Workshop 2

- Examples from metaD and TPS
- Details of the *shooting* approach
- Details of MD engines

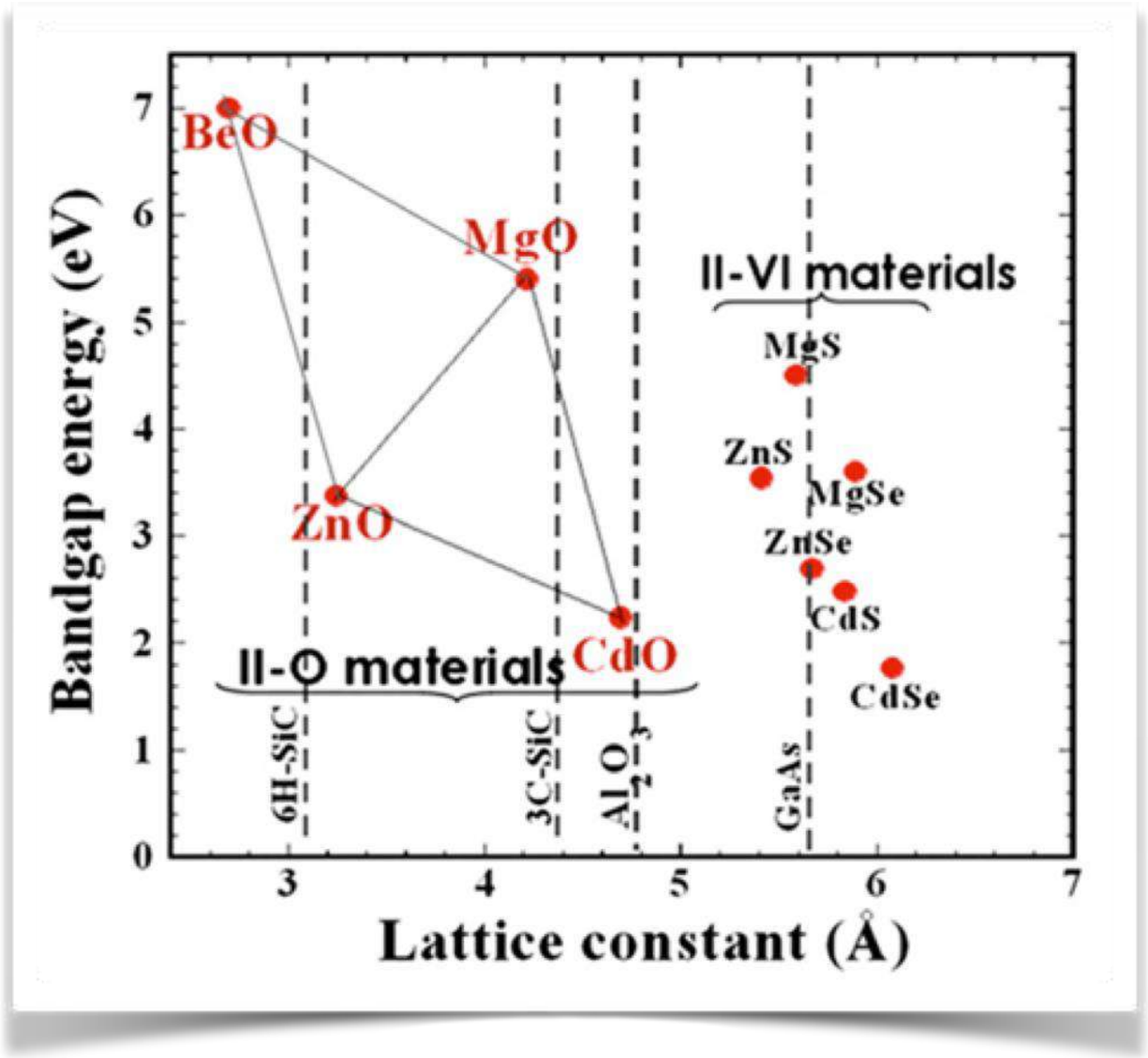
Metashooting

- combine metaD and TPS
- based on an external driver
- cp2k/plumed/shooter

ZnO

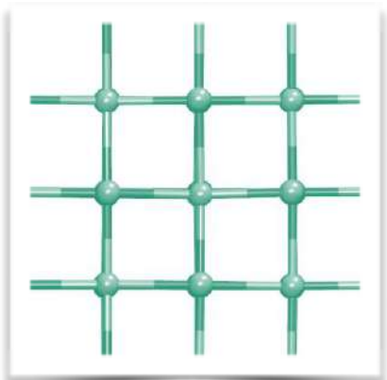
Binary oxide, small lattice constant (d shell)

Wurtzite normal state, zincblende metastable, transformation to B1 (rocksalt) under pressure

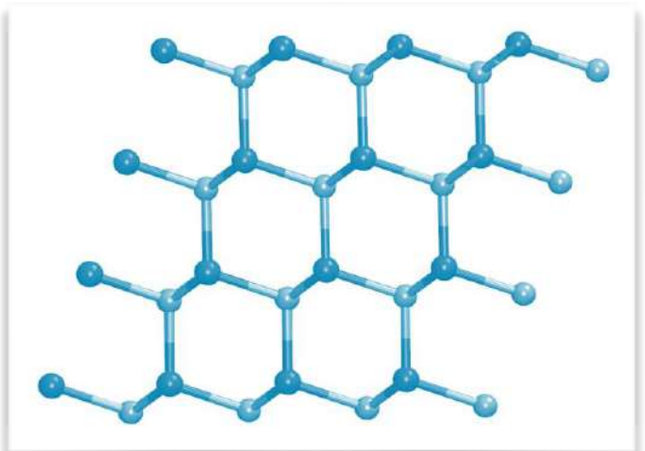


Zinc Oxide (ZnO)

B4



B1



B3

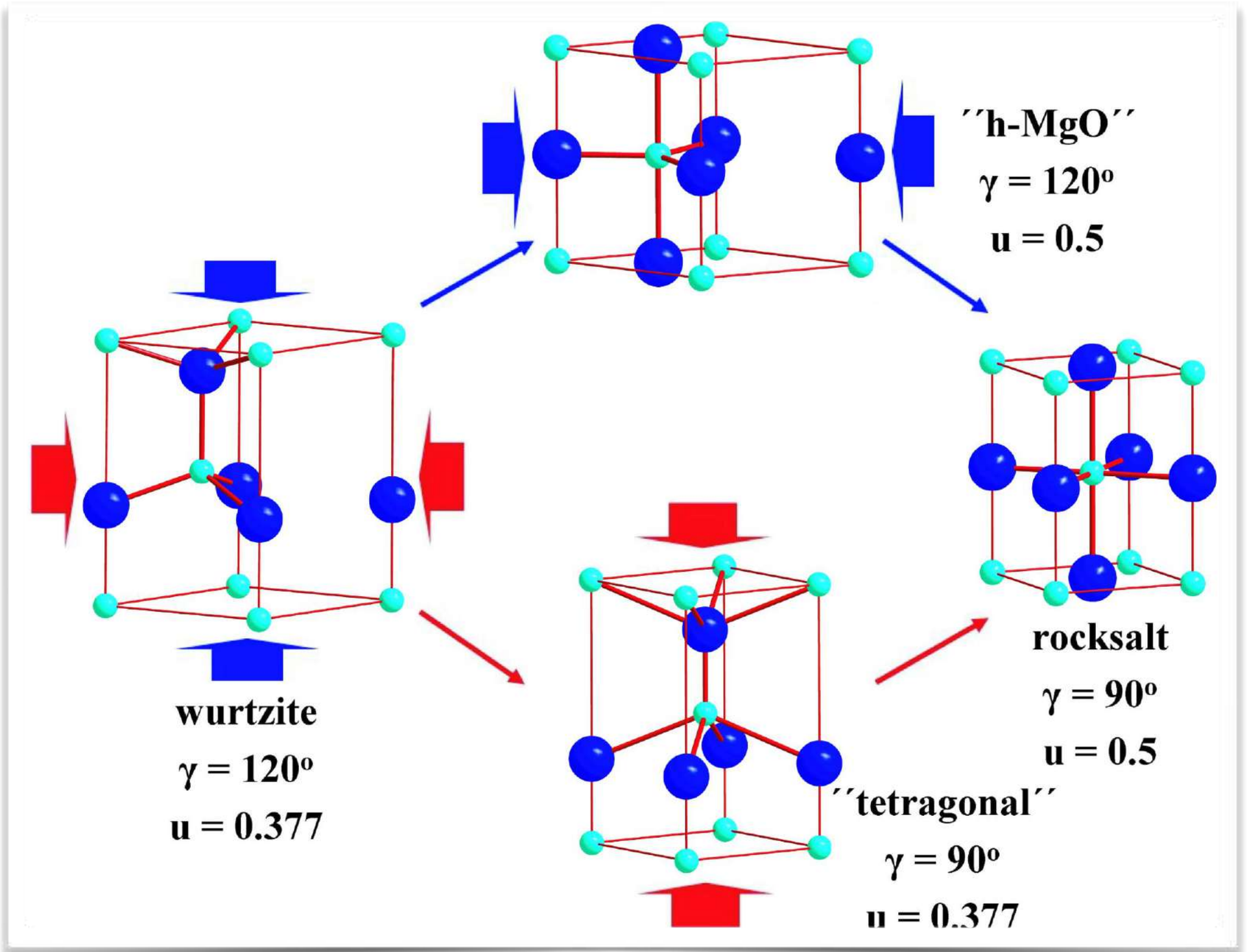
Hexagonal **wurtzite** (WZ, B4, $P6_3mc$) structure under ambient conditions

High pressure **rocksalt** (RS, B1, Fm3m) accessible under extreme conditions

Cubic **zincblende** (ZB, B3, F43m), also known as sphalerite, is metastable

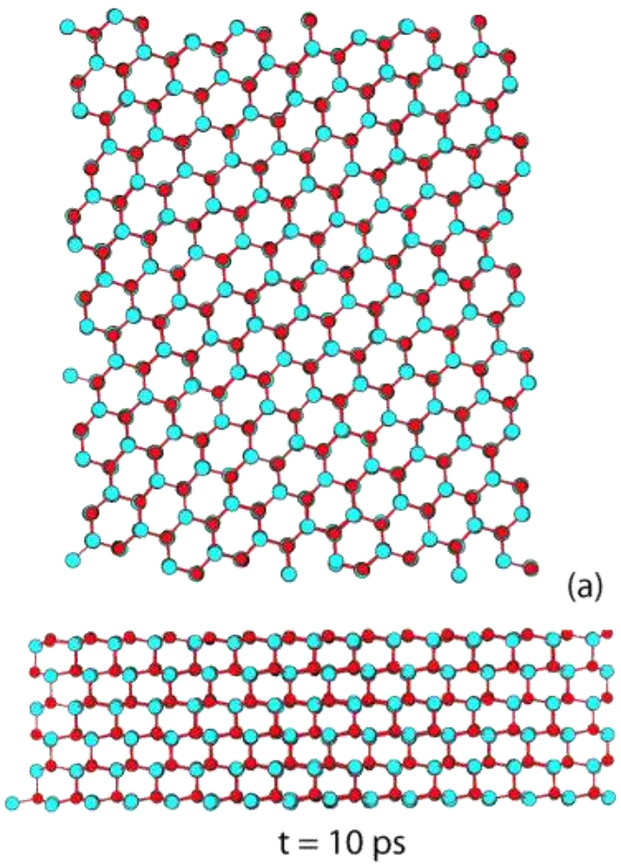
Intermediate Competition

GaN
ZnO



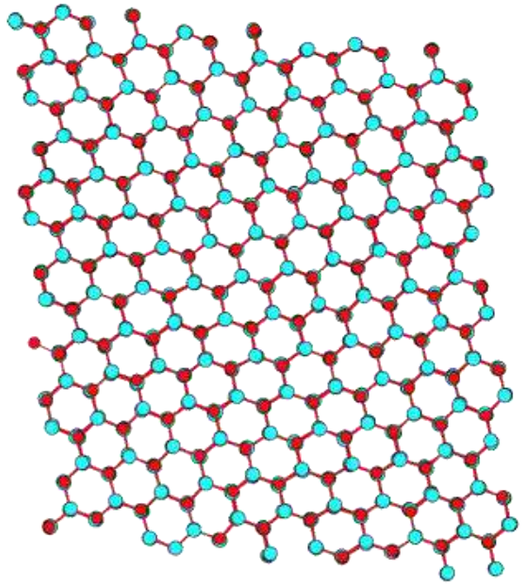
A. M. Saitta and F. Decremps, PRB 70, 035214 (2004).
S. E. Boulfelfell, S. Leoni, PRB 78, 125204 (2008)

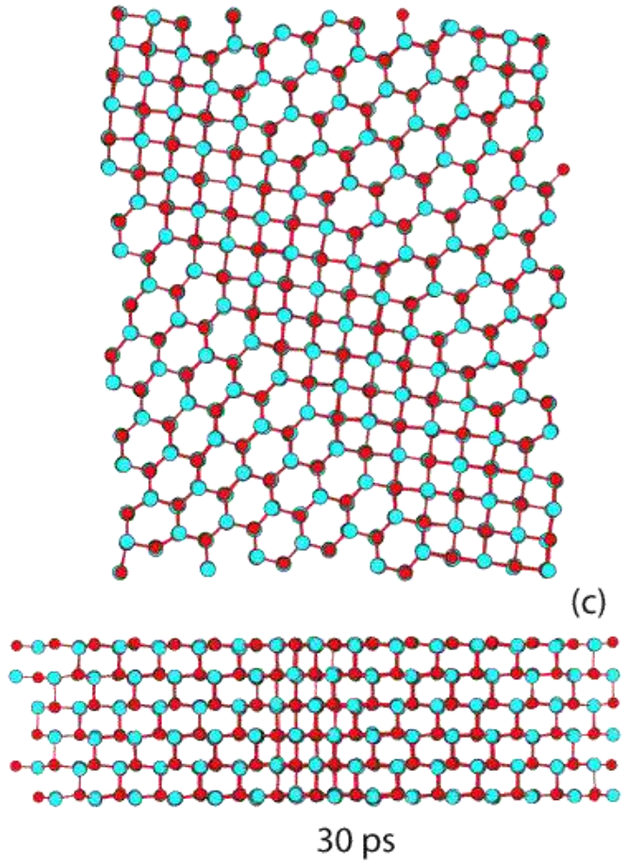
ZnO: Competing Intermediates



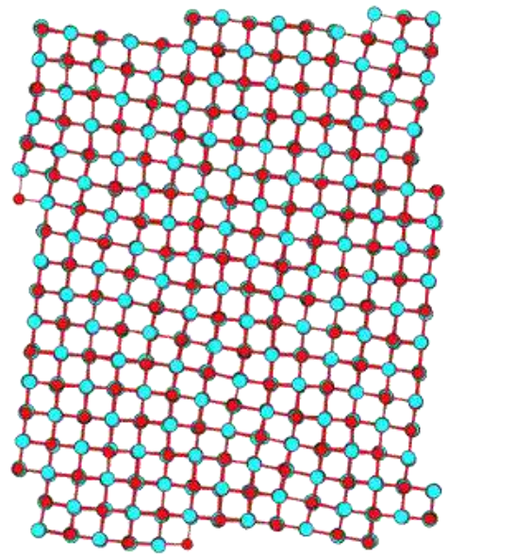
B4

iH





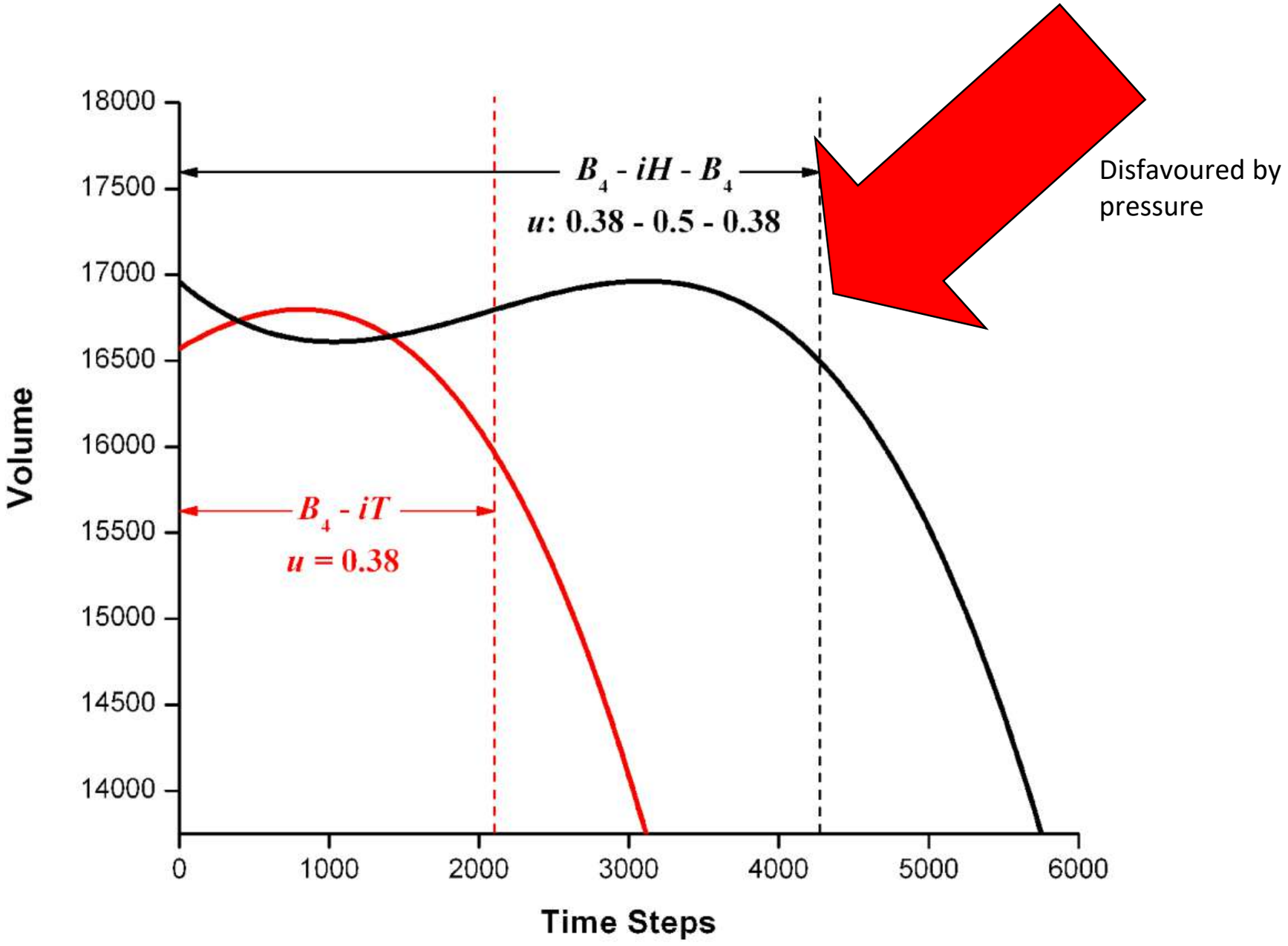
B1



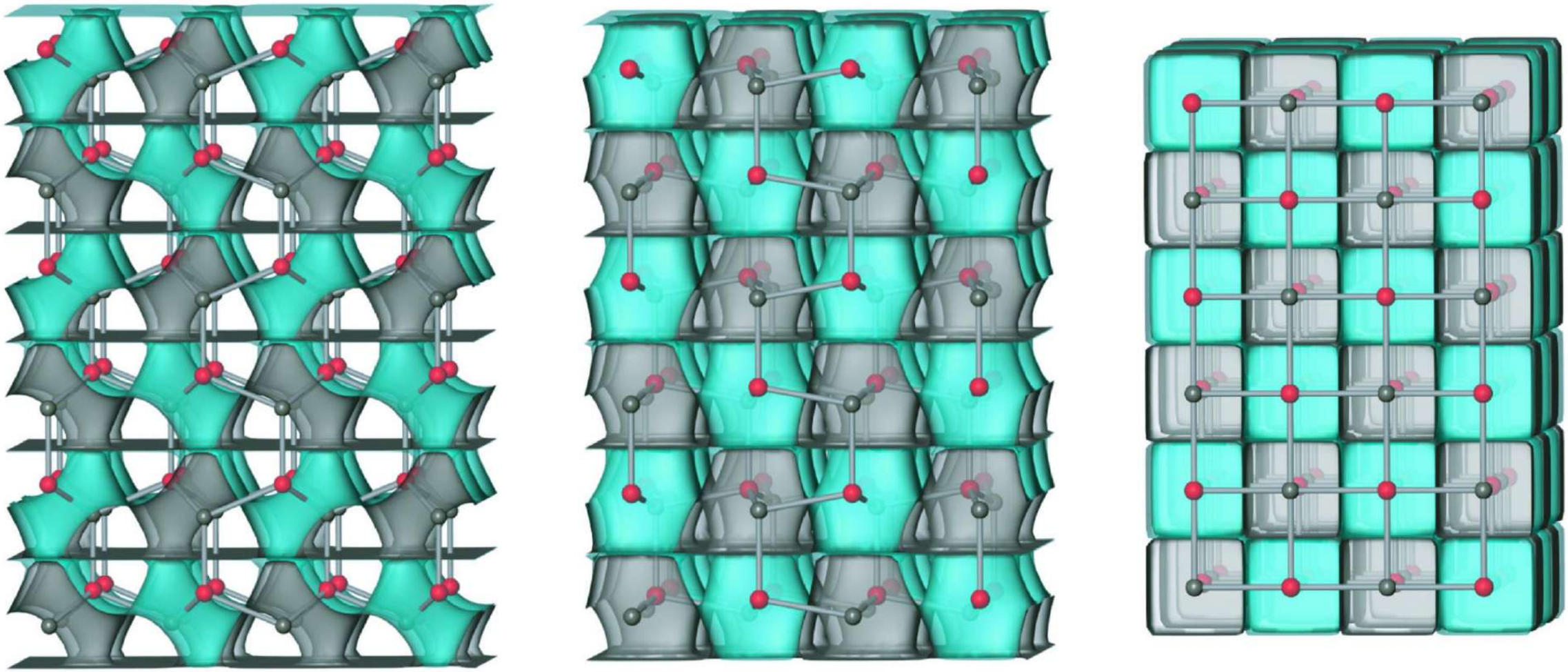
long lived intermediate

S. E. Boulfelfell, S. Leoni, PRB 78, 125204 (2008)

Effect/role of pressure



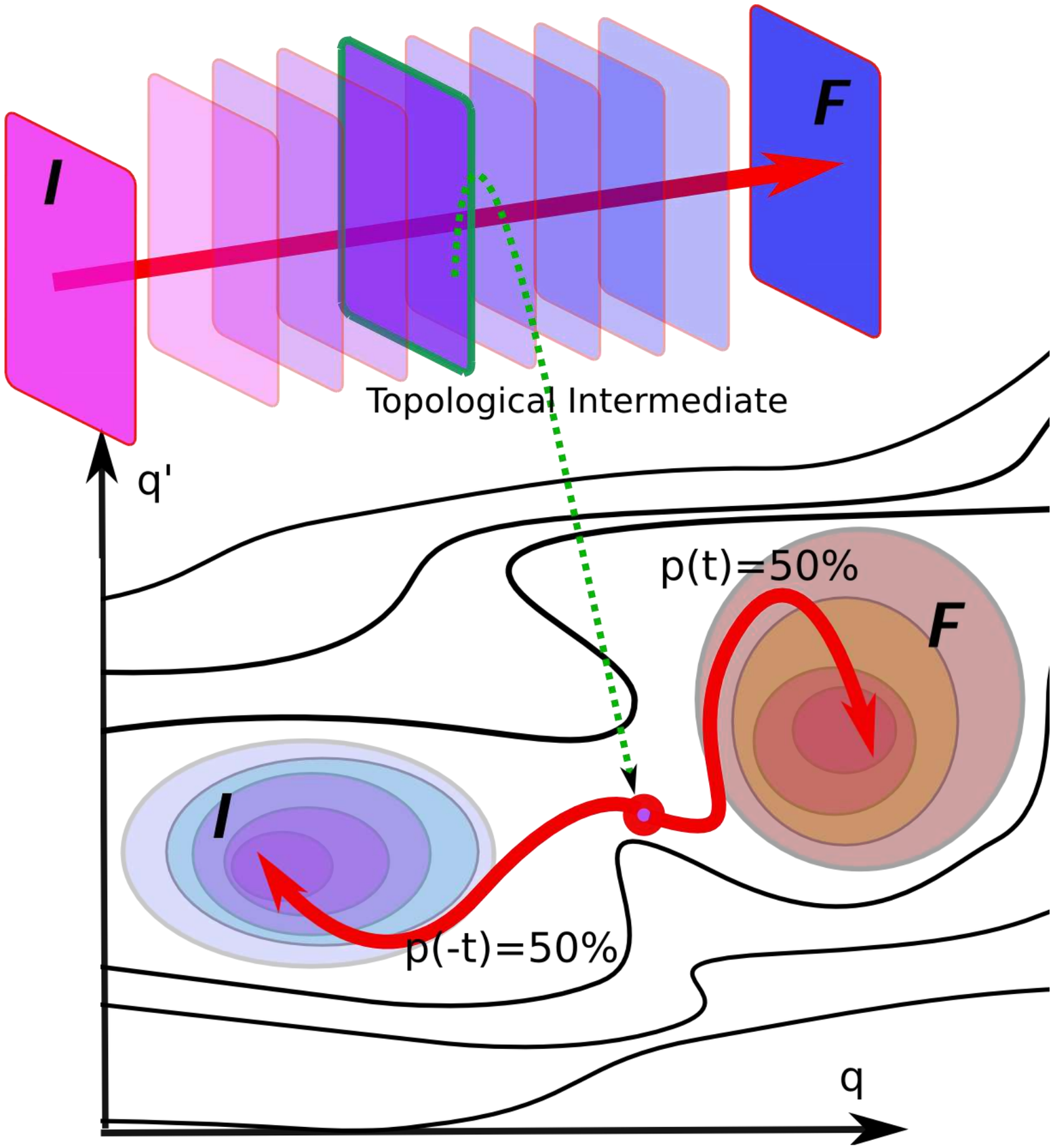
B4 to B1 Phase Transition



(wurtzite) Topological Intermediate (rocksalt)

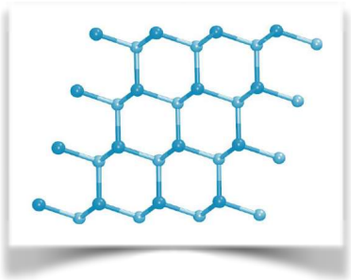
B4 → **B1**

Topology

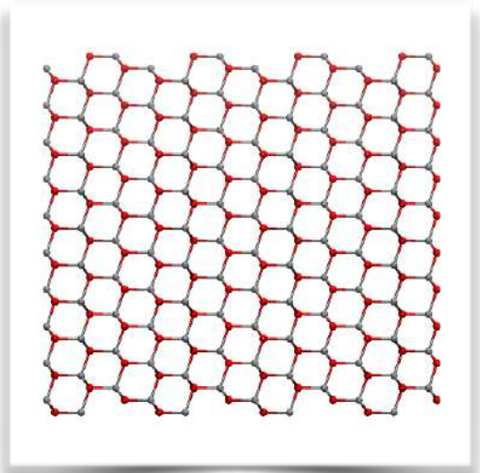


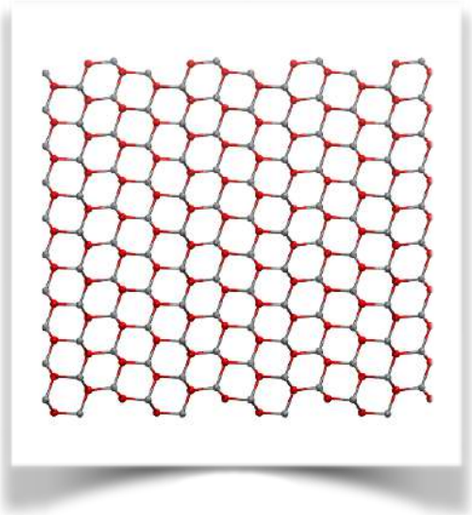
MD

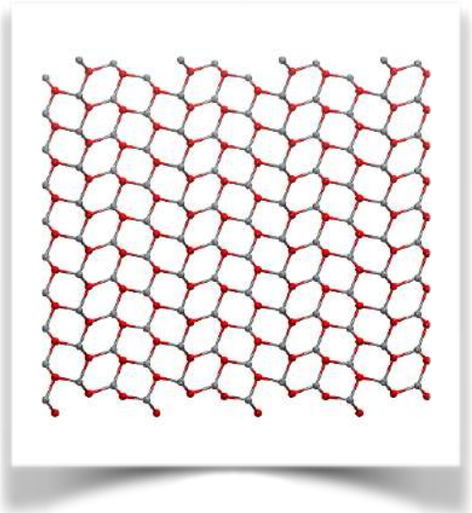
First Trajectory

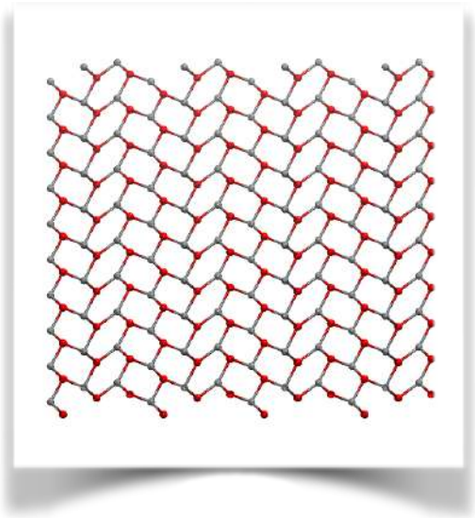


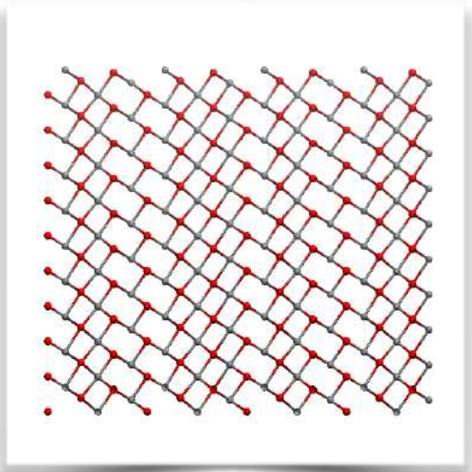
B3

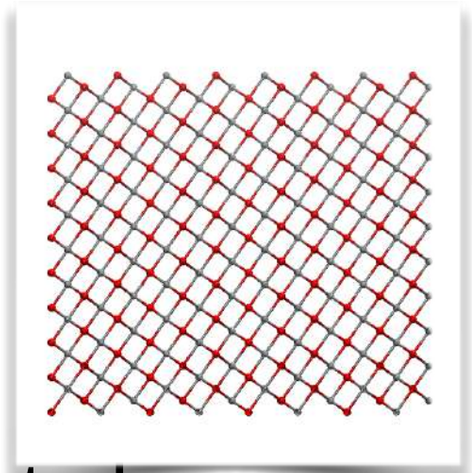


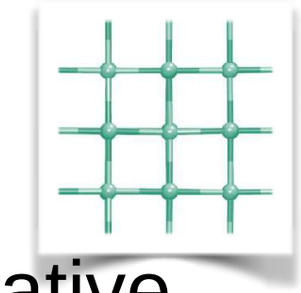








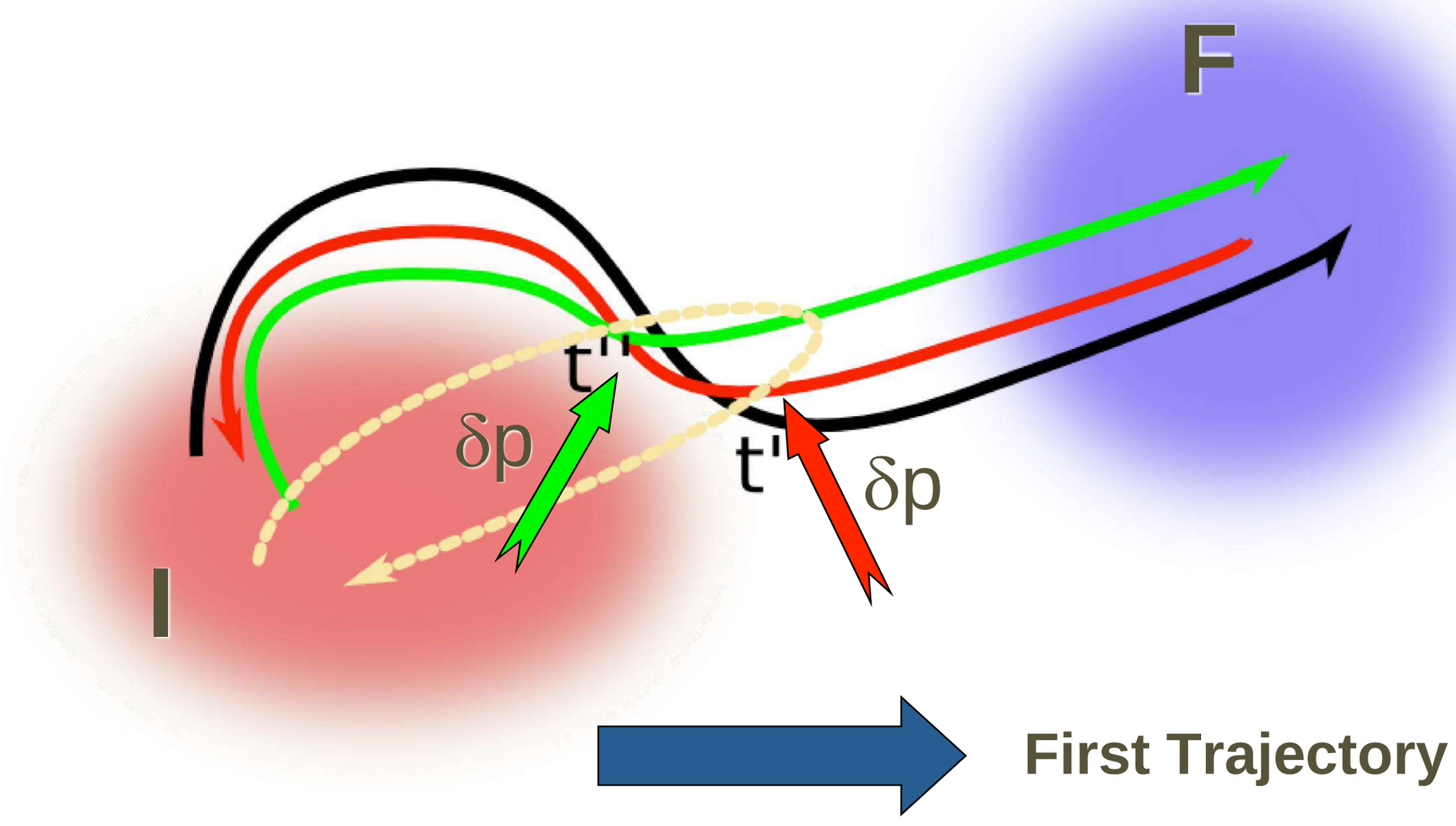




A given trajectory does not need to be representative of the REAL transformation mechanism (TPS will weight its importance)

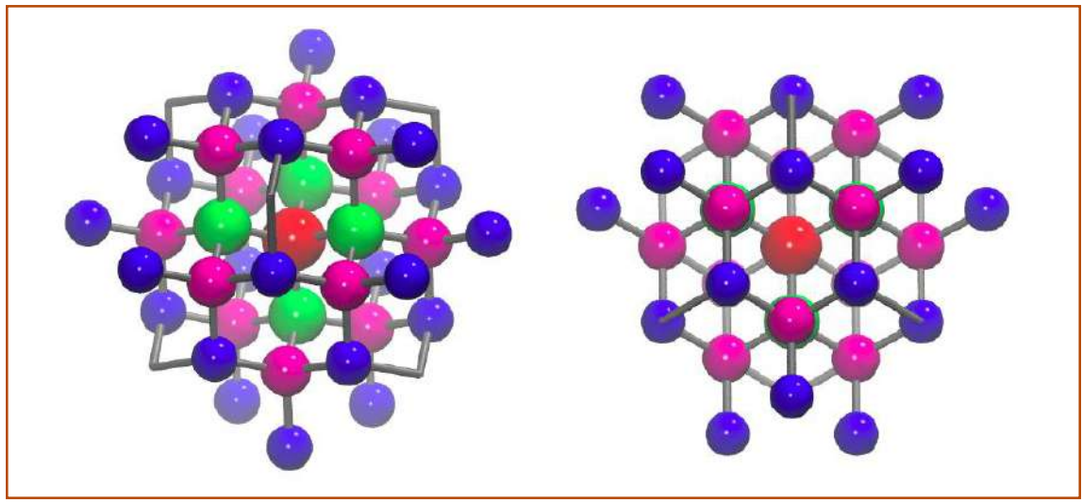
B1

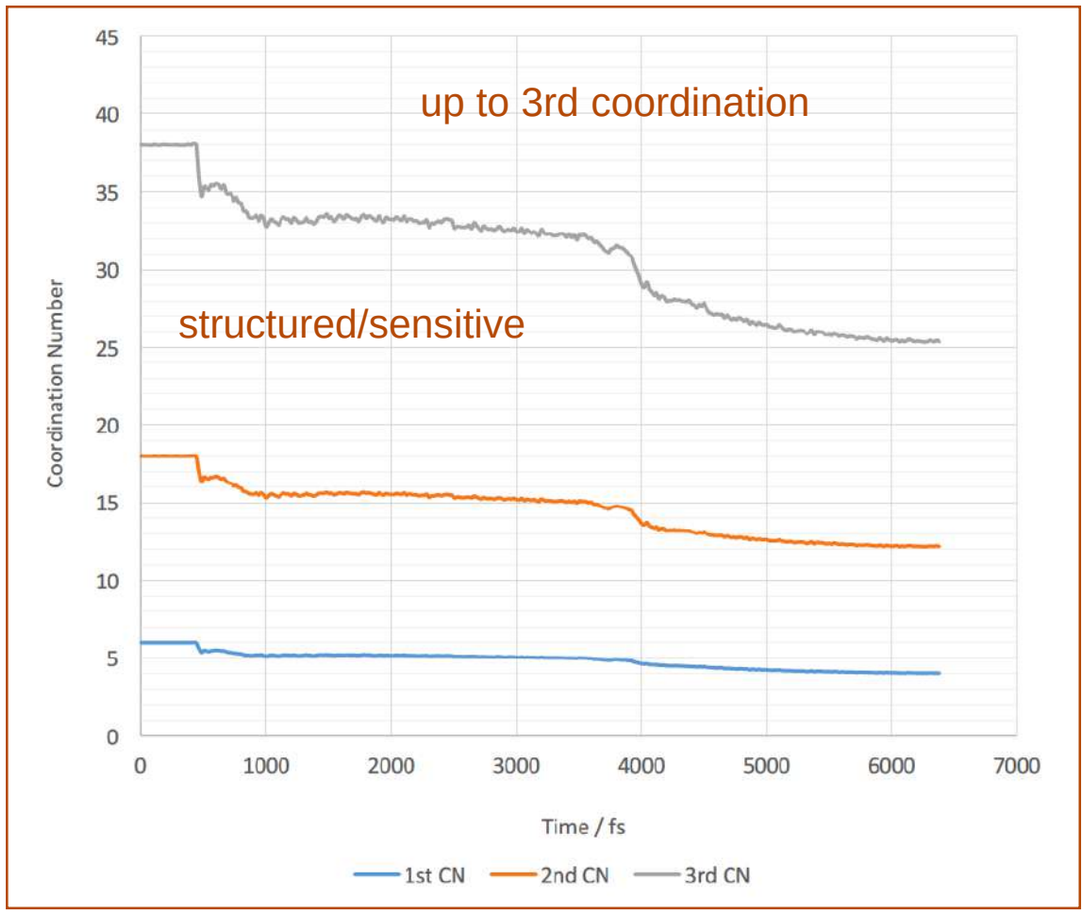
Monte Carlo in Trajectory Space

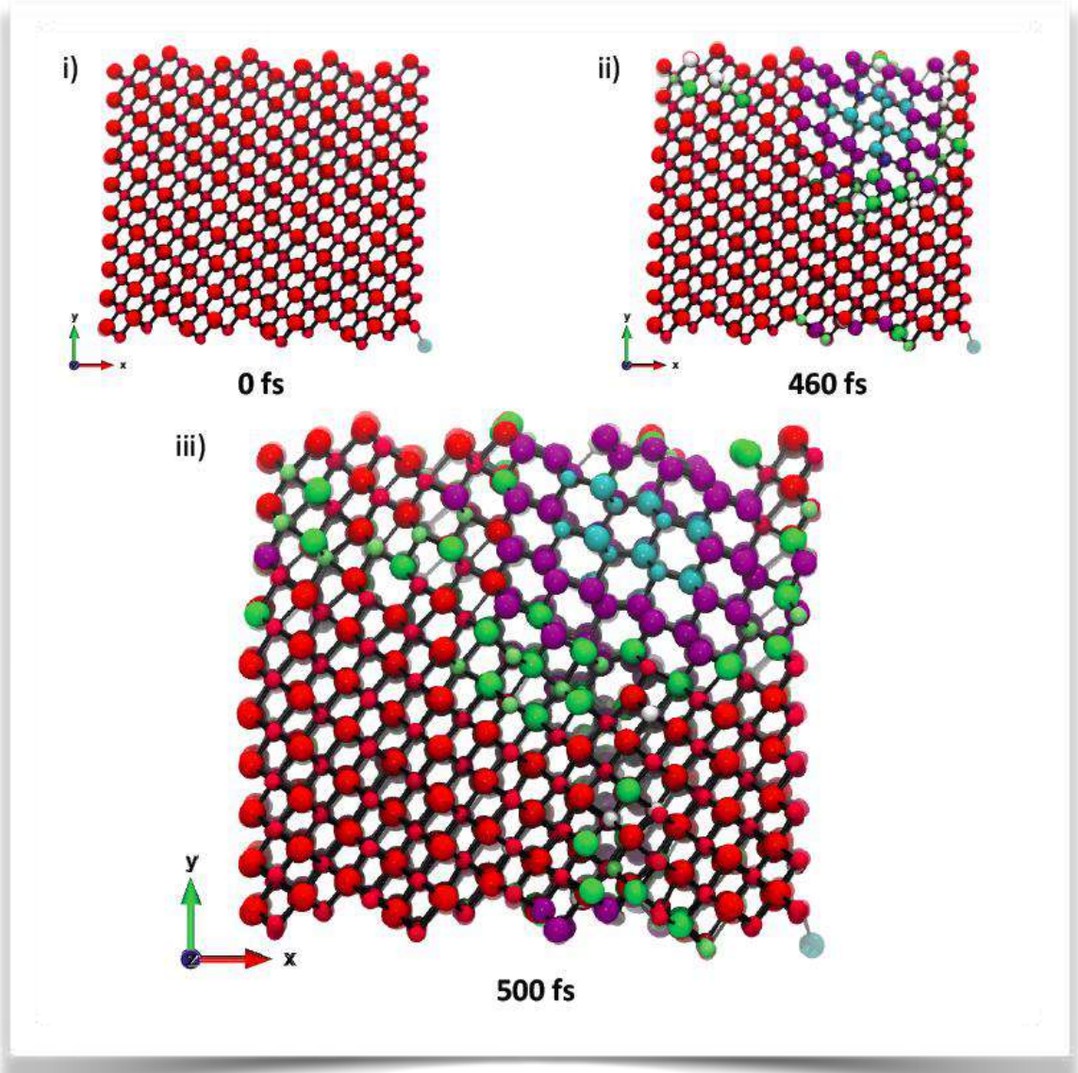


„Shooting Algorithm“ (C. Dellago, D. Chandler)

Order Parameter (CV) - coordination number/sequence

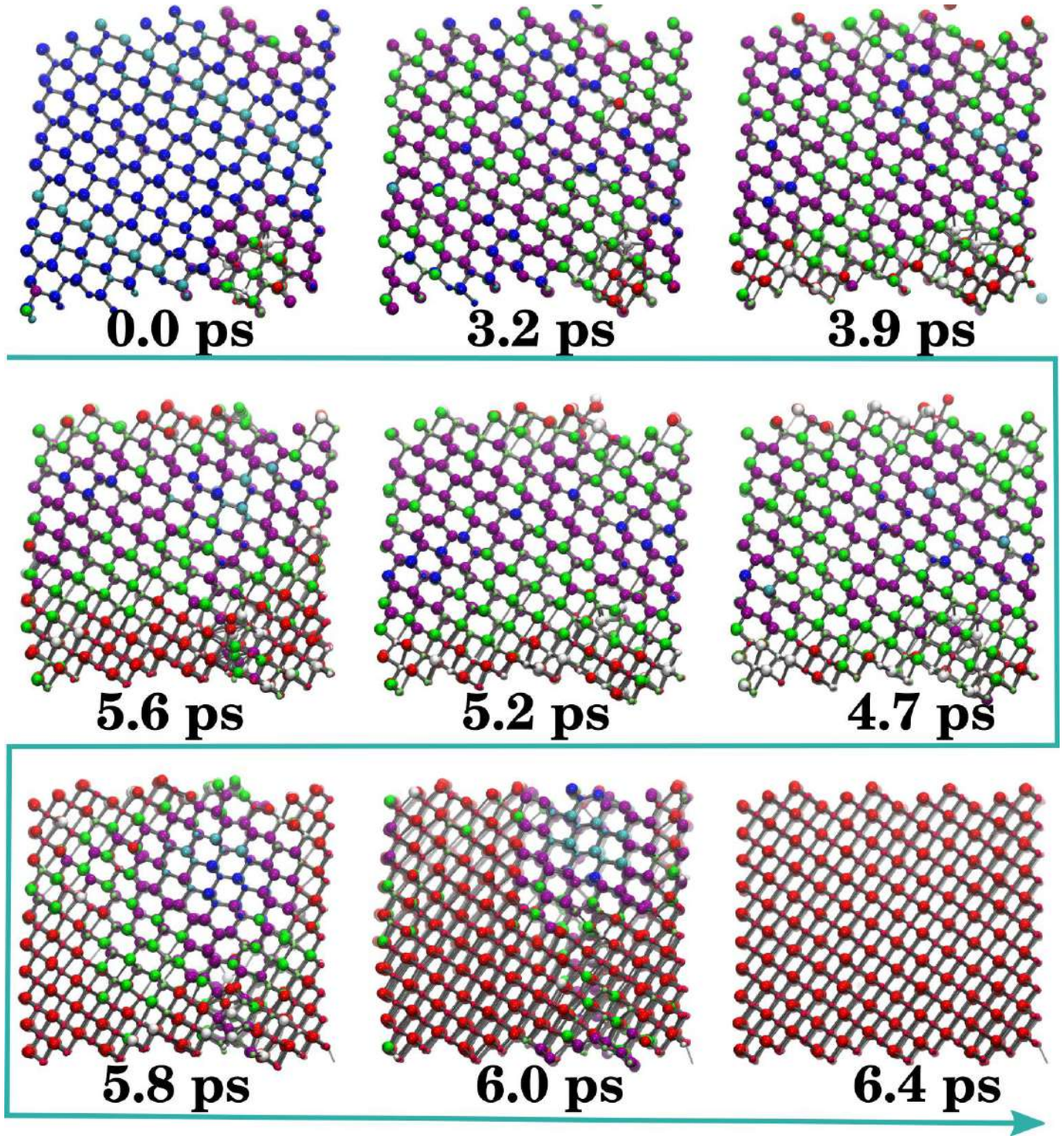






Mechanism from TPS - forwards

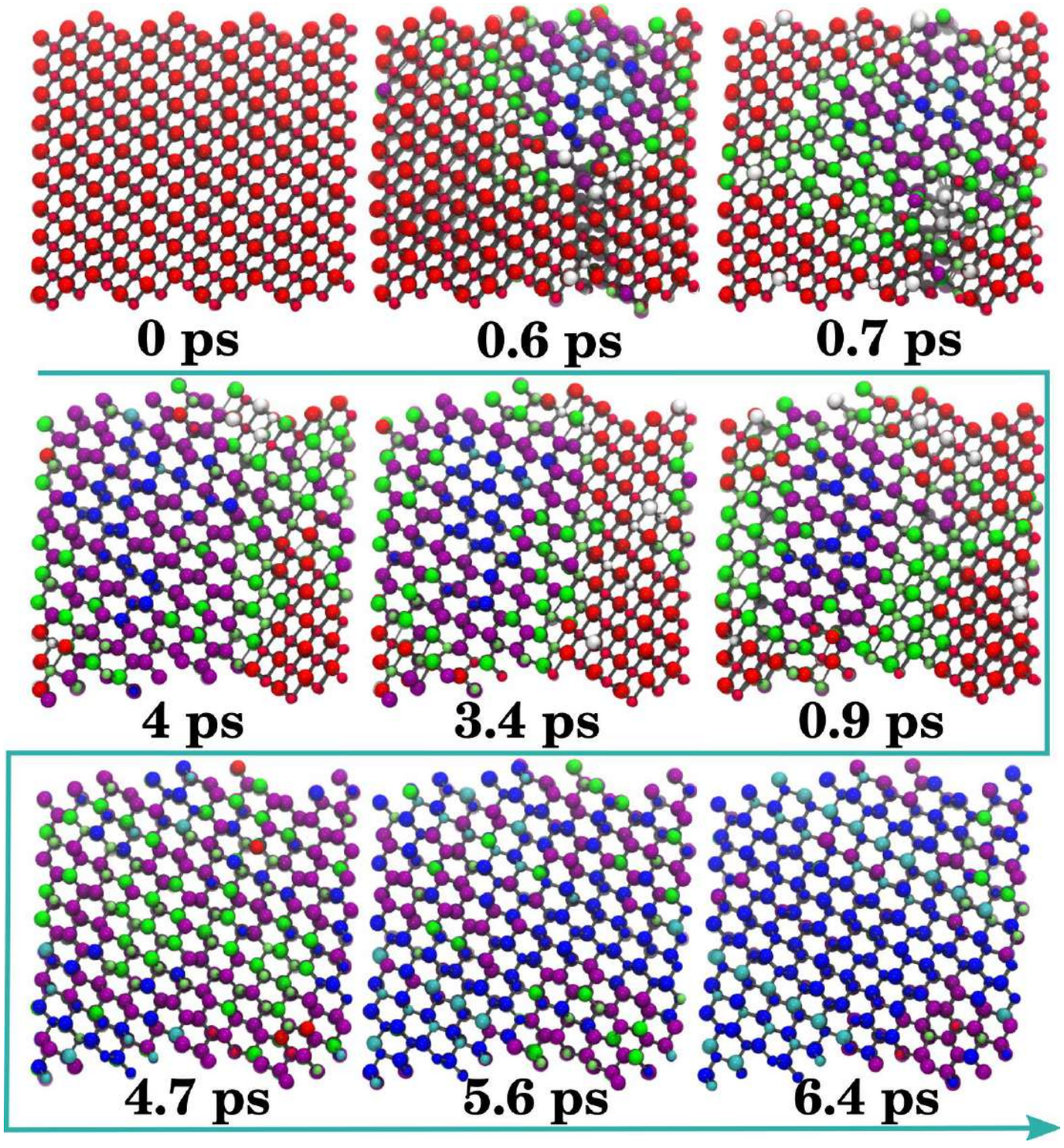
B3



B1

Mechanism from TPS - backwards

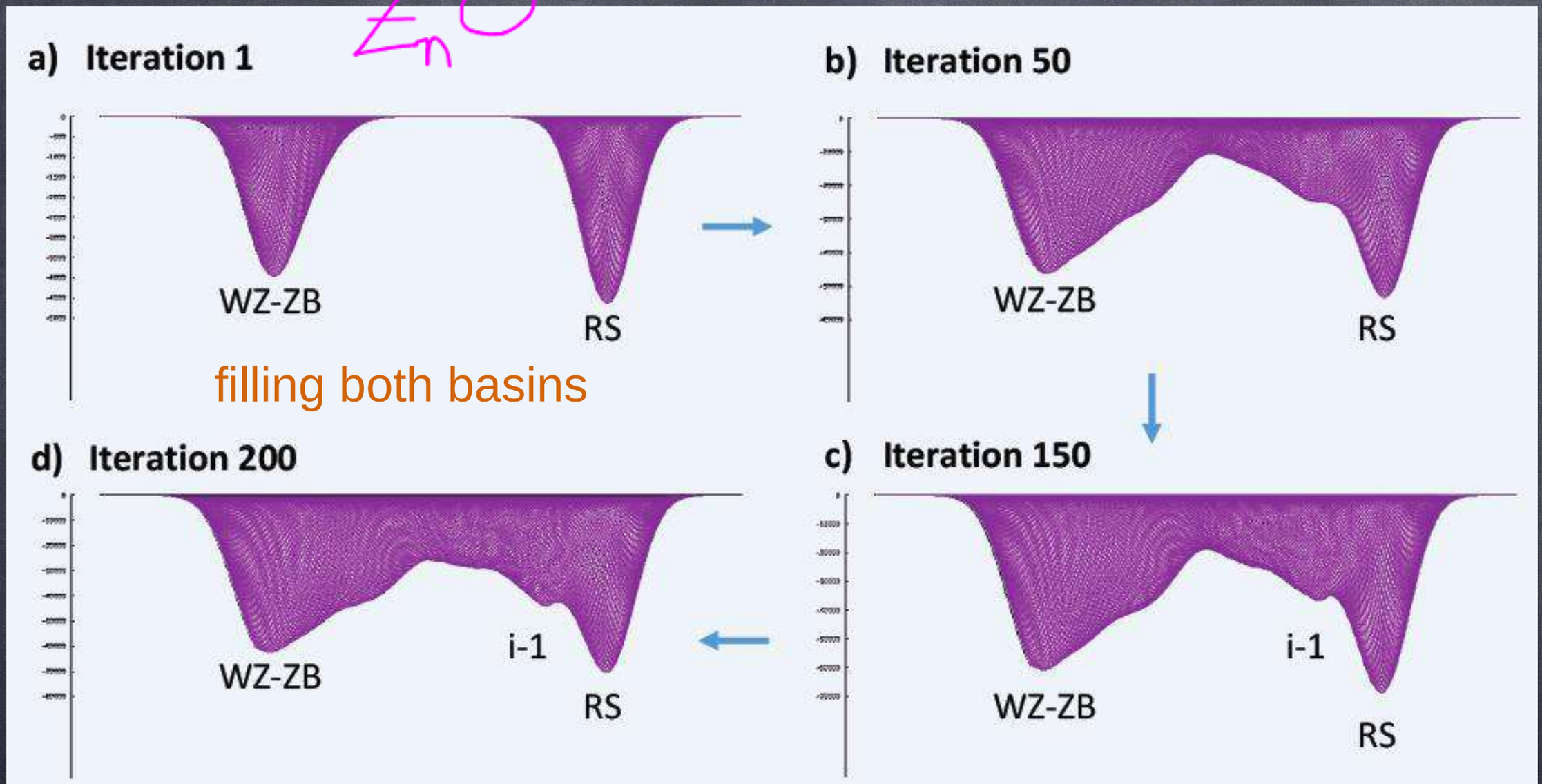
B1



B4/B3

Free Energy Reconstruction (TPS/metaD)

ZnO



CV controlled by TPS,
PE filling by Gaussians

1. TPS step 1: shoot off a new trajectory and time propagate.

2. MetaD step 1: deposit a bias using a metadynamics scheme, locally partially filling the as yet uncharacterised energy well.

3. TPS step 2: Generate another trajectory (as in step 1) and propagate into the now biased basin A, to generate a true MD velocity distribution on the biased potential.

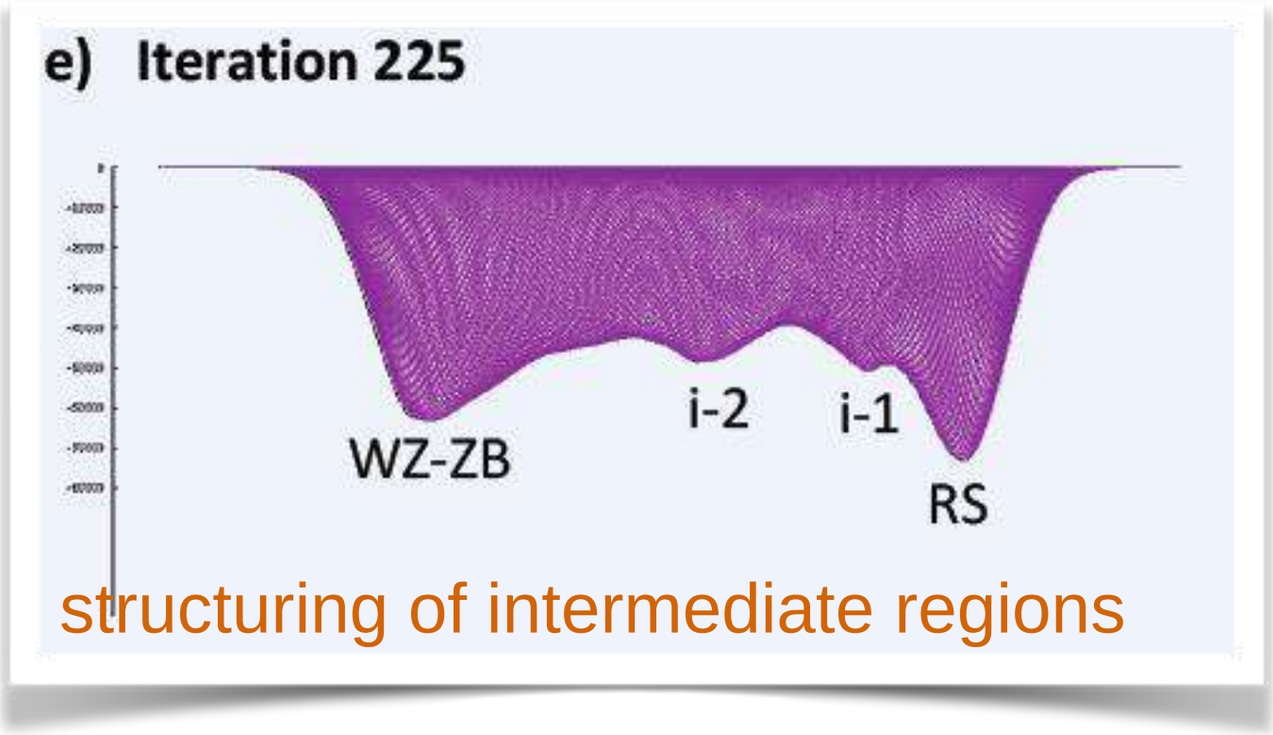
4. TPS step 3: shoot off a new trajectory from the same snapshot as above and propagate, only this time backwards in time, to basin B.

5. MetaD step 2: In basin B, apply the same metadynamics scheme as above for a number of steps, in order to partially fill this second basin of attraction.

6. TPS step 4: Re-shoot a novel trajectory from a random snapshot of the previous trajectory. Propagate into the now biased basin B.

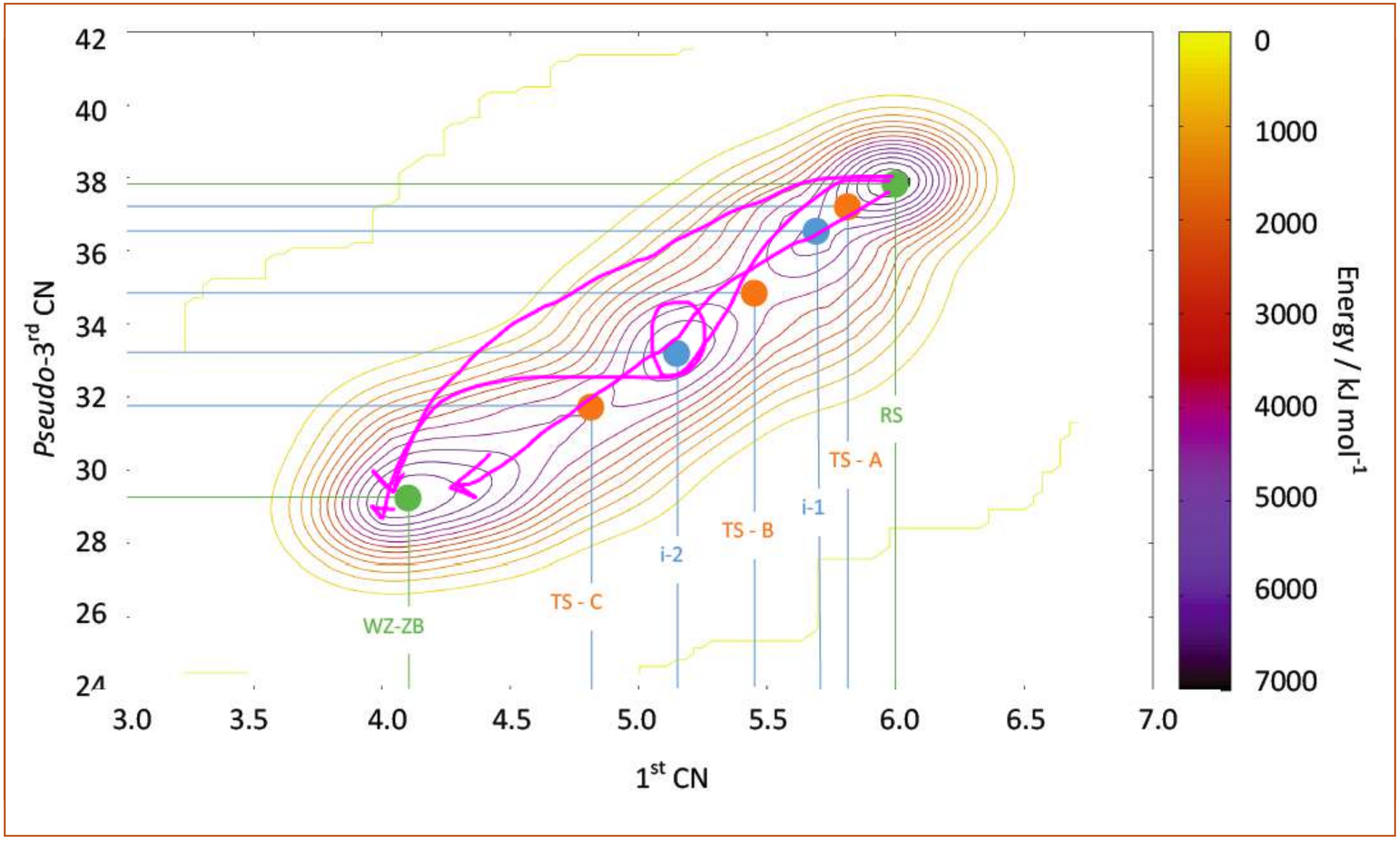
Repeat the above iterations of metadynamics and TPS moves, until the underlying free energy profile is fully converged.

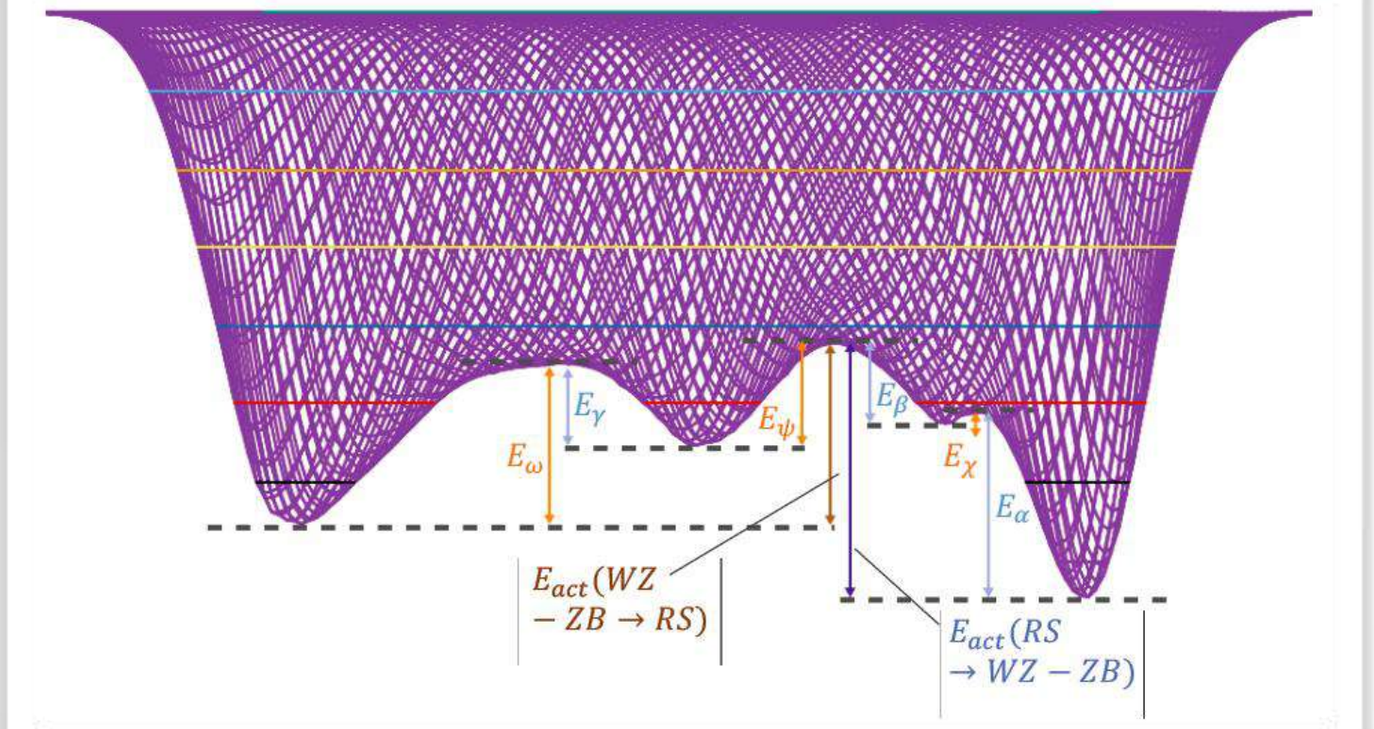
S.A. Jobbins, S.E. Boulfelfel, S. Leoni, Faraday Discussions (2018)



Population of intermediate basins in the late stage only

2D map of two-dimensional CV

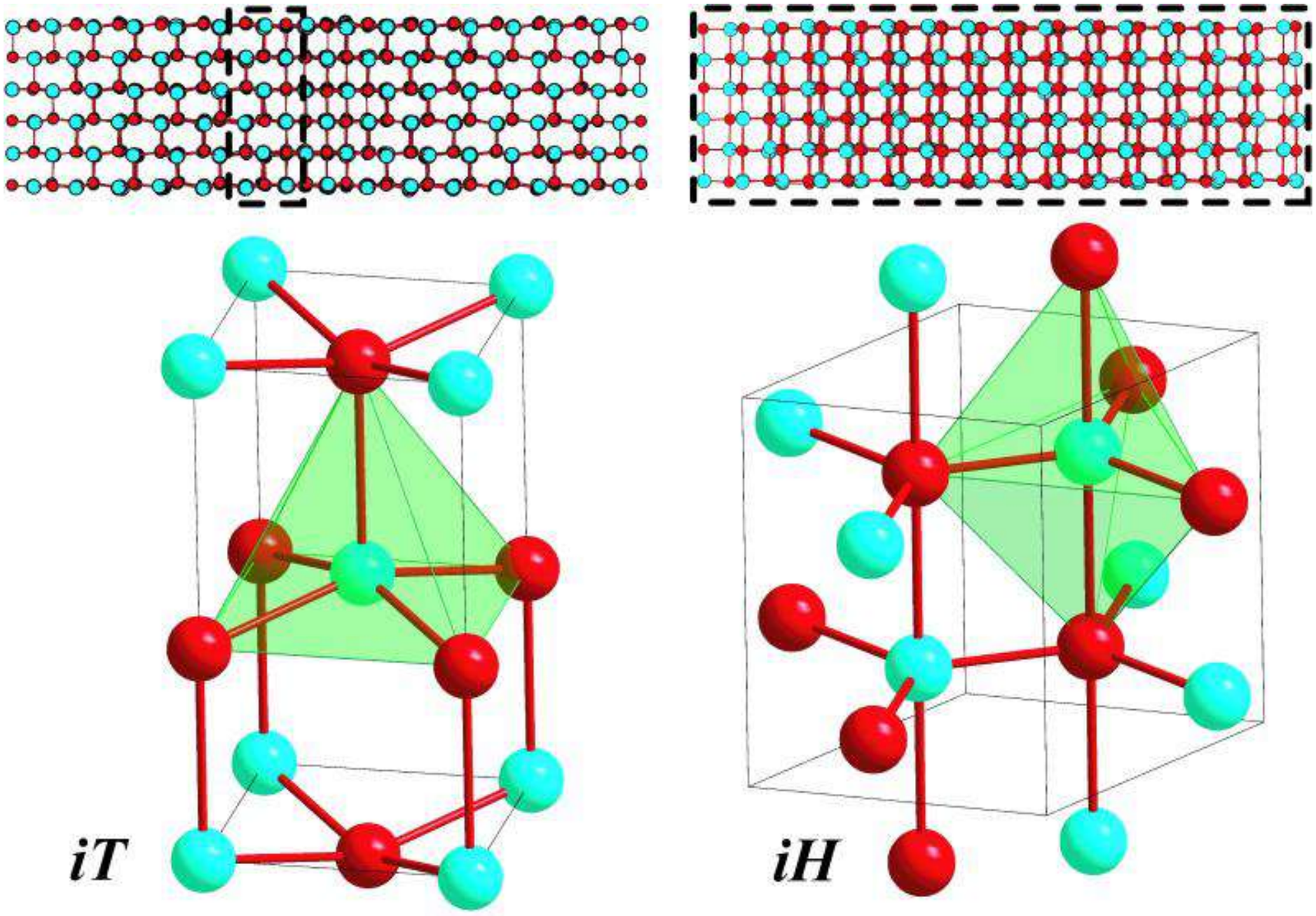




	Energy /kJ mol^{-1}	Energy /kJ mol^{-1} pair^{-1}	Energy /eV pair^{-1}	Energy /k_BT pair^{-1}
E_χ	20 447.0	17.1	0.18	6.8
E_ψ	13 085.9	10.9	0.11	4.4
E_ω	1 357.0	1.3	0.01	0.5
$E_{act}(WZ - ZB \rightarrow RS)$	23 049.1	19.2	0.20	7.7

	Energy /kJ mol^{-1}	Energy /kJ mol^{-1} pair^{-1}	Energy /eV pair^{-1}	Energy /k_BT pair^{-1}
E_χ	20 447.0	17.1	0.18	6.8
E_ψ	13 085.9	10.9	0.11	4.4
E_ω	1 357.0	1.3	0.01	0.5
$E_{act}(RS \rightarrow WZ - ZB)$	32 565.9	27.1	0.28	10.9

i2 - intermediate

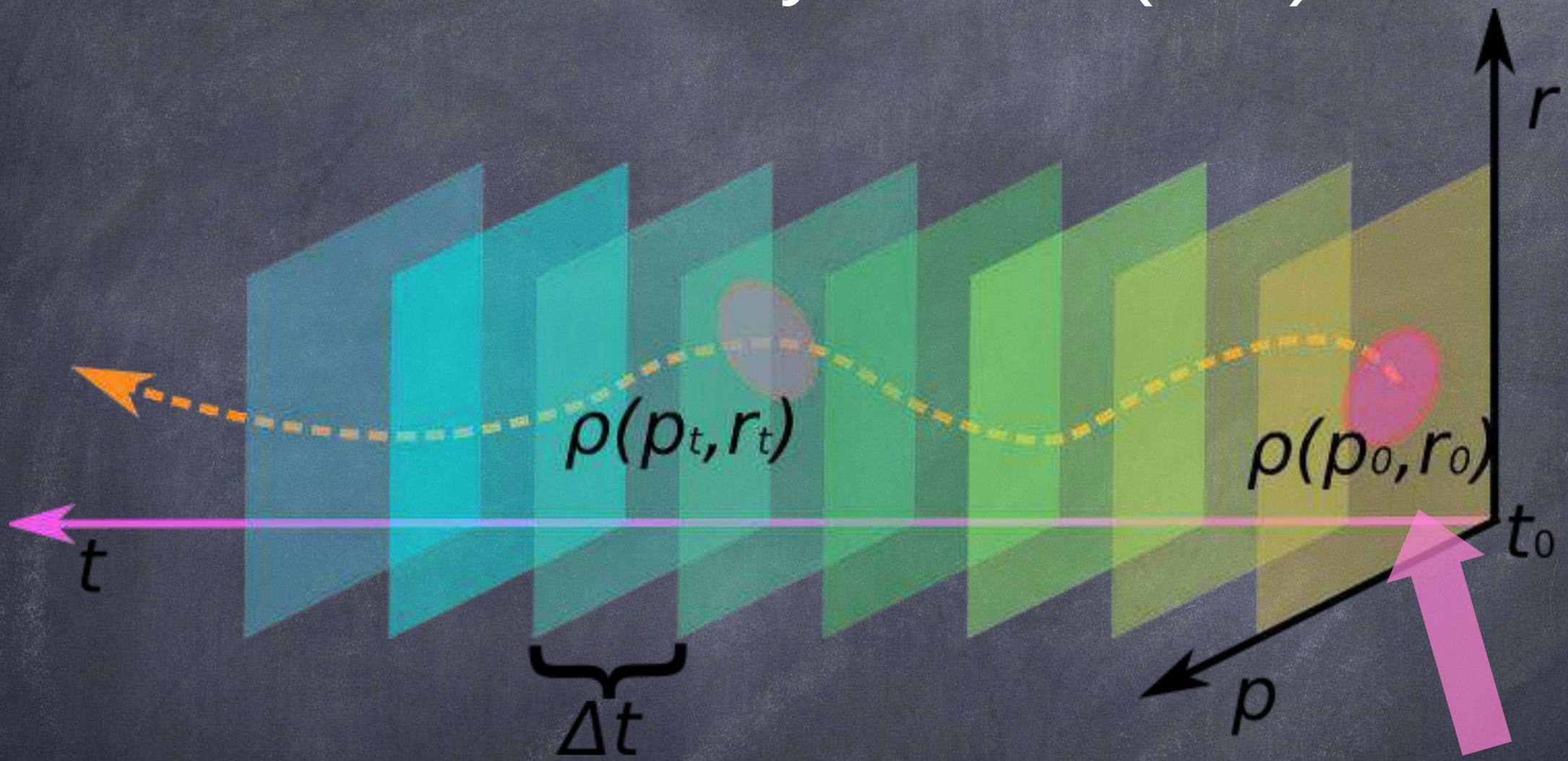


Boulfelfel & Leoni, PRB 78, 125204 (2008).

Workshop 2

- Examples from metaD and TPS
- Details of the *shooting* approach
- Details of MD engines

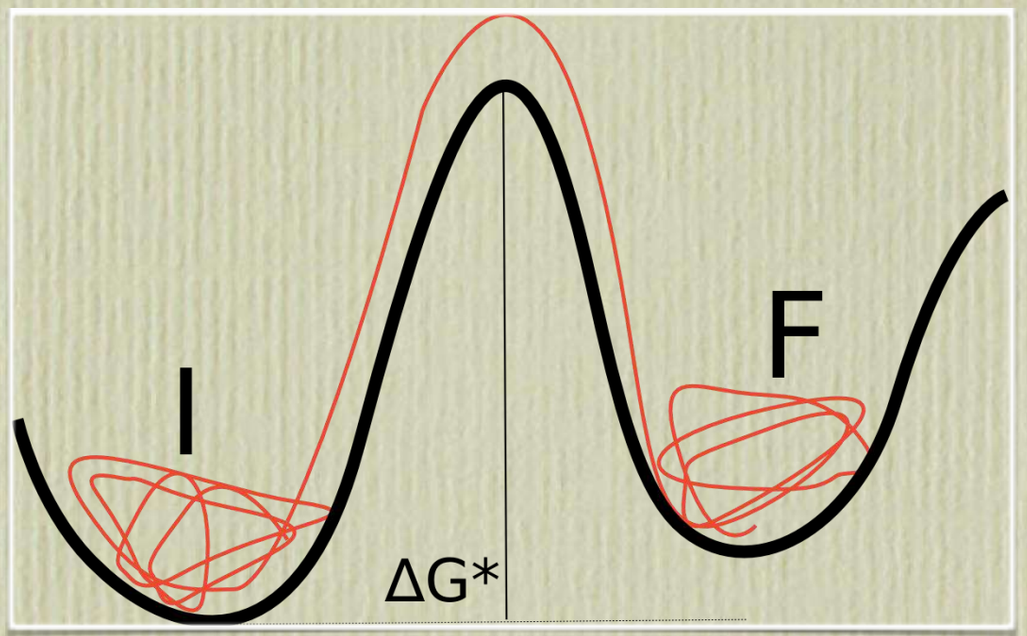
Time-Evolution of a System
Molecular Dynamics (MD)

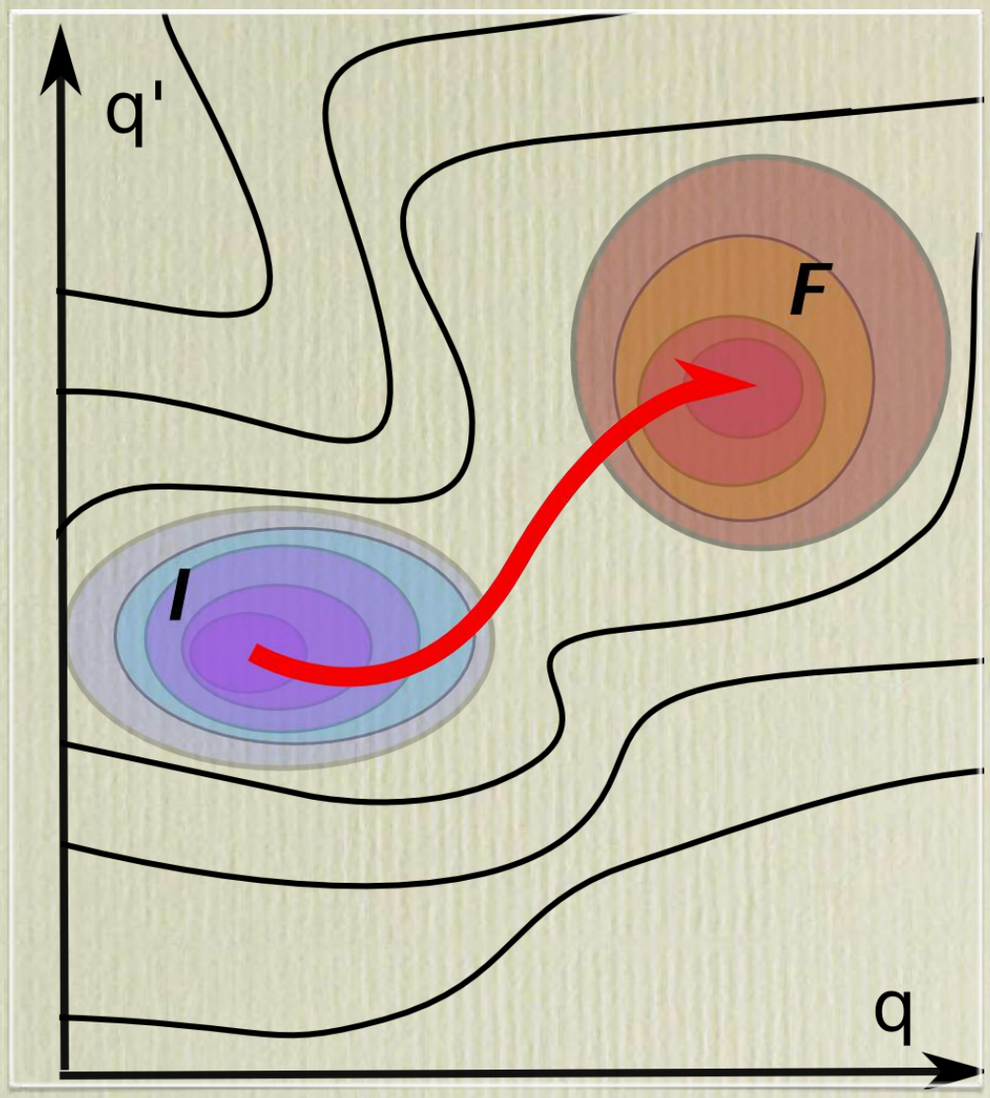


Calculate forces on atoms and propagate in time

Initial configuration:
Specify positions and velocitiy distribution at temperature T.

Different time scales (MD)





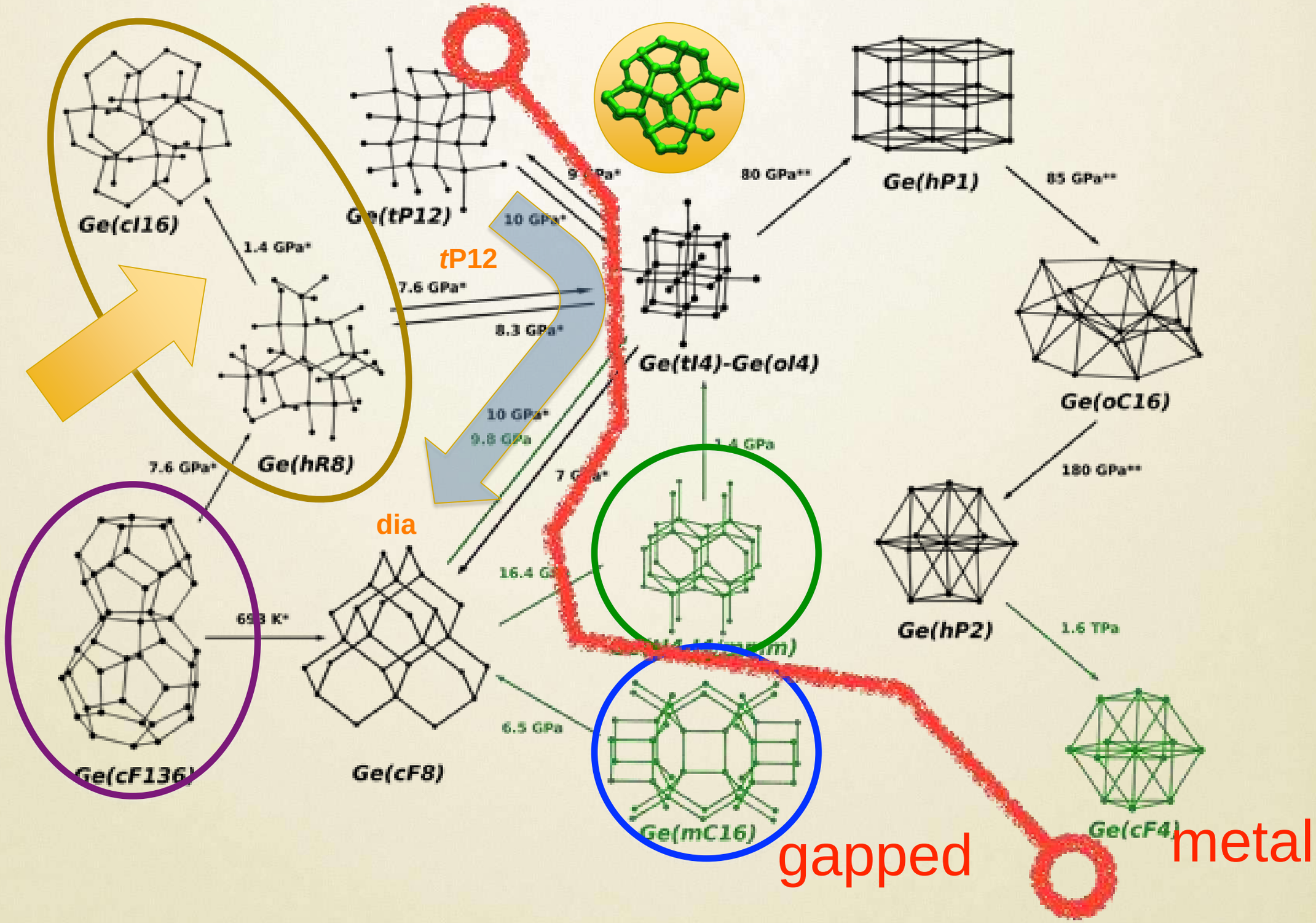
Frequent and slow vs.
Rare and quick

MetaD 1

Details

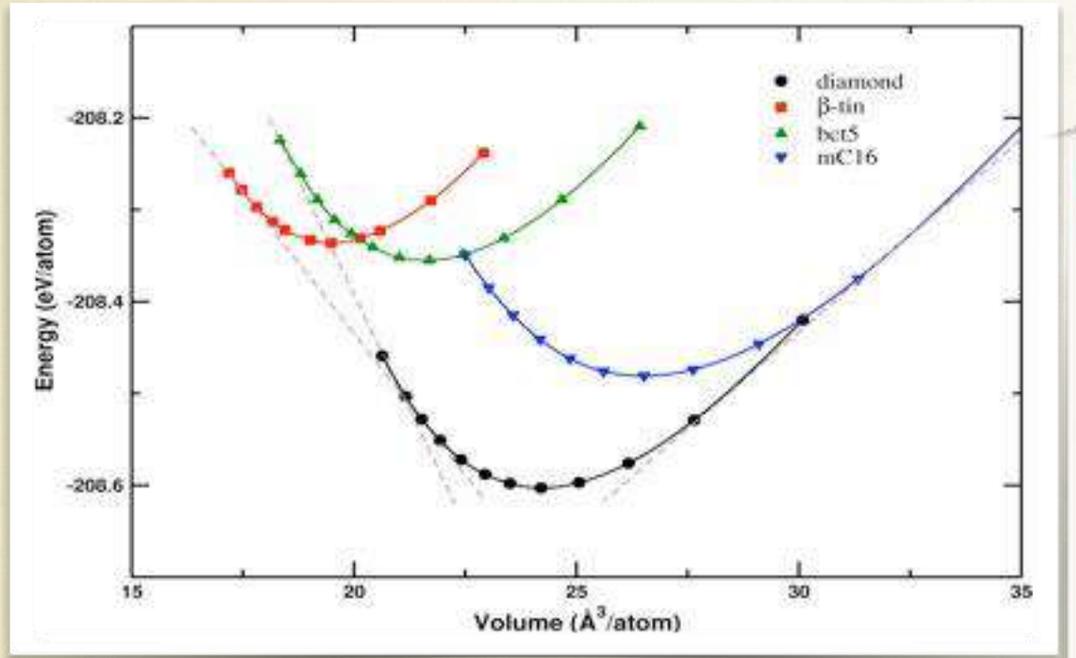
- siesta as MD/Force engine (DFT)
- box as CV
- external driver (metaD)
- chain of NVT - metaD - NVT simulations

Ge - Refinement of the Phase Diagram

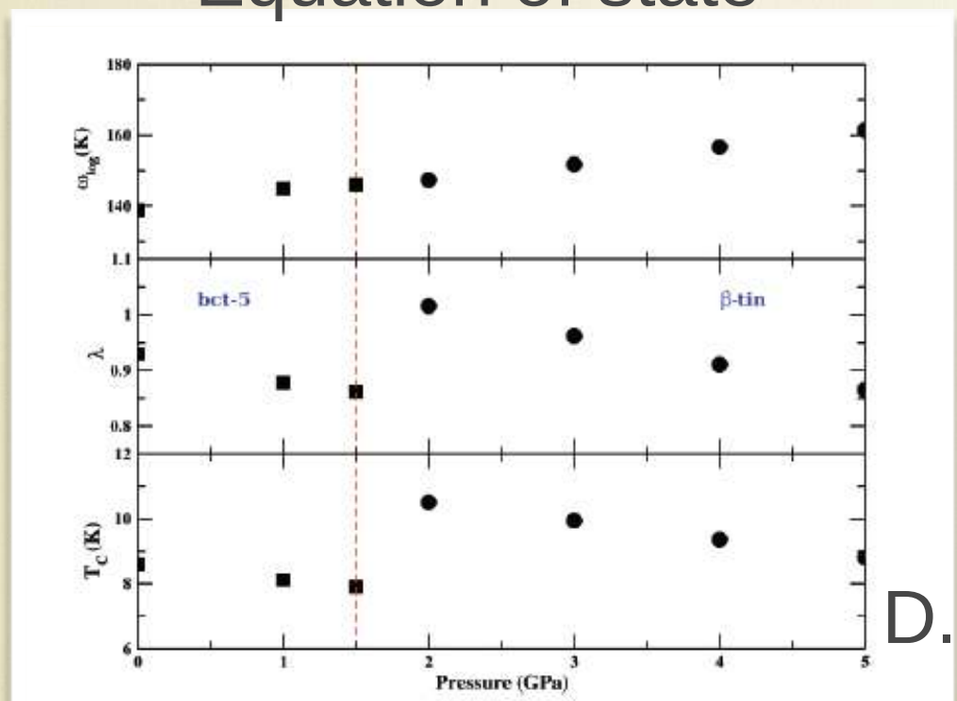


Guloy, A., Ramlau, R., Tang, Z. *et al.* A guest-free germanium clathrate. *Nature* **443,** 320–323 (2006).

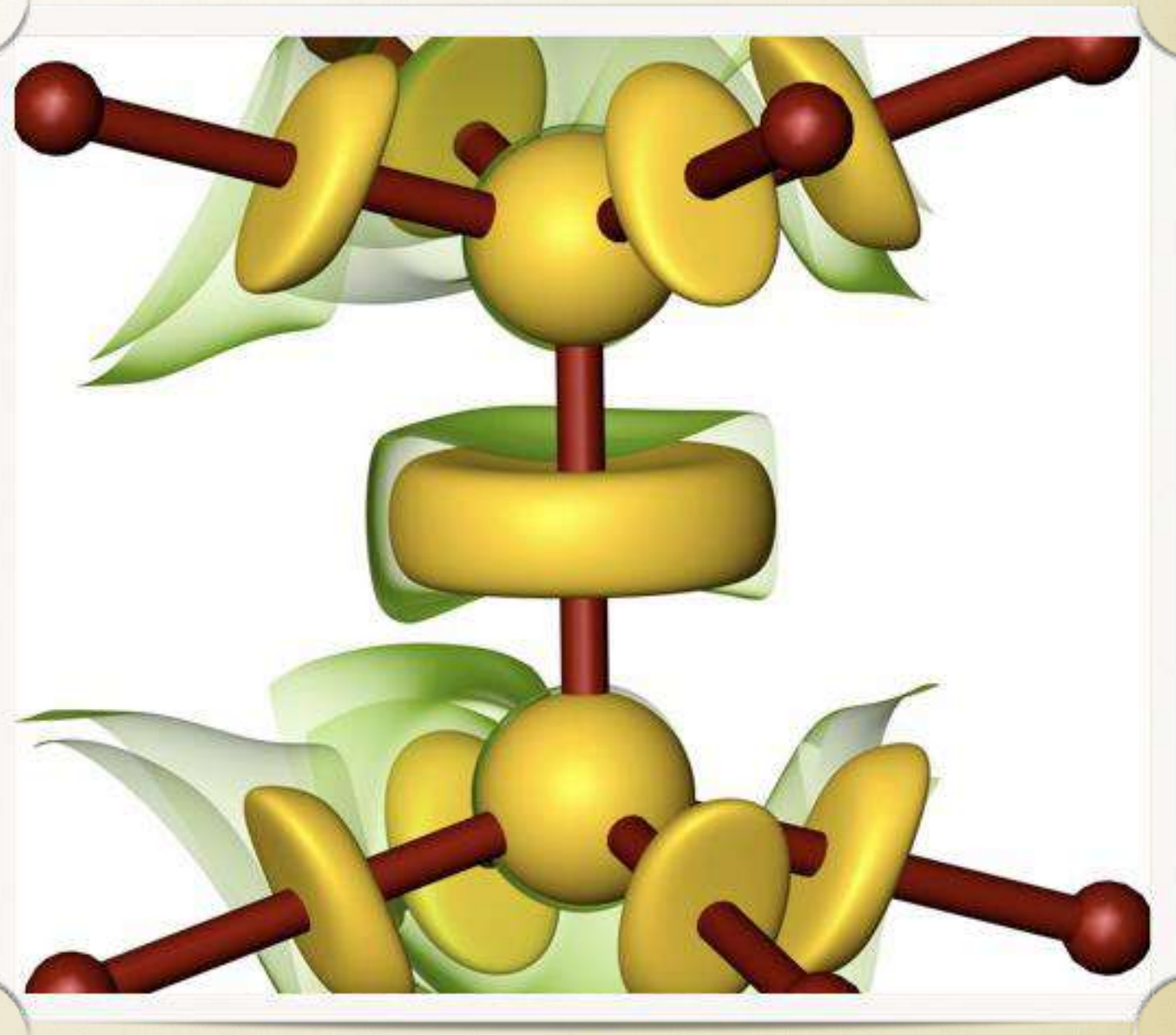
Ge - Metallic & Superconducting



Equation of state



Superconductivity



D. Selli *et al*., Scientific Reports 3, 1466 (2013)

D. Selli *et al.*, arXiv:1209.3753 (2012)

Gibbs free energy

- Crystal structures correspond to minima of the Gibbs free energy
  G(**h**) = F(**h**) + PV

$$-\frac{\partial \mathcal{G}}{\partial h_{ij}} = V\left[\mathbf{h}^{-1}(\mathbf{p}-P)\right]_{ji}$$

box volume

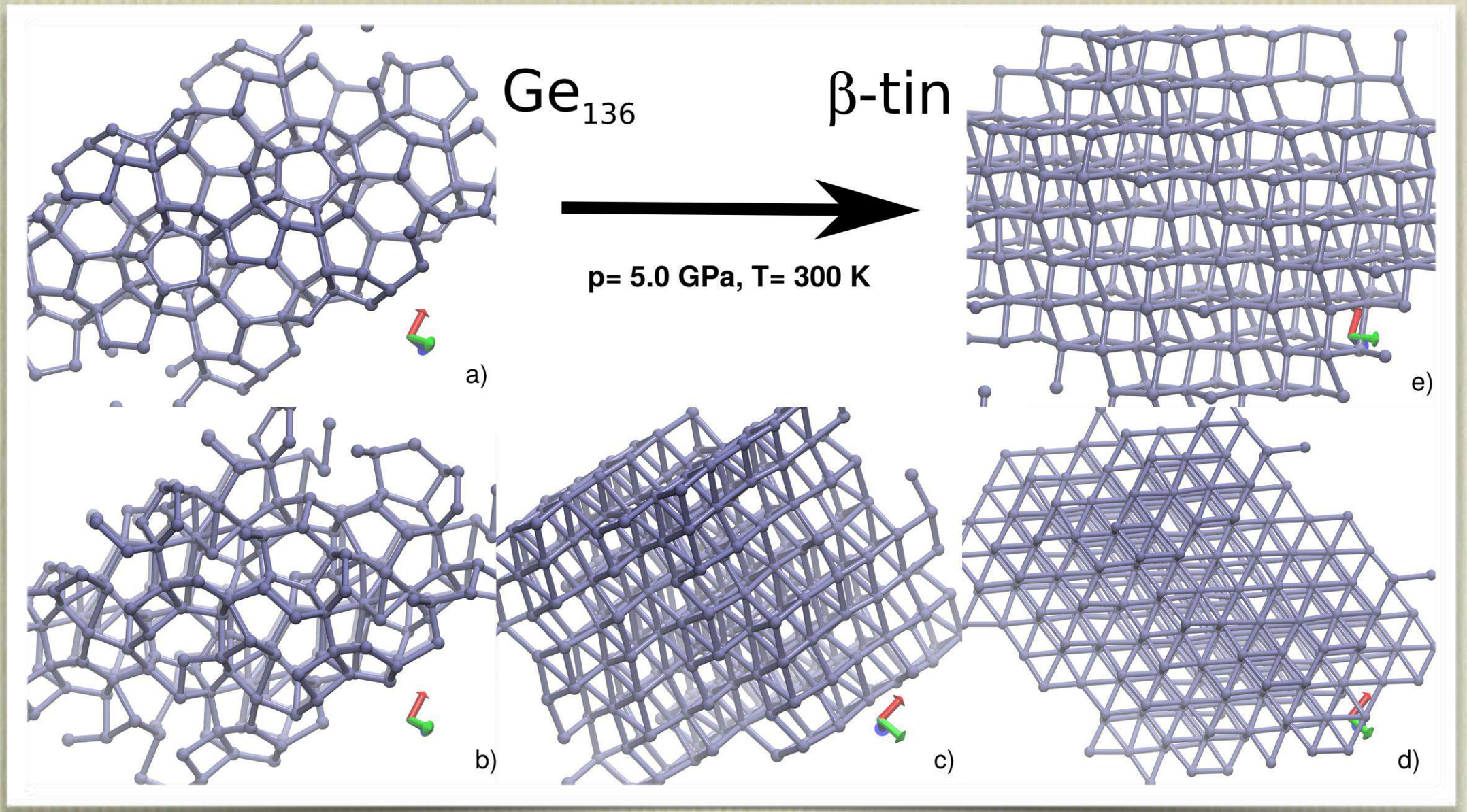
internal pressure

external pressure

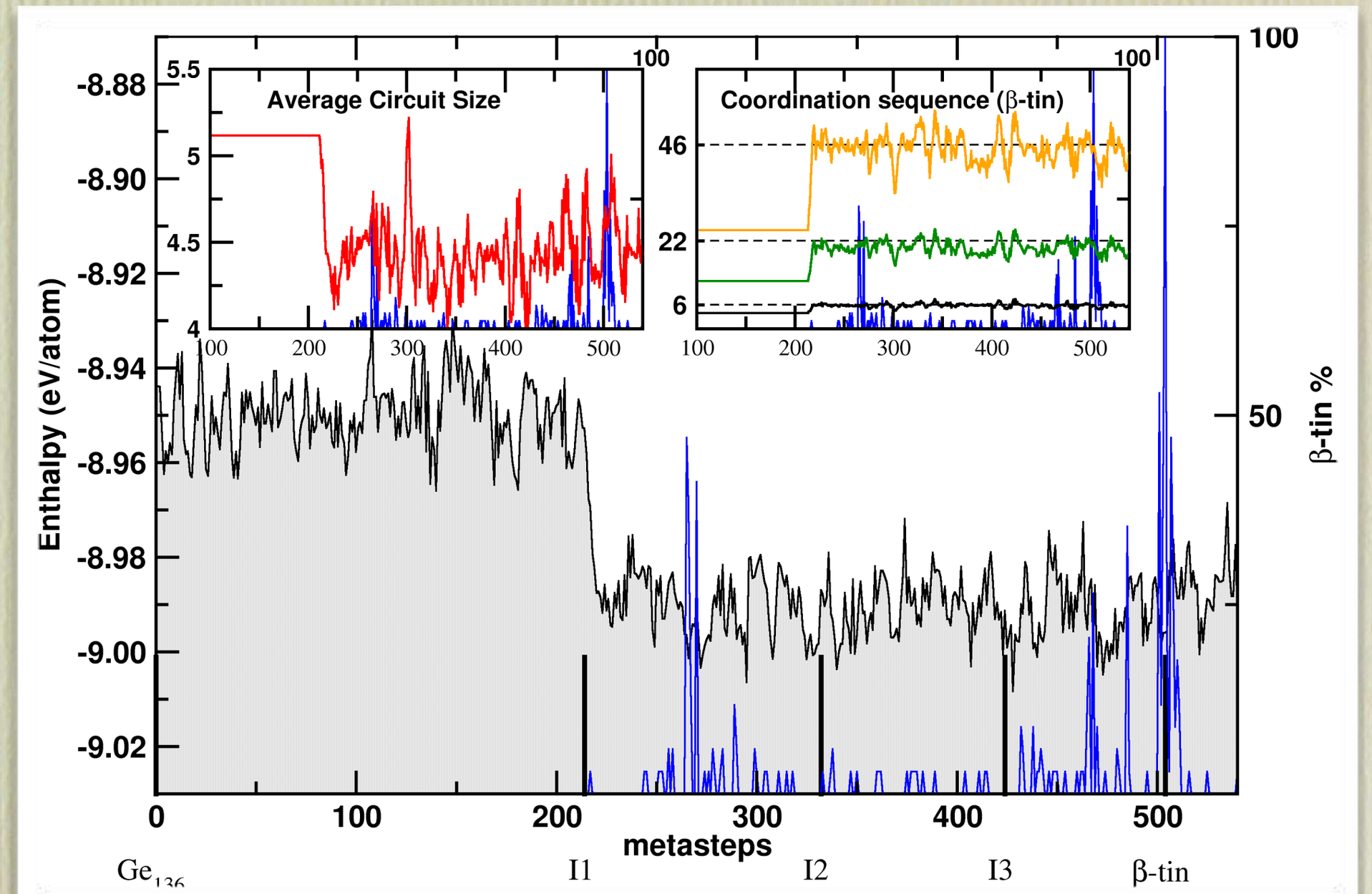
- Different crystal structures, and different symmetries.
- MD simulation box matrix **h** as order parameter
- ***6 independent components*** of the matrix **h**

R. Martoňák, A. Laio and M. Parrinello, Phys. Rev. Lett **90**, 075503 (2003)

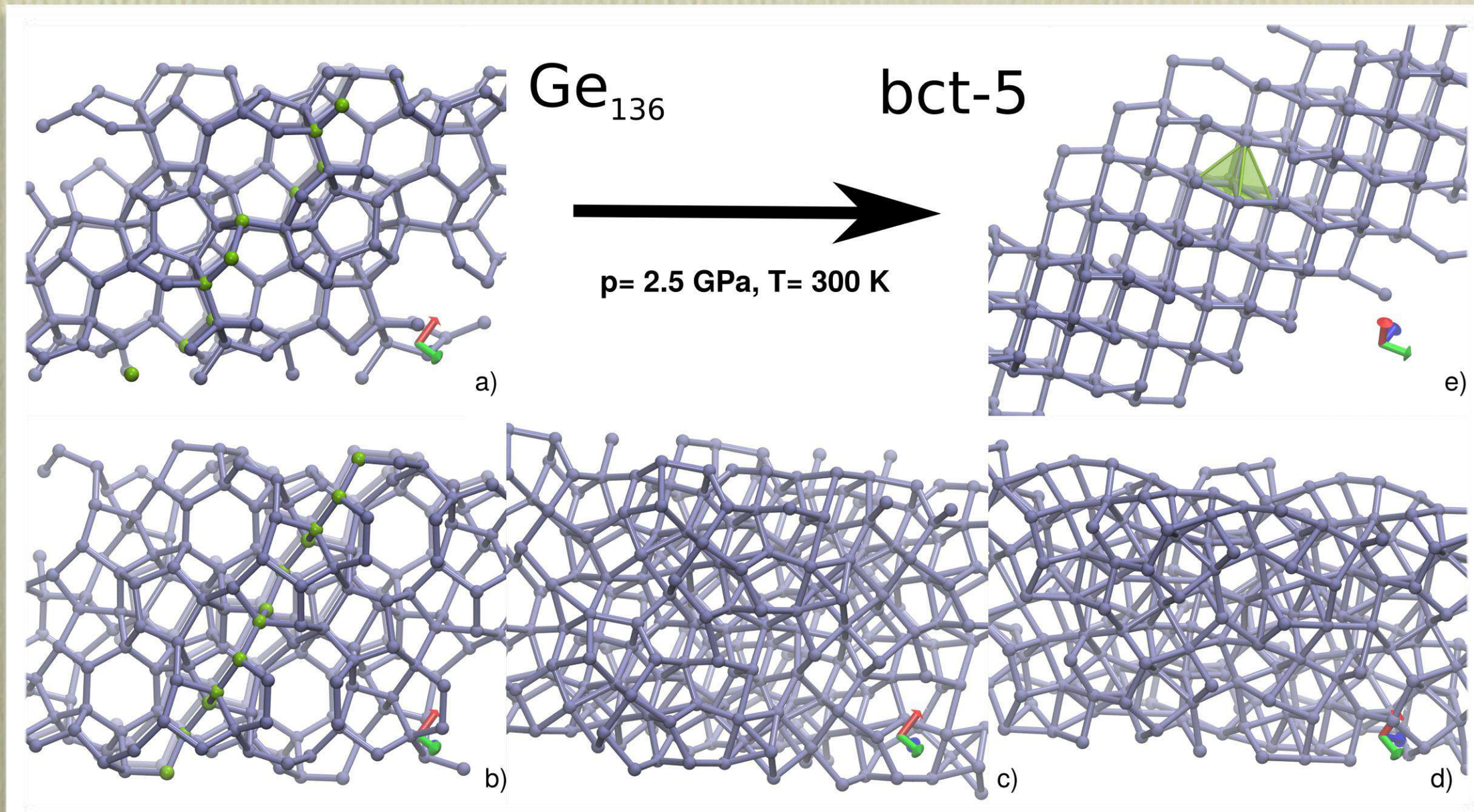
Ge_{136} (cF136) as precursor



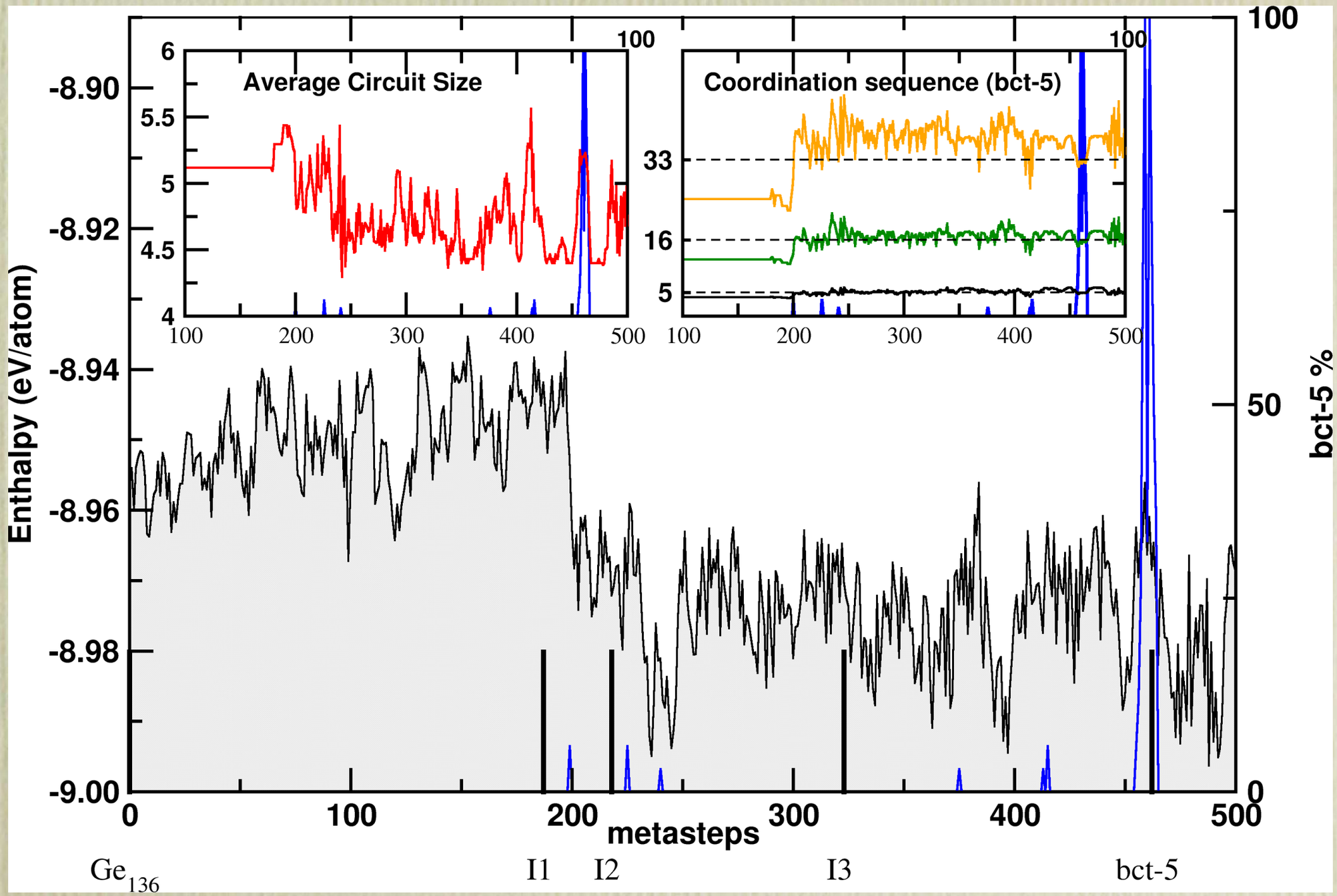
Ge_{136} (cF136) as precursor



Formation of bct-5

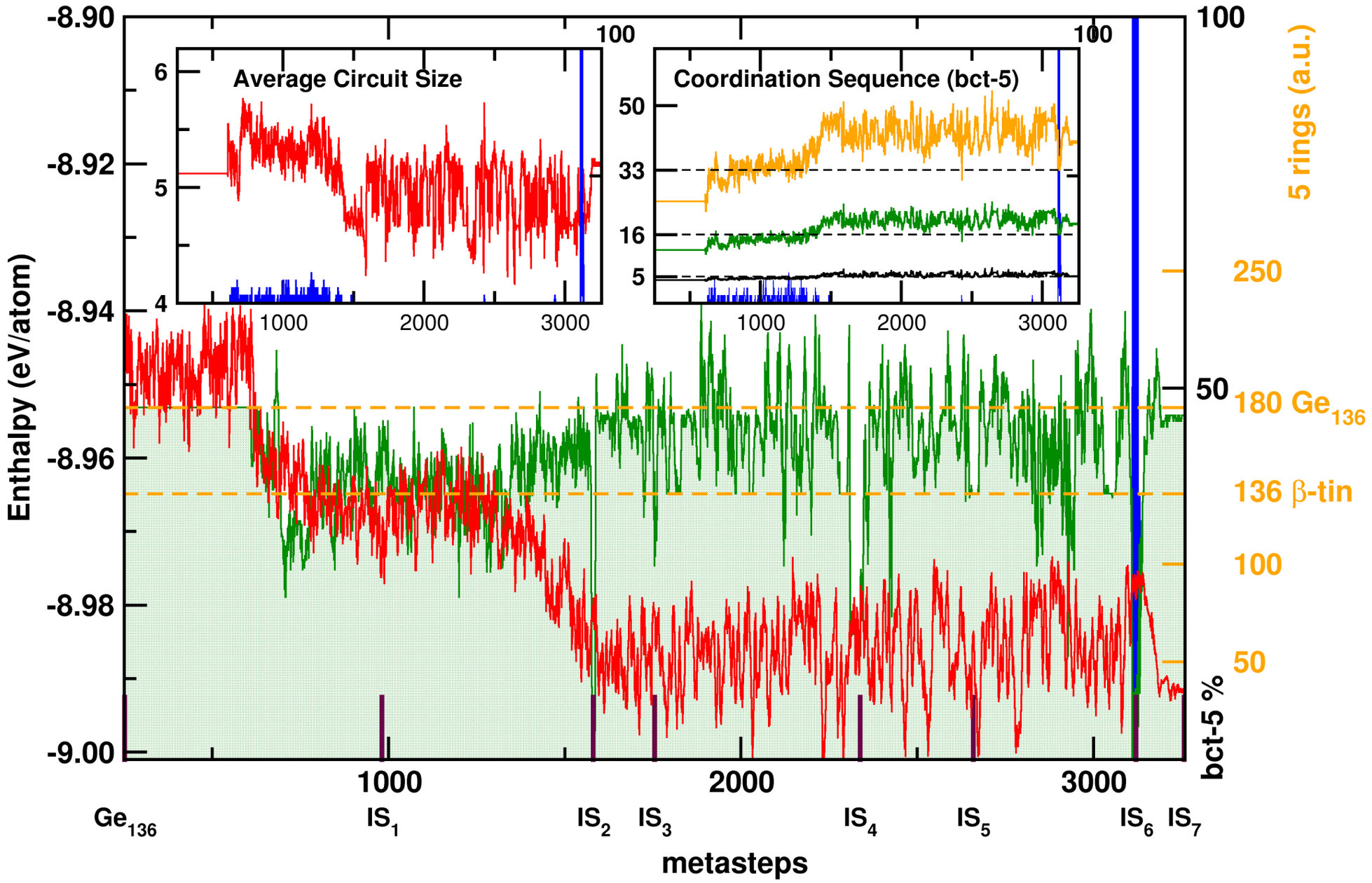


Descriptors

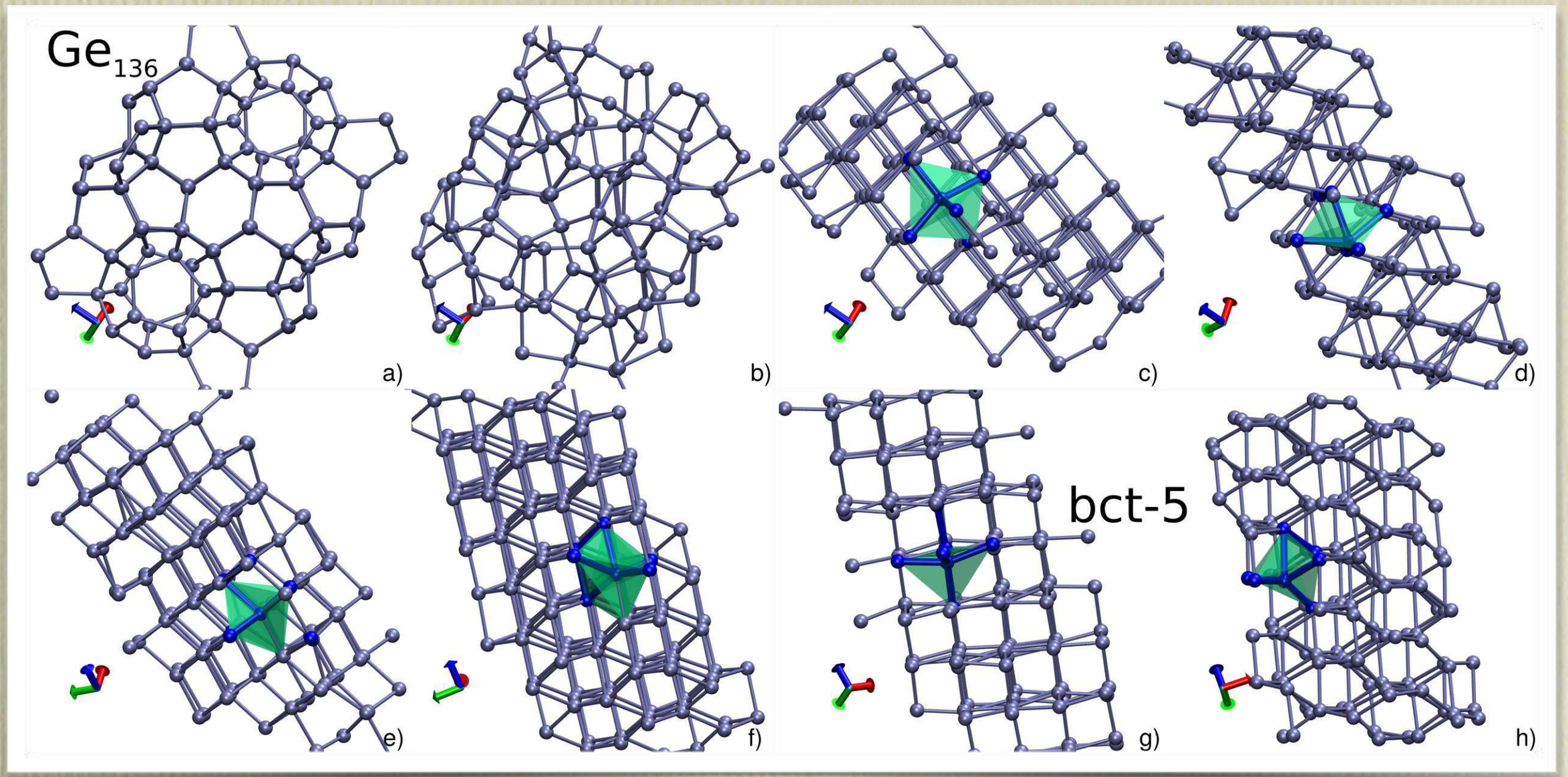


Ge_{136} I1 I2 I3 bct-5

Low Temperature (77K)



Metadynamics at 77K

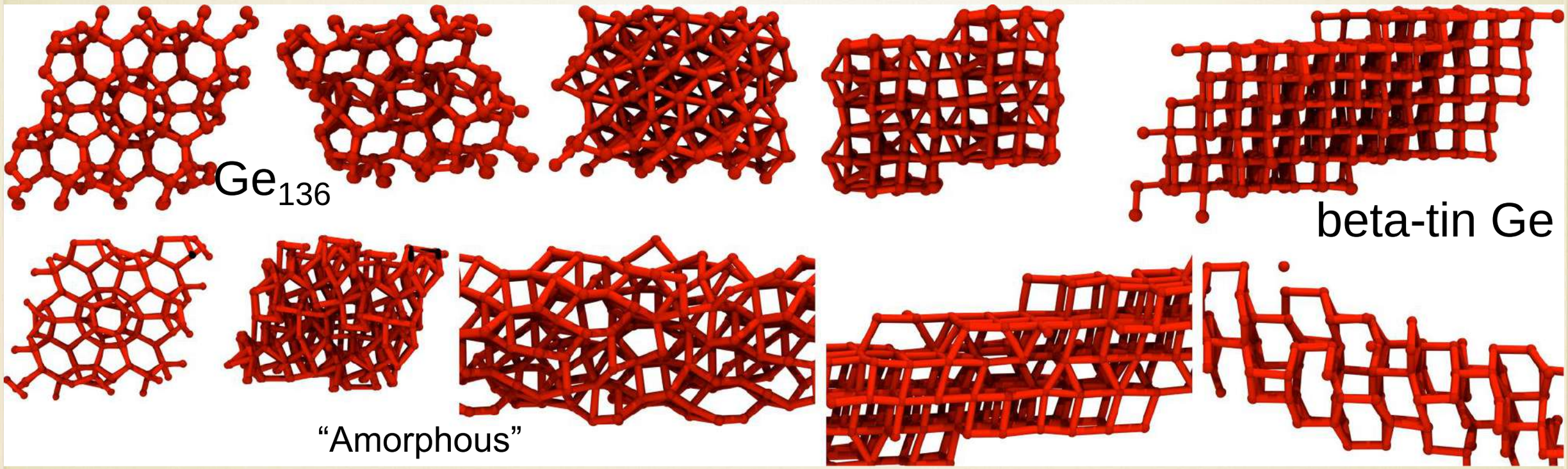


Looking for a formation mechanisms

Clathrate Ge_{136}

—> Control nucleation!

Higher Pressure, Room Temperature Path



Lower pressure, Low Temperature Path

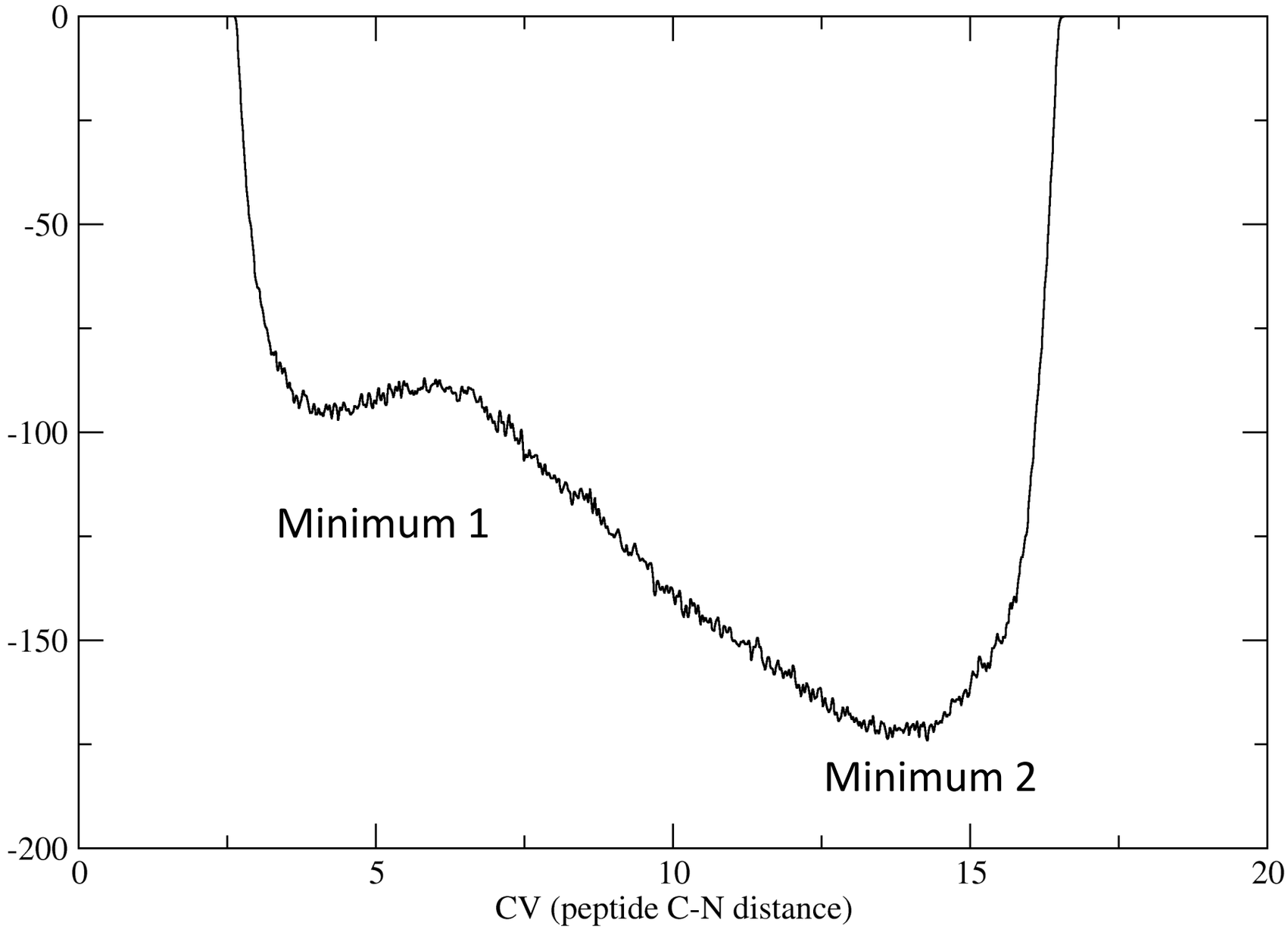
Different Paths, Intermediates & Nucleation History

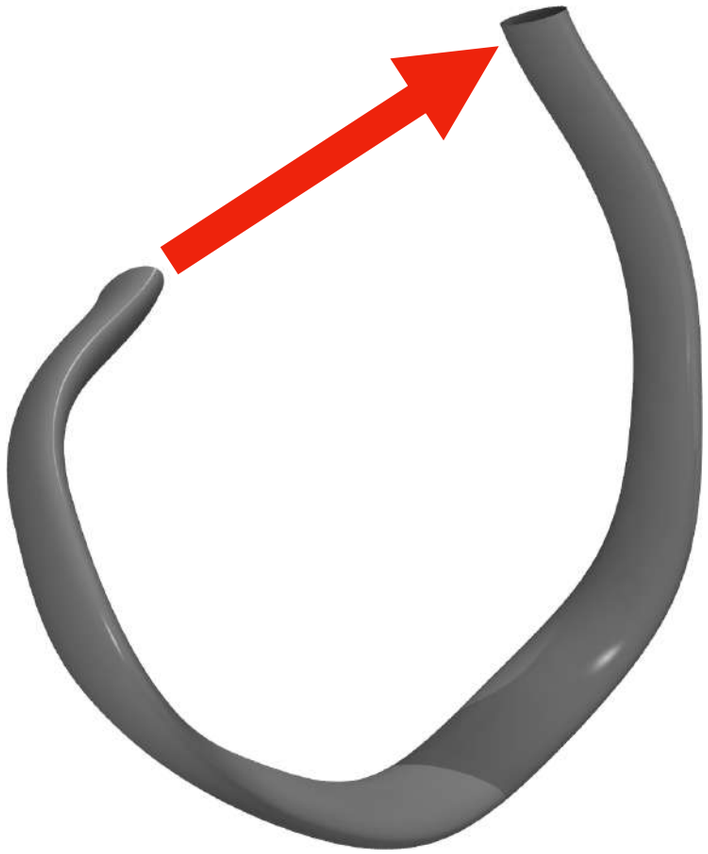
D. Selli *et al.* (2017), in preparation

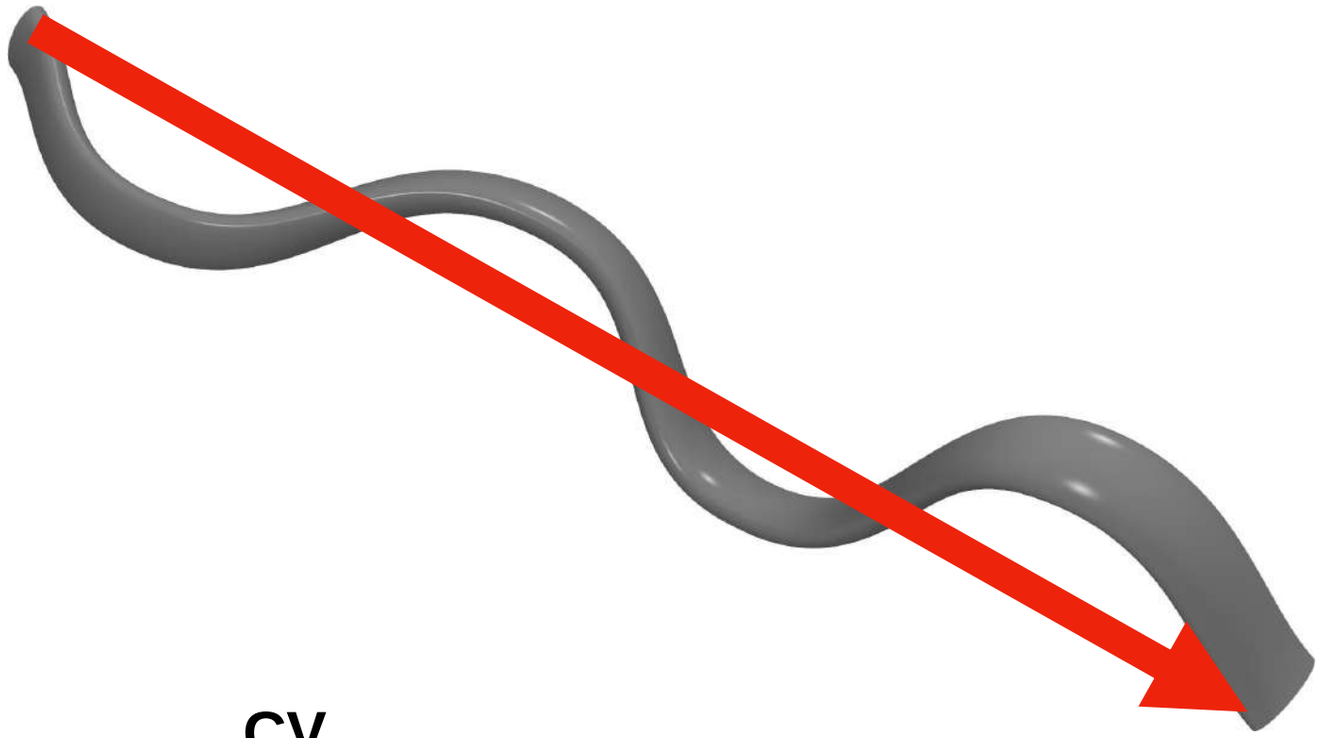
MetaD 2

Details

- cp2k as MD/Force
- based on FF (attempted with DFTB as QM/MM)
- external driver (plumed), distance as CV


0
-50
-100
-150
-200
0
5
10
15
20
CV (peptide C-N distance)
Minimum 1
Minimum 2





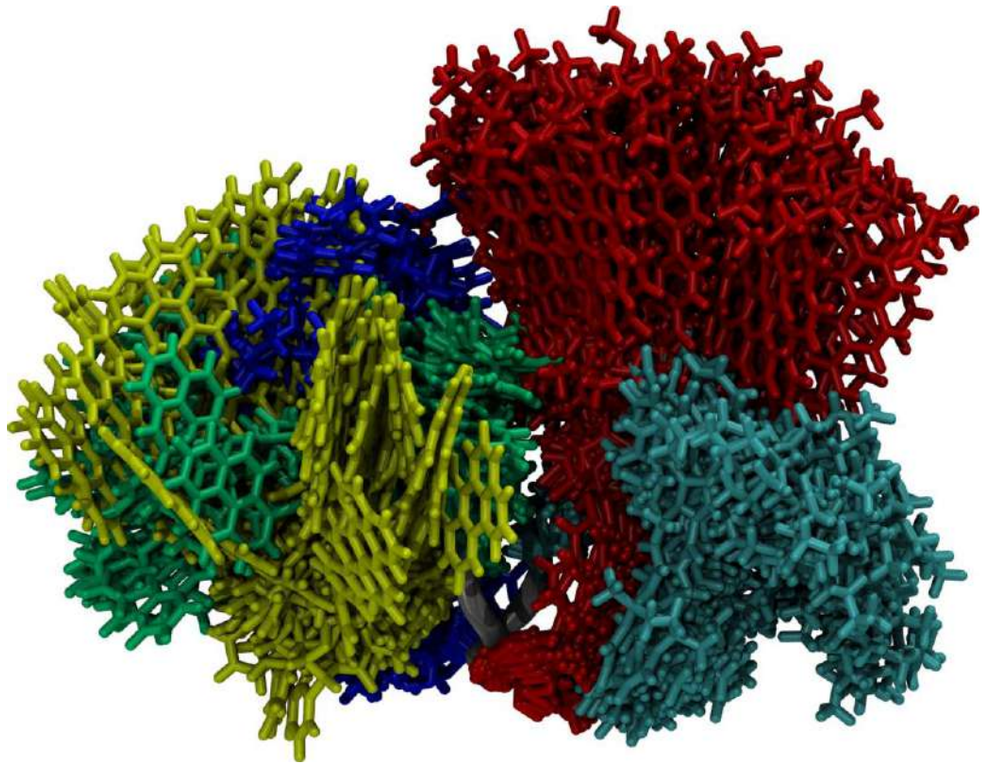
CV

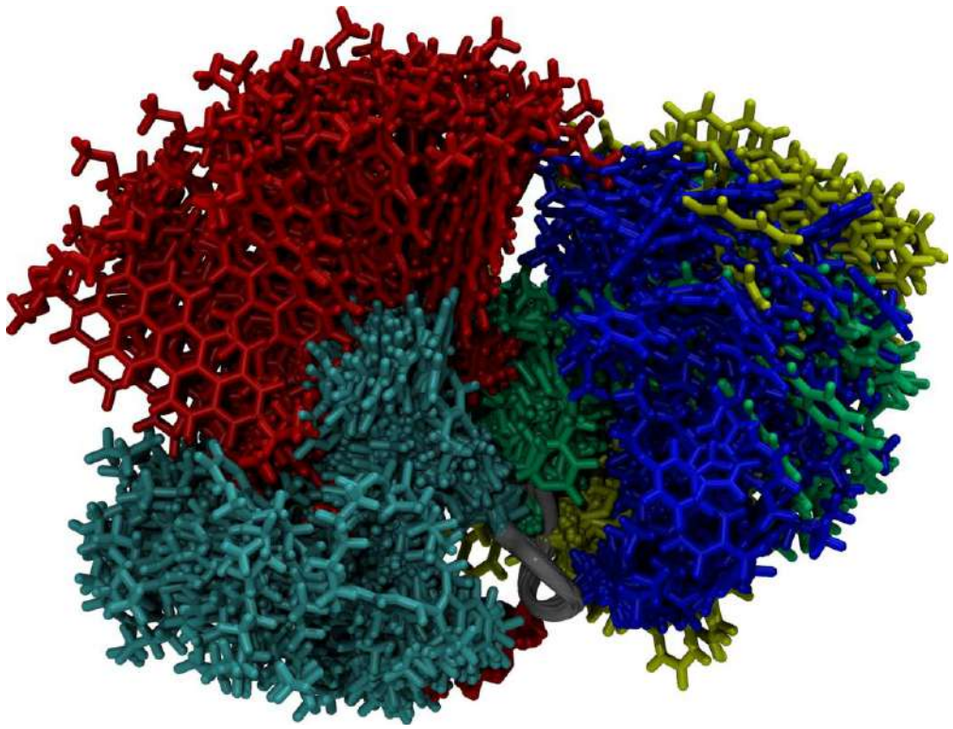
Min1 { within 1.0%
within 0.5%

Free Energy -182.17 kJ/mol

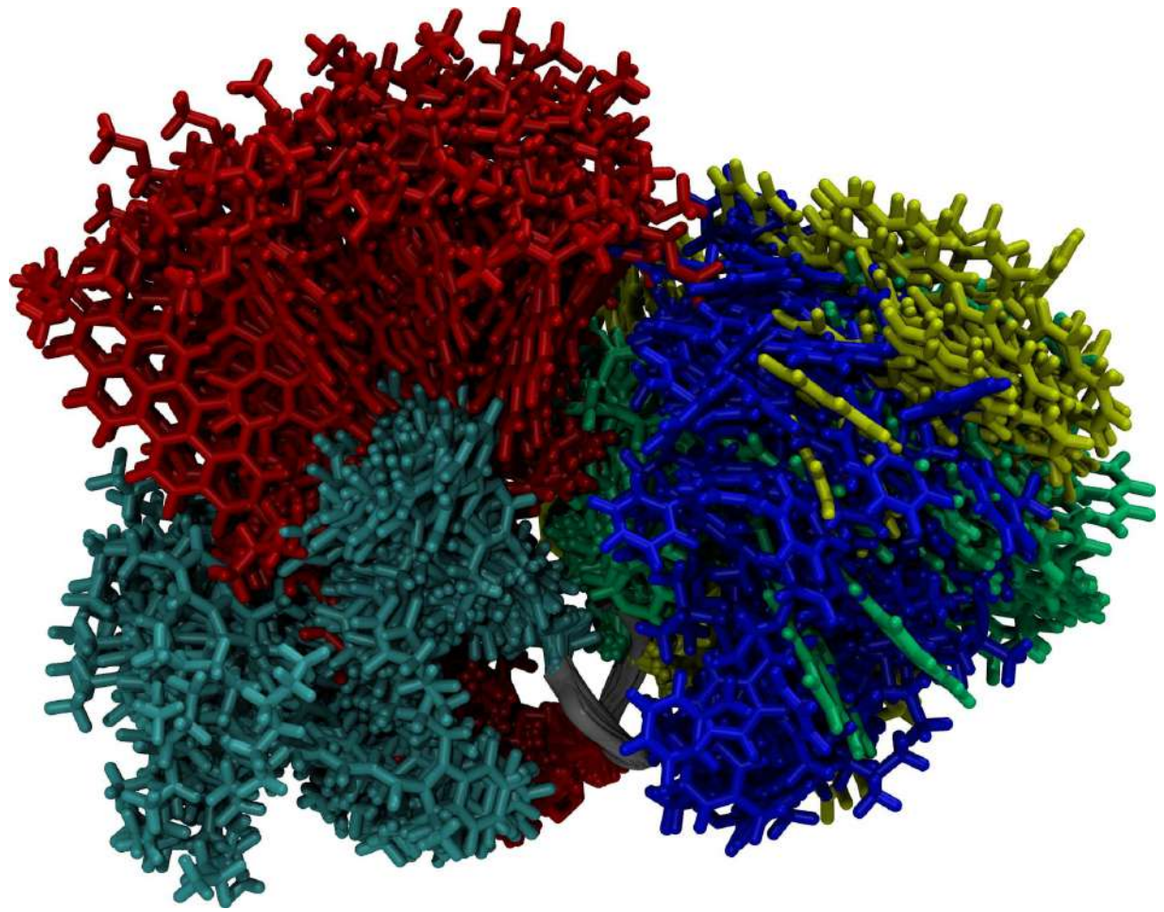
Min2 { within 1.0%
within 0.5% { A (40%)
B (60%)

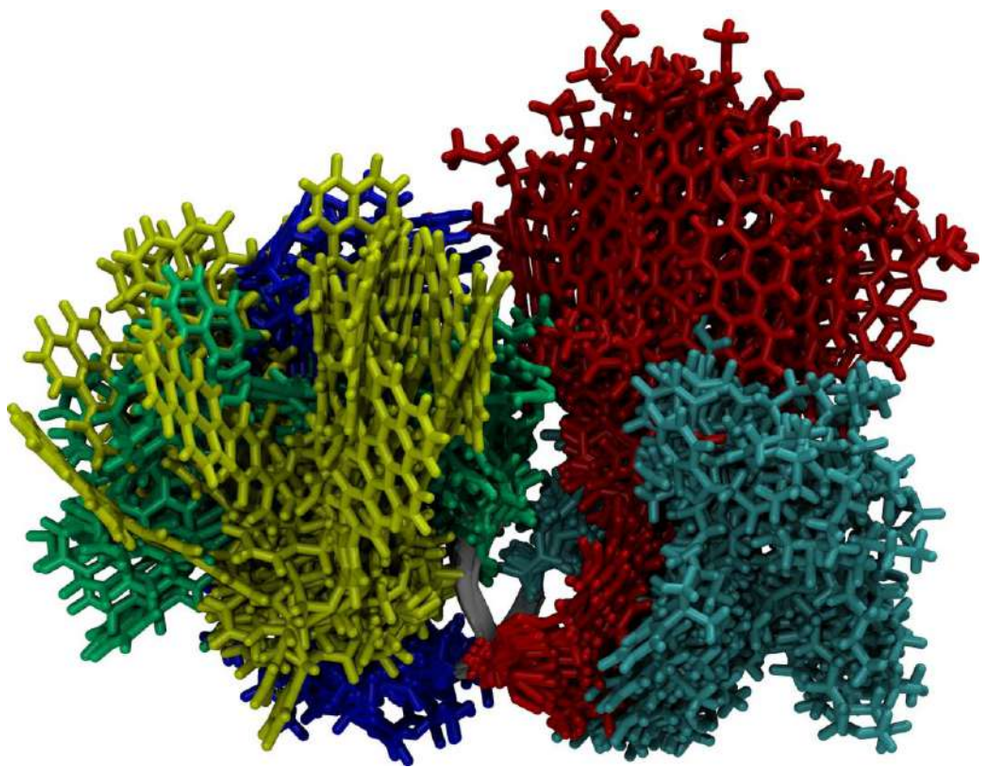
Free Energy -245.54 kJ/mol

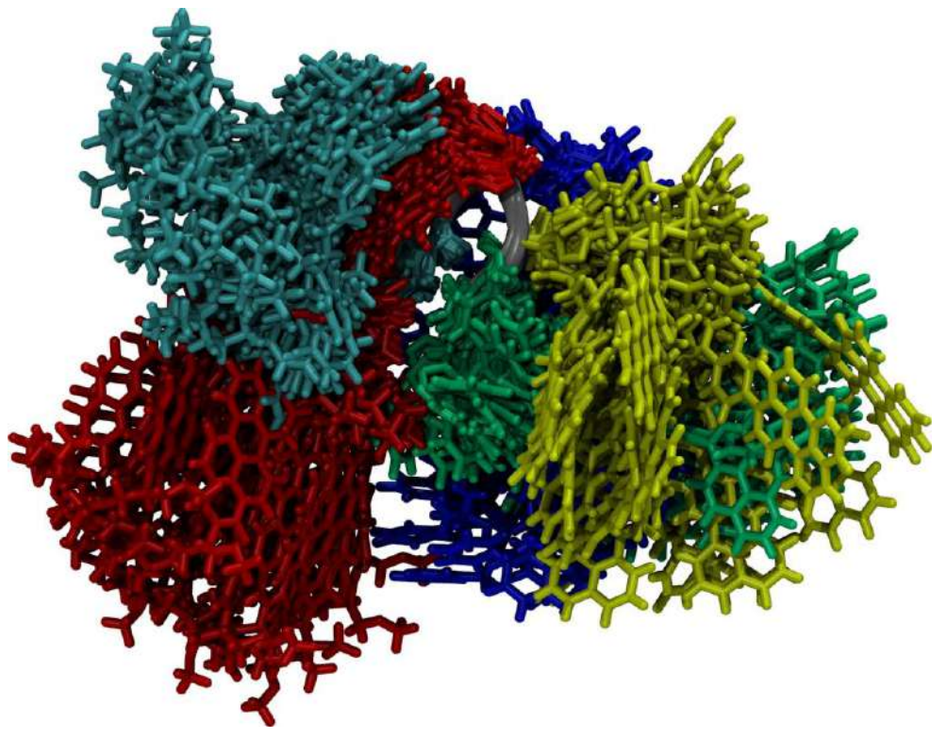




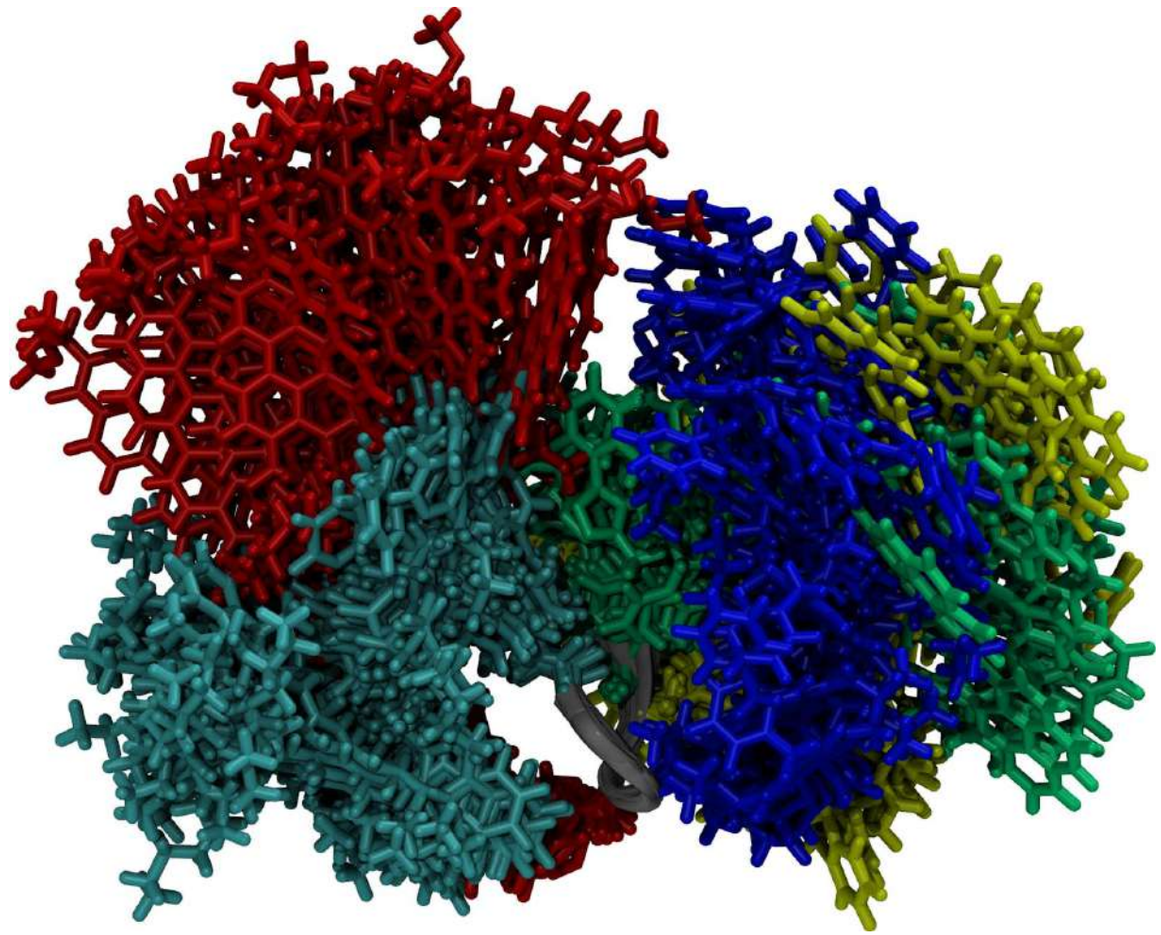
Min1, conf1







Min1, conf0

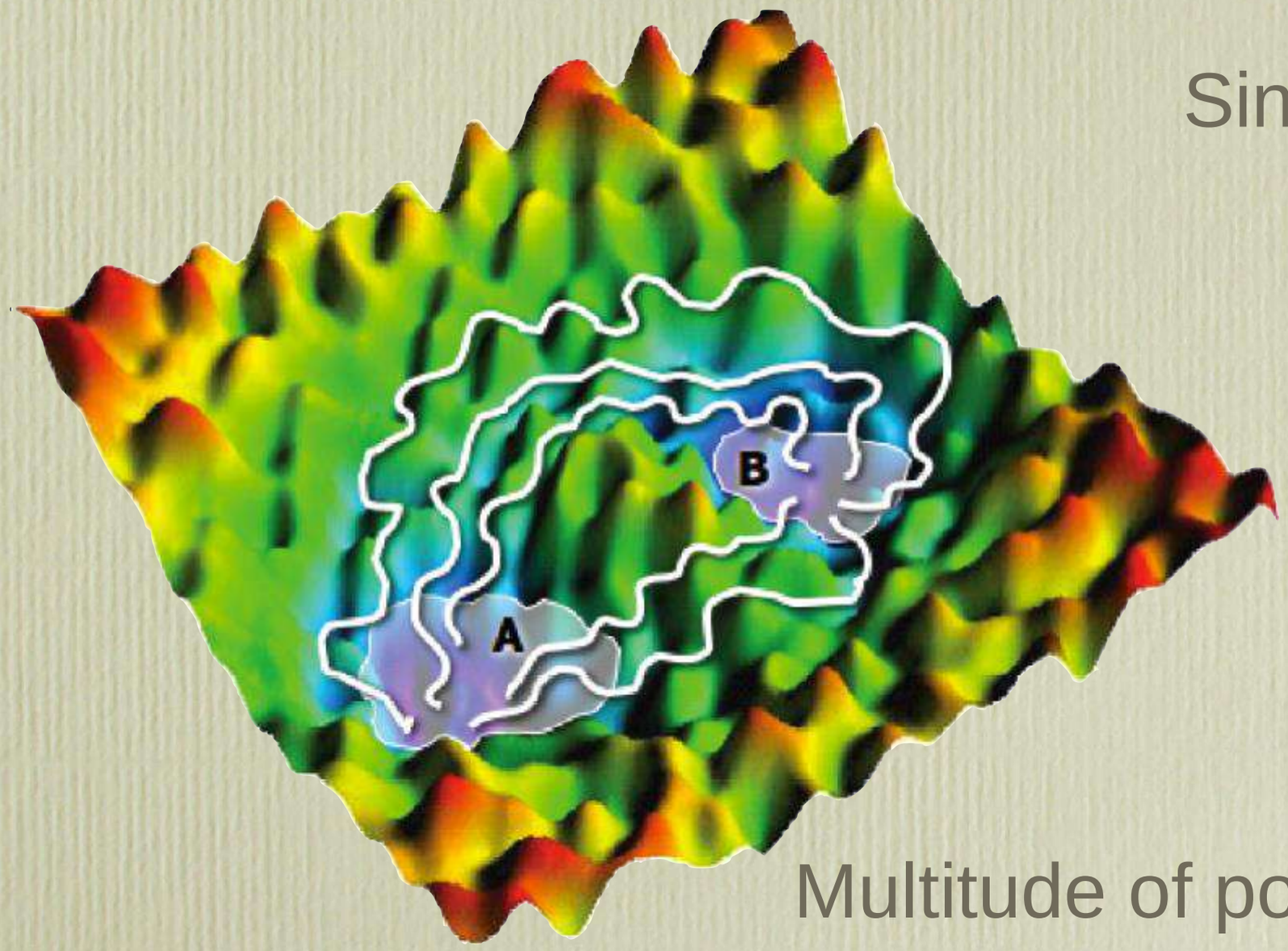


TPS 1

Details

- Carbon
- DFTB/cp2k C-C
- Graphite—> Diamond, then lower T
- shooter, external script
- MD —> shooting move —> MD —> ….

Corrugated Landscape of Complex Systems



(D. Chandler, C. Dellago)

Transition *path*

Single Mechanism → saddle point(s)

Multitude of points become relevant, only some of them stationary.

Transition path *ensemble*

```
&FORCE_EVAL
 &DFT
  &QS
    METHOD DFTB
    &DFTB
      SELF_CONSISTENT    F
      ORTHOGONAL_BASIS   F
      DO_EWALD           F
      &PARAMETER
        PARAM_FILE_PATH  .
        SK_FILE   C C   ../../cc
      &END PARAMETER
    &END DFTB
  &END QS
  &SCF
    SCF_GUESS NONE
    MAX_SCF  1
    &MIXING
       METHOD DIRECT_P_MIXING
       ALPHA   1.
    &END
  &END SCF
 &END DFT
STRESS_TENSOR DIAGONAL_NUMERICAL
&END FORCE_EVAL
```

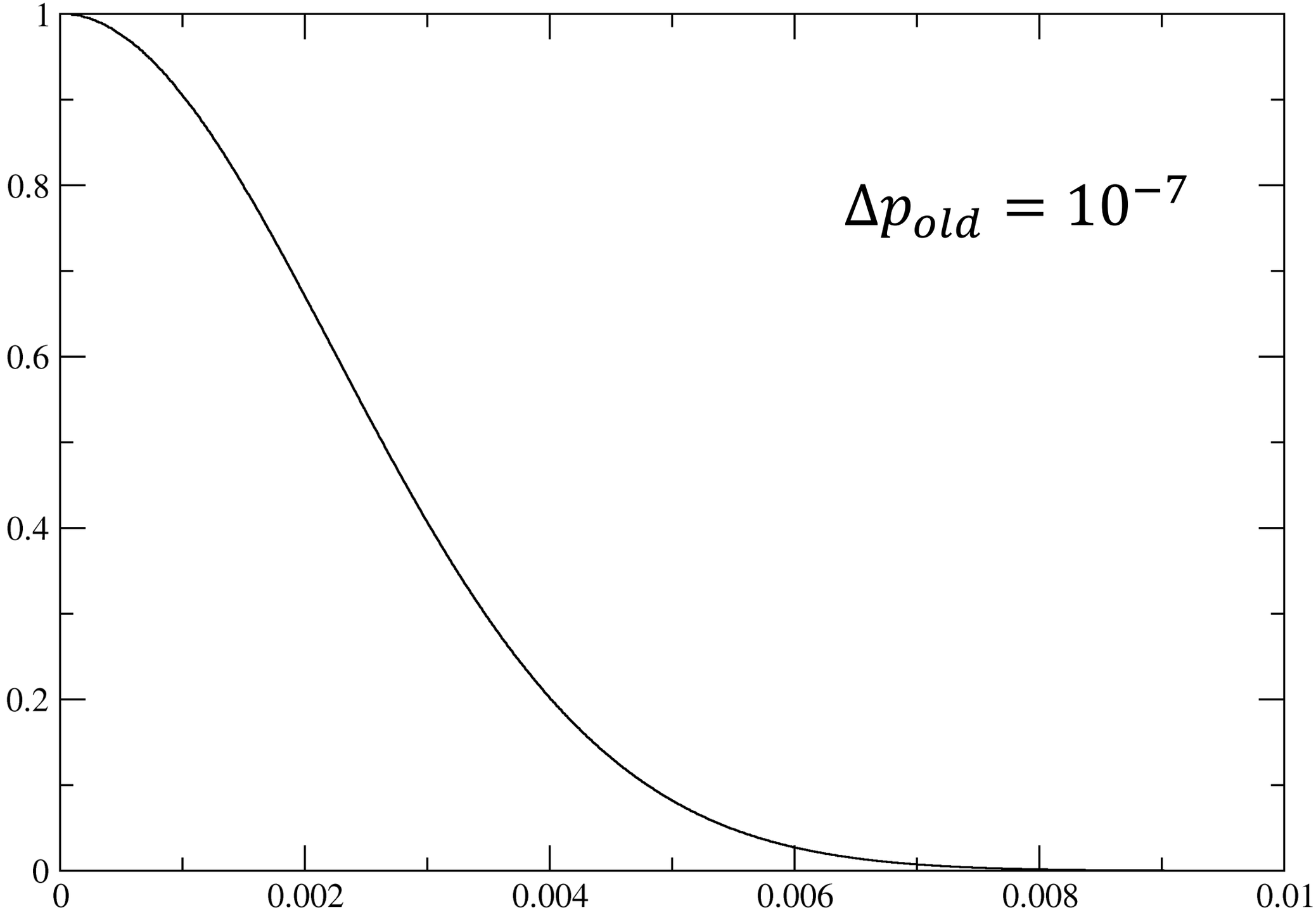
```
&MOTION
 &MD
  ENSEMBLE NPT_F
  STEPS xstepsx
  TIMESTEP xtimestepx
  TEMPERATURE 300.0
  &THERMOSTAT
   &NOSE
    TIMECON 300
    LENGTH 6
    YOSHIDA 3
    MTS 2
   &END NOSE
  &END
  &BAROSTAT
   PRESSURE [kbar] 150.0
   TIMECON 50000
  &END BAROSTAT
 &END MD
 &PRINT
  &RESTART_HISTORY ON
   &EACH
    MD 1000
   &END
  &END
  &VELOCITIES ON
   &EACH
    MD 100
   &END
  &END
  &TRAJECTORY
   &EACH
    MD 10
   &END
  &END TRAJECTORY
  &CELL LOW
   &EACH
    MD 10
   &END
  &END CELL
  &RESTART LOW
   &EACH
    MD 1000
   &END
  &END RESTART
 &END PRINT
&END MOTION
```

Acceptance Criteria

Shooter

$$\mathcal{P}_{\Delta p_{o\to n}} \propto e^{\frac{-\Delta p_{shooting}{}^2}{\Delta p_{old}}}$$

$\mathcal{P}_{\Delta p_{o\to n}}$



$\Delta p_{shooting}$

Details

- CdSe
- FF (LJ + partial charges on Cd/Se)
- W—>RS (model)
- shooter, external script
- MD —> shooting move —> MD —> ….

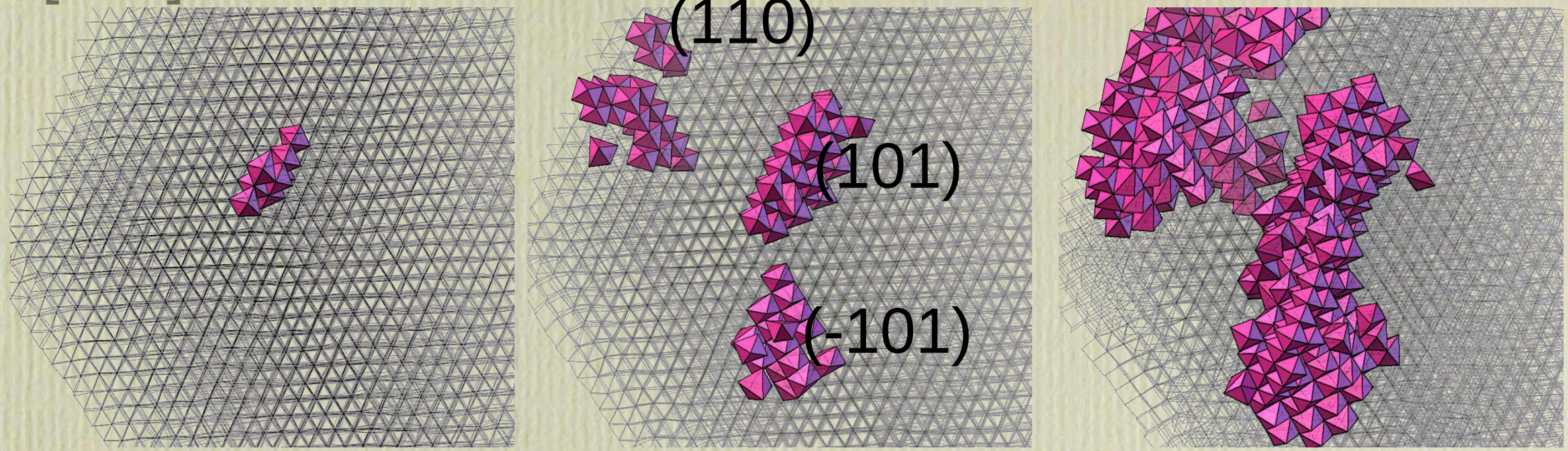
Focus on nucleation

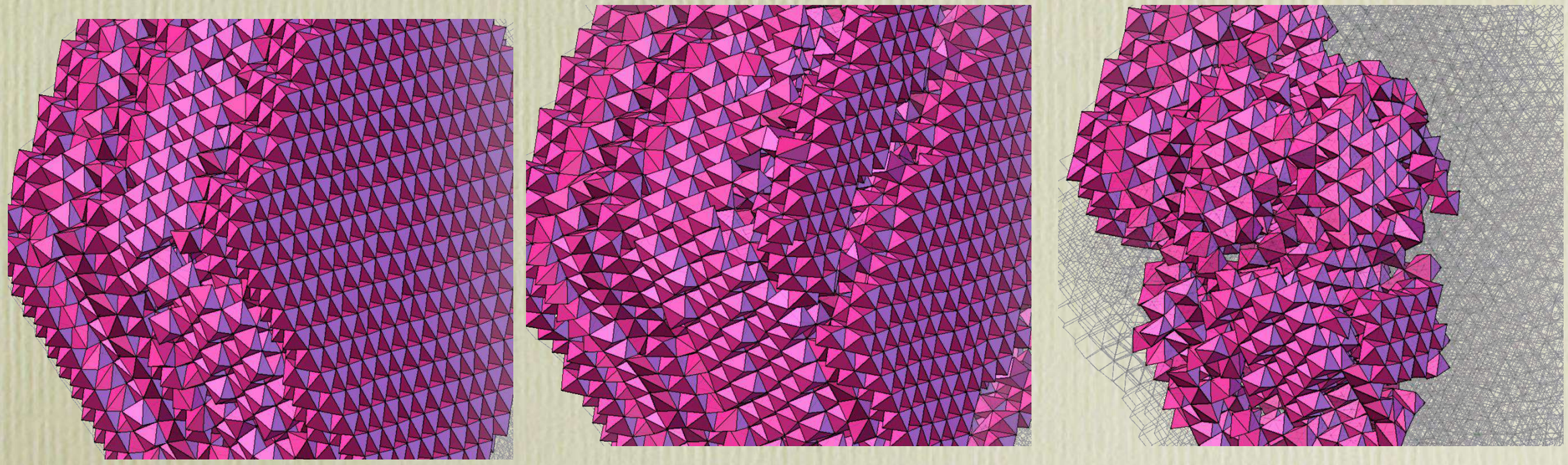
[111]

(110)

(101)

(-101)





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