Short-sighted colloids: birth, structure and evolution of a gel.

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with:

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Synopsis

A) The strange world of short-range potentials: from depletion forces to sticky hard spheres

B) Unraveling depletion forces: sedimentation, phase diagram, and equation of state.

C) Birth of a gel: the spinodal route to gelation

D) Collapse and ageing of a settling gel: microscopic vs. macroscopic dynamics
A) THE STRANGE WORLD OF VERY SHORT-RANGED POTENTIALS

MOLECULAR SYSTEMS

\[ U(r) \]

\[ T \]

\[ \rho \]

GAS

LIQUID

SOLID

CP

TP
The liquid-gas transition becomes metastable with respect to freezing. Nonetheless, the latter:

- Has huge effect on crystal nucleation (ten Wolte & Frenkel, 1997)
- Is strongly related to the formation of structurally arrested phases (glasses/gels)
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DEPLETION EFFECTS IN COLLOIDS

ADDING TO A SUSPENSION OF LARGE SPHERES SMALLER SPHERES (POLYMERS, SURFACTANT MICELLES)...

FORCE VIEW

Osmotic pressure unbalance yields an ATTRACTIVE force between colloids

IF the depletant can be regarded as an IDEAL GAS

AO POTENTIAL \[ U = \Pi V_{exc} \]

ENTROPY VIEW

Large particles subtract free volume to the small ones (which DOMINATE ENTROPY)

Small spheres gain entropy by PHASE SEGREGATION of the large colloids
Very short-ranged depletion: THE “STICKY” HS (AHS) LIMIT

Shrink the well, increase the depth by keeping thermodynamic functions finite

A SINGLE PARAMETER POTENTIAL: “STICKINESS” $\tau$ (a reciprocal temperature)

ANALYTICALLY SOLUBLE
B) Unraveling depletion forces: the experimental system

COLLOID:
MFA (modified PTFE) particles

- Low refractive index \((<n> = 1.35)\) → Low turbidity
- High density \((\rho > 2 \text{ g/cm}^3)\) → “Fast” sedimentation

\[ R = 78 \pm 3 \text{ nm} \]
B) Unraveling depletion forces: the experimental system

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**DISTINCTIVE OPTICAL PROPERTIES**

- PARTIALLY CRYSTALLINE
- OPTICALLY ANISOTROPIC
- DEPOLARIZED SCATTERING

$I_{VV}$ is insensitive to particle interactions!
(Useful for sedimentation studies – see below)
DEPLETANT: Triton X100

- A nonionic surfactant forming globular micelles in a wide conc. range
  - Hydrophilic head
  - Hydrophobic tail
  - $r \approx 3.4 \text{ nm}$
  - Aggregation number $N \approx 100$

- When added to a MFA suspension, first adsorbs on the particles, leading to colloid stabilization even in the presence of salt

- At higher surfactant concentration:
  - MICELLAR DEPLETION
EXPLOITING EQUILIBRIUM SEDIMENTATION TO PROBE THE EQUATION OF STATE & PHASE DIAGRAM

Depletant: Triton X100, a similar (but cheaper) nonionic surfactant

Depolarized scattering intensity

Local particle concentration

\[ \Pi(z) = g \Delta \rho \int_{z}^{h} dz' \Phi(z') \]

CONC. PROFILES

From \( \Pi(z) \) and \( \Phi(z) \)
EQUATIONS OF STATE

- **A → NO SURF**
- **B → c_s = 2.7 %**
- **C → c_s = 6 %**
- **D → c_s = 6.5 %**
- **E → c_s = 7 %**
- **F → c_s = 8.2 %**

**A (solid branch)**
- HS crystal
  - \[ Z(\Pi) = \frac{3}{1 - \Phi/0.74} \]

**A (fluid branch)**
- HS Carnahan-Starling
  - (no fit parameter)

**B-E (fluid branches)**
- BAXTER EQUATION OF STATE FOR AHS
  - (\(\tau\) is the only fit parameter)
C) BIRTH OF A GEL
At higher surfactant concentration:

FAST SEDIMENTATION
(hours vs. months!)

A MUCH MORE EXPANDED PHASE
FULL PHASE DIAGRAM:
TO THE ROOTS OF GELATION

Miller & Frenkel coex. line for AHS
FULL PHASE DIAGRAM:
TO THE ROOTS OF GELATION

- Fluid
- Gel
- Solid

Miller & Frenkel coex. line for AHS
FULL PHASE DIAGRAM: TO THE ROOTS OF GELATION

GELATION AS ARRESTED SPINODAL DECOMPOSITION

Miller & Frenkel coex. line for AHS

FLUID

GEL

SOLID
CONCENTRATION PROFILES FOR GELS

G (\(\Phi_s = 0.094\))

H (\(\Phi_s = 0.119\))
COMPRESSION MODULUS: A POWER LAW BEHAVIOR

\[ \Pi \sigma^3 / k_B T \]
HOW TO STUDY SLOW GEL DYNAMICS: TRC (Space-Time Resolved Correlation)
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Multi-speckle correlations

Imaging through a stopped-down lens

“Speckled” image of the beam
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Continuous dynamics → Smooth changes
Intermittent dynamics → Sudden changes
HOW TO STUDY SLOW GEL DYNAMICS: TRC (Space-Time Resolved Correlation)

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\[
 c_I(t, \tau) = \frac{\langle I_p(t)I_p(t+\tau) \rangle_p}{\langle I_p(t) \rangle_p \langle I_p(t+\tau) \rangle_p}
\]

Continuous dynamics → Smooth changes
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D) Collapse and ageing of a gel: macroscopic dynamics

Time evolution of the gel height \((\Phi_p \approx 0.12, U_{att} \approx 4.5 \, k_B T)\)
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Spinodal decomposition and cluster formation
D) Collapse and ageing of a gel: macroscopic dynamics

Time evolution of the gel height \( (\Phi_p \approx 0.12, U_{att} \approx 4.5 \, k_B T) \)

Settling of a cluster phase (linear in time)
D) Collapse and ageing of a gel: macroscopic dynamics

Time evolution of the gel height ($\Phi_p \approx 0.12, U_{\text{att}} \approx 4.5 \, k_B T$)
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Time evolution of the gel height ($\Phi_p \approx 0.12, U_{att} \approx 4.5 k_B T$)
THE POROELASTIC REGIME

PICTURE: A FLUID (COUNTER)FLOWING THROUGH AN ELASTIC POROUS MEDIUM

- GENERAL EQUATION:

\[
\frac{\partial \Phi}{\partial t} = \frac{\partial}{\partial z} \left[ \Phi \kappa(\Phi) \left( \frac{\Delta \rho g \Phi}{\eta} + \frac{K(\Phi)}{\Phi} \frac{\partial \Phi}{\partial z} \right) \right]
\]

PERMEABILITY

GRAVITATIONAL STRESS

ELASTIC RESPONSE

- INPUT FOR NUMERICAL SIMULATIONS:

\[ K(\Phi) = \Phi \frac{\partial \sigma}{\partial \Phi} \]

EFFECTIVE COMPRESSIONAL MODULUS

IN RESPONSE TO AN APPLIED STRESS \( \sigma \)

FROM STEADY-STATE PROFILE

\[ \kappa(\Phi) = \kappa_0 \frac{(1 - \Phi)^m}{\Phi} \]

WITH \( \kappa_0 \) AND \( m \) CHOSEN TO FIT THE TIME-DEPENDENCE OF THE GEL HEIGHT

\[ \sigma = a \Phi^{3 \pm 0.3} \]
VELOCIMETRY

NO HORIZONTAL COMPONENT OF THE DISPLACEMENT DURING GEL COMPRESSION

\[ \downarrow \]

NEGLIGIBLE STRESS ON THE CELL WALLS (CONFIRMED BY POLARIMETRY)

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POISSON RATIO ≈ 0 (LIKE CORK)
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NEGLIGIBLE STRESS ON THE CELL WALLS (CONFIRMED BY POLARIMETRY)

POISSON RATIO \( \approx 0 \) (LIKE CORK)

LOCAL SETTLING VELOCITY \( v(t) \) (AT VARIOUS SETTLING TIMES)

- THE VELOCITY PROFILE IS ALMOST LINEAR FOR ANY SETTLING TIME, EXCEPT IN THE UPPERMOST LAYER OF THE GEL.
- A \( z \)-INDEPENDENT (BUT \( t \)-DEPENDENT)

STRAIN RATE:
\[
\dot{\varepsilon}(t) = \frac{dv}{dz}
\]

- ON A PLANE AT CONSTANT \( \sigma \) (SAME WEIGHT ON TOP)

EFFECTIVE “COMPRESSIONAL” VISCOSITY:
\[
\eta(t) = \frac{\sigma}{\dot{\varepsilon}(t)} \approx \dot{\varepsilon}(t)^{-1}
\]
D) Collapse and ageing of a gel: microscopic dynamics

Local TRC correlation functions in the gel

![Graph showing the local TRC correlation functions in the gel. The graph plots $g_2(z, t, \tau)$ against $\tau$ for different times $t$. The curves represent the decay of the correlation functions as a function of time and lag time $\tau$.](image)
D) Collapse and ageing of a gel: microscopic dynamics

Local TRC correlation functions in the gel

SAME decay time at all values of $z$ (as for strain rate!)
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Local TRC correlation functions in the gel

SAME decay time at all values of \( z \) (as for strain rate!)

\( \tau_{1/e} \) scales as \( \varepsilon^{-1} \)
REFERENCES


Thanks, and… ARRIVEDERCI!