## Supplemental Information: Linking slow dynamics and microscopic connectivity in dense suspensions of charged colloids

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## 1 Synthesis

All materials are purchased from Sigma-Aldrich (SA) and used as received, unless specified otherwise. For the synthesis of polymethyl methacrylate (PMMA) colloidal particles we use: Methyl methacrylate (MMA, SA M55909), Methacrylic acid (MA, SA 155721), Hexane (SA 208752), Mineral Oil BioUltra (SA 69794), 2,2'-Azobis(2-methyl-propionitrile) (AIBN, SA 441090), 1-Octanethiol(SA 471836), and 3,3'-Dioctadecyloxacarbocyanine Perchlorate (DiO, ThermoFischer Scientific D-275). For the synthesis of Poly(12-hydroxystearic acid)-graft-poly(methyl methacrylate) (PHSA-g-PMMA) we use: 12-Hydroxystearic Acid (TCI Chemicals, H0308), Toluene (SA, 179965), Methanesulfonic Acid (SA 471356), 4-*tert*-Butylcatechol (SA 124249), Glycidyl methacrylate (GMA, SA 151238), N,N-Dimethyldodecylamine (SA 284386), Ethyl acetate (SA 16371), and Butyl acetate (SA 537454). We also use *cis*-Decahydronaphthalene (cDec, TCI Chemicals D0009), Tetrachloroethylene (TCE, SA 270393), and Docusate sodium salt (AOT, SA 86140).

Synthesis of poly(methyl methacrylate)-graft-poly(12-hydroxystearic acid) Our synthetic procedure for poly(methyl methacrylate)-graft-poly(12-hydroxystearic acid) (PMMA-g-PHSA), the stabiliser used in the synthesis of colloidal PMMA particles, follows the general three-step procedure as detailed in literature<sup>59</sup>, with some minor changes. Step I - We begin by creating oligomers of 12-Hydroxystearic acid (HSA), aiming for oligomers of around 5 monomers in length, using a polycondensation reaction. To this end we weigh 50 g HSA and 9 g toluene in a 500 mL two necked round-bottom flask equipped with a reflux condenser and a 15 mL Dean-Stark trap, with 12 mL of toluene added to receiver leg. We heat the setup via an oil bath set at 110  $^{\circ}C$  and wait for the HSA to fully melt and dissolve in the toluene, while vigorously stirring the solution. After the HSA has fully dissolved we add 0.11 g of methanesulfonic acid and set the temperature of the oil bath to 150  $^{\circ}C$ . We let the reaction reflux for 20 hours, during which the reaction goes from a very pale yellow to a dark brown in colour and the viscosity of the solution increases strongly. During the condensation reaction a total of  $\sim 1.5 mL$  of water are extracted from the flask into the Dean-Stark trap. Step II - After 20 hours we empty the receiver leg of the Dean-Stark trap and add 20 mL of toluene to the reaction. We azeotropically distill 15 ml of the added toluene to remove all condensation water from the reaction. We then react the terminal carboxylic group on the PHSA with glycidyl methacrylate (GMA), to create reactive PHSA macromonomers. In a separate beaker we combine 5.2 g GMA, 0.073 g tert-Butylcatechol, 0.20 g N,N-Dimethyldodecylamine, and 10 g toluene. We add this solution to the refluxing reaction and allow it to react for another 7 hours while stirring vigorously. At completion the reaction is cooled and stored at 4°C until further use. Step III - In the third step we co-polymerize MMA and the PHSA macromonomer, to create the PMMA-graft-PHSA stabiliser. We prepare a mixture of 31 g PHSA macromonomer, as synthesised in steps I & II, 9.2 g toluene, 18.32 g methyl metacrylate, 2.05 g glycidyl methacrylate, and 0.307 g AIBN. We slowly add this mixture dropwise, using a syringe pump, over a period of three hours to a round-bottom flask equipped with a reflux condenser, containing 13.94 g ethyl acetate and 6.97 g butyl acetate which is immersed in a 110 °C oil bath. After the reaction mixture has been added to the flask we let the reaction proceed under reflux for two hours after which we add a solution of 140 mg AIBN in 1.5 g ethyl acetate and 0.75 g butyl acetate. When another two hours have elapsed we add another dose of AIBN. After addition of the second injection of AIBN we dilute the reaction with 16.6 g ethyl acetate and 8.3 g butyl acetate. We let the reaction proceed for 15 hours. After cooling to room temperature, the stabiliser reaction mixture is used directly in the synthesis of the particles. The resulting product is highly viscous and has a golden colour.

Synthesis of PMMA colloidal particles For the synthesis of colloidal particles made out of poly(methyl methacrylate) (PMMA)<sup>60</sup> we add 49.0 g Methyl metacrylate (98% of total monomer weight), 1.0 g Methacrylic acid (2% of total monomer weight), 29.8 g Hexane, 14.3 g Mineral Oil, and approximately 10 mg of DiO-C18 fluorescent dye to a 250 mL round-bottom flask. We add a small magnetic stirring bar and stir the solution until all the dye has dissolved. We then add 5 g of PMMA-g-PHSA stabiliser, 390 mg AIBN, and 300 mg 1-Octanethiol. The reaction takes place under reflux conditions at 80 °C and proceeds for 2 hours under slow magnetic stirring. We then filter the reaction mix through glass wool. Reaction products are removed by cleaning the suspension through centrifugation against hexane (2x). The resulting particles have a radius of 710 nm as

measured by static light scattering (Fig. S1A). By increasing the monomer amount in the reaction, the particle size can be increased. Using this method we synthesise a second batch of particles with a radius of 975 nm as determined by SLS (Fig. S1B).



**Fig. S1. Size determination of colloidal particles with SLS.** (**A**) Rayleigh ratio as a function of scattering vector for the smaller particles **q**, solid red line is a theoretical fit as calculated using Mie theory giving a radius of gyration of 710 nm (black circles). (**B**) Same as in (**A**) but for particles with a radius of gyration of 975 nm.

## 2 Sample preparation

*Washing and density matching of particle suspension* - We start by washing, by sequential centrifugation and re-suspension steps, the particle suspensions two times with a 50/50 volume-% mix of *cis*-Decahydronaphthalene (cDec) and Tetrachloroethylene (TCE) with 10 mM AOT. By varying the relative volumes of cDec and TCE we can density match our particles with the solvent mix. We achieve this by adding small amounts of TCE or cDec until we can no longer observe sedimentation after centrifugation at 2000 g for one hour. The density matched suspension is also matched well enough in refractive index to allow us to examine the samples using confocal microscopy up to depths of approximately 100  $\mu m$ , without loss of resolution due to scattering. After density matching the particle suspensions we concentrate the suspension by centrifuging at 2500 g and 35 °C until we observe a clear supernatant. We decant the supernatant and store it for later use. All subsequent samples are made from this concentrated stock suspension and are diluted with the supernatant.



**Fig. S2.** Side view of the sample chambers used in this study. The shaded blue area represents the hollow where the sample is loaded.

Sample chamber fabrication - Our sample chambers are constructed by gluing, using Norland Optical Adhesive 61 UV curable glue, two 21 mm x 26 mm microscopy cover slips on a larger round cover slip (radius of 2.5 cm); leaving a space between them of approximately 0.5 cm. We than glue a microscope slide (26 mm x 76 mm) across the two rectangular cover slips using the same UV glue. This creates a hollow chamber with dimension of approximately 5 mm x 26 mm x 150  $\mu m$ . The sample chamber construct is depicted as a side-view in Figure S2 with the loaded

sample shaded in blue. We load the sample chambers using capillary forces and seal both ends of the chamber with 2-component gel epoxy from VersaChem.

## **3** Pair potential U(r)

The pair potentials U(r) is obtained from the measured radial distribution function g(r) using the Ornstein-Zernike relation:

$$h(r) = c(r) + \rho \int h(r)c(r-r)d\mathbf{r}$$
(1)

where h(r) = g(r) - 1 is the total correlation function, c(r) the direct correlation function, and  $\rho$  the number density of particles. We solve this equation by Fourier transformation, using the hypernetted chain (HNC) closure approximation:

$$c(r) = -U(r)/k_BT + h(r) - lng(r)$$
<sup>(2)</sup>

This closure approximation is known to give accurate results for soft potentials at not too high densities<sup>61</sup>.

4 Supplemental Figures and Movies



**Fig. S3.** Probability distribution of cluster sizes,  $P(S_C)$ , for the small particles (**A**) and the large particles (**B**) in our binary mixture, calculated for the sample with volume fraction  $\phi = 0.18$ . We find no clusters of any significant sizes for either particle species. (**A inset**) Probability distribution of the particle radii as identified by the locating algorithm; we use this to determine a rough cutoff radius (dashed line) by which we can identify the two different particle populations. For the cluster analysis we use the DBSCAN algorithm with parameter  $\epsilon$ , the maximum allowable neighbourhood radius, equal to the first minimum distance in the pair-correlation function, g(r), and a minimum cluster size of one. (**B inset**) Pair-correlation function, g(r), for the two particle populations: large particles (blue triangles) and small particles (red circles).



**Fig. S4.** Heterogeneous depercolation of bond networks. Computer-generated renderings of bond networks showing all nearest-neighbours bonds, those that are intact at a lag time t are shown in dark purple, those that have broken due to thermal fluctuations in green at  $\phi = 0.31$ . For lag times **A** t = 0 s, **B** t = 50 s **C** t = 100 s.



Fig. S5. Raw confocal data - High volume fraction. Raw experimental data for  $\phi = 0.35$ 

with a real time duration of 10 s. Shown here is a still from the movie.



Fig. S6. Raw confocal data - Low volume fraction. Raw experimental data for  $\phi = 0.18$  with a real time duration of 10 s. Shown here is a still from the movie.



Fig. S7. Decay of *Z* with increasing lag time. We show the decay of the long-lived bond network with increasing delay  $\tau$ . Particles are coloured according to *Z* at constant experimental time *t* and varying delay  $\tau$  from 0.5 s to 171 s, as shown in the video. Shown here is a still from the movie.



Fig. S8. Dynamics of *Z* clusters. Here we show the dynamical behaviour of *Z* at a constant delay time  $\tau = \tau_0$  while varying the experimental time as indicated in the video. Shown here is a still from the movie.

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