A fascinating feature of colloidal dispersion is that the specific pair interactions can be tuned. Repulsive interactions are often caused by surface-released charges. This allows us to vary the range of repulsion by changing the salt content. For significant differences in the colloid and solvent dielectric constants, also the short-range van der Waals attraction plays a role. A depletion-induced longer-ranged attractive interaction can be imposed by adding free polymer chains.

In colloidal systems with competing attractive and repulsive interactions, the phase separation process can interfere with the colloid cluster aggregation process. To study this interference, we have analyzed an aqueous mixture of charged, nanosized silica particles and dextran polymers using photon correlation spectroscopy and visual inspection [1,3]. We have investigated the effect of salt-induced screening, the influence of increasing the colloid volume fraction, $\phi$, and the effect of increasing the polymer concentration, $c$, on the initial cluster growth by measuring the collective diffusion coefficient of the aggregates. The hydrodynamic radius, $R$, was determined from the Stokes-Einstein relation. We find that the cluster aggregation process is enhanced with increasing $\phi$ and $c$, and increasing salt content. Furthermore, the aggregation time, $\tau_a$, increases with increasing polymer-to-colloid size ratio $q$. From the exponential time behaviour of $R(t)$, we conclude that the cluster growth is induced by a reaction-limited aggregation process (RLA). Our experiments can be quantitatively understood by the standard dimer formation theory based on the DLVO pair potential in conjunction with the Asakura-Oosawa-Vrij (AOV) depletion potential. Deviations from the theoretically predicted aggregation times are observed for $c$ close to the polymer overlap concentration, $c^*$, where non-ideal solution behaviour of dextran is expected.

At higher $\phi$ and $c$, and lower salt content, the sample becomes turbid right after mixing, with a turbid viscous phase formed at the sample bottom. By rediluting the samples within a couple of hours after preparation we find that the colloidal particles do not form larger aggregates. By comparing the experimental non-equilibrium phase diagram to the equilibrium phase diagram obtained from a generalised free-volume theory (GFVT) [2], we find that the experimental phase line observed after two days nearly coincides with the GFVT spinodal line. We argue that the colloid-polymer mixture undergoes an initial phase separation into a denser and a less dense phase, accompanied by a more slowly progressing irreversible aggregation process in the denser phase. The formation of a gel-like bottom phase, which cannot be rediluted, is indicative of an irreversible aggregation process at later times.
