Supplementary Information - Exploring Guest Molecule Uptake in pH-Responsive Polyelectrolyte Microgels via Monte Carlo Simulations

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I. NETWORK GENERATION

To generate the network, tetra-functional crosslinks were placed on the lattice points of a cropped cubic-diamond lattice. The cut-off radius of the cropped cubic-diamond lattice was 71.0σ ($\sigma = 2.0$ Å). Starting from each crosslink, $N_{\mathrm{seg}} = 9$ monomers in the distance of 2.5σ to the next monomer were placed in four different directions (unless monomers did not exist in this position yet) and building chains. In total, $N_{\mathrm{chain}} = 184$ chains were placed. The networks consisted of $N_{\mathrm{cl}} = 71$ crosslinks and $N_{\mathrm{mon}} = 1656$ titratable beads with radius 1.0 σ. The network was placed in the center of the simulation box.

II. SIMULATION DETAILS

This section contains different tables with the simulation parameters.

TABLE I. Simulation parameters of the reference system

Parameter	Symbol	value
segments per chain	N_{seg}	9
number of chains	N_{chain}	184
crosslinks	N_{cl}	71
number of acidic monomers	N_{acid}	1656
number of counterions network	N_{acid}	1656
number of guest	N_{guest}	125
number of counterions guest	N_{guest}	1250
number of positive salt ions	$N_{\mathrm{s,+}}$	0
number of negative salt ions	$N_{\mathrm{s,-}}$	0
charge crosslink	z_{cl}	0
charge network monomer	z_{a}	-1/0
charge guest bead	z_{guest}	+10
charge counterion network	$z_{\mathrm{c+}}$	+1/0
charge counterion guest	$z_{\mathrm{c-}}$	-1/0
pK network	pK	5.0
radius of network beads	R	1.0 σ
radius of counterions	R	1.0 σ
radius of guest beads	R	5.0 σ
box length	L	750 σ
force constants of bonds	k	3.89 $\sigma^{-2} k_{\mathrm{B}}T$
zero force distance of bonds	r_{eq}	2.5 σ
Bjerrum length	l_{b}	3.58 σ
temperature	T	298.15 K
pH		3-11 in 0.5 steps

TABLE II. Simulation details of the varied parameters. In the simulations, the box size L, the pK values, and the number of oligomer chains were varied.

simulation row	value
influence charge	$z_{\text{guest}} = +1$, $N_{\text{guest}} = 1250$
	$z_{\text{guest}} = +5$, $N_{\text{guest}} = 250$
	$z_{\text{guest}} = +10$, $N_{\text{guest}} = 125$
	$z_{\text{guest}} = +15$, $N_{\text{guest}} = 83$
	$z_{\text{guest}} = +20$, $N_{\text{guest}} = 62$
influence size	$R_{\text{guest}} = 2.5\sigma$
	$R_{\text{guest}} = 5.0\sigma$
	$R_{\text{guest}} = 10.0\sigma$
influence concentration	$N_{\text{guest}} = 50$
	$N_{\text{guest}} = 83$
	$N_{\text{guest}} = 125$
	$N_{\text{guest}} = 166$
	$N_{\text{guest}} = 199$
influence ionic strength	$z_{\text{s},+} = 0$, $N_{\text{s},+} = 0$, $N_{\text{s},-} = 0$, $I_{\text{s}} = 0.0$mM
	$z_{\text{s},+} = +1$, $N_{\text{s},+} = 2032$, $N_{\text{s},-} = 2032$, $I_{\text{s}} = 0.0$mM
	$z_{\text{s},+} = +1$, $N_{\text{s},+} = 10162$, $N_{\text{s},-} = 10162$, $I_{\text{s}} = 5.0$mM
	$z_{\text{s},+} = +2$, $N_{\text{s},+} = 3387$, $N_{\text{s},-} = 3387$, $I_{\text{s}} = 5.0$mM
	$z_{\text{s},+} = +3$, $N_{\text{s},+} = 1694$, $N_{\text{s},-} = 1694$, $I_{\text{s}} = 5.0$mM

TABLE III. Monte Carlo parameters

Parameter	value
Monte Carlo steps equilibration run	$1.5{\cdot}10^6$
Monte Carlo steps production run	$1.0{\cdot}10^6$
max. displacement crosslink bead	2.5 σ
max. displacement network monomer bead	4.0 σ
max. displacement guest bead	12.5 σ
max. displacement counterions	12.5 σ
probability single particle move crosslink	1.0
probability single particle move network monomer	0.995
probability charge-change network monomer	0.005
probability single particle move guest	1.000
probability single particle move counterion	1.0

TABLE IV. Parameters used in Ewald summation

Parameter	Symbol	value
cut-off real space	r_{cut}	$L/2$
Largest number of k-vectors in one direction	n_{cut}	9
k-vectors	nkvec	238
surface term	lsurf	.true.
damping factor	ualpha	0.0040
potential energy tolerance	uewaldtol	$0.515 \cdot 10^{-6}$

III. INFLUENCE OF SIZE

Figure 1 illustrates the uptake and swelling behavior of the polyelectrolyte network at $\mathrm{pH} - \mathrm{p}K = 2$ for different guest bead sizes. While attractive electrostatic interactions lead to a collapse of the network for small guest beads (left), the excluded volume of large guest beads leads to a swelling of the network (right).

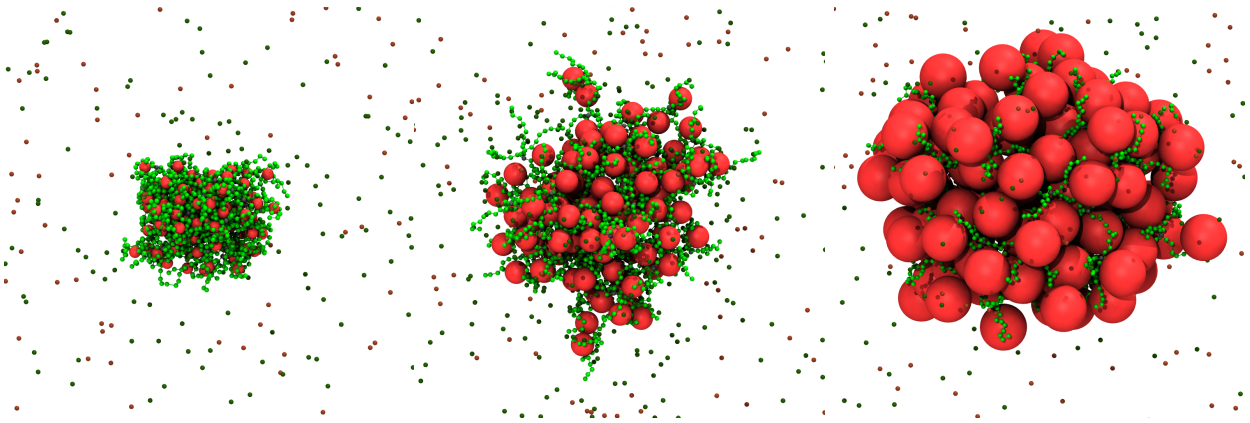

FIG. 1. Snapshots for different network/guest bead-system with $R_{\mathrm{guest}} = 2.5\,\sigma$ (left), $R_{\mathrm{guest}} = 5.0\,\sigma$ (middle), and $R_{\mathrm{guest}} = 10.0\,\sigma$ (right) at $\mathrm{pH} - \mathrm{p}K = 2$

IV. DISTRIBUTION OF COUNTERIONS

If charges within the network cannot compensated by the guest beads, counterions compensate for the charges. Figure 2 shows the concentration profiles of counterions for different charges and concentrations of guest beads at different $\mathrm{pH}-\mathrm{p}K$. Since for low $\mathrm{pH}-\mathrm{p}K$ guest beads compensated the network charges, no counterions were within the network. Only at high $\mathrm{pH}-\mathrm{p}K$, counterions could be found within the network. For guest bead concentrations higher than the acidic monomer concentration, the charges were completely compensated by guest beads, and no counterions were inside the network. For lower concentrations, the counterion concentration within the network shows a rather homogeneous distribution for guest bead charges of $z = +10$.

For guest bead charges of $z = +5$, an increase of counterion concentration close to the center of mass was observed. This increase can be explained by the higher charge density of the network in this regime, which cannot be compensated by the guest beads since their charge density is not sufficiently large. For charges of $z = +20$, the electrostatic repulsion between the guest beads cannot compensated by the network in its core region. Therefore, the counterions compensated the network charges, leading to a high counterion concentration close to the center of mass.

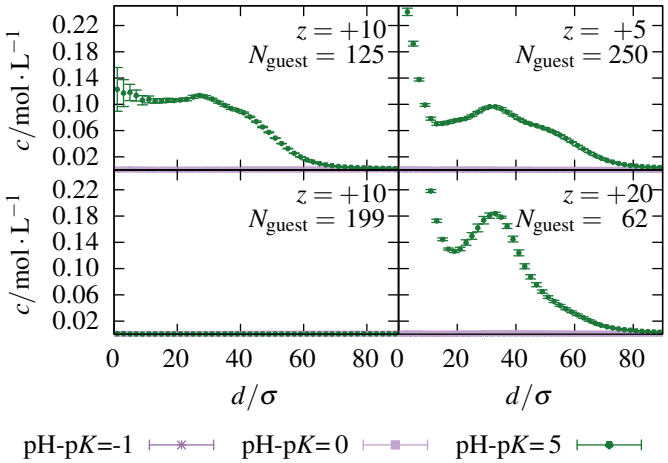

FIG. 2. Concentration of counterions for different numbers of guest beads and valencies as a function of distance to the center of mass of the network.

V. GUEST MOLECULES WITH CHARGE $z_{\mathbf{guest}} = +20$

Figure 3 illustrates the uptake and swelling behavior of the polyelectrolyte network in the presence of guest molecules with charge $z_{\mathrm{guest}} = +20$ at $\mathrm{pH}-\mathrm{p}K = 0$ (left) and $\mathrm{pH}-\mathrm{p}K = +5$ (right). The snapshot for $\mathrm{pH} - \mathrm{p}K = 0$ shows that the guest molecules bind in the location of the dangling chains preferred to the crosslinks, leading to an enhanced ionization in monomers close to these crosslinks while outer chain segments were rather not ionized. The snapshot for $\mathrm{pH} - \mathrm{p}K = 5$ visualizes the swelling of the network due to the repulsive interactions between the highly charged guest molecules.

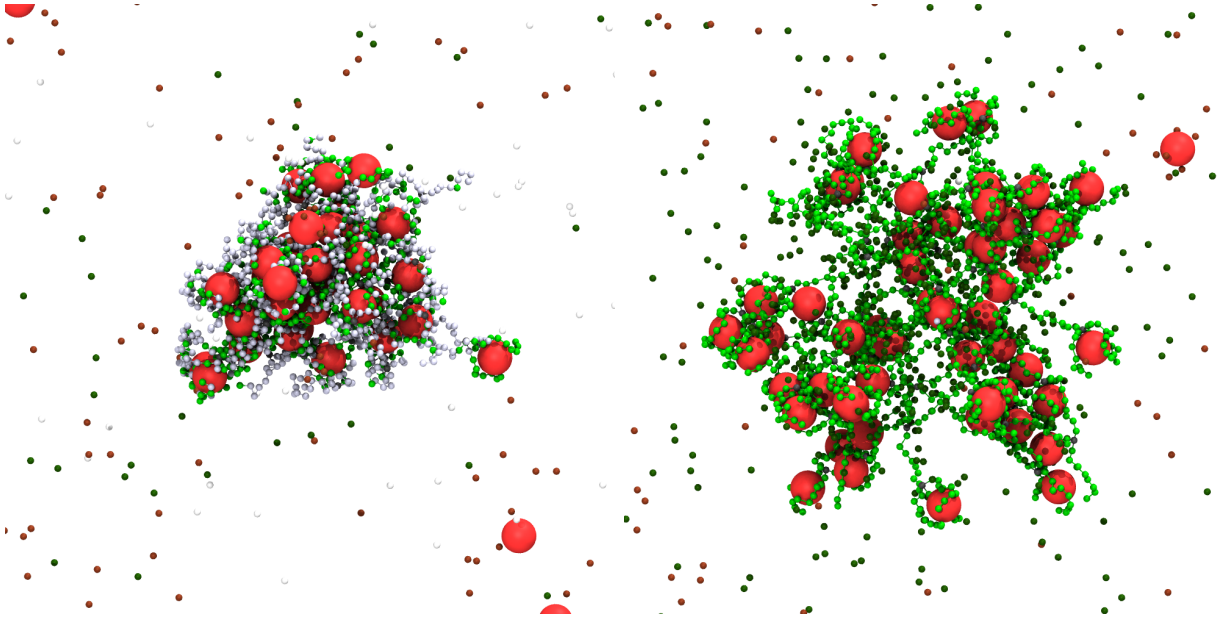

FIG. 3. Snapshots for different network/guest bead-system with $z_{\mathrm{guest}} = +20$. Left:$\mathrm{pH} - \mathrm{p}K = 0$, right: $\mathrm{pH} - \mathrm{p}K = +5$. Green beads represent ionized monomers.