

Lecture IV

Path Analysis: Finding the Mechanism

Outline

1. Reaction coordinate, committor and all that
2. Transition state ensemble
3. Committor distributions
4. Likelihood maximization

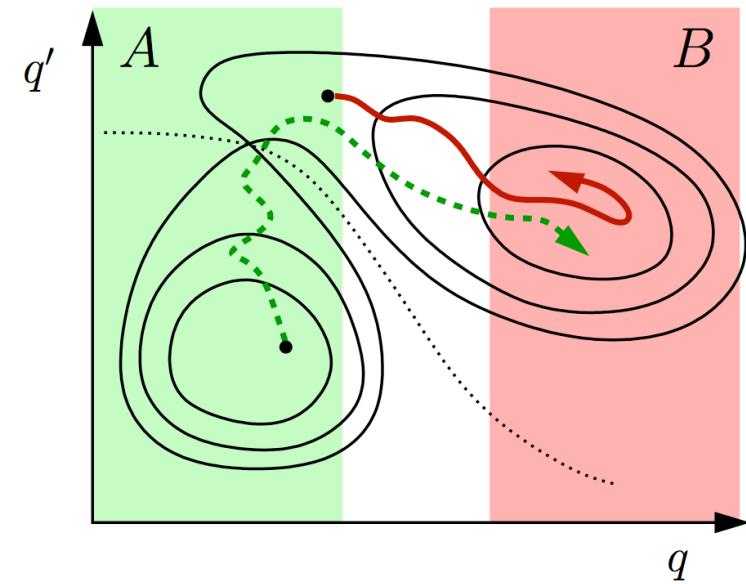
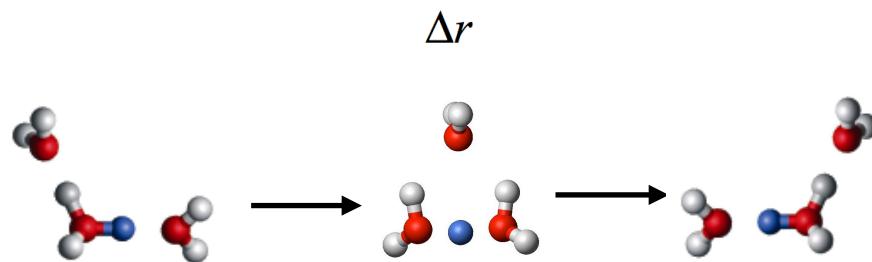
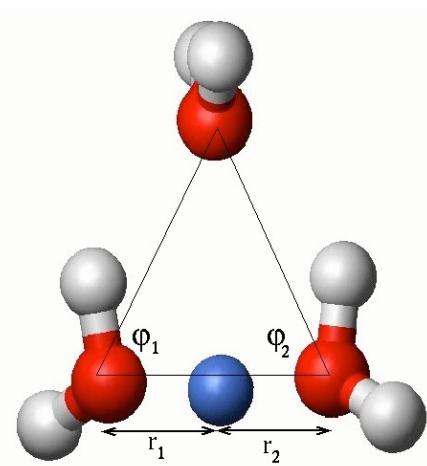
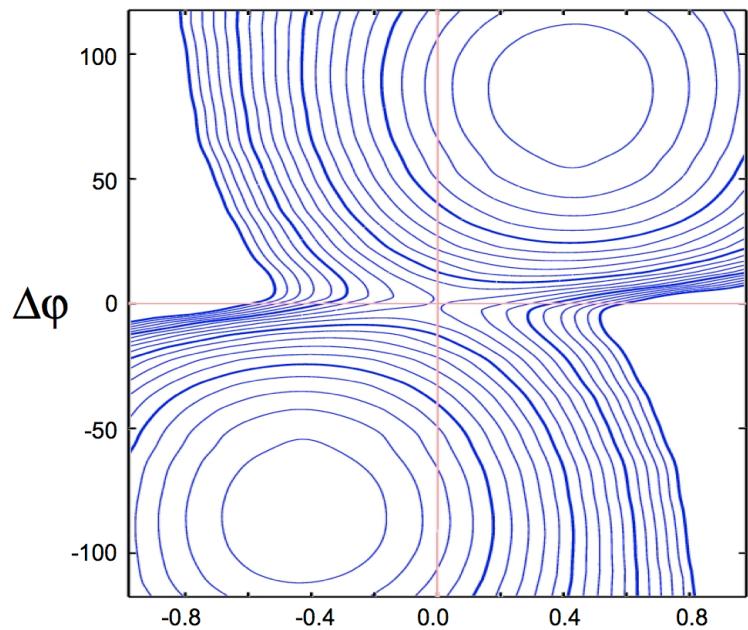
Analyzing transition pathways



”It is nice to know that the computer understands the problem. But I would like to understand it too.”

(E. P. Wigner)

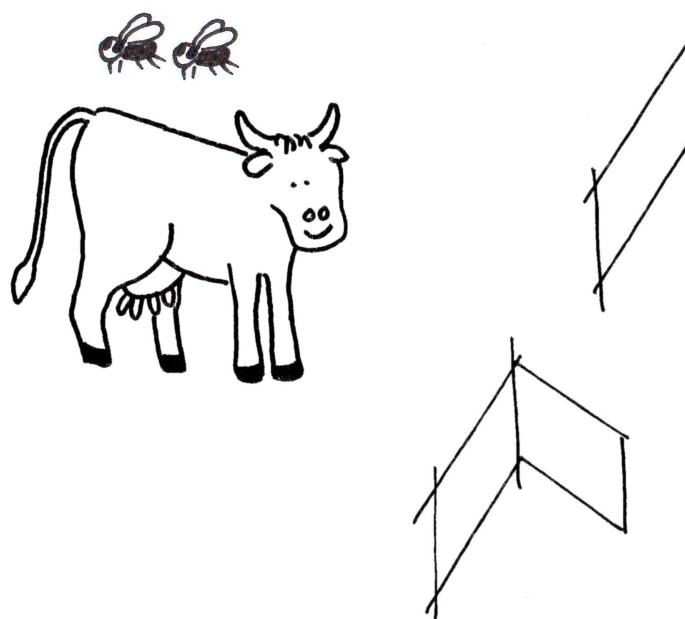
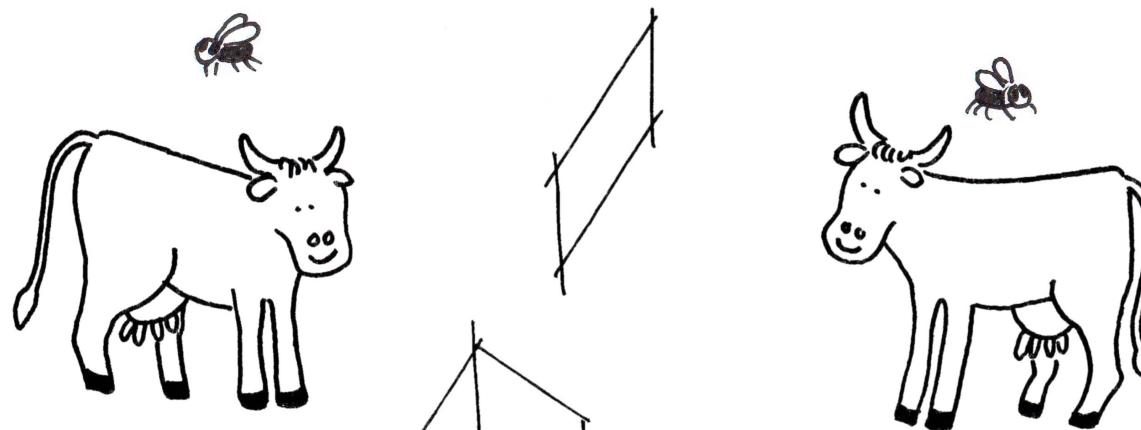
Order parameter vs. reaction coordinate



“Choosing an order parameter is an art”

J. Sethna

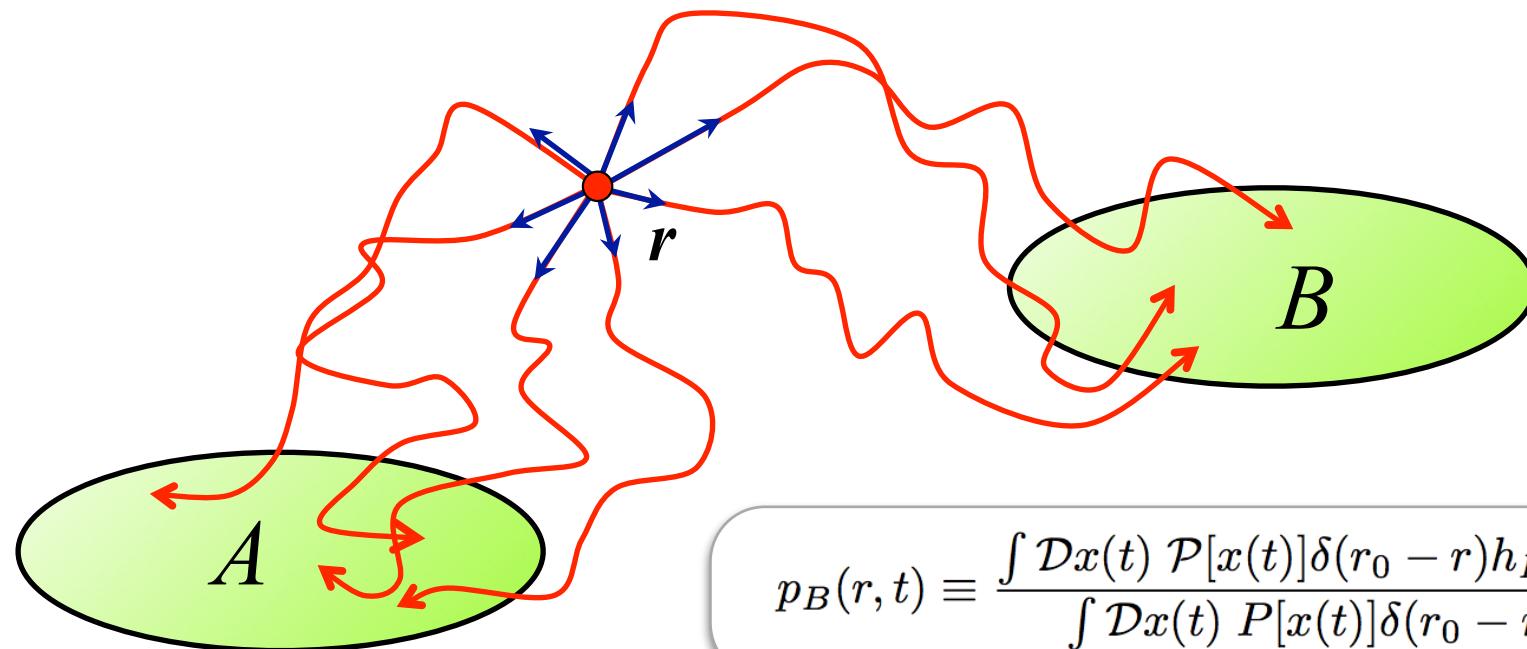
Order parameter vs. reaction coordinate



Committer

(aka p-fold, splitting probability)

$p_B(r, t) =$ Probability that a trajectory initiated at r relaxes into B



$$p_B(r, t) \approx \frac{1}{N} \sum_{i=1}^N h_B(x_t^{(i)})$$

$$\sigma = \sqrt{\langle (p_B^{(N)} - p_B)^2 \rangle} = \sqrt{\frac{p_B(1 - p_B)}{N}}$$

L. Onsager, Phys. Rev. **54**, 554 (1938).

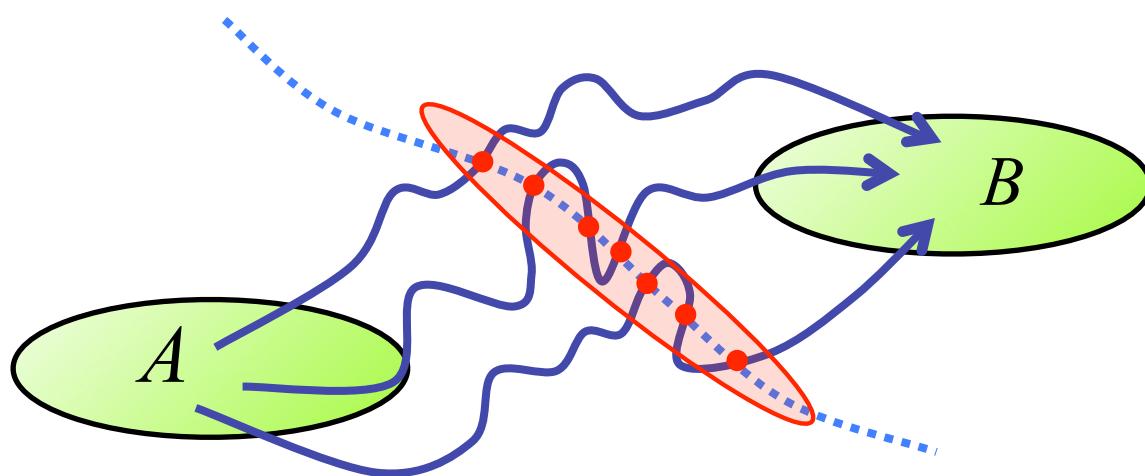
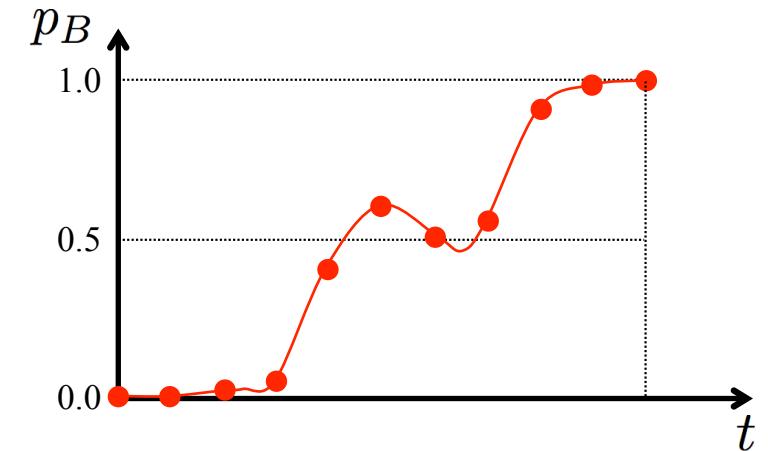
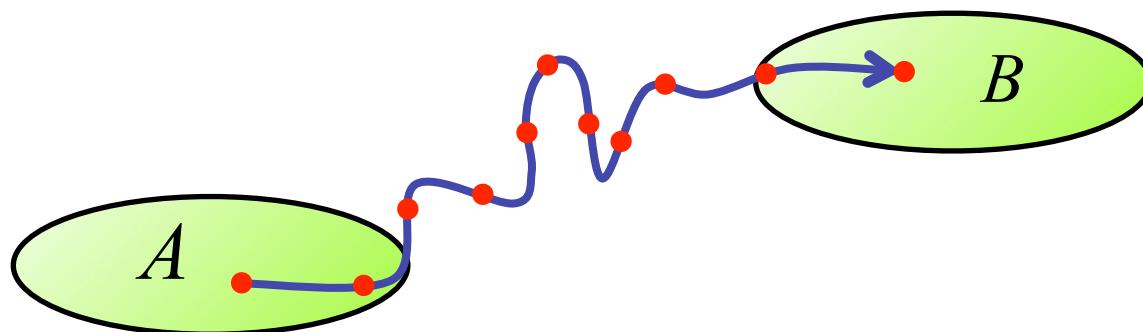
M. M. Klosek, B. J. Matkowsky, Z. Schuss, Ber. Bunsenges. Phys. Chem. **95**, 331 (1991)

V. Pande, A. Y. Grosberg, T. Tanaka, E. I. Shakhnovich, J. Chem. Phys. **108**, 334 (1998)

Transition state ensemble

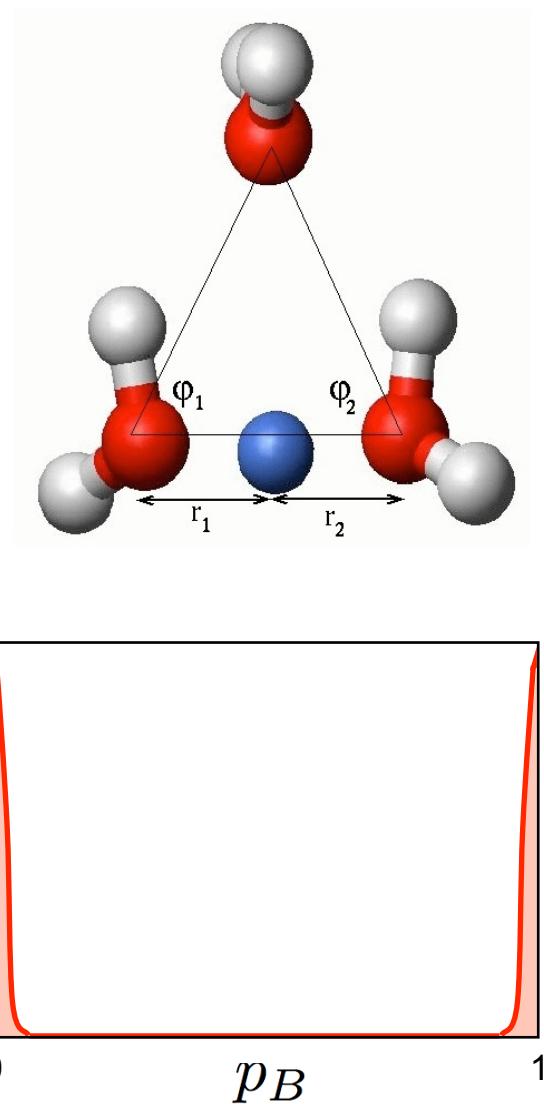
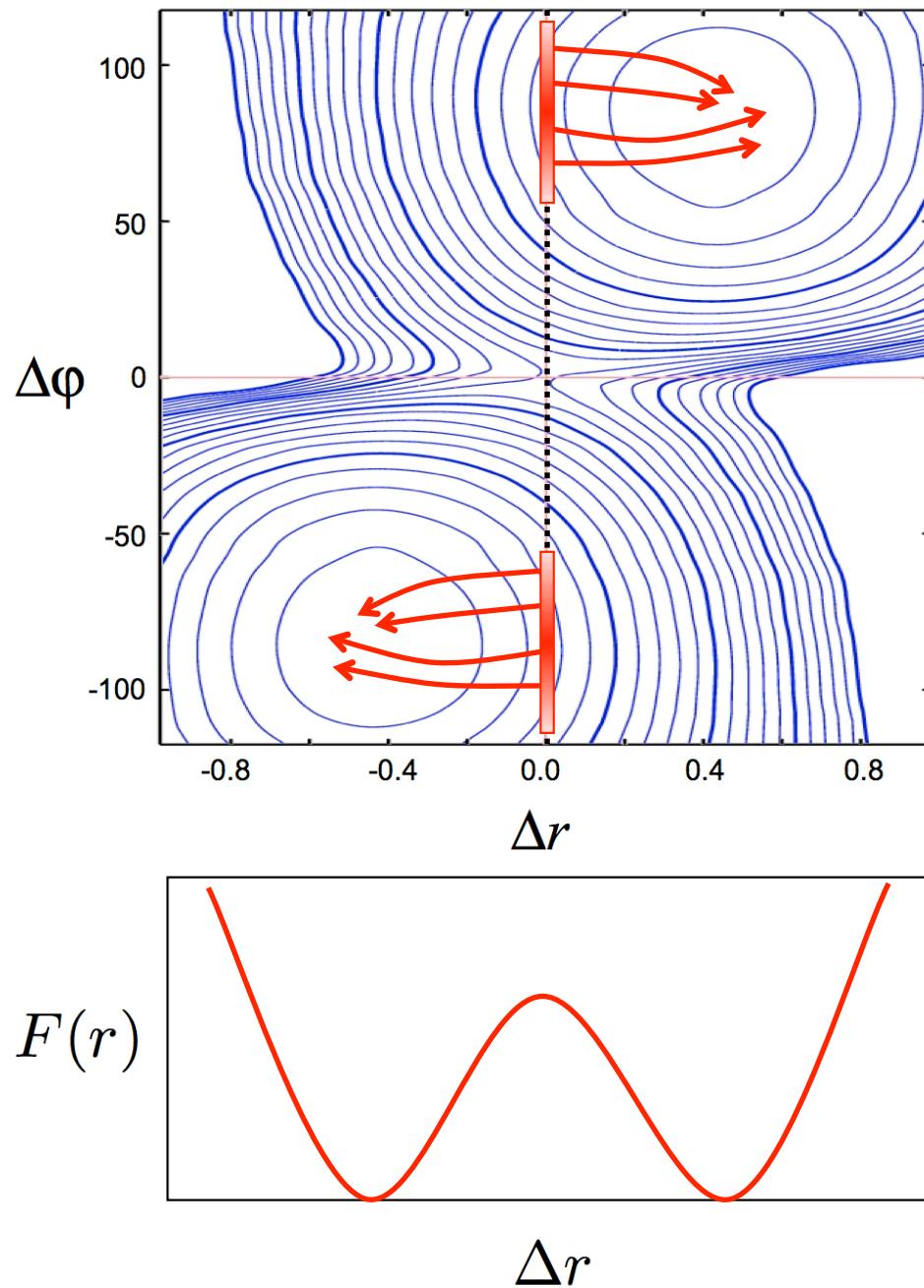
r is a **transition state (TS)** if

$$p_B(r) = p_A(r)$$

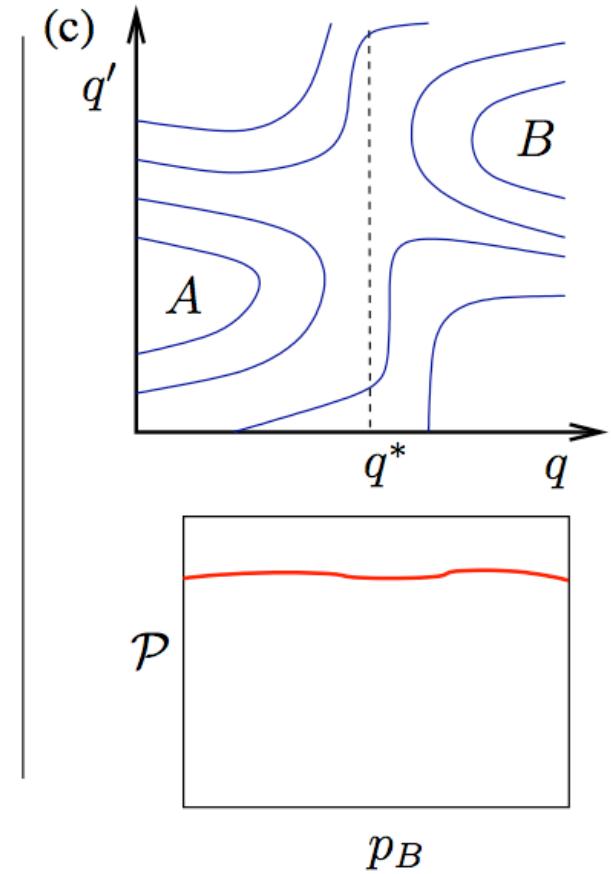
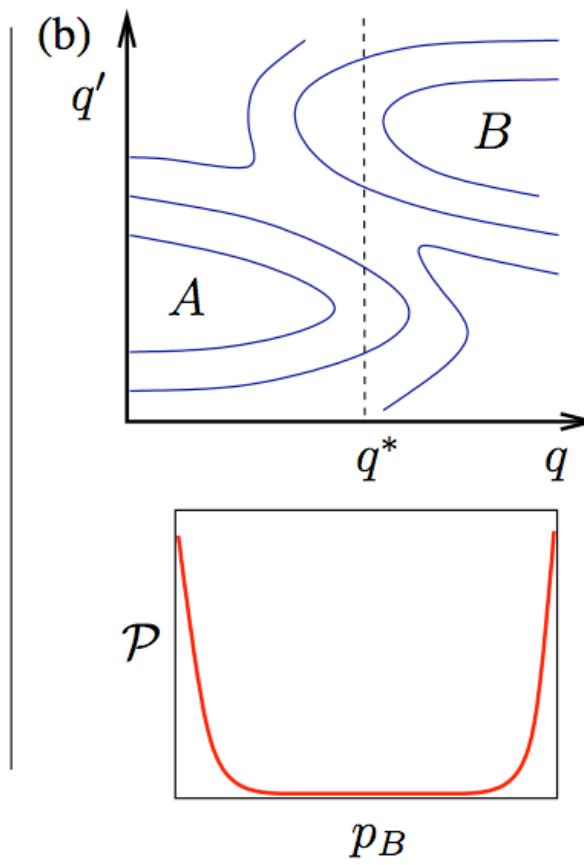
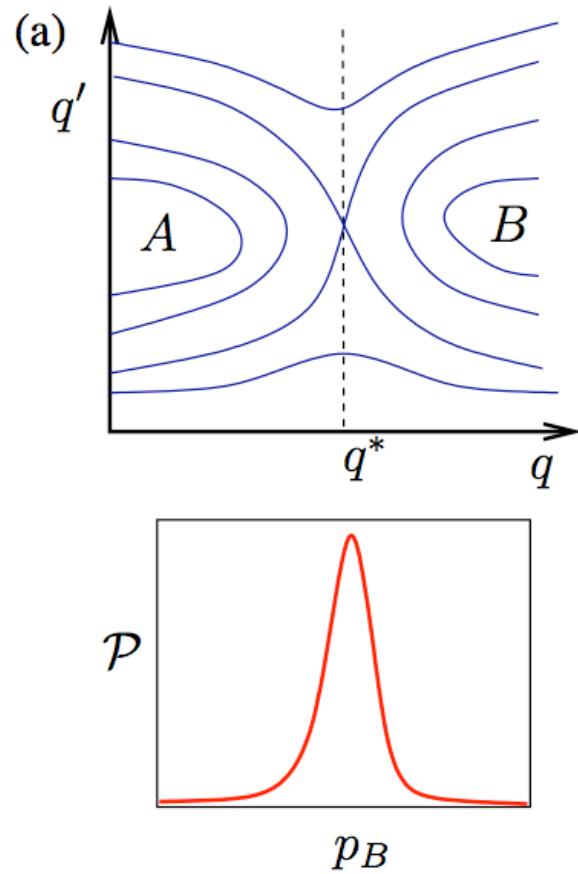


TSE: Intersections of
transition pathways with
the $p_B=1/2$ surface

Committer distributions



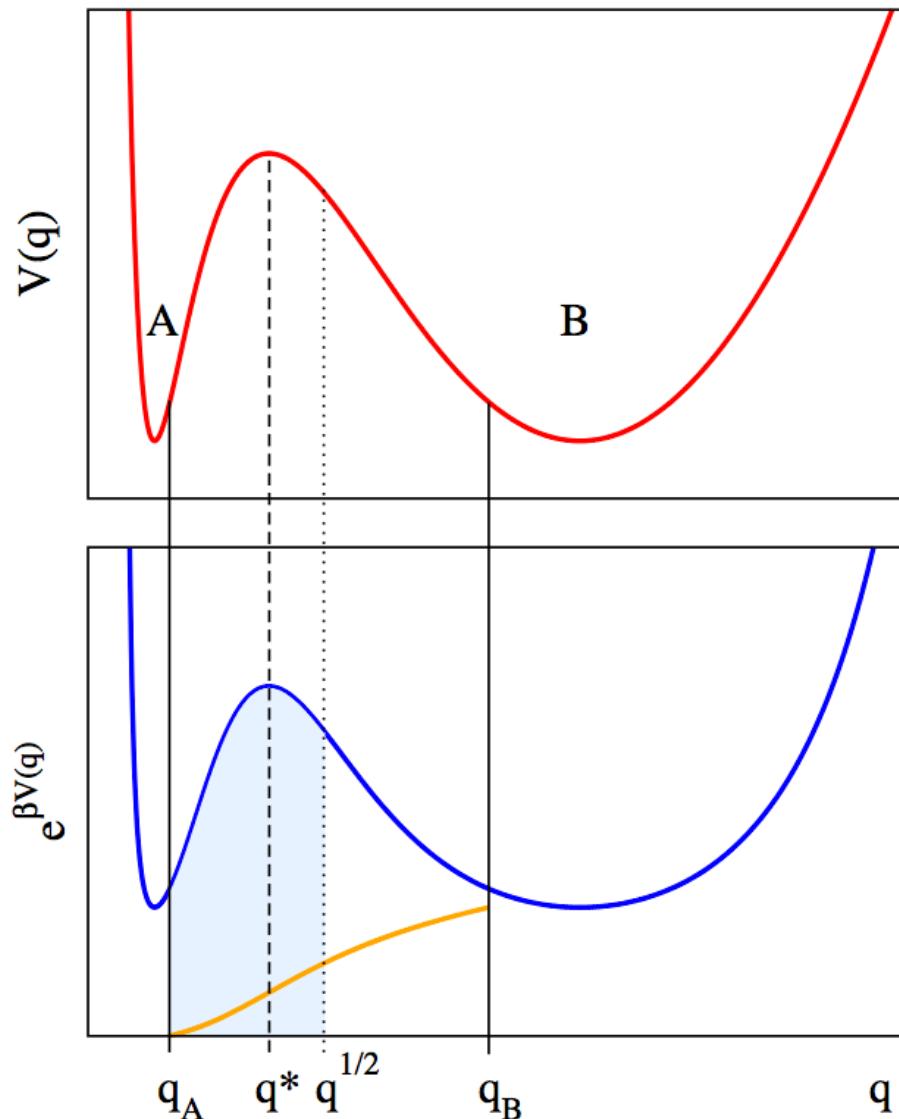
Committer distributions



Perfect reaction coordinate $q(x)$:

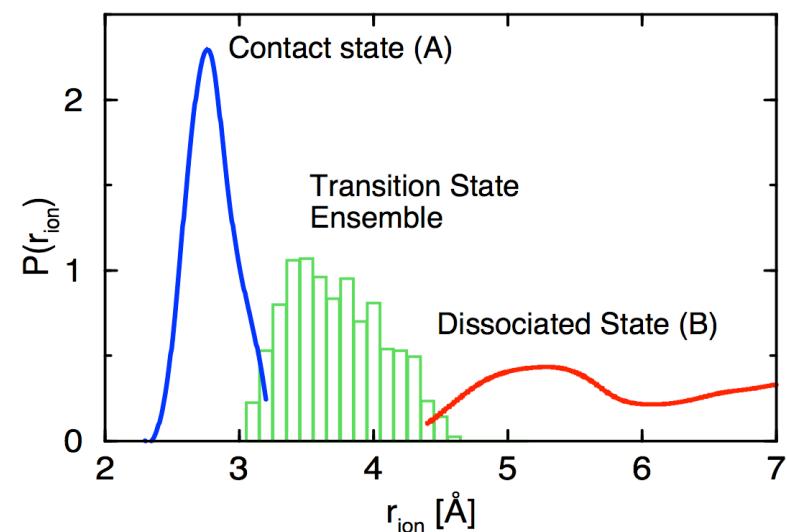
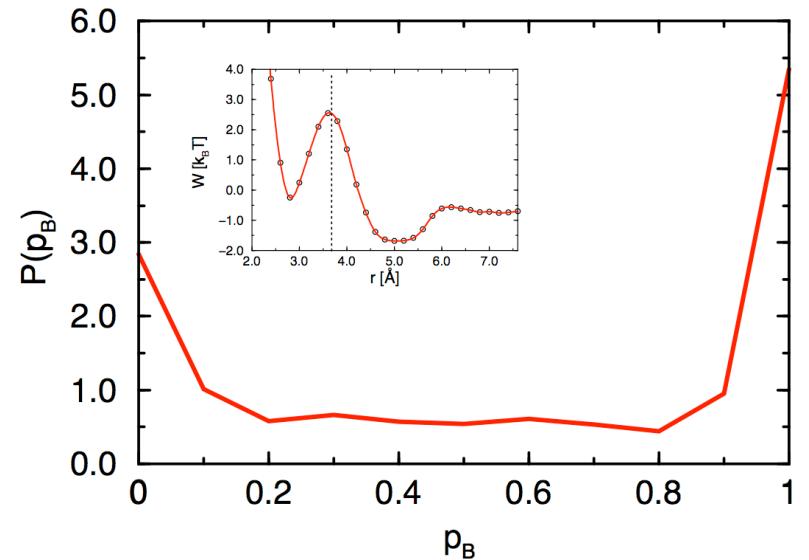
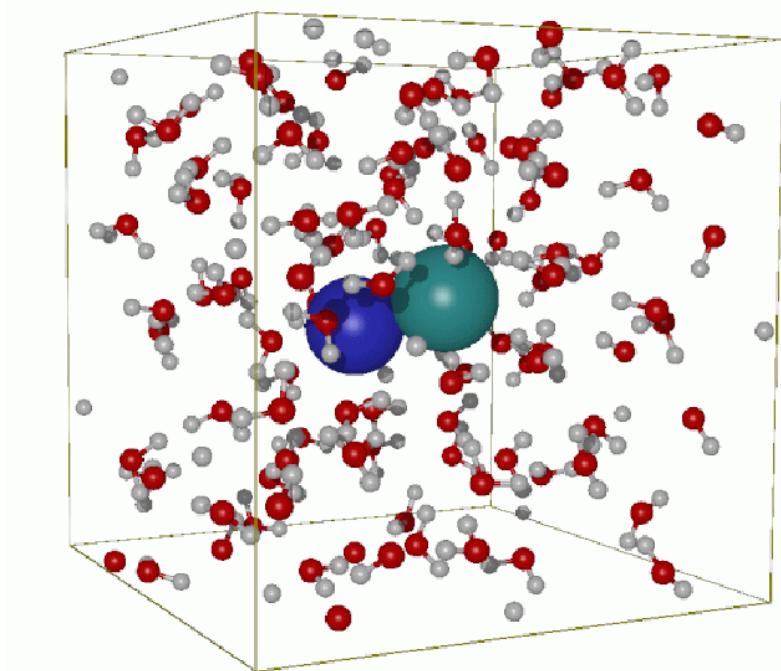
$$p_B(x) = p_B[q(x)]$$

$p_{1/2}$ -surface at top of barrier?

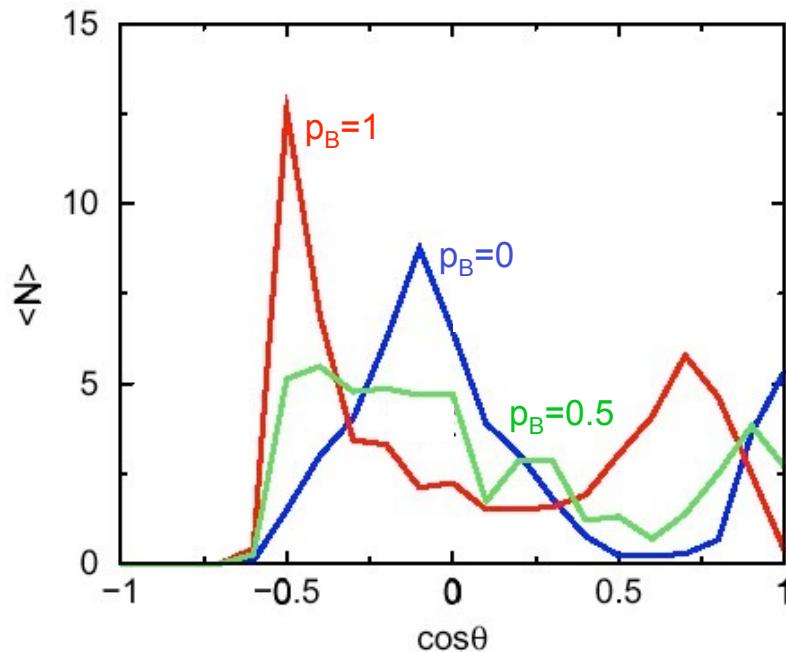
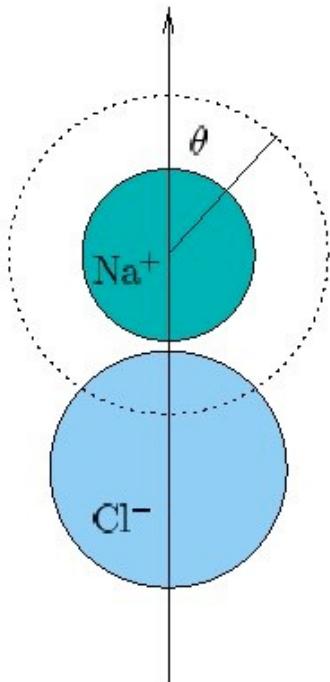


$$p_B(q) = \frac{\int_{q_A}^q \exp[\beta V(q')] dq'}{\int_{q_A}^{q_B} \exp[\beta V(q')] dq'}$$

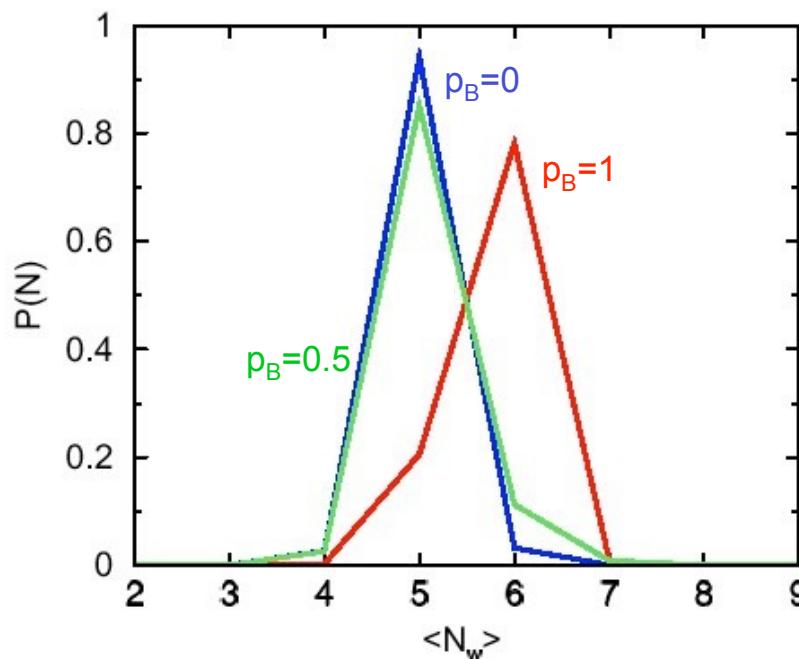
Ionic dissociation in aqueous solution



Constrained ensemble $r=r^*$

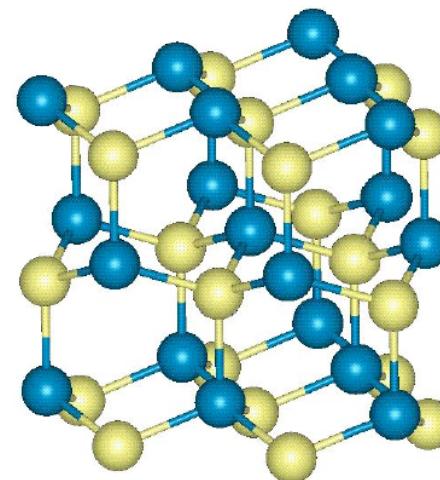


Structure of first coordination shell of Na^+



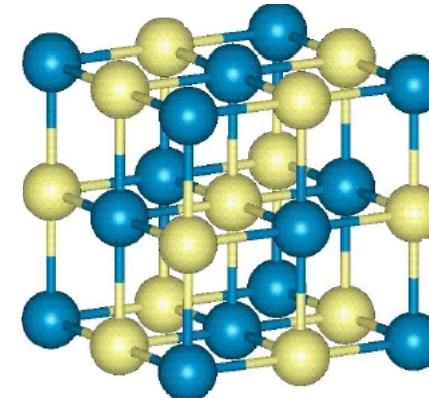
Number of coordinating water molecules @ Na^+

Structural transformation in CdSe

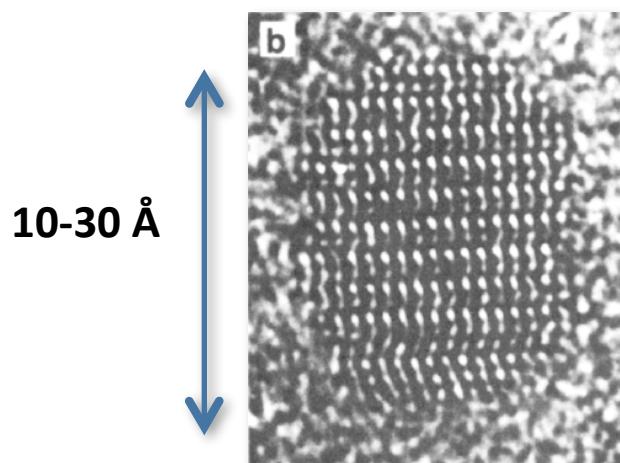
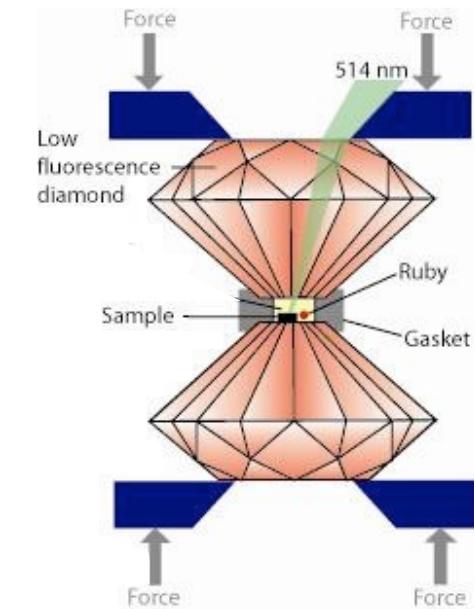


Wurtzite

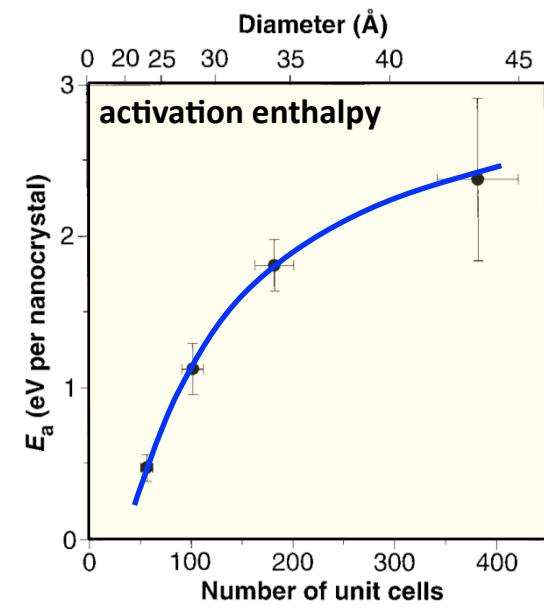
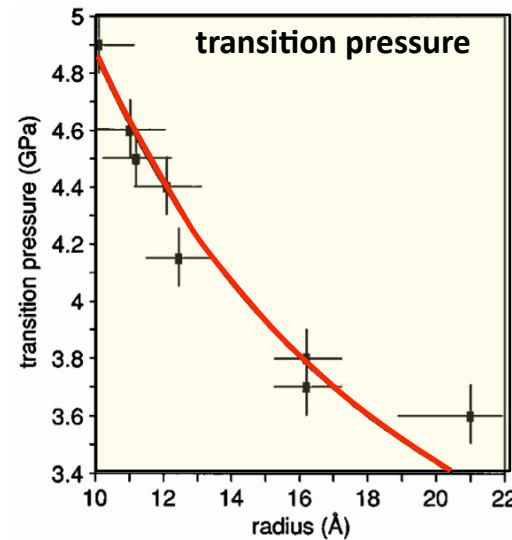
2.5 GPa



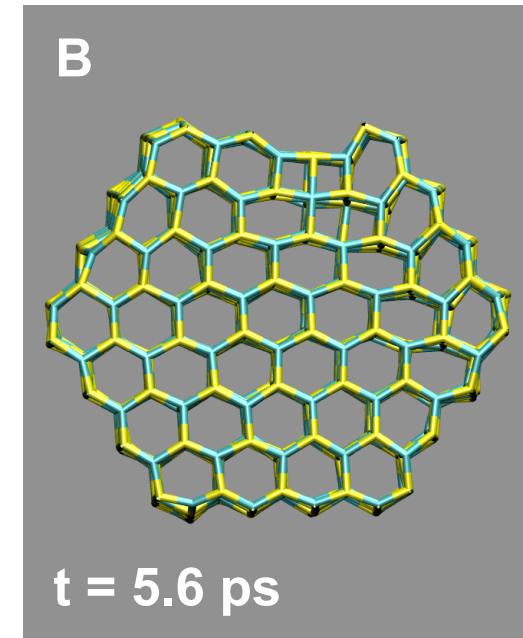
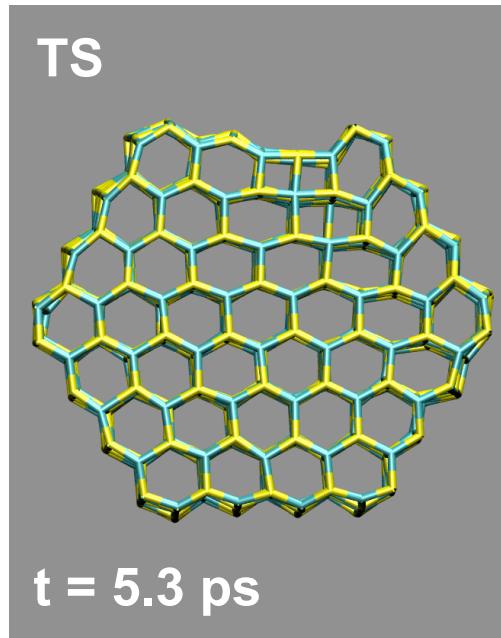
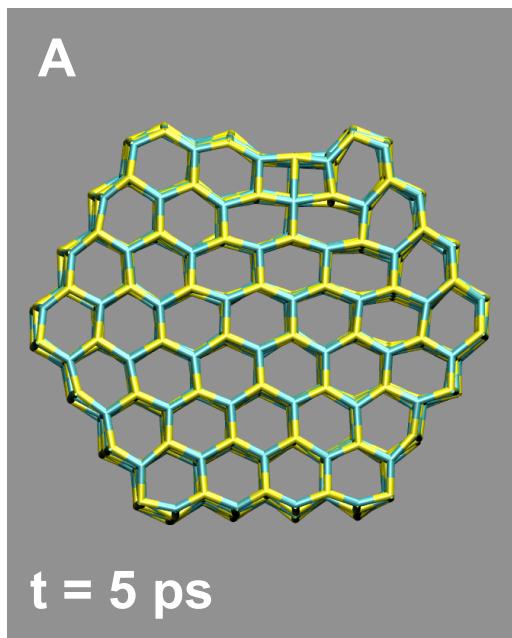
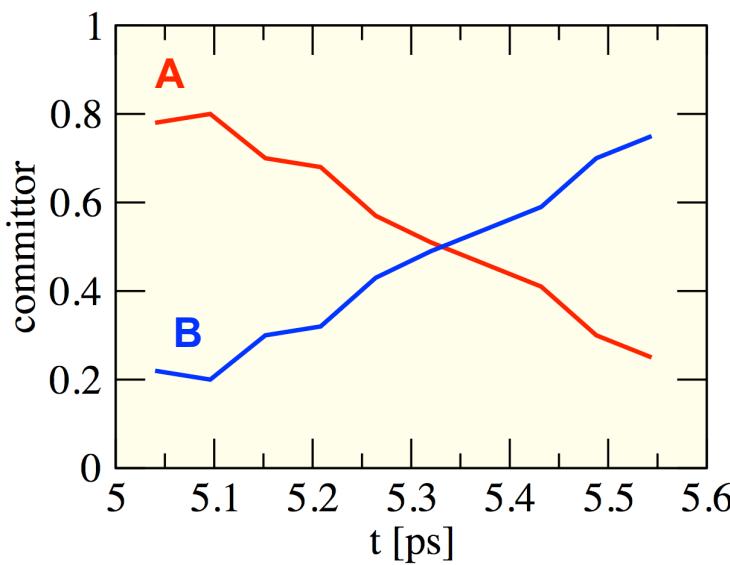
Rocksalt



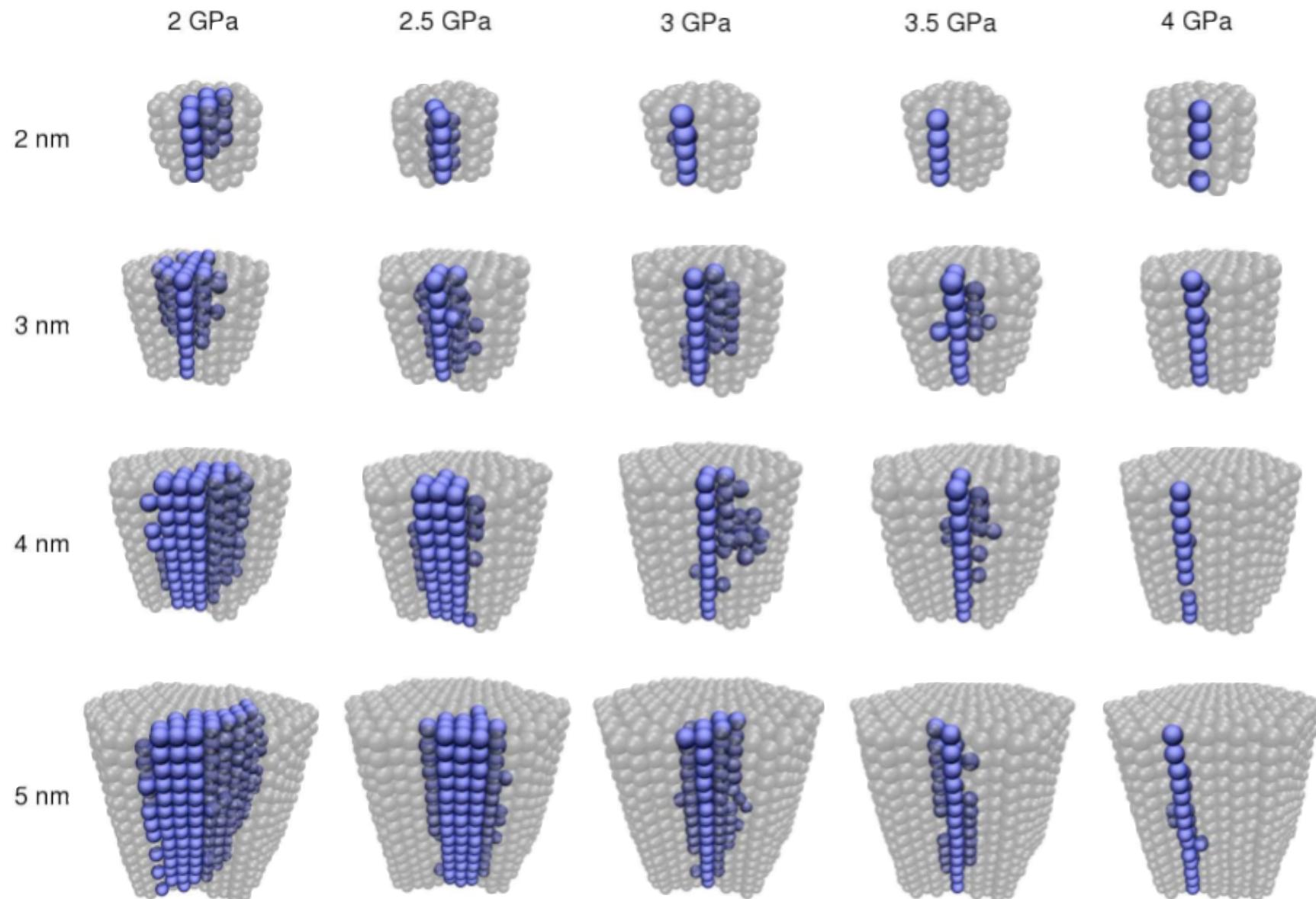
10-30 Å



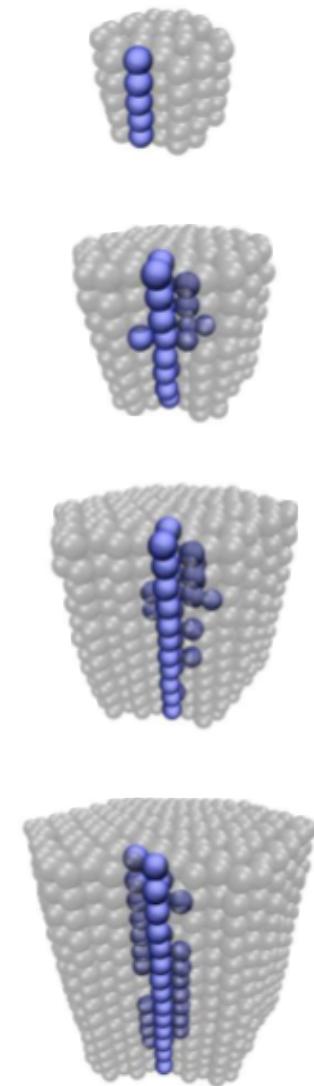
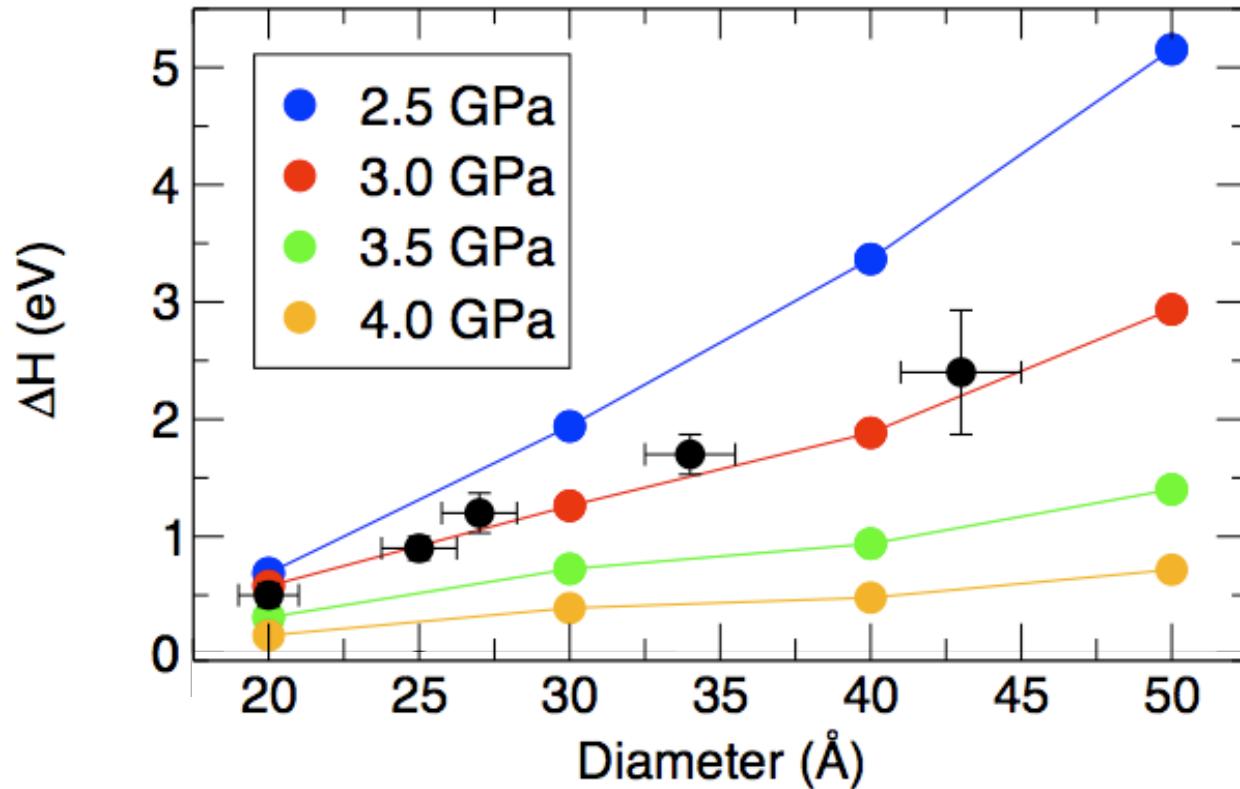
Transition state



Critical nuclei



Nucleaton barrier - size dependence

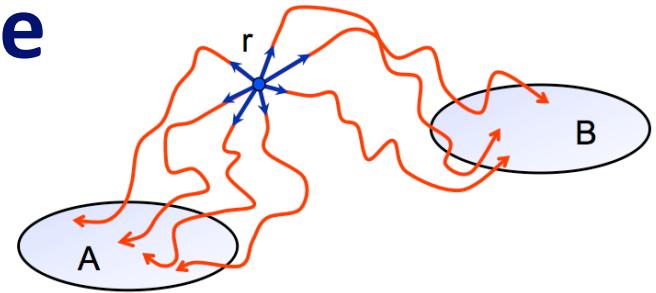


M. Grünwald and C. Dellago, Nano Letters 9, 2099 (2009)

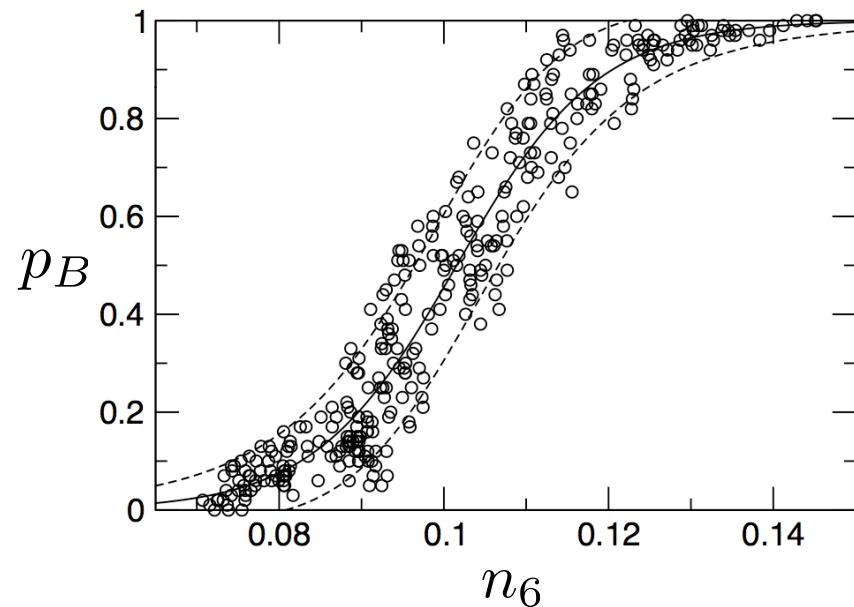
C.-C. Chen, A. B. Herhold, C. S. Johnson, and A. P. Alivisatos, Science 276, 398 (1997)

K. Jacobs, D. Zaziski, E. C. Scher, A. B. Herhold, and A. P. Alivisatos, Science 293, 1803 (2001)

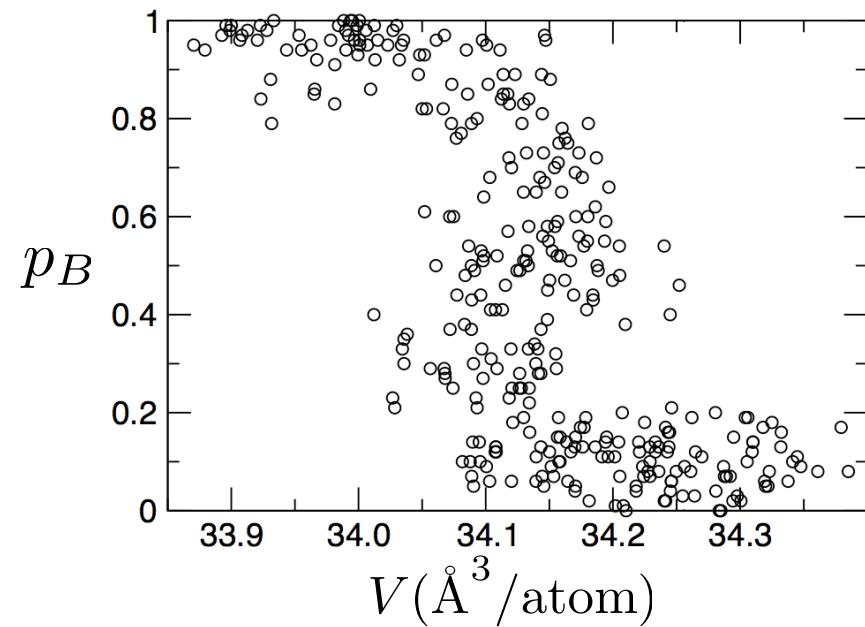
Reaction coordinate



Good RC q parametrizes committor: $p_B(x) = p_B[q(x)]$



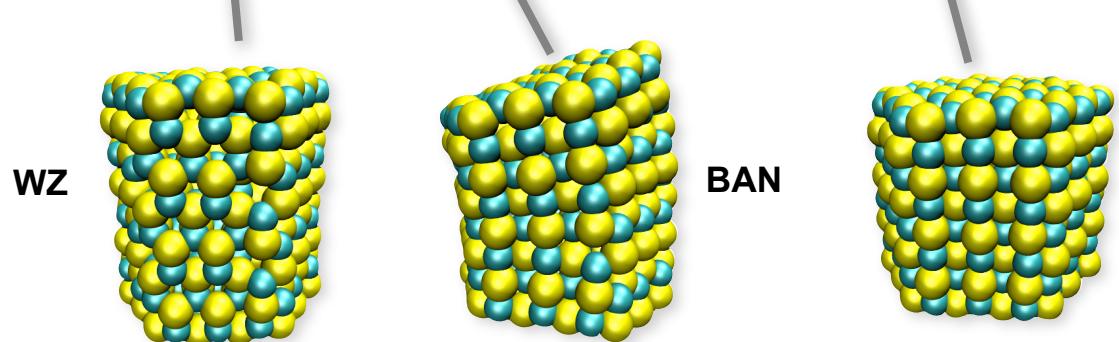
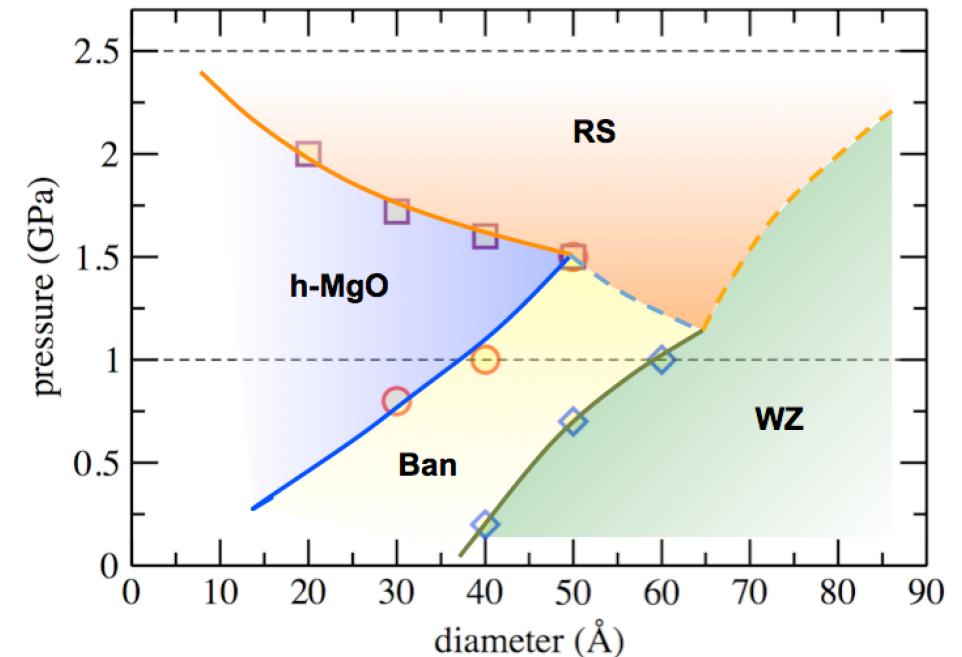
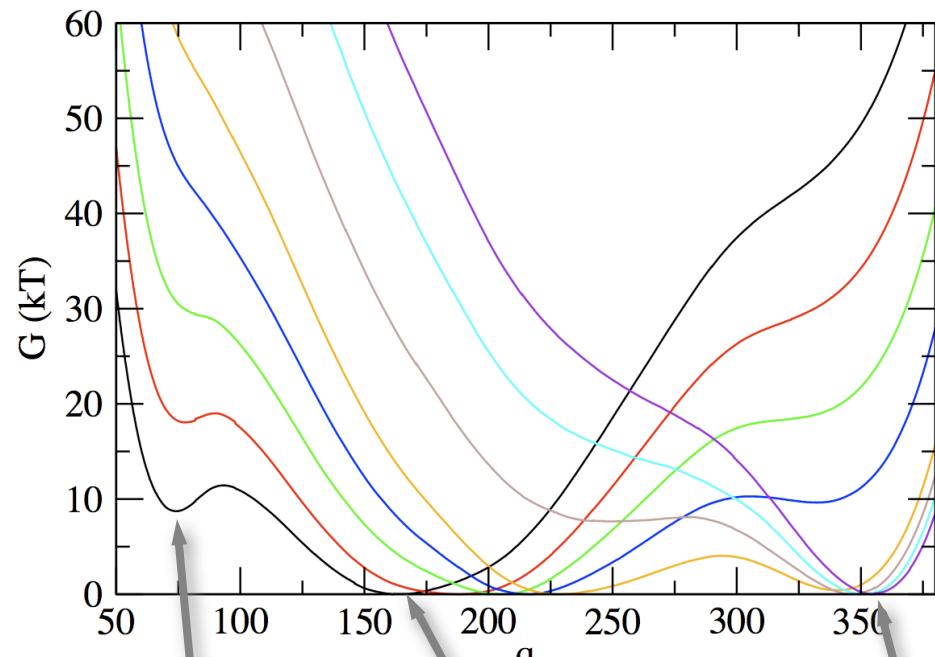
good RC



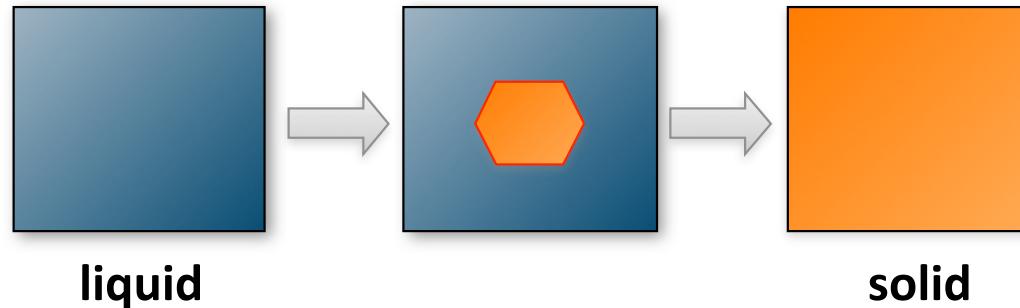
poor RC

From free energy to phase diagram

T=575 K, flat histogram sampling



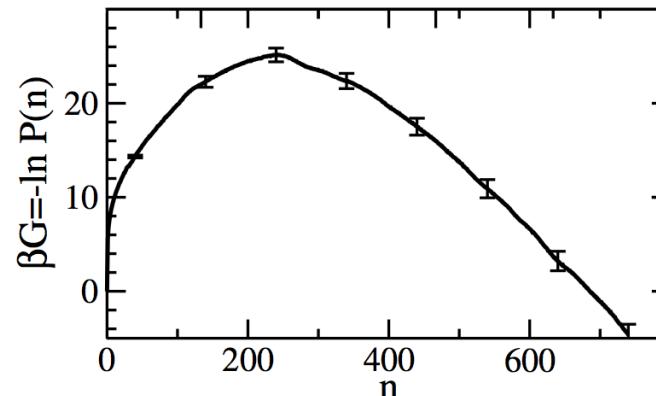
Crystallization in Lennard-Jonesium



$$\mu_l > \mu_s$$

$$F(r) = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \rho_s \Delta \mu$$

Lennard-Jones fluid
25% undercooling

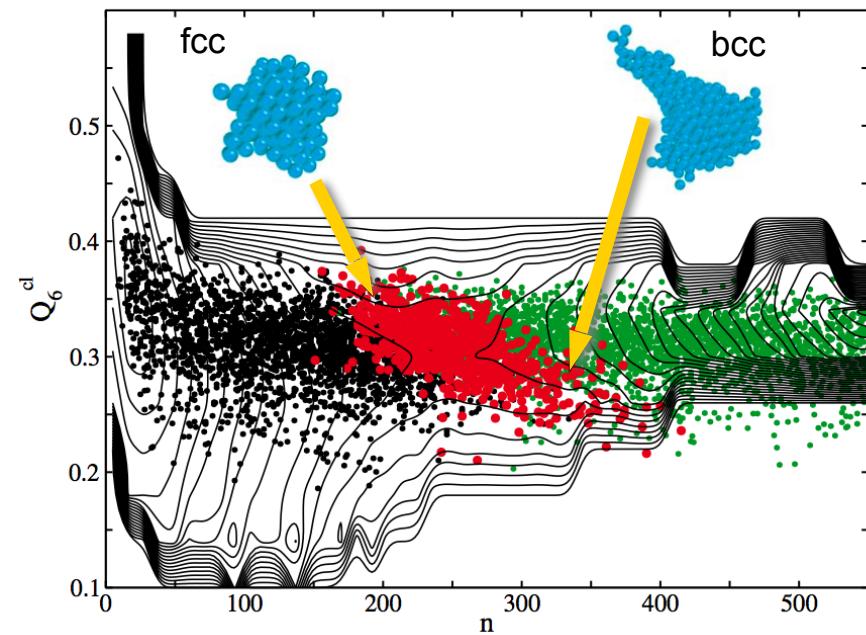
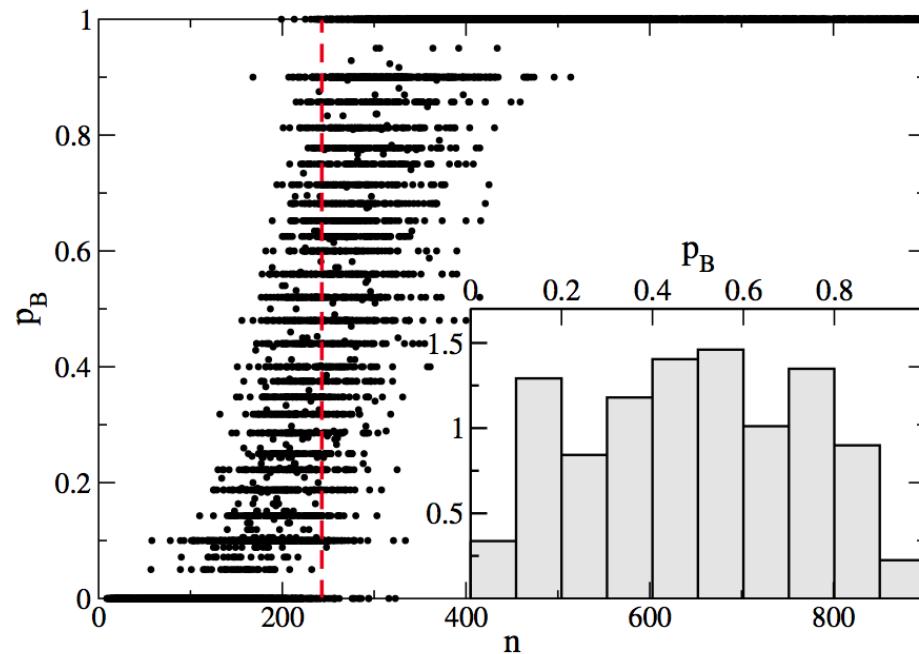


Structure of critical nucleus

critical nucleus $p_{\text{grow}} = p_{\text{shrink}}$

Mandell, McTague, Rahman (1976)

J. D. Honeycutt and H. C. Andersen, CPL 108, 535 (1984); JPC 90, 1585 (1986)



Ostwald's step rule and other rules

Ostwald's rule (1897)

“The phase that nucleates need not be the stable phase, but the one that is closest in free energy to the parent phase ...”



Wilhelm Ostwald (1853-1932)

“Only energy is real - believing in atoms is like worshipping idols...”

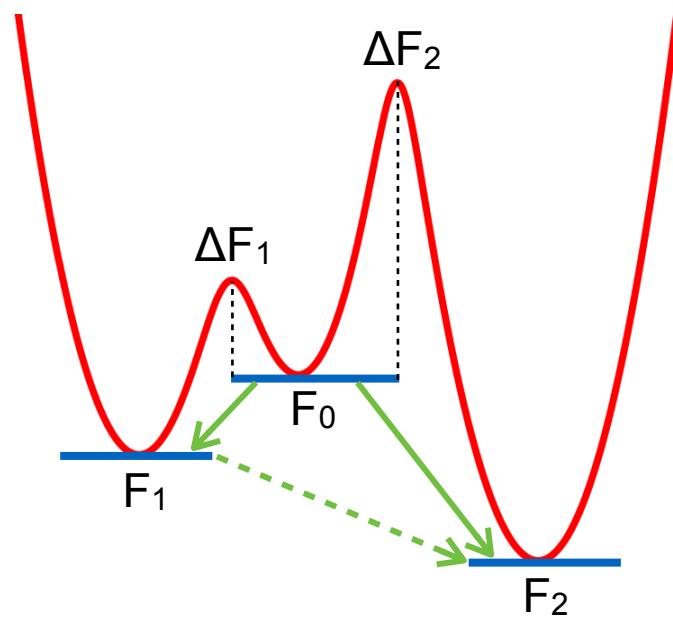
Stranski and Totomatov (1930's)

“The phase that nucleates is the one with the lowest free energy barrier...”

Alexander and McTague (1980)

“On the basis of Landau theory, one would expect the following crystal phases to form easily from the melt:

1. hexagonal (2d)
2. icosahedral
3. bcc crystal

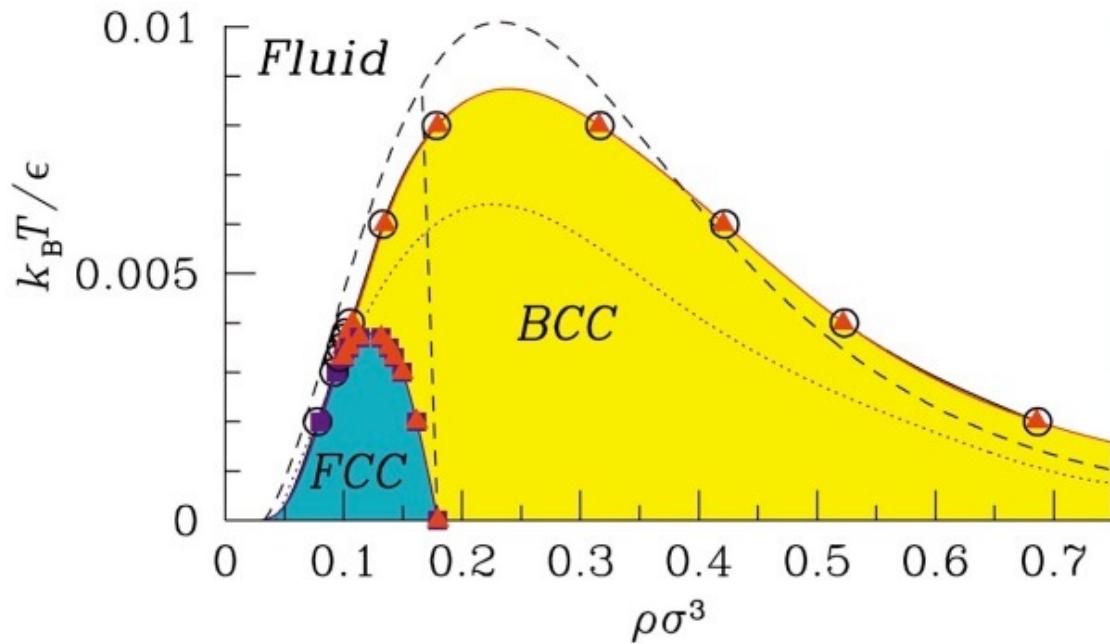


Freezing - Finding the reaction coordinate

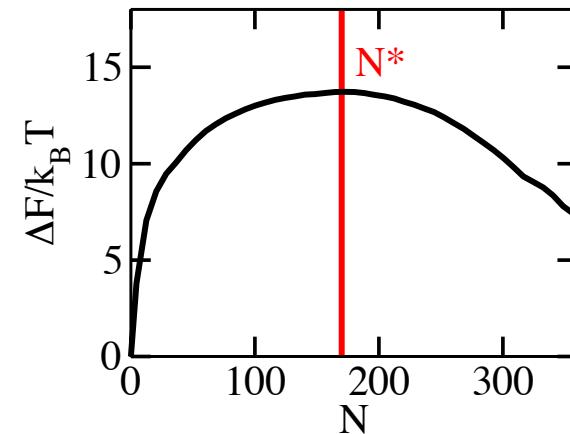
Gaussian core model

Gaussian pair interactions

$$\phi(r) = \varepsilon \exp[-(r/\sigma)^2]$$

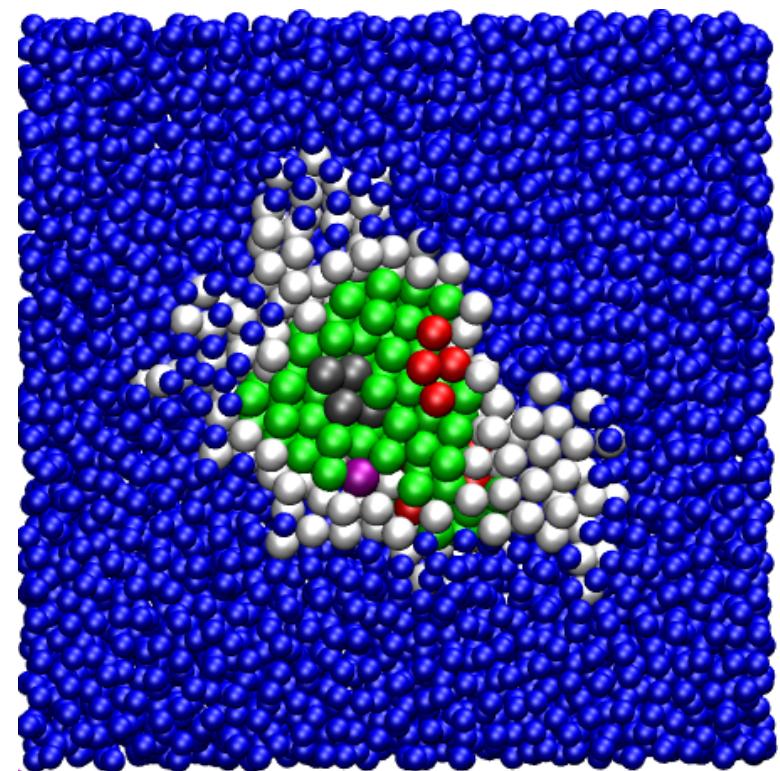
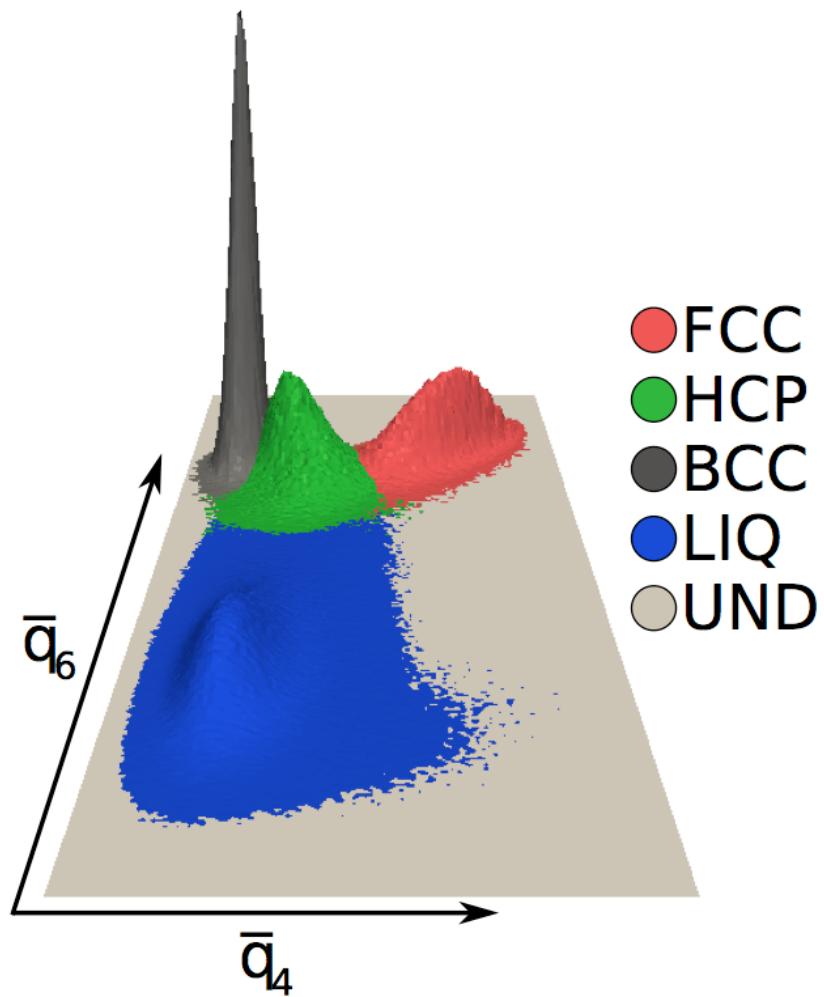


- Reentrant melting
- Low temperature: bcc or fcc



Prestipino, Sajta, Giaquinta, Phys. Rev. E 71, 050102 (2005)
Lechner, Dellago, Bolhuis, Phys. Rev. Lett. 106, 085701 (2011)

Structural information



Likelihood maximization

linear RC

$$q(r) = \sum_i^M \alpha_i q_i(r) + \alpha_0$$

model

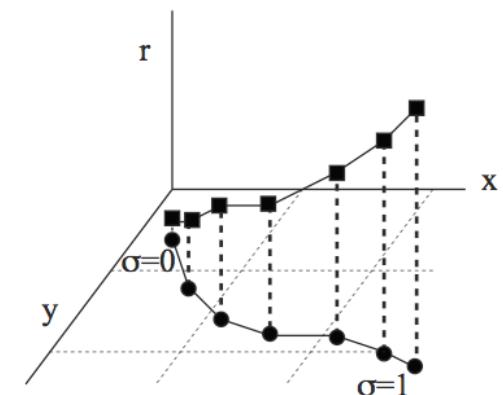
$$p_B[q(r)] = \frac{1}{2}(1 + \tanh[q(r)])$$

likelihood

$$\mathcal{L}(\{\alpha_i\}) = \prod_{r_i \rightarrow B} p_B[q(r_i)] \prod_{r_i \rightarrow A} (1 - p_B[q(r_i)])$$

String method

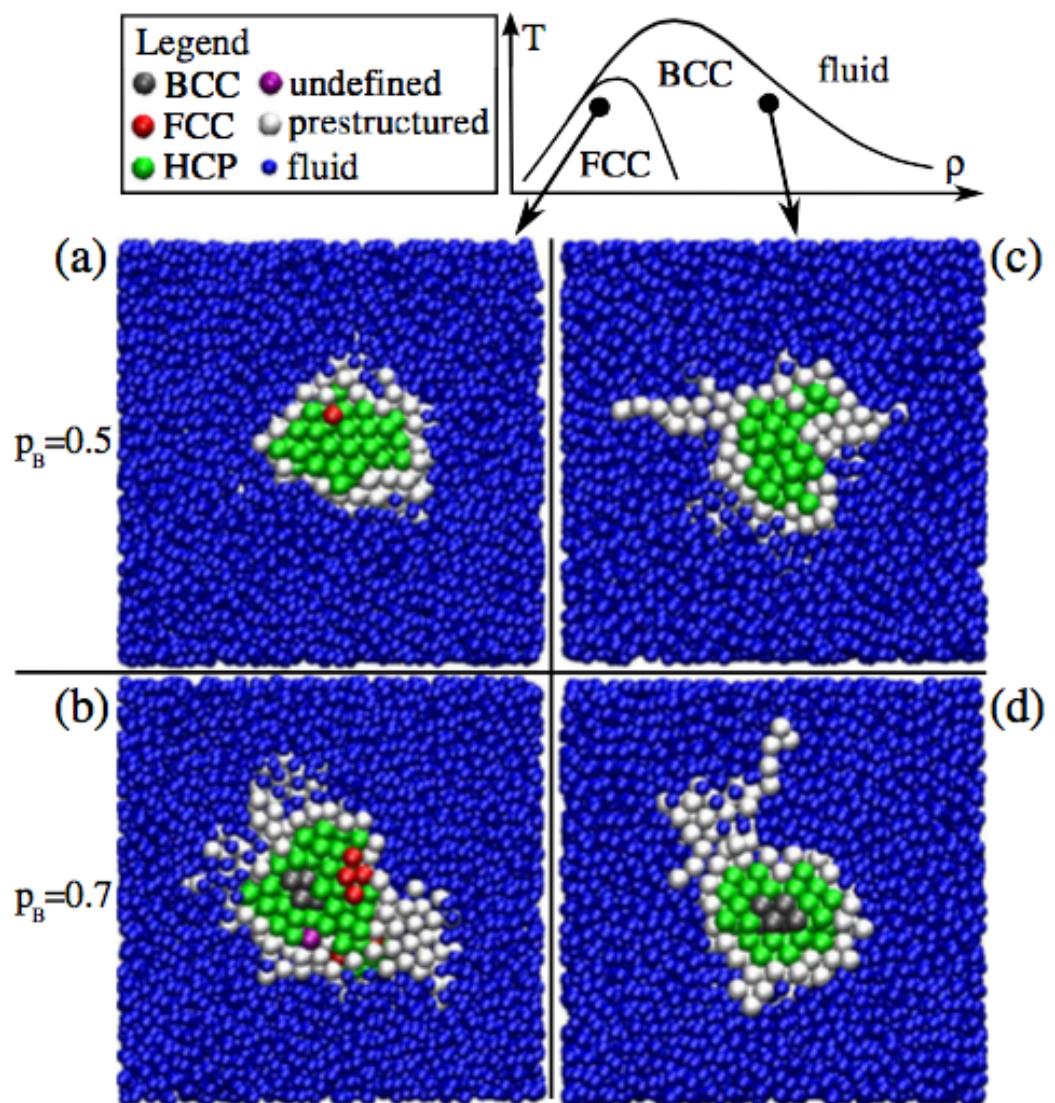
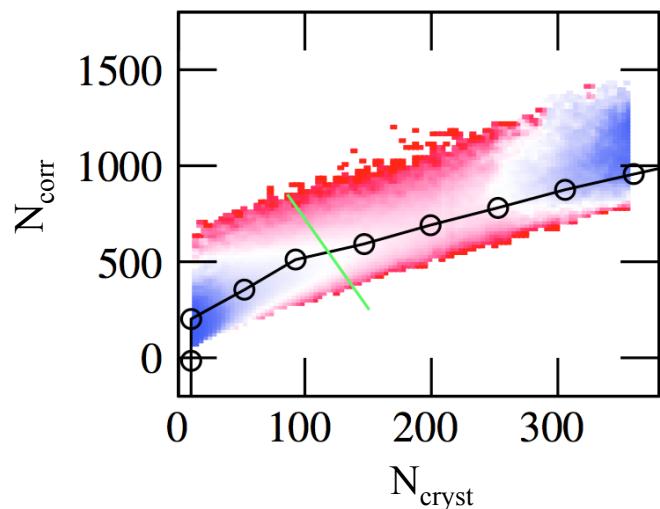
- Non-linear RC
- RC is progress along string
- String is optimized to explain observed data



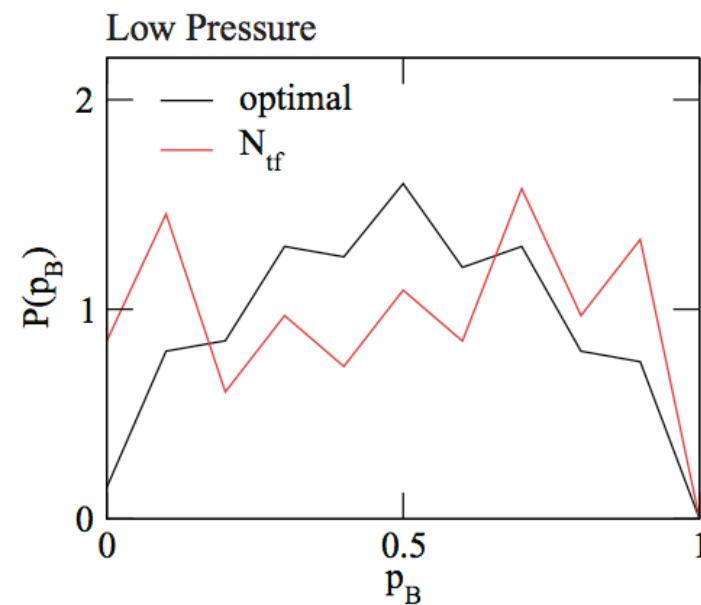
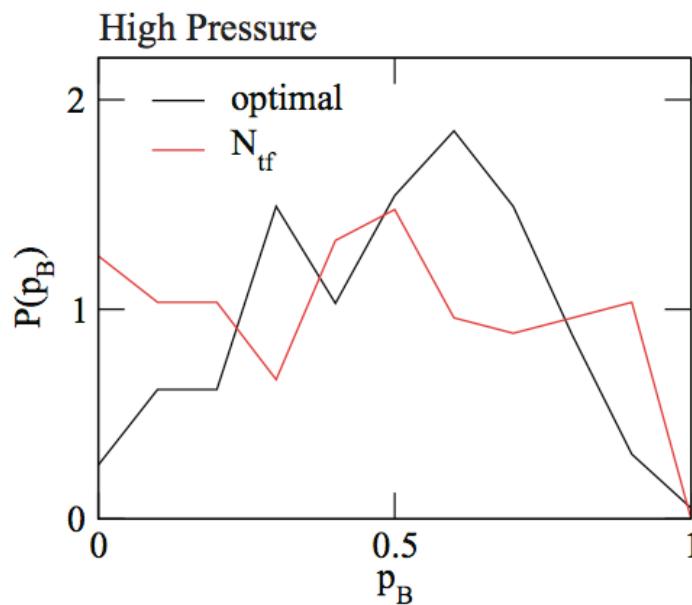
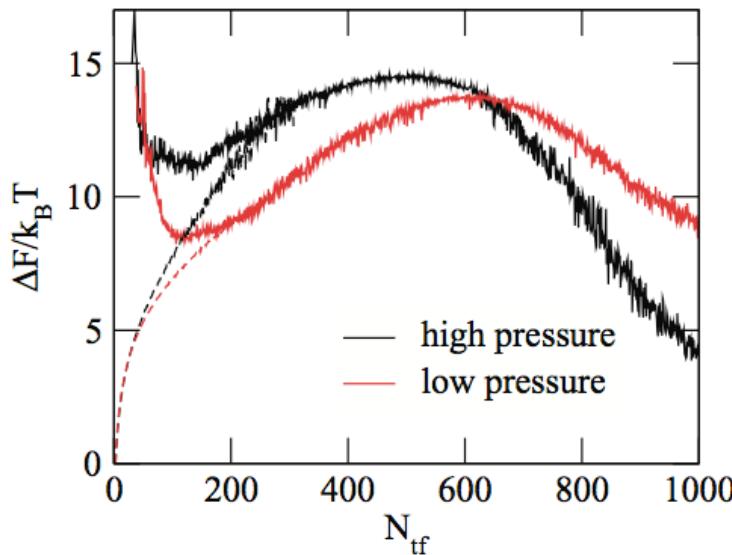
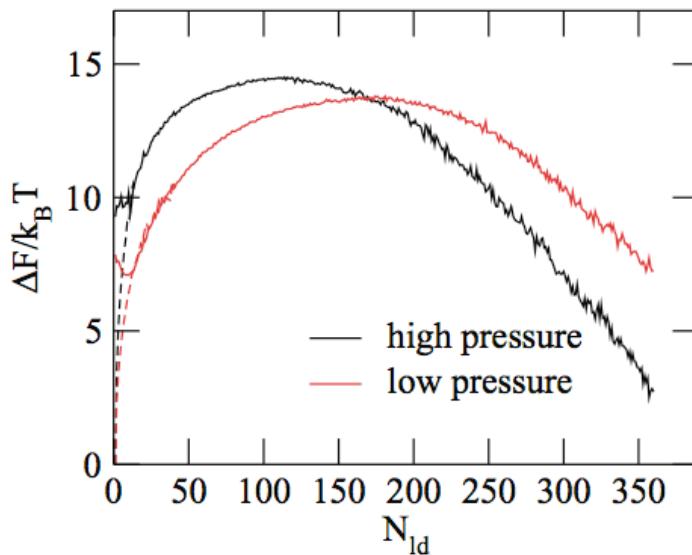
Best reaction coordinate for freezing prestructured surface cloud

N_{cryst} = cluster size of crystalline particles

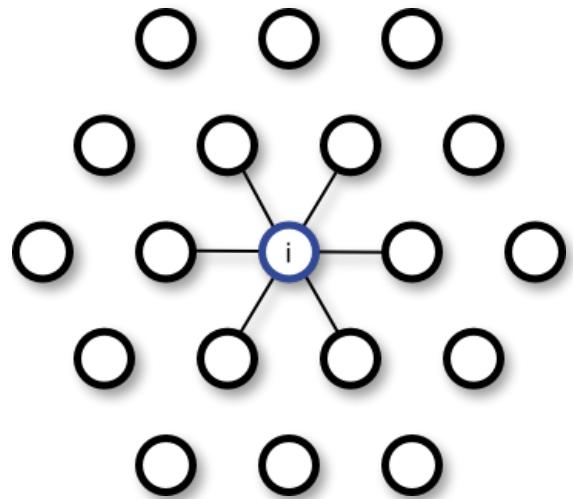
N_{corr} = cluster size correlated particles



Size of largest crystalline cluster as RC?



Optimizing the definition of crystallinity



$$n(x; d_{th}, s_{th}, n_{th})$$

d_{th} = threshold for neighbor distance

s_{th} = threshold for correlation

n_{th} = threshold for number of connections

$$q_{6m}(i) = \frac{1}{n_b} \sum_{j=1}^{n_b} Y_{6m} (\theta(\mathbf{r}_{ij}), \phi(\mathbf{r}_{ij}))$$

$$s_{ij} = \frac{\sum_{m=-6}^6 q_{6m}(i) q_{6m}^*(j)}{\left(\sum_{m=-6}^6 |q_{6m}(i)|^2 \right)^{1/2} \left(\sum_{m=-6}^6 |q_{6m}(j)|^2 \right)^{1/2}}$$

