Evolutionary Metadynamics (and Beyond)

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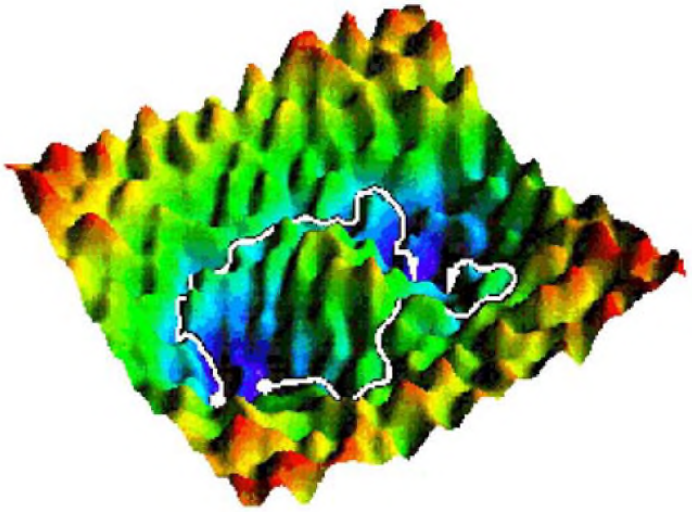
(Free) energy landscape: key to thermodynamics and kinetics



E
H=E+PV
F=E-TS
G=E+PV-TS

Transition paths, rate constants etc.

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Transition path sampling: throwing ropes over mountains in the dark

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Global minimum & low-energy local minima

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Crystal structure prediction using *ab initio* evolutionary techniques: Principles and applications

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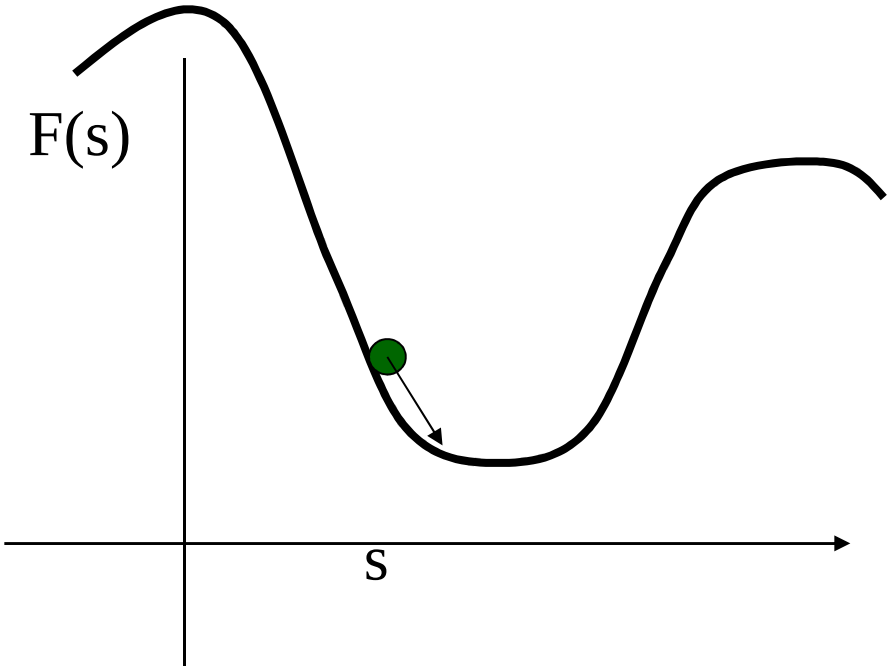
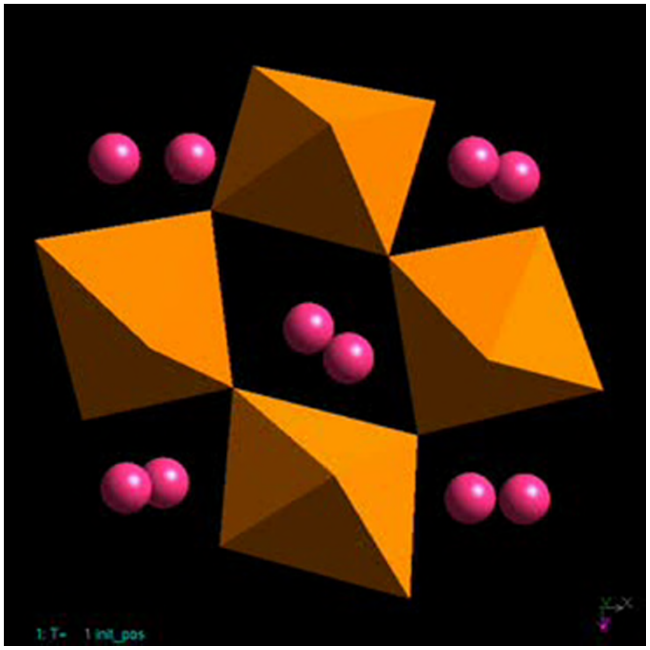
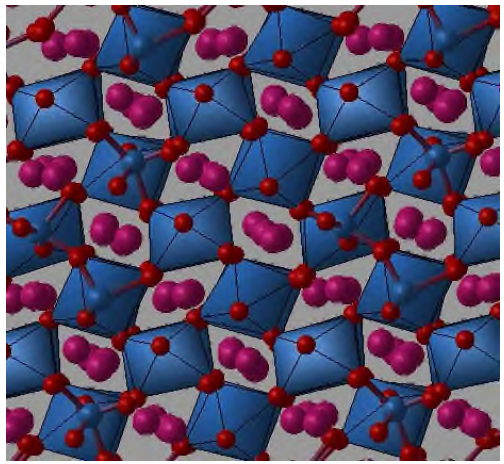
Molecular dynamics



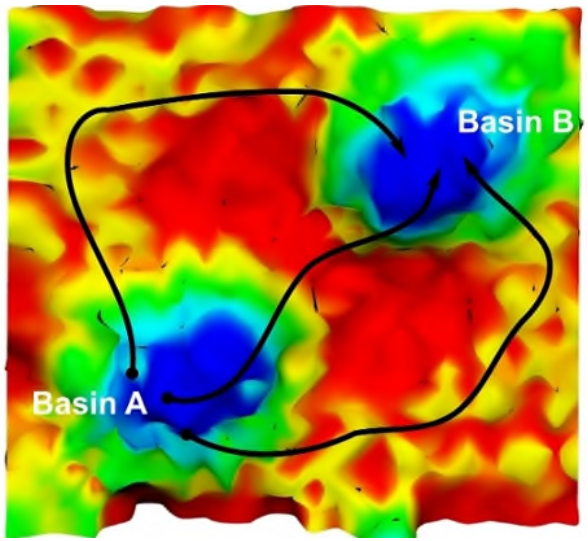


- **Used to study dynamics of atoms, thermodynamics, transport properties.**
- **Problematic to observe phase transitions: simulation timescale is ~10^{-9} sec.**

Evolutionary metadynamics is a new powerful technique for exploring energy landscapes

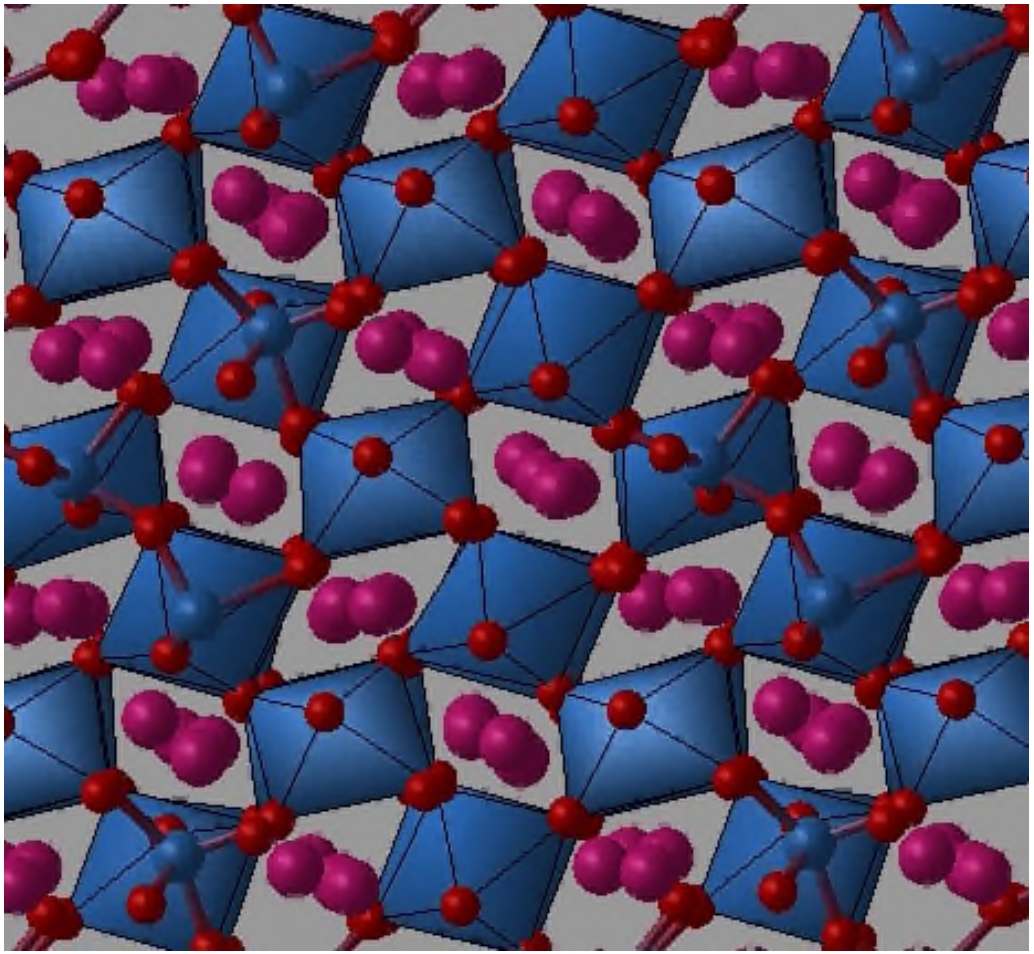


I. Metadynamics, lattice dynamics, and evolution



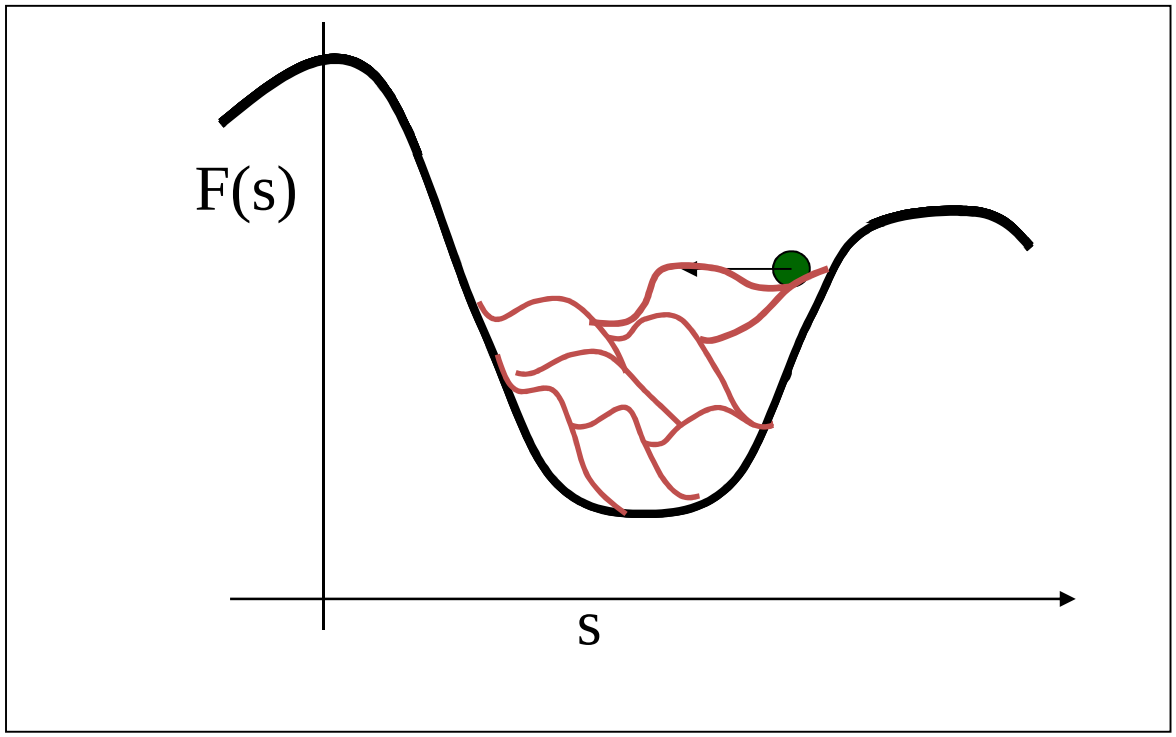
II. Towards predicting metastable synthesis

I. Metadynamics, lattice dynamics, and evolution



Metadynamics: accelerating the rare event (phase transition)

$$\mathbf{h}^{t+1} = \mathbf{h}^{t} + \delta h \frac{\phi^{t}}{|\phi^{t}|} \qquad G^{t}(\mathbf{h}) = G(\mathbf{h}) + \sum_{t'<t} We^{\frac{|h-h^{t'}|^2}{2\delta h^2}} \qquad -\frac{\partial G}{\partial h_{ij}} = V[\mathbf{h}^{-1}(p-P)]_{ji}$$



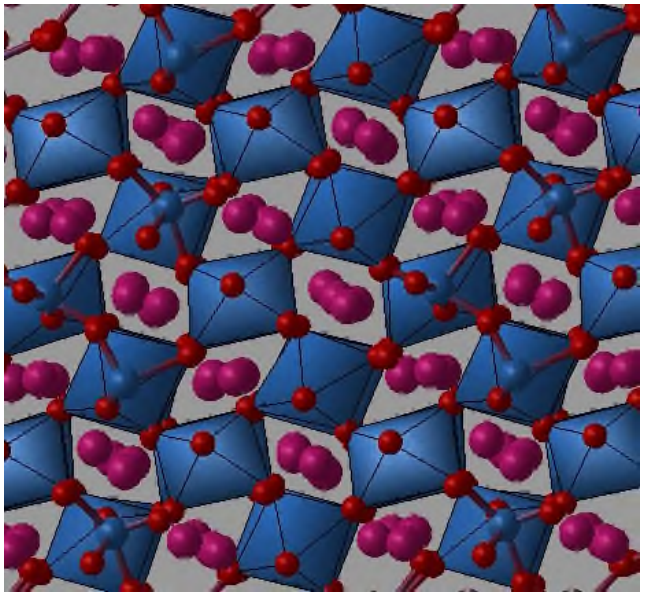
(Laio & Parrinello, 2002; Martonak et al., 2003)

- Works in reduced dimensionality space

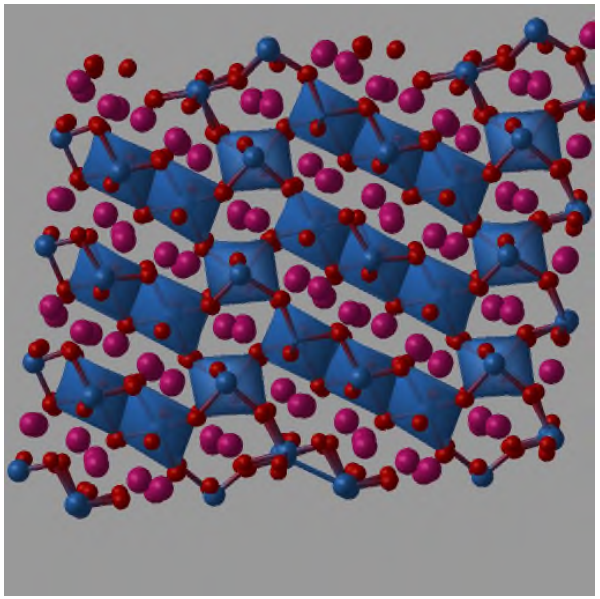
(usually 6D – lattice).

- Requires a good starting structure.
- Finding lowest transition paths, may find the ground-state structure.
- Suitable for large systems.
- Requires only two parameters – W and δh.

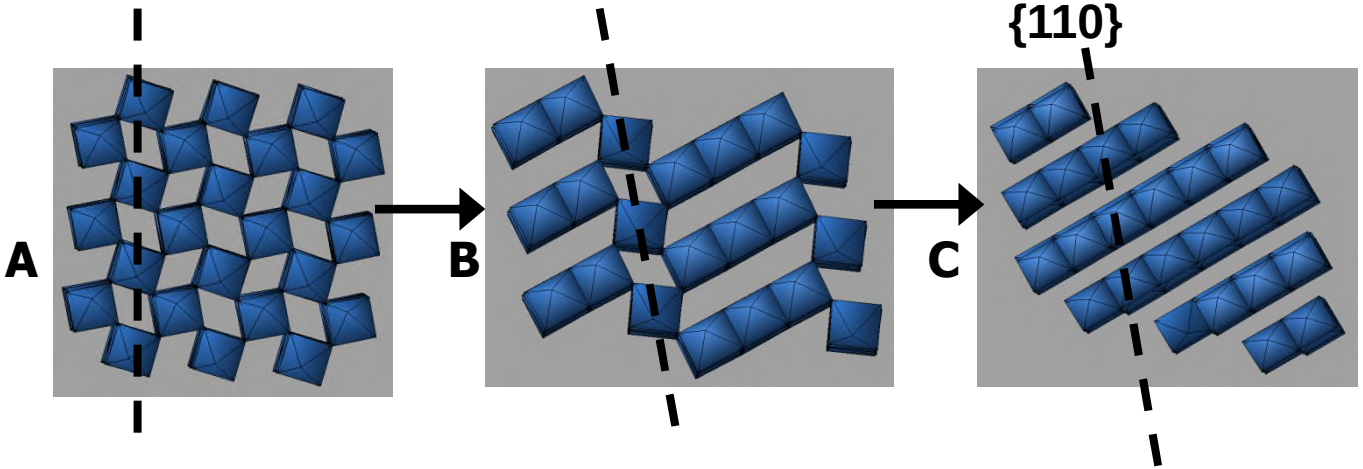
Post-perovskite transition in Earth's mantle involves stacking faults (ARO et al., Nature 2005)



Perovskite to stacking-fault



Stacking-fault to post-perovskite



Metadynamics: pros and contras

PROS

1. **Simultaneously obtains stable structure and transition pathways.**

2. **Efficient for large systems (no scaling with *N*)**

3. **Requires only 2 parameters.**

CONTRAS

1. **Success rate for finding stable structure is moderate. Transition pathway is not necessarily the best one.**

2. **Solves problem reduced from 3N+3 dimensions to 6 dimensions.**

3. **Requires a good initial structure.**

Points to address:

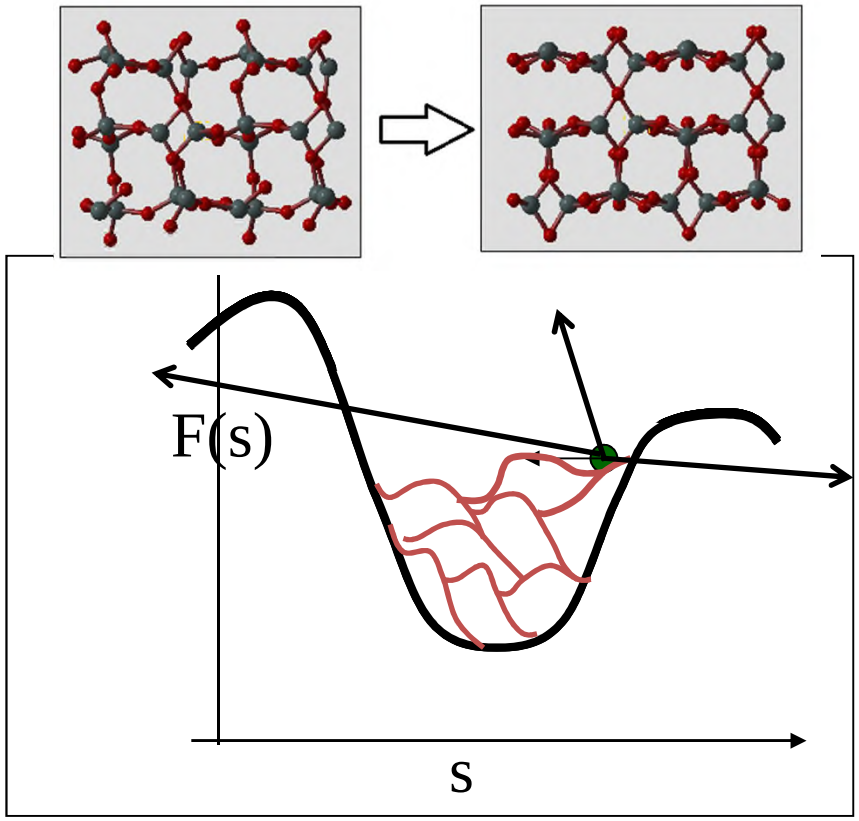
1. **Equilibration at each metastep is done by MD. Too expensive and equilibration is incomplete – often get amorphization.**

2. **Original formulation is not invariant to cell transformations.**

3. **At each (long!) metastep get only 1 structure.**

Evolutionary metadynamics: marrying strengths of metadynamics and USPEX (Zhu, ARO, Lyakhov, 2012)

Softmutation instead of MD!



- Much faster equilibration
- Produces multiple structures

Zhu, ARO, Lyakhov, 2012

$$G^t(\mathbf{h}) = G(\mathbf{h}) + \sum_{t'<t} We^{\frac{|h-h^{t'}|^2}{2\delta h^2}}$$

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

$$\mathbf{h}^{t+1} = \mathbf{h}^t + \delta h \frac{\phi^t}{|\phi^t|}$$

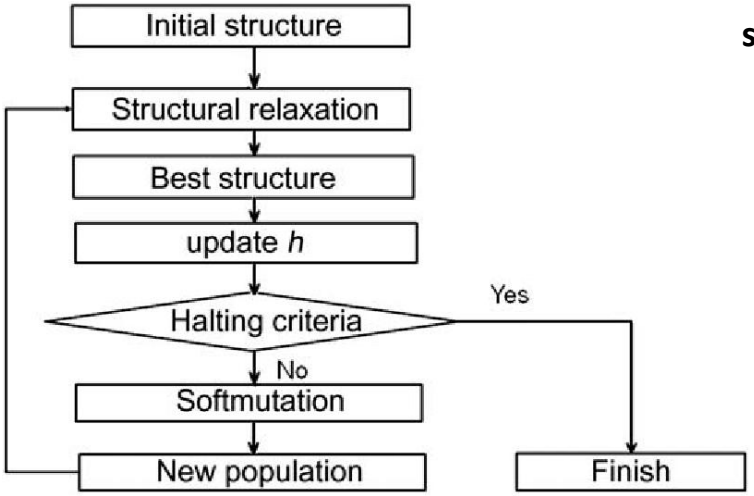
to achieve invariance, replaced with:

$$h_{im}(t+1) = h_{im}(t) + \frac{\delta h}{|f|V^{1/3}} S_{ijkl} f_{kl} h_{jm}(t),$$

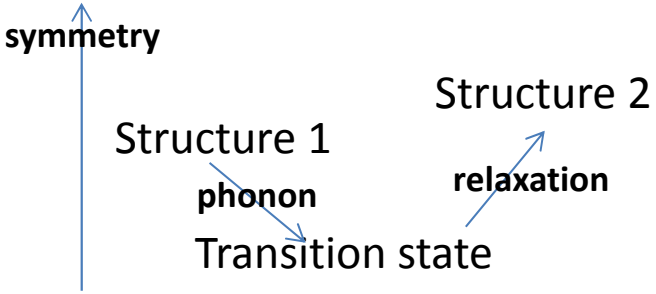
where S is the elastic compliance tensor corresponding to an elastically isotropic medium with Poisson ratio 0.26, which corresponds to the border between brittle and ductile materials[25] and is a good average value to describe both metals and insulators.

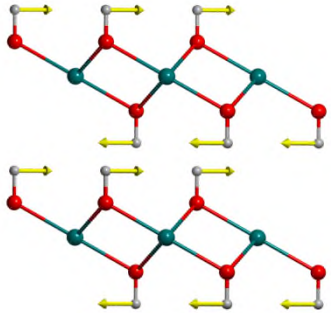
1. **Rapid and reliable equilibration.**
2. **Amorphization does not happen.**
3. **Rich structural information: obtain numerous low-energy metastable structures.**
4. **New formulation is invariant to cell transformations.**

Evolution, group-subgroup relations, metastable synthesis



I. Flowchart of evolutionary metadynamics. The method is evolutionary because in each metastep (generation) there are many structures, and the one with lowest energy (at fixed cell!) is selected to produce offspring.





II. Displacement along an eigenvector lowers symmetry. Subsequent relaxation may increase it afterwards.

III. Extensively sampling low-barrier paths, evolutionary metadynamics produces a nearly exhaustive list of low-energy metastable phases synthesizable from the given starting structure.

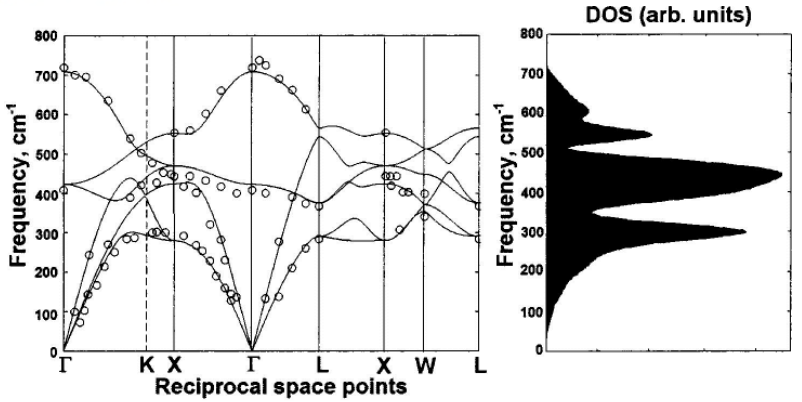
A (very) brief introduction to lattice dynamics

Force constants matrix: $\Phi^{ij}_{\alpha\beta}(l, l') = \dfrac{\partial^2 E}{\partial u^i_\alpha(l)\partial u^j_\beta(l')}$

Dynamical matrix: $\mathbf{D}^{ik}_{\alpha\beta}(\mathbf{k}) = \dfrac{1}{(\mathrm{m}_i \mathrm{m}_j)^{1/2}} \sum_l \mathbf{\Phi}^{ij}_{\alpha\beta}(0, l) \exp[\mathbf{ik}(\mathbf{r}_j(l) - \mathbf{r}_i(0)]$

Secular equation: $\omega^2(\mathbf{k},\nu)\mathbf{e}(\mathbf{k},\nu) = \mathbf{D}(\mathbf{k})\,\mathbf{e}(\mathbf{k},\nu)$

ω is the mode eigenfrequency, $\mathbf{e}$ is the mode eigenvector.

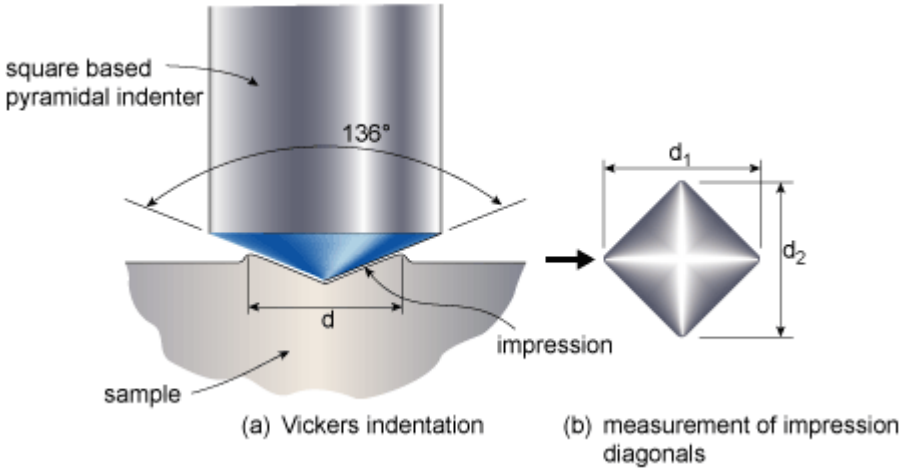


Phonon dispersion curves of MgO (ARO, 2003)

1. If we set all masses =1, $\omega_i^2 \sim \partial^2 E / \partial Q i^2$.
2. Negative ω_i^2 – instability towards a better structure, without a barrier. Low ω_i^2 – low transition barrier. Need eigenvectors of lowest-frequency phonons.

3. Phonon calculations are too expensive.
4. For approximate phonons in USPEX, use model of central nearest-neighbour interactions: $E = 1/2 \sum k_{ij}(r_{ij} - r_{0,\,ij})^2$

Bond hardness – used in USPEX both for hardness computation and for softmutation



Single-bond crystals:

$$H_k(\mathrm{GPa}) = 423.8 N_v X_{ab} e^{-2.7 f_i} - 3.4$$

Multibond crystals:

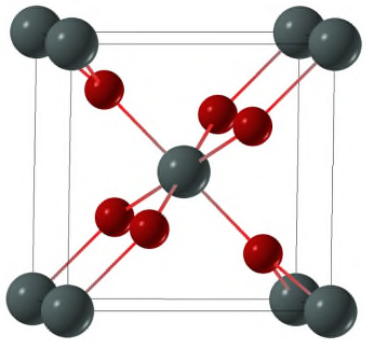
$$H_k(\mathrm{GPa}) = \frac{423.8}{V} n \left[\prod_{a,b=1}^{n} N_{ab} X_{ab} e^{-2.7 f_{i(ab)}} \right]^{1/n} - 3.4$$

Nv - bond density
V - volume
Nab - number of bonds of type ab
Xab - "bond electronegativity"
fi - bond ionicity

$$X_k = \sqrt{\frac{\chi_i^k \chi_j^k}{CN_i^k CN_j^k}}$$

Material	Model of Li et al. (2009)	Lyakhov & ARO (2011)	Exp.
Diamond	91.2	89.7	90
Graphite	57.4	0.17	0.14
TiO_2 rutile	12.4	12.3	8-10
β-Si_3N_4	23.4	23.4	21
SiO_2 stishovite	31.8	30.8	33

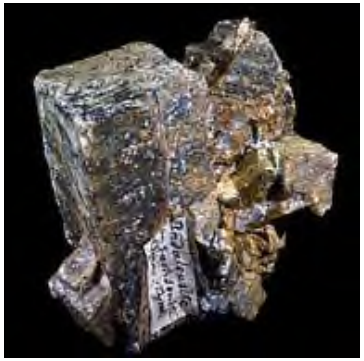
For softmutation, force constant k_i is taken equal to "bond electronegativity" X_k

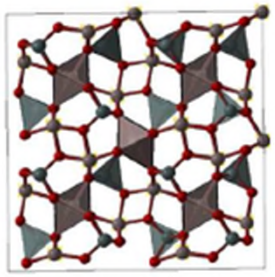


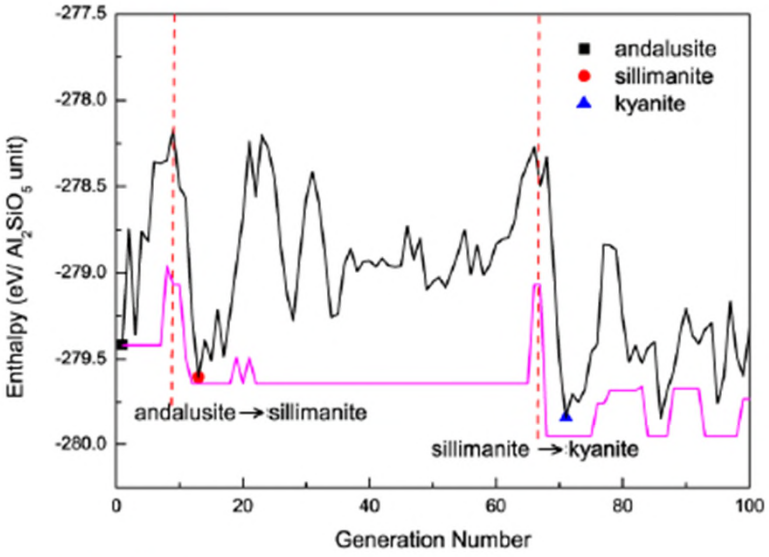
What evolutionary metadynamics can give?

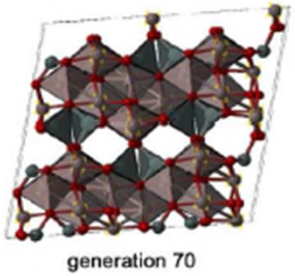
- **Global energy minimum – provided the starting structure is not too far**
- **Phase transition pathways**
- **Numerous low-energy metastable structures**
- **List of phases synthesizable from initial phase**

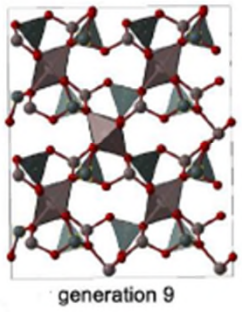
Searching for the global minimum and transition pathways: phases of Al_2SiO_5 (Zhu & ARO, 2012)

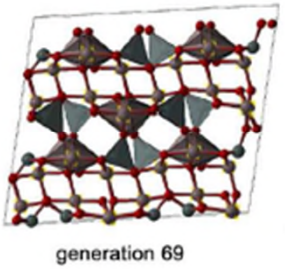


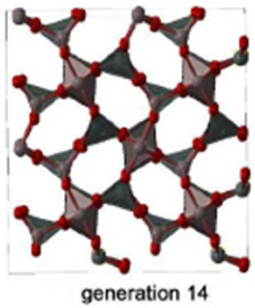


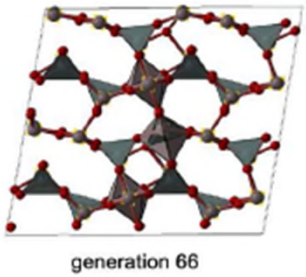


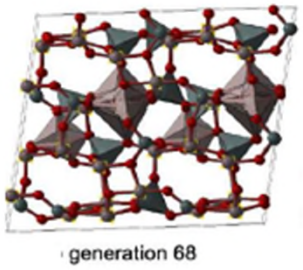








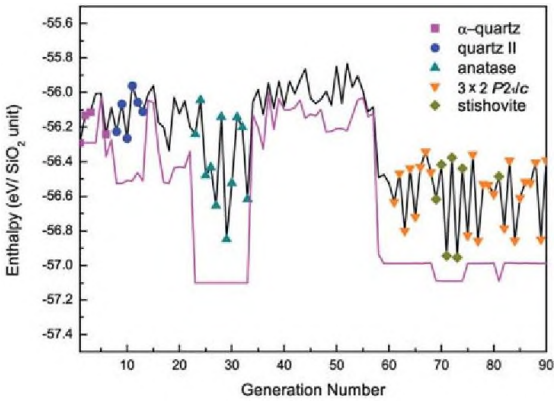




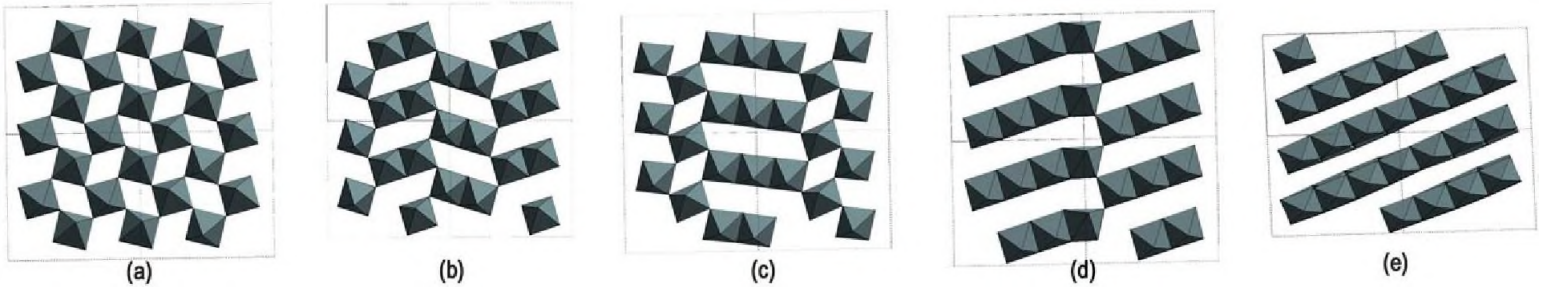
The mechanism is perfectly reasonable and non-intuitive!

ATTENTION: Do not trust “barriers” for polymorphic transitions from metadynamics

A few simple tests: SiO2 and MgSiO3 (Zhu & ARO, 2012)



Metadynamics results for compressed SiO_2. After a disordered state is formed, the system recrystallized!



Metadynamics results for compressed $MgSiO_3$. Transition from perovskite to post-perovskite is compatible with (ARO et al., Nature 2005).

Evolutionary metadynamics and USPEX-evolution: complementary

Evolutionary metadynamics.

Requires a good initial structure.

Very efficient. Does not scale with N, i.e. can handle large systems easily!

Success rate depends entirely on starting structure: danger!

Deterministic.

Produces numerous good and synthesizable metastable structures.

Produces a good guess of transition mechanism.

USPEX.

Requires no initial structure.

Very efficient. Scales ~ exp(aN). Works up to N~100-500, but never more.

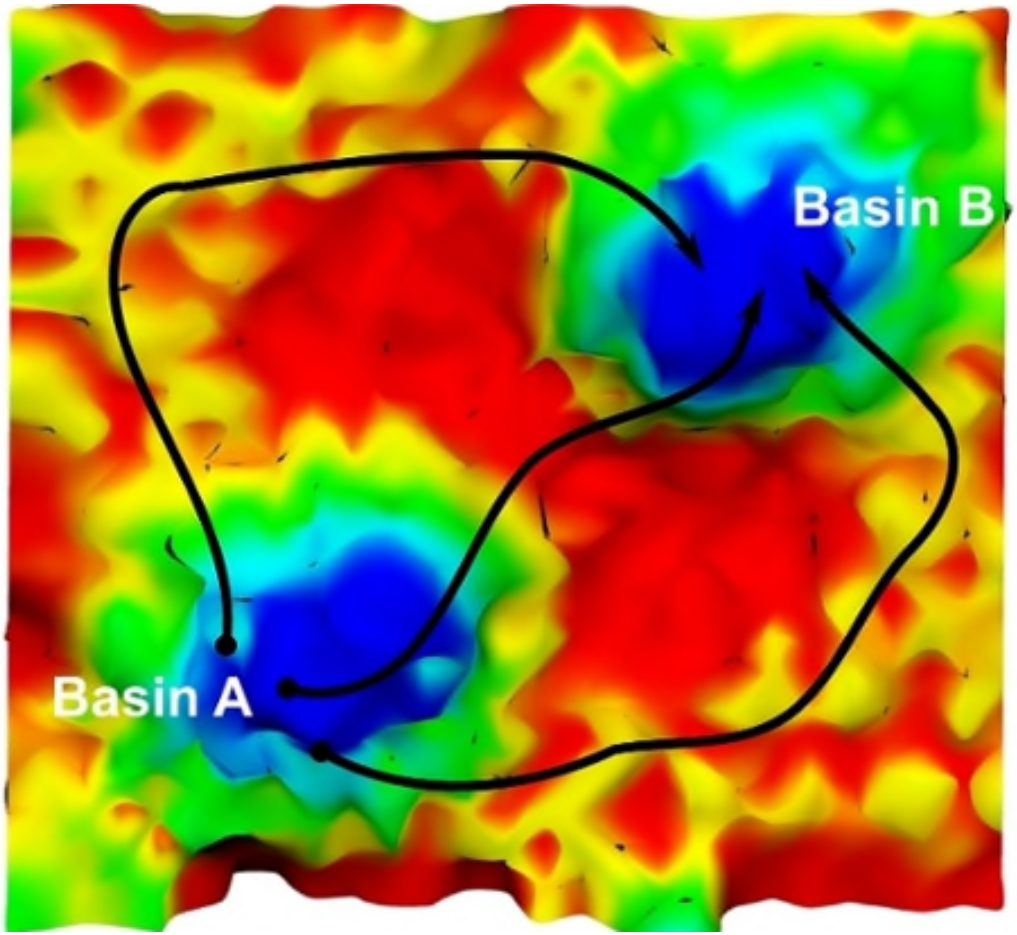
Success rate ~100% for fixed-composition, ~70% for variable-composition calcs.

Stochastic.

Does not explore transition pathways, synthesis, etc. Metastable phases are byproduct of global search.

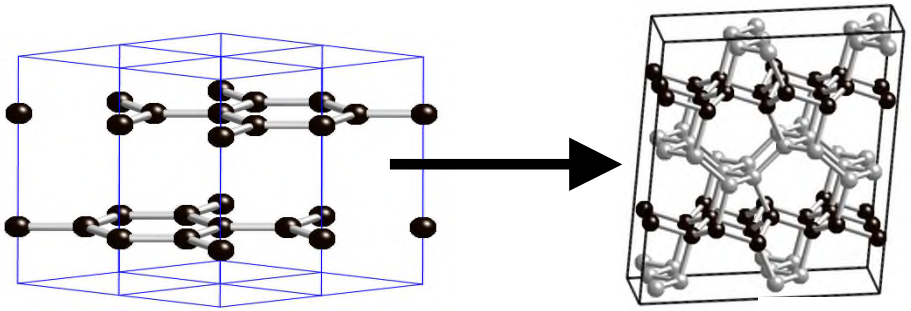
The only good way to do variable-composition search. More suitable for low-dimensional systems.

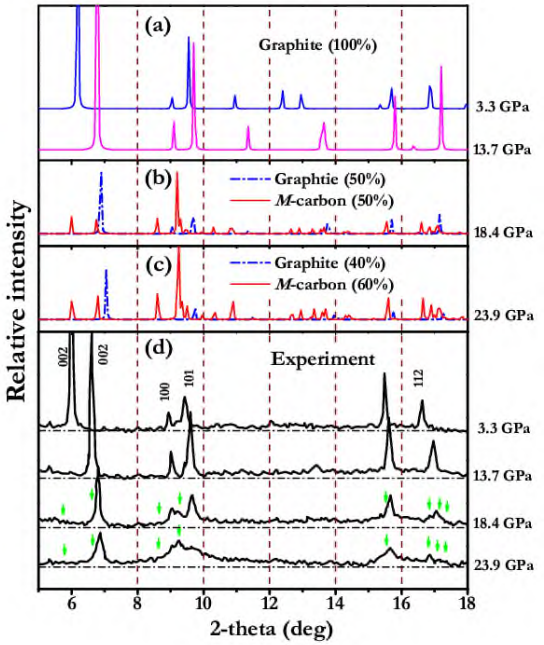
II. Towards predicting synthesis



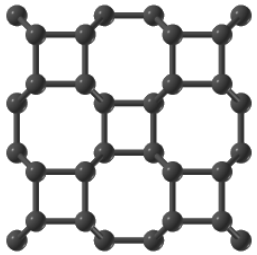
Puzzle: Cold compression of graphite yielded a new allotrope of carbon, of unknown nature

•Without catalysts, graphite converts to diamond at >15 GPa but at very high temperatures (1600–2500 K).
•Compression at 300 K converts graphite into a superhard transparent phase at ~17 GPa (Drickamer, 1963; Goncharov, 1990; Yagi, 1991; Mao, 2003).
•ARO & Glass (2006) – predicted low-energy sp^3-structure, which matches (Li & ARO, 2009) observations: M-carbon.



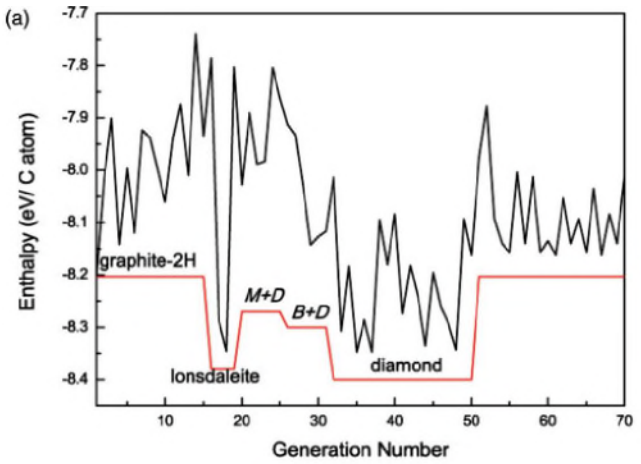


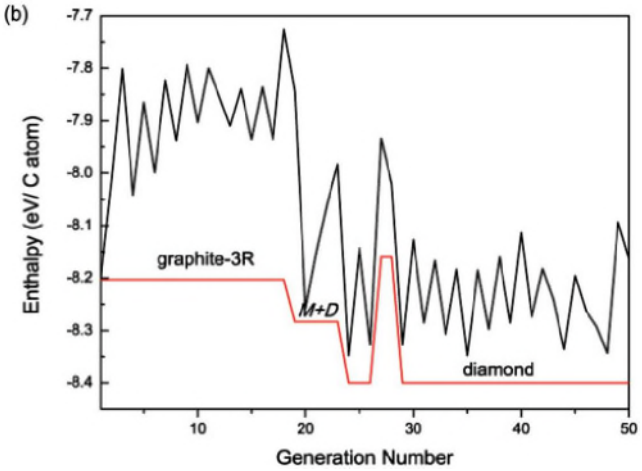
•Umemoto (2010) – observations can be explained by another structure, bct4.

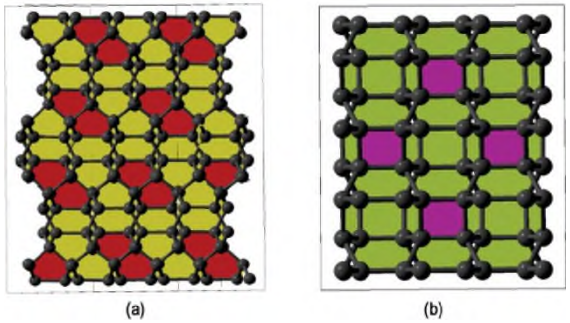


•Wang (2011) – proposed W-carbon.
•Amsler (2011), Zhao (2011) – proposed Z-carbon.
•2012: P-, Q-, R-, S-, X-, Y-, Z-carbon structures were proposed.

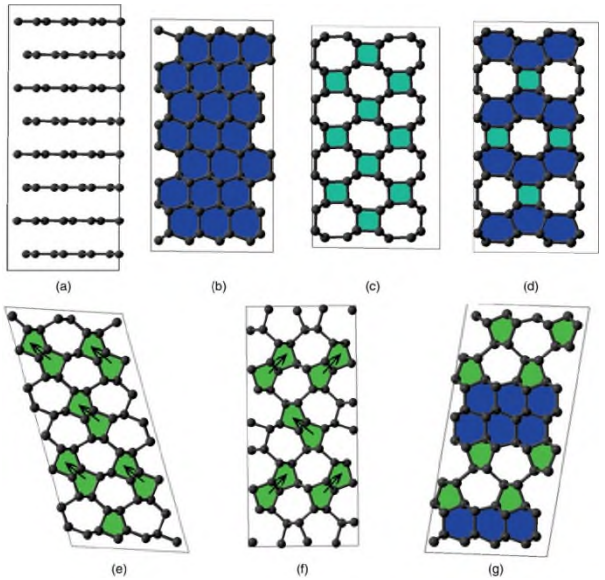
Evolutionary metadynamics: metastable phases of C at 20 GPa (Zhu, Zeng, ARO, 2012)

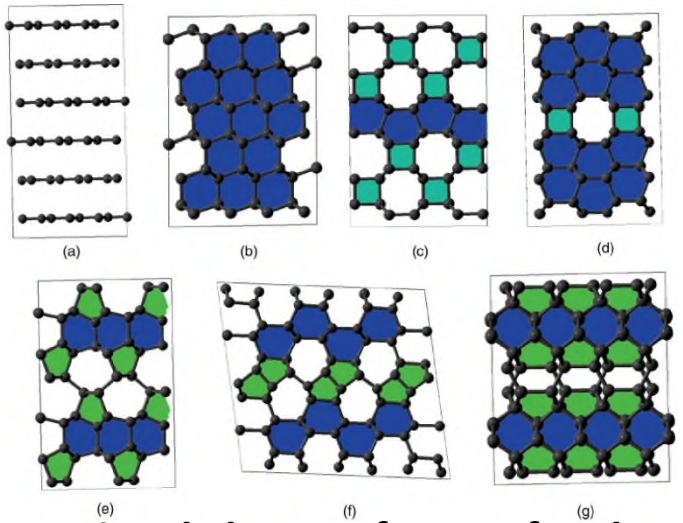






New forms of carbon



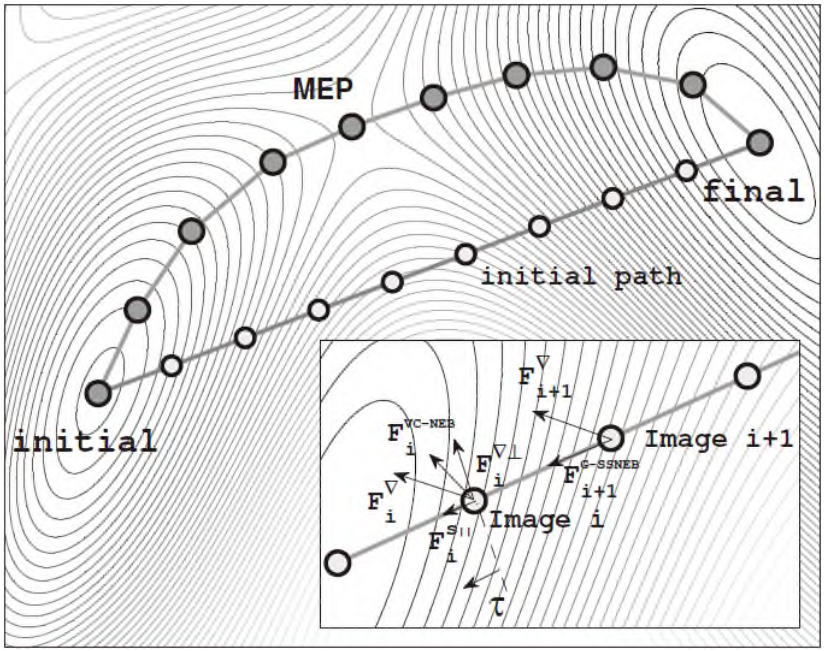


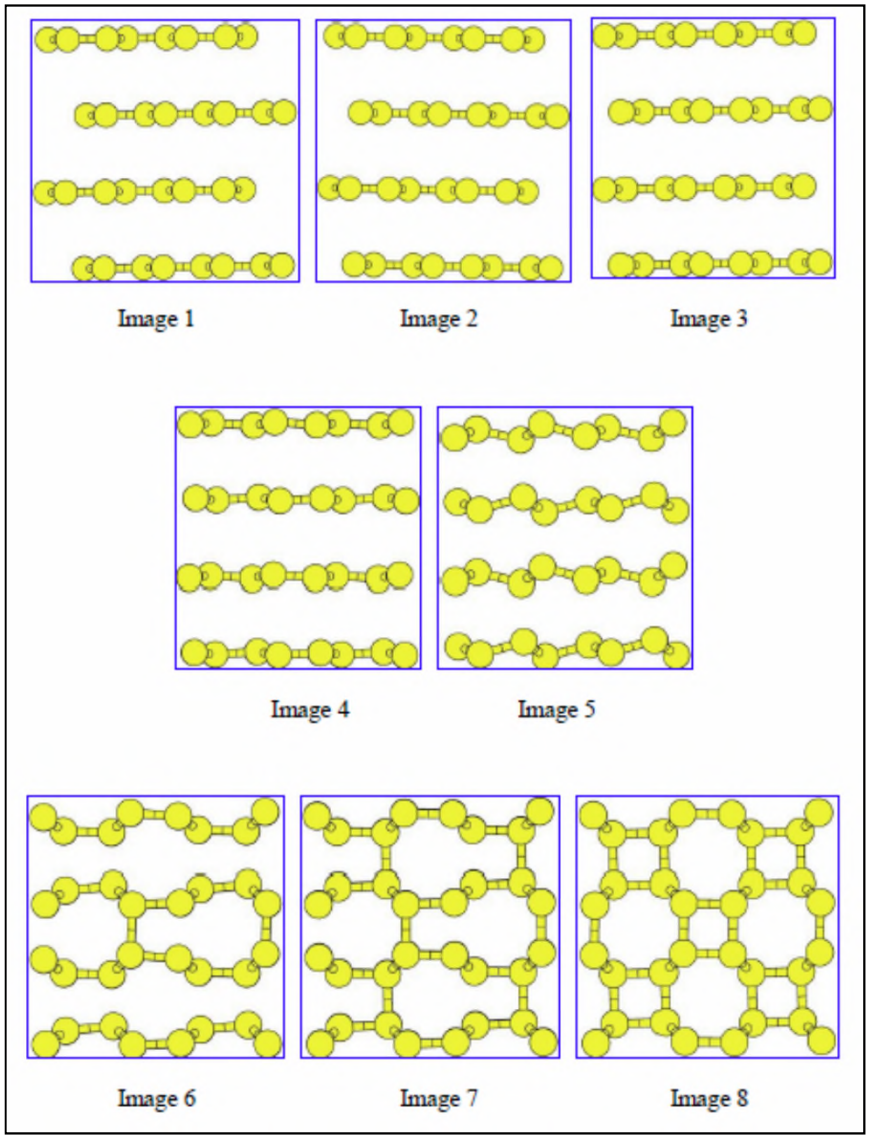
Previously known forms of carbon

Synthesis route and activation barriers

Variable-cell nudged elastic bands (vcNEB)

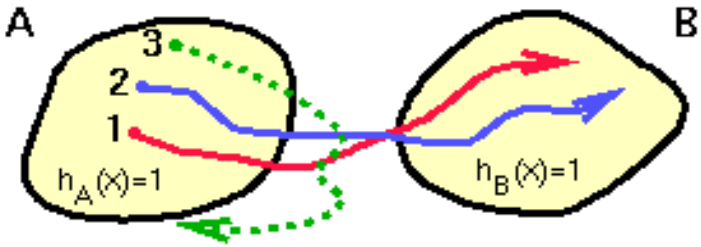
Work of Guangrui Qian





Graphite => bct, 20GPa

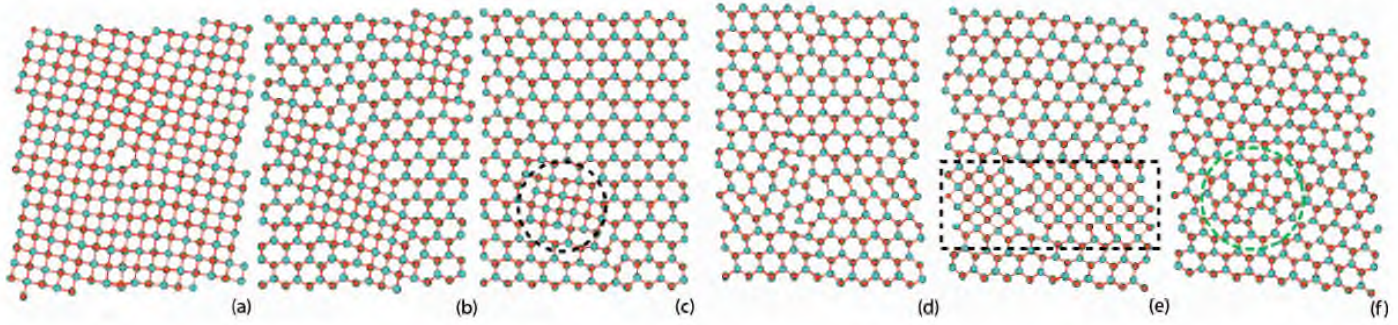
Transition path sampling (TPS) – a way to assess synthesizability of a material



TPS (Dellago et al., 1998) is a combination of Monte Carlo and molecular dynamics methods.

Look for the statistically likeliest pathway.

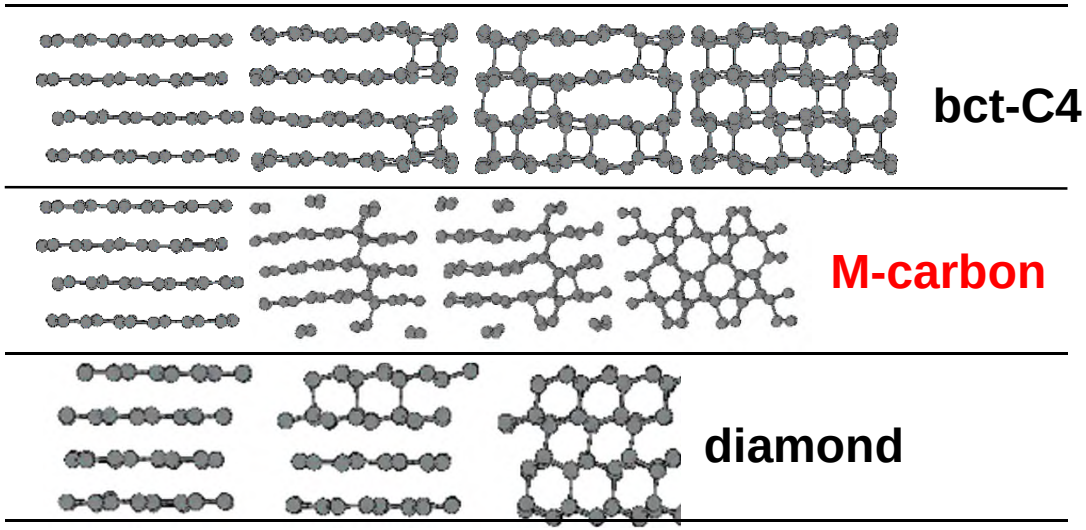
TPS is the best method for predicting activation barriers, because it adequately accounts for nucleation and growth.

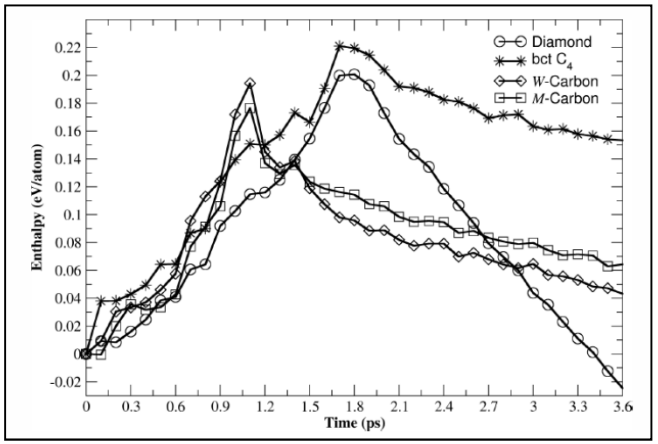


B1-B4 transition pathway in ZnO [Boulfelfel et al. (2007)]

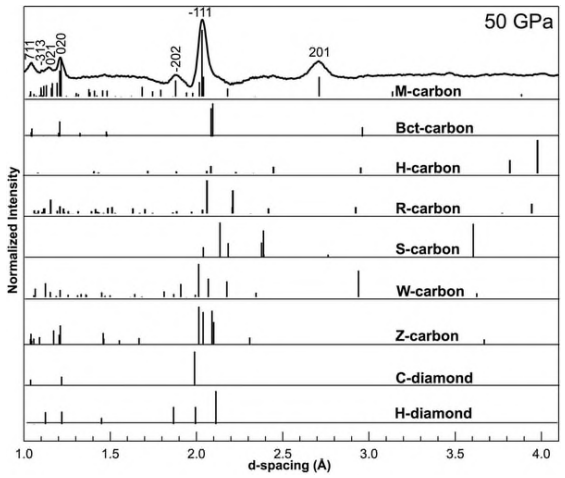
Cold compression of graphite produces M-carbon

TPS at 17 GPa, 300 K, starting from graphite: M-carbon is kinetically easiest [Boulfelfel, ARO, Leoni, *Sci. Reports*, 2012]

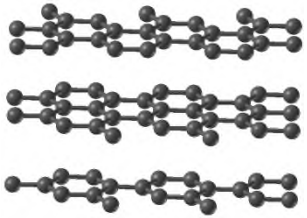




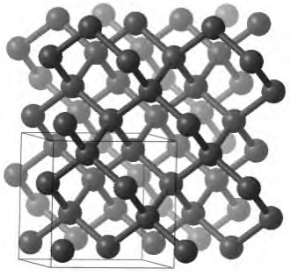
M-carbon confirmed by latest experiments [Yuejian Wang, et al., *Sci. Reports*, 2012]



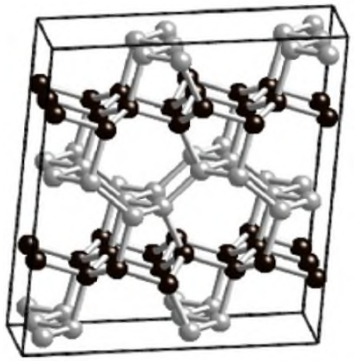
M-carbon - a new established carbon allotrope



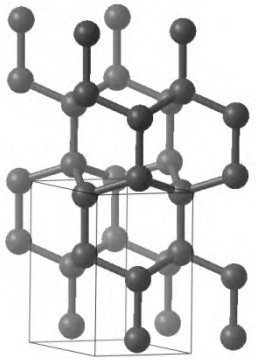
graphite



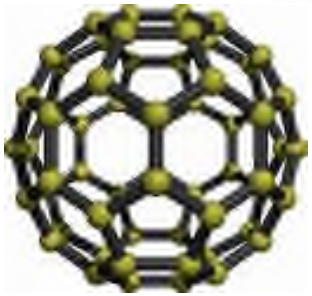
diamond



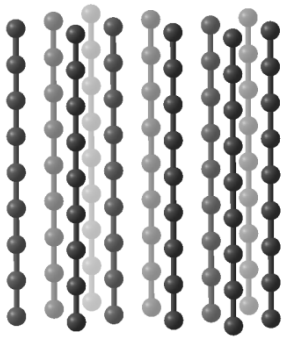
M-carbon



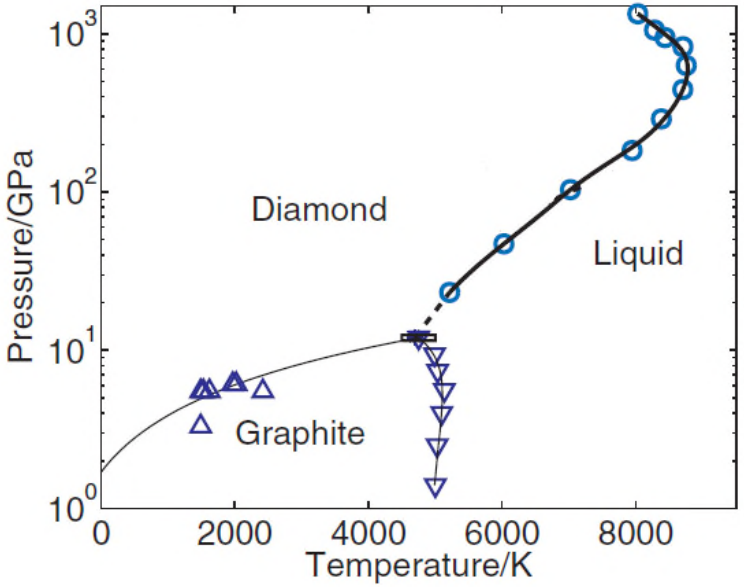
lonsdaleite



fullerenes

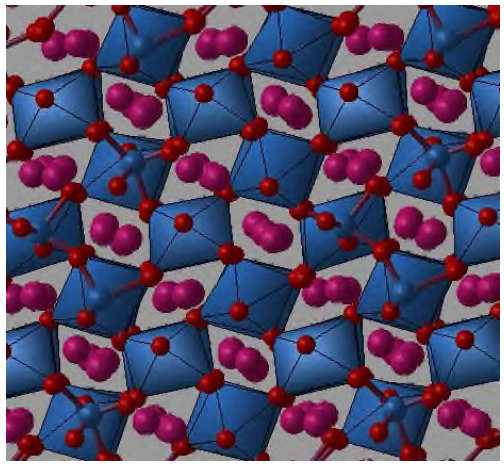


carbynes

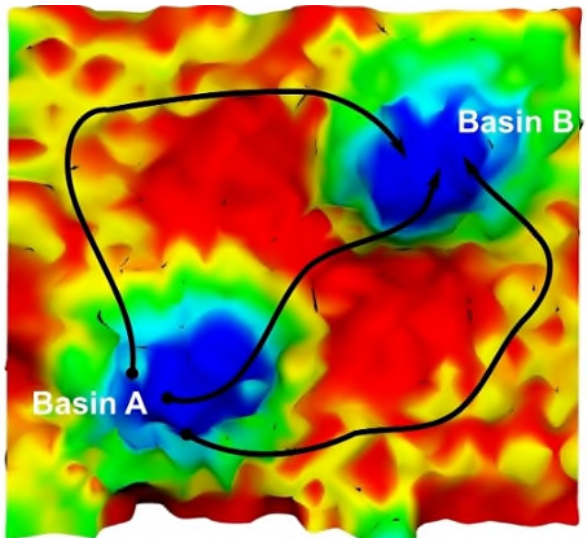


Theoretical phase diagram of carbon [Wang et al. (2005)]

Evolutionary metadynamics is a new powerful technique for exploring energy landscapes



I. It addresses issues of MD- metadynamics



II. Complementary to USPEX - efficient to predict crystal structures, transition mechanisms, synthesizable structures