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

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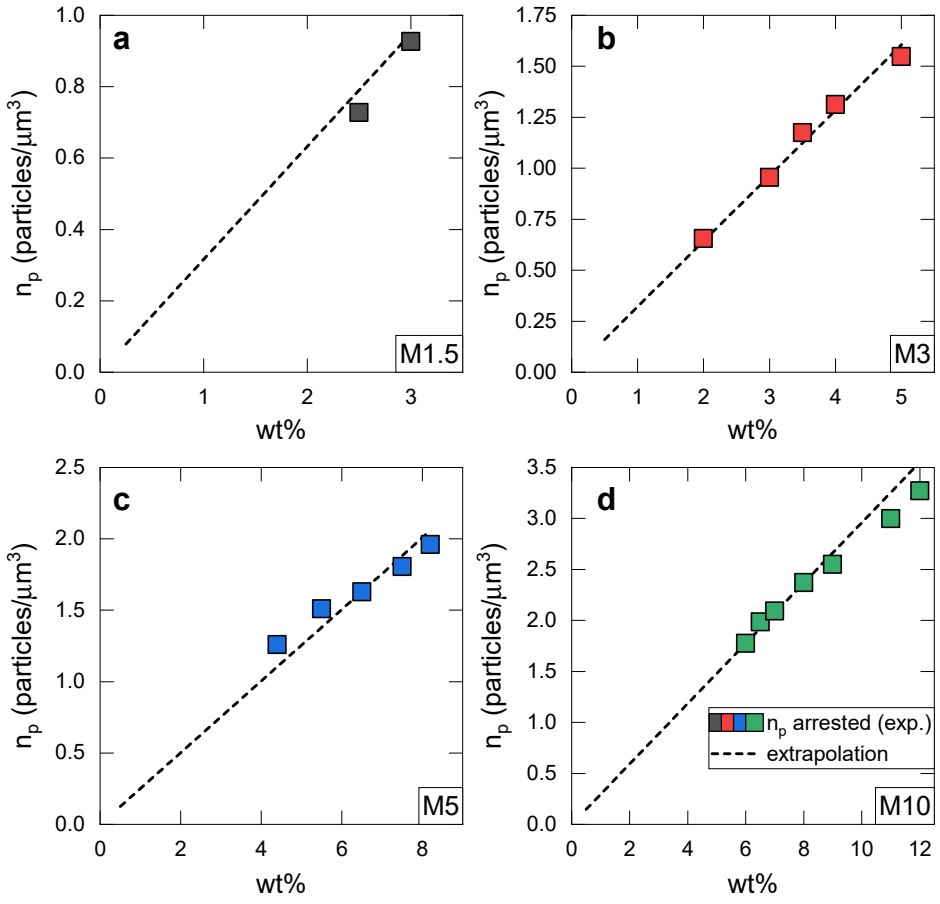
EXPERIMENTAL PARAMETERS

M1.5 (1.5 mol%)			M3 (3 mol%)			M5 (5 mol%)			M10 (mol%)		
liquid state points											
wt%	n_p (μm^{-3})	ϕ_{RH}	wt%	n_p (μm^{-3})	ϕ_{RH}	wt%	n_p (μm^{-3})	ϕ_{RH}	wt%	n_p (μm^{-3})	ϕ_{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
									5.5	1.56	0.74
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 ϕ_{RH} is calculated using number density and hydrodynamic radius R_{H} under deionized conditions.

EXPERIMENTAL NUMBER DENSITIES

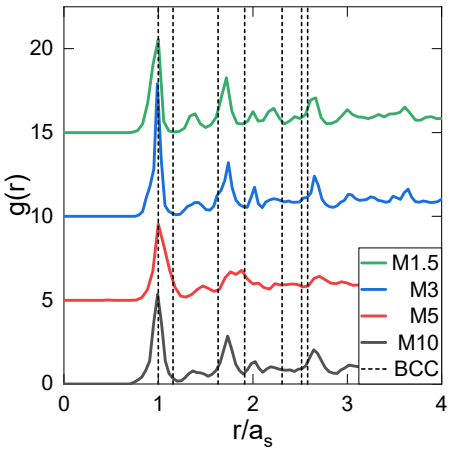
In SI-Figure 1 the experimental number densities n_p are shown for arrested samples (symbols) as well as the linear extrapolation to zero concentration (dashed lines). We note again that the microgels with crosslinker content 1.5 mol%, 3 mol%, 5 mol% and 10 mol% are indicated with the names M1.5, M3,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

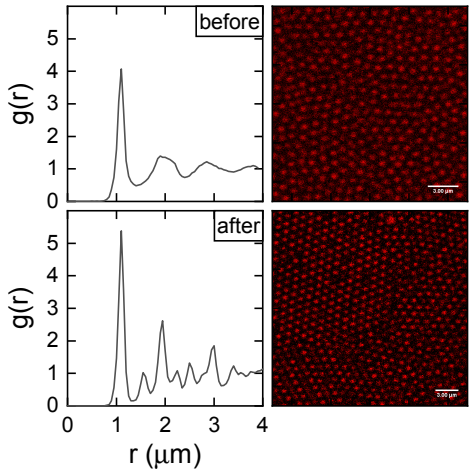
In SI-Figure 2 four typical crystal $g(r)$s are shown (solid lines) for each crosslinker density (data also shown in Figure 4 in main text). We compare the peak positions to the predicted peak positions for a BCC crystal structure (dashed lines) [1]. The discrepancy between prediction and experiment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

ANNEALING OF M1.5

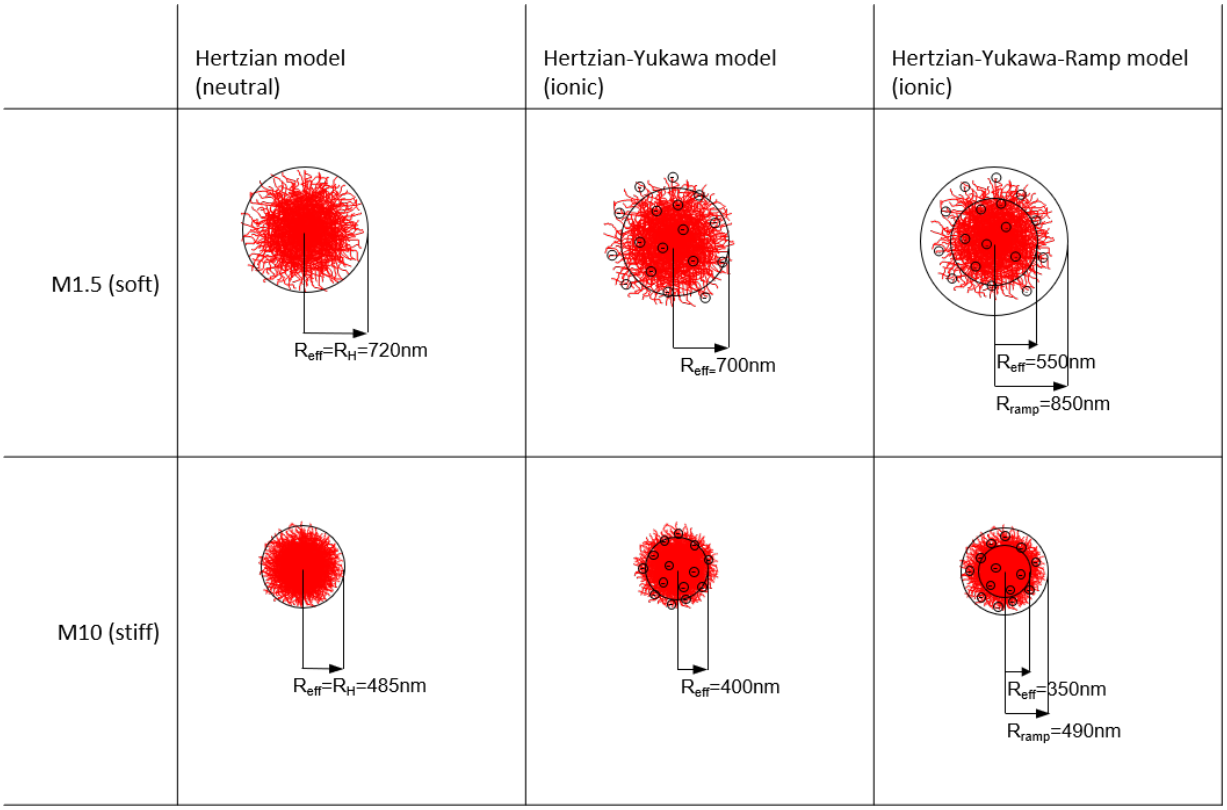
In SI-Figure 3 we show the effect of temperature annealing on the structural order of the M1.5 sample at 3wt%. The upper row shows the $g(r)$ and typical image before annealing, i.e. immediately after preparation of the confocal microscopy sample. The bottom row indicates the crystalline order achieved 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.**

ILLUSTRATION OF R_{eff} FOR SOFT AND STIFF MICROGELS FOR EACH MODEL

SI-Figure 4 gives an example of the best-scoring R_{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 $R_{\mathrm{eff}} = R_{\mathrm{H}}$. For ionic microgels under deionised conditions, R_{eff} with highest χ^2-value is generally smaller than R_{H}.



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 $R_{\mathrm{eff}} = R_{\mathrm{H}}$, the HY model and the HYR model. Sizes are not drawn to scale.

PARAMETER CHOICE AND FITTING HERTZIAN + YUKAWA (HY) MODEL

In the Hertzian + Yukawa model, key parameters are the Debye screening length κ, the Hertzian interaction strength ϵ_{H}, the effective charge Z_{eff}, the effective volume fraction ϕ_{eff}, and the effective interaction radius R_{eff}.

The Debye screening length is set to $\kappa = 5.3\ \mu\mathrm{m}^{-1}$, 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 ϵ_{H} depends on crosslinker content. Because the electrostatic interactions dominate in the liquid regime, however, an estimate for ϵ_{H} suffices here. Published experimental work on 5 mol% crosslinked PNIPAM microgels suggests $\epsilon_{\mathrm{H}} \sim 500\ k_{\mathrm{B}}T$ [4–6]. In a recent simulation study $\epsilon_{\mathrm{H}} \simeq 200, 350, 600\ k_{\mathrm{B}}T$ 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 $\epsilon_{\mathrm{H}} = 200, 350, 500$, and $750\ k_{\mathrm{B}}T$ for M1.5, M3, M5 and M10, respectively.

This leaves Z_{eff}, R_{eff} and ϕ_{eff} as free parameters for each state point. Per crosslinker series, we consider $R_{\mathrm{eff}} = [R_{\mathrm{core}}, R_{\mathrm{H}}]$, 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. ϕ_{eff} follows from R_{eff} and n_p: $\phi_{\mathrm{eff}} = \frac{4}{3\pi} n_p R_{\mathrm{eff}}^3$. Z_{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_{eff}, the best-scoring SSE is kept per state point — this selects the fit parameter Z_{eff}. The SSEs are then summed per R_{eff} and the best-scoring SSE is kept per crosslinker series. We thus keep the effective interaction radius R_{eff} constant allowing Z_{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
ϵ_{H} ($k_{\mathrm{B}}T$)	200	350	500	750
$[R_{\mathrm{core}}, R_{\mathrm{H}}]$ (nm)	[450,750]	[400,700]	[350,600]	[350,500]
$R_{\mathrm{eff}}^{\text{best SSE}}$ (nm)	700	550	550	400
Z_{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	10 000	1000	1.90
0.5	0.15	723	0.24	10 000	400	0.57
0.75	0.23	723	0.36	10 000	200	4.62
1.0	0.30	723	0.48	10 000	0	22.58

SI-Table 4: Fit parameters for the HY model test on the first four state points of M1.5 with $\epsilon_{\text{H}} = 10^4\ k_BT$ and $R_{\text{eff}} = R_{\text{H}}$ (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 κ, the Hertzian interaction strength ϵ_{H}, the effective charge Z_{eff}, the effective volume fraction ϕ_{eff}, the effective interaction radius R_{eff}, the ramp strength ϵ_{ramp} and relative ramp radius R_{ramp}.

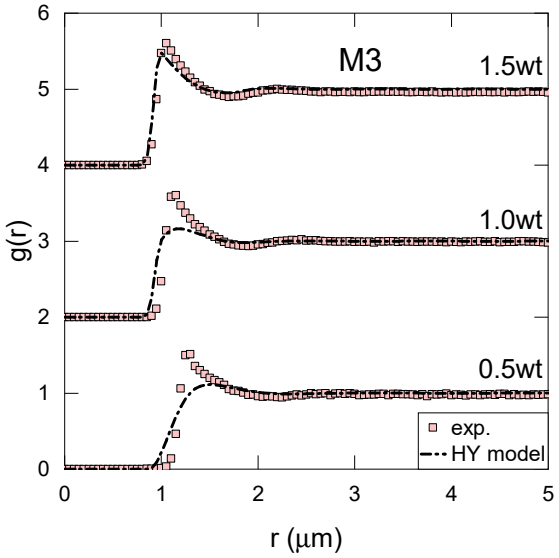
κ, ϵ_{H}, Z_{eff}, ϕ_{eff} and R_{eff} are used as defined for the HY model. Ramp strength ϵ_{ramp} indicates the interaction strength at $R_{\mathrm{eff}} = 0$ and is considered between 0 – 50 $k_{\mathrm{B}}T$. Relative ramp radius R_{ramp} is considered between R_{eff} – $2R_{\mathrm{eff}}$. SI-Table 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_{eff}, the best-scoring fit per statepoint is kept, thus setting Z_{eff}. SSEs are summed per R_{eff} to select the highest-scoring R_{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.

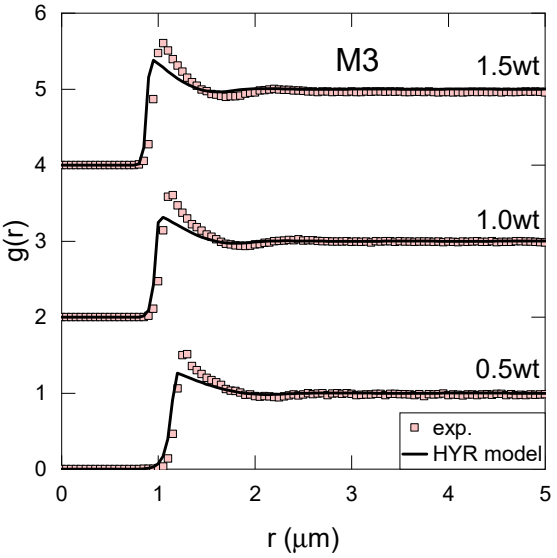
Fit parameter	M1.5	M3	M5	M10
ϵ_{H} ($k_{\mathrm{B}}T$)	200	350	500	750
$[R_{\mathrm{core}}, R_{\mathrm{H}}]$ (nm)	[450,750]	[400,700]	[350,600]	[350,500]
$R_{\mathrm{eff}}^{\mathrm{best\ SSE}}$ (nm)	550	450	400	350
Z_{eff}	100-1000			
ϵ_{ramp} ($k_{\mathrm{B}}T$)	0-50			
R_{ramp} (R_{eff})	1-2			

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.



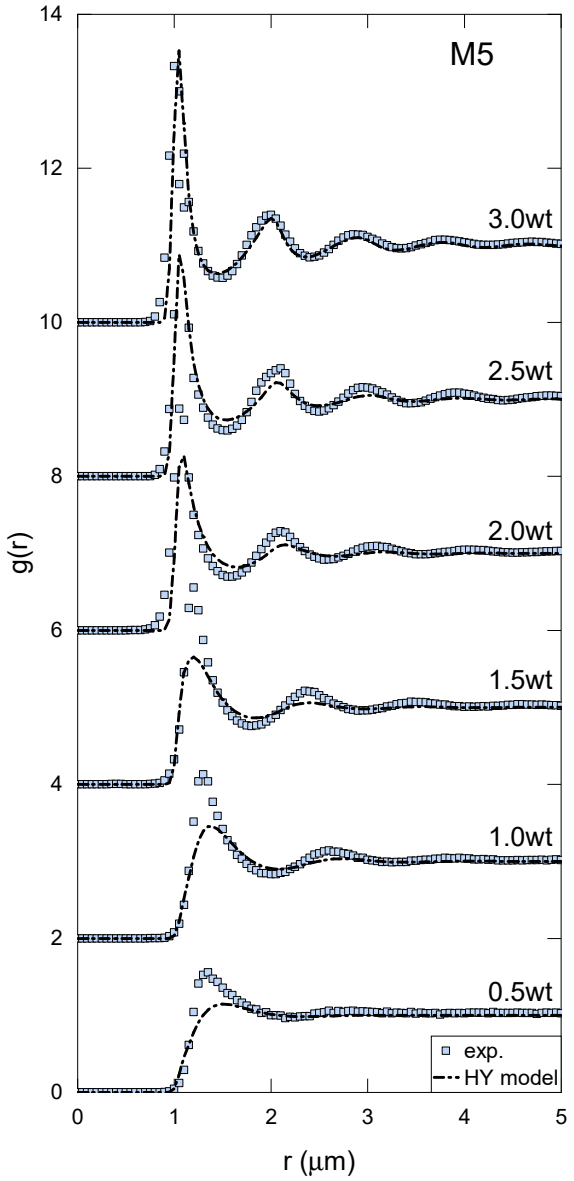
SI-Fig. 6: Pair correlation functions for liquid state points crosslinker series M3 (symbols) and fits with HYR model (solid line). Corresponding fit parameters are given in table below.

wt	n_p	R_{eff}	ϕ_{eff}	ϵ_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

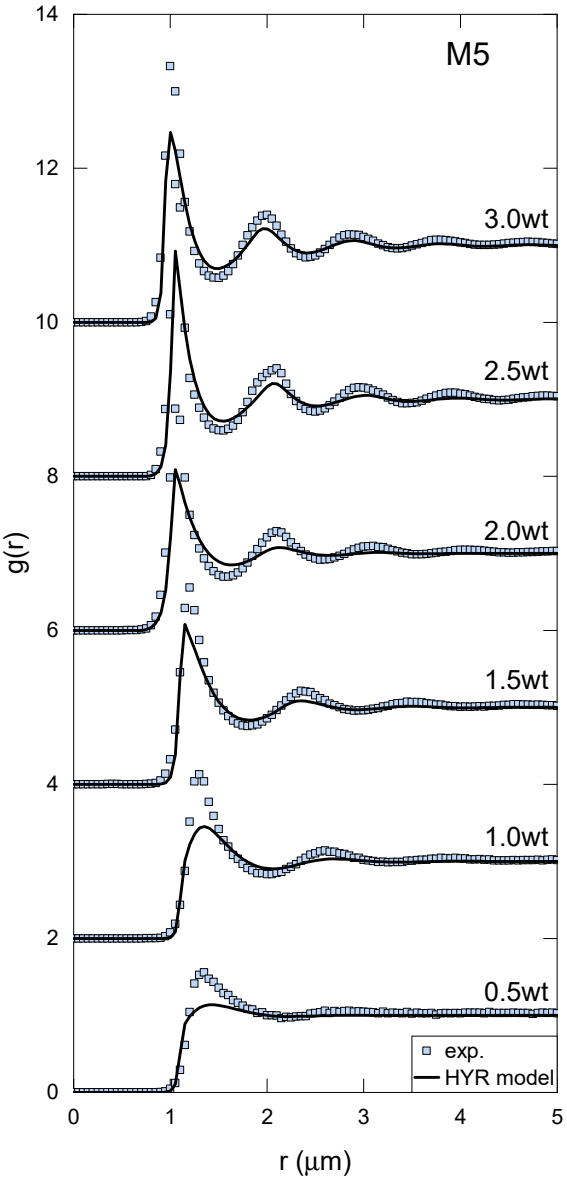
SI-Table 7: Crosslinker series M3. Fit parameters for HY model.

wt%	n_p	R_{eff}	ϕ_{eff}	ϵ_H	Z_{eff}	R_{ramp}	ϵ_{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.



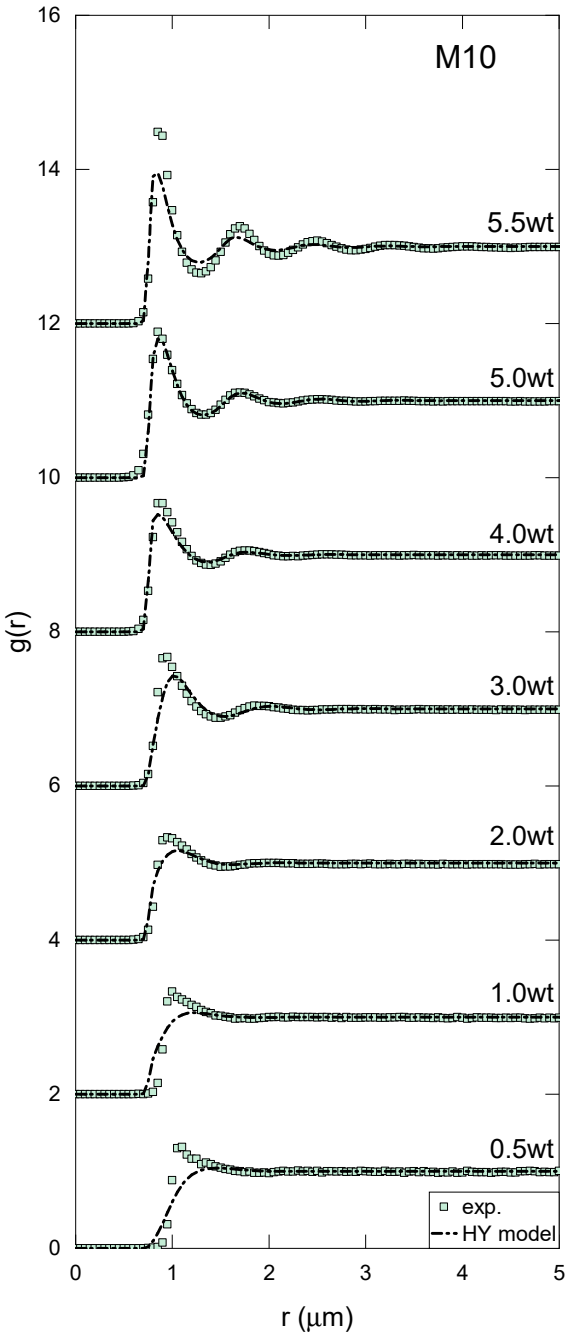
SI-Fig. 8: Pair correlation functions for liquid state points crosslinker series M5 (symbols) and fits with HYR model (solid line). Corresponding fit parameters are given in table below.

wt%	n_p	R_{eff}	ϕ_{eff}	ϵ_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

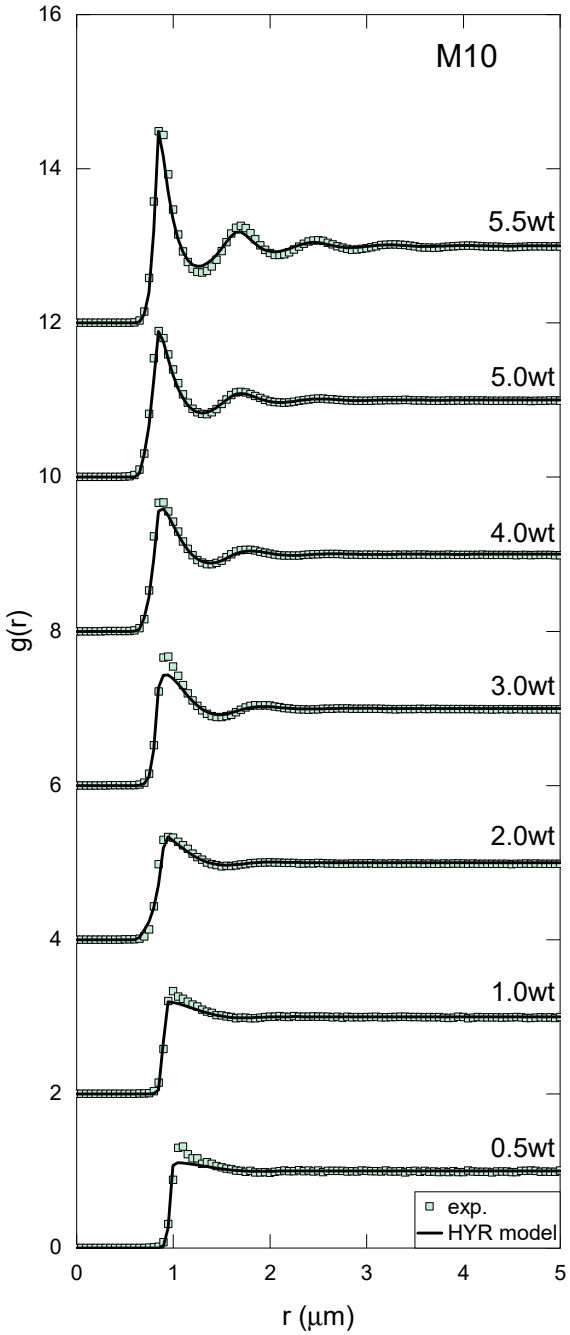
SI-Table 9: Crosslinker series M5. Fit parameters for HY model.

wt%	n_p	R_{eff}	ϕ_{eff}	ϵ_H	Z_{eff}	R_{ramp}	ϵ_{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-Table 10: Crosslinker series M5. Fit parameters for HYR model.



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-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.

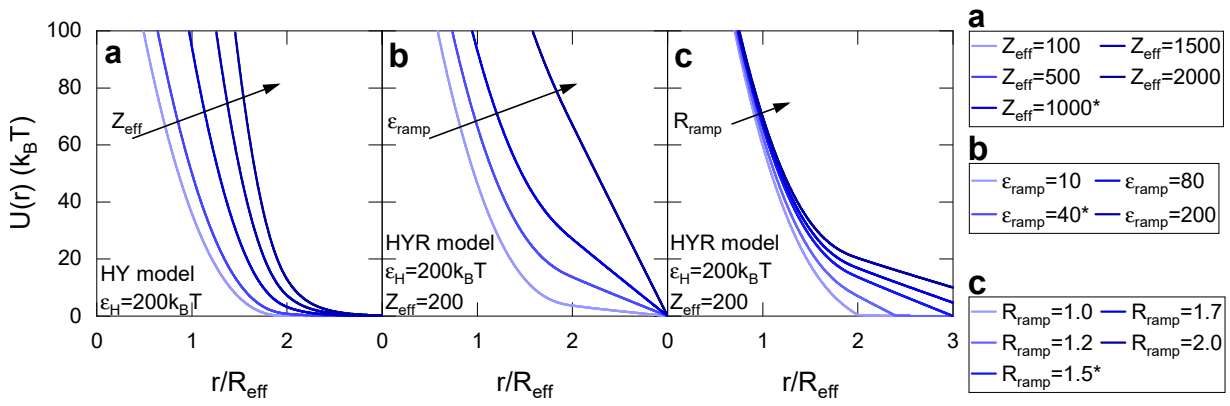
wt%	n_p	R_{eff}	ϕ_{eff}	ϵ_H	Z_{eff}	SSE
0.5	0.14	400	0.038	750	300	0.91
1.0	0.28	400	0.076	750	200	0.86
2.0	0.57	400	0.152	750	200	0.31
3.0	0.85	400	0.227	750	300	0.50
4.0	1.13	400	0.303	750	200	0.22
5.0	1.42	400	0.379	750	300	0.17
5.5	1.56	400	0.417	750	300	1.28

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

wt%	n_p	R_{eff}	ϕ_{eff}	ϵ_H	Z_{eff}	R_{ramp}	ϵ_{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-Table 12: Crosslinker series M10. Fit parameters for HYR model.

POTENTIALS USED FOR FIG. 8



SI-Fig. 11: Potentials used to calculate $g(r)$s shown in Figure 8. With increasing repulsion (a: Z_{eff}, b: ϵ_{ramp}) the potential becomes harder. With increasing R_{ramp} (c) interactions become longer ranged. ϵ_{ramp} is in units of k_BT. R_{ramp} is defined in units of R_{eff}. Starred values indicate best scoring $g(r)$fits.

FIT PARAMETERS USED FOR FIG. 8

Model	n_p (μm^{-3})	R (nm)	ϕ	ϵ_H (kT)	Z_{eff}	R_{ramp}	ϵ_{ramp}
	0.25wt% 1.5 mol% crosslinker						
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	-	-	-
	0.5wt% 3 mol% crosslinker						
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	-	-	-
	0.5wt% 5 mol% crosslinker						
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	-	-	-
	0.5wt% 10 mol% crosslinker						
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.

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