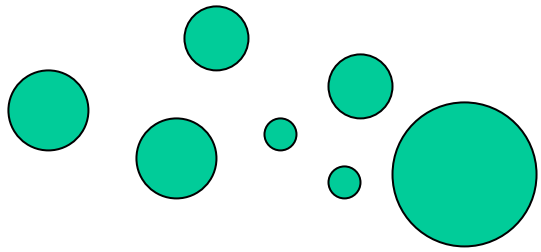
Why Disorder is Interesting

All argon atoms are the same….

…but every colloidal particles is different.

This has interesting consequences for their physical behavior.

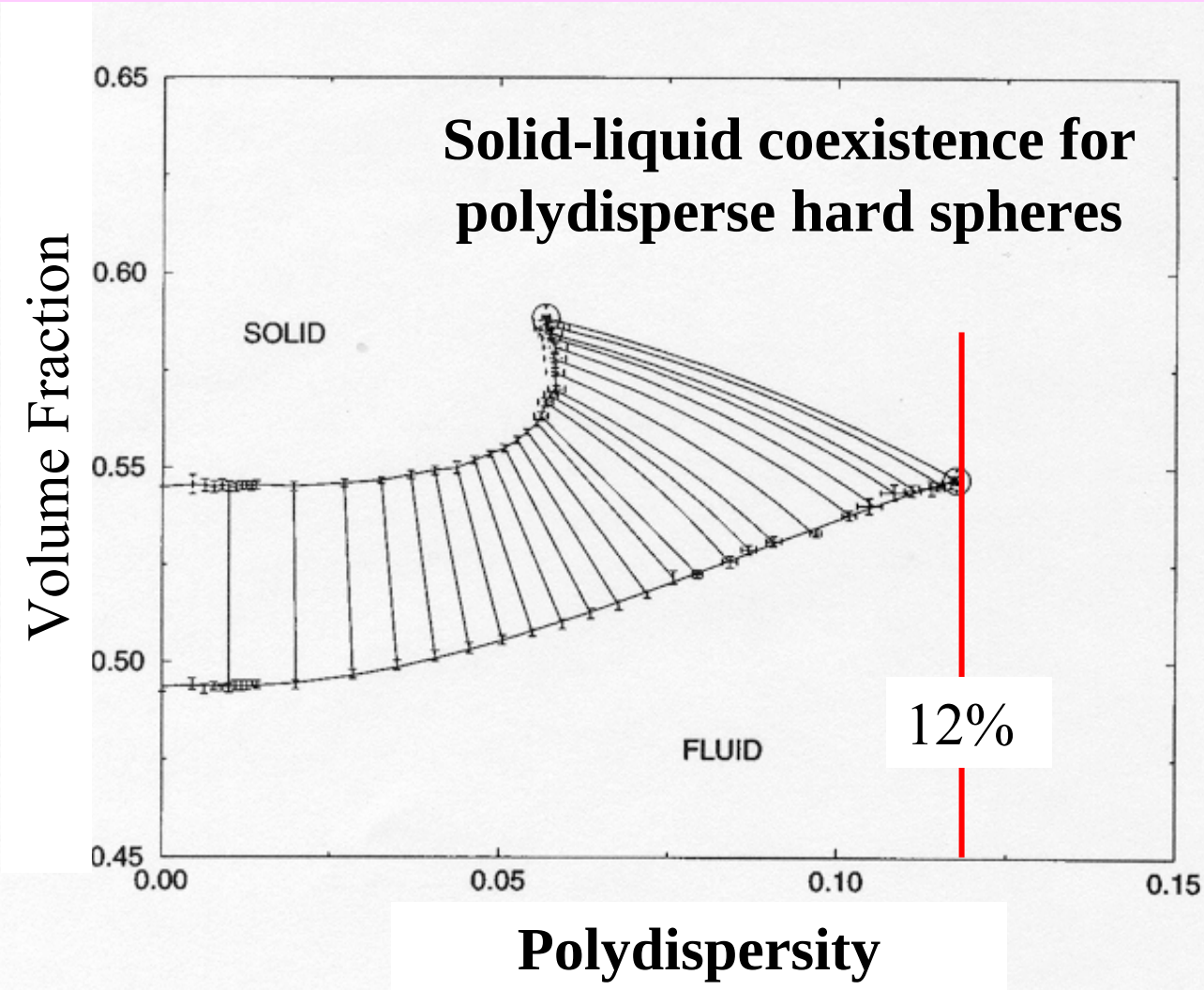
POLYDISPERSITY IN HARD-SPHERE COLLOIDS



Polydispersity postpones, and eventually suppresses, hard-sphere freezing)

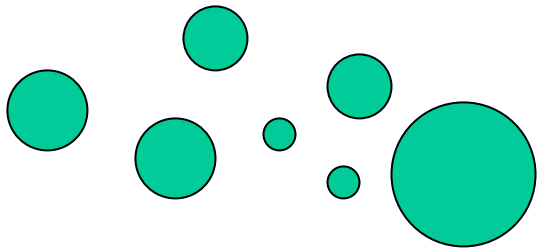
Polydispersity: $s \equiv (\langle r^2 \rangle - \langle r \rangle^2)^{1/2} / \langle r \rangle$

Phase diagram of polydisperse hard spheres



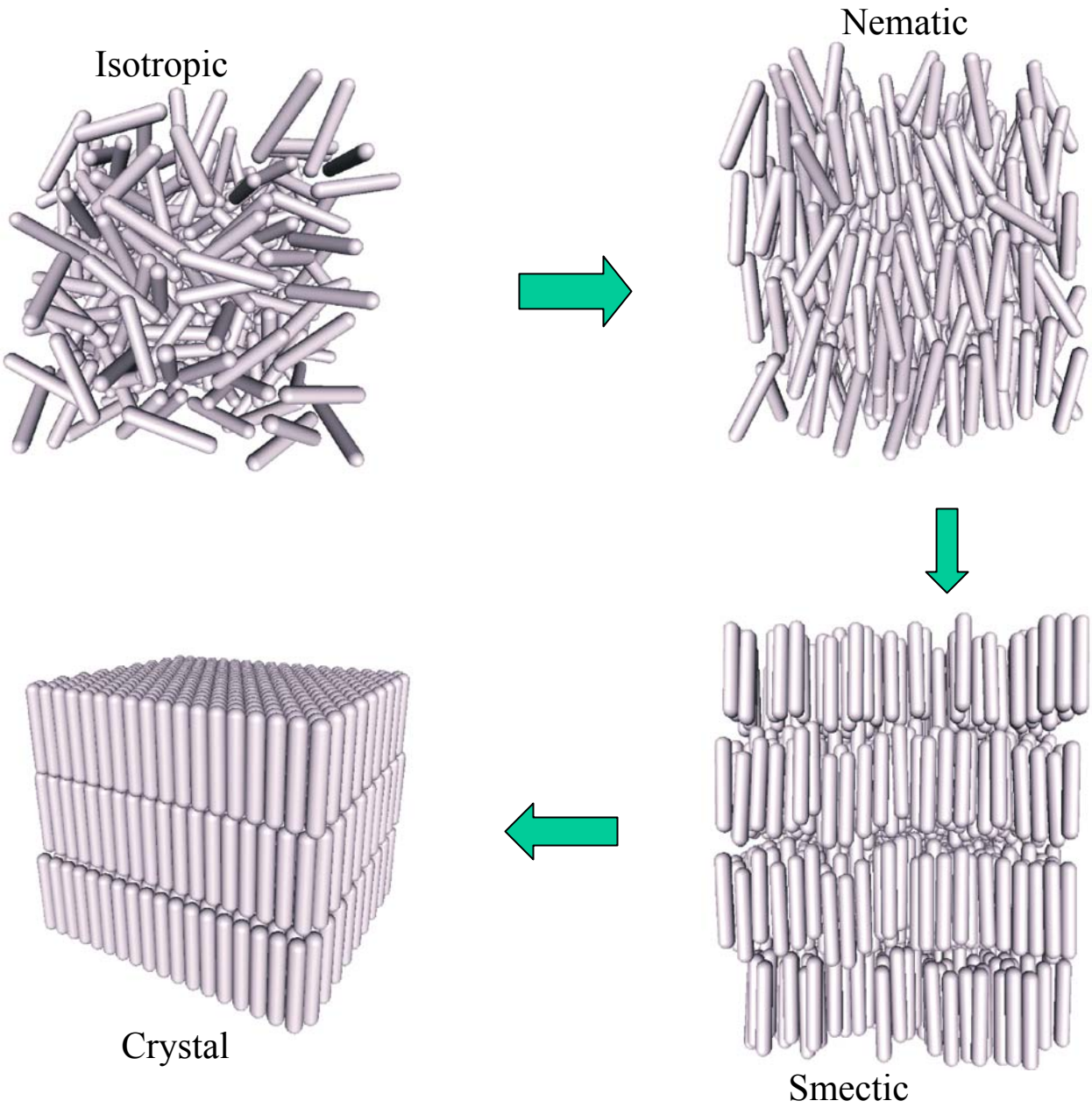
(Bolhuis & Kofke, PRE, 54:634(1996))

POLYDISPERSITY IN LYOTROPIC LIQUID CRYSTALS



Lyotropic liquid crystals:
Liquid crystals consisting of mesoscopic (10nm-1μm) building blocks.
(Examples: colloids, virus particles, rigid polymers).

Hard-core liquid lyotropic crystals ⇒
Ordering is entropy-driven

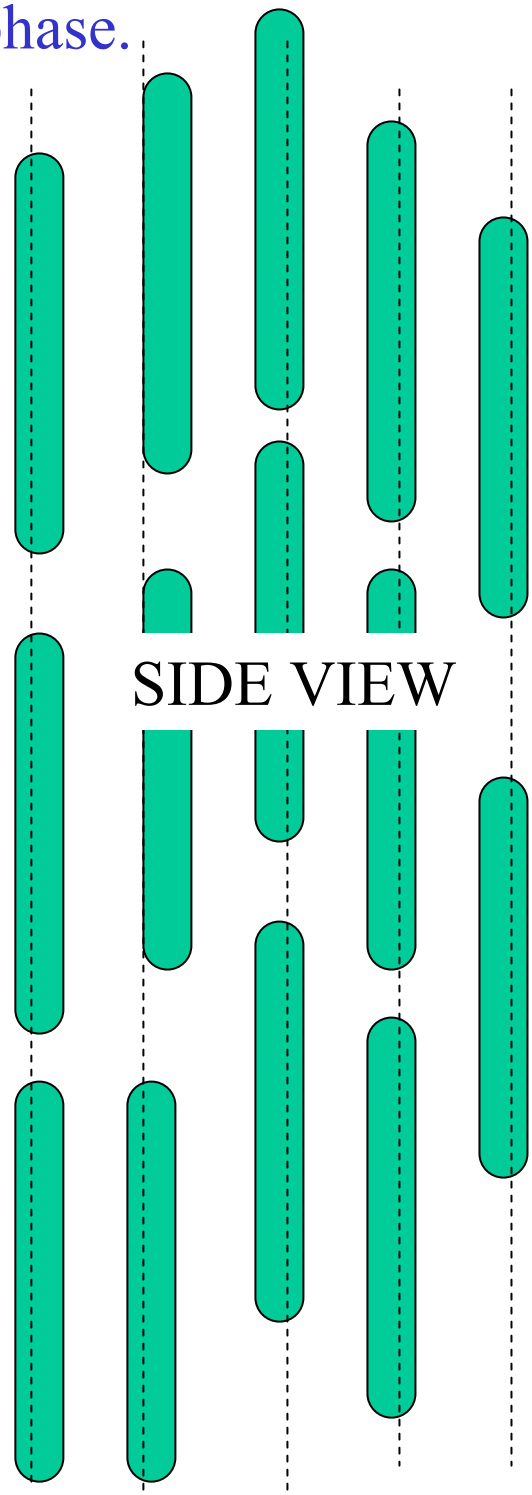


Entropy driven formation of liquid crystals of rod-like colloids

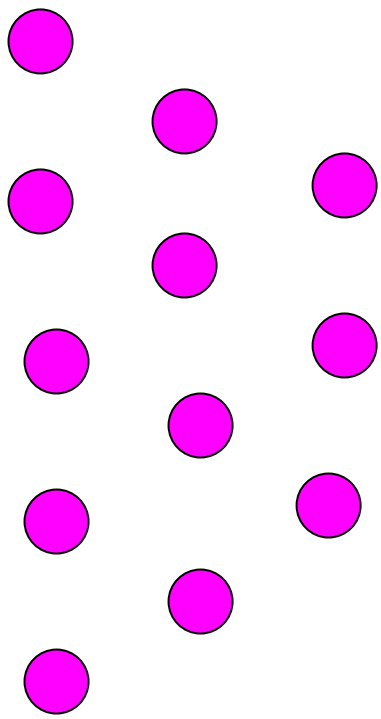
= Direction of increasing density

But there is one other possibility to consider:

Rodlike particles could form a COLUMNAR phase.



SIDE VIEW

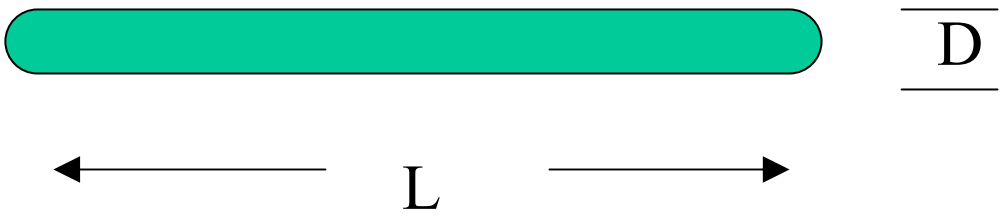


TOP VIEW

Can hard, rodlike particles form a columnar phase?

Simulations (JCP, 106:666(1997)) show:

No columnar phase for "short" rods (L/D < 60)



Maybe for very long rods??

($L/D \Rightarrow \infty$)

Problem...

Limit L/D $\Rightarrow \infty$:

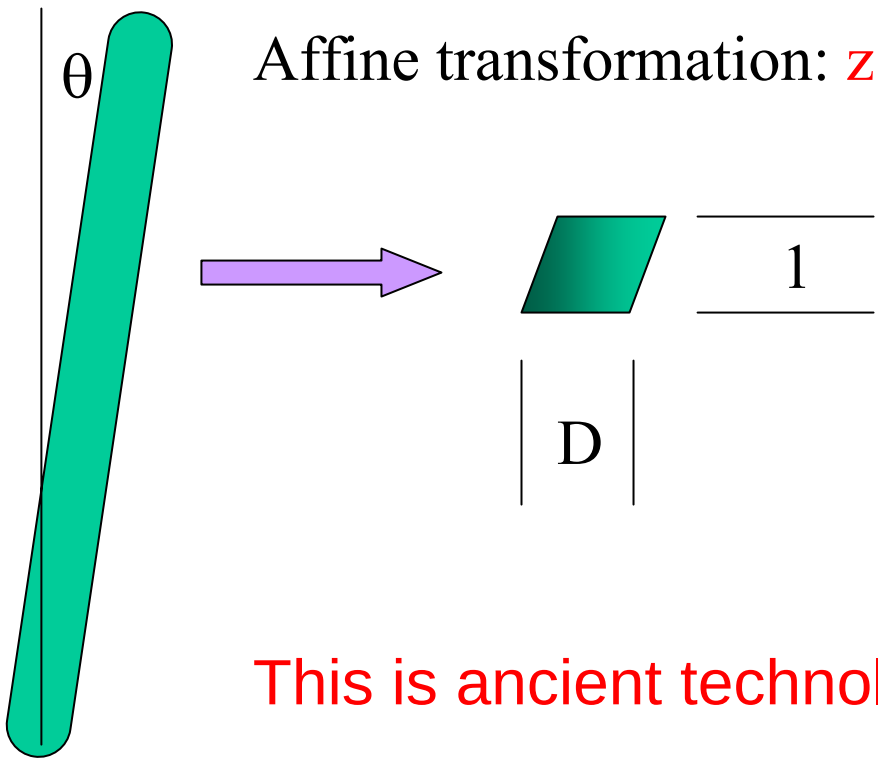
Simulations impossible???

Box volume ~ L^3

$N \sim L^3/(LD^2) = O(L^2/D^2) \Rightarrow \infty$

* * * * *

At high densities, the nematic phase is strongly aligned. $\{\theta = O(D/L) \Rightarrow 0\}$



Affine transformation: z'==(D/L) z

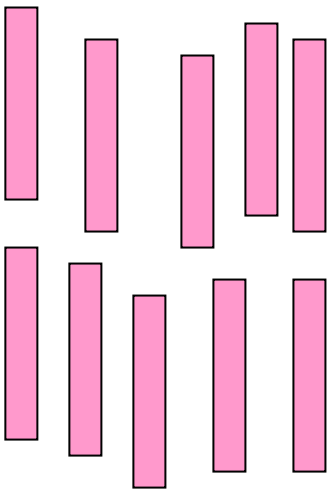
This is ancient technology…

… No columnar phase.

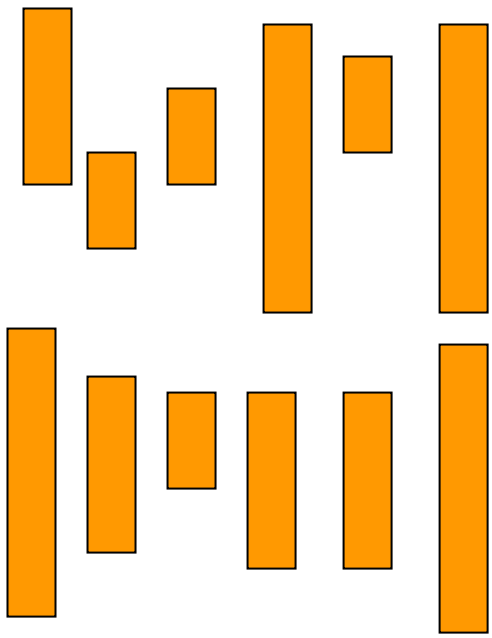
Clearly, we need something else.

Polydispersity

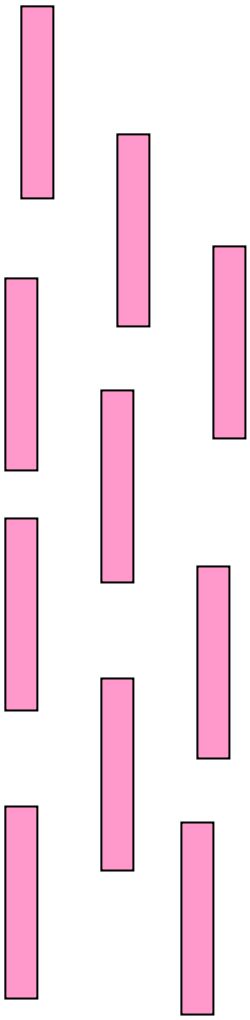
WHY?



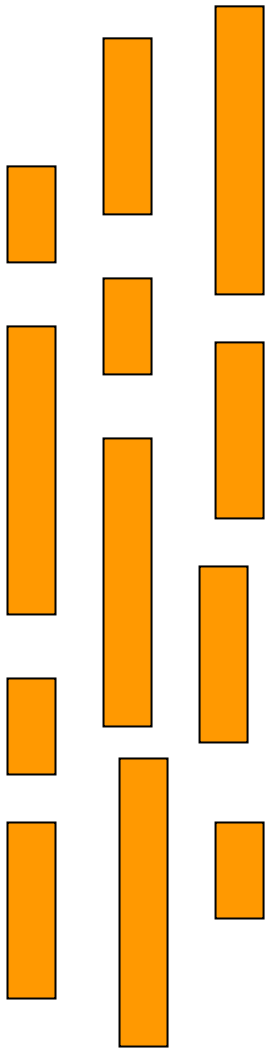
Monodisperse smectic



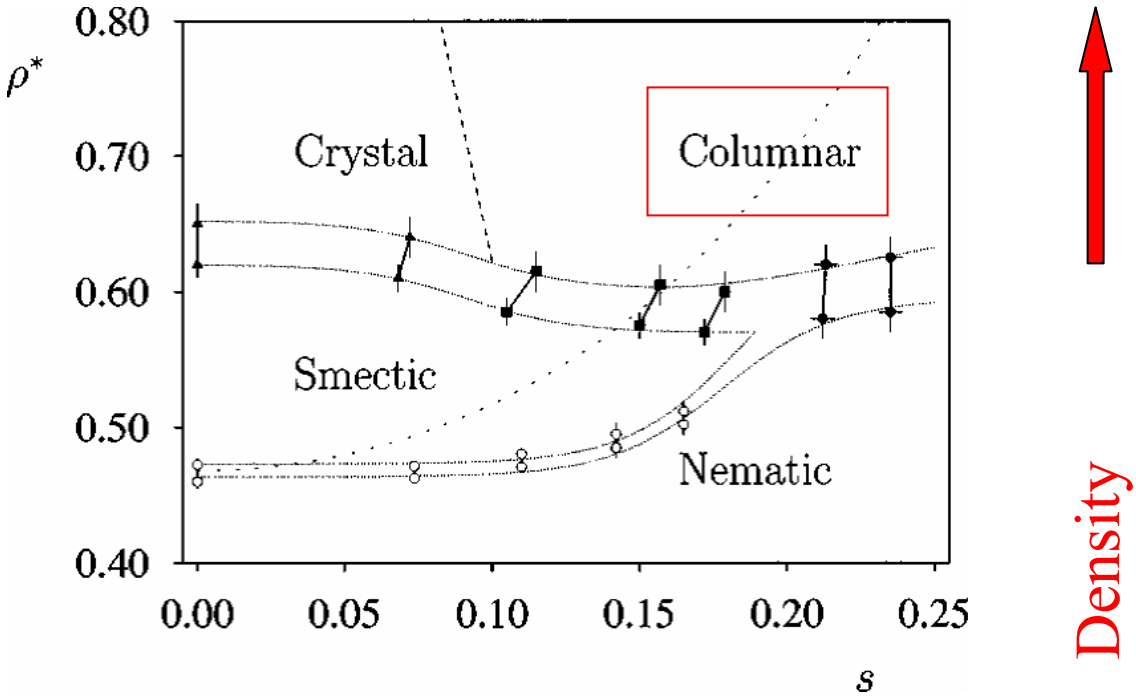
Polydisperse smectic



Monodisperse columnar



Polydisperse columnar



Polydispersity can be a good thing:

It can *induce* phases that are not stable in mono-disperse systems.

CRYSTAL NUCLEATION in COLLOIDS

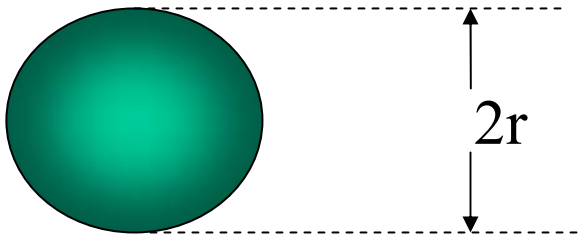
1. The effect of polydispersity
2. The effect of the interaction range

Homogeneous nucleation…

…the basics

Nucleation requires supercooling

(e.g. : $\mu_{solid} < \mu_{liquid}$)



Physicist's Crystal nucleus

r^3

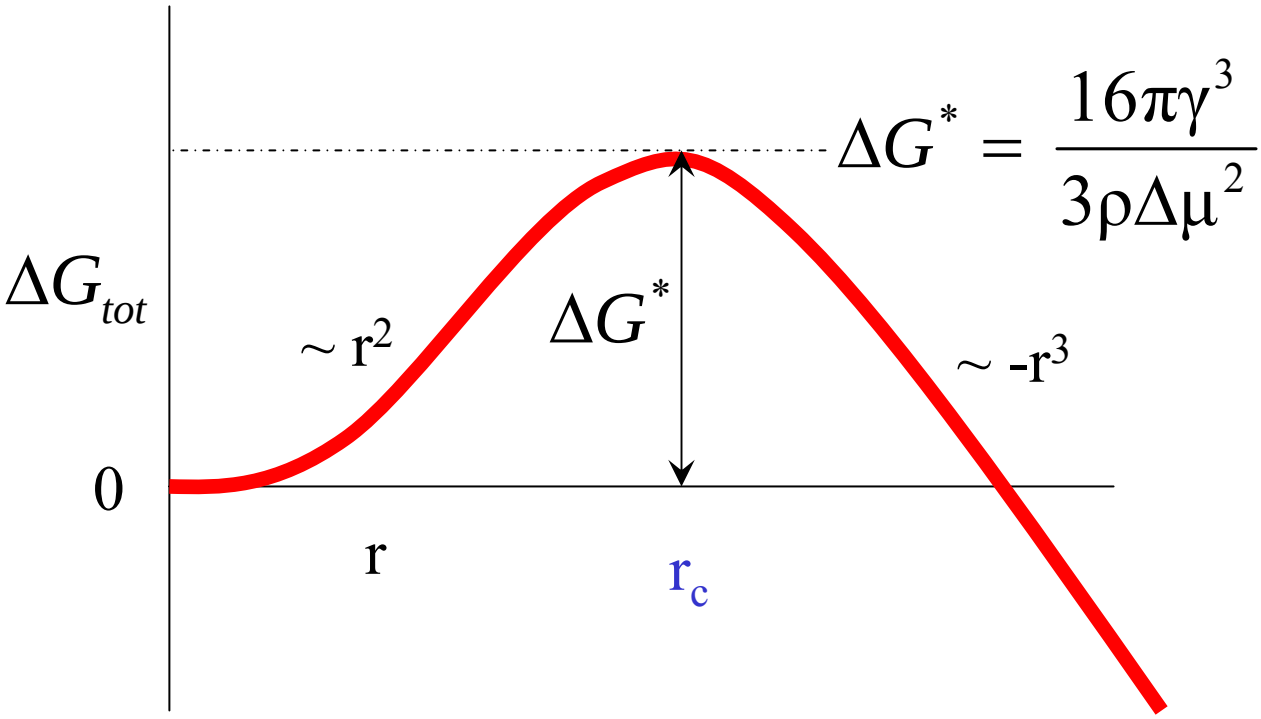
Free - energy gain

$$\Delta G_{Bulk} = \frac{4\pi}{3}\rho r^3 \Delta\mu_{s,l} < 0$$

Free - energy loss :

r^2

$$\Delta G_{Surface} = 4\pi r^2 \gamma_{s,l} > 0$$



How good is this description?

Classical Nucleation Theory

(CNT)

assumes that:

Crystal nuclei have the same properties

(structure, density, surface free energy)

as bulk crystals.

…is that true?

Test by "Computer Experiment"

HOWEVER:

NUCLEATION IS A

RARE EVENT

Hence:

1. EXPERIMENTS ARE DIFFICULT, and
2. BRUTE-FORCE SIMULATIONS WON'T WORK…

What is the problem?

Experimental nucleation rates:

$O(1)$ cm^{-3} s^{-1}

Simulation:

Volume is much smaller (e.g. for one million particles): $V = O(10^{-15})$ cm^3

$\Rightarrow$ **Nucleation rate** $O(10^{-15})$ s^{-1} **!!**

$\Rightarrow$ *One event per* 10^{15} s

$\Rightarrow$ *One event per* 10^{30} **MD time steps**

$=10^{15}$ years with

"Blue Gene"

Solution:

1. **Compute height of the free-energy barrier ΔG^* (MC/MD)**
2. **Compute transmission coefficient Γ (MD)**

$$\text{Rate} = \Gamma \quad \boxed{\exp(-\beta \Delta G^*)}$$

Probability of "critical" fluctuation

(strong function of T)

Kinetic Prefactor
(usually weak function of T)

Determine Free-energy Barrier, using:

Biased sampling

("umbrella sampling")

Simulation allows us to study:

1. The structure of the critical nucleus.
2. The height of the nucleation barrier
3. The nucleation rate

Testing Classical Nucleation Theory

CRYSTAL NUCLEATION of COLLOIDAL HARD SPHERES

(entropic freezing transition)

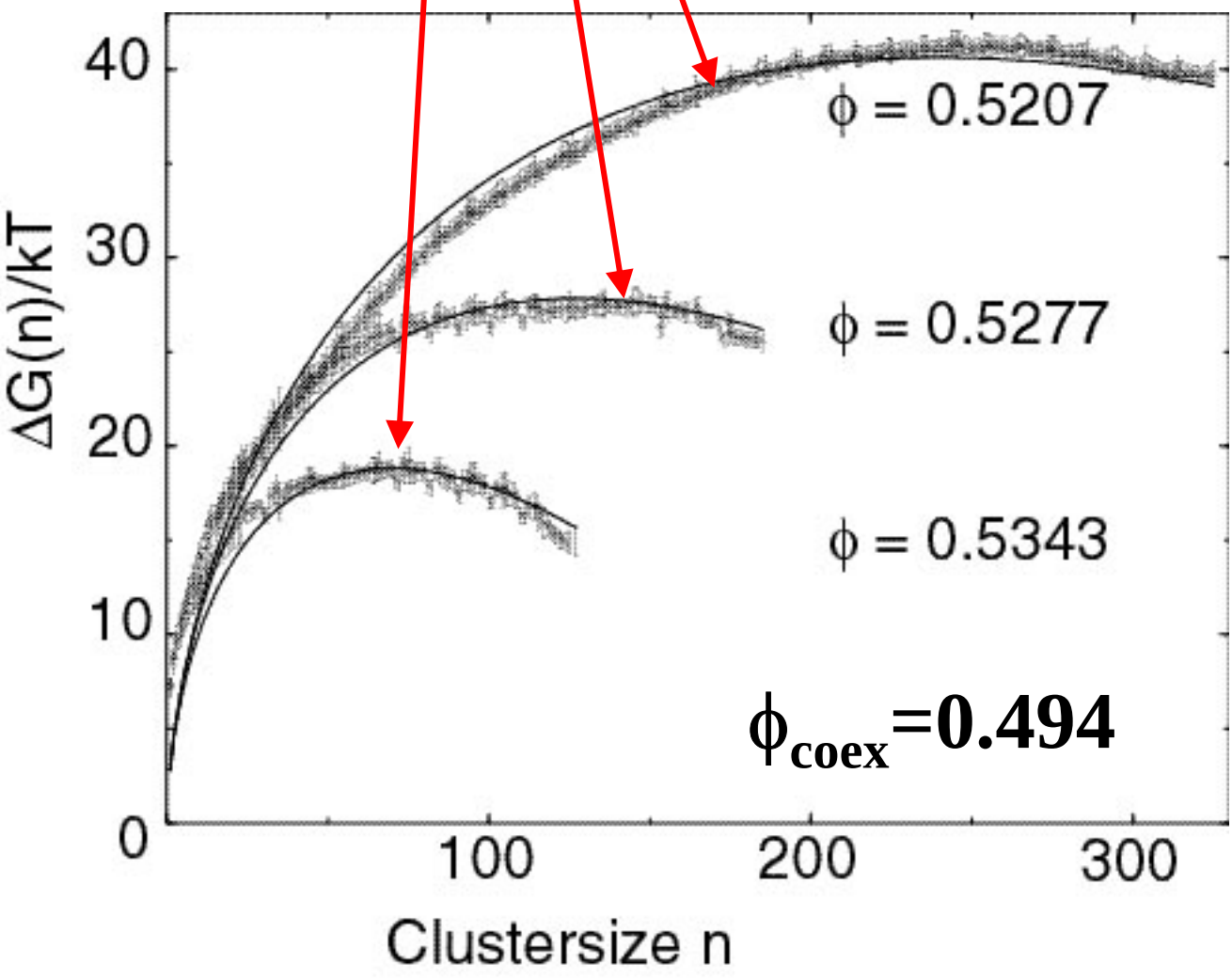
WHY THIS SYSTEM?

1. **THEORY/SIMULATION: We know "everything" about the equilibrium properties of hard spheres.**
2. **EXPERIMENT: Suspensions of uncharged *silica* or *PMMA* colloids really behave like hard-sphere systems**
3. **..AND: There is experimental information on hard-sphere nucleation**.(Ackerson & Schaetzel, Harland & van Megen:on earth. Cheng, Zhu, Chaikin et al.: in μ-gravity)

However:

Entropy-driven freezing is not universally loved…

SIMULATION RESULTS
for BARRIER HEIGHT



Nothing special???

As $\Delta\mu$ is known, we can deduce γ from the barrier heights.

SIMULATIONS:

Supersaturated: $\gamma_{eff} \approx 0.72\ kT/\sigma^2$

At coexistence: $\gamma \approx 0.62\ kT/\sigma^2$

In contrast, CNT ASSUMES THAT γ IS CONSTANT.

20% error does not seem much, but:

$$\Delta G^* \sim \gamma^3$$

And the nucleation rate is proportional to

$$\exp[-16\pi\gamma^3/(3\rho^2\Delta\mu^2 kT)]$$

Absolute nucleation rates ?

Assume : Brownian motion
Approximate : Hydrodynamic Interactions

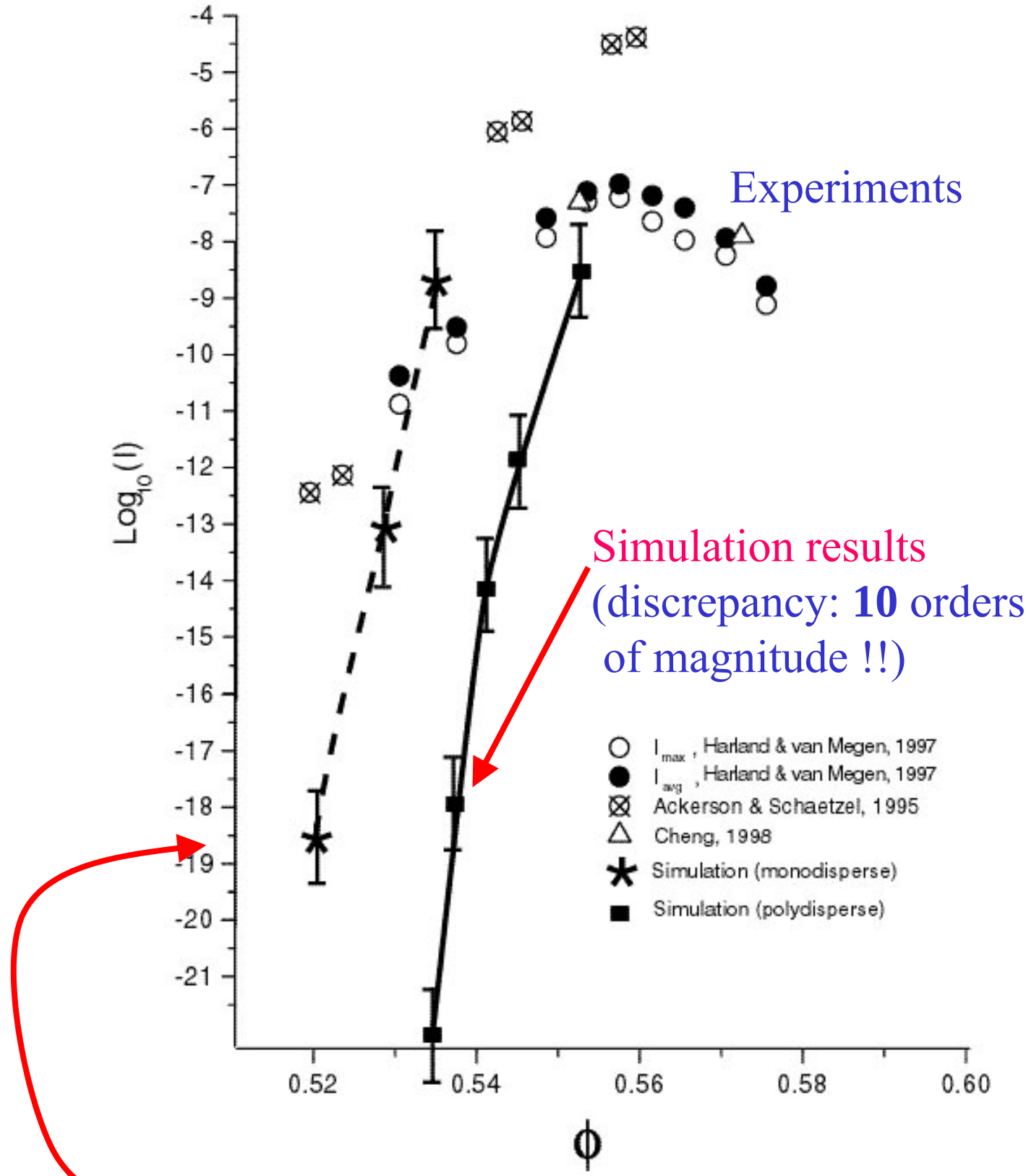
Nucleation rate:

Zeldovich Factor

$$I = k^{+}_{N^*} Z \rho \exp(-\Delta G^*/kT)$$

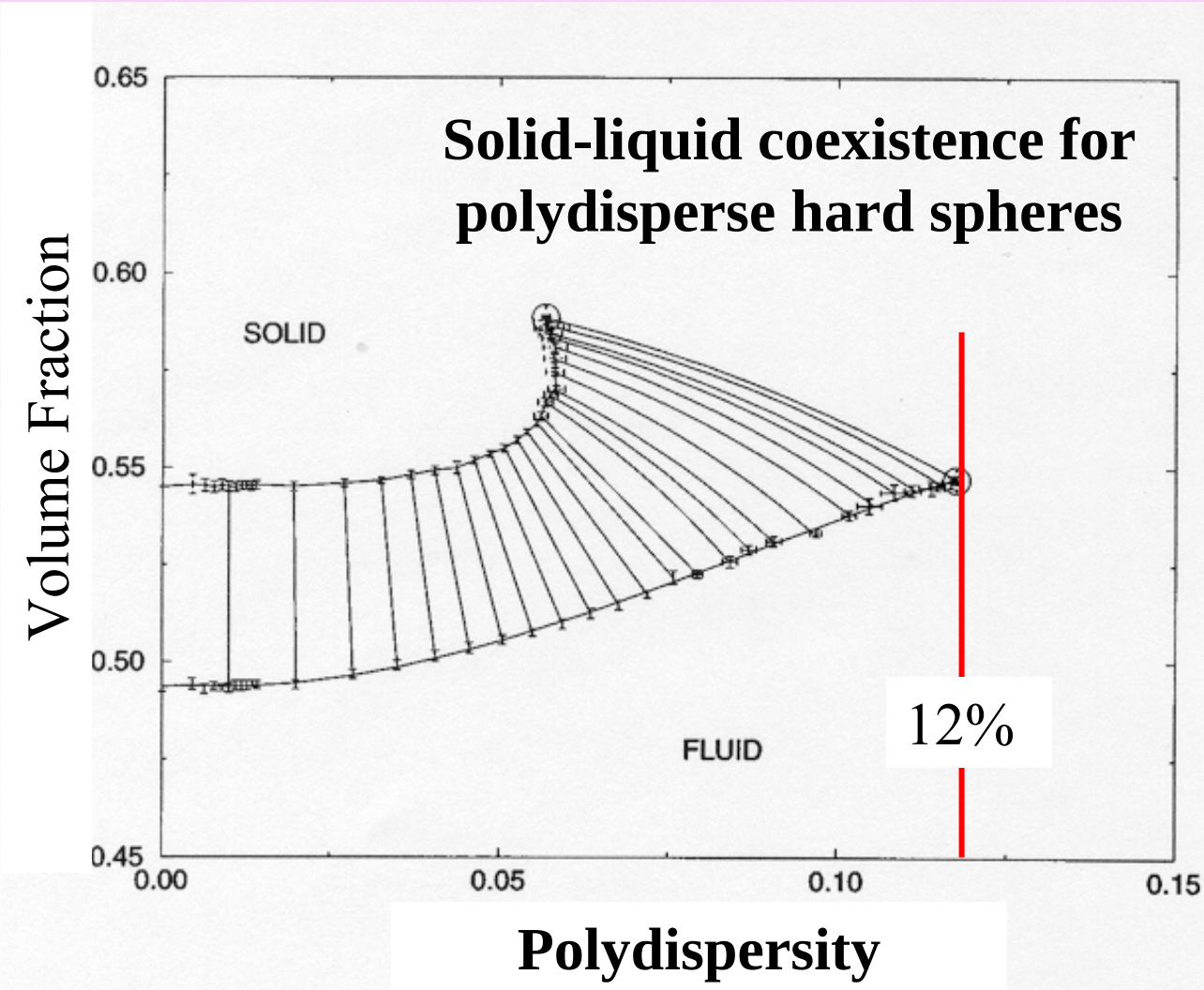
$k^{+}_{N^*}$, Z, ΔG^* can all be computed numerically

COMPARISON WITH EXPERIMENT

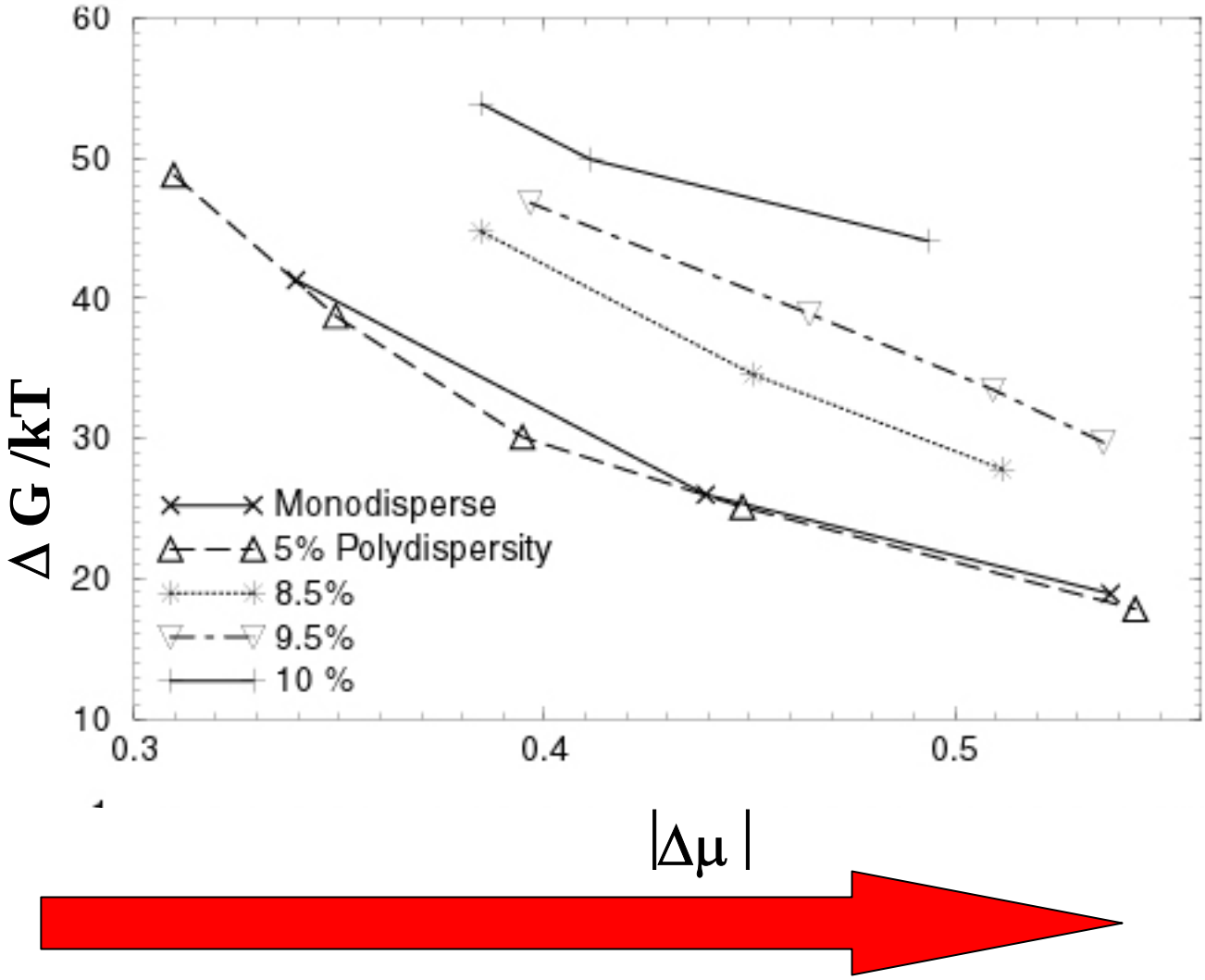


THE EFFECT OF POLYDISPERSITY

Phase diagram of polydisperse hard spheres



(Bolhuis & Kofke, PRE, 54:634(1996))



Increasing supersaturation

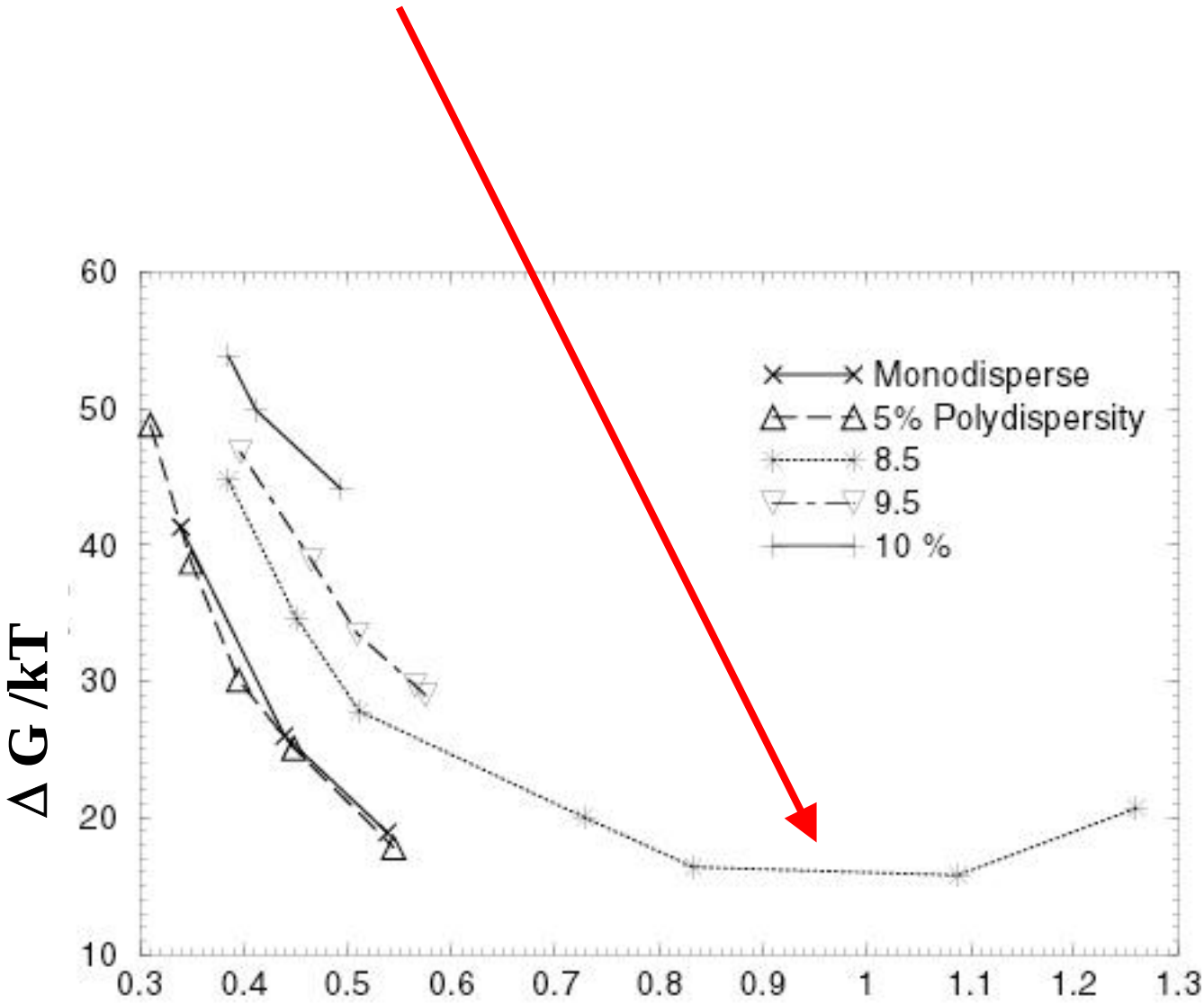
×	**monodisperse**
Δ	**5% polydispersity**
*	**8.5 %**
∇	**9.5 %**
+	**10 %**

For low polydispersity (up to 5%), the nucleation barrier is the same as for monodisperse spheres.

But for larger polydispersity, the barrier becomes **much** larger…

Moreover…

It goes through a minimum!!!



Increasing supersaturation

That is not predicted by standard CNT…

Implications for glass formation

Experiments:

Hard sphere liquids with polydispersity larger than 12 % do not crystallize (Pusey, 1987)

Why not?

"Conventional" answer:

The polydisperse fluid vitrifies before it freezes.

This slows down both **nucleation** and **growth**.

But the nucleation barrier itself will be low.

If this were true, glasses should contain very many, very small crystallites that simply cannot grow.

We find:

In polydisperse colloids, the nucleation barrier is **large**.

Colloidal glasses are therefore NOT nano-crystalline but truly amorphous.

Any experimental evidence???

Maybe…

Logarithm of average crystallite SIZE should be proportional to

$$\Delta G^*/k_B T$$

F. Shi et al. Appl.Phys.Lett. **67**, 350(1995)

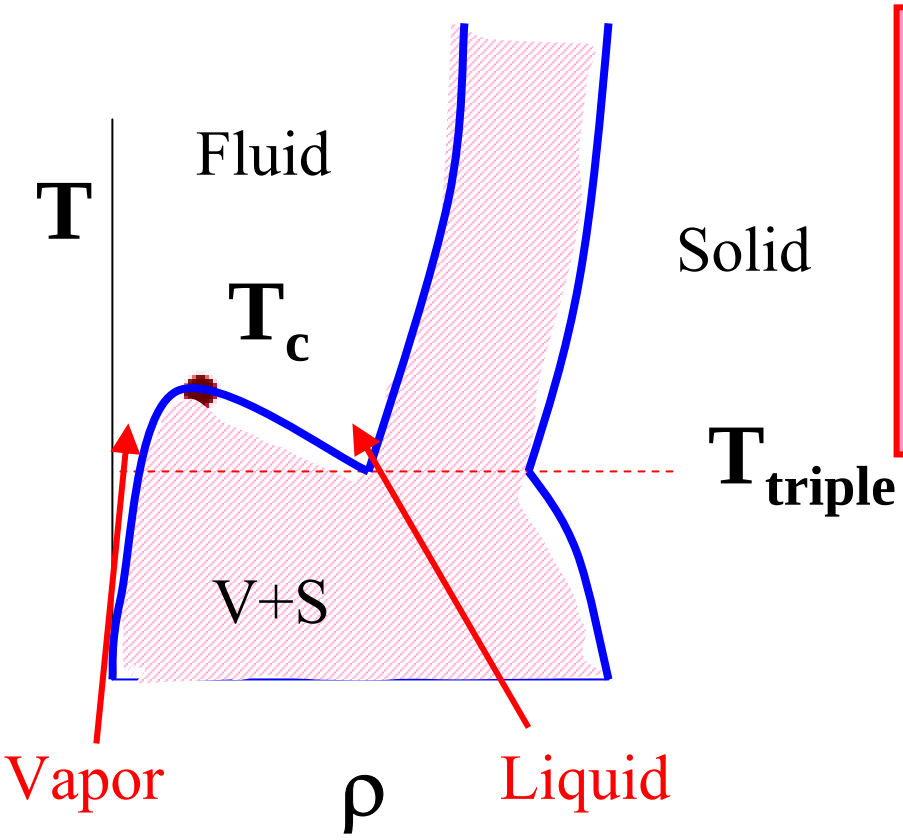
A minimum in the nucleation barrier then implies:

1. For small supersaturation:
   LARGE CRYSTALS
2. For higher supersaturation:
   SMALL CRYSTALS
3. For still higher supersaturation:
   LARGE CRYSTALS

Evidence?

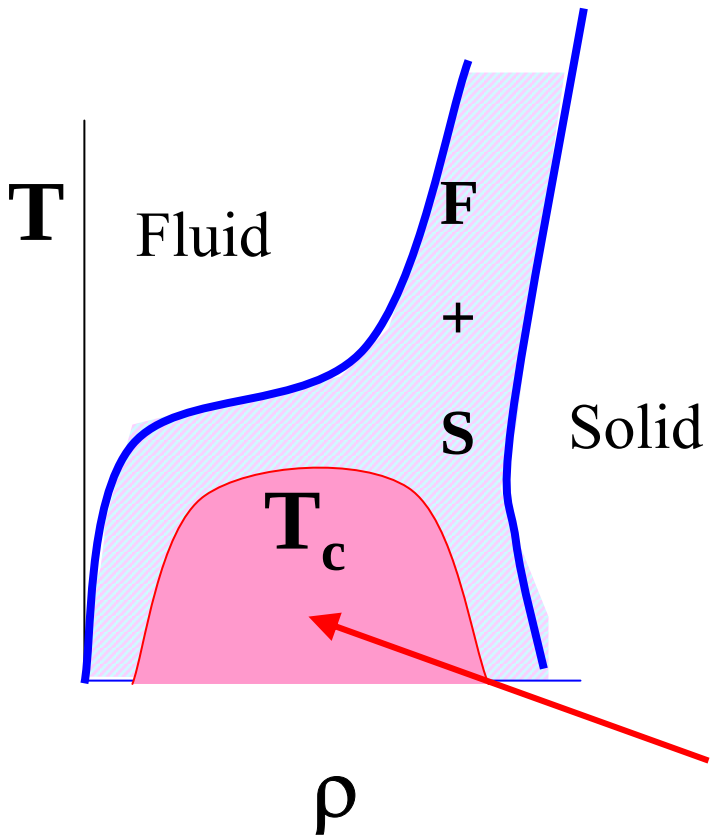
Effect of short-ranged attractions on crystallization

Recall: Short-ranged attractive forces change the appearance of the phase diagram of colloidal suspensions:



Hard spheres with

LONG-RANGED attraction



Hard spheres with

SHORT-RANGED attraction

GLOBULAR PROTEINS

Problem:

HUMAN GENOME PROJECT

⇓

$3\ 10^4$ proteins

BUT WHAT IS THEIR 3D STRUCTURE?

X-RAY CRYSTALLOGRAPHY REQUIRES GOOD CRYSTALS

CRYSTALLIZED PROTEINS:

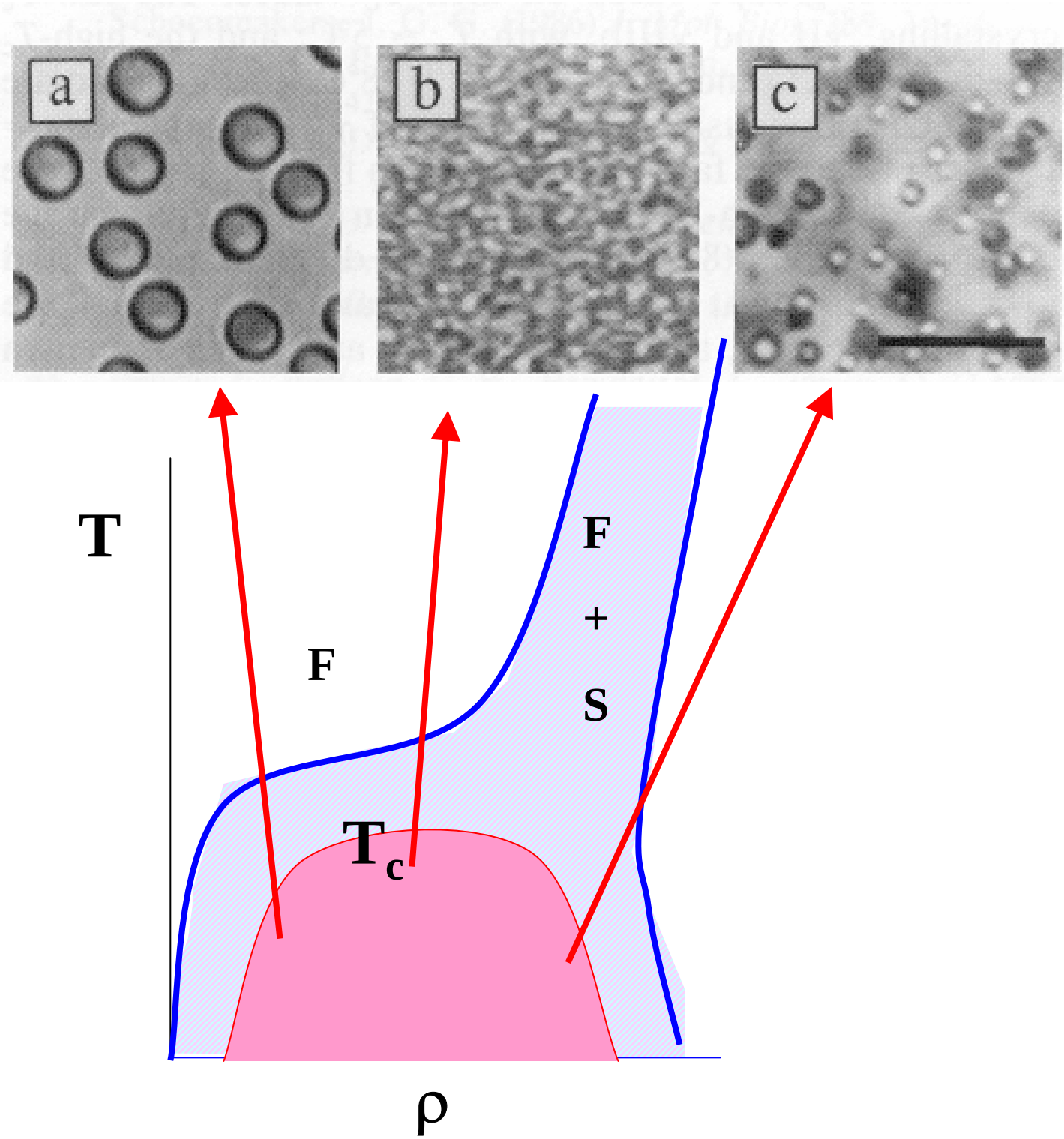
$O(8\ 10^3)$ - globular proteins

$O(20)$ - membrane proteins

M. Broide *et al.* , PNAS **88**,5660(1991)

Phase diagram of **GLOBULAR PROTEINS**

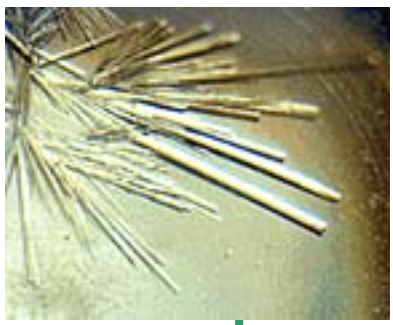
(γ-crystallin)

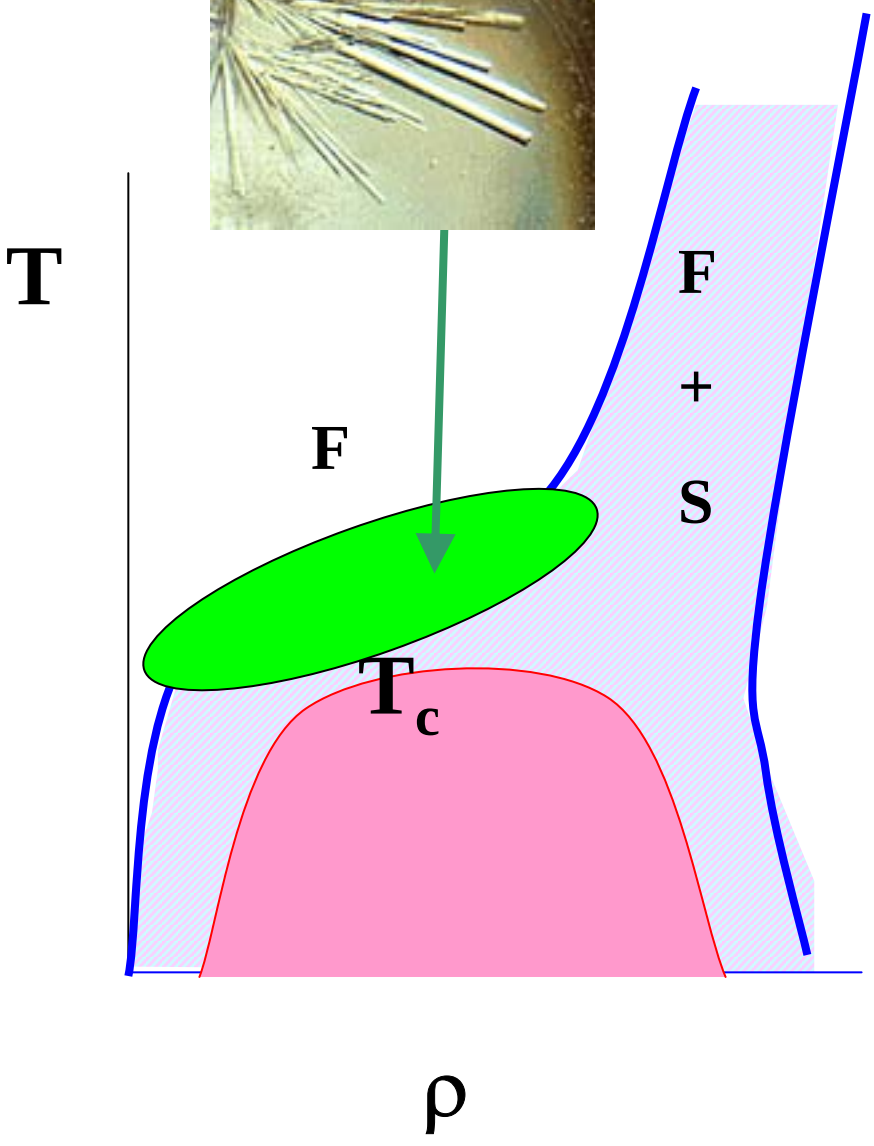


D. Rosenbaum, P.C. Zamora and C.F. Zukoski.
PRL, 76150(1996)

RELATION BETWEEN PHASE DIAGRAM AND

PROTEIN-CRYSTALLIZATION "WINDOW"

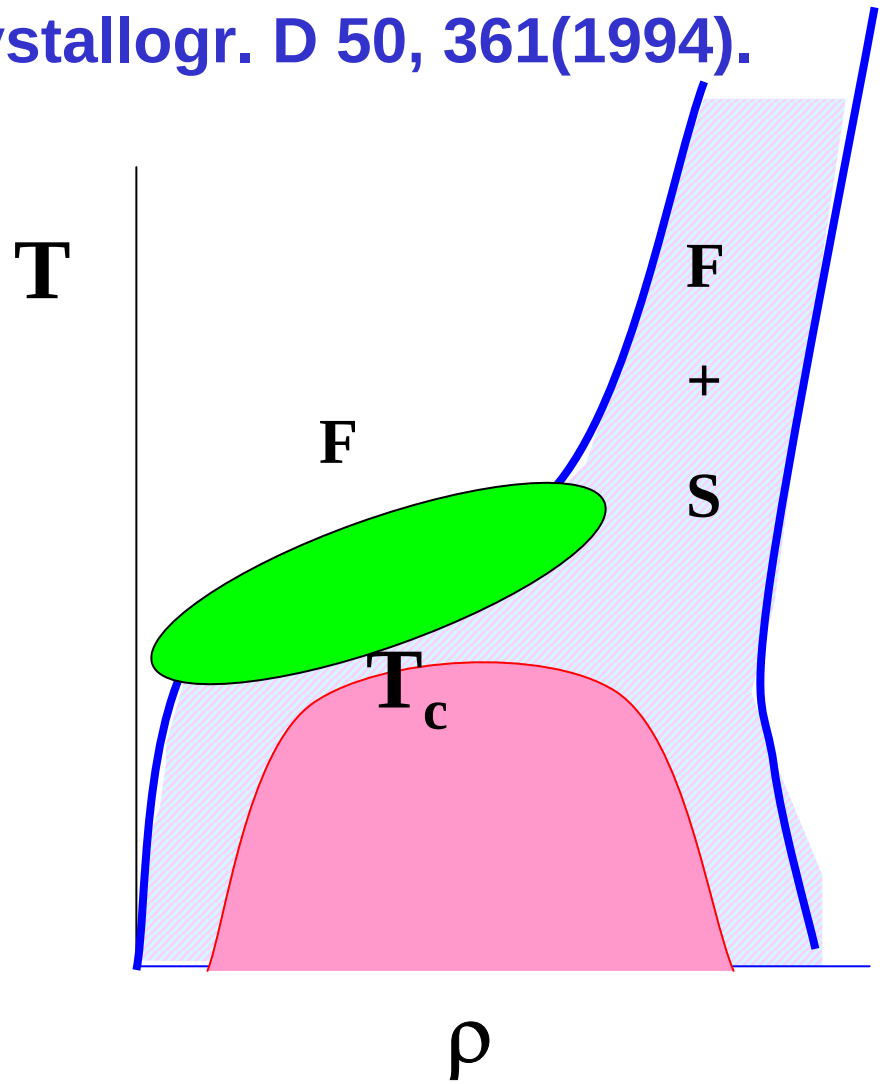




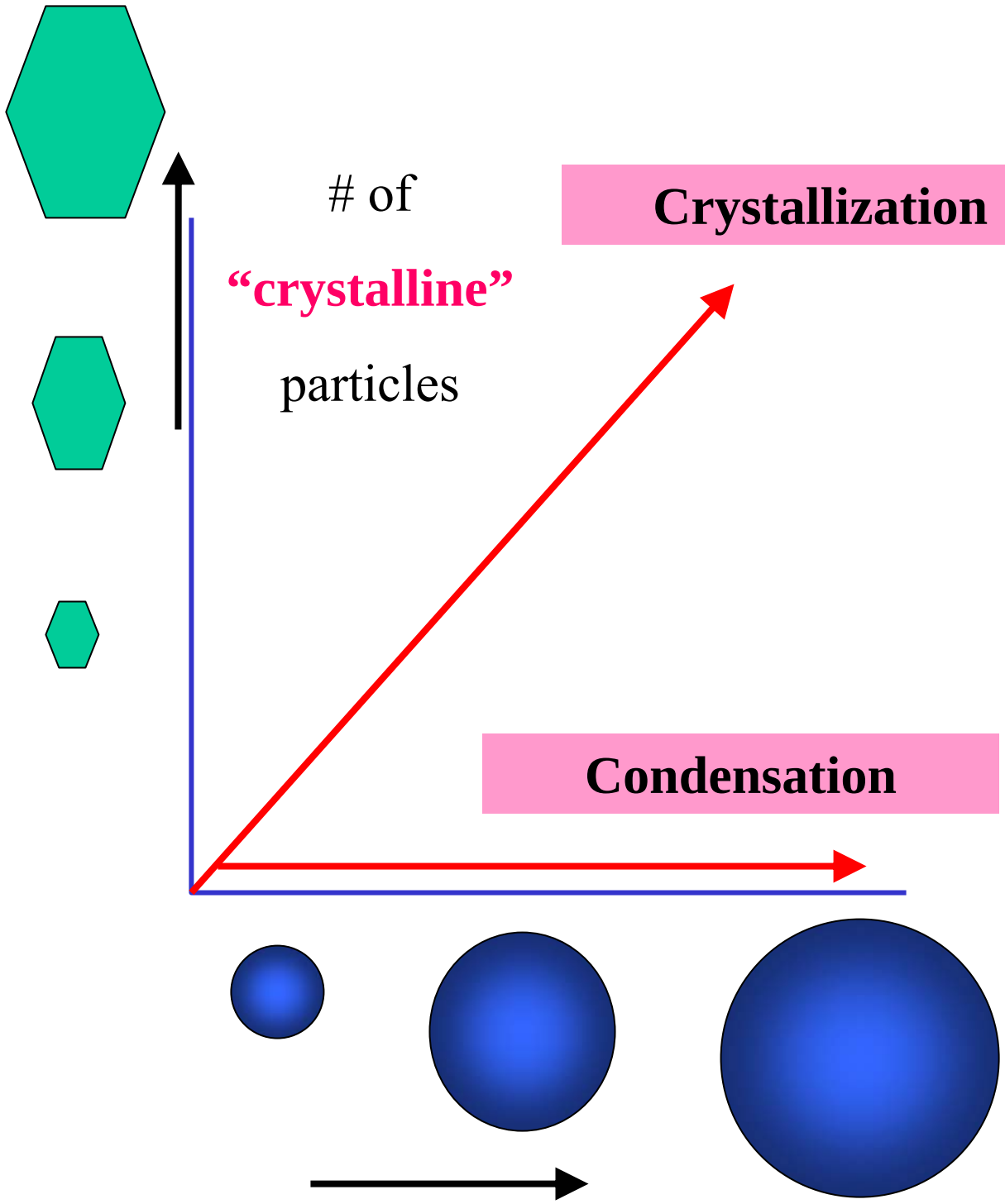
WHY DO GLOBULAR PROTEINS CRYSTALLIZE IN A NARROW "WINDOW" ??

A. George and W. Wilson,

Acta.Crystallogr. D 50, 361(1994).

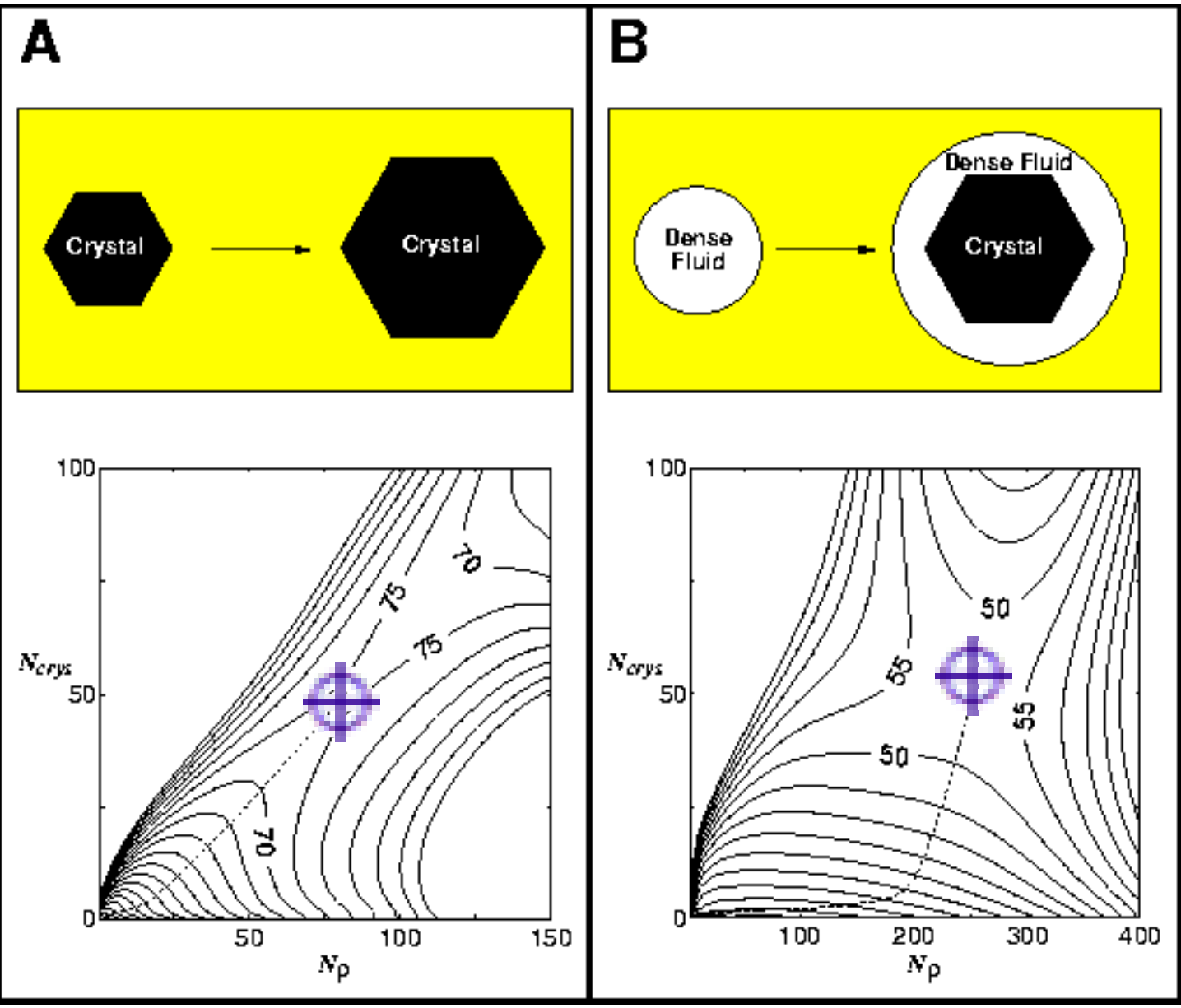


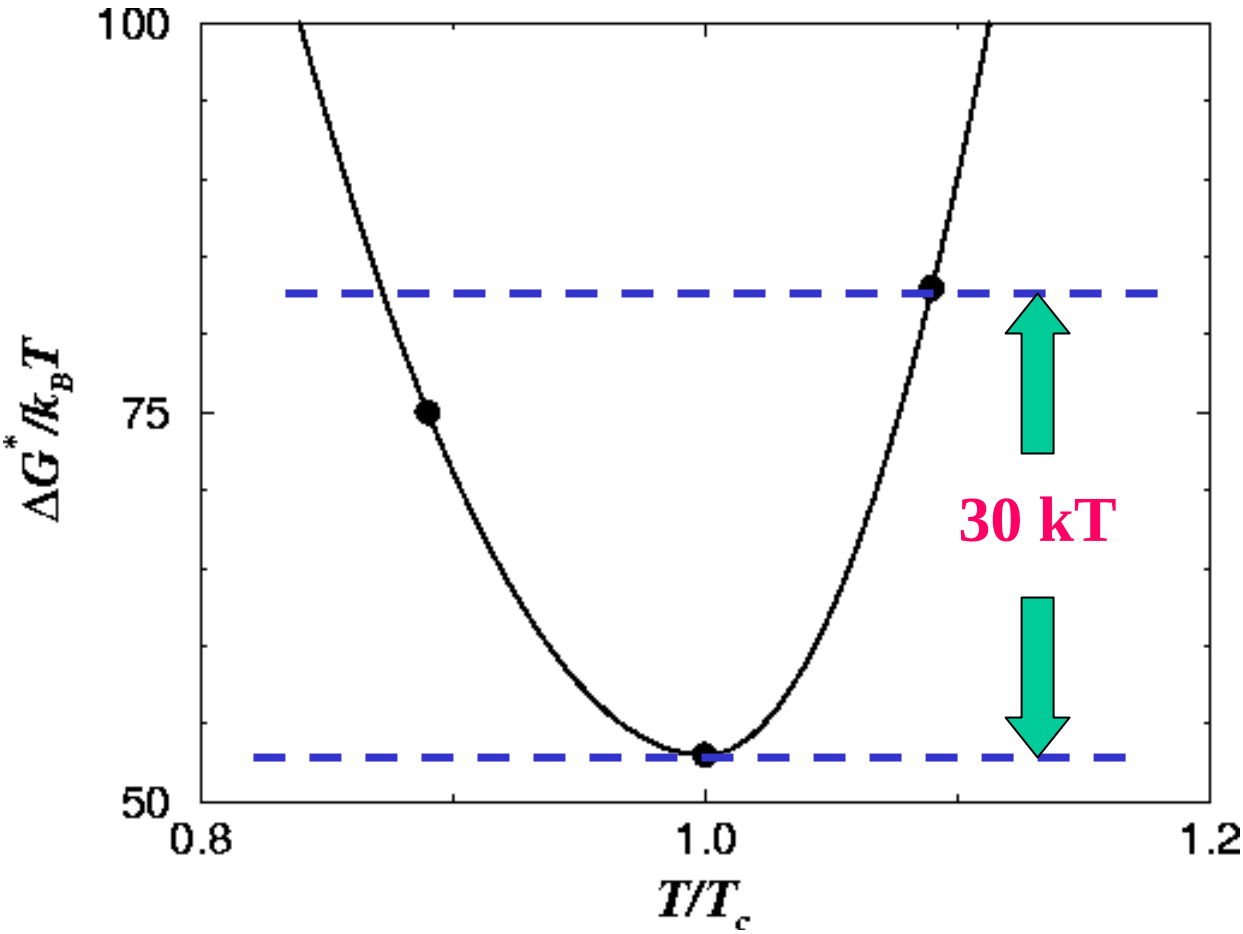
USE **SIMULATION** TO STUDY THE **NUCLEATION PATHWAY...**


of
"crystalline"
particles
Crystallization
Condensation
# of particles in a **dense cluster**
(e.g. a droplet)

P.R. ten Wolde & D.F.

SCIENCE, **277**,1975(1997)

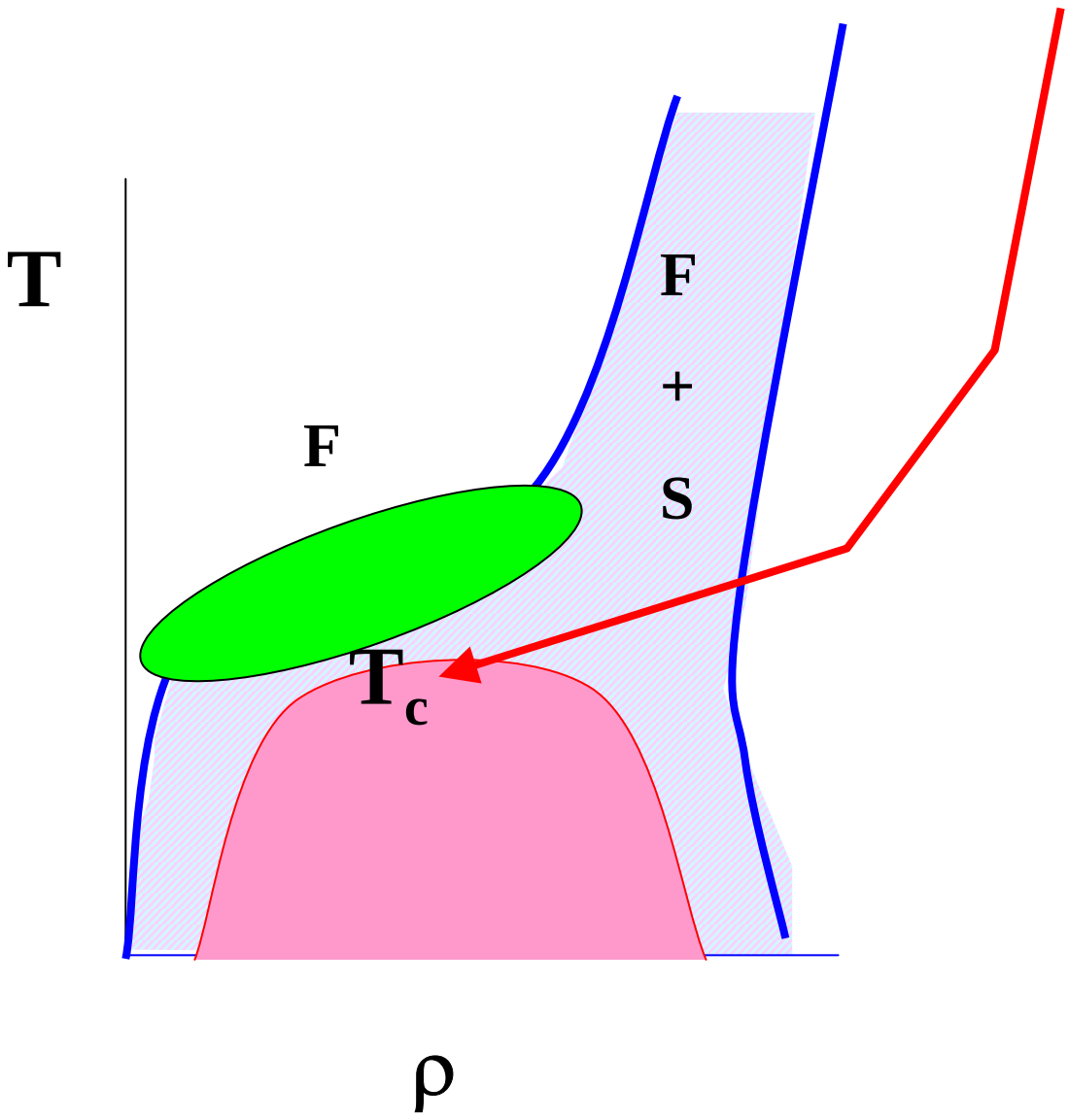


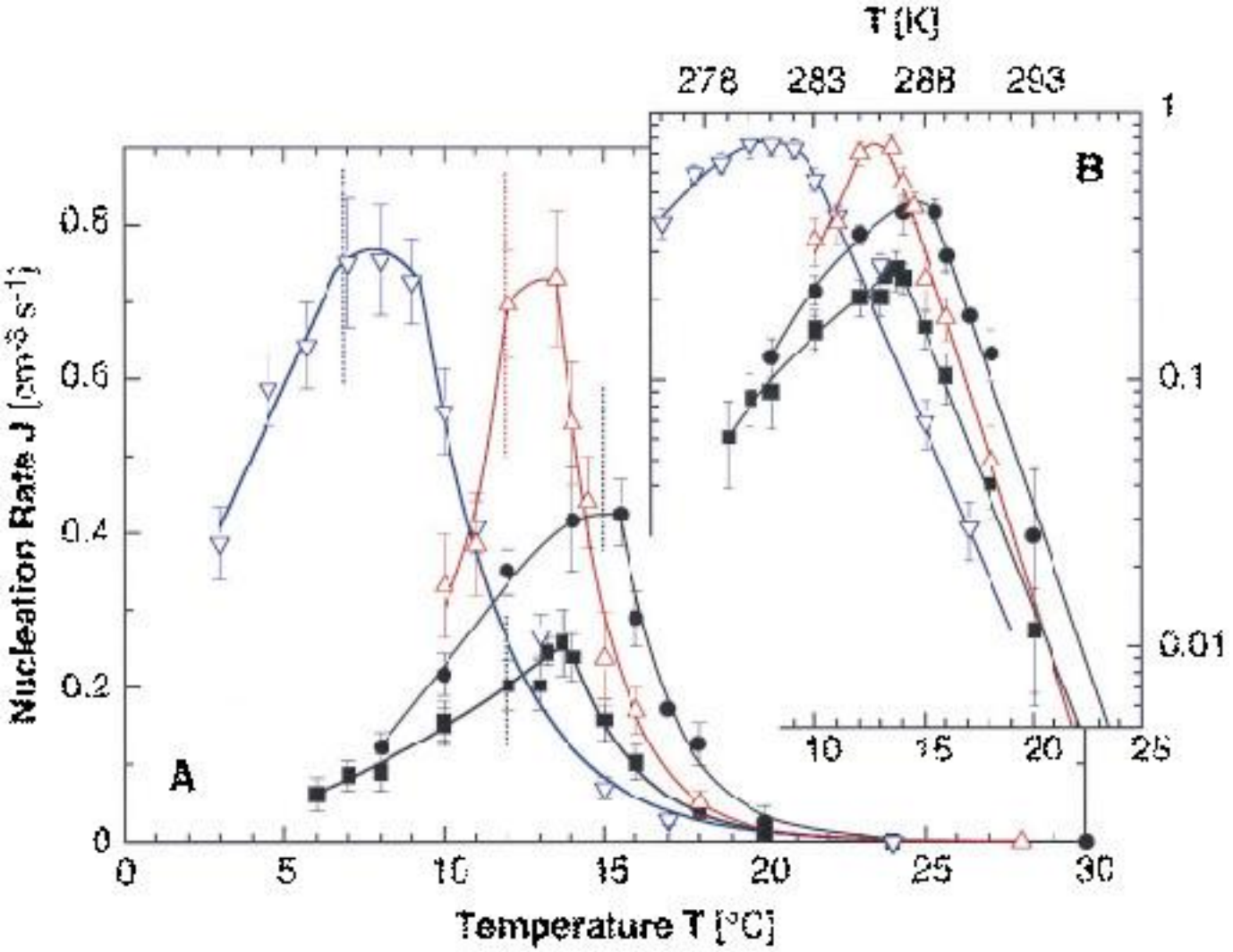

100
75
50
0.8
1.0
1.2
$\Delta G^*/k_BT$
T/T_c
30 kT

At fixed supersaturation, this corresponds to an increase in the nucleation rate by a factor:

$$10^{13}\ !$$

A hidden critical point helps!




T [K]
278
283
288
293
1
0.1
0.01
B
10
15
20
25
0.8
0.6
0.4
0.2
0
A
0
5
10
15
20
25
30
Nucleation Rate J [cm⁻³s⁻¹]
Temperature T [°C]

SUMMARY

1. **Nucleation can be studied by simulation**
2. **The structure of the critical nucleus is (often) not as predicted, and…**
3. **The barrier height is not as predicted, and …**
4. **The rate is not as predicted…**

In short: we need better experiments and better theories….