Methods for predicting phase transition: VCNEB and TPS approaches

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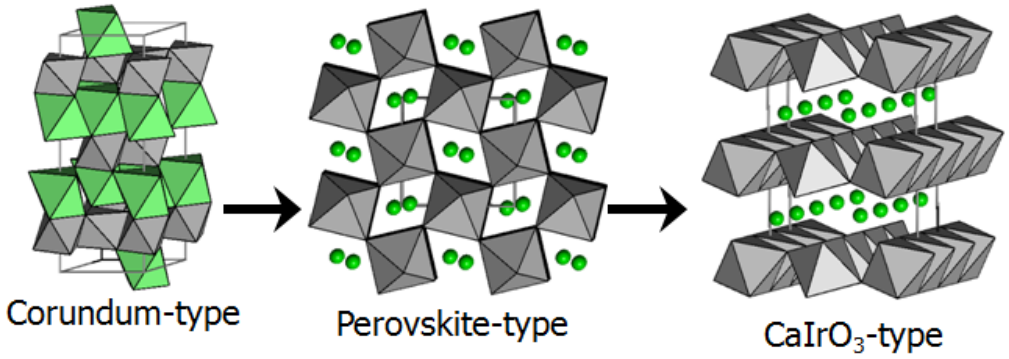
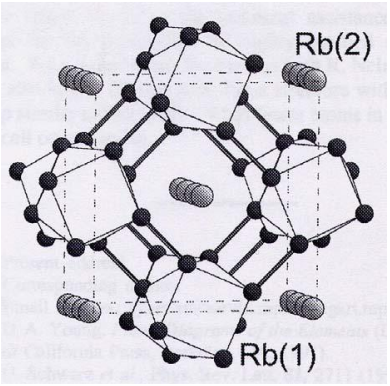
Materials at High Pressure

- New physics and new chemistry
- New crystallography
- Exotic materials, novel structures and properties
- Phase transitions





Rb: Schwarz et al. (1999)

Solid-solid phase transition under Pressure

- Displacive(continuous) phase transition
  - Order parameter
- Reconstructive Phase Transitions

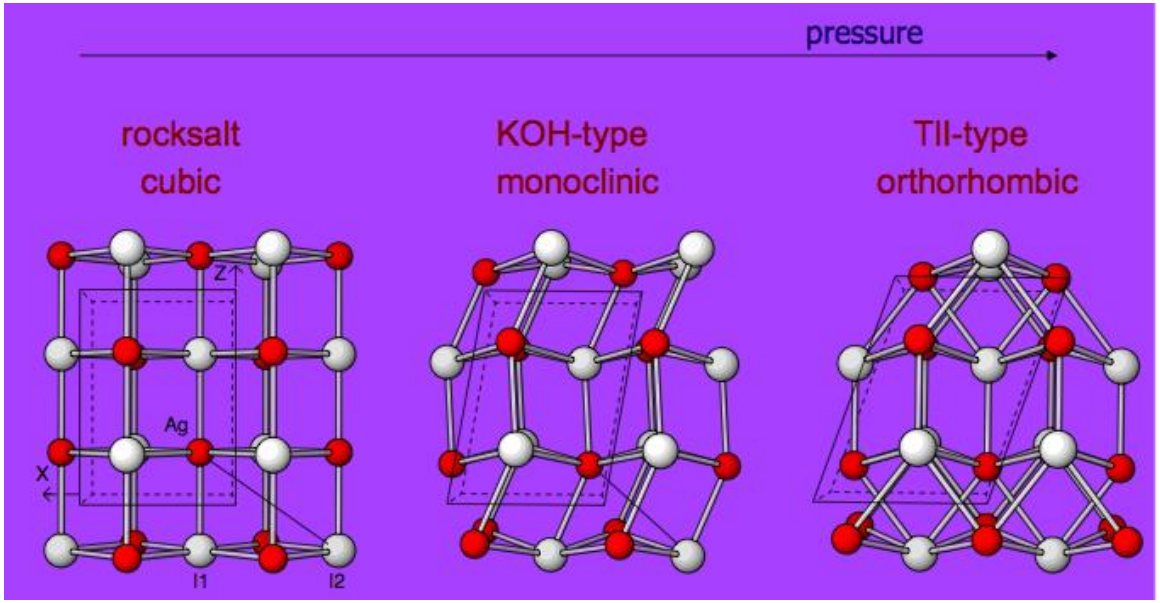
Displacive phase transitions in AgI

- Fm-3m →$P2_1/m$
- $P2_1/m$ → *Cmcm*

Coordinate Number change in AgI

- 6 → 6+1 → 7

AgI : Catti M., PRB (2005)

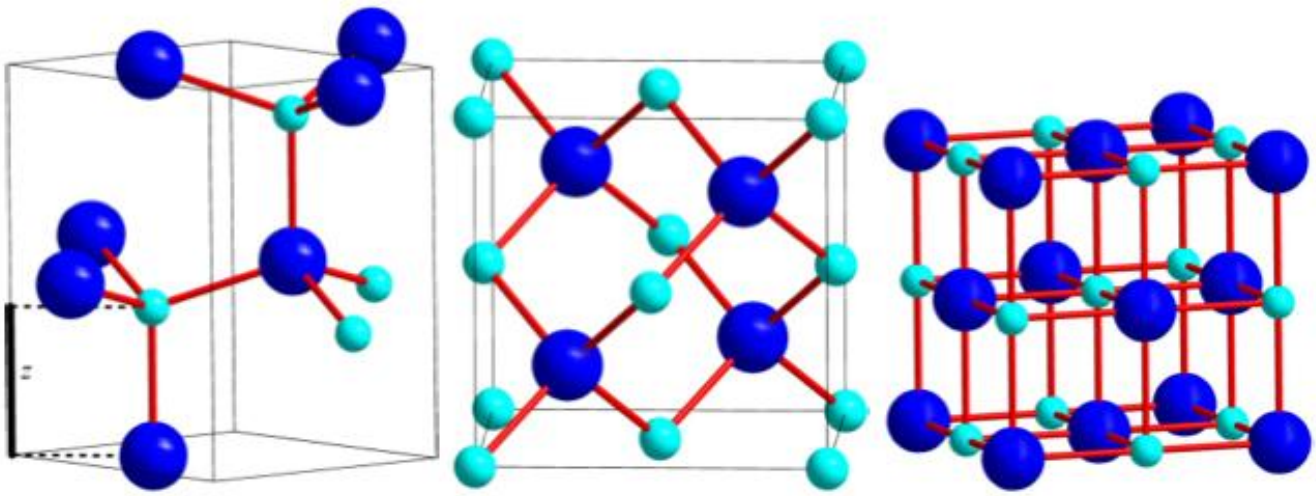


Reconstructive Phase Transitions

- The symmetry of the phases are not related
- Broken and reformation of the bonds
  - Coordinate Number (C.N.)

B4(CN=4) – Wurtzite
B3(CN=4) – Zincblende
B1(CN=6) – Rocksalt

B4→B1, B3→B1

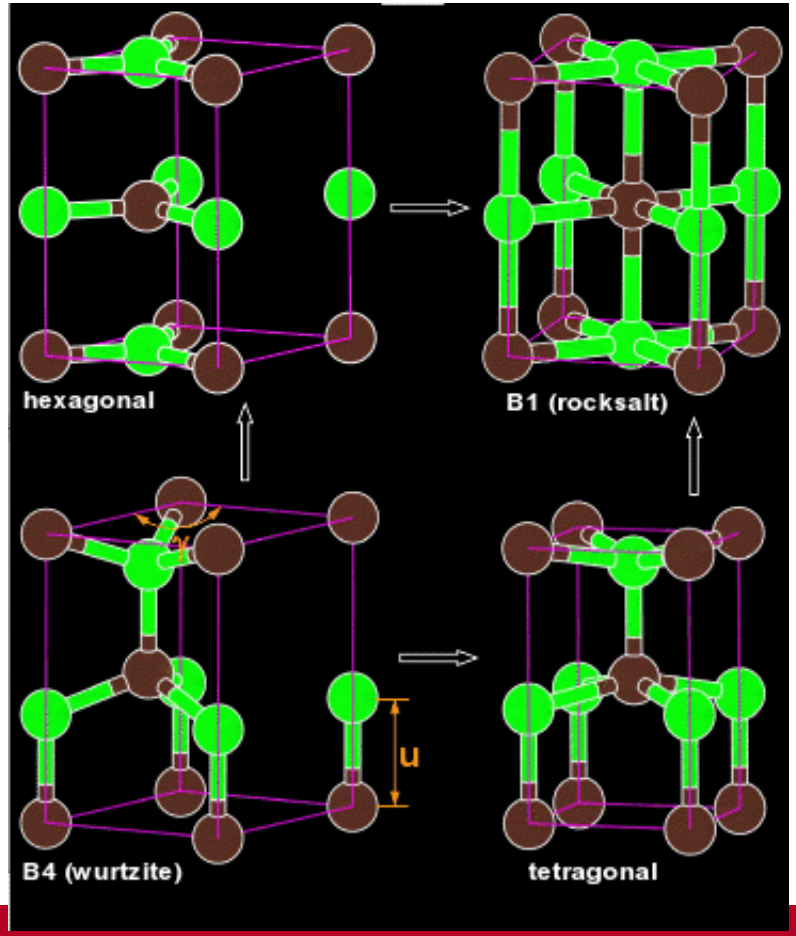


Phase transition pathway

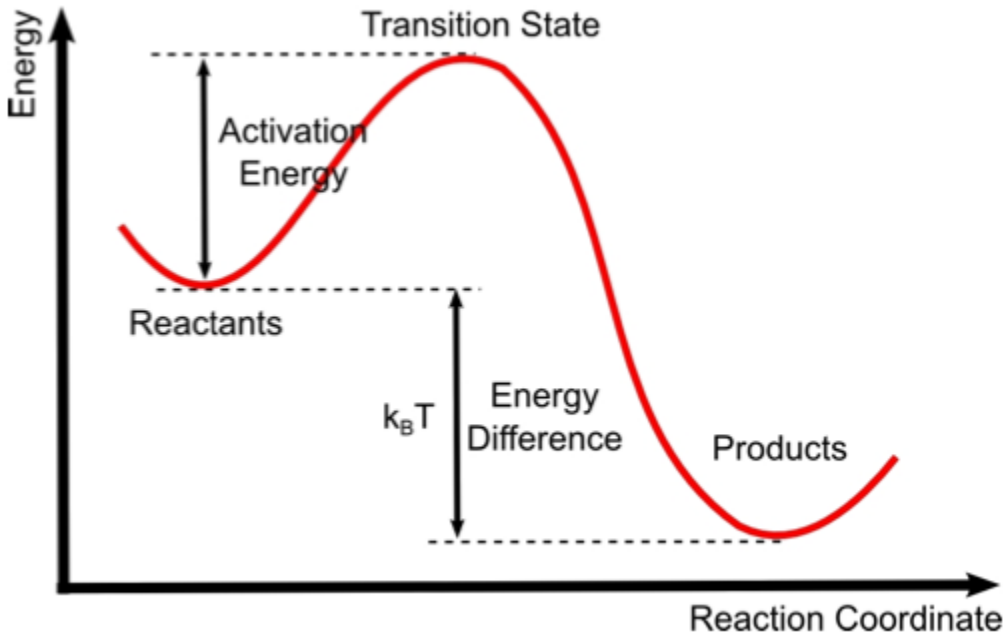
Two transition models for B4-to-B1 phase transformation in semiconducting materials (GaN, AlN, InN, ZnO, CdSe, et al . . .).

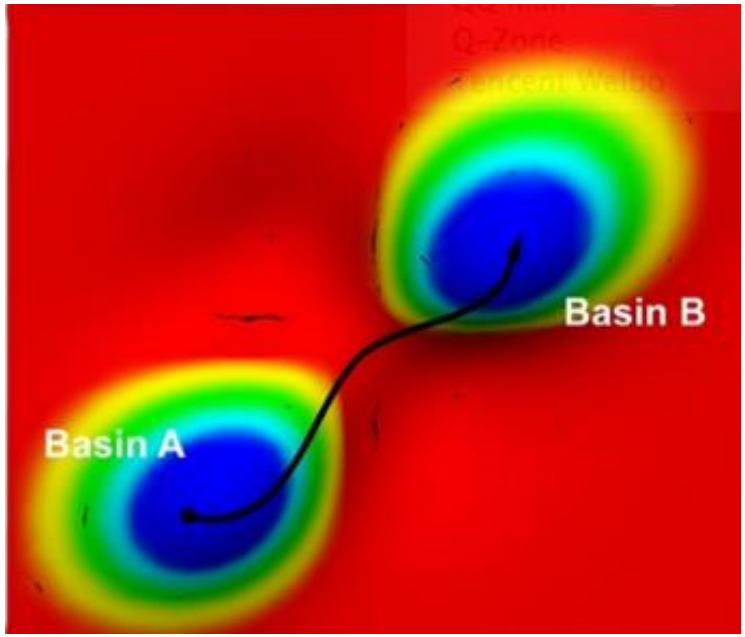
- **A hexagonal intermediate structure ($P6_3/mmc$)**
- **A tetragonal intermediate structure (I4mm)**

Both intermediates have fivefold coordinated atoms.



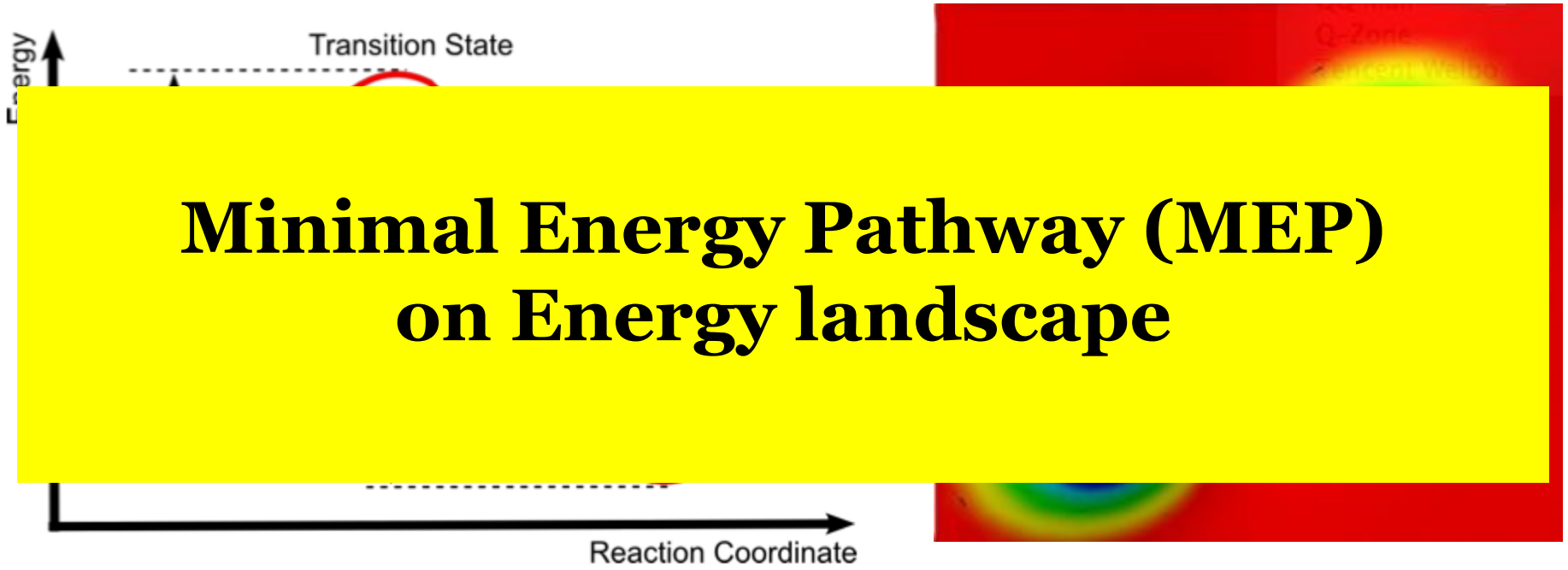
Phase transition pathway and energy landscape





Transition State Theory: The basic idea of TST is the assumption of a dividing surface in configuration space between stable states which are defined as adjacent sets separated by this surface.

Phase transition pathway and energy landscape

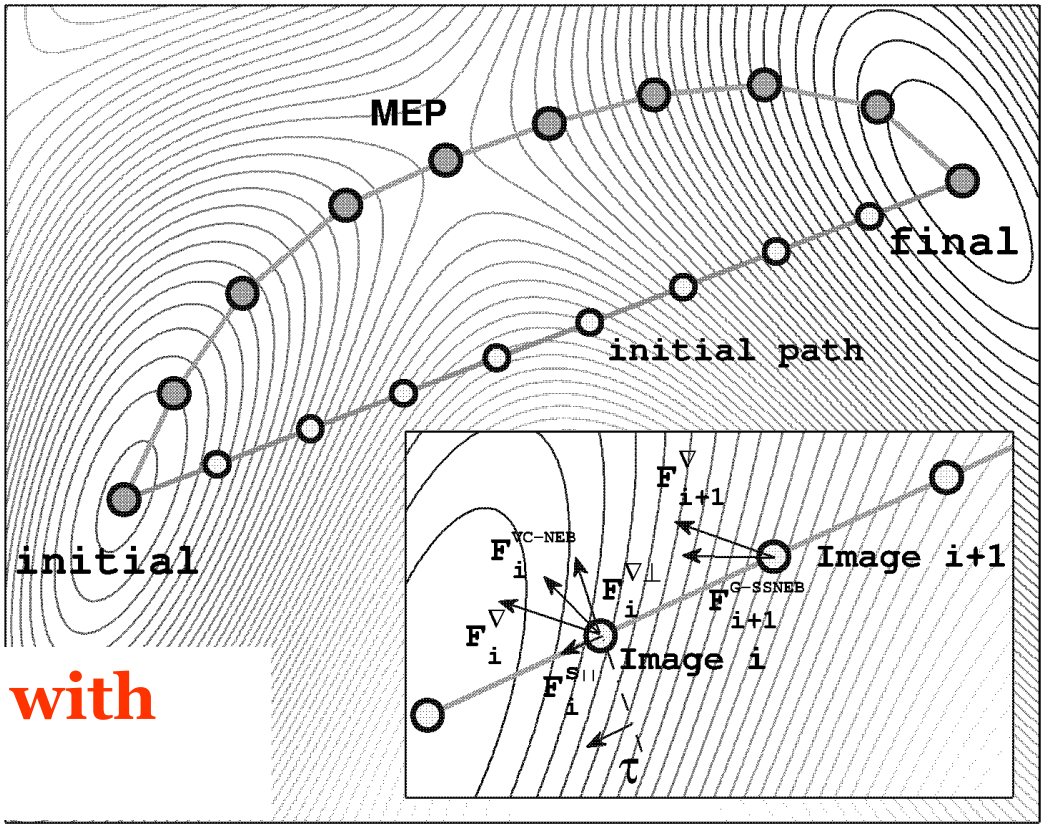


Minimal Energy Pathway (MEP) on Energy landscape

Transition State Theory: The basic idea of TST is the assumption of a dividing surface in configuration space between stable states which are defined as adjacent sets separated by this surface.

Variable-Cell Nudged Elastic Band Method

- Images (structures) Chain
- Adjusted forces on the images
- Evolution of the images chain
- Minimal Energy Pathway



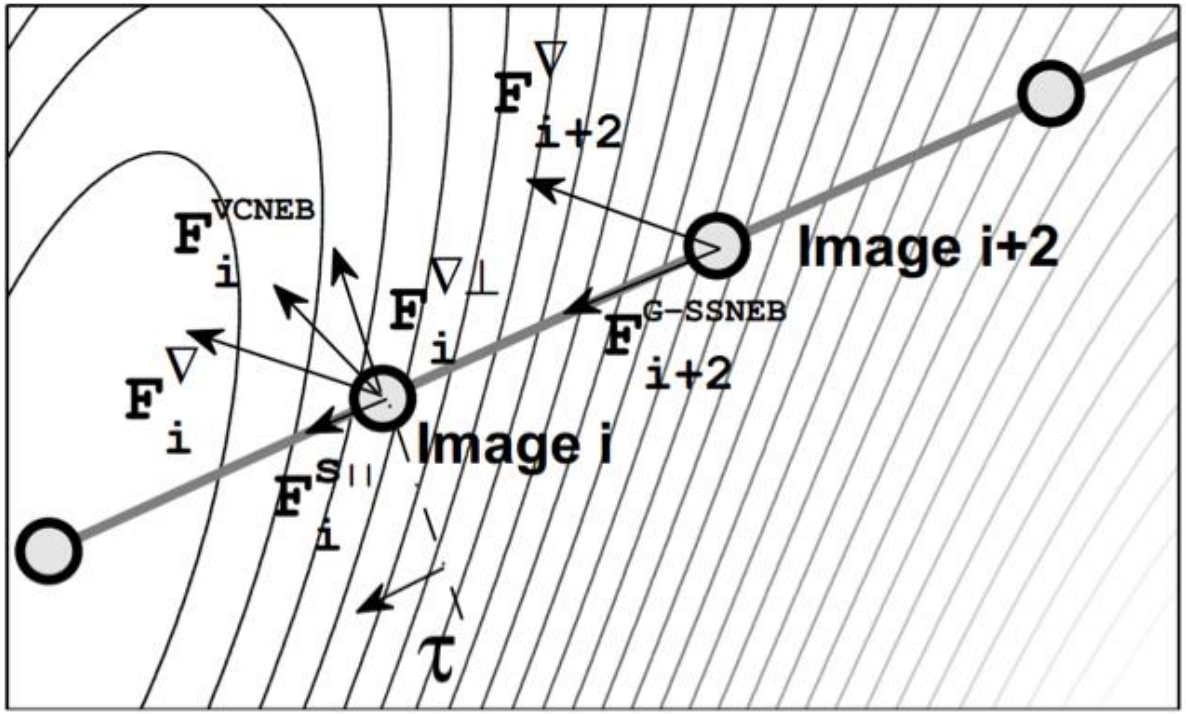
Structural Relaxations with Constraints !

Variable-Cell Nudged Elastic Band Method

$$H = E + P\Omega$$

$$\mathbf{F} = -\left.\frac{\partial H}{\partial \mathbf{X}}\right|_P .$$

$$\mathbf{F} = (f_{(\bar{\bar{\varepsilon}})}, gf_1, \ldots, gf_N)^T$$



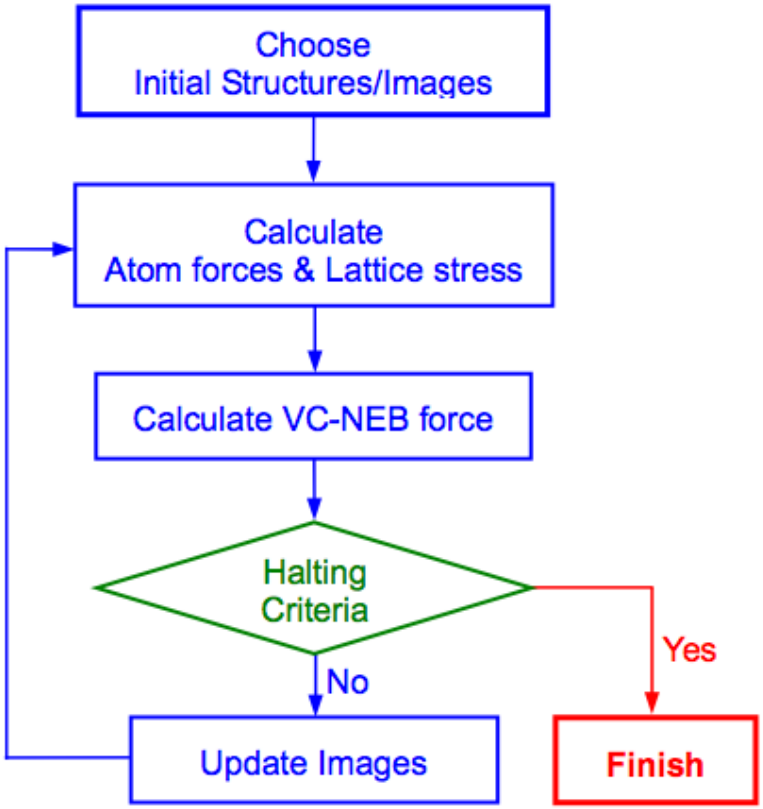
$$f_{(\bar{\bar{\varepsilon}})}^{VCNEB} = f_{(\bar{\bar{\varepsilon}})}^{s\parallel} + f_{(\bar{\bar{\varepsilon}})}^{\nabla\perp},$$

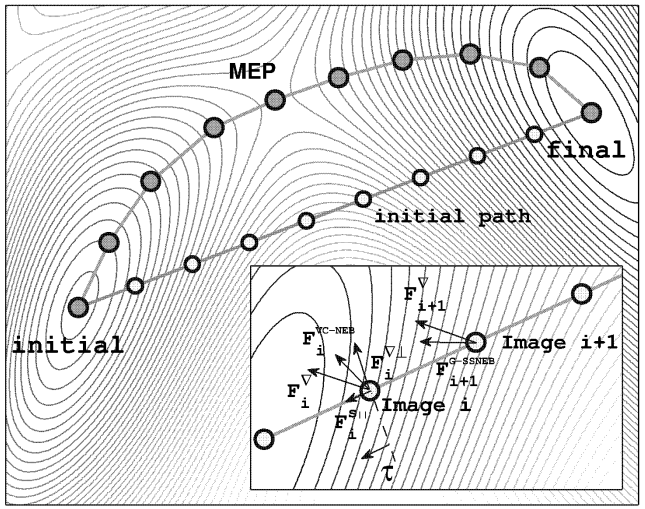
$$f_v^{VCNEB} = f_v^{s\parallel} + f_v^{\nabla\perp},$$

$$\mathbf{F}^{VCNEB} = \left(f_{(\bar{\bar{\varepsilon}})}^{VCNEB}, gf_1^{VCNEB}, \ldots, gf_N^{VCNEB}\right)^T$$

G.R. Qian, *et al, CPC*, 2013

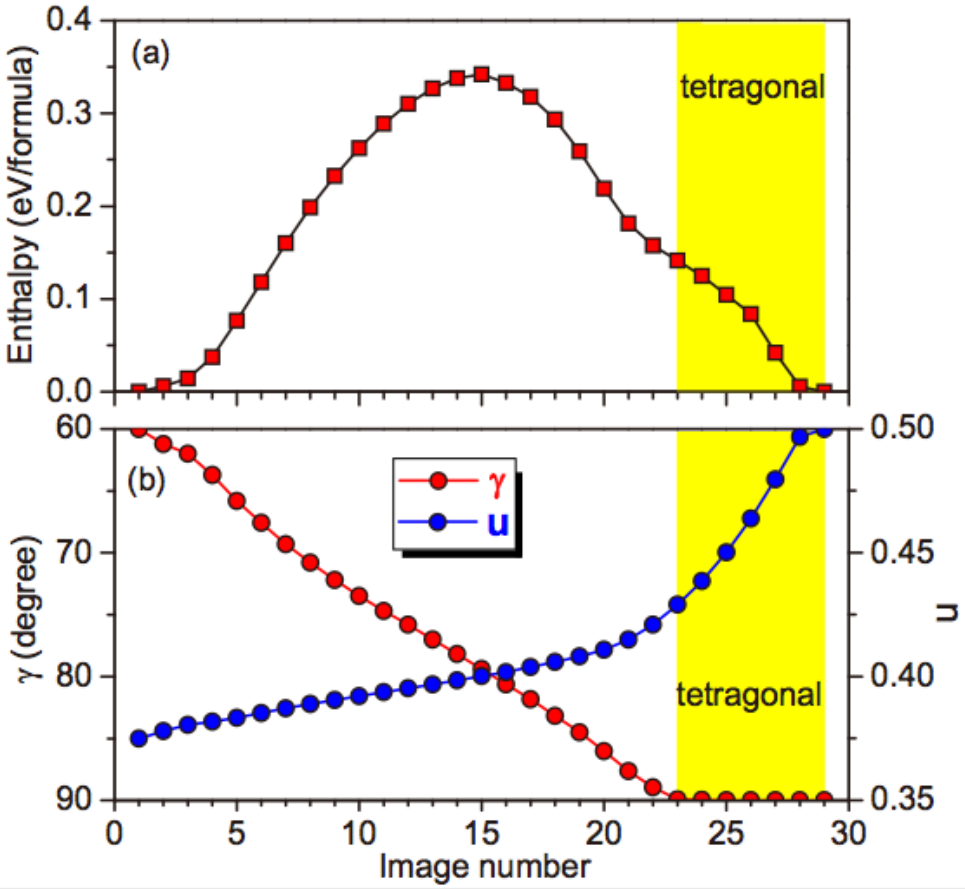
Variable-Cell Nudged Elastic Band Method

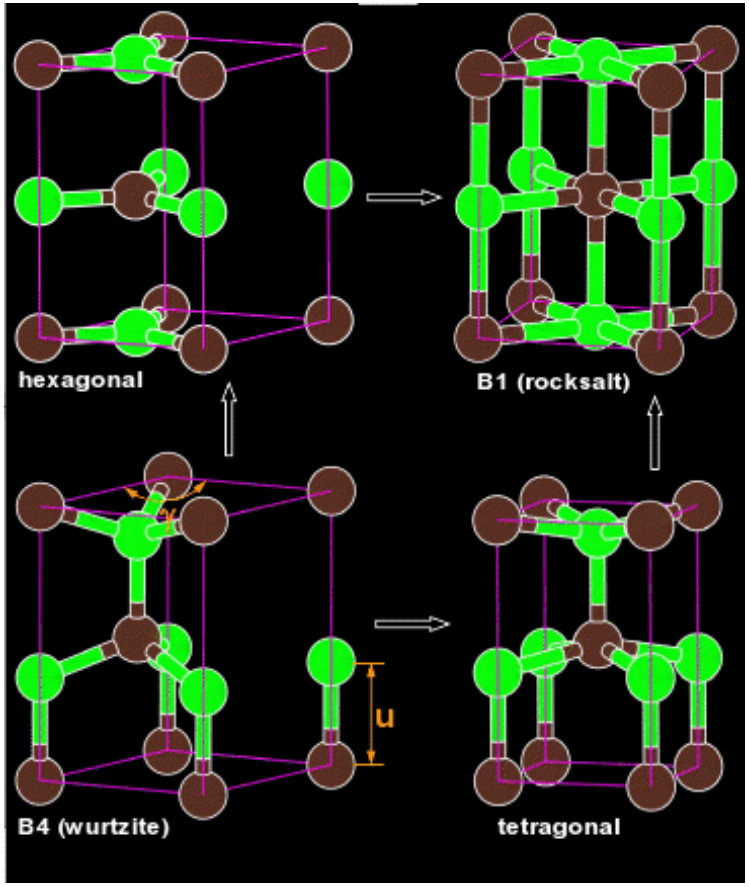




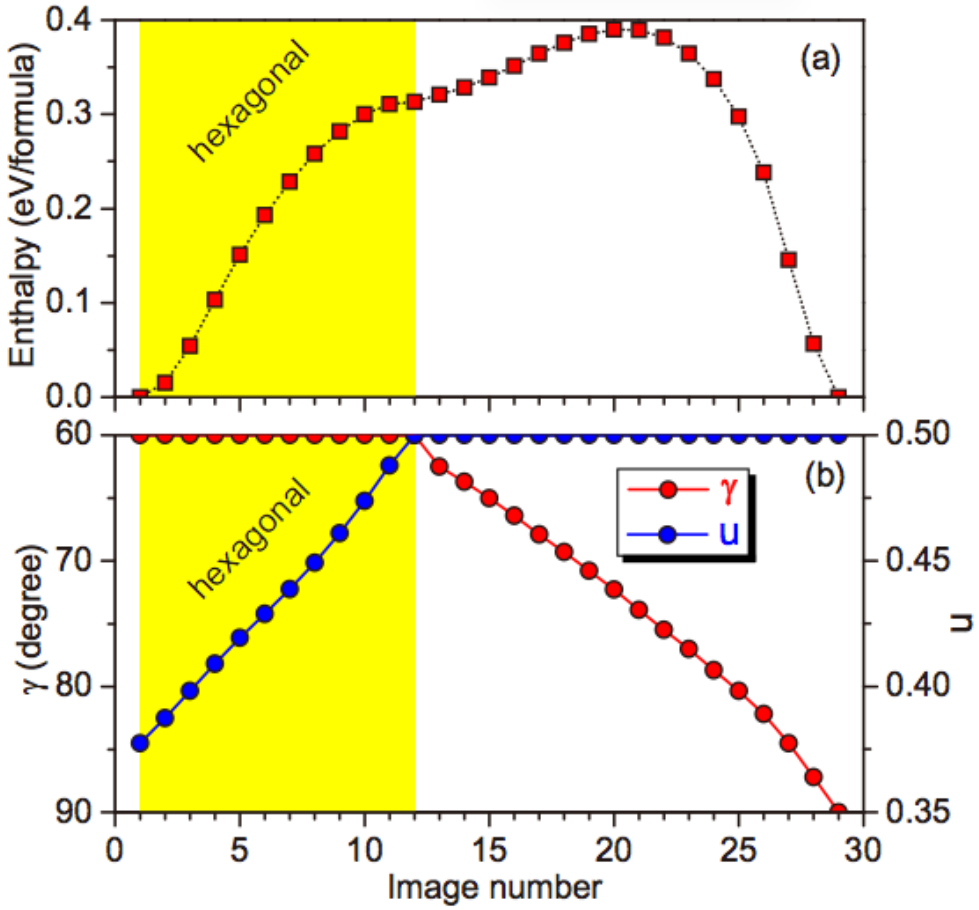
- Images (structures) Chain
- Adjusted forces on the images
- Evolution of the images chain
- Minimal Energy Pathway

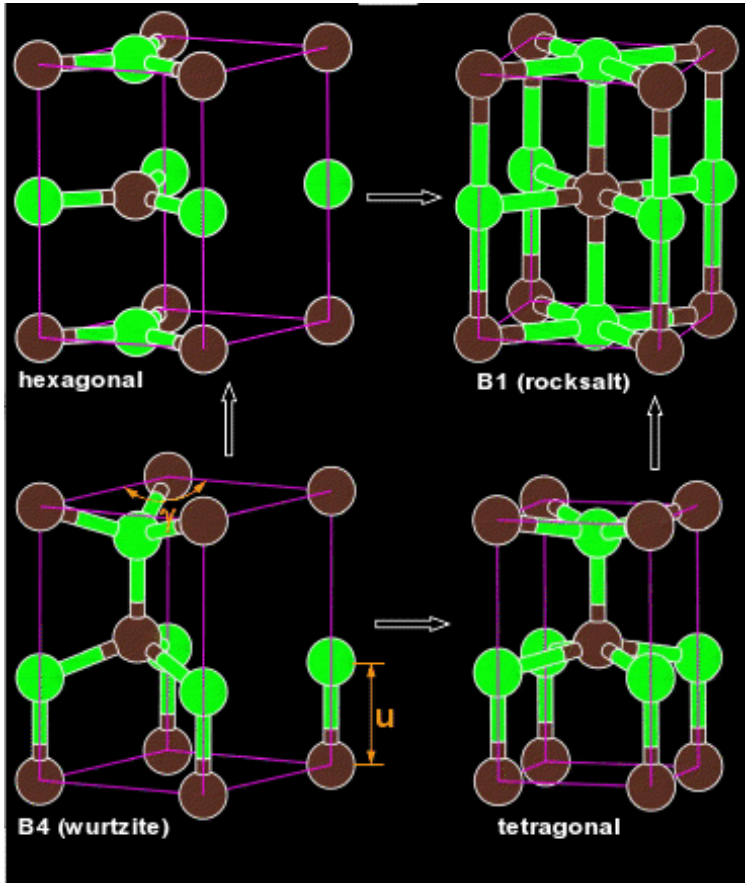
B4(wutzite) → B1 (rocksalt) Phase transition in GaN





B4(wutzite) → B1 (rocksalt) Phase transition in GaN





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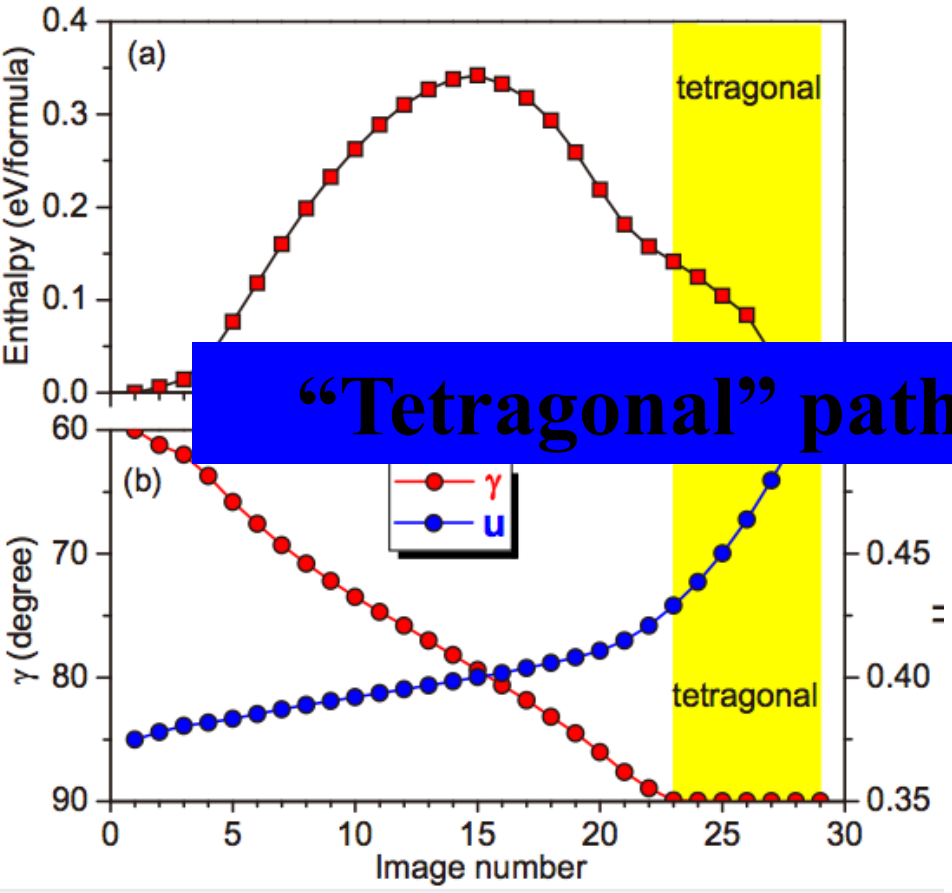
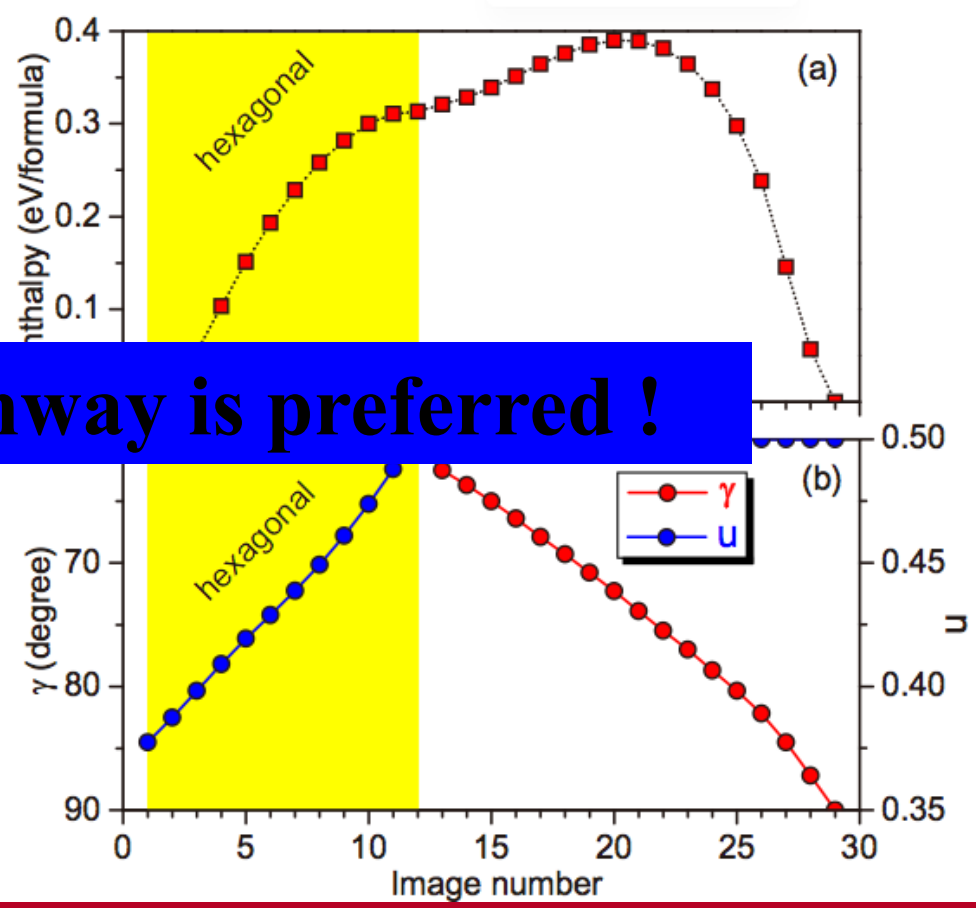
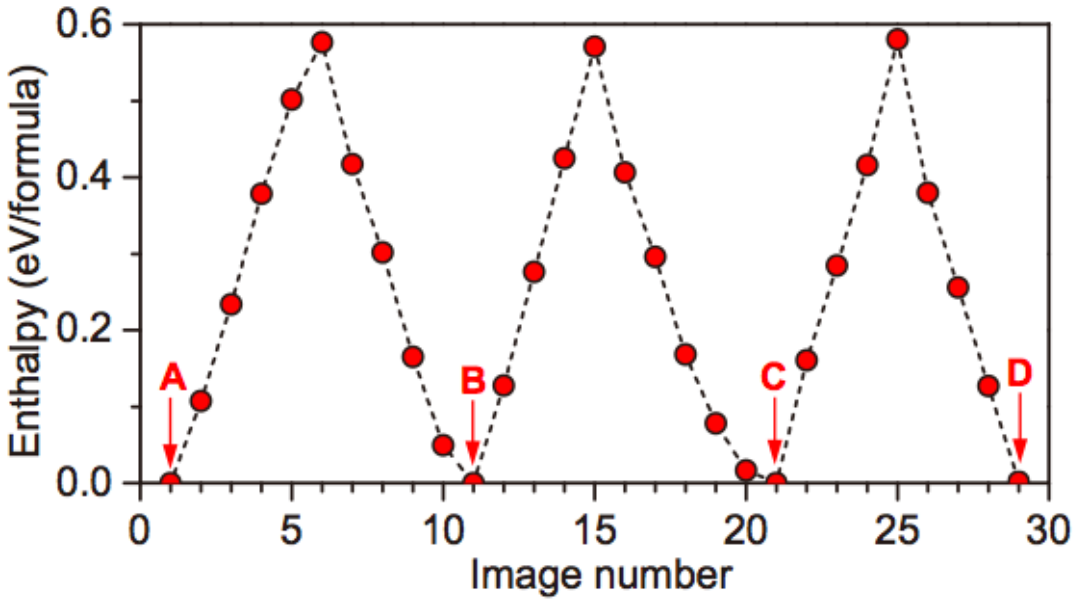
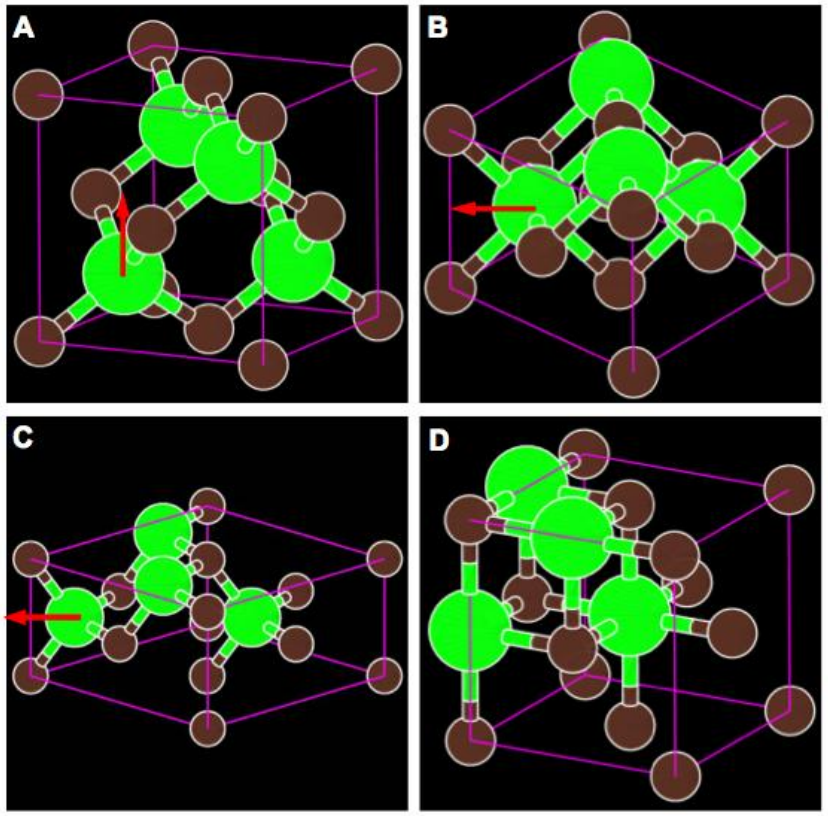


"Tetragonal" pathway is preferred !



B3(Zincblende) → B1 (rocksalt) Phase transition in GaN

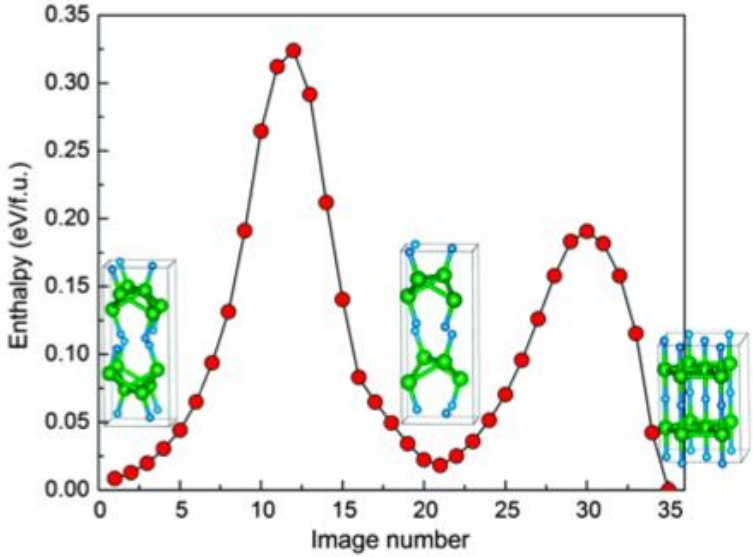




Imm2 Transition State

Other publication with VCNEB method

- X.F. Zhou, *et al*, *PRB*, **82** 134126 (2010)
- F. Tian, *et al*, *JPCM*, **24**, 165504 (2012)
- Z.S. Zhao, *et al*, *JACS*, **30**, 134 (2012)
- C. H. Hu, *et al*, *PRL*,**110**, 165504 (2013)
- X. Dong, *et al*, *JPCM*, **25**, 145402 (2013)

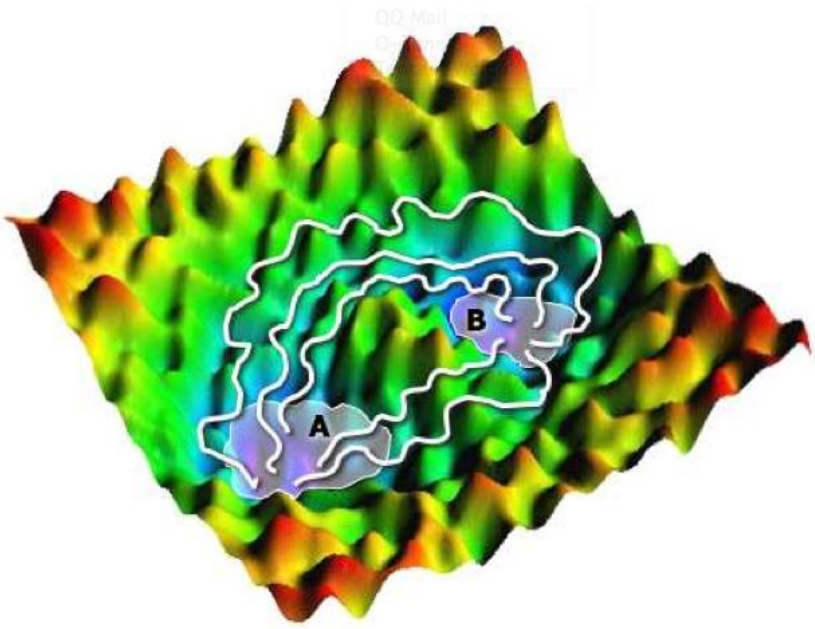


Further Discussion of the VCNEB method

- **How to generate/choose the initial pathway**
  - Various transition models (group/subgroup analyze)
  - Difficulty in paring the atoms in the initial and final images
- **How many images we should use?**
- **How to speed up the VCNEB calculation?**
- **Is the VCNEB result believable?**
  - VCNEB is a static method, works well in smooth topography of potenial energy landscapes
  - VCNEB has difficulty in find global minimal pathway

Transition Path Sampling Approach

"For systems containing large number of atoms, PES topologies are rough on the scale of thermal energies, k_BT , and dense in saddle points. Therefore, there is generally an uncountable number of transition states. The accurate determination of relevant points is not possible. Instead, one wants to locate and sample an ensemble of transition states. Transition path sampling accomplishes this task"



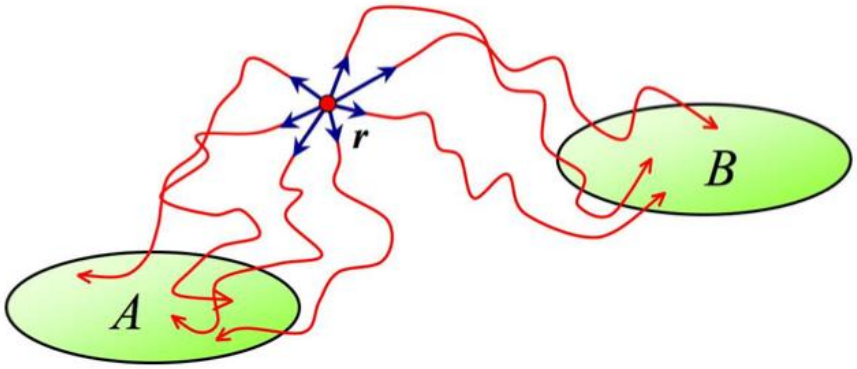
- *C.Dellago, P.G.Bolhuis and P.L. Geissler, "Transition Path Sampling", Adv. Chem. Phys. 123 (2002)*

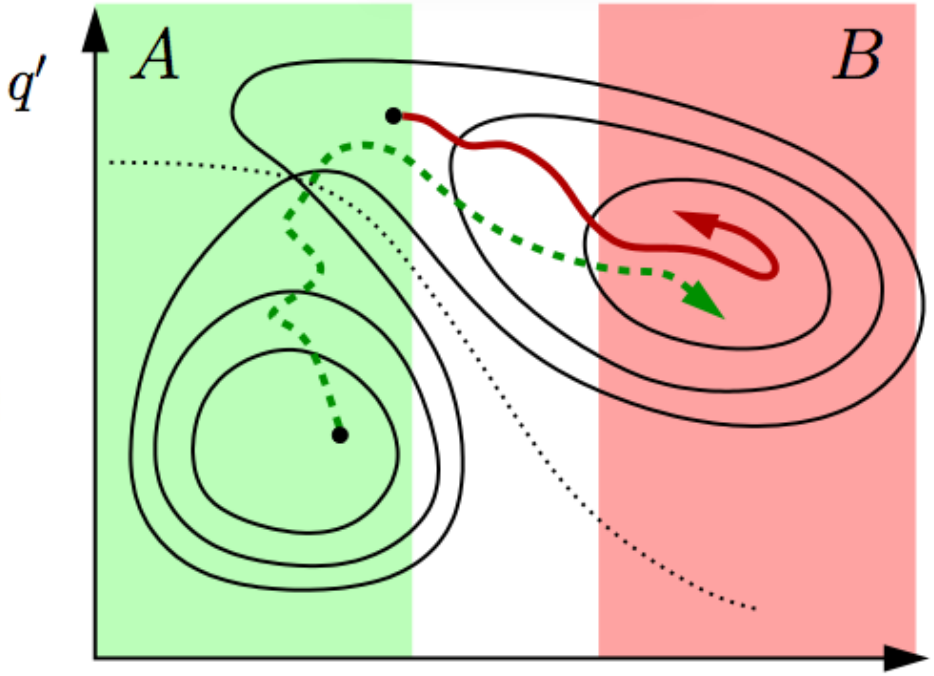
Introduction to TPS approach

Molecular Dynamic Simulation

+

Monte Carlo techniques

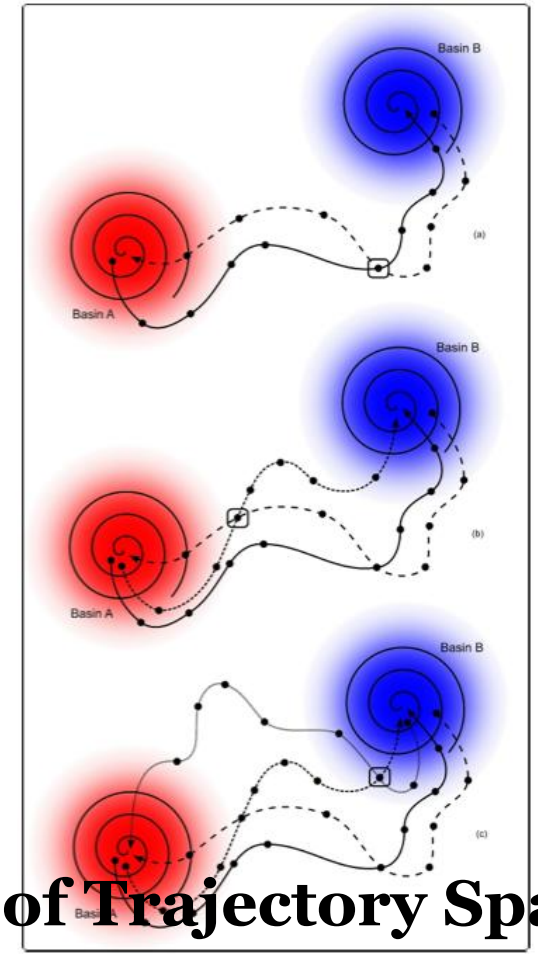


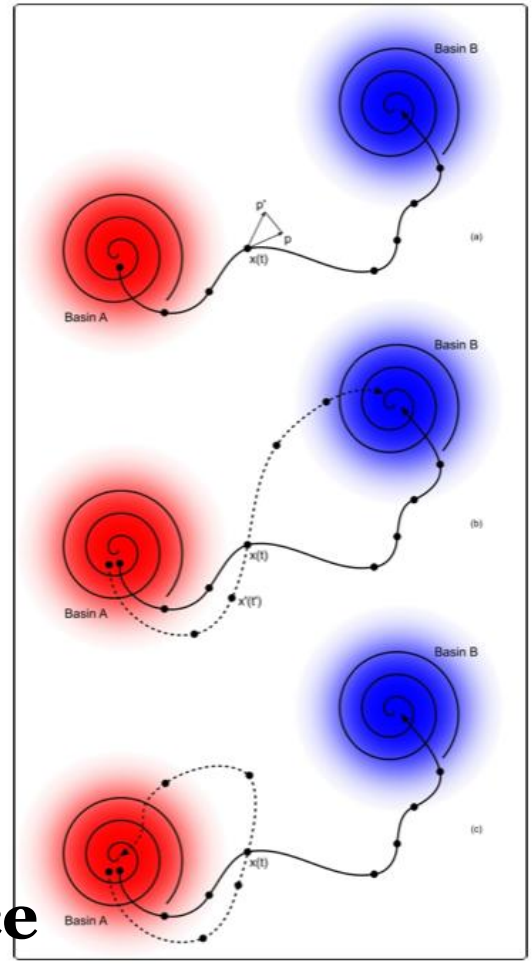


Basic idea : Sampling of Trajectory Space

Shooting and Shifting Moves

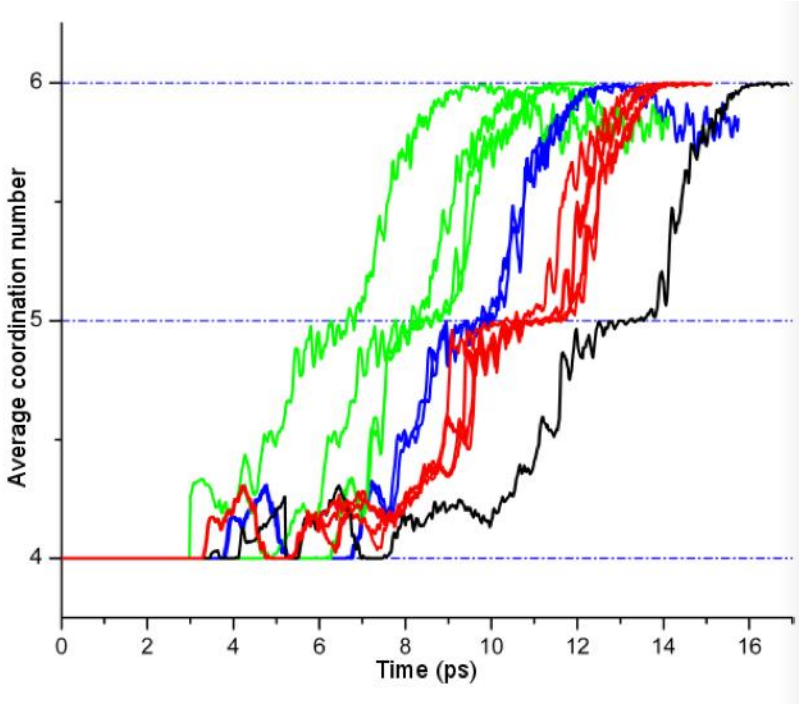
1. Define the parameter of the initial and final phase
2. Find the initial trajectory
3. Sampling the trajectory ensemble with shooting and shifting move
4. Find the transition pathway



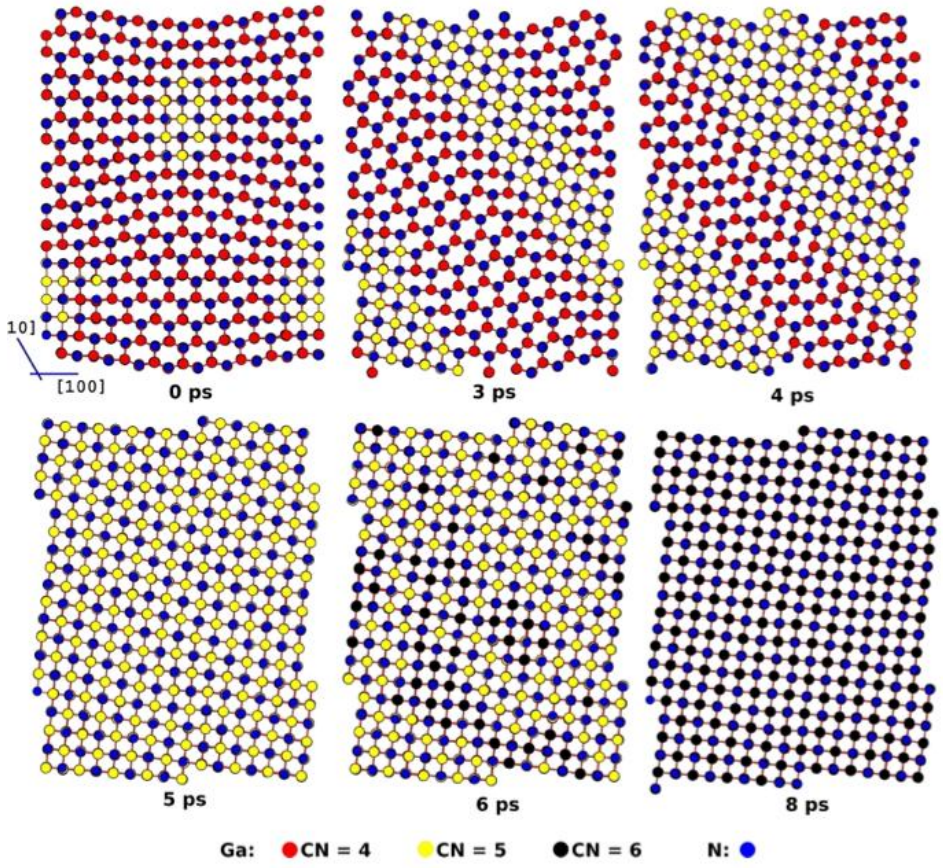


Basic idea : Sampling of Trajectory Space

Studying the Wurtzite-to-Rocksalt (B4-B1) in GaN with TPS



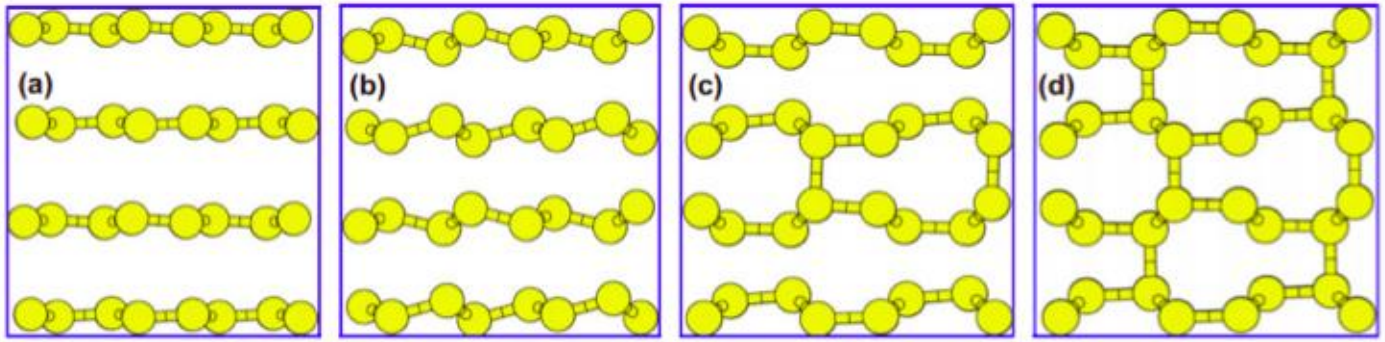
S. E. Boulfelfel, ***PRL*** (2007)

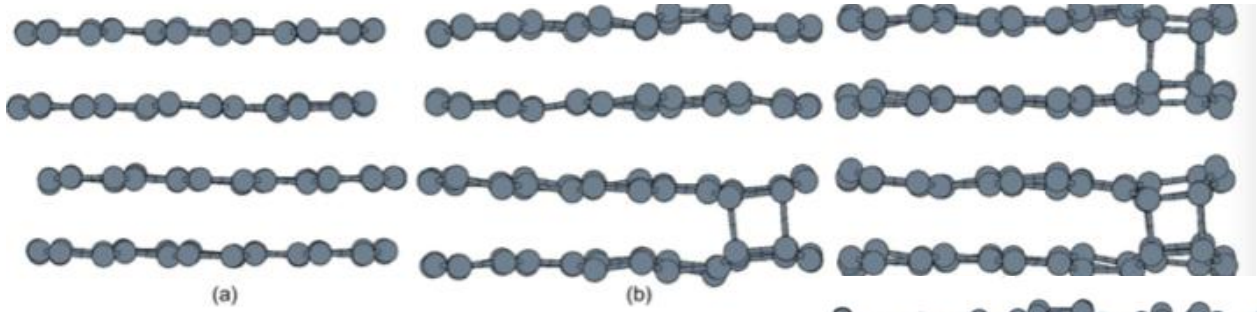


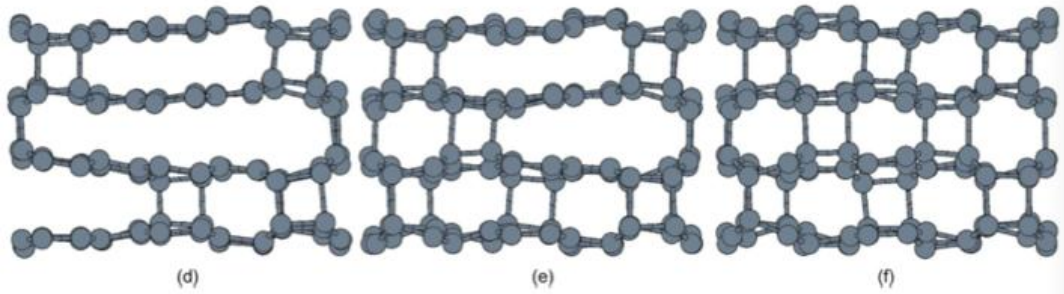
Using the VCNEB and TPS studying Carbon system

Graphite →

bct-Carbon





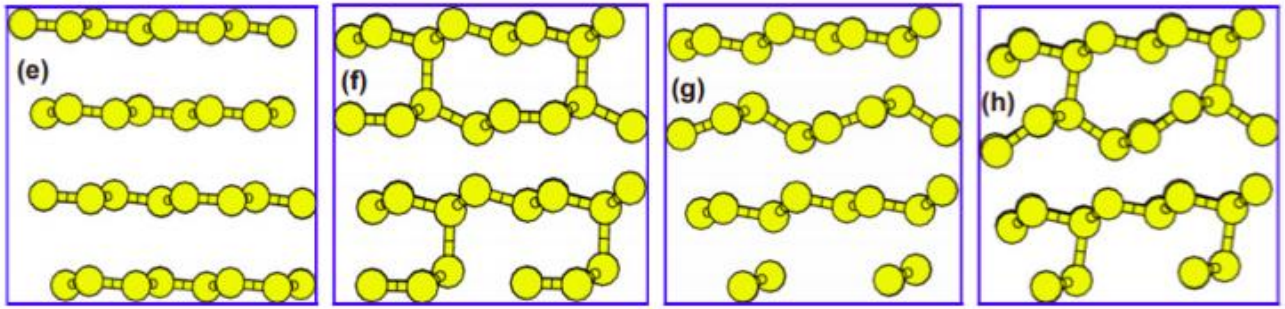


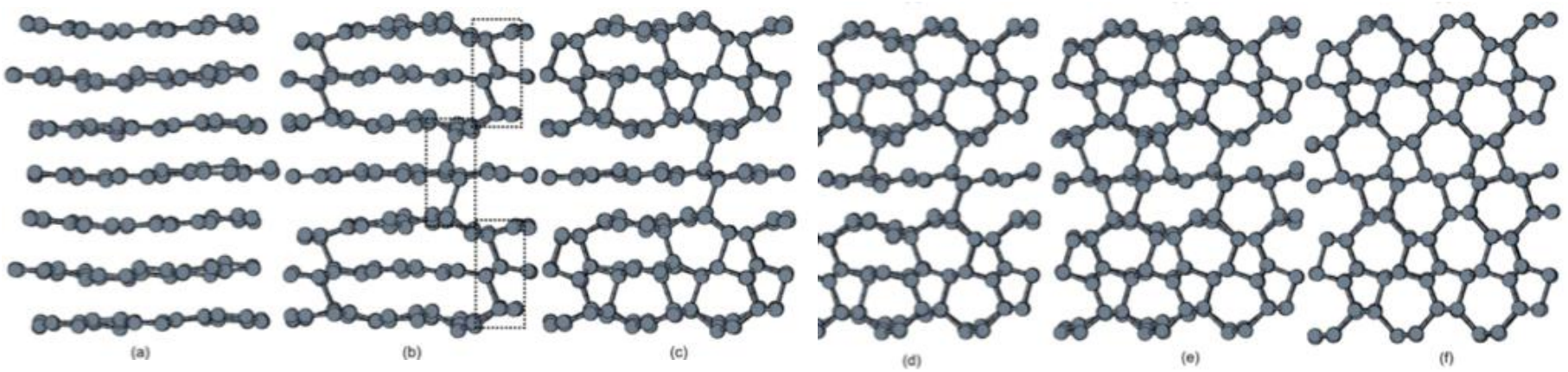
X.F. Zhou, *et al, PRB*, (2010)

S. E. Boulfelfel, *et al, Scientific Reports* (2012)

Using the VCNEB and TPS studying Carbon system

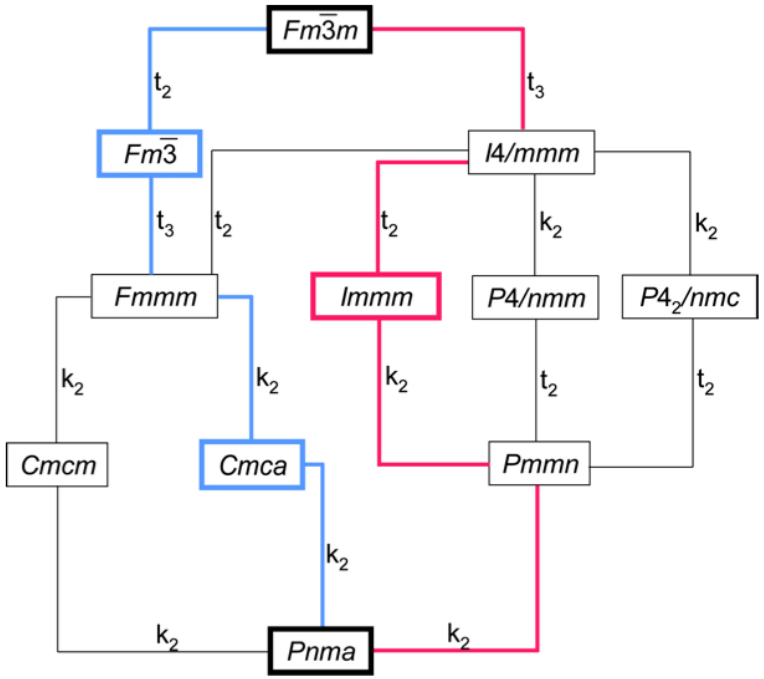
Graphite → M-Carbon





Further Discussion of the TPS method

- Very difficult to generate the first trajectory
- MD software must support "-t" simulation and NPT ensemble
- VCNEB is a complementary of TPS
- Size effect in TPS simulation
- Time consuming



Applying the VCNEB pathway to get the first trajectory!

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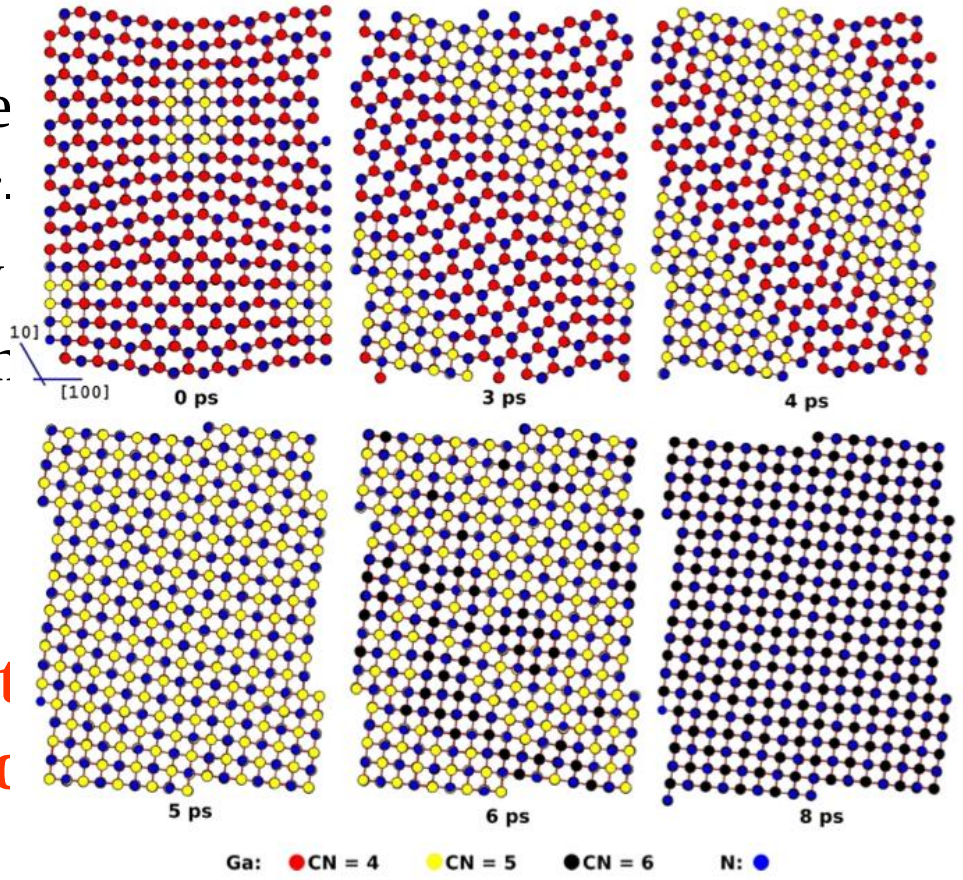


Applying the VCNEB pat
to get the first trajecto

Salah Eddine Boulfelfel

Atomic Scale Investigation of Pressure Induced Phase Transitions in the Solid State

DISSERTATION

zur Erlangung des akademischen Grades

Doctor rerum naturalium

(Dr. rer. nat.)

vorgelegt

der Fakultät Mathematik und Naturwissenschaften

der Technischen Universität Dresden

von

M. Sc. Salah Eddine Boulfelfel

Snapshots of VCNEB codes

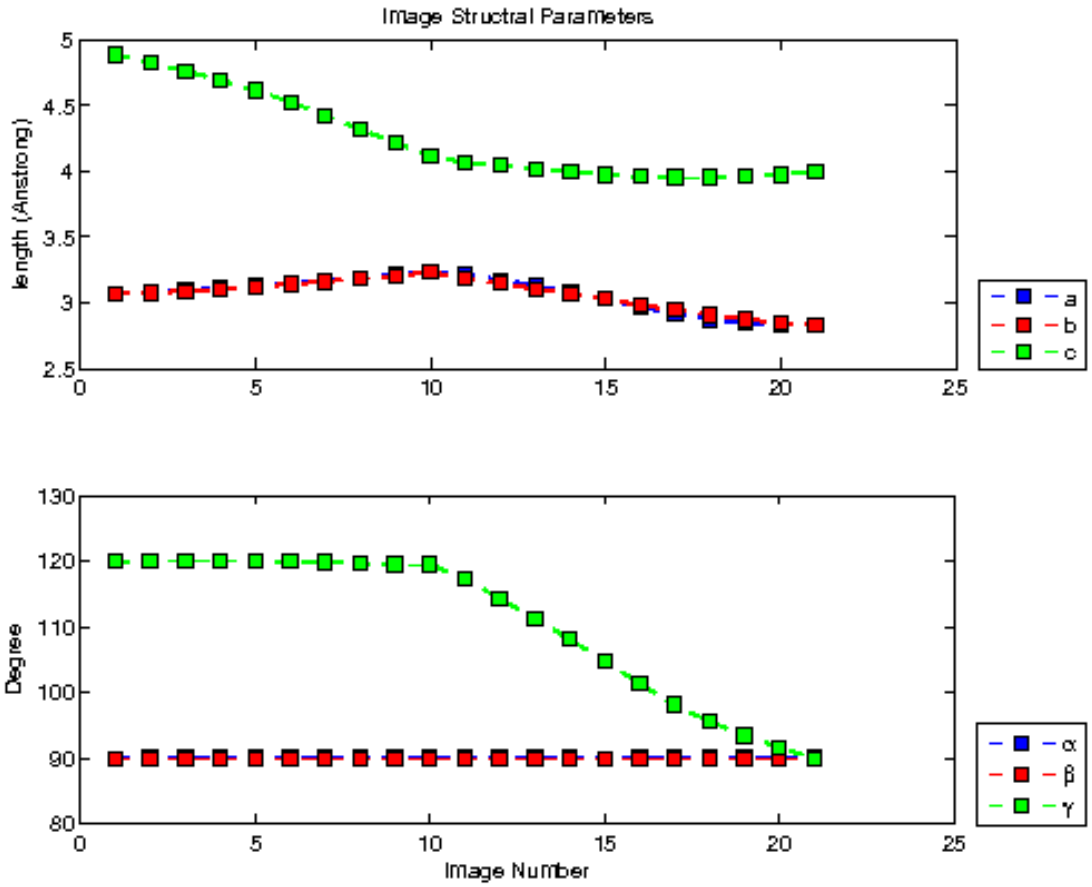
---------- VCNEB step : 400 ----------

Image	Energy-(eV)	Cell Forces RMS(eV/A) Total, Project, Elastic	Atom Forces RMS(eV/A) Total, Project, Elastic	F	Dist	SpaceG	
1	-26.4053383	[0.000, 0.000, 0.000]	[0.000, 0.000, 0.000]	0	0.0000	186	
2	-26.3966007	[0.005, 0.005, 0.000]	[0.005, 0.005, 0.000]	0	0.1050	186	
3	-26.3724992	[0.011, 0.010, 0.002]	[0.007, 0.009, 0.002]	0	0.1053	186	
4	-26.3394881	[0.017, 0.014, 0.005]	[0.008, 0.012, 0.004]	0	0.1135	186	
5	-26.2901382	[0.022, 0.017, 0.007]	[0.009, 0.014, 0.005]	0	0.1329	186	
6	-26.2256773	[0.023, 0.019, 0.007]	[0.010, 0.015, 0.005]	0	0.1591	186	
7	-26.1598812	[0.019, 0.016, 0.006]	[0.008, 0.012, 0.004]	0	0.1853	186	
8	-26.1128024	[0.007, 0.006, 0.003]	[0.004, 0.005, 0.002]	0	0.2069	186	<-TS->
9	-26.1160149	[0.010, 0.008, 0.004]	[0.006, 0.007, 0.002]	0	0.2164	186	
10	-26.1515661	[0.012, 0.009, 0.005]	[0.010, 0.009, 0.003]	0	0.2042	186	->LM<-
11	-26.1335112	[0.011, 0.011, 0.001]	[0.007, 0.006, 0.001]	0	0.1886	63	
12	-26.0686401	[0.018, 0.017, 0.001]	[0.008, 0.009, 0.001]	0	0.1863	63	
13	-25.9863780	[0.019, 0.018, 0.002]	[0.007, 0.009, 0.002]	0	0.1901	63	
14	-25.9105485	[0.014, 0.013, 0.002]	[0.004, 0.006, 0.002]	0	0.1963	63	
15	-25.8702263	[0.001, 0.001, 0.000]	[0.000, 0.000, 0.000]	0	0.2027	63	<-TS->
16	-25.9013573	[0.019, 0.017, 0.004]	[0.003, 0.007, 0.005]	0	0.2033	63	
17	-26.0182132	[0.042, 0.037, 0.010]	[0.003, 0.015, 0.012]	0	0.1899	63	
18	-26.1786445	[0.053, 0.047, 0.013]	[0.002, 0.018, 0.016]	0	0.1585	63	
19	-26.3066966	[0.042, 0.037, 0.009]	[0.001, 0.013, 0.012]	0	0.1184	63	
20	-26.3746645	[0.018, 0.016, 0.003]	[0.001, 0.005, 0.004]	0	0.0898	139	
21	-26.3935964	[0.000, 0.000, 0.000]	[0.000, 0.000, 0.000]	0	0.0801	225	

activation energy (->) = 0.535112 eV
activation energy (<-) = 0.523370 eV

Snapshots of VCNEB codes

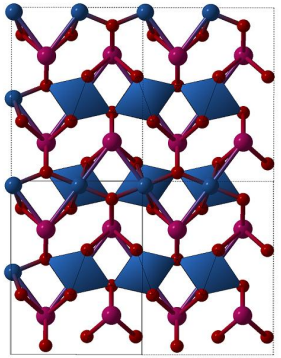
- **VCNEB : calculationMethod**
- Variable Image technique
- Variable Spring Constant method
- Climbing-Image technique

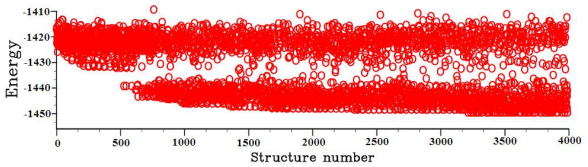


USPEX

-- Universal Structure Predictor: Evolution Xtallography

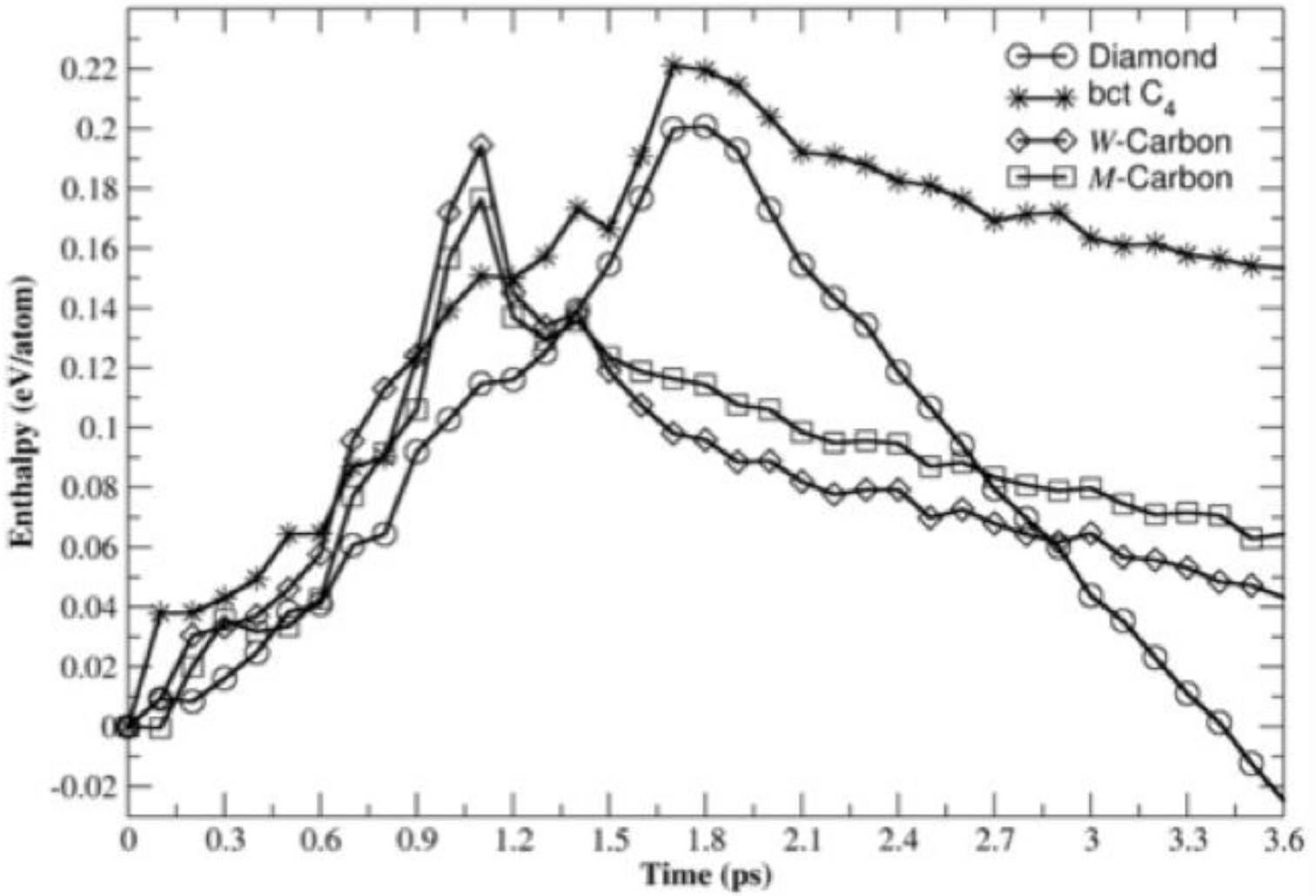
- **Evolutionary methods**
  - 3D and molecular systems
  - Surface and low dimension systems
- **Evolutionary metadynamics method**
- **Variable-Cell-Nudged-Elastic-Band method**
- **Transition path sampling approach**
- **Other new methods/features are under developing …**





Thanks~

Please enjoy the USPEX !


Diamond
bct C4
W-Carbon
M-Carbon
Enthalpy (eV/atom)
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
0
0.3
0.6
0.9
1.2
1.5
1.8
2.1
2.4
2.7
3
3.3
3.6
Time (ps)

Stony Brook University

USPEX

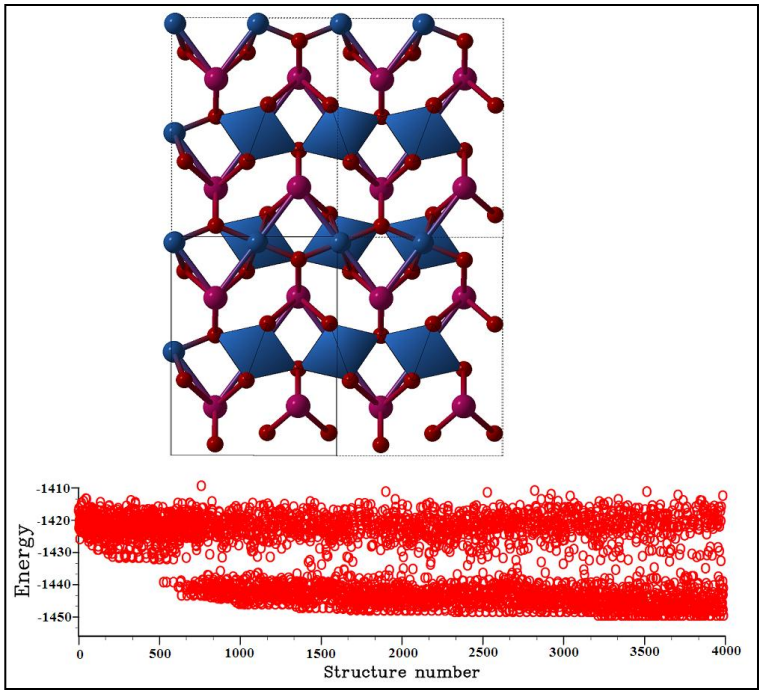
Universal Structure Predictor: Evolutionary Xtallography

- ***Evolutionary Algorithm***
- ***Ab initio* determination**

  Given information as least as possible
- ***Powerful Searching***

  invariant with the system

  Self-improved learning process



Website: http://uspex.stonybrook.edu

Oganov A.R., Lyakhov A.O., Valle M. (2011).
How evolutionary crystal structure prediction works - and why.
***Acc. Chem. Res.* 44, 227-237.**