Depletion forces on soft colloids

Christos N. Likos

Faculty of Physics, University of Vienna, Austria

Enrico Fermi Summer School
Course 193: Soft Matter Self-Assembly
Villa Monastero, Varenna, 29 June - 7 July 2015

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Outline

Introduction

Star polymer solutions with no depletion

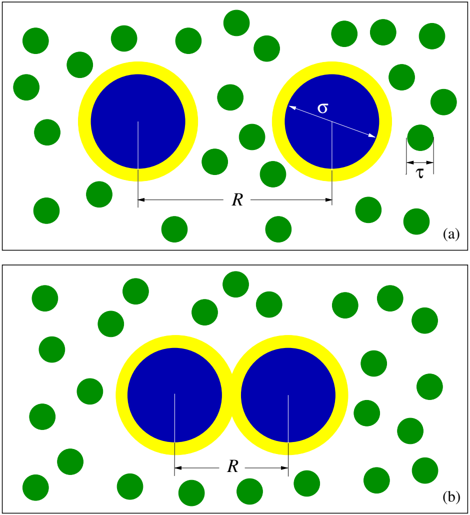
Linear polymers as depletants of soft colloids

Hard colloids as depletants of soft colloids

Conclusions

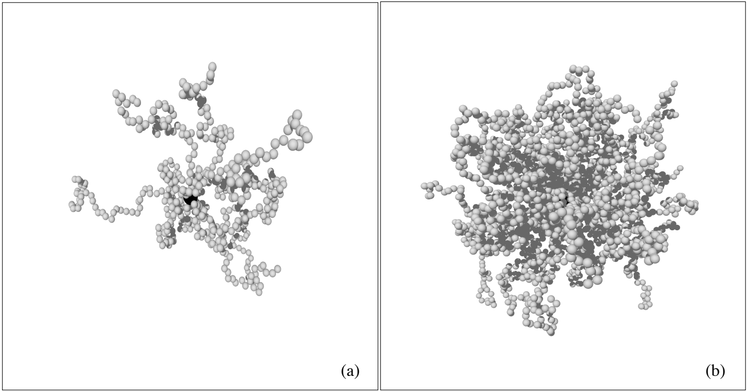
Introduction

- The classical Asakura-Oosawa depletion picture

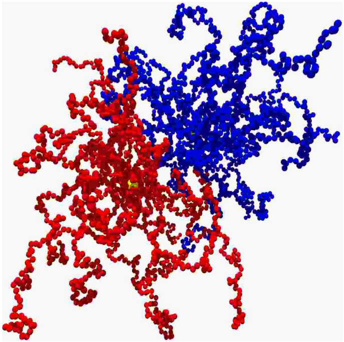


Star polymers

- Chemically anchor *f* polymers on a common center
- *f* is called *functionality* of the star
- Below: $f = 10$ (left), $f = 50$ (right)



One-component star polymer solutions



- Center-to-center effective interaction[1]

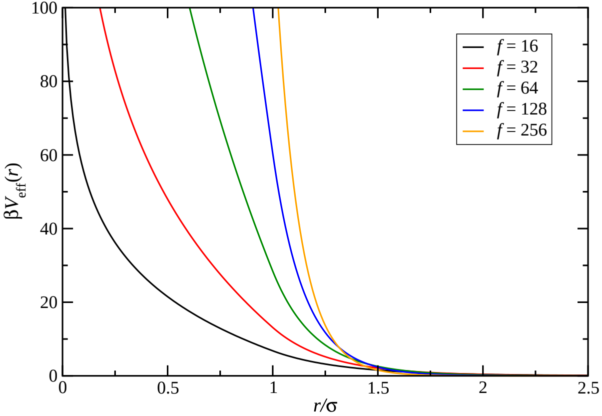
$$\beta V(r) = \frac{5}{18} f^{3/2} \begin{cases} -\ln\left(\frac{r}{\sigma}\right) + \frac{1}{1+\sigma\kappa} & \text{for } r \leq \sigma \\ \frac{1}{1+\sigma\kappa}\frac{\sigma}{r}\exp[-\kappa(r-\sigma)] & \text{for } r > \sigma, \end{cases}$$

where $\kappa = \sqrt{f}/(2\sigma)$ and $\sigma \cong 1.3\, R_g$.

[1] CNL *et al.*, Phys. Rev. Lett. **80**, 4450 (1998)

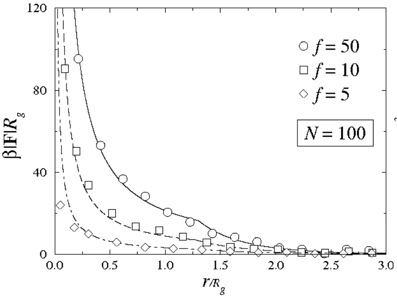
Effective interaction

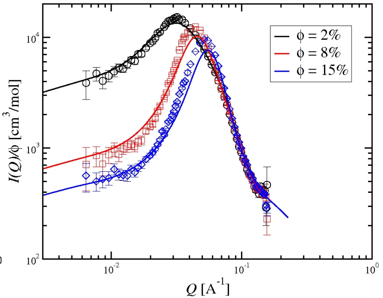
- Dependence on f: Bridging between polymer and hard-sphere behavior



Effective interaction

- Comparison with simulations[2] and SANS[3]





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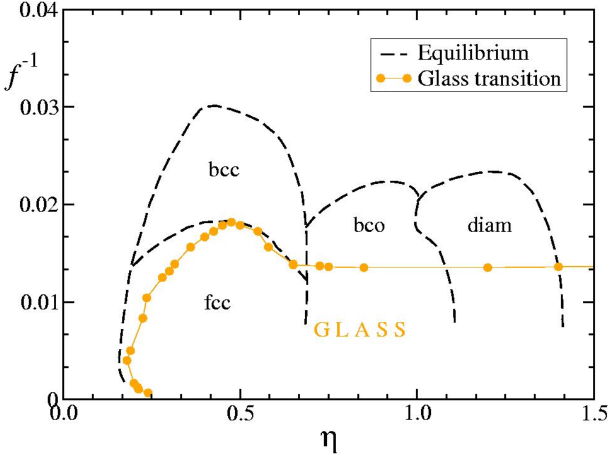
[2] A. Jusufi *et al.*, Macromolecules **32**, 4470 (1999).
[3] CNL *et al.*, Phys. Rev. Lett. **80**, 4450 (1998).

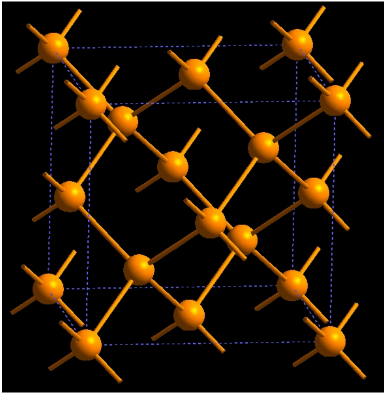
Phase behavior

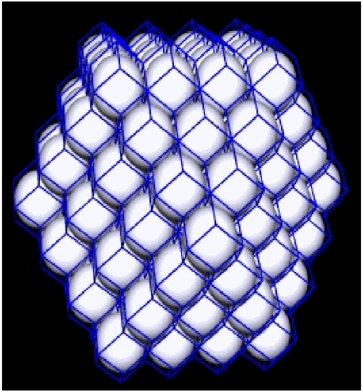
- Equilibrium[4] and glass[5] phase diagrams



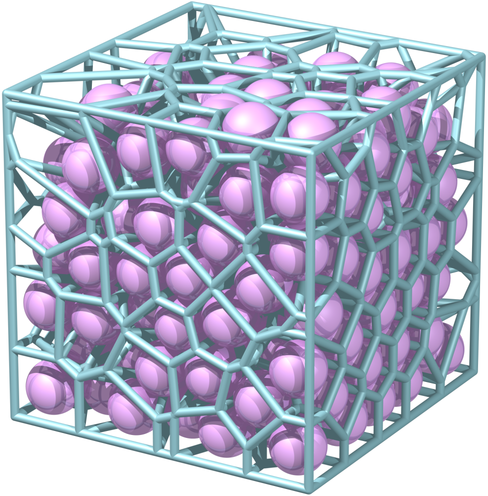
[4] M. Watzlawek *et al.*, Phys. Rev. Lett. **82**, 5289 (1999)
[5] G. Foffi *et al.*, Phys. Rev. Lett. **90**, 238301 (2003)

Crystals ...



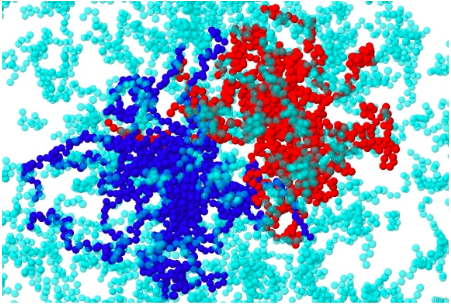


... and glasses



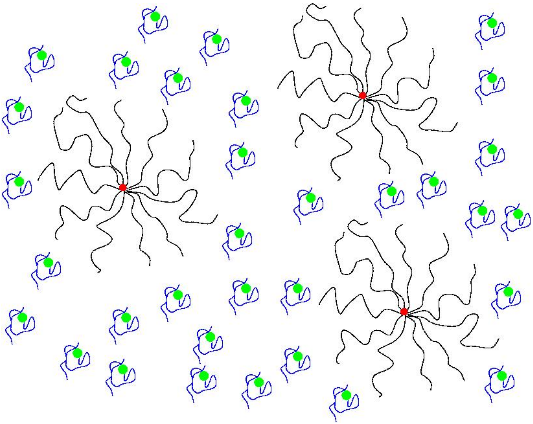
Star-chain mixtures

- Add some homopolymer chains
- Why? Sheer curiosity!



Star-chain mixtures

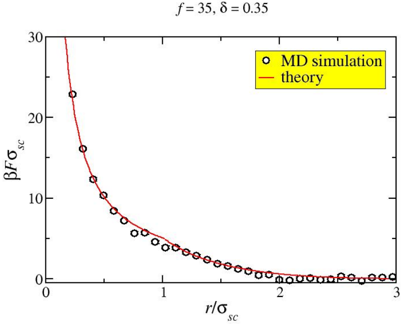
- Star centers and chain central monomers as effective coordinates

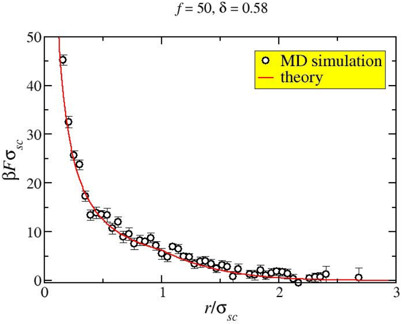


Star-chain mixtures

Cross interaction $V_{12}(r)$: MD and theory:[6]

- For $r \leq \sigma_{\mathrm{sc}}$, scaling form, $V_{12}(r) \sim -\ln(r/\sigma_{\mathrm{sc}})$.
- For $r > \sigma_{\mathrm{sc}}$, apply a Flory theory for overlapping density profiles.





[6] C. Mayer, CNL, Macromolecules **40**, 1196 (2007).

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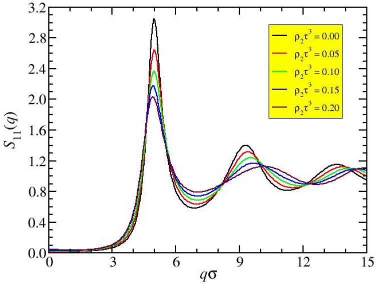
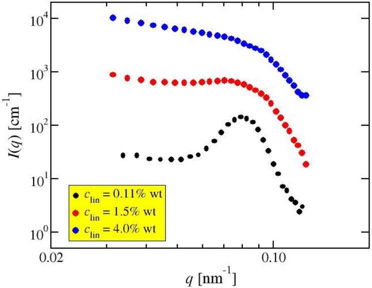
Pair structure: theory and experiment

Here: $f = 263$ and $\delta = 0.3$

Star solution at the overlap concentration c^*_{star}

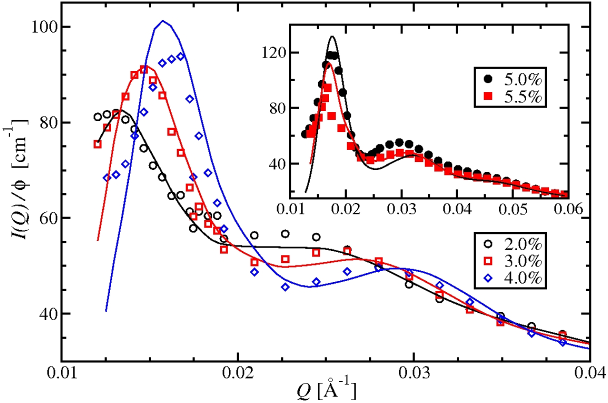




- The added chains cause a loss of structure of the stars.

Pair structure: theory and experiment

Here: $f = 91$ and $\delta = 0.3$, increasing concentration[7]



- Quantitative agreement without free parameters in a broad density range.

[7] B. Lonetti, M. Camargo, CNL *et al.*, Phys. Rev. Lett. **106**, 228301 (2011).

Chain-mediated depletion forces between stars

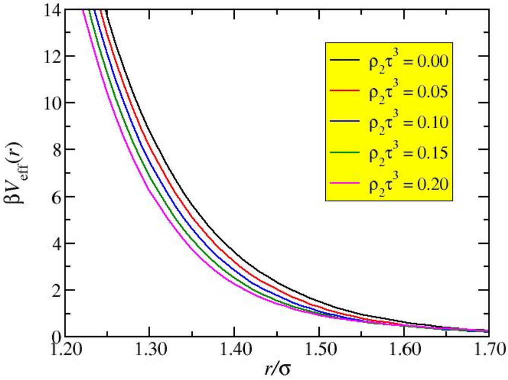
- Consider $N_1 = 2$ stars in a sea of linear chains, density ρ_2;
- Volume $\Omega \to \infty$, hence $\rho_1 \to 0$;
- Star-star distance is r, direct and chain-mediated force is $\mathbf{F}_{\mathrm{eff}}(r; \rho_2) = -\nabla V_{\mathrm{eff}}(r; \rho_2)$;
- Obtain as

$$V_{\mathrm{eff}}(r; \rho_2) = -\lim_{\rho_1 \to 0} \left[\ln g_{11}(r; \rho_1, \rho_2)\right];$$

- Readily available from liquid structure.

Chain-mediated depletion forces between stars

- Here: $f = 263$, $\delta = 0.3$



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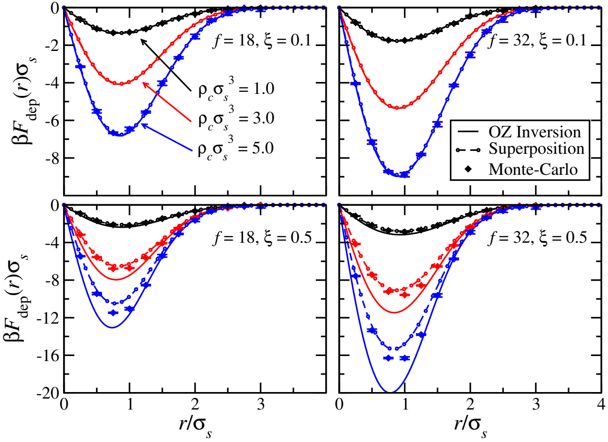
Chain-mediated depletion forces between stars[8]

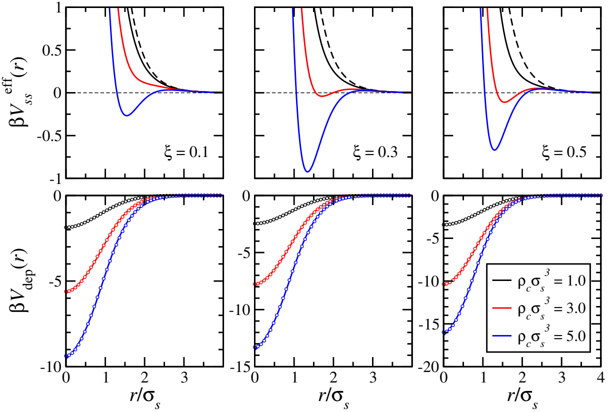
- Here: $f = 18, 32$, varying $\xi \equiv \delta$ and chain density



[8]M. Camargo and CNL, Phys. Rev. Lett. **104**, 078301 (2010).

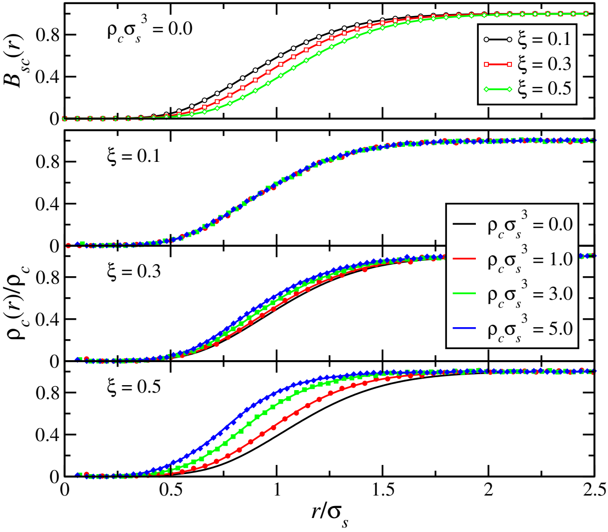
Chain-mediated depletion forces between stars

- Here: $f = 18$, variying $\xi \equiv \delta$ and chain density



Polymer density profiles around a star

- Here: $f = 32$, variying $\xi \equiv \delta$ and chain density



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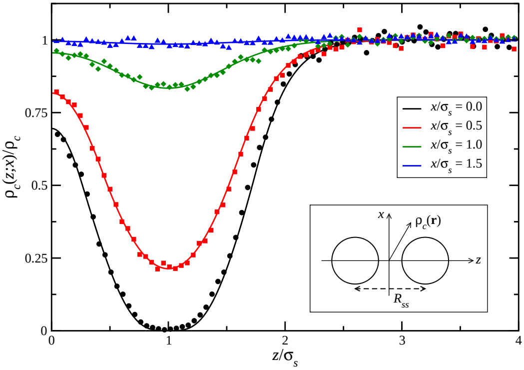
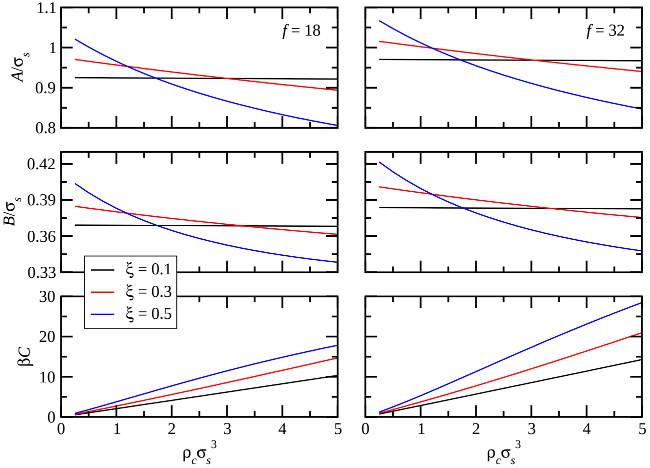
Polymer density profiles around two interacting stars

- Here: $f = 18$, variiying $\xi = 0.5$ and $\rho_c\sigma_s^3 = 4.0$



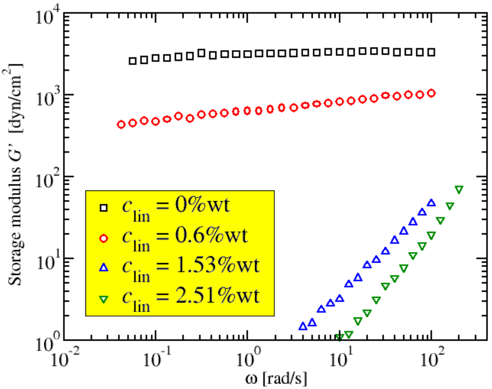
Chain-mediated depletion forces between stars

- Fit to $\beta V_{\mathrm{dep}}(r) = -\frac{C}{\exp[(r-A)/B]+1}$



Star-chain mixtures: glass melting

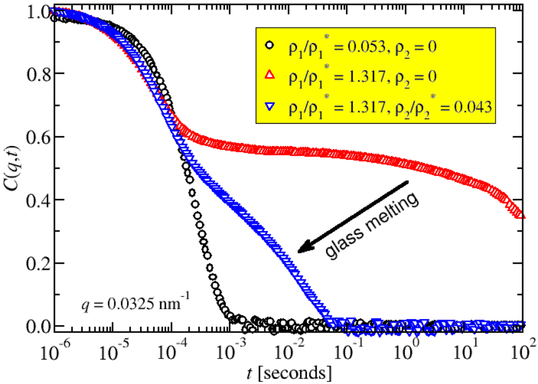
- $f = 263$, $\delta = 0.3$, rheology[9]



[9] E. Stiakakis *et al.*, Phys. Rev. Lett. **89**, 208302 (2002).

Star-chain mixtures: glass melting

- $f = 122$, $\delta = 0.44$, Dynamic Light Scattering[10]



[10] E. Stiakakis *et al.*, Europhys. Lett. **72**, 664 (2005).

Mode Coupling Theory

- Focus only on stars, chains implicit.
- Consider $\hat{\rho}(\mathbf{q}, t) = \sum_\ell \exp[-\mathrm{i}\mathbf{q} \cdot \mathbf{r}_\ell]$.
- Non-ergodicity factor $f(q)$ of the stars[11]

$$f(q) = \lim_{t\to\infty} \langle \hat{\rho}^*(\mathbf{q}, 0)\hat{\rho}(\mathbf{q}, t)\rangle / \langle \hat{\rho}^*(\mathbf{q}, 0)\hat{\rho}(\mathbf{q}, 0)\rangle.$$

- MCT:

$$\frac{f(q)}{1 - f(q)} = \frac{1}{2(2\pi)^3} \int d\mathbf{k}\, V^{(2)}(q, k, |\mathbf{q} - \mathbf{k}|) f(k) f(|\mathbf{q} - \mathbf{k}|),$$

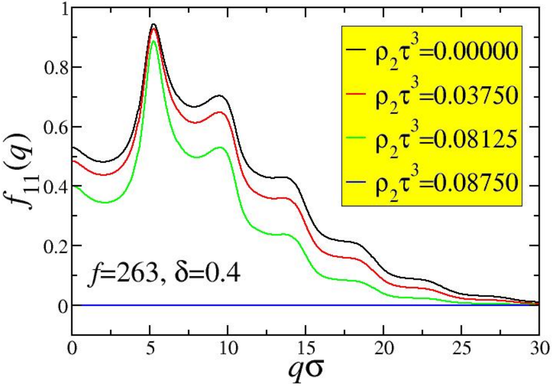
- where

$$\begin{aligned} V^{(2)}(q, k, |\mathbf{q} - \mathbf{k}|) &= \frac{\rho}{q^2} S(q) S(k) S(|\mathbf{q} - \mathbf{k}|) \\ &\times \left(\frac{\mathbf{q}}{q} [\mathbf{k} c(k) + (\mathbf{q} - \mathbf{k}) c(|\mathbf{q} - \mathbf{k}|)] \right)^2 . \end{aligned}$$

[11] C. Mayer, CNL, Macromolecules **40**, 1196 (2007).

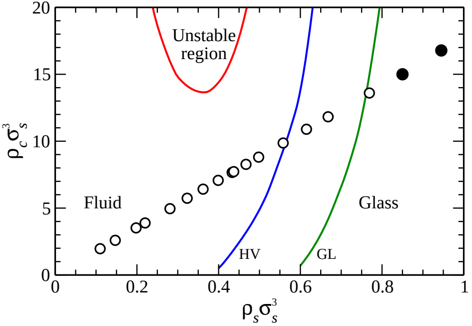
Star-linear mixtures: glass melting

- MCT-results



Star-linear mixtures: glass melting

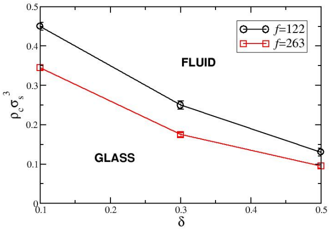
- Shifting of glass line[12]

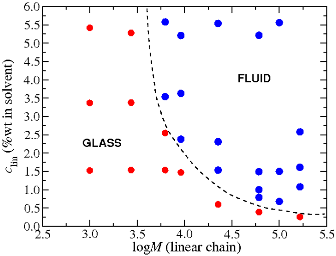


[12] B. Lonetti, M. Camargo, CNL *et al.*, Phys. Rev. Lett. **106**, 228301 (2011).

Star-linear mixtures: glass melting

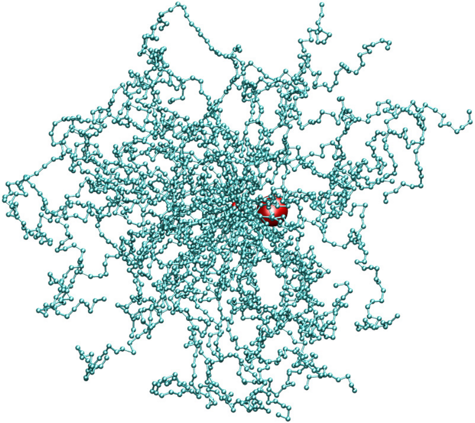
- Comparison with experiment[13]





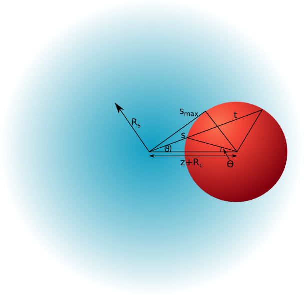
[13] E. Stiakakis *et al.*, Phys. Rev. Lett. **89**, 208302 (2002).

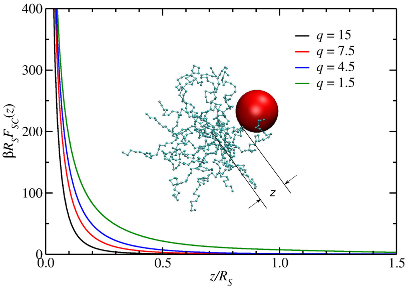
Turn it around: big stars, small colloids



Turn it around: big stars, small colloids

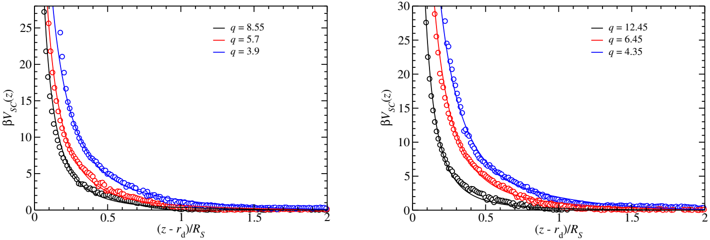
- Coarse-graining: calculate $V_{sc}(r)$





Turn it around: big stars, small colloids

- $V_{sc}(r)$: left, $f = 30$; right, $f = 50$. Compare with simulations[14]

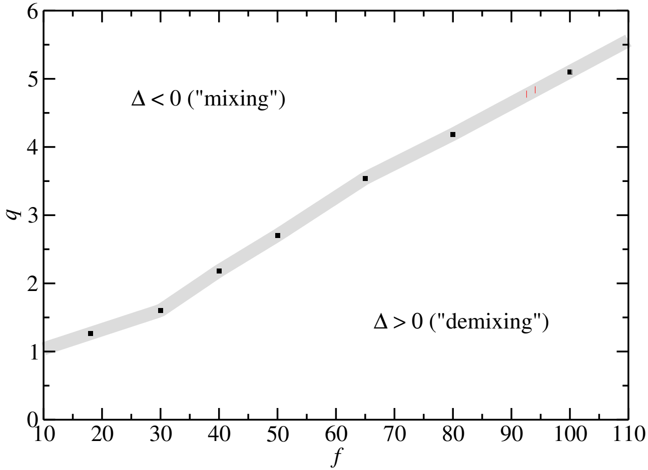


- NB, $V_{sc}(z) \sim -\ln z$ as $z \to 0$.

[14] D. Marzi, CNL, B. Capone, J. Chem. Phys. **137**, 014902 (2012).

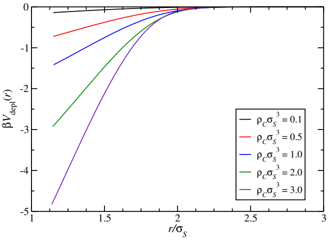
Turn it around: big stars, small colloids

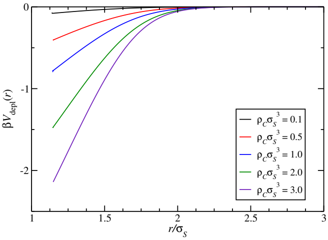
- A rough-and-ready prediction on phase behavior



Depletion potentials on the stars due to colloids

- $V_{depl}(r)$: left, $f = 200, q = 3$; right, $f = 200, q = 4$.





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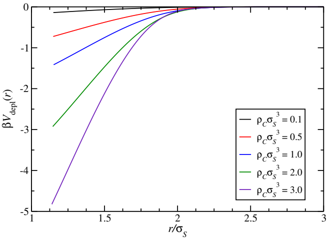
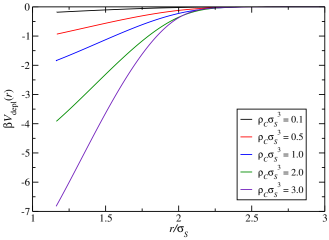
Depletion potentials on the stars due to colloids

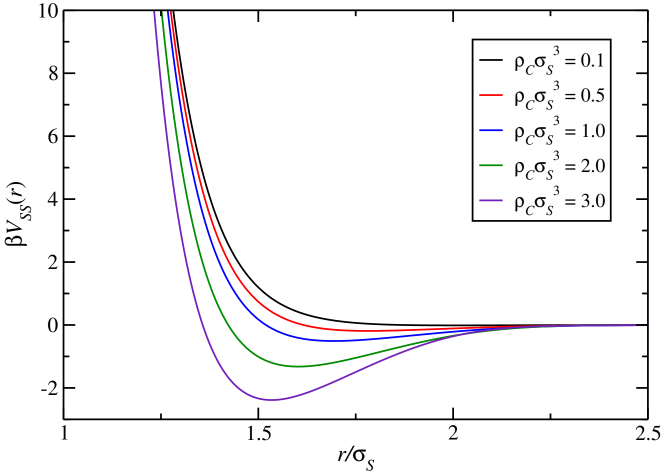
- $V_{depl}(r)$: left, $f = 200, q = 3$; right, $f = 300, q = 3$.





Total effective star-star potential

- $f = 300$, $q = 3$



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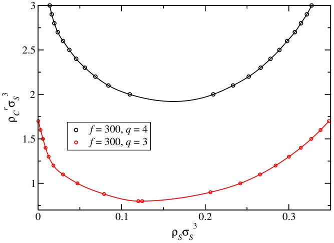
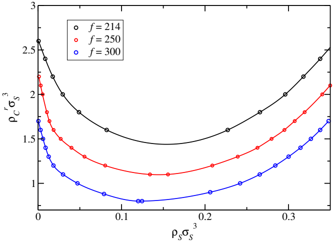
Phase behavior of star-polymer/colloid mixtures

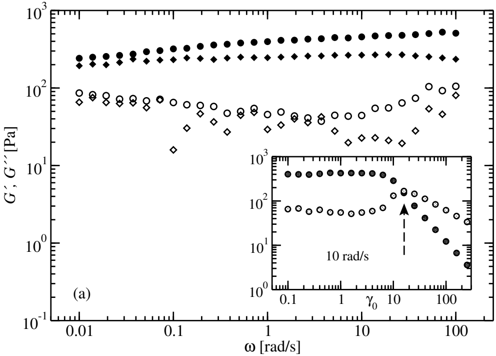
- Demixing binodals





Glossy behavior – influence of colloids[15]

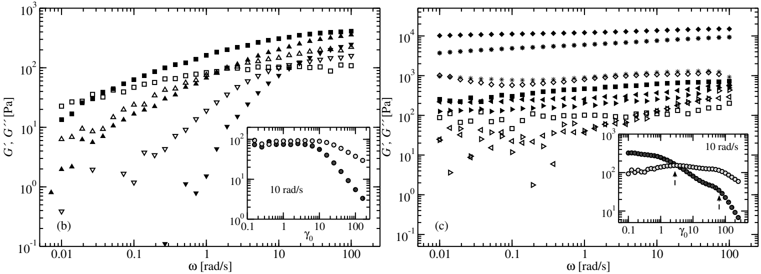
- The stars: 1,4 PB, $f_s = 214$, $M_a = 67\,000\,\mathrm{g/mol}$.
- The colloids: 1,4 PB, $f_c = 1109$, $M_a = 1270\,\mathrm{g/mol}$.
- Oscillatory shear rheology: measure $G'(\omega)$ and $G''(\omega)$.



[15] D. Truzzolillo *et al.*, Phys. Rev. Lett. **111**, 208301 (2013).

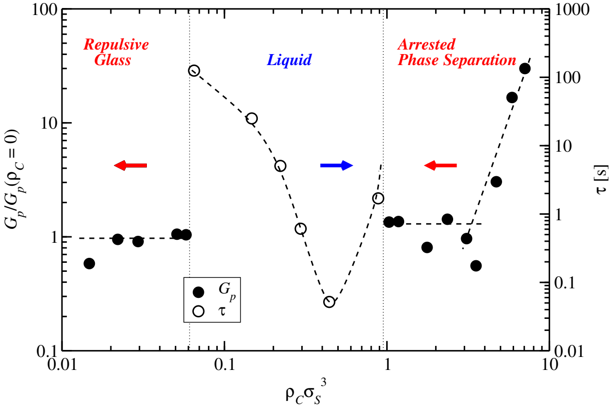
Glassy behavior

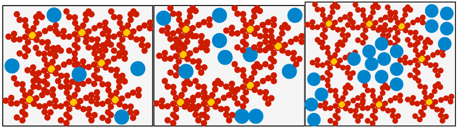
- Rheology



Glassy behavior

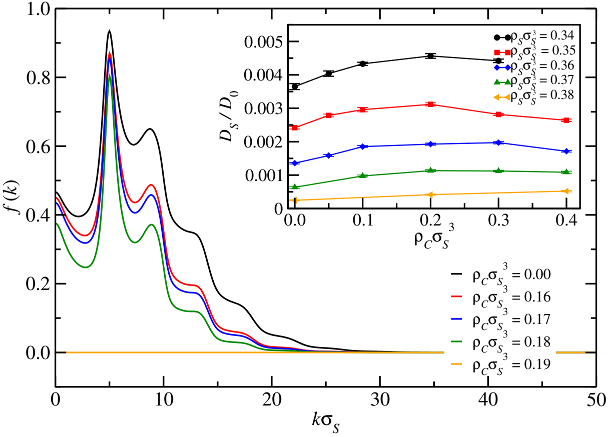
- Rheology – Summary





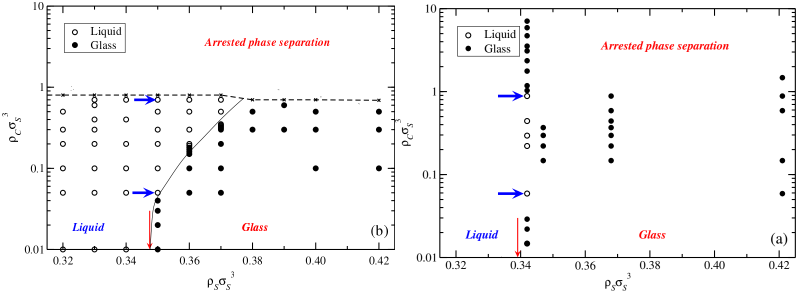
Glassy behavior

- Mode-Coupling-Theory and simluations



Glassy behavior

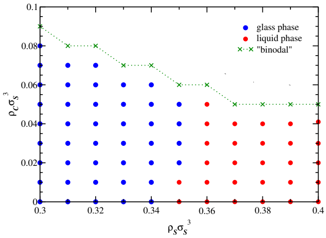
- Comparison experiment-theory

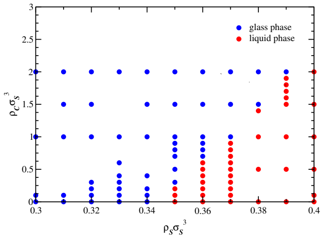


- Re-entrant glass due to arrested phase separation

Glassy behavior

- Interplay between glass melting and demixing
- Left: $f = 214$, $q = 2$; right: $f = 214$, $q = 4$.





Conclusions

- Soft colloids hide many surprises
- Depletion potentials have novel, unexpected properties
- Multitude of arrested states in concentrated soft colloids
- Depletion dictates phase- and glassy-behavior

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- Asakura-Oosawa theory has set a paradigm ...

Conclusions

- Soft colloids hide many surprises
- Depletion potentials have novel, unexpected properties
- Multitude of arrested states in concentrated soft colloids
- Depletion dictates phase- and glassy-behavior
- Asakura-Oosawa theory has set a paradigm ...
- ... but it can be quantitatively misleading!

Acknowledgments

- **Dimitris Vlassopoulos** (FORTH, Greece)
- **Dieter Richter** (FZ Jülich)
- **Emanuela Zaccarelli** (University of Rome *La Sapienza*)
- **Manuel Camargo** (University of Vienna $\rightarrow$ Universidad Antonio Nariño, Colombia)
- **Daniela Marzi** (University of Vienna)
- **Barbara Capone** (University of Vienna)

comploids
PHYSICS OF COMPLEX COLLOIDS

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