Drying microgel dispersions:
at the crosspoint of colloidal and molecular scales

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Bringing an aqueous dispersion or solution into open air leads to water evaporation. The resulting drying process initiates the build-up of spatial heterogeneities as non-volatile solutes and colloids concentrate. Such gradients lead to complex flow within multicomponent systems, which has triggered a large research effort to describe the resulting hydrodynamics. However, less attention has been paid to the deviations from thermodynamic ideality stemming from water depletion in the vicinity of the air/liquid interface, which leads to drastic water activity changes and a collapse of water transport. We have shown before the relevance of these effects in solutions of amphiphiles[1] and predicted its generality for complex fluids[2], for instance polymer solutions. Yet, hard-sphere colloidal dispersions behave differently due to water excess content even in the driest regions of the film, so that water properties remain unchanged throughout drying. Still, many colloidal dispersions actually include both length-scales due to polymer grafting on particles’ surfaces or the presence of polymeric or amphiphilic solutes in the solvent. The transition between molecular and colloidal length-scales thus needs to be assessed, which we do using microgels dispersions as a system combining both.

We evidence an original drying behavior intermediate between colloidal and solution drying, in which a diffusional scaling of the drying front is observed together with a weak dependence on the air relative humidity[3]. Mapping composition and structuration gradients using Raman spectroscopy and small-angle scattering techniques, we show that this behavior stems from the ability of microgels to both interpenetrate and compact. As a result, water activity and transport is drastically decreased in the vicinity of the air/liquid interface. This mechanism will be at play in a large diversity of complex colloidal systems, including physiological fluids that carry viruses in air, and is thus pivotal for the mastering of drying processes.

Figure 1. Microgels dispersions are evaporated in a millifluidic channel and observed with polarized optical microscopy. A drying front is observed and grows as the square root of time but rather independently of the air relative humidity. Microgels are packing, interpenetrating and deswelling in the film causing large water activity changes along a complex concentration gradient.
