Dynamic Assemblies of Soft Colloids

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Nano@Tech, March 13, 2007

Acknowledgements

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Ashlee St. John

Bart Blackburn

Neetu Singh

Courtney Sorrell

Zhiyong Meng

Toni Bonhivert

Grant Hendrickson

Support

NIH - NIBIB

GT-Emory ERC on the Engineering of Living Tissues

Johnson & Johnson

ACS-PRF

CCNE

...also: Dr. Jonathan McGrath (paint-on photonics) and Prof. Victor Breedveld, ChBE (particle tracking).

Nanoscience and Colloids

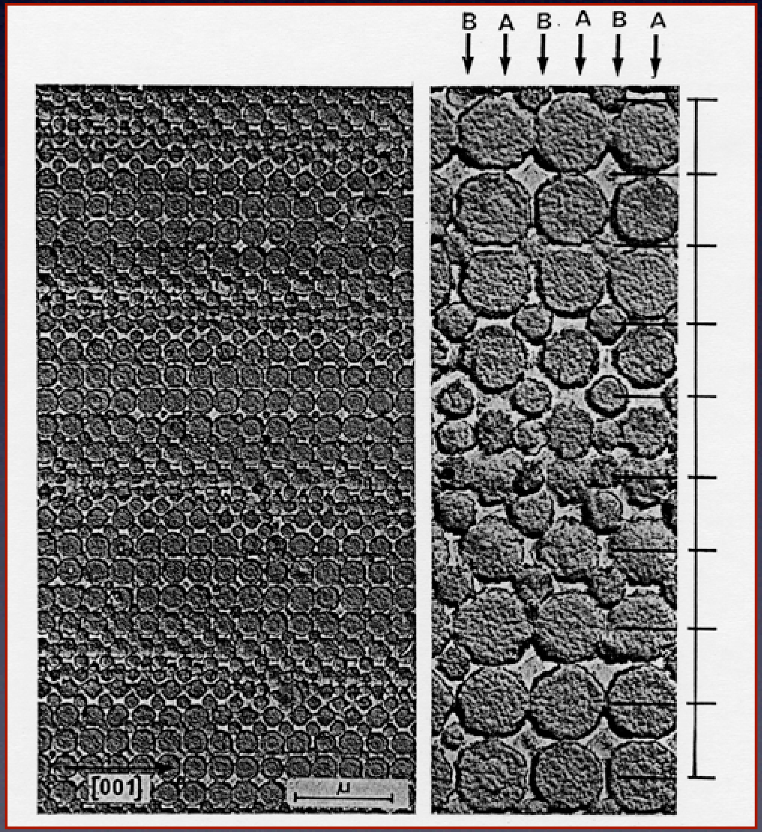
Colloidal media have occupied a critical place in the history of "nanoscience"...

- *Quantum confinement:*
  - Semiconductor nanoparticles/clusters
- *Plasmonics:*
  - Metal nanoparticles
- *Nanocomposites for reinforcement:*
  - Carbon nanotube dispersions

Colloidal Dispersions

...while colloidal dispersions/assemblies have existed far longer than “nano”.

Sanders, J. V. *Phil. Mag. A* **1980**, *42*, 705-720.



Royal Institution of Great Britain

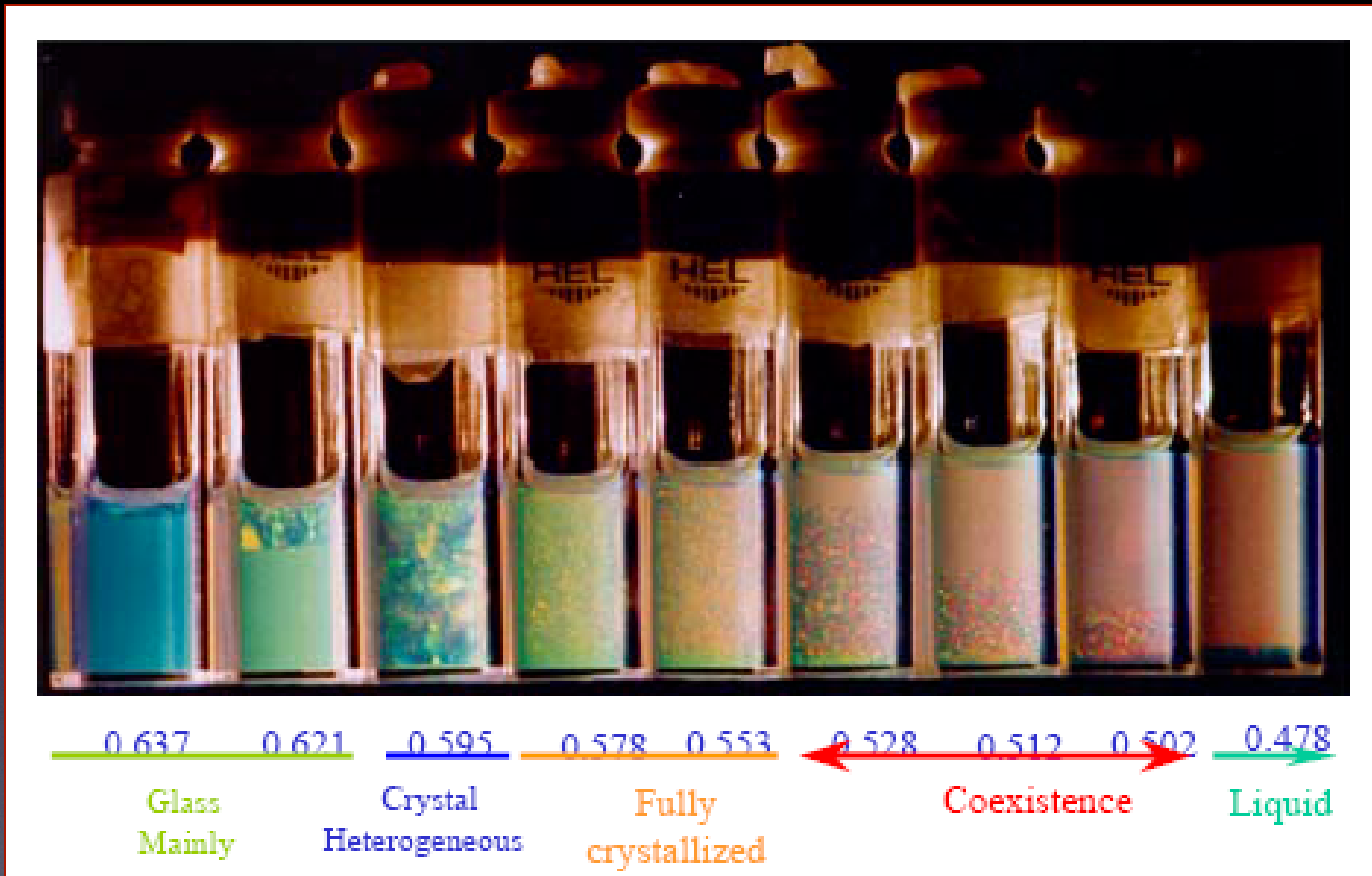
Colloidal Energetics/Dynamics

How do colloidal assemblies differ from atomic/molecular assemblies?

- *Number Density*
  - ~10^{13} cm^{-3} (colloidal) vs. ~10^{22} cm^{-3} (atomic).
- *Stability*
  - because "strength" $\propto$ density, colloidal crystals are *~1 billion* times weaker than atomic crystals.
- *Dynamics (Relaxation Time)*
  - ~10^{-2} s (colloidal) vs. ~10^{-11} s (atomic)

Hard- and Soft-Sphere Phases

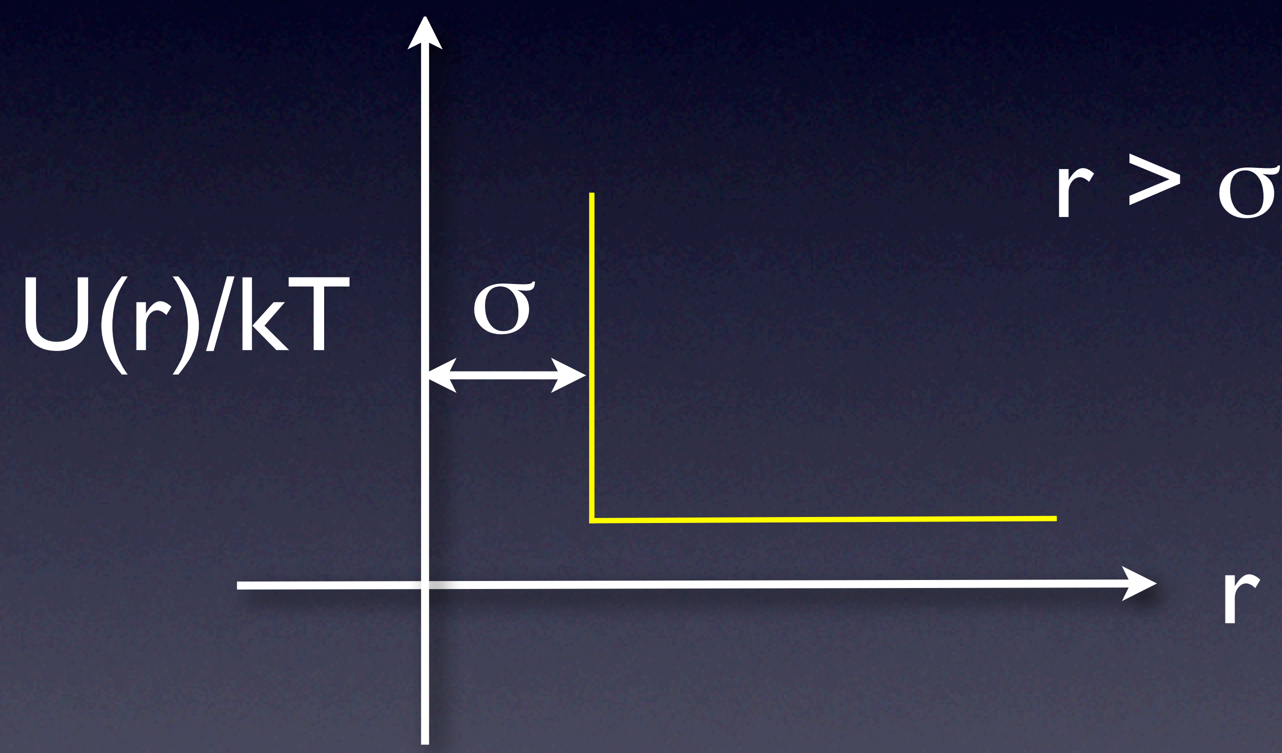
Hard Sphere Phases



Pusey, P. N.; van Megan, W. *Nature* **1986,** *330*, 340-342.

Interparticle Interactions

Repulsive hard sphere interactions can be modeled as a square potential.

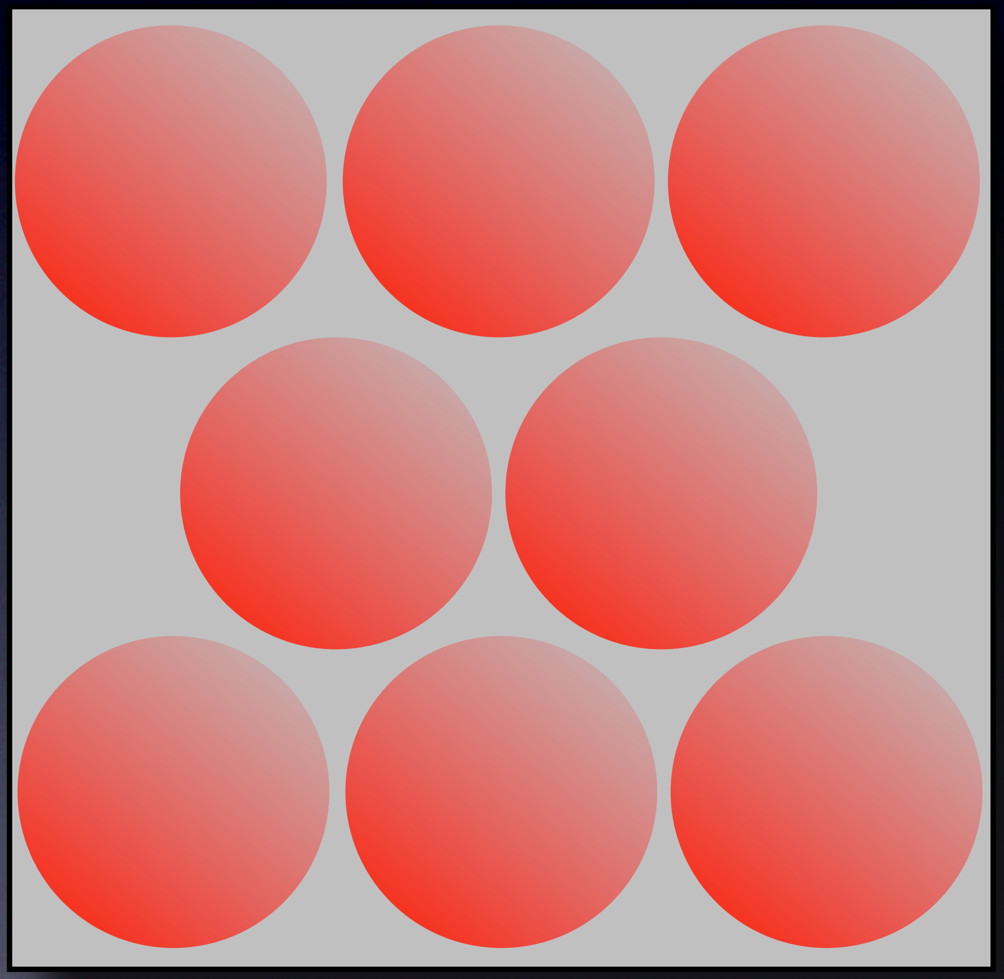


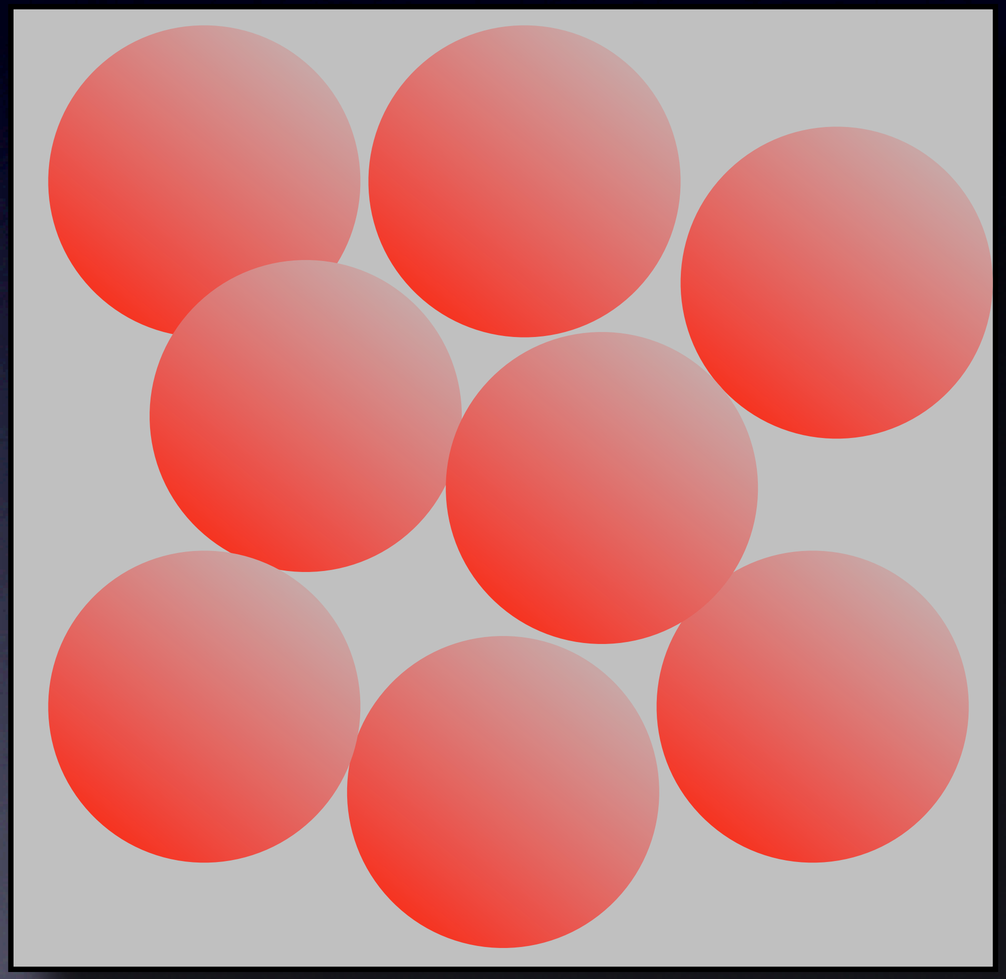
r > σ (diameter) : No Interaction

r = σ : Infinite Repulsion

Entropic Crystallization

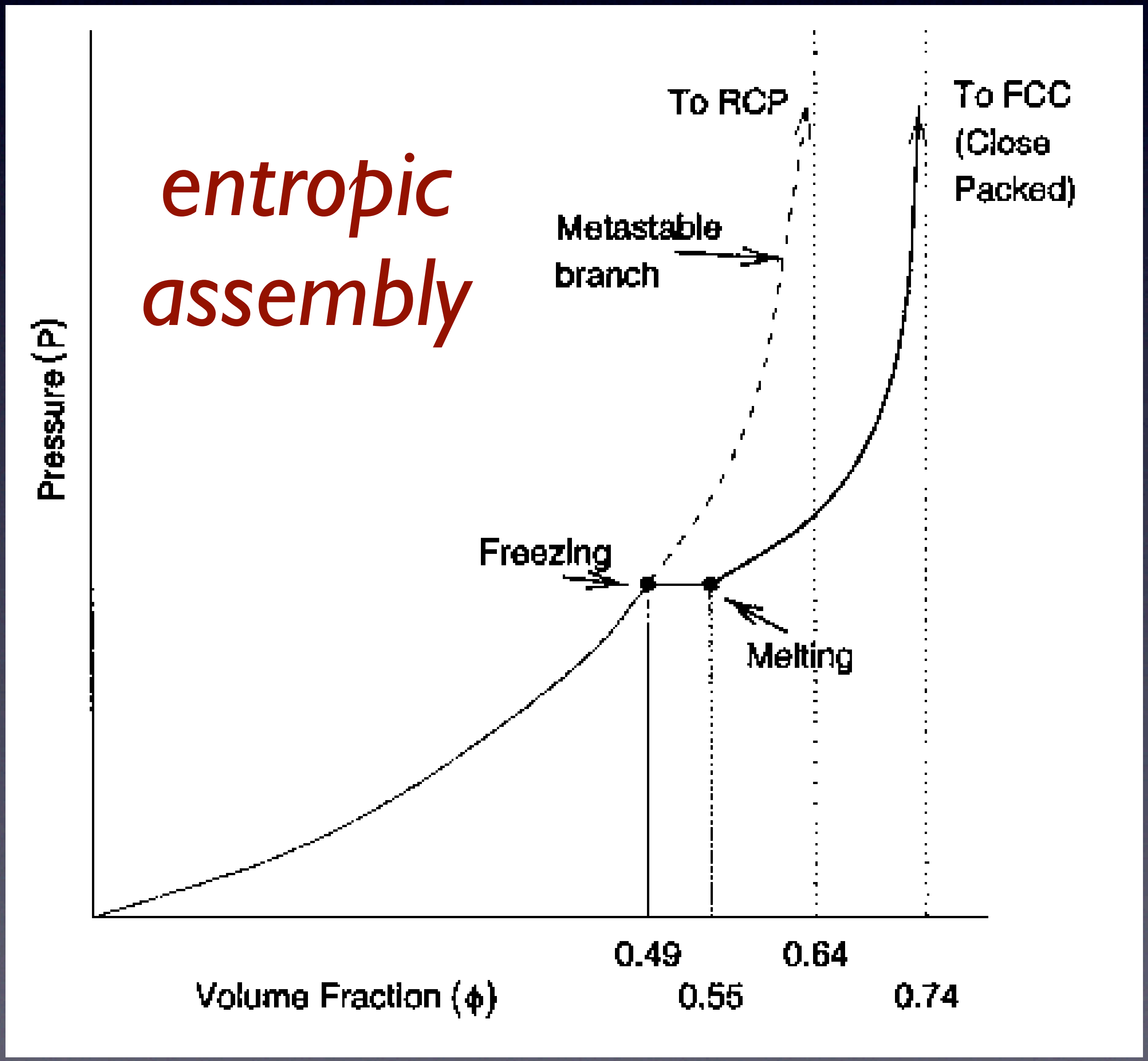
Hard spheres self-organize to maximize entropy.



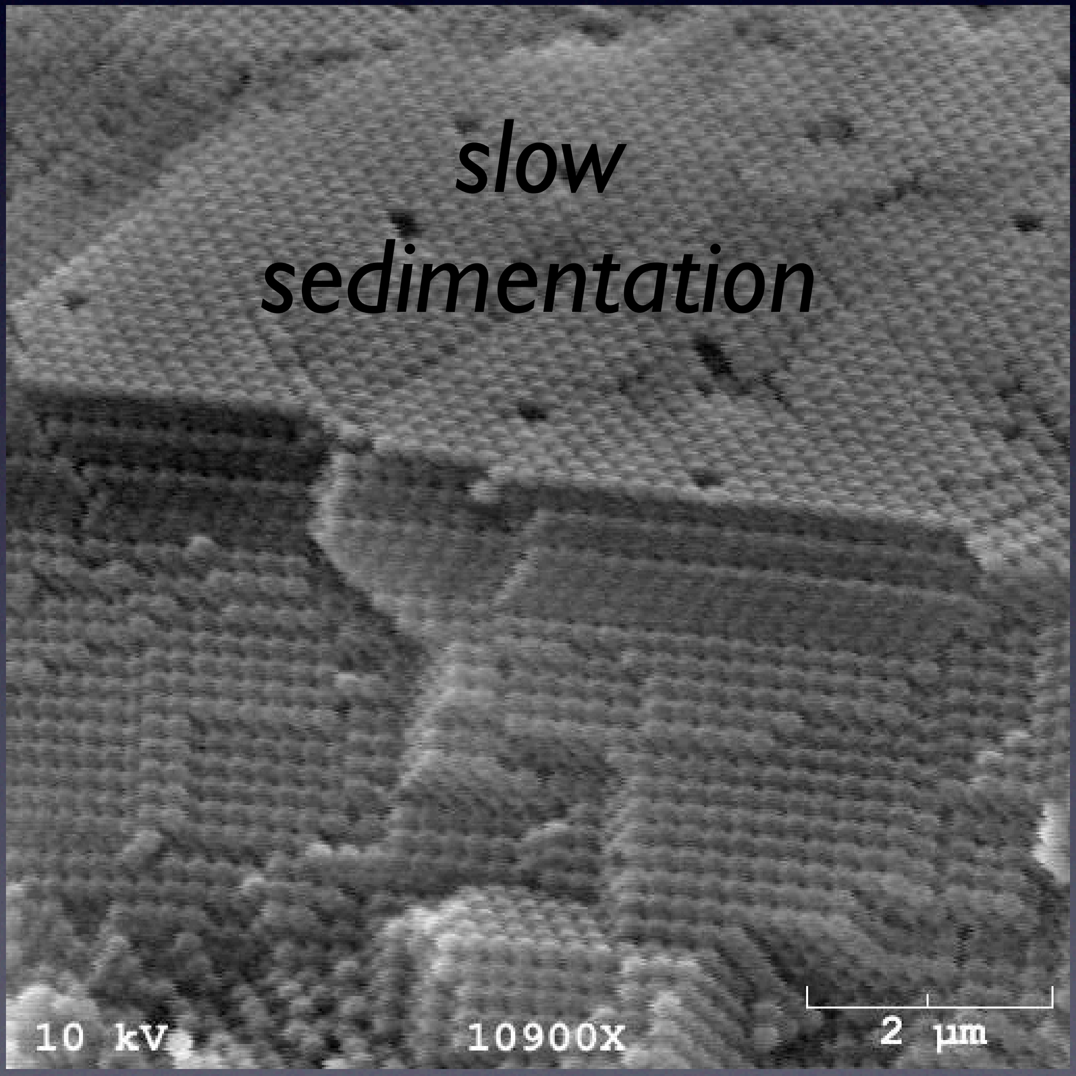


Hard Sphere Assembly

From a practical standpoint, energetically-minimized, close-packed phases of hard spheres cannot be easily prepared.

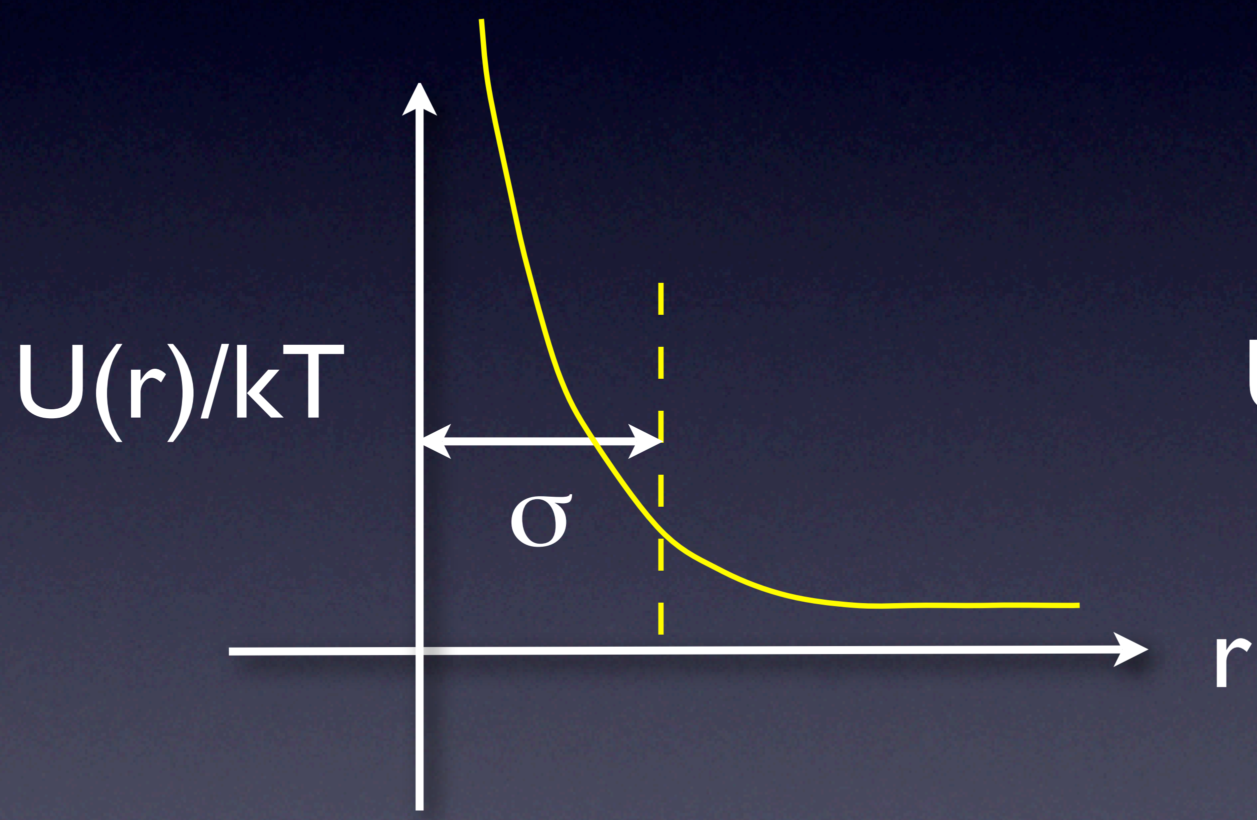


versus



What about Soft Interactions?

A power law potential can be used describe interpenetrating or deformable spheres.



$U(r) \propto (\sigma/r^{n})$

Soft Colloidal Phases

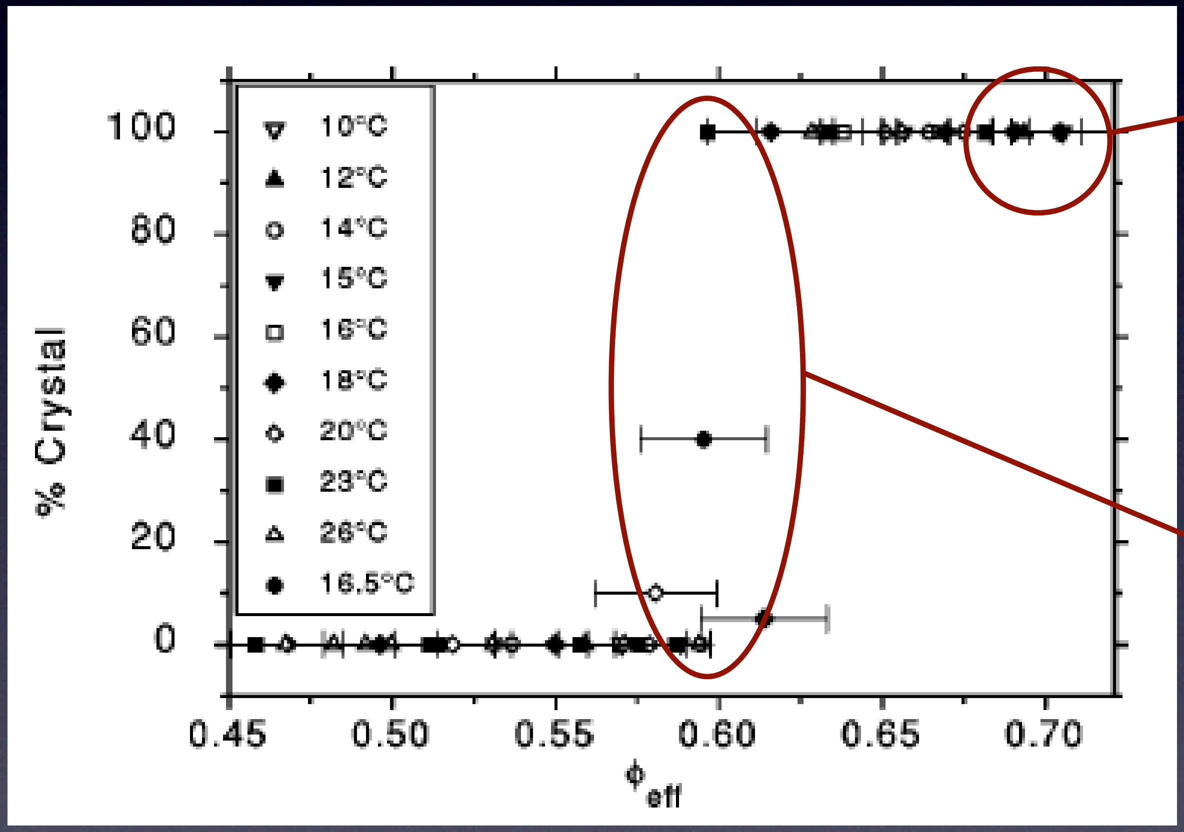
How does *particle softness* manifest itself...

- ...in the phase behavior?
- ...in the optical properties?
- ...in defect healing?
- ...in the assembly's dynamics?

What are the appropriate tools to study phenomena in soft assemblies?

Soft Colloidal Phases

Some evidence (experimental and theoretical) of softness impacting the phase behavior.



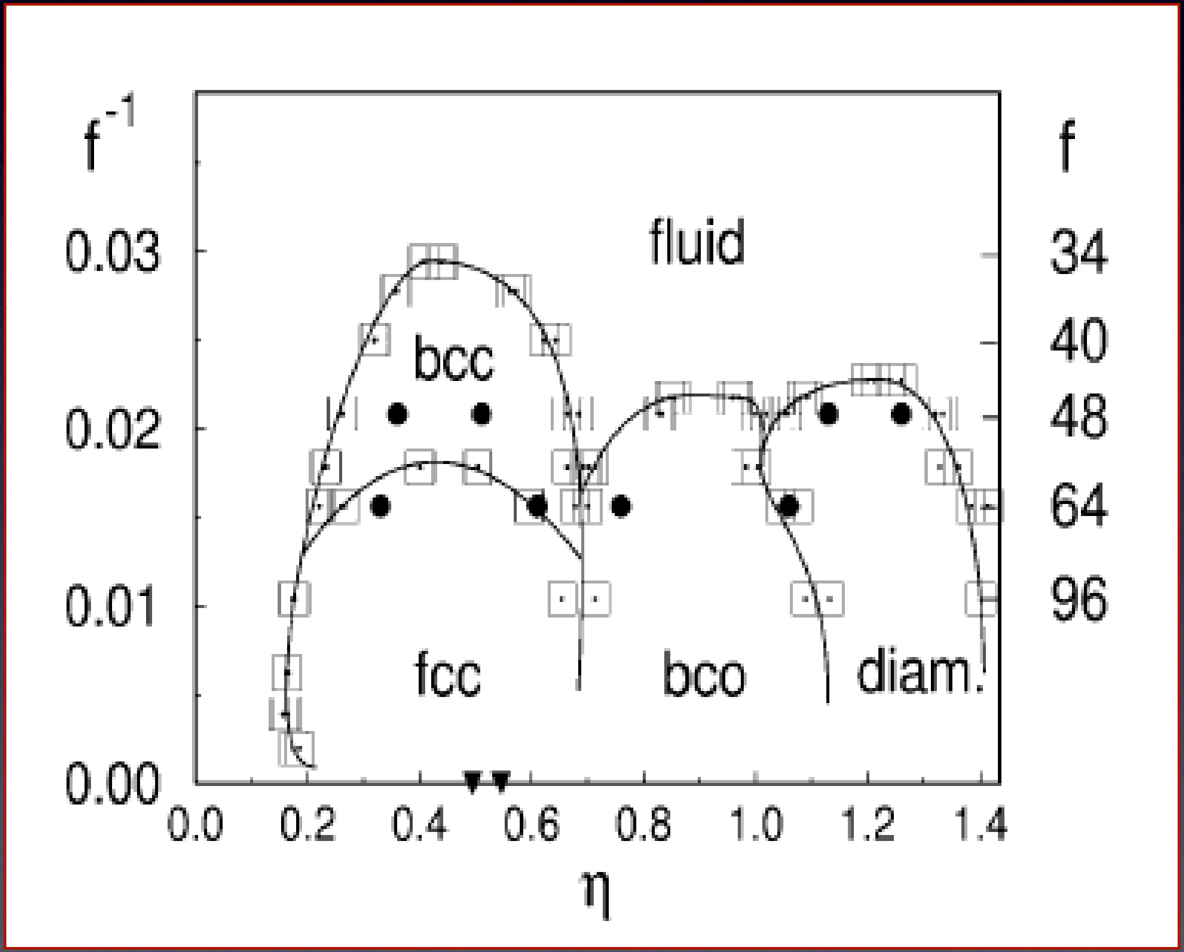
Senff, H.; Richtering, W. *J. Chem. Phys.* **1999**, *111*, 1705-1711.

"True" thermodynamic close-packed phases can be prepared.

Liquid-to-crystal transition for hydrogel particles occurs at higher volume fractions and over a more narrow concentration range than for hard spheres.

Soft Colloidal Phases

Some evidence (experimental and theoretical) of softness impacting the phase behavior.



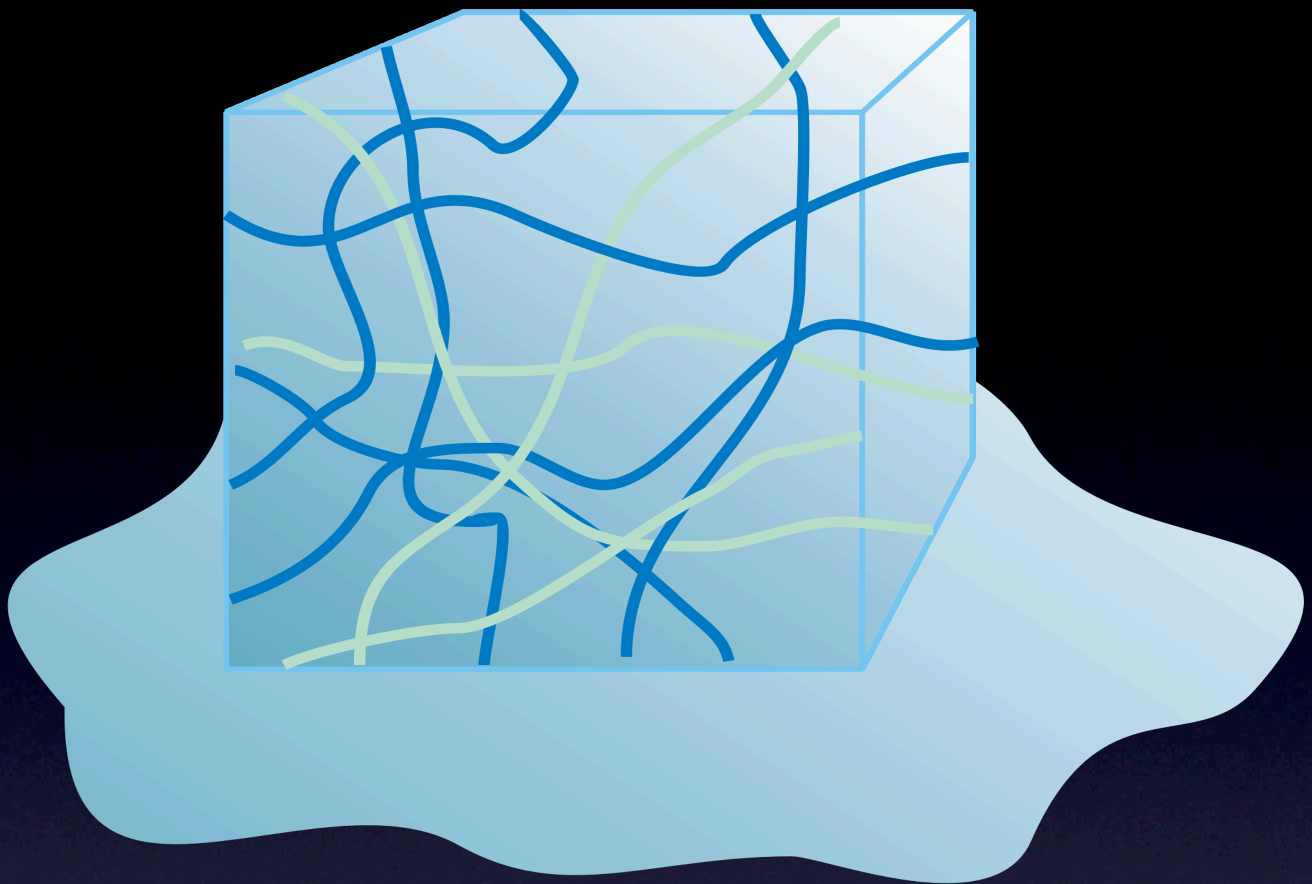
M. Watzlawek, et al., *Phys. Rev. Lett.* **1999**, *82(26)*, 5289.

Unusual non-close packed and anisotropic phases predicted.

Microgels as a Soft Sphere Model System

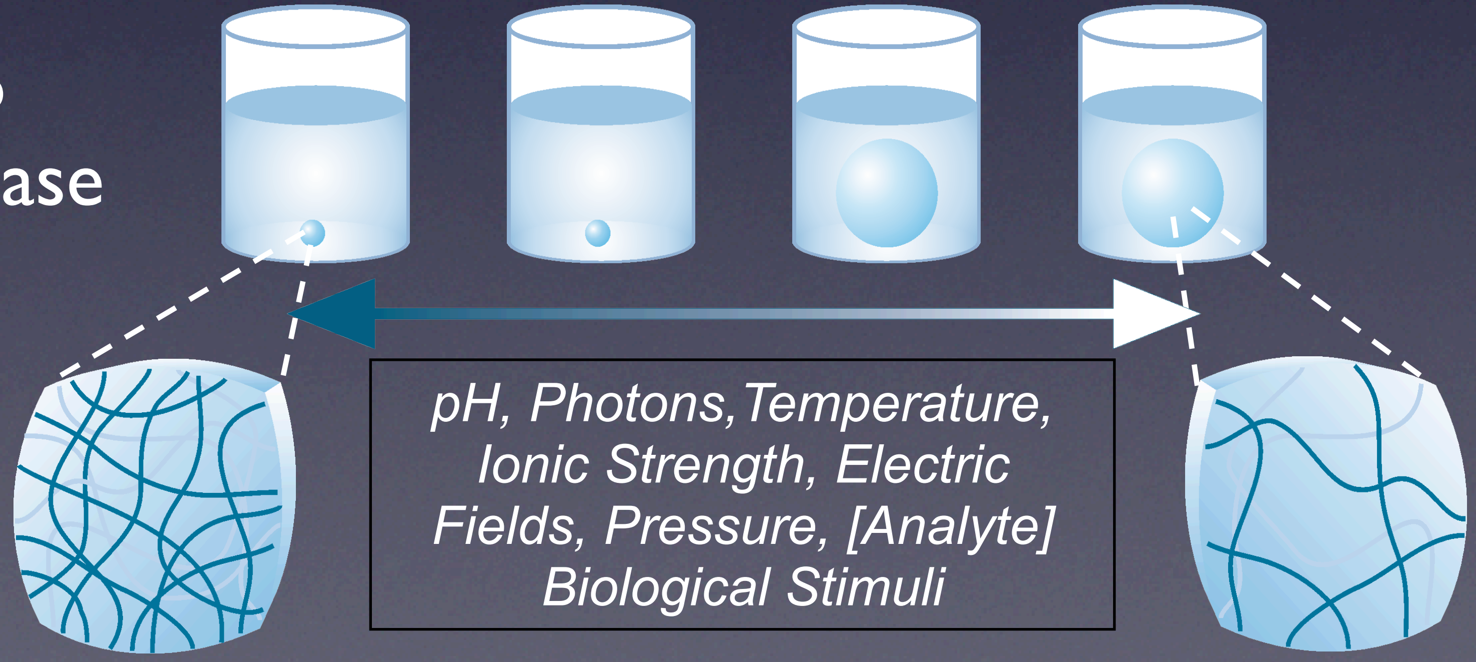
Hydrogels

- Cross-linked water soluble polymers - a physically restricted, dimensionally-stable, polymer solution.



Responsive Hydrogels

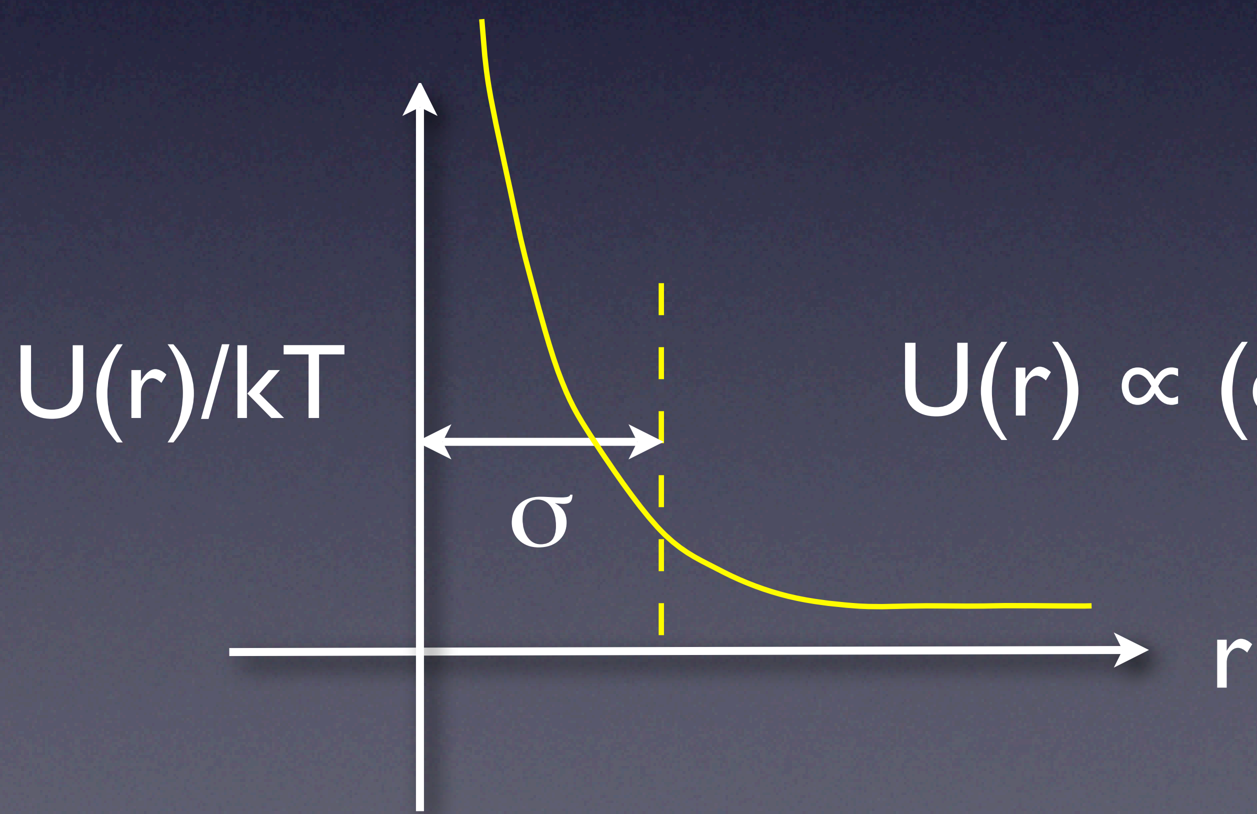
- Polymeric gels that undergo environmentally initiated phase separation events (volume phase transition)



Gel Swelling Thermodynamics

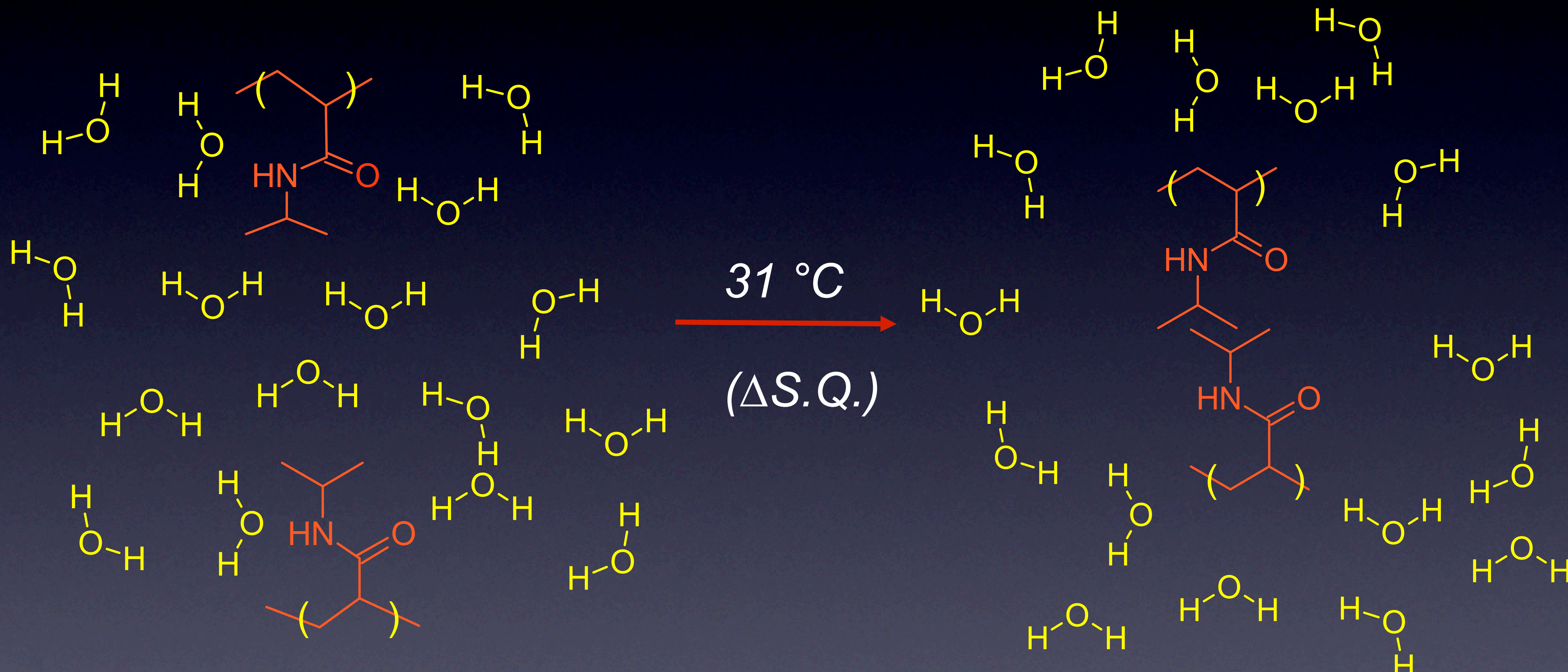
Gel swelling includes contributions from the free energy of mixing and chain elasticity.

$$\frac{\pi}{k_B T} = \frac{\pi_{el} + \pi_M}{k_B T} = \frac{n_0}{N_x}\left[\frac{1}{2}\left(\frac{n}{n_0}\right) - \left(\frac{n}{n_0}\right)^{\frac{1}{3}}\right] - \frac{1}{v}\left[\ln(1 - nv) + nv + \chi n^2 v^2\right]$$



Responsive Polymers

poly(*N*-isopropylacrylamide) (pNIPAm)

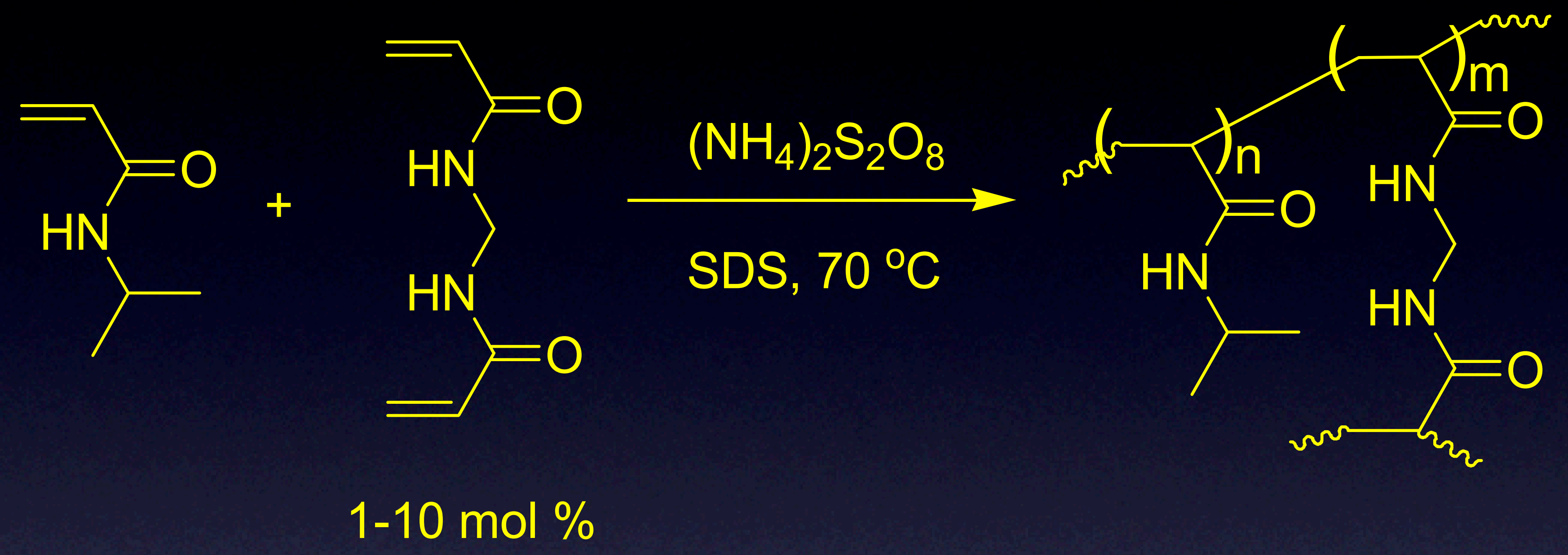


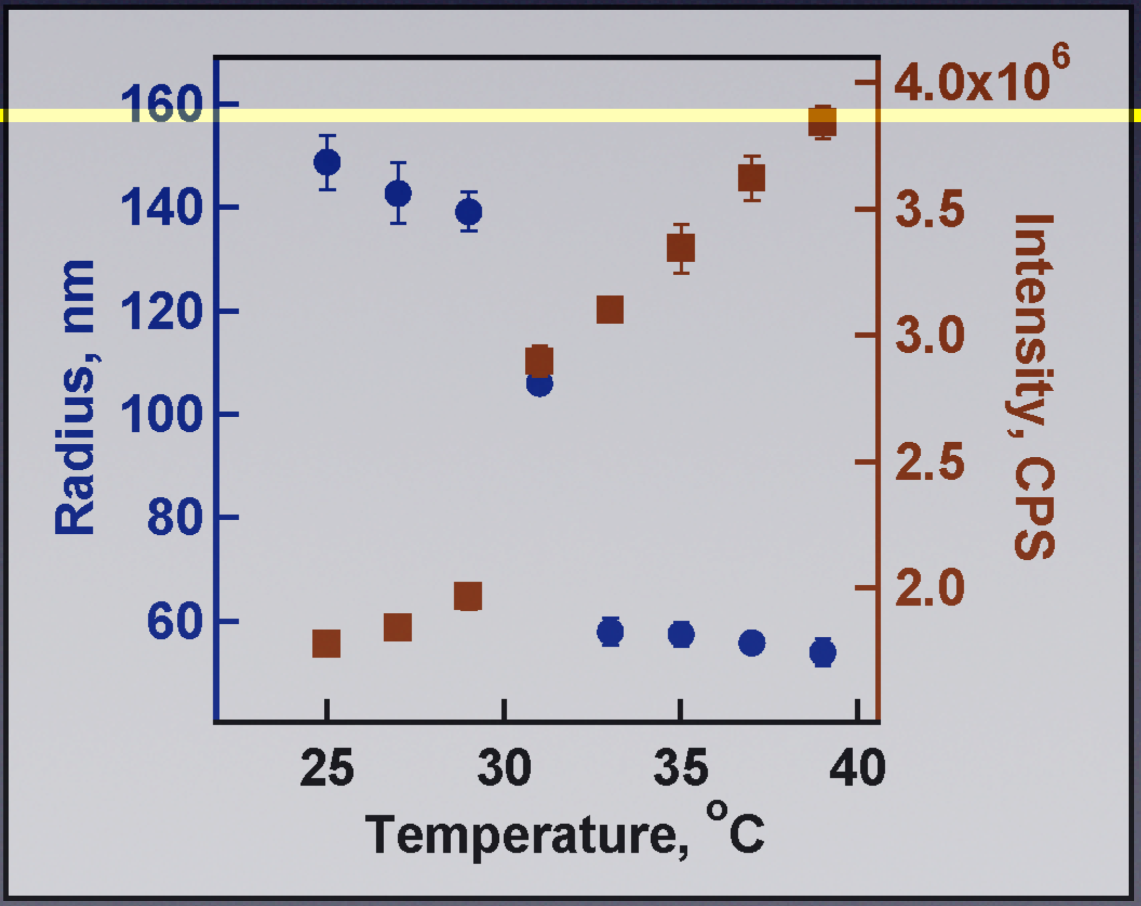
Swollen/Hydrophilic

Collapsed/Hydrophobic

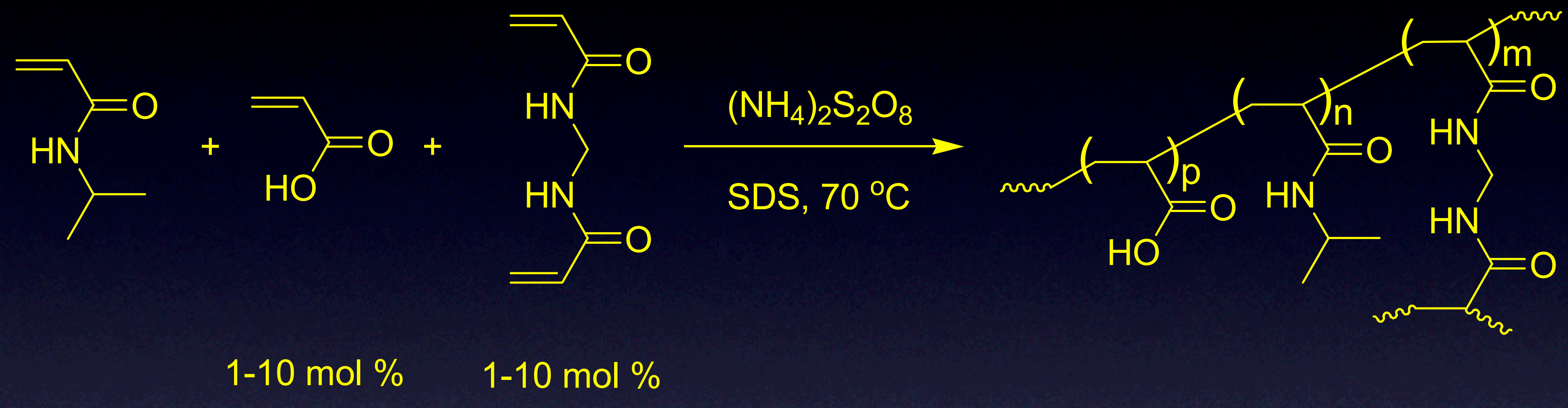
Heskins, M.; Guillet, J. E., *J. Macromol. Sci. Chem.* **1968,** *A2*, 1441-1455.
Tanaka, T., *Phys. Rev. Lett.* **1978,** *40*, 820-823.
Annaka, M.; Tanaka, T., *Nature* **1992,** *355*, 430-432.

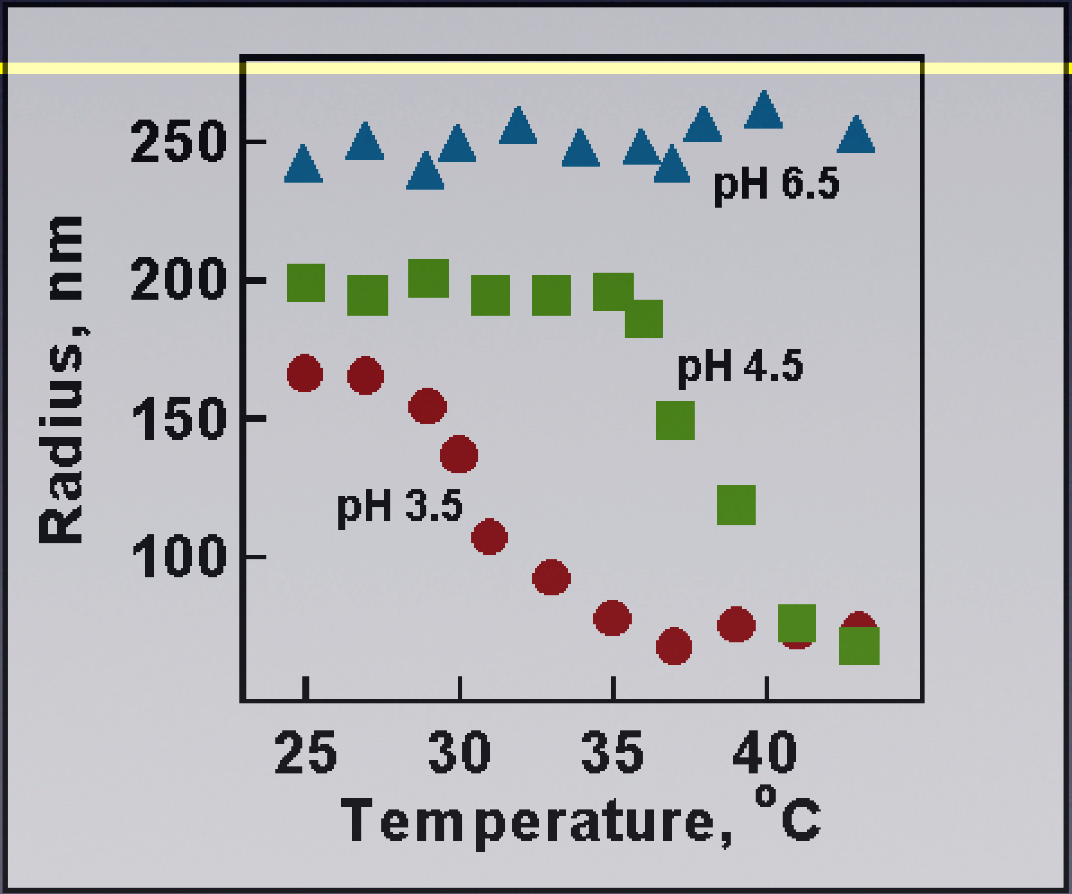
Hydrogel Synthesis





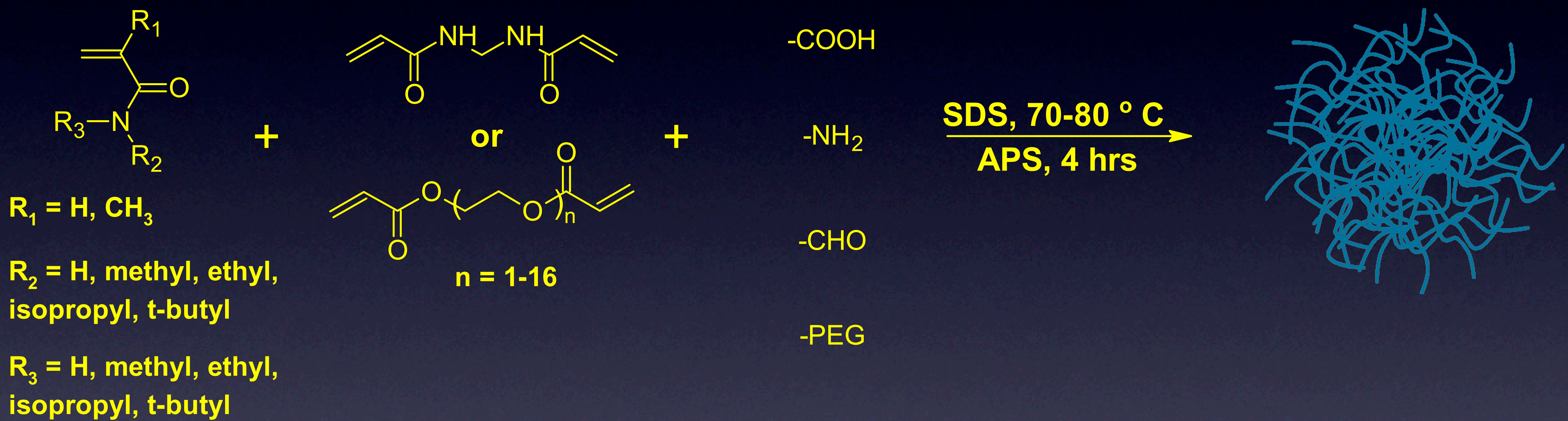
“Multiresponsive” Hydrogels

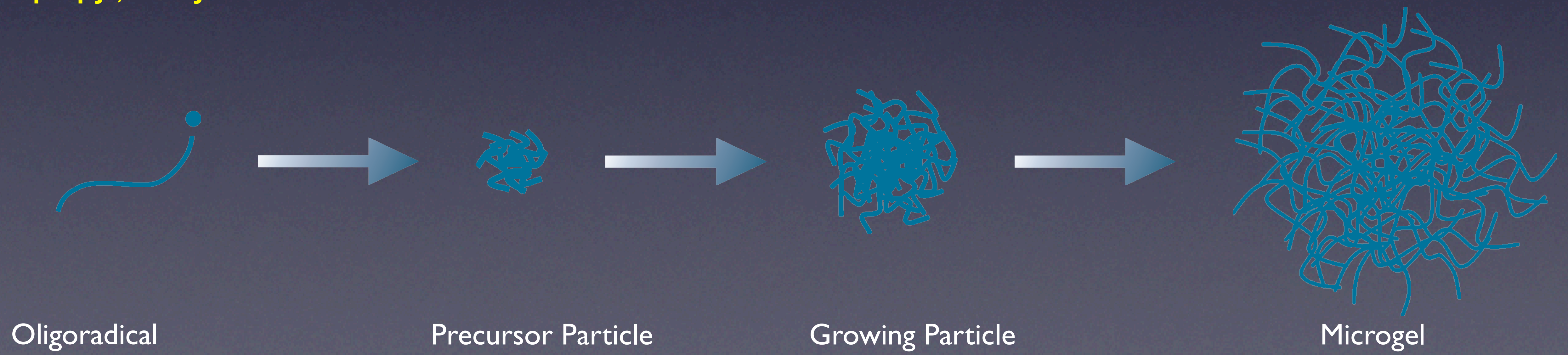




Hydrogel Nano/Microparticles

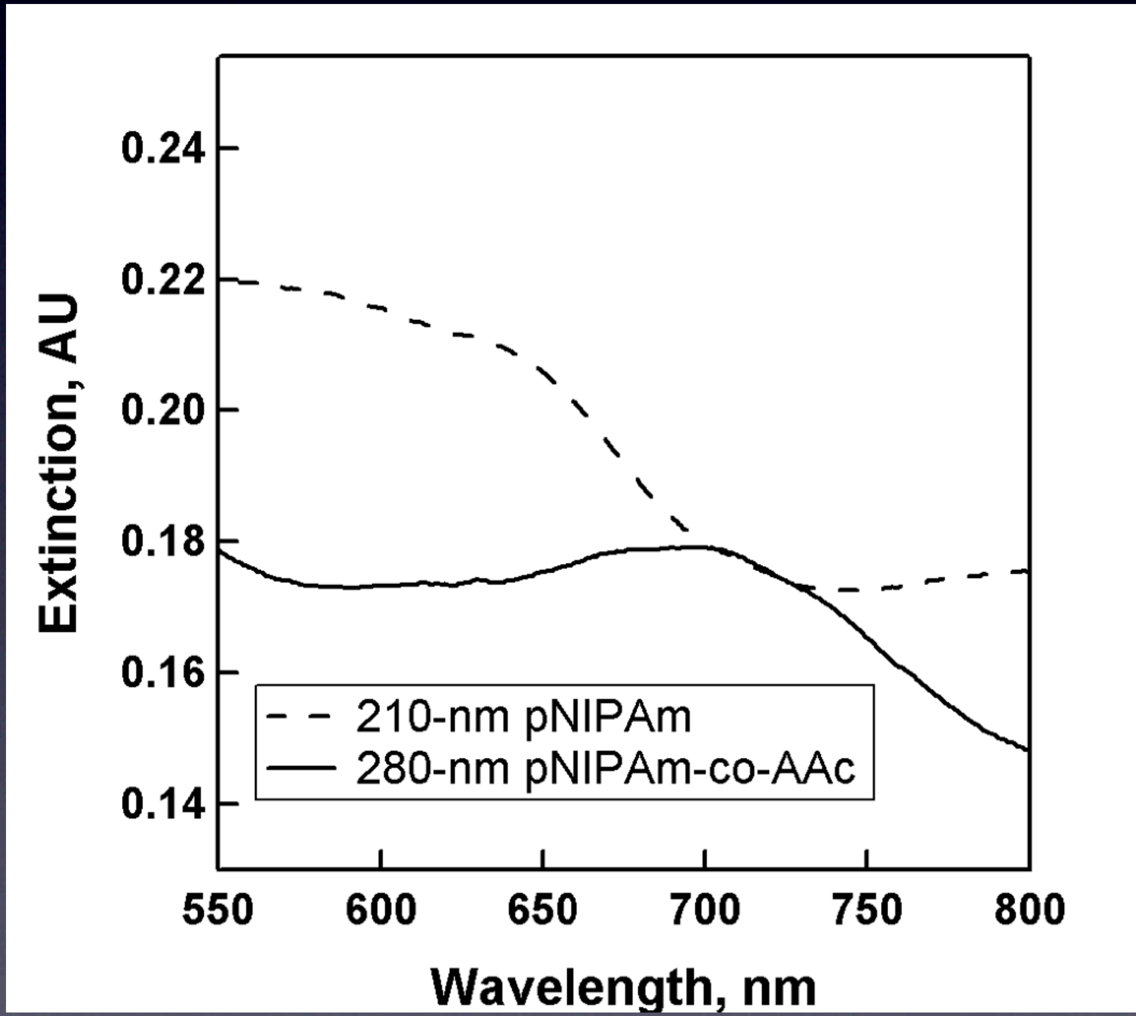
Thermoresponsivity as a route to well-defined colloidal materials.

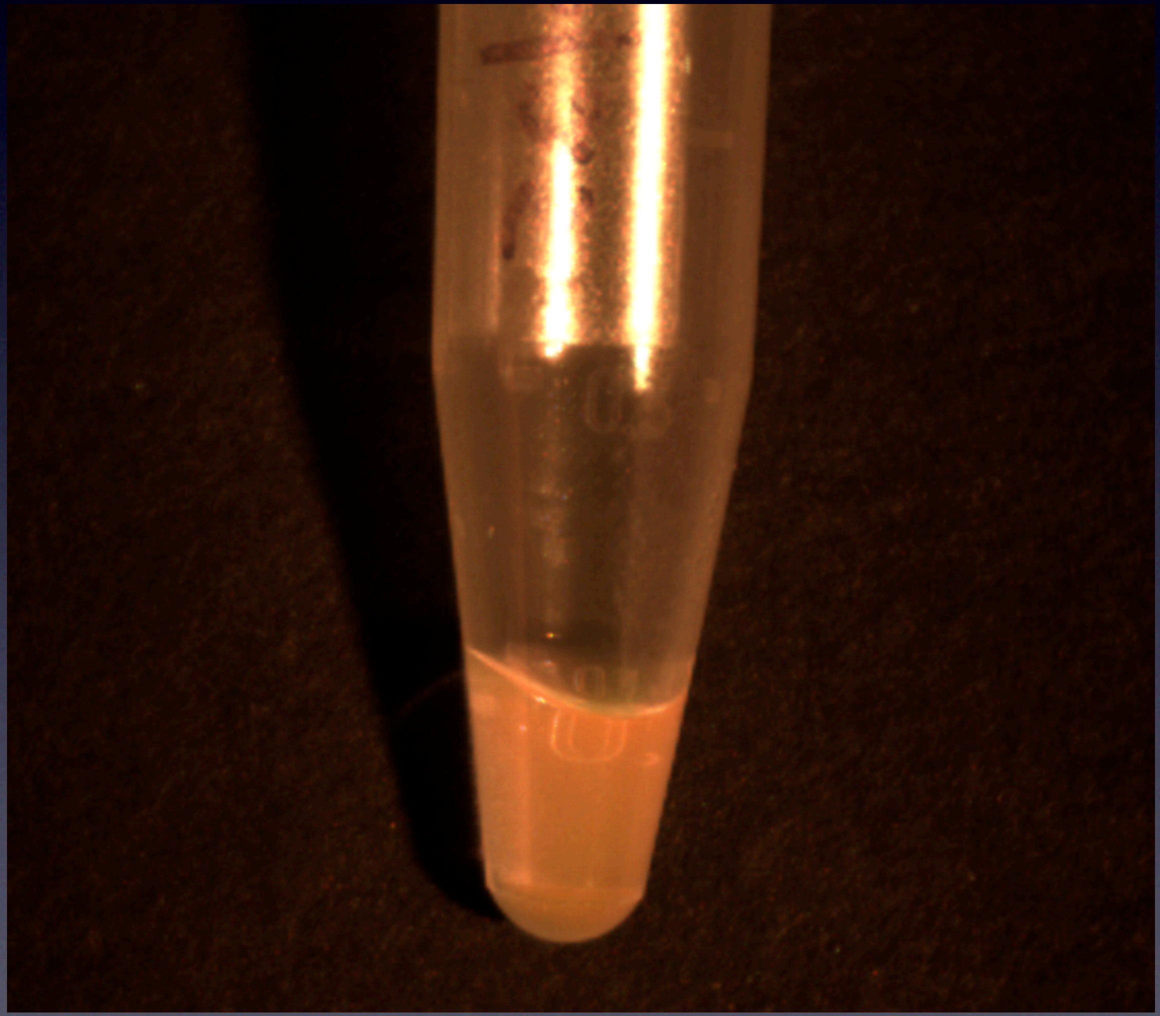




Microgel Assemblies

Centrifugal sedimentation (16,000 x g) of microgels yields an amorphous glassy phase.

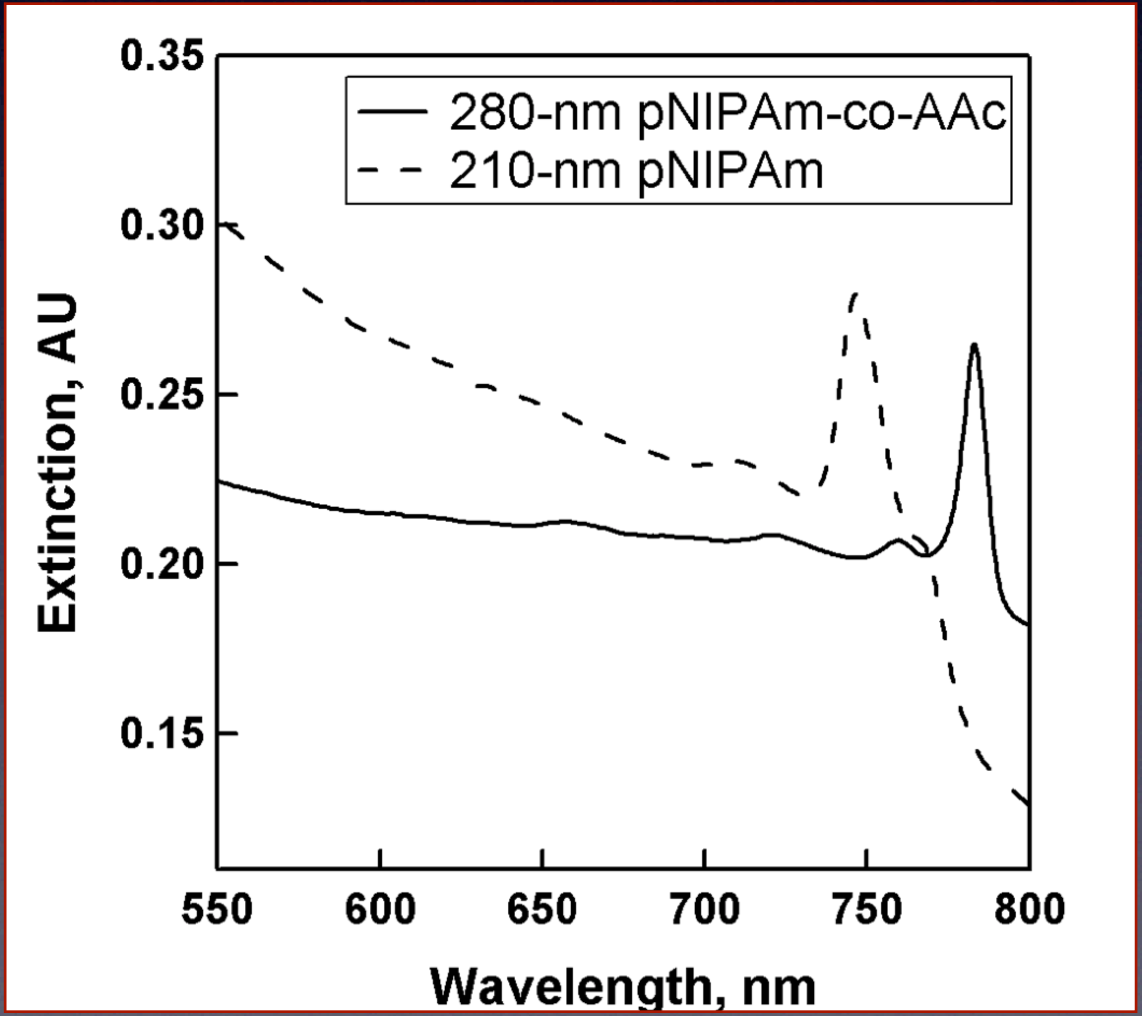


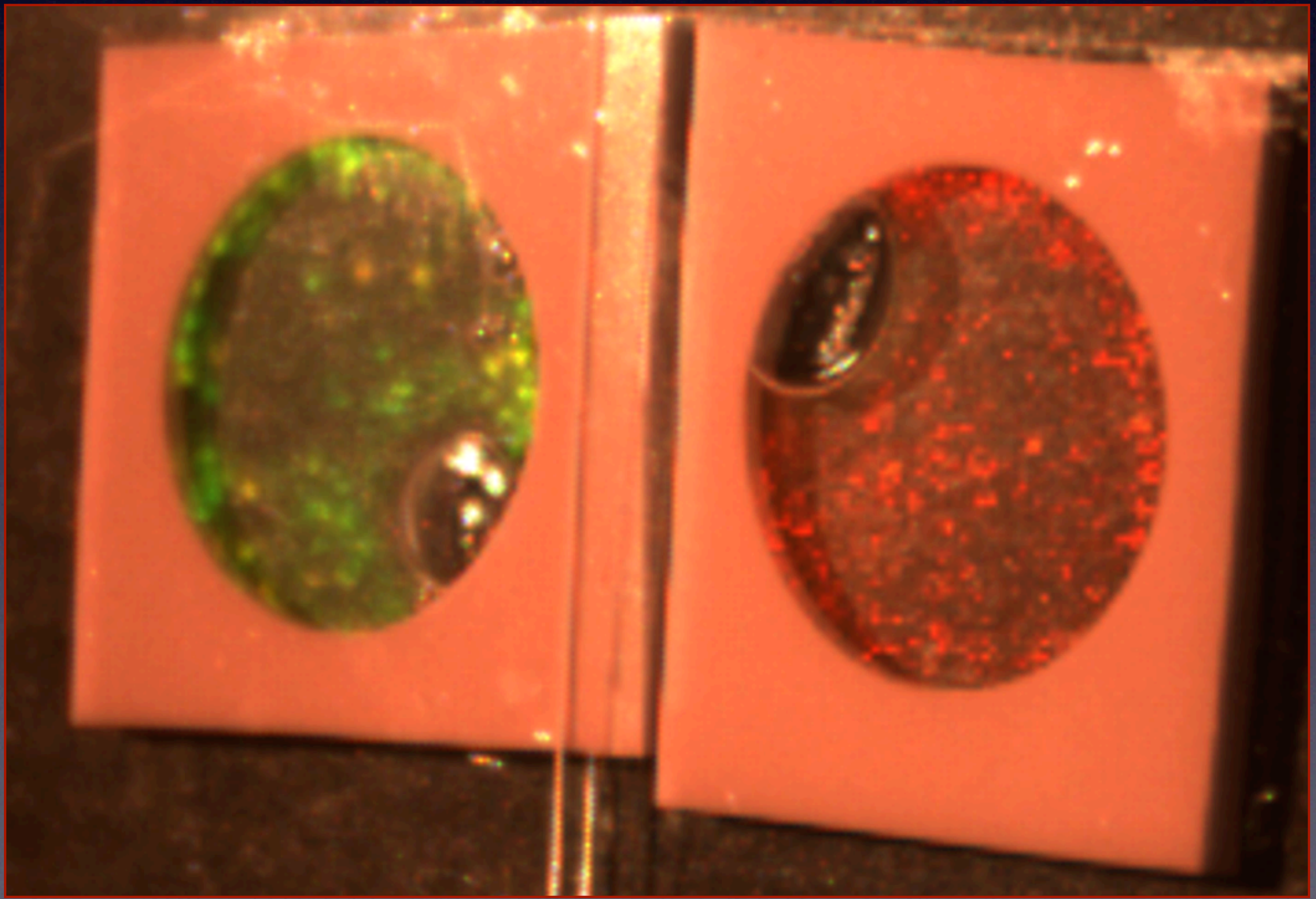


Thermal Annealing

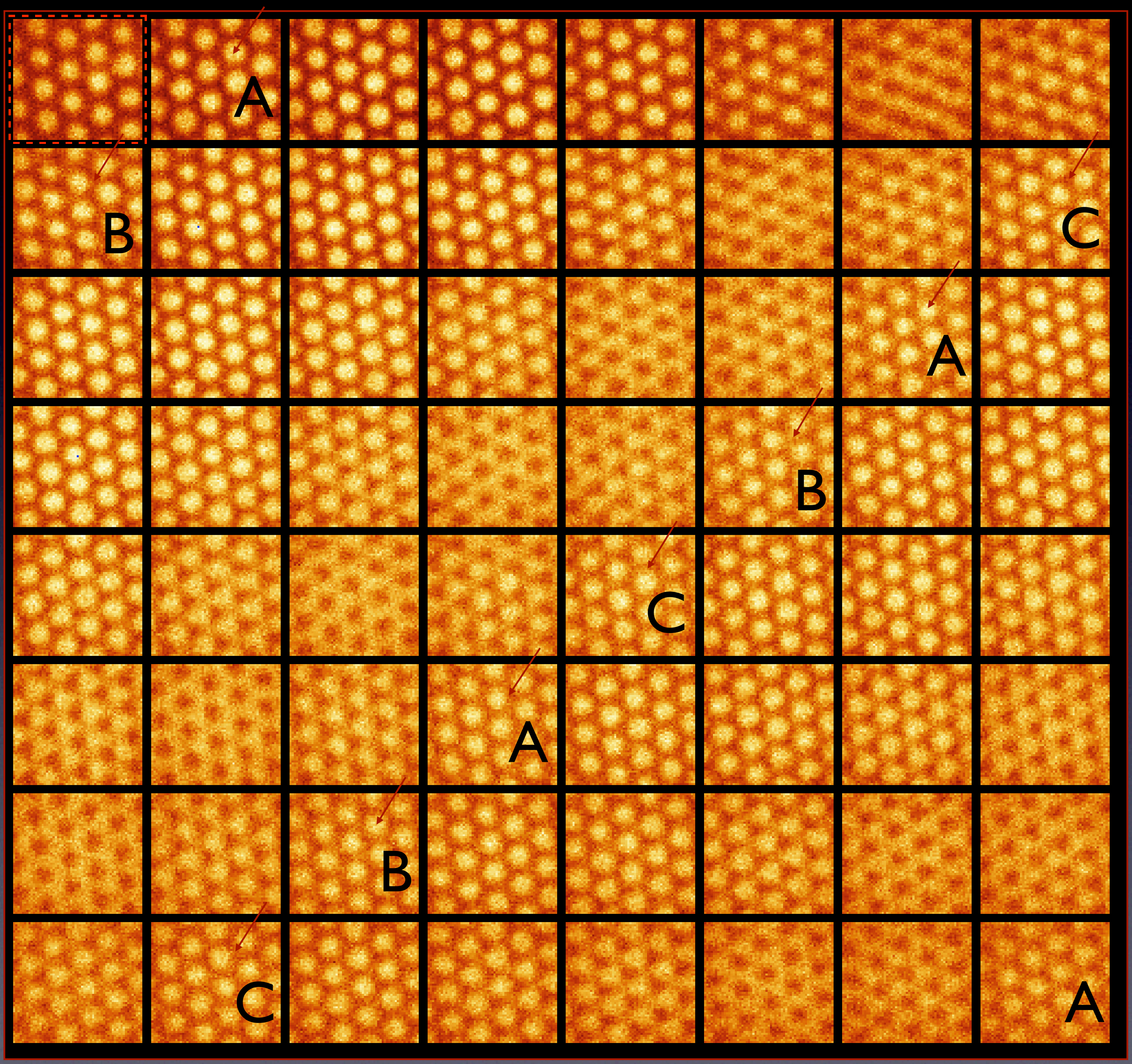
Thermal cycling across the *particle volume phase transition temperature* yields the thermodynamically preferred crystal.

Temperature tunes the volume fraction.





3-D Structure



Confocal Microscopy ~810-nm diam. particles

Regular A-B-C-A packing - FCC crystal structure

Thermodynamics more controlled than in sedimented hard sphere crystals; High volume fractions accessible

Colloidal Gel Phases

How does *particle softness* manifest itself...

- ...in the phase diagram?
- ...in the optical properties?
- ...in defect healing?
- ...in the assembly's responsivity?

What are the appropriate tools to study phenomena in soft assemblies?

How do we quantitatively measure these phenomena?

Problem #1: Determine the Volume Fraction

It is non-trivial to calculate the volume fraction of a dispersion of spheres if there is *uncertainty* in the particle:

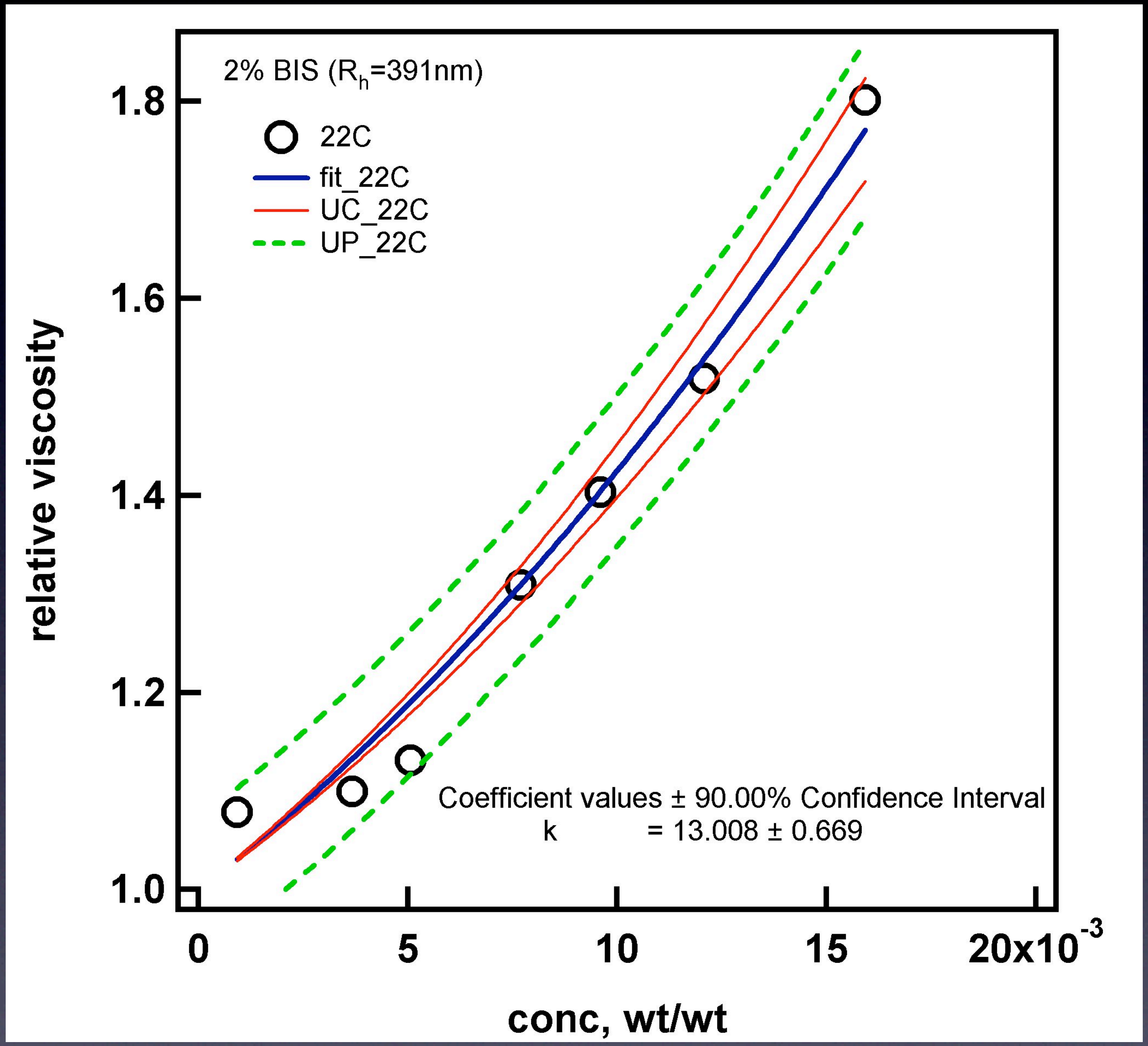
size

density

structure/topology

number density

Solution: Relative Viscosities



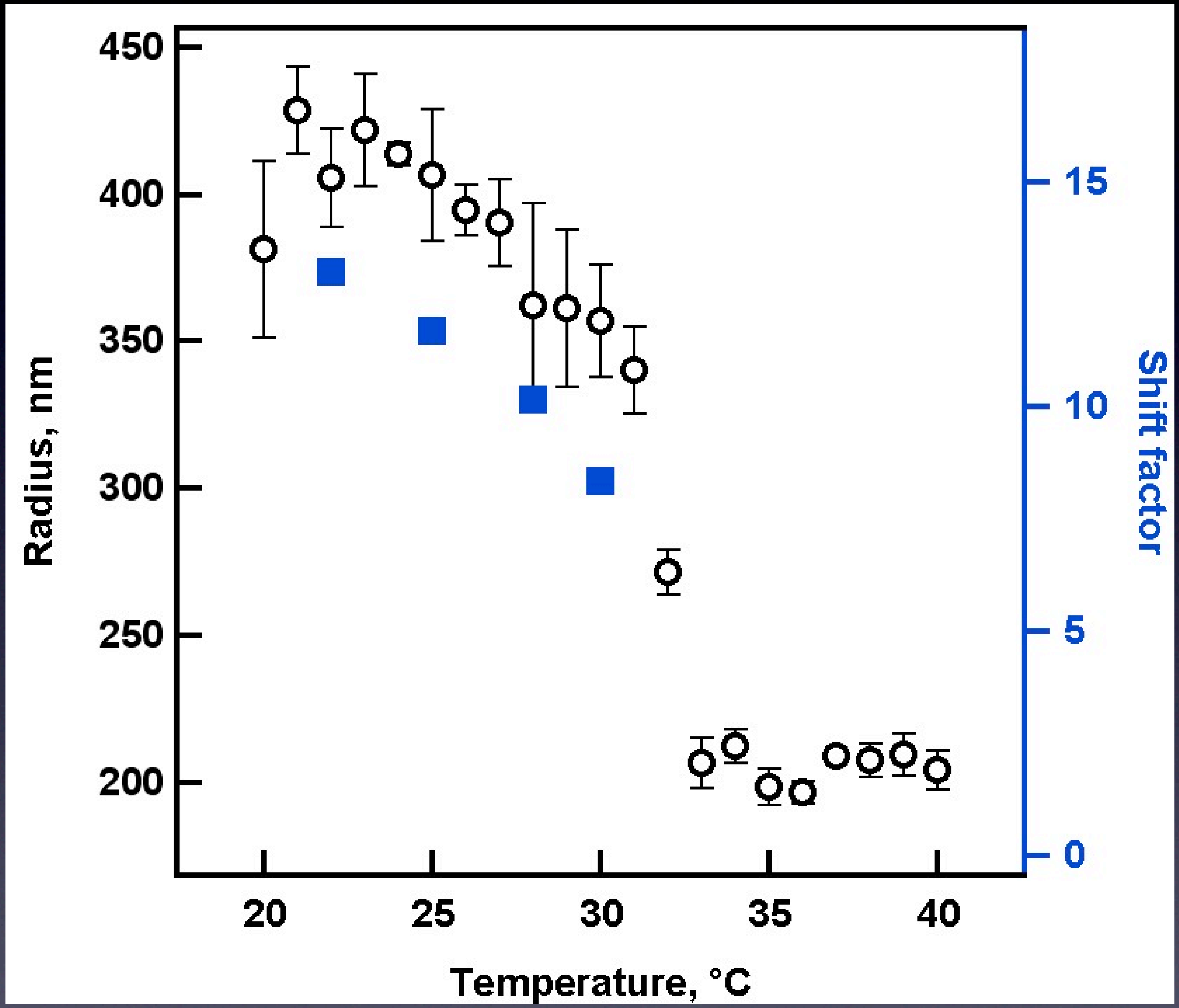
At low concentrations, soft spheres behave "hard". The Batchelor equation relates the viscosity to the hard sphere volume fraction.

$$\phi_{eff} = kc$$

$$\eta = 2.5\phi_{eff} + 5.9\phi_{eff}^{\ 2} + 1$$

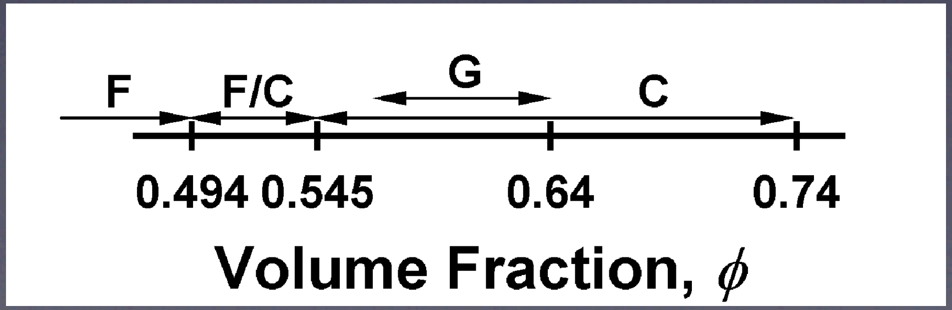
H. Senff and W. Richtering, *J. Chem. Phys.* **1999** *111*, 1705.
Batchelor, Journal of Fluid Mechanics **1976** *74*, Pt. 1, 1.

Correlation with the VPT



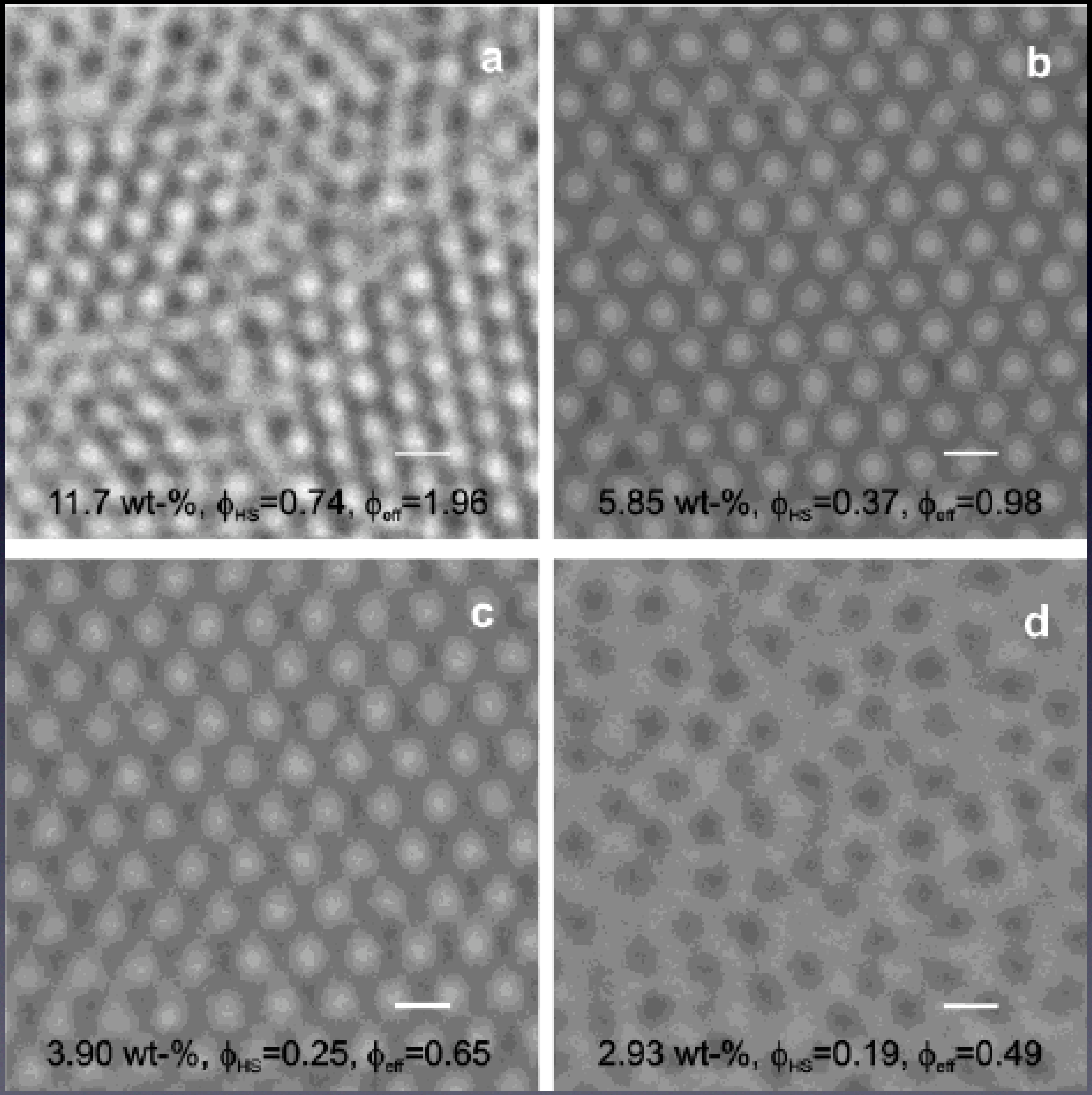
Direct relationship between volume deswelling (DLS) and shift factor (viscosity).

Temperature tunes the volume fraction.



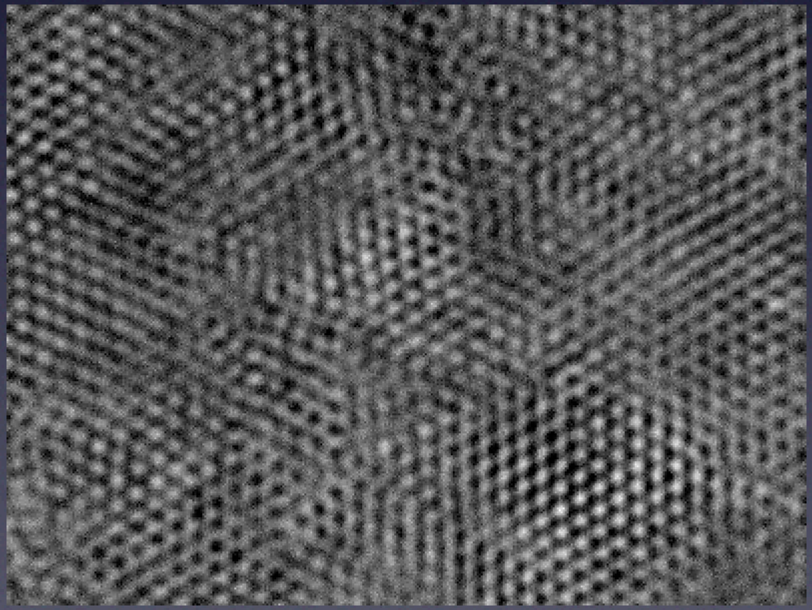
Soft Particle Overpacking

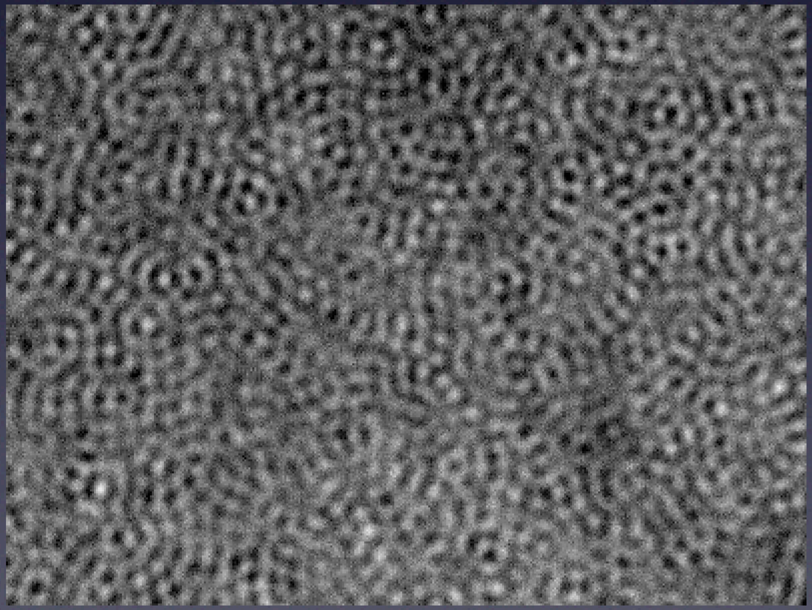
Soft particles can be packed into crystals in a deswollen, "overpacked" form via thermal annealing.

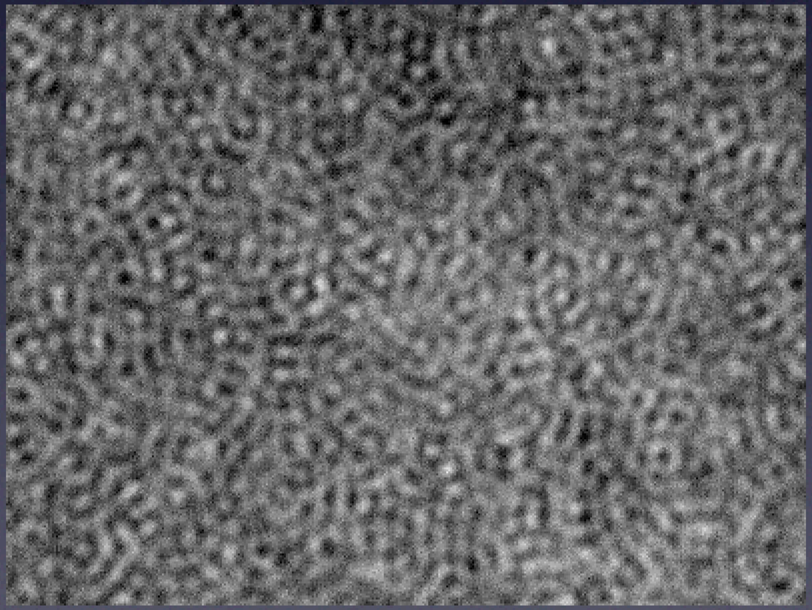


Problem #2: Objective Determination of the Phase

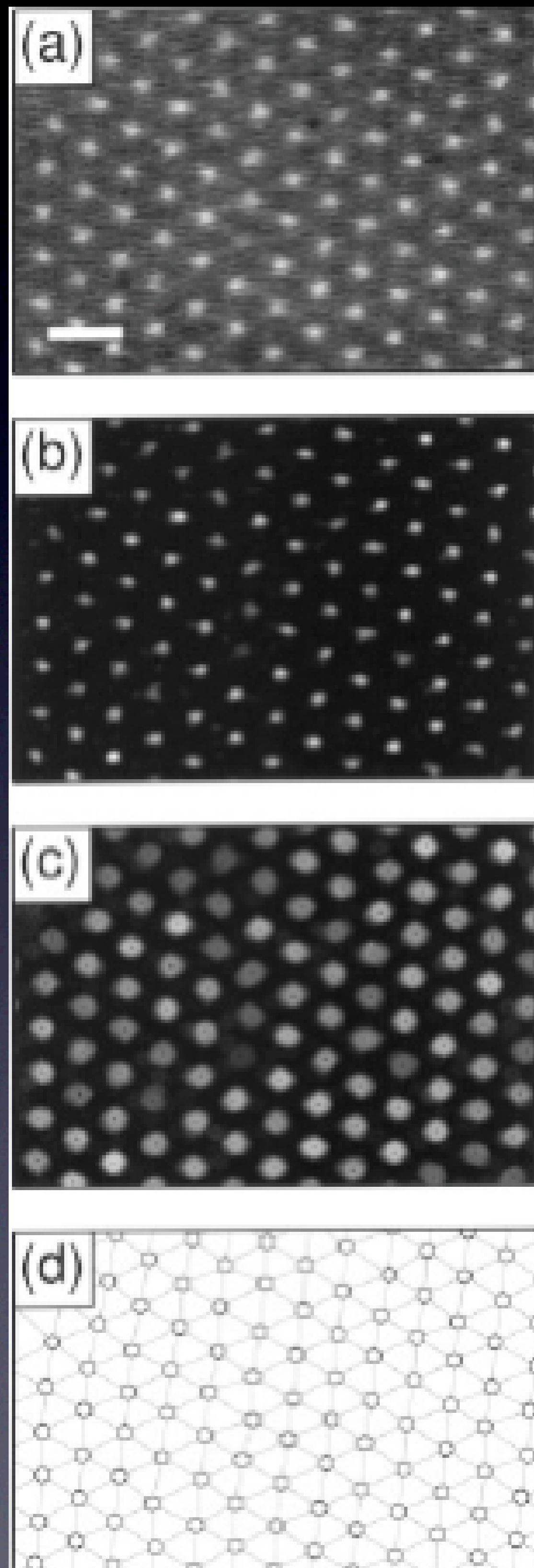
Is there a method (besides visual inspection) that will permit quantitative analysis of the assembly motif?







Solution: Image Analysis



Original microscopic image

Filtered microscopic image after reducing the noise

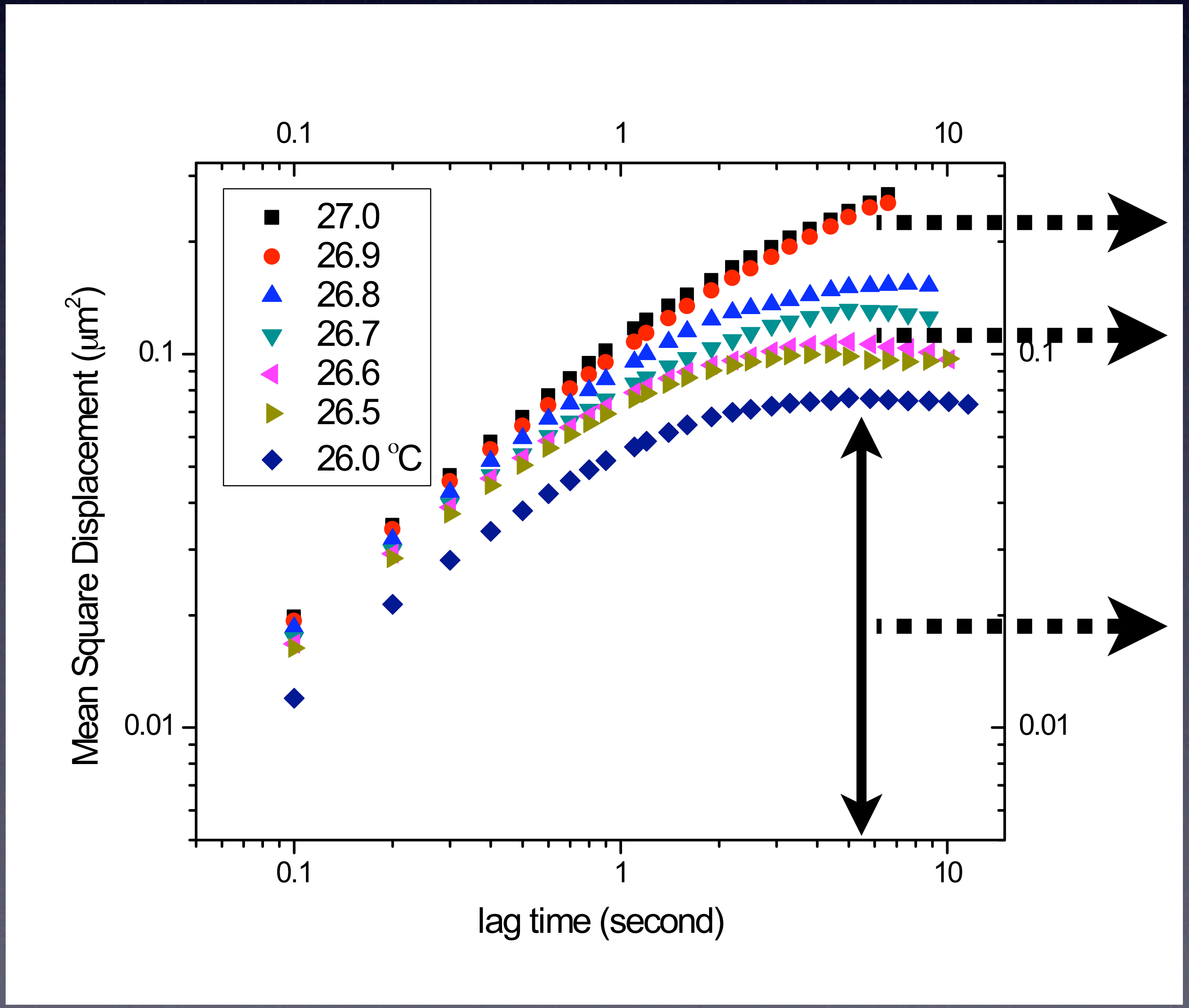
Gray-scale dilation of the microscopic image

Particle location estimation

Particle Tracking: Dynamics

By measuring all particle positions over time, one can calculate the Mean Square Displacement (MSD)

$$MSD = \langle |r_i(t) - r_i(0)|^2 \rangle \text{ or } \langle |\Delta r_i(t)|^2 \rangle$$

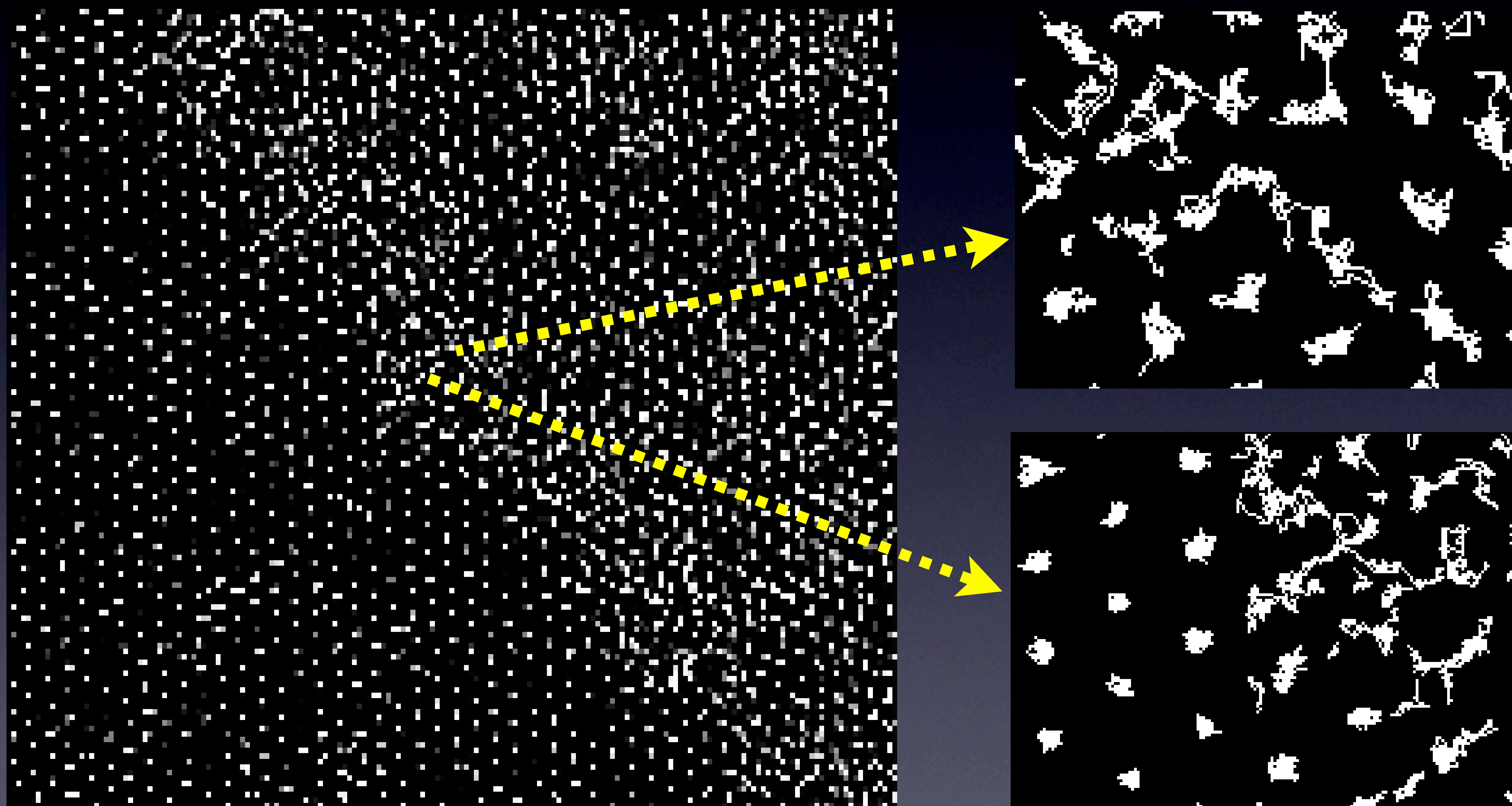


Diffusive: MSD ~ t

Cage effect: subdiffusive

$MSD_\infty \sim D_{cage}^2$

Particle Tracking: Trajectories

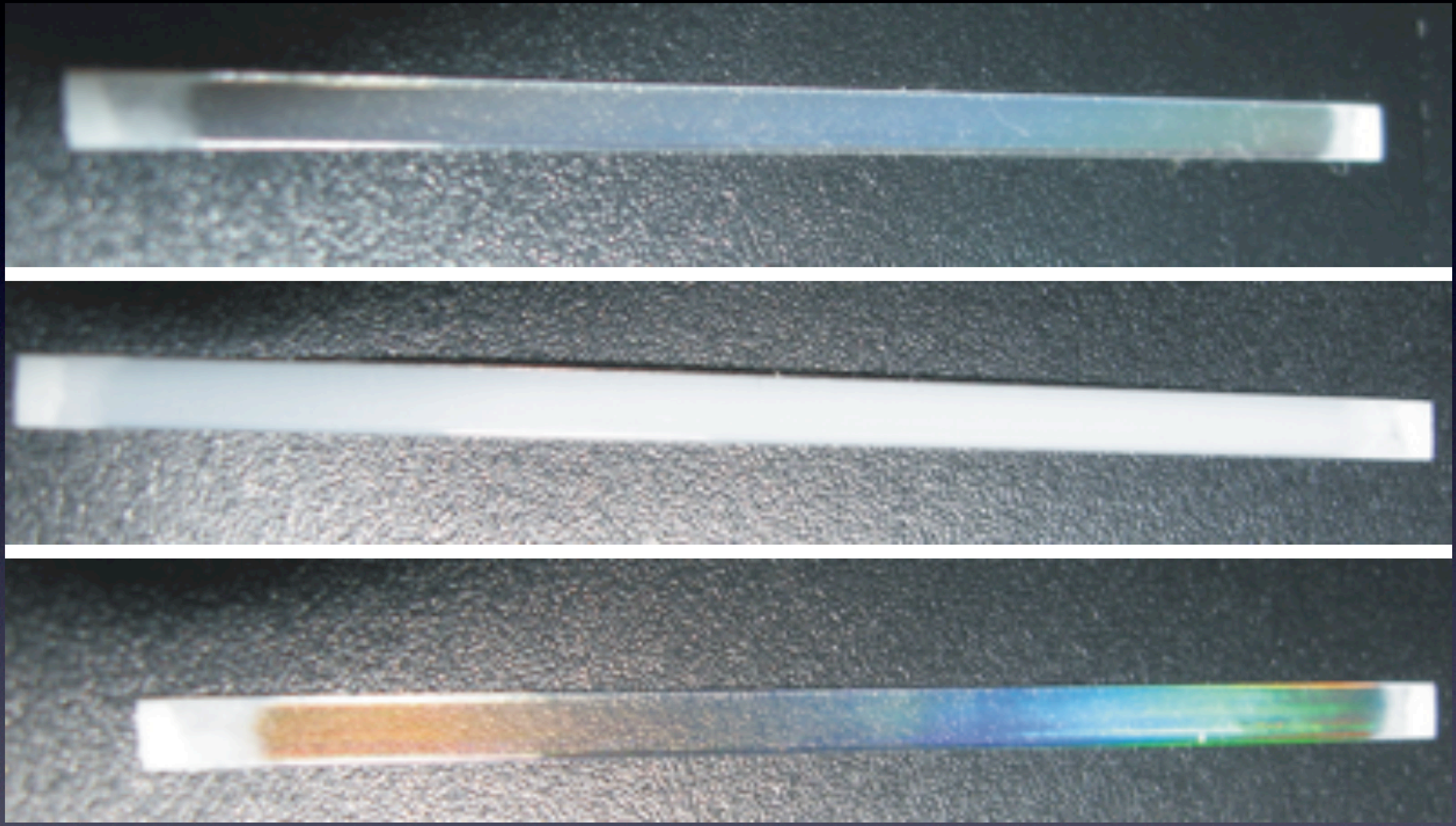


Visualizing Melting

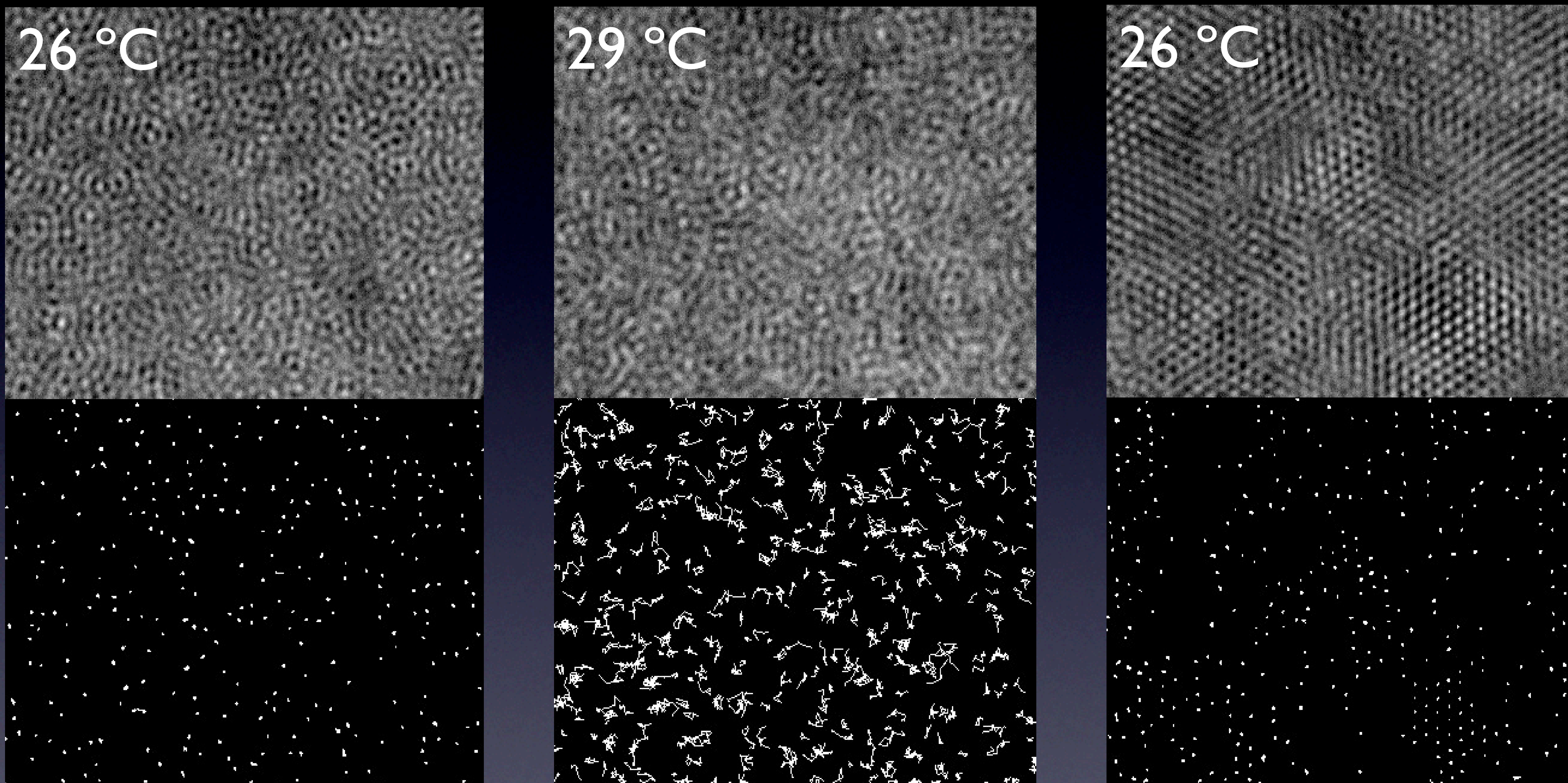
Glass

Fluid

Crystal

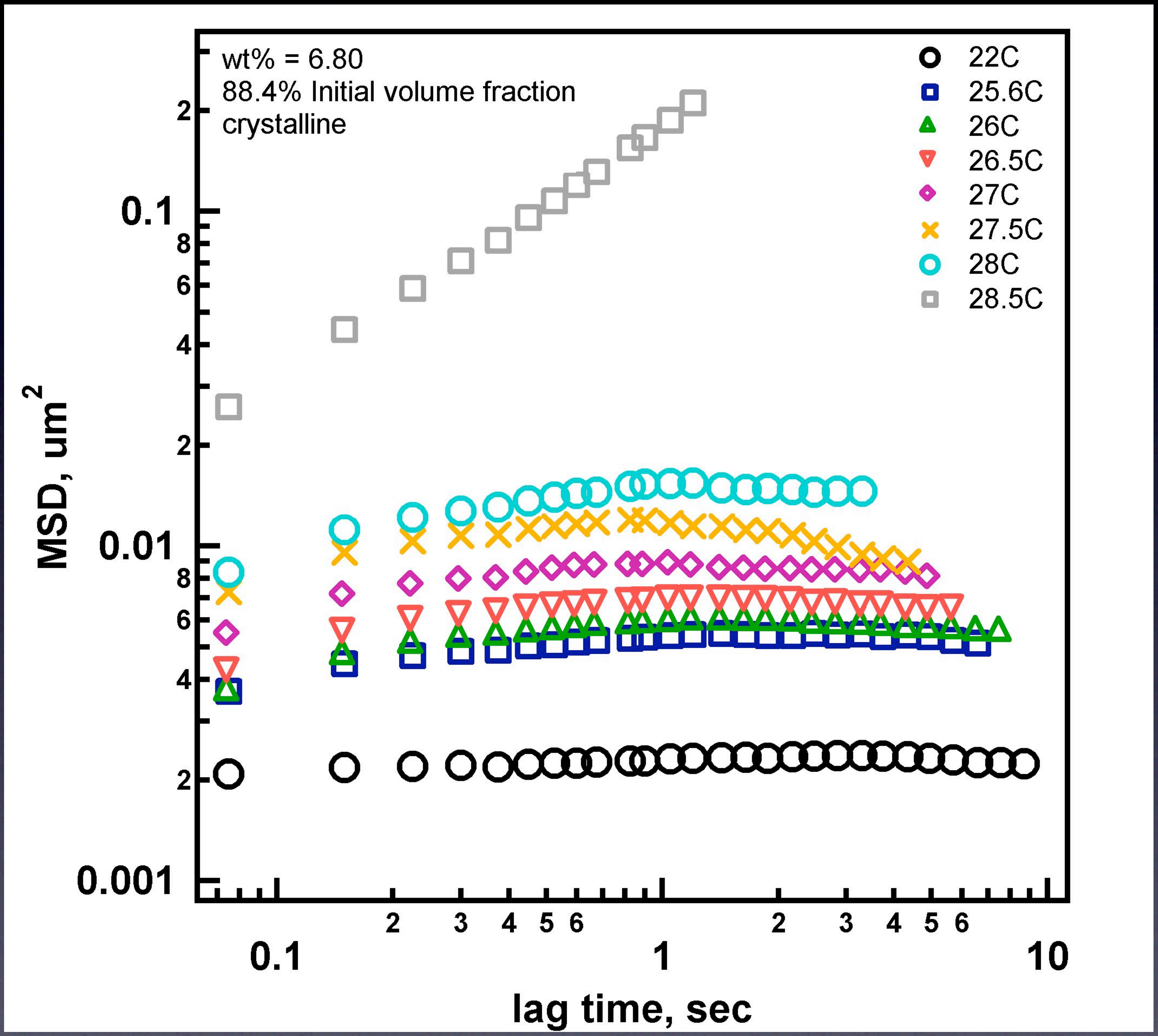


Visualizing Melting



Glass   Fluid   Crystal

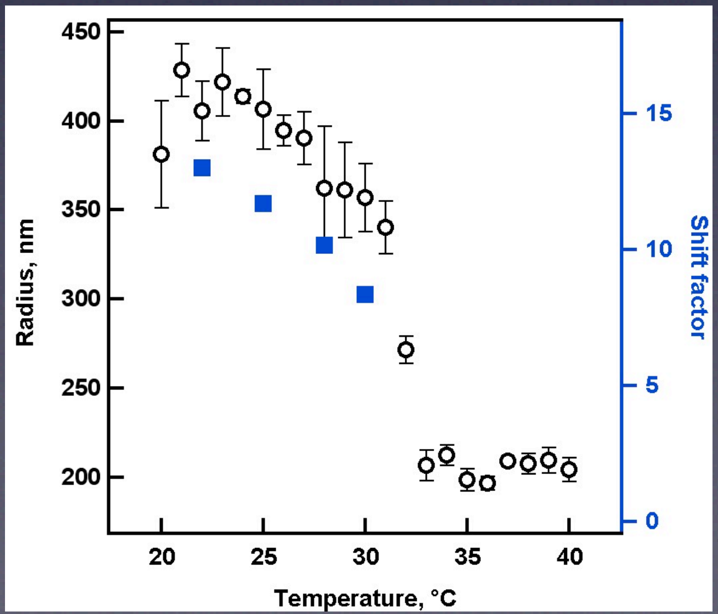
Crystal Melting



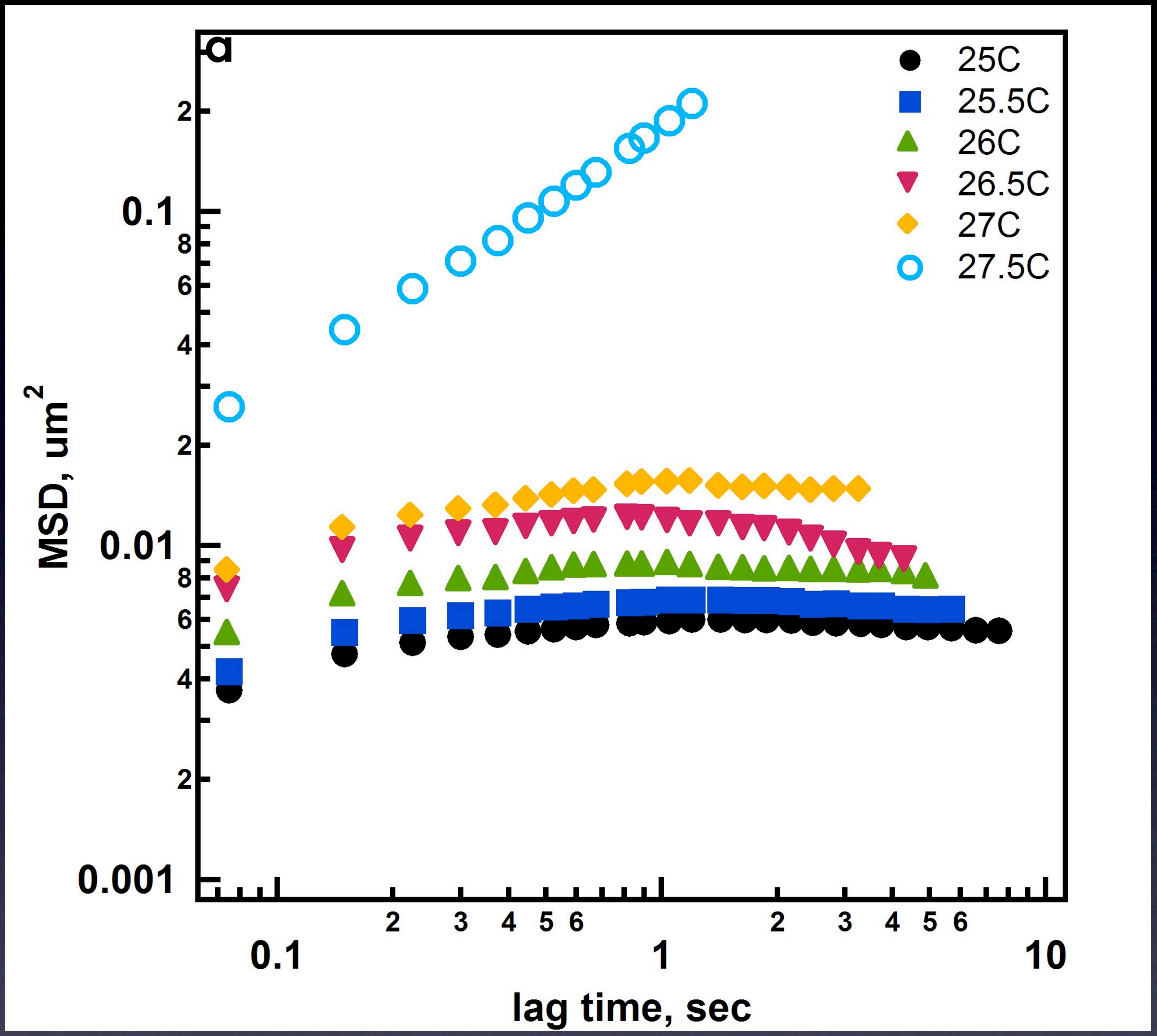
~800-nm diameter pNIPAm spheres

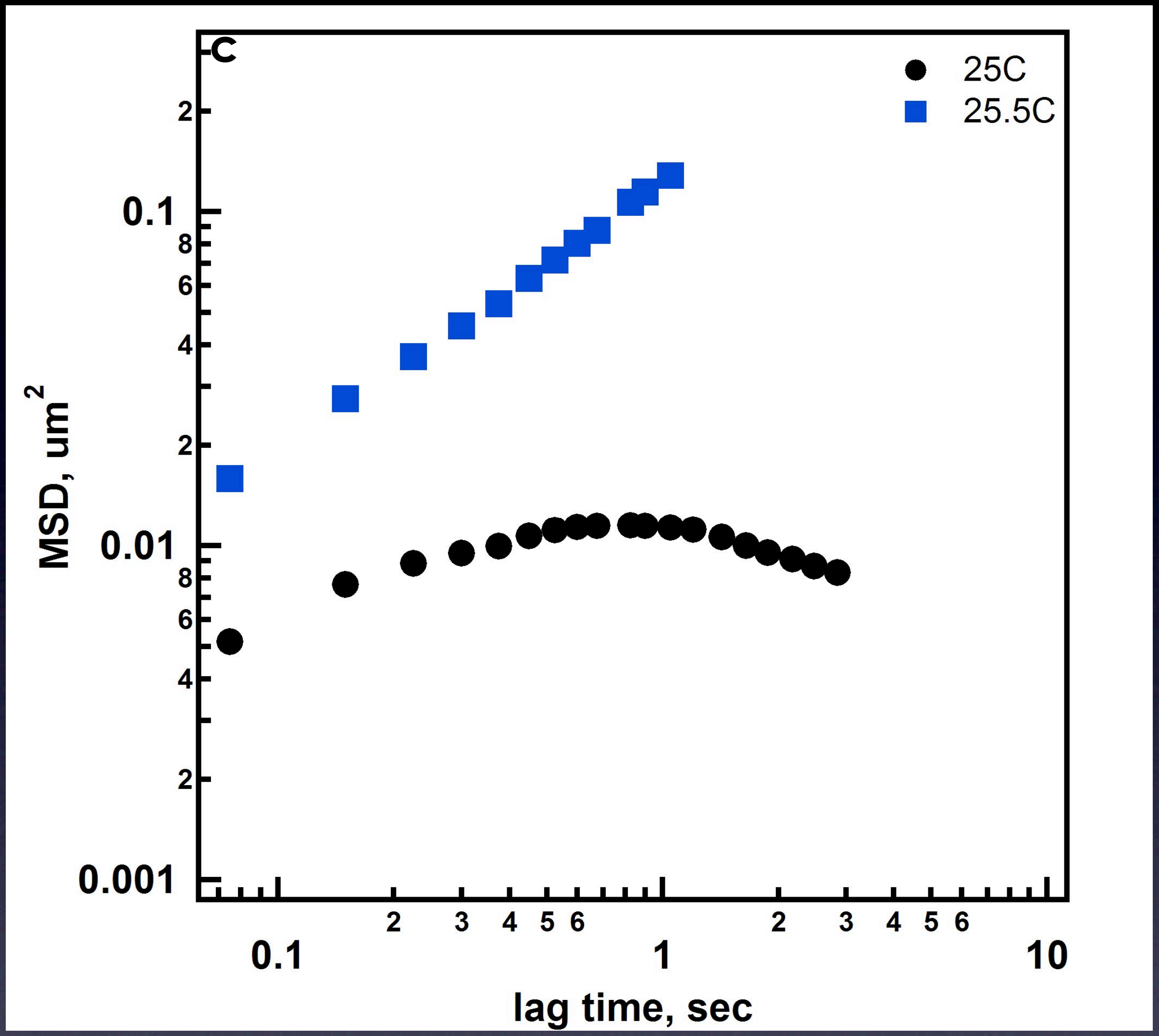
ϕ = 88.4%

2% cross-linked with *N,N'*-methylenebisacrylamide



Effect of Initial Packing



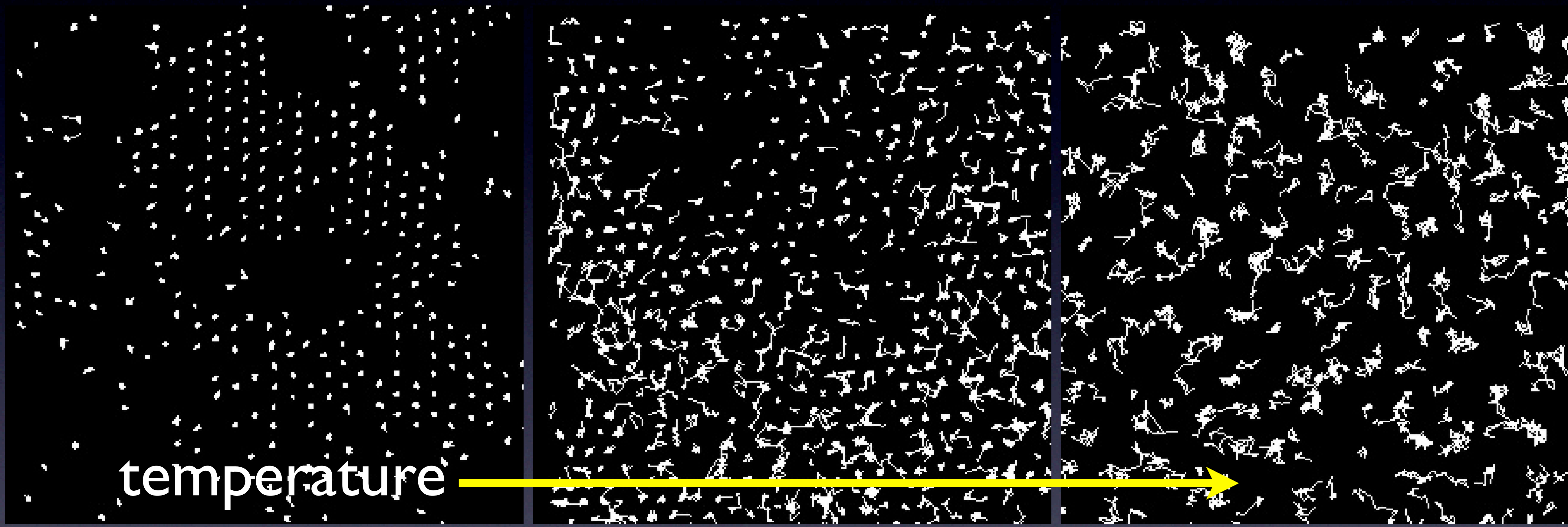


MSD of samples packed at Room Temperature.

ϕ_{eff} = 89.8% (6.80wt%) (left) and 71.7% (5.44wt%) (right).

Melting vs. $\phi_{\text{eff, initial}}$

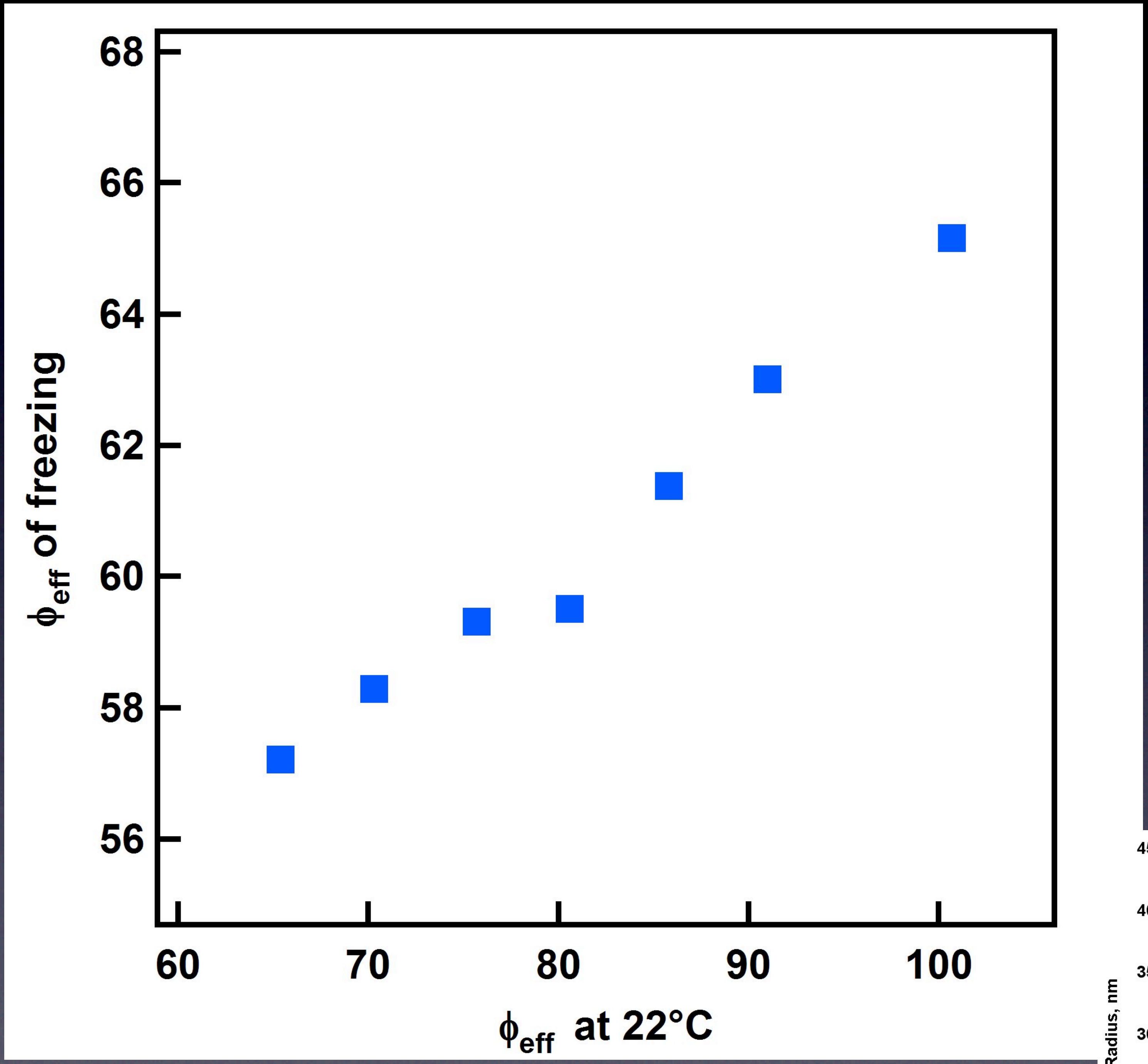
Three assemblies with a thermally regulated effective volume fraction of ~64-66%.

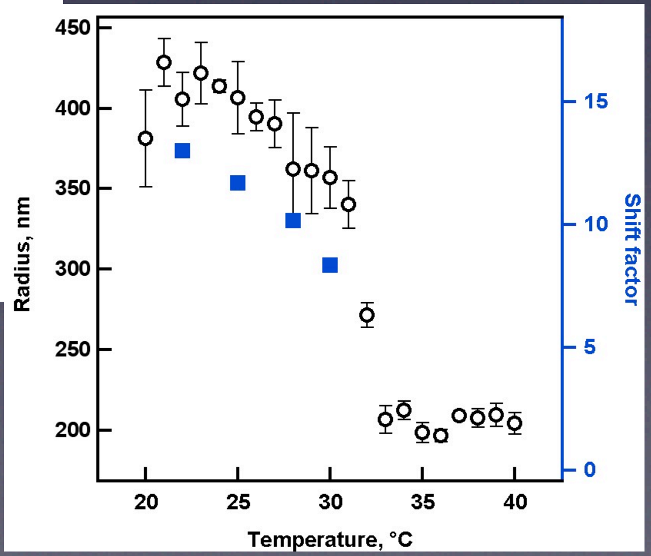


5.71 wt%　　6.34 wt%　　6.80 wt%

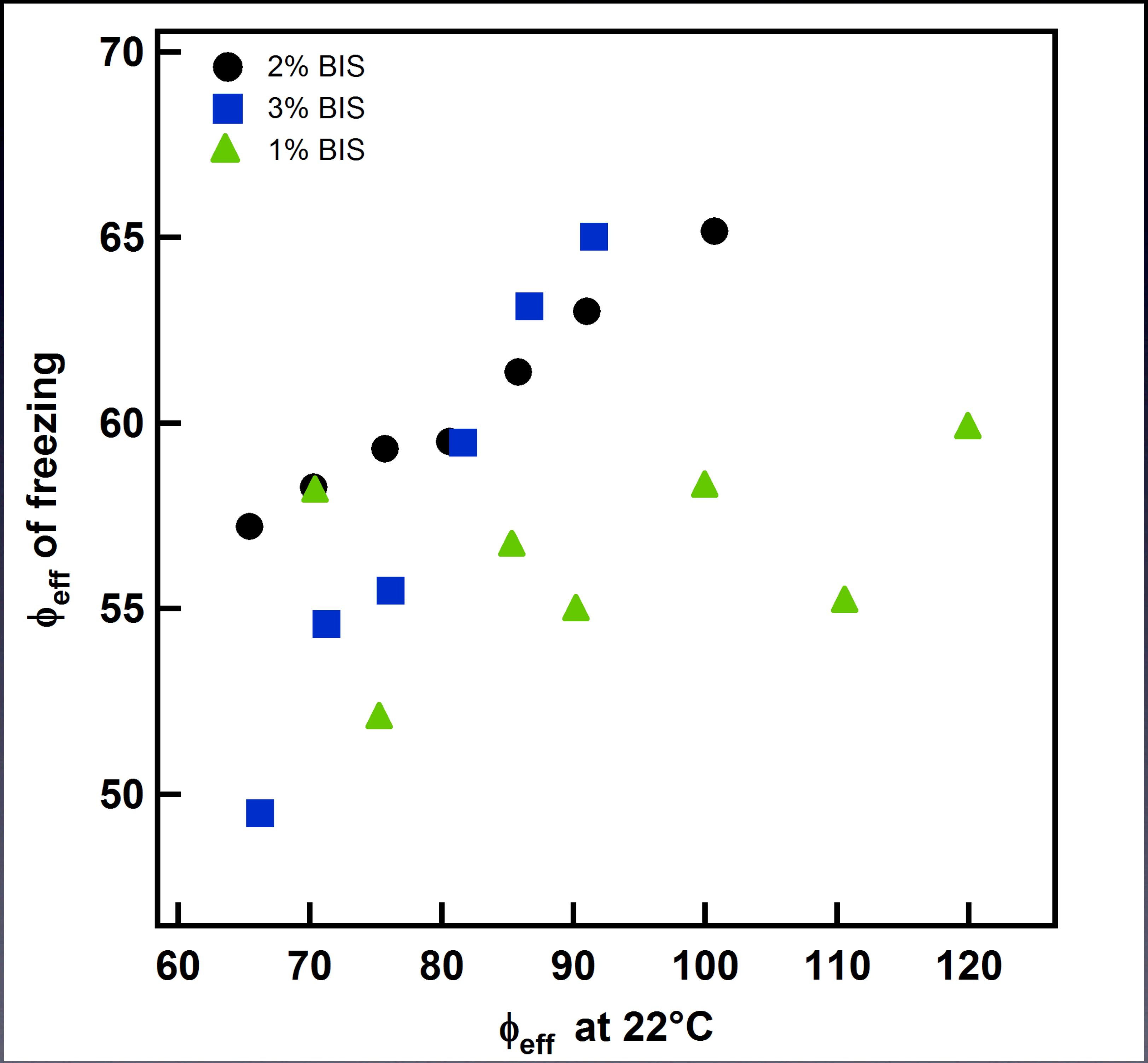
Denser asemblies melt easier?

Melting vs. $\phi_{eff,\ initial}$





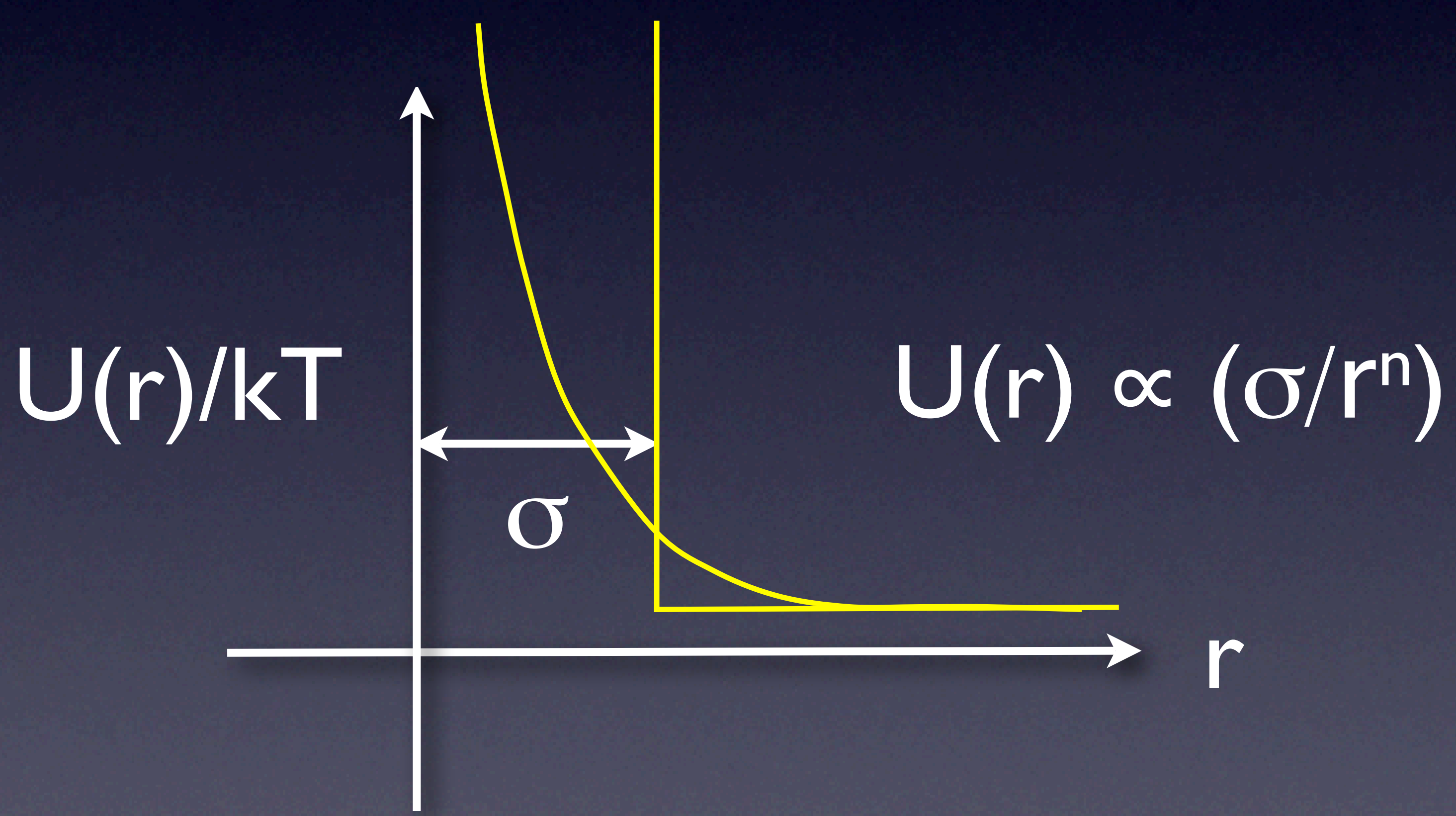
Dependence on Softness

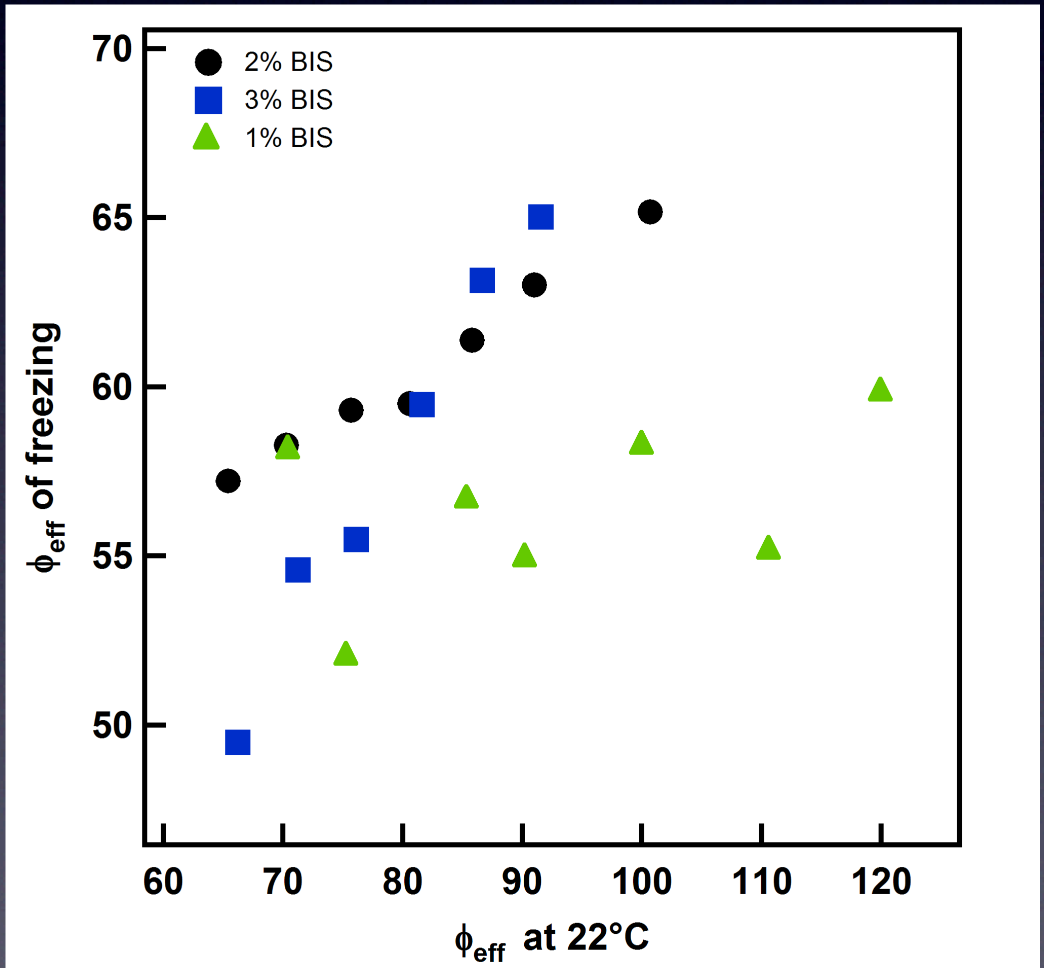


Softer particles show less packing dependence.

Swelling and Softness

$$\frac{\pi}{k_B T} = \frac{\pi_{el} + \pi_M}{k_B T} = \frac{n_0}{N_x}\left[\frac{1}{2}\left(\frac{n}{n_0}\right) - \left(\frac{n}{n_0}\right)^{\frac{1}{3}}\right] - \frac{1}{v}\left[\ln(1 - nv) + nv + \chi n^2 v^2\right]$$





Summary: Microgel Packing

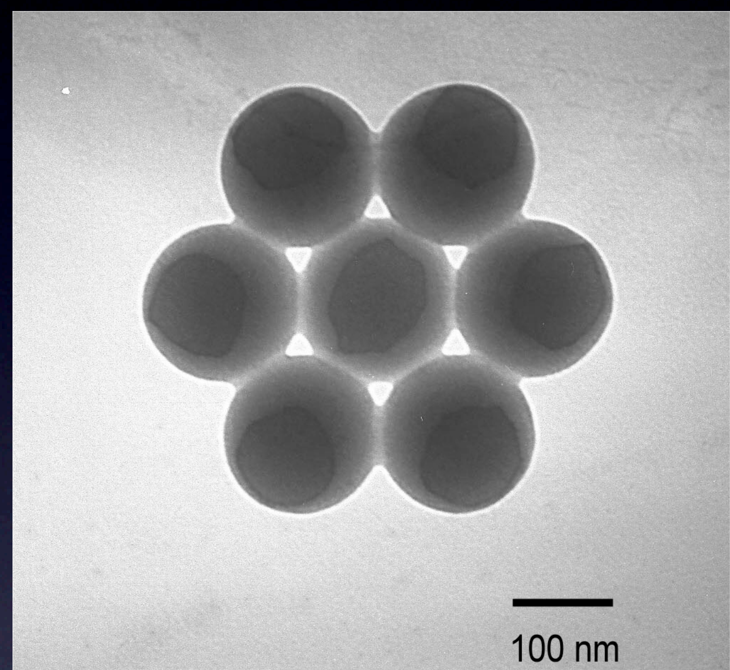
- Microgels represent a good model system for soft sphere packing.
- Particle tracking methods allow for objective determination of melting points/phase behavior.
- *The effective melting point provides insight into the local curvature/slope of the pair potential.*

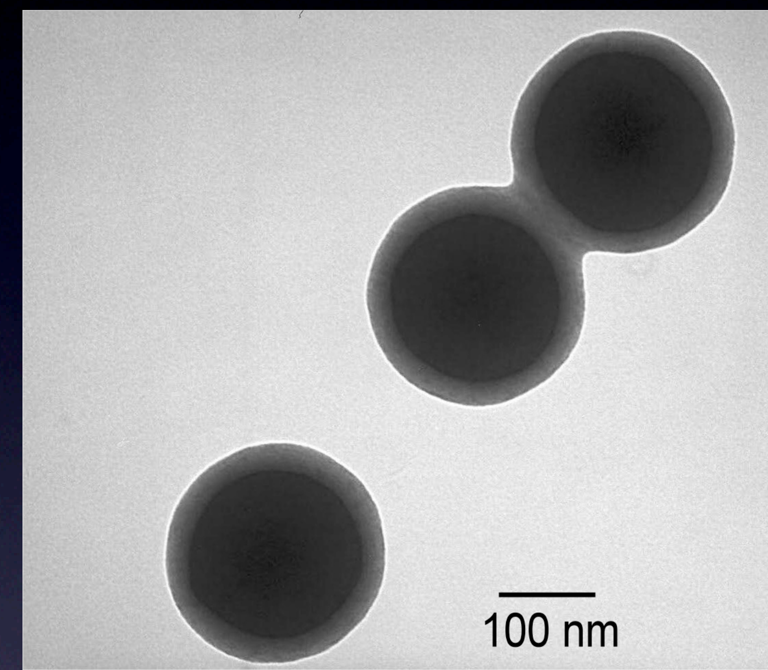
Soft Interactions: Utility

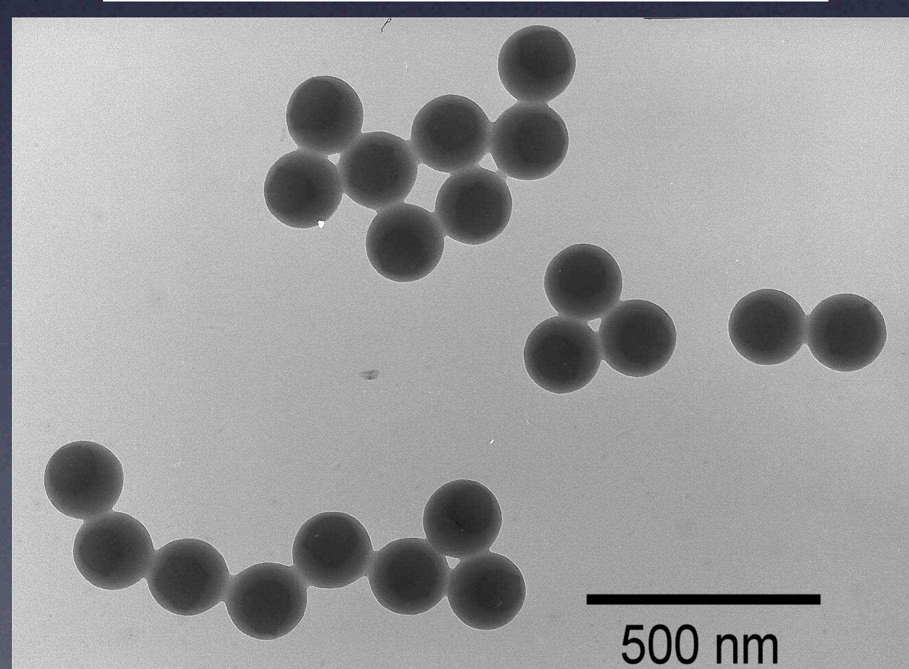
Paint-On Photonics

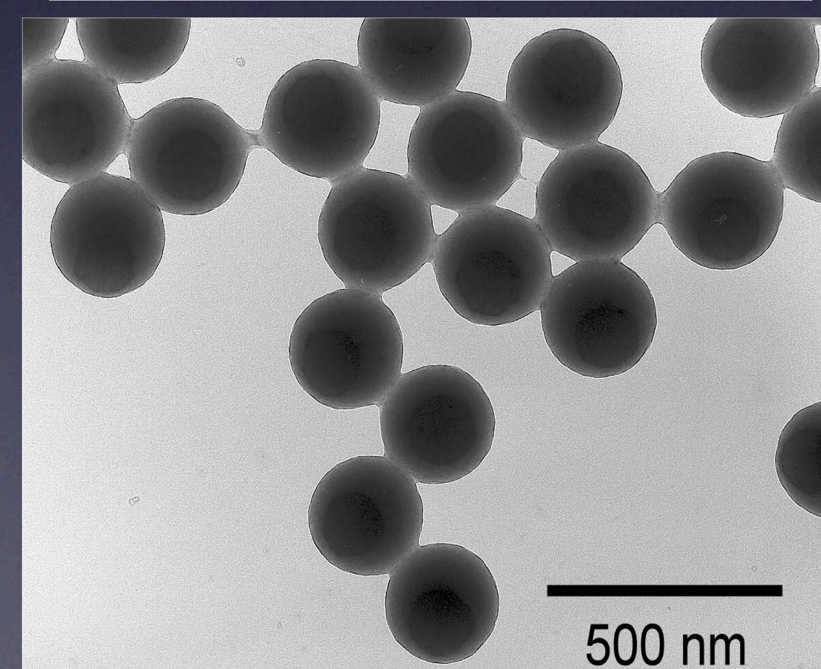
Core/Shell Latex

poly(styrene) core + pNIPAm shell



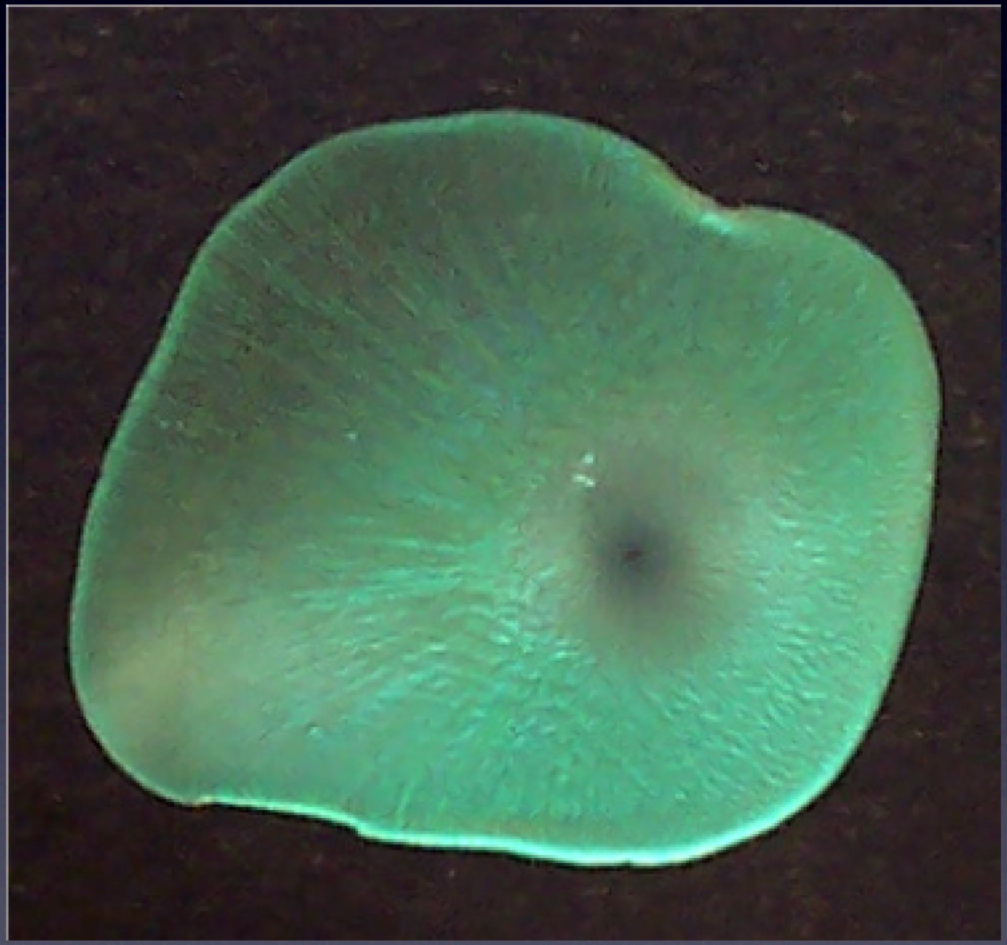


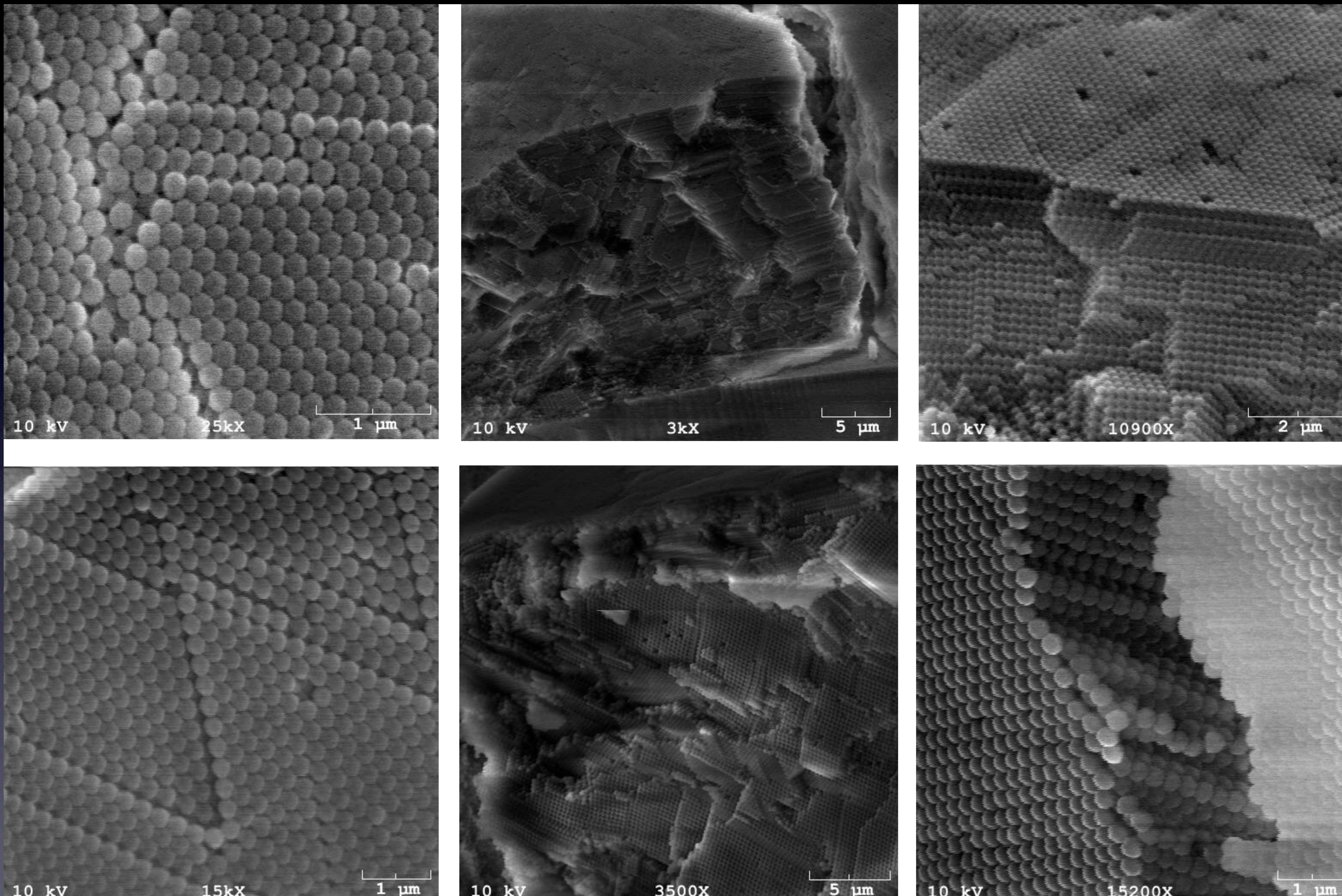




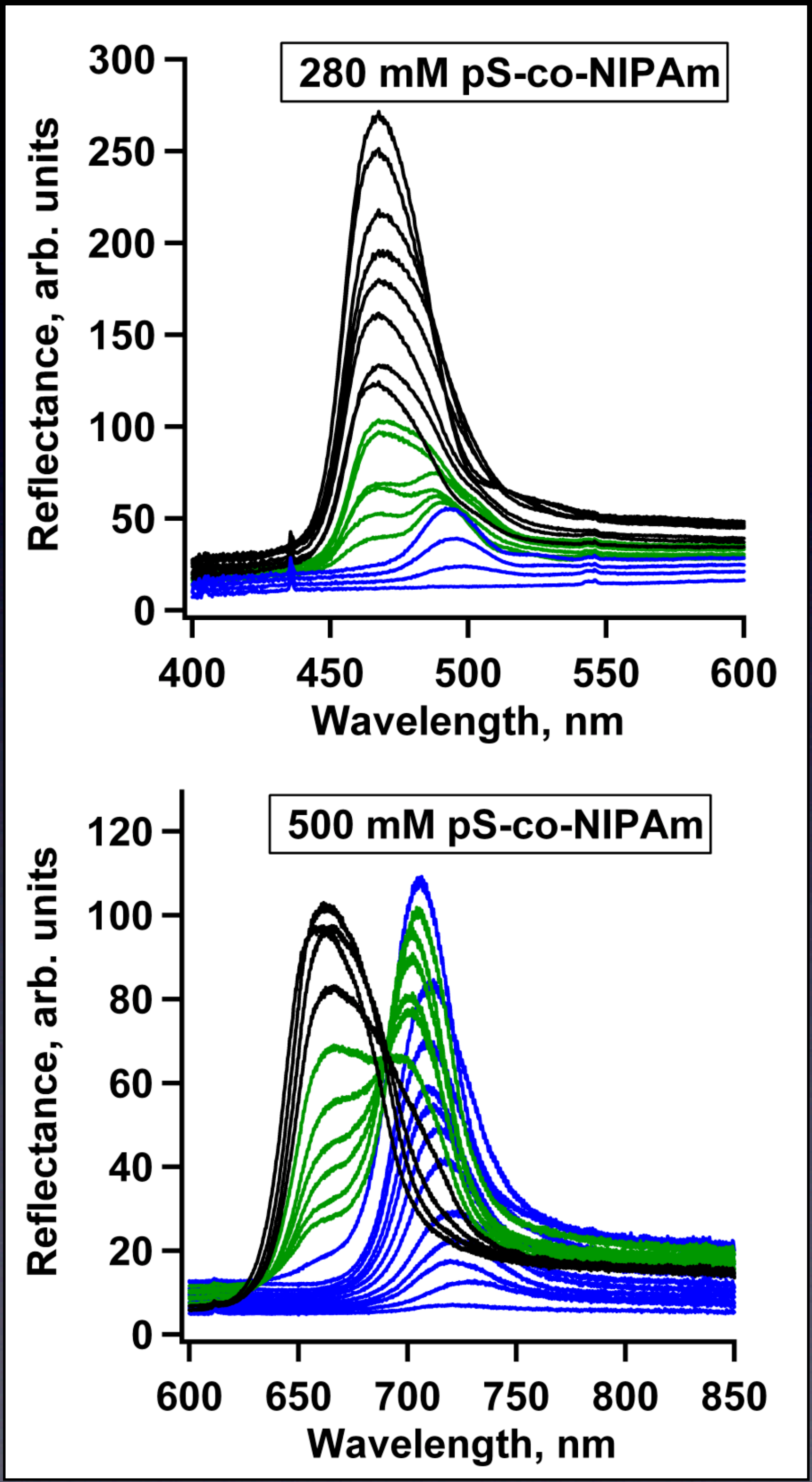
Photonic Inks

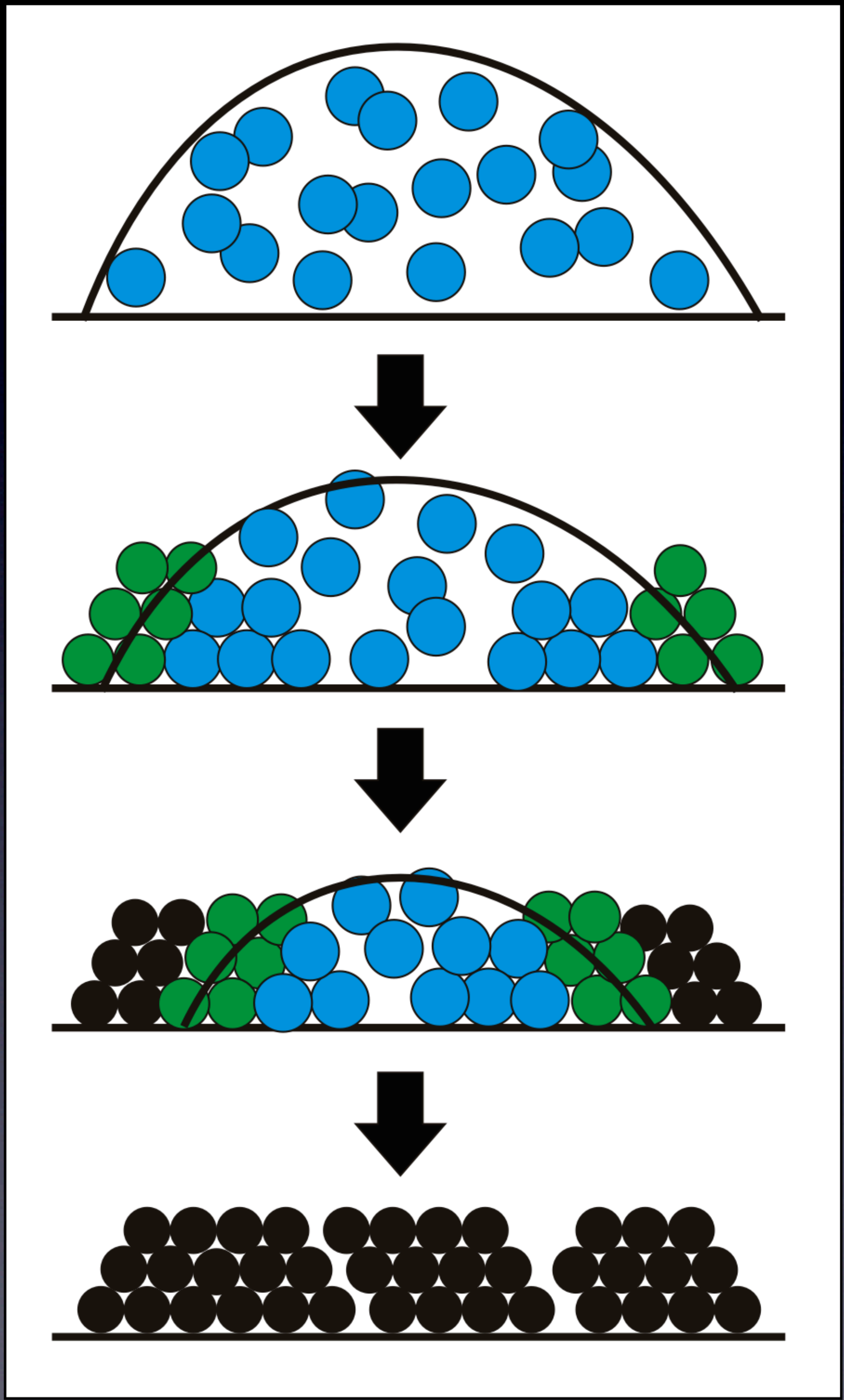
Hard/soft core/shell latexes spontaneously assemble upon drying.




10 kV
25kX
1 µm
10 kV
3kX
5 µm
10 kV
10900X
2 µm
10 kV
15kX
1 µm
10 kV
3500X
5 µm
10 kV
15200X
1 µm

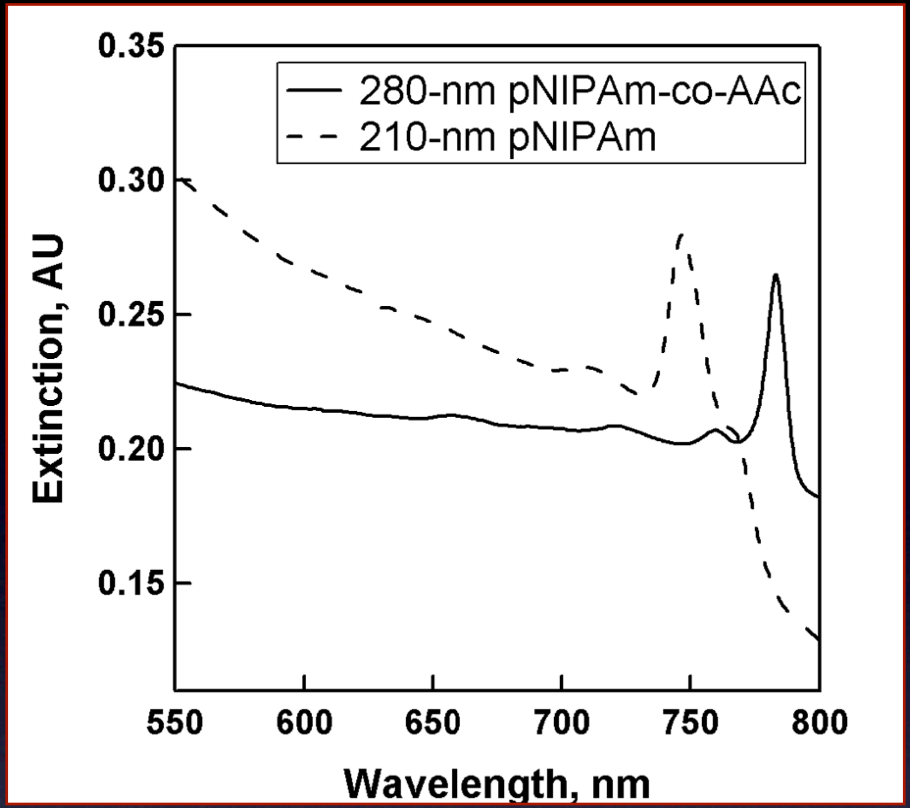
Assembly Process

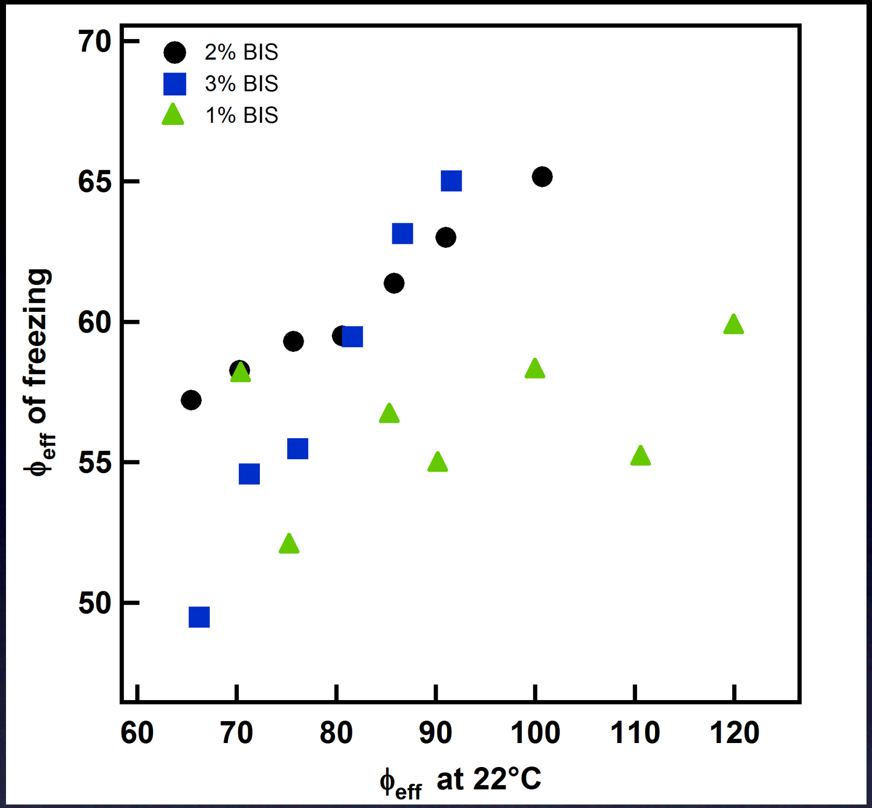


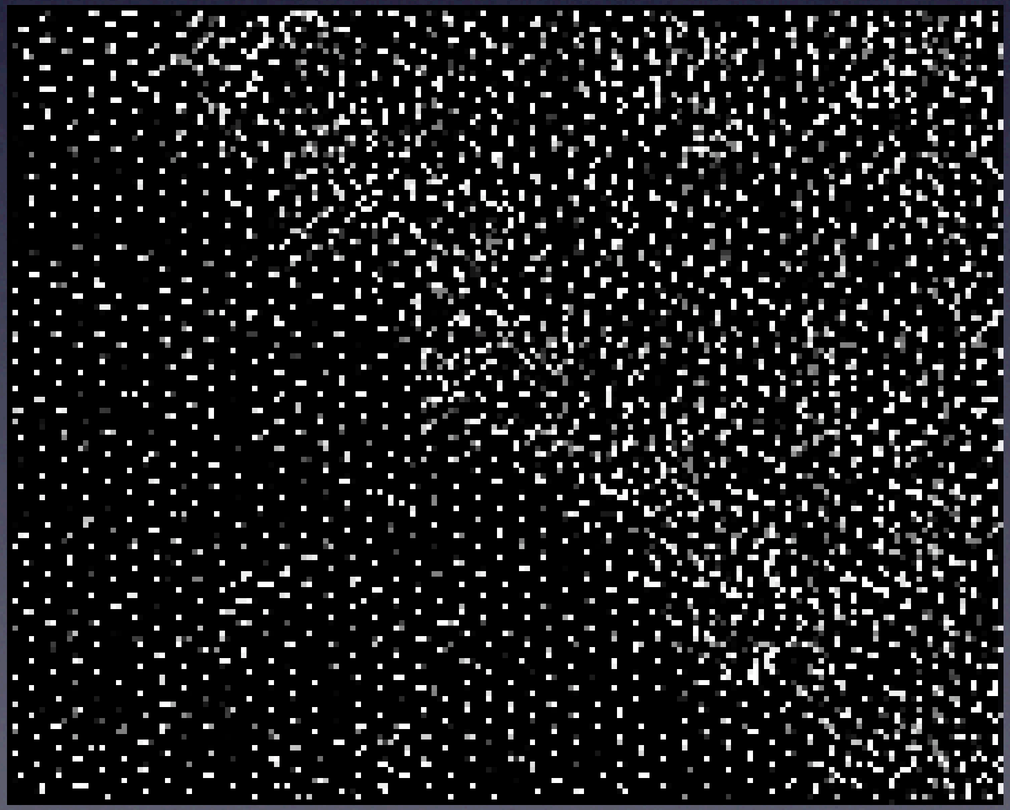


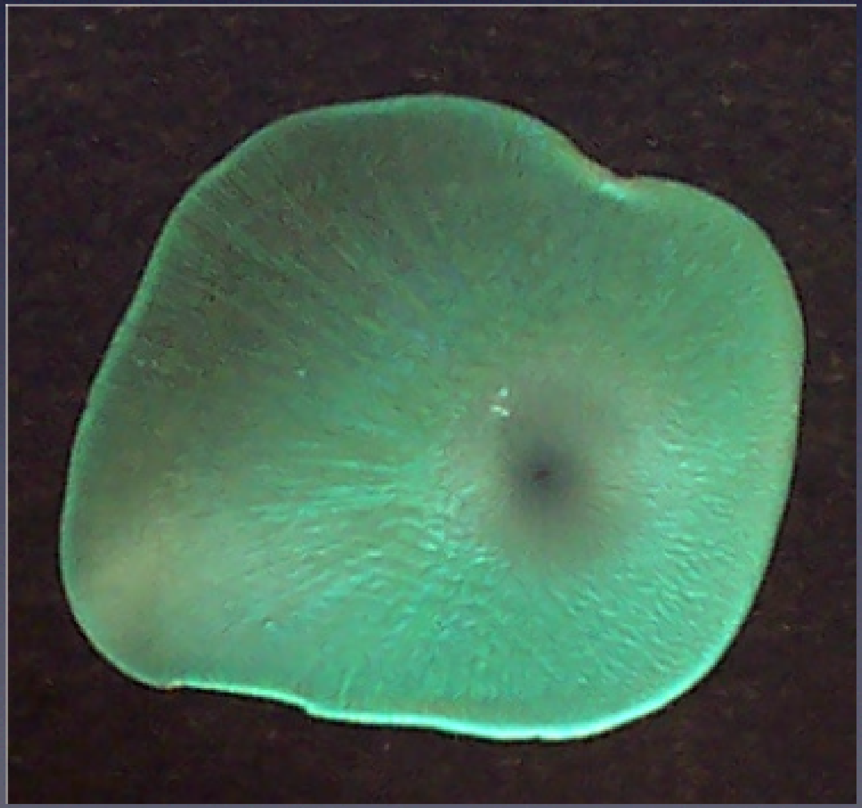
Dynamic transition from soft (repulsive) to soft (attractive, pNIPAm entanglement + hydrophobic) to hard (repulsive; polystyrene).

Conclusions









Acknowledgements

The Group

Ashlee St. John

Bart Blackburn

Neetu Singh

Courtney Sorrell

Zhiyong Meng

Toni Bonhivert

Grant Hendrickson

Support

NIH - NIBIB

GT-Emory ERC on the Engineering of Living Tissues

Johnson & Johnson

ACS-PRF

CCNE

...also: Dr. Jonathan McGrath (paint-on photonics) and Prof. Victor Breedveld (particle tracking).