Field-driven self-assembly near and far from equilibrium

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Soft materials group at Memorial

- **Equilibrium:** diffusion in crowded multi-component macromolecular systems
- **Near equilibrium:** kinetics of crystal-crystal phase transitions
- **Far from equilibrium:** electrically driven hydrodynamic interactions in emulsions

Payam Bagheri (Memorial), Priti Mohanty (KIIT, India), Sofi Nöjd, P. Schurtenberger (Lund, Sweden)
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- **Near equilibrium**: kinetics of crystal-crystal phase transitions
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- **Phase transformation kinetics in colloids**: Payam Bagheri (Memorial), Priti Mohanty (KIIT, India), Sofi Nöjd, P. Schurtenberger (Lund, Sweden)
- **Electrohydrodynamics in emulsions**: Somayeh Khajehpour Tadavani (Memorial), Atul Varshney, Sheshagiri Rao, S. Ghosh, S. Bhattacharya (TIFR, India)
Phase transformations from solid to solid

- G. Olson & W. Owen, Martensite
- K. Otsuka & C. Wayman, Shape Memory Materials

Experimentally, we need a link between microstructural evolution and macroscopic phase transition kinetics.

www.lassp.cornell.edu/sethna/Tweed/What_Are_Martensites.html
Solid-solid transitions in colloids


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  **The current work moves a step closer to 3D.**
Phase transitions in hard-sphere colloids

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- **An isotropic fluid at low densities.** The particle excluded volume is much smaller than the total volume → lots of free volume.
- **At high packing, the crystal is entropically favoured over the fluid,** due to the limited free volume.
- **At high densities, a glassy state is seen,** for somewhat polydisperse hard spheres.

Colloids with electrostatic repulsions

- **Left:** $\phi = 0.002 \kappa^{-1} \sim 10 \mu m$. A. Yethiraj & A. van Blaaderen, *Nature*, 2003
- **Middle:** $\phi = 0.02$, **face-centred cubic (FCC)**, no salt (large $\kappa^{-1}$).
- **Right:** $\phi = 0.02$, **fluid phase**, salt added
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An intervening body-centred cubic (BCC) phase emerges at $\kappa R \sim 2$

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But to have a knob to control kinetics $\rightarrow$ tunable interactions

*AY, Soft Matter review (2007)*
Colloids with electric dipolar interactions

Spheres form chains:

The external electric field $\vec{E}_{\text{ext}}$ induces dipoles in each microsphere.

The dipolar interaction energy is

$$U_{\text{dipolar}}(d)/k_B T = -\frac{\Lambda}{(d/\sigma)^3} \left( \frac{3 \cos^2 \theta - 1}{2} \right)$$

where

$$\Lambda = \frac{\pi \epsilon_0 \epsilon_f \beta^2}{16k_B T} \sigma^3 E_{\text{ext}}^2$$

and

$$\beta = \frac{\epsilon_p - \epsilon_f}{\epsilon_p + 2\epsilon_f}.$$
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Structures are 3D, but can be tracked in quasi-2D.

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![Diagram showing spheres forming chains](image)

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- Chains **stack** or chains **stagger**:

![Graphs showing energy vs. distance for different chain configurations](image)

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Interactions plus tunable dipolar interactions

- **Attraction-dominated:** BCT-string fluid coexistence (Tao & Sun, *PRL*, 1991) and a low-density cluster phase (A. Agarwal & AY, *PRL*, 2009).


- **Short-range attractions + dipolar:** more compact complex tubular structures (Yan et al., *Nature*, 491, 578 (2012)).
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- **Repulsion-dominated**: more open space-filling body-centred tetragonal (BCT) and body-centred orthorhombic (BCO) phases \( (AY, \textit{Soft Matter} 3, 1099 (2007); AY \& A. van Blaaderen, \textit{Nature} 421, 513 (2003)) \).
Interactions plus tunable dipolar interactions


- **Short-range attractions + dipolar**: *more compact* complex tubular structures (Yan et al., *Nature*, 491, 578 (2012))
“Ultra-soft” microgel colloids

What about short-ranged repulsions and longer ranged dipolar forces?

- What happens when soft steric repulsions compete with dipolar forces?
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**A strong field effect!**


- Low $\phi_{eff}$: strings - BCT
“Ultra-soft” microgel colloids

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![Diagram showing phase transformations under different electric fields](image)

A strong field effect!


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- Intermediate: FCC - BCT
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A strong field effect!


- **Low** $\phi_{eff}$: strings - BCT
- **Intermediate**: FCC - BCT
- **High**: glassy - arrested phase separated state
Phase Transition kinetics: FCC - BCT
Field on: FCC to BCT ($\phi_{\text{eff}} = 1.36$)

$E = 0$

FCC

$E = 0.11$

BCT
Field on: FCC to BCT ($\phi_{\text{eff}} = 1.36$)

- Melting near grain boundaries precedes crystal formation.

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- **Quantify:** bond order parameters ($\psi_6$ and $\psi_4$) and population fractions $f_6$ and $f_4$. 
Melting near grain boundaries precedes crystal formation.

**Quantify:** bond order parameters ($\psi_6$ and $\psi_4$) and population fractions $f_6$ and $f_4$.

**Avrami form:** $f_4 \sim 1 - \exp(-Kt^\alpha)$, with $\alpha = 4.0$. $V \sim N_g \times V_g$
Field off: BCT to ??

- BCT to body-centred orthorhombic (BCO), the action $\sim 50$ s.
Field off: BCT to ??

- BCT to body-centred orthorhombic (BCO), the action $\sim 50$ s.
- The reverse transition is collective ("martensitic").
Order parameters start to change everywhere close to $t = 50s$.

- **High $\phi_{\text{eff}}$:** final state is not the (FCC) field-off state.
- **Lower $\phi_{\text{eff}}$:** final state is the (fluid) field-off state.
Field off: BCT to BCO

Forcing into Avrami form: \( f_4 \sim 1 - \exp(-Kt^\alpha) \) yields \( \alpha = 8.5 \): not classical nucleation and growth.
Field off: BCO to FCC

- The BCO state is long-lived, but anneals back to FCC at higher temperatures.
Kinetics of a solid-solid transition

- The ionic microgel colloidal system is a great model system to gain microscopic insights into 3-dimensional solid-solid phase transformations. *Phys. Rev. X* 5, 011030 (2015)
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- The forward FCC to BCT transition is polymorphic and **diffusive**, similar to phase transformations in metals and ceramics
Introduction

Phase transformation kinetics in colloids

Electrohydrodynamics in emulsions

Conclusions

Kinetics of a solid-solid transition

The ionic microgel colloidal system is a great model system to gain microscopic insights into 3-dimensional solid-solid phase transformations. *Phys. Rev. X* 5, 011030 (2015)

The forward FCC to BCT transition is polymorphic and diffusive, similar to phase transformations in metals and ceramics.

The reverse transition - the BCT to BCO structural sequence - is diffusionless and martensitic, and occurs through cooperative rearrangements.
Kinetics of a solid-solid transition

In both the 2D study (Peng et al) and our electric-field studies in the forward direction, there is an external field that picks out the orientation of the $c$ axis in addition to simply driving the transition.
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- Therefore, the new crystal structure cannot pick out the most favourable face to show to the old crystal, and melting occurs as an intermediate → this is not generically true.
Kinetics of a solid-solid transition

- In both the 2D study (Peng et al) and our electric-field studies in the forward direction, there is an external field that picks out the orientation of the $c$ axis in addition to simply driving the transition.

- *Therefore, the new crystal structure cannot pick out the most favourable face to show to the old crystal, and melting occurs as an intermediate → this is not generically true.*

- On the other hand, *the reverse (martensitic) transition* into a metastable crystalline intermediate is likely to exist “in solid-solid transitions of most metals and alloys”
Unanswered questions

- What governs the 50 s waiting time in the martensitic transition?
  - Waiting time could be related to finding the collective “golf hole”, i.e. finding the right collective deformation that gets you into the new state in a large landscape.
  - Waiting times should be a function of quench depth.
Unanswered questions

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  - Waiting times should be a function of quench depth.

- the metastable-BCO to BCT transformation is reversible!, so we can carry out the BCO to BCT transition as a function of quench depth

- bond order parameters are convenient, but there are other suggestions, e.g. measuring non-affineness of deformations (S. Sengupta, TIFR-Hyderabad)
Can we tune hydrodynamics?
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- Nucleation of large-scale *coherent* crystalline structures...

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- Large-scale *incoherent* structures such as clouds involve both electrostatics and hydrodynamics.
  - E. Bodenschatz et al., *Can we understand clouds without turbulence*? Science 327, 970 (2010).
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Hydrodynamics is important, but hard to include.
Electric stresses on a liquid drop

Dielectric liquid drop in a dielectric liquid medium

- Dipolar forces $\rightarrow$ normal stresses $\rightarrow$ prolate deformations.
- Electrohydrodynamic forces $\rightarrow$ tangential stresses $\rightarrow$ oblate deformations.

Silicone oil drop in castor oil. $E = 10$ kV/mm, pointing along $y$. 

5 kHz

70 Hz
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Droplet shape prolate or oblate depending on electrical properties of the two fluids, which is frequency-tunable.
Electric stresses on a liquid drop

Electrohydrodynamics forces for a single drop in a leaky dielectric medium have been well-studied

Electric stresses on a liquid drop

- Electrohydrodynamics forces for a single drop in a leaky dielectric medium have been well-studied


Our challenge now is to study the collective, many-particle behaviours.
Above 70 Hz, drops adopt a steady-state shape, balancing dipolar forces and electrohydrodynamic (EHD) flows.

- High-frequency, dipolar forces $\rightarrow$ prolate
- Low-frequency, EHD forces $\rightarrow$ oblate

\[ \tau_c = \epsilon_m \epsilon_0 / \sigma_m \sim 0.01 \text{s} \]

\[ f_c^{\text{expt}} = 100 \text{Hz} \sim 1 / \tau_c \]

\[ 0.7 < f / f_c^{\text{expt}} < 50 \]

Silicone oil drop in castor oil. AC field along $y$. 5 kHz

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Frequency-tunable hydrodynamics

Below 70 Hz, drops exhibit time-dependent deformations due to electrohydrodynamic (EHD) flows.

\[ \frac{f}{f_{c}^{\text{expt}}} < 0.7 \]

\[ E = 3V/\mu m, \frac{f}{f_{c}} = 0.035 \]
Onset of collective motions

- $f = 3 \text{ Hz}, 2 \text{ Hz}, 1 \text{ Hz}$.
- $f / f_c^{\text{expt}} < 0.03$

A critical size above which drop is unstable to break up.
Chaotic flows in DC fields

- $f / f_c^{\text{expt}} \rightarrow 0$
- Onset of convective flows
- Apparently turbulent behaviours

**Forcing is DC, but a 1 to 3 Hz oscillation emerges: its like Rayleigh-Bènard convection.**
Chaotic flows in DC fields

\[ E = 6\text{V/\mu m, DC} \]
Chaotic flows in DC fields

$E = 6V/\mu m$, DC

$E = 10.7V/\mu m$, DC
Measurement modalities

Optical microscopy and PIV

Rheometry

Cantilever sensing
Temporal power spectra

Low frequencies: $a -1.4$ power law, reminiscent of Rayleigh-Bénard turbulence.

$1$ Hz

$0.00$ s

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Temporal power spectra

Low frequencies: a -1.4 power law, reminiscent of Rayleigh-Bénard turbulence.
Spatiotemporal power spectrum

also a -1.4 power law!
Summary

Electrohydrodynamics

- a model system for tunable hydrodynamics
- rich, dynamical phase diagram in field frequency and amplitude
- turbulence at low $Re$
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**Electrohydrodynamics**
- a model system for tunable hydrodynamics
- rich, dynamical phase diagram in field frequency and amplitude
- turbulence at low $Re$

**Phase transformation kinetics**
- a model system for controlling field quenches
- two-parameter space: temperature and electric field.
Looking beyond near-equilibrium self-assemblies, new coherent structures emerge far from equilibrium.

Frequency quench from 3 to 8 Hz
Void phase: is hydrodynamics important?

Void size scales with sample thickness and chain length.