Supporting information for:
On the role of softness in ionic microgel interactions

M. J. Bergman,1,2 S. Nöjd,1 P. S. Mohanty,1,3 N. Boon,1 J. N. Immink,1,4 J. J. E. Maris,1,5 J. Stenhammar,1 and P. Schurtenberger1,6

1 Physical Chemistry, Department of Chemistry, Lund University, Lund, Sweden.
2 current address: Department of Physics, University of Fribourg, Fribourg, Switzerland.
3 current address: School of Chemical Technology, Kalinga Institute of Industrial Technology (KIIT), Bhubaneswar, India.
4 Current address: Condensed Matter Physics Laboratory, Heinrich-Heine-University, Düsseldorf, Germany
5 current address: Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, Utrecht, Netherlands.
6 Lund Institute for advanced Neutron and X-ray Science (LINXS), Lund University, Lund, Sweden.
EXPERIMENTAL PARAMETERS

| M1.5 (1.5 mol%) | M3 (3 mol%) | M5 (5 mol%) | M10 (mol%) |
|-----------------|-------------|-------------|-------------|
| **liquid state points** | **liquid state points** | **liquid state points** | **liquid state points** |
| wt% $n_p$ ($\mu m^{-3}$) | $\phi_{RH}$ | wt% $n_p$ ($\mu m^{-3}$) | $\phi_{RH}$ | wt% $n_p$ ($\mu m^{-3}$) | $\phi_{RH}$ | wt% $n_p$ ($\mu m^{-3}$) | $\phi_{RH}$ |
| 0.25 | 0.08 0.12 | 0.5 | 0.16 0.19 | 0.5 | 0.13 0.22 | 0.5 | 0.14 0.07 |
| 0.5 | 0.15 0.24 | 1.0 | 0.32 0.39 | 1.0 | 0.25 0.33 | 1.0 | 0.28 0.13 |
| 0.75 | 0.23 0.36 | 1.5 | 0.48 0.59 | 1.5 | 0.38 0.46 | 2.0 | 0.57 0.27 |
| 1.0 | 0.30 0.48 | | 2.0 | 0.50 0.70 | 3.0 | 0.85 0.40 | |
| 1.5 | 0.45 0.72 | | 2.5 | 0.63 0.76 | 4.0 | 1.13 0.54 | |
| 2 | 0.60 0.96 | | 3.0 | 0.75 0.83 | 5.0 | 1.42 0.67 | |
| | | | | | | | |
| **arrested state points** | **arrested state points** | **arrested state points** | **arrested state points** |
| 2.5 | 0.73 1.15 | 2.0 | 0.64 0.79 | 4.4 | 1.26 1.02 | 6.0 | 1.78 0.84 |
| 3 | 0.93 1.47 | 3.0 | 0.96 1.18 | 5.5 | 1.51 1.22 | 6.5 | 1.98 0.94 |
| | | | | | | | |
| 3.5 | 1.12 1.38 | 6.5 | 1.63 1.32 | 7.0 | 2.09 0.99 | |
| 4.0 | 1.28 1.58 | 7.5 | 1.81 1.46 | 8.0 | 2.37 1.13 | |
| 5.0 | 1.61 1.97 | 8.2 | 1.96 1.59 | 9.0 | 2.55 1.21 | |
| | | | | | 11.0 | 3.00 1.42 | |
| | | | | | 12.0 | 3.27 1.55 | |

SI-Table 1: Experimental parameters. Number density ($n_p$) for liquid state points is derived from linear extrapolation of experimental number density of arrested state points. Effective volume fraction $\phi_{RH}$ is calculated using number density and hydrodynamic radius $R_H$ under deionized conditions.
EXPERIMENTAL NUMBER DENSITIES

In SI-Figure 1, the experimental number densities $n_p$ are shown for arrested samples (symbols) as well as the linear extrapolation to zero concentration (dashed lines). We note again that the microgels with crosslinker content 1.5 mol%, 3 mol%, 5 mol% and 10 mol% are indicated with the names M1.5, M3, M5 and M10, respectively.

SI-Fig. 1: Number densities in the liquid regime based on the fits (squares) and experimental number densities in the solid regime (circles) as function of wt%. Panels a, b, c, d contain data for M1.5, M3, M5 and M10, respectively.

Also shown are the linear fits (dashed lines) for each regime, which have been forced to go through zero.
COMPARISON OF CRYSTAL $g(r)$ TO BCC STRUCTURE

In SI-Figure 2, four typical crystal $g(r)$s are shown (solid lines) for each crosslinker density (data also shown in Figure 4 in main text). We compare the peak positions to the predicted peak positions for a BCC crystal structure (dashed lines) [1]. The discrepancy between prediction and experiment confirms that all crystals possess the FCC structure.

SI-Fig. 2: Typical crystal $g(r)$s for each crosslinker density. From bottom to top M1.5 at 2.5 wt%, M3 at 3 wt%, M5 at 4.4 wt% and M10 at 6.5 wt% are shown. Dashed lines represent the characteristic peak positions for a BCC crystal. The graphs are offset in y for clarity. The x-axis is normalized by the first peak position as of each g(r).
In SI-Figure 3 we show the effect of temperature annealing on the structural order of the M1.5 sample at 3wt%. The upper row shows the $g(r)$ and typical image before annealing, i.e. immediately after preparation of the confocal microscopy sample. The bottom row indicates the crystalline order achieved via temperature annealing. The sample was heated to 30 °C overnight, then allowed to cool down to 20 °C in steps of 5 °C, with equilibration time of several days at each step.

SI-Fig. 3: Crystallisation can be achieved through annealing for M1.5.
SI-Figure 4 gives an example of the best-scoring $R_{\text{eff}}$ values for M1.5 (softest) and M10 (stiffest) microgels for each considered model. For neutral microgels – or screened microgels – the Hertzian model quantitatively describes structural correlations in the liquid regime, and conveniently $R_{\text{eff}} = R_H$. For ionic microgels under deionised conditions, $R_{\text{eff}}$ with highest $\chi^2$-value is generally smaller than $R_H$.

| Model  | Hertzian model (neutral) | Hertzian-Yukawa model (ionic) | Hertzian-Yukawa-Ramp model (ionic) |
|--------|--------------------------|-------------------------------|-----------------------------------|
| M1.5   | ![Image](image1)          | ![Image](image2)              | ![Image](image3)                  |
|        | $R_{\text{eff}} = 720\,\text{nm}$ | $R_{\text{eff}} = 700\,\text{nm}$ | $R_{\text{eff}} = 550\,\text{nm}$ |
|        | $R_{\text{H}} = 465\,\text{nm}$ | $R_{\text{H}} = 400\,\text{nm}$ | $R_{\text{H}} = 490\,\text{nm}$ |
| M10    | ![Image](image4)          | ![Image](image5)              | ![Image](image6)                  |

SI-Fig. 4: Illustration of effective radii considered per model for the softest (M1.5, top row) and stiffest (M10, bottom row) microgel type. From left to right: the Hertzian model where $R_{\text{eff}} = R_H$, the HY model and the HYR model. Sizes are not drawn to scale.
In the Hertzian + Yukawa model, key parameters are the Debye screening length $\kappa$, the Hertzian interaction strength $\epsilon_H$, the effective charge $Z_{\text{eff}}$, the effective volume fraction $\phi_{\text{eff}}$, and the effective interaction radius $R_{\text{eff}}$.

The Debye screening length is set to $\kappa = 5.3 \, \mu m^{-1}$, reflecting the very low ion concentrations in the ionic double layers in the presence of ion-exchange resins [2]. Although samples are kept on resins before measurements, the confocal microscopy samples are free of resins in order to avoid salt gradients, which are known to promote crystallisation [3].

The Hertzian interaction strength $\epsilon_H$ depends on crosslinker content. Because the electrostatic interactions dominate in the liquid regime, however, an estimate for $\epsilon_H$ suffices here. Published experimental work on 5 mol% crosslinked PNIPAM microgels suggests $\epsilon_H \approx 500 \, k_B T$ [4-6]. In a recent simulation study $\epsilon_H \approx 200, 350, 600 \, k_B T$ was computed for simulated microgels with crosslinker density 3.2, 5, 10 mol% [7]. We increase these literature values to correspond to the experimental values and use $\epsilon_H = 200, 350, 500, 750 \, k_B T$ for M1.5, M3, M5 and M10, respectively.

This leaves $Z_{\text{eff}}$, $R_{\text{eff}}$ and $\phi_{\text{eff}}$ as free parameters for each state point. Per crosslinker series, we consider $R_{\text{eff}} = [R_{\text{core}}, R_{\text{H}}]$, spanning the size range described in Figure 1a. The number density $n_p$ is derived from counting particles in the crystalline state and extrapolating back to zero. $\phi_{\text{eff}}$ follows from $R_{\text{eff}}$ and $n_p$: $\phi_{\text{eff}} = \frac{4}{3}\pi n_p R_{\text{eff}}^3$. $Z_{\text{eff}}$ is a free fitting parameter per state point. The fit parameters are summarised in SI-Table 2.

The squared sum of error (SSE) is calculated for each fit at each statepoint. For each considered $R_{\text{eff}}$, the best-scoring SSE is kept per state point — this selects the fit parameter $Z_{\text{eff}}$. The SSEs are then summed per $R_{\text{eff}}$ and the best-scoring SSE is kept per crosslinker series. We thus keep the effective interaction radius $R_{\text{eff}}$ constant allowing $Z_{\text{eff}}$ to vary per statepoint. Resultant fits are shown in Figure 6a and SI-Figures 5, 7, 9 with fit parameters summarised in SI-Tables 3, 7, 9, 11.

| Fit parameter                     | M1.5 | M3  | M5  | M10 |
|-----------------------------------|------|-----|-----|-----|
| $\epsilon_H (k_B T)$             | 200  | 350 | 500 | 750 |
| $[R_{\text{core}}, R_{\text{H}}]$ (nm) | [450,750] | [400,700] | [350,600] | [350,500] |
| $R_{\text{eff}}^\text{best SSE}$ (nm) | 700  | 550 | 550 | 400 |
| $Z_{\text{eff}}$                   | 100-1000 |     |     |     |

SI-Table 2: Fit parameters HY model tested for all crosslinker series.
### FIT PARAMETERS USED IN FIG. 6

| wt% | n_p | R_eff | φ_eff | ϵ_H | Z_eff | SSE |
|-----|-----|-------|-------|------|-------|-----|
| 0.25 | 0.08 | 700 | 0.114 | 200 | 1000 | 1.55 |
| 0.5  | 0.15 | 700 | 0.227 | 200 | 600  | 1.24 |
| 0.75 | 0.23 | 700 | 0.341 | 200 | 500  | 0.75 |
| 1.0  | 0.30 | 700 | 0.455 | 200 | 200  | 0.12 |
| 1.5  | 0.45 | 700 | 0.682 | 200 | 300  | 0.65 |
| 2    | 0.60 | 700 | 0.91  | 200 | 600  | 1.39 |

SI-Table 3: Crosslinker series M1.5. Fit parameters for HY model (solid lines in Figure 6a).

| wt% | n_p | R_eff | φ_eff | ϵ_H | Z_eff | SSE |
|-----|-----|-------|-------|------|-------|-----|
| 0.25 | 0.08 | 723 | 0.12 | 10000 | 1000 | 1.90 |
| 0.5  | 0.15 | 723 | 0.24 | 10000 | 400  | 0.57 |
| 0.75 | 0.23 | 723 | 0.36 | 10000 | 200  | 4.62 |
| 1.0  | 0.30 | 723 | 0.48 | 10000 | 0    | 22.58 |

SI-Table 4: Fit parameters for the HY model test on the first four state points of M1.5 with \( \epsilon_H = 10^4 \ k_B T \) and \( R_{\text{eff}} = R_H \) (solid lines in Figure 6b).

| wt% | n_p | R_eff | φ_eff | ϵ_H | Z_eff | R_ramp | ϵ_ramp | SSE |
|-----|-----|-------|-------|------|-------|--------|--------|-----|
| 0.25 | 0.08 | 550 | 0.055 | 200 | 200  | 1.5    | 40     | 0.39 |
| 0.5  | 0.15 | 550 | 0.11 | 200 | 500  | 1.3    | 40     | 0.51 |
| 0.75 | 0.23 | 550 | 0.166 | 200 | 200  | 1.3    | 20     | 0.58 |
| 1.0  | 0.30 | 550 | 0.221 | 200 | 200  | 1.2    | 20     | 0.42 |
| 1.5  | 0.45 | 550 | 0.331 | 200 | 600  | 1.1    | 30     | 0.69 |
| 2    | 0.60 | 500 | 0.42 | 200 | 400  | 1.1    | 30     | 0.48 |

SI-Table 5: Crosslinker series M1.5. Fit parameters for HYR model (solid lines in Figure 6c).
PARAMETER CHOICE AND FITTING HERTZIAN + YUKAWA + RAMP (HYR) MODEL

In the Hertzian + Yukawa + ramp model, the key parameters that need to be considered are: the Debye screening length $\kappa$, the Hertzian interaction strength $\epsilon_H$, the effective charge $Z_{\text{eff}}$, the effective volume fraction $\phi_{\text{eff}}$, the effective interaction radius $R_{\text{eff}}$, the ramp strength $\epsilon_{\text{ramp}}$ and relative ramp radius $R_{\text{ramp}}$.

$\kappa$, $\epsilon_H$, $Z_{\text{eff}}$, $\phi_{\text{eff}}$ and $R_{\text{eff}}$ are used as defined for the HY model. Ramp strength $\epsilon_{\text{ramp}}$ indicates the interaction strength at $R_{\text{eff}} = 0$ and is considered between 0 – 50 $k_BT$. Relative ramp radius $R_{\text{ramp}}$ is considered between $R_{\text{eff}} - 2R_{\text{eff}}$. SI-Table 6 summarizes the parameter space probed.

The fitting approach used for the HY model is reproduced here: the SSE is calculated for each fit at each statepoint, with considered fit parameters summarised in SI-Table 6. For each $R_{\text{eff}}$, the best-scoring fit per statepoint is kept, thus setting $Z_{\text{eff}}$. SSEs are summed per $R_{\text{eff}}$ to select the highest-scoring $R_{\text{eff}}$. These fits are shown in Figure 6c and SI-Figures 6, 8, 10 with fit parameters summarised in SI-Tables 5, 8, 10, 12.

| Fit parameter | M1.5 | M3   | M5   | M10  |
|---------------|------|------|------|------|
| $\epsilon_H$  | 200  | 350  | 500  | 750  |
| $[R_{\text{core}}, R_H]$ (nm) | [450,750] | [400,700] | [350,600] | [350,500] |
| $R_{\text{eff}}$ (nm) | 550  | 450  | 400  | 350  |
| $Z_{\text{eff}}$ | 500-1000 |
| $\epsilon_{\text{ramp}}$  | 0-50 |
| $R_{\text{ramp}}$  | 1-2 |

SI-Table 6: Fit parameters HYR model tested for all crosslinker series.
HY AND HYR FITS TO ALL CROSSLINKER SERIES

SI-Fig. 5: Pair correlation functions for liquid state points crosslinker series M3 (symbols) and fits with HY model (dash-dotted line). Corresponding fit parameters are given in table below.

| wt% | n_p | R_{eff} | \phi_{eff} | \epsilon_H | Z_{eff} | SSE |
|-----|-----|---------|-----------|-----------|---------|-----|
| 0.5 | 0.16 | 500 | 0.082 | 350 | 400 | 1.13 |
| 1.0 | 0.32 | 500 | 0.164 | 350 | 200 | 0.73 |
| 1.5 | 0.48 | 500 | 0.246 | 350 | 100 | 0.28 |

SI-Table 7: Crosslinker series M3. Fit parameters for HY model.

SI-Fig. 6: Pair correlation functions for liquid state points crosslinker series M3 (symbols) and fits with HYR model (solid line). Corresponding fit parameters are given in table below.

| wt% | n_p | R_{eff} | \phi_{eff} | \epsilon_H | Z_{eff} | R_{ramp} | \epsilon_{ramp} | SSE |
|-----|-----|---------|-----------|-----------|---------|----------|--------------|-----|
| 0.5 | 0.16 | 450 | 0.06 | 350 | 100 | 1.3 | 20 | 0.26 |
| 1.0 | 0.32 | 450 | 0.119 | 350 | 100 | 1.1 | 30 | 0.31 |
| 1.5 | 0.48 | 450 | 0.179 | 350 | 100 | 1.0 | 30 | 0.37 |

SI-Table 8: Crosslinker series M3. Fit parameters for HYR model.
SI-Fig. 7: Pair correlation functions for liquid state points crosslinker series M5 (symbols) and fits with HY model (dash-dotted line). Corresponding fit parameters are given in table below.

**SI-Table 9**: Crosslinker series M5. Fit parameters for HY model.

| wt% | n_p | R_eff | \phi_{eff} | \epsilon_H | Z_{eff} | SSE  |
|-----|-----|-------|------------|------------|--------|------|
| 0.5 | 0.14| 550   | 0.112      | 500        | 400    | 1.25 |
| 1.0 | 0.28| 550   | 0.225      | 500        | 500    | 2.01 |
| 1.5 | 0.42| 550   | 0.337      | 500        | 400    | 2.19 |
| 2.0 | 0.56| 550   | 0.449      | 500        | 200    | 3.34 |
| 2.5 | 0.70| 550   | 0.562      | 500        | 200    | 2.88 |
| 3.0 | 0.84| 550   | 0.674      | 500        | 200    | 4.08 |

SI-Fig. 8: Pair correlation functions for liquid state points crosslinker series M5 (symbols) and fits with HYR model (solid line). Corresponding fit parameters are given in table below.

**SI-Table 10**: Crosslinker series M5. Fit parameters for HYR model.

| wt% | n_p | R_eff | \phi_{eff} | \epsilon_H | Z_{eff} | R_{ramp} | \epsilon_{ramp} | SSE |
|-----|-----|-------|------------|------------|--------|----------|-----------------|-----|
| 0.5 | 0.14| 400   | 0.043      | 500        | 400    | 1.4      | 30              | 1.04|
| 1.0 | 0.27| 400   | 0.086      | 500        | 600    | 1.4      | 30              | 1.73|
| 1.5 | 0.42| 400   | 0.13      | 500        | 300    | 1.4      | 30              | 1.18|
| 2.0 | 0.56| 400   | 0.173     | 500        | 100    | 1.3      | 20              | 2.85|
| 2.5 | 0.70| 400   | 0.216     | 500        | 100    | 1.3      | 30              | 3.31|
| 3.0 | 0.84| 400   | 0.259     | 500        | 400    | 1.2      | 30              | 2.19|
SI-Fig. 9: Pair correlation functions for liquid state points crosslinker series M10 (symbols) and fits with HY model (dash-dotted line). Corresponding fit parameters are given in table below.

SI-Table 11: Crosslinker series M10. Fit parameters for HY model.

| wt% | n_p | R_eff | phi_eff | epsilon_H | Z_eff | SSE |
|-----|-----|-------|---------|------------|-------|-----|
| 0.5 | 0.14| 400   | 0.038   | 750        | 300   | 0.91|
| 1.0 | 0.28| 400   | 0.076   | 750        | 200   | 0.86|
| 2.0 | 0.57| 400   | 0.152   | 750        | 200   | 0.31|
| 3.0 | 0.85| 400   | 0.227   | 750        | 200   | 0.50|
| 4.0 | 1.13| 400   | 0.303   | 750        | 200   | 0.22|
| 5.0 | 1.42| 400   | 0.379   | 750        | 300   | 0.17|
| 5.5 | 1.56| 400   | 0.417   | 750        | 300   | 1.28|

SI-Fig. 10: Pair correlation functions for liquid state points crosslinker series M10 (symbols) and fits with HYR model (solid line). Corresponding fit parameters are given in table below.

SI-Table 12: Crosslinker series M10. Fit parameters for HYR model.

| wt% | n_p | R_eff | phi_eff | epsilon_H | Z_eff | R_ramp | epsilon_ramp | SSE |
|-----|-----|-------|---------|------------|-------|---------|--------------|-----|
| 0.5 | 0.14| 350   | 0.025   | 750        | 100   | 1.4     | 50           | 0.19|
| 1.0 | 0.28| 350   | 0.051   | 750        | 100   | 1.3     | 50           | 0.10|
| 2.0 | 0.57| 350   | 0.102   | 750        | 100   | 1.3     | 10           | 0.18|
| 3.0 | 0.85| 350   | 0.152   | 750        | 200   | 1.2     | 20           | 0.19|
| 4.0 | 1.13| 350   | 0.203   | 750        | 200   | 1.2     | 20           | 0.15|
| 5.0 | 1.42| 350   | 0.254   | 750        | 200   | 1.2     | 10           | 0.15|
| 5.5 | 1.56| 350   | 0.279   | 750        | 200   | 1.2     | 20           | 0.40|
SI-Fig. 11: Potentials used to calculate $g(r)$s shown in Figure 8. With increasing repulsion (a: $Z_{\text{eff}}$, b: $\epsilon_{\text{ramp}}$) the potential becomes harder. With increasing $R_{\text{ramp}}$ (c) interactions become longer ranged. $\epsilon_{\text{ramp}}$ is in units of $k_B T$. $R_{\text{ramp}}$ is defined in units of $R_{\text{eff}}$. Starred values indicate best scoring $g(r)$ fits.
### FIT PARAMETERS USED FOR FIG. 8

| Model | \(n_p \text{ (}\mu\text{m}^{-3}\)) | \(R \text{ (nm)}\) | \(\phi\) | \(\epsilon_H \text{ (kT)}\) | \(Z_{\text{eff}}\) | \(R_{\text{ramp}}\) | \(\epsilon_{\text{ramp}}\) |
|-------|------------------|------------------|-------|------------------|------------|------------------|------------------|
| HY    | 0.075            | 700              | 0.11  | 200 1000         | -          | -                | -                |
| HYR   | 0.075            | 550              | 0.05  | 200 200          | 1.5 40     | -                | -                |
| HS    | 0.075            | 850              | 0.194 | 100000           | -          | -                | -                |
| HY    | 0.16             | 550              | 0.11  | 350 700          | -          | -                | -                |
| HYR   | 0.15             | 550              | 0.10  | 350 200          | 1.3 10     | -                | -                |
| HS    | 0.16             | 650              | 0.18  | 100000           | -          | -                | -                |
| HY    | 0.16             | 550              | 0.11  | 500 400          | -          | -                | -                |
| HYR   | 0.16             | 400              | 0.04  | 500 400          | 1.4 30     | -                | -                |
| HS    | 0.14             | 675              | 0.18  | 100000           | -          | -                | -                |
| HY    | 0.15             | 400              | 0.04  | 600 300          | -          | -                | -                |
| HYR   | 0.15             | 350              | 0.03  | 600 100          | 1.4 30     | -                | -                |
| HS    | 0.14             | 550              | 0.10  | 100000           | -          | -                | -                |

SI-Table 13: Fit parameters used in Figure 8 for most dilute state point per crosslinker series.

### REFERENCES

* maxime.bergman@unifr.ch
† peter.schurtenberger@fem1.lu.se

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