SUPPLEMENTARY INFORMATION:

Deformable particles with anisotropic interactions: unusual field-induced structural transitions in ultrasoft ionic microgel colloids

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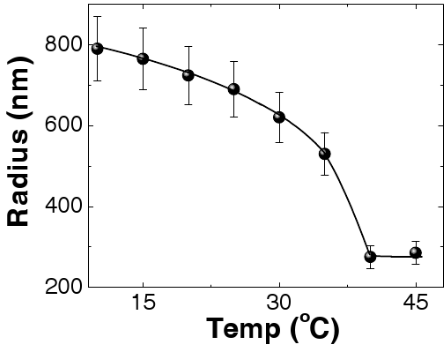
I. SYNTHESIS AND SWELLING BEHAVIOR OF PNIPAM CO AMP MICROGEL COLLOIDS

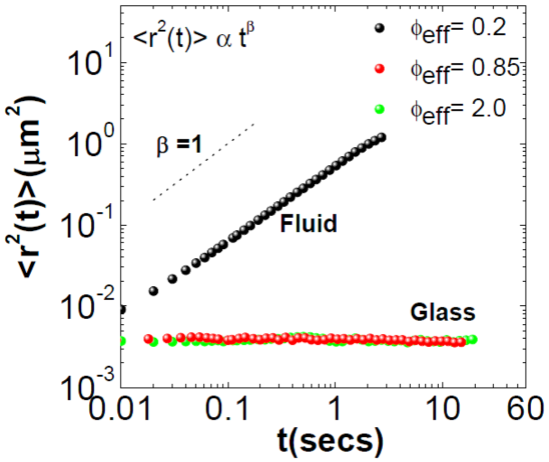
Ionic PNIPAm microgels were synthesized by free-radical precipitation polymerization using 2-acrylamido-2-methyl-1-propanesulfonic acid as an ionic co-monomer (references 7 and 9 of the paper), and fluorescently labelled with the covalently linked dye methacryloxyethyl thiocarbamoyl rhodamine B. N, N-methylene-bis-acrylamide was used as a cross-linker (with a 2.74 mol% cross-link density) and potassium per sulfate (KPS) as a free-radical initiator. After the synthesis, the suspensions were purified using multiple centrifugation and redispersion steps, followed by dialysis using deionized ($< 1\mu$S/cm) Millipore water for 2 weeks. The ionic comonomer 2-acrylamido-2-methyl-1-propanesulfonic (AMPS) is a strong acid , which accordingly ionizes completely in an aqueous medium. Hence in MilliQ water, it is expected that PNIPAM co AMPS microgels will be maximally charged. Therefore, for the purpose of the current study we made no attempt to characterize and vary the pH. [1] The temperature dependence of the hydrodynamic radius of these particles, as obtained by dynamic light scattering at very low concentrations, is shown in Supplementary Figure 1.

With increasing temperature, the radius decreases, reflecting the typical thermoresponsive nature of PNIPAM based microgels. However, in our case, the volume phase transition (VPT) is slightly shifted to higher temperatures (39°C) as compared to pure neutral PNIPAM microgels. This is due to the fact that swelling of the microgels is now due to a combined effect of two contributions, a strong Coulomb repulsion between neighbouring ionic groups in the polymer chain and the osmotic pressure of counterions. Moreover, a shift of the VPT to higher temperatures has also been seen in the case of other types of ionic microgels. The estimated swelling ratio ($= [\mathrm{R_h}(20^{\circ}\mathrm{C})/\mathrm{R_h}(45^{\circ}\mathrm{C})]^3$) of our microgel is 17.



Supplementary Fig. 1: Hydrodynamic radius of the ionic microgel colloids used in this study measured by DLS as a function of temperature for thermoresponsive ionic PNIPAm microgel with a cross-linking density of 2.74 mol%. The volume phase transition (VPT) occurs at 39°C, higher than the VPT of the PNIPAm microgel.

II. DYNAMICS IN THE FLUID AND GLASS PHASE AT ZERO FIELD

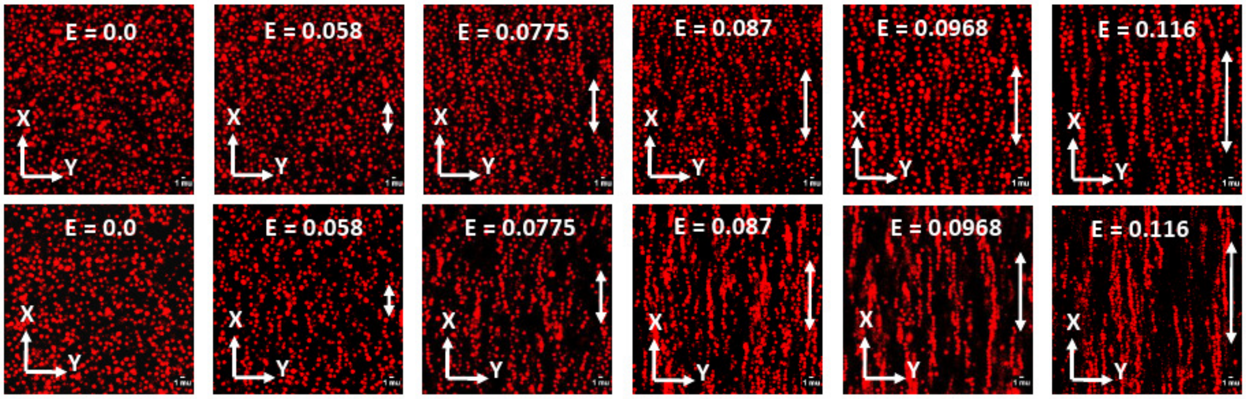


Supplementary Fig. 2: MSD vs time at zero field in the fluid and glass states. In the fluid state, diffusive $\beta = 1$ behaviour is observed, while in the glassy state, the MSD reaches a plateau value at very short times.

The disordered state at high volume fraction ($\phi_{\rm eff} = 0.85$, 2.0) is confirmed to be glass by measuring the mean square displacement (MSD) from XY time series. Usually, MSD $\propto t^{\beta}$, where β is 1 for free diffusion. In the highly concentrated glassy regime $\beta << 1$.

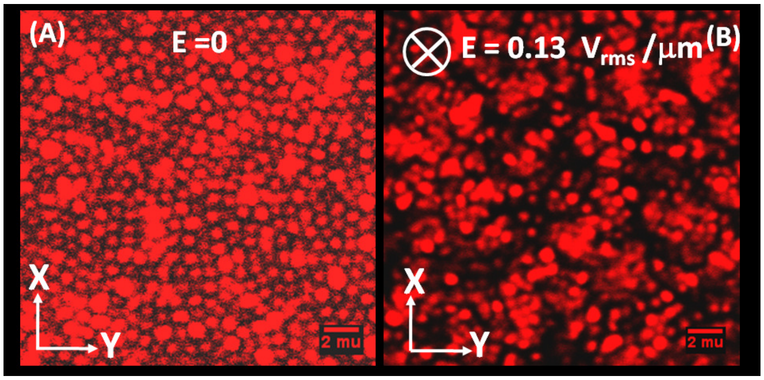
Supplementary Figure 2 shows the MSD vs time both in fluid and glassy state. The MSD vs time in the glassy state clearly shows a plateau indicating arrested long-time diffusion.

III. COMPARISON OF THE FIELD RESPONSE AT TWO TEMPERATURES



Supplementary Fig. 3: Microgels at $\phi_{\text{eff}} = 0.2$ in an applied electric field (in units of $\mathrm{V_{rms}}/\mu\mathrm{m}$). 2d confocal images taken in the bulk (10 particle diameters from the cover glass surface) at different electric fields (E) at temperature (TOP) : 20°C (BOTTOM) : 35°C

It is already known that with increasing temperature the dielectric constant of a PNIPAM microgel decreases from 63 at 15°C to 17 at 40°C (reference 32 of the paper) due to the change in water content. Since the ionic microgels used in our study show different swelling behavior, the dependence of the dielectric constant on temperature is also expected to be different; however it is also expected to decrease with increasing temperature. Hence, if one neglects the effect of mobile counterions, one would naively expect to have a larger field response at higher temperature. We have carried out experiments at two temperatures (20°C and 35°C) with increasing different field strength (Supplementary Figure 3). Upon comparing the observed structures for an effective volume fraction $\phi_{\text{eff}} = 0.2$ at different field strengths, it is apparent that the chain structure emerges at a lower field threshold at the higher temperature. A more comprehensive study involving dielectric spectroscopy as a function of temperature is planned.



Supplementary Fig. 4: Microgels at $\phi_{\text{eff}} = 1.6$ in an applied electric field (in units of $\mathrm{V_{rms}}/\mu\mathrm{m}$) show a transition from (a) a zero-field amorphous state to (b) a heterogeneous disordered state that does not evolve significantly. As in Figure 3 in the main text, we identify this as arrested phase separation. Field is along the Z direction.

IV. FIELD-DRIVEN ARRESTED PHASE SEPARATION AT $\phi_{\text{eff}} = 1.6$

Figure 3 in the main text shows a transition, at $\phi_{\text{eff}} = 2.0$, from an amorphous phase to a disordered state where there are large holes, that appears to be a phase separation that is arrested dynamically. This experiment was repeated for $\phi_{\text{eff}} = 1.6$ (Supplementary Figure 4). In this case the samples were contained between two ITO-coated cover glasses separated by a 70 mm spacer (similar sample geometry as in Figure 4 in the main text). As observed for $\phi_{\text{eff}} = 2.0$, there is no sign of further structure evolution and confirms the picture of arrested phase separation.

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[1] J. L. Velada, Y. Liu and M. B. Hugh, *Macromol. Chem. Phys.*, 1998, **199**, 1127.