## **Supplementary Information**

## Lysozyme fibrillation induced by convective flow under quasi contact-free conditions

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**MICROSCOPY.** Residues of the evaporation experiments were examined off-line by optical microscopy (Olympus inverted microscope) and by scanning electron microscopy (Zeiss Leo 1530).

**SYNCHROTRON RADIATION BEAM.** The beam from a low- $\beta$  undulator with 18 mm period and 6 mm gap was monochromated to a wavelength of  $\lambda = 0.10004$  nm by a liquid nitrogen-cooled Si-111 monochromator. Crossed-mirror optics was used to generate a 1.7\*1.7  $\mu$ m<sup>2</sup> full-width-at-half-maximum (fwhm) focal spot at the sample position.<sup>1,2</sup> The beam profile was determined by transmission knife-edge scans. The beam divergence of about 1 mrad provides a moderate small-angle X-ray scattering (SAXS) resolution. A flux of ~10<sup>11</sup> photons/sec at 200 mA ring current was determined by a calibrated photodiode. The beam intensity before the sample was monitored continuously by a mini-ionization chamber.<sup>3</sup>

**SAMPLE STAGE.** The superhydrophobic PMMA surface was supported on the arcs of a stepping motor driven Huber 1006 goniometer head which was attached to a raster-scanning goniometer composed of orthogonal x/y/z linear stepping motor driven stages and a motorized z-rotation stage.<sup>2</sup> The PMMA surface was aligned by a water level parallel to the beam. (Fig. S1)



**Fig.S1** A 3x3cm<sup>2</sup> sheet of superhydrophobic PMMA is attached to a metal support plate. The plate is fixed to a cylinder carried by the goniometer head arcs.(not visible) A drop has been deposited on the surface but not yet positioned in the X-ray beam.

The sample was aligned in the beam by an on-axis Olympus microscope.<sup>2</sup> 2D raster-scans of the drops and residues were performed with the y/z axes of an x/y/z raster-scanning goniometer.<sup>1</sup> Typical raster-increments were 100  $\mu$ m increment at the onset of evaporation and 20-30  $\mu$ m in the final stages of evaporation. The residues were attached with a small amount of fast glue to a borosilicate glass capillary tip and were centered on the raster-scanning rotation axis.

**DETECTOR.** The X-ray diffraction patterns were recorded by a 16 bit readout FReLoN charge coupled device (CCD) detector<sup>4</sup> with 2048\*2048 pixels of 50.8\*50.8  $\mu$ m<sup>2</sup> size which was 2\*2 or 4\*4 binned in order to increase the readout speed. For the highest readout speed a 4x4 binning was used

**CALIBRATION.** The raw detector data were corrected for flat field and geometric errors. The distance of the sample to the detector was determined by corundum powder (ASTM SRM676 standard). The corundum powder rings were also used to refine the alignment of the detector and the effective detector pixel size.<sup>5</sup> We compared the refined alignment parameters based on the corundum standard.

**DATA REDUCTION&ANALYSIS.** Data reduction was performed using the FIT2D program.<sup>5</sup> Diffraction patterns were corrected for background scattering by patterns measured in the same run. In order to scale diffraction patterns from consecutive mesh-scans of the same liquid drop during evaporation we used the integrated intensity of the diffuse water scattering. (Fig. S2A,B)



**Figure S2 A**: Raw diffraction pattern from a water drop. The pattern has been azimuthally integrated within the indicated boundaries to avoid an intensity reduction due to the PMMA substrate; **B**: Fit of the intensity profile by 2 Gaussian functions (in blue) and a 0-order polynomial. The fitted curve (solid blue line) matches the experimental points (crosses). The difference between experimental and calculated intensity values ( $\Delta I$ ) is shown below.

In general microbeam diffraction patterns of mineral powders do not show powder rings but are more or less spotty due to individual crystallites. Azimuthal averaging of the pattern provides a 1D intensity distribution. The reflection positions of the calcium carbonate phases were calculated using the CARIne 3.1 software (Divergent S.A. France) based on the unit cell parameters for calcite<sup>6</sup>, vaterite<sup>7</sup> and aragonite<sup>8</sup>.

**LYSOZYME SOLUTION SCATTERING.** The low angle lysozyme solution scattering overlaps with the diffuse aqueous solution scattering. (Figure S3)





**MORPHOLOGIES OF SOLUTION DROP RESIDUES.** The evaporation of solution drops results in various morphologies depending on the nature of the solutions.

The presence of lysozyme results in hollow residues.<sup>9</sup> (Figures S4 A,B) The residues can be easily detached from the PMMA substrate and attached to a glass capillary by a small amount of glue. Calcite crystallites can be seen to be deposited at the outer edge of the hollow residue. (Fig.4B)



**Fig. S4 A**: Optical image of hollow residue from 10 mg/ml lysozyme solution drop with calcium bicarbonate; **B**: close-up of Fig.S4 A showing the precipitation of calcite crystallites on the outside of the residue.

**DIFFRACTION PATTERNS OF DROP-RESIDUES.** The pattern from the edge of the 10 mg/ml lysozyme residue shown in Fig. S3 of the text has been azimuthally averaged. (Fig. 5A) The intensity profile is shown together with the indices of calcite and vaterite reflections. The principal crystalline phase is calcite with a small fraction of vaterite. Fig. 5B shows the azimuthally averaged pattern from the interface zone to the glass capillary of the 50 mg/ml lysozyme SDR. (Fig. 3B of the text) The intensity profile is shown in Figure 5B together with the indices of calcite and vaterite reflections which match a large part of the pattern. Three strong peaks with d=0.649, 0.556 and 0.483 nm cannot, however, be matched by these calcium carbonate phase, by monohydrocalcite<sup>10</sup> or fibrous lysozyme deposit (main text: Fig. 4B). The intensity of these peaks appears also too high for a metastable vaterite model-phase.<sup>11</sup>



**Fig. S5 A**: Intensity profile of diffraction pattern from the edge of a 10 mg/ml lysozyme residue. **B**: Intensity profile of diffraction pattern from the edge of a 50 mg/ml lysozyme residue. Miller's indices for the calcite and vaterite unit cells are indicated. The d-spacings of 3 reflections due to an unknown phase are indicated.

**POWDER-AVERAGE PATTERNS.** The center of the goniometer  $\Omega$ -rotation axis was calibrated using the beamline on-axis microscope and a fine glass tip. The tip was then replaced by the sample (Figure S6) and a specific part of the sample was centered on the rotation axis which coincided with the X-ray beam. The sample was rotated by n  $\delta\omega$  angular steps through an angle  $\Delta\Omega$  and a diffraction pattern was collected after each step. Typical values used in the present work are n:180;  $\delta\omega:0.5^{\circ}$ ;  $\Delta\Omega:180^{\circ}$ . The patterns can either be analyzed individually to search for fibrillar orientation or an average pattern is calculated. For the parameters indicated before, the average pattern corresponds in good approximation to a two-dimensional powder pattern obtained with continuous rotation during data collection.



Fig. S6 Schematic design of obtaining a powderaveraged pattern. The microscope image shows a 50 mg/ml lysozyme solution residue glued to glass capillary. The rotation axis is centered to the point in the middle of the residue which also coincides with the direction of the X-ray beam. The capillary is rotated by n steps of  $\delta\omega$  angular increment. An average pattern is derived from all n-patterns. No crystalline calcium carbonate reflections are observed for this lysozyme concentration.

**CONTACT ANGLE MEASUREMENTS.** Experiments were performed at room temperature (21 <sup>0</sup>C) using a Kruss EasyDrop contact angle meter.

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