From the Atomistic to the Macromolecular Scale: Distinct Simulation Approaches for Polyelectrolyte Solutions

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Contents

Abstract

Polyelectrolytes reveal interesting properties in solution. At short length scales, the dissociation of counterions is heavily affected by the chemical structure of the polyelectrolyte, the properties of the solution, and specific ion effects. At larger length scales, the structure of polyelectrolyte solutions is dominated by long-range interactions. In the special case of dissolved polyanions and polycations, polyelectrolyte complexes or multilayers can form. In this review we present distinct simulation approaches to study the corresponding effects at different

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length scales in more detail. Whereas at short length scales, atomistic molecular dynamics simulation is often the method of choice, semi-coarse-grained and coarse-grained models with a lower level of details reveal their benefits at larger length scales.

1 Introduction

In accordance with the IUPAC definition, polyelectrolytes are charged macromolecules, in which a substantial portion of the constitutional units contains ionic or ionizable groups, or both (McNaught and Wilkinson 1997). Strong polyelectrolytes like DNA are completely ionized, whereas weak polyelectrolytes like polyacrylic acid show an incomplete and pH-dependent dissociation behavior. Consequently, the properties of polyelectrolytes are dominated by a combination of electrostatic and molecular interactions, which heavily affect the occurring conformations and the resulting ion dissociation behavior. In contrast to uncharged polymers, the long-range decay of electrostatic interactions between the ionic groups impedes the derivation of scaling relations in terms of simple mean-field approaches (de Gennes 1979; Doi and Edwards 1988; Dobrynin and Rubinstein 2005; Dobrynin 2008). Thus, the complex interplay between the polyelectrolyte, the ions in the solution, and the solvent reveals many interesting phenomena at different length scales, which can be studied in more detail with the help of distinct molecular dynamics (MD) simulation approaches in combination with appropriate models for the considered species.

At short length scales, previous atomistic MD simulations demonstrated that the molecular solvation behavior significantly influences the amount of ionized groups and thus the corresponding conformation with regard to counterion condensation effects and repulsive electrostatic interactions along the polyelectrolyte backbone (Smiatek et al. 2014). Vice versa, the behavior of the surrounding solvent molecules is also modified by the presence of ionic groups, which is reflected by local variations concerning the dielectric permittivity and the solvation of ions (Fahrenberger et al. 2015a; Mukhopadhyay et al. 2012). In contrast to these local interactions, the aggregation of polyelectrolytes becomes important at larger length scales, such that polycations and polyanions form polyelectrolyte complexes and multilayers, whose stability significantly depends on enthalpic and entropic contributions and the properties of the embedded solvent molecules (Cerdà et al. 2009; Qiao et al. 2011, 2012). Also in bulk solution, molecular properties determine the configurational behavior of the polyelectrolyte, as can be seen by the formation of polyelectrolyte micelles, pearl-necklace structures, or the onset of microphase separation processes between polar and apolar regions (Limbach and Holm 2003; Limbach et al. 2004; Dormidontova et al. 1994). Thus, appropriate models with a sufficient degree of detail are needed for reliable simulations of polyelectrolyte solutions in order to elucidate the properties of interest.

In this chapter, we introduce several well-established approaches for the simulation of polyelectrolyte systems at different length and time scales. The benefits and drawbacks of atomistic, semi-coarse-grained and simple coarse-grained models are discussed, and we will present representative examples for various applications. In the last section, we summarize the main points and address current limitations concerning the general applicability of the methods.

2 Simulation Approaches for Polyelectrolyte Solutions at Different Length Scales

The discussion of methods in this section follows a bottom-up approach, which means that we start with atomistic models and the description of molecular force fields. Hereafter, we decrease the level of resolution in terms of semi- and simple coarse-grained approaches, which are best suited for the simulation of processes at large length and long time scales. All models rely on the consideration of explicit particles in combination with molecular dynamics or Monte Carlo time integration schemes. It has to be noted that other continuum or self-consistent field approaches can also be used, for instance, as described in Schmid (1998). Over the last years, multiscale simulation approaches were also developed, which rely on a combined consideration of the following methods in terms of matching and adaptive resolution schemes. The reader is referred to Fritz et al. (2011) and Praprotnik et al. (2008) for more details and for other contributions to this volume.

2.1 Atomistic Models: Importance of Chemical and Molecular Details

Due to the massive increase of computational power over the last years, it is nowadays possible to study the properties of short polyelectrolyte chains, the so-called oligoelectrolytes, for hundreds of nanoseconds via atomistic MD simulations in combination with accurate molecular force fields. In terms of modern force fields, molecular properties are dictated by bonded and nonbonded interactions, which are represented by classical potential functions in order to avoid an extremely expensive evaluation of the electronic behavior. In more detail, standard atomistic force fields like OPLS/AA (Jorgensen et al. 1996) include parameters for bonded, angular, and dihedral potentials in addition to nonbonded interactions, which are usually represented by Coulomb and Lennard-Jones contributions. In combination with advanced electrostatics algorithms (Deserno and Holm 1998; Arnold et al. 2013) and the sophisticated use of graphics processing units (GPUs), the properties of polyelectrolyte solutions with a dimension up to several nanometers can be studied for hundreds of nanoseconds by standard atomistic MD approaches. Hence, detailed information on the molecular interactions, the solvent behavior, and the corresponding distribution functions are accessible.

As an illustrative example, the stable conformations for a sulfonated oligosulfonic acid with sodium counterions in water and chloroform are displayed in Fig. 1, where more details of this system can be found in Smiatek et al. (2014). It can

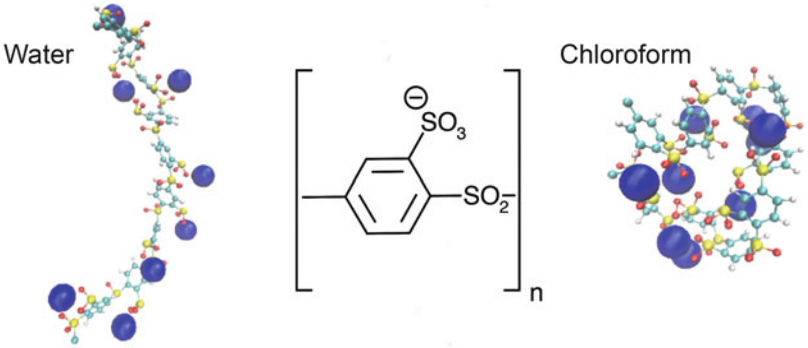

Fig. 1 Sulfonated oligosulfonic acid with nine monomers according to $N_p = 9$ and an equivalent number of sodium counterions (blue spheres) in water (left side) and chloroform (right side). The solvent molecules are not shown for reasons of clarity, and the chemical structure of one monomer is depicted in the middle

be clearly seen that the oligoelectrolyte reveals a swollen conformation in polar solvents like water when compared with chloroform. This finding can be related to molecular solvation effects and standard polymer theories, which distinguish between good, poor, and theta solvents (de Gennes 1979). Thus, the average size of the polyelectrolyte with N_p monomers can be described by a power-law behavior according to $R \sim N_p^{\nu}$ with the excluded-volume parameter ν, which is usually $\nu = 0.588$ for uncharged polymers in good solvents (Doi and Edwards 1988). Depending on the actual value of the excluded-volume parameter, good and poor solvents are defined by $\nu > 1/2$ and $\nu < 1/2$, respectively, whereas a theta solvent is characterized by $\nu = 1/2$. A polyelectrolyte chain at infinite dilution should scale with $\nu = 1$. Hence, the molecular properties of the polyelectrolyte adapt directly to the polarity of the solvent, which is reflected by an increase or a decrease of the solvent-accessible surface area and the size.

Interestingly, further analysis concerning atomistic models for polyelectrolytes revealed that the counterion behavior differs significantly from standard theoretical descriptions (Manning 1969, 1996; Deserno et al. 2000; Deserno and Holm 2001), which highlights the benefits of atomistic MD approaches in order to verify molecular theories and to study the corresponding deviations. As a result of these simulations (Lund et al. 2008; Heyda and Dzubiella 2012; Smiatek et al. 2014; Batys et al. 2017), it was found that the counterion distribution around the polyelectrolyte can deviate from standard mean-field predictions in terms of the Poisson-Boltzmann theory (Andelman 1995), which can be attributed to specific solvation effects and molecular interactions (Smiatek et al. 2014). Furthermore, it was also observed that specific ion effects (Marcus 2009; Kunz 2010; Lo Nostro and Ninham 2012) and conformational properties of polyelectrolytes (Wohlfarth et al. 2015) influence the corresponding counterion distribution and yield results in good agreement with experimental data. To summarize, also atomistic simulations reveal short-range deviations from simple mean-field theories; however, Poisson-Boltzmann theory and its generalizations often agree surprisingly well for global observables like the osmotic pressure or effects that are dominated by the Coulomb interactions (Deserno et al. 2001; Antypov et al. 2005; Antypov and Holm 2006; Lu et al. 2008).

2.2 Semi-Coarse-Grained Approaches: MARTINI Force Fields and Refined Models

Atomistic MD simulations mainly intend to study the properties of short oligoelectrolyte chains and their molecular interactions with counterions and other components of the solution. Although also larger systems were studied, for instance, polyelectrolyte complexes and multilayers (Farhat et al. 1999; Micciulla et al. 2014), it has to be mentioned that these simulations are very CPU-time demanding and usually restricted to several tens of nanoseconds, such that even a reasonable equilibration of these complex solutions is hard to achieve. In order to introduce efficient but still accurate models for these larger systems, the use of semi-coarse-grained approaches is highly beneficial. In general, coarse-grained approaches intend to reduce the degrees of freedom when compared with atomistic simulations, which results in a significant acceleration of the computation times and the possibility of using larger time steps (Winger et al. 2009; Marrink et al. 2010). Standard coarse-grained frameworks for polyelectrolytes and polymers include the introduction of simple bead-spring models (Doi and Edwards 1988). Hence, several atoms of a monomer are represented by one interaction site, the so-called bead, while the individual beads are connected with springs, which are usually modeled by classic harmonic or modified Finitely Extensible Nonlinear Elastic (FENE) potentials. In contrast to the most simple coarse-grained methods, semi-coarse-grained approaches like the MARTINI force field (Marrink and Tieleman 2013) refine these very generic models by consideration of important chemical details. For instance, the MARTINI force field usually relies on a 4:1 mapping scheme, such that four heavy atoms are combined into one interaction site (CG bead) with parameterized polarity values and hydrogen bond acceptor and donor abilities (Marrink et al. 2007). In more detail, the MARTINI CG beads can be divided into different particle-type classes (polar (P), nonpolar (N), apolar (C), and charged (Q) species). The subtypes within these classes are categorized due to their ability to form hydrogen bonds (donor (d), acceptor (a), both donor and acceptor (da), and none of them (0)) and with regard to their polarity (from 1 = low polarity to 5 = high polarity) (Marrink et al. 2007; Marrink and Tieleman 2013). Further subclasses were also defined to increase the local resolution (Marrink et al. 2007). All CG beads reveal different Lennard-Jones parameters and partial charges, which were parameterized according to partitioning coefficients for similar atomic groups in oil/water mixtures (Marrink et al. 2007; Marrink and Tieleman 2013).

Over the last years, several MARTINI models for polymers and polyelectrolytes were developed. Specific examples are DNA (Uusitalo et al. 2015), poly(styrene sulfonate) (PSS) and poly(diallyldimethylammonium) (PDADMA), which were both used for the study of polyelectrolyte complexes (Vögele et al. 2015a). The

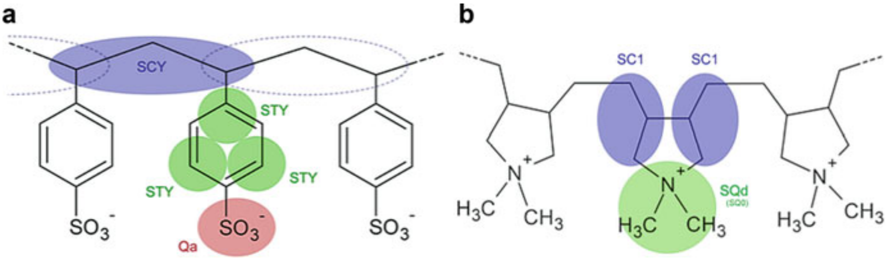

Fig. 2 Chemical structure of PSS (left side) and PDADMA (right side) with three monomers. The differently shaded regions denote spherical MARTINI CG beads with particle-type classes as defined in Marrink et al. (2007)

molecular topologies of PSS and PDADMA in terms of the MARTINI force field and the corresponding particle types according to Marrink et al. (2007) are shown in Fig. 2. In combination with refined polarizable water models (Yesylevskyy et al. 2010; Michalowsky et al. 2017), it was shown that MARTINI simulations are well suited to study the properties of highly charged systems at large length and time scales (Vögele et al. 2015a,b; Uusitalo et al. 2015).

The advantages of MARTINI models are mostly given by their flexibility and their transferability, but it has to be noted that solvent particles indeed have to be considered explicitly. In order to circumvent time-consuming calculations, the matching of potential of mean forces between atomistic and coarse-grained simulations provides a computationally efficient route in terms of tabulated potentials and thus an implicit solvent approach (Brini et al. 2013; Reith et al. 2002; Li et al. 2012; Lyubartsev and Laaksonen 1999; Savelyev and Papoian 2010; Hsu et al. 2012). Although this method, which is also often called iterative Boltzmann inversion technique (Reith et al. 2003), avoids time-consuming calculation of interactions between solvent particles and between solvent and polyelectrolyte groups, it has to be mentioned that the force-matching method is mostly applicable for homogeneous solutions without interfaces. More refined coarse-grained models for DNA and ionomer systems, based on the matching of ion mobilities, were published in Lu et al. (2014), Weik et al. (2016), and Rau et al. (2017). A semi-coarse-grained approach for the simulation of weak polyelectrolytes was recently introduced in Landsgesell et al. (2017a,b). Furthermore, the well-known decrease of the dielectric permittivity around charged objects and the corresponding consequences were recently studied in coarse-grained polyelectrolyte solution via a modification of the Maxwell equation molecular dynamics algorithm (Fahrenberger and Holm 2014; Fahrenberger et al. 2015a,b).

In summary, refined or semi-coarse-grained models can be used for the study of systems at intermediate length and time scales. Nevertheless, for the study of long time-scale processes like transport behavior or the influence of hydrodynamics on polyelectrolyte motion, the use of simple coarse-grained methods remains the most suitable choice.

2.3 Simple Coarse-Graining: Generic Bead-Spring Models with Explicit Charges

In general, all simple coarse-grained models are composed of single interaction sites, which have a lower resolution when compared with semi-coarse-grained approaches and thus usually correspond to individual monomers or the number of monomers within the corresponding persistence length (Doi and Edwards 1988). All adjacent beads are connected by springs in terms of simple harmonic or FENE potentials, which restrict the length of the bonds to the equilibrium distance in order to avoid entanglement effects in polymer melts (Kremer and Grest 1990; Stevens and Kremer 1993a,b). In contrast to semi-coarse-grained approaches, simple bead-spring models do not include angular or dihedral potentials per definition, and the corresponding nonbonded interactions are represented by simple Lennard-Jones (LJ) and Coulomb interactions. Most often, the WCA potential, a purely repulsive shifted and truncated version of the Lennard-Jones potential, is used to mimic hard spheres for beads and ions (Weeks et al. 1971). In contrast to MARTINI models, the solvent is often modeled implicitly by consideration of a global dielectric constant, which is thus inserted into the Coulomb potential. Furthermore, the model can be even more simplified by using a screened electrostatic potential or neglecting Coulomb interactions all together (Hickey et al. 2012; Szuttor et al. 2017; Roy et al. 2017). Specifically in solvents with high values of the dielectric constant, for instance, water, electrostatic interactions between charged groups and ions dominate only at short distances (Collins 2004). This can be mostly attributed to the low value of the Bjerrum length at room temperature $\lambda_B = e^2/4\pi\epsilon_0\epsilon_r k_B T$ with the elementary charge e, the vacuum permittivity ϵ_0, the dielectric constant ϵ_r, the temperature T, and the Boltzmann constant k_B. The Bjerrum length estimates the distance where the thermal energy dominates over the electrostatic energy and which is for water at 300 K around $\lambda_B \approx 0.7$ nm corresponding to two hydration shells (Collins 2004; Marcus and Hefter 2006). For larger and highly charged objects like polyelectrolytes or colloidal particles, also the salt concentration plays a significant role in order to induce a fast decay of electrostatic interactions. Hence, by a simple linearization of the Poisson-Boltzmann equation in terms of the Debye-Hückel approximation, the corresponding electrostatic screening length reads $\lambda_D = (\epsilon_r \epsilon_0 k_B T/(\sum_i 2z_i^2 e^2 \rho_i))^{1/2}$ with the valency z_i and the ion density ρ_i (Andelman 1995). With regard to this relation, one usually obtains a screening length of $\lambda_D \approx 1$ nm for water at room temperature with a salt concentration of 0.1 mol/L, which implies that the monomers are only weakly affected by the electric field of the surrounding polyelectrolyte groups (Szuttor et al. 2017). Hence, for large objects like λ-DNA, it is often sufficient to neglect electrostatic interactions between the monomers, if the Debye and the Bjerrum length are significantly smaller than the size of the polyelectrolyte in accordance with $\lambda_D \approx \lambda_B \ll R$ (Szuttor et al. 2017; Roy et al. 2017).

Most of these simple coarse-grained models are used to study the dynamics of polyelectrolytes and other components in solution, often under the influence of external forces in order to induce transport processes. Recent reviews highlighted the benefits of these models in combination with sophisticated mesoscopic simulation techniques for the study of transport processes and electrokinetic effects in microchannels (Slater et al. 2009; Pagonabarraga et al. 2010; Smiatek et al. 2012). In more detail, mesoscopic simulation approaches induce a stochastic motion of the solute species in the system, which is related to the behavior at long time scales. A simple but effective and thermodynamically consistent approach is represented by Langevin or Brownian dynamics (Kremer and Grest 1990). However, as it has been pointed out in Dünweg (1993), momentum is not conserved in Langevin dynamics, such that this approach cannot capture any hydrodynamical effects (Doi and Edwards 1988; Ober and Thomas 1997; Grass et al. 2008; Frank and Winkler 2009). Most often, one is indeed specifically interested in hydrodynamic effects, such that either the Langevin dynamics approach can be modified by introducing the Oseen tensor (Ermak and McCammon 1978) or efficient Navier-Stokes solvers have to be used. In terms of mesoscopic approaches, the most common techniques are dissipative particle dynamics (DPD) (Groot and Warren 1997; Smiatek et al. 2012), coupled lattice Boltzmann/molecular dynamics (LBMD) (Dünweg and Ladd 2009) or multiparticle collision dynamics (MPCD) (Gompper et al. 2008). Previous articles highlighted the good quantitative agreement between DPD and LBMD simulations (Smiatek et al. 2009) and their applicability to study transport processes in confined geometries (Smiatek and Schmid 2010, 2011; Smiatek et al. 2012; Weik et al. 2016). In general, the use of mesoscopic simulation methods can be nowadays regarded as a standard approach in order to study the influence of hydrodynamics in many different research fields.

Furthermore, simple coarse-grained models were often used to validate analytical mean-field approaches like counterion condensation theories (Deserno et al. 2000), stretching forces on tethered polymers (Szuttor et al. 2017), electrohydrodynamic screening effects (Grass et al. 2008), or the combined influence of electroosmotic and electrophoretic motion (Smiatek and Schmid 2010). Interestingly, also the influence of the solvent quality on the resulting conformations can be studied via the use of simple approaches. In terms of experimental and atomistic simulation results, it is known that poor solvents imply collapsed conformations, whereas good solvents lead to a swelling of the polyelectrolyte. Hence, these findings can be transferred to tunable attractive or repulsive interactions between the beads in order to correct for the presence of an implicit solvent. Hence, in combination with electrostatic interactions and attractive bead potentials, it was even possible to enforce the occurrence of pearl-necklace polyelectrolyte structures (Dobrynin et al. 1996; Micka et al. 1999; Limbach et al. 2002; Limbach and Holm 2003). Furthermore, also more complicated topologies like in polymeric ionic liquids (PILs) (Mecerreyes 2011; Yuan et al. 2013) can be modeled via simple coarse-grained approaches (Weyman et al. 2018). A simple example for a common alkylimidazolium-based PIL and a snapshot of a system conformation are shown in Fig. 3. As can be seen in the bottom, a simulation of 30 PIL chains with $N_p = 30$ reveals the occurrence of a microphase separation between polar and apolar beads. The aggregation of apolar beads was initiated by attractive LJ interactions, which initiate the formation

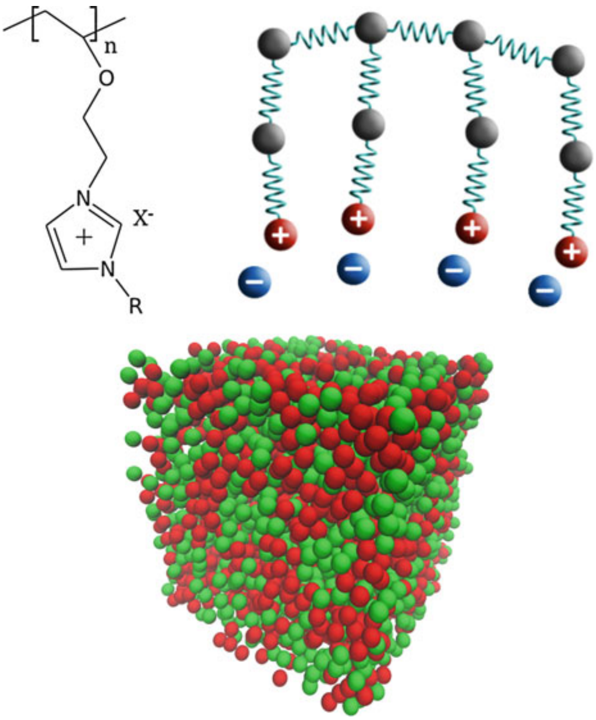

Fig. 3 Chemical structure of a typical alkylimidazolium-based PIL with counterions X^- (top left). The corresponding simple bead-spring model with $N_p = 4$ is shown at the upper right part. The charged terminal groups are shown as red spheres and the counterions as blue spheres. All neutral beads have a gray color. A snapshot of the simulation with 30 polymers with $N_p = 30$ in terms of the coarse-grained model is shown at the bottom. Neutral beads are colored in red, while charged beads and counterions are colored in green

of apolar and polar microphases for larger side chain lengths. In summary, simple coarse-grained polyelectrolyte models are computationally efficient and can be used for the study of different systems at larger scales. The consideration of further details can be simply achieved via effective generic or tunable potentials and provides reasonable results, if the specific molecular details and processes are of minor importance.

3 Summary and Conclusion

In this chapter, we described distinct approaches for the simulation of polyelectrolyte solutions at different length and time scales. For the study of fast processes and molecular interactions at short length scales, the use of atomistic models with regard to appropriate force fields is advised. In terms of larger length and longer time scales, semi- and simple coarse-grained models with different levels of detail can often be considered as the method of choice. A promising approach is the MARTINI force field, which provides a beneficial transferability between different systems without the need of a proper reparameterization for distinct models. Furthermore, also tabulated potential methods as well as refined coarse-grained models were also developed that can be interpreted as coarse-grained approaches with basic molecular properties. For the simulation of transport processes and hydrodynamic effects, simple coarse-grained models in combination with mesoscopic simulation methods are highly beneficial, which can be rationalized by the fact that polymers show a universal scaling behavior at large scales, such that specific molecular details are of minor importance (de Gennes 1979; Doi and Edwards 1988).

In summary, the presented methods can be used for a broad range of systems at different time and length scales. However, which method is most appropriate will depend crucially on the question to be answered, and one cannot give any general advice. However, it has to be emphasized that all methods rely on crucial approximations, and thus, if possible, one should always verify the simulation results with experimental findings or theoretical predictions. A prominent example are specific ion effects, which are modeled explicitly only in few atomistic MD force fields (Fyta and Netz 2012). It is thus a challenging task to transfer this information to coarse-grained models. Moreover, the study of apolar organic solvents is significantly more complicated in comparison to polar solvents, due to the fact that the Debye and the Bjerrum lengths can easily exceed the simulation box size, which induces electrostatic correlation effects between the polyelectrolyte and its periodic images. These finite-size effects modify structural and dynamic properties of the solution and are thus a crucial problem in order to bring simulation outcomes in quantitative agreement with experimental results. Moreover, also non-ideal effects, as they are well known for higher component solutions (Krishnamoorthy et al. 2016), are often not correctly reproduced. In general, all considered methods rely on potential functions to mimic the electronic behavior. Hence, an accurate study of bond formation and cleavage processes in combination with varying pH values of the solution is often impossible. A promising new route is the introduction of reactive force fields (Senftle et al. 2016), which are, although time consuming, less computationally expensive than ab initio simulations. In accordance with the simplification of the electronic behavior, atomic polarization effects are also usually neglected, which have nowadays become an active field of research and model improvement (Lemkul et al. 2016; Bordin et al. 2016).

Despite their limitations, the presented methods and models are the most promising approaches for the reliable study of effects and processes in polyelectrolyte solutions. It can be expected that new and refined approaches in combination with longer simulation times will allow a more accurate study of these systems in the coming years.

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