Colloidal Crystals of Responsive Hydrogels

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School of Chemistry and Biochemistry
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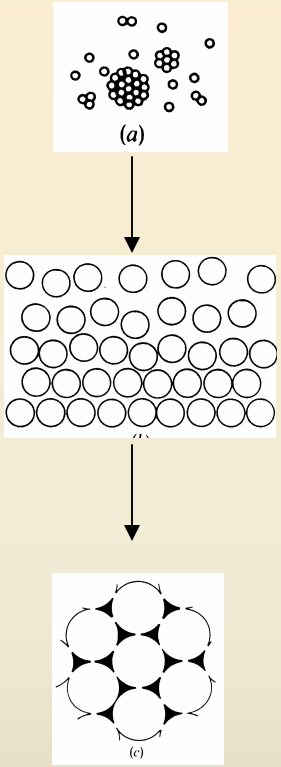
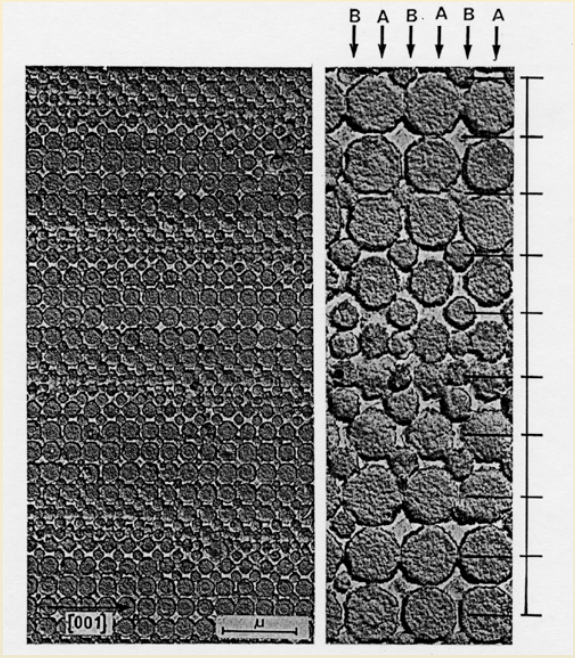
Opals: Structure and Optics

Assembly



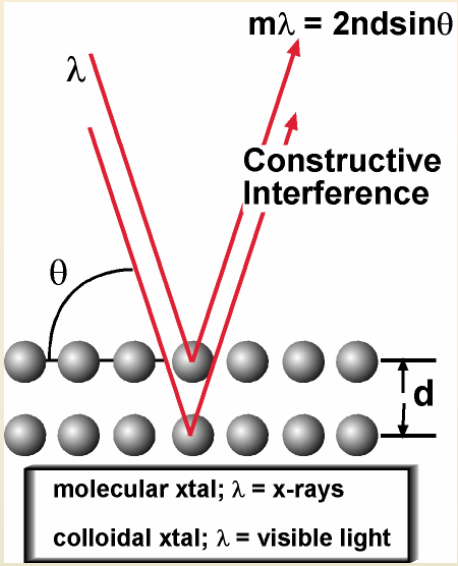
Pieranski, P. *Contemp. Phys.* **1983**, *24*, 25-73.

Structure



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

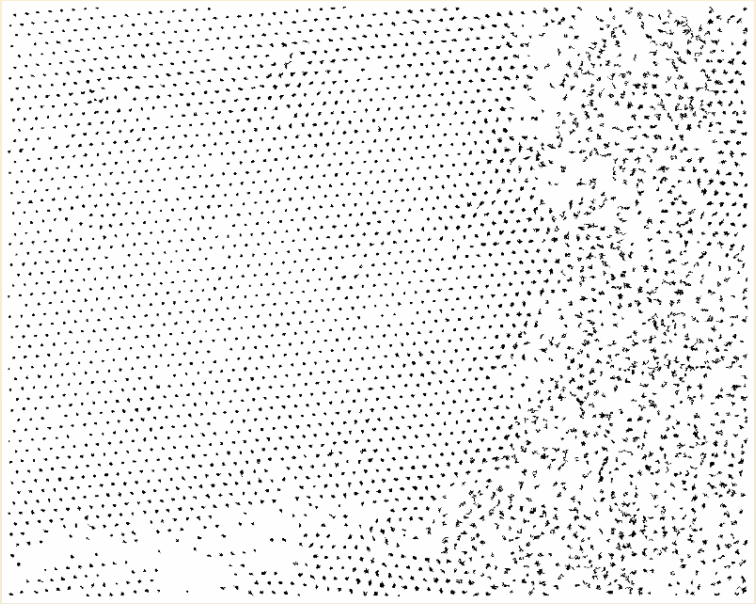
Optics

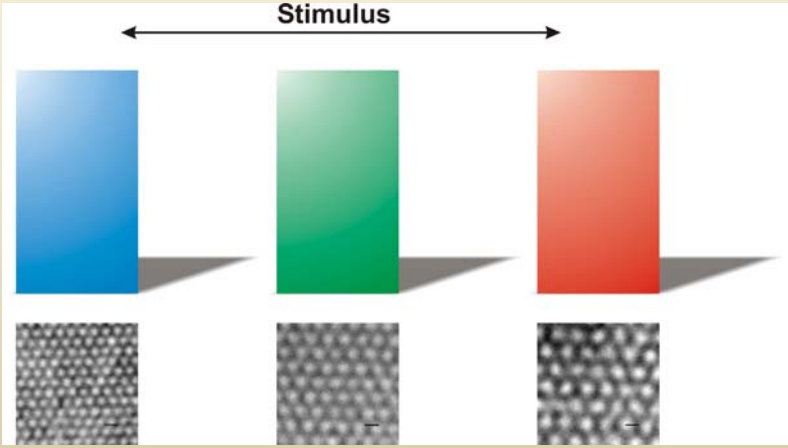


Opals represent primitive photonic lattices

Colloidal Crystals - Motivation

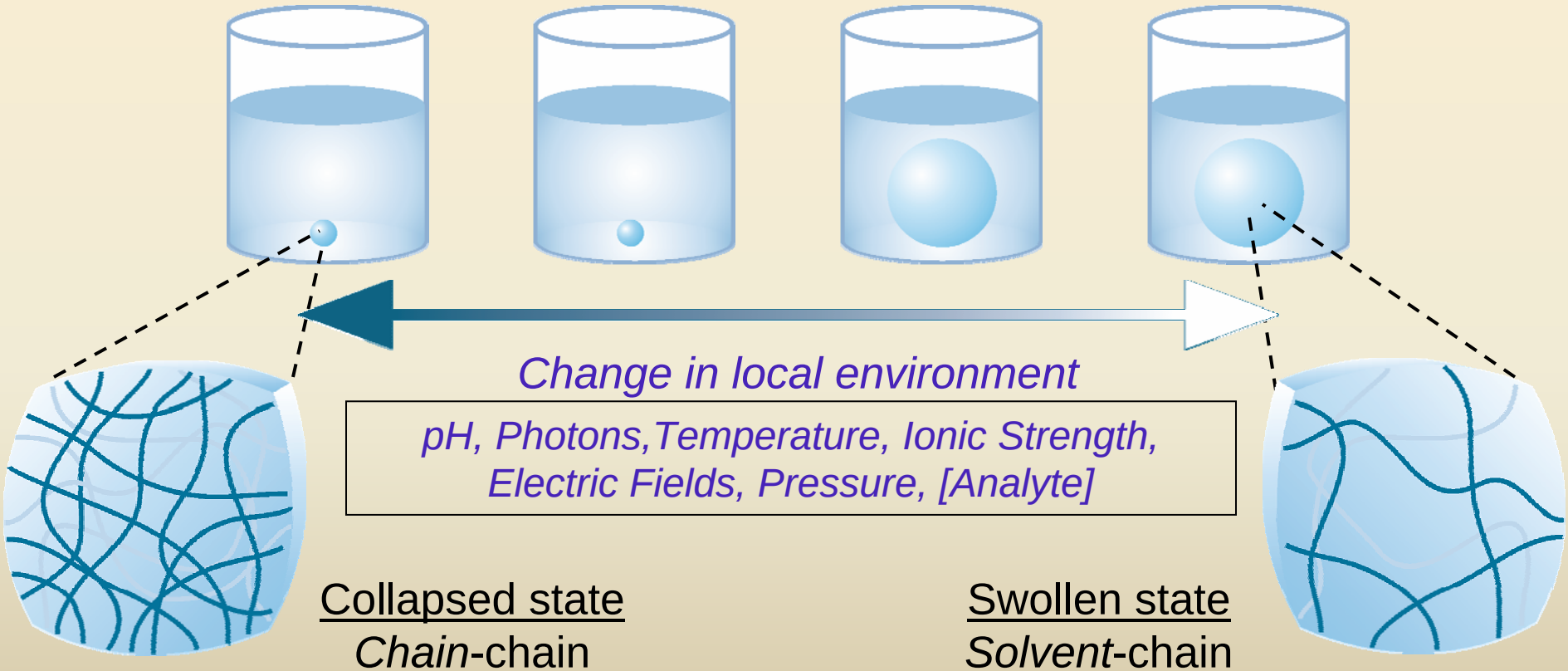
- ***Models of Condensed Phases***
  - Crystallization energetics
  - Crystallization kinetics
- ***New Optical Materials***
  - Precursors to photonic band gap structures
  - Dynamic optics (filters, switches)
  - Reconfigurable optical materials
- ***Silica is a little boring.***





Responsive Hydrogels

Polymeric gels that can be designed to undergo *environmentally-initiated* phase separation events (volume phase transition).



Change in local environment

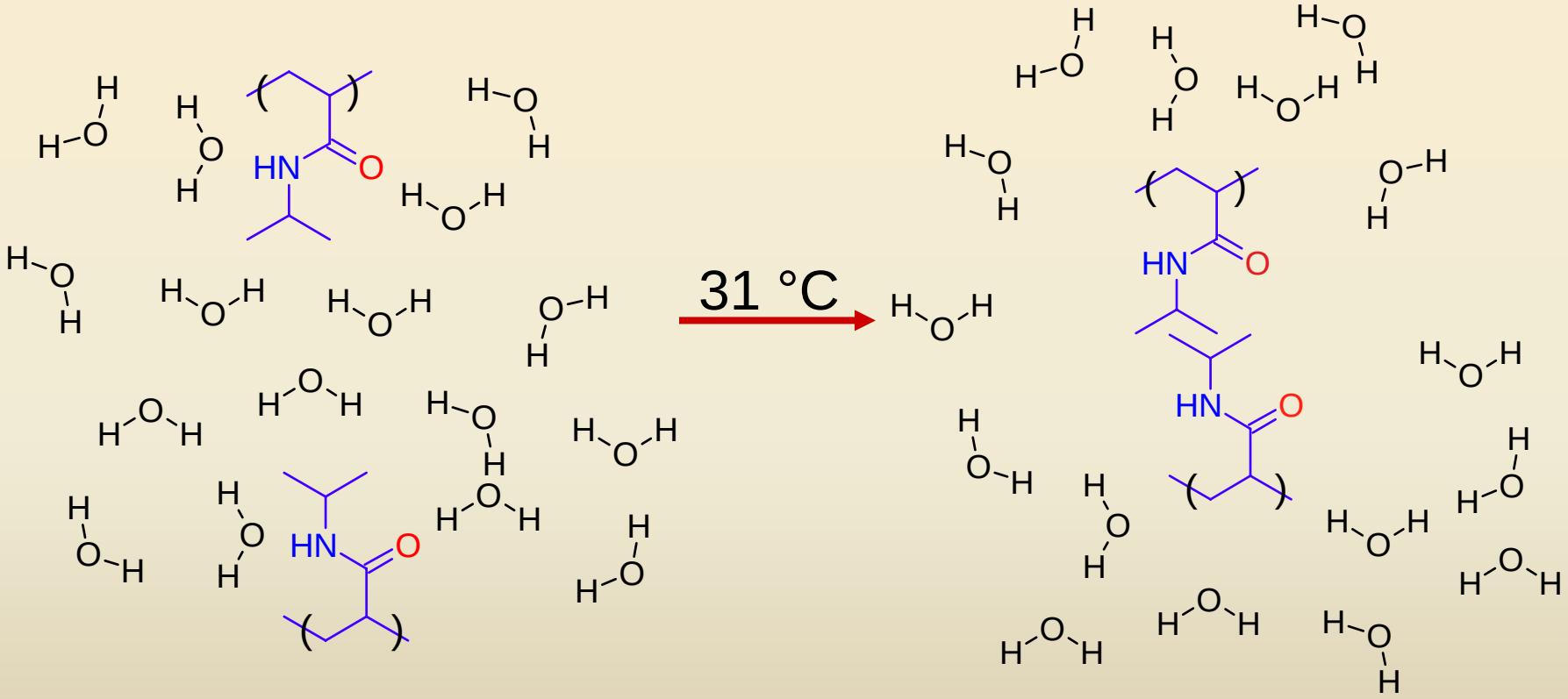
pH, Photons,Temperature, Ionic Strength, Electric Fields, Pressure, [Analyte]

Collapsed state
Chain-chain interactions dominate

Swollen state
Solvent-chain interactions dominate

Thermo-Responsive Gels

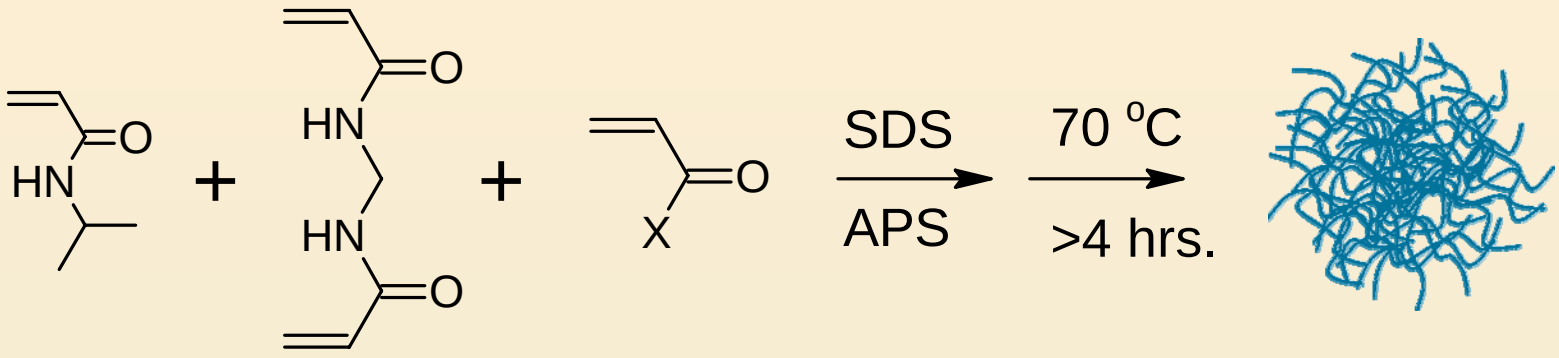
poly(*N*-isopropylacrylamide) (*p*NIPAm)



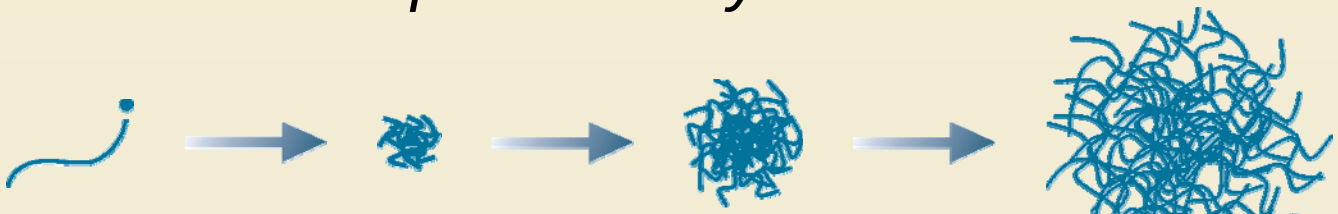
Swollen/Hydrophilic

Collapsed/Hydrophobic

pNIPAm Microgel Synthesis



Precipitation Polymerization



Oligoradical

Precursor Particle

Growing Particle

Microgel

Controllable Parameters:

particle porosity/solvent content (crosslinker identity/conc.)

size – 50 nm to 5 μm (initiator, surfactant conc.)

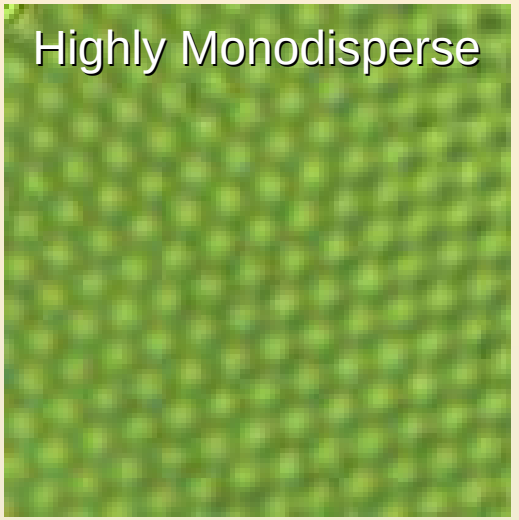
phase transition magnitude

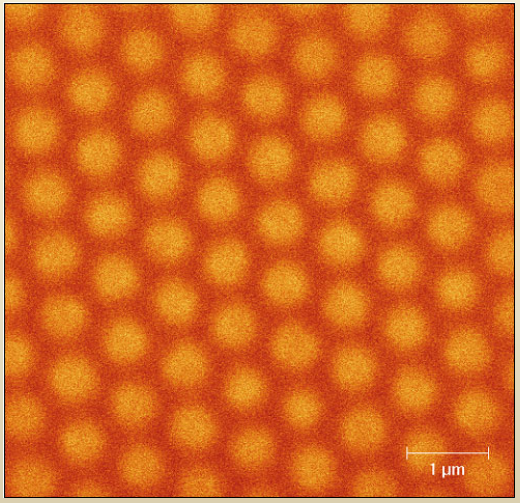
volume phase transition shape

Hydrogel Particle Characteristics

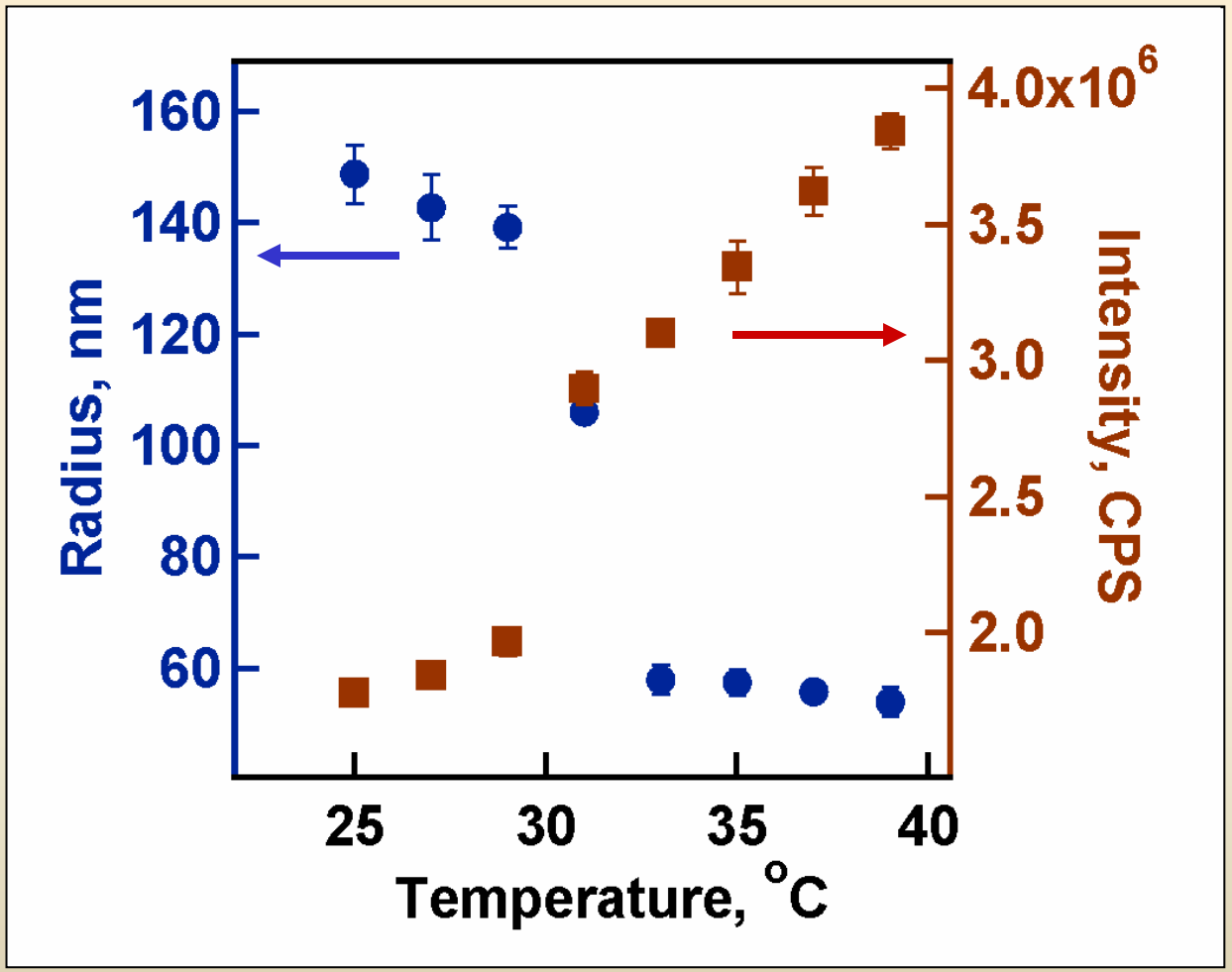
Infinite Spherical Network

High water content (90-99% v/v) a microgel is effectively *all surface area*





Volume Phase Transitions



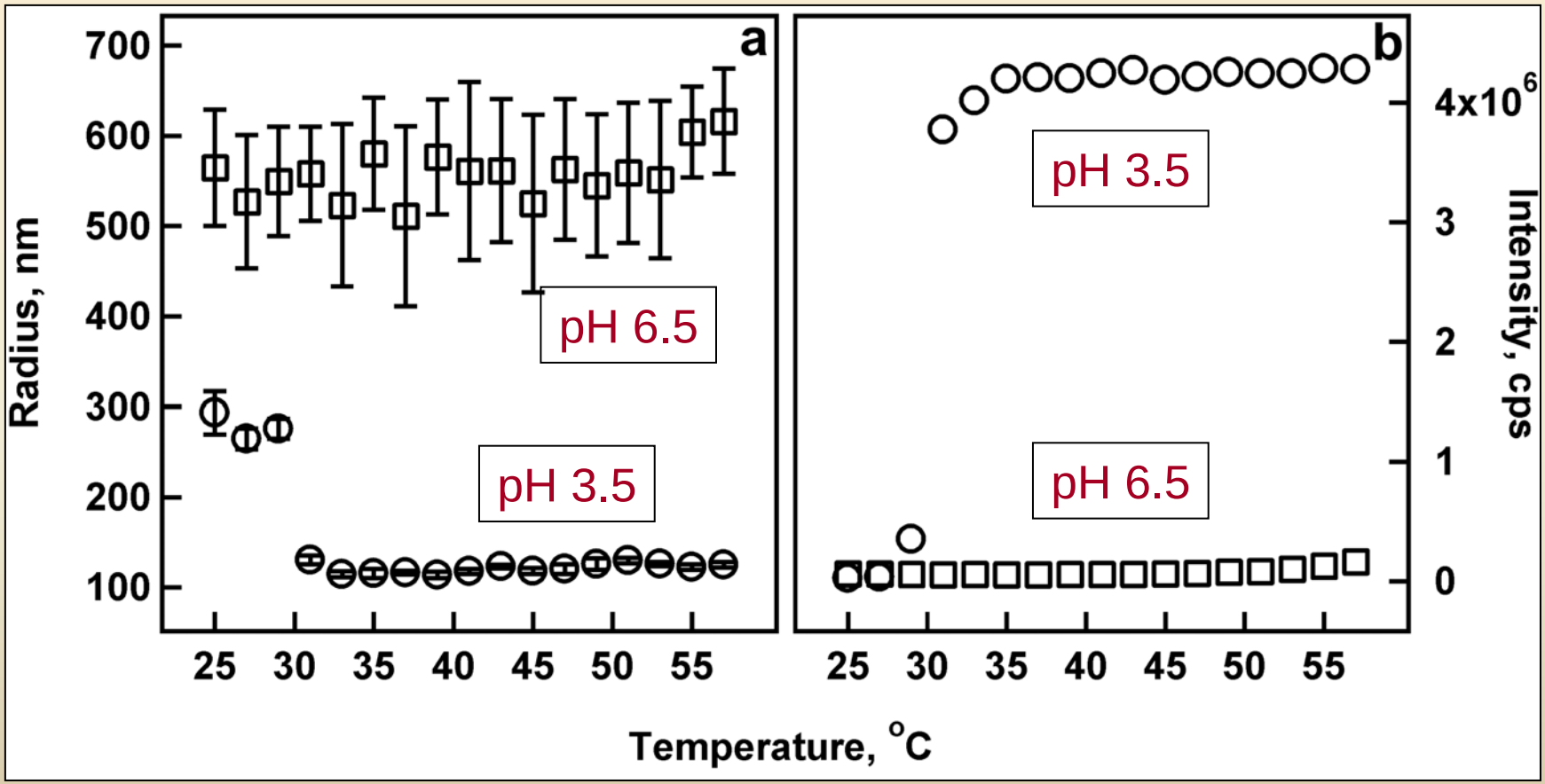
2 mol% crosslinked pNIPAm in water

Dynamic Light Scattering (Photon Correlation Spectroscopy)

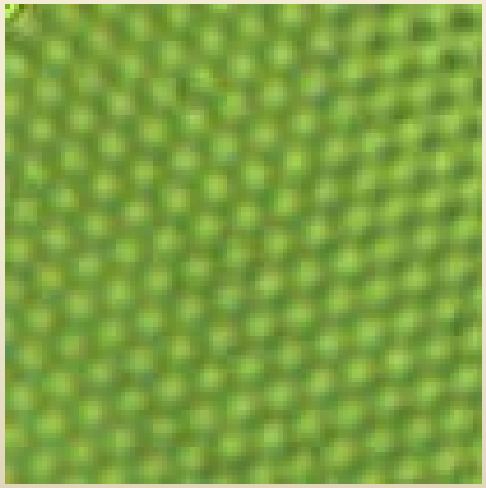
Dual-Response Microgels

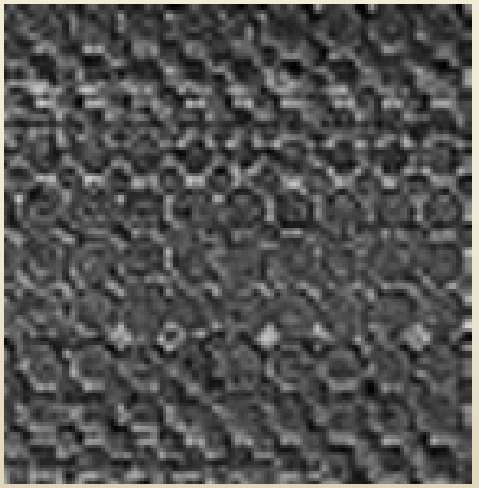
pNIPAm-co-Acrylic Acid

pH dependent size and phase transition temperature



Responsive Hydrogel “Opals”





Questions:

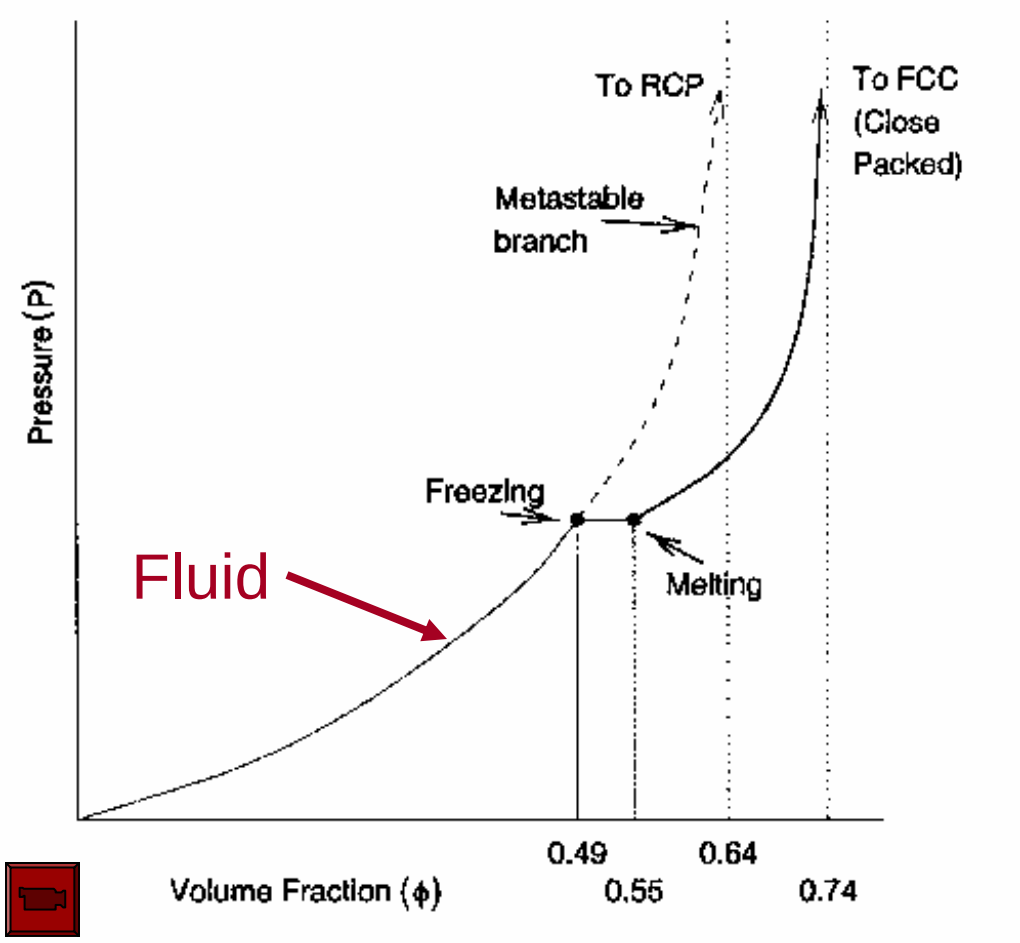
Is there any fundamental utility in the use of soft particles in crystalline assemblies?

How does the physics of packing change with the “softness of the interaction potential?

Can responsive assemblies be used to achieve optical materials not obtainable from hard sphere systems?

Colloidal Hard Sphere Phases

Entropic Crystallization



Colloidal Hard Sphere Phases

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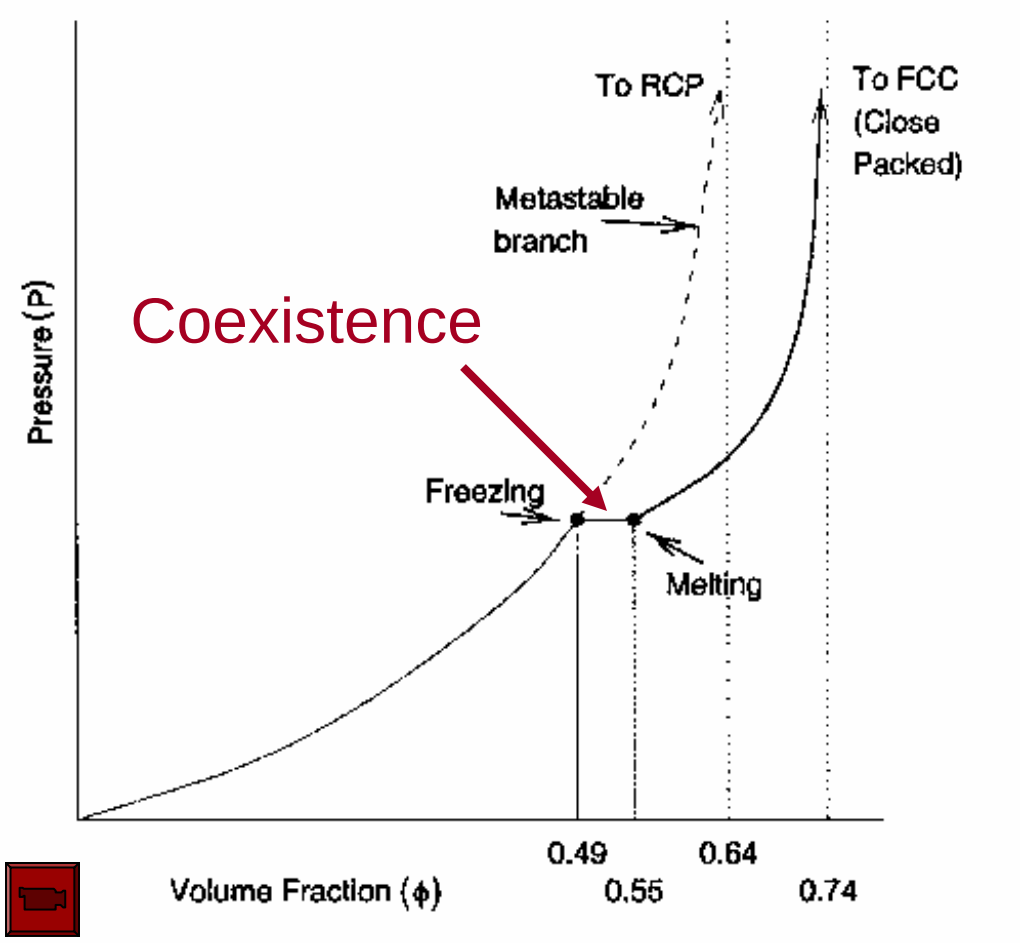
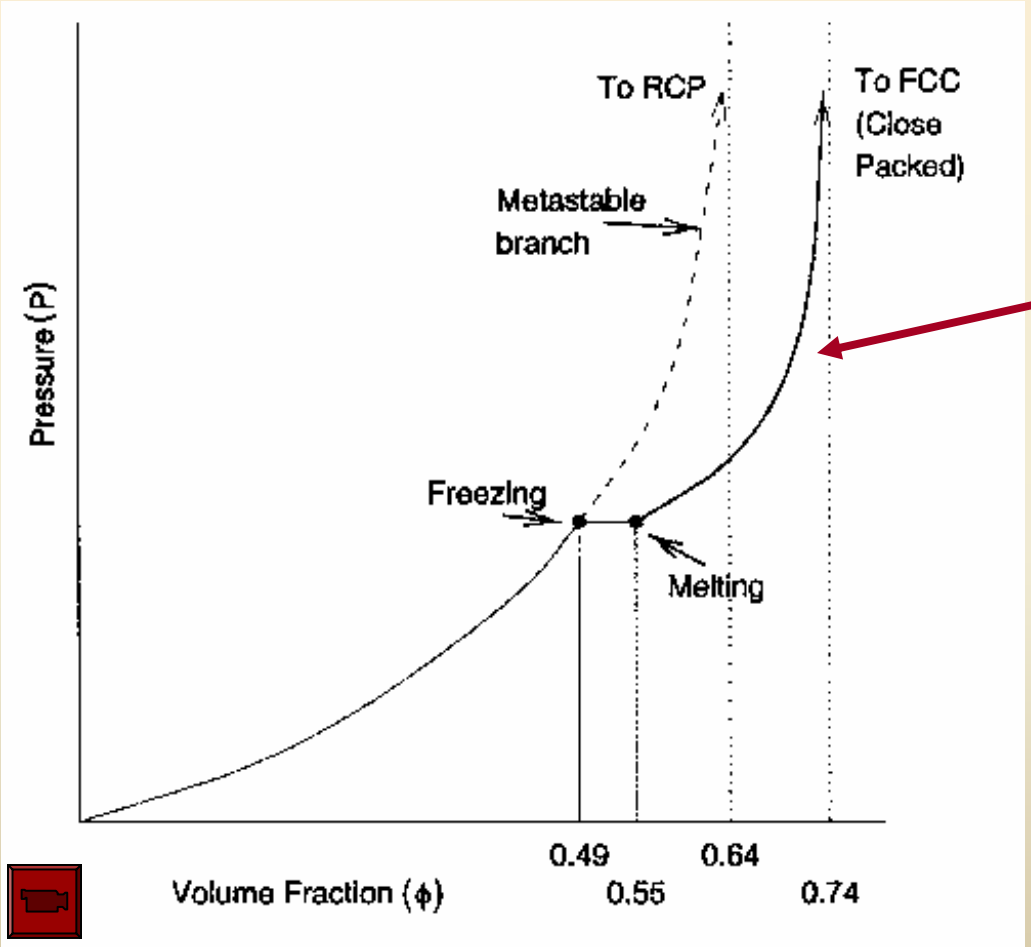


Colloidal Hard Sphere Phases

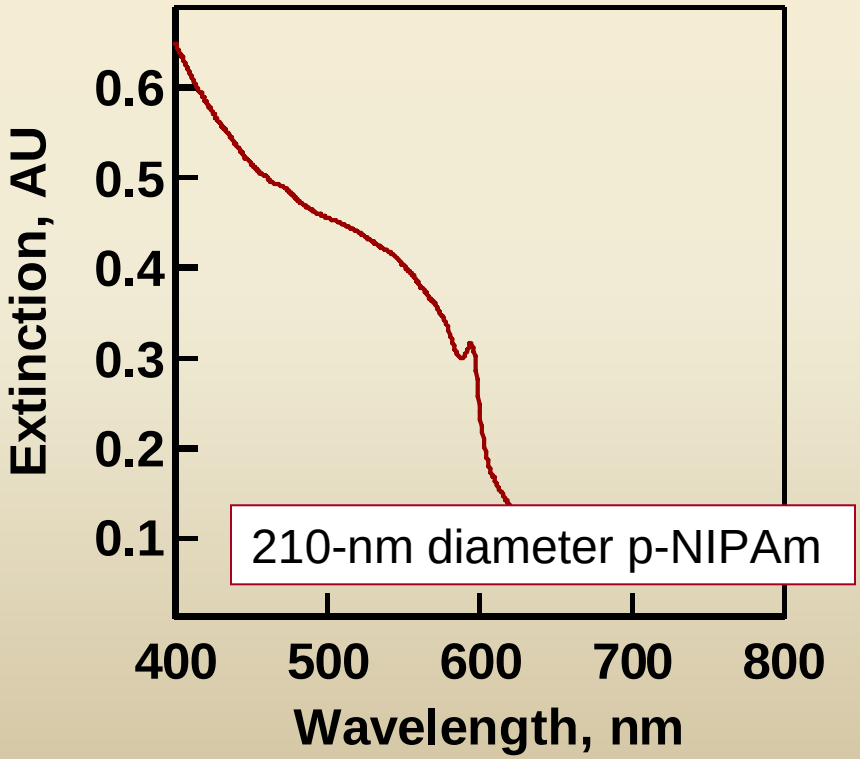
Entropic Crystallization

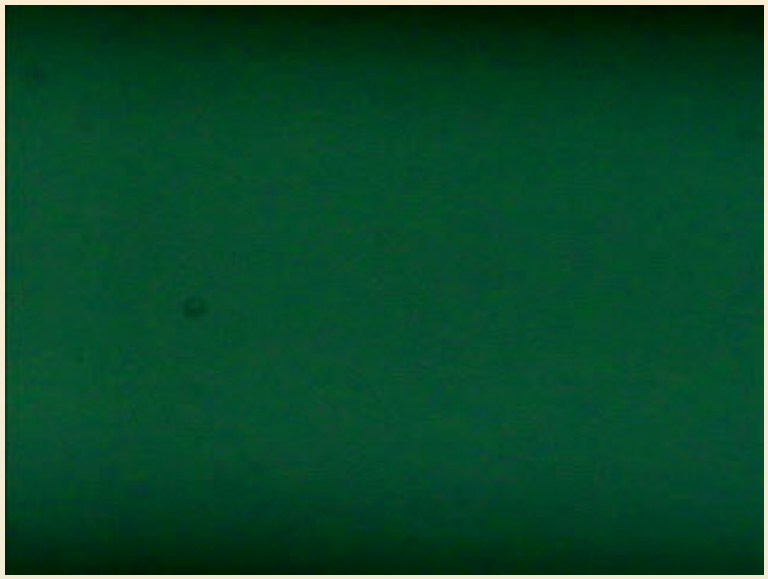


Crystal

Centrifugal Assembly–Glassy Gels

Centrifugation at 16,000 g (1 hour) packs particles into amorphous "jammed" phase.

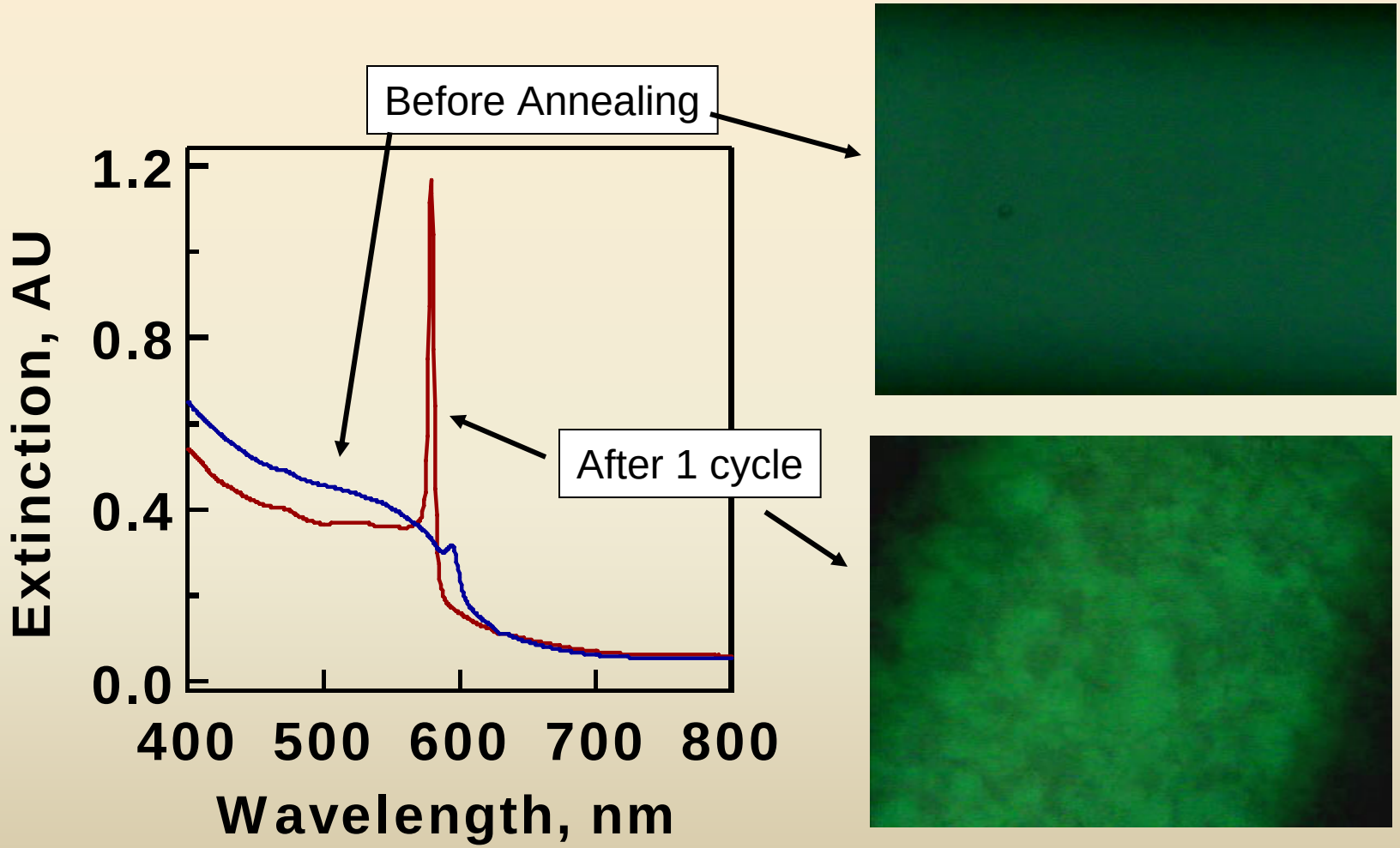




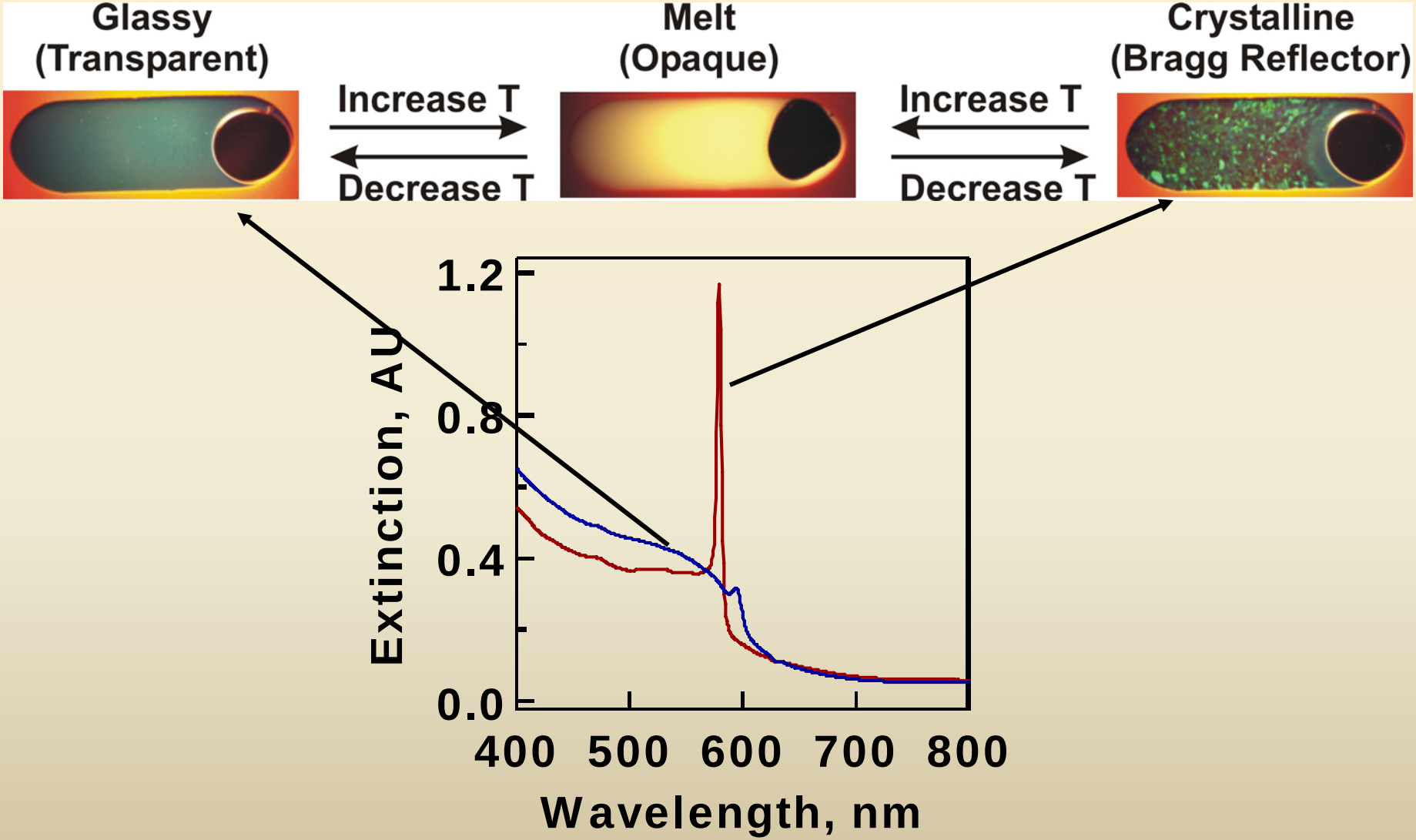
Low-mag (15X) brightfield reflectance microscopy shows no evidence of crystallites.

Thermal Annealing

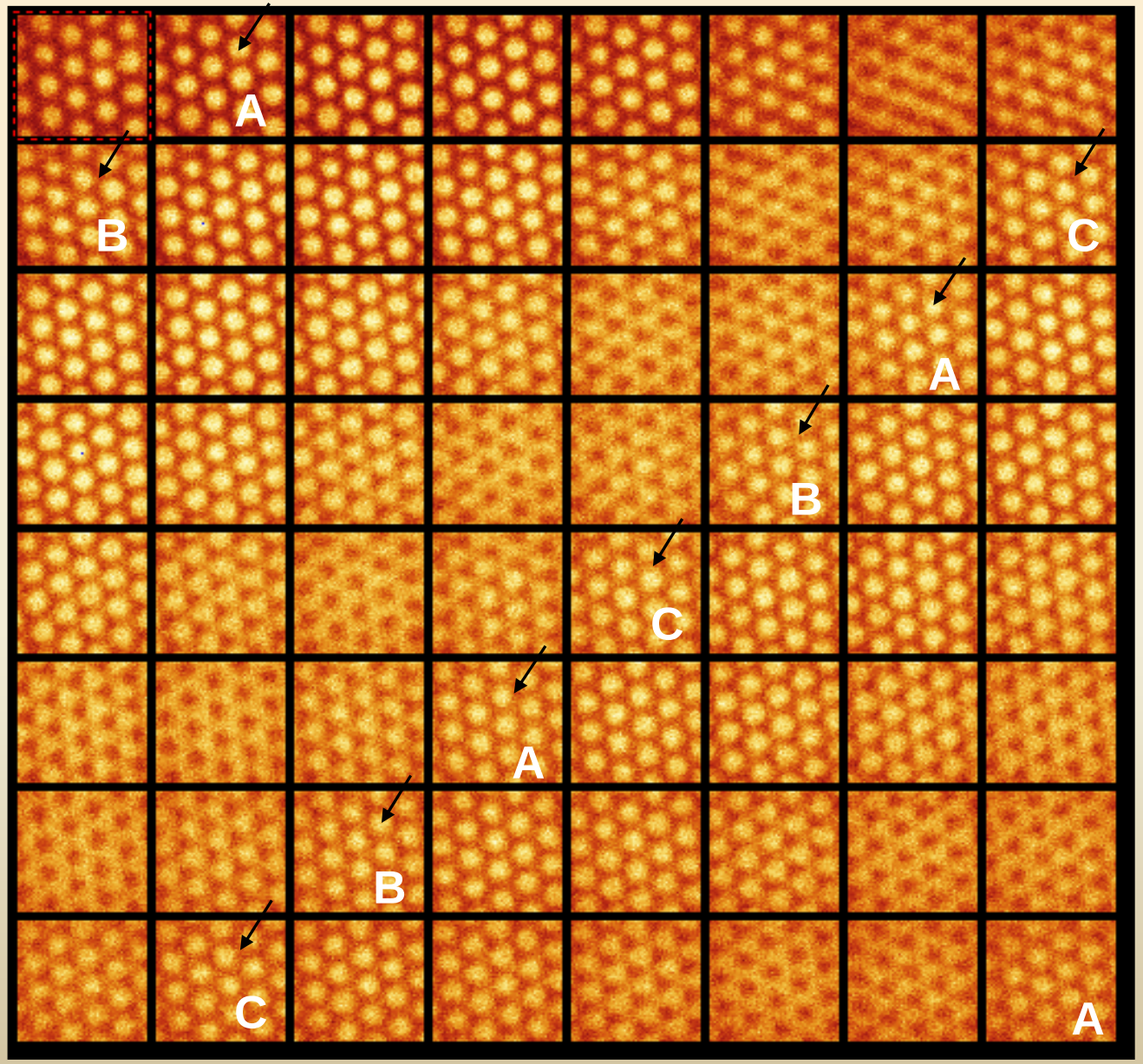
Thermal cycling across the *particle phase transition temperature* yields a highly crystalline, strongly photonic material.



States of Hydrogel Crystals



3-D Structure



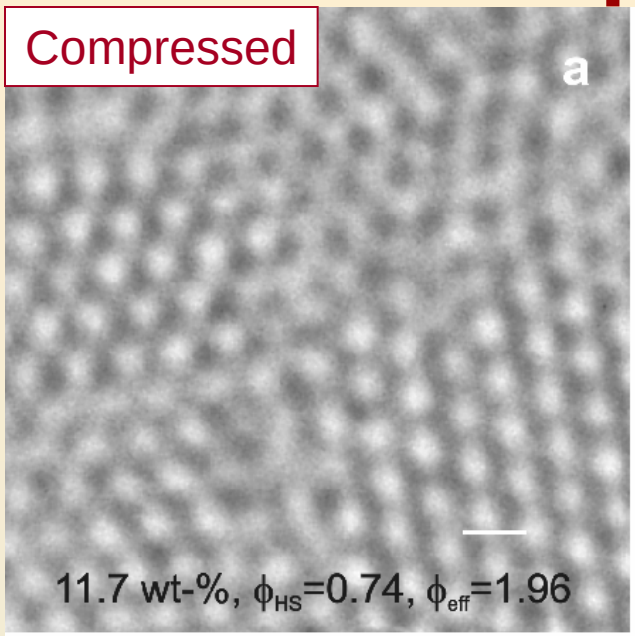
Confocal Microscopy - ~810-nm Diam. particles.

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

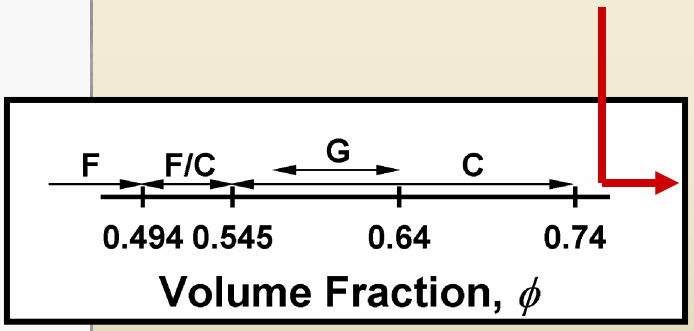
Thermodynamics more controlled than in sedimented hard sphere crystals; High volume fractions accessible

Soft Sphere Phase Behavior

Compressed



DIC Microscopy:
810-nm diam.
pNIPAm spheres



Soft Sphere Phase Behavior

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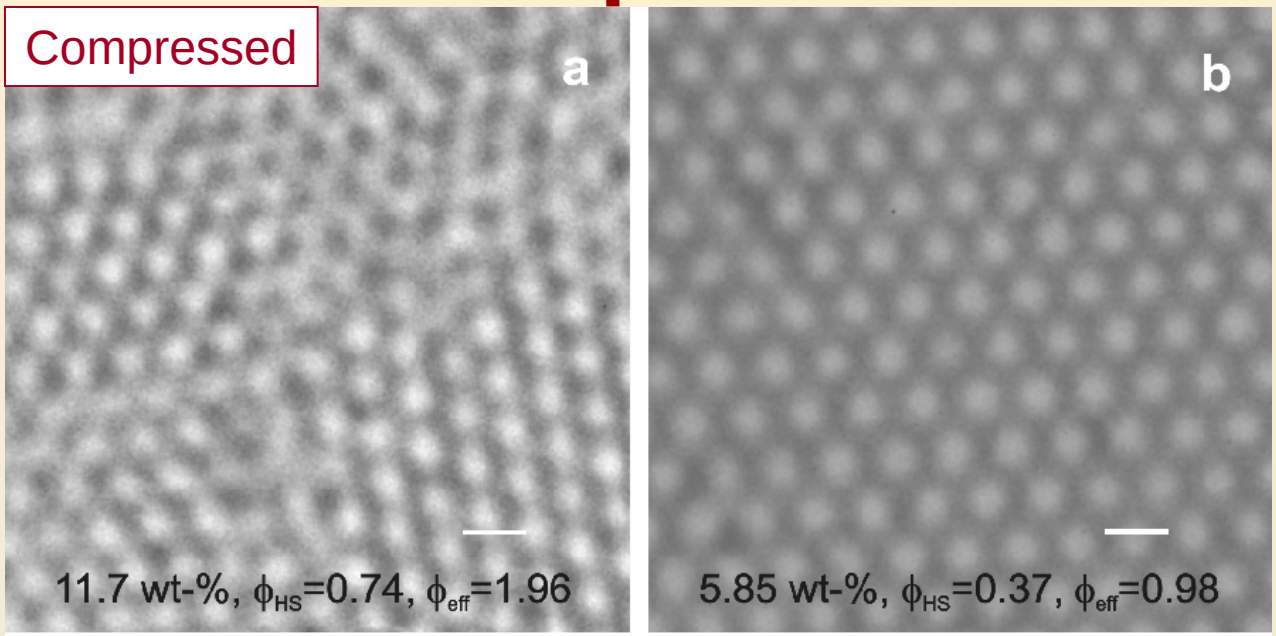

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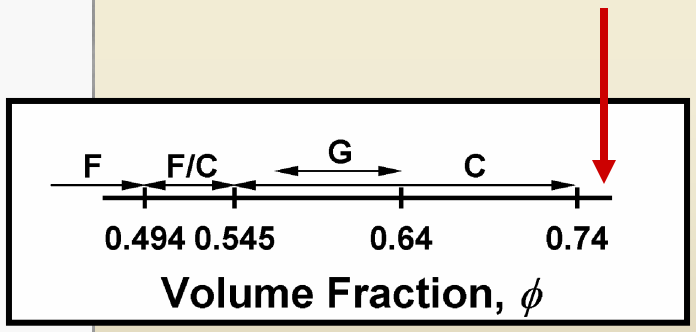
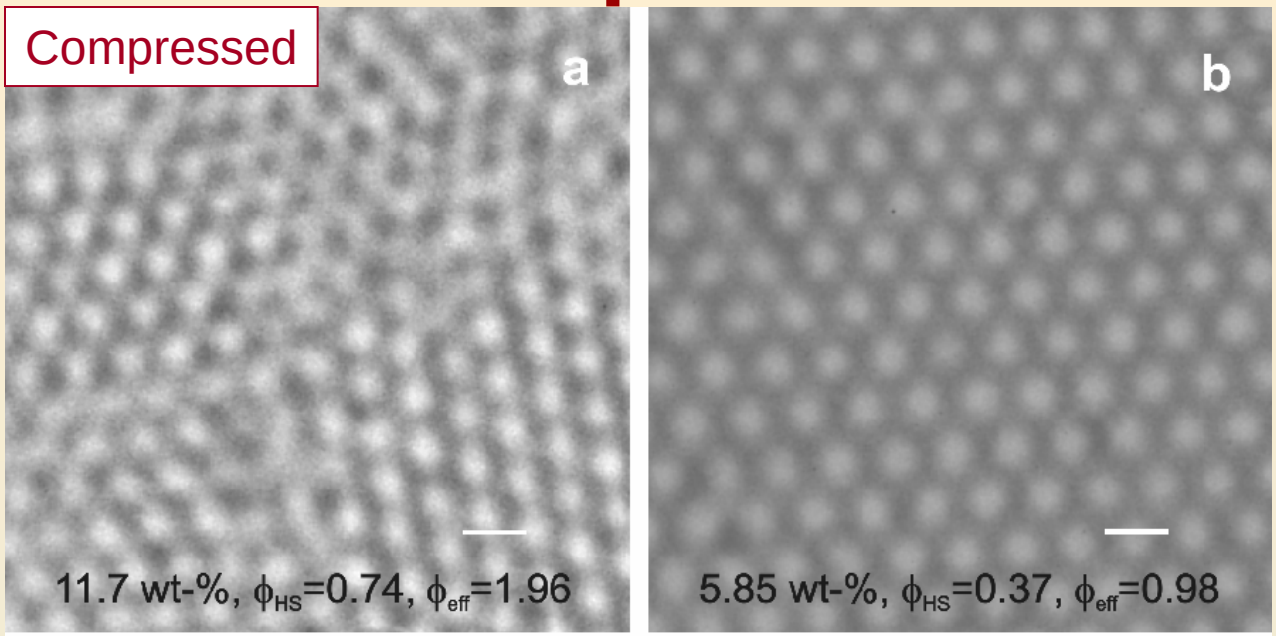
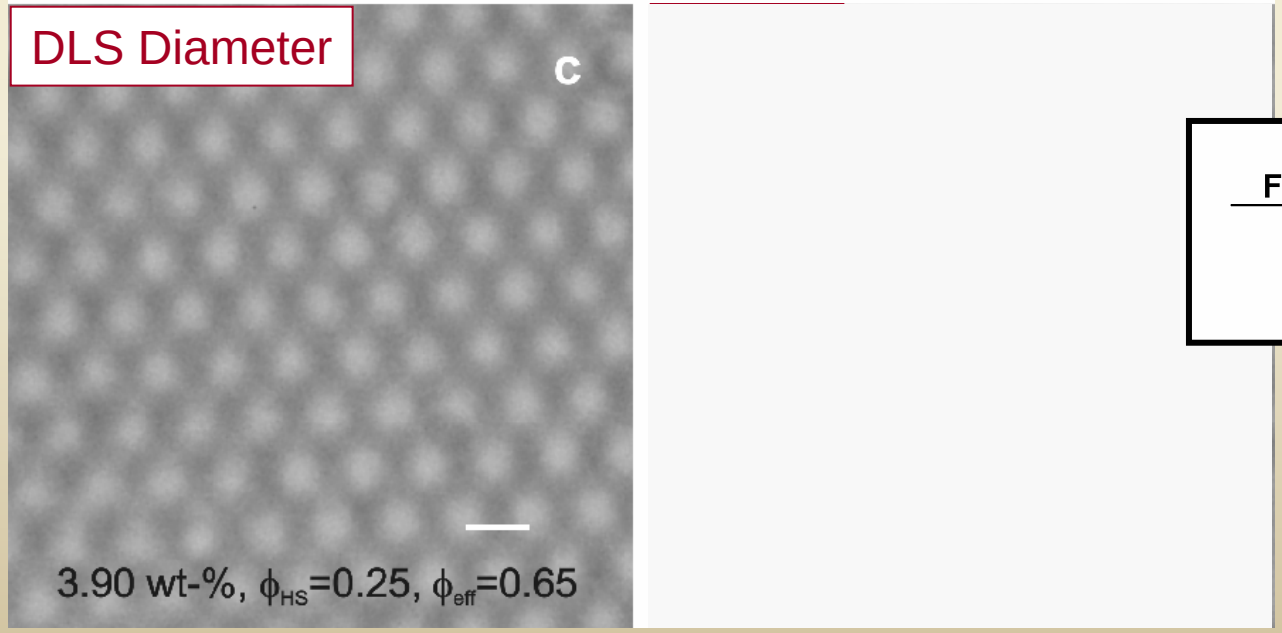


Soft Sphere Phase Behavior

Compressed



DLS Diameter



DIC Microscopy:
810-nm diam.
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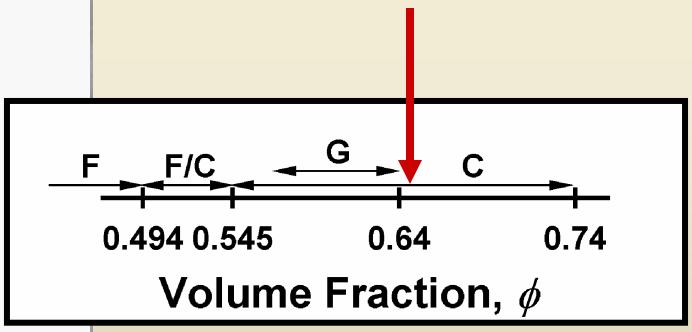
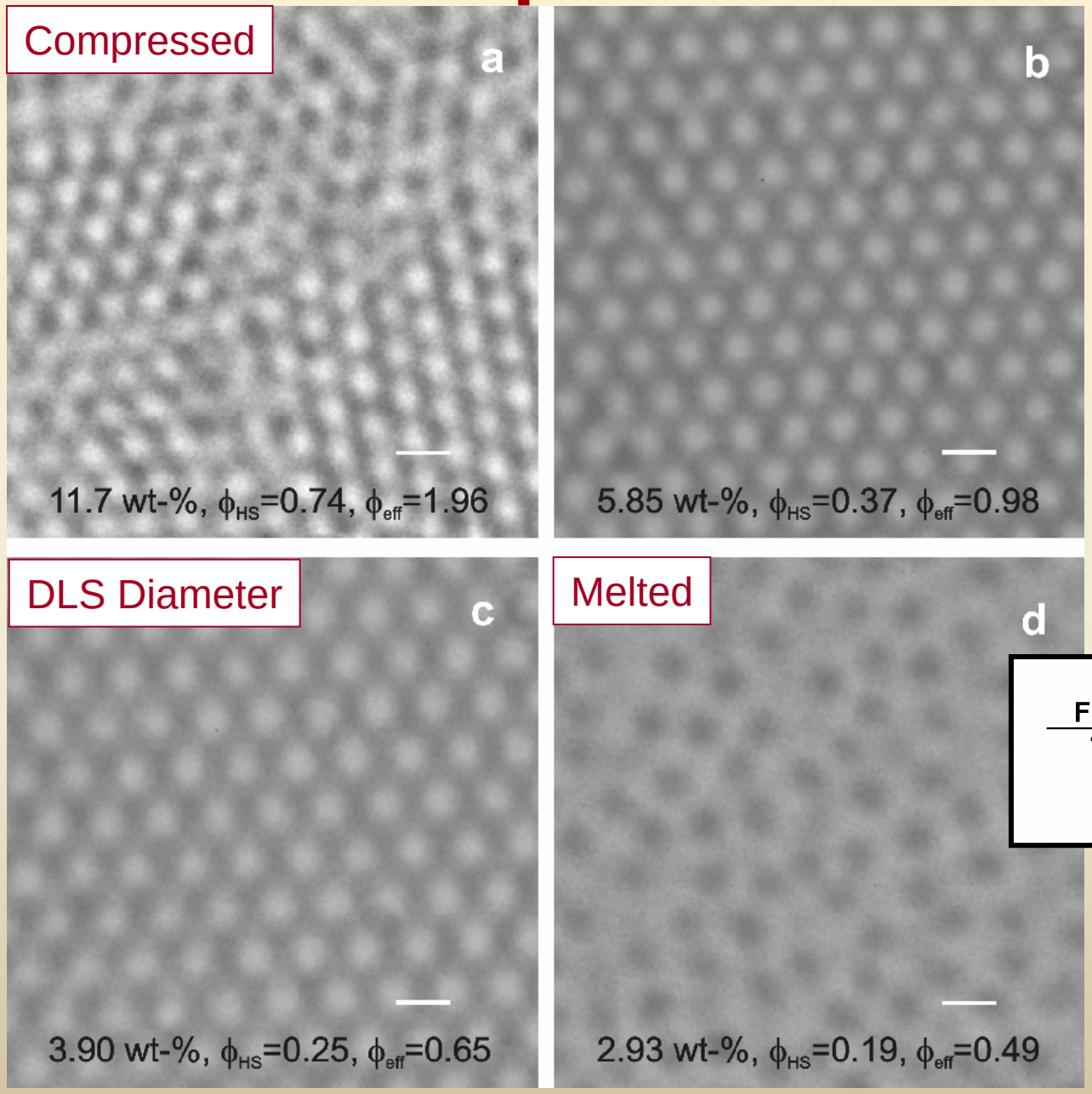


Soft Sphere Phase Behavior



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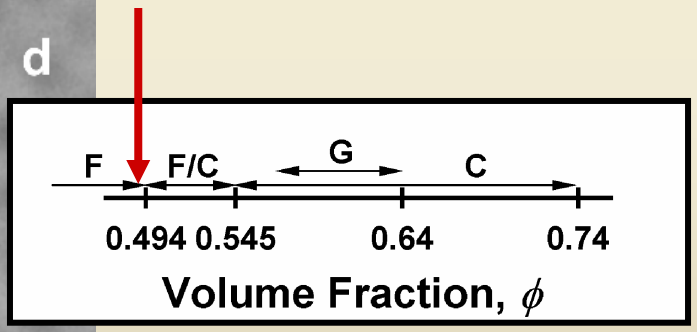
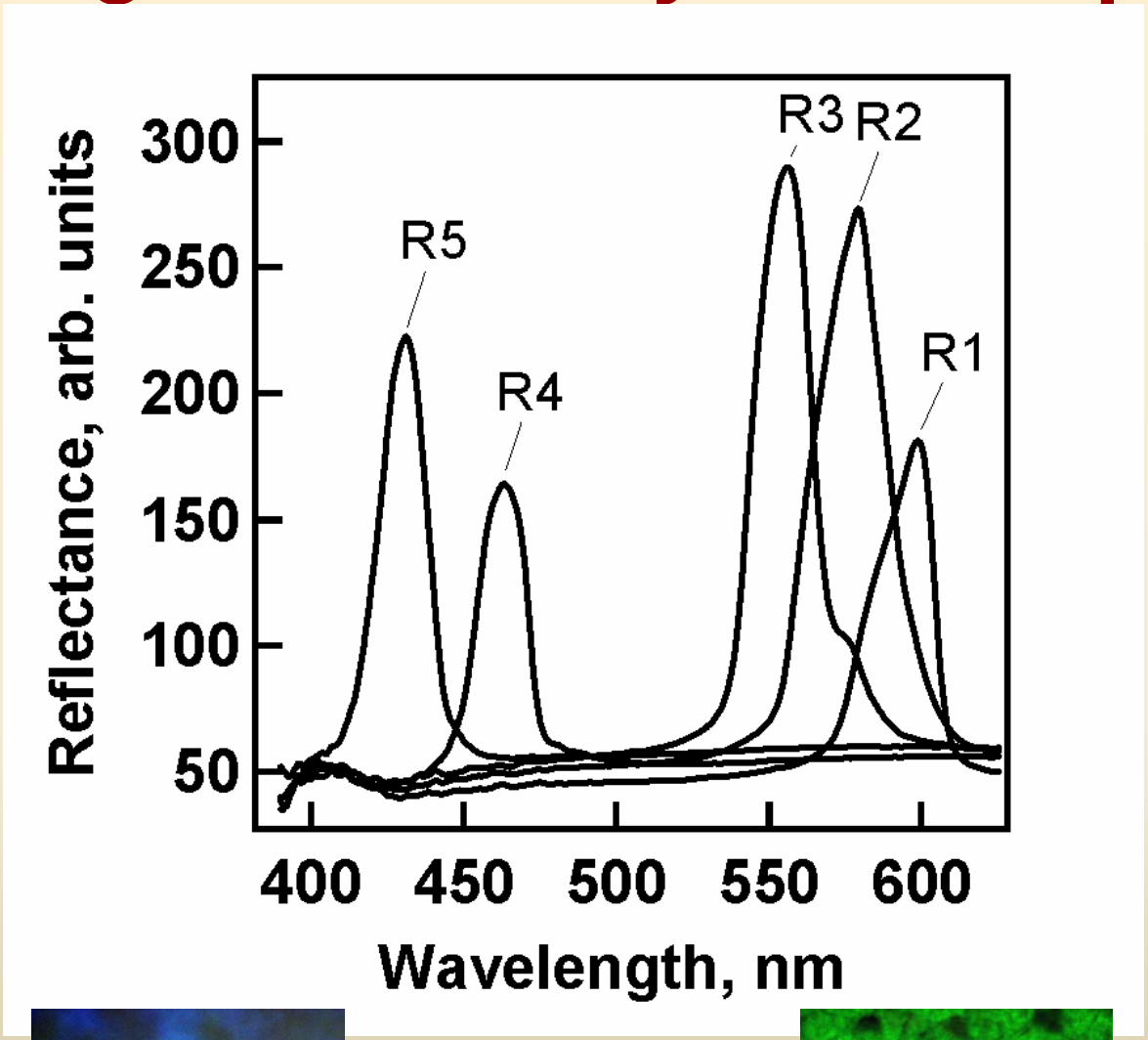
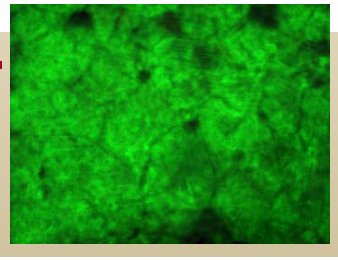


Wavelength Tunability *via* Compression



Hydrogel Compression



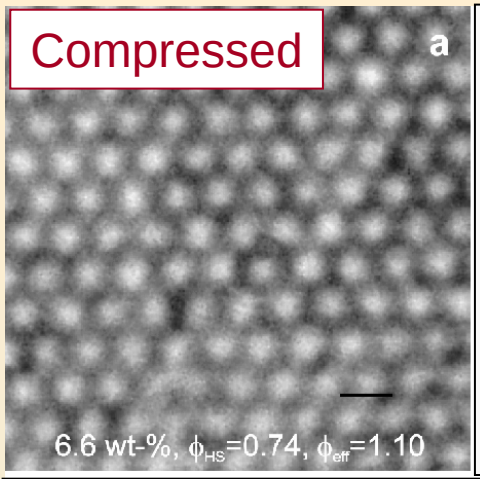
$R_{initial}$ = 260 nm

R1 = 275 nm
R2 = 266 nm
R3 = 254 nm
R4 = 210 nm
R5 = 197 nm

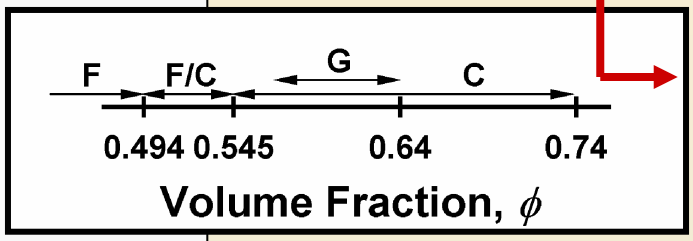
Debord, J. D.; Eustis, S.; Debord, S.; Lofye, M. T.; Lyon, L. A. *Adv. Mater.*, **2002**, *14 (9)*, 658-661.

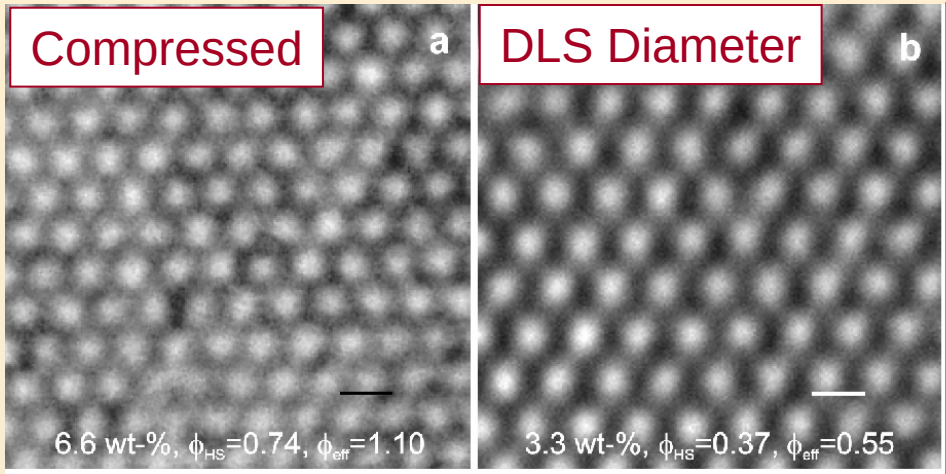
(Slightly) More Complex Interactions??

Compressed



pNIPAm-*co*-*AAc*
(pH=3.8)





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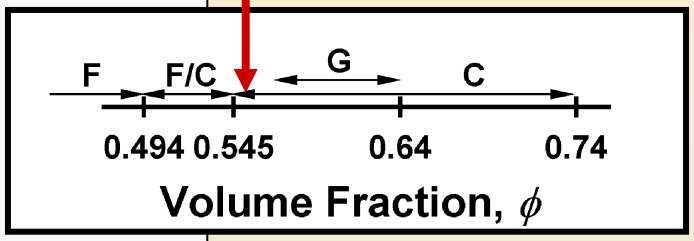

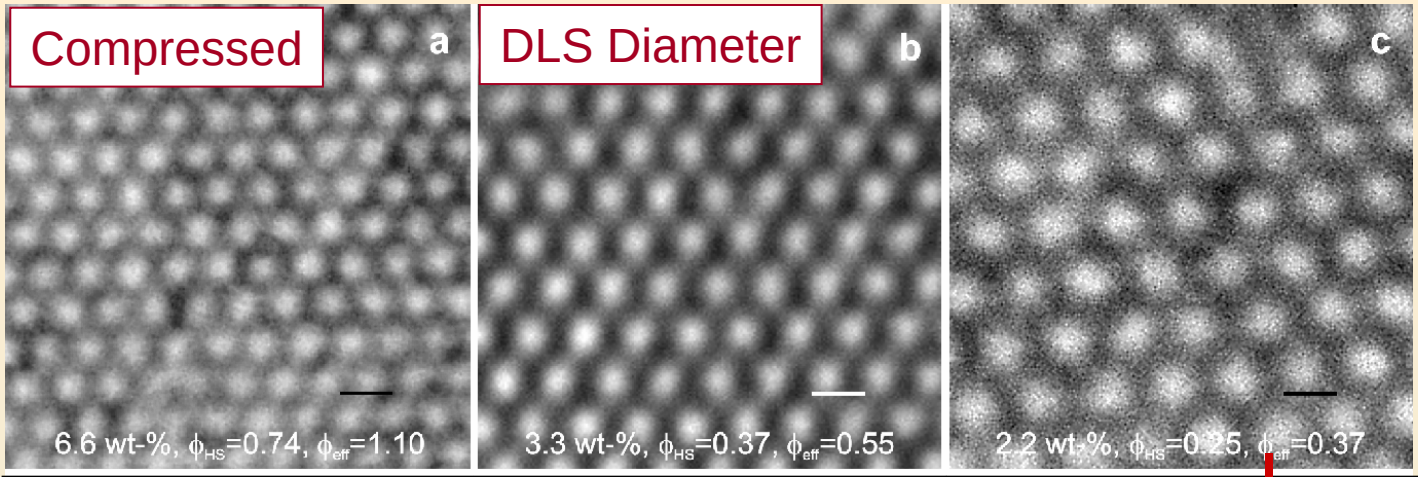

pNIPAm-*co*-*AAc*
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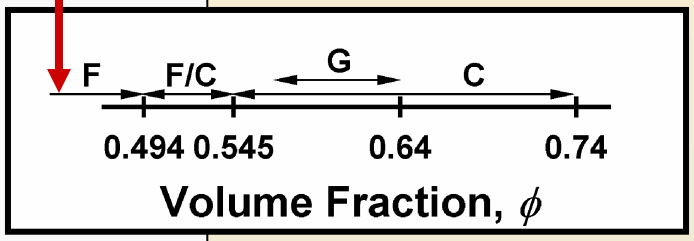
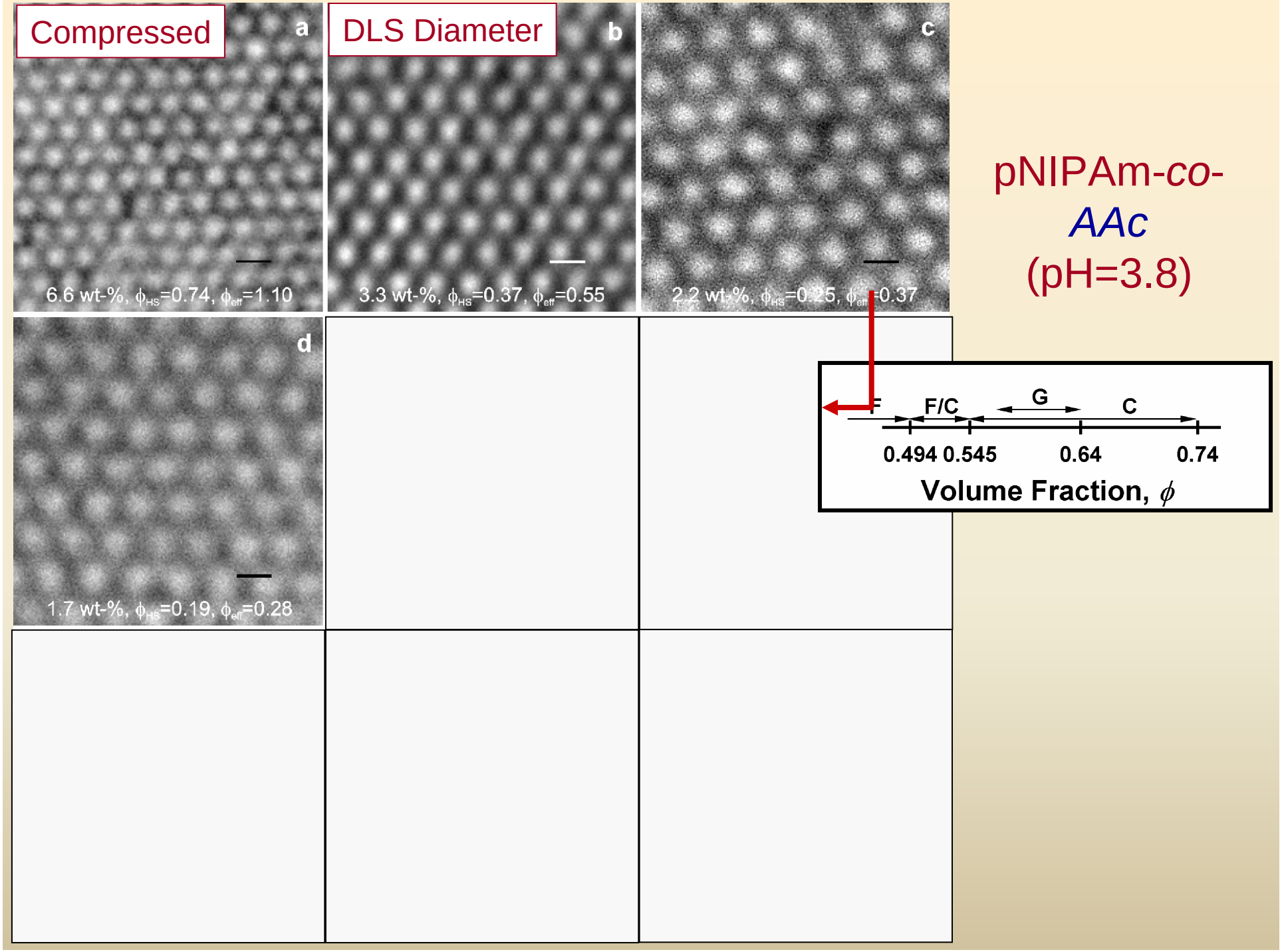
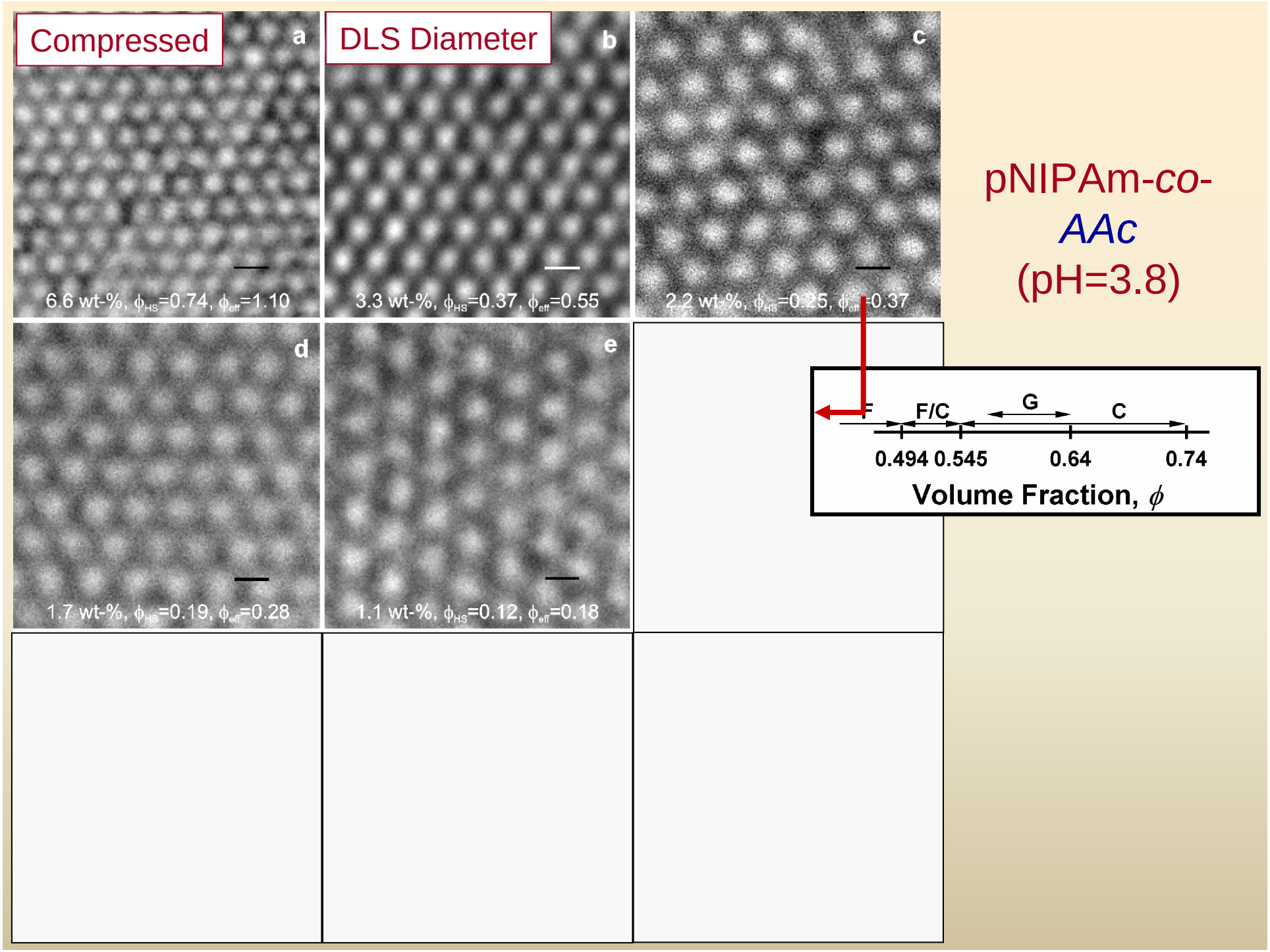



Compressed
a
DLS Diameter
b
c
6.6 wt-%, ϕ_{HS}=0.74, ϕ_{eff}=1.10
3.3 wt-%, ϕ_{HS}=0.37, ϕ_{eff}=0.55
2.2 wt-%, ϕ_{HS}=0.25, ϕ_{eff}=0.37
d
1.7 wt-%, ϕ_{HS}=0.19, ϕ_{eff}=0.28
pNIPAm-*co*-*AAc*
(pH=3.8)
F
F/C
G
C
0.494 0.545
0.64
0.74
Volume Fraction, ϕ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(pH=3.8)
d
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1.7 wt-%, ϕ_{HS}=0.19, ϕ_{eff}=0.28
1.1 wt-%, ϕ_{HS}=0.12, ϕ_{eff}=0.18
F
F/C
G
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0.494 0.545
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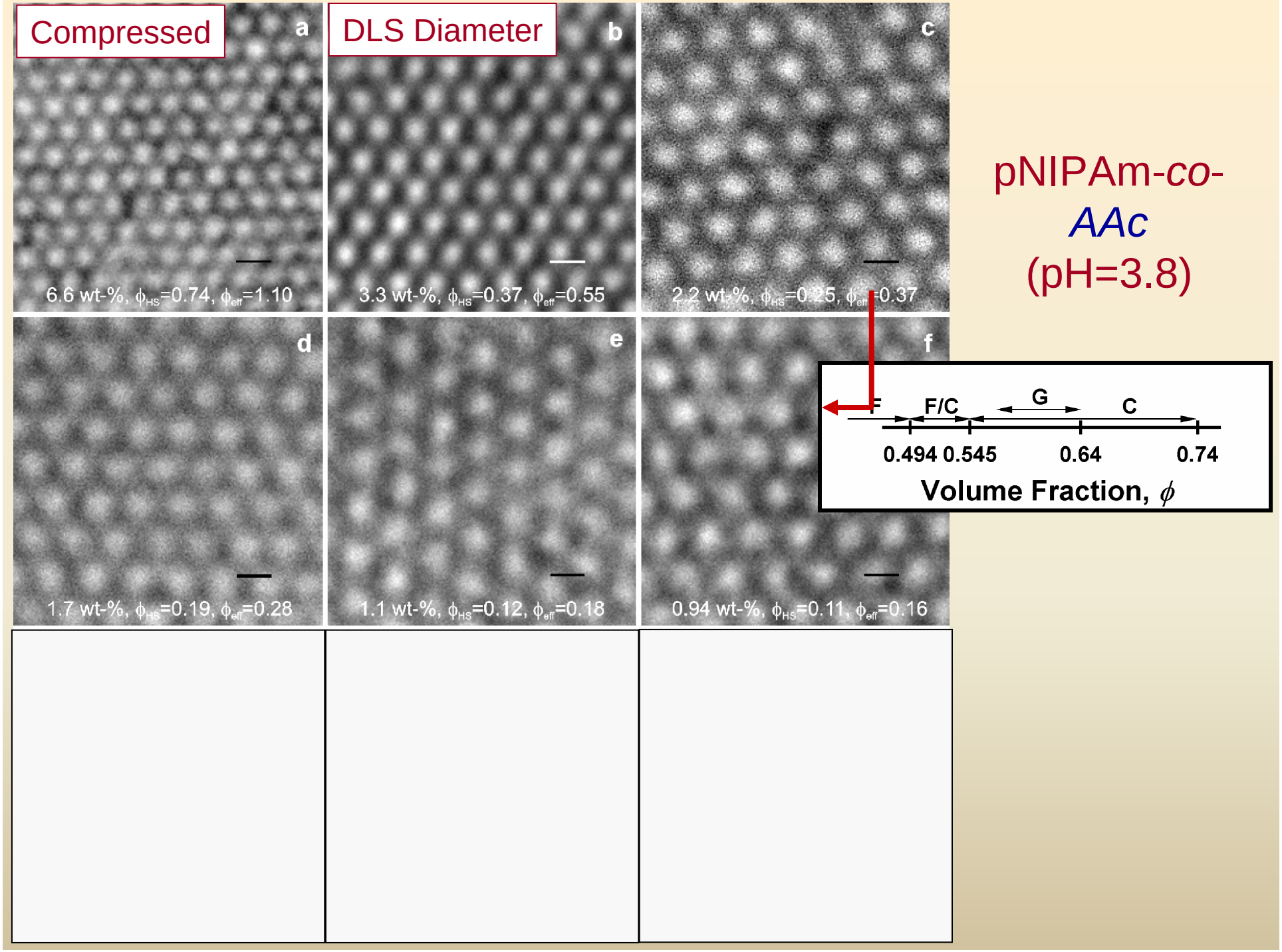
Volume Fraction, ϕ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d
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f
1.7 wt-%, ϕ_{HS}=0.19, ϕ_{eff}=0.28
1.1 wt-%, ϕ_{HS}=0.12, ϕ_{eff}=0.18
0.94 wt-%, ϕ_{HS}=0.11, ϕ_{eff}=0.16
F
F/C
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0.494 0.545
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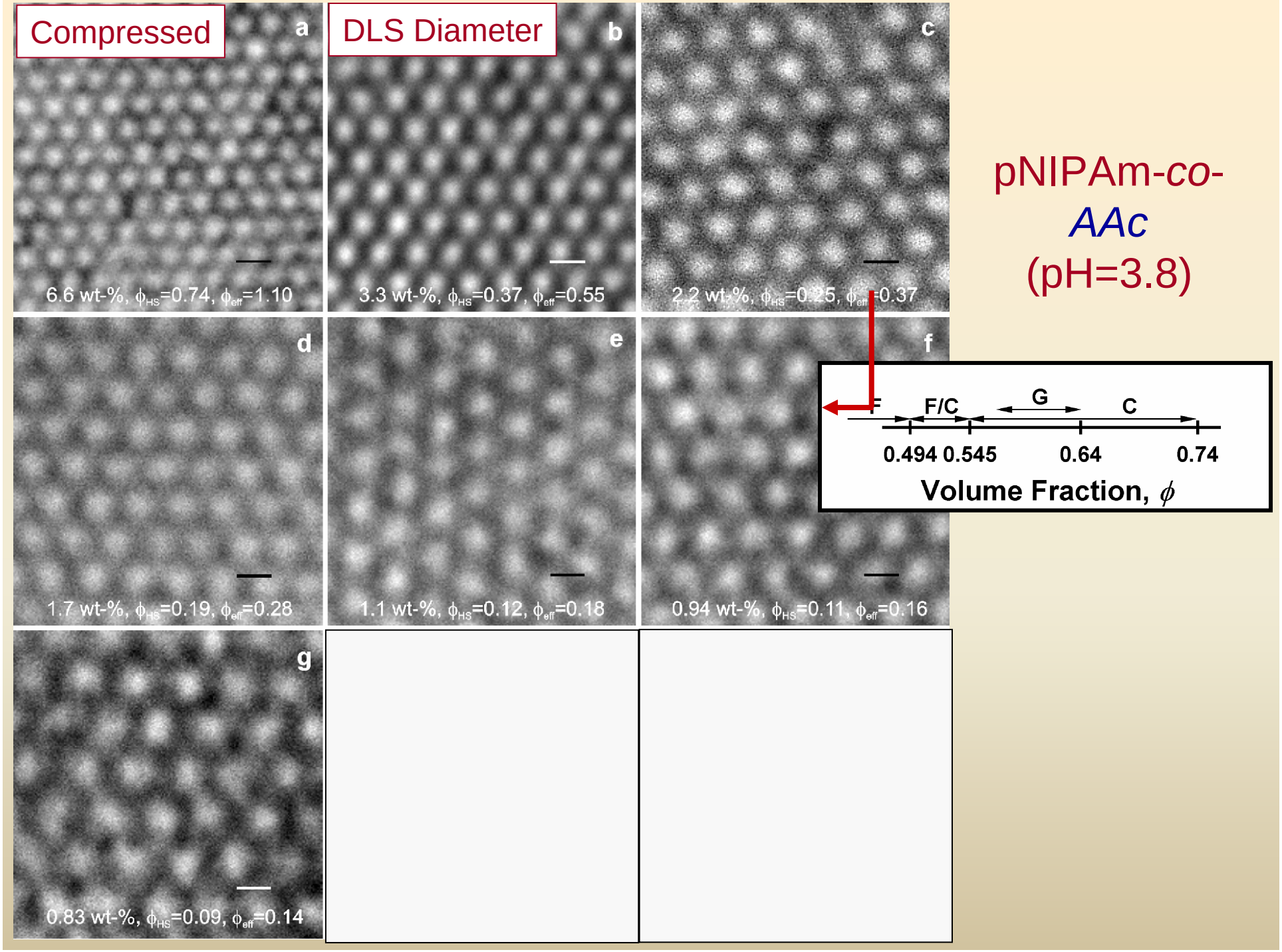
Volume Fraction, ϕ
pNIPAm-*co*-*AAc*
(pH=3.8)


Compressed
DLS Diameter
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6.6 wt-%, ϕ_{HS}=0.74, ϕ_{eff}=1.10
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1.7 wt-%, ϕ_{HS}=0.19, ϕ_{eff}=0.28
1.1 wt-%, ϕ_{HS}=0.12, ϕ_{eff}=0.18
0.94 wt-%, ϕ_{HS}=0.11, ϕ_{eff}=0.16
0.83 wt-%, ϕ_{HS}=0.09, ϕ_{eff}=0.14
F
F/C
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0.494 0.545
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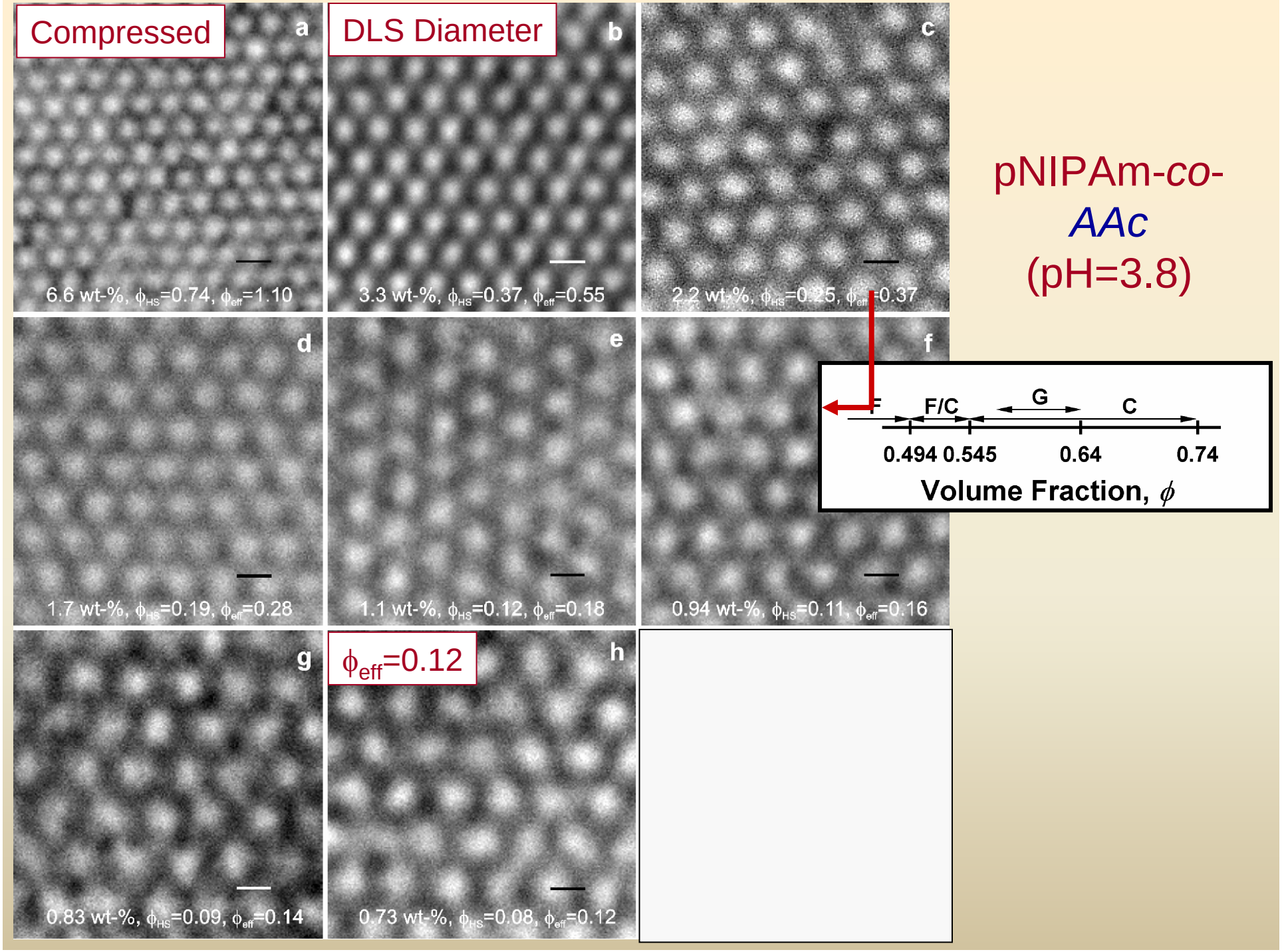
0.74
Volume Fraction, ϕ
pNIPAm-*co*-*AAc*
(pH=3.8)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DLS Diameter
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d
1.7 wt-%, ϕ_{HS}=0.19, ϕ_{eff}=0.28
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1.1 wt-%, ϕ_{HS}=0.12, ϕ_{eff}=0.18
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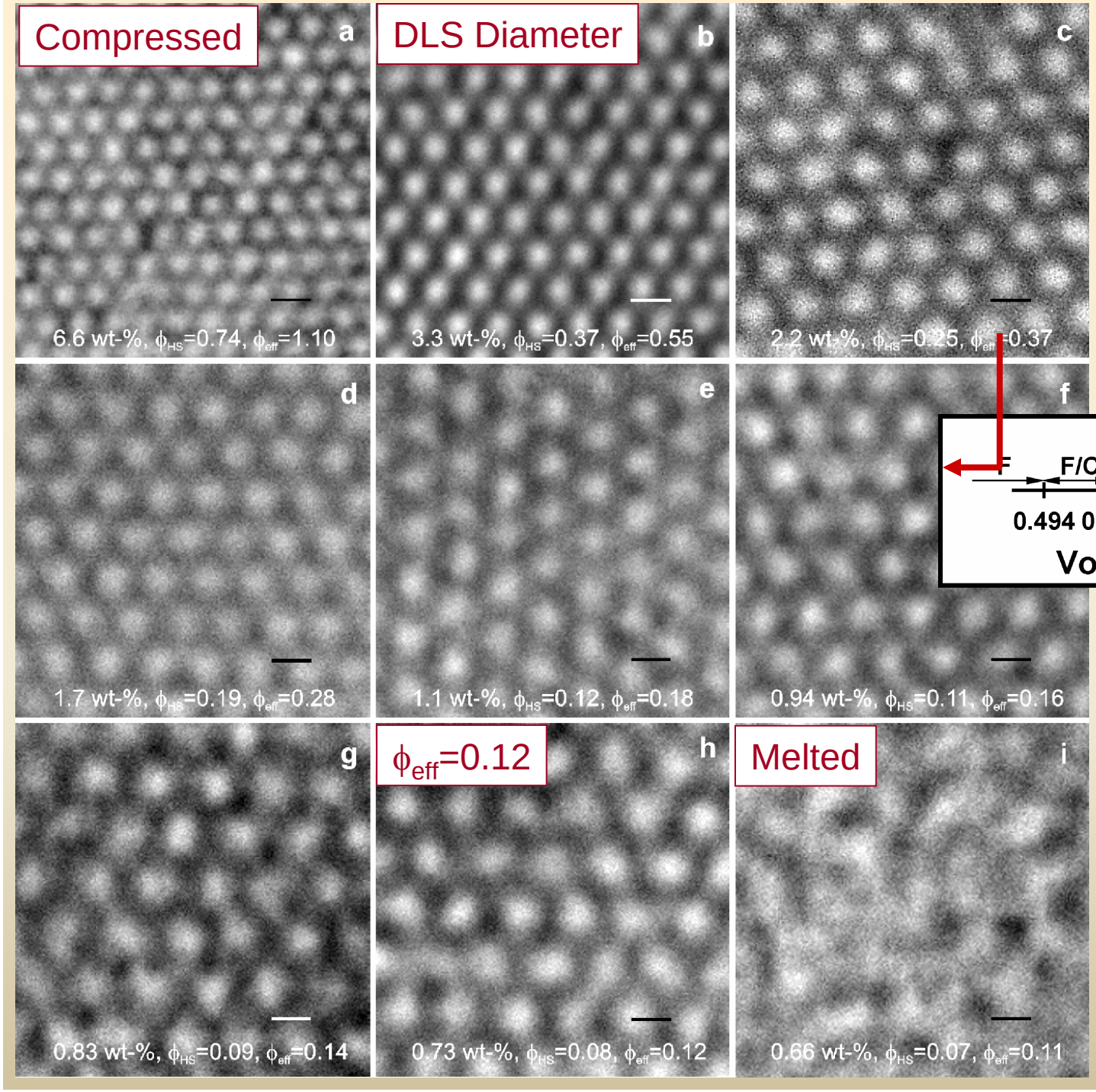
F
F/C
G
C
0.494 0.545
0.64
0.74
Volume Fraction, ϕ
g
0.83 wt-%, ϕ_{HS}=0.09, ϕ_{eff}=0.14
ϕ_{eff}=0.12
h
0.73 wt-%, ϕ_{HS}=0.08, ϕ_{eff}=0.12



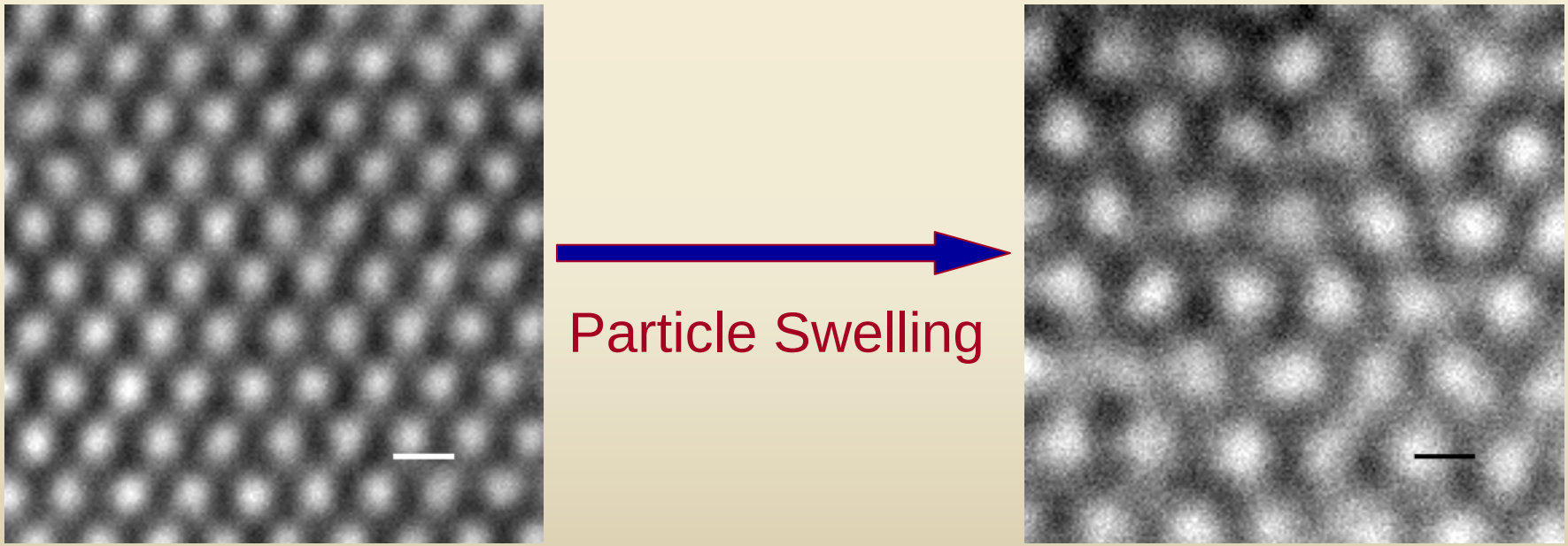
pNIPAm-*co*-*AAc*
(pH=3.8)

Increased thermal phase stability also observed.
T_m>50 C for most samples.

pNIPAm-AAc Crystal Stability

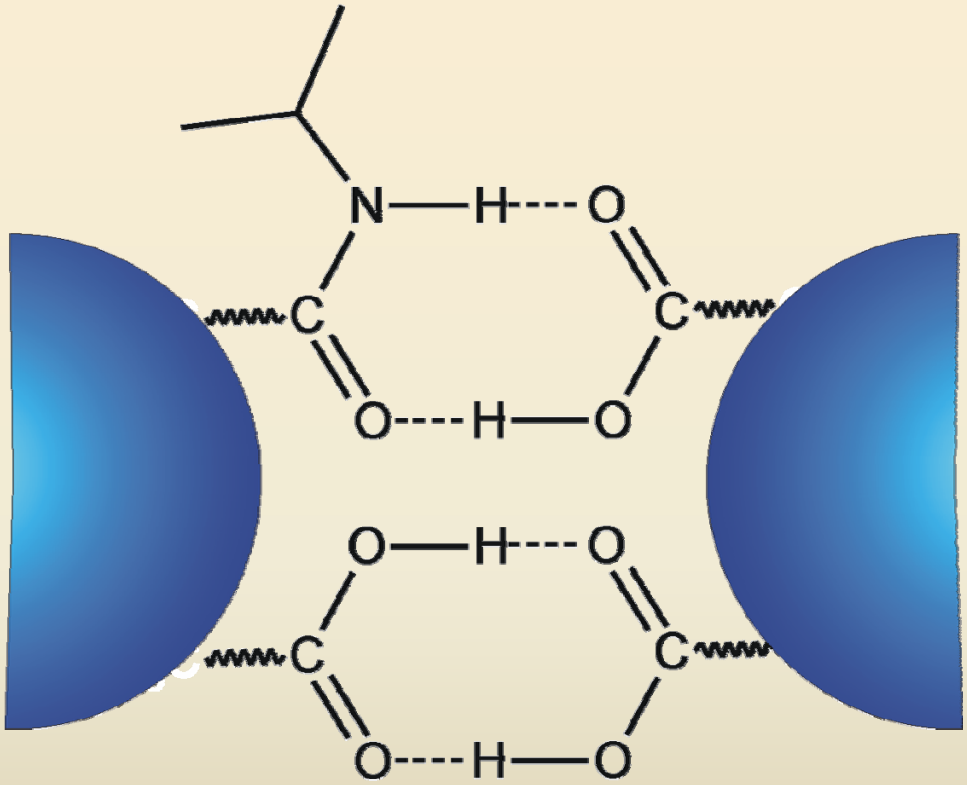
How can particles remain crystallized at such low particle concentrations/high temperatures?
How can the particle size be *larger* than that measured in dilute solution by DLS?

This is all Entropically UPHILL



Crystals via Attractive Forces

Hypothesis: Soft ATTRACTIVE forces must be at work.



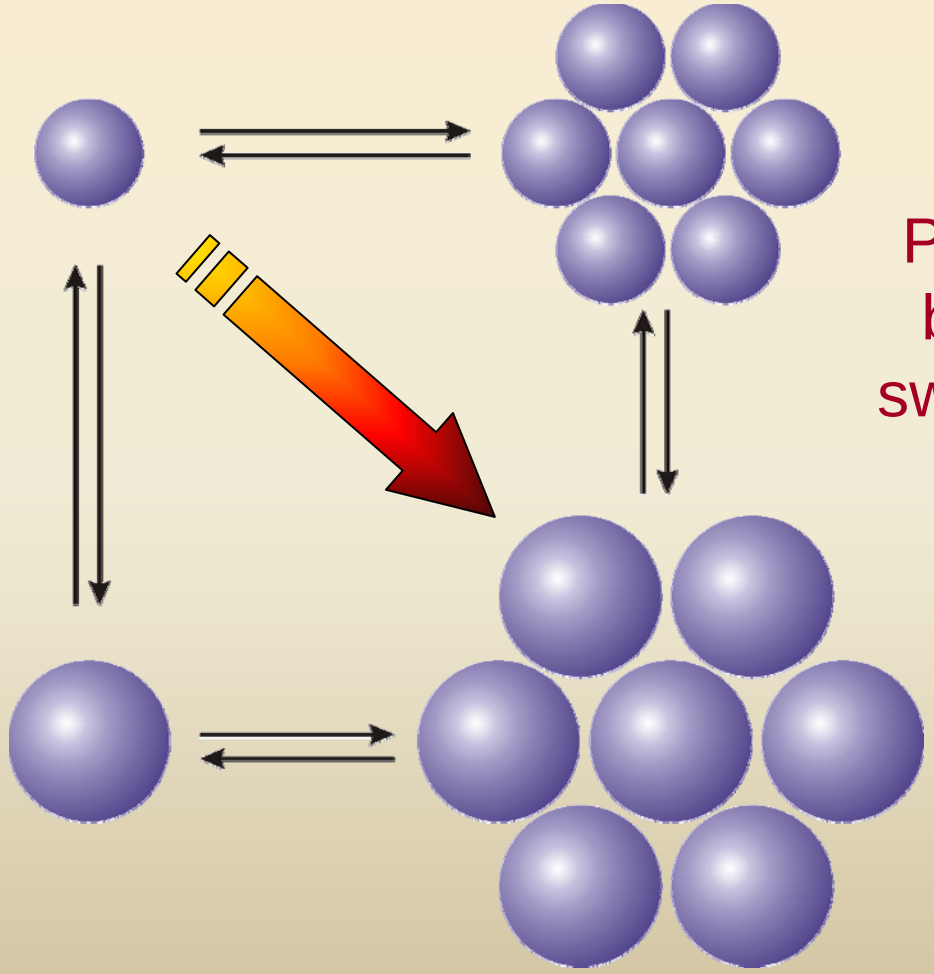
If attractive/repulsive forces are balanced correctly, soft attractive forces can dominate crystallization.

"Normal" phases at pH<3.5 → poor H-bonding.

Debord, S. B.; Lyon, L. A. *J. Phys. Chem. B*, **2003**, *107*, 2927-2932.

What is the Crystallization Mechanism?

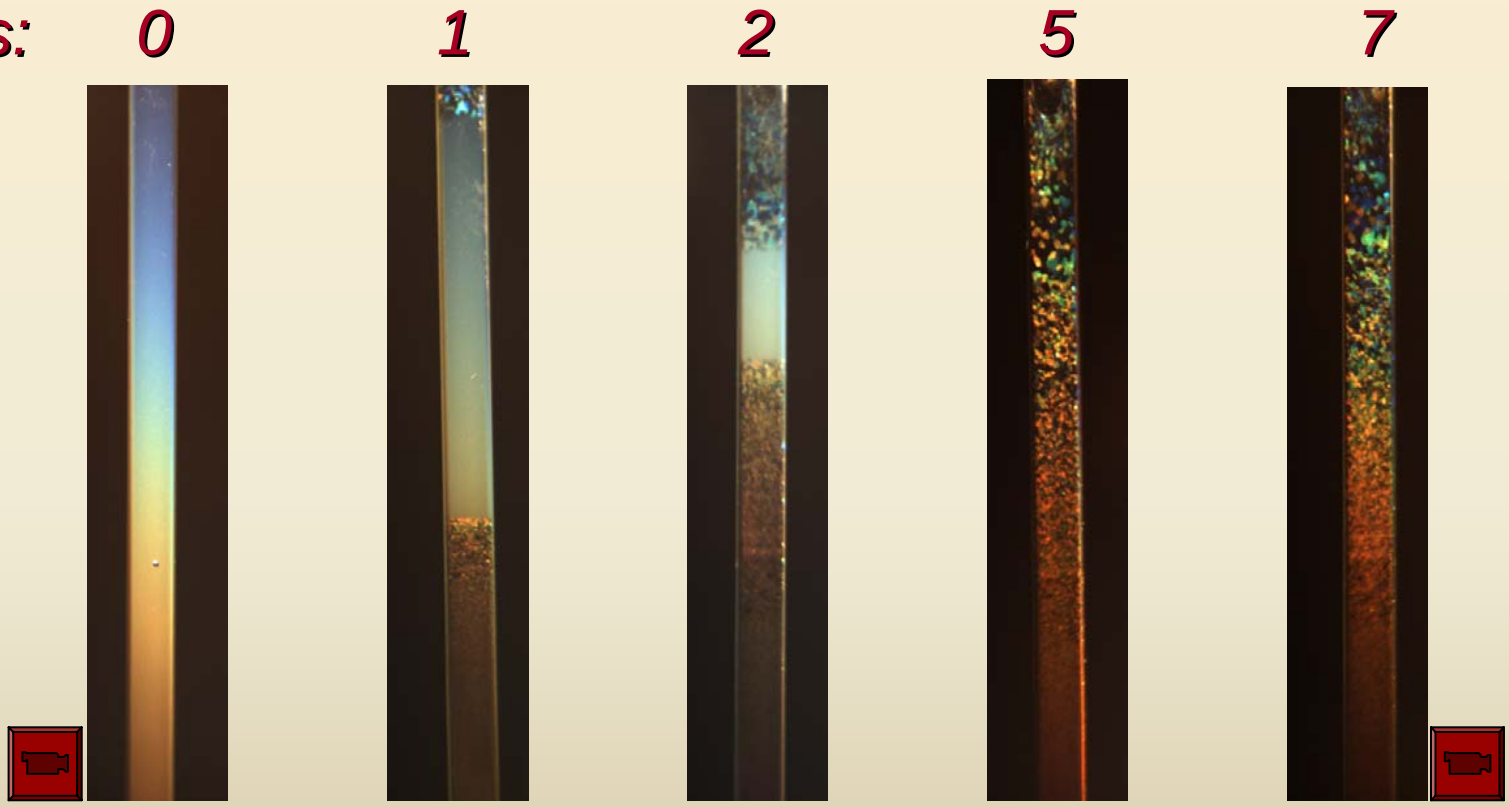
Enthalpic crystallization *without* aggregation must be dependent on a swelling-dependent, MULTIBODY interaction event.



Particle association must be coupled with particle swelling ⇨ both processes are apparently unfavorable.

Crystallization Dynamics

At the macroscopic scale, slow crystallization kinetics are observed for low volume fraction samples.

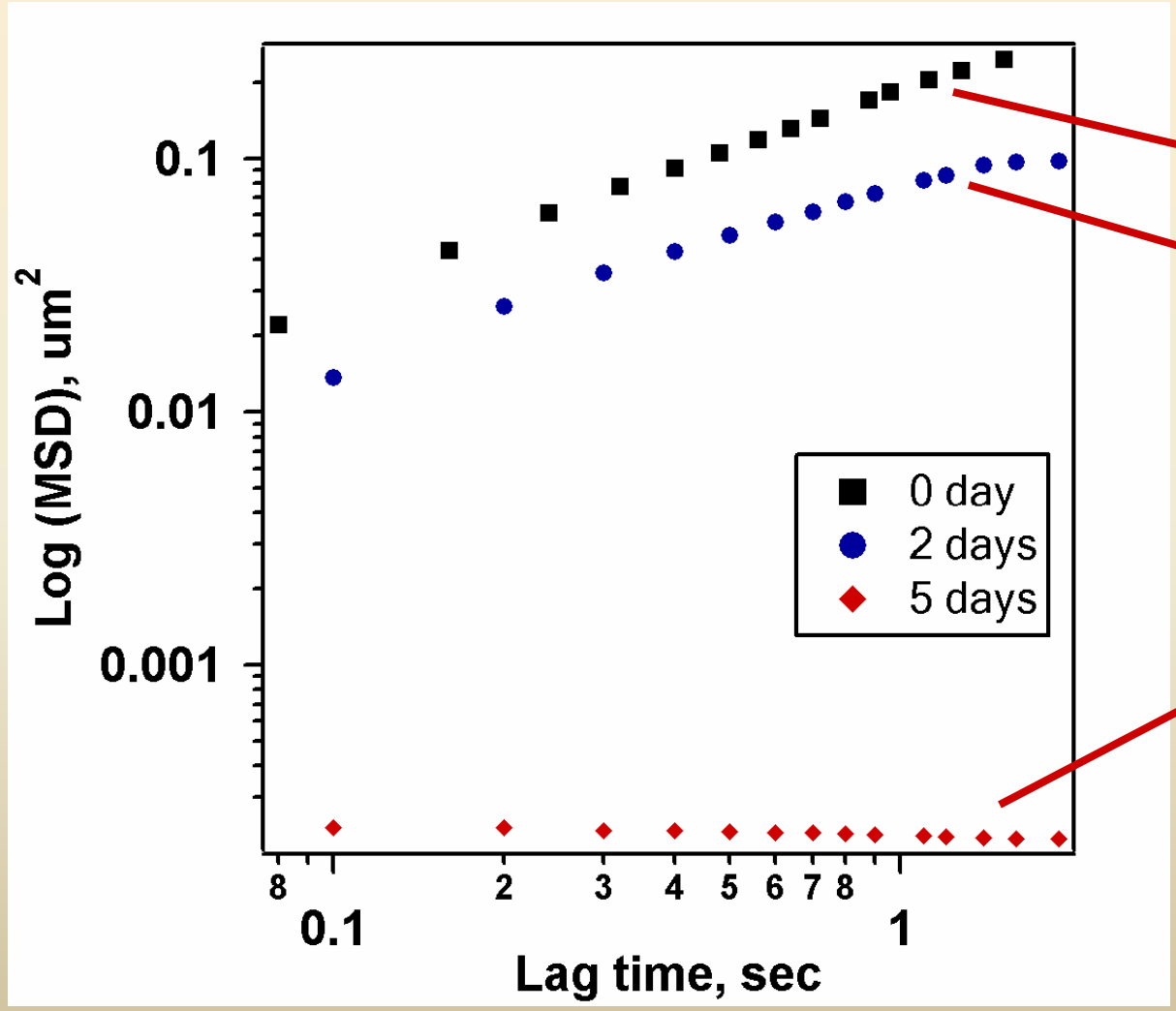


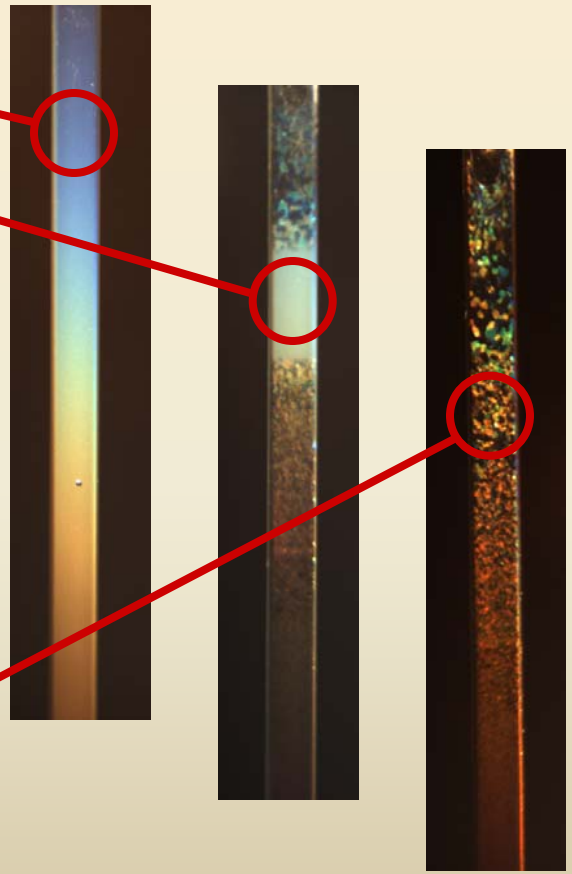
~35% effective volume fraction

~820-nm diameter pNIPAm-AAc; pH 3.8

Particle Tracking Analysis

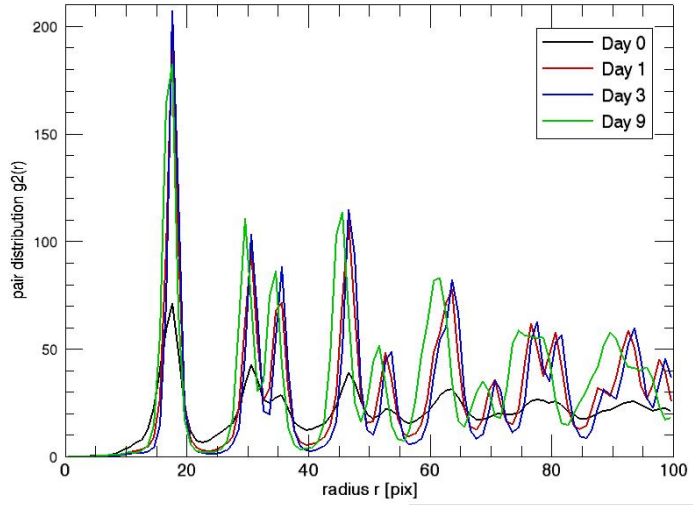
Microscopic tracking analyses illustrate "freezing" trend.



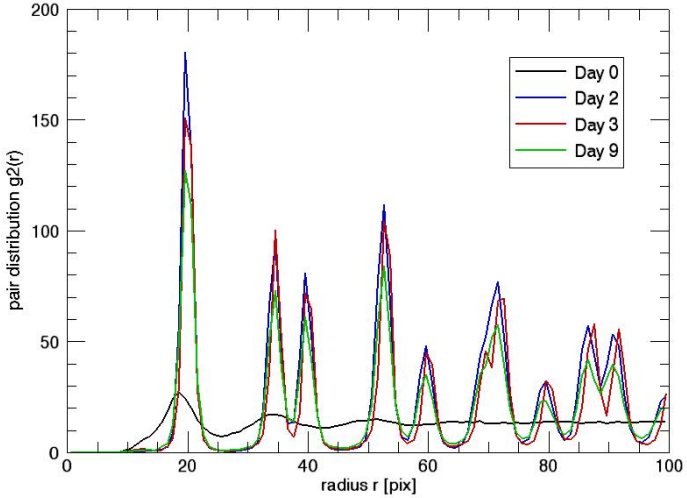


Evolution of Structure

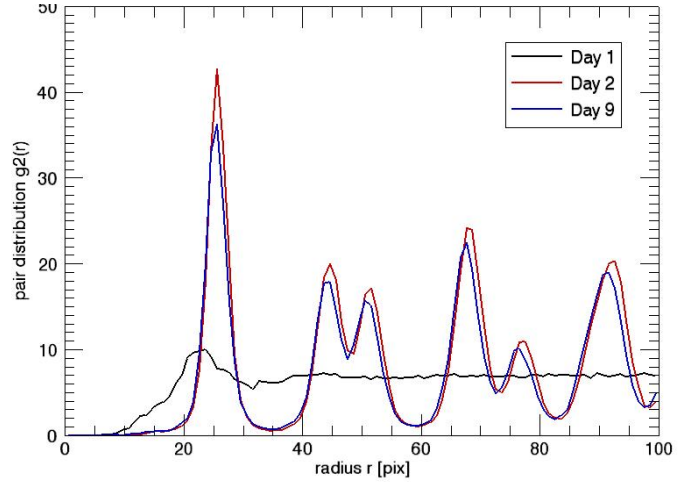
~54% volume fraction



~36% volume fraction

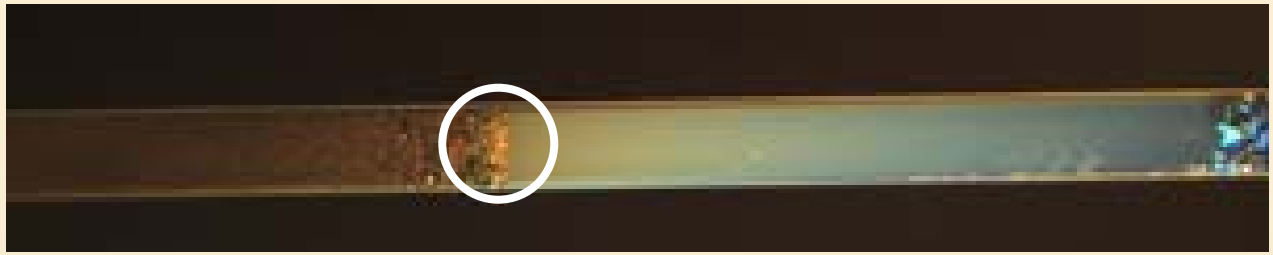


~17% volume fraction

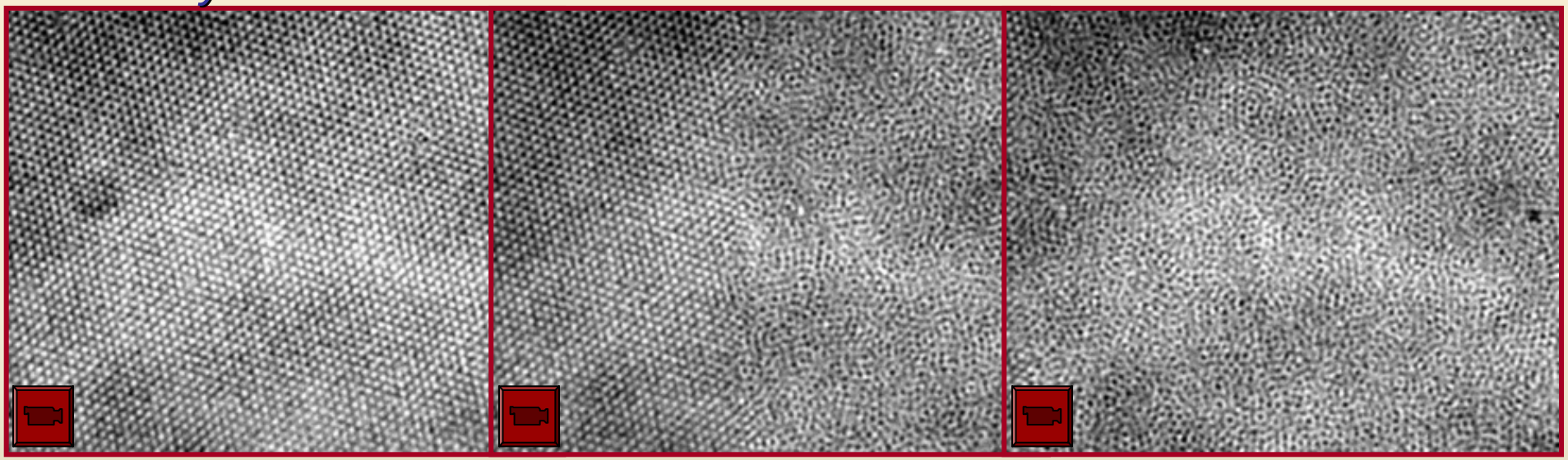


Radial pair distribution functions [*g(r)*] show degree of order.

Crystallization Dynamics II



Crystal *Phase Coexistence* *Fluid*

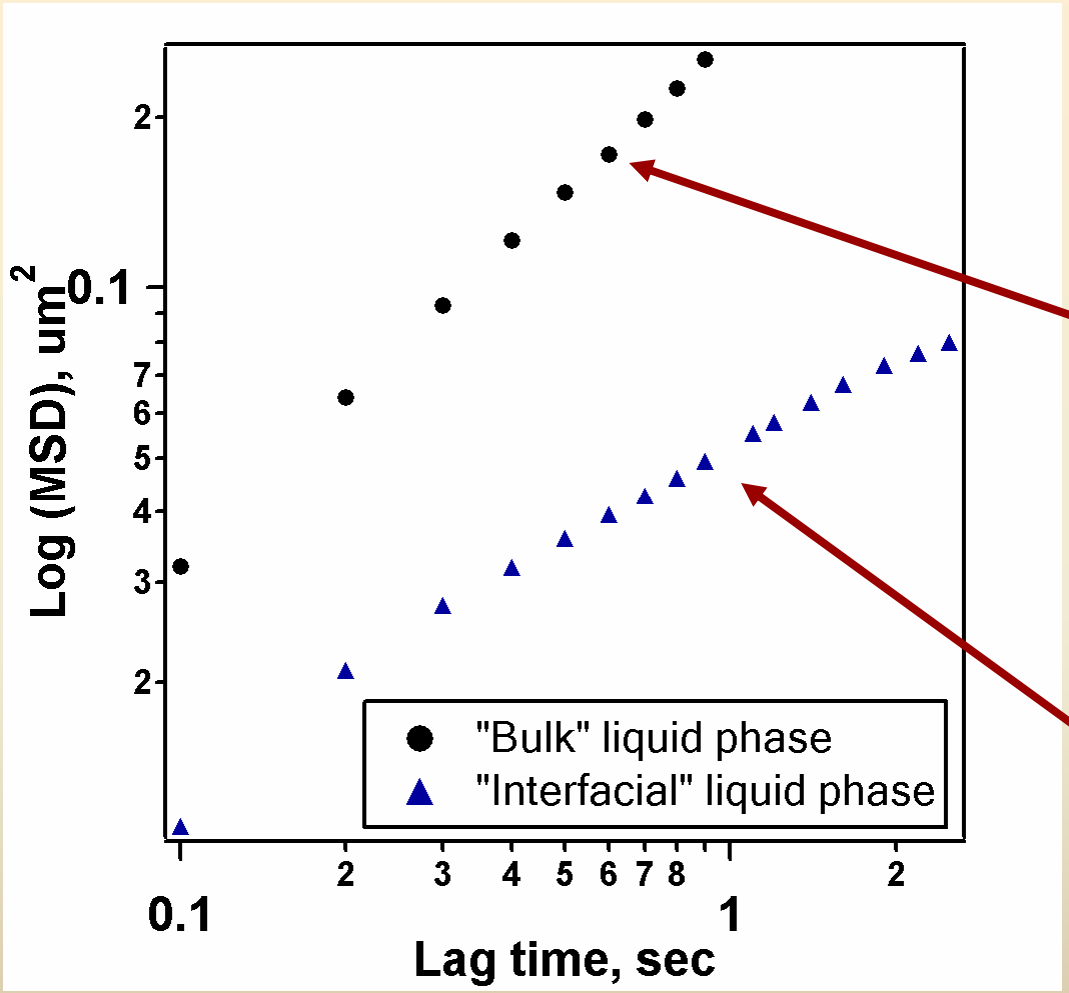


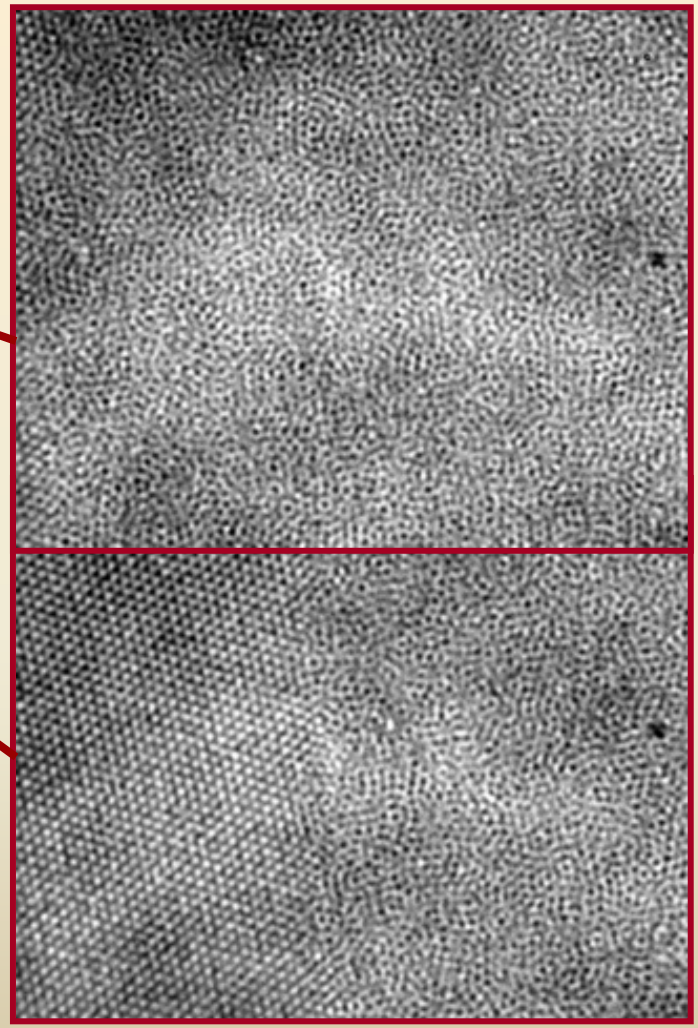
1 day old sample; ~**35%** effective volume fraction

~820-nm diameter pNIPAm-AAc; pH 3.8

Phase Dependent Diffusion

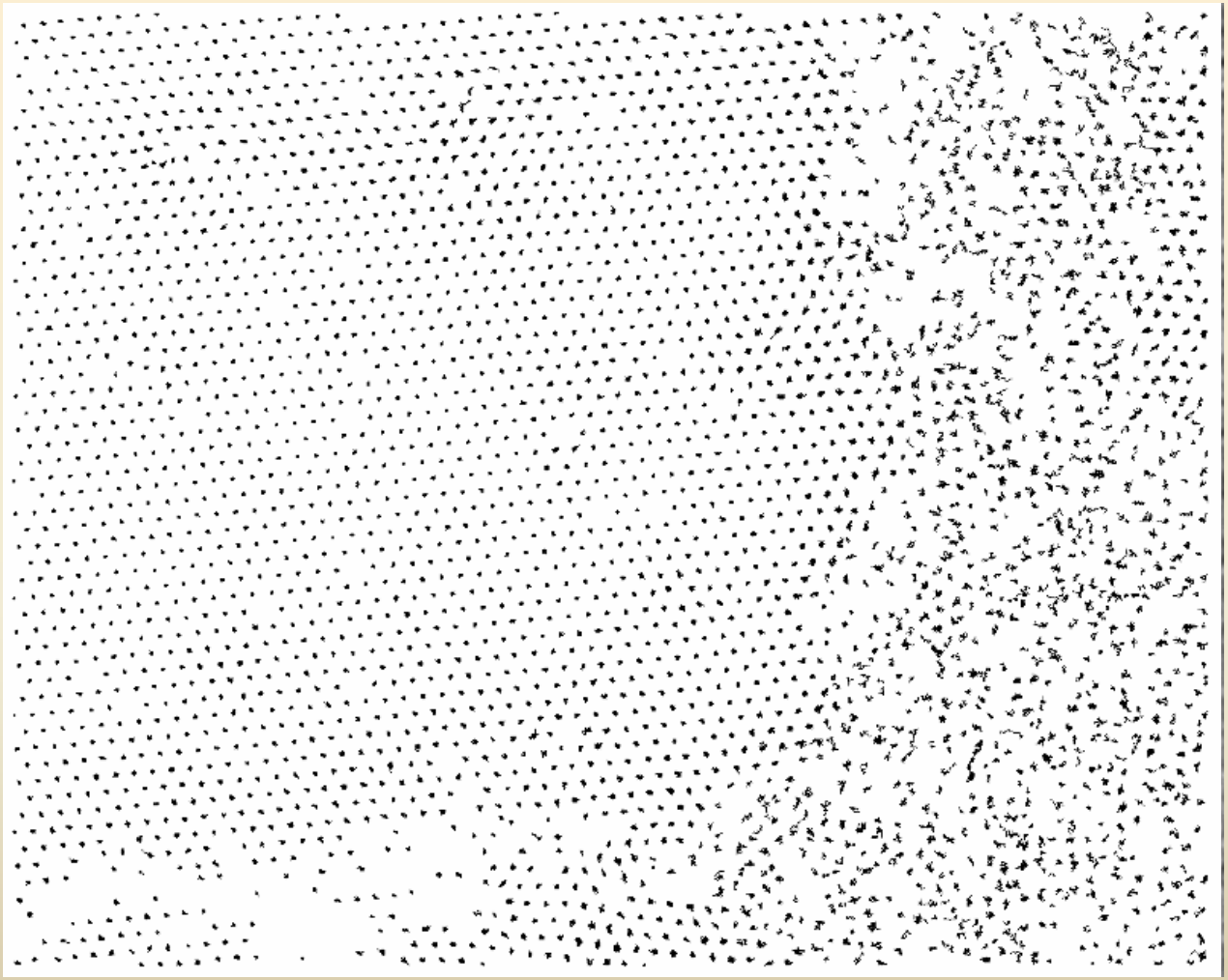
Tracking analysis reveals dynamics of growing interface.





Crystallization Dynamics

Tracking analysis of growing crystal – 36% volume fraction.



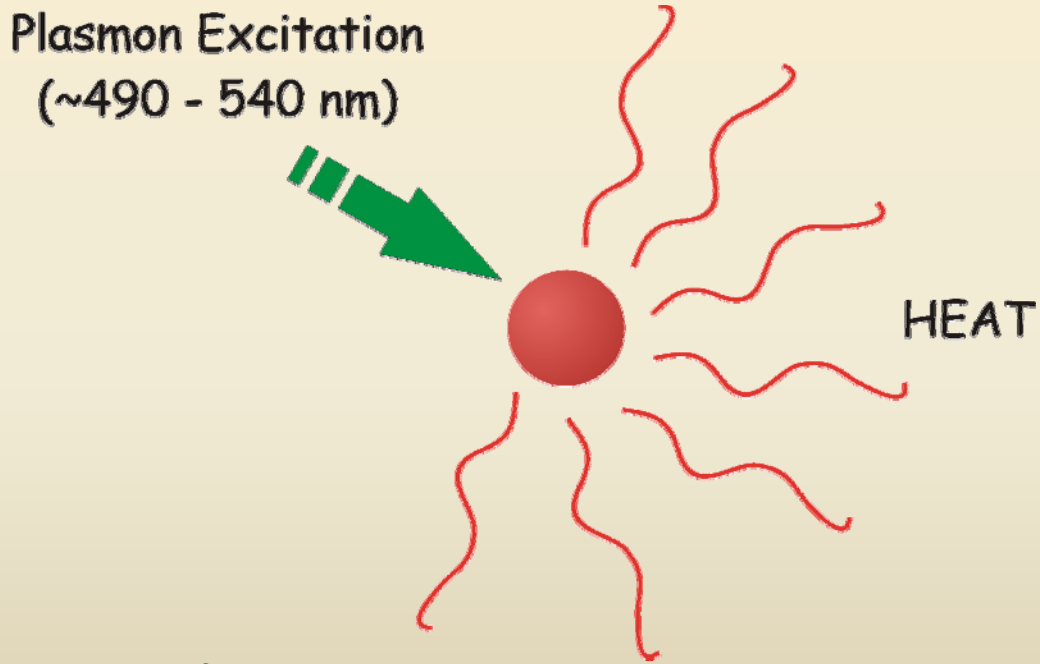
Summary: Attractive Assembly

- Unusual phase behavior for AAc-modified particles
- Thermal stability of xtals not correlated with LCST
- H-bonding implicated in attractive assembly
- Slow Assembly via Attractive Forces
- Phase dependent diffusion → long range forces in fluids?
- Sharp crystalline interfaces → extremely stable crystal facets

Part II: Can We Exploit T-Responsive Xtals?

Au nanoparticles are optically-addressable heaters ⇨ strong plasmon resonances.

Route to photo-manipulation of hydrogel crystals?



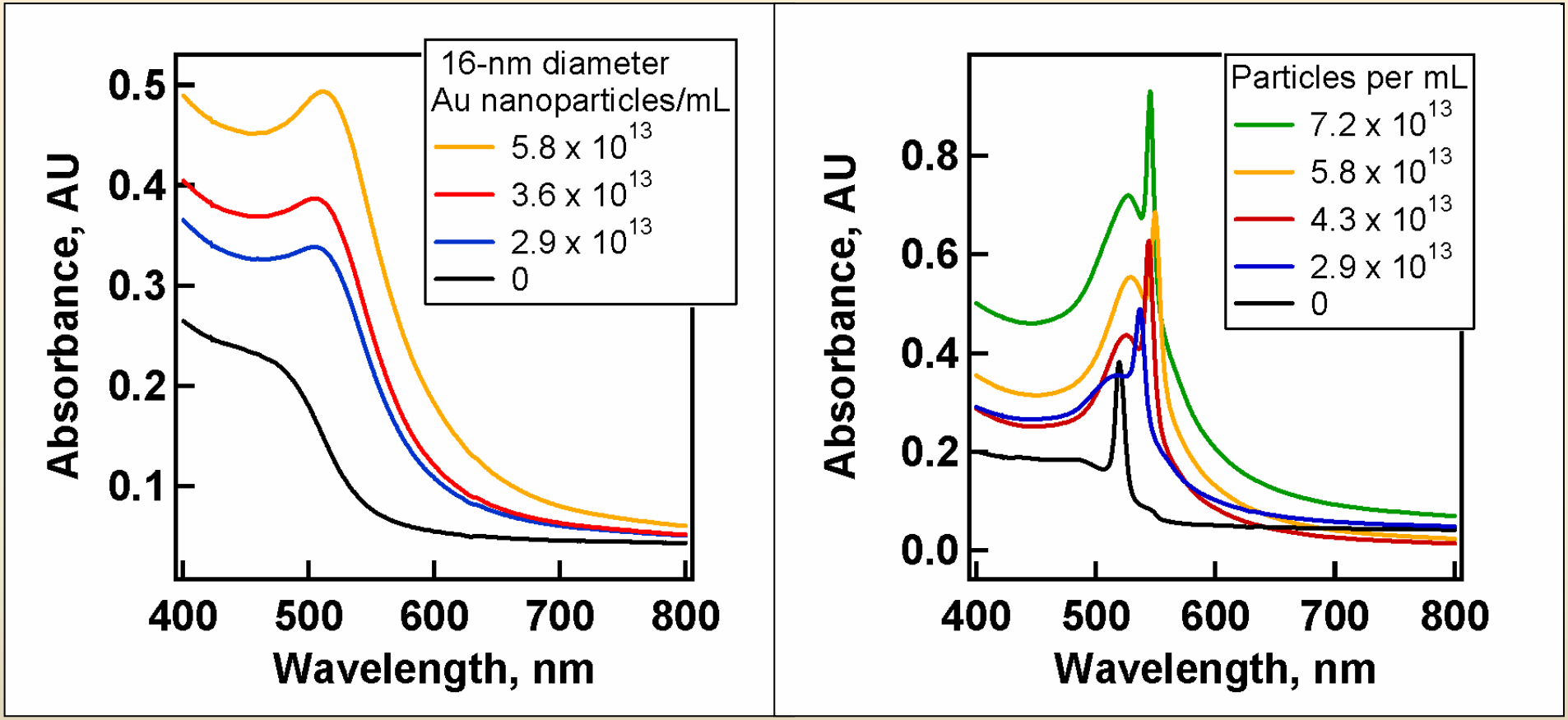
$\varepsilon \sim 1 \times 10^{9}\ M^{-1}cm^{-1}$ *(20 nm particle at 520 nm)*

photoemission yield ~ 0%

fast lattice relaxation ~ 10-100 ps

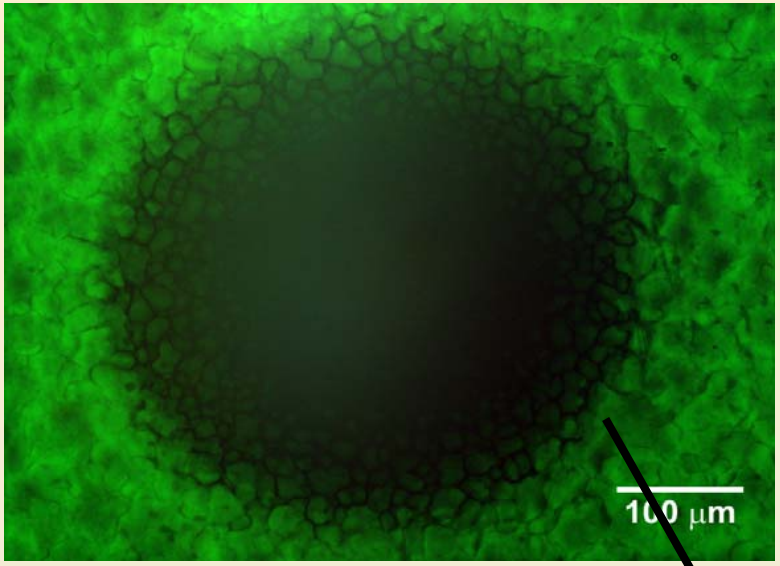
Au@Crystal Composites

Co-centrifugation of Au NPs with Microgels

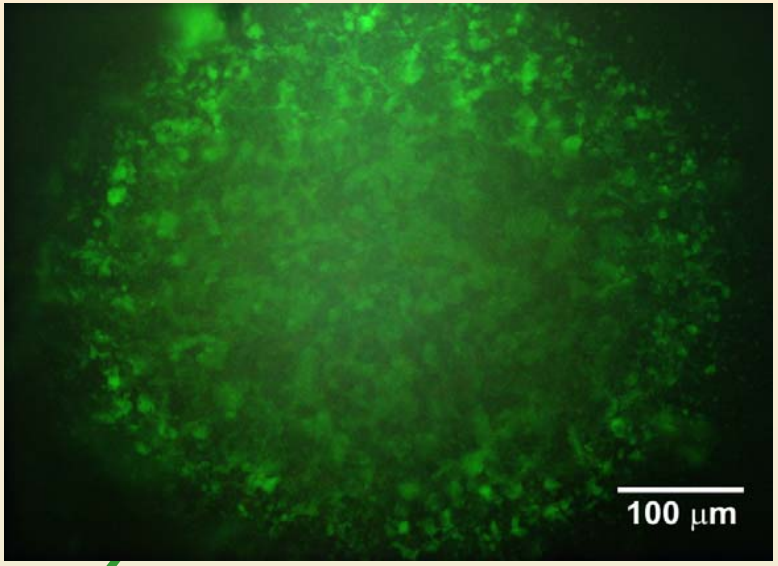


Thermal Anneal

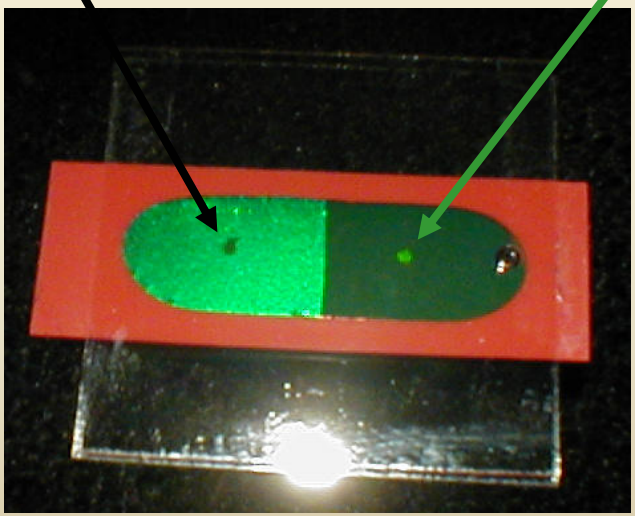
Laser Annealing/Melting



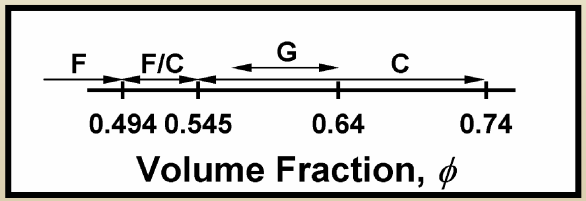
λ_{ex} = 532 nm



High Flux:
Glassy patterned into crystalline

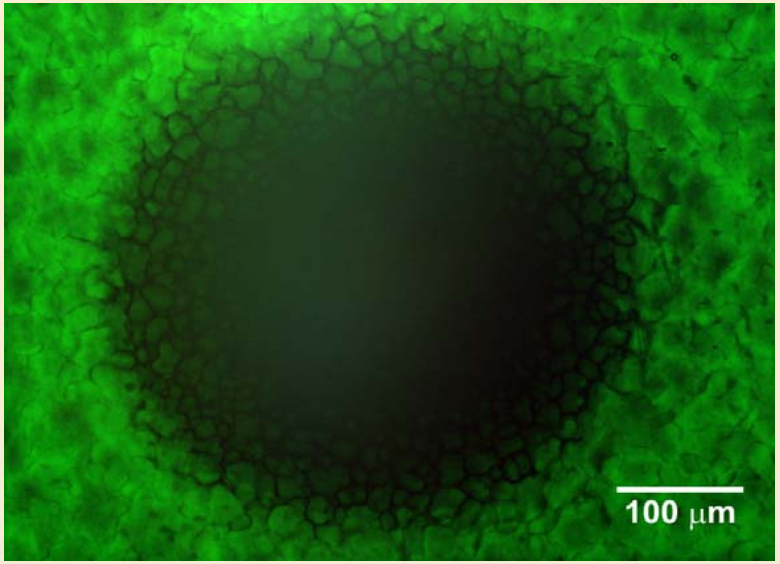


Low Flux:
Crystalline patterned into glassy

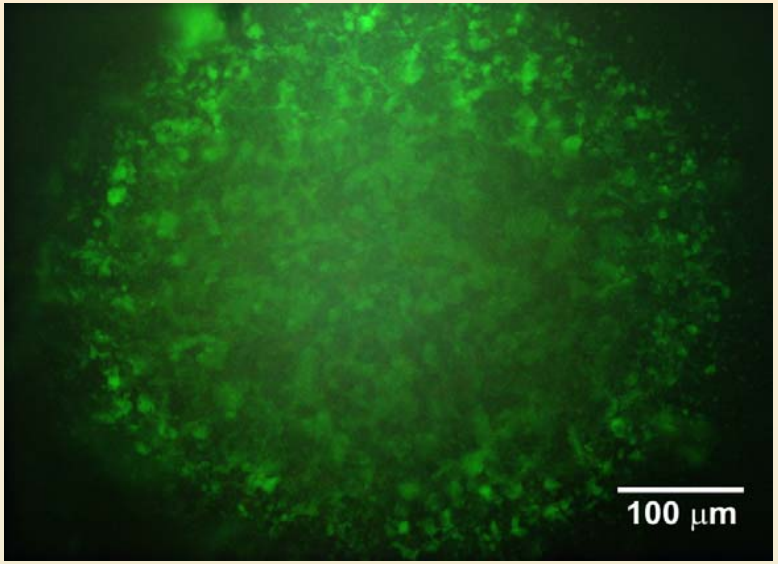


Jones, C. D.; Lyon, L. A. *J. Am. Chem. Soc.* **2003**, 125, 460-465.

Laser Annealing/Melting



λ_{ex} = 532 nm



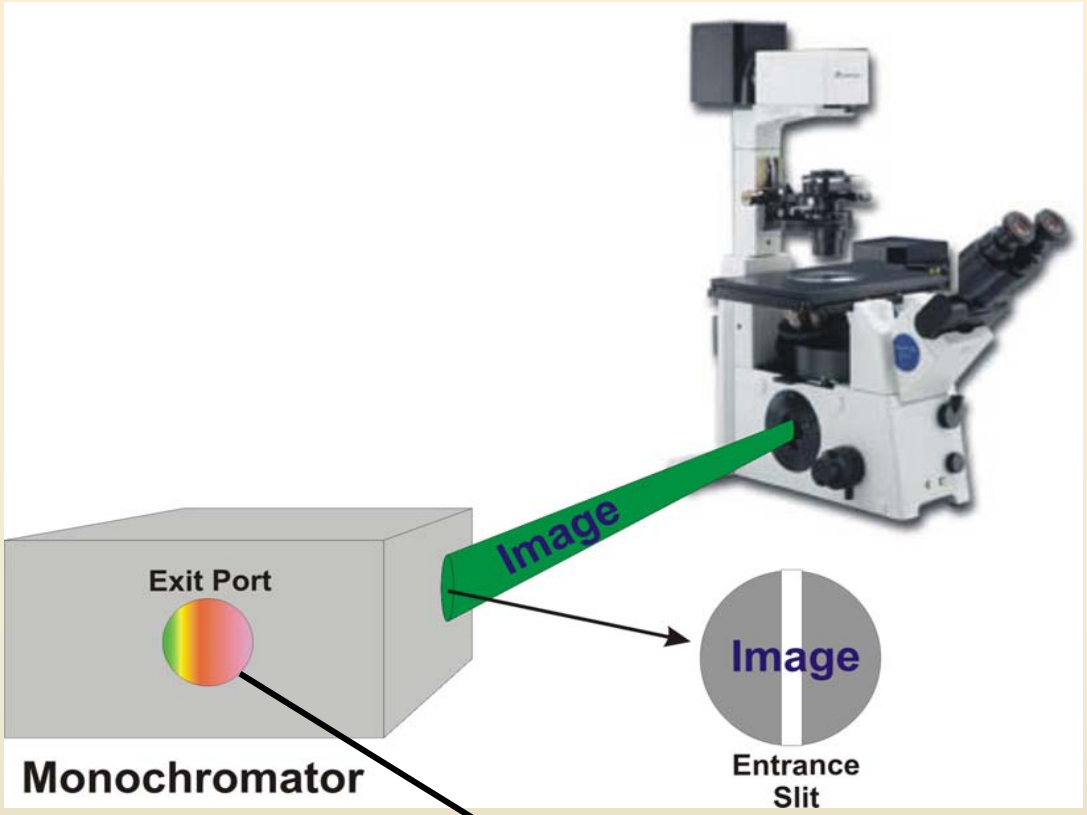
High Flux:
Glassy patterned
into crystalline

Low Flux:
Crystalline patterned
into glassy

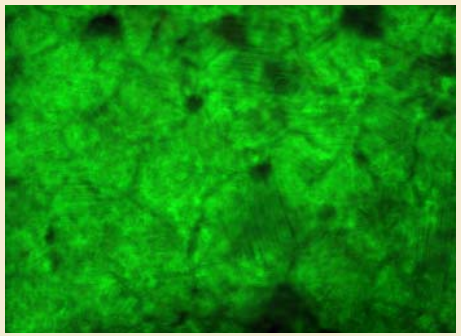
Laser flux determines local temperature and the effective cooling rate → Flux determines crystal phase.

Jones, C. D.; Lyon, L. A. *J. Am. Chem. Soc.* **2003**, 125, 460-465.

Microspectrophotometry

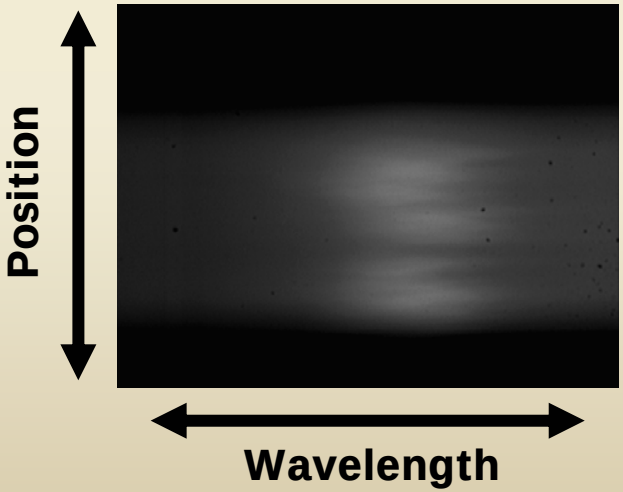


Analysis of single crystal optical properties.

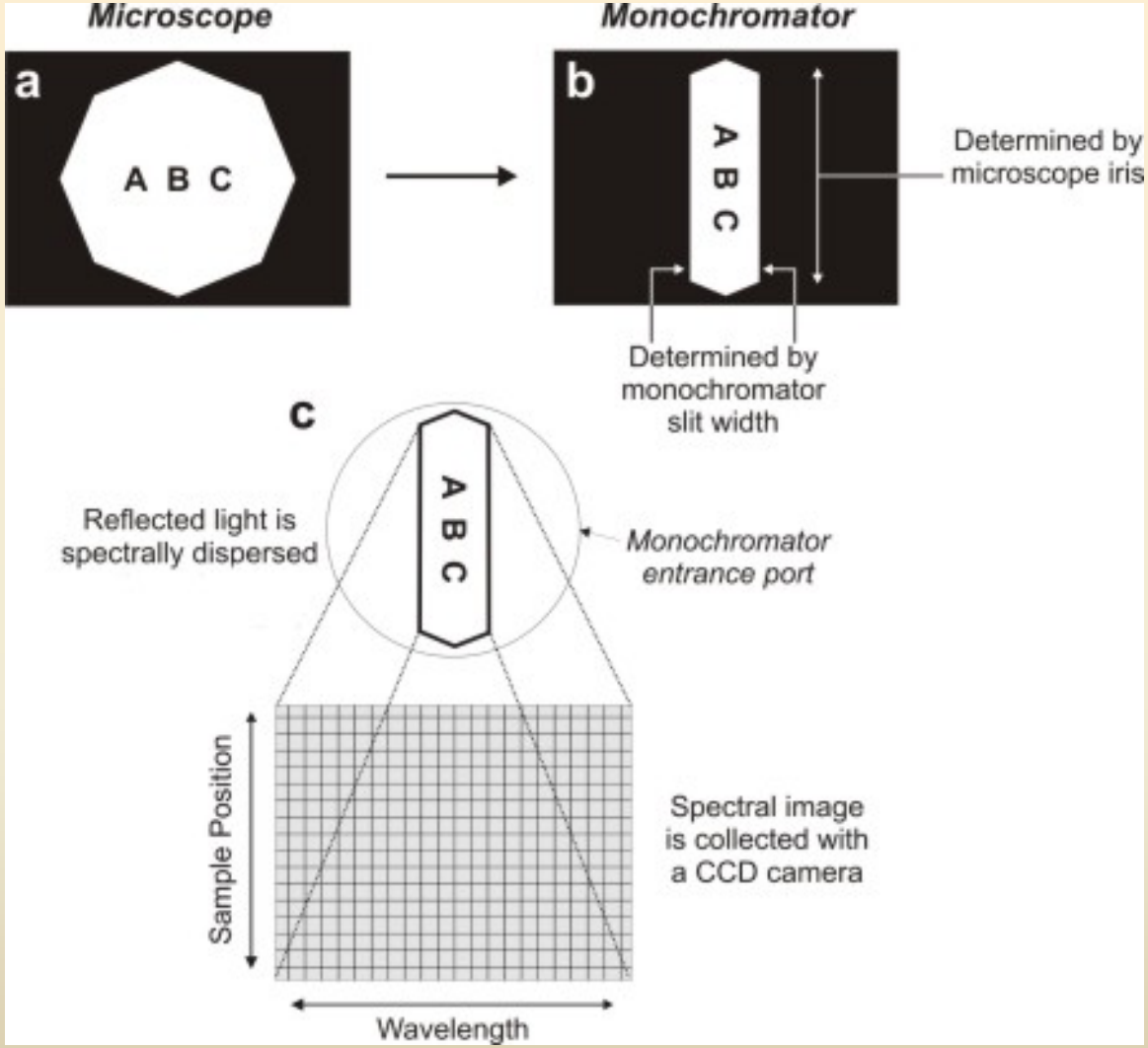


CCD Camera

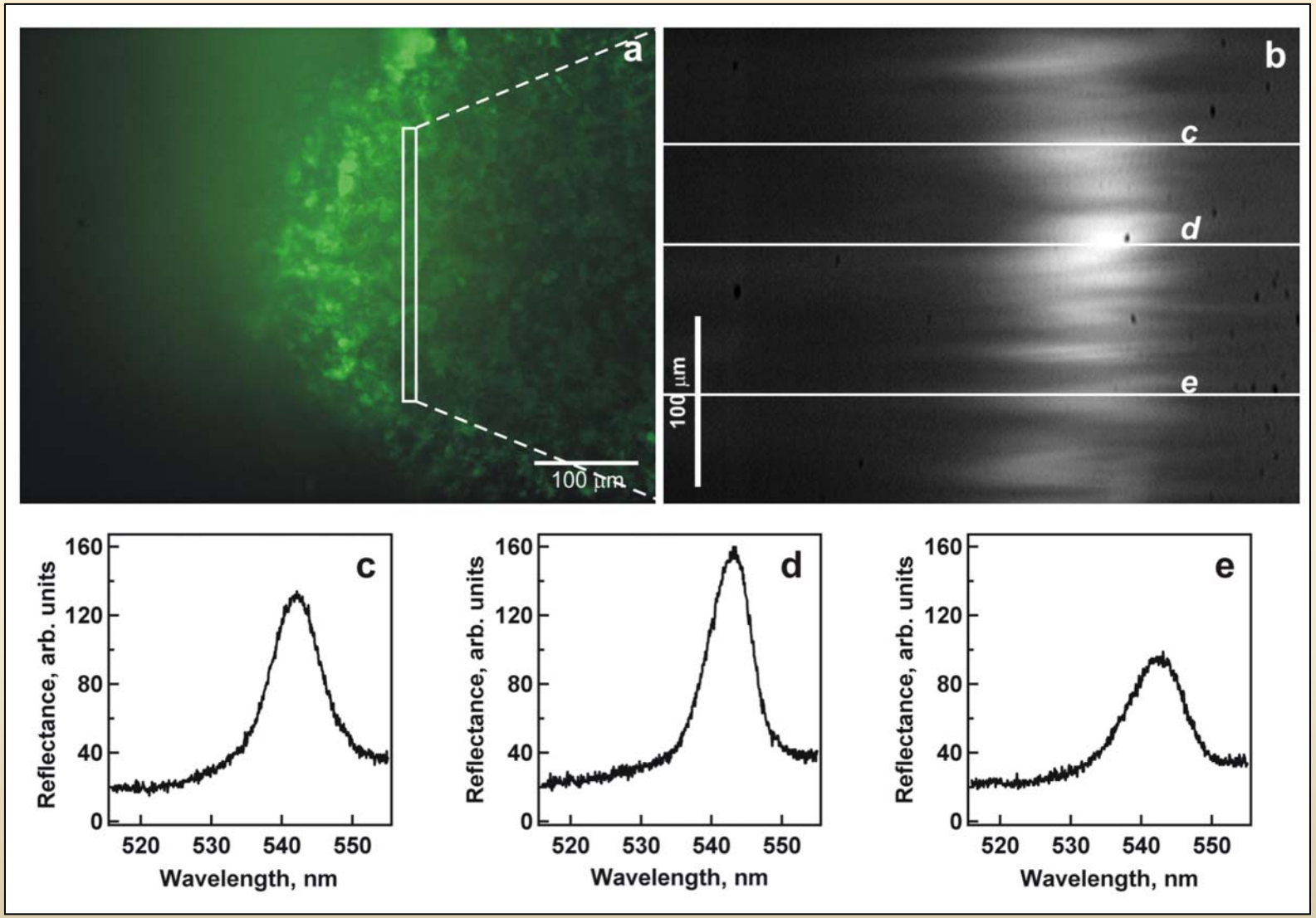
CPU



Microspectrophotometry

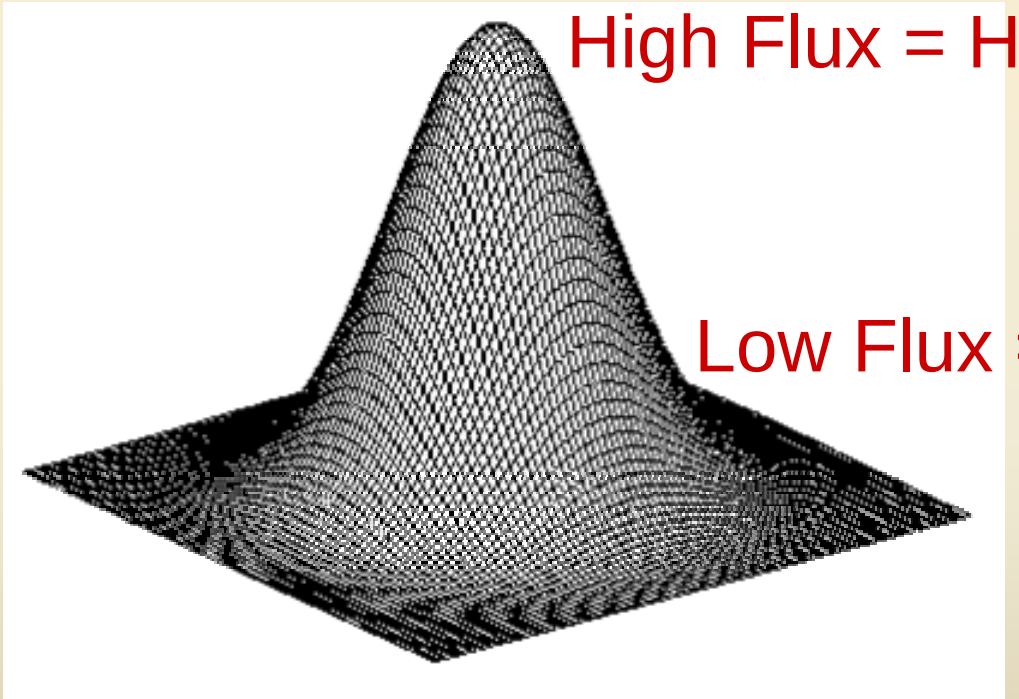


Spectral Imaging



Fine Tuning Phase Manipulation

Beam with Gaussian intensity profile → spatial (photothermal) control over crystallization?

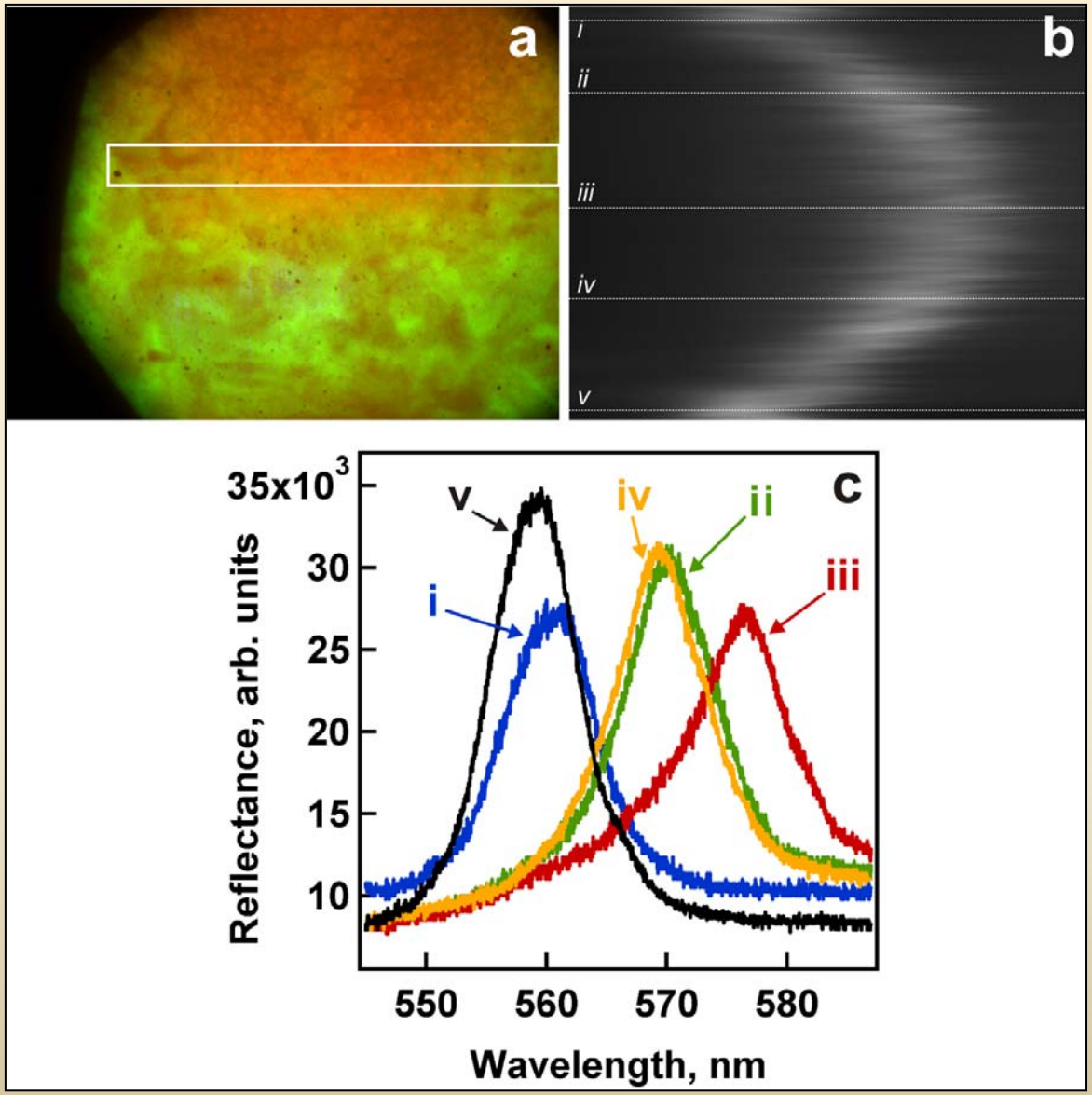


High Flux = High T = Fast Cooling

Low Flux = Low T = Slow Cooling

What is the resultant structure?

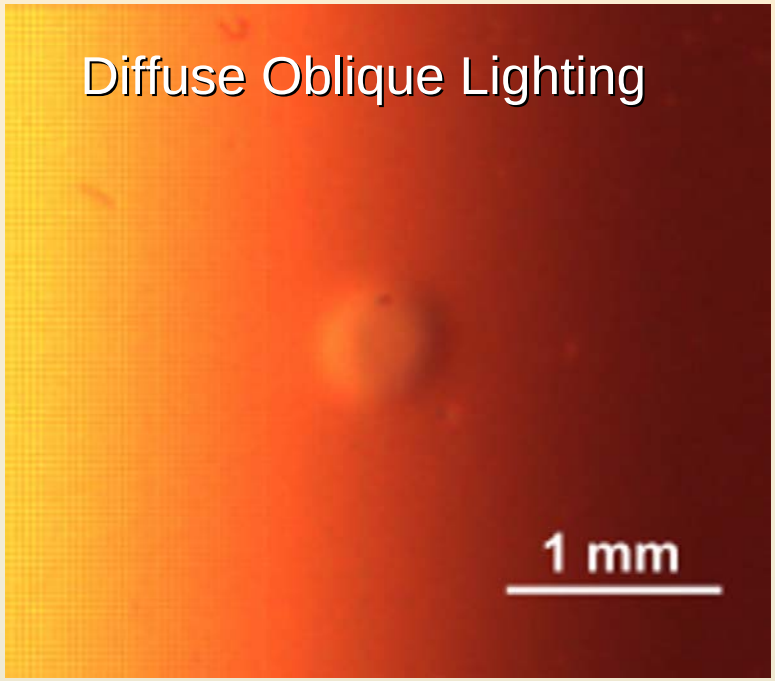
Lattice Constant Gradients

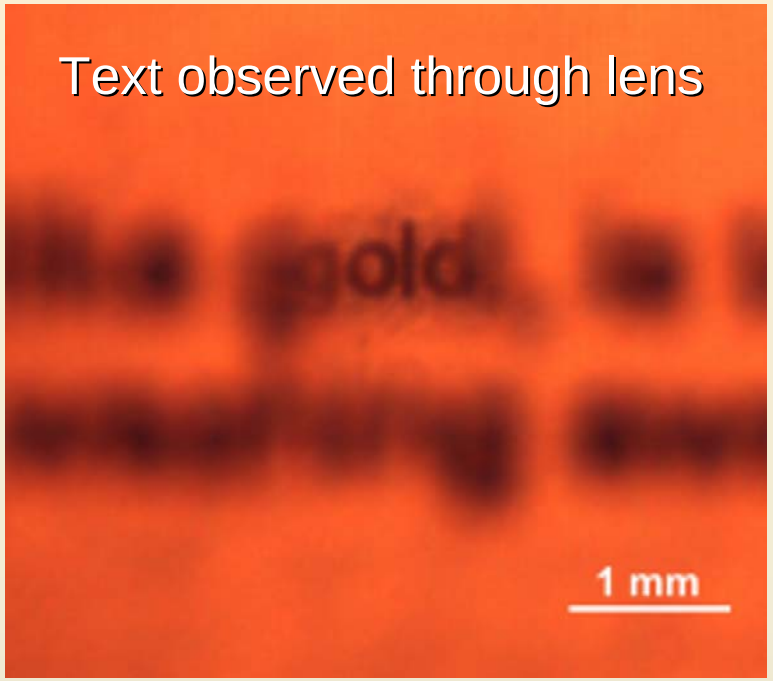


Patterned region imaged immediately after irraditation →

Bragg Peak (lattice constant) varies radially across area.

Microlenses from Bragg Gradients

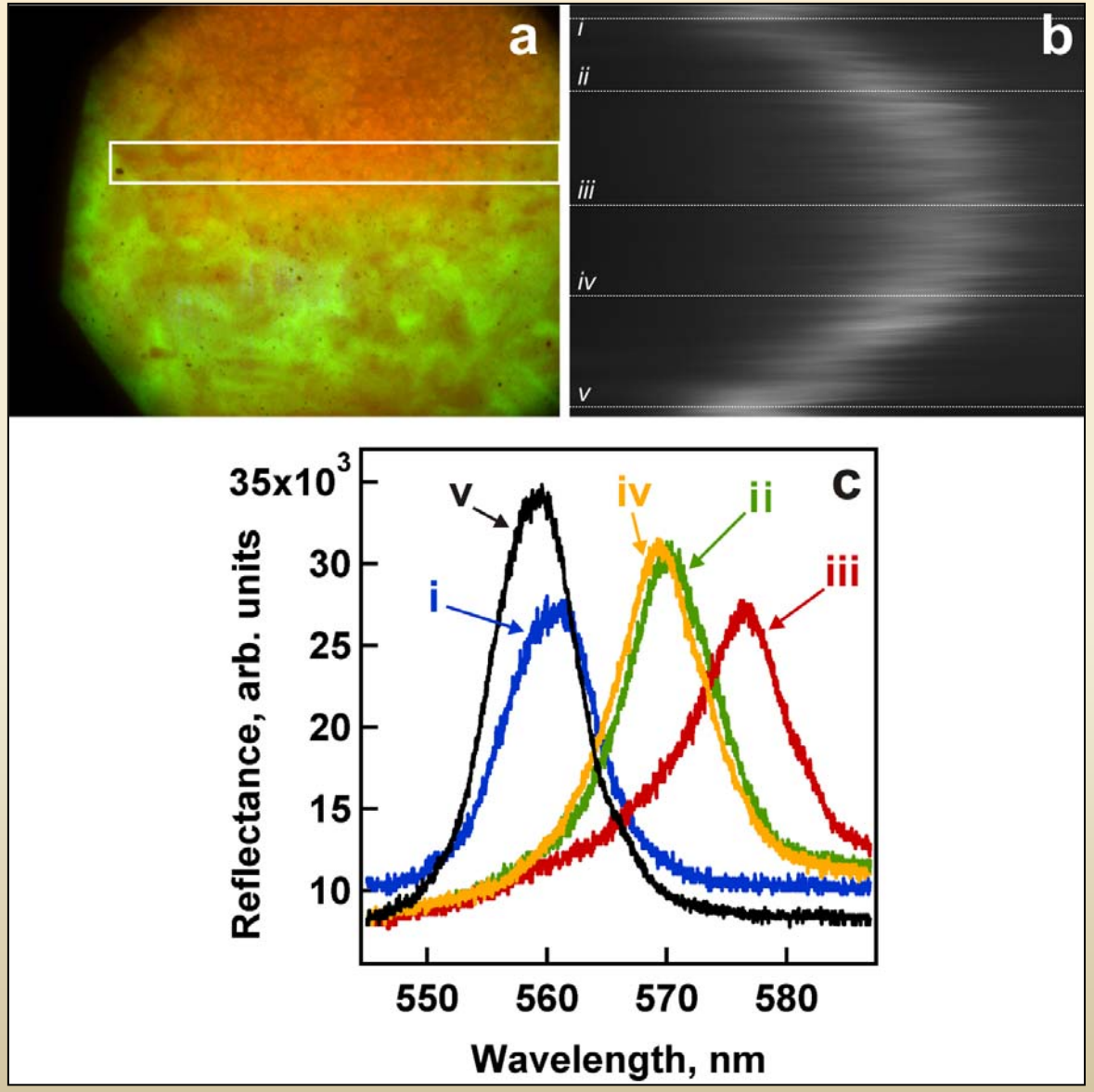




Structures with gradient structure are highly effective (fluid) microlenses.

Jones, C. D.; Serpe, M. J.; Schroeder, L.; Lyon, L. A., *J. Am. Chem. Soc.,* **2003**; *125,* 5292-5293.

Wavefront GRIN (GRadient INdex) Lenses



Lens “curvature” arises from a radial refractive index gradient.

Observed as a gradient in crystal lattice constants.

Conclusions

Responsive hydrogel nanoparticles (nanogels) offer opportunities to assemble “self-healing” colloidal crystalline materials with tunability and responsivity.

Crystallization can be *Repulsive* or *Attractive* if the soft, multibody interaction potentials are balanced.

Attractive forces dramatically change the phase diagram for soft spheres.

Soft, thermoresponsive assemblies can be manipulated through photothermally directed crystal/glass transitions.

Lens-like structures can be made by spatial control of heating/cooling rates.

Acknowledgements

The Group

Justin Debord (g) – Bioconjugates
Clint Jones (g) – Core-Shell/Crystals (now at PSU)
Christine Nolan (g) – Thin Films/Insulin Delivery
Satish Nayak (g) – Bioconjugates
SaetByul (Stella) Debord (g) – Colloidal Crystals
Mike Serpe (g) –Thin Films/Lenses/Drug Delivery
Jonathan McGrath (g) – Templated Microgels
Jongseong Kim (g) – Films/Polyelectrolytes/Lenses
Ashlee St.John (g) – Colloidal Crystals
Bart Blackburn (g) – Cell Targeting
Neetu Singh (g) – Bioconjugates
Ryan Mulkeen (ug) – Colloidal Crystals

Collaborators

Victor Breedveld (GT-ChE)
Mohan Srinivasarao (GT-PTFE)
Jean Chmielewski (Purdue-Chem)
Mike Ogawa (BGSU-Chem)
Joe LeDoux (GT-BME)

Support

NSF-CAREER
NSF-DMR
NSF-STC (MDITR)
Office of Naval Research
DARPA (BOSS)
Beckman Foundation
Sloan Foundation
Dreyfus Foundation
GT Blanchard Fellowship