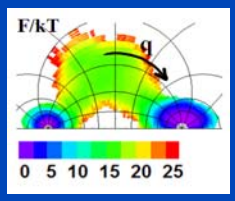
The Peters Lab

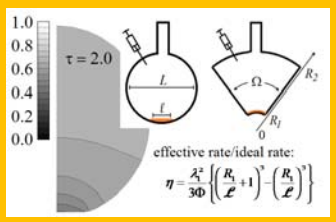
where the future is a random variable

reaction rate theory



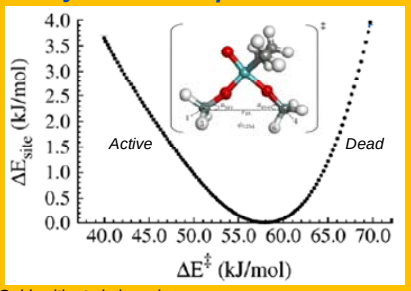
Peters et al. JACS (2008)

reactor models, etc.



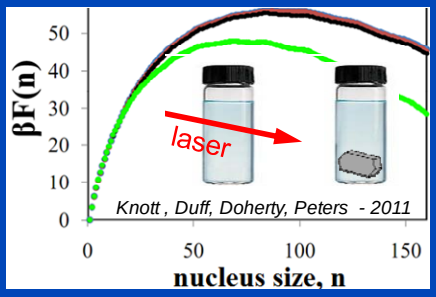
Peters, Chem. Eng. Sci. (2012)

catalysis on *amorphous* materials

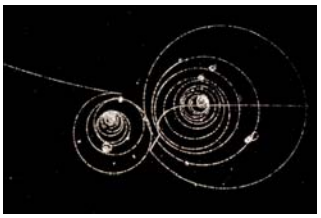


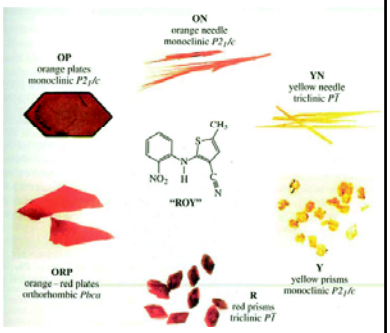
Goldsmith et al., in review

solute precipitate nucleation



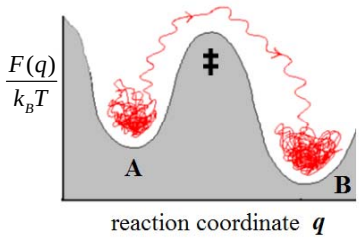
Nucleation is a rare event ?

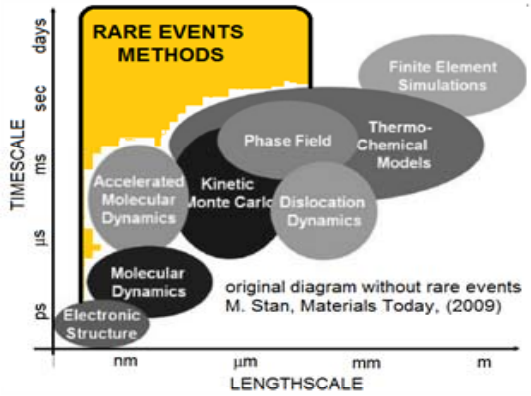




Dendrite, napolitano group, iowa state
Bubble chamber, nuclear engr uc davis
Crystal glazes (american pottery)
Gypsum crystals, Naica cave, Mexico
Seltzer water and finger, HEN
Lian Yu, Polymorphs of ROY

Rare events: TST, CNT, Kramers, Grote-Hynes, etc.





$\tau_{escape} >> \tau_{relax}$

necessary for existence of rate constant
otherwise, fully detailed initial condition matters

caution! slow processes may lack a *separation* of time-scales, e.g. ripening, glass aging, etc.

Baron Peters UCSB

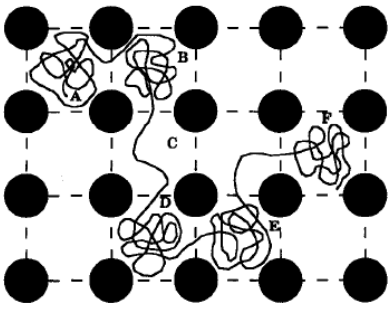
From brute force MD to discrete master equation

kinetic **M**onte **C**arlo, Bortz et al. *J. Comp. Phys*. (1975)

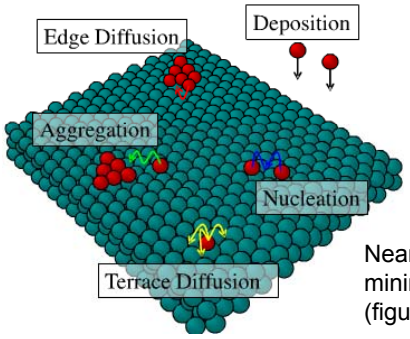
1. How long until next hop ? $\Delta t = -(\ln X)/\Sigma k_j$
2. Which hop will occur ? $p_i = k_i/\Sigma k_j$

Master equation construction
‡-search tools: NEB, Cerjan-Miller, etc.
transition state theory (usually harmonic)

Build master equation before kMC or
on-the-fly, e.g. Voter's Bond Boost method or
Mousseau's Activation Relaxation Techniques

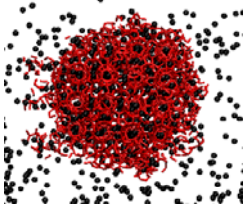


H-migration on Ni(100),
Zhang, Haug, Metiu, J. Chem. Phys. (1990)



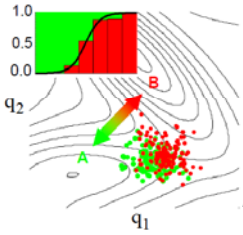
Nearly perfect when states correspond to minima on PES with high saddles between (figure from K. Fichthorn, PSU)

Atomistic simulations



Knott et al., J. Am. Chem. Soc. (2012)

Path sampling & high-through-put H_0-testing

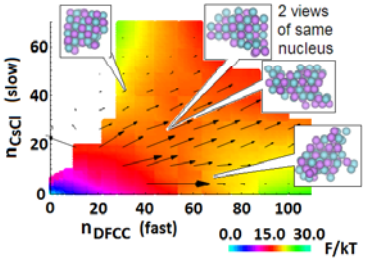


Peters et al. J. Chem. Phys. (2007)

Lattice models

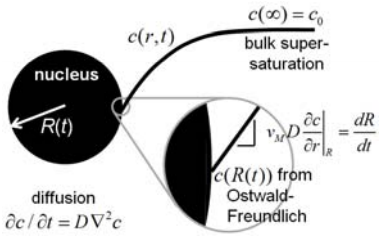
Duff, Knott et al., J. Chem. Phys. (2011)

Fokker-Planck parameterization



Peters, J. Chem. Phys. (2009)

Continuum analysis



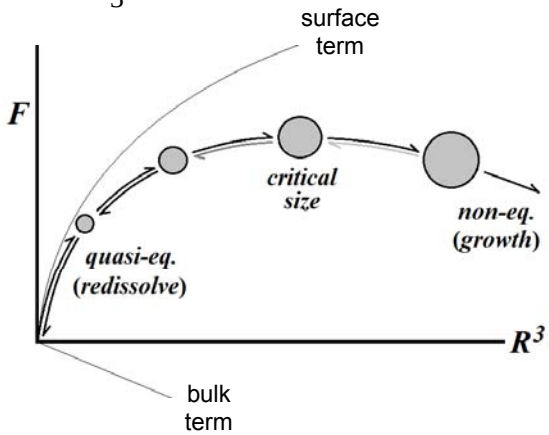
Peters, J. Chem. Phys. (2011)

classical nucleation theory

Gibbs, Volmer, Weber

surface *bulk*

$$F_{CNT}(R) = \gamma 4\pi R^2 - \Delta\mu \frac{4\pi}{3} R^3 v_M^{-1}$$



Agarwal & Peters, Adv. Chem. Phys. (in press)

Baron Peters UCSB

classical nucleation theory (details)

the driving force ['pushes' n to larger size…]

$$\Delta\mu = k_B T \ln\left(a_0 / a_{sat}\right)$$

replace *R* with *n*: equally valid and easily connected to simulation

$$F_{CNT}(n) = -n\Delta\mu + \gamma a n^{2/3} \quad \Leftarrow \quad F_{CNT}(R) = \gamma 4\pi R^2 - \Delta\mu \frac{4\pi}{3} R^3 v_0^{-1}$$

v_0 = volume per molecule in the nucleating (more stable) phase

$nv_0 = 4\pi R^3/3$ (for a sphere)

a = shape factor, $\gamma_{eff} = A_{total}^{-1} \sum_{[ijk]} A_{[ijk]} \gamma_{[ijk]}$

$$a = 4\pi \left(\frac{3v_0}{4\pi}\right)^{2/3} = 4.84 v_0^{2/3}$$

tetrahedra $a = 7.21 v_0^{2/3}$
cubes $a = 6 v_0^{2/3}$
octahedra $a = 5.72\ v_0^{2/3}$

Agarwal & Peters, Adv. Chem. Phys. (in press)

Baron Peters UCSB

classical nucleation theory (details)

What is the free energy in classical nucleation theory?

$$F_{CNT}(n) - F_{CNT}(1) = -k_B T \ln\left(\rho_{EQ}(n) / \rho_{EQ}(1)\right).$$

(important – not a Landau free energy, c.f. Maibaum PRL 2008)

Which nucleus is least common at equilibrium? $dF_{CNT}/dn = 0$

$$n^{\ddagger} = (2\gamma a / 3\Delta\mu)^3$$

The free energy 'barrier' is

$$F_{CNT}(n^{\ddagger}) = \frac{4(\gamma a)^3}{27\Delta\mu^2}$$

remarkable simplicity stems from the assumption that nuclei are of fixed shape (a) and properties (γ, $\Delta\mu$) at every size *n* down to *n = 1* molecule.

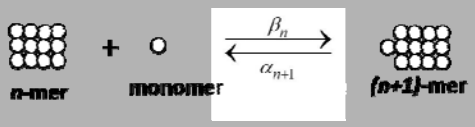
Are we there yet? No. This is just a static equilibrium description.

Agarwal & Peters, Adv. Chem. Phys. (in press)

Baron Peters UCSB

classical nucleation theory (details)

master equation: one atom at a time
skip some beautiful analysis
treat *n* as continuous variable
obtain Zeldovich-Frenkel eqn



$$\frac{d\rho}{dt} = \frac{\partial}{\partial n}\left(\beta \rho_{EQ} \frac{\partial}{\partial n}\left(\frac{\rho}{\rho_{EQ}} \right) \right)$$

change vars to Smoluchowski equation: $\Phi(n,t) \equiv \rho(n,t)/\rho_{eq}(n)$

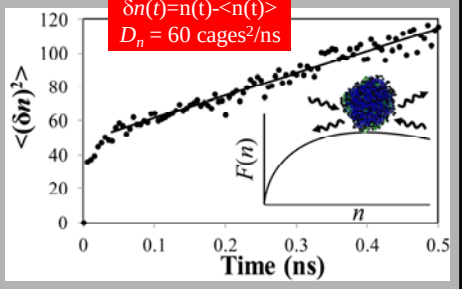
$$\frac{\partial \Phi}{\partial t} = e^{F(n)/k_B T} \frac{\partial}{\partial n}\left(e^{-F(n)/k_B T} D(n) \frac{\partial \Phi}{\partial n} \right)$$

what is this *D* ?

$$2Dt = <\delta n^2(t)>$$

a random walk in nucleus size via monomer attachment/detachment.

$2D_n t = <\delta n(t)^2>$
$\delta n(t) = n(t) - <n(t)>$
D_n = 60 cages²/ns



Agarwal & Peters, Adv. Chem. Phys. (in press)

Baron Peters UCSB

classical nucleation theory (details)

Are we there yet? almost

All of the action is happening at the barrier top where

$$F(n^{\ddagger} + \delta n) \approx F(n^{\ddagger}) - \pi k_B T Z^2 \delta n^2$$

in writing *F* this way we have defined the Zeldovich factor $Z = \sqrt{\frac{1}{2\pi k_B T} \frac{d^2 F}{dn^2}\Big|_{n^{\ddagger}}}$

Now solve steady state Smoluchowski equation with 'rescue and replace' boundary conditions:

$\Phi = 1$ for $n << n^{\ddagger}$
$\Phi = 0$ for $n >> n^{\ddagger}$

$$\frac{\partial \Phi}{\partial t}^{SS} = e^{F(n)/k_B T} \frac{\partial}{\partial n}\left(e^{-F(n)/k_B T} D(n) \frac{\partial \Phi}{\partial n} \right)$$

i.e. for the steady state situation where large nuclei are always removed and replaced by metastable solution

$$\Phi_{SS}(n) = \frac{1}{2} erfc[Z\sqrt{\pi}(n - n^{\ddagger})]$$

Φ_{SS} predicts steady leak to stable state. How fast is the leak? That's *J*.

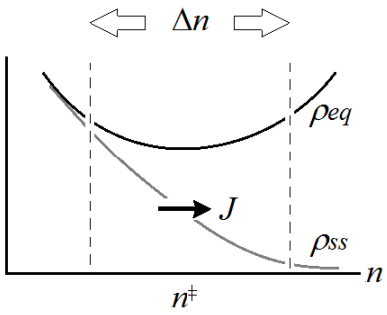
Agarwal & Peters, Adv. Chem. Phys. (in press)

Baron Peters UCSB

classical nucleation theory

$$J_{CNT} = -D(n^{\ddagger})\left.\frac{\partial \rho_{SS}}{\partial n}\right|_{n^{\ddagger}}$$
$$= -D(n^{\ddagger})\left.\frac{\partial \Phi_{SS}}{\partial n}\right|_{n^{\ddagger}} \rho_{EQ}(n^{\ddagger})$$
$$= \rho_1 D(n^{\ddagger})\, Z \exp[\{F(1) - F(n^{\ddagger})\}/k_B T]$$
$$= (prefactor)\exp\left[-\frac{4(\gamma a/k_B T)^3}{27\ln^2 S}\right]$$

with $\Delta\mu \cong k_B T \ln S$



$$\ln J_{CNT} = \ln A - B/\ln^2 S$$
$$B \sim \gamma^3/T^3$$

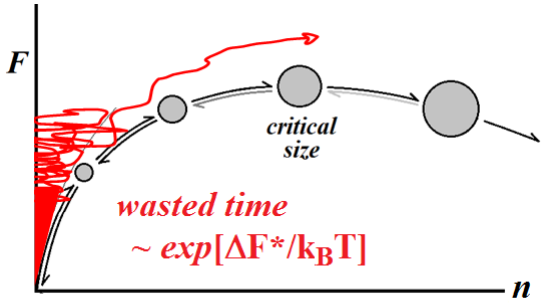
Agarwal & Peters, Adv. Chem. Phys. (in press)

Baron Peters UCSB

CNT assumptions: spherical nuclei, sharp interface, macroscopic γ, Δμ

J_{CNT} is notoriously inaccurate, but can simulation do better?

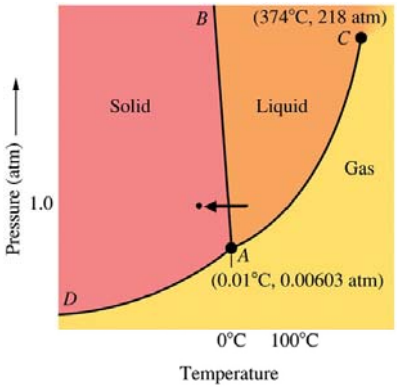
nucleation is a **rare event**
a fast rate: $J \sim 10^{21}$/cc/s
typical simulation box 100(nm)^3
→ waiting time for event: **1s !**

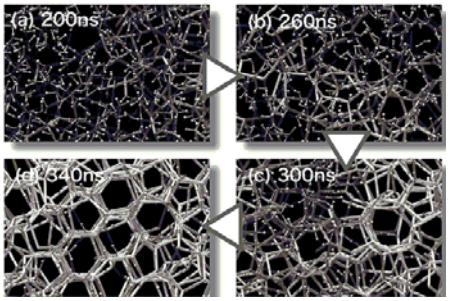


brute-force MD *and kMC* waste exponential CPU time on boring pre-critical dynamics

Baron Peters UCSB

Example: nucleation with brute force





Matsumoto's 7-yrs of simulation of supercooled water turning to ice, Nature, 2002

When does a calculation take so long that it will finish faster if you waitfor next yrs processors?

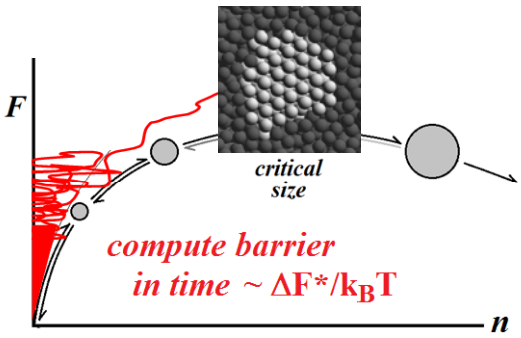
stevengoddard.wordpress.com/

Baron Peters UCSB

rare events methods

1996: ten Wolde, Frenkel
- local order parameter (n_{YLM})
- distinguish liquid vs. solid atoms
- umbrella sampling for barriers
- short trajectories for prefactors

Auer, Frenkel, Nature, 2001



Baron Peters UCSB

Umbrella Sampling 101

Torrie and Valleau, Mol. Phys. (1976)

$$e^{-F(q)/kT} \equiv \int d\mathbf{x} e^{-E(\mathbf{x})/kT} \delta[q - q(\mathbf{x})]$$

multiply both sides by exp[-V_{bias}(q)/kT]

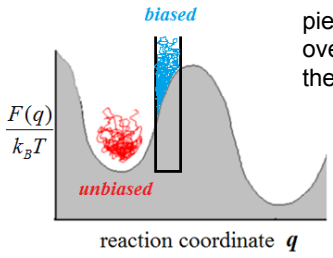
$$e^{-[F(q)+V_{bias}(q)]/kT} = \int d\mathbf{x} e^{-[E(\mathbf{x})+V_{bias}(q(\mathbf{x}))]/kT} \delta[q - q(\mathbf{x})]$$

solve for F(q):

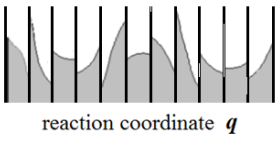
sample with biased Hamiltonian

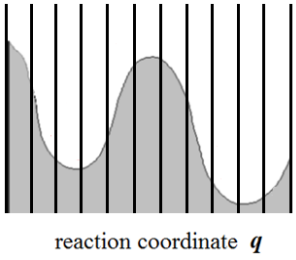
$$F(q) = -kT \ln \int d\mathbf{x} e^{-[E(\mathbf{x})+V_{bias}(q(\mathbf{x}))]/kT} \delta[q - q(\mathbf{x})] - V_{bias}(q)$$

www.flickr.com



piecewise $F(q)$ from many overlapping bias "windows" then stitch together WHAM





Baron Peters UCSB

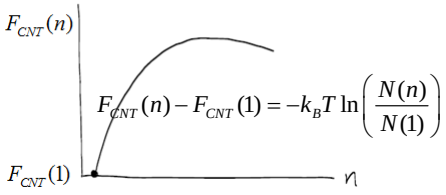
Even the best methods can be used badly…

- free energy barriers are not observables
- HEN rate is not "*faster than*" HON rate (they have different units)
- what happens en route to bottleneck is kinetically irrelevant
- no hypothesis, no control, no test, no science
- ensembles matter: solute precipitate nucleation in grand or semigrand
- guessing coordinates is so '90s – we have ways to get them right now
- use the correct free energy with the correct rate theory

Which F for which rate theory?

CNT formulation

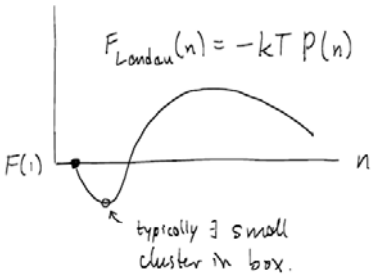
$N(n)$ average number of nuclei of size n in simulation box



YouTube

Landau-MFPT formulation

n_{max} largest nucleus in simulation box and $P(n) = Prob[n_{max} = n]$

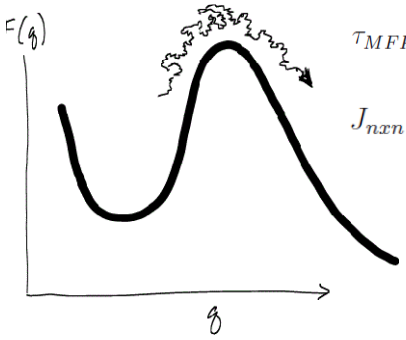


"[CNT] breaks down at large supersaturation or supercooling."

- two formulations are different routes to same rate *when CNT correct*
- Landau formulation more general, not tied to assumptions of CNT

Rates without the CNT assumptions: Kramers theory

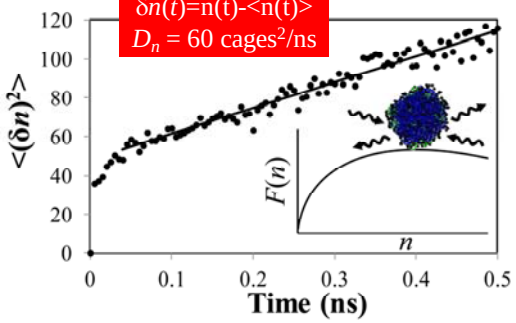
Physica A(1940): here concerned only with overdamped limit and "rescue and replace" steady state diffusion current



$$\tau_{MFPT} = \int_{\cup} exp[-\beta F(n)]dn \int_{\cap} \frac{exp[\beta F(n)]}{\mathcal{D}(n_{\ddagger})}dn$$

$$J_{nxn} = (\tau_{MFPT} V)^{-1}$$

$2D_n t = \langle \delta n(t)^2 \rangle$
$\delta n(t) = n(t) - \langle n(t) \rangle$
D_n = 60 cages^2/ns



One last pitfall

- **which metric *n* gives correct *J* ?**
- **unlike inertial barrier crossing,**
  ∃ no correction for bad n !

Baron Peters 2012

Kramers-Langer-Berezhkovskii-Szabo theory

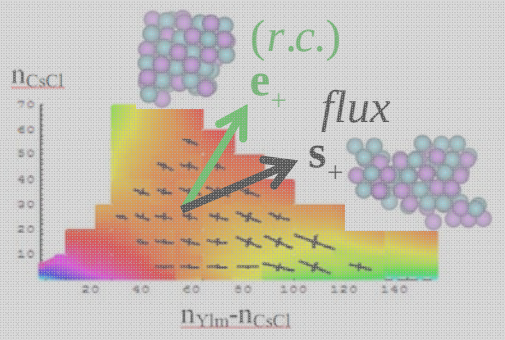
J. Langer, *Ann. Phys.* (1969)

$$\beta F[\mathbf{q}] = \beta F_{\neq} + \frac{1}{2}\mathbf{q}^T \mathbf{A}\mathbf{q}$$

$$k_N = \frac{1}{2\pi}\left(\frac{\det \mathbf{A}_R}{\det \mathbf{A}}\right)^{1/2} \lambda_+ \exp[-\beta F_{\neq}]$$

$$\mathbf{DA}\mathbf{s}_+ = -\lambda_+ \mathbf{s}_+$$

- **A** = Hessian of F(**q**)
- **D** = diffusivity tensor



Berezhkovskii and Szabo, *JCP* (2005)

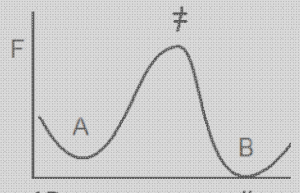
project everything onto 1 direction **e**

$$k(\mathbf{e}) = \frac{1}{2\pi}\left(\frac{\det \mathbf{A}_R}{\det \mathbf{A}}\right)^{1/2}\left(\frac{\mathbf{e}^T\mathbf{D}\mathbf{e}}{|\mathbf{e}^T\mathbf{A}\mathbf{e}|}\right)\exp[-\beta F_{\neq}]$$

projection $\mathbf{e}_+$ minimizes $k(\mathbf{e})$ and gives *same rate as Langer*. ($\mathbf{A}\mathbf{D}\mathbf{e}_+ = -\lambda_+\mathbf{e}_+$)

reaction coord direction $\mathbf{e}_+$ *is* $\partial p_B/\partial \mathbf{q}$

$$p_B(\mathbf{q}) = \frac{1}{2} erfc\left(\mathbf{e}_+^T\mathbf{q}\Big/\sqrt{2\,|\,\mathbf{e}_+^T\mathbf{A}^{-1}\mathbf{e}_+\,|}\right)$$



1D rxn.coor = p_B dirxn

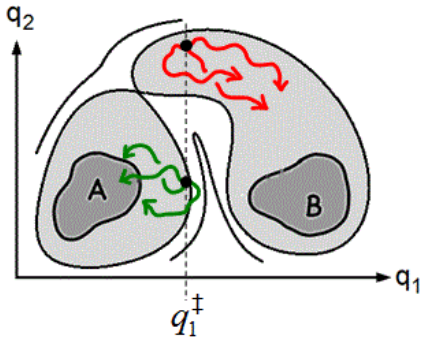
Example from Peters, J. Chem. Phys. (2009)

KLBS theory (multidimensional Kramers) tells us that

(1) flux direction ≠ reaction coordinate, i.e. movies can be mechanistically misleading

(2) MFEP direction, e.g. from String method, is neither flux nor reaction coordinate but rather something between the two

(3) the committor is the correct (1D) reaction coordinate for overdamped problems



*except in very special cases where all variables diffuse at same rate. then all three directions are equivalent.

143 7. Crystal Nucleation of LJ particles

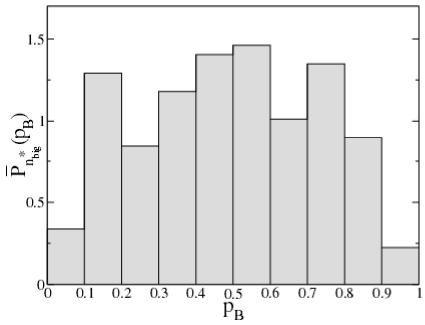


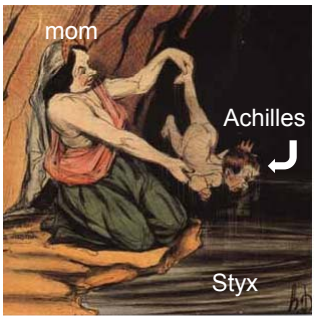
Figure 7.14: Path committor probability $\bar{P}_{n_{\rm big}^*}(p_B)$ restricted to the transition ensemble. The curve is computed using points for which $n_{\rm big} \in [240, 246]$. Even if transitions only are considered the distribution is substantially flat, indicating $n_{\rm big}$ is not a good reaction coordinate.

For a good coordinate, the histogram would be narrow and centered at ½.

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

rates without reaction coordinate by path sampling

Transition Path Sampling, Forward Flux Sampling, Transition Interface Sampling, etc.



Transition path sampling is inefficient for processes that take longer than a picosecond.

- Allen, ten Wolde, Frenkel, *J. Chem. Phys.* (2005).

Determining [variables] that reflect the dynamics of the system is a trial and error procedure.

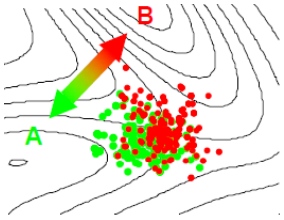
- Hagan, Dinner, Chakraborty, and Chandler, PNAS, (2004).

A prospective reaction coordinate can be tested … This is an extremely costly procedure.

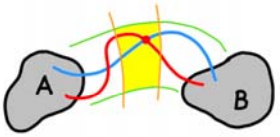
- Juraszek and Bolhuis, Biophysical Journal (2008)

**c.f. Hillier et al. J. Phys. Chem. B. 2004*

Aimless Shooting, i.e. *efficient Transition Path Sampling*

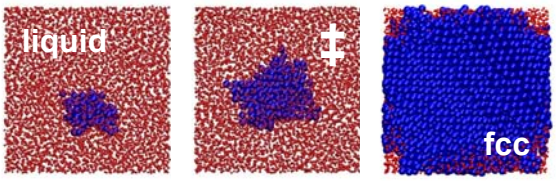


shooting points automatically generated in bottleneck region!



example: nucleation in the supercooled Lennard-Jones fluid

*"**TPS is inefficient for processes that take longer than a picosecond.**" - Allen, ten Wolde, Frenkel (2005)*



P*=5.68, T*=0.888, R_{cutoff}=2.5σ

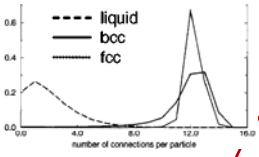
- 3000 trajectories
- **400ps duration**
- **30% acceptance**

and rapid decorrelation!

Peters and Trout, J. Chem. Phys. (2006)
Peters, Beckham, Trout, J.Chem.Phys. (2007)
Beckham and Peters, J. Phys. Chem. Lett. (2011)
γ=100, Langevin dynamics, 4kT per contour

likelihood maximization = high throughput hypothesis testing

- **Structure**
  - q_2^{box}, q_4^{box}, q_6^{box}, q_8^{box}
  - w_2^{box}, w_4^{box}, w_6^{box}, w_8^{box}
  - q_2^{cl}, q_4^{cl} , q_6^{cl} , q_8^{cl}
  - w_2^{cl}, w_4^{cl}, w_6^{cl}, w_8^{cl}
  - $\underline{q}_2^{box}$, $\underline{q}_4^{box}$, $\underline{q}_6^{box}$, $\underline{q}_8^{box}$
  - $\underline{q}_2^{cl}$, $\underline{q}_4^{cl}$, $\underline{q}_6^{cl}$, $\underline{q}_8^{cl}$
  - Q_2^{glob}, Q_4^{glob}, Q_6^{glob}, Q_8^{glob}
  - W_2^{glob}, W_4^{glob}, W_6^{glob}, W_8^{glob}
  - $\langle C_{ss} \rangle$ = average coordination of solid particles [Parrinello et al.]
  - Lechner-Dellago avg. local q_ℓ's



ten Wolde, Ruiz-Montero, Frenkel, *JCP*, 1996

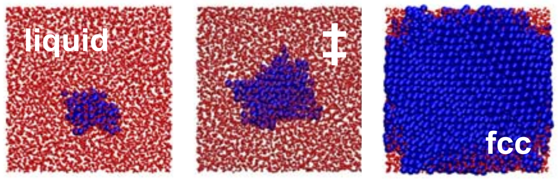
previous OPs for nucleation in the super-cooled LJ fluid

- **Size**:
  - $n_{Dellago}$(2008)
  - $n_{Frenkel}$=n_{YLM}
  - $\det(I_1 \cdot I_2 \cdot I_3)$
  - $[\det(I_1 \cdot I_2 \cdot I_3)]^{1/3}$
  - $[\det(I_1 \cdot I_2 \cdot I_3)]^{1/6}$
- **Shape:**
  - I_{max} / I_{min}
  - $[\det(I_1 \cdot I_2 \cdot I_3)]^{1/3} / I_{min}$
  - $n_{surface} / (n_{cluster})$
- **Size · Structure:**
  - $q_6^{cl} \cdot n$
  - $\underline{q}_6^{cl} \cdot n$
  - $\langle c_{ss} \rangle \cdot n$
- **Size/(elongatedness):**
  - $n / (I_{max} / I_{min})$

some that Beckham & I added

Steinhardt, van Duijnveldt and Frenkel, ten Wolde and Frenkel, Ruiz-Montero, Donadio and Parrinello, Degranges and Delhommelle, Torquato, Debenedetti, Moroni, Bolhuis, Glotzer, Lechner and Dellago,… PRL, JCP, JACS, JPCB, PRE,…. from 1981 to 2011

Beckham, Peters, *JPCLett*, (2011)

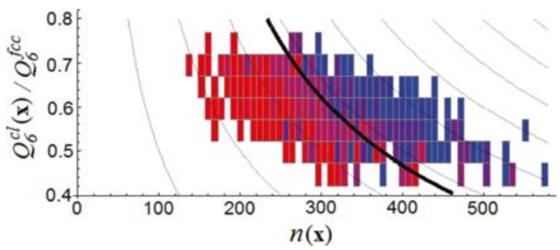


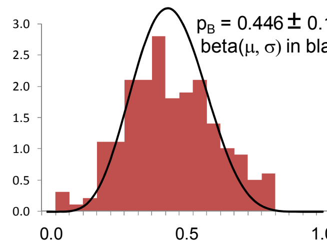
P*=5.68, T*=0.888, R_{cutoff}=2.5σ

Likelihood maximization tests 60 mechanistic hypotheses in minutes

unprecedented accuracy: by trial and error or by any other method

~100K d.o.f but only one matters: ($Q_6^{cl} \cdot n$)
i.e. Frenkel x Bolhuis





Beckham, Peters, *JPCLett*, (2011)
coming soon, Dellago et al. (2013)

Path sampling advantages

- unbiased dynamics
- rates, free energies, and (most important) identify reaction coordinates
- don't need MC moves
- new path sampling algorithms are efficient
- don't need forces on q
- q can be *anything,* even dynamical quantity, e.g. studies of jamming via Chandler's s-ensemble.

*Transition path sampling is **inefficient** for processes that are longer than a picosecond.*
- Allen, ten Wolde, Frenkel, *J. Chem. Phys.* (2005).

aimless shooting

*Determining [variables] that reflect the dynamics of the system is a **trial and error** procedure.*
Ma, Dinner, Chakraborty, and Chandler, PNAS, (2004).

likelihood maximization

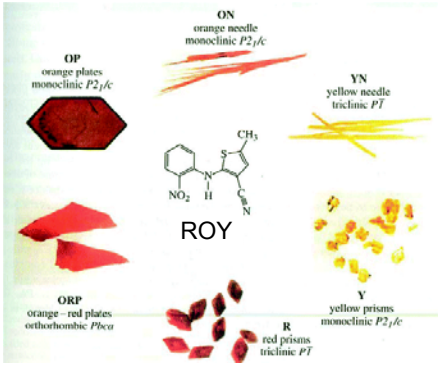
*A prospective reaction coordinate can be tested … This is **extremely costly** procedure.*
Juraszek and Bolhuis, Biophysical Journal (2008)

binomial deconvolution

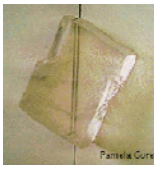
Path sampling : dynamics
: :
Metropolis MC : equilibrium

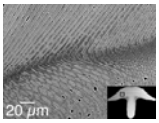
See:
B. Peters, *Molec. Sim.* (2010)
Ma and Dinner, J. Phys. Chem. B. (2005)
Bolhuis and Dellago, *Adv. Polym. Sci.* (2009)

polymorph selection



calcite aragonite vaterite



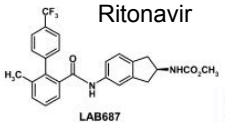


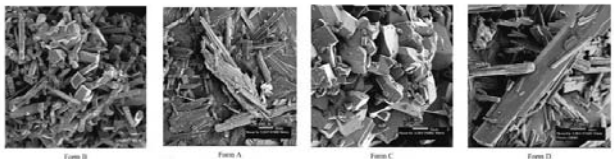
urchin teeth P. Gilbert

abalone nacre P. Gilbert

human pearl Bassi et al.

Ritonavir



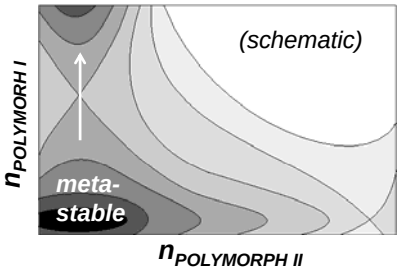


Bernstein, Chem. Comm. 5007, 2005
Chemburkar et al., Org. Process Res. Dev. (2000)
Somerdjik et al. Science (2009)

Bassi et al. Curr. Therapeutic Res. 55, 1169, (1994)
http://en.wikipedia.org
http://home.physics.wisc.edu/gilbert/

free energy landscape for polymorph selection

Ivan Stranski: nucleation via channel with lowest barrier

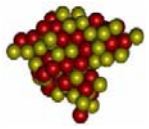


Baron Peters UCSB

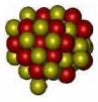
(2007) PHYSICAL REVIEW LETTERS

Evidence for Out-of-Equilibrium Crystal Nucleation in Suspensions of Oppositely Charged Colloids

Eduardo Sanz,[1,*] Chantal Valeriani,[2] Daan Frenkel,[2] and Marjolein Dijkstra[1]



Forward Flux Sampling (n_{YLM})



DFCC

natural brownian dynamics

dynamics governing polymorph selection?

artificial dynamics ±swaps

CsCl

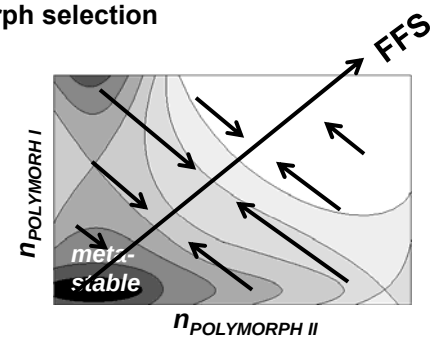
- assumed ∃ two separate pathways one to CsCl and one to DFCC
- concluded ∃ breakdown in quasi-equilibrium for pre-critical nuclei

but evidence from projection (dynamics and free energy) onto 1D n_{YLM}

Baron Peters UCSB

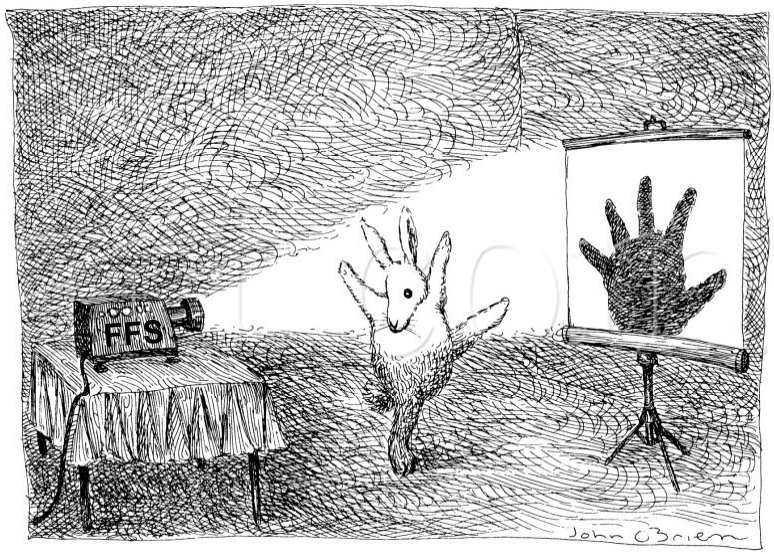
free energy landscape for polymorph selection

Ivan Stranski: nucleation via channel with lowest barrier



Baron Peters UCSB

Projection to lower dimension can cause confusion

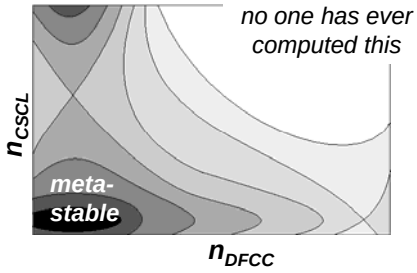


Baron Peters UCSB

understanding polymorph selection

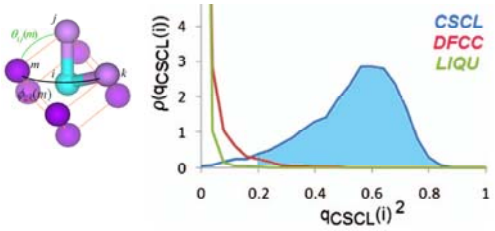
requires one coordinate per polymorph

Ivan Stranski: channel with the lower barrier wins



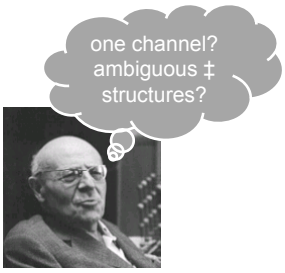
polymorph specific nucleus size coordinates

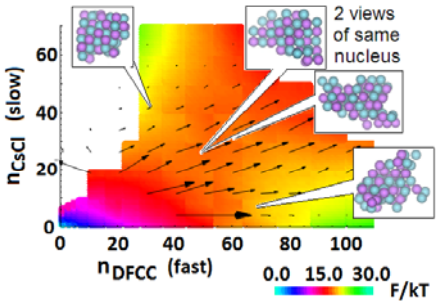
n_{CSCL} and n_{DFCC} to replace n_{YLM}



Peters, J. Chem. Phys. (2009)

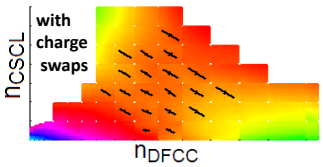
free energy landscape for polymorph selection



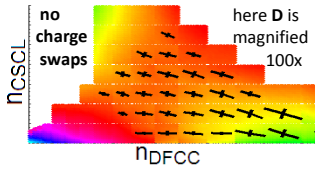


$$2\mathbf{D}t = \begin{bmatrix} \langle \delta n_{DFCC}(t)^2 \rangle_{\mathbf{n}(0)} & \langle \delta n_{DFCC}(t)\delta n_{CSCL}(t) \rangle_{\mathbf{n}(0)} \\ \langle \delta n_{DFCC}(t)\delta n_{CSCL}(t) \rangle_{\mathbf{n}(0)} & \langle \delta n_{CSCL}(t)^2 \rangle_{\mathbf{n}(0)} \end{bmatrix}$$

diffusion tensor & free energy into Fokker-Planck = FFS results



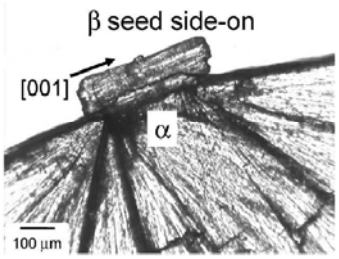
selection governed by dynamics at and beyond ‡

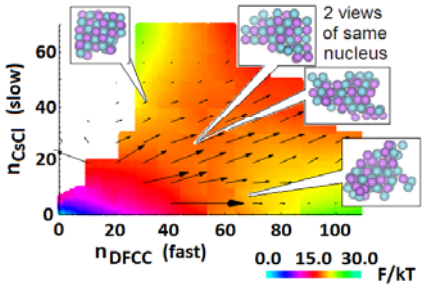


Peters, J. Chem. Phys. (2009)

D-mannitol from water, Tao et al., *Cryst. Growth & Des.* (2007)

thermo. stability: solution $< \alpha < \beta$
growth rate from solution: $\alpha > \beta$



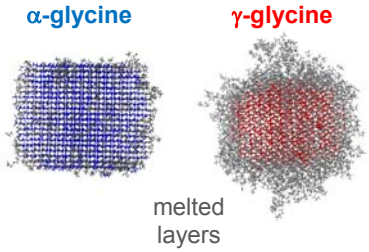


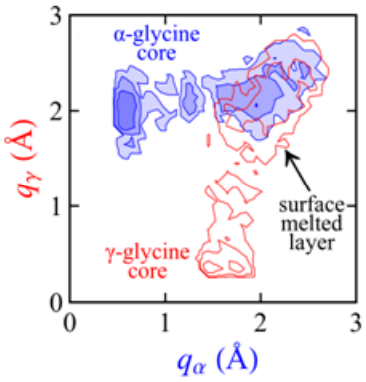
- **high mobility downhill from ‡ in DFCC direction**
- ~~breakdown in quasi-equilibrium for pre-critical nuclei~~
- **"*Direction of the nucleation current through the saddle point in the binary nucleation theory and the saddle point avoidance*",**
  Berezhkovskii, Zitserman, *J.Chem. Phys.* (*1995*).

n = (n_I, n_{II}) → ***D*(n), *F*(n) → Fokker-Planck → polymorph selection**

Baron Peters UCSB

fast, easy, general polymorph specific local order parameters for molecular crystals and nuclei





$$\ln J_{CNT} = \ln A - B / \ln^2 S$$

$$B \sim \gamma^3 / T^3$$

300K, 1atm
Forcefield: S.Price et al. (AMBER), Mol. Sim. (2006)

Duff, Peters, J. Chem. Phys. (2011)

Solvated glycine crystallites

γ-glycine, α-glycine, melted layers, NaCl, water not shown

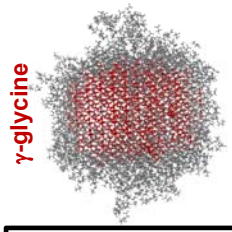
expected double layer forms

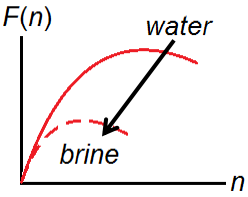
$$\psi(r,\theta) = \psi_0 \left(\frac{1+Kr}{1+K}\right) \frac{e^{-K(r-1)}}{r^2} \cos\theta$$

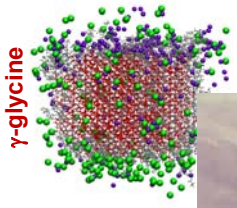
in water

schematic ΔΔF

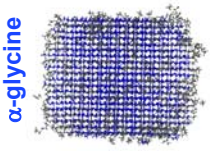
in brine

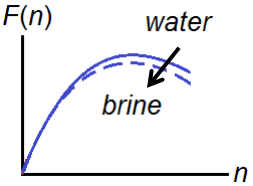


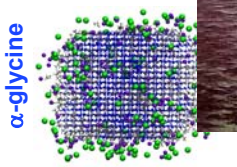




can Nathan turn water into brine?

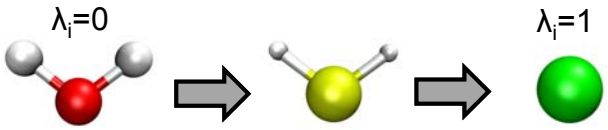






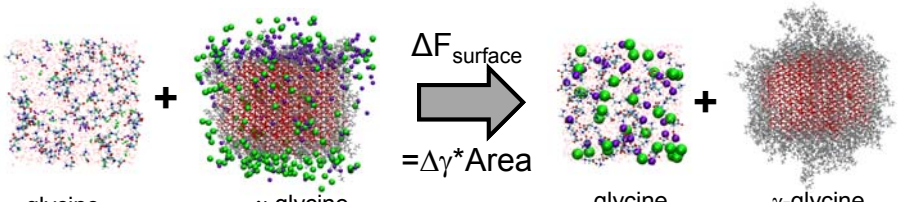
Duff, Peters, in progress

alchemical transformation of the entire solvent



$$\Delta F = -kT \sum_{i=1}^{N} \ln \left\langle \exp\left\{-\left[H(\lambda_{i+1}) - H(\lambda_i)\right]/kT\right\}\right\rangle_i$$

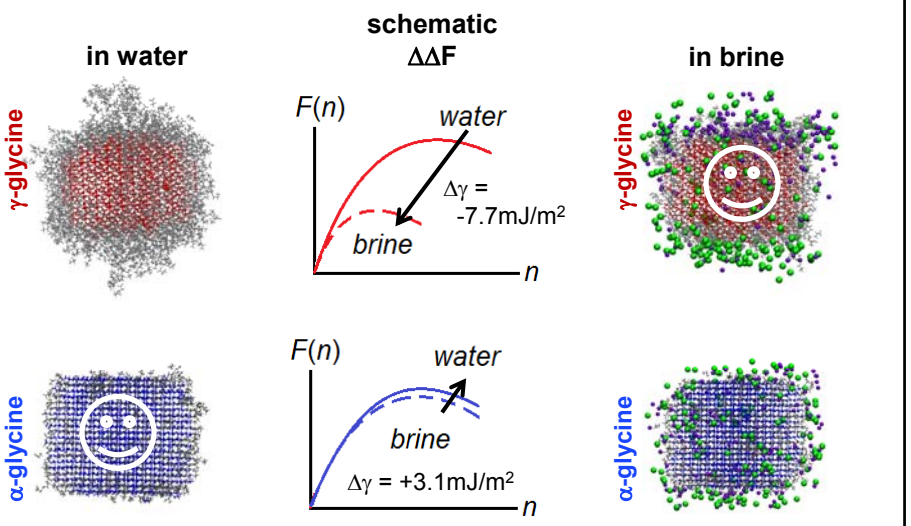
'transfer' crystallite to isolate the interfacial free energy:



glycine in water + γ-glycine nxs in brine → glycine in brine + γ-glycine nxs in water

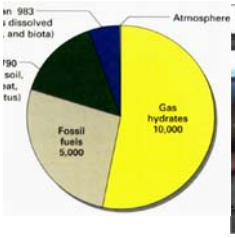
R. Zwanzig, J. Chem. Phys. 22, 1420, (1954)

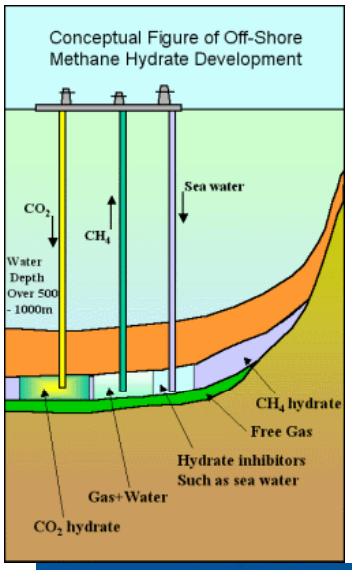
Duff, Peters, in progress


in water
schematic
ΔΔF
in brine
γ-glycine
F(n)
water
Δγ =
-7.7mJ/m²
brine
n
γ-glycine
α-glycine
F(n)
water
brine
Δγ = +3.1mJ/m²
n
α-glycine

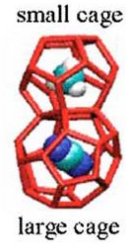
diffusion in methane hydrates

$CH_4 \cdot 7H_2O + CO_{2(g)} \rightarrow CO_2 \cdot 7H_2O + CH_{4(g)}$





enclathrated methanes in crystal array



Images: Amadeu Sum, Werner Kuhs, Dornan et al, (Us), and http://www.aist.go.jp/NIRE/eco_tec_e/new-ene_e.htm

Baron Peters UCSB

Off lattice, non-spherical, two components?

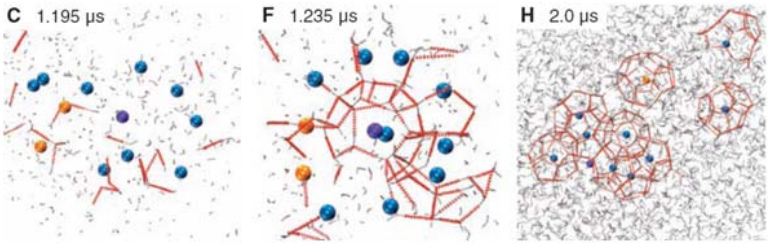
many studies crank up $\Delta\mu$ so t_{nxn} ~ ns
untestably fast rates ☹ is the mechanism altered? is that spinodal decomp?

SCIENCE VOL 326 20 NOVEMBER 2009

Microsecond Simulations of Spontaneous Methane Hydrate Nucleation and Growth

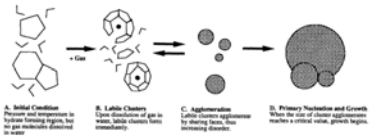
Matthew R. Walsh,[1] Carolyn A. Koh,[1] E. Dendy Sloan,[1] Amadeu K. Sum,[1]* David T. Wu[1,2]*

- best effort to date, but:
- estimated rate: **k ~ 10^{26}/cc/s** much faster than measurable
- expect fast b/c simulations at effective P_{CH4}=32000atm!



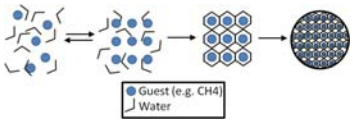
Baron Peters UCSB

Proposed (**homogeneous**) mechanisms of hydrate nucleation



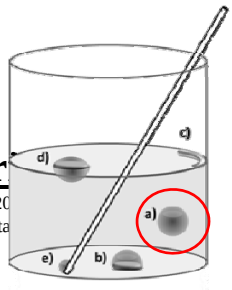
Labile cluster

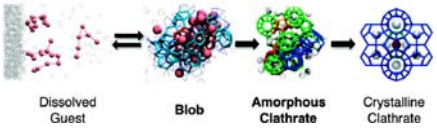
Sloan and coworkers
(figure: Christiansen and Sloan
Annals of the NYAS (1994))



Local structur

Radhakrishnan and Trout JCP (20
(figure: current author's representa





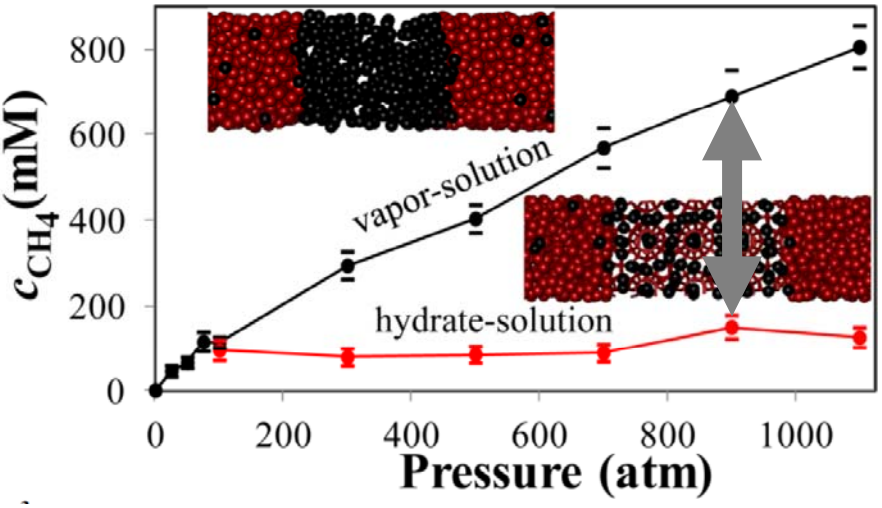
Blob (two – step)

Jacobson, Hugo, and Molinero JACS (2010)
Jacobson, Hugo, and Molinero JPC B (2010)
(figure: Jacobson et al JPC B (2010))

Baron Peters UCSB

Supersaturation at T = 273K

P = 900 atm
c/c_{sat} = 5.8



Knott et al. J. Am. Chem. Soc. (2012)
using FF: Jacobson, Hugo, and Molinero JPC B (2010)

Baron Peters UCSB

Average over noise in overdamped Langevin equation

$$\frac{d\langle n\rangle}{dt} = -\frac{D_n}{k_B T}\frac{\partial F}{\partial n}$$

D_n = attach. freq. ✓

What is $\partial F/\partial n$?

$$\frac{\partial F}{\partial n} = -\Delta\mu + \frac{2}{3}\phi\gamma n^{-1/3}$$

ϕ = shape factor ✓

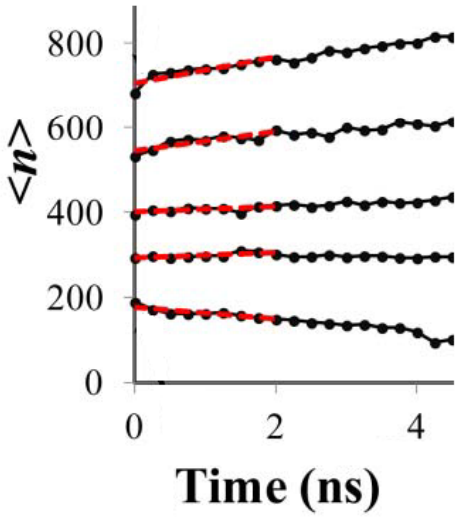
$\Delta\mu = kT\ln[c/c_{sat}]$ ✓

n = cluster size ✓

$d\langle n\rangle / dt$ ✓

γ = surface tension **?**

one parameter least squares fit

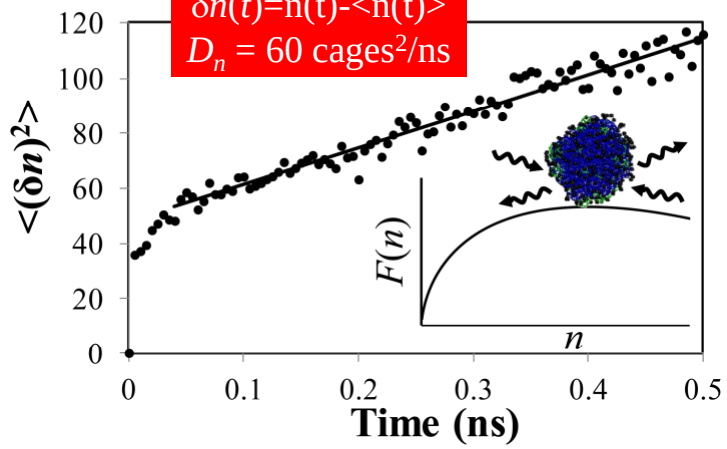


Baron Peters UCSB

$2D_n t = \langle \delta n(t)^2 \rangle$

$\delta n(t) = n(t) - \langle n(t) \rangle$

D_n = 60 cages^2/ns



Knott et al. J. Am. Chem. Soc. (2012)

Baron Peters UCSB

for realistic conditions must use nucleation theory and rare events

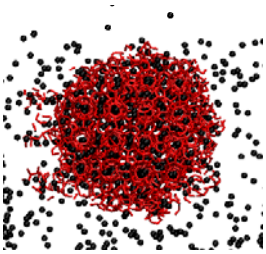
$\gamma = 31$ mJ/m^2

expt: 32±3mJ/m^2

$\Delta G^{\ddagger} = 305\ k_B T$

$J = 3 \times 10^{-112}$ nuclei/cc/s

$$J = \rho_1 D(n^{\ddagger})\, Z\, \exp[\{\Delta G(1) - \Delta G(n^{\ddagger})\} / k_B T]$$



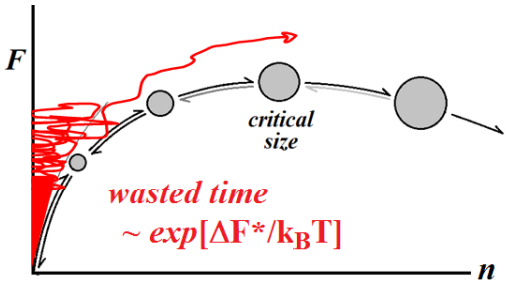
the transition state
(critical nucleus)

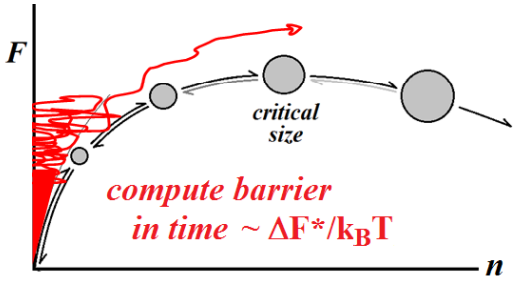
not homogeneous nucleation? heterogeneous how?

Knott et al. J. Am. Chem. Soc. 2012

Baron Peters UCSB

1 nucleus per 10^{79} years per earth!
not by parallelization, coarse-graining, etc.

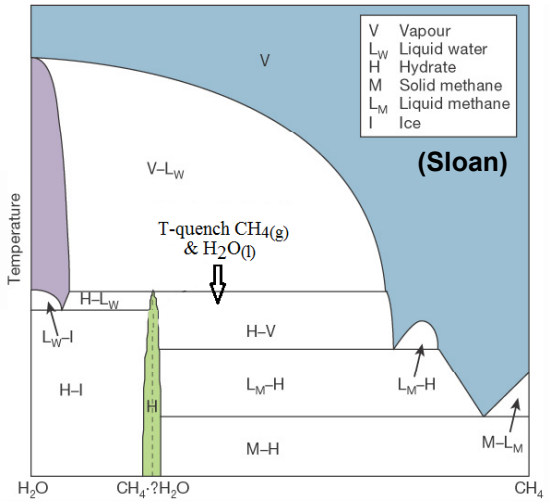




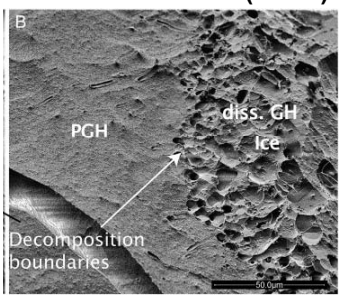
only rare events methods

Hydrates made by cycling T around their freezing point

(Kuhs)



(Sloan)

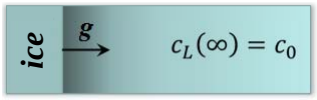


but hydrate and ice interfaces are incompatible (Molinero)

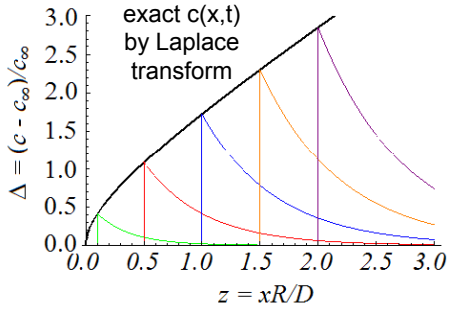
Poon, Peters, *in preparation*

ice growth creates zone of giant hydrate supersaturation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + g\frac{\partial c}{\partial x}$$



Tiller et al. 1953



stochastic "survival probability" model: $t_{nxn} = t_{nxn}(g, S_0, Area, D)$

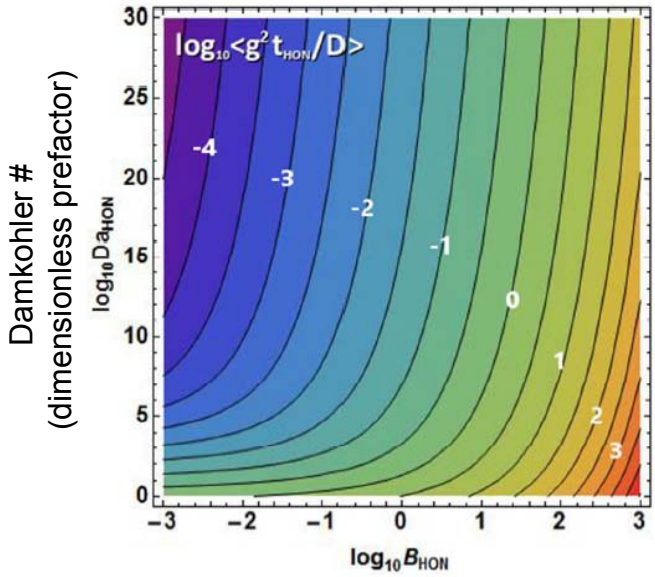
$$J_{nxn} = J_0 \exp\left[-\mathrm{B}/\ln^2(c(\mathbf{x},t)/c_{sat})\right]$$

$$P_{no\ nxn}(t) = \exp\left[-\int_0^t dt \int_V d\mathbf{x} \cdot J_{nxn}(\mathbf{x},t)\right]$$

Poon, Peters, *in review*

Baron Peters UCSB

dimensionless induction time



Poon, Peters, *in review*

Poon, Peters, *in review*

How important is nucleation in the freeze concentration boundary layer?

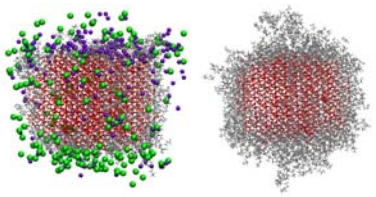
Reasonable parameters for hydrates/ice…

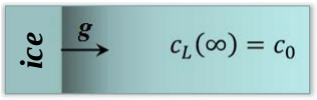
Poon, Peters, *in review*

	freeze conc.	*homog. nxn*
initial supersaturation, $S(t=0)$	1	5.8
observation area or volume, a or V	1 cm^2	1 cm^3
ice growth velocity, g	1 μm/s	--
methane diffusivity, D	1.46×10^{-9} m^2/s	--
average induction time, $\langle\tau\rangle$	22 hours	10^{103} years

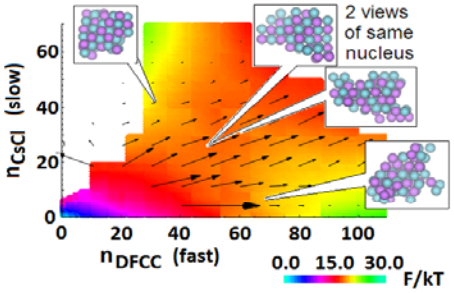
… a googol-fold acceleration.

Poon, Peters, *in review*

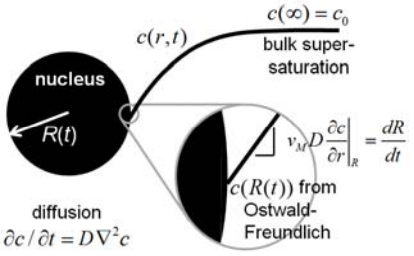




Tiller et al. 1953



thank you:
Nathan Duff, Brandon Knott, Geoff Poon, Gregg Beckham, Bernhardt Trout, Mike Doherty, Vale Molinero, Vishal Agarwal



LANL
IMMS
NSF CAREER
NSF CDI-TypeII

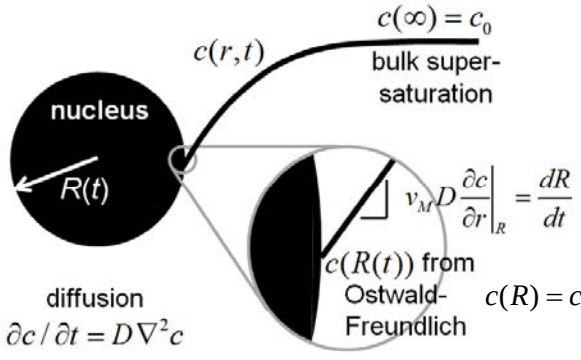
Baron Peters UCSB

Table 1: S dependence of pre-exponential factor

attachment kinetics	$\rho_1 Z D(n_\ddagger)\exp[F(1)/k_B T]$	S-dependence
diffusion controlled	$4\pi \mathcal{D} R_\ddagger \rho_1^2 Z \exp[F(1)/k_B T]$	$\sim S \ln S$
surface reaction controlled	$4\pi R_\ddagger^2 k_S \rho_1^2 Z \exp[F(1)/k_B T]$	$\sim S$

Concentration fluctuation gating in nucleation

- Volmer's CNT (1926) was for vapor condensation
  concentration fluctuations decay rapidly and $\lambda_{MFP} > R_{CNT}$
- <u>everyone</u> uses CNT in solution too:
  We will mostly use "vapor" and "liquid" for simplicity but the reader can replace these with "dilute" and "concentrated" … Sear, Cryst. Growth and Des. (2012)
- in solution $R_{CNT}^2/D >>$ ps (attachment time) ⇒ 1st shell quasi-equilibrates to slowly changing R



$$c(R) = c_0 \exp[-\beta \Delta\mu_0 (1 - R_{CNT}/R)]$$

Peters, *J. Chem. Phys*. (2011)

Baron Peters UCSB

$F(n) = -n\Delta\mu_0 + \gamma n^{2/3}$

obvious:

$\Delta\mu_0 = kT \ln[c_0 / c_{SAT}]$

$4\pi R^3 / 3 = n v_M$

less obvious: (Volmer-Weber):

$$\mu(n) \equiv \partial F / \partial n = -\Delta\mu_0 + \frac{2\gamma}{3} n^{-1/3}$$

$$= kT \ln[c(n) / c_0]$$

combine two expressions for $\mu(n)$:

$$\ln[c(R)/c_0] = \ln[c_0 / c_{SAT}] + \frac{2\gamma}{3kT}\left(\frac{3v_M}{4\pi}\right)^{1/3}\frac{1}{R}$$

require $c(R_{CNT}) = c_0$

$$c(R) = c_0 \exp\left[-\beta\Delta\mu_0(1 - R_{CNT}/R)\right]$$

classical nucleation theory

c(n) = concentration that would be in equilibrium with cluster of size n

Ostwald-Freundlich as boundary condition

Peters, *J. Chem. Phys.* (2011)

Baron Peters UCSB

diffusion coupled nucleation model

rescaled independent variables

$\tau = tD / R_{CNT}^2$ *scaled time*

$\xi = r / R(\tau)$ *scaled distance*

rescaled dependent variables

$u(\xi,\tau) = \left(c(\xi,\tau) - c_0\right)/c_0$

$\sigma(\tau) = R(\tau)/R_{CNT}$

eliminate moving boundary in exchange for extra terms

$$\frac{\partial}{\partial r} = \frac{\partial\xi}{\partial r}\frac{\partial}{\partial\xi} + \frac{\partial\tau}{\partial r}\frac{\partial}{\partial\tau}^{0} = \frac{1}{R(\tau)}\frac{\partial}{\partial\xi}$$

$$\frac{\partial}{\partial t} = \frac{\partial\tau}{\partial t}\frac{\partial}{\partial\tau} + \frac{\partial\xi}{\partial t}\frac{\partial}{\partial\xi} = \frac{D}{R_{CNT}^2}\left(\frac{\partial}{\partial\tau} - \frac{\sigma'(\tau)}{\sigma(\tau)}\xi\frac{\partial}{\partial\xi}\right)$$

ODE for R(t)

$$\frac{1}{2}\frac{d\sigma^2}{d\tau} = \varepsilon\left.\frac{\partial u}{\partial\xi}\right|_{\xi=1}$$

PDE for c(r, t)

$$\sigma^2\frac{\partial u}{\partial\tau} = \frac{1}{2}\frac{d\sigma^2}{d\tau}\xi\frac{\partial u}{\partial\xi} + \frac{1}{\xi^2}\frac{\partial}{\partial\xi}\left[\xi^2\frac{\partial u}{\partial\xi}\right]$$

Boundary conditions

at interface

$u(1,\tau) = \exp[-\beta\Delta\mu_0(1 - 1/\sigma(\tau))]$

at infinity

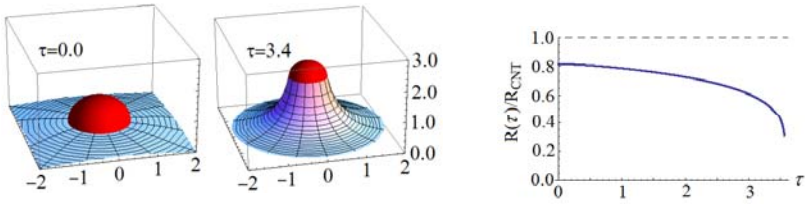
$u(\infty,\tau) = 1$

Peters, *J. Chem. Phys.* (2011)

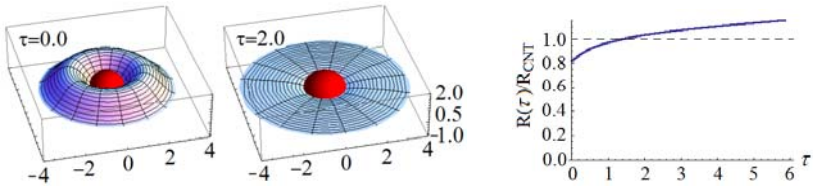
Baron Peters UCSB

diffusion transport coupled nucleation

pre-critical nucleus in uniform c_0 dissolves



but same nucleus within a concentrated zone grows

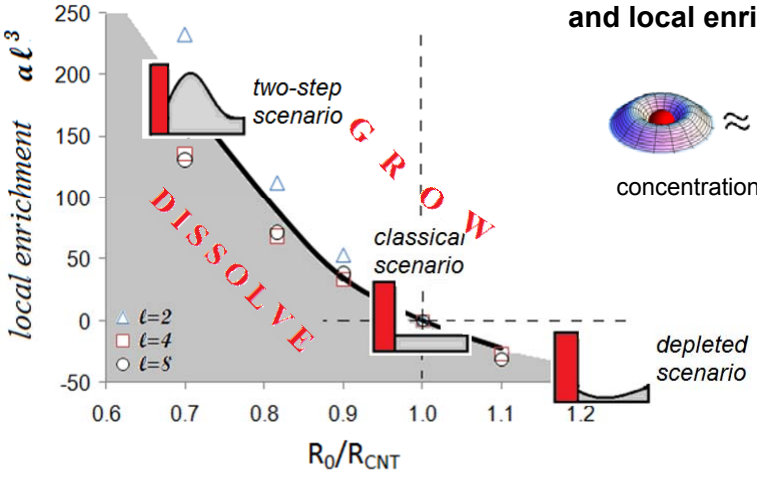


fluctuations up and down happen all the time…

Peters, *J. Chem. Phys*. (2011)

Baron Peters UCSB

separatrix: nucleus size and local enrichment



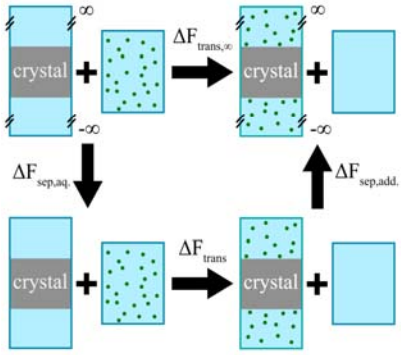
concentration profiles

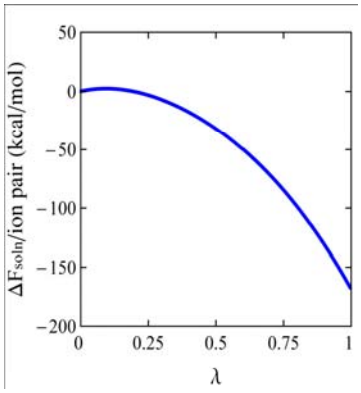
Myerson: "two-step mechanism may underlie most crystallization processes from solutions."

slow diffusion in condensed phase favors two-step nxn.

Peters, *J. Chem. Phys*. (2011)

Baron Peters UCSB


crystal
crystal
crystal
crystal
∞
-∞
∞
-∞
ΔF trans,∞
ΔF sep,aq.
ΔF sep,add.
ΔF trans


ΔF soln/ion pair (kcal/mol)
50
0
−50
−100
−150
−200
0
0.25
0.5
0.75
1
λ