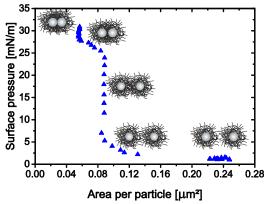
## Influence of the shell-to-core ratio of hard core/soft shell particles at liquid/liquid interfaces

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Understanding and controlling the microstructures formed by nanoparticles at liquid/liquid interfaces is of significant importance for many applications including surface patterning, stabilization of emulsions and biological membranes. For a systematic investigation of the effect of shell thickness, we synthesized core/shell particles with hard silica cores encapsulated in soft hydrogel shells of poly-Nisopropylacrylamide.[1] In particular, we used silica cores of the same size for all particles and systematically varied the shell-to-core ratio. Due to a similar cross-linking density in the shells with different thicknesses, the degree of swelling was comparable for all samples. The overall particle diameter, however, was significantly different, independently of the swelling state. We assembled these particles at water/n-hexane interfaces in a Langmuir-Blodgett trough. Upon compression the particle microstructures were directly transferred onto silicon wafers while the surface pressure was simultaneously measured.[2] The microstructures were investigated by atomic force microscopy (AFM). A representative compression curve obtained for such an experiment is shown in Figure 1. Freeze-Fracture Shadow-Casting cryogenic Scanning Electron Microscopy (FreSCa cryo SEM)[3] was also used to reveal the morphology of the particles at the liquid/liquid interface. The combination of FreSCa cryo SEM and structural analysis by AFM allows drawing conclusions on correlations of the particle architecture to the microstructure as a function of surface pressure. At low surface pressures we found that interfacial distortion caused by the wetting of the particle shells creates attractive capillary forces resulting into crystalline clusters of particles in shell-to-shell contact, at odds with pure microgel particles with a deformable core. At higher compressions, the particles are squeezed into contact. Consequently, adjusting the shell thickness allows tuning the interaction forces and tailoring a specific interface microstructure.[4]



**Figure 1:** Compression curve for core-shell particles with a shell-to-core ratio of 2.2 adsorbed at the liquid/liquid interface along with a schematic depiction of the underlying microstructure of the particles.

[1]M. Karg *et al.*, *Colloid and Polymer* Science, 2010, **289**, 699-709. [2]M. Rey *et al.*, Soft Matter, 2016, **12**, 3545-3557. [3]L. Isa *et al.*, *Nat. Comm.*, 2011, **2**, 1-9. [4]A. Rauh *et al.*, *Soft Matter*, 2016, *in preparation*.