

B4: Colloidal stabilization by unattached homo- and copolymers

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Presentations

- 2⁺ oral IRTG
- 3⁺, 2* posters IRTG
- 3⁺ oral other
- 1⁺ posters other

Publications

Shvets, A. A., Semenov, A. N., J. Chem. Phys. 139, 054905, (2013).

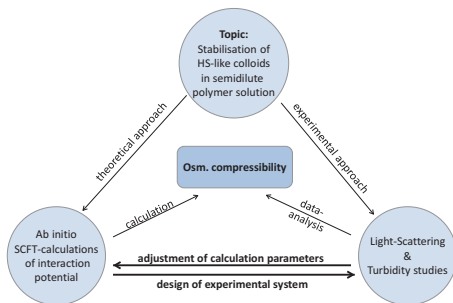
Other activities

- IRTG summer school Master Class, 2013⁺
- Organization of IRTG-Training Camp "Soft skills in Science", Freiburg, 2014⁺

Introduction

From theory to experiment and vice versa

Dealing with colloidal dispersions, one of the most important tasks is to prevent particle aggregation due to van-der-Waals forces. Besides standard stabilisation techniques (i.e. electrostatic and/or steric) another method may be the addition of a certain amount of free non-adsorbing polymer. This effect is known in the literature but not well understood. Current theoretical models describing this polymer-induced (PI) stabilisation are oversimplified and are, for example, not able to predict the dependence on solution parameters.



Theory: To improve the understanding of the PI stabilisation we developed a numerical model for the particle interaction potential $U(h)$ based on self-consistent field theory (SCFT), which is in agreement with the recent theoretical approach by Semenov et al. (*Macromolecules* 41, 2243, 2008).

Experiment: To validate the theoretical predictions potential dependent properties accessible by light scattering and turbidity experiments are measured (i.e. the osmotic compressibility of the system).

Collaboration: The physical parameters of the experimental system can be used to tune the model calculations, while the theoretical predictions were taken into account for the selection of the experimental system.

Theoretical approach

Self consistent field theory

In order to simplify the problem in its original form we reduce the space from 3d to 1d geometry using the Derjaguin approximation. The polymer is modeled as a random walk in a self consistent field that satisfied to the diffusion-like equation:

$$\frac{\partial q_{\omega}(x, s)}{\partial s} = \frac{\partial^2 q_{\omega}(x, s)}{\partial x^2} - \omega(x)q_{\omega}(x, s)$$

where $q(x, s)$ is a statistical weight of the chain of length s whose end point is fixed at x . The self-consistent field is a function of monomer concentration between plates, so

$$\omega(x) = v_N(c(x)/c_b - 1) + w_N((c(x)/c_b)^2 - 1) \quad c(x)/c_b = \int_0^1 ds q_{\omega}(x, s)q_{\omega}(x, 1-s)$$

Where c_b is the bulk concentration of monomers, $v_N = v_c N$, $w_N = w_c N^2$ are virial coefficients and N is the degree of polymerisation. The free energy of the system between plates in dimensionless units is

$$W[\omega, h] = -Q[\omega, h] - h - \int_0^h dx \left(\frac{v_N}{2} ((c/c_b)^2 - 1) + \frac{2w_N}{3} ((c/c_b)^3 - 1) \right)$$

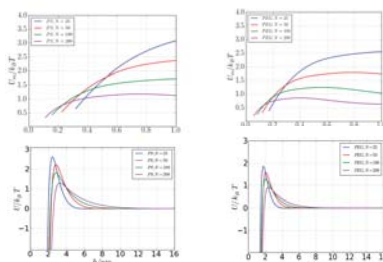
and

$$Q[\omega, h] = \int_0^h dx q_{\omega}(x, 1)$$

The free energy in "real" variables is

$$U(h)/k_B T = \pi R_c^2 c_b R_c^2 / N W(h)$$

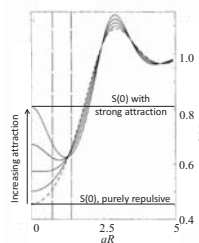
Changing the virial parameters all concentration ranges for certain polymers with a fixed length can be covered. Numerically, solving the above system of equations, we can draw the dependence of the free energy barrier U_m height vs. polymer volume fraction Φ_{pol} and the free energy $U(h)$ vs. particle distance.



Free energy barrier height U_m vs. polymer volume fraction Φ_{pol} (upper half) and free energy $U(h)$ at fixed Φ_{pol} (lower half) for different chain lengths of polystyrene in toluene (left) and polyethylenglycol in water (right). Colloidal radius: $R_c = 200$ nm.

Experimental approach

Osmotic compressibility from turbidity data



Influence of particle attraction on the zero-q-limit of scattering data.

Here $S(0)$ (i.e. the osm. compressibility) can be obtained from the turbidity structure factor $Z(\lambda)$, but only in the limit of small R/λ -values.

To gain reasonable PI-stabilisation the theoretical work demands particle sizes sufficiently larger than the ones accessible in the conventional turbidity approach. ($\lambda_{max} = 1100$ nm $\rightarrow R_{max} \approx 60$ nm)

Therefore the studied wavelength range was further increased into the NIR-region (up to 1600 nm) to double the particle radii accessible by the method.

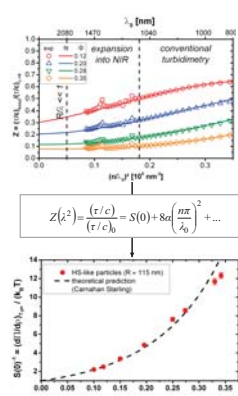
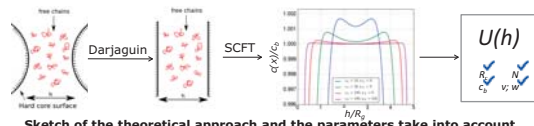


Illustration of data evaluation and the advantage of the expansion into NIR.

Summary

Current Work



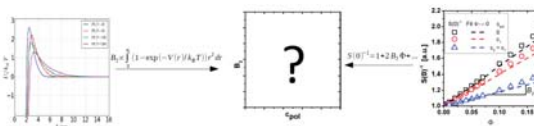
Sketch of the theoretical approach and the parameters take into account.

We established a SCFT approach to study polymer induced colloidal interactions in semidilute solutions. In contrast to other approaches our theory is able to predict a repulsive contribution to the particle interaction potential $U(h)$ caused by the polymer. Furthermore we are able to calculate $U(h)$ as function of colloid- and polymer-size as well as solvent parameters.

We modified the known turbidity approach of measuring $S(0)$ to access larger particles. The behaviour of a pure HS-like system could be reproduced, measurements on colloid polymer mixtures are planned.

Future Work

The derived potentials can be used to calculate the osmotic compressibility of a hard sphere like system. To ease the calculation we are planning to concentrate on the low colloidal volume fraction limit.



Schematic drawing on how to bring theory and experiment finally together: Calculation of the second virial coefficient B_2 of the osmotic compressibility from theoretical and experimental data.

In order to enhance the agreement between the theoretical and the experimental model system we are currently introducing adsorbed surfaces and soft shell layers to the theoretical model which are considered along with the free polymer.



Future steps: Extending the theoretical model from hard spheres towards hard spheres with decorated walls and soft particles to enhance the agreement with the experimental model systems and to increase the PI-stabilisation.

Based on the current work and the discussions between the groups in Strasbourg and Freiburg we now know how to extend the theoretical and the experimental work away from the pure HS-systems to systems where the PI-induced stabilisation will be much stronger. This will be the topic of our continuation project. (See renewal proposal, Project C1).

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⁺joint contributions