# **Supplementary Information**

#### 1. Zero-average contrast approach

The ZAC solvent, in which Hm and Dm contribute to the scattered intensity equally, was determined to be at 48 vol% of H<sub>2</sub>O in D<sub>2</sub>O. This ratio is reflected by the data in Figure S.1, in which the particle contrast in different H<sub>2</sub>O/D<sub>2</sub>O mixtures was obtained from  $I_0 \equiv I(q \rightarrow 0)$ .



**Fig. S.1** Contrast variation curves in  $H_2O/D_2O$  solvent mixtures for hydrogenated (squares) and deuterated (circles) particles. In all cases the number density was kept constant and the structure factors were cancelled by additions of KCI. The solid red lines are linear fits to the data.

## 2. Fit to SAXS data

The *q*-dependent intensity, I(q), of the SAXS data can be described by  $I(q) \propto P_{\rm m}(q)S_{\rm m}(q)$ , where  $P_{\rm m}(q)$  and  $S_{\rm m}(q)$  are the measured form and structure factor, respectively. The form factor  $P_{\rm m}(q)$  is assumed to satisfy

$$P_{\rm m}(q) = \frac{\int_0^\infty P(q, R_{\rm HC}, \sigma) D(R_{\rm HC}, \sigma_{\rm PD}) V_{\rm sphere}^2 \, dR}{\int_0^\infty D(R_{\rm HC}, \sigma_{\rm PD}) V_{\rm sphere}^2 \, dR} + I_{\rm fluct}, \qquad (S.1)$$

where  $D(R_{\rm HC}, \sigma_{\rm PD})$  the Gaussian size distribution,  $I_{\rm fluc}$  is the Lorentzian function to account for polymer network fluctuations,  $V_{\rm sphere}$  the particle volume and  $P(q, R_{\rm HC}, \sigma)$  the fuzzy sphere form factor,

$$P(q, R_{\rm HC}, \sigma) = \left[\frac{3(\sin(qR_{\rm HC}) - qR_{\rm HC}\cos(qR_{\rm HC}))}{(qR_{\rm HC})^3}\exp\left(-\frac{(\sigma q)^2}{2}\right)\right]^2$$
(S.2)

Here,  $R_{\rm HC}$  and  $\sigma$  are the hard-core radius and the fuzziness parameter, respectively. We approximate the exact  $S_{\rm m}(q)$  by the decoupling approximation in the same way as Westermeier *et. al.*<sup>1</sup>

$$S_{\rm m}(q) = [1 - X(q)] + X(q)S(q), \tag{S.3}$$

where S(q) is the monodisperse structure factor calculated through the established *modified penetrating background-corrected rescaled mean sphere approximation* (MPB-RMSA) scheme used in previous publications.<sup>2,3</sup> The decoupling amplitude factor X(q) is defined as

$$X(q) = \frac{\left[\int_0^\infty D(R,\sigma) f(q,R) V_{\text{sphere}} \ dR\right]^2}{P_{\text{m}}(q) \int_0^\infty D(R,\sigma) V_{\text{sphere}}^2 \ dR},$$
(S.4)

where f(q, R) is the normalised form amplitude of a particle with radius *R*, i.e.  $P(q, R) = f(q, R)^2$ .

### 3. pH vs. concentration

The pH was measured as a function of the microgel weight fraction and is represented as points in Figure S.2. The fitted curve corresponds to an acid with pKa 4.2.



Fig. S.2 pH vs. concentration (circles). The line are the best fit for an acid with a pKa 4.2.

#### 4. S(q) with additional Ornstein-Zernike term

In order to account for the low-q deviation we have added an Ornstein-Zernike,  $S_{OZ}(q)$  term to the structure factor,

$$S_{\rm OZ}(q) = \frac{A}{(1+\xi^2 q^2)},$$
 (S.5)

where  $\xi$  is the correlation length and *A* the amplitude. The total *S*(*q*) is then described as

$$S(q) = S_{\text{OZ}}(q) + S_{\text{MPBRMSA}}(q), \qquad (S.6)$$

where  $S_{\text{MPBRMSA}}(q)$  is the monodisperse structure factor calculated through the established MPB-RMSA scheme. We then follow Equations S.1-3 for obtaining I(q), as the red line in Figure S.3 A shows. Note that the black curve shows the best fit without the Ornstein-Zernike contribution. We also used the calculated S(q) as an input to calculate the dynamic function, D(q). As can be seen in



**Fig. S.3** I(q), A, and D(q), B, as a function of q at a concentration of 0.3 wt%. The red curves are the best fit with an added Ornstein-Zernike contribution, while the black curves do not include this term.

Figure S.3 B, an equally good fit can be see for D(q) in comparison to with out the Ornstein-Zernike contribution, black curve.

### 5. High-ionic strengths

In a few test sample, 0.1, 0.02 and 0.005 wt% we added 10 mM NaCl to screen the electrostatic interactions. The resulting hydrodynamic radius, open red circles, and static radius, black open circles, can be seen in Figure S.4. The same result for de-ionised samples are shown as solid circles in the same figure.



**Fig. S.4** The hydrodynamic radius, red, and static radius, black, radius vs. concentration. Data for the microgels with 10 mM added NaCl is shown by open circles. The data for the deionized microgels is shown by the full circles.

### 6. Electric field profiles

The Poisson-Boltzmann cell model is used to numerically calculate the electrostatic potential inside the microgel particle, as well as in its vicinity. As described in the main text, the cell size is determined by the number density of the microgels. Charge neutrality dictates that the electric field should vanish at the boundary of the cell, which results in a density-dependent field profile. The calculated profiles are shown in in Figure S.5.



**Fig. S.5** The electric field strength for heterogeneously crosslinked microgels with a swollen radius of 70 nm, at weight fractions 1.8 wt %, 0.18 wt %, and 0.018 wt %. The corresponding cell radii  $R_{cell}$  at these weight fractions are 622 nm, 289 nm, and 134 nm, respectively.

- F. Westermeier, B. Fischer, W. Roseker, G. Grübel, G. Nägele, and M. Heinen, J. Chem. Phys. 137, 114504 (2012).
- 2 M. Heinen, P. Holmqvist, A. J. Banchio, and G. Nägele, J. Chem. Phys. **134**, 044532 (2011).
- 3 P. Holmqvist, P. S. Mohanty, G. Nägele, P. Schurtenberger, and M. Heinen, Phys. Rev. Lett. 109, 048302 (2012).