SUPPORTING INFORMATION

Chain stiffness and attachment dependent attraction between polyelectrolyte grafted colloids

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Table S1: Breakdown of the total energy $\Delta\mathcal{U}$ into its individual components for the four colloids types at two charge combinations: (q_c, q_p) = $(1e, -1e)$ and $(2e, -2e)$.

Energy[a]	Free,flexible		Free,stiff		Constrained,flexible		Constrained,stiff	
(kcal/mol)	$(1e,-1e)$	$(2e,-2e)$	$(1e,-1e)$	$(2e,-2e)$	$(1e,-1e)$	$(2e,-2e)$	$(1e,-1e)$	$(2e,-2e)$
ΔE_{cc}	4.3 ± 0.0	17.6 ± 0.1	4.3 ± 0.1	17.4 ± 0.2	4.3 ± 0.1	17.6 ± 0.1	4.3 ± 0.1	17.0 ± 0.2
ΔE_{pp1}	0.2 ± 0.1	0.0 ± 0.5	0.3 ± 0.1	-0.4 ± 0.8	0.2 ± 0.1	0.1 ± 0.5	0.2 ± 1.6	-11.4 ± 3.1
ΔE_{pp2}	5.0 ± 0.0	17.8 ± 0.2	5.3 ± 0.0	19.5 ± 0.5	5.2 ± 0.1	18.1 ± 0.3	6.3 ± 0.4	29.5 ± 1.1
ΔE_{pp}	5.1 ± 0.1	17.8 ± 0.6	5.6 ± 0.1	19.1 ± 1.0	5.3 ± 0.2	18.2 ± 0.6	6.5 ± 1.6	18.1 ± 3.4
ΔE_{cp1}	-0.2 ± 0.1	9.6 ± 0.8	-0.5 ± 0.3	19.4 ± 2.0	-0.1 ± 0.2	12.2 ± 1.0	-0.3 ± 4.2	77.0 ± 5.5
ΔE_{cp2}	-12.1 ± 0.1	-50.1 ± 0.5	-13.7 ± 0.1	-55.4 ± 1.8	-12.8 ± 0.1	-52.2 ± 0.6	-18.4 ± 1.3	-104.7 ± 5.1
ΔE_{cp}	-12.3 ± 0.1	-40.5 ± 1.1	-14.1 ± 0.3	-35.9 ± 2.8	-12.9 ± 0.2	-40.0 ± 1.2	-18.7 ± 5.0	-27.7 ± 7.6
ΔE_s	-0.2 ± 0.4	-0.2 ± 0.6	-0.1 ± 0.4	0.2 ± 1.1	0.2 ± 0.4	-0.1 ± 0.5	0.6 ± 1.5	0.5 ± 3.9
ΔE_b	0.0 ± 0.1	0.1 ± 0.1	0.6 ± 0.3	1.5 ± 0.9	-0.2 ± 0.3	-0.7 ± 0.8	2.2 ± 2.7	-32.1 ± 5.1
$\Delta\mathcal{U}$	-2.6 ± 0.5	-5.6 ± 0.9	-3.0 ± 0.5	1.9 ± 1.1	-2.8 ± 0.7	-5.3 ± 1.2	-3.7 ± 0.6	-23.9 ± 7.5

[a] ΔE_{cc}: electrostatic repulsion between colloid surfaces; $\Delta E_{pp1}, \Delta E_{pp2}, \Delta E_{pp}$: electrostatic repulsion between chains from same and different colloids and their net effect, respectively; $\Delta E_{cp1}, \Delta E_{cp2}, \Delta E_{cp}$: electrostatic attraction between chains and surfaces of same and different colloids and their net effect; respectively; $\Delta E_s, \Delta E_b$: total stretching and bending energy

Why colloids with stiff, constrained chains exhibit a broad attractive regime

Table S1 tabulates the total energy and its different various contributions (see main text) at (q_c, q_p) = $(1e, -2.5e)$ and $(2.5e, -1e)$ for three colloidal systems (constrained, flexible; regular,stiff, and constrained, stiff). The energies for colloids with regular, flexible chains are not shown as they are very similar to those with constrained, flexible chains. These two charge values were picked because they fall in the attractive regime for colloids with stiff, constrained chains and fall outside the attractive regime for the other two colloid types. We observe that the bending energy change ΔE_b is strongly negative for both charge combinations in colloids with constrained, stiff chains, and it is the main contributor to the observed attraction observed (-11.6 and -21.7 kcal/mol for the two charges, respectively). The bending contribution is small for the other two colloids. Hence, colloids with stiff, constrained chains exhibit a broad regime of attraction.

Table S2: Breakdown of the total energy $\Delta\mathcal{U}$ into its individual components for three colloids types at two charge combinations: (q_c, q_p) = $(1e, -2.5e)$ and $(2.5e, -1e)$.

Energy[a]	$(1e, -2.5e)$			$(2.5e, -1e)$		
(kcal/mol)	Constrained,flexible	Regular,Stiff	Constrained,stiff	Constrained,flexible	Regular,Stiff	Constrained,stiff
ΔE_{cc}	4.3 ± 0.1	4.4 ± 0.5	4.3 ± 0.1	27.3 ± 0.1	27.0 ± 0.3	26.1 ± 0.2
ΔE_{pp1}	1.0 ± 0.2	0.9 ± 0.5	-3.0 ± 1.6	-0.2 ± 0.1	0.0 ± 0.3	-2.0 ± 1.3
ΔE_{pp2}	17.7 ± 0.2	16.6 ± 0.3	26.5 ± 0.4	7.2 ± 0.1	9.7 ± 0.2	10.8 ± 0.4
ΔE_{pp}	18.7 ± 0.4	17.5 ± 0.8	23.4 ± 2.0	7.0 ± 0.2	9.7 ± 0.5	8.8 ± 1.7
ΔE_{cp1}	3.9 ± 0.9	7.0 ± 1.5	14.3 ± 4.2	6.2 ± 0.6	14.6 ± 1.5	32.3 ± 4.5
ΔE_{cp2}	-27.1 ± 1.1	-26.4 ± 0.3	-51.6 ± 1.3	-38.0 ± 0.3	-47.7 ± 0.7	-67.2 ± 1.4
ΔE_{cp}	-23.3 ± 2.0	-19.4 ± 1.8	-37.3 ± 5.5	-31.8 ± 0.9	-33.2 ± 2.2	-35.0 ± 5.9
ΔE_s	0.3 ± 0.8	-0.4 ± 0.9	3.1 ± 1.5	0.2 ± 0.4	0.0 ± 0.8	3.9 ± 1.7
ΔE_b	0.2 ± 1.5	0.2 ± 0.7	-11.6 ± 2.7	-0.6 ± 0.5	2.1 ± 0.9	-21.7 ± 3.0
$\Delta\mathcal{U}$	0.2 ± 1.9	2.4 ± 1.6	-16.5 ± 2.3	2.2 ± 0.7	6.0 ± 1.6	-16.6 ± 2.9

[a] Energy components same as in Table 2

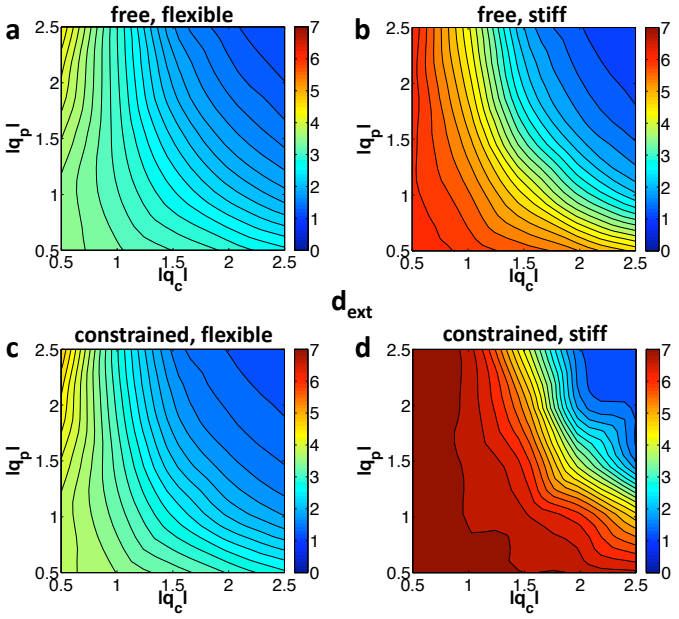

Fig. S1: Chain extension (d_{ext}) as a function of surface and polyelectrolyte charge in isolated colloids with (a) free, flexible (b) free, stiff; (c) constrained, flexible; and (d) constrained, stiff chains.

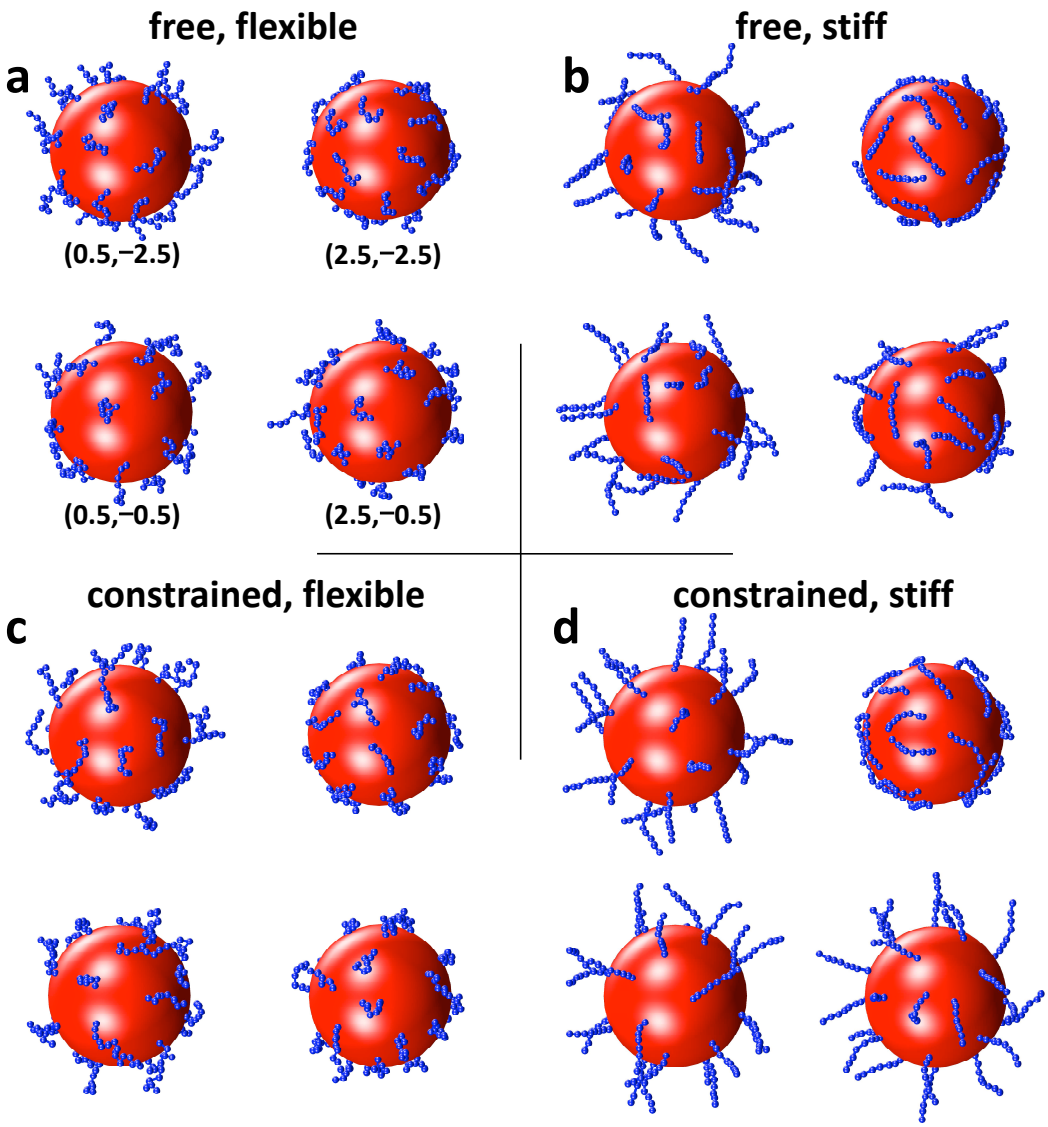

Fig. S2: Representative snapshots of isolated colloids with (a) free, flexible; (b) free, stiff; (c) constrained, flexible; and (d) constrained, stiff chains highlighting chain configurations and their transitions from extended to collapsed states. For each colloid type, four snapshots at (q_c, q_p) = $(0.5e, -0.5e)$, $(0.5e, -2.5e)$, $(2.5e, -0.5e)$, and $(2.5e, -2.5e)$. The surface charges have not been shown for clarity.

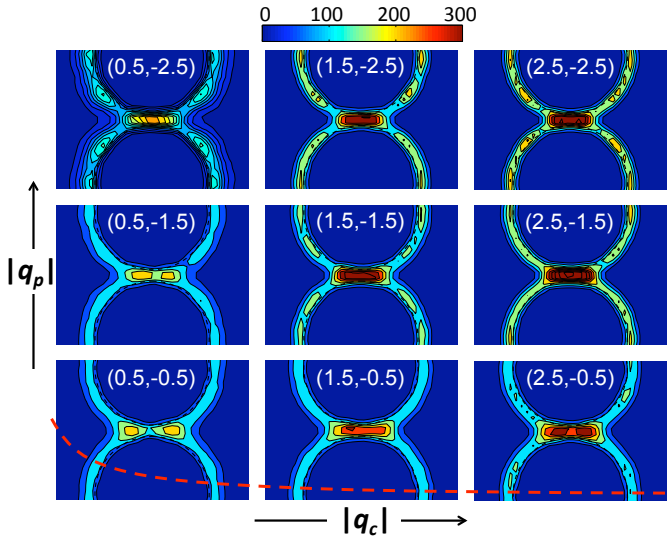

Fig. S3: Polyelectrolyte chain density for colloids with free, flexible chains at $d = 22$ nm. The plots are shown for nine different combinations of surface and polyelectrolyte charges (q_c, q_p). The red dashed line corresponds roughly to the transition between collapsed and extended states of the chains. The color bar is set to an arbitrary scale.

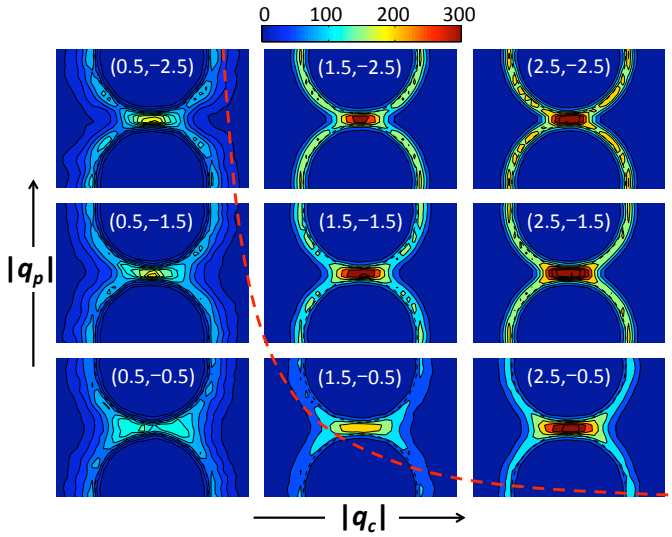

Fig. S4: Same as Fig. S3 except that the results are for colloids with free, stiff chains.

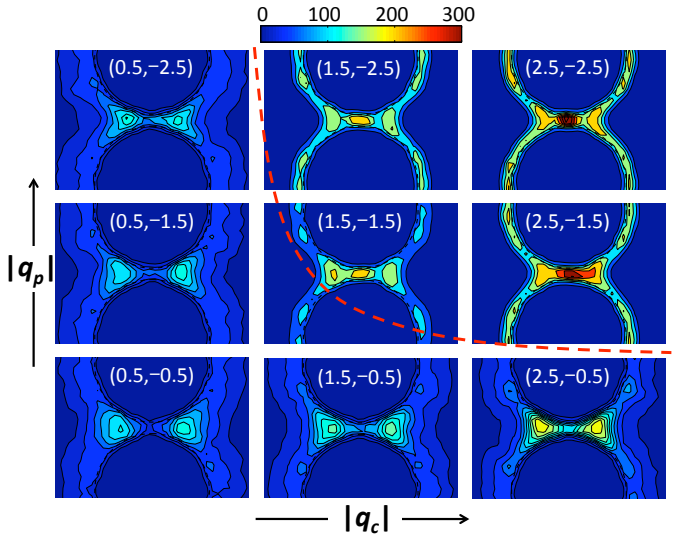

Fig. S5: Same as Fig. S3 except that the results are for colloids with constrained, stiff chains.

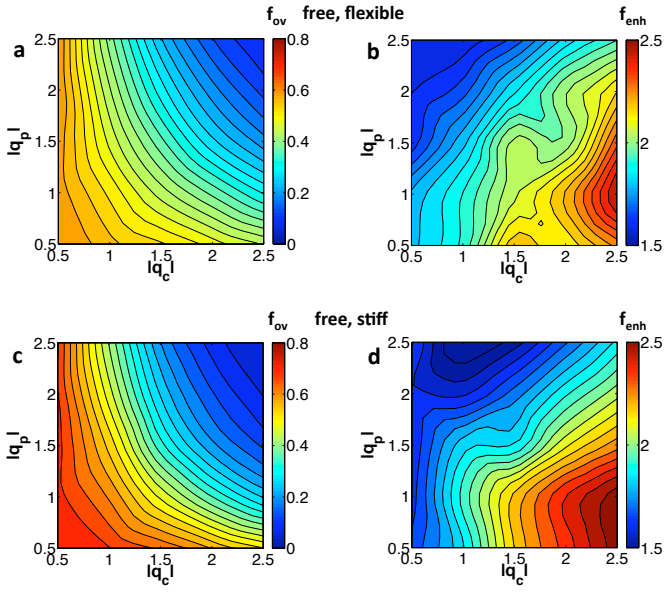

Fig. S6: Fraction of chains overlapping (f_{ov}) and enhancement in chain density within the gap (f_{enh}) when the colloids are brought from infinity to a distance $d = 22$ nm for colloids with free, flexible and free, stiff chains.