ADAPTIVE MICROGELS IN COMPLEXES AND AT INTERFACES

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Microgels are macromolecular networks swollen by the solvent they are dissolved in. They are unique systems that are distinctly different from common colloids, such as, e.g., rigid nanoparticles, flexible macromolecules, micelles or vesicles. When swollen, they are soft and have a fuzzy surface with dangling chains and the presence of cross-links provides structural integrity - in contrast to linear and (hyper-) branched polymers. Obviously, the cross-linker content will allow controlling whether microgels behave more ”colloidal” or ”macromolecular”. Finally, microgels reveal interfacial activity without being amphiphilic.

The combination of being soft and porous while still having a stable structure through the cross-linked network allows for the possibility to introduce chemical functionality at different positions. The architectural diversity and compartmentalization of reactive groups enable thus short-range coexistence of otherwise unstable combinations of chemical reactivity. The capability of microgels to adjust both their shape and volume in response to external stimuli provides the opportunity to reversibly tune their physico-chemical properties. From a physics point of view, microgels are particularly intriguing and challenging, since their intra-particle properties are intimately linked to their inter-particle behavior.

We will discuss the interaction of microgels of different architecture as, e.g., core-shell, hollow and multi-shell hollow microgels with polyelectrolytes and proteins. The formation of polyelectrolyte complexes was studied and especially amphoteric microgels enable controlled uptake and release. The solution structure was determined by means of neutron and light scattering as well as by (super-resolved) fluorescence microscopy.

Furthermore, we investigate the influence of the structure of microgels on their behavior at interfaces. Here, the structure was probed by means of scanning force and electron microscopy. Compression isotherms of the microgel-laden oil-water interfaces reveal spreading of the microgels at the interface and counter-intuitive influences of charged groups and cross-link density on the compression modulus.

The experimental results are fully supported by computer simulations and illustrate the special behavior of soft microgels at interfaces.

Plamper, F. A.; Richtering, W. Functional Microgels and Microgel Systems. Accounts of Chemical Research
2017, 50, 131–140.
Yaroslavov, A.; Panova, I.; Sybachin, A.; Spiridonov, V.; Zezin, A.; Mergel, O.; Gelissen, A.; Tiwari, R.; Plamper, F.; Richtering, W.; et al. Payload Release by Liposome Burst: Thermal Collapse of Microgels Induces Satellite Destruction. Nanomedicine: nanotechnology, biology, and medicine 2017, DOI:10.1016/j.nano.2017.02.001
Gelissen, A. P. H.; Oppermann, A.; Caumanns, T.; Hebbeker, P.; Turnhoff, S. K.; Tiwari, R.; Eisold, S.; Simon, U.; Lu, Y.; Mayer, J.; et al. 3D Structures of Responsive Nanocompartmentalized Microgels. Nano Lett. 2016, 16, 7295–7301.
Schmid, A. J.; Dubbert, J.; Rudov, A. A.; Pedersen, J. S.; Lindner, P.; Karg, M.; Potemkin, I. I.; Richtering, W. Multi-Shell Hollow Nanogels with Responsive Shell Permeability. Scientific Reports 2016, 6, 22736.
Sigolaeva, L. V.; Mergel, O.; Evtushenko, E. G.; Gladyr, S. Y.; Gelissen, A. P. H.; Pergushov, D. V.; Kurochkin, I. N.; Plamper, F. A.; Richtering, W. Engineering Systems with Spatially Separated Enzymes via Dual-Stimuli-Sensitive Properties of Microgels. Langmuir 2015, 31, 13029–13039.
Geisel, K.; Isa, L.; Richtering, W. The Compressibility of pH-Sensitive Microgels at the Oil-Water Interface: Higher Charge Leads to Less Repulsion. Angew. Chem. Int. Ed. Engl. 2014, 53, 4905–4909