Hydration of polyelectrolytes studied by molecular dynamics simulation

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Abstract

Molecular dynamics simulations of diluted (≈ 2.5 weight percent) aqueous solutions of two polyelectrolytes, namely sodium carboxy methyl cellulose (CMC) and sodium poly(acrylate) (PAA) have been performed. Water and counterions were taken into account explicitly.

For CMC the substitution pattern and starting conformation is all-important. Two simulations of CMC oligomers resulted in different structures: One molecule takes a stretched conformation, while the second one keeps a globule-like, toroidal one. PAA is stretched during the whole simulation, with an average characteristic ratio of 8.3.

On a local atomistic scale CMC and PAA have different hydrogen-bond properties. The COO\(^{-}\) groups of PAA can only act as hydrogen bond acceptors, but due to the high negative charge density there are still more water molecules assembled around PAA than around CMC. There are 0.036 bonds/amu respectively 0.029 bonds/amu to water for the two CMC oligomers, but more than twice as many for PAA: 0.083 bonds/amu. Beside intermolecular hydrogen bonding, there is a significant amount of intramolecular H-bonding for CMC, which is influenced by the COO\(^{-}\) groups, which act as strong H-acceptor. In contrast to hydroxy- and carboxylic groups, ether oxygens are hardly involved into hydrogen bonding.

1 Introduction

Polyelectrolytes play an important role in industrial chemistry. The fields of application range from tailor-made thickeners to paper finishing or ore preparation. Polysaccharide derivatives represent one interesting class of polyelectrolytes. In particular, cellulose products are important compounds. For our simulation study carboxy methyl cellulose (CMC) is chosen as an example for a polyelectrolyte derived from a natural polymer. Aqueous CMC solutions exhibit valuable properties, like a wide range of viscosity, non-toxicity and biodegradability. Particularly for the high-purity consumer-product market (cosmetics, food stuffs), CMC is used. However, pricing becomes more important in bulk applications (clay and ore treatment, oil-drilling). Hence it is desirable to replace some of the high-cost–high-selective chemicals with low-cost equivalents, like poly(acrylic acid) (PAA), which is the prototype of industrial synthetic polyelectrolytes. PAA is the other polymer studied in this work.

Most published work on aqueous CMC and PAA solutions was done experimentally using chromatography, \(^{13}\)C nuclear magnetic resonance and rheological techniques. Theoretical approaches are scarce. We are aware of only one paper, which treats CMC by the worm-like-chain theory. This electrostatic theory successfully rationalizes some of the global properties of CMC, but as a rather generic approach it does not allow for detailed predictions on an atomistic time and length scale. Similar restrictions apply also to Monte Carlo simulations of polyelectrolyte chains in a cell model, where the solvent is treated as a dielectric continuum. Especially local...
interactions hydrogen bonds (hydrogen bridges) are neglected in theories and non-atomistic simulations. With two or three hydrogen-bond donor groups per repeat unit and even more acceptor sites (including charged COO\(^-\) groups), this type of interaction is likely to be very important for the behaviour of CMC in water. Experimental techniques, on the other hand, suffer from different problems: NMR provides averaged local properties. Rheology derives and verifies scaling laws, but different polyelectrolytes lose their chemical “identity” and show the generic behaviour of excluded-volume chains. Atomistic molecular dynamics (MD) simulations cannot overcome all these problems, but they can provide some more detailed information.

The aim of this study is to understand better the structural and dynamic aspects of the hydration of CMC and PAA and to compare the two polymers. To this end, we investigate both the chain properties and the interaction of chains with their immediate solvent environment. Atomistic simulation is confined to the study of small system sizes. However, in combination with coarse-graining methods \[7, 8, 9\] even some mesoscopic properties may be explored. Thus, a second goal of this study was to produce atomistic structural information, from which coarse-grained models of e. g. PAA can be generated.

## 2 Computational Details

The exact molecular composition of CMC is a consequence of the molecule’s production history. Usually OH-groups are randomly substituted by carboxy methyl units \[2, 10\] and the degree of substitution (DS) for most commercial CMC’s lies in the range DS=0.6–1.2 substitutions per anhydroglucose unit (AGU). There is evidence for a preferential substitution during heterogeneous, wet conversion of cellulose to CMC: Heinze and coworkers used liquid chromatography to analyse the substitution pattern of Sodium-CMC. Their analysis was preceded by hydrolysis of the glucosidic link, by which information on the ring-substitution sequence is lost. For the AGU, the following substitution statistics was found \[11\]: 23\% of all O2-oxygens were substituted, followed by the O6 (15\%) and O3 with 11\% of all respective atoms. The glucose nomenclature is shown in figure 1. The diversity of molecular substitution patterns of CMC makes it difficult to model such a compound by an oligomer, because there is no “typical” molecule or structure.

To have at least some variety, two CMC oligomers were simulated. Substitution patterns were generated at random, with weights for the three exocyclic oxygens \((P(O2) = 0.23, P(O3) = 0.12, P(O6) = 0.15)\). They are summarized in table 1. The first molecule (CMC I) consists of seven AGUs and is substituted five times, the second one (CMC II) consist of eight AGUs with six OH groups substituted. The degrees of substitution are DS=0.70 and DS=0.75, respectively. Due to three sites, at which substitution can take place (neglecting the chain ends) there are eight different possible substitution patterns on a single AGU. Four of these (O2 O3, O3, O2, O6) are present in the first simulated CMC oligomer and one further pattern (O3 O6) in the second CMC.
Anhydroglucose unit number

|    | 1 | 2 | 3 | 4 | 5 | 6 | 7 | (8) |
|----|---|---|---|---|---|---|---|-----|
| O2 | I | I | I | II| I, II | |
| O3 | II| I | I | II|        | |
| O6 | I | I | II|   |        | |

Table 1: Substitution pattern of both simulated carboxy methyl cellulose (CMC) molecules. An entry in the table for one of the CMC molecules (I or II) indicates a substitution at the respective OH-Group (O2, O3 and O6). Anhydroglucose units are numbered from 1 to 7 (CMC I) or 1 to 8 (CMC II).

Oligomer.

All carboxylic acid groups were assumed to be dissociated, neutrality of the systems was maintained by five, respectively six sodium counterions. As the carboxylic acid group has a pK$_A$ of about 4, the system is basic. Molecular weights are 1440 amu (seven AGUs, CMC I) and 1660 amu (eight AGUs, CMC II), respectively. Molecule CMC I was solvated in 3789, molecule II in 3917 water molecules. The concentrations are about 2.1 and 2.4 weight percent (excluding the sodium-counterions). Therefore both simulations were performed in the dilute regime (no added salt), where polyelectrolytes are expected to be stretched [4].

Polyacrylic acid (PAA) was modeled as one atactic oligomer strand, with 23 repeat units (1636 amu) solvated in 3684 water molecules (concentration excluding counterions 2.4 weight percent). All COO$^{-}$ groups are negatively charged and there are 23 sodium counterions. Runs were performed under the same conditions as for CMC, including the GROMOS force field [12] as detailed in table 2 and 3.

To ensure a consistent forcefield, we used simple point charge (SPC) water [14] with the GROMOS parameter set. This combination has proven useful in several simulations of sugars in water [16, 17]. Lennard-Jones interactions were truncated and shifted at a cutoff of $r_c = 0.9$ nm. An isotropic pressure correction term was applied for site-site distances greater than the cutoff $r_c$. Electrostatics were dealt with using the Coulomb-Potential with a reaction-field correction [18, 19]:

$$V_q(r_{ij}) = \frac{q_i q_j}{4 \pi \varepsilon_0} \left( \frac{1}{r_{ij}} + \frac{\varepsilon_{RF} - 1}{2 \varepsilon_{RF} + 1} \frac{r_{ij}^2}{r_c^2} \right)$$

with the reaction field dielectric $\varepsilon_{RF}$ equal to the value for water ($\varepsilon_{RF} = 78.5$). All atoms – except aliphatic hydrogens – are explicitly modeled. In the GROMOS forcefield, aliphatic hydrogens are accounted for by a change of the parameters for the parent carbons.

Bond lengths were held constant using the Shake procedure [20]. Equations of motion were integrated using the leap-frog algorithm with a timestep of 2 fs. Other simulation parameters were a neighbor list, which was updated every 15 steps with a list cutoff of 1 nm, weak coupling to a temperature ($T = 333.15$ K) and pressure ($p = 1$ atm) bath [21] with coupling times of $\tau_T = 0.5$ ps and $\tau_p = 2.5$ ps (water compressibility $4.5 \cdot 10^{-10}$ kPa$^{-1}$). For later analysis, coordinates were written every 195 steps. The overall simulation time was 4.5 ns for CMC I and 2.5 ns for CMC II, each after 1 ns of equilibration.

We used different starting geometries for both CMC I and CMC II. The first one was started in a stretched conformation, the second, CMC II, was prepared in a folded starting conformation: During the first 150 ps of equilibration, a globule-like conformation was enforced by five artificial harmonic bonds (force constant of 100 kJ mol$^{-1}$nm$^{-2}$ with a minimum energy at 1 nm between C1 atoms of different glucose rings). PAA was started in the stretched (all-trans) conformation, equilibrated for 1 ns and simulated for about 4.5 ns.

For analysis purpose, the center of mass of a repeat unit is calculated using all its atoms, including any side groups if present. The CMC repeat unit begins at C1 and ends at O4 according to the numbering in figure 3. The acrylate repeat unit coincides with the propylate unit.
Nonbonded Parameters CMC

| Name | Type          | σ [nm] | ε [kJ mol\(^{-1}\)] | q [e] | m [amu] |
|------|---------------|--------|----------------------|-------|---------|
| C    | COO\(^-\)     | 0.3361 | 0.405870             | 0.2700| 12.0100 |
| CH\(_1\) | O-C\(_3\)-O | 0.38004| 0.313940             | 0.4000| 13.0190 |
| CH\(_2\) | C\(_2\)-OH, C\(_4\)-OH | 0.38004| 0.313940             | 0.1500| 13.0190 |
|      | C\(_4\)-OR\(_2\), C\(_5\)-C-OH | 0.38004| 0.313940             | 0.1600| 13.0190 |
| RCH\(_2\)-OH | and | | | | |
| RCH\(_2\)-O-CH\(_2\)-COO\(^-\) | 0.39199| 0.489590             | 0.1500| 14.0270 |
| RCH\(_2\)-O-CH\(_2\)-COO\(^-\) | 0.39199| 0.489590             | 0.2080| 14.0270 |
| O    | -O-H          | 0.28706| 1.010650             | -0.5480| 15.9994 |
| R-O-CH\(_2\) | and | | | | |
| OCH\(_2\)-O-CH\(_2\)-COO\(^-\) | 0.28706| 1.010650             | -0.3580| 15.9994 |
| R-O-R (ether) | 0.28706| 1.010650             | -0.3600| 15.9994 |
| -COO\(^-\) | 0.26259| 1.725440             | -0.6350| 15.9994 |
| H    | -O-H (chain end) | 0.00000| 0.000000             | 0.3980| 1.0080 |
| H    | -O-H (chain end) | 0.00000| 0.000000             | 0.3730| 1.0080 |
| OW   | water         | 0.31650| 0.650300             | -0.8200| 15.9994 |
| HW   | water         | 0.00000| 0.000000             | 0.4100| 1.0080 |
| Na\(^+\) | 0.27300| 0.358000             | 1.0000| 22.9898 |

Additional Nonbonded Parameters PAA

| Name | Type |
|------|------|
| C    | CH\(_1\) | 0.38004| 0.313940| 0.000| 13.0190 |
|      | CH\(_2\) | 0.39199| 0.489590| 0.000| 14.0270 |
|      | CH\(_3\) | 0.38750| 0.73227| 0.000| 15.0350 |

Table 2: Overview of all nonbonded force field parameter of our simulations. A united-atom model is used, so no explicit aliphatic hydrogens are present. Lennard Jones and electrostatic interactions between atoms less than 3 bonds apart are switched off. Lennard-Jones interactions between unlike atoms are treated using the Lorentz-Berthelot mixing rules. \( \text{R} \) refers to an aliphatic site. Underlining is used to make the assignment unambiguous.

-CH\(_2\)-CH-COO\(^-\).

The simulations were done with our molecular dynamics package YASP, which is described in ref. 14.

3 Results

3.1 Global Chain Properties

Carboxy methyl cellulose I (CMC I) and CMC II have very different structures: CMC I is an extended, almost straight chain, whereas CMC II assumes a cyclic conformation (Fig. 2). Poly(acrylic acid) (PAA) behaves more like CMC I, having mostly a straight conformation with only some bending (Fig. 2). These structural features cause the end-to-end distance distributions (figure 4) of CMC I and CMC II to be very different. The end-to-end distance \( R_{ee} \) is calculated between the center of mass of the first and last AGU in the chain. For PAA it is calculated from the center of mass of the terminate repeat units. For CMC I there are two conformers, a major one at 2.6 nm and a second state at 1.8 nm. This second state corresponds to a bent conformation, which shows up several times in the simulation. Its probability is about 15% of the stretched structure and on average this state is kept for about 80 ps until the oligomer’s end-to-end distance lengthens again. For CMC II the situation is different: The end-to-end distribution is very narrow. The short distance corresponds to a stable ring conformer. Poly(acrylic acid) shows a wider distribution than either CMC, resulting from the larger number of torsional degrees of freedom. The shoulder at 2.8 nm is due to the bent conformation shown in Fig. 2.

The shapes of the molecules are also reflected in the the eigenvalues of the gyration tensor (table 4). The stretched conformations of CMC I and PAA, lead to one large and two small eigenvalues, whereas CMC II has more isotropic eigenvalues, with only a factor of two between the
Bond constraints CMC and PAS

| Name          | $r_0$ [nm] |
|---------------|------------|
| CH$_n$-(COO)$^-$ | 0.1530    |
| CH$_n$-CH$_{12}$ | 0.1520    |
| CH$_2$-O        | 0.1435    |
| C-(OO)         | 0.1250    |
| O-H            | 0.1000    |

Bond angles CMC and PAS

| Name          | $\phi_0$ [degree] | $K_\phi$ [kJ mol$^{-1}$ rad$^{-2}$] |
|---------------|-------------------|-----------------------------------|
| CH$_2$-O-H    | 109.5             | 450.0                             |
| CH$_n$-CH$_n$-CH$_n$ | 109.5          | 285.0                             |
| CH$_n$-CH$_n$-O | 109.5             | 320.0                             |
| CH$_n$-O-CH$_n$ | 109.5             | 380.0                             |
| O-CH$_n$-O    | 109.5             | 285.0                             |
| CH$_n$-(COO)-(OO) | 117.0           | 635.0                             |
| (COO)-CH$_n$-O | 109.5             | 520.0                             |
| (OO)-(COO)-(OO) | 126.0            | 770.0                             |
| CH$_2$-CH$_2$-CH$_2$ | 111.0            | 530.0                             |

Harmonic dihedrals CMC and PAS

| Name          | $\delta_0$ [degree] | $K_\delta$ [kJ mol$^{-1}$ rad$^{-2}$] |
|---------------|---------------------|--------------------------------------|
| C1-O5-O4-O2   | 35.3                | 334.9                                |
| C5-O5-C6-C4   | 35.3                | 334.9                                |
| C4-C3-O4-C5   | 35.3                | 334.9                                |
| C3-O3-C2-C4   | 35.3                | 334.9                                |
| C2-O2-C3-C1   | 35.3                | 334.9                                |
| CH$_2$-(OO)-(OO)-(COO) | 0.0               | 167.5                                |

Torsional angles

| Name          | $\tau_0$ [degree] | $n$ | $K_\tau$ [kJ mol$^{-1}$] |
|---------------|-------------------|-----|------------------------|
| CMC           |                   |     |                        |
| H4-O4-C1-C2   | 60.0              | 3   | 2.520                  |
| O4-C1-C2-C3   | 60.0              | 3   | 11.720                 |
| O4-C1-C2-C3   | 90.0              | 2   | 0.836                  |
| O5-C1-C2-C3   | 90.0              | 2   | 0.836                  |
| O5-C1-C2-O2   | 90.0              | 2   | 4.180                  |
| O4-C1-C2-O2   | 90.0              | 2   | 4.180                  |
| C1-C2-O2-H2   | 60.0              | 3   | 2.520                  |
| C1-C2-C3-C4   | 60.0              | 3   | 11.720                 |
| C1-C2-C3-O3   | 90.0              | 2   | 0.836                  |
| O2-C2-C3-C4   | 90.0              | 2   | 0.836                  |
| O2-C3-C3-O3   | 90.0              | 2   | 4.180                  |
| O2-C3-O3-H3   | 60.0              | 3   | 2.520                  |
| C2-C3-C4-C5   | 60.0              | 3   | 11.720                 |
| C2-C3-C4-O4   | 90.0              | 2   | 0.836                  |
| O3-C3-C4-C5   | 90.0              | 2   | 0.836                  |
| O3-C3-C4-O4   | 90.0              | 2   | 4.180                  |
| C2-C1-O5-C5   | 60.0              | 3   | 7.540                  |
| C1-O5-C5-C4   | 60.0              | 3   | 7.540                  |
| C4-C5-C6-O6   | 60.0              | 3   | 11.720                 |
| O5-C5-C6-O6   | 90.0              | 2   | 0.836                  |
| O5-C5-C6-O6   | 90.0              | 2   | 4.180                  |
| C5-C6-O6-H6   | 60.0              | 3   | 2.520                  |
| C6-C5-C4-C3   | 60.0              | 3   | 11.720                 |
| O5-C5-C4-C3   | 90.0              | 2   | 0.836                  |
| O5-C5-C4-O4   | 90.0              | 2   | 4.180                  |
| C3-C4-O4-C1   | 60.0              | 3   | 7.540                  |
| C2-C3-O3-C4   | 60.0              | 3   | 7.540                  |
| C3-O3-(CH$_2$-(COO) | 60.0           | 3   | 7.540                  |
| O2-CH$_2$-(COO)-(OO) | 0.0              | 6   | 2.000                  |
| O3-CH$_2$-(COO)-(OO) | 0.0              | 6   | 2.000                  |

PAA

| Name          |     |       |
|---------------|-----|-------|
| CH$_3$-CH$_1$-CH$_2$-CH$_1$ | 60.0 | 3 11.720 |
| CH$_3$-CH$_2$-CH$_1$-CH$_2$ | 60.0 | 3 11.720 |
| CH$_3$-CH$_2$-CH$_2$-CH$_1$ | 60.0 | 3 11.720 |
| CH$_2$-CH$_2$-CH$_2$-(COO) | 30.0 | 6 2.000 |

Table 3: Overview of bonding parameters of our simulations. “(COO)” is carboxylic carbon, “(OO)” carboxylic oxygen. All other atom type names are self-explanatory (see figure [ ]). Analytical forms of force field term are as explained in ref. [4].
Figure 2: Snapshots of CMC I (left) and CMC II (right).
Figure 3: Snapshots of the PAA molecule after 3564 ps and 4460 ps runtime.

Figure 4: End-to-end distance probabilities for CMC I (middle), II (left) and PAA (right).
The correlation between the eigenvalues of the gyration tensor follows opposite trends (table 4): Whereas CMC I and PAA exhibit a negative correlation (−0.86 and −0.76) between the two largest eigenvalues, there is a small positive correlation (0.14) for CMC II. This shows how structural fluctuations happen: CMC I and PAA behave like bending rods – they shrink in one dimension and necessarily grow in another. In contrast the ring pulsation of CMC II, leads to the two largest eigenvalues growing and shrinking simultaneously.

Both the gyration radius and the end-to-end distance have multiple time regimes even in the first 80ps. At higher correlation times the correlation function’s statistics get worse. The time correlation function of the radius of gyration (figure 5) of CMC I displays two time regimes: on the first 15ps a fast one with a time constant of 41ps followed by a slow decay with \( \tau = 92 \)ps. A Kohlrausch-Williams-Watt fit \( f(t) = \exp\left(-\frac{(t/A)^B}{B}\right) \) from 0 to 80ps reveals a total correlation time of 80ps by analytical integration \[22\]. Contrary, the CMC II gyration radius decay has four domains: within the first picosecond there is a very fast and sharp decay (not resolved in figure 5).

### Table 4: Averages of the end-to-end distance \( R_{\text{ete}} \), the gyration radius \( R_{\text{gyr}} \) and the eigenvalues of the gyration tensor \( \langle R_{11} \rangle \geq \langle R_{22} \rangle \geq \langle R_{33} \rangle \) of CMC I and II and PAA. Additionally, correlation coefficients between the eigenvalues \( c_{R_{11}R_{22}} \), etc.) and characteristic ratios \( C_\infty \) are given.

|              | CMC I | CMC II | PAA   |
|--------------|-------|--------|-------|
| \( R_{\text{ete}} \) | 2.5 nm | 0.70 nm | 3.6 nm |
| \( R_{\text{gyr}} \) | 0.95 nm | 0.66 nm | 1.27 nm |
| \( \langle R_{11} \rangle \) | 0.758 nm | 0.245 nm | 1.346 nm |
| \( \langle R_{22} \rangle \) | 0.111 nm | 0.126 nm | 0.213 nm |
| \( \langle R_{33} \rangle \) | 0.047 nm | 0.067 nm | 0.049 nm |
| \( c_{R_{11}R_{22}} \) | −0.86 | 0.14 | −0.76 |
| \( c_{R_{11}R_{33}} \) | −0.31 | −0.60 | −0.30 |
| \( c_{R_{22}R_{33}} \) | −0.05 | −0.28 | −0.15 |
| \( C_\infty \) | 6.7 | 1.0 | 8.3 |

**Figure 5:** Auto correlation functions for the radius of gyration of CMC I (■), II (●) and PAA (▲). Up to 30ps PAA has the slowest decay. (Only every third point shown for clarity.)
Table 5: Inter-ring, glucosidic torsions’ occupancy probability (in percent) for CMC I. Each link is characterized by two torsions: φ: C4-O4-C1’-C2’ and ψ: C3-C4-O4-C1’. The table summarizes all torsional trajectories for CMC I. To allow better comparison, we classify the torsions into states for each link: The ψ-torsion is assigned to two states, the first one covering angles from 0 to 115 degrees, the second one, all remaining conformations. The φ-torsion exhibits three possible distinct maxima. One from 240 to 360, another from 0 to 120 and the last from 120 to 240. However, the second state is only populated in the link between ring two and three.

| Link 1-2 | ψ [%] | Link 2-3 | ψ [%] | Link 3-4 | ψ [%] | Link 4-5 | ψ [%] | Link 5-6 | ψ [%] | Link 6-7 | ψ [%] |
|---------|------|---------|------|---------|------|---------|------|---------|------|---------|------|
|         | 0°–115° | 115°–360° | 240°–360° | 0°–120° | 120°–240° | 0°–115° | 115°–360° | 240°–360° | 0°–120° | 120°–240° | 0°–115° | 115°–360° | 240°–360° | 0°–120° | 120°–240° | 0°–115° | 115°–360° | 240°–360° | 0°–120° | 120°–240° |
| Link 1-2 | 65  | 35  | 28  | 0   | 72  |
| Link 2-3 | 59  | 41  | 57  | 1   | 42  |
| Link 3-4 | 66  | 34  | 33  | 0   | 67  |
| Link 4-5 | 67  | 33  | 25  | 0   | 75  |
| Link 5-6 | 85  | 15  | 11  | 0   | 89  |
| Link 6-7 | 57  | 43  | 35  | 0   | 65  |

followed by a decay comparable to the first one for CMC I with a time constant of 37 ps. The mid-time relaxation is in the same order of magnitude as for CMC I, but there is a vast difference in the long time decay, where CMC II has a very slow mode with a time constant of ≈ 2200 ps. Averaging the whole range from 0 to 80 ps with a Kohlrausch-Williams-Watt fit we calculate a total correlation time of 900 ps.

The decay of the PAA gyration radius is less complex. It is almost monoexponential with a correlation time of 110 ps. Compared with CMC – where monomers are larger and intramolecular hydrogen bonding is an issue (see section 3.3) – PAA lacks any fast decay. One may speculate about the reason for the different relaxation behaviour. Poly(acrylic acid) behaves monoexponentially as expected for a generic polymer chain in solution. The relaxation time of ~ 100 ps is also found for both CMCs at some time scales which supports the idea that it is somehow characteristic for a polyelectrolyte of this size in water. The extremely slow long time relaxation (at least 2 ns) of CMC II is also easily explained by its rigid globular conformation. The origin of the short-time (t ≲ 15 ps) relaxation behaviour of both CMCs (characteristic time ~ 40 ps), which is faster than for PAA, is as yet not clear. It is possibly due to the weaker hydration of CMC (chapter 3.3.2) which could decrease the short-time local friction experienced by the polymer.

3.2 Local Chain Properties

Two selected CMC I glucosidic torsional angle’s φ (C4-O4-C1’-C2’) and ψ (C3-C4-O4-C1’) trajectories are shown in figure 6. The positions of the maxima differ (for all angles) from results found for unsubstituted cellubiose in vacuum [23] and in water [24]. For aqueous solutions there are maxima for (φ, ψ) at (284, 63), (274, 193), (294, 242) and (50, 237) degrees (in our definition). We found most of the linking dihedral angles to be unimodally distributed. Deviation from unimodality depend on the position along the chain and the substitution pattern: Torsion ψ is unimodal for chain-terminating glucosidic links. A second ψ-state is populated only for links connecting repeat unit three with its neighbors. Occupancies of the individual states for CMC I are given in table 3. Since there are no significant barriers between the states, transitions or, rather, oscillations between them occur on a picosecond scale for all torsions. The terminal torsion φ relaxes faster than the others (2 ps rather than 3–4 ps). Other than this, no significant trends can be found. The relaxation time is calculated from the torsional angle auto correlation function ⟨Φ(t)Φ(0)⟩ and a subsequent fit and integration.

There is hardly any torsional dynamics for CMC II, which is a consequence of the static folded state, with torsional links less mobile than those of CMC I. Example torsions are shown in figure 7.
Figure 6: Two selected trajectories of ring linking torsions for CMC I ($\phi$: C4-O4-C1'-C2' and $\psi$: C3-C4-O4-C1'). The link between rings 1 and 2 is shown at the top and the link from ring 5 to 6 at bottom. Distribution histograms are shown on the right. Only link 1-2 undergoes a significant transition, all other links are fluctuating around with only minor transitions. They are well represented by the second link shown.

Figure 7: Selected trajectories of ring linking torsions for CMC II ($\phi$: C4-O4-C1'-C2' and $\psi$: C3-C4-O4-C1'), link 1-2 (top), link 3-4 (bottom). The sharp one-state peak for the 3-4 link distribution is also characteristic for CMC II glucosidic links in the chain centre such as links 4-5 or 5-6. Distributions are shown on the right.
Figure 8: Histograms of four representative PAA backbone torsions (Torsions between unit seven and eight and ten-eleven are shown on the top, torsions between unit one and two, three and four are shown at the bottom). The above two torsions have two maxima, with a clear minimum between them. The lower histogram shows one almost unimodal torsion and a second one with three (or four) maxima. PAA has two backbone torsions per repeat unit.

Torsions are more complex for PAA (figure 8), with up to three states for each torsion. The time in which the torsions change ($\approx 2–5$ ps) is in the same order of magnitude as for CMC I. There is no apparent correlation between the tacticity of adjacent PAA monomers and their backbone torsional statistics.

3.3 Hydrogen Bonding

For biopolymers and modified biopolymers hydrogen bonding (H-bonds) is one of the most significant interactions on atomistic scales, both intramolecular (conformation) and intermolecular (solvation, aggregation). Both CMC and PAA undergo intensive hydrogen bonding. In CMC hydroxy groups, carboxylic oxygens, and to a smaller extent, ether oxygens are involved. Poly(acrylic acid) can only form H-acceptor bonds via carboxylic groups.

Our definition of a hydrogen bond is geometric: If the two oxygens are within a distance of less than 0.29 nm with the hydrogen between them, so that the angle O-H-O is greater than 130$^\circ$, a hydrogen bond is assumed. In our polyelectrolyte-water systems, we find both solute-solute, solute-solvent and solvent-solvent hydrogen bonding. The latter is only analyzed in the solute’s first hydration shell as defined from radial distribution functions (below).

The lifetimes $\tau$ of hydrogen bonds may be calculated from bond-correlation functions: For each possible hydrogen-bond we calculate an array, which contains 'true=1' in case of a bond, otherwise 'false=0'. The time-correlation function is calculated on this array, integration leads to the lifetime $\tau$. The integration was done by fitting a stretched exponential (Kohlrausch-Williams-Watt) $\exp[-(t/\alpha)\beta]$ in the range 0 to 80 ps and followed analytical integration.

3.3.1 Solute-Solute Hydrogen Bonding

The average absolute numbers of intramolecular hydrogen bonds are 1.8 for CMC I and 7.5 for CMC II respectively (see table 3 and figure 5). The large number of intramolecular hydrogen bonds stabilizes the much more compact structure of CMC II compared to CMC I.
Figure 9: Probability distribution of the number of intramolecular hydrogen bonds for CMC I (left) and CMC II (right).

|       | max | min | average | τ    |
|-------|-----|-----|---------|------|
| CMC I | 5   | 0   | 1.8     | 35 ps|
| CMC II| 12  | 4   | 7.5     | 205 ps|

Table 6: Number of solute-solute hydrogen bonds in one conformation: maximum (max), minimum (min), average (avrg) and lifetime τ (fit from t = 0 ps to 80 ps).

For CMC, the hydrogen bonds lifetime τ differs considerably between the CMC I and CMC II molecule: CMC I has a bond lifetime of 35 ps, CMC II of 205 ps (table 6), indicating that the cyclic compact structure of CMC II is stabilized by long-lived hydrogen bonds.

Intramolecular hydrogen bonds can be further separated into two subsets: (a) intra-ring and (b) inter-ring bonds, which connect two distinct glucose moieties and which are presumed to influence the overall chain structure of CMC: The ratio of inter- and intra-ring bonds for CMC I is 3 : 1. Lifetimes are shorter for intra-ring bonds (τ = 23 ps), which demonstrates a lower stability, compared to inter-ring bond with τ = 40 ps. Further differences can be spotted in the hydrogen bonding atom types: intra-ring bonds involve O3-O6 hydrogen bonds (20%) and to a larger amount O3-COO− bonds (70%). Bonds between rings involve mainly O2-COO− (60%) and O3-COO− and O6-COO− (15% each) oxygen atoms.

Thus the picture of intramolecular hydrogen bonds in CMC I is as follows: There is a high fraction of long-lived, ring-connecting hydrogen bonds, intra-ring bonds are of less importance. Inter-ring hydrogen bonding happens mostly via COO− groups, which makes (a) the interaction

| n   | 0  | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
|-----|----|----|----|----|----|----|----|----|
| CMC I P[%]| 22 | 78 | 0  | 0  | 0  | 0  | 0  | -  |
| CMC II P[%]| 11 | 18 | 13 | 13 | 18 | 4  | 11 | 12 |

Table 7: Solute-solute hydrogen bonds for CMC. First row (n) contains the distance along the chain between two rings involved in a hydrogen bond, the second row (P) is probability of occurrence. n = 0 denotes intra-ring hydrogen bonds.
Figure 10: Time evolution of six selected hydrogen bonds for CMC II. For bond pairs (like #1/#2 or #3/#4) most of the time there is only one bond out of a pair intact (indicated by a bar). Bond #1 and #2 bridges two glucosidic links, #3 bridges seven links, #4 three links and the last two bonds one and five links, respectively. (Description of the H-bonds, subscripts indicate the AGU number. (#1:O6$_5$-COO$_7$, #2:O6$_5$-COO$'$_7, #3:O3$_1$-O6$_8$, #4:O6$_4$-COO$_7$, #5:O2$_8$-COO$_7$ and #6:O6$_1$-COO$_6$) energy favourable and \( b \) involves a flexible, exocyclic group into binding. For this reason, changes in the global chain conformation may be compensated by carboxy methyl torsional changes to keep the \( \text{OH-O} \) alignment in an energetically low geometry. Intra-ring H-bonds, on the other hand, are either formed by neutral OH groups, which have a lower energy, or they necessitate sharp turns of the carboxy methyl group, which leads to distortions.

In CMC I, inter-ring hydrogen bonds are limited to neighboring rings (table 7). This is different for CMC II, where also more distant rings are connected by inter-ring hydrogen bonds: In contrast to CMC I, 90% of the inter-ring hydrogen bonds connect rings which are not nearest neighbors: on average bonds span 3–4 rings. These bonds are found to be very stable, some of them are intermittently present for an overall time of 1.7 ns, thus living for more than half of the simulation.

Furthermore, in CMC II there are several pairs of hydrogen bonds (about 15), which bind almost exclusively (see figure 10). Out of these pairs, there is solely one bond present, but alternating with the second one. The presence of one bonds prevents the second bond. Even, if the mean lifetime of an individual bond is short, both bonds together form a steady connection between two glucose rings. One example is the bond pair O6(ring 3)-COO(ring 7) and O6(ring 5)-COO(ring 7), where the carboxylate oxygen flips between the two alcohol oxygens. Each bond lives 1 ns and together they span not less than 2 ns. However, for 1.7 ns only one of them is exclusively present. Thus, for most of the time, one bond excludes the other. This evident for H-bonds formed via a COO$^-$ group, which account for every second (56%) of all solute-solute bonds.

A distribution of all bond-bond cross correlation coefficients for CMC II is shown in figure 12. They are calculated as

\[
c_{ij} = \frac{\langle (h_i(t) - \langle h_i \rangle)(h_j(t) - \langle h_j \rangle) \rangle \cdot \langle (h_i(t) - \langle h_i \rangle)^2 \langle h_j(t) - \langle h_j \rangle)^2 \rangle^{-1/2}}{2}
\]

where \( h_i(t) \) is 1 when hydrogen bond \( i \) is present and 0 otherwise. Most hydrogen bonds do not have a significant correlation: 10 hydrogen-bond-pairs have a strong negative \( c_{ij} < -0.30 \), 45 bond-pairs a positive correlation \( c_{ij} > 0.3 \). The anti-correlated bond pairs often involve one common oxygen of a COO$^-$ group, which alternates between two different hydrogen-donor groups. High correlations \( c_{ij} > 0.6 \) occur particularly, if the compact configuration of the CMC II oligomer allows for some bonds to form simultaneously, like H-bonds involving O2H and O6H donor groups of one, and a single carboxylic group of a second ring. The COO$^-$ group is embedded between
Figure 11: Local configuration of solute-solute hydrogen bonds for CMC II. There are two inter-ring H-bonds, which occur only simultaneously and one short (oxygen-oxygen distance: 2.4 nm) intra-ring bond which forms an eight-membered-ring. The two inter-ring bond occur only simultaneously.

The two H-donors (figure 11). The effect is very strong for the flexible COO$^-$ group at rings 7 and 8, but is still noticeable for other acceptors. Examples of hydrogen bond trajectories (Fig 13) illustrate the cases of (anti) correlated H-bonds.

The cross correlation coefficient $c$

$$c = \frac{\langle (n - \langle n \rangle)(r - \langle R_{ete} \rangle) \rangle}{\sqrt{\langle (n - \langle n \rangle)^2 \rangle \langle (R_{ete} - \langle R_{ete} \rangle)^2 \rangle}}$$

shows some coincidence between the number of solute-solute hydrogen-bonds $n$ and the polyelectrolyte’s end-to-end distance $R_{ete}$ for CMC I. Whereas there is hardly any correlation of extension and the total number of intra-CMC hydrogen-bonds ($c = -0.05$), it is slightly more pronounced ($c = -0.16$) for the number of intra-ring hydrogen bonds versus the end-to-end distance: If the molecular extension shrinks, the number of intramolecular hydrogen bonds increases. The compact polymer structure favours more contacts. Similar correlations for CMC II would not be very meaningful, because of the rigid structure which fixes the end-to-end distance.

Figure 12: H-Bond-H-bond cross correlations for CMC II. Distribution of correlation coefficients between all intramolecular hydrogen-bonds emerging during the CMC II simulation. The majority of all hydrogen bonds does not show correlations with other bonds. Only a small part shows (negative and positive) correlations. Correlation coefficients are calculated as described in section 3.3.1.
3.3.2 Hydrogen Bonds to Solvent

A general picture of the solvent distribution around CMC is given by radial distribution functions (RDF) between the center of mass (defined as in section 2) of the glucose unit and water oxygens (figure 14). The differences in the peak heights can be described and explained as follows: The outermost glucose rings exhibit the best defined hydration shell. Environments of inner rings are more perturbed, either by neighboring rings or by attached carboxylic groups. This is evident for the doubly substituted ring 3 in CMC I, whose first solvation peak disappears entirely. The CMC II radial distributions for rings 1 and 3 show multiple peaks with the first maximum at approximately 0.45 nm. Only ring 7 shows two different peaks centered at 0.33 nm and 0.36 nm, where the first peak at 0.3 nm is caused by the solvation of the C6 carboxymethyl group. Thus from the appearance of the RDFs, the CMC I solvation shell seems to be more intact than that at CMC II. This is the consequence of the open-chain configuration of CMC I as opposed to the compact structure of CMC II, which excludes solvent molecules from the vicinity of different monomers to a different extent.

As PAA has a simple configuration, the solvation shell is more uniform: the chain ends attract more water than inner segments, but, apart from that, the center of mass-water RDF is the same with the first peak at 0.35 nm.

On average the CMC I oligomer has 13 donor and 38 acceptor hydrogen bonds with water, CMC II 9 donor and 35 acceptor bonds (table 8). The difference is in line with the result for intramolecular bonds: The CMC II molecule, which heavily bonds with itself, has fewer free sites for hydrophilic interaction with the solvent. Poly(acrylic acid), with no hydrogen bond donors of its own, has on average no less than 136 bonds with water. As an estimate, this corresponds to water molecules with a total mass of 2300 amu, which is 1.5 times the polymer’s own mass. The mass of associated water is smaller for CMC: About 60% of the polymer’s mass for CMC I and only 50% for CMC II. The detailed distributions of H-Bonds are shown in figure 15. They are approximately Gaussian in all cases and they reflect the trends already seen in the averages.

In order to compare the hydration of the different molecules on an equal basis, one may normalize the number of H-bonds by the mass of the polymer. This yields the H-bonds per weight, which should in some way be correlated with the specific enthalpy of solvation. One finds 0.036 bonds/amu for CMC I, 0.029 bonds/amu for CMC II and more than twice as many for PAA: 0.083 bonds/amu. Thus there seems to be a competition between inter- and intra-molecular hydrogen bonds for car-
Figure 14: Pair distribution functions $g(r)$ of selected CMC glucose rings and PAA monomer units (center of mass) with water oxygens. a) CMC I, b) CMC II, c) PAA. For CMC I one identifies a first hydration shell with on average 15 next neighbors to the first minimum. The first shell of CMC II is more irregular, with hydration numbers ranging from 10 to 18. PAA has the most regular and smooth hydration shell. As a general result, end monomers have more water molecules in their neighborhood than inner monomers.

|                   | CMC I | CMC II | PAA   |
|-------------------|-------|--------|-------|
| Donor-OH          | 13 (0.72) | 9 (0.45) |       |
| Acceptor COO$^-$  | 26 (2.60) | 23 (1.92) | 136 (2.9) |
| Acceptor OH       | 10 (0.56) | 11 (0.55) |       |
| Acceptor ether-O  | 1.5 (0.10) | 1.3 (0.01) |       |

Table 8: Average number of hydrogen bonds to solvent, grouped according to solute binding sites. In parentheses: numbers with respect to hydroxy, ether and carboxylic oxygen sites of the polyelectrolytes. For the two CMC oligomers, there is hardly any difference in the number of OH-acceptor H-bonds per site. In contrast the number of CMC I donor-OH and acceptor COO$^-$ bonds per site is lower than for CMC II. From this follows that the intrapolymer H-bonding happens in many cases trough -OH-COO$^-$ bonds.
Figure 15: a) Total number of donor and acceptor hydrogen bonds between water and CMC I (grey) and CMC II (black) and PAA. b) Histogram of the number of solute-solvent hydrogen bonds for CMC I, CMC II and PAA (from left to right). Normalized with respect to the appropriate number of binding sites of the polyelectrolytes (all polymer-oxygens as acceptor, all hydroxy-groups as donor to water). Acceptor bonds are grey, donor bonds are dark.
boxy methyl cellulose, which is dominated by the intramolecular bonds in case of CMC II and to a lesser extent for CMC I. In PAA, there is no competition from intramolecular hydrogen-bonds. In addition, one can reasonably expect that hydrogen-bonds to COO\(^-\) with its negative charge are energetically more favorable than to \(-\text{OH}\) or \(-\text{O}\). Hence, PAA should have a more negative enthalpy of solvation than CMC. We are, however, only aware of experimental data for PAA to compare with \[26\]. Klein et al. used solution calorimetric measurements to determine the solution enthalpy of about 25 kJ/(mol repeat unit) (0.27 kJ/g) for sodium-PAA, this value corresponds to 575 kJ/mol for the PAA 23-mer.

3.4 Structure of the solvation shell

The arrangement of water molecules in the vicinity of the polymer chains has been investigated. To this end, all water molecules within 0.6 nm of any polymer atom were sorted into clusters. A water molecule was taken to be part of a cluster if it formed a hydrogen bond to any other water molecule of that cluster. Hence, the assignment of molecules to clusters depends on our geometrical definition of a hydrogen bond (Sect. 3.3).

For the three polymers, examples of water clusters in the immediate vicinity of the solute are shown in Figure 16. For both CMCs, such clusters consist of 2–5 molecules and are attached to the solute via 2–3 hydrogen bonds (in addition to individual water molecules hydrogen-bonded to CMC which are not shown). Depending on their size, the clusters can connect two (CMC I: a, b; CMC II: a-c) or more (CMC I: c,d) cellulose rings. Poly(acrylate) is quite different due to the shorter distances between repeat units. Typically, one finds single water molecules, that are not part of water clusters and that bridge neighboring carboxylate groups (Fig 16, PAA I). The clusters are, however, fragile arrangements undergoing rapid exchange (order of picoseconds, Fig 17) with other water molecules and they do provide little if any stabilisation to particular CMC conformations. Only a small difference is found between both CMC oligomers (figure 17), whereas clusters in the hydration sphere of PAA tend to live longer. This could be due to the high concentration of negative charges on the PAA backbone, which slow down the general motion of hydration water by their strong electrostatic field.

3.5 Counterions

The distribution of counterions around the solute molecules has also been investigated. The solutes are fragments of polyelectrolytes, and since the work of Manning \[27\] the distribution of counterions in the field of polyelectrolytes has been of considerable theoretical interest (see, e.g., ref. \[28\] and references therein). Because of the small size of the charged solutes investigated here and the small number of counterions, this study has to be limited to the molecular neighborhood of the solutes.

Radial distribution functions (RDFs) between the centres of mass of the repeat units (for definition, see Sect. 2) and the Na\(^+\) are summarised in Figure 18a. Both CMCs are similar in shape, but different in intensity: They have a close peak at about 0.4 nm and a broad second peak centered at about 0.7 nm. Figure 18b shows that the first peak (\(r < 0.5 \text{ nm}\)) is dominated by Na\(^+\) approaching the O2 oxygen of the cellulose moiety, whereas the second peak (0.5–1 nm) arises from Na\(^+\) ions near the carboxylic groups which, in CMC, are more remote from the centre of mass. Both the (dynamic) flexibility of the carboxylate and the (static) different substitution patterns on different AGUs account for the large width of the second peak. CMC II has a lower intensity, especially at short distance. This arises from its more compact structure which prevents counterions from approaching it freely from all sides. This behaviour is similar to what was already seen for the solute-solvent H-bonds.

The RDF of poly(acrylate) is better defined due to the larger number of counterion-monomer pairs. It shows a relatively sharp first maximum at about 0.5 nm caused by Na\(^+\) ions near the carboxylate and a broader second maximum (\(\approx 0.8 \text{ nm}\)) possibly due to solvent-separated ion pairs.

It is interesting to note that on average the CMC oligomer keeps much fewer counterions (\(\approx 0.41\)) in its electrostatic vicinity (distance to any atom of the polymer lower than the electrostatic
Figure 16: Examples of water cluster in the vicinity of CMC I, II and PAA. Dotted lines denote hydrogen bonds.
Figure 17: Average lifetimes of water clusters in the vicinity of the polyelectrolytes as a function of size. Two pathways are responsible for the disappearance of a cluster: Either it is overtaken by a larger one and inherits its identity, or it diminishes by losing all of its molecules.

screening length of the solvent < 0.64 nm) than the PAA oligomer (≈ 13), in spite of both being of similar molecular weight. This is caused by the difference in charge.

4 Conclusions

Even though poly(acrylate) and carboxy methyl cellulose both are water-soluble polyelectrolytes, their behaviour in water and towards water differs markedly. This is due to the different charge density as well as to the different type and quality of hydrogen bonds that either forms with water. In PAA, there is one strong hydrogen bond with the deprotonated carboxylate acting as an acceptor. In CMC, the smaller density of carboxylates is only partly set off by the possibility of forming both donor and acceptor hydrogen bonds to the alcoholic OH groups of the cellulose. (Hydrogen bonds to the ether oxygens are irrelevant.) Taken per molecular weight of the polymer, it seems safe to say that PAA forms at least twice as many hydrogen bonds as CMC and that they are of larger binding energy (charge-dipole, rather than, dipole-dipole). Based on this argument, the solvation of PAA in water should be more exothermic than that of CMC. Unfortunately, no measurements appear to be available for comparison.

The comparison of the two CMC oligomers shows that the particular carboxy methylation pattern has an immense influence on the local structure in solution. The two assume entirely different conformations: CMC I is stretched and flexible, whereas CMC II remains in a rigid cyclic conformation. While it cannot be ruled out completely that one molecule may not have reached equilibrium and may still be stuck in a local minimum, this is unlikely in view of the long simulation times of several nanoseconds. If there are metastable conformations they have to be long-lived. We are therefore left to conclude that industrial CMC with its statistical substitution of OH groups, behaves locally very diversely. As a consequence of its globular structure, CMC II shows more intramolecular hydrogen bonds than CMC I, fewer hydrogen bonds to water, slower
Figure 18: a) Monomer(center of mass)-sodium radial distribution. Both CMC molecules show the same shape RDF, but CMC II has smaller peak heights. All radial distributions reach unity at about $r = 1.9\text{ nm}$. b) The figure shows the preference of docking sites for sodium ions approaching CMC I. The histogram is divided into two parts. The first (grey) includes ions close to the chain (distance sodium-ring-com lower 0.5 nm), the second one (black) is for all ions in the distance of the second peak in the pair distribution function ($\in [0.5 \text{ nm}, 1.0 \text{ nm}]$).

hydrogen bond dynamics, and fewer contacts with the counterions.

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