Monte Carlo simulations of weak polyelectrolyte microgels: pH-dependence of conformation and ionization

Electronic Supplementary Information

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In this study, we investigated the effect of pH on single weak acidic polyelectrolyte microgels under salt-free conditions with (i) varying microgel concentration, (ii) varying content of acidic groups and (iii) different crosslinking densities using Monte Carlo simulations under explicit consideration of the protonation/deprotonation reaction. We assessed both, global properties, like the degree of ionization, the degree of swelling and the counterion distribution, as well as local properties like the radial network ionization profile and the ionization along the polymer chains in dependence of pH. We found a pronounced suppression of the pH-dependent ionization of the microgels, as compared to the ideal titration behavior and a shift of the titration curve to higher pH originating in the proximity of acidic groups in the microgel. In contrast to macroscopic gels, counterions can leave the microgel, resulting in an effective charge of the network, which hinders the ionization. A decreasing microgel concentration leads to an increased effective charge of the microgel and a more pronounced shift of the titration curve. The number of acidic groups showed only a weak effect on the ionization behavior of the microgels. For two different microgels with different crosslinking densities, similar scaling of the gel size was observed. A distinct transition from an uncharged and unswollen to a highly charged and expanded polymer network was observed for all investigated microgels. The degree of swelling mainly depends on the degree of ionization. An inhomogeneous distribution of the degree of ionization along the radial profile of the microgel was found.

1 Details on the modeling of the polymer network

The polymer network was modeled by placing tetra-functional cross-linking units on the vertexes of the diamond cubic lattice. The generated lattice positions are subsequently cropped to obtain $N^{\mathrm{cl}} = 71$ tetra-functional cross-linking sites in an approximately spherical arrangement. In total, 100 twofold cross-linked polymer chains are used to interconnect the cross-links, each of them being represented as a string of N^{seg} freely jointed hard spheres. Besides the inner chains, another 84 polymer chains form the surface of the polymer network, each of them being connected on one end to only one cross-link of the network. As one end of these chains dangles freely in space, these chains are referred to as "dangling chains". The described network structure has already been used in various other studies [1–9].

2 Reference System

Here, we present additional data of the reference system. The degree of swelling as a function of the $\mathrm{pH} - \mathrm{p}K_0$ is given in Figure 1. The charge density of the network charges as a function of the distance to the center of mass of the polymer network is shown in Figure 2. The charge density of the counterions as a function of the distance to the center of mass of the polymer network is shown in Figure 3.

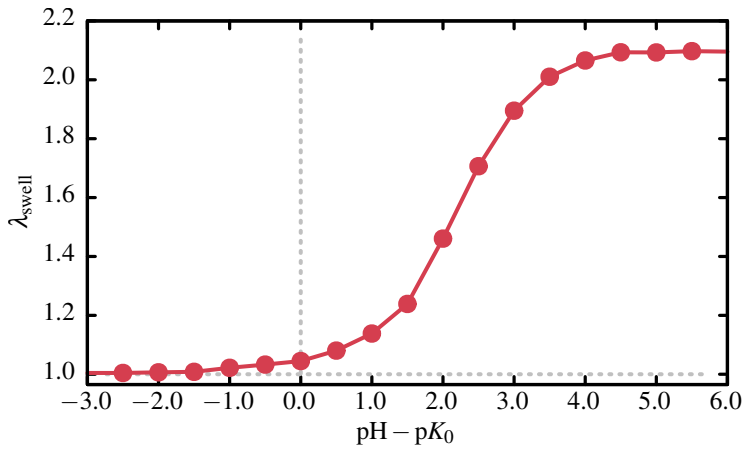

Figure 1 Degree of swelling λ_{swell} of the reference microgel particle (solid line with red circles) as a function of $\mathrm{pH} - \mathrm{p}K_0$. Error bars are smaller than the symbol size.

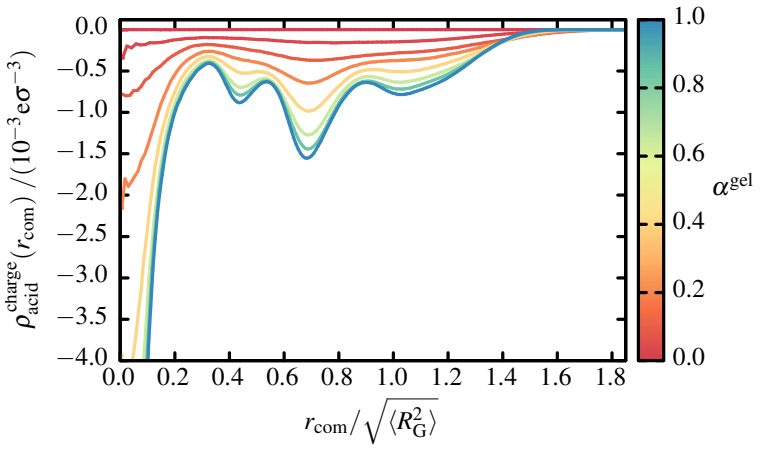

Figure 2 Radial volume charge density of the network charges as a function of the distance r_{com} to the center of mass of the reference polymer network normalized by its radius of gyration $\sqrt{\langle R_{\mathrm{G}}^2\rangle}$. The global degree of ionization α^{gel} associated with the respective curves can be seen from the color bar on the right hand side of the graph.

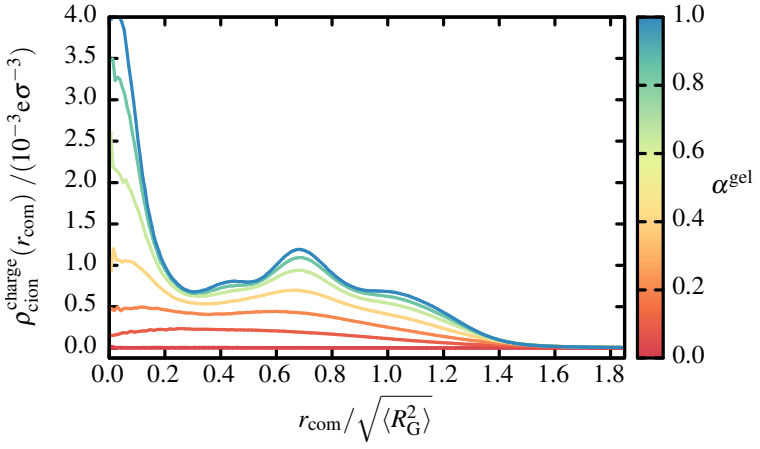

Figure 3 Radial volume charge density of the counterion charges as a function of the distance r_{com} to the center of mass of the reference polymer network normalized by its radius of gyration $\sqrt{\langle R_{\mathrm{G}}^2\rangle}$. The global degree of ionization α^{gel} associated with the respective curves can be seen from the color bar on the right hand side of the graph.

3 Variation of the size of the simulation cell

Here, we present additional data concerning the systems with varying size of the simulation cell. The degree of swelling as a function of the $\mathrm{pH}-\mathrm{p}K_0$ is given in Figure 4.

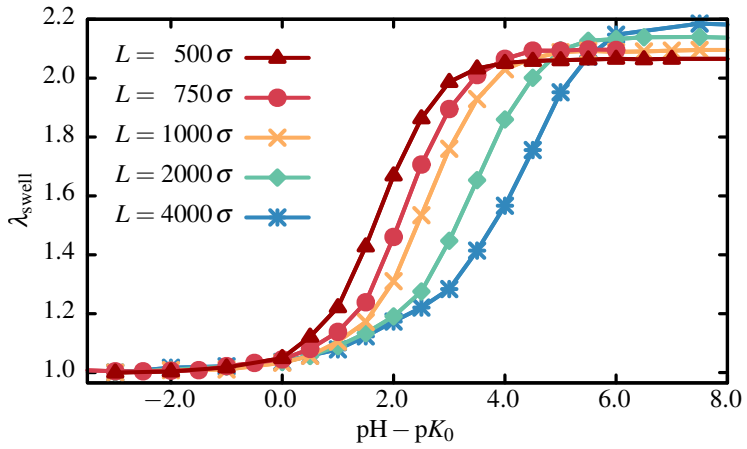

Figure 4 Degree of swelling λ_{swell} of the microgels at various simulation cell lengths L as a function of $\mathrm{pH}-\mathrm{p}K_0$. Error bars are smaller than the symbol size.

4 Variation of the fraction of ionizable segments per chain

Here, we present additional data on the systems with varying fraction of ionizable segments per chain. The degree of swelling is given in Figure 5. The degree of swelling as a function of the $\mathrm{pH}-\mathrm{p}K_0$ is given in Figure 6. In Figure 7 the normalized degree of ionization α^*_{gel} is given as a function of $\mathrm{pH}-\mathrm{p}K_0$.

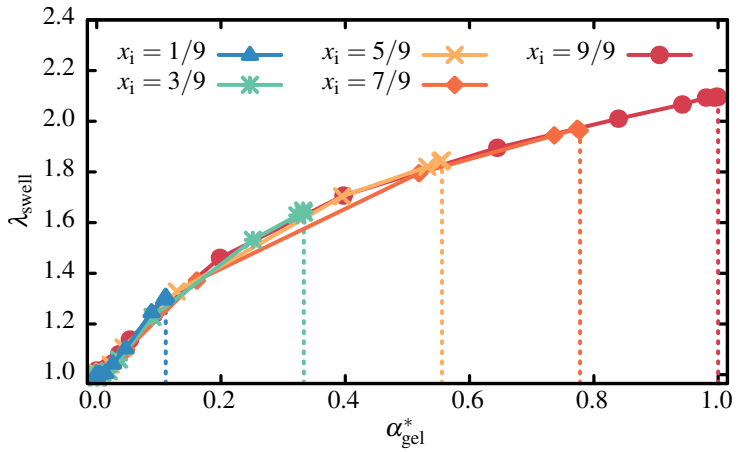

Figure 5 Degree of swelling λ_{swell} of microgel particles with various fractions of ionizable segments per chain x_{i} as a function of their normalized degree of ionization α^*_{gel}. Error bars are smaller than the symbol size.

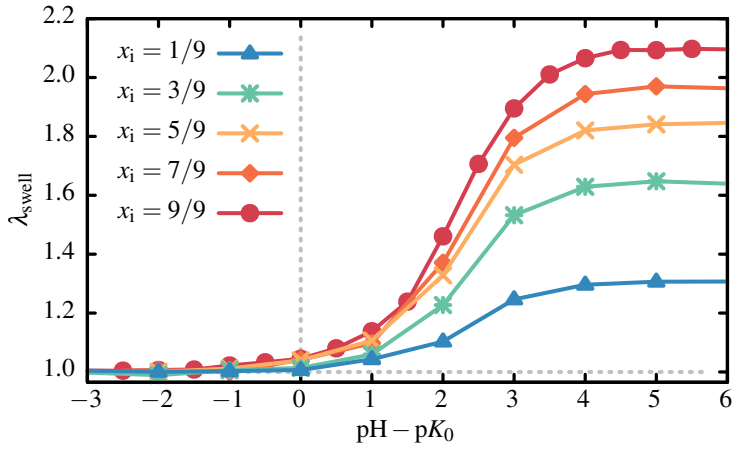

Figure 6 Degree of swelling λ_{swell} of microgel particles with various fractions of ionizable segments per chain x_{i} as a function of $\mathrm{pH} - \mathrm{p}K_0$. Error bars are smaller than the symbol size.

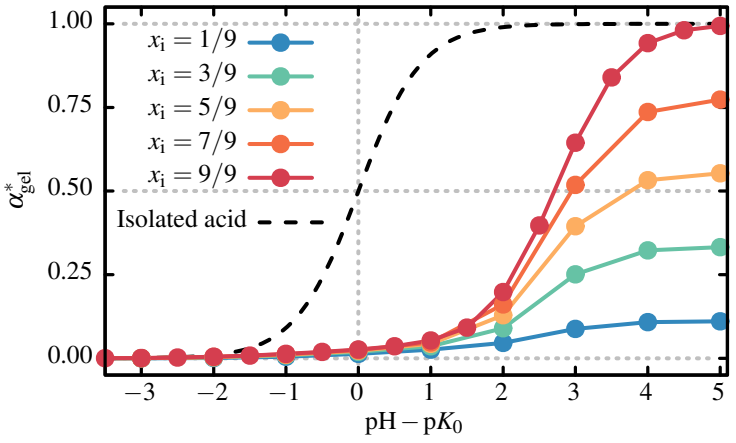

Figure 7 Normalized degree of ionization α^*_{gel} of microgel particles with various fractions of ionizable segments per chain x_{i} as a function of $\mathrm{pH} - \mathrm{p}K_0$. Error bars are smaller than the symbol size. The black dashed line represents the theoretical titration curve of the isolated acid monomer with $\mathrm{p}K_{\mathrm{A}} = \mathrm{p}K_0$ at infinite dilution.

5 Variation of the number of segments per chain

Here, we present additional data on the systems with varying number of segments per strand. The degree of swelling λ_{swell} is given in Figure 8. The degree of swelling as a function of the $\text{pH} - \text{p}K_0$ is given in Figure 9

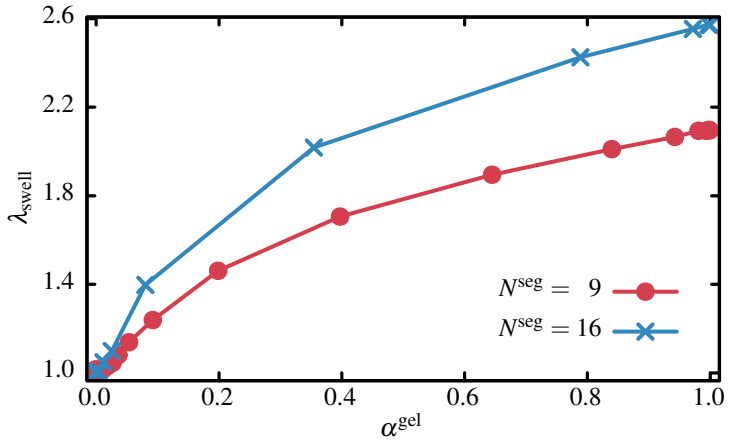

Figure 8 Degree of swelling λ_{swell} of the reference microgel particle (solid line with red circles) and the microgel with a higher number of segments per chain (solid line with blue crosses) as a function of their degree of ionization α^{gel}. Error bars are smaller than the symbol size.

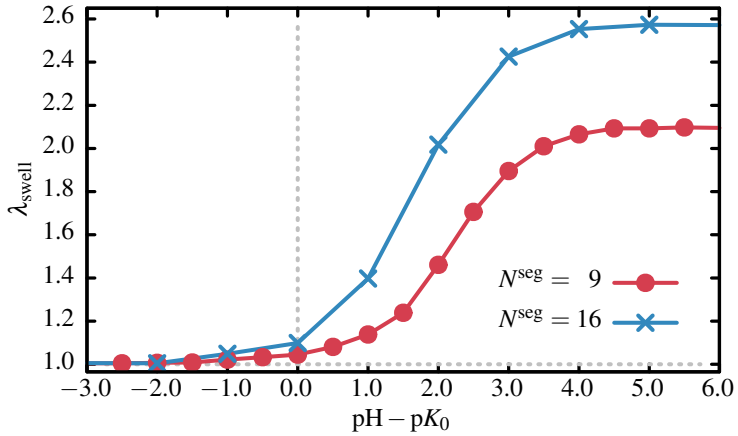

Figure 9 Degree of swelling λ_{swell} of the reference microgel particle (solid line with red circles) and the microgel with a higher number of segments per chain (solid line with blue crosses) as a function of $\text{pH} - \text{p}K_0$. Error bars are smaller than the symbol size.

References

[1] P. K. Jha, J. W. Zwanikken, F. A. Detcheverry, J. J. de Pablo and M. O. de la Cruz, *Soft Matter*, 2011, **7**, 5965–5975.

[2] M. Quesada-Perez and A. Martin-Molina, *Soft Matter*, 2013, **9**, 7086–7094.

[3] H. Kobayashi and R. Winkler, *Polymers*, 2014, **6**, 1602–1617.

[4] M. Quesada-Pérez, S. Ahualli and A. Martín-Molina, *The Journal of Chemical Physics*, 2014, **141**, 124903.

[5] R. Schroeder, A. A. Rudov, L. A. Lyon, W. Richtering, A. Pich and I. I. Potemkin, *Macromolecules*, 2015, **48**, 5914–5927.

[6] H. Kobayashi and R. G. Winkler, *Scientific Reports*, 2016, **6**, 19836.

[7] L. G. Rizzi and Y. Levin, *The Journal of Chemical Physics*, 2016, **144**, 114903.

[8] H. Kobayashi, R. Halver, G. Sutmann and R. Winkler, *Polymers*, 2017, **9**, 15.

[9] I. Adroher-Benítez, A. Martín-Molina, S. Ahualli, M. Quesada-Pérez, G. Odriozola and A. Moncho-Jordá, *Physical Chemistry Chemical Physics*, 2017, **19**, 6838–6848.