Nanoscale Landscapes: Unveiling the Lateral and Vertical Architecture of Microgels at Fluid Interfaces

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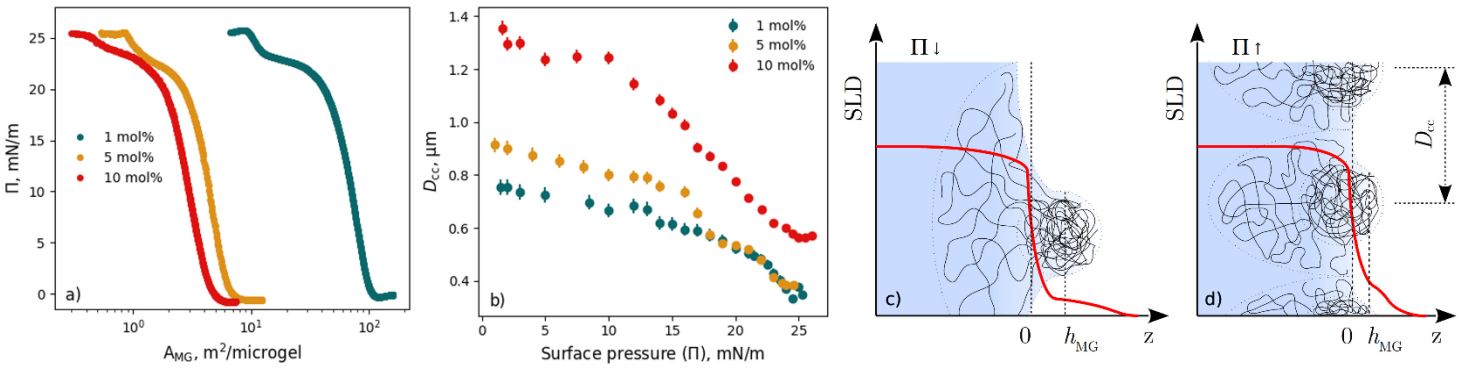
Microgels are soft, three-dimensional colloidal networks comprised of cross-linked polymers, whose surface activity [1] and mechanical properties [2] can be precisely tuned via cross-linker density. In the bulk phase, particularly when composed of thermoresponsive polymers like poly(oligoethylene glycol methacrylate), these microgels exhibit stimuli-responsive behaviour, allowing their size and surface charge density to be controlled via temperature modulations. However, transitioning these particles from the bulk to an interface alters their physicochemical behaviour [3].

Here we map the structural evolution of polymer microgels as they transition from bulk solutions to distinct interfacial environments. At the solid-water interface, *ex situ* atomic force microscopy (AFM) reveals decorated microgel surfaces can impart functional, stimuli-responsive elasticity. In contrast, adsorption at the fluid air-water interface induces significant structural deformation relative to the bulk state, causing the core-shell particles to flatten dramatically into a two-dimensional core-corona (or "fried-egg") morphology.

Accurately capturing these disparate behaviours requires tailored characterisation. While AFM provides essential, high-resolution structural insight at solid substrates, it is inherently limited when evaluating long-range lateral structure over delicate fluid boundaries. To address this, *in situ* specular and off-specular X-ray reflectivity (XRR) is utilised to directly probe the air-water interface without doping or transfer-induced artefacts. This technique successfully resolves the long-range vertical and lateral ordering of the microgels as a function of surface pressure [4]. Furthermore, by directly comparing this *in situ* XRR data with *ex situ* AFM measurements, we explicitly confirm and quantify the structural transfer effects that occur during Langmuir-Blodgett deposition, highlighting the critical need for *in situ* methodologies when evaluating interfacial microgel behaviour.

Keywords:
microgel, reflectometry, X-ray, air-water interface, structure



(a) Langmuir isotherms and (b) corresponding centre-to-centre distances (Dcc) of microgels at the air-water interface as a function of surface pressure and cross-linker concentration. Visualisation of microgels at the air-water interface are also shown for (c) low and (d) high surface pressures [4].

References:

[1] Karg et al., *Langmuir* 35 (2019) 6231–6255.
[2] Burmistrova et al., *Colloid Polym Sci* 289 (2011) 613–624.
[3] Kuk et al., *Soft Matter* 19 (2023) 175–188.
[4] Robertson et al., *Soft Matter* 22 (2026) 127–138.

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