Star-like thermoresponsive microgels: a new class of soft colloids with Gaussian effective interactions

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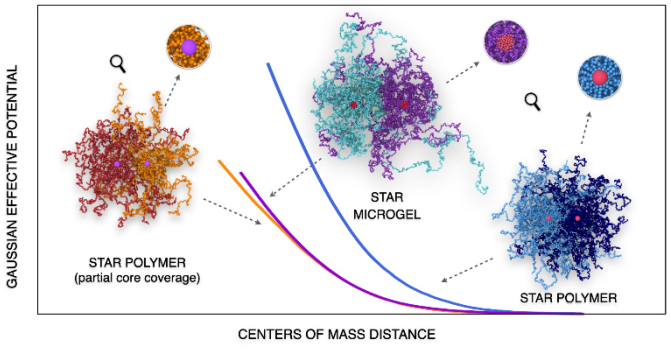
Microgels are soft colloidal particles with micro- to nanoscale dimensions, consisting of a crosslinked polymer network with the ability to respond to various external stimuli. Among the most widely investigated microgels are those based on poly(N-isopropylacrylamide) (PNIPAM), a thermoresponsive polymer that exhibits a volume phase transition (VPT) in response to temperature changes. PNIPAM microgels are typically synthesized via free radical polymerization in the presence of a crosslinking agent, most commonly N,N′-methylenebis(acrylamide) (BIS).
Star polymers, consisting of multiple arms radiating from a central small core, are instead the prototypes of ultrasoft colloids. However, the chemical synthesis of multi-arm stars is quite involved, requiring deep expertise. Furthermore, the polymers used to produce stars are usually not thermoresponsive.
In this contribution I will present recent experimental and simulation results on PNIPAM microgels where the cross linker is ethylenglykol dimethacrylate (EGDMA), building on the pioneering work of Hellweg group back in 2002 [1]. Thanks to the much faster reactivity of EGDMA with respect to BIS, these microgels adopt a peculiar star-like structure, with a crosslinker-rich core and crosslinker-free arms, at low crosslinker concentration. This is confirmed by the comparison between Small Angle X-ray Scattering and monomer-resolved computer simulations of star polymers and of star-like microgels [2]. For all studied EGDMA concentrations, these microgels undergo a very sharp Volume Phase Transition and manifest a high deswelling ability, in contrast with standard PNIPAM-BIS microgels. We also assess the role of crosslinker concentration and added surfactant stabilizers to ensure the formation of star-like topologies across different microgel sizes.
Next, we investigate the effective interactions of star-like microgels by computer simulations finding that they are Gaussian, in contrast to the Hertzian-like potential of regular microgels [3], and that they closely resemble stars with a core partially covered by arms, in contrast to ideal star polymers whose core is fully covered. We conclude by discussing the possible role of these unusual interactions on the phase diagram and dynamical arrest of these microgels under dense conditions.

Keywords:
microgels, star polymers, monomer-resolved simulations, soft colloids, effective interactions



Calculated Gaussian effective potentials between star-like microgels, star polymers and star polymers with a partially covered core as a function of the centers of mass distance.

References:

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