

**Supplementary Information for:**

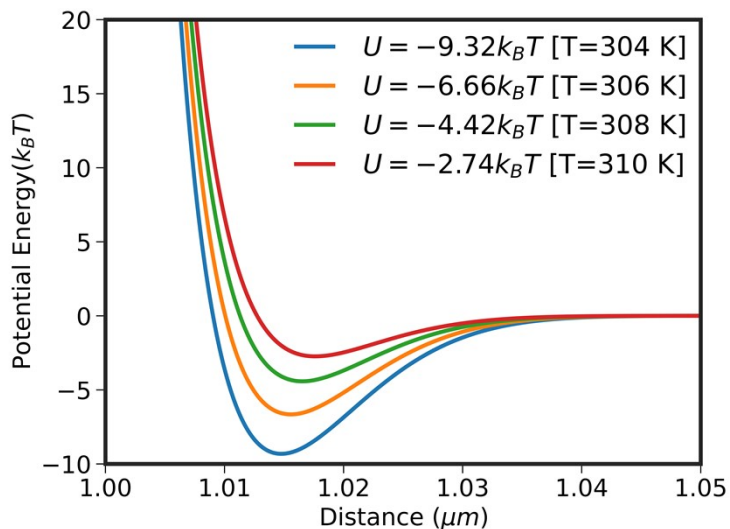
**Modelling the Role of Interaction Heterogeneity in the Gelation of Micron-Scale Colloidal Systems**

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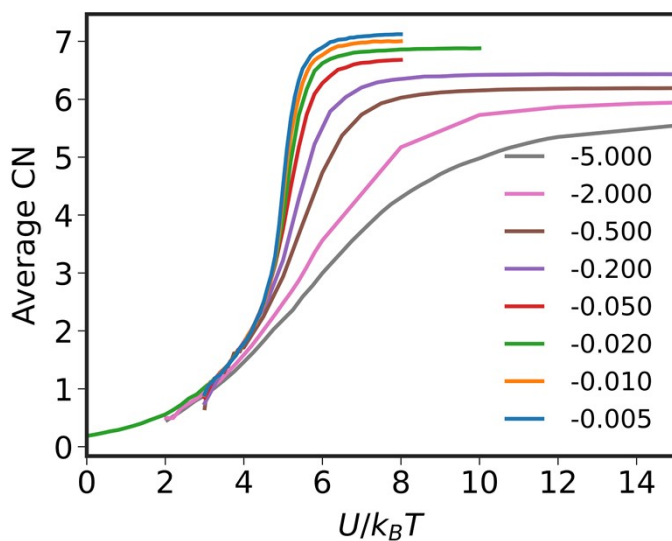
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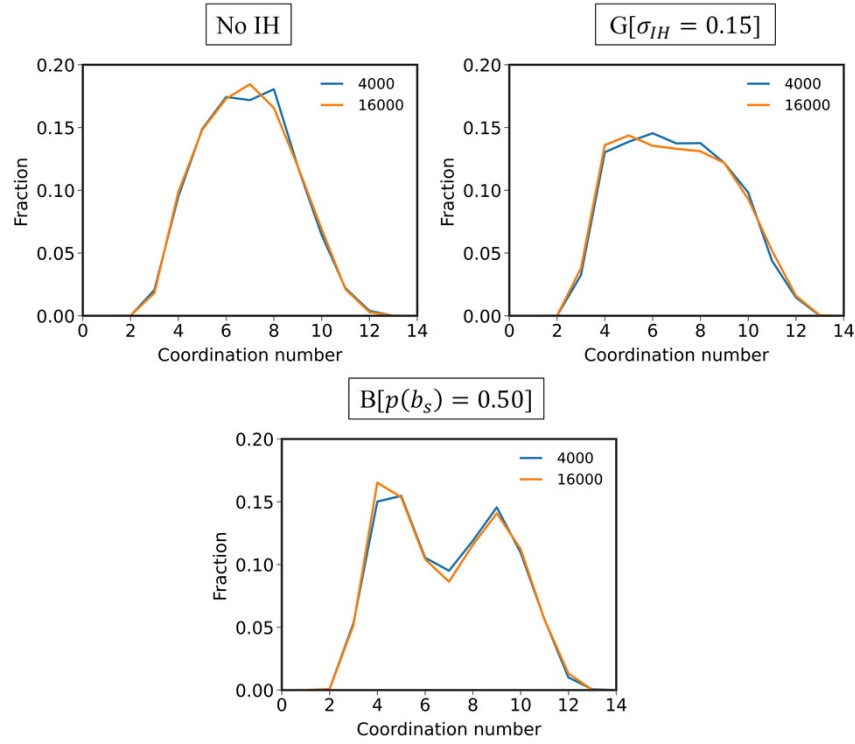
## S1. Supplemental figures



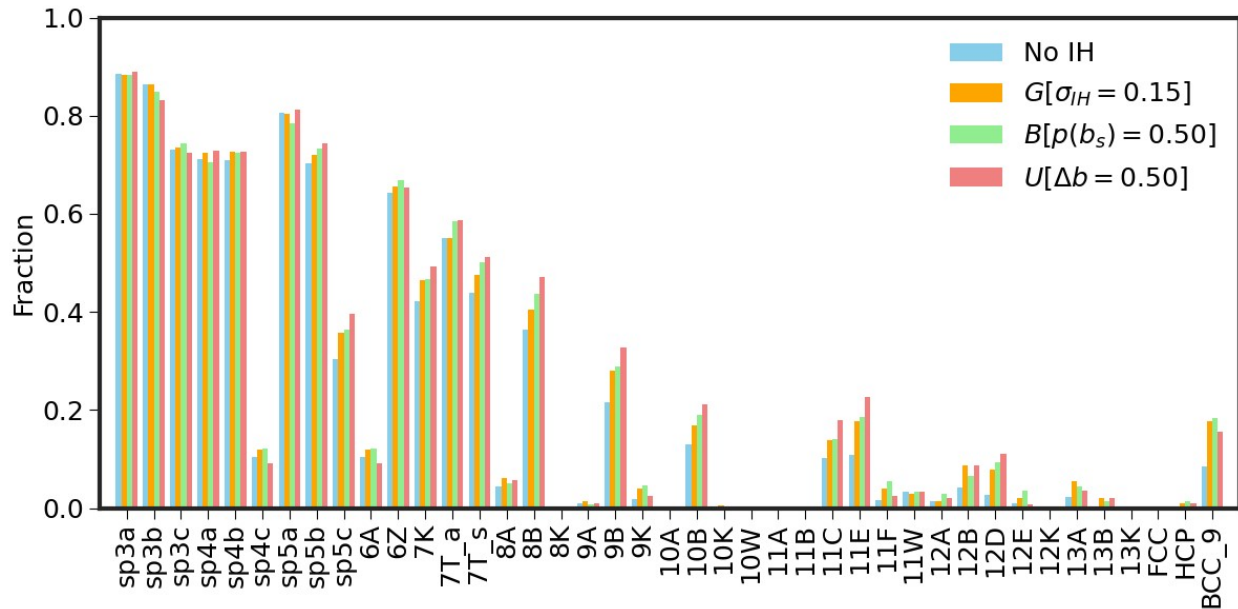
**Fig. S1** Examples of the interparticle potential for DNA-grafted colloids at various interaction strengths. The depth of the potential well increases with decreasing temperature due to the thermodynamics of DNA bridge formation.



**Fig. S2** Average coordination number (CN) as a function of  $U$  at different quench rates (in units of  $k_B T S^{-1}$ ) without IH.



**Fig. S3** CN distributions across different IH types with 4000 and 16000 particles at a quench rate of  $dU/dt = -0.02 k_B T s^{-1}$ .



**Fig. S4** TCC analysis showing fraction of topological clusters with selected IH distributions in an arrested gel formed at a quenching rate  $dU/dt = -0.020 k_B T s^{-1}$  and overall particle volume fraction  $\phi = 0.20$ .

## S2. Principal component analysis (PCA) on Steinhardt order parameters $q_4$ and $q_6$

Steinhardt order parameters were calculated using the Python package *Freud*.<sup>1,2</sup> Briefly, a neighbor list is generated based on a cutoff distance defined as the sum of radii of neighboring particles plus a shell thickness of  $0.04 \mu m$ . The Steinhardt order parameter  $q_l$  is calculated by evaluating spherical harmonics over its neighbors. First, for a particle  $i$ , the quantity  $q_{lm}(i)$  is determined by

$$q_{lm}(i) = \frac{1}{N_b} \sum_{j=1}^{N_b} Y_{lm}(\theta(\vec{r}_{ij}), \phi(\vec{r}_{ij})), \#(S1)$$

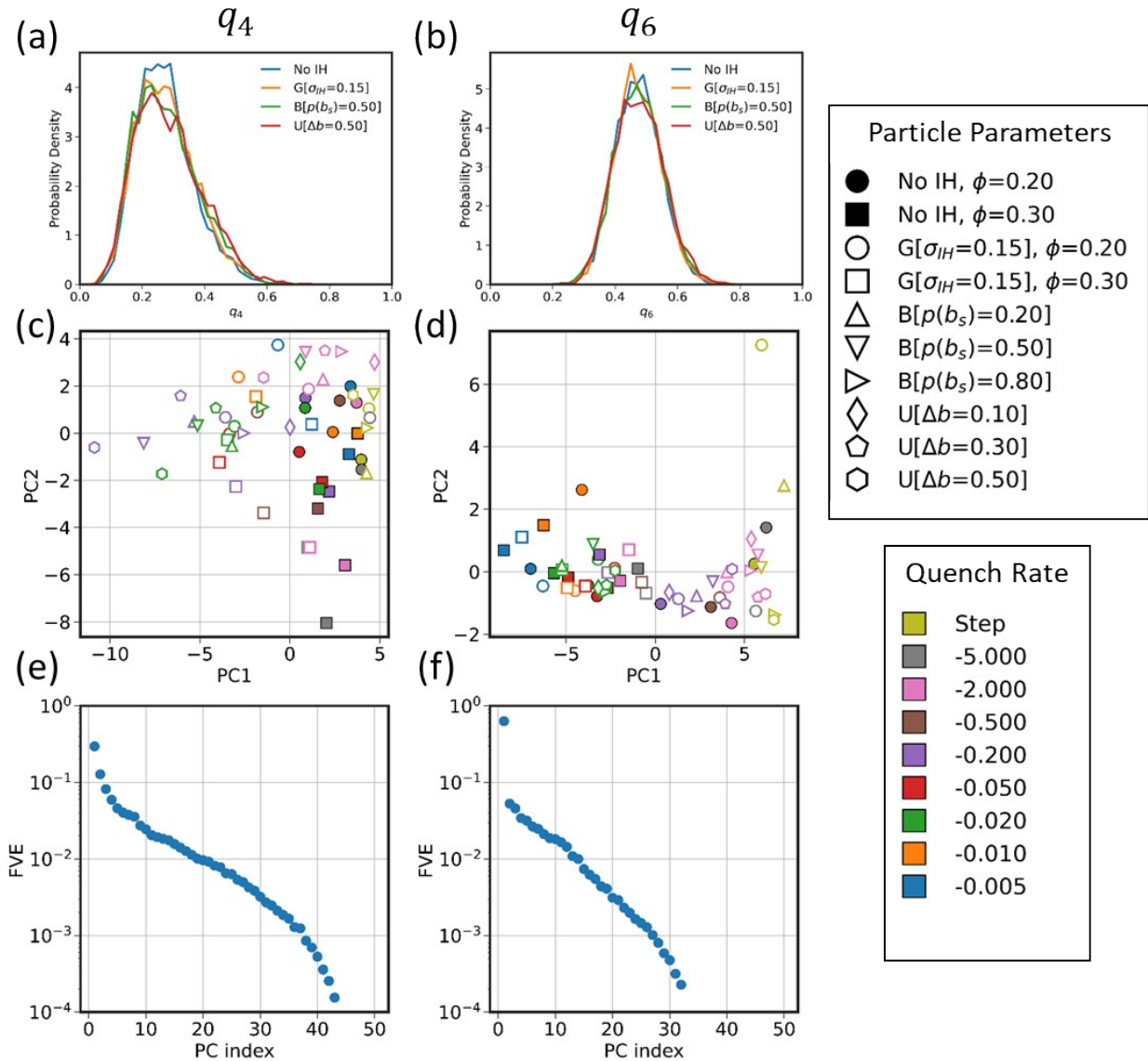
where  $N_b$  is the number of neighbors of particle  $i$ , and  $Y_{lm}$  denotes spherical harmonics. Then  $q_l$  is obtained from

$$q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |q_{lm}(i)|^2}. \#(S2)$$

The resulting values of  $q_l$  are histogrammed with a bin size of 0.02 over the range from 0 to 1.

The Steinhardt parameters  $q_4$  and  $q_6$  are widely used to quantify local structural order in colloidal self-assembly, effectively distinguishing crystalline and disordered arrangements. Specifically,  $q_4$  characterizes local cubic symmetries, such as simple cubic or body-centered cubic structures, while  $q_6$  efficiently identifies close-packed or icosahedral arrangements typically associated with face-centered cubic (FCC) and hexagonal close-packed (HCP) structures.<sup>3,4</sup> The distributions of  $q_4$  and  $q_6$  with different IH types are shown in **Fig. S5 (a-b)**. While the peaks of the  $q_4$  and  $q_6$  distributions appear to be somewhat impacted by IH, no definitive trend is obvious. **Fig. S5 (c-f)** summarize PCA results based on the distributions of Steinhardt order parameters  $q_4$  and  $q_6$ , respectively. PCA based on  $q_4$  distributions fails to distinguish gel structures produced at

different quench rates, while IH appears to shift the data to the left; correspondingly, PC1 and PC2 collectively capture less than 50% of the total explained variance. PCA on the  $q_6$  distributions does effectively capture differences arising from quench rates, predominantly through PC1. However, it still does not differentiate structures with different IH types. The first two principal components of the PCA on  $q_6$  account for approximately 68% of the total variance, predominantly explained by PC1.



**Fig. S5** Evaluation of quench rate and IH based on Steinhardt order parameters. (a, b)  $q_4$  and  $q_6$  distributions with various IH distributions at  $dU/dt = -0.020 k_B T s^{-1}$  and  $\phi = 0.20$ . (c, d) Two-

dimensional projections of the first two principal components obtained from PCA of  $q_4$  and  $q_6$  distributions, respectively. (e, f) Corresponding fraction of variance explained (FVE) by each principal component. Symbols indicate different IH conditions and particle volume fractions ( $\phi$ ), while colors represent varying quench rates.

#### S4. Movie caption

**Movie S1.** Configurations for bidisperse IH with  $b_{s/w} = 1.50$  and  $p(b_s) = 0.50$  at  $dU/dt = -0.020 k_B T s^{-1}$  showing (a) all particles, (b) strong-binding species only, and (c) weak-binding species only. (Red: strong-binding species. Blue: weak-binding species.)

#### REFERENCES

- 1 P. J. Steinhardt, D. R. Nelson and M. Ronchetti, *Phys. Rev. B*, 1983, **28**, 784.
- 2 V. Ramasubramani, B. D. Dice, E. S. Harper, M. P. Spellings, J. A. Anderson and S. C. Glotzer, *Comput. Phys. Commun.*, 2020, **254**, 107275.
- 3 U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey and D. A. Weitz, *Science*, 2001, **292**, 258–262.
- 4 W. Mickel, S. C. Kapfer, G. E. Schröder-Turk and K. Mecke, *J. Chem. Phys.*, 2013, **138**, 044501.