SUPPLEMENTARY MATERIAL:
Coarse-grained simulations of polyelectrolyte complexes:
MARTINI models for poly(styrene sulfonate) and
poly(diallyldimethylammonium)

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I. NOTE ON THE PARAMETERIZATION SCHEME

We tested our coarse-grained MARTINI models for PSS and PDADMA and the validity of our coarse-grained (CG) parameterization scheme by comparing the results with atomistic simulations. For this purpose, we simulated single PSS and PDADMA polyelectrolytes in dilute solution with the MARTINI model (parameters given in the main article) and with atomistic OPLS-AA force-field approaches1 that have been published in Refs. 2, 3 and slightly modified in Ref. 4. For a final comparison, we chose the model and the simulations presented in Ref. 4. In addition, we developed our own PSS and PDADMA atomistic models which are based on the generalized AMBER force field (GAFF)5 with the help of the acpype routine6 and the ANTECHAMBER suite7. Using two atomistic force fields (GAFF and OPLS-AA) in combination with different water models was motivated by the reference atomistic OPLS-AA PDADMA and PSS approach4 in presence of SPC/E water8 instead of TIP3P or TIP4P water9 as it was originally recommended1. Hence, for the mapping of the MARTINI CG scheme, we chose four different atomistic force field combinations: i) PDADMA/PSS (OPLS-AA) + SPC/E water (as in Ref. 4), ii) PDADMA/PSS (OPLS-AA) + TIP3P water, iii) PDADMA/PSS (OPLS-AA) + TIP4P water and iv) PDADMA/PSS (GAFF) + TIP3P water. The deviations of the MARTINI coarse-grained models should ideally be in the same range as the deviations between the atomistic models.

II. POLYELECTROLYTES IN DILUTE SOLUTION

In both atomistic and MARTINI simulations, a polyelectrolyte chain with 30 monomers was dissolved in a cubic box of water with periodic boundary conditions in all directions. 30 counterions were added (Cl− for PDADMA and Na+ for PSS) such that the system in total was uncharged. All simulations were performed with GROMACS 4.5.610 and a leap-frog algorithm.

A. MARTINI simulation protocol: single chains in dilute solution

For the MARTINI simulations, the initial cubic box edge lengths in our simulations were 7.15 nm for PSS and 6.95 nm for PDADMA. The simulation parameters were identical to the parameters for the polyelectrolyte complex simulations presented in the main article. After energy minimization, a NVT simulation run of 60 ns was performed followed by a 90 ns equilibration run in the NPT ensemble. For both runs, the time step was chosen to be 1 fs. After equilibration, a production run of 200 ns was performed, again in the NPT ensemble but with a time step of 2 fs. Considering the MARTINI dynamics speedup factor of four, the effective time interval of this simulation was 800 ns.

B. Atomistic simulation protocol: single chains in dilute solution

The OPLS-AA atomistic force field parameters adopted from Refs. 2, 3 were modified and presented as force fields for PSS and PDADMA in Ref. 4. The initial cubic box edge lengths in our simulations were 7.15 nm for PSS and 6.95 nm for PDADMA. After energy minimization, first a 2 ns run in the NVT ensemble was performed followed by a 3 ns run in the NPT ensemble. For both runs, the timestep was chosen to be 1 fs. After equilibration, a production run of 100 ns was performed, again using the NPT ensemble but with a timestep of 2 fs. Long-range electrostatic interactions were treated with a smooth particle mesh Ewald summation method (SPME)11 using a Fourier grid spacing of 0.12 nm, fourth-order interpolation and a cut-off radius of 1.2 nm. Covalent bonds with hydrogen atoms were constrained by the LINCS algorithm12. In the NVT equilibration, temperature was controlled by a velocity rescaling algorithm13 with a characteristic time of τ = 0.5 ps. In the NPT simulations, temperature and pressure were controlled by a Nosé-Hoover thermostat14 with a characteristic time interval of τ = 0.5 ps and a Parrinello-Rahman barostat15 (characteristic time: τ = 4 ps, reference pressure: 1 bar, compressibility: 4.5 · 10−5 bar−1). Frames used for the analysis were saved every 0.2 ps. The above presented parameters were chosen equal or similar.

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to the all-atom simulations of polyelectrolyte complexes that have been already published in Ref. 4.

III. ATOMIC SIMULATION PROTOCOL OF PREVIOUS POLYELECTROLYTE COMPLEX SIMULATIONS ACCORDING TO REF. 15

In accordance to Ref. 4, the atomistic OPLS/AA force field parameters for PSS have been adopted from Ref. 3 and for PDADMA building blocks from Ref. 2. The SPC/E water model was used and the degree of polymerization was 12 for each PDADMA and PSS chain. Slight modifications to the original force fields have been also performed as discussed in more detail in Ref. 4. The simulated system was given by an initial cubic box of side length 40 nm, where 35 PSS and 35 PDADMA chains with NaCl salt and water molecules were inserted. The simulation protocol follows the one that we used for the MARTINI PEC simulations. Cycles of ascendant and descendant temperatures were used for a proper equilibration of the complex. The final production run had a length of 100 ns.

IV. COMPUTING TIME: MARTINI VS. ATOMIC APPROACHES

In order to determine the computational speed up for MARTINI simulations, identical systems, identical simulation times and identical hardware architectures have to be taken into account. Thus, we are not able to compare the computational acceleration factor for the PEC simulations in detail. However, with regard to the simulation of single polyelectrolytes in dilute solution, we estimated a speed up factor of 20 to 30 for MARTINI simulations, identical systems, identical simulation times and identical hardware architectures have to be taken into account. Thus, we are not able to compare the computational acceleration factor for the PEC simulations in detail. However, with regard to the simulation of single polyelectrolytes in dilute solution, we estimated a speed up factor of 20 to 30 for MARTINI simulations compared to atomistic simulations without detailed benchmark tests.

V. MARTINI BEAD TYPES, COUNTERION BINDING BEHAVIOR AND BACKBONE ANGLE OF PDADMA

A. MARTINI bead types for PDADMA and PSS

For PSS, we adopted the backbone structure of the existing MARTINI model for PS, where any further geometrical parameterization except the addition of the sulfonate group was not necessary. For the sulfonate group, we chose the bead type 'Qa' which denotes a charged hydrogen acceptor bead. The corresponding molecular topology of our MARTINI PSS model is described in the main article.

In contrast to PSS, the MARTINI PDADMA model has to be built from scratch. First, we chose the bead type ‘SC1’ for the backbone atoms in accordance to the parameterization approach for cyclohexane. As an initial guess for the dimethylammonium group, we chose the bead type SQ0 which stands for 'small, charged, no hydrogen bonds'.

B. Counterion binding

As a crucial test case, we compared the chloride ion binding strength of the MARTINI model with the atomistic force field results. To estimate the chloride binding strength, the local preferential binding coefficient between the nitrogen atom in the dimethylammonium group of PDADMA (denoted with the index 2) and the chloride ions (denoted as 3) can be calculated according to

\[ \nu_{23}(r) = \rho_3(G_{23}(r) - G_{21}(r)) \]

with the chloride bulk number density \( \rho_3 \) and the local Kirkwood-Buff integral

\[ G_{23}(r) = 4\pi \int_0^r R^2 (g_{23}(R) - 1) dR \]

where \( g_{23}(r) \) is the radial distribution function. As shown in Fig. 1 (top), the bead type SQ0 significantly underestimates the binding behavior when compared to the atomistic force field results. Therefore, we changed the bead type to SQd due to the fact that this bead type shows a stronger affinity for chloride ions. It can be seen in Fig. 1 that the introduction of SQd reproduces the ion binding behavior quite well within the range of deviations already present between the atomistic force fields. Furthermore, it has to be noticed that the MARTINI results for PSS are in good agreement with the atomistic results such that no additional reparameterization was necessary.

C. Radius of gyration

The squared radius of gyration is given by

\[ R_g^2 = \frac{1}{2N^2} \sum_{i,j} (\mathbf{r}_i - \mathbf{r}_j)^2 \]

with the monomer positions \( \mathbf{r}_i \) and \( \mathbf{r}_j \) and the number of monomers \( N \) which can be also equivalently denoted by the degree of polymerization \( dp \). As monomer reference groups in dilute solution, we chose the Qa and SQd beads in the MARTINI models and the sulfur and nitrogen atoms of the atomistic polyelectrolytes. The results for different polymer lengths but for an identical monomer concentration are shown in Fig. 2. It becomes obvious that the PSS MARTINI model for very small chain lengths \( N \leq 25 \) underestimates the atomistic values only slightly. In contrast, the result for PDADMA are in reasonable agreement. For the MARTINI chain lengths studied in the main article \( (N = 30) \), nearly comparable values with the atomistic models for \( R_g \) can be seen.

The
FIG. 1. Preferential binding coefficients between Na$^+$/Cl$^-$ ions and the charged groups in the MARTINI model and the nitrogen, respectively sulfur atoms in the atomistic models for polyelectrolytes in dilute solution (top: PDADMA, bottom: PSS) fits according to the function $R_g = b N^\nu$ for infinite chain behavior give the Flory exponents $\nu = 0.64 \pm 0.02$ for PDADMA and $\nu = 0.88 \pm 0.02$ for PSS. It has to be noticed that the infinite chain behavior can be only reached for $N \to \infty$ which is clearly out of reach for our simulations. Thus, it becomes clear that deviations can be observed which can be mainly attributed to the importance of chemical details and electrostatic interactions at short length scales.

VI. ATOMIC POLYELECTROLYTE COMPLEX SIMULATIONS AND MARTINI FORCE FIELD CHECK

After the matching of the MARTINI bead types for polyelectrolytes in dilute solution, we finally used these models for the simulation of a polyelectrolyte complex with the simulation protocol presented in the main article. The MARTINI results were compared to the atomistic findings presented in Ref. 4. In addition, we also simulated the same system with our own GAFF force field parameter set in combination with the TIP3P water model. The polyelectrolyte complex was composed of 35 PSS and PDADMA chains with a degree of polymerization of 12.

A. Backbone angle distribution

As a prerequisite for a reasonable MARTINI model, we also evaluated the backbone angle distribution for PDADMA in all considered atomistic force fields with different water models. The results in Fig. 3 indicate a favorable backbone angle of $136^\circ$ which was also chosen for the MARTINI PDADMA model. The corresponding backbone angle distribution function for PDADMA in the complex is shown in Fig. 4 and for PSS in Fig. 5. It can be clearly seen that the results of the backbone angle distribution for PDADMA nicely coincide with the
results for the atomistic models. The mean backbone angle for the MARTINI PDADMA model is 136.4° with a standard deviation of 10.3°. In addition, we have found a value of 135.2° with a standard deviation of 8.8° for MARTINI PDADMA chains in dilute solution. It has to be mentioned, that the second peak at 105° in the atomistic models cannot be exactly reproduced due to the limited degrees of freedom in a CG model such that we had to neglect it.

In contrast, the results for MARTINI PSS in Fig. 5 slightly differ to the atomistic models. The reason for this difference can be mainly explained with regard to the original parameterization scheme for PS which remains unchanged for our PSS model to ensure maximum compatibility with existing MARTINI topologies. Finally it has to be mentioned that especially for CG models, the exact fitting of a specific force-field parameter to a well-defined atomistic representation might lead to severe deviations for other parameters (“overfitting”). The redefinition of existing bead types or adding new types would put up a huge barrier for the usage of other existing compounds due to the fact that all interactions have to be reparameterized. This would impair the compatibility between different systems which is a huge advantage of the MARTINI approach. With this in mind and due to a good agreement with the atomistic models in terms of the structural properties shown in section VI, we consider the accuracy of the MARTINI models to be appropriate.

To further verify this conclusion, we have also calculated the angle between three neighbored charged beads (SQd-SQd-SQd for PDADMA and Qa-Qa-Qa for PSS) and compared the results with the values for the atomistic models (N-N-N for PDADMA and S-S-S for PSS). The corresponding results for PDADMA are shown in Fig. 6 and for PSS in Fig. 7. We have found a good agreement for the PDADMA model whereas the results for PSS overestimate the preference of an angle of 38° when compared with the atomistic results. However, this discrepancy does not affect the results for the radius of gyration or the end-to-end distance as more crucial parameters for polymer properties which will be discussed in more detail in the following sections.

B. Potential of mean force between ions and polyelectrolytes in the complex

In order to estimate the ionic binding strength, we have calculated the potential of mean force between the polyelectrolytes and the counterions according to

$$\Delta V_{PMF} = -RT \log \left( \frac{g(r_{1st})}{g(r_0)} \right)$$  (4)
with the bulk value distance $r_0$, the maximum value for the radial distribution function at the position of the first counterion shell $g(r_{1,ct})$, the universal gas constant $R$ and the temperature $T$. The corresponding results for the MARTINI and the atomistic model are presented in Tab. I. With regard to the presented values, it can be seen that the total differences between the models are given by $|\Delta \Delta V_{PMF}| \approx 1.3$ kJ/mol (PDADMA) and $|\Delta \Delta V_{PMF}| \approx 0.9$ kJ/mol (PSS) which are acceptable values with regard to the thermal energy at room temperature of $k_B T = 2.477$ kJ/mol. Moreover, in terms of the energetic values it can be clearly seen that PDADMA has a lower ion binding affinity than PSS (energetic difference

![FIG. 6. Angle distribution for three neighbored nitrogen atoms (atomistic model) and SQd beads (MARTINI) for PDADMA chains in the polyelectrolyte complex.](image)

![FIG. 7. Angle distribution for three neighbored sulfur atoms (atomistic model) and Qa beads (MARTINI) for PSS chains in the polyelectrolyte complex.](image)

### Table I. Values for the potential of mean force $\Delta V_{PMF}$ in the atomistic simulations between the sulfonate group in PSS and sodium ions (S - Na) and the dimethylammonium group in PDADMA and chloride ions (N - Cl) and the corresponding results for the MARTINI model for chloride binding to PDADMA (SQd - Cl) and sodium ion binding to PSS (Qa - Na).

<table>
<thead>
<tr>
<th>Method</th>
<th>Polymer</th>
<th>Beads/Atoms</th>
<th>$\Delta V_{PMF}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MARTINI</td>
<td>PDADMA</td>
<td>SQd - Cl</td>
<td>-4.4</td>
</tr>
<tr>
<td>Atomistic</td>
<td>PDADMA</td>
<td>N - Cl</td>
<td>-3.1</td>
</tr>
<tr>
<td>MARTINI</td>
<td>PSS</td>
<td>Qa - Na</td>
<td>-5.8</td>
</tr>
<tr>
<td>Atomistic</td>
<td>PSS</td>
<td>S - Na</td>
<td>-6.7</td>
</tr>
</tbody>
</table>

with PDADMA and PSS of roughly 1.4 kJ/mol in the MARTINI approach and 3.6 kJ/mol in the atomistic simulations). These results are only weakly influenced by the chosen excess salt concentration. As a final remark, it has to be noted that even the atomistic force field results might be erroneous. Previous publications\textsuperscript{21,22} have discussed the occurrence of artificial ion pairing effects for standard force fields. Therefore, a qualitative agreement (same order of magnitude) with the MARTINI models can be regarded as sufficient for our parameterization scheme.

### C. Charge compensation mechanism, coordination numbers and dielectric constants for atomistic approaches

The results for the atomistic force fields (GAFF+TIP3P and OPLS-AA + SPC/E) indicate that the charge compensation mechanism coincides for both atomistic approaches within small deviations as shown in Tab. II. The coordination numbers (corresponding explanation in the main text) are very similar according to the values shown in Tab. III. Therefore we can assume that both atomistic force fields give comparable results with regard to electrostatic properties. It has to be mentioned, that the results of the MARTINI model are in reasonable agreement with both atomistic approaches.

### Table II. Probability (in %) for charge compensation mechanisms in the all-atom complex simulations with standard deviation. The values for the OPLS-AA models were calculated from the raw data of Ref. 4

<table>
<thead>
<tr>
<th></th>
<th>OPLS-AA$^4$</th>
<th>GAFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>S intrinsic</td>
<td>89.27 ± 0.82</td>
<td>89.88 ± 0.88</td>
</tr>
<tr>
<td>N intrinsic</td>
<td>91.78 ± 0.90</td>
<td>93.43 ± 0.89</td>
</tr>
<tr>
<td>S extrinsic</td>
<td>10.11 ± 0.77</td>
<td>9.07 ± 0.82</td>
</tr>
<tr>
<td>N extrinsic</td>
<td>7.43 ± 0.92</td>
<td>5.47 ± 0.81</td>
</tr>
</tbody>
</table>
TABLE III. Coordination numbers in the all-atom complex simulations for the force fields OPLS-AA and GAFF. The values for OPLS-AA were already presented in Ref. 4

<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>OPLS-AA</th>
<th>GAFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-N</td>
<td>2.39</td>
<td>2.35</td>
</tr>
<tr>
<td>S-Na</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>N-Cl</td>
<td>0.16</td>
<td>0.14</td>
</tr>
</tbody>
</table>

D. Density of polyelectrolyte complexes (PECs)

The equilibrated size of the box edges was 6.22 nm (volume: 241 nm³) and the density of the resulting system was 1270 kg/m³ for the MARTINI model. For the PEC simulated with the OPLS-AA force field and the SPC/E water model, we found a polyelectrolyte density of 1237 kg/m³ which is slightly smaller than in the MARTINI simulations. Accordingly, the box is bigger (edge length: 6.28 nm, volume: 248 nm³).

E. Internal structural arrangement of PSS and PDADMA chains

For the study of the internal structure of the polyelectrolyte complex, we have additionally calculated the radial distribution function between the \(N−N\) and \(S−S\) groups in PDADMA and PSS and the corresponding rdf values for SQd-SQd and Qa-Qa in the MARTINI models. The results are shown in Fig. 8. In general, it can be seen that the sulfonate groups in PSS are more ordered at larger distances than the dimethylammonium groups in PDADMA. This general result is valid for the atomistic and the MARTINI simulations and can be related to the chemical structure of PSS where the sulfonate groups are covalently bound to the flexible phenyl rings.

An acceptable agreement in terms of peak locations and peak heights can be found for the dimethylammonium groups (\(N−N\)), respectively SQd-SQd groups of PDADMA. The absence of a well-ordered long range structure can be observed for the atomistic and the MARTINI simulations at distances larger than 1.7 nm. Indeed, also the position of the first peak is roughly identical within distances of 0.6 to 0.8 nm (MARTINI) and 0.7 to 1.0 nm (atomistic simulations). Thus, the size of the beads and the corresponding excluded volume is therefore correctly reproduced by the MARTINI model. In contrast to PDADMA, the MARTINI results for PSS indicate a highly ordered PSS polyelectrolyte complex structure due to the presence of three distinct rdf peaks with a well-defined distance of 0.5 nm and nearly identical heights. The constant distance between the peaks can be attributed to the MARTINI CG bead size of 0.47 nm as well as intra- and intermolecular contributions. As a remark, a distinction between intra- or intermolecular contributions cannot be drawn due to some limitations of this analysis method. Hence, it can be assumed that excluded volume effects due to the spherical bead size approximation as well as intra- and intermolecular contributions significantly influence the occurrence of higher order peaks.

The corresponding cumulative number distribution functions for PSS and PDADMA shown in Fig. 8 emphasize the fact that the local density is well reproduced. Thus, the net number of monomer groups in both MARTINI models is roughly comparable with the atomistic findings. Larger deviations can be only recognized at distances \(r ≥ 1.1\) nm. Hence, the short-scale local structure of the polyelectrolyte complex is correctly reproduced. Nevertheless, the corresponding deviations in the peak height of the radial distribution functions are evident. Thus, the local order for the bead distances as it is shown in the main article might represent a better analysis tool for intramolecular order effects.
F. Dielectric constant of water: Atomistic force fields

The dielectric constant is calculated via the fluctuations of the total dipole moment \( \mu_t \) as described in the main article. For the OPLS-AA force field and SPC/E water, we found a value of \( \varepsilon_r = 11.1 \pm 1.2 \) and for GAFF with TIP3P water \( \varepsilon_r = 11.5 \pm 1.7 \). The difference therefore is not significant, which means that both force fields behave similarly for long-range electrostatics interactions.

G. Structural and dynamic properties of the MARTINI polyelectrolyte complex

We compared the internal structure of the MARTINI polyelectrolyte complex to the original atomistic data and again to simulations using GAFF models. In addition to the simulations presented in the main article, we also modeled a PSS/PDADMA MARTINI complex for chains with \( dp = 12 \) for a better comparison with the atomistic results. The MARTINI complex consisted of 35 PSS and 35 PDADMA chains with 25 sodium and chloride excess ions. In addition, 735 polarizable water beads were inserted. The simulation procedure was identical to the one described in the main article.

1. Radius of gyration

<table>
<thead>
<tr>
<th>Force Field</th>
<th>PSS</th>
<th>PDADMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAFF</td>
<td>1.79 ± 0.94</td>
<td>1.98 ± 0.87</td>
</tr>
<tr>
<td>OPLS-AA</td>
<td>1.91 ± 0.95</td>
<td>2.03 ± 0.86</td>
</tr>
<tr>
<td>MARTINI</td>
<td>1.83 ± 0.88</td>
<td>1.96 ± 0.88</td>
</tr>
</tbody>
</table>

TABLE IV. Average radius of gyration \( R_g \) in nm for chains (\( dp = 12 \)) in a PSS/PDADMA complex.

The corresponding \( R_g \) values over time for PSS and PDADMA chains with a degree of polymerization of \( dp = 12 \) are presented in Fig. 9 and the mean values are shown in Tab. IV. It can be clearly seen that fluctuations are minimal which indicates the presence of well-equilibrated polyelectrolyte conformations. The absence of fluctuations for the same timescale is also evident for MARTINI chains with \( dp = 30 \) (Fig. 10). Furthermore, the deviations between the atomistic force field results (GAFF and OPLS-AA) are also evident. However, with regard to our MARTINI results, we can safely assume that a simulation time of 100 ns, even for longer chains (\( dp = 30 \)) with a previous equilibration procedure as described in the main article validates the presence of stable states. Moreover, a good agreement between the MARTINI model and the atomistic model results is evident.

2. End-to-end distance

The end-to-end distance\(^{20} \) between the first and the last monomer \( \vec{r}_1 \) and \( \vec{r}_N \) is given by

\[
R_e^2 = (\vec{r}_1 - \vec{r}_N)^2
\]

and can be regarded as an important value to estimate the polymer size. The corresponding time averaged results for chains with \( dp = 12 \) in a PSS/PDADMA complex are presented in Tab. V and the results for \( R_e \) over time are shown in Fig. 11. In agreement with the results for the radius of gyration, slight deviations can be observed between the atomistic force field results. In addition, an acceptable agreement for the MARTINI results can be found which is slightly better for PSS than for PDADMA. These findings are also valid for MARTINI chains with a larger number of monomers \( dp = 30 \) in Fig. 12.
FIG. 10. Radius of gyration over time in the simulation of a PSS/PDADMA (chains with $dp = 30$) complex with the MARTINI model and the atomistic approaches. Top: PSS, Bottom: PDADMA.

FIG. 11. End-to-end distance over time for chains ($dp = 12$) in a PSS/PDADMA complex with the MARTINI model and the atomistic approaches. Top: PSS, Bottom: PDADMA

<table>
<thead>
<tr>
<th>Force Field</th>
<th>PSS</th>
<th>PDADMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAFF</td>
<td>2.12 ± 0.60</td>
<td>2.27 ± 0.71</td>
</tr>
<tr>
<td>OPLS-AA</td>
<td>2.13 ± 0.65</td>
<td>2.12 ± 0.76</td>
</tr>
<tr>
<td>MARTINI</td>
<td>2.08 ± 0.49</td>
<td>2.06 ± 0.73</td>
</tr>
</tbody>
</table>

TABLE V. End-to-end distance $R_e$ in nm in the simulations of a PSS/PDADMA complex with $dp = 12$.

3. Monomer distance

As a quantity that does not depend on the degree of polymerization, the distance between neighboring monomers is well-suited for the comparison of the local structure. The distance was measured between sulfur, respectively nitrogen atoms in the atomistic representations and between the charged beads in the MARTINI model. The corresponding averaged results are shown in Tab. VI and the distribution is shown in Fig. 13. The average numbers for the monomer distance are in good agreement between the models. Therefore, it can be safely assumed that the MARTINI model resembles the internal structure found in the atomistic simulations. Slighter deviations can be only seen with regard to the distribution function (Fig. 13) whereas the mean values are comparable.

<table>
<thead>
<tr>
<th>Force Field</th>
<th>PSS</th>
<th>PDADMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAFF</td>
<td>1.06 ± 0.22</td>
<td>0.75 ± 0.06</td>
</tr>
<tr>
<td>OPLS-AA</td>
<td>1.07 ± 0.17</td>
<td>0.76 ± 0.05</td>
</tr>
<tr>
<td>MARTINI</td>
<td>1.13 ± 0.24</td>
<td>0.69 ± 0.07</td>
</tr>
</tbody>
</table>

TABLE VI. Monomer distance in nm in the simulations of a PSS/PDADMA complex.
4. Mean squared displacement (MSD)

Finally, we show the comparison of the polyelectrolyte center-of-mass mean squared displacement\textsuperscript{18}

\[ \langle (\vec{r}_{cm}(t) - \vec{r}_{cm}(t_0)) \rangle = 6D_{cm} \lim_{t \to \infty} t \]  

(6)

with the center-of-mass positions $\vec{r}_{cm}$ for different times $t$ and the diffusion coefficient $D_{cm}$ for the MARTINI and the atomistic models. The corresponding results are shown in Fig. 14. The values for the calculated diffusion coefficients are presented in Tab. VII. A reasonable agreement between the MARTINI results and the atomistic force fields becomes evident. This becomes specifically true with regard to the results for shorter MARTINI PSS and PDADMA chains ($dp = 12$). Furthermore, it has to be noticed that the ratio $r_D = D_{PDADMA}/D_{PSS}$ for the MARTINI models with $dp = 12$ ($r_D = 1.37$) nicely coincides with the results for the atomistic model (OPLS-AA: $r_D = 1.3$). Thus, the MARTINI models are in reasonable agreement with the atomistic models which validates our approach.

<table>
<thead>
<tr>
<th>Force Field</th>
<th>$D_{PSS}$ [cm$^2$/s]</th>
<th>$D_{PDADMA}$ [cm$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MARTINI ($dp = 30$)</td>
<td>$3.08 \cdot 10^{-8}$</td>
<td>$3.65 \cdot 10^{-8}$</td>
</tr>
<tr>
<td>MARTINI ($dp = 12$)</td>
<td>$6.03 \cdot 10^{-8}$</td>
<td>$8.27 \cdot 10^{-8}$</td>
</tr>
<tr>
<td>OPLS-AA</td>
<td>$4.52 \cdot 10^{-8}$</td>
<td>$5.86 \cdot 10^{-8}$</td>
</tr>
<tr>
<td>GAFF</td>
<td>$6.42 \cdot 10^{-8}$</td>
<td>$9.59 \cdot 10^{-8}$</td>
</tr>
</tbody>
</table>

TABLE VII. Diffusion coefficients of the polyelectrolytes in the polyelectrolyte complex simulations.
VII. REFERENCES

FIG. 14. Mean squared displacement of the polyelectrolytes ($dp = 30$ (top) and $dp = 12$ (middle)) in the MARTINI complex simulation with 1 mol/L NaCl and in the OPLS-AA simulations (bottom) by Qiao et al\textsuperscript{4}.

FIG. 14. Mean squared displacement of the polyelectrolytes ($dp = 30$ (top) and $dp = 12$ (middle)) in the MARTINI complex simulation with 1 mol/L NaCl and in the OPLS-AA simulations (bottom) by Qiao et al\textsuperscript{4}.