## **Supporting Information**

# Compression, expansion and relaxation of soft colloidal monolayers at the air/water interface

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#### Data extraction and calculation from SALS diffraction images

Starting with a .avi (.tiff or .jpeg) file, we extract the radial profile from the 2D images with a Matlab code in a batch process, where the primary beam position is needed. The grayscale translated radial averaged intensity was plotted against the distance from the primary beam position in pixel. Gaussian fits in OriginPro 2021b (version 9.8.5.201) were used to determine the peak position and FWHM. The example in Figure S1 gives the peak position of 88.4 pixels with an FWHM of 11.3 pixels.



**Fig. S1.** Left: Exemplary diffraction image from SALS with the beam center marked with a red circle and the diffraction pattern in blue. Right: Radially averaged intensity profile, where the intensity is plotted against the distance from the beam center with an exemplary Gaussian fit for determination of the peak position and FWHM (inset).

The following equations were used to calculate the magnitude of the scattering vector q and the interparticle distance  $d_{c-c}$ :

$$q_{\max} = \frac{4\pi n}{\lambda} \sin\left(\frac{\operatorname{atan}\left(\frac{x \cdot y}{D_{\mathrm{S-D}}}\right)}{2}\right) \tag{1}$$
$$d_{\mathrm{c-c}} = \frac{2}{\sqrt{3}} \frac{2\pi}{q_{\max}} \tag{2}$$

Here,  $q_{\text{max}}$  is the magnitude of the scattering vector at the peak position in  $\mu$ m<sup>-1</sup>, *n* is the refractive index (refractive index of air, *n* = 1),  $\lambda$  the wavelength of the light in  $\mu$ m (0.405  $\mu$ m), *x* the distance from the primary beam in pixel (peak position from Gaussian-fit), *y* the conversion factor in mm per pixel (= 0.146 mm/pixel) and *D*<sub>S-D</sub> the sample-to-detector distance in mm (= 28 mm). Errors for *d*<sub>c-c</sub> were calculated using the FWHM from peak analysis and standard Gaussian error propagation.

#### Compression isotherm and in situ microscopy images

Fig. S2 shows the nearest neighbor interparticle distance,  $d_{c-c}$ , plotted as a function of surface pressure,  $\Pi$ , with six selected microscopy images taken *in situ* at the air/water interface at various  $\Pi$ . The values of  $d_{c-c}$  were determined by Gaussian fits to the first peak of the radial distribution functions, g(r), computed from the microscopy images (black squares). The red circles correpond to data from SALS shown and discussed in the main manuscript. The shaded areas in red and grey correspond to the standard deviations (obtained from the FWHM of the respective peaks analysed). Both data oberlap and show good agreement not only in region I but also in the regime of high surface pressures where we transition from region II to III.



**Fig. S2.** Nearest neighbor interparticle distance  $d_{c-c}$  as a function of surface pressure  $\Pi$  from a standard uniaxial compression experiment (Fig. 2 b). Data from LT-SALS in red are supplemented by the measured  $d_{c-c}$  (black data points) from the real-space *in situ* light microscopy images of CS microgels at the air/water interface. Six selected images are shown with numbers corresponding to the surface pressure  $\Pi$  in mN/m where the images were taken. The scale bars correspond to 10 µm.

#### Area per particle and measured vs. calculated interparticle distance

Due to the large size of our CS microgels, we can simply count the number of particles from optical microscopy images. For this we used microscopy images that were recorded at the air/water interface (*in situ*) with examples shown in Fig. S2. Considering the total area of the microscopy images, we can then claculate the number of particles per total area,  $A_p$ . We want to note, that these values of A<sub>p</sub> account for a homogeneous distribution of particles over the available area. The clear linear trend in Fig. S3a confirms that we deal with a constant number of CS microgels at the interface independent on the available total trough area A in this regime of the compression isotherm. Values of  $A_p$  starting with approximately 2.2  $\mu$ m<sup>2</sup> at 18.7 mN/m (region I) decrease linearly with decreasing available interfacial area until reaching region III (30.9 mN/m). We can now calculate the theoretical avaerage interparticle distance,  $d_{\text{c-c,calculated}}$  that would correspond to a close-packed, 2-dimensional layer of circles in contact (area fraction of 0.91). Fig. S3b shows that the calculated values are always larger than experimentally measured values of  $d_{c-c}$ . This implies that we do not deal with a homogeneous distribution of CS microgels as for example in a defect-free, perfectly ordered lattice. The fact that we obtained very similar  $d_{c-c,measured}$  from microscopy (local, small area probed) as well as from SALS (macroscopic area probed), underlines that this is not a local observation (see Fig. S2). If we now consider our estimated interfacial diameter of the laterally stretched CS microgels,  $d_i = 1.52 \,\mu m$  (from Fig. 2, main manuscript), we can map this to a measured value of  $d_{c-c,measured} = 1.25 \,\mu m$ . This is a very important finding, because a) it means that indeed in region I we deal with a monolayer that contains clusters of CS microgels surrounded by voids that are subsequently closed as we reduce the trough area, and b) the value of 1.25 µm conicides nicely with the value where we enter region II (see Fig. 2b in the main manuscript). In other words, based on the counted number of microgels per area and our estimated value of  $d_i$ , we should theoretically deal with a homogeneous monolayer of microgels in their stretched shell-shell contacts when entering region II at approximately 26 - 27 mN/m. The fact that we measure smaller values of  $d_{c-c}$  (by SALS and microscopy) in this range means that attractive capillary interactions lead to clustering of microgels with  $d_{c-c} < d_i$  and that these cluster must be surrounded by voids. The linear trend in Fig. S3b allows to estimate the interparticle distances in region I also for smaller surface pressures:

$$d_{\rm c-c,calculated} = -0.2\,\mu m + 1.38\,\cdot\,d_{\rm c-c,measured} \tag{3}$$

For example at the start of our experiments shown in Fig. 2 in the main manuscript ( $\Pi \approx$  8 mN/m,  $d_{c-c,measured} \approx$  1.43 µm), we calculate a theoretical  $d_{c-c}$  of 1.77 µm that is significanly larger than our estimated  $d_i$ .



**Fig. S3.** a) Trough area as a function of area per particle,  $A_P$ , that was determined from the real space, microscopy data shown in Fig. S2 and additional microscopy images (not shown). The red line corresponds to a linear fit to the data. b) Calculated vs. measured interparticle distance, dc-c. The  $d_{c-c,calculated}$  was estimated using the trough area and  $A_P$  assuming a close packing (area fraction of 0.91). The solid black line corresponds to a linear fit to the data. The horizontal dashed line marks the extrapolated  $d_{c-c}$  at  $\Pi = 0$  mN/m from the linear fit in Fig. 2 b in region I from the main manuscript, i.e. the estimated interfacial diameter,  $d_i$ . The vertical dashed line marks the corresponding value of  $d_{c-c,measured}$  (1.25 µm).

#### Compression isotherm for various compression speeds



**Fig. S4.** Data from Fig. 5 a with calculated  $d_{c-c}$  (without normalization). The small black arrow close to the left ordinate indicates the drop of  $d_{c-c}$  after fast compression and 5 seconds equilibration. Compression isotherms for various speeds of compression (black line: 3 mm/min, gray line: 30 mm/min and light gray line: 270 mm/min), surface pressure  $\Pi$  and interparticle distance  $d_{c-c}$  (in red) as a function of normalized area  $A/A_0$ . The brightness of the red curves correlates with the speeds described above. Numbers mark positions on the isotherms. All three compression experiments were performed with freshly prepared monolayers. Red dotted horizontal lines indicate the hydrodynamic diameter  $d_h$  of the CS microgels in the swollen (20 °C) and collapsed (50 °C) state.

### First compression/expansion cycle



**Fig. S5.** First cycle of the experiment from Fig. 4. Top left: Surface pressure as a function of normalized area  $A/A_0$  for compression from position 1 to 3 (black) and the immediately following expansion from position 4 to 6 (blue). Top right: Corresponding SALS images for the six positions highlight along the isotherms. Bottom left: Radially averaged intensity profiles in the *q*-range of the structure factor peak computed from the SALS images shown in the top right.