Self-Assembly of Two Dimensional Colloidal Alloys

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Outline of talk

1. Colloids at fluid interfaces (2D colloids)
2. Interaction between interfacial colloids
3. Two dimensional colloidal alloys
4. Conclusions & future work
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1. Colloids at fluid interfaces

- Partially wetting colloids spontaneously adsorb at oil/water interface [1]
- Particle position at interface depends on wettability
- For $R \sim 1 \, \mu m$, $\Delta E_{\text{det}} >> kT$, adsorption irreversible $\rightarrow$ 2D colloidal system

2. Interaction between interfacial colloids

- Silica particles at octane/water interface
- Interaction can be tuned by changing $\theta$ \[1\]
- Repulsion between hydrophilic particles sensitive to salt
- Repulsion between hydrophobic particles insensitive to salt

Repulsion between hydrophobic particles

- Interactions more complex than in bulk. Contributions from:
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Repulsion between hydrophobic particles

- Interactions more complex than in bulk. Contributions from:
  - Asymmetric double layer [1]
  - Residual charges (oil side) [2]
  - Stern layer [3]
- Residual charge unscreened - strong and long ranged
- Dipole-dipole form:
  \[ \beta U(r) = \Gamma \frac{l^3}{r^3} \]


\[ \Gamma = \text{interaction strength} \approx 1700 \]
Attraction between hydrophilic particles

- Electrostatic repulsion between hydrophilic particles much weaker.
- Residual charge negligible, repulsion due to charge at particle/water interface.
- $d \approx 2 \mu m \rightarrow$ VdW attraction negligible.
- Attraction most probably from capillary interaction due to contact line undulations [1]

$$U_{cap}(r) = -\frac{12\pi\gamma R_c^4 \delta^2}{r^4}$$

$\delta \approx 10$nm

3. Two Dimensional Colloidal Alloys

Hydrophobicity

A
hydrophobic particles

\[ \theta = 152^\circ \]

B
hydrophilic particles

\[ \theta = 65^\circ \]

Hydrophobic/hydrophobic mixtures

Hydrophobic/hydrophilic mixtures

- Large (3 µm)
- Small (1 µm)
Hydrophobic/hydrophobic monolayers (experiment)

- Interaction strength $\Gamma kT = 1700kT$
- Dipole moment ratio $m_{SA} = P_{SA}/P_{LA} \approx 0.03$
- Vary small particle fraction $\xi = \frac{n_{SA}}{n_{LA} + n_{SA}}$

- Rich variety of hexagonal superlattices with medium to long ranged order
- Progressive filling of interstitial sites as $\xi$ increased
- Minimum distortion of large particle lattice by small particles

Lattice Sum Method

• Calculate structure at T=0 using lattice sum method

• Energy per unit cell

\[ E = \frac{1}{2} \sum_{hk} U_{LALA}(ha + kb) + \frac{1}{2} n_{SA} \sum_{hk} U_{SASA}(ha + kb) \]

\[ + \sum_{hk} \sum_{i=1}^{n_{SA}} U_{LASA}(r_{i}^{SA} ha + kb) + \sum_{hk} \sum_{i=1}^{n_{SA}-1} \sum_{j=i+1}^{n_{SA}} U_{SASA}(r_{i}^{SA} + r_{j}^{SA} + ha + kb) \]

• Minimise \( E \) wrt \( \phi, \gamma, \{ r_{i}^{SA} \} \) to find minimum energy configuration (MEC)

\[ \gamma = \frac{b}{a} \]
Lattice Sum Calculations

Superlattice structures reproduced by T = 0 calculations

Hydrophobic/hydrophilic monolayers (experiment)

- Rich variety of superlattice cluster structures formed
- Structure of mixed clusters controlled by composition and packing geometry
- Attraction between hydrophobic and hydrophilic particles
- Repulsion between hydrophilic particles within a cluster

Induced dipole interactions

- Postulate interactions in mixed systems due to polarisation of hydrophilic particles by hydrophobic particles.

- Induced dipole interactions:
  - Attractive between A, B
  - Repulsive between B, B

- Diagram showing the interaction between hydrophilic and hydrophobic particles in oil and water phases.

- Induced dipole interactions:
  - **Attractive** between A, B
  - **Repulsive** between B, B
Lattice Sum Calculations

2D cluster structures reproduced by $T=0$ calculations

4. Conclusions

• Mixed colloidal monolayers of hydrophobic/hydrophilic silica particles at oil/water interface exhibit rich variety of 2D superlattice and cluster structures.

• Structure of mixed monolayers can be controlled by tuning particle interactions, compositions and packing geometry.

• Structure of mixed monolayers in excellent agreement with $T=0$ calculations and finite $T$ simulations.

• 2D structures stabilised by long range electrostatic repulsion and short ranged induced dipole interactions mediated through the oil phase.
Future work

• Metal/dielectric mixed monolayers
• Anisotropic particles at oil/water interface
• Scaling down to nanoscale
• Functional metamaterials with unique electromagnetic properties
Thank you!