Colloidal Crystals of Responsive Hydrogels

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Opals: Structure and Optics

**Assembly**

**Structure**

**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).

- **Collapsed state**: *Chain-chain* interactions dominate.
- **Swollen state**: *Solvent-chain* interactions dominate.

*Change in local environment:
  - pH, Photons, Temperature, Ionic Strength, Electric Fields, Pressure, [Analyte]*
Thermo-Responsive Gels

\textit{poly}(N\text{-isopropylacrylamide}) (pNIPAm)

Swollen/Hydrophilic $\rightarrow$ Collapsed/Hydrophobic

31 °C
pNIPAm Microgel Synthesis

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 \textit{all surface area}

Highly Monodisperse
Volume Phase Transitions

Dynamic Light Scattering (Photon Correlation Spectroscopy)

2 mol% crosslinked pNIPAm in water
Dual-Response Microgels

*pNIPAm-co-Acrylic Acid*

pH dependent size and phase transition temperature

![Graph showing pH dependent size and phase transition temperature](image)
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

Fluid
Colloidal Hard Sphere Phases

Entropic Crystallization

Coexistence

Pressure ($P$)

Volume Fraction ($\phi$)

To RCP

Metastable branch

Freezing

Melting

To FCC (Close Packed)

0.49

0.56

0.74
Colloidal Hard Sphere Phases

**Entropic Crystallization**

Crystal
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

- **Glassy (Transparent)**
- **Melt (Opaque)**
- **Crystalline (Bragg Reflector)**

Wavelength, nm

Extinction, AU
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

DIC Microscopy:
810-nm diam.
pNIPAm spheres

11.7 wt-%, $\phi_{HS}=0.74$, $\phi_{eff}=1.96$
DIC Microscopy: 810-nm diam. pNIPAm spheres
Soft Sphere Phase Behavior

Compressed

DIC Microscopy:
810-nm diam.
pNIPAm spheres

DLS Diameter

11.7 wt-%, $\phi_{HS}=0.74, \phi_{eff}=1.96$

5.85 wt-%, $\phi_{HS}=0.37, \phi_{eff}=0.98$

3.90 wt-%, $\phi_{HS}=0.25, \phi_{eff}=0.65$

Volume Fraction, $\phi$

494 545 64 74
Soft Sphere Phase Behavior

Compressed

DIC Microscopy: 810-nm diam. pNIPAm spheres

DLS Diameter

Melted

11.7 wt-%, $\phi_{HS}=0.74$, $\phi_{eff}=1.96$

5.85 wt-%, $\phi_{HS}=0.37$, $\phi_{eff}=0.98$

3.90 wt-%, $\phi_{HS}=0.25$, $\phi_{eff}=0.65$

2.93 wt-%, $\phi_{HS}=0.19$, $\phi_{eff}=0.49$

Volume Fraction, $\phi$

0.494 0.545 0.64 0.74
Wavelength Tunability via Compression

R_{initial} = 260 \text{ nm}
R1 = 275 \text{ nm}
R2 = 266 \text{ nm}
R3 = 254 \text{ nm}
R4 = 210 \text{ nm}
R5 = 197 \text{ nm}


Hydrogel Compression
(Slightly) More Complex Interactions??
Compressed

6.6 wt-%, $\phi_{\text{is}}=0.74$, $\phi_{\text{ex}}=1.10$

pNIPAm-co-AAc (pH=3.8)

Volume Fraction, $\phi$
pNIPAm-co-AAc (pH=3.8)

Compressed

DLS Diameter

\[ \phi_{\text{eff}} = 0.12 \]

6.6 wt-%, \( \phi_{\text{cp}} = 0.74 \), \( \phi_{\text{cr}} = 1.10 \)

3.3 wt-%, \( \phi_{\text{cp}} = 0.37 \), \( \phi_{\text{cr}} = 0.55 \)
pNIPAm-co-AAc
(pH=3.8)

Volume Fraction, $\phi$
pNIPAm-co-AAc (pH=3.8)

6.6 wt-%, $\phi_{\text{eq}}=0.74, \phi_{\text{car}}=1.10$

3.3 wt-%, $\phi_{\text{eq}}=0.37, \phi_{\text{car}}=0.55$

2.2 wt-%, $\phi_{\text{eq}}=0.25, \phi_{\text{car}}=0.37$

1.7 wt-%, $\phi_{\text{eq}}=0.19, \phi_{\text{car}}=0.28$
pNIPAm-co-AAc (pH=3.8)
pNIPAm-co-AAc (pH=3.8)

Compressed

DLS Diameter

φ_{eff}=0.12
pNIPAm-co-AAc (pH=3.8)
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*

![Particle Swelling](image_url)
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.

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 $\Rightarrow$ both processes are apparently unfavorable.
Crystallization Dynamics

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

Days: 0 1 2 5 7

~35% effective volume fraction
~820-nm diameter pNIPAm-AAc; pH 3.8
Particle Tracking Analysis

Microscopic tracking analyses illustrate “freezing” trend.
Evolution of Structure

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

~54% volume fraction

~36% volume fraction

~17% volume fraction
Crystallization Dynamics II

1 day old sample; \(\sim 35\%\) 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?*

\[ \varepsilon \approx 1 \times 10^9 \text{ M}^{-1}\text{cm}^{-1} \text{ (20 nm particle at 520 nm)} \]

photoemission yield \( \approx 0\% \)

fast lattice relaxation \( \approx 10\text{-}100 \text{ ps} \)
Au@Crystal Composites

Co-centrifugation of Au NPs with Microgels

![Graphs showing absorbance vs wavelength with different concentrations of Au nanoparticles and microgels.](image)
Laser Annealing/Melting

High Flux: Glassy patterned into crystalline

Low Flux: Crystalline patterned into glassy

$\lambda_{ex} = 532$ nm

Laser Annealing/Melting

**High Flux:**
Glassy patterned into crystalline

**Low Flux:**
Crystalline patterned into glassy

\[ \lambda_{\text{ex}} = 532 \text{ nm} \]

*Laser flux determines local temperature and the effective cooling rate* \( \Rightarrow \) *Flux determines crystal phase.*

Microspectrophotometry

Analysis of single crystal optical properties.
Microspectrophotometry

- Microscope
- Monochromator
- Determined by microscope iris
- Determined by monochromator slit width
- Reflected light is spectrally dispersed
- Monochromator entrance port
- Spectral image is collected with a CCD camera
Spectral Imaging
Fine Tuning Phase Manipulation

Beam with Gaussian intensity profile $\rightarrow$ 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 irradiation →

Bragg Peak (lattice constant) varies radially across area.
Microlenses from Bragg Gradients

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

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.
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