Towards understanding gelation in complex model mixtures

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Neutrons and Food Workshop
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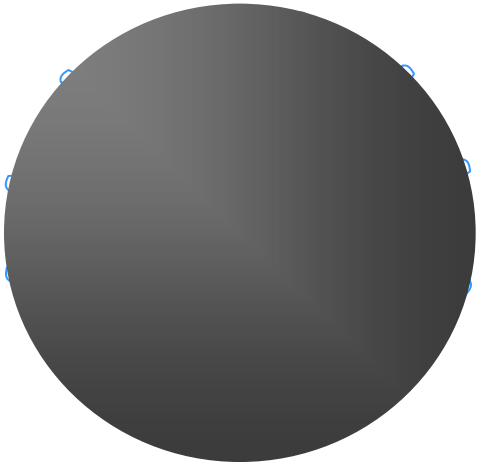
Inspiration

Stabilization *via* attractions
Pourable "gel"

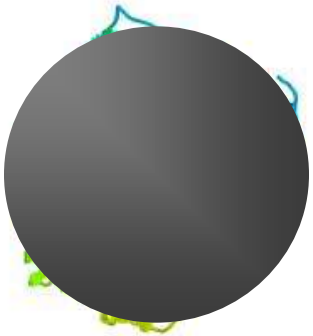
Structure *via* attractions
(More) solid gel

Can we predict gelation & gel properties?

Structure builders in food



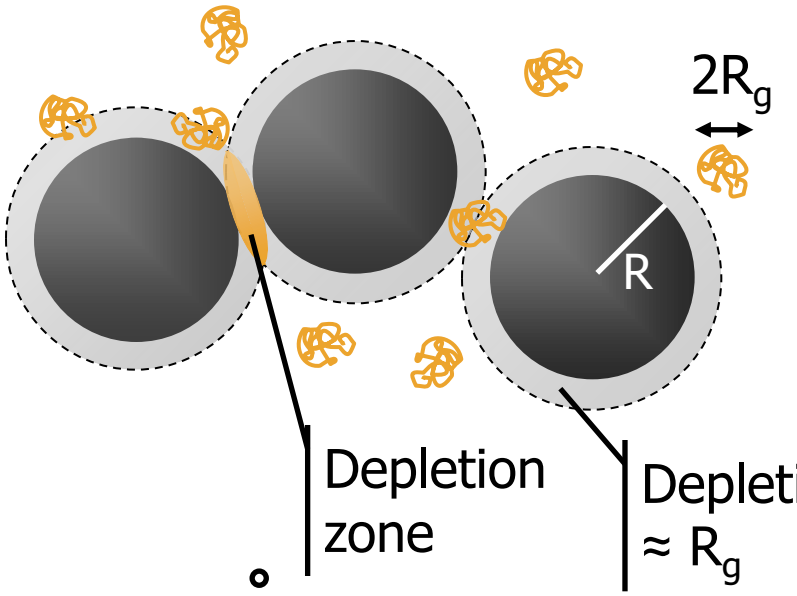
Emulsion droplet



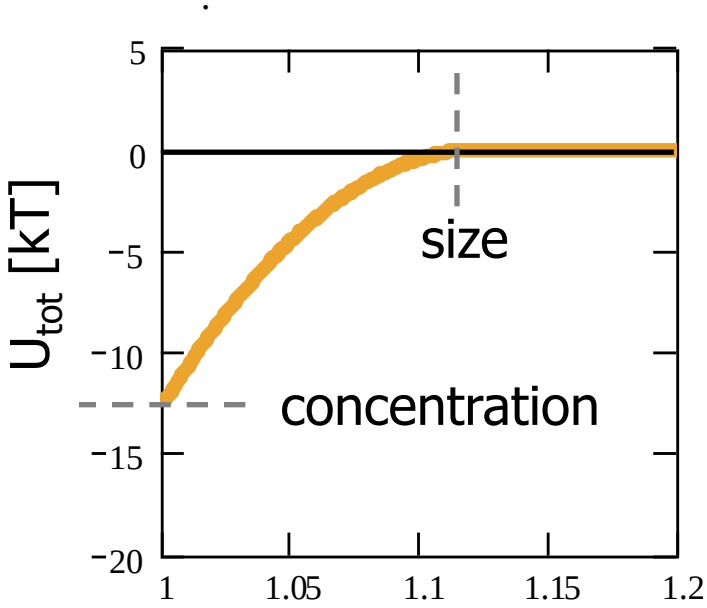
Protein
(aggregate)

Polymer-induced attractions

Colloid + Polymer



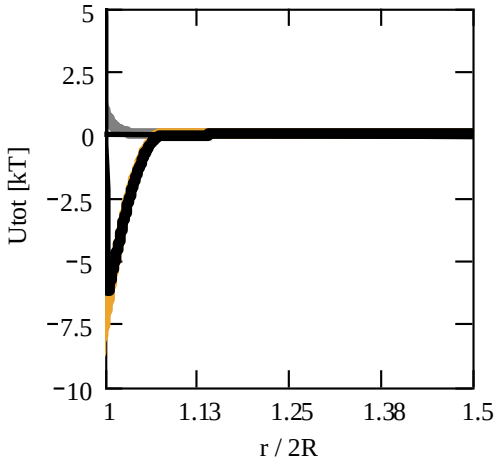
Colloid-colloid pair potential

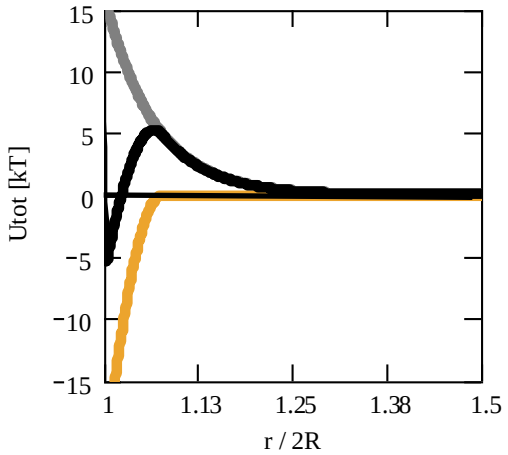


colloid-colloid distance / colloid diameter

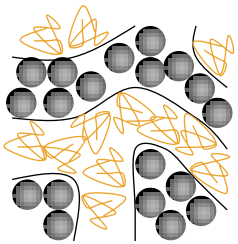
Repulsion & attraction => gelation

repulsion
attraction
total

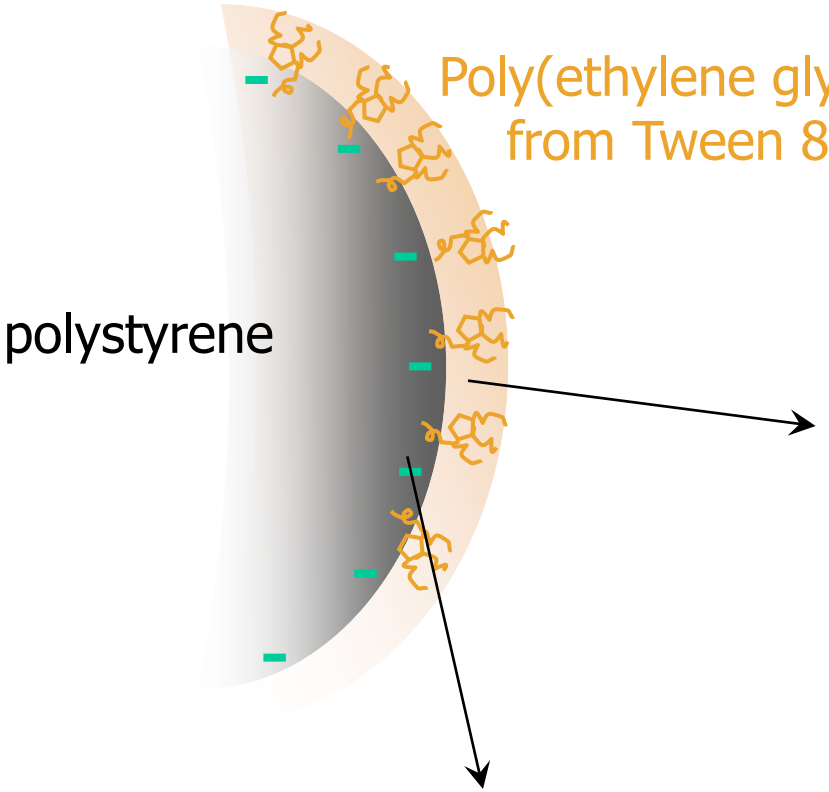




Range repulsion vs attraction vs colloid size	short short
Increasing c/c* in equilibrium	fluid - fluid
Gelation	arrested spinodal decomposition non-equilibrium



Colloids



In-house synthesized
model colloids in water

SANS contrast variation of form factor:

$R_{core} \approx$ 57 nm

$d_{shell} =$ 4 nm

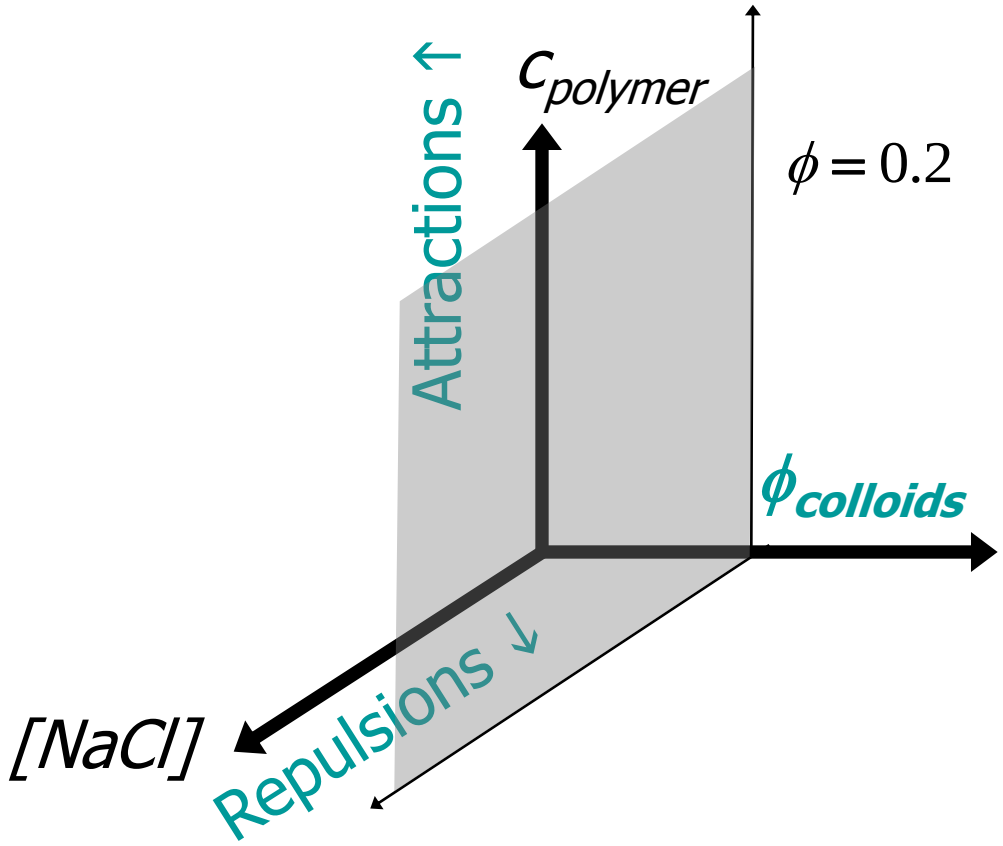
SANS / SAXS structure factors:

Effective volume fraction and surface charge
as function of salt & colloid concentration

Complex mixtures

Poly(ethylene oxide) polymer

R_g = 4.7 nm

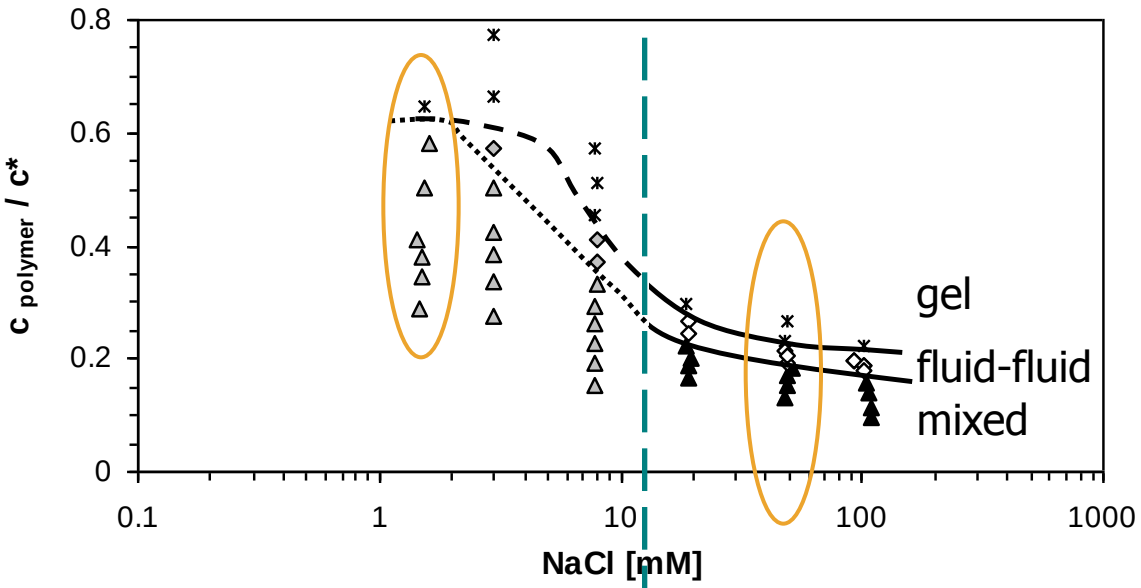


Phase diagram

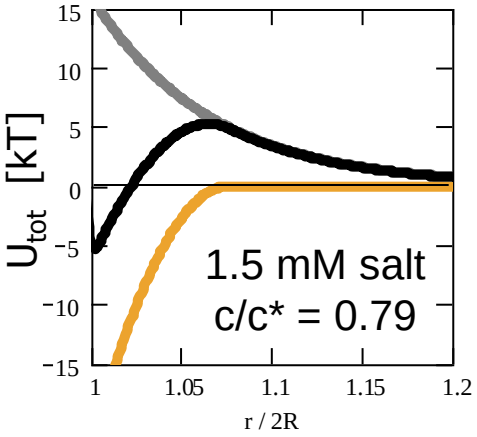
Strong repulsions ← Weak repulsions

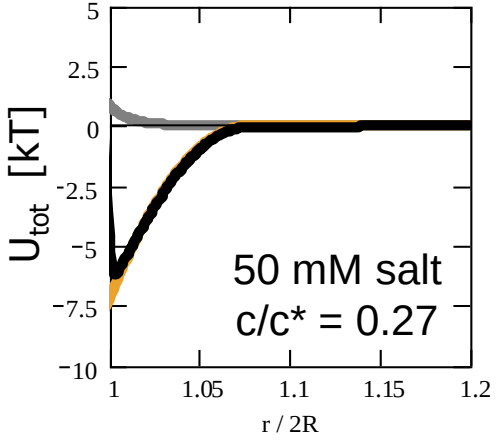
Strong attractions

Weak attractions



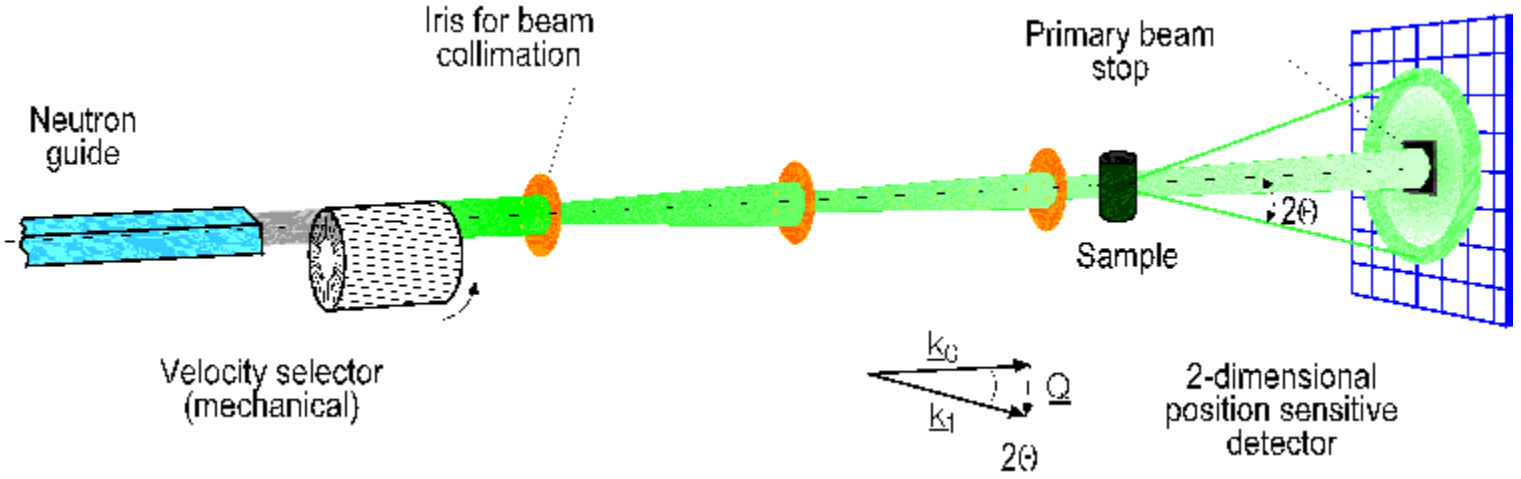
repulsion
attraction
total





Characterization - SANS

Small angle neutron scattering



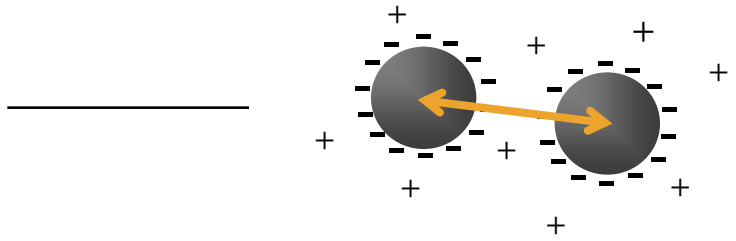
Intensity = form factor x structure factor

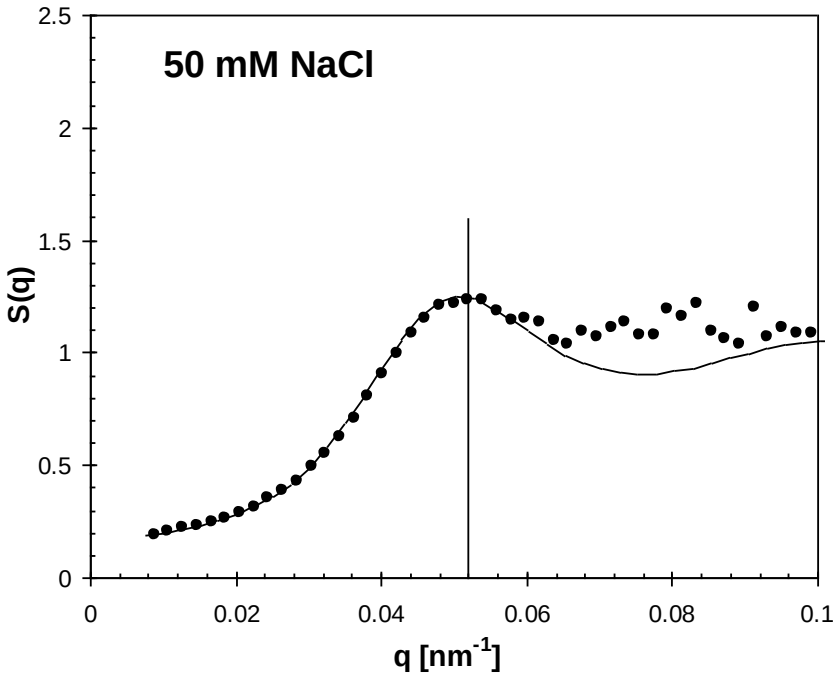
SANS I, PSI, Villigen

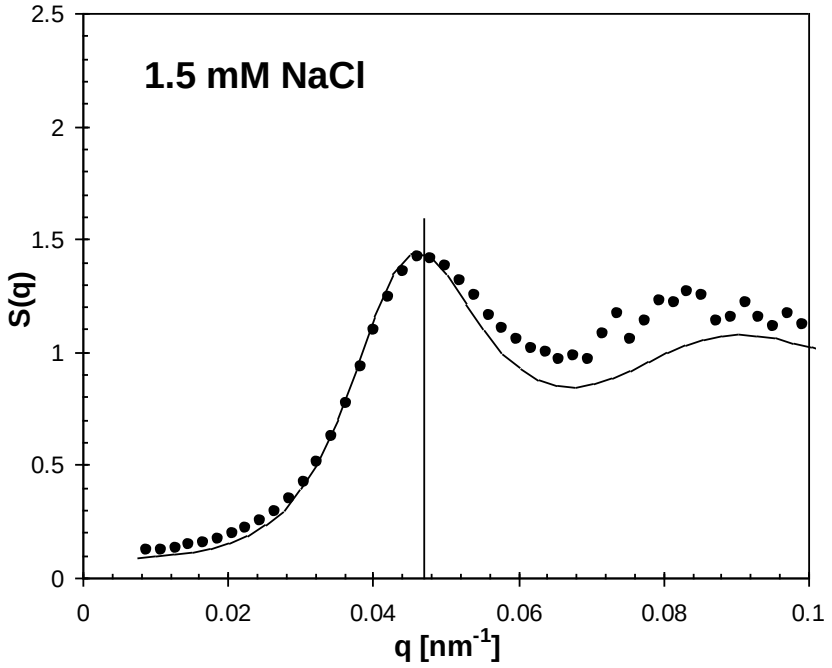
Characterization phases

Structure factors from SANS

Scattered intensity I(q) => S(q)



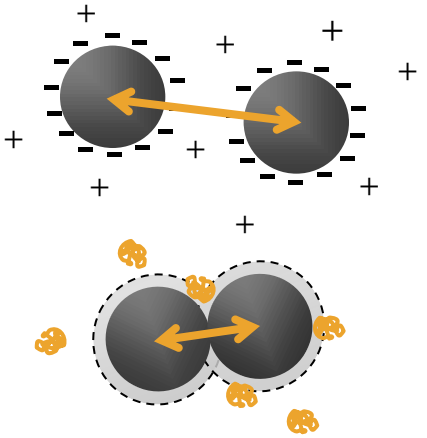


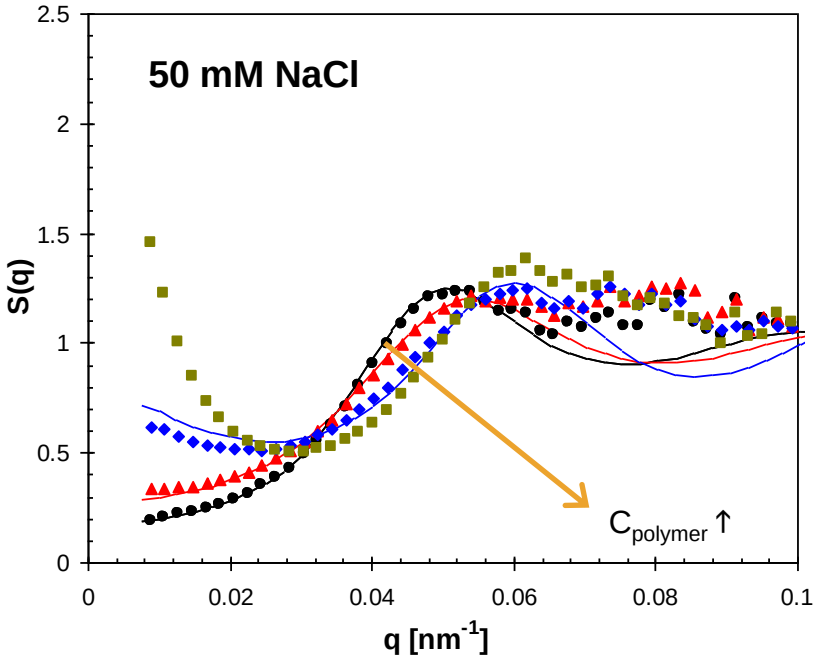


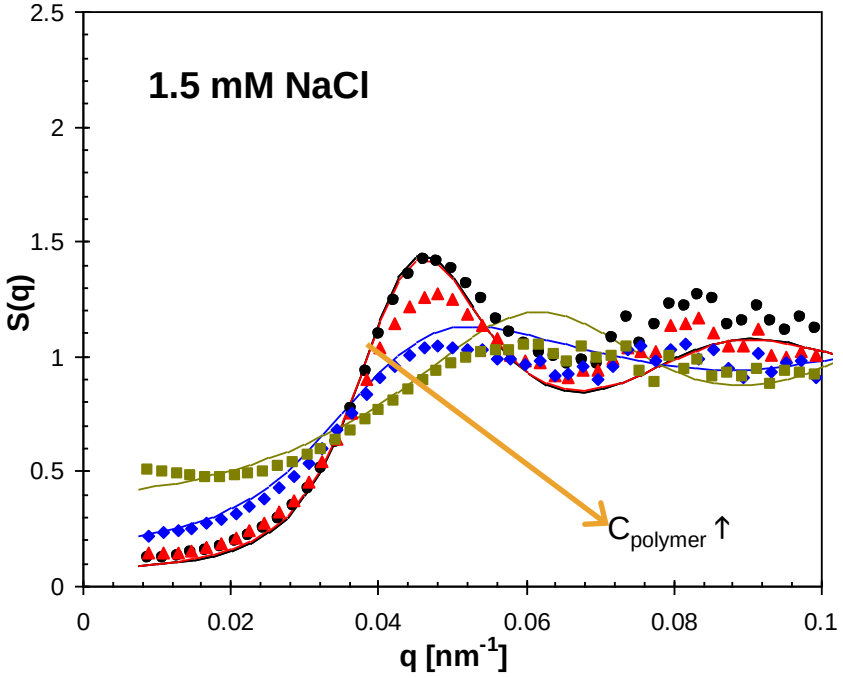
Characterization phases

Structure factors from SANS

Visually homogeneous samples



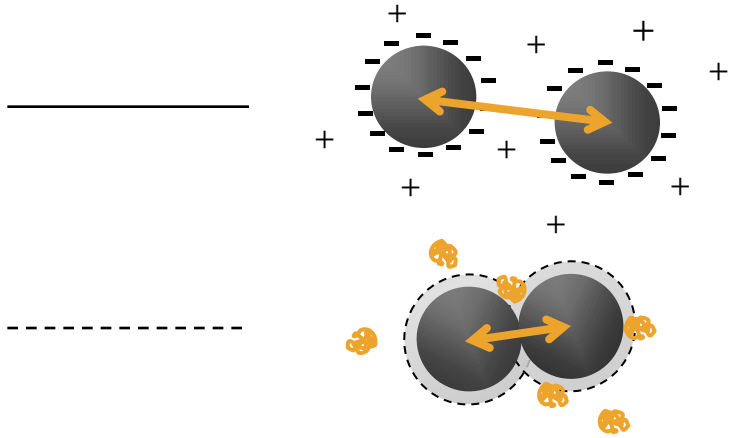


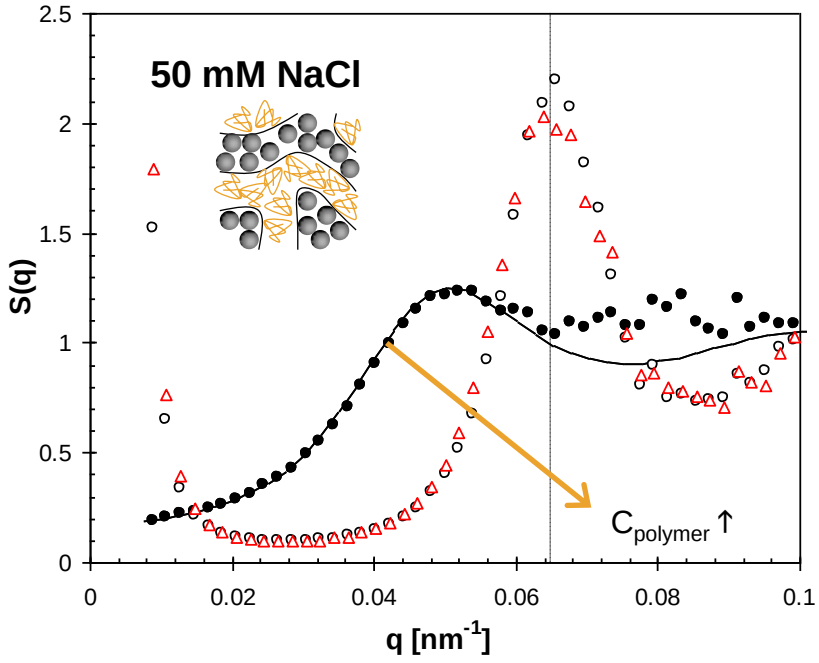


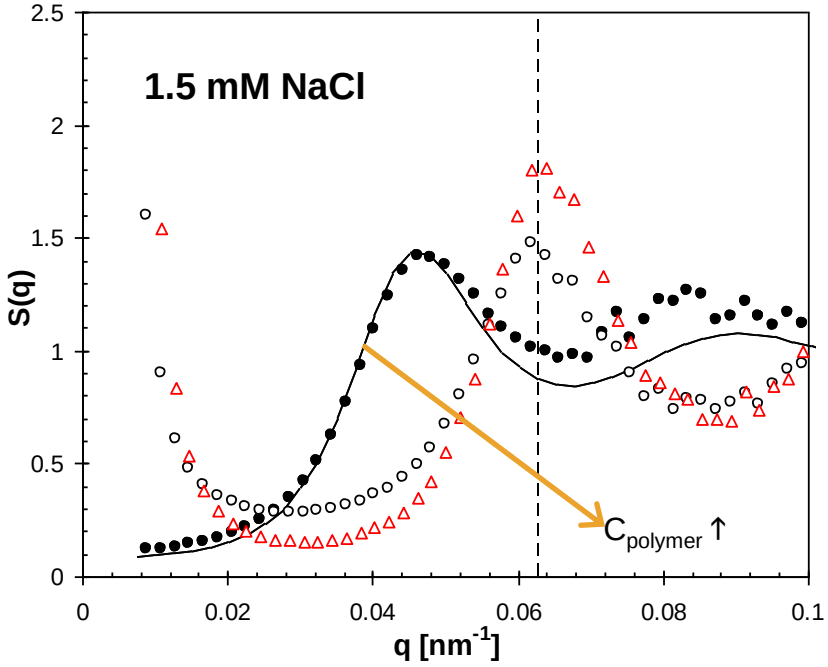
Characterization phases

Structure factors from SANS:

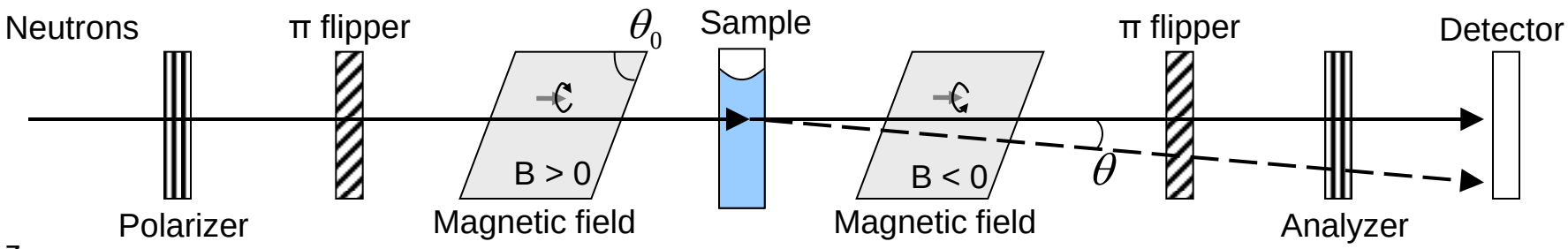
- Stronger gel peak in 50 mM
- Opposite effects for stronger attractions

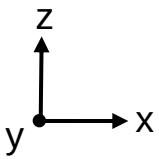


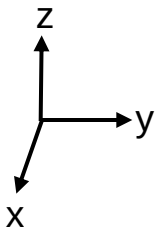




Characterization - SESANS



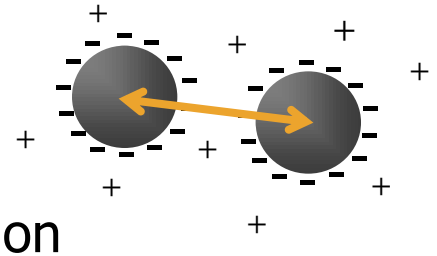




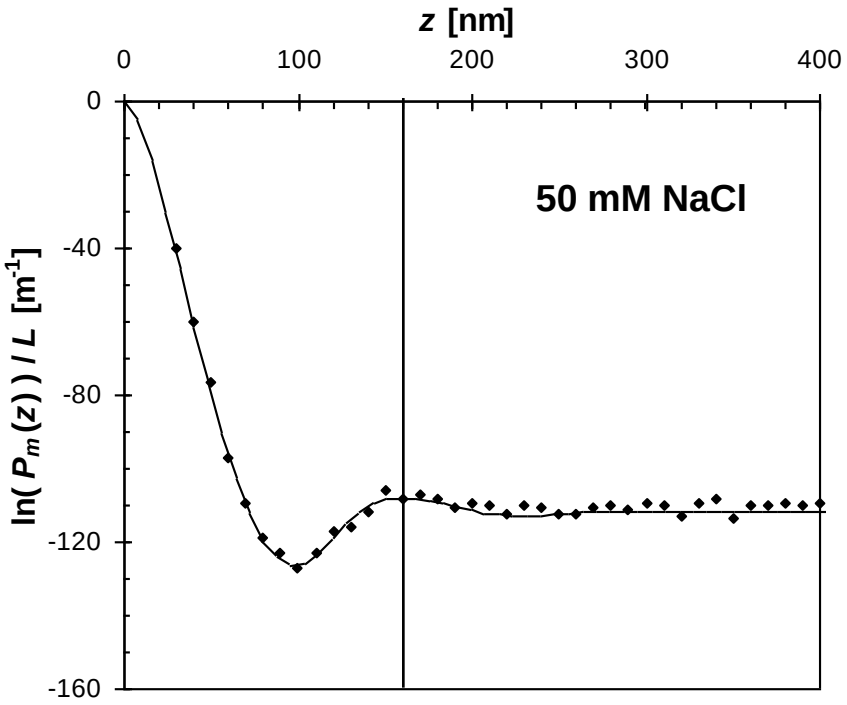
SESANS, RID, Delft

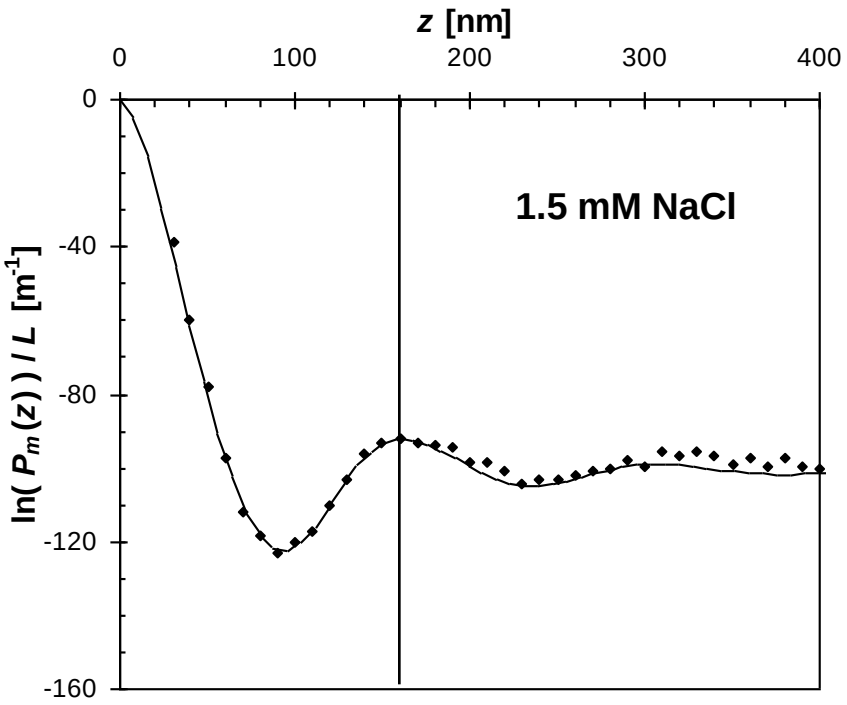
Characterization colloids

SESANS data



Measured polarization ~ density correlation function

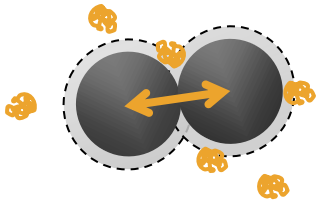


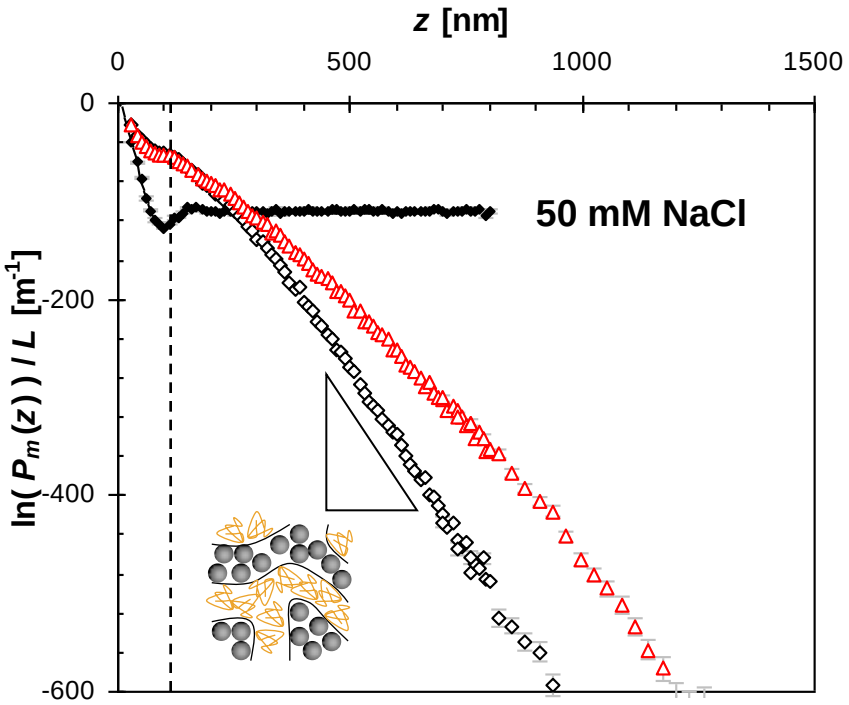


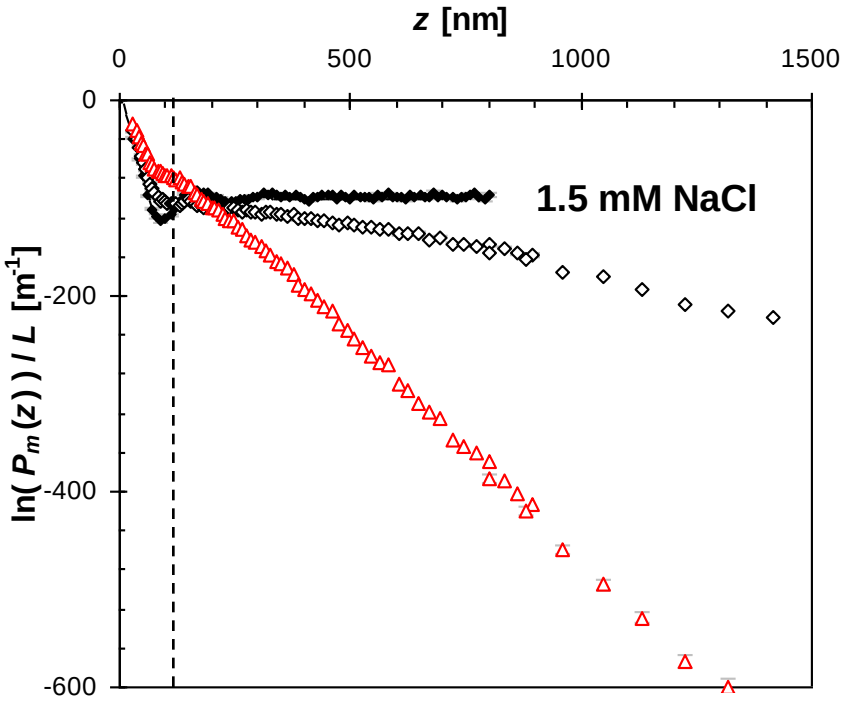
Characterization - SESANS

SESANS data:

- Correlation over long length scales
- Estimate density of colloid-rich backbone from slope of curve



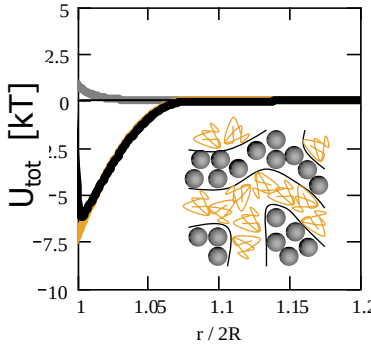




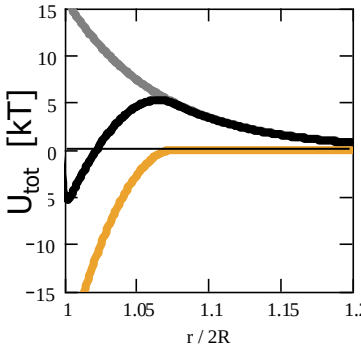
Conclusions & Outlook

What have we learned about the effect of charges on gelation?

- **Repulsions shorter ranged than attraction**
  - **Phase behaviour of purely attractive systems**
  - **Gelation *via* spinodal decomposition**



- **Repulsions longer ranged than attraction & shorter ranged than colloid size**
  - **Cluster fluid phase**
  - **Gel structure is more open**
  - **Neither *via* spinodal decomposition, nor DLCA/RLCA**



Acknowledgements

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Thank you for your attention!

Physics

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Synthesis

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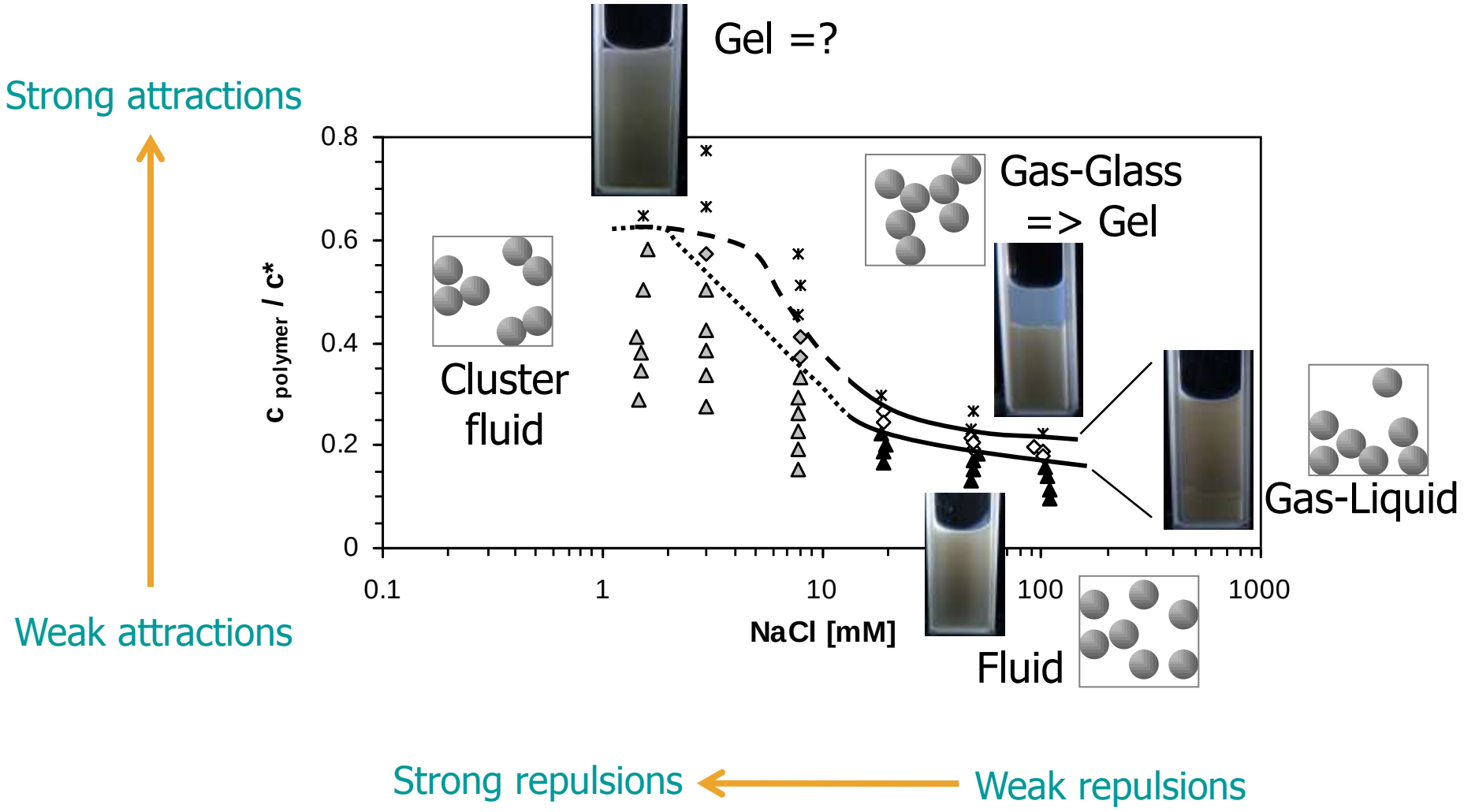
Chantal Rufier

Liliane Ackermann-Hirschi

Phase diagram

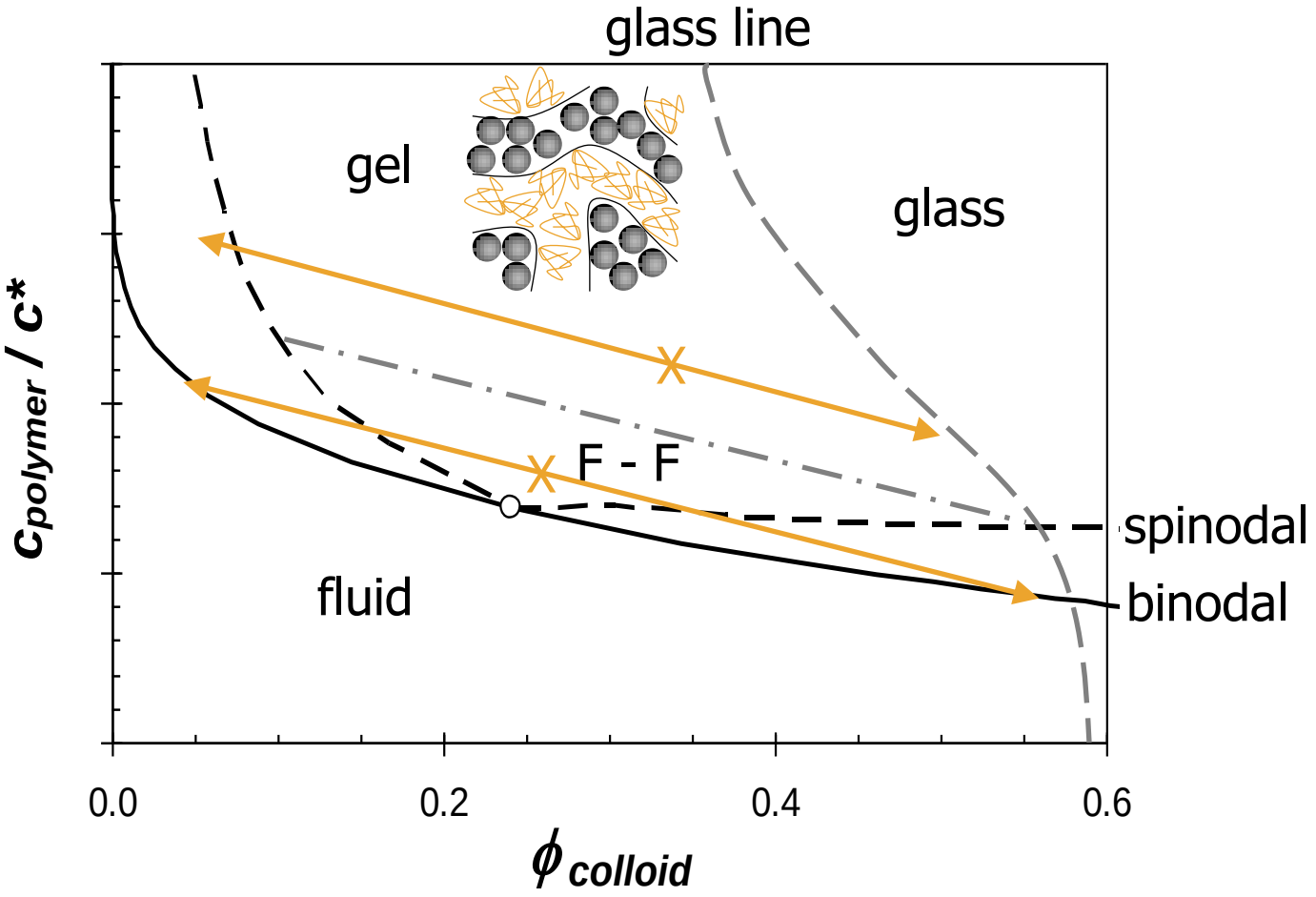


Attractions => gelation

Phase diagram

spinodal decomposition: instantaneous demixing

Increasing attractions



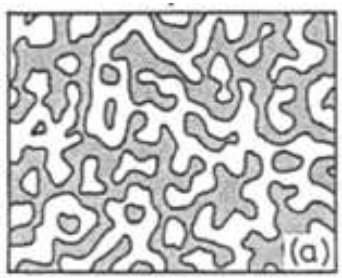
$R_g / R < 0.2$

Gelation

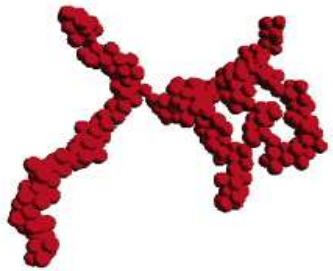
Routes to gelation

1. RL or DL cluster aggregation
   Driving force: typically Van der Waals
   Arrest: space spanning aggregate

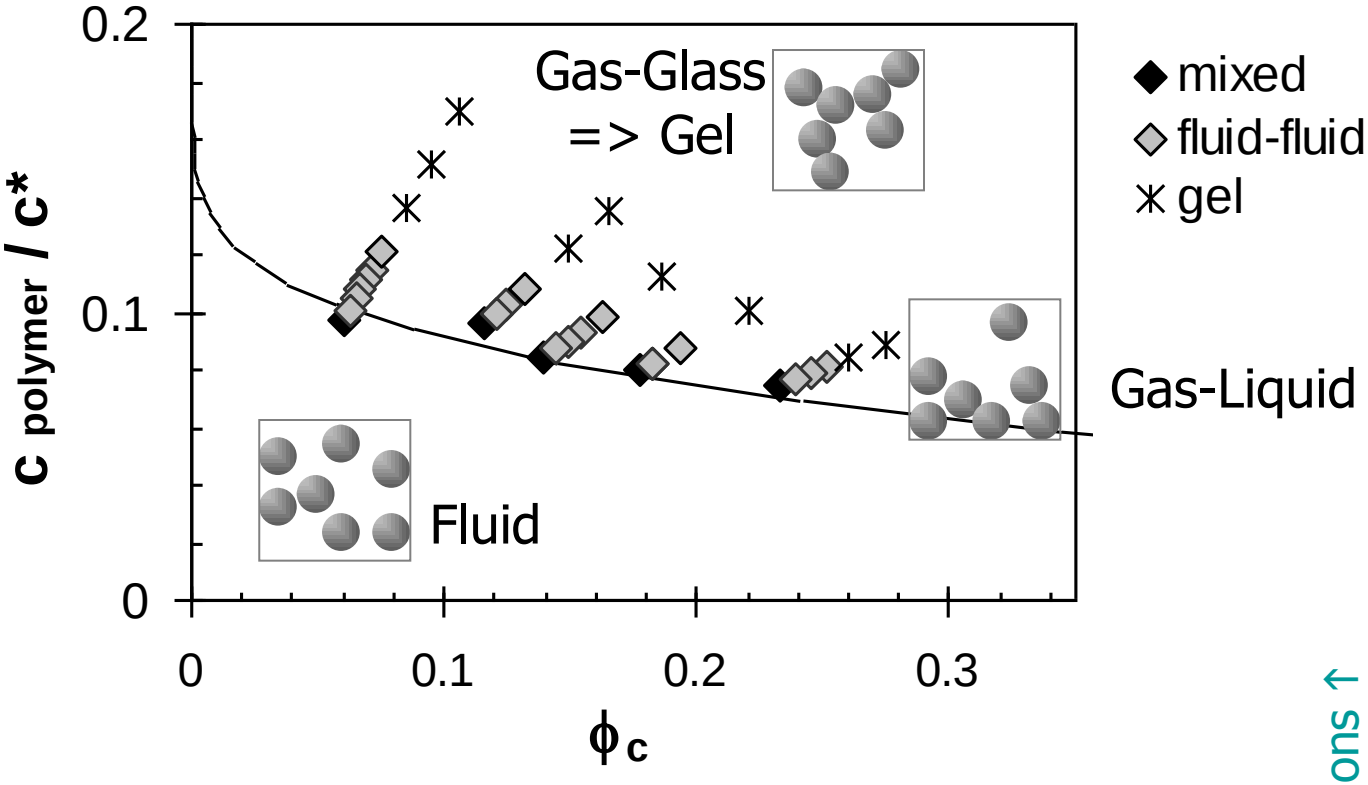
2. Thermodynamic instability / phase separation
   Driving force: for instance depletion interactions
   Arrest: space spanning dense phase that
   reaches the attractive glass transition

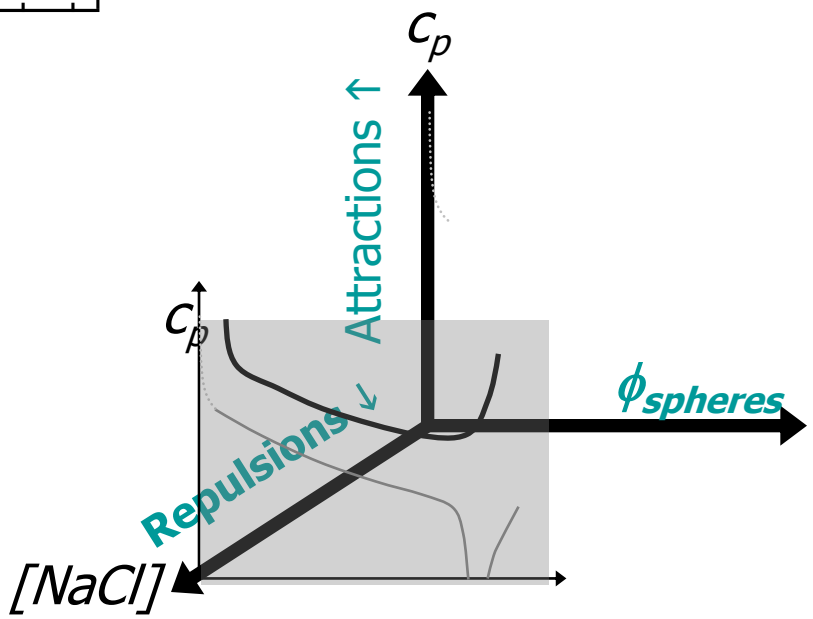


3. Equilibrium gelation
   Driving force: short-range attraction vs
   long-range repulsion
   Arrest: space spanning equilibrium cluster



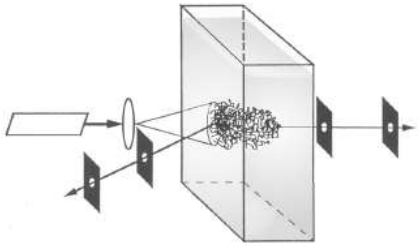
Phase diagram – high salt

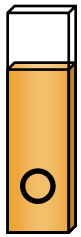




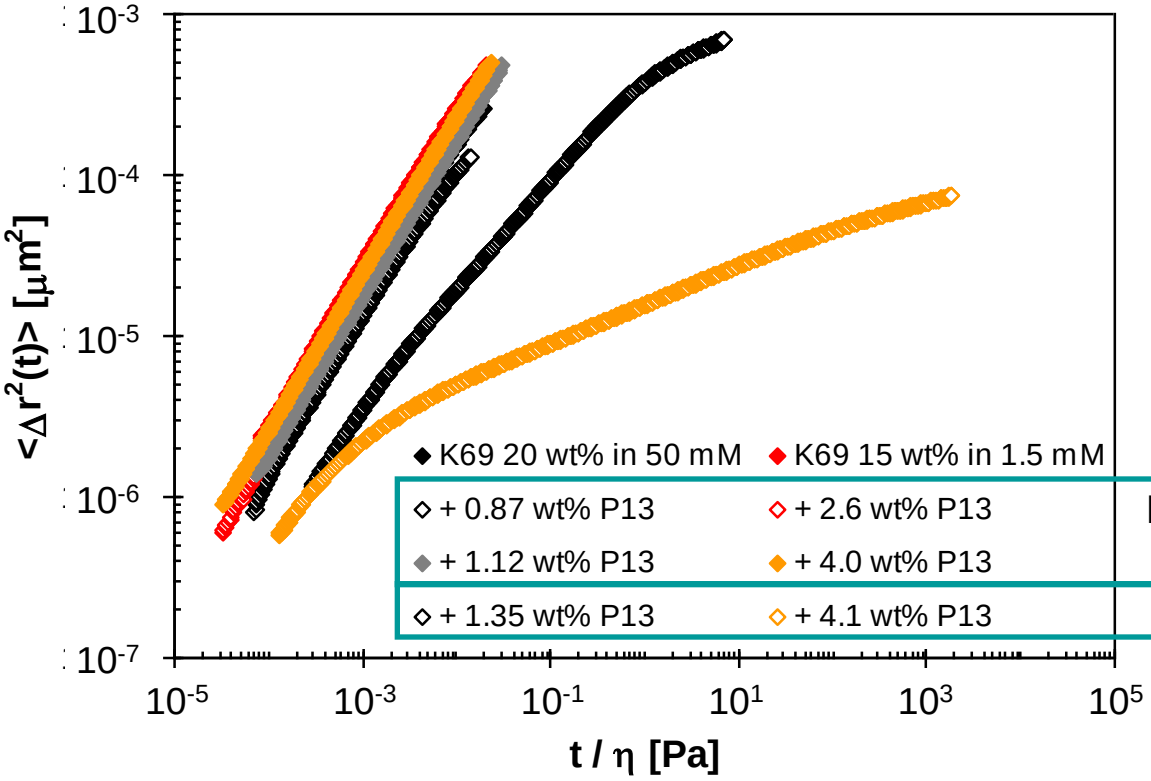
Fleer & Tuinier 2007

Characterization - dynamics



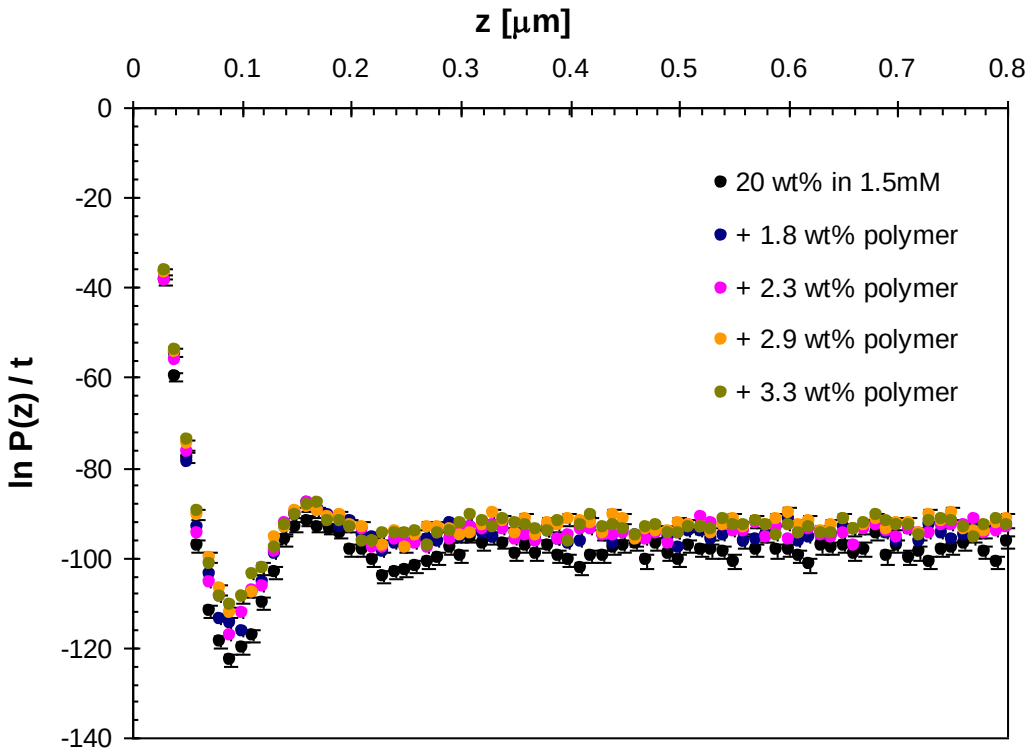


Diffusing Wave Spectroscopy

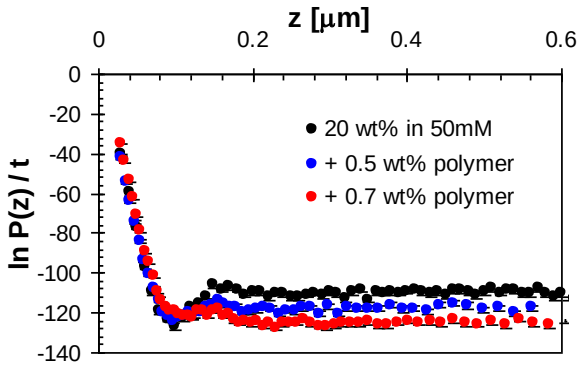


$$< \Delta r^2(t) > \propto \frac{1}{R_h}$$

Characterization phases



Gradient samples
Within 24 h



Mixtures