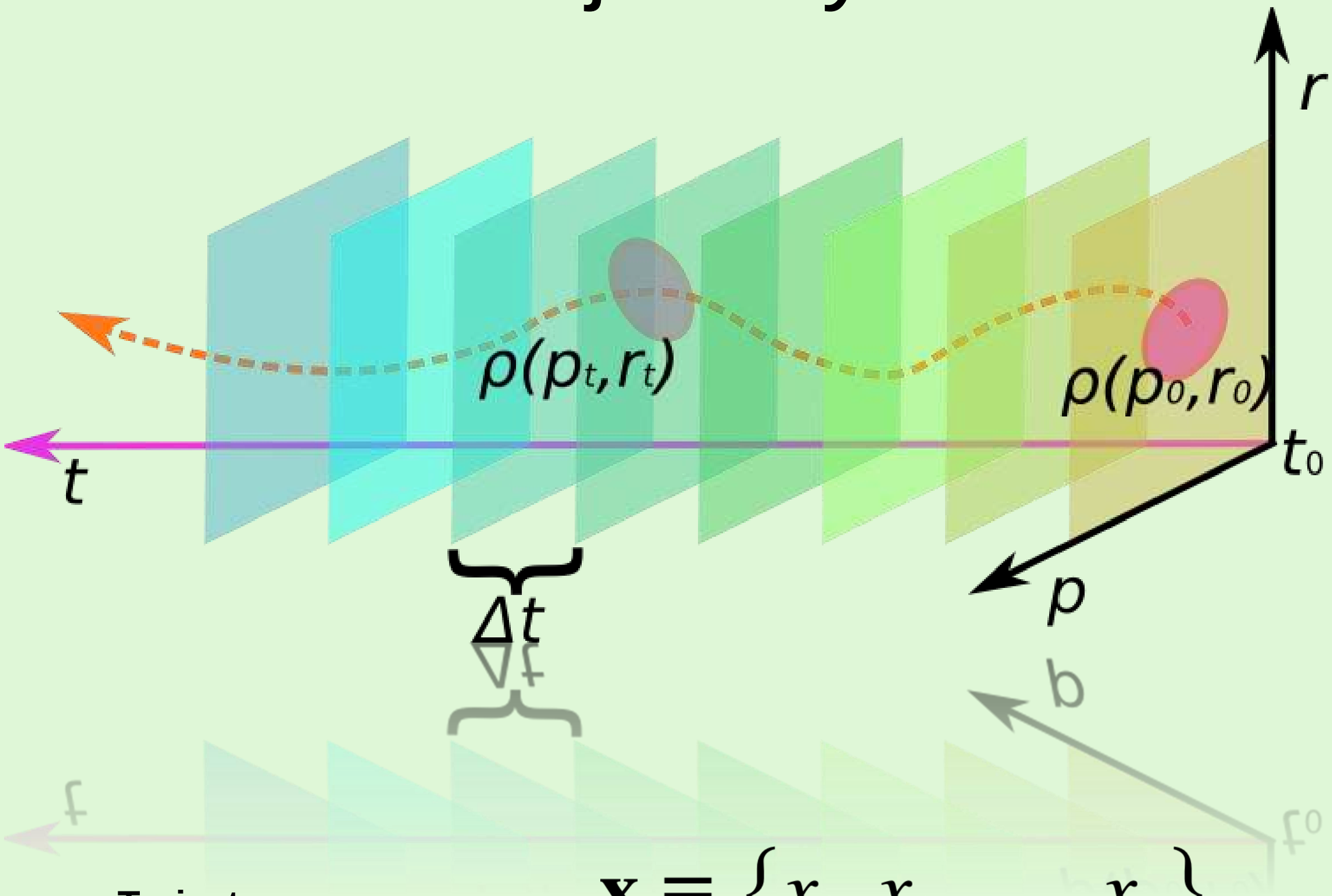
Lecture 2

Advanced techniques: rare events,
metadynamics (metaD), transition path sampling (TPS), metashooting

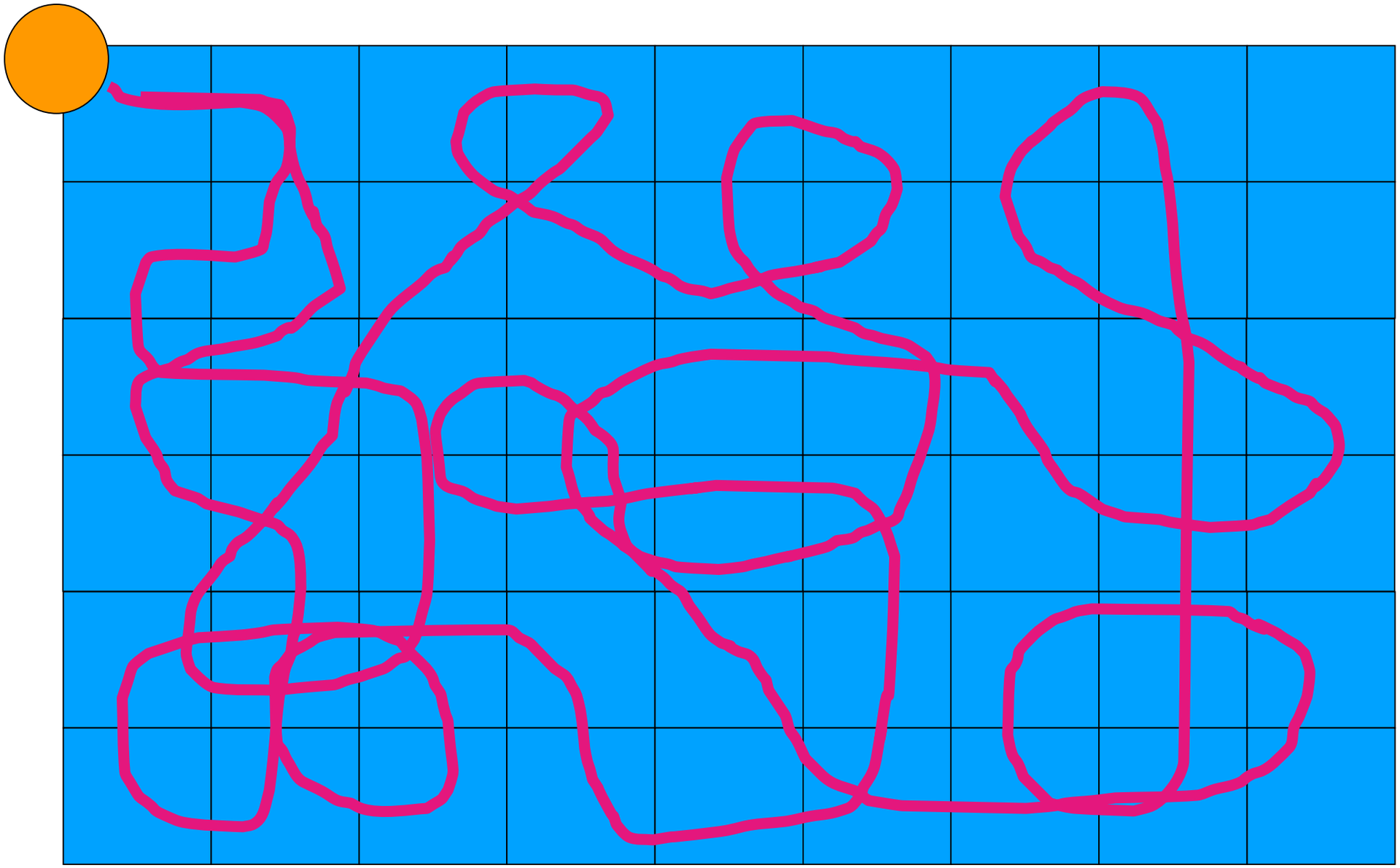
Trajectory



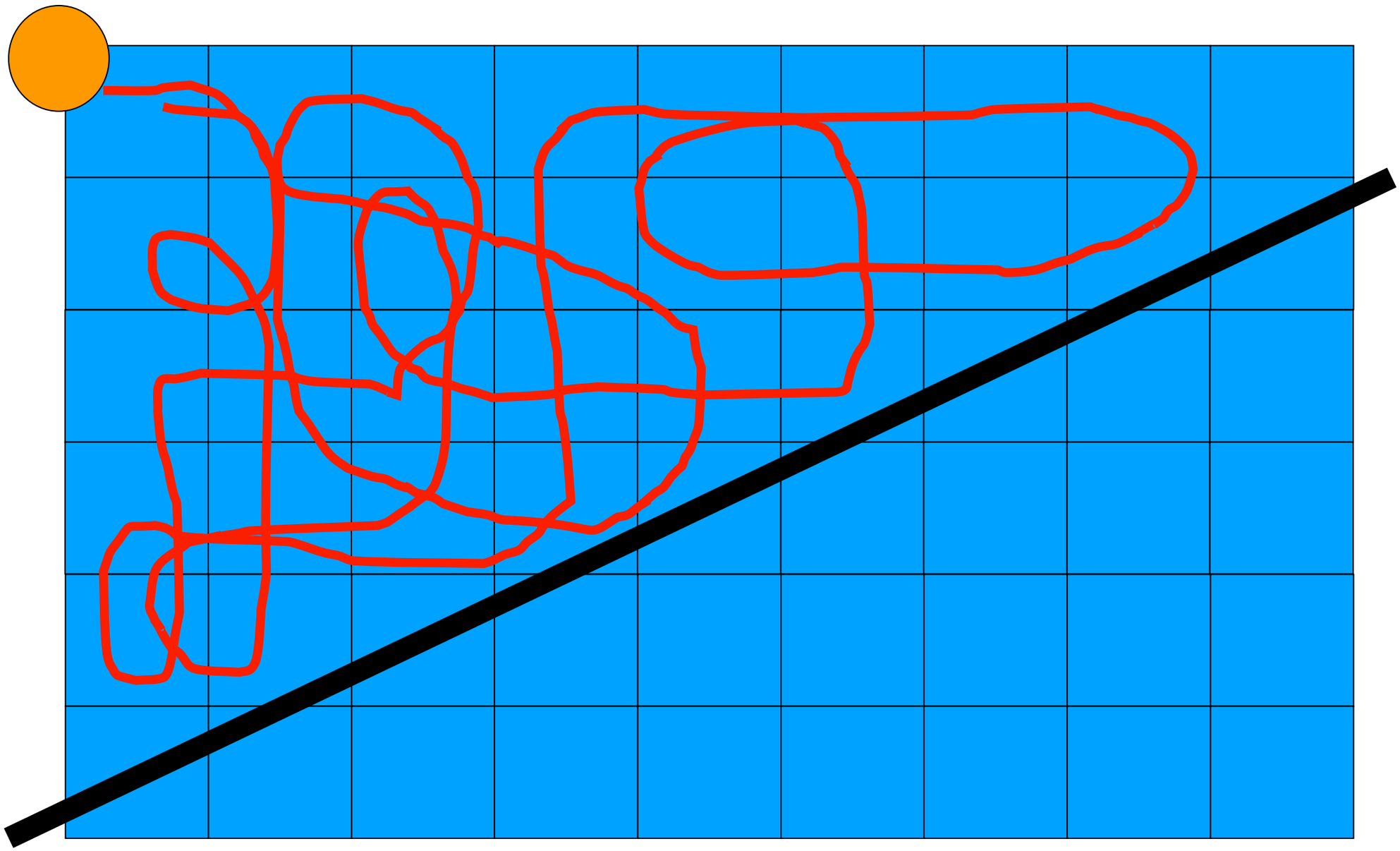
Trajectory

$$\mathbf{x} \equiv \{x_0, x_1, \ldots, x_L\}$$

Ergodic system (see lecture 1)
(all states are visited)

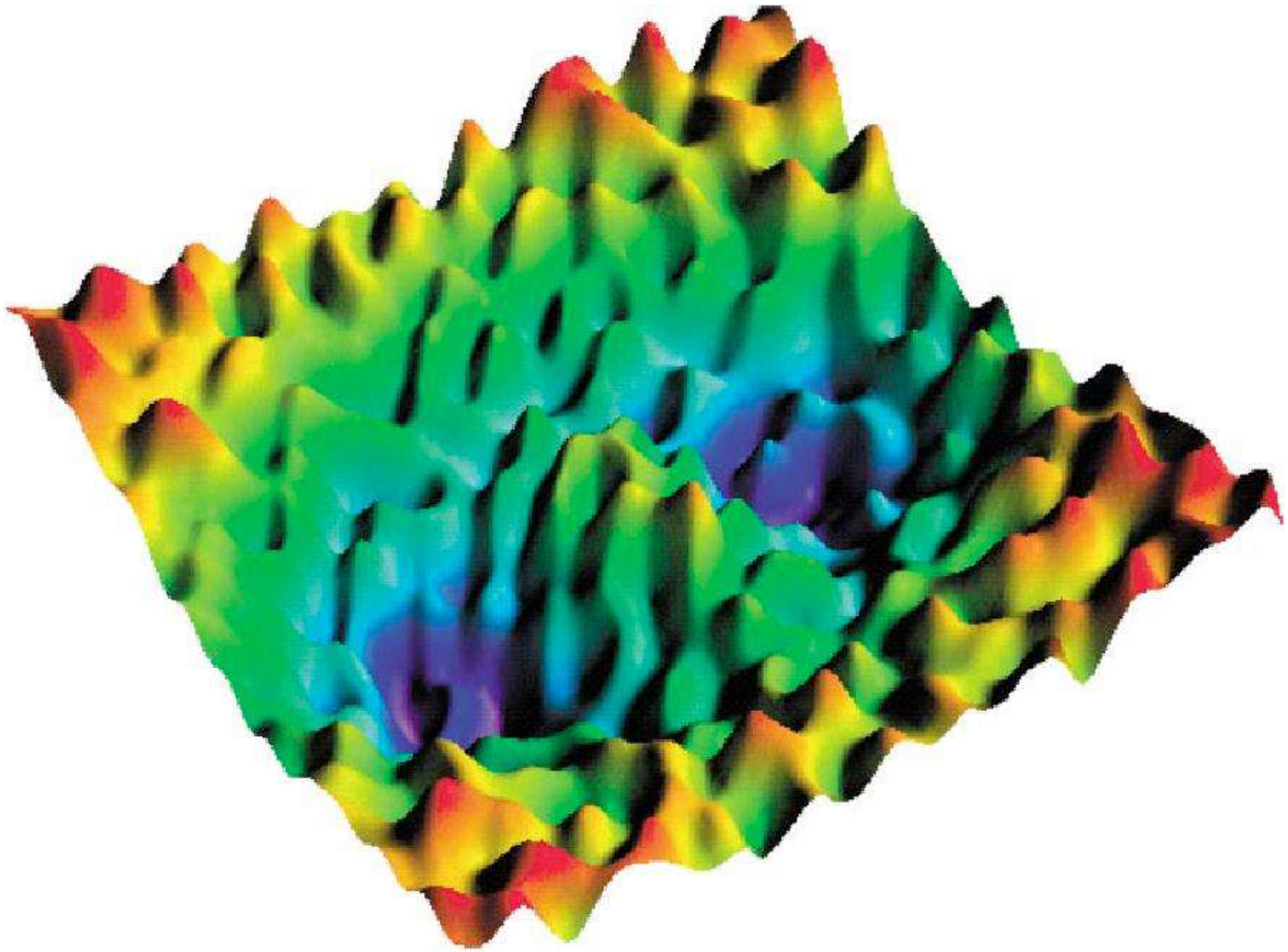


Broken ergodicity
(some regions inaccessible)



Associated with highly corrugated energy landscapes

Corrugated Energy Landscape



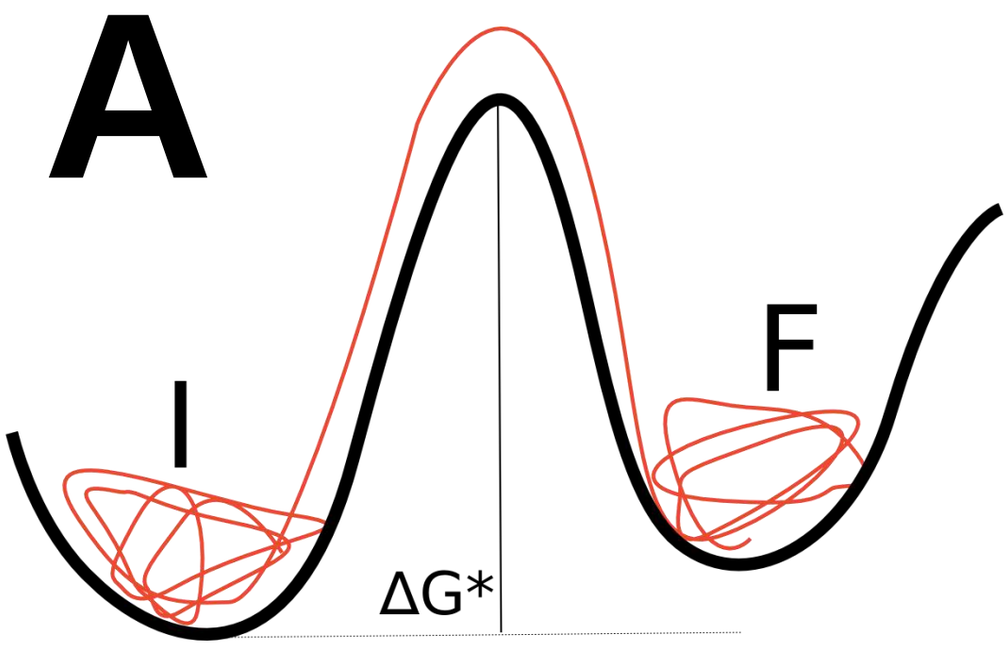
https://www.semanticscholar.org/paper/Transition-path-sampling%3A-throwing-ropes-over-rough-Bolhuis-Chandler/b36f22f2fae776ad0723a92d659d056e27cc41f3

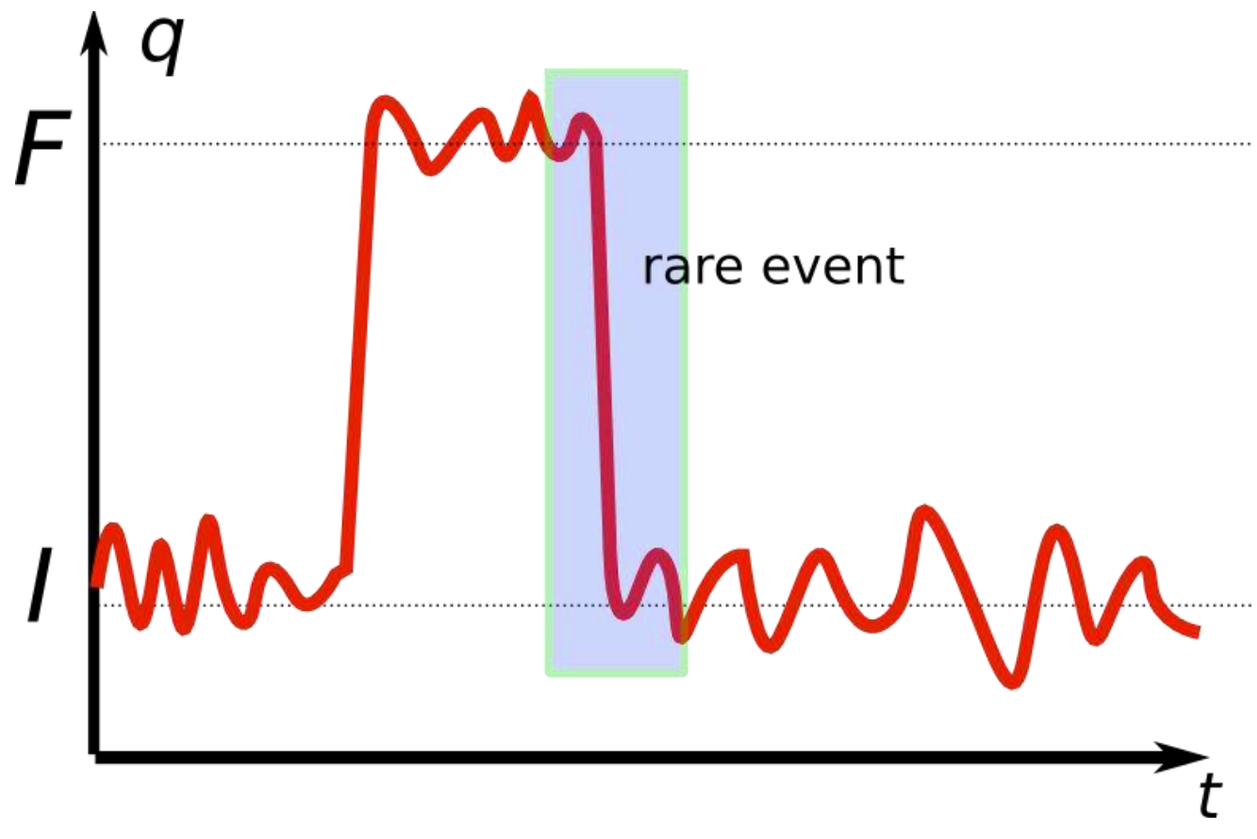
rare event

- plain molecular dynamics can be applied “universally”, to a broad range of problems, to understand equilibrium properties of a system. Therein, the inherent time-scale of fluctuation decay is short (~10^{-8} s).

- Diffusion, which implies a slower dynamics, can nonetheless still be described with plain MD (see diffusion coefficient, Kubo-Green formulas)

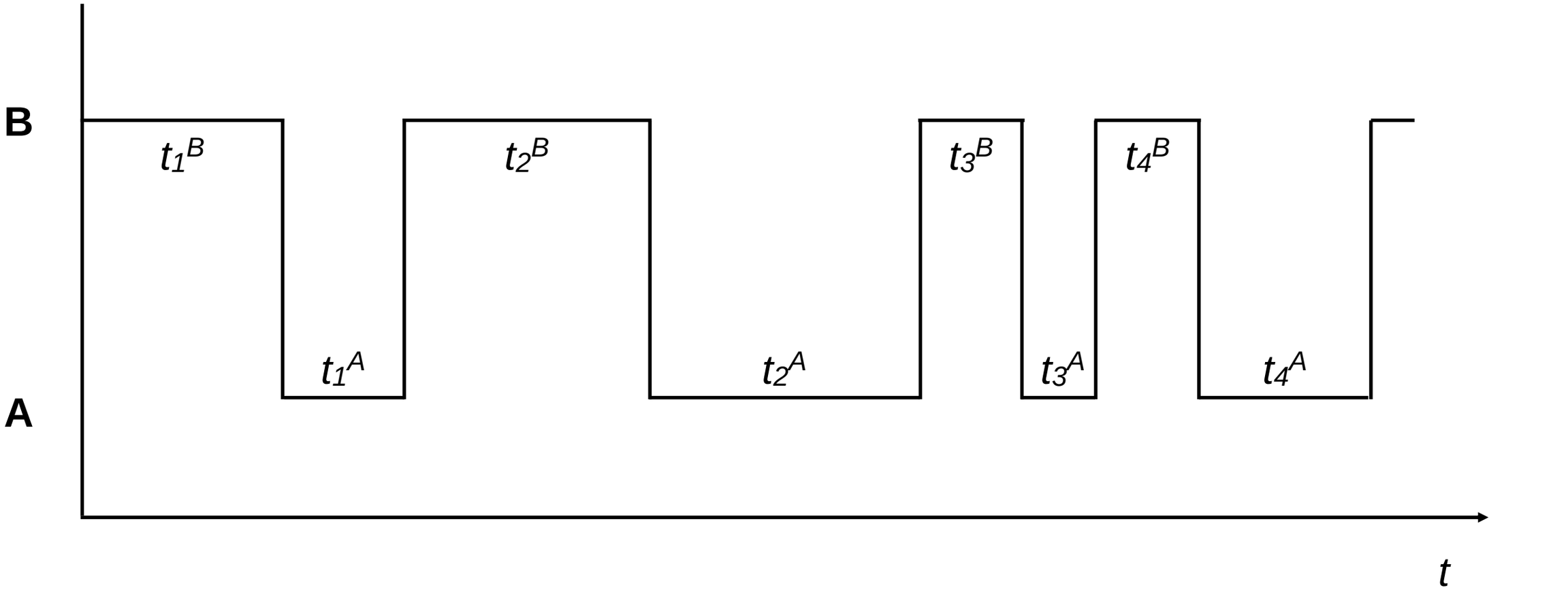
- If however the process is activated (ie there is a large energy barrier somewhere along the process), then the chances of a crossing over the barrier are small to tiny, for a typical time scale simulation. (large means energy barrier >> $k_B T$)





Frequent and slow vs.
Rare and quick

Random dynamical trajectory



W(A,B): transition probability A to B per unit of time

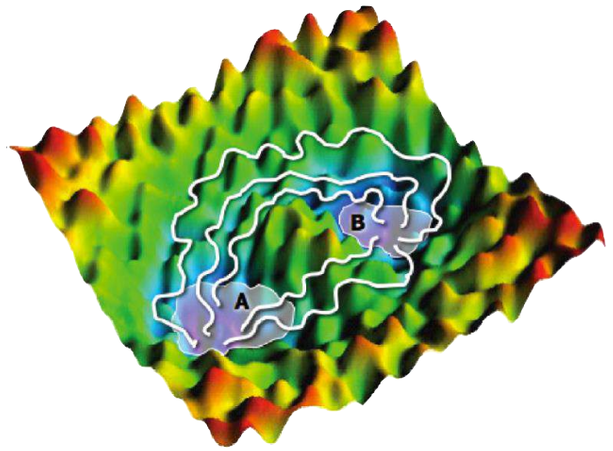
$$k_{AB} = W(A,B)$$
$$k_{AB} = (t_A^{mr})^{-1}$$

t_A^{mr} = mean residence time in state A

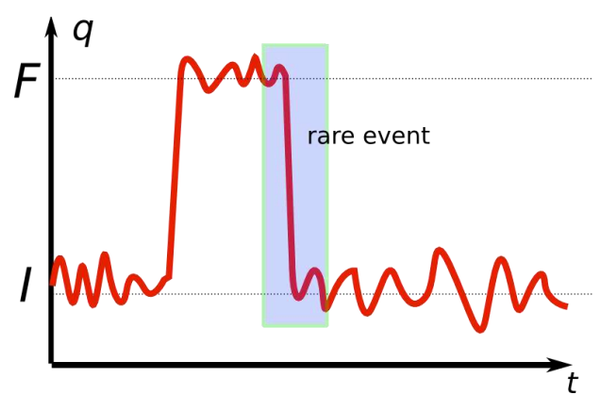
Importance of a state reflected in the total time spend in it

activated processes

- Activated processes are characterised by an activation (free energy) barrier. They span phase transitions, chemical reaction, protein folding processes, crystallisation, nucleation…



- If an event can be observed at all, it will be *quick* on the timescale of the simulation, and will characterise a *narrow* region of the overall simulation time.



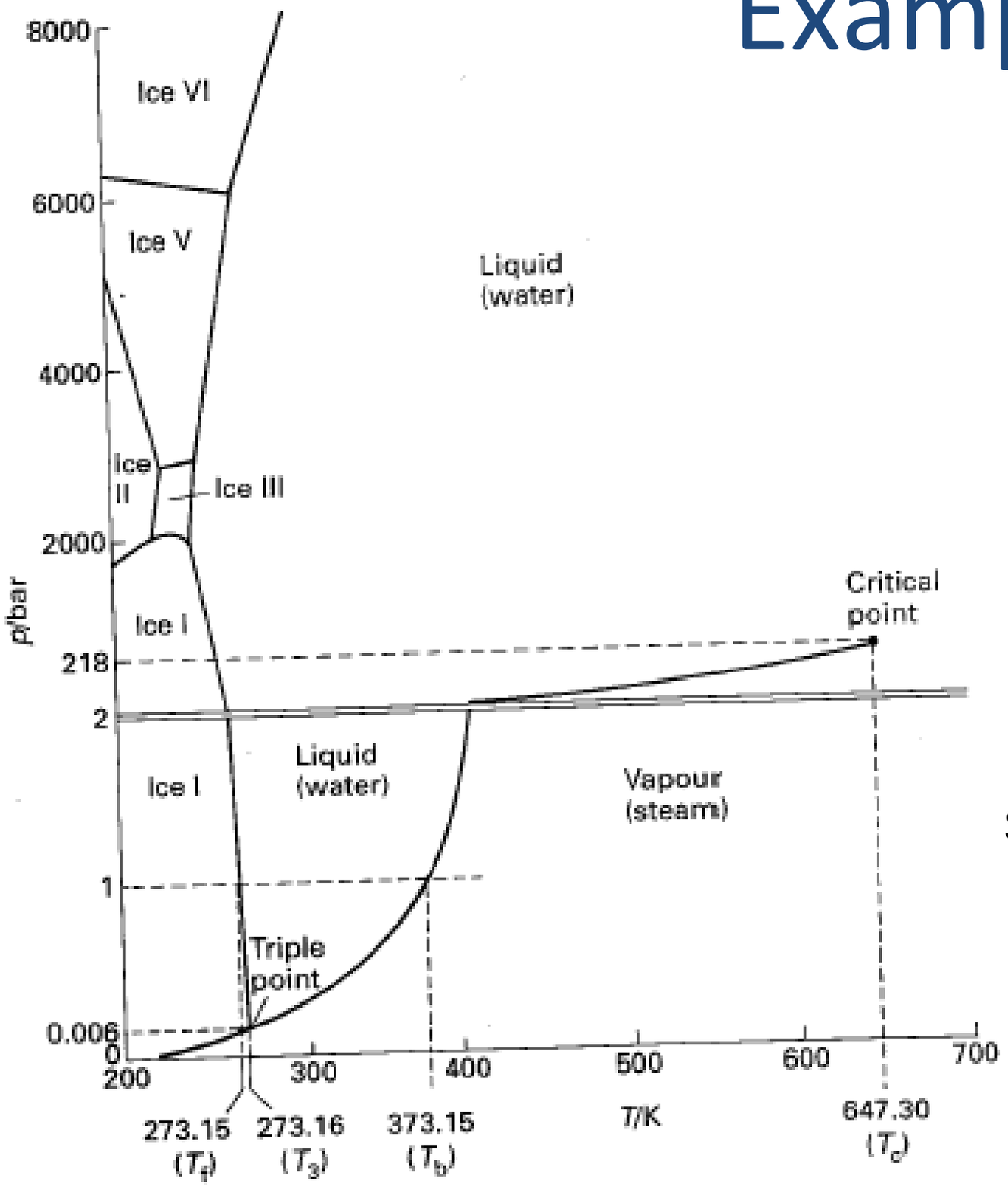
Solutions

- Plain MD can be overdriven, which may imply the choice of a different temperature or pressure from equilibrium values, increasing concentration/activity, a.s.o

- This approach may allow observing the event of interest, it will however spoil the dynamics to some extent. Nonetheless, this typically allows for the observation of a single event, in the direction of equilibrium displacement.

- There are nowadays dedicated, accelerated methods of MD, among them Metadynamics (MetaD) and Transition Path Sampling (TPS).

Example: Water



Slope at triple point positive

Density of Ice < density of water.

Simulation of Water Crystallisation by MD

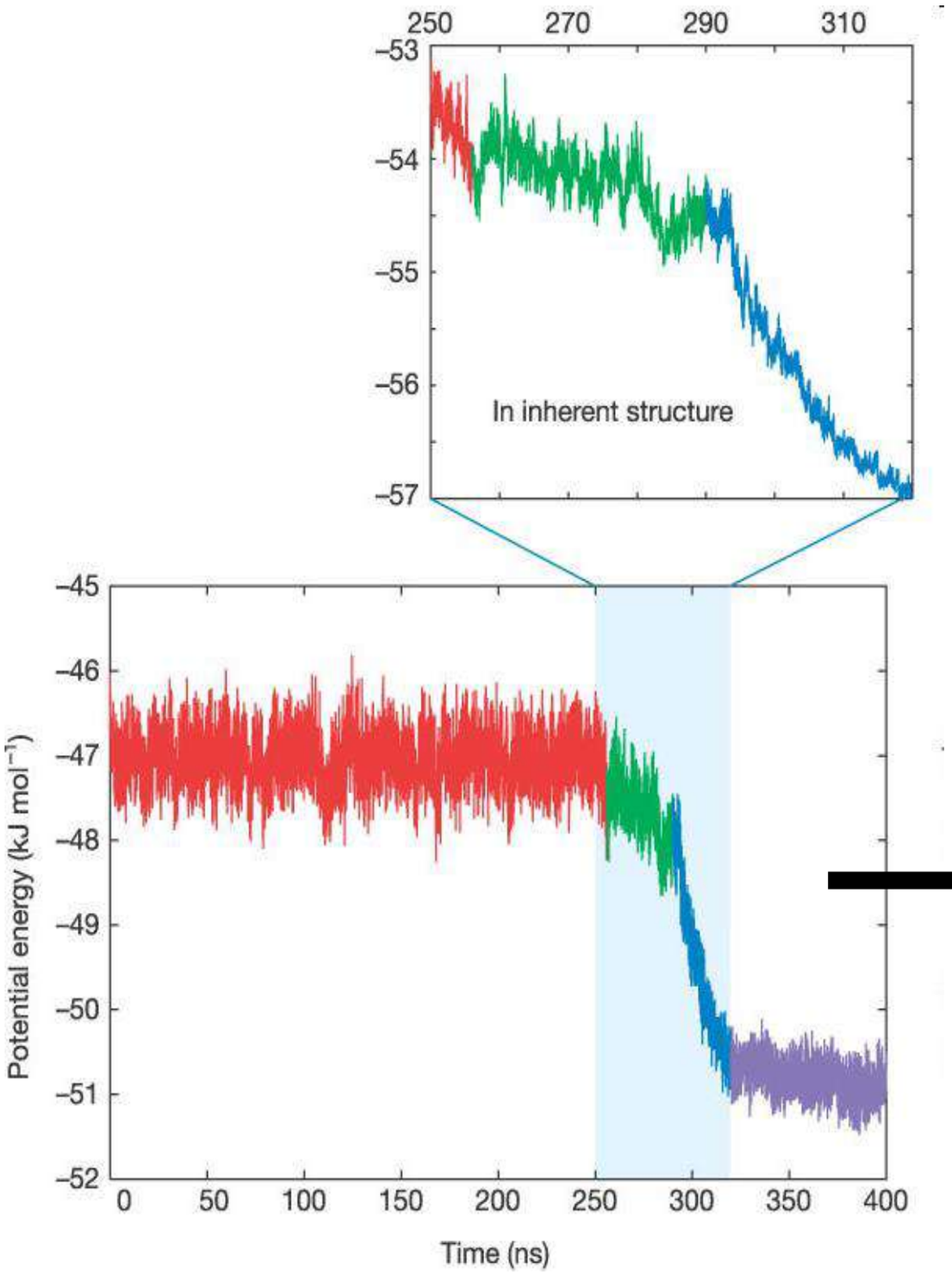
- Thermalisation at high(er) Temp
- Quenching to lower T (230 K)
- Supercooled state (overdriven conditions)
- Time evolution, const-T, const-p
- 512 molecules (ab initio MD)
- Observation of nuclei formation and growth

Molecular dynamics simulation of the ice nucleation and growth process leading to water freezing

Masakazu Matsumoto, Shinji Saito & Iwao Ohmine

Chemistry Department, Nagoya University, Chikusa-ku, Nagoya, Japan 464-8602

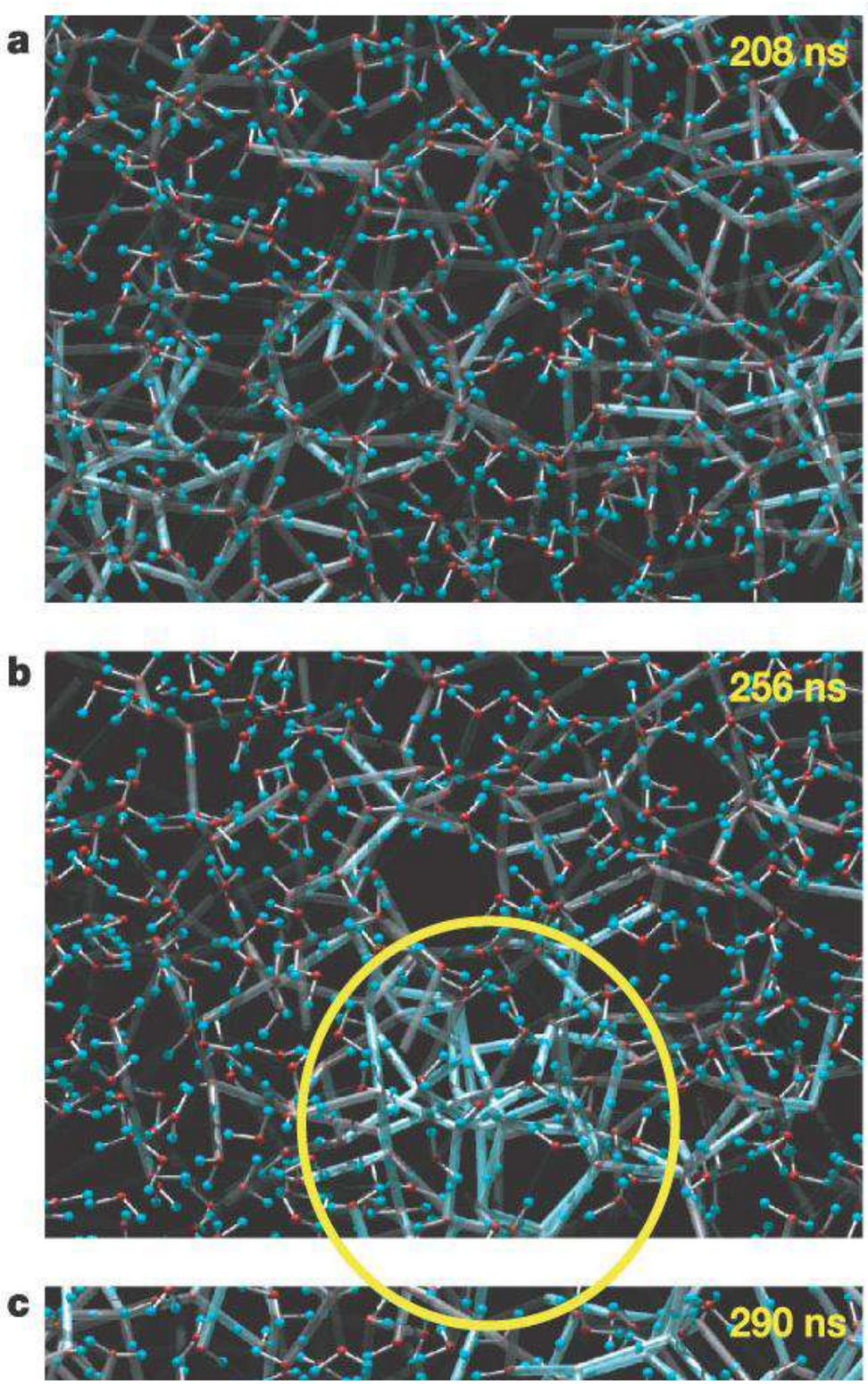
Inherent Structure

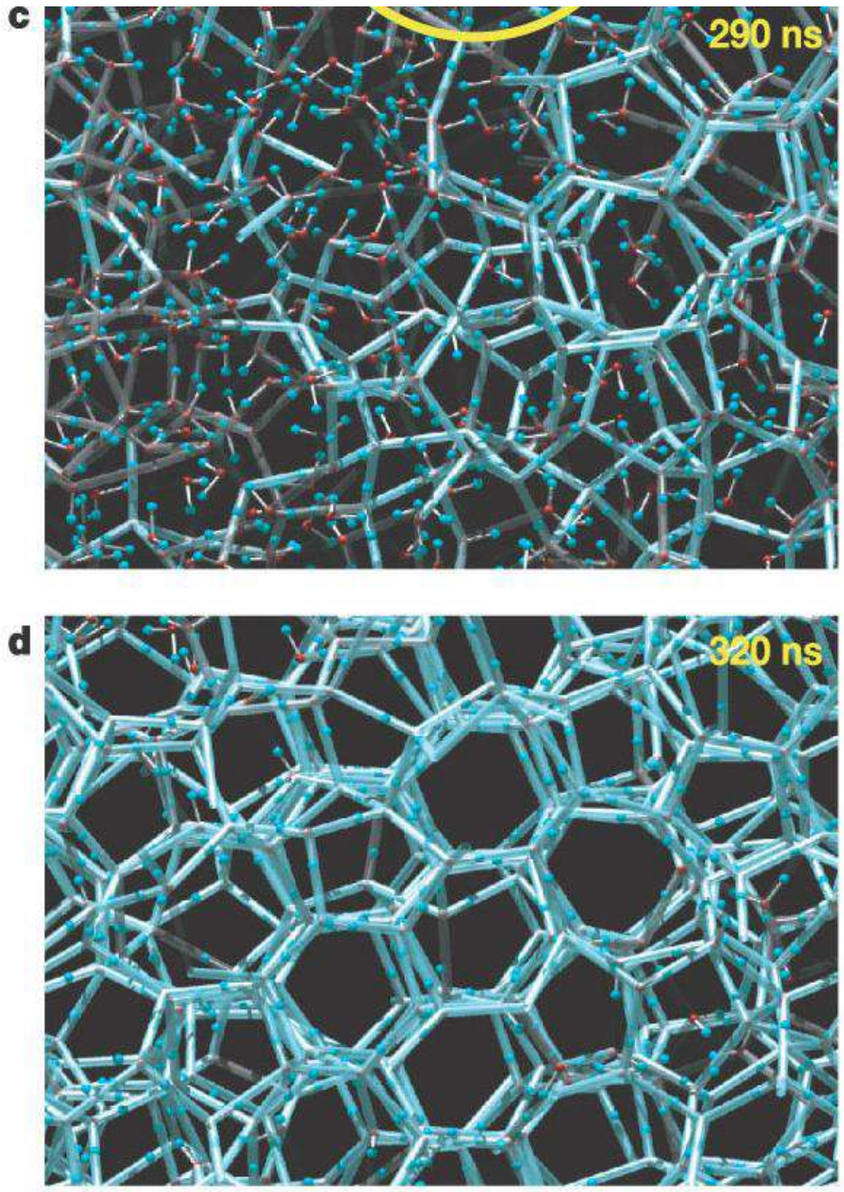


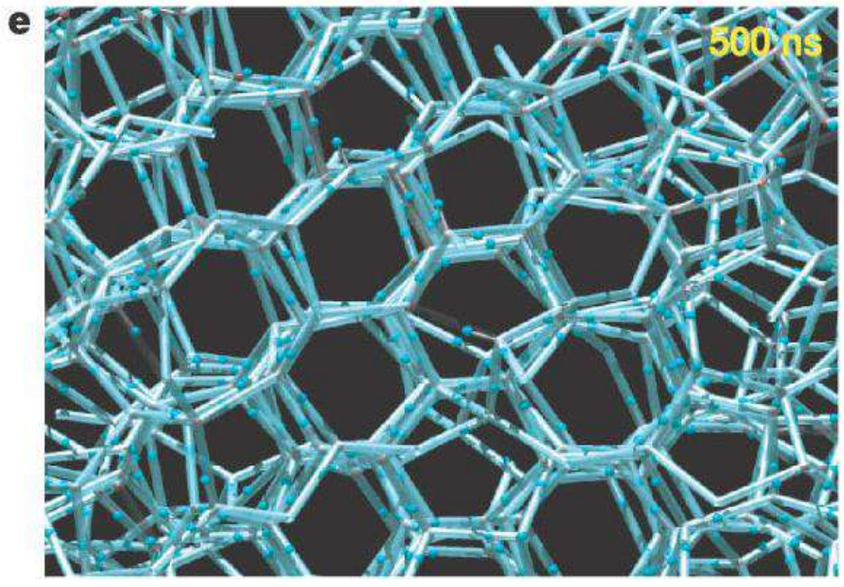
Samples of structures at 10 ps intervals,

Evolution of potential energy

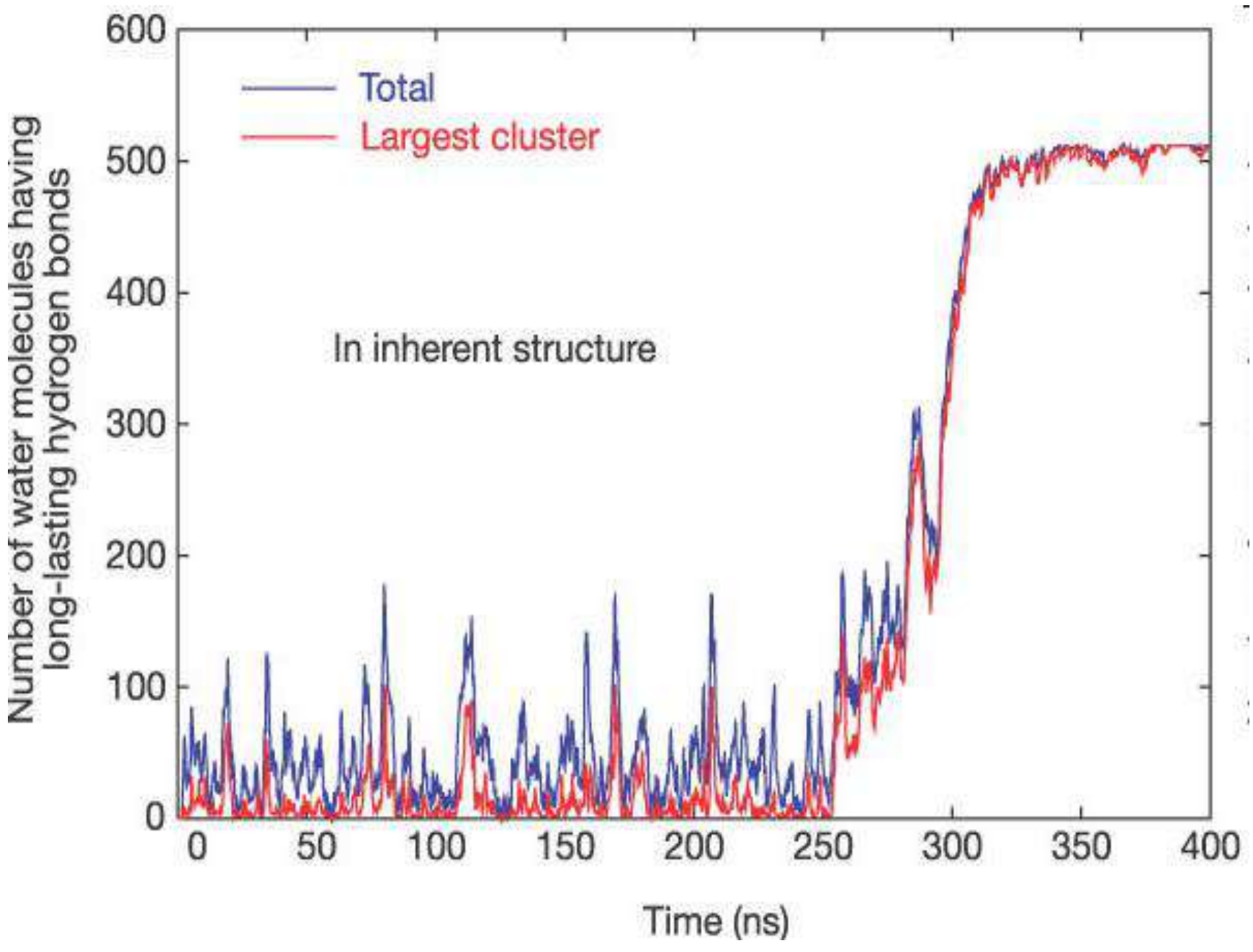
H-bonds Structure (nucleation and growth)







Monitoring of PT progress



Metadynamics

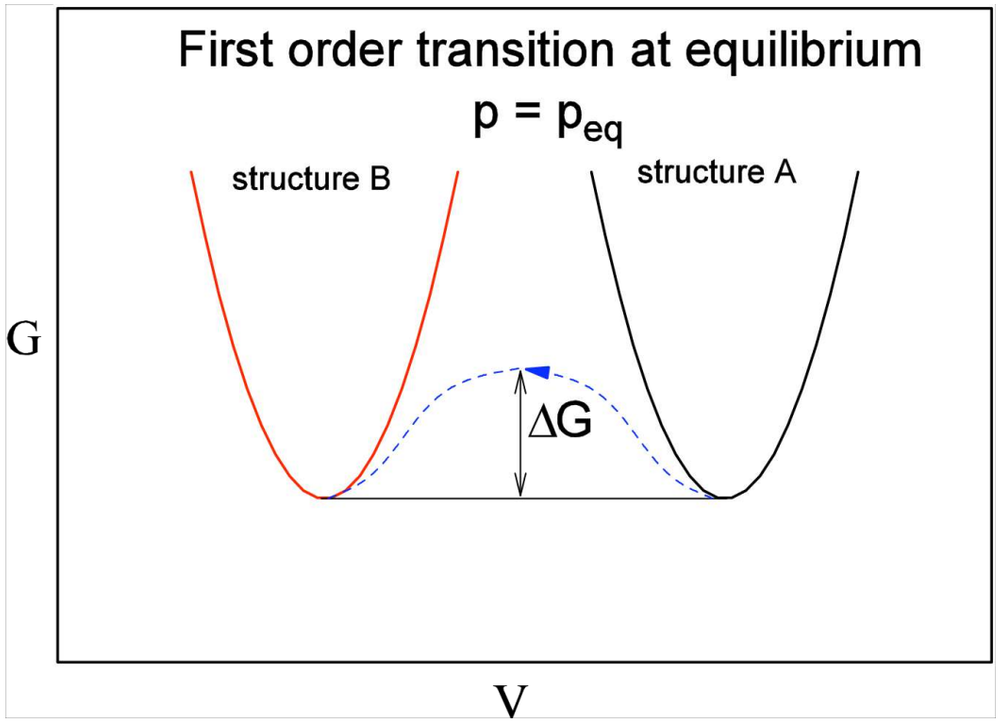
Structural Phase Transitions: Metadynamics

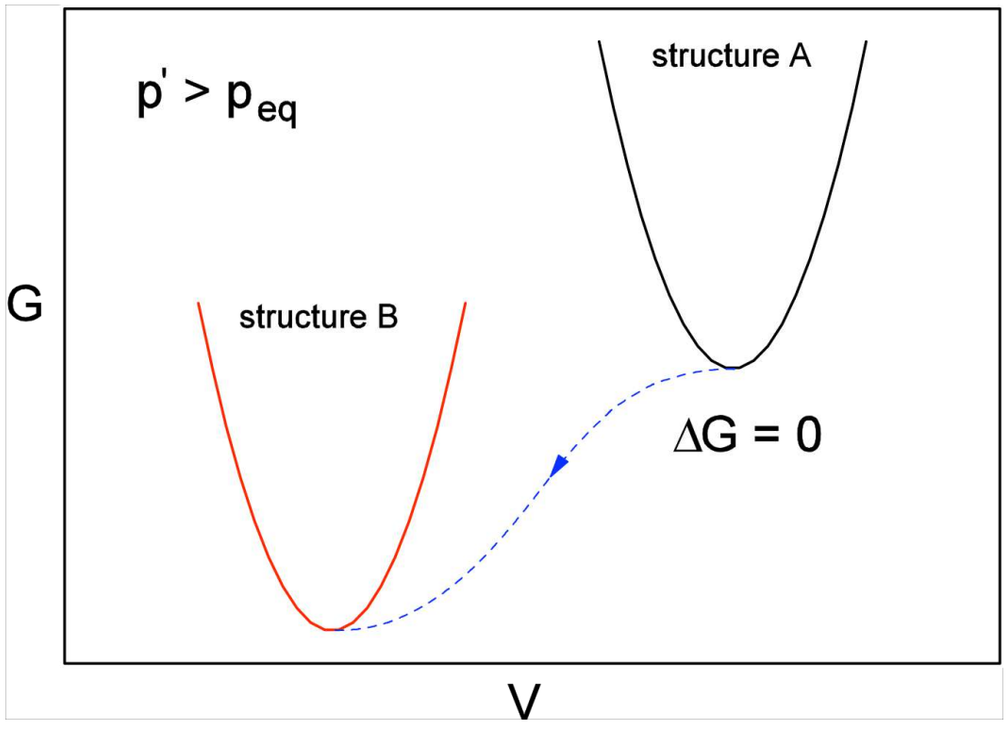
- structural transitions often 1st order
- characterised by nucleation and growth
- $\Delta G >> k_B T$, barrier crossing will take a long time (rare event scenario)

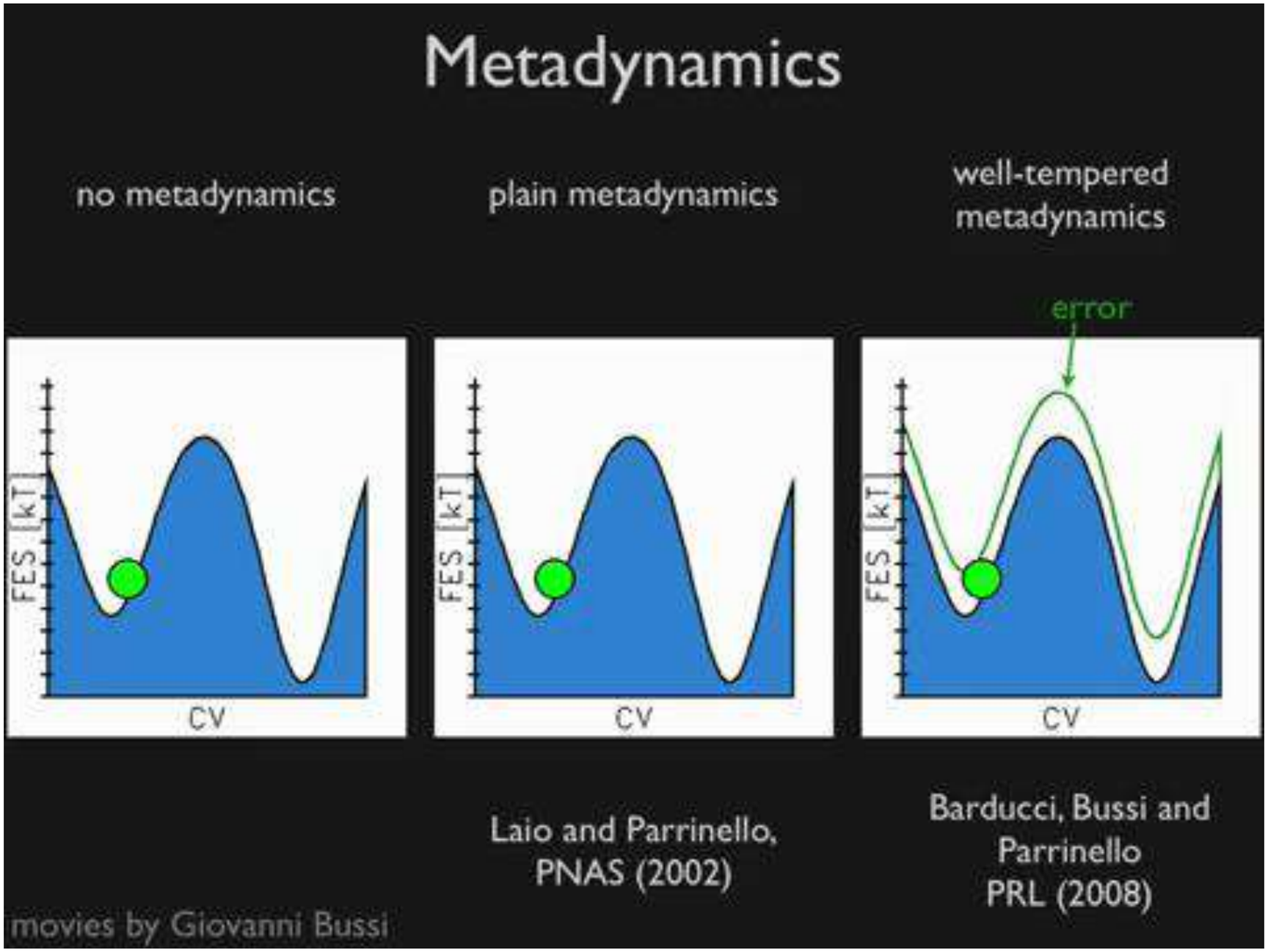
- over-pressurisation (p') of the system to the point of mechanical instability

- as $p' > p_{eq}$, some phases may be overlooked, transformation too quick, details missed, possibly not even the correct mechanism!

- origin of the problem – time scale gap (rare event)





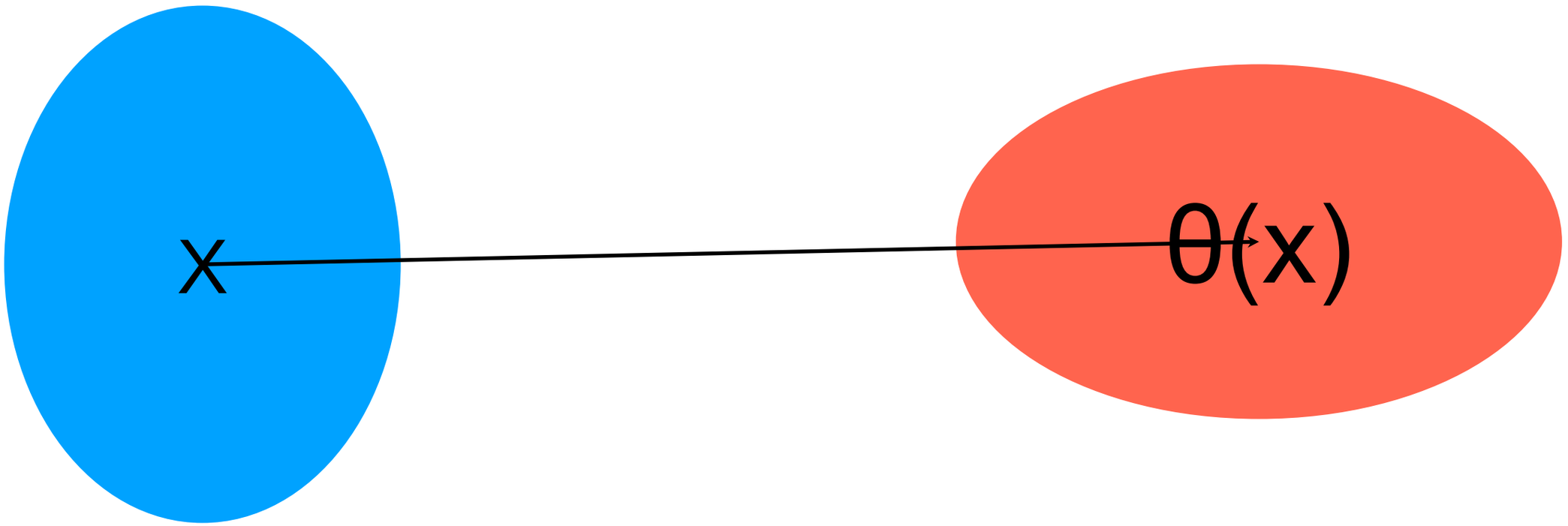


A Laio & M Parrinello (2002), R. Martonak & M. Parrinello (2003)

https://www.youtube.com/watch?v=IzEBpQ0c8TA

Collective Variable(s), CV

result from a mapping: x —> θ(x)



Physical Space (x, y, z)

Collective Variable space, θ(x)

Underlying maths

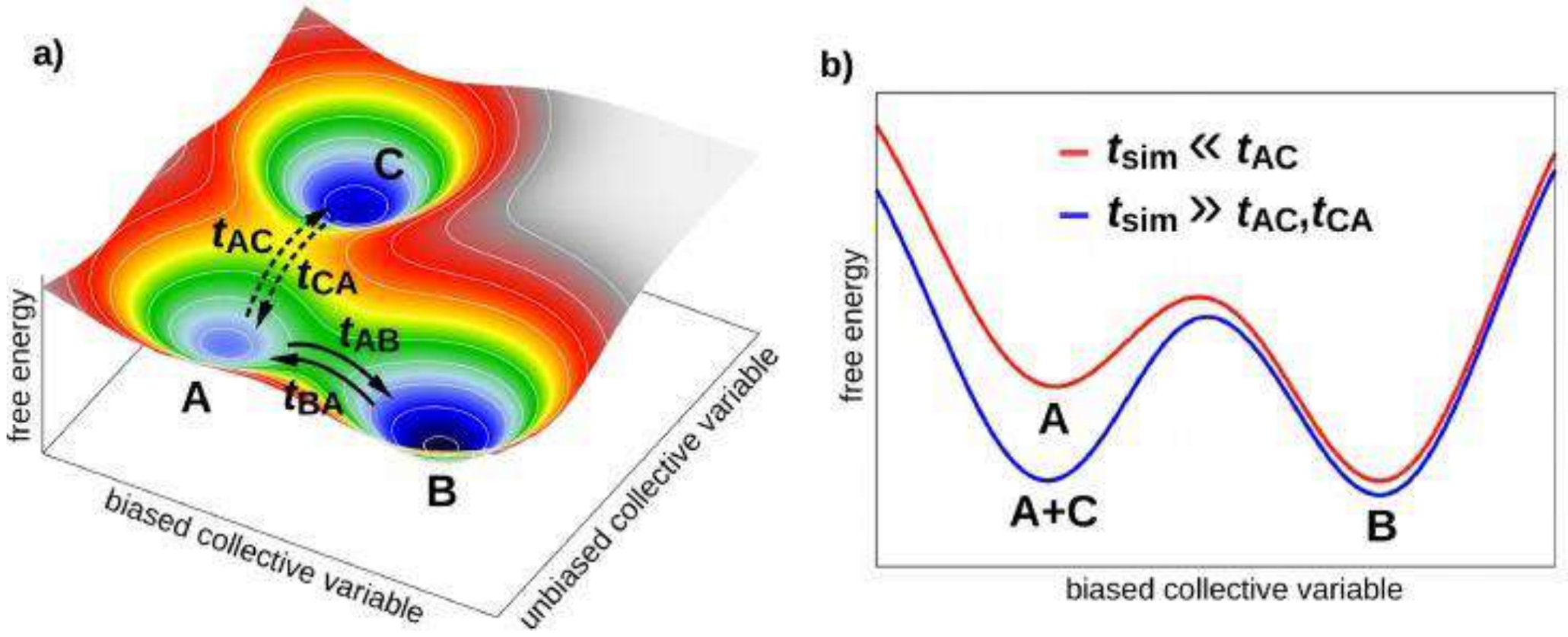
$$V(\mathbf{x}) = V_0(\mathbf{x}) + \Delta V(\mathbf{x}, t)$$ **bias potential**

$$\Delta V(\mathbf{x}, t) = w \sum_{t'=\tau_G, 2\tau_G, \ldots} e^{\frac{|\theta(x(t)) - \theta(x(t'))|^2}{2\delta\theta^2}}$$

implemented as **regular deposition of gaussian functions**

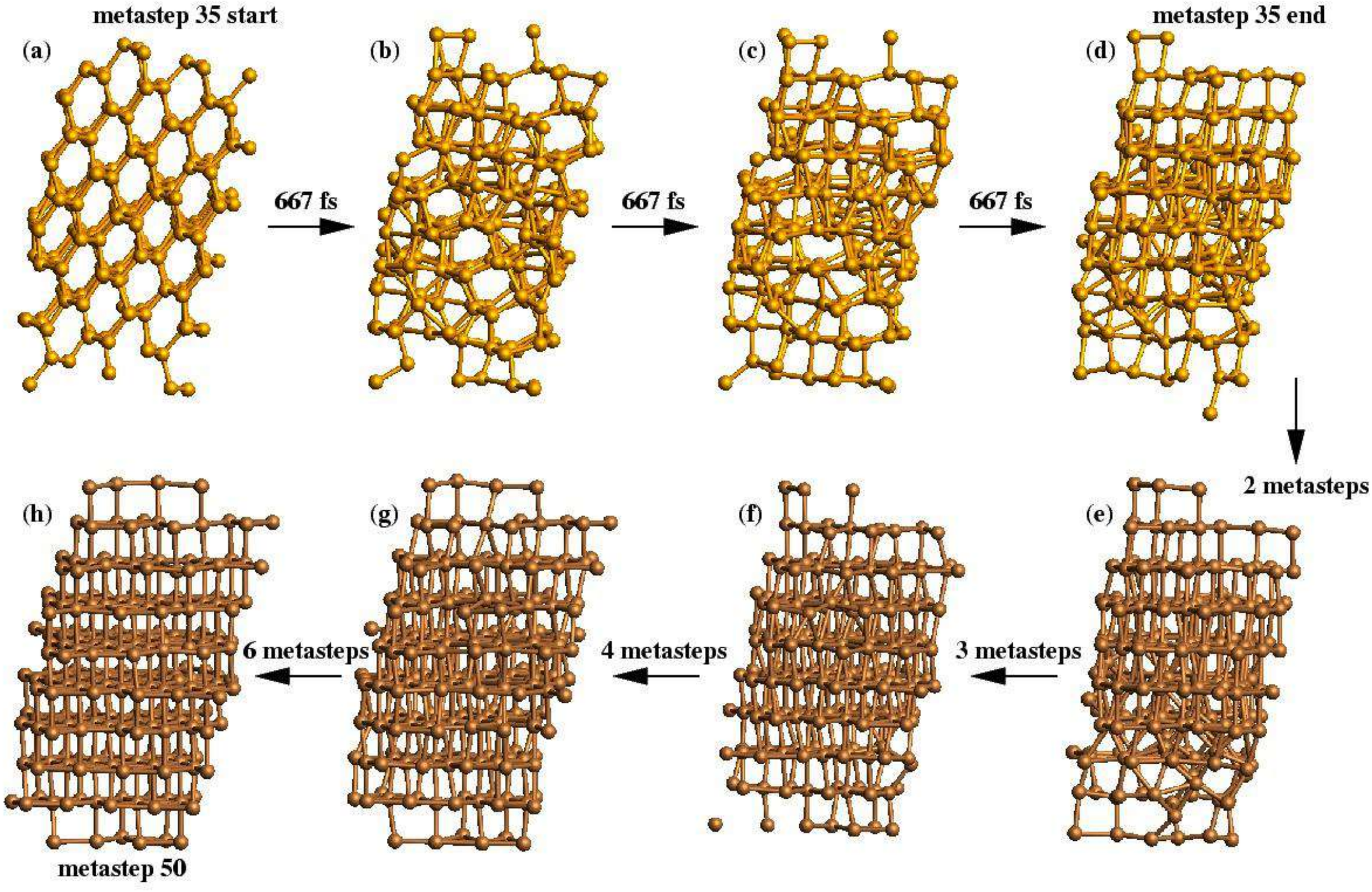
https://www.mdpi.com/1099-4300/16/1/163/htm

Dependence of the free energy from the choice of collective variables, the bias imposed thereof, and the overall simulation time.



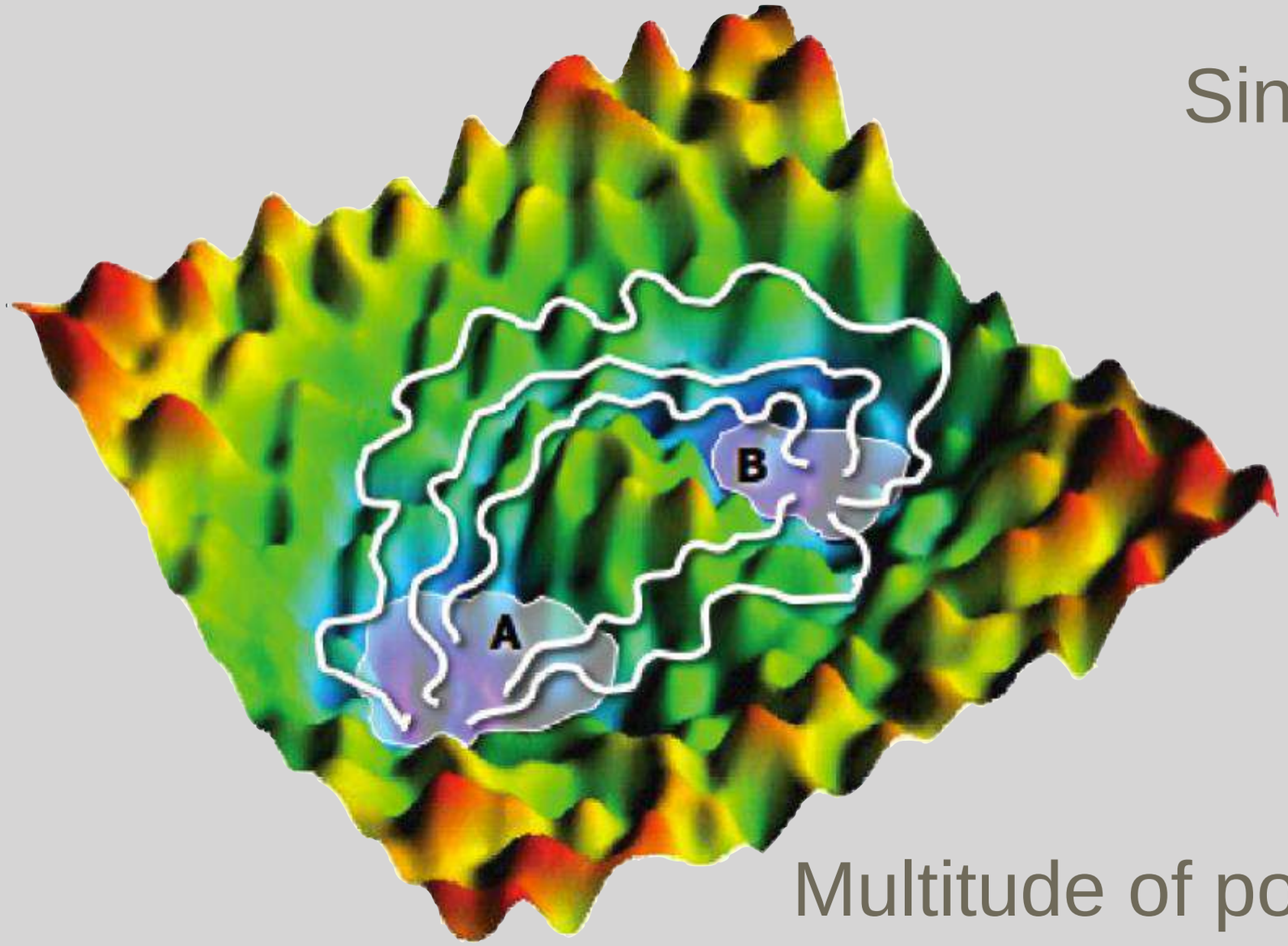
https://doi.org/10.1016/j.revip.2017.05.001

structural transformations



Transition Path Sampling (TPS)

Corrugated Landscape of Complex Systems



(D. Chandler, C. Dellago)

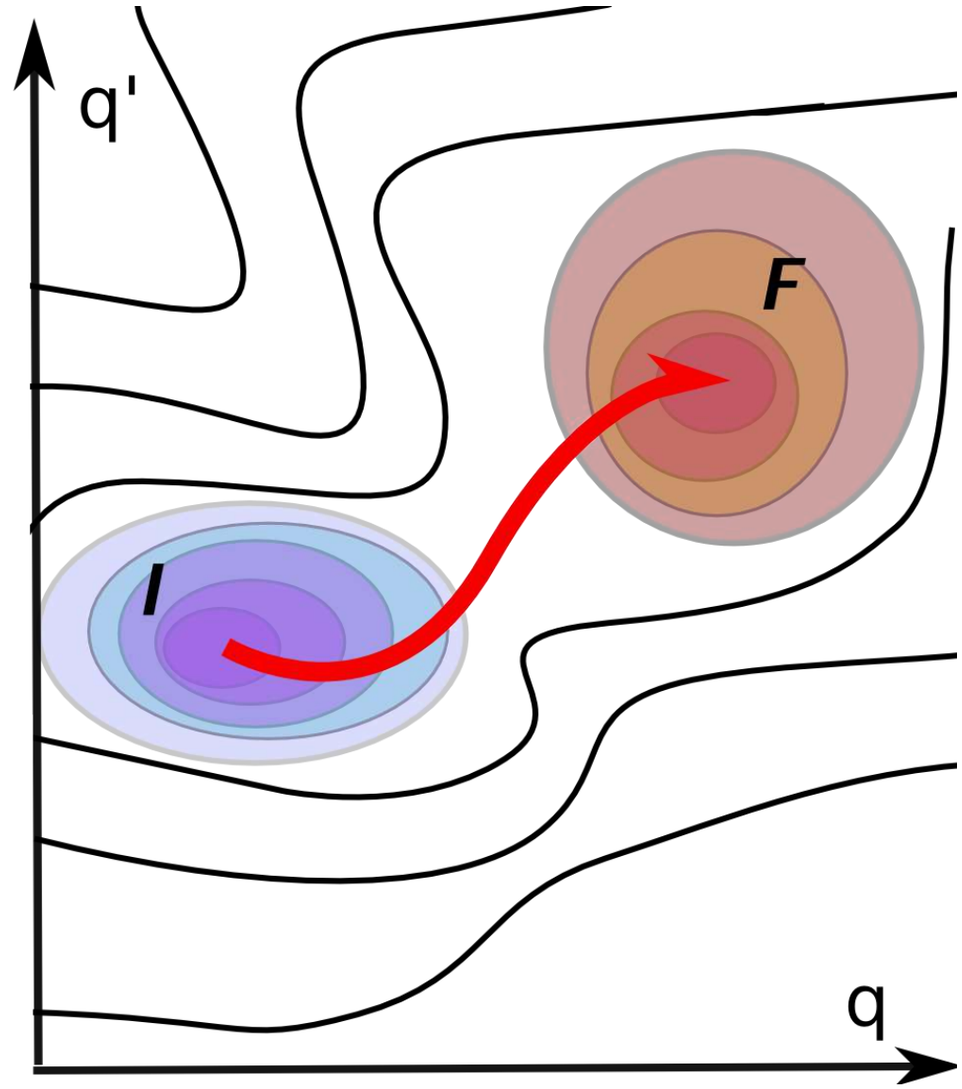
Transition *path*

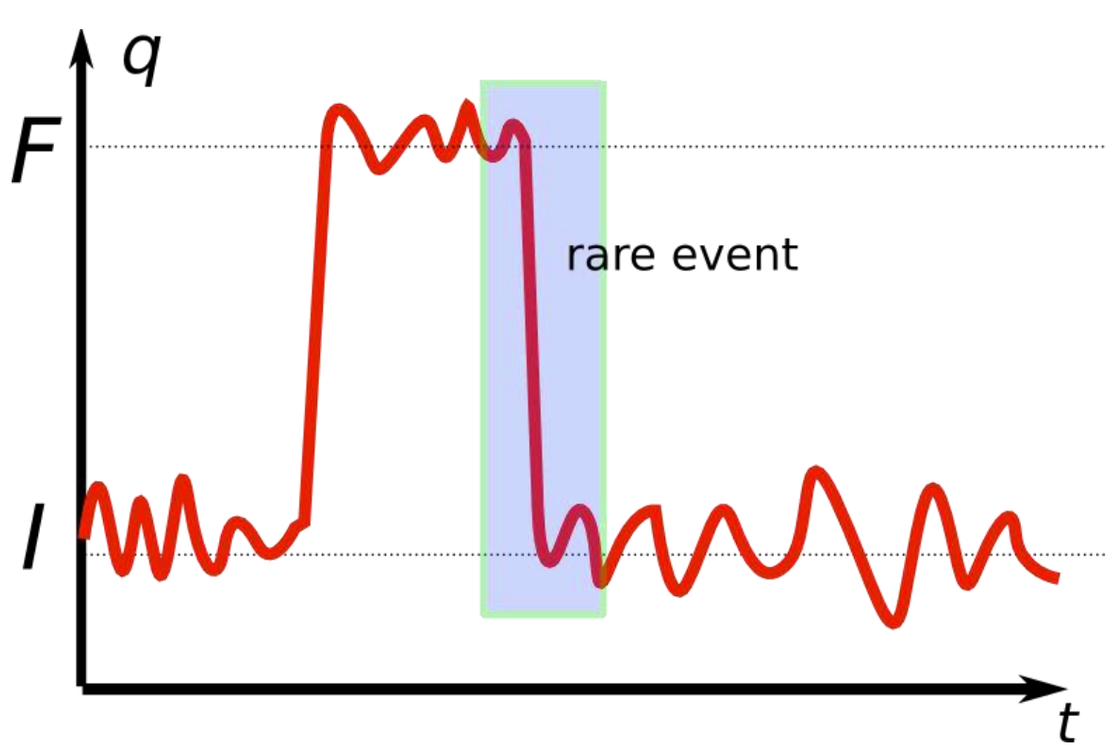
Single Mechanism → saddle point(s)

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

Transition path *ensemble*

TPS focuses entirely on the intermediate region of the process,



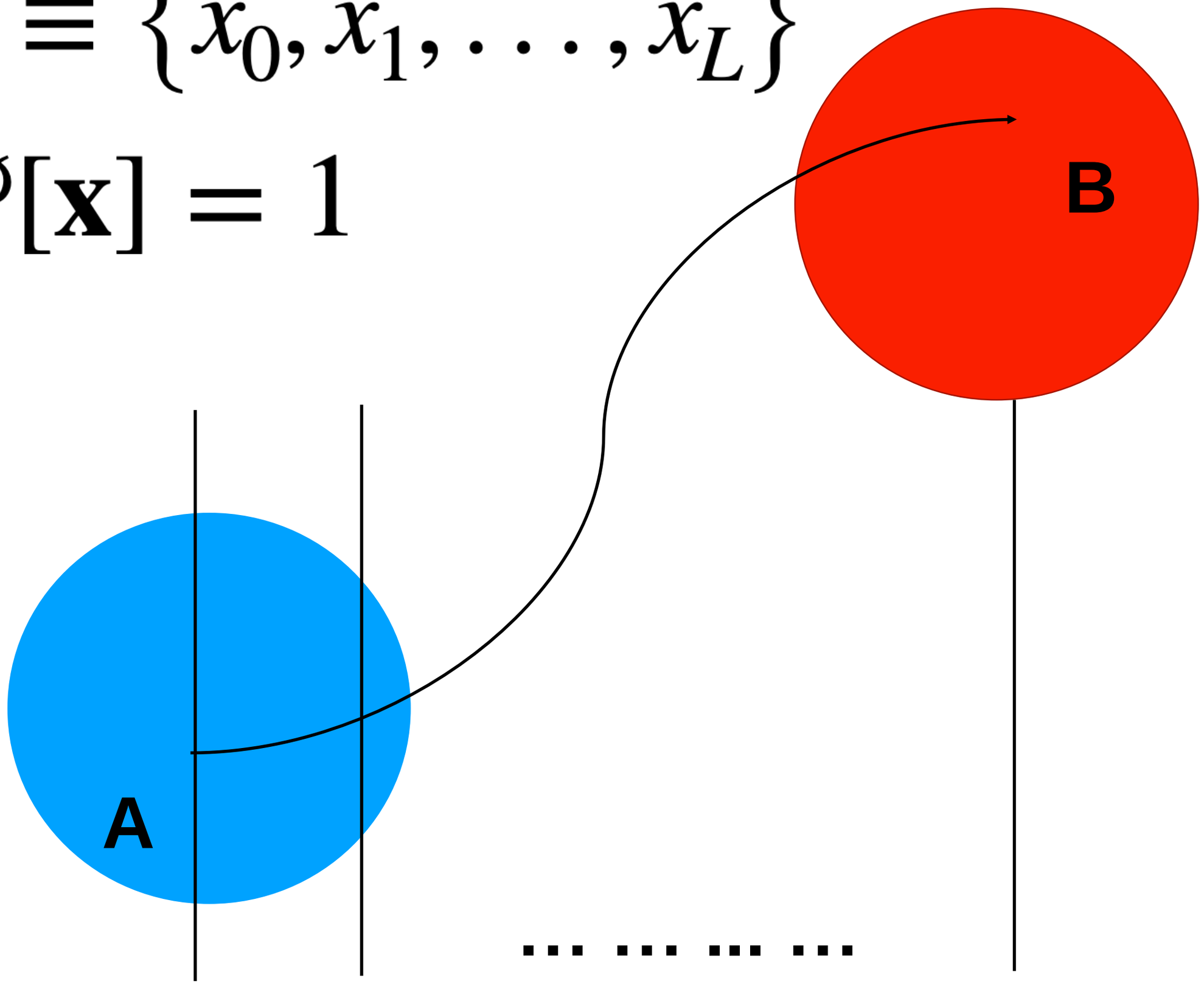


Frequent and slow vs.
Rare and quick

see also: http://statisticalbiophysicsblog.org/?p=115

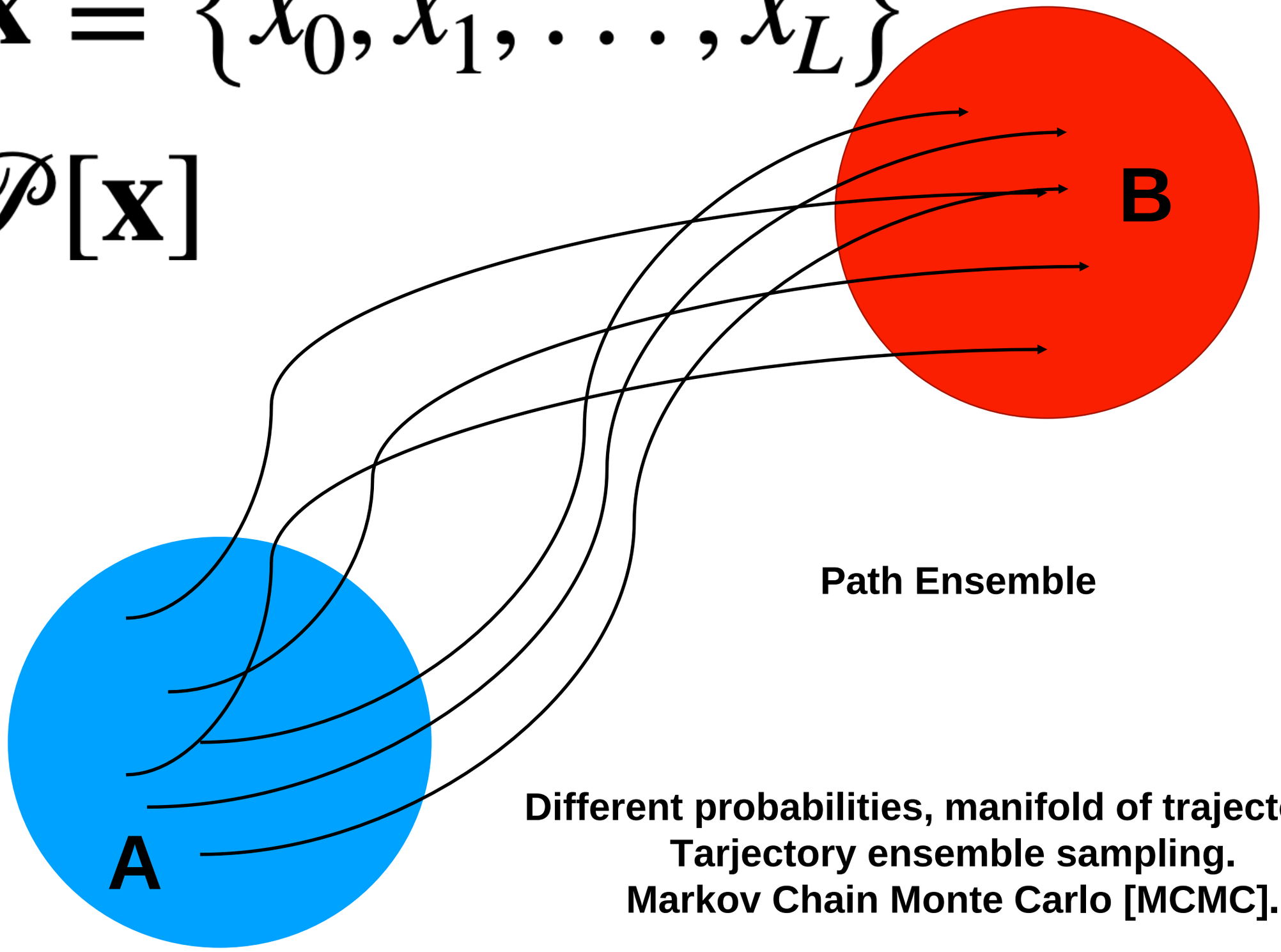
$$\mathbf{x} \equiv \{x_0, x_1, \ldots, x_L\}$$

$$\mathscr{P}[\mathbf{x}] = 1$$



$$\mathbf{x} \equiv \{x_0, x_1, \ldots, x_L\}$$

$$\mathscr{P}[\mathbf{x}]$$



Path Ensemble

Different probabilities, manifold of trajectories.
Tarjectory ensemble sampling.
Markov Chain Monte Carlo [MCMC].

Note: The use of Markov chains authomatically samples trajectory probabilities.

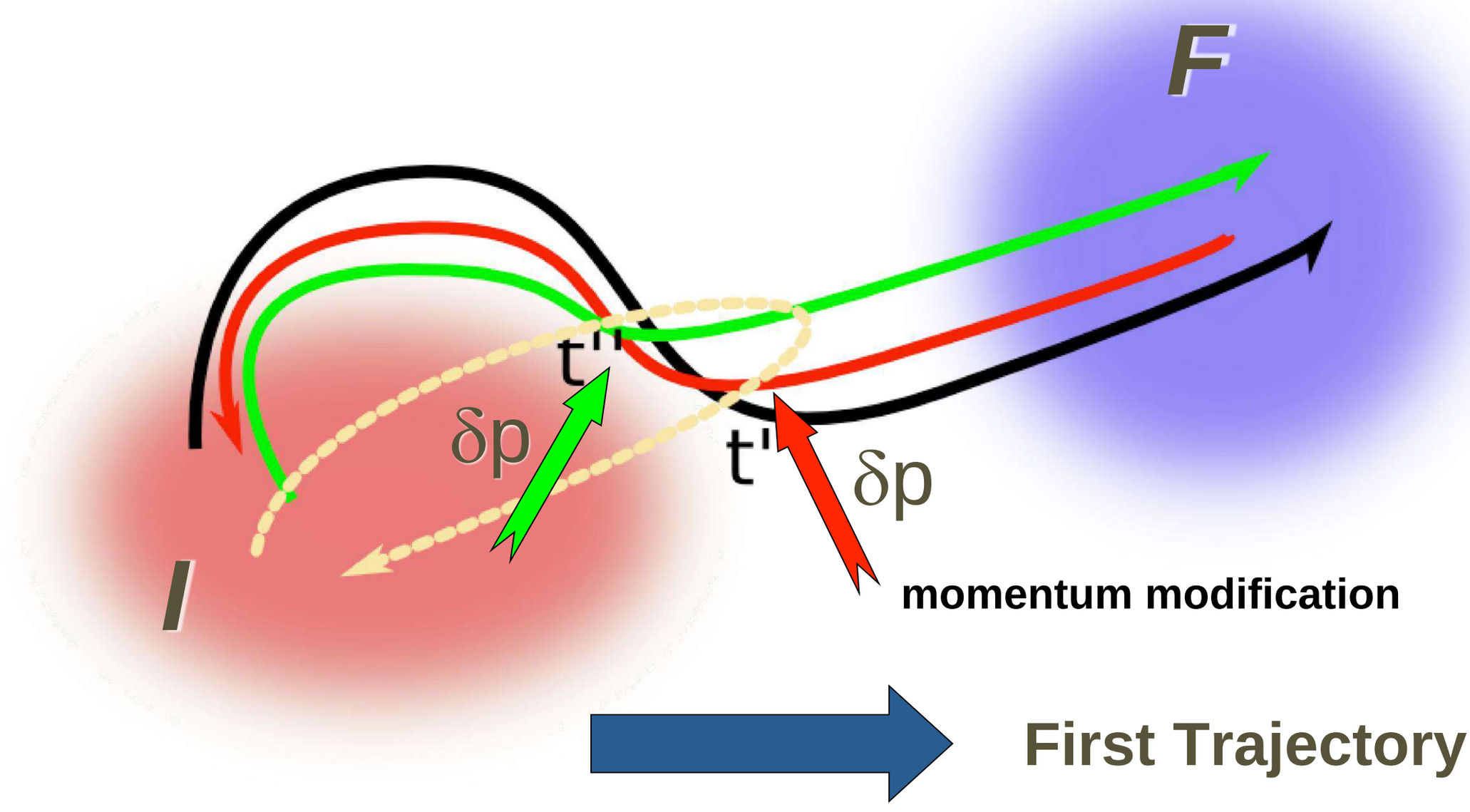
Constrained Path

$$\mathbf{x} \equiv \{x_0, x_1, \ldots, x_L\}$$

$$\mathscr{P}_{AB}[x] \propto \mathbf{1}_A(x_0)\mathbf{1}_B(x_L)\mathscr{P}[x]$$

$\mathscr{P}_{AB}[x]$	**AB Path ensemble**
$\mathbf{1}_A(x_0)$	**Trajectory starts with x_0 in A**
$\mathbf{1}_B(x_L)$	**Trajectory ends with x_L in B**
$\mathscr{P}[x]$	**Equilibrium path probability**

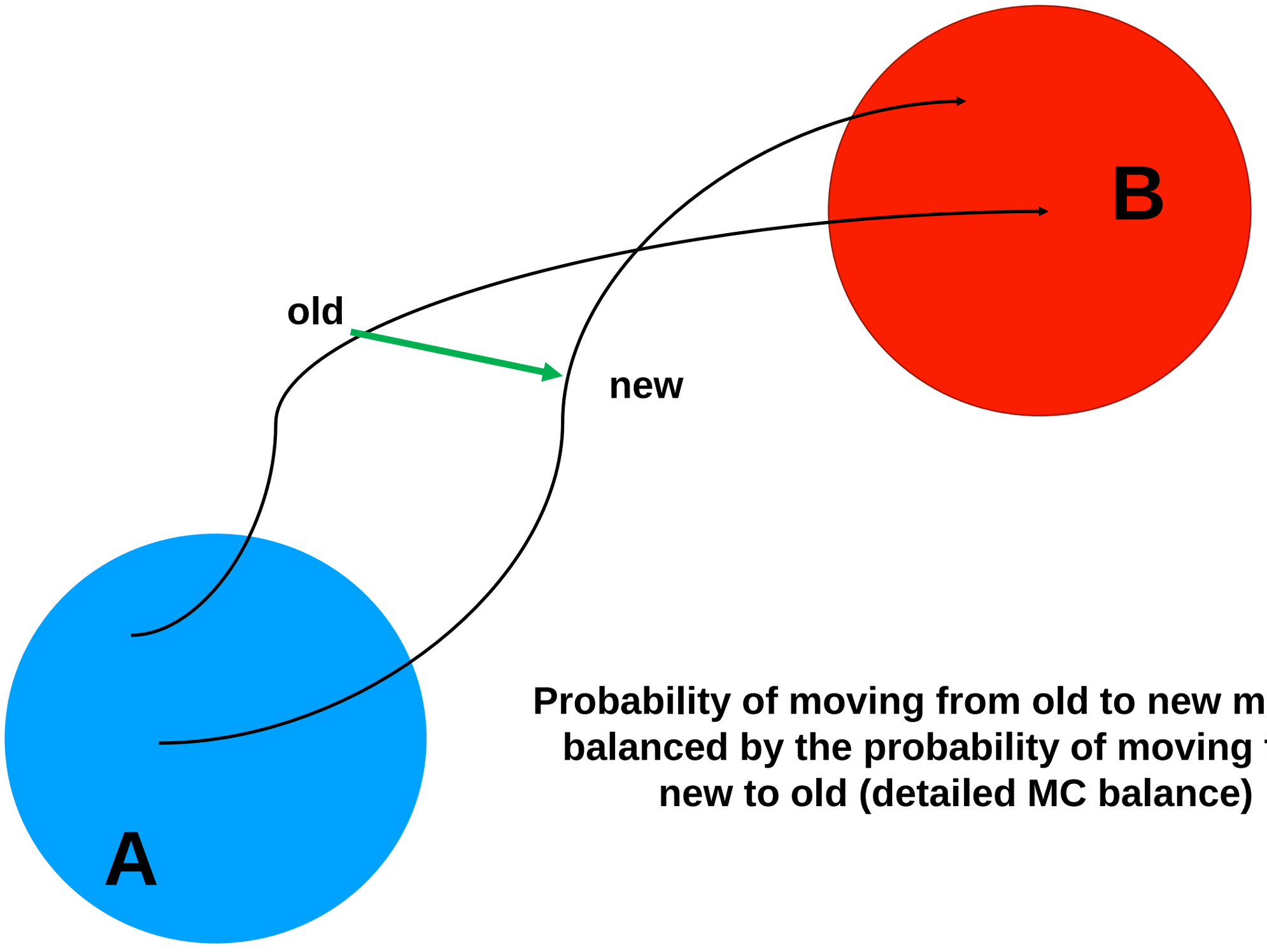
In *practice*, TPS implements a Monte Carlo run in Trajectory Space



„Shooting Algorithm“

based on time reversibility of MD trajectories

Monte Carlo Move



Probability of moving from old to new must be balanced by the probability of moving from new to old (detailed MC balance)

Move Acceptance

$$\mathcal{P}_{acc}[x^{old} \rightarrow x^{new}] = \frac{\mathcal{P}[n]P_{gen}[n \rightarrow o]}{\mathcal{P}[o]P_{gen}[o \rightarrow n]}$$

$$\mathcal{P}_{acc}[x^{old} \rightarrow x^{new}]$$

Unreactive (not AB) → rejected

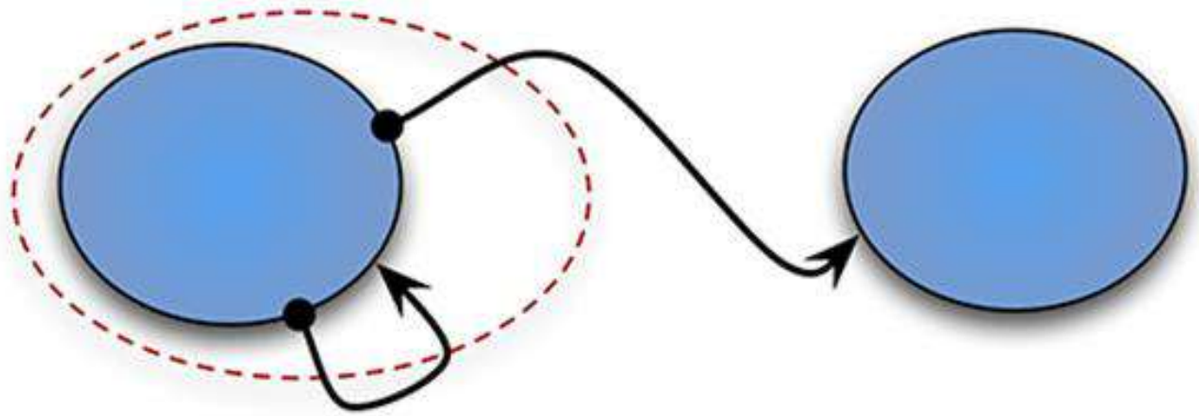
$\mathcal{P}_{acc}$ > 1 → accepted

$\mathcal{P}_{acc}$ <1, accept if $\mathcal{P}_{acc}$ > random number within [0,1] (uniform)

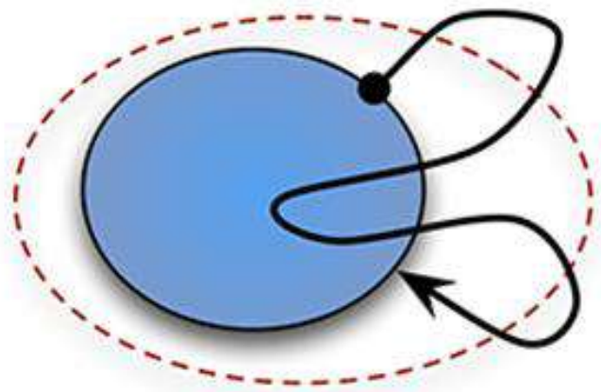
(a) Flexible-length TPS

(b) Fixed-length TPS

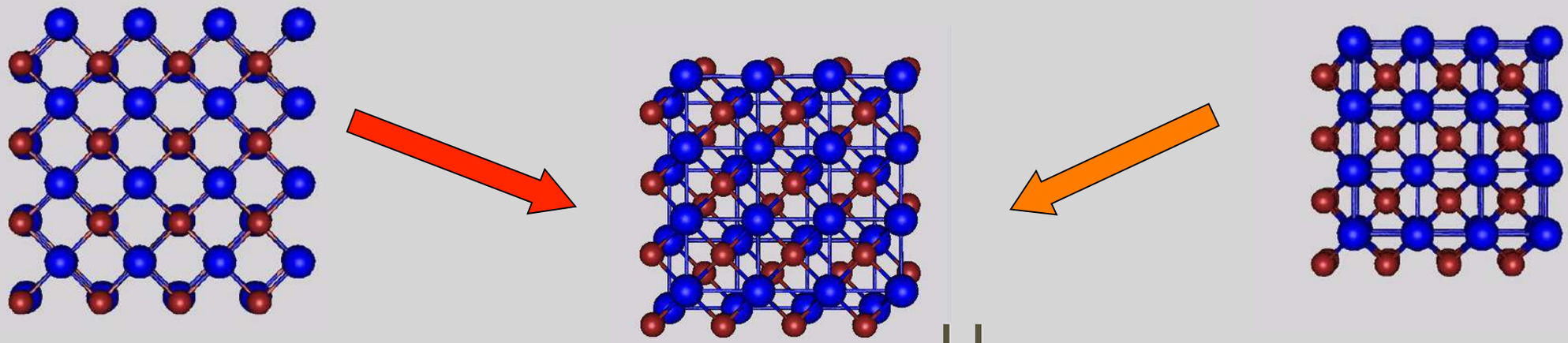
(c) TIS



(d) Minus interface



First Trajectory - direct mapping by means of symmetry groups



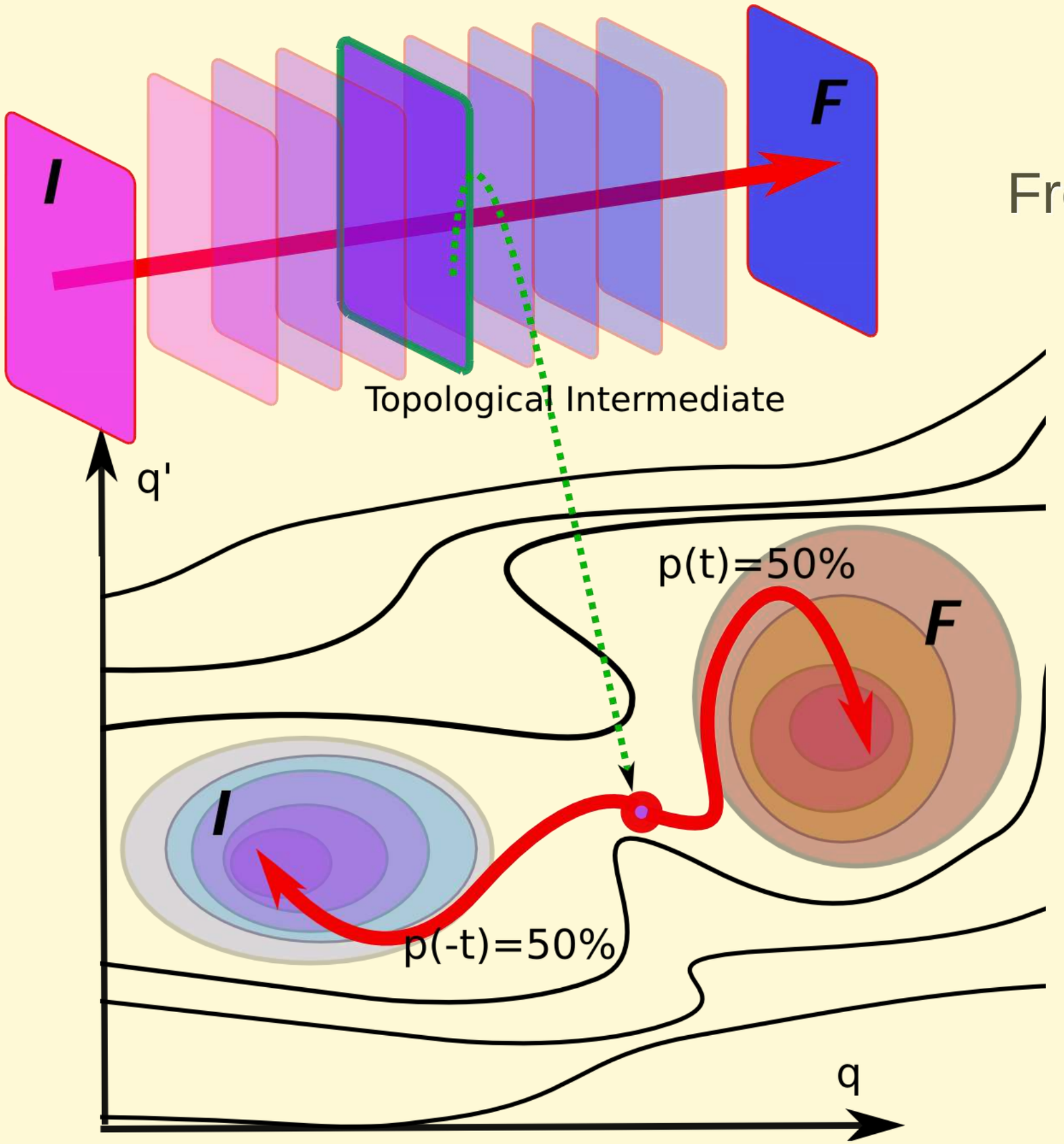
$G_{0,A}$ U $G_{0,B}$

NaCl

#	Space Group Symmetry	Energy (eV)
1	$R\bar{3}m$ (166)	0.077
2	$C2$ (1) (5)	0.91
3	$C2$ (2) (5)	0.90
4	$Cmc2_1$ (36)	2.08
5	$Pmmn$ (59)	0.10
6	$P2/c$ (1) (13)	1.17
7	$P2/c$ (2) (13)	1.04
8	$P2_1/m$ (11)	2.15
9	Pc (7)	0.92
10	$C2/c$ (15)	0.58
11	$P\bar{1}$ (2)	0.40
12	$Iba2$ (45)	1.33

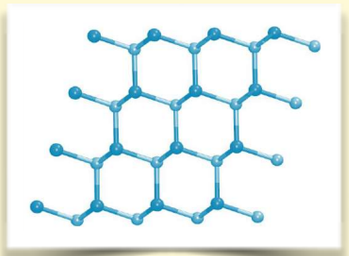
P. Toledano *et al.*, PRB 67, 144106 (2003)

From a **Model**

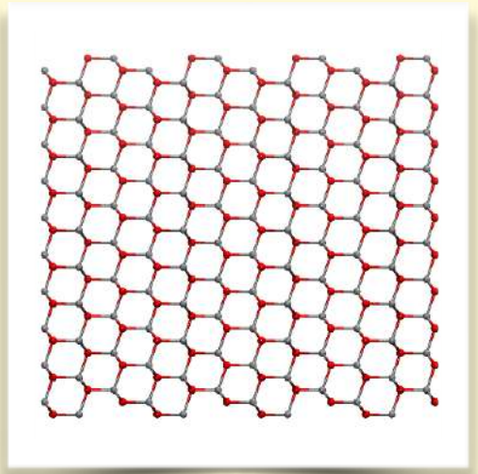


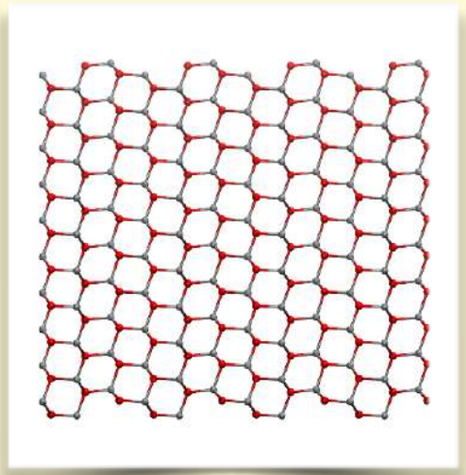
To **MD**

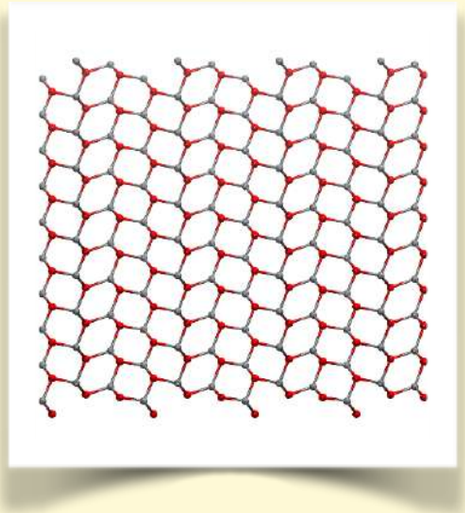
First Trajectory

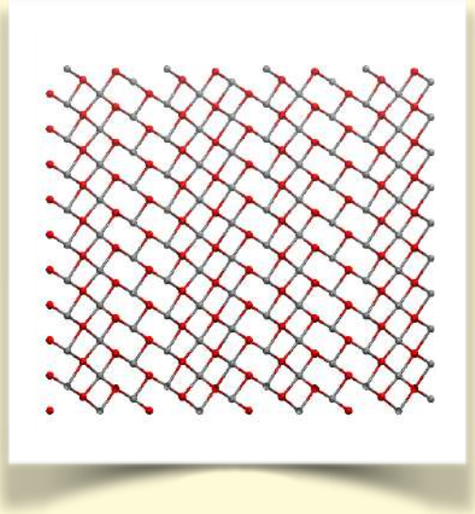


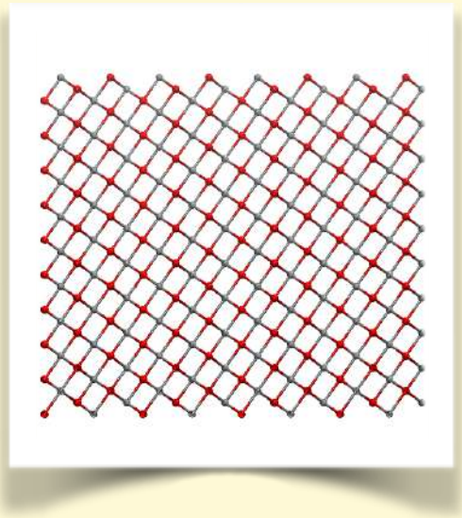
B3

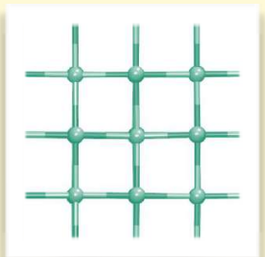








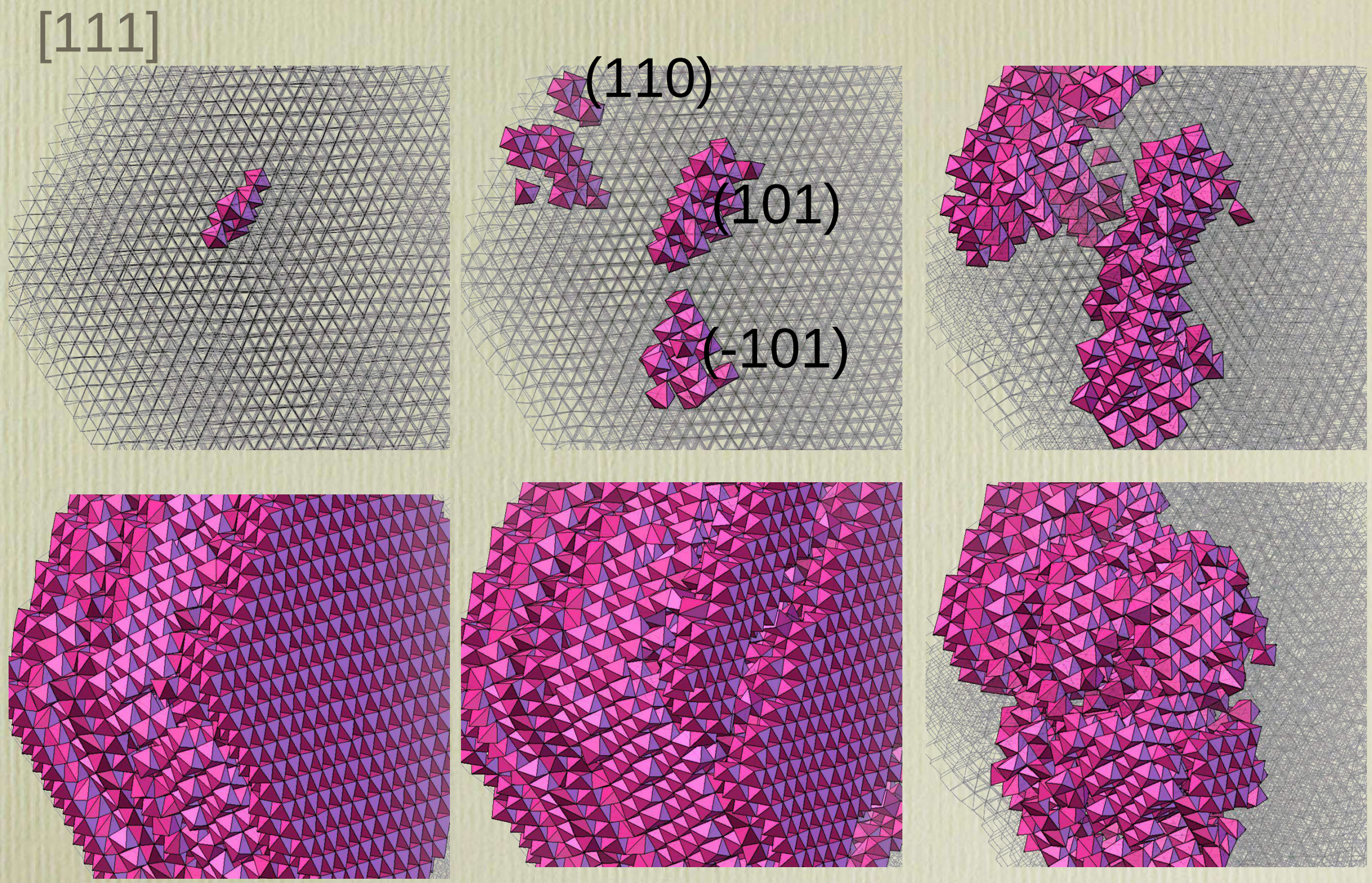




B1

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

A typical nucleation scenario



S. Leoni, R. Ramlau, K. Meier, M. Schmidt, U. Schwarz, PNAS 105, 19612 (2008)
S.Leoni, S. E. Boulfelfel, in “Modern Methods of Crystal Structure Predictions”, Wiley (2011)
S. Leoni, D. Selli, I. Baburin. D. Selli, Chemical Modelling Vol. 11, RCS Books (2015).
S. Jobbins, S.E. Boulfelfel, S. Leoni, Faraday Discussions (2018)

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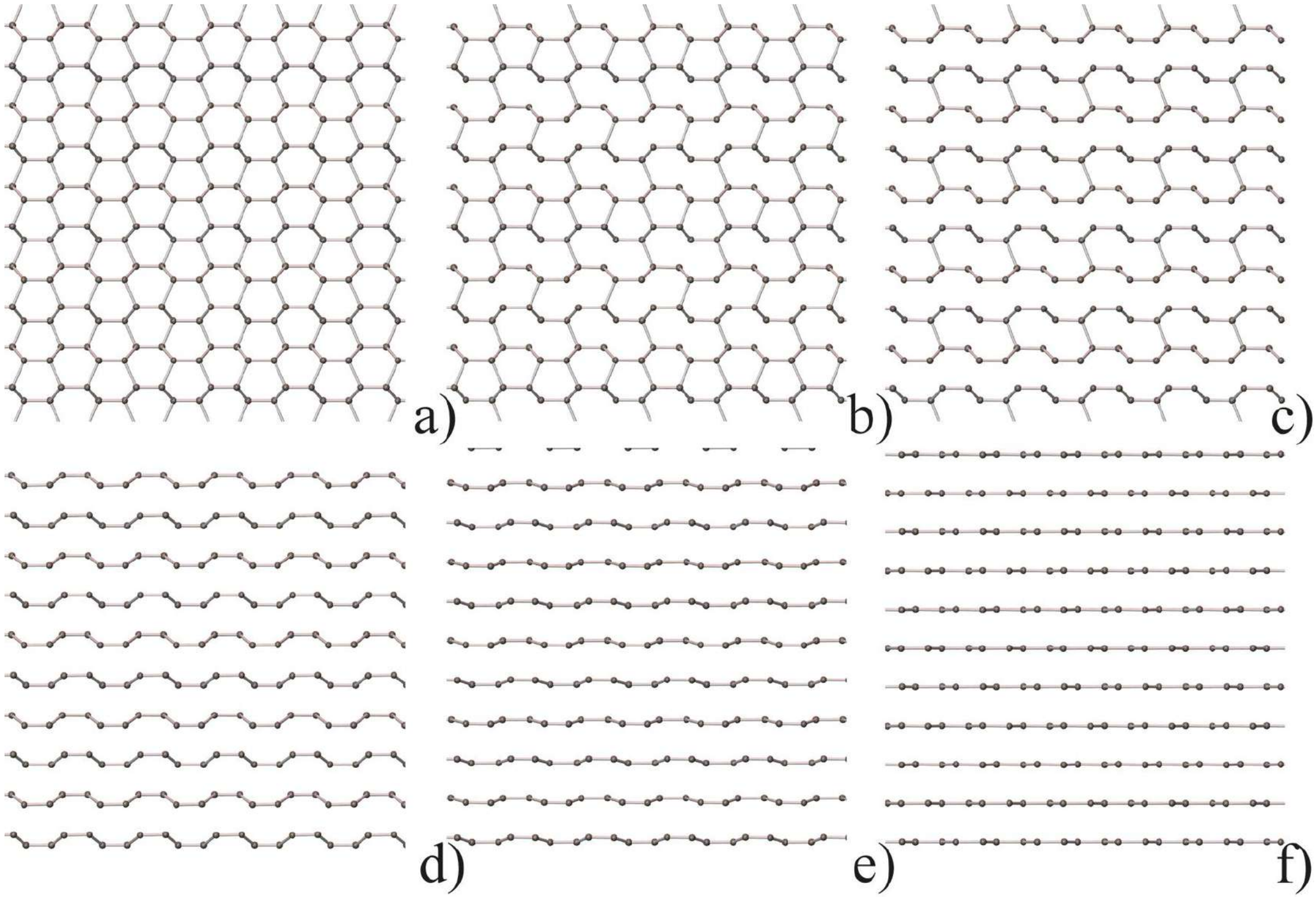
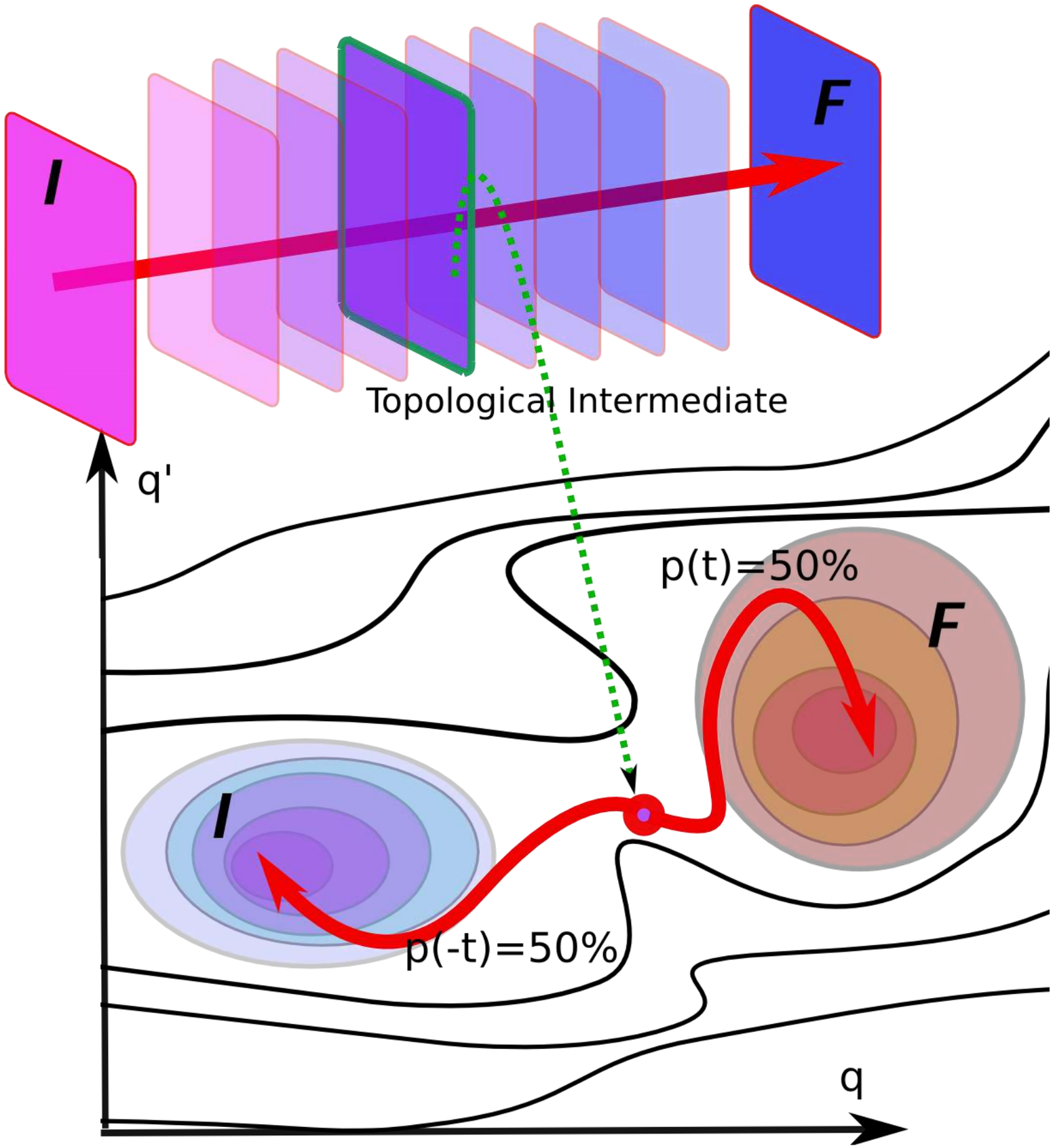
The role of Models

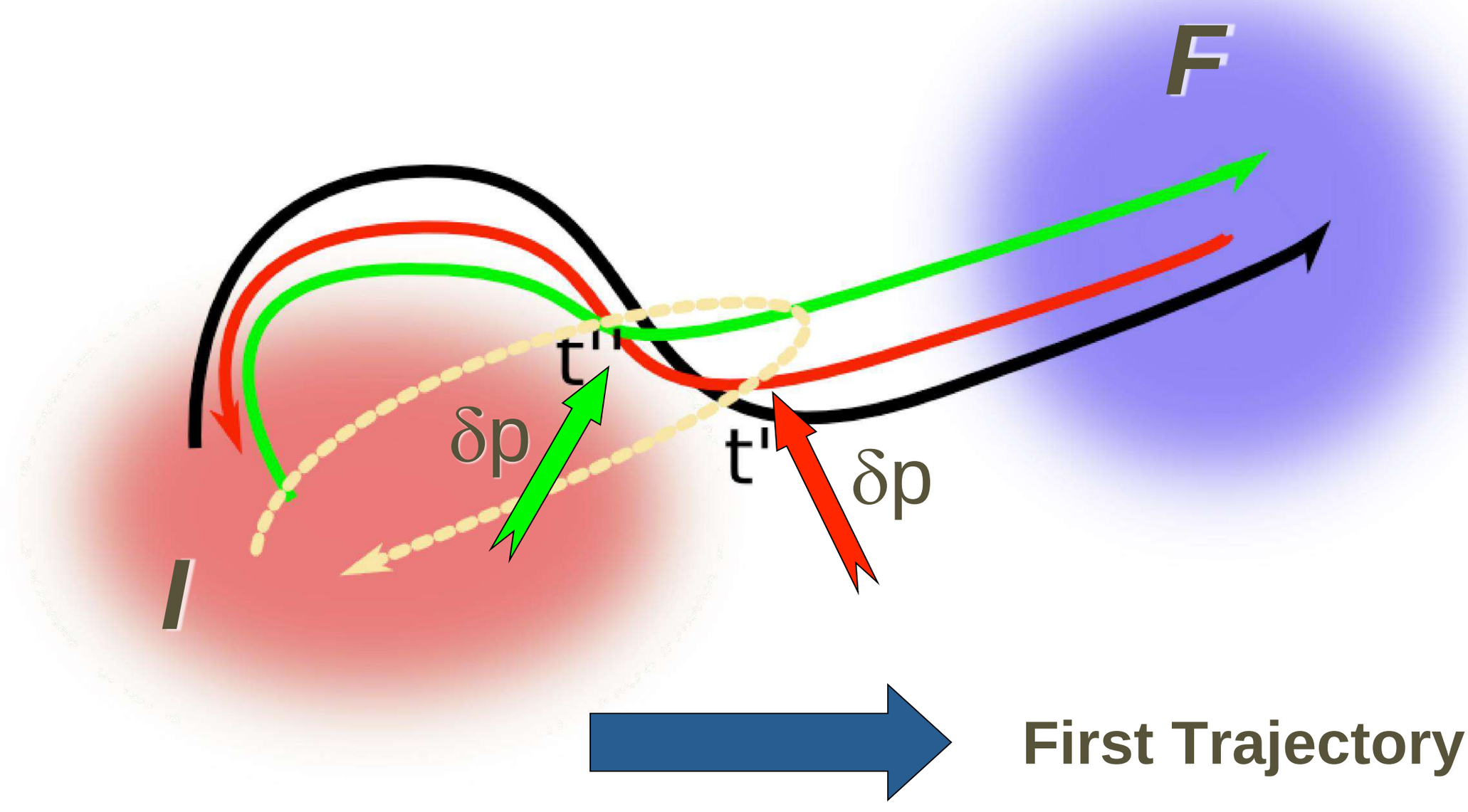


Topology



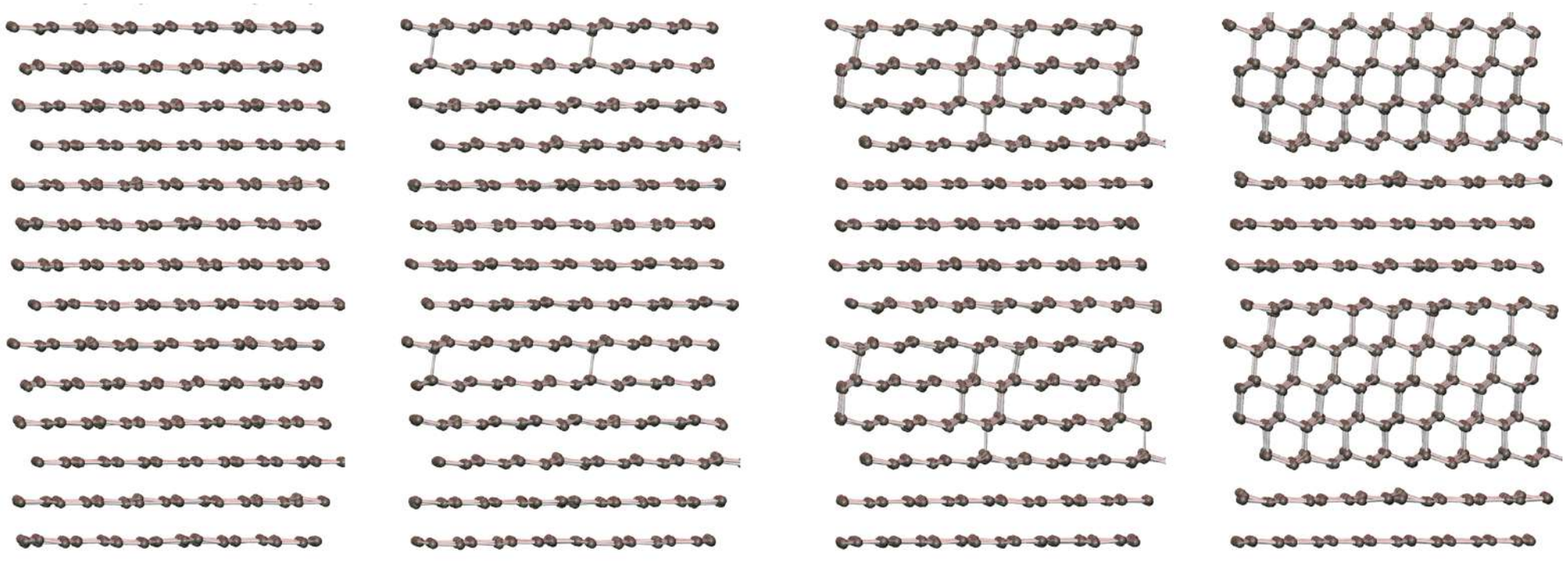
MD

Monte Carlo in Trajectory Space



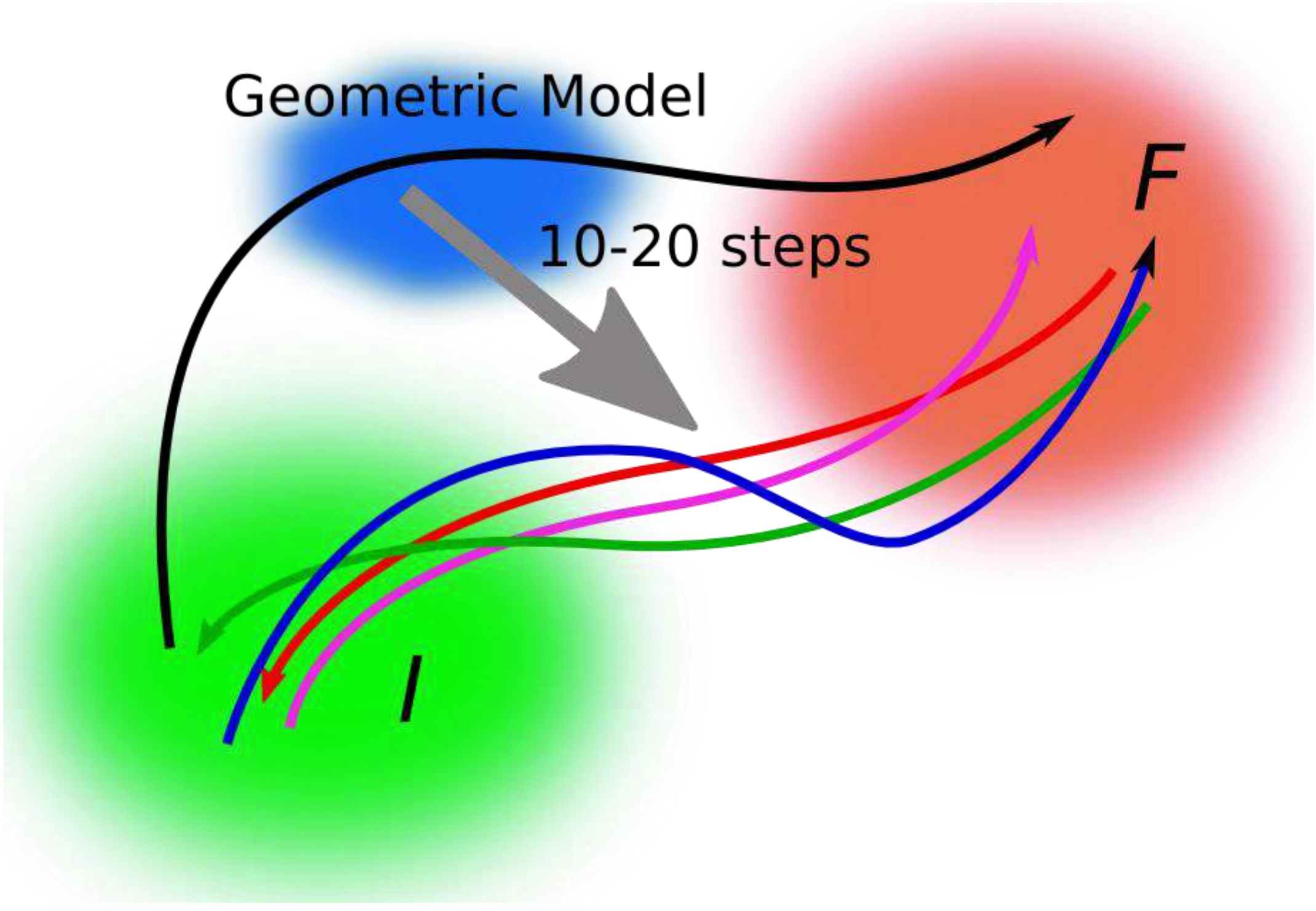
„Shooting Algorithm“ (C. Dellago, D. Chandler)

Initial Steps and Time Evolution

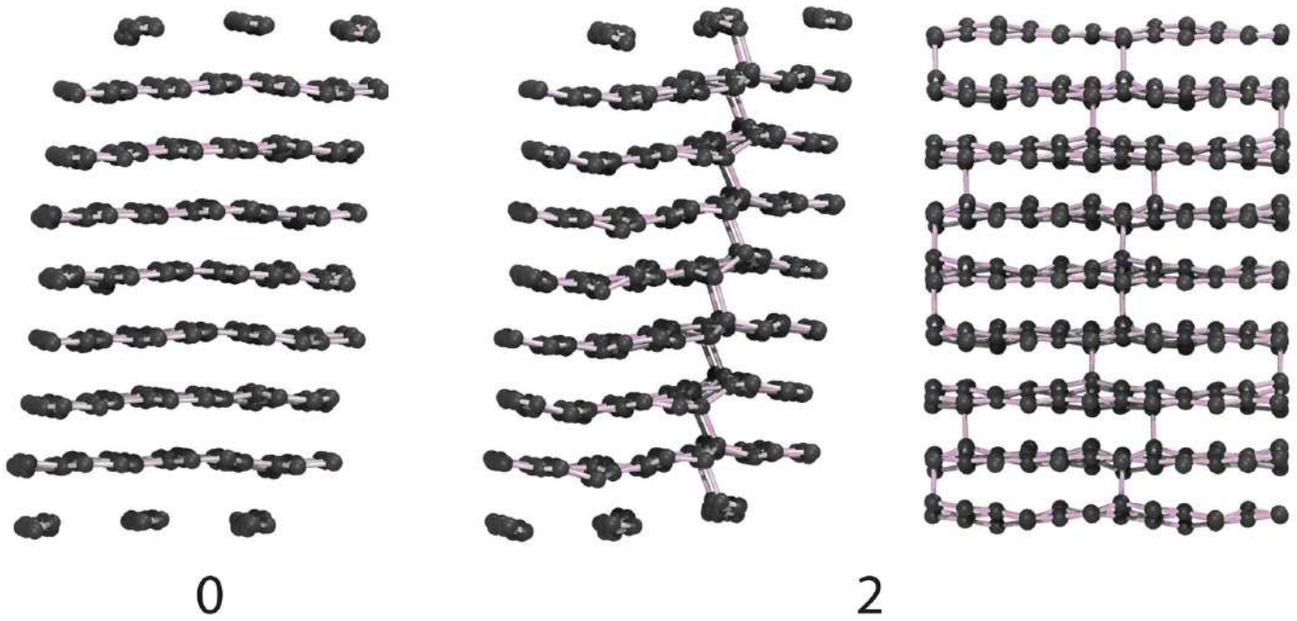


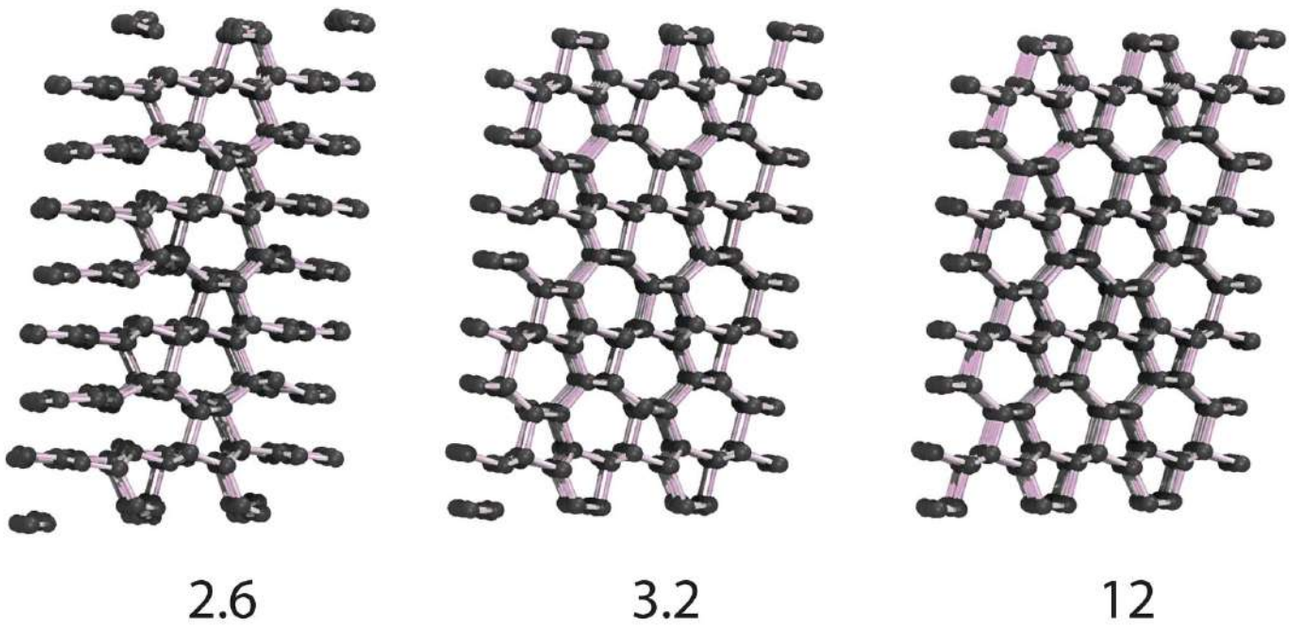
System Response on lowering temperature

Trajectory Regime Evolution



What you end up whit…

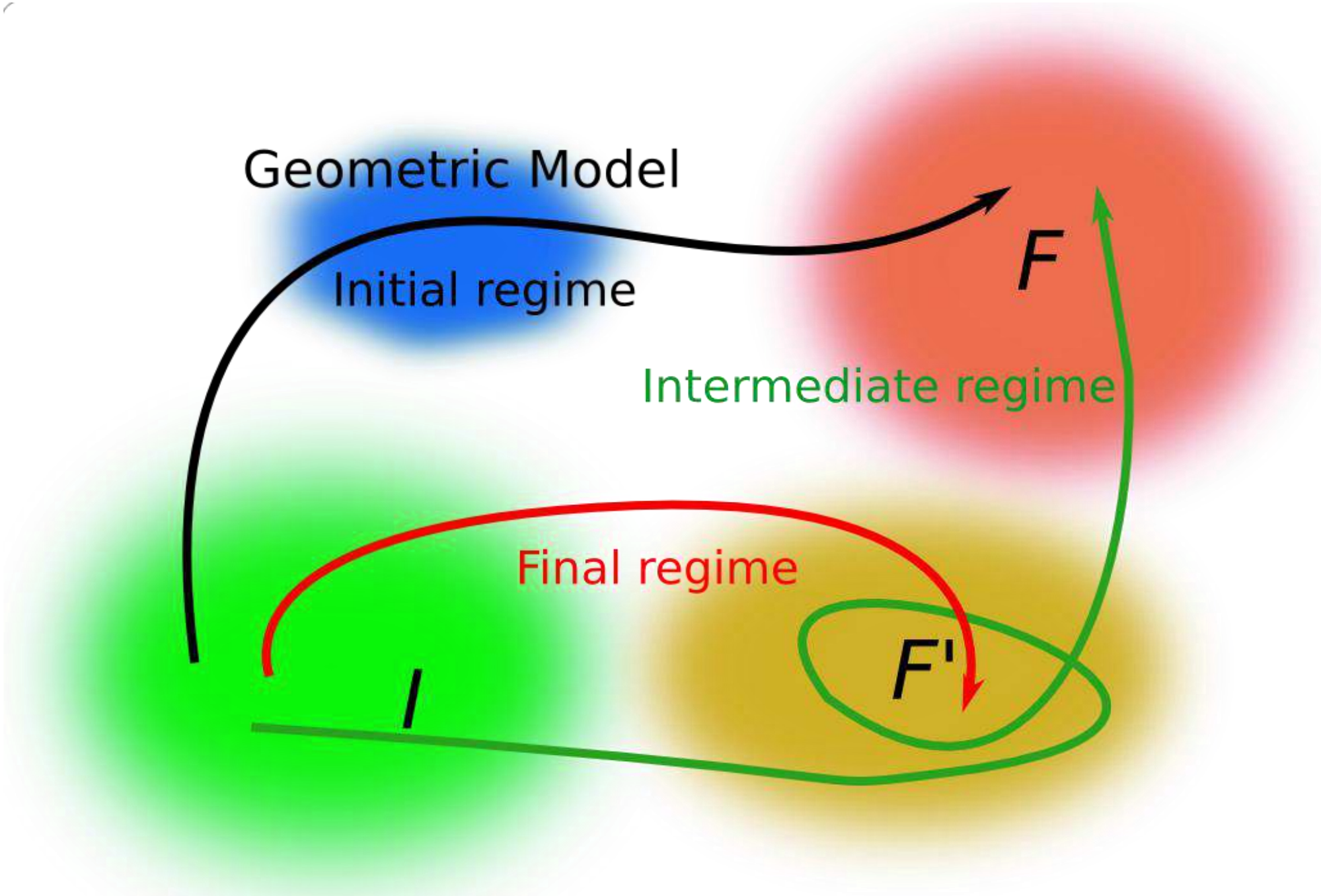




Final regime is distinct from the initial guess
Trajectories are neither pinned nor constrained, so longer transformation times can be expected.

In this case, layer interconnections after compression, followed by formation of odd rings is a characteristic pattern of this low temperature process

Trajectory Regime

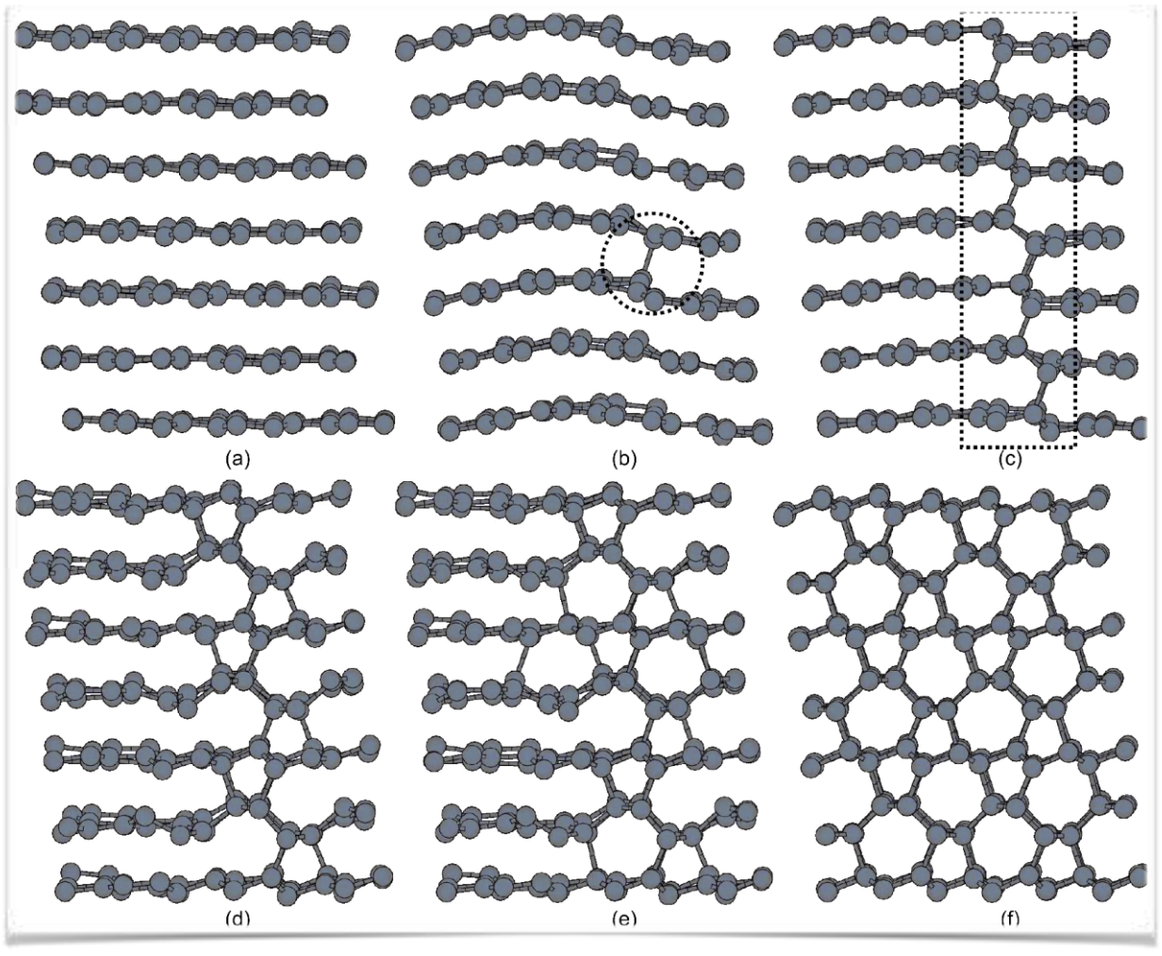


Final Product may be different - “structure prediction” from the correct mechanism!

M & W Carbons

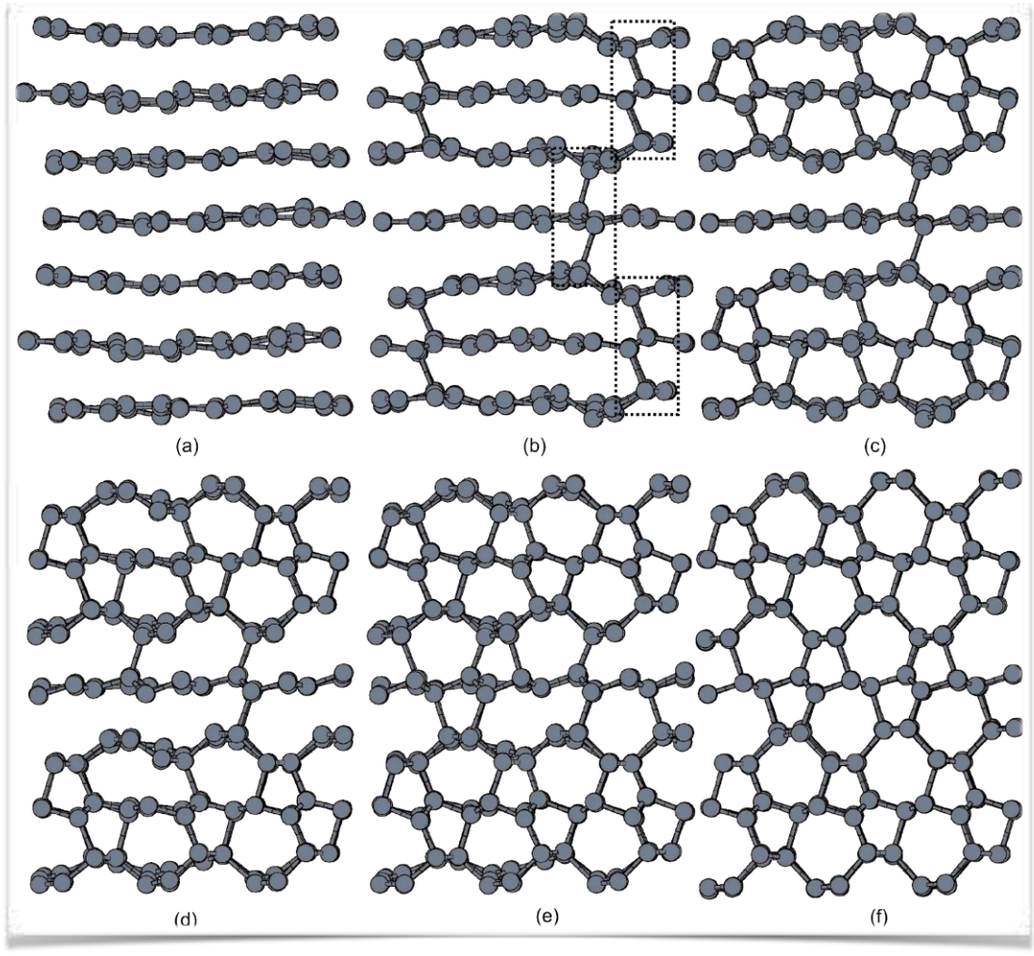
Probable

M



Less Probable

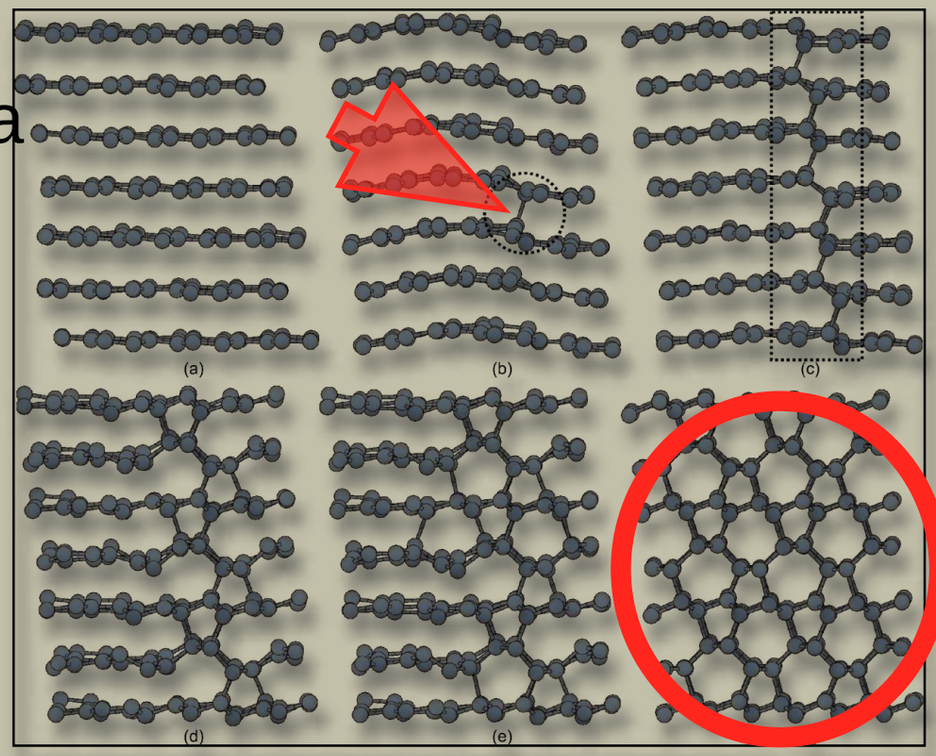
W



Distinct Nucleation History
(Competing Mechanisms - A Free Lunch ?)

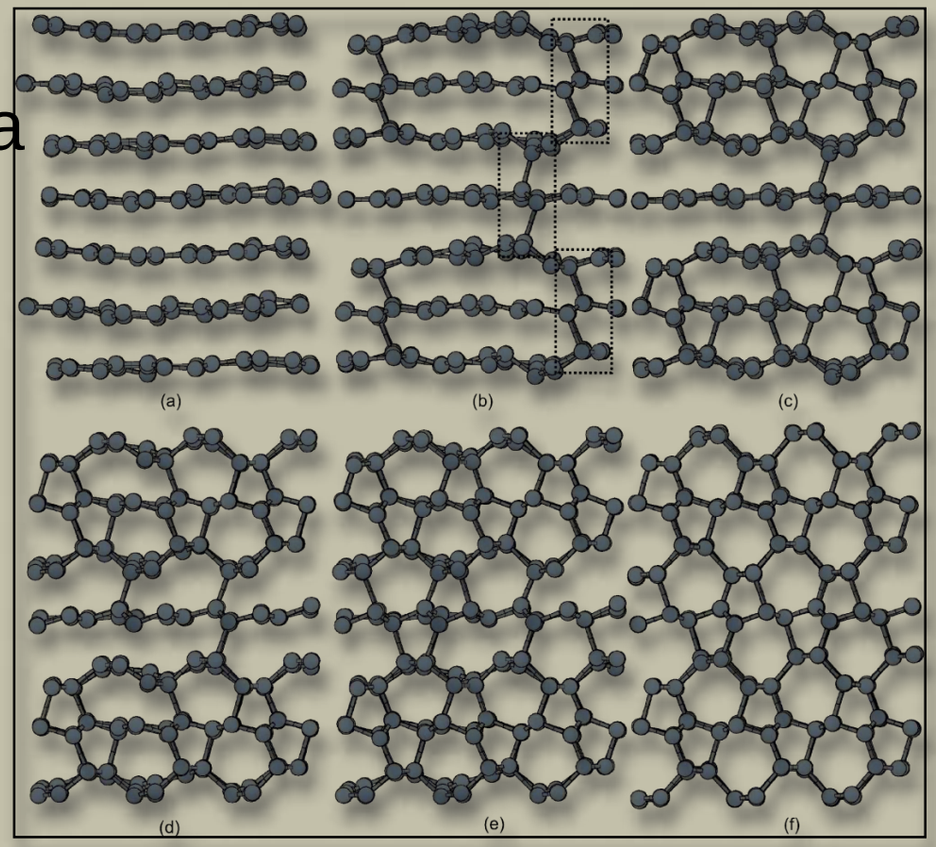
S. E. Boulfelfel, A. Oganov, S. Leoni, Scientific Reports, 2 (2012)

Gra

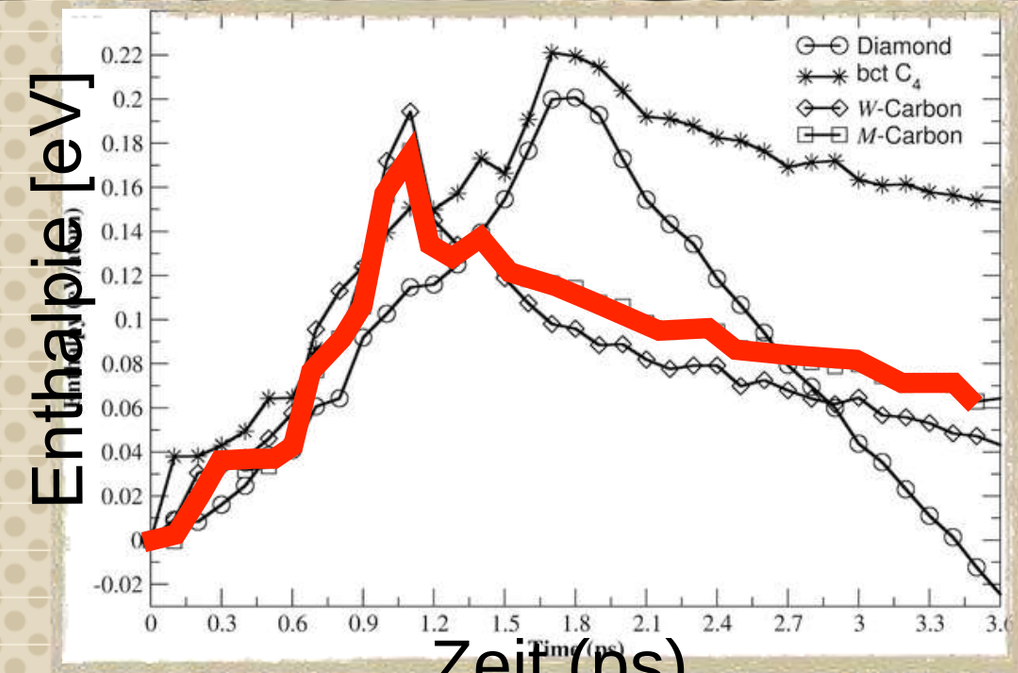


M

Gra



W



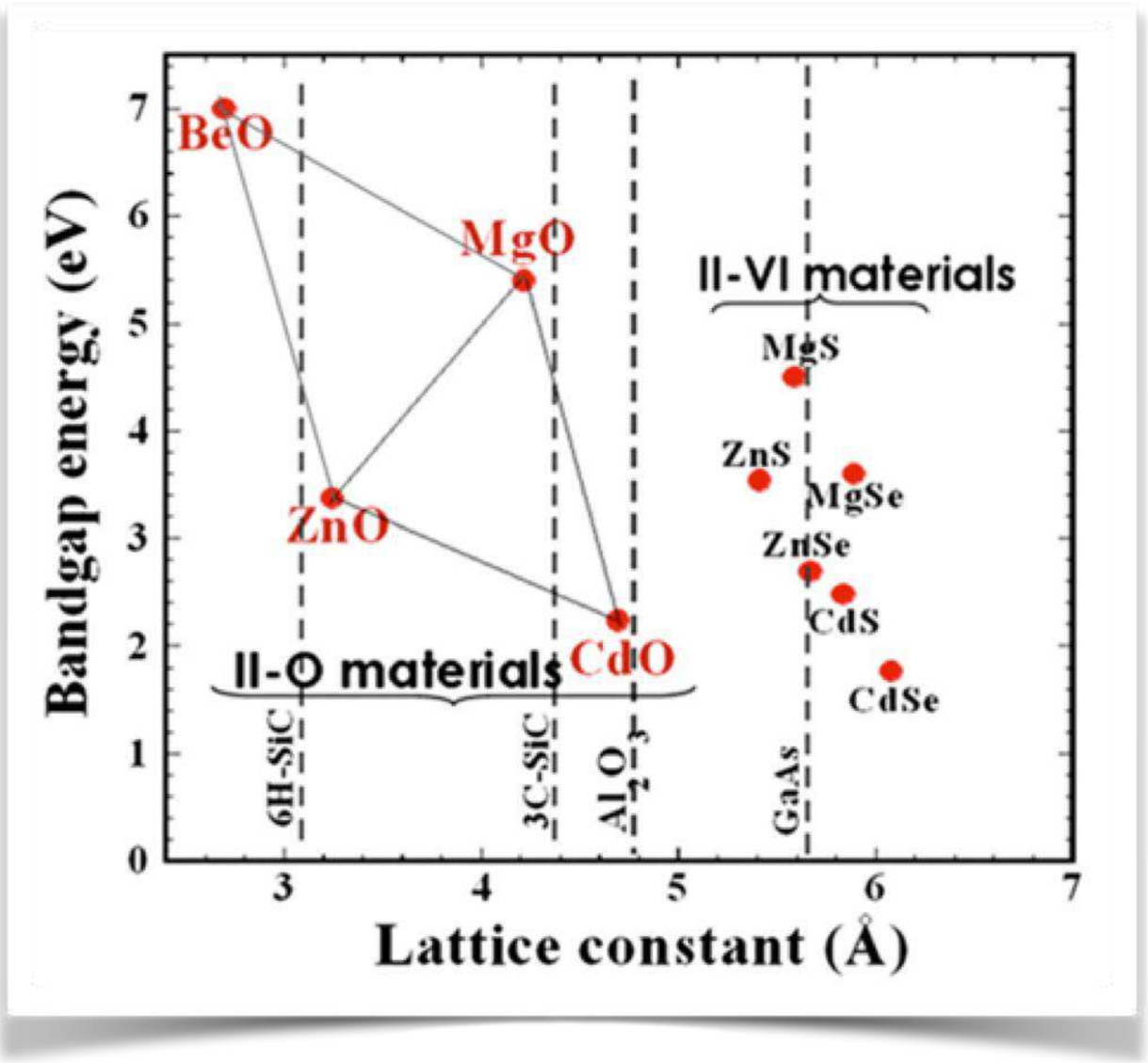
Nucleation History

Overall lower activation energy (Enthalpy)

Transition Path Sampling (TPS)

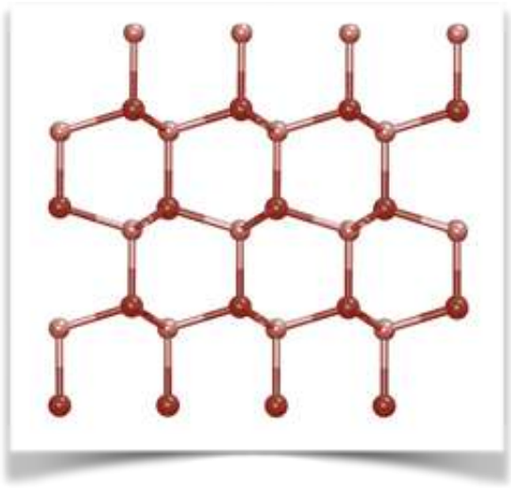
ZnO

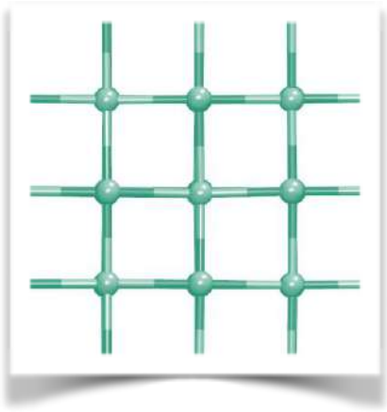
- Binary oxide, small lattice constant (d shell)
- Wurtzite normal state, zincblende metastable, transformation to B1 (rocksalt) under pressure



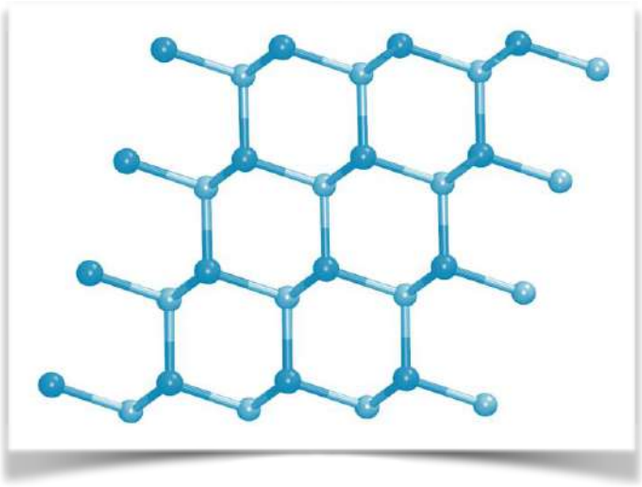
Zinc Oxide (ZnO)

B4





B1



B3

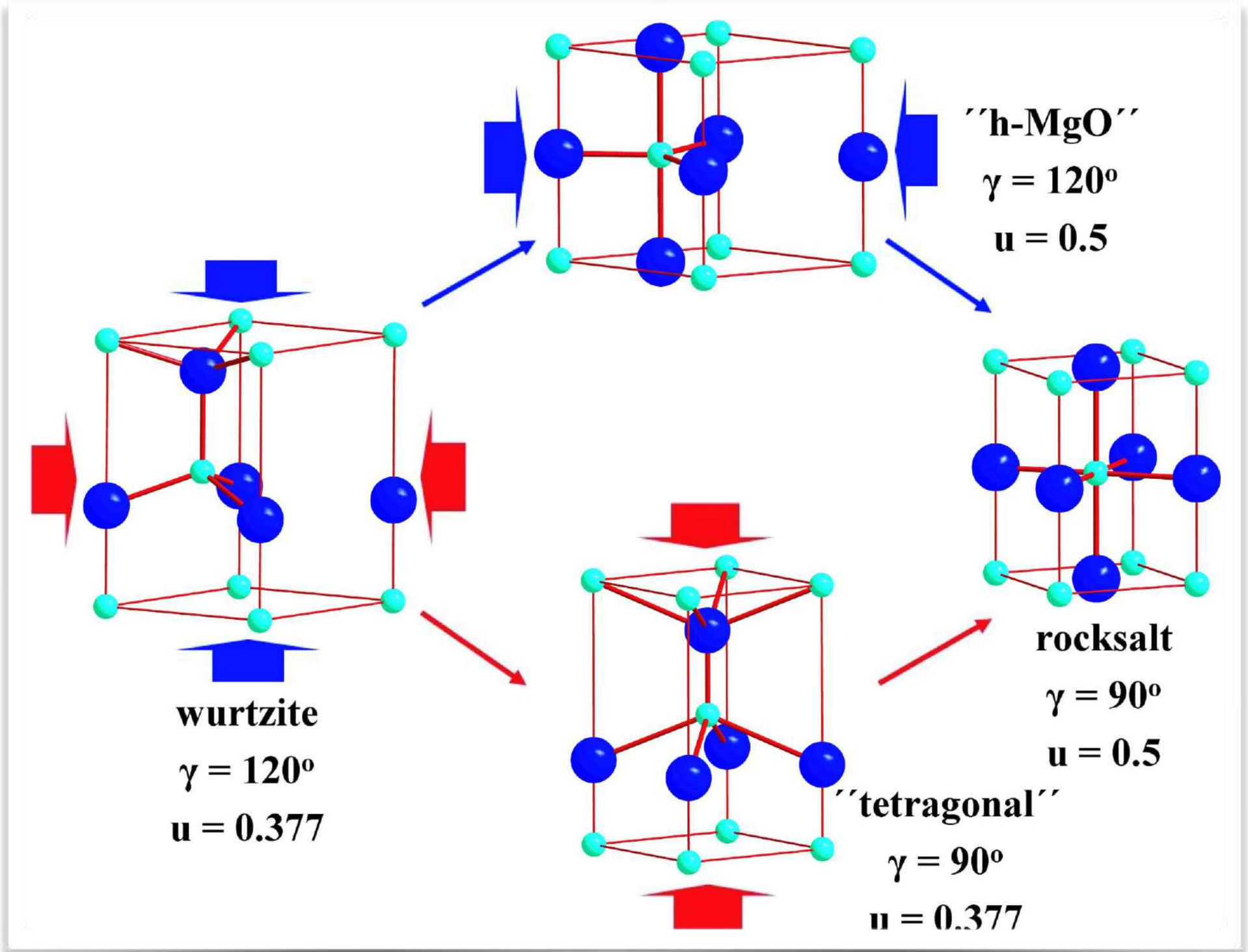
Hexagonal **wurtzite** (WZ, B4, $P6_3mc$) structure under ambient conditions

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

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

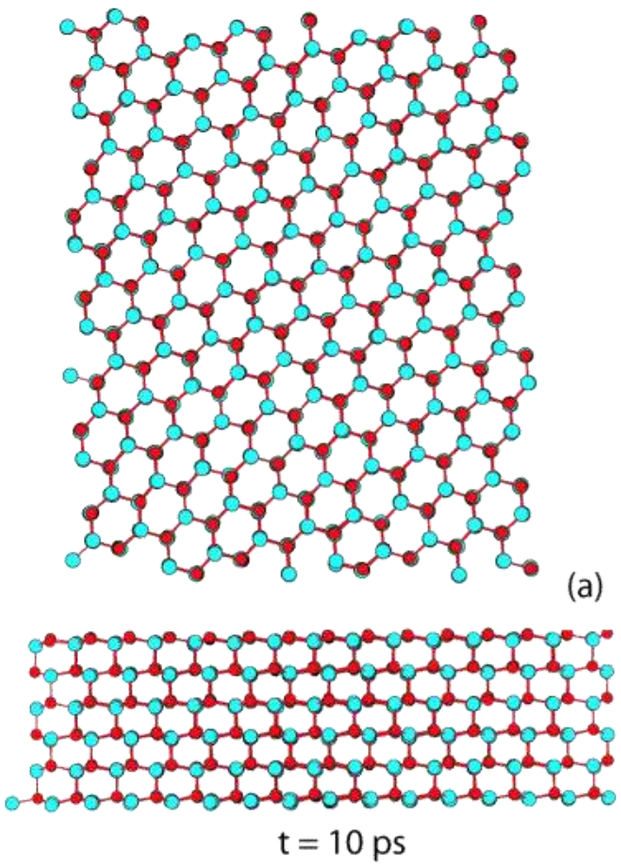
Intermediate Competition

GaN
ZnO



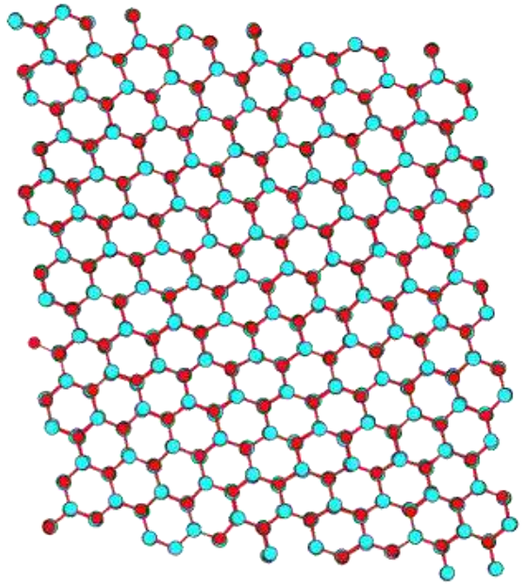
A. M. Saitta and F. Decremps, PRB 70, 035214 (2004).
S. E. Boulfelfell, S. Leoni, PRB 78, 125204 (2008)

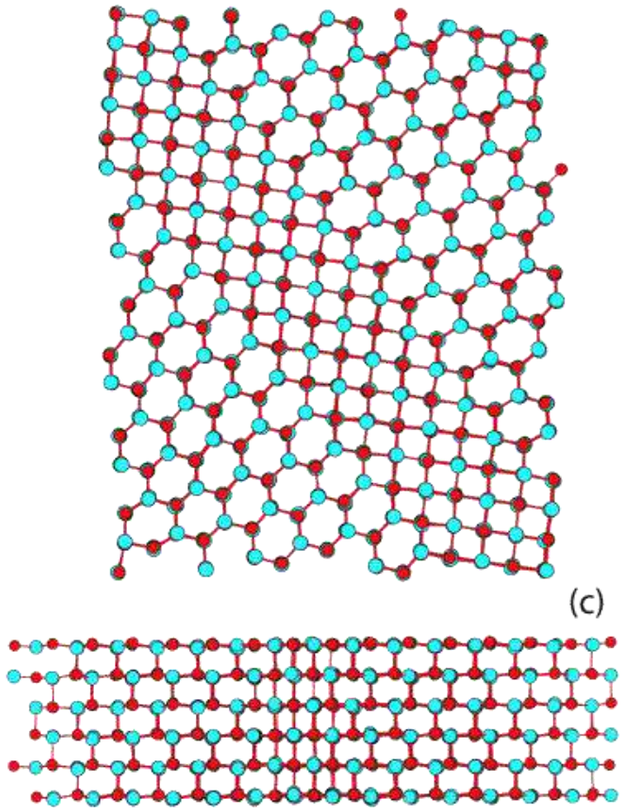
ZnO: Competing Intermediates



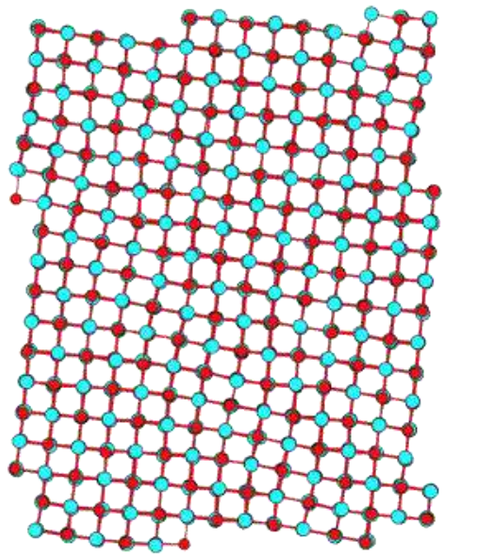
B4

iH





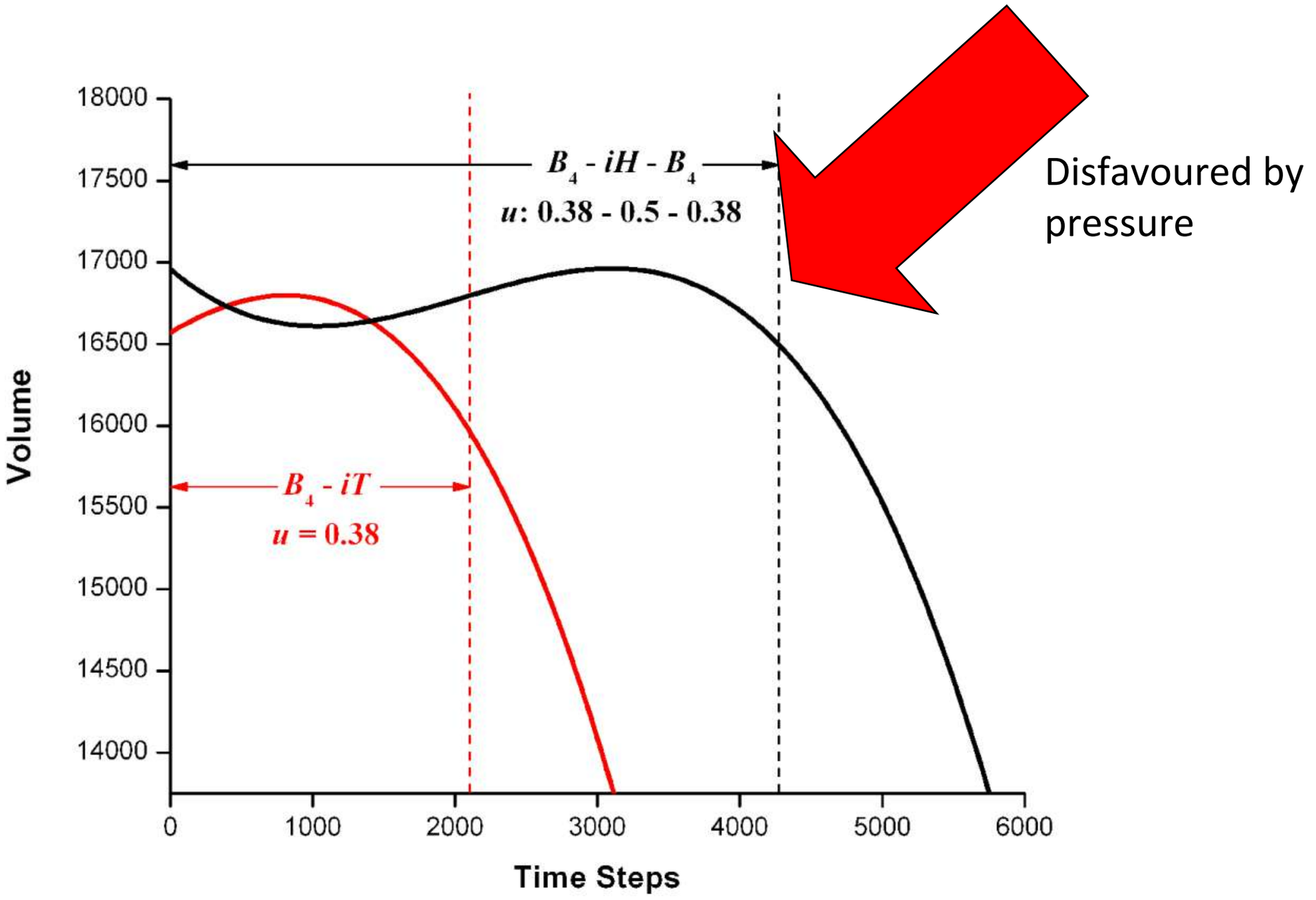
B1



long lived intermediate

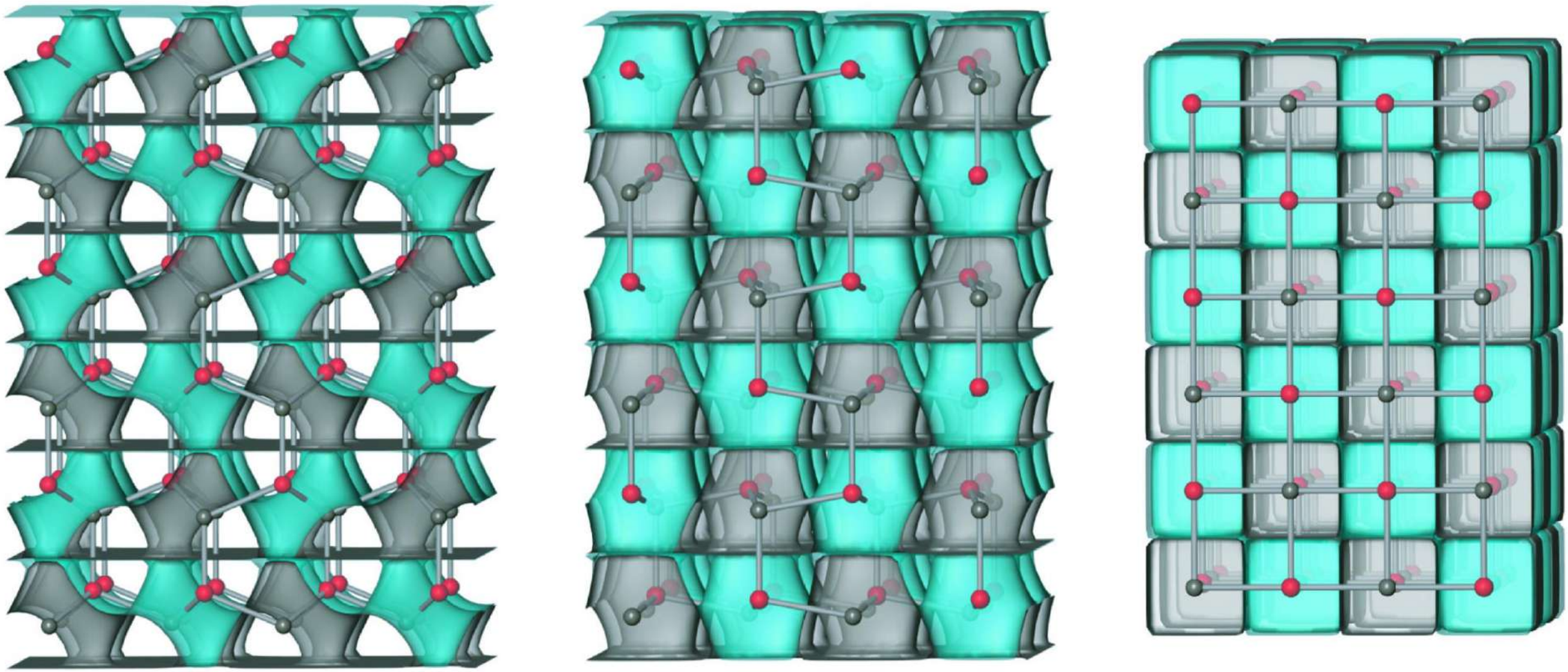
S. E. Boulfelfell, S. Leoni, PRB 78, 125204 (2008)

Effect/role of pressure



Disfavoured by pressure

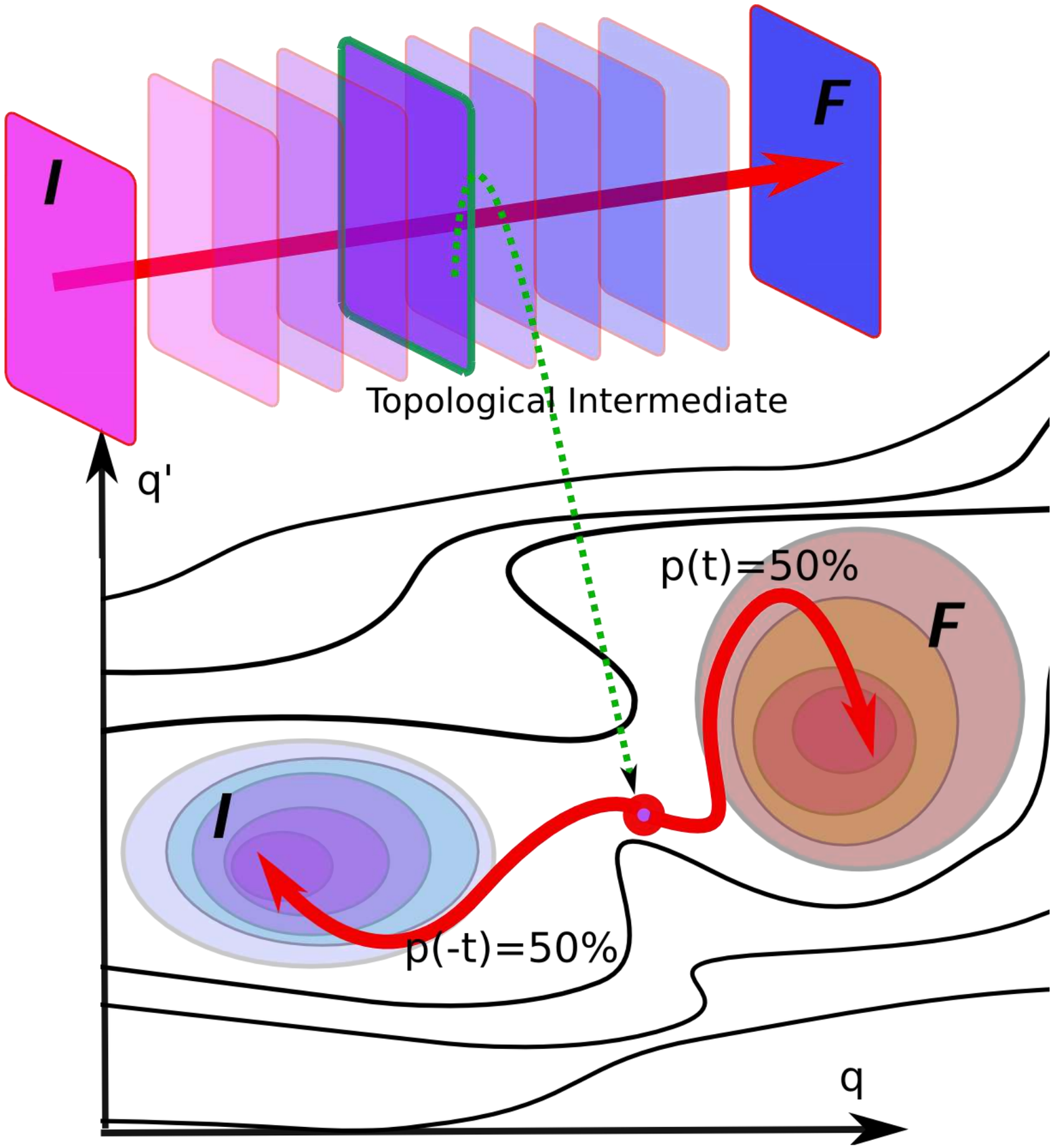
B4 to B1 Phase Transition



(wurtzite) *Topological Intermediate* (rocksalt)

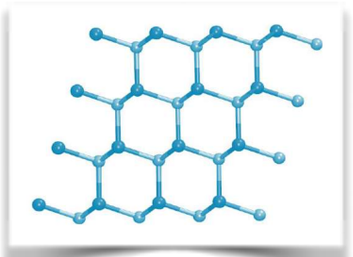
B4 → **B1**

Topology

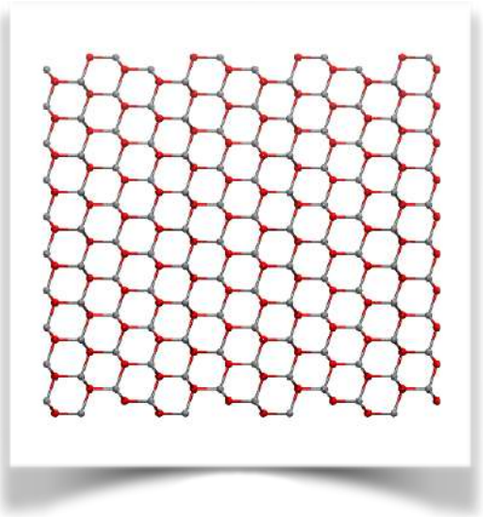


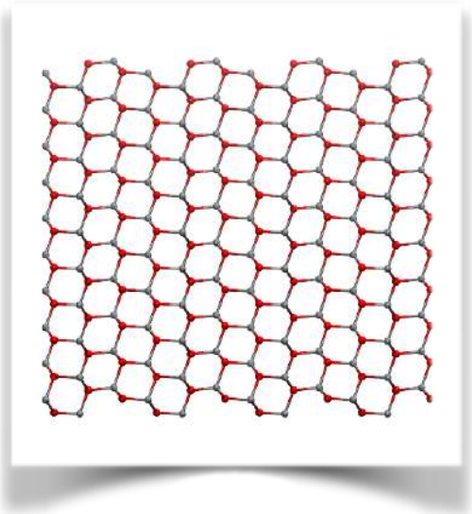
MD

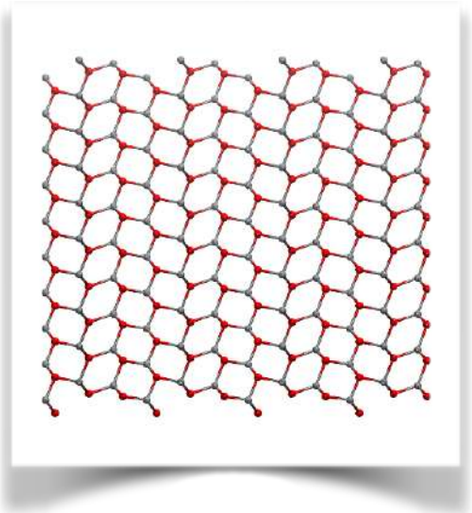
First Trajectory

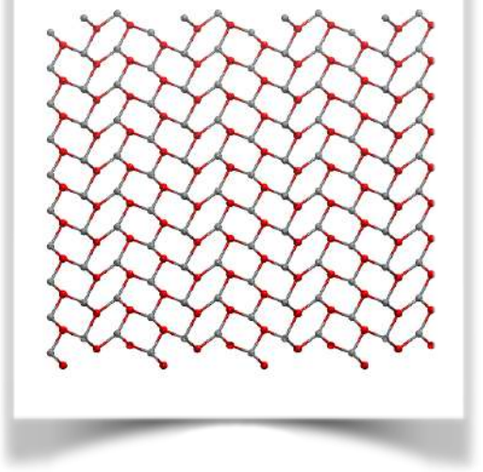


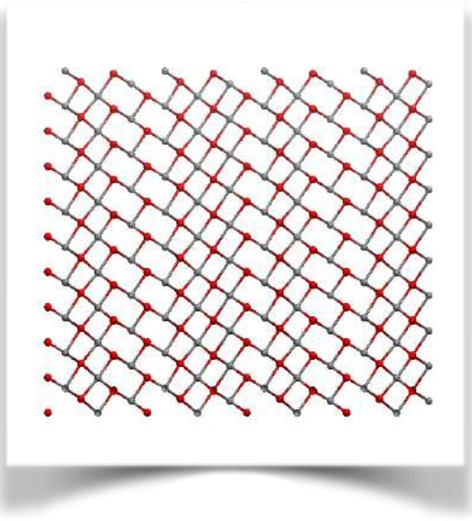
B3

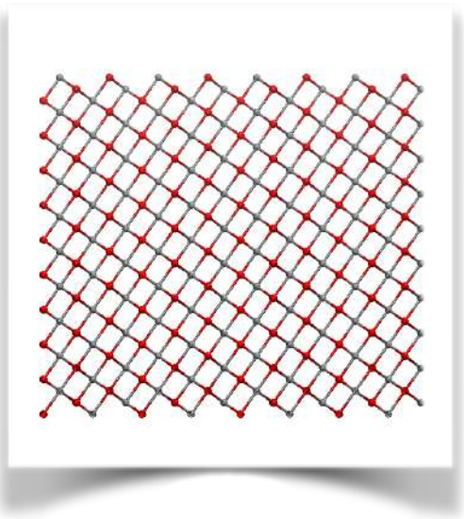


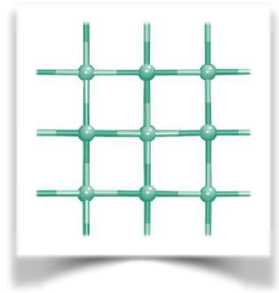








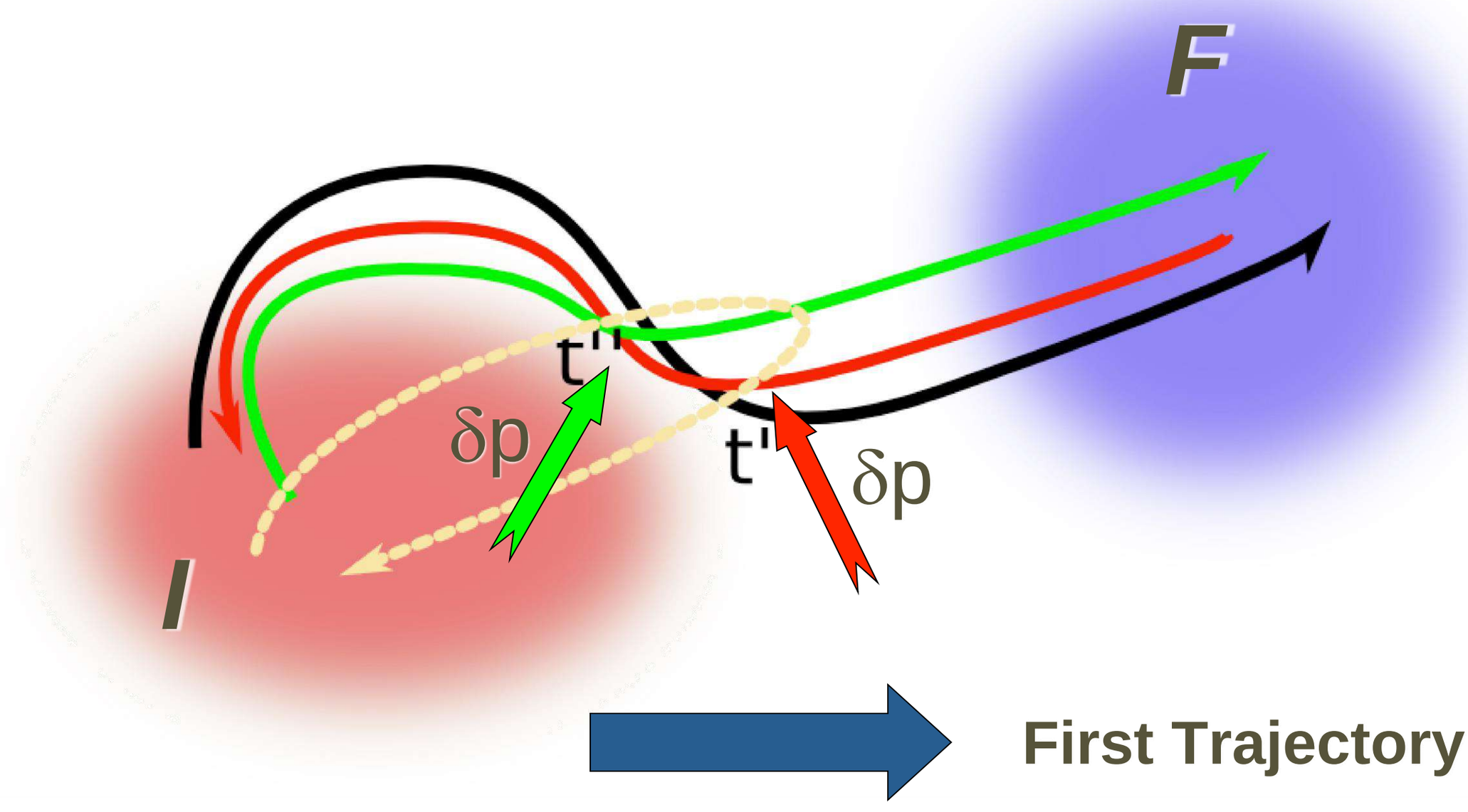




B1

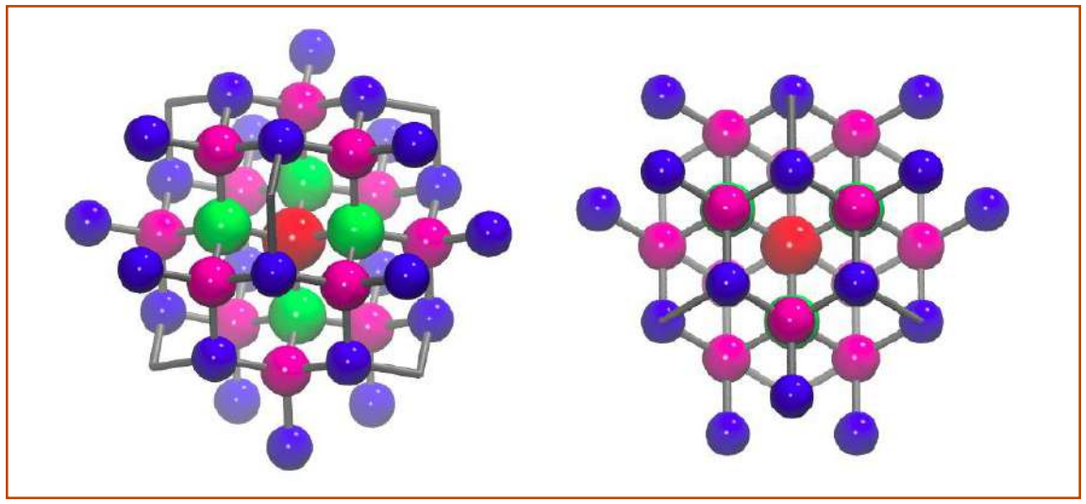
A given trajectory does not need to be representative of the REAL transformation mechanism (TPS will weight its importance)

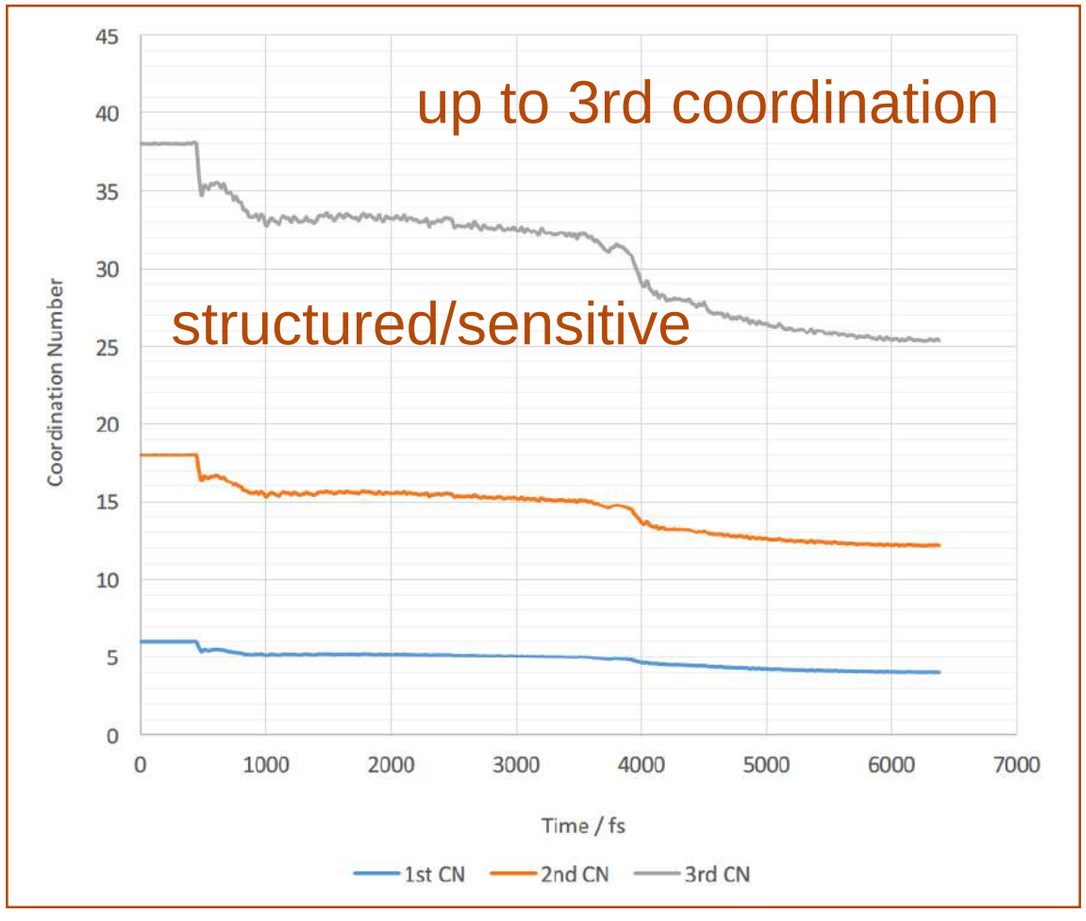
Monte Carlo in Trajectory Space

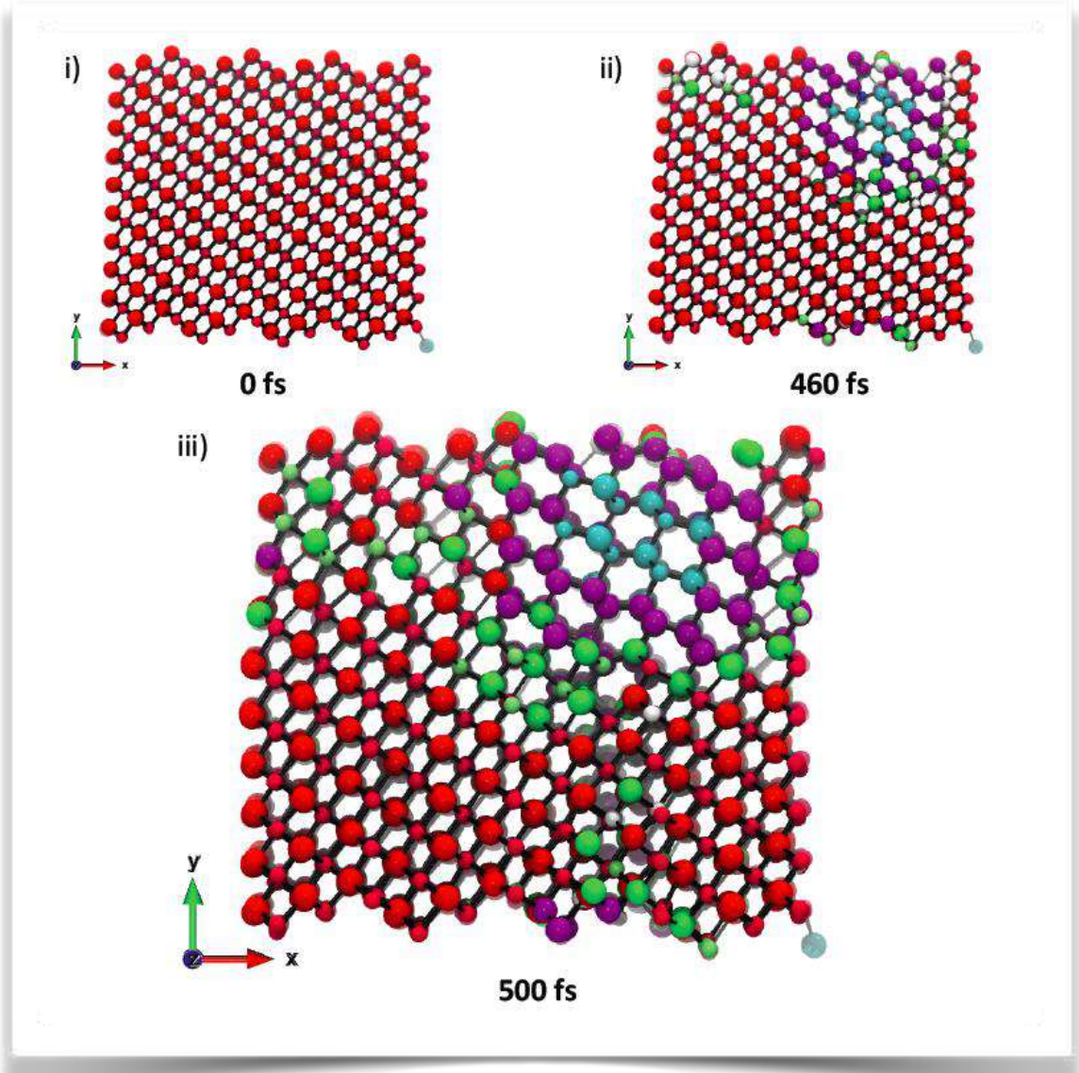


„Shooting Algorithm“ (C. Dellago, D. Chandler)

Order Parameter (CV) - coordination number/sequence

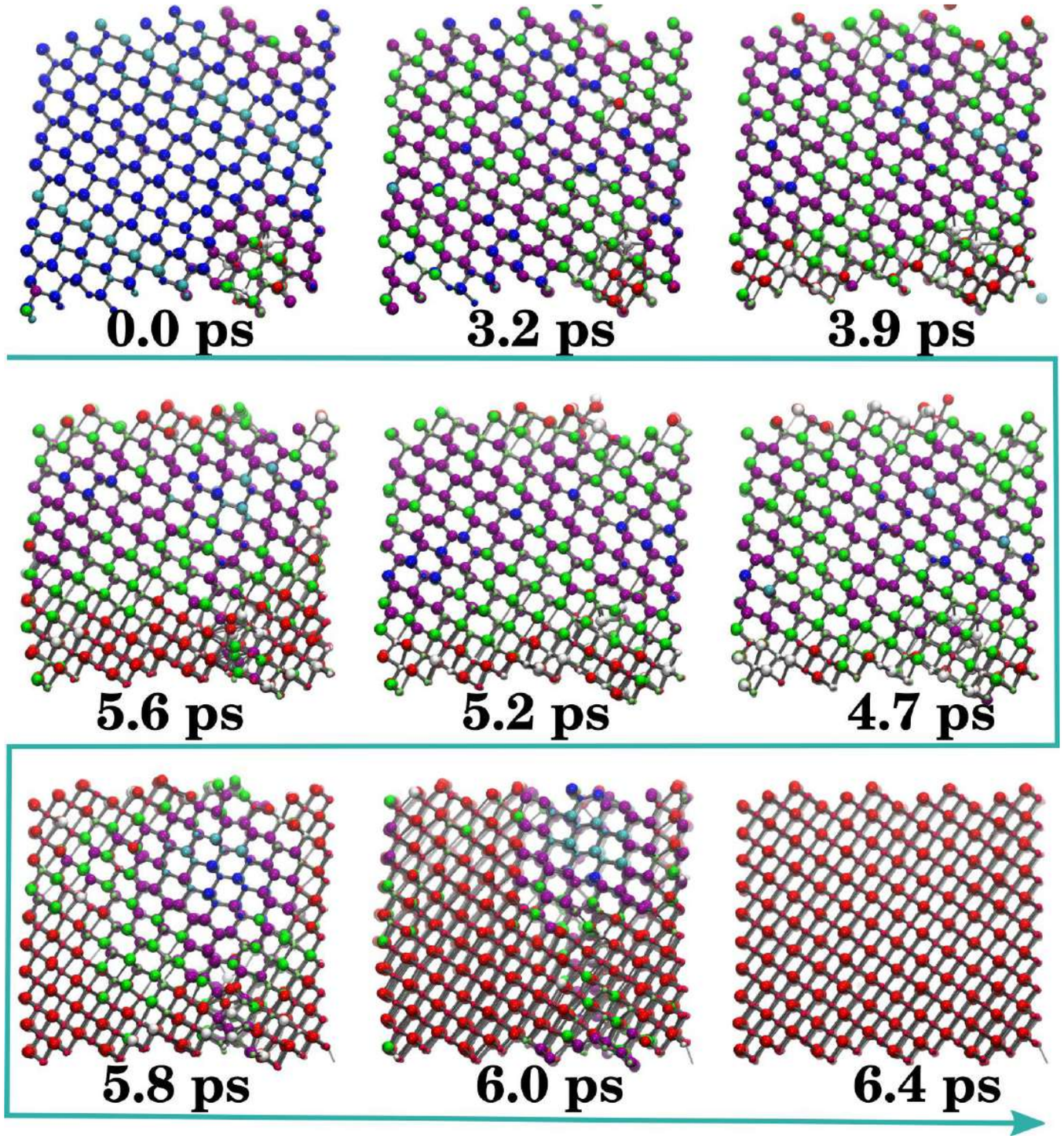






Mechanism from TPS - forwards

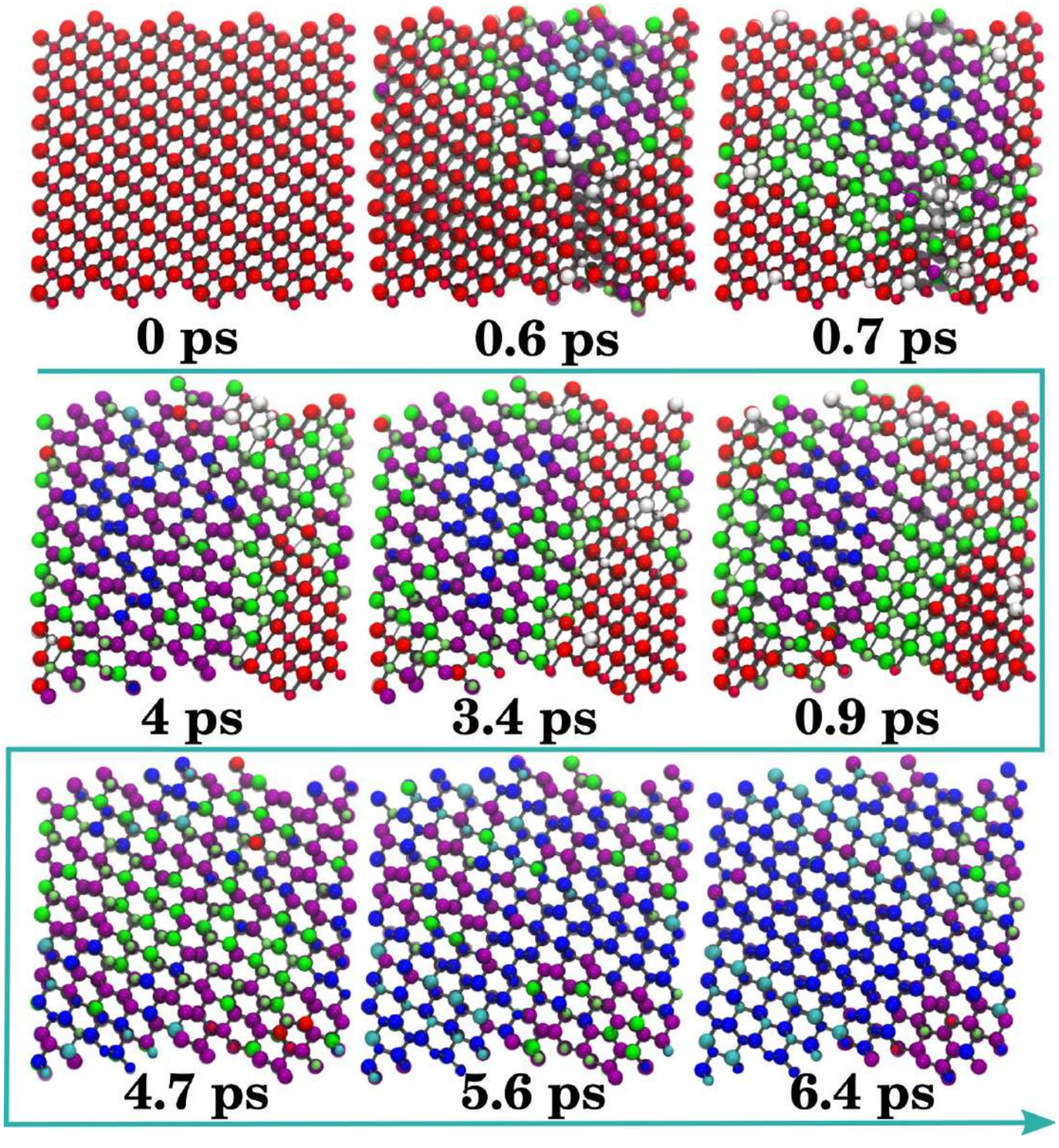
B3



B1

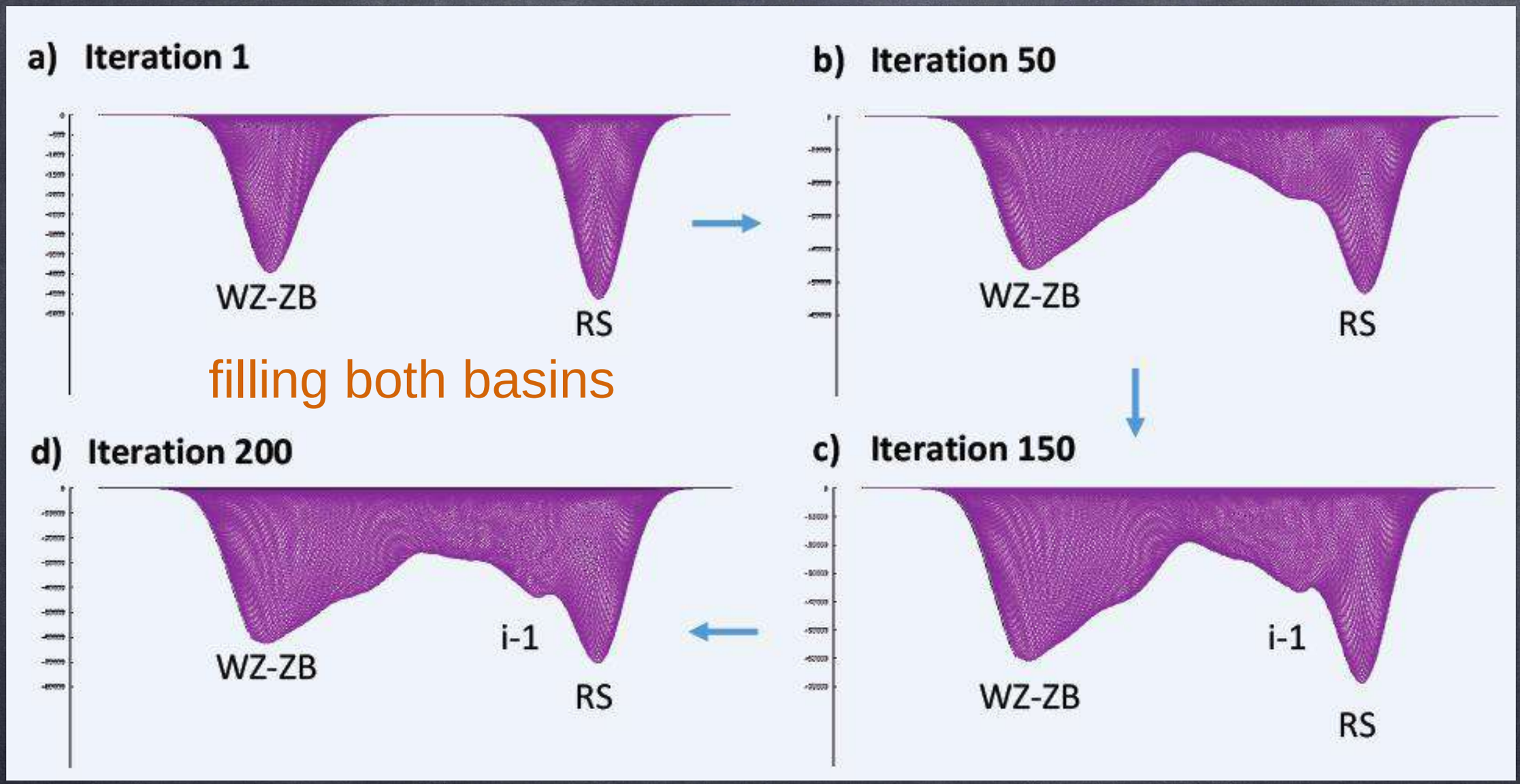
Mechanism from TPS - backwards

B1



B4/B3

Free Energy Reconstruction (TPS/metaD)



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.

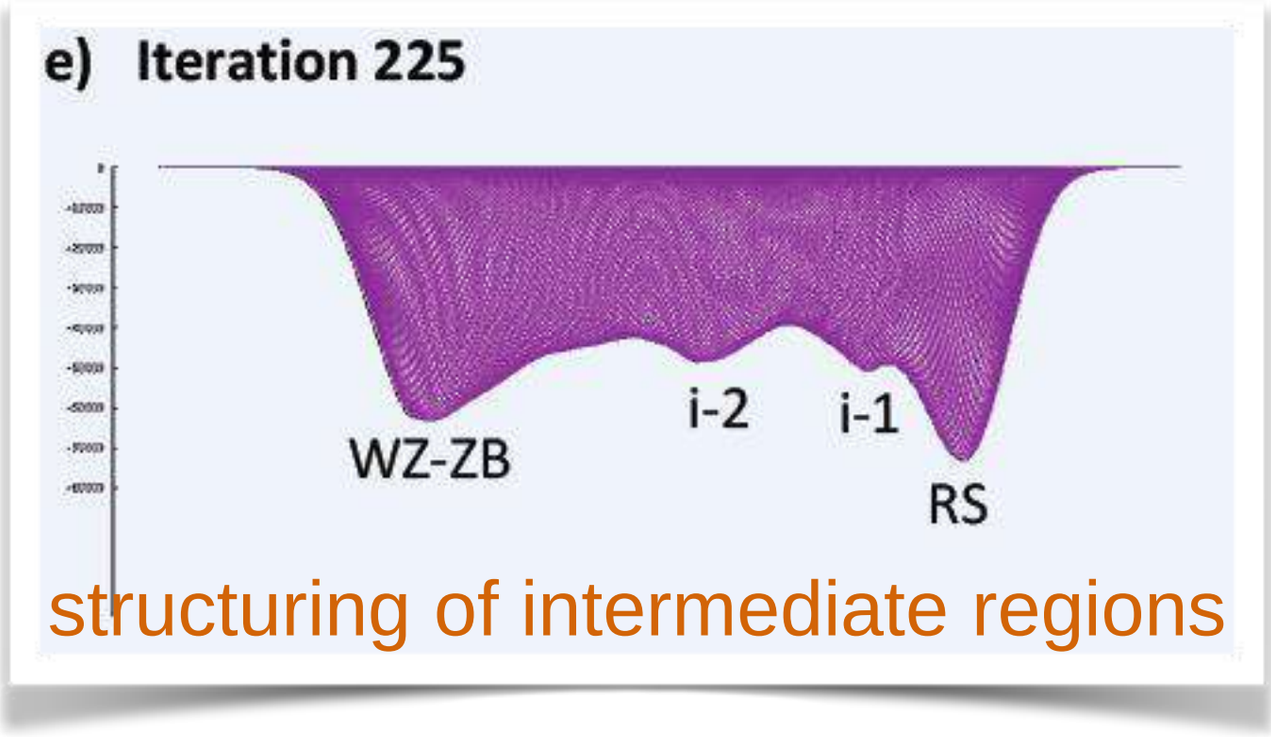
4. TPS step 3: shoot off a new trajectory from the same snapshot as above and propagate, only this time backwards in time, to basin B.

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.

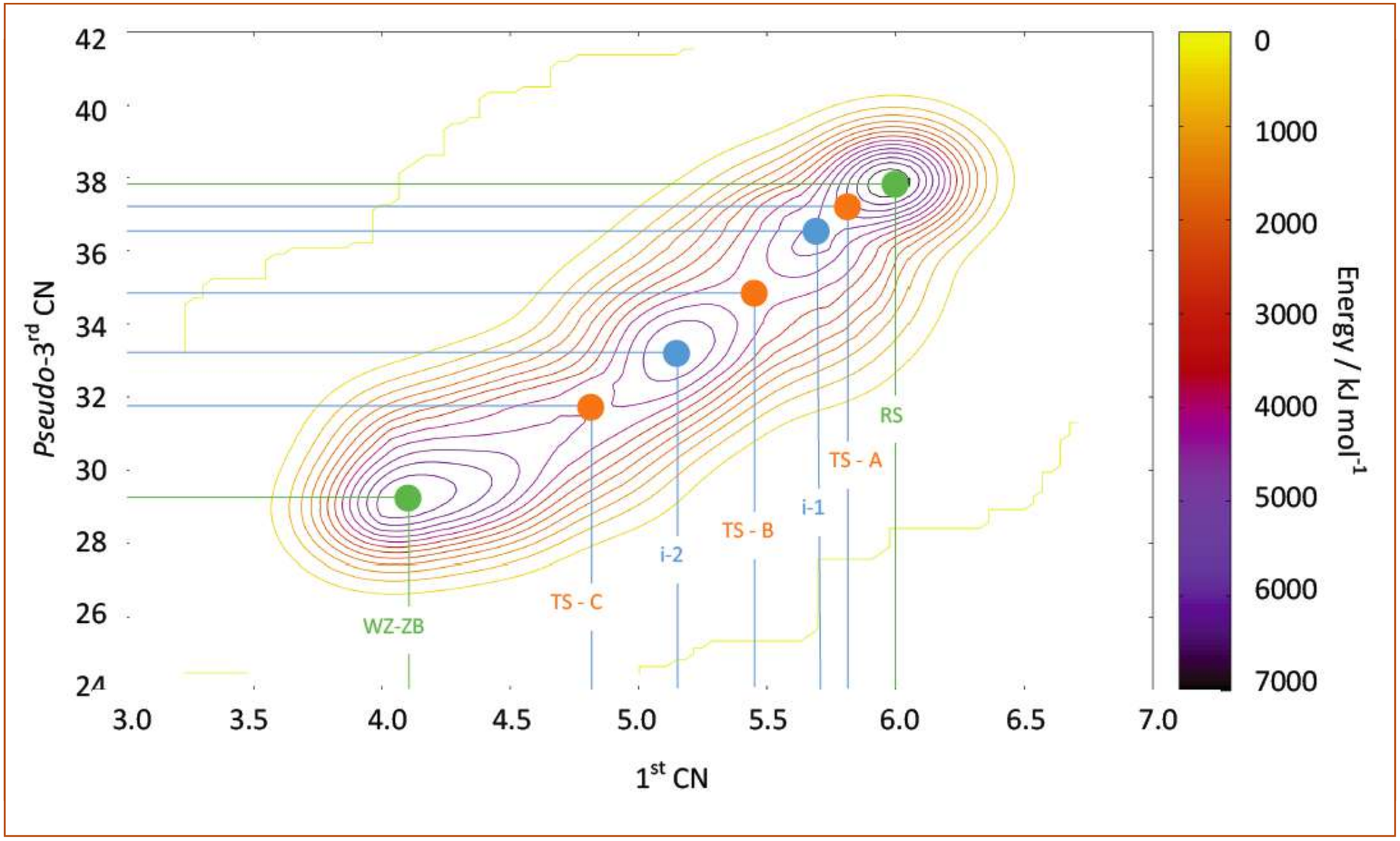
Repeat the above iterations of metadynamics and TPS moves, until the underlying free energy profile is fully converged.

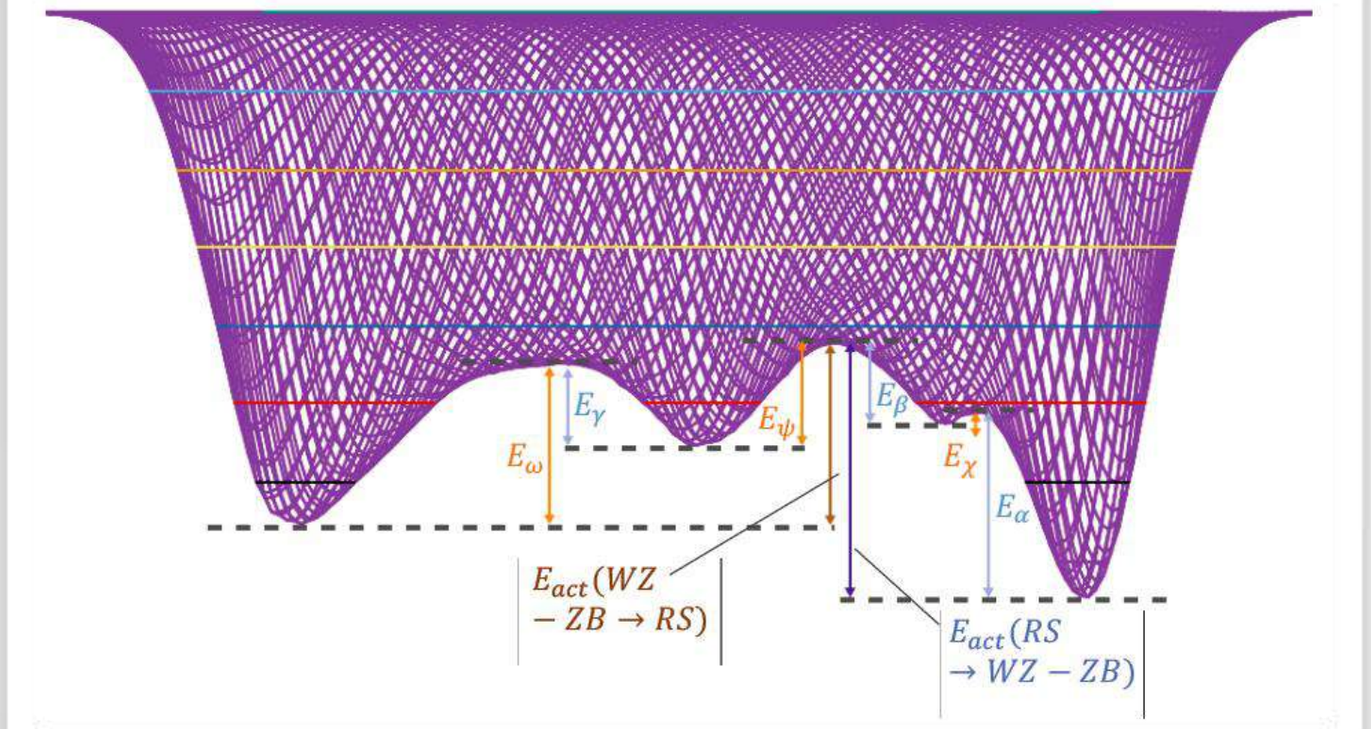
S.A. Jobbins, S.E. Boulfelfel, S. Leoni, Faraday Discussions (2018)



Population of intermediate basins in the late stage only

2D map of two-dimensional CV

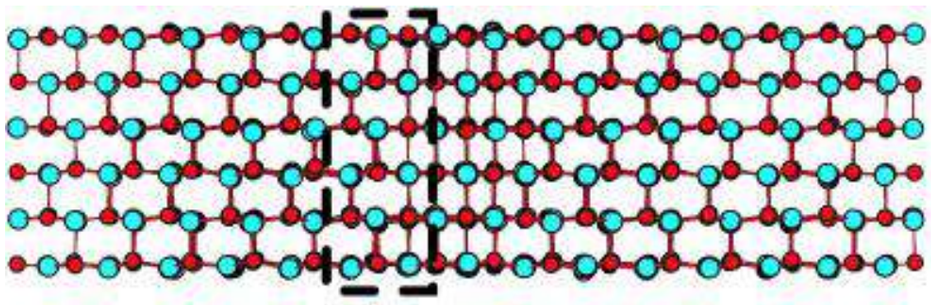


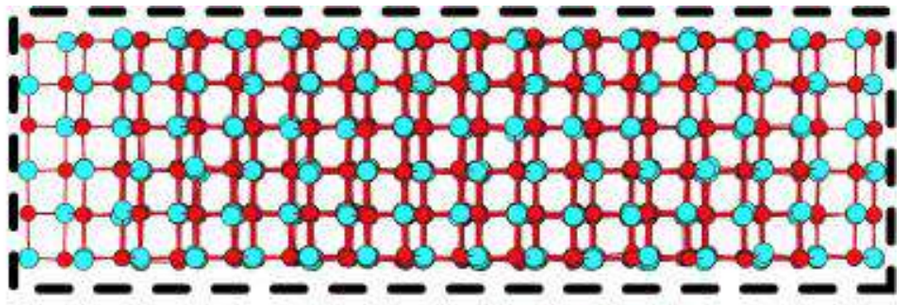


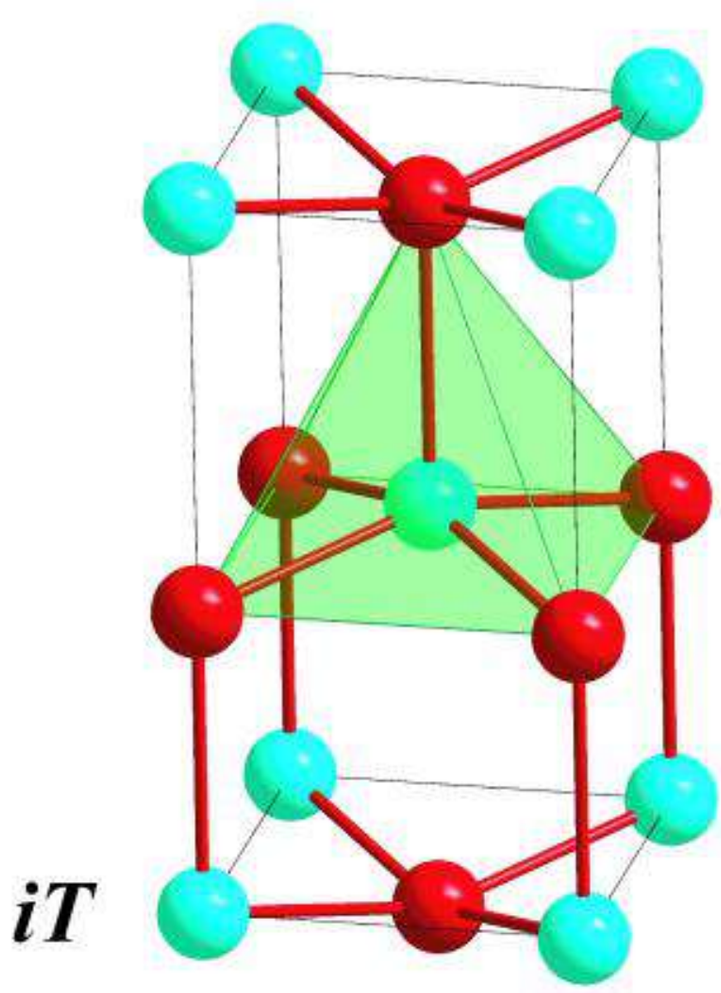
	Energy /kJ mol^{-1}	Energy /kJ mol^{-1} pair^{-1}	Energy /eV pair^{-1}	Energy /k_BT pair^{-1}
E_χ	20 447.0	17.1	0.18	6.8
E_ψ	13 085.9	10.9	0.11	4.4
E_ω	1 357.0	1.3	0.01	0.5
$E_{act}(WZ - ZB \rightarrow RS)$	23 049.1	19.2	0.20	7.7

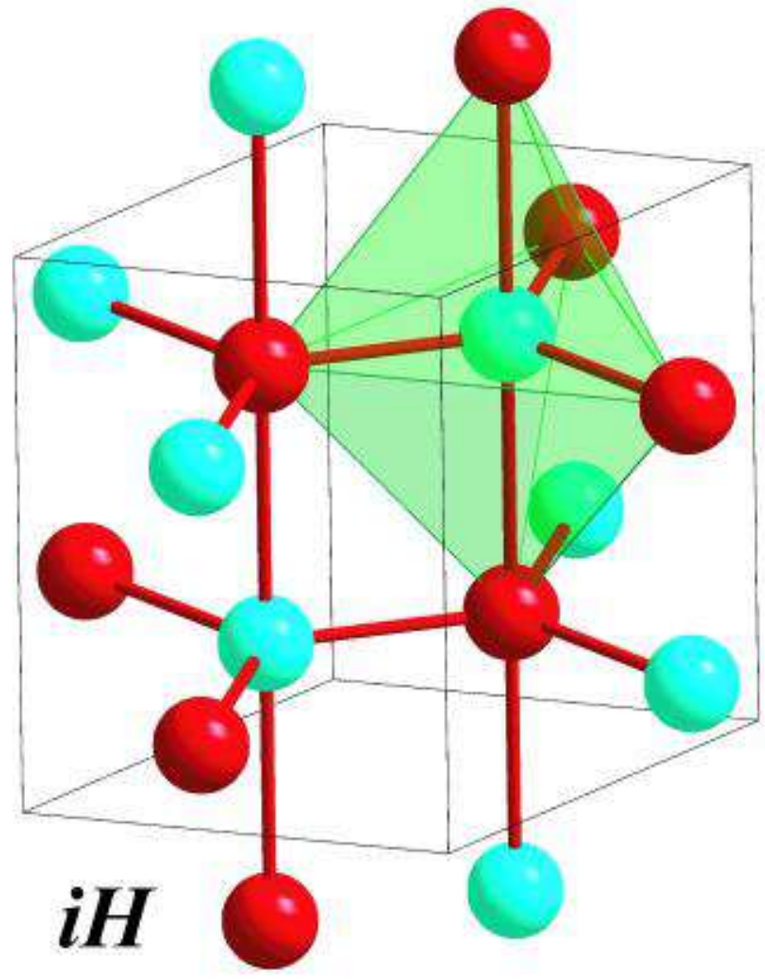
	Energy /kJ mol^{-1}	Energy /kJ mol^{-1} pair^{-1}	Energy /eV pair^{-1}	Energy /k_BT pair^{-1}
E_χ	20 447.0	17.1	0.18	6.8
E_ψ	13 085.9	10.9	0.11	4.4
E_ω	1 357.0	1.3	0.01	0.5
$E_{act}(RS \rightarrow WZ - ZB)$	32 565.9	27.1	0.28	10.9

i2 - intermediate









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

explicit