

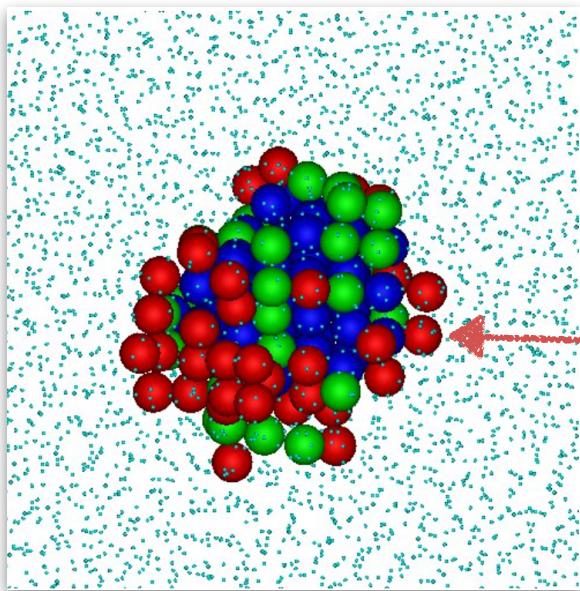
# Lecture II

## Classical nucleation theory

# Outline

1. Kramers theory
2. Classical Nucleation Theory (CNT)
3. Seeding method: crystallization of water
4. Detecting crystalline regions
5. Hard sphere freezing
6. Free energies are not unique
7. Dynamical corrections: Bennett-Chandler

# Homogeneous vs. heterogeneous nucleation

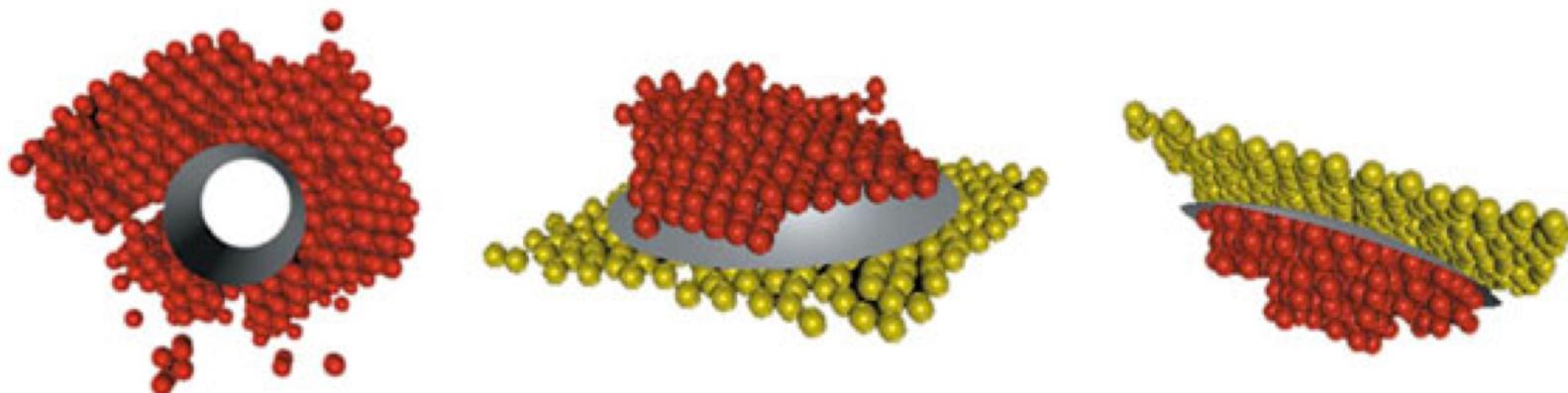


**homogeneous nucleation**

nucleus, crystallite, embryo, cluster, nanoparticle

Filion, Hermes, Ni, Dijkstra, JCP (2010)

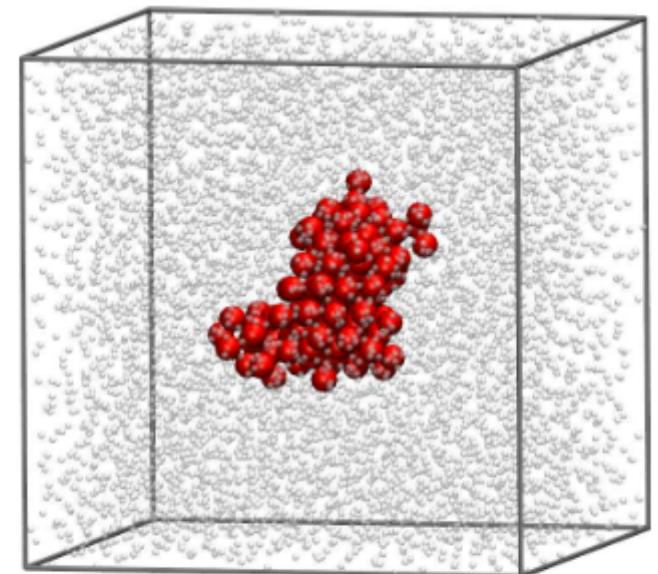
**heterogeneous nucleation**



Cacciuto, Auer and Frenkel, Nature (2004)

# Assumptions of CNT

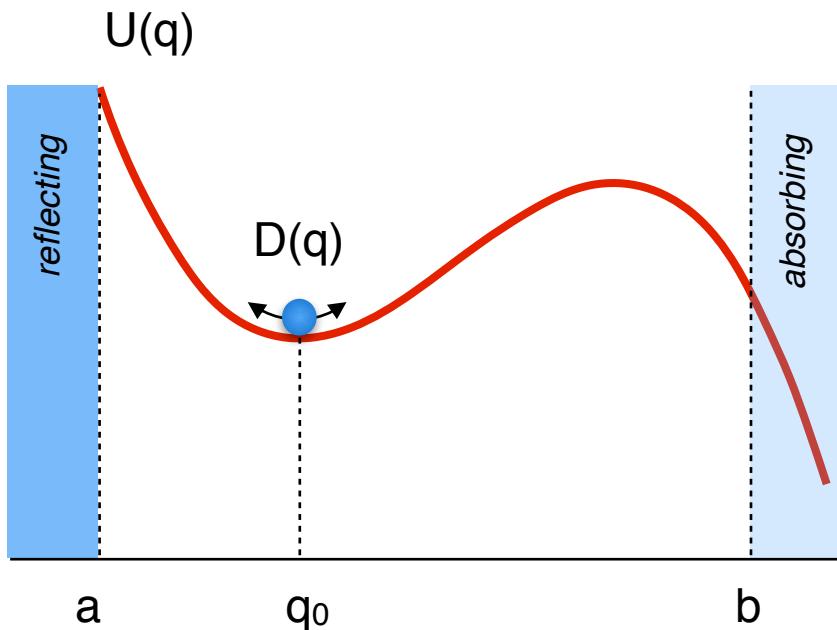
1. One-step process: only one barrier significant; nucleus consists of a piece of new bulk phase
2. Nucleus grows one monomer at a time
3. Crystal lattice can be neglected, nucleus is spherical
4. Only long time scale is that of barrier crossing (microscopic kinetics are fast)
5. Nucleation rate does not depend on history
6. Nucleation occurs over saddle point in free energy (nucleus size is reaction coordinate)



# Escape over barrier - the Kramers problem

$$\beta = 1/k_B T$$

Time evolution of  $q$



$$\dot{q} = -D(q)\beta \frac{\partial U(q)}{\partial q} + \sqrt{2D(q)}\xi(t)$$

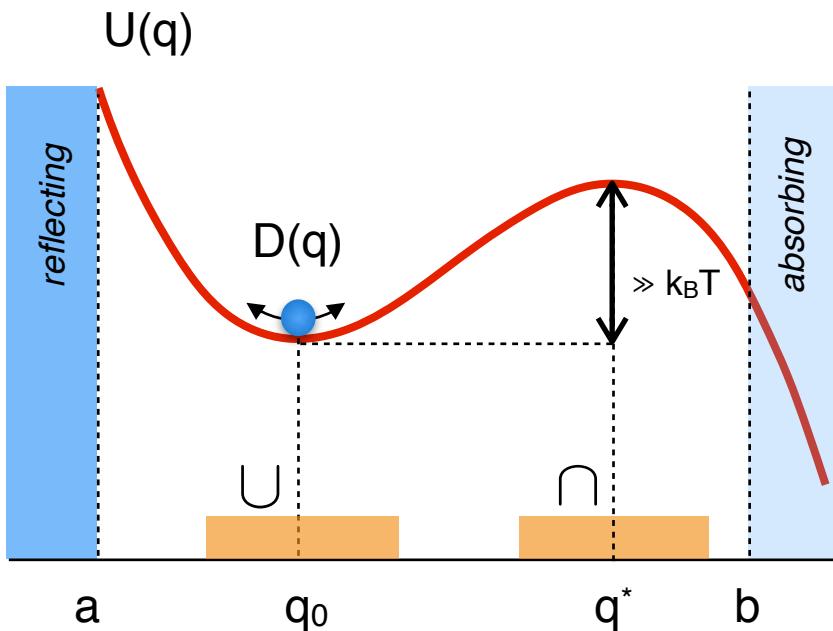
Smoluchowski equation

$$\frac{\partial \rho(q, t)}{\partial t} = \frac{\partial}{\partial q} \left[ D(q) \frac{\partial \beta U(q)}{\partial q} \rho(q, t) + D(q) \frac{\partial \rho(q, t)}{\partial q} \right]$$

Mean first passage time

$$\tau(q_0) = \int_{q_0}^b dy \frac{e^{\beta U(y)}}{D(y)} \int_a^y dz e^{-\beta U(y)}$$

# Escape over barrier - the Kramers problem



Mean first passage time

$$\tau(q_0) = \int_{q_0}^b dy \frac{e^{\beta U(y)}}{D(y)} \int_a^y dz e^{-\beta U(y)}$$

Escape rate

$$k^{-1} = \int_{\cap} dq \frac{e^{\beta U(q)}}{D(q)} \int_{\cup} dq e^{-\beta U(q)}$$

Expand  $U(q)$  around  $q^*$

$$U(q) \approx U(q^*) + \frac{1}{2}\omega^2(q - q^*)^2$$

- \* Barrier high compared to  $k_B T$
- \* Diffusions constant  $D(q)$  constant on barrier
- \* Top of barrier parabolic

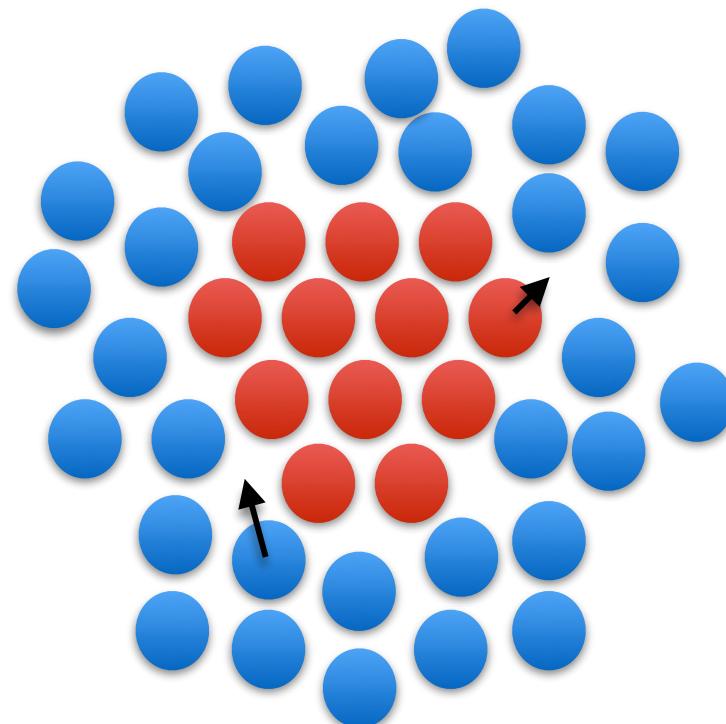
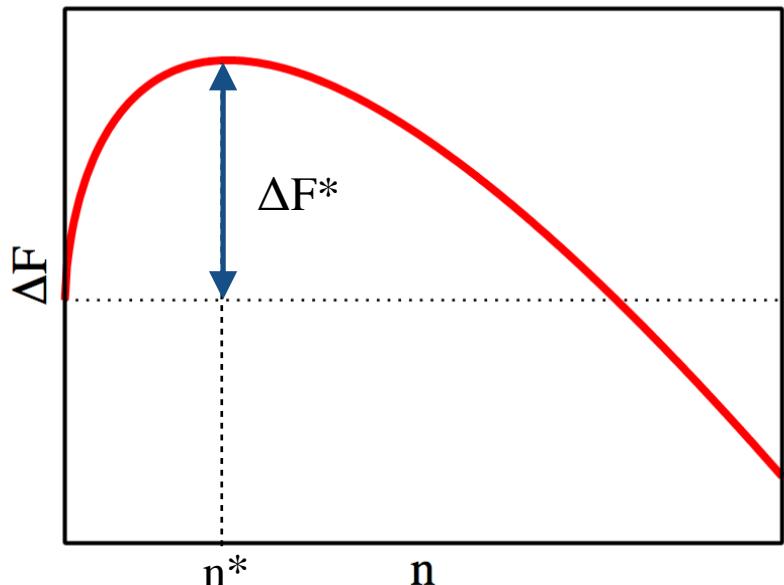
Kramers' result

$$k = \frac{\omega D(q^*)}{\sqrt{2\pi k_B T}} \frac{e^{-\beta U(q^*)}}{\int_{\cup} dq e^{-\beta U(q)}}$$

$P(q^*)$

# Crystal growth as diffusion process

$n$  = size of the crystalline cluster



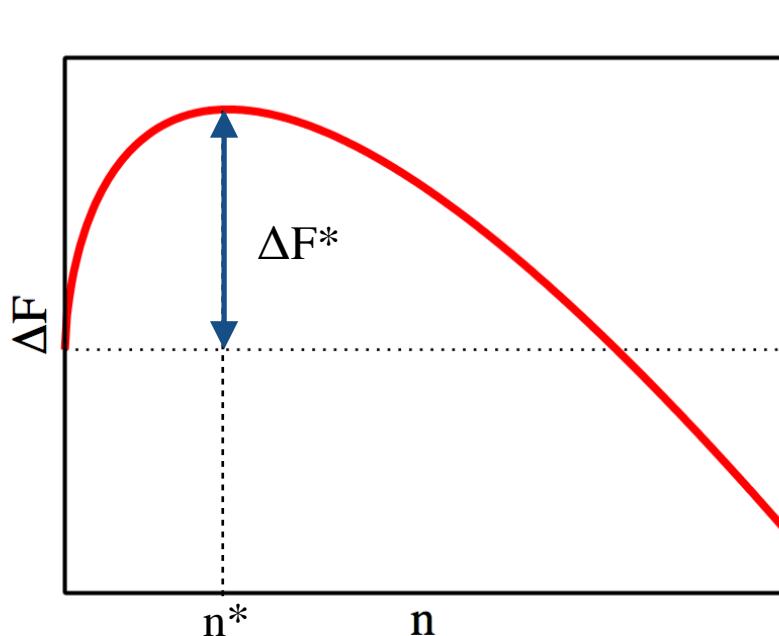
$D(n)$  = diffusion constant of cluster size  $n$

$P(n)$  = equilibrium cluster size distribution

Escape rate  $k = \frac{\omega D(n^*)}{\sqrt{2\pi k_B T}} P(n^*)$

Nucleation rate  $J = \frac{k}{V}$

# Classical nucleation theory



Nucleation free energy

$$\Delta F(n) = (36\pi)^{1/3} (nv)^{2/3} \gamma - n|\Delta\mu|$$

Critical cluster size and barrier

$$n^* = \frac{32\pi}{3} \frac{\gamma^3 v^2}{|\Delta\mu|^3} \quad \Delta F^* = \frac{16\pi}{3} \frac{\gamma^3 v^2}{|\Delta\mu|^2}$$

Probability of having critical nucleus

$$P(n^*) = Ne^{-\beta\Delta F^*}$$

Curvature of barrier

$$\omega^2 = \frac{|\Delta\mu|}{3n^*}$$

Diffusion constant

$$D(n^*) = 24 \frac{D_S}{\lambda^2} n^{*2/3}$$

Nucleation rate

$$J = \sqrt{\frac{\beta|\Delta\mu|}{6\pi n^*}} 24 \frac{D_S}{\lambda^2} n^{*2/3} \rho \exp \left\{ -\frac{16\pi}{3k_B T} \frac{\gamma^3}{|\Delta\mu|^2 \rho^2} \right\}$$

kinetic pre-factor

Zeldovich factor

# Nucleation theorem

$$J = \kappa \exp \left\{ -\frac{16\pi}{3k_B T} \frac{\gamma^3}{|\Delta\mu|^2 \rho^2} \right\}$$

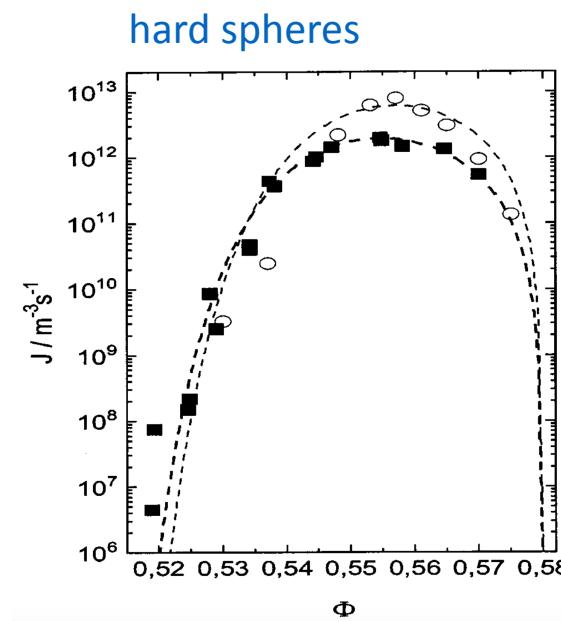
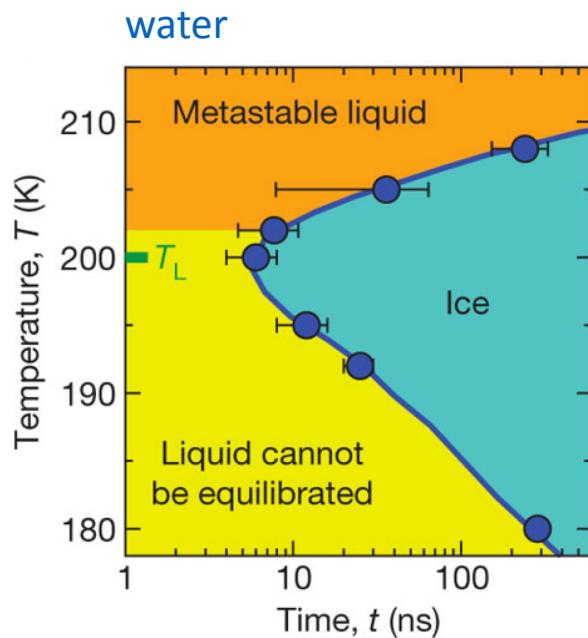
$$n^* = \frac{32\pi}{3} \frac{\gamma^3 v^2}{|\Delta\mu|^3}$$

*Microscopic:* size critical nucleus

*Macroscopic:* from temperature dependence of nucleation rate

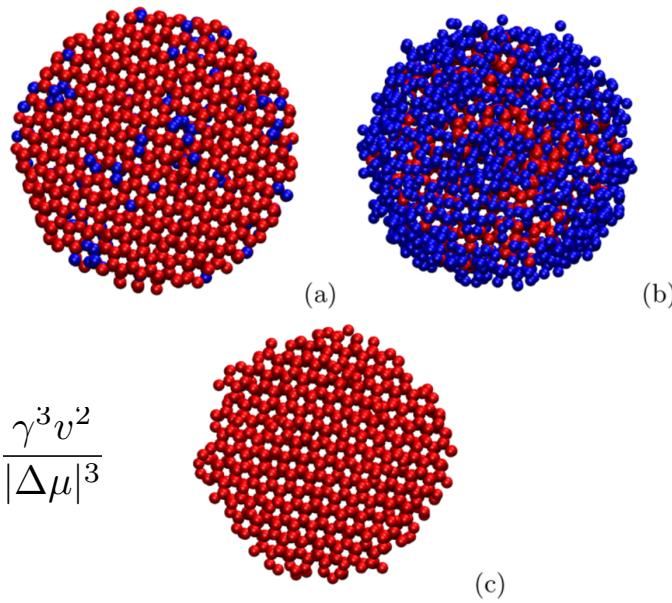
$$n^* = \frac{\partial k_B T \ln J}{\partial \Delta\mu} - \frac{\partial k_B T \ln \kappa}{\partial \Delta\mu}$$

Nucleation theorem does not depend on CNT



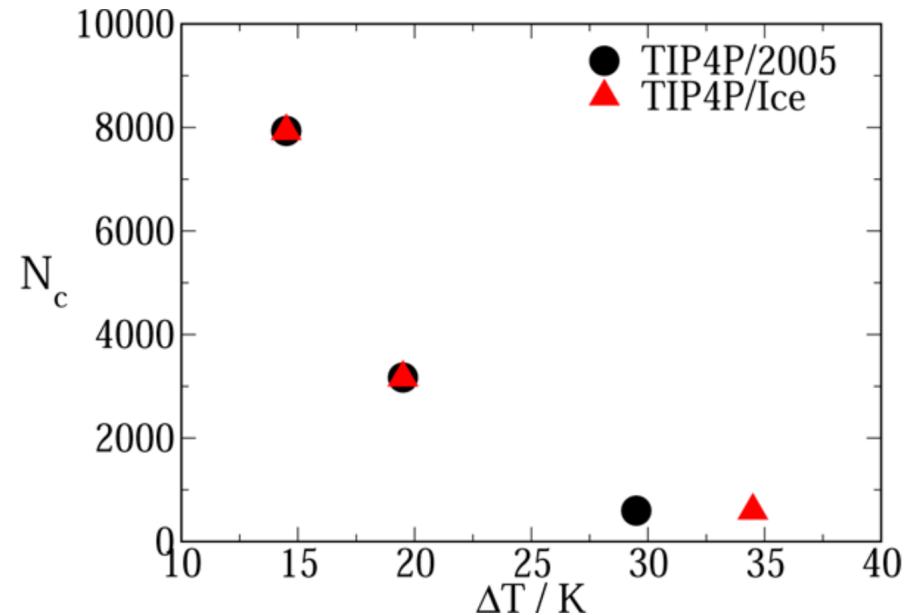
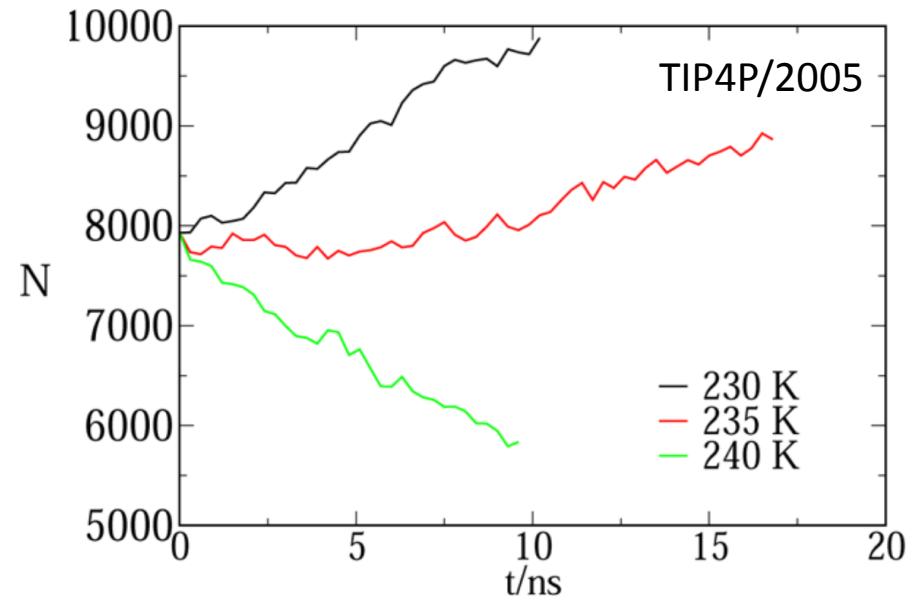
# Seeding method

- \* Size of critical cluster
- \* Surface free energy
- \* Nucleation rate



$$n^* = \frac{32\pi}{3} \frac{\gamma^3 v^2}{|\Delta\mu|^3}$$

TIP4P/ice & TIP4P/2005  
15K-35K below melting (moderate undercooling)  
 $\gamma=29$  mN/m (by fitting CNT)  
 $\Delta\mu$  from thermodynamic integration  
 $N=2 \times 10^5$   
 $T_m = 252$  K for TIP4P/2005  
 $T_m = 272$  K for TIP4P/ice

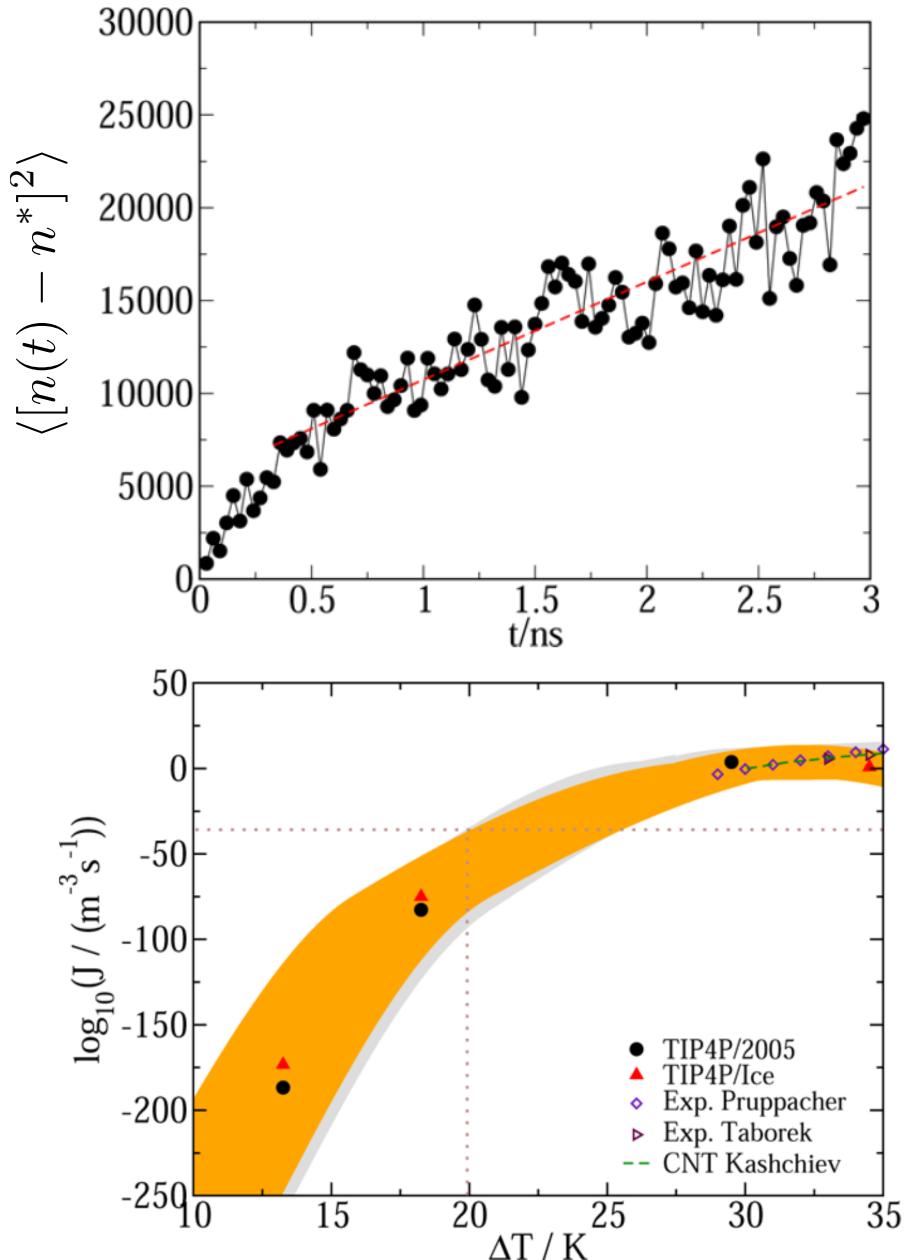


# Nucleation rate from seeding method

$$J = \sqrt{\frac{\beta|\Delta\mu|}{6\pi n^*}} D(n^*) \rho \exp \left\{ -\frac{16\pi}{3} \frac{\beta\gamma^3}{|\Delta\mu|^2 \rho^2} \right\}$$

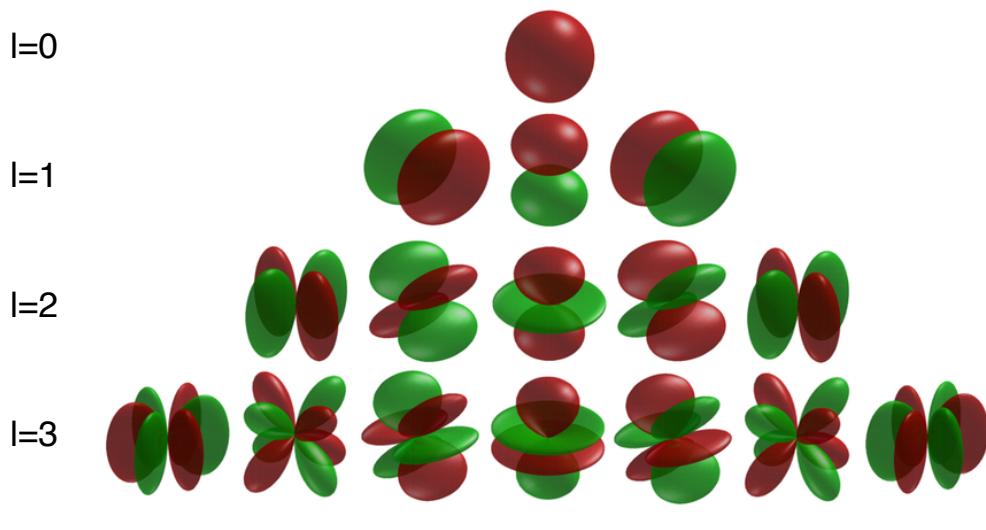
$$\langle [n(t) - n^*]^2 \rangle \approx 2D(n^*)t$$

It is impossible that ice nucleates *homogeneously* at temperatures above -20 C



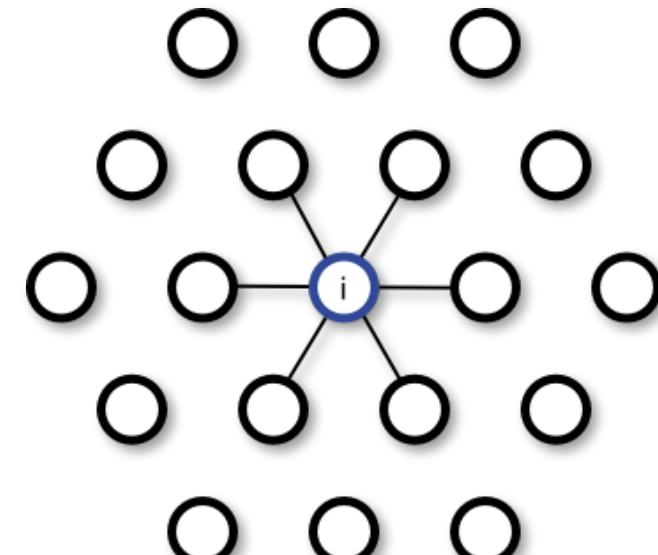
# Detecting local order

## Steinhardt bond order parameter



spherical harmonics

$$Y_{lm}(\vartheta, \varphi)$$

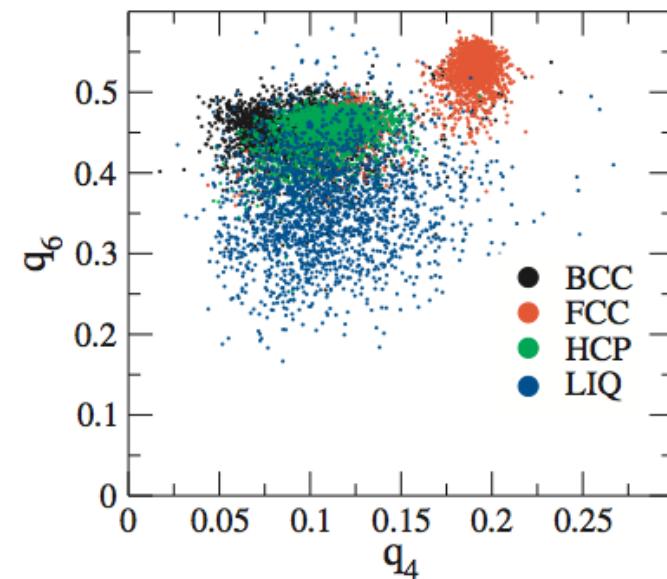
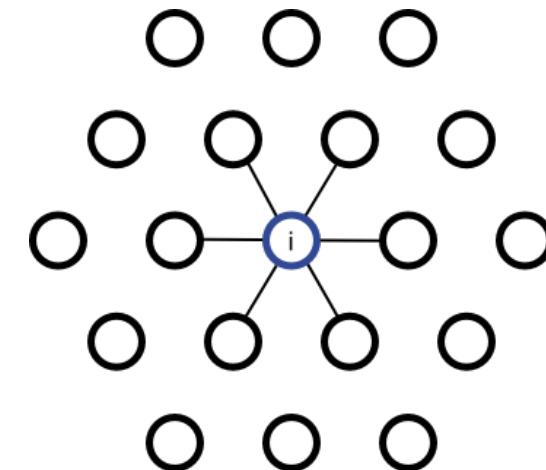
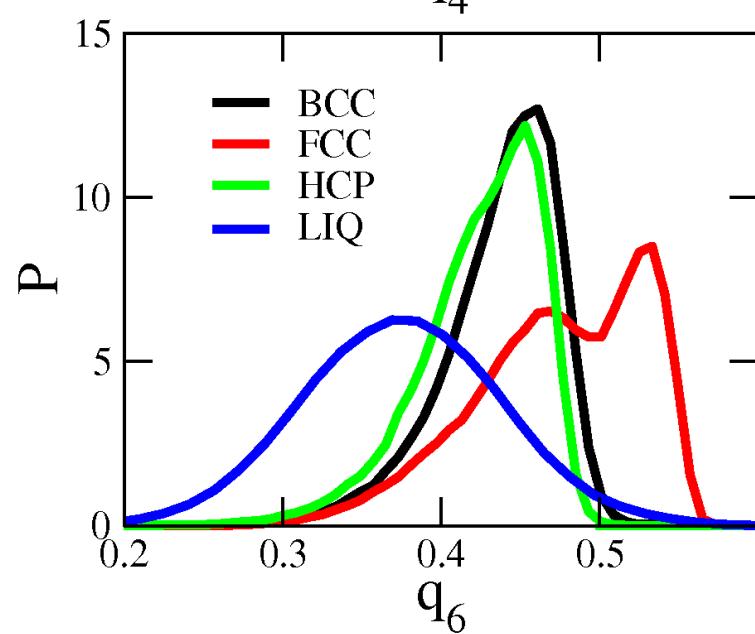
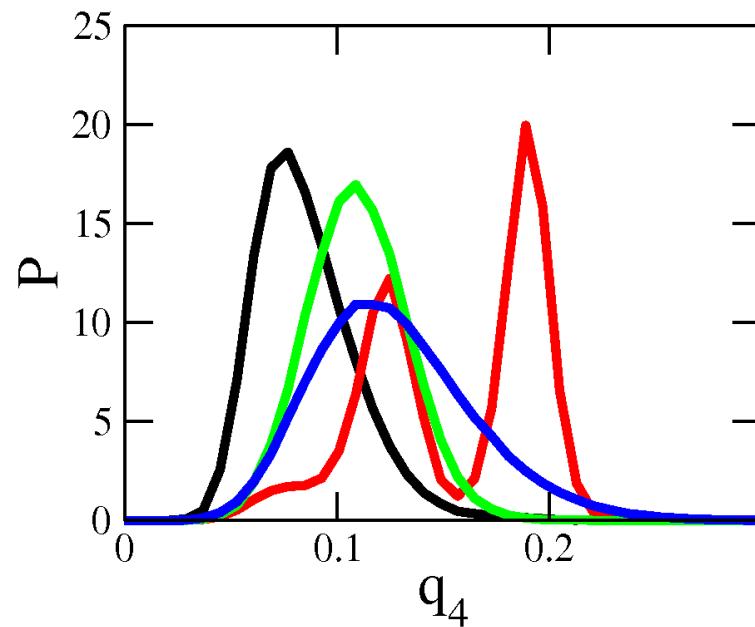


$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(r_{ij})$$

rotationally invariant

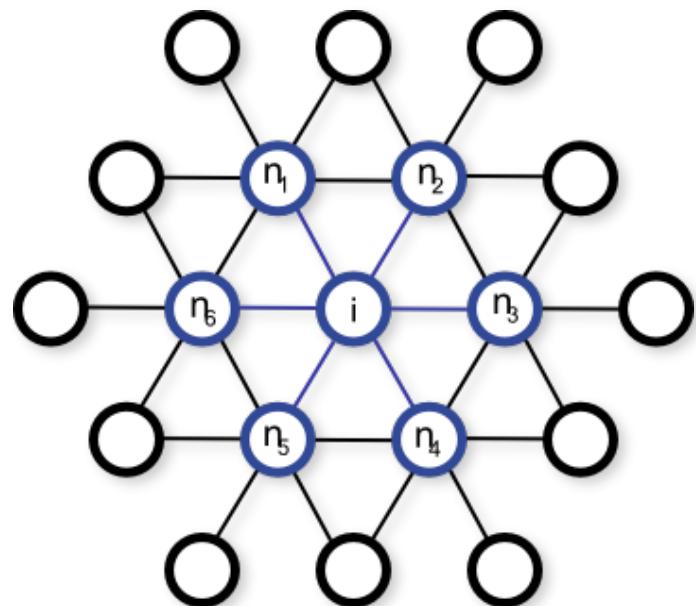
$$q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |q_{lm}(i)|^2}$$

# Distinguishing solid structures

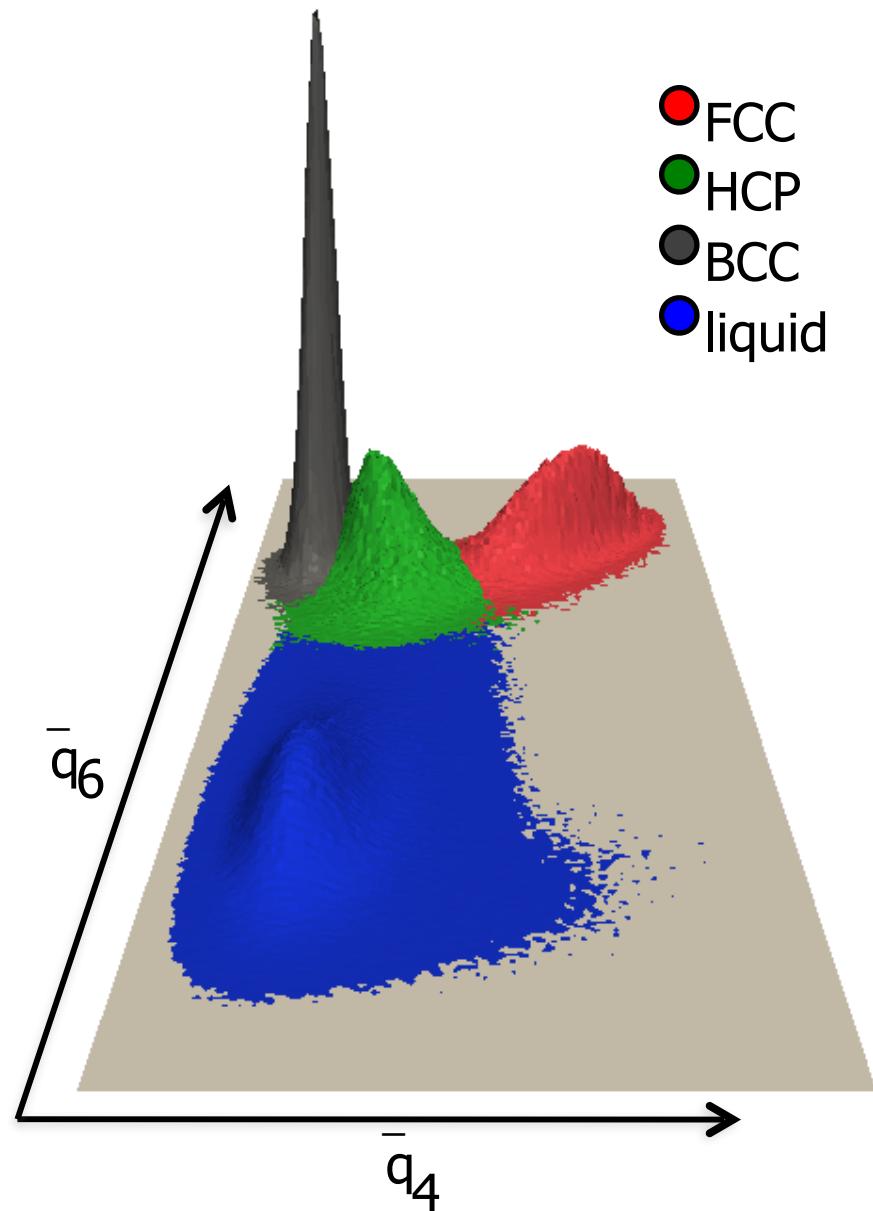


# Averaged local order parameter

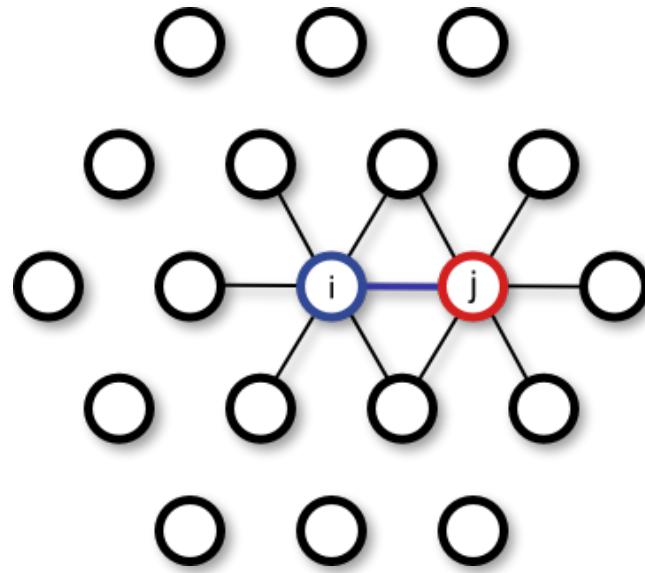
$$\bar{q}_{lm}(i) = \frac{1}{N_b + 1} \left[ q_{lm}(i) + \sum_{k=1}^{N_b} q_{lm}(n_k) \right]$$



$$\bar{q}_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{q}_{lm}(i)|^2}$$

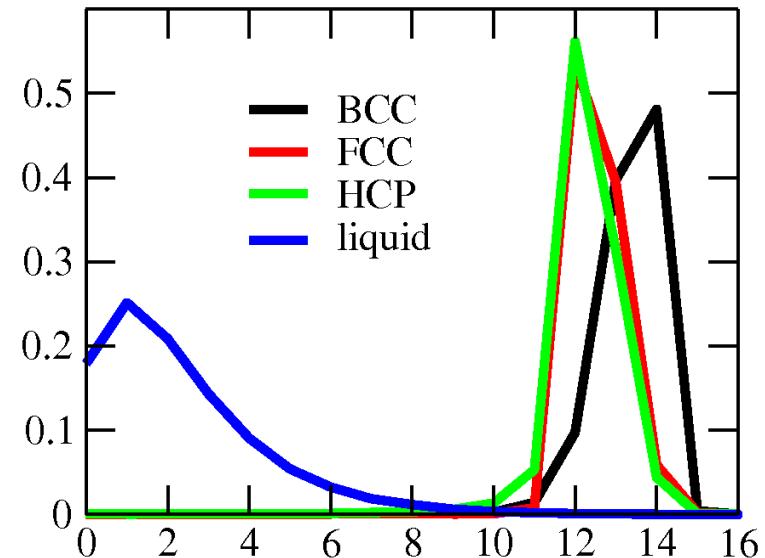


# Distinguishing liquid from solid



if  $s_{ij} > 0.5$ : i and j connected

$$N_{bonds} = \sum_{N_b} \Theta(s_{ij} - 0.5)$$



structural correlations

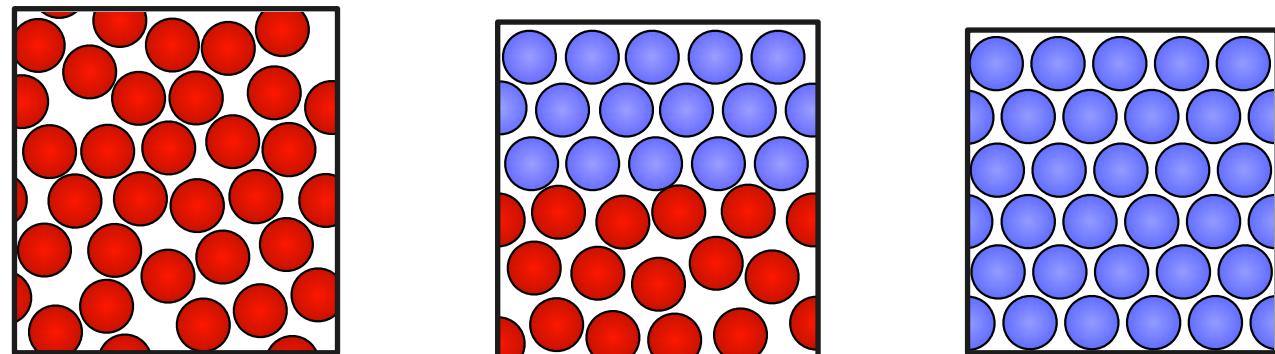
$$s_{ij} = \frac{4\pi}{2l+1} \sum_{m=-l}^l q_{lm}(i)q_{lm}^*(j)$$

$s_{ij} = 1$  perfect crystal  
 $s_{ij} = 0$  liquid

n = size of largest cluster of crystalline particles

# Freezing of hard spheres

Hard sphere freezing  
Kirkwood (1941)

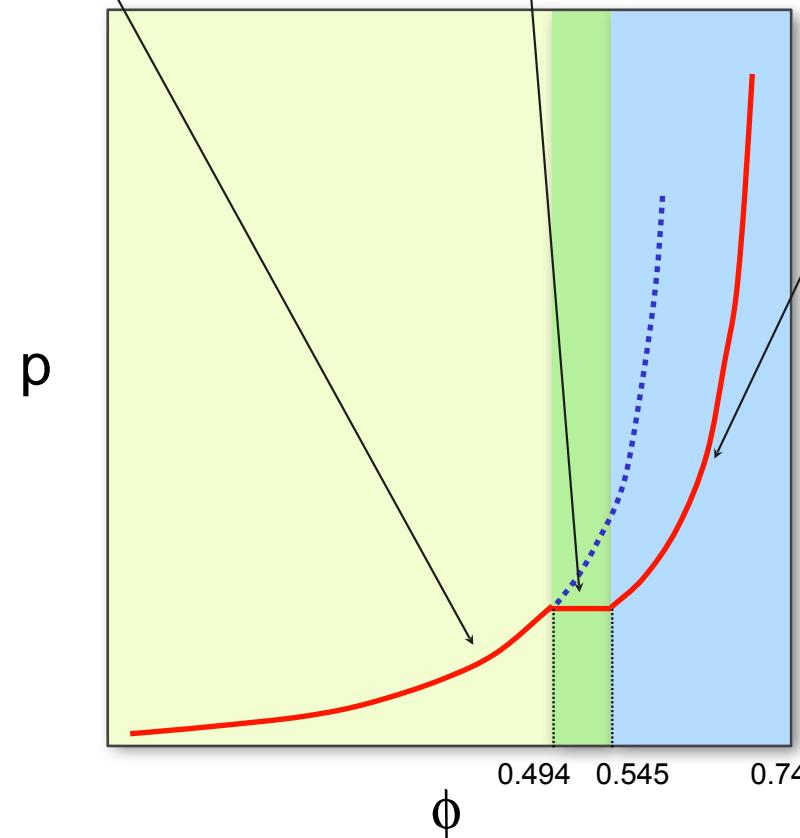


$$F = U - TS$$

$$S = k \cdot \log W$$

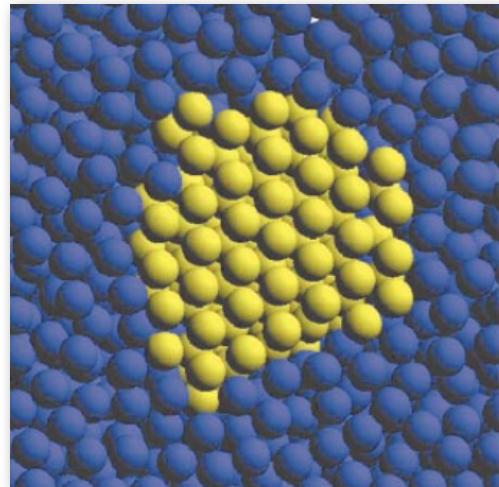
$\phi$  = packing fraction

Alder and Wainwright (1957)  
Wood and Jacobsen (1957)



# Nucleation of hard sphere crystals

$n(x)$  = size of the **largest** crystalline cluster

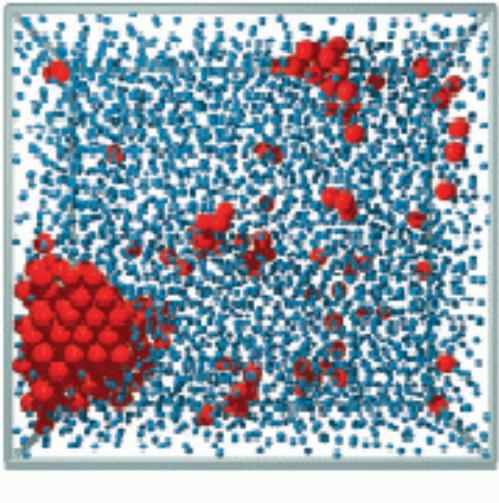


critical  
cluster

$$k = \frac{\omega D(n^*)}{\sqrt{2\pi k_B T}} P(n^*)$$

Compute  $P(n)$  in computer simulation

$$P(n) = \int dx \rho(x) \delta[n - n(x)] = \langle \delta[n - n(x)] \rangle$$



Free energy  $F(n)$

$$F(n) = -k_B T \ln P(n)$$

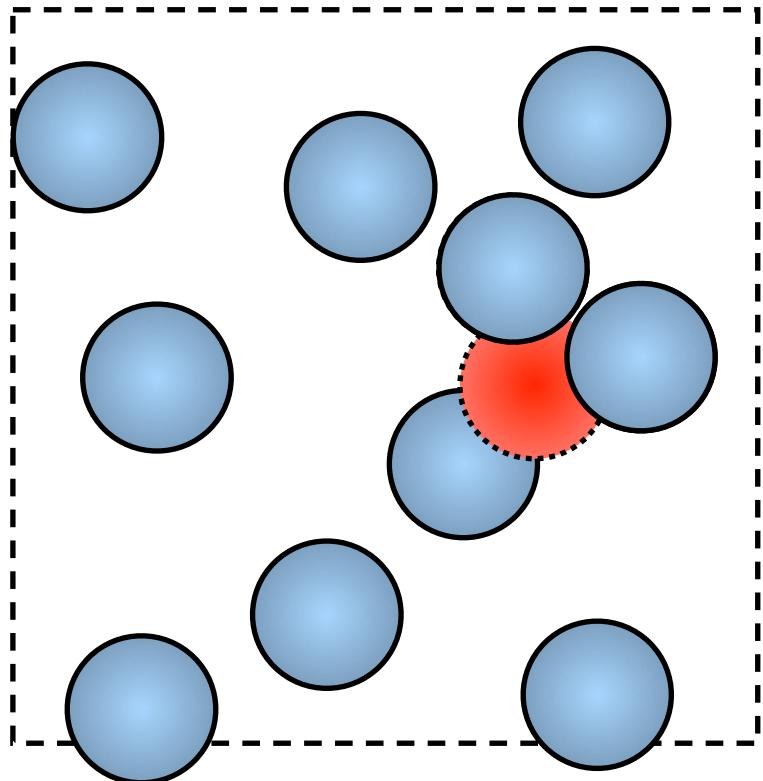
Rate

$$k = \frac{\omega D(n^*)}{\sqrt{2\pi k_B T}} e^{-\beta F(n^*)}$$

Auer and Frenkel, Nature (2001)

Gasser, Weeks, Schofield, Pusey, Weitz, Science (2001)

# Markov chain Monte Carlo simulation

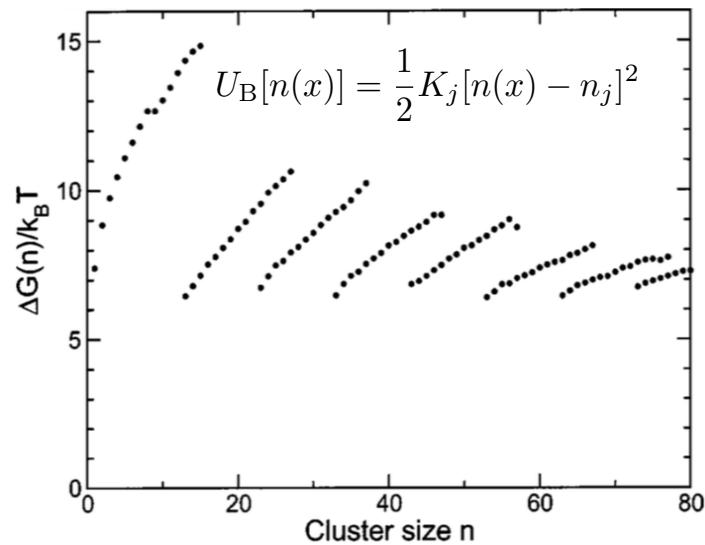


- Generate test configuration
- Calculate energy
- Accept or reject

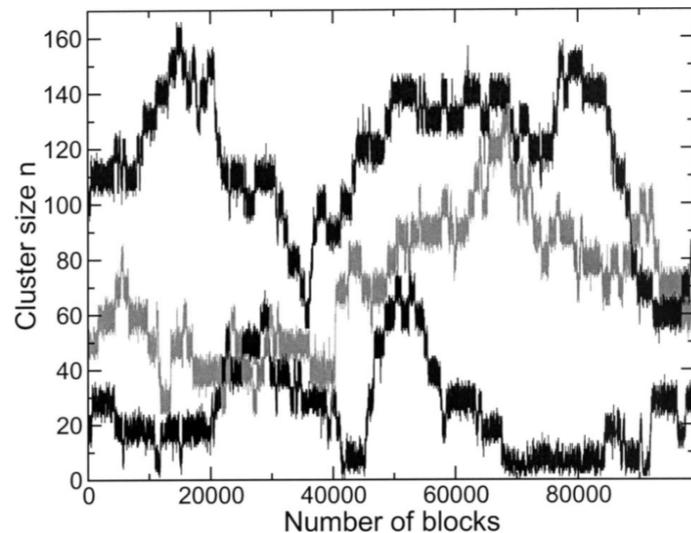
$$\text{acc}(o \rightarrow n) = \begin{cases} \exp\{-\beta[H(n) - H(o)]\} & \text{if } H(n) > H(o) \\ 1 & \text{if } H(n) \leq H(o) \end{cases}$$

# Computing the nucleation free energy

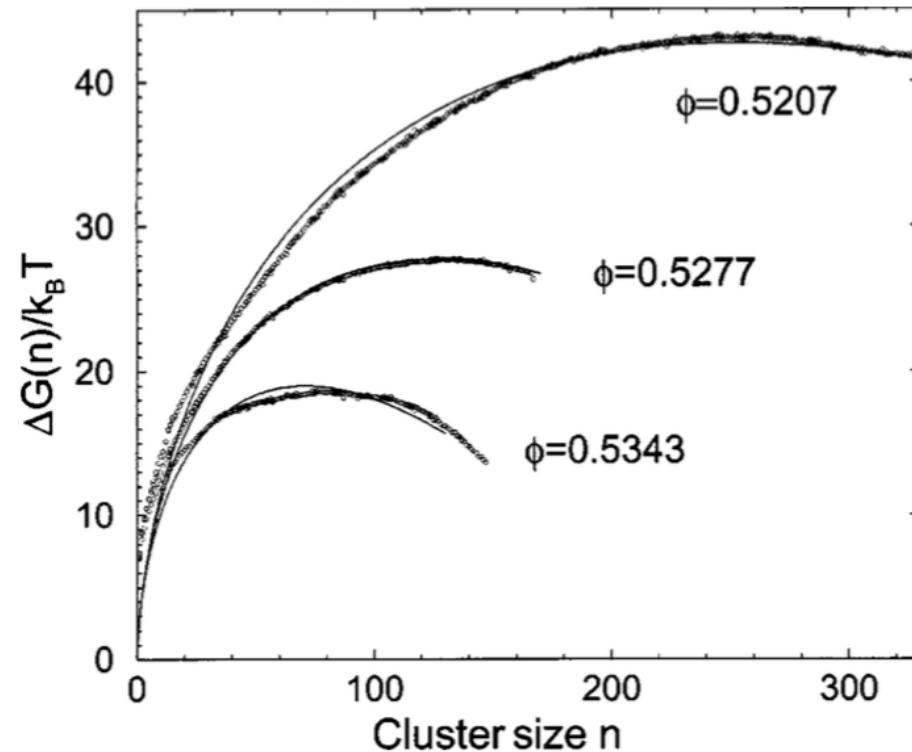
Umbrella sampling with bias  $U_B(x)$



Parallel replica



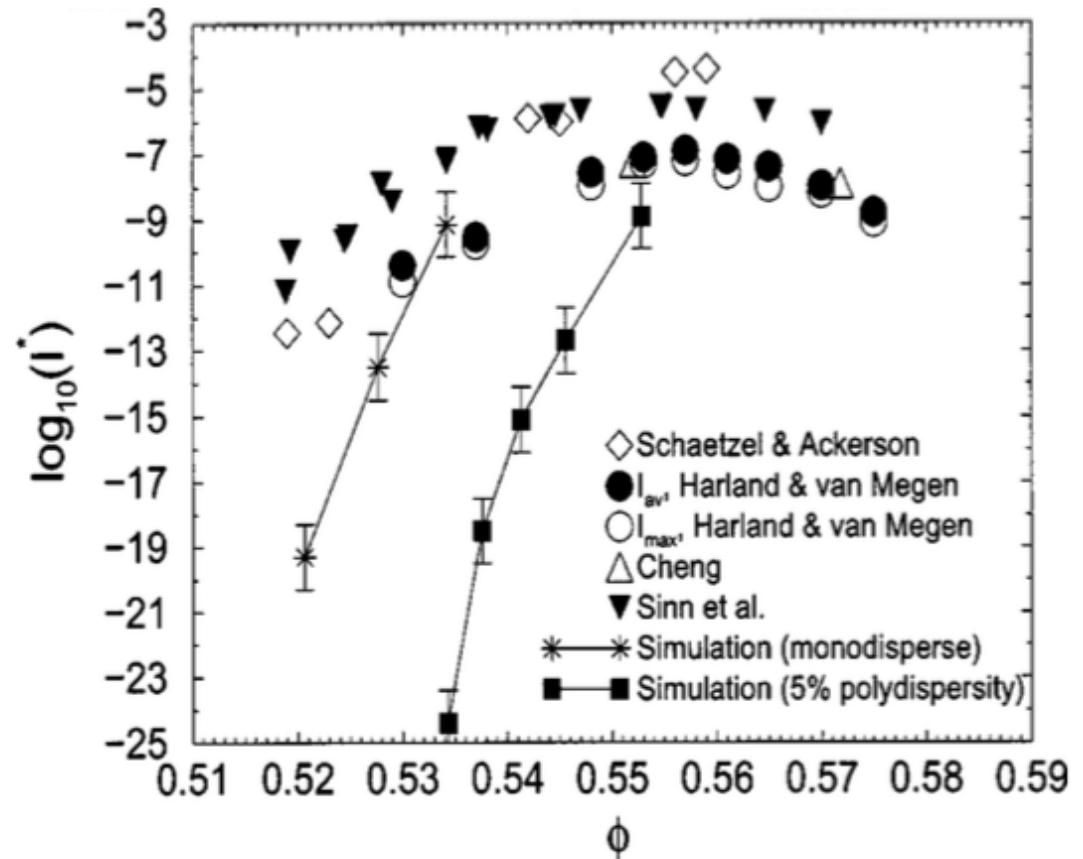
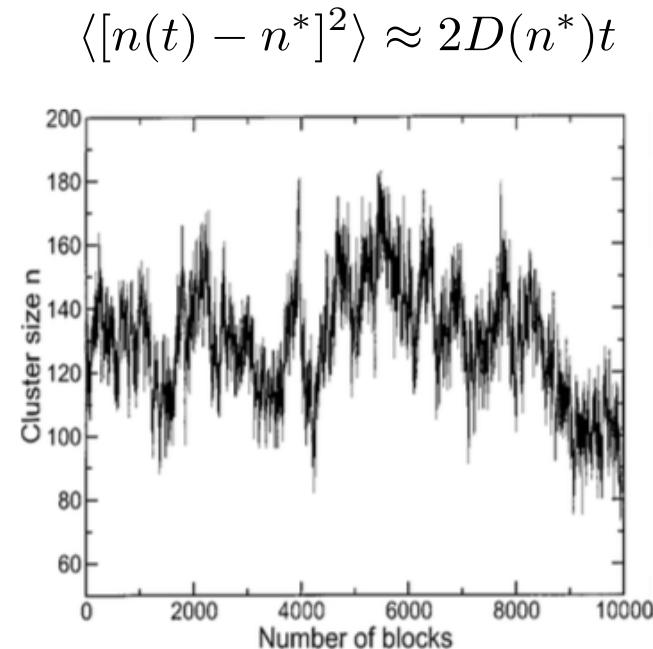
Nucleation free energy



# Computing the kinetic prefactor

$$k = \frac{\omega D(n^*)}{\sqrt{2\pi k_B T}} P(n^*)$$

Kinetic prefactor

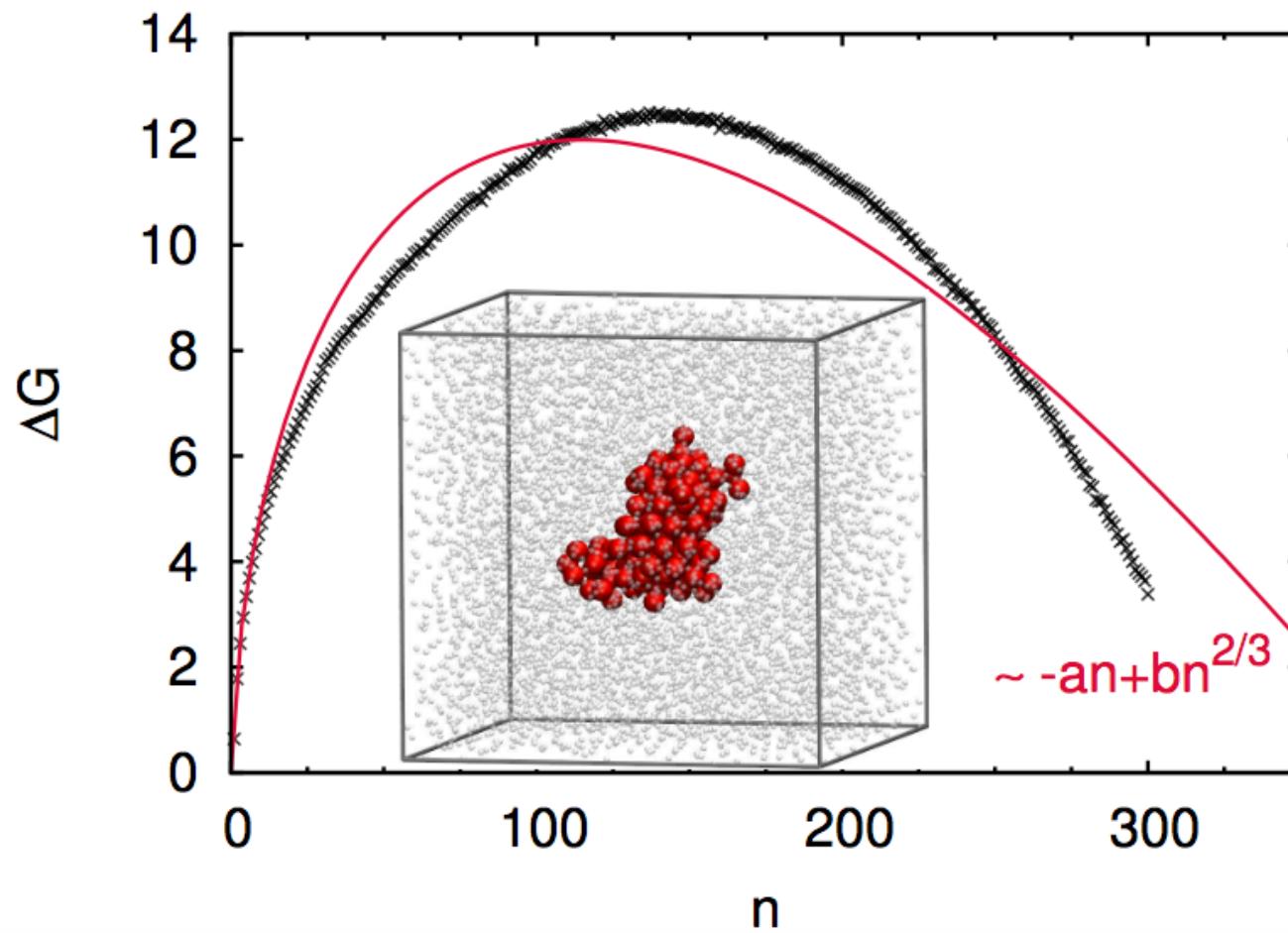


$$\phi = 0.5277$$

- \* Does not rely on shape of barrier
- \* Only assumption: diffusive in  $n$

# Nucleation free energy

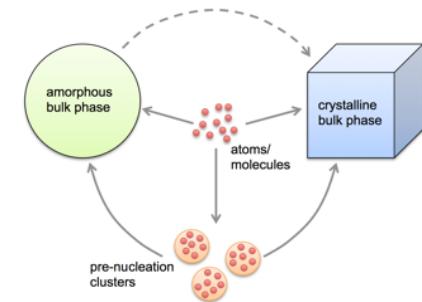
Lennard-Jones, T=0.5 (28% undercooling)



# How classical is nucleation?

1. One-step process: only one barrier significant; nucleus consists of a piece of new bulk phase
2. Nucleus grows one monomer at a time
3. Crystal lattice can be neglected, nucleus is spherical
4. Only long time scale is that of barrier crossing (microscopic kinetics are fast)
5. Nucleation rate does not depend on history
6. Nucleation occurs over saddle point in free energy (nucleus size is reaction coordinate)

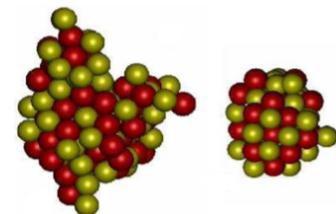
Ostwald's step rule(1897)  
(ice from cold vapor)



non-classical nucleation

Nucleation near **curved objects**  
Role of **defects?**

Other **slow processes**  
(charge ordering, glassy dynamics)

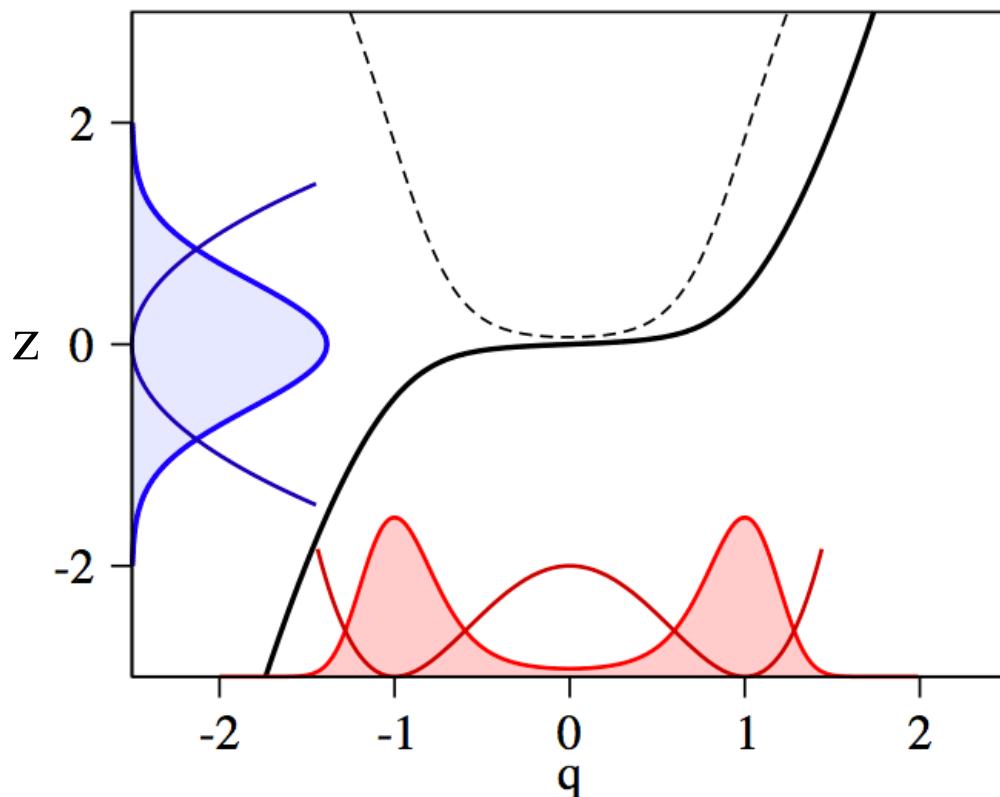


**Thermal history** in porous media

**Shape, structure** matter

# Free energy landscapes are not unique

$$F_Z(z) = z^2 + C'$$



$$F_Q(q) = (1 - q^2)^2 + C$$

$$P_Q(q) = \int dx \rho(x) \delta[q - q(x)]$$

$$F_Q(q) = -k_B T \ln P_Q(q)$$

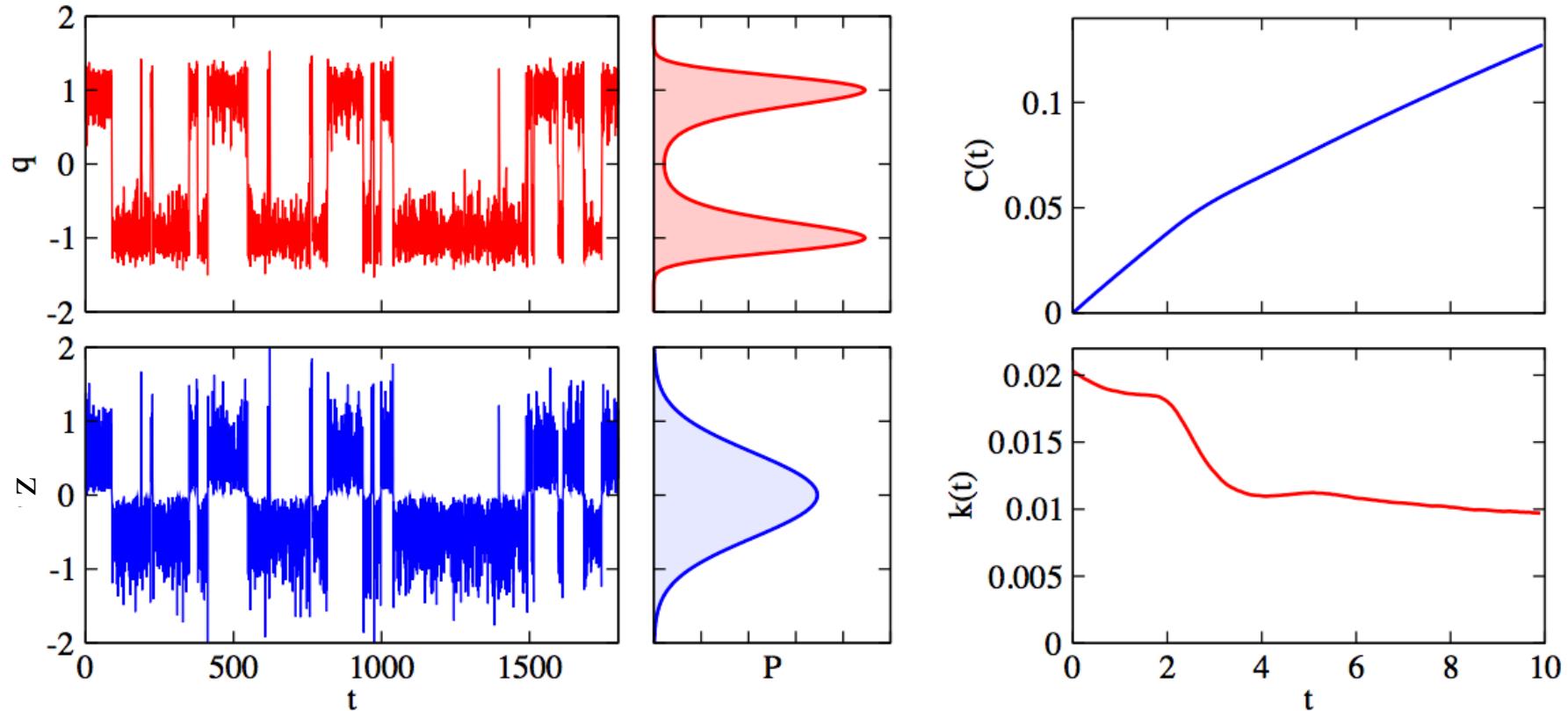
$$z = \varphi(q) \quad q = \varphi^{-1}(z)$$

$$P_Z(z) = P_Q[\varphi^{-1}(z)] \left| \frac{d\varphi^{-1}}{dz} \right|$$

$$F_Z(z) = F_Q[\varphi^{-1}(z)] - k_B T \ln \left| \frac{d\varphi^{-1}}{dz} \right|$$

# Transition rates are unique

$q$  evolves according to Langevin equation

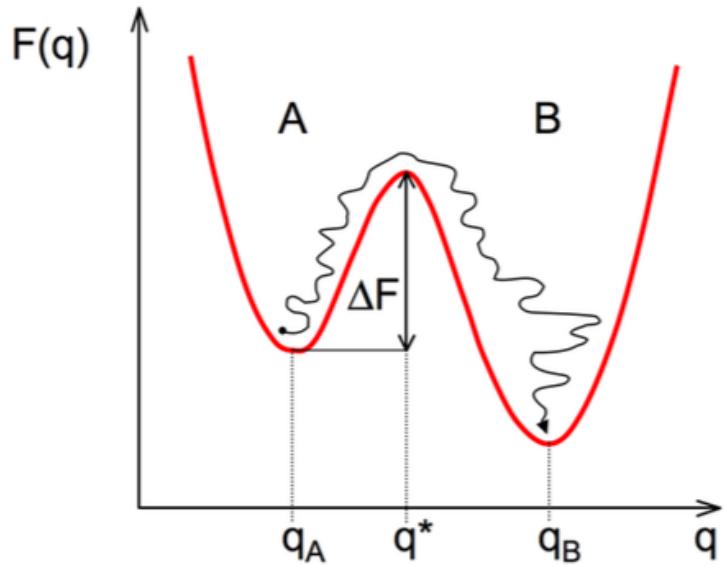


$$C(t) = \frac{\langle h_A [q(0)] h_B [q(t)] \rangle}{\langle h_A \rangle}$$

$$h_A(x) = 1 - \theta[q(x)]$$

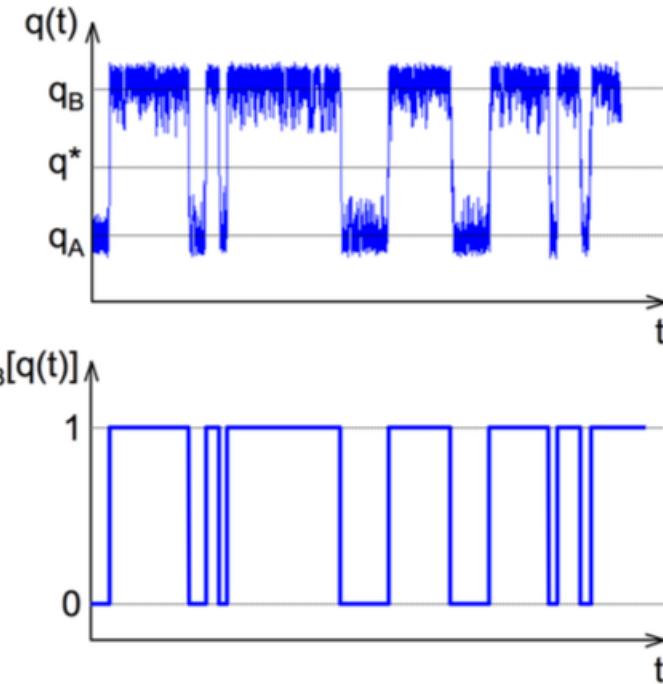
$$h_B(x) = \theta[q(x)]$$

# Bennett-Chandler approach



Time correlation function

$$C(t) = \frac{\langle h_A(x_0)h_B(x_t) \rangle}{\langle h_A \rangle}$$



$$\tau_{\text{rxn}}^{-1} = k_{AB} + k_{BA}$$

Phenomenological kinetics

$$\tau_{\text{mol}} < t \ll \tau_{\text{rxn}}$$

$$\frac{\langle h_A(x_0)h_B(x_t) \rangle}{\langle h_A \rangle} = \langle h_B \rangle \left( 1 - e^{-t/\tau_{\text{rxn}}} \right)$$

$$C(t) \approx k_{AB}t$$

# Bennett-Chandler approach

$$k(t) = \frac{dC(t)}{dt}$$

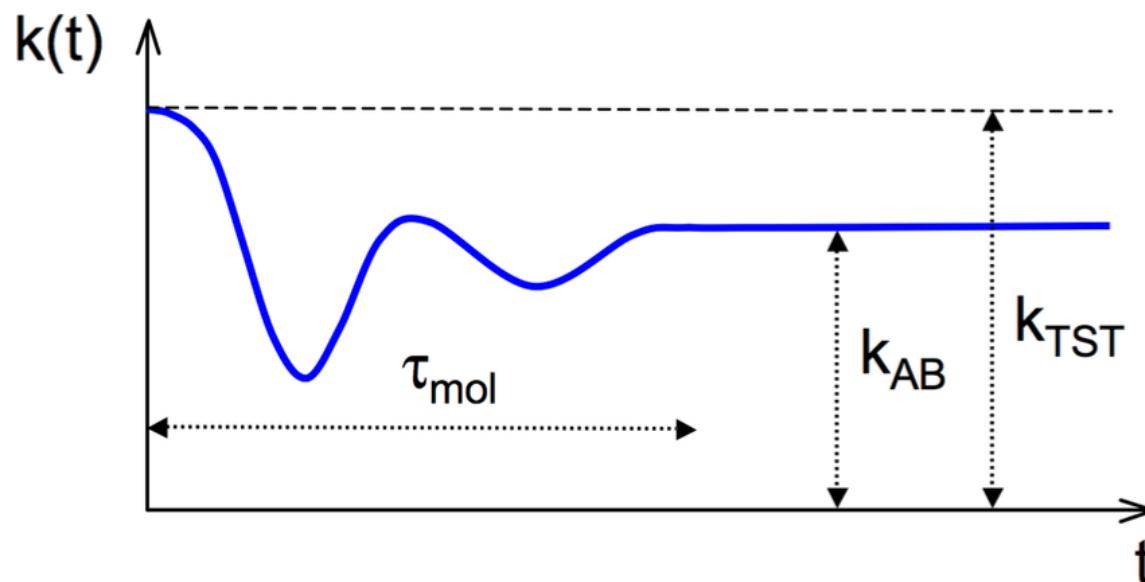
$$k(t) = \frac{\langle \dot{q}(0) \delta[q(0) - q^*] \theta[q(t) - q^*] \rangle}{\langle \delta[q^* - q(0)] \rangle} \times \frac{\langle \delta[q^* - q(0)] \rangle}{\langle \theta[q^* - q(0)] \rangle}$$



dynamical correction



from free energy

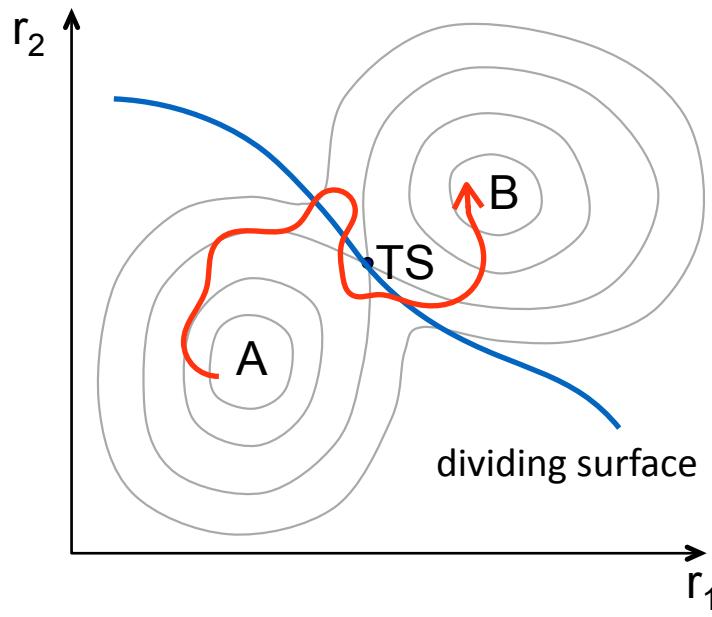


transmission coefficient

$$\kappa = k_{AB}/k_{TST}$$

# Transition state theory (TST)

Assumption of TST: **no recrossings** of dividing surface



$$k_{\text{TST}} = \frac{\langle \dot{q} \delta[q - q^*] \theta[\dot{q}] \rangle}{\langle \delta[q^* - q] \rangle} \times \frac{\langle \delta[q^* - q] \rangle}{\langle \theta[q^* - q] \rangle}$$

$$k_{\text{TST}} = \frac{1}{2} \langle |\dot{q}| \rangle_{q=q^*} \frac{e^{-\beta F(q^*)}}{\int_{-\infty}^{q^*} e^{-\beta F(q)} dq}.$$

Harmonic TST

$$k = \frac{1}{2\pi} \frac{\prod_{i=1}^n \omega_i^A}{\prod_{i=1}^{n-1} \omega_i^{TS}} \exp(-\beta \Delta V)$$

# Kramers turnover

