	Experiment title: Time-resolved study of the drying front in thin colloidal films	Experiment number:
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Shifts: 6	**Local contact(s)**: SZTUCKI Michael	*Received at ESRF:*

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Report: In this SAXS experiment, we spread a film of aqueous silica dispersion (particle radius 8 nm, volume fraction $\phi_s = 0.14$) on a thin sheet of mica. During evaporation, a lateral drying front swept across the film. The X-ray beam was focused at one spot of the film, and SAXS patterns were periodically recorded. As the drying fronts passed across the beam, the spectra measured the ordering of particles, their volume fraction, the film thickness and the water content.

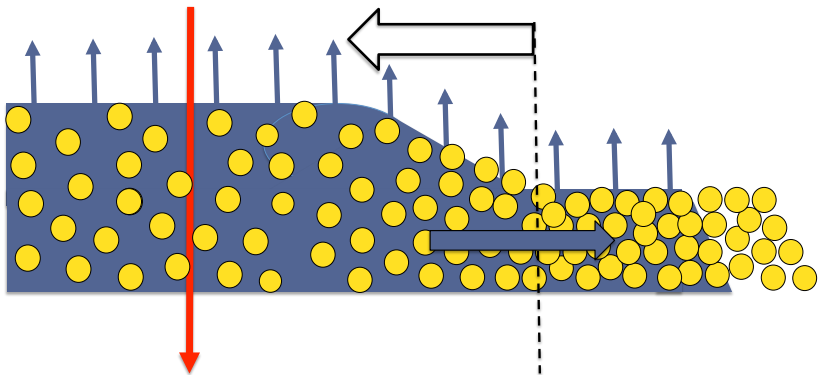
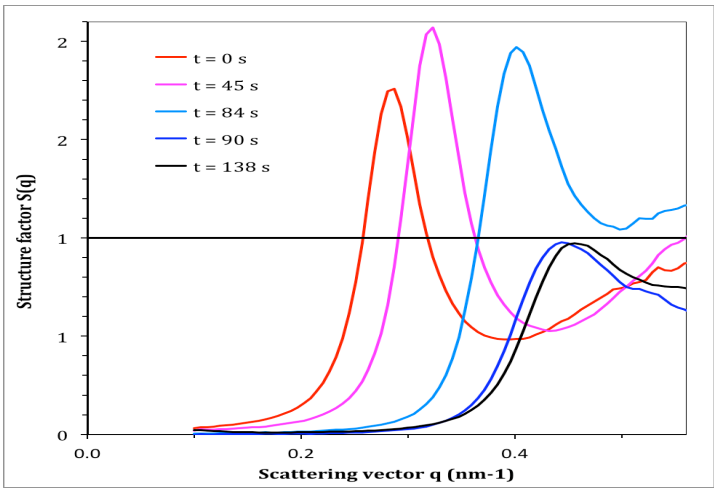


FIGURE 1 Particle ordering and aggregation during evaporation of a colloidal film. Left: liquid film, the particles are concentrated through surface evaporation. Right, wet solid, and extreme right, dry solid. Center: transition region where the particles aggregate and the liquid flows toward the wet solid. The liquid – solid boundary progresses from right to left whereas the flow of liquid is from left to right.

We compared the intensity from the film and that of a dilute dispersion, and we extracted the structure factor of the dispersion, $S(q)$ (Figure 2). The position of the primary peak of the structure factor, q_{peak}, was related to the local silica volume fraction ϕ_s. Using calibration standards of known ϕ_s we found good agreement with the law expected for a face-centred cubic structure. Through this relation, we calculated how the silica volume fraction ϕ_s, at the location irradiated by the beam, evolved over time (Fig. 3). During the course of drying, this volume fraction rose progressively until $t = 93$ s.



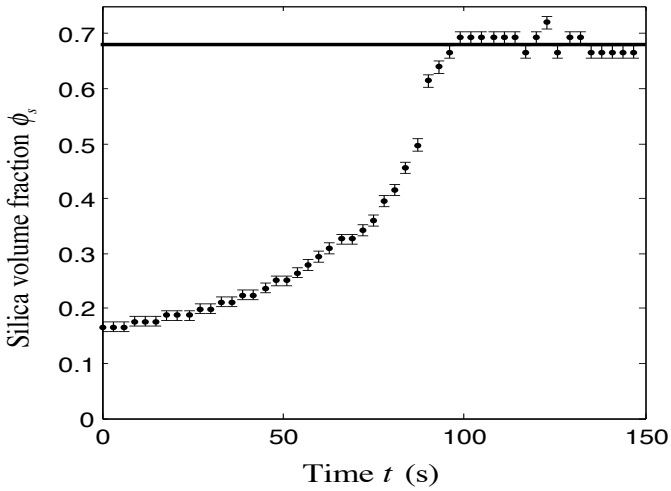
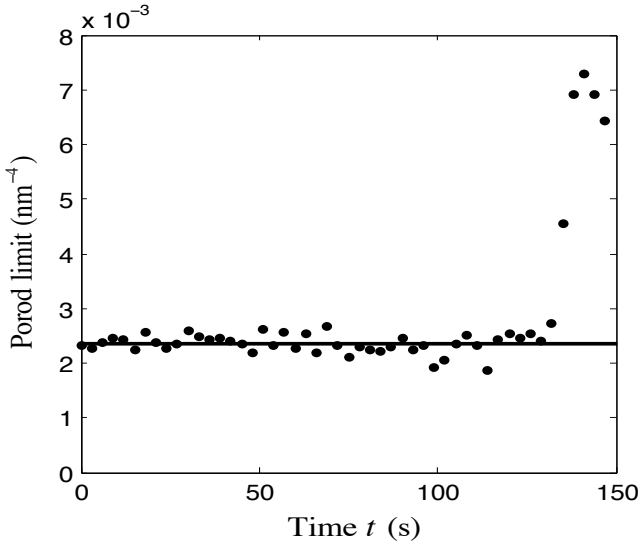


Figure 2. A few structure factors taken at selected times during the drying of the film.
Figure 3. Drying curve (volume fraction versus time). The volume fraction of particles has been calculated from the position of the main peak in S(q).

Fig. 4 presents the variation of the Porod limit throughout the drying process. Surprisingly, it remained constant through the liquid-solid transition (at 93 s). Accordingly, the number of particles at the spot irradiated by the beam was conserved through all the stages of drying. The shap rise at t = 130 s was caused by the change in contrast that occurred when air entered into the film. Figure 5 presents the variation of the integral Q of the scattered intensity. In the liquid film, this quantity was proportional to the water volume fraction. As air entered the film, it also rose abruply, due to the change in contrast.



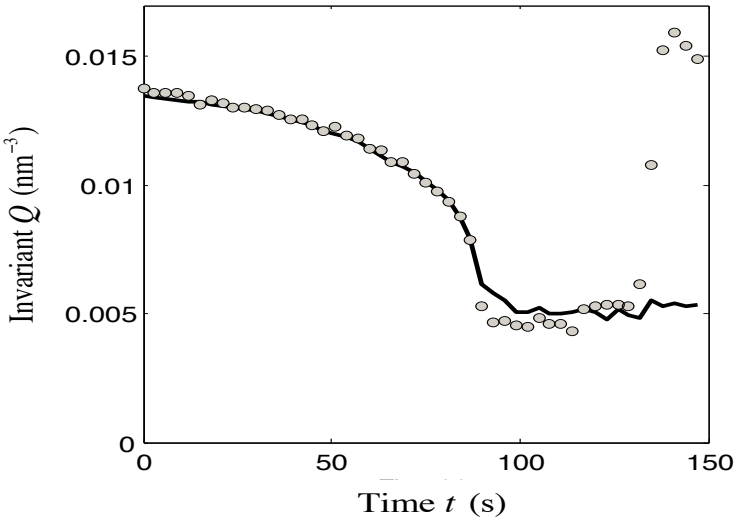


Figure 4. Variation of the Porod limit of the intensity during drying. The constant value up to t = 130 s indicates a constant number of particles at the spot irradiated by the beam. The jump at t = 130 s was caused by increase in contrast, as air entered the pore space of the film.
Figure 5. Changes in the invariant Q, during drying. For t < 93 s, the film was in the liquid state, for 93 s < t < 130 s in the wet solid state and at t = 130 s air entered the film.

An important finding is that, in any spot, the number of particles was conserved throughout this drying process, leading to the formation of a homogeneous deposit. This implies that no flow of particles occured during drying, a behavior distinct to that encountered in the iconic coffee stain drying

Reference: *Langmuir*, **2012**, volume *28*, pp 200-208