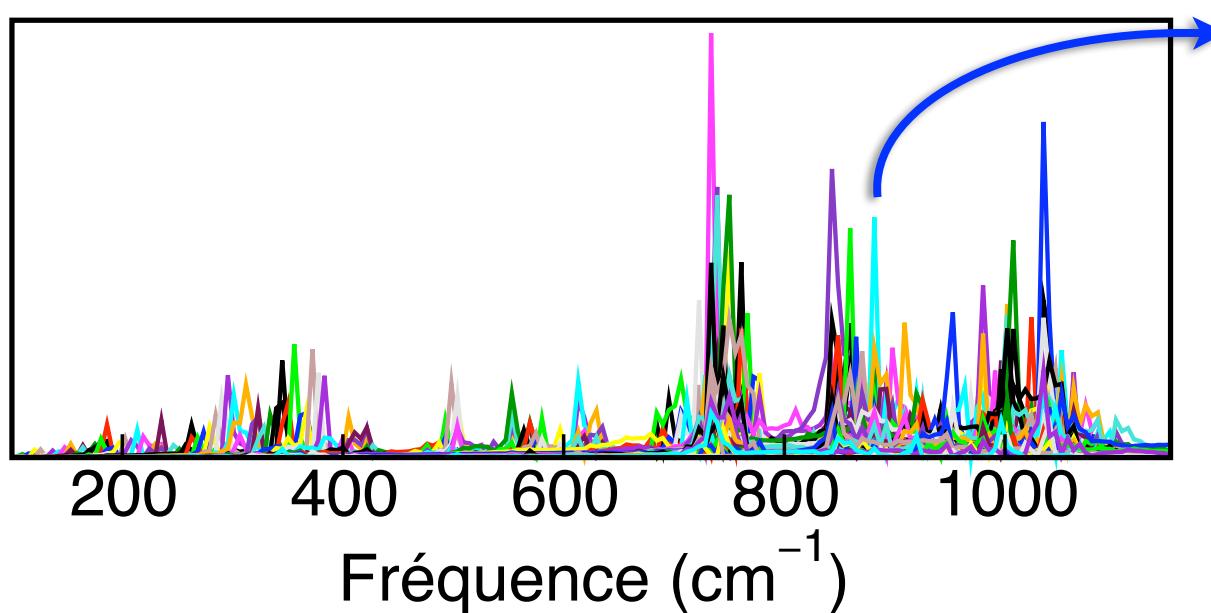
# X-ray absorption

As for NMR, ab initio calculations on a series of snapshots



# Vibrational spectroscopy

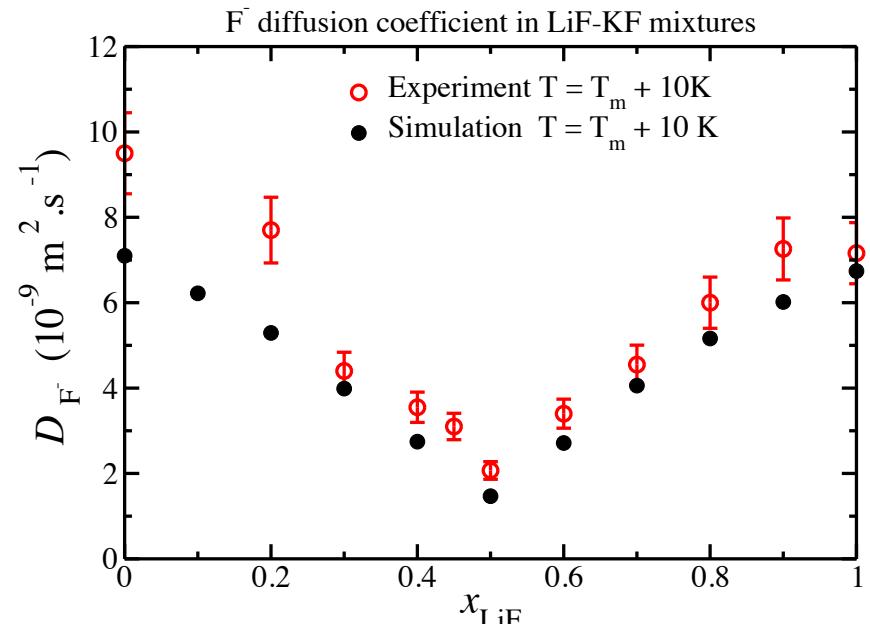
Infra-red: current auto-correlation function  
Raman: polarization auto-correlation function



$$\nu_{151} = 897 \text{ cm}^{-1}$$

# Transport coefficients

Diffusion coefficients:  
Mean-squared displacements



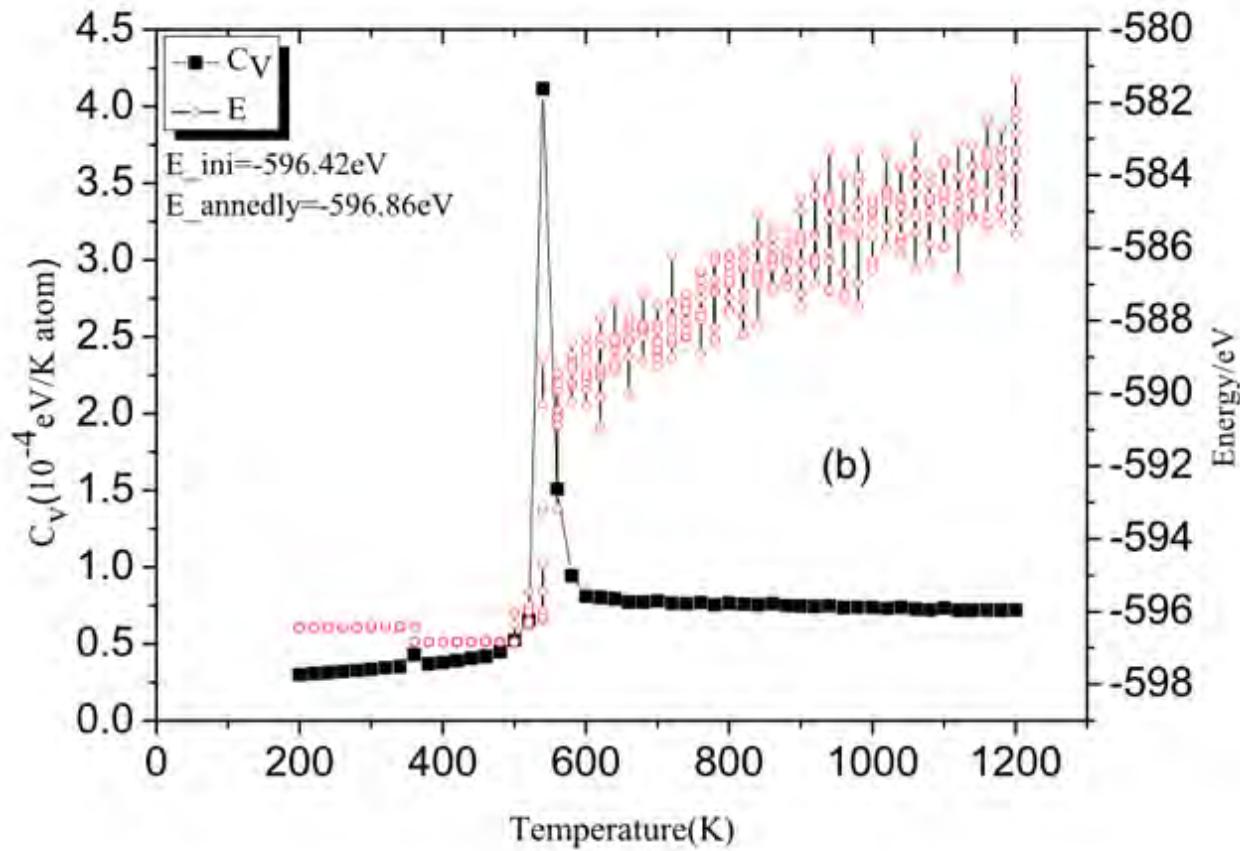
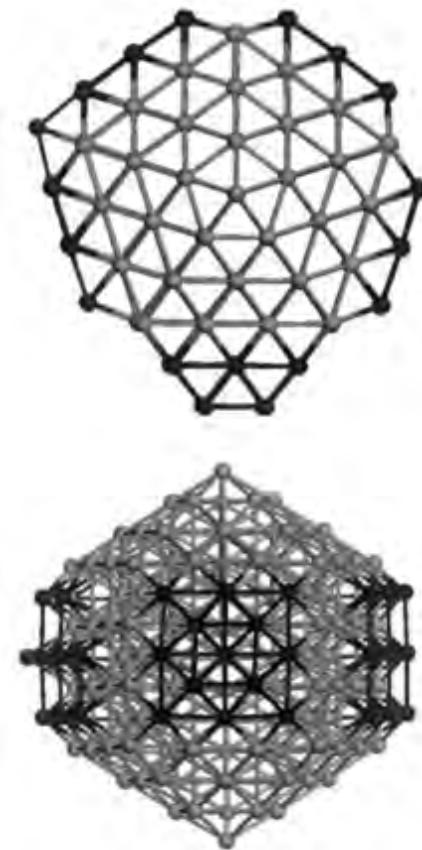
Viscosity: stress tensor auto-correlation function

Ionic conductivity: displacements of charged species

# Thermodynamic properties

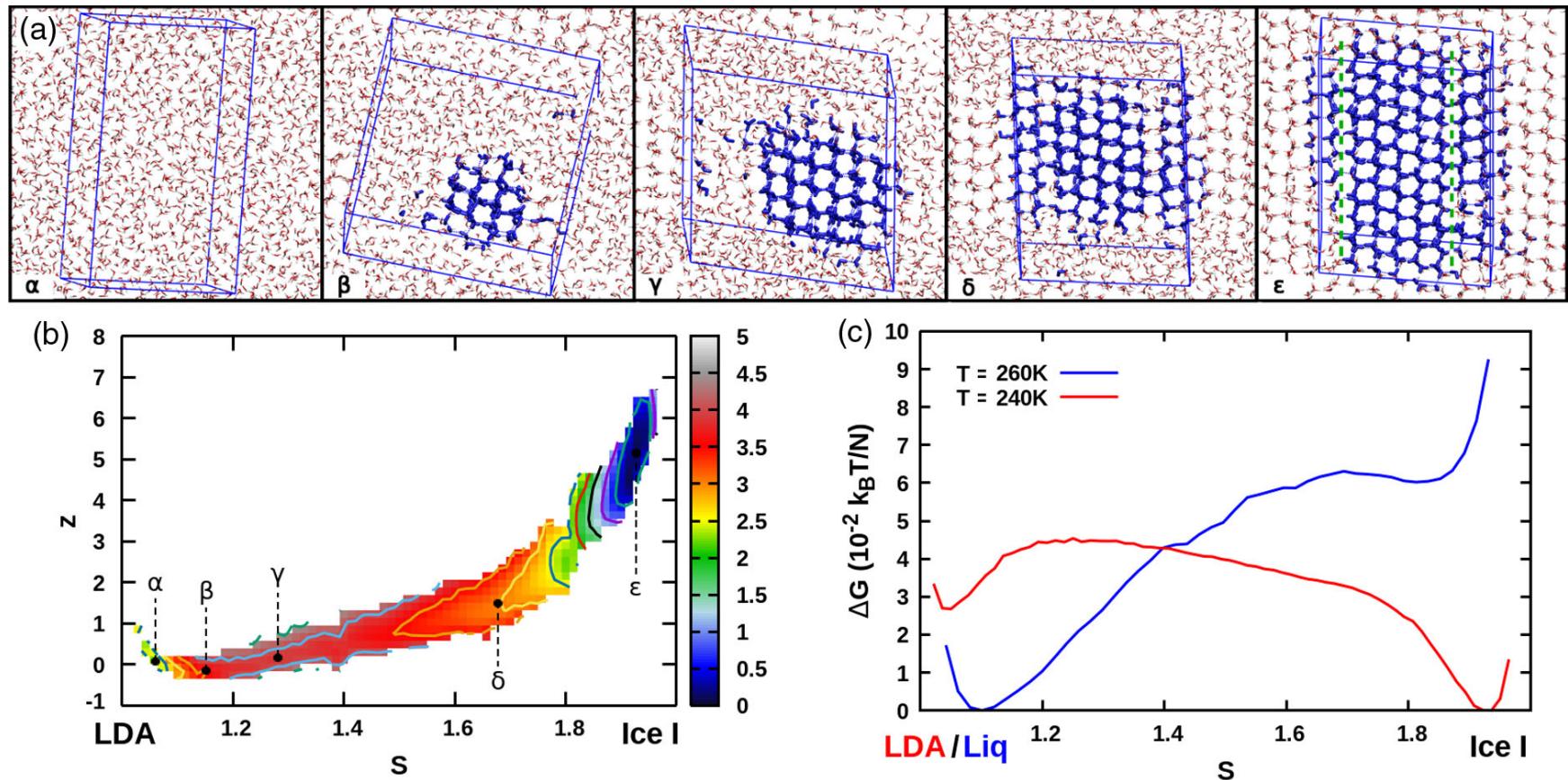
Melting of  $\text{Al}_{196}$  nanoparticle

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



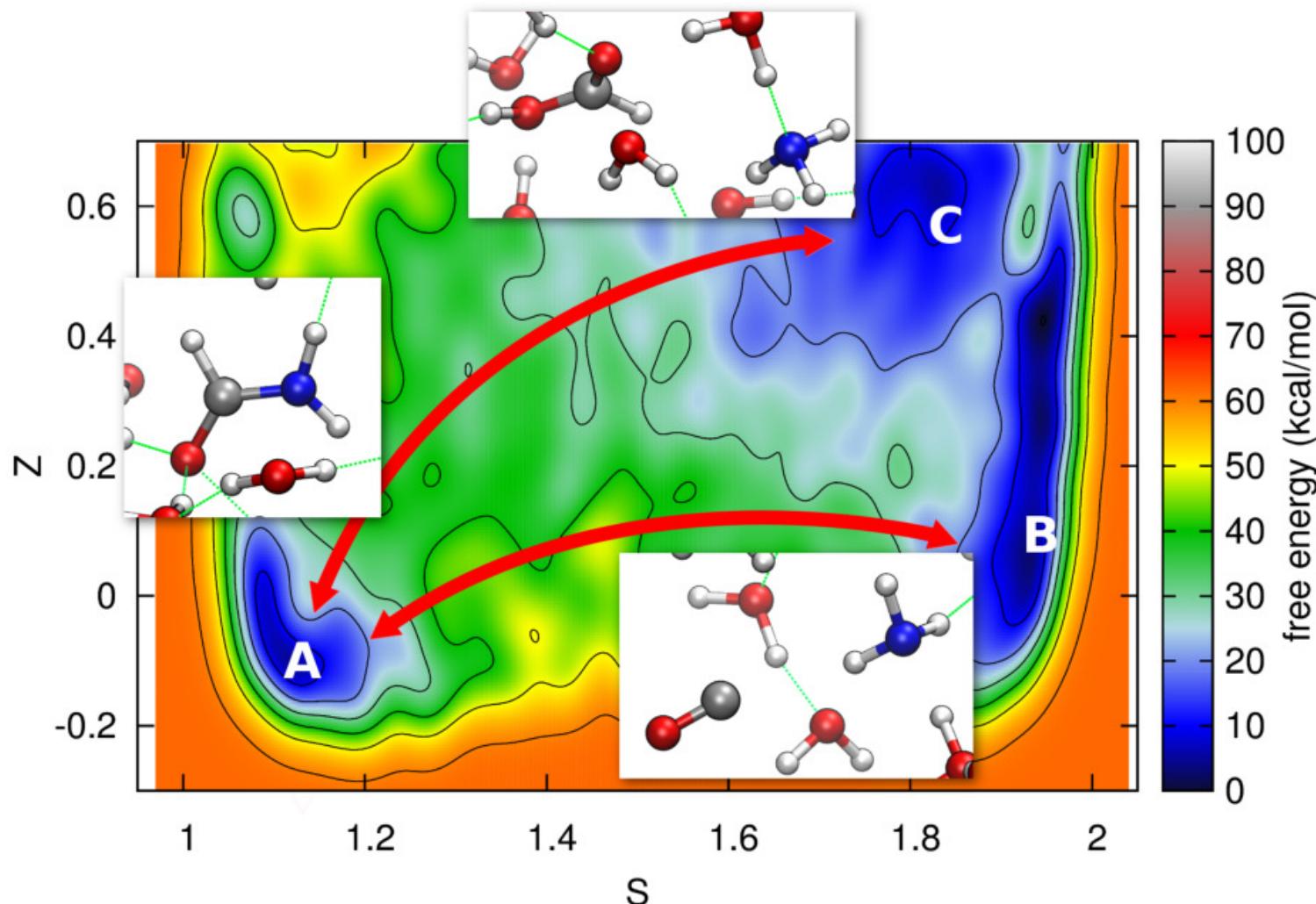
Heat capacity, phase diagram, compressibility, etc

# Free energy: physical transformation



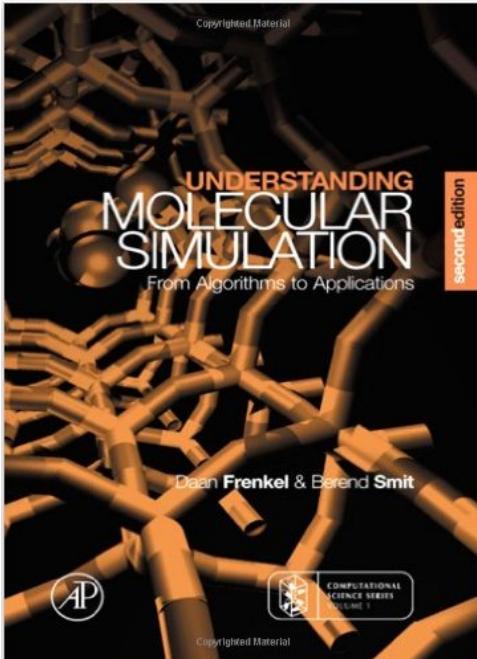
Crystallization of liquid water

# Free energy: chemical transformation

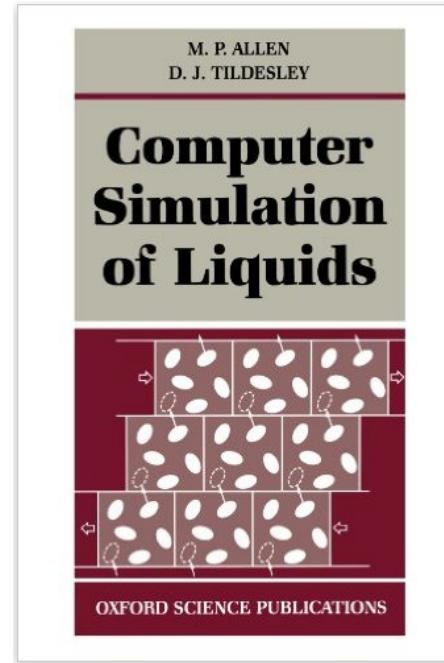


Generally requires ab initio molecular dynamics

# Further reading



Frenkel & Smit



Allen & Tildesley

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