Field-driven self-assembly near and far from equilibrium

Anand Yethiraj
Associate Professor, Department of Physics & Physical Oceanography
Memorial University of Newfoundland
St. John's, Canada
Visiting Professor, TIFR Hyderabad

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Soft materials group at Memorial

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

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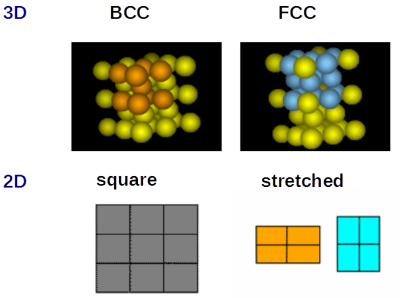
3. **Far from equilibrium:** electrically driven hydrodynamic interactions in emulsions

- **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



www.lassp.cornell.edu/sethna/Tweed/What_Are_Martensites.html

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

Solid-solid transitions in colloids

- **Martensitic transition in 2D:** J. Weiss, D. W. Oxtoby, D. G. Grier, C. A. Murray, *J. Chem. Phys.* **103**, 1180 (1995).

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The current work moves a step closer to 3D.

Phase transitions in hard-sphere colloids

Thermodynamics of monodisperse, hard spheres:

P. Pusey & W. van Megen, *Nature 1986*

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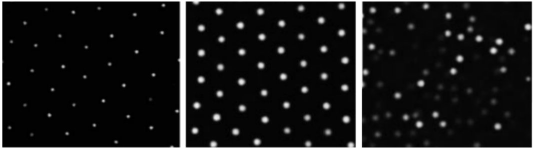
- **At high densities, a glassy state is seen**, for somewhat polydisperse hard spheres.

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 κ^{-1}).
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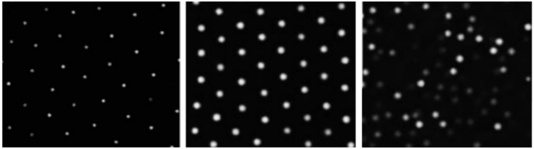

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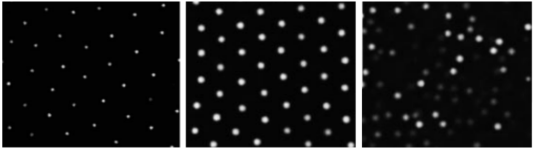

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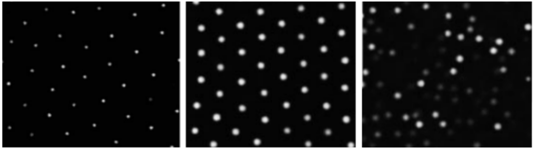

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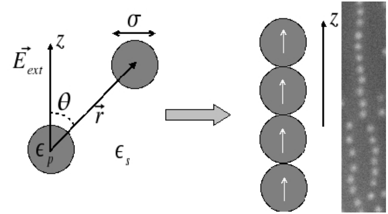
  But to have a knob to control kinetics → tunable interactions

  AY, *Soft Matter* review (2007)

Colloids with electric dipolar interactions

Spheres form chains:



The dipolar interaction energy is

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

where $\Lambda = \frac{\pi\epsilon_0\epsilon_f\beta^2}{16 k_B T}\sigma^3 E_{ext}^2$ and $\beta = \frac{\epsilon p - \epsilon_f}{\epsilon p + 2\epsilon_f}$.

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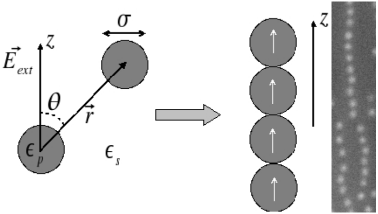

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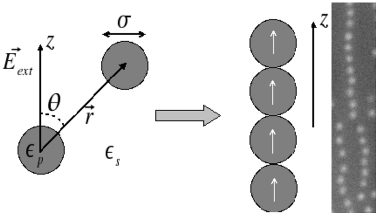

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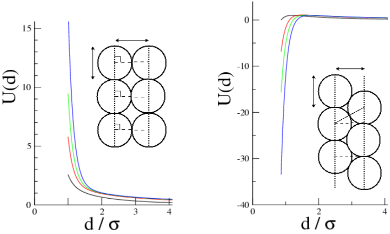

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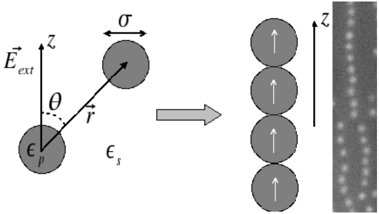

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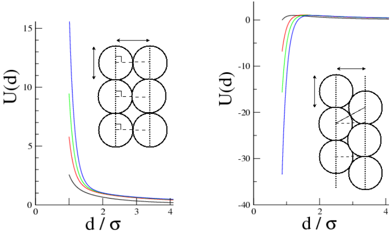

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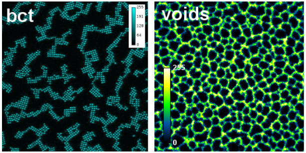
Structures are 3D, but can be tracked in quasi-2D

Interactions **plus** tunable dipolar interactions



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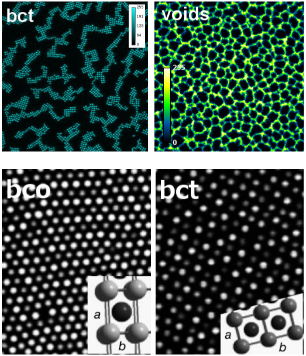

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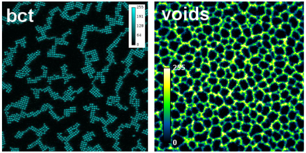

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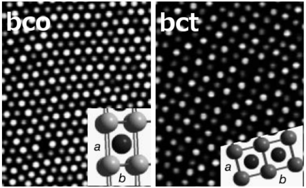

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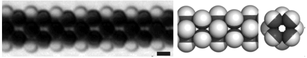

- **Short-range attractions + dipolar:** *more compact* complex tubular structures (Yan *et al.*, *Nature*, **491**, 578 (2012))

“Ultra-soft” microgel colloids

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

- Thermo-sensitive particle size (driven by polymer collapse) allows dynamical control of packing fraction (H. Senff & W. Richtering, *J. Chem. Phys*, 1999).
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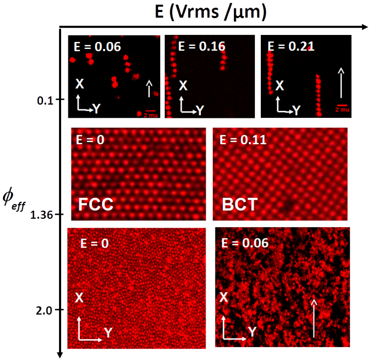

A strong field effect!

S. Nöjd, P. Mohanty, P. Bagheri, AY, P. Schurtenberger *Soft Matter* **9**, 9199 (2013); P. Mohanty, AY, PS, *Soft Matter* **8**, 10819 (2012)

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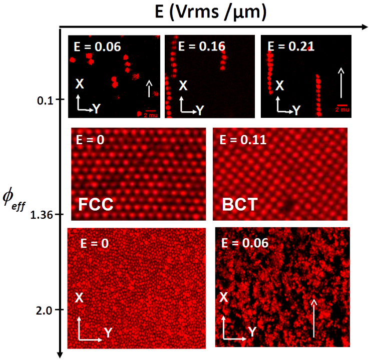

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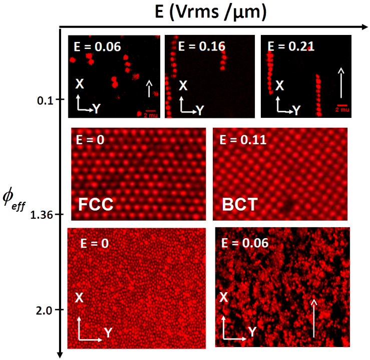

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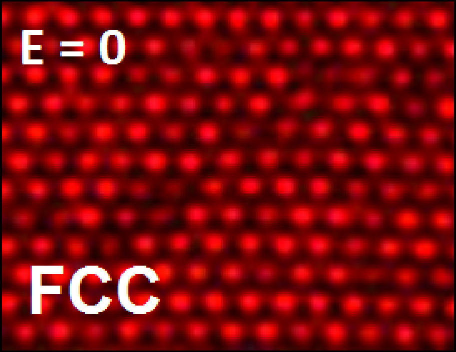
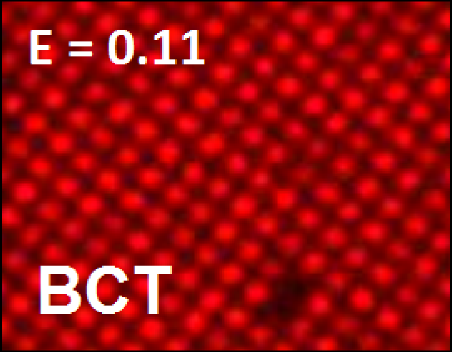
- **High:** glassy - arrested phase separated state

Phase Transition kinetics: FCC - BCT

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





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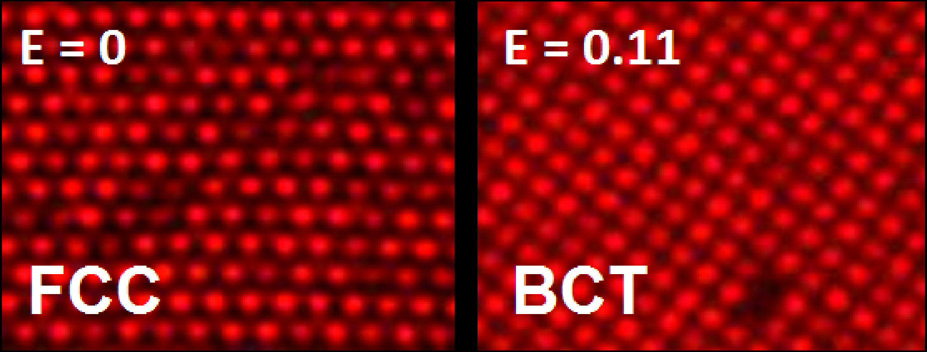

- Melting near grain boundaries precedes crystal formation. Similar two-step nucleation process reported in quasi-2D (Peng *et al*, Nature Materials, 2014).

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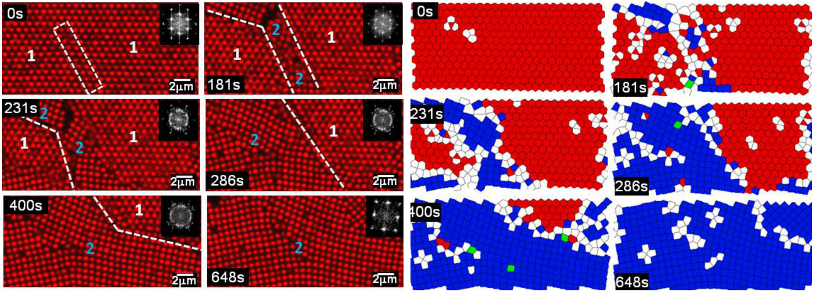

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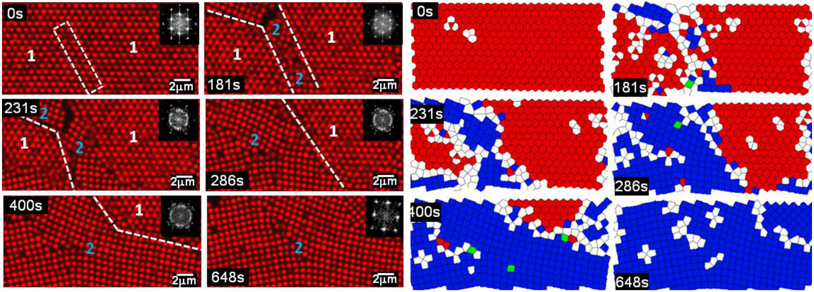

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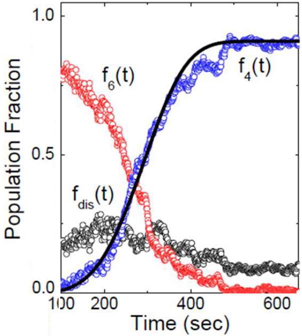

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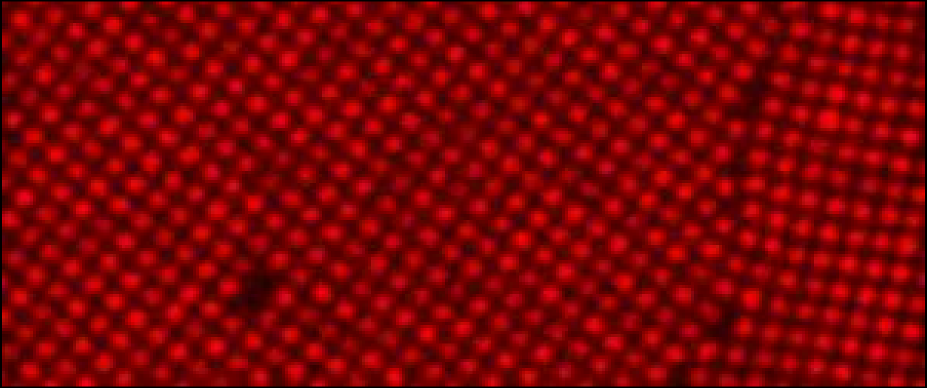
- **Avrami form:** $f_4 \sim 1 - \exp(-Kt^\alpha)$, with $\alpha = 4.0$. $V \sim N_g \times V_g$

Field off: BCT to ??



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

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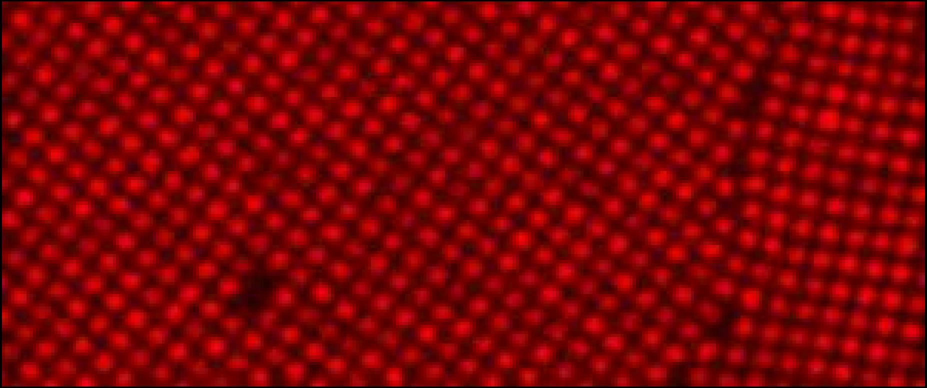
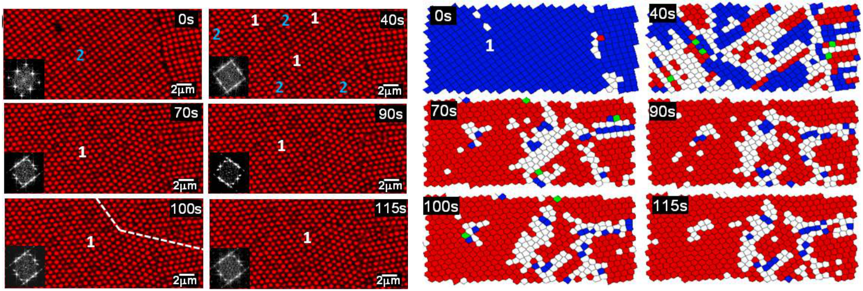


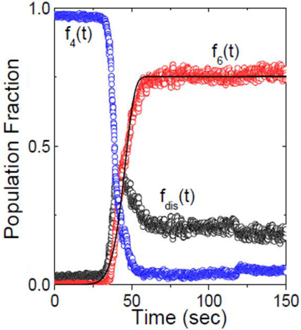
- BCT to body-centred orthorhombic (BCO), the action $\sim$ 50 s.
- **The reverse transition is collective (“martensitic”).**

Field off: BCT to BCO



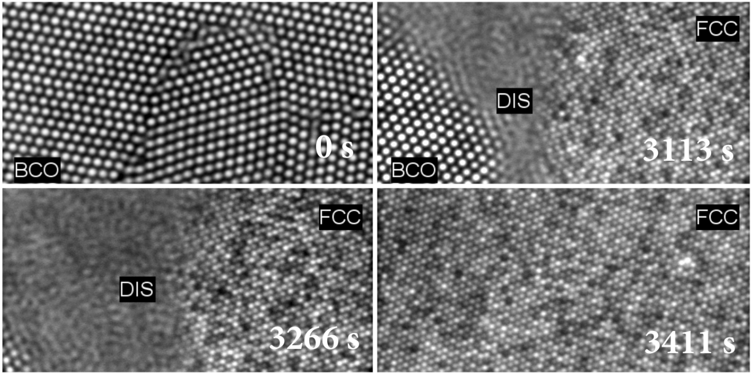
- Order parameters start to change everywhere close to t = 50s.
- **High** ϕ_{eff}: final state is not the (FCC) field-off state.
- **Lower** ϕ_{eff}: final state is the (fluid) field-off state.

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

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- **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

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- 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.

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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?

Can we tune hydrodynamics?

- Nucleation of large-scale *coherent* crystalline structures...

  – **L. Filion, R. Ni, D. Frenkel, M. Dijkstra, Simulation of nucleation in almost hard-sphere colloids:** the discrepancy between experiment and simulation persists, J. Chem. Phys. 134, 134901 (2011).

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- Large-scale *incoherent* structures such as clouds involve both electrostatics and hydrodynamics.

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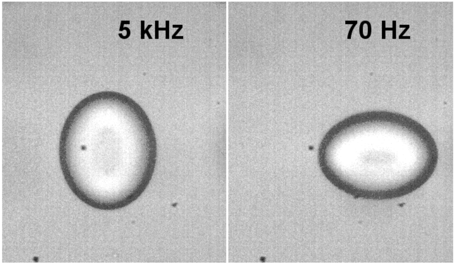
Hydrodynamics is important, but hard to include.

Electric stresses on a liquid drop

Dielectric liquid drop in a dielectric liquid medium

- Dipolar forces → normal stresses → prolate deformations.
- Electrohydrodynamic forces → tangential stresses → oblate deformations.



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

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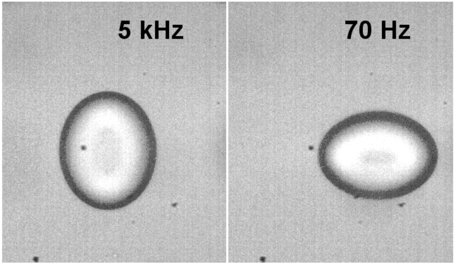


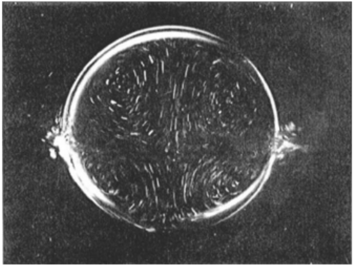
Silicone oil drop in castor oil. E = 10 kV/mm, pointing along *y*.

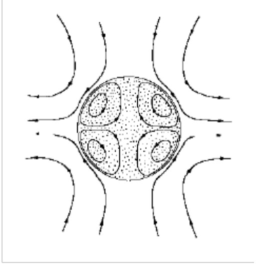
Droplet shape prolate or oblate depending on electrical properties of the two fluids, which is frequency-tunable.

Electric stresses on a liquid drop

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

Melcher & Taylor, *Ann. Rev. Fluid Mech.* **1**, 111 (1965); D. Saville, *Ann. Rev. Fluid Mech.* **29**, 27 (1997); Salipante & Vlahovska, *Physics of Fluids* **22**, 112110 (2010).





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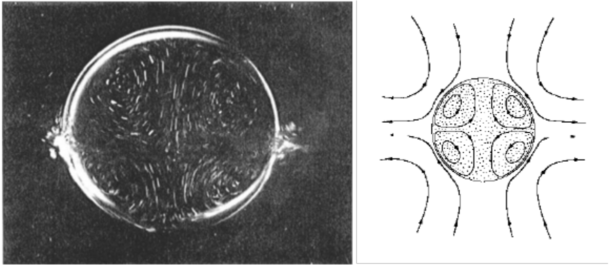
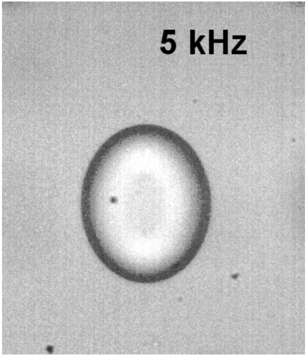


Our challenge now is to study the collective, many-particle behaviours.

Frequency-tunable hydrodynamics

Above 70 Hz, drops adopt a steady-state shape, balancing dipolar forces and electrohydrodynamic (EHD) flows.

- High-frequency, dipolar forces → prolate
- Low-frequency, EHD forces → oblate
- $\tau_c = \epsilon_m \epsilon_0 / \sigma_m \sim 0.01s$
- $f_c^{expt} = 100Hz \sim 1/\tau_c$
- $0.7 < f/f_c^{expt} < 50$

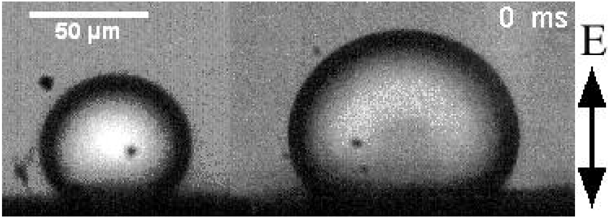


Silicone oil drop in castor oil. AC field along y.

Frequency-tunable hydrodynamics

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

- $f/f_c^{expt} < 0.7$

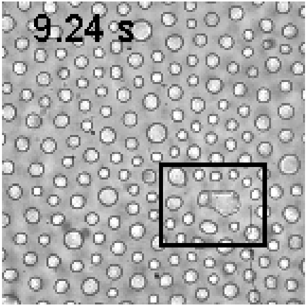


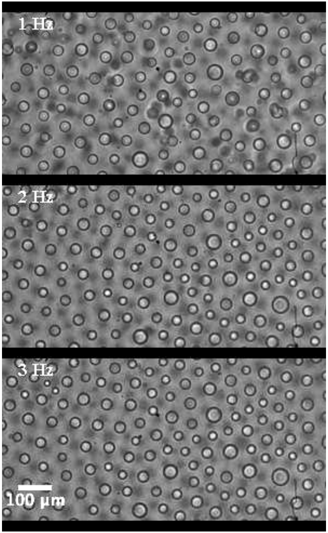
E = 3V/μm, $f/f_c = 0.035$

Onset of collective motions

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

A critical size above which drop is unstable to break up.

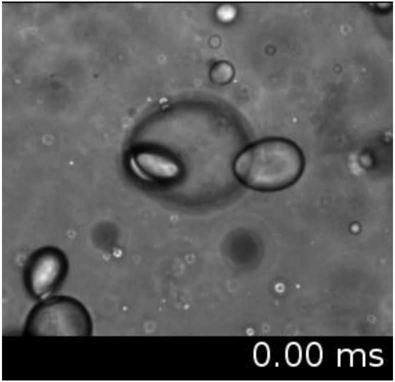




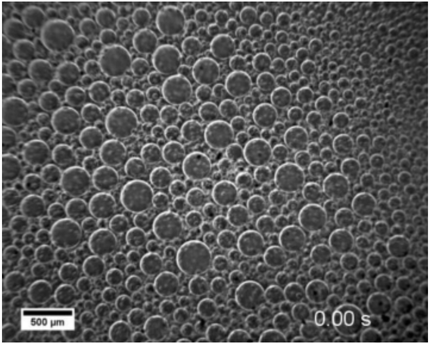
Chaotic flows in DC fields

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

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

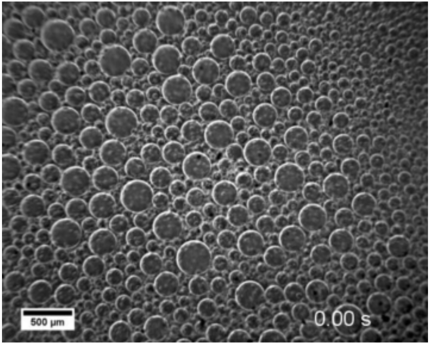


Chaotic flows in DC fields



E = 6V/μm, DC

Chaotic flows in DC fields



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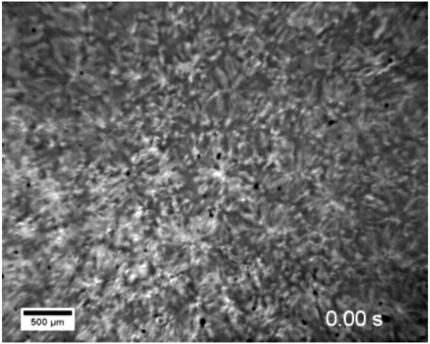
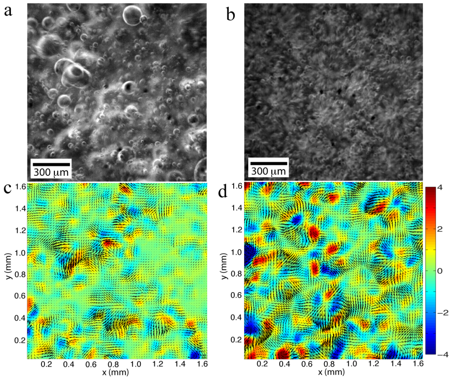


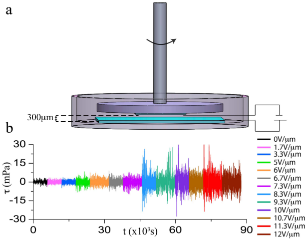
E = 10.7V/μm, DC

Measurement modalities

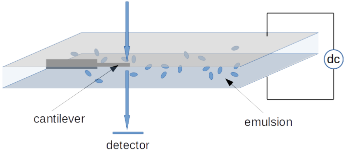
Optical microscopy and PIV



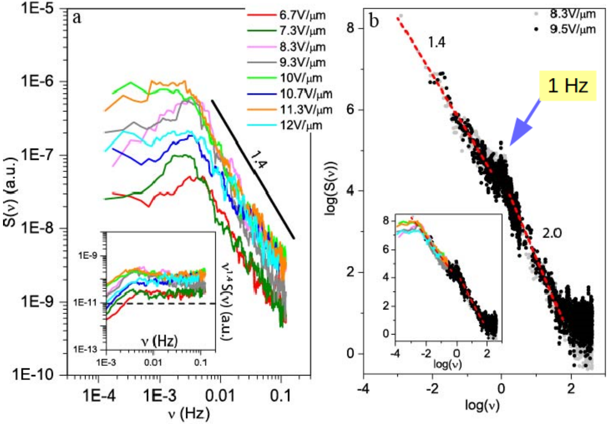
Rheometry



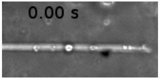
Cantilever sensing



Temporal power spectra



1 Hz



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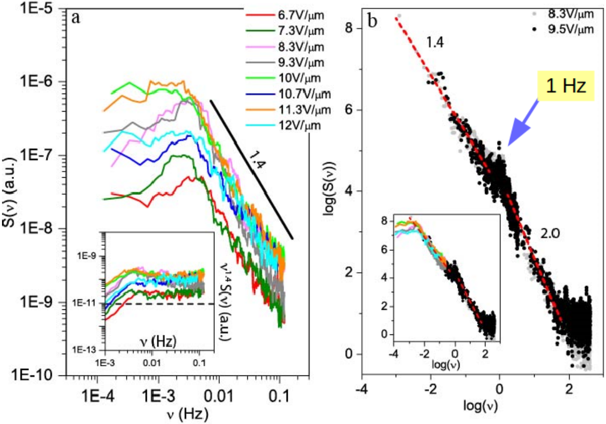
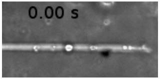
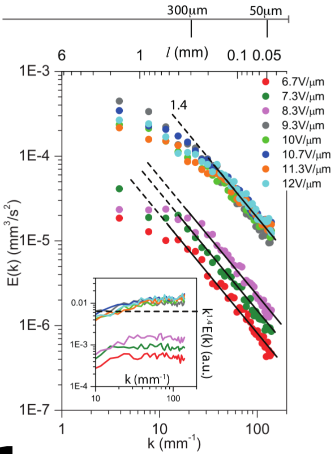




Low frequencies: a -1.4 power law, reminiscent of Rayleigh Bénard turbulence.

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

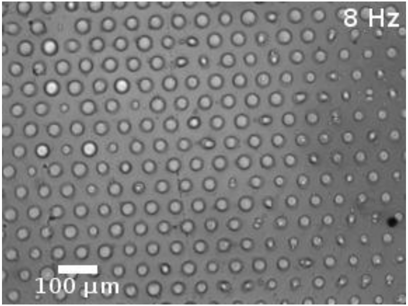
- a model system for tunable hydrodynamics
- rich, dynamical phase diagram in field frequency and amplitude
- turbulence at low *Re*

Phase transformation kinetics

- a model system for controlling field quenches
- two-parameter space: temperature and electric field.

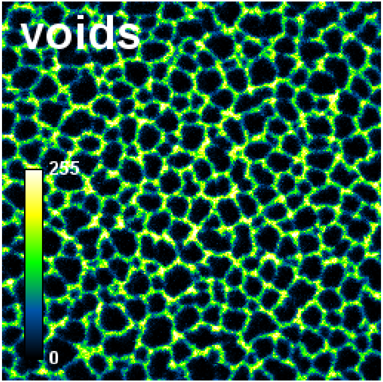
Conclusions

- **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.