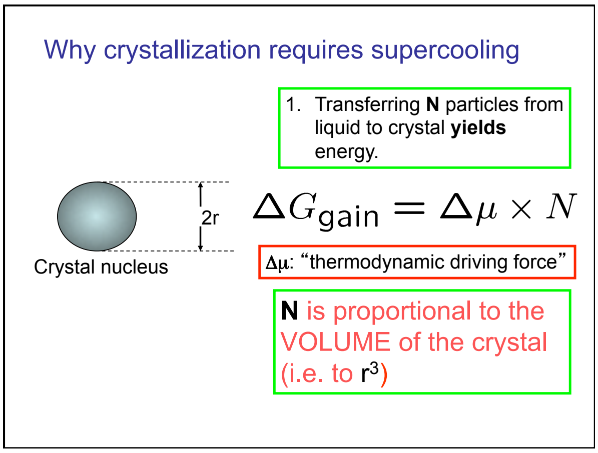
(Crystal) Nucleation:

The language



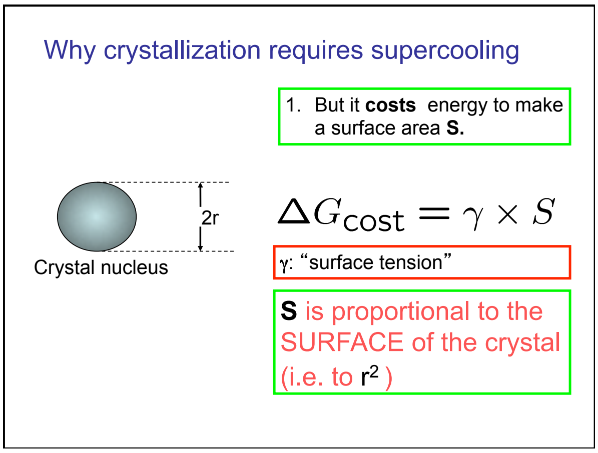
Why crystallization requires supercooling

1. Transferring **N** particles from liquid to crystal **yields** energy.

$$\Delta G_{\text{gain}} = \Delta\mu \times N$$

$\Delta\mu$: “thermodynamic driving force”

N is proportional to the VOLUME of the crystal (i.e. to r^3)



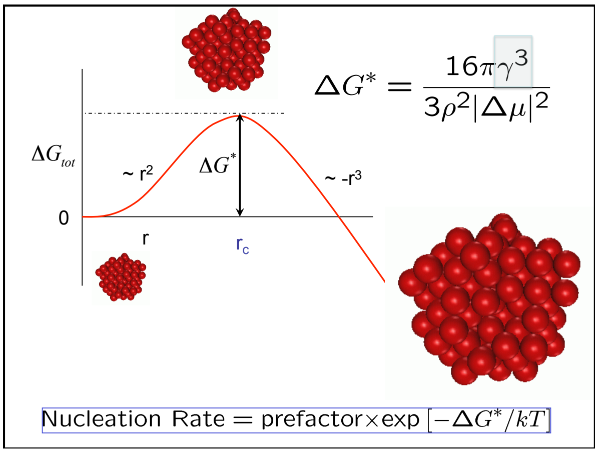
Why crystallization requires supercooling

1. But it **costs** energy to make a surface area **S.**

$$\Delta G_{\text{cost}} = \gamma \times S$$

γ: “surface tension”

S is proportional to the SURFACE of the crystal (i.e. to r^2)

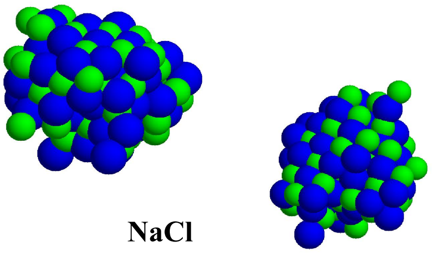


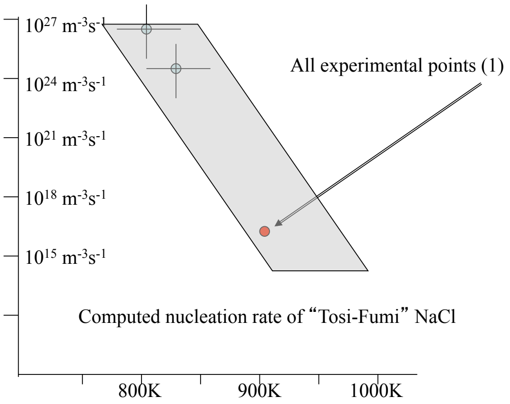
$$\Delta G^* = \frac{16\pi\gamma^3}{3\rho^2|\Delta\mu|^2}$$

$$\text{Nucleation Rate} = \text{prefactor} \times \exp\left[-\Delta G^*/kT\right]$$

Computing absolute nucleation rates

Crystallization of NaCl from melt





Other example: hard sphere colloids.

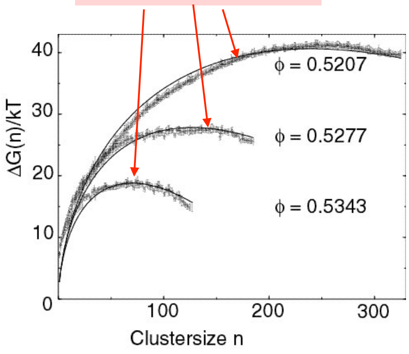
Crystal nucleation of hard-sphere colloids

Equilibrium phase behavior:

Pusey and van Megen *Nature* 320 340 (1986)

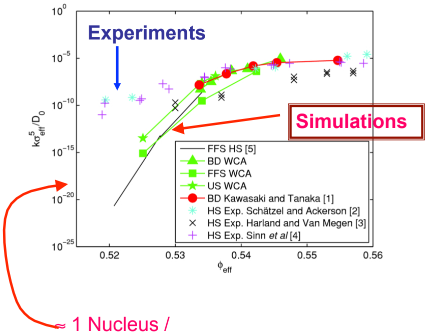
NUCLEATION BARRIER

SIMULATION RESULTS



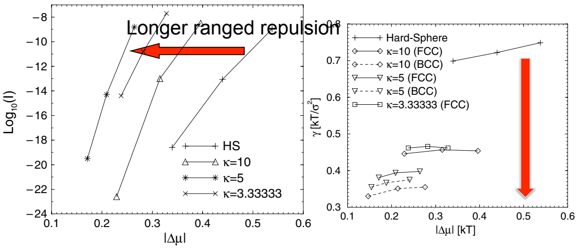
Nucleation RATES

Discrepancy: >20 orders of magnitude.

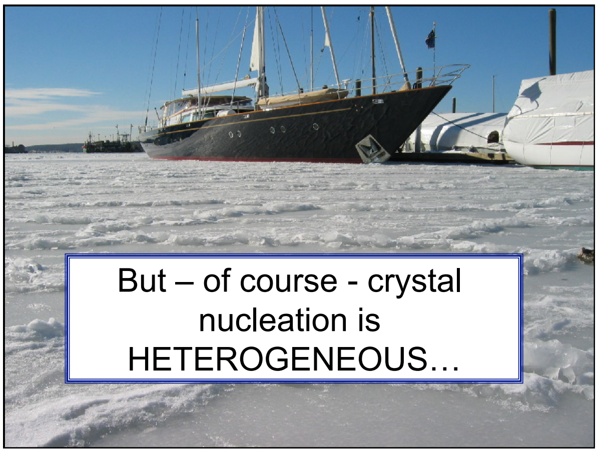


≈ 1 Nucleus / (month cm^3)

Nucleation Rate depends strongly on strength and range of repulsion (lower γ)

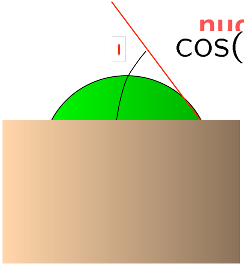


Hard core + Yukawa (“screened Coulomb”) interaction



But – of course - crystal nucleation is HETEROGENEOUS…

Effect of a flat wall on nucleation



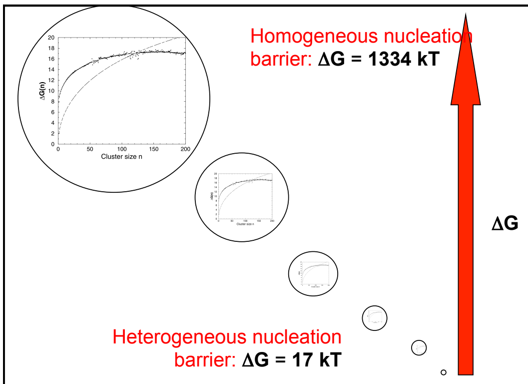
$$\cos(\theta) = (\gamma_{wl} - \gamma_{ws})/\gamma_{ls}$$

CNT:

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma_{ls}^3 f(\theta)}{(\rho_s \Delta\mu)^2}$$

with:

$$f(\theta) = (2 + \cos(\theta))(1 - \cos(\theta))^2/4$$



Homogeneous nucleation barrier: **ΔG = 1334 kT**

Heterogeneous nucleation barrier: **ΔG = 17 kT**

Flat wall speeds up nucleation by a factor **10^{570}**

That is why homogeneous nucleation is the exception

The effect of surface free energy:

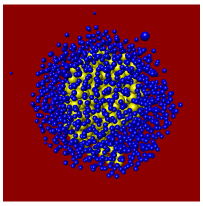
$$\Delta G^* = \frac{16\pi\gamma^3}{3\rho^2|\Delta\mu|^2}$$

Observation: $\gamma_{\text{Solid-Liquid}}$

is about one order of magnitude smaller than $\gamma_{\text{Solid-Vapour}}$

Therefore:

this



is easier than

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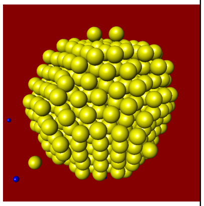
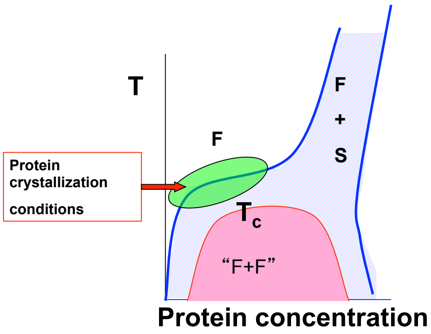


Consequence:

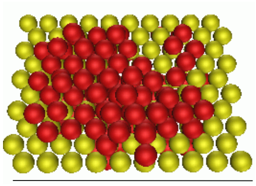
`two-step' nucleation is plausible



Protein crystallization conditions

Seeded nucleation?

Seeded Crystallization



If the crystal fits well on the template, it is easy to nucleate… however:

RANDOM (!) SUBSTRATES CAN ACT AS UNIVERSAL NUCLEATION SEEDS

(Experiments: Naomi Chayen, Imperial College)

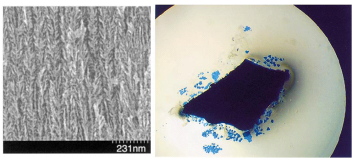


Figure 1: Electron micrograph of micro-porous silicon (left) shows that the sample contains a network of pores with sizes between 5 and 10 nanometers. The figure on the right hand shows a number of protein crystals (phycobili protein) that have formed on the micro-porous silicon. (N.E. Chayen et al., Ref.. [1])

Explanation (Richard Sear)

“For every Cinderella there is a shoe that fits…”

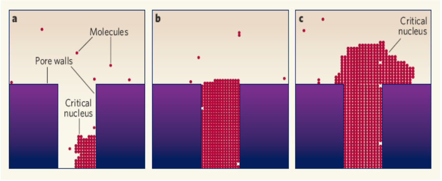
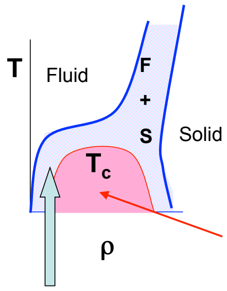


Figure 1 | Crystal nucleation in a pore. Page and Sear[2] propose a model to explain why porous materials induce protein crystallization. **a**, The pore walls weakly attract the molecules to be crystallized. Crystals start to grow in the corners of the pore when a critical nucleus of molecules forms. **b**, The crystal grows until the pore is filled. **c**, Another critical nucleus of molecules forms on the outside of the pore, which allows the ‘breakout’ of a bulk crystal from the pore. The rates of nucleus formation and breakout vary independently according to the width of the pore.

Theory: Richard Sear

D. Frenkel, NATURE, 443, 641, 2006

But this is not the whole story.

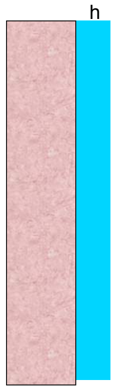


Hard particles with

SHORT-RANGED attraction

Meta-stable fluid-fluid

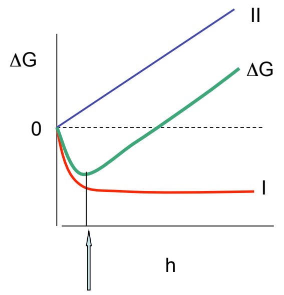
Liquid may form a wetting layer



I II

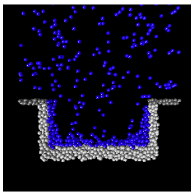
$$\Delta G/S = (\gamma_{sl} + \gamma_{lv} - \gamma_{sv}) f(h) + \rho_l h \Delta\mu$$

< 0 > 0



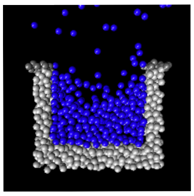
Study crystal nucleation in a regime where the bulk liquid is not even metastable

In this regime, the dense liquid may wet walls



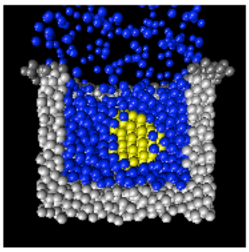
Wetting layer in “large” pore

In this regime, the dense liquid may wet walls

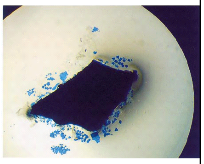


Capillary condensation in “small” pore

Crystal nucleation in filled pore



$\overset{?}{=}$

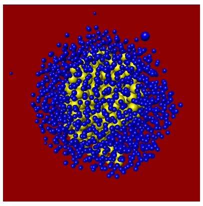


Disordered substrate yields perfect crystal that nucleates in wetting layer ….

J. A. van Meel, R. P. Sear and DF, Phys. Rev. Lett. **105**, 205501 (2010)

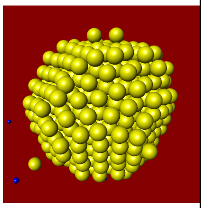
Which illustrates that:

this



is easier than

this



Beyond Newtonian dynamics:

1. Langevin dynamics
2. Brownian dynamics
3. Stokesian dynamics
4. Dissipative particle dynamics
5. Stochastic rotation/multi-particle collision dynamics
6. Lattice Boltzmann
7. Etc. etc.

Why ?

Saving time.

These algorithms are often used to simulate molecular motion in a viscous medium, without solving the equations of motion for the solvent particles.

Friction force

Conservative force

First, consider mo with friction alone:

$$\cancel{m\dot{\vec{v}} = -\gamma\vec{v}(t') - \nabla U \ ,}$$

After a short while, all particles will stop moving, due to the friction..

"random" force

Better:

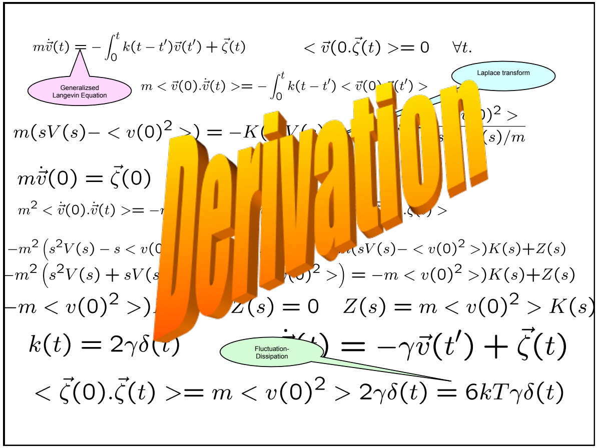
$$m\dot{\vec{v}} = -\gamma\vec{v}(t') - \nabla U + \vec{\zeta}(t) \ ,$$

There is a relation between the correlation function of the random force and the friction coefficient:

$$< \zeta_x(0)\zeta_x(t) >= 2kT\gamma\delta(t)$$

The derivation is straightforward, but beyond the scope of this lecture. The KEY point is that the friction force and the random force ARE RELATED.

$$< \vec{\zeta}(0).\vec{\zeta}(t) >= m < v(0)^2 > 2\gamma\delta(t) = 6kT\gamma\delta(t)$$



$m\dot{\vec{v}}(t) = -\int_0^t k(t-t')\vec{v}(t') + \vec{\zeta}(t) \qquad < \vec{v}(0.\vec{\zeta}(t) >= 0 \quad \forall t.$

Generalizsed Langevin Equation

$m < \vec{v}(0).\dot{\vec{v}}(t) >= -\int_0^t k(t-t') < \vec{v}(0)$ [illegible] $(t') >$

Laplace transform

$m(sV(s)- < v(0)^2 >) = -K($ [illegible] $)^2 >$ [illegible] $(s)/m$

$m\dot{\vec{v}}(0) = \vec{\zeta}(0)$

$m^2 < \dot{\vec{v}}(0).\dot{\vec{v}}(t) >= -$ [illegible] $.\zeta(0) >$

$-m^2\left(s^2V(s) - s < v(0\right.$ [illegible] $(sV(s)- < v(0)^2 >)K(s)+Z(s)$

$-m^2\left(s^2V(s) + sV(s\right.$ [illegible] $\left.(0)^2 >\right) = -m < v(0)^2 >)K(s)+Z(s)$

$-m < v(0)^2 >)$ [illegible] $Z(s) = 0 \quad Z(s) = m < v(0)^2 > K(s)$

$k(t) = 2\gamma\delta(t)$ [illegible] $) = -\gamma\vec{v}(t') + \vec{\zeta}(t)$

Fluctuation-Dissipation

$< \vec{\zeta}(0).\vec{\zeta}(t) >= m < v(0)^2 > 2\gamma\delta(t) = 6kT\gamma\delta(t)$

Limiting case of Langevin dynamics:

No inertial effects (m=0)

$$m\dot{\vec{v}} = -\gamma\vec{v}(t') - \nabla U + \vec{\zeta}(t) \ ,$$

Becomes:

$$0 = -\gamma\vec{v}(t') - \nabla U + \vec{\zeta}(t) \ ,$$

“Brownian Dynamics”

(But still the friction force and the random force are related)

What is missing in Langevin dynamics and Brownian dynamics?

1. Momentum conservation
2. Hydrodynamics

(1 implies 2).

Is this serious?

Not always: it depends on the time scales.

Momentum “diffuses” away in a time L^2/ν. After that time, a “Brownian” picture is OK.

However: hydrodynamics makes that the friction constant depends on the positions of all particles (and so do the random forces…).

Momentum conserving, coarse-grained schemes:

Dissipative particle dynamics

Stochastic Rotation Dynamics/Multi-particle collision dynamics

Lattice-Boltzmann simulations

These schemes represent the solvent explicitly (i.e. as particles), but in a highly simplified way.

Recursive sampling

Outline:

1. Recursive enumeration
   a) Polymer statistics (simulation)
   b) ..
2. Molecular Motors (experiments!)
   (well, actually, simulated experiments)

Lattice polymers:

Consider a lattice (e.g. 2D-square).

At a given point x_i, the potential energy is $U(x_i)$.

The Boltzmann factor for a particle at point x_i is

$\exp(-\beta U(x_i)) \equiv z_i^1$

Consider a lattice (e.g. 2D-square).

At a given point x_i, the potential energy is $U(x_i)$.

The Boltzmann factor for a particle at point x_i is

$\exp(-\beta U(x_i)) \equiv z_i^1$

The partition function for a single point particle is

$Z_1 \equiv \sum_i z_i^1$

Dimers

The Boltzmann factor for a dimer on points x_i and x_{i+1} is

$\exp(-\beta(U(x_i) + U(x_{i+1})) = z_i^1 \times z_{i+1}^1$

The Boltzmann factor for all dimers terminating

on point x_i is

$z_i^{(2)} \equiv z_i^1 \times \sum_{jnni} z_j^1$

The partition function for a single dimer is

$Z_2 \equiv \sum_i z_i^{(2)}$

n-mers

The Boltzmann weight for an n-mer terminating on point x_i is

$$z_i^{(n)} = z_i^1 \times \sum_{jnni} z_j^{(n-1)}$$

and the corresponding partition function is

$$Z^{(n)} = \sum_i z_i^{(n)}$$

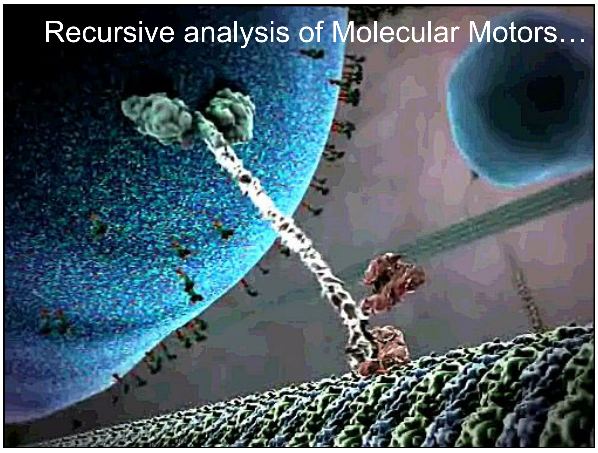
This method is exact for non-self-avoiding, non-interacting lattice polymers.

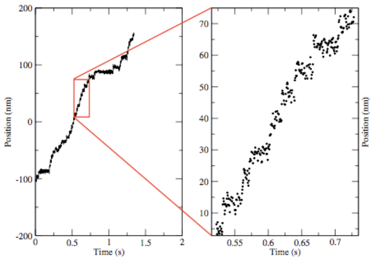
It can be used to speed up MC sampling of (self)interacting polymers

B. Bozorgui and DF, Phys. Rev. E 75, 036708 (2007))

NOTE: `MFOLD' also uses recursive sampling to predict RNA secondary structures.

Recursive analysis of Molecular Motors…

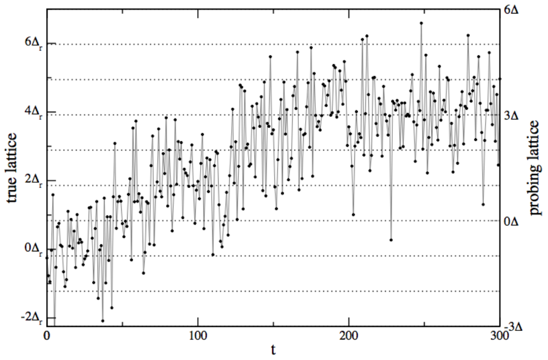




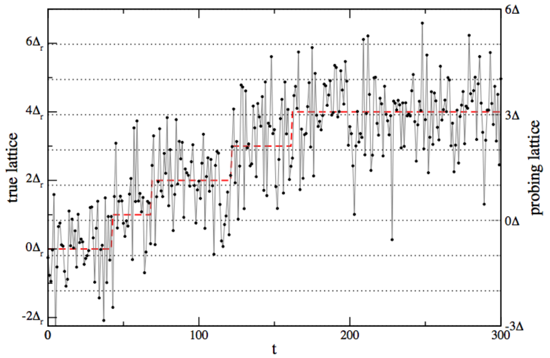
Kinesin motor steps along micro-tubules with a step size of 8nm

Experimentally, the step size is measured by fitting the (noisy) data.

Example: noisy “synthetic data”

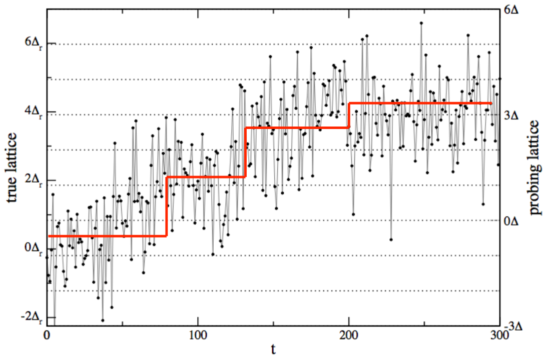


Example: noisy “synthetic data”



- - - - - - - : “true” trace

Best practice: “fit steps to data”



J.W.J. Kerssemakers et al. , Nature 442,709 (2006)

How well does it perform?

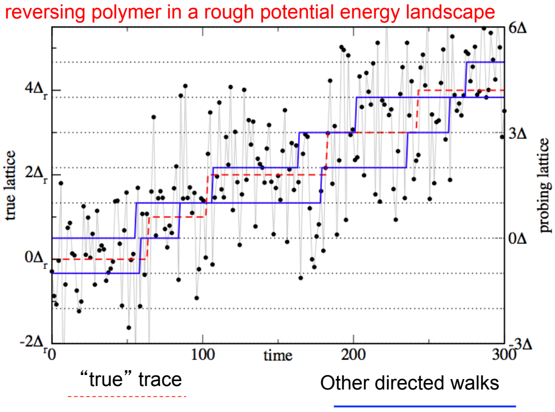
1. It can be used if the noise is less than 60% of the step size.
2. It yields a distribution of step sizes (even if the underlying process has only one step size)

Observation:

We want to know the step size and the step frequency but…

<u>We do not care which trace is the “correct” trace.</u>

Bayesian approach: compute the partition function **Q** of non-reversing polymer in a rough potential energy landscape

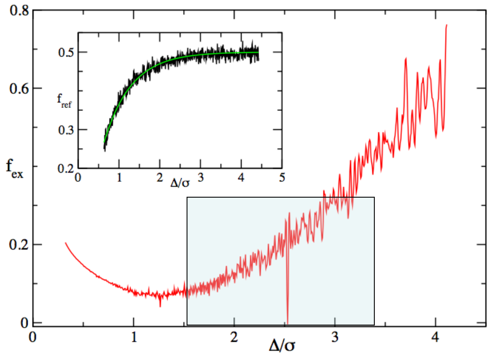


As shown before: we can enumerate **Q** exactly (and cheaply).

From **Q** we can compute a “free energy”

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

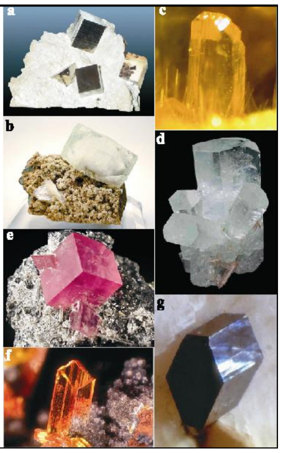
Compute the “excess free energy” with respect to reference data



What have we learned?

1. What is Soft Matter?

Hard Matter



Dark Matter

Soft Matter

Airport security measures
Prepare for security

If you have any of these items you must return to Check-in or dispose of them safely.

Any items purchased after Security can be taken on board. Special restrictions may apply to items taken onto flights to the USA.

One bag only

35cm
45cm
16cm
Maximum dimensions

No liquids

No cosmetics

No toiletries

No gels or pastes
Including food stuffs

No sharp items

No lighters
Not allowed in baggage or through security. Please dispose of safely.

From 24 August 2006

BAA

Time to stop!