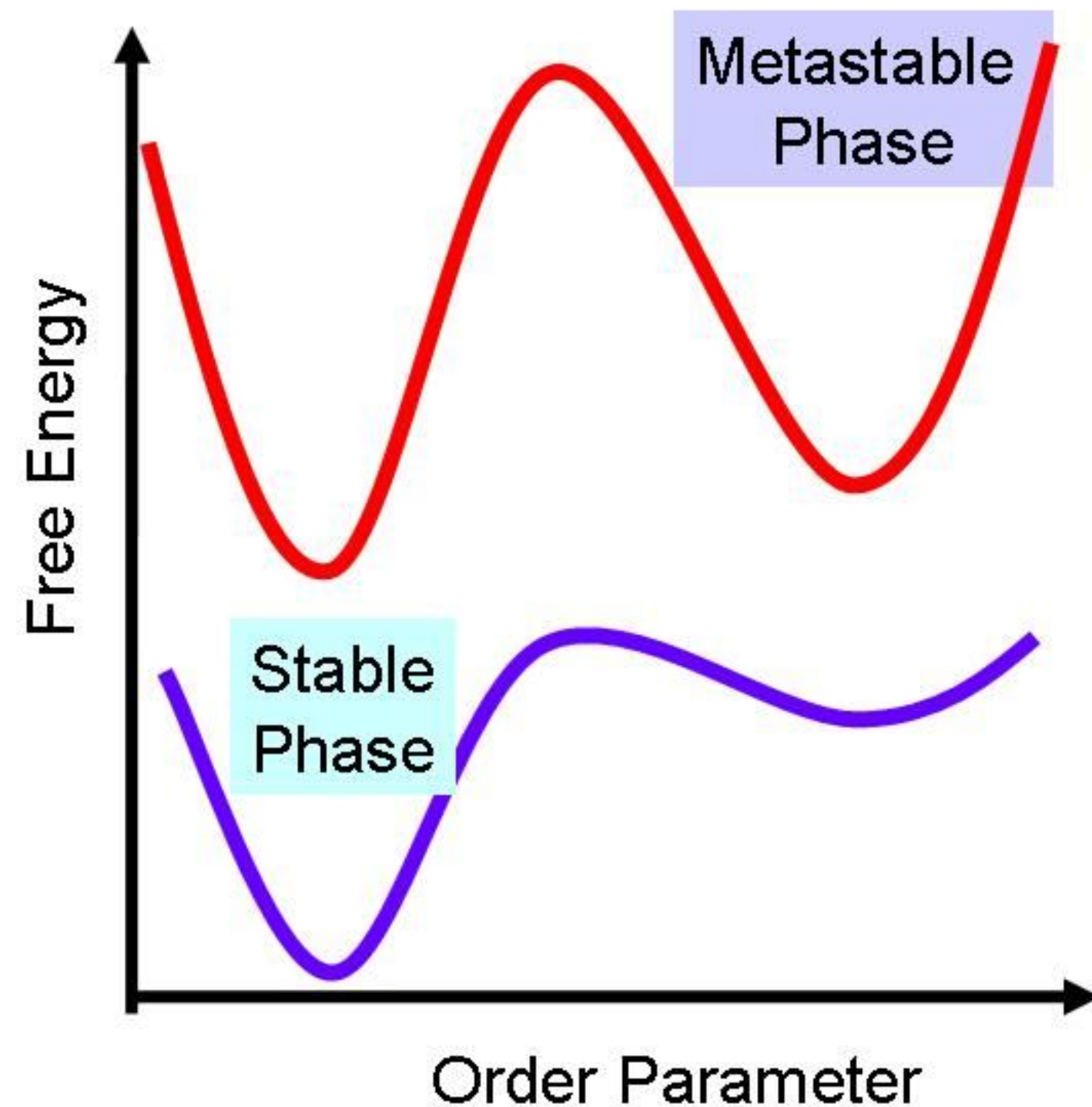


Computational Methods for the Study of Nucleation

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Nucleation Regimes and Computational Methods



Crystallization in the Lennard-Jones Liquid
Weak/moderate supercooling
 $0.8 < T/T_m < 1.0$
Rare-event regime
Classical Nucleation Theory

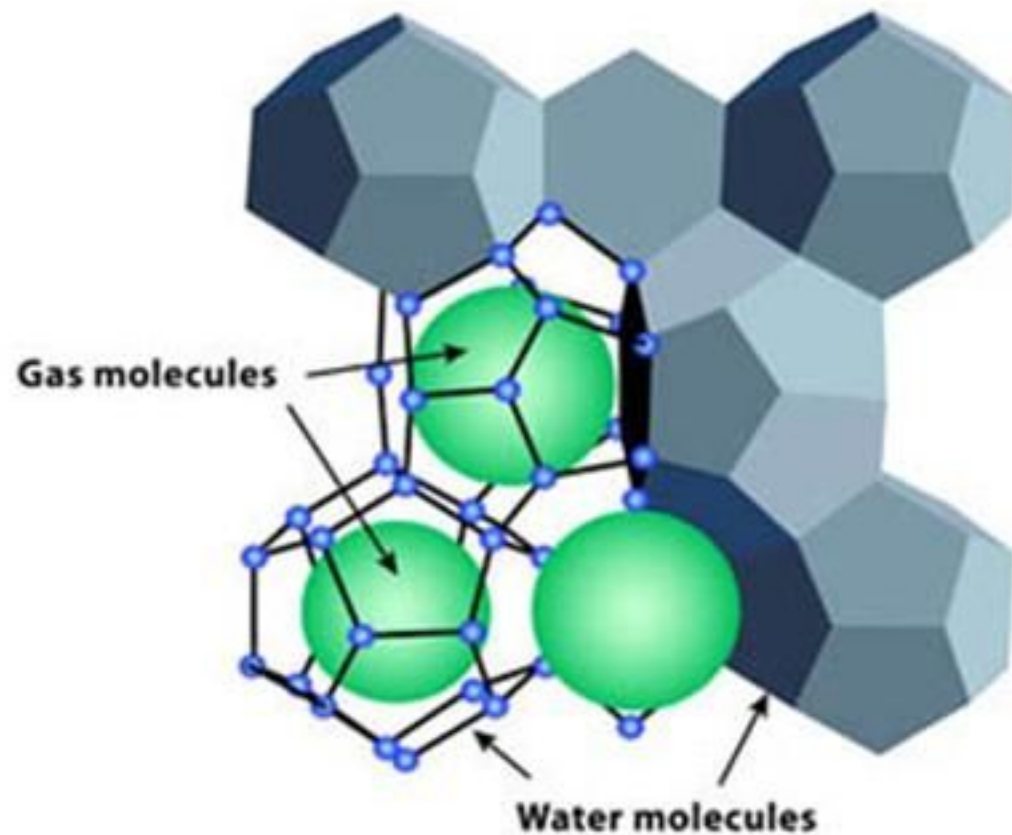
Strong supercooling
 T/T_m about 0.6
“Brute-force” Molecular Dynamics approach of running long trajectories

Molecular Dynamics

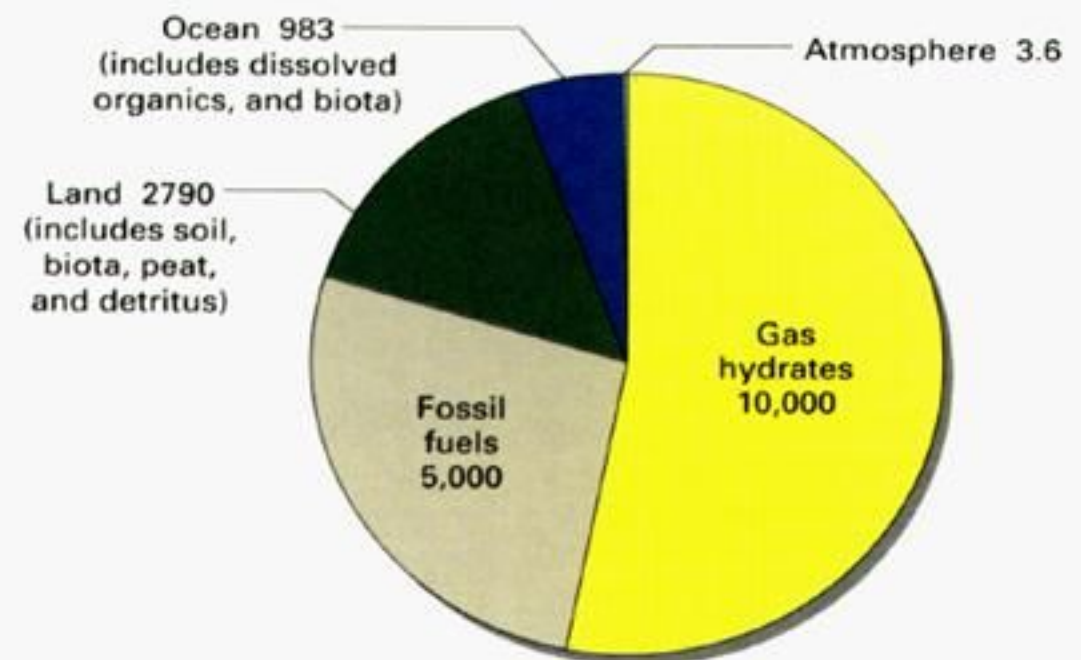
- Insight into order parameters and microscopic reorganisations
- Nucleation mechanism may be different in weak and strong supercooling regimes
- Nucleation is a stochastic process, so we require an ensemble of trajectories to get information on the nucleation rate.
- Must be able to identify the time when a system has nucleated

$$k = \frac{1}{\langle t \rangle V}$$

Methane Hydrate Formation

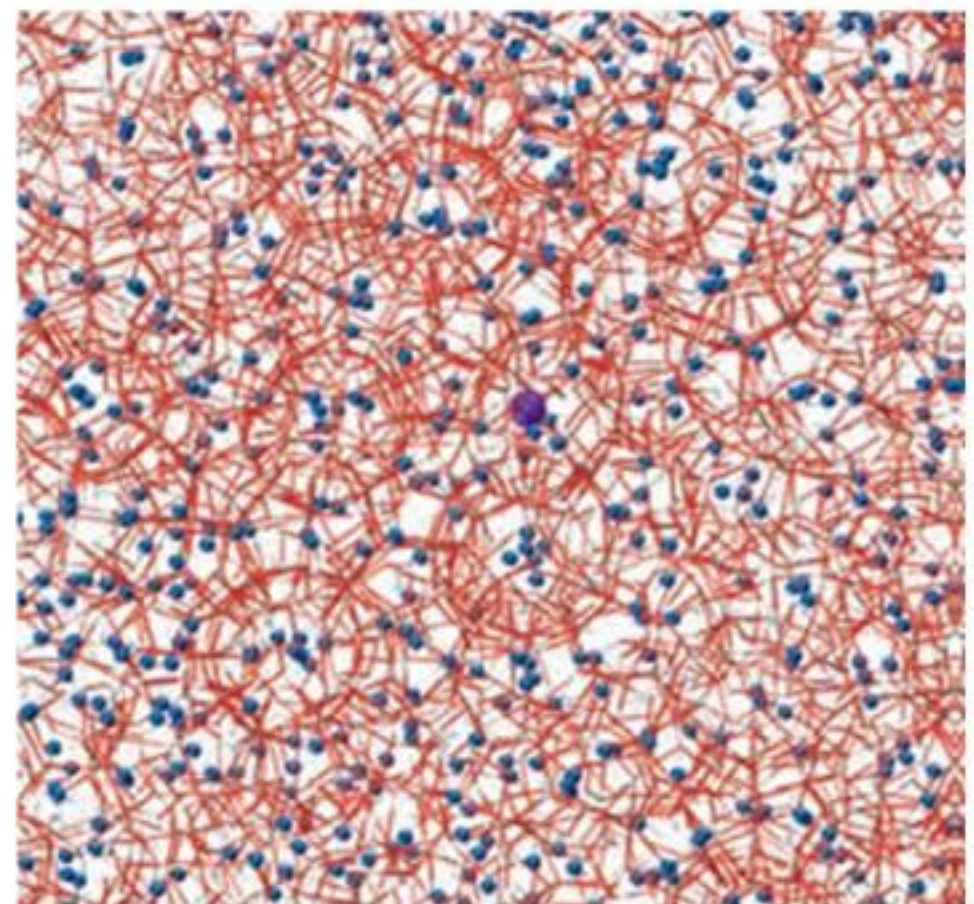
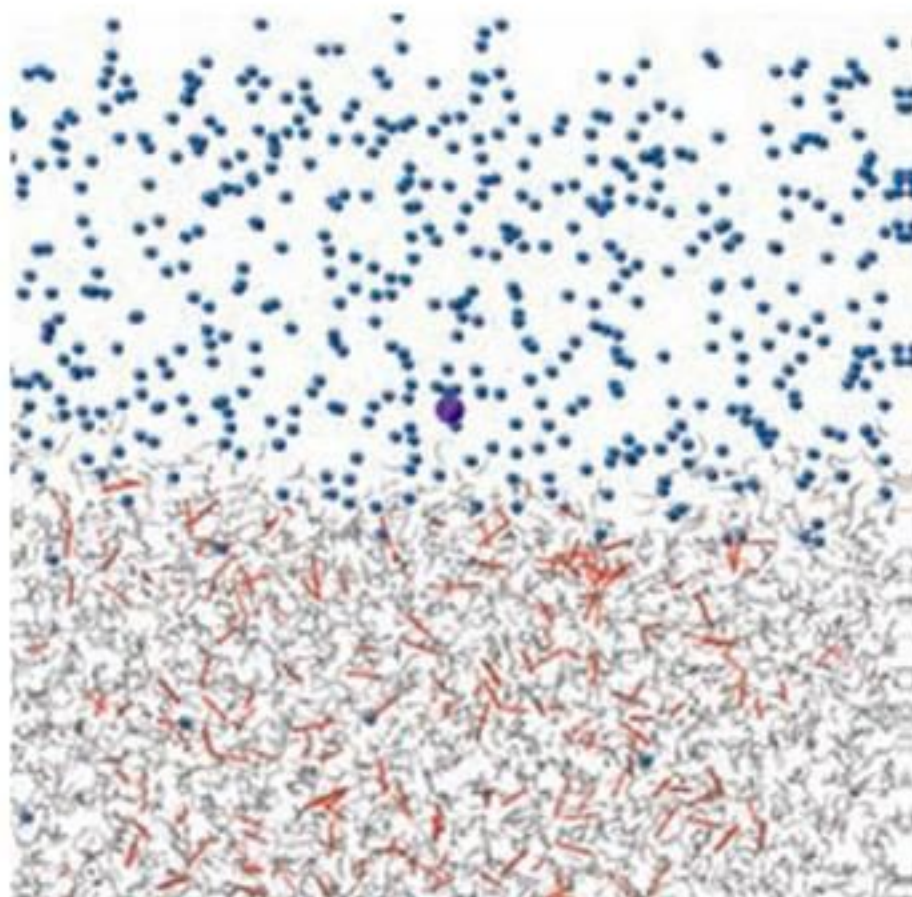


A gas hydrate is a crystalline solid; its building blocks consist of a gas molecule surrounded by a cage of water molecules. Potential energy resource



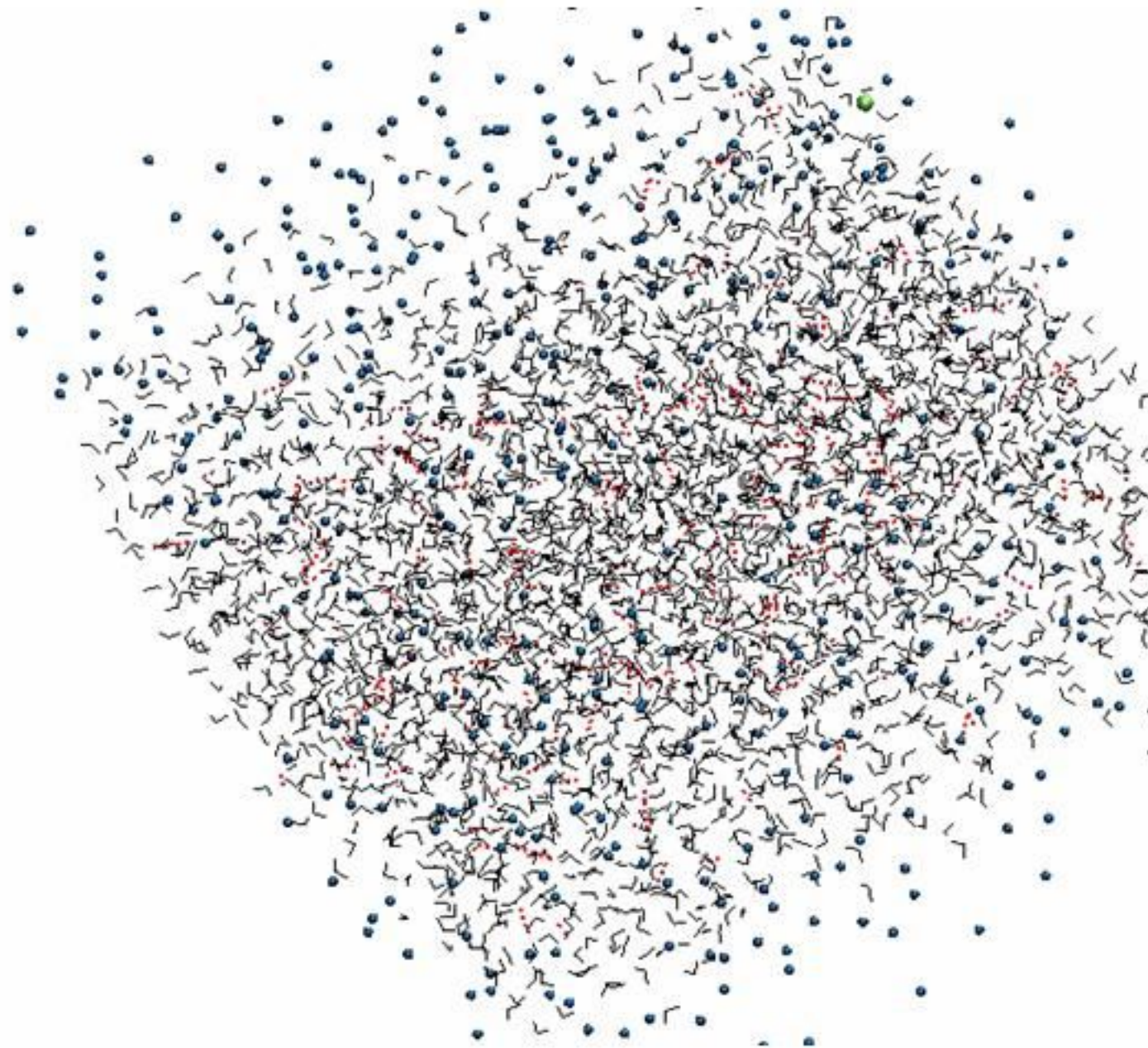
Microsecond Simulations of Spontaneous Methane Hydrate Nucleation and Growth

(Walsh et al, Science, **326**, 1095 (2009))

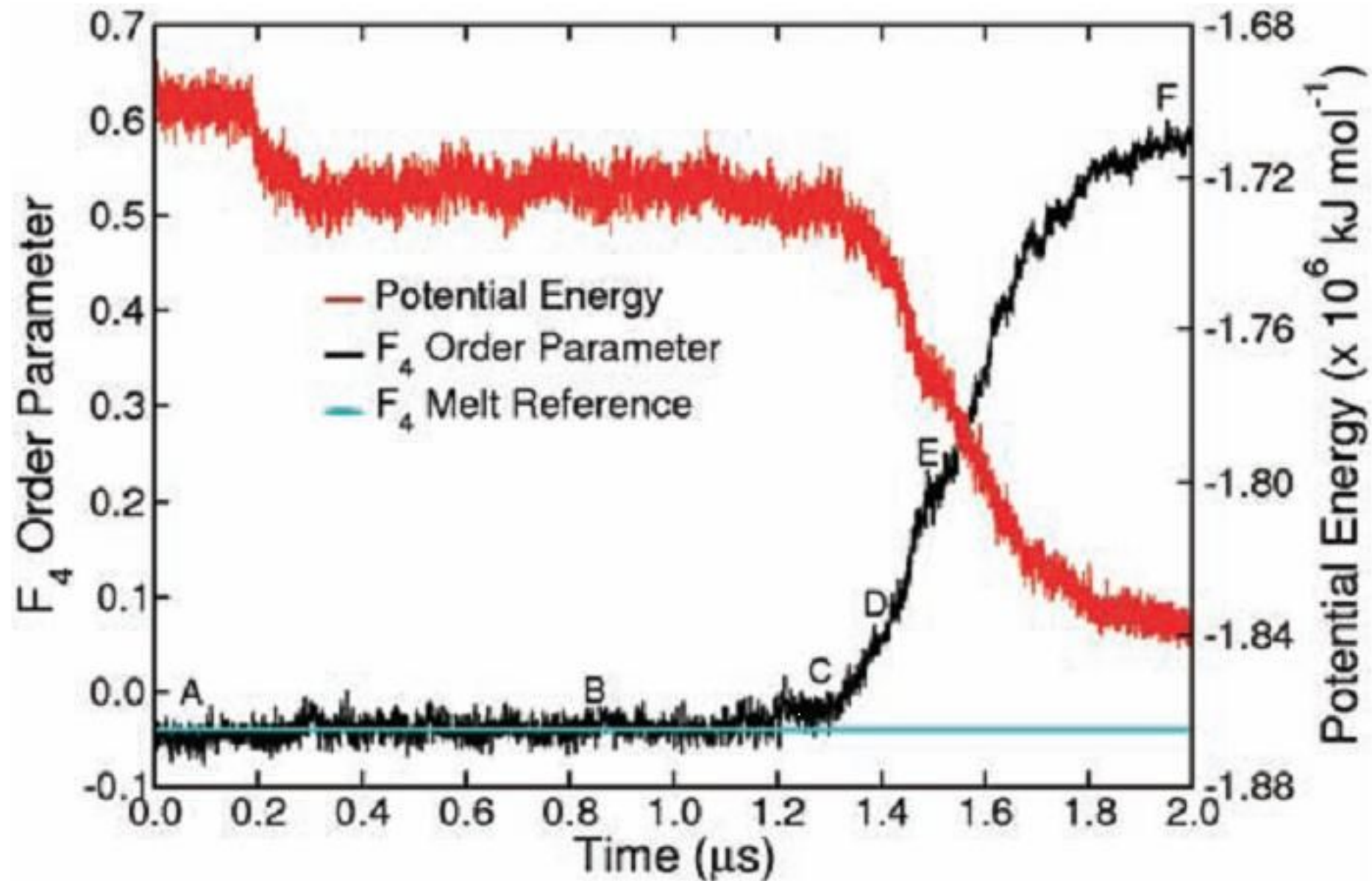


250K, 50 MPa, 0.0015 of methane mole fraction

Formation of S₁ Clathrate Structure



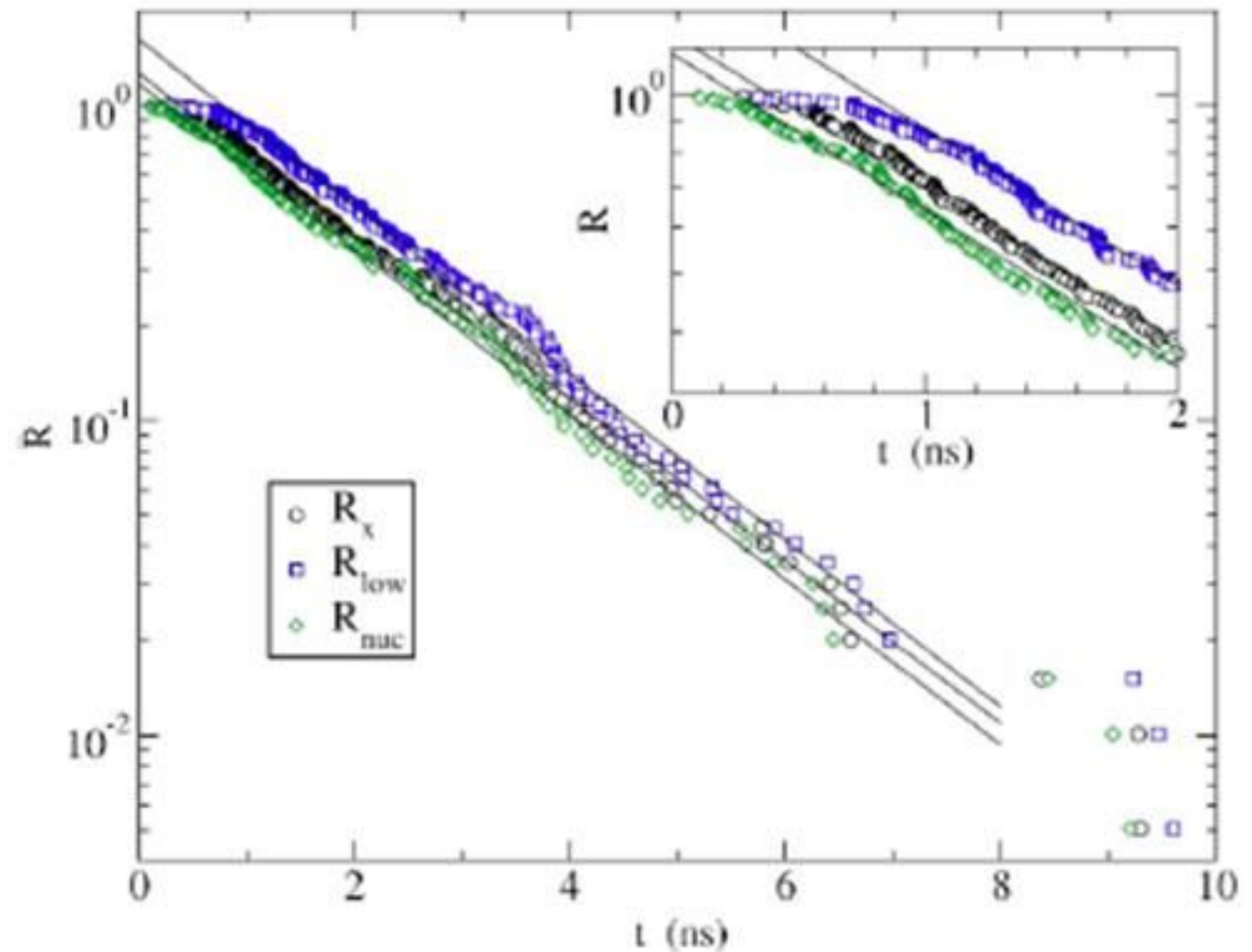
Order Parameters and Energy



Nucleation Rates from MD

Crystallization of deeply supercooled liquid silica,
I. Saika-Voivod, P. H. Poole and R. K. Bowles, **124**,
224709 (2006)

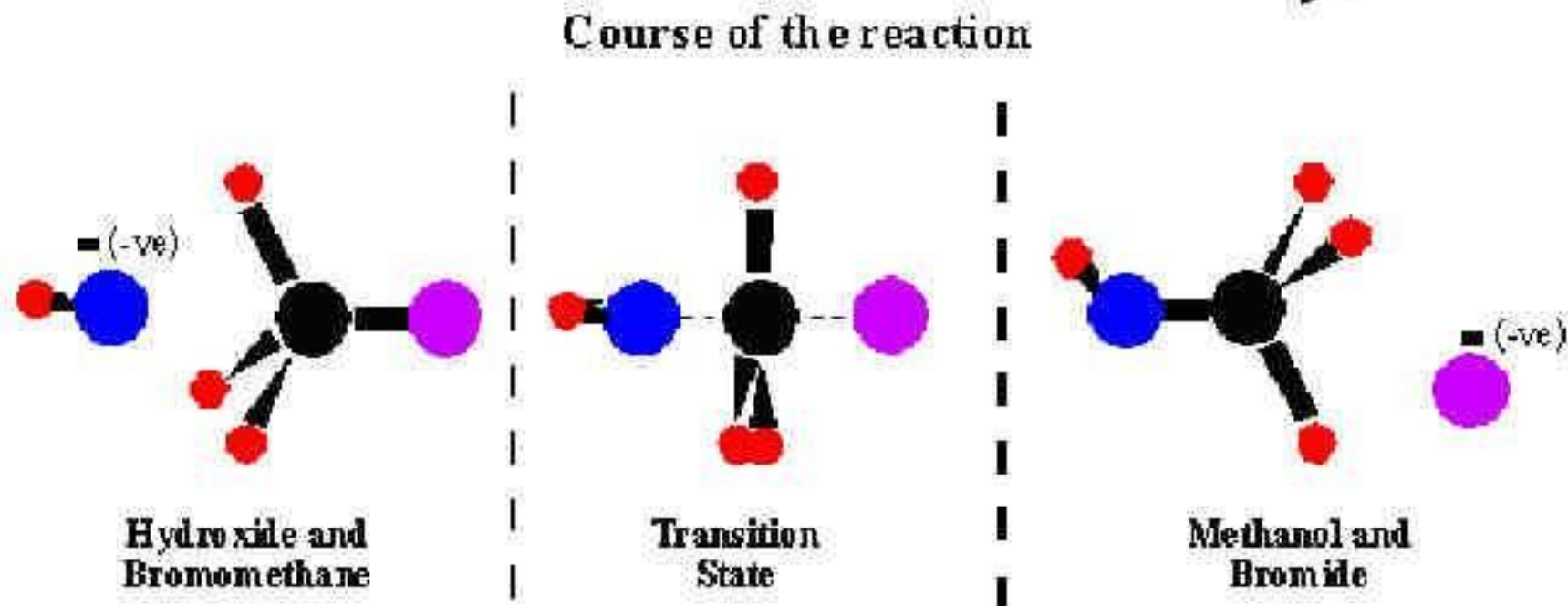
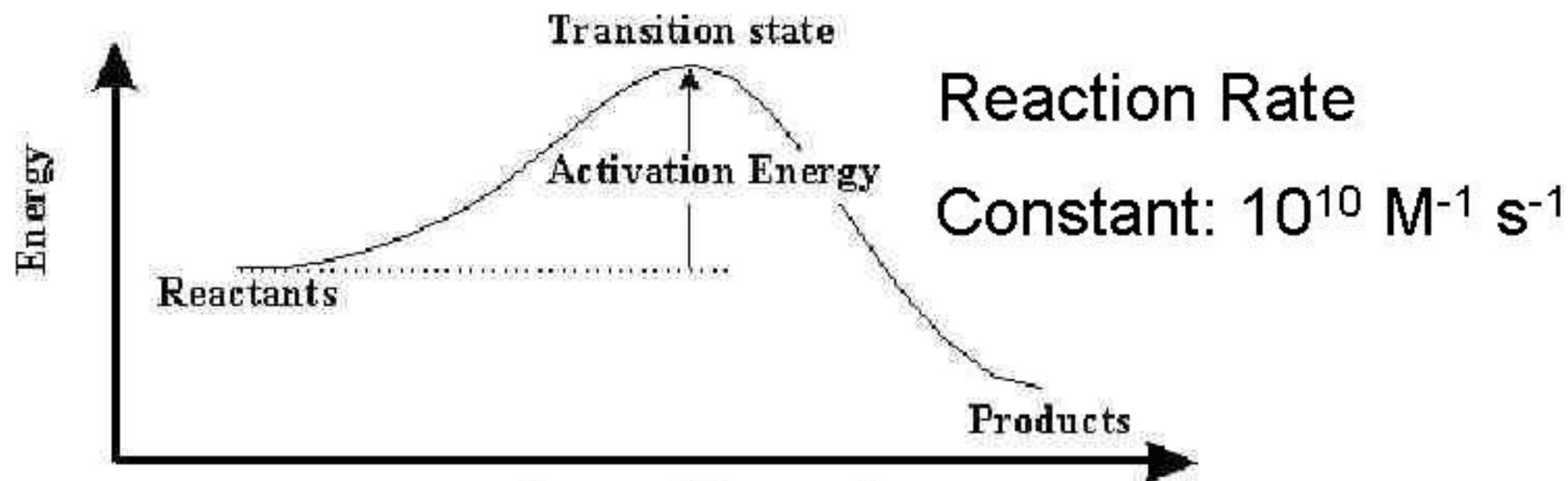
$$\ln[R(t)] = -JV(t - t_0)$$



Rare Event Simulations

- **Transition State Theory**
 - Gas-Phase/Condensed Phase Reactions
 - Factor reaction rate into the product of a dynamical term and an equilibrium term
 - Must define a reaction coordinate and a transition state
- **Bennett-Chandler Formulation**
 - Must define a reaction coordinate
 - Combining Classical Nucleation Theory with Bennett-Chandler Formulation of Transition State Theory
- **Sampling Pathways:** multiple order parameters /pathways/ no quasi-equilibrium assumption

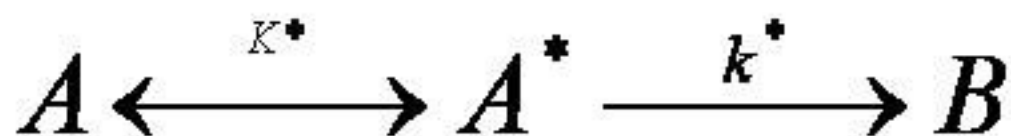
Chemical Kinetics



Transition State Theory

Quasi-equilibrium between reactant(A) and transition state(A*) with equilibrium constant K^* (Eyring (1935), M. Polyani)

Transformation of A* to B with determined by first-order rate constant k^* . Assumed to be the product of some characteristic vibration frequency ν , associated with unstable mode, and transmission coefficient k



$$\frac{d[B]}{dt} = \kappa \nu [A^*] = \kappa \nu K^* [A] = \kappa \nu \exp(-\Delta G / kT) [A]$$

$$k = \kappa \nu \exp(-\Delta G / kT)$$

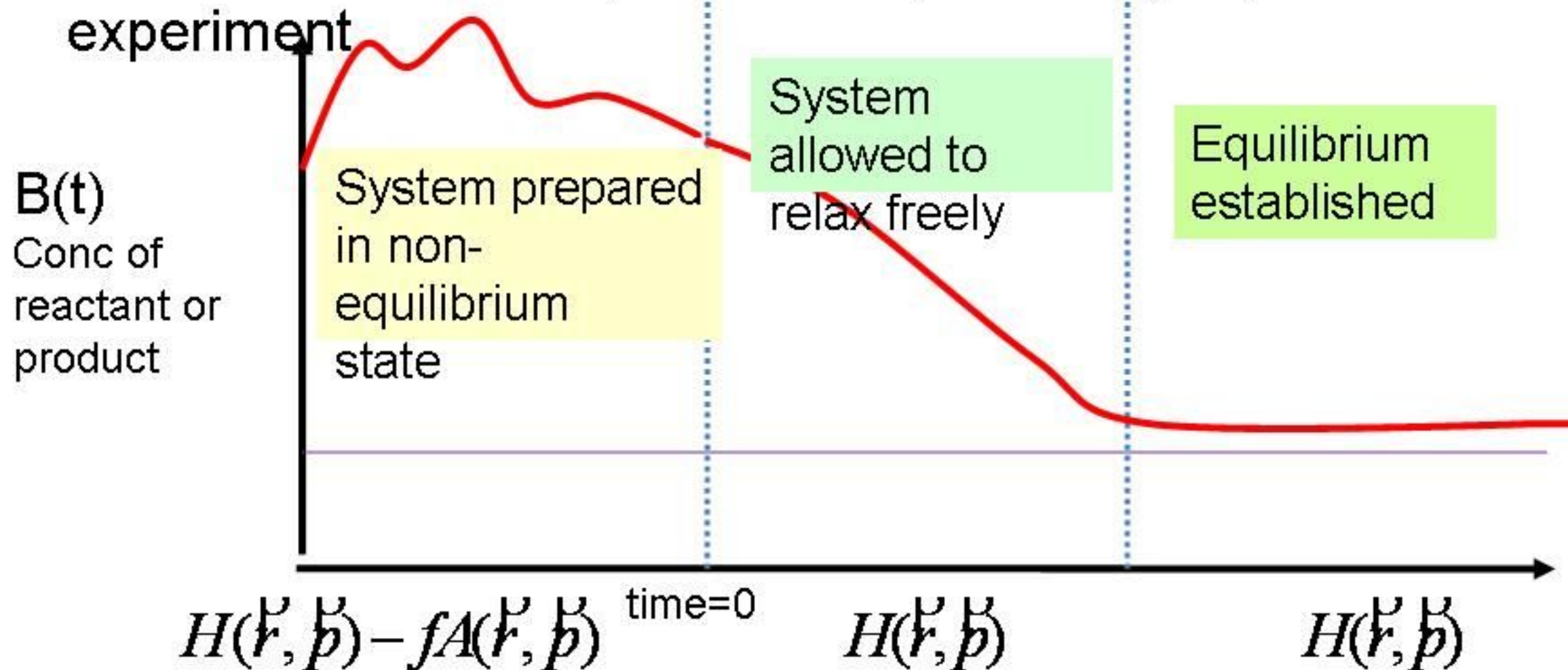
Kinetic prefactor
Very short-time
dynamics

Probability for being on barrier top:
Use equilibrium methods

Bennett-Chandler Formulation of Transition State Theory(1): Classical Linear Response Theory

Apply a perturbation to the system that results in a small deviation from equilibrium.

Chemical Kinetics: Temperature or pressure jump experiment



Bennett-Chandler Formulation (2): Onsager's regression hypothesis

The relaxation of macroscopic non-equilibrium disturbances is governed by the same dynamics as the regression of spontaneous microscopic fluctuations in the equilibrium system

$$\bar{B}(t) - \langle B \rangle = \beta f \left[\langle A(0)B(t) \rangle - \langle A \rangle \langle B \rangle \right]$$

$$\Delta \bar{B}(t) = \beta f \left[\langle \delta A(0) \delta B(t) \rangle \right]$$

Macroscopic Relaxation:
Deviation of conc. From
equilibrium at time t

Equilibrium Time-correlation
function:
Need a dynamical variable
proportional to concentration of
reactant

Bennett-Chandler Formulation(3)



$$\frac{dc_A(t)}{dt} = -k_{A \rightarrow B} c_A(t) + k_{B \rightarrow A} c_B(t)$$

Total number of molecules

$$\frac{d[c_A(t) + c_B(t)]}{dt} = 0$$

$$\frac{dc_B(t)}{dt} = +k_{A \rightarrow B} c_A(t) - k_{B \rightarrow A} c_B(t)$$

Equilibrium:

$$\frac{\langle c_B \rangle}{\langle c_A \rangle} = \frac{k_{A \rightarrow B}}{k_{B \rightarrow A}} = K$$

$$\mathcal{E}_A(t) = \mathcal{E}_B(t) = 0$$

Make a small perturbation and observe the time-dependent variation of concentrations

$$c_A(t) = \langle c_A \rangle + \Delta c_A(t)$$

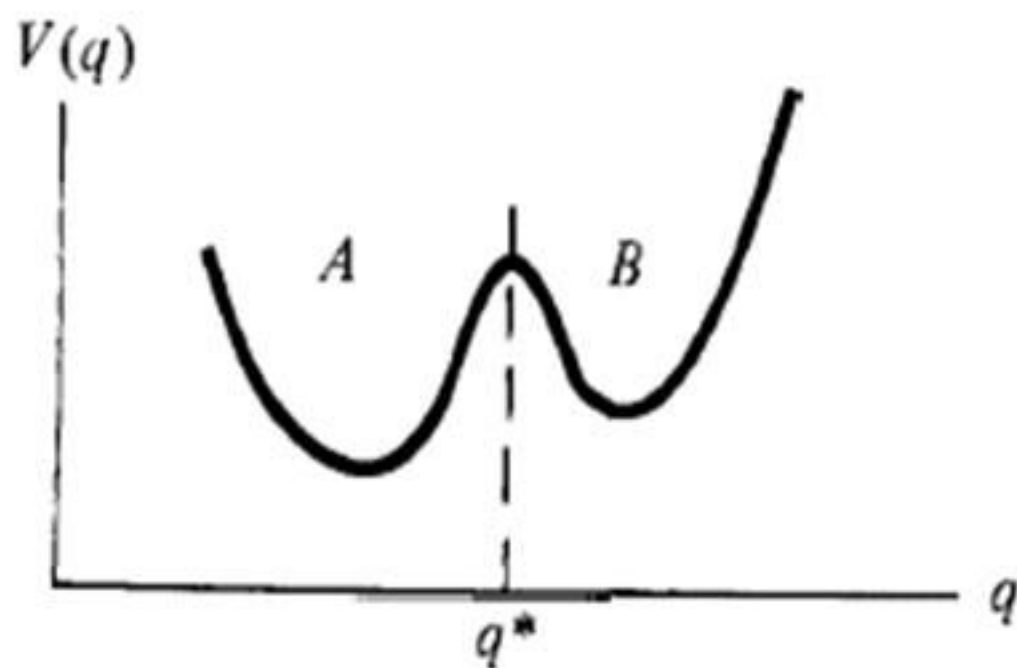
$$c_B(t) = \langle c_B \rangle - \Delta c_A(t)$$

Bennett-Chandler Formulation(4)

$$\frac{d\Delta c_A(t)}{dt} = -k_{A \rightarrow B} \Delta c_A(t) - k_{B \rightarrow A} \Delta c_A(t)$$

$$\Delta c_A(t) = \Delta c_A(0) \exp[-(k_{A \rightarrow B} + k_{B \rightarrow A})t] = \Delta c_A(0) \exp[-t/\tau]$$

$$\tau = (k_{A \rightarrow B} + k_{B \rightarrow A})^{-1} = k_{A \rightarrow B}^{-1} \left(1 + \frac{\langle c_A \rangle}{\langle c_B \rangle}\right)^{-1} = \frac{\langle c_B \rangle}{k_{A \rightarrow B}}$$



$$\overline{n_A(t)} \propto c_A(t)$$

$$n_A(t) = H_A[q(t)]$$

$$H_A[z] = 1, \quad z < q^*$$

$$= 0, \quad z > q^*$$

Bennett-Chandler Formulation(5)

Fluctuation-dissipation theorem $n_A(t) = H_A[q(t)]$

$$\Delta c_A(t) / \Delta c_A(0) = \langle \delta n_A(0) \delta n_A(t) \rangle / \langle (\delta n_A)^2 \rangle$$

$$\exp(-t/\tau_{rxn}) = \langle \delta n_A(0) \delta n_A(t) \rangle / \langle (\delta n_A)^2 \rangle$$

$$\langle H_A^2 \rangle = \langle H_A \rangle = x_A \quad \langle H_A \rangle = x_A = \langle c_A \rangle / (\langle c_A \rangle + \langle c_B \rangle)$$

$$\langle (\delta H_A)^2 \rangle = x_A(1 - x_A)$$

$$\equiv x_A x_B$$

$$\exp(-t/\tau_{rxn}) = (x_A x_B)^{-1} [\langle H_A(0) H_A(t) \rangle - x_A^2]$$

Bennett-Chandler Formulation(6)

$$\exp(-t/\tau_{rxn}) = (x_A x_B)^{-1} [\langle H_A(0) H_A(t) \rangle - x_A^2]$$

Taking the time derivative:

$$\tau_{rxn}^{-1} \exp(-t/\tau_{rxn}) = -(x_A x_B)^{-1} \langle H_A(0) \dot{H}_A(t) \rangle$$

Stationarity $-\langle H_A(0) \dot{H}_A(t) \rangle = \langle \dot{H}_A(0) H_A(t) \rangle$

$$\dot{H}_A[q] = \dot{q} \frac{d}{dq} H_A[q] = -\dot{q} \delta(q - q^*).$$

$$\begin{aligned} -\langle H_A(0) \dot{H}_A(t) \rangle &= -\langle \dot{q}(0) \delta[q(0) - q^*] H_A[q(t)] \rangle \\ &= \langle \dot{q}(0) \delta[q(0) - q^*] H_B[q(t)] \rangle, \end{aligned}$$

Bennett-Chandler Formulation(7)

$$\tau_{rxn}^{-1} \exp(-t/\tau_{rxn}) = (x_A x_B)^{-1} \langle v(0) \delta[q(0) - q^*] H_B[q(t)] \rangle$$

$$\tau_{rxn}^{-1} = (x_A x_B)^{-1} \langle v(0) \delta[q(0) - q^*] H_B[q(\Delta t)] \rangle$$

Flux-position correlation function for rate
If $t_{rxn} \gg t \gg t_{mol}$

$$k_{BA} = x_A^{-1} \langle v(0) \delta[q(0) - q^*] H_B[q(\Delta t)] \rangle$$

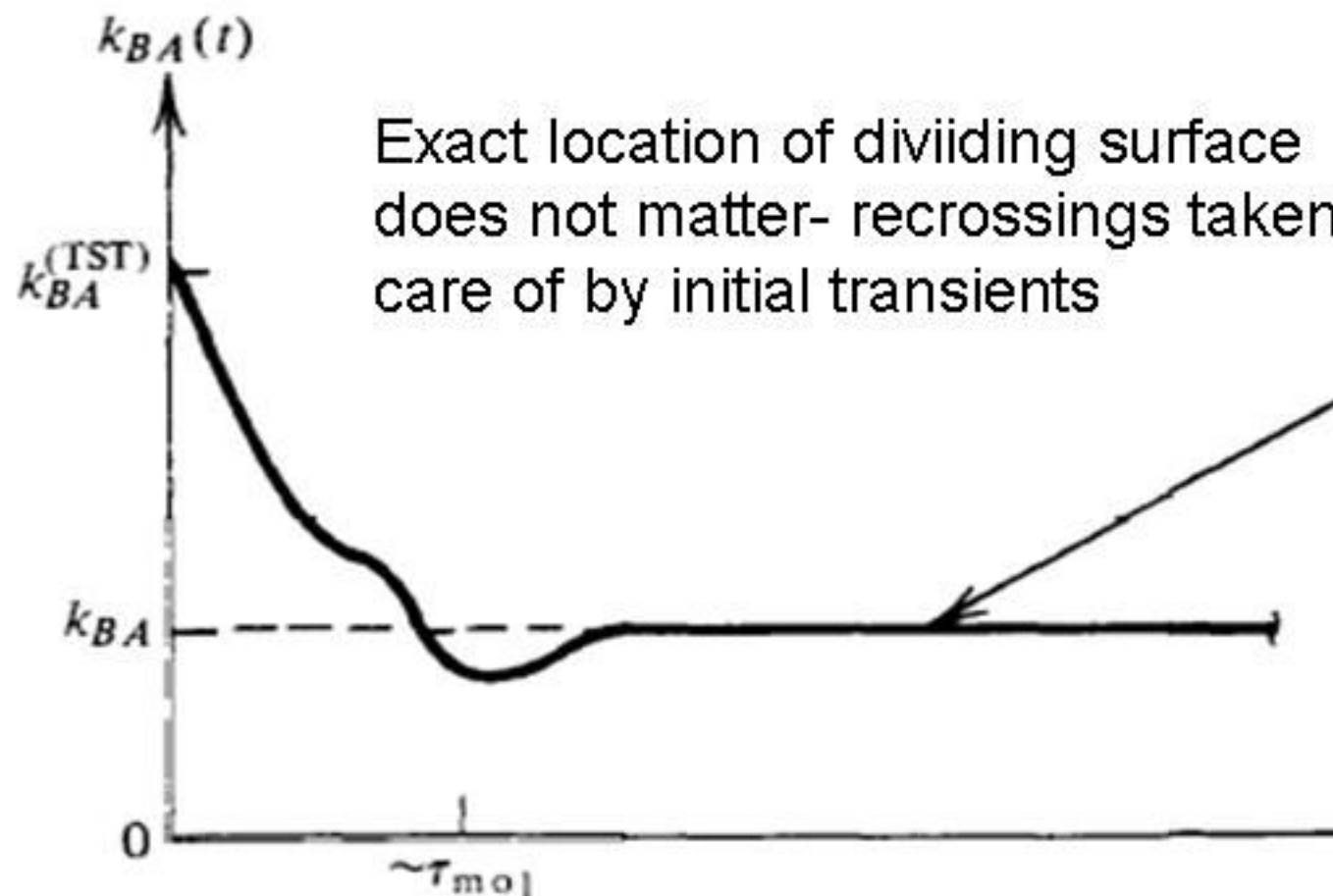
$$k_{A \rightarrow B} = \frac{\langle v(0) \delta(q(0) - q^*) H_B(q(t)) \rangle}{\langle \delta(q(0) - q^*) \rangle} \times \frac{\langle \delta(q(0) - q^*) \rangle}{\langle H_A(q(t)) \rangle}$$

Bennett-Chandler Formulation(8)

$$k_{A \rightarrow B} = \frac{\langle v(0) \delta(q(0) - q^*) H_B(q(t)) \rangle}{\langle \delta(q(0) - q^*) \rangle} \times \frac{\langle \delta(q(0) - q^*) \rangle}{\langle H_A(q(t)) \rangle}$$

Dynamical prefactor- evaluate using short MD trajectories starting at barrier

Probability of observing system at the barrier top- evaluate as a relative free energy by umbrella sampling



Umbrella Sampling

- Free energy curves as a function of an order parameter

$$F(Q) = -kT \ln P(Q)$$

- Bistable free energy curves: MC or MD simulation will sample either the stable or metastable free energy basin, depending in the initial conditions.
- To judge the relative free energies of the two phases it is essentially to sample the intermediate configurations and transform continuously from one phase to another along the nucleation path
- Use Biasing or Umbrella potential that favours intermediate configurations with a low Boltzmann weight

NPT Ensemble

$$Z = \int \exp[-\beta(U(x) + PV)] dx dV$$

$$P(Q) = (1/Z) \int \delta(Q(x) - Q) \exp[-\beta(U(x) + PV)] dV dx$$

In the presence of a biasing potential $W(Q)$

$$\begin{aligned} P_W(Q) &= (1/Z_W) \int \delta(Q(x) - Q) \exp[-\beta(U(x) + PV + W(Q))] dV dx \\ &= (Z/Z_W) \exp(-\beta W(Q)) (1/Z) \int \delta(Q(x) - Q) \exp[-\beta(U(x) + PV)] dV dx \end{aligned}$$

Free energy curve

$$F(Q) = -kT \ln P_W(Q) - W(Q) + kT \ln(Z/Z_W)$$

Choosing the biasing potential:

Free energy curve

$$F(Q) = -kT \ln P_W(Q) - W(Q) + kT \ln(Z / Z_W)$$

Flat distribution :

$$W(Q) = -F(Q)$$

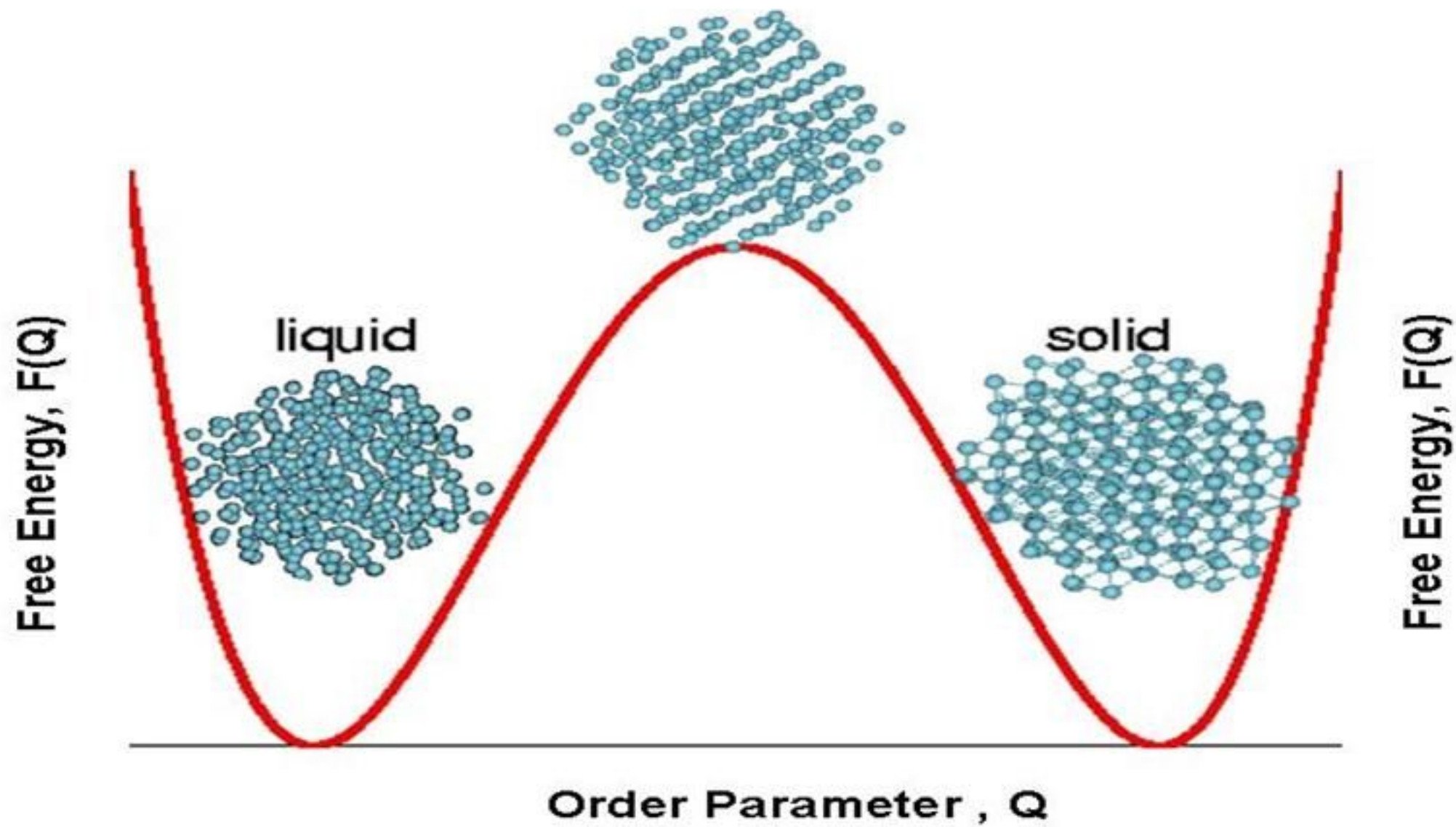
Harmonic window potentials :

$$W(Q_i) = 0.5k_i(Q - Q_i)^2$$

Sequential construction of $W(Q)$:

$$W(Q) = \sum_{i=0} a_i Q^i$$

Solid-Liquid Transformation: Using Umbrella Sampling



Van Duijneveldt and Frenkel, 1992
Lynden-Bell et al, 1993

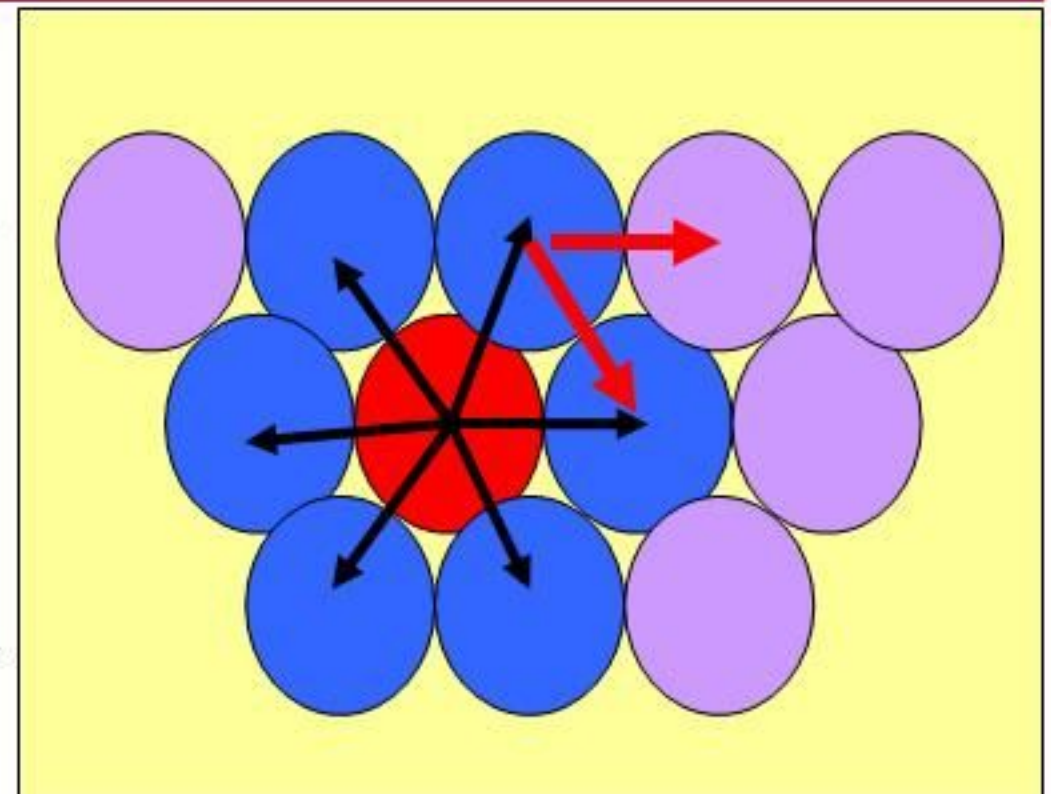
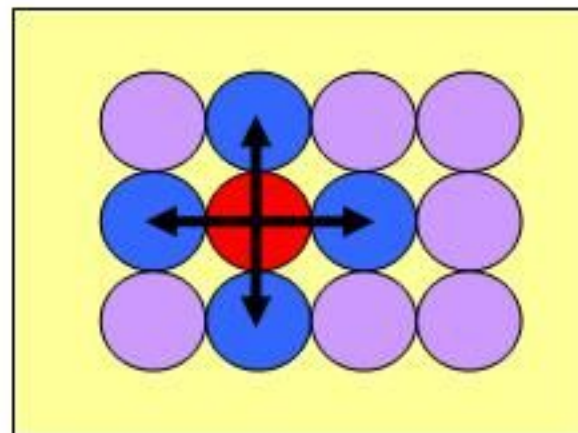
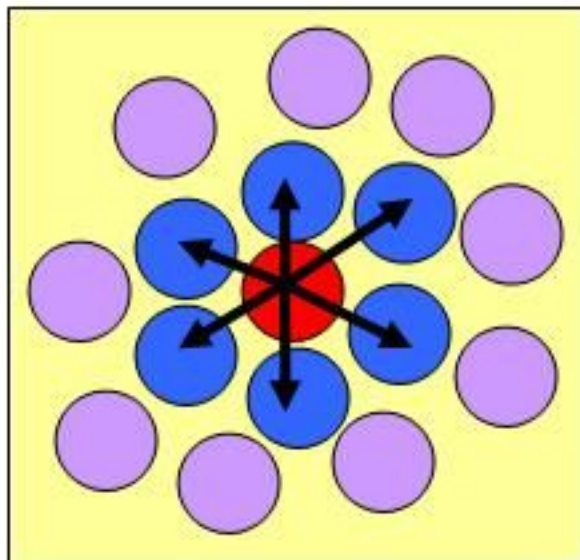
Global bond orientational order parameter(1)

Bond Orientational Order Parameters(Steinhardt, 1983)

More convenient than translational order because we will eventually need to generalise to a small solid-like nucleus in a disordered melt.

Bond: vector joining two atoms lying within the first neighbour shell

Local clusters in liquids contain 10 or 11 nearest neighbours with distorted icosahedral, rather than cubic, packing



Global bond orientational order parameter (2)

$$Q_{lm}(r) \equiv Y_{lm}(\theta(\mathbf{r}))(\phi(\mathbf{r}))$$

$$\bar{Q}_{lm}$$

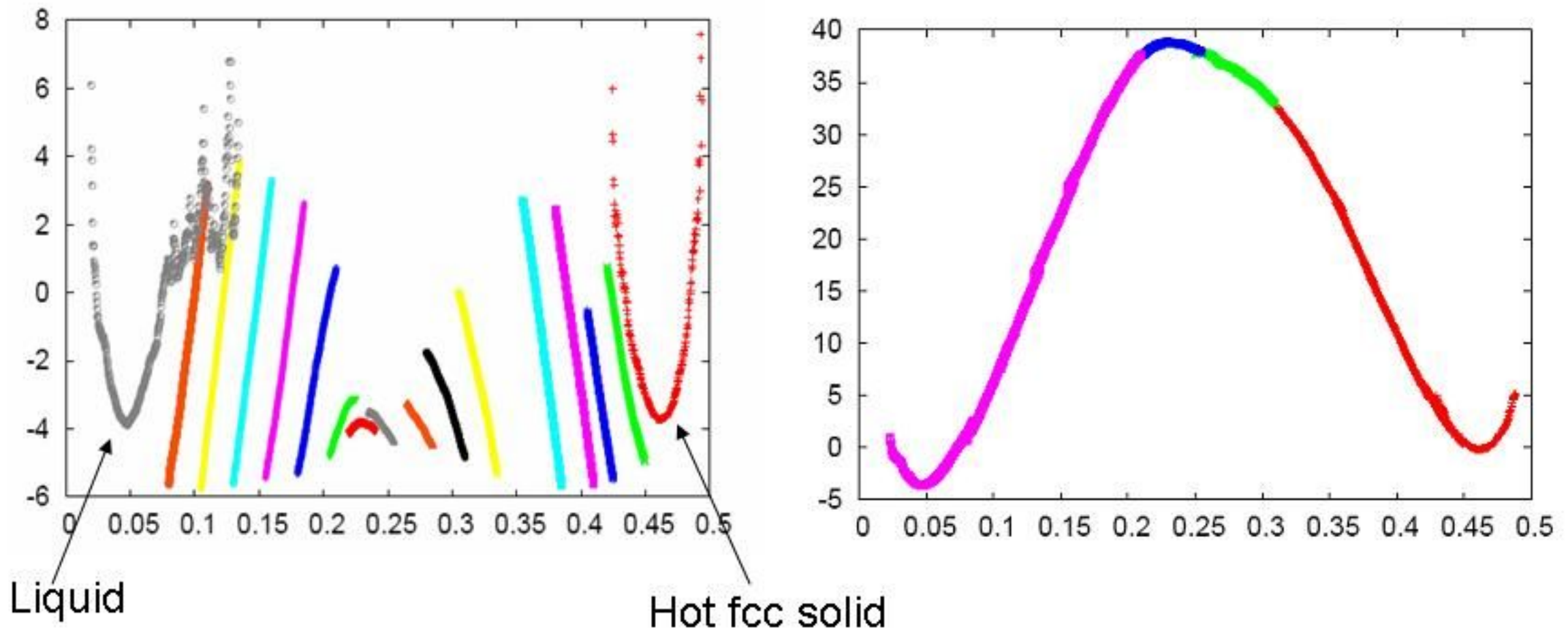
Average over all bonds in sample

	Q_4	Q_6
fcc	0.191	0.575
hcp	0.097	0.485
bcc	0.036	0.511
s.c	0.764	0.354

$$Q_l \equiv \left(\frac{4\pi}{(2l+1)} \sum_{m=-l}^l \bar{Q}_{lm} \right)^{1/2}$$

Using umbrella sampling to construct free energy curves for melting

Lennard-Jones with a smooth cutoff: $T=0.70$, $P=0.67$
Free energy (F/kT) as a function of Q_6



Committer Probability Distributions

How do we know if we have found a good reaction coordinate?

Committer: probability that a trajectory initiated from a given configuration ends up in the product state

Run trajectories with configurations sampled from configurations located at the top of the barrier and with different choices of Maxwell-Boltzmann distribution of initial velocities

If 50% of the trajectories from each configuration lying in this transition state ensemble reach the products, we have found a good transition state.

Global order parameters are NOT good for studying nucleation

Free Energy Barrier for Nucleation(1): Defining a solid-like Cluster

CNT: reaction coordinate for nucleation is size of critical nucleus

Need to define local order parameters for crystalline clusters

Sum over spherical harmonics with $l=6$ for nearest neighbour bonds of particle i

$$q_{6m}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{6m}(\hat{\mathbf{r}}_{ij})$$

Local order around particle i

$$q_6(i) = \left(\frac{4\pi}{13} \sum_{m=-6}^6 |q_{6m}(i)|^2 \right)^{1/2}$$

Degree of correlation between local order between particles i and j :

$$\mathbf{q}_6(i) \cdot \mathbf{q}_6(j) = \sum_{m=-6}^6 q_{6m}(i) \cdot q_{6m}^*(j)$$

Two neighbouring particles are said to be connected if the dot product exceeds a threshold.

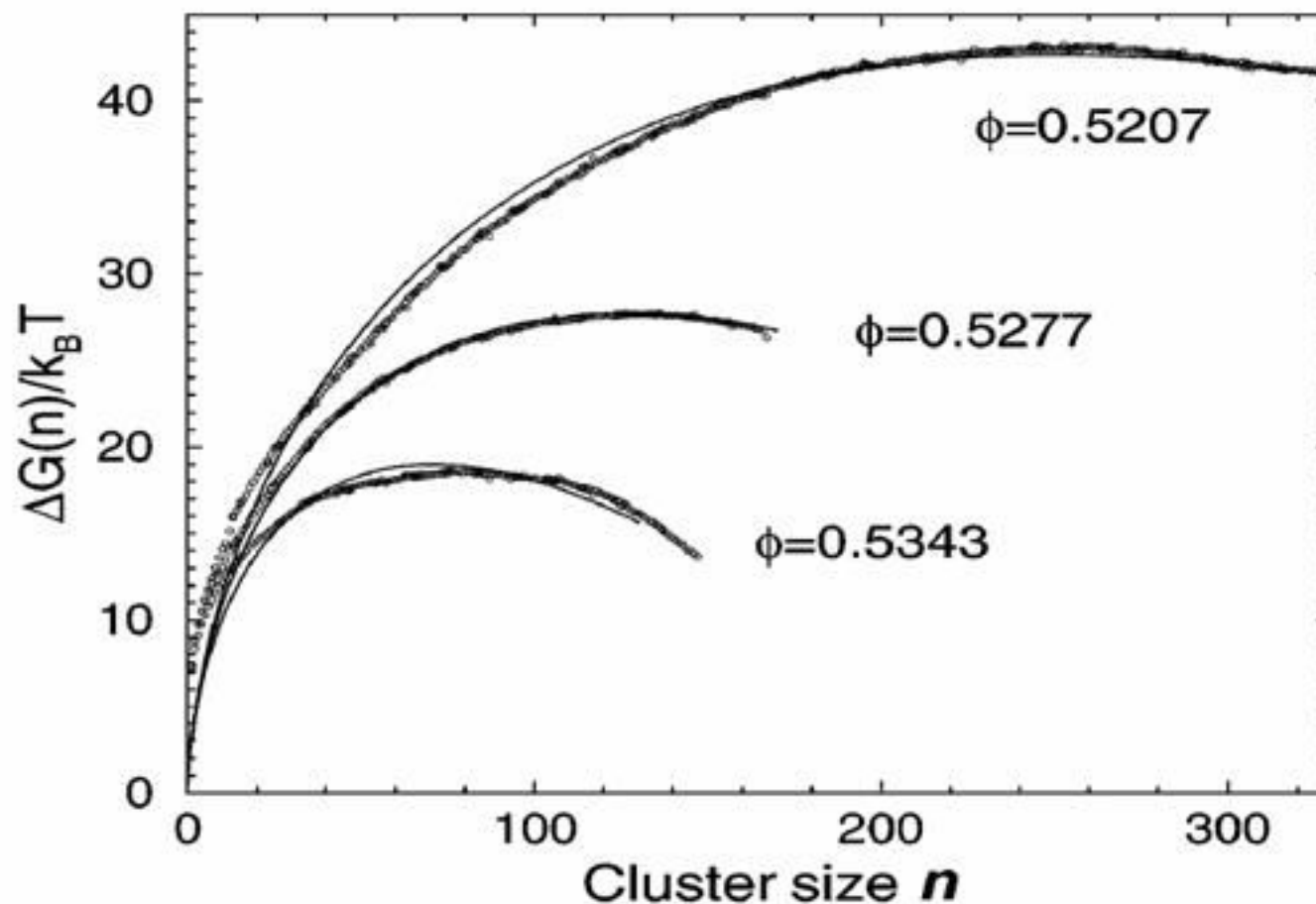
Use a cluster identification algorithm (e.g. Allen and Tildesley)

Free Energy Barrier for Nucleation(2):

Bias potential that controls the size of the largest cluster in the system

$$\omega[n(\mathbf{r}^N)] = \frac{1}{2}k_n[n(\mathbf{r}^N) - n_0]^2$$

Use narrow but overlapping windows for different cluster sizes.
Run a parallel tempering scheme and allow exchange of clusters
between adjacent windows



Hard-sphere
Colloids

Kinetic Prefactor for Nucleation (1)

$$\Gamma = Z\rho_l f_c^+$$

Diffusive, rather than ballistic, barrier crossing
Run a large number of dynamical trajectories starting with configurations at the barrier top
Can use molecular dynamics or kinetic Monte Carlo
Zeldovich factor (Z):
Attachment rate to cluster

$$f_c^+ = \frac{24D_S n_c^{2/3}}{\lambda^2}$$

Kinetic Prefactor for Nucleation (2)

Mean square change in the number of particles in the critical cluster

$$\Delta n_{n_c}^2(t) = [n_c(t) - n_c(t=0)]^2$$

Effective diffusion constant for change in cluster size

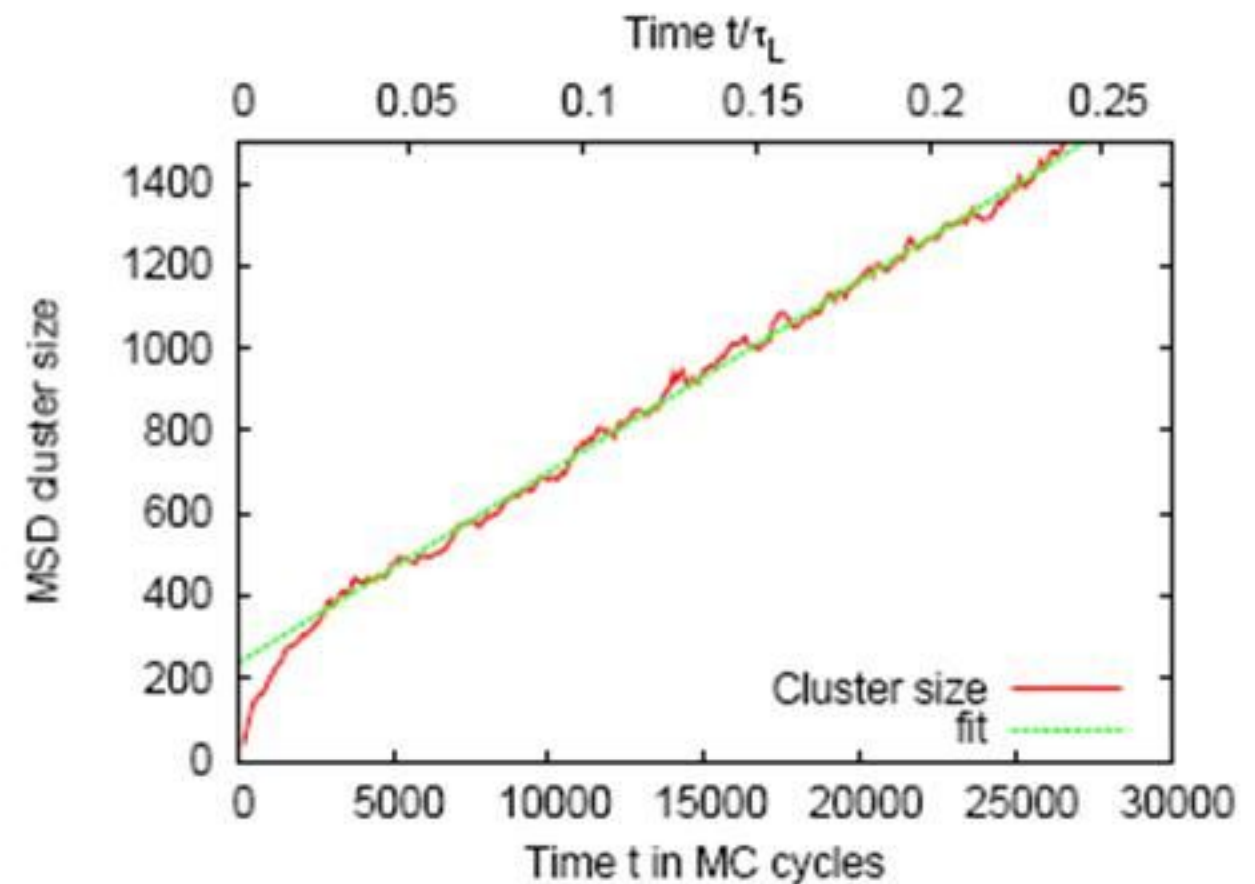
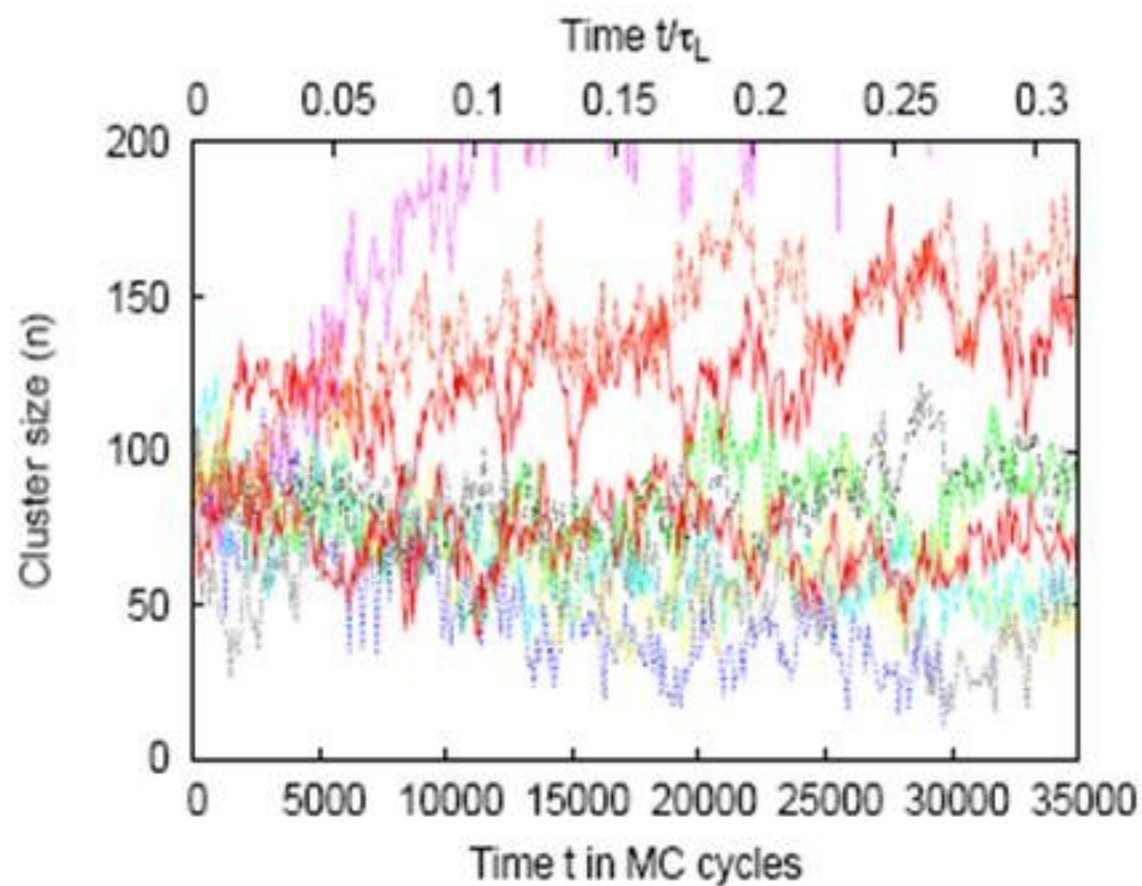
$$D_{n_c}^{att} = \frac{1}{2} \frac{\langle \Delta n_c^2(t) \rangle}{t}$$

Expressing in terms of attachment and detachment rates:

$$\langle \Delta n_c^2(t) \rangle / t = (f_{n_c}^+ + f_{n_c}^-) / 2, \quad f_{n_c}^+ \approx f_{n_c}^-$$

$$f_{n_c}^+ = \frac{1}{2} \frac{\langle \Delta n_c^2(t) \rangle}{t}$$

Kinetic Prefactor for Nucleation (3)

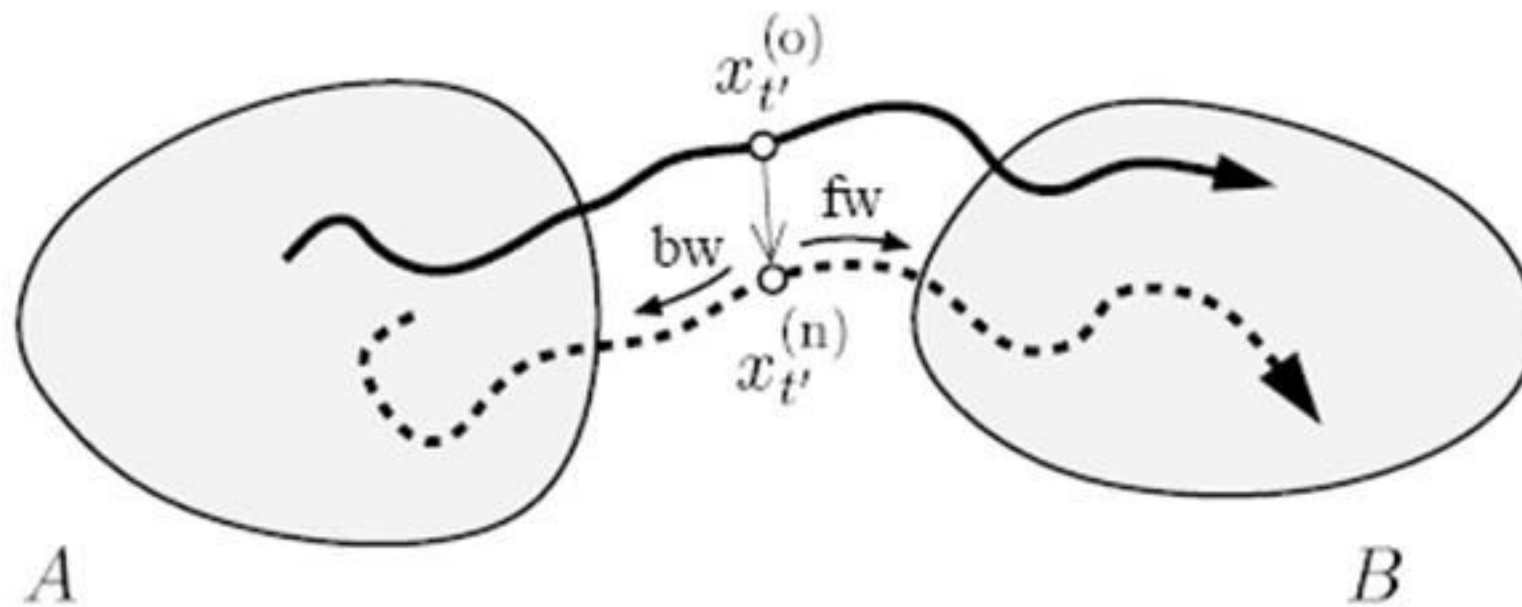


Transition Path Sampling

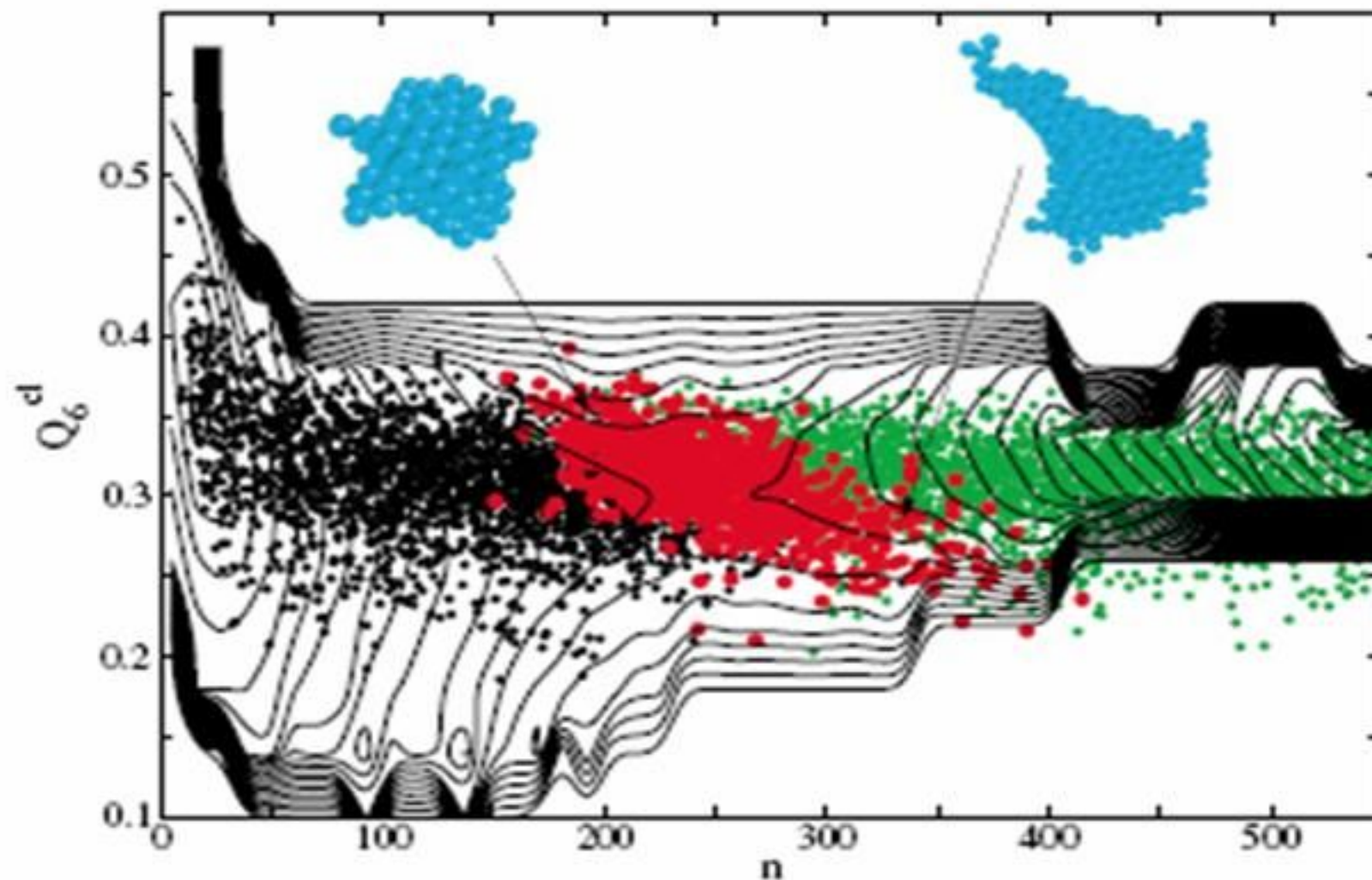
Create an ensemble of reactive paths

Multiple order parameters can be obtained by analysing paths

Fluctuations about minimum free energy path



Transition Path Sampling: Structure and Size of a Critical Crystal Nucleus

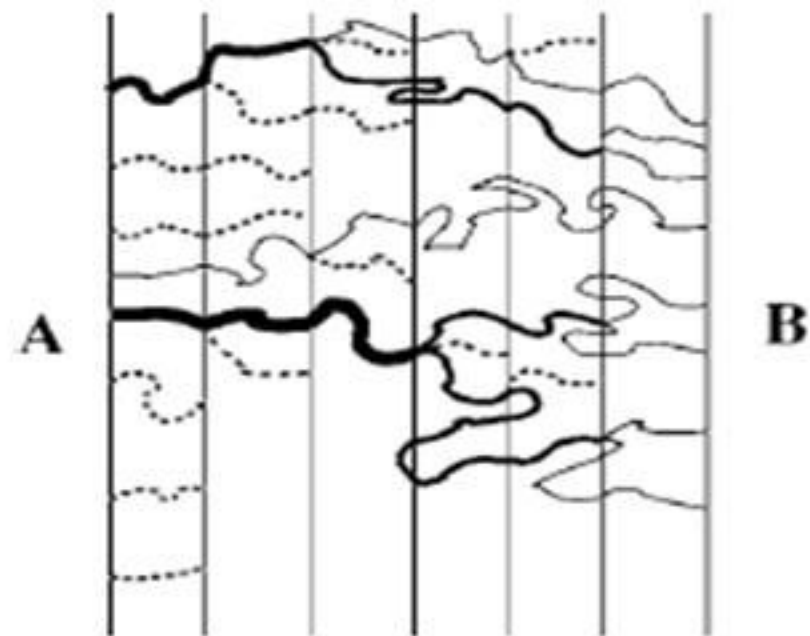


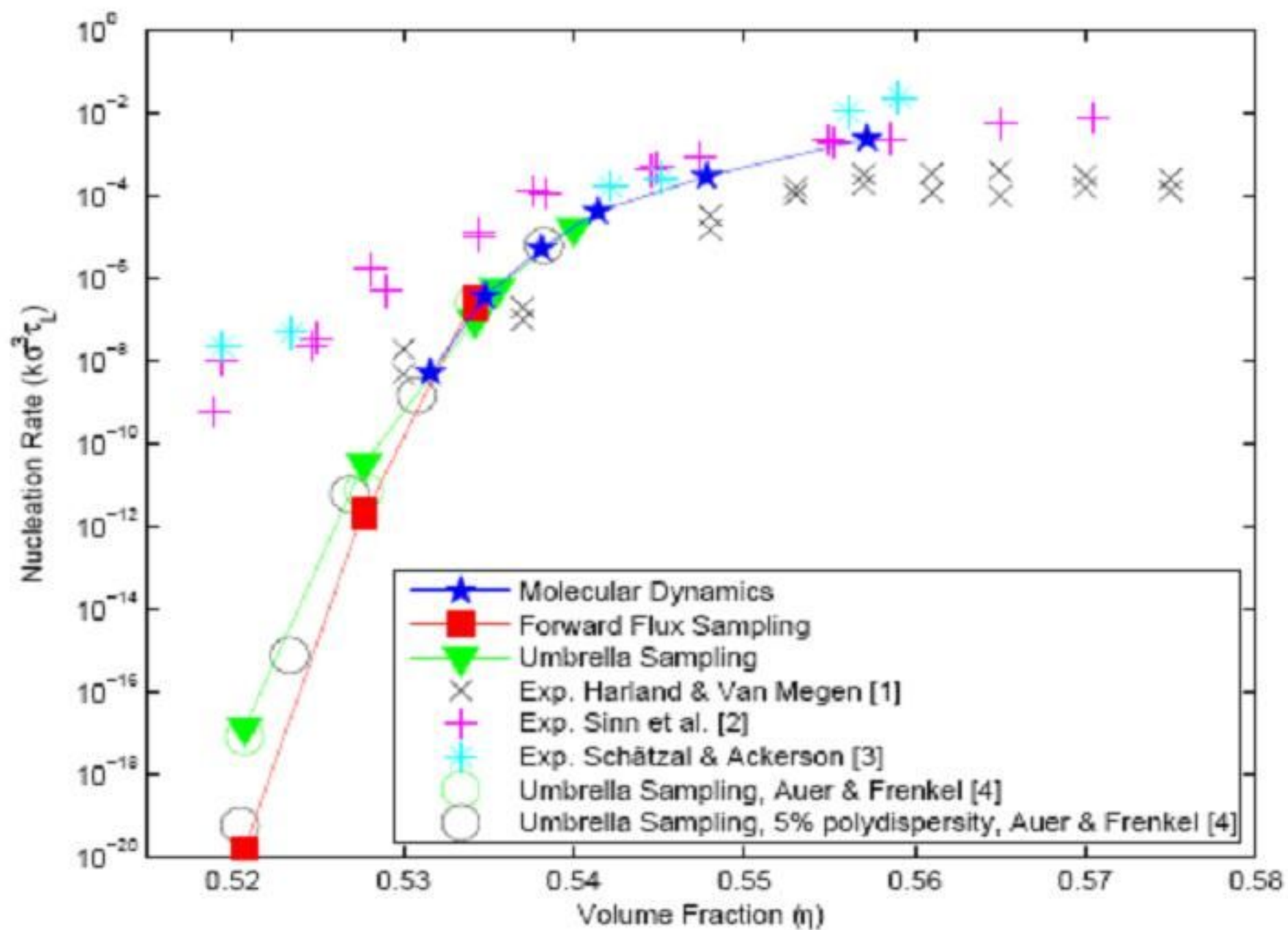
Moroni, ten Wolde and Bolhuis, Phys. Rev. Lett., 95,235704 (2005)

Forward-flux method

A series of non-intersecting interfaces λ_i are chosen such that $\lambda < \lambda_0$ corresponds to A and $\lambda > \lambda_n$ corresponds to B.

$$k_{AB} = \frac{\bar{\Phi}_{A,n}}{\bar{h}_A} = \frac{\bar{\Phi}_{A,0}}{\bar{h}_A} P(\lambda_n | \lambda_0).$$





References

- D. Chandler, An Introduction to Modern Statistical Mechanics
- S. Auer and D. Frenkel, Annu. Rev. Phys. Chem., **55**, 333 (2004)
- D. Frenkel and B. Smit, Understanding Molecular Simulations: From Algorithms to Applications