Project C1: Colloid stabilization by unattached polymers in solution - from hard walls to soft and sterically stabilized colloids

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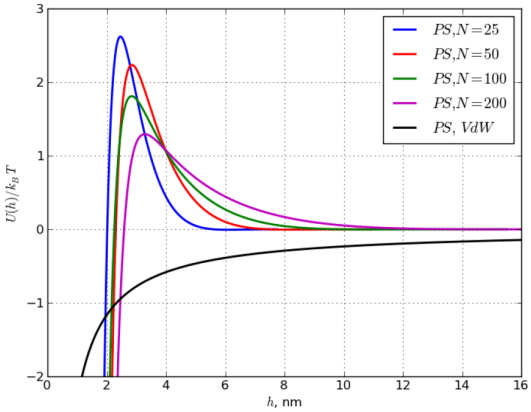
Current state of the research. Colloidal dispersions are indispensable for many technologically important applications. Here the main problem is that the colloidal particles tend to aggregate due to van-der-Waals attraction. Stabilization is therefore required. It is known that a certain amount of free polymer added to a colloidal system may enhance its stability ("depletion stabilization"). This effect was largely ignored, contrary to the well-understood depletion attraction which is intensively studied in the context of arrest scenarios (attractive glass *versus* gel transitions). However, depletion stabilization could open new ways to control colloid stability. Previous theoretical studies of free-polymer-induced (PI) stabilization have been based on simplified models so that even basic features of the stabilization effect are still unknown (e.g., dependence on solution parameters, polymer structure, monomer/surface interactions, etc.). It is the aim of this project to identify the regimes where the PI stabilization can be harnessed to efficiently control the stability of colloidal suspensions.

Contributions of the principal investigators. Semenov *et al.* have considered the PI interactions by a rigorous theoretical approach. Two main contributions to the PI repulsion in semidilute solutions were elucidated: *i*) the anti-Casimir effect; *ii*) the chain-end effect. A theory of PI interactions between hard walls was elaborated in the first funding period (PhD thesis of A. Shvets). Calculations for one experimental system from Freiburg – polystyrene (PS) microgel colloids with linear PS as free polymer – showed that free polymers can indeed improve colloidal stability, but the maximum barrier height of about 2 *kT* (see Figure on the right) will in general not be sufficient to warrant the stability, which requires barriers of about 20 *kT*. A pre-stabilization by other means would thus be required. However, we stress that the current theory developed by A. Shvets considers hard-core nonattractive colloids and does not incorporate the following effects: (1) finite thickness of the microgel/solvent interface due to dangling chains; (2) anti-Casimir effect. Preliminary theoretical results show that both effects can enhance stabilization. The results also indicate that the most promising effect is expected for soft particles or for solid particles with attached polymer layers.



Current work focuses on calculating static structure factor $S(q)$ via integral equation theories for the PS microgel system and comparing the result with the measured $S(q)$ as well as with previous approaches. On the experimental side, we have also developed another system based on perfluorinated polyacrylate (PFA) particles sterically stabilized with polyethyleneoxide (PEO) chains grafted to the particle surface. Various ratios between shell thickness and core radius were achieved, allowing to vary the softness of the repulsion.

Research project and collaborations. Building on the results from the first funding period we will study more complicated systems (soft particles, pre-stabilized hard surfaces). The Strasbourg group will extend the theory in two directions: *i*) penetrable particles of variable softness and *ii*) hard particles decorated with polymers of variable grafting density and chain length. In collaboration with the Freiburg group the theoretical parameters will be adjusted to the experimental systems and $S(q)$ will be calculated. Extensions to blockcopolymers and other complex architectures (triblock copolymer, star-like homo- and block copolymers) will also be started because they are expected to enhance the stabilization effect significantly. The Freiburg group will extend the studies of the developed systems: *i*) The experiments on

the highly crosslinked PS microgel system will be continued and also extended to less crosslinked particles in order to systematically study the influence of particle softness. The latter extension can build on recent work. *ii*) The system consisting of PFA colloids stabilized by surface-grafted PEO with free PEO as depletion polymer will be explored as it is a suitable model system for the planned theoretical work. As this model system is rather new, it requires systematic study on the dependence of particle interactions on particle architecture (grafting density and chain length dependence). An experimental protocol to study structure and dynamics of these particles at low volume fractions with light scattering will be set up and the parameter range for the occurrence of the stabilization will be determined. An interpretation of the data together with the theory group is planned.

Work plan. Two doctoral researchers will work on this project.

Doctoral researcher from France. *Phase 1 (1 Year; Strasbourg with one short visit to Freiburg):* Calculation of force profiles for PI interactions between walls in semidilute homopolymer solutions. Variations of the wall softness. Visit to Freiburg: a short stay to learn about the experimental systems and methods. Setting up and adjusting the program for numerical calculation of $S(q)$. *Phase 2 (1 Year; Strasbourg with short visits to Freiburg; 3-4 times):* Study of PI interactions between solid surfaces with grafted polymer chains in semidilute solutions of the same polymer, osmotic pressure calculations and elaboration of the phase diagrams for colloid/grafted-polymer/free-polymer systems. Calculation of $S(q)$ and comparison with the experimental $S(q)$ on the PEO and PS systems. *Phase 3 (1 Year; Strasbourg with several longer stays in Freiburg; 3-4 times):* Theoretical study of PI interactions between colloids in solutions of diblock-copolymers and telechelic polymers with adsorbing ends, investigation of the effects of the length of non-adsorbing and sticky segments. Determination of the optimum stabilization regimes in terms of the block length, number of blocks, concentration, adsorption energy and other parameters. Visits to Freiburg: Calculation of $S(q)$ for the PFA-PEO colloid/PEO free polymer system and comparison with experimental data. Analysis and documentation of the results, and defence of the thesis.

Doctoral researcher from Germany. *Phase 1 (1 year, Freiburg with frequent short visits to Strasbourg):* Setting up the PS model systems with different crosslink. Determination of kinetic arrest transitions for several degree of polymerization of free polymer for volume fractions 0.1 to 0.3. Measurement of $S(q)$ around the transition lines. Frequent short visits to Strasbourg (introduction to the theory; definition of system parameters for adaptation of the theory to the experimental systems). *Phase 2 (1 year, Freiburg with several longer stays (3-4 times):* Continuation of light scattering on the PS system. Setting up the PFA-PEO systems. Definition of bare potentials via $S(q)$ and viscosity measurements of the particles without free polymer. Determination of kinetic arrest lines and verification of depletion stabilization effect. Measurement of $S(q)$. Visits to Strasbourg (collaborative calculation of $S(q)$ for the PS system and comparison with experimental data; tentative extension to calculation of dynamics with mode coupling theory (MCT); definition of systems parameters for the PFA-PEO). *Phase 3 (1 year; Freiburg with frequent short visits to Strasbourg):* Continuation of light scattering experiments on PFA-PEO systems. Calculations of $S(q)$ for the PFA-PEO and PS systems and comparison with experimental data. Exploratory experiments on PFA-PEO colloids with added block copolymers, triblock copolymers and/or star polymers (these special architecture free polymers will be obtained via collaboration from other polymer chemistry groups). Visits to Strasbourg: discussions about results of theory on depletion stabilization with complex free polymer structures; decision on system for exploratory experiments. Analysis and documentation of the results, and defence of the thesis.