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 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

Solid-liquid coexistence for polydisperse hard spheres

Volume Fraction

Polydispersity

12%

(Bolhuis & Kofke, PRE, 54:634(1996))
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 $\sim L^3$

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

** * * * * * **

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 Diagram]

**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. : \( \mu_{\text{solid}} < \mu_{\text{liquid}} \) )

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

Free-energy gain

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

Free-energy loss:

Physicist’s Crystal nucleus
$$\Delta G^* = \frac{16\pi \gamma^3}{3\rho \Delta \mu^2}$$

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:**

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

**Simulation:**

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

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

$\Rightarrow$ 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 $\Delta G^*$ (MC/MD)

2. Compute transmission coefficient $\Gamma$ (MD)

\[
\text{Rate} = \Gamma \exp(-\beta \Delta G^*)
\]

- 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


However:

Entropy-driven freezing is not universally loved…
SIMULATION RESULTS for BARRIER HEIGHT

\[ \Delta G(n)/kT \]

Clustersize \( n \)

\( \phi = 0.5207 \)

\( \phi = 0.5277 \)

\( \phi = 0.5343 \)

\( \phi_{\text{coex}} = 0.494 \)

Nothing special???
As $\Delta \mu$ is known, we can deduce $\gamma$ from the barrier heights.

SIMULATIONS:

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

At coexistence: $\gamma \approx 0.62 \frac{kT}{\sigma^2}$

In contrast, CNT ASSUMES THAT $\gamma$ IS CONSTANT.

20% error does not seem much, but:

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

And the nucleation rate is proportional to

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

Assume: Brownian motion
Approximate: Hydrodynamic Interactions

Nucleation rate: Zeldovich Factor

\[ I = k^+ N^* Z \rho \exp(-\Delta G^*/kT) \]

\[ k^+ N^* , Z, \Delta G^* \text{ can all be computed numerically} \]
COMPARISON WITH EXPERIMENT

Simulation results (discrepancy: 10 orders of magnitude !!)

≈ 1 Nucleus / (month cm³)
THE EFFECT OF POLYDISPERSITY
Phase diagram of polydisperse hard spheres

Solid-liquid coexistence for polydisperse hard spheres

12% Polydispersity

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

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

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?
Recall: Short-ranged attractive forces change the appearance of the phase diagram of colloidal suspensions:
**Phase Diagrams**

- **Tc** (critical temperature)
- **T_{triple}** (triple point)
- **V+S** (vapor + solid)
- **F+S** (fluid + solid)

**Hard Spheres**

- **Long-ranged** attraction
- **Short-ranged** attraction

**Meta-stable fluid-fluid**
GLOBULAR PROTEINS

**Problem:**

HUMAN GENOME PROJECT

\[ \downarrow \]

3 \(10^4\) proteins

BUT WHAT IS THEIR 3D STRUCTURE?

**X-RAY CRYSTALLOGRAPHY**

REQUIRES GOOD CRYSTALS

CRYSTALLIZED PROTEINS:

\[ O \left(8 \times 10^3\right) \] - globular proteins

\[ O \left(20\right) \] - membrane proteins
M. Broide et al., PNAS 88, 5660 (1991)

Phase diagram of GLOBULAR PROTEINS

(γ-crystallin)
RELATION BETWEEN PHASE DIAGRAM AND PROTEIN-CRYSTALLIZATION “WINDOW”
WHY DO GLOBULAR PROTEINS CRYSTALLIZE IN A NARROW “WINDOW”??

A. George and W. Wilson,


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)
\[ \frac{\Delta G^*}{k_B T} \]
At fixed supersaturation, this corresponds to an increase in the nucleation rate by a factor: 

\[ 10^{13} \! \] 

*A hidden critical point helps!*
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....