DRYING AQUEOUS COLLOIDAL SYSTEMS:
MOLECULAR INTERACTIONS, SELF-ASSEMBLY AND HOMEOSTATIC BEHAVIOR

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Evaporation is a ubiquitous process in aqueous systems, which may be advantageous for processing materials through drying or deadly for living systems. Since surfactants, polymers and particles are usually non-volatile, water evaporation will lead to the build-up of concentration gradients in the system, from the air/liquid interface into the dispersion's bulk. These concentration gradients will in turn generate structuration gradients in the colloidal system, which lead to changes in transport properties along the gradients. We will show that such a feedback loop on water evaporation can lead to non-linear behaviors, which are crucial for land-living animals' survival and opens new avenues in drying and filtration processes.
We designed millifluidic drying cells, which consist of a small capillary attached to a large reservoir, with one tip exposed to air at a controlled relative humidity. Chemical potential boundary conditions are thus set and controlled during drying. We monitored drying with time with a combination of mapping techniques: polarized microscopy, infra-red microscopy and coherent small-angle scattering, which yields both concentration and structuration gradients. We also measured independently the evaporation rate through gravimetry.
Using simple surfactant aqueous solutions, we show that the evaporation rate is nearly independent of water evaporation driving force, the air relative humidity [1]. Strikingly, this behavior is identical to that of stratum corneum, skin's outer layer. We demonstrate that this non-linear behavior stems from the feedback loop on water transport. Dryer air should lead to a higher evaporation rate due to an increased chemical potential difference between the air and the solution. However, this variation is absorbed in a very thin and dry phase at the air/water interface. This phase corresponds to dramatically low water diffusion coefficients, which in turn efficiently decrease water evaporation [2]. Uncovering the mechanism of this homeostatic behavior opens new strategies to evaluate the impact of a formulation on skin, lung or tear films.
We will also show that this mechanism becomes relevant when drying, or filtering, dispersions of interpenetrable colloids, such as microgels or "hairy" particles [3]. Indeed, large changes in water chemical potential and permeabilities will occur in the concentrated regime, in contrast to the drying of more conventional colloidal dispersions. Taking these molecular interactions into account is crucial for the processing of more complex, and thus realistic, colloidal dispersions into materials.

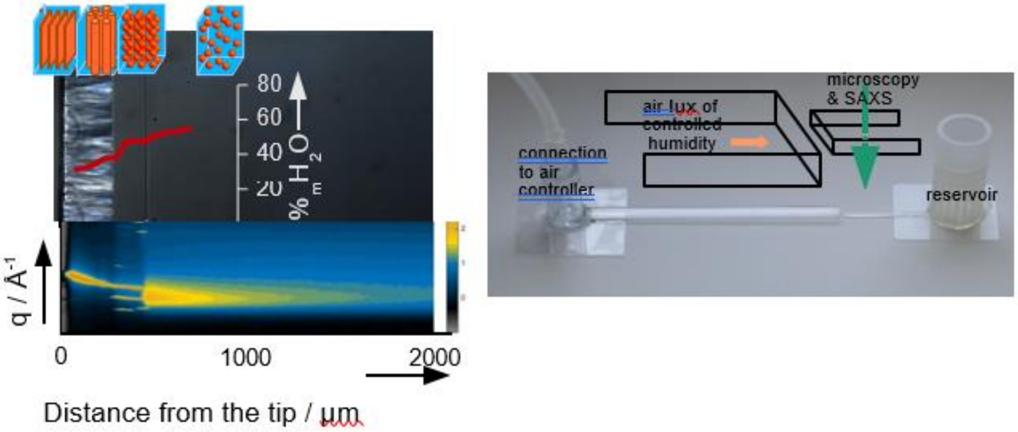

Figure 1: Left: experimental monitoring of composition and structural gradients through microscopy, infra-red microscopy and small angle-scattering; Right: capillary cell enabling controlled drying with set boundaries.

[1] K. Roger, M. Liebi, J. Heimdal, D. Pham, E. Sparr, PNAS, 2016, doi: 10.1073/pnas.1604134113 [2] K. Roger, E. Sparr, H. Wennerström, draft, 2017
[3] J. Crassous, K. Roger, draft, 2017