

Supporting Information for: In-Situ Characterization of Microgel Monolayers: Controlling Isostructural Phase Transitions for Homogeneous Crystal Drying Patterns

Antonio Rubio-Andrés, Delfi Bastos-González, Miguel Angel Fernandez-Rodriguez

Laboratory of Surface and Interface Physics, Biocolloid and Fluid Physics Group, Department of Applied Physics, Faculty of Sciences, University of Granada, Campus de Fuentenueva s/n, 18071 Granada, Spain

E-mail: mafernandez@ugr.es

Synthesis Protocol

For regular microgels, 1009 mg of N-isopropylacrylamide (NIPAM) and 69 mg of N,N'-methylene-bisacrylamide (BIS) were dissolved in 50 mL of Milli-Q water, resulting in a crosslinking density of 4.8 mol%. This nominal crosslinking density was calculated by dividing the amount of BIS used by the total amount of NIPAM and BIS mixture. The solution was degassed with nitrogen (N_2) for 15 minutes while being heated to 80°C. At that point, 26 mg of potassium persulfate (KPS), dissolved in 2 mL of Milli-Q water, was added to initiate the reaction. The reaction was allowed to proceed for 5 hours. Afterward, the milky microgel solution was cooled to room temperature and purified by centrifugation. The solution was centrifuged at 39400 rcf for 1 hour (Sigma 3-30ks), the supernatant was discarded and the pellet was re-suspended in Milli-Q water. This purification step was repeated three times.

For low crosslinked microgels, 4.52g of N-vinylcaprolactam (VCL) and 0.0816 g of N,N'-methylene-bisacrylamide (BIS) were dissolved in 200 mL of Milli-Q water, resulting in a crosslinking density of 1.6 mol%. The solution was degassed with nitrogen (N_2) for 15 minutes while being heated to 60°C. At that point, 0.0816 g of 2,2'-azobis (2-amidinopropane) dihydrochloride (V50), dissolved in 2 mL of Milli-Q water, was added to initiate the reaction. The reaction was allowed to proceed for 7 hours. Afterward, the milky microgel solution was cooled to room temperature and purified by centrifugation. The solution was centrifuged at 39400 rcf for 1 hour (Sigma 3-30ks), the supernatant was discarded and the pellet was re-suspended in Milli-Q water. This purification step was repeated three times.

Substrate functionalization

The hydrophobic silicon substrates were silanized using Aquapel. Briefly, the substrates were immersed in Aquapel for 15 minutes. Then, they were washed with ethanol to remove any unreacted species and dried with N_2 . Finally, the treated samples were heated in the oven at 100 °C for 30 minutes to promote a covalent binding between the silane and the substrate.

The hydrophobicity of the samples was assessed by measuring the static contact angle. For that, 10 μ l Milli-Q water were placed on top of the substrate. Then, a lateral image of the droplet was taken and the droplet profile was extracted using the software Dynaten, from which the contact angle was measured.

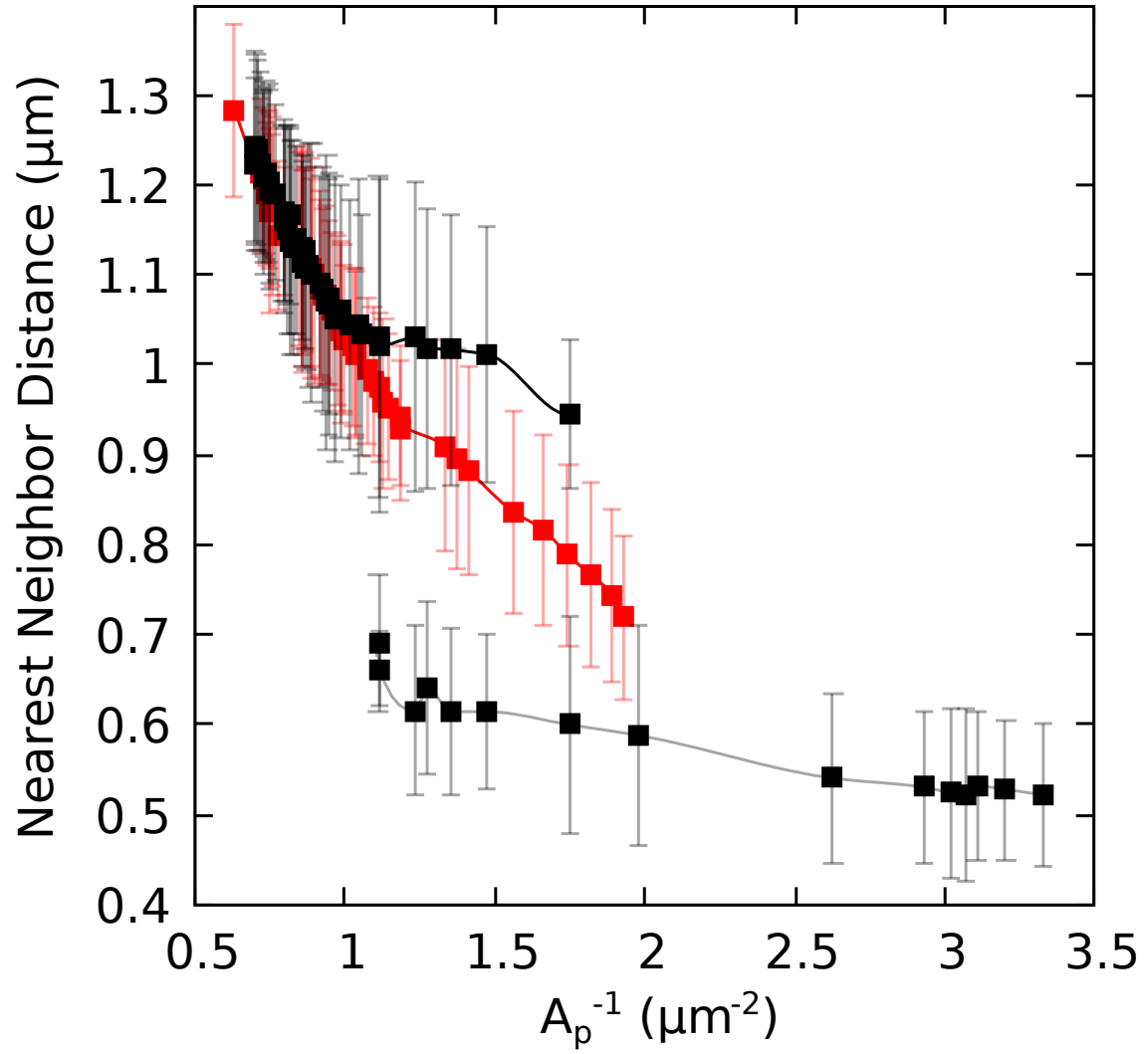


Figure S1. Nearest Neighbor Distance as a function of microgels per Area (A_p^{-1}) observed in-situ at the interface (■) and deposited ex-situ. Lines are guides to the eye.

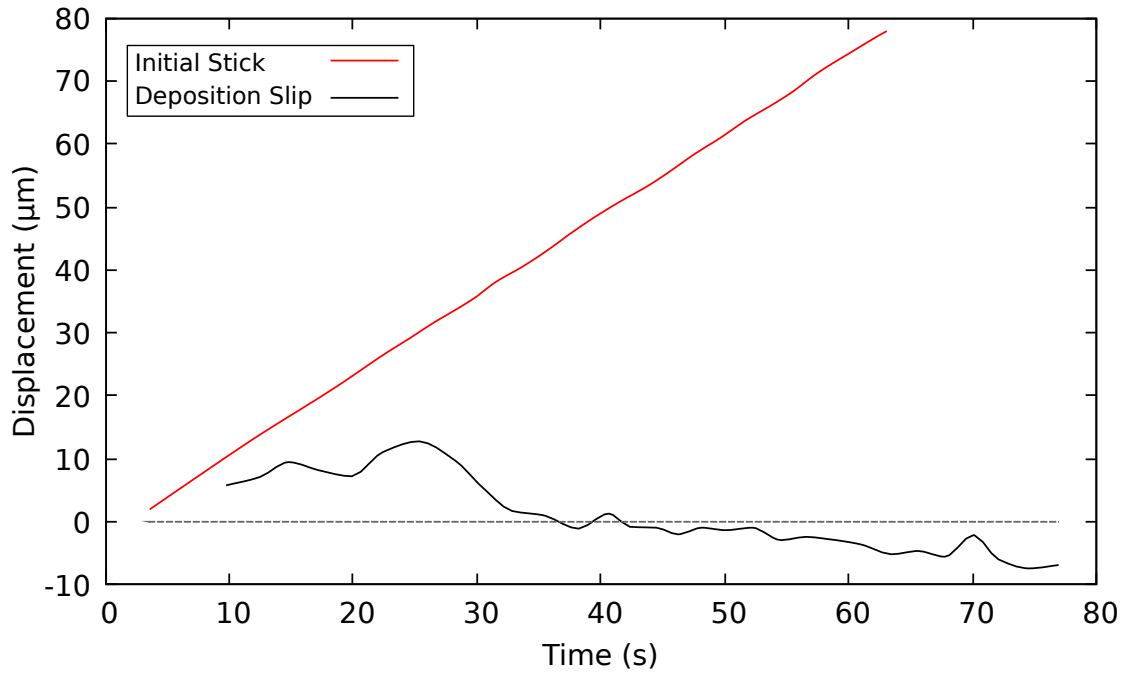


Figure S2. Evolution of the position of the meniscus over time upon starting the deposition (red) and once the monolayer is being transferred (black).

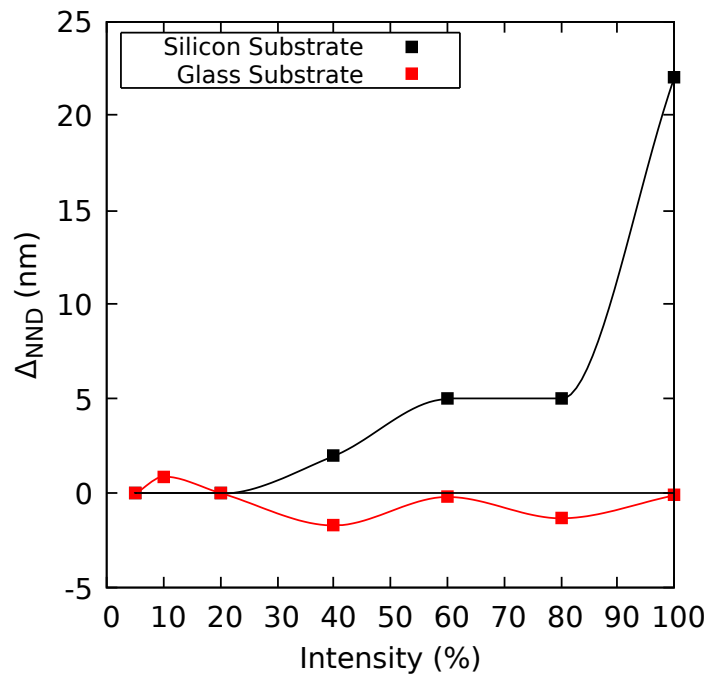


Figure S3. Difference between the NND measured in-situ at the three-phase line and at the bulk of the interface, Δ_{NND} , for a microgel monolayer at $\Pi = 23\text{mN m}^{-1}$ as a function of the microscope light intensity. Red points (■) and black points (■) represents measurements done using a glass and silicon substrate, respectively. Lines are guides to the eye.

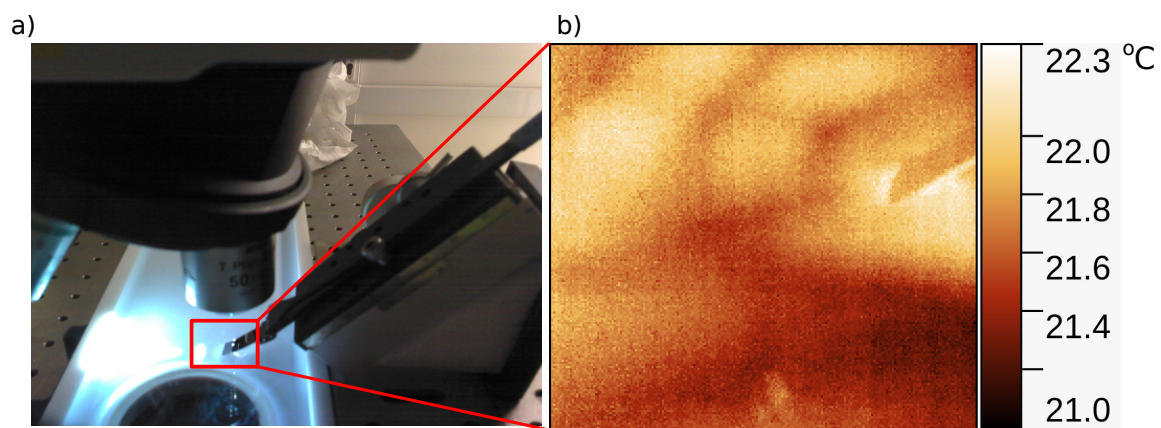


Figure S4. a) RGB picture of the experimental set-up to observe the three-phase line. b) Infrared image of the substrate placed at the air/water interface while being illuminated by the optical microscope. Lighter colors show regions with higher temperature.

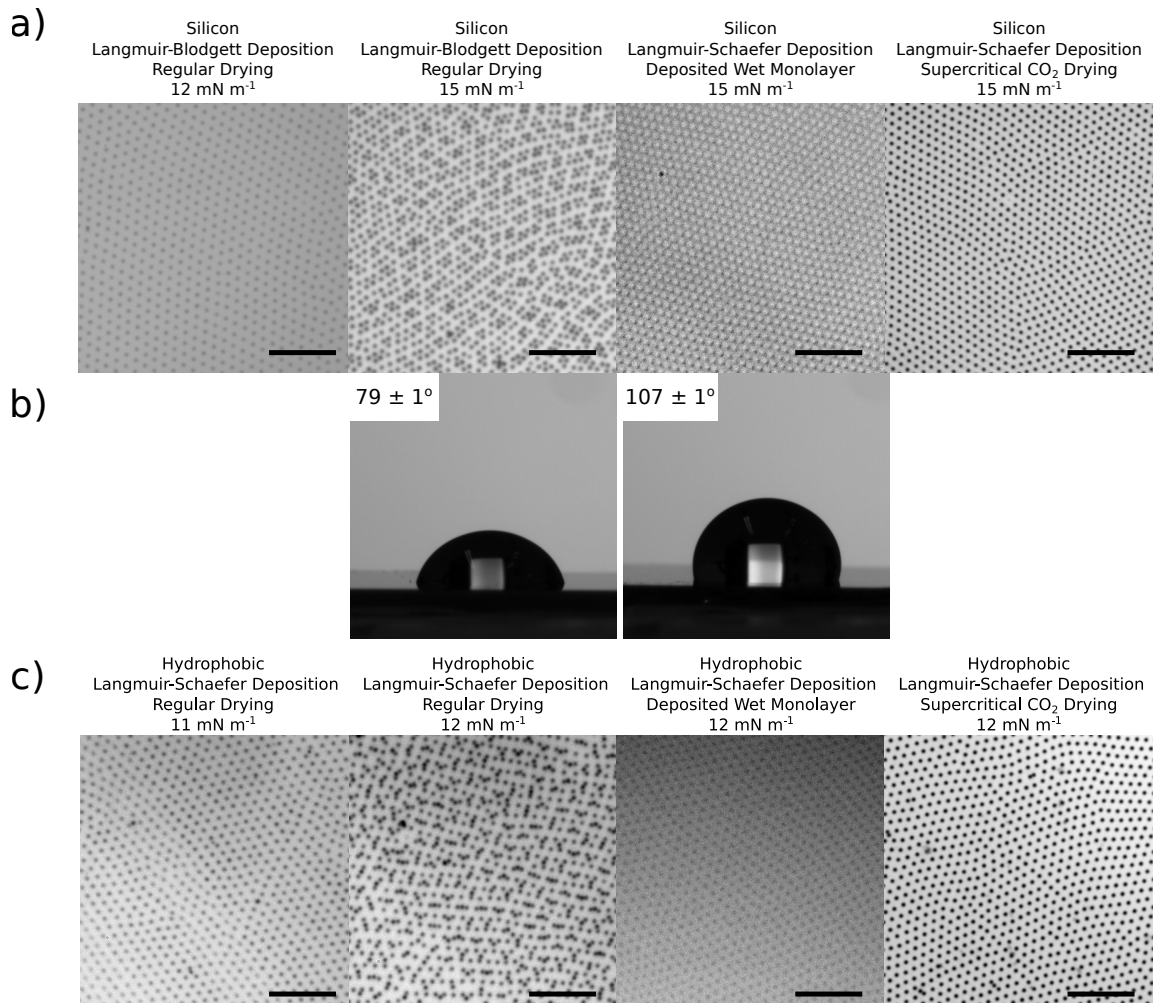


Figure S5. a) Optical microscope images of the 1% crosslinked pVCL microgel deposited on silicon substrates. From left to right: Langmuir-Blodgett monolayer at 12 mN m^{-1} and at 15 mN m^{-1} , showing IPT only for the later. Then we show the still wet deposited monolayer at the higher Π via Langmuir-Schaefer technique showing no IPT. Finally, we show the Langmuir-Schaefer technique plus supercritical CO_2 drying, in the same conditions, avoiding the IPT. $10 \mu\text{m}$ -scale bars. b) Images of a $10 \mu\text{l}$ Milli-Q water droplet on top of a silicon surface (left) and an hydrophobic, silane-functionalized silicon surface (right). c) Optical microscope images of the 1% crosslinked pVCL microgel deposited silane-functionalized, hydrophobic silicon. From left to right: Langmuir-Schaefer monolayer at 11 mN m^{-1} and at 12 mN m^{-1} , showing IPT only for the later. Then we show the still wet deposited monolayer at the higher Π via Langmuir-Schaefer technique showing no IPT. Finally, we show the Langmuir-Schaefer technique plus supercritical CO_2 drying, in the same conditions, avoiding the IPT. $10 \mu\text{m}$ -scale bars.

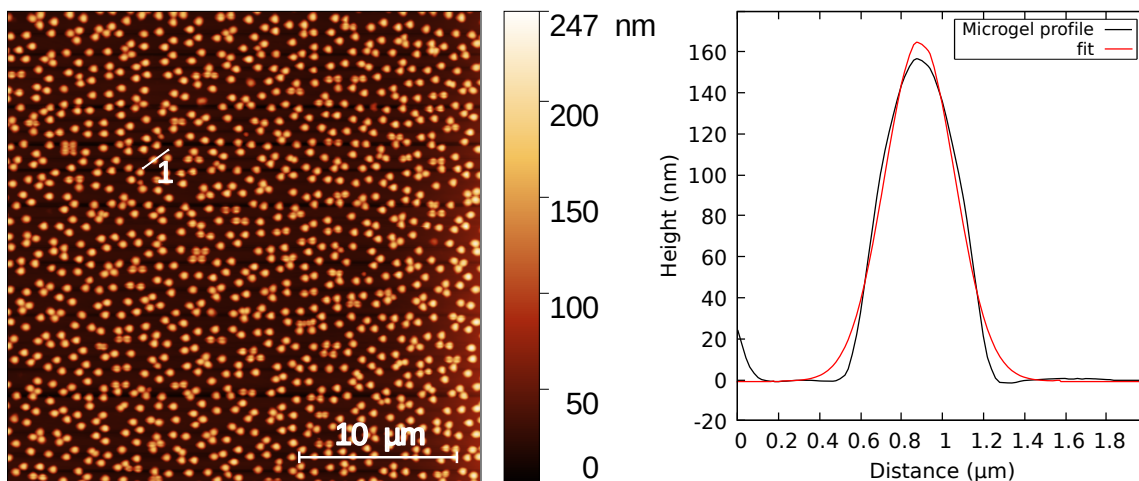


Figure S6. Atomic force microscopy image of a microgel monolayer deposited at $\Pi = 23\text{mN m}^{-1}$, and the profile of a selected microgel, labeled in the image as 1. The black line corresponds to the profile of the microgel, while the red line shows the Gaussian fit used to extract the height and width of the microgel.

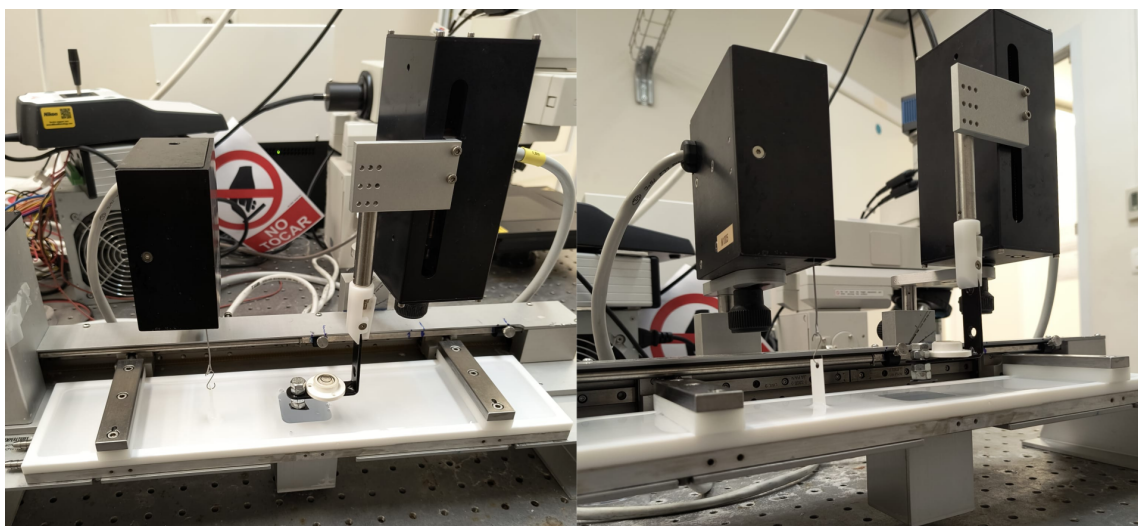


Figure S7. Experimental set-up to perform the Langmuir-Schaefer depositions. An adapted holder is attached to the dipper to place the substrate parallel to the interface. A level is used to set the holder completely parallel. Then, to avoid the use of any surface active compound, the substrate is attached to the holder with paraffin or wax. Upon monolayer formation, the dipper is lowered until the substrate makes contact with the interface. At that point, the dipper is rapidly lifted and the substrate is stored inside a petri dish filled with water.

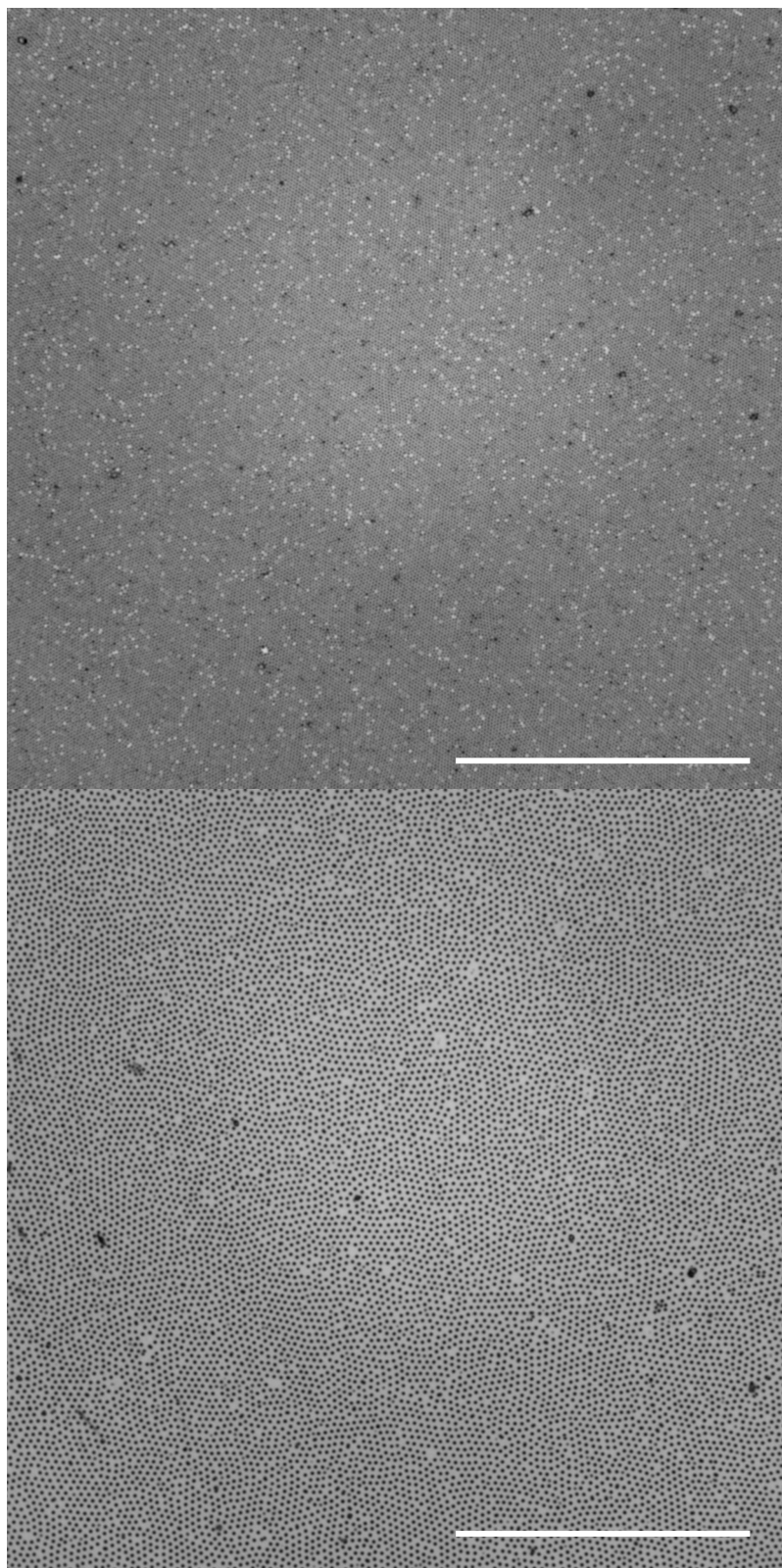


Figure S8. Low magnification optical microscope images of microgel monolayer deposited with the Schaefer method and dried using supercritical CO_2 at surface pressures of $\Pi = 30$ and 10 mNm^{-1} , respectively. Scale bars denote $50 \mu\text{m}$.

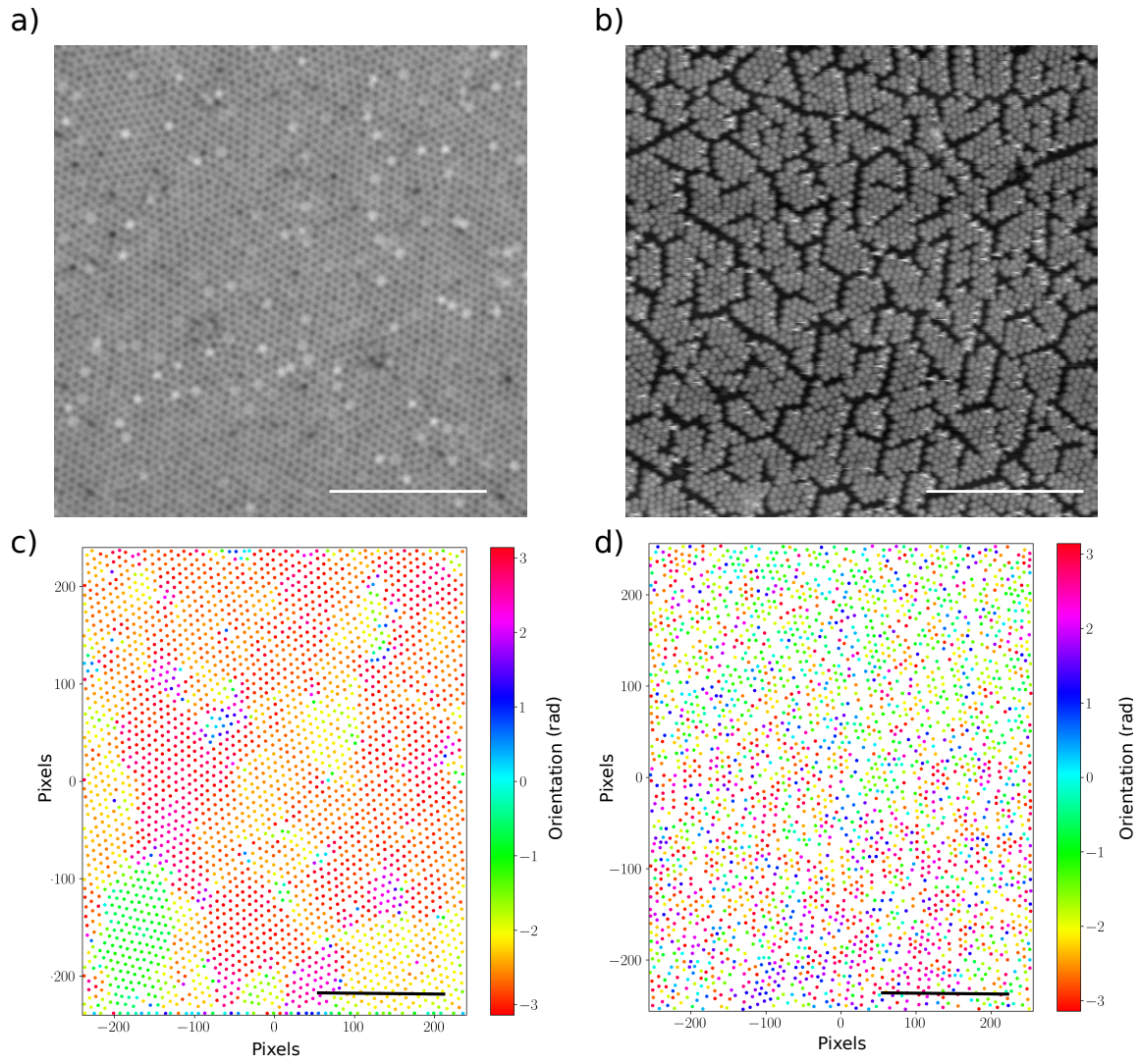


Figure S9. Pictures of microgel monolayer deposited at $\Pi = 30\text{mN m}^{-1}$ with **a)** the Schaefer method and dried with supercritical CO_2 drying and **b)** with the classical deposition method. Panels **c)** and **d)** show the orientation of the microgel crystals corresponding to each deposition method. Scale bars denote $10\ \mu\text{m}$

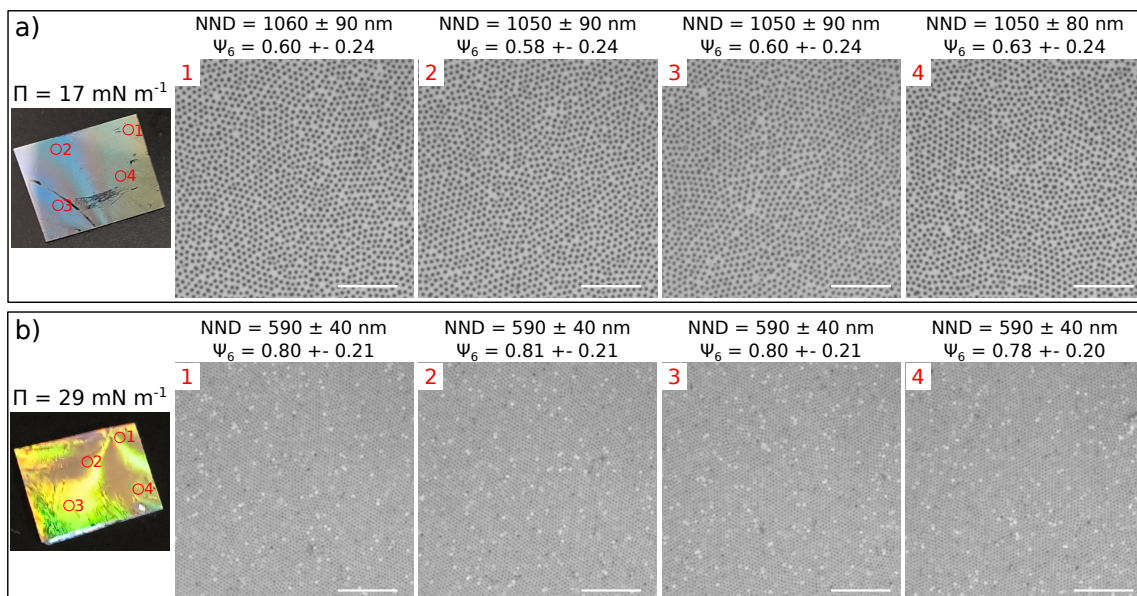


Figure S10. Details of the microstructure of the deposited microgel monolayer at a) 17 mN m^{-1} and b) 29 mN m^{-1} , through the Langmuir-Schaefer method and dried with supercritical CO_2 , in different parts of the same substrate. Scale bars represents $10 \mu\text{m}$.

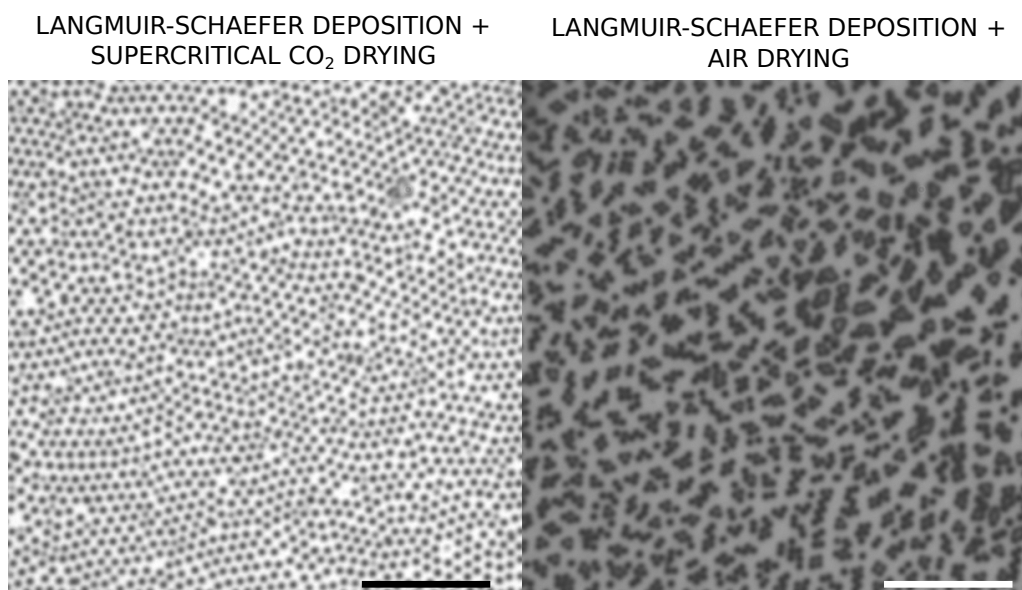


Figure S11. Optical Microscope of the microgel monolayer deposited at $\Pi = 23 \text{ mN m}^{-1}$ through the Langmuir-Schaefer deposition method and dried (left) with supercritical CO_2 and (right) against air. Scale bars denotes $10 \mu\text{m}$.

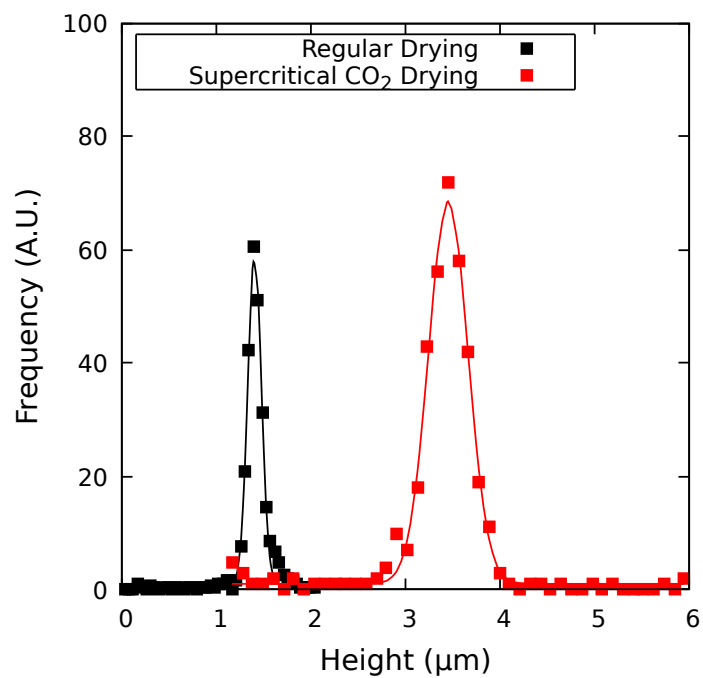


Figure S12. Height Distribution of a microgel monolayer deposited at $\Pi = 15\text{mN m}^{-1}$ by regular Langmuir-Blodgett deposition (■) and by Langmuir-Schaefer deposition and dried using supercritical CO_2 (■)

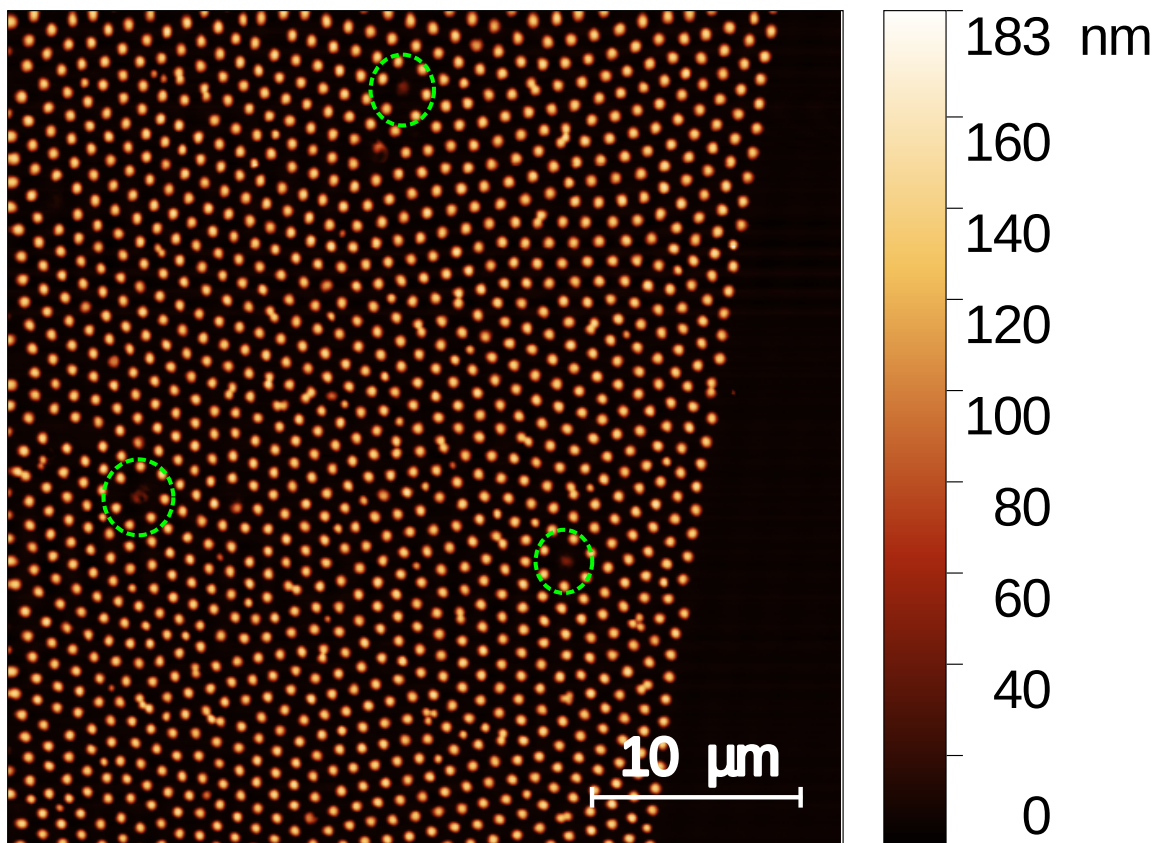


Figure S13. Atomic force microscopy image of microgels deposited at $\Pi = 10 \text{ mN m}^{-1}$. Green dotted circles show less crosslinked microgels.

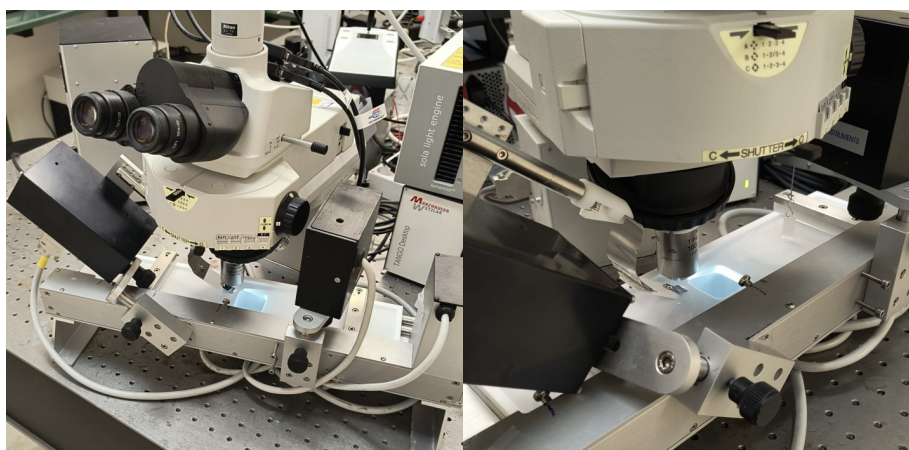


Figure S14. Experimental set-up for the in-situ observation of the microgel monolayer.

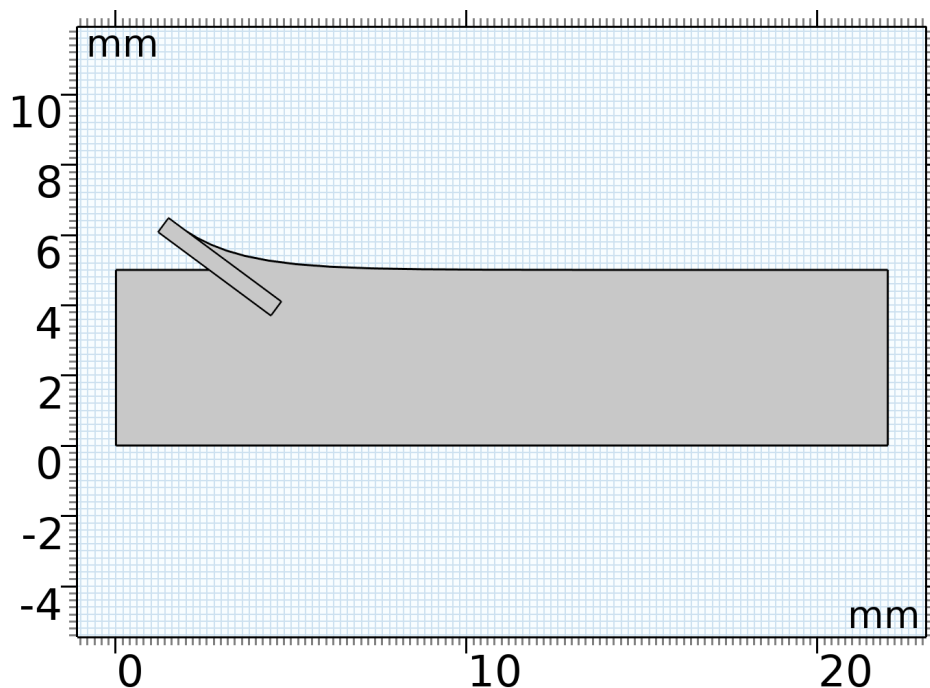


Figure S15. Geometry used to calculate the Marangoni and Capillary forces for the green curve in Figure 3 with the COMSOL Multiphysics software.

Supplementary Movies

Movie M1. Initial stick of the microgel monolayer to the the three-phase line and posterior transfer to the solid substrate. The three-phase line is the line where the wrinkles start. The movie has been speed up 4x. The movie frame has a size of $130 \times 40 \mu\text{m}^2$.

Movie M2. Transition from a wet deposited monolayer to a dried deposited monolayer. Collapse of the microgels into core-core contact can be observed. The movie frame has a size of $66 \times 36 \mu\text{m}^2$.

Movie M3. Iridescence patterns as the angle of light changes of the deposited microgel monolayer trough Langmuir-Schaefer deposition and supercritical CO_2 drying at 5 and 30 mN m^{-1} .

Movie M4. Langmuir-Schaefer deposition method, phase exchange and supercritical drying.