Simulazioni Montecarlo e Dinamica Molecolare applicate a problemi di fisica, chimica ed energia
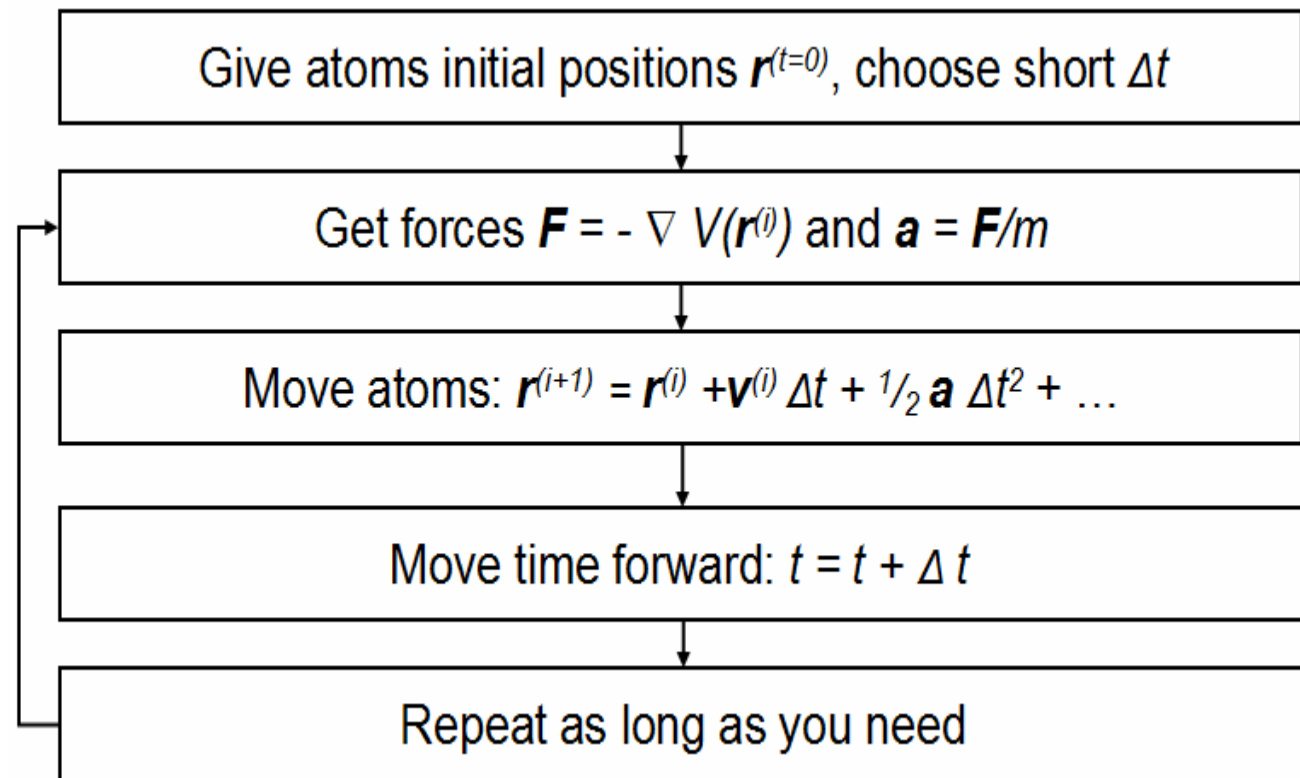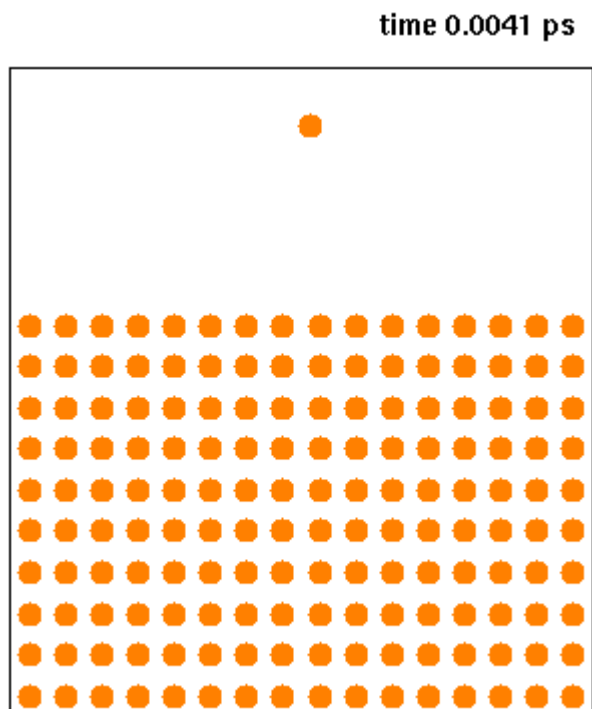
Marco Cogoni

30 05 2012

time 0.0041 ps

Give atoms initial positions $r^{(t=0)}$, choose short Δt

Get forces $\mathbf{F} = -\nabla V(r^{(i)})$ and $\mathbf{a} = \mathbf{F}/m$

Move atoms: $r^{(i+1)} = r^{(i)} + v^{(i)} \Delta t + \frac{1}{2} \mathbf{a} \Delta t^2 + \ldots$

Move time forward: $t = t + \Delta t$

Repeat as long as you need

L'affidabilità di una simulazione MD dipende essenzialmente dal force field

Esplorazione dello spazio delle fasi secondo una traiettoria "non fisica" nel senso che l'evoluzione è verso configurazioni ad energia vicina e non configurazione spaziale simile
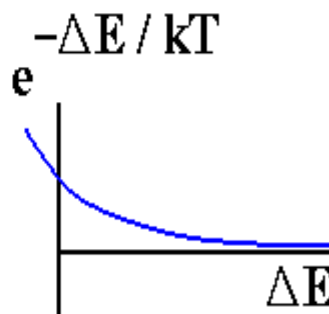
Le uniche "manopole" che possiamo usare per governare l'evoluzione sono la temperatura T e il meccanismo che genera le nuove configurazioni di prova

MC compares energies. No forces calculated.
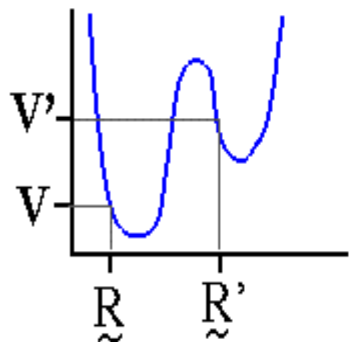
In equilibrium at T:

$$\frac{p(E')}{p(E)} = e^{-(E'-E)/kT}$$

$e^{-\Delta E / kT}$

ΔE

$E_{old} \leftarrow$ Calculate energy

Build trial configuration

$E_{trial} \leftarrow$ Calculate energy

$\Delta E \leftarrow E_{trial} - E_{old}$

ran() returns a random uniform number between 0 and 1.

if (exp(-$\beta\Delta E$) > ran()) **then**

    Accept trial configuration

else

    Reject trial configuration

end if

- L'idea base è quella di integrare le equazioni del moto per un set di atomi caratterizzati da posizione, velocità e accelerazione

- L'evoluzione temporale del sistema non è "reale", ma costituisce solamente un modo di esplorazione dello spazio delle fasi per ottenere valori medi di osservabili fisiche (statiche o dinamiche)

  diffidare sempre dei bei filmati senza valore statistico

- Il force field (FF) deve essere "buono quanto basta": qualche volta è sufficiente un'approssimazione classica, altre volte anche un approccio *ab initio* può essere inadeguato

- *Forma funzionale:* somma di diversi contributi

$E\_tot = E\_bonded + E\_nonbonded$

$E\_bonded=E\_bond+E\_angle+E\_dihedral+...$
Usually modeled as harmonic, Morse, etc...

$E\_nonbonded=E\_elec+E\_vdW+...$
Usually Coulomb and Lennard-Jones

- *Table based approach:* fit da esperimenti o da simulazioni *ab initio*

In this case no analitycal expression
for the force field exists.
No explicit "physical meaning".
Often used for pair-wise interactions.

## Nessun FORCE FIELD ha valenza generale

- Nessun Force Field classico può descrivere del tutto il diagramma delle fasi dell'acqua

- Difficoltà nel trattare il legame H fra molecole H2O

- Estremamente difficile riprodurre cristallizzazione

- Necessità di simulazioni molto lunghe per osservare transizioni di fase
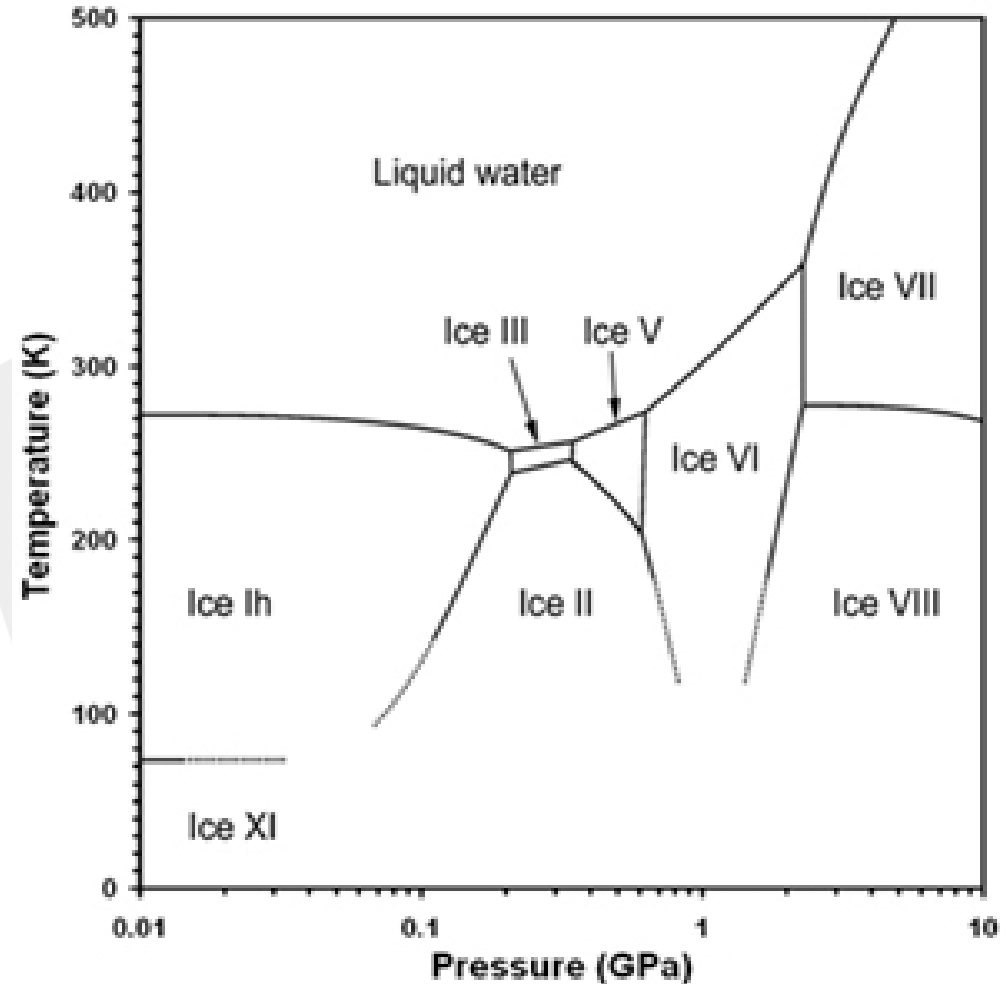
- Goal is to fit a set of experimental neutron diffraction diagrams of liquid water

- Tabular format, pair-wise potential

- Long range: Coulomb continuation

- Allows bond breaking/reforming

DWM Hofmann et al. *Chemical Physics Letters* **448** (2007) 138–143
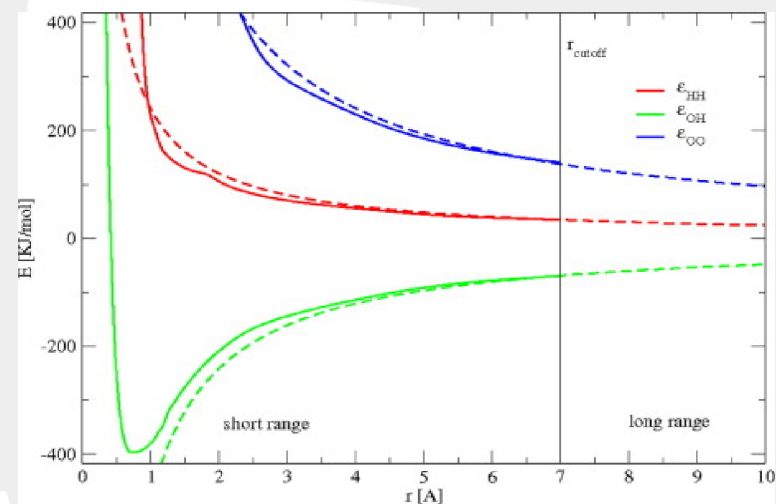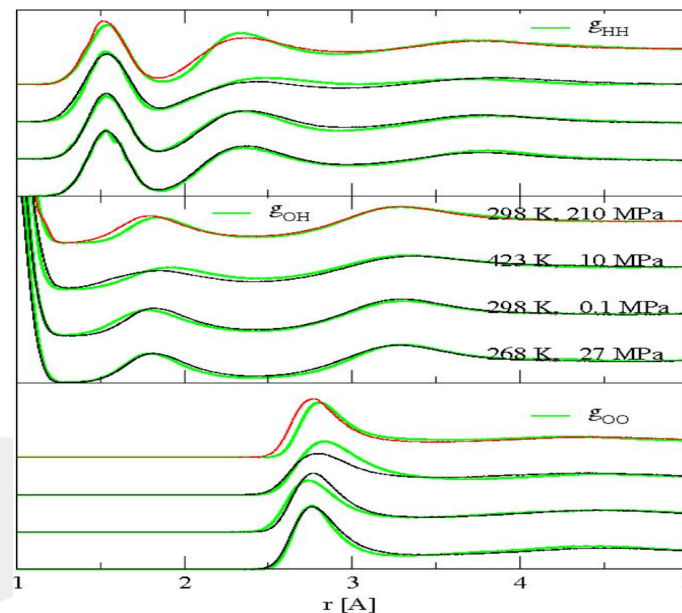
- RWFF describes all known ice polymorphs

- Their relative energies are in the correct order

- Able to describe Ice X which is not made by "standard" water molecules

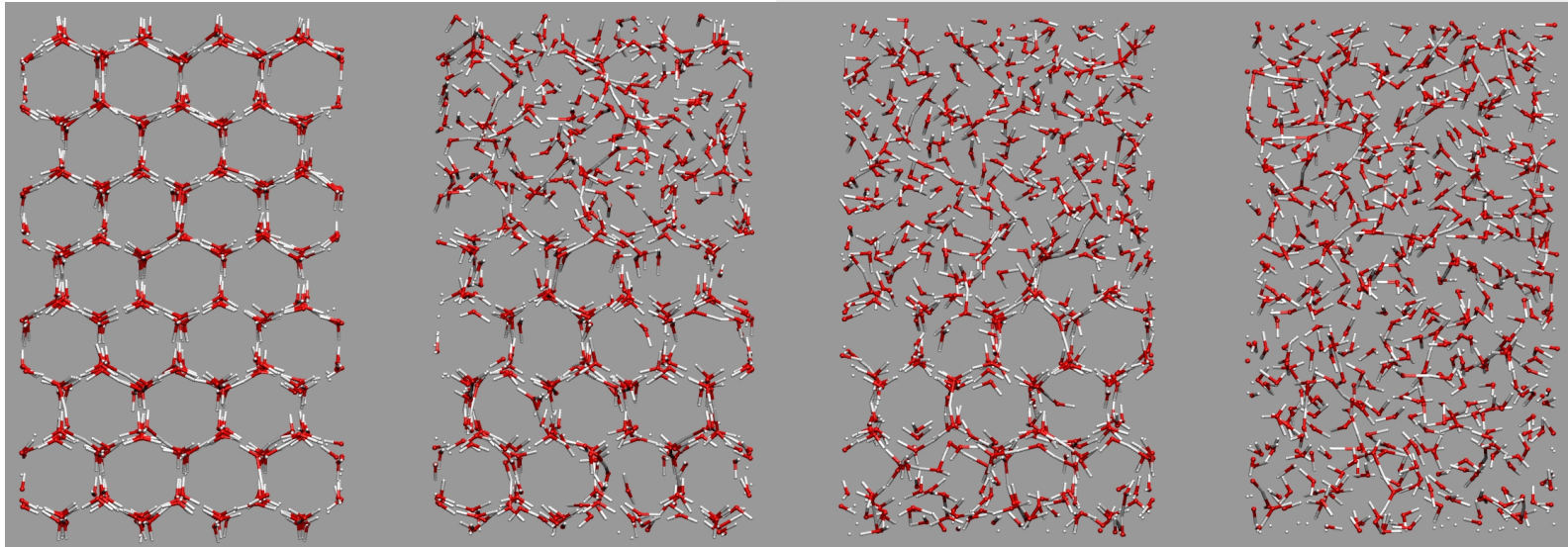- Negative side: small timestep ~0.1 fs vs 1 fs (hydrogen motion is very fast)
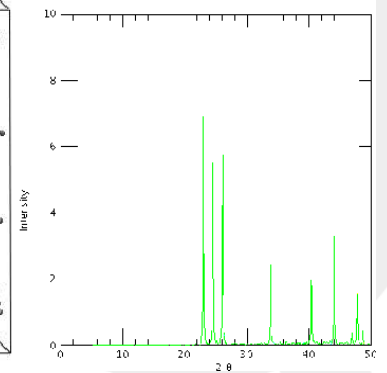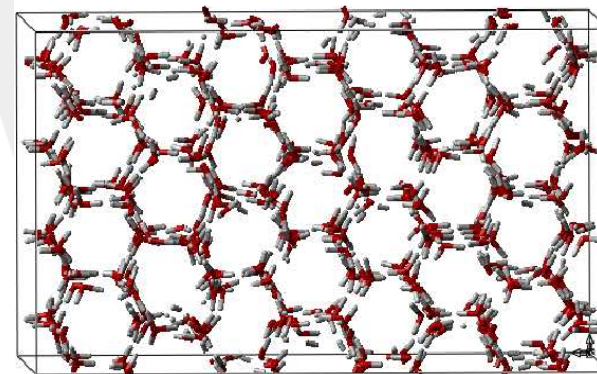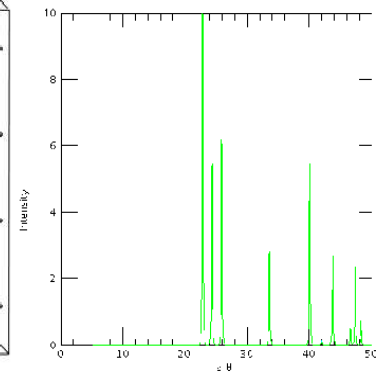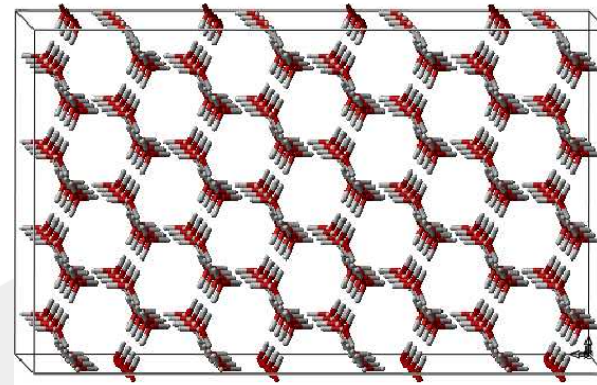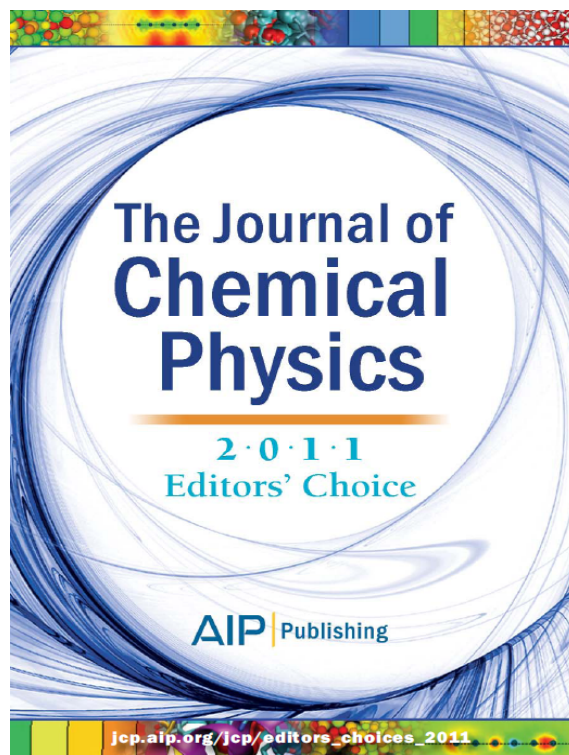
A powerful computational crystallography method to study ice polymorphism

*M. Cogoni, B. D'Aguanno, L. N. Kuleshova, and D. W. M. Hofmann*

Classical molecular dynamics simulations are used to investigate the structural properties of ice crystals under several temperature and pressure conditions. The study demonstrates the ability of the interaction potential model to estimate the relative stability of the 16 known crystal structures and to simulate the temperature and pressure dependence of static properties of ice crystals, such as structure, proton order-disorder relations, and phase stability.

- Sorprendente accordo della T di fusione del ghiaccio Ih

- Riprodotta una transizione di fase (nota sperimentalmente) ad alta pressione del ghiaccio VIII / VII

- Ottimo accordo coi valori sperimentali di diffusione sia dei protoni che dei difetti intrinseci del ghiaccio Ih
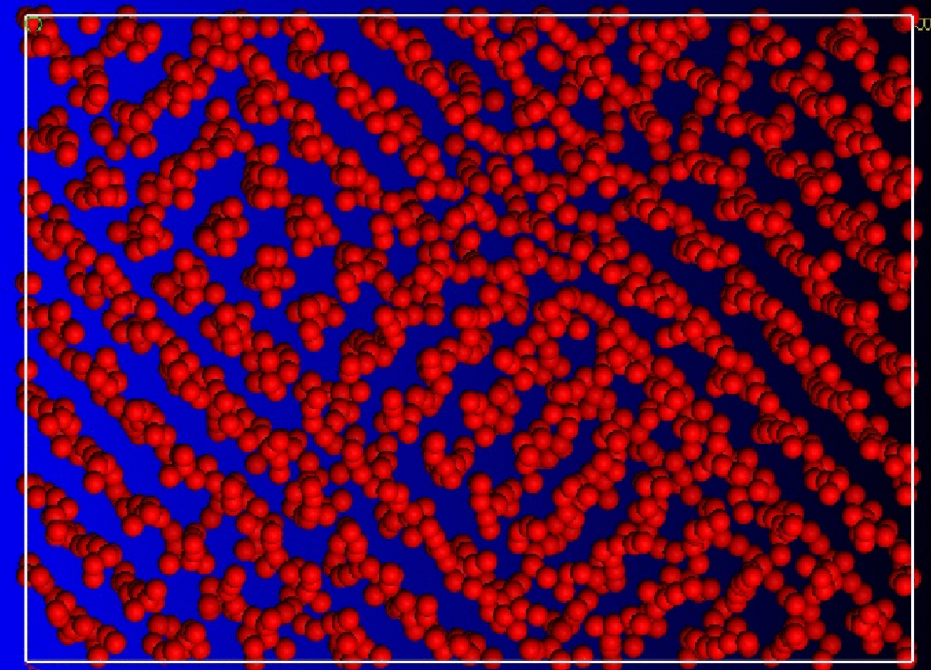

{filmato esterno}

M. Cogoni, B. D'Aguanno, L. N. Kuleshova, and D. W. M. Hofmann J. Chem. Phys. (to be submitted)

Transizione di fase reversibile ghiaccio
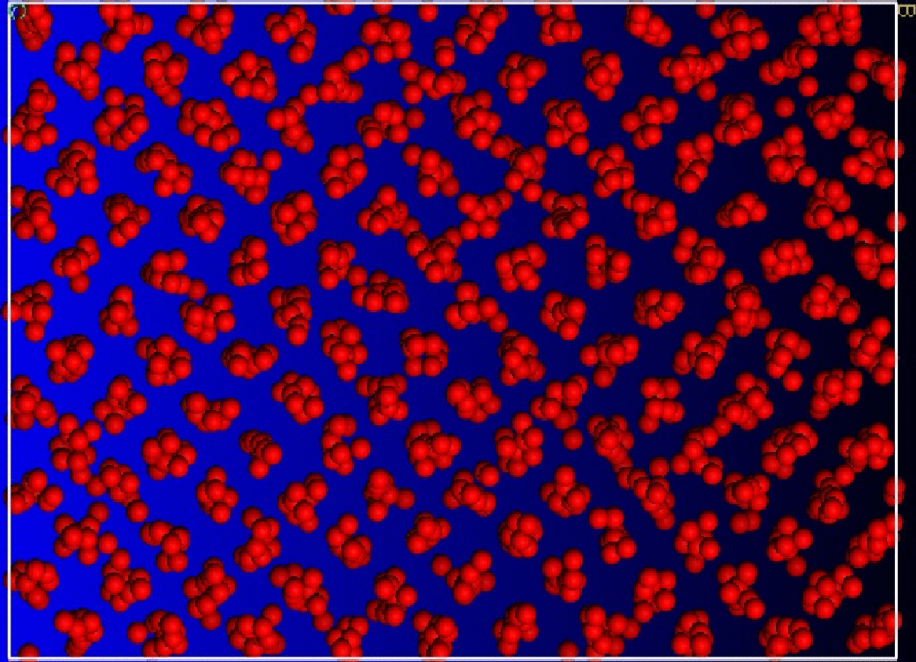
Ice VIII $\rightleftharpoons$ Ice VII

5GPa – 300K

14GPa - 300K

(a)

(b)
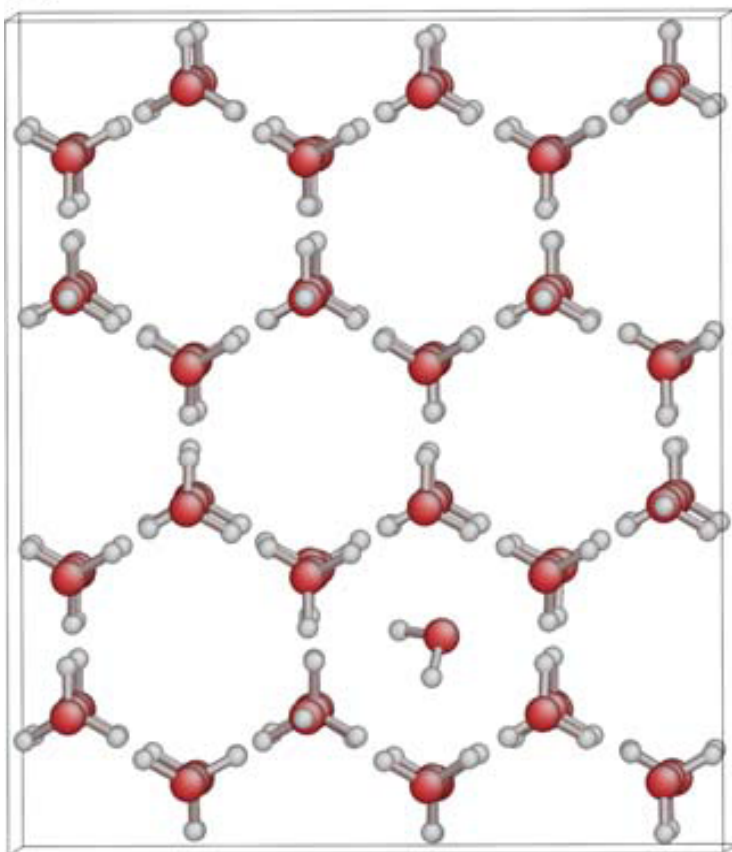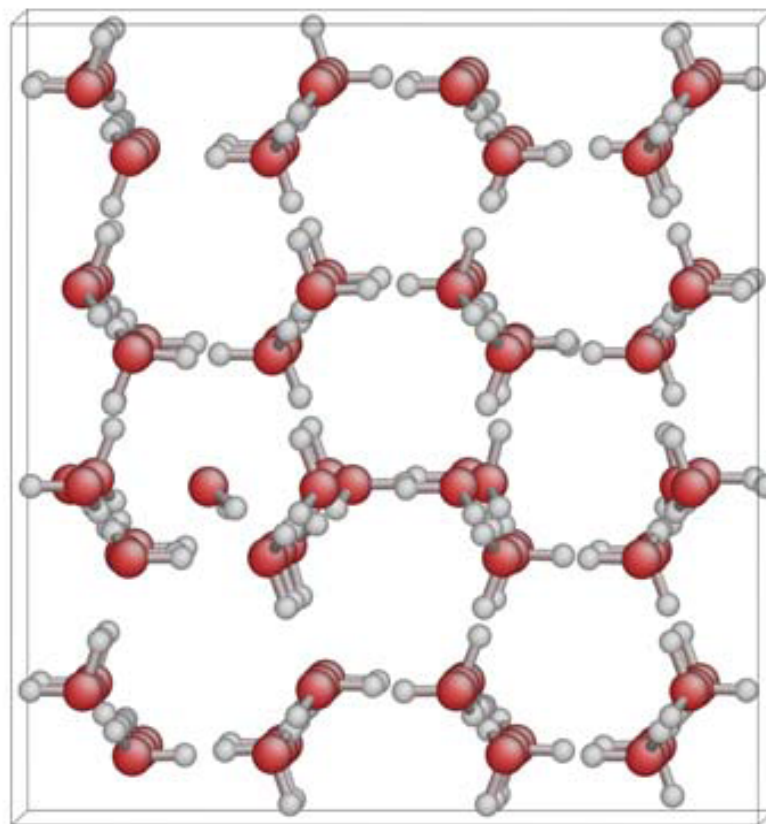
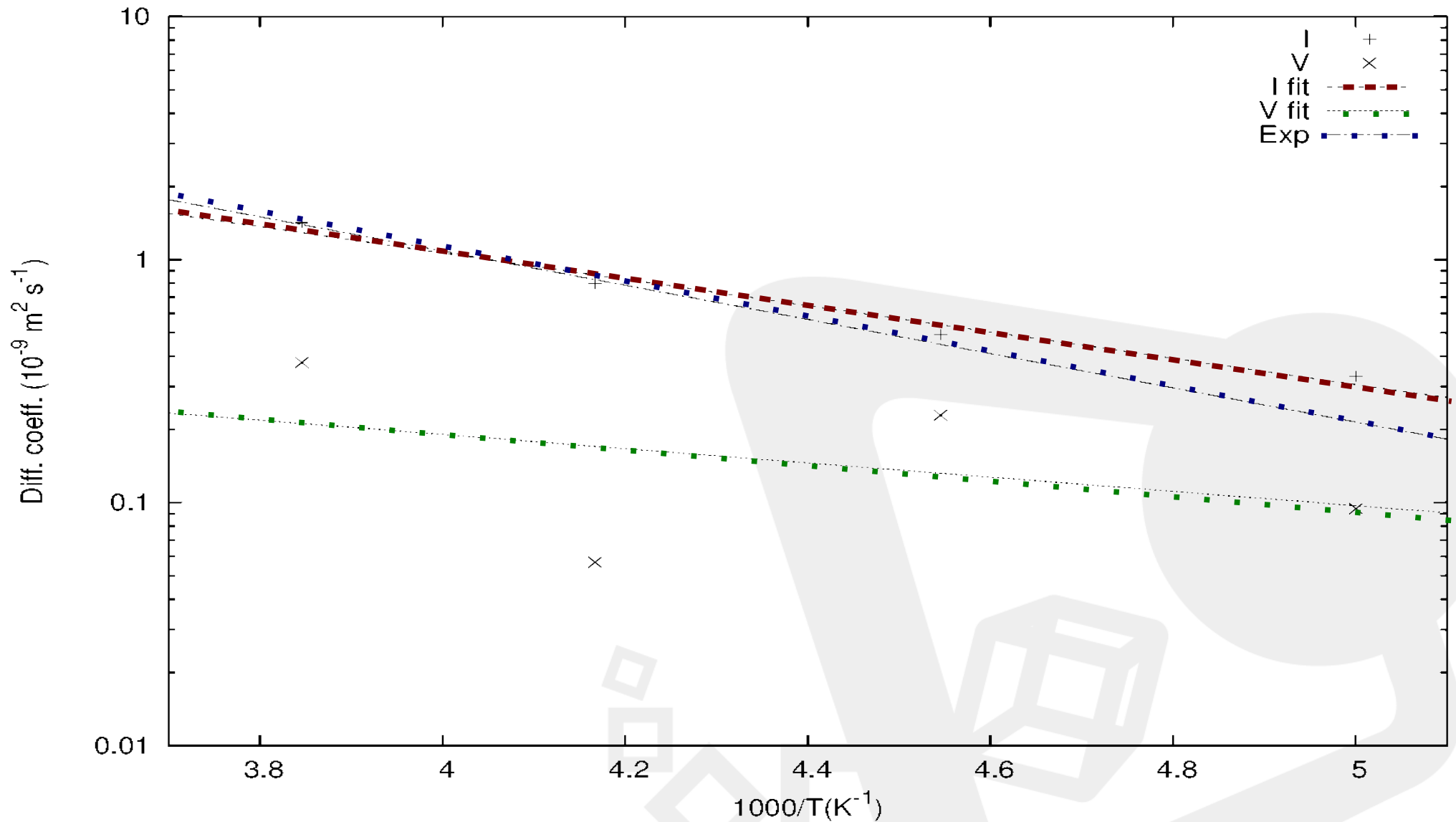# Sostituzione isotopica (D/H)

Collaborazione con il gruppo sperimentale del Dipartimento di Chimica Inorganica dell'Università di Bochum:

Effetti di sostituzione isotopica (D/H) nel packing di cristalli molecolari
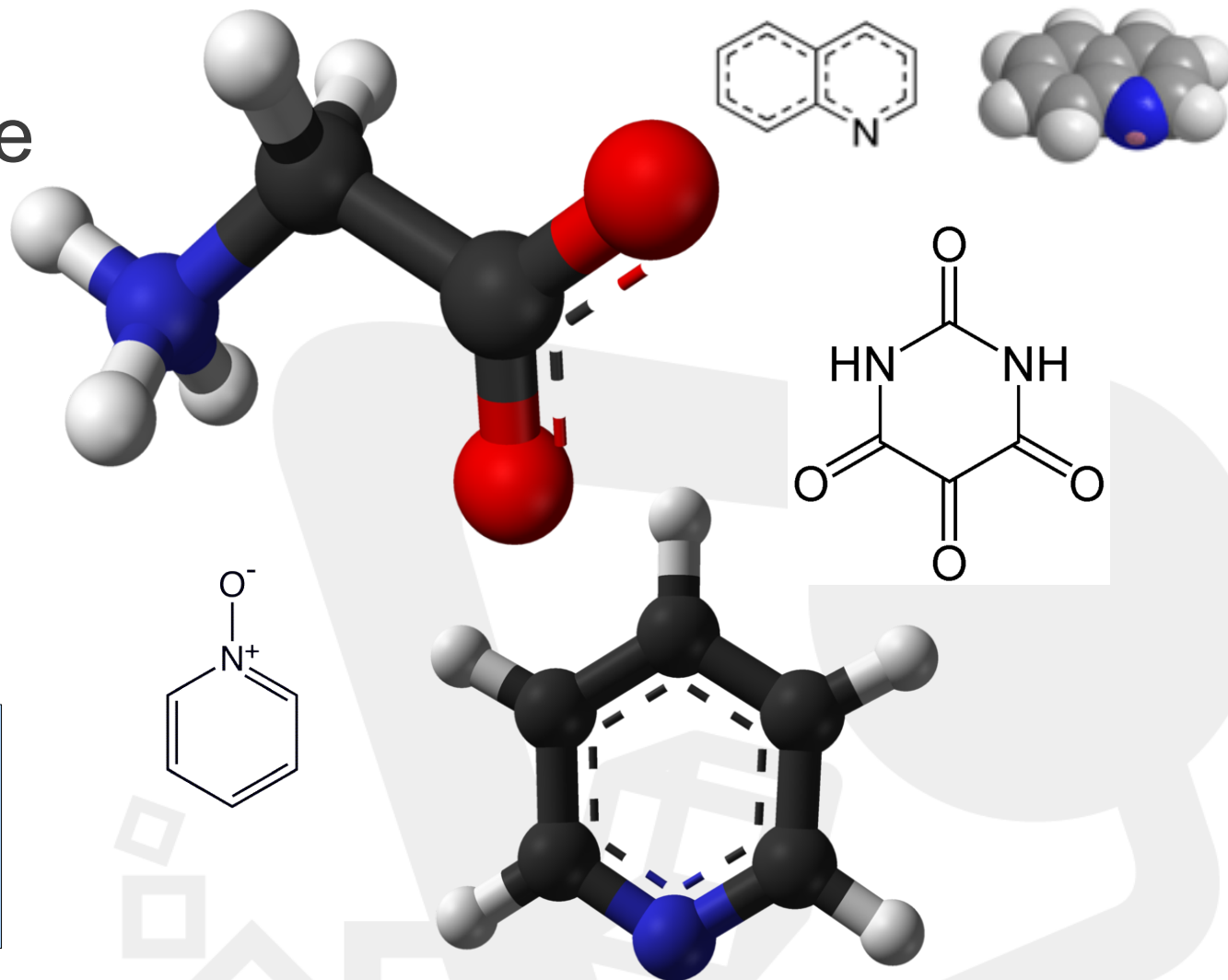
Klaus Merz - Vera Vasylieva

- Ice non-bonded interactions are single H-bonds and Coulomb

- Many FFs exist for heterocyclic compounds: UFF, Dreiding, CFF91, COMPASS (ab initio fit)

- Can fit new FFs from dispersion-corrected DFT

- FF even if for few el have large number of params
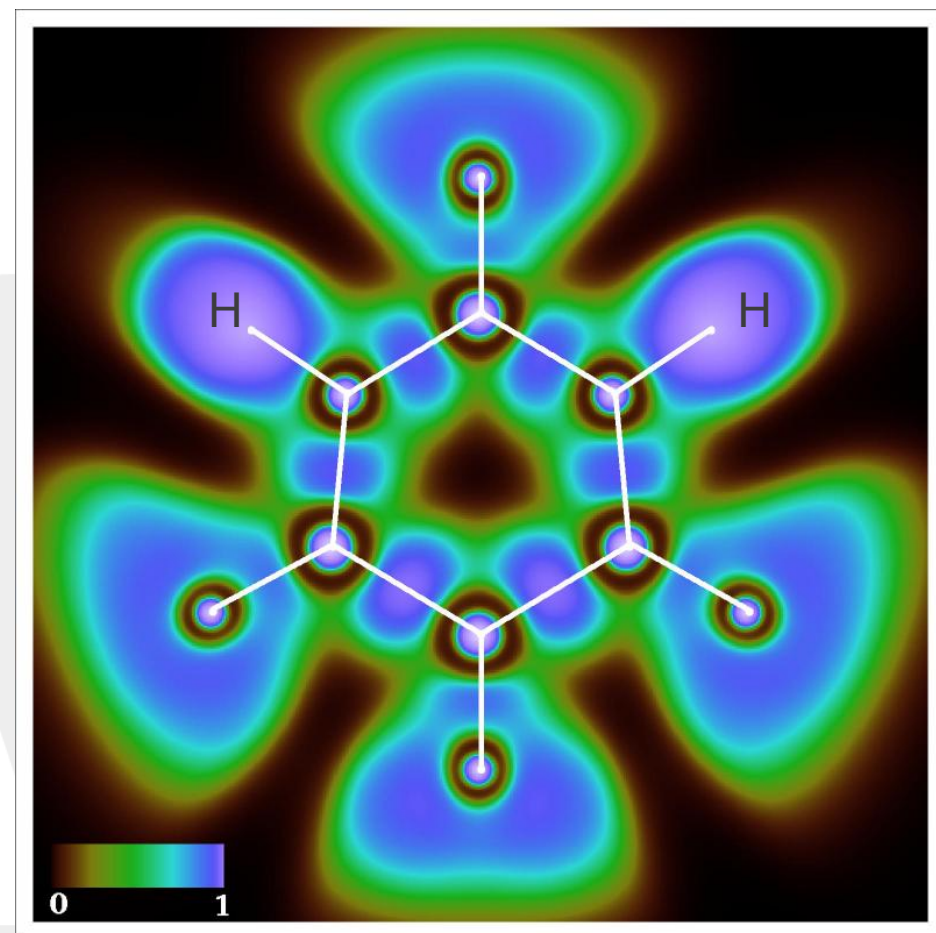
- Pyridine
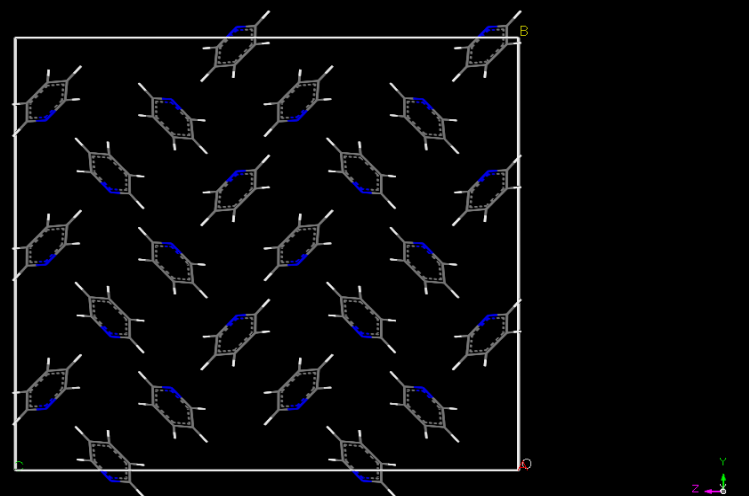- Pyridine N Oxide
- Alloxan
- Glycine
- Quinolin

Main goal is try to observe isotopic substitution effects on crystal packing

- Static optimizations see no structural difference for H and D

- **Entropic effect** to be checked with finite T and P

- Need long NPT simulations with large crystals: anharmonic lattice vibrations (D/H non uniformity...)
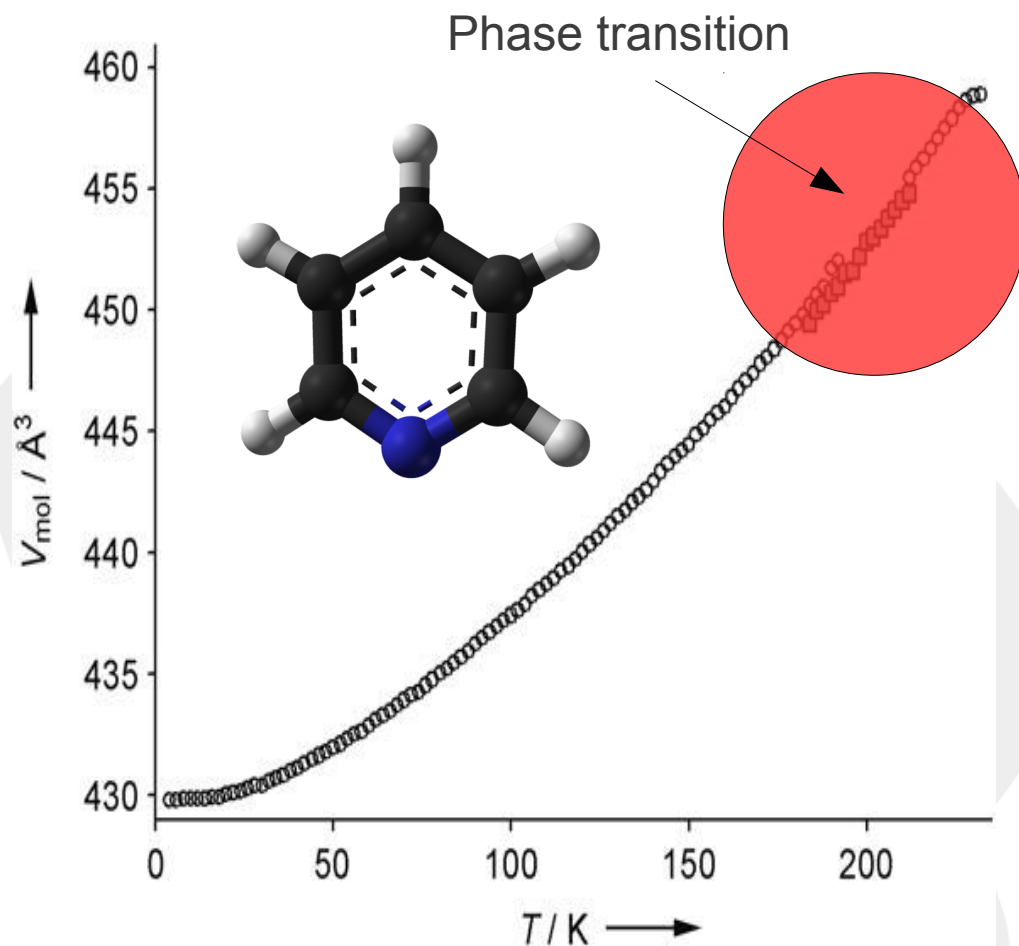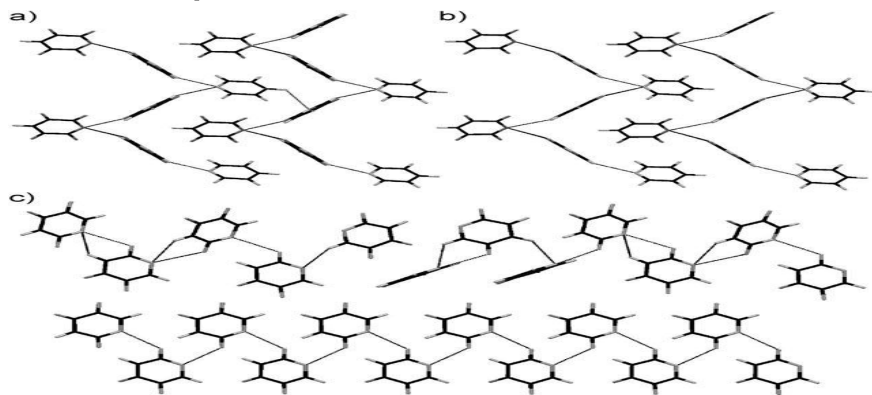
PYR I
Z'=4
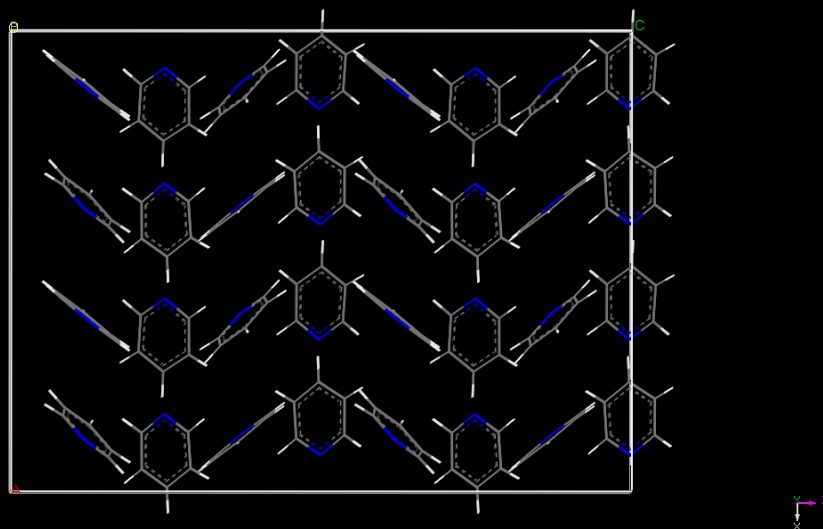
PYR II
Z'=1

- ## Transition observed with fully deuterated pyridine

- ## Transition from Z'=4 to Z'=1 in a narrow T range

- CH⋯π interaction in the middle of the phase I chain is converted into a CH⋯N contact in phase II

Phase transition

R Boese et al. - *Angew. Chem.* 2009, **121**, 769 –771

- ## T=195K
  - P_I=12.66(3)
  - P_II=12.71(3)
  - DP_I=12.61(3)
  - DP_II=12.64(3)
- ## T=220K
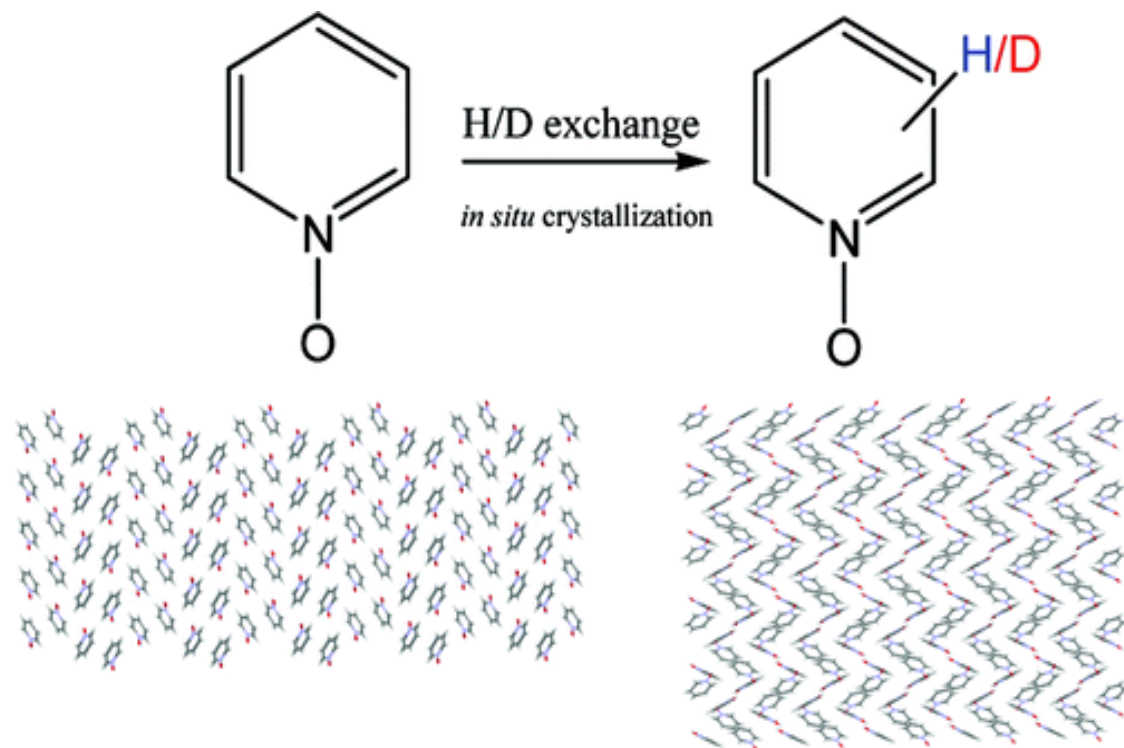 - P_I=14.37(3)
  - P_II=14.42(3)
  - DP_I=14.33(3)
  - DP_II=14.32(3)

At 0K DeltaE=0.3 kcal/mol
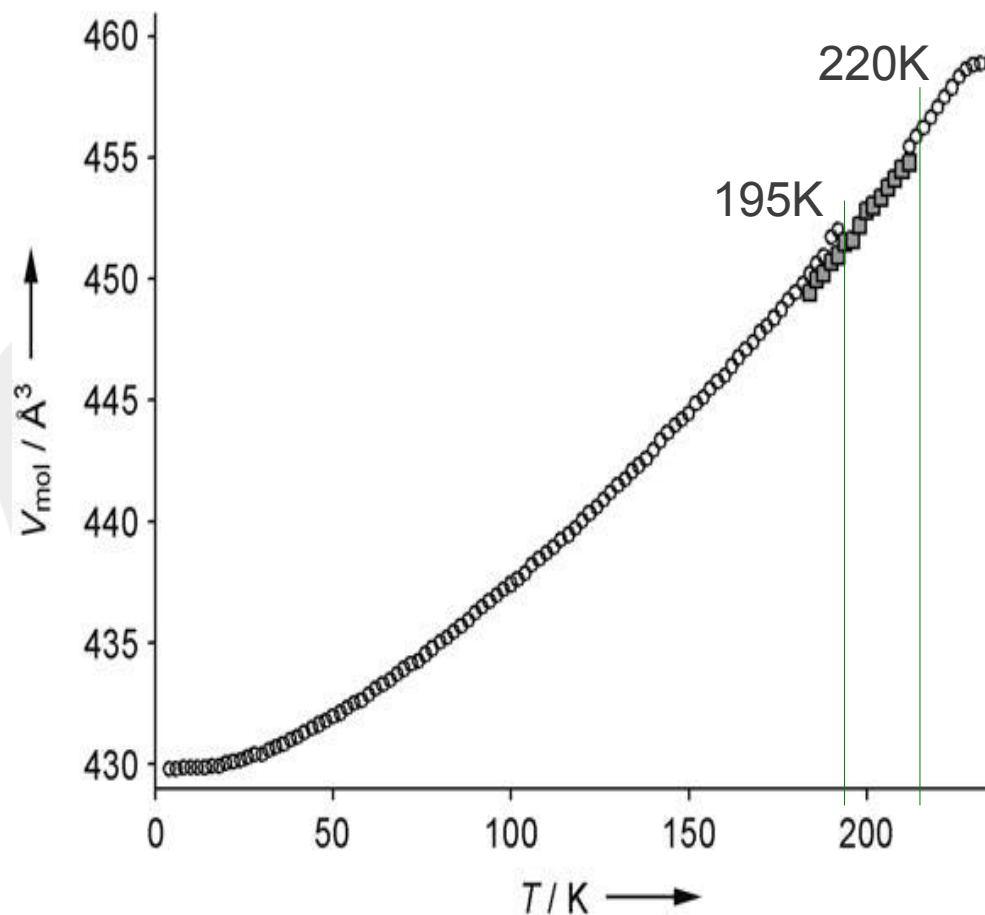
- Full deuteration → no change in polymorphism

- H2D3: new crystal packing

- Change in hydrogen bond network

T=225K P=1bar

NON DEUTERATED

- PNO2   11,38(3)
- PNO1   11,30(3)

T=225K P=1bar

Fully DEUTERATED

- D-PNO2   11,58
- D-PNO1   11,31

Partly DEUTERATED

- D3-PNO2   11,44
- D3-PNO1   11,49

M Cogoni V Vasylieva K Merz (in preparation)

# Rapid MD-based conformer discovery method for small molecules in water
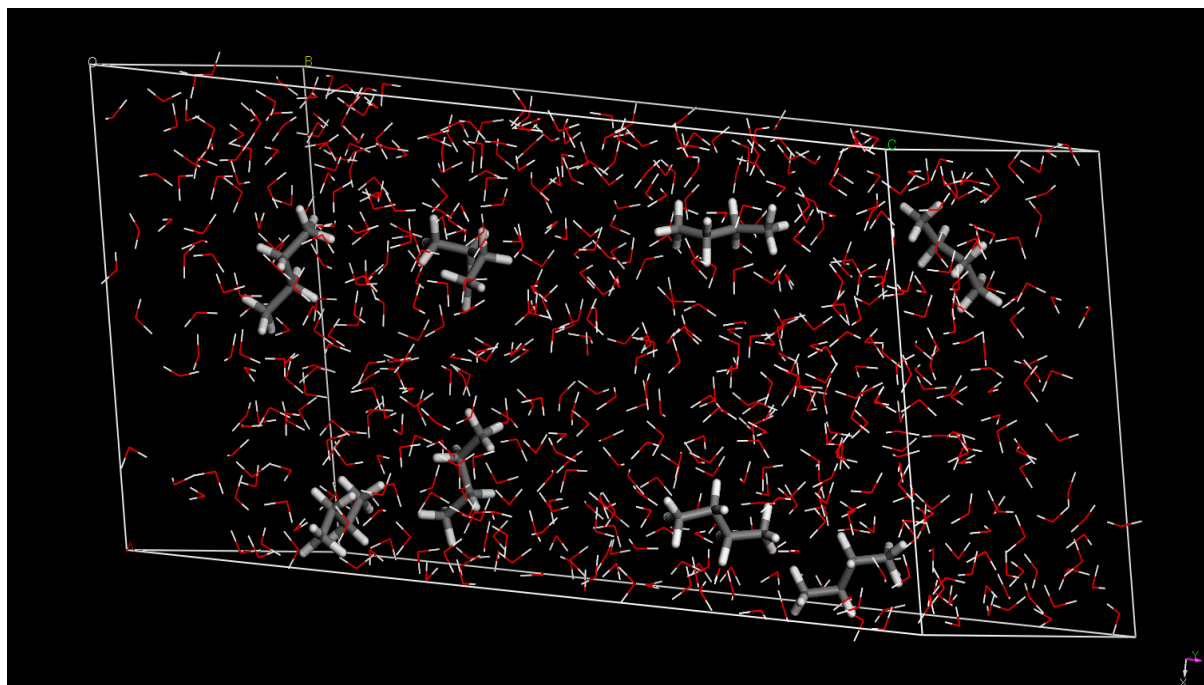
SMALL MOLECULES IN INTERACTIONS
INTERNATIONAL SYMPOSIUM MARCH 26 - 27 2012
BOCHUM

Vacuum Approach

- The easiest approach to the **exploration of the conformational landscape** for a given molecule is to treat it in vacuum (separated from its usual environment such as water) and **to apply a certain number of deformations to the initial structure**.
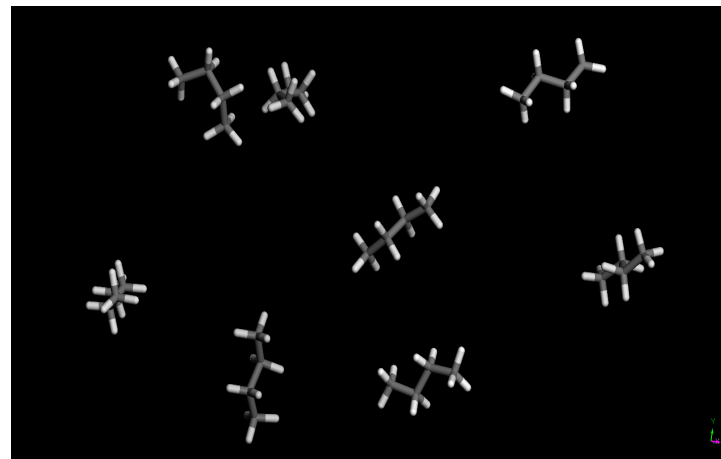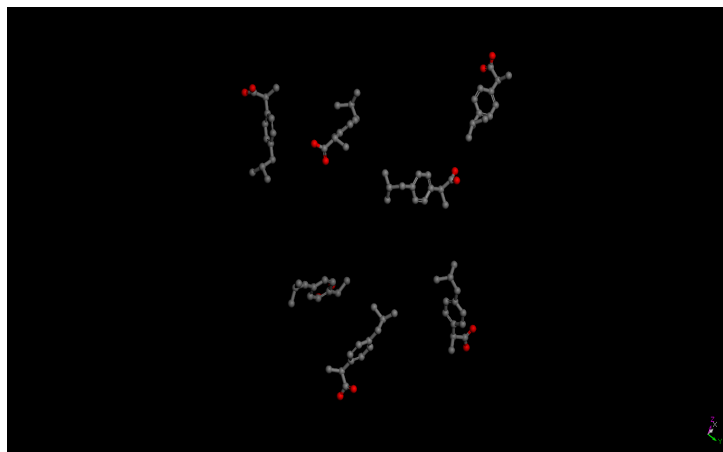
- *Repeating this action several times and optimizing the geometry for each different structural modification*, one finally obtains a set of (possibly) different conformations of the original.

Vacuum Approach

The problem with this approach is that one makes very bold assumptions such as:

- Molecule in vacuum behaves like in water

- Potential energy surface has many artificial local minima in which the optimization can easily be stuck

- Difficult to enumerate the possible structural deformations depending on the specific intramolecular bonds

A **different** approach: **Many molecules in a single water box**

We build a box of explicit water large enough to contain a set of several copies of the molecule under investigation

• The number of needed replicas is roughly estimated from the degrees of freedom associated with each bond type and scales with some power of molecular size.

• The molecular dynamics is performed in the NPT ensemble at ambient conditions with a quite long time step which in this case favours the exploration of the configurational space (LTMD).

• In this specific showcase we used the COMPASS forcefield as implemented in Materials Studio, and verified the results on DL_POLY with the simpler Dreiding and PCFF force fields.

Showcases: Butane and Ibuprofen

 For both molecules we have been able to reproduce the known energetically favoured structures

• To obtain the final structures we have the flexibility to operate the minimization procedure (Conjugate Gradients or Steepest Descent methods) both on the solvated box or we can remove the water molecules and proceed.

• Sometimes the minimization gets stuck in some artificial minimum typical of this kind of force fields with rather short cutoffs.

• The final clustering procedure (at this time still under heavy development) gets rid of the unstable conformers.
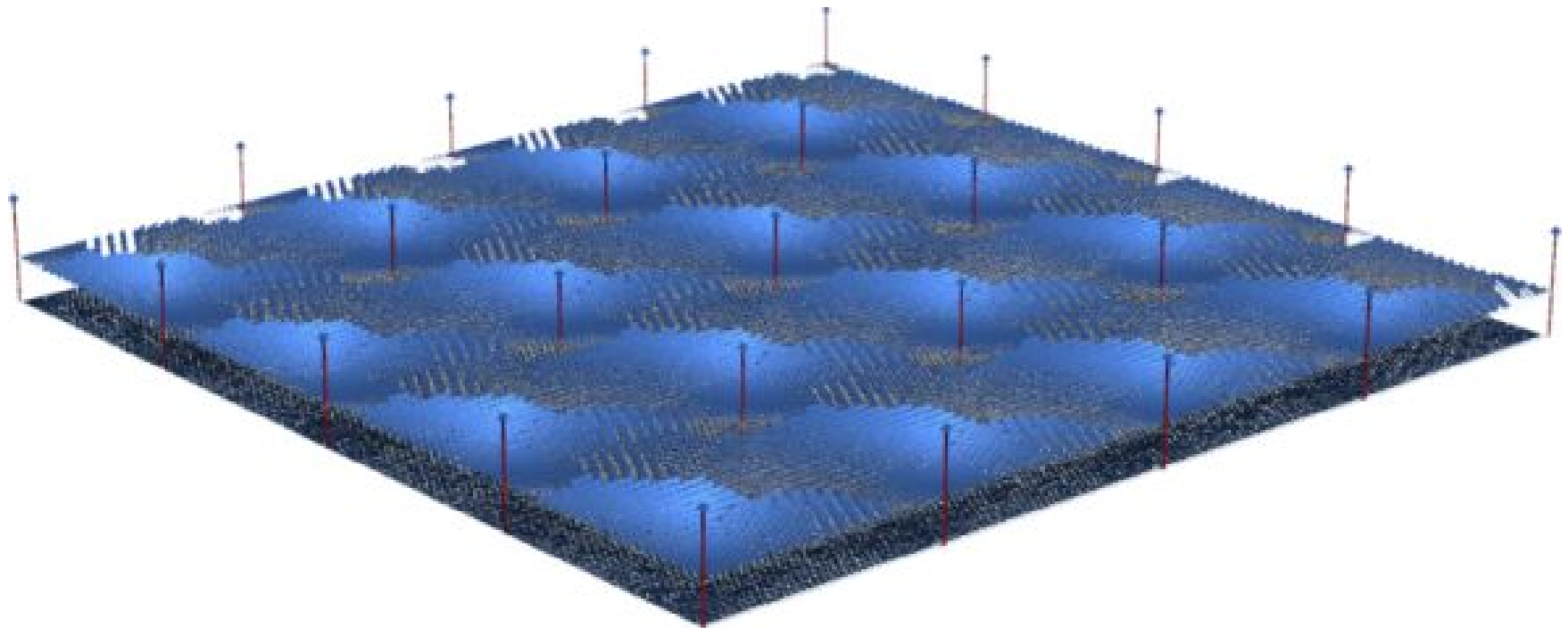
Clustering of conformers
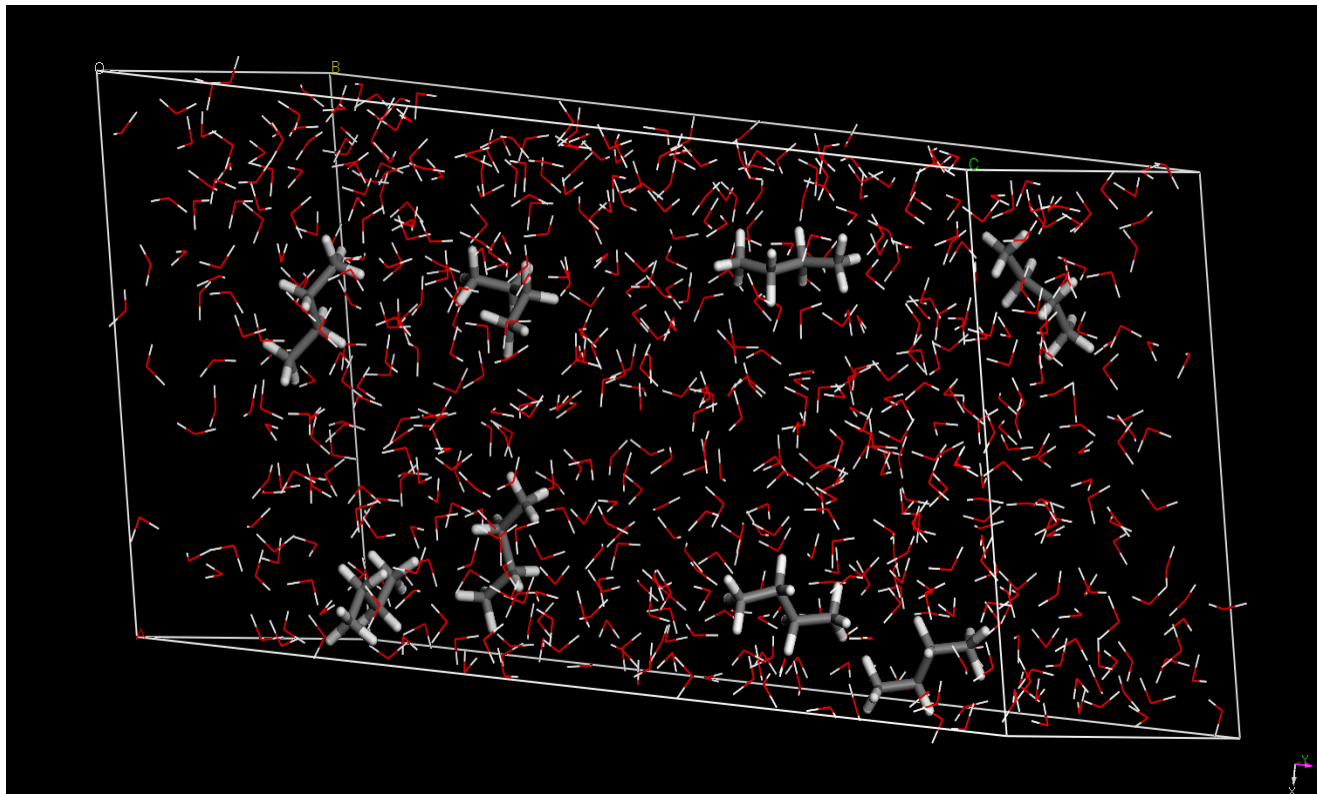
dendrogram
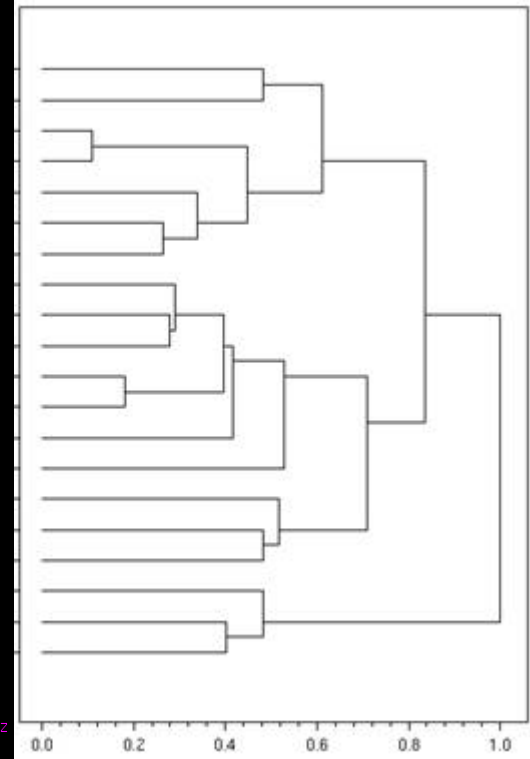
similarity index

Smart Multiple Tower Solar Plants

C o n f i d e n t i a l