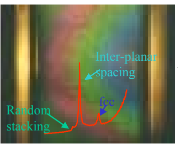
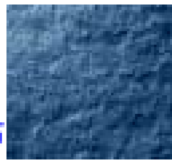


Structure and Dynamics of Colloidal Suspensions



We studied **colloidal suspensions** at different phases, using **SAXS**, **XPCS**, **Two-colour light scattering (TCLS)** techniques and direct observations.
The inter-particle attraction in these systems is induced by the presence of hard sphere repulsion and depletion interactions due to presence of non-adsorbing polymer. The topology of the phase diagrams is known to depend on the volume fraction and on the ratio of the polymer to colloid sizes, ξ. The measurements chart the development of the structure for the liquid, the crystal and the gel phases. For the **Colloidal liquid**, appearing at for $\xi > 0.24$, we find that while the *local* structure remains almost unchanged, long-ranged fluctuations appear. At small size ratio, i.e. deep and narrow depletion attraction, two kind of **Colloidal gel** have been found.

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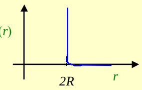
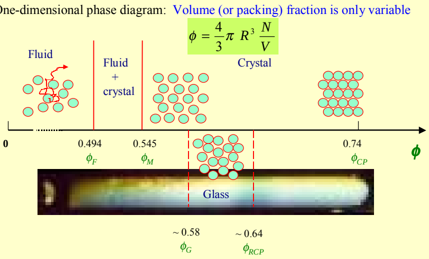
Phase behaviour of hard-sphere colloids [1]

Inter-particle Potential

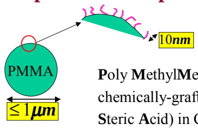


No attraction ⇒ $T_C = 0$ no colloidal liquid
Hard particles (+ incompressible liquid)
⇒ Phase boundaries vertical
One-dimensional phase diagram: Volume (or packing) fraction is only variable

$$\phi = \frac{4}{3}\pi R^3 \frac{N}{V}$$



Example of Hard Sphere colloid

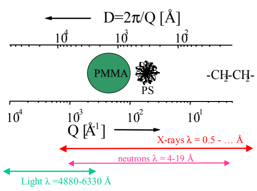


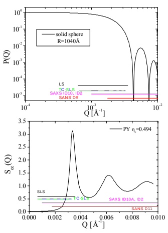
Poly **M**ethyl**M**eth**A**crylate particles Stabilised by chemically-grafted polymer brush (**P**oly **H**ydroxy **S**teric **A**cid) in Cis-Decalin

Volume fraction φ studied form 0.005 to 0.64

Scattering methods

scattering vector: $Q = \frac{4\pi}{\lambda}\sin(\Theta)$ [1/Å]

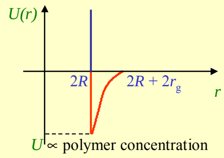


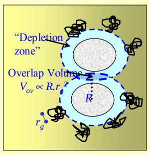


Colloid-Polymer Mixture

The addition of a non-adsorbing polymer to colloidal suspension induces an effective attraction between the particles [2]:
The Depletion Mechanism

⇒ Overlap of Depletion zones gives polymer more free volume (Higher entropy)
⇒ Osmotic force pushes particles together: "depletion potential"



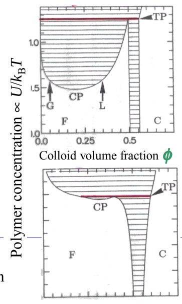


Phase diagrams of colloid-polymer mixtures

The topology of the phase diagrams depends on the volume fraction φ, polymer concentration c_p and on the ratio of the polymer to colloid sizes, $(\xi = r_g/R)$.

Theoretical phase diagrams

Calculated phase diagrams for two size ratios $\xi \approx 0.57$ (top) and $\xi \approx 0.37$ (bottom). **CP** is the critical point, **TP** triple line, **F** fluid, **L** liquid, **G** gas and **C** crystal. Liquid phase is 'marginal' at small size ration: critical point **CP** almost emerges into triple coexistence line **TP.**



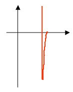
The Liquid State

-A stable liquid (or equivalently a critical point in the p-T phase diagram) only exists in a system with sufficiently long-ranged inter-particle attraction [3]
-The hard-spheres have only a single fluid state, no critical point to distinguish 'gas' and 'liquid'
-Particles with Lennard-Jones potential have a liquid phase
- colloid-polymer mixtures exhibit a liquid phase at $\xi \geq 0.24$. This liquid phase at triple coexistence is the most characteristic liquid phase in any particular phase diagram

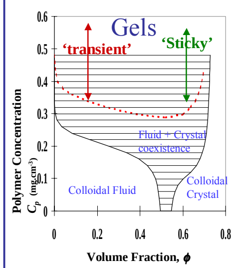
Colloidal-Polymer Gels

•Small Polymer $\xi = (r_g/R) < 1/3$

•Repulsion + deep Narrow Attraction

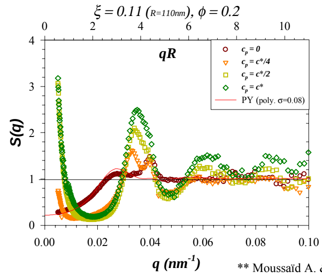


⇒At low φ (≈ 0.2) Transient Gel [6]
⇒A high φ (≈ 0.6) Sticky glass [7]



At small size ratio ξ and high polymer concentration c_p, i.e. deep and narrow depletion attraction, two kind of frozen state have been found:
-At low volume fractions of particles, variety of *non-equilibrium* aggregates are observed at high enough polymer concentrations, including certain **'transient' gels**
-At volume fractions above 0.58, hard-sphere glass is first *melted* upon addition of polymer (i.e. turning up the attraction); at high enough polymer concentration, another **'sticky' glass**, driven by attraction, is formed [7]

SAXS measurements:
Structure of Transient Gels (PMMA + PS)**

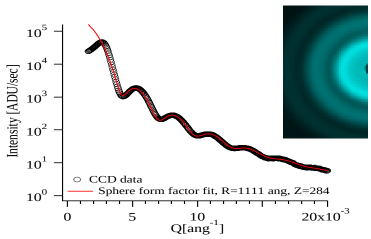


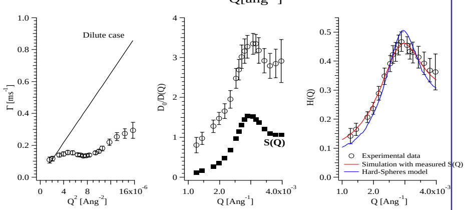
Well developed peak in *S(q)*, at *qR* ≈ *3.6* is evidence of the existence of compact structure. Local structure is also consistent with the highly non-ergodic dynamics [6]. The rise at small angles is result of aggregations of particles.

** Moussaïd A. & Narayan T., to be published

Example of SAXS & XPCS Study at ID10A PMMA particles in Cis-decalin

*Federico Zontone et al**



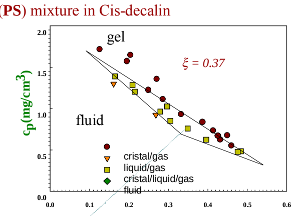


Good agreement with theory

* *Zontone F., Grübel G., Moussaïd A., to be pubilshed*

Experimental Results

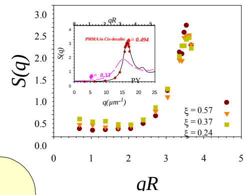
Example of phase diagram of **PMMA** particles and Polystyrene polymer (**PS**) mixture in Cis-decalin



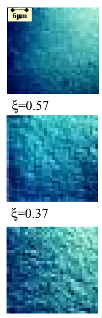
Samples

3 colloidal liquids at their triple points are studied

ξ =	0.57	0.37	0.24
ϕ_{liquid} =	0.44 well-developed liquid	0.40	0.33 marginal liquid



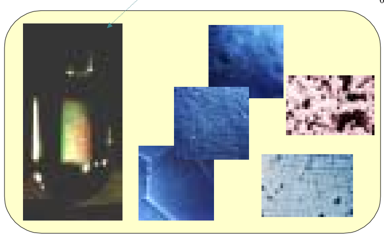
Measured S(q) of triple-coexistence colloidal liquid phase of 3 mixtures PMMA-PS for 3 different values of ξ. Inset: S(q) of PMMA at the freezing volume fraction $\phi = 0.494$ [8], compared with the theoretical Percus-Yevick prediction



ξ=0.57

ξ=0.37

ξ=0.24



Photograph of 3-phase coexistence sample and direct microscope observation of the phases using differential interference contrast (DIC) and scanning electron microscope (SEM)

- For the 3 colloidal liquids, the main peaks of *S(q)* have similar amplitudes [4]
-Long-ranged fluctuations appear in all liquids and increase as ξ is reduced, interpretation confirmed by direct observation using DIC optics
- Good agreement with theory [5]

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