Colloidal Superstructures in Space

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Colloidal Superstructures in Space

- Anisotropic interactions
- $T$ control of interactions
- Superstructures: Formation + Growth
- Direct + reciprocal imaging

Anisotropic Interaction by critical Casimir forces
Colloids - Hard Spheres

\[ V(\phi) \]

\[ r \]

\[ \phi \]

\[ \text{fluid} \quad 0.49 \quad \text{fluid + crystal} \quad 0.54 \quad \text{crystal} \]
Colloids - Hard Spheres

\[ V(r) \]

\[ r \]

\[ \phi \]

\[ \text{fluid} \quad 0.49 \quad \text{fluid + crystal} \quad 0.54 \quad \text{crystal} \]

Chaikin, Russel et al.
Colloids - Charged Spheres

Science Overview

Leunissen et al. (Nature 2005)
Colloidal Phase behavior - Depletion

Colloid-polymer

Volume fraction $U/kT$

Gel
attr. glass
HS glass

equilibrium
out of equilibrium
Colloidal Phase behavior - Depletion

Colloid-polymer

\[ V(r) \]

\[ r \]

\[ \frac{U}{kT} \]

Volume fraction

\[ G \]

\[ G+L \]

\[ G+C \]

\[ F \]

Gel

attr. glass

HS glass

equilibrium

out of equilibrium

Chaikin, Weitz
Science Overview

Control Interactions - Critical Casimir effect

1. Active Potential Control

2. Anisotropic Interaction
Control Interactions - Critical Casimir effect

Bechinger et al. (Nature 2008)
The Critical Casimir effect

Science Overview

Fraction of 3MP in water

Temperature

2 phases

Colloidal aggregation

Phase Separation Line

1 phase

C_c

3MP + water

water

3MP
Particle interactions

Coulomb repulsion

\[ V_{el}(a) \propto \lambda_d^2 e^{-a/\lambda_d} \]

\( \lambda_d \rightarrow \) Salt concentration

+ Casimir attraction

\[ V_{\text{casimir}}(a) \propto -\frac{1}{\xi} e^{-a/\xi} \]

\( \xi \rightarrow \) Temperature

\[ \frac{U}{kT} \]

Particle interactions

Coulomb repulsion

\[ V_{el}(a) \propto \lambda_d^2 e^{-a/\lambda_d} \]

\( \lambda_d \rightarrow \text{Salt concentration} \)

+ Casimir attraction

\[ V_{casimir}(a) \propto -\frac{1}{\xi} e^{-a/\xi} \]

\( \xi \rightarrow \text{Temperature} \)

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Scientific Merit

Control Anisotropic Interactions

Critical Fluctuation

Hydrophilic
Hydrophobic
Control Anisotropic Interactions

- Living polymer chains (Particles 2)
- Diamond structure (Particles 4)
- Colloidal Micelles Helices (Particles 1)
- Molecules (Particle Mixtures)

D.J. Kraft et al, JACS, 131, (2009) 1182-1186
Need for ISS environment

1. Follow the growth of structures

\[ F_g = \Delta \rho g V \]

\[ \Delta \rho = \rho_{\text{Colloid}} - \rho_{\text{Solvent}} \]
1. Follow the growth of structures

\[ F_g = \Delta \rho g V \]

\[ \Delta \rho = \rho_{\text{Colloid}} - \rho_{\text{Solvent}} \]
2. Temperature is control parameter

- Change Temperature $\Delta \rho$ changes
- Temperature $\rightarrow$ Convection disrupts growth
Ground-based work

Microscopy

$\Delta T = 0.9^\circ C$

$1 \mu m$
Ground-based work

Microscopy

$\Delta T = 0.9^\circ C$

$0.5^\circ C$

$1\mu m$
Ground-based work

Microscopy

Gas $\Delta T = 0.9^\circ C$

Liquid $0.5^\circ C$

Crystal $0.2^\circ C$

$1\mu m$
Ground-based work

Microscopy

Gas \( \Delta T = 0.9^\circ C \)

Liquid \( 0.5^\circ C \)

Crystal \( 0.2^\circ C \)

- 1\( \mu \)m
Microscopy

2 µm
Microscopy

2 µm
Microscopy

2 µm
Ground-based work

Potential measurement

Pair distribution function

Particle distribution

\[ G(r) \]

- \( \Delta T = 0.30 \, ^\circ\text{C} \)
- \( \Delta T = 0.35 \, ^\circ\text{C} \)
- \( \Delta T = 0.40 \, ^\circ\text{C} \)
- \( \Delta T = 0.50 \, ^\circ\text{C} \)
- Room temperature
Ground-based work

Potential measurement

Pair distribution function

\[ G(r) = \exp\left(-\frac{U(r)}{k_B T}\right) \]

Potential

\[ \Delta T = \{1.5K, 0.8K, 0.6K, 0.4K\} \]

\[ \Delta T = \{0.3K, 0.35K, 0.4K, 0.5K\} \]
\[ U_{\text{total}} = U_{\text{el}} + U_{\text{Casimir}} \]

\[ A_{\text{el}} e^{-\left(\frac{r}{\lambda_d}\right)} \quad A_{\text{Cas}} e^{-\left(\frac{r}{\xi}\right)} \]

**Ground-based work**

**Potential measurement**

ΔT = 0.3K, 0.6K, 0.8K, 1.5K, 0.4K

ΔT = 0.3K, 0.4K, 0.5K

Room temperature

\[ \frac{U(r)}{kT} \]
Ground-based work

Potential measurement

\[ U_{\text{total}} = U_{\text{el}} + U_{\text{Casimir}} \]

\[ A_{\text{el}} e^{-(r'/\lambda_d)} \quad A_{\text{Cas}} e^{-(r'/\xi)} \]
Van der Waals model

\[(v - b) \left( p + \frac{a}{v^2} \right) = k_B T \]

Excluded volume

\[ b = \frac{16}{3} \pi r_0^3 \]

Effect. attraction

\[ a = -2\pi \int_{r_1}^{\infty} U(r) r^2 dr \]

Israelachvili, Intermolecular and surface forces
Ground-based work

Van der Waals model

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Israelachvilli, Intermolecular and surface forces

\[ \Delta T = 1.5K \]

\[ 0.8K \]

\[ 0.6K \]

\[ 0.4K \]
Ground-based work

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Israelachvili, Intermolecular and surface forces

\[ \Delta T = 1.5K \]
\[ 0.8K \]
\[ 0.6K \]
\[ 0.4K \]
Ground-based work

Monte Carlo Simulations

Extrapolate potential

Equilibrium phase diagram

\[ U(r) / k_B T \]

\[ (T-T_c)/K \]

D. Triet, D. Nguyen, P. Bolhuis and P. Schall, in preparation
Ground-based work

Colloidal Molecules

Single protrusion

Making molecules

D.J. Kraft et al, JACS, 131, (2009) 1182-1186
Ground-based work

Adjusting the surface properties

Add Fluorecein

Creating differences:
- Different monomer (PS/PMMA)
- Charged/uncharged initiator

Current system:
- Charged protrusion
- PolyStyrene/PS particles
- Readily suspendable in water/3MP
- Promising ground-based measurement

Ground-based work

Adjusting the surface properties

Simple calculation
Charge density difference only
Same temperature

R_{seed} = 1.15 \text{ nm}
R_{cap} = 1.45 \text{ nm}
\sigma_{seed} = 10 \times \sigma_{cap}
Proposed Experiment

**Temperature control** → Attraction on/off → Follow structure formation → “Reaction kinetics“

Vary **Temperature** → Vary attraction strength

Vary **Rate of change** → Eqilibrium vs. out-of equilibrium

**Reverse Temperature** → Repeat Experiment

**Image in real + reciprocal space**
Proposed Experiment

Direct imaging + Near Field Scattering

\[ d_{sp} \approx R \]

Far Field

\[ d_{sp} = \frac{z\lambda}{D} \]

Proposed Experiment

1. Sample Cells
   - Stirrer
   - No bubbles in field of view
   - Quartz cells
   - Max 3 mm thick
2. Temperature control

- 0.5 °C steps, better 0.2°C

- Possible to heat samples individually
3. Camera

- 1024x1280 pixels
- Dynamic range: 12 bit
- Low signal to noise ratio
4. Direct Imaging Mode

- White light illumination on
- Laser off
- Focus in sample
5. Near field scattering Mode

- White light off
- Laser on:
  Beam Collimated
  Coherence length ~ 3mm
- Focus above sample
Proposed Experiment

Raw image at $t_i$

Raw Image at $t = t_i + \Delta t$

Subtracted Image

Power Spectrum

Azimuthal averaging

$D_i(x, y)$

$S(q_x, q_y) = \left| \text{FFT}[D_i(x, y)] \right|^2$

$I(q)$

Proposed Experiment - Samples

1. Mono Patch

D.J. Kraft et al, JACS, 131, (2009) 1182-1186
Proposed Experiment - Samples

1. Mono Patch

Colloidal Micelles

Helices

vary aspect ratio

200nm

D.J. Kraft et al, JACS, 131, (2009) 1182-1186

Israelachvili, Intermolecular and surface forces
Proposed Experiment - Samples

2. Di-Patch

Colloidal Polymers
Proposed Experiment - Samples

2. Di-Patch

Colloidal Polymers

3. Mixtures Mono Patch + Di-Patch

Molecules Superstructures
Proposed Experiment - Samples

3. Mixtures Tetra Patch + Di-Patch

CH₄, organic molecules

4. Tetra-Patch

Diamond structure
Succes Criteria

- What do we want to see?
  - Temperature-controlled assembly + Imaging
  - Novel structures from anisotropic potential
  - Control structure with attraction strength
  - Follow Dynamics of ‘molecular reactions’
Summary

- Growth of colloidal superstructures
- Direct T control of anisotropic potential
  → New equilibrium + out-of-equilibrium structures
- Real+reciprocal space imaging
- Colloidal Micelles, Helices, Polymer chains, Diamond structure, complex molecules
Collaborators

- Willem Kegel, Daniela Kraft (Utrecht)
- Peter Bolhuis (Simulations, Amsterdam)
- T. Narayanan (ESRF Grenoble)
- D. Nguyen, D. Triet, J. Moons (PhD, Amsterdam)