Stony Brook University

Predicting Low Dimensional Systems

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USPEX: Computational Materials Design

Crystal Structure Prediction

System

- **Dimension**

0: Nano-particle;
1: polymers;
2: surfaces/crystals;
3: Bulk

- **Stoichiometry**

0: fixed; 1: variable

- **Building block**

0: atom; 1: molecule

Target

- Density
- Hardness
- Dielectric constants
- Band gap
- Magnetic moment
- ….

Crystal Structure:

300: Sunday

310: Sunday

301: Monday

311: Monday

Materials Discovery:

Monday

USPEX: Computational Materials Design

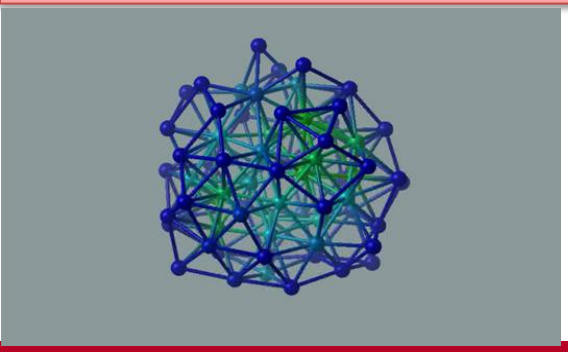
(Crystal) Structure Prediction

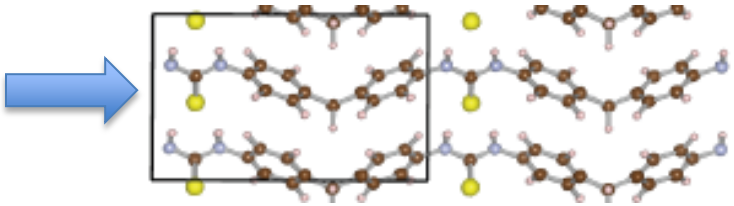
System

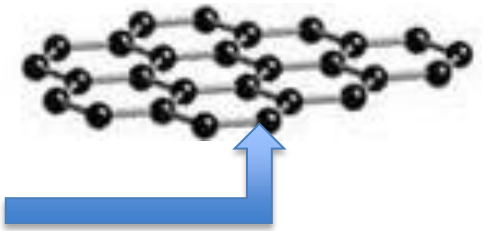
- **Dimension**
  - 0: Nano-particle;
  - 1: polymers;
  - 2: surfaces/2D crystals;
  - 3: Bulk
- **Stoichiometry**

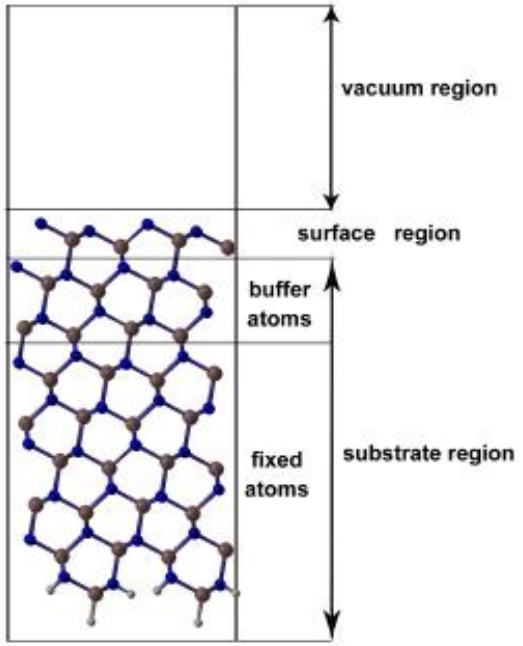
  0: fixed; 1: variable
- **Building block**

  0: atom; 1: molecule

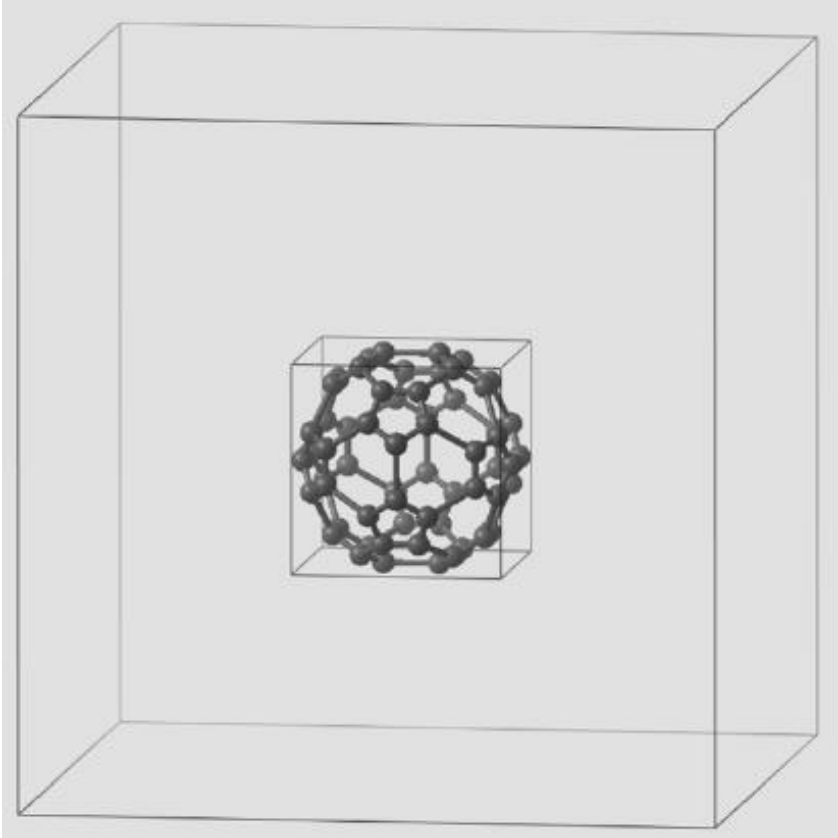






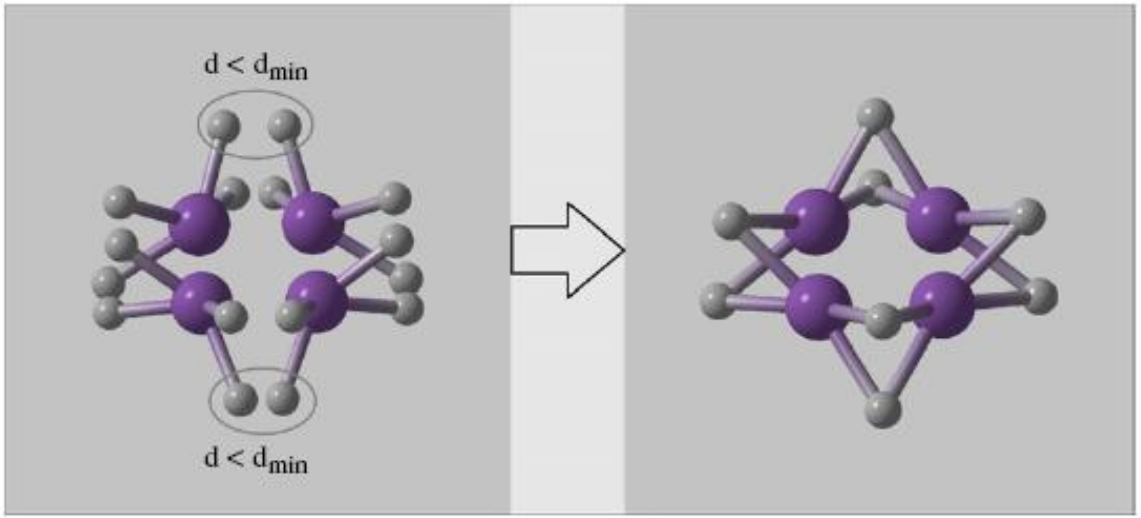


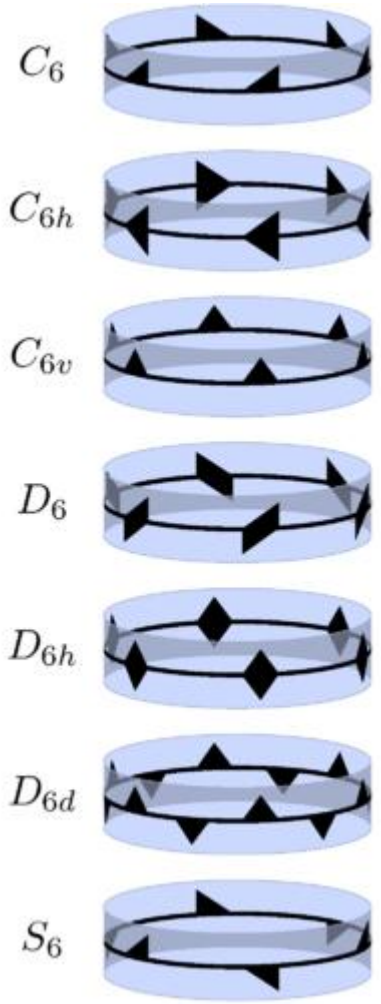
Cluster: 000



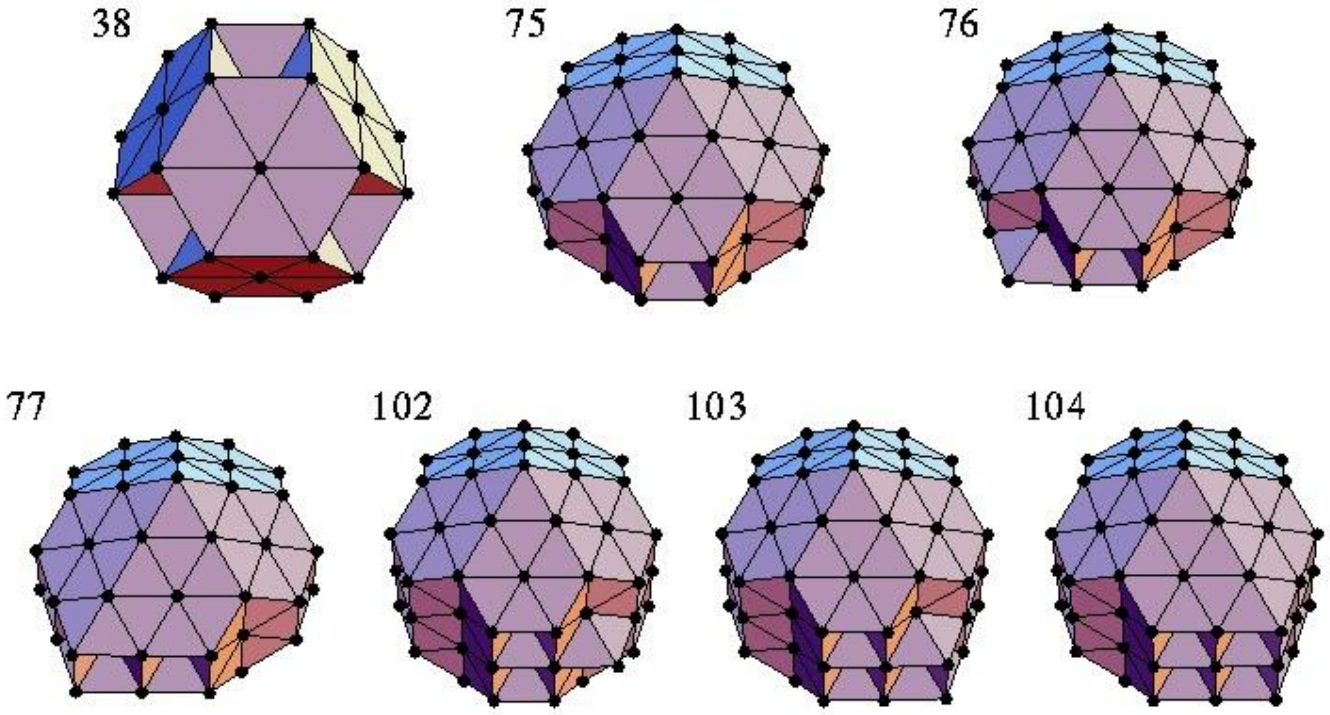
Cluster: 000

32 crystallographic point groups
Some other important non-cryst point groups



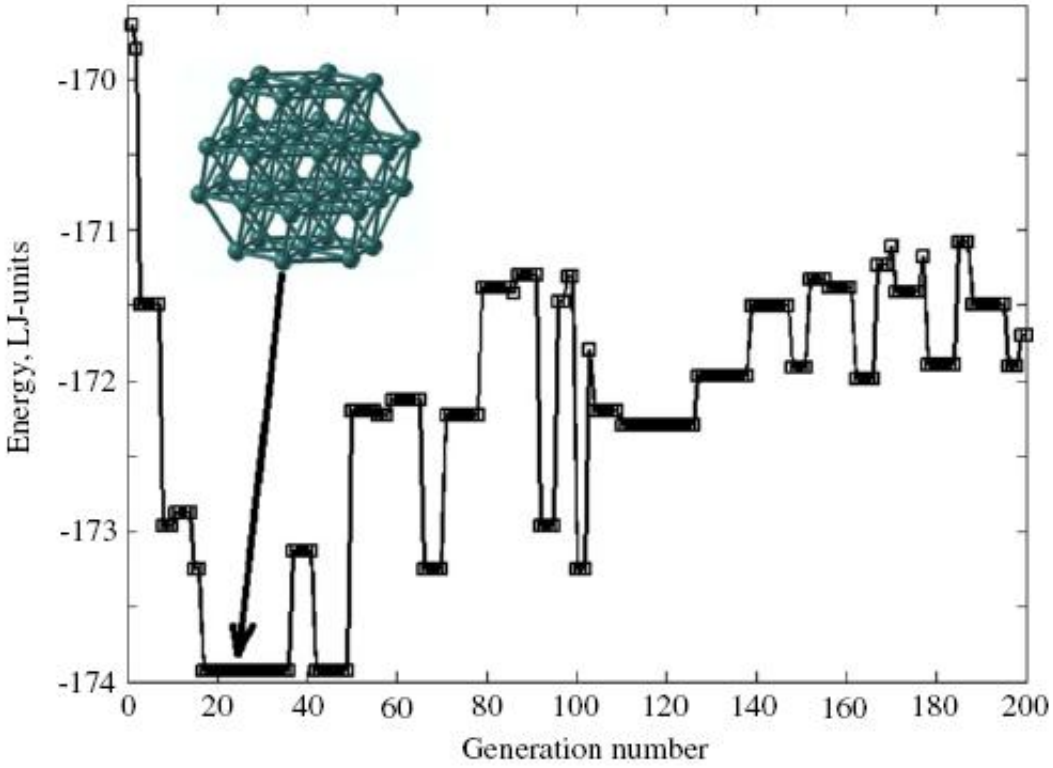


Lennard-Jones Clusters



http://doye.chem.ox.ac.uk/jon/structures/LJ/pictures/LJ.nonicos.gif

Prediction using USPEX



LJ-38 with antiseeds technique

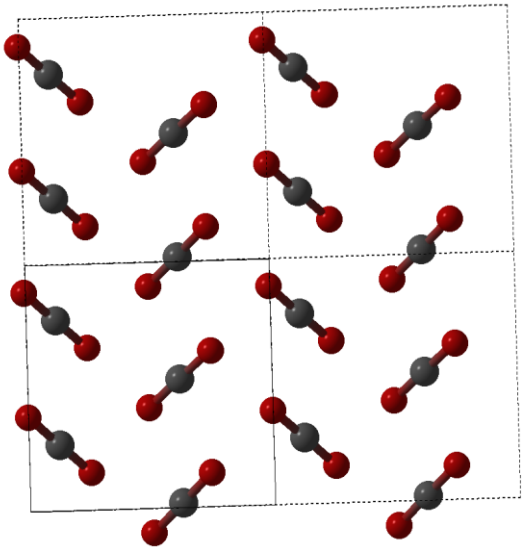
Statistics for Lennard-Jones clusters with different algorithms. Best algorithms are highlighted in bold.

	Symmetric initialization	Antiseeds	Order	Success rate (%)	Average number of structures until global minimum is found	Dispersion	Number of calculations
LJ_{38} (PSO [48])	+	−	−	100	605	N/a	100
LJ_{38}(USPEX)	+	+	−	**100**	**35**	**58**	**183**
LJ_{38}(USPEX)	−	−	−	67	2291	1443	100
LJ_{38}(USPEX)	−	+	−	98	3080	2119	100
LJ_{38} (EA [46])[b]	−	−	−	N/a	1265	N/a	100
LJ_{38} (MH [46])[b]	−	−	−	100	1190	N/a	100
LJ_{38} (EA [47])[b]	−	−	−	N/a	~2000[a]	N/a	N/a
LJ_{38} (PSO [48])	−	−	−	100	1649	N/a	20
LJ_{44}(USPEX)	−	−	−	100	1510	1079	35
LJ_{44}(USPEX)	−	+	+	**100**	**859**	**524**	**37**
LJ_{44}(USPEX)	+	+	+	100	1129	765	41
LJ_{44}(USPEX)	+	−	−	86	1551	1020	35
LJ_{44}(USPEX)	+	+	−	94	1423	867	35
LJ_{55} (PSO [48])	+	−	−	100	159	N/a	100
LJ_{55}(USPEX)	+	−	−	**100**	**11**	**30**	**60**
LJ_{55}(USPEX)	−	−	−	100	717	407	103
LJ_{55} (EA [46])[b]	−	−	−	100	100	N/a	100
LJ_{55} (MH [46])[b]	−	−	−	100	190	N/a	100
LJ_{75} (PSO [48])	+	−	−	98	2858	N/a	50
LJ_{75}(USPEX)	+	+	+	**100**	**2145**	**2024**	**53**
LJ_{75}(USPEX)	+	+	−	100	5419	4513	47

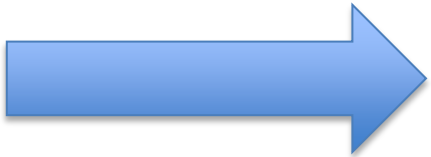
[a] Depending on algorithm parameters, 2000–12 000 structures were required to reach the global minimum in [47].

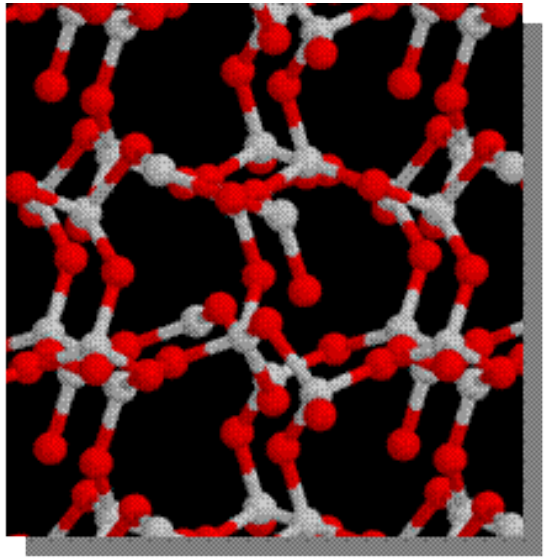
[b] Results for algorithms [46,47] are given for optimized algorithm parameters. We did not attempt to optimize USPEX parameters and chose them based on intuition and experience. We could achieve even greater advantage over other approaches with parameter optimization, but did not do this because in realistic calculations (using quantum-mechanical energy evaluations) one cannot afford parameter tuning.

Extended Systems



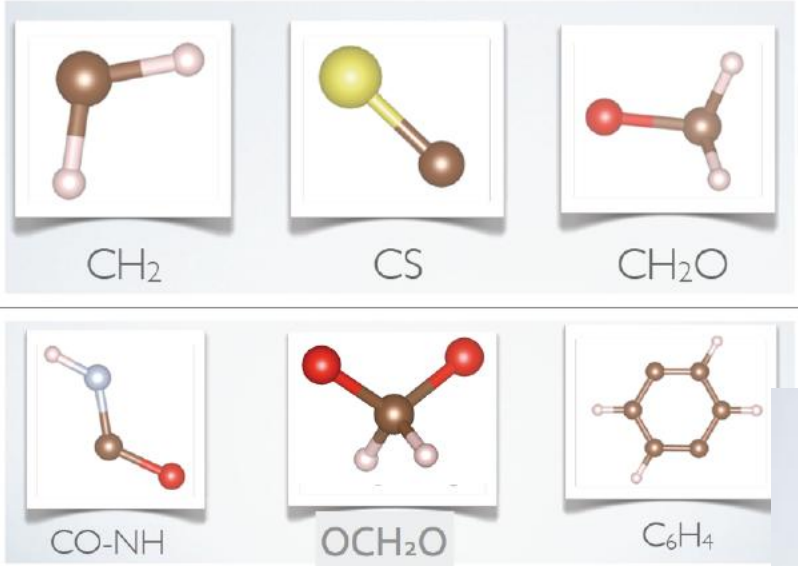
Packing



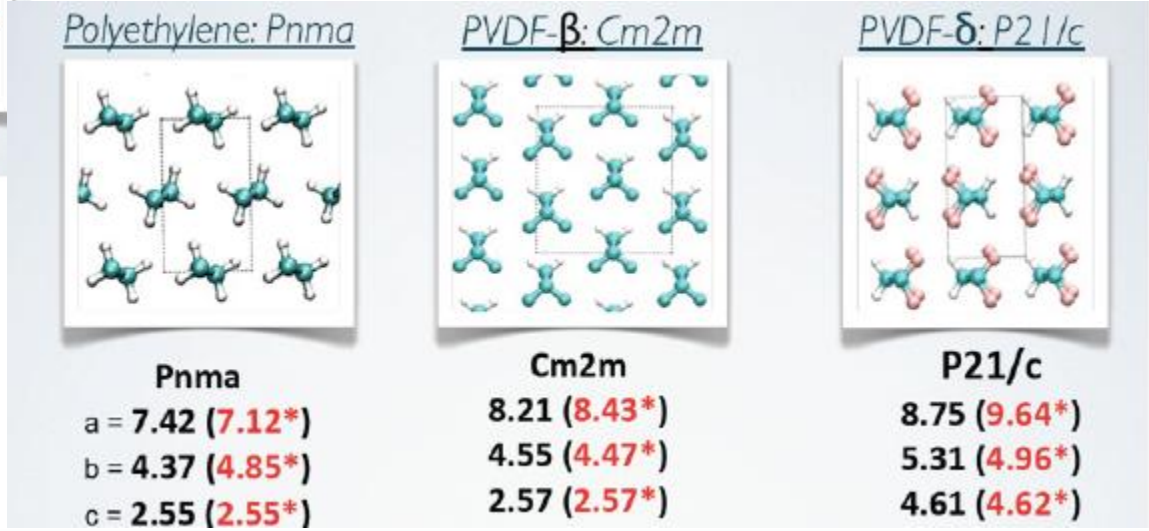


Polymerization

Packing of Polymers

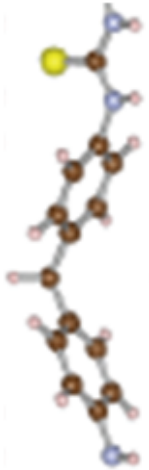


Fix bond connectivity



Zhu & Sharma, In preparation

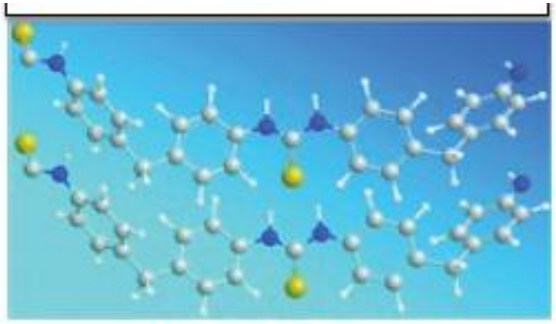
Polymers: 110



connectivity

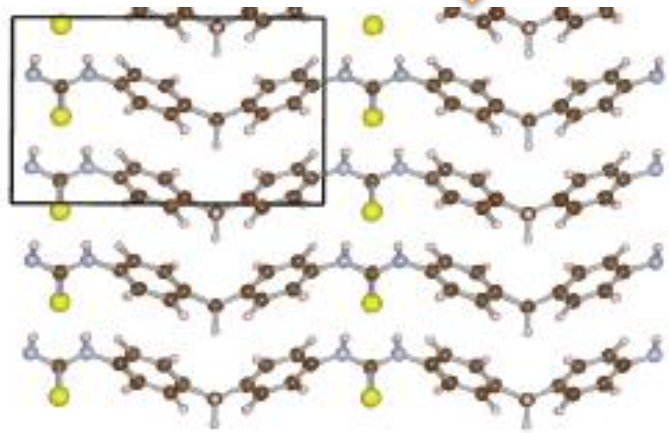
orientation

Polythiourea
-[CS-NH-C6H4-CO-C6H4]-



Expt.*

* Wu *et. al.* Adv. Mater., **25** (2013) 1734.



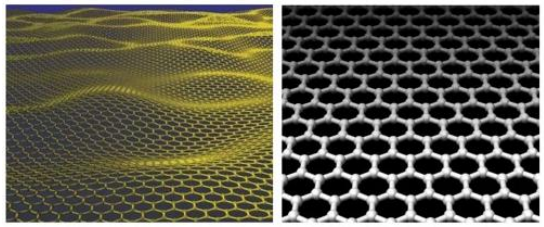
Space group $Pmc2_1$

Predicted

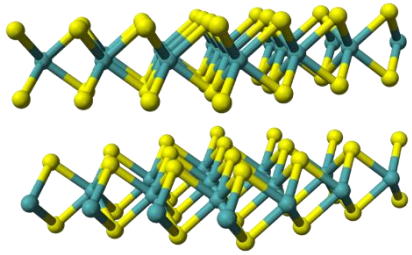
Sharma & Zhu, In preparation

2D crystals: -200

1. Layered material (Bulk)
   van der waals /ionic interactions

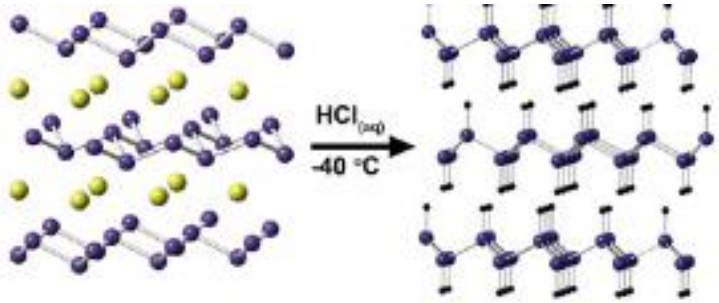


graphene



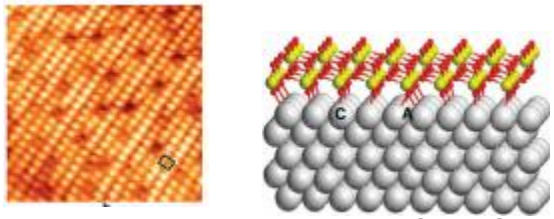
MoS_2/WS_2

2. Metal Atom Intercalated layered material (Bulk), Exfoliation(monolayer)



SiH/GeH from Ca2Si/Ca2Ge + HCl

3. Thin layer grown on substrate

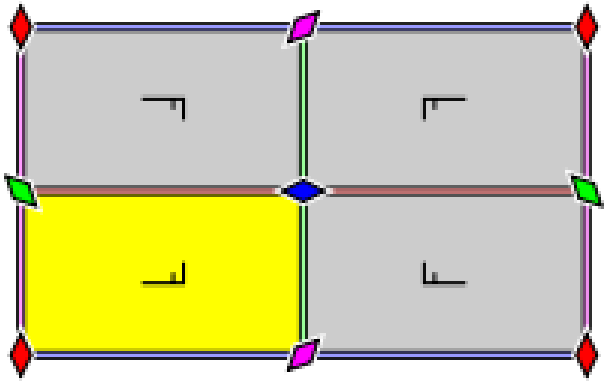


TiO2 grow on Ag (100)

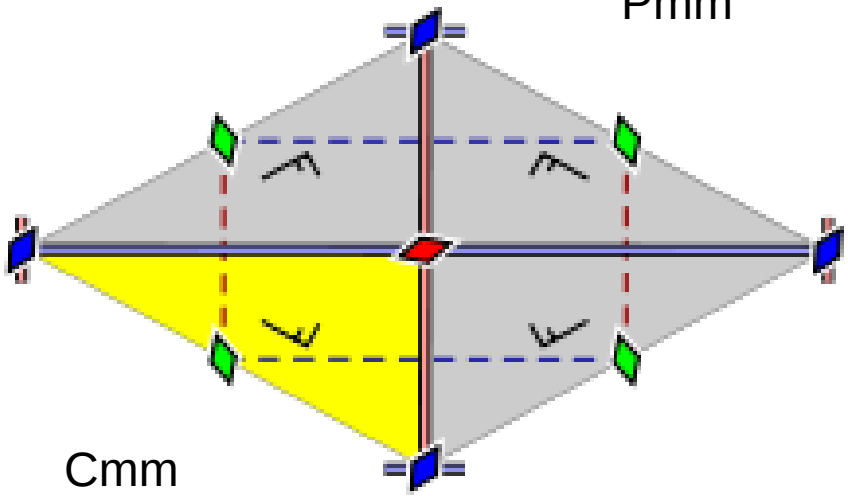
2D crystals: -200

17 Plane Groups
- Translation
- Rotation
- Reflection
- Glide Reflections

Finite thickness
Mono/Bi layer…

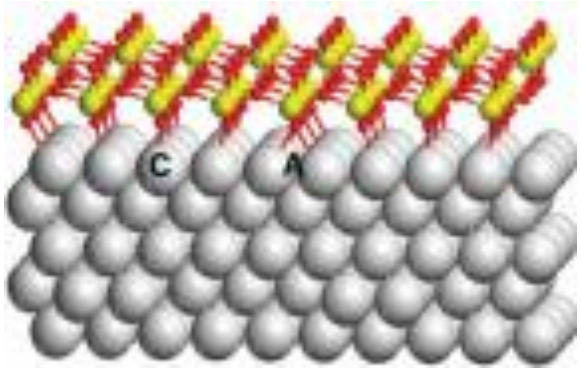


Pmm

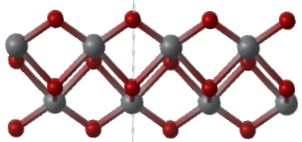


Cmm

2D crystals: -200

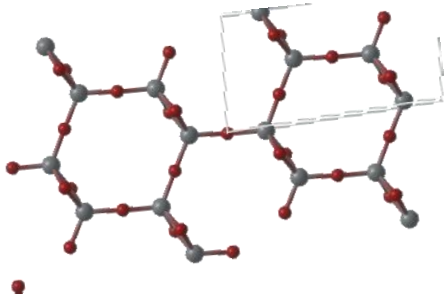


Lepidocrocite
0 eV/atom

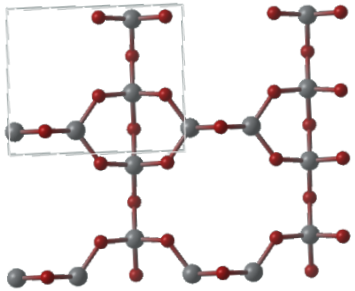


Anatase
+0.032eV/atom

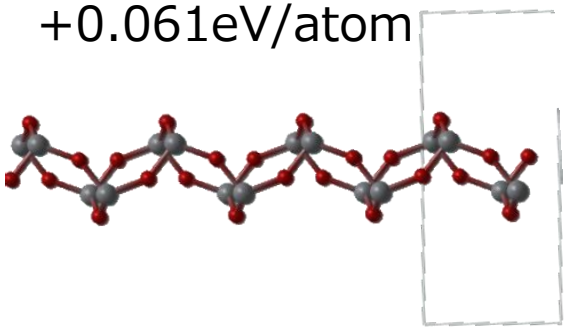
+0.2eV/atom



+0.2eV/atom

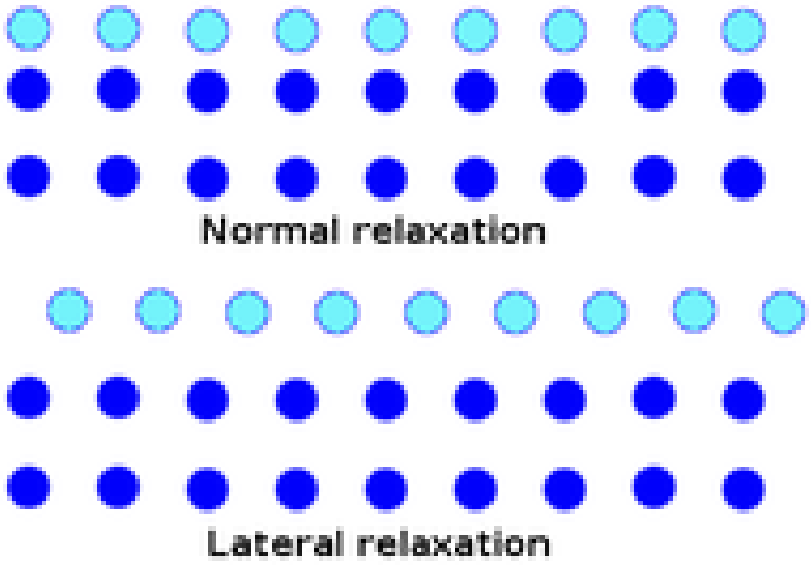


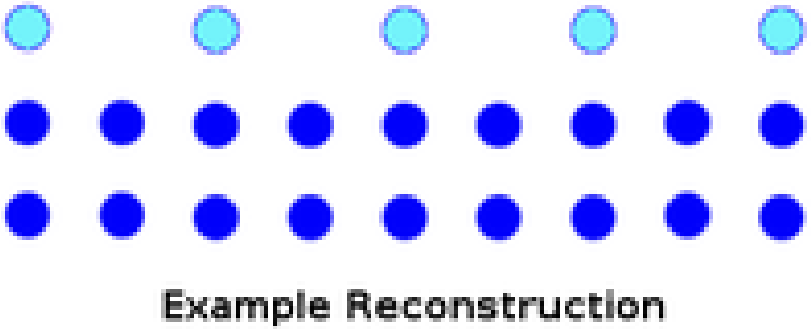
+0.061eV/atom



Atrei , et al, PCCP, 2010

Surfaces: 200/201





From Wikipedia

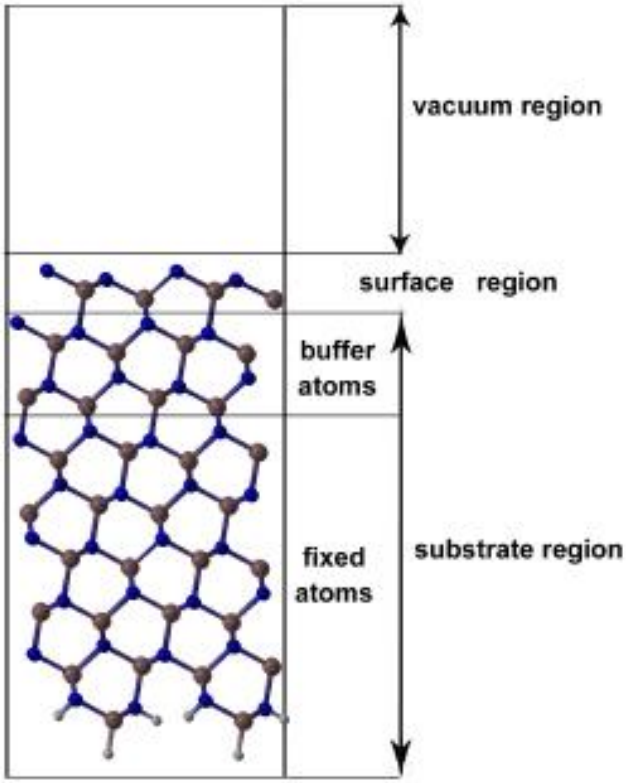


FIG. 1. Surface model used in the evolutionary algorithm.

Stony Brook University

STEP 1
Initialization

Vacuum layer

Adlayer
(for add atoms)

Substrate layer
(for substate atoms
& Passivation)

STEP 2
Relaxation
(By VASP)

Free part

Fixed part

STEP 3
Evolution

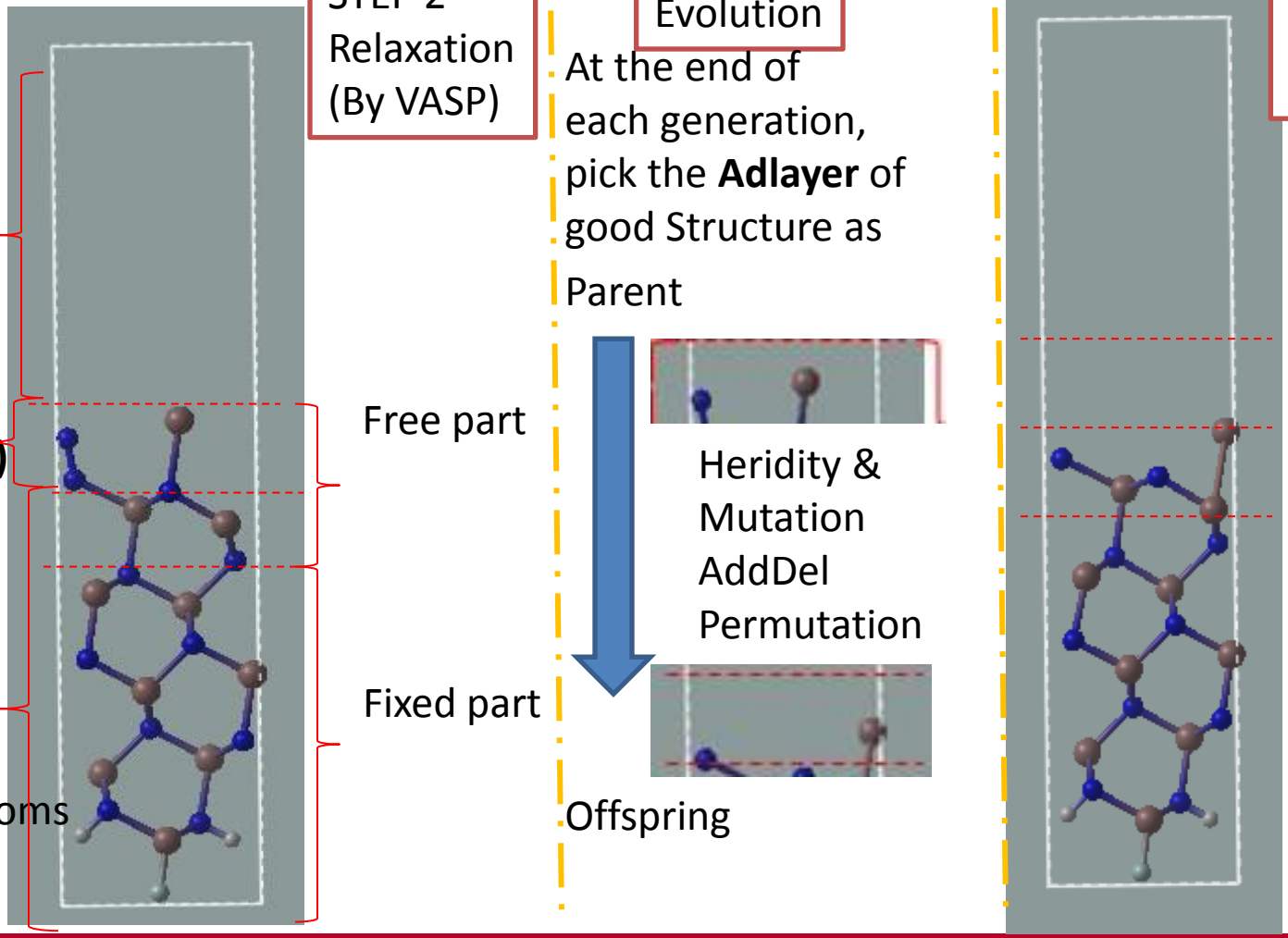
At the end of each generation, pick the **Adlayer** of good Structure as Parent

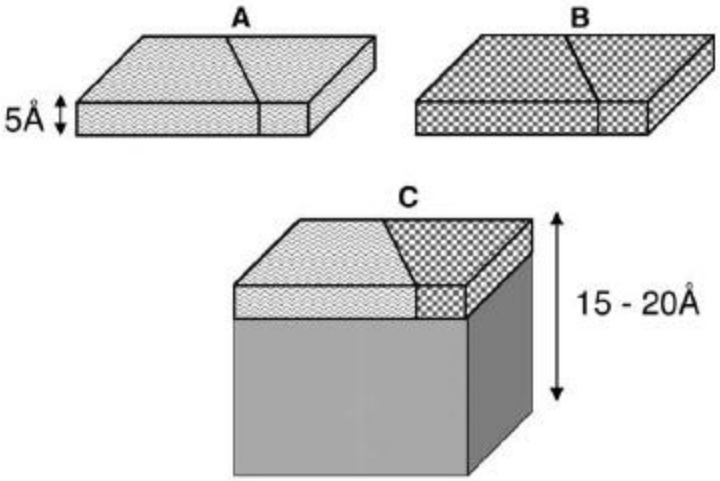
Heridity &
Mutation
AddDel
Permutation

Offspring

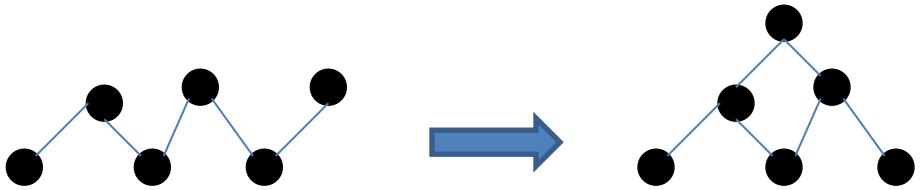
Offspring

STEP 4
Go back
to Step 2

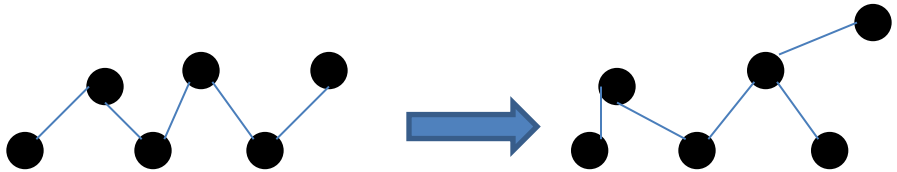




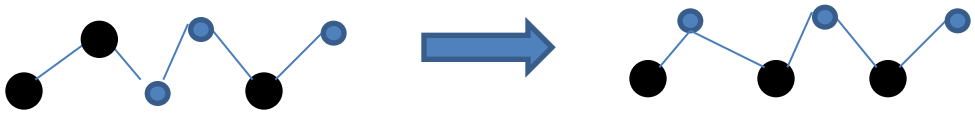
1. Heredity



2. shuffling



3. Mutation



4. Permutation

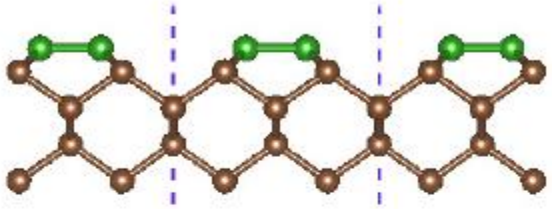
Simple input information (200)

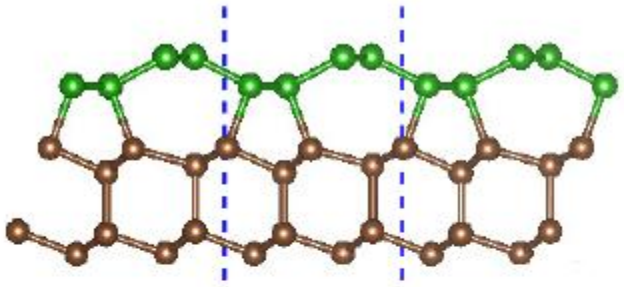
- Adlayer – the type of surface atom
- substrate

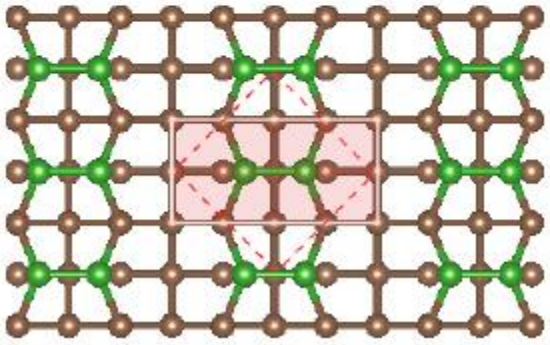
Even more intelligent (201)

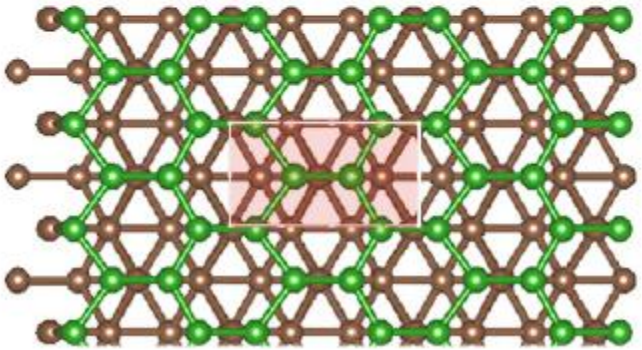
- Variable number of surface atoms
- Variable reconstruction cell (from 1*1 to N*N)

Surfaces: 200





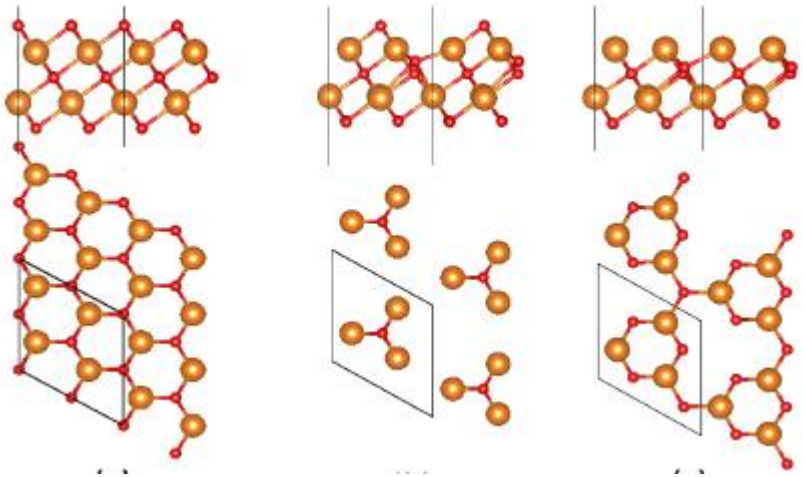




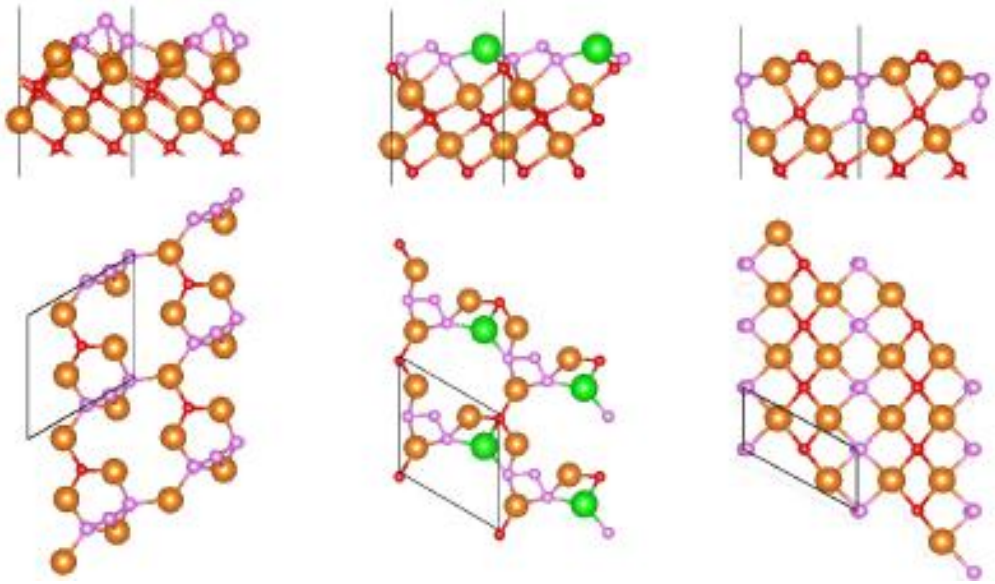
Diamond (100) 2*1 reconstruction

Diamond (111) 2*1 reconstruction

Surfaces: 200

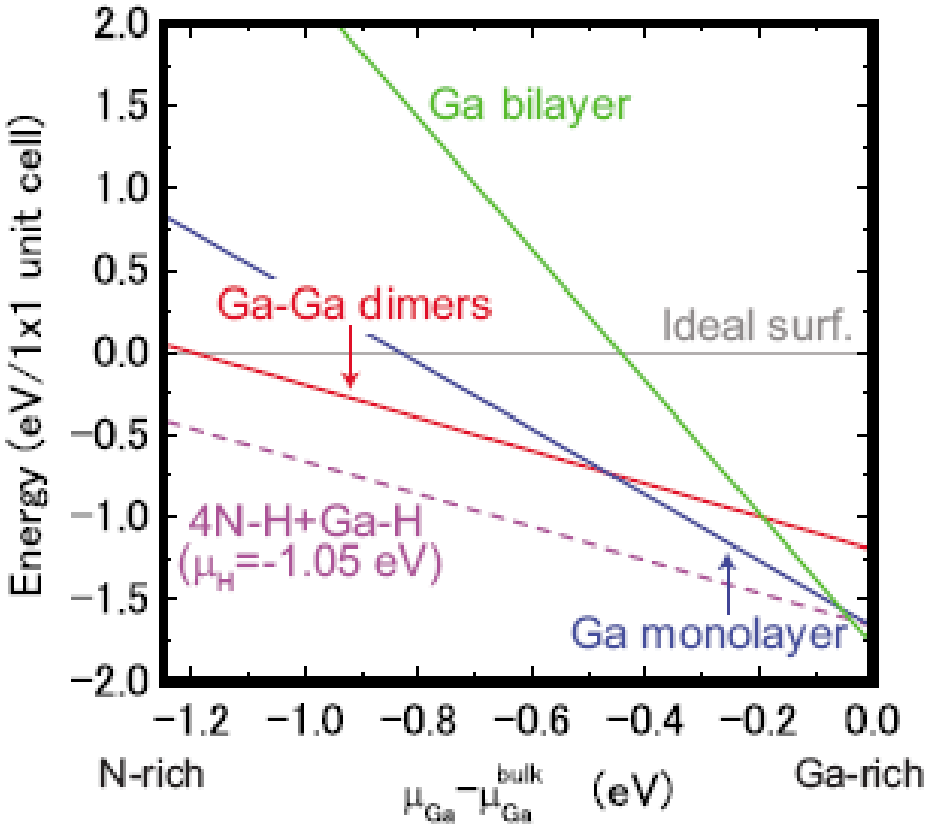


MgO-(111) known reconstruction



MgO-(111) new reconstruction from USPEX

Surface stability depends on chemical potential



Akiyama, PRB, 2010

Simple input information (200)

- Adlayer – the type of surface atom
- substrate

Even more intelligent (201)

- Variable number of surface atoms
- Variable reconstruction cell (from 1*1 to N*N)

Formation Energy of Surfaces

$$E_{\text{formation}} = E_{\text{total}} - E_{\text{ref}} - \sum_i n_i \mu_i,$$

$$\mu_{\text{A}} + \mu_{\text{B}} = E_{\text{AB}}.$$

$$\mu_{\text{A}} \leq E_{\text{A}}.$$

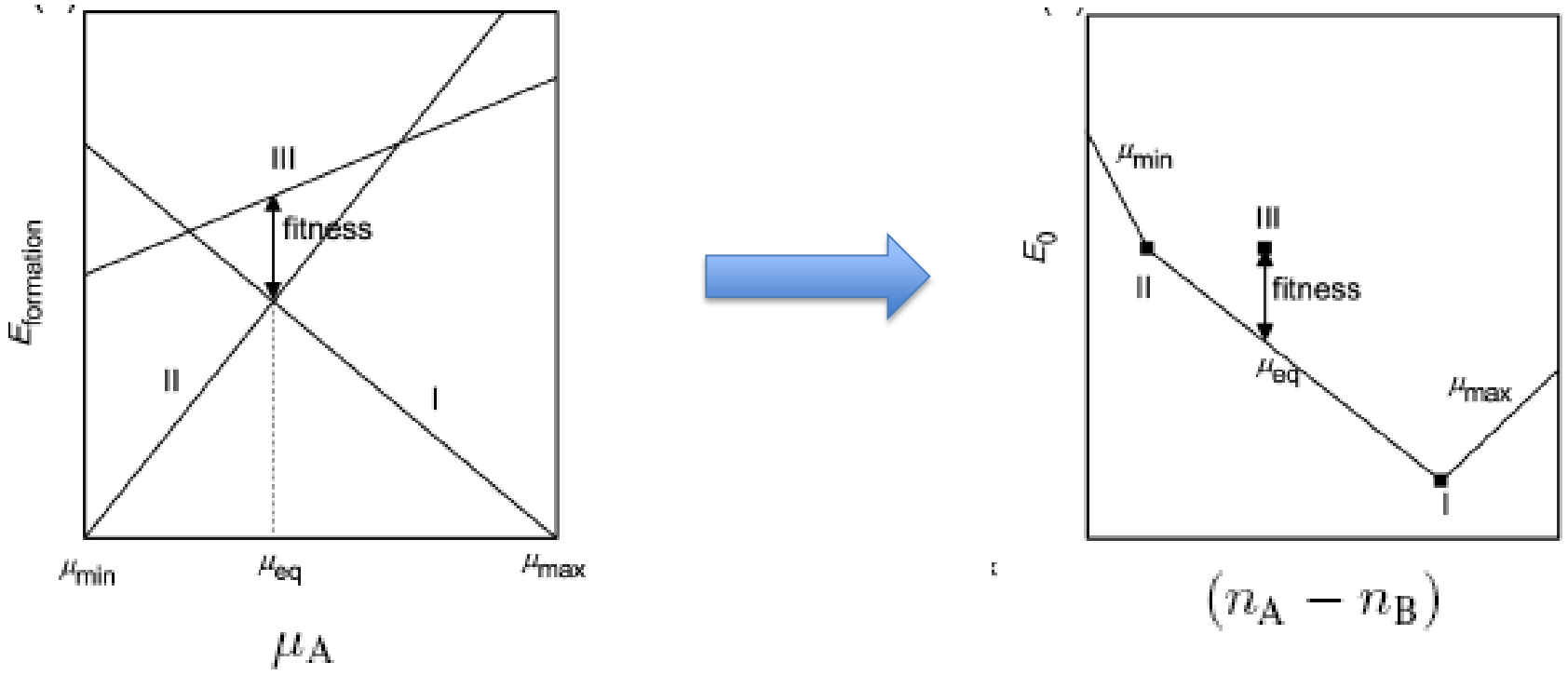
$$\mu_{\text{B}} \leq E_{\text{B}}.$$

$$E_{\text{formation}} = E_{\text{tot}} - E_{\text{ref}} - n_{\text{B}} E_{\text{AB}} - \mu_{\text{A}}(n_{\text{A}} - n_{\text{B}})$$

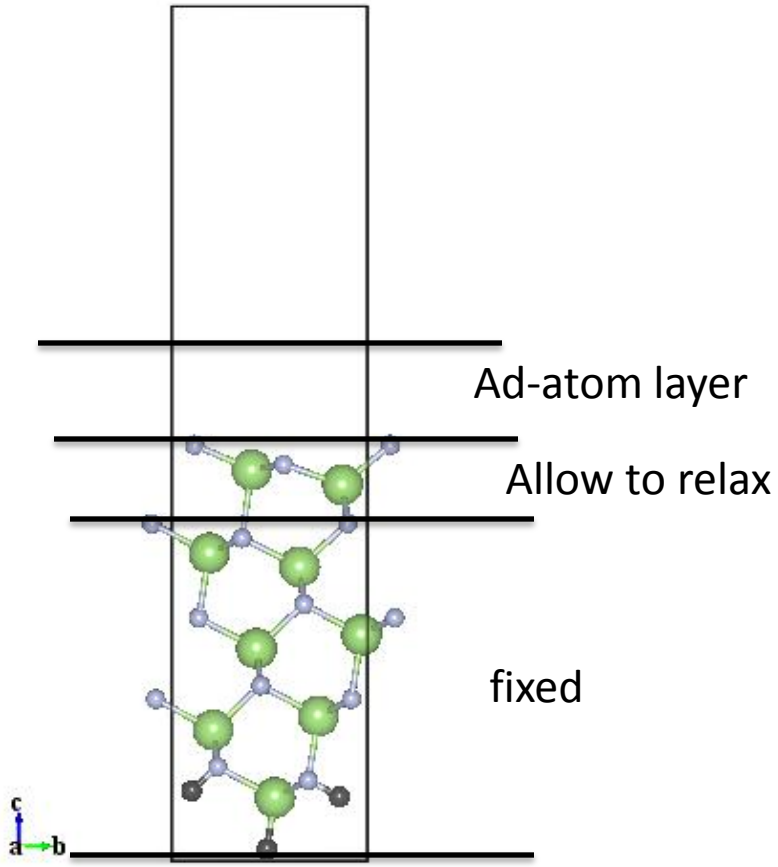
$$E_{\text{AB}} - E_{\text{B}} \leq \mu_{\text{A}} \leq E_{\text{A}}$$

Convex hull representation

$$E_{\text{formation}} = E_{\text{tot}} - E_{\text{ref}} - n_{\text{B}} E_{\text{AB}} - \mu_{\text{A}}(n_{\text{A}} - n_{\text{B}})$$



Surfaces: 201



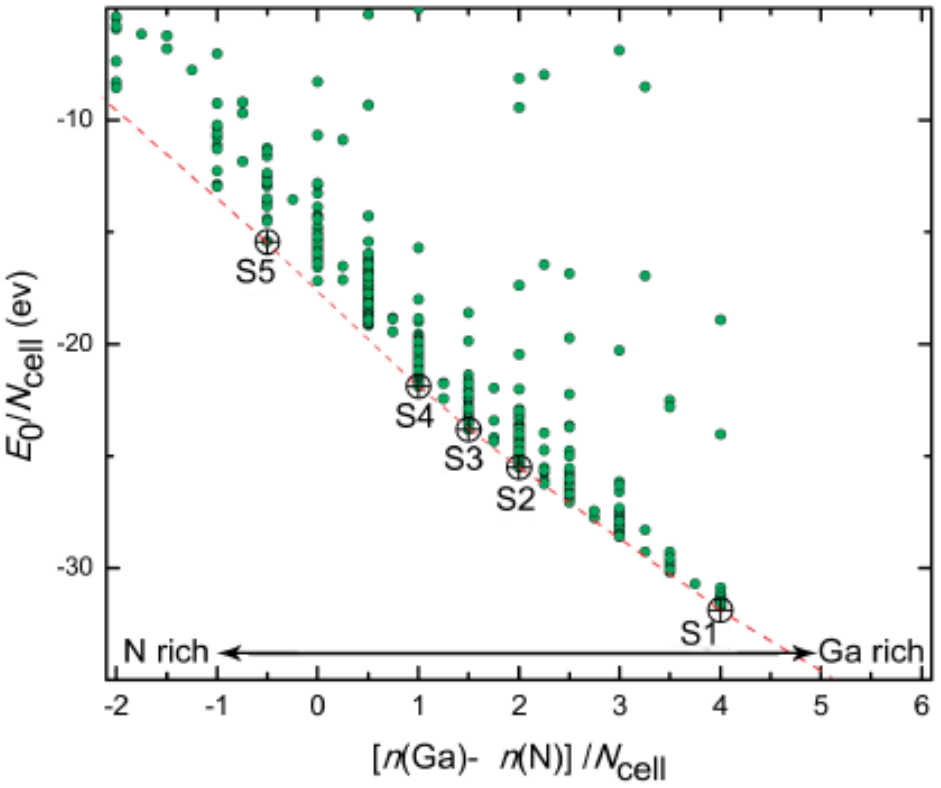
GaN: (10$\bar{1}$1) surface

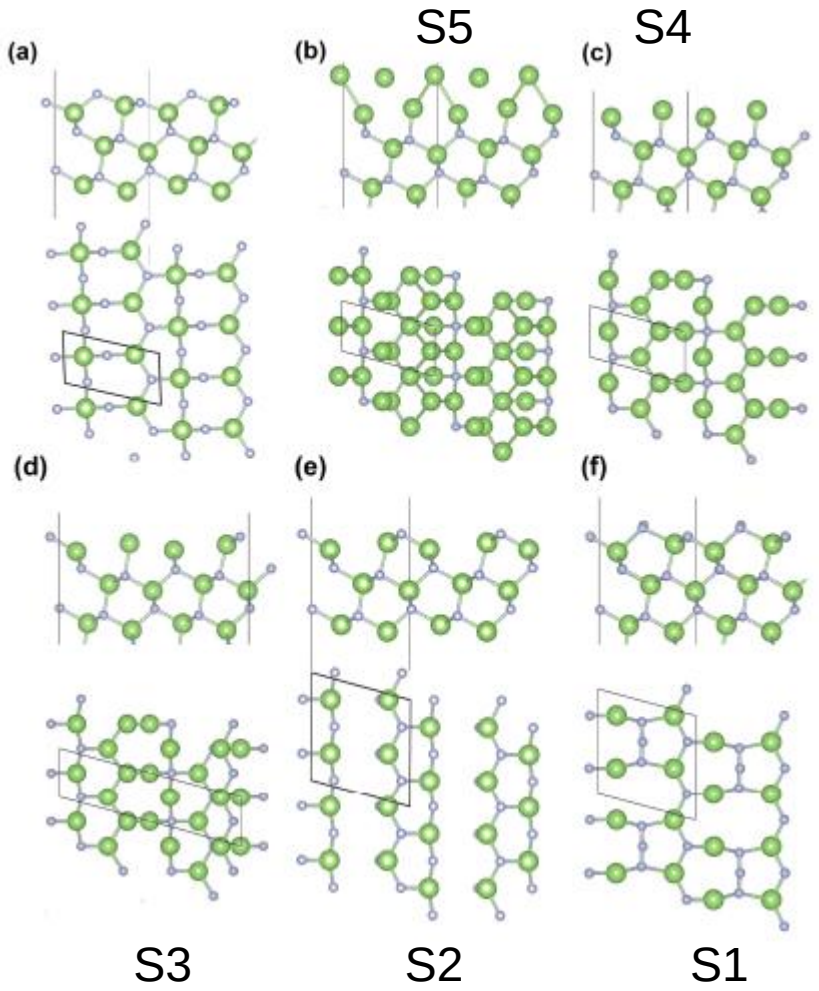
VASP, PBE+U, 400eV planewave cutoff. Only 1x1, 1x2,2x1,2x2 supercells

Maximally 2 Ga and 2 N per surface unit cell are added into the ad-atom layer

The system is then relaxed. Atoms relaxed into the vacuum are thrown away. The remaining part is relaxed again.

GaN-O: (10$\bar{1}$1) surface





Two dimensional convex hull

GaN-O: (10$\underline{1}$1) surface

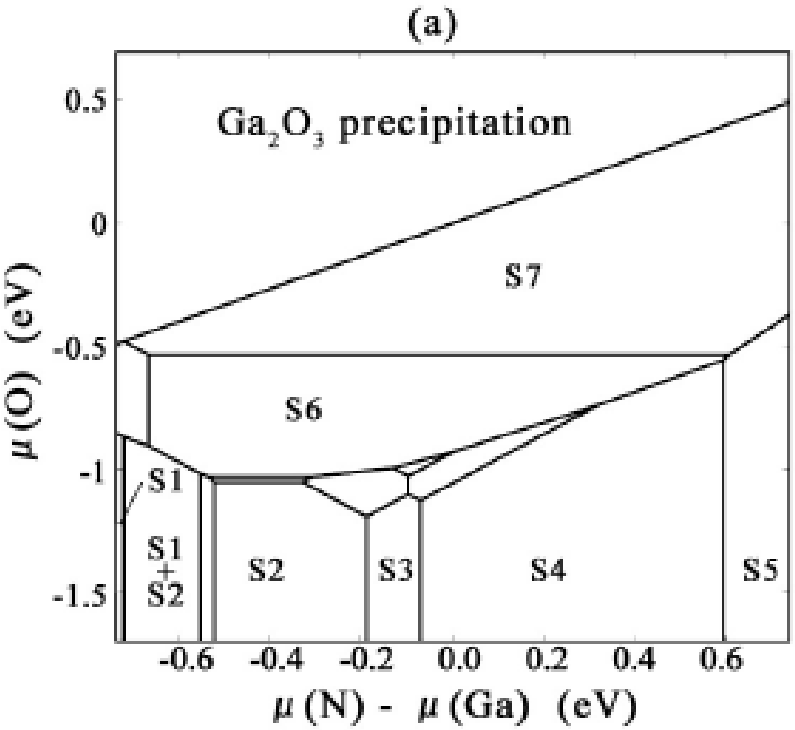
$$E_{\text{formation}} = E_0 - \mu(\text{Ga})[n(\text{Ga}) - n(\text{N})] - \mu(\text{O})n(\text{O})$$

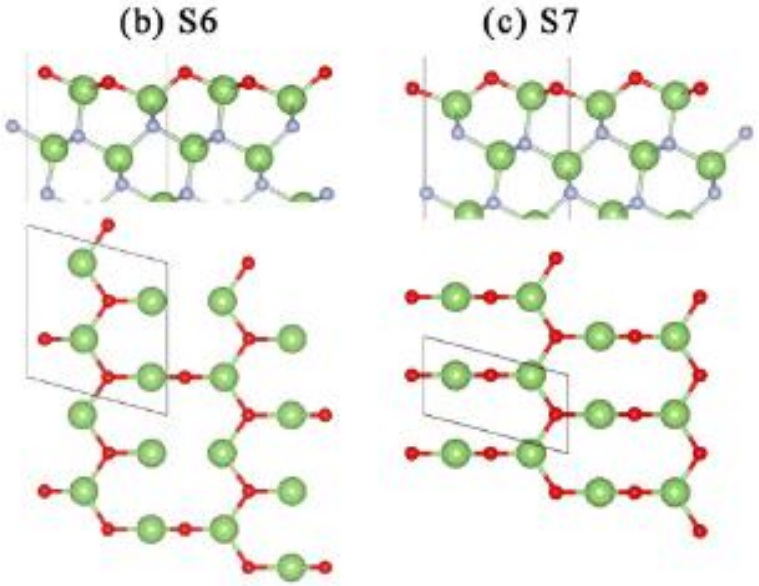
$$\begin{aligned} \mu(\text{O}) &\leq \frac{1}{2}E(\text{O}_2), \\ 2\mu(\text{Ga}) + 3\mu(\text{O}) &\leq E(\text{Ga}_2\text{O}_3), \\ x\mu(\text{Ga}) + y\mu(\text{O}) &\leq E(\text{N}_x\text{O}_y). \end{aligned}$$

Zhu et al, PRB, 2010

Two dimensional convex hull

GaN-O: (10$\underline{1}$1) surface





Zhu et al, PRB, 2010

USPEX: Computational Materials Design

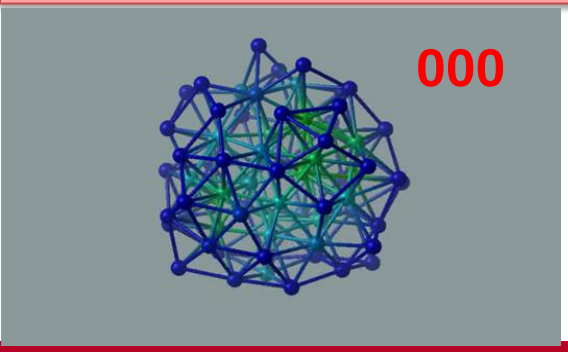
(Crystal) Structure Prediction

System

- **Dimension**
  - 0: Nano-particle;
  - 1: polymers;
  - 2: surfaces/2D crystals;
  - 3: Bulk
- **Stoichiometry**

  0: fixed; 1: variable
- **Building block**

  0: atom; 1: molecule



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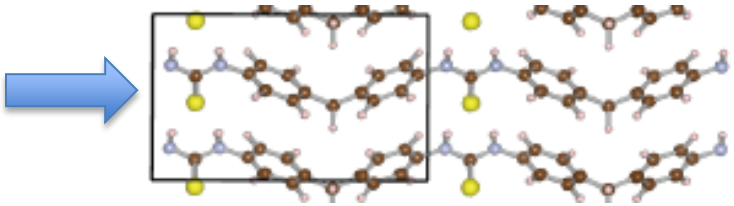

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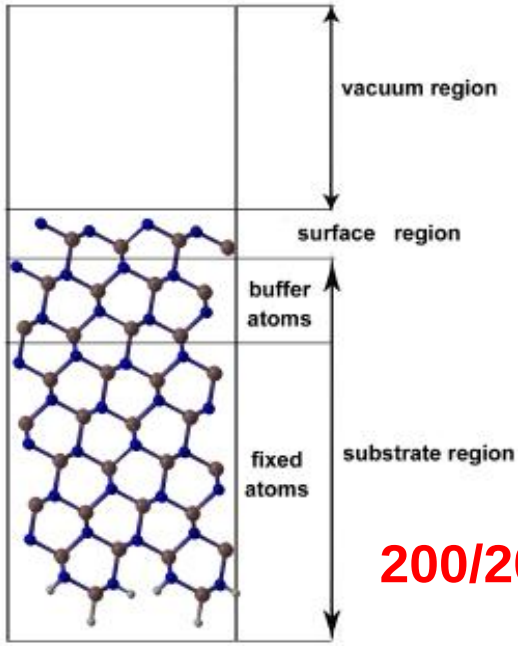

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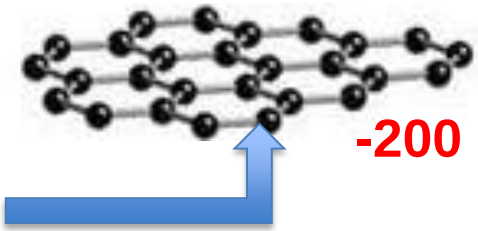

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